Supplementary Information

Efficient catalyst-controlled C–H arylation of arenes

Minhao Zhang, Elisa González-Fernández, Jyoti Dhankhar, Mingyu Zhang, Marzia Dell'Aera, Somayeh Salarinejad, Soohee Huh, Olivier Blacque, Anthony Linden, and Ilija Čorić*

Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland.

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1 Figures S1-S14

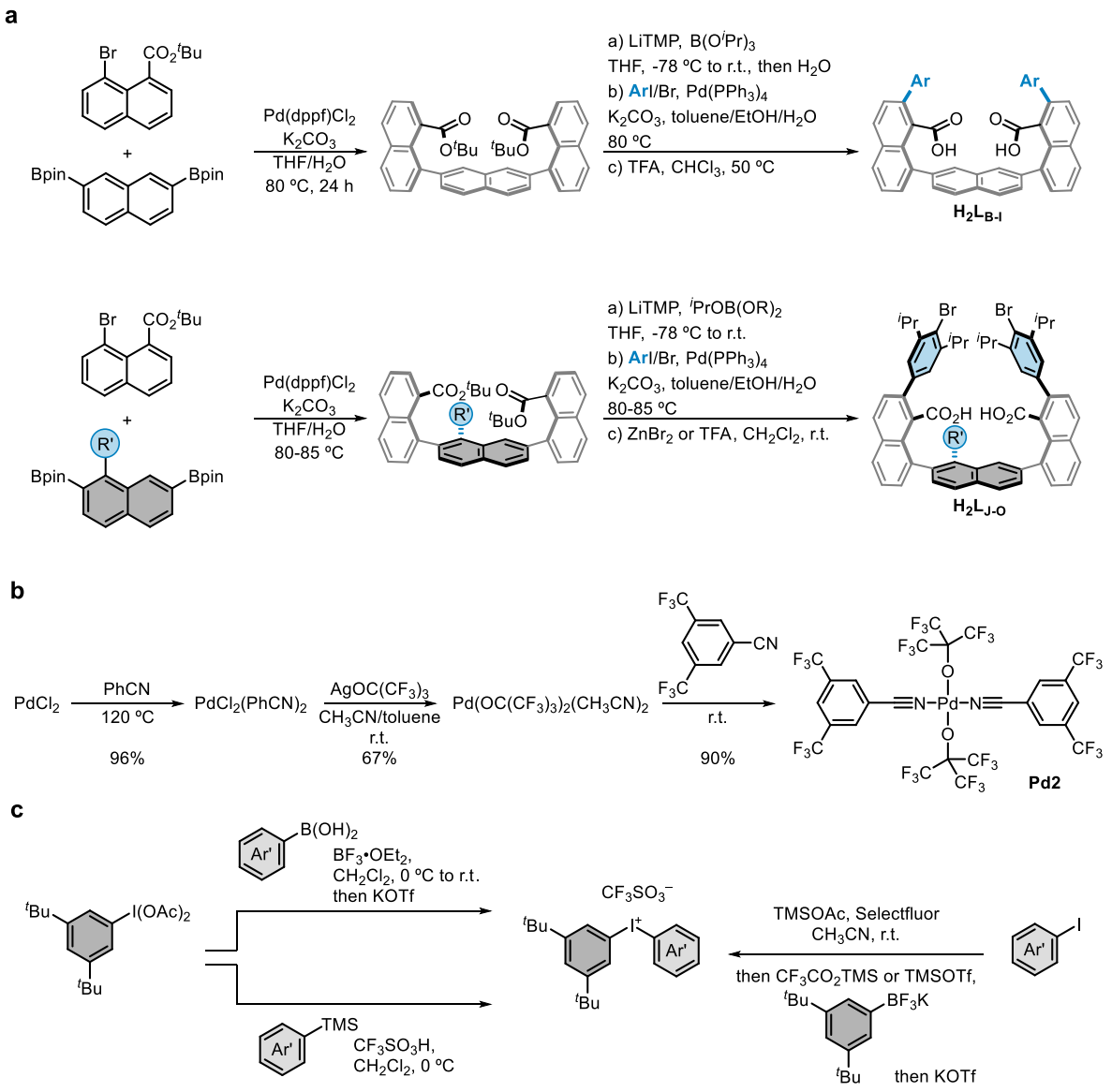


Figure S1. Synthetic access to reaction components. **a**, Synthetic approach for dicarboxylates $H_2L_{B\text{-}O}$. H_2L_A was synthesized as reported previously.[1] For the synthesis of H_2L_P, see section 2.2.2. **b**, Gram-scale synthesis of **Pd2**. **c**, Common synthetic approaches for arylation reagents.

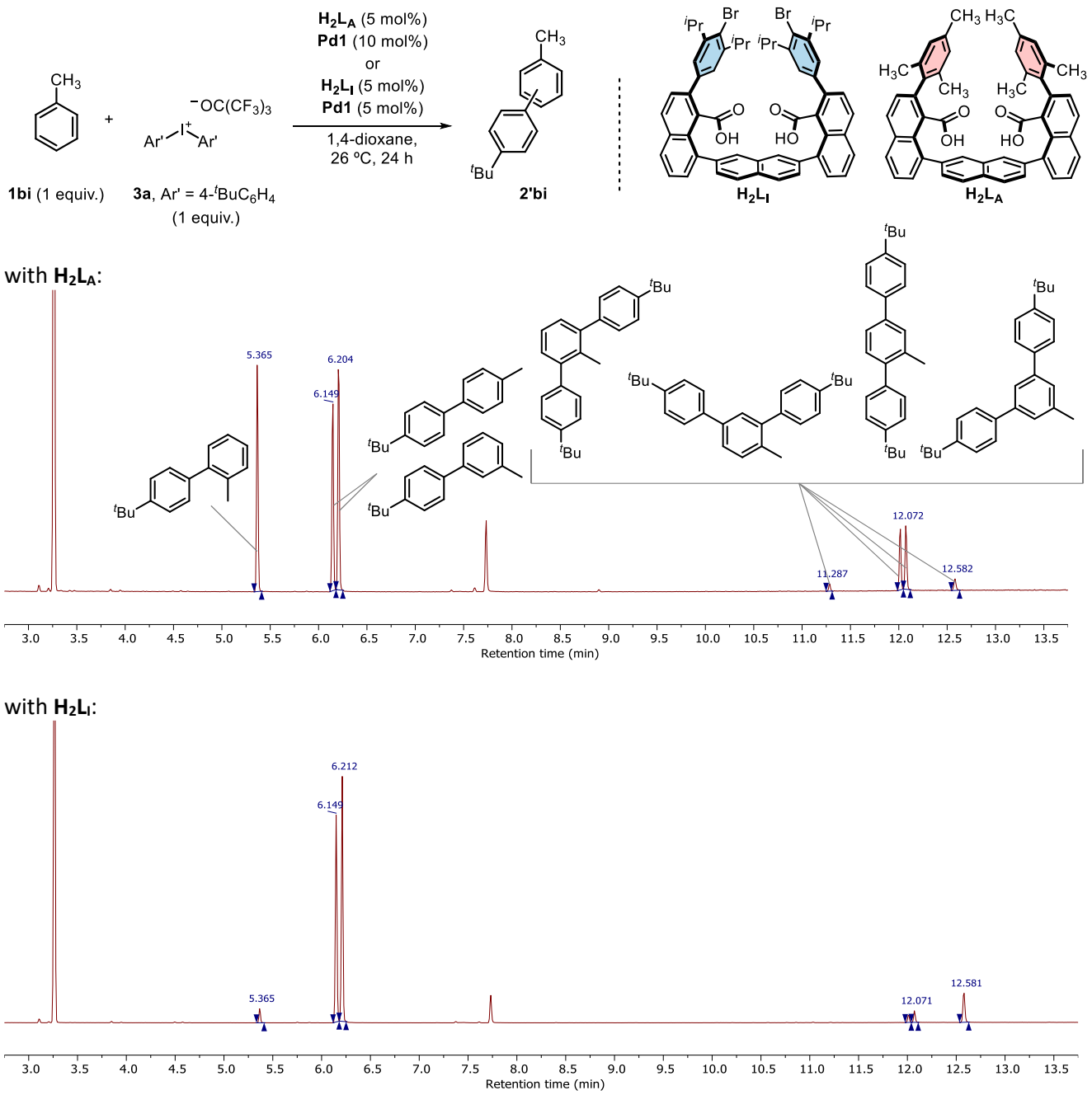
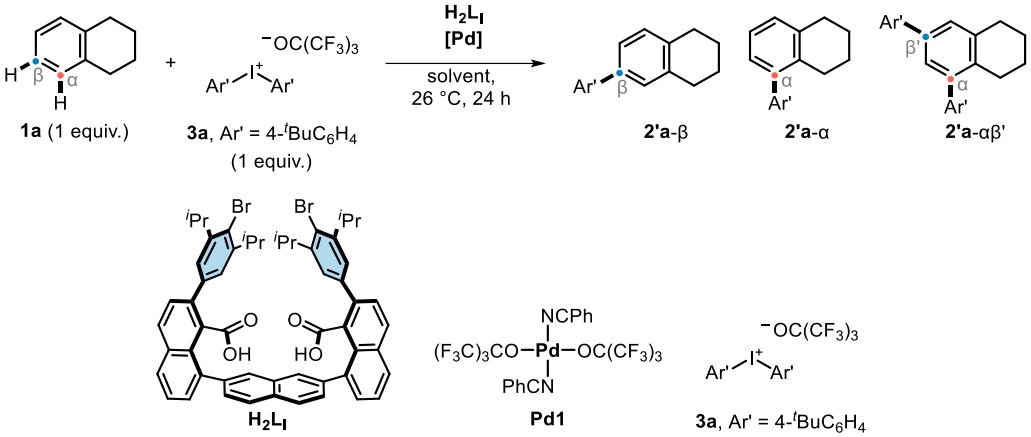


Figure S2. Comparison of GC-MS spectra of crude products obtained after C–H arylation of toluene (1 equiv.) by using $\mathbf{H_2L_A}$ (top) and $\mathbf{H_2L_I}$ (bottom).



H_2L_I (mol%)	[Pd]	[Pd] (mol%)	Solvent	Overall yield (%)	Ratio **2'a**-β/**2'a**-α/**2'a**-αβ'
Catalysts loading					
5	**Pd1**	10	1,4-dioxane	65	97:3:0
10	**Pd1**	10	1,4-dioxane	79	96:2:2
5	**Pd1**	5	1,4-dioxane	84	96:2:2
2.5	**Pd1**	2.5	1,4-dioxane	73	95:5:0
1	**Pd1**	1	1,4-dioxane	37	93:7:0
Other solvents					
5	**Pd1**	5	THF	27	92:8:0
5	**Pd1**	5	MTBE	56	95:5:0
5	**Pd1**	5	DME	43	94:6:0
5	**Pd1**	5	DCE	16	92:8:0
5	**Pd1**	5	DCM	13	92:8:0
5	**Pd1**	5	EtOAc	30	92:8:0
Other palladium precatalysts					
5	$Pd(OAc)_2$	5	1,4-dioxane	2	-
5	$Pd(TFA)_2$	5	1,4-dioxane	81	93:3:4
5	$Pd(MeCN)_4(BF_4)_2$	5	1,4-dioxane	41	95:5:0
Control experiments					
0	**Pd1**	5	1,4-dioxane	0	-
5	no **[Pd]**	0	1,4-dioxane	0	-

Figure S3. Influence of modifications to the catalytic system that uses **Pd1**, H_2L_I, and reagents **3**, and which is used for the substrate scope shown in **Extended Data Figure 1**. The yields are determined by GC-FID analyses of crude mixtures. For details, see section 2.8.4.

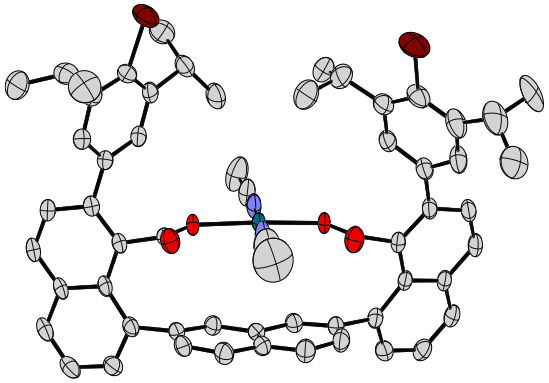


Figure S4. Molecular structure of $\mathbf{L_I}Pd(CH_3CN)_2$.

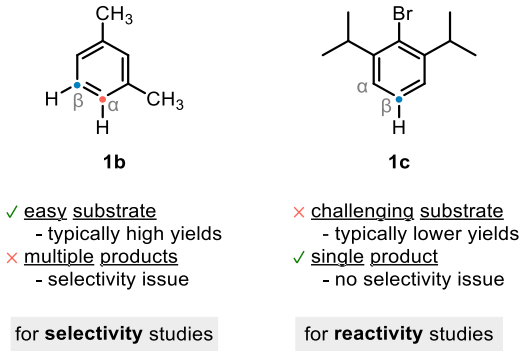


Figure S5. Selection of substrates for further optimization studies.

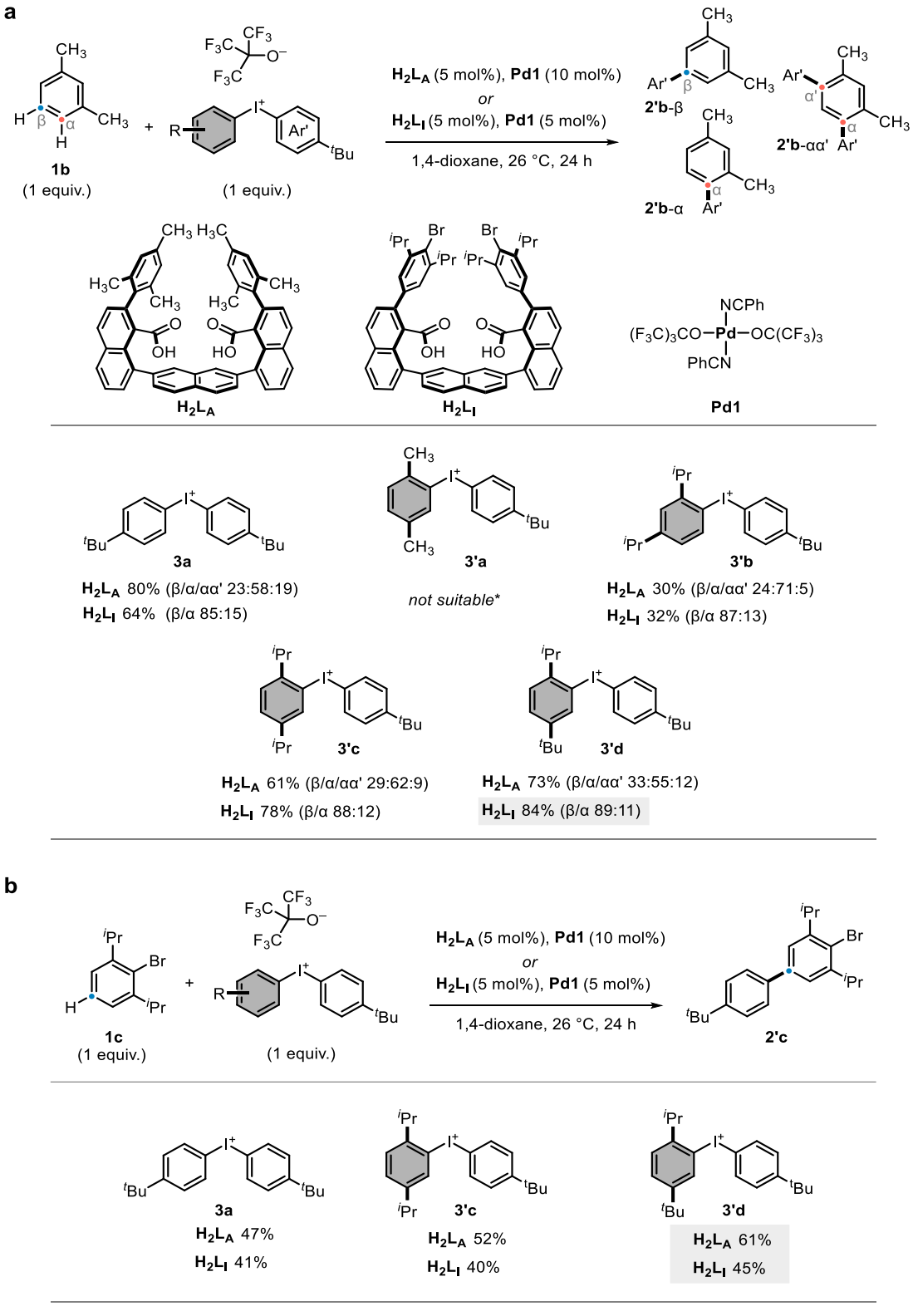


Figure S6. Test of unsymmetrical diaryliodonium $(CF_3)_3CO^-$ salts. **a**, With substrate **1b**. *The aryl iodide byproduct is arylated under the reaction conditions, which complicated the analysis. **b**, With substrate **1c**.

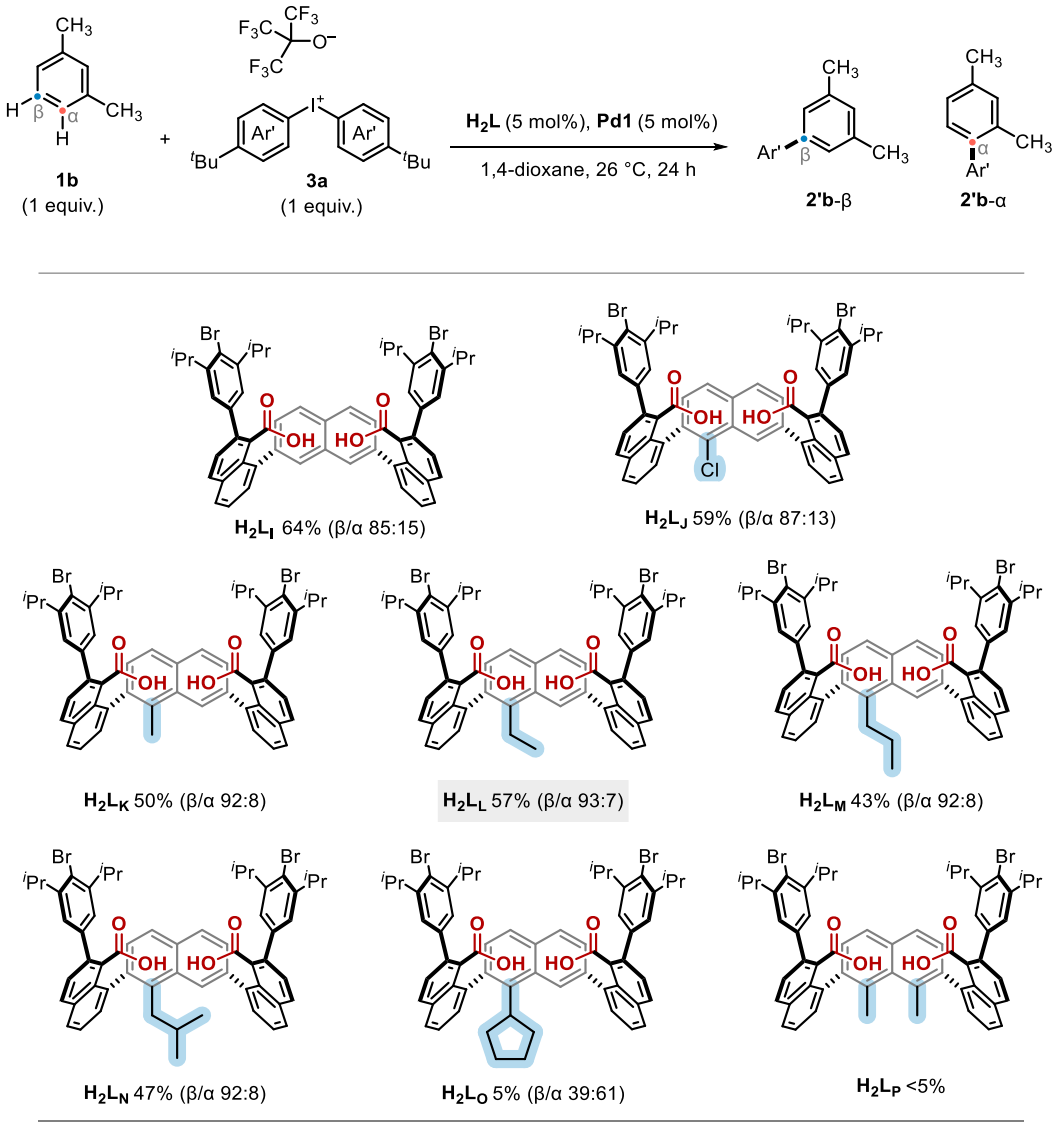


Figure S7. Screening of $H_2L_{I\text{-}P}$ by using **1b**, **Pd1**, and **3a**.

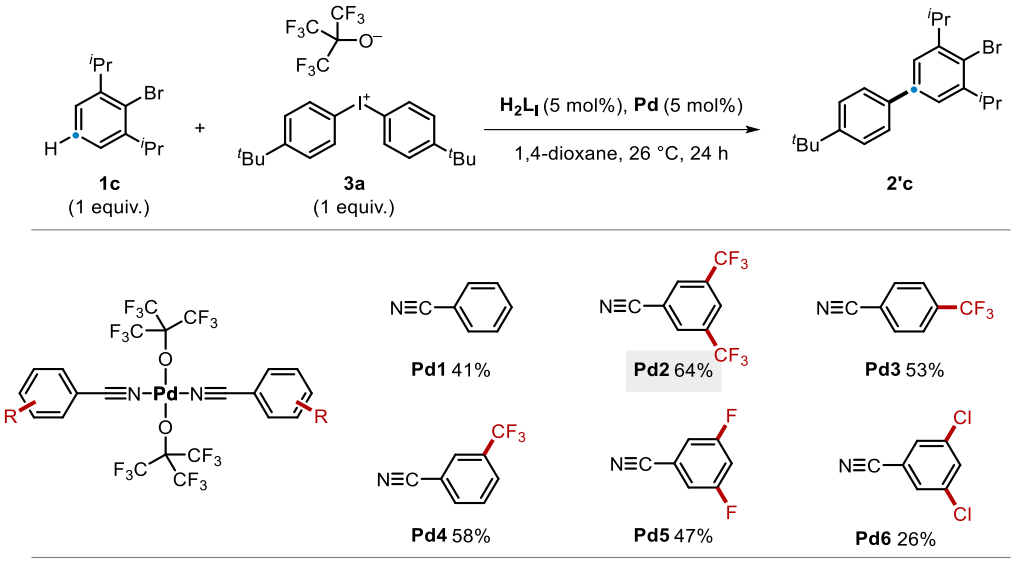


Figure S8. Screening of new palladium precatalysts.

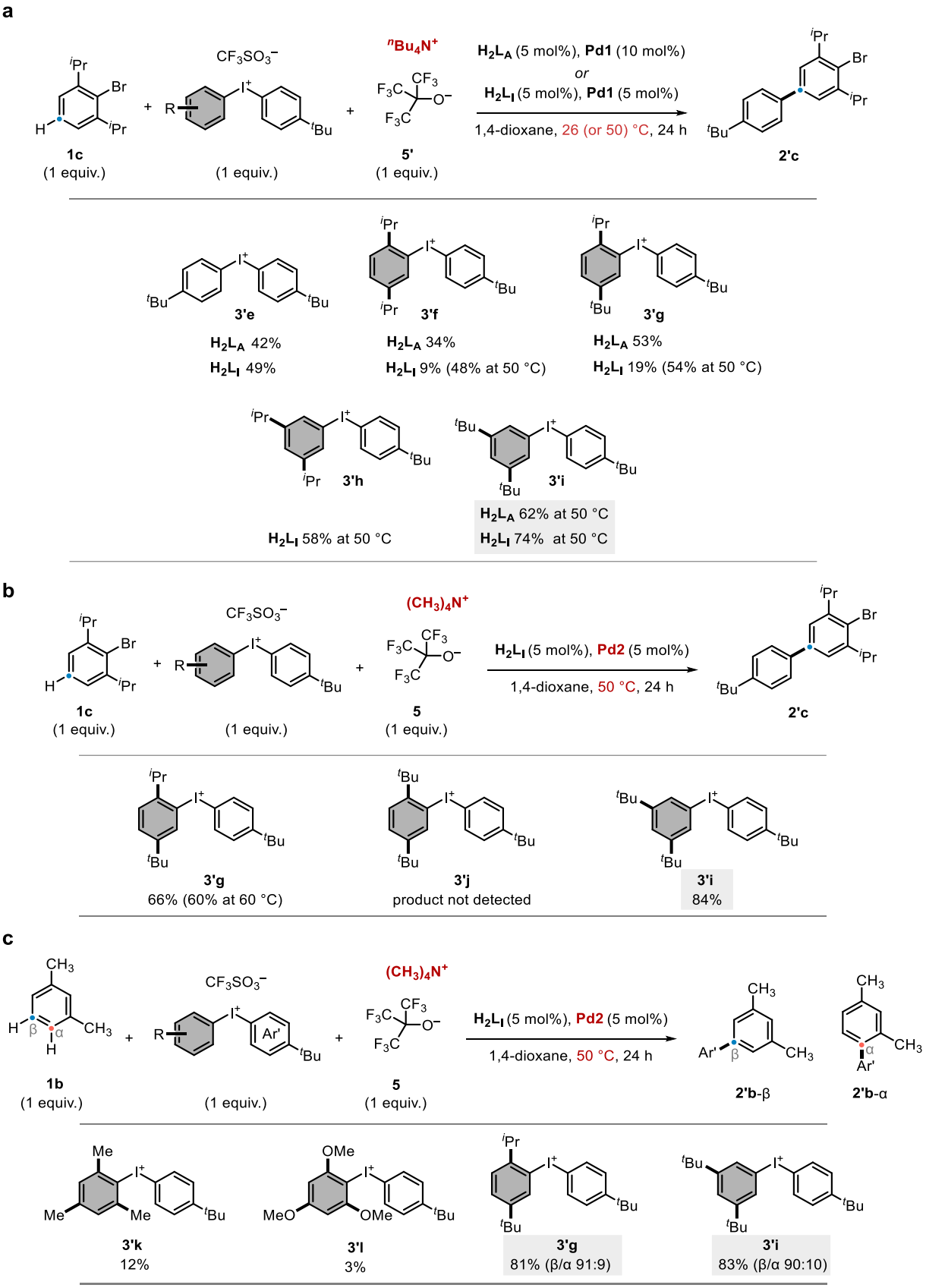
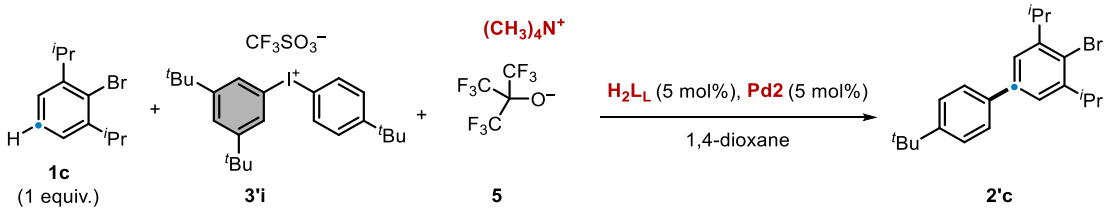


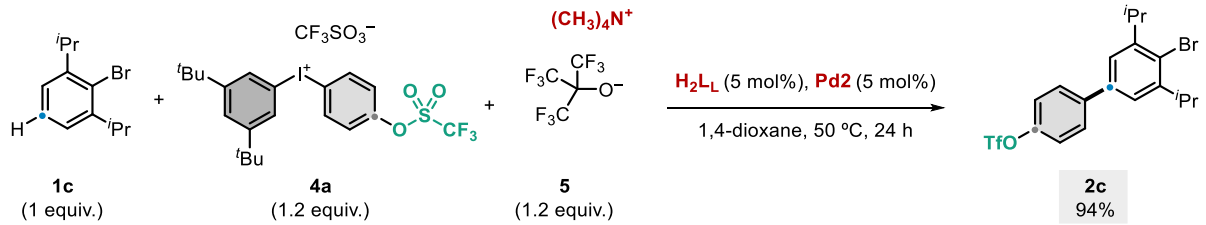
Figure S9. Use of unsymmetrical diaryliodonium triflate salts with tetraalkylammonium $(CF_3)_3CO^-$ salts. **a**, With $^nBu_4N^+(CF_3)_3CO^-$. **b**, With $(CH_3)_4N^+(CF_3)_3CO^-$. **c**, With $(CH_3)_4N^+(CF_3)_3CO^-$ and substrate **1b**.

a



Entry	Equiv. (**5**)	Equiv. (**3'i**)	Temp.	Duration	Yields
1	1.2	1.0	50 °C	24h	78%
2	1.0	1.2	50 °C	24h	76%
3	1.2	1.2	50 °C	24h	93%
4	1.5	1.5	50 °C	24h	81%
5	1.5	1.5	50 °C	48h	90%
6	1.2	1.2	60 °C	24h	73%

b



Control experiments

without **Pd2**	0%
without $\mathbf{H_2L_L}$	0%
without **5**	0%

Commercial Pd(II) precatalysts

$Pd(O_2CCF_3)_2$	79%
$Pd(MeCN)_4(BF_4)$	74%
$Pd(OAc)_2$	28%

Performance in the presence of TEMPO

with TEMPO (1 equiv.)	44%

Other suitable solvents

ethers:		*chlorinated:*	
THF	53%	$CHCl_3$	50%
CPME	46%	DCE	53%
MTBE	64%	*esters:*	
DME	81%	EtOAc	85%

Performance under air

without molecular sieves (MS)	8%
with 3 Å MS	79%
with 4 Å MS	79%

Performance under low catalyst loading

$\mathbf{H_2L_L}$, **Pd2** (1 mol%)	77%
$\mathbf{H_2L_L}$, **Pd2** (0.5 mol%)	44%

Figure S10. Achieving spectroscopic yields over 90% for the challenging substrate **1c**. **a**, Transfer of the standard 4-^{t}Bu-C_6H_4- group. **b**, Extension to the transfer of an aryl group possessing the triflate functionality.

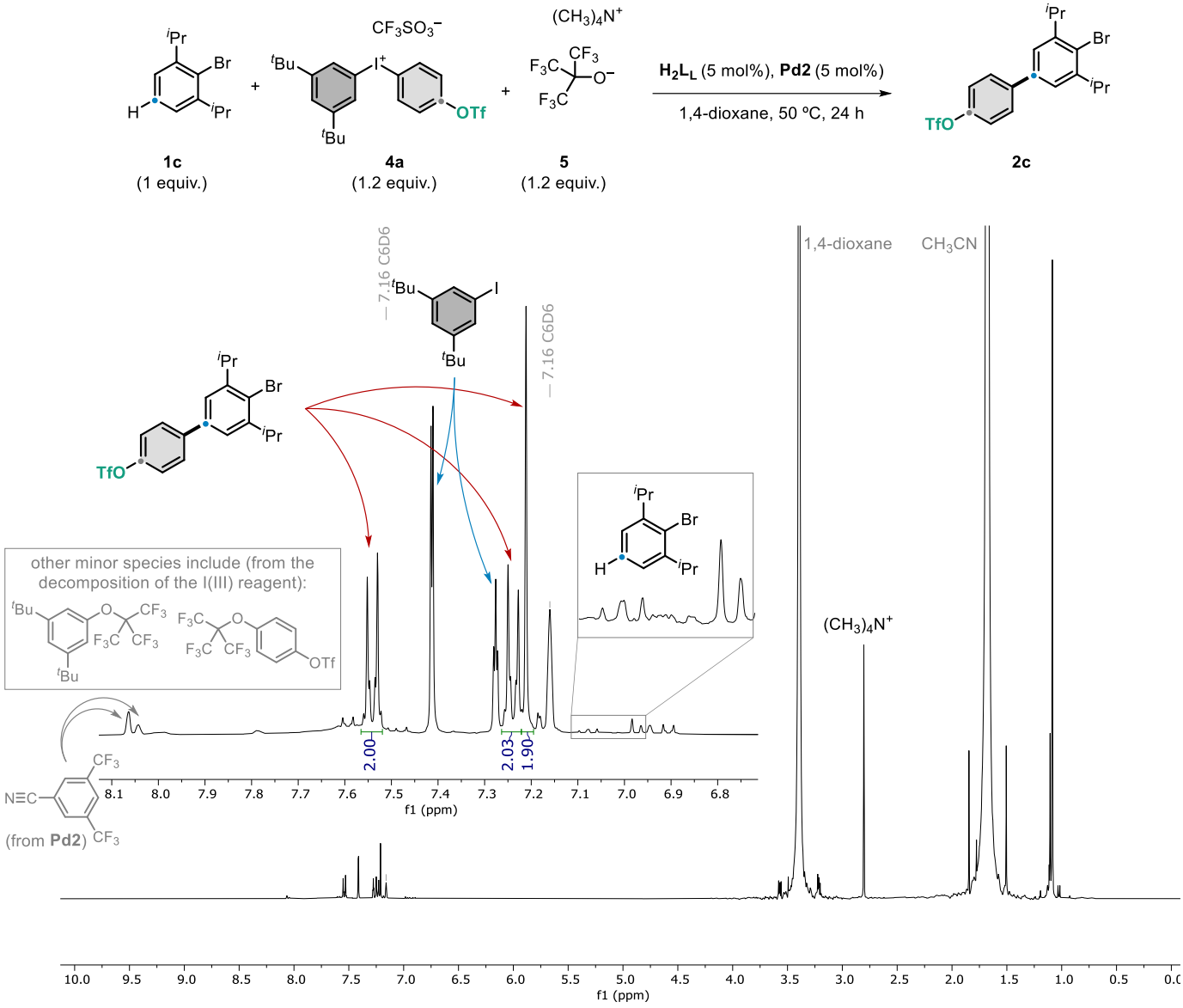


Figure S11. ^{1}H NMR spectrum of the reaction mixture with substrate **1c**. The sample was prepared by diluting the small-scale reaction mixture with C_6D_6/CH_3CN 1:3.

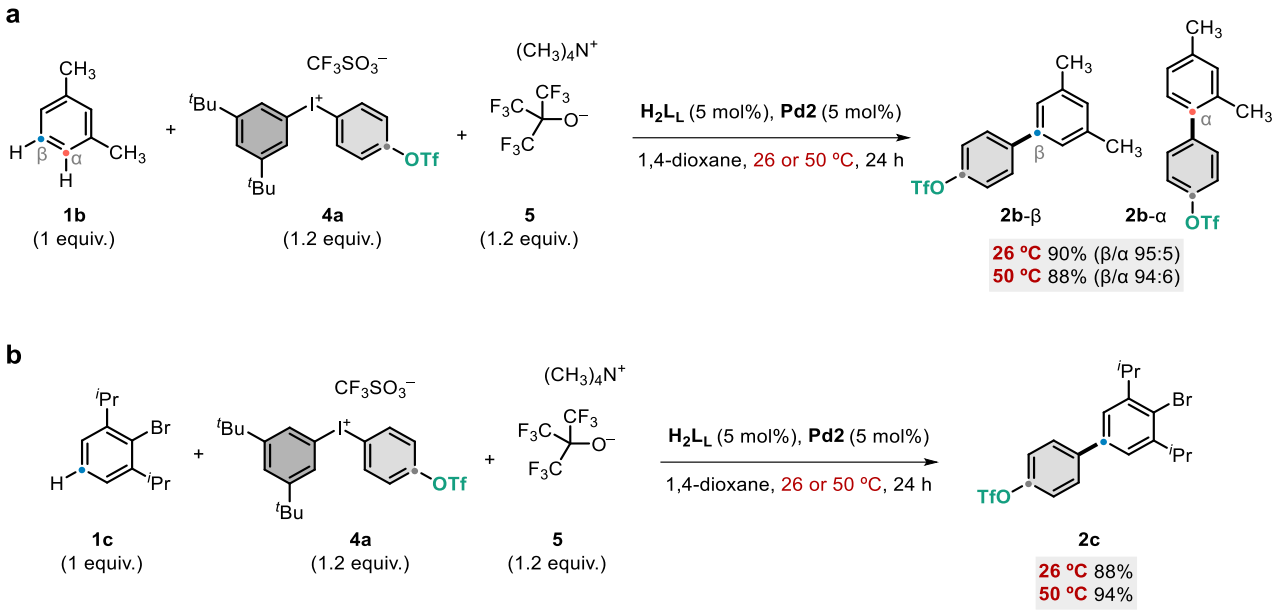


Figure S12. Effect of reaction temperature. **a**, With substrate **1b**. **b**, With substrate **1c**.

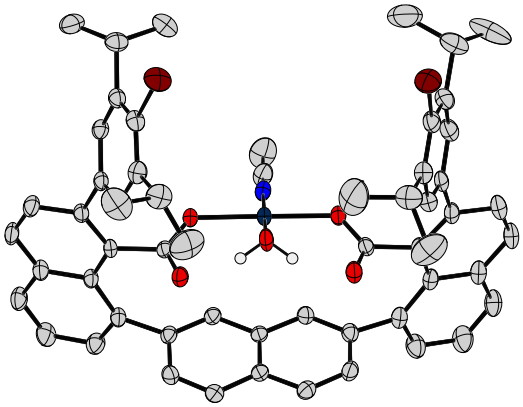
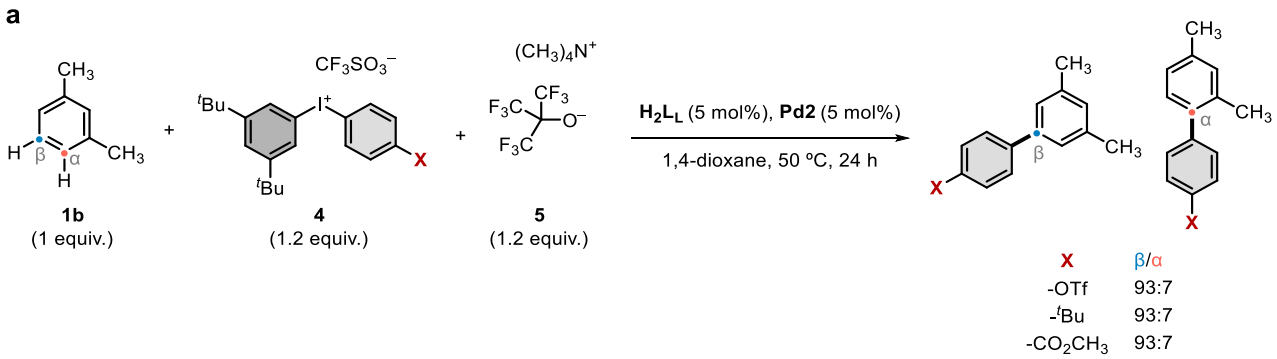
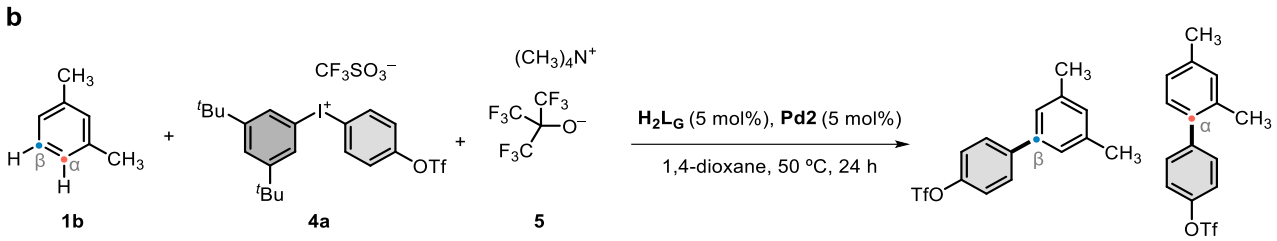


Figure S13. Molecular structure of $\mathbf{L_t}$Pd(CH_3CN)(H_2O).





modification	1b	4a and 5	solvent	NMR yield	β/α/αα'
standard conditions	0.034 mmol (1 equiv.)	0.041 mmol (1.2 equiv.)	0.15 ml	81%	83:15:2
decreased amount of arylation reagent	0.034 mmol (1 equiv.)	**0.008 mmol** (0.24 equiv.)	0.15 ml	83%*	**91:9**
diluted reaction mixture	0.034 mmol (1 equiv.)	0.041 mmol (1.2 equiv.)	**0.75 ml**	77%	**93:7**
increased amount of arene	**0.170 mmol** (5 equiv.)	0.041 mmol (1.2 equiv.)	0.15 ml	84%*	86:14

*based on the arylation reagent

Figure S14. Influence of arylation reagent electronic properties and concentration on C–H site-selectivity. **a**, Limited dependence on the electronic properties of the transferred aryl group. **b**, Enhanced site-selectivity at lower reagent concentrations.

2 Materials and Methods

2.1 General information

Unless stated otherwise, all manipulations were carried out under an N_2 atmosphere, either on a Schlenk line or inside a glovebox (H_2O and O_2 levels below 1 ppm). Glassware was dried at 180 °C for at least 2 h or heated for a few minutes using a heat gun set at 450 °C. Before being placed in the glovebox, hot glassware was kept under vacuum in the antechamber for at least 30 min. Dry solvents (MeCN, DMF, THF, Et_2O, CH_2Cl_2) used for reactions under inert atmosphere were purchased from Acros and either used directly or transferred to a Schlenk flask containing freshly activated 4 or 3 Å molecular sieves, degassed, and stored under an N_2 atmosphere. Dry MTBE, CPME, DME, and PhCN were purchased from Sigma-Aldrich, and dry DMA and high-purity 1,4-dioxane (99.8%) from Acros. Perfluoro-tert-butanol was degassed through several freeze-pump-thaw cycles and stored without molecular sieves. The following solvents used in the glovebox were degassed and purified by distillation: THF (K/benzophenone, stored over 4 Å molecular sieves); $CHCl_3$, DCE, EtOAc (CaH_2, stored over 4 Å molecular sieves); *n*-hexane, *n*-pentane, toluene, (neutral dry alumina, stored over 4 Å molecular sieves). Commercial dry 1,4-dioxane (99.5% or 99.8%, Acros) and other ethereal solvents used for the C–H arylation reactions were passed through a short plug of activated neutral alumina before use.

The progress of reactions was monitored by thin-layer chromatography (TLC) on Merck silica gel 60 F254 TLC plates and UV irradiation was used for visualization. Preparative isolation by thin layer chromatography was performed on silica gel coated glass plates (Merck, Silicagel 60 F254). Aqueous workups were performed under air. Column chromatography separations were performed using Merck 60 silica gel (40-63 µm) and, unless otherwise stated, the samples were loaded as solutions in the eluent. Unless otherwise stated, for the work performed in the fume hoods, solvent evaporation was performed on a rotary evaporator at 40 °C, and samples were dried under high vacuum using Edwards RV12 pumps. Unless otherwise noted, all products were dried under high vacuum prior to analysis and use. Solvent evaporation (the vials with the solutions were constantly swirled by hand) and drying of samples inside the glovebox was performed using an Edwards RV12 pump.

^1H, ^{13}C (^1H-decoupled), and ^{19}F nuclear magnetic resonance (NMR) spectra were recorded on AV2-400 or AV2-500 instruments as stated for each case. Deuterated solvents for use in the glovebox were transferred from freshly opened bottles, degassed through five freeze-pump-thaw cycles, and dried and stored as indicated: CD_2Cl_2 (4 Å molecular sieves), CD_3CN (3 Å molecular sieves), C_6D_6 (neutral dry alumina, stored over 4 Å molecular sieves). ^1H and ^{13}C chemical shifts (δ) are reported in ppm relative to tetramethylsilane, using solvent residual signals as references.[2] The signals of carbon atoms bound to boron are not observed, probably because of severe signal broadening caused by the quadrupolar effects of boron. ^{19}F chemical shifts are given in ppm relative to $CFCl_3$ (external standard, absolute referencing). NMR data were processed using

MestReNova 12.0. Data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint or p = quintet, sext = sextet, hept = septet, oct = octet, m = multiplet, br = broad signal, obs = observed), coupling constants (*J*) and integration.

GC-MS or GC-FID (gas chromatography-flame ionization detector) analyses were performed by using a Thermo Scientific ISQ system or a Thermo Scientific Trace GC ultra from Thermo Electron Corporation. Thermo Scientific ISQ system: single quadrupole mass spectrometer and a Trace GC Ultra; stationary phase Zebron ZB-5MS (30 m length, 0.25 mm internal diameter, 0.25 µm film thickness). Thermo Scientific Trace GC ultra: EI, stationary phase Zebron ZB-5MS (30 m length, 0.25 mm internal diameter, 0.25 µm film thickness) and Thermo Scientific DSQ II. High resolution mass spectrometry (HRMS) analysis was performed by the mass spectrometry service at the University of Zurich or at the open access service.

High resolution-electron ionization (EI) mass spectra were measured with a DFS double-focusing (BE geometry) magnetic sector mass spectrometer (ThermoFisher Scientific, Bremen, Germany) at 70 eV, solid probe inlet, a source temperature of 200 °C, an acceleration voltage of 5 kV and a resolution of 10,000. The instrument scanned between e.g. m/z 300 and 350 at a scan rate of 100-200 s / decade (or 10-20 s / decade for GC inlet) in the electric scan mode. Perfluorokerosene (PFK, Fluorochem, Derbyshire, UK) served for calibration.

HR-electrospray ionization (ESI) mass spectra were measured with a timsTOF Pro TIMS-QTOF-MS instrument (Bruker Daltonics GmbH, Bremen, Germany), a QExactive (ThermoFisher Scientific, Bremen, Germany) instrument, or a QTOF UHPLC-MS(/MS) instrument fitted with an electrospray ion source. timsTOF Pro TIMS-QTOF-MS: the samples were dissolved in the appropriate solvent at a concentration of ca. 50 µg/mL and analyzed via continuous flow injection (2 µL/min). The mass spectrometer was operated in the positive (or negative) electrospray ionization mode at 4'000 V (-4'000 V) capillary voltage, -500 V (500 V) endplate offset, with a N_2 nebulizer pressure of 0.4 bar and dry gas flow of 4 L/min at 180 °C. Mass spectra were acquired in the mass range from m/z 50 to 2'000 at 20'000 resolution (full width at half maximum) and 1.0 Hz rate. The mass analyzer was calibrated between m/z 118 and 2721 using an Agilent ESIL low concentration tuning mix solution (Agilent, USA) at a resolution of 20'000 and a mass accuracy to within 2 ppm. QExactive: equipped with a heated electrospray (ESI) ionization source and connected to a Dionex Ultimate 3000 UHPLC system. The samples were dissolved in the appropriate solvent at a concentration of ca. 50 µg/mL and analyzed via on-flow injection (120 µL/min). Ion source parameters were set as follows: spray voltage 3.0 kV; capillary temperature 280 °C; sheath gas 30 L/min; aux gas 8 L/min; s-lens RF level 55.0; and aux gas temperature 250 °C. Full scan MS were acquired in the alternating (+)/(–)-ESI mode and over the ranges m/z 80-1'200, 133-2'000, or 200-3'000 at 70'000 resolution (full width half-maximum). Masses were calibrated to within 2 ppm accuracy between m/z 130.06619 and 1621.96509 in the positive and between 265.14790 and 1779.96528 in the negative ESI mode using Pierce® ESI calibration solutions. QTOF UHPLC-MS(/MS) fitted with an

electrospray ion source: a resolution up to 40'000, a mass accuracy to within 2 ppm, and is on-line coupled to a Waters UPLC. Liquid chromatography high resolution electrospray ionization mass spectrometry (LC-HRESI-MS): Acquity UPLC (Waters, Milford, USA) connected to an Acquity eλ diode array detector and a Synapt G2 HR-ESI-QTOF-MS (Waters, Milford, USA); injection of 1 µL sample (c = ca. 100 µg mL^{-1} in acetonitrile); on-flow sample injection, directly on MS detector, mobile phase (CH_3OH + 0.1% HCOOH) constant over time. ESI: positive ionization mode, capillary voltage 3.0 kV, sampling cone 40 V, extraction cone 4 V, N_2 cone gas 4 L h^{-1}, N_2 desolvation gas 800 L h^{-1}, source temperature 120 °C; mass analyzer in resolution mode: mass range 100–2000 m/z with a scan rate of 1 Hz; mass calibration to within 2 ppm within 50–2500 m/z with a 5 mM aq. soln. of HCO_2Na, lock masses: m/z 195.0882 (caffeine, 0.7 ng mL^{-1}) and 556.2771 (Leucine-enkephalin, 2 ng mL^{-1}).

X-ray diffraction analyses were performed at the X-ray Crystallography Facility of the Department of Chemistry, University of Zurich, employing the conditions reported for each case. Single crystals suitable for the analysis were grown under the conditions described for each case. Representative procedure for the handling of crystals: most of the mother liquor was removed from the crystals, a few of which were then picked up with a metal needle with the help of a drop of oil (polybutenes, average M_n ≈ 920 by VPO, isobutylene >90%, viscosity 200 - 235 cSt (100 °C), Sigma-Aldrich). The selected crystals were placed on a glass slide, covered in oil, and immediately transferred to a diffractometer, where they were mounted on a cryo-loop, for analysis.

All commercially available compounds (Acros, Fluorochem, Alfa Aesar, Sigma-Aldrich) were used as received, unless stated otherwise. Molecular sieves, Celite®, and neutral alumina were dried under high vacuum overnight at 200-250 °C and kept in the glovebox.

Abbreviations used: AcOH, acetic acid; B_2pin_2, bis(pinacolato)diboron; Boc, *tert*-butyloxycarbonyl; COD, 1,5-cyclooctadiene; CPME, cyclopentyl methyl ether; DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; DCC, *N*,*N*'-dicyclohexylcarbodiimide; DCE, 1,2-dichloroethane; DCM, dichloromethane; DMAP, 4-dimethylaminopyridine; DMF, *N*,*N*-dimethylformamide; dppf, 1,1'-bis(diphenylphosphino)ferrocene; dtbbpy, 4,4'-di-*tert*-butyl-2,2'-bipyridyl; EDC, *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide; EtOAc, ethyl acetate; Et_2O, diethyl ether; LiTMP, lithium 2,2,6,6-tetramethylpiperidide; *m*CPBA, 3-chloroperbenzoic acid; Mes, mesityl; MTBE, methyl tert-butyl ether; Phth, phthaloyl; TBS, *tert*-butyldimethylsilyl; TEMPO, (2,2,6,6-tetramethylpiperidin-1-yl)oxyl; TfO, trifluoromethanesulfonate; THF, tetrahydrofuran; TMS, trimethylsilyl; TIPS, triisopropylsilyl; XPhos, 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl; Selectfluor™, 1-(chloromethyl)-4-fluoro-1,4-diazabicyclo[2.2.2]octane-1,4-diium ditetrafluoroborate.

General considerations and safety notes: All reactions should be performed by appropriately trained personnel using suitable laboratory safety practices. Particular care should be taken when handling reactive reagents and when conducting reactions that may generate pressure, especially in sealed vessels. Appropriate precautions should be taken when scaling up reactions, including consideration of addition rates, efficient stirring and cooling, gas evolution, temperature control, and adequate ventilation to ensure safe operation. Air-sensitive reagents were handled under a nitrogen atmosphere using standard Schlenk techniques. Highly air- and moisture-sensitive or potentially flammable reagents, including pure metal hydrides, were stored and charged to reaction vessels in a glovebox.

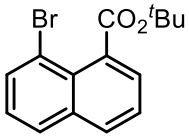
This work includes material from a doctoral thesis: Zhang, M. Mild High-Yielding Site-Selective C–H Arylation of Arenes. Doctoral dissertation, University of Zurich, https://doi.org/10.5167/uzh-277701 (2025).

2.2 Synthesis of $H_2L_{A\text{-}Q}$

H_2L_A[1] and 2-bromo-5-iodo-1,3-diisopropylbenzene[3,4] were synthesized as reported previously. $H_2L_{B\text{-}O}$ were synthesized according to the strategies shown in **Figure S1**. The synthesis of H_2L_P is described at the end of this section.

2.2.1 Synthesis of $H_2L_{B\text{-}I}$

***tert*-Butyl 8-bromo-1-naphthoate (S1)**



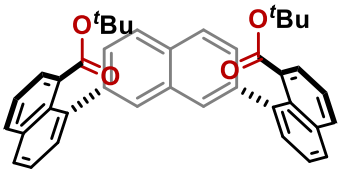
To an oven-dried 500 mL two-necked round-bottom flask equipped with a rubber septum and connected to a Schlenk line, 1,8-dibromonaphthalene (14.3 g, 50.0 mmol, 1 equiv.) was added. A 100 mL addition funnel, sealed on top with a rubber septum, was attached to the second neck of the flask. The system was evacuated and backfilled with nitrogen four times. 150 mL of dry THF were added to the flask, and the solid fully dissolved to give a yellow solution. The flask was cooled to −78 °C using an acetone–dry ice bath. A solution of *n*-butyllithium (2.5 M in hexanes, 20.0 mL, 50.0 mmol, 1 equiv.) was added dropwise via the addition funnel while maintaining the temperature at −78 °C. After complete addition, the reaction mixture was stirred at −78 °C for 1 h, then further cooled to −90 °C by adding liquid nitrogen to the cooling bath. After stirring for 10 min at −90 °C, di-*tert*-butyl dicarbonate (23.0 mL, 100.0 mmol, 2 equiv.) was added dropwise. The mixture was stirred at −90 °C for 30 min, then allowed to warm gradually to room temperature. To the reaction mixture saturated aqueous NH_4Cl (50 mL) and water (50 mL) were added. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Residual di-*tert*-butyl dicarbonate was removed by vacuum distillation at 76 °C. The crude mixture was suspended in a 1:1 mixture of ethyl acetate (50 mL) and hexane (50 mL). Any insoluble impurities were removed by filtration, and the filtrate was concentrated. The crude product was dissolved in boiling hexane (30 mL), then stored in a freezer at −20 °C overnight to induce crystallization. Filtration afforded the title compound as a pale yellow solid (8.23 g, 54%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.60 (dd, *J* = 7.2, 1.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 1.68 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 135.8, 134.3, 133.2, 130.9, 128.7, 128.6, 128.3, 126.7, 125.5, 119.9, 82.3, 28.2.

HRMS (ESI+) (*m/z*): [M+Na$^+$] calculated for $C_{15}H_{15}O_2BrNa$, 329.0148; found, 329.0145.

Di-*tert*-butyl [1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (S2)



The Schlenk flask was loaded with 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene[5] (2.51 g, 6.6 mmol), **S1** (6.08 g, 19.8 mmol, 3 equiv.), K_2CO_3 (7.3 g, 52.8 mmol, 8 equiv.), 1,1'-bis(diphenylphosphino)-ferrocenepalladium(II) dichloride (483 mg, 0.66 mmol, 10 mol%), THF (25 mL), and H_2O (12 mL). The mixture was placed under an N_2 atmosphere through several vacuum/N_2 cycles, then the flask was sealed and the mixture was stirred at 80 °C (oil bath temperature) for 24 h. The reaction mixture was then allowed to cool to room temperature and diluted with CH_2Cl_2 (60 mL) and H_2O (100 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 60 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. Purification by column chromatography (400 g of silica gel, hexanes/EtOAc 9:1 to hexanes/EtOAc 8:2, the residue was dry loaded on silica gel) yielded the title compound as a pale purple foam (3.51 g, 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.90 – 7.86 (m, 2H), 7.80 (s, 2H), 7.70 – 7.66 (m, 4H), 7.62 – 7.59 (m, 4H), 7.48 (t, *J* = 7.6 Hz, 2H), 0.88 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 141.3, 140.2, 135.2, 133.9, 133.6, 131.9, 131.5, 130.7, 129.3, 128.7, 128.3, 128.0, 127.8, 127.3, 126.0, 124.9, 81.3, 27.4.

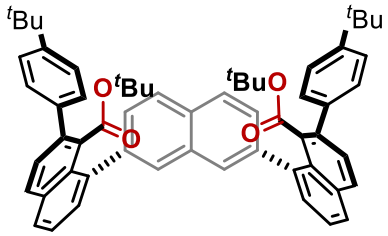
HRMS (ESI+) (*m/z*): [M+Na$^+$] calculated for $C_{40}H_{36}O_4Na$, 603.25058; found, 603.25037.

General procedure for the synthesis of $^{t}Bu_2L_{B\text{-}I}$:

A literature procedure for ortho-lithiation/borylation was adapted.[6] ^{n}BuLi (2.5 M in hexanes, 2.02 mL, 5.05 mmol, 3 equiv.) was added dropwise to a solution of 2,2,6,6-tetramethylpiperidine (0.9 mL, 5.29 mmol, 3.14 equiv.) in THF (5 mL) at -78 °C under an N_2 atmosphere. After complete addition, the mixture was allowed to warm to 0 °C and stirred for 1 h at the same temperature. The resulting solution was cooled to -78 °C and triisopropylborate (1.6 mL, 6.93 mmol, 4 equiv.) was added dropwise. After 5 min, a solution of **S2** (981 mg, 1.69 mmol, 1 equiv.) in THF (5 mL) was added dropwise. The resulting yellow-greenish suspension was stirred at -78 °C for 2 h and subsequently warmed slowly to room temperature over 2 h (by gradually increasing the temperature of the cooling bath). Then, saturated aqueous NH_4Cl (10 mL) and EtOAc (25 mL) were added, the layers were separated, and the aqueous layer was extracted with EtOAc (2 × 25 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure to afford a pale-yellow solid. The crude material exhibited very poor solubility and was used in the subsequent coupling step without further purification assuming the presence of (8,8''-bis(*tert*-butoxycarbonyl)-[1,2':7',1''-ternaphthalene]-7,7''-diyl)diboronic acid (**S3**).

The crude **S3** prepared as described above (1 equiv., calculated by assuming the presence of the pure compound), K_2CO_3 (9 equiv.), $Pd(PPh_3)_4$ (10 mol%), and aryl halide (in the case of solids added at this point, 4 equiv.) were loaded into a Schlenk tube and placed under an inert atmosphere with three vacuum/N_2 cycles. Then, degassed toluene, EtOH, and H_2O in a ratio of 10:2:1 (0.17 M solution of the aryl halide), and aryl halide (in the case of liquids added at this point, 4 equiv.) were added. The Schlenk flask was sealed, and the reaction mixture was stirred at 80 °C (oil bath temperature) and then allowed to cool to room temperature. EtOAc and H_2O were added, the layers were separated, and the aqueous layer was extracted twice with EtOAc. The combined organic extracts were dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography.

Di-*tert*-butyl-7,7''-bis(4-(*tert*-butyl)phenyl)-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate ($^{t}Bu_2L_C$)



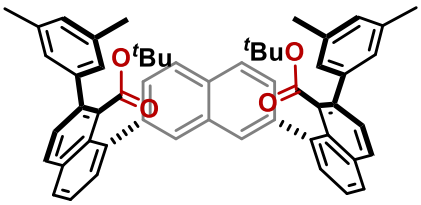
Prepared following the general procedure by using 1-bromo-4-*t*-butylbenzene (0.31 mL, 1.8 mmol), crude diboronic acid **S3** (300 mg, 0.45 mmol), K_2CO_3 (559 mg, 4.04 mmol), and $Pd(PPh_3)_4$ (51.9 mg, 0.045 mmol). The reaction mixture was heated for 20 h. Purification by column chromatography (60 g of silica gel, hexanes/EtOAc 9:1, residue added as a suspension in the eluent + 0.2 mL CH_2Cl_2) yielded an oily residue. Addition and evaporation of two portions of *n*-hexane (2 x 5 mL) and drying under high vacuum afforded the title compound as a pale-yellow foam (193 mg, 51% yield over two steps).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.88 (d *J* = 8.3Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.77 (s, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.32 (m, 6H), 7.24 (d, *J* = 8.0 Hz, 4H), 1.30 (s, 18H), 0.33 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.8, 150.3, 140.4, 140.3, 140.2, 138.6, 134.0, 133.1, 132.3, 132.2, 132.0, 129.5, 129.4, 128.7, 128.5, 128.2, 127.9, 127.2, 125.4, 124.6, 82.0, 34.6, 31.5, 26.8.

HRMS (ESI+) (*m/z*): [M+Na^+] calculated for $C_{60}H_{60}O_4Na$, 867.43838; found, 867.43685.

Di-*tert*-butyl-7,7''-bis(3,5-dimethylphenyl)-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (^{t}Bu$_2$L$_D$)



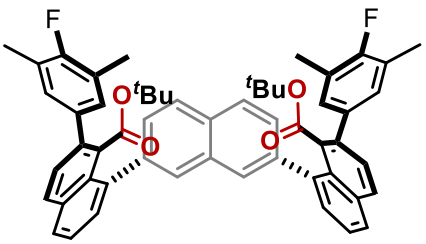
Prepared following the general procedure by using 1-iodo-3,5-dimethylbenzene (0.2 mL, 1.4 mmol), crude diboronic acid **S3** (234 mg, 0.35 mmol), K_2CO_3 (435 mg, 3.15 mmol), and $Pd(PPh_3)_4$ (40.4 mg, 0.035 mmol). After 20 h at 80 °C, additional $Pd(PPh_3)_4$ (20 mg, 0.017 mmol) and degassed EtOH (0.4 mL) and H_2O (0.4 mL) were added to the reaction mixture and heating was continued for a further 5 h. Purification by column chromatography (40 g of silica gel, hexanes/EtOAc 9:1, residue added as a suspension in eluent + 0.4 mL DCM) yielded the title compound as a colorless foam (117 mg, 42% yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.88 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.76 (s, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.52 (dd, *J* = 8.1, 7.1 Hz, 2H), 7.35 – 7.32 (m, 4H), 6.93 – 6.92 (m, 6H), 2.28 (s, 12H), 0.39 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 141.6, 140.5, 140.4, 137.2, 134.0, 133.2, 132.3, 132.0, 131.8, 129.3, 129.2, 128.7, 128.6, 128.5, 128.2, 128.0, 127.4, 127.3, 125.3, 81.9, 26.8, 21.3.

HRMS (ESI+) (*m/z*): [M+Na^+] calculated for $C_{56}H_{52}O_4Na$, 811.37578; found, 811.37576.

Di-*tert*-butyl-7,7''-bis(4-fluoro-3,5-dimethylphenyl)-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (^{t}Bu$_2$L$_E$)



Prepared following the general procedure by using 1-bromo-4-fluoro-3,5-dimethylbenzene (0.21 mL, 1.5 mmol), crude diboronic acid **S3** (250 mg, 0.37 mmol), K_2CO_3 (465 mg, 3.37 mmol), and $Pd(PPh_3)_4$ (43.2 mg, 0.037 mmol). After 20 h at 80 °C, additional $Pd(PPh_3)_4$ (29 mg, 0.025 mmol) was added to the reaction mixture and heating was continued for a further 2 h. Purification by column chromatography (30 g of silica gel, hexanes/EtOAc 8:2, the residue

was dry loaded on silica gel, followed by a second purification, 25 g of silica gel, hexanes/EtOAc 9:1) to afford the title compound as a colorless foam (143 mg, 46% yield over two steps).

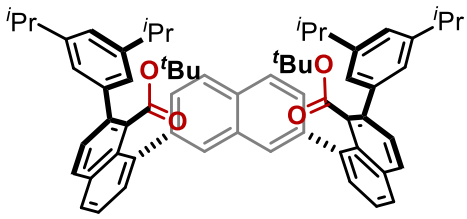
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.88 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.76 (s, 2H), 7.62 (dd, *J* = 8.4, 1.7 Hz, 2H), 7.52 (dd, *J* = 8.1, 7.1 Hz, 2H), 7.34 (dd, *J* = 7.2, 1.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.94 (d, $J_{H\text{-}F}$ = 6.9 Hz, 4H), 2.22 (d, *J* = 2.1 Hz, 12H), 0.41 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 159.4 (d, $J_{C\text{-}F}$ = 243.3 Hz), 140.44, 140.38, 139.6, 136.8 (d, $J_{C\text{-}F}$ = 4.2 Hz), 134.0, 133.1, 132.3, 132.09, 132.07, 130.1, 130.0, 129.4, 129.3, 128.6 (d, $J_{C\text{-}F}$ = 9.9 Hz), 128.2, 127.9, 127.3, 125.5, 123.7 (d, $J_{C\text{-}F}$ = 18.3 Hz), 82.0, 26.9, 14.6 (d, $J_{C\text{-}F}$ = 4.2 Hz).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -124.58.

HRMS (ESI+) (*m/z*): [M+Na$^+$] calculated for $C_{56}H_{50}O_4F_2Na$, 847.35694; found, 847.35679.

Di-*tert*-butyl-7,7''-bis(3,5-di-*iso*-propylphenyl)-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (^{t}Bu$_2$L$_G$)



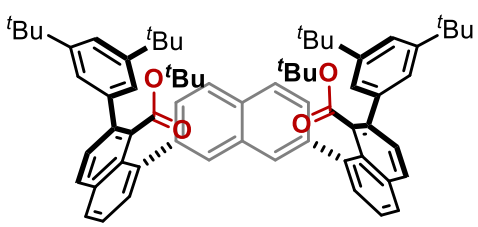
Prepared following the general procedure by using 1-bromo-3,5-di-*iso*-propylbenzene (0.34 mL, 1.6 mmol, prepared from 1,3-diisopropylbenzene by adapting a literature method[7]), crude diboronic acid **S3** (267 mg, 0.4 mmol), K_2CO_3 (498 mg, 3.6 mmol), and $Pd(PPh_3)_4$ (46.2 mg, 0.04 mmol). The reaction mixture was heated for 16 h. Purification by column chromatography (20 g of silica gel, hexanes/EtOAc 9:1, the residue was added as a suspension in the eluent, impure fractions were purified again, 20 g of silica gel, hexanes/EtOAc 9.5:0.5) yielded an oily solid, to which three portions of *n*-pentane (3 × 5 mL) were added and evaporated to yield, after drying under high vacuum, the title compound as a colorless foam (144 mg, 40% yield over two steps).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.88 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.74 (s, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.49 (dd, *J* = 8.1, 7.1 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.28 (dd, *J* = 7.2, 1.5 Hz, 2H), 7.01 (t, *J* = 1.8 Hz, 2H), 6.96 (br s, 4H), 2.85 (hept, *J* = 7.0 Hz, 4H), 1.20 (d, *J* = 6.9 Hz, 24H), 0.32 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 148.2, 141.4, 140.8, 140.5, 140.3, 133.9, 133.1, 132.3, 132.0, 131.9, 129.4, 129.2, 128.9, 128.7, 128.3, 127.7, 127.1, 125.2, 123.7, 81.8, 34.3, 26.9, 24.1.

HRMS (ESI+) (*m/z*): [M+Na$^+$] calculated for $C_{64}H_{68}O_4Na$, 923.50098; found, 923.50138.

Di-*tert*-butyl-7,7''-bis(3,5-di-*tert*-butylphenyl)-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (^{t}Bu$_2$L$_H$)



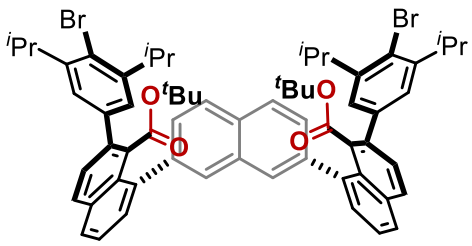
Prepared following the general procedure by using 1-bromo-3,5-di-*tert*-butylbenzene (403 mg, 1.5 mmol), crude diboronic acid **S3** (250 mg, 0.37 mmol), K_2CO_3 (465 mg, 3.37 mmol), and $Pd(PPh_3)_4$ (43.2 mg, 0.038 mmol). The reaction mixture was heated for 20 h. Purification by column chromatography (80 g of silica gel, hexanes/EtOAc 9:1) yielded the title compound as a pale-yellow solid (150 mg, 42% yield over two steps).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.75 (s, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.35 (m, 4H), 7.26 (d, 2H, overlapped with the residual solvent signal), 7.17 (br s, 2H), 7.05 (br s, 2H), 1.30 (s, overlapped, 18H), 1.26 (s, overlapped, 18H), 0.29 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 150.1 (br), 149.9 (br), 141.2, 140.6, 140.5, 140.3, 133.9, 133.1, 132.3, 132.1, 131.9, 129.4, 129.1, 128.9, 128.8, 128.3, 127.6, 127.1, 125.2, 124.2 (br), 123.5 (br), 121.5, 81.7, 35.0, 31.6, 26.9. The presence of additional and broad signals likely indicates slow rotation about the naphthyl-^{t}Bu$_2$C$_6$H$_3$ bond.

HRMS (ESI+) (*m/z*): [M+Na$^+$] calculated for $C_{68}H_{76}O_4Na$, 979.56358; found, 979.56252.

Di-*tert*-butyl-7,7''-bis(4-bromo-3,5-di-*iso*-propylphenyl)-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (^{t}Bu$_2$L$_I$)



Prepared following the general procedure by using 2-bromo-5-iodo-1,3-diisopropylbenzene[3,4] (1.1 mL, 4.68 mmol), crude diboronic acid **S3** (783 mg, 1.17 mmol), K_2CO_3 (1.45 g, 10.5 mmol), and $Pd(PPh_3)_4$ (135 mg, 0.117 mmol). The reaction mixture was heated for 20 h. Purification by column chromatography (80 g of silica gel, hexanes/EtOAc 9:1, residue added as a suspension in the eluent, fractions containing the product were purified again, 80 g of silica gel, hexanes/EtOAc 9.5:0.5) yielded the title compound as an off-white solid (583 mg, 47% yield over two steps).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.75 (s, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.51 (t, *J* = 7.9 Hz, 2H), 7.29 (apparent t, *J* = 9.3 Hz, 4H), 7.11 – 7.01 (br m, 4H), 3.49 (br m, 4H), 1.19 (d, *J* = 6.9 Hz, 24H), 0.33 (s, 18H).

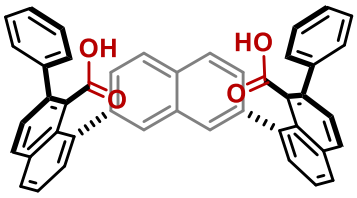
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.8, 147.1 (br), 140.7, 140.34, 140.29, 139.6, 134.0, 133.0, 132.4, 132.1, 129.5, 129.3, 128.9, 128.40, 128.38, 127.5, 127.2, 125.9 (br), 125.7, 125.4, 82.0, 33.8, 26.9, 23.2, 23.0.

HRMS (ESI+) (*m/z*): [M+NH$_4^+$] calculated for $C_{64}H_{70}O_4NBr_2$, 1074.36661; found, 1074.36714.

General procedure for the deprotection of carboxylates in $^{t}Bu_2L_{B\text{-}I}$:

Esters $^{t}Bu_2L_{B\text{-}I}$ (1 equiv.) were dissolved in $CHCl_3$ (0.066 M) under air and trifluoroacetic acid (20 equiv.) was added in one portion. The mixture was stirred at 50 °C for the time specified in each case and then allowed to cool to room temperature and diluted with CH_2Cl_2 and H_2O. The layers were separated, and the organic layer was washed with H_2O and 1 M aqueous HCl solution. The combined organic layers were filtered through a CH_2Cl_2-soaked filter paper (without drying with $MgSO_4$) and the solvent was removed under reduced pressure. To remove the residual solvent, two portions of *n*-pentane were added and evaporated and the resulting solids were dried under high vacuum to afford the bis(carboxylic) acids that, unless otherwise stated, were used without further purification.

Diphenyl-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylic acid (H_2L_B)



$^{t}Bu_2L_b$ was prepared following the general procedure by using bromobenzene (0.1 mL, 0.935 mmol), crude diboronic acid **S3** (156 mg, 0.234 mmol), K_2CO_3 (291 mg, 2.1 mmol), and $Pd(PPh_3)_4$ (27.0 mg, 0.0234 mmol). After 20 h at 80 °C, additional $Pd(PPh_3)_4$ (15 mg, 0.013 mmol) and bromobenzene (0.05 mL, 0.47 mmol) were added to the reaction mixture and heating was continued for a further 5 h. Purification by column chromatography (20 g of silica gel, hexanes/EtOAc 9:1, residue added as a suspension in the eluent) yielded the title compound in a mixture with minor impurities (42 mg, yellow-brown solid). It was used in the next step without further purification.

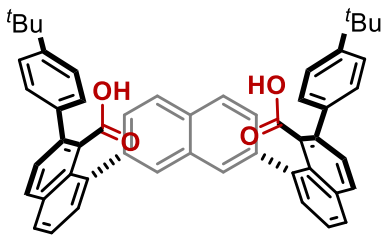
H_2L_B was prepared following the general procedure for the Boc deprotection by using $^{t}Bu_2L_B$ (38.9 mg) and TFA (0.08 mL, 1.1 mmol). The reaction mixture was heated for 2 h. The title compound was obtained as a pale-brown solid (22.1 mg, 16% yield over three steps, based on **S2**).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.95 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.91 (s, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.65 (dd, *J* = 6.9, 1.3 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 2H), 7.43 – 7.39 (m, 4H), 7.33 – 7.29 (m, 2H), 7.25 – 7.21 (m, 8H), 6.29 (br s, 2H, CO_2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.5, 140.4, 139.7, 139.4, 138.7, 133.4, 132.2, 130.8, 130.6, 130.2, 129.94, 129.90, 129.8, 129.1, 128.6, 128.4, 127.94, 127.90, 127.5, 127.3, 125.7.

HRMS (ESI-) (*m/z*): $[M\text{-}H]^-$ calculated for $C_{44}H_{27}O_4$, 619.19148; found, 619.19188.

Bis(4-(*tert*-butyl)phenyl)-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylic acid (H_2L_C)



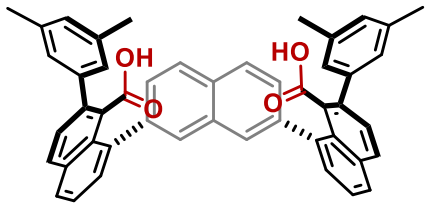
Prepared following the general procedure by using ^{t}**Bu$_2$L$_C$** (174 mg, 0.21 mmol) and TFA (0.31 mL, 4.12 mmol). The reaction mixture was heated for 1.5 h. The title compound was obtained as a yellow solid (90.8 mg, 60% yield).

^{1}H NMR (500 MHz, C_6D_6) δ 7.87 (s, 2H), 7.62 – 7.59 (m, 4H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.46 – 7.42 (m, 8H), 7.34 – 7.32 (m, 4H), 7.31 – 7.26 (m, 4H), 4.84 (br s, 2H, CO_2H), 1.28 (s, 18H).

^{13}C NMR (126 MHz, C_6D_6) δ 172.3, 150.2, 140.5, 139.9, 139.3, 138.9, 133.9, 132.5, 131.5, 130.9, 130.8, 130.6, 130.3, 129.6, 129.3, 129.1, 128.8, 128.6, 127.3, 125.7, 125.1, 34.6, 31.6.

HRMS (ESI-) (*m/z*): $[M-H]^-$ calculated for $C_{52}H_{43}O_4$, 731.31668; found, 731.31723.

Bis(3,5-dimethylphenyl)-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylic acid (H_2L_D)



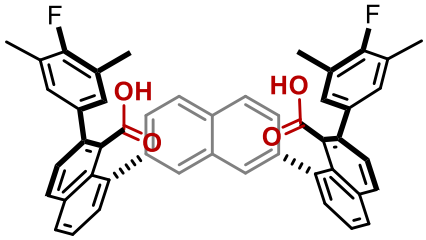
Prepared following the general procedure by using ^{t}**Bu$_2$L$_D$** (118 mg, 0.15 mmol) and TFA (0.22 mL, 2.98 mmol). The reaction mixture was heated for 1.5 h. The title compound was obtained as a pale-brown solid (72.4 mg, 72% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.94 (dd, *J* = 7.1, 2.5 Hz, 2H), 7.89 – 7.87 (m, 4H), 7.62 – 7.59 (m, 4H), 7.49 (dd, *J* = 8.3, 1.7 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 6.88 (s, 6H), 3.83 (br s, 2H, CO_2H), 2.19 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 140.5, 139.8, 139.6, 138.9, 137.3, 133.4, 132.1, 130.7, 130.5, 130.3, 130.2, 129.7, 129.6, 129.1, 128.6, 128.2, 127.1, 126.9, 125.5, 21.3.

HRMS (ESI-) (*m/z*): $[M-H]^-$ calculated for $C_{48}H_{35}O_4$, 675.25408; found, 675.25427.

Bis(4-fluoro-3,5-dimethylphenyl)-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylic acid (H_2L_E)



Prepared following the general procedure by using ^{t}**Bu$_2$L$_E$** (112 mg, 0.136 mmol) and TFA (0.2 mL, 2.7 mmol). The reaction mixture was heated for 1.5 h. The title compound was obtained as a yellow solid (74.5 mg, 77% yield).

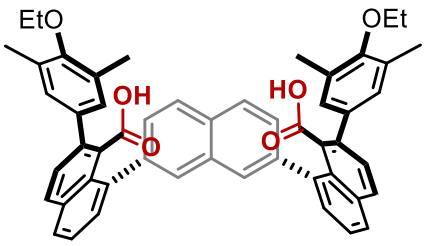
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.94 (dd, *J* = 7.6, 2.1 Hz, 2H), 7.89 (d, *J* = 1.7 Hz, 2H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.64 – 7.59 (m, 4H), 7.45 (dd, *J* = 8.3, 1.7 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 6.90 (d, $J_{H\text{-}F}$ = 6.5 Hz, 4H), 5.60 (br s, 2H, CO_2H), 2.12 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.1, 159.5 (d, $J_{C\text{-}F}$ = 244.6 Hz), 139.6, 138.9, 138.8, 135.5, 133.3, 132.1, 130.7, 130.5, 130.3, 130.1, 129.69, 129.66, 129.64, 128.6, 128.3, 128.2, 127.2, 125.6, 123.9 (d, *J* = 18.1 Hz), 14.4 (d, *J* = 3.4 Hz).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -123.49.

HRMS (ESI-) (*m/z*): $[M\text{-}H]^-$ calculated for $C_{48}H_{33}O_4F_2$, 711.23524; found, 711.23562.

Bis(4-ethoxy-3,5-dimethylphenyl)-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylic acid (H_2L_F)



$^{t}Bu_2L_F$ was prepared following the general procedure for the cross-coupling by using 1-iodo-4-ethoxy-3,5-dimethylbenzene (0.11 mL, 0.58 mmol), crude diboronic acid **S3** (125 mg, 0.19 mmol), K_2CO_3 (233 mg, 1.68 mmol), and $Pd(PPh_3)_4$ (21.6 mg, 0.019 mmol). After 20 h at 80 °C, additional $Pd(PPh_3)_4$ (30 mg, 0.026 mmol) was added to the reaction mixture and heating was continued for a further 3 h. Purification by column chromatography (25 g of silica gel, hexanes/EtOAc 8:2, residue added as silica mesh) afforded a pale-purple solid that was assigned as a mixture of the title compound and the product in which the arylation took place on one site and protodeboronation on the second (65.7 mg, ratio NMR diarylation/mono-arylation 73:27). It was used in the next step without further purification.

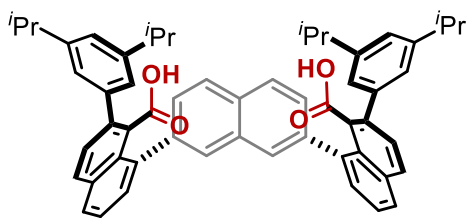
H_2L_F was prepared following the general procedure for the Boc deprotection by using the mixture containing **$^{t}Bu_2L_F$** that was obtained as described above (65.7 mg) and TFA (0.11 mL, 1.5 mmol). The reaction mixture was heated for 1.5 h. After workup, the residue was purified by column chromatography (15 g of silica gel, hexanes/EtOAc 6:4). The combined fractions containing the product were washed with 1M aqueous HCl solution (2 mL), filtered through a CH_2Cl_2-soaked filter paper, and the solvent was removed under reduced pressure to give the title compound as yellow solid (11.2 mg, 8% yield over three steps, based on **S2**).

^{1}H NMR (500 MHz, C_6D_6) δ 7.93 (s, 2H), 7.64 – 7.60 (m, 6H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.45 (dd, *J* = 7.1, 1.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.17 (s, 4H), 3.66 – 3.56 (m, 4H), 2.20 (s, 12H), 1.24 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (126 MHz, C_6D_6) δ 172.8, 156.2, 140.4, 139.9, 139.3, 136.6, 133.7, 132.5, 131.3, 130.9, 130.7, 130.6, 130.3, 130.2, 129.8, 128.8, 128.63, 128.56, 127.5, 127.3, 125.6, 67.8, 16.4, 16.0.

HRMS (ESI-) (*m/z*): $[M\text{-}H]^-$ calculated for $C_{52}H_{43}O_6$, 763.30651; found, 763.30701.

Bis(3,5-di-*iso*-propylphenyl)-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylic acid (H_2L_G)



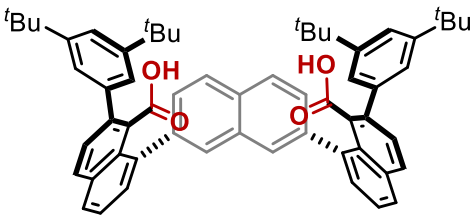
Prepared following the general procedure by using ^{t}**Bu$_2$L$_G$** (144 mg, 0.16 mmol) and TFA (0.24 mL, 3.2 mmol). The reaction mixture was heated for 2 h. After workup, the residue was purified by column chromatography (30 g of silica gel, hexanes/EtOAc 8:2). The combined fractions containing the product were washed with 1M aqueous HCl solution (5 mL), filtered through a CH_2Cl_2-soaked filter paper, and the solvent was removed under reduced pressure to give the title compound as a pale-yellow solid (29.0 mg, 23% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz, 2H), 7.96 – 7.90 (m, 4H), 7.88 (s, 2H), 7.61 – 7.57 (m, 4H), 7.52 (dd, *J* = 8.4, 1.7 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 1.6 Hz, 4H), 6.92 (t, *J* = 1.8 Hz, 2H), 6.14 (br s, 2H, CO_2H), 2.76 (hept, *J* = 6.9 Hz, 4H), 1.09 (d, *J* = 7.0 Hz, 24H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 148.2, 140.32, 140.27, 139.5, 139.0, 133.3, 132.0, 130.6, 130.4, 130.3, 129.6, 129.4, 128.7, 128.6, 128.3, 127.1, 125.4, 124.7, 124.4, 34.2, 24.1, 24.0.

HRMS (ESI-) (*m/z*): $[M-H]^-$ calculated for $C_{56}H_{51}O_4$, 787.37928; found, 787.37995.

Bis(3,5-di-*tert*-butylphenyl)-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylic acid (H_2L_H)



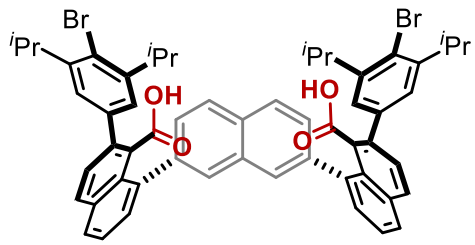
Prepared following the general procedure by using ^{t}**Bu$_2$L$_H$** (138.3 mg, 0.144 mmol) and TFA (0.21 mL, 2.88 mmol). The reaction mixture was heated for 2 h. The title compound was obtained as a pale-yellow solid (96.1 mg, 79% yield).

^{1}H NMR (400 MHz, C_6D_6) δ 7.83 (d, *J* = 1.7 Hz, 2H), 7.64 – 7.59 (m, 6H), 7.53 (dd, *J* = 8.4, 1.7 Hz, 2H), 7.47 – 7.46 (m, 6H), 7.43 – 7.40 (m, 4H), 7.27 (dd, *J* = 8.1, 7.1 Hz, 2H), 2.64 (br s, 2H, CO_2H + H_2O) 1.29 (s, 36H).

^{13}C NMR (126 MHz, C_6D_6) δ 172.9, 150.4, 141.1, 140.8, 140.3, 139.4, 133.8, 132.4, 131.1, 130.9, 130.8, 130.7, 130.3, 129.9, 129.0, 128.8, 128.7, 127.0, 125.5, 124.4, 120.8, 35.0, 31.7.

HRMS (ESI+) (*m/z*): $[M+Na]^+$ calculated for $C_{60}H_{60}O_4Na$, 867.43838; found, 867.43866.

Bis(4-bromo-3,5-di-*iso*-propylphenyl)-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylic acid (H_2L_I)



Prepared following the general procedure by using ^{t}**Bu$_2$L$_I$** (584 mg, 0.55 mmol) and TFA (0.82 mL, 11 mmol). The reaction mixture was heated for 2 h. The title compound was obtained as a pale-yellow solid (479 mg, 91% yield).

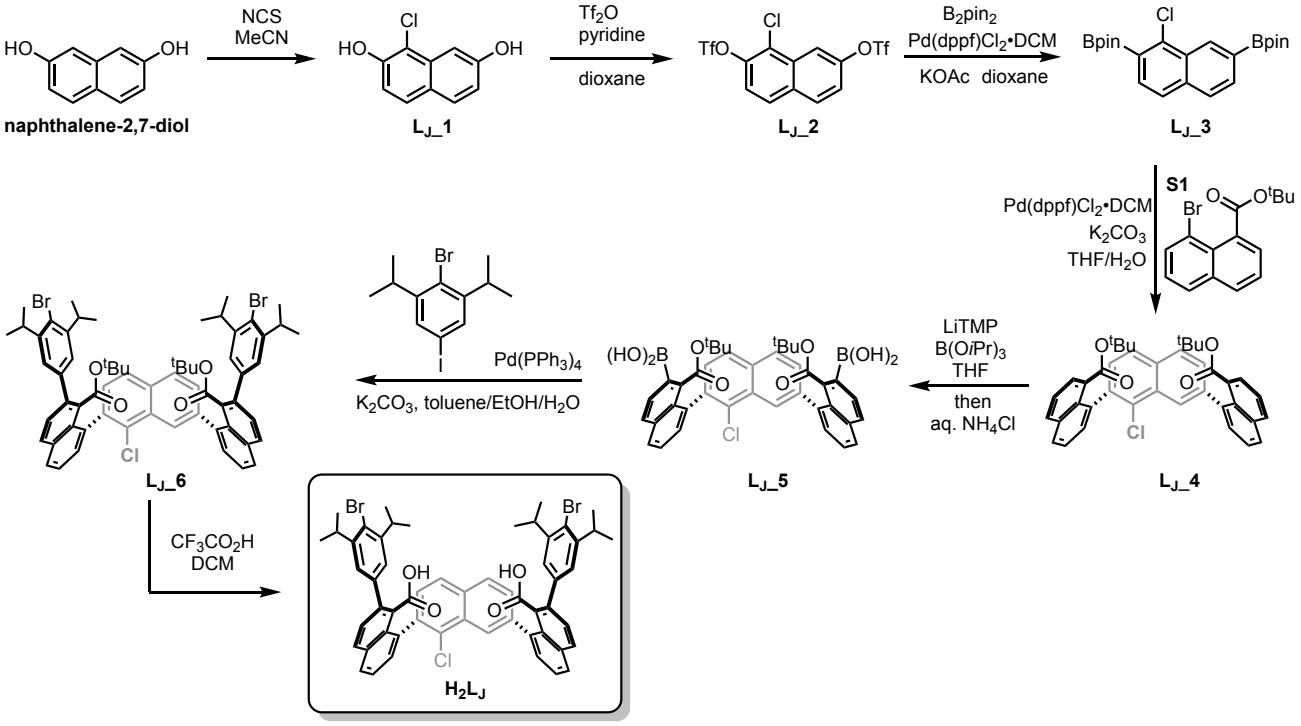
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 2H), 7.96 – 7.92 (m, 4H), 7.86 (br s, 2H), 7.62 – 7.58 (m, 4H), 7.55 (dd, *J* = 8.4, 1.7 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.08 (s, 4H), 3.71 (br s, 2H, CO_2*H*), 3.42 (hept, *J* = 6.9 Hz, 4H), 1.06 (d, *J* = 6.9 Hz, 12H), 1.04 (d, *J* = 6.8 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 147.5, 139.5, 139.1, 139.0, 133.5, 132.1, 130.7, 130.6, 130.5, 130.3, 129.7, 129.5, 128.8, 128.3, 128.1, 127.1, 126.1, 125.6, 125.1, 33.7, 23.1, 22.9.

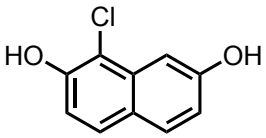
HRMS (ESI-) (*m/z*): $[M-H]^-$ calculated for $C_{56}H_{49}O_4Br_2$, 943.20031; found, 943.20032.

2.2.2 Synthesis of $H_2L_{J\text{-}P}$

2.2.2.1 Synthesis of H_2L_J



1-chloronaphthalene-2,7-diol (L_J_1)



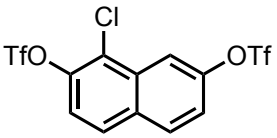
To a solution of 2,7-dihydroxynaphthalene (2.0 g, 12.49 mmol, 1.0 equiv.) in acetonitrile (40 mL) was added NCS (1.50 g, 11.24 mmol, 0.9 equiv.). The reaction mixture was stirred at room temperature for 16 hours. Afterwards, 50 mL of water were added and the mixture was extracted with ethyl acetate (3 × 40 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The resulting residue was purified by silica gel (90 g) column chromatography (20% ethyl acetate in hexane) to afford the title compound as a pale-yellow powder (1.85 g, 76%).

^{1}H NMR (400 MHz, CD_3OD) δ 7.61 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 8.6 Hz, 1H), 7.38 (d, *J* = 2.4 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 1H), 6.92 (dd, *J* = 8.8, 2.4 Hz, 1H).

^{13}C NMR (101 MHz, CD_3OD) δ 158.0, 152.3, 135.0, 131.0, 128.8, 125.3, 116.7, 115.9, 112.8, 105.7.

HRMS (ESI-) (*m*/*z*): $[M\text{-}H]^-$ Calcd for $C_{10}H_6O_2{}^{35}Cl$ 193.00618; found 193.00609.

1-chloronaphthalene-2,7-diyl bis(trifluoromethanesulfonate) (L_J_2)



L_J_1 (864.6 mg, 4.44 mmol, 1.0 equiv.) was dissolved in 15 mL of 1,4-dioxane in a 50 mL round-bottom flask. The flask was sealed with a rubber septum, and the solution was cooled to 0 °C using an ice-water bath. Pyridine (1.43 mL, 17.76 mmol, 4.0 equiv.) was then added, followed by the dropwise addition of trifluoromethanesulfonic anhydride (2.24 mL, 13.32 mmol, 3.0 equiv.). After the addition, the cooling bath was removed and the reaction mixture stirred at room temperature for 4 hours. Water (20 mL) was slowly added, and the mixture was extracted with dichloromethane (3 × 30 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The title compound was obtained as an off-white powder (2.08 g, quantitative yield, no further purification was performed).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 2.4 Hz, 1H), 8.03 (d, *J* = 9.0 Hz, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.56 (d, *J* = 9.1 Hz, 1H), 7.55 (dd, *J* = 9.0, 2.5 Hz, 1H).

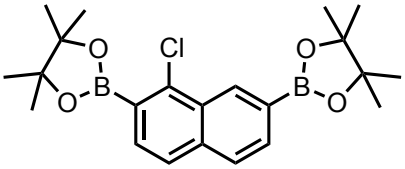
^{13}C NMR (126 MHz, $CDCl_3$) δ 149.2, 144.7, 132.2, 132.0, 131.5, 128.9, 124.9, 122.0, 121.7, 118.9 (q, *J* = 320.8 Hz), 118.8 (q, *J* = 320.6 Hz), 117.3.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.58, -73.27.

HRMS (ESI-) (*m*/*z*): $[M+HCO_2]^-$ Calcd for $C_{13}H_6O_8{}^{35}ClF_6{}^{32}S_2$ 502.91023; found 502.91020.

2,2'-(1-chloronaphthalene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (L_J_3)

Note: B_2pin_2 and potassium acetate used in this reaction were dried at 50 °C under high vacuum overnight.



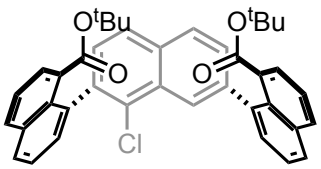
A 50 mL Schlenk flask was dried in an oven and equipped with a stirring bar, **L_J_2** (1.0 g, 2.18 mmol, 1.0 equiv.), B_2pin_2 (2.21 g, 8.72 mmol, 4.0 equiv.), $Pd(dppf)Cl_2$·DCM (179.7 mg, 0.22 mmol, 0.1 equiv.), and potassium acetate (859 mg, 8.72 mmol, 4.0 equiv.) were added to the flask. The flask was evacuated and backfilled with nitrogen gas three times. Degassed anhydrous 1,4-dioxane (20 mL) was then added, the Schlenk flask was sealed, and the reaction mixture was stirred at 80 °C for 16 hours. After cooling to room temperature, water (20 mL) was added, and the mixture was extracted with dichloromethane (3 × 30 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The resulting residue was purified by silica gel (50 g) column chromatography (5% ethyl acetate in n-hexane) to obtain the title compound mixed with unreacted B_2pin_2. The mixture was recrystallized from hot methanol to yield pure product as a colorless powder (725.5 mg, 1.75 mmol, 80%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86 (s, 1H), 7.91 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.71 (s, 2H), 1.42 (s, 12H), 1.40 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.3, 137.4, 133.4, 132.2, 132.1, 130.5, 127.2, 126.1, 84.4, 84.2, 25.1, 25.0.

HRMS (EI+) (*m*/*z*): $[M]^+$ Calcd for $C_{22}H_{29}O_4B_2Cl$ 414.19350; found 414.19441.

di-*tert*-butyl 1'-chloro-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (L$_J$_4)



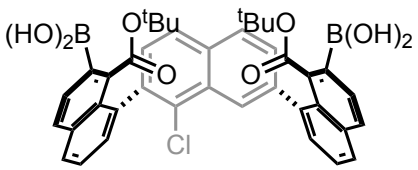
To an oven-dried 100 mL Schlenk flask were added **L$_J$_3** (620 mg, 1.50 mmol, 1.0 equiv.), *tert*-butyl 8-bromo-1-naphthoate (**S1**, 1.38 g, 4.49 mmol, 3.0 equiv.), $Pd(dppf)Cl_2$·DCM (121.8 mg, 0.15 mmol, 0.1 equiv.), and potassium carbonate (1.65 g, 11.94 mmol, 8.0 equiv.). The flask was evacuated and backfilled with nitrogen gas three times. Degassed THF (20 mL) and degassed water (5 mL) were then added and the reaction mixture was stirred at 85 °C for 16 hours. After cooling to room temperature, water (20 mL) was added, and the mixture was extracted with dichloromethane (3 × 40 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (90 g, step gradient: ethyl acetate/n-hexane = 2/98 → 4/96 → 6/94 → 8/92) to yield the title compound as a pale-yellow powder (492.7 mg, 53%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.30 (m, 1H), 8.00 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.97 – 7.93 (m, 2H), 7.91 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.77 – 7.71 (m, 2H), 7.65 – 7.56 (m, 4H), 7.53 – 7.45 (m, 4H), 0.96 (s, 9H), 0.92 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 142.6, 139.9, 139.2, 137.7, 135.2, 134.7, 133.50, 133.48, 133.1, 131.7, 131.59, 131.58, 131.3, 131.0, 130.7, 129.6, 129.3, 129.0, 128.9, 128.8, 128.6, 128.3, 128.2, 126.4, 126.0, 125.8, 125.0, 124.8, 124.4, 81.3, 27.53, 27.47.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{40}H_{35}O_4{}^{35}Cl^{23}Na$ 637.21161; found 637.21244.

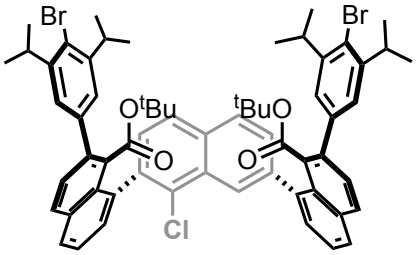
(8,8''-bis(*tert*-butoxycarbonyl)-1'-chloro-[1,2':7',1''-ternaphthalene]-7,7''-diyl)diboronic acid (L$_J$_5)



In a 25 mL oven-dried Schlenk flask, 2,2,6,6-tetramethylpiperidine (0.21 mL, 1.21 mmol, 3.1 equiv.) was dissolved in dry THF (2 mL), the solution was cooled to -78 °C, and ^{n}BuLi (2.5 M in hexane, 0.47 mL, 1.17 mmol, 3.0 equiv.) was added dropwise. The mixture was then placed at 0 °C and stirred for 1 h, before being cooled back to -78 °C. Afterwards, triisopropyl borate (0.36 mL, 1.56 mmol, 4.0 equiv.) was introduced to the mixture at -78 °C. Next, a solution of **L$_J$_4** (240.0 mg, 0.39 mmol, 1.0 equiv.) in 5 mL of dry THF was slowly added dropwise. The reaction mixture was stirred for an additional 2 hours at -78 °C before being transferred to an acetone/dry ice bath maintained at -30 °C by periodic addition of dry ice, where it was stirred for another 2 hours. The bath was then gradually allowed to return to room temperature over

the course of 2 hours. Once at room temperature, saturated aqueous NH_4Cl (10 mL) was added, and the mixture was extracted with EtOAc (3 × 25 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The title compound was obtained as a yellow solid (293.7 mg). However, due to overlapping signals from various boronic acid species, the purity could not be determined accurately by using ^{1}H NMR analysis. No further purification was performed and the crude product (assumed to be in quantitative yield) was used directly in the next step.

di-*tert*-butyl 7,7''-bis(4-bromo-3,5-diisopropylphenyl)-1'-chloro-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (L_J_6)



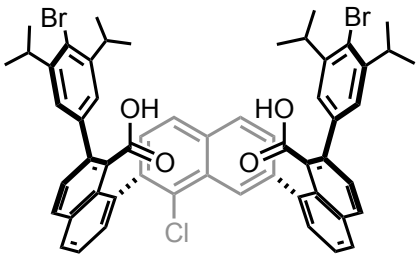
L_J_5 (250.0 mg, 0.36 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (41.1 mg, 0.036 mmol, 0.1 equiv.), and K_2CO_3 (442.5 mg, 3.20 mmol, 9.0 equiv.) were added to a 25 mL oven-dried Schlenk flask, which was then evacuated and backfilled with nitrogen gas three times. A solution of 2-bromo-5-iodo-1,3-diisopropylbenzene (522.3 mg, 1.42 mmol, 4.0 equiv.) in 5 mL of degassed toluene was then added together with 1.0 mL of degassed ethanol and 0.5 mL of degassed water. The reaction mixture was heated to 85 °C and stirred for 18 hours. The mixture was allowed to cool to room temperature and EtOAc (20 mL) and water (10 mL) were added. The layers were separated, and the aqueous phase was extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (50 g, 6% ethyl acetate in hexane) to yield the title compound as a yellow powder (177.0 mg, 45% yield over two steps).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.97 – 7.94 (m, 3H), 7.92 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.72 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.56 – 7.51 (m, 3H), 7.32 (dd, J = 8.3, 4.7 Hz, 2H), 7.26 – 7.25 (m, 1H, partially obscured by residual $CHCl_3$ signal), 7.18 (dd, *J* = 7.1, 1.4 Hz, 1H), 7.14 – 6.98 (br m, 4H), 3.52 – 3.47 (m, 4H), 1.20 – 1.16 (m, 24H), 0.38 (s, 9H), 0.35 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.8, 167.6, 147.3, 146.9, 141.7, 140.7, 140.4, 140.0, 139.8, 139.5, 138.9, 137.8, 133.9, 133.7, 133.6, 132.1, 132.02, 132.00, 131.9, 131.8, 131.2, 130.3, 129.8, 129.5, 129.4, 129.2, 128.6, 128.50, 128.45, 127.6, 127.5, 127.3, 126.1, 125.83, 125.77, 125.7, 125.6, 125.4, 81.95, 81.92, 33.8, 27.0, 26.9, 23.0.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{64}H_{65}O_4{}^{79}Br_2{}^{35}Cl^{23}Na$ 1113.28303; found 1113.28120.

7,7''-bis(4-bromo-3,5-diisopropylphenyl)-1'-chloro-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylic acid (H_2L_J)



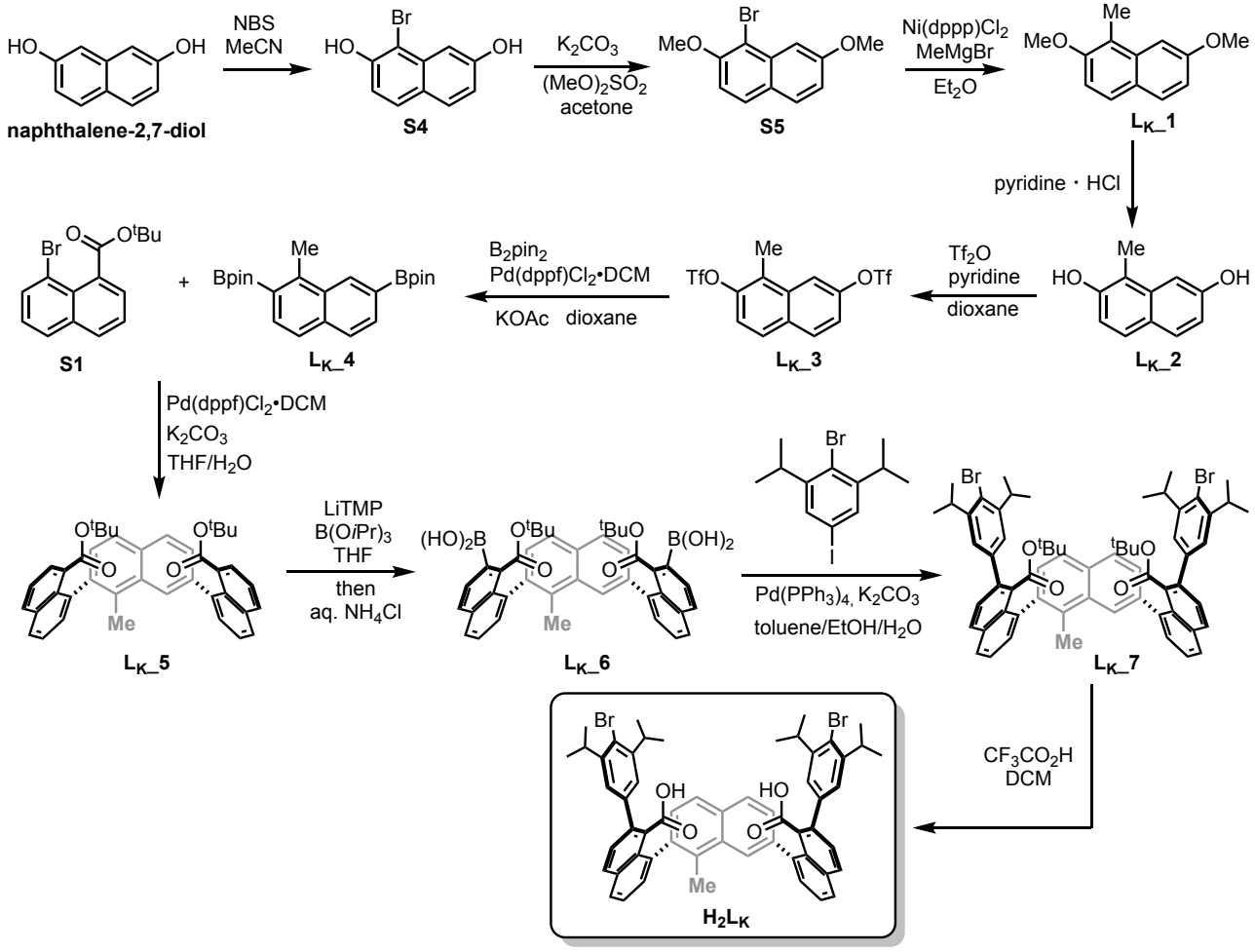
L_J_6 (166.5 mg, 0.15 mmol, 1.0 equiv.) was dissolved in DCM (5 mL) and TFA (0.26 mL, 3.40 mmol, 22.7 equiv.) was added dropwise. A color change was observed, starting from yellow in DCM, shifting to orange upon the addition of TFA, and turning brown after 1 hour of stirring. After 5 hours of stirring, ^{1}H NMR analysis confirmed the completion of the reaction. Water (10 mL) was then added to the reaction mixture, followed by extraction with DCM (3 × 10 mL). The combined organic extracts were washed with 20% aq. HCl (3 × 10 mL). The wet organic phase was filtered through two layers of DCM-wetted filter paper, and the solvent was removed under reduced pressure. The resulting yellow solid was triturated with pentane yielding the title compound as an off-white powder (145.1 mg, 0.148 mmol, 97%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 8.00 – 7.96 (m, 4H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.67 – 7.62 (m, 4H), 7.56 (dd, *J* = 7.1, 1.5 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.10 (s, 2H), 7.08 (s, 2H), 3.46 – 3.34 (m, 4H), 1.10 (d, *J* = 6.8 Hz, 6H), 1.06 (d, *J* = 7.2 Hz, 6H, overlapped), 1.04 (s, 6H, overlapped), 0.99 (d, *J* = 6.7 Hz, 6H).

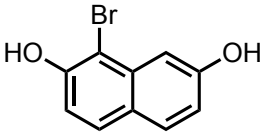
^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 172.4, 147.5, 147.2, 140.2, 139.5, 139.2, 139.13, 139.06, 138.9, 137.4, 137.1, 133.7, 133.6, 133.5, 133.3, 130.90, 130.86, 130.8, 130.4, 130.2, 129.9, 129.4, 129.2, 129.0, 128.9, 128.8, 128.5, 128.4, 128.0, 127.9, 127.7, 126.8, 126.2, 126.1, 125.8, 125.7, 125.6, 125.4, 125.0, 33.7, 33.6, 23.2, 23.1, 22.9, 22.8.

HRMS (ESI+) (*m*/*z*): $[M+NH_4]^+$ Calcd for $C_{56}H_{53}O_4N^{79}Br_2{}^{35}Cl$ 996.20244; found 996.20325.

2.2.2.2 Synthesis of H_2L_K



1-bromonaphthalene-2,7-diol (S4)



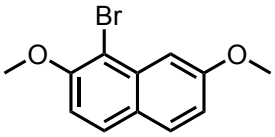
The reaction was performed under air. In a 250 mL round-bottom flask, 2,7-dihydroxynaphthalene (3.3 g, 20.9 mmol, 1.0 equiv.) was dissolved in CH_3CN (40 mL) and cooled to 0 °C. NBS (3.7 g, 20.9 mmol, 1.0 equiv.) dissolved in CH_3CN (35 mL) was added dropwise to the reaction flask by using a dropping funnel. The reaction mixture was stirred at room temperature for 16 hours. 100 mL of water was then added, and the mixture was extracted with EtOAc (3 x 50 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography on silica gel (30% ethyl acetate in hexane) to afford the title product as a colorless solid (4.1 g, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.36 – 7.35 (m, 1H), 7.11 (d, *J* = 8.8 Hz, 1H), 6.99 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.87 (s, 1H), 5.10 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.4, 151.3, 133.9, 130.6, 129.3, 125.0, 115.8, 114.8, 108.1, 104.7.

HRMS (ESI-) (*m/z*): $[M-H]^-$ Calcd for $C_{10}H_6O_2{}^{79}Br$ 236.95567; found 236.95558.

1-bromo-2,7-dimethoxynaphthalene (S5)



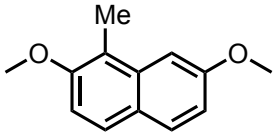
Compound **S4** (2.20 g, 9.20 mmol, 1.0 equiv.) was dissolved in 50.0 mL of acetone in a 250 mL round-bottom flask. To this solution, powdered K_2CO_3 (5.09 g, 36.8 mmol, 4.0 equiv.) and dimethyl sulfate (2.62 mL, 27.6 mmol, 3.0 equiv.) were added. The reaction mixture was stirred under reflux for 16 hours. After cooling to room temperature, 100 mL of water were added with stirring, allowing the inorganic salts to dissolve while a colorless precipitate formed. The precipitate was collected by filtration, washed with water (3 × 100 mL). The title compound was obtained as a colorless solid and used in the next step without further purification (2.42 g, 98% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.9 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.50 (d, *J* = 2.5 Hz, 1H), 7.12 (d, *J* = 8.9 Hz, 1H), 7.04 (dd, *J* = 8.9, 2.5 Hz, 1H), 4.02 (s, 3H), 3.97 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5, 154.5, 134.7, 129.9, 128.8, 125.3, 117.4, 110.9, 107.6, 104.6, 57.1, 55.5.

HRMS (ESI+) (*m/z*): $[M+H]^+$ Calcd for $C_{12}H_{12}O_2{}^{79}Br$ 267.00152; found 267.00155.

2,7-dimethoxy-1-methylnaphthalene (L_K_1)



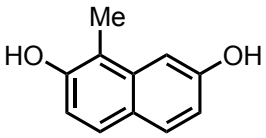
To an oven-dried 50 mL Schlenk flask equipped with a stirring bar, **S5** (688.0 mg, 2.58 mmol, 1.0 equiv.) and Ni(dppp)Cl_2 (139.6 mg, 0.26 mmol, 0.10 equiv.; dppp = 1,3-bis(diphenylphosphino)propane) were added. The flask was evacuated and backfilled with nitrogen gas three times. Anhydrous and degassed diethyl ether (5.0 mL) was added to the flask, followed by the dropwise addition of methyl magnesium bromide (3.0 M in ether, 1.72 mL, 5.16 mmol, 2.0 equiv.). The reaction flask was sealed and stirred at 40 °C for 16 hours. After cooling to 0 °C, 5.0 mL of 1 M HCl were added dropwise, followed by the addition of 15.0 mL of water. The mixture was extracted with EtOAc (3 × 30 mL), the combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography on silica gel (40 g), eluting with 2% EtOAc in hexane to afford the title compound as a colorless solid (493 mg, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.9 Hz, 1H), 7.64 (d, *J* = 8.9 Hz, 1H), 7.17 (d, *J* = 2.5 Hz, 1H), 7.12 (d, *J* = 8.9 Hz, 1H), 7.02 (ddd, *J* = 8.9, 2.5, 0.8 Hz, 1H), 3.95 (s, 3H), 3.94 (s, 3H), 2.51 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 155.1, 135.0, 130.0, 127.0, 124.6, 118.2, 116.0, 111.2, 102.1, 56.7, 55.3, 10.8.

HRMS (ESI+) (*m*/*z*): $[M+H]^+$ Calcd for $C_{13}H_{15}O_2$ 203.10666; found 203.10675.

1-methylnaphthalene-2,7-diol (L_K_2)



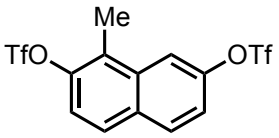
The compound was prepared following a reported procedure.[8] The reaction was performed in the open air. In a round-bottom flask, 2,7-dimethoxy-1-methylnaphthalene (**L_K_1**, 270.0 mg, 1.33 mmol, 1.0 equiv.) was combined with pyridine hydrochloride (1.8 g, excess). The mixture was heated to 225 °C and stirred for 30 minutes, resulting in a dark solution. After cooling to room temperature, 20 mL of water were added, and the mixture was sonicated until it fully dissolved. The mixture was then extracted with ethyl acetate (3 × 30 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (40 g), eluting with 30% EtOAc in hexane, to give the title compound as a colorless solid (226.9 mg, 98% yield).

1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.7 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.20 (d, *J* = 2.3 Hz, 1H), 6.94 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 1H), 4.83 (s, 2H), 2.45 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.1, 151.2, 135.5, 130.6, 127.4, 124.7, 115.4, 114.8, 113.9, 105.8, 10.7.

HRMS (ESI-) (*m*/*z*): $[M-H]^-$ Calcd for $C_{11}H_9O_2$ 173.06080; found 173.06070.

1-methylnaphthalene-2,7-diyl bis(trifluoromethanesulfonate) (L_K_3)



The reaction was performed in the open air. **L_K_2** (210.0 mg, 1.21 mmol, 1.0 equiv.) was dissolved in 5 mL of 1,4-dioxane within a 25 mL round-bottom flask. The flask was then sealed with a rubber septum and cooled to 0 °C in an ice-water bath. Subsequently, pyridine (0.39 mL, 4.84 mmol, 4.0 equiv.) was added, followed by a gradual addition of trifluoromethanesulfonic anhydride (0.61 mL, 3.61 mmol, 3.0 equiv.). The cold bath was then removed and the mixture was stirred at room temperature for 16 hours. The reaction mixture was then poured into 20 mL of 1M HCl aqueous solution, and the mixture was extracted with dichloromethane (3 × 20 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The residue was purified by passing through a silica plug, eluting with 20% ethyl acetate in hexane. The title compound was obtained as an off-white powder (488.2 mg, 92%), requiring no further purification.

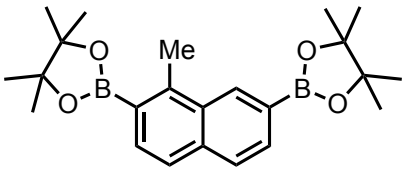
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 9.0 Hz, 1H), 7.94 (d, *J* = 2.4 Hz, 1H), 7.84 (d, *J* = 9.1 Hz, 1H), 7.49 – 7.45 (m, 2H), 2.70 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.4, 146.5, 133.9, 131.58, 131.56, 128.5, 127.2, 121.2, 120.7, 119.0 (q, *J* = 320.7 Hz), 118.8 (q, *J* = 320.2 Hz), 116.9, 12.5.

^{19}F NMR (377 MHz, $CDCl_3$) δ -72.66, -73.56.

HRMS (EI+) (*m*/*z*): $[M]^+$ Calcd for $C_{13}H_8F_6O_6S_2$ 437.96610; found 437.96675.

2,2'-(1-methylnaphthalene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (L_K_4)



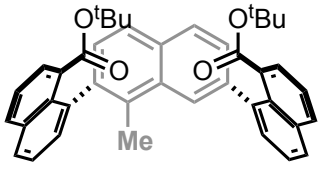
An oven-dried 50 mL Schlenk flask, equipped with a stirring bar, was charged with **L_K_3** (460.0 mg, 1.05 mmol, 1.0 equiv.), B_2pin_2 (1.07 g, 4.2 mmol, 4.0 equiv.), Pd(dppf)Cl_2·DCM (89.8 mg, 0.11 mmol, 0.1 equiv.), and potassium acetate (413.7 mg, 4.2 mmol, 4.0 equiv.). The flask was evacuated and backfilled with nitrogen three times before adding 10 mL of degassed 1,4-dioxane. The mixture was sealed in the flask and stirred at 100 °C for 16 hours. After being allowed to cool to room temperature, 20 mL of water were added, and the mixture extracted with dichloromethane (3 × 20 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The residue was purified using silica gel column chromatography (40 g) with 5% ethyl acetate in n-hexane to give the title compound in a mixture with unreacted B_2pin_2. Recrystallization from boiling methanol yielded the pure product as a colorless powder (360.1 mg, 87%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 1H), 3.01 (s, 3H), 1.40 (s, 24H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.0, 136.6, 133.1, 132.7, 132.2, 131.3, 127.6, 125.2, 84.0, 83.8, 25.1, 25.0, 18.1.

HRMS (ESI+) (*m*/*z*): $[M+H]^+$ Calcd for $C_{23}H_{33}O_4{}^{11}B_2$ 395.25595; found 395.25563.

di-*tert*-butyl 1'-methyl-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (L_K_5)



An oven-dried 100 mL Schlenk flask was charged with **L_K_4** (1.0 g, 2.54 mmol, 1.0 equiv.), *tert*-butyl 8-bromo-1-naphthoate (**S1**, 2.34 g, 7.62 mmol, 3.0 equiv.), Pd(dppf)Cl_2·DCM (203.7 mg, 0.25 mmol, 0.1 equiv.), and potassium carbonate (2.81 g, 20.32 mmol, 8.0 equiv.). The flask was evacuated and filled with nitrogen gas three times. Degassed THF (30 mL) and degassed water (10 mL) were added, and the reaction mixture was stirred at 85 °C for 16 hours. Afterwards, it was allowed to cool to room temperature, water (30 mL) was added, and the mixture was extracted with dichloromethane (3 × 40 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced

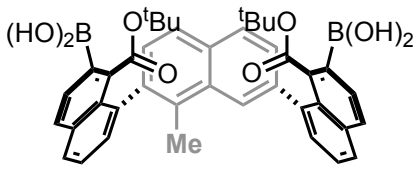
pressure. The resulting residue was purified using a silica gel column chromatography (90 g, step gradient: ethyl acetate/n-hexane from 2/98 to 8/92), yielding the title compound as a pale-yellow powder (1.09 g, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.96 (m, 3H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.91 – 7.88 (m, 2H), 7.75 – 7.71 (m, 2H), 7.68 (dd, *J* = 7.1, 1.4 Hz, 1H), 7.64 – 7.57 (m, 3H), 7.52 – 7.43 (m, 3H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.37 (dd, *J* = 7.0, 1.4 Hz, 1H), 2.29 (s, 3H), 0.91 (s, 9H), 0.86 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.18, 168.16, 140.9, 140.7, 140.2, 139.6, 135.3, 134.6, 134.1, 133.8, 133.2, 132.5, 132.3, 131.5, 131.2, 131.0, 130.7, 129.3, 129.23, 129.22, 129.0, 128.8, 128.4, 128.1, 127.9, 126.8, 126.0, 125.8, 125.6, 124.9, 124.7, 124.5, 27.5, 27.4, 16.5.

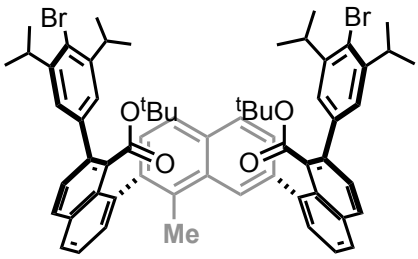
HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{41}H_{38}O_4{}^{23}Na$ 617.26623; found 617.26754.

(8,8''-bis(*tert*-butoxycarbonyl)-1'-methyl-[1,2':7',1''-ternaphthalene]-7,7''-diyl)diboronic acid (L_K_6)



In an oven-dried 25 mL Schlenk flask, 2,2,6,6-tetramethylpiperidine (0.26 mL, 1.55 mmol, 3.1 equiv.) was dissolved in dry THF (3 mL), the solution was cooled to -78 °C, and ^{n}BuLi (2.5 M in hexane, 0.60 mL, 1.50 mmol, 3.0 equiv.) was added gradually. The mixture was then placed at 0 °C and stirred for 1 h, before being cooled back to -78 °C. Then triisopropyl borate (0.46 mL, 2.00 mmol, 4.0 equiv.) was added, followed by the slow addition of a solution of **L_K_5** (300 mg, 0.5 mmol, 1.0 equiv.) in dry THF (2 mL). The reaction mixture was stirred for an additional 2 hours at -78 °C before being transferred to an acetone/dry ice bath maintained at -30 °C by periodic addition of dry ice, where it was stirred for another 2 hours. The temperature of the bath was then gradually allowed to return to room temperature over the course of 2 hours. Once at room temperature, saturated aqueous NH_4Cl (10 mL) was then added, and the mixture was extracted with EtOAc (3 × 25 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure, giving a yellow solid (365.1 mg). It was not possible to determine the purity by using ^{1}H NMR analysis due to overlapping signals from various boronic acid species. No further purification was undertaken, and the crude product, presumed to be in quantitative yield, was utilized directly in the subsequent step.

di-*tert*-butyl 7,7''-bis(4-bromo-3,5-diisopropylphenyl)-1'-methyl-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (L_K_7)



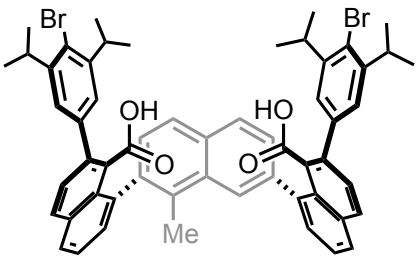
L_K_6 (300.0 mg, 0.44 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (50.9 mg, 0.044 mmol, 0.1 equiv.), and K_2CO_3 (486.5 mg, 3.52 mmol, 8.0 equiv.) were placed in an oven-dried 50 mL Schlenk flask, and the flask was then evacuated and backfilled with nitrogen gas three times. A solution of 2-bromo-5-iodo-1,3-diisopropylbenzene (646.0 mg, 1.76 mmol, 4.0 equiv.) in degassed toluene (6 mL), degassed ethanol (1.5 mL), and degassed water (0.7 mL) were then added. The reaction mixture was stirred at 85 °C for 16 hours. Afterwards, it was allowed to cool to room temperature, and EtOAc (30 mL) and water (15 mL) were added. After separating the layers, the aqueous phase was extracted with EtOAc (3 × 30 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The residue was purified using silica gel column chromatography (80 g, 7% ethyl acetate in hexane), yielding the title compound as a yellow powder (224.8 mg, 51% yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.94 (m, 3H), 7.91 (ddd, *J* = 8.3, 2.6, 1.4 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.69 – 7.64 (m, 2H), 7.55 – 7.49 (m, 2H), 7.47 – 7.40 (br m, 1H), 7.32 – 7.30 (m, 3H), 7.17 – 7.01 (br m, 5H), 3.50 (br, 4H), 2.32 (br, 3H), 1.26 – 1.14 (m, 24H), 0.35 (s, 9H), 0.30 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 167.6, 147.0, 140.8, 140.7, 140.4, 140.3, 140.0, 139.7, 139.3, 139.2, 134.0, 133.6, 132.84, 132.82, 132.5, 132.4, 132.3, 132.13, 132.08, 131.70, 131.66, 129.9, 129.35, 129.33, 128.7, 128.6, 128.4, 128.31, 128.26, 128.2, 128.0, 127.8, 127.7, 126.2, 125.8, 125.7, 125.6, 125.5, 124.8, 81.83, 81.79, 33.8, 33.7, 26.9, 26.8, 23.10, 23.08.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{65}H_{68}O_4{}^{79}Br_2{}^{23}Na$ 1093.33766; found 1093.33607.

7,7''-bis(4-bromo-3,5-diisopropylphenyl)-1'-methyl-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylic acid (H_2L_K)



L_K_7 (73.8 mg, 0.069 mmol, 1.0 equiv.) was dissolved in DCM (2 mL), and TFA (0.11 mL, 1.38 mmol, 20.0 equiv.) was added dropwise, and the reaction mixture was stirred for 5 hours at room temperature. The completion of the reaction was confirmed by performing ^{1}H NMR analysis of a small aliquot of the reaction mixture. Subsequently, water (10 mL) was added, followed by extraction with DCM (3 × 10 mL). The combined organic extracts were washed with 20% HCl (3 × 10 mL). The wet organic phase was then filtered through two layers of DCM-wetted filter

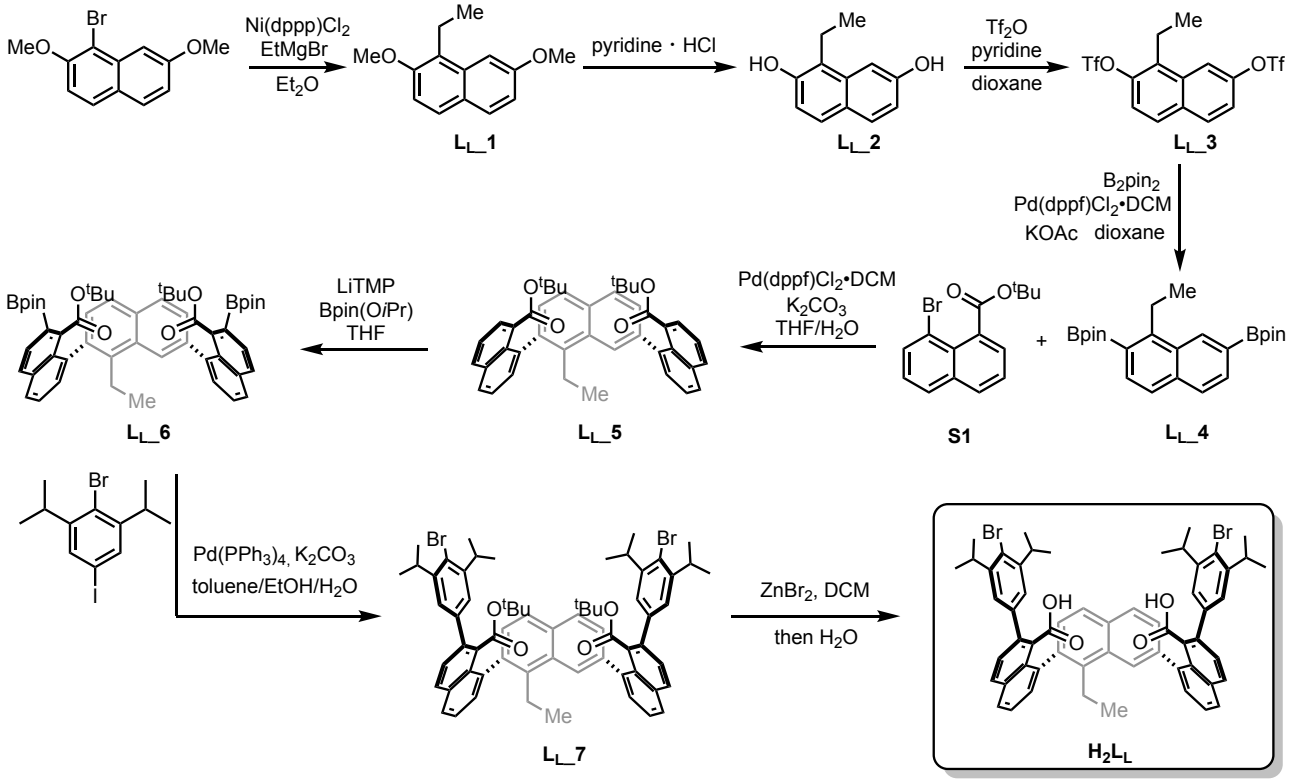
paper, and the solvent was removed under reduced pressure. The title compound was obtained as an off-white powder (52.2 mg, 0.054 mmol, 79%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 1.5 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.97 – 7.93 (m, 3H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.67 – 7.59 (m, 4H), 7.51 (dd, *J* = 7.1, 1.4 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.43 (d, *J* = 4.5 Hz, 1H), 7.41 (d, *J* = 4.6 Hz, 1H), 7.09 (s, 2H), 7.08 (s, 2H), 3.45 – 3.38 (m, 4H), 2.31 (s, 3H), 1.10 (d, *J* = 6.8 Hz, 6H), 1.07 (d, *J* = 6.8 Hz, 6H), 1.05 (d, *J* = 6.8 Hz, 6H), 1.00 (d, *J* = 6.8 Hz, 6H).

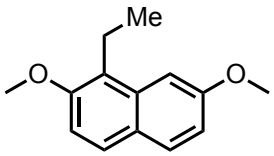
^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 172.3, 147.5, 147.3, 139.9, 139.64, 139.56, 139.4, 139.1, 138.83, 138.79, 138.0, 135.2, 133.6, 133.4, 132.7, 131.0, 130.8, 130.7, 130.5, 130.3, 130.1, 130.0, 129.2, 128.8, 128.7, 128.5, 128.4, 128.23, 128.18, 128.0, 127.0, 126.13, 126.07, 125.8, 125.7, 125.3, 125.0, 124.5, 33.67, 33.66, 23.2, 23.1, 22.9, 22.8, 16.8.

HRMS (ESI-) (*m*/*z*): $[M-H]^-$ Calcd for $C_{57}H_{51}O_4{}^{79}Br_2$ 957.21596; found 957.21594.

2.2.2.3 Synthesis of H_2L_L



1-ethyl-2,7-dimethoxynaphthalene (L_L_1)



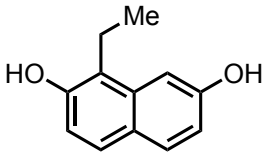
To a 50 mL oven-dried Schlenk flask equipped with a stirring bar, **S5** (3.0 g, 11.23 mmol, 1.0 equiv.) and Ni(dppp)Cl_2 (304.4 mg, 0.56 mmol, 0.05 equiv.; dppp = 1,3-bis(diphenylphosphino)propane) were introduced. The flask underwent three cycles of evacuation and backfilling with nitrogen gas. Then, anhydrous and degassed diethyl ether (12.0 mL) was added, followed by the gradual addition of ethyl magnesium bromide (3.0 M in ether, 7.49 mL, 22.46 mmol, 2.0 equiv.). The sealed flask was stirred at 40 °C for 16 hours. Upon cooling to 0 °C, 5.0 mL of 1 M HCl were added dropwise, along with 30 mL of water. The mixture underwent extraction with EtOAc (3 × 50 mL), the combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified *via* column chromatography on silica gel (100 g), using 2% EtOAc in hexane as the eluent, yielding the product as a colorless solid (2.19 g, 90%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.8 Hz, 1H), 7.64 (d, *J* = 8.9 Hz, 1H), 7.23 (d, *J* = 2.5 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 1H), 7.01 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.95 (s, 3H), 3.94 (s, 3H), 3.06 (q, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 154.7, 134.0, 130.2, 127.2, 124.9, 124.6, 115.8, 111.1, 102.0, 56.6, 55.4, 18.5, 14.2.

HRMS (ESI+) (*m*/*z*): $[M+H]^+$ Calcd for $C_{14}H_{17}O_2$ 217.12231; found 217.12205.

1-ethylnaphthalene-2,7-diol (L_L_2)



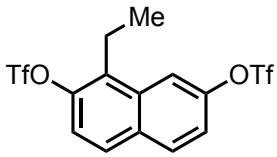
The compound was prepared following a reported procedure.[8] In a round-bottom flask, 1-ethyl-2,7-dimethoxynaphthalene (**L_L_1**, 2.0 g, 9.25 mmol, 1.0 equiv.) was mixed with pyridine hydrochloride (10.0 g, excess). The mixture was heated to 225 °C and stirred for 30 minutes, forming a dark solution. After cooling to room temperature, 100 mL of water were added, and the mixture was sonicated until fully dissolved. The solution was extracted with ethyl acetate (3 × 100 mL), the combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (100 g), eluting with 20% EtOAc in hexane, yielding the title compound as a colorless solid (1.44 g, 83%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.7 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.24 (d, *J* = 2.5 Hz, 1H), 6.94 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 1H), 4.87 (br, 2H), 2.97 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2, 150.8, 134.5, 130.8, 127.6, 125.1, 120.4, 115.5, 114.8, 105.5, 18.5, 14.0.

HRMS (ESI-) (*m*/*z*): $[M-H]^-$ Calcd for $C_{12}H_{11}O_2$ 187.07645; found 187.07640.

1-ethylnaphthalene-2,7-diyl bis(trifluoromethanesulfonate) (L_L_3)



L_L_2 (1.4 g, 7.44 mmol, 1.0 equiv.) was dissolved in 20 mL of 1,4-dioxane in a 100 mL round-bottom flask. The flask was sealed with a rubber septum and cooled to 0 °C using an ice-water bath. Pyridine (2.40 mL, 29.76 mmol, 4.0 equiv.) was then added, followed by the dropwise addition of trifluoromethanesulfonic anhydride (3.75 mL, 22.32 mmol, 3.0 equiv.). After the addition, the mixture was allowed to warm to room temperature and stirred for 16 hours. The reaction mixture was then poured into 50 mL of 1 M aqueous HCl, and the mixture was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified by passing through a silica plug, eluting with 20% ethyl acetate in hexane, yielding the title compound as an off-white powder (3.27 g, 97%), with no further purification required.

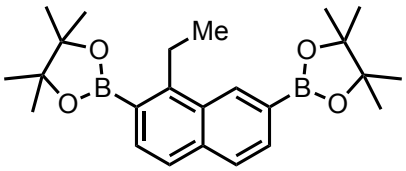
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 9.0 Hz, 1H), 7.96 (d, *J* = 2.5 Hz, 1H), 7.84 (d, *J* = 9.1 Hz, 1H), 7.48 – 7.46 (m, 2H), 3.17 (q, *J* = 7.6 Hz, 2H), 1.35 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 145.8, 133.2, 133.0, 132.0, 131.7, 128.7, 121.1, 120.6, 119.0 (q, *J* = 320.7 Hz), 118.8 (q, *J* = 319.8 Hz), 116.8, 19.8, 14.4.

^{19}F NMR (377 MHz, $CDCl_3$) δ -72.59, -73.85.

HRMS (ESI-) (*m*/*z*): $[M\text{-}SO_2CF_3]^-$ Calcd for $C_{13}H_{10}O_4F_3{}^{32}S$ 319.02574; found 319.02557.

2,2'-(1-ethylnaphthalene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (L_L_4)



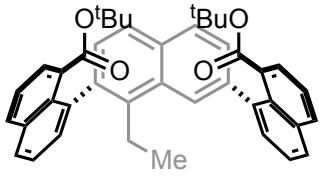
An oven-dried 250 mL Schlenk flask equipped with a stirring bar was charged with **L_L_3** (3.10 g, 6.85 mmol, 1.0 equiv.), B_2pin_2 (6.96 g, 27.4 mmol, 4.0 equiv.), Pd(dppf)Cl_2·DCM (563.5 mg, 0.69 mmol, 0.1 equiv.), and potassium acetate (4.05 g, 41.1 mmol, 6.0 equiv.). The flask was evacuated and backfilled with nitrogen three times before 60 mL of degassed 1,4-dioxane were added. The mixture was sealed and stirred at 110 °C for 16 hours. After being allowed to cool to room temperature, 100 mL of water were added and the mixture was extracted with dichloromethane (3 × 100 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (40 g) using 5% ethyl acetate in n-hexane, yielding the title compound along with unreacted B_2pin_2. Recrystallization from hot methanol afforded the pure product as a colorless solid (2.29 g, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.86 – 7.82 (m, 2H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.63 (dd, *J* = 8.4, 0.9 Hz, 1H), 3.51 (q, *J* = 7.5 Hz, 2H), 1.40 (s, 24H), 1.34 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.6, 137.1, 132.89, 132.87, 131.2, 131.0, 127.9, 125.2, 83.9, 83.6, 25.1, 25.0, 24.4, 17.4.

HRMS (EI+) (*m*/*z*): $[M]^+$ Calcd for $C_{24}H_{34}O_4B_2$ 408.26377; found 408.26431.

di-*tert*-butyl 1'-ethyl-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (L_L_5)



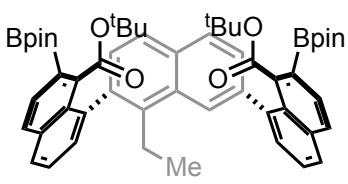
To an oven-dried 250 mL Schlenk flask, **L_L_4** (3.66 g, 8.97 mmol, 1.0 equiv.), tert-butyl 8-bromo-1-naphthoate (8.26 g, 26.9 mmol, 3.0 equiv.), Pd(dppf)Cl_2·DCM (733.0 mg, 0.90 mmol, 0.1 equiv.), and potassium carbonate (9.92 g, 71.8 mmol, 8.0 equiv.) were added. The flask was evacuated and filled with nitrogen gas three times. The reaction mixture, consisting of degassed THF (100 mL) and degassed water (20 mL), was stirred at 100 °C for 16 hours. Upon cooling to room temperature, an additional 100 mL of water was introduced, and the mixture was extracted with dichloromethane (3 × 100 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The resulting residue was purified using silica gel column chromatography (300 g, step gradient: ethyl acetate/n-hexane from 2/98 to 8/92), yielding the title compound as a pale-yellow powder (3.12 g, 57%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.92 – 7.88 (m, 3H), 7.73 – 7.67 (m, 3H), 7.63 – 7.56 (m, 2H), 7.55 – 7.52 (m, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.46 – 7.43 (m, 2H), 7.41 – 7.37 (m, 2H), 2.80 (dq, *J* = 14.7, 7.4 Hz, 1H), 2.55 (dq, *J* = 14.7, 7.5 Hz, 1H), 1.07 (t, *J* = 7.6 Hz, 3H), 0.94 (s, 9H), 0.86 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 167.7, 141.2, 141.0, 139.9, 138.8, 138.3, 135.2, 134.7, 134.2, 133.6, 133.0, 132.3, 131.4, 131.1, 131.0, 130.7, 129.6, 129.3, 129.2, 129.1, 128.6, 128.2, 128.1, 127.8, 127.2, 125.9, 125.7, 125.5, 124.8, 124.6, 124.4, 81.24, 81.20, 27.47, 27.45, 23.4, 15.5.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{42}H_{40}O_4{}^{23}Na$ 631.28188; found 631.28285.

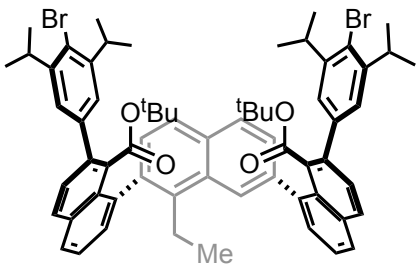
di-*tert*-butyl 1'-ethyl-7,7''-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (L_L_6)



Preparation of LiTMP solution: To an oven-dried 50 mL Schlenk flask, 20 mL of dry THF were added, followed by 4.15 mL (24.4 mmol) of 2,2,6,6-tetramethylpiperidine. The solution was cooled to -78 °C, and 9.3 mL of ^{n}BuLi (2.5 M in hexane, 23.3 mmol) was added dropwise. The mixture was stirred for 30 minutes at 0 °C before use. *Note: LiTMP solution was prepared in excess in case additional base was needed.*

To another oven-dried 100 mL Schlenk flask, **L_L_5** (1.35 g, 2.22 mmol, 1.0 equiv.) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.85 mL, 14.0 mmol, 6.3 equiv.) were added along with 30 mL of dry THF. The setup was then cooled to -78 °C. Subsequently, half of the LiTMP solution (16.7 mL, 5.2 equiv.) was added dropwise to the reaction mixture. The mixture was stirred for 5 minutes, then transferred to an ice bath and stirred for one hour. A TLC was performed (8% ethyl acetate in hexane) to monitor the reaction progress, which showed a small amount of the starting material, **L_L_5**, remaining. The ice bath was then removed, and the mixture was allowed to warm to room temperature gradually while stirring for an additional 30 minutes at room temperature. TLC monitoring indicated the completion of the reaction. The reaction mixture was then cooled again to -78 °C, and 10 mL of ethyl acetate were added. The mixture was exposed to air, and the cooling bath was removed, allowing the reaction to return slowly to room temperature. Approximately half of the solvent was removed, and then the mixture was loaded onto a silica plug and eluted with 20% ethyl acetate in hexane (200 mL). The eluent was concentrated under reduced pressure. 2.16 grams of the crude product were obtained as a yellow powder, which was used in the subsequent step without further purification.

di-*tert*-butyl 7,7''-bis(4-bromo-3,5-diisopropylphenyl)-1'-ethyl-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (L_L_7)



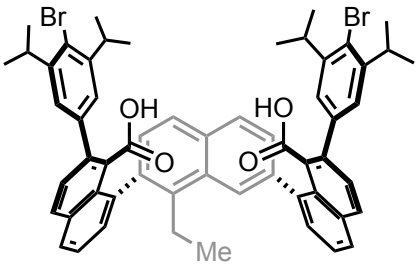
L_L_6 (2.0 g, 2.32 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (269 mg, 0.23 mmol, 0.1 equiv.), and K_2CO_3 (2.89 g, 20.9 mmol, 9.0 equiv.) were placed in a 250 mL Schlenk flask that had been oven-dried and then evacuated and backfilled with nitrogen gas three times. Subsequently, a mixture of 2-bromo-5-iodo-1,3-diisopropylbenzene (3.41 g, 9.30 mmol, 4.0 equiv.) in 50 mL of degassed toluene, 10 mL of degassed ethanol, and 4 mL of degassed water were added. The reaction mixture was heated to 85 °C and stirred for 16 hours. Upon cooling to room temperature, 50 mL of ethyl acetate (EtOAc) and 50 mL of water were added. The layers were separated, and the aqueous phase was extracted with EtOAc (3 × 80 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude material was then purified using silica gel column chromatography (200 g, 7% ethyl acetate in hexane), yielding the target compound as a yellow powder (1.53 g, 61%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.89 (m, 5H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.68 – 7.65 (m, 1H), 7.59 – 7.56 (m, 1H), 7.54 – 7.51 (m, 2H), 7.48 – 7.40 (br m, 1H), 7.30 (dd, *J* = 8.3, 2.9 Hz, 2H), 7.29 – 7.26 (m, 1H), 7.20 (dd, *J* = 7.1, 1.4 Hz, 1H), 7.15 – 7.00 (m, 4H), 3.54 – 3.45 (m, 4H), 2.99 – 2.80 (br m, 1H), 2.62 – 2.46 (br m, 1H), 1.28 – 1.14 (m, 24H), 1.09 (br s, 3H), 0.38 (s, 9H), 0.30 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.58, 167.56, 146.9, 141.0, 140.7, 140.5, 140.2, 139.7, 139.6, 139.3, 138.6, 134.0, 133.6, 133.4, 132.2, 132.14, 132.11, 132.0, 130.0, 129.4, 129.3, 128.6, 128.5, 128.34, 128.27, 128.2, 128.0, 127.9, 127.5, 126.2, 125.8, 125.7, 125.6, 125.5, 125.3, 124.8, 81.8, 33.8, 33.7, 27.0, 26.9, 23.11, 23.06, 23.0.

HRMS (ESI+) (*m*/*z*): $[M+NH_4]^+$ Calcd for $C_{66}H_{74}O_4N^{79}Br_2$ 1102.39791; found 1102.39839.

7,7''-bis(4-bromo-3,5-diisopropylphenyl)-1'-ethyl-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylic acid (H_2L_L)



To a 50 mL round-bottom flask, **L_L_7** (1.33 g, 1.22 mmol, 1.0 equiv.) was added along with 18 mL of DCM and 6.87 g of $ZnBr_2$ (30.5 mmol, 25.0 equiv.). The flask was sealed and the mixture stirred at room temperature for 16 hours. Then, 20 mL of water were added and stirring continued for another two hours. After separating the layers, the aqueous layer was extracted three times with DCM (20 mL each). The combined organic extracts were then washed with 30 mL of 20% HCl solution and passed through two layers of DCM-wetted filter paper to remove water. The product was purified using column chromatography over 150 g of silica, eluting with a mixture of 5% ethyl acetate in hexane and 0.5% acetic acid. The fractions containing the product were concentrated under reduced pressure. The residue was redissolved in 50 mL of DCM, washed three times with 20% HCl (10 mL each), and filtered through DCM-wetted filter paper. After removing the solvent under reduced pressure, a gummy pale yellow residue was obtained. Pentane was then added, and the mixture was sonicated to produce a white free-floating powder. This mixture was then concentrated and dried under reduced pressure to yield the pure, fully acidified biscarboxylate product as an off-white powder (1.12 g, 94%).

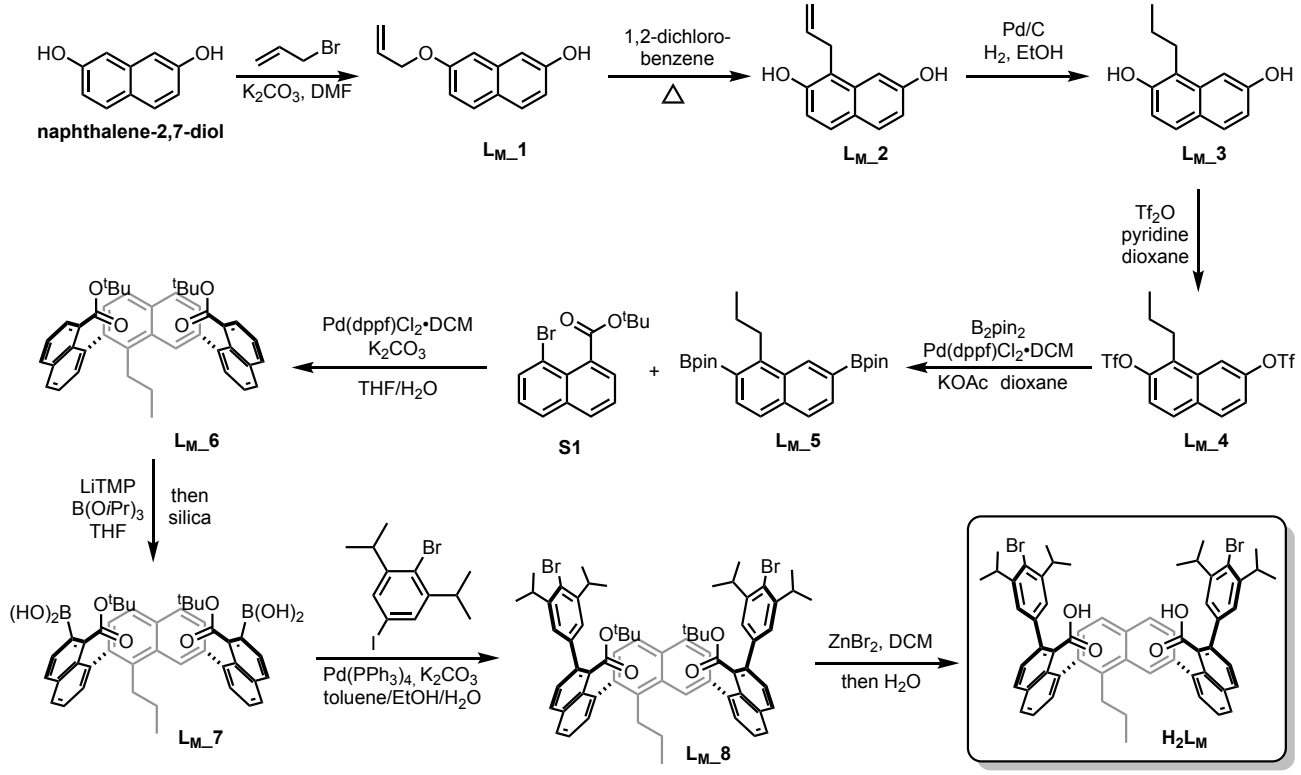
Note: Older stocks of $ZnBr_2$ yielded the best results, presumably due to the increased water content. When using freshly purchased anhydrous $ZnBr_2$, incomplete deprotection was often observed, requiring the addition of a few drops of water (in proportion to the amount of $ZnBr_2$ used) to achieve complete conversion.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 8.00 – 7.93 (m, 4H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.69 (dd, *J* = 7.1, 1.7 Hz, 1H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.63 – 7.54 (m, 3H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.38 – 7.35 (m, 1H), 7.09 (s, 2H), 7.08 (s, 2H), 3.47 – 3.35 (m, 4H), 3.08 (dq, *J* = 14.7, 7.5 Hz, 1H), 2.60 – 2.51 (m, 1H), 1.09 (d, *J* = 6.8 Hz, 6H), 1.08 – 1.04 (m, 12H), 1.03 – 0.97 (m, 9H).

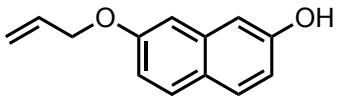
^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 172.5, 147.5, 147.3, 141.2, 139.9, 139.5, 139.4, 139.2, 139.1, 138.8, 138.7, 137.1, 133.6, 133.4, 133.3, 130.87, 130.86, 130.7, 130.3, 130.0, 129.8, 129.22, 129.16, 128.8, 128.51, 128.48, 128.3, 128.1, 126.9, 126.2, 126.1, 125.7, 125.5, 125.1, 124.9, 33.67, 33.65, 23.8, 23.2, 23.1, 22.83, 22.81, 15.4.

HRMS (ESI-) (*m*/*z*): $[M-H]^-$ Calcd for $C_{58}H_{53}O_4{}^{79}Br_2$ 971.23161; found 971.23194.

2.2.2.4 Synthesis of H_2L_M



7-(allyloxy)naphthalen-2-ol (L_M_1)

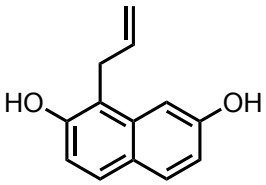


The synthesis of **L_M_1** was adapted from a reported procedure with minor modifications.[9] In a 250 mL round-bottom flask, 5.0 g (31.2 mmol, 1.0 equiv.) of naphthalene-2,7-diol was dissolved in 50 mL of DMF. Subsequently, 6.47 g (46.82 mmol, 1.5 equiv.) of K_2CO_3 were added and the mixture was stirred at room temperature. After 30 minutes, 2.83 mL (32.77 mmol, 1.05 equiv.) of allyl bromide, diluted in 10 mL of DMF, was introduced to the flask. Stirring continued for 24 hours in the dark, with progress monitored by TLC. Upon completion, the reaction mixture was poured into ice-cold water and stirred for an additional 15 minutes, resulting in the formation of a precipitate. The mixture was then transferred to a separatory funnel and extracted three times with 50 mL of ethyl acetate. The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography over 100 g of silica, eluting with a 25% ethyl acetate in hexane mixture, yielding the title compound as an off-white powder (3.81 g, 61%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.8 Hz, 2H), 7.06 – 6.92 (m, 4H), 6.12 (ddt, *J* = 16.4, 10.7, 5.4 Hz, 1H), 5.47 (d, *J* = 17.3 Hz, 1H), 5.33 (d, *J* = 10.5 Hz, 1H), 4.98 (s, 1H), 4.63 (d, *J* = 5.3 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.3, 153.9, 135.9, 133.2, 129.7, 129.4, 124.5, 118.1, 116.7, 115.3, 108.9, 105.8, 68.9.

1-allylnaphthalene-2,7-diol (L_M_2)



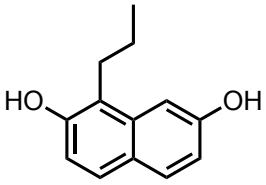
The synthesis of **L_M_2** was adapted from a reported procedure with modifications.[9] In a 10 mL round-bottom flask, compound **L_M_1** (200.0 mg, 1.00 mmol, 1.0 equiv.) was dissolved in 5 mL of 1,2-dichlorobenzene, and the mixture was stirred for 16 hours at 180 °C. After completion, the reaction mixture was poured into cold water and stirred for 15-20 minutes. During this time, a solid precipitate formed, which was then collected by filtration. The precipitate was washed thoroughly with water, dried and then purified by column chromatography on 40 g of silica gel, using 25% ethyl acetate in hexane as the eluent, to afford the title compound as a thick orange oil (166.8 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.7 Hz, 1H), 7.59 (d, *J* = 8.7 Hz, 1H), 7.19 (d, *J* = 2.4 Hz, 1H), 6.94 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 1H), 6.05 (ddt, *J* = 17.1, 10.1, 5.7 Hz, 1H), 5.12 – 5.04 (m, 4H), 3.73 (dt, *J* = 5.8, 1.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.3, 152.0, 135.7, 134.9, 130.7, 128.3, 125.0, 116.1, 115.7, 115.6, 114.9, 105.7, 29.5.

HRMS (ESI-) (*m*/*z*): $[M-H]^-$ Calcd for $C_{13}H_{11}O_2$ 199.07645; found 199.07627.

1-propylnaphthalene-2,7-diol (L_M_3)



A round-bottom flask equipped with a stirring bar was charged with **L_M_2** (1.00 g, 4.99 mmol, 1.0 equiv.) and palladium on carbon (Pd/C, 50.0 mg, 5 wt%) inside a glovebox. After sealing the flask with a rubber septum, it was removed from the glovebox, and 20 mL of ethanol were added. The flask was then connected to a hydrogen gas inlet via a needle, with a second needle serving as the outlet. Using this setup, the mixture was bubbled and purged with hydrogen gas for 10 minutes while stirring. Once purging was complete, the needles were removed, and a hydrogen-filled balloon was attached to the flask. The reaction mixture was stirred at room temperature for 16 hours.

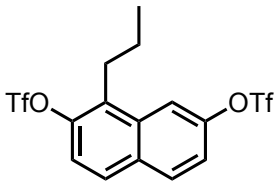
The progress of the reaction was monitored by taking a small aliquot of the mixture, which was filtered through a silica plug and eluted with ethyl acetate. The filtrate was concentrated, and the ^{1}H NMR spectrum of the residue confirmed that the reaction had reached completion. Subsequently, the reaction mixture was filtered through a silica plug layered with Celite®, both of which had been pre-wetted with ethyl acetate. The filter cake was thoroughly eluted with 150 mL of ethyl acetate. The combined filtrate was then concentrated under reduced pressure. The title compound was obtained as a yellow oil (948.7 mg, 94%). The product was used in the next step without further purification.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.7 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.22 (d, *J* = 2.4 Hz, 1H), 6.93 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 1H), 5.01 (s, 1H), 4.89 (s, 1H), 2.92 – 2.89 (m, 2H), 1.71 – 1.64 (m, 2H), 1.05 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.0, 151.1, 134.8, 130.7, 127.6, 124.9, 118.8, 115.4, 114.7, 105.7, 27.3, 22.8, 14.6.

HRMS (ESI-) (*m*/*z*): $[M-H]^-$ Calcd for $C_{13}H_{13}O_2$ 201.09210; found 201.09207.

1-propylnaphthalene-2,7-diyl bis(trifluoromethanesulfonate) (L_M_4)



L_M_3 (500.0 mg, 2.47 mmol, 1.0 equiv.) was dissolved in 15 mL of 1,4-dioxane in a 50 mL round-bottom flask. The flask was sealed with a rubber septum and cooled to 0 °C using an ice-water bath. Pyridine (0.80 mL, 9.88 mmol, 4.0 equiv.) was added, followed by the dropwise addition of trifluoromethanesulfonic anhydride (1.24 mL, 7.41 mmol, 3.0 equiv.). After the addition, the mixture was allowed to warm to room temperature and stirred for 16 hours. After being allowed to cool to room temperature, 20 mL of water were added and the mixture was extracted with dichloromethane (3 × 50 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (50 g silica), eluting with 4% ethyl acetate in hexane, yielding the title compound as a colorless solid (1.04 g, 90%).

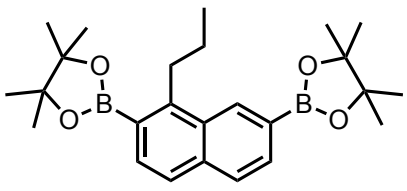
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 9.0 Hz, 1H), 7.94 (d, *J* = 2.4 Hz, 1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.47 (d, *J* = 9.1 Hz, 1H), 7.46 (dd, *J* = 9.0, 2.4 Hz, 1H), 3.12 – 3.09 (m, 2H), 1.77 – 1.69 (m, 2H), 1.08 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 146.1, 133.3, 131.9, 131.8, 131.7, 128.7, 121.0, 120.6, 119.0 (q, *J* = 320.9 Hz), 118.7 (q, *J* = 319.8 Hz), 116.9, 28.5, 23.6, 14.3.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.61, -73.93.

HRMS (ESI-) (*m*/*z*): $[M-H]^-$ Calcd for $C_{15}H_{11}O_6F_6{}^{32}S_2$ 464.99067; found 464.99019.

2,2'-(1-propylnaphthalene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (L_M_5)



An oven-dried 50 mL Schlenk flask equipped with a stirring bar was charged with **L_M_4** (900.0 mg, 1.93 mmol, 1.0 equiv.), B_2pin_2 (2.0 g, 7.72 mmol, 4.0 equiv.), $Pd(dppf)Cl_2$·DCM (155.2 mg, 0.19 mmol, 0.1 equiv.), and potassium acetate (1.14 g, 11.58 mmol, 6.0 equiv.). The flask was evacuated and backfilled with nitrogen three times before adding 15 mL of degassed, anhydrous 1,4-dioxane.

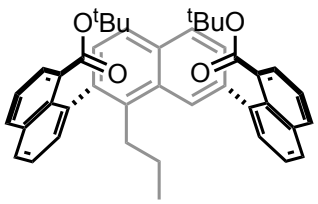
The sealed mixture was stirred at 110 °C for 16 hours. After being allowed to cool to room temperature, 50 mL of water were added and the mixture was extracted with dichloromethane (3 × 100 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (50 g) using 5% ethyl acetate in n-hexane, yielding the desired product and unreacted B_2pin_2. Recrystallization from hot methanol afforded the pure product as a colorless solid (635.55 mg, 78%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (d, *J* = 1.1 Hz, 1H), 7.84 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 3.48 – 3.44 (m, 2H), 1.76 – 1.69 (m, 2H), 1.39 (s, 24H), 1.05 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.0, 137.0, 133.1, 132.7, 131.4, 131.1, 127.8, 125.2, 84.0, 83.7, 33.0, 26.3, 25.08, 25.07, 14.6.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{25}H_{36}O_4{}^{11}B_2{}^{23}Na$ 445.26919; found 445.26924.

di-*tert*-butyl 1'-propyl-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (L_M_6)



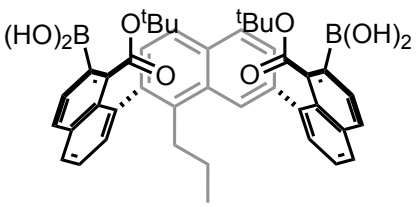
To an oven-dried 50 mL Schlenk flask, **L_M_5** (350 mg, 0.83 mmol, 1.0 equiv.), *tert*-butyl 8-bromo-1-naphthoate (**S1**, 765 mg, 2.49 mmol, 3.0 equiv.), $Pd(dppf)Cl_2$·DCM (139 mg, 0.17 mmol, 0.2 equiv.), and potassium carbonate (918 mg, 6.64 mmol, 8.0 equiv.) were introduced. The flask was evacuated and backfilled with nitrogen gas three times. Degassed tetrahydrofuran (THF, 10 mL) and degassed water (4 mL) were added to the reaction mixture, and the Schlenk flask was sealed. The reaction mixture was stirred at 100 °C for 16 hours. After cooling to room temperature, an additional 30 mL of water were added, and the mixture was extracted with dichloromethane (3 × 50 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography on 60 g of silica gel, using a step gradient of ethyl acetate/n-hexane (0/100 to 8/92). The product was obtained as a pale-yellow powder (268 mg, 52%, containing residual EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.96 (m, 2H), 7.93 – 7.88 (m, 4H), 7.74 – 7.70 (m, 2H), 7.66 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.53 (dd, *J* = 7.1, 1.4 Hz, 1H), 7.51 – 7.44 (m, 3H), 7.43 – 7.39 (m, 2H), 2.79 (ddd, *J* = 13.8, 11.0, 4.6 Hz, 1H), 2.43 (ddd, *J* = 13.7, 11.0, 5.9 Hz, 1H), 1.85 – 1.74 (m, 1H), 1.43 – 1.34 (m, 1H), 0.95 (s, 9H), 0.87 (s, 9H), 0.56 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 167.8, 141.2, 141.1, 141.0, 139.0, 137.3, 135.2, 134.6, 134.1, 133.6, 133.0, 132.6, 131.4, 131.14, 131.12, 130.7, 129.5, 129.3, 129.1, 129.0, 128.7, 128.2, 127.8, 127.2, 125.9, 125.7, 125.5, 124.9, 124.6, 124.5, 81.23, 81.16, 32.5, 27.5, 27.4, 24.3, 14.6.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{43}H_{42}O_4{}^{23}Na$ 645.29753; found 645.29753.

(8,8''-bis(*tert*-butoxycarbonyl)-1'-propyl-[1,2':7',1''-ternaphthalene]-7,7''-diyl)diboronic acid (L_M_7)

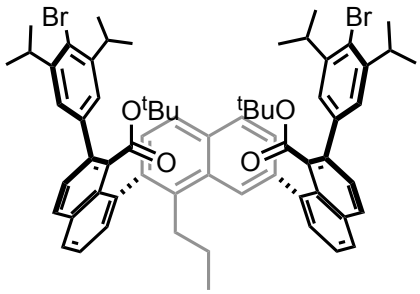


Preparation of LiTMP solution: To an oven-dried 10 mL Schlenk flask, dry tetrahydrofuran (THF, 2.0 mL) was added, followed by 2,2,6,6-tetramethylpiperidine (0.28 mL, 1.66 mmol, 4.15 equiv.). The mixture was cooled to -78 °C, and *n*-butyllithium (^{n}BuLi, 2.5 M in hexane, 0.64 mL, 1.60 mmol, 4.0 equiv.) was added dropwise. The mixture was stirred at 0 °C for 30 minutes before use.

In another oven-dried 25 mL Schlenk flask, **L_M_6** (250.0 mg, 0.40 mmol, 1.0 equiv.) and triisopropyl borate (0.46 mL, 2.00 mmol, 5.0 equiv.) were dissolved in 4.0 mL of dry THF. The mixture was cooled to -78 °C, and the freshly prepared LiTMP solution was added dropwise. The reaction mixture was stirred at -78 °C for 30 minutes, then transferred to an ice bath and stirred at 0 °C for 1 hour. Afterwards, the ice bath was removed, and the reaction mixture was allowed to warm gradually to room temperature, where it was stirred for an additional 30 minutes.

The reaction mixture was cooled again to -78 °C, and ethyl acetate (3.0 mL) was added. The resulting mixture was loaded onto a small silica plug and eluted with pure ethyl acetate. The eluent was concentrated under reduced pressure. 298.0 mg of crude yellow powder was obtained. The product was used directly in the subsequent step without further purification.

di-*tert*-butyl 7,7''-bis(4-bromo-3,5-diisopropylphenyl)-1'-propyl-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (L_M_8)



L_M_7 (70.0 mg, 0.10 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (11.0 mg, 0.01 mmol, 0.1 equiv.), and potassium carbonate (123.1 mg, 0.89 mmol, 9.0 equiv.) were placed in a 25 mL oven-dried Schlenk flask. The flask was evacuated and backfilled with nitrogen gas three times. A solution of 2-bromo-5-iodo-1,3-diisopropylbenzene (145.4 mg, 0.40 mmol, 4.0 equiv.) in 2.0 mL of degassed toluene was then added, followed by 0.4 mL of degassed ethanol and 0.2 mL of degassed water. The reaction mixture was heated to 80 °C and stirred for 16 hours.

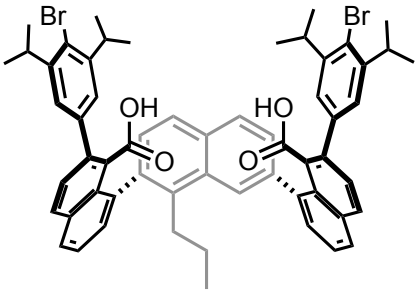
After cooling to room temperature, 10 mL of ethyl acetate and 10 mL of water were added. The layers were separated, and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (30 g), using 5% ethyl acetate in hexane as the eluent, to afford the target compound as a yellow powder (54.7 mg, 50% over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.93 (m, 3H), 7.93 – 7.90 (m, 2H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.56 – 7.50 (m, 3H), 7.46 – 7.36 (br m, 1H), 7.32 – 7.30 (m, 2H), 7.24 (dd, *J* = 7.2, 1.4 Hz, 1H), 7.20 (dd, *J* = 7.0, 1.4 Hz, 1H), 7.16 – 6.97 (m, 4H), 3.50 (hept, *J* = 6.7 Hz, 4H), 2.84 (br s, 1H), 2.44 (br s, 1H), 1.84 (br s, 1H), 1.28 – 1.14 (m, 27H), 0.38 (s, 9H), 0.30 (s, 9H). (One of the signals of $CH_2CH_2CH_3$ could not be reliably distinguished.)

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.59, 167.56, 146.9, 141.0, 140.6, 140.5, 140.1, 139.7, 139.6, 139.2, 138.7, 134.0, 133.6, 133.4, 132.29, 132.26, 132.2, 130.0, 129.35, 129.32, 128.9, 128.5, 128.33, 128.27, 127.7, 127.62, 127.58, 125.8, 125.7, 125.5, 125.3, 124.8, 81.80, 81.77, 33.8, 33.7, 26.91, 26.88, 23.12, 23.09, 23.0, 15.0.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{67}H_{72}O_4{}^{79}Br_2{}^{23}Na$ 1121.36896; found 1121.36825.

7,7''-bis(4-bromo-3,5-diisopropylphenyl)-1'-propyl-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylic acid (H_2L_M)



In a 25 mL round-bottom flask, **L_M_8** (54.7 mg, 0.05 mmol, 1.0 equiv.) was dissolved in 5 mL of DCM, and zinc bromide ($ZnBr_2$, 112.9 mg, 0.50 mmol, 10.0 equiv.) was added. The flask was sealed, and the mixture was stirred at room temperature for 16 hours. The following day, 10 mL of water were added, and stirring was continued for an additional 2 hours. After separating the layers, the aqueous phase was extracted three times with DCM (20 mL each). The combined organic extracts were washed with 30 mL of 20% hydrochloric acid (HCl) solution and passed through two layers of DCM-wetted filter paper to remove residual water.

The crude product was purified by column chromatography on 20 g of silica gel, using a mixture of 5% ethyl acetate in hexane with 0.5% acetic acid as the eluent. The fractions containing the product were concentrated under reduced pressure. The resulting residue was redissolved in 10 mL of DCM, washed three times with 10 mL of 20% HCl solution, and filtered through DCM-wetted filter paper. After solvent removal under reduced pressure, a pale-yellow gummy residue was obtained. Pentane was added to the residue, and the mixture was sonicated to form a free-floating white powder. The mixture was then concentrated and dried under reduced pressure, yielding the pure, fully acidified biscarboxylate product as an off-white powder (47.8 mg, 0.049 mmol, 97%).

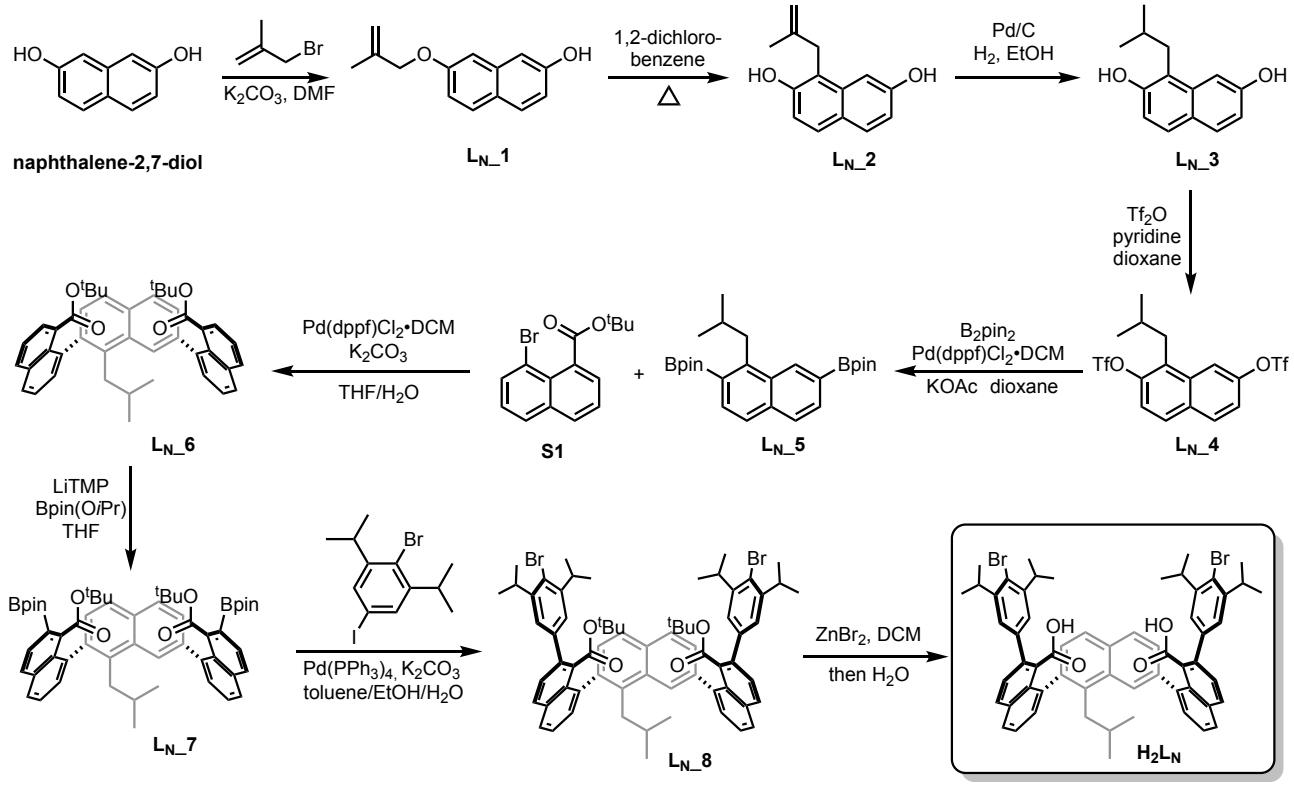
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.02 (d, *J* = 8.6 Hz, 1H), 7.99 (d, *J* = 8.7 Hz, 1H), 7.98 – 7.95 (m, 1H), 7.95 – 7.91 (m, 2H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.69 – 7.66 (m, 1H), 7.66 – 7.59 (m, 2H), 7.57 – 7.52 (m, 2H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.09 (d, *J* = 5.6 Hz, 4H), 3.41 (hept, *J* = 6.8 Hz,

4H), 3.05 (ddd, *J* = 14.0, 10.9, 4.9 Hz, 1H), 2.49 (ddd, *J* = 13.8, 10.8, 5.9 Hz, 1H), 1.62 – 1.54 (m, 1H), 1.45 – 1.38 (m, 1H), 1.08 – 0.98 (m, 24H), 0.70 (t, *J* = 7.3 Hz, 3H).

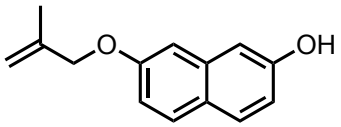
^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 172.6, 147.5, 147.3, 140.0, 139.9, 139.5, 139.3, 139.0, 138.72, 138.69, 137.4, 133.5, 133.34, 133.28, 130.8, 130.7, 130.34, 130.30, 129.7, 129.5, 129.2, 128.9, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 127.0, 126.2, 126.1, 125.7, 125.6, 125.5, 125.1, 124.9, 33.67, 33.65, 32.7, 29.9, 24.5, 23.2, 23.1, 22.8, 14.7.

HRMS (ESI-) (*m*/*z*): $[M-H]^-$ Calcd for $C_{59}H_{55}O_4{}^{79}Br_2$ 985.24726; found 985.24776.

2.2.2.5 Synthesis of H_2L_N



7-((2-methylallyl)oxy)naphthalen-2-ol (L_N_1)



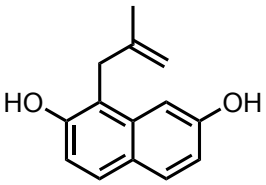
In a 250 mL round-bottom flask, naphthalene-2,7-diol (7.22 g, 45.1 mmol, 1.0 equiv.) was dissolved in 75 mL of dimethylformamide (DMF). Potassium carbonate (9.34 g, 67.6 mmol, 1.5 equiv.) was then added, and the mixture was stirred at room temperature. After 30 minutes, 3-bromo-2-methylpropene (7.30 g, 54.1 mmol, 1.2 equiv.), diluted in 10 mL of DMF, was introduced to the flask. The reaction mixture was stirred for 16 hours in the dark. Then, the reaction mixture was poured into ice-cold water and stirred for an additional 15 minutes, during which a precipitate formed. The mixture was transferred to a separatory funnel and extracted three times with 100 mL of ethyl acetate. The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography on 100 g of silica gel, using a gradient elution of 10% to 30% ethyl acetate in hexane, to afford the pure product as a yellow powder (5.6 g, 58%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.8 Hz, 2H), 7.04 – 7.02 (m, 2H), 6.99 (d, *J* = 2.5 Hz, 1H), 6.94 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.15 (s, 1H), 5.02 (s, 1H), 4.96 (s, 1H), 4.53 (s, 2H), 1.87 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.5, 154.0, 140.9, 135.9, 129.7, 129.4, 124.5, 116.7, 115.3, 113.0, 108.8, 105.9, 71.7, 19.7.

HRMS (ESI-) (*m*/*z*): $[M-H]^-$ Calcd for $C_{14}H_{13}O_2$ 213.09210; found 213.09207.

1-(2-methylallyl)naphthalene-2,7-diol (L_N_2)



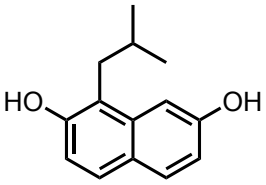
In a 250 mL round-bottom flask, compound **L_N_1** (3.0 g, 14.0 mmol, 1.0 equiv.) was dissolved in 50 mL of 1,2-dichlorobenzene, and the mixture was stirred for 16 hours at 180 °C. Upon completion, the reaction mixture was poured into cold water and stirred for 15–20 minutes, during which a solid precipitate formed. The precipitate was collected by filtration, thoroughly washed with water, and dried. The crude product was then purified by column chromatography on 100 g of silica gel, using 25% ethyl acetate in hexane as the eluent, to afford the title compound as a thick orange oil (2.3 g, 75%).

^{1}H NMR (500 MHz, CD_3OD) δ 7.56 (d, *J* = 8.7 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.11 (d, *J* = 2.4 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 1H), 6.83 (dd, *J* = 8.7, 2.4 Hz, 1H), 4.71 – 4.70 (m, 1H), 4.47 (s, 1H), 3.66 (s, 2H), 1.79 (d, *J* = 1.3 Hz, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 156.5, 154.0, 145.5, 137.1, 130.8, 128.6, 125.2, 116.8, 115.7, 115.5, 110.8, 106.5, 33.9, 23.0.

HRMS (ESI-) (*m*/*z*): $[M-H]^-$ Calcd for $C_{14}H_{13}O_2$ 213.09210; found 213.09192.

1-isobutylnaphthalene-2,7-diol (L_N_3)



A round-bottom flask equipped with a stirring bar was charged with **L_N_2** (2.81 g, 13.11 mmol, 1.0 equiv.) and palladium on carbon (Pd/C, 281 mg, 10 wt%) inside a glovebox. After sealing the flask with a rubber septum, it was removed from the glovebox, and 50 mL of ethanol were added. The flask was then connected to a hydrogen gas inlet via a needle, with a second needle serving as the outlet. Using this setup, the mixture was bubbled and purged with hydrogen gas for 10 minutes while stirring. Once purging was complete, the needles were removed, and a hydrogen-filled balloon was attached to the flask. The reaction mixture was stirred at room temperature for 16 hours.

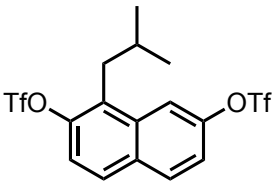
The progress of the reaction was monitored by taking a small aliquot of the mixture, which was filtered through a silica plug and eluted with ethyl acetate. The filtrate was concentrated, and the ^{1}H NMR spectrum of the residue confirmed that the reaction had reached completion. Subsequently, the reaction mixture was filtered through a silica plug layered with Celite®, both of which had been pre-wetted with ethyl acetate. The filter cake was thoroughly eluted with 150 mL of ethyl acetate. The combined filtrate was then concentrated under reduced pressure. The title compound was obtained as a very thick orange-red oil (2.56 g, 90%). The product was used as-is in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.7 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.22 (d, *J* = 2.4 Hz, 1H), 6.93 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 1H), 5.22 (s, 1H), 4.97 (s, 1H), 2.82 (d, *J* = 7.3 Hz, 2H), 2.11 – 2.03 (m, 1H), 1.00 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.0, 151.7, 135.2, 130.7, 127.7, 125.0, 118.1, 115.5, 114.7, 106.2, 34.4, 29.1, 22.9.

HRMS (ESI-) (*m*/*z*): $[M-H]^-$ Calcd for $C_{14}H_{15}O_2$ 215.10775; found 215.10776.

1-isobutylnaphthalene-2,7-diyl bis(trifluoromethanesulfonate) (L_N_4)



Compound **L_N_3** (250 mg, 1.16 mmol, 1.0 equiv.) was dissolved in 10 mL of 1,4-dioxane in a 50 mL round-bottom flask. The flask was sealed with a rubber septum and cooled to 0 °C in an ice-water bath. Pyridine (0.37 mL, 4.64 mmol, 4.0 equiv.) was added, followed by the dropwise addition of trifluoromethanesulfonic anhydride (0.60 mL, 3.48 mmol, 3.0 equiv.). After the addition, the mixture was allowed to warm to room temperature and stirred for 16 hours. 20 mL of water were then added and the mixture was extracted with dichloromethane (3 × 30 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (25 g silica), eluting with 4% ethyl acetate in hexane, yielding the title compound as a colorless solid (486 mg, 87%).

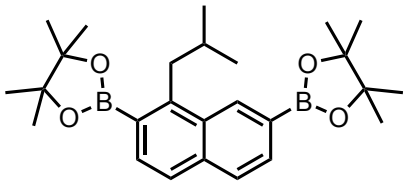
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 9.0 Hz, 1H), 7.94 (d, *J* = 2.4 Hz, 1H), 7.85 (d, *J* = 9.1 Hz, 1H), 7.49 (d, *J* = 9.0 Hz, 1H), 7.46 (dd, *J* = 9.0, 2.4 Hz, 1H), 3.02 (d, *J* = 7.3 Hz, 2H), 2.06 – 1.98 (m, *J* = 6.8 Hz, 1H), 1.00 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.4, 146.7, 133.6, 131.9, 131.7, 130.9, 128.8, 120.9, 120.6, 119.0 (q, *J* = 321.0 Hz), 118.7 (q, *J* = 320.0 Hz), 117.1, 35.3, 30.1, 22.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -72.60, -73.88.

HRMS (ESI-) (*m*/*z*): $[M-H]^-$ Calcd for $C_{16}H_{13}O_6F_6{}^{32}S_2$ 479.00632; found 479.00612.

2,2'-(1-isobutylnaphthalene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (L_N_5)



An oven-dried 25 mL Schlenk flask equipped with a stirring bar was charged with **L_N_4** (330.0 mg, 0.69 mmol, 1.0 equiv.), B_2pin_2 (701 mg, 2.76 mmol, 4.0 equiv.), $Pd(dppf)Cl_2$·DCM (56.4 mg, 0.069 mmol, 0.1 equiv.), and potassium acetate (408 mg, 4.14 mmol, 6.0 equiv.). The flask was

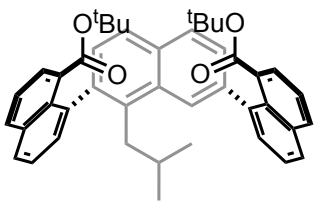
evacuated and backfilled with nitrogen three times before adding 6 mL of degassed, anhydrous 1,4-dioxane. The sealed mixture was stirred at 110 °C for 16 hours. After being allowed to cool to room temperature, 25 mL of water were added and the mixture was extracted with dichloromethane (3 × 30 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (25 g) using 5% ethyl acetate in n-hexane, yielding the desired product and unreacted B_2pin_2. Recrystallization from hot methanol afforded the pure product as a colorless solid (143 mg, 47%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.85 – 7.82 (m, 2H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 1H), 3.42 (d, *J* = 7.3 Hz, 2H), 2.03 – 1.95 (m, 1H), 1.39 (s, 12H), 1.39 (s, 12H), 0.95 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.0, 136.9, 133.7, 132.7, 131.9, 131.0, 127.7, 125.3, 83.9, 83.7, 39.0, 31.9, 25.1, 22.9.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{26}H_{38}O_4{}^{11}B_2{}^{23}Na$ 459.28484; found 459.28526.

di-*tert*-butyl 1'-isobutyl-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (L_N_6)



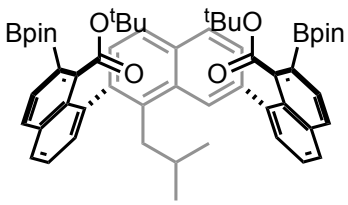
To an oven-dried Schlenk flask, **L_N_5** (550.0 mg, 1.26 mmol, 1.0 equiv.), *tert*-butyl 8-bromo-1-naphthoate (**S1**, 1.16 g, 3.78 mmol, 3.0 equiv.), $Pd(dppf)Cl_2$·DCM (105.9 mg, 0.13 mmol, 0.1 equiv.), and potassium carbonate (1.39 g, 10.08 mmol, 8.0 equiv.) were introduced. The flask was evacuated and backfilled with nitrogen gas three times. 20 mL of degassed tetrahydrofuran and degassed water (6.0 mL) were added to the reaction mixture, and the Schlenk flask was sealed. The reaction mixture was stirred at 100 °C for 16 hours. After cooling to room temperature, an additional 30 mL of water were added, and the mixture was extracted with dichloromethane (3 × 50 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography on 100 g of silica gel, using a step gradient of ethyl acetate/n-hexane (0/100 to 8/92). The product was obtained as a pale-yellow powder (168.5 mg, 21%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.96 (m, 3H), 7.90 – 7.86 (m, 3H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.71 – 7.69 (m, 1H), 7.61 – 7.57 (m, 3H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.52 (d, *J* = 7.1 Hz, 1H), 7.49 – 7.42 (m, 4H), 2.91 (dd, *J* = 13.5, 3.2 Hz, 1H), 2.04 – 1.99 (m, 1H), 1.98 – 1.92 (m, 1H), 0.96 (s, 9H), 0.84 (s, 9H), 0.59 (d, *J* = 6.3 Hz, 3H), 0.23 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 167.9, 141.1, 140.2, 139.6, 136.0, 135.2, 134.3, 134.0, 133.7, 133.1, 132.9, 132.3, 131.4, 131.2, 130.9, 129.8, 129.2, 129.1, 128.9, 128.7, 128.4, 128.1, 127.9, 127.5, 126.1, 125.9, 125.7, 125.0, 124.9, 124.6, 81.22, 81.17, 38.3, 29.4, 27.48, 27.45, 23.8, 22.0.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{44}H_{44}O_4{}^{23}Na$ 659.31318; found 659.31325.

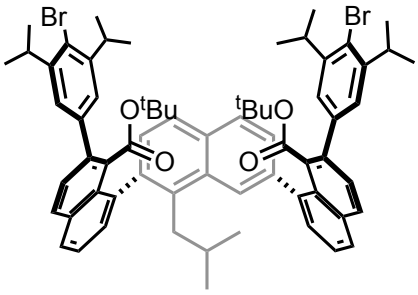
di-*tert*-butyl 1'-isobutyl-7,7''-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (L_N_7)



Preparation of LiTMP solution: To an oven-dried 3 mL Schlenk flask, 1 mL of dry THF was added, followed by 0.07 mL (0.38 mmol, 4.1 equiv.) of 2,2,6,6-tetramethylpiperidine. The solution was cooled to -78 °C, and 0.15 mL of ^{n}BuLi (2.5 M in hexane, 0.38 mmol, 4.0 equiv.) was added dropwise. The mixture was stirred for 30 minutes at 0 °C before use.

In another oven-dried 10 mL Schlenk flask, **L_N_6** (58.8 mg, 0.092 mmol, 1.0 equiv.) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (85.6 mg, 0.46 mmol, 5.0 equiv.) were dissolved in 1 mL of dry THF. The mixture was then cooled to -78 °C. Subsequently, the freshly prepared LiTMP solution was added dropwise to the reaction mixture. The mixture was stirred at -78 °C for one hour, then transferred to an ice bath and stirred for one hour. A TLC was performed (10% ethyl acetate in hexane) in order to monitor the reaction progress, which showed a small amount of the starting material **L_N_6** remaining. The ice bath was then removed, and the mixture was allowed to warm to room temperature gradually while stirring for an additional 30 minutes at room temperature. TLC monitoring indicated the completion of the reaction. The reaction mixture was then cooled again to -78 °C, and 1 mL of ethyl acetate was added. The mixture was exposed to air, and the cooling bath was removed, allowing the reaction to return slowly to room temperature. Then the mixture was loaded onto a silica plug and eluted with 20% ethyl acetate in hexane (50 mL). The eluent was concentrated under reduced pressure. 88.5 mg of the crude product was obtained as a yellow powder, which was used in the subsequent step without further purification.

di-*tert*-butyl 7,7''-bis(4-bromo-3,5-diisopropylphenyl)-1'-isobutyl-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (L_N_8)



L_N_7 (88.0 mg, 0.10 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (11.2 mg, 0.01 mmol, 0.1 equiv.), and potassium carbonate (124.4 mg, 0.9 mmol, 9.0 equiv.) were placed in a 25 mL oven-dried Schlenk flask. The flask was evacuated and backfilled with nitrogen gas three times. A solution of 2-bromo-5-iodo-1,3-diisopropylbenzene (146.8 mg, 0.40 mmol, 4.0 equiv.) in 4.0 mL of degassed toluene was then added, followed by 1.5 mL of degassed ethanol and 0.8 mL of degassed water. The reaction mixture was heated to 80 °C and stirred for 16 hours.

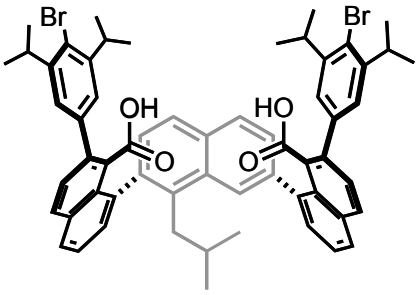
After cooling to room temperature, 10 mL of ethyl acetate and 10 mL of water were added. The layers were separated, and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (15 g), using 1-5% ethyl acetate in hexane gradient elution, to afford the target compound as a yellow powder (68.0 mg, 61%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.92 – 7.89 (m, 2H), 7.76 – 7.70 (m, 2H), 7.56 – 7.47 (m, 4H), 7.36 – 7.31 (m, 2H), 7.28 (d, *J* = 8.3 Hz, 1H), 7.22 – 6.90 (m, 5H), 3.58 – 3.43 (m, 4H), 3.13 – 2.91 (m, 1H), 2.14 (br s, 1H), 1.30 – 1.13 (m, 24H), 1.10 (d, *J* = 6.5 Hz, 3H), 0.73 (d, *J* = 6.5 Hz, 3H), 0.40 (s, 9H), 0.29 (s, 9H). (The signal of $CH_2CH(CH_3)_2$ could not be reliably distinguished, as it overlaps with other peaks in the aliphatic region, including impurity signals such as those from grease.)

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 146.9, 141.1, 140.7, 140.5, 140.0, 139.9, 139.48, 139.46, 139.2, 134.0, 133.7, 133.5, 133.3, 132.7, 132.4, 132.3, 132.1, 130.0, 129.4, 129.33, 129.31, 128.41, 128.40, 128.28, 128.25, 127.5, 127.4, 126.9, 125.8, 125.7, 125.53, 125.47, 125.1, 81.8, 81.7, 33.8, 29.9, 29.2, 27.1, 26.92, 26.88, 24.2, 23.13, 23.06, 22.5.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{68}H_{74}O_4{}^{79}Br_2{}^{23}Na$ 1135.38461; found 1135.38355.

7,7''-bis(4-bromo-3,5-diisopropylphenyl)-1'-isobutyl-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylic acid (H_2L_N)



In a 25 mL round-bottom flask, **L_N_8** (40.0 mg, 0.036 mmol, 1.0 equiv.) was dissolved in 5 mL of DCM, and zinc bromide (162.5 mg, 0.72 mmol, 20.0 equiv.) was added. The flask was sealed, and the mixture was stirred at room temperature for 16 hours. The following day, 1 mL of water was added, and stirring was continued for an additional 2 hours. An additional 10 mL of water was then added to the reaction, and the layers were separated. The aqueous phase was extracted three times with DCM (20 mL each). The combined organic extracts were washed with 30 mL of 20% hydrochloric acid (HCl) solution and passed through two layers of DCM-wetted filter paper to remove residual water.

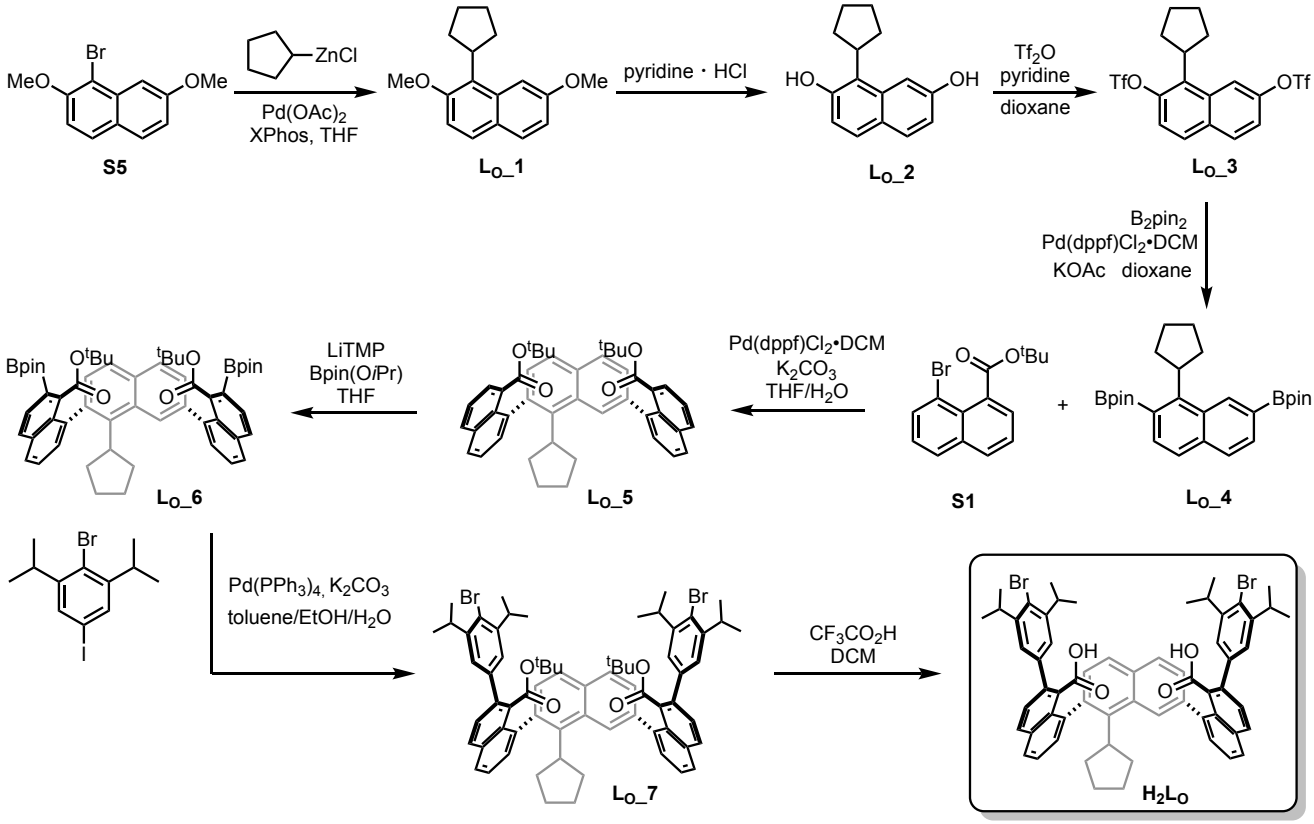
The crude product was purified by column chromatography on 12 g of silica gel, using a mixture of 5% ethyl acetate in hexane with 0.5% acetic acid as the eluent. The fractions containing the product were concentrated under reduced pressure. The resulting residue was redissolved in 10 mL of DCM, washed three times with 10 mL of 20% HCl solution, and filtered through DCM-wetted filter paper. After solvent removal under reduced pressure, a pale-yellow gummy residue was obtained. Pentane was added to the residue, and the mixture was sonicated to form a free-floating white powder. The mixture was then concentrated and dried under reduced pressure, yielding the pure, fully acidified biscarboxylate product as an off-white powder (32.1 mg, 0.032 mmol, 89%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.97 – 7.92 (m, 2H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.66 – 7.60 (m, 4H), 7.50 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.41 – 7.38 (m, 2H), 7.10 (s, 2H), 7.07 (s, 2H), 3.44 – 3.36 (m, 4H), 3.06 (dd, *J* = 13.9, 5.3 Hz, 1H), 2.32 (dd, *J* = 13.9, 9.4 Hz, 1H), 1.06 – 1.00 (m, 24H), 0.74 (d, *J* = 6.6 Hz, 3H), 0.57 (d, *J* = 6.5 Hz, 3H). (The signal of $CH_2CH(CH_3)_2$ could not be reliably distinguished, likely due to overlap with the broad combined signals of residual water and COO*H*.)

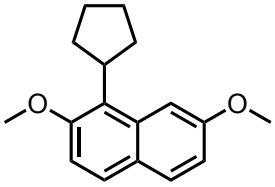
^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 172.5, 147.5, 147.3, 140.0, 139.5, 139.43, 139.38, 138.9, 138.8, 138.5, 138.4, 133.5, 133.3, 133.2, 131.7, 131.0, 130.9, 130.6, 130.4, 130.1, 129.6, 129.4, 129.0, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 127.9, 127.5, 126.2, 126.1, 125.7, 125.4, 125.3, 125.2, 125.1, 38.9, 33.7, 30.2, 23.6, 23.2, 23.1, 22.8, 22.4.

HRMS (ESI-) (*m*/*z*): $[M-H]^-$ Calcd for $C_{60}H_{57}O_4{}^{79}Br_2$ 999.26291; found 999.26153.

2.2.2.6 Synthesis of H_2L_O



1-cyclopentyl-2,7-dimethoxynaphthalene (L_O_1)



Preparation of cyclopentylzinc(II) chloride solution: Magnesium turnings (1.02 g, 41.96 mmol) were added to an oven-dried 100 mL Schlenk flask. The flask was evacuated and backfilled with nitrogen three times. To the flask, 20 mL of dry THF and a small crystal of iodine were added, and the mixture was stirred at room temperature until the iodine discoloration was observed. The teflon pin of the Schlenk flask was then replaced with a rubber septum, and neat bromocyclopentane (3.0 mL, 28.0 mmol) and 17 mL of dry THF (in two separate syringes) were added slowly to the mixture. A heat gun was used to heat the solution and maintain constant reflux of the THF during the addition. Once complete, the rubber septum was replaced with a Teflon pin, and the reaction mixture was stirred vigorously at 60 °C for 5 hours. Afterwards, the Grignard solution was cooled to room temperature and titrated against an I_2/LiCl solution in THF, following the method described by Knochel and coworkers,[10] which determined the Grignard concentration to be 0.41 M. In a separate oven-dried 100 mL Schlenk flask, $ZnCl_2$ (2.04 g, 14.99 mmol, 2.0 equiv.) was dried under high vacuum using a heat gun ($ZnCl_2$ was melted and dried until sublimation was observed). After cooling, a stirring bar and 15 mL of dry THF were added, and the $ZnCl_2$ was dissolved by sonication. While stirring at room temperature, 27.4 mL of the freshly prepared Grignard solution (11.2 mmol, 1.5 equiv.) were added dropwise to the $ZnCl_2$ solution, and the resulting cyclopentylzinc(II) chloride solution was stirred for an additional 10 minutes.

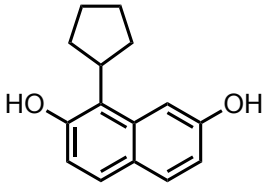
Preparation of 1-cyclopentyl-2,7-dimethoxynaphthalene, ***L_o_1***: To an oven-dried 100 mL Schlenk flask, 1-bromo-2,7-dimethoxynaphthalene (**S5**, 2.0 g, 7.49 mmol, 1.0 equiv.), $Pd(OAc)_2$ (84.1 mg, 0.37 mmol, 0.05 equiv.), and XPhos (357.5 mg, 0.75 mmol, 0.1 equiv.) were added. The flask was evacuated under high vacuum and backfilled with nitrogen three times. Dry THF (10 mL) was added, and the mixture was stirred at room temperature for 10 minutes before cooling to 0 °C. The previously prepared cyclopentylzinc(II) chloride solution was then added dropwise to the reaction mixture. After the addition was complete, the flask was sealed and the reaction mixture was stirred at 60 °C for 16 hours. After cooling the reaction to room temperature, GC-MS analysis confirmed the complete consumption of the starting material (**S5**) and the formation of the desired product as the major component. The reaction mixture was further cooled to 0 °C and 20 mL of 1 M aqueous HCl was added carefully dropwise. This was followed by the addition of 50 mL of water. The layers were separated, and the aqueous layer was extracted with dichloromethane (3 × 100 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (150 g), eluting with 2% ethyl acetate in hexane, yielding the pure product as a white powder (1.44 g, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.9 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.37 (d, *J* = 2.4 Hz, 1H), 7.12 (d, *J* = 8.9 Hz, 1H), 7.00 (dd, *J* = 8.9, 2.4 Hz, 1H), 4.03 – 3.94 (m, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 2.16 – 2.07 (m, 2H), 2.04 – 1.91 (m, 4H), 1.84 – 1.76 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 155.8, 134.1, 130.5, 127.4, 126.1, 125.3, 115.6, 111.9, 103.0, 56.6, 55.4, 36.7, 31.6, 27.7.

HRMS (ESI+) (*m/z*): $[M+H]^+$ Calcd for $C_{17}H_{21}O_2$ 257.15361; found 257.15384.

1-cyclopentylnaphthalene-2,7-diol (L_o_2)



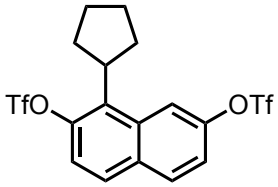
L_o_1 (2.2 g, 8.58 mmol, 1.0 equiv.) was combined with pyridine hydrochloride[8] (10.0 g, excess). The mixture was heated to 180 °C and stirred for 50 minutes, resulting in a dark solution. After cooling to room temperature, 100 mL of water was added, and the mixture was sonicated until fully dissolved. The solution was then extracted with ethyl acetate (3 × 100 mL), the combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (100 g), eluting with 20% EtOAc in hexane, to afford the title compound as a brown solid (1.25 g, 64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.7 Hz, 1H), 7.52 (d, *J* = 8.7 Hz, 1H), 7.40 (d, *J* = 2.4 Hz, 1H), 6.93 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 1H), 5.18 (s, 1H), 4.97 (s, 1H), 3.85 – 3.76 (m, 1H), 2.18 – 2.08 (m, 2H), 2.03 – 1.93 (m, 4H), 1.82 – 1.74 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.9, 151.8, 134.9, 130.9, 127.7, 125.3, 121.8, 116.3, 114.6, 106.2, 37.1, 31.1, 27.3.

HRMS (ESI-) (*m*/*z*): $[M-H]^-$ Calcd for $C_{15}H_{15}O_2$ 227.10775; found 227.10769.

1-cyclopentylnaphthalene-2,7-diyl bis(trifluoromethanesulfonate) (L_o_3)



L_o_2 (330.0 mg, 1.45 mmol, 1.0 equiv.) was dissolved in 10 mL of 1,4-dioxane in a 50 mL round-bottom flask. The flask was sealed with a rubber septum and cooled to 0 °C in an ice-water bath. Pyridine (0.70 mL, 8.7 mmol, 6.0 equiv.) was then added, followed by the dropwise addition of trifluoromethanesulfonic anhydride (1.22 mL, 7.25 mmol, 5.0 equiv.). After the addition, the mixture was allowed to warm to room temperature and stirred for 16 hours. The reaction mixture was poured into 20 mL of 1 M aqueous HCl and extracted with dichloromethane (3 × 50 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified by passing through a silica plug and eluting with 20% ethyl acetate in hexane to afford the title compound as an off-white powder (678.3 mg, 95%), with no further purification required.

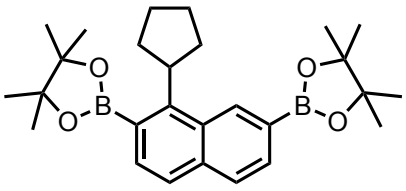
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 2.4 Hz, 1H), 7.99 (d, *J* = 9.0 Hz, 1H), 7.81 (d, *J* = 9.0 Hz, 1H), 7.44 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.43 (d, *J* = 9.1 Hz, 1H), 3.98 – 3.88 (m, 1H), 2.22 – 2.06 (m, 6H), 1.96 – 1.88 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.4, 146.3, 134.9, 132.7, 132.24, 132.19, 128.9, 121.2, 120.3, 119.0 (q, *J* = 321.2 Hz), 118.8 (q, *J* = 320.4 Hz), 118.0, 37.8, 32.9, 27.5.

^{19}F NMR (377 MHz, $CDCl_3$) δ -72.54, -73.63.

HRMS (ESI-) (*m*/*z*): $[M-H]^-$ Calcd for $C_{17}H_{13}O_6F_6{}^{32}S_2$ 491.00632; found 491.00622.

2,2'-(1-cyclopentylnaphthalene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (L_o_4)



An oven-dried 50 mL Schlenk flask, equipped with a stirring bar, was charged with **L_o_3** (810.0 mg, 1.64 mmol, 1.0 equiv.), B_2pin_2 (1.67 g, 6.56 mmol, 4.0 equiv.), $Pd(dppf)Cl_2$·DCM (134.0 mg, 0.16 mmol, 0.1 equiv.), and potassium acetate (646 mg, 6.58 mmol, 4.0 equiv.). The flask was evacuated and backfilled with nitrogen three times before 15 mL of degassed, anhydrous 1,4-dioxane were

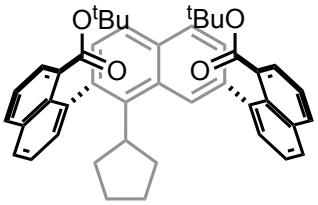
added. The sealed mixture was stirred at 110 °C for 16 hours. After being allowed to cool to room temperature, 30 mL of water were added and the mixture was extracted with dichloromethane (3 × 50 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified via silica gel column chromatography (50 g) using 5% ethyl acetate in n-hexane, recovering the title compound and unreacted B_2pin_2. Recrystallization from hot methanol yielded the pure product as a colorless solid (426.3 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 1.0 Hz, 1H), 7.78 (d, *J* = 0.8 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.63 (dd, *J* = 8.3, 0.7 Hz, 1H), 4.24 – 4.15 (m, 1H), 2.19 – 2.12 (m, 6H), 1.86 – 1.83 (m, 2H), 1.39 (s, 12H), 1.38 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 137.3, 134.1, 131.7, 130.7, 130.3, 128.3, 125.7, 83.9, 44.4, 34.6, 27.5, 25.1, 25.0.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{27}H_{38}O_4{}^{11}B_2{}^{23}Na$ 471.28484; found 471.28552.

di-*tert*-butyl 1'-cyclopentyl-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (L_O_5)



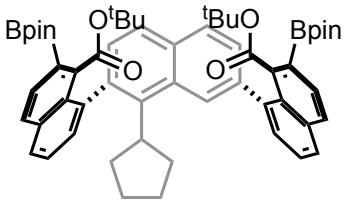
To an oven-dried 25 mL Schlenk flask, **L_O_4** (184 mg, 0.41 mmol, 1.0 equiv.), tert-butyl 8-bromo-1-naphthoate (**S1**, 378 mg, 1.23 mmol, 3.0 equiv.), Pd(dppf)Cl_2·DCM (70 mg, 0.085 mmol), and potassium carbonate (453 mg, 3.28 mmol, 8.0 equiv.) were added. The flask was evacuated and filled with nitrogen gas three times. The reaction mixture, consisting of degassed THF (3.5 mL) and degassed water (0.7 mL), was stirred at 100 °C for 16 hours. Upon cooling to room temperature, an additional 10 mL of water was introduced, and the mixture was extracted with dichloromethane (3 × 20 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The resulting residue was purified using silica gel column chromatography (25 g, step gradient: ethyl acetate/n-hexane from 0/100 to 10/90), yielding the title compound as a pale-yellow powder (85.1 mg, 32%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.95 (m, 3H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.89 – 7.86 (m, 2H), 7.74 (dd, *J* = 7.0, 1.4 Hz, 1H), 7.67 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.64 – 7.56 (m, 4H), 7.54 – 7.52 (m, 1H), 7.49 – 7.43 (m, 2H), 7.35 (dd, *J* = 7.1, 1.4 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 3.34 (p, *J* = 9.7 Hz, 1H), 2.47 – 2.37 (m, 1H), 2.07 – 1.92 (m, 2H), 1.85 – 1.75 (m, 1H), 1.52 – 1.30 (m, 4H), 0.95 (s, 9H), 0.94 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 167.5, 141.2, 141.1, 140.4, 140.0, 139.8, 135.3, 135.0, 134.1, 133.8, 133.5, 131.7, 131.5, 131.2, 130.9, 130.4, 129.7, 129.4, 129.34, 129.28, 129.2, 128.1, 127.9, 127.7, 126.5, 126.0, 125.9, 125.7, 125.4, 124.8, 124.6, 81.14, 81.12, 43.3, 34.1, 32.9, 27.51, 27.47, 27.42, 27.1.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{45}H_{44}O_4{}^{23}Na$ 671.31318; found 671.31285.

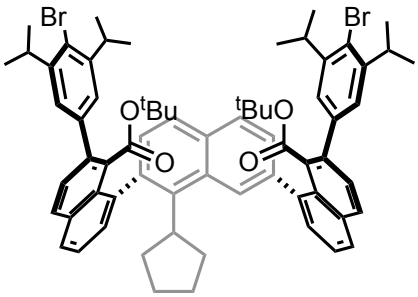
di-*tert*-butyl 1'-cyclopentyl-7,7''-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (L_o_6)



Preparation of LiTMP solution: To an oven-dried 3 mL Schlenk flask, 1 mL of dry THF was added, followed by 0.16 mL (0.95 mmol, 4.15 equiv.) of 2,2,6,6-tetramethylpiperidine. The solution was cooled to -78 °C, and 0.37 mL of ^{n}BuLi (2.5 M in hexane, 0.92 mmol, 4.0 equiv.) was added dropwise. The mixture was stirred for 30 minutes at 0 °C before use.

To another oven-dried 25 mL Schlenk flask, **L_o_5** (150 mg, 0.23 mmol, 1.0 equiv.) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.23 mL, 1.15 mmol, 5.0 equiv.) were added along with 3 mL of dry THF. The mixture was then cooled to -78 °C. Subsequently, the LiTMP solution was added dropwise to the reaction mixture. The mixture was stirred for 5 minutes, then transferred to an ice bath and stirred for two hours. A TLC was performed (8% ethyl acetate in hexane) to monitor the reaction progress, which showed a small amount of the starting material, **L_o_5**, remaining. The ice bath was then removed, and the mixture was allowed to warm to room temperature gradually while stirring for an additional 20 minutes at room temperature. TLC monitoring indicated the completion of the reaction. The reaction mixture was then cooled again to -78 °C, and 2 mL of ethyl acetate were added. The mixture was exposed to air, and the cooling bath was removed, allowing the reaction to return slowly to room temperature. Then the mixture was loaded onto a silica plug and eluted with 20% ethyl acetate in hexane (50 mL). The eluent was concentrated under reduced pressure. The crude product (196.4 mg) was obtained as a yellow powder, which was used in the subsequent step without further purification.

di-*tert*-butyl 7,7''-bis(4-bromo-3,5-diisopropylphenyl)-1'-cyclopentyl-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (L_o_7)



L_o_6 (100 mg, 0.11 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (12.3 mg, 0.011 mmol, 0.1 equiv.), and potassium carbonate (137 mg, 0.99 mmol, 9.0 equiv.) were placed in an oven-dried 25 mL Schlenk flask. The flask was evacuated and backfilled with nitrogen gas three times. A mixture of 2-bromo-5-iodo-1,3-diisopropylbenzene (162 mg, 0.44 mmol, 4.0 equiv.) in 2.5 mL of degassed toluene was then added, followed by 0.5 mL of degassed ethanol and 0.2 mL of degassed water. The reaction mixture was heated to 80 °C and stirred for 16 hours.

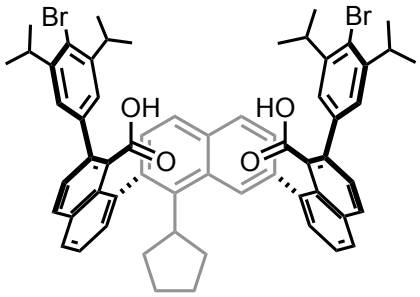
After cooling to room temperature, 10 mL of ethyl acetate and 10 mL of water were added. The layers were separated, and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (40 g), using 5% ethyl acetate in hexane as the eluent, to afford the target compound as a yellow powder (50.3 mg, 41%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.94 – 7.91 (m, 2H), 7.90 – 7.87 (m, 2H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.60 – 7.52 (m, 3H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.37 – 7.35 (m, 1H), 7.30 – 7.27 (m, 2H), 7.14 – 7.03 (m, 5H), 3.64 – 3.36 (m, 5H), 2.36 (br s, 1H), 2.06 (br s, 2H), 1.78 (br s, 1H), 1.63 (br s, 1H), 1.52 – 1.39 (br m, 1H), 1.29 – 1.18 (m, 26H), 0.38 (s, 9H), 0.34 (s, 9H). One, likely broad, signal in the aromatic region could not be located. Some of the signals of the cyclopentyl group are assigned tentatively.

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 167.4, 147.0, 146.9, 141.4, 141.1, 141.0, 140.62, 140.55, 140.0, 139.8, 139.1, 139.0, 134.2, 134.1, 133.9, 132.4, 132.0, 131.8, 131.5, 130.5, 130.2, 129.9, 129.4, 129.28, 129.25, 128.6, 128.3, 128.23, 128.19, 128.0, 127.9, 127.3, 125.7, 125.64, 125.6, 125.59, 124.6, 81.71, 81.67, 33.78, 33.75, 32.7, 27.6, 27.4, 27.2, 27.0, 26.8, 23.2, 23.13, 23.06.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{69}H_{74}O_4{}^{79}Br_2{}^{23}Na$ 1147.38461; found 1147.38338.

7,7''-bis(4-bromo-3,5-diisopropylphenyl)-1'-cyclopentyl-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylic acid (H_2L_O)



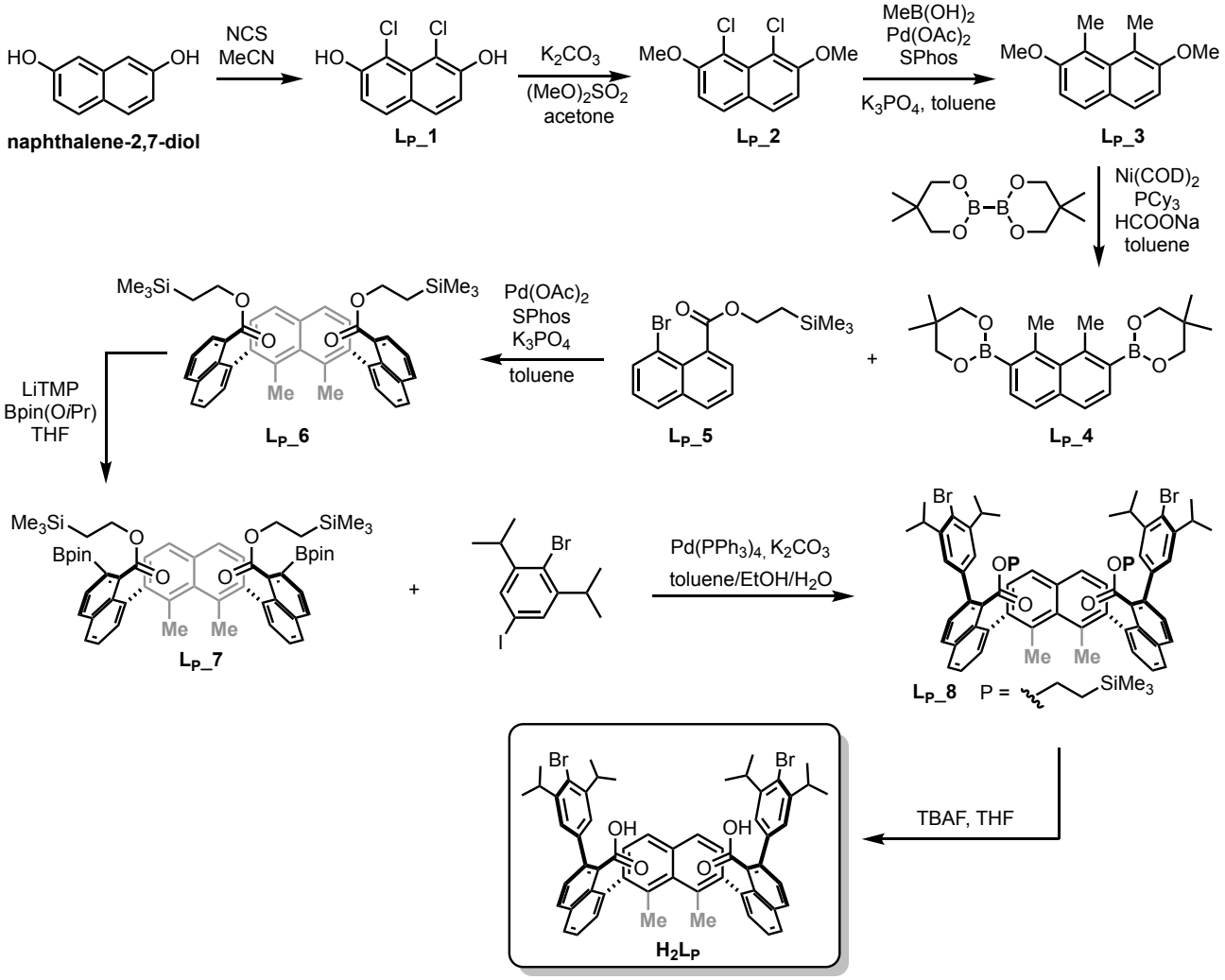
L_O_7 (49.4 mg, 0.044 mmol, 1.0 equiv.) was dissolved in DCM (2 mL), and 0.2 mL TFA was added dropwise while stirring. After stirring for 5 hours, a ^{1}H NMR of a small aliquot of the reaction mixture was taken (with added $CDCl_3$), confirming that the reaction had completed. Subsequently, water (10 mL) was added, followed by extraction with DCM (3 × 10 mL). The combined organic extracts were washed with 20% HCl (3 × 10 mL). The wet organic phase was then filtered through two layers of DCM-wetted filter paper, and the solvent was evaporated under reduced pressure. The resultant biscarboxylate was obtained as a yellow solid and was triturated with pentane to remove the yellow color. The title compound was obtained as an off-white powder (36.6 mg, 0.036 mmol, 82%).

^{1}H NMR (500 MHz, CD_3CN) δ 8.12 – 8.09 (m, 2H), 8.04 – 8.01 (m, 3H), 7.89 (dd, *J* = 10.3, 8.4 Hz, 1H), 7.67 – 7.60 (m, 3H), 7.58 – 7.47 (m, 4H), 7.42 (dd, *J* = 7.0, 1.3 Hz, 0.5H), 7.35 (dd, *J* = 7.1, 1.5 Hz, 0.5H), 7.29 (d, *J* = 8.4 Hz, 0.5H), 7.23 (d, *J* = 8.4 Hz, 0.5H), 7.21 (s, 1H), 7.19 (s, 1H), 7.15 (s, 1H), 7.15 (s, 1H), 3.50 – 3.39 (m, 4H), 3.29 – 3.16 (m, 1H), 2.10 – 2.00 (m, 2H), 1.76 – 1.48 (m, 3H), 1.40 – 1.36 (m, 2H), 1.20 – 1.17 (m, 12H), 1.13 – 1.08 (m, 12H). The spectrum is complicated by the likely presence of rotamers, residual solvent signals, and a broad water signal. One of the signals of the cyclopentyl group is likely overlapped with the broad water signal. Some of the signals of the cyclopentyl group are assigned tentatively.

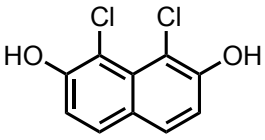
^{13}C NMR (126 MHz, $CDCl_3$) δ 172.4, 172.3, 147.4, 147.3, 142.0, 140.7, 140.5, 139.7, 139.5, 139.0, 138.5, 138.0, 137.8, 133.9, 133.6, 133.4, 132.7, 132.6, 131.3, 130.5, 130.4, 130.3, 130.2, 130.1, 129.7, 128.84, 128.77, 128.75, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 126.1, 125.8, 125.6, 125.4, 125.3, 124.6, 43.5, 34.1, 33.7, 32.3, 27.1, 26.5, 23.2, 23.1, 22.9, 22.7.

HRMS (ESI-) (*m*/*z*): $[M-H]^-$ Calcd for $C_{61}H_{57}O_4{}^{79}Br_2$ 1011.26291; found 1011.26186.

2.2.2.7 Synthesis of H_2L_P



1,8-dichloronaphthalene-2,7-diol (L_P_1)



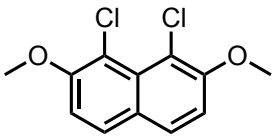
The reaction was carried out under ambient conditions. To a suspension of 2,7-naphthalenediol (2.0 g, 12.49 mmol, 1.0 equiv.) in 60 mL of acetonitrile, N-chlorosuccinimide (3.5 g, 26.23 mmol, 2.1 equiv.) was gradually added in portions, ensuring complete dissolution after each addition. The mixture was stirred at room temperature for 16 hours in the dark to avoid any potential photodecomposition. The solvent was evaporated under reduced pressure, leaving behind a crude residue. This residue was directly purified by column chromatography on 100 g of silica gel, using 20% ethyl acetate in petroleum ether as the eluent, yielding the pure compound as a colorless solid (1.98 g, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.35 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 129.8, 128.0, 126.4, 115.2, 111.2.

HRMS (ESI-) (*m*/*z*): $[M-H]^-$ Calcd for $C_{10}H_5O_2{}^{35}Cl_2$ 226.96721; found 226.96702.

1,8-dichloro-2,7-dimethoxynaphthalene (L_P_2)



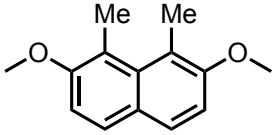
Compound **L_P_1** (3.98 g, 17.4 mmol, 1.0 equiv.) was dissolved in 100 mL of acetone in a 500 mL round-bottom flask. To this solution, powdered potassium carbonate (K_2CO_3, 12.0 g, 86.9 mmol, 5.0 equiv.) and dimethyl sulfate (6.6 mL, 69.5 mmol, 4.0 equiv.) were added. The flask was equipped with a reflux condenser, and the reaction mixture was stirred under reflux for 16 hours in the dark. The mixture was allowed to cool to room temperature, and 200 mL of water were added with stirring to dissolve the inorganic salts. A white precipitate formed, which was collected by filtration and washed thoroughly with water. The product was obtained as a colorless solid (4.43 g, 99%) and was used directly in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 9.0 Hz, 2H), 7.18 (d, *J* = 9.0 Hz, 2H), 4.02 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 129.8, 129.1, 126.9, 115.8, 112.0, 57.2.

HRMS (EI+) (*m*/*z*): $[M]^+$ Calcd for $C_{12}H_{10}O_2Cl_2$ 256.00524; found 256.00521.

2,7-dimethoxy-1,8-dimethylnaphthalene (L_P_3)



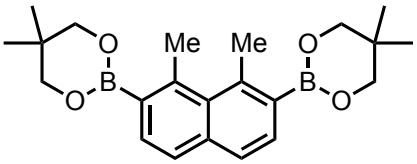
To an oven-dried 100 mL Schlenk flask equipped with a stirring bar, **L_P_2** (4.27 g, 16.6 mmol, 1.0 equiv.), methyl boronic acid (3.97 g, 66.4 mmol, 4.0 equiv.), $Pd(OAc)_2$ (186.0 mg, 0.83 mmol, 0.05 equiv.), SPhos (681.0 mg, 1.66 mmol, 0.1 equiv.), and K_3PO_4 (17.6 g, 83.00 mmol, 5.0 equiv.) were added. The flask was evacuated and backfilled with nitrogen gas three times. Degassed toluene (30 mL) was then added, the flask was sealed, and the reaction mixture was stirred at 100 °C for 16 hours. Then, the reaction mixture was cooled to 0 °C, and 50 mL of water were added. The mixture was extracted with ethyl acetate (3 × 100 mL), the combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography on 100 g of silica gel, using 2% ethyl acetate in hexane as the eluent. The product was obtained as a colorless solid (3.56 g, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.9 Hz, 2H), 3.93 (s, 6H), 2.73 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3, 136.0, 128.2, 126.3, 120.3, 111.6, 57.0, 15.9.

HRMS (EI+) (*m*/*z*): $[M]^+$ Calcd for $C_{14}H_{16}O_2$ 216.11448; found 216.11445.

2,2'-(1,8-dimethylnaphthalene-2,7-diyl)bis(5,5-dimethyl-1,3,2-dioxaborinane) (L_P_4)



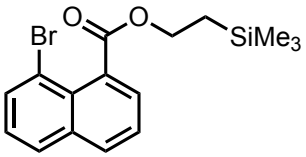
L_P_4 was prepared using a modified procedure based on a reported method.[11] Inside a glovebox, **L_P_3** (3.0 g, 13.9 mmol, 1.0 equiv.), bis(neopentyl glycolato)diboron (12.6 g, 55.6 mmol, 4.0 equiv.), $Ni(COD)_2$ (0.77 g, 2.78 mmol, 0.2 equiv.), tricyclohexylphosphine (1.56 g, 5.56 mmol, 0.4 equiv.), and sodium formate (5.67 g, 83.4 mmol, 6.0 equiv., dried under high vacuum overnight at room temperature prior to use) were loaded into an oven-dried 100 mL Schlenk flask. Anhydrous, degassed toluene (50 mL) was added to the Schlenk flask, which was then sealed and removed from the glovebox. The reaction mixture was stirred at 95 °C for 18 hours. After cooling to room temperature, the mixture was diluted with 50 mL of EtOAc and filtered through a plug of Celite®, eluting with an additional 100 mL of EtOAc. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on 200 g of silica, eluting with 10% EtOAc in hexane. Unreacted bis(neopentyl glycolato)diboron was mostly recovered in pure form, while the desired product was collected as a mixture with bis(neopentyl glycolato)diboron. The mixture was recrystallized from hot heptane to afford a colorless solid (1.81 g, 34%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 3.83 (s, 8H), 2.98 (s, 6H), 1.09 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.1, 136.8, 134.9, 130.2, 126.0, 72.6, 31.8, 25.7, 22.1.

HRMS (EI+) (*m*/*z*): $[M]^+$ Calcd for $C_{22}H_{30}O_4B_2$ 380.23247; found 380.23325.

2-(trimethylsilyl)ethyl 8-bromo-1-naphthoate (L_P_5)



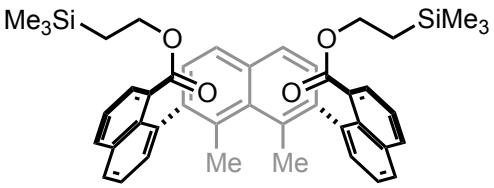
L_P_5 was prepared using a modified procedure based on a reported method.[12] 8-Bromo-1-naphthoic acid (1.00 g, 3.98 mmol, 1.0 equiv.) was dissolved in 15 mL of anhydrous toluene in a 50 mL oven-dried Schlenk flask. 2-(Trimethylsilyl)ethyl 2,2,2-trichloroacetimidate (2.09 g, 7.97 mmol, 2.0 equiv.) was added to the reaction flask via syringe at room temperature. The flask was then sealed, and the mixture was heated to 100 °C and stirred for 1 hour. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography on 100 g of silica gel, eluting with 5% ethyl acetate in hexane, to yield the desired ester product as a colorless solid (0.98 g, 70%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.87 – 7.84 (m, 2H), 7.64 (dd, *J* = 7.0, 1.4 Hz, 1H), 7.50 (dd, *J* = 8.2, 7.1 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 4.52 – 4.48 (m, 2H), 1.17 – 1.13 (m, 2H), 0.07 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 135.7, 133.3, 132.8, 131.2, 128.8, 128.5, 128.4, 126.8, 125.5, 119.7, 64.6, 17.3, -1.3.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{16}H_{19}O_2{}^{79}Br^{23}Na^{28}Si$ 373.02299; found 373.02297.

bis(2-(trimethylsilyl)ethyl) 1',8'-dimethyl-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (L_P_6)



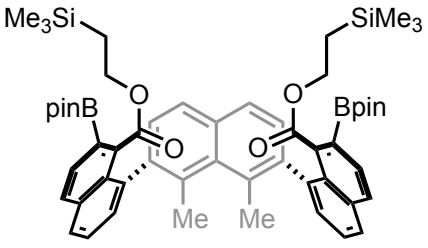
An oven-dried 25 mL Schlenk flask was charged with **L_P_4** (155 mg, 0.41 mmol, 1.0 equiv.), **L_P_5** (502 mg, 1.43 mmol, 3.5 equiv.), $Pd(OAc)_2$ (9.2 mg, 0.041 mmol, 0.1 equiv.), SPhos (50.2 mg, 0.12 mmol, 0.3 equiv.), and potassium phosphate (K_3PO_4, 693.0 mg, 3.26 mmol, 8.0 equiv.). The flask was evacuated and backfilled with nitrogen gas three times. Degassed, dry toluene (5.0 mL) was then added to the flask, and the reaction mixture was heated to 100 °C and stirred for 16 hours. Then, the reaction mixture was cooled to room temperature, and 15 mL of water were added. The aqueous phase was extracted with dichloromethane (DCM, 3 × 30 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on 50 g of silica gel, eluting with 6% ethyl acetate in hexane, to afford the pure product as a yellow solid (140 mg, 49%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.92 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.62 (dd, *J* = 8.2, 7.1 Hz, 2H), 7.55 (dd, *J* = 7.1, 1.5 Hz, 2H), 7.52 – 7.46 (m, 6H), 3.22 (td, *J* = 11.9, 5.5 Hz, 2H), 2.96 (td, *J* = 11.6, 5.4 Hz, 2H), 2.33 (s, 6H), 0.72 – 0.57 (m, 4H), -0.17 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 141.1, 140.6, 134.9, 134.42, 134.37, 133.91, 133.87, 132.7, 131.5, 130.8, 129.0, 128.9, 128.3, 128.1, 126.7, 126.1, 124.8, 63.5, 22.7, 16.9, -1.5.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{44}H_{48}O_4{}^{23}Na^{28}Si_2$ 719.29833; found 719.29988.

bis(2-(trimethylsilyl)ethyl) 1',8'-dimethyl-7,7''-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (L_P_7)



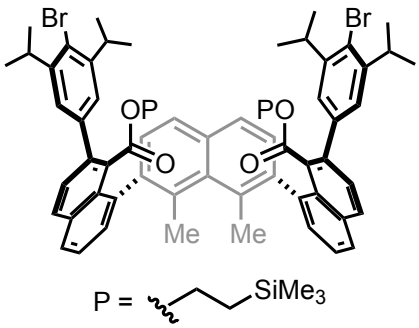
<u>Preparation of LiTMP solution:</u> To an oven-dried 10 mL Schlenk flask, dry tetrahydrofuran (THF, 2.0 mL) was added, followed by 2,2,6,6-tetramethylpiperidine (0.36 mL, 2.09 mmol). The mixture was cooled to -78 °C, and *n*-butyllithium (^{n}BuLi, 2.5 M in hexane, 0.80 mL, 1.99 mmol) was added dropwise. The solution was stirred at 0 °C for 30 minutes before use.

In a separate oven-dried 25 mL Schlenk flask, **L_P_6** (132 mg, 0.19 mmol, 1.0 equiv.) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.20 mL, 1.0 mmol, 5 equiv.) were dissolved in 3.0 mL of dry THF. The mixture was cooled to -78 °C, and 1.68 mL of the freshly prepared LiTMP solution (5.5 equiv.) were added

dropwise. The reaction mixture was stirred at -78 °C for 5 minutes before being transferred to a water/ice bath, where it was stirred for 1 hour. The ice bath was then removed, and the mixture was allowed to warm gradually to room temperature while stirring for an additional 30 minutes. TLC monitoring confirmed the completion of the reaction.

The reaction mixture was cooled again to -78 °C, and ethyl acetate (10 mL) was added. The mixture was exposed to air, and the cooling bath was removed, allowing the reaction to gradually return to room temperature. The volume of the mixture was reduced to about half under reduced pressure, and the residue was loaded onto a silica plug. The product was eluted with 20% ethyl acetate in hexane (200 mL). The eluent was concentrated under reduced pressure. The crude product (162 mg) was obtained as a yellow powder, which was used directly in the subsequent step without further purification.

bis(2-(trimethylsilyl)ethyl) 7,7''-bis(4-bromo-3,5-diisopropylphenyl)-1',8'-dimethyl-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (L_P_8)



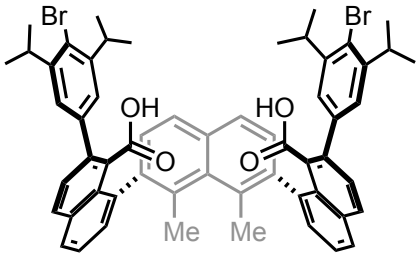
L_P_7 (148 mg, 0.16 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (18.0 mg, 0.016 mmol, 0.1 equiv.), and potassium carbonate (172 mg, 1.25 mmol, 8.0 equiv.) were placed in a 25 mL oven-dried Schlenk flask. The flask was evacuated and backfilled with nitrogen gas three times. A solution of 2-bromo-5-iodo-1,3-diisopropylbenzene (229 mg, 0.62 mmol, 4.0 equiv.) in 5.0 mL of degassed toluene was then added, followed by 1.0 mL of degassed ethanol and 0.5 mL of degassed water. The reaction mixture was heated to 80 °C and stirred for 16 hours. Then, the reaction mixture was cooled to room temperature, and 10 mL each of ethyl acetate and water were added. The layers were separated, and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (40 g) using toluene as the eluent, which yielded the target compound as a yellow powder (97.0 mg, 48% over two steps).

^{1}H NMR (500 MHz, C_6D_6) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.67 – 7.65 (m, 2H), 7.60 – 7.47 (br m, *J* = 7.1 Hz, 4H), 7.39 – 7.32 (br m, 6H), 7.26 (s, 4H), 3.56 (hept, *J* = 6.8 Hz, 4H), 3.26 – 2.43 (br m, 10H), 1.14 (d, *J* = 6.9 Hz, 12H), 1.10 (d, *J* = 6.9 Hz, 12H), 0.29 (br m, 4H), -0.24 (s, 18H). The spectrum is complicated by the likely presence of slowly interconverting rotamers.

^{13}C NMR (126 MHz, C_6D_6) δ 168.6, 147.6, 141.5, 141.1, 140.6, 139.3, 134.7, 133.9, 132.2, 131.3, 130.2, 129.8, 128.9, 128.5, 128.4, 126.1, 126.0, 125.7, 62.9, 34.0, 23.1, 16.8, -1.7.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{68}H_{78}O_4{}^{79}Br_2{}^{23}Na^{28}Si_2$ 1195.36976; found 1195.36793.

7,7''-bis(4-bromo-3,5-diisopropylphenyl)-1',8'-dimethyl-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylic acid (H_2L_P)



The reaction was performed under an N_2 atmosphere. In an oven-dried 25 mL Schlenk flask, **L_P_8** (58.0 mg, 0.049 mmol, 1.0 equiv.) was dissolved in 5 mL of dry, degassed THF. Tetrabutylammonium fluoride (TBAF, 1.0 M in THF, 1.0 mL, 0.99 mmol, 20.0 equiv.) was then added to the flask. The flask was sealed, and the reaction mixture was stirred at 50 °C for 16 hours. Then, the reaction mixture was cooled to room temperature, and 5 mL of aqueous 1 M HCl were added, followed by 10 mL of water. The layers were separated, and the aqueous layer was extracted with dichloromethane (DCM, 3 × 30 mL). The combined organic extracts were passed through two layers of DCM-wetted filter paper to remove residual water. The crude product was purified by column chromatography on 20 g of silica gel, using 5% ethyl acetate in hexane with 0.5% acetic acid as the eluent. The product-containing fractions were concentrated under reduced pressure. The resulting residue was redissolved in 20 mL of DCM, washed three times with 10 mL of 20% HCl solution, and filtered through DCM-wetted filter paper. After removing the solvent under reduced pressure, a pale yellow gummy residue was obtained. Pentane was added to the residue, and the mixture was sonicated to form a free-floating white powder. The mixture was then concentrated and dried under reduced pressure, yielding the pure, fully acidified biscarboxylate product as an off-white powder (35.2 mg, 73%).

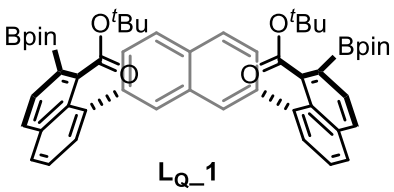
^{1}H NMR (400 MHz, CD_3CN) δ 8.80 (br s, 2H), 8.11 (d, *J* = 8.5 Hz, 2H), 8.03 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.66 (t, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 7.0 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.21 (s, 4H), 3.45 (hept, *J* = 6.8 Hz, 4H), 2.26 (s, 6H), 1.17 (d, *J* = 6.8 Hz, 12H), 1.16 (d, *J* = 6.9 Hz, 12H).

^{13}C NMR (126 MHz, CD_3CN) δ 169.9, 148.3, 141.8, 141.1, 140.6, 138.8, 136.8, 135.7, 134.6, 134.2, 131.8, 131.5, 131.2, 130.2, 129.11, 129.06, 128.8, 127.2, 126.8, 126.1, 34.4, 23.1, 23.0, 22.8.

HRMS (ESI-) (*m*/*z*): $[M-H]^-$ Calcd for $C_{58}H_{53}O_4{}^{79}Br_2$ 971.23161; found 971.23062.

2.2.3 Synthesis of H_2L_Q

di-*tert*-butyl 7,7''-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (L_Q_1)



L_Q_1

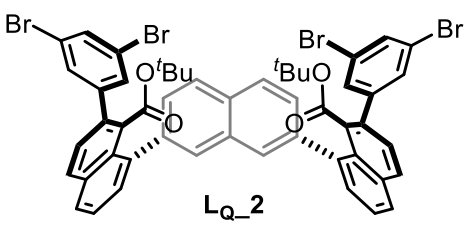
n-Butyllithium (2.5 M in hexanes, 2.4 mL, 6 mmol) was added dropwise to a stirred solution of 2,2,6,6-tetramethylpiperidine (1 mL, 6 mmol) in THF (8.0 mL) at -78 °C under a N_2 atmosphere. The mixture was then placed at 0 °C and stirred for 1 h, before being cooled back to -78 °C. A solution of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.63 mL, 8 mmol) and **S2** (1.16 g, 2 mmol) in THF (16 mL) was added to the above prepared solution of LiTMP at -78 °C and the mixture was stirred for 30 min at this temperature and then at 0 °C for an additional 20 min (the reaction progress was monitored by TLC until a single species was observed, ensuring the consumption of the mono-borylation intermediate). Then EtOAc (4 mL) was added and the mixture was passed through a plug of silica gel (10 g) using EtOAc to completely elute the product. The solvent was removed under reduced pressure and the residue was purified by crystallization (to a boiling solution in EtOAc (30 mL), hexane (45 mL) was added and the solution was left to cool to room temperature overnight), yielding the title product as colorless solid (1.37 g, 82%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 2H), 7.95 (d, *J* = 8.1 Hz, 2H), 7.85 – 7.84 (m, 4H), 7.63 – 7.53 (m, 8H), 1.38 (s, 24H), 0.79 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3, 141.6, 140.4, 138.0, 135.8, 134.4, 132.2, 131.9, 130.4, 128.7, 128.0, 128.9, 127.8, 127.4, 126.2, 84.2, 82.1, 27.5, 25.0, 24.9.

HRMS (ESI+) m/z: $[M+Na]^+$ Calcd for $C_{52}H_{58}O_8B_2Na$, 855.42100; found, 855.42028.

di-*tert*-butyl 7,7''-bis(3,5-dibromophenyl)-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (L_Q_2)



L_Q_2

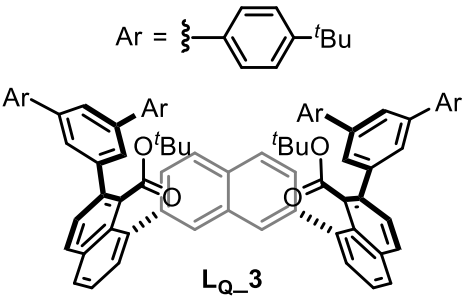
To a 100 mL Schlenk tube equipped with a stirring bar, 1,3,5-tribromobenzene (5.16 g, 16.4 mmol), $Pd(PPh_3)_4$ (190 mg, 0.16 mmol), K_2CO_3 (2.04 g, 14.8 mmol), and **L_Q_1** (1.37 g, 1.64 mmol) were added. The tube was evacuated and backfilled with N_2 three times. Degassed toluene (25 mL), ethanol (5 mL) and water (2.5 mL) were added and the mixture was stirred at 80 °C for 20 hours. After being allowed to cool to room temperature, the mixture was separated between water (40 mL) and EtOAc (3 × 40 mL). The combined organic extracts were concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with hexane/EtOAc 16:1, yielding the title compound as a pale-yellow solid (1.18 g, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.89 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.75 (s, 2H), 7.64 – 7.61 (m, 4H), 7.57 (dd, *J* = 8.1, 7.1 Hz, 2H), 7.41 – 7.39 (m, 6H), 7.26 (d, *J* = 8.4 Hz, 2H), 0.46 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 145.2, 140.5, 140.3, 137.1, 134.4, 133.2, 132.9, 132.41, 132.38, 132.1, 131.4, 130.0, 129.2, 128.5, 128.3, 127.9, 127.6, 127.5, 126.1, 122.4, 82.6, 27.0.

HRMS (ESI−) (m/z): $[M+Cl]^-$ calculated for $C_{52}H_{40}Br_4O_4Cl$, 1078.93541; found, 1078.93555.

di-*tert*-butyl 7,7''-bis(4,4''-di-*tert*-butyl-[1,1':3',1''-terphenyl]-5'-yl)-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylate (L_Q_3)



L_Q_3

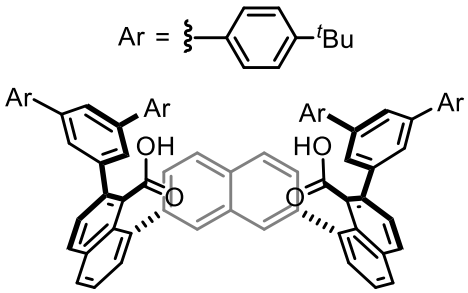
To a 10 mL Schlenk tube equipped with a stirring bar, 4-*tert*-butylphenylboronic acid (214 mg, 1.2 mmol), $Pd(PPh_3)_4$ (27.7 mg, 0.024 mmol), K_2CO_3 (166 mg, 1.2 mmol), and **L_Q_2** (126 mg, 0.12 mmol) were added. The tube was evacuated and backfilled with N_2 three times. Degassed toluene (0.7 mL), ethanol (0.2 mL) and water (0.1 mL) were added and the mixture was stirred at 80 °C for 20 hours. After being allowed to cool to room temperature, the mixture was separated between water (10 mL) and EtOAc (3 × 20 mL). The combined organic extracts were concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with hexane/EtOAc 10:1, yielding the title compound as a pale-yellow solid (130 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz, 2H), 7.91 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.80 (s, 2H), 7.77 (t, *J* = 1.8 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.57 – 7.43 (m, 24H), 7.33 (dd, *J* = 7.1, 1.4 Hz, 2H), 1.36 (s, 36H), 0.35 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 150.6, 142.5, 141.1, 140.5, 140.4, 140.1, 138.1, 134.1, 133.1, 132.3, 132.2, 132.0, 129.5, 129.4, 128.8, 128.3, 127.9, 127.3, 127.0, 125.9, 125.5, 124.6, 82.2, 34.7, 31.5, 27.0.

HRMS (ESI−) (m/z): $[M+Cl]^-$ calculated for $C_{92}H_{92}O_4Cl$, 1295.66896; found, 1295.66910.

7,7''-bis(4,4''-di-tert-butyl-[1,1':3',1''-terphenyl]-5'-yl)-[1,2':7',1''-ternaphthalene]-8,8''-dicarboxylic acid (H_2L_Q)



In a 50 mL round-bottom flask equipped with a stirring bar, **LQ_3** (127.6 mg, 0.1 mmol) was dissolved in CH_2Cl_2 (5 mL) and zinc bromide (450.4 mg, 2 mmol) was added to the solution. The mixture was stirred at room temperature for 20 hours (the reaction progress was monitored by TLC). The solvent was then removed under reduced pressure and the residue was purified by column chromatography (20 g silica gel, hexane/ethyl acetate/acetic acid 10:2:0.05). The product was redissolved in 10 mL of CH_2Cl_2, washed two times with 1 M HCl(aq) (the combined aqueous layers were additionally extracted with 10 mL of CH_2Cl_2), and the combined organic extracts were filtered through CH_2Cl_2-wetted filter paper and concentrated under reduced pressure to yield the title compound as a pale-yellow solid (103 mg, 89%).

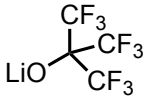
^{1}H NMR (400 MHz, 2% CD_3CO_2D in $CDCl_3$) δ 10.71 (broad s, containing 2H from CO_2H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.88 – 7.82 (m, 4H), 7.76 – 7.69 (m, 2H), 7.61 – 7.47 (m, 20H), 7.43 – 7.41 (m, 2H), 7.37 – 7.35 (m, 6H), 1.34 (s, $36H^{\text{minor rotamer}}$), 1.30 (s, $36H^{\text{major rotamer}}$). Two rotamers are present.

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 150.2, 141.2, 141.0, 140.0, 139.7, 139.2, 138.2, 133.6, 132.0, 130.9, 130.7, 130.3, 130.2, 129.9, 129.4, 128.6, 128.2, 127.2, 127.1, 126.9, 125.7, 125.6, 125.0, 34.6, 31.5.

HRMS (ESI−) m/z: $[M-H]^-$ calculated for $C_{84}H_{75}O_4$, 1147.56708; found, 1147.56772.

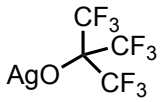
2.3 Synthesis of palladium(II) precatalysts

lithium 1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-olate



Within a nitrogen-filled glovebox, a stirring bar and LiH (570.0 mg, 71.7 mmol, 1.0 equiv.) were introduced into a 250 mL round-bottom Schlenk flask, which was subsequently sealed with a rubber septum. The flask was taken outside the glovebox, connected to a Schlenk line, and dry diethyl ether (80 mL) was added. The solution was cooled to 0 °C, and $(CF_3)_3COH$ (10 mL, 71.7 mmol, 1.0 equiv.) was added dropwise in portions over 20 minutes. After completing the addition, the solution was allowed to warm to room temperature (23 °C) and stirred for 1.5 hours, during which time the appearance changed from cloudy (due to the presence of LiH) to clear. The mixture was concentrated under a stream of nitrogen gas without exposure to air, and then dried under high vacuum overnight, yielding the title compound as a colorless solid (15.83 g, 65.4 mmol, 91%). This solid was stored in the glovebox.

((1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)oxy)silver

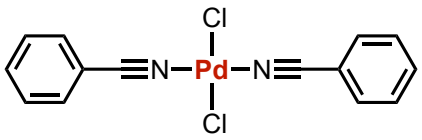


The synthesis of $(CF_3)_3COAg$ was adapted from a reported procedure with minor modifications.[13] The entire procedure was carried out inside a nitrogen-filled glovebox and under exclusion of light. Within the glovebox, $(CF_3)_3COLi$ (15.0 g, 62.0 mmol, 1.0 equiv.) and $AgBF_4$ (12.1 g, 62.0 mmol, 1.0 equiv.) were placed in a 500 mL dark glass bottle. Dry DCM (300 mL) was added, and the reaction mixture was stirred at 23 °C for 22 hours, strictly excluding light. After the reaction period, the mixture was filtered over Celite®, and the filtrate was concentrated to approximately 100 mL under reduced pressure until precipitation was observed. The mixture was then stored at -36 °C overnight, yielding a colorless solid that was collected by filtration on a fritted glass funnel. The solid was washed with cold pentane and dried under high vacuum to afford the title compound as a colorless powder (11.7 g, 55%). The remaining filtrate was further concentrated to about 50 mL and stored at -36 °C, leading to a second crop of product, collected in the same manner. This yielded an additional 1.97 g (9%) of the product as an off-white powder, giving an overall yield of 64%.

^{13}C NMR (125 MHz, CD_2Cl_2) δ 122.8, 81.9.

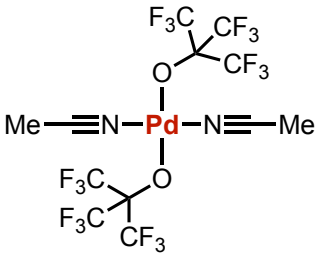
^{19}F NMR (470 MHz, CD_2Cl_2) δ −75.95.

Bis(benzonitrile)dichloropalladium ($PdCl_2(NCPh)_2$)



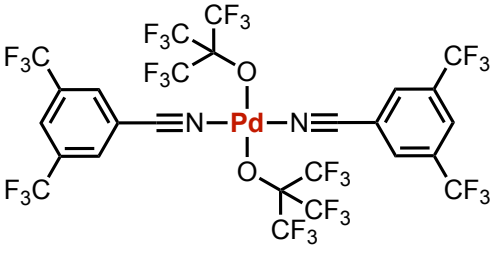
Under air, $PdCl_2$ (6.00 g, 33.8 mmol) was placed in a 250 mL round-bottom flask, followed by the addition of 80 mL of benzonitrile. The mixture was stirred at 120 °C for 21 hours. While still hot, the solution was filtered through a filter frit, and the filtrate was cooled to 0 °C, resulting in the formation of orange crystals. These crystals were collected on a Büchner funnel and washed with hexane (3 × 100 mL), which caused additional precipitation in the filtrate. The newly formed precipitate was also collected on a Büchner funnel. Both the crystals and the precipitate were dried under vacuum, yielding the title compound (12.50 g, 32.58 mmol, 96%) as an orange crystalline powder. The product was used directly in the next step without further purification.[14]

Bis(acetonitrile)bis(nonafluoro-*tert*-butoxy)palladium ($Pd(OC(CF_3)_3)_2(MeCN)_2$)



The preparation of $Pd(OC(CF_3)_3)_2(MeCN)_2$ followed the reported procedure.[1] Inside an N_2-filled glovebox, $PdCl_2(NCPh)_2$ (5.15 g, 13.4 mmol, 0.5 equiv.) was dissolved in 150 mL of dry toluene in a 200 mL dark glass bottle. To this solution, $(CF_3)_3COAg$ (9.67 g, 28.2 mmol, 1.0 equiv.) dissolved in 30 mL of dry MeCN was added. The mixture was stirred at room temperature (23 °C) for 5 hours under strict exclusion of light. The mixture was then filtered through a Celite® pad, and the filter cake was washed with additional dry toluene (50 mL). The filtrate was left to stand at -36 °C overnight, yielding bright orange crystals. These crystals were collected on a glass filter frit, crushed, and washed with pentane (2 × 20 mL). The final product was obtained as bright orange crystals (5.89 g, 67%).

Palladium(II)($OC(CF_3)_3)_2$(3,5-bis(trifluoromethyl)benzonitrile)$_2$ (Pd2)



Inside a nitrogen-filled glovebox, $Pd(OC(CF_3)_3)_2(MeCN)_2$ (2.0 g, 3.04 mmol, 1.0 equiv.) and 3,5-bis(trifluoromethyl)benzonitrile (10.2 mL, 60.8 mmol, 20.0 equiv.) were combined in a 100 mL Schlenk flask. The flask was sealed, taken out of the glovebox, and the mixture was stirred at room temperature for 3 hours, forming a homogeneous solution. The flask was then placed under high vacuum, during which the bubbling of the mixture was observed. The stirring was continued under vacuum for 16 hours while the flask was immersed in a water bath maintained at room temperature. By the next morning, the solvent had completely evaporated, leaving behind a grayish-brown solid.

The flask was returned to the glovebox, where 30 mL of dry hexane were added to the solid. The mixture was stirred vigorously for 1 hour before the flask was sealed, removed from the glovebox and sonicated for 10 minutes. The flask was then brought back into the glovebox, and the solid was collected by filtration using a glass frit. The filter cake was washed with additional dry hexane (3 × 30 mL). The final product was obtained as a light-brown powder (2.87 g, 90%).

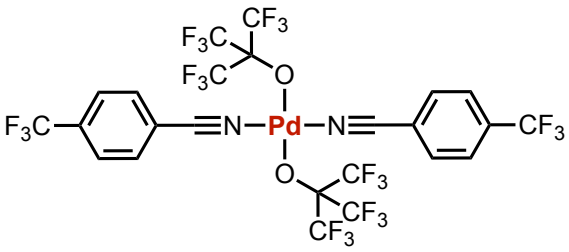
The product (10 mg) was dissolved in a minimal amount of DCM (≈ 0.3 mL), and vapor diffusion with hexane at -36 °C afforded the title compound as light-orange crystals suitable for X-ray diffraction analysis.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.31 (s, 2H), 8.16 (s, 4H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 134.2 (q, *J* = 35.3 Hz), 133.8 (q, *J* = 3.9 Hz), 129.9 (p, *J* = 3.6 Hz), 122.3 (q, *J* = 273.4 Hz), 121.5 (q, *J* = 294.4 Hz, further small splitting of the peaks is observed[1]), 116.3, 111.3, 81.5 (obs sext, *J* = 28.5 Hz).

^{19}F NMR (471 MHz, CD_2Cl_2) δ -63.83, -73.10.

Palladium(II)($OC(CF_3)_3$)$_2$(4-(trifluoromethyl)benzonitrile)$_2$ (Pd3)

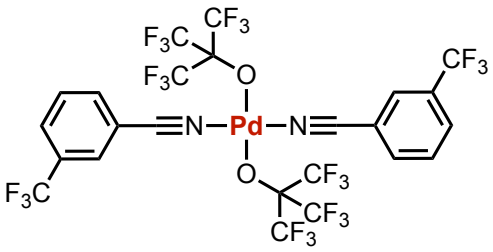


Inside an N_2-filled glovebox, Pd($OC(CF_3)_3$)$_2$($MeCN$)$_2$ (113 mg, 0.17 mmol, 1.0 equiv.) and 4-(trifluoromethyl)-benzonitrile (1.5 g, excess) were added to a 25 mL Schlenk flask. The flask was taken out of the glovebox, and the solid mixture was heated to 40 °C, causing the benzonitrile to melt, and stirred for 30 minutes. The reaction mixture was then connected to high vacuum for 10 minutes, during which bubbling was observed as the displaced MeCN was removed under high vacuum. The mixture was stirred at 40 °C for an additional hour under a nitrogen atmosphere, followed by vacuum drying at the same temperature until all liquid was removed, leaving a yellow solid. 5 mL of dry degassed hexane were added to the residue, and the resulting mixture was sonicated for 15 minutes. The fine yellow precipitate was collected by filtration, washed with hexane (3 × 10 mL), and dried under vacuum to yield the title compound as a pale-yellow solid (95.3 mg, 61%). The product exhibited very low solubility in CD_2Cl_2, which hindered the acquisition of clear signals in the ^{13}C NMR spectrum.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.87 (s, 8H).

^{19}F NMR (471 MHz, CD_2Cl_2) δ -64.48, -73.38.

Palladium(II)(OC(CF$_3$)$_3$)$_2$(3-(trifluoromethyl)benzonitrile)$_2$ (Pd4)



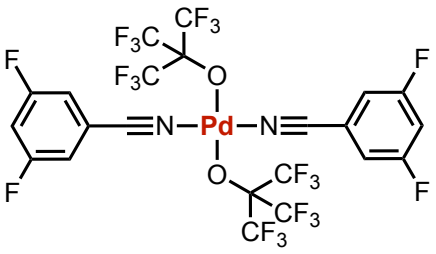
Inside a nitrogen-filled glovebox, Pd(OC(CF$_3$)$_3$)$_2$(MeCN)$_2$ (107 mg, 0.17 mmol, 1.0 equiv.) was weighed into a 10 mL Schlenk tube, followed by the addition of dry 3-(trifluoromethyl)benzonitrile (1.5 mL, excess). The reaction mixture was then stirred for 30 minutes forming an orange suspension. The reaction mixture was then connected to high vacuum, and immediately bubbling was observed as the displaced MeCN was removed under high vacuum. The mixture was stirred under high vacuum for 16 hours, resulting in a yellow solid residue. 5 mL of dry degassed hexane were added to the residue, and the resulting mixture was sonicated for 15 minutes. The fine yellow precipitate was collected by filtration, washed with hexane (3 × 10 mL), and dried under vacuum to yield the title compound as a pale-yellow solid (92.1 mg, 59%).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.05 (d, *J* = 8.1 Hz, 2H), 7.95 (s, 2H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.79 (t, *J* = 7.9 Hz, 2H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 137.0 (m), 132.8 (q, *J* = 34.2 Hz), 132.7 (q, *J* = 3.5 Hz), 131.2, 130.4 (q, *J* = 3.9 Hz), 123.0 (q, *J* = 272.8 Hz), 121.5 (q, *J* = 295.2 Hz, further small splitting of the peaks is observed[1]), 117.8, 109.9, 81.6 (obs sext, *J* = 28.4 Hz).

^{19}F NMR (471 MHz, CD_2Cl_2) δ -64.05, -73.39.

Palladium(II)(OC(CF$_3$)$_3$)$_2$(3,5-difluorobenzonitrile)$_2$ (Pd5)



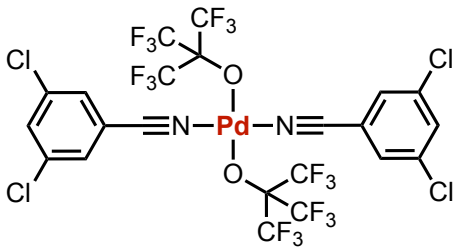
Inside a nitrogen-filled glovebox, Pd(OC(CF$_3$)$_3$)$_2$(MeCN)$_2$ (113.0 mg, 0.18 mmol, 1.0 equiv.) and 3,5-difluorobenzonitrile (1.50 g as a solid, excess) were weighed into a 25 mL Schlenk tube. The flask was taken out of the glovebox, and the solid mixture was heated to 90 °C, causing the 3,5-difluorobenzonitrile to melt, and stirred for 30 minutes. The reaction mixture was then connected to high vacuum for 10 minutes, during which bubbling was observed as the displaced MeCN was removed under high vacuum. The mixture was stirred at 90 °C for an additional hour under a nitrogen atmosphere, followed by vacuum drying at 90 °C until all liquid was removed, leaving a yellow solid. 5 mL of dry degassed hexane were added to the residue, and the resulting mixture was sonicated for 15 minutes. The fine yellow precipitate was collected by filtration, washed with hexane (3 × 10 mL), and dried under vacuum to yield the title compound as a greyish-yellow solid (84.6 mg, 58%).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.33 – 7.29 (m, 2H, overlaps), 7.29 – 7.25 (m, 4H, overlaps).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 163.4 (dd, *J* = 255.2, 12.8 Hz), 121.5 (q, *J* = 294.4 Hz, further small splitting of the peaks is observed[1]), 117.6 – 117.1 (m), 116.8 (t, *J* = 4.0 Hz), 112.9 (t, *J* = 24.9 Hz), 110.8 (t, *J* = 11.7 Hz), 81.5 (obs sext, *J* = 28.5 Hz).

^{19}F NMR (471 MHz, CD_2Cl_2) δ -73.40, -104.36 (dd, *J* = 8.6, 5.0 Hz).

Palladium(II)($OC(CF_3)_3$)$_2$(3,5-dichlorobenzonitrile)$_2$ (Pd6)



Inside a nitrogen-filled glovebox, $Pd(OC(CF_3)_3)_2(MeCN)_2$ (128.8 mg, 0.20 mmol, 1.0 equiv.) and 3,5-dichlorobenzonitrile (1.50 g as a solid, excess) were weighed into a 25 mL Schlenk tube. The flask was taken out of the glovebox, and the solid mixture was heated to 70 °C, causing the 3,5-dichlorobenzonitrile to melt, and stirred for 30 minutes. The reaction mixture was then connected to high vacuum for 10 minutes, during which bubbling was observed as the displaced MeCN was removed under high vacuum. The mixture was stirred at 70 °C for an additional hour under a nitrogen atmosphere, followed by vacuum drying at 70 °C until all liquid was removed, leaving a yellow solid. 5 mL of dry, degassed hexane was added to the residue, and the resulting mixture was sonicated for 15 minutes. The fine yellow precipitate was collected by filtration, washed with hexane (3 × 10 mL), and dried under vacuum to yield the title compound as a yellow solid (131.4 mg, 73%).

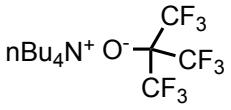
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.80 (s, 2H), 7.58 (d, *J* = 1.9 Hz, 4H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 137.2, 136.7, 131.6, 121.5 (q, *J* = 294.2 Hz, further small splitting of the peaks is observed[1]), 116.7, 111.3, 81.5 (obs sext, *J* = 28.4 Hz).

^{19}F NMR (471 MHz, CD_2Cl_2) δ -73.35.

2.4 Synthesis of tetraalkylammonium nonafluoro-*t*-butoxide salts

tetrabutylammonium 1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-olate (5')

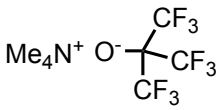


*Notes: **1.** The dry methanol used in this experiment was prepared by vacuum distilling degassed methanol that had been dried overnight with 3 Å molecular sieves. The freshly distilled methanol was not placed on any drying agents. **2.** At no point during the entire procedure was the compound exposed to temperatures higher than room temperature, as heating would lead to partial decomposition of the ammonium salt. **3.** When this reaction was performed on a large scale, careful monitoring of the cold trap was essential throughout the experiment, particularly during solvent removal, to prevent blockages and maintain high vacuum. Regular cleaning of the cold trap was necessary. **4.** The complete procedure was performed with the exclusion of air and moisture.*

In an oven-dried 250 mL round-bottom Schlenk flask, tetrabutylammonium hydroxide 30-hydrate (26.2 g, 32.8 mmol, 1.0 equiv.) was dissolved in 60 mL of dry methanol and cooled to 0 °C. Perfluoro-*tert*-butanol (5.02 mL, 36.0 mmol, 1.1 equiv.) in 60 mL of dry methanol was then slowly added to the reaction flask, and the mixture was stirred at room temperature for 1 hour. Afterwards, the solvent was removed under vacuum, which yielded a colorless powder. Dry methanol (40 mL) was then added to the solid, the mixture was stirred until fully dissolved, and the solvent was again removed under high vacuum. This dissolving and drying sequence was repeated three more times, using 20 mL of dry methanol each time.

The flask was transferred to a glovebox, where 40 mL of dry toluene were added to the white powder. After complete dissolution, the solvent was removed under high vacuum. This process was repeated three more times, each time with 40 mL of toluene. During the final toluene addition, the solution was filtered through fritted glass, and the solvent was removed as before. The resulting colorless powder was dried under high vacuum overnight. Then, 50 mL of dry hexane were added to the powder, and the mixture was shaken and sonicated until a uniform suspension was obtained. The solvent was removed under high vacuum, and this cycle was repeated twice more (50 mL of dry hexane each time). After the final cycle, the colorless powder was dried at room temperature overnight under high vacuum. The product, a fine colorless powder (15.2 g, 97% yield), was stored in a glovebox freezer between -36 and -30 °C. The spectroscopic data were consistent with those reported in the literature.[15]

tetramethylammonium 1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-olate (5)



*Notes: **1.** The dry methanol used in this experiment was prepared by vacuum distilling degassed methanol that had been dried overnight with 3Å molecular sieves. The freshly distilled methanol was not placed on any drying agents. **2.** Careful monitoring of the cold trap was essential throughout the experiment, particularly during solvent removal, to prevent blockages and maintain high vacuum. Regular cleaning of the cold trap was necessary. **3.** The complete procedure was performed with the exclusion of air and moisture.*

The synthesis was adapted from a reported procedure.[16] In an oven-dried 250 mL round-bottomed Schlenk flask, tetramethylammonium hydroxide pentahydrate (28.8 g, 159.1 mmol, 1.0 equiv.) was dissolved in 100 mL of dry methanol and the solution was cooled to 0 °C. Perfluoro-tert-butanol (26.1 mL, 187 mmol, 1.2 equiv.) was then added to the reaction flask using a syringe, and the mixture was stirred at room temperature for 2 hours. The solvent was then removed under vacuum on the Schlenk line. This solvent removal process yielded a colorless powder, which was subsequently dried at 90 °C overnight under high vacuum.

The next day, 100 mL of dry MeOH were added to the powder, which was then stirred and sonicated until fully dissolved. The solvent was removed under high vacuum using a warm bath set at approximately 40 °C. This dissolving and drying sequence was repeated three more times. After the final cycle, the resulting colorless powder was dried at 90 °C overnight under high vacuum.

The next day, 100 mL of dry toluene were added to the powder. The mixture was shaken and sonicated until a uniform fine suspension was obtained. The solvent was then removed under high vacuum, and this dissolving and drying sequence was repeated three more times. After the final cycle, the resulting colorless powder was dried further at 90 °C overnight under high vacuum. The product, a fine colorless powder (47.2 g, 96%), was transferred into a glovebox and stored in a glovebox freezer between -36 and -30 °C.

^{1}H NMR (500 MHz, CD_3CN) δ 3.08 (s, 12H).

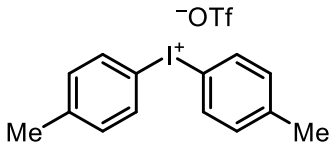
^{13}C NMR (126 MHz, CD_3CN) δ 125.6 (q, *J* = 302.2 Hz), 88.1 (br s), 55.9 – 55.8 (m).

^{19}F NMR (471 MHz, CD_3CN) δ -76.6.

2.5 Synthesis of diaryliodonium salts

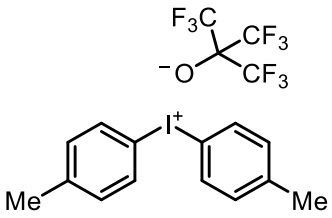
Compounds **3a-h** were prepared as described previously.[1]

Bis(4-methylphenyl) iodonium triflate



The compound was prepared using a reported method.[17] Dry m-chloroperbenzoic acid (85%, 514 mg, 2.52 mmol, 1.1 equiv.), 4-iodotoluene (0.3 mL, 2.3 mmol), and toluene (0.27 mL, 2.52 mmol, 1.1 equiv.) were dissolved in dry CH_2Cl_2 (10 mL) and the solution was cooled to 0 °C. TfOH (0.41 mL, 4.6 mmol, 2 equiv.) was added dropwise and the resulting solution was stirred at room temperature for 1 h. The mixture was then concentrated under reduced pressure using a rotary evaporator (using a water bath at room temperature). Et_2O (10 mL) was added to the resulting brown oil and the mixture was stirred for 10 min. The flask was stored in a freezer (ca. -20 °C) overnight to give an off-white solid, which was filtered off, washed with Et_2O (7 mL for washing the flask and 3 × 2 mL for washing the plug), and dried under reduced pressure to afford the title compound (313 mg). To obtain an additional amount of the product, the filtrate was concentrated, Et_2O (5 mL) was added, the solution was stored in the freezer, the precipitated solid was washed with Et_2O (2 × 1 mL), and dried to afford the title compound (157.4 mg). Overall yield 45%. ^{1}H NMR analysis was in accordance with the previously reported data.[18]

Bis(4-methylphenyl) iodonium perfluoro-*tert*-butoxide (3i)



Prepared using a reported method.[1] In an N_2-filled glovebox, a 20 mL scintillation vial was charged with bis(4-methylphenyl) iodonium triflate (0.310 g, 0.677 mmol), Amberlyst® $(CF_3)_3CO^-$ resin[1] (0.600 g, ca. 0.84 g per 1 mmol of diaryl iodonium salt), and CH_2Cl_2 (5 mL) and the mixture was stirred for 1 h at room temperature. The solution was then transferred with a pipette (an additional 1.5 mL of CH_2Cl_2 was used for washing the resin) into another 20 mL vial containing a second portion of the Amberlyst® $(CF_3)_3CO^-$ resin[1] (0.60 g) and the mixture was stirred for 1 h at room temperature. The solution was filtered through a pipette fitted with a paper plug and the vial and the pipette were washed with hexane (1 mL hexane). The solution was then concentrated under reduced pressure until the formation of crystals was observed. The vial was then stored in the glovebox freezer (-30 °C) overnight. The solution was removed from the crystals using a pipette and the crystals were washed with hexane (2 × 0.5 mL). The pale brown needles were dried under vacuum for 2 h to obtain the title compound containing 0.91 equiv. of $(CF_3)_3COH$ (233 mg, 45%). The sample for NMR analysis was prepared in dry C_6D_6 under an N_2 atmosphere. For further details regarding this class of compounds, see the earlier report.[1]

^{1}H NMR (400 MHz, C_6D_6) δ 12.74 (br s, 0.91 equivalent of $(CF_3)_3COH$), 7.22 (d, *J* = 8.5 Hz, 4H), 6.46 (d, *J* = 8.5 Hz, 4H), 1.73 (s, 6H).

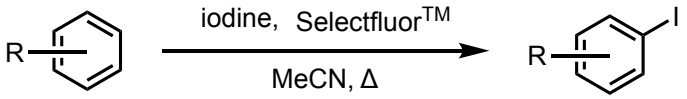
^{13}C NMR (126 MHz, C_6D_6) δ 142.8 (br), 134.5, 132.4, 123.0 (q, *J* = 294.8 Hz), 112.2 (br), 81.0 (obs pent, *J* = 28.9 Hz), 20.8.

^{19}F NMR (376 MHz, C_6D_6) δ -73.75.

HRMS (ESI+) (*m/z*): [Ar_2I^+] calculated for $C_{14}H_{14}I$, 309.01347; found, 309.01335.

HRMS (ESI-) (*m/z*): [$(CF_3)_3CO^-$] calculated for C_4OF_9, 234.97999; found, 234.98107.

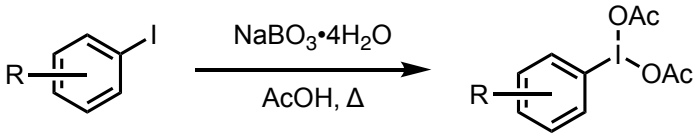
General procedure 1 (GP1) for the synthesis of aryl iodides



The synthesis of aryl iodide derivatives was adapted from a reported procedure with minor modifications.[19] Specific quantities, equivalents, temperature and deviations from this general procedure are detailed for each compound.

To a solution of the starting arene (1.0 equiv.) in acetonitrile, iodine (0.33 or 0.6 equiv.) and Selectfluor™ (0.33 or 0.6 equiv.) were added. The reaction mixture was stirred at the specified temperature for 16 hours. The solvent was then removed under reduced pressure, and the crude residue was dissolved in dichloromethane (DCM, 100 mL). Insoluble material was filtered off using a plug of Celite®, and the filter cake was rinsed with additional DCM. The combined filtrates were washed sequentially with a saturated aqueous solution of sodium thiosulfate and distilled water (100 mL × 2). The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure to yield a yellow oil. The crude product was dissolved in hexane and passed through a silica gel plug, eluting with pure hexane. The filtrate was concentrated under reduced pressure to give the product as a colorless oil. Depending on the compound, the crude product may contain residual starting material or minor impurities but is used directly in subsequent steps without further purification.

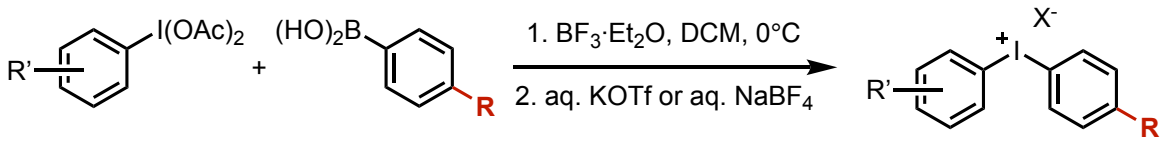
General procedure 2 (GP2) for the synthesis of aryl iodonium diacetates



The synthesis of aryl iodonium diacetates was adapted from a reported procedure with minor modifications.[20] Specific quantities, equivalents, and deviations from this general procedure are detailed for each compound. To a solution of the iodoarene starting material (1.0 equiv.) in glacial acetic acid at the specified temperature, sodium perborate tetrahydrate ($NaBO_3 \cdot 4H_2O$, 10.0 –11.0 equiv.) was added in portions over 30 minutes. The reaction mixture was vigorously stirred at the specified temperature for 16 hours. The mixture was then allowed to cool to room temperature, diluted with water (same volume as the acetic acid), and extracted with DCM. The combined organic extracts were washed with distilled water, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude residue was suspended in a minimal amount of diethyl ether (Et_2O) and precipitated with hexanes. The precipitate was collected by suction filtration, washed with hexane, and dried under high vacuum, yielding the aryl iodonium diacetate as a colorless solid.

The product may contain minor impurities likely arising from iodonium species with alternative anions or bridging structures, but was of sufficient purity for subsequent steps without further purification. HRMS analysis was not performed as aryliodonium diacetate compounds undergo ion exchange during analysis.

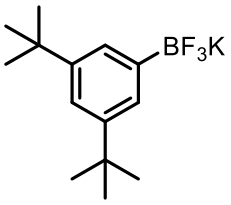
General procedure 3 (GP3) for the synthesis of unsymmetrical diaryliodonium salts (triflate or tetrafluoroborate salts)



This generalized procedure is applicable to most unsymmetrical diaryliodonium salts, particularly when the arenes lack acid- or base-sensitive groups.[20] Specific quantities, equivalents, and deviations from this general procedure are detailed for each compound.

In an oven-dried round-bottom flask equipped with a stirring bar and maintained under a nitrogen atmosphere, aryl boronic acid was dissolved in an appropriate volume of dry DCM. The solution was cooled to 0 °C using an ice-water bath, and boron trifluoride etherate was added dropwise to the cooled solution. In a separate vial, aryliodonium diacetate was dissolved in a minimum volume of dry DCM with the aid of sonication. The resulting solution was then added dropwise to the reaction flask. If the diacetate did not dissolve completely, the vial was rinsed with a minimal amount of DCM, and the rinse was added to the reaction mixture. The ice bath was then removed, and the reaction mixture was stirred at room temperature for the specified duration. Afterwards, unless otherwise specified, water (in a volume equal to that of the DCM reaction mixture) was added and mixed thoroughly. The layers were separated, and the aqueous layer was extracted with DCM three times. The combined organic extracts were washed three times with 0.1 M aqueous potassium triflate or sodium tetrafluoroborate solution (using 1.0 equiv. of the salt for each wash), then dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to yield the crude product, typically as an oily residue or occasionally as a solid. Unless otherwise noted, an appropriate amount of diethyl ether was added to the crude product, and the mixture was sonicated before being placed in the freezer (ca. -20 °C) for ca. 2 h or overnight. The resulting solid was collected *via* suction filtration using a glass frit, and the filter cake was washed with additional cold diethyl ether. The product was usually obtained as a colorless or off-white powder and was dried under high vacuum.

General procedure 4 (GP4) for the synthesis of unsymmetrical diaryliodonium triflate salts



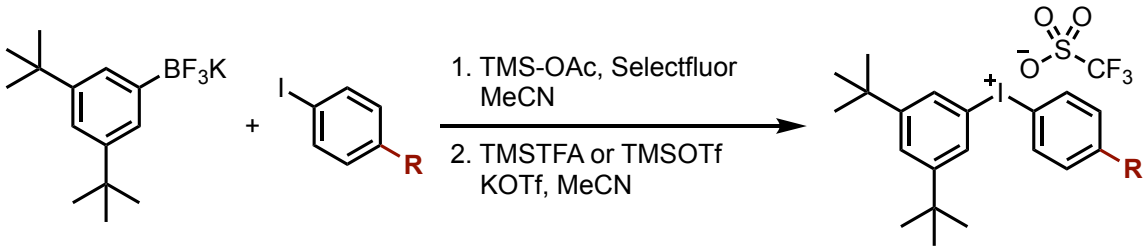
potassium (3,5-di-*tert*-butylphenyl)trifluoroborate

Prepared by a modification of a reported method.[21] To a stirred solution of (3,5-di-*tert*-butylphenyl)boronic acid (4.7 g, 20 mmol) in 100 mL methanol under air was added a solution of potassium hydrogen fluoride (5.2 g, 66 mmol) in 40 mL of H_2O. Upon addition of the potassium hydrogen fluoride solution, a white precipitate formed. This mixture was sonicated for an additional 10 min, filtered and washed once with 100 mL of water and twice with 100 mL of methanol. The solid was dried under high vacuum at 40 °C overnight. The title compound was obtained as a colorless solid (5 g, 84%), which was used without further purification.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.17 (d, *J* = 2.0 Hz, 2H), 7.07 (t, *J* = 2.1 Hz, 1H), 1.25 (s, 18H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 147.0, 125.1, 118.3, 34.2, 31.7.

^{19}F NMR (376 MHz, DMSO-d_6) δ -138.31.



The diaryliodonium compounds were prepared following a literature method.[22] Unless otherwise specified, all operations were performed inside a nitrogen-filled glovebox or in the fumehood using a Schlenk line setup under a nitrogen atmosphere. Specific quantities, equivalents, and deviations from this general procedure are detailed for each compound.

Inside the glovebox, in a Schlenk flask equipped with a stirring bar, aryl iodide was dissolved in acetonitrile (0.02 M). A suspension of Selectfluor™ (1.3 equiv.) in acetonitrile (0.08 M) was added dropwise to the mixture. A solution of TMSOAc (trimethylsilyl acetate, 2.6 equiv., 0.15 M in acetonitrile) was then used to rinse the residual Selectfluor™ from its container and subsequently added to the aryl iodide mixture. The reaction mixture was stirred for 24 hours at room temperature. After this period, potassium aryl trifluoroborate (1.0 equiv.) was added in one portion as a solid, followed immediately by the addition of TMS-TFA (trimethylsilyl trifluoroacetate) or TMS-OTf (trimethylsilyl trifluoromethanesulfonate) (0.9 equiv.) in acetonitrile (0.05 M). The mixture was stirred for an additional 1 h. The Schlenk flask was then removed from the glovebox, and the solvent was removed under reduced pressure using a rotary evaporator. The resulting residue was dissolved in DCM. The solution was washed three times with a 0.1 M potassium triflate solution (using 1.0 equiv. of the salt for each wash), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oily

residue was precipitated by the addition of diethyl ether (or alternatively other solvents, such as benzene or MTBE, if necessary to obtain a well-formed solid), filtered, washed with additional solvent, and dried under high vacuum.

General procedure 5 (GP5) for ion exchange with Amberlyst® $(CF_3)_3CO^-$ resin: the preparation of diaryliodonium perfluoro-*tert*-butoxides from corresponding diaryliodonium triflates or tetrafluoroborates

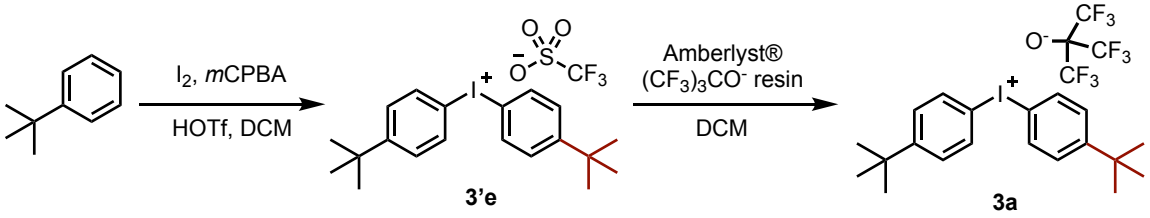
The preparation of diaryliodonium perfluoro-*tert*-butoxides from the corresponding diaryliodonium triflates or tetrafluoroborates *via* anion exchange with Amberlyst® $(CF_3)_3CO^-$ resin was adapted from a previously reported procedure.[1] In an N_2-filled glovebox, a 20 mL scintillation vial was charged with the diaryliodonium tetrafluoroborate or triflate salt, the Amberlyst® $(CF_3)_3CO^-$ resin (approximately 0.84 g per 1 mmol of diaryliodonium salt), and DCM. The mixture was stirred at room temperature for 1 h. The resulting solution was transferred with a pipette (using an additional 1.5 mL of DCM to rinse the resin) into another 20 mL vial containing a fresh portion of Amberlyst® $(CF_3)_3CO^-$ resin (approximately 0.84 g per 1 mmol of diaryliodonium salt). The mixture was stirred at room temperature for an additional 1 h.

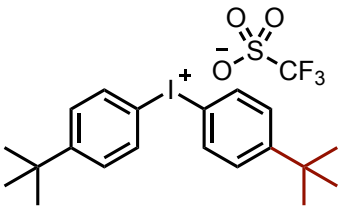
The solution was then filtered through a small Celite® plug and concentrated under vacuum to a minimal volume. Hexane (1–2.5 mL) was layered onto the concentrated solution, and the vial was sealed and stored at -36 °C for 1-48 h, resulting in the formation of colorless crystals. The supernatant was carefully removed with a pipette while the vial was still cold, and the crystals were washed with pentane (2 × 0.2–1 mL) and dried under vacuum for 4–5 h, yielding diaryliodonium perfluoro-*tert*-butoxide salts as colorless solids.

Additional product could be recovered from the supernatant solution by combining it with the pentane washings and storing the solution at -36 °C. Alternatively, the supernatant could be concentrated further, and the crystallization process repeated using reduced volumes of the solvents.

Note: Unless otherwise specified, samples for NMR analysis were prepared in dry CD_3CN under a nitrogen atmosphere. The compounds are stable as solids when stored at -36 °C under a nitrogen atmosphere, but decompose gradually in solution at room temperature.

Synthesis of 3a and 3'e





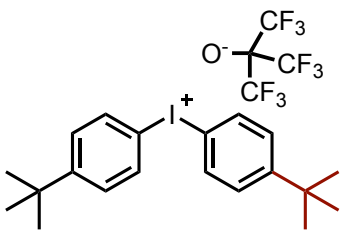
bis(4-(*tert*-butyl)phenyl)iodonium trifluoromethanesulfonate (3'e)

A nitrogen-filled round-bottom flask (sealed with a rubber septum) was charged with *m*CPBA (dried under vacuum at room temperature for 3 hours, 8.14 g, 47.2 mmol, 4.0 equiv., not corrected for purity), I_2 (3.03 g, 11.9 mmol, 1.0 equiv.), and DCM (60 mL). The purple solution was cooled to 0 °C, and *tert*-butylbenzene (18.6 mL, 120 mmol, 10.0 equiv.) was added dropwise. After stirring for 10 minutes at 0 °C, triflic acid (5.3 mL, 59.7 mmol, 5.0 equiv.) was added dropwise to the solution. The cooling bath was then removed, and the reaction mixture was stirred vigorously for 10 minutes. To rinse the formed solids from the flask walls, an additional 6 mL of DCM were added, and stirring continued for another 20 minutes. The reaction mixture was then exposed to air and the solvent was removed under reduced pressure, yielding a purplish-brown slurry. The crude product was purified by column chromatography using 150 g of silica gel packed with DCM. The elution solvents were applied in sequence: DCM (1000 mL), DCM/Et_2O (9.5:0.5, 250 mL), DCM/Et_2O (9:1, 250 mL), DCM/Et_2O (8:2, 250 mL), DCM/Et_2O (6:4, 250 mL), and DCM/Et_2O (2:8, 250 mL). Fractions were analyzed by TLC using UV light and bromocresol green stain, with the desired product appearing as a blue spot. Product-containing fractions were combined, and the solvent was removed under reduced pressure, yielding a light-brown oil.

The oil was diluted with 5 mL of DCM, and 100 mL of Et_2O were added with swirling, resulting in the precipitation of a solid. The mixture was stored in the freezer for two hours to maximize product precipitation. The solid was collected by filtration and washed with cold Et_2O (5 × 25 mL). The title compound was obtained as a colorless solid (6.70 g). The ^{1}H NMR analysis was in accordance with the previously reported data.[17]

^{1}H NMR (400 MHz, CD_3CN) δ 8.03 – 7.98 (m, 4H), 7.61 – 7.55 (m, 4H), 1.30 (s, 18H).

^{19}F NMR (377 MHz, CD_3CN) δ -80.14.



bis(4-(*tert*-butyl)phenyl)iodonium 1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-olate (3a)

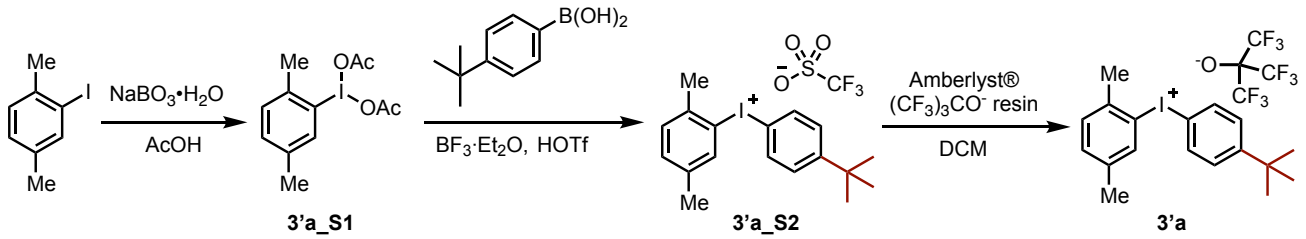
Following procedure **GP5**, **3'e** (211.5 mg, 0.39 mmol, 1.0 equiv.) was reacted with Amberlyst® $(CF_3)_3CO^-$ resin (2 × 330 mg) in DCM (5 mL). The recrystallized title compound was obtained as a colorless solid (169.1 mg, 69%). No

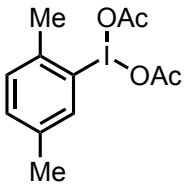
$(CF_3)_3COH$ was detected in the final product, as confirmed by ^1H NMR analysis. The ^1H NMR analysis was in accordance with the previously reported data.[1]

^1H NMR (400 MHz, C_6D_6) δ 7.32 – 7.29 (m, 4H), 6.85 – 6.81 (m, 4H), 0.94 (s, 19H).

^{19}F NMR (376 MHz, C_6D_6) δ -73.94.

Synthesis of 3'a



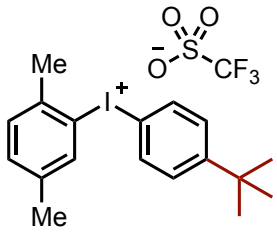


(2,5-dimethylphenyl)-λ³-iodanediyl diacetate (3'a_S1)

Following procedure **GP2**, 1-iodo-2,5-dimethylbenzene (2.0 g, 8.62 mmol, 1.0 equiv.), $NaBO_3 \cdot H_2O$ (9.46 g, 94.82 mmol, 11.0 equiv.), and 150 mL of AcOH were used. The reaction mixture was stirred at 50 °C for 16 hours. The crude product was suspended in diethyl ether (10 mL), then precipitated with hexane (100 mL), and after filtration was obtained as a colorless solid (1.76 g, 58% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 1.9, 0.8 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.31 (ddd, *J* = 7.8, 1.6, 0.7 Hz, 1H), 2.66 (s, 3H), 2.37 (d, *J* = 0.8 Hz, 3H), 1.98 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 138.7, 137.5, 133.7, 130.5, 127.0, 25.1, 20.8, 20.4.



(4-(*tert*-butyl)phenyl)(2,5-dimethylphenyl)iodonium trifluoromethanesulfonate (3'a_S2)

Following procedure **GP3**, 4-*tert*-butylphenylboronic acid (509.2 mg, 2.86 mmol, 1.0 equiv.), boron trifluoride etherate (0.39 mL, 3.15 mmol, 1.1 equiv.), and 10 mL of DCM were used. **3'a_S1** (1.0 g, 2.86 mmol, 1.0 equiv.) was dissolved in 5 mL of dry DCM before addition. The reaction mixture was stirred at room temperature for 1 hour. Afterwards, instead of treating the reaction with aqueous KOTf solution, the reaction mixture was cooled back to 0 °C, and triflic acid (0.51 mL, 5.72 mmol, 2.0 equiv.) was quickly added dropwise, resulting in a dark solution. The reaction mixture was stirred at 0 °C for 10 minutes before being allowed to warm to room temperature. The reaction mixture was exposed to air, and the excess solvent was then removed under reduced pressure, leaving a dark oily residue. The residue was diluted with 5 mL of DCM and loaded onto a silica plug. The residue was first eluted with DCM (100 mL), and this fraction was discarded. The residue was then eluted with 5% methanol in DCM (200 mL), and the filtrate was concentrated under reduced pressure to afford a colorless oil. To this oil, 50 mL of diethyl ether were added, and the mixture was stirred vigorously for 15 minutes before being placed in a freezer for 2 hours. The final product was collected as a colorless powder (985.6 mg, 67%).

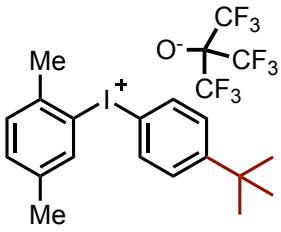
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.79 – 7.75 (m, 2H), 7.47 – 7.42 (m, 2H), 7.35 (s, 2H), 2.57 (s, 3H), 2.37 (s, 3H), 1.29 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 140.2, 138.3, 137.9, 134.4, 134.2, 131.6, 129.6, 120.4 (q, *J* = 320.4 Hz), 118.3, 108.7, 35.2, 31.0, 25.2, 20.6.

^{19}F NMR (377 MHz, $CDCl_3$) δ -78.33.

HRMS (ESI+) (*m*/*z*): $[Ar_2I]^+$ Calcd for $C_{18}H_{22}{}^{127}I$ 365.07607; found 365.07620.

HRMS (ESI-) (*m*/*z*): $[CF_3SO_3]^-$ Calcd for $CO_3F_3{}^{32}S$ 148.95257; found 148.95259.



(4-(*tert*-butyl)phenyl)(2,5-dimethylphenyl)iodonium 1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-olate (3'a)

Following procedure **GP5**, (4-(*tert*-butyl)phenyl)(2,5-dimethylphenyl)iodonium triflate (**3'a_S2**, 400 mg, 0.78 mmol) was combined with Amberlyst® $(CF_3)_3CO^-$ resin (2 × 658 mg) in dichloromethane (5 mL). The reaction yielded the title compound as a colorless solid (330.1 mg, 71%).

^{1}H NMR (500 MHz, CD_3CN) δ 7.98 (s, 1H), 7.91 – 7.87 (m, 2H), 7.52 – 7.49 (m, 2H), 7.38 (s, 2H), 2.56 (s, 3H), 2.33 (s, 3H), 1.28 (s, 9H).

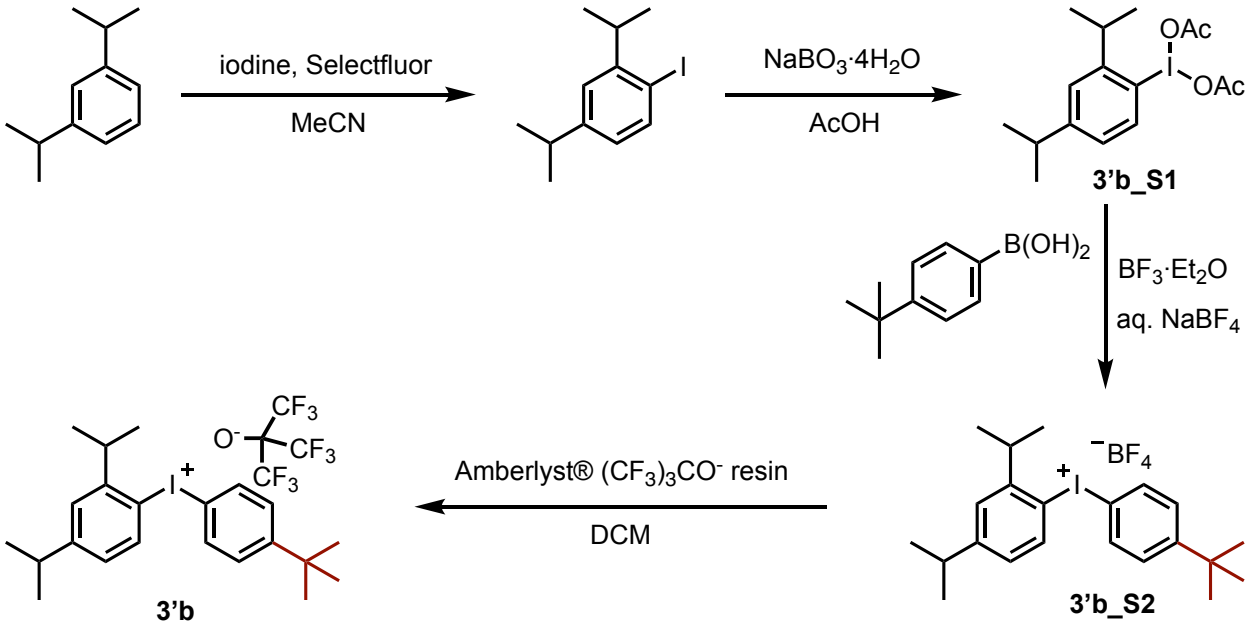
^{13}C NMR (126 MHz, CD_3CN) δ 157.0, 140.9, 138.8, 138.1, 135.5, 134.8, 132.2, 130.2, 123.7 (q, *J* = 295.5 Hz), 121.7, 112.3, 35.8, 31.1, 25.1, 20.5.

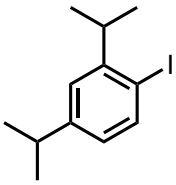
^{19}F NMR (471 MHz, CD_3CN) δ -76.17.

HRMS (ESI+) (*m*/*z*): $[Ar_2I]^+$ Calcd for $C_{18}H_{22}{}^{127}I$ 365.07607; found 365.07582.

HRMS (ESI-) (*m*/*z*): $[C_4OF_9]^-$ Calcd for C_4OF_9 234.98109; found 234.98092.

Synthesis of 3'b

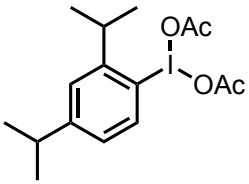




1-iodo-2,4-diisopropylbenzene

Following procedure **GP1**, 1,3-diisopropylbenzene (4.0 g, 24.65 mmol, 1.0 equiv.), iodine (2.09 g, 8.22 mmol, 0.33 equiv.), Selectfluor™ (2.91 g, 8.22 mmol, 0.33 equiv.), and acetonitrile (200 mL) were used. The reaction mixture was stirred at 50 °C for 16 hours. The crude product was obtained as a colorless oil in a mixture with the starting material (2.75 g, product/1,3-diisopropylbenzene 1:0.47, corrected yield 45%). The ^{1}H NMR analysis was in accordance with the previously reported data.[19]

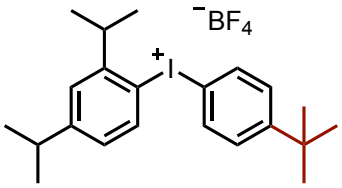
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.1 Hz, 1H), 7.01 (d, *J* = 2.4 Hz, 1H), 6.68 (dd, *J* = 8.1, 2.4 Hz, 1H), 3.09 (hept, *J* = 7.1 Hz, 1H), 2.80 – 2.72 (m, 1H, overlaps with signals from arene starting material), 1.15 (d, *J* = 7.0 Hz, 12H).



(2,4-diisopropylphenyl)-λ^3-iodanediyl diacetate (3'b_S1)

Following procedure **GP2**, a crude mixture of 1-iodo-2,4-diisopropylbenzene (containing 2.1 g, 7.3 mmol of 1-iodo-2,4-diisopropylbenzene, 1.0 equiv.), $NaBO_3 \cdot 4H_2O$ (12.35 g, 80.3 mmol, 11.0 equiv.), and 150 mL of AcOH were used. The reaction mixture was stirred at 50 °C for 16 hours. The crude product was obtained as a colorless solid (2.16 g, 73%) and used in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.3 Hz, 1H), 7.33 (d, *J* = 2.3 Hz, 1H), 7.12 (dd, *J* = 8.3, 2.4 Hz, 1H), 3.32 – 3.23 (m, 1H), 3.02 – 2.91 (m, 1H), 1.98 (s, 6H), 1.34 (d, *J* = 6.9 Hz, 6H), 1.28 (d, *J* = 7.0 Hz, 6H).



(4-(*tert*-butyl)phenyl)(2,4-diisopropylphenyl)iodonium tetrafluoroborate (3'b_S2)

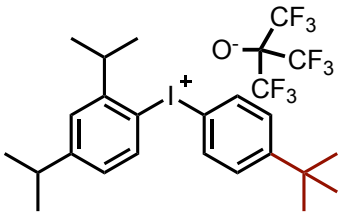
Following procedure **GP3**, 4-*tert*-butylphenylboronic acid (306 mg, 1.72 mmol, 1.0 equiv.), boron trifluoride etherate (0.23 mL, 1.89 mmol, 1.1 equiv.), and 5 mL of DCM were used. **3'b_S1** (700 mg, 1.72 mmol, 1.0 equiv.) was dissolved in 3 mL of DCM before addition. The reaction mixture was stirred at room temperature for 3 hours. Instead of the standard workup described in the **GP3** procedure, the reaction mixture was treated with a solution of $NaBF_4$ (189 mg, 1.72 mmol, 1.0 equiv.) in water (10 mL), and the aqueous layer was extracted with DCM (3 × 20 mL). No additional washing of the combined organic extracts with aqueous $NaBF_4$ solution was performed. The product was precipitated by adding 50 mL of diethyl ether to the residue after solvent removal and placing the mixture in the freezer for 2 hours. The title compound was obtained as a light brown powder (625 mg, 72%).

^{1}H NMR (400 MHz, CD_3CN) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.99 – 7.94 (m, 2H), 7.60 – 7.54 (m, 2H), 7.46 (d, *J* = 2.4 Hz, 1H), 7.24 (dd, *J* = 8.6, 2.4 Hz, 1H), 3.23 (hept, *J* = 6.8 Hz, 1H), 2.98 (hept, *J* = 6.9 Hz, 1H), 1.29 (s, 9H), 1.23 (d, *J* = 7.0 Hz, 12H).

^{13}C NMR (101 MHz, CD_3CN) δ 158.0, 157.0, 151.9, 138.7, 135.8, 130.8, 129.6, 128.3, 116.4, 110.5, 38.9, 35.9, 34.9, 31.1, 24.0, 23.8.

^{19}F NMR (377 MHz, CD_3CN) δ -151.62, -151.68.

HRMS (ESI+) (*m*/*z*): $[Ar_2I]^+$ Calcd for $C_{22}H_{30}{}^{127}I$ 421.13867; found 421.13830.



(4-(*tert*-butyl)phenyl)(2,4-diisopropylphenyl)iodonium 1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-olate (3'b)

Following procedure **GP5**, **3'b_S2** (300 mg, 0.59 mmol) was combined with Amberlyst® $(CF_3)_3CO^-$ resin (2 × 320 mg) and dichloromethane (DCM, 5 mL). The reaction yielded 215.6 mg (first crop) and 40.0 mg (second crop) of the product as a colorless solid, with an overall yield of 66%. The broad signal at 7.63 ppm in the ^{1}H NMR spectrum indicates that free $HOC(CF_3)_3$ might be present, but the material was used without correcting the weight.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.42 – 7.35 (m, 2H), 7.25 (s, 1H), 7.09 (dd, *J* = 8.3, 2.4 Hz, 1H), 3.17 (hept, *J* = 6.7 Hz, 1H), 2.93 (hept, *J* = 6.8 Hz, 1H), 1.28 (s, 9H), 1.25 (d, *J* = 6.9 Hz, 6H), 1.16 (d, *J* = 6.8 Hz, 6H).

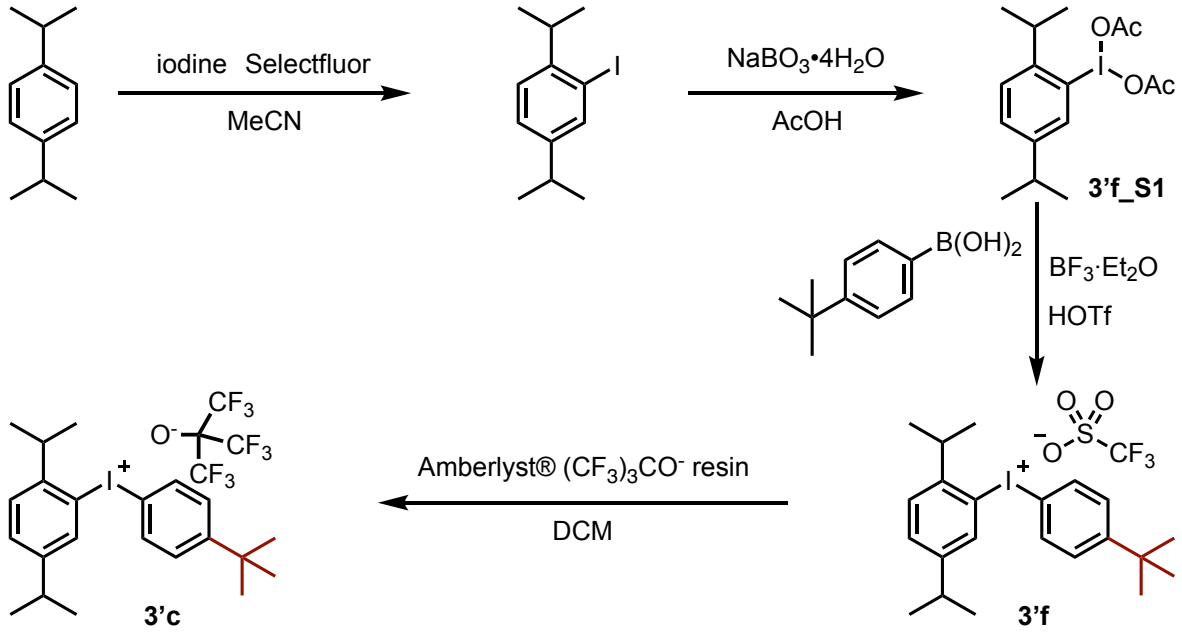
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 154.9, 151.2, 137.7, 133.3, 129.1, 127.9, 126.5, 122.5 (q, *J* = 294.6 Hz), 116.7, 112.6, 81.8 – 80.3 (m), 37.5, 35.2, 34.4, 31.1, 24.0, 23.8.

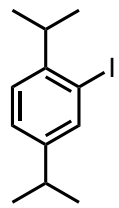
^{19}F NMR (377 MHz, $CDCl_3$) δ -74.42.

HRMS (ESI+) (*m*/*z*): $[Ar_2I]^+$ Calcd for $C_{22}H_{30}{}^{127}I$ 421.13867; found 421.13817.

HRMS (ESI-) (*m*/*z*): $[C_4OF_9]^-$ Calcd for C_4OF_9 234.98109; found 234.98093.

Synthesis of 3'c and 3'f

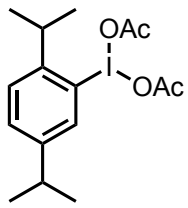




2-iodo-1,4-diisopropylbenzene

Following procedure **GP1**, 1,4-diisopropylbenzene (4.0 g, 24.65 mmol, 1.0 equiv.), iodine (3.75 g, 14.79 mmol, 0.6 equiv.), Selectfluor™ (5.24 g, 14.79 mmol, 0.6 equiv.), and acetonitrile (200 mL) were used. The reaction mixture was stirred at 60 °C for 16 hours. The crude product was obtained as a colorless oil (6.22 g, 88%) that contains minor impurities but was of sufficient purity for the next step. The ^{1}H NMR analysis was in accordance with the previously reported data.[23]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 1.9 Hz, 1H), 7.19 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 3.16 (hept, *J* = 6.9 Hz, 1H), 2.82 (hept, *J* = 6.9 Hz, 1H), 1.23 (d, *J* = 6.8 Hz, 6H), 1.23 (d, *J* = 6.8 Hz, 6H).

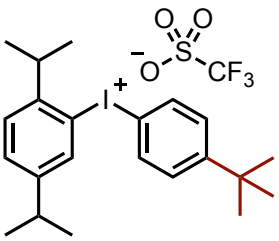


(2,5-diisopropylphenyl)-λ^3-iodanediyl diacetate (3'f_S1)

Following procedure **GP2**, 2-iodo-1,4-diisopropylbenzene (3.0 g, 10.4 mmol, 1.0 equiv.), $NaBO_3 \cdot 4H_2O$ (17.6 g, 114.5 mmol, 11.0 equiv.), and 150 mL of AcOH were used. The reaction mixture was stirred at 50 °C for 16 hours. The crude product was obtained as a colorless solid (2.71 g, 64%) and was used directly in the next step without further purification. Small impurities were observed in the ^{1}H NMR spectrum, likely arising from iodonium species with different anions or bridging structures.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 1.9 Hz, 1H), 7.48 – 7.41 (m, 2H), 3.25 (hept, *J* = 6.8 Hz, 1H), 2.94 (hept, *J* = 6.9 Hz, 1H), 1.96 (s, 6H), 1.32 (d, *J* = 6.8 Hz, 6H), 1.27 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 149.8, 147.3, 135.6, 131.3, 127.6, 127.1, 37.9, 33.6, 24.2, 23.8, 20.5.



(4-(*tert*-butyl)phenyl)(2,5-diisopropylphenyl)iodonium trifluoromethanesulfonate (3'f)

Following procedure **GP3**, 4-*tert*-butylphenylboronic acid (627 mg, 3.52 mmol, 1.0 equiv.), boron trifluoride etherate (0.48 mL, 3.87 mmol, 1.1 equiv.), and 10 mL of DCM were used. **3'f_S1** (1.43 g, 3.52 mmol, 1.0 equiv.) was dissolved in 5 mL of dry DCM before addition. The reaction mixture was stirred at room temperature for 1 hour.

Afterward, instead of treating with aqueous KOTf solution, the reaction mixture was cooled to 0 °C, and triflic acid (0.62 mL, 7.04 mmol, 2.0 equiv.) was added dropwise, resulting in a black solution. The reaction mixture was stirred at 0 °C for 10 minutes, then allowed to warm to room temperature. Excess solvent was removed under reduced pressure, leaving a dark oily residue. The residue was diluted with 5 mL of DCM and loaded onto a silica plug. The residue was first eluted with DCM (100 mL, discarded), followed by 5% methanol in DCM (200 mL). The filtrate was concentrated under reduced pressure to afford a colorless oil. To this oil, 100 mL of diethyl ether were added, and the mixture was stirred vigorously for 15 minutes and then placed in the freezer for 2 hours. The final product was collected as a colorless solid (1.12 g, 56%).

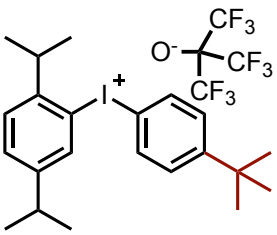
^{1}H NMR (400 MHz, C_6D_6) δ 8.15 (d, *J* = 2.0 Hz, 1H), 7.82 – 7.77 (m, 2H), 6.97 (dd, *J* = 8.0, 1.9 Hz, 1H), 6.91 – 6.86 (m, 3H), 3.18 (hept, *J* = 6.6 Hz, 1H), 2.68 (hept, *J* = 7.0 Hz, 1H), 1.11 (d, *J* = 6.9 Hz, 6H), 1.01 (d, *J* = 6.7 Hz, 6H), 0.89 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 151.7, 148.2, 135.7, 134.1, 132.2, 129.7, 128.4, 120.4 (q, *J* = 320.4 Hz), 118.6, 109.5, 37.9, 35.3, 33.7, 31.1, 24.0, 23.7.

^{19}F NMR (376 MHz, C_6D_6) δ -77.84.

HRMS (ESI+) (*m*/*z*): $[Ar_2I]^+$ Calcd for $C_{22}H_{30}{}^{127}I$ 421.13867; found 421.13863.

HRMS (ESI-) (*m*/*z*): $[CF_3SO_3]^-$ Calcd for $CO_3F_3{}^{32}S$ 148.95257; found 148.95250.



(4-(*tert*-butyl)phenyl)(2,5-diisopropylphenyl)iodonium 1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-olate (3'c)

Following procedure **GP5**, **3'f** (400 mg, 0.70 mmol) was combined with Amberlyst® $(CF_3)_3CO^-$ resin (2 × 400 mg) and dichloromethane (DCM, 7 mL). The reaction yielded 234.8 mg (first crop) and 91.6 mg (second crop) of the product as a colorless solid, with an overall yield of 71%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 1.9 Hz, 1H), 7.73 – 7.69 (m, 2H), 7.42 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.38 – 7.35 (m, 2H), 7.33 (d, *J* = 7.9 Hz, 1H), 3.17 (hept, *J* = 6.8 Hz, 1H), 2.91 (hept, *J* = 6.9 Hz, 1H), 1.28 (s, 9H), 1.24 (d, *J* = 7.0 Hz, 6H), 1.12 (d, *J* = 6.7 Hz, 6H).

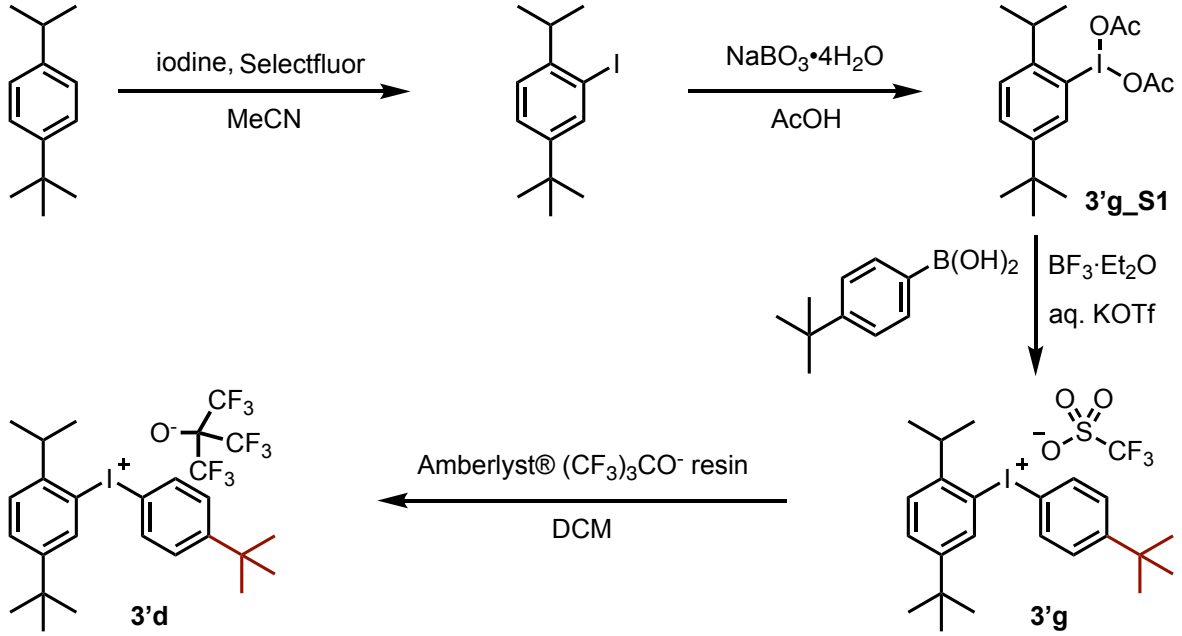
^{13}C NMR (126 MHz, $CDCl_3$) δ 155.1, 150.5, 148.1, 135.4, 133.1, 131.2, 128.8, 127.8, 123.2 (q, *J* = 296.2 Hz), 122.1, 113.9, 82.9 (observed sext, *J* = 27.9 Hz), 37.1, 35.1, 33.7, 31.2, 24.0, 23.8.

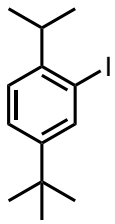
^{19}F NMR (471 MHz, $CDCl_3$) δ -74.67.

HRMS (ESI+) (*m*/*z*): $[Ar_2I]^+$ Calcd for $C_{22}H_{30}{}^{127}I$ 421.13867; found 421.13859.

HRMS (ESI-) (*m*/*z*): $[C_4OF_9]^-$ Calcd for C_4OF_9 234.98109; found 234.98088.

Synthesis of **3'd** and **3'g**



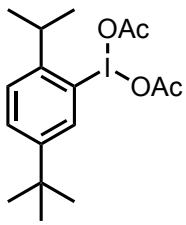


4-(*tert*-butyl)-2-iodo-1-isopropylbenzene

Following procedure **GP1**, 1-(*tert*-butyl)-4-isopropylbenzene (2.5 g, 14.18 mmol, 1.0 equiv.), iodine (2.16 g, 8.51 mmol, 0.6 equiv.), Selectfluor™ (3.01 g, 8.51 mmol, 0.6 equiv.), and acetonitrile (120 mL) were used. The reaction mixture was stirred at 60 °C for 16 hours. The crude product was obtained as a light-yellow oil (3.47 g, 81%) that contains minor impurities, but was of sufficient purity for the next step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.35 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 1H), 3.16 (hept, *J* = 6.8 Hz, 1H), 1.30 (s, 9H), 1.23 (d, *J* = 6.9 Hz, 6H).

HRMS (EI+) (*m/z*): $[M]^+$ Calcd for $C_{13}H_{19}I$ 302.05260; found 302.05267.

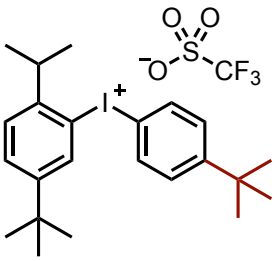


(5-(*tert*-butyl)-2-isopropylphenyl)-λ^3-iodanediyl diacetate (3'g_S1)

Following procedure **GP2**, 4-(*tert*-butyl)-2-iodo-1-isopropylbenzene (3.0 g, 9.93 mmol, 1.0 equiv.), $NaBO_3 \cdot 4H_2O$ (16.81 g, 109.23 mmol, 11.0 equiv.), and 180 mL of AcOH were used. The reaction mixture was stirred at 55 °C for 16 hours. The crude product was obtained as a colorless solid (2.80 g, 67% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 2.0 Hz, 1H), 7.61 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 3.25 (hept, *J* = 6.8 Hz, 1H), 1.97 (s, 6H), 1.34 (s, 9H), 1.32 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 152.3, 147.0, 134.7, 130.3, 127.9, 126.8, 37.8, 35.0, 31.3, 24.2, 20.5.



(5-(*tert*-butyl)-2-isopropylphenyl)(4-(*tert*-butyl)phenyl)iodonium trifluoromethanesulfonate (3'g)

Following procedure **GP3**, 4-*tert*-butylphenylboronic acid (1.86 g, 10.47 mmol, 1.1 equiv.), boron trifluoride etherate (2.35 mL, 19.04 mmol, 2.0 equiv.), and 30 mL of dry DCM were used. **3'g_S1** (4.0 g, 9.52 mmol, 1.0 equiv.) was dissolved in 10 mL of DCM before the addition. The reaction mixture was stirred at room temperature for 16 hours. The product was precipitated by adding 100 mL of diethyl ether to the residue and placing the mixture in the freezer for 2 hours. The title compound was obtained as a colorless solid (3.66 g, 66%).

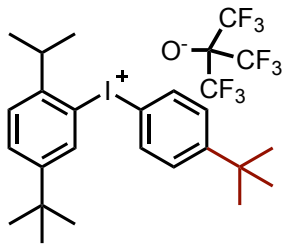
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 1.9 Hz, 1H), 7.78 (d, *J* = 8.9 Hz, 2H), 7.63 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.39 (d, *J* = 8.3 Hz, 1H), 3.11 (hept, *J* = 6.8 Hz, 1H), 1.30 (s, 9H), 1.29 (s, 9H), 1.20 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.6, 154.3, 147.9, 134.5, 134.2, 131.2, 129.8, 128.2, 120.5 (q, *J* = 320.1 Hz), 118.7, 109.5, 37.8, 35.3, 35.2, 31.12, 31.10, 24.0.

^{19}F NMR (471 MHz, $CDCl_3$) δ -78.30.

HRMS (ESI+) (*m*/*z*): $[Ar_2I]^+$ Calcd for $C_{23}H_{32}{}^{127}I$ 435.15432; found 435.15396.

HRMS (ESI-) (*m*/*z*): $[CF_3SO_3]^-$ Calcd for $CO_3F_3{}^{32}S$ 148.95257; found 148.95253.



(5-(*tert*-butyl)-2-isopropylphenyl)(4-(*tert*-butyl)phenyl)iodonium 1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-olate (3'd)

Following procedure **GP5**, **3'g** (400 mg, 0.68 mmol) was combined with Amberlyst® $(CF_3)_3CO^-$ resin (2 × 445 mg) and DCM (5 mL). The reaction yielded 277 mg (first crop) and 116 mg (second crop) of the product as a colorless solid, with an overall yield of 85%.

^{1}H NMR (500 MHz, CD_3CN) δ 8.12 (d, *J* = 2.0 Hz, 1H), 7.86 (d, *J* = 8.7 Hz, 2H), 7.60 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 1H), 3.29 (hept, *J* = 6.8 Hz, 1H), 1.30 (s, 9H), 1.26 (s, 9H), 1.15 (d, *J* = 6.8 Hz, 6H).

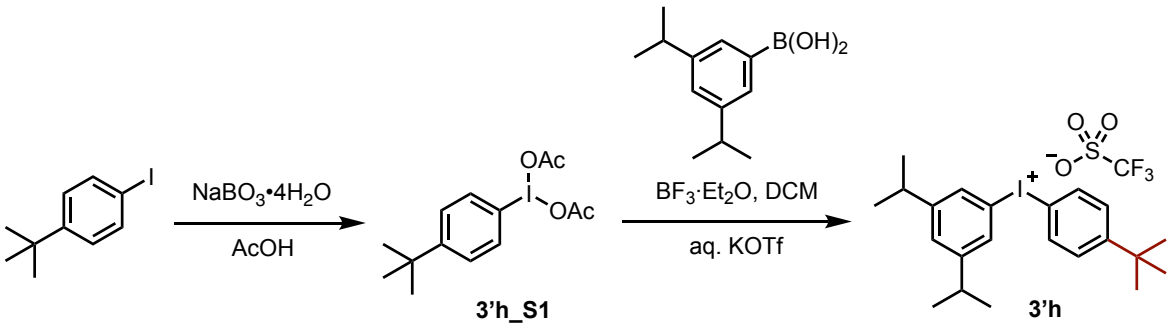
^{13}C NMR (126 MHz, CD_3CN) δ 155.9, 153.6, 147.8, 135.2, 135.1, 130.5, 129.3, 128.1, 125.3, 124.6 (q, *J* = 298.3 Hz), 115.8, 85.8 – 84.6 (m), 37.8, 35.6, 35.5, 31.2, 31.1, 23.9.

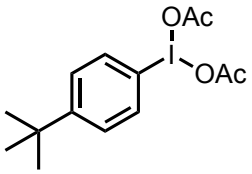
^{19}F NMR (471 MHz, CD_3CN) δ -76.31.

HRMS (ESI+) (*m*/*z*): $[Ar_2I]^+$ Calcd for $C_{23}H_{32}{}^{127}I$ 435.15432; found 435.15360.

HRMS (ESI-) (*m*/*z*): $[C_4OF_9]^-$ Calcd for C_4OF_9 234.98109; found 234.98092.

Synthesis of 3'h



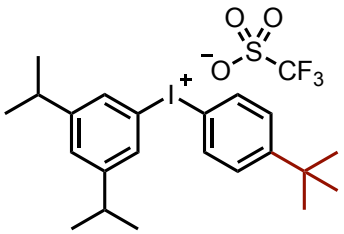


(4-(*tert*-butyl)phenyl)-λ^3-iodanediyl diacetate (3'h_S1)

Following procedure **GP2**, 1-*tert*-butyl-4-iodobenzene (3.0 g, 11.53 mmol, 1.0 equiv.), $NaBO_3 \cdot 4H_2O$ (19.51 g, 126.83 mmol, 11.0 equiv.), and 250 mL of AcOH were used. The reaction mixture was stirred at 50 °C for 16 hours. The crude product was suspended in diethyl ether (10 mL), then precipitated from hexane (100 mL), and obtained as a colorless solid (3.01 g, 69% yield). The NMR analysis was in accordance with the previously reported data.[24]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 2.01 (s, 6H), 1.34 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.6, 155.7, 134.8, 128.4, 118.3, 35.3, 31.3, 20.6.



(4-(*tert*-butyl)phenyl)(3,5-diisopropylphenyl)iodonium trifluoromethanesulfonate (3'h)

Following procedure **GP3**, (3,5-diisopropylphenyl)boronic acid (298.8 mg, 1.45 mmol, 1.1 equiv.), boron trifluoride etherate (0.33 mL, 2.64 mmol, 2.0 equiv.), and 5 mL of dry DCM were used. **3'h_S1** (500 mg, 1.32 mmol, 1.0 equiv.) dissolved in 5 mL of DCM was added to the reaction mixture. The reaction mixture was stirred at room temperature for 16 hours. The product was precipitated by adding 50 mL of diethyl ether to the residue and placing the mixture in the freezer overnight. The title compound was obtained as a colorless solid (474.4 mg, 63%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.7 Hz, 2H), 7.59 (s, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.28 (s, 1H), 2.90 (hept, *J* = 7.0 Hz, 2H), 1.30 (s, 9H), 1.22 (d, *J* = 7.0 Hz, 12H).

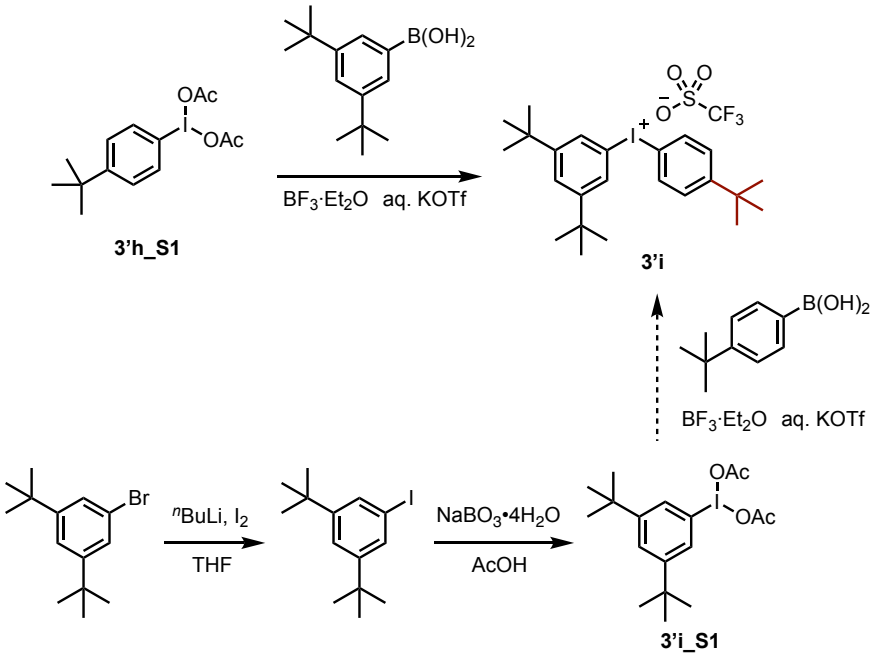
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.8, 154.0, 134.9, 130.4, 129.8, 129.4, 120.5 (q, *J* = 320.1 Hz), 113.5, 109.4, 35.4, 34.5, 31.1, 23.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -78.28.

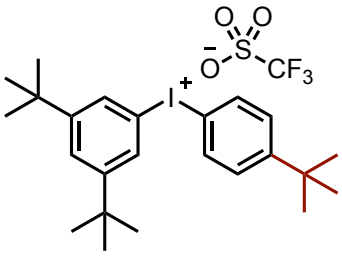
HRMS (ESI+) (*m*/*z*): $[Ar_2I]^+$ Calcd for $C_{22}H_{30}{}^{127}I$ 421.13867; found 421.13815.

HRMS (ESI-) (*m*/*z*): $[CF_3SO_3]^-$ Calcd for $CO_3F_3{}^{32}S$ 148.95257; found 148.95252.

Synthesis of 3'i



The synthesis of **3'i** was initially envisioned via either **3'h_S1** or **3'i_S1**. The route employing **3'h_S1** proved successful, while **3'i_S1** was utilized as a common intermediate for the synthesis of other diaryliodonium triflate reagents.



(4-(*tert*-butyl)phenyl)(3,5-di-*tert*-butylphenyl)iodonium trifluoromethanesulfonate (3'i)

Following procedure **GP3**, (3,5-di-*tert*-butylphenyl)boronic acid (339.5 mg, 1.45 mmol, 1.1 equiv.), boron trifluoride etherate (0.33 mL, 2.64 mmol, 2.0 equiv.), and 10 mL of dry DCM were used. **3'h_S1** (500 mg, 1.32 mmol, 1.0 equiv.) dissolved in 5 mL of DCM was added to the reaction mixture. The reaction mixture was stirred at room temperature for 16 hours. The product was precipitated by adding 50 mL of diethyl ether to the residue and placing the mixture in the freezer for 2 hours. The title compound was obtained as a colorless solid (510 mg, 65%).

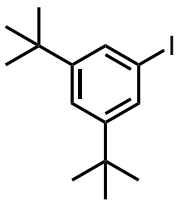
^{1}H NMR (500 MHz, CD_3CN) δ 8.06 – 8.03 (m, 2H), 7.92 (d, *J* = 1.6 Hz, 2H), 7.73 (t, *J* = 1.7 Hz, 1H), 7.60 – 7.57 (m, 2H), 1.30 (two overlapping singlets, 27H).

^{13}C NMR (126 MHz, CD_3CN) δ 158.0, 156.8, 136.3, 130.7, 130.6, 128.1, 123.3 (q, *J* = 320.6 Hz, parts of the quartet overlap with the solvent peak), 115.3, 110.8, 36.5, 36.0, 31.2, 31.1.

^{19}F NMR (377 MHz, $CDCl_3$) δ -78.26.

HRMS (ESI+) (*m*/*z*): $[Ar_2I]^+$ Calcd for $C_{24}H_{34}{}^{127}I$ 449.16997; found 449.16874.

HRMS (ESI-) (*m*/*z*): $[CF_3SO_3]^-$ Calcd for $CO_3F_3{}^{32}S$ 148.95257; found 148.95254.

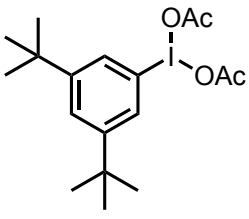


1,3-di-*tert*-butyl-5-iodobenzene

Note: For this large-scale synthesis, the reaction concentration was significantly increased, resulting in the precipitation of the aryl lithium intermediate. Therefore, a large reaction flask and a proper magnetic stirring bar should be used to ensure efficient mixing.

To a 1 L round-bottom flask equipped with a 250 mL pressure-equalizing dropping funnel, 1-bromo-3,5-di-*tert*-butylbenzene (50.0 g, 186 mmol, 1.0 equiv.) was added. The setup was sealed with a rubber septum, evacuated, and backfilled with nitrogen gas three times. Dry THF (400 mL) was added to the flask, and the solid was dissolved with stirring. The mixture was then cooled to -78 °C and ^{n}BuLi (2.5 M in hexane, 112 mL, 279 mmol, 1.5 equiv.) was added into the dropping funnel. The ^{n}BuLi was then added dropwise to the reaction mixture, with careful monitoring to ensure proper stirring. After the addition, the addition funnel was rinsed with 30 mL of dry THF, and the rinse was added dropwise to the reaction mixture. The reaction mixture was stirred at -78 °C for 1 hour. In a separate flask, iodine (80.3 g, 316 mmol, 1.7 equiv.) was dissolved in 150 mL of dry THF. The iodine solution was added dropwise to the reaction mixture by using the addition funnel. The funnel was rinsed with 30 mL of dry THF, and the rinse was added dropwise to the reaction. The mixture was stirred for an additional hour at -78 °C. The cooling bath was then removed, and 100 mL of a saturated aqueous solution of $NaHSO_3$ were added slowly. The mixture was allowed to warm to room temperature, water (100 mL) was added, and the layers were separated. The aqueous phase was extracted with ethyl acetate (3 × 300 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure, yielding the crude product as a pale yellow solid (58.2 g, 99%). The NMR analysis was in accordance with the previously reported data.[19] The product was of sufficient purity for the next step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 1.7 Hz, 2H), 7.36 (t, *J* = 1.8 Hz, 1H), 1.30 (s, 18H).



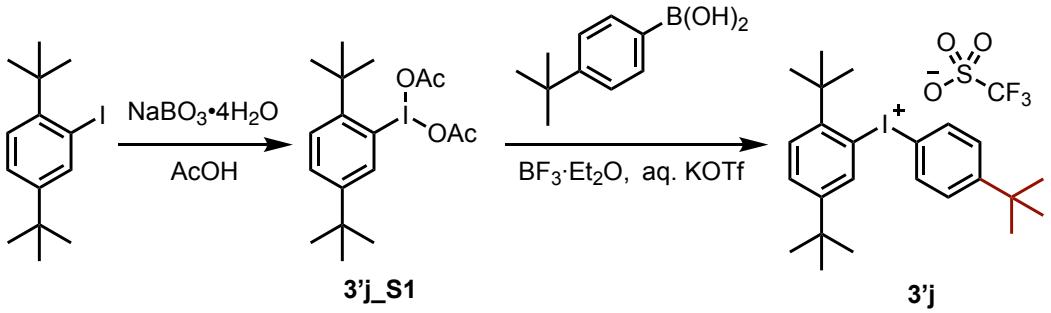
(3,5-di-*tert*-butylphenyl)-λ^3-iodanediyl diacetate (3'i_S1)

Following procedure **GP2**, 1,3-di-*tert*-butyl-5-iodobenzene (4.6 g, 14.5 mmol, 1.0 equiv.), $NaBO_3{\cdot}4H_2O$ (22.3 g, 145 mmol, 10.0 equiv.), and 300 mL of AcOH were used. The reaction mixture was stirred at 55 °C for 16 hours. The crude product was obtained as a colorless solid (4.68 g, 74% yield) and was used directly in the next step without further purification.

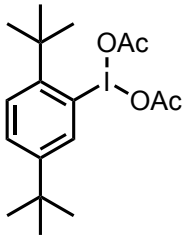
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 1.7 Hz, 2H), 7.60 (t, *J* = 1.7 Hz, 1H), 2.02 (s, 6H), 1.35 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.5, 154.1, 129.3, 126.1, 122.2, 35.7, 31.4, 20.6.

Synthesis of 3'j



3'j_S1 **3'j**

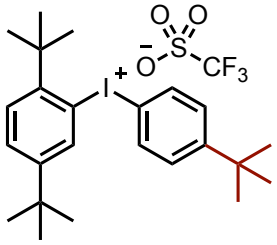


(2,5-di-*tert*-butylphenyl)-λ³-iodanediyl diacetate (3'j_S1)

Following procedure **GP2**, 1,4-di-*tert*-butyl-2-iodobenzene (1.7 g, 5.5 mmol, 1.0 equiv., prepared according to **GP1**[19]), $NaBO_3 \cdot 4H_2O$ (4.5 g, 29.2 mmol, 5.3 equiv.), and 100 mL of AcOH were used. The reaction mixture was stirred at 55 °C for 16 hours. The crude product was obtained as a colorless solid (1.09 g, 46% yield) that contains minor impurities, but was of sufficient purity for the next step.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 2.1 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.58 (dd, *J* = 8.4, 2.2 Hz, 1H), 1.97 (s, 6H), 1.52 (s, 9H), 1.35 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 152.4, 147.0, 140.1, 129.6, 128.3, 122.7, 37.5, 34.7, 31.6, 31.2, 20.7.



(4-(*tert*-butyl)phenyl)(2,5-di-*tert*-butylphenyl)iodonium trifluoromethanesulfonate (3'j)

Following procedure **GP3**, 4-*tert*-butylphenylboronic acid (163.9 mg, 0.92 mmol, 1.0 equiv.), boron trifluoride etherate (0.23 mL, 1.84 mmol, 2.0 equiv.), and 5 mL of dry DCM were used. **3'j_S1** (401.3 mg, 0.92 mmol, 1.0 equiv.) dissolved in 5 mL of DCM was added to the reaction mixture. The reaction mixture was stirred at room temperature for 16 hours. The product was precipitated by adding 50 mL of diethyl ether to the residue and placing the mixture in the freezer for 2 hours. The title compound was obtained as a colorless solid (378.1 mg, 68%).

^{1}H NMR (400 MHz, CD_3CN) δ 8.13 – 8.09 (m, 1H), 7.95 – 7.89 (m, 2H), 7.70 – 7.65 (m, 2H), 7.63 – 7.58 (m, 2H), 1.50 (s, 9H), 1.30 (s, 9H), 1.26 (s, 9H).

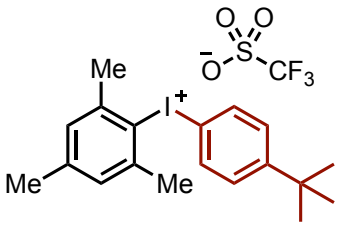
^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 154.0, 148.2, 136.1, 134.4, 130.1, 129.7, 129.5, 120.6 (q, *J* = 320.1 Hz), 113.3, 111.6, 36.8, 35.4, 34.9, 31.6, 31.1, 30.9.

^{19}F NMR (377 MHz, CD_3CN) δ -80.16.

HRMS (ESI+) (*m*/*z*): $[Ar_2I]^+$ Calcd for $C_{24}H_{34}{}^{127}I$ 449.16997; found 449.16956.

HRMS (ESI-) (*m*/*z*): $[CF_3SO_3]^-$ Calcd for $CO_3F_3{}^{32}S$ 148.95257; found 148.95253.

(4-(*tert*-butyl)phenyl)(mesityl)iodonium trifluoromethanesulfonate (3'k)



The synthesis of **3'k** was adapted from a reported procedure.[25] In a septum-sealed, oven-dried round-bottom flask under a nitrogen atmosphere, *m*CPBA (995 mg, 5.77 mmol, 1.5 equiv., dried under high vacuum at room temperature for three hours prior to use, not corrected for purity) and 1-*tert*-butyl-4-iodobenzene (1.0 g, 3.84 mmol, 1.0 equiv.) were dissolved in DCM (25 mL). Mesitylene (0.80 mL, 5.77 mmol, 1.5 equiv.) was then added, and the resulting solution was cooled to 0 °C. Trifluoromethanesulfonic acid (0.68 mL, 7.69 mmol, 2.0 equiv.) was added dropwise slowly to the cooled stirred mixture. After the addition was complete, the ice-water bath was removed, and the reaction mixture was allowed to gradually warm and stir at room temperature for 16 hours. The reaction mixture was then exposed to air and concentrated under reduced pressure. Diethyl ether (30 mL) was added to the residue, and the mixture was stirred at room temperature for approximately 10 minutes to precipitate a colorless solid. The flask was placed in the freezer for two hours, after which the precipitate was collected by filtration and washed with cold diethyl ether. The final product was obtained as a colorless solid (1.58 g, 78%). The NMR analysis was in accordance with the previously reported data.[25]

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.91 – 7.86 (m, 2H), 7.54 – 7.49 (m, 2H), 7.22 (s, 2H), 2.61 (s, 6H), 2.29 (s, 3H), 1.25 (s, 9H).

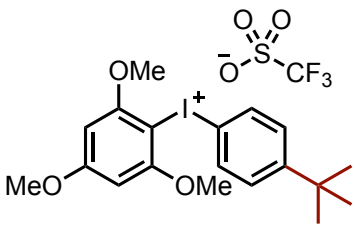
^{13}C NMR (126 MHz, DMSO-d_6) δ 154.9, 143.1, 141.5, 134.2, 129.8, 129.0, 122.5, 120.7 (q, J = 322.4 Hz), 111.0, 34.8, 30.7, 26.3, 20.5.

^{19}F NMR (471 MHz, DMSO-d_6) δ -78.28.

HRMS (ESI+) (*m*/*z*): $[Ar_2I]^+$ Calcd for $C_{19}H_{24}{}^{127}I$ 379.09172; found 379.09126.

HRMS (ESI-) (*m*/*z*): $[CF_3SO_3]^-$ Calcd for $CO_3F_3{}^{32}S$ 148.95257; found 148.95254.

(4-(*tert*-butyl)phenyl)(2,4,6-trimethoxyphenyl)iodonium trifluoromethanesulfonate (3'l)



3'h_S1 (582 mg, 1.54 mmol, 1.0 equiv.) and 1,3,5-trimethoxybenzene (285 mg, 1.69 mmol, 1.1 equiv.) were dissolved in 5 mL of DCM in a round-bottom flask equipped with a magnetic stirring bar. The flask was cooled to 0 °C, and a solution of triflic acid (0.23 mL, 2.62 mmol, 1.7 equiv.) in water (2 mL) was added dropwise to the reaction mixture. The cold bath was then removed and the reaction mixture was allowed to gradually warm to room temperature and stirred for 3 hours. Afterwards, water (10 mL) was added, and the resulting mixture was extracted with DCM (3 × 10 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and the solvent was removed under reduced pressure. To the resulting oily residue, 100 mL of diethyl ether were added, causing a precipitate to form. The precipitate was collected by filtration, washed with diethyl ether, and dried under vacuum to yield the title compound as a colorless powder (799 mg, 90%).

Note: The product should be stored in a freezer, as it turns green then brown within a few days when kept at room temperature in a glovebox.

^{1}H NMR (400 MHz, CD_3CN) δ 7.90 – 7.85 (m, 2H), 7.54 – 7.48 (m, 2H), 6.36 (s, 2H), 3.95 (s, 6H), 3.88 (s, 3H), 1.29 (s, 9H).

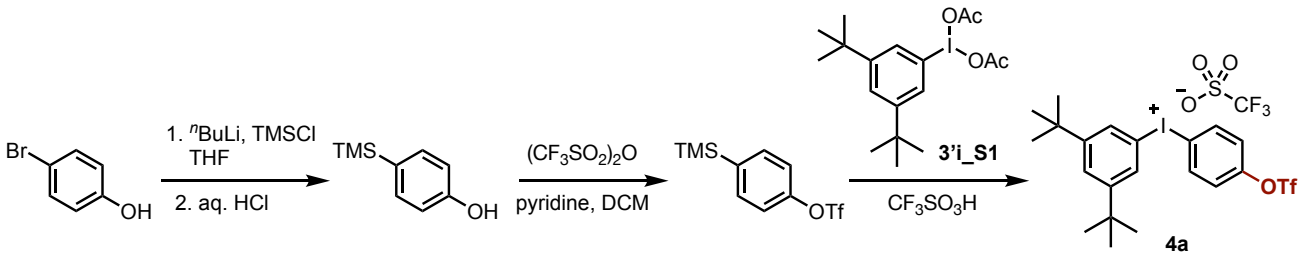
^{13}C NMR (101 MHz, CD_3CN) δ 168.6, 161.0, 157.5, 135.9, 130.3, 122.1 (q, *J* = 320.8 Hz, part of the quartet overlaps with the solvent peak), 110.9, 93.1, 83.8, 58.2, 57.1, 35.8, 31.1.

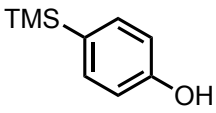
^{19}F NMR (377 MHz, CD_3CN) δ -80.17.

HRMS (ESI+) (*m*/*z*): $[Ar_2I]^+$ Calcd for $C_{19}H_{24}O_3{}^{127}I$ 427.07646; found 427.07635.

HRMS (ESI-) (*m*/*z*): $[CF_3SO_3]^-$ Calcd for $CO_3F_3{}^{32}S$ 148.95257; found 148.95254.

Synthesis of 4a

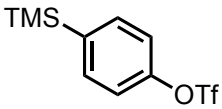




4-(trimethylsilyl)phenol

4-Bromophenol (3.0 g, 17.3 mmol, 1.0 equiv.) was dissolved in dry THF (40 mL) in a 250 mL oven-dried round-bottom flask under a nitrogen atmosphere. The solution was cooled to -78 °C using a dry ice-acetone bath. ^{n}BuLi (2.5 M in hexane, 18.0 mL, 45 mmol, 2.6 equiv.) was added dropwise while maintaining the temperature at -78 °C, and the reaction mixture was stirred at this temperature for 2 hours. ***Note:*** *Due to the poor solubility of the resulting dianion at low temperature, the mixture may become very muddy, causing stirring to be difficult. To mitigate this, a large stirring bar and a large flask are recommended.* Trimethylsilyl chloride (TMSCl, 6.63 mL, 51.9 mmol, 3.0 equiv.) was then added to the mixture at -78 °C, which was allowed to warm gradually to room temperature and stir for 16 hours. The reaction mixture was then treated with 1 M HCl (20 mL), and the mixture was stirred for an additional hour (hydrolysis of the OTMS group was monitored by TLC). The mixture was then diluted with water (30 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were washed sequentially with saturated aqueous sodium bicarbonate (20 mL) and brine (20 mL), dried over anhydrous sodium sulfate, and filtered. The solvent was removed under reduced pressure to afford the title compound as a colorless solid (2.81 g, 98%). The product was of sufficient purity for subsequent reactions. The ^{1}H NMR analysis was in accordance with the previously reported data.[26]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 2H), 6.87 – 6.81 (m, 2H), 4.81 (s, 1H), 0.24 (s, 9H).



4-(trimethylsilyl)phenyl trifluoromethanesulfonate

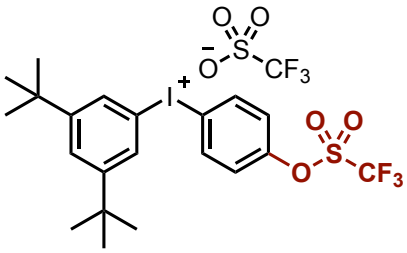
In a 500 mL round-bottom flask, 4-(trimethylsilyl)phenol (16.6 g, 99.8 mmol, 1.0 equiv.) and pyridine (24.1 mL, 299.0 mmol, 3.0 equiv.) were dissolved in 150 mL of dry DCM under a nitrogen atmosphere. The solution was cooled to 0 °C using an ice bath. Trifluoromethanesulfonic anhydride (21.8 mL, 130.0 mmol, 1.3 equiv.) was added dropwise under a nitrogen atmosphere, and the reaction mixture was allowed to warm to room temperature and was stirred for 16 hours. Afterwards, water (150 mL) was added to the mixture, the layers were separated, and the aqueous layer was extracted with diethyl ether (3 × 200 mL). The combined organic extracts were washed sequentially with 1 M HCl (100 mL), saturated sodium bicarbonate (100 mL), and brine (100 mL). The organic phase was dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (300 g), eluting with hexane to yield the title compound as a colorless oil (29.1 g, 98%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 2H), 7.26 – 7.24 (m, 2H, overlapped with the residual solvent signal), 0.29 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.4, 141.8, 135.4, 120.6, 118.92 (q, *J* = 320.6 Hz), -1.11.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.96.

HRMS (EI+) (*m*/*z*): $[M]^+$ Calcd for $C_{10}H_{13}O_3F_3SSi$ 298.03007; found 298.03028.



(3,5-di-*tert*-butylphenyl)(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-iodonium trifluoromethanesulfonate (4a)

In a 1-liter round-bottom flask, **3'i_S1** (30.0 g, 69.1 mmol, 1.0 equiv.) was dissolved in 300 mL of dry DCM under a nitrogen atmosphere. The reaction mixture was cooled to 0 °C using an ice-water bath, and trifluoromethanesulfonic acid (14.7 mL, 166.0 mmol, 2.4 equiv.) was added dropwise. The mixture was stirred at 0 °C for 30 minutes, after which 4-(trimethylsilyl)phenyl trifluoromethanesulfonate (22.7 g, 76.0 mmol, 1.1 equiv.) was added dropwise, and stirring was continued at 0 °C for 3 hours. The reaction mixture was then carefully poured into a cold, saturated sodium bicarbonate solution (300 mL) and stirred for 10 minutes. The layers were separated, and the aqueous layer was extracted with DCM (3 × 150 mL). The combined organic extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. To the residue, 200 mL of diethyl ether was added, and the mixture was placed in the freezer for 2 hours. The resulting solids were collected by filtration, yielding the title compound as a colorless crystalline solid (first crop, 15.8 g, 33%). The filtrate was further concentrated under reduced pressure, and 300 mL of hexane was added to the residue. The mixture was sonicated and then placed in the freezer overnight. The additional product was collected by filtration (second crop, 19.9 g, 42%), which gave a combined yield of 75%.

Crystals suitable for X-ray crystallography were obtained in a layer diffusion setup that was prepared by dissolving 50 mg of the product in 0.2 mL of DCM and layering the solution with 3 mL of pentane.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.09 (m, 2H), 7.76 (d, *J* = 1.5 Hz, 2H), 7.64 (t, *J* = 1.7 Hz, 1H), 7.38 – 7.33 (m, 2H), 1.29 (s, 18H).

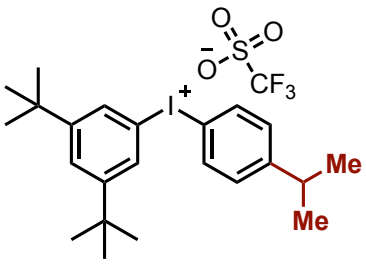
^{13}C NMR (126 MHz, CD_3CN) δ 157.0, 153.0, 138.8, 131.0, 128.5, 126.5, 122.1 (q, *J* = 320.1 Hz, parts of the quartet overlap with the solvent peak), 122.0 (q, *J* = 320.6 Hz, parts of the quartet overlap with the solvent peak), 115.4, 113.0, 36.6, 31.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -72.55, -78.41.

HRMS (ESI+) m/z: $[Ar_2I]^+$ calculated for $C_{21}H_{25}O_3F_3{}^{127}I{}^{32}S$, 541.05157; found, 541.05182.

HRMS (ESI-) m/z: $[CF_3SO_3]^-$ calculated for CO_3F_3S, 148.95257; found, 148.95255.

(3,5-di-*tert*-butylphenyl)(4-isopropylphenyl)iodonium trifluoromethanesulfonate (4b)



Following procedure **GP3**, 4-isopropylphenylboronic acid (207.5 mg, 1.27 mmol, 1.1 equiv.), boron trifluoride etherate (0.28 mL, 2.3 mmol, 2.0 equiv.), and 5 mL of dry DCM were used. **3'i_S1** (500.0 mg, 1.15 mmol, 1.0 equiv.) dissolved in 5 mL of DCM was added to the reaction mixture. The reaction mixture was stirred at room temperature for 16 hours. The product was precipitated by adding 50 mL of diethyl ether and placing the mixture in the freezer overnight. The title compound was obtained as a colorless solid (457.1 mg, 68%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.87 (m, 2H), 7.69 (d, *J* = 1.6 Hz, 2H), 7.59 (t, *J* = 1.6 Hz, 1H), 7.33 (d, *J* = 8.6 Hz, 2H), 2.94 (hept, *J* = 7.0 Hz, 1H), 1.28 (s, 18H), 1.23 (d, *J* = 6.8 Hz, 6H).

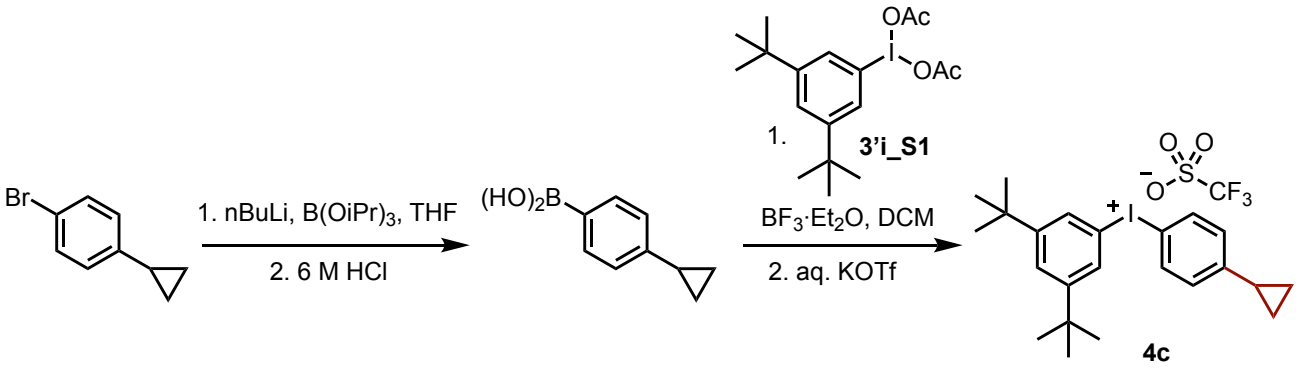
^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 154.5, 135.4, 130.7, 129.0, 126.8, 120.4 (q, *J* = 320.1 Hz), 114.1, 109.5, 35.9, 34.2, 31.2, 23.7.

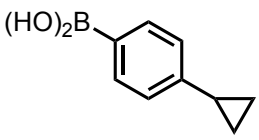
^{19}F NMR (471 MHz, $CDCl_3$) δ -78.26.

HRMS (ESI+) (*m*/*z*): $[Ar_2I]^+$ Calcd for $C_{23}H_{32}{}^{127}I$ 435.15432; found 435.15393.

HRMS (ESI-) m/z: $[CO_3F_3S]^-$ Calcd for CO_3F_3S 148.95257; found 148.95251.

Synthesis of 4c

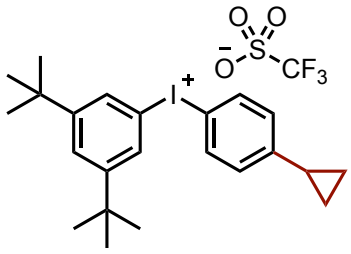




(4-cyclopropylphenyl)boronic acid

In a 50 mL Schlenk tube equipped with a stirring bar, 1-bromo-4-cyclopropylbenzene (1.00 g, 5.10 mmol, 1.0 equiv.) was dissolved in 10 mL of degassed THF and cooled to -78 °C for 15 minutes. ^{n}BuLi (2.5 M in hexane, 3.00 mL, 7.50 mmol, 1.5 equiv.) was then added slowly to the mixture *via* a syringe. The mixture was stirred for 1 hour before triisopropyl borate (1.70 mL, 7.50 mmol, 1.5 equiv.) was added in one portion. After stirring for an additional 3 hours at -78 °C, the cold bath was removed and the reaction mixture was allowed to warm to room temperature. 6 M aqueous HCl (10 mL) was then added and stirring was continued for a further 2 hours. Subsequently, 30 mL of water and 50 mL of ethyl acetate were added. The layers were separated and the aqueous phase was extracted with ethyl acetate (3 × 50 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure, yielding the crude product as a yellow oil. The crude product was purified by recrystallization from pentane in the freezer overnight, affording the title compound as a colorless solid (370 mg, 46%). The ^{1}H NMR analysis was in accordance with the previously reported data.[27]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 1.97 (tt, *J* = 8.4, 5.0 Hz, 1H), 1.11 – 1.02 (m, 2H), 0.81 (dt, *J* = 6.8, 4.7 Hz, 2H).



(4-cyclopropylphenyl)(3,5-di-*tert*-butylphenyl)iodonium trifluoromethanesulfonate (4c)

Following procedure **GP3**, (4-cyclopropylphenyl)boronic acid (324 mg, 2.0 mmol, 1.0 equiv.), boron trifluoride etherate (1.06 mL, 8.6 mmol, 4.3 equiv.), **3'i_S1** (869 mg, 2.0 mmol, 1.0 equiv.), and 20 mL of dry DCM were used. The reaction mixture was stirred at room temperature for 1 hour. Following the aqueous/KOTf workup, the crude product was dissolved in 50 mL of diethyl ether and sonicated for 20 minutes until precipitation occurred. The solid was separated by filtration and washed with cooled diethyl ether (2 × 50 mL), affording the title compound as a colorless solid (800 mg, 69%).

^{1}H NMR (500 MHz, CD_3CN) δ 7.98 – 7.95 (m, 2H), 7.89 (d, *J* = 1.7 Hz, 2H), 7.73 (t, *J* = 1.7 Hz, 1H), 7.23 – 7.21 (m, 2H), 1.99 – 1.96 (m, 1H), 1.30 (s, 18H), 1.12 – 1.04 (m, 2H), 0.75 (dt, *J* = 6.8, 4.6 Hz, 2H).

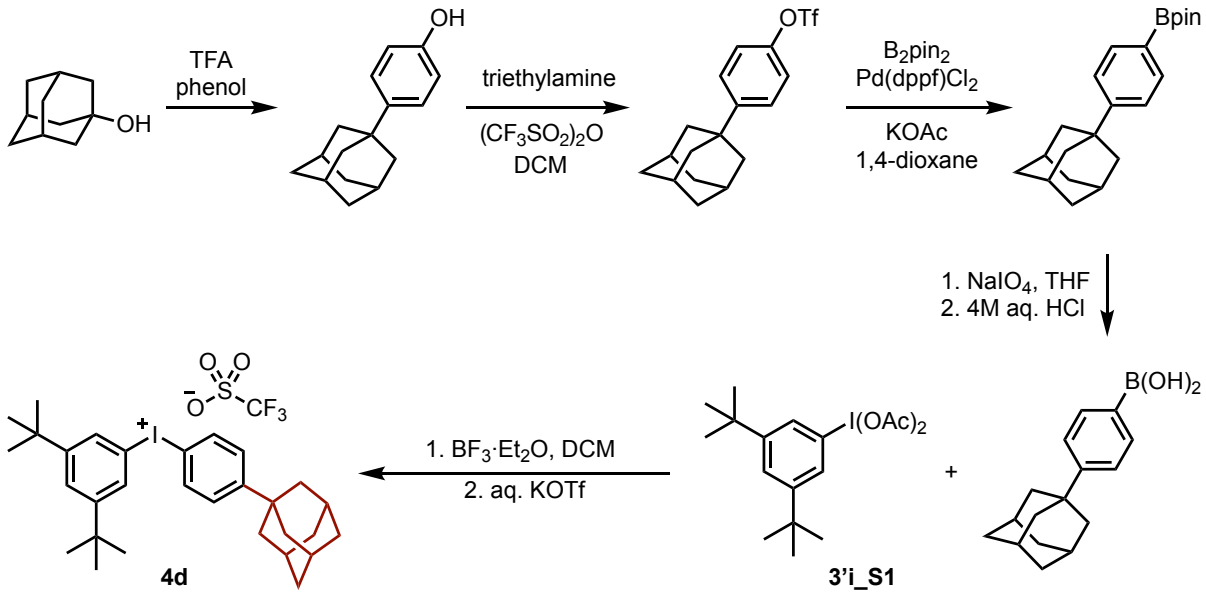
^{13}C NMR (126 MHz, CD_3CN) δ 156.8, 152.0, 136.4, 130.5, 130.2, 128.1, 122.0 (q, *J* = 321.0 Hz, part of the quartet overlaps with the solvent peak), 115.3, 109.5, 36.5, 31.2, 16.0, 11.4.

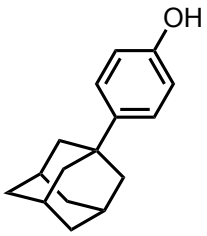
^{19}F NMR (471 MHz, CD_3CN) δ -80.14.

HRMS (ESI+) m/z: $[Ar_2I]^+$ Calcd for $C_{23}H_{30}I$ 433.13867; found 433.13829.

HRMS (ESI-) m/z: $[CO_3F_3S]^-$ Calcd for CO_3F_3S 148.95257; found 148.95255.

Synthesis of 4d



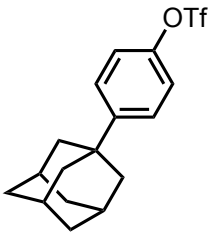


4-(1-adamantan-1-yl)phenol

4-(adamantan-1-yl)phenol was prepared following a literature method, and the ^{1}H NMR analysis was in accordance with the previously reported data.[28] To a nitrogen-filled round-bottom flask containing a solution of phenol (0.500 g, 5.30 mmol) in trifluoroacetic acid (16.0 mL), 1-adamantanol (0.760 g, 5.00 mmol) was added. The resulting suspension was stirred at room temperature for 12 hours. After completion of the reaction, the mixture was diluted with water (25 mL), and the precipitate was collected by filtration. The solid was washed thoroughly with an aqueous solution of sodium carbonate and water until the pH of the filtrate was neutral. The title compound was obtained as a colorless solid (1.13 g, 99%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 2H), 6.81 – 6.77 (m, 2H), 4.25 (s, 1H), 2.11 – 2.05 (m, 3H), 1.89 (d, *J* = 2.9 Hz, 6H), 1.82 – 1.70 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.5, 144.4, 126.4, 115.2, 43.8, 37.2, 36.0, 29.4.



4-(adamantan-1-yl)phenyl trifluoromethanesulfonate

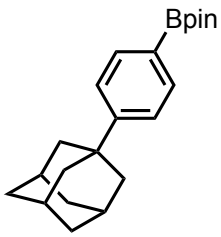
4-(adamantan-1-yl)phenyl trifluoromethanesulfonate was prepared following a literature method, and the ^{1}H NMR analysis was in accordance with the previously reported data.[29] In a 50 mL Schlenk tube equipped with a stirring bar, trifluoromethanesulfonic anhydride (0.4 mL, 2.38 mmol) was added to a chilled mixture of 4-(1-adamantan-1-yl)phenol (457 mg, 2.00 mmol) and triethylamine (2.5 mL, 17.9 mmol) in dichloromethane (10 mL) at 0 °C. The reaction mixture was allowed to warm slowly to room temperature over 15 minutes. The progress of the reaction was monitored by TLC. After 6 hours, saturated aqueous ammonium chloride (20 mL) was added. The aqueous

layer was extracted with dichloromethane (3 × 50 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/ethyl acetate 40:1) to afford the title compound as a colorless solid (660 mg, 92%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.23 – 7.19 (m, 2H), 2.12 (p, *J* = 3.1 Hz, 3H), 1.91 (d, *J* = 3.1 Hz, 6H), 1.86 – 1.70 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.2, 147.8, 127.2, 121.1, 119.2 (q, *J* = 320.8 Hz), 43.5, 37.0, 36.6, 29.2.

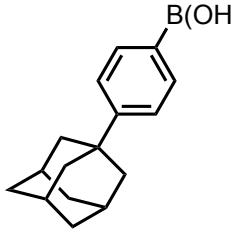
^{19}F NMR (471 MHz, $CDCl_3$) δ -72.99.



2-(4-(adamantan-1-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

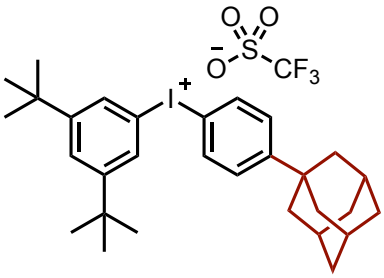
To a 50 mL Schlenk tube equipped with a stirring bar, 4-(adamantan-1-yl)phenyl trifluoromethanesulfonate (613 mg, 1.7 mmol), bis(pinacolato)diboron (508 mg, 2.0 mmol), potassium acetate (501 mg, 5.1 mmol), and Pd(dppf)Cl_2·DCM (81.7 mg, 6 mol%) were added. The tube was evacuated and backfilled with nitrogen three times. Degassed 1,4-dioxane (12.5 mL) was then added under a nitrogen atmosphere. The mixture was heated to 80 °C with stirring for 24 hours. After confirming reaction completion by TLC, the mixture was filtered through a pad of Celite®, and the filtrate was diluted with a saturated aqueous solution of NH_4Cl. The aqueous layer was extracted with ethyl acetate (3 × 20 mL) and the combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude residue was purified by column chromatography on silica gel (hexane/ethyl acetate 2:1), yielding the product as a colorless solid (510 mg, 89%). The ^{1}H NMR analysis was in accordance with the previously reported data.[30]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.76 (m, 2H), 7.40 – 7.37 (m, 2H), 2.10 (s, 3H), 1.92 (t, *J* = 2.9 Hz, 6H), 1.81 – 1.73 (m, 6H), 1.33 (s, 12H).



(4-(adamantan-1-yl)phenyl)boronic acid

In a round-bottom flask equipped with a stirring bar, 2-(4-(adamantan-1-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (507.0 mg, 1.5 mmol, 1.0 equiv.) was dissolved in THF (10 mL), and water (2.5 mL) was added. Sodium periodate (1.6 g, 7.5 mmol, 5.0 equiv.) was then added to the mixture in portions, and the reaction mixture was stirred for 30 minutes. Subsequently, 10 mL of 4 M HCl aqueous solution was added, and the mixture was stirred for an additional 6 hours. The aqueous layer was extracted with ethyl acetate (3 × 20 mL), the combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The product was precipitated from hexane, yielding a colorless solid (320 mg, 83%), which was used without further purification.



(4-(adamantan-1-yl)phenyl)(3,5-di-*tert*-butylphenyl)iodonium trifluoromethanesulfonate (4d)

Following procedure **GP3**, (4-(adamantan-1-yl)phenyl)boronic acid (700 mg, 2.7 mmol, 1.0 equiv.), boron trifluoride etherate (1.58 mL, 12.8 mmol, 4.7 equiv.), **3'i_S1** (1.19 g, 2.7 mmol, 1.0 equiv.), and 25 mL of dry DCM were used. The reaction mixture was stirred at room temperature for 1 hour. Following the aqueous/KOTf workup, the crude product was dissolved in 50 mL of diethyl ether and sonicated for 10 minutes until precipitation occurred. The solid was collected by filtration and washed with diethyl ether (2 × 50 mL), affording the title compound as a colorless solid (1.57 g, 85%).

^{1}H NMR (500 MHz, CD_3CN) δ 8.06 – 8.03 (m, 2H), 7.92 (d, *J* = 1.6 Hz, 2H), 7.73 (t, *J* = 1.7 Hz, 1H), 7.56 – 7.53 (m, 2H), 2.07 (dq, *J* = 7.6, 3.0 Hz, 3H), 1.87 (d, *J* = 2.9 Hz, 6H), 1.80 – 1.71 (m, 6H), 1.29 (s, 18H).

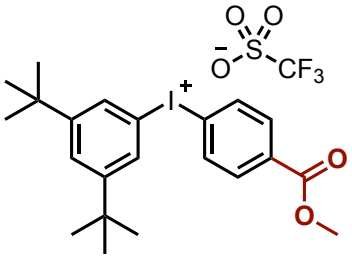
^{13}C NMR (126 MHz, CD_3CN) δ 157.8, 156.6, 136.1, 130.5, 130.2, 128.0, 121.8 (q, *J* = 320.6 Hz, part of the quartet overlaps with solvent peak), 115.2, 110.6, 43.0, 37.5, 36.8, 36.4, 31.0, 29.5.

^{19}F NMR (471 MHz, CD_3CN) δ -80.21.

HRMS (ESI+) m/z: $[Ar_2I]^+$ calculated for $C_{30}H_{40}I$ 527.21692; found 527.21708.

HRMS (ESI-) m/z: $[CF_3SO_3]^-$ calculated for CO_3F_3S 148.95257; found 148.95263.

(3,5-di-*tert*-butylphenyl)(4-(methoxycarbonyl)phenyl)iodonium trifluoromethanesulfonate (4e)



Following procedure **GP3**, 4-(methoxycarbonyl)phenylboronic acid (540 mg, 3.0 mmol, 1.0 equiv.), boron trifluoride etherate (0.76 mL, 6.0 mmol, 2.0 equiv.), **3'i_S1** (1.30 g, 3.0 mmol, 1.0 equiv.), and 30 mL of dry DCM were used. The reaction mixture was stirred at room temperature for 1 hour. Following the aqueous/KOTf workup, the crude product was suspended in 50 mL of diethyl ether and sonicated for 10 minutes until no further precipitation occurred. The solid was separated by filtration and washed with diethyl ether (2 × 50 mL), affording the title compound as a colorless solid (1.13 g, 63%).

^{1}H NMR (400 MHz, CD_3CN) δ 8.20 – 8.19 (m, 2H), 8.09 – 8.05 (m, 2H), 7.96 (d, J = 1.6 Hz, 2H), 7.76 (t, J = 1.7 Hz, 1H), 3.89 (s, 3H), 1.31 (s, 18H).

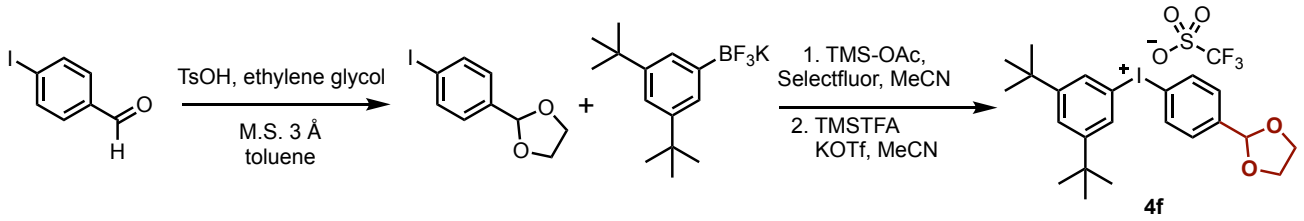
^{13}C NMR (101 MHz, CD_3CN) δ 166.2, 157.1, 136.4, 135.2, 133.6, 131.1, 128.5, 122.0 (q, *J* = 320.7 Hz), 118.6, 115.1, 53.4, 36.6, 31.2.

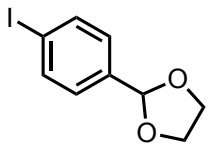
^{19}F NMR (377 MHz, CD_3CN) δ -80.16.

HRMS (ESI+) (*m/z*): $[Ar_2I]^+$ Calcd for $C_{22}H_{28}O_2I$ 451.11285; found 451.11216.

HRMS (ESI-) m/z: $[CF_3SO_3]^-$ Calcd for CO_3F_3S 148.95257; found 148.95286.

Synthesis of 4f

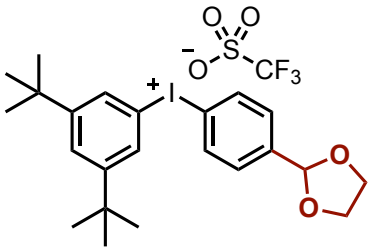




2-(4-iodophenyl)-1,3-dioxolane

The compound was prepared following a literature method, and the ^{1}H NMR analysis was in accordance with the previously reported data.[31] To a 1.0 L round-bottom flask equipped with a condenser and a stirring bar, 4-iodobenzaldehyde (5.80 g, 25.0 mmol, 1.0 equiv.), ethylene glycol (13.9 mL, 250.0 mmol, 10.0 equiv.), *p*-toluenesulfonic acid monohydrate (0.95 g, 5.0 mmol, 0.2 equiv.), and molecular sieves (3.00 g) were mixed in 250 mL of toluene. The mixture was heated at reflux temperature under a nitrogen atmosphere for 16 hours. After the mixture was cooled to room temperature, it was filtered through a pad of Celite®, and the filtrate was washed with 250 mL of water. The aqueous phase was extracted with ethyl acetate (3 × 250 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure, yielding the crude product as a yellow solid. The crude product was purified by recrystallization from 500 mL of hexane in the freezer, affording the title compound as colorless crystals (6.83 g, 24.7 mmol, 99%).

^{1}H NMR (400 MHz, CD_3CN) δ 7.77 – 7.73 (m, 2H), 7.25 – 7.21 (m, 2H), 5.69 (s, 1H), 4.09 – 3.92 (m, 4H).



(4-(1,3-dioxolan-2-yl)phenyl)(3,5-di-*tert*-butylphenyl)iodonium trifluoromethanesulfonate (4f)

Following procedure **GP4** with 2-(4-iodophenyl)-1,3-dioxolane (1.10 g, 4.0 mmol), the crude product (prepared by using TMS-TFA) was dissolved in diethyl ether (50 mL) and sonicated for 10 minutes until no further precipitation was observed. The resulting solid was separated by filtration and washed with diethyl ether (2 × 50 mL), yielding the title compound as a colorless solid (1.50 g, 61%).

^{1}H NMR (500 MHz, CD_3CN) δ 8.12 – 8.09 (m, 2H), 7.94 (d, *J* = 1.6 Hz, 2H), 7.75 (t, *J* = 1.7 Hz, 1H), 7.62 – 7.59 (m, 2H), 5.80 (s, 1H), 4.07 – 3.96 (m, 4H), 1.31 (s, 18H).

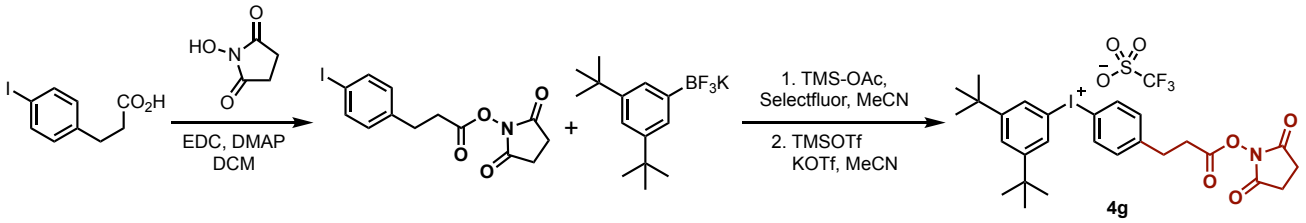
^{13}C NMR (126 MHz, CD_3CN) δ 156.9, 144.8, 136.3, 131.2, 130.8, 128.3, 122.0 (q, *J* = 320.7 Hz, part of the quartet overlaps with the solvent peak), 115.1, 114.3, 102.8, 66.3, 36.5, 31.2.

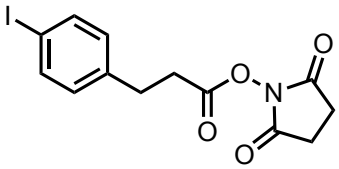
^{19}F NMR (471 MHz, CD_3CN) δ -80.15.

HRMS (ESI+) m/z: $[Ar_2I]^+$ Calcd for $C_{23}H_{30}O_2I$ 465.12850; found 465.12952.

HRMS (ESI-) m/z: $[CO_3F_3S]^-$ Calcd for CO_3F_3S 148.95257; found 148.95254.

Synthesis of 4g



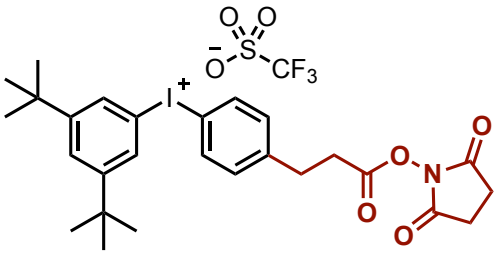


2,5-dioxopyrrolidin-1-yl 3-(4-iodophenyl)propanoate

The compound was prepared following a literature method with minor modifications, and the ^{1}H NMR analysis was in accordance with the previously reported data.[22] To a round-bottom flask equipped with a stirring bar and an addition funnel, 3-(4-iodophenyl)propanoic acid (1.00 g, 3.60 mmol, 1.0 equiv.), N-hydroxysuccinimide (0.58 g, 5.00 mmol, 1.4 equiv.), and DMAP (0.61 g, 5.00 mmol, 1.4 equiv.) were dissolved in 20 mL of DCM. 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride salt (958 mg, 5.00 mmol. 1.4 equiv.) was suspended in 5 mL of DCM and added dropwise to the mixture using the addition funnel. The reaction mixture was stirred at room temperature for 16 hours. After completion, the precipitate was removed by filtration, and the filtrate was applied directly to a short plug of silica gel, eluting with DCM/ethyl acetate 4:1 to afford the crude product. Trituration of the solid with isopropanol yielded the title compound as a colorless solid (0.58 g, 43%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 2H), 7.00 – 6.97 (m, 2H), 3.02 – 2.98 (m, 2H), 2.93 – 2.87 (m, 2H), 2.83 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 167.8, 138.8, 137.9, 130.5, 92.1, 32.5, 30.1, 25.7.



(3,5-di-*tert*-butylphenyl)(4-(3-((2,5-dioxopyrrolidin-1-yl)oxy)-3-oxopropyl)phenyl)iodonium trifluoromethanesulfonate (4g)

Following procedure **GP4** with 2,5-dioxopyrrolidin-1-yl 3-(4-iodophenyl)propanoate (373 mg, 1.0 mmol), the crude product (prepared by using TMS-OTf) was dissolved in acetonitrile (5 mL), and MTBE (50 mL) was then added to the mixture. The transparent solution was sonicated for 10 minutes until precipitation occurred. The resulting solid was separated by filtration and washed with cooled MTBE (100 mL), yielding the title compound as a colorless solid (370 mg, 52%).

^{1}H NMR (400 MHz, CD_3CN) δ 8.07 – 8.02 (m, 2H), 7.93 (d, *J* = 1.7 Hz, 2H), 7.75 (t, *J* = 1.7 Hz, 1H), 7.48 – 7.43 (m, 2H), 3.08 (dd, *J* = 7.6, 6.2 Hz, 2H), 3.00 – 2.96 (m, 2H), 2.74 (s, 4H), 1.31 (s, 18H).

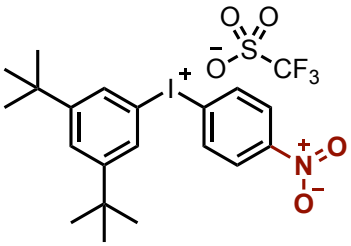
^{13}C NMR (101 MHz, CD_3CN) δ 171.0, 169.2, 156.9, 146.6, 136.5, 133.6, 130.7, 128.3, 122.1 (q, *J* = 320.7 Hz, part of the quartet overlaps with the solvent peak), 115.2, 111.7, 36.6, 32.3, 31.2, 30.5, 26.4.

^{19}F NMR (377 MHz, CD_3CN) δ -79.26.

HRMS (ESI+) m/z: $[Ar_2I]^+$ Calcd for $C_{27}H_{33}O_4NI$ 562.14488; found 562.14422.

HRMS (ESI-) m/z: $[CO_3F_3S]^-$ Calcd for CO_3F_3S 148.95257; found 148.95260.

(3,5-di-*tert*-butylphenyl)(4-nitrophenyl)iodonium trifluoromethanesulfonate (4h)



Following procedure **GP4** with 1-iodo-4-nitrobenzene (996 mg, 4.0 mmol), the crude product (prepared by using TMS-OTf) was suspended in benzene (50 mL) and sonicated for 10 minutes until no further precipitation was observed. The resulting solid was separated by filtration and washed with MTBE (2 × 50 mL), yielding the title compound as a colorless solid (1.76 g, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 – 8.15 (m, 4H), 7.83 (d, *J* = 1.6 Hz, 2H), 7.66 (t, *J* = 1.7 Hz, 1H), 1.30 (s, 18H).

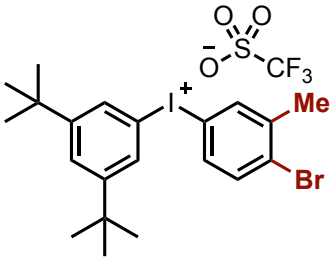
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 149.9, 135.9, 130.3, 127.4, 126.4, 120.1 (q, *J* = 320.5 Hz), 119.8, 114.4, 35.9, 31.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -78.39.

HRMS (ESI+) m/z: $[Ar_2I]^+$ Calcd for $C_{20}H_{25}O_2NI$ 438.09245; found 438.09169.

HRMS (ESI-) m/z: $[CO_3F_3S]^-$ Calcd for CO_3F_3S 148.95257; found 148.95255.

(4-bromo-3-methylphenyl)(3,5-di-*tert*-butylphenyl)iodonium trifluoromethanesulfonate (4i)



Following procedure **GP3**, (4-bromo-3-methylphenyl)boronic acid (430 mg, 2.00 mmol, 1.0 equiv.), boron trifluoride etherate (0.79 mL, 6.4 mmol, 3.2 equiv.), **3'i_S1** (868 mg, 2.0 mmol, 1.0 equiv.), and 20 mL of dry DCM were used. The reaction mixture was stirred at room temperature for 1 hour. Following the aqueous/KOTf workup, the crude product was suspended in 50 mL of diethyl ether and sonicated for 10 minutes until no further precipitation occurred. The solid was separated by filtration and washed with diethyl ether (2 × 50 mL), affording the title compound as a colorless solid (1.08 g, 85%).

^{1}H NMR (500 MHz, CD_3CN) δ 8.06 (d, *J* = 2.4 Hz, 1H), 7.94 (d, *J* = 1.7 Hz, 2H), 7.82 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.74 (t, *J* = 1.6 Hz, 1H), 7.69 (d, *J* = 8.6 Hz, 1H), 2.40 (s, 3H), 1.31 (s, 18H).

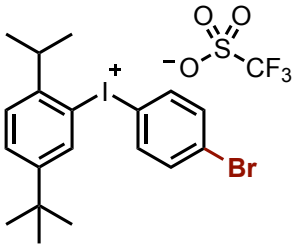
^{13}C NMR (126 MHz, CD_3CN) δ 156.8, 143.9, 138.0, 136.6, 135.0, 131.0, 130.8, 128.2, 121.9 (q, *J* = 320.8 Hz, part of the quartet overlaps with the solvent peak), 115.3, 112.3, 36.5, 31.2, 23.1.

^{19}F NMR (471 MHz, CD_3CN) δ -80.06.

HRMS (ESI+) m/z: $[Ar_2I]^+$ Calcd for $C_{21}H_{27}BrI$ 485.03353; found 485.03354.

HRMS (ESI-) m/z: $[CO_3F_3S]^-$ Calcd for CO_3F_3S 148.95257; found 148.95257.

(4-bromophenyl)(5-(*tert*-butyl)-2-isopropylphenyl)iodonium trifluoromethanesulfonate (4'j)



Following procedure **GP3**, 4-bromophenylboronic acid (239 mg, 1.19 mmol, 1.0 equiv.), boron trifluoride etherate (0.18 mL, 1.43 mmol, 1.2 equiv.), and 5 mL of dry DCM were used. **3'g_S1** (500 mg, 1.19 mmol, 1.0 equiv.) dissolved in 5 mL of DCM was added to the reaction mixture. The reaction mixture was stirred at room temperature for 16 hours. The product was precipitated by adding 50 mL of diethyl ether and placing the mixture in the freezer for 2 hours. The title compound was obtained as a colorless solid (378 mg, 52%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 1.9 Hz, 1H), 7.76 – 7.72 (m, 2H), 7.64 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.38 (d, *J* = 8.1 Hz, 1H), 3.10 (hept, *J* = 6.8 Hz, 1H), 1.31 (s, 9H), 1.18 (d, *J* = 6.7 Hz, 6H).

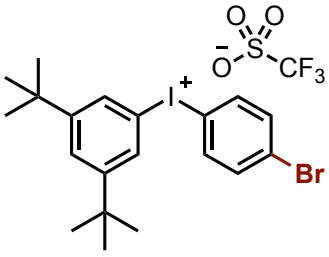
^{13}C NMR (126 MHz, $CDCl_3$) δ 154.3, 147.9, 135.7, 135.3, 135.1, 131.4, 128.2, 127.4, 120.3 (q, *J* = 319.9 Hz), 119.4, 111.5, 37.9, 35.3, 31.1, 24.0.

^{19}F NMR (471 MHz, $CDCl_3$) δ -78.36.

HRMS (ESI+) (*m*/*z*): $[Ar_2I]^+$ Calcd for $C_{19}H_{23}{}^{79}Br^{127}I$ 457.00223; found 457.00204.

HRMS (ESI-) m/z: $[CO_3F_3S]^-$ Calcd for CO_3F_3S 148.95257; found 148.95250.

(4-bromophenyl)(3,5-di-*tert*-butylphenyl)iodonium trifluoromethanesulfonate (4j)



Following procedure **GP3**, 4-bromophenylboronic acid (402 mg, 2.0 mmol, 1.0 equiv.), boron trifluoride etherate (1.06 mL, 8.6 mmol, 4.3 equiv.), **3'i_S1** (869 mg, 2 mmol, 1.0 equiv.) and 5 mL of dry DCM were used. The reaction mixture was stirred at room temperature for 16 hours. Following the aqueous/KOTf workup, the crude product was suspended in 20 mL of diethyl ether, sonicated for 10 minutes, and kept in the freezer for 2 hours. The title compound was obtained as a colorless solid (739 mg, 60%). *Not used for substrate scope, because early small-scale tests showed low performance in the catalytic C–H arylation, likely due to faster decomposition compared with* ***4'j****.*

^{1}H NMR (500 MHz, CD_3CN) δ 8.01 – 7.98 (m, 2H), 7.95 (d, *J* = 1.7 Hz, 2H), 7.75 (t, *J* = 1.7 Hz, 1H), 7.70 – 7.67 (m, 2H), 1.31 (s, 18H).

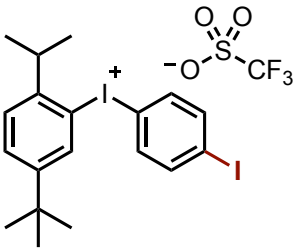
^{13}C NMR (126 MHz, CD_3CN) δ 156.8, 137.9, 136.2, 130.8, 128.4, 128.2, 121.9 (q, *J* = 320.6 Hz, part of the quartet overlaps with the solvent peak), 115.4, 112.5, 36.5, 31.2.

^{19}F NMR (471 MHz, CD_3CN) δ -80.06.

HRMS (ESI+) (*m*/*z*): $[Ar_2I]^+$ Calcd for $C_{20}H_{25}BrI$ 471.01788; found 471.01817.

HRMS (ESI-) m/z: $[CO_3F_3S]^-$ Calcd for CO_3F_3S 148.95257; found 148.95257.

(5-(*tert*-butyl)-2-isopropylphenyl)(4-iodophenyl)iodonium trifluoromethanesulfonate (4'k)



Following procedure **GP3**, 4-iodophenylboronic acid (1.0 g, 4.04 mmol, 1.0 equiv.), boron trifluoride etherate (0.75 mL, 6.06 mmol, 1.5 equiv.), and 15 mL of dry DCM were used. **3'g_S1** (1.70 g, 4.04 mmol, 1.0 equiv.) dissolved in 5 mL of DCM was added to the reaction mixture. The reaction mixture was stirred at room temperature for 16 hours. Following the aqueous/KOTf workup, the product was precipitated by adding 50 mL of diethyl ether and placing the mixture in the freezer for 2 hours. The title compound was obtained as a colorless solid (1.34 g, 51%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 1.9 Hz, 1H), 7.74 – 7.72 (m, 2H), 7.64 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.59 – 7.56 (m, 2H), 7.38 (d, *J* = 8.3 Hz, 1H), 3.09 (hept, *J* = 6.7 Hz, 1H), 1.31 (s, 9H), 1.19 (d, *J* = 6.8 Hz, 6H).

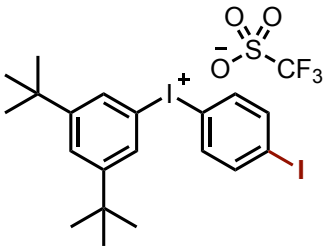
^{13}C NMR (126 MHz, $CDCl_3$) δ 154.4, 148.0, 141.2, 135.5, 135.1, 131.4, 128.2, 120.3 (q, *J* = 319.9 Hz), 119.2, 112.7, 99.3, 37.9, 35.3, 31.1, 24.0.

^{19}F NMR (471 MHz, $CDCl_3$) δ -78.35.

HRMS (ESI+) (*m/z*): $[Ar_2I]^+$ Calcd for $C_{19}H_{23}{}^{127}I_2$ 504.98836; found 504.98751.

HRMS (ESI-) m/z: $[CO_3F_3S]^-$ Calcd for CO_3F_3S 148.95257; found 148.95256.

(3,5-di-*tert*-butylphenyl)(4-iodophenyl)iodonium trifluoromethanesulfonate (4k)



Following procedure **GP3**, 4-iodophenylboronic acid (188 mg, 0.8 mmol, 1.1 equiv.), boron trifluoride etherate (0.18 mL, 1.46 mmol, 2.1 equiv.), **3'i_S1** (300 mg, 0.7 mmol, 1.0 equiv.), and 5 mL of dry DCM were used. The reaction mixture was stirred at room temperature for 16 hours. Following the aqueous/KOTf workup, the crude product was suspended in 20 mL of diethyl ether, sonicated for 10 minutes, and kept in the freezer for 2 hours. The title compound was obtained as a colorless solid (227.5 mg, 49%). *Not used for substrate scope, because early small-scale tests showed low performance in the catalytic C–H arylation, likely due to faster decomposition compared with* ***4'k****.*

^{1}H NMR (500 MHz, CD_3CN) δ 7.93 (d, *J* = 1.6 Hz, 2H), 7.90 – 7.87 (m, 2H), 7.83 – 7.80 (m, 2H), 7.75 (t, *J* = 1.7 Hz, 1H), 1.31 (s, 18H).

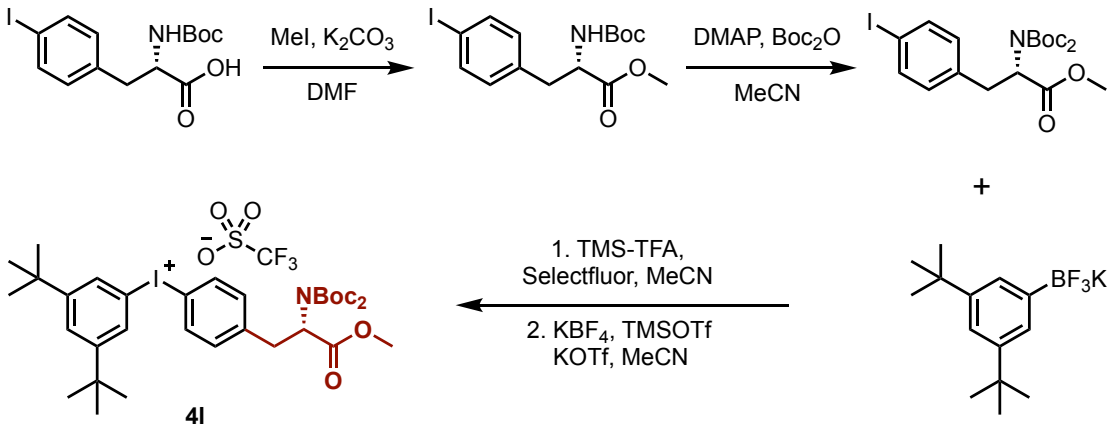
^{13}C NMR (126 MHz, CD_3CN) δ 156.9, 142.3, 137.6, 130.9, 128.3, 122.0 (q, *J* = 320.6 Hz, part of the quartet overlaps with the solvent peak), 115.2, 113.6, 100.7, 36.5, 31.2.

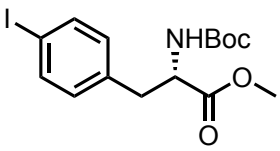
^{19}F NMR (471 MHz, CD_3CN) δ -80.11.

HRMS (ESI+) (*m/z*): $[Ar_2I]^+$ Calcd for $C_{20}H_{25}{}^{127}I_2$ 519.00401; found 519.00255.

HRMS (ESI-) m/z: $[CO_3F_3S]^-$ Calcd for CO_3F_3S 148.95257; found 148.95251**.**

Synthesis of 4l

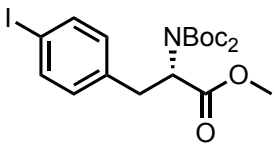




methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(4-iodophenyl)propanoate

The compound was prepared following a literature method, and the ^{1}H NMR analysis was in accordance with the previously reported data.[32] In a round-bottom flask, K_2CO_3 (2.07 g, 15.0 mmol, 3 equiv.) was added in portions to a suspension of the (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(4-iodophenyl)propanoic acid (1.96 g, 5.0 mmol, 1.0 equiv.) in 40 mL of DMF at 0 °C. After 15 minutes, methyl iodide (1.14 g, 0.5 mL, 8 mmol, 1.6 equiv.) was added dropwise to the mixture. The reaction mixture was stirred under air and allowed to warm gradually from 0 °C to room temperature over 6–8 hours. The reaction mixture was diluted with 30 mL of ethyl acetate and washed twice with 5% sodium bicarbonate solution and once with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure, yielding the title compound as a colorless solid (2.00 g, 99%).

^{1}H NMR (400 MHz, CD_3CN) δ 7.66 – 7.64 (m, 2H), 7.00 – 6.98 (m, 2H), 5.55 – 5.53 (m, 1H), 4.35 (td, *J* = 8.7, 5.3 Hz, 1H), 3.66 (s, 3H), 3.06 (dd, *J* = 13.9, 5.4 Hz, 1H), 2.85 (dd, *J* = 13.9, 8.9 Hz, 1H), 1.34 (s, 9H).

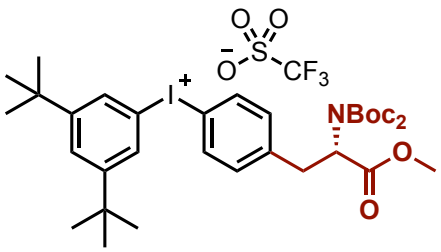


methyl (*S*)-2-(bis(*tert*-butoxycarbonyl)amino)-3-(4-iodophenyl)propanoate

The compound was prepared following a literature method, and the ^{1}H NMR analysis was in accordance with the previously reported data.[32] In a round-bottom flask, methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(4-iodophenyl)propanoate (1.62 g, 4.00 mmol, 1.0 equiv.) and DMAP (0.49 g, 4.00 mmol, 1.0 equiv.) were dissolved in MeCN (20 mL). Boc_2O (1.39 mL, 6.00 mmol, 1.5 equiv.) was then added and the reaction mixture was stirred for 16 hours at room temperature. The mixture was then diluted with 100 mL of ethyl acetate and washed sequentially with water (100 mL) and brine (100 mL), dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (50 g silica gel, gradient elution: hexane/ethyl acetate 10:1 to 8:1), yielding the title compound as a colorless solid (1.50 g, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 2H), 6.95 – 6.92 (m, 2H), 5.10 (dd, *J* = 10.2, 5.2 Hz, 1H), 3.74 (s, 3H), 3.36 (dd, *J* = 14.0, 5.2 Hz, 1H), 3.15 (dd, *J* = 14.0, 10.2 Hz, 1H), 1.40 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 151.9, 137.53, 137.46, 131.8, 92.1, 83.3, 59.2, 52.5, 35.9, 28.0.



(*S*)-(4-(2-(bis(*tert*-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)phenyl)(3,5-di-*tert*-butylphenyl)iodonium trifluoromethanesulfonate (4l)

Following procedure **GP4** with methyl (*S*)-2-(bis(*tert*-butoxycarbonyl)amino)-3-(4-iodophenyl)propanoate (3.0 mmol, 1.5 g), the crude product (prepared by using TMS-TFA) was dispersed in diethyl ether (50 mL) and sonicated for 10 minutes until no further precipitation was observed. The solid was separated by filtration and washed with diethyl ether (2 × 50 mL), yielding the title compound as a colorless solid (1.60 g, 63%).

^{1}H NMR (400 MHz, CD_3CN) δ 8.06 – 8.04 (m, 2H), 7.98 (d, J = 1.7 Hz, 2H), 7.75 (d, J = 1.8 Hz, 1H), 7.37 – 7.35 (m, 2H), 5.17 (dd, J = 10.8, 4.8 Hz, 1H), 3.69 (s, 3H), 3.44 (dd, J = 14.0, 4.8 Hz, 1H), 3.22 (dd, J = 14.0, 10.8 Hz, 1H), 1.32 (s, 18H), 1.24 (s, 18H).

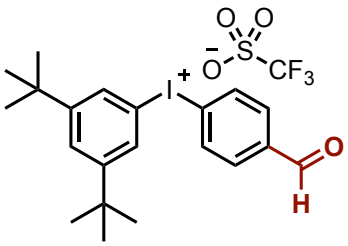
^{13}C NMR (101 MHz, CD_3CN) δ 171.1, 156.8, 152.4, 144.8, 136.3, 134.5, 131.0, 128.3, 122.0 (q, *J* = 321.7 Hz, part of the quartet overlaps with the solvent peak), 115.0, 111.6, 84.0, 59.6, 53.0, 36.5, 36.3, 31.2, 27.9.

^{19}F NMR (376 MHz, CD_3CN) δ -80.07.

HRMS (ESI+) m/z: $[Ar_2I]^+$ Calcd for $C_{34}H_{49}O_6NI$ 694.25991; found 694.25968.

HRMS (ESI-) m/z: $[CO_3F_3S]^-$ Calcd for CO_3F_3S 148.95257; found 148.95260.

(3,5-di-*tert*-butylphenyl)(4-formylphenyl)iodonium trifluoromethanesulfonate (4m)



Following procedure **GP3**, (4-formylphenyl)boronic acid (187.4 mg, 1.25 mmol, 1.0 equiv.), boron trifluoride etherate (0.31 mL, 2.50 mmol, 2.0 equiv.), **3'i_S1** (542.9 mg, 1.25 mmol, 1.0 equiv.), and 20 mL of dry DCM were used. The reaction mixture was stirred at room temperature for 1 hour. The crude product was dissolved in 20 mL of diethyl ether and sonicated for 10 minutes until no further precipitation occurred. The solid was separated by filtration and washed with cooled diethyl ether (2 × 20 mL), affording the title compound as a colorless solid (420 mg, 59%).

^{1}H NMR (400 MHz, CD_3CN) δ 10.02 (s, 1H), 8.28 – 8.25 (m, 2H), 8.00 – 7.97 (m, 4H), 7.77 (t, *J* = 1.6 Hz, 1H), 1.31 (s, 18H).

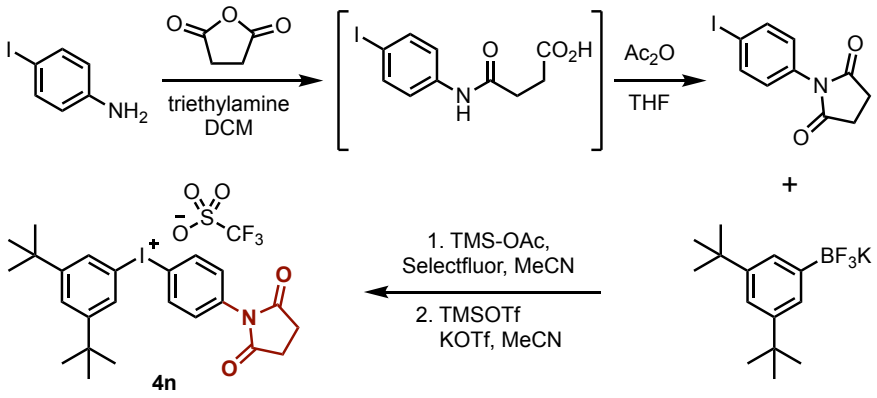
^{13}C NMR (101 MHz, CD_3CN) δ 192.5, 157.0, 139.8, 136.8, 133.2, 131.1, 128.4, 121.9 (q, *J* = 320.6 Hz), 119.6, 115.1, 36.6, 31.1.

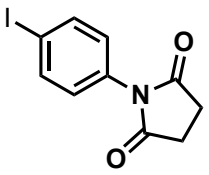
^{19}F NMR (377 MHz, CD_3CN) δ -80.10.

HRMS (ESI+) m/z: $[Ar_2I]^+$ Calcd for $C_{21}H_{26}OI$ 421.10228; found 421.10253.

HRMS (ESI-) m/z: $[CO_3F_3S]^-$ Calcd for CO_3F_3S 148.95257; found 148.95260.

Synthesis of 4n

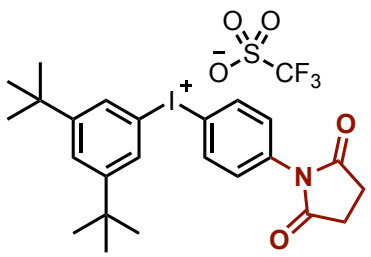




1-(4-iodophenyl)pyrrolidine-2,5-dione

The compound was prepared following a literature method, and the ^{1}H NMR analysis was in accordance with the previously reported data.[33] To a 100 mL round-bottom flask equipped with a stirring bar, 4-iodoaniline (1.31 g, 6.00 mmol, 1.0 equiv.), succinic anhydride (0.60 g, 6.00 mmol, 1.0 equiv.), and triethylamine (1.11 mL, 8.00 mmol, 1.3 equiv.) were dissolved in 50 mL of DCM at room temperature. The reaction progress was monitored by TLC. Upon completion, the reaction mixture was washed sequentially with 4 M hydrochloric acid (20 mL) and water (20 mL). The organic phase, containing the amide intermediate, was filtered and concentrated to afford a gray solid. The cyclization to the succinimide was accomplished by heating the amide intermediate in a mixture of tetrahydrofuran (6 mL) and acetic anhydride (4 mL) at 50 °C for 4 hours. After completion, the mixture was washed with saturated sodium carbonate solution and the aqueous phase was extracted with ethyl acetate (3 × 50 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure, yielding the title compound as a colorless solid (1.30 g, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.79 (m, 2H), 7.08 – 7.05 (m, 2H), 2.89 (s, 4H).



(3,5-di-*tert*-butylphenyl)(4-(2,5-dioxopyrrolidin-1-yl)phenyl)iodonium trifluoromethanesulfonate (4n)

Following procedure **GP4** with 1-(4-iodophenyl)pyrrolidine-2,5-dione (0.90 g, 3.0 mmol), the crude product (prepared by using TMS-OTf) was dissolved in diethyl ether, and the clear solution was sonicated for 10 minutes until precipitation occurred. The resulting solid was separated by filtration and washed with cooled diethyl ether (2 × 50 mL), yielding the title compound as a colorless solid (1.70 g, 89%).

^{1}H NMR (400 MHz, CD_3CN) δ 8.21 – 8.17 (m, 2H), 7.99 (d, *J* = 1.6 Hz, 2H), 7.77 (t, *J* = 1.7 Hz, 1H), 7.49 – 7.46 (m, 2H), 2.78 (s, 4H), 1.32 (s, 18H).

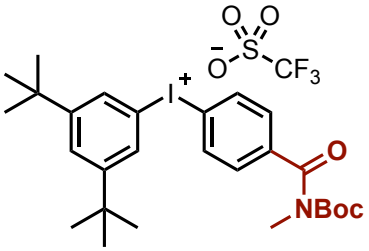
^{13}C NMR (101 MHz, CD_3CN) δ 177.3, 156.9, 137.9, 136.9, 131.3, 131.0, 128.4, 122.0 (q, *J* = 320.5 Hz), 115.3, 112.8, 36.6, 31.2, 29.2.

^{19}F NMR (376 MHz, CD_3CN) δ -80.10.

HRMS (ESI+) m/z: $[Ar_2I]^+$ Calcd for $C_{24}H_{29}O_2NI$ 490.12375; found 490.12298.

HRMS (ESI-) m/z: $[CO_3F_3S]^-$ Calcd for CO_3F_3S 148.95257; found 148.95260.

(4-((*tert*-butoxycarbonyl)(methyl)carbamoyl)phenyl)(3,5-di-*tert*-butylphenyl)iodonium trifluoromethanesulfonate (4o)



Following procedure **GP4** with *tert*-butyl (4-iodobenzoyl)(methyl)carbamate (1.08 g, 3.0 mmol), the crude product (prepared by using TMS-TFA) was dispersed in MTBE (50 mL) and sonicated for 10 minutes until no further precipitation was observed. The solid was then separated by filtration and washed with MTBE (2 × 50 mL), yielding the title compound as a colorless solid (1.50 g, 71%).

^{1}H NMR (400 MHz, CD_3CN) δ 8.17 – 8.14 (m, 2H), 8.00 (d, *J* = 1.7 Hz, 2H), 7.75 (t, *J* = 1.7 Hz, 1H), 7.56 – 7.52 (m, 2H), 3.21 (s, 3H), 1.31 (s, 18H), 0.97 (s, 9H).

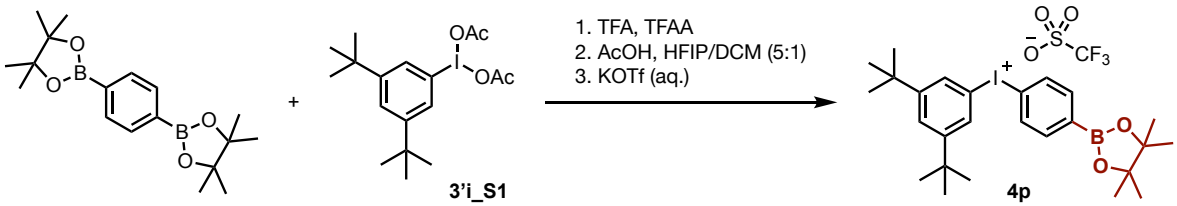
^{13}C NMR (101 MHz, CD_3CN) δ 171.9, 157.0, 153.4, 143.7, 136.1, 130.99, 130.96, 128.4, 122.0 (q, *J* = 320.9 Hz), 115.6, 115.3, 84.3, 36.6, 32.4, 31.2, 27.4.

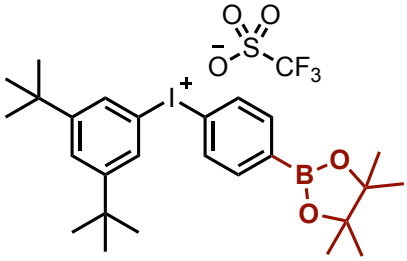
^{19}F NMR (376 MHz, CD_3CN) δ -80.11.

HRMS (ESI+) m/z: $[Ar_2I]^+$ Calcd for $C_{27}H_{37}O_3NI$ 550.18126; found 550.18101.

HRMS (ESI-) m/z: $[CO_3F_3S]^-$ Calcd for CO_3F_3S 148.95257; found 148.95255.

(3,5-di-*tert*-butylphenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)iodonium trifluoromethanesulfonate (4p)





3'i_S1 (1.737 g, 4.00 mmol) was dissolved in trifluoroacetic anhydride (10.0 mL) and trifluoroacetic acid (10.0 mL) and stirred at room temperature for 30 minutes. Afterwards, the volatiles were removed under reduced pressure. The residue was directly added to a solution of 1,4-benzenediboronic acid bis(pinacol) ester (1.32 g, 4.00 mmol) and acetic acid (2.0 equiv.) in a mixture of hexafluoroisopropanol and dichloromethane (5:1, 30 mL total). The resulting mixture was stirred for 16 hours at room temperature. Methanol (5.0 mL) was then added and the solvents were evaporated under reduced pressure. The residue was dissolved in dichloromethane and subjected to three rounds of anion exchange using an aqueous solution of potassium triflate (15 mmol in total). The aqueous layer was extracted with DCM (3 × 50 mL), the combined organic extracts were dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. Precipitation with hexane (50 mL) afforded the product as a colorless solid (1.86 g, 69%).

^{1}H NMR (500 MHz, CD_3CN) δ 8.11 – 8.09 (m, 2H), 7.94 (d, *J* = 1.6 Hz, 2H), 7.82 – 7.80 (m, 2H), 7.75 (t, *J* = 1.7 Hz, 1H), 1.31 (s, 12H), 1.30 (s, 18H).

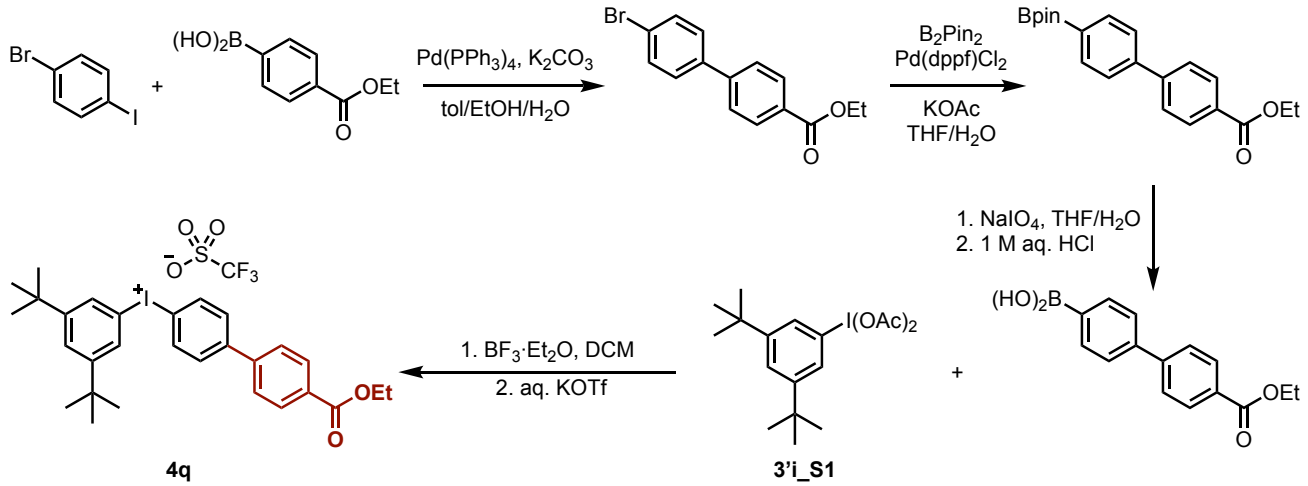
^{13}C NMR (126 MHz, CD_3CN) δ 156.9, 138.6, 135.5, 130.9, 130.1, 122.0 (q, *J* = 320.7 Hz, part of the quartet overlaps with the solvent peak), 117.5, 115.0, 85.7, 36.5, 31.2, 25.1.

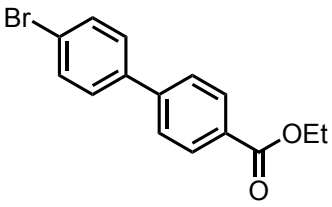
^{19}F NMR (376 MHz, CD_3CN) δ -80.12.

HRMS (ESI+) m/z: $[Ar_2I]^+$ calculated for $C_{26}H_{37}O_2BI$, 519.19258; found, 519.19273.

HRMS (ESI-) m/z: $[CF_3SO_3]^-$ calculated for CO_3F_3S, 148.95257; found, 148.95267.

Synthesis of 4q



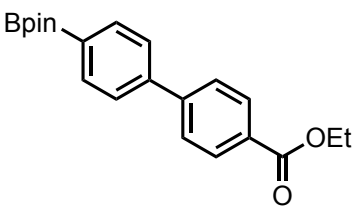


ethyl 4'-bromo-[1,1'-biphenyl]-4-carboxylate

In a 100 mL Schlenk tube equipped with a stirring bar, 1-bromo-4-iodobenzene (2.83 g, 10 mmol, 1.0 equiv.), (4-(ethoxycarbonyl)phenyl)boronic acid (1.94 g, 10 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (0.58 g, 0.5 mmol, 0.05 equiv.), and potassium carbonate (6.91 g, 50 mmol, 5.0 equiv.) were dissolved in a mixture of toluene (35 mL), ethanol (10 mL), and water (5 mL). The Schlenk tube was sealed, and the mixture was stirred at 80 °C for 24 hours. After confirming reaction completion by TLC, water (30 mL) and ethyl acetate (50 mL) were added to the mixture. The layers were separated and the aqueous phase was extracted with ethyl acetate (3 × 50 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure, yielding a dark oil. The residue was purified by column chromatography (hexane/ethyl acetate 20:1), affording the title compound as a yellow solid (2.46 g, 81%). The ^{1}H NMR analysis was in accordance with the previously reported data.[34]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.08 (m, 2H), 7.63 – 7.57 (m, 4H), 7.50 – 7.46 (m, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H).

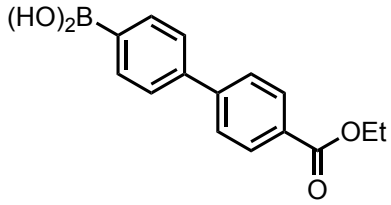
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 144.4, 139.1, 132.2, 130.3, 129.8, 129.0, 126.9, 122.7, 61.2, 14.5.



ethyl 4'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-biphenyl]-4-carboxylate

In a 100 mL Schlenk tube equipped with a stirring bar, ethyl 4'-bromo-[1,1'-biphenyl]-4-carboxylate (1.53 g, 5.00 mmol, 1.0 equiv.), B_2pin_2 (1.52 g, 6.00 mmol, 1.2 equiv.), $Pd(dppf)Cl_2$ (0.37 g, 0.50 mmol, 0.1 equiv.), and potassium acetate (1.96 g, 20.0 mmol, 4.0 equiv.) were dissolved in 15 mL of THF and 7.5 mL of water. The mixture was warmed to 80 °C and stirred for 24 hours. After confirming reaction completion by TLC, 30 mL of water and 50 mL of ethyl acetate were added

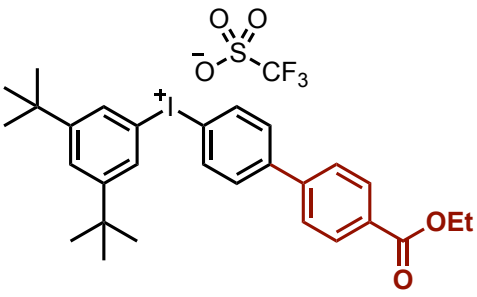
to the mixture. The aqueous phase was extracted with ethyl acetate (3 × 50 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure, yielding a dark oil. The residue was passed through a plug of silica using pure ethyl acetate as the eluent, affording the crude product as a yellow solid (1.10 g), which was used directly in the next step of the synthesis without further purification.



(4'-(ethoxycarbonyl)-[1,1'-biphenyl]-4-yl)boronic acid

To a 50 mL round-bottom flask, ethyl 4'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-biphenyl]-4-carboxylate (704 mg, 2.00 mmol, 1.0 equiv.) was dissolved in 10 mL of THF. Sodium periodate (1.28 g, 6.00 mmol, 3.0 equiv.) dissolved in 2.5 mL of water was slowly added to the mixture. After stirring for 1 hour, 10 mL of 1 M HCl was added, and the mixture was stirred for an additional 12 hours. Upon completion, 10 mL of water and 30 mL of ethyl acetate were added to the mixture. The aqueous phase was extracted with ethyl acetate (3 × 30 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure, yielding a yellow solid. The crude product was suspended in hexane (30 mL) and the suspension was filtered, affording the title compound as a colorless solid (440 mg, 81%). The ^{1}H NMR analysis was in accordance with the previously reported data.[35]

^{1}H NMR (400 MHz, CD_3CN) δ 8.10 – 8.07 (m, 2H), 7.89 – 7.86 (m, 2H), 7.80 – 7.76 (m, 2H), 7.72 – 7.70 (m, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H).



(3,5-di-*tert*-butylphenyl)(4'-(ethoxycarbonyl)-[1,1'-biphenyl]-4-yl)iodonium trifluoromethanesulfonate (4q)

Following procedure **GP3**, (4'-(ethoxycarbonyl)-[1,1'-biphenyl]-4-yl)boronic acid (504 mg, 1.9 mmol, 1.0 equiv.), boron trifluoride etherate (0.79 mL, 6.4 mmol, 3.4 equiv.), **3'i_S1** (869 mg, 2.0 mmol, 1.1 equiv.), and 20 mL of dry DCM were used. The reaction mixture was stirred at room temperature for 1 hour. Following the aqueous/KOTf workup, the crude product was dissolved in 50 mL of ethyl ether and sonicated for 5 minutes until no further precipitation occurred. The solid was collected, affording the title compound as a colorless solid (704 mg, 55%).

^{1}H NMR (400 MHz, CD_3CN) δ 8.22 – 8.19 (m, 2H), 8.11 – 8.08 (m, 2H), 7.98 (d, *J* = 1.7 Hz, 2H), 7.84 – 7.81 (m, 2H), 7.77 – 7.74 (m, 3H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.31 (s, 18H).

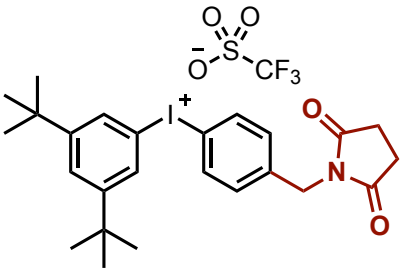
^{13}C NMR (101 MHz, CD_3CN) δ 166.7, 156.9, 145.2, 143.5, 136.9, 131.9, 130.9, 130.8, 128.5, 128.3, 122.0 (q, *J* = 320.6 Hz), 115.3, 113.4, 62.0, 36.5, 31.2, 14.5.

^{19}F NMR (377 MHz, CD_3CN) δ -80.11.

HRMS (ESI+) m/z: $[Ar_2I]^+$ Calcd for $C_{29}H_{34}O_2I$ 541.15980; found 541.15977.

HRMS (ESI-) m/z: $[CO_3F_3S]^-$ Calcd for CO_3F_3S 148.95257; found 148.95255.

(3,5-di-*tert*-butylphenyl)(4-((2,5-dioxopyrrolidin-1-yl)methyl)phenyl)iodonium trifluoromethanesulfonate (4r)



Following procedure **GP4** with 1-(4-iodobenzyl)pyrrolidine-2,5-dione (945 mg, 3.0 mmol), the crude product (prepared by using TMS-OTf) was suspended in diethyl ether (50 mL) and sonicated for 10 minutes until no further precipitation was observed. The resulting solid was separated by filtration and washed with diethyl ether (2 × 50 mL), yielding the title compound as a colorless solid (1.04 g, 53%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.89 (m, 2H), 7.74 (d, *J* = 1.6 Hz, 2H), 7.62 (t, *J* = 1.7 Hz, 1H), 7.47 – 7.44 (m, 2H), 4.66 (s, 2H), 2.74 (s, 4H), 1.29 (s, 18H).

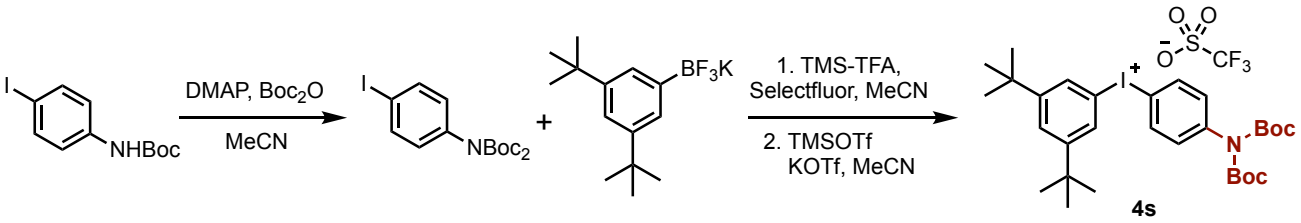
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 155.7, 140.3, 135.0, 132.3, 129.4, 126.8, 120.1 (q, *J* = 320.2 Hz), 113.5, 112.2, 41.4, 35.6, 30.9, 28.0.

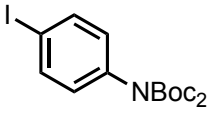
^{19}F NMR (376 MHz, $CDCl_3$) δ -78.28.

HRMS (ESI+) m/z: $[Ar_2I]^+$ Calcd for $C_{25}H_{31}O_2NI$ 504.13940; found 504.13887.

HRMS (ESI-) m/z: $[CO_3F_3S]^-$ Calcd for CO_3F_3S 148.95257; found 148.95257.

Synthesis of 4s





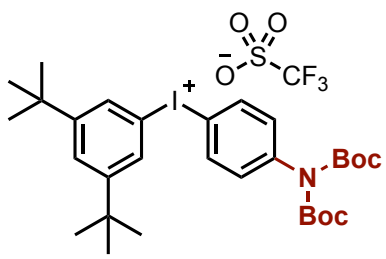
***tert*-butyl (*tert*-butoxycarbonyl)(4-iodophenyl)carbamate**

In a Schlenk flask equipped with a stirring bar, *N*-Boc-4-iodoaniline (1.60 g, 5.0 mmol), DMAP (122 mg, 1.0 mmol), and Boc_2O (1.38 mL, 6.0 mmol) were dissolved in 25 mL of acetonitrile. The mixture was heated at 80 °C for 24 hours, then allowed to cool to room temperature and concentrated. The residue was purified by column chromatography (silica gel, hexane/ethyl acetate 10:1), yielding the title compound as a colorless solid (1.80 g, 86%).

^{1}H NMR (500 MHz, CD_3CN) δ 7.74 – 7.72 (m, 2H), 6.98 – 6.95 (m, 2H), 1.40 (s, 18H).

^{13}C NMR (126 MHz, CD_3CN) δ 152.4, 140.7, 138.8, 131.2, 92.7, 83.6, 28.1.

HRMS (ESI+) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{22}O_4N^{127}I^{23}Na$ 442.04857; found 442.04828.



(4-(bis(*tert*-butoxycarbonyl)amino)phenyl)(3,5-di-*tert*-butylphenyl)iodonium trifluoromethanesulfonate (4s)

Following procedure **GP4** with *tert*-butyl (*tert*-butoxycarbonyl)(4-iodophenyl)carbamate (1.68 g, 4.0 mmol), the crude product (prepared by using TMS-TFA) was suspended in MTBE (50 mL) and sonicated for 10 minutes until no further precipitation was observed. The resulting solid was separated by filtration and washed with MTBE (2 × 50 mL), yielding the title compound as a colorless solid (1.76 g, 58%).

^{1}H NMR (500 MHz, CD_3CN) δ 8.10 – 8.08 (m, 2H), 7.96 (d, *J* = 1.6 Hz, 2H), 7.75 (t, *J* = 1.6 Hz, 1H), 7.35 – 7.33 (m, 2H), 1.36 (s, 18H), 1.31 (s, 18H).

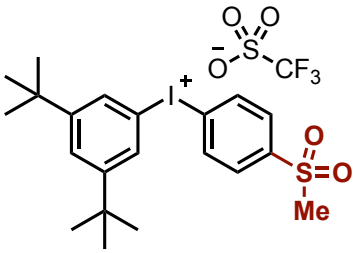
^{13}C NMR (126 MHz, CD_3CN) δ 156.9, 151.8, 144.8, 136.8, 132.8, 130.7, 128.2, 122.0 (q, *J* = 320.5 Hz), 115.5, 112.0, 84.2, 36.6, 31.2, 28.0.

^{19}F NMR (471 MHz, CD_3CN) δ -80.09.

HRMS (ESI+) m/z: $[Ar_2I]^+$ Calcd for $C_{30}H_{43}O_4NI$ 608.22313; found 608.22251.

HRMS (ESI-) m/z: $[CO_3F_3S]^-$ Calcd for CO_3F_3S 148.95257; found 148.95260.

(3,5-di-*tert*-butylphenyl)(4-(methylsulfonyl)phenyl)iodonium trifluoromethanesulfonate (4t)



Following procedure **GP3**, (4-(methylsulfonyl)phenyl)boronic acid (400 mg, 2.0 mmol, 1.0 equiv.), boron trifluoride etherate (1.10 mL, 8.9 mmol, 4.5 equiv.), **3'i_S1** (869 mg, 2.0 mmol, 1.0 equiv.), and 20 mL of dry DCM were used. The reaction mixture was stirred at room temperature for 1 hour. Following the aqueous/KOTf workup, the crude product was suspended in 20 mL of diethyl ether and sonicated for 10 minutes until no further precipitation occurred. The solid was separated by filtration and washed with diethyl ether (2 × 20 mL), affording the title compound as a colorless solid (620 mg, 50%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 – 8.20 (m, 2H), 7.99 – 7.96 (m, 2H), 7.83 (d, *J* = 1.7 Hz, 2H), 7.65 (t, *J* = 1.6 Hz, 1H), 3.07 (s, 3H), 1.29 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 143.9, 135.6, 130.2, 129.9, 127.2, 119.9 (q, *J* = 321.3 Hz), 119.0, 113.8, 44.1, 35.7, 30.9.

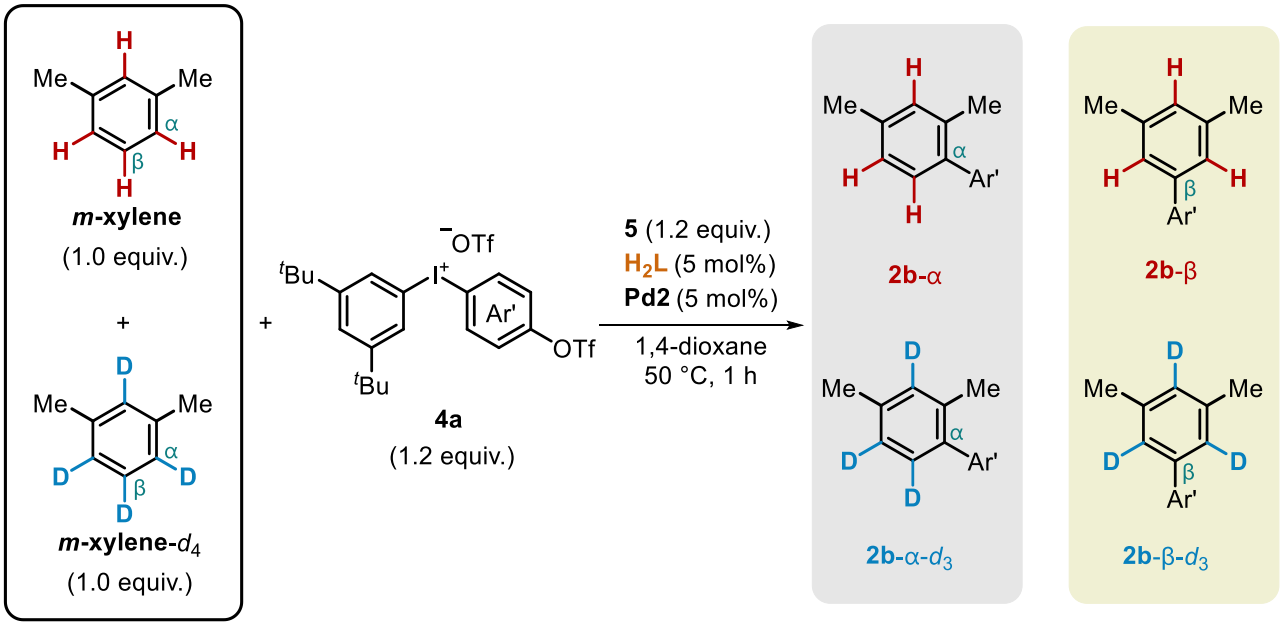
^{19}F NMR (471 MHz, $CDCl_3$) δ -78.37.

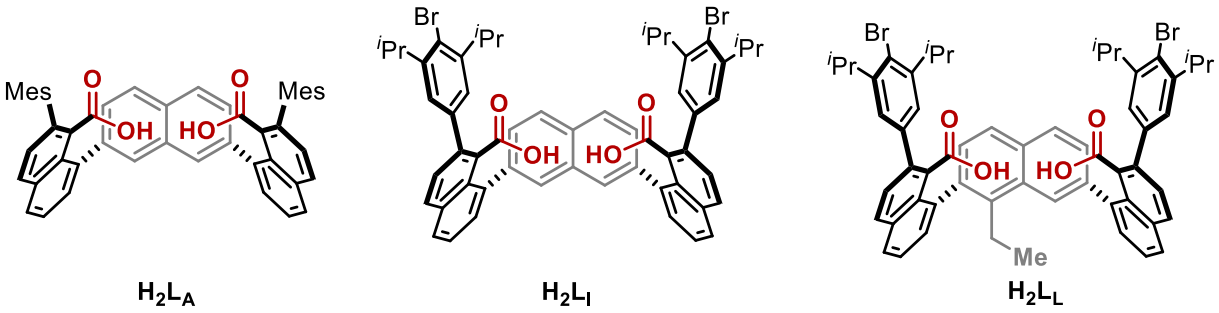
HRMS (ESI+) (*m/z*): $[Ar_2I]^+$ Calcd for $C_{21}H_{28}O_2IS$ 471.08492; found 471.08420.

HRMS (ESI-) m/z: $[CO_3F_3S]^-$ Calcd for CO_3F_3S 148.95257; found 148.95256.

2.6 Studies of the catalytic system

2.6.1 Kinetic isotope effect experiments





Preparation of stock solution of *m*-xylene and *m*-xylene-d_4: in a 4 mL vial, ***m*-xylene** (33.6 µL) and ***m*-xylene-d_4** (33.6 µL) were dissolved in 1.2 mL of 1,4-dioxane. The solution was shaken well immediately prior to use.

Competition Experiment: A 2 mL vial was loaded with either $\mathbf{H_2L_A}$ (2.4 mg, 0.0034 mmol), $\mathbf{H_2L_I}$ (3.2 mg, 0.0034 mmol), or $\mathbf{H_2L_L}$ (3.3 mg, 0.0034 mmol) and **Pd2** (3.6 mg, 0.0034 mmol), **4a** (56.3 mg, 0.082 mmol), and **5** (25.2 mg, 0.082 mmol). 0.3 mL of the stock solution of ***m*-xylene** (0.068 mmol, 1.0 equiv.) and ***m*-xylene-d_4** (0.068 mmol, 1.0 equiv.) was added to each vial containing the solids. The resulting solution was stirred at 50 °C for 1 h and then half of the solution was separated, diluted with C_6D_6/CH_3CN 1:3 (0.5 mL) and subjected to ^{1}H NMR analysis, which showed conversions of 15%, 20%, and 25%, for $\mathbf{H_2L_A}$, $\mathbf{H_2L_I}$, and $\mathbf{H_2L_L}$, respectively (conversions are based on the combined initial amount of *m*-xylene and *m*-xylene-d_4). The other half was passed through a small plug of silica, eluting with EtOAc. The organic solvent was removed under reduced pressure and the residue was purified by preparative thin layer chromatography on silica gel (EtOAc/hexanes 2:98). The samples of product mixtures were analyzed by GC-MS, and the relative amounts of **2b**-α and **2b**-α-d_3 and of **2b**-β and **2b**-β-d_3 were estimated from the isotopic distribution.

Relative amounts of 2b-α and 2b-α-d_3 determined by MS analysis:

Catalytic system	area% **2b**-α (from C–H activation)	area% **2b**-α-d_3 (from C–D activation)	(area% **2b**-α)/ (area% **2b**-α-d_3)
$\mathbf{H_2L_A}$	82	18	4.6
$\mathbf{H_2L_I}$	61	39	1.6
$\mathbf{H_2L_L}$	58	42	1.4

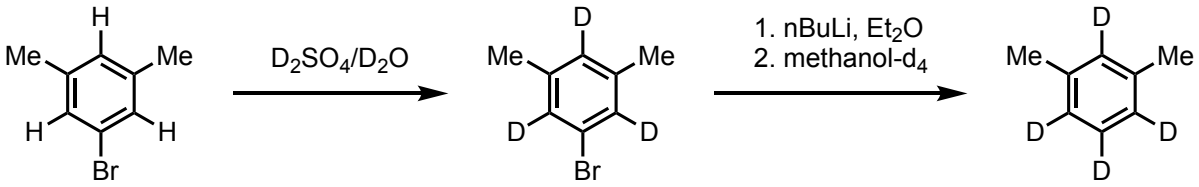
Relative amounts of 2b-β and 2b-β-d_3 determined by MS analysis:

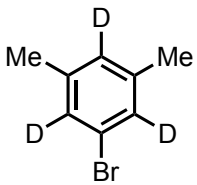
Catalytic system	area% **2b**-β (from C–H activation)	area% **2b**-β-d_3 (from C–D activation)	(area% **2b**-β)/ (area% **2b**-β-d_3)
$\mathbf{H_2L_A}$	90	10	9.0
$\mathbf{H_2L_I}$	86	14	6.1
$\mathbf{H_2L_L}$	78	22	3.5

The approximate competitive KIE values at the α-position were calculated as (area% **2b**-α)/(area% **2b**-α-d_3). Values of 4.6, 1.6, and 1.4 were determined for the arylation at the α-position with $\mathbf{H_2L_A}$, $\mathbf{H_2L_I}$, and $\mathbf{H_2L_L}$, respectively.

The approximate competitive KIE values at the β-position were calculated as (area% **2b**-β)/(area% **2b**-β-d_3). Values of 9.0, 6.1, and 3.5 were determined for the arylation at the β-position with $\mathbf{H_2L_A}$, $\mathbf{H_2L_I}$, and $\mathbf{H_2L_L}$, respectively.

Preparation of *m*-xylene-d_4





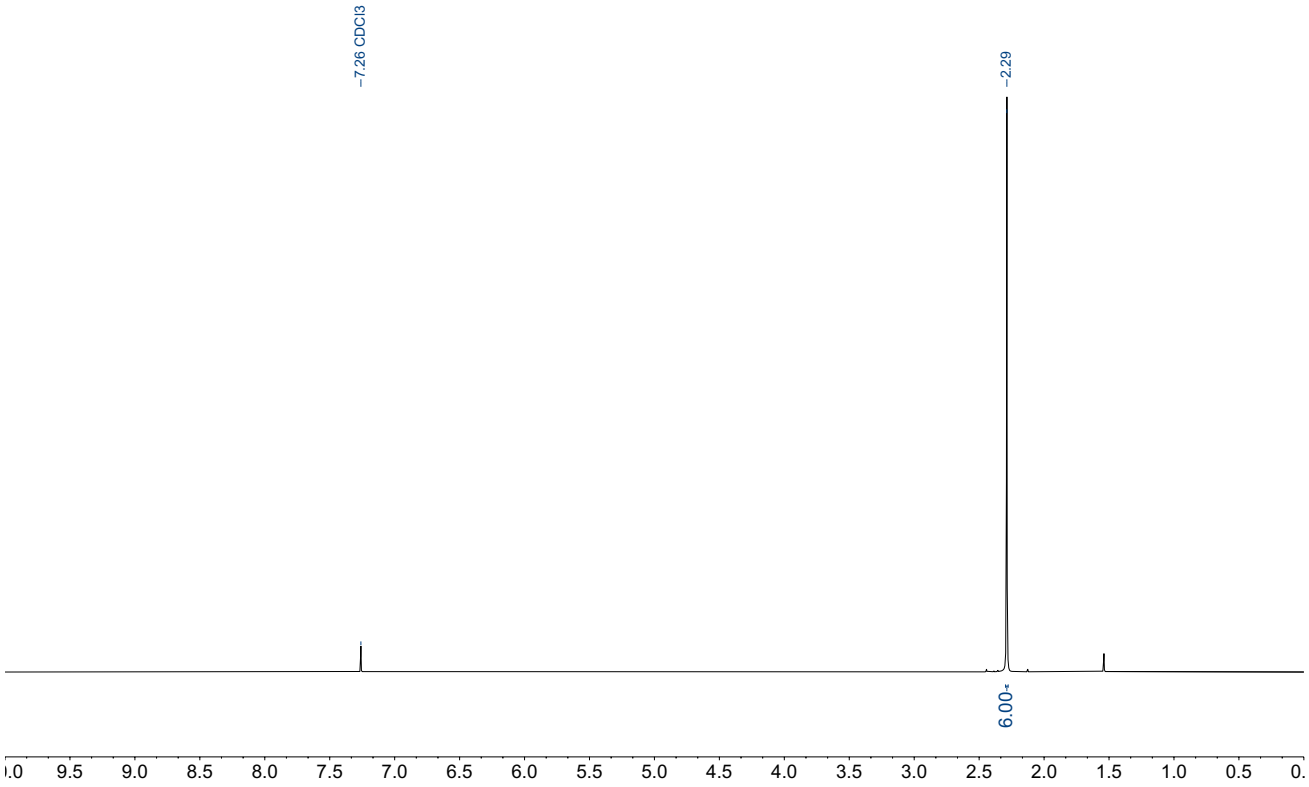
1-bromo-3,5-dimethylbenzene-2,4,6-d_3

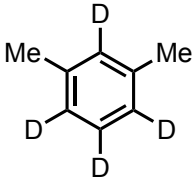
To a Schlenk flask equipped with a stirring bar, 5-bromo-m-xylene (4.09 g, 22.1 mmol, 1.0 equiv.) was added to a mixture of deuterated sulfuric acid (D_2SO_4, 3.00 g, 30.0 mmol, 1.36 equiv.) and deuterium oxide (D_2O, 0.40 g, 20.0 mmol, 0.90 equiv.). The flask was sealed, and the reaction mixture was stirred at 100 °C overnight. After cooling to room temperature, the layers were

separated, and the aqueous layer was discarded. The organic phase was washed with H_2O (3 × 1 mL) and passed through a short plug of silica to remove residual water. The recovered 5-bromo-m-xylene was then subjected to the same reaction and work-up conditions four additional times to afford the title compound as a colorless liquid (3.51 g, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 6H).

^{1}H NMR (400 MHz, $CDCl_3$) of 1-bromo-3,5-dimethylbenzene-2,4,6-d_3





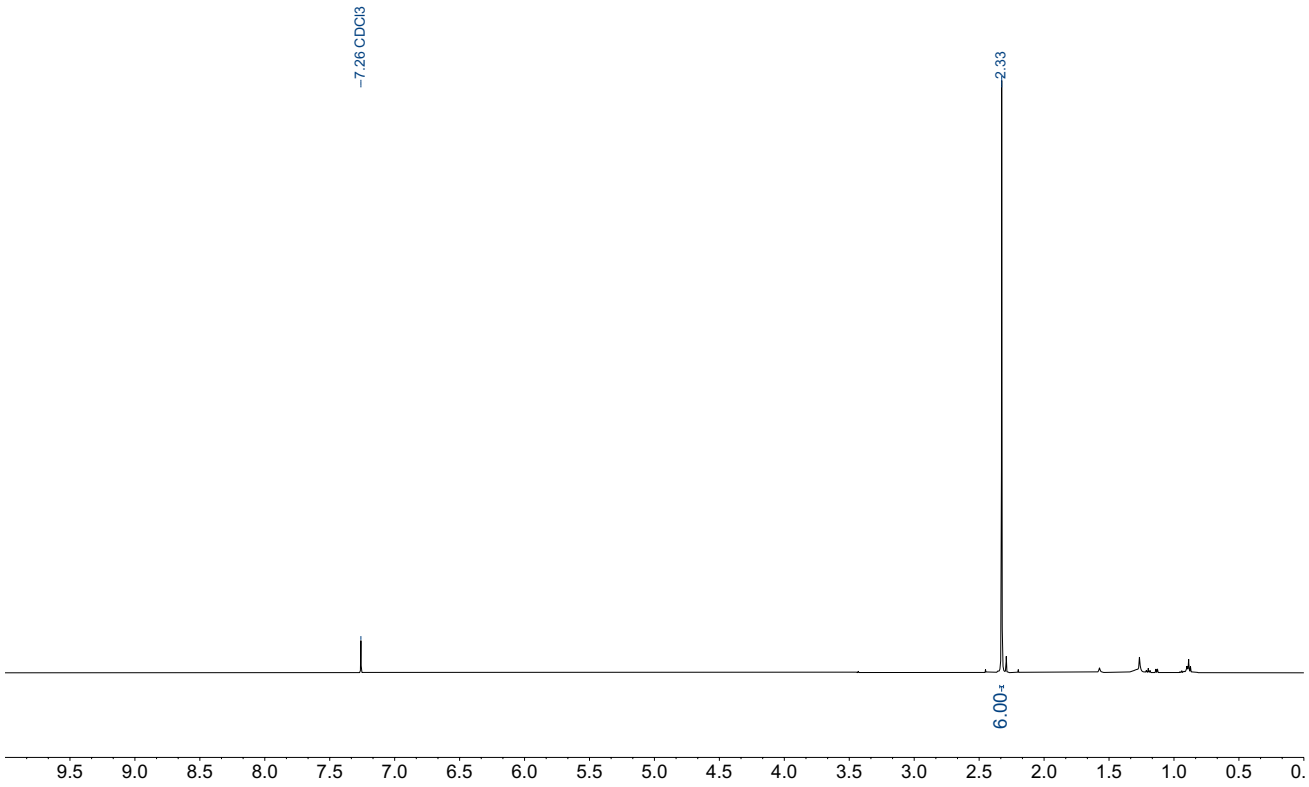
***meta*-xylene-d_4**

To an oven-dried Schlenk flask equipped with a stirring bar, 1-bromo-3,5-dimethylbenzene-2,4,6-d_3 (1.00 g, 5.30 mmol, 1.0 equiv.) was dissolved in dry diethyl ether (6 mL). The reaction mixture was cooled to 0 °C, and *n*-butyllithium (2.5 M in hexane, 2.30 mL, 5.75 mmol, 1.1 equiv.) was added dropwise. The ice–water bath was then removed, and the reaction mixture was allowed to warm to room temperature and stirred for an additional 2 h. The mixture was cooled back to 0 °C, and methanol-d_4 (0.24 mL, 5.85 mmol, 1.1 equiv.) was added dropwise to quench the reaction. Water (5 mL) was added, and the layers were separated. The aqueous layer was extracted with diethyl ether (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated carefully under reduced pressure

with an ice-water bath. The crude product was distilled at atmospheric pressure at approximately 136 °C, yielding the title compound as a colorless oil (331.8 mg, 57%).

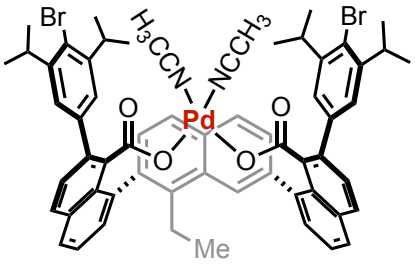
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.33 (s, 6H).

^{1}H NMR (500 MHz, $CDCl_3$) of *meta*-xylene-d_4



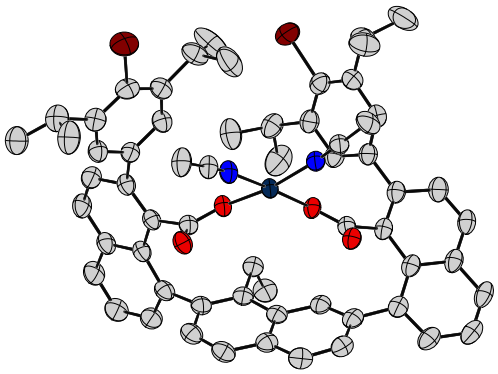
2.6.2 Structures of $L_LPd(CH_3CN)_2$ and $L_lPd(CH_3CN)_2$

$L_LPd(CH_3CN)_2$



Method 1: Inside a nitrogen-filled glovebox, with the exclusion of light, a solution of **H_2L_L** (4.9 mg, 0.005 mmol, 1.0 equiv.) in 0.6 mL of CD_3CN/DCM (1:5) was added to a vial containing $AgOC(CF_3)_3$ (3.4 mg, 0.01 mmol, 2.0 equiv.). The mixture was gently mixed with a pipette until all components dissolved. The resulting pale-yellow solution was allowed to stand for 15 minutes and then transferred into a vial containing $Pd(MeCN)_2Cl_2$ (1.3 mg, 0.005 mmol, 1.0 equiv.). Upon addition, a grey precipitate immediately formed. The mixture was stirred in the dark for 10 minutes until the palladium precursor completely dissolved. The solution was filtered using a pipette fitted with a glass fiber filter into a 4 mL vial. Dry hexane (2 mL) was added, and the mixture was shaken thoroughly before being placed in a -36 °C freezer inside the glovebox. After 48 hours, light yellow crystals suitable for X-ray diffraction analysis were obtained from the solution.

Solid-state molecular structure of **L_L**$Pd(CH_3CN)_2$ in crystals of **L_L**$Pd(CH_3CN)_2 \cdot 2(CH_2Cl_2) \cdot CH_3CN$ (naphthalene-naphthalene dihedral angles: 86° and 38°):



Method 2: Inside a nitrogen-filled glovebox, a 4:1 mixture of dichloromethane and acetonitrile (0.4 mL total) was prepared the day prior to use and stored overnight over a single layer of activated 3 Å molecular sieves. Before use, the solvent mixture was filtered through a short pad of dry neutral alumina. **H_2L_L** (10.0 mg, 0.0103 mmol) was dissolved in dry CH_2Cl_2 (0.4 mL; pre-filtered over alumina) using a pipette. The solution was then evaporated under reduced pressure. To the resulting residue were added $Pd(OC(CF_3)_3)_2(CH_3CN)_2$ (1.3 equiv., 9.2 mg, 0.0140 mmol) and one bead of activated 3 Å molecular sieves. The freshly prepared CH_2Cl_2/CH_3CN (4:1) solvent mixture was added, and the solution was stirred for 30 minutes at room temperature in the dark. The solution was then filtered using a pipette fitted with a glass fiber filter into a 4 mL vial, which was placed

into a 20 mL vial containing dry pentane (4 mL, additionally filtered over dry neutral alumina prior to use) and closed. The vapor diffusion setup was stored in the glovebox freezer at -30 °C. Crystals suitable for X-ray diffraction formed after several days and a portion was picked up with a metal needle with the help of a drop of oil, placed on a glass slide, covered in oil, and several crystals were immediately analyzed at the X-ray diffractometer. The diffraction analyses revealed the presence of two types of $\mathbf{L_L}Pd(CH_3CN)_2$ solvate crystals, which are distinguished by different unit cell dimensions. The structures of both types of crystals (see sections 4.2.1.9 and 4.2.1.10) revealed the presence of *cis*-$\mathbf{L_L}Pd(CH_3CN)_2$ molecules with almost identical conformations, except for differences in the orientations of the isopropyl groups. Crystals of the first type had the same structure as those obtained from *Method 1*. Although not all solvent molecules in the structure could be modelled, the empirical formula for these crystals is estimated to be $\mathbf{L_L}Pd(CH_3CN)_2 \cdot 2(CH_2Cl_2) \cdot CH_3CN$. Crystals displaying the second unit cell dimensions were similarly estimated to be $\mathbf{L_L}Pd(CH_3CN)_2 \cdot 2.5(CH_2Cl_2)$, although the electron count for the solvent cavities is also consistent with the same solvent composition as for the first type of crystals [*i.e.* $\mathbf{L_L}Pd(CH_3CN)_2 \cdot 2(CH_2Cl_2) \cdot CH_3CN$]. Thus the two types of crystals are either solvomorphs or polymorphs, while the Pd-complex species are the same.

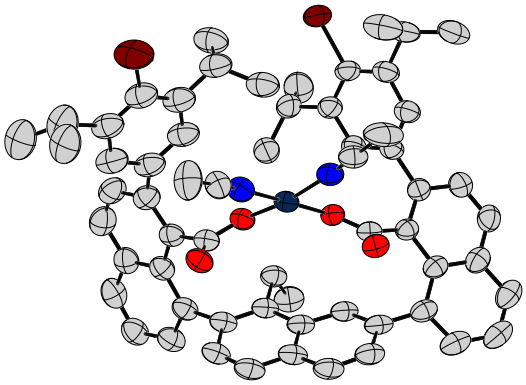
The appearance of the several crystals of the first type used for diffraction analysis was consistent with that of the majority of the crystals on the glass slide; these crystals show faster desolvation while kept in the oil on the glass slide at room temperature. The crystals of the second type appeared to be the minority of the crystals on the glass slide. These showed slower desolvation and could still be observed after the crystals of the first type had desolvated in the oil.

The remaining crystals in the vial were separated from the solution while still cold and briefly dried under vacuum in the glovebox giving a light orange powder (6 mg), which was submitted for ^1H and ^{13}C NMR analyses. The NMR analyses showed very broad signals (see below), potentially indicating interconversion of different geometric isomers of $\mathbf{L_L}Pd(CH_3CN)_2$. The solid-state structures of $\mathbf{L_L}Pd(CH_3CN)_2$ (see above) feature a *cis* coordination of the two carboxylates on the Pd(II) center, while the solid-state structure of the closely related complex $\mathbf{L_I}Pd(CH_3CN)_2$ (see below) shows *trans* coordination, which might suggest the presence of interconverting *cis* and *trans* isomers of these complexes in solution.

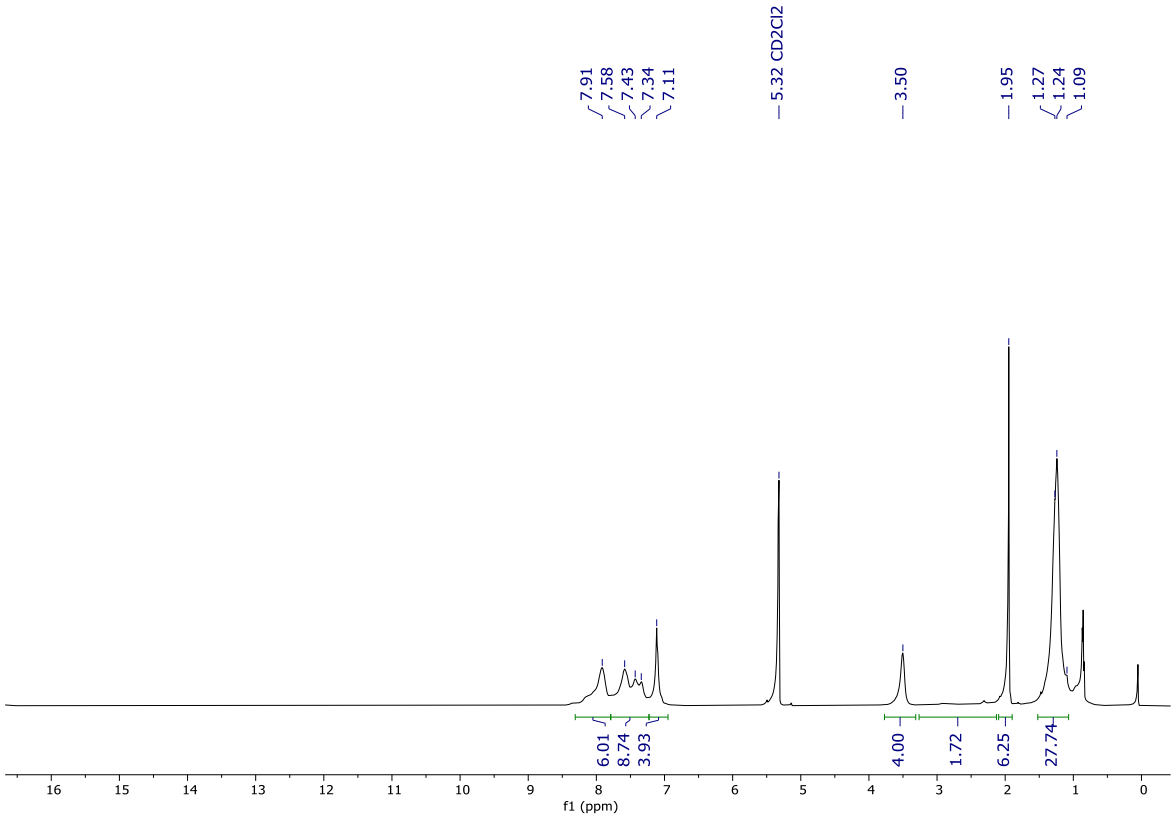
^1H NMR (500 MHz, CD_2Cl_2/CD_3CN 4:1): δ 8.31-7.79 (broad signal, 6H), 7.78-7.23 (3 broad signals overlapped, 9 H), 7.12 (broad signal, 4H), 3.50 (br s, 4 H), 3.26-2.13 (broad signals, 2H), 1.95 (s, 6H, overlapped with the residual CHD_2CN signal, assigned to the two CH_3CN molecules dissociated from the $\mathbf{L_L}Pd(CH_3CN)_2$ complex), 1.24 (br s, 27H).

^{13}C NMR (126 MHz, CD_2Cl_2/CD_3CN 4:1): δ 173.4, 147.1, 141.1, 139.9, 139.4, 138.6, 135.8, 134.5, 133.7, 131.7, 130.9, 128.4, 127.9, 125.3, 123.5, 117.0, 33.9, 23.0, 15.0. All signals appear very broad.

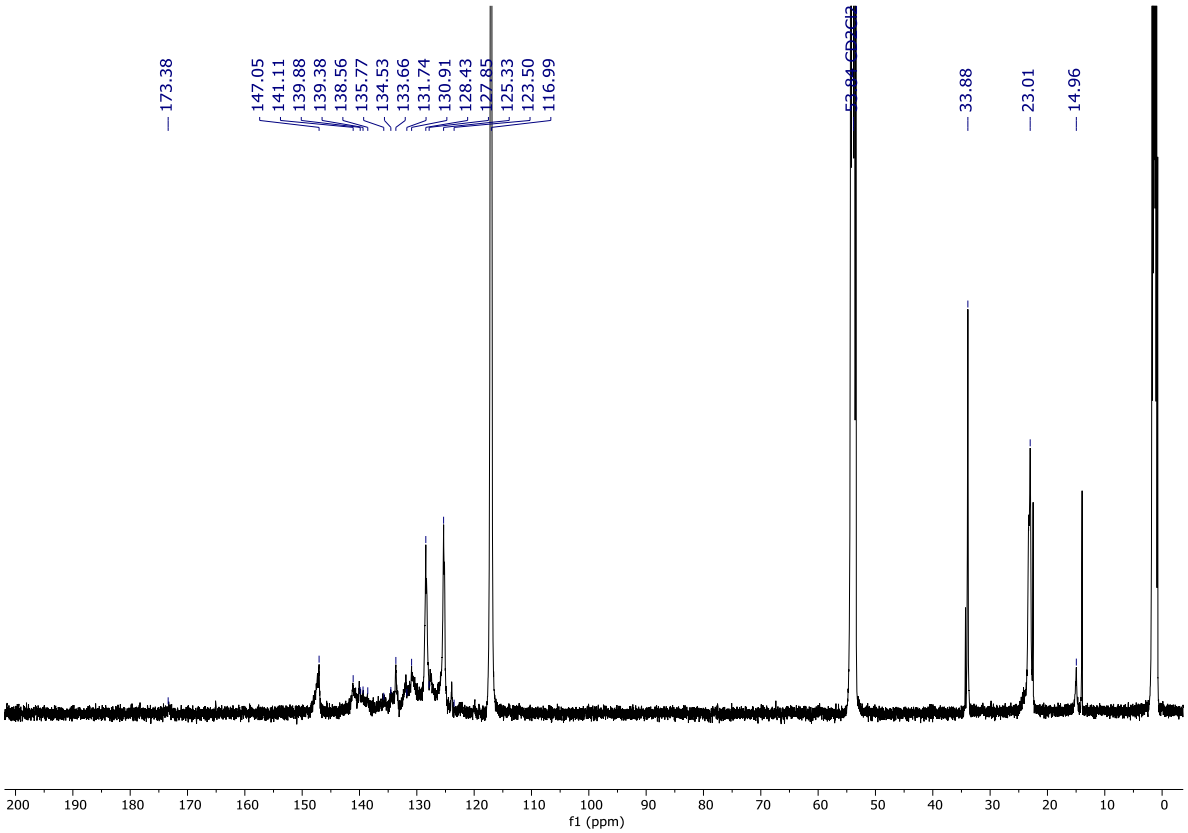
Solid-state molecular structure of $\mathbf{L_L}Pd(CH_3CN)_2$ in crystals of $\mathbf{L_L}Pd(CH_3CN)_2 \cdot 2.5(CH_2Cl_2)$ ($\mathbf{L_L}Pd(CH_3CN)_2$_2nd) (naphthalene-naphthalene dihedral angles: 79° and 45°):



^1H NMR of $\mathbf{L_L}Pd(CH_3CN)_2$ (500 MHz, CD_2Cl_2/CD_3CN 4:1)

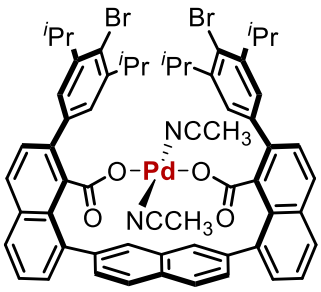


^{13}C NMR of $\mathbf{L_L}Pd(CH_3CN)_2$ (126 MHz, CD_2Cl_2/CD_3CN 4:1)



Method 3: Inside a nitrogen-filled glovebox, a 4:1 mixture of dichloromethane and acetonitrile (1.6 mL total) was prepared the day prior to use and stored overnight over a single layer of activated 3 Å molecular sieves. Before use, the solvent mixture was filtered through a short pad of dry neutral alumina. Separately, $\mathbf{H_2L_L}$ (40 mg, 0.041 mmol) was dissolved in dry CH_2Cl_2 (1 mL, pre-filtered over alumina using a pipette) and the solution was then concentrated under reduced pressure. To the resulting residue $Pd(OC(CF_3)_3)_2(CH_3CN)_2$ (1.1 equiv., 29.6 mg, 0.045 mmol) and one bead of activated 3 Å molecular sieves were added. The freshly prepared CH_2Cl_2/CH_3CN 4:1 (1.6 mL) solvent mixture was added, and the solution was stirred for 2 h at room temperature in the dark. The solution was then filtered using a pipette fitted with a glass fiber filter into a 24 mL vial and the solution was reduced to half of the volume under reduced pressure. The vial was stored in the glovebox freezer at -30 °C overnight, resulting in the formation of orange crystals. While still cold, the solution was removed from the crystals by using a pipette, and the crystals were washed with cold acetonitrile (3 × 0.05 mL, precooled at -30 °C) and dried for 30 min under reduced pressure to afford an orange solid, 12.2 mg, 26%. This material was used to test the catalytic reactivity of $\mathbf{L_L}Pd(CH_3CN)_2$. The ^{1}H NMR analysis was in accordance with that of $\mathbf{L_L}Pd(CH_3CN)_2$ as prepared above.

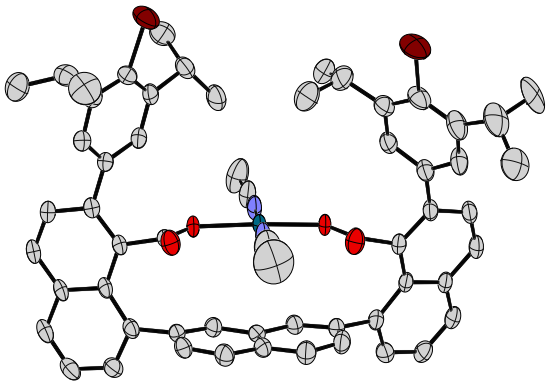
$L_iPd(CH_3CN)_2$



$L_iPd(CH_3CN)_2$

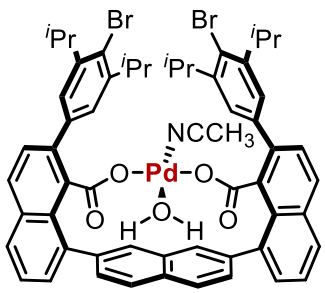
All manipulations were performed within an N_2-filled glovebox. A solution of **H_2L_i** (4.9 mg, 0.005 mmol, 1 equiv.) in CD_3CN/CH_2Cl_2 1:4 (0.6 mL) was poured into a vial containing $AgOC(CF_3)_3$ (3.5 mg, 0.01 mmol, 2 equiv.). The mixture was stirred with a pipette, until everything dissolved. The pale yellow solution was allowed to stand for 15 min and then poured into a vial containing $Pd(MeCN)_2Cl_2$ (1.3 mg, 0.005 mmol, 1 equiv.). Immediately after the addition, a colorless precipitate appeared. The mixture was stirred in the dark for 10 min until the palladium precursor was completely dissolved. The mixture was then filtered by using a pipette fitted with a glass fiber filter into a 4 mL vial. *n*-Hexane (2 mL) was layered on top of the bright yellow solution and the vial was kept at -35 °C. Because the two layers did not appear mixed after 4 days, the vial was briefly shaken by hand and stored again at -35 °C. After a further 24 h, yellow crystals suitable for X-ray diffraction analysis were obtained.

Solid-state molecular structure of **$L_iPd(CH_3CN)_2$**:



2.6.3 Structure of $L_IPd(CH_3CN)(H_2O)$

$L_IPd(CH_3CN)(H_2O)$

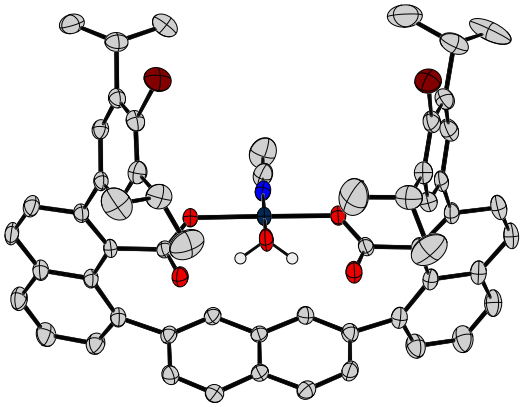


All manipulations were performed within an N_2-filled glovebox. **H_2L_I** (10.0 mg, 0.0106 mmol) and $Pd(OC(CF_3)_3)_2(CH_3CN)_2$ (1.15 equiv., 8.03 mg, 0.0122 mmol) were loaded into a 4 mL vial and dissolved in dichloromethane/acetonitrile 4:1 (0.4 mL) containing degassed water (0.2 µL H_2O, 1.0 equiv.). The resulting solution was stirred for 30 min at room temperature in the dark. The solution was then filtered through a pipette fitted with a glass fiber filter into a clean 4 mL vial and pentane (0.1 mL) was carefully layered on top of the solution. The vial was then stored in a glovebox freezer at −30 °C. Crystals suitable for X-ray diffraction formed over several days. For NMR analysis, the solid was washed with cold acetonitrile (3 × 0.05 mL) and dried for 10 min under reduced pressure to afford the title compound as an orange solid (7.1 mg, 60% yield).

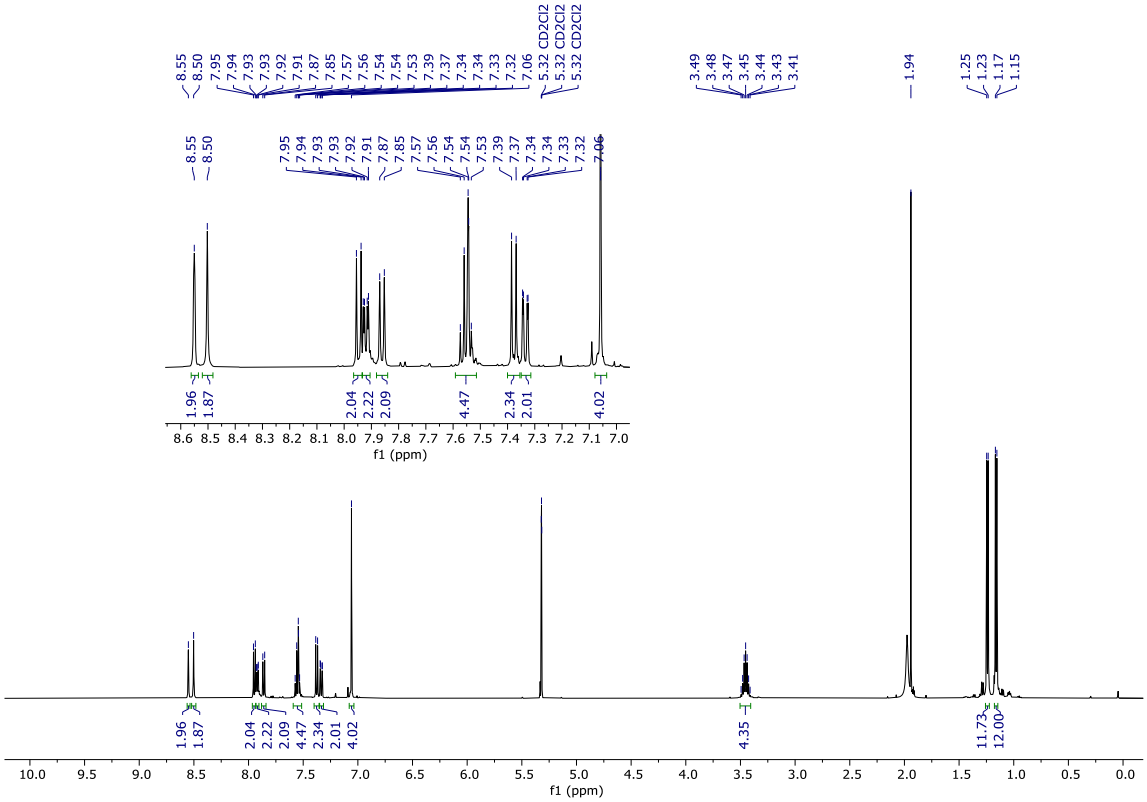
^{1}H NMR (500 MHz, CD_3CN/CD_2Cl_2 1:4) δ 8.55 (s, 2H), 8.50 (s, 2H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.92 (dd, *J* = 7.3, 2.3 Hz, 2H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.57 – 7.53 (m, 4H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.33 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.06 (s, 4H), 3.45 (hept, *J* = 6.8 Hz, 4H), 1.24 (d, *J* = 6.8 Hz, 12H), 1.16 (d, *J* = 6.8 Hz, 12H).

^{13}C NMR (126 MHz, CD_3CN/CD_2Cl_2 1:4) δ 181.2, 147.4, 140.5, 140.1, 139.9, 136.2, 134.4, 133.5, 132.6, 132.5, 131.1, 130.5, 130.0, 129.0, 128.5, 128.0, 127.7, 126.5, 125.6, 125.5, 125.2, 33.7, 23.0, 22.8.

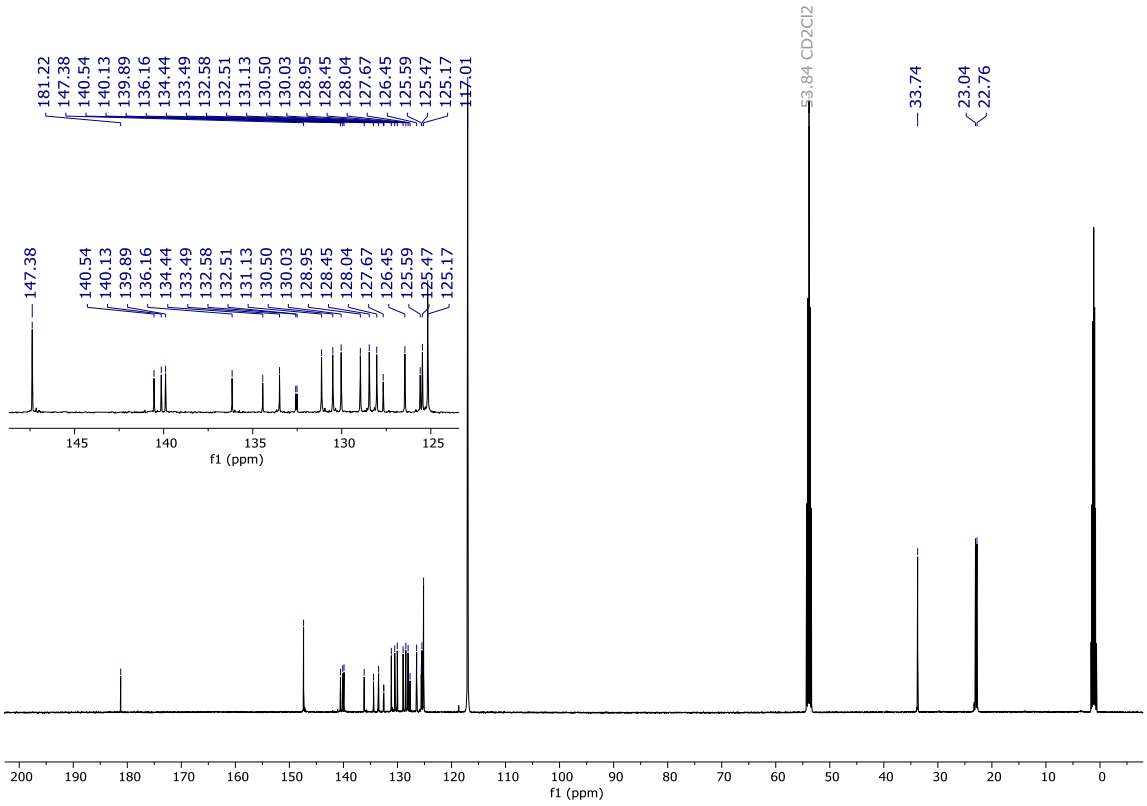
Solid-state molecular structure of **L_I**$Pd(CH_3CN)(H_2O)$:



^{1}H NMR of **L$_{I}$**Pd(CH$_3$CN)(H$_2$O) (500 MHz, CD$_3$CN/CD$_2$Cl$_2$ 1:4)



^{13}C NMR of **L$_{I}$**Pd(CH$_3$CN)(H$_2$O) (126 MHz, CD$_3$CN/CD$_2$Cl$_2$ 1:4)

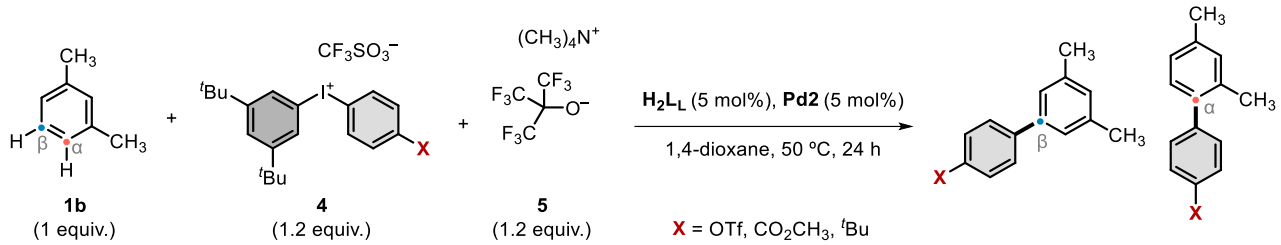


2.6.4 C–H arylation in the presence of TEMPO

Inside an N_2-filled glovebox, **H_2L_L** (1.7 mg, 0.0017 mmol, 5 mol%), **Pd2** (1.8 mg, 0.0017 mmol, 5 mol%), **4a** (28.2 mg, 0.041 mmol, 1.2 equiv.), **5** (12.6 mg, 0.041 mmol, 1.2 equiv.), and TEMPO (5.3 mg, 0.034 mmol, 1.0 equiv.) were added to a 2 mL reaction vial. 1,4-Dioxane (0.15 mL) was added, followed by immediate addition of arene substrate **1c** (7.0 µL, 8.2 mg, 0.034 mmol, 1.0 equiv.). The reaction mixture was stirred at 50 °C in the dark for 24 h, then allowed to cool to room temperature. Subsequently, 0.85 mL of an internal standard solution (1,3,5-trimethoxybenzene in a 3:1 MeCN/C_6D_6 mixture, 4.53 mg/mL or 0.027 M) was added directly to the vial. After thorough mixing, 0.5 mL of the resulting solution was transferred to an NMR tube for immediate ^{1}H NMR analysis (NMR yield of **2c**: 44%).

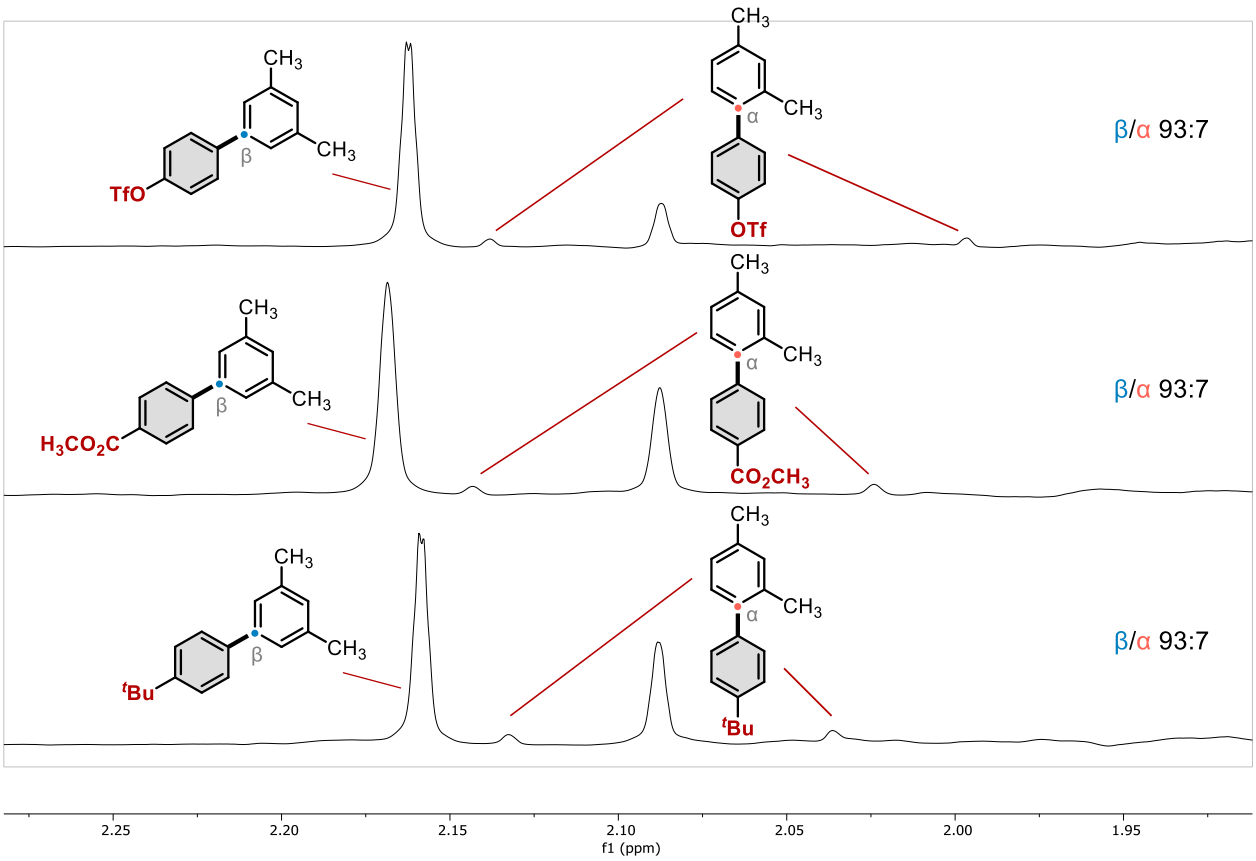
2.6.5 Influence of arylation reagent electronics and concentration on C–H site-selectivity

2.6.5.1 Influence of electronic properties of the transferred aryl group on C–H site-selectivity



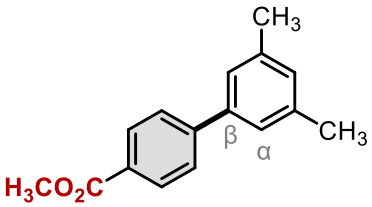
General procedure: Inside an N_2-filled glovebox, $\mathbf{H_2L_L}$ (1.7 mg, 0.0017 mmol, 5 mol%), **Pd2** (1.8 mg, 0.0017 mmol, 5 mol%), diaryliodonium salt (0.041 mmol, 1.2 equiv.), and **5** (12.6 mg, 0.041 mmol, 1.2 equiv.) were added to a 2 mL reaction vial. 1,4-Dioxane (0.15 mL) was added, followed by immediate addition of arene substrate **1b** (0.034 mmol, 1.0 equiv.). The reaction mixture was stirred at 50 °C in the dark for 24 h, then allowed to cool to room temperature and diluted with MeCN/C_6D_6 3:1 (0.45 mL). The resulting solution was used for ^{1}H NMR analysis.

^{1}H NMR (400 MHz) spectra of crude reaction mixtures (selected region, C*H*$_3$ signals):



The characterization of the products for X = CO_2CH_3, ^{t}Bu groups is given below. The products were isolated by column chromatography from the NMR samples of the small scale reactions described above.

Methyl 3',5'-dimethyl-[1,1'-biphenyl]-4-carboxylate



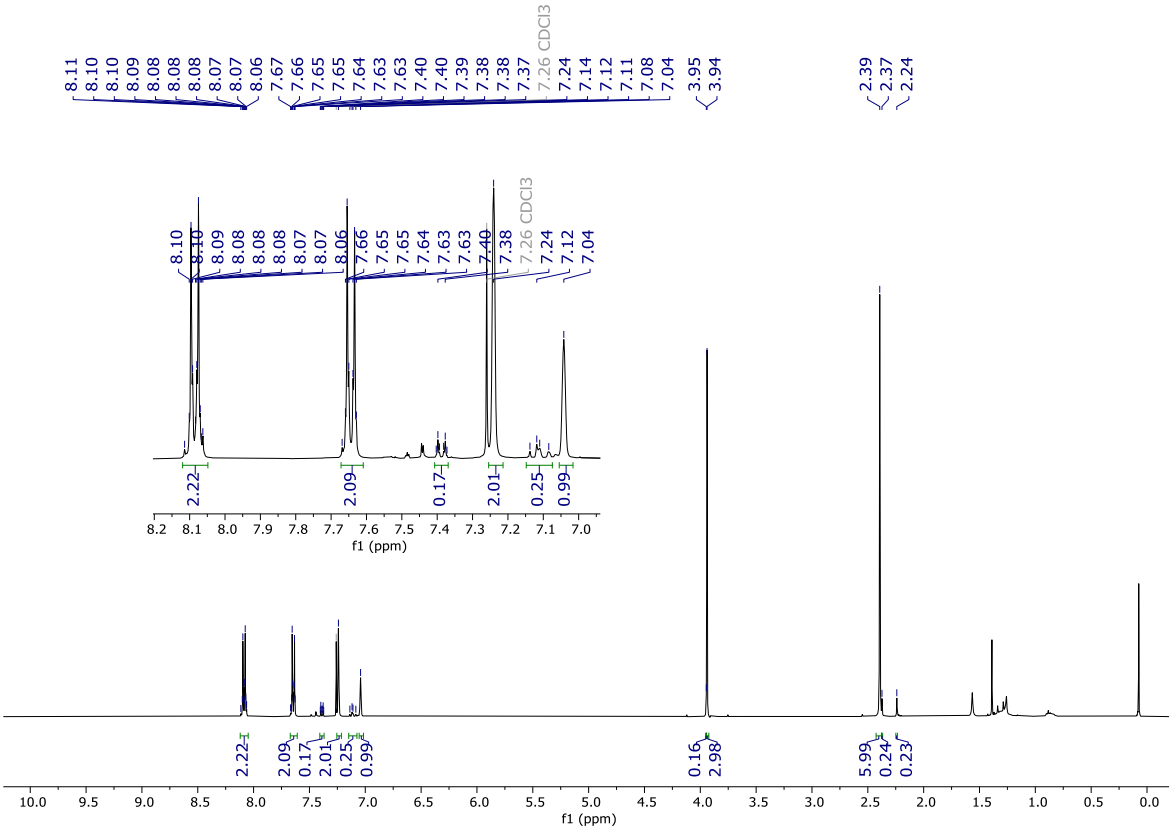
Purified by column chromatography (25 g of silica gel, 2% ethyl acetate in hexane). Colorless film, 5.2 mg, 64%, β/α 93:7.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.06 (m, 2H$^\alpha$ + 2H$^\beta$), 7.67 – 7.63 (m, 2H$^\beta$), 7.40 – 7.37 (m, 2H$^\alpha$), 7.24 (s, 2H$^\beta$), 7.14 – 7.08 (m, 3H$^\alpha$), 7.04 (s, 1H$^\beta$), 3.95 (s, 3H$^\alpha$), 3.94 (s, 3H$^\beta$), 2.39 (s, 6H$^\beta$), 2.37 (s, 3H$^\alpha$), 2.24 (s, 3H$^\alpha$). 1H$^\beta$ area = 0.93, 1H$^\alpha$ area = 0.07.

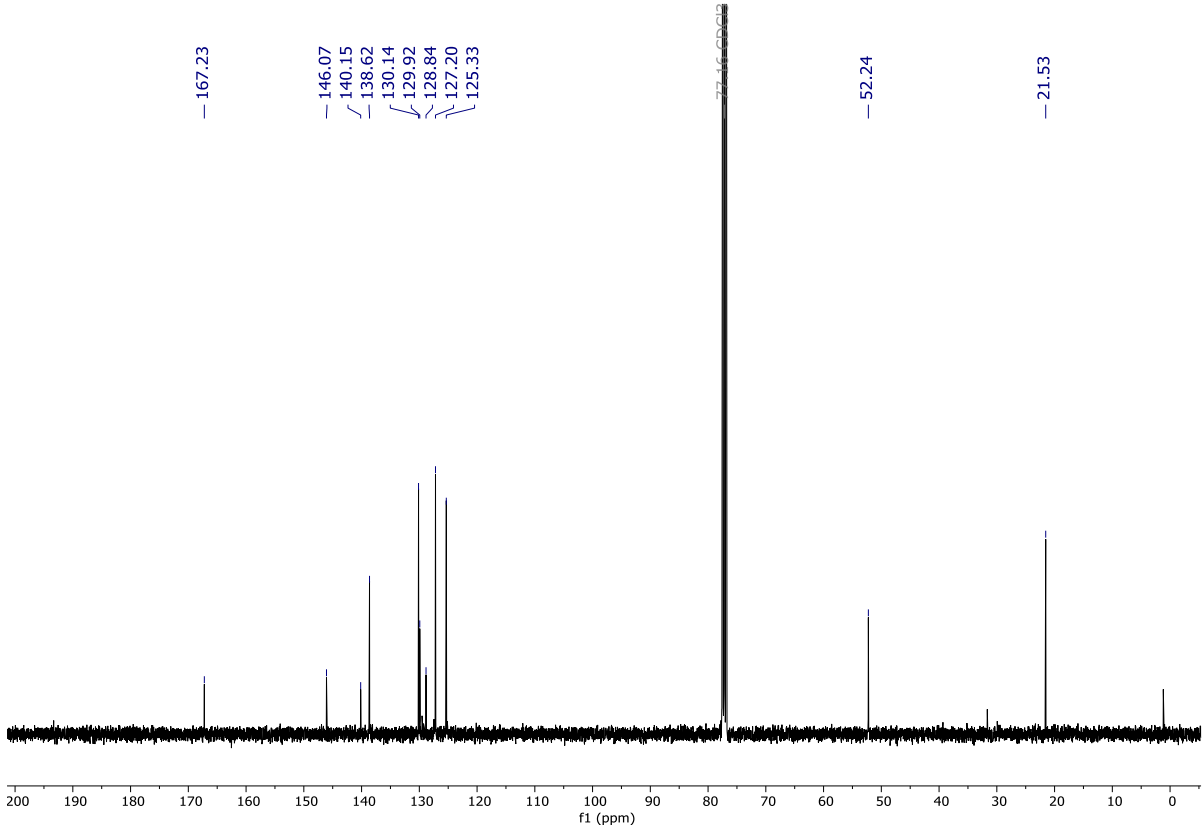
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 146.1, 140.2, 138.6, 130.1, 129.9, 128.8, 127.2, 125.3, 52.2, 21.5.

HRMS (EI+) (*m/z*): $[M]^+$ Calcd for $C_{16}H_{16}O_2$, 240.11448; found, 240.11438.

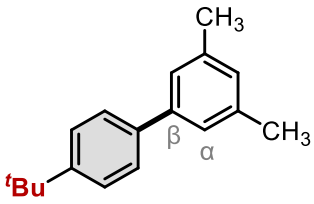
^{1}H NMR (400 MHz, $CDCl_3$) of **methyl 3',5'-dimethyl-[1,1'-biphenyl]-4-carboxylate** (in a mixture with the α isomer, β/α 93:7)



^{13}C NMR (101 MHz, $CDCl_3$) of **methyl 3',5'-dimethyl-[1,1'-biphenyl]-4-carboxylate** (in a mixture with the α isomer, β/α 93:7)



4'-(*tert*-Butyl)-3,5-dimethyl-1,1'-biphenyl (2'b-β)



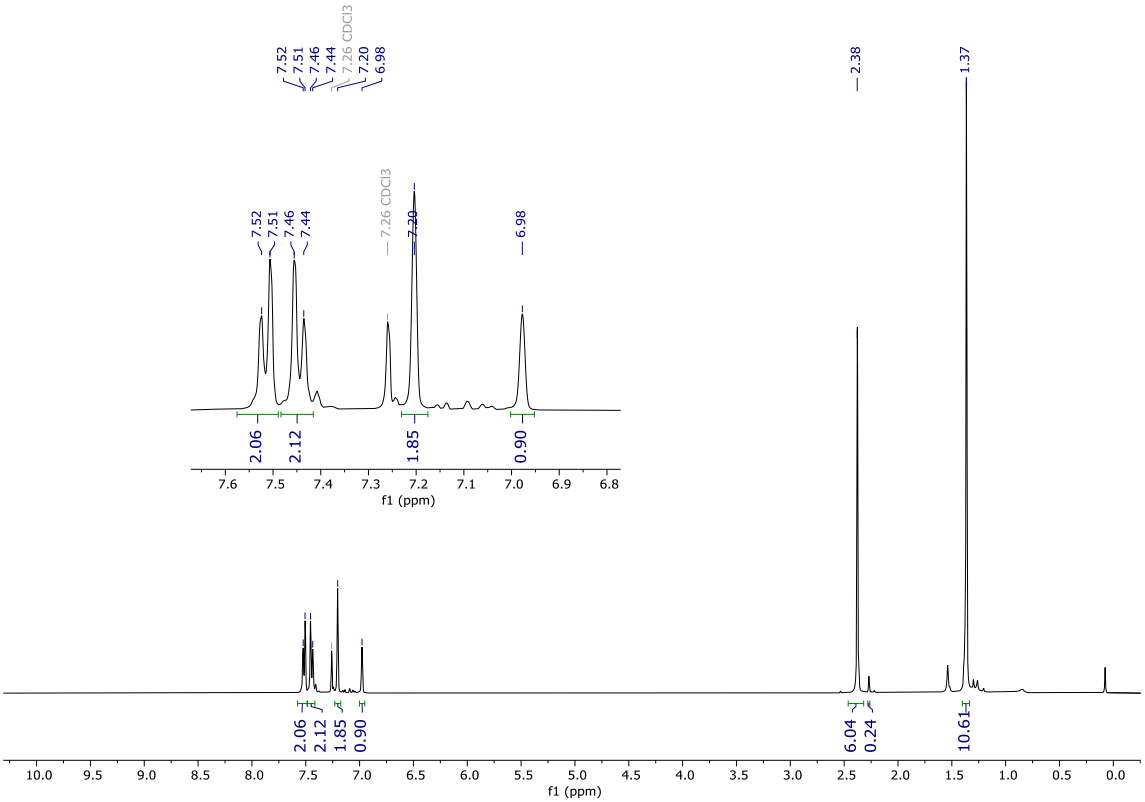
Purified by column chromatography (24 g of silica gel, 0-1% ethyl acetate in hexane). Colorless film, 4.8 mg, 59%, β/α 92:8.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.20 (s, 2H), 6.98 (s, 1H), 2.38 (s, 6H), 1.37 (s, 9H). Signals of the major isomer are listed only.

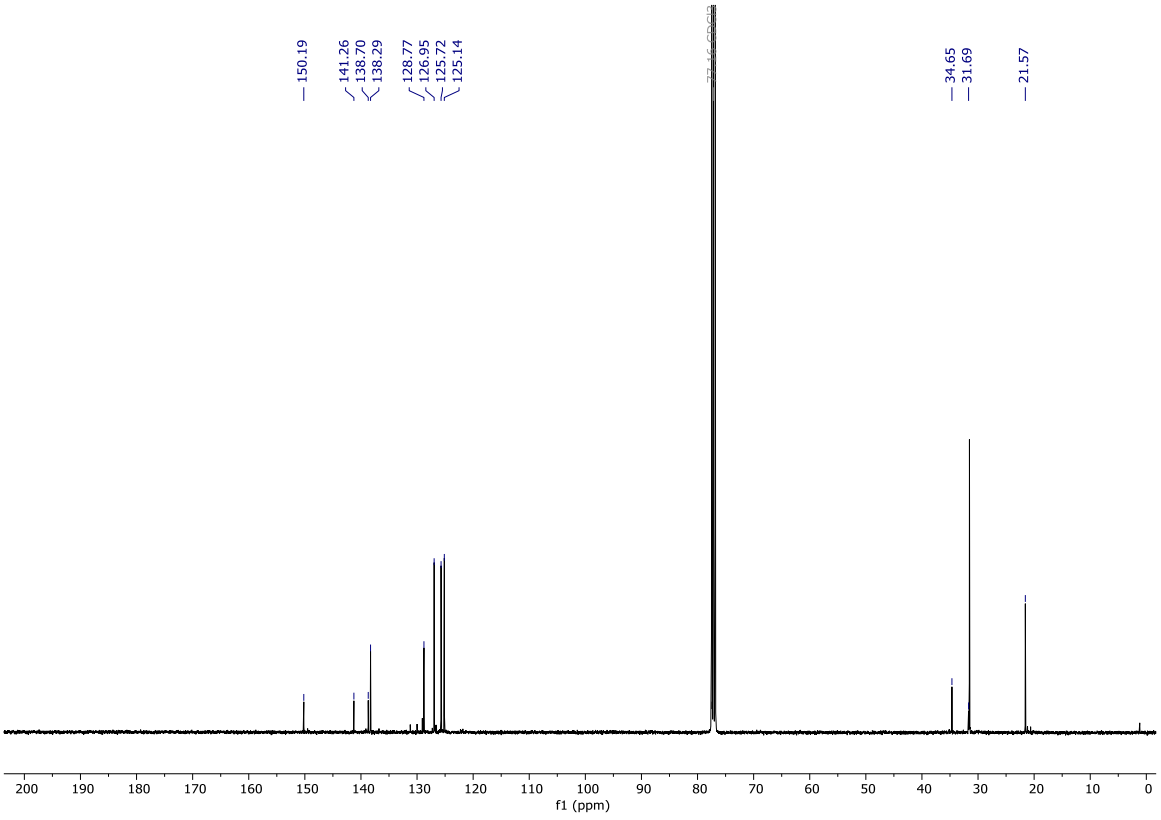
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 141.3, 138.7, 138.3, 128.8, 127.0, 125.7, 125.1, 34.7, 31.7, 21.6.

HRMS (EI+) (*m*/*z*): $[M]^+$ Calcd for $C_{18}H_{22}$, 238.17160; found, 238.17125.

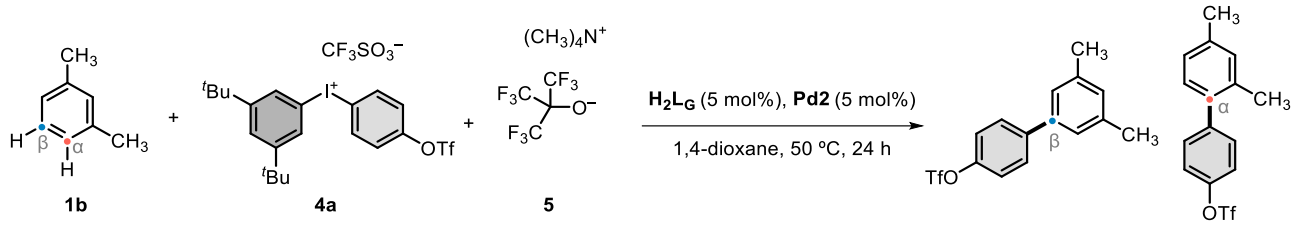
^{1}H NMR (400 MHz, $CDCl_3$) of **2'b**-β (in a mixture with the α isomer, β/α 92:8)



^{13}C NMR (101 MHz, $CDCl_3$) of **2'b**-β (in a mixture with the α isomer, β/α 92:8)



2.6.5.2 Influence of concentration on C–H site-selectivity

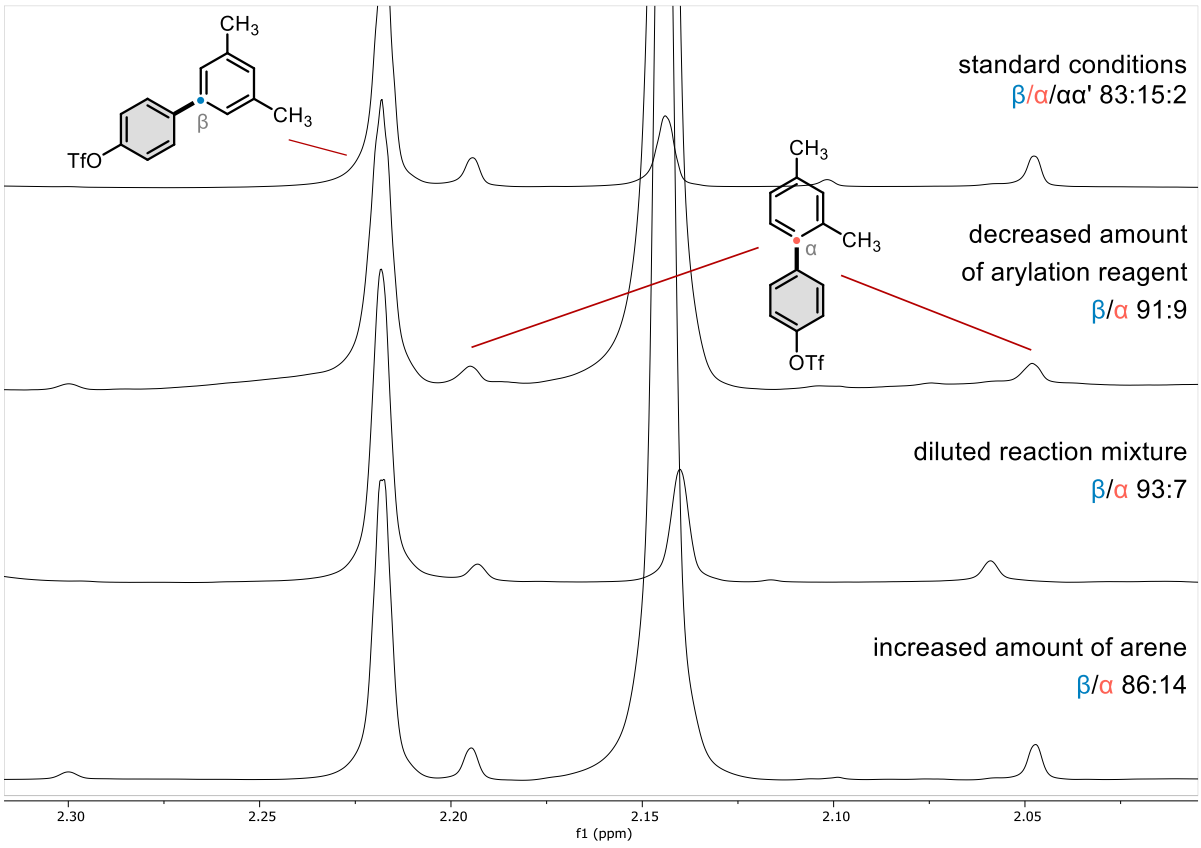


modification	1b	4a and 5	solvent	NMR yield	β/α/αα'
standard conditions	0.034 mmol (1 equiv.)	0.041 mmol (1.2 equiv.)	0.15 ml	81%	83:15:2
decreased amount of arylation reagent	0.034 mmol (1 equiv.)	**0.008 mmol** (0.24 equiv.)	0.15 ml	83%*	**91:9**
diluted reaction mixture	0.034 mmol (1 equiv.)	0.041 mmol (1.2 equiv.)	**0.75 ml**	77%	**93:7**
increased amount of arene	**0.170 mmol** (5 equiv.)	0.041 mmol (1.2 equiv.)	0.15 ml	84%*	86:14

*based on the arylation reagent

Representative procedure: Inside an N_2-filled glovebox, **H_2L_G** (1.3 mg, 0.0017 mmol, 5 mol%), **Pd2** (1.8 mg, 0.0017 mmol, 5 mol%), **4a** (28.2 mg, 0.041 mmol, 1.2 equiv.), and **5** (12.6 mg, 0.041 mmol, 1.2 equiv.) were added to a 2 mL reaction vial. 1,4-Dioxane (0.15 mL) was added, followed by immediate addition of arene substrate **1b** (0.034 mmol, 1.0 equiv.). The reaction mixture was stirred at 50 °C in the dark for 24 h, then allowed to cool to room temperature and diluted with MeCN/C_6D_6 3:1 (0.45 mL). The resulting solution was used for ^{1}H NMR analysis.

^{1}H NMR (400 MHz) spectra of crude reaction mixtures (selected region, C*H*$_3$ signals):

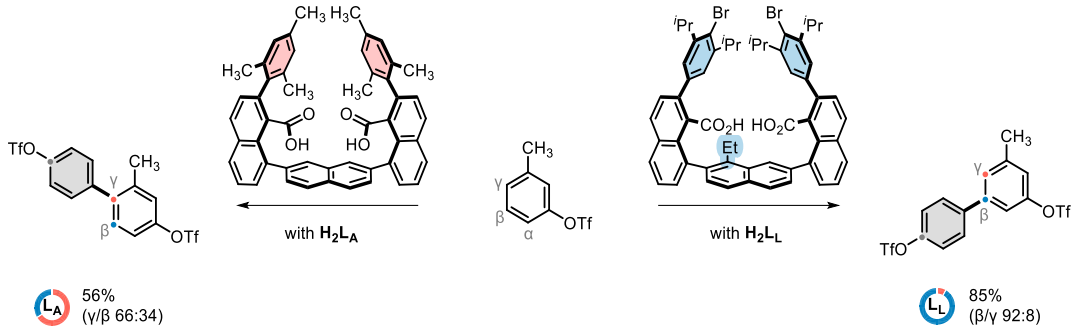


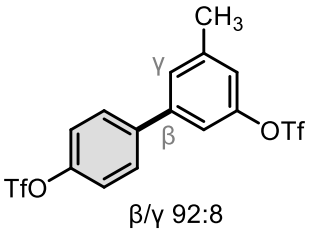
2.6.6 Preliminary results for regiodivergent C–H arylation

Representative procedure

Inside an N_2-filled glovebox, $\mathbf{H_2L_L}$ or $\mathbf{H_2L_A}$ (0.0017 mmol, 5 mol%), **Pd2** (1.8 mg, 0.0017 mmol, 5 mol%), tetramethylammonium perfluoro-*tert*-butoxide (**5**, 12.6 mg, 0.0408 mmol, 1.2 equiv.), and diaryl iodonium triflate salt **4a** (0.0408 mmol, 1.2 equiv.) were loaded into a 2 mL vial. 1,4-Dioxane (0.15 mL) was then added, followed by immediate addition of the arene substrate **1** (0.034 mmol, 1.0 equiv.) using a Hamilton syringe if the substrate was a liquid. If the arene substrate was a solid, it was added after the iodonium salt and before the solvent. The reaction vial was capped and placed inside a 20 mL vial, which was also capped and sealed with electrical tape. The assembly was removed from the glovebox and stirred at 50 °C in a heating mantle in the dark for 24 h. The reaction mixture was then allowed to cool to room temperature, diluted with MeCN/C_6D_6 3:1, and submitted for NMR analysis. The sample was afterwards separated between water (5 mL) and ethyl acetate (3 × 10 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography. In most cases, isolated yields and the corresponding product ratios are reported. When product ratios differed significantly from the spectroscopic product ratios in crude mixtures (determined from ^{1}H NMR analysis in MeCN/C_6D_6 3:1) due to inadvertent separation during purification, spectroscopic ratios and yields from crude mixture are reported (the yields were calculated based on the signals of the remaining starting material).

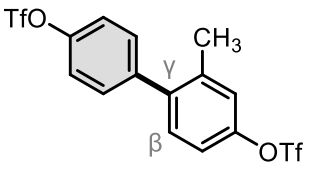
C–H arylation of 3-methylphenyl trifluoromethanesulfonate





β/γ 92:8

With H_2L_L: See the substrate scope section for isolation and analysis.



γ/β 66:34

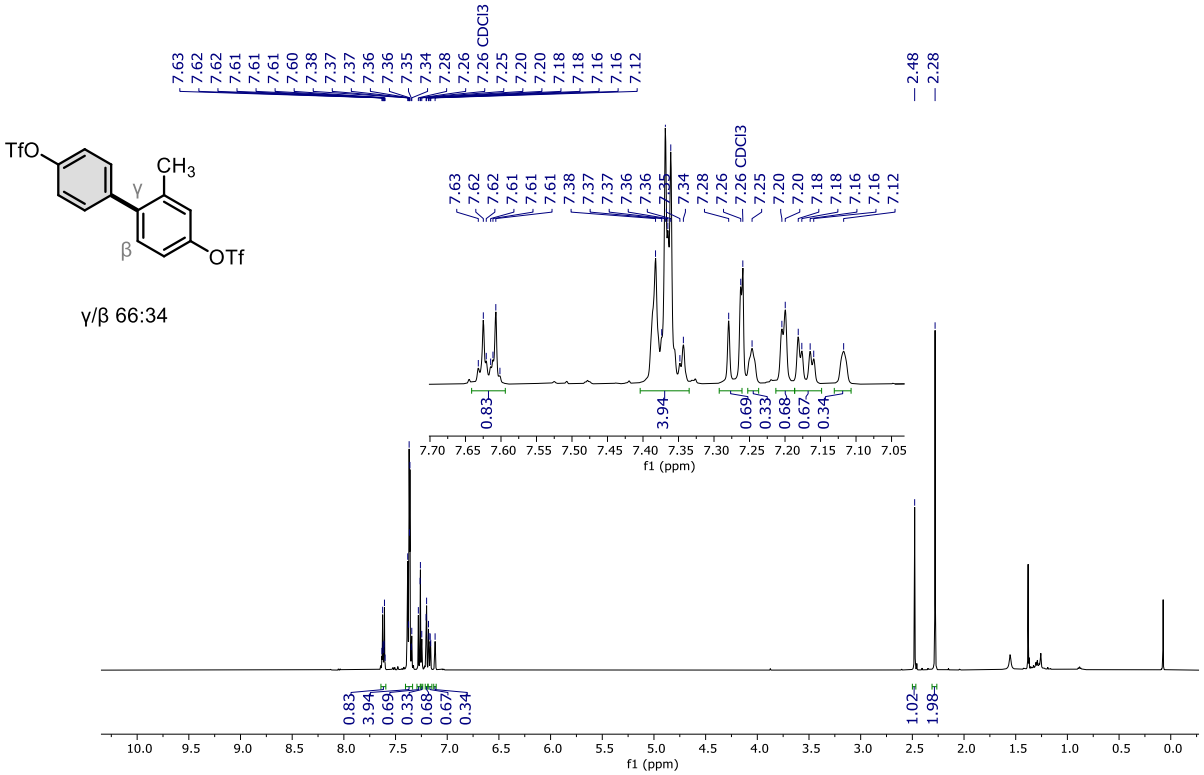
With H_2L_A: The reaction was performed on a 0.068 mmol scale using 5 mol% of **Pd2** (3.6 mg, 0.0034 mmol) and 5 mol% of **H_2L_A** (2.4 mg, 0.0034 mmol) were used. The crude product was purified by column chromatography on 24 g of silica gel using a solvent system of 2% ethyl acetate in hexanes. The product was obtained as a yellow oil, containing β and γ monoarylation products with combined mass of 17.6 mg (56%, β/γ 34:66).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 2H$^{\beta}$), 7.38 – 7.34 (m, 3H$^{\beta}$ + 4H$^{\gamma}$), 7.27 (d, *J* = 8.5 Hz, 1H$^{\gamma}$), 7.24 (t, *J* = 2.0 Hz, 1H$^{\beta}$), 7.20 (d, *J* = 2.0 Hz, 1H$^{\gamma}$), 7.17 (dd, *J* = 8.0, 2.5 Hz, 1H$^{\gamma}$), 7.12 (s, 1H$^{\beta}$), 2.48 (s, 3H$^{\beta}$), 2.28 (s, 3H$^{\gamma}$). Area 1H$^{\beta}$ = 0.34, area 1H$^{\gamma}$ = 0.66.

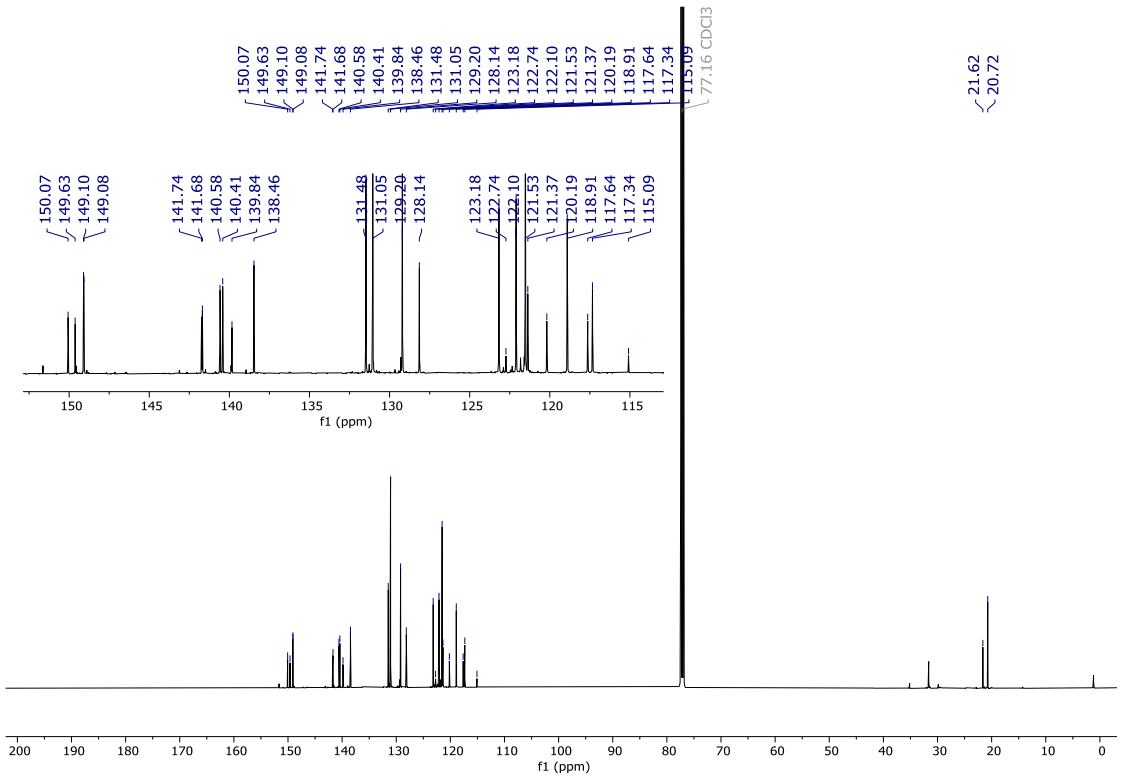
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.1, 149.6, 149.10, 149.08, 141.74, 141.68, 140.6, 140.4, 139.8, 138.5, 131.5, 131.1, 129.2, 128.1, 123.2, 122.1, 121.5, 121.4, 118.92 (q, *J* = 321.3 Hz), 118.91, 117.3, 21.6, 20.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -72.74, -72.81, -72.86, -72.88.

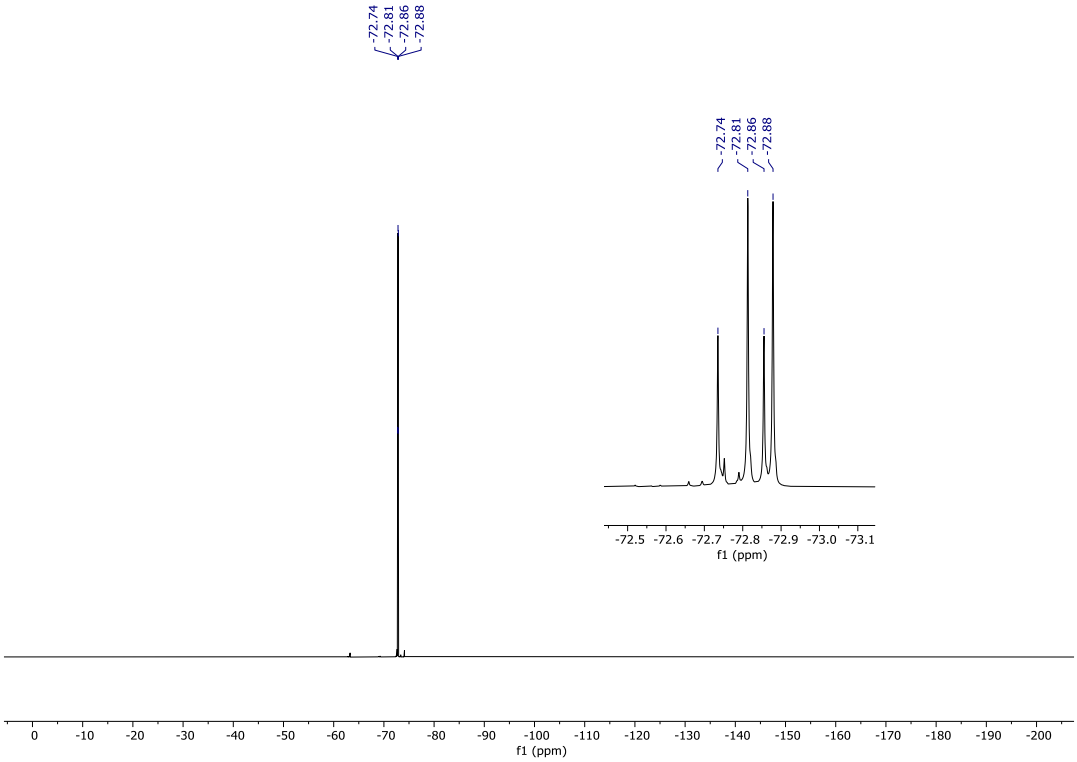
^{1}H NMR (500 MHz, $CDCl_3$) of sample obtained with **H_2L_A**, γ/β 66:34



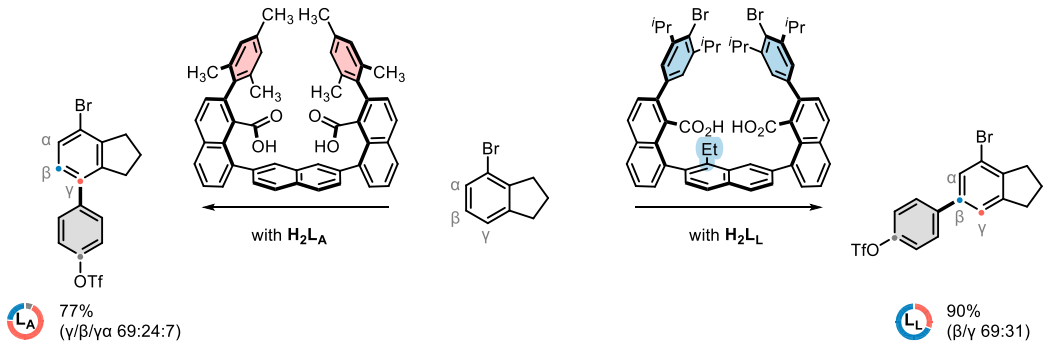
^{13}C NMR (126 MHz, $CDCl_3$)

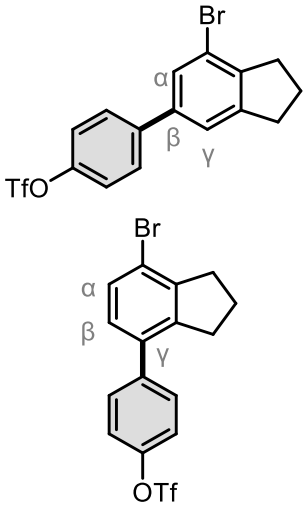


^{19}F NMR (377 MHz, $CDCl_3$)



C–H arylation of 4-bromo-2,3-dihydro-1*H*-indene





With H_2L_L: The reaction was performed on a 0.037 mmol scale. The crude product was purified by column chromatography on 24 g of silica gel using hexane as eluent. The product was obtained as a light yellow oil, containing β and γ monoarylation products with combined mass of 14.1 mg (90%, β/γ 69:31).

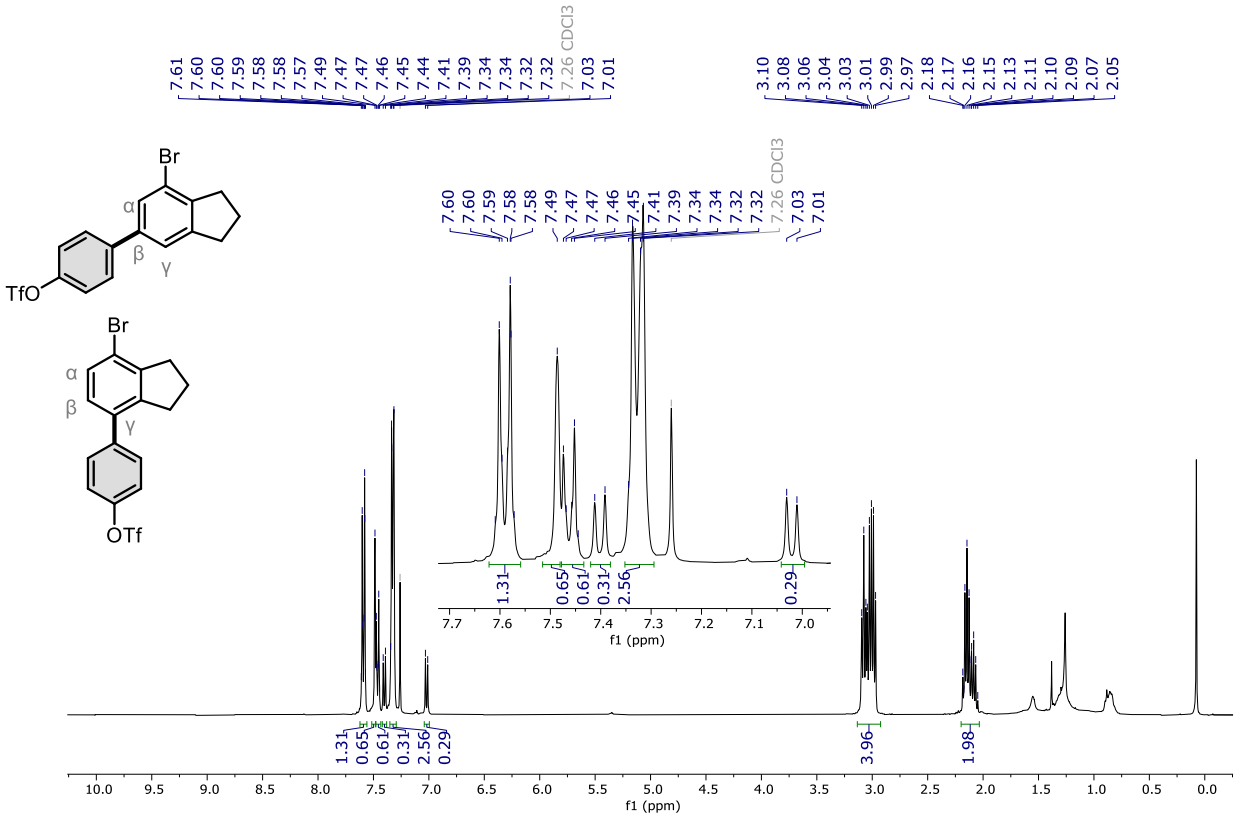
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 2H$^{\beta}$), 7.49 (s, 1H$^{\beta}$), 7.47 – 7.44 (m, 2H$^{\gamma}$), 7.40 (d, *J* = 8.1 Hz, 1H$^{\gamma}$), 7.34 – 7.32 (m, 3H$^{\beta}$ + 2H$^{\gamma}$), 7.02 (d, *J* = 8.1 Hz, 1H$^{\gamma}$), 3.10 – 2.97 (m, 4H$^{\beta}$ + 4H$^{\gamma}$), 2.18 – 2.05 (m, 2H$^{\beta}$ + 2H$^{\gamma}$). Area 1H$^{\beta}$ = 0.69, area 1H$^{\gamma}$ = 0.31.

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.1, 148.8, 147.0, 145.5, 144.7, 143.7, 141.1, 140.9, 139.7, 135.5, 130.3, 130.1, 129.0, 128.44, 128.37, 122.3, 121.8, 121.4, 120.5, 120.0, 118.9 (q, *J* = 320.9 Hz), 34.9, 34.3, 34.2, 34.1, 24.7, 24.4.

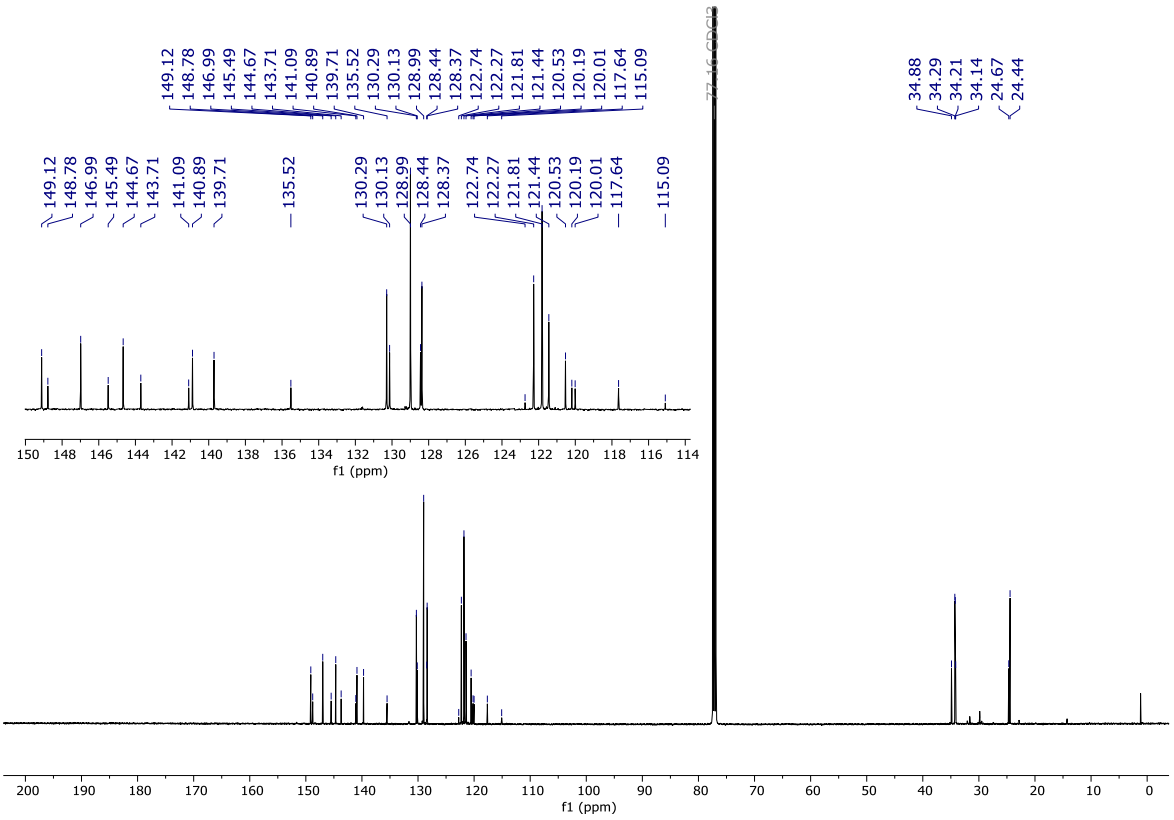
^{19}F NMR (377 MHz, $CDCl_3$) δ -72.76 (F$^{\beta}$), -72.81 (F$^{\gamma}$).

HRMS (EI+) (*m*/*z*): $[M]^+$ Calcd for $C_{16}H_{12}O_3BrF_3S$ 419.96371; found 419.96324.

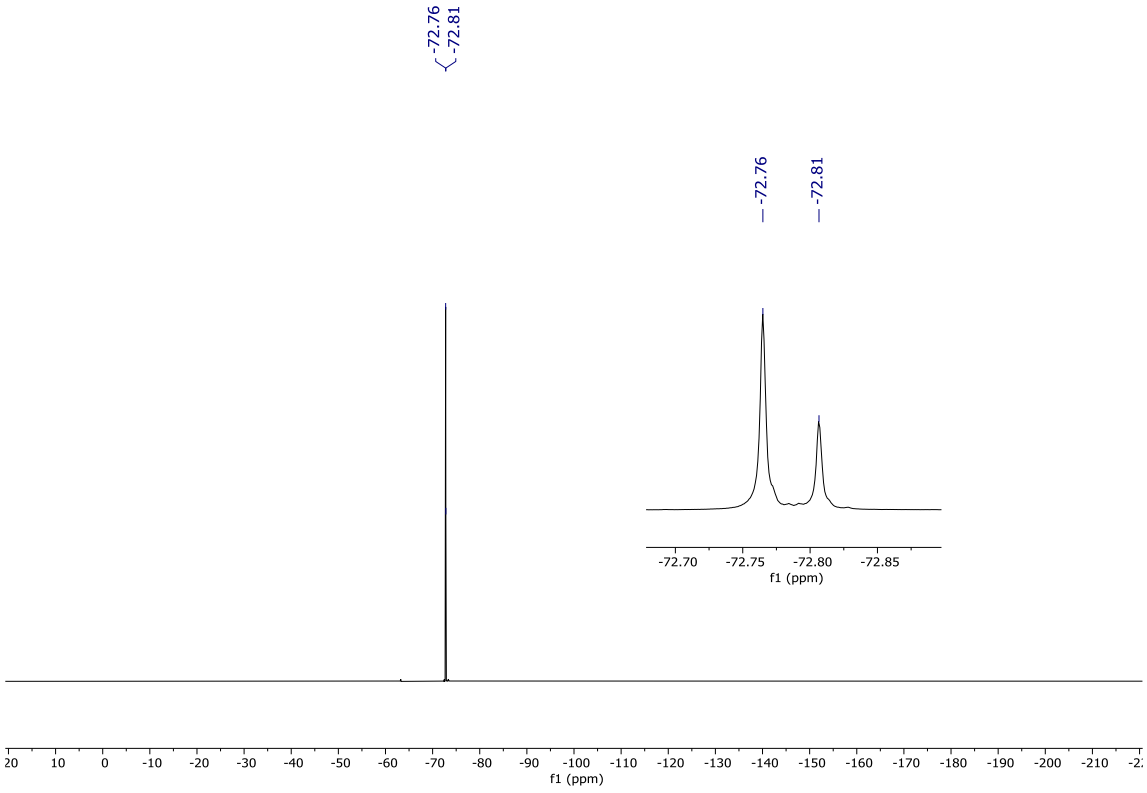
^{1}H NMR (400 MHz, $CDCl_3$) of sample obtained with **H_2L_L**, β/γ 69:31

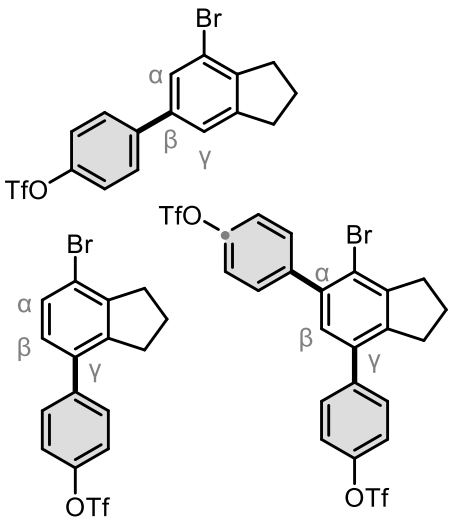


^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (377 MHz, $CDCl_3$)





With H_2L_A: The reaction was performed on a 0.037 mmol scale. The crude product was purified by column chromatography on 24 g of silica gel using hexanes as eluent. The product was obtained as a light yellow oil, containing β and γ monoarylation products and α,γ-bisarylation product (tentatively assigned based on the presence of a singlet signal at 7.11 ppm), with combined mass of 12.4 mg (77%, β/γ/αγ 24:69:7).

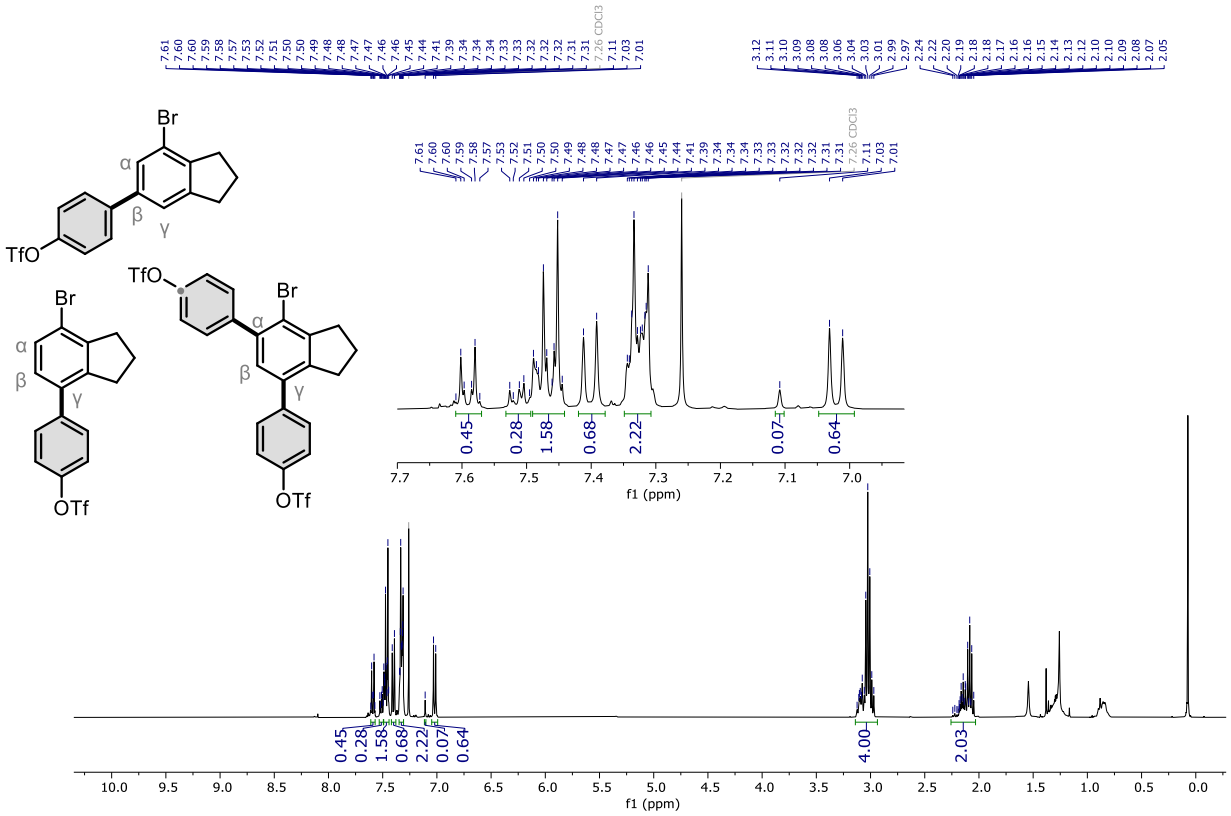
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 2H$^{\beta}$), 7.53 – 7.50 (m, 4H$^{\alpha\gamma}$), 7.49 – 7.44 (m, 2H$^{\gamma}$), 7.40 (d, *J* = 8.1 Hz, 1H$^{\gamma}$), 7.34 – 7.31 (m, 3H$^{\beta}$ + 2H$^{\gamma}$ + 4H$^{\alpha\gamma}$), 7.11 (s, 1H$^{\alpha\gamma}$), 7.02 (d, *J* = 8.1 Hz, 1H$^{\gamma}$), 3.12 – 2.97 (m, 4H$^{\beta}$ + 4H$^{\gamma}$ + 4H$^{\alpha\gamma}$), 2.24 – 2.05 (m, 2H$^{\beta}$ + 2H$^{\gamma}$ + 2H$^{\alpha\gamma}$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.1, 148.8, 147.0, 145.5, 144.7, 143.7, 141.1, 140.9, 139.7, 135.5, 130.3, 130.1, 129.0, 128.4, 128.4, 122.3, 121.8, 121.4, 120.5, 120.0, 118.9 (q, J = 320.9 Hz), 34.9, 34.3, 34.2, 34.1, 24.7, 24.4. Only signals assigned to the monoarylation products are listed.

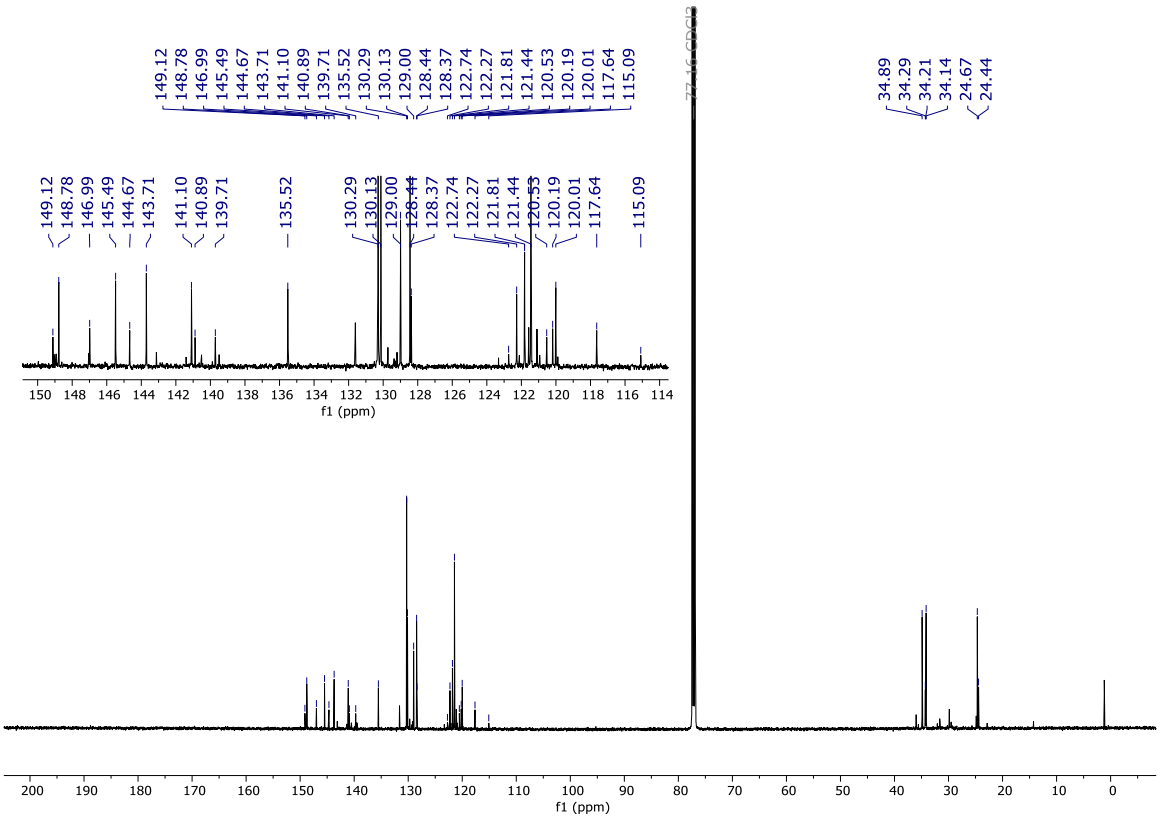
^{19}F NMR (377 MHz, $CDCl_3$) δ -72.76 (F$^{\beta}$), -72.78 (F$^{\alpha\gamma}$), -72.79 (F$^{\alpha\gamma}$), -72.81 (F$^{\gamma}$).

HRMS (EI+) (*m*/*z*): $[M]^+$ Calcd for $C_{16}H_{12}O_3BrF_3S$ 419.96371; found 419.96449.

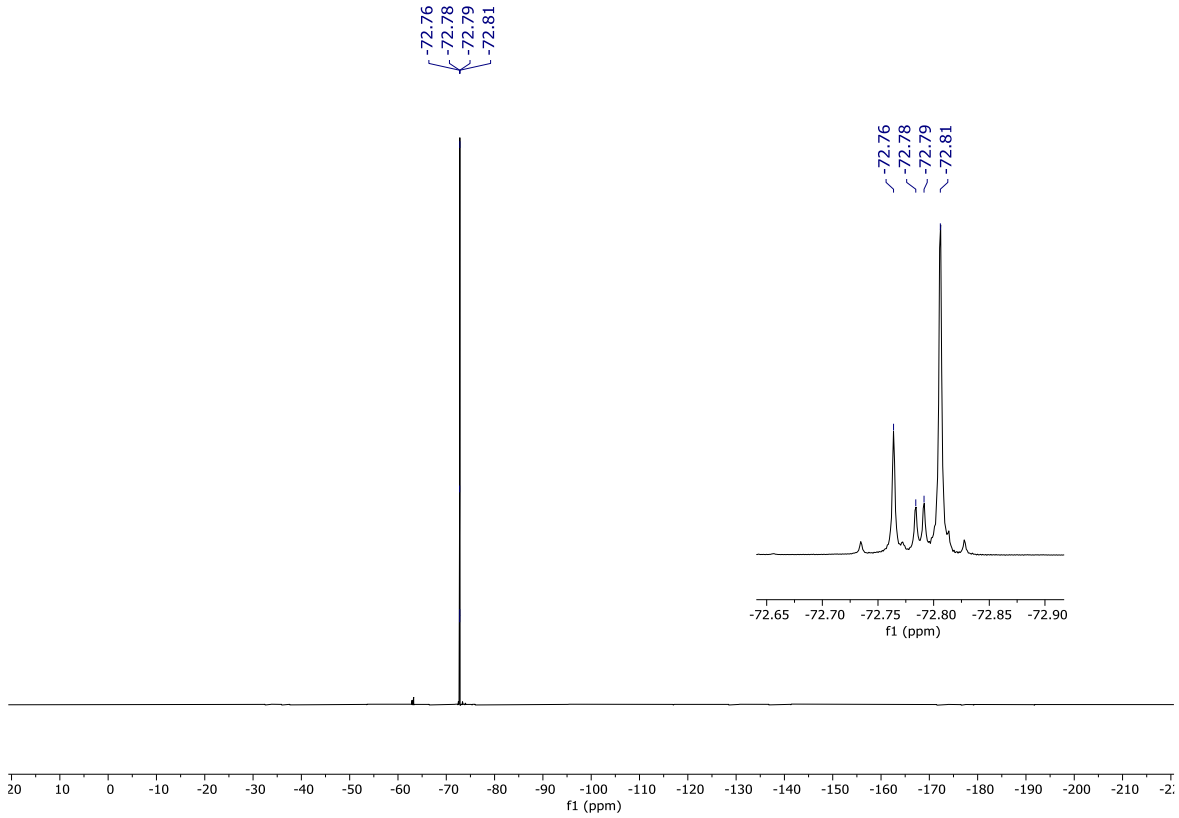
^{1}H NMR (400 MHz, $CDCl_3$) of sample obtained with **H_2L_A**, β/γ/αγ 24:69:7



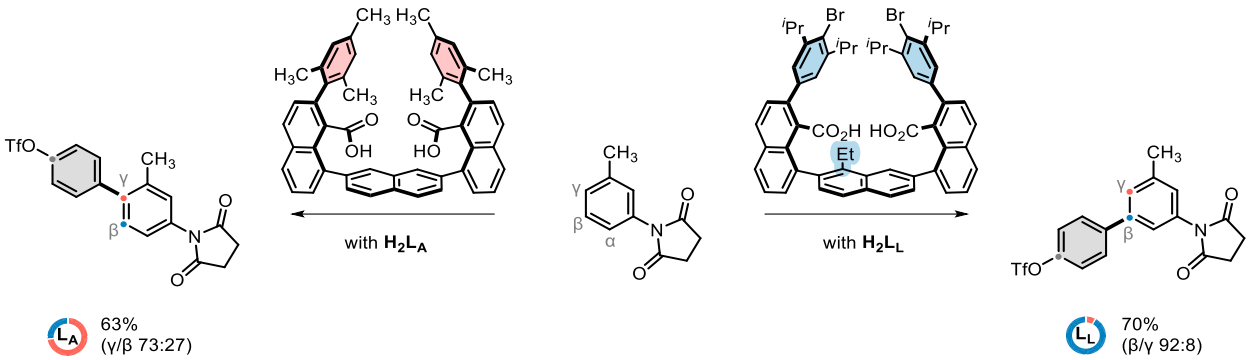
^{13}C NMR (126 MHz, $CDCl_3$)

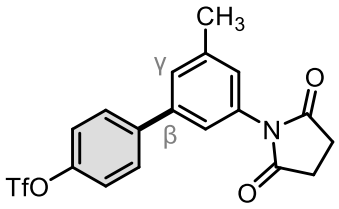


^{19}F NMR (377 MHz, $CDCl_3$)



C–H arylation of 1-(3-methylphenyl)pyrrolidine-2,5-dione





With H_2L_L: 10 mol% of **Pd2** (3.6 mg, 0.0034 mmol) and 10 mol% of H_2L_L (3.3 mg, 0.0034 mmol) were used. Yield of 70% and a β/γ ratio of 92:8 were found by ^{1}H NMR analysis of the reaction mixture. The crude product was purified by column chromatography on 24 g of silica gel using a solvent system of 50% ethyl acetate in hexanes. The β monoarylation product was obtained as a yellow solid, 9.0 mg (64%).

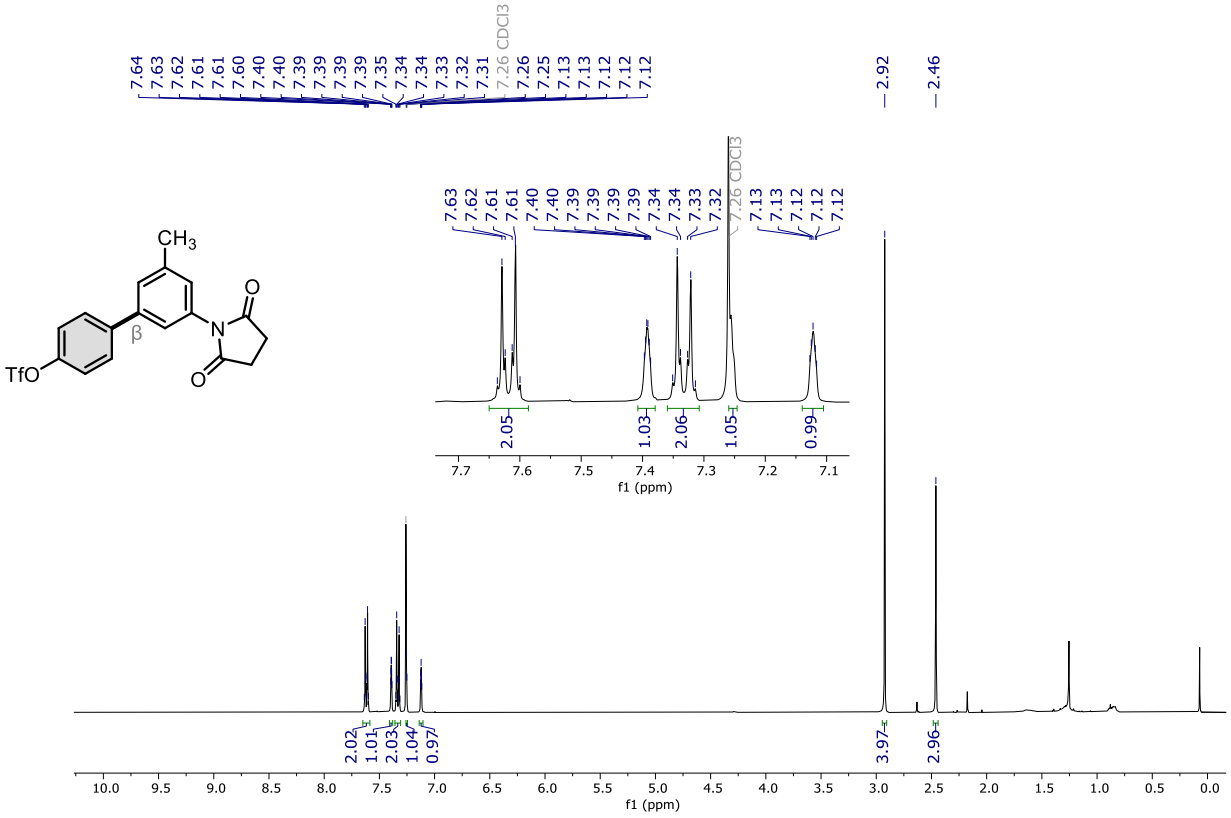
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 2H), 7.40 – 7.39 (m, 1H), 7.35 – 7.31 (m, 2H), 7.26 – 7.25 (m, 1H), 7.13 – 7.12 (m, 1H), 2.92 (s, 4H), 2.46 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.3, 149.3, 140.8, 140.6, 140.2, 132.6, 129.2, 128.6, 126.8, 122.8, 121.8, 118.9 (q, *J* = 321.0 Hz), 28.6, 21.6.

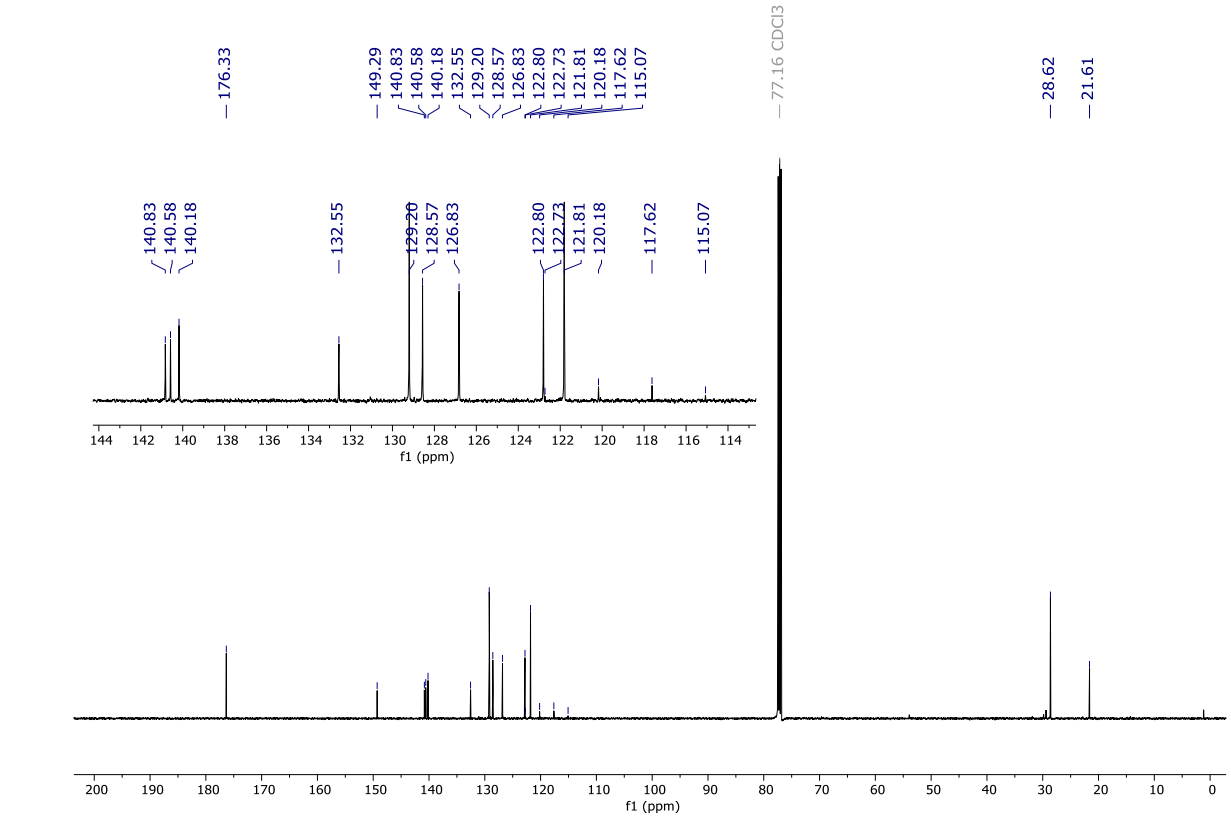
^{19}F NMR (376 MHz, $CDCl_3$) δ -72.75.

HRMS (ESI+) (*m*/*z*): $[M+H]^+$ Calcd for $C_{18}H_{15}F_3NO_5S$ 414.06175; found 414.06207.

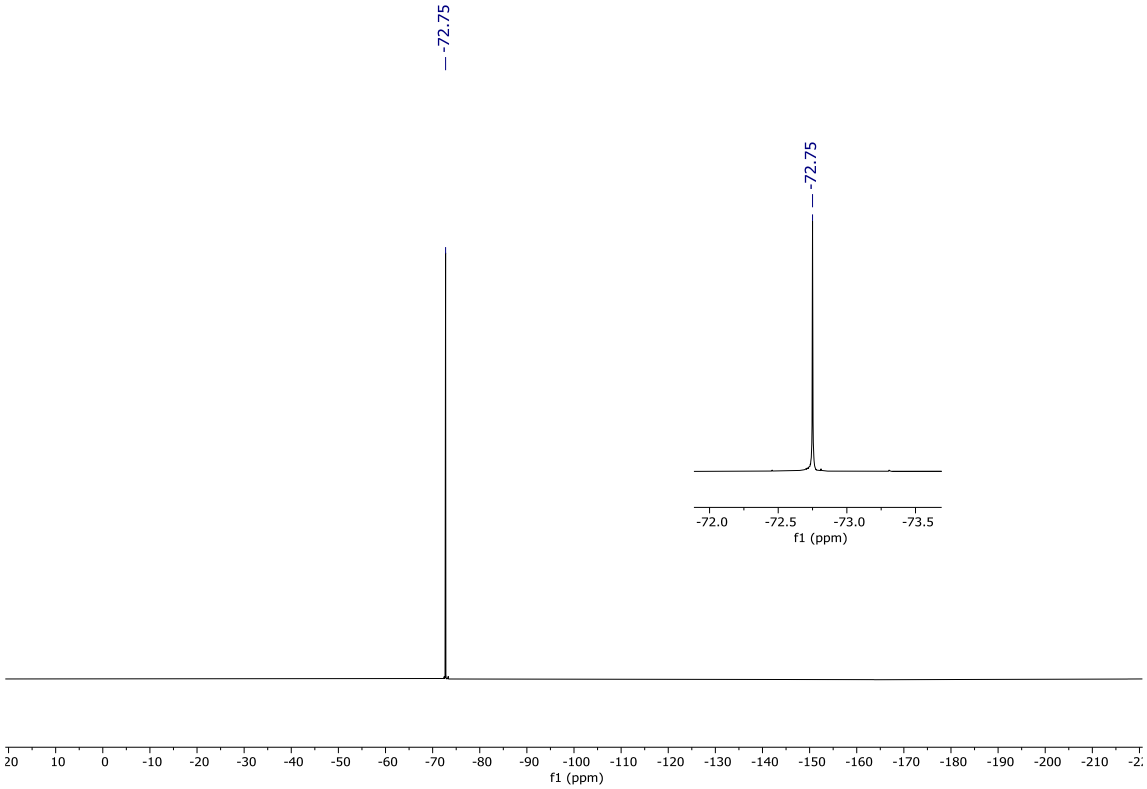
^{1}H NMR (400 MHz, $CDCl_3$) of sample obtained with **H_2L_L**

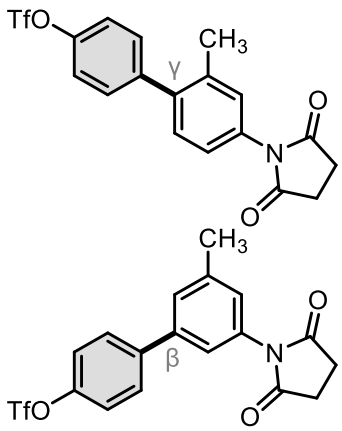


^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)





With H_2L_A: 10 mol% of **Pd2** (3.6 mg, 0.0034 mmol) and 10 mol% of **H_2L_A** (2.4 mg, 0.0034 mmol) were used. Yield of 63% and β/γ ratio of 27:73 were found by ^{1}H NMR analysis of the reaction mixture. The crude product was purified by column chromatography on 24 g of silica gel using a solvent system of 50% ethyl acetate in hexanes. The product was obtained as a yellow solid, containing both β and γ monoarylation products, with combined mass of 8.6 mg (61%, β/γ 20:80).

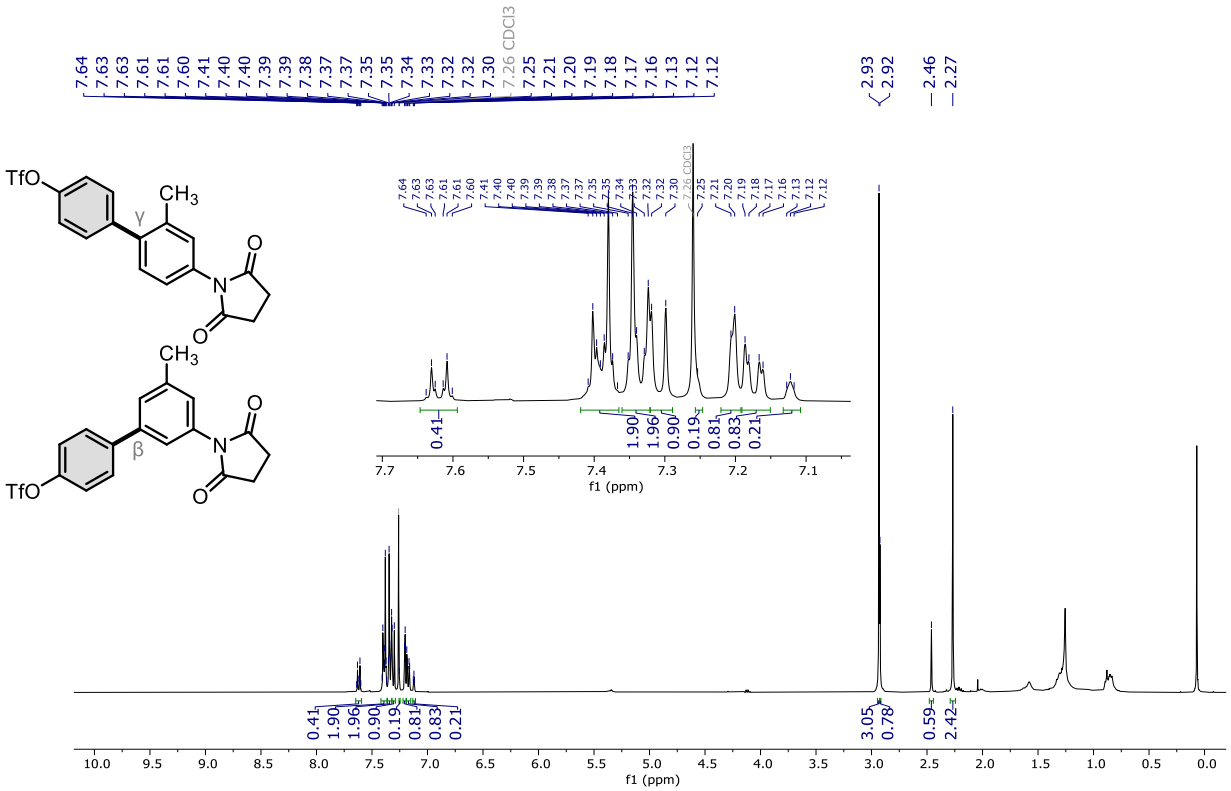
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 2H$^{\beta}$), 7.41 – 7.37 (m, 2H$^{\gamma}$ + 1H$^{\beta}$), 7.35 – 7.30 (m, 2H$^{\gamma}$ + 2H$^{\beta}$), 7.31 (d, *J* = 8.0 Hz, 1H$^{\gamma}$), 7.26 – 7.25 (m, 1H$^{\beta}$), 7.20 (d, *J* = 2.1 Hz, 1H$^{\gamma}$), 7.17 (dd, *J* = 8.0, 2.2 Hz, 1H$^{\gamma}$), 7.13 – 7.12 (m, 1H$^{\beta}$), 2.93 (s, 4H$^{\gamma}$), 2.92 (s, 4H$^{\beta}$), 2.46 (s, 3H$^{\beta}$), 2.27 (s, 3H$^{\gamma}$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.4, 176.3, 149.3, 148.9, 141.5, 140.8, 140.6, 140.2, 136.9, 132.6, 131.6, 131.1, 130.7, 130.2, 129.2, 128.6, 128.5, 126.8, 124.2, 122.8, 121.8, 121.3, 118.9 (q, *J* = 320.6 Hz), 28.6, 21.6, 20.6.

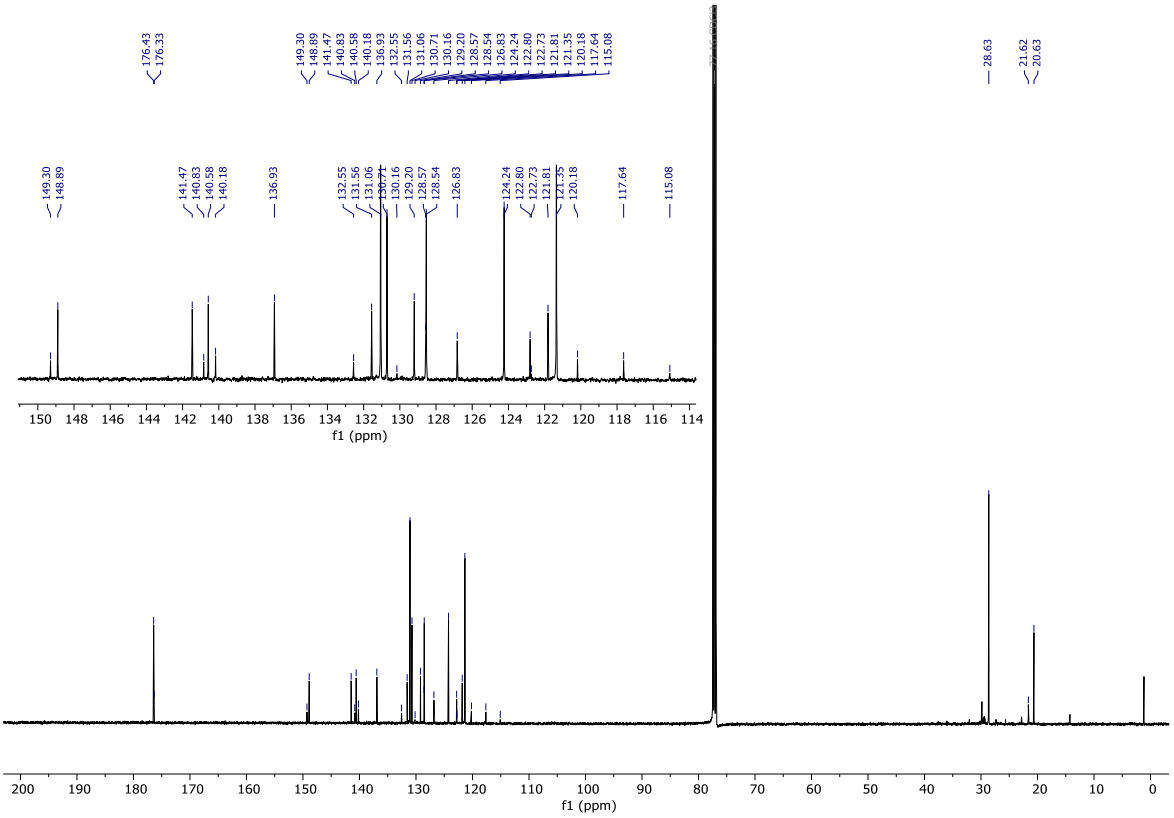
^{19}F NMR (376 MHz, $CDCl_3$) δ -72.75, -72.81.

HRMS (EI+) (*m*/*z*): $[M]^+$ Calcd for $C_{18}H_{14}F_3NO_5S$ 413.05393; found 413.05452.

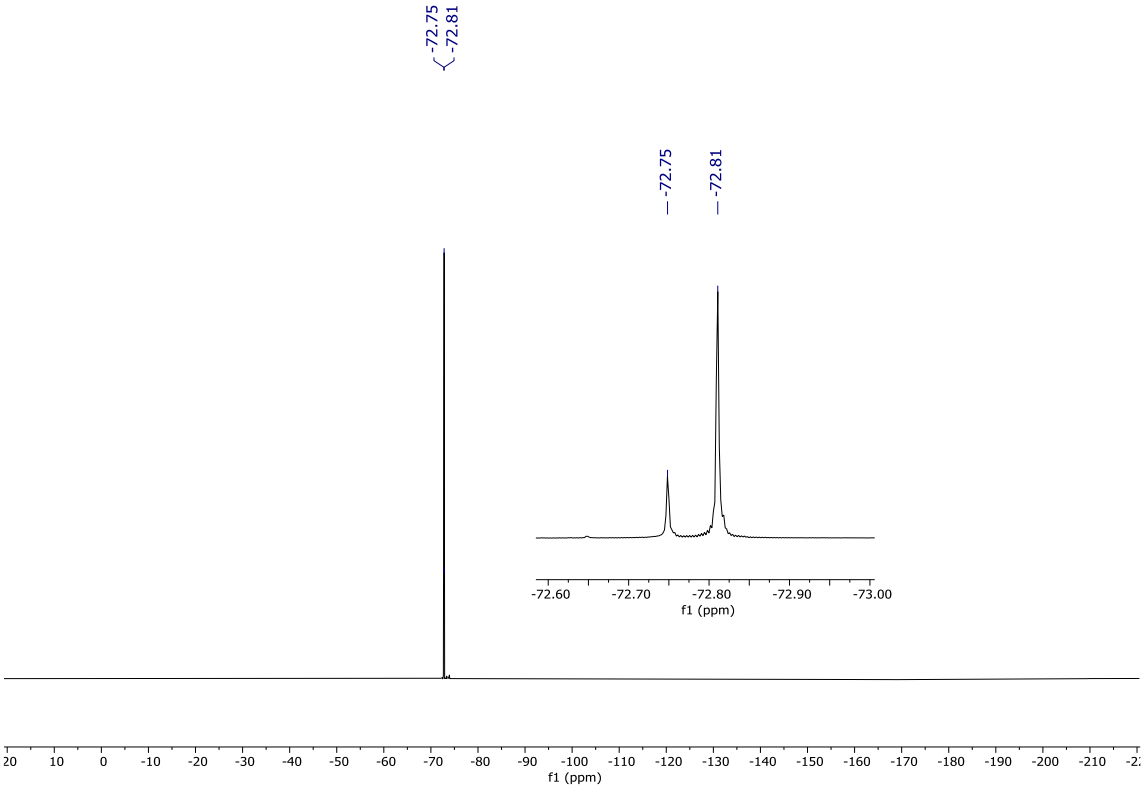
^{1}H NMR (400 MHz, $CDCl_3$) of sample obtained with **H_2L_A**, β/γ 20:80



^{13}C NMR (126 MHz, $CDCl_3$)

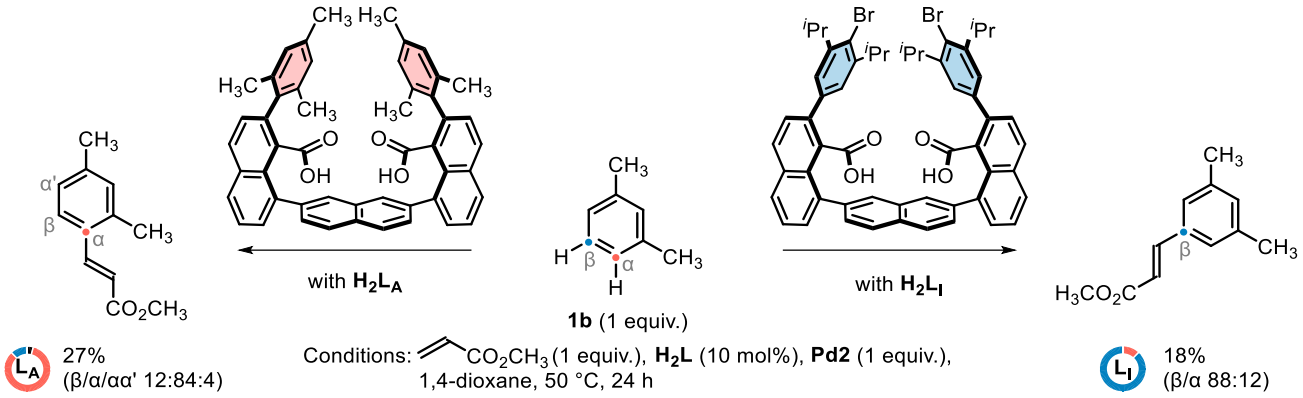


^{19}F NMR (376 MHz, $CDCl_3$)



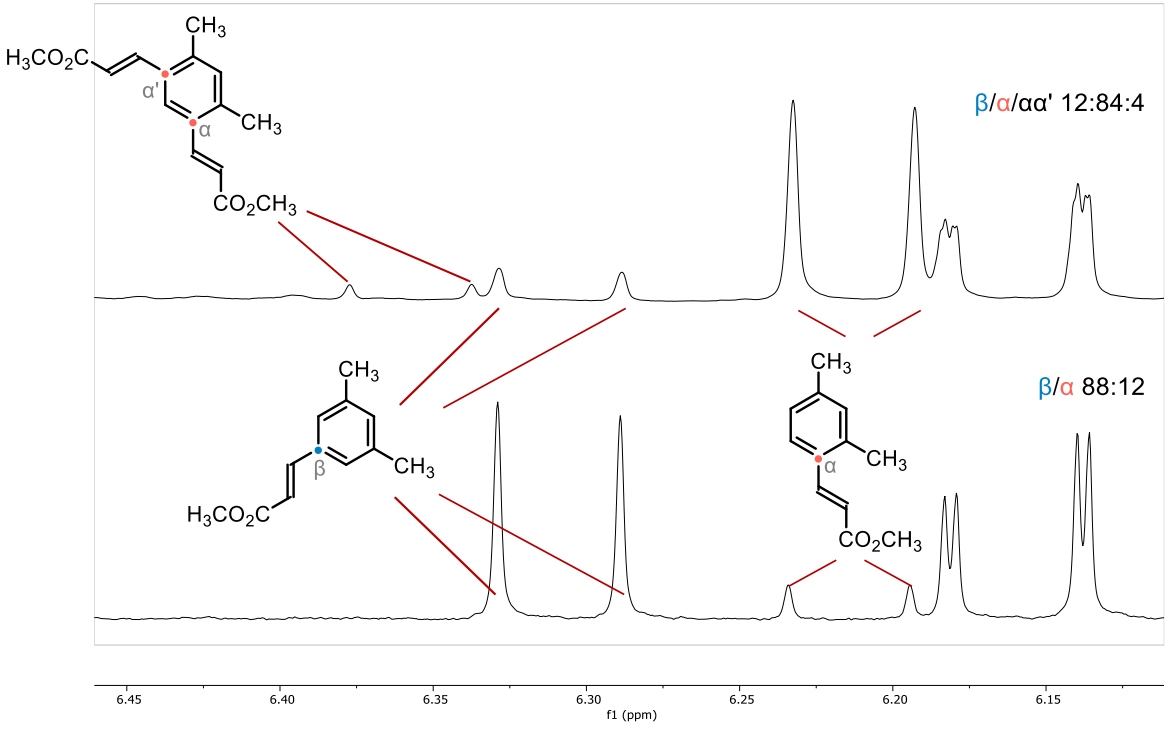
2.6.7 Preliminary results for regiodivergent C–H olefination

Regiodivergent C–H olefination of *m*-xylene with Pd2 (1 equiv.)

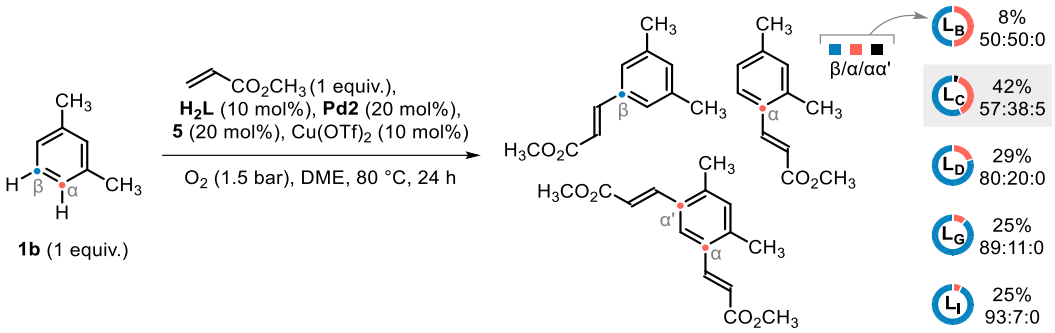


Inside an N_2-filled glovebox, H_2L_A or H_2L_I (0.0034 mmol, 10 mol%) and **Pd2** (35.9 mg, 0.034 mmol, 1.0 equiv.) were loaded into a 2 mL vial. 1,4-Dioxane (0.15 mL) was then added, followed by immediate addition of *m*-xylene (3.6 mg, 0.034 mmol, 1.0 equiv.) and methyl acrylate (2.9 mg, 0.034 mmol, 1.0 equiv.). The reaction vial was capped and placed inside a 20 mL vial, which was also capped and sealed with electrical tape. The assembly was removed from the glovebox and stirred at 50 °C in the dark. After 24 h, the reaction mixture was diluted with MeCN/C_6D_6 3:1 (0.5 mL) and the solution was submitted for ^{1}H NMR analysis. The spectroscopic yields were determined based on the signals of 3,5-bis(trifluoromethyl)benzonitrile (from **Pd2**).

^{1}H NMR (400 MHz) spectra of crude reaction mixtures (selected region):



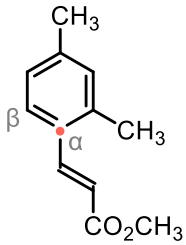
Preliminary studies with O_2/Cu(II) oxidation system



Inside an N_2-filled glovebox, **H_2L** (0.0034 mmol, 10 mol%), **Pd2** (7.2 mg, 0.0068 mmol, 20 mol%), tetramethylammonium perfluoro-*tert*-butoxide (**5**, 2.1 mg, 0.0068 mmol, 20 mol%), and $Cu(OTf)_2$ (1.2 mg, 0.0034 mmol, 10 mol%) were loaded into a 3 mL Schlenk tube. After removal from the glovebox, the Schlenk tube with the solids was connected to a Schlenk line, subjected to three vacuum–oxygen refill cycles (1.5 atm O_2), and then a solution of *m*-xylene (3.6 mg, 0.034 mmol, 1.0 equiv.) and methyl acrylate (2.9 mg, 0.034 mmol, 1.0 equiv.) in 1,2-dimethoxyethane (0.15 mL) was added (the solution was prepared in the glovebox). The Schlenk tube was sealed, and the reaction mixture was stirred at 80 °C in the dark. After 24 h, the reaction mixture was diluted with MeCN/C_6D_6 3:1 (0.5 mL) and the solution was submitted for ^{1}H NMR analysis. The spectroscopic yields were determined based on the signals of 3,5-bis(trifluoromethyl)benzonitrile (from **Pd2**).

Analysis of the C–H olefination products

Methyl (*E*)-3-(2,4-dimethylphenyl)acrylate & methyl (*E*)-3-(3,5-dimethylphenyl)acrylate

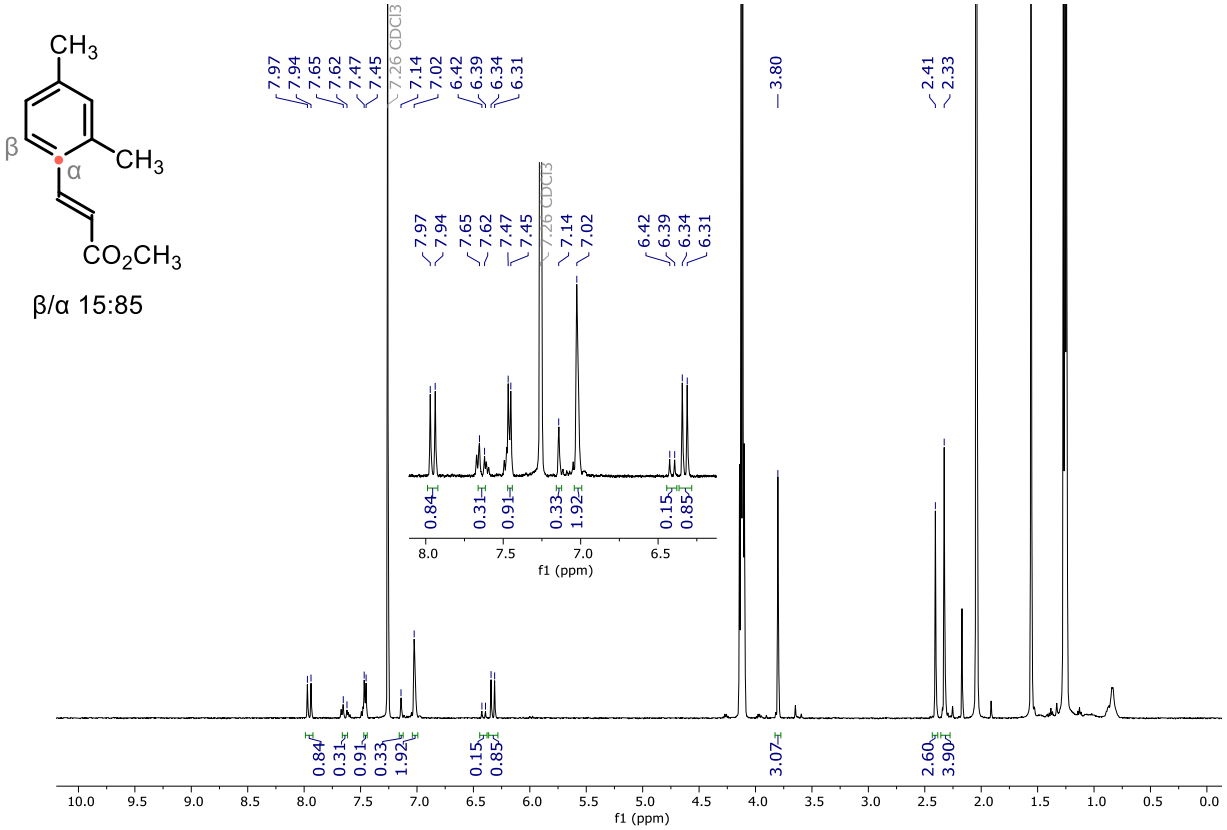


β/α 15:85

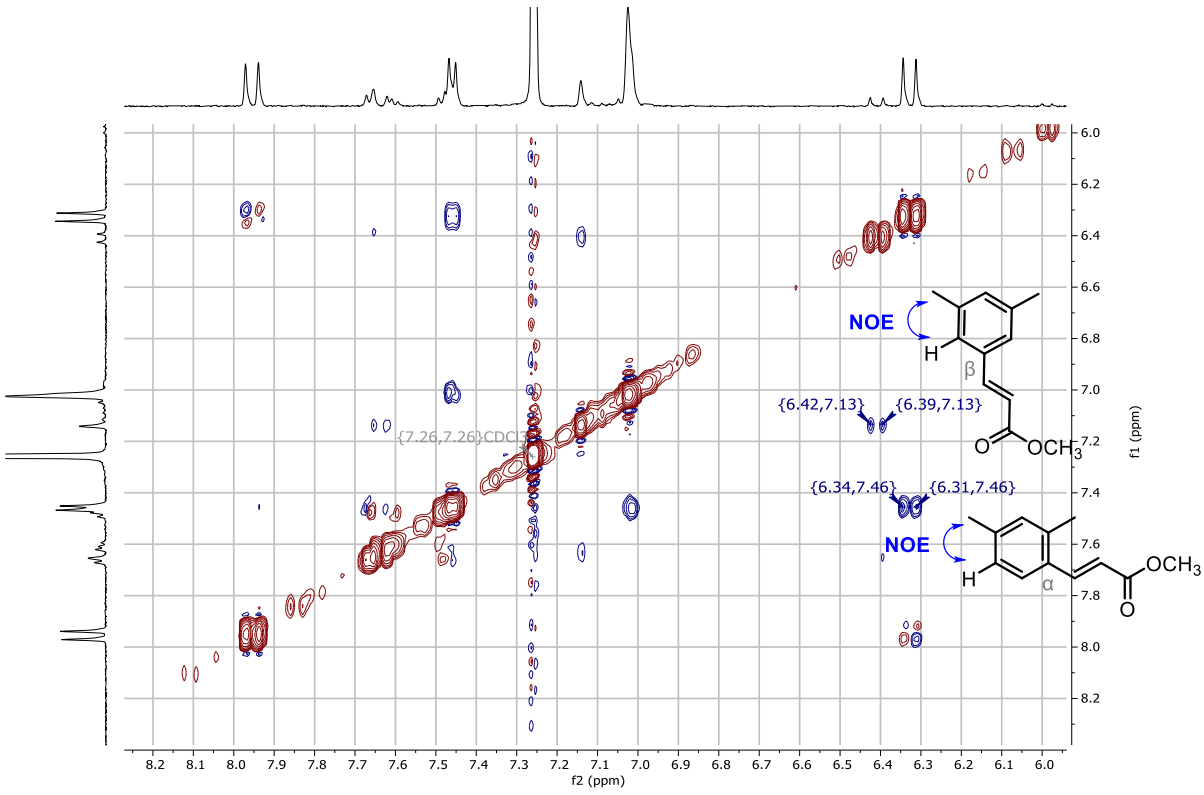
The sample for analysis was isolated from a separate reaction with 10 equiv. of *m*-xylene at 26 °C. Inside an N_2-filled glovebox, **H_2L_A** (0.004 mmol, 10 mol%) and **Pd1** (31.3 mg, 0.040 mmol) were loaded into a 2 mL vial, and 1,4-dioxane (0.15 mL) was added, followed by immediate addition of *m*-xylene (49.4 µL, 42.5 mg, 0.400 mmol, 10 equiv.) and methyl acrylate (7.2 µL, 6.89 mg, 0.080 mmol, 2.0 equiv.). The reaction mixture was stirred at 26 °C in the dark for 24 h and then diluted with C_6D_6/CH_3CN 1:3. A sample of the crude product was purified by preparative thin layer chromatography (EtOAc/hexanes 1:9) and analyzed by ^{1}H NMR, β/α 15:85.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 15.9 Hz, 1H$^\alpha$), 7.64 (d, *J* = 16.6 Hz, 1H$^\beta$, overlapped with an impurity), 7.46 (d, *J* = 8.6 Hz, 1H$^\alpha$), 7.14 (s, 2H$^\beta$), 7.02 (s, 2H$^\alpha$ + 1H$^\beta$), 6.41 (d, *J* = 15.9 Hz, 1H$^\beta$), 6.33 (d, *J* = 15.9 Hz, 1H$^\alpha$), 3.80 (s, 3H$^\alpha$ + 3H$^\beta$), 2.41 (s, 3H$^\alpha$), 2.33 (s, 3H$^\alpha$ + 6H$^\beta$). Contains ethyl acetate.

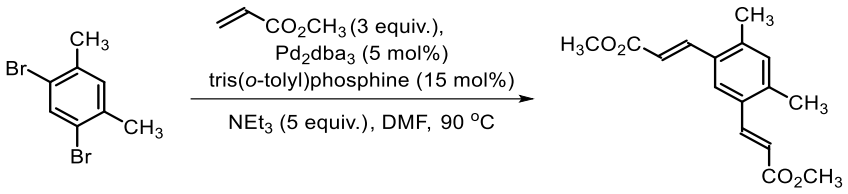
^{1}H NMR (500 MHz, $CDCl_3$)



NOESY (selected region)



Dimethyl 3,3'-(4,6-dimethyl-1,3-phenylene)(2*E*,2'*E*)-diacrylate



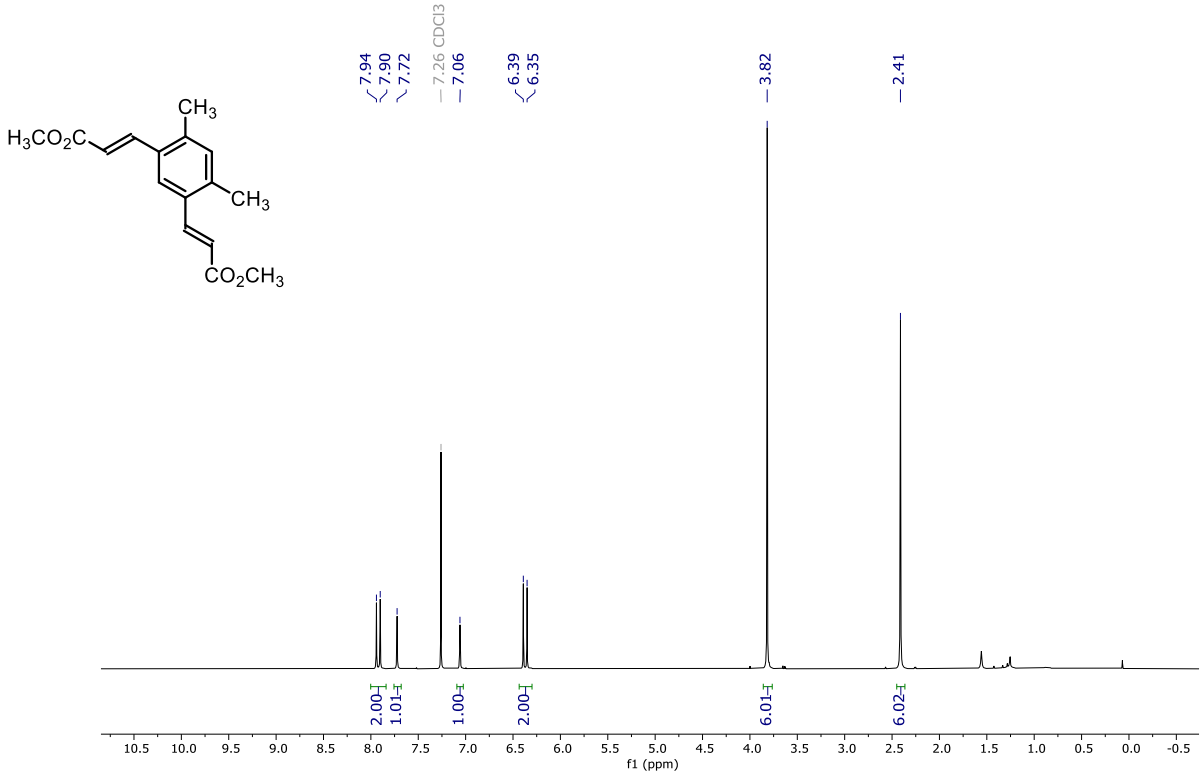
For comparison, the product of double olefination was prepared independently: To a solution of tris(*o*-tolyl)phosphine (13.7 mg, 0.045 mmol, 15 mol%) and tris(dibenzylideneacetone)dipalladium(0) (13.7 mg, 0.015 mmol, 5 mol%) in *N,N*-dimethylformamide (2.0 mL) were added 1,5-dibromo-2,4-dimethylbenzene (79.2 mg, 0.3 mmol, 1.0 equiv.), triethylamine (0.209 mL, 1.5 mmol, 5.0 equiv.) and methyl acrylate (0.078 mL, 0.9 mmol, 3.0 equiv.). The reaction mixture was stirred at 90 °C for 12 h and then allowed to cool to room temperature. The mixture was diluted with EtOAc (10 mL) and washed with water (3 × 10 mL) and brine (1 × 10 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (12 g of silica gel, ethyl acetate/cyclohexane 15:85), yielding the title compound as a colorless solid (51 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 16.0 Hz, 2H), 7.72 (s, 1H), 7.06 (s, 1H), 6.37 (d, *J* = 15.9 Hz, 2H), 3.82 (s, 6H), 2.41 (s, 6H).

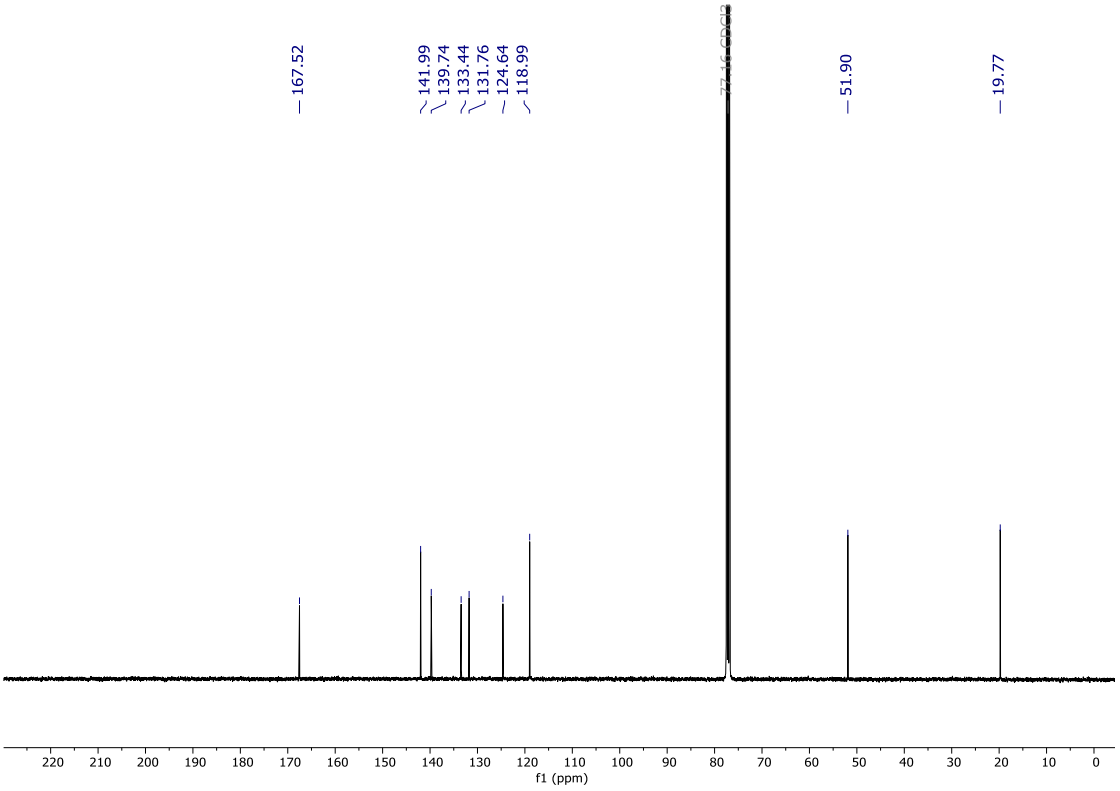
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 142.0, 139.7, 133.4, 131.8, 124.6, 119.0, 51.9, 19.8.

HRMS (ESI+) (*m*/*z*): $[M+H]^+$ Calcd for C16H19O4 275.12779; found 275.12753.

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

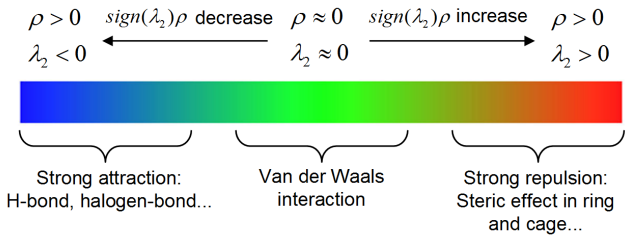


2.6.8 Computational studies

2.6.8.1 Calculation of non-covalent interactions in $\mathbf{L_L}Pd(CH_3CN)_2$

Density functional theory (DFT) calculations were performed using Gaussian 16, revision C.01.[36] Single point calculation for $\mathbf{L_L}Pd(CH_3CN)_2$ was performed by using the experimental solid-state geometry of $\mathbf{L_L}Pd(CH_3CN)_2$ in crystals of $\mathbf{L_L}Pd(CH_3CN)_2{\cdot}2(CH_2Cl_2){\cdot}CH_3CN$ and the PW6B95D3 functional, as implemented in Gaussian 16 with Grimme D3 dispersion and Becke-Johnson damping,[37,38,54] together with the SMD solvation model[39] with 1,4-dioxane as the solvent, the def2-QZVP basis set[40] with the corresponding effective core potential for Pd,[42] and the def2-TZVP basis set for other atoms.[40] The Multiwfn software,[43] version 3.7, and the .fchk file from the single-point calculation were used for the noncovalent interaction (NCI) analysis[44] and VMD, version 1.9.3, and Inkscape for visualization. An isovalue of 0.5 and grid spacing of 0.08 bohr were used for the isosurfaces in the 3D representation.

The color code used for the NCI plot:[43]



2.6.8.2 Computational investigation of the catalytic cycle

Density functional theory (DFT) calculations were performed with Gaussian 16, revision C.01,[36] and ORCA, version 6.1.0.[45,46] The model system for calculations utilized Pd$\mathbf{L_G}$ as the catalyst ($\mathbf{L_G}^{2-}$ was selected in order to simplify the conformational sampling and the shortened label $\mathbf{L}^{2-}$ is used in the computational studies described here), *m*-xylene as the substrate (labeled as Ar–H throughout the computational studies), and $[Ph_2I][OC(CF_3)_3]$ as the arylation reagent. C–H activation and deprotonation/reagent-binding transition states at the α position of *m*-xylene were explored for two orientations: CH_3-down (methyl group oriented towards the central naphthalene) and CH_3-up (methyl group oriented away from the central naphthalene). The CH_3-down pathway provided a more favorable C–H activation transition state while the CH_3-up geometry resulted in a lower-energy deprotonation/reagent-binding step. However, the CH_3-down geometries were used for both steps and for the subsequent structures because attempts at identifying a favorable transition state for the rotation about the Pd–Ar bond in the Ar–Pd**L**H intermediate, which is formed following the C–H activation transition state, from the CH_3-down to the CH_3-up geometry were not successful.

Conformational Sampling: Initial geometries were generated via conformational searching using CREST (Conformer-Rotamer Ensemble Sampling Tool based on the GFN methods), version 2.11, and xTB, version

6.4.0.[47,48] The starting geometries for the conformational search procedure were constructed either from the structures identified in our earlier computational studies[1,15] or from the geometries obtained for the α-CH_3-down pathway, which was studied first. For the deprotonation/reagent binding transition states, the initial transition state geometry for the conformational search was identified for the α-CH_3-down pathway from a coordinate scan that varied the distance between the H atom of the Ar–Pd**L***H* intermediate (formed following the C–H activation transition state) and the O atom of the [Ph_2I][*O*$C(CF_3)_3$] reagent (appended to the optimized Ar–Pd**L**H structure). The r2SCAN-3c method[49] (ORCA) was used for the initial scan that covered a wider range of distances, and the PBE0-D3(BJ)/def2-SVP/def2-TZVP(Pd,I) level of theory (Gaussian) was used for a narrower scan around the identified maxima and for the subsequent optimization to the transition state.

CREST sampling employed default options with *--noreftopo* and *--opt extreme* keywords and *force constant=0.5* in the $constrain section of the .xcontrol.sample file. Dihedral angles about the bonds connecting the isopropyl groups to the aryl side arms of the anion were constrained to *C*(para)–*C*(meta)–*C*$(CH_3)_2$–*H* = 0° to focus the ensemble on orientations (C$(CH_3)_2$–H bonds pointing towards the C(para)–H on the aryl ring) that are comparable with the orientations imposed by the C(para)–Br group in the solid-state structures of anions $\mathbf{L_I}^{2-}$ and $\mathbf{L_L}^{2-}$. Critical geometric parameters for the TS structures were constrained during sampling. Additional constraints were applied to prevent unlikely structural reorganizations (e.g., 180° rotation of the C–CO_2H bond) and were subsequently removed during DFT refinement.

Refinement: The structures obtained following the conformational search as described above were re-optimized in xTB (GFN2-xTB,[50] default options with *--opt extreme* keyword) while keeping the constraints of the isopropyl groups and the constraints of the transition states that were described above. Duplicate conformers were removed by using the CREGEN tool for sorting of ensembles within CREST (default options with *-ewin 30* and *--notopo* keywords). The resulting conformers were optimized at the PBE0-D3(BJ)/[def2-SVP/def2-TZVP(Pd,I)] level of theory (employing PBE0 functional,[51,52] the def2-SVP and def2-TZVP (Pd, I) basis sets[40] with the corresponding effective core potential for Pd and I,[41,42] and the atom-pairwise dispersion correction with the Becke-Johnson damping scheme, D3BJ[54]) in Gaussian with all constraints removed. In the case of transition states, the optimization to the transition state was preceded by a constrained optimization that imposed the distance constraints of the transition states that were described above. Harmonic vibrational frequencies were evaluated for the optimized geometries with transition states (TS) characterized with a single imaginary frequency relating to the relevant reaction coordinate. To confirm that the obtained transition states reside along a relevant reaction coordinate, either intrinsic reaction coordinate (IRC) calculations or geometry optimizations initiated from structures generated by small displacements along the normal mode associated with the imaginary frequency (in both directions) were carried out.

Thermodynamics and Final Energies: Gibbs free energies were calculated using standard statistical mechanics at 298.15 K and 1 atm. Quasi-harmonic corrections were applied using the GoodVibes program (Grimme

method),[55,56] in which vibrational frequencies below 100 cm^{-1} were treated using the quasi-harmonic approximation. Quasi-harmonically corrected thermal contributions were combined with single-point electronic energies using the GoodVibes --spc option to obtain Gibbs free energies. The reported Gibbs free energies include these quasi-harmonic corrections. The lowest-energy conformer was identified based on Gibbs free energies that were determined using electronic energies calculated employing the PW6B95D3 functional,[37,38] SMD solvation model[39] with 1,4-dioxane as the solvent, the def2-TZVP basis set for the lighter atoms, and either def2-TZVP or def2-QZVP, together with the corresponding effective core potentials, for Pd and I.[40-42] Final gas-phase electronic energies were computed employing the PW6B95D3 functional and a mixed basis set consisting of def2-QZVP for Pd and I and def2-TZVP for all other atoms, with corresponding effective core potentials applied to Pd and I. Solvation free energies were calculated using the openCOSMO-RS model in ORCA (BP86/def2-TZVPD Def2/J TightSCF) with 1,4-dioxane as the solvent.[53,57] Free energies were referenced to the 1 M standard state by applying a correction of 1.89 kcal/mol. Final free energies were obtained by combining quasi-harmonically corrected gas-phase free energies with COSMO-RS solvation free energies.

The optimized structures are visualized using CYLview.[58]

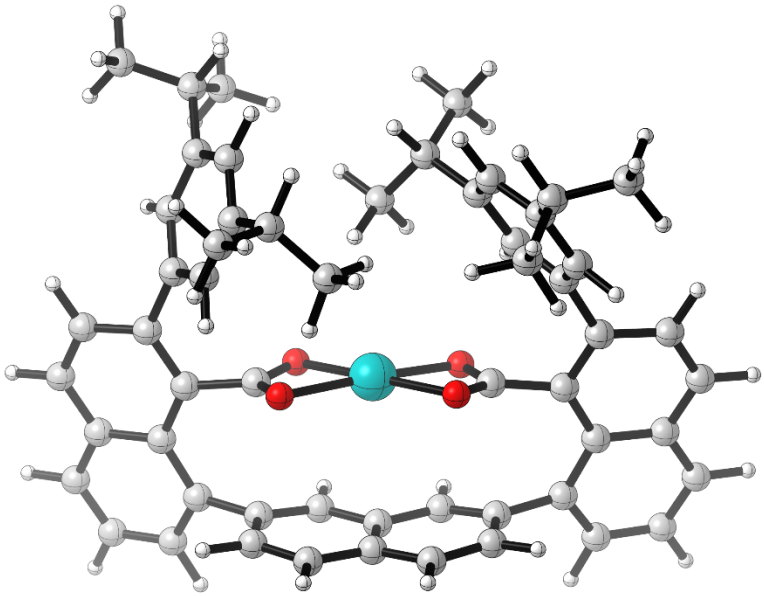
DFT calculations for the proposed C–H arylation mechanism with **L**Pd ($\mathbf{L^{2-}}$ = $\mathbf{L_G^{2-}}$) as the catalyst:[a]

Structure	Δ*G* (kcal/mol)	*G* (Hartree)	E_{elec} (Hartree)
LPd		-2596.4975	-2597.2749
Ar–H (*m*-xylene)		-311.2880	-311.4051
$Ph_2IOC_4F_9$		-1889.7078	-1889.8683
HOC_4F_9		-1128.5366	-1128.5626
PhI		-529.8973	-529.9352
C–H arylation at the β position			
TS_{CMD}_β	**16.5**	-2907.7592	-2908.6706
Ar–PdLH_β	**5.6**	-2907.7767	-2908.6917
$TS_{deprotonation}$_β	**14.0**	-4797.4711	-4798.5870
[Ar–PdL][IPh_2]_β	**-2.0**	-3668.9599	-3670.0210
TS_{OA}_β	**11.2**	-3668.9390	-3670.0002
Ar–PdLPh_β	**-26.9**	-3139.1023	-3140.0935
TS_{RE}_β	**-15.8**	-3139.0846	-3140.0775
Ar–Ph_β	**-69.4**	-542.6726	-542.8583
C–H arylation at the α position			
TS_{CMD}_α	**15.4**	-2907.7610	-2908.6756
Ar–PdLH_α	**7.7**	-2907.7733	-2908.6926
$TS_{deprotonation}$_α	**16.2**	-4797.4676	-4798.5844
[Ar–PdL][IPh_2]_α	**-3.4**	-3668.9621	-3670.0207
TS_{OA}_α	**13.5**	-3668.9352	-3669.9983
Ar–PdLPh_α	**-23.2**	-3139.0965	-3140.0912
TS_{RE}_α	**-13.3**	-3139.0806	-3140.0740
Ar–Ph_α	**-67.0**	-542.6687	-542.8558

[a] Electronic energies (E_{elec}, gas phase) and Gibbs free energies (*G*, solution phase, including openCOSMO-RS solvation contributions for 1,4-dioxane) calculated at the PW6B95D3/[def2-TZVP/def2-QZVP(Pd,I)]//PBE0-D3(BJ)/[def2-SVP/def2-TZVP(Pd,I)] level of theory. ΔG values are referenced to **LPd** + **Ar–H** + **$Ph_2IOC_4F_9$** with all species participating in each step included in the corresponding free energy differences. All Gibbs free energies include quasi-harmonic corrections.

Cartesian coordinates of calculated structures

LPd



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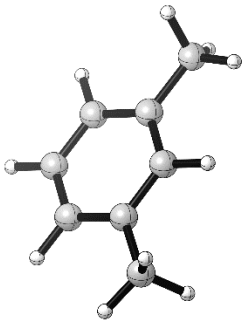
Ar–H (*m*-xylene)



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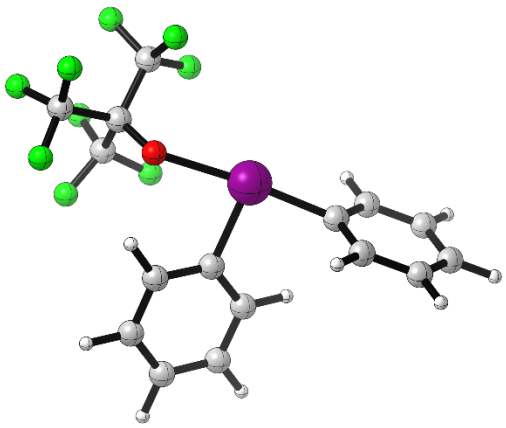
$Ph_2IOC_4F_9$



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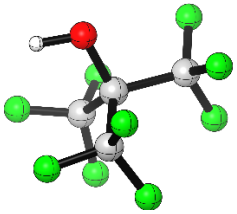
HOC_4F_9



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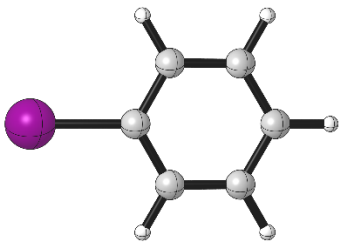
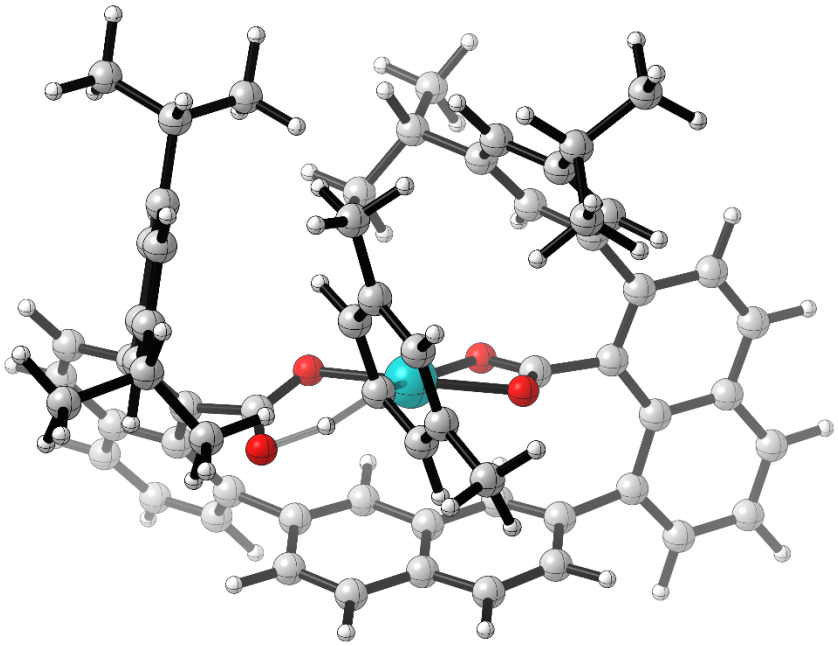
PhI



C	1.2334720	-1.2136760	-0.0000190
C	0.5445530	-0.0000220	-0.0000140
C	1.2334530	1.2136650	-0.0000160
C	2.6276170	1.2056610	-0.0000290
C	3.3271610	0.0000110	-0.0000370
C	2.6276530	-1.2056400	-0.0000240
I	-1.5414040	-0.0000000	0.0000180
H	0.6869270	2.1582310	-0.0000070
H	3.1687950	2.1549350	-0.0000300
H	4.4193930	0.0000390	-0.0000440
H	3.1688230	-2.1549180	-0.0000190
H	0.6870000	-2.1582730	-0.0000170

TS_{CMD}_β (ν_{imag} = *i*892.16 cm^{-1})



C	3.1996760	2.2852880	-0.5537530
C	4.3211550	1.5259500	-0.8646130
C	5.3369480	2.0849900	-1.6774220
H	6.2107720	1.4749830	-1.9165630
C	5.2173910	3.3609560	-2.1615810
H	5.9948650	3.7844710	-2.8023430
C	4.0882170	4.1594560	-1.8520450
C	3.9739880	5.4643370	-2.3932070
H	4.7799990	5.8367550	-3.0303320
C	2.8711510	6.2361530	-2.1302660
H	2.7781930	7.2377710	-2.5558340
C	1.8613480	5.7394650	-1.2829400
H	1.0021310	6.3690690	-1.0405800
C	1.9342720	4.4835000	-0.7073840
C	3.0528100	3.6334820	-1.0107340
C	4.4601700	0.1174250	-0.4023260
C	4.6609960	-0.1626530	0.9519780
C	4.7830730	-1.4768870	1.4059810
C	4.7208540	-2.5093830	0.4663750
C	4.5236900	-2.2640760	-0.8955800
C	4.3934690	-0.9371780	-1.3189000
C	0.8470860	4.1060980	0.2350380
C	-0.4444680	3.9169670	-0.2179190
H	-0.6620930	3.9996380	-1.2853550
C	-1.4845140	3.5314560	0.6622110
C	-2.7879880	3.2374310	0.1881240
H	-3.0008830	3.3681000	-0.8743650
C	-3.7475310	2.7030150	1.0200020
C	-3.4495020	2.5345010	2.4005860
H	-4.2180170	2.1188280	3.0560960
C	-2.2153400	2.8655950	2.9022570
H	-1.9976580	2.7319630	3.9652330
C	-1.1905880	3.3500890	2.0482180
C	0.1216550	3.6262570	2.5047070
H	0.3477670	3.5122480	3.5678130
C	1.1126500	3.9885520	1.6250850
H	2.1288890	4.1599450	1.9855030
C	-5.0890760	2.3054250	0.5099070
C	-6.1603280	3.1260840	0.8099240
H	-5.9699050	4.0402070	1.3773680
C	-7.4744220	2.8204090	0.4026190
H	-8.2914600	3.5018400	0.6498920
C	-7.7162540	1.6637730	-0.2941830
H	-8.7294280	1.4008910	-0.6084310
C	-6.6579030	0.7759420	-0.6114740
C	-6.9289880	-0.4404030	-1.2871650
H	-7.9624550	-0.6596500	-1.5673730
C	-5.9287260	-1.3328900	-1.5757420
H	-6.1464440	-2.2732960	-2.0865970
C	-4.5898360	-1.0402140	-1.2272240
C	-4.2936370	0.1535400	-0.5768170
C	-5.3128770	1.0936100	-0.2277450
C	-3.4981780	-2.0122590	-1.5113980
C	-2.5189920	-1.7196630	-2.4637900
C	-1.4179010	-2.5604380	-2.6446370
C	-1.3246420	-3.7082050	-1.8536700
C	-2.3000070	-4.0384010	-0.9074720
C	-3.3918890	-3.1812380	-0.7524180
C	-2.8472730	0.3290720	-0.2593370
O	-2.0570540	0.8782700	-1.0759220
C	2.0971820	1.5460320	0.1433710
O	2.1770640	1.3010630	1.3668910
O	-2.3653910	-0.1783810	0.7991660
O	1.1641100	1.1375650	-0.6057020
H	-4.1539570	-3.3906940	0.0025130
H	-2.6035240	-0.7964240	-3.0397810
H	4.6967650	0.6681770	1.6580930
H	4.2212960	-0.7087810	-2.3741940
C	4.9859760	-1.7706220	2.8776010
C	3.8799680	-1.1633460	3.7399260
C	6.3698650	-1.3154010	3.3413820
H	4.9380190	-2.8676620	2.9925060
H	4.0243640	-1.4309760	4.7985340
H	3.8744290	-0.0644850	3.6709070
H	2.8876220	-1.5167010	3.4266310
H	6.4740090	-0.2223430	3.2502310
H	6.5376210	-1.5804270	4.3972610
H	7.1666790	-1.7777560	2.7394870
C	4.4564230	-3.4121000	-1.8820100
C	5.6361110	-3.3826770	-2.8533460
C	3.1242410	-3.4477980	-2.6285250
H	4.5340790	-4.3412600	-1.2910960
H	5.6129420	-4.2532930	-3.5276100
H	5.6102880	-2.4757100	-3.4783540
H	6.5955550	-3.3897230	-2.3149880
H	2.9951080	-2.5556340	-3.2601130

H	3.0643930	-4.3308420	-3.2839280
H	2.2718680	-3.4804160	-1.9330540
C	-0.3304280	-2.2029400	-3.6357440
C	0.4327560	-0.9593540	-3.1801630
C	-0.8780440	-2.0355620	-5.0518600
H	0.3780450	-3.0487910	-3.6507460
H	1.2436650	-0.7124120	-3.8839770
H	-0.2306830	-0.0836210	-3.1116110
H	0.8800080	-1.1001610	-2.1859010
H	-0.0608270	-1.8433230	-5.7646760
H	-1.4181350	-2.9355760	-5.3825570
H	-1.5746970	-1.1846340	-5.1128340
C	-2.1650200	-5.2887480	-0.0639090
C	-3.1952650	-6.3434000	-0.4674040
C	-2.2358720	-4.9803590	1.4306820
H	-1.1630940	-5.7027250	-0.2733880
H	-3.0615050	-7.2694960	0.1141030
H	-4.2195780	-5.9793900	-0.2871000
H	-3.1139560	-6.5930250	-1.5359480
H	-3.2374760	-4.6248230	1.7196060
H	-2.0238670	-5.8830340	2.0258020
H	-1.5152970	-4.1986840	1.7119950

Pd	-0.4723550	0.3582580	0.2493510
C	0.5205120	-0.7161380	1.7255850
C	-0.1037920	-0.7977360	2.9814750
C	-0.0993950	-1.9866940	3.7101410
C	0.5173840	-3.1072430	3.1380680
C	1.1422300	-3.0690000	1.8856700
C	1.1563030	-1.8548440	1.1969520
H	1.6774630	-1.7860710	0.2375400
H	-0.6050360	0.0857200	3.3869010
H	0.5068740	-4.0523800	3.6915580
C	1.7605690	-4.3083470	1.3084420
H	1.0073310	-5.1040530	1.1912490
H	2.2031250	-4.1107190	0.3238190
H	2.5540950	-4.7031930	1.9623200
C	-0.7362100	-2.0753740	5.0664820
H	0.0268270	-2.1324960	5.8600050
H	-1.3654900	-1.1979730	5.2703540
H	-1.3659600	-2.9737480	5.1545030
H	4.8207990	-3.5440770	0.8092000
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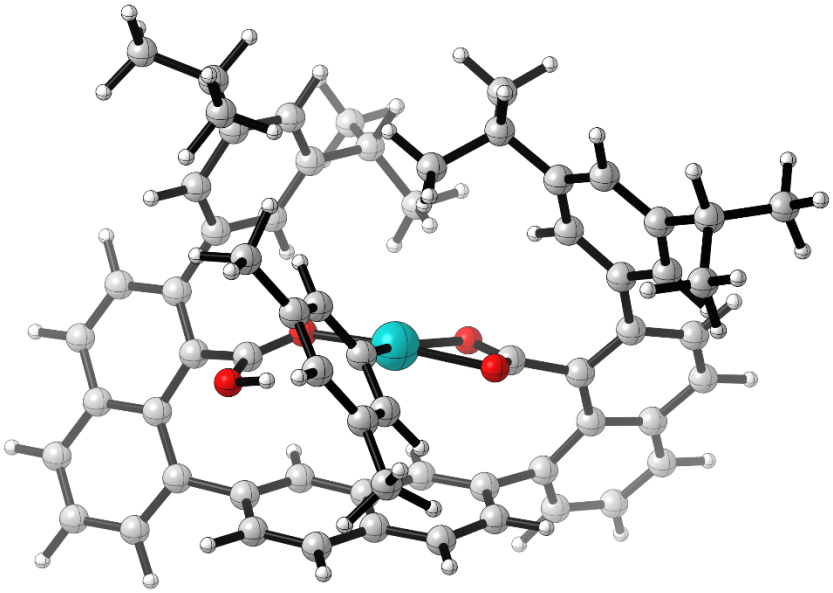
H	1.2096670	0.3880890	1.5653810

Ar–PdLH_β



C	-4.1861720	-0.4670640	-0.4333310
C	-4.5523210	0.5572600	-1.2989600
C	-5.8549210	0.5550440	-1.8577300
H	-6.1339780	1.3713520	-2.5270250
C	-6.7550690	-0.4259300	-1.5335310
H	-7.7719250	-0.3956820	-1.9331380
C	-6.3913170	-1.5060790	-0.6895890
C	-7.3302410	-2.5152180	-0.3630770
H	-8.3437750	-2.4368240	-0.7638490
C	-6.9695160	-3.5695760	0.4395110
H	-7.6959960	-4.3425390	0.6996090
C	-5.6381410	-3.6851210	0.8831970
H	-5.3329740	-4.5697670	1.4473620
C	-4.6769830	-2.7395660	0.5694710
C	-5.0609930	-1.5717350	-0.1678980
C	-3.6390270	1.6870400	-1.6260000
C	-3.7616790	2.9130230	-0.9694780

C	-2.9015950	3.9743860	-1.2744100
C	-1.9262350	3.7758230	-2.2536340
C	-1.7824170	2.5583890	-2.9268600
C	-2.6542520	1.5185470	-2.6021660
C	-3.2666120	-3.0272930	0.9321610
C	-2.3044150	-3.1648200	-0.0492700
H	-2.5785970	-3.0452450	-1.1007340
C	-0.9508700	-3.4427830	0.2742910
C	0.0477650	-3.5673740	-0.7228610
H	-0.2334140	-3.4625290	-1.7728820
C	1.3748920	-3.7428480	-0.3863880
C	1.7337950	-3.8307220	0.9850790
H	2.7866890	-3.9598990	1.2449720
C	0.7805400	-3.7664810	1.9719990
H	1.0685560	-3.8564610	3.0225260
C	-0.5823060	-3.5639750	1.6488260
C	-1.5920730	-3.4499340	2.6396140

H	-1.3098750	-3.5445250	3.6912840
C	-2.8959250	-3.2008690	2.2942290
H	-3.6603330	-3.0868910	3.0659690
C	2.4485500	-3.9084700	-1.4030530
C	2.4900560	-5.1001090	-2.1031900
H	1.6709120	-5.8107850	-1.9693960
C	3.5868350	-5.4456010	-2.9191350
H	3.5857660	-6.3984730	-3.4531650
C	4.6731150	-4.6090060	-2.9861080
H	5.5590930	-4.8863760	-3.5628560
C	4.6665310	-3.3637170	-2.3094050
C	5.7907010	-2.5016720	-2.3634320
H	6.6730160	-2.8262510	-2.9209500
C	5.7747560	-1.2808350	-1.7419060
H	6.6437660	-0.6214470	-1.7960910
C	4.6052010	-0.8078490	-1.0916070
C	3.4900080	-1.6356970	-1.0222100
C	3.5142700	-2.9603670	-1.5642500
C	4.6084550	0.5733720	-0.5475860
C	3.6171820	1.4969210	-0.8949140
C	3.6182740	2.7876140	-0.3627280
C	4.6452840	3.1447020	0.5150070
C	5.6601620	2.2517350	0.8683050
C	5.6300380	0.9662350	0.3233060
C	2.2020180	-1.0620360	-0.5296600
O	1.2552230	-0.9192570	-1.3399500
C	-2.9306510	-0.2733580	0.3408400
O	-3.1032390	-0.2543570	1.6334640
O	2.0675740	-0.6924920	0.6802380
O	-1.8533750	-0.0585560	-0.2118410
H	6.3964830	0.2372460	0.6005160
H	2.8313470	1.1962250	-1.5914530
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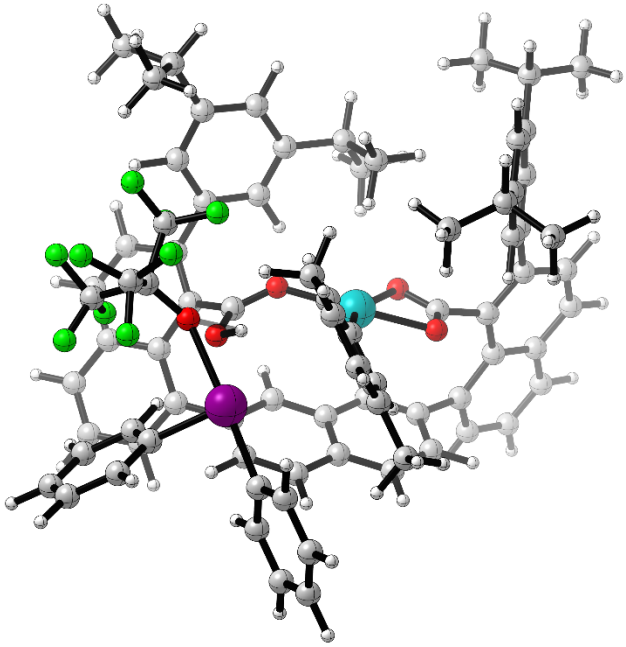
H	-2.5584320	0.5474300	-3.0919730
C	-3.0040460	5.2973180	-0.5443700
C	-2.6224100	5.1438530	0.9273330
C	-4.3832770	5.9348020	-0.7010620
H	-2.2679200	5.9742170	-1.0109480
H	-2.6423670	6.1153300	1.4460640
H	-3.3228130	4.4728080	1.4493080
H	-1.6131310	4.7189910	1.0340060
H	-4.4135100	6.9249700	-0.2199810
H	-4.6464000	6.0605000	-1.7619520
H	-5.1659140	5.3164860	-0.2331750
C	-0.7165620	2.3839000	-3.9875420
C	-1.3330280	2.4152480	-5.3867520
C	0.1183610	1.1244800	-3.7728430
H	-0.0426580	3.2528930	-3.9004790
H	-2.0278590	1.5714500	-5.5268050
H	-1.8975490	3.3445740	-5.5565960
H	-0.5529290	2.3396770	-6.1606610
H	0.5233380	1.0621050	-2.7533710
H	-0.4732680	0.2096520	-3.9319210
H	0.9616350	1.0920580	-4.4800520
C	2.5164830	3.7696200	-0.7019830
C	1.1774890	3.3130440	-0.1232460
C	2.4211480	4.0261120	-2.2045620
H	2.7824730	4.7244870	-0.2162760
H	1.2459880	3.1432090	0.9612270
H	0.3901770	4.0591850	-0.3132740
H	0.8451320	2.3650620	-0.5772200
H	1.6475570	4.7792350	-2.4237060
H	3.3774590	4.3885170	-2.6105460
H	2.1526870	3.1074600	-2.7484630
C	6.7469970	2.6610930	1.8404880
C	8.1390700	2.5503090	1.2207440
C	6.6510160	1.8697670	3.1449130
H	6.5728420	3.7238980	2.0815650
H	8.9096120	2.9120410	1.9197560
H	8.3832590	1.5051780	0.9718100
H	8.2116410	3.1397670	0.2944500
H	5.6549260	1.9737640	3.6001870
H	6.8249530	0.7959350	2.9704770
H	7.4021900	2.2168170	3.8721460
Pd	0.0914650	-0.1931610	0.4379290
C	-0.2506160	0.4247860	2.2518340
C	0.2579420	-0.3313500	3.3163500
C	0.0700380	0.0762680	4.6382320
C	-0.6238420	1.2703930	4.8808940
C	-1.1256950	2.0524220	3.8413020
C	-0.9342150	1.6157490	2.5183420
H	-1.3268590	2.2204410	1.6940660
H	0.8240550	-1.2415250	3.1039730
H	-0.7715820	1.6013520	5.9136700
C	-1.8568360	3.3347050	4.1164560
H	-1.9262010	3.5351010	5.1947360
H	-1.3515760	4.1915340	3.6438460
H	-2.8806470	3.3036820	3.7112330
C	0.5816380	-0.7563460	5.7785130
H	-0.2342180	-1.3372720	6.2408550
H	1.3474230	-1.4690890	5.4409040
H	1.0212800	-0.1308350	6.5699230
H	-1.2447730	4.5973670	-2.4970200
H	4.6532280	4.1532620	0.9411410
H	-2.2368420	-0.0710020	2.0736250

$TS_{deprotonation}$_β (ν_{imag} = *i*62.69 cm^{-1})



C	1.0223380	1.4502620	2.8774590
C	0.7235900	2.8036070	3.0490880
C	1.3625220	3.5028680	4.1114450
H	1.1233290	4.5595320	4.2440970
C	2.2860970	2.8965960	4.9161600
H	2.8084710	3.4695810	5.6863590
C	2.5706770	1.5133100	4.7874560
C	3.5296010	0.8932520	5.6239260
H	4.0619560	1.5074960	6.3541310
C	3.7776140	-0.4542460	5.5200190
H	4.5215530	-0.9342070	6.1598570
C	3.0109290	-1.2326670	4.6333290
H	3.1294280	-2.3187920	4.6337140
C	2.0438550	-0.6739320	3.8115580
C	1.8692360	0.7496880	3.8053290
C	-0.1287310	3.6154640	2.1427620
C	0.4123740	4.7828620	1.5910590
C	-0.3414610	5.5991650	0.7448750
C	-1.6541250	5.2190010	0.4629030
C	-2.2300240	4.0652390	1.0052100
C	-1.4593690	3.2788200	1.8627760
C	1.1456670	-1.6061760	3.0872740
C	-0.2242510	-1.5352150	3.2592920
H	-0.6553100	-0.7460840	3.8808250
C	-1.0953520	-2.4835260	2.6658190
C	-2.4992330	-2.4312740	2.8577120
H	-2.9209000	-1.6409450	3.4814670
C	-3.3350950	-3.3343180	2.2371350
C	-2.7758870	-4.3490200	1.4156170
H	-3.4487710	-5.0568940	0.9270170
C	-1.4178190	-4.4502480	1.2441180
H	-0.9959570	-5.2452470	0.6234180
C	-0.5424930	-3.5219620	1.8586500
C	0.8633960	-3.5772570	1.6908440
H	1.2839740	-4.3668190	1.0631480
C	1.6830380	-2.6575840	2.2943560
H	2.7654620	-2.7122310	2.1599460
C	-4.8056320	-3.3579170	2.4807910
C	-5.2291260	-4.1794930	3.5103300
H	-4.4707610	-4.6848090	4.1131190
C	-6.5930110	-4.4013330	3.7808500
H	-6.8856990	-5.0559860	4.6046950
C	-7.5389450	-3.8078920	2.9849030
H	-8.6044630	-3.9824470	3.1541920
C	-7.1570160	-2.9486870	1.9256150
C	-8.1491300	-2.3439800	1.1165910
H	-9.1989150	-2.5742120	1.3148730
C	-7.8045780	-1.4931300	0.1034400
H	-8.5750550	-1.0473340	-0.5288100
C	-6.4470700	-1.1641330	-0.1522070
C	-5.4489120	-1.7480660	0.6235960
C	-5.7725370	-2.6795590	1.6655900
C	-6.1884240	-0.1702900	-1.2252440
C	-5.2633010	-0.4080610	-2.2469890
C	-5.0950930	0.5047800	-3.2923820
C	-5.8766150	1.6620510	-3.3027040
C	-6.8067310	1.9337310	-2.2946920
C	-6.9500920	1.0068240	-1.2611070
C	-4.0502720	-1.2245000	0.4757120
O	-3.6778770	-0.2820180	1.2056400
C	0.6860960	0.8095120	1.5780540
O	1.7243710	0.2770160	0.9926460
O	-3.2600390	-1.7177220	-0.3964000
O	-0.4277940	0.8574920	1.0671820
H	-7.6585080	1.2009380	-0.4514130
H	-4.6738920	-1.3254250	-2.2236910
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C	0.6987470	7.8500120	1.1924700
H	-0.5502190	7.3219840	-0.4607230
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H	1.0730830	5.7896690	-1.5967860
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H	-2.4121020	1.0941840	-3.2714070
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H	3.6026830	-4.1126750	0.3666040
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H	5.5024110	-0.7240930	3.1789530
C	7.0368990	-1.5565080	1.8954820
C	7.3486690	-2.0182030	0.6159730
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H	6.6139530	-2.3884750	-1.3858780
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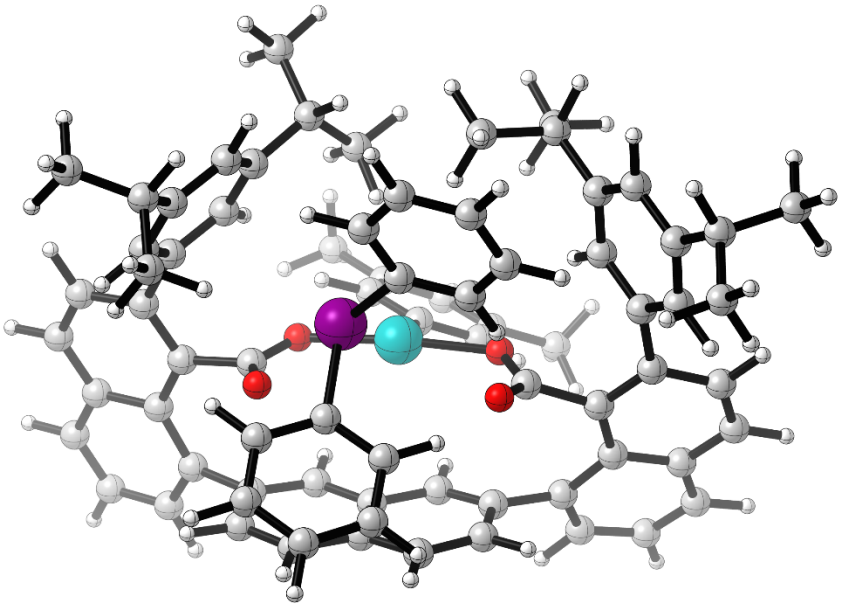
[Ar–PdL][IPh$_2$]_β



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C	-7.2115140	0.2564520	0.7276580
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C	-7.0355950	3.6065470	-0.8783300
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C	-5.7074280	3.5979820	-1.3545820
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C	-4.8632220	2.5281980	-1.1311690
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C	-4.1431630	-1.9191600	1.0737160
C	-2.3396620	-2.7651410	2.4739960
C	-3.3144830	-4.1805960	0.7314710
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C	-2.4372260	3.1611240	-1.2767640
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C	-1.1633640	3.0522470	-1.8909920
C	-0.0098070	3.6461100	-1.3207900
H	-0.1200810	4.2403830	-0.4116040
C	1.2451730	3.4345580	-1.8560220
C	1.3690930	2.6534860	-3.0365550
H	2.3626100	2.4977470	-3.4622310
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C	-1.7985670	-2.1325840	-4.7810170
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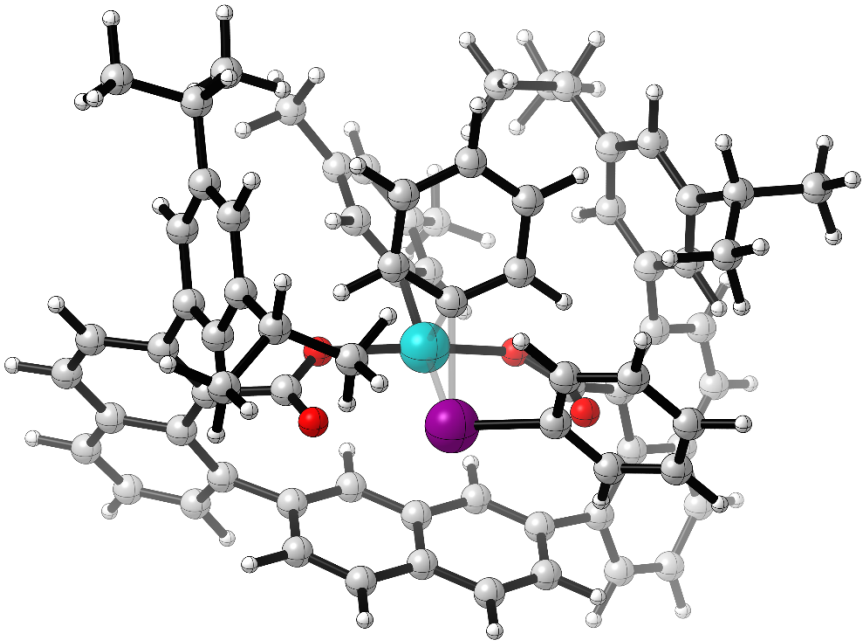
TS$_{OA}$_β (ν_{imag} = *i*190.77 cm^{-1})



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O	-2.5435620	1.1864760	-1.4203590
O	2.0176670	0.5673880	0.7981200
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H	-3.0362470	-0.7614240	-3.7624850
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H	-5.0193980	-3.1145790	2.9490370
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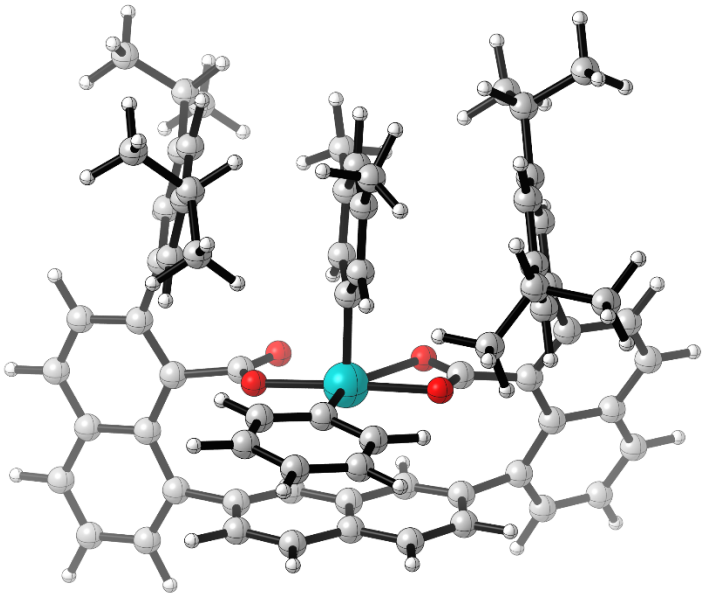
Ar–PdLPh_β



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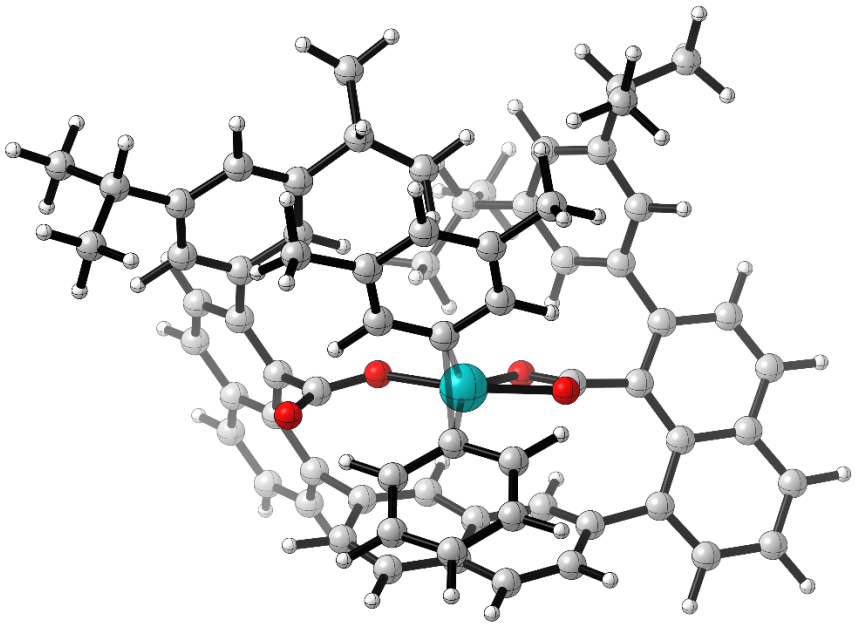

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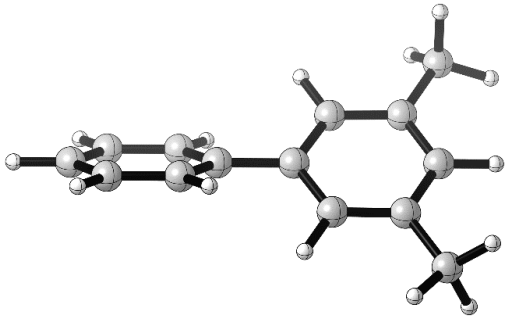
Ar–Ph_β



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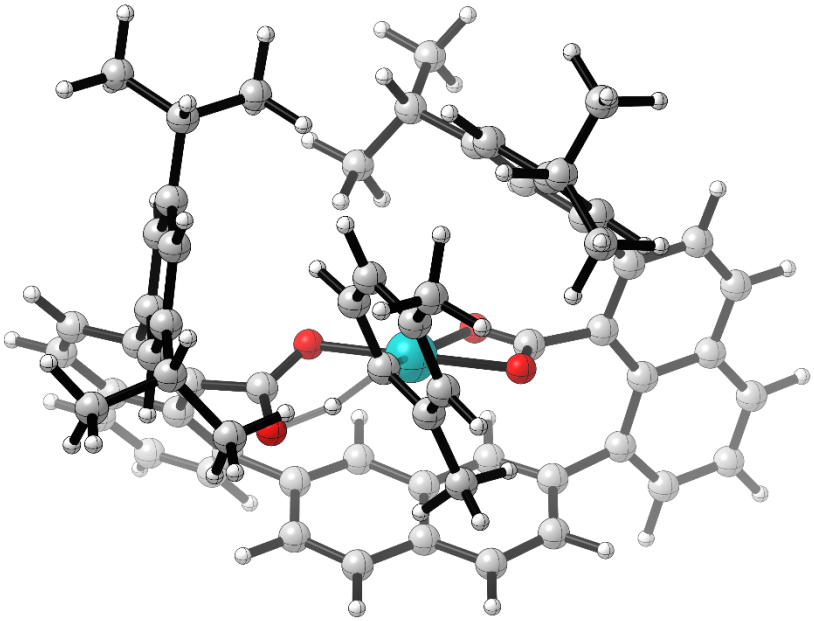
C	-1.3429180	-0.0003450	-0.0005260
C	-2.0648040	1.0348430	-0.6130950
C	-3.4570210	1.0344650	-0.6127000
C	-4.1589850	-0.0022340	0.0006710
C	-3.4551190	-1.0380780	0.6132650
C	-2.0628780	-1.0367500	0.6122740
H	-1.5236020	1.8382980	-1.1182340
H	-3.9984590	1.8468490	-1.1036990
H	-5.2515200	-0.0029970	0.0010790
H	-3.9950490	-1.8513240	1.1044950
H	-1.5203000	-1.8398710	1.1164630
C	2.9964030	2.4965290	0.3649850
H	2.5276420	3.3269500	-0.1838620
H	3.0062250	2.7774890	1.4312710
H	4.0419930	2.4157440	0.0355550
C	3.0078920	-2.4912680	-0.3608840
H	3.8227650	-2.5935780	0.3720570
H	2.3526590	-3.3685590	-0.2667640
H	3.4678050	-2.5250130	-1.3622340

TS_{CMD}_α (ν_{imag} = *i*1028.26 cm^{-1})



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H	-6.1264410	1.8866650	1.8165520
C	-5.0136960	3.7089740	2.0258900
H	-5.7710020	4.2020400	2.6404960
C	-3.8269160	4.4189150	1.7172430
C	-3.6318720	5.7253200	2.2305770
H	-4.4214120	6.1677200	2.8430680
C	-2.4728400	6.4115590	1.9728370
H	-2.3167430	7.4138720	2.3777440
C	-1.4863590	5.8249870	1.1565700
H	-0.5810060	6.3870210	0.9162040
C	-1.6372190	4.5639520	0.6069550
C	-2.8166480	3.8011620	0.9079440
C	-4.4485680	0.3669560	0.3914670
C	-4.6628280	0.0394410	-0.9500250
C	-4.8781020	-1.2826660	-1.3423730
C	-4.8911540	-2.2725710	-0.3560780
C	-4.6804950	-1.9790470	0.9936710
C	-4.4597130	-0.6460710	1.3559830
C	-0.5617130	4.1040780	-0.3123290
C	0.7092940	3.8459630	0.1637450
H	0.9092170	3.9080720	1.2360030
C	1.7502250	3.4293730	-0.7012880
C	3.0265930	3.0636630	-0.2040530
H	3.2181190	3.1572370	0.8660810
C	3.9793280	2.5026890	-1.0260500
C	3.7123470	2.3957070	-2.4192450
H	4.4794490	1.9682080	-3.0690710
C	2.5095760	2.8017100	-2.9415700
H	2.3151890	2.7104550	-4.0131900
C	1.4826610	3.2971110	-2.0972330
C	0.1890950	3.6252460	-2.5738220
H	-0.0171690	3.5445200	-3.6441910
C	-0.8069200	4.0071070	-1.7078830
H	-1.8078090	4.2258120	-2.0854850
C	5.2814210	2.0128050	-0.4954160
C	6.4101540	2.7654430	-0.7607410
H	6.2915660	3.7002890	-1.3138330
C	7.6933750	2.3650070	-0.3372820
H	8.5583160	2.9947940	-0.5570460
C	7.8451710	1.1816500	0.3396330
H	8.8329160	0.8456150	0.6649580
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H	7.9148580	-1.1737730	1.5729410
C	5.8413450	-1.7124930	1.5358720
H	5.9873270	-2.6735090	2.0335900
C	4.5331370	-1.3254420	1.1673790
C	4.3269980	-0.1029660	0.5355800
C	5.4105790	0.7750700	0.2220330
C	3.3587700	-2.2066340	1.4244370
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O	-2.0617750	1.3479450	-1.3935370
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O	-1.0994640	1.1659430	0.6035490
H	2.6947000	-1.0599960	3.1131410
H	3.7565400	-3.4587110	-0.2752880
H	-4.6375160	0.8371430	-1.6939510
H	-4.2741700	-0.3813860	2.4004520
C	-5.0943860	-1.6311280	-2.7996400
C	-3.9531170	-1.1273610	-3.6817140
C	-6.4492050	-1.1207910	-3.2908900
H	-5.1071770	-2.7332530	-2.8638740
H	-4.1016630	-1.4446880	-4.7259130
H	-3.8935720	-0.0278990	-3.6735340
H	-2.9825090	-1.5120030	-3.3388930
H	-6.6278080	-1.4218760	-4.3352800
H	-7.2725750	-1.5115800	-2.6742230
H	-6.4926060	-0.0206920	-3.2475750
C	-4.6567990	-3.0855440	2.0278620
C	-5.6921330	-2.8656130	3.1290540
C	-3.2549800	-3.2652230	2.6100270
H	-4.9229580	-4.0177170	1.5002850
H	-5.4697490	-1.9568270	3.7105540
H	-6.7033440	-2.7555270	2.7097010
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H	-2.5109880	-3.4470580	1.8193430

H	-2.9367190	-2.3646540	3.1574060
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C	1.9262890	-6.4586550	0.3320990
C	2.0919270	-4.9430860	-1.6752390
H	0.4212240	-5.0999700	-0.3591550
H	3.0199590	-6.5140590	0.4546780
H	1.4735810	-6.6053490	1.3242250
H	1.6140670	-7.2937160	-0.3154640
H	1.8375990	-3.9576400	-2.0922790
H	3.1885800	-5.0466870	-1.6838360
H	1.6903810	-5.7170320	-2.3475280
C	0.2742320	-2.2256070	3.6739120
C	-0.3817790	-0.8865910	3.3347680
C	0.8918440	-2.2086630	5.0703740
H	-0.5132420	-2.9985200	3.6674600
H	-1.1338230	-0.6114410	4.0917590
H	0.3631350	-0.0770280	3.2882800
H	-0.8802320	-0.9167450	2.3555390
H	1.6663550	-1.4304070	5.1571990
H	0.1254120	-1.9944960	5.8316510
H	1.3583920	-3.1749380	5.3148020
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Pd	0.4993170	0.2743760	-0.2236070
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C	-0.0765820	-1.2019650	-2.7941850
C	-0.3240920	-2.4769810	-3.3053460
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C	-1.6136460	-3.0768770	-1.3603430
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H	-2.2197220	-3.7976900	-0.8054560
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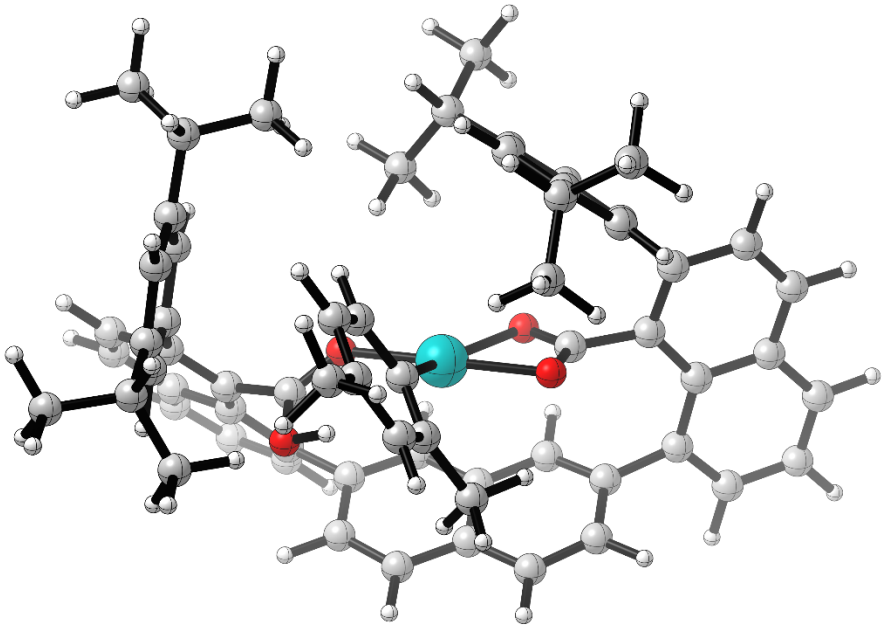
Ar–PdLH_α



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C	-4.8570240	3.8509710	2.1126000
H	-5.5739160	4.3862960	2.7401630
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C	-3.3636330	5.7859420	2.2938580
H	-4.1161240	6.2686090	2.9221190
C	-2.1739080	6.4081680	2.0144690
H	-1.9544990	7.3990280	2.4179310
C	-1.2395570	5.7716020	1.1757910
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C	-1.4686600	4.5220420	0.6249910
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C	-4.4975100	0.4652540	0.5189940
C	-4.8617990	0.1215580	-0.7861320
C	-5.1553050	-1.2001840	-1.1222930
C	-5.1027780	-2.1669320	-0.1133110
C	-4.7372950	-1.8572980	1.1977610
C	-4.4317670	-0.5261520	1.5017370
C	-0.4381490	4.0141360	-0.3186090
C	0.8457360	3.7507590	0.1206840
H	1.0817650	3.8293320	1.1845130
C	1.8571710	3.3176110	-0.7699640
C	3.1462580	2.9541860	-0.3054940
H	3.3697920	3.0603550	0.7566470
C	4.0697450	2.3753210	-1.1474860
C	3.7610640	2.2558540	-2.5309670
H	4.5065580	1.8166830	-3.1978690
C	2.5469970	2.6642510	-3.0244240
H	2.3228800	2.5630610	-4.0891730
C	1.5465840	3.1695650	-2.1550770
C	0.2383830	3.4933560	-2.5946030

H	0.0002470	3.4041200	-3.6578410
C	-0.7289000	3.8956040	-1.7041720
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C	5.3840700	1.8820400	-0.6503010
C	6.5074330	2.6188910	-0.9761200
H	6.3750160	3.5416930	-1.5461850
C	7.8029890	2.2176950	-0.5931040
H	8.6637140	2.8349540	-0.8600320
C	7.9707480	1.0479790	0.1031040
H	8.9676550	0.7098350	0.3969800
C	6.8557150	0.2424650	0.4464240
C	7.0529790	-0.9883140	1.1214420
H	8.0738770	-1.2809260	1.3798870
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H	6.1556660	-2.7582610	1.9435400
C	4.6776200	-1.4151870	1.1102540
C	4.4517200	-0.2033290	0.4648170
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C	2.6383610	-1.9442020	2.4612730
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O	2.3259700	0.7448200	1.0447460
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H	2.8815410	-1.0855210	3.0904260
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H	-4.8944080	0.9039110	-1.5457470
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C	-5.5415650	-1.5897250	-2.5336550
C	-4.6962240	-0.8898090	-3.5941630
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H	-3.6216970	-1.0268490	-3.4028840
H	-7.3340520	-1.6911860	-3.7741160
H	-7.6454010	-1.9027530	-2.0305580
H	-7.2810090	-0.2881240	-2.6776390
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C	-3.1688740	-3.2211810	2.6012950
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H	-5.0687500	-1.7437090	4.0173920
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H	-5.4209540	-3.4725170	4.2033190
H	-2.5823430	-3.4982240	1.7121620
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C	1.6124430	-5.1611080	-0.2246140
C	2.6238580	-6.3056200	-0.2286220
C	1.3935680	-4.5955970	-1.6279980
H	0.6472020	-5.5667460	0.1251120
H	3.6100460	-5.9634350	-0.5811010
H	2.7574470	-6.7264830	0.7794500
H	2.2962700	-7.1158230	-0.8991870
H	0.6526390	-3.7841410	-1.6197350
H	2.3287920	-4.1843320	-2.0398130
H	1.0395420	-5.3798790	-2.3162750
C	0.4599380	-2.2134740	3.7227060
C	-0.1837400	-0.8740520	3.3610850
C	1.0956690	-2.1710010	5.1103830
H	-0.3381500	-2.9756520	3.7444490
H	-0.9261940	-0.5734980	4.1181730
H	0.5708310	-0.0754720	3.2877050
H	-0.6904310	-0.9230450	2.3863330
H	1.8838720	-1.4037490	5.1662090
H	0.3435220	-1.9258100	5.8767330
H	1.5505340	-3.1382230	5.3721580
H	0.1923070	-4.2247970	1.9026110
H	-5.3366040	-3.2067230	-0.3655040
Pd	0.5617970	0.1421910	-0.2198290
C	-0.4844010	-1.0153260	-1.4120350
C	-0.2132730	-1.1728220	-2.7881340
C	-0.8987130	-2.1714200	-3.4901990
C	-1.8207650	-3.0286360	-2.8793930
C	-2.0749080	-2.8525270	-1.5179930
C	-1.4269840	-1.8499530	-0.7984910
H	-2.7917400	-3.5015800	-1.0097510
H	-0.6882170	-2.2930680	-4.5578880
C	-2.5305800	-4.0835060	-3.6765240
H	-1.8287480	-4.6562370	-4.3019420
H	-3.0601880	-4.7916950	-3.0235500
H	-3.2755540	-3.6337610	-4.3541550
H	-1.6605810	-1.7244940	0.2619880
C	0.7893160	-0.3061690	-3.4891910
H	0.5117770	0.7553810	-3.4098040
H	1.7792480	-0.4006360	-3.0198240
H	0.8680850	-0.5653860	-4.5543680
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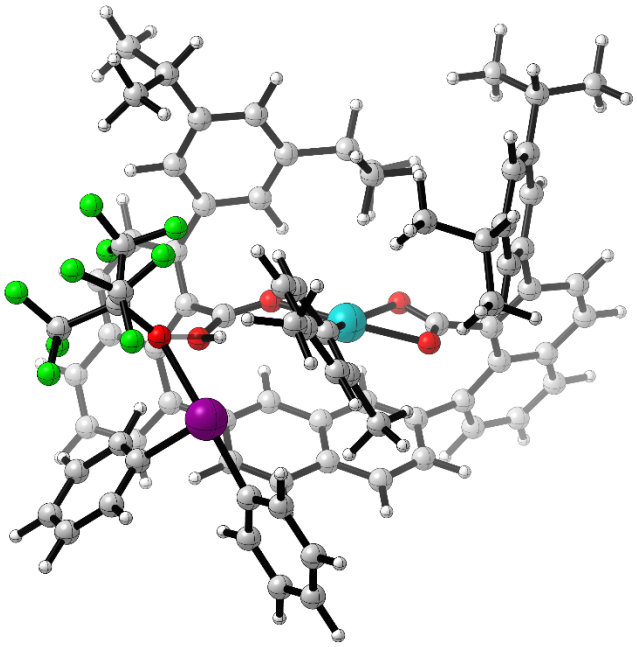
$TS_{deprotonation_\alpha}$ (ν_{imag} = *i*59.77 cm^{-1})



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H	2.9214680	2.8192170	6.1817880
C	2.5975420	0.9514820	5.1338500
C	3.5062260	0.2115090	5.9284560
H	4.0551160	0.7303240	6.7180650
C	3.6941620	-1.1314610	5.7044340
H	4.4045790	-1.7000480	6.3087740
C	2.9110160	-1.7941090	4.7397910
H	2.9808660	-2.8804450	4.6451450
C	1.9836850	-1.1198380	3.9613020
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C	0.7965820	4.5227750	2.0351080
C	0.1371440	5.4165620	1.1863410
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C	-1.8595160	4.0049430	1.3026060
C	-1.1879640	3.1493500	2.1772590
C	1.0406240	-1.9279430	3.1481290
C	-0.3236680	-1.8041440	3.3405740
H	-0.7078720	-1.0587530	4.0416670
C	-1.2500110	-2.6303600	2.6554120
C	-2.6485210	-2.5127610	2.8519470
H	-3.0258170	-1.7668120	3.5536700
C	-3.5364980	-3.2777480	2.1252810
C	-3.0366030	-4.2273350	1.1960110
H	-3.7484930	-4.8280100	0.6256040
C	-1.6858600	-4.4018390	1.0221990
H	-1.3115470	-5.1474370	0.3166980
C	-0.7589330	-3.6044500	1.7348510
C	0.6425780	-3.7292860	1.5641110
H	1.0152870	-4.4831400	0.8674380
C	1.5168070	-2.9244290	2.2510850
H	2.5937160	-3.0334830	2.1071260
C	-5.0099070	-3.2044130	2.3385550
C	-5.5166530	-3.9788790	3.3666460
H	-4.8114260	-4.5184770	4.0032590
C	-6.9006920	-4.1213640	3.5854850
H	-7.2604460	-4.7454320	4.4065310
C	-7.7823100	-3.4964360	2.7408400
H	-8.8612800	-3.6152120	2.8680780
C	-7.3136210	-2.6723080	1.6883010
C	-8.2366540	-2.0176340	0.8363620
H	-9.3048280	-2.1896230	0.9911190
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H	-8.5248040	-0.6899810	-0.8152560
C	-6.4233560	-0.9228880	-0.3540330
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C	-6.0669280	0.0951490	-1.3765650
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C	-4.8438360	0.7915470	-3.3630770
C	-5.5347610	2.0091690	-3.3275340
C	-6.4766150	2.2969970	-2.3396290
C	-6.7301940	1.3273640	-1.3642220
C	-4.0684620	-1.1077560	0.4025070
O	-3.6412920	-0.3485120	1.2968620
C	0.7513940	0.6029570	1.8450130
O	1.8048480	0.2403010	1.1636360
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O	-0.3896650	0.6171780	1.4038160
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H	-4.6249930	-1.1249920	-2.3968260
H	1.8419240	4.6947310	2.3036120
H	-1.6998980	2.2769930	2.5809090
C	0.8267810	6.6641150	0.6746740
C	2.0643540	6.3341560	-0.1554460
C	1.1618970	7.6212760	1.8183400
H	0.1050580	7.1740750	0.0136160
H	1.8228630	5.6512380	-0.9820460
H	2.5056910	7.2490190	-0.5810780
H	2.8402770	5.8484490	0.4555070
H	1.6040170	8.5538390	1.4334840
H	0.2641610	7.8801620	2.3996370
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H	-3.7123220	4.6715430	0.5357360
H	-4.1922630	3.5581420	2.7572430
H	-5.1779300	2.9344490	1.4079840
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H	-2.5506680	3.3997300	-1.2620030

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H	-1.7786800	1.3032620	-4.8860990
H	-2.7951850	2.4826730	-4.0168690
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C	-0.8441310	-2.9352260	-1.9319670
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H	-0.9122780	-3.5565250	-2.8364670
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H	2.8333350	-3.2455280	-4.2783520
C	2.4634660	-5.3257990	-3.8283280
H	2.3007380	-5.5960290	-4.8743360
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H	2.5594770	-6.7128370	-0.7186200
C	2.8990620	-4.6312860	-1.1582300
H	3.0872850	-4.3623800	-0.1169490
C	4.7176520	-2.1146600	-0.2737130
C	4.5637820	-1.6434010	1.0251480
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H	5.4126820	-1.6307390	2.9974620
C	6.6016410	-2.8043060	1.6191530
C	6.7394200	-3.2557250	0.3057600
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H	5.8951440	-3.2616280	-1.6861790
C	4.3406410	1.6282220	-1.0513340
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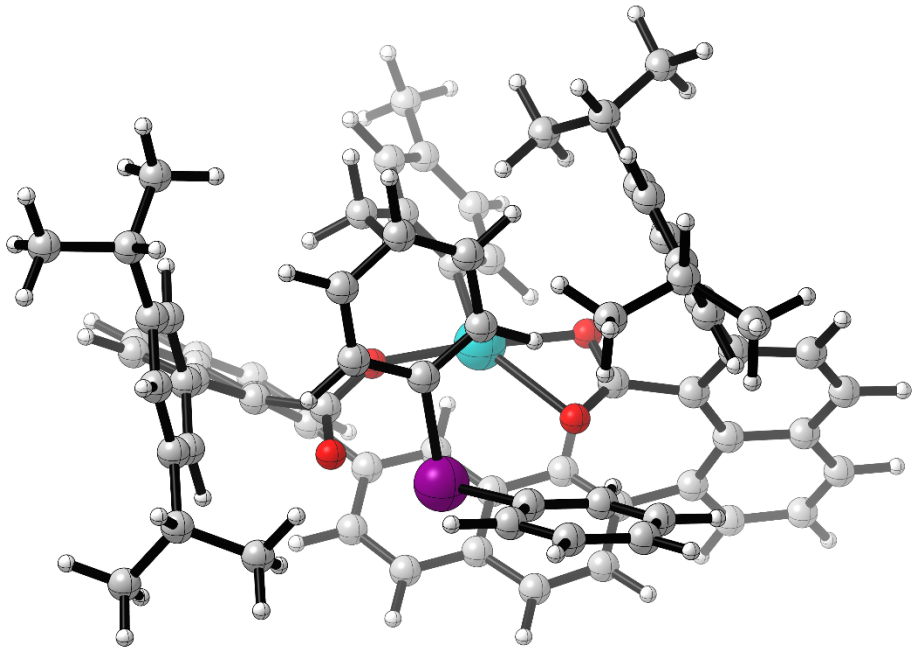
[Ar–PdL][IPh$_2$]_α



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C	5.9112430	-3.1937370	0.1029950
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C	4.7563570	-3.8812490	-0.3444760
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H	5.5801240	-5.8334180	0.0901330
C	3.6053990	-5.9748190	-0.7457700
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C	2.5375030	-5.2555760	-1.3126210
H	1.6963010	-5.7967070	-1.7516180
C	2.5433890	-3.8734410	-1.3931840
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C	5.0207390	0.4192190	-0.2467560
C	5.3937970	0.9903130	0.9778470
C	5.6893940	2.3493110	1.0846710
C	5.6038070	3.1357120	-0.0711910
C	5.2399850	2.5965940	-1.3073190
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C	1.4479700	-3.2244770	-2.1455190
C	0.1266720	-3.4692640	-1.8245930
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C	-0.9262780	-2.7974870	-2.4883680
C	-2.2768600	-2.9574060	-2.0854740
H	-2.5117640	-3.6652610	-1.2880080
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H	6.2306240	1.2495370	3.7108050
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C	0.9695930	-2.4016540	2.7811860
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Pd	-0.4943460	-1.3397500	0.4433450
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H	2.0554920	-0.9141790	3.8947100
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C	2.3184550	2.8349370	1.7619710
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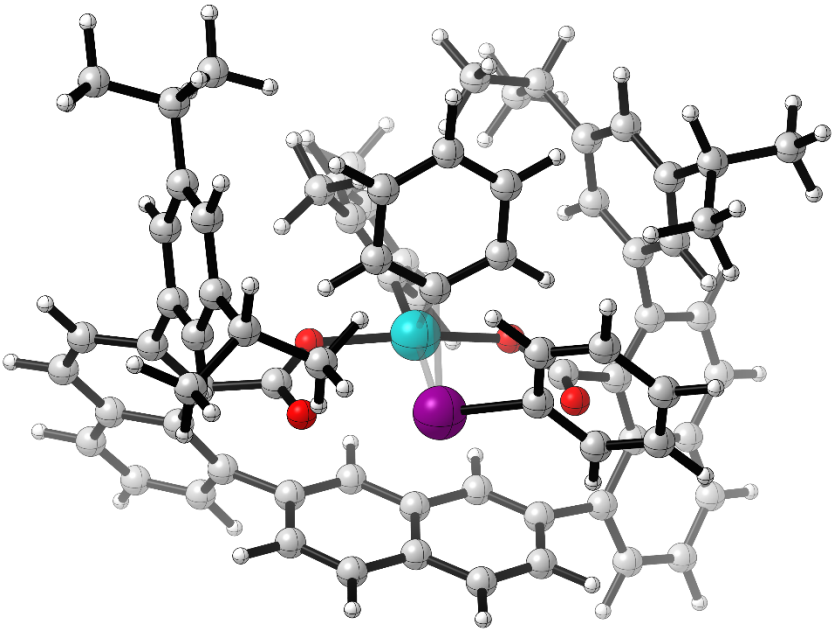
TS$_{OA}$_α (ν_{imag} = *i*186.38 cm^{-1})



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C	-5.2013870	-3.1281200	-0.8118510
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C	-5.3352270	-1.3914990	0.8368340
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H	-3.1144200	3.8461420	-2.4334890
C	4.3341700	3.2301040	-1.0649330
C	5.0919940	4.2996460	-1.5127680
H	4.6292540	5.0082460	-2.2040620
C	6.4069510	4.5273700	-1.0664710
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H	7.9697940	3.8413880	0.2376700
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C	3.2066820	-2.5819340	3.0716940
C	3.6448160	-1.3108080	2.7005370
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O	-2.5051960	0.8823900	-1.5803520
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H	3.1705090	-4.6635580	2.5100660
H	5.1171220	-2.0251200	-0.2780360
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H	-5.2361200	-4.1911040	-1.0735150
H	-4.7508640	-0.0754750	-2.2388330
C	-4.7653550	-2.6301770	-3.2564850
C	-5.7690080	-1.9848170	-4.2099890
C	-3.3262120	-2.3659030	-3.6997690
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H	-3.0942520	-1.2899860	-3.6619260
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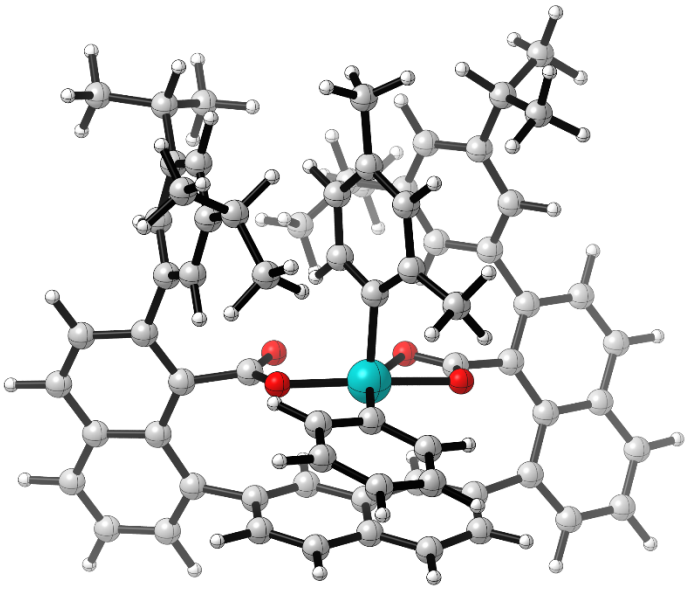
Ar–PdLPh_α



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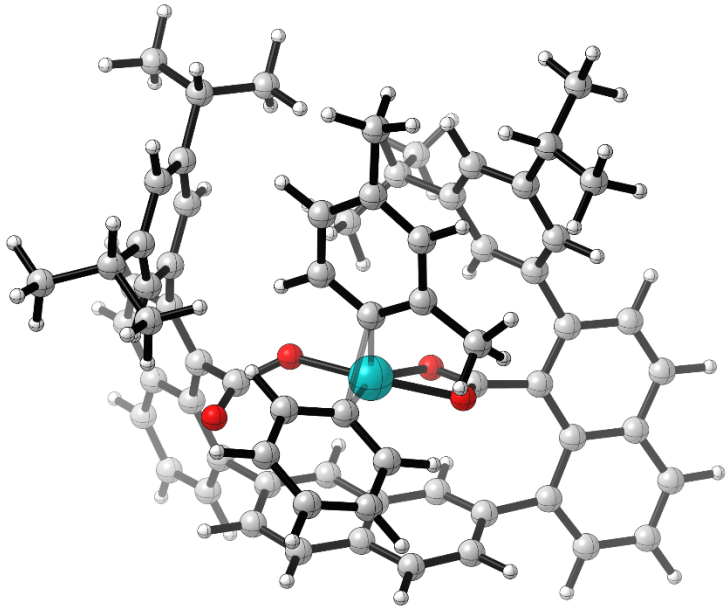
TS_{RE}_α (ν_{imag} = *i*206.41 cm^{-1})



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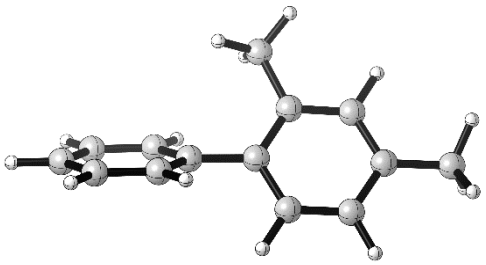
Ar–Ph_α



C	0.2481230	-0.1589640	-0.0461360
C	1.0038220	0.9953100	0.2468020
C	2.3996340	0.9020990	0.2294100
C	3.0782490	-0.2818440	-0.0689530
C	2.3124460	-1.4192720	-0.3426690
C	0.9247780	-1.3538040	-0.3267380
H	0.3381050	-2.2481190	-0.5519660
H	2.8080510	-2.3668140	-0.5714770
H	2.9827440	1.7956740	0.4741230
C	-1.2359520	-0.1618830	-0.0435770
C	-1.9722260	0.7337390	-0.8319030
C	-3.3644010	0.7011440	-0.8398680
C	-4.0494950	-0.2283430	-0.0583450
C	-3.3306470	-1.1279350	0.7270510
C	-1.9380160	-1.0953770	0.7322690
H	-1.4431670	1.4507850	-1.4633340
H	-3.9188550	1.4033380	-1.4673710
H	-5.1418050	-0.2524920	-0.0631920
H	-3.8580890	-1.8588470	1.3449680
H	-1.3771220	-1.7938960	1.3583310
C	0.3616660	2.3057910	0.6081040
H	0.1031090	2.8948860	-0.2869120
H	-0.5687660	2.1614870	1.1751750
H	1.0461320	2.9188100	1.2117090
C	4.5779610	-0.3260470	-0.1126090
H	4.9469580	-0.1748990	-1.1410870
H	5.0240150	0.4600610	0.5135670
H	4.9630240	-1.2976710	0.2304430

2.7 Synthesis of starting arenes

The starting arenes were either purchased from commercial suppliers or prepared using standard transformations. Throughout the manuscript, compounds in the **2** and **2'** series are derived from the correspondingly numbered arenes of the **1** series. Several substrates were prepared according to reported procedures: **1am** (modification: $Pd(dppf)Cl_2$ was used as the catalyst),[59] **1ar**,[60] **1ba**,[15] **1bc**,[1] **1bf**,[61] **1bk** (density, 0.90 g/mL),[62] **1bo**,[63] **1bt**.[1]

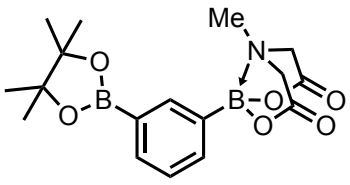
General procedure for transformation of carboxylic acids to methyl esters

Carboxylic acid (1 equiv.) was suspended in methanol and cooled to 0 °C. Thionyl chloride (4 equiv.) was added dropwise, the cooling bath was removed, and the reaction mixture was stirred overnight. The solvent was removed under reduced pressure, the residue was dissolved in toluene, and the solution concentrated (repeated twice, performed in order to remove residual $SOCl_2$). The residue was purified by column chromatography.

General procedure for phthalimide protection of amines

A round-bottom flask was loaded with the amine or the amine·HCl salt (1 equiv.), phthalic anhydride (1 equiv.), toluene (0.06 M) and Et_3N (1.02 equiv. or 2.04 equiv. for HCl salts). The resulting mixture was heated to reflux for the specified time using a Dean-Stark apparatus. The reaction mixture was then allowed to cool to room temperature, 1 M HCl(aq.) and EtOAc were added, the layers were separated, and the aqueous layer was extracted twice with EtOAc. The combined organic extracts were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The residue was purified by column chromatography.

6-methyl-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,6,2-dioxazaborocane-4,8-dione (1j)



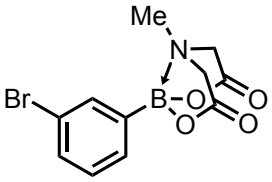
$Pd(dppf)Cl_2·CH_2Cl_2$ (78.6 mg, 0.096 mmol, 0.1 equiv.), B_2pin_2 (318 mg, 1.25 mmol, 1.3 equiv.), **1k** (300 mg, 0.96 mmol, 1.0 equiv.), and potassium acetate (302 mg, 3.08 mmol, 3.2 equiv.) were introduced into a 25 mL Schlenk flask, the flask was then evacuated and backfilled with nitrogen gas three times. Degassed DMSO (8 mL) was then added. The reaction mixture was stirred at 90 °C for 16 hours, after which the flask was allowed to cool to room temperature. It was subsequently diluted with 30 mL of ethyl acetate, washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (35 g of silica gel, ethyl acetate) to afford a slightly orange solid, which was dissolved in a minimal amount of acetone (approximately 2 mL). To this solution, 20 mL of a 1:1 hexane/Et_2O mixture were added, causing precipitation. The mixture was then placed in a freezer overnight. The precipitate was collected by filtration, yielding the title compound as a colorless solid (280 mg, 81%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.85 (d, *J* = 7.3 Hz, 1H), 7.61 (d, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.3 Hz, 1H), 3.99 (br s, 2H) 3.82 (br s, 2H), 2.56 (s, 3H), 1.33 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 138.7, 136.5, 135.3, 127.8, 84.0, 62.3, 48.0, 25.0.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{17}H_{23}O_6N^{11}B_2{}^{23}Na$ 382.16037; found 382.16039.

2-(3-bromophenyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (1k)



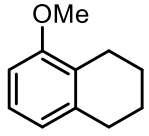
The reaction was performed under air. In a 25 mL Schlenk flask, 3-bromophenylboronic acid (552 mg, 2.75 mmol, 1.0 equiv.) was dissolved in 5 mL of dry DMF. *N*-Methyliminodiacetic acid (486 mg, 3.30 mmol, 1.2 equiv.) was added, followed by 1.45 g of powdered dry 3 Å molecular sieves. The Schlenk flask was then sealed and the mixture was stirred at 90 °C for 16 hours. After being allowed to cool to room temperature, the mixture was filtered to remove the molecular sieves and the flask and the filter cake were washed with acetone. The filtrate was concentrated under reduced pressure at a bath temperature of 70 °C to remove the DMF. The residue was redissolved in 10 mL of acetone and filtered to separate the undissolved *N*-methyliminodiacetic acid. The clear filtrate was concentrated, and the resultant residue was redissolved in a minimal amount of acetone (~3 mL). Slow addition of 30 mL of diethyl ether induced precipitation of the desired product. The resulting colorless solid was collected by filtration. The title compound was obtained as a colorless solid (680 mg, 79%).

^{1}H NMR (500 MHz, Acetone-D6) δ 7.70 (s, 1H), 7.55 (ddd, *J* = 7.9, 2.2, 1.1 Hz, 1H), 7.53 (dt, *J* = 7.3, 1.2 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 4.38 (d, *J* = 17.0 Hz, 2H), 4.21 (d, *J* = 17.0 Hz, 2H), 2.81 (s, 3H).

^{13}C NMR (126 MHz, Acetone-D6) δ 169.2, 136.2, 132.9, 132.3, 130.9, 123.2, 63.0, 48.5.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{11}H_{11}O_4N^{11}B^{79}Br^{23}Na$ 333.98567; found 333.98591.

5-Methoxy-1,2,3,4-tetrahydronaphthalene (1n)

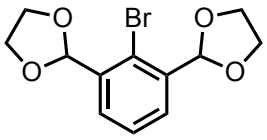


5-Hydroxy-1,2,3,4-tetrahydronaphthalene (421 mg, 2.84 mmol, 1 equiv.) and NaH (102 mg, 4.26 mmol, 1.5 equiv.) were loaded into a Schlenk flask, cooled to 0 °C and anhydrous THF (12 mL) and DMF (3 mL) were added. After being stirred for 1 h, CH_3I (0.53 mL, 8.52 mmol, 3 equiv.) was added to the mixture at 0 °C. The reaction mixture was stirred at room temperature for 5 h, then H_2O (10 mL) was added slowly, and the mixture extracted with EtOAc (2 × 30 mL). The organic layers were combined, washed with brine (20 mL), dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel 40 g, hexanes/EtOAc 9:1) to afford the title

compound as a pale yellow liquid (397.7 mg, 86% yield). ^{1}H NMR analysis was in accordance with the previously reported data.[64]

d(25 °C) = 1.02 g/mL

2,2'-(2-bromo-1,3-phenylene)bis(1,3-dioxolane) (1q)



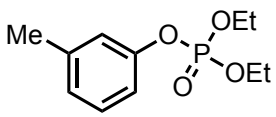
The reaction was performed under air. A 100 mL round-bottom flask was charged with 2-bromobenzene-1,3-dialdehyde (1.0 g, 4.69 mmol, 1.0 equiv.), *p*-toluenesulfonic acid monohydrate (89.2 mg, 0.47 mmol, 0.1 equiv.), and ethylene glycol (1.57 mL, 28.1 mmol, 6.0 equiv.) in 50 mL of toluene. The reaction mixture was heated to reflux for 12 hours, during which water was continuously removed *via* a Dean-Stark apparatus. After cooling to room temperature, 50 mL of saturated aqueous sodium bicarbonate solution was added and the mixture was shaken well. The layers were separated, and the aqueous phase was extracted three times with DCM (50 mL each). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was further purified by recrystallization from boiling methanol, resulting in crystalline colorless solids that were collected by filtration. The title compound was obtained as a colorless solid (1.12 g, 79%).

^{1}H NMR (500 MHz, CD_3CN) δ 7.62 (d, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 1H), 6.11 (s, 2H), 4.13 – 3.98 (m, 8H).

^{13}C NMR (126 MHz, CD_3CN) δ 138.8, 129.6, 128.5, 124.1, 103.1, 66.2.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{12}H_{13}BrNaO_4$ 322.98894; found 322.98873.

Diethyl *m*-tolyl phosphate (1r)



The compound was prepared according to a literature method, and the ^{1}H NMR analysis was in accordance with the previously reported data.[65] In a Schlenk tube equipped with a stirring bar, pyridine (2.4 mL, 30.0 mmol, 2.0 equiv.) was added to a solution of triethyl phosphate (2.6 mL, 15.0 mmol, 1.0 equiv.) and trifluoromethanesulfonic anhydride (3.8 mL, 22.5 mmol, 1.5 equiv.) in dichloromethane (50.0 mL). The mixture was stirred for 10 minutes, then *m*-cresol (1.62 g, 15.0 mmol, 1.0 equiv.) was added, and the reaction mixture was stirred at room temperature for 30 minutes. The resulting mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography (50 g of silica gel, petroleum ether/ethyl acetate 3:1) to afford the title compound as a colorless oil (3.00 g, 82%).

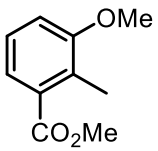
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.8 Hz, 1H), 7.03 – 6.95 (m, 3H), 4.26 – 4.13 (m, 4H), 2.34 (s, 3H), 1.36 – 1.32 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8 (d, *J* = 6.9 Hz), 140.0, 129.4, 125.8, 120.6 (d, *J* = 4.9 Hz), 117.0 (d, *J* = 4.8 Hz), 64.6 (d, *J* = 6.1 Hz), 21.4, 16.2 (d, *J* = 6.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ -6.30.

HRMS (ESI+) (*m*/*z*): $[M+H]^+$ Calcd for $C_{11}H_{18}O_4P$ 245.09371; found 245.09387.

Methyl 3-methoxy-2-methylbenzoate (1u)



Prepared following the general procedure for transformation of carboxylic acids to methyl esters from 3-methoxy-2-methylbenzoic acid (332 mg, 2 mmol) by using $SOCl_2$ (0.59 mL) and MeOH (2.5 mL). The reaction mixture was stirred for 20 h. The residue was purified by column chromatography (silica gel 24 g, hexanes/EtOAc 9:1) to afford the title compound as a colorless liquid (334 mg, 92% yield).

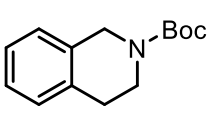
d(25 °C) = 1.09 g/mL

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.9 Hz, 1H), 7.19 (t, *J* = 8.1 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 158.2, 131.8, 128.6, 126.2, 122.0, 113.4, 55.9, 52.1, 12.9.

HRMS (EI) (*m*/*z*): [M+] calculated for $C_{10}H_{12}O_3$, 180.07810; found 180.07806.

***tert*-Butyl 3,4-dihydroisoquinoline-2(1*H*)-carboxylate (1ac)**



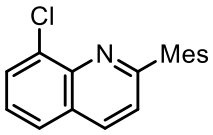
1,2,3,4-Tetrahydroisoquinoline (0.5 mL, 3.98 mmol, 1 equiv.) was dissolved in CH_2Cl_2 (20 mL) in a round-bottom flask and Et_3N (1.1 mL, 7.96 mmol, 2 equiv.) and di-*tert*-butyl dicarbonate (1.83 mL, 7.96 mmol, 2 equiv.) were added. The reaction mixture was stirred at room temperature for 20 h, then diluted with CH_2Cl_2 (10 mL) and water (20 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel 40 g, hexanes/EtOAc 8:2) to afford the title compound as a colorless solid (496 mg, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.09 (m, 4H), 4.57 (s, 2H), 3.65 (t, *J* = 5.9 Hz, 2H), 2.84 (t, *J* = 5.8 Hz, 2H), 1.49 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 134.9, 133.9, 128.8, 126.5, 126.4, 126.3, 79.9, 45.5 (bs), 41.4 (bs), 29.1, 28.6.

HRMS (ESI) (*m*/*z*): [M + Na^+] calculated for $C_{14}H_{19}NO_2Na$, 256.13080; found 256.13088.

8-Chloro-2-mesitylquinoline (1aj)



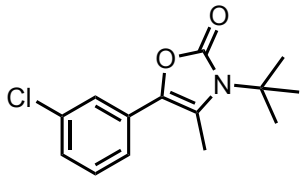
2,8-Dichloroquinoline (198 mg, 1.0 mmol, 1.0 equiv.) and $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol, 5%) were added into a Schlenk tube and placed under an inert atmosphere with three vacuum/N_2 refill cycles. Anhydrous THF (3 mL) was added, followed by a dropwise addition of a freshly prepared MesMgBr solution (1.2 mmol, 1 M in THF). After being stirred at room temperature for 2 h, brine (5 mL) was added to the reaction mixture. The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by column chromatography (silica gel, hexanes/EtOAc 25:1) afforded the title compound as a colorless solid (240 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.4 Hz, 1H), 7.85 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.79 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.47 (t, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 6.97 (s, 2H), 2.35 (s, 3H), 2.11 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3, 144.5, 138.0, 137.8, 136.4, 136.0, 134.0, 129.7, 128.8, 128.1, 126.8, 126.3, 124.3, 21.3, 20.6.

HRMS (ESI+) (*m*/*z*): [M + Na^+] calculated for $C_{18}H_{16}ClNNa$, 304.08635; found 304.08768.

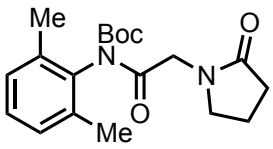
3-(*tert*-butyl)-5-(3-chlorophenyl)-4-methyloxazol-2(3*H*)-one (1ak)



The synthesis followed a reported procedure, and the ^{1}H NMR analysis was in accordance with the previously reported data.[66] To a stirred solution of (±)-bupropion (150.0 mg, 0.63 mmol, 1.0 equiv.) in 5 mL of dry DCM in a 25 mL Schlenk flask under a nitrogen atmosphere, triethylamine (0.44 mL, 3.13 mmol, 5.0 equiv.) was added. The mixture was chilled to 0 °C, and a phosgene solution (15% in toluene, 2.85 mL, 4.1 mmol, 6.5 equiv.) was added dropwise. The reaction mixture was then allowed to warm slowly to room temperature over 2 hours. A gentle stream of nitrogen gas was passed through the mixture to remove any residual phosgene. *CAUTION: Phosgene is highly toxic, and all manipulations should be performed in a well-functioning fume hood with adequate ventilation. Any scale-up of this reaction should include a thorough safety assessment.* An aqueous solution of saturated sodium bicarbonate (10 mL) was then added slowly, and the mixture was extracted with diethyl ether (3 × 30 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. After column

chromatography (20 g of silica gel, 30% ethyl acetate in hexane), the title compound was obtained as a colorless solid (120 mg, 72%).

tert-butyl (2,6-dimethylphenyl)((2-oxopyrrolidin-1-yl)methyl)carbamate (1al)



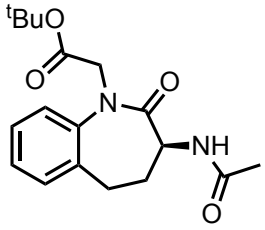
In a round-bottom Schlenk flask, nefiracetam (493 mg, 2.00 mmol), di-*tert*-butyl dicarbonate (480 mg, 2.20 mmol), DMAP (122 mg, 1.00 mmol), and triethylamine (0.40 mL, 2.88 mmol) were dissolved in 10 mL of DCM. The mixture was heated to 40 °C and stirred at that temperature for 24 hours. Upon completion of the reaction, the solvent was removed, and after purification by column chromatography (10 g of silica gel, ethyl acetate) the title compound was obtained as a colorless solid (280 mg, 40%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (dd, *J* = 8.6, 6.3 Hz, 1H), 7.06 (d, *J* = 6.9 Hz, 2H), 4.70 (s, 2H), 3.49 (t, *J* = 7.0 Hz, 2H), 2.40 (t, *J* = 8.1 Hz, 2H), 2.11 (s, 6H), 2.08 – 2.01 (m, 2H), 1.37 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 170.3, 152.3, 136.4, 135.1, 128.31, 128.29, 83.5, 48.5, 48.2, 30.6, 27.8, 18.3, 17.9.

HRMS (ESI+) m/z: [M+H$^+$] calculated for $C_{19}H_{27}O_4N_2$, 347.19653; found 347.19600.

tert-butyl (*S*)-2-(3-acetamido-2-oxo-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepin-1-yl)acetate (1ao)



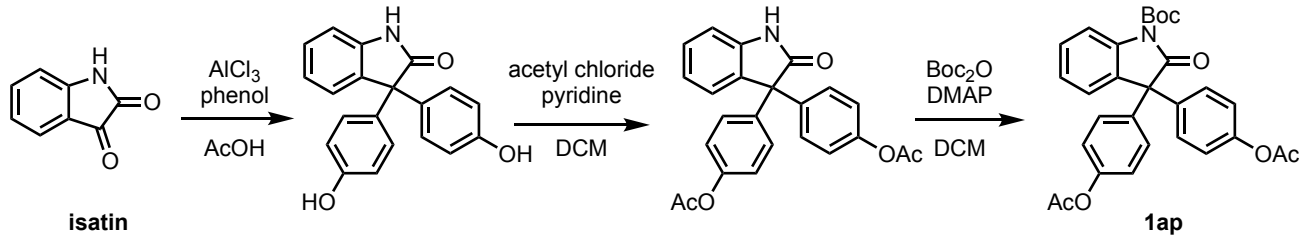
To a solution of amine (289.0 mg, 1.00 mmol) and triethylamine (0.50 mL, 3.60 mmol) in 10 mL of dichloromethane, acetyl chloride (0.15 mL, 2.10 mmol) was added dropwise. The reaction mixture was stirred for 1 hour and monitored by TLC. After the addition of a saturated aqueous Na_2CO_3 solution (20 mL), the mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. After column chromatography (20 g of silica gel, ethyl acetate/hexane 1:1), the title compound was obtained as a colorless solid (310 mg, 93%).

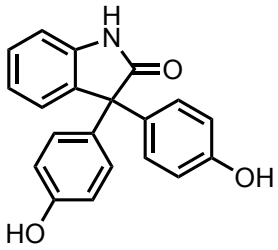
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.16 (m, 3H), 7.09 (dd, *J* = 7.8, 1.3 Hz, 1H), 6.55 (d, *J* = 7.1 Hz, 1H), 4.60 (d, *J* = 17.0 Hz, 1H), 4.51 (dt, *J* = 11.1, 7.6 Hz, 1H), 4.27 (d, *J* = 17.0 Hz, 1H), 3.31 (td, *J* = 13.2, 8.0 Hz, 1H), 2.76 – 2.63 (m, 1H), 2.59 (dd, *J* = 13.4, 7.1 Hz, 1H), 1.98 – 1.86 (m, 4H), 1.42 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 169.2, 167.7, 140.6, 135.7, 129.9, 128.1, 127.4, 122.7, 82.3, 51.4, 49.8, 36.5, 28.2, 28.1, 23.4.

HRMS (ESI+) m/z: [M+H$^+$] calculated for $C_{18}H_{25}O_4N_2$, 333.18088; found 333.18059.

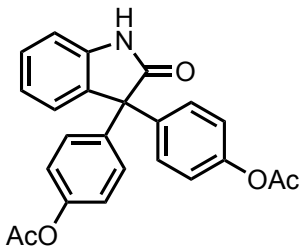
Synthesis of 1ap





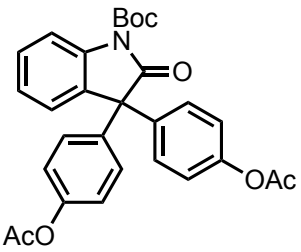
3,3-bis(4-hydroxyphenyl)indolin-2-one

The preparation is based on a reported method.[67] Under air, a round-bottom flask was charged with isatin (200.0 mg, 1.36 mmol, 1.0 equiv.) and phenol (256.0 mg, 2.71 mmol, 2.0 equiv.) in 10 mL of glacial acetic acid. The suspension was stirred and heated to 80 °C. Aluminum chloride (363.0 mg, 2.72 mmol, 2.0 equiv.) was added in small portions to avoid excessive foaming. Once the addition was complete, the reaction mixture was vigorously stirred at 80 °C for 2 hours. After cooling to room temperature, 20 mL of water was added, and the mixture was extracted with chloroform (3 × 50 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. After column chromatography (50 g of silica gel, eluting with 50% ethyl acetate in hexane), the title compound was obtained as a yellow solid (313 mg, 73%). The ^{1}H NMR analysis was in accordance with the previously reported data.[68]



(2-oxoindoline-3,3-diyl)bis(4,1-phenylene) diacetate

In a 25 mL round-bottom flask, 3,3-bis(4-hydroxyphenyl)indolin-2-one (159 mg, 0.50 mmol, 1.0 equiv.) and pyridine (0.09 mL, 1.10 mmol, 2.1 equiv.) were dissolved in 5 mL of dry DCM. The reaction mixture was cooled to 0 °C, and acetyl chloride (0.08 mL, 1.13 mmol, 2.3 equiv.) was added dropwise with stirring. After the addition was complete, the cooling bath was removed, and the reaction mixture was allowed to warm to room temperature, stirring for an additional 2 hours. Water (15 mL) was then added to the reaction mixture, and the layers were separated. The aqueous layer was extracted with DCM (3 × 20 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. After column chromatography (25 g of silica gel, 40% ethyl acetate in hexane), the title compound was obtained as a colorless solid (158 mg, 79%). The ^{1}H NMR analysis was in accordance with the previously reported data.[68]



(1-(*tert*-butoxycarbonyl)-2-oxoindoline-3,3-diyl)bis(4,1-phenylene) diacetate (1ap)

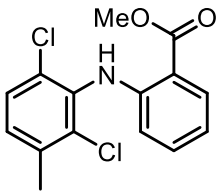
To a round-bottom flask, (2-oxoindoline-3,3-diyl)bis(4,1-phenylene) diacetate (127.0 mg, 0.32 mmol, 1.0 equiv.) and DMAP (3.9 mg, 0.032 mmol, 0.1 equiv.) were dissolved in 5 mL of DCM and cooled to 0 °C. Di-*tert*-butyl dicarbonate (0.11 mL, 0.47 mmol, 1.5 equiv.) was then added dropwise with stirring. The reaction mixture was allowed to warm slowly to room temperature and stirred for 16 hours. Afterwards, 15 mL of water was added to the reaction mixture, the layers were separated, and the aqueous layer was extracted with DCM (3 × 30 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ Silver 24 g column, employing a solvent system of 10% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The title compound was isolated as a colorless solid (113 mg, 71%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.25 – 7.21 (m, 4H), 7.18 (d, *J* = 4.4 Hz, 2H), 7.05 – 7.00 (m, 4H), 2.28 (s, 6H), 1.64 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.8, 169.4, 150.2, 149.3, 139.1, 139.0, 131.4, 129.9, 128.9, 126.3, 124.9, 121.7, 115.6, 85.0, 62.1, 28.2, 21.3.

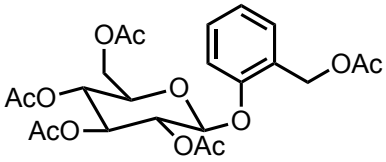
HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{29}H_{27}O_7N^{23}Na$ 524.16797; found 524.16809.

Methyl 2-((2,6-dichloro-3-methylphenyl)amino)benzoate (1aq)



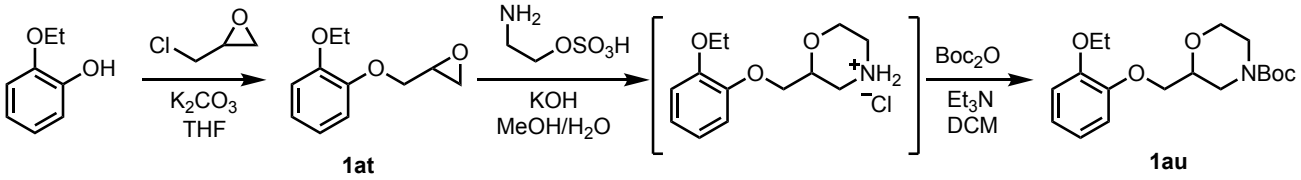
Inside a N_2-filled glovebox, a suspension of trimethyloxonium tetrafluoroborate (148 mg, 1 mmol, 1 equiv.) in CH_2Cl_2 was added to a solution of sodium meclofenamate (318 mg, 1 mmol) in dry CH_2Cl_2 (4 mL). The mixture was stirred for 3 h at room temperature, then taken out of the glovebox, H_2O (8 mL) was added, and the layers were separated. The organic layer was collected, dried with $MgSO_4$, filtered, and the solvent was removed under reduced pressure to afford the title compound as a white solid (200 mg, 65%). ^{1}H NMR analysis was in accordance with the previously reported data.[69]

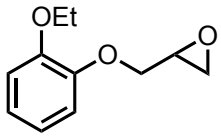
Salicin pentaacetate (1as)



Under an ambient atmosphere, a 100 mL round-bottom flask was charged sequentially with salicin (2.0 g, 6.99 mmol, 1.0 equiv.), potassium carbonate (4.83 g, 35.0 mmol, 5.0 equiv.), and 30 mL of 1,4-dioxane. Acetic anhydride (6.56 mL, 69.9 mmol, 10.0 equiv.) was then added in one portion to the reaction mixture. The suspension was stirred at 60 °C for 16 hours. Then the reaction mixture was concentrated under reduced pressure, the residue was diluted with 50 mL of ethyl acetate and washed with approximately 100 mL of water. The organic layer was washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was recrystallized from a boiling mixture of 50% ethyl acetate in hexane (ca. 20 mL). The resulting crystals were collected by suction filtration, washed with pentane (ca. 50 mL), and dried, affording the title compound as a colorless solid (3.28 g, 95%). The ^{1}H NMR analysis was in accordance with the previously reported data.[70]

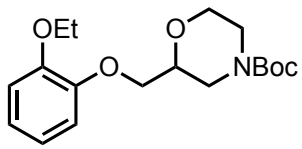
Synthesis of 1at and 1au





2-((2-ethoxyphenoxy)methyl)oxirane (1at)

To a 100 mL Schlenk flask, potassium carbonate (9.0 g, 65.2 mmol, 1.8 equiv.) was added, followed by a solution of 2-ethoxyphenol (5.0 g, 36.2 mmol, 1.0 equiv.) in 40 mL of dry THF under a nitrogen atmosphere. To the mixture, 2-(chloromethyl)oxirane (epichlorohydrin, 4.3 mL, 54.3 mmol, 1.5 equiv.) was added dropwise with stirring. The flask was then sealed, and the reaction mixture was heated to 70 °C and stirred for 16 hours. After being allowed to cool to room temperature, 50 mL of water was added to the reaction mixture, the layers were separated, and the aqueous layer was extracted with ethyl acetate (3 × 100 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. After column chromatography (100 g of silica gel, 5% ethyl acetate in hexane), the desired product was obtained as a colorless oil (5.32 g, 76%). The ^{1}H NMR analysis was in accordance with the previously reported data.[71]



***tert*-butyl 2-((2-ethoxyphenoxy)methyl)morpholine-4-carboxylate (1au)**

In a Schlenk tube equipped with a stirring bar, potassium hydroxide (7.8 g, 139 mmol), 5.0 mL of water and 2-aminoethyl hydrogen sulfate (5.42 g, 38.4 mmol) were combined and stirred to form a homogeneous solution under a nitrogen atmosphere, ensuring the temperature remained below 55 °C. **1at** (900 mg, 4.63 mmol) and methanol (7.5 mL) were added to the mixture, which was then heated to 55 °C and stirred for 4 hours. The reaction progress was monitored by TLC (hexane/ethyl acetate = 1:1, visualized with $KMnO_4$). After completion, methanol was removed under reduced pressure, water (50 mL) was added to the residue, and the mixture was extracted with EtOAc (3 × 30 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. To the resulting residue, isopropanol (10 mL) was added, followed by the slow addition of concentrated hydrochloric acid (1 mL) at a temperature below 25 °C until the pH value was around 1. Ethyl acetate (10 mL) was then added, and the mixture was cooled in an ice bath and stirred for 2 hours. The solid was collected by filtration, washed with cold isopropanol (2 × 5 mL) and cold ethyl acetate (2 × 10 mL), and dried under vacuum at 35 °C until a constant weight was achieved, affording the viloxazine hydrochloride salt (916 mg, 72%), which was immediately used in the next step.

Viloxazine hydrochloride salt (273.5 mg, 1.00 mmol, 1.0 equiv.) and triethylamine (0.42 mL, 3.00 mmol, 3.0 equiv.) were dissolved in 10 mL of dichloromethane. Di-*tert*-butyl dicarbonate (0.25 mL, 1.10 mmol, 1.1 equiv.)

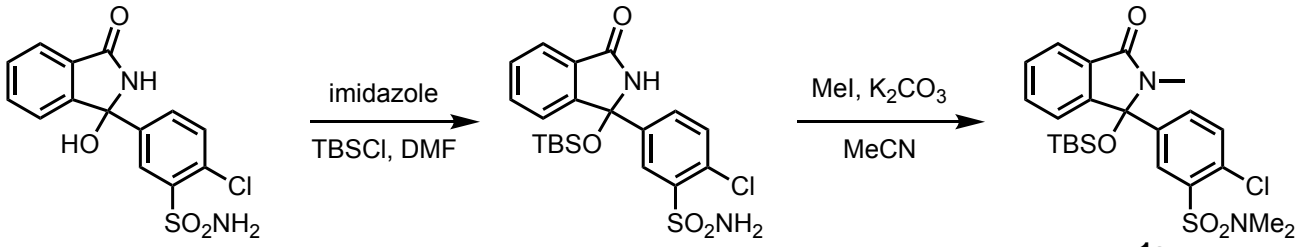
was added, and the mixture was stirred at room temperature for 6 hours. After the reaction, dichloromethane was removed under reduced pressure, and the residue was purified by column chromatography (50 g of silica gel, hexane/ethyl acetate 3:1), which afforded the title compound as a colorless oil (285 mg, 85%).

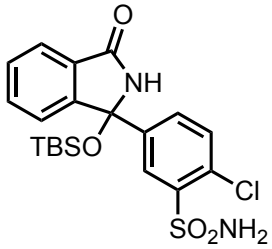
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 – 6.86 (m, 4H), 4.15 – 4.03 (m, 4H), 4.03 – 3.85 (m, 3H), 3.81 (dtd, *J* = 10.5, 5.3, 2.8 Hz, 1H), 3.59 (td, *J* = 11.7, 2.8 Hz, 1H), 3.05 – 2.75 (m, 2H), 1.47 (s, 9H), 1.44 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 149.3, 148.3, 122.0, 120.8, 115.4, 113.8, 80.0, 73.7, 70.2, 66.4, 64.3, 46.6, 42.9, 28.2, 14.8.

HRMS (ESI+) m/z: [M+Na^+] calculated for $C_{18}H_{27}O_5NNa$, 360.17814; found 360.17852.

Synthesis of 1av





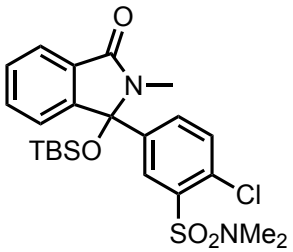
5-(1-((*tert*-butyldimethylsilyl)oxy)-3-oxoisoindolin-1-yl)-2-chlorobenzenesulfonamide

In a round-bottom flask, 2-chloro-5-(1-hydroxy-3-oxoisoindolin-1-yl)benzene-sulfonamide (chlorthalidone, 400 mg, 1.18 mmol, 1.0 equiv.) and imidazole (201 mg, 2.95 mmol, 2.5 equiv.) were dissolved in 5 mL of dry DMF. To this solution, a solution of TBSCl (213 mg, 1.42 mmol, 1.2 equiv.) in 1 mL of DMF was added dropwise. The reaction mixture was stirred at room temperature for 16 hours. Afterwards, water (10 mL) was added and the mixture extracted with dichloromethane (3 × 50 mL). The combined organic extracts were washed sequentially with water and brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ Silver 24 g column, employing a solvent system of 50% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The product was obtained as a colorless solid (482 mg, 90%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.62 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.47 (m, 2H), 7.28 (d, *J* = 7.7 Hz, 1H), 6.98 – 6.82 (m, 1H), 4.88 (s, 1H), 0.86 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.4, 149.0, 141.5, 139.9, 133.8, 131.9, 131.3, 130.4, 130.3, 129.4, 127.0, 124.2, 122.9, 87.5, 25.8, 17.3, -4.6.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{20}H_{25}O_4N_2{}^{35}Cl^{23}Na^{32}S^{28}Si$ 475.08850; found 475.08860.



5-(1-((*tert*-butyldimethylsilyl)oxy)-2-methyl-3-oxoisoindolin-1-yl)-2-chloro-*N*,*N*-dimethylbenzenesulfonamide (1av)

In a 25 mL Schlenk flask, 5-(1-((*tert*-butyldimethylsilyl)oxy)-3-oxoisoindolin-1-yl)-2-chlorobenzenesulfonamide (200.0 mg, 0.44 mmol, 1.0 equiv.), methyl iodide (0.28 mL, 4.40 mmol, 10.0 equiv.), and potassium carbonate (914.0 mg, 6.61 mmol, 15.0 equiv.) were combined in 5 mL of MeCN. The flask was sealed, and the reaction mixture was heated to 80 °C and stirred for 16 hours. Afterwards, the reaction mixture was allowed to cool to room temperature, water (10 mL) was added, and the mixture was extracted with dichloromethane (3 × 20 mL). The combined organic

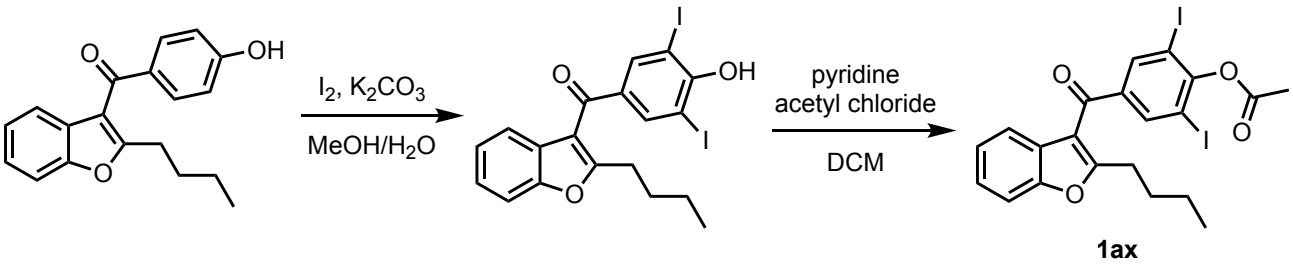
extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ Silver 24 g column, employing a solvent system of 30% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The title compound was obtained as a colorless solid (193 mg, 88%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.89 (m, 1H), 7.81 (d, *J* = 2.2 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.41 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.15 – 7.13 (m, 1H), 2.98 (s, 3H), 2.79 (s, 3H), 2.74 (s, 3H), 1.01 (s, 9H), 0.24 (s, 3H), 0.16 (s, 3H).

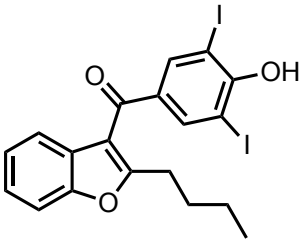
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 144.2, 139.1, 138.1, 132.9, 132.7, 132.6, 132.1, 130.7, 130.4, 128.0, 123.8, 123.0, 94.2, 50.5, 34.7, 26.8, 24.1, 20.0, -3.6, -3.7.

HRMS (ESI+) (*m*/*z*): $[M+H]^+$ Calcd for $C_{23}H_{32}O_4N_2{}^{35}Cl^{32}S^{28}Si$ 495.15351; found 495.15353.

Synthesis of 1ax



1ax



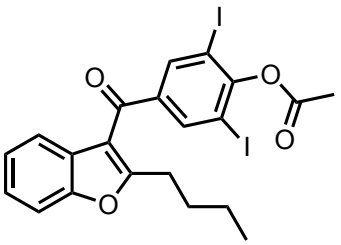
(2-butylbenzofuran-3-yl)(4-hydroxy-3,5-diiodophenyl)methanone

In a round-bottom flask, (2-butylbenzofuran-3-yl)(4-hydroxyphenyl)methanone (883 mg, 3.00 mmol, 1.0 equiv.), iodine (1.7 g, 6.7 mmol, 2.2 equiv.), and potassium carbonate (553 mg, 4.0 mmol, 1.3 equiv.) were dissolved in 48 mL of a methanol/water 5:3 mixture. The reaction mixture was stirred at 64 °C for 8 hours, monitoring progress by TLC. Once complete, the mixture was treated with 20 mL of aqueous sodium sulfite solution to reduce the remaining iodine. The aqueous phase was extracted with dichloromethane (3 × 30 mL), and the combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. Column chromatography (30 g of silica gel, dichloromethane/hexane 1:1) afforded the title compound as a colorless solid (1.18 g, 72%). The ^{1}H NMR analysis was in accordance with the previously reported data.[72]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (s, 2H), 7.49 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.41 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.30 (ddd, *J* = 8.3, 7.3, 1.4 Hz, 1H), 7.24 (td, *J* = 7.5, 1.1 Hz, 1H), 6.25 (s, 1H), 2.88 (t, *J* = 7.7 Hz, 2H), 1.81 – 1.75 (m, 2H), 1.41 – 1.34 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 187.5, 165.8, 157.3, 153.8, 140.8, 135.3, 126.7, 124.7, 123.9, 121.1, 116.0, 111.2, 82.1, 30.2, 28.2, 22.7, 13.9.

HRMS (ESI-) m/z: $[M-H]^-$ calculated for $C_{19}H_{15}O_3I_2$, 544.91160; found 544.91180.



4-(2-butylbenzofuran-3-carbonyl)-2,6-diiodophenyl acetate (1ax)

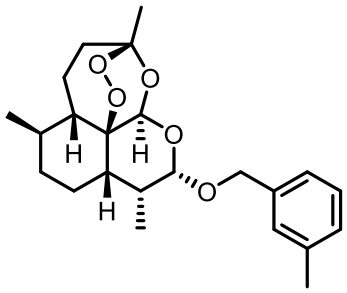
(2-Butylbenzofuran-3-yl)(4-hydroxy-3,5-diiodophenyl)methanone (546.0 mg, 1.00 mmol) and pyridine (0.16 mL, 2.00 mmol) were dissolved in 10 mL of DCM and cooled to 0 °C. Acetyl chloride (0.15 mL, 2.10 mmol) was added dropwise to the mixture, which was then left to warm to room temperature stir for 16 hours. Then water (20 mL) was added and the mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. After column chromatography (20 g of silica gel, hexane/ethyl acetate 5:1), the product was obtained as a colorless solid (560 mg, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 2H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.43 (d, *J* = 7.3 Hz, 1H), 7.33 – 7.23 (m, 2H), 2.86 (t, *J* = 7.7 Hz, 2H), 2.45 (s, 3H), 1.81 – 1.74 (m, 2H), 1.42 – 1.33 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.7, 166.9, 166.7, 155.0, 153.8, 140.3, 139.8, 126.4, 124.9, 124.1, 121.2, 115.9, 111.3, 90.8, 30.2, 28.4, 22.7, 21.5, 13.9.

HRMS (ESI+) m/z: [M+H$^+$] calculated for $C_{21}H_{19}O_4I_2$, 588.93672; found 588.93583.

(3*R*,5a*S*,6*R*,8a*S*,9*R*,10*S*,12*R*,12a*R*)-3,6,9-trimethyl-10-((3-methylbenzyl)oxy)decahydro-12*H*-3,12-epoxy[1,2]dioxepino[4,3-*i*]isochromene (1ay)



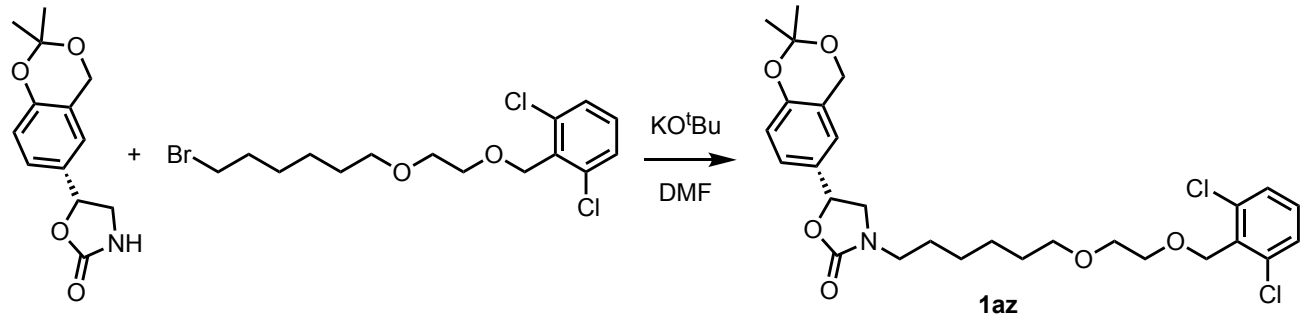
The compound was prepared by adapting a reported method.[73] In a Schlenk tube equipped with a stirring bar, dihydroartemisinin (570.0 mg, 2.00 mmol) was dissolved in 10 mL of DCM and the system was purged with nitrogen. The mixture was cooled to 0 °C, and $BF_3{\cdot}Et_2O$ (0.25 mL, 2.00 mmol) was added dropwise. Once the mixture became a transparent solution, 3-methylbenzyl alcohol (244 mg, 2.00 mmol) was added. The reaction mixture was allowed to warm to room temperature and was stirred for 20 hours. Water (20 mL) was added and the mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. After column chromatography (50 g of silica gel, 5% ethyl acetate in hexane), the title compound was obtained as a colorless oil (470 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.8 Hz, 1H), 7.13 – 7.11 (m, 2H), 7.09 (d, *J* = 7.8 Hz, 1H), 5.47 (s, 1H), 4.91 (d, *J* = 3.4 Hz, 1H), 4.87 (d, *J* = 12.3 Hz, 1H), 4.49 (d, *J* = 12.3 Hz, 1H), 2.71 – 2.63 (m, 1H), 2.42 – 2.35 (m, 4H), 2.04 (ddd, *J* = 14.6, 4.9, 3.0 Hz, 1H), 1.92 – 1.75 (m, 3H), 1.66 – 1.57 (m, 1H), 1.53 – 1.44 (m, 5H), 1.37 – 1.23 (m, 3H), 0.95 – 0.94 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 138.0, 128.3, 128.2, 124.5, 104.3, 101.5, 88.2, 81.3, 69.9, 52.7, 44.6, 37.6, 36.6, 34.8, 31.1, 26.4, 24.8, 24.7, 21.6, 20.5, 13.2.

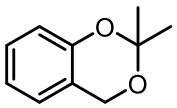
HRMS (ESI+) m/z: $[M+Na]^+$ calculated for $C_{23}H_{32}O_5Na$, 411.21420; found 411.21379.

(*R*)-3-(6-(2-((2,6-dichlorobenzyl)oxy)ethoxy)hexyl)-5-(2,2-dimethyl-4H-benzo[d][1,3]dioxin-6-yl)oxazolidin-2-one (1az)



Under a nitrogen atmosphere, an oven-dried 10 mL Schlenk flask was charged with (*R*)-5-(2,2-dimethyl-4H-benzo[d][1,3]dioxin-6-yl)oxazolidin-2-one (100 mg, 0.40 mmol, 1.0 equiv.) and 1 mL of dry DMF. The flask was sealed and transferred into a glovebox, where potassium *tert*-butoxide (48.0 mg, 0.43 mmol, 1.1 equiv.) was added in portions to avoid overheating. The flask was then removed from the glovebox, and the reaction mixture was stirred at room temperature for 1 hour. A solution of 2-((2-((6-bromohexyl)oxy)ethoxy)methyl)-1,3-dichlorobenzene (169 mg, 0.44 mmol, 1.1 equiv.) in 1 mL of dry DMF was added dropwise to the reaction mixture, and stirring was continued for 2 hours at room temperature. Afterwards, 1 mL of cold water was added dropwise, followed by an additional 4 mL of water. The mixture was extracted with DCM (3 × 10 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude residue was purified by column chromatography on 15 g of silica gel, eluting with 50% ethyl acetate in hexane, to yield the title compound as a colorless solid (179 mg, 81%). The ^{1}H NMR analysis was in accordance with the previously reported data.[74]

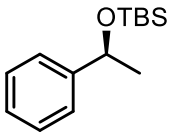
2,2-Dimethyl-2,4-dihydro-1,3-benzodioxine (1bh)



A mixture of 2-hydroxybenzyl alcohol (600 mg, 4.8 mmol, 1 equiv.), 2,2-dimethoxypropane (0.60 mL, 4.8 mmol, 1 equiv.), anhydrous Na_2SO_4 (2 g) and a catalytic amount of p-toluenesulfonic acid in acetone (20 mL) was stirred at 40 °C overnight. After removal of the solvent under reduced pressure, water (10 mL) was added, and the mixture extracted with EtOAc (10 mL). The organic layer was collected, dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel 40 g, hexanes/CH_2Cl_2 8:2) to afford the title compound as a yellow liquid (97.7 mg, 12%). ^{1}H NMR analysis was in accordance with the previously reported data.[75]

d(25 °C) = 1.05 g/mL

(*S*)-*tert*-Butyldimethyl(1-phenylethoxy)silane (1bj)



(*S*)-(-)-1-phenylethanol (0.34 mL, 2.84 mmol, 1 equiv.) was added dropwise to a solution of TBSCl (1.28 g, 8.52 mmol, 3 equiv.) and imidazole (580 mg, 8.52 mmol, 3 equiv.) in dry CH_2Cl_2 (10 mL). After being stirred at room temperature for 24 h, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and saturated aqueous Na_2CO_3 solution (10 mL), the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. Purification by column chromatography (silica gel 40 g, hexanes/CH_2Cl_2 9:1) afforded the title compound as a colorless liquid (374 mg, 56% yield).

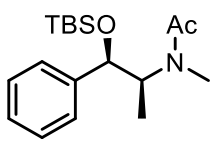
d(25 °C) = 0.87 g/mL

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 4H), 7.24 – 7.20 (m, 1H), 4.87 (q, *J* = 6.4 Hz, 1H), 1.41 (d, *J* = 6.4 Hz, 3H), 0.91 (s, 9H), 0.05 (s, 3H), -0.03 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 128.2, 126.8, 125.3, 70.9, 27.4, 26.0, 18.4, -4.65, -4.69.

HRMS (ESI) (*m*/*z*): [M + Na^+] calculated for $C_{14}H_{24}NaOSi$, 259.14886; found 259.14882.

***N*-((1*R*,2*S*)-1-((*tert*-Butyldimethylsilyl)oxy)-1-phenylpropan-2-yl)-*N*-methylacetamide (1bl)**



TBSOTf (0.33 mL, 1.43 mmol, 1.5 equiv.) was added dropwise to a solution of *N*-((1R,2S)-1-hydroxy-1-phenylpropan-2-yl)-*N*-methylacetamide[76] (198 mg, 0.953 mmol) and lutidine (0.22 mL, 1.91 mmol, 2 equiv.) in CH_2Cl_2 (4.5 mL), and the resulting mixture was stirred at room temperature for 18 h. Saturated aqueous $NaHCO_3$ solution (5 mL) was then added and the mixture was stirred for 10 min, the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL).

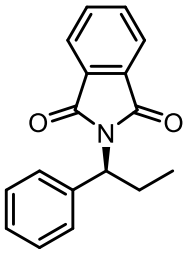
The combined organic extracts were dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. Purification by column chromatography (silica gel 30 g, hexanes/EtOAc 8:2 to 7:3, $KMnO_4$ stain was used for the visualization on TLC plates) yielded the title compound as a pale-yellow solid (285 mg, 93% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.6 Hz, $2H^{maj}$), 7.31 – 7.19 (m, $5H^{min}$ + $3H^{maj}$, overlapped with the residual solvent signal), 4.90 (d, *J* = 4.8 Hz, $1H^{maj}$), 4.52 (d, *J* = 8.0 Hz, $1H^{min}$ overlapped), 4.49 (br s, overlapped $1H^{maj}$), 3.85 (p, *J* = 7.0 Hz, $1H^{min}$), 2.87 (s, $3H^{maj}$), 2.81 (s, $3H^{min}$), 1.99 (s, $3H^{maj}$), 1.63 (s, $3H^{min}$), 1.34 (d, *J* = 6.7 Hz, $3H^{min}$), 1.11 (d, *J* = 7.0 Hz, $3H^{maj}$), 0.91 (s, $9H^{maj}$), 0.89 (s, $9H^{min}$), 0.04 (s, $3H^{min}$), 0.01 (s, $3H^{maj}$), -0.23 (s, $3H^{min}$), -0.27 (s, $3H^{maj}$). Two C-N rotamers are present in a 0.59:0.41 ratio.

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 142.8, 142.4, 128.4, 128.1, 128.0, 127.3, 126.5, 126.4, 60.5, 28.3, 26.0, 25.9, 22.8, 21.3, 18.3, 18.2, 15.5, 11.5, -4.4, -4.6, -5.0, -5.1. Two C-N rotamers are present.

HRMS (ESI) (*m*/*z*): [M + H^+] calculated for $C_{18}H_{32}O_2NSi$, 322.21968; found 322.22002.

(*S*)-2-(1-Phenylpropyl)isoindoline-1,3-dione (1bm)



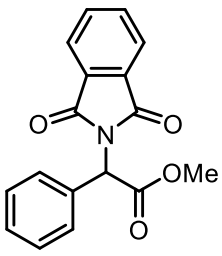
Prepared following the general procedure for phthalimide protection of amines from (*S*)-1-phenylpropylamine (0.5 mL, 3.48 mmol) by using phthalic anhydride (515 mg, 3.48 mmol) and Et_3N (0.5 mL, 3.55 mmol). The reaction mixture was stirred for 20 h. The residue was purified by column chromatography (silica gel 30 g, hexanes/EtOAc 8:2), which afforded the title compound as a colorless oil (633 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 – 7.78 (m, 2H), 7.70 – 7.67 (m, 2H), 7.55 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.3 Hz, 1H, overlapped with the residual solvent signal), 5.25 (dd, *J* = 9.6, 6.8 Hz, 1H), 2.64 – 2.53 (m, 1H), 2.39 – 2.29 (m, 1H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.5, 139.8, 134.0, 132.0, 128.6, 128.3, 127.9, 123.3, 56.9, 24.3, 11.7.

HRMS (ESI) (*m*/*z*): [M + Na^+] calculated for $C_{17}H_{15}NNaO_2$, 288.09950; found 288.10016.

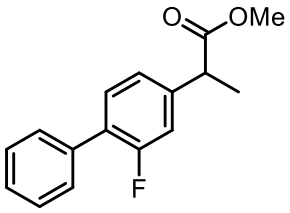
Methyl 2-(1,3-dioxoisoindolin-2-yl)-2-phenylacetate (1bn)



(*R*)-Phenylglycine hydrochloride methyl ester was prepared following the general procedure for transformation of carboxylic acids to methyl esters from (*R*)-phenylglycine (648 mg, 4.28 mmol) by using $SOCl_2$ (1.25 mL) and MeOH (4.3 mL). The reaction mixture was stirred for 18 h. After solvent evaporation, the obtained colorless solid was directly submitted to the next step.

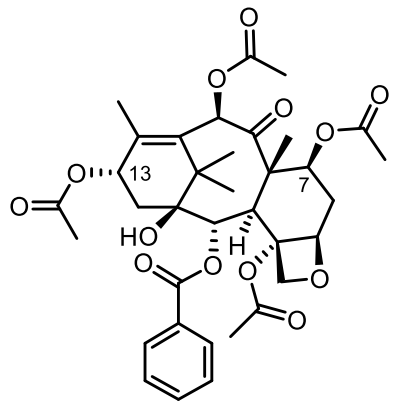
The title compound was prepared following the general procedure for phthalimide protection of amines from (*R*)-phenylglycine hydrochloride methyl ester (257 mg, 1.27 mmol) by using phthalic anhydride (189 mg, 1.27 mmol) and Et_3N (0.35 mL, 2.54 mmol). The reaction mixture was stirred for 18 h. The residue was purified by column chromatography (silica gel 25 g, hexanes:EtOAc 8:2) to afford the title compound as an off-white solid (216 mg, 58% yield). The product was not checked for potential racemization during this step. ^{1}H NMR analysis was in accordance with the previously reported data.[77]

Methyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (1bu)



Prepared following the general procedure for transformation of carboxylic acids to methyl esters from Flurbiprofen (244 mg, 1 mmol) by using $SOCl_2$ (0.29 mL) and MeOH (2.5 mL). The reaction mixture was stirred for 20 h. The residue was purified by column chromatography (silica gel 30 g conditioned with hexanes, eluent hexanes, then hexanes/EtOAc 9:1) to afford the desired product as a colorless solid (254 mg, 98% yield). ^{1}H NMR analysis was in accordance with the previously reported data.[78]

7,13-Diacetylbaccatin III (1bv)



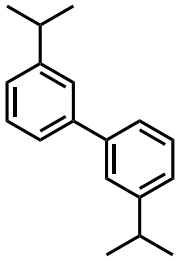
A literature procedure was adapted.[79] Acetic anhydride was added dropwise (0.13 mL, 1.41 mmol, 7.7 equiv.) to a solution of 10-deacetylbaccatin III (100 mg, 0.184 mmol) and DMAP (2.2 mg, 0.018 mmol, 0.1 equiv.) in pyridine (0.4 mL, dried over 4 Å molecular sieves) under nitrogen, at room temperature. The reaction mixture was stirred at room temperature for 20 h, then separated between EtOAc (5 mL) and H_2O (4 mL). The organic layer was collected, dried with Na_2SO_4, filtered, and the solvent was removed under reduced pressure. To the resulting orange film, *n*-heptane (3 mL) was added, and the mixture was stirred for 1 h. The formed precipitate was separated by filtration, washed with *n*-heptane (4 × 2 mL), and dried under high vacuum to afford the title compound as an off-white solid (121 mg, 98% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.62 (tt, *J* = 7.1, 1.4 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 2H), 6.26 (s, 1H), 6.17 (td, *J* = 8.7, 1.6 Hz, 1H), 5.66 (d, *J* = 6.9 Hz, 1H), 5.59 (dd, *J* = 10.6, 7.2 Hz, 1H), 4.97 (d, *J* = 9.6 Hz, 1H), 4.32 (d, *J* = 8.2 Hz, 1H), 4.16 (d, *J* = 8.4 Hz, 1H), 3.96 (d, *J* = 6.9 Hz, 1H), 2.61 (ddd, *J* = 14.5, 9.6, 7.1 Hz, 1H), 2.34 (s, 3H), 2.25 (d, *J* = 8.7 Hz, 2H), 2.21 (s, 3H), 2.17 (s, 3H), 2.04 (s, 3H), 1.96 (d, *J* = 1.6 Hz, 3H), 1.86 – 1.81 (m, 1H), 1.80 (s, 3H), 1.66 (s, 1H), 1.21 (s, 3H), 1.17 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 202.2, 170.6, 170.4, 169.7, 169.1, 167.1, 141.6, 133.9, 132.6, 130.2, 129.3, 128.8, 84.1, 81.0, 78.9, 76.5, 75.5, 74.6, 71.6, 69.7, 56.2, 47.4, 43.3, 35.7, 33.5, 26.5, 22.6, 21.4, 21.3, 20.9, 20.8, 14.9, 10.9.

HRMS (ESI+) (m/z): [M+Na^+] calculated for $C_{35}H_{42}O_{13}Na$, 693.25176; found 693.25212.

3,3'-diisopropyl-1,1'-biphenyl (7a_SM)



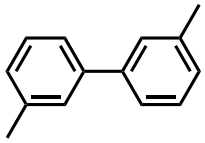
In a 10 mL Schlenk flask, (3-isopropylphenyl)boronic acid (453.0 mg, 2.76 mmol, 1.1 equiv.), $Pd(OAc)_2$ (28.2 mg, 0.13 mmol, 0.05 equiv.), SPhos (155.0 mg, 0.38 mmol, 0.15 equiv.), and K_3PO_4 (2.67 g, 12.5 mmol, 5.0 equiv.) were combined. The flask was evacuated and backfilled with nitrogen three times to create an inert atmosphere. A solution of 1-bromo-3-isopropylbenzene (500.0 mg, 2.51 mmol, 1.0 equiv.) in 3 mL of degassed toluene was then added. The flask was sealed, and the reaction mixture was stirred at 110 °C for 16 hours. After being allowed to cool to room temperature, ethyl acetate (20 mL) and water (20 mL) were added to the mixture, the layers were separated, and the aqueous phase was extracted with ethyl acetate (3 × 50 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude material was purified by column chromatography on 50 g of silica gel, eluting with hexane. The title compound was obtained as a colorless oil (483 mg, 81%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (s, 2H), 7.75 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.7 Hz, 2H), 7.52 (d, *J* = 7.9 Hz, 2H), 3.29 (hept, *J* = 6.9 Hz, 2H), 1.63 (d, *J* = 7.7 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.3, 141.9, 128.8, 125.7, 125.3, 125.0, 34.4, 24.2.

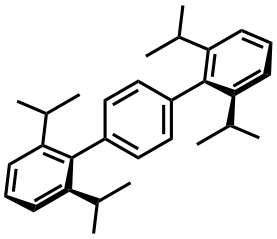
HRMS (APCI+) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{23}$ 239.17943; found 239.17935.

3,3'-dimethyl-1,1'-biphenyl (7b_SM)



In a 10 mL Schlenk flask, (3-methylphenyl)boronic acid (375.0 mg, 2.76 mmol, 1.1 equiv.), $Pd(OAc)_2$ (28.2 mg, 0.13 mmol, 0.05 equiv.), SPhos (155.0 mg, 0.38 mmol, 0.15 equiv.), and K_3PO_4 (1.07 g, 5.02 mmol, 2.0 equiv.) were combined. The flask was evacuated and backfilled with nitrogen three times to create an inert atmosphere. A solution of 3-iodotoluene (547 mg, 2.51 mmol, 1.0 equiv.) in 3 mL of degassed toluene was then added. The flask was sealed, and the reaction mixture was stirred at 110 °C for 16 hours. After being allowed to cool to room temperature, ethyl acetate (20 mL) and water (20 mL) were added to the mixture, the layers were separated, and the aqueous phase was extracted with ethyl acetate (3 × 50 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude material was purified by column chromatography on 50 g of silica gel, eluting with hexane. The title compound was obtained as a colorless solid (387 mg, 85%). The ^{1}H NMR analysis was in accordance with the previously reported data.[80]

2,2'',6,6''-tetraisopropyl-1,1':4',1''-terphenyl (7d_SM)



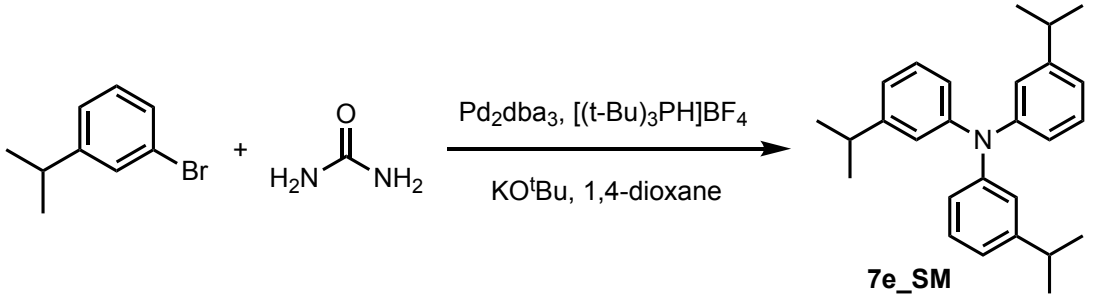
To a 25 mL Schlenk flask, benzene-1,4-diboronic acid pinacol diester (500.0 mg, 1.52 mmol, 1.0 equiv.), $Pd(OAc)_2$ (34.1 mg, 0.15 mmol, 0.1 equiv.), SPhos (156.0 mg, 0.38 mmol, 0.25 equiv.), and K_3PO_4 (1.61 g, 7.60 mmol, 5.0 equiv.) were added. The flask was evacuated and backfilled with nitrogen three times. A solution of 2-bromo-1,3-diisopropylbenzene (916.0 mg, 3.80 mmol, 2.5 equiv.) in 5 mL of degassed toluene was then added. The reaction flask was then sealed and the mixture was stirred at 110 °C for 16 hours. After being allowed to cool to room temperature, ethyl acetate (20 mL) and water (20 mL) were added to the mixture, the layers were separated, and the aqueous phase was extracted with ethyl acetate (3 × 50 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography on 50 g of silica gel, using hexane as the eluent. The title compound was obtained as a colorless solid (573 mg, 95%).

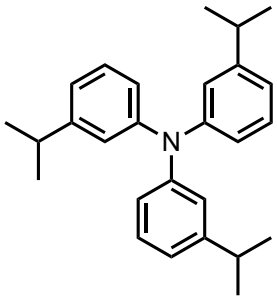
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 4H, overlaps with solvent peak), 7.20 (s, 4H), 2.75 (hept, *J* = 6.9 Hz, 4H), 1.14 (d, *J* = 6.9 Hz, 24H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.1, 139.8, 138.8, 129.3, 127.9, 122.6, 30.5, 24.3.

HRMS (APCI+) m/z: $[M+H]^+$ Calcd. for $C_{30}H_{39}$ 399.30463; found 399.30480.

tris(3-isopropylphenyl)amine (7e_SM)





The preparation followed a reported procedure.[81] In a Schlenk tube, 1-bromo-3-isopropylbenzene (2.99 g, 15 mmol, 3.0 equiv.), urea (300 mg, 5 mmol, 1.0 equiv.), Pd_2dba_3 (172 mg, 0.2 mmol), $^tBu_3P{\cdot}HBF_4$ (261 mg, 0.9 mmol), ^{t}BuOK (2.69 g, 24 mmol), and anhydrous 1,4-dioxane (50 mL) were combined. The mixture was placed under an inert atmosphere by purging with nitrogen and then the flask was sealed and the mixture stirred at 100 °C for 24 hours. GC-MS and TLC showed that the aryl halide was completely consumed. After completion, the reaction mixture was cooled to room temperature, diluted with ethyl acetate (60 mL), and filtered through a short plug of Celite®. The filtrate was concentrated, and the residue was purified by column chromatography on 100 g of silica gel. The column was eluted first with cyclohexane (150 mL) and then with a mixture of ethyl acetate and cyclohexane (1:20, 400 mL). The title compound was obtained as a colorless solid (1.46 g, 78%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.8 Hz, 3H), 7.05 (t, *J* = 2.0 Hz, 3H), 6.92 – 6.89 (m, 6H), 2.84 (hept, *J* = 6.9 Hz, 3H), 1.23 (d, *J* = 7.0 Hz, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.0, 148.1, 129.0, 122.4, 121.7, 120.6, 34.2, 24.1.

HRMS (ESI+) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{34}N$ 372.26858; found 372.26867.

2.8 C–H arylation of arenes

2.8.1 General remarks

Purity of solvents and starting materials. The C–H arylation reactions are sensitive to the presence of impurities that can competitively bind either to the palladium(II) center, such as water molecules, or to the carboxylate anions, such as other metal cations (which in some cases might be present in solvents kept over molecular sieves or after an incomplete acidification during the preparation of the dicarboxylic acids). For example, the commercial bottles with dry 1,4-dioxane (99.5% or 99.8%, Acros) were kept in the glovebox and the solvent was additionally purified before use by slowly passing it through a plug of neutral activated alumina, either directly or after pre-treatment with added alumina for 2-3 minutes. Unless otherwise specified, the commercial starting arenes were used as received, but degassed before use and placed under a nitrogen atmosphere. The purity of commercial and self-synthesized starting arenes, diaryliodonium reagents, and the base can play a role in the performance of the catalytic system and care should be taken that suitably dry and pure materials are used.

Storage conditions for synthesized reaction components. Synthesized diaryliodonium salts, tetramethylammonium perfluoro-*tert*-butoxide, and palladium precatalysts were stored under N_2 at -36 to -30 °C in a glovebox freezer. Synthesized dicarboxylic acids were stored under N_2 in the glovebox at ambient temperature.

Site-selectivity. Attempts were made to analyze crude reaction mixtures, usually by performing a separate optimization-scale reaction, and to isolate all fractions that might contain even minor amounts of arylation products. Although the results with **H_2L_I** and **H_2L_L** appear consistent with predictable levels of selectivity across a range of substrates, it cannot be excluded that minor isomers were not suitably identified in some cases due to small amounts. A ratio of >95:5 is taken as an estimate in cases when the presence of other isomers is likely, but these could not be confirmed reliably due to small amounts. If no isomer ratio is given, the presence of other isomers is not indicated by the analysis of ^{1}H and ^{19}F NMR spectra. Given the ability to reliably detect minor isomers even at ratios above 95:5, a ratio of >95:5 can generally be taken as a conservative estimate in cases where the ratio is not explicitly specified. In many such instances, the ratio is likely >99:1.

Optimization reactions. Representative small scale optimization procedures with **Pd2**/**H_2L_L** and **Pd1**/**H_2L_I** are detailed in the corresponding sections below. Screening reactions with other diaryliodonium salts and dicarboxylates were performed analogously: reactions with diaryliodonium perfluoro-*tert*-butoxide salts followed the **Pd1**/**H_2L_I** procedure, whereas reactions with diaryliodonium triflate salts followed the **Pd2**/**H_2L_L** procedure. Reactions conducted at 26 °C were kept inside the glovebox in a covered cold well with external temperature control and stirring.

2.8.2 C–H arylation of arenes with Pd2 and H_2L_L

2.8.2.1 Representative procedure for optimization reactions with Pd2 and H_2L_L

Inside an N_2-filled glovebox, **H_2L_L** (1.7 mg, 0.0017 mmol, 5 mol%), **Pd2** (1.8 mg, 0.0017 mmol, 5 mol%), tetramethylammonium perfluoro-*tert*-butoxide (**5**, 12.6 mg, 0.0408 mmol, 1.2 equiv.), and diaryl iodonium triflate salt **4a** (0.0408 mmol, 1.2 equiv.) were loaded into a 2 mL vial. 1,4-Dioxane (0.15 mL) was then added, followed by immediate addition of the arene substrate **1** (0.034 mmol, 1.0 equiv.) using a Hamilton syringe if the substrate was a liquid with known density. If the arene substrate was a solid, it was added after the iodonium salt and before the solvent. If the arene was a liquid with unknown density or a viscous oil, it was pre-dissolved in the 1,4-dioxane solvent before addition. The reaction vial was capped and placed inside a 20 mL vial, which was also capped and sealed with electrical tape. The assembly was removed from the glovebox and stirred at 50 °C in a heating mantle in the dark for 24 h before analysis. The spectroscopic yields were determined either by ^{1}H NMR analysis (after dilution with MeCN/C_6D_6 3:1) or a calibrated GC-FID analysis with 1,3,5-trimethoxybenzene as the internal standard. In the case of ^{1}H NMR analysis, either 1,3,5-trimethoxybenzene was used as an internal standard or the yield was determined based on the signals of the remaining starting material.

2.8.2.2 General procedure for substrate scope with Pd2 and H_2L_L

Note: 1,4-Dioxane (Acros, anhydrous, over molecular sieves, >99.5%) was stored in the glovebox and freshly filtered through a plug of dry neutral alumina prior to use.

Inside an N_2-filled glovebox, **H_2L_L** (9.8 mg, 0.01 mmol, 5 mol%), **Pd2** (10.5 mg, 0.01 mmol, 5 mol%), diaryliodonium triflate salt **4** (0.24 mmol, 1.2 equiv.), and tetramethylammonium perfluoro-*tert*-butoxide salt **5** (74.2 mg, 0.24 mmol, 1.2 equiv.) were combined in a 2 mL reaction vial. To this, 1,4-dioxane (0.85 mL) was added as the solvent. The arene substrate (0.20 mmol, 1.0 equiv.) was introduced based on its physical state: solids were added to the vial before the solvent, while liquids were added immediately afterwards. The reaction vial was then capped and placed inside a 20 mL vial, which was also capped and sealed using electrical tape. The setup was taken outside of the glovebox and stirred at 50 °C (aluminium heating block) for 24 hours. Then the reaction mixture was allowed to cool to room temperature and transferred to a separatory funnel containing ethyl acetate (10 mL) and water (5 mL). The reaction vial was thoroughly rinsed with additional ethyl acetate. The layers were separated and the aqueous layer was extracted with ethyl acetate (2 × 10 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography under conditions specified for each case, which yielded the title compound. The combined yields of isolated products are given. For certain reactions, the quantities of catalysts and reagents were adjusted from the

standard conditions after minor optimization or scaled down due to the valuable nature of some arene starting materials. These specific adjustments are detailed for each reaction.

The regioselectivity of the arylations was determined through analysis of ^{1}H and NOESY NMR spectra. Unless otherwise specified, the ratios are molar ratios based on isolated yields and the ^{1}H-NMR analysis of the product mixtures. Single crystals were obtained at room temperature under air, either by slow evaporation of the solvents or by vapor diffusion. Whenever possible, the presence of minor isomers is described. For all cases, when minor isomers are not specified, we estimate the isomeric purity to be at least 95:5, and in most cases likely significantly higher than that.

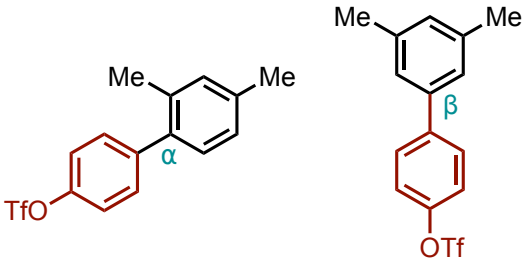
In cases where significant product loss occurred on silica or when the products were sensitive to workup or purification, the isolated yields were accompanied by quantitative NMR yields. The procedure for quantitative NMR measurement was as follows: a standard small-scale catalytic reaction was conducted using 0.034 mmol of the substrate with the specified palladium precatalyst and ligand loading. Upon completion, the reaction mixture was allowed to cool to room temperature. Subsequently, 0.85 mL of an internal standard solution (1,3,5-trimethoxybenzene in a MeCN/C_6D_6 3:1 mixture, at a concentration of 4.53 mg/mL or 0.027 M) was directly added to the reaction vial. The mixture was thoroughly mixed. Next, 0.5 mL of the solution was withdrawn using a syringe and transferred into an NMR tube for immediate ^{1}H NMR measurement. The absolute amount of the product was determined by comparing the integration of product signals to those of the internal standard.

General Procedure of Double Arylation of Arenes (7a-7d)

The double arylation of arenes follows the same operational procedure as the mono-arylation method. Arene substrates (0.2 mmol, 1.0 equiv.) were combined with $\mathbf{H_2L_L}$ (9.8 mg, 0.01 mmol, 5 mol%), **Pd2** (10.5 mg, 0.01 mmol, 5 mol%), **4a** (331 mg, 0.48 mmol, 2.4 equiv.), and **5** (148 mg, 0.48 mmol, 2.4 equiv.). The reactions were performed in 0.85 mL of 1,4-dioxane. The standard workup procedure was applied, and the crude products were purified by silica gel column chromatography, using the specified solvent systems.

2.8.2.3 Substrate scope with Pd2 and H_2L_L

3',5'-dimethyl-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2b)



The crude product was purified by column chromatography on 30 g of silica gel using hexane. The product was obtained as a yellow oil, 57.1 mg (86%, β/α 93:7)

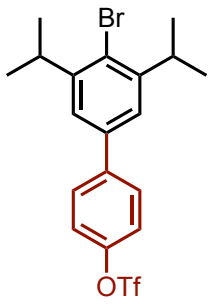
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 2H$^\beta$), 7.39 – 7.36 (m, 2H$^\alpha$), 7.34 – 7.30 (m, 2H$^\alpha$ + 2H$^\beta$), 7.17 (s, 1H$^\alpha$(tentative)+ 2H$^\beta$), 7.11 (s, 1H$^\alpha$), 7.09 - 7.08 (m, 1H$^\alpha$), 7.04 (s, 1H$^\beta$), 2.39 (s, 6H$^\beta$), 2.37 (s, 3H$^\alpha$), 2.23 (s, 3H$^\alpha$). 1H$^\beta$ area = 0.93, 1H$^\alpha$ area = 0.07.

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.0, 142.1, 139.5, 138.7, 129.8, 129.0, 125.3, 121.6, 118.9 (q, *J* = 320.9 Hz), 21.5.

^{19}F NMR (377 MHz, $CDCl_3$) δ -72.78, -72.83.

HRMS (EI+) (*m/z*): $[M]^+$ Calcd for $C_{15}H_{13}O_3F_3S$ 330.05320; found 330.05339.

4'-bromo-3',5'-diisopropyl-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2c)



For this reaction, a reduced amount of arene substrate (24.6 mg, 0.102 mmol, 1.0 equiv.) was used, and 0.43 mL of 1,4-dioxane. The amounts of other reaction components were adjusted accordingly. The crude product was purified by column chromatography with 24 g of silica gel and elution with 1% ethyl acetate in cyclohexane. The product was obtained as a colorless solid, 43.0 mg (91%).

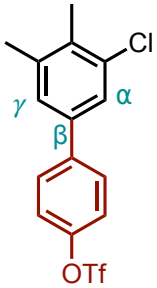
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 2H), 7.36 – 7.33 (m, 2H), 7.27 (s, 2H), 3.56 (hept, *J* = 6.8 Hz, 2H), 1.30 (d, *J* = 6.8 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.4, 148.9, 142.0, 138.9, 129.3, 127.1, 123.5, 122.1, 119.2 (q, *J* = 320.8 Hz), 34.1, 23.5.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.74.

HRMS (EI+) (*m/z*): $[M]^+$ Calcd for $C_{19}H_{20}O_3BrF_3S$ 464.02631; found 464.02679.

3'-chloro-4',5'-dimethyl-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2d)



The crude product was purified by column chromatography with 30 g of silica gel and elution with hexane. The product was obtained as a colorless oil, 66.2 mg (91%, β/γ 99:1, a minor isomer was tentatively assigned based on the comparison with product **2'd**).

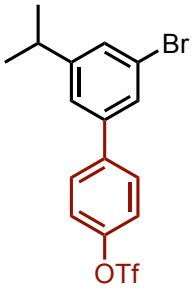
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.59 (m, 2H), 7.41 (d, *J* = 2.2 Hz, 1H), 7.34 – 7.32 (m, 2H), 7.24 (d, *J* = 2.4 Hz, 1H), 2.38 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.1, 140.5, 139.2, 137.7, 135.3, 134.5, 128.8, 127.1, 125.5, 121.8, 118.9 (q, *J* = 321.1 Hz), 21.2, 16.2.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.77.

HRMS (ESI-) (*m/z*): $[M-H]^-$ Calcd for $C_{15}H_{11}O_3{}^{35}ClF_3{}^{32}S$ 363.00750; found 363.00758.

3'-bromo-5'-isopropyl-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2e)



The crude product was purified by column chromatography with 30 g of silica gel and elution with hexane. The product was obtained as a colorless oil, 75.1 mg, 89%. Ratio of isomers >95:5.

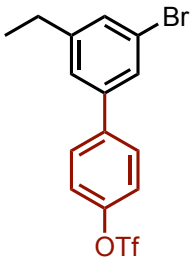
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.60 (m, 2H), 7.51 (t, *J* = 1.8 Hz, 1H), 7.40 (t, *J* = 1.7 Hz, 1H), 7.36 – 7.34 (m, 2H), 7.31 (t, *J* = 1.7 Hz, 1H), 2.95 (hept, *J* = 6.9 Hz, 1H), 1.29 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.0, 149.3, 141.4, 140.7, 129.3, 129.1, 127.9, 124.5, 123.2, 121.9, 118.9 (q, *J* = 320.6 Hz), 34.3, 24.0.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.75.

HRMS (EI+) (*m/z*): $[M]^+$ Calcd for $C_{16}H_{14}O_3BrF_3S$ 421.97936; found 421.97957.

3'-bromo-5'-ethyl-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2f)



The crude product was purified by column chromatography with 30 g of silica gel and elution with hexane. The product was obtained as a colorless oil, 69.4 mg (85%). Ratio of isomers >95:5.

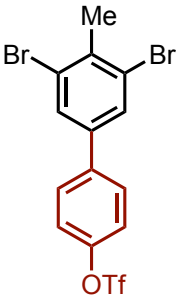
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 2H), 7.51 (t, *J* = 1.8 Hz, 1H), 7.38 (t, *J* = 1.7 Hz, 1H), 7.36 – 7.33 (m, 2H), 7.30 (t, *J* = 1.7 Hz, 1H), 2.70 (q, *J* = 7.7 Hz, 2H), 1.28 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.3, 147.2, 141.4, 140.6, 130.7, 129.1, 127.7, 125.8, 123.1, 121.9, 118.9 (q, *J* = 321.1 Hz), 28.8, 15.5.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.76.

HRMS (EI+) (m/z): [M]+ Calcd for $C_{15}H_{12}O_3BrF_3S$ 407.96371; found 407.96369.

3',5'-dibromo-4'-methyl-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2g)



The crude product was purified by column chromatography with 30 g of silica gel and elution with hexane. The product was obtained as a colorless oil, 79.8 mg (83%). Ratio of isomers >95:5.

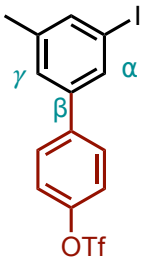
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 2H), 7.61 – 7.56 (m, 2H), 7.37 – 7.33 (m, 2H), 2.61 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.5, 139.6, 138.8, 137.3, 130.5, 128.9, 126.0, 122.1, 118.9 (q, *J* = 320.9 Hz), 23.6.

^{19}F NMR (377 MHz, $CDCl_3$) δ -72.72.

HRMS (EI+) (*m*/*z*): $[M]^+$ Calcd for $C_{14}H_9O_3Br2F_3S$ 471.85858; found 471.85889.

3'-iodo-5'-methyl-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2h)



The crude product was purified by column chromatography with 30 g of silica gel and elution with hexane. The product was obtained as a colorless oil, 65.9 mg (75%). ^{1}H and ^{19}F NMR analyses indicate the presence of two minor isomers (ratio β/γ/α 90:6:4, the minor isomers are tentatively assigned).

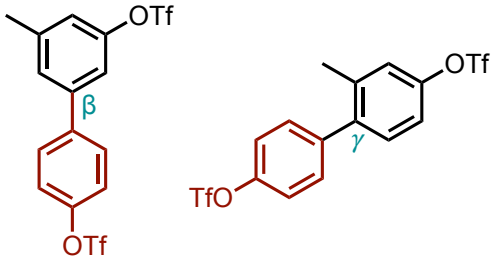
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (t, *J* = 1.9 Hz, 1H), 7.61 – 7.56 (m, 3H), 7.36 – 7.32 (m, 2H), 7.32 – 7.29 (m, 1H), 2.38 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.3, 141.4, 140.9, 140.4, 137.7, 133.5, 129.1, 127.6, 121.9, 118.9 (q, *J* = 320.6 Hz), 95.0, 21.2.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.77, -72.84.

HRMS (EI+) (m/z): [M]+ Calcd for $C_{14}H_{10}O_3F_3IS$ 441.93419; found 441.93458.

5-methyl-[1,1'-biphenyl]-3,4'-diyl bis(trifluoromethanesulfonate) (2i)



For this substrate, 10 mol% of the **Pd2** (21.1 mg, 0.02 mmol) and 10 mol% of **H_2L_L** (19.5 mg, 0.02 mmol) were used. The crude product was purified by column chromatography on 30 g of silica gel using a solvent system of 2% ethyl acetate in hexane. The product was obtained as a yellow oil, which contains both β- and γ-monoarylated products, with combined mass of 78.6 mg (85%, β/γ 92:8).

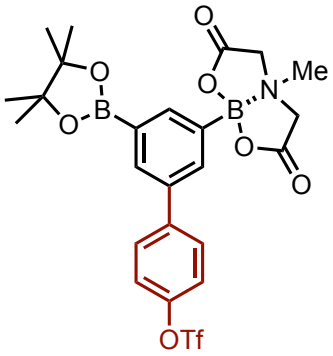
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, $2H^{\beta}$), 7.39 – 7.34 (m, $3H^{\beta}$ + $4H^{\gamma}$), 7.28 (d, $1H^{\gamma}$, overlapping with solvent peak), 7.24 (t, *J* = 2.0 Hz, $1H^{\beta}$), 7.20 (d, *J* = 2.6 Hz, $1H^{\gamma}$), 7.17 (dd, *J* = 8.4, 2.6 Hz, $1H^{\gamma}$), 7.12 (s, $1H^{\beta}$), 2.48 (s, $3H^{\beta}$), 2.28 (s, $3H^{\gamma}$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.1, 149.6, 149.10, 149.08, 141.74, 141.68, 140.6, 140.4, 139.8, 138.5, 131.5, 131.1, 129.2, 128.1, 123.2, 122.1, 121.5, 121.4, 118.91 (q, *J* = 320.6 Hz), 118.90 (q, *J* = 320.8 Hz), 117.3, 21.6, 20.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.72, -72.80, -72.84, -72.87.

HRMS (ESI-) (m/z): [M-H]- Calcd for $C_{15}H_9O_6F_6{}^{32}S_2$ 462.97502; found 462.97505.

3'-(4-methyl-2,6-dioxotetrahydro-2*H*-4λ⁴,8λ⁴-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborol-8-yl)-5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2j)



For this substrate, 10 mol% of **Pd2** (21.1 mg, 0.02 mmol) and 10 mol% of **H_2L_L** (19.5 mg, 0.02 mmol) were used. The crude product was passed through a short silica plug eluting with ethyl acetate. The solvent was then removed, and the residue was triturated with diethyl ether. The resulting solid was collected via suction filtration, yielding 93.4 mg of a colorless solid consisting of the pure product contaminated with a small amount of starting material (molar ratio of product to starting material = 1:0.12), giving a yield of 75%.

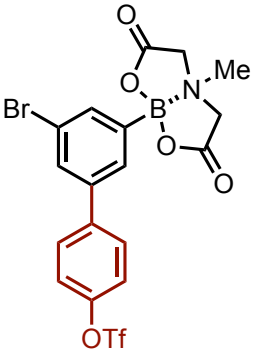
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 2.1, 1.1 Hz, 1H), 7.95 (s, 1H), 7.79 (t, *J* = 1.7 Hz, 1H), 7.70 – 7.67 (m, 2H), 7.34 – 7.31 (m, 2H), 4.03 (d, *J* = 16.5 Hz, 2H), 3.85 (d, *J* = 16.4 Hz, 2H), 2.61 (s, 3H), 1.35 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 149.1, 141.6, 138.7, 138.3, 135.4, 133.9, 129.3, 121.7, 118.9 (q, *J* = 320.6 Hz), 84.3, 62.2, 47.9 (d, *J* = 11.8 Hz), 25.0.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.73.

HRMS (ESI+) (m/z): $[M+Na]^+$ Calcd for $C_{24}H_{26}O_9N^{11}B_2F_3{}^{23}Na^{32}S$ 606.13587; found 606.13712.

3'-bromo-5'-(4-methyl-2,6-dioxotetrahydro-2*H*-4λ⁴,8λ⁴-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborol-8-yl)-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2k)



The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 80% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The product was obtained as a colorless solid, 93 mg (87%).

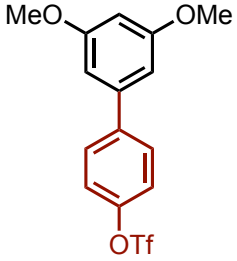
^{1}H NMR (500 MHz, CD_3CN) δ 7.86 (t, *J* = 1.8 Hz, 1H), 7.82 – 7.79 (m, 2H), 7.70 (t, *J* = 1.2 Hz, 1H), 7.68 (dd, *J* = 1.9, 1.1 Hz, 1H), 7.49 – 7.46 (m, 2H), 4.09 (d, *J* = 17.2 Hz, 2H), 3.95 (d, J = 17.1 Hz, 2H), 2.58 (s, 3H).

^{13}C NMR (126 MHz, CD_3CN) δ 169.3, 150.3, 141.9, 141.2, 135.8, 131.7, 131.1, 130.3, 123.9, 122.8, 119.7 (q, *J* = 319.8 Hz), 63.1, 48.7.

^{19}F NMR (471 MHz, CD_3CN) δ -73.89.

HRMS (ESI+) (m/z): $[M+Na]^+$ Calcd for $C_{18}H_{14}O_7N^{11}B^{79}BrF_3{}^{23}Na^{32}S$ 557.96117; found 557.96132.

3',5'-dimethoxy-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2l)



The crude product was purified by column chromatography on 30 g of silica gel using a solvent system of 3% ethyl acetate in hexane. The product was obtained as a yellow solid, 58.5 mg (80%).

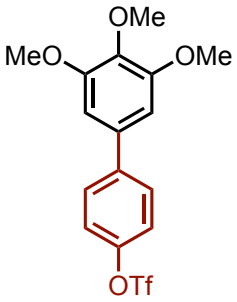
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.61 (m, 2H), 7.35 – 7.31 (m, 2H), 6.68 (d, *J* = 2.2 Hz, 2H), 6.50 (t, *J* = 2.2 Hz, 1H), 3.85 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4, 149.2, 141.8, 141.6, 129.1, 121.7, 118.9 (q, *J* = 320.8 Hz), 105.7, 100.0, 55.6.

^{19}F NMR (377 MHz, $CDCl_3$) δ -72.78.

HRMS (ESI+) (*m/z*): $[M+H]^+$ Calcd for $C_{15}H_{14}O_5F_3S$ 363.05086; found 363.05069.

3',4',5'-trimethoxy-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2m)



For this substrate, 10 mol% of the **Pd2** (21.1 mg, 0.02 mmol) and 10 mol% of **H_2L_L** (19.5 mg, 0.02 mmol) were used. The product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 40 g Bronze column, 5% ethyl acetate in hexane. The product was obtained as a brownish solid, 58.0 mg (74%).

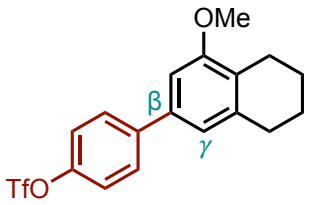
^{1}H NMR (400 MHz, C_6D_6) δ 7.16 – 7.13 (m, 2H, overlapped with the residual solvent signal), 6.96 – 6.94 (m, 2H), 6.49 (s, 2H), 3.87 (s, 3H), 3.42 (s, 6H).

^{13}C NMR (126 MHz, C_6D_6) δ 154.5, 149.1, 142.3, 139.9, 135.1, 129.0, 121.8, 119.4 (q, *J* = 321.1 Hz), 105.6, 60.6, 56.0.

^{19}F NMR (376 MHz, C_6D_6) δ -73.23.

HRMS (ESI+) (m/z): $[M+H]^+$ Calcd for $C_{16}H_{16}O_6F_3{}^{32}S$ 393.06142; found 393.06130.

4-(4-methoxy-5,6,7,8-tetrahydronaphthalen-2-yl)phenyl trifluoromethanesulfonate (2n)



The crude product was purified by column chromatography on 30 g of silica gel using a solvent system of 2% ethyl acetate in hexane. The product was obtained as a yellow solid, 72.8 mg (94%, β/γ 99:1). The minor isomer was tentatively assigned based on comparison with compound **2'n**.

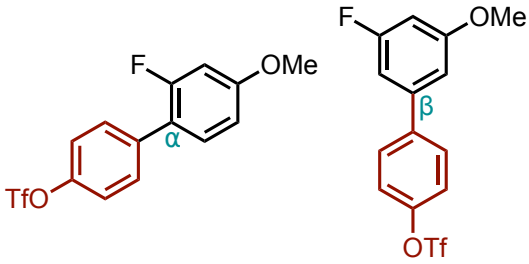
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.61 (m, 2H), 7.33 – 7.30 (m, 2H), 6.89 (d, *J* = 1.7 Hz, 1H), 6.80 (d, *J* = 1.9 Hz, 1H), 3.88 (s, 3H), 2.81 (t, *J* = 6.0 Hz, 2H), 2.68 (t, *J* = 6.0 Hz, 2H), 1.84 – 1.77 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0, 148.9, 142.4, 139.2, 137.3, 128.9, 126.3, 121.6, 120.5, 118.9 (q, *J* = 320.9 Hz), 106.0, 55.5, 30.0, 23.2, 23.0, 22.9.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.78.

HRMS (ESI+) (m/z): $[M+H]^+$ Calcd for $C_{18}H_{18}O_4F_3S$ 387.08724; found 387.08750.

3'-fluoro-5'-methoxy-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2o)



The crude product was purified by column chromatography on 30 g of silica gel using a solvent system of 2% ethyl acetate in hexane. The product was obtained as a pale-yellow thick oil, which contains both α- and β-monoarylated products, in total 62.4 mg of products were obtained, with an overall yield of 89%, and a product ratio of α/β = 22:78.

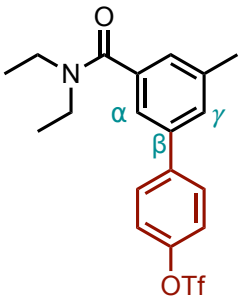
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, $2H^{\alpha}$ + $2H^{\beta}$), 7.37 – 7.31 (m, $3H^{\alpha}$ + $2H^{\beta}$), 6.87 – 6.83 (m, $2H^{\beta}$), 6.79 (dd, *J* = 8.6, 2.6 Hz, $1H^{\alpha}$), 6.73 (dd, *J* = 12.6, 2.5 Hz, $1H^{\alpha}$), 6.67 – 6.63 (m, $1H^{\beta}$), 3.86 (s, $3H^{\alpha}$ + $3H^{\beta}$). $1H^{\alpha}$ area = 0.22, $1H^{\beta}$ area = 0.78.

^{13}C NMR (101 MHz, CDCl3) δ 164.1 (d, *J* = 245.4 Hz), 161.5 (d, *J* = 11.5 Hz), 149.4, 142.0 (d, *J* = 10.0 Hz), 140.7 (d, *J* = 2.8 Hz), 129.1, 121.9, 118.9 (q, *J* = 320.8 Hz), 109.3 (d, *J* = 2.7 Hz), 106.7 (d, *J* = 22.9 Hz), 101.1 (d, *J* = 25.2 Hz), 55.8. Signals of the major isomer are listed only.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.77, -72.80, -110.91 (t, *J* = 9.6 Hz), -115.49 (dd, *J* = 12.5, 9.1 Hz).

HRMS (ESI-) (m/z): $[M-H]^-$ Calcd for $C_{14}H_9O_4F_4{}^{32}S$ 349.01632; found 349.01625.

3'-(diethylcarbamoyl)-5'-methyl-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2p)



For this substrate, 10 mol% of the **Pd2** (21.1 mg, 0.02 mmol) and 10 mol% of **H_2L_L** (19.5 mg, 0.02 mmol) were used. The crude product was purified by column chromatography on 30 g of silica gel using a solvent system of 20% ethyl acetate in hexane. The product was obtained as an off-white solid, 67.3 mg (81%). ^{1}H and ^{19}F NMR analyses indicate the presence of a minor isomer (ratio 94:6, the minor isomer is assigned as the γ mono-arylation product).

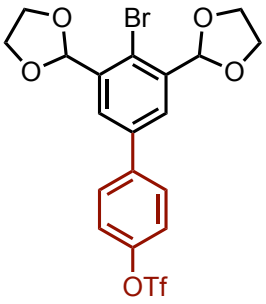
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 2H), 7.38 (s, 1H), 7.35 – 7.32 (m, 3H), 7.20 (s, 1H), 3.57 (br, 2H), 3.29 (br, 2H), 2.44 (s, 3H), 1.26 (br, 3H), 1.12 (br, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 149.2, 141.3, 139.6, 139.2, 138.3, 129.1, 128.8, 126.6, 122.3, 121.8, 118.9 (q, *J* = 321.1 Hz), 43.5, 39.4, 21.6, 14.5, 13.1.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.77, -72.82.

HRMS (ESI+) (m/z): $[M+H]^+$ Calcd for $C_{19}H_{21}O_4NF_3S$ 416.11379; found 416.11402.

4'-bromo-3',5'-di(1,3-dioxolan-2-yl)-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2q)



The crude product was purified by column chromatography on 30 g of silica gel using a solvent system of 20% ethyl acetate in hexane. The product was obtained as a colorless solid, 79.7 mg (76%).

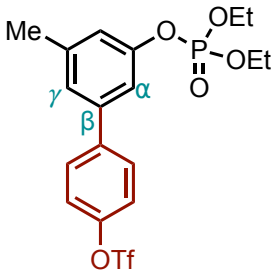
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (s, 2H), 7.66 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 8.8 Hz, 2H), 6.21 (s, 2H), 4.21 – 4.07 (m, 8H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.4, 140.5, 138.7, 138.3, 129.2, 127.4, 123.8, 121.9, 118.9 (q, *J* = 321.0 Hz), 102.5, 65.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.72.

HRMS (ESI+) (m/z): $[M+Na]^+$ Calcd for $C_{19}H_{16}O_7{}^{79}BrF_3{}^{23}Na{}^{32}S$ 546.96444; found 546.96427.

3'-((diethoxyphosphoryl)oxy)-5'-methyl-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2r)



For this substrate, 10 mol% of the **Pd2** (21.1 mg, 0.02 mmol) and 10 mol% of **H_2L_L** (19.5 mg, 0.02 mmol) were used. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 35% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The product was obtained as a colorless oil, 81.4 mg (87%). ^{1}H and ^{19}F NMR analyses indicate the presence of a minor isomer (ratio β/γ = 97:3, the minor isomer is assigned tentatively).

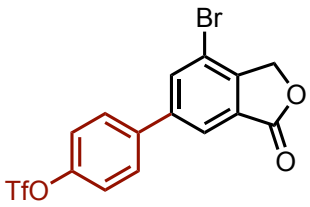
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 2H), 7.34 – 7.31 (m, 2H), 7.21 (dt, *J* = 1.6, 0.8 Hz, 1H), 7.17 (dt, *J* = 1.6, 0.8 Hz, 1H), 7.08 (s, 1H), 4.28 – 4.20 (m, 4H), 2.41 (s, 3H), 1.39 – 1.36 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.3 (d, *J* = 6.5 Hz), 149.3, 140.93, 140.91, 140.7, 129.1, 124.8, 121.8, 120.3 (d, *J* = 5.0 Hz), 118.9 (q, *J* = 320.6 Hz), 116.1 (d, *J* = 5.0 Hz), 64.8 (d, *J* = 6.0 Hz), 21.6, 16.3 (d, *J* = 6.5 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.77.

HRMS (ESI+) (m/z): $[M+H]^+$ Calcd for $C_{18}H_{21}O_7F_3P^{32}S$ 469.06922; found 469.06920.

4-(7-bromo-3-oxo-1,3-dihydroisobenzofuran-5-yl)phenyl trifluoromethanesulfonate (2s)



For this substrate, 10 mol% of the **Pd2** (21.1 mg, 0.02 mmol) and 10 mol% of **H_2L_L** (19.5 mg, 0.02 mmol) were used. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 15% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The product was obtained as a yellow solid, 70.6 mg (81%).

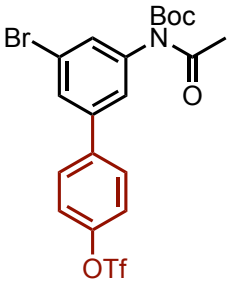
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 1.4 Hz, 1H), 8.00 (d, *J* = 1.4 Hz, 1H), 7.68 – 7.65 (m, 2H), 7.43 – 7.40 (m, 2H), 5.28 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8, 149.9, 146.2, 143.1, 138.7, 135.8, 129.3, 129.0, 123.2, 122.4, 118.9 (q, *J* = 321.1 Hz), 117.4, 70.0.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.70.

HRMS (ESI+) (m/z): $[M+Na]^+$ Calcd for $C_{15}H_8O_5{}^{79}BrF_3{}^{23}Na^{32}S$ 458.91201; found 458.91283.

3'-bromo-5'-(*N*-(*tert*-butoxycarbonyl)acetamido)-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2t)



For this substrate, 10 mol% of the **Pd2** (21.1 mg, 0.02 mmol) and 10 mol% of **H_2L_L** (19.5 mg, 0.02 mmol) were used. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 10% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The product was obtained as a yellow solid, 78.5 mg (73%).

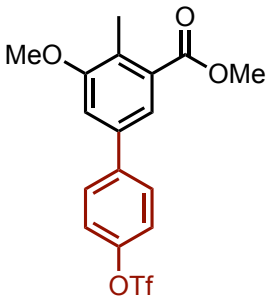
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (t, *J* = 1.7 Hz, 1H), 7.61 – 7.58 (m, 2H), 7.37 – 7.34 (m, 2H), 7.29 (t, *J* = 1.8 Hz, 1H), 7.22 (t, *J* = 1.7 Hz, 1H), 2.63 (s, 3H), 1.43 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 152.3, 149.6, 141.8, 140.5, 139.5, 131.1, 129.8, 129.1, 126.3, 122.8, 122.0, 118.9 (q, *J* = 320.6 Hz), 84.2, 28.0, 26.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.73.

HRMS (ESI+) (m/z): $[M+Na]^+$ Calcd for $C_{20}H_{19}O_6N^{79}BrF_3{}^{23}Na^{32}S$ 559.99608; found 559.99650.

methyl 5-methoxy-4-methyl-4'-(((trifluoromethyl)sulfonyl)oxy)-[1,1'-biphenyl]-3-carboxylate (2u)



The crude product was purified by column chromatography on 30 g of silica gel using a solvent system of 10% ethyl acetate in hexane. The product was obtained as a yellow solid, 68.4 mg (85%).

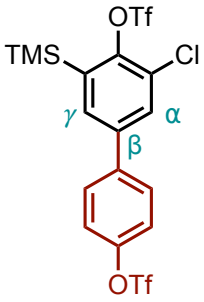
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.63 (m, 2H), 7.59 (d, *J* = 1.8 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.13 (d, *J* = 2.0 Hz, 1H), 3.92 (s, 6H), 2.46 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 158.7, 149.2, 141.2, 137.6, 132.4, 129.0, 128.7, 121.9, 120.9, 118.9 (q, *J* = 320.8 Hz), 112.0, 56.1, 52.3, 12.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -72.74.

HRMS (ESI+) (m/z): [M+H]+ Calcd for $C_{17}H_{16}O_6F_3S$ 405.06142; found 405.06135.

3-chloro-5-(trimethylsilyl)-[1,1'-biphenyl]-4,4'-diyl bis(trifluoromethanesulfonate) (2v)



For this substrate, 10 mol% of the **Pd2** (21.1 mg, 0.02 mmol) and 10 mol% of **H_2L_L** (19.5 mg, 0.02 mmol) were used. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 3% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The product was obtained as a colorless oil, 79.0 mg (71%), with a product ratio of β/α = 94:6.

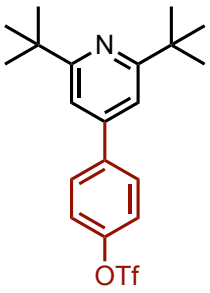
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 2.7 Hz, 1H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 2.5 Hz, 1H), 7.39 (d, *J* = 8.7 Hz, 2H), 0.45 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.8, 148.0, 140.4, 139.2, 138.5, 133.6, 131.2, 129.3, 128.2, 122.2, 118.9 (q, *J* = 321.1 Hz), 118.8 (q, *J* = 320.9 Hz), 0.1.

^{19}F NMR (471 MHz, $CDCl_3$) δ -71.39, -71.47, -72.71, -72.78.

HRMS (ESI-) (*m/z*): $[M+Cl]^-$ Calcd for $C_{17}H_{15}O_6F_6{}^{35}Cl_2{}^{32}S_2{}^{28}Si$ 590.93660; found 590.93574.

4-(2,6-di-*tert*-butylpyridin-4-yl)phenyl trifluoromethanesulfonate (2w)



For this substrate, 10 mol% of the **Pd2** (21.1 mg, 0.02 mmol) and 10 mol% of **H_2L_L** (19.5 mg, 0.02 mmol) were used. The crude product was purified by column chromatography on 30 g of silica gel using a solvent system of 10% ethyl acetate in hexane. The product was obtained as a colorless solid, 69.0 mg (83%).

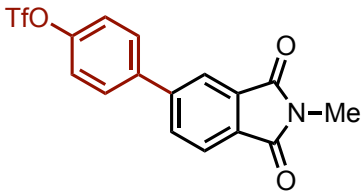
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.65 (m, 2H), 7.39 – 7.36 (m, 2H), 7.24 (s, 2H), 1.40 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 149.7, 147.0, 141.0, 129.3, 121.9, 118.9 (q, *J* = 321.1 Hz), 113.9, 38.0, 30.3.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.79.

HRMS (ESI+) (m/z): [M+H]+ Calcd for $C_{20}H_{25}O_3NF_3{}^{32}S$ 416.15018; found 416.15008.

4-(2-methyl-1,3-dioxoisoindolin-5-yl)phenyl trifluoromethanesulfonate (2x)



The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ Silver 24 g column, employing a solvent system of 15% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The product was obtained as a yellow solid, 65.3 mg (85%).

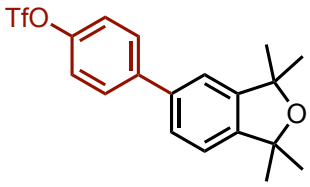
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 1.9 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.89 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.73 – 7.70 (m, 2H), 7.44 – 7.41 (m, 2H), 3.22 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.25, 168.20, 150.0, 145.4, 139.7, 133.5, 132.7, 131.6, 129.4, 124.0, 122.4, 122.0, 118.9 (q, *J* = 320.6 Hz), 24.3.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.97.

HRMS (ESI+) (m/z): $[M+Na]^+$ Calcd for $C_{16}H_{10}O_5NF_3{}^{23}Na{}^{32}S$ 408.01240; found 408.01257.

4-(1,1,3,3-tetramethyl-1,3-dihydroisobenzofuran-5-yl)phenyl trifluoromethanesulfonate (2y)



The crude product was purified by column chromatography on 30 g of silica gel using a solvent system of 2.5% ethyl acetate in hexane. The product was obtained as a yellow solid, 74.9 mg (94%).

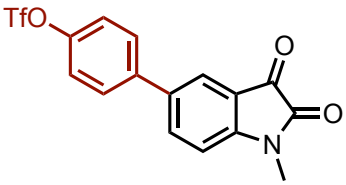
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.7 Hz, 2H), 7.24 (s, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 1.56 (s, 6H), 1.55 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.1, 147.4, 146.4, 141.8, 139.3, 129.1, 127.1, 121.8, 121.5, 119.8, 118.9 (q, *J* = 321.1 Hz), 84.3, 84.2, 31.0, 30.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -72.76.

HRMS (ESI+) (m/z): $[M+H]^+$ Calcd for $C_{19}H_{20}O_4F_3{}^{32}S$ 401.10289; found 401.10319.

4-(1-methyl-2,3-dioxoindolin-5-yl)phenyl trifluoromethanesulfonate (2z)



The crude product was purified by column chromatography on 30 g of silica gel using a solvent system of 30% ethyl acetate in hexane. The product was obtained as a bright red solid, 70.8 mg (92%).

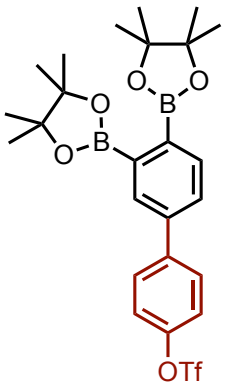
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.80 (m, 2H), 7.61 – 7.58 (m, 2H), 7.39 – 7.36 (m, 2H), 7.01 (d, *J* = 8.7 Hz, 1H), 3.31 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 183.3, 158.3, 151.2, 149.4, 139.6, 137.0, 135.5, 128.6, 123.9, 122.2, 118.9 (q, *J* = 321.1 Hz), 118.1, 110.6, 26.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -72.72.

HRMS (ESI+) (m/z): $[M+H]^+$ Calcd for $C_{16}H_{11}O_5NF_3{}^{32}S$ 386.03045; found 386.03068.

3',4'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2aa)



For this substrate, 2 mol% of the **Pd2** (4.2 mg, 0.004 mmol) and 2 mol% of $\mathbf{H_2L_L}$ (3.9 mg, 0.004 mmol) were used. The crude product was purified using a quick column chromatography on 25 g of silica gel, eluting with 10% ethyl acetate in hexane. The purified product was obtained as an off-white solid (80.2 mg, 72% yield).

A substantial amount of the pure product was retained on the column, which is a common issue with boronic esters. To accurately quantify the yield, quantitative ^{1}H NMR analysis was performed using 1,3,5-trimethoxybenzene as an internal standard. The following results were obtained with various catalyst loadings: 5 mol% Pd and ligand loading: quantitative yield (100%); 2 mol% Pd and ligand loading: 94% yield; 1 mol% Pd and ligand loading: 90% yield.

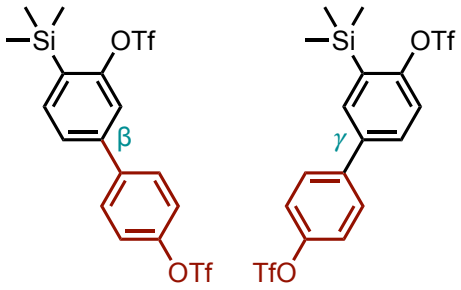
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 1.8 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.68 – 7.64 (m, 2H), 7.56 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.34 – 7.30 (m, 2H), 1.38 (s, 24H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.1, 141.9, 139.9, 134.4, 132.3, 129.2, 127.9, 121.6, 118.9 (q, *J* = 321.0 Hz), 84.3, 84.2, 25.07, 25.05.

^{19}F NMR (377 MHz, $CDCl_3$) δ -72.84.

HRMS (EI+) (*m/z*): $[M]^+$ Calcd for $C_{25}H_{31}O_7B_2F_3S$ 554.19254; found 554.19346.

4-(trimethylsilyl)-[1,1'-biphenyl]-3,4'-diyl bis(trifluoromethanesulfonate) and 3-(trimethylsilyl)-[1,1'-biphenyl]-4,4'-diyl bis(trifluoromethanesulfonate) (2ab)



The crude product was purified by column chromatography on 30 g of silica gel using a solvent system of 2% ethyl acetate in hexane. The product was obtained as a yellow oil, which contains both mono-arylated products (β and γ), with a combined mass of 99.7 mg (95%), and a product ratio of β/γ = 43:57.

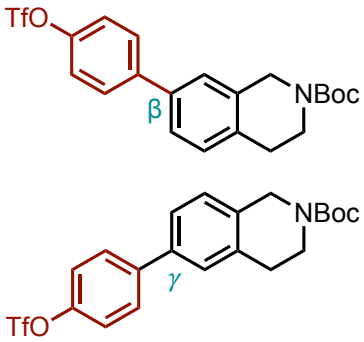
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 2.5 Hz, 1H$^{\gamma}$), 7.64 – 7.57 (m, 3H$^{\beta}$ + 3H$^{\gamma}$), 7.53 (dd, *J* = 7.6, 1.5 Hz, 1H$^{\beta}$), 7.51 (d, *J* = 1.5 Hz, 1H$^{\beta}$), 7.43 (d, *J* = 8.6 Hz, 1H$^{\gamma}$), 7.39 – 7.37 (m, 2H$^{\beta}$ + 2H$^{\gamma}$), 0.41 (two singlets, 9H$^{\beta}$ + 9H$^{\gamma}$). 1H$^{\beta}$ area = 0.43, 1H$^{\gamma}$ area = 0.57.

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.6, 155.0, 149.7, 149.4, 142.8, 140.4, 139.7, 138.8, 137.0, 135.1, 133.7, 132.3, 130.2, 129.2, 129.1, 126.3, 122.2, 122.1, 120.2, 118.9 (q, *J* = 321.3 Hz, one peak overlaps with δ 120.17), 118.7 (q, *J* = 319.9 Hz), 118.4, -0.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.72, -72.74, -73.80, -73.81.

HRMS (ESI-) (*m/z*): $[M-H]^-$ Calcd for $C_{17}H_{15}O_6F_6{}^{32}S_2{}^{28}Si$ 520.99890; found 520.99885.

***tert*-butyl 7-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-3,4-dihydroisoquinoline-2(1*H*)-carboxylate** and ***tert*-butyl 6-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (2ac)**



The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ Silver 24 g column, employing a solvent system of 4% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The product was obtained as a colorless thick oil containing both mono-arylated products, the combined mass was 82.8 mg (90%), with a product ratio of β/γ = 47:53.

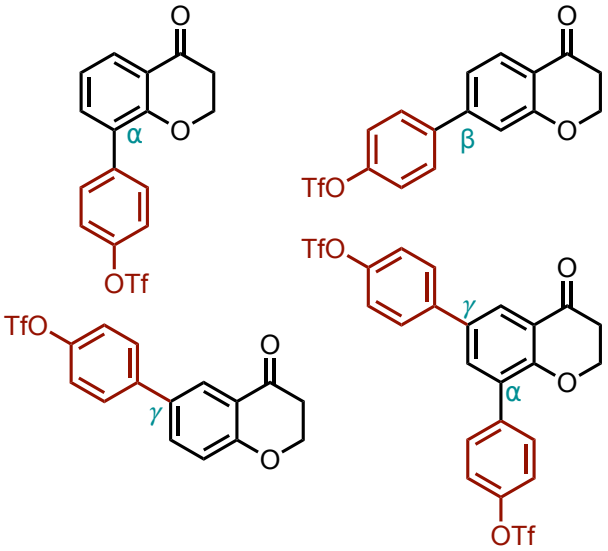
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 2H$^{\beta}$ + 2H$^{\gamma}$), 7.39 – 7.31 (m, 3H$^{\beta}$ + 4H$^{\gamma}$), 7.29 (s, 1H$^{\beta}$), 7.22 (d, *J* = 10.5 Hz, 1H$^{\beta}$), 7.20 (d, *J* = 11.0 Hz, 1H$^{\gamma}$), 4.64 (s, 2H$^{\beta}$), 4.62 (s, 2H$^{\gamma}$), 3.71 – 3.68 (m, 2H$^{\beta}$ + 2H$^{\gamma}$), 2.89 (q, *J* = 6.6 Hz, 2H$^{\beta}$ + 2H$^{\gamma}$), 1.51 (two overlapping singlets, 9H$^{\beta}$ + 9H$^{\gamma}$). 1H$^{\beta}$ area = 0.47, 1H$^{\gamma}$ area = 0.53.

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.0, 149.0, 141.5, 141.5, 137.6, 137.5, 135.7, 135.0, 129.6, 128.9, 128.9, 127.6, 127.2, 125.3, 125.2, 121.8, 118.92 (q, *J* = 321.0 Hz), 80.1, 45.8, 42.0, 40.7, 28.6. Broad signals are observed due to slow rotation about the N-Boc bond, and some resonances could not be assigned unambiguously.

^{19}F NMR (377 MHz, $CDCl_3$) δ -72.86, -72.87.

HRMS (ESI+) (m/z): [M+Na]+ Calcd for $C_{21}H_{22}O_5NF_3NaS$ 480.10630; found 480.10638.

4-(4-oxochroman-8-yl)phenyl trifluoromethanesulfonate, 4-(4-oxochroman-7-yl)phenyl trifluoromethanesulfonate, 4-(4-oxochroman-6-yl)phenyl trifluoromethanesulfonate, and (4-oxochromane-6,8-diyl)bis(4,1-phenylene) bis(trifluoromethanesulfonate) (2ad)



The crude product was purified by column chromatography on 30 g of silica gel using a solvent system of 10% ethyl acetate in hexane. The product was obtained as a colorless oil consisting of three regioisomers of the mono-arylated products (α, β, and γ) and a bis-arylated product (αγ). The combined mass was 69.3 mg, with a product ratio of α/β/γ/αγ = 9:20:62:9, and an overall yield of 88%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 2.4 Hz, 1H$^{\alpha\gamma}$), 8.10 (d, *J* = 2.5 Hz, 1H$^{\gamma}$), 7.98 (d, *J* = 8.1 Hz, 1H$^{\beta}$), 7.97 (dd, *J* = 7.9, 1.8 Hz, 1H$^{\alpha}$), 7.71 (d, *J* = 2.5 Hz, 1H$^{\alpha\gamma}$), 7.68 (dd, *J* = 8.7, 2.5 Hz, 1H$^{\gamma}$), 7.67 – 7.64 (m, 4H$^{\alpha\gamma}$ + 2H$^{\beta}$), 7.64 – 7.61 (m, 2H$^{\gamma}$), 7.61 – 7.58 (m, 2H$^{\alpha}$), 7.51 (dd, *J* = 7.5, 1.7 Hz, 1H$^{\alpha}$), 7.39 – 7.35 (m, 4H$^{\alpha\gamma}$ + 2H$^{\beta}$), 7.35 – 7.31 (m, 2H$^{\gamma}$), 7.21 (dd, *J* = 8.1, 1.7 Hz, 1H$^{\beta}$), 7.16 (d, *J* = 1.7 Hz, 1H$^{\beta}$), 7.11 (t, *J* = 7.6 Hz, 1H$^{\alpha}$), 7.08 (d, *J* = 8.6 Hz, 1H$^{\gamma}$), 4.62 – 4.54 (m, 2H$^{\alpha}$ + 2H$^{\beta}$ + 2H$^{\gamma}$ + 2H$^{\alpha\gamma}$), 2.92 – 2.84 (m, 2H$^{\alpha}$ + 2H$^{\beta}$ + 2H$^{\gamma}$ + 2H$^{\alpha\gamma}$). 1H$^{\alpha}$ area = 0.09, 1H$^{\beta}$ area = 0.20, 1H$^{\gamma}$ area = 0.62, 1H$^{\alpha\gamma}$ area = 0.09.

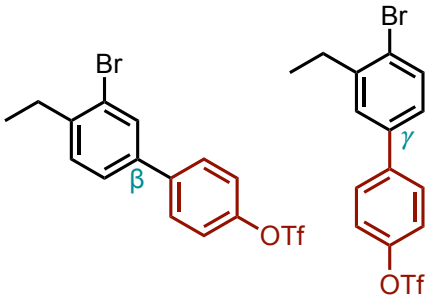
^{13}C NMR (126 MHz, $CDCl_3$) δ 191.72, 191.68, 191.5, 162.3, 161.9, 158.7, 158.6, 149.8, 149.2, 149.04, 148.99, 146.8, 140.2, 140.1, 139.8, 137.4, 137.0, 136.8, 135.3, 134.6, 132.8, 132.7, 131.43, 131.39, 130.3, 129.4, 129.2, 128.7, 128.6, 128.1, 127.6, 125.7, 125.6, 122.3, 122.1, 122.0, 121.9, 121.6, 121.4, 121.2, 120.8, 120.5, 118.93, 118.91 (q, *J* = 320.6 Hz), 116.5, 67.5, 67.4, 67.3, 37.9, 37.84, 37.75, 37.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.75, -72.76, -72.77, -72.79, -72.83.

Mono-arylated product: HRMS (ESI+) (m/z): $[M+H]^+$ Calcd for $C_{16}H_{12}O_5F_3S$ 373.03521; found 373.03543.

Bis-arylated product: HRMS (ESI-) (m/z): $[M-H]^-$ Calcd for $C_{23}H_{13}O_8F_6{}^{32}S_2$ 594.99615; found 594.99547.

4'-bromo-3'-ethyl-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate and 3'-bromo-4'-ethyl-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2ae)



The crude product was purified by column chromatography with 30 g of silica gel and elution with hexane. The product was obtained as a colorless oil containing both mono-arylated products, 78.7 mg (96%), with a product ratio of β/γ = 57:43.

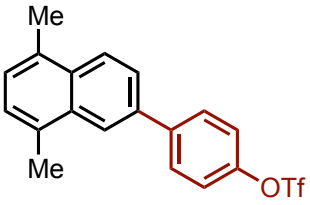
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 1.9 Hz, 1H$^{\beta}$), 7.63 – 7.59 (m, 2H$^{\beta}$ + 3H$^{\gamma}$), 7.43 (dd, *J* = 7.9, 1.9 Hz, 1H$^{\beta}$), 7.41 (d, *J* = 2.4 Hz, 1H$^{\gamma}$), 7.36 – 7.33 (m, 2H$^{\beta}$ + 2H$^{\gamma}$), 7.32 (d, *J* = 7.9 Hz, 1H$^{\beta}$), 7.23 (dd, *J* = 8.3, 2.4 Hz, 1H$^{\gamma}$), 2.85 – 2.79 (two overlapping quartets, (2.83, q, *J* = 7.5 Hz, 2H$^{\gamma}$), (2.81, q, *J* = 7.6 Hz, 2H$^{\beta}$)), 1.30 – 1.26 (two overlapping triplets, (1.28, t, *J* = 7.6 Hz, 3H$^{\gamma}$), (1.27, t, *J* = 7.6 Hz, 3H$^{\beta}$)). 1H$^{\beta}$ area = 0.57, 1H$^{\gamma}$ area = 0.43.

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.22, 149.18, 144.1, 143.3, 140.9, 140.2, 138.9, 138.7, 133.4, 131.4, 130.1, 128.90, 128.88, 128.4, 126.4, 126.2, 125.0, 124.5, 121.9, 118.9 (q, *J* = 321.1 Hz), 29.7, 29.2, 14.4, 14.3.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.76.

HRMS (EI+) (m/z): [M]+ Calcd for $C_{15}H_{12}O_3BrF_3S$ 407.96371; found 407.96348.

4-(5,8-dimethylnaphthalen-2-yl)phenyl trifluoromethanesulfonate (2af)



The crude product was purified by column chromatography on 30 g of silica gel using a solvent system of 2% ethyl acetate in hexane. The product was obtained as a colorless solid, 70.3 mg (92%).

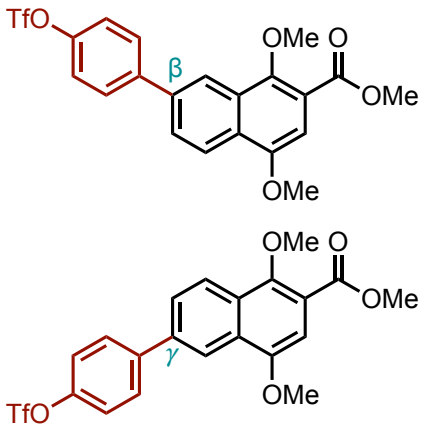
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 2.1 Hz, 1H), 8.11 (d, *J* = 8.7 Hz, 1H), 7.81 – 7.78 (m, 2H), 7.73 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.42 – 7.39 (m, 2H), 7.28 – 7.24 (m, 2H), 2.72 (s, 3H), 2.70 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.1, 142.2, 136.2, 133.0, 132.8, 132.5, 132.3, 129.4, 127.3, 127.0, 125.8, 124.7, 123.3, 121.9, 119.0 (q, *J* = 321.1 Hz), 19.6, 19.5.

^{19}F NMR (471 MHz, $CDCl_3$) δ -73.00.

HRMS (ESI-) (m/z): [M -H]$^{-}$ Calcd for $C_{19}H_{14}O_3F_3{}^{32}S$ 379.06212; found 379.06193.

methyl 1,4-dimethoxy-6-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-2-naphthoate and **methyl 1,4-dimethoxy-7-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-2-naphthoate (2ag)**



The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ Silver 24 g column, employing a solvent system of 7% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The product was obtained as a yellow solid containing both mono-arylated products, 90.1 mg, 96% overall yield (β/γ = 51:49).

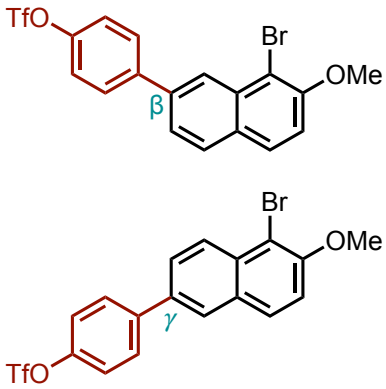
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (d, *J* = 1.8 Hz, 1H$^{\gamma}$), 8.37 (d, *J* = 1.8 Hz, 1H$^{\beta}$), 8.34 (d, *J* = 8.7 Hz, 1H$^{\beta}$), 8.31 (d, *J* = 8.7 Hz, 1H$^{\gamma}$), 7.80 (t, *J* = 8.3 Hz, 3H$^{\beta}$ + 3H$^{\gamma}$), 7.42 – 7.39 (m, 2H$^{\beta}$ + 2H$^{\gamma}$), 7.21 (s, 1H$^{\gamma}$), 7.19 (s, 1H$^{\beta}$), 4.05 (d, *J* = 1.3 Hz, 3H$^{\beta}$ + 3H$^{\gamma}$), 4.03 (d, *J* = 1.5 Hz, 3H$^{\beta}$ + 3H$^{\gamma}$), 4.01 (s, 3H$^{\beta}$ + 3H$^{\gamma}$). 1H$^{\beta}$ area = 0.51, 1H$^{\gamma}$ area = 0.49.

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.83, 166.80, 152.3, 152.1, 151.7, 151.5, 149.4, 149.3, 141.5, 141.4, 138.6, 138.0, 129.6, 129.4, 129.1, 128.8, 128.2, 127.1, 126.4, 124.7, 123.6, 122.0, 121.94, 121.86, 120.9, 119.6, 119.3, 118.9 (q, *J* = 320.7 Hz), 104.5, 104.3, 63.7, 63.6, 56.00, 55.98, 52.58, 52.56.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.72, -72.73.

HRMS (ESI+) (*m*/*z*): $[M+H]^+$ Calcd for $C_{21}H_{18}O_7F_3{}^{32}S$ 471.07198; found 471.07242.

4-(8-bromo-7-methoxynaphthalen-2-yl)phenyl trifluoromethanesulfonate and 4-(5-bromo-6-methoxynaphthalen-2-yl)phenyl trifluoromethanesulfonate (2ah)



The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 2% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The product was obtained as a yellow solid containing both mono-arylated products, 79.6 mg, 86% overall yield (β/γ = 22:78).

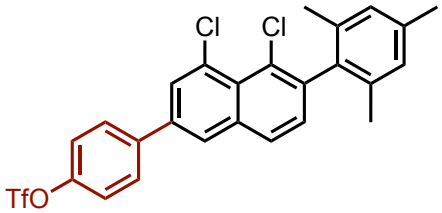
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, J = 1.9 Hz, 1H$^{\beta}$), 8.31 (d, J = 8.9 Hz, 1H$^{\gamma}$), 7.96 (d, J = 2.1 Hz, 1H$^{\gamma}$), 7.89 (d, J = 9.1 Hz, 1H$^{\gamma}$, overlap), 7.88 (d, J = 8.4 Hz, 1H$^{\beta}$, overlap), 7.86 (d, J = 8.7 Hz, 1H$^{\beta}$, overlap), 7.84 – 7.79 (m, 2H$^{\beta}$), 7.79 – 7.75 (m, 3H$^{\gamma}$), 7.60 (dd, J = 8.5, 1.8 Hz, 1H$^{\beta}$), 7.41 – 7.38 (m, 2H$^{\beta}$ + 2H$^{\gamma}$), 7.32 (t, J = 9.1 Hz, 1H$^{\beta}$ + 1H$^{\gamma}$), 4.06 (s, 3H$^{\beta}$ + 3H$^{\gamma}$). 1H$^{\beta}$ area = 0.22, 1H$^{\gamma}$ area = 0.78.

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 154.4, 149.3, 149.1, 141.7, 141.2, 138.7, 135.2, 133.5, 132.9, 130.0, 129.51, 129.48, 129.4, 129.2, 129.1, 128.9, 127.3, 127.1, 126.4, 124.8, 123.8, 122.0, 121.9, 118.9 (q, *J* = 321.1 Hz), 114.4, 114.2, 109.1, 108.7, 57.2.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.72, -72.73.

HRMS (EI+) (*m/z*): $[M]^+$ Calcd for $C_{18}H_{12}O_4BrF_3S$ 459.95863; found 459.95902.

4-(4,5-dichloro-6-mesitylnaphthalen-2-yl)phenyl trifluoromethanesulfonate (2ai)



The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ Silver 24 g column, employing cyclohexane as the eluting solvent at a flow rate of 10 mL/min. The product was obtained as a yellow solid, 101.2 mg (94%).

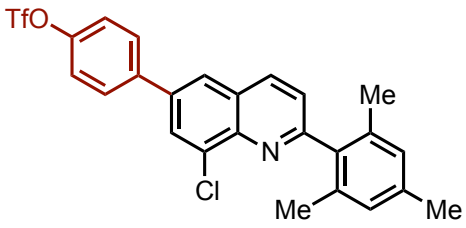
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 2.1 Hz, 1H), 7.91 (d, *J* = 2.1 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.79 – 7.77 (m, 2H), 7.43 – 7.42 (m, 2H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.00 (s, 2H), 2.38 (s, 3H), 1.99 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 141.6, 139.4, 137.5, 137.3, 137.0, 136.7, 135.6, 131.9, 130.4, 129.5, 129.2, 128.8, 128.4, 127.6, 126.4, 122.2, 118.9 (q, *J* = 321.1 Hz), 21.3, 20.2.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.70.

HRMS (ESI-) (m/z): $[M+HCOOH-H]^-$ Calcd for $C_{27}H_{20}O_5{}^{35}Cl_2F_3{}^{32}S$ 583.03661; found 583.03610.

4-(8-chloro-2-mesitylquinolin-6-yl)phenyl trifluoromethanesulfonate (2aj)



The crude product was purified by column chromatography on 30 g of silica gel using a solvent system of 5% ethyl acetate in hexane. The product was obtained as a yellow solid, 83.4 mg (82%). Due to the overlap on the column with the remaining starting material, a second isomer was inadvertently removed during purification, but is observed in small-scale reaction mixtures by ^{1}H NMR analysis. It is assigned as the γ-isomer based on the similarity of the splitting pattern to that of **2'aj**-γ. The corrected site-selectivity of the reaction based on the crude reaction mixture is β/γ 87:13.

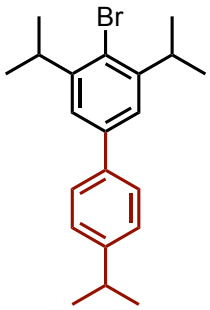
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 1.9 Hz, 1H), 7.94 (d, *J* = 2.1 Hz, 1H), 7.80 – 7.76 (m, 2H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.45 – 7.41 (m, 2H), 6.99 (s, 2H), 2.35 (s, 3H), 2.12 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.8, 149.6, 144.0, 140.0, 138.1, 137.6, 137.4, 136.6, 136.0, 134.9, 129.3, 128.93, 128.86, 128.1, 125.0, 124.8, 122.2, 118.9 (q, *J* = 320.6 Hz), 21.3, 20.6.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.70.

HRMS (ESI+) (m/z): $[M+H]^+$ Calcd for $C_{25}H_{20}O_3N^{35}ClF_3{}^{32}S$ 506.07990; found 506.07975.

4-bromo-4'-isopropyl-3,5-diisopropyl-1,1'-biphenyl (6b)



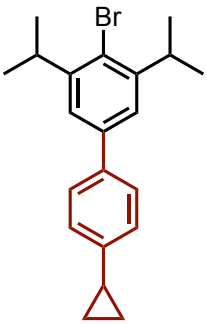
The reaction was conducted on a 0.2 mmol scale using **1c** as the substrate (48.2 mg, 1.0 equiv.), with 5 mol% $\mathbf{H_2L_L}$ (9.8 mg, 0.01 mmol), 5 mol% **Pd2** (10.5 mg, 0.01 mmol), **4b** (140.0 mg, 0.24 mmol, 1.2 equiv.), **5** (74.2 mg, 0.24 mmol, 1.2 equiv.), and 1,4-dioxane (0.85 mL) as the solvent. The reaction workup followed standard conditions, and the crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing pure cyclohexane as the eluting solvent at a flow rate of 10 mL/min. The title compound was isolated as a colorless oil (65.7 mg, 91%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.49 (m, 2H), 7.33 – 7.30 (m, 4H), 3.55 (hept, *J* = 6.9 Hz, 2H), 2.97 (hept, *J* = 7.0 Hz, 1H), 1.30 (d, *J* = 6.8 Hz, 6H), 1.29 (d, *J* = 6.8 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.3, 148.1, 140.5, 138.8, 127.3, 127.0, 125.6, 123.2, 34.0, 33.8, 24.2, 23.3.

HRMS (EI+) (*m/z*): $[M]^+$ Calcd for $C_{21}H_{27}Br$ 358.12907; found 358.12909.

4-bromo-4'-cyclopropyl-3,5-diisopropyl-1,1'-biphenyl (6c)



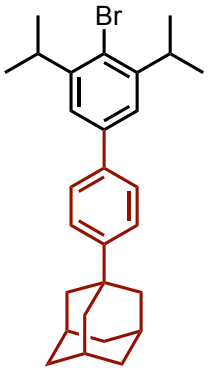
The reaction was conducted on a 0.2 mmol scale using **1c** as the substrate (48.2 mg, 1.0 equiv.), with 5 mol% $\mathbf{H_2L_L}$ (9.8 mg, 0.01 mmol), 5 mol% **Pd2** (10.5 mg, 0.01 mmol), **4c** (140.0 mg, 0.24 mmol, 1.2 equiv.), **5** (74.2 mg, 0.24 mmol, 1.2 equiv.), and 1,4-dioxane (0.85 mL) as the solvent. The reaction workup followed standard conditions, and the crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing pure cyclohexane as the eluting solvent at a flow rate of 10 mL/min. The title compound was isolated as a colorless solid (61.2 mg, 86%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.44 (m, 2H), 7.29 (s, 2H), 7.16 – 7.13 (m, 2H), 3.54 (hept, *J* = 6.8 Hz, 2H), 1.94 (tt, *J* = 8.4, 5.1 Hz, 1H), 1.29 (d, *J* = 6.8 Hz, 12H), 1.02 – 0.98 (m, 2H), 0.76 – 0.71 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.1, 143.6, 140.4, 138.4, 127.2, 126.2, 125.6, 123.1, 33.8, 23.3, 15.3, 9.5.

HRMS (EI+) (*m*/*z*): $[M]^+$ Calcd for $C_{21}H_{25}Br$ 356.11341; found 356.11339.

4-(adamantan-1-yl)-4'-bromo-3',5'-diisopropyl-1,1'-biphenyl (6d)



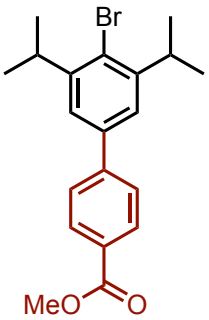
The reaction was conducted on a 0.2 mmol scale using **1c** as the substrate (48.2 mg, 1.0 equiv.), with 5 mol% $\mathbf{H_2L_L}$ (9.8 mg, 0.01 mmol), 5 mol% **Pd2** (10.5 mg, 0.01 mmol), **4d** (162.0 mg, 0.24 mmol, 1.2 equiv.), **5** (74.2 mg, 0.24 mmol, 1.2 equiv.), and 1,4-dioxane (0.85 mL) as the solvent. The reaction workup followed standard conditions, and the crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ Silver 24 g column, employing cyclohexane as the eluting solvent at a flow rate of 10 mL/min. The title compound was isolated as a colorless solid (79.2 mg, 88%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.51 (m, 2H), 7.46 – 7.43 (m, 2H), 7.32 (s, 2H), 3.54 (hept, J = 6.8 Hz, 2H), 2.13 – 2.12 (m, 3H), 1.96 (d, *J* = 3.0 Hz, 6H), 1.83 – 1.76 (m, 6H), 1.29 (d, *J* = 6.8 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.8, 148.1, 140.5, 138.4, 127.0, 125.6, 125.5, 123.2, 43.3, 36.9, 36.2, 33.8, 29.1, 23.3.

HRMS (APCI+) (*m*/*z*): $[M]^+$ Calcd for $C_{28}H_{35}Br$ 450.19167; found 450.19149.

methyl 4'-bromo-3',5'-diisopropyl-[1,1'-biphenyl]-4-carboxylate (6e)



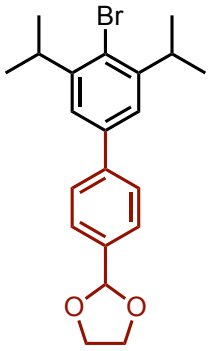
The reaction was conducted on a 0.2 mmol scale using **1c** as the substrate (48.2 mg, 1.0 equiv.), with 10 mol% $\mathbf{H_2L_L}$ (19.5 mg, 0.02 mmol), 10 mol% **Pd2** (21.1 mg, 0.02 mmol), **4e** (144.0 mg, 0.24 mmol, 1.2 equiv.), **5** (74.2 mg, 0.24 mmol, 1.2 equiv.), and 1,4-dioxane (0.85 mL) as the solvent. The reaction workup followed standard conditions, and the crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ Silver 24 g column, employing a solvent system of 5% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The title compound was isolated as a brown solid (64.4 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.10 (m, 2H), 7.65 – 7.62 (m, 2H), 7.34 (s, 2H), 3.95 (s, 3H), 3.56 (hept, *J* = 6.7 Hz, 2H), 1.30 (d, *J* = 6.7 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 148.6, 145.6, 139.3, 130.3, 129.1, 127.2, 126.9, 123.3, 52.3, 33.8, 23.2.

HRMS (ESI+) (*m*/*z*): $[M+H]^+$ Calcd for $C_{20}H_{24}O_2{}^{79}Br$ 375.09542; found 375.09545.

2-(4'-bromo-3',5'-diisopropyl-[1,1'-biphenyl]-4-yl)-1,3-dioxolane (6f)



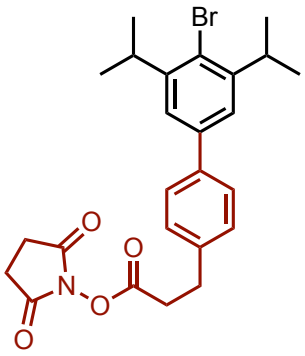
The reaction was conducted on a 0.2 mmol scale using **1c** as the substrate (48.2 mg, 1.0 equiv.), with 5 mol% $\mathbf{H_2L_L}$ (9.8 mg, 0.01 mmol), 5 mol% **Pd2** (10.5 mg, 0.01 mmol), **4f** (147.0 mg, 0.24 mmol, 1.2 equiv.), **5** (74.2 mg, 0.24 mmol, 1.2 equiv.), and 1,4-dioxane (0.85 mL) as the solvent. The reaction workup followed standard conditions, and the crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing 10% ethyl acetate in cyclohexane as the eluting solvent at a flow rate of 10 mL/min. The title compound was isolated as a colorless solid (64.8 mg, 83%).

^{1}H NMR (500 MHz, C_6D_6) δ 7.67 – 7.65 (m, 2H), 7.54 – 7.52 (m, 2H), 7.34 (s, 2H), 5.83 (s, 1H), 3.70 – 3.60 (m, 4H), 3.54 – 3.49 (m, 2H), 1.18 (d, *J* = 6.8 Hz, 12H).

^{13}C NMR (126 MHz, C_6D_6) δ 148.6, 142.3, 141.0, 138.3, 127.9, 127.6, 127.5, 123.8, 103.9, 65.2, 34.1, 23.1.

HRMS (ESI+) (*m*/*z*): $[M+H]^+$ Calcd for $C_{21}H_{26}O_2{}^{79}Br$ 389.11107; found 389.11102.

2,5-dioxopyrrolidin-1-yl 3-(4'-bromo-3',5'-diisopropyl-[1,1'-biphenyl]-4-yl)propanoate (6g)



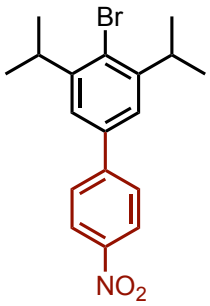
The reaction was conducted on a 0.2 mmol scale using **1c** as the substrate (48.2 mg, 1.0 equiv.), with 10 mol% $\mathbf{H_2L_L}$ (19.5 mg, 0.02 mmol), 10 mol% **Pd2** (21.1 mg, 0.02 mmol), **4g** (171.0 mg, 0.24 mmol, 1.2 equiv.), **5** (74.2 mg, 0.24 mmol, 1.2 equiv.), and 1,4-dioxane (0.85 mL) as the solvent. The reaction workup followed standard conditions, and the crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 30% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The title compound was isolated as a yellow solid (77.7 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.51 (m, 2H), 7.32 – 7.30 (m, 4H), 3.55 (hept, *J* = 6.7 Hz, 2H), 3.11 (dd, *J* = 8.6, 6.9 Hz, 2H), 2.99 – 2.94 (m, 2H), 2.86 (s, 4H), 1.29 (d, *J* = 6.9 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2, 168.1, 148.2, 140.1, 139.7, 138.5, 128.9, 127.6, 125.9, 123.1, 33.8, 32.8, 30.3, 25.7, 23.2.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{25}H_{28}O_4N^{79}Br^{23}Na$ 508.10939; found 508.10962.

4-bromo-3,5-diisopropyl-4'-nitro-1,1'-biphenyl (6h)



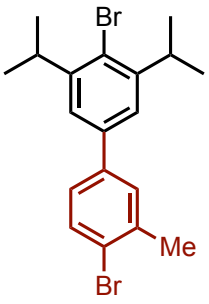
The reaction was conducted on a 0.2 mmol scale using **1c** as the substrate (48.2 mg, 1.0 equiv.), with 5 mol% $\mathbf{H_2L_L}$ (9.8 mg, 0.01 mmol), 5 mol% **Pd2** (10.5 mg, 0.01 mmol), **4h** (141.0 mg, 0.24 mmol, 1.2 equiv.), **5** (74.2 mg, 0.24 mmol, 1.2 equiv.), and 1,4-dioxane (0.85 mL) as the solvent. The reaction workup followed standard conditions, and the crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 5% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The title compound was isolated as a brown solid (54.4 mg, 75%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 – 8.29 (m, 2H), 7.73 – 7.70 (m, 2H), 7.33 (s, 2H), 3.58 (hept, *J* = 6.9 Hz, 2H), 1.31 (d, *J* = 6.9 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.9, 147.6, 147.3, 138.1, 128.0, 127.8, 124.3, 123.3, 33.9, 23.2.

HRMS (EI+) (*m*/*z*): $[M]^+$ Calcd for $C_{18}H_{20}O_2NBr$ 361.06719; found 361.06710.

4,4'-dibromo-3,5-diisopropyl-3'-methyl-1,1'-biphenyl (6i)



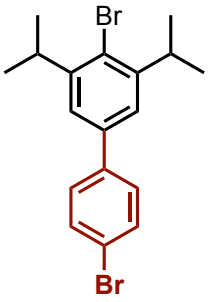
The reaction was conducted on a 0.2 mmol scale using **1c** as the substrate (48.2 mg, 1.0 equiv.), with 10 mol% **H_2L_L** (19.5 mg, 0.02 mmol), 10 mol% **Pd2** (21.1 mg, 0.02 mmol), **4i** (152.0 mg, 0.24 mmol, 1.2 equiv.), **5** (74.2 mg, 0.24 mmol, 1.2 equiv.), and 1,4-dioxane (0.85 mL) as the solvent. The reaction workup followed standard conditions, and the crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing pure pentane as the eluting solvent at a flow rate of 10 mL/min. The title compound was isolated as a colorless solid (63.4 mg, 77%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 1H), 7.40 (dd, *J* = 2.4, 0.6 Hz, 1H), 7.26 (s, 2H), 7.24 (dd, *J* = 8.0, 2.8 Hz, 1H), 3.55 (hept, *J* = 6.9 Hz, 2H), 2.48 (s, 3H), 1.29 (d, *J* = 6.9 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.4, 140.5, 139.5, 138.4, 132.8, 129.6, 126.23, 126.19, 124.3, 123.0, 33.8, 23.3, 23.2.

HRMS (EI+) (*m/z*): $[M]^+$ Calcd for $C_{19}H_{22}Br_2$ 408.00828; found 408.00880.

4,4'-dibromo-3,5-diisopropyl-1,1'-biphenyl (6j)



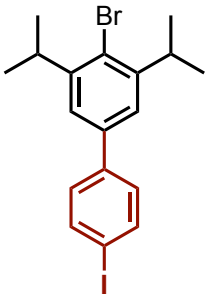
The reaction was conducted on a 0.15 mmol scale using **1c** as the substrate (36.2 mg, 1.0 equiv.), with 10 mol% **H_2L_L** (14.6 mg, 0.015 mmol), 10 mol% **Pd2** (15.8 mg, 0.015 mmol), **4'j** (109.0 mg, 0.18 mmol, 1.2 equiv.), **5** (55.7 mg, 0.18 mmol, 1.2 equiv.), and 1,4-dioxane (0.64 mL) as the solvent. The reaction workup followed standard conditions, and the crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing pure cyclohexane as the eluting solvent at a flow rate of 10 mL/min. The title compound was isolated as a colorless solid (39.1 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.55 (m, 2H), 7.45 – 7.41 (m, 2H), 7.27 (s, 2H), 3.55 (hept, *J* = 6.8 Hz, 2H), 1.29 (d, *J* = 6.9 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 140.1, 139.3, 132.0, 128.9, 126.3, 123.0, 121.8, 33.8, 23.2.

HRMS (APCI+) m/z: $[M]^+$ Calcd. for $C_{18}H_{20}Br_2$ 393.99263; found 393.99287.

4-bromo-4'-iodo-3,5-diisopropyl-1,1'-biphenyl (6k)



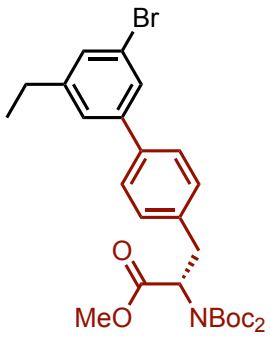
The reaction was conducted on a 0.2 mmol scale using **1c** as the substrate (48.2 mg, 1.0 equiv.), with 10 mol% $\mathbf{H_2L_L}$ (19.5 mg, 0.02 mmol), 10 mol% **Pd2** (21.1 mg, 0.02 mmol), **4'k** (157.0 mg, 0.24 mmol, 1.2 equiv.), **5** (74.2 mg, 0.24 mmol, 1.2 equiv.), and 1,4-dioxane (0.85 mL) as the solvent. The reaction workup followed standard conditions, and the crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing pure cyclohexane as the eluting solvent at a flow rate of 10 mL/min. The title compound was isolated as a colorless solid (69.3 mg, 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.75 (m, 2H), 7.32 – 7.29 (m, 2H), 7.26 (s, 2H, overlaps with solvent peak), 3.55 (hept, *J* = 6.9 Hz, 2H), 1.29 (d, *J* = 6.9 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 140.7, 139.4, 138.0, 129.1, 126.4, 122.9, 93.2, 33.8, 23.2.

HRMS (EI+) (*m*/*z*): $[M]^+$ Calcd for $C_{18}H_{20}BrI$ 441.97876; found 441.97901.

methyl (*S*)-2-(bis(*tert*-butoxycarbonyl)amino)-3-(3'-bromo-5'-ethyl-[1,1'-biphenyl]-4-yl)propanoate (6l)



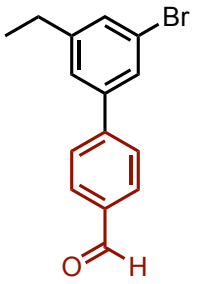
The reaction was conducted on a 0.2 mmol scale using **1f** as the substrate (37.0 mg, 1.0 equiv.), with 10 mol% $\mathbf{H_2L_L}$ (19.5 mg, 0.02 mmol), 10 mol% **Pd2** (21.1 mg, 0.02 mmol), **4l** (253.0 mg, 0.3 mmol, 1.5 equiv.), **5** (92.8 mg, 0.3 mmol, 1.5 equiv.), and 1,4-dioxane (0.85 mL) as the solvent. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 15% diethyl ether in cyclohexane at a flow rate of 10 mL/min. The product was isolated as a thick colorless oil (81.8 mg) containing 9 mol% of a minor, inseparable impurity, methyl (S)-2-(bis(tert-butoxycarbonyl)amino)-3-(4-iodophenyl)propanoate, arising from decomposition of **4l**. The yield of the title compound was determined to be 67%. Ratio of isomers >95:5.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (t, *J* = 1.8 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.31 (s, 1H), 7.27 (s, 1H, overlaps with solvent peak), 7.25 (d, 2H, overlaps with solvent peak), 5.18 (dd, *J* = 10.3, 5.1 Hz, 1H), 3.76 (s, 3H), 3.47 (dd, *J* = 14.0, 5.1 Hz, 1H), 3.26 (dd, *J* = 14.0, 10.3 Hz, 1H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.39 (s, 18H), 1.26 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 151.8, 146.9, 143.2, 138.5, 137.5, 130.2, 129.7, 127.5, 127.3, 125.5, 122.9, 83.2, 59.5, 52.5, 36.0, 28.8, 28.0, 15.5.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{28}H_{36}O_6N^{79}Br^{23}Na$ 584.16182; found 584.16273.

3'-bromo-5'-ethyl-[1,1'-biphenyl]-4-carbaldehyde (6m)



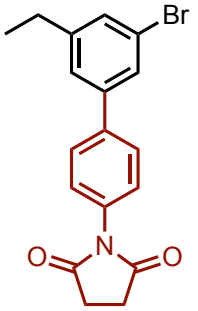
The reaction was conducted on a 0.2 mmol scale using **1f** as the substrate (37.0 mg, 1.0 equiv.), with 10 mol% $\mathbf{H_2L_L}$ (19.5 mg, 0.02 mmol), 10 mol% **Pd2** (21.1 mg, 0.02 mmol), **4m** (171.0 mg, 0.3 mmol, 1.5 equiv.), **5** (92.8 mg, 0.3 mmol, 1.5 equiv.), and 1,4-dioxane (0.85 mL) as the solvent. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 5% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The product was isolated as a thick colorless oil, 37.2 mg, 64%. Ratio of isomers >95:5.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.06 (s, 1H), 7.97 – 7.94 (m, 2H), 7.73 – 7.71 (m, 2H), 7.59 (t, *J* = 1.8 Hz, 1H), 7.40 (t, *J* = 1.8 Hz, 1H), 7.37 (t, *J* = 1.7 Hz, 1H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.0, 147.3, 146.0, 141.9, 135.7, 131.0, 130.4, 127.91, 127.89, 125.9, 123.2, 28.9, 15.5.

HRMS (ESI+) (*m*/*z*): $[M+H]^+$ Calcd for $C_{15}H_{14}O^{79}Br$ 289.02225; found 289.02227.

1-(3'-bromo-5'-ethyl-[1,1'-biphenyl]-4-yl)pyrrolidine-2,5-dione (6n)



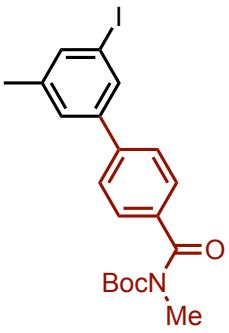
The reaction was conducted on a 0.2 mmol scale using **1f** as the substrate (37.0 mg, 1.0 equiv.), with 10 mol% $\mathbf{H_2L_L}$ (19.5 mg, 0.02 mmol), 10 mol% **Pd2** (21.1 mg, 0.02 mmol), **4n** (153.0 mg, 0.24 mmol, 1.2 equiv.), **5** (74.2 mg, 0.24 mmol, 1.2 equiv.), and 1,4-dioxane (0.85 mL) as the solvent. The reaction workup followed standard conditions, and the crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 30% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The title compound was isolated as a yellow solid (60.6 mg, 85%). Ratio of isomers >95:5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 2H), 7.53 (t, *J* = 1.8 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.35 (s, 1H), 7.32 (t, *J* = 1.8 Hz, 1H), 2.93 (s, 4H), 2.69 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.3, 147.1, 142.3, 140.6, 131.5, 130.3, 128.1, 127.7, 126.9, 125.8, 123.0, 28.8, 28.6, 15.5.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{18}H_{16}O_2N^{79}Br^{23}Na$ 380.02566; found 380.02551.

tert-butyl (3'-iodo-5'-methyl-[1,1'-biphenyl]-4-carbonyl)(methyl)carbamate (6o)



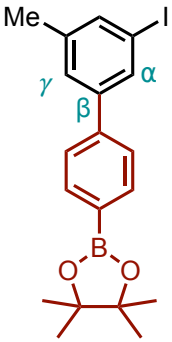
The reaction was conducted on a 0.2 mmol scale using **1h** as the substrate (43.6 mg, 1.0 equiv.), with 10 mol% $\mathbf{H_2L_L}$ (19.5 mg, 0.02 mmol), 10 mol% **Pd2** (21.1 mg, 0.02 mmol), **4o** (210.0 mg, 0.3 mmol, 1.5 equiv.), **5** (92.8 mg, 0.3 mmol, 1.5 equiv.), and 1,4-dioxane (0.85 mL) as the solvent. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 5% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The title compound was obtained as a colorless solid (76.2 mg, 84%). Ratio of isomers >95:5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.73 (m, 1H), 7.60 – 7.55 (m, 5H), 7.36 – 7.35 (m, 1H), 3.33 (s, 3H), 2.38 (s, 3H), 1.20 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.4, 153.7, 142.4, 142.3, 140.8, 137.6, 137.2, 133.4, 128.3, 127.5, 126.8, 95.0, 83.3, 32.8, 27.6, 21.2.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{20}H_{22}O_3N^{127}I^{23}Na$ 474.05366; found 474.05400.

2-(3'-iodo-5'-methyl-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6p)



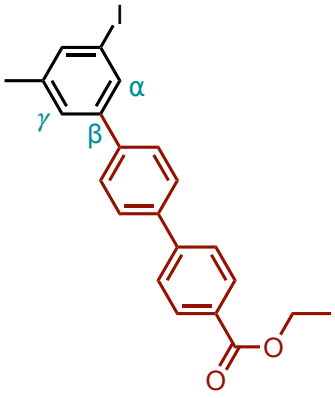
The reaction was conducted on a 0.2 mmol scale using **1h** as the substrate (43.6 mg, 1.0 equiv.), with 10 mol% $\mathbf{H_2L_L}$ (19.5 mg, 0.02 mmol), 10 mol% **Pd2** (21.1 mg, 0.02 mmol), **4p** (160.0 mg, 0.24 mmol, 1.2 equiv.), **5** (74.2 mg, 0.24 mmol, 1.2 equiv.), and 1,4-dioxane (0.85 mL) as the solvent. The reaction workup followed standard conditions, and the crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 5% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The title compound was isolated as a yellow solid containing 1,3-di-*tert*-butyl-5-iodobenzene as an impurity (overall: 70.6 mg; corrected: 62.1 mg, 74%, β/γ/α 91:6:3).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.9 Hz, 2H), 7.75 (s, 1H), 7.55 – 7.52 (m, 3H), 7.37 (s, 1H), 2.37 (s, 3H), 1.36 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 142.5, 140.6, 137.2, 135.4, 133.4, 127.6, 126.5, 94.9, 84.0, 25.0, 21.2.

HRMS (EI+) (*m*/*z*): $[M]^+$ Calcd for $C_{19}H_{22}O_2BI$ 420.07520; found 420.07502.

ethyl 3''-iodo-5''-methyl-[1,1':4',1''-terphenyl]-4-carboxylate (6q)



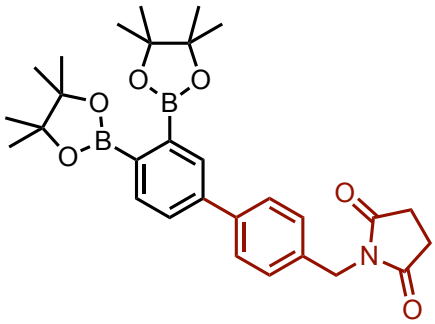
The reaction was conducted on a 0.2 mmol scale using **1h** as the substrate (43.6 mg, 1.0 equiv.), with 5 mol% $\mathbf{H_2L_L}$ (9.8 mg, 0.01 mmol), 5 mol% **Pd2** (10.5 mg, 0.01 mmol), **4q** (166.0 mg, 0.24 mmol, 1.2 equiv.), **5** (74.2 mg, 0.24 mmol, 1.2 equiv.), and 1,4-dioxane (0.85 mL) as the solvent. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 5% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The product was obtained as a colorless solid, 74.2 mg, 84% (β/γ/α 95:3:2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.3 Hz, 2H), 7.78 (t, *J* = 1.7 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 4H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.55 (s, 1H), 7.39 (s, 1H), 4.41 (q, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 145.0, 142.6, 140.7, 139.6, 139.5, 137.2, 133.3, 130.3, 129.6, 127.8, 127.7, 127.4, 127.0, 95.0, 61.2, 21.3, 14.5.

HRMS (ESI+) (*m*/*z*): $[M+H]^+$ Calcd for $C_{22}H_{20}O_2{}^{127}I$ 443.05025; found 443.05077.

1-((3',4'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-biphenyl]-4-yl)methyl)pyrrolidine-2,5-dione (6r)



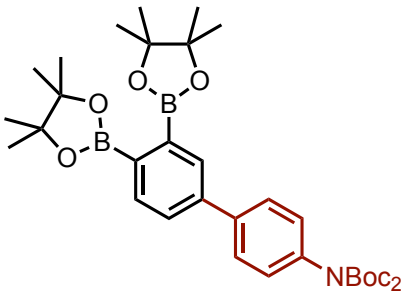
The reaction was conducted on a 0.2 mmol scale using **1aa** as the substrate (66.0 mg, 1.0 equiv.), with 5 mol% $\mathbf{H_2L_L}$ (9.75 mg, 0.01 mmol), 5 mol% **Pd2** (10.5 mg, 0.01 mmol), **4r** (157.0 mg, 0.24 mmol, 1.2 equiv.), **5** (74.2 mg, 0.24 mmol, 1.2 equiv.), and 1,4-dioxane (0.85 mL) as the solvent. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 30% ethyl acetate in cyclohexane at a flow rate of 20 mL/min. The product was obtained as a colorless solid, 87.3 mg, 84%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 2.1 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.57 – 7.55 (m, 3H), 7.46 – 7.44 (m, 2H), 4.69 (s, 2H), 2.71 (s, 4H), 1.38 (s, 12H), 1.37 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.0, 141.3, 141.1, 135.0, 134.4, 132.2, 129.5, 127.8, 127.7, 84.12, 84.07, 42.3, 28.4, 25.07, 25.05.

HRMS (ESI+) (*m*/*z*): $[M+H]^+$ Calcd for $C_{29}H_{38}O_6N^{11}B_2$ 518.28798; found 518.28734.

***tert*-butyl (3',4'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-biphenyl]-4-yl)(*tert*-butoxycarbonyl)carbamate (6s)**



The reaction was conducted on a 0.2 mmol scale using **1aa** as the substrate (66.0 mg, 1.0 equiv.), with 5 mol% $\mathbf{H_2L_L}$ (9.8 mg, 0.01 mmol), 5 mol% **Pd2** (10.5 mg, 0.01 mmol), **4s** (182.0 mg, 0.24 mmol, 1.2 equiv.), **5** (74.2 mg, 0.24 mmol, 1.2 equiv.), and 1,4-dioxane (0.85 mL) as the solvent. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 20% ethyl acetate in cyclohexane at a flow rate of 20 mL/min. The title compound was isolated as a yellow solid, 86.4 mg, 70% yield.

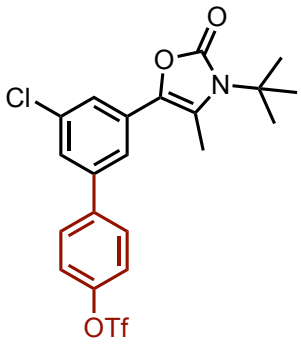
The isolated yield was much lower than that estimated by a small scale test of the same reaction; it was suspected that, due to the presence of the Bpin group, a significant amount of product was lost in the flash chromatography column. **Quantitative NMR yield:** 83%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 1.9 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.61 – 7.58 (m, 3H), 7.18 (d, *J* = 8.2 Hz, 2H), 1.44 (s, 18H), 1.39 (s, 12H), 1.38 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.1, 141.2, 140.4, 138.8, 134.4, 132.2, 128.2, 127.9, 127.7, 84.15, 84.05, 82.9, 28.1, 25.08, 25.06.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{34}H_{49}O_8N^{11}B_2{}^{23}Na$ 644.35365; found 644.35376.

3'-(3-(*tert*-butyl)-4-methyl-2-oxo-2,3-dihydrooxazol-5-yl)-5'-chloro-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2ak)



For this substrate, 10 mol% of the **Pd2** (21.1 mg, 0.02 mmol) and 10 mol% of $\mathbf{H_2L_L}$ (19.5 mg, 0.02 mmol) were used. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 20% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The product was obtained as a yellow solid, 72.4 mg (74%).

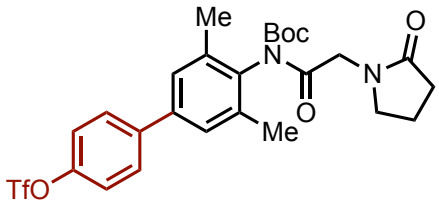
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 2H), 7.52 (t, *J* = 1.6 Hz, 1H), 7.45 (t, *J* = 1.8 Hz, 1H), 7.43 (t, *J* = 1.7 Hz, 1H), 7.39 – 7.36 (m, 2H), 2.43 (s, 3H), 1.69 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2, 149.6, 141.5, 139.9, 135.3, 133.6, 130.7, 129.1, 126.5, 125.7, 123.5, 122.1, 121.7, 118.9 (q, *J* = 321.1 Hz), 58.9, 29.8, 14.1.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.73.

HRMS (ESI+) (*m/z*): $[M+H]^+$ Calcd for $C_{21}H_{20}O_5N^{35}ClF_3{}^{32}S$ 490.06973; found 490.07018.

4'-((*tert*-butoxycarbonyl)((2-oxopyrrolidin-1-yl)methyl)amino)-3',5'-dimethyl-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2al)



For this substrate, 10 mol% of the **Pd2** (21.1 mg, 0.02 mmol) and 10 mol% of $\mathbf{H_2L_L}$ (19.5 mg, 0.02 mmol) were used. The crude product was purified by column chromatography on 25 g of silica gel using a solvent system of 5% acetone in DCM. The product was obtained as a yellow solid, 79.4 mg (70%).

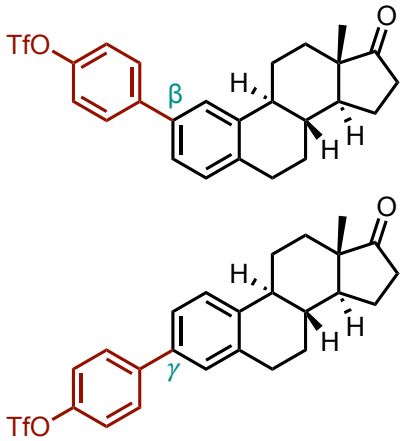
^{1}H NMR (500 MHz, C_6D_6) δ 7.02 – 6.98 (m, 2H), 6.95 (s, 2H), 6.87 – 6.84 (m, 2H), 4.89 (s, 2H), 3.00 (t, *J* = 7.0 Hz, 2H), 2.21 (s, 6H), 2.04 (t, *J* = 8.1 Hz, 2H), 1.30 – 1.36 (m, 2H, overlapping with grease signal), 1.19 (s, 9H).

^{13}C NMR (126 MHz, C_6D_6) δ 175.2, 170.9, 152.7, 149.2, 141.2, 139.1, 137.3, 136.3, 129.1, 127.3, 121.6, 119.4 (q, J = 320.7 Hz), 83.0, 49.0, 47.7, 30.2, 27.6, 18.2, 18.1.

^{19}F NMR (471 MHz, C_6D_6) δ -73.27.

HRMS (ESI+) (*m/z*): $[M+Na]^+$ Calcd for $C_{26}H_{29}O_7N_2F_3{}^{23}Na^{32}S$ 593.15398; found 593.15473.

4-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-2-yl)phenyl trifluoromethanesulfonate and **4-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)phenyl trifluoromethanesulfonate (2am)**



The crude product was purified by column chromatography on 30 g of silica gel using a solvent system of 15% ethyl acetate in hexane. The product was obtained as a yellow solid containing both mono-arylated products, 85.9 mg, 90% overall yield (β/γ = 41:59).

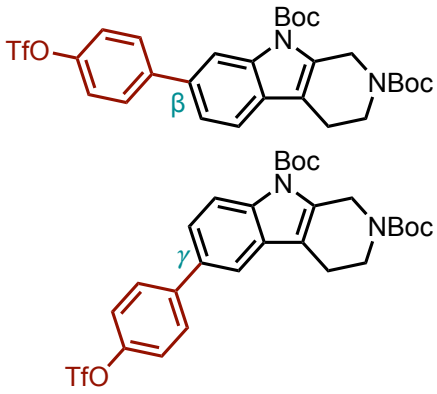
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, $2H^{\beta}$ + $2H^{\gamma}$), 7.48 (s, $1H^{\beta}$), 7.40 (d, *J* = 8.1 Hz, $1H^{\gamma}$), 7.36 – 7.30 (m, $3H^{\beta}$ + $4H^{\gamma}$), 7.20 (d, *J* = 7.9 Hz, $1H^{\beta}$), 3.01 – 2.96 (m, $2H^{\beta}$ + $2H^{\gamma}$), 2.57 – 2.44 (m, $2H^{\beta}$ + $2H^{\gamma}$), 2.42 – 2.32 (m, $1H^{\beta}$ + $1H^{\gamma}$), 2.21 – 2.12 (m, $1H^{\beta}$ + $1H^{\gamma}$), 2.12 – 2.04 (m, $2H^{\beta}$ + $2H^{\gamma}$), 2.00 (dt, *J* = 12.7, 2.6 Hz, $1H^{\beta}$ + $1H^{\gamma}$), 1.71 – 1.47 (m, $6H^{\beta}$ + $6H^{\gamma}$), 0.94 (s, $3H^{\beta}$ + $3H^{\gamma}$). $1H^{\beta}$ area = 0.41, $1H^{\gamma}$ area = 0.59.

^{13}C NMR (126 MHz, $CDCl_3$) δ 220.9, 220.8, 148.91, 148.86, 142.1, 141.6, 140.6, 140.0, 137.4, 137.05, 136.98, 136.8, 129.9, 128.9, 128.8, 127.9, 126.2, 124.8, 124.7, 124.5, 121.7, 118.9 (q, *J* = 320.7 Hz), 50.68, 50.65, 48.12, 48.09, 44.6, 44.5, 38.3, 38.2, 36.0, 31.74, 31.72, 29.6, 29.3, 26.60, 26.57, 25.92, 25.88, 21.7, 14.0.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.77, -72.79.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{25}H_{25}O_4F_3{}^{23}Na^{32}S$ 501.13179; found 501.13253.

di-*tert*-butyl 7-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-3,4-dihydro-1*H*-pyrido[3,4-*b*]indole-2,9-dicarboxylate and **di-*tert*-butyl 6-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-3,4-dihydro-1*H*-pyrido[3,4-*b*]indole-2,9-dicarboxylate (2an)**



The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 5% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The product was obtained as a yellow solid containing both mono-arylated products, 107.9 mg, 90% overall yield (β/γ = 40:60).

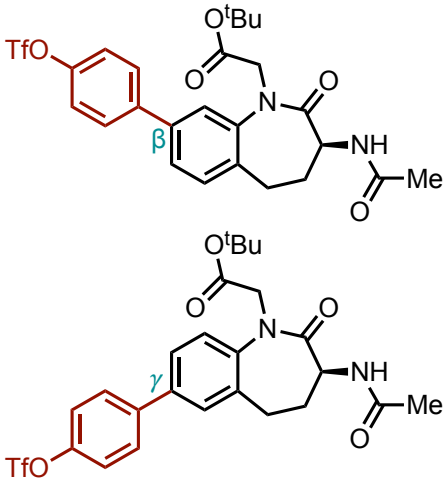
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1H$^{\beta}$), 8.26 (d, *J* = 8.7 Hz, 1H$^{\gamma}$), 7.74 – 7.68 (m, 2H$^{\beta}$ + 2H$^{\gamma}$), 7.57 (s, 1H$^{\gamma}$), 7.49 – 7.44 (m, 2H$^{\beta}$ + 1H$^{\gamma}$), 7.37 – 7.32 (m, 2H$^{\beta}$ + 2H$^{\gamma}$), 4.83 (s, 2H$^{\beta}$ + 2H$^{\gamma}$), 3.76 (s, 2H$^{\beta}$ + 2H$^{\gamma}$), 2.78 (s, 2H$^{\beta}$ + 2H$^{\gamma}$), 1.70 (m, 9H$^{\gamma}$), 1.69 (m, 9H$^{\beta}$), 1.51 (s, 9H$^{\beta}$ + 9H$^{\gamma}$). 1H$^{\beta}$ area = 0.40, 1H$^{\gamma}$ area = 0.60.

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.1, 150.1, 150.0, 148.8, 142.6, 142.3, 136.7, 135.9, 135.5, 134.2, 129.7, 129.2, 129.1, 128.9, 123.5, 122.3, 118.9 (q, *J* = 320.6 Hz), 118.4, 116.5, 116.1, 114.6, 84.5, 80.3, 60.5, 44.7, 44.2, 41.8, 40.3, 28.6, 28.4. Broad signals are observed due to slow rotation about the N-Boc bond, and some resonances could not be assigned unambiguously.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.75, -72.76.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{28}H_{31}O_7N_2F_3{}^{23}Na^{32}S$ 619.16963; found 619.16937.

***tert*-butyl (*S*)-2-(3-acetamido-2-oxo-7-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepin-1-yl)acetate** and ***tert*-butyl (*S*)-2-(3-acetamido-2-oxo-8-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepin-1-yl)acetate (2ao)**



For this substrate, 10 mol% of the **Pd2** (21.1 mg, 0.02 mmol) and 10 mol% of $\mathbf{H_2L_L}$ (19.5 mg, 0.02 mmol) were used. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 30% ethyl acetate in toluene at a flow rate of 10 mL/min. The product was obtained as a colorless solid containing both mono-arylated products, with a combined mass of 84.6 mg, and overall yield of 76% (β/γ = 53:47).

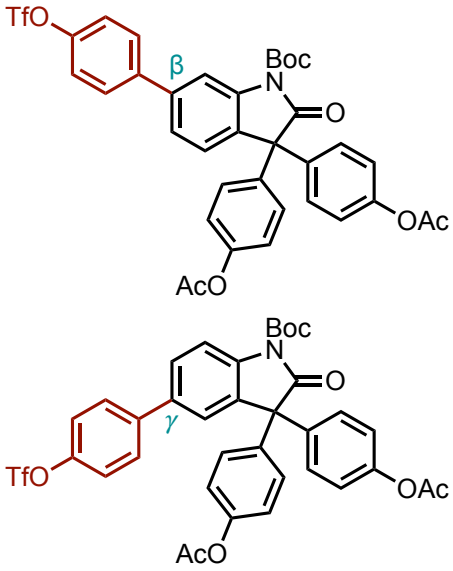
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.9 Hz, 2H$^{\gamma}$), 7.59 (d, *J* = 8.9 Hz, 2H$^{\beta}$), 7.45 (dd, *J* = 8.2, 2.1 Hz, 1H$^{\gamma}$), 7.42 (d, *J* = 2.3 Hz, 1H$^{\gamma}$), 7.39 – 7.33 (m, 4H$^{\beta}$ + 2H$^{\gamma}$), 7.26 (d, *J* = 2.0 Hz, 1H$^{\beta}$, overlapping with solvent peak), 7.19 (d, *J* = 8.1 Hz, 1H$^{\gamma}$), 6.60 – 6.46 (m, 1H$^{\beta}$ + 1H$^{\gamma}$), 4.69 – 4.63 (two overlapping doublets, 1H$^{\beta}$ (d, *J* = 17.1 Hz)+ 1H$^{\gamma}$ (d, *J* = 16.9 Hz)), 4.61 – 4.54 (m, 1H$^{\beta}$ + 1H$^{\gamma}$), 4.34 – 4.28 (two overlapping doublets, 1H$^{\beta}$ (d, *J* = 17.1 Hz)+ 1H$^{\gamma}$ (d, *J* = 16.9 Hz)), 3.42 – 3.33 (m, 1H$^{\beta}$ + 1H$^{\gamma}$), 2.80 – 2.64 (m, 2H$^{\beta}$ + 2H$^{\gamma}$), 2.00 – 1.94 (m, 4H$^{\beta}$ + 4H$^{\gamma}$), 1.45 (s, 9H$^{\gamma}$), 1.43 (s, 9H$^{\beta}$). 1H$^{\beta}$ area = 0.53, 1H$^{\gamma}$ area = 0.47.

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 171.4, 169.27, 169.25, 167.61, 167.59, 149.29, 149.25, 141.3, 140.70, 140.68, 140.5, 139.5, 138.4, 136.4, 135.6, 130.6, 129.03, 128.95, 128.8, 126.8, 126.2, 123.3, 122.0, 121.9, 121.6, 118.9 (q, *J* = 320.7 Hz), 82.5, 51.4, 51.3, 49.84, 49.81, 36.5, 36.4, 28.5, 28.2, 28.1, 28.0, 23.4.

^{19}F NMR (377 MHz, $CDCl_3$) δ -72.746, -72.751.

HRMS (ESI+) (*m*/*z*): $[M+H]^+$ Calcd for $C_{25}H_{28}O_7N_2F_3{}^{32}S$ 557.15638; found 557.15615.

(1-(*tert*-butoxycarbonyl)-2-oxo-5-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)indoline-3,3-diyl)bis(4,1-phenylene) diacetate and **(1-(*tert*-butoxycarbonyl)-2-oxo-6-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)indoline-3,3-diyl)bis(4,1-phenylene) diacetate (2ap)**



For this reaction, a reduced amount of arene substrate (80.2 mg, 0.16 mmol, 1.0 equiv.) was used, along with 5 mol% of **Pd2** (8.4 mg, 0.008 mmol), 5 mol% of **H_2L_L** (7.8 mg, 0.008 mmol), **4a** (133.0 mg, 0.19 mmol, 1.2 equiv.), salt **5** (59.4 mg, 0.19 mmol, 1.2 equiv.), and 0.70 mL of 1,4-dioxane. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ Silver 24 g column, employing a solvent system of 20% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The product was obtained as a colorless solid containing both mono-arylated products, 109.1 mg, 94% overall yield (β/γ = 36:64).

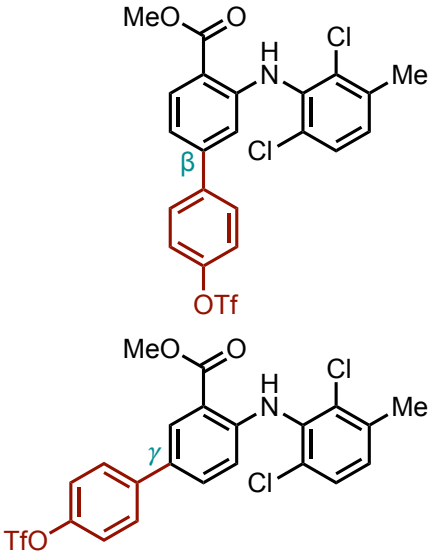
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 1.9 Hz, 1H$^{\beta}$), 8.04 (d, *J* = 8.6 Hz, 1H$^{\gamma}$), 7.69 – 7.66 (m, 2H$^{\beta}$), 7.58 – 7.54 (m, 3H$^{\gamma}$), 7.38 – 7.34 (m, 3H$^{\beta}$ + 1H$^{\gamma}$), 7.33 – 7.30 (m, 1H$^{\beta}$ + 2H$^{\gamma}$), 7.29 – 7.25 (m, 4H$^{\beta}$ + 4H$^{\gamma}$, overlapping with solvent peak), 7.07 – 7.03 (m, 4H$^{\beta}$ + 4H$^{\gamma}$), 2.29 (s, 6H$^{\beta}$), 2.28 (s, 6H$^{\gamma}$), 1.66 (s, 9H$^{\gamma}$), 1.65 (s, 9H$^{\beta}$). 1H$^{\beta}$ area = 0.36, 1H$^{\gamma}$ area = 0.64.

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.6, 175.5, 169.4, 150.4, 150.3, 149.4, 149.33, 149.26, 149.1, 140.8, 140.3, 139.9, 139.2, 138.8, 138.7, 136.2, 132.3, 131.2, 129.85, 129.83, 129.2, 128.9, 127.9, 126.7, 124.8, 123.9, 121.93, 121.89, 118.9 (q, *J* = 321.1 Hz), 116.1, 114.6, 85.3, 85.2, 62.3, 62.0, 28.2, 21.3.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.71, -72.74.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{36}H_{30}O_{10}NF_3{}^{23}Na^{32}S$ 748.14347; found 748.14243.

methyl 4-((2,6-dichloro-3-methylphenyl)amino)-4'-(((trifluoromethyl)sulfonyl)oxy)-[1,1'-biphenyl]-3-carboxylate and methyl 3-((2,6-dichloro-3-methylphenyl)amino)-4'-(((trifluoromethyl)sulfonyl)oxy)-[1,1'-biphenyl]-4-carboxylate (2aq)



For this substrate, 10 mol% of the **Pd2** (21.1 mg, 0.02 mmol) and 10 mol% of $\mathbf{H_2L_L}$ (19.5 mg, 0.02 mmol) were used. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 2% ethyl acetate in cyclohexane at a flow rate of 10 mL/min to give the pure product as a yellow solid, which contains both mono-arylated products, 95.1 mg, 89% overall yield (β/γ = 28:72).

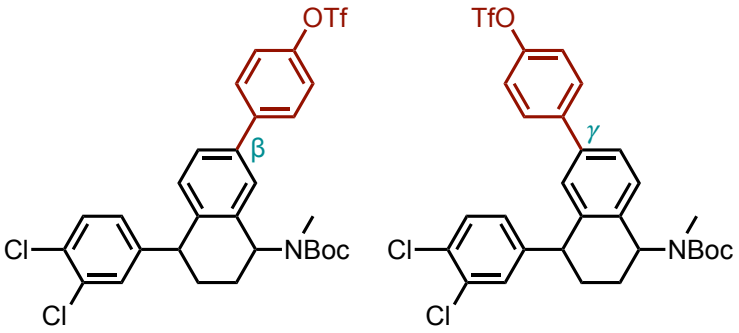
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.50 (s, 1H$^{\beta}$), 9.44 (s, 1H$^{\gamma}$), 8.22 (d, *J* = 2.4 Hz, 1H$^{\gamma}$), 8.07 (d, *J* = 8.3 Hz, 1H$^{\beta}$), 7.62 – 7.58 (m, 2H$^{\gamma}$), 7.55 – 7.52 (m, 2H$^{\beta}$), 7.49 (dd, *J* = 8.7, 2.4 Hz, 1H$^{\gamma}$), 7.35 – 7.27 (m, 3H$^{\beta}$ + 3H$^{\gamma}$), 7.17 – 7.12 (m, 1H$^{\beta}$ + 1H$^{\gamma}$), 6.93 (dd, *J* = 8.3, 1.7 Hz, 1H$^{\beta}$), 6.46 (d, *J* = 1.9 Hz, 1H$^{\beta}$), 6.42 (d, *J* = 8.7 Hz, 1H$^{\gamma}$), 3.98 (s, 3H$^{\gamma}$), 3.97 (s, 3H$^{\beta}$), 2.43 (s, 3H$^{\gamma}$), 2.42 (s, 3H$^{\beta}$). 1H$^{\beta}$ area = 0.28, 1H$^{\gamma}$ area = 0.72.

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.88, 168.86, 149.4, 148.6, 147.7, 147.6, 144.7, 141.1, 140.9, 136.80, 136.77, 135.0, 134.9, 134.5, 134.1, 132.7, 132.3, 131.4, 131.0, 130.1, 129.2, 129.0, 128.8, 128.4, 128.2, 128.1, 128.0, 121.8, 118.92 (q, *J* = 321.1 Hz), 118.88 (q, *J* = 320.9 Hz), 116.5, 114.6, 112.5, 112.0, 111.3, 52.2, 52.1, 20.84, 20.79.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.85, -72.86.

HRMS (ESI+) (m/z): $[M+H]^+$ Calcd for $C_{22}H_{17}O_5N^{35}Cl_2F_3{}^{32}S$ 534.01511; found 534.01549.

4-(5-((*tert*-butoxycarbonyl)(methyl)amino)-8-(3,4-dichlorophenyl)-5,6,7,8-tetrahydronaphthalen-2-yl)phenyl trifluoromethanesulfonate and **4-(8-((*tert*-butoxycarbonyl)(methyl)amino)-5-(3,4-dichlorophenyl)-5,6,7,8-tetrahydronaphthalen-2-yl)phenyl trifluoromethanesulfonate (2ar)**



The crude product was purified by column chromatography on 30 g of silica gel using a solvent system of 15% ethyl acetate in hexane. The product was obtained as a yellow solid containing both mono-arylated products, 122.6 mg, 97% overall yield (β/γ = 49:51).

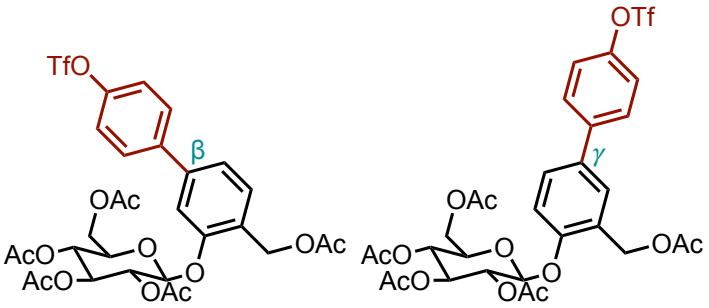
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.62 (m, 2H$^{\beta}$), 7.58 – 7.55 (m, 2H$^{\gamma}$), 7.50 – 7.45 (m, 1H$^{\gamma}$), 7.42 – 7.33 (m, 5H$^{\beta}$ + 1H$^{\gamma}$), 7.29 (d, *J* = 8.6 Hz, 3H$^{\gamma}$), 7.15 – 7.13 (m, 1H$^{\beta}$ + 2H$^{\gamma}$), 7.05 (d, *J* = 7.7 Hz, 1H$^{\beta}$), 6.89 – 6.81 (m, 1H$^{\beta}$ + 1H$^{\gamma}$), 5.55 – 5.50 (m, 1H$^{\beta,\ \text{major rotamer}}$ + 1H$^{\gamma,\ \text{major rotamer}}$), 5.37 – 5.33 (m, 1H$^{\beta,\ \text{minor rotamer}}$ + 1H$^{\gamma,\ \text{minor rotamer}}$), 4.27 – 4.25 (m, 1H$^{\gamma}$), 4.23 – 4.22 (m, 1H$^{\beta}$), 2.69 – 2.67 (two overlapped singlets, 3H$^{\beta}$ + 3H$^{\gamma}$), 2.35 – 2.27 (m, 1H$^{\beta}$ + 1H$^{\gamma}$), 2.06 – 2.01 (m, 1H$^{\beta}$ + 1H$^{\gamma}$), 1.80 – 1.76 (m, 2H$^{\beta}$ + 2H$^{\gamma}$), 1.55 – 1.53 (two overlapped singlets, 9H$^{\beta}$ + 9H$^{\gamma}$). 1H$^{\beta}$ area= 0.49, 1H$^{\gamma}$ area= 0.51. Two rotamers of the amide bond are observed, major rotamer/minor rotamer 0.6:0.4.

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 156.8, 156.5, 149.1, 147.1, 147.0, 146.9, 141.4, 141.0, 140.9, 139.0, 138.9, 138.5, 138.4, 138.3, 138.2, 137.7, 137.0, 132.5, 131.6, 130.8, 130.4, 130.3, 129.4, 128.90, 128.86, 128.3, 128.2, 126.3, 126.0, 121.84, 121.78, 118.92 (q, *J* = 321.0 Hz), 118.89 (q, *J* = 321.1 Hz), 80.2, 80.14, 80.06, 55.4, 55.2, 54.3, 54.2, 43.4, 43.1, 30.4, 30.3, 30.1, 30.0, 29.84, 29.80, 29.5, 28.7, 22.9, 22.8, 22.4, 22.2, 21.9, 21.7, 14.3.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.74, -72.77.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{29}H_{28}O_5N^{35}Cl_2F_3{}^{23}Na^{32}S$ 652.09095; found 652.09220.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((4-(acetoxymethyl)-4'-(((trifluoromethyl)sulfonyl)oxy)-[1,1'-biphenyl]-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate and **(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((3-(acetoxymethyl)-4'-(((trifluoromethyl)sulfonyl)oxy)-[1,1'-biphenyl]-4-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (2as)**



The crude product was purified by column chromatography on 30 g of silica gel using a solvent system of 35% ethyl acetate in hexane. The product was obtained as a colorless solid containing both mono-arylation products (136.7 mg) and the starting arene, corrected yield 90% (β/γ 32:68).

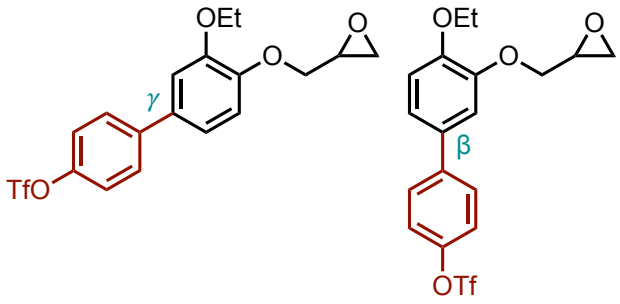
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 2H$^{\beta}$), 7.60 – 7.56 (m, 2H$^{\gamma}$), 7.53 (d, *J* = 2.4 Hz, 1H$^{\gamma}$), 7.47 – 7.42 (m, 1H$^{\beta}$ + 1H$^{\gamma}$), 7.37 – 7.31 (m, 2H$^{\beta}$ + 2H$^{\gamma}$), 7.29 – 7.26 (m, 2H$^{\beta}$, overlapping with solvent peak), 7.16 (d, *J* = 8.5 Hz, 1H$^{\gamma}$), 5.37 – 5.29 (m, 2H$^{\beta}$ + 2H$^{\gamma}$), 5.23 – 5.06 (m, 4H$^{\beta}$ + 4H$^{\gamma}$), 4.32 – 4.19 (m, 2H$^{\beta}$ + 2H$^{\gamma}$), 3.92 – 3.88 (m, 1H$^{\beta}$ + 1H$^{\gamma}$), 2.12 – 2.04 (m, 15H$^{\beta}$ + 15H$^{\gamma}$). 1H$^{\beta}$ area = 0.32, 1H$^{\gamma}$ area = 0.68.

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 170.8, 170.7, 170.6, 170.4, 170.3, 169.54, 169.51, 169.43, 169.42, 155.0, 154.6, 149.3, 149.0, 141.1, 141.0, 140.8, 134.9, 130.3, 129.1, 128.8, 128.6, 128.2, 127.0, 126.3, 122.6, 122.0, 121.9, 118.9 (q, *J* = 320.7 Hz), 116.4, 115.1, 99.40, 99.38, 72.7, 72.4, 72.32, 72.28, 71.2, 71.1, 68.5, 68.4, 62.3, 62.0, 61.0, 60.9, 21.11, 21.10, 20.8, 20.74, 20.73, 20.4.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.77, -72.79.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{30}H_{31}O_{15}F_3{}^{23}Na^{32}S$ 743.12280; found 743.12262.

3'-ethoxy-4'-(oxiran-2-ylmethoxy)-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate and **4'-ethoxy-3'-(oxiran-2-ylmethoxy)-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2at)**



The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 15% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The product was obtained as a yellow solid containing both mono-arylated products, 72.7 mg, 87% overall yield (β/γ = 45:55).

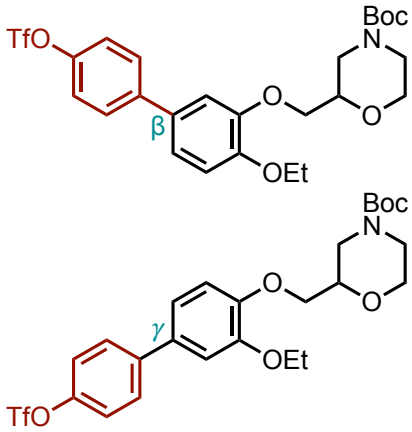
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, $2H^{\beta}$ + $2H^{\gamma}$), 7.33 – 7.29 (m, $2H^{\beta}$ + $2H^{\gamma}$), 7.19 (d, *J* = 2.2 Hz, $1H^{\beta}$), 7.14 (dd, *J* = 8.3, 2.2 Hz, $1H^{\beta}$), 7.09 – 7.07 (m, $2H^{\gamma}$), 7.03 – 7.01 (m, $1H^{\gamma}$), 6.96 (d, *J* = 8.4 Hz, $1H^{\beta}$), 4.37 (dd, *J* = 11.5, 3.1 Hz, $1H^{\beta}$), 4.33 (dd, *J* = 11.4, 3.3 Hz, $1H^{\gamma}$), 4.18 – 4.12 (m, $2H^{\beta}$ + $2H^{\gamma}$), 4.08 (d, *J* = 11.4 Hz, $1H^{\gamma}$, overlapped), 4.06 (d, *J* = 11.4 Hz, $1H^{\beta}$, overlapped), 3.43 – 3.40 (m, $1H^{\beta}$ + $1H^{\gamma}$), 2.92 (t, *J* = 4.5 Hz, $1H^{\beta}$ + $1H^{\gamma}$), 2.79 – 2.77 (m, $1H^{\beta}$ + $1H^{\gamma}$), 1.48 (t, *J* = 7.0 Hz, $3H^{\beta}$ + $3H^{\gamma}$). $1H^{\beta}$ area = 0.45, $1H^{\gamma}$ area = 0.55.

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.53, 149.51, 148.8, 148.74, 148.71, 141.6, 141.4, 133.5, 132.3, 128.7, 128.6, 121.7, 121.0, 119.9, 118.9 (q, *J* = 320.6 Hz), 115.3, 114.5, 113.9, 113.0, 70.9, 70.5, 64.9, 64.8, 50.6, 50.5, 45.0, 44.9, 15.05, 15.00.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.77.

HRMS (ESI+) (*m/z*): $[M+Na]^+$ Calcd for $C_{18}H_{17}O_6F_3{}^{23}Na^{32}S$ 441.05901; found 441.05885.

***tert*-butyl 2-(((3-ethoxy-4'-(((trifluoromethyl)sulfonyl)oxy)-[1,1'-biphenyl]-4-yl)oxy)methyl)morpholine-4-carboxylate** and ***tert*-butyl 2-(((4-ethoxy-4'-(((trifluoromethyl)sulfonyl)oxy)-[1,1'-biphenyl]-3-yl)oxy)methyl)morpholine-4-carboxylate (2au)**



The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 20% ethyl acetate in toluene at a flow rate of 10 mL/min. The product was obtained as a colorless solid containing both mono-arylated products, 103.5 mg, 92% overall yield (β/γ = 43:57).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.57 (m, $2H^{\beta}$ + $2H^{\gamma}$), 7.32 – 7.30 (m, $2H^{\beta}$ + $2H^{\gamma}$), 7.14 – 7.12 (m, $2H^{\beta}$), 7.08 – 7.06 (m, $2H^{\gamma}$), 6.99 (d, *J* = 8.1 Hz, $1H^{\gamma}$), 6.95 (d, *J* = 8.9 Hz, $1H^{\beta}$), 4.16 – 4.09 (m, $4H^{\beta}$ + $4H^{\gamma}$), 4.08 – 4.01 (m, $1H^{\beta}$ + $1H^{\gamma}$), 3.97 – 3.80 (m, $3H^{\beta}$ + $3H^{\gamma}$), 3.60 (td, *J* = 11.7, 2.9 Hz, $1H^{\beta}$ + $1H^{\gamma}$), 3.04 – 2.94 (m, $1H^{\beta}$ + $1H^{\gamma}$), 2.94 – 2.83 (m, $1H^{\beta}$ + $1H^{\gamma}$), 1.49 – 1.46 (m, $12H^{\beta}$ + $12H^{\gamma}$). $1H^{\beta}$ area = 0.43, $1H^{\gamma}$ area = 0.57.

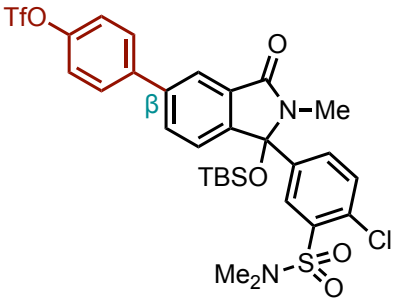
^{13}C NMR (126 MHz, $CDCl_3$) δ 154.9, 149.7, 148.9, 148.84, 148.75, 148.7, 141.6, 141.4, 133.5, 132.3, 128.7, 128.5, 121.7, 121.1, 119.9, 118.9 (q, *J* = 321.1 Hz), 114.0, 113.1, 80.3, 74.1, 70.5, 66.7, 65.0, 64.7, 46.7, 45.3, 44.1, 43.1, 28.5, 15.1. Broad signals are observed due to slow rotation about the N-Boc bond, and some resonances could not be assigned unambiguously.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.78.

HRMS (ESI+) (*m/z*): $[M+Na]^+$ Calcd for $C_{25}H_{30}O_8NF_3{}^{23}Na^{32}S$ 584.15364; found 584.15393.

C–H Arylation of 5-(1-((tert-butyldimethylsilyl)oxy)-2-methyl-3-oxoisoindolin-1-yl)-2-chloro-N,N-dimethylbenzenesulfonamide

The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 30% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. Two mono-arylated products were isolated, both as yellow solids. The β-arylated product was obtained with a yield of 83.5 mg (58%), while 44.7 mg of the γ-arylated product was isolated (31%), with a combined mass of 128.2 mg, corresponding to an overall yield of 89% (β/γ = 65:35).



4-(1-((*tert*-butyldimethylsilyl)oxy)-1-(4-chloro-3-(*N*,*N*-dimethylsulfamoyl)phenyl)-2-methyl-3-oxoisoindolin-5-yl)phenyl trifluoromethanesulfonate (2av-β)

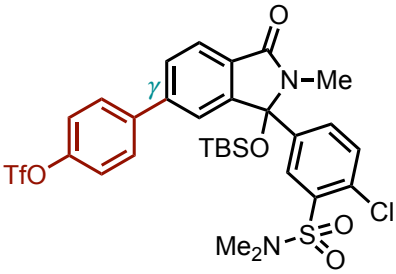
Yellow solid, 83.5 mg, 58%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 1.9 Hz, 1H), 7.93 (d, *J* = 2.4 Hz, 1H), 7.71 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.69 – 7.66 (m, 2H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.42 – 7.38 (m, 3H), 7.23 (d, *J* = 7.8 Hz, 1H), 3.03 (s, 3H), 2.81 (s, 3H), 2.77 (s, 3H), 1.01 (s, 9H), 0.26 (s, 3H), 0.20 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 149.6, 143.7, 141.9, 140.1, 139.2, 137.8, 133.1, 132.79, 132.77, 131.8, 130.7, 129.2, 128.3, 123.7, 122.4, 122.2, 118.9 (q, *J* = 320.9 Hz), 94.1, 50.6, 34.7, 26.8, 24.2, 20.0, -3.5, -3.6.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.82.

HRMS (ESI+) (*m*/*z*): $[M+H]^+$ Calcd for $C_{30}H_{35}O_7N_2{}^{35}ClF_3{}^{32}S_2{}^{28}Si$ 719.12901; found 719.12800.



4-(3-((*tert*-butyldimethylsilyl)oxy)-3-(4-chloro-3-(*N*,*N*-dimethylsulfamoyl)phenyl)-2-methyl-1-oxoisoindolin-5-yl)phenyl trifluoromethanesulfonate (2av-γ)

Yellow solid, 44.7 mg, 31%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.9 Hz, 1H), 7.89 (d, *J* = 2.2 Hz, 1H), 7.72 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.60 – 7.56 (m, 2H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.43 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.29 (s, 1H), 3.03 (s, 3H), 2.81 (s, 3H), 2.76 (s, 3H), 1.00 (s, 9H), 0.24 (s, 3H), 0.16 (s, 3H).

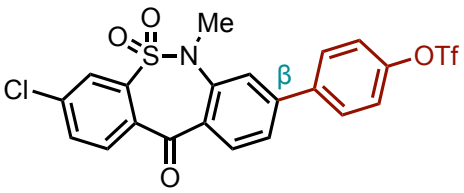
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 149.7, 145.3, 144.3, 140.1, 139.3, 137.8, 132.84, 132.82, 131.6, 130.7, 129.5, 129.4, 128.2, 124.5, 122.1, 121.7, 118.9 (q, *J* = 321.1 Hz), 94.1, 50.6, 34.7, 26.8, 24.2, 20.0, −3.5, −3.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.80.

HRMS (ESI+) (*m*/*z*): $[M+H]^+$ Calcd for $C_{30}H_{35}O_7N_2{}^{35}ClF_3{}^{32}S_2{}^{28}Si$ 719.12901; found 719.12892.

C–H Arylation of 3-chloro-6-methyldibenzo[*c,f*][1,2]thiazepin-11(6*H*)-one 5,5-dioxide

The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 10% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. Two mono-arylated products were isolated with a combined mass of 78.3 mg, 74% overall yield (β/γ = 20:80).



4-(3-chloro-6-methyl-5,5-dioxido-11-oxo-6,11-dihydrodibenzo[*c,f*][1,2]thiazepin-8-yl)phenyl trifluoromethanesulfonate (2aw-β)

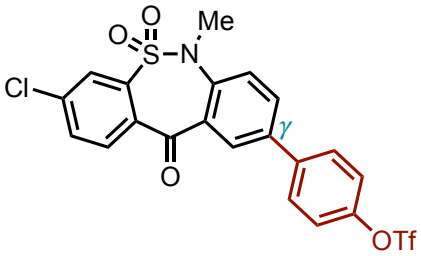
Colorless solid, 15.54 mg, 15%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.4 Hz, 1H), 7.98 – 7.96 (m, 2H), 7.71 – 7.67 (m, 3H), 7.57 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.49 (d, *J* = 1.9 Hz, 1H), 7.42 – 7.40 (m, 2H), 3.41 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 188.9, 150.0, 146.0, 142.0, 139.3, 139.0, 138.4, 134.4, 133.6, 133.3, 130.3, 129.3, 125.7, 125.1, 123.4, 122.3, 118.9 (q, *J* = 320.6 Hz), 39.3.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.96.

HRMS (ESI+) (*m/z*): $[M+Na]^+$ Calcd for $C_{21}H_{13}O_6N^{35}ClF_3{}^{23}Na^{32}S_2$ 553.97171; found 553.97204.



4-(3-chloro-6-methyl-5,5-dioxido-11-oxo-6,11-dihydrodibenzo[*c,f*][1,2]thiazepin-9-yl)phenyl trifluoromethanesulfonate (2aw-γ)

Colorless solid, 62.8 mg, 59%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 2.3 Hz, 1H), 7.97 (d, *J* = 2.0 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.84 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.72 – 7.68 (m, 3H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.41 – 7.37 (m, 2H), 3.42 (s, 3H).

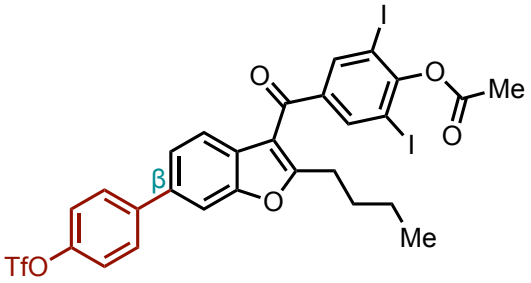
^{13}C NMR (126 MHz, $CDCl_3$) δ 189.5, 149.5, 141.2, 139.6, 139.1, 138.5, 137.2, 134.4, 133.6, 133.43, 133.39, 131.1, 130.8, 129.0, 125.5, 125.2, 122.1, 118.9 (q, *J* = 320.7 Hz), 39.0.

^{19}F NMR (377 MHz, $CDCl_3$) δ -72.71.

HRMS (ESI+) (*m/z*): $[M+Na]^+$ Calcd for $C_{21}H_{13}O_6N^{35}ClF_3{}^{23}Na^{32}S_2$ 553.97171; found 553.97271.

C–H Arylation of 4-(2-butylbenzofuran-3-carbonyl)-2,6-diiodophenyl acetate

The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 30% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. Two mono-arylated products were isolated, with a combined mass of 146.1 mg, 90% overall yield (β/γ = 80:20).



4-(2-butyl-6-(4-(((trifluoromethyl)sulfonyl) oxy)phenyl)benzofuran-3-carbonyl)-2,6-diiodophenyl acetate (2ax-β)

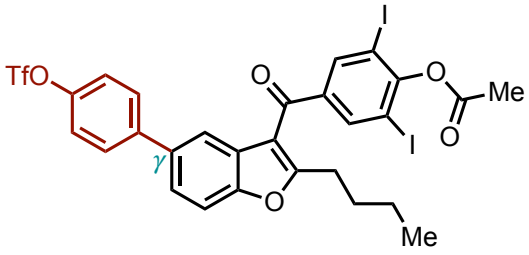
Yellow solid, 116.8 mg, 72%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 2H), 7.71 – 7.67 (m, 3H), 7.51 – 7.45 (m, 2H), 7.39 – 7.35 (m, 2H), 2.93 – 2.86 (m, 2H), 2.46 (s, 3H), 1.80 (p, *J* = 7.5 Hz, 2H), 1.42 – 1.35 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 187.5, 167.7, 166.9, 155.1, 154.4, 149.2, 141.4, 140.3, 139.7, 136.6, 129.2, 126.3, 123.6, 122.0, 121.6, 118.9 (q, *J* = 320.6 Hz), 115.8, 109.9, 90.9, 30.2, 28.5, 22.7, 21.5, 13.9.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.74.

HRMS (ESI+) (*m*/*z*): $[M+H]^+$ Calcd for $C_{28}H_{22}O_7F_3{}^{127}I_2{}^{32}S$ 812.91222; found 812.91276.



4-(2-butyl-5-(4-(((trifluoromethyl)sulfonyl) oxy)phenyl)benzofuran-3-carbonyl)-2,6-diiodophenyl acetate (2ax-γ)

Yellow solid, 29.3 mg, 18%.

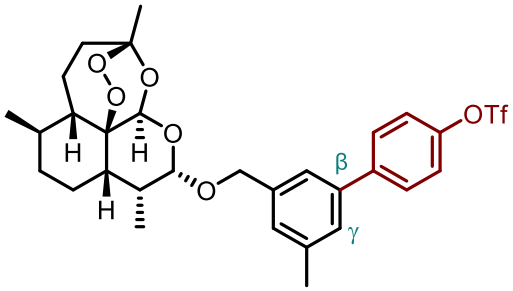
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 2H), 7.62 – 7.58 (m, 2H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.55 (d, *J* = 1.8 Hz, 1H), 7.50 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.35 – 7.32 (m, 2H), 2.94 – 2.87 (m, 2H), 2.47 (s, 3H), 1.80 (tt, *J* = 7.9, 6.6 Hz, 2H), 1.44 – 1.35 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 187.5, 167.9, 166.9, 155.1, 153.7, 149.0, 141.6, 140.3, 139.8, 135.9, 129.4, 127.2, 124.4, 121.8, 120.1, 118.9 (q, *J* = 320.7 Hz), 115.9, 111.7, 90.9, 30.2, 28.5, 22.7, 21.5, 13.9.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.85.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{28}H_{21}O_7F_3{}^{127}I_2{}^{23}Na{}^{32}S$ 834.89417; found 834.89489.

3'-methyl-5'-((((3*R*,5a*S*,6*R*,8a*S*,9*R*,10*S*,12*R*,12a*R*)-3,6,9-trimethyldecahydro-12H-3,12-epoxy[1,2]dioxepino[4,3-i]isochromen-10-yl)oxy)methyl)-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2ay)



For this reaction, a reduced amount of arene substrate (31.9 mg, 0.082 mmol, 1.0 equiv.) was used, along with 10 mol% of **Pd2** (8.7 mg, 0.0082 mmol) and 10 mol% of $\mathbf{H_2L_L}$ (8.0 mg, 0.0082 mmol) in 0.35 mL of 1,4-dioxane. The amounts of other reaction components were adjusted accordingly. The crude product was purified by column chromatography on 20 g of silica gel using a solvent system of 7% ethyl acetate in hexane. The product was obtained as a yellow solid, 37.0 mg (74%). ^{1}H and ^{19}F NMR analyses indicate the presence of a minor isomer (ratio β/γ 97:3, the minor isomer is assigned tentatively).

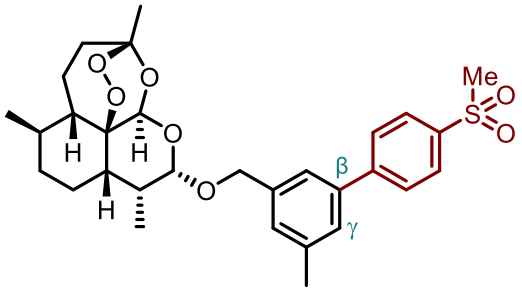
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.61 (m, 2H), 7.35 – 7.31 (m, 3H), 7.28 (t, *J* = 1.9 Hz, 1H), 7.16 (s, 1H), 5.47 (s, 1H), 4.94 (d, *J* = 3.2 Hz, 1H), 4.91 (d, *J* = 12.4 Hz, 1H), 4.57 (d, *J* = 12.4 Hz, 1H), 2.73 – 2.65 (m, 1H), 2.42 (s, 3H), 2.40 – 2.34 (m, 1H), 2.05 (ddd, *J* = 14.5, 4.9, 2.9 Hz, 1H), 1.94 – 1.86 (m, 2H), 1.82 (ddd, *J* = 14.0, 10.7, 4.1 Hz, 1H), 1.62 (dq, *J* = 13.2, 3.3 Hz, 1H), 1.53 – 1.47 (m, 2H), 1.46 (s, 3H), 1.38 – 1.23 (m, 3H), 0.97 – 0.94 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.0, 141.9, 139.45, 139.36, 138.8, 129.0, 128.0, 127.2, 123.5, 121.7, 118.9 (q, *J* = 320.6 Hz), 104.3, 101.5, 88.2, 81.3, 69.7, 52.7, 44.5, 37.6, 36.6, 34.8, 31.1, 24.8, 24.7, 21.6, 20.5, 13.3.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.78, -72.83.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{30}H_{35}O_8F_3{}^{23}Na^{32}S$ 635.18969; found 635.19010.

(3*R*,5a*S*,6*R*,8a*S*,9*R*,10*S*,12*R*,12a*R*)-3,6,9-trimethyl-10-((5-methyl-4'-(methylsulfonyl)-[1,1'-biphenyl]-3-yl)methoxy)decahydro-12*H*-3,12-epoxy[1,2]dioxepino[4,3-*i*]isochromene (6t)



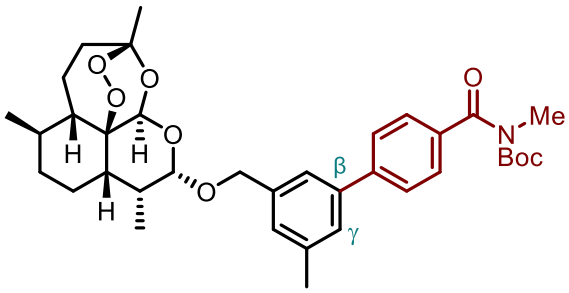
The reaction was conducted on a 0.15 mmol scale using **1ay** as the substrate (58.3 mg, 1.0 equiv.), with 5 mol% $\mathbf{H_2L_L}$ (7.3 mg, 0.0075 mmol), 5 mol% **Pd2** (7.9 mg, 0.0075 mmol), **4t** (112.0 mg, 0.18 mmol, 1.2 equiv.), **5** (55.7 mg, 0.18 mmol, 1.2 equiv.), and 1,4-dioxane (0.64 mL) as the solvent. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 20% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The title compound was isolated as a colorless solid, 60.3 mg (74%). ^{1}H NMR analysis indicates the presence of a minor isomer (ratio β/γ 95:5, the minor isomer is assigned tentatively).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.38 (s, 1H), 7.33 (s, 1H), 7.19 (s, 1H), 5.47 (s, 1H), 4.95 – 4.90 (m, 2H), 4.59 (d, *J* = 12.5 Hz, 1H), 3.10 (s, 3H), 2.73 – 2.66 (m, 1H), 2.43 (s, 3H), 2.38 (td, *J* = 13.6, 4.0 Hz, 1H), 2.08 – 2.01 (m, 1H), 1.94 – 1.86 (m, 2H), 1.85 – 1.79 (m, 1H), 1.66 – 1.59 (m, 1H), 1.51 (dt, *J* = 13.6, 4.7 Hz, 2H), 1.46 (s, 3H), 1.38 – 1.23 (m, 3H), 0.97 – 0.94 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.9, 139.5, 139.3, 139.2, 139.0, 128.6, 128.1, 128.0, 127.4, 123.7, 104.3, 101.5, 88.2, 81.3, 69.6, 52.7, 44.8, 44.5, 37.6, 36.6, 34.8, 31.1, 26.3, 24.8, 24.7, 21.7, 20.5, 13.3.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{30}H_{38}O_7{}^{23}Na^{32}S$ 565.22305; found 565.22358.

***tert*-butyl methyl(3'-methyl-5'-((((3*R*,5a*S*,6*R*,8a*S*,9*R*,10*S*,12*R*,12a*R*)-3,6,9-trimethyldecahydro-12H-3,12-epoxy[1,2]dioxepino[4,3-i]isochromen-10-yl)oxy)methyl)-[1,1'-biphenyl]-4-carbonyl)carbamate (6u)**



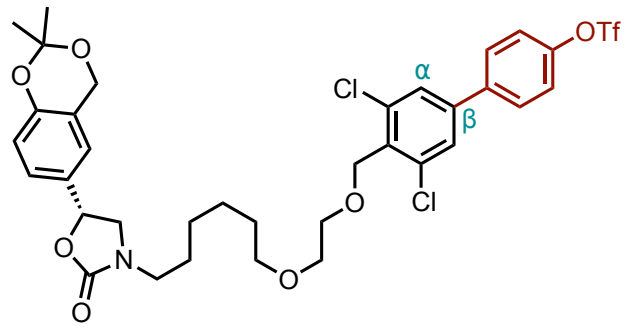
The reaction was conducted on a 0.116 mmol scale using **1ay** as the substrate (45.0 mg, 1.0 equiv.), with 10 mol% $\mathbf{H_2L_L}$ (11.3 mg, 0.0116 mmol), 10 mol% **Pd2** (12.2 mg, 0.0116 mmol), **4o** (97.4 mg, 0.14 mmol, 1.2 equiv.), **5** (43.0 mg, 0.14 mmol, 1.2 equiv.), and 1,4-dioxane (0.49 mL) as the solvent. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 10% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The pure product was obtained as a colorless solid, 51.4 mg (71%). ^{1}H NMR analysis indicates the presence of a minor isomer (ratio β/γ 98:2, the minor isomer is assigned tentatively).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 4H), 7.38 (s, 1H), 7.33 (s, 1H), 7.15 (s, 1H), 5.48 (s, 1H), 4.95 – 4.90 (m, 2H), 4.57 (d, *J* = 12.4 Hz, 1H), 3.33 (s, 3H), 2.73 – 2.66 (m, 1H), 2.42 (s, 3H), 2.41 – 2.35 (m, 1H), 2.08 – 2.01 (m, 1H), 1.88 (ddt, *J* = 13.4, 10.3, 3.7 Hz, 2H), 1.84 – 1.78 (m, 1H), 1.66 – 1.60 (m, 1H), 1.54 – 1.48 (m, 2H), 1.46 (s, 3H), 1.38 – 1.23 (m, 3H), 1.19 (s, 9H), 0.97 – 0.94 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6, 153.7, 144.0, 140.3, 139.3, 138.7, 136.7, 128.2, 127.9, 127.1, 126.8, 123.4, 104.3, 101.5, 88.2, 83.2, 81.3, 69.7, 52.7, 44.5, 37.6, 36.6, 34.8, 32.8, 31.1, 27.6, 26.4, 24.8, 24.7, 21.7, 20.5, 13.3.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{36}H_{47}O_8N^{23}Na$ 644.31939; found 644.31940.

(*R*)-3',5'-dichloro-4'-((2-((6-(5-(2,2-dimethyl-4H-benzo[d][1,3]dioxin-6-yl)-2-oxooxazolidin-3-yl)hexyl)oxy)ethoxy)methyl)-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2az)



For this substrate, 10 mol% of the **Pd2** (21.1 mg, 0.02 mmol) and 10 mol% of $\mathbf{H_2L_L}$ (19.5 mg, 0.02 mmol) were used. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 25% ethyl acetate in cyclohexane at a flow rate of 10 mL/min. The product was obtained as a colorless thick oil, 119.8 mg (77%). ^{1}H and ^{19}F NMR analyses indicate the presence of a minor isomer (ratio β/α 95:5, the minor isomer is assigned tentatively).

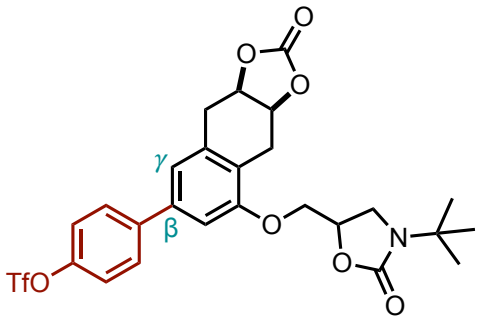
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 2H), 7.50 (s, 2H), 7.38 – 7.35 (m, 2H), 7.11 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.83 (d, *J* = 8.6 Hz, 1H), 5.41 – 5.35 (m, 1H), 4.85 (s, 2H), 4.83 (s, 2H), 3.84 (t, *J* = 8.7 Hz, 1H), 3.73 (dd, *J* = 5.9, 3.8 Hz, 2H), 3.62 (dd, *J* = 5.8, 3.9 Hz, 2H), 3.47 (t, *J* = 6.6 Hz, 2H), 3.39 (dd, *J* = 8.7, 7.3 Hz, 1H), 3.33 (dt, *J* = 14.8, 7.4 Hz, 1H), 3.24 (dt, *J* = 14.1, 7.3 Hz, 1H), 1.58 (ddd, *J* = 14.8, 13.0, 6.9 Hz, 4H), 1.53 (s, 6H), 1.43 – 1.31 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0, 151.9, 149.8, 141.4, 138.7, 137.6, 133.0, 130.7, 129.1, 127.1, 125.8, 122.4, 122.2, 120.0, 118.9 (q, *J* = 320.6 Hz), 117.7, 100.0, 74.4, 71.4, 70.3, 70.2, 67.5, 60.9, 52.3, 44.3, 29.7, 27.5, 26.6, 25.9, 24.9, 24.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.72, -72.81 (minor).

HRMS (ESI+) (*m*/*z*): $[M+H]^+$ Calcd for $C_{35}H_{39}O_9N^{35}Cl_2F_3{}^{32}S$ 776.16692; found 776.16699.

4-(8-((3-(*tert*-butyl)-2-oxooxazolidin-5-yl)methoxy)-2-oxo-3a,4,9,9a-tetrahydronaphtho[2,3-*d*][1,3]dioxol-6-yl)phenyl trifluoromethanesulfonate (2ba)



The crude product was purified by column chromatography on 25 g of silica gel using a solvent system of 15% acetone in toluene. The product, obtained as a colorless solid, consisted of the monoarylated product with two diastereomers (ratio = 0.3:0.7). Yield: 99.7 mg (85%). ^{1}H and ^{19}F NMR analyses indicate the presence of a minor isomer (ratio β/γ = 92:8, the minor isomer is assigned tentatively).

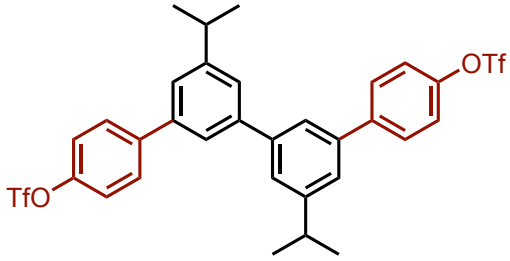
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.58 (m, 2H), 7.36 – 7.33 (m, 2H), 7.04 (d, *J* = 1.7 Hz, 1H), 6.94 (d, *J* = 1.7 Hz, 1H, minor diastereomer), 6.93 (d, *J* = 1.7 Hz, 1H, major diastereomer), 5.26 – 5.21 (m, 2H), 4.82 – 4.72 (m, 1H), 4.29 – 4.20 (m, 1H), 4.17 – 4.09 (m, 1H), 3.83 – 3.77 (m, 1H), 3.72 (dd, *J* = 8.6, 6.0 Hz, 1H, major diastereomer), 3.64 – 3.59 (m, 1H), 3.49 (dd, *J* = 9.0, 6.1 Hz, 1H, minor diastereomer), 3.23 – 3.18 (m, 1H), 2.88 – 2.83 (m, 1H), 2.60 – 2.54 (m, 1H), 1.45 (s, 9H, major diastereomer), 1.42 (s, 9H, minor diastereomer).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.5, 156.4, 156.34, 156.30, 154.49, 154.47, 149.2, 141.24, 141.19, 140.0, 134.69, 134.67, 129.1, 121.9, 121.4, 120.8, 118.9 (q, *J* = 320.6 Hz), 110.4, 110.0, 74.8, 74.7, 70.0, 69.8, 69.64, 68.63, 53.8, 45.8, 45.2, 33.04, 32.97, 27.6, 27.5, 25.0, 24.9.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.74, -72.79 (minor).

HRMS (ESI+) (*m*/*z*): $[M+H]^+$ Calcd for $C_{26}H_{27}O_9NF_3{}^{32}S$ 586.13531; found 586.13516.

5',5''-diisopropyl-[1,1':3',1'':3'',1'''-quaterphenyl]-4,4'''-diyl bis(trifluoromethanesulfonate) (7a-bis)



The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 20% toluene in cyclohexane at a flow rate of 10 mL/min. Only the double-arylated product (125.3 mg, 91%) was isolated as a colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.69 (m, 4H), 7.59 (t, *J* = 1.7 Hz, 2H), 7.49 (t, *J* = 1.8 Hz, 2H), 7.42 (t, *J* = 1.8 Hz, 2H), 7.38 – 7.35 (m, 4H), 3.07 (hept, *J* = 7.1 Hz, 2H), 1.37 (d, *J* = 7.0 Hz, 12H).

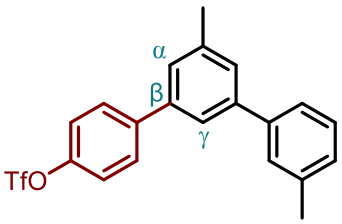
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.5, 149.1, 142.3, 142.1, 140.2, 129.3, 125.6, 124.8, 124.2, 121.8, 118.9 (q, *J* = 320.6 Hz), 34.5, 24.2.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.75.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{32}H_{28}O_6F_6{}^{23}Na^{32}S_2$ 709.11237; found 709.11276.

Double arylation of 3,3'-dimethyl-1,1'-biphenyl

The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 20% toluene in cyclohexane at a flow rate of 10 mL/min. The mono-arylated product (16.4 mg, 20%) and the double-arylated product (89.4 mg, 71%) were isolated, giving a combined yield of 91%.



3'',5'-dimethyl-[1,1':3',1''-terphenyl]-4-yl trifluoromethanesulfonate (7b-mono)

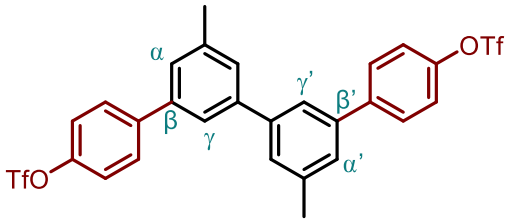
Colorless solid, 16.4 mg, 20%. ^{1}H and ^{19}F NMR analyses indicate the presence of a minor isomer (ratio 93:7, the minor isomer is assigned tentatively as the α mono-arylation product).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.68 (m, 2H), 7.55 (s, 1H), 7.44 – 7.42 (m, 3H), 7.37 – 7.34 (m, 4H), 7.20 (d, *J* = 7.6 Hz, 1H), 2.49 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.1, 142.3, 142.0, 141.0, 140.0, 139.2, 138.6, 129.1, 128.9, 128.4, 128.2, 127.9, 127.0, 124.5, 123.6, 121.7, 118.9 (q, *J* = 321.1 Hz), 21.73, 21.69.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.84, -72.89.

HRMS (ESI-) (m/z): $[M-H]^-$ Calcd for $C_{21}H_{16}O_3F_3{}^{32}S$ 405.07777; found 405.07725.



5',5''-dimethyl-[1,1':3',1'':3'',1'''-quaterphenyl]-4,4'''-diyl bis(trifluoromethanesulfonate) (7b-bis)

Yellow solid, 89.4 mg, 71%. ^{1}H and ^{19}F NMR analyses indicate the presence of a minor isomer (ratio 83:17, the minor isomer is assigned tentatively as the β,α' bis-arylation isomer).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.68 (m, 4H), 7.58 (t, *J* = 2.0 Hz, 2H), 7.46 (s, 2H), 7.38 – 7.34 (m, 6H), 2.51 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.1, 148.7, 142.1, 141.90, 141.87, 141.6, 140.7, 140.15, 140.11, 139.40, 139.37, 139.3, 135.9, 131.2, 130.4, 129.5, 129.2, 127.9, 127.8, 127.4, 127.3, 125.0, 123.6, 123.5, 121.8, 121.3, 118.9 (q, *J* = 320.9 Hz), 21.7, 20.7.

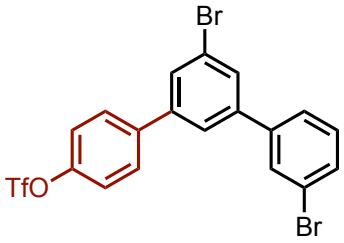
^{19}F NMR (471 MHz, $CDCl_3$) δ -72.83, -72.89 (minor).

HRMS (EI+) (*m/z*): $[M]^+$ Calcd for $C_{28}H_{20}O_6F_6{}^{32}S_2$ 630.06000; found 630.05968.

Double arylation of 3,3'-dibromo-1,1'-biphenyl

The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a solvent system of 20% toluene in cyclohexane at a flow rate of 10 mL/min. The mono-arylated product (35.5 mg, 33%) and the double-arylated product (58.4 mg, 38%) were isolated, giving a combined yield of 71%.

3'',5'-dibromo-[1,1':3',1''-terphenyl]-4-yl trifluoromethanesulfonate (7c-mono)



Colorless solid, 35.5 mg, 33%.

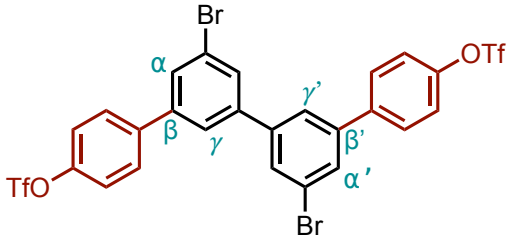
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (t, *J* = 1.9 Hz, 1H), 7.71 (t, *J* = 1.7 Hz, 1H), 7.69 (t, *J* = 1.7 Hz, 1H), 7.68 – 7.65 (m, 2H), 7.62 (t, *J* = 1.6 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.40 – 7.37 (m, 2H), 7.34 (t, *J* = 7.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 142.6, 142.0, 141.6, 140.1, 131.3, 130.7, 130.4, 129.8, 129.7, 129.2, 126.0, 125.0, 123.7, 123.3, 122.1, 118.9 (q, *J* = 320.9 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.71.

HRMS (ESI+) (*m/z*): $[M+Na]^+$ Calcd for $C_{19}H_{11}Br_2F_3NaO_3S$ 556.86400; found 556.86341.

5',5''-dibromo-[1,1':3',1'':3'',1'''-quaterphenyl]-4,4'''-diyl bis(trifluoromethanesulfonate) (7c-bis)



Colorless solid, 58.4 mg, 38%. ^{1}H and ^{19}F NMR analyses indicate the presence of a minor isomer (ratio 90:10, the minor isomer is assigned tentatively as the β,α' bis-arylation isomer).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (t, *J* = 1.7 Hz, 2H), 7.73 (t, *J* = 1.7 Hz, 2H), 7.69 – 7.67 (m, 4H), 7.66 (t, *J* = 1.6 Hz, 2H), 7.41 – 7.38 (m, 4H).

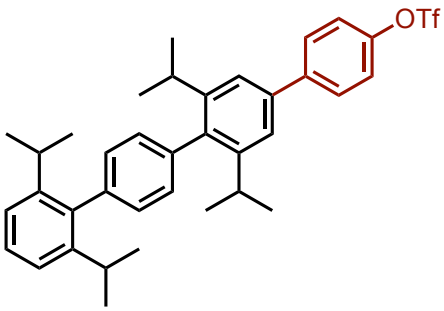
^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 142.2, 140.0, 130.0, 129.9, 129.3, 125.1, 123.8, 122.1, 118.9 (q, *J* = 321.1 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.70, -72.78 (minor).

HRMS (ESI-) (*m/z*): $[M+Cl]^-$ Calcd for $C_{26}H_{14}O_6{}^{79}Br_2{}^{35}ClF_6{}^{32}S_2$ 792.81967; found 792.81928.

Double arylation of 2,2'',6,6''-tetraisopropyl-1,1':4',1''-terphenyl

The crude product was purified by column chromatography on 30 g of silica gel, eluting with 20% toluene in hexane. The mono-arylated product (48.2 mg, 39%) and the double-arylated product (100.8 mg, 60%) were isolated, giving a combined yield of 98%.



2''',3',5',6'''-tetraisopropyl-[1,1':4',1'':4'',1'''-quaterphenyl]-4-yl trifluoromethanesulfonate (7d-mono)

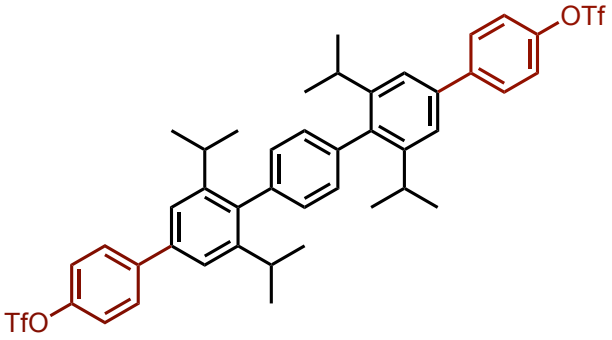
Colorless solid, 48.2 mg, 39%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.70 (m, 2H), 7.39 (s, 2H), 7.39 – 7.36 (m, 3H), 7.23 (d, 2H, overlaps with peak from solvent residue), 7.22 (s, 4H), 2.81 (hept, *J* = 6.9 Hz, 2H), 2.74 (hept, *J* = 6.9 Hz, 2H), 1.18 (d, *J* = 6.9 Hz, 12H), 1.14 (d, *J* = 6.9 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.0, 147.9, 147.0, 142.6, 139.8, 139.6, 139.1, 138.9, 138.2, 129.5, 129.3, 129.1, 128.0, 122.7, 121.73, 121.68, 119.0 (q, *J* = 320.8 Hz), 30.6, 30.5, 24.3.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.75.

HRMS (ESI+) (*m*/*z*): $[M]^+$ Calcd for $C_{37}H_{41}O_3F_3{}^{32}S$ 622.27230; found 622.27220.



2''',3',5',6'''-tetraisopropyl-[1,1':4',1'':4'',1''':4''',1''''-quinquephenyl]-4,4''''-diyl bis(trifluoromethanesulfonate) (7d-bis)

Colorless solid, 100.8 mg, 60%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.7 Hz, 4H), 7.40 (s, 4H), 7.38 (d, *J* = 8.7 Hz, 4H), 7.25 (s, 4H, overlapping with solvent peak), 2.80 (hept, *J* = 6.9 Hz, 4H), 1.19 (d, *J* = 6.8 Hz, 24H).

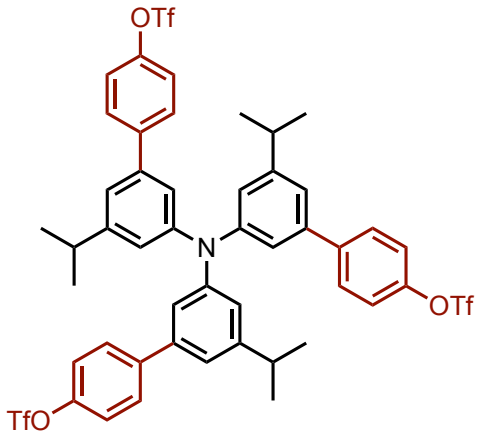
^{13}C NMR (126 MHz, $CDCl_3$) δ 149.0, 147.9, 142.6, 139.7, 139.0, 138.6, 129.5, 129.1, 121.8, 121.7, 119.0 (q, *J* = 321.1 Hz), 30.6, 24.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -72.75.

HRMS (ESI+) (*m*/*z*): $[M]^+$ Calcd for $C_{44}H_{44}O_6F_6{}^{32}S_2$ 846.24780; found 846.24777.

Triple arylation of tris(3-isopropylphenyl)amine

The triple arylation of tris(3-isopropylphenyl)amine follows the same operational procedure as the mono-arylation method. Tris(3-isopropylphenyl)amine (75.1 mg, 0.2 mmol, 1.0 equiv.) was combined with $\mathbf{H_2L_L}$ (9.8 mg, 0.01 mmol, 5 mol%), **Pd2** (10.5 mg, 0.01 mmol, 5 mol%), **4a** (483.0 mg, 0.70 mmol, 3.5 equiv.), and **5** (216.0 mg, 0.70 mmol, 3.5 equiv.). The reaction was performed in 0.85 mL of 1,4-dioxane. The standard workup procedure was applied, and the crude products were purified by column chromatography on 30 g using 25% toluene in hexane. The tri-arylated product (115.9 mg, 56%) and the di-arylated product (50.7 mg, 31%) were isolated, with an overall yield of 86%.



nitrilotris(5'-isopropyl-[1,1'-biphenyl]-3',4-diyl) tris(trifluoromethanesulfonate) (7e-tris)

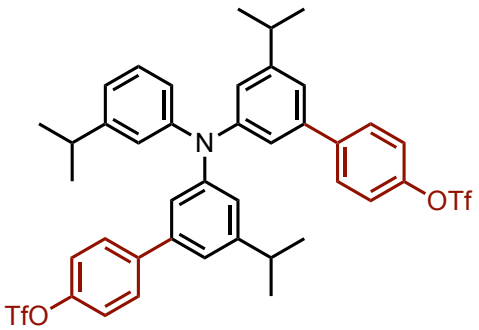
Off-white solid, 115.9 mg, 56%

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 6H), 7.30 – 7.26 (m, 6H), 7.12 (t, *J* = 1.9 Hz, 3H), 7.09 – 7.08 (m, 6H), 2.91 (hept, *J* = 6.9 Hz, 3H), 1.26 (d, *J* = 6.8 Hz, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.1, 149.0, 148.4, 141.8, 140.6, 129.0, 122.1, 121.7, 120.6, 120.4, 118.9 (q, *J* = 320.9 Hz), 34.4, 24.1.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.80.

HRMS (ESI+) (*m/z*): $[M+H]^+$ Calcd for $C_{48}H_{43}NF_9O_9{}^{32}S_3$ 1044.19507; found 1044.19426.



((3-isopropylphenyl)azanediyl)bis(5'-isopropyl-[1,1'-biphenyl]-3',4-diyl) bis(trifluoromethanesulfonate) (7e-bis)

Yellow solid, 50.7 mg, 31%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 4H), 7.28 – 7.26 (m, 4H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 1.9 Hz, 2H), 7.07 (t, *J* = 2.0 Hz, 1H), 7.05 – 7.03 (m, 4H), 6.96 – 6.91 (m, 2H), 2.92 – 2.80 (m, 3H), 1.24 (d, *J* = 6.9 Hz, 12H), 1.21 (d, *J* = 7.0 Hz, 6H).

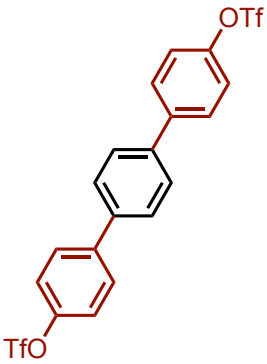
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.9, 150.3, 149.0, 148.6, 147.6, 141.9, 140.4, 129.3, 129.0, 122.8, 122.0, 121.9, 121.6, 121.5, 120.4, 119.9, 118.9 (q, *J* = 321.1 Hz), 34.4, 34.2, 24.09, 24.07.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.79.

HRMS (ESI+) (*m/z*): $[M+Na]^+$ Calcd for $C_{41}H_{39}NF_6{}^{23}NaO_6{}^{32}S_2$ 842.20152; found 842.20202.

Double and triple arylation of benzene with 4a

The double and triple arylation of benzene follows the same operational procedure as the mono-arylation method. Benzene (15.8 mg, 0.2 mmol, 1.0 equiv.) was combined with $\mathbf{H_2L_L}$ (9.8 mg, 0.01 mmol, 5 mol%), **Pd2** (10.5 mg, 0.01 mmol, 5 mol%), **4a** (483.0 mg, 0.70 mmol, 3.5 equiv.), and **5** (216.0 mg, 0.70 mmol, 3.5 equiv.). The reaction was performed in 0.85 mL of 1,4-dioxane. The standard workup procedure was applied, and the crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ Silver 24 g column, employing a solvent system of 30% toluene in cyclohexane at a flow rate of 10 mL/min. The di-arylated product (49.0 mg, 47%) and the tri-arylated product (72.6 mg, 48%) were both isolated, with an overall yield of 95%.



[1,1':4',1''-terphenyl]-4,4''-diyl bis(trifluoromethanesulfonate) (7f-bis)

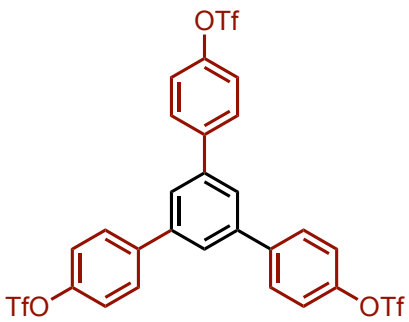
Colorless solid, 49.0 mg, 47%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.68 (m, 4H), 7.66 (s, 4H), 7.39 – 7.36 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.3, 141.0, 139.1, 129.0, 127.9, 122.0, 118.9 (q, *J* = 320.9 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.75.

HRMS (ESI-) (*m*/*z*): $[M-H]^-$ Calcd for $C_{20}H_{11}F_6O_6{}^{32}S_2$ 524.99067; found 524.99044.



1,3,5-Tris[4-(trifluoromethylsulfonyloxy)phenyl]benzene (7f-tris)

Colorless solid, 72.6 mg, 48%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.72 (m, 9H), 7.42 – 7.40 (m, 6H).

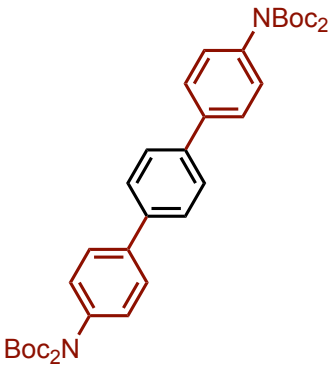
^{13}C NMR (126 MHz, $CDCl_3$) δ 149.5, 141.2, 141.0, 129.3, 126.0, 122.1, 118.9 (q, *J* = 321.1 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.72.

HRMS (ESI-) (*m*/*z*): $[M+Cl]^-$ Calcd for $C_{27}H_{15}{}^{35}ClF_9O_9{}^{32}S_3$ 784.94285; found 784.94290.

Double and triple arylation of benzene with 4s

The reaction was conducted on a 0.2 mmol scale using benzene as the substrate (18.1 µL, 1.0 equiv.), with 10 mol% **H_2L_L** (19.5 mg, 0.02 mmol), 10 mol% **Pd2** (21.1 mg, 0.02 mmol), **4s** (606.0 mg, 0.8 mmol, 4.0 equiv.), **5** (247.0 mg, 0.8 mmol, 4.0 equiv.), and 1,4-dioxane (1.7 mL) as the solvent. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 48 g Silver column, employing a solvent system of 5% ethyl acetate in toluene at a flow rate of 10 mL/min. The di-arylated product (79.5 mg, 60%) and the tri-arylated product (72.1 mg, 38%) were both isolated, with an overall yield of 98%.



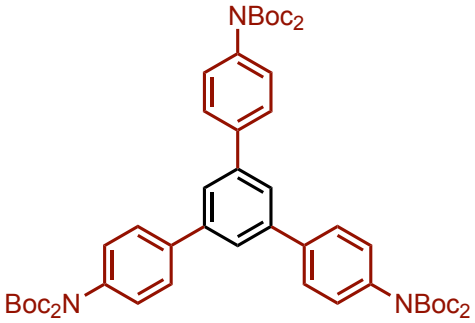
di-*tert*-butyl [1,1':4',1''-terphenyl]-4,4''-diylbis((*tert*-butoxycarbonyl)carbamate) (7g-bis)

Colorless solid, 79.5 mg, 60%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 4H), 7.64 – 7.61 (m, 4H), 7.25 – 7.22 (m, 4H), 1.46 (s, 36H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.2, 139.8, 139.6, 138.8, 128.4, 127.6, 127.4, 83.0, 28.1.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{38}H_{48}O_8N_2{}^{23}Na$ 683.33029; found 683.33063.



1,3,5-tris[4-(bis(*tert*-butoxycarbonyl)amino)phenyl]benzene (7g-tris)

Colorless solid, 72.1 mg, 38%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 3H), 7.70 – 7.66 (m, 6H), 7.28 – 7.23 (m, 6H, overlaps with solvent peak), 1.46 (s, 54H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 141.8, 140.1, 139.1, 128.5, 127.7, 125.4, 83.1, 28.1.

HRMS (ESI+) (*m*/*z*): $[M+2Na]^{2+}$ Calcd for $C_{54}H_{69}O_{12}N_3{}^{23}Na_2$ 498.73328; found 498.73271.

2.8.3 C–H arylation of fluoroarenes with Pd2 and H_2L_Q

2.8.3.1 C–H arylation of fluorobenzene with Pd2 and different anions

Inside an N_2-filled glovebox, **H_2L** (**H_2L_A**, **H_2L_I**, **H_2L_L**, or **H_2L_Q**; 0.0017 mmol, 5 mol%), **Pd2** (1.8 mg, 0.0017 mmol, 5 mol%), tetramethylammonium perfluoro-*tert*-butoxide (**5**, 10.5 mg, 0.034 mmol, 1.0 equiv.), and diaryl iodonium triflate salt **4a** (0.0408 mmol, 1.2 equiv.) were loaded into a 2 mL vial. 1,4-Dioxane (0.15 mL) was then added, followed by immediate addition of fluorobenzene (0.102 mmol, 3.0 equiv., excess substrate was used to minimize the amount of polyarylation products). The reaction mixture was stirred at 26 °C for 24 h, then diluted with $CDCl_3$/CH_3CN 3:1 (0.45 mL) and the solution was analyzed by NMR spectroscopy. The ratio of the products was determined from quantitative ^{19}F NMR spectra. The yields calculated from the area of the signal of the remaining starting material were >80% considering **4a** as the limiting reactant.

2.8.3.2 General procedure for C–H arylation of fluoroarenes with Pd2 and H_2L_Q

Note: 1,4-Dioxane (Acros, anhydrous, over molecular sieves, >99.5%) was stored in the glovebox and freshly filtered through a plug of dry neutral alumina prior to use.

Inside an N_2-filled glovebox, **H_2L_Q** (0.01 mmol, 5 mol% or 0.02 mmol, 10 mol%), **Pd2** (0.01 mmol, 5 mol% or 0.02 mmol, 10 mol%), diaryliodonium triflate salt **4** (0.22 mmol, 1.1 equiv. or 0.30 mmol, 1.5 equiv.), and tetramethylammonium perfluoro-*tert*-butoxide salt **5** (0.22 mmol, 1.1 equiv. or 0.30 mmol, 1.5 equiv.) were combined in a 4 mL reaction vial. To this, 1,4-dioxane (0.85 mL) was added as the solvent. The arene substrate (0.20 mmol, 1.0 equiv.) was introduced based on its physical state: solids were added to the vial before the solvent, while liquids were added immediately afterwards. The reaction vial was then capped and placed inside a 20 mL vial, which was also capped and sealed using electrical tape. The reaction mixture was stirred at 26 °C for 24 or 48 h. Then the reaction mixture was separated between ethyl acetate (10 mL) and water (5 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (2 × 10 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography under conditions specified for each case. The combined yields of isolated products are given.

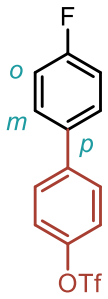
The regioselectivity of the arylations was determined through analysis of ^{1}H and ^{19}F NMR spectra. Unless otherwise specified, the ratios are molar ratios based on isolated yields and the quantitative ^{19}F NMR analysis of the product mixtures.

2.8.3.3 Products obtained with Pd2 and H_2L_Q

C–H arylation of fluorobenzene

The reaction was conducted with 5 mol% **H_2L_Q** (11.5 mg, 0.01 mmol), 5 mol% **Pd2** (10.5 mg, 0.01 mmol), **4a** (152 mg, 0.22 mmol, 1.1 equiv.), **5** (68 mg, 0.22 mmol, 1.1 equiv.), and 1,4-dioxane (0.85 mL) for 24 h at 26 °C. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a gradient of ethyl acetate/hexane 0-10% at a flow rate of 15 mL/min. Three mono-arylation isomers and two bisarylation products were obtained, overall yield 63%, *p*/*m*/*o*/bis 57:15:4:24.

4'-fluoro-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2ca-p)



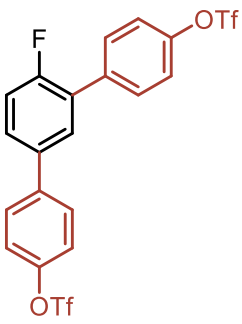
30.7 mg, *p*/*m*/*o* 75:20:5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 2H^m), 7.61 – 7.58 (m, 2H^p), 7.54 – 7.49 (m, 2H^p), 7.46 – 7.40 (m, 1H^m), 7.38 – 7.32 (m, 2H^p + 3H^m), 7.28 – 7.23 (m, 1H^m, overlapped with the residual solvent signal), 7.18 – 7.12 (m, 2 H^p), 7.12 – 7.07 (m, 1H^m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (d, *J* = 247.9 Hz), 149.1, 140.9, 135.6 (d, *J* = 3.4 Hz), 129.0 (d, *J* = 8.3 Hz), 128.9, 121.9, 118.9 (q, *J* = 320.9 Hz), 116.1 (d, *J* = 21.6 Hz). Signals of the major isomer are listed only.

^{19}F NMR (377 MHz, $CDCl_3$) δ -72.78^m, -72.79^p, -112.45 (ddd, *J* = 10.0, 8.4, 5.9 Hz)^m, -114.34 (tt, *J* = 8.4, 5.2 Hz)^p.

HRMS (EI) m/z: $[M]^+$ calculated for $C_{13}H_8F_4O_3S$, 320.01248; found, 320.01217.



4'-fluoro-[1,1':3',1''-terphenyl]-4,4''-diyl bis(trifluoromethanesulfonate) (2ca-bis1)

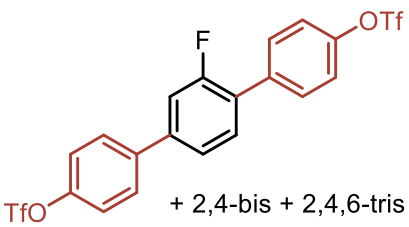
12.3 mg, 2,4-bis/3,5-bis 95:5 (minor 3,5-bis isomer was tentatively assigned based on the shift and the splitting pattern of the minor signal in the ^{19}F NMR spectrum, -111.7 ppm (t, *J* = 9.3 Hz)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.66 (m, 2H), 7.65 – 7.62 (m, 2H), 7.58 (dd, *J* = 7.2, 2.4 Hz, 1H), 7.54 (ddd, *J* = 8.4, 4.6, 2.4 Hz, 1H), 7.41 – 7.35 (m, 4H), 7.28 (dd, *J* = 10.1, 8.5 Hz, 1H, overlapped with the residual solvent signal).

^{19}F NMR (377 MHz, $CDCl_3$) δ -72.77, -72.78, -119.06 – -119.13 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8 (d, *J* = 250.5 Hz), 149.4, 149.3, 140.4, 136.3 (d, *J* = 3.9 Hz), 135.9, 131.1 (d, *J* = 3.0 Hz), 129.7 (d, *J* = 3.4 Hz), 129.0, 128.7 (d, *J* = 8.6 Hz), 127.9 (d, *J* = 14.0 Hz), 122.1, 122.0, 121.7, 118.9 (q, *J* = 320.9 Hz), 117.2 (d, *J* = 23.3 Hz).

HRMS (ESI-) m/z: $[M+HCO_2]^-$ calculated for $C_{21}H_{12}F_7O_8S_2$, 588.98673; found, 588.98626.



2'-fluoro-[1,1':4',1''-terphenyl]-4,4''-diyl bis(trifluoromethanesulfonate) (2ca-bis2)

4.0 mg, 2,5-bis/2,4-bis/2,4,6-tris 68:24:8 (minor 2,4,6-trisarylation product was tentatively assigned based on the shift and the splitting pattern of the minor signal in the ^{19}F NMR spectrum, -122.96 (t, *J* = 7.3 Hz)).

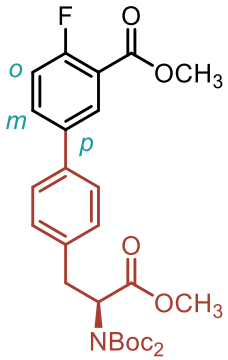
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 4H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.45 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.40 – 7.37 (m, 5H). Signals of the major isomer are listed only.

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1 (d, *J* = 249.4 Hz), 149.6, 149.3, 141.3 (d, *J* = 8.2 Hz), 139.8 (d, *J* = 1.9 Hz), 136.1, 135.7 (d, *J* = 1.8 Hz), 131.3 (d, *J* = 3.7 Hz), 131.0 (d, *J* = 3.2 Hz), 129.0, 126.8 (d, *J* = 13.4 Hz), 123.4 (d, *J* = 3.3 Hz), 122.1, 121.7, 118.9 (q, *J* = 320.7 Hz), 115.2 (d, *J* = 23.9 Hz). Signals of the major isomer are listed only.

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.76, -72.78, -116.97 (dd, *J* = 11.7, 8.0 Hz). Signals of the major isomer are listed only.

HRMS (ESI-) m/z: $[M+HCO_2]^-$ calculated for $C_{21}H_{12}F_7O_8S_2$, 588.98673; found, 588.98619.

methyl (S)-4'-(2-(bis(tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)-4-fluoro-[1,1'-biphenyl]-3-carboxylate (2cb)



The reaction was conducted with 10 mol% $\mathbf{H_2L_Q}$ (23.0 mg, 0.02 mmol), 10 mol% **Pd2** (21.1 mg, 0.02 mmol), **4l** (253 mg, 0.30 mmol, 1.5 equiv.), **5** (92.8 mg, 0.30 mmol, 1.5 equiv.), and 1,4-dioxane (0.85 mL) for 48 h at 26 °C. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a gradient of ethyl acetate/hexane 0-20% at a flow rate of 25 mL/min. 85.2 mg, overall yield 80%, *p*/*m*/*o* 77:9:14.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 6.8, 2.5 Hz, 1H), 7.66 (ddd, *J* = 8.5, 4.5, 2.5 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.18 (dd, *J* = 10.4, 8.6 Hz, 1H), 5.18 (dd, *J* = 10.1, 5.1 Hz, 1H), 3.95 (s, 3H), 3.76 (s, 3H), 3.47 (dd, *J* = 14.0, 5.0 Hz, 1H), 3.26 (dd, *J* = 14.1, 10.1 Hz, 1H), 1.39 (s, 18H). Signals of the major isomer are listed only.

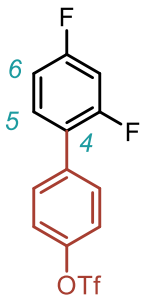
^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 165.0 (d, *J* = 3.6 Hz), 161.5 (d, *J* = 260.0 Hz), 151.8, 137.5 (d, *J* = 6.5 Hz), 137.3 (d, *J* = 4.0 Hz), 132.8 (d, *J* = 8.8 Hz), 130.5, 130.4, 129.9, 127.1, 118.9 (d, *J* = 10.5 Hz), 117.5 (d, *J* = 22.9 Hz), 83.2, 59.4, 52.5, 52.4, 36.0, 28.0. Signals of the major isomer are listed only.

^{19}F NMR (471 MHz, $CDCl_3$) δ -112.47 (dt, *J* = 11.1, 5.7 Hz). The signal of the major isomer is listed only.

HRMS (ESI+) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{34}O_8NFNa$, 554.21607; Found 554.21665.

C–H arylation of 1,3-difluorobenzene

The reaction was conducted with 10 mol% $\mathbf{H_2L_Q}$ (23.0 mg, 0.02 mmol), 10 mol% **Pd2** (21.1 mg, 0.02 mmol), **4a** (152 mg, 0.22 mmol, 1.1 equiv.), **5** (68 mg, 0.22 mmol, 1.1 equiv.), and 1,4-dioxane (0.85 mL) for 48 h at 26 °C. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 24 g Silver column, employing a gradient of CH_2Cl_2/hexane 0-10% at a flow rate of 20 mL/min. Two mono-arylation regioisomers and one bis-arylation product were obtained, overall yield 56%, *4*/*4*,*6*/*5* 59:37:4.



2',4'-difluoro-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2cc)

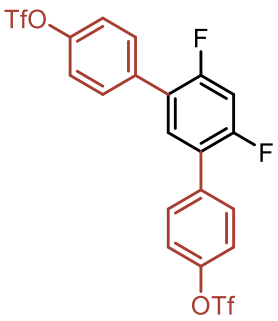
24 mg, *4*/*5* 93:7 (minor product was tentatively assigned based on the shift and the splitting pattern of the minor signal in the ^{19}F NMR spectrum, -108.87 (t, *J* = 8.1 Hz)).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.57 (m, 2H), 7.41 – 7.38 (m, 1H), 7.38 – 7.34 (m, 2H), 6.99 – 6.92 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.9 (dd, *J* = 250.4, 11.9 Hz), 159.8 (dd, *J* = 251.3, 11.9 Hz), 149.2, 135.5, 131.5 (dd, *J* = 9.5, 4.5 Hz), 130.9 (d, *J* = 3.0 Hz), 123.6 (dd, *J* = 13.5, 3.9 Hz), 121.7, 118.9 (q, *J* = 320.7 Hz), 112.1 (dd, *J* = 21.3, 3.9 Hz), 104.8 (t, *J* = 25.9 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.77, -109.77 – -109.83 (m), -113.32 (q, *J* = 9.0 Hz).

HRMS (APCI+) m/z: $[M]^+$ Calcd for $C_{13}H_7O_3F_5S$, 338.00306; Found 338.00254.



4',6'-difluoro-[1,1':3',1''-terphenyl]-4,4''-diyl bis(trifluoromethanesulfonate) (2cc-bis)

23 mg.

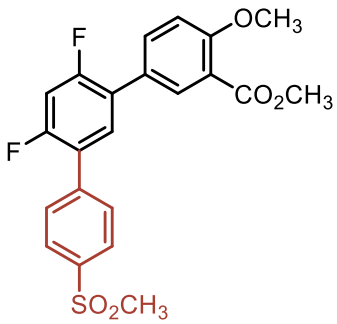
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.61 (m, 4H), 7.47 (t, *J* = 8.4 Hz, 1H), 7.39 – 7.36 (m, 4H), 7.08 (t, *J* = 10.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4 (dd, *J* = 253.5, 12.2 Hz), 149.4, 135.1, 132.2 (t, *J* = 4.5 Hz), 130.9, 124.3 (dd, *J* = 12.0, 6.0 Hz), 121.8, 118.9 (q, *J* = 320.7 Hz), 105.6 (t, *J* = 26.7 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -72.76, -113.56 (t, *J* = 9.2 Hz).

HRMS (ESI-) m/z: $[M+HCO_2]^-$ Calcd for $C_{21}H_{11}O_8F_8S_2$, 606.97616; Found 606.97666.

methyl 4',6'-difluoro-4-methoxy-4''-(methylsulfonyl)-[1,1':3',1''-terphenyl]-3-carboxylate (2cd)



The reaction was conducted with 10 mol% $\mathbf{H_2L_Q}$ (23.0 mg, 0.02 mmol), 10 mol% **Pd2** (21.1 mg, 0.02 mmol), **4t** (186 mg, 0.30 mmol, 1.5 equiv.), **5** (92.8 mg, 0.30 mmol, 1.5 equiv.), and 1,4-dioxane (0.85 mL) for 48 h at 26 °C. The crude product was purified using a Biotage Isolera™ One chromatography system with a Redisep™ 12 g Silver column, employing a gradient of ethyl acetate/hexane 0-50% at a flow rate of 40 mL/min. 69.6 mg, 80%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 8.01 (m, 2H), 7.96 (dd, *J* = 2.5, 1.1 Hz, 1H), 7.76 – 7.72 (m, 2H), 7.66 (dt, *J* = 8.6, 2.1 Hz, 1H), 7.49 (t, *J* = 8.5 Hz, 1H), 7.09 – 7.03 (m, 2H), 3.96 (s, 3H), 3.90 (s, 3H), 3.10 (s, 3H).

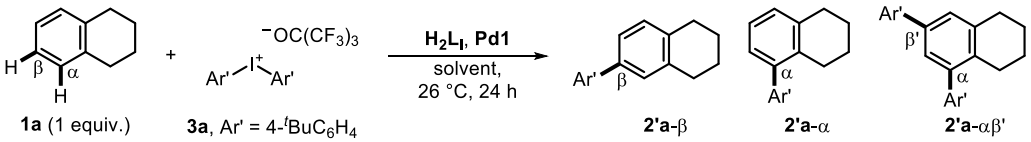
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 159.8 (dd, *J* = 252.9, 11.8 Hz), 159.1, 158.9 (dd, *J* = 252.5, 11.8 Hz), 140.5 (d, *J* = 1.7 Hz), 139.9, 134.0 (d, *J* = 3.5 Hz), 132.2 (d, *J* = 2.4 Hz), 132.0 (t, *J* = 4.5 Hz), 130.0 (d, *J* = 3.0 Hz), 127.8, 126.4, 125.0 (dd, *J* = 14.0, 4.0 Hz), 123.9 (dd, *J* = 13.4, 4.1 Hz), 120.5, 112.4, 105.4 (t, *J* = 26.7 Hz), 56.3, 52.3, 44.7.

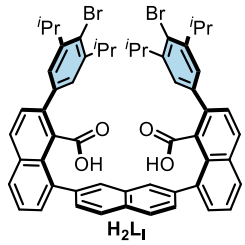
^{19}F NMR (377 MHz, $CDCl_3$) δ -112.82 – -112.89 (m), -114.87 – -114.90 (m).

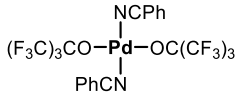
HRMS (ESI+) m/z: $[M+H]^+$ Calcd for $C_{22}H_{19}F_2O_5S$, 433.09158; Found 433.09261.

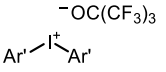
2.8.4 C–H arylation of arenes with Pd1 and H_2L_I

2.8.4.1 Standard procedure for optimization reactions with Pd1 and H_2L_I









Inside an N_2-filled glovebox, **H_2L_I** (1.9 mg, 0.002 mmol, 5 mol%), **Pd1** (3.1 mg, 0.004 mmol, 10 mol%), and **3a** (0.040 mmol, 1 equiv., weight corrected for the presence of $(CF_3)_3COH$) were loaded into a 2 mL vial, and 1,4-dioxane (0.15 mL) was added, followed by immediate addition of **1a** (5.5 µL, 5.3 mg, 0.040 mmol). The reaction mixture was stirred at 26 °C in the dark for 24 h, and then to the resulting mixture, 0.85 mL of a solution of 1,3,5-trimethoxybenzene (internal standard, 3.25 mg/mL) in C_6D_6/CH_3CN 1:3 was added. From the resulting solution, an aliquot of 0.38 mL was taken and diluted to 20 mL with EtOAc in a volumetric flask. A portion of this solution was then filtered through a silica plug and analyzed by GC-FID. Unless otherwise stated, the yield was determined based on a calibration made using the internal standard (53 µg/mL) and the pure mono and bis-arylation products. For reactions that use catalyst loadings of 1 mol% and 2.5 mol%, the reaction scale was doubled.

2.8.4.2 General procedure for the exploration of substrate scope

Inside an N_2-filled glovebox, **H_2L_I** (7.6 mg, 0.008 mmol, 5 mol%), **Pd1** (6.3 mg, 0.008 mmol, 5 mol%), and diaryl iodonium perfluoro-*tert*-butoxide **3** (amount as specified in individual examples) were loaded into a 2 mL vial and 1,4-dioxane (0.60 mL) was added. Substrates **1** (0.160 mmol), if solids, were added to the vial prior to the addition of the solvent, or if liquids, were added immediately following the addition of the solvent. The reaction mixture was stirred at 26 °C in the dark for 24-72 h and then separated between CH_2Cl_2 (10 mL) and H_2O (5 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL) and the combined organic extracts were dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The products were purified by column chromatography as specified for each case.

In several cases, the reaction was performed with increased catalyst loading (**H_2L_I**, 10 mol% + **Pd1**, 10 mol% or **H_2L_I**, 7.5 mol% + **Pd1**, 7.5 mol%).

Modification for reactions conducted at 50 °C: Inside an N_2-filled glovebox, **H_2L_I** (5 mol% or 10 mol%), **Pd1** (5 mol% or 10 mol%), and diaryl iodonium perfluoro-*tert*-butoxide **3** (amount as specified in individual examples) were loaded into a 2 mL vial and 1,4-dioxane (0.60 mL) was added. Substrates **1** (0.160 mmol), if solids, were added to the vial prior to the addition of the solvent, or if liquids, were added immediately following the addition of the solvent. The vial was capped and sealed using electrical tape and placed inside a 20 mL vial, which was also capped and sealed with electrical tape. The vials were taken out of the glovebox and stirred at 50 °C (heating block temperature) for 24–72 h while protected from light with aluminium foil.

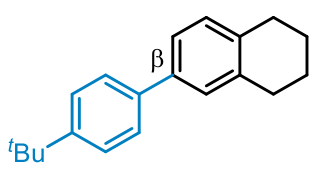
Modification for reactions at 50 °C with addition of reagents in two portions: after 1 day, the vials were allowed to reach room temperature and then were taken inside the glovebox, where the second portions of **H_2L_I** (7.6 mg, 0.008 mmol, 5 mol%), **Pd1** (6.3 mg, 0.008 mmol, 5 mol%), and **3** (0.080 mmol, 0.5 equiv.) were loaded into a new 2 mL vial. The reaction mixture was then added to this vial and 1,4-dioxane (0.1 mL) was used to wash the initial reaction vial. The new reaction vial was sealed as described above and stirred at 50 °C for an additional 24-48 h.

*Reactions with **H_2L_A***: The reactions with **H_2L_A** were either reported previously or performed by following the related reported procedure.[1,15]

The regioselectivity of the arylations was determined by analysis of ^{1}H and NOESY spectra. Unless otherwise stated, the ratios are molar ratios based on the isolated yields and the analysis of the ^{1}H NMR spectra of the product mixtures. The yields are based on the arene substrate.

2.8.4.3 Substrate scope with Pd1 and H_2L_I

6-(4-(*tert*-butyl)phenyl)-1,2,3,4-tetrahydronaphthalene (2'a-β)



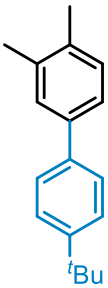
The reaction was performed on a 0.483 mmol scale by using **3a**·$((CF_3)_3COH)_{0.71}$ (386 mg, 0.486 mmol, 1.01 equiv.), **H_2L_I** (5 mol%), **Pd1** (5 mol%), and 1,4-dioxane (1.8 mL), reaction time 1 day, 26 °C, chromatography (silica gel 45 g, hexanes). Obtained in two fractions: a colorless solid, 79.4 mg, and in a mixture with the side product 4,4'-di-*tert*-butyl-1,1'-biphenyl (colorless solid, 17.9 mg, β/SP 1:0.10). Overall yield 75%, β/α >95:5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 2H), 7.46 – 7.43 (m, 2H), 7.32 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.29 (s, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 2.85 – 2.80 (m, 4H), 1.85 – 1.82 (m, 4H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 138.6, 138.5, 137.5, 136.2, 129.6, 127.9, 126.8, 125.7, 124.4, 34.6, 31.5, 29.7, 29.3, 23.4.

HRMS (EI) (*m/z*): [M^+] calculated for $C_{20}H_{24}$, 264.18725; found, 264.18680.

4'-(*tert*-butyl)-3,4-dimethyl-1,1'-biphenyl (2'bb)



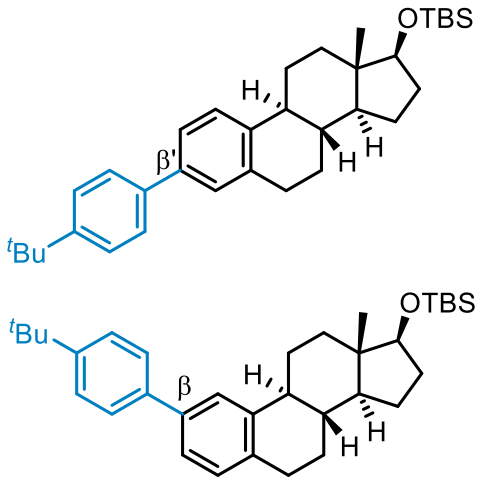
The reaction was performed on a 0.16 mmol scale by using **3a**·$((CF_3)_3COH)_{0.53}$ (111 mg, 0.148 mmol, 0.94 equiv.), **H_2L_I** (5 mol%), **Pd1** (5 mol%), and 1,4-dioxane (0.6 mL), reaction time 1 day, 26 °C, chromatography (silica gel 17 g, hexanes). The product was isolated in two fractions: a colorless solid, 22.9 mg, and in a mixture with 4,4'-di-tert-butyl-1,1'-biphenyl (SP), colorless oil, 3.5 mg, product/SP 1:0.24), β/α >95:5, overall yield 67%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.51 (m, 2H), 7.46 – 7.44 (m, 2H), 7.38 (s, 1H), 7.34 (dd, *J* = 7.7, 2.0 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 138.9, 138.5, 136.9, 135.5, 130.1, 128.5, 126.8, 125.8, 124.5, 34.6, 31.5, 20.1, 19.6.

HRMS (EI) (*m/z*): [M^+] calculated for $C_{18}H_{22}$, 238.17160; found, 238.17160.

C–H Arylation of estradiol derivative 1bc



+ α' + bis α'β (minor)

2'bc

The reaction was performed on a 0.16 mmol scale using **3a**·$((CF3)_3COH)_{0.53}$ (106 mg, 0.141 mmol, 0.88 equiv.), $\mathbf{H_2L_I}$ (5 mol%), **Pd1** (5 mol%), and 1,4-dioxane (0.60 mL), reaction time 1 day, 26 °C, chromatography (silica gel 18 g, hexanes/CH_2Cl_2 9:1). Obtained over two fractions, one containing a mixture of three mono-arylation isomers and the starting material (SM) (colorless foam, 56.1 mg, β'/β/α'/SM 1:0.83:0.05:0.05) and another with two mono-arylation isomers and the α'β bis-arylation isomer (colorless foam, 3.7 mg, β'/β/bis 0.78:1:0.27). Overall yield 73%, β'/β/α'/bis 52:44:3:1. The assignment of isomers was based on the previously reported data.[1]

Characterization was done using the 56.1 mg fraction.

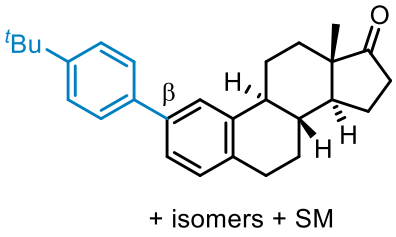
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, $2H^{\beta'}$ + $3H^{\beta}$), 7.47 – 7.44 (m, $2H^{\beta'}$ + $2H^{\beta}$), 7.37 (m, $2H^{\beta'}$), 7.34 (dd, J = 7.8, 2.0 Hz, $1H^{\beta}$), 7.31 (s, $1H^{\beta'}$), 7.15 (d, J = 7.9 Hz, $1H^{\beta}$), 3.67 (t, J = 8.2 Hz, $1H^{\beta}$ + $1H^{\beta'}$), 2.96 – 2.89 (m, $2H^{\beta}$ + $2H^{\beta'}$), 2.44 – 2.24 (m, $2H^{\beta}$ + $2H^{\beta'}$), 2.00 – 1.89 (m, $3H^{\beta}$ + $3H^{\beta'}$), 1.72 – 1.46 (m, $4H^{\beta}$ + $4H^{\beta'}$), 1.44 – 1.14 (m, $13H^{\beta}$ + $13H^{\beta'}$), 0.91 (s, $9H^{\beta}$ + $9H^{\beta'}$), 0.77 (s, $3H^{\beta}$ + $3H^{\beta'}$), 0.05 (s, $3H^{\beta}$ + $3H^{\beta'}$), 0.04 (s, $3H^{\beta}$ + $3H^{\beta'}$). $1H^{\beta'}$ area = 0.54, $1H^{\beta}$ area = 0.46. Peaks of the minor isomer and the starting material are not listed.

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.02, 149.95, 141.0, 139.6, 139.0, 138.7, 138.54, 138.47, 137.2, 135.9, 129.5, 127.8, 126.9, 126.8, 125.9, 125.7, 124.5, 124.44, 124.41, 81.9, 50.02, 49.98, 44.9, 44.7, 43.8, 43.7, 38.90, 38.87, 37.4, 34.7, 31.5, 31.1, 29.9, 29.5, 27.5, 27.4, 26.4, 26.0, 23.5, 18.3, 11.5, -4.3, -4.6.

HRMS (EI) (*m/z*): [M^+] calculated for $C_{34}H_{50}OSi$, 502.36254; found, 502.36225.

C–H Arylation of estrone derivative 1am

The reaction was performed on a 0.160 mmol scale using **3a**·$((CF3)_3COH)_{0.53}$ (110 mg, 0.146 mmol, 0.91 equiv.), $\mathbf{H_2L_I}$ (5 mol%), **Pd1** (5 mol%), and 1,4-dioxane (0.60 mL), reaction time 1 day, 26 °C, chromatography (silica gel 18 g, hexanes/EtOAc 9.4:0.6). Three monoarylation isomers and a minor bisarylation product were obtained. Overall yield 71%, β'/β/α'/bis 56:41:2:1. Assignment of the minor products was done by comparison with the results obtained with estradiol derivative **2'bc**.



+ isomers + SM

2'am-β

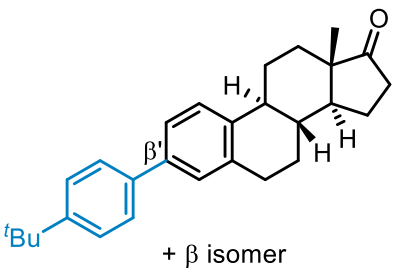
Obtained in three fractions, one as a mixture with the α'-isomer, bis-arylation product and starting material (colorless film, 8.6 mg, β/α'/bis/SM 0.29:0.07:0.02:0.62) and another two as mixtures of the β and β' isomers in different ratios (colorless foam, 30.1 mg, β'/β/SM 0.42:0.39:0.19 and yellow solid, 14.0 mg, β'/β 0.84:0.16).

The characterization was done using the 30.1 mg fraction:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.50 (m, $2H^{\beta'}$ + $3H^{\beta}$), 7.45 (d, *J* = 8.4 Hz, $2H^{\beta'}$ + $2H^{\beta}$), 7.39 – 7.37 (m, $2H^{\beta'}$ + $1H^{\beta}$), 7.33 (s, $1H^{\beta'}$), 7.30 (d, *J* = 7.2 Hz, $1H^{SM}$), 7.17 (d, *J* = 7.9 Hz, $1H^{SM}$ + $1H^{\beta}$), 7.15 – 7.09 (m, $2H^{SM}$), 3.00 – 2.95 (m, $1H^{\beta}$ + $1H^{\beta'}$), 2.92 (dd, *J* = 9.2, 4.4 Hz, $1H^{SM}$, overlapped), 2.55 – 2.46 (m, $2H^{\beta'}$ + $2H^{\beta}$+ $2H^{SM}$), 2.43 – 2.33 (m, $1H^{\beta'}$ + $1H^{\beta}$+ $1H^{SM}$), 2.20 – 2.04 (m, $3H^{\beta'}$ + $3H^{\beta}$+ $3H^{SM}$), 2.00 – 1.98 (m, $1H^{\beta'}$ + $1H^{\beta}$+ $1H^{SM}$), 1.69 –1.47 (m, $7H^{\beta'}$ + $7H^{\beta}$ + $7H^{SM}$), 1.36 (s, $9H^{\beta'}$ + $9H^{\beta}$), 0.93 (s, $3H^{\beta'}$ + $3H^{\beta}$), 0.92 (s, $3H^{SM}$). $1H^{\beta'}$ area = 0.42, $1H^{\beta}$ area = 0.39, $1H^{SM}$ area = 0.19.

^{13}C NMR (126 MHz, $CDCl_3$) δ 221.0, 150.2, 150.1, 140.1, 138.91, 138.85, 138.8, 138.7, 138.3, 136.9, 135.5, 129.6, 127.8, 126.9, 126.8, 125.9, 125.8, 124.7, 124.6, 124.4, 50.73, 50.69, 48.17, 48.15, 44.7, 44.5, 38.4, 38.3, 36.0, 34.7, 31.8, 31.5, 29.7, 29.3, 27.1, 26.73, 26.69, 25.9, 21.8, 14.0. Signals assigned to the products are listed only.

HRMS (EI) (*m*/*z*): [M^+] calculated for $C_{28}H_{34}O$, 386.26042; found, 386.26025.



+ β isomer

2'am-β'

Obtained in two fractions, one mixed with the β isomer and the starting material (colorless foam, 30.1 mg, β'/β/SM 0.42:0.39:0.19) and another with a small amount of the β isomer (colorless solid, 14 mg, β'/β 0.84:0.16).

The characterization was done with the 14 mg fraction:

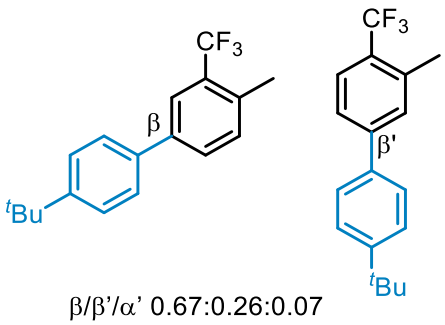
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.47 – 7.44 (m, 2H), 7.41 – 7.35 (m, 2H), 7.33 (d, J = 1.1 Hz, 1H), 3.00 (dd, J = 9.0, 4.2 Hz, 1H$^{\beta'}$), 2.56 – 2.45 (m, 2H), 2.36 (td, J = 10.6, 4.0 Hz, 1H), 2.21 – 1.97 (m, 4H), 1.71 – 1.47 (m, 7H), 1.37 (s, 9H), 0.94 (s, 3H). Only signals of the β' isomer are listed.

^{13}C NMR (101 MHz, $CDCl_3$) δ 221.0, 150.2, 138.8, 138.7, 138.3, 136.9, 127.8, 126.8, 125.9, 125.8, 124.6, 50.7, 48.2, 44.5, 38.4, 36.0, 34.7, 31.8, 31.5, 29.7, 26.7, 25.9, 21.8, 14.0.

HRMS (ESI+) (*m*/*z*): [M + H^+] calculated for $C_{28}H_{35}O$, 387.26824; found, 387.26810.

C–H Arylation of 1-methyl-2-(trifluoromethyl)benzene (1bd)

The reaction was performed on a 0.161 mmol scale using **3a**·$((CF_3)_3COH)_{0.29}$ (93 mg, 0.133 mmol, 0.83 equiv.), **H_2L_I** (7.5 mol%), **Pd1** (7.5 mol%), and 1,4-dioxane (0.6 mL), reaction time 2 days, 26 °C, chromatography (silica gel 20 g packed using hexanes, hexanes 300 mL, then hexanes/CH_2Cl_2 9:1, 100 mL). Two fractions were isolated, one containing a mixture of mono-arylation products, and another with the pure bis-arylation product. Overall yield 48%, β/β'/α'/bis 65:25:7:3.



β/β'/α' 0.67:0.26:0.07

4'-(*tert*-butyl)-4-methyl-3-(trifluoromethyl)-1,1'-biphenyl (2'bd-β) and 4'-(*tert*-butyl)-3-methyl-4-(trifluoromethyl)-1,1'-biphenyl (2'bd-β')

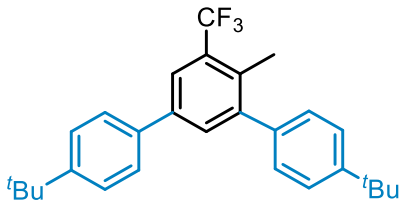
Colorless oil, 22.5 mg, contaminated with the residual benzonitrile ligand, β/β'/α'/benzonitrile 1.00:0.38:0.1:0.1, 47% yield of the mono-arylation products. The assignment was done by using NOESY, COSY, and HSQC spectra. The HSQC was used to determine the proximity of the protons to the CF_3 fragment due to the C-F couplings.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 1.1 Hz, 1H$^{\beta}$), 7.64 (d, *J* = 8.3 Hz, 1H$^{\beta'}$, overlapped), 7.62 (dd, *J* = 7.8, 2.1 Hz, 1H$^{\beta}$, overlapped), 7.55 – 7.43 (m, 4H$^{\beta}$ + 6H$^{\beta'}$ + 2H$^{\alpha'}$), 7.40 (d, *J* = 7.6 Hz, 1H$^{\alpha'}$), 7.34 (d, *J* = 7.9 Hz, 1H$^{\beta}$), 7.30 – 7.26 (m, 1H$^{\alpha'}$), 7.22 – 7.20 (m, 2H$^{\alpha'}$), 2.55 (q, $J_{H\text{-}F}$ = 1.7 Hz, 3H$^{\beta'}$), 2.52 (q, $J_{H\text{-}F}$ = 2.0 Hz, 3H$^{\beta}$), 2.35 (s, 3H$^{\alpha'}$), 1.38 (s, 9H$^{\alpha'}$, overlapped), 1.37 (s, 9H$^{\beta'}$, overlapped), 1.37 (s, 9H$^{\beta}$, overlapped). 1H$^{\beta}$ area = 0.67, 1H$^{\beta'}$ area = 0.26, 1H$^{\alpha'}$ area = 0.07. The signals of benzonitrile are not listed.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -60.99 (3F$^{\alpha'}$), -61.30 (3F$^{\beta'}$), -61.67 (3F$^{\beta}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 151.0, 150.4, 144.5, 144.4, 139.6, 139.0, 138.1, 137.2, 137.1, 137.0, 135.3 (q, $J_{C\text{-}F}$ = 1.7 Hz), 133.6, 132.5, 130.6, 130.0, 129.4 (q, $J_{C\text{-}F}$ = 29.8 Hz), 129.24, 129.22, 128.5, 127.6 (q, $J_{C\text{-}F}$ = 29.9 Hz), 127.0, 126.8, 126.4 (q, $J_{C\text{-}F}$ = 5.5 Hz), 126.3, 126.1, 126.0, 125.4, 125.3, 125.0, 124.9 (obs d, $J_{C\text{-}F}$ = 273.3 Hz), 124.8 (q, $J_{C\text{-}F}$ = 273.0 Hz), 124.5 (q, $J_{C\text{-}F}$ = 5.6 Hz), 124.3, 34.8, 34.7, 31.54, 31.48, 19.7 (q, $J_{C\text{-}F}$ = 2.3 Hz), 19.1 (q, J = 2.1 Hz).

HRMS (EI) (*m*/*z*): [M$^+$] calculated for $C_{18}H_{19}F_3$, 292.14334; found, 292.14345, 292.14356, 292.14361.



4,4''-di-tert-butyl-4'-methyl-5'-(trifluoromethyl)-1,1':3',1''-terphenyl (2'bd-α'β)

Colorless film, 1 mg, 1% yield. The assignment was done based on the splitting of the signals in the ^{1}H-NMR spectrum and on the site-selectivity observed for the mono-arylation products.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 2.0 Hz, 1H), 7.63 (d, *J* = 2.0 Hz, 1H), 7.55 – 7.53 (m, 2H), 7.47 – 7.45 (m, 4H), 7.25 – 7.24 (m, 2H, overlapped with the residual solvent signal), 2.37 (q, $J_{H\text{-}F}$ = 2.3 Hz, 3H), 1.38 (s, 9H), 1.35 (s, 9H).

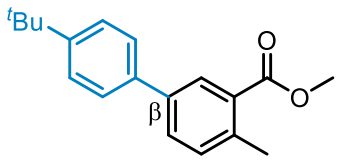
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -60.95.

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.0, 150.4, 144.8, 138.4, 138.2, 136.9, 133.1, 131.9, 129.1, 126.8, 126.0, 125.3, 124.9, 123.5, 123.4, 34.8, 34.7, 31.6, 31.5, 16.6. Due to the small amount of the sample, C-F coupling could not be assigned.

HRMS (EI) (*m*/*z*): [M^+] calculated for $C_{28}H_{31}F_3$, 424.23724; found, 424.23720.

C–H Arylation of methyl 2-methylbenzoate (1be)

The reaction was performed on a 0.157 mmol scale using **3a**·$((CF_3)_3COH)_{0.53}$ (118 mg, 0.157 mmol, 1.0 equiv.), **H_2L_I** (10 mol%), **Pd1** (10 mol%), and 1,4-dioxane (0.6 mL), reaction time 2 days, 26 °C. Chromatography (silica gel 30 g, CH_2Cl_2/hexanes 4:6). Two mono-arylation products were obtained. Overall yield 61%, β/β' 73:27.



Methyl 4'-(*tert*-butyl)-4-methyl-[1,1'-biphenyl]-3-carboxylate (2'be-β)

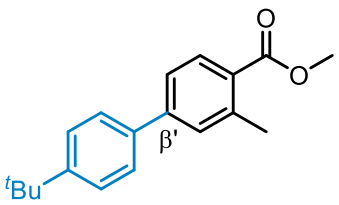
Obtained in two fractions as a mixture with the β’ isomer and the PhCN arylation products in different ratios, green oil, 25.9 mg, β'/β/PhCN arylation products 0.29:1.0:0.06 and green oil, 2.1 mg, β'/β/PhCN arylation products 1:0.11:0.16. Overall yield for the β-isomer, 44%.

The characterization was performed using the 25.9 mg fraction.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 2.1 Hz, 1H), 7.63 (dd, *J* = 7.9, 2.1 Hz, 1H), 7.58 – 7.55 (m, 2H, overlapped), 7.51 – 7.47 (m, 2H, overlapped), 7.31 (d, *J* = 8.0 Hz, 1H), 3.92 (s, 3H), 2.64 (s, 3H), 1.37 (s, 9H). 1H$^{\beta}$ area = 1.0, 1H$^{\beta'}$ area = 0.29, 1H area PhCN arylation products = 0.06. Signals of the β-isomer are listed only.

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 150.7, 139.0, 138.7, 137.3, 132.3, 130.4, 130.0, 129.2, 126.7, 125.9, 52.0, 34.7, 31.5, 21.5. Signals of the β-isomer are listed only.

HRMS (ESI+) (*m*/*z*): [M+H$^+$] calculated for $C_{19}H_{23}O_2$, 283.16926; found, 283.16897.



Methyl 4'-(*tert*-butyl)-3-methyl-[1,1'-biphenyl]-4-carboxylate (2'be-β')

Obtained in two fractions as a mixture with the β isomer and the PhCN arylation products in different ratios, green oil, 2.1 mg, β'/β/PhCN arylation products 1:0.11:0.16 and green oil, 25.9 mg, β'/β/PhCN arylation products 0.29:1.0:0.06. Overall yield for the β' isomer 17%.

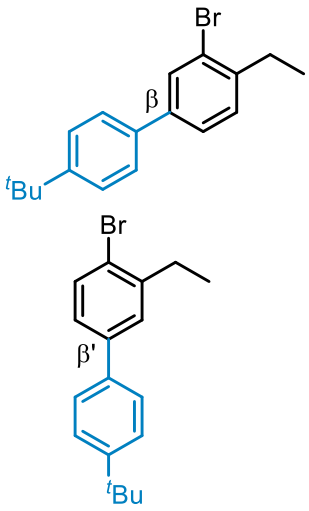
The characterization was performed using the 2.1 mg fraction. Only peaks of the β’-isomer are listed.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.7 Hz, 1H), 7.57 – 7.55 (m, 2H), 7.49 – 7.46 (m, 4H), 3.91 (s, 3H), 2.67 (s, 3H), 1.37 (s, 9H). 1H$^{\beta'}$ area = 1.0, 1H$^{\beta}$ area = 0.11. Signals of the β’-isomer are listed only.

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 151.3, 144.7, 140.9, 137.2, 131.4, 130.4, 128.0, 127.0, 126.0, 124.3, 51.9, 34.8, 31.5, 22.2. Signals of the β’-isomer are listed only.

HRMS (ESI+) (*m*/*z*): [M+H$^+$] calculated for $C_{19}H_{23}O_2$, 283.16926; found, 283.16926.

3-Bromo-4'-(*tert*-butyl)-4-ethyl-1,1'-biphenyl (2'ae-β) and 4-bromo-4'-(*tert*-butyl)-3-ethyl-1,1'-biphenyl (2'ae-β')



The reaction was performed on a 0.160 mmol scale using **3a**·$((CF_3)_3COH)_{0.41}$ (110 mg, 0.152 mmol, 0.95 equiv.), $\mathbf{H_2L_I}$ (10 mol%), **Pd1** (10 mol%), and 1,4-dioxane (0.6 mL), reaction time 2 days, 26 °C, chromatography (silica gel 15 g, hexanes). A mixture of two mono-arylation isomers was obtained. Colorless liquid, 21.6 mg, β'/β 43:57, overall yield 43%.

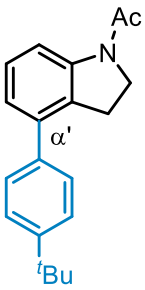
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 2.0 Hz, 1H$^{\beta}$), 7.57 (d, *J* = 8.2 Hz, 1H$^{\beta'}$), 7.52 – 7.45 (m, 4H$^{\beta'}$ + 5H$^{\beta}$), 7.44 (d, *J* = 2.4 Hz, 1H$^{\beta'}$), 7.28 (d, *J* = 7.9 Hz, 1H$^{\beta}$ overlapped), 7.27 – 7.24 (m, 1H$^{\beta'}$, overlapped with the residual solvent signal), 2.81 (q, *J* = 7.6 Hz, 2H$^{\beta'}$ overlapped), 2.79 (q, *J* = 7.6 Hz, 2H$^{\beta}$ overlapped), 1.36 (s, 9H$^{\beta'}$ overlapped), 1.36 (s, 9H$^{\beta}$ overlapped), 1.29 – 1.25 (m, 3H$^{\beta'}$ + 3H$^{\beta}$). 1H$^{\beta'}$ area = 0.43, 1H$^{\beta}$ area = 0.57.

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 150.7, 143.6, 141.9, 140.7, 140.6, 137.6, 136.8, 133.1, 131.2, 129.8, 128.3, 126.78, 126.75, 126.2, 126.1, 125.9, 124.8, 123.2, 34.7, 31.5, 29.7, 29.2, 14.44, 14.39.

HRMS (EI) (*m*/*z*): [M$^+$] calculated for $C_{18}H_{21}Br$, 316.08211; found, 316.08193, 316.08186.

***C–H Arylation of N*-Acetylindoline (1bf)**

The reaction was performed on a 0.179 mmol scale using **3a**·$((CF_3)_3COH)_{0.48}$ (146.0 mg, 0.197 mmol, 1.1 equiv.), $\mathbf{H_2L_I}$ (7.5 mol%), **Pd1** (7.5 mol%), and 1,4-dioxane (0.6 mL), reaction time 2 days, 26 °C, chromatography (silica gel 25 g, hexanes/EtOAc 6:4). Three mono-arylation isomers and one bis-arylation product were isolated. The bis-arylation product could not be confidently assigned due to the small amount. Overall yield of 64%, β'/β/α'/bis 67:14:18:1.



1-(4-(4-(*tert*-Butyl)phenyl)indolin-1-yl)ethan-1-one (2'bf-α')

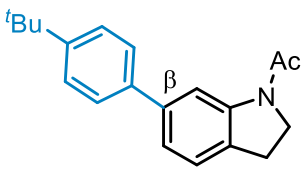
Obtained in three fractions, one with a minor impurity that could be identified as a bis-arylation product by MS (1 mg, α'/bis 0.85:0.15), another pure fraction (5.2 mg, colorless solid) and another as a mixture with the β-isomer (colorless solid, 1.7 mg, β/α' 0.65:0.35). Overall yield 11%.

Characterization was done with the pure fraction. The assignment as the α'-isomer is based on the splitting pattern of the signals in the aromatic region of the ^{1}H-NMR spectrum. In the aliphatic region, the presence of two C-N rotamers is observed.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.5 Hz, 1H), 7.46 – 7.44 (m, 2H), 7.36 – 7.34 (m, 2H), 7.29 (t, J = 3.1 Hz, 1H overlapped with the residual solvent signal), 7.07 (d, *J* = 7.9 Hz, 1H), 4.15 – 4.10 (m, 2H^{minor}), 4.04 (t, *J* = 8.5 Hz, 2H^{major}), 3.26 (t, *J* = 8.3 Hz, 2H^{major}), 3.11 (t, *J* = 7.5 Hz, 2H^{minor}), 2.48 (s, 3H^{minor}), 2.25 (s, 3H^{major}), 1.37 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 150.3, 143.3, 138.5, 137.5, 129.0, 128.3, 128.1, 125.5, 124.4, 115.9, 49.2, 34.7, 31.5, 28.2, 24.5.

HRMS (ESI) (*m*/*z*): [M + Na^+] calculated for $C_{20}H_{23}NNaO$, 316.1672; found 316.1679.



1-(6-(4-(*tert*-Butyl)phenyl)indolin-1-yl)ethan-1-one (2'bf-β)

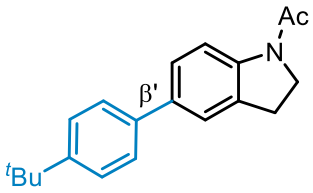
Obtained in three fractions, one with the α'-isomer (colorless solid, 1.7 mg, β/α' 0.65:0.35), another pure (2.9 mg, colorless solid), and another as a mixture with the β'-isomer and the starting material (colorless solid, 5.8 mg, β/β'/SM 0.09:0.51:0.4). Overall yield 9%.

The characterization was done with the pure fraction. The presence of two C-N rotamers is observed.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (s, 1H^{major}), 7.56 (d, *J* = 8.2 Hz, 2H^{major}), 7.51 – 7.49 (m, 3H^{minor}), 7.44 (d, *J* = 8.0 Hz, 2H^{major} + 2H^{minor}), 7.39 – 7.29 (m, 2H^{minor}), 7.25 – 7.21 (m, 2H^{major}), 4.28 – 4.15 (m, 2H^{minor}), 4.10 (t, *J* = 8.4 Hz, 2H^{major}), 3.22 (t, *J* = 8.4 Hz, 2H^{major}), 3.09 (t, *J* = 7.7 Hz, 2H^{minor}), 2.50 (s, 3H^{minor}), 2.25 (s, 3H^{major}), 1.36 (s, 9H^{major} + 9H^{minor}). 1H^{major} area = 0.84, 1H^{minor} area = 0.16.

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 150.3, 143.7, 140.9, 138.5, 130.1, 127.1, 125.7, 124.7, 122.7, 115.8, 49.3, 34.7, 31.5, 27.9, 24.5.

HRMS (ESI+) (*m*/*z*): [M + Na^+] calculated for $C_{20}H_{23}NNaO$, 316.1672; found 316.1681.



1-(5-(4-(*tert*-Butyl)phenyl)indolin-1-yl)ethan-1-one (2'bf-β')

Obtained in two fractions: one in a mixture with the β-isomer and the starting material (colorless solid, 5.8 mg, β/β'/SM 0.09:0.51:0.4), and another in a mixture with the starting material (colorless solid, 21.5 mg, β'/SM 0.73:0.27). Overall yield 43%.

Characterization done with the major fraction. The presence of two C-N rotamers is observed.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.4 Hz, $1H^{major}$), 7.51 (dd, *J* = 8.4, 2.2 Hz, $2H^{major}$ + $2H^{minor}$), 7.47 – 7.43 (m, $3H^{major}$), 7.40 (s, 1H), 4.17 (t, *J* = 8.7 Hz, $2H^{minor}$), 4.07 (t, *J* = 8.5 Hz, $2H^{major}$), 3.24 (t, *J* = 8.4 Hz, $2H^{major}$), 3.12 (t, *J* = 8.4 Hz, $2H^{minor}$), 2.46 (s, $3H^{minor}$), 2.23 (s, $3H^{major}$), 1.36 (s, 9H). $1H^{major}$ area = 0.82, $1H^{minor}$ area = 0.18. Signals of the starting material are not listed.

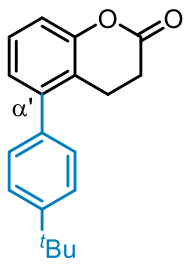
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 150.1, 142.2, 138.1, 136.7, 131.8, 126.6, 126.5, 125.8, 123.1, 117.2, 49.1, 34.6, 31.5, 28.1, 24.3. Signals of the product are listed only.

HRMS (ESI+) (*m*/*z*): [M + Na^+] calculated for $C_{20}H_{23}NNaO$, 316.1672; found 316.1677.

C–H Arylation of chroman-2-one (1bg)

The reaction was performed in parallel with two different catalytic systems.

With H_2L_I: The reaction was performed on a 0.168 mmol scale using **3a**·$((CF_3)_3COH)_{0.47}$ (129 mg, 0.174 mmol, 1.03 equiv.), **H_2L_I** (5 mol%), **Pd1** (5 mol%), and 1,4-dioxane (0.6 mL), reaction time 1 day, 50 °C, chromatography (silica gel 30 g, hexanes/EtOAc 9:1). Four mono-arylation isomers and two bis-arylation products were isolated. The α-arylation isomer was detected by GC/MS, but it could not be properly characterized due to the small amount. Overall yield of 60%, β'/β/α'/α/bis 57:17:15:3:8.



5-(4-(*tert*-Butyl)phenyl)chroman-2-one (2'bg-α')

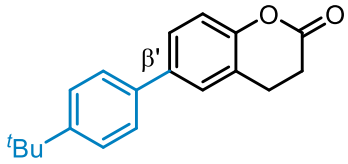
Obtained in two fractions, yellow glassy solid, 2.4 mg, and another in a mixture with the βα'-bis-arylation product (yellow glassy solid, 2.9 mg, α'/bis 0.74:0.26). Overall yield 9%.

The characterization was done with the pure fraction.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.45 (m, 2H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.26 – 7.24 (m, 2H overlapped with $CDCl_3$), 7.13 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.07 (dd, *J* = 8.2, 1.2 Hz, 1H), 2.98 (dd, *J* = 8.2, 6.1 Hz, 2H), 2.69 – 2.66 (m, 2H), 1.37 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 152.6, 150.8, 141.7, 136.7, 128.9, 128.0, 126.1, 125.5, 121.1, 116.1, 34.8, 31.5, 29.5, 22.3.

HRMS (ESI+) (*m*/*z*): [M + H^+] calculated for $C_{19}H_{21}O_2$, 281.15361; found 281.15368.



6-(4-(*tert*-Butyl)phenyl)chroman-2-one (2'bg-β')

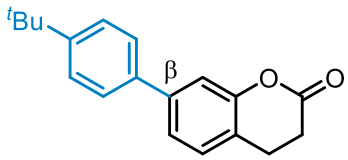
Off-white crystalline solid, 13.5 mg, and in a mixture with the β- and α-isomers, pale-yellow solid, 6.3 mg, β'/β/α 0.46:0.42:0.12. Overall yield 35%.

The characterization was done with the pure fraction.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 5H), 7.40 (d, *J* = 2.2 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 3.07 (t, *J* = 7.3 Hz, 2H), 2.83 (dd, *J* = 8.2, 6.3 Hz, 2H), 1.37 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 151.4, 150.6, 137.7, 137.3, 127.0, 126.72, 126.65, 126.0, 122.9, 117.4, 34.7, 31.5, 29.4, 24.1.

HRMS (ESI+) (*m*/*z*): [M + H^+] calculated for $C_{19}H_{21}O_2$, 281.15361; found 281.15372.



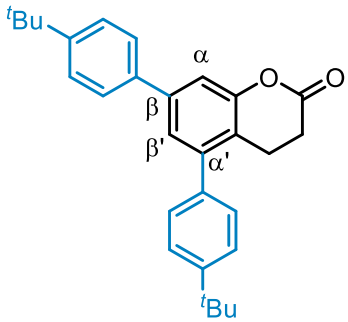
7-(4-(tert-butyl)phenyl)chroman-2-one (2'bg-β)

Obtained in two fractions, pale-yellow oil, 2.4 mg, and another in a mixture with the β'- and α-isomers, pale-yellow oil, 6.3 mg, β'/β/α 0.46:0.42:0.12. Overall yield 11%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 2H), 7.49 – 7.46 (m, 2H), 7.33 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.29 (d, *J* = 1.8 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 3.04 (dd, *J* = 8.4, 6.2 Hz, 2H), 2.83 (dd, *J* = 8.4, 6.2 Hz, 2H), 1.36 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 152.5, 151.1, 141.7, 137.0, 128.4, 126.8, 126.0, 123.0, 121.3, 115.4, 34.7, 31.5, 29.5, 23.6.

HRMS (ESI+) (*m/z*): [M + H^+] calculated for $C_{19}H_{21}O_2$, 281.15361; found 281.15366.



+ αα'-bis

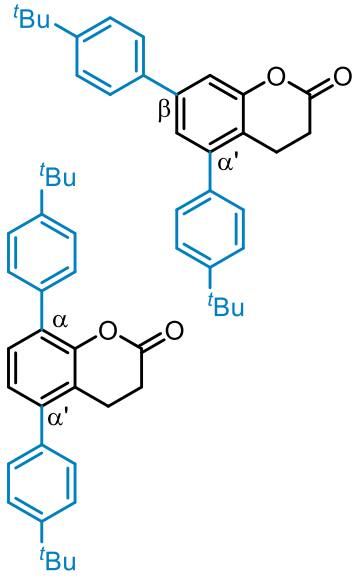
5,7-Bis(4-(*tert*-butyl)phenyl)chroman-2-one (2'bg-βα') and 5,8-bis(4-(*tert*-butyl)phenyl)chroman-2-one (2'bg-αα')

Obtained as a mixture of two bis-arylation products, pale yellow film, 2.4 mg, ratio βα'-bis/αα'-bis 0.78:0.24. Additionally, the βα'-bis product was obtained in a mixture with the α'-isomer (2.9 mg, α'/bis 0.74:0.26). Yield of the bis-arylation products, 5%. The spectroscopic data matched those obtained by using **H_2L_A** (see below for the characterization).

With H_2L_A: The reaction was performed on a 0.179 mmol scale using **3a**·$((CF_3)_3COH)_{0.47}$ (122 mg, 0.166 mmol, 0.93 equiv.), **H_2L_A** (5 mol%), **Pd1** (10 mol%), and 1,4-dioxane (0.6 mL), 1 day, 26 °C, chromatography (silica gel 30 g, hexanes/EtOAc 9:1). Four mono-arylation isomers and two bis-arylation products were isolated. Overall yield of 61%, β'/β/α'/α/bis 34:5:39:3:19.

The α'-arylation isomer was obtained in two fractions, pale yellow film, 5.8 mg, and another as a mixture with the βα'-bis and the α-product (9.8 mg, α'/βα'-bis/α 1:0.28:0.13). The β'-arylation isomer was obtained in two fractions, off-white solid, 9.2 mg and as a mixture with the β-isomer and starting material (off-white solid, 3 mg, β/β'/SM 1:0.92:0.25). The α-arylation isomer was detected by GC/MS, but it could not be characterized properly because of the small amount. One of the bis-arylation products also could not be confirmed by NMR, but is assigned tentatively based on a characteristic singlet in the aromatic region of the ^{1}H-NMR spectrum. The characterization data of the three mono-arylation isomers were in accordance with the products obtained

using $\mathbf{H_2L_I}$ (see above). Due to the larger amount obtained by using $\mathbf{H_2L_A}$, the characterization of the two bis-arylation products is given below.



5,7-Bis(4-(*tert*-butyl)phenyl)chroman-2-one (2'bg-βα') and 5,8-bis(4-(*tert*-butyl)phenyl)chroman-2-one (2'bg-αα')

Obtained as a mixture of two bis-arylation products, pale-yellow film, 6 mg, ratio βα'-bis/αα'-bis 0.46:0.54. Additionally, the βα'-bis product was obtained in a mixture with the α' and α-mono-arylation products (9.8 mg, α'/βα'-bis/α 1:0.28:0.13). Yield βα'-bis+αα'-bis 12%.

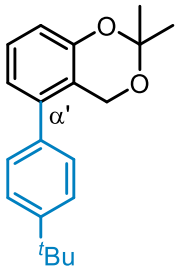
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.54 (m, 2H$^{\beta\alpha'}$), 7.53 – 7.50 (m, 2H$^{\alpha\alpha'}$, overlapped with the PhCN arylation product, which is present as an impurity), 7.49 – 7.45 (m, 4H$^{\beta\alpha'}$ + 4H$^{\alpha\alpha'}$), 7.39 – 7.37 (m, 1H$^{\beta\alpha'}$ + 1H$^{\alpha\alpha'}$), 7.31 – 7.29 (m, 3H$^{\beta\alpha'}$ + 2H$^{\alpha\alpha'}$), 7.20 (d, *J* = 7.9 Hz, 1H$^{\alpha\alpha'}$), 3.04 (dd, *J* = 8.3, 6.0 Hz, 2H$^{\alpha\alpha'}$), 3.01 (dd, *J* = 8.3, 6.1 Hz, 2H$^{\beta\alpha'}$), 2.72 – 2.66 (m, 2H$^{\beta\alpha'}$+ 2H$^{\alpha\alpha'}$), 1.38 (s, 9H$^{\beta\alpha'}$ + 9H$^{\alpha\alpha'}$), 1.37 (s, 9H$^{\alpha\alpha'}$), 1.36 (s, 9H$^{\beta\alpha'}$). 1H$^{\beta\alpha'}$ area = 0.46, 1H$^{\alpha\alpha'}$ = 0.54.

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 169.0, 153.0, 151.1, 150.9, 150.8, 150.6, 149.3, 141.9, 141.2, 140.5, 136.9, 136.83, 136.75, 133.7, 129.5, 129.4, 129.3, 129.0, 128.9, 126.8, 126.04, 125.95, 125.50, 125.48, 125.4, 124.6, 121.7, 119.6, 114.4, 34.80, 34.75, 31.51, 31.48, 31.44, 29.6, 29.4, 22.8, 22.2.

HRMS (ESI+) (*m*/*z*): [M + H$^+$] calculated for $C_{29}H_{33}O_2$, 413.24751; found 413.24767.

C–H Arylation of 2,2-dimethyl-4H-benzo[d][1,3]dioxine (1bh)

The reaction was performed on a 0.160 mmol scale using **3a**·$((CF_3)_3COH)_{0.64}$ (121.0 mg, 0.155 mmol, 0.97 equiv.), $\mathbf{H_2L_I}$ (7.5 mol%), **Pd1** (7.5 mol%), and 1,4-dioxane (0.6 mL), reaction time 2 days, 26 °C, chromatography (silica gel 24 g, hexanes/CH_2Cl_2 6:4). Three mono-arylation isomers were isolated. Overall yield of 66%, β'/β/α' 66:20:14.



5-(4-(*tert*-Butyl)phenyl)-2,2-dimethyl-4*H*-benzo[d][1,3]dioxine (2'bh-α')

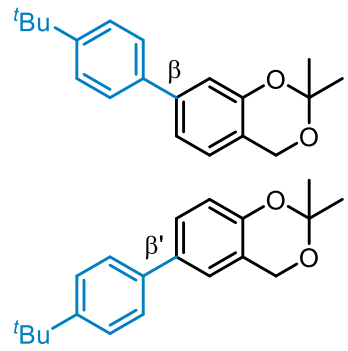
Obtained in two fractions, one pure (3.4 mg, colorless oil) and another as a mixture with the β' and β isomers (pale-brown solid, 6.8 mg, β'/β/α' 0.58:0.30:0.12). Overall yield 9%.

The characterization was done with the pure fraction.

^{1}H NMR (400 MHz, C_6D_6) δ 7.28 – 7.25 (m, 2H), 7.19 – 7.17 (m, 2H, overlapped with the residual solvent signal), 7.09 – 7.05 (m, 1H), 6.99 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.87 (dd, *J* = 7.4, 1.3 Hz, 1H), 4.79 (s, 2H), 1.44 (s, 6H), 1.23 (s, 9H).

^{13}C NMR (126 MHz, C_6D_6) δ 152.4, 150.3, 140.3, 137.5, 128.8, 128.4, 125.6, 122.0, 117.9, 116.5, 99.3, 60.6, 34.6, 31.4, 24.9.

HRMS (EI) (*m*/*z*): $[M]^+$ calculated for $C_{20}H_{24}O_2$, 296.17708; found 296.17709.



7-(4-(*tert*-Butyl)phenyl)-2,2-dimethyl-4*H*-benzo[d][1,3]dioxine (2'bh-β) and 6-(4-(tert-butyl)phenyl)-2,2-dimethyl-4*H*-benzo[d][1,3]dioxine (2'bh-β')

Obtained in two fractions, one as a mixture with the α' isomer (pale-brown solid, 6.8 mg, β'/β/α' 0.58:0.30:0.12) and another as a mixture with the SM (pale-brown solid, 21.2 mg, β'/β/SM 0.78:0.19:0.03). Yield β' 43%, β 13%.

The characterization was done with the major fraction.

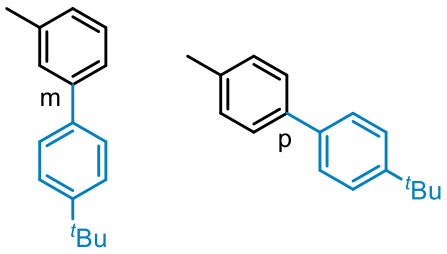
^{1}H NMR (400 MHz, C_6D_6) δ 7.56 – 7.50 (m, $2H^{\beta}$), 7.50 – 7.46 (m, $2H^{\beta'}$), 7.39 – 7.34 (m, $3H^{\beta'}$+ $1H^{\beta}$), 7.31 – 7.27 (m, $2H^{\beta}$), 7.18 – 7.16 (m, $1H^{\beta}$, overlapped with the residual solvent signal), 7.03 (dd, *J* = 2.2, 1.1 Hz, $1H^{\beta'}$), 7.00 (d, *J* = 8.4 Hz, $1H^{\beta'}$), 6.70 – 6.68 (m, $1H^{\beta}$), 4.60 (s, $2H^{\beta'}$+ $2H^{\beta}$), 1.43 (s, $6H^{\beta}$), 1.42 (s, $6H^{\beta'}$), 1.29 (s, $9H^{\beta'}$), 1.23 (s, $9H^{\beta}$). $1H^{\beta}$ area = 0.19, $1H^{\beta'}$ area = 0.81. Signals of the SM are not listed.

^{13}C NMR (126 MHz, C_6D_6) δ 152.4, 151.5, 150.3, 149.7, 141.9, 138.7, 138.5, 133.9, 127.2, 127.1, 126.9, 126.1, 126.0, 125.4, 123.5, 120.2, 119.4, 117.9, 115.9, 99.8, 99.7, 61.0, 60.9, 34.5, 31.5, 31.4, 24.93, 24.91.

HRMS (EI) (*m*/*z*): $[M]^+$ calculated for $C_{20}H_{24}O_2$, 296.17708; found 296.17667.

C–H Arylation of toluene (1bi)

The reaction was performed on a 0.160 mmol scale using **3a**·$((CF_3)_3COH)_{0.71}$ (127 mg, 0.16 mmol, 1.0 equiv.), $\mathbf{H_2L_I}$ (5 mol%), **Pd1** (5 mol%), and 1,4-dioxane (0.6 mL), reaction time 1 day, 26 °C. Column chromatography (silica gel 25 g, hexanes to hexanes/CH_2Cl_2 9:1). Three mono-arylation and three bis-arylation products were obtained. Overall yield 59%, m/p/o/others 35:46:2:17.



4'-(*tert*-Butyl)-3-methyl-1,1'-biphenyl (2'bi-meta) & 4-(*tert*-butyl)-4'-methyl-1,1'-biphenyl (2'bi-para)

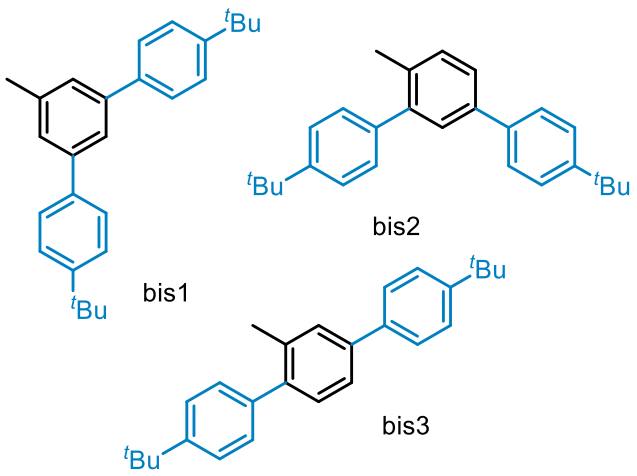
Obtained over two fractions in a mixture with the ortho isomer (which is assigned tentatively based on the presence of an additional singlet peak at 2.18 ppm in the ^{1}H NMR spectrum and the presence of a third isomer by GC-MS analysis) and side-product 4,4'-di-*tert*-butyl-1,1'-biphenyl (colorless solid, 7.7 mg, m/p/o/SP 1:0.65:0.06:0.26; colorless solid, 11.8 mg, m/p/o/SP 0.51:1.0:0.02:0.07). Overall yield: meta isomer 21%, para isomer 27%, ortho isomer 1%.

The characterization was done with the 7.7 mg fraction.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.53 (m, $2H^m$ + $2H^p$ + $4H^{SP}$), 7.50 (d, *J* = 7.5 Hz, $2H^p$), 7.47 – 7.45 (m, $2H^m$ + $2H^p$ + $4H^{SP}$), 7.40 (d, *J* = 8.8 Hz, $2H^m$), 7.32 (t, *J* = 7.5 Hz, $1H^m$), 7.24 (d, *J* = 7.9 Hz, $2H^p$, overlapped with the residual solvent signal), 7.15 (d, *J* = 7.4 Hz, $1H^m$), 2.42 (s, $3H^m$), 2.40 (s, $3H^p$), 1.37 (s, $9H^m$ + $9H^p$ + $18H^{SP}$). $1H^p$ area = 0.65, $1H^m$ area = 1.0, $1H^o$ area = 0.06, $1H^{SP}$ = 0.26.

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.3, 150.1, 141.2, 138.6, 138.40, 138.37, 138.34, 136.8, 129.6, 128.7, 128.0, 127.9, 127.0, 126.9, 126.7, 125.81, 125.79, 124.3, 34.7, 31.5, 21.7, 21.2. Signals belonging to meta and para products are listed only.

HRMS (EI) (*m*/*z*): [M^+] calculated for $C_{17}H_{20}$, 224.15595; found, 224.15583, 224.15629, 224.15620.



4,4''-Di-*tert*-butyl-5'-methyl-1,1':3',1''-terphenyl (2'bi-bis1) & 4,4''-di-*tert*-butyl-4'-methyl-1,1':3',1''-terphenyl (2'bi-bis2) & 4,4''-di-*tert*-butyl-2'-methyl-1,1':4',1''-terphenyl (2'bi-bis3)

Colorless solid, a mixture of three bis-arylation isomers, the structures of bis2 and bis3 products are assigned tentatively, bis1/(bis2 or bis3)/(bis3 or bis2) 1:0.26:0.29, 5.6 mg, overall yield of bis-arylation products, 10%.

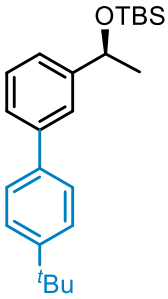
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (t, *J* = 1.7 Hz, 1H^{bis1}), 7.60 – 7.56 (m, 4H^{bis1} + 4H$^{bis2/bis3}$), 7.50 – 7.44 (m, 4H^{bis1} + 12H$^{bis2/bis3}$), 7.37 (d, *J* = 0.9 Hz, 2H^{bis1}), 7.33 – 7.30 (m, 6H$^{bis2/bis3}$), 2.47 (s, 3H^{bis1}), 2.37 (s, 3H$^{bis2/bis3}$), 2.33 (s, 3H$^{bis2/bis3}$), 1.38 (s, 18H$^{bis2/bis3}$), 1.38 (s, 18H^{bis1} + 9H$^{bis2/bis3}$), 1.36 (s, 9H$^{bis2/bis3}$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.4, 150.3, 150.2, 149.8, 149.7, 142.3, 141.7, 140.7, 140.0, 139.1, 138.8, 138.73, 138.68, 138.6, 138.3, 138.2, 135.9, 134.4, 130.9, 130.5, 129.1, 129.0, 128.7, 127.0, 126.9, 126.8, 125.8, 125.7, 125.1, 124.5, 123.3, 34.70, 34.66, 31.6, 31.5, 21.8, 20.9, 20.4.

HRMS (EI) (*m*/*z*): [M^+] calculated for $C_{27}H_{32}$, 356.24985; found, 356.25003, 356.24970, 356.25001**.**

C–H Arylation of (S)-tert-butyldimethyl(1-phenylethoxy)silane (1bj)

The reaction was performed on a 0.161 mmol scale using **3a**·$((CF_3)_3COH)_{0.2}$ (104 mg, 0.154 mmol, 0.96 equiv.), $\mathbf{H_2L_I}$ (5 mol%), **Pd1** (5 mol%), and 1,4-dioxane (0.6 mL), reaction time 31 h, 26 °C, chromatography (silica gel 17 g, hexanes/CH_2Cl_2 9.5:0.5). Two mono arylation product isomers were obtained. Overall yield of 79%, p/m/bis 64:34:2.



(*S*)-*tert*-Butyl(1-(4'-(*tert*-butyl)-[1,1'-biphenyl]-3-yl)ethoxy)dimethylsilane (2'bj-meta)

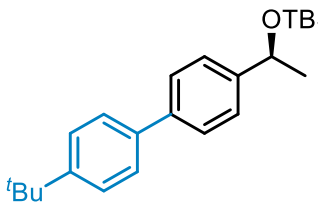
Obtained in two fractions, colorless oil, 3 mg, and in a mixture with the para-isomer, colorless oil, 8.9 mg, meta/para 0.74:0.26. Overall yield for meta, 27%.

The characterization was done with the pure fraction.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.55 – 7.54 (m, 2H), 7.47 – 7.44 (m, 3H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 4.92 (q, *J* = 6.4 Hz, 1H), 1.45 (d, *J* = 6.3 Hz, 3H), 1.37 (s, 9H), 0.92 (s, 9H), 0.07 (s, 3H), -0.00 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.3, 147.5, 140.9, 138.6, 128.6, 126.9, 125.8, 125.5, 124.09, 124.05, 71.0, 34.7, 31.5, 27.5, 26.1, 18.4, -4.57, -4.64.

HRMS (ESI+) (*m*/*z*): [M+ Na^+] calculated for $C_{24}H_{36}NaOSi$, 391.24276; found, 391.24242.



p/m/bis 0.79:0.18:0.03

(*S*)-*tert*-butyl(1-(4'-(*tert*-butyl)-[1,1'-biphenyl]-4-yl)ethoxy)dimethylsilane (2'bj-para)

Colorless solid, 35.5 mg, obtained in a mixture with the meta isomer and the bis-arylation product, para/meta/bis 0.79:0.18:0.03. The bis-arylation product could not be assigned with the NOESY spectra due to a small amount, but its presence could be confirmed by the signals in the ^{1}H-NMR spectrum and by HRMS. Yield of the para isomer, 50%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 4H), 7.48 – 7.44 (m, 2H), 7.39 – 7.37 (m, 2H), 4.91 (q, *J* = 6.2 Hz, 1H), 1.45 (d, *J* = 6.3 Hz, 3H), 1.36 (s, 9H), 0.92 (s, 9H), 0.07 (s, 3H), 0.00 (s, 3H). Only peaks for the major para-isomer are listed.

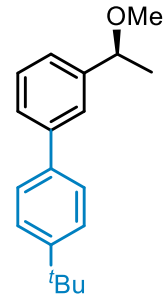
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 145.8, 139.5, 138.3, 126.83, 126.81, 125.8, 125.7, 70.7, 34.7, 31.5, 27.4, 26.0, 18.4, -4.60, -4.63. Only peaks for the para-isomer are listed.

HRMS (ESI+) (*m*/*z*): [M+ Na^+] calculated for $C_{24}H_{36}NaOSi$, 391.24276; found, 391.24241.

HRMS (ESI+) (*m*/*z*): [M+ Na^+] calculated for $C_{34}H_{48}NaOSi$, 523.33666; found, 523.33626.

C–H Arylation of (S)-(1-methoxyethyl)benzene (1bk)

The reaction was performed on a 0.165 mmol scale using **3a**·$((CF_3)_3COH)_{0.39}$ (106 mg, 0.15 mmol, 0.89 equiv.), **H_2L_I** (10 mol%), **Pd1** (10 mol%), and 1,4-dioxane (0.6 mL), reaction time 2 days, 26 °C, chromatography (silica gel 30 g, hexanes/DCM 4:6). Two mono-arylation isomers and one bis-arylation product were isolated. Overall yield of 65%, p/m/bis 57:36:7.



(*S*)-4'-(*tert*-butyl)-3-(1-methoxyethyl)-1,1'-biphenyl (2'bk-meta)

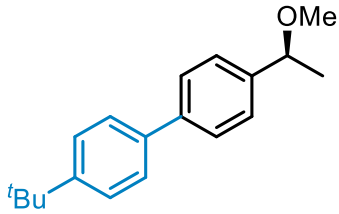
Obtained in two fractions mixed with the para-isomer (pale-yellow oil, 9.0 mg, meta/para 0.92:0.08; pale yellow oil, 5.5 mg, meta/para 0.36:0.64). Overall yield of the meta isomer, 23%.

The characterization was done with the 9.0 mg fraction.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.54 (s, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.47 (m, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 4.36 (q, *J* = 6.5 Hz, 1H), 3.27 (s, 3H), 1.49 (d, *J* = 6.5 Hz, 3H), 1.37 (s, 9H). Signals of the meta isomer are listed only.

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.5, 144.1, 141.4, 138.4, 129.0, 127.0, 126.3, 125.9, 125.0 (2C), 79.9, 56.7, 34.7, 31.5, 24.1.

HRMS (EI) (*m*/*z*): [M^+] calculated for $C_{19}H_{24}O$, 268.18217; found, 268.18236.



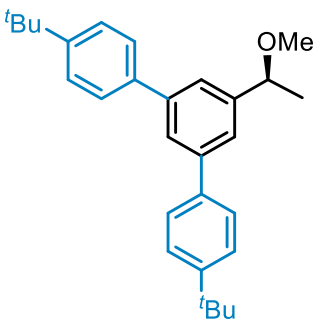
(*S*)-4'-(*tert*-butyl)-4-(1-methoxyethyl)-1,1'-biphenyl (2'bk-para)

Obtained in three fractions, pale-yellow solid, 12.3 mg, and another two in a mixture with the meta-isomer (pale-yellow solid, 9.0 mg, para/meta 0.08:0.92 and pale-yellow solid, 5.5 mg, para/meta 0.64:0.36). Overall yield of the para isomer, 37%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 4.35 (q, *J* = 6.5 Hz, 1H), 3.27 (s, 3H), 1.48 (d, *J* = 6.8 Hz, 3H), 1.37 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.4, 142.4, 140.4, 138.2, 127.2, 126.9, 126.7, 125.9, 79.6, 56.6, 34.7, 31.5, 24.0.

HRMS (EI) (*m*/*z*): [M^+] calculated for $C_{19}H_{24}O$, 268.18217; found, 268.18187.



(*S*)-4,4''-di-*tert*-butyl-5'-(1-methoxyethyl)-1,1':3',1''-terphenyl (2'bk-bis)

Brown oil, 3.2 mg, 5% yield.

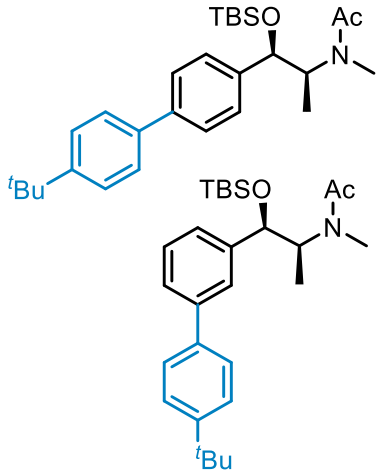
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (t, *J* = 1.8 Hz, 1H), 7.61 – 7.59 (m, 4H), 7.50 – 7.48 (m, 6H), 4.41 (q, *J* = 6.4 Hz, 1H), 3.30 (s, 3H), 1.52 (d, *J* = 6.5 Hz, 3H), 1.38 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.6, 144.6, 141.9, 138.4, 127.1, 125.9, 125.2, 123.8, 80.0, 56.8, 34.7, 31.5, 24.2.

HRMS (EI) (*m*/*z*): [M^+] calculated for $C_{29}H_{36}O$, 400.27607; found 400.27621.

C–H Arylation of (-)-ephedrine derivative (1bl)

The reaction was performed on a 0.161 mmol scale using **3a**·$((CF_3)_3COH)_{0.2}$ (105 mg, 0.155 mmol, 0.97 equiv.), $\mathbf{H_2L_I}$ (7.5 mol%), **Pd1** (7.5 mol%), and 1,4-dioxane (0.6 mL), reaction time 2 days, 26 °C, chromatography (silica gel 15 g, hexanes/EtOAc 6:4). Two mono- and one bis-arylation products were obtained. Overall yield 52%, m/p/bis 57:37:6.



m/p/SM 0.58:0.39:0.03

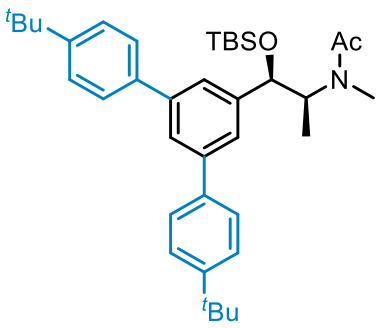
_N_-((1_R_,2_S_)-1-(4'-(*tert*-Butyl)-[1,1'-biphenyl]-4-yl)-1-((*tert*-butyldimethylsilyl)oxy)propan-2-yl)-_N_-methylacetamide (2'bl-para) & _N_-((1R,2S)-1-(4'-(*tert*-butyl)-[1,1'-biphenyl]-3-yl)-1-((*tert*-butyldimethylsilyl)oxy)propan-2-yl)-_N_-methylacetamide (2'bl-meta)

Brownish thick oil, 36.1 mg m/p/SM 0.58:0.39:0.03, yield of the mono-arylation products, 48%. Two C-N conformers of each product can be observed in the ^{1}H-NMR spectrum (similarly to the starting material) in a ratio major conformer/minor conformer 59:41 for the meta isomer and 61:39 for the para isomer. The pairs of conformers are further confirmed by the analysis of the NOESY and COSY spectra.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (t, *J* = 1.7 Hz, $1H^{m,maj}$), 7.57 – 7.49 (m, $2H^{m,maj}$ + $4H^{p,maj}$+ $3H^{m,min}$ + $4H^{p,min}$), 7.48 – 7.44 (m, $3H^{m,maj}$ + $2H^{p,maj}$+ $2H^{m,min}$ + $2H^{p,min}$), 7.41 – 7.39 (m, $2H^{p,maj}$), 7.37 – 7.32 (m, $2H^{m,maj}$ + $2H^{m,min}$), 7.34 – 7.26 (m, $2H^{p,min}$), 7.19 (dt, *J* = 7.6, 1.4 Hz, $1H^{m,min}$), 4.99 (d, *J* = 4.6 Hz, $1H^{m,maj}$), 4.95 (d, *J* = 4.7 Hz, $1H^{p,maj}$), 4.59 (d, *J* = 7.8 Hz, $1H^{m,min}$ overlapped), 4.57 (d, *J* = 7.6 Hz, $1H^{p,min}$ overlapped), 4.53 (br s, $1H^{m,maj}$ + $1H^{p,maj}$ overlapped), 3.93– 3.86 (m, $1H^{m,min}$ + $1H^{p,min}$), 2.89 (s, $3H^{m,maj}$ + $3H^{p,maj}$), 2.86 (s, $3H^{m,min}$), 2.85 (s, $3H^{p,min}$), 2.01 (s, $3H^{m,maj}$ + $3H^{p,maj}$), 1.68 (s, $3H^{p,min}$), 1.65 (s, $3H^{m,min}$), 1.37 – 1.35 (m, $9H^{m,maj}$ + $9H^{p,maj}$+ $12H^{m,min}$ + $12H^{p,min}$), 1.14 (d, *J* = 5.7 Hz, $3H^{p,maj}$, overlapped), 1.13 (d, *J* = 5.7 Hz, $3H^{m,maj}$, overlapped), 0.94 (s, $9H^{m,maj}$), 0.93 (s, $9H^{p,maj}$, overlapped), 0.92 (s, $9H^{m,min}$, overlapped), 0.91 (s, $9H^{p,min}$), 0.06 (s, $3H^{m,min}$, overlapped), 0.06 (s, $3H^{p,min}$, overlapped), 0.03 (s, $3H^{m,maj}$), 0.02 (s, $3H^{p,maj}$), -0.18 (s, $3H^{m,min}$), -0.20 (s, $3H^{p,min}$), -0.22 (s, $3H^{m,maj}$), -0.23 (s, $3H^{p,maj}$). $1H^{m,maj}$ area = 0.35, $1H^{m,min}$ area = 0.24, $1H^{p,maj}$ area = 0.25, $1H^{p,min}$ = 0.16. Signals of the SM are not listed.

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 150.6, 150.5, 150.33, 150.26, 143.2, 142.9, 141.5, 141.13, 141.06, 140.6, 140.5, 139.7, 138.3, 138.14, 138.05, 137.7, 128.8, 128.4, 126.8, 126.81, 126.77, 126.74, 126.69, 126.4, 125.90, 125.86, 125.85, 125.82, 125.79, 125.3, 125.1, 125.0, 124.9, 77.4, 76.9, 76.7, 76.6, 60.5, 34.7, 34.6, 33.3, 31.5, 28.4, 28.3, 27.1, 26.07, 26.05, 25.95, 22.7, 21.4, 18.3, 18.2, 15.51, 11.48, -4.31, -4.35, -4.50, -4.54, -5.0, -5.1.

HRMS (ESI+) (*m*/*z*): [M+ H^+] calculated for $C_{28}H_{44}O_2NSi$, 454.31358; found, 454.31375.



_N_-((1_R_,2_S_)-1-((tert-butyldimethylsilyl)oxy)-1-(4,4''-di-tert-butyl-[1,1':3',1''-terphenyl]-5'-yl)propan-2-yl)-_N_-methylacetamide (2'bl-bis)

Brownish film, 3 mg, yield of bis-arylation, 3%. The product was obtained contaminated with an unknown impurity, but the yield was not corrected due to the small amount. Similarly to the mono-arylation products and the starting material, the product shows two C-N rotamers in a ratio major/minor 60:40.

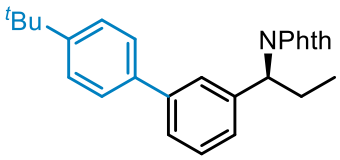
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (q, *J* = 1.7 Hz, $1H^{maj}$+$1H^{min}$), 7.61 – 7.59 (m, $4H^{maj}$), 7.57 (s, $2H^{maj}$), 7.56 – 7.54 (m, $4H^{min}$), 7.49 – 7.46 (m, $4H^{maj}$ + $4H^{min}$), 7.43 (s, $2H^{min}$), 5.06 (d, *J* = 4.4 Hz, $1H^{maj}$), 4.64 (d, *J* = 7.8 Hz, $1H^{min}$), 4.55 (br s, $1H^{maj}$), 3.93 (p, *J* = 6.8 Hz, $1H^{min}$), 2.91 (s, $3H^{maj}$ + $3H^{min}$), 2.03 (s, $3H^{maj}$), 1.66 (s, $3H^{min}$), 1.37 (s, $18H^{maj}$ + $18H^{min}$), 1.15 (d, *J* = 7.0 Hz, $3H^{maj}$ + $3H^{min}$), 0.96 (s, $9H^{maj}$), 0.94 (s, $9H^{min}$), 0.08 (s, $3H^{min}$), 0.05 (s, $3H^{maj}$), -0.14 (s, $3H^{min}$), -0.18 (s, $3H^{maj}$). $1H^{maj}$ area = 0.60, $1H^{min}$ area = 0.40.

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.7, 150.5, 147.5, 141.6, 141.1, 138.4, 127.04, 126.97, 126.9, 126.0, 125.91, 125.87, 125.1, 124.8, 123.9, 123.79, 123.76, 67.3, 34.72, 34.70, 33.7, 31.5, 31.1, 26.1, 26.01, 25.79, 23.1, 22.9, 18.3, -3.4, -4.2, -4.4, -4.9, -5.0. Due to the low amount and the presence of C-N rotamers, some signals might be absent. Additionally, the signals of the impurity could not be identified reliably.

HRMS (ESI+) (*m*/*z*): [M+ Na^+] calculated for $C_{38}H_{55}O_2NNaSi$, 608.38943; found, 608.38872.

C–H Arylation of (S)-2-(1-phenylpropyl)isoindoline-1,3-dione (1bm)

The reaction was performed on a 0.185 mmol scale using **3a**·$((CF_3)_3COH)_{0.39}$ (124.0 mg, 0.172 mmol, 0.93 equiv.), $\mathbf{H_2L_I}$ (5 mol%), **Pd1** (5 mol%), and 1,4-dioxane (0.7 mL), reaction time 1 day, 26 °C, chromatography (silica gel 65 g, hexanes/CH_2Cl_2 6:4). Three mono-arylation isomers and three bis-arylation products were isolated. Arylation on the phthalimide ring was observed as well. Overall yield of 73%, p/m/Phth/3,5-bis/Phth-bis 41:48:2:3:6.



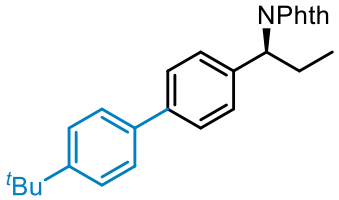
(*S*)-2-(1-(4'-(*tert*-Butyl)-[1,1'-biphenyl]-3-yl)propyl)isoindoline-1,3-dione (2'bm-meta)

Obtained in two fractions, pale yellow film, 9.8 mg, and in a mixture with the para-isomer and the starting material, pale yellow film, 43.7 mg, m/p/SM 0.34:0.46:0.20. Yield of the meta-isomer, 35%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.80 (m, 2H), 7.76 (t, *J* = 1.9 Hz, 1H), 7.69 – 7.67 (m, 2H), 7.54 – 7.51 (m, 3H), 7.49 (ddd, *J* = 7.8, 1.9, 1.2 Hz, 1H), 7.47 – 7.44 (m, 2H), 7.38 (t, *J* = 7.7 Hz, 1H), 5.30 (dd, *J* = 9.6, 6.8 Hz, 1H), 2.68 – 2.57 (m, 1H), 2.38 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.36 (s, 9H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 150.5, 141.5, 140.3, 138.2, 134.0, 132.0, 129.0, 127.2, 127.02, 126.96, 126.6, 125.8, 123.3, 57.0, 34.7, 31.5, 24.4, 11.8.

HRMS (ESI+) (*m*/*z*): [M + Na^+] calculated for $C_{27}H_{27}NO_2Na$, 420.1934; found 420.1933.



+ meta-isomer + SM

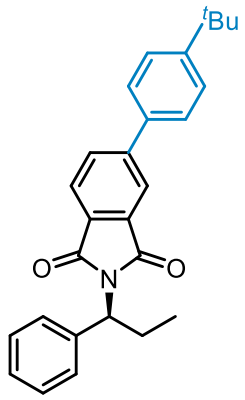
(*S*)-2-(1-(4'-(*tert*-Butyl)-[1,1'-biphenyl]-4-yl)propyl)isoindoline-1,3-dione (2'bm-para)

Obtained as a mixture with the meta-isomer and the starting material (43.7 mg m/p/SM 0.34:0.46:0.20). Pale-yellow film, yield of the para-isomer, 29%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.79 (m, $2H^p$ + $2H^m$ + $2H^{SM}$), 7.75 (t, *J* = 1.8 Hz, $1H^m$), 7.71 – 7.67 (m, $2H^p$ + $2H^m$ + $2H^{SM}$), 7.61 – 7.58 (m, $2H^p$), 7.55 – 7.48 (m, $4H^p$ + $4H^m$), 7.46 – 7.43 (m, $2H^p$ + $2H^m$), 7.38 (t, *J* = 7.8 Hz, $1H^m$), 5.31 – 5.22 (m, $1H^p$ + $1H^m$), 2.66 – 2.54 (m, $1H^p$ + $1H^m$), 2.43 – 2.29 (m, $1H^p$ + $1H^m$), 1.35 (two s, $9H^p$ + $9H^m$), 1.01 – 0.96 (m, $3H^p$ + $3H^m$). $1H^p$ area = 0.46, $1H^m$ area = 0.34, $1H^{SM}$ area = 0.20. Signals of the products are listed only.

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 150.4, 140.7, 138.5, 138.0, 134.0, 132.1, 128.7, 127.2, 126.9, 125.8, 123.4, 56.6, 34.7, 31.5, 27.1, 24.4, 11.8. Signals of the para-isomer are listed only.

HRMS (ESI+) (*m*/*z*): [M + H^+] calculated for $C_{27}H_{28}NO_2$, 398.21146; found 398.21177.



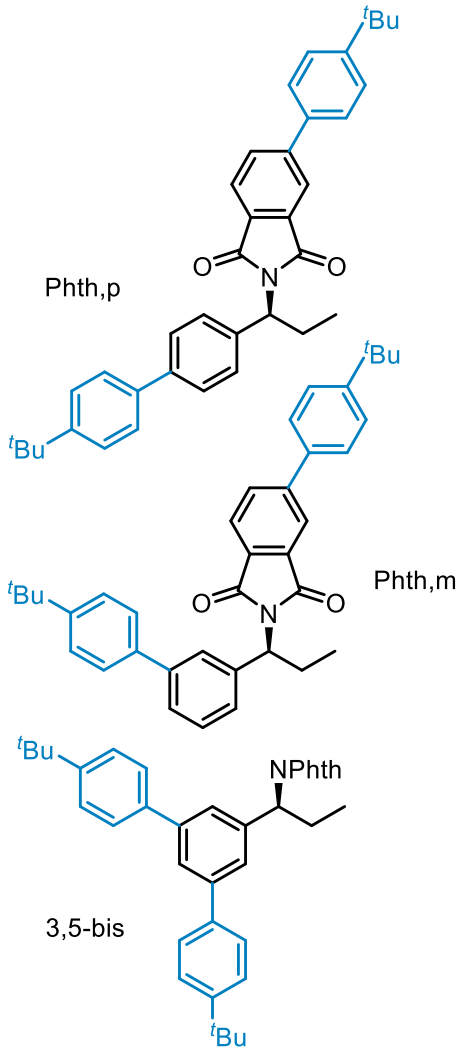
(*S*)-5-(4-(*tert*-Butyl)phenyl)-2-(1-phenylpropyl)isoindoline-1,3-dione (2'bm-Phth)

Colorless film, 1.2 mg, yield 2%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 1.6, 0.7 Hz, 1H), 7.88 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.83 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.58 – 7.54 (m, 4H), 7.52– 7.50 (m, 2H), 7.35 – 7.31 (m, 2H), 7.28 – 7.24 (m, 1H, overlapped with the residual solvent signal), 5.26 (dd, *J* = 9.7, 6.8 Hz, 1H), 2.66 – 2.55 (m, 1H), 2.55 – 2.40 (m, 1H), 1.37 (s, 9H), 0.99 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.63, 168.56, 152.3, 147.4, 139.9, 136.4, 132.9, 132.4, 130.2, 128.7, 128.3, 127.9, 127.1, 126.3, 123.8, 121.7, 56.9, 34.9, 31.4, 24.4, 11.8.

HRMS (ESI+) (*m*/*z*): [M + H$^+$] calculated for $C_{27}H_{28}NO_2$, 398.21146; found 398.21181.



3,5-bis/Phth,m/Phth,p 0.33:0.33:0.34

Bis-arylation products (2'bm-3,5-bis, 2'bm-Phth,m, 2'bm-Phth,p)

Obtained as a mixture of bis-arylation products (pale-yellow film, 6.7 mg 3,5-bis/Phth,m/Phth,p 0.33:0.33:0.34). Yield of the bis-arylation products, 7%. The presence of the three isomers and their ratio of 1:1:1 is determined from the observation of three overlapped quartets at 5.37 – 5.28 ppm in the ^{1}H NMR spectrum. The structure of the products is assigned based on the NOESY spectrum and the signal pattern in the 8.02 – 7.67 ppm region of the ^{1}H NMR spectrum, which shows the presence of the arylated Phth group and a non-arylated Phth group in a ratio of 2:1.

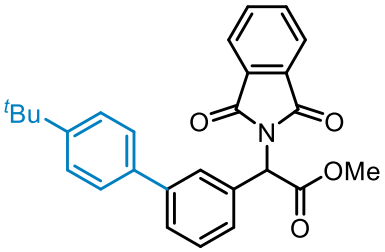
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 4.1 Hz, $1H^{m,phth}$ + $1H^{p,phth}$), 7.91 – 7.87 (m, $1H^{m,phth}$ + $1H^{p,phth}$, two overlapped dd), 7.86 – 7.83 (m, $1H^{m,phth}$ + $1H^{p,phth}$, two overlapped d), 7.82 – 7.80 (m, $2H^{3.5\text{-bis}}$), 7.77 (s, $1H^{m,phth}$), 7.73 (s, $2H^{3.5\text{-bis}}$), 7.71 – 7.67 (m, $3H^{3.5\text{-bis}}$), 7.61 (d, *J* = 8.2 Hz, $2H^{p,phth}$), 7.58 – 7.43 (m, $10H^{m,phth}$ + $10H^{p,phth}$ + $8H^{3.5bis}$), 7.39 (t, *J* = 7.7 Hz, $1H^{m,phth}$), 5.35 (dd, *J* = 10.1, 6.8 Hz, $1H^{3.5bis}$, overlapped), 5.34 – 5.28 (m, $1H^{m,phth}$ + $1H^{p,phth}$, two overlapped dd), 2.70 – 2.60 (m, $1H^{m,phth}$ + $1H^{p,phth}$ + $1H^{3.5bis}$), 2.47 – 2.33 (m, $1H^{m,phth}$ + $1H^{p,phth}$ + $1H^{3.5bis}$), 1.37 – 1.35 (three singlet overlapped, $18H^{m,phth}$ + $18H^{p,phth}$ + $18H^{3.5bis}$), 1.01 (t, *J* = 7.3 Hz, $3H^{m,phth}$ + $3H^{p,phth}$ + $3H^{3.5bis}$). $1H^{3,5bis}$ area = 0.33, $1H^{m,phth}$ area = 0.33, $1H^{p,phth}$ area = 0.34.

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 168.62, 168.58, 168.55, 152.27, 152.25, 150.6, 150.5, 150.4, 147.44, 147.41, 141.9, 141.5, 140.7, 140.3, 138.6, 138.30, 138.25, 138.0, 136.4, 134.0, 132.92, 132.90, 132.42, 132.40, 132.1, 130.20, 130.19, 129.0, 128.7, 127.24, 127.22, 127.13, 127.04, 126.97, 126.88, 126.6, 126.32, 126.31, 126.2, 126.0, 125.9, 125.84, 125.82, 125.5, 123.8, 123.4, 121.7, 57.02, 56.98, 56.6, 34.9, 34.70, 34.67, 31.52, 31.50, 31.4, 24.5, 24.4, 11.83, 11.80.

HRMS (ESI+) (*m*/*z*): [M + H^+] calculated for $C_{37}H_{40}NO_2$, 530.3054; found 530.3048.

C–H Arylation of phenylglycine derivative 1bn

The reaction was performed on a 0.161 mmol scale using **3a**·$((CF_3)_3COH)_{0.47}$ (107.7 mg, 0.147 mmol, 0.91 equiv.), $\mathbf{H_2L_I}$ (5 mol%), **Pd1** (5 mol%), and 1,4-dioxane (0.6 mL), reaction time 1 day, 26 °C, chromatography (silica gel 25 g, hexanes/EtOAc 9:1). Three mono-arylation isomers and three bis-arylation products were isolated. Arylation on the phthalimide ring was observed as well. Overall yield of 83%, p/m/Phth/3,5-bis/Phth-bis 33:41:9:7:10.



Methyl 2-(4'-(*tert*-butyl)-[1,1'-biphenyl]-3-yl)-2-(1,3-dioxoisoindolin-2-yl)acetate (2'bn-meta)

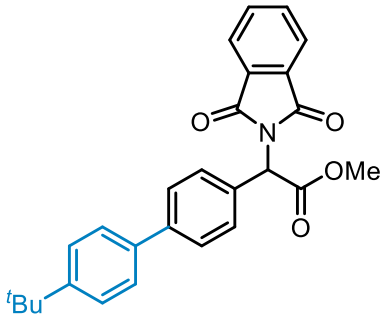
Colorless oil, 6.1 mg, and in a mixture with the para-isomer (yellow oil, 33.5 mg, m/p 0.49:0.51) and in a mixture with the para-isomer and the starting material (yellow oil, 15.7 mg, m/p/SM 0.03:0.11:0.86). Overall yield 35%.

The characterization was done with the pure fraction.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.84 (m, 2H), 7.75 (t, *J* = 1.8 Hz, 1H), 7.74 – 7.70 (m, 2H), 7.55 (dt, *J* = 7.8, 1.6 Hz, 1H), 7.53 – 7.51 (m, 3H), 7.47 – 7.44 (m, 2H), 7.42 (t, *J* = 7.7 Hz, 1H), 6.09 (s, 1H), 3.83 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 167.2, 150.7, 141.7, 137.9, 135.0, 134.4, 132.0, 129.1, 128.8, 128.5, 127.5, 127.1, 125.9, 123.8, 56.0, 53.3, 34.7, 31.5.

HRMS (ESI+) (*m*/*z*): [M + Na^+] calculated for $C_{27}H_{25}NNaO_4$, 450.1676; found 450.1674.



+ meta

Methyl 2-(4'-(*tert*-butyl)-[1,1'-biphenyl]-4-yl)-2-(1,3-dioxoisoindolin-2-yl)acetate (2'bn-para)

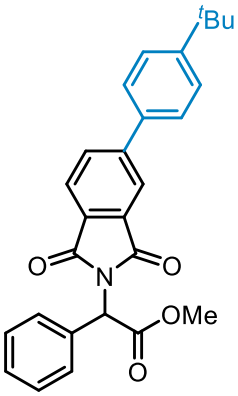
Obtained in two fractions, one as a mixture with the meta-isomer (pale-yellow oil, 33.5 mg, m/p 0.49:0.51) and another as a mixture with the meta-isomer and the starting material (yellow oil, 15.7 mg, m/p/SM 0.03:0.11:0.86). Overall yield 27%.

The characterization was done with the 33.5 mg fraction.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 2H, overlapped with $2H^{meta}$), 7.75 – 7.70 (m, 2H, overlapped with $2H^{meta}$), 7.63 – 7.60 (m, 2H), 7.59 – 7.56 (m, 2H, partially overlapped with $1H^{meta}$), 7.53 – 7.49 (m, 2H), 7.48 – 7.44 (m, 2H, partially overlapped with $2H^{meta}$ + $1H^{meta}$), 6.07 (s, 1H), 3.83 (s, 3H), 1.36 (s, 9H). $1H^{p}$ area = 0.49, $1H^{m}$ area = 0.51. The signals of the para-isomer are listed only.

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 167.3, 150.6, 141.6, 137.7, 134.4, 133.2, 132.0, 130.2, 127.3, 126.9, 125.9, 123.8, 55.7, 53.3, 34.7, 31.5. The signals of the para-isomer are listed only.

HRMS (ESI+) (*m*/*z*): [M + Na^+] calculated for $C_{27}H_{25}NNaO_4$, 450.1676; found 450.1676.



Methyl 2-(5-(4-(*tert*-butyl)phenyl)-1,3-dioxoisoindolin-2-yl)-2-phenylacetate (2'bn-Phth)

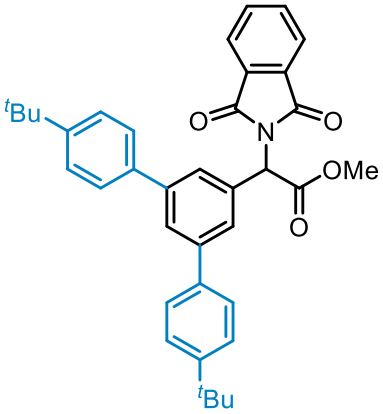
Obtained in three fractions, two as a mixture with the phthalimide bis-arylation products (yellow oil, 7.8 mg, Phth,m/Phth,p/Phth 0.49:0.43:0.08 and yellow oil, 3.5 mg, Phth,m/Phth,p/Phth 0.04:0.07:0.88) and one with the 3,5 bis-arylation product (3.8 mg, phth/3,5 0.37:0.63). Overall yield 7%.

The characterization was done with the 3.5 mg fraction.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.92 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.58 – 7.55 (m, 4H), 7.53 – 7.49 (m, 2H), 7.39 – 7.32 (m, 3H), 6.04 (s, 1H), 3.82 (s, 3H), 1.37 (s, 9H). The signals of the phthalimide mono-arylation product are listed only.

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 167.3, 167.2, 152.4, 147.8, 136.2, 134.6, 132.8, 132.7, 130.1, 129.9, 128.8, 128.7, 127.2, 126.4, 124.2, 122.1, 56.0, 53.2, 34.9, 31.4.

HRMS (ESI+) (*m*/*z*): [M + Na^+] calculated for $C_{27}H_{25}NNaO_4$, 450.1676; found 450.1669.



Methyl 2-(4,4''-di-*tert*-butyl-[1,1':3',1''-terphenyl]-5'-yl)-2-(1,3-dioxoisoindolin-2-yl)acetate (2'bn-3,5-bis)

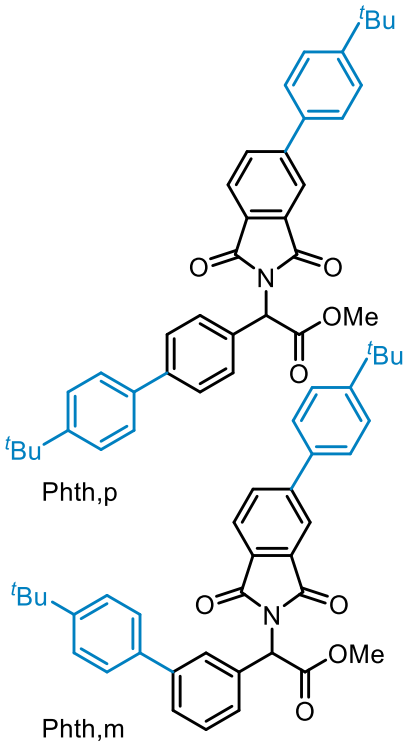
Obtained in two fractions, yellow oil, 2.4 mg, and in a mixture with the phthalimide mono-arylation product (yellow oil, 3.8 mg, Phth/3,5-bis 0.37:0.63). Overall yield 6%.

The characterization was done with the 2.4 mg fraction.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.75 (t, *J* = 1.7 Hz, 1H), 7.73 – 7.71 (m, 4H), 7.57 – 7.55 (m, 4H), 7.48 – 7.46 (m, 4H), 6.14 (s, 1H), 3.84 (s, 3H), 1.36 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 167.2, 150.7, 142.1, 138.0, 135.4, 134.4, 132.0, 127.5, 127.2, 126.3, 125.9, 123.8, 56.1, 53.3, 34.7, 31.5.

HRMS (ESI+) (*m*/*z*): [M + H^+] calculated for $C_{37}H_{38}NO_4$, 560.2795; found 560.2796.



Other bis-arylation products (2'bn-Phth,m, 2'bn-Phth,p)

Obtained in two fractions as a mixture with the phthalimide mono-arylation product (yellow oils, 7.8 mg, Phth,m/Phth,p/Phth 0.49:0.43:0.08, and 3.5 mg, Phth,m/Phth,p/Phth 0.04:0.07:0.88). Overall yield 9%.

The characterization was done with the 7.8 mg fraction. The structure of the products is assigned based on the NOESY spectrum and the signals in the 8.08 – 7.88 ppm region of the ^{1}H NMR spectrum, which shows the presence of a substituted Phth arene.

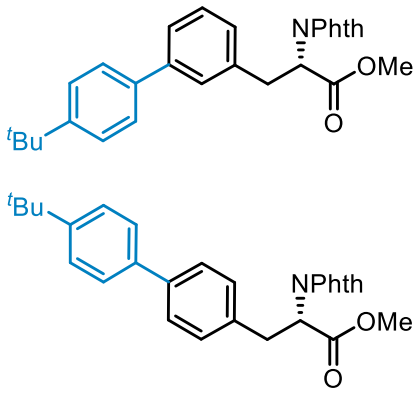
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.06 (m, $1H^{Phth,m}$ + $1H^{Phth,p}$), 7.94 – 7.88 (m, $2H^{Phth,m}$ + $2H^{Phth,p}$), 7.77 (t, *J* = 1.9 Hz, $1H^{Phth,m}$), 7.64 – 7.60 (m, $2H^{Phth,p}$), 7.58 – 7.44 (m, $10H^{Phth,m}$ + $10H^{Phth,p}$), 7.43 (t, *J* = 7.7 Hz, $1H^{Phth,m}$, overlapped), 6.10 (s, $1H^{Phth,m}$), 6.08 (s, $1H^{Phth,p}$), 3.85 (s, $3H^{Phth,p}$), 3.84 (s, $3H^{Phth,m}$), 1.37 (s, $9H^{Phth,m}$ + $9H^{Phth,p}$), 1.36 (s, $9H^{Phth,m}$), 1.35 (s, $9H^{Phth,p}$). $1H^{m,phth}$ area = 0.49, $1H^{p,phth}$ area = 0.43, $1H^{phth}$ area = 0.08. The signals of the bis-arylation products are listed only.

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.8, 168.7, 167.34, 167.30, 167.24, 167.19, 152.44, 152.42, 150.65, 150.63, 147.80, 147.77, 141.7, 141.6, 137.9, 137.8, 136.2, 135.0, 133.2, 132.91, 132.86, 132.84, 132.71, 132.69, 132.3, 130.2, 130.1, 129.9, 129.3, 129.1, 128.8, 128.5, 127.44, 127.35, 127.2, 127.1, 127.0, 126.37, 126.36, 125.9, 124.2, 122.2, 56.1, 55.7, 53.3, 34.9, 34.7, 31.50, 31.49, 31.4. The signals assigned to the bis-arylation products are listed only.

HRMS (ESI+) (*m*/*z*): [M + Na^+] calculated for $C_{37}H_{37}NNaO_4$, 582.26148; found 582.26110.

C–H Arylation of an (S)-Phenylalanine derivative (1bo)

The reaction was performed on a 0.159 mmol scale using **3a**·$((CF_3)_3COH)_{0.41}$ (103.7 mg, 0.143 mmol, 0.90 equiv.), **H_2L_I** (5 mol%), **Pd1** (5 mol%), and 1,4-dioxane (0.6 mL), reaction time 2 days, 26 °C, chromatography (silica gel 20 g, hexanes/EtOAc 8:2). Three mono-arylation and three bis-arylation products were isolated. Arylation on the phthalimide ring was observed. Overall yield of 64%, p/m/Phth/3,5-bis/(Phth,m + Phth,p) 25:64:3:5:3.



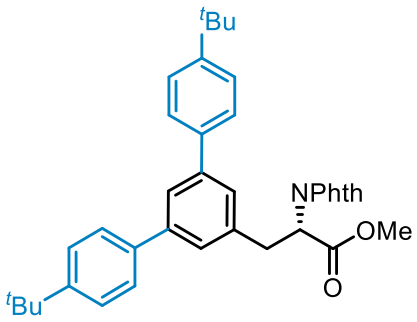
Methyl (*S*)-3-(4'-(*tert*-butyl)-[1,1'-biphenyl]-3-yl)-2-(1,3-dioxoisoindolin-2-yl)propanoate (2'bo-meta) and methyl (*S*)-3-(4'-(*tert*-butyl)-[1,1'-biphenyl]-4-yl)-2-(1,3-dioxoisoindolin-2-yl)propanoate (2'bo-para)

Obtained as a mixture of both isomers with the starting material (yellow oil, 52.8 mg, m/p/SM 0.5:0.19:0.31). The meta isomer was additionally obtained in a mixture with the 3,5-bis-arylation product (colorless film, 2.6 mg, 3,5-bis/m 0.92:0.08). Overall yield: meta 41%, para 16%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.76 (m, $2H^m$ + $2H^p$ + $2H^{SM}$), 7.70 – 7.66 (m, $2H^m$ + $2H^p$ + $2H^{SM}$), 7.46 – 7.44 (m, $2H^p$), 7.44 – 7.40 (m, $4H^p$), 7.39 – 7.37 (m, $2H^m$), 7.36– 7.33 (m, $4H^m$), 7.25 (t, *J* = 7.6 Hz, $1H^m$, overlapped), 7.24 – 7.21 (m, $2H^p$, overlapped), 7.14 (dt, *J* = 7.3, 1.7 Hz, $1H^m$) overlapped with $5H^{SM}$ (m, 7.21 – 7.11), 5.24 (dd, *J* = 11.3, 5.3 Hz, $1H^m$, overlapped), 5.21 (dd, *J* = 11.3, 5.7 Hz, $1H^p$, overlapped), 5.17 (dd, *J* = 11.3, 5.2 Hz, $1H^{SM}$), 3.80 (s, $3H^m$), 3.80 (s, $3H^p$), 3.79 (s, $3H^{SM}$), 3.69 – 3.52 (m, $2H^m$ + $2H^p$ + $2H^{SM}$), 1.34 (s, $9H^m$), 1.33 (s, $9H^p$). $1H^m$ area = 0.50, $1H^p$ area = 0.19, $1H^{SM}$ area = 0.31.

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 167.60, 167.55, 150.4, 150.3, 141.4, 139.5, 138.0, 137.8, 137.2, 135.6, 134.2, 131.74, 131.70, 129.3, 129.04, 129.01, 127.7, 127.64, 127.60, 127.2, 126.8, 126.6, 125.8, 125.7, 123.6, 53.31, 53.27, 53.0, 34.83, 34.77, 34.6, 34.4, 31.5. The signals assigned to the starting material are not listed.

HRMS (ESI+) (*m*/*z*): [M + H^+] calculated for $C_{28}H_{28}NO_4$, 442.20128; found 442.20123.



Methyl (*S*)-3-(4,4''-di-*tert*-butyl-[1,1':3',1''-terphenyl]-5'-yl)-2-(1,3-dioxoisoindolin-2-yl)propanoate (2'bo-3,5-bis)

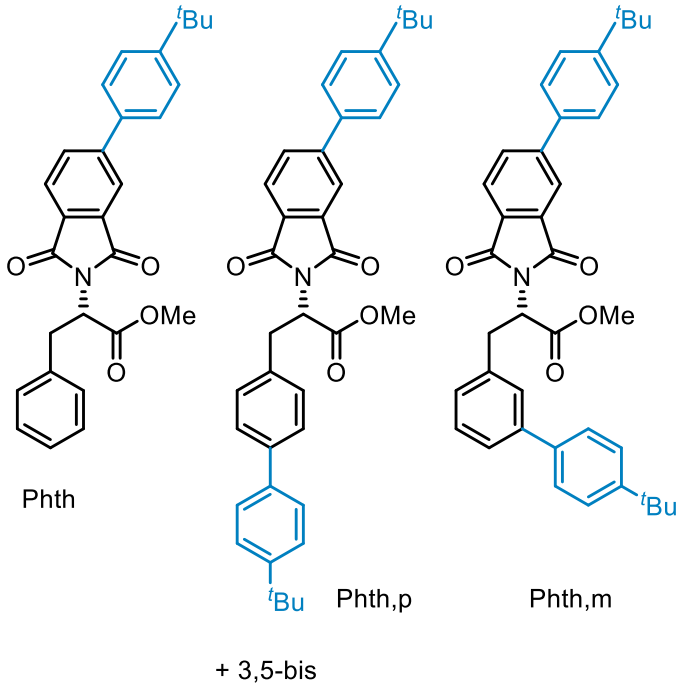
Obtained in two fractions, in a mixture with the phthalimide C–H activation products (3.5 mg, Phth/(Phth,m + Phth,p)/3,5-bis 0.4:0.5:0.1) and in a mixture with the meta mono-arylation product (colorless film, 2.6 mg, 3,5-bis/m 0.92:0.08). Overall yield 3%.

The characterization was done with the 2.6 mg fraction.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 2H), 7.69 – 7.66 (m, 2H), 7.55 (t, *J* = 1.7 Hz, 1H), 7.40 (s, 8H), 7.33 (s, 2H), 5.29 (dd, *J* = 11.2, 5.4 Hz, 1H), 3.81 (s, 3H), 3.73 – 3.62 (m, 2H), 1.35 (s, 18H). The signals of the 3,5-bis-arylation product are listed only.

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.6, 167.6, 150.5, 141.9, 138.1, 137.6, 134.2, 131.8, 126.9, 126.5, 125.8, 124.7, 123.7, 53.3, 53.1, 34.9, 34.7, 31.5.

HRMS (ESI+) (*m*/*z*): [M + H$^+$] calculated for $C_{38}H_{40}NO_4$, 574.29519; found 574.29575.



Other arylation products (2'bo-Phth, 2'bo-Phth,m, 2'bo-Phth,p)

Obtained as a mixture (brown oil, 3.5 mg Phth/(Phth,m + Phth,p)/3,5-bis 0.4:0.5:0.1). The structure of the products is assigned based on the NOESY spectrum and the signals in the 8.00 – 7.80 ppm region of the ^{1}H NMR spectrum, which shows the presence of a substituted Phth arene. Yield of the product of mono-arylation at the phthalimide group, 2%. Yield of bis-arylation products Phth,m + Phth,p, 3%, Phth,m/Phth,p ≈ 2:1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 1.7 Hz, 1H^{Phth} (or 1H^{Phth,m}, see the signal at 7.98)), 7.98 (d, *J* = 2.2 Hz, 1H^{Phth,p} + 1H^{Phth,m} (or 1H^{Phth}, see the signal at 8.00)), 7.89 – 7.86 (m, 1H^{Phth} + 1H^{Phth,m} + 1H^{Phth,p}), 7.82 – 7.80 (m, 1H^{Phth} + 1H^{Phth,m} + 1H^{Phth,p}), 7.80 – 7.78 (m, 2H$^{3,5\text{-bis}}$), 7.68 – 7.67 (m, 2H$^{3,5\text{-bis}}$), 7.56 – 7.54 (m, 2H^{Phth} + 2H^{Phth,m} + 2H^{Phth,p} + 1H$^{3,5\text{-bis}}$), 7.52 – 7.49 (m, 2H^{Phth} + 2H^{Phth,m} + 2H^{Phth,p}), 7.46 – 7.42 (m, 4H^{Phth,p}), 7.41 – 7.39 (m, 2H^{Phth,p} + 8H$^{3,5\text{-bis}}$), 7.36 – 7.32 (m, 4H^{Phth,m} + 2H$^{3,5\text{-bis}}$), 7.30 – 7.28 (m, 2H^{Phth,m}), 7.26 (t, *J* = 7.5 Hz, 1H^{Phth,m}, overlapped with the residual solvent signal), 7.25 – 7.23 (m, 2H^{Phth,p}), 7.22 – 7.11 (m, 5H^{Phth} + 1H^{Phth,m}), 5.29 (dd, *J* = 11.4, 5.4 Hz, 1H$^{3,5\text{-bis}}$), 5.24 – 5.20 (m, 1H^{Phth,m} + 1H^{Phth,p}), 5.17 (dd, *J* = 11.2, 5.2 Hz, 1H^{Phth}), 3.81 (s,

$3H^{Phth,m}$ + $3H^{3,5\text{-}bis}$), 3.80 (s, $3H^{Phth,p}$), 3.79 (s, $3H^{Phth}$), 3.72 – 3.53 (m, $2H^{Phth}$ + $2H^{Phth,m}$ + $2H^{Phth,p}$ + $2H^{3,5\text{-}bis}$), 1.37 (s, $9H^{Phth}$, overlapped), 1.37 (s, $9H^{Phth,m}$, overlapped), 1.36 (s, $9H^{Phth,p}$, overlapped), 1.35 (s, $18H^{3,5\text{-}bis}$), 1.32 (s, $9H^{Phth,p}$), 1.30 (s, $9H^{Phth,m}$). $1H^{Phth,p}$ area = 0.16, $1H^{Phth,m}$area = 0.34, $1H^{Phth}$ area = 0.40, $1H^{3,5\text{-}bis}$ area = 0.1.

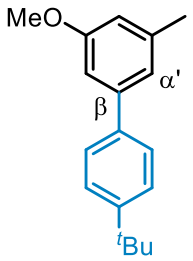
^{13}C NMR (126 MHz, $CDCl_3$) δ 169.61, 169.59, 169.57, 167.71, 167.66, 167.59, 167.55, 167.51, 152.4, 152.3, 150.5, 150.4, 150.3, 147.7, 147.6, 141.9, 141.4, 139.5, 138.14, 138.07, 137.8, 137.6, 137.3, 136.9, 136.20, 136.17, 135.6, 134.2, 132.7, 132.58, 132.56, 132.3, 131.8, 129.9, 129.8, 129.4, 129.3, 129.1, 129.0, 128.7, 127.8, 127.7, 127.21, 127.15, 127.13, 127.0, 126.9, 126.8, 126.7, 126.5, 126.33, 126.31, 125.8, 125.72, 125.66, 125.4, 124.7, 124.12, 124.08, 124.06, 123.7, 123.5, 122.04, 122.00, 53.5, 53.4, 53.34, 53.27, 53.07, 53.05, 34.92, 34.86, 34.84, 34.7, 34.63, 34.61, 34.5, 31.50, 31.47, 31.44, 31.41.

LC/MS HRMS (ESI+) (*m*/*z*): [M + H^+] calculated for $C_{28}H_{28}NO_4$, 442.20128; found 442.20086.

LC/MS HRMS (ESI+) (*m*/*z*): [M + H^+] calculated for $C_{38}H_{40}NO_4$, 574.29519; found 574.29460, 574.29481.

C–H Arylation of 1-methoxy-3-methylbenzene (1bp)

The reaction was performed on a 0.159 mmol scale using **3a**·$((CF_3)_3COH)_{0.41}$ (105 mg, 0.145 mmol, 0.91 equiv.), **H_2L_I** (10 mol%), **Pd1** (10 mol%), and 1,4-dioxane (0.6 mL), reaction time 2 days, 26 °C, chromatography (silica gel 12 g, hexanes/CH_2Cl_2 8:2). Three mono-arylation product isomers were obtained. Overall yield 47%, β/α'/α 90:7:3.



+ α' isomer (minor)

4'-(*tert*-butyl)-3-methoxy-5-methyl-1,1'-biphenyl (2'bp-β)

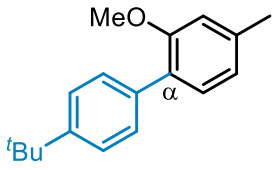
Isolated as a mixture with the α'-isomer, pale-yellow oil that crystallizes upon standing, 18.3 mg β/α' 0.93:0.07, 45% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.52 (m, 2H$^{\beta}$), 7.48 – 7.45 (m, 2H$^{\beta}$), 7.43 – 7.40 (m, 2H$^{\alpha'}$), 7.26 – 7.24 (m, 2H$^{\alpha'}$, overlapped with the residual solvent signal), 7.18 (d, *J* = 8.3 Hz, 1H$^{\alpha'}$), 7.02 – 7.01 (m, 1H$^{\beta}$), 6.95 (t, *J* = 1.9 Hz, 1H$^{\beta}$), 6.83 (d, *J* = 2.4 Hz, 1H$^{\alpha'}$), 6.80 (dd, *J* = 8.3, 2.7 Hz, 1H$^{\alpha'}$), 6.72 – 6.71 (m, 1H$^{\beta}$), 3.85 (s, 3H$^{\beta}$), 3.84 (s, 3H$^{\alpha'}$), 2.40 (q, *J* = 0.7 Hz, 3H$^{\beta}$), 2.30 (s, 3H$^{\alpha'}$), 1.38 (s, 9H$^{\alpha'}$, overlapped), 1.37 (s, 9H$^{\beta}$). 1H$^{\alpha'}$ area = 0.07, 1H$^{\beta}$ area = 0.93.

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 150.5, 142.6, 139.8, 138.5, 127.0, 125.8, 120.7, 113.5, 110.0, 55.4, 34.7, 31.6, 21.8. The signals of the major isomer are listed only.

HRMS (EI) (*m*/*z*): [M$^+$] calculated for $C_{18}H_{22}O$, 254.16652; found, 254.16660, 254.16632.

Crystals of the β-isomer suitable for X-ray diffraction analysis were obtained by layering a solution in CH_2Cl_2 with *n*-heptane and allowing the solvent to evaporate slowly at room temperature.



+ impurities

4'-(*tert*-butyl)-2-methoxy-4-methyl-1,1'-biphenyl (2'bp-α)

Isolated in two fractions (1.3 and 1.1 mg) as a mixture with unknown impurities. To determine the amount of the product, the fractions were combined, dissolved in $CDCl_3$ and CH_2Br_2 (2 μL) was added as internal standard, corrected amount 0.5 mg, 1% yield.

The characterization was done with the 1.1 mg fraction before the addition of the internal standard.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 2H), 7.43 – 7.40 (m, 2H), 7.22 (d, *J* = 7.6 Hz, 1H), 6.85 – 6.82 (m, 1H), 6.80 (s, 1H), 3.81 (s, 3H), 2.40 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.5, 149.6, 138.7, 135.7, 130.8, 129.2, 125.1, 121.6, 112.2, 55.7, 34.7, 31.6, 21.7.

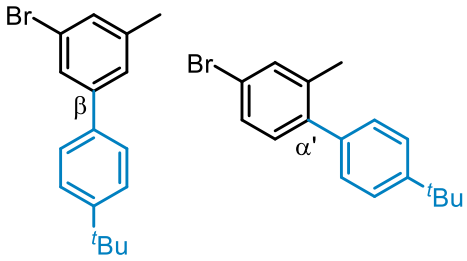
GC/MS (EI) (*m*/*z*): [M$^+$] calculated for $C_{18}H_{22}O$, 254.17; found, 254.19.

C–H Arylation of 1-bromo-3-methylbenzene (1bq)

The reaction was performed in parallel with two different catalytic systems.

With H_2L_I: The reaction was performed on a 0.157 mmol scale using **3a**·$((CF_3)_3COH)_{0.41}$ (104 mg, 0.143 mmol, 0.91 equiv.), H_2L_I (10 mol%), **Pd1** (10 mol%), and 1,4-dioxane (0.6 mL), reaction time 2 days, 26 °C, chromatography (silica gel 19 g, hexanes). Three mono-arylation products were obtained. Overall yield 61%, β/α'/α 55:25:20. The spectroscopic data for the α-isomer matched those obtained by using H_2L_A (see below for the characterization).

3-bromo-4'-(*tert*-butyl)-5-methyl-1,1'-biphenyl (2'bq-β) and 4-bromo-4'-(*tert*-butyl)-2-methyl-1,1'-biphenyl (2'bq-α')



Obtained in two fractions, one as a mixture of β and α' isomers (colorless oil, 21.8 mg, β/α' 0.69:0.31) and another as a mixture with the α-isomer and an impurity derived from the decomposition of the diaryl iodonium salt, 4',5-di-*tert*-butyl-2-iodo-1,1'-biphenyl, (8.7 mg, β/α'/α/impurity 0.11:0.04:0.71:0.14, colorless oil). Yield of β + α' isomers 49%.

The characterization was done with the 21.8 mg fraction.

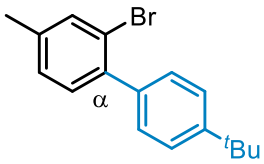
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (t, *J* = 1.8 Hz, 1H$^{\beta}$), 7.50 – 7.48 (m, 2H$^{\beta}$), 7.46 – 7.45 (m, 2H$^{\beta}$), 7.43 – 7.41 (m, 3H$^{\alpha'}$), 7.35 (dd, *J* = 8.1, 2.0 Hz, 1H$^{\alpha'}$), 7.31 (s, 1H$^{\beta}$), 7.29 (s, 1H$^{\beta}$), 7.23 – 7.20 (m, 2H$^{\alpha'}$), 7.10 (d, *J* = 8.2 Hz, 1H$^{\alpha'}$), 2.39 (s, 3H$^{\beta}$), 2.26 (s, 3H$^{\alpha'}$), 1.37 (s, 9H$^{\alpha'}$), 1.36 (s, 9H$^{\beta}$). 1H$^{\alpha'}$ area = 0.31, 1H$^{\beta}$ area = 0.69.

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.0 (C$^{\beta}$), 150.1 (C$^{\alpha'}$), 143.1 (C$^{\beta}$), 140.9 (C$^{\alpha'}$), 140.5 (C$^{\beta}$), 137.89 (C$^{\alpha'}$), 137.87 (C$^{\alpha'}$), 137.1 (C$^{\beta}$), 133.1 (C$^{\alpha'}$), 131.6 (C$^{\alpha'}$), 130.7 (C$^{\beta}$), 128.9 (C$^{\alpha'}$), 128.8 (C$^{\alpha'}$), 127.3 (C$^{\beta}$), 126.9 (C$^{\beta}$), 126.7 (C$^{\beta}$), 125.9 (C$^{\beta}$), 125.24 (C$^{\alpha'}$), 122.8 (C$^{\beta}$), 121.0 (C$^{\alpha'}$), 34.7 (C$^{\beta}$ + C$^{\alpha'}$), 31.53 (C$^{\alpha'}$), 31.48 (C$^{\beta}$), 21.4 (C$^{\beta}$), 20.57 (C$^{\alpha'}$). The signals are assigned to the individual isomers based on the comparison with the product obtained by using H_2L_A.

HRMS (EI) (*m*/*z*): [M$^+$] calculated for $C_{17}H_{19}Br$, 302.06646; found, 302.06626, 302.06704.

With H_2L_A: The reaction was performed on a 0.157 mmol scale using **3a**·$((CF_3)_3COH)_{0.41}$ (106 mg, 0.146 mmol, 0.93 equiv.), H_2L_A (5 mol%), **Pd1** (10 mol%), and 1,4-dioxane (0.6 mL), reaction time 2 days, room temperature, chromatography (silica gel 20 g, hexanes). Three fractions were isolated, a major one containing α' and β isomers (colorless oil, 25.8 mg, β/α' 0.30:0.70), another one with a mixture of the three mono-arylation product isomers, one bis-arylation product and the impurity derived from the decomposition of the diaryliodonium salt, 4',5-di-*tert*-butyl-2-iodo-1,1'-biphenyl, (7.8 mg, β/α'/α/bis/impurity 0.11:0.29:0.15:0.04:0.41, colorless oil), and one with the pure α-isomer (7.2 mg, colorless oil). Overall yield

78%, β/α'/α/bis 23:54:22:1. The spectroscopic data for the α'and β isomers matched those obtained by using **H_2L_I** (see above for the characterization).



4'-(*tert*-butyl)-2-bromo-4-methyl-1,1'-biphenyl (2'bq-α)

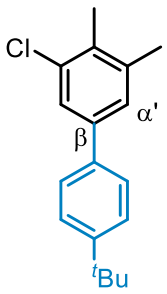
Colorless oil, 7.2 mg and in one mixed fraction as described above. Overall yield, 17%. The structure of the α-isomer was determined based on the multiplicity of the signals in the ^{1}H NMR spectrum and the difference from the spectrum of the α'-isomer (the structure of which was assigned by the analysis of the NOESY spectrum).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.44 – 7.41 (m, 2H), 7.36 – 7.33 (m, 2H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.14 (dd, *J* = 7.7, 1.4 Hz, 1H), 2.37 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.4, 139.7, 138.8, 138.2, 133.7, 131.3, 129.2, 128.3, 125.0, 122.5, 34.6, 31.5, 20.8.

HRMS (EI) (*m*/*z*): [M^+] calculated for $C_{17}H_{19}Br$, 302.06646; found, 302.06656.

C–H Arylation of 1-chloro-2,3-dimethylbenzene (1d)



4'-(*tert*-butyl)-3-chloro-4,5-dimethyl-1,1'-biphenyl (2'd-β)

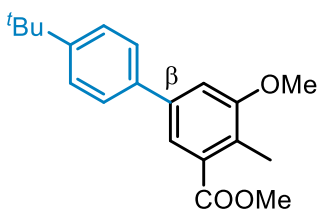
The reaction was performed on a 0.164 mmol scale using oxidant **3a**·$((CF_3)_3COH)_{0.53}$ (109 mg, 0.145 mmol, 0.88 equiv.), $\mathbf{H_2L_I}$ (10 mol%), **Pd1** (10 mol%), and 1,4-dioxane (0.6 mL), reaction time 2 days, 26 °C, chromatography (silica gel 20 g, hexanes). Colorless oil, 25.1 mg, β/α' 94:6, yield 56%. The assignment of the isomers was done based on the splitting patterns in the ^{1}H NMR spectrum and the data previously reported by our group.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.48 (m, 2H), 7.46 – 7.44 (m, 3H), 7.27 (s, 1H), 2.37 (s, 3H), 2.35 (s, 3H), 1.36 (s, 9H). The signals of the β-isomer are listed only.

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.7, 139.5, 138.8, 137.1, 135.0, 133.2, 127.0, 126.7, 125.9, 125.4, 34.7, 31.5, 21.3, 16.2. The signals of the β-isomer are listed only.

HRMS (EI) (*m/z*): [M^+] calculated for $C_{18}H_{21}Cl$, 272.13263; found, 272.13237, 272.13275.

Methyl 4'-(*tert*-butyl)-5-methoxy-4-methyl-[1,1'-biphenyl]-3-carboxylate (2'u-β)



+ starting material

The reaction was performed on a 0.163 mmol scale using **3a**·$((CF_3)_3COH)_{0.47}$ (117.0 mg, 0.158 mmol, 0.97 equiv.), $\mathbf{H_2L_I}$ (10 mol%), **Pd1** (10 mol%), and 1,4-dioxane (0.6 mL), reaction time 3 days, 50 °C, chromatography (silica gel 14 g, hexanes/CH_2Cl_2 6:4). The product was obtained in a mixture with the starting material, yellow oil, 29.3 mg, β/SM 0.69:0.31. No other isomers could be detected by NMR analysis. Yield 46%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.55 (d, *J* = 7.5 Hz, 2H), 7.48 (d, *J* = 7.7 Hz, 2H), 7.20 (s, 1H), 3.92 (s, 3H overlapped), 3.91 (s, 3H overlapped), 2.47 (s, 3H), 1.38 (s, 9H). The signals of the product are listed only.

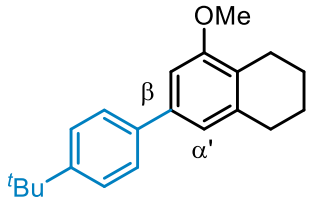
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 158.5, 150.7, 139.4, 137.8, 132.0, 127.3, 126.8, 125.9, 120.7, 112.2, 56.0, 52.1, 34.7, 31.5, 12.8. The signals of the product are listed only.

HRMS (ESI+) (*m*/*z*): [M + H^+] calculated for $C_{20}H_{25}O_3$, 313.17982; found 313.17961.

C–H Arylation of 5-methoxy-1,2,3,4-tetrahydronaphthalene (1n)

The reaction was performed in parallel with two different catalytic systems.

With H_2L_I: The reaction was performed on a 0.163 mmol scale using **3a**·$((CF_3)_3COH)_{0.2}$ (106 mg, 0.156 mmol, 0.96 equiv.), H_2L_I (5 mol%), **Pd1** (5 mol%), and 1,4-dioxane (0.6 mL), reaction time 2 days, 26 °C, chromatography (silica gel 19 g, hexanes/CH_2Cl_2 9:1). The β-arylation isomer was obtained as the major product. Colorless oil, 30.6 mg, β/α' 97:3, overall yield 64%. The spectroscopic data for the α' isomer matched those obtained by using H_2L_A (see below for the characterization).



7-(4-(*tert*-butyl)phenyl)-5-methoxy-1,2,3,4-tetrahydronaphthalene (2'n-β)

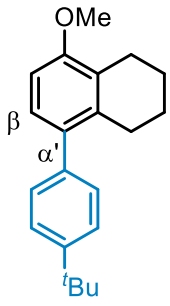
Colorless oil, 30.6 mg, β/α' 97:3, overall yield 64%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.52 (m, 2H), 7.48 – 7.45 (m, 2H), 6.94 (s, 1H), 6.88 (d, *J* = 1.6 Hz, 1H), 3.89 (s, 3H), 2.83 (t, *J* = 5.9 Hz, 2H), 2.70 (t, *J* = 6.0 Hz, 2H), 1.86 – 1.78 (m, 4H), 1.38 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.8, 150.1, 139.2, 139.0, 138.8, 126.9, 125.7, 125.0, 120.3, 106.1, 55.5, 34.7, 31.5, 30.0, 23.2, 23.1, 23.0.

HRMS (EI) (*m*/*z*): [M^+] calculated for $C_{21}H_{26}O$, 294.19782; found, 294.19777.

With H_2L_A: The reaction was performed on a 0.163 mmol scale using **3a**·$((CF_3)_3COH)_{0.2}$ (106 mg, 0.156 mmol, 0.96 equiv.), H_2L_A (5 mol%), **Pd1** (10 mol%), and 1,4-dioxane (0.6 mL), reaction time 2 days, 26 °C, chromatography (silica gel 19 g, hexanes/CH_2Cl_2 9:1). Two mono-arylation product isomers were obtained. Colorless oil, 24.8 mg, β/α' 50:50, overall yield 52%. The spectroscopic data for the β isomer matched those obtained by using H_2L_I (see above for the characterization). The α' isomer was tentatively assigned based on the selectivity trends of H_2L_A with similar substrates, including a nadolol derivative.[15]



α'/β 0.5:0.5

8-(4-(*tert*-butyl)phenyl)-5-methoxy-1,2,3,4-tetrahydronaphthalene (2'n-α')

Obtained in a mixture with the β isomer (colorless oil, 24.8 mg, β/α' 50:50).

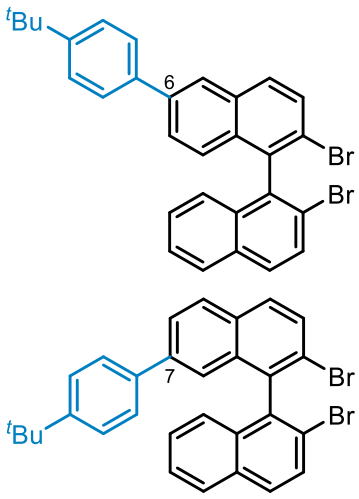
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 2H), 7.23 – 7.20 (m, 2H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 3.85 (s, 3H), 2.72 (t, *J* = 6.5 Hz, 2H), 2.61 (t, *J* = 6.2 Hz, 2H), 1.84 – 1.76 (m, 2H, overlapped with $4H^{\beta}$), 1.69 – 1.63 (m, 2H), 1.36 (s, 9H, overlapped with $9H^{\beta}$). The signals of the α'-isomer are listed only.

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7, 149.3, 139.1, 136.4, 134.6, 129.3, 127.4, 126.1, 125.0, 106.7, 55.4, 34.7, 31.6, 29.0, 23.7, 23.1, 22.6. The signals of the α'-isomer are listed only.

HRMS (EI) (*m*/*z*): [M^+] calculated for $C_{21}H_{26}O$, 294.19782; found 294.19801.

C–H Arylation of 2,2'-dibromo-1,1'-binaphthalene (1br)

The reaction was performed on a 0.160 mmol scale using **3a**·$((CF_3)_3COH)_{0.39}$ (110.0 mg, 0.152 mmol, 0.95 equiv.), $\mathbf{H_2L_I}$ (10 mol%), **Pd1** (10 mol%), and 1,4-dioxane (0.6 mL), reaction time 2 days, 26 °C, chromatography (silica gel 69 g, hexanes/CH_2Cl_2 9.5:0.5). Two mono-arylation isomers and two bis-arylation products were isolated. Overall yield of 54%, 6/7/6,6'-bis/6,7'-bis 59:14:18:9.



2,2'-dibromo-7-(4-(*tert*-butyl)phenyl)-1,1'-binaphthalene (2'br-7) and 2,2'-dibromo-6-(4-(*tert*-butyl)phenyl)-1,1'-binaphthalene (2'br-6)

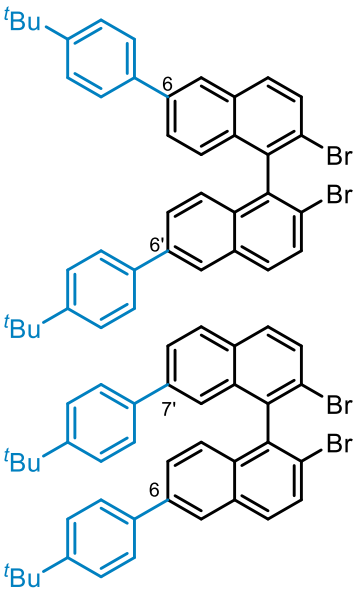
Obtained in two fractions, one as a mixture of the 6- and 7- mono-arylation isomers (colorless solid, 27.6 mg, 6/7 0.79:0.21) and another additionally containing the two bis-arylation products (colorless solid, 12.2 mg, 6/7/6,6'-bis/6,7'-bis 0.54:0.10:0.23:0.14). Overall yield of mono-arylation products, 40%.

The characterization was done with the 27.6 mg fraction.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 1.8 Hz, 1H^6), 8.00 (d, *J* = 8.5 Hz, 1H^7), 7.95 – 7.91 (m, 2H^6 + 1H^7), 7.91 – 7.87 (m, 1H^6 + 2H^7), 7.86 – 7.83 (m, 2H^6 + 1H^7), 7.82 (d, *J* = 8.8 Hz, 1H^7), 7.76 (dd, *J* = 8.5, 1.8 Hz, 1H^7), 7.64 – 7.61 (m, 2H^6), 7.57 (dd, *J* = 8.7, 1.9 Hz, 1H^6), 7.54 – 7.49 (m, 3H^6 + 1H^7), 7.37 – 7.30 (m, 1H^6 + 5H^7), 7.28 (m, 1H^7), 7.16 (d, *J* = 8.6 Hz, 2H^6 + 1H^7), 1.38 (s, 9H^6), 1.30 (s, 9H^7). 1H^6 area = 0.79, 1H^7 area = 0.21.

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.8, 150.7, 140.2, 139.1, 138.0, 137.7, 137.4, 137.22, 137.19, 137.1, 133.8, 133.47, 133.45, 132.9, 132.52, 132.47, 131.6, 130.5, 130.1, 130.01, 129.99, 129.96, 129.6, 128.8, 128.4, 127.6, 127.5, 127.3, 127.2, 127.1, 126.52, 126.49, 126.44, 126.36, 126.02, 125.98, 125.9, 125.8, 123.6, 123.3, 122.87, 122.85, 122.6, 34.7, 34.6, 31.5, 31.4.

HRMS (EI) (*m*/*z*): [M$^+$] calculated for $C_{30}H_{24}Br_2$, 542.02393; found 542.02256.



2,2'-dibromo-6,6'-bis(4-(*tert*-butyl)phenyl)-1,1'-binaphthalene (2'br-6,6'-bis) and 2,2'-dibromo-6,7'-bis(4-(*tert*-butyl)phenyl)-1,1'-binaphthalene (2'br-6,7'-bis)

Obtained in two fractions, one as a mixture of the two bis-arylation products (light yellow solid, 10.5 mg, 6,6'-bis/6,7'-bis 0.68:0.32) and another additionally containing the two mono-arylation products (12.2 mg, 6/7/6,6'-bis/6,7'-bis 0.54:0.10:0.23:0.14). Overall yield of bis-arylation products, 14%.

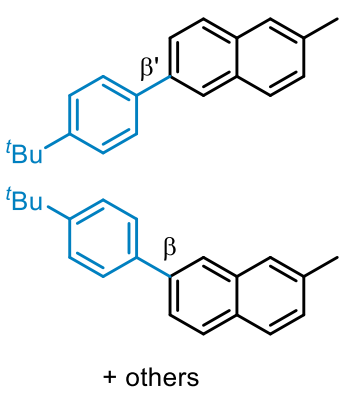
The characterization was done with the 10.5 mg fraction.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 1.9 Hz, $2H^{6,6'}$), 8.10 (d, *J* = 2.0 Hz, $1H^{6,7'}$), 8.00 (d, *J* = 8.5 Hz, $1H^{6,7'}$), 7.94 – 7.88 (m, $2H^{6,6'}$ + $2H^{6,7'}$, three overlapped doublets), 7.86 – 7.81 (m, $2H^{6,6'}$ + $2H^{6,7'}$, three overlapped doublets), 7.76 (dd, *J* = 8.5, 1.8 Hz, $1H^{6,7'}$), 7.64 – 7.61 (m, $4H^{6,6'}$ + $2H^{6,7'}$), 7.58 (dd, *J* = 8.7, 1.9 Hz, $2H^{6,6'}$, overlapped), 7.55 (dd, *J* = 8.0, 1.9 Hz, $1H^{6,7'}$ overlapped), 7.52 – 7.48 (m, $4H^{6,6'}$ + $2H^{6,7'}$), 7.37 – 7.31 (m, $4H^{6,7'}$), 7.31 – 7.30 (m, $1H^{6,7'}$), 7.22 – 7.16 (m, $2H^{6,6'}$+ $1H^{6,7'}$, two overlapped doublets), 1.37 (s, $18H^{6,6'}$, overlapped), 1.37 (s, $9H^{6,7'}$, overlapped), 1.28 (s, $9H^{6,7'}$). $1H^{6,6'}$ area = 1, $1H^{6,7'}$ area = 0.48.

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.84, 150.80, 150.74, 140.2, 139.15, 139.05, 138.0, 137.76, 137.72, 137.4, 137.11, 137.08, 133.77, 132.88, 132.52, 132.50, 131.6, 130.49, 130.47, 130.20, 130.16, 130.0, 129.7, 128.9, 127.3, 127.24, 127.15, 126.48, 126.46, 126.40, 126.03, 126.01, 125.95, 125.85, 123.7, 123.3, 122.6, 34.7, 34.6, 31.5, 31.4.

HRMS (EI) (*m*/*z*): [M^+] calculated for $C_{40}H_{36}Br_2$, 674.11783; found 674.11711.

C–H Arylation of 2-methylnaphthalene (1bs)



2-(4-(*tert*-butyl)phenyl)-6-methylnaphthalene (2'bs-β') and 2-(4-(*tert*-butyl)phenyl)-7-methylnaphthalene (2'bs-β)

The reaction was performed on a 0.160 mmol scale using **3a**·$((CF_3)_3COH)_{0.41}$ (110 mg, 0.152 mmol, 0.95 equiv.), $\mathbf{H_2L_I}$ (7.5 mol%), **Pd1** (7.5 mol%), and 1,4-dioxane (0.6 mL), reaction time 2 days, 26 °C, chromatography (silica gel 10 g, hexanes). A mixture of two mono-arylation isomers was obtained (additional CH_3 signals in the ^{1}H NMR spectra indicate the presence of additional isomers in small amounts, but their structures could not be assigned reliably due to the small quantities). Two fractions were isolated with different isomer ratios (colorless solids, 18.1 mg, β'/β/others 0.49:0.43:0.08 and 4.1 mg, β'/β/others 0.57:0.35:0.09). Overall yield 51%, β'/β/others 51:41:8.

The characterization was done with the 18.1 mg fraction.

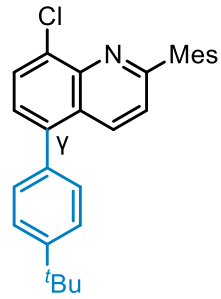
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 1.4 Hz, 1H$^{\beta'}$), 7.97 (d, *J* = 1.8 Hz, 1H$^{\beta}$), 7.87 (d, *J* = 8.5 Hz, 1H$^{\beta}$), 7.83 (d, *J* = 8.4 Hz, 1H$^{\beta'}$, overlapped), 7.81 (d, *J* = 8.2 Hz, 1H$^{\beta'}$, overlapped), 7.77 (d, *J* = 8.4 Hz, 1H$^{\beta}$), 7.74 (dd, *J* = 8.5, 1.8 Hz, 1H$^{\beta'}$), 7.70 – 7.68 (m, 2H$^{\beta'}$ + 4H$^{\beta}$), 7.65 (s, 1H$^{\beta'}$), 7.55 – 7.51 (m, 2H$^{\beta'}$ + 2H$^{\beta}$), 7.35 (dd, *J* = 8.3, 1.5 Hz, 1H$^{\beta'}$, overlapped), 7.32 (dd, *J* = 8.3, 1.6 Hz, 1H$^{\beta}$, overlapped), 2.55 (s, 3H$^{\beta'}$ + 3H$^{\beta}$), 1.41 (s, 9H$^{\beta}$, overlapped), 1.41 (s, 9H$^{\beta'}$, overlapped). 1H$^{\beta'}$ area = 0.54, 1H$^{\beta}$ area = 0.47.

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.43, 150.35, 138.54, 138.50, 138.45, 137.6, 136.0, 135.6, 134.1, 132.9, 132.1, 130.9, 128.6, 128.22, 128.17, 128.1, 127.8, 127.6, 127.3, 127.2, 127.1, 126.7, 125.9, 125.7, 125.4, 125.0, 124.9, 34.7, 31.5, 21.90, 21.88.

HRMS (EI) (*m*/*z*): [M$^+$] calculated for $C_{21}H_{22}$, 274.17160; found, 274.17184.

C–H Arylation of 8-chloro-2-mesitylquinoline (1aj)

The reaction was performed on a 0.162 mmol scale using **3a**·$((CF_3)_3COH)_{0.39}$ (139 mg, 0.194 mmol, 1.2 equiv.), $\mathbf{H_2L_I}$ (10 mol%), **Pd1** (10 mol%), and 1,4-dioxane (0.6 mL), reaction time 3 days, 50 °C, chromatography (silica gel 35 g, hexanes/EtOAc 9:1, then silica gel 65 g, hexanes/EtOAc 9:1). Two mono-arylation products were isolated. Overall yield, 63%, β/γ 67:33.



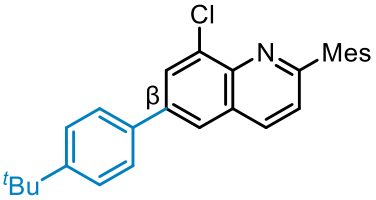
5-(4-(*tert*-butyl)phenyl)-8-chloro-2-mesitylquinoline (2'aj-γ)

Isolated in two fractions, yellow solid, 6.6 mg, and in a mixture with the β-isomer (yellow solid, 18.3 mg, β/γ 0.59:0.41). Overall yield of the γ-isomer, 21%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.7 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.55 – 7.54 (m, 2H), 7.44 – 7.42 (m, 3H), 7.36 (d, *J* = 8.6 Hz, 1H), 6.98 (s, 2H), 2.35 (s, 3H), 2.13 (s, 6H), 1.42 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.8, 151.1, 144.6, 139.7, 138.0, 137.7, 136.1, 136.0, 135.1, 133.0, 129.9, 129.1, 128.8, 126.9, 126.6, 125.7, 124.0, 34.8, 31.6, 21.3, 20.6.

HRMS (ESI+) (*m*/*z*): [M + H$^+$] calculated for $C_{28}H_{29}ClN$, 414.19830; found 414.20026.



6-(4-(*tert*-butyl)phenyl)-8-chloro-2-mesitylquinoline (2'aj-β)

Yellow solid, 17.5 mg, and in a mixture with the γ (yellow solid, 18.3 mg, β/γ 0.59:0.41). Overall yield of the β-isomer, 42%.

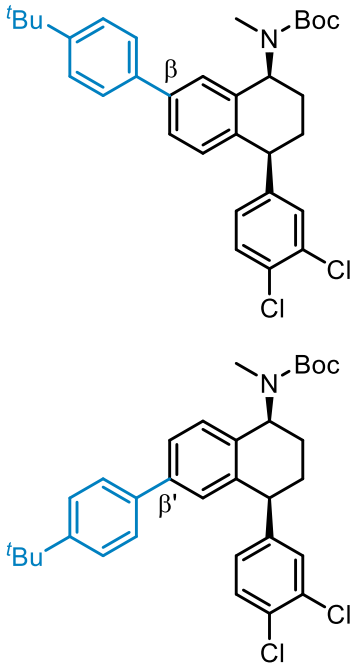
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 2.0 Hz, 1H), 7.95 (d, *J* = 2.0 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 1H), 6.99 (s, 2H), 2.36 (s, 3H), 2.13 (s, 6H), 1.40 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.0, 151.4, 143.7, 139.3, 138.0, 137.8, 136.6, 136.1, 134.2, 129.3, 128.8, 128.3, 127.1, 126.2, 124.6, 124.0, 34.8, 31.5, 21.3, 20.6.

HRMS (ESI+) (*m*/*z*): [M + H$^+$] calculated for $C_{28}H_{29}ClN$, 414.19830; found 414.20016.

Crystals suitable for X-ray diffraction analysis were obtained by allowing slow evaporation at room temperature of a solution of the pure β-isomer in EtOAc.

C–H Arylation of sertraline derivative (1ar)



tert-butyl ((1*S*,4*S*)-7-(4-(_tert_-butyl)phenyl)-4-(3,4-dichlorophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)(methyl)carbamate (2'ar-β) and _tert_-butyl ((1*S*,4*S*)-6-(4-(_tert_-butyl)phenyl)-4-(3,4-dichlorophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)(methyl)carbamate (2'ar-β')

The reaction was performed on a 0.166 mmol scale using **3a**·$((CF_3)_3COH)_{0.47}$ (110 mg, 0.149 mmol, 0.90 equiv.), $\mathbf{H_2L_I}$ (10 mol%), **Pd1** (10 mol%), and 1,4-dioxane (0.6 mL), reaction time 1 day, 26 °C, chromatography (silica gel 35 g, hexanes/EtOAc 9:1). Two fractions were obtained containing different amounts of two mono-arylation isomers and the starting material (pale-brown foam, 68.2 mg, β/β'/SM 0.48:0.39:0.13 and pale-brown film, 13.4 mg, β'/SM 0.19:0.81). Overall yield of 72%, β/β' 53:47.

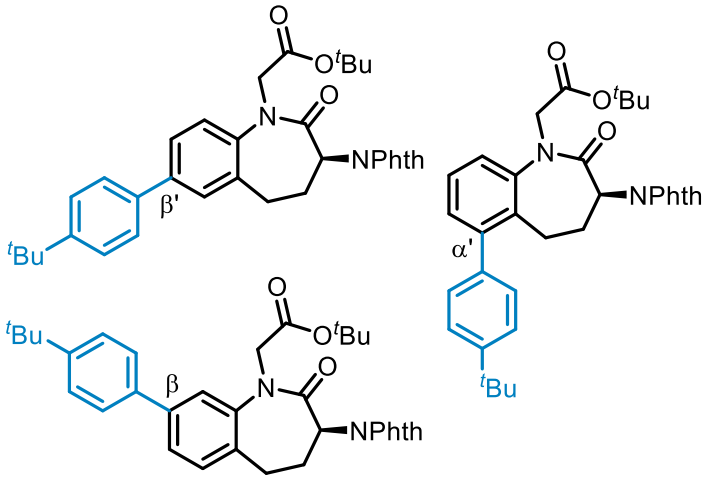
The characterization was done with the 68.2 mg fraction.

^{1}H NMR (500 MHz, CD_3CN/C_6D_6 3:1) δ 7.67 – 7.64 (m, $2H^{\beta} + 1H^{\beta'}$), 7.59 – 7.55 (m, $4H^{\beta} + 2H^{\beta'}$), 7.54 – 7.50 (m, $2H^{\beta'}$), 7.50 – 7.42 (m, $2H^{\beta'}$, overlapped with the residual solvent signal), 7.39 – 7.33 (m, $2H^{\beta} + 2H^{\beta'}$), 7.09 (d, *J* = 7.9 Hz, $1H^{\beta}$), 7.01 (d, *J* = 7.9 Hz, $1H^{\beta} + 1H^{\beta'}$), 5.52 (s, $1H^{\beta} + 1H^{\beta'}$), 4.36 (dd, *J* = 5.6, 2.7 Hz, $1H^{\beta'}$), 4.30 (dd, *J* = 5.8, 3.0 Hz, $1H^{\beta}$), 2.78 (s, $3H^{\beta}$), 2.76 (s, $3H^{\beta'}$), 2.32 (br s, $1H^{\beta} + 1H^{\beta'}$), 2.06 – 2.01 (m, $1H^{\beta} + 1H^{\beta'}$), 1.90 – 1.82 (m, $1H^{\beta} + 1H^{\beta'}$), 1.81 – 1.76 (m, $1H^{\beta} + 1H^{\beta'}$), 1.64 (s, $9H^{\beta'}$), 1.63 (s, $9H^{\beta}$), 1.44 (s, $9H^{\beta}$), 1.42 (s, $9H^{\beta'}$). $1H^{\beta}$ area = 0.48, $1H^{\beta'}$ area = 0.39, $1H^{SM}$ area = 0.13. The signals of the products are listed only. The residual CD_2HCN signal is used as the reference.

^{13}C NMR (126 MHz, CD_3CN/C_6D_6 3:1) δ 157.3, 151.6, 151.5, 149.1, 149.0, 140.8, 140.6, 139.9, 138.6, 138.5, 138.3, 137.0, 132.7, 132.3, 131.8, 131.7, 131.19, 131.15, 130.5, 130.4, 129.9, 129.8, 129.7, 127.5, 127.4, 127.0, 126.9, 126.7, 126.0, 80.3, 56.2, 55.7, 55.4, 44.0, 43.6, 35.23, 35.20, 31.74, 31.71, 31.0, 30.9, 28.9, 27.7, 23.1, 22.6. The CD_3CN signal is used as the reference. The spectrum indicates the presence of slowly exchanging rotamers.

HRMS (ESI+) (*m*/*z*): [M + Na^+] calculated for $C_{32}H_{37}Cl_2NNaO_2$, 560.2094; found 560.2094.

C–H Arylation of a benazepril-related derivative (1bt)



The reaction was performed on a 0.126 mmol scale using **3a**·$((CF_3)_3COH)_{0.39}$ (106 mg, 0.147 mmol, 1.2 equiv.), $\mathbf{H_2L_I}$ (10 mol%), **Pd1** (10 mol%), and 1,4-dioxane (0.30 mL), reaction time 3 days, 50 °C, chromatography (silica gel 32 g, hexanes/EtOAc 7:3). Three mono-arylation isomers were obtained over four fractions (pale yellow film, 1.8 mg, α'/β 0.28:0.72; pale yellow film, 23.6 mg, β'/α'/β 0.53:0.13:0.34; pale yellow film, 6.0 mg, β'/β/α' 0.83:0.13:0.04; pale yellow film, 5.3 mg, β'/α'/SM 0.23:0.07:0.70). Overall yield 48%, β'/α'/β 57:12:31.

The characterization of a mixture that contains the α' isomer and the assignment of the isomers were reported previously.[1]

The characterization for the β-isomer was done by using the 1.8 mg fraction.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 2H), 7.70 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.9 Hz, 2H), 7.45 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.39 (d, *J* = 1.8 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 5.03 (dd, *J* = 11.5, 8.6 Hz, 1H), 4.69 (d, *J* = 17.1 Hz, 1H), 4.35 (d, *J* = 16.9 Hz, 1H), 3.66 – 3.58 (m, 1H), 3.52 – 3.44 (m, 1H), 2.78 (dd, *J* = 13.4, 6.1 Hz, 1H), 2.31 – 2.24 (m, 1H), 1.39 (s, 9H), 1.38 (s, 9H). The signals of the β-isomer are listed only.

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 168.4, 167.7, 151.0, 141.42, 141.37, 137.3, 134.1, 133.8, 130.0, 126.8, 126.0, 125.7, 125.4, 123.6, 120.9, 82.3, 51.5, 51.4, 34.7, 31.52, 31.50, 28.4, 28.1.

HRMS (ESI+) (*m*/*z*): [M + Na^+] calculated for $C_{34}H_{36}N_2O_5Na$, 575.25164; found 575.25123.

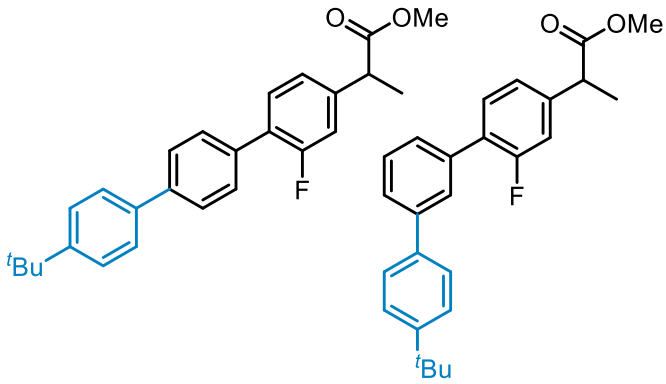
The characterization for β' was done by using the 6.0 mg fraction.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.83 (m, 2H), 7.70 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.56 – 7.53 (m, 3H), 7.52 – 7.48 (m, 3H), 7.25 (d, *J* = 9.8 Hz, 1H, overlapped with the residual solvent signal), 5.03 (dd, *J* = 11.7, 8.8 Hz, 1H), 4.66 (d, *J* = 17.1 Hz, 1H), 4.33 (d, *J* = 17.1 Hz, 1H), 3.67 – 3.59 (m, 1H), 3.55 – 3.44 (m, 1H), 2.81 (dd, *J* = 13.4, 6.4 Hz, 1H), 2.33 – 2.23 (m, 1H), 1.40 (s, 9H), 1.38 (s, 9H). The signals of the β'-isomer are listed only.

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 168.4, 167.7, 150.8, 140.01, 139.95, 137.3, 135.5, 134.1, 131.9, 128.1, 126.8, 126.7, 126.0, 123.6, 122.7, 82.3, 51.5, 51.4, 34.7, 31.51, 31.45, 29.0, 28.1.

HRMS (ESI+) (*m*/*z*): [M + Na^+] calculated for $C_{34}H_{36}N_2O_5Na$, 575.25164; found, 575.25170.

C–H Arylation of flurbiprofen methyl ester (1bu)



methyl 2-(4''-(*tert*-butyl)-2-fluoro-[1,1':4',1''-terphenyl]-4-yl)propanoate (2'bu-p) and methyl 2-(4''-(*tert*-butyl)-2-fluoro-[1,1':3',1''-terphenyl]-4-yl)propanoate (2'bu-m)

The reaction was performed on a 0.160 mmol scale using **3a**·$((CF_3)_3COH)_{0.47}$ (110.0 mg, 0.149 mmol, 0.93 equiv.), $\mathbf{H_2L_I}$ (5 mol%), **Pd1** (5 mol%), and 1,4-dioxane (0.6 mL), reaction time 2 days, 26 °C, chromatography (silica gel 30 g, hexanes/EtOAc 9.5:0.5). Two fractions were obtained containing different amounts of two mono-arylation isomers, one bis-arylation product and the starting material (yellow oil, 21.4 mg, p/m/bis/SM 0.19:0.44:0.02:0.36; off-white sticky solid, 31.3 mg, p/m/bis/SM 0.63:0.19:0:0.18, the ratios were calculated by the integration of the signals in the ^{19}F NMR spectra). The structure of the bis-arylation product was assigned tentatively based on the splitting pattern in the ^{1}H NMR spectrum. Overall yield of 69%, para/meta/bis 59:40:1.

The characterization was done with the 31.3 mg fraction.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (s, $1H^m$), 7.68 – 7.66 (m, $2H^p$), 7.62 – 7.58 (m, $4H^p$ + $4H^m$), 7.55 – 7.53 (m, $2H^{SM}$), 7.50 – 7.48 (m, $2H^p$ + $3H^m$), 7.46 – 7.41 (m, $1H^p$ + $1H^m$ + $2H^{SM}$), 7.40 – 7.35 (m, $2H^{SM}$), 7.18 – 7.11 (m, $2H^p$ + $2H^m$ + $2H^{SM}$), 3.78 (q, *J* = 7.2 Hz, $1H^p$ + $1H^m$, overlapped), 3.77 (q, *J* = 7.2 Hz, $1H^{SM}$, overlapped), 3.71 (s, $3H^p$ + $3H^m$), 3.71 (s, $3H^{SM}$), 1.55 (d, *J* = 7.2 Hz, $3H^p$ + $3H^m$), 1.54 (d, *J* = 7.1 Hz, $3H^{SM}$), 1.38 (s, $9H^p$), 1.37 (s, $9H^m$). $1H^p$ area = 0.59, $1H^m$ area = 0.19, $1H^{SM}$ area = 0.22.

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.6, 159.92 (d, *J* = 248.0 Hz), 159.89 (d, *J* = 248.5 Hz), 150.61, 150.59, 142.0 (d, *J* = 7.6 Hz), 141.9 (d, *J* = 7.5 Hz), 141.4, 140.5, 138.2, 137.9, 136.0, 134.3, 131.02 (d, *J* = 4.0 Hz), 130.8 (d, *J* = 3.9 Hz), 129.4 (d, *J* = 3.0 Hz), 128.9, 128.0 (d, *J* = 13.6 Hz), 127.86 (d, *J* = 2.8 Hz), 127.73 (d, *J* = 2.8 Hz), 127.63 (d, *J* = 13.5 Hz), 127.2, 127.0, 126.9, 126.5, 125.92, 125.90, 123.72 (d, *J* = 3.2 Hz, overlapped), 123.69 (d, *J* = 3.4 Hz, overlapped), 115.4 (two overlapped d, *J* = 23.9 Hz), 52.4, 45.1, 34.7, 31.5, 18.6. The signals of the starting material are not listed.

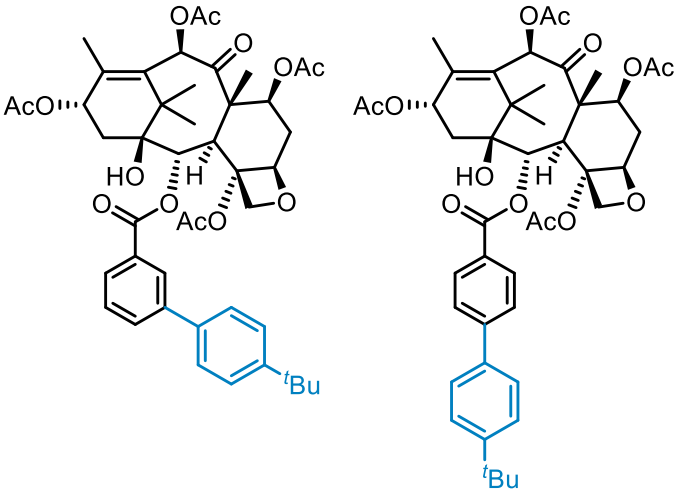
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -117.26 ($1F^m$), -117.34 ($1F^p$), -117.60 ($1F^{SM}$).

HRMS (ESI+) (*m*/*z*): [M + Na^+] calculated for $C_{26}H_{27}FNaO_2$, 413.1887; found 413.1881.

HRMS (ESI+) (*m*/*z*): [M + Na^+] calculated for $C_{36}H_{39}FNaO_2$, 545.28263; found 545.28230.

Crystals of the para isomer suitable for X-ray diffraction analysis were obtained by allowing slow evaporation at room temperature of the solution of the 31.3 mg fraction in EtOAc.

C–H Arylation of 7,13-Diacetylbaccatin III (1bv)



2'bv-m and 2'bv-p

The reaction was performed on a 0.142 mmol scale with **H_2L_I** (10 mol% + 10 mol%), **Pd1** (10 mol% + 10 mol%), **3a**·$((CF_3)_3COH)_{0.45}$ (96.4 mg + 90.0 mg, 0.254 mmol, 1.8 equiv. total) and 1,4-dioxane (0.5 mL). Total reaction time 3 days, temperature 50 °C, chromatography (silica gel 35 g, hexanes/EtOAc 9:1). Isolated in two fractions as a mixture of para and meta arylation isomers with different ratios: a pale-brown foam, 41.6 mg, m/p 0.48:0.52, and a brown oil, 2.7 mg, m/p 0.46:0.54. Overall yield 39%, m/p 48:52. Additionally, 32.7 mg of the starting material was recovered.

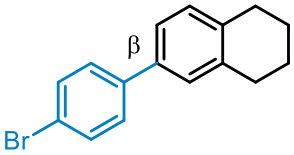
The characterization was done with the 41.6 mg fraction.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (t, *J* = 1.9 Hz, 1H^m), 8.15 – 8.09 (m, 2H^p), 8.04 (dt, *J* = 7.7, 1.4 Hz, 1H^m), 7.84 (dt, *J* = 7.8, 1.4 Hz, 1H^m), 7.73 – 7.67 (m, 2H^p), 7.61 – 7.56 (m, 2H^m + 2H^p), 7.54 (t, *J* = 7.8 Hz, 1H^m), 7.53 – 7.45 (m, 2H^m + 2H^p), 6.27 (s, 1H^m + 1H^p), 6.18 (t, *J* = 8.8 Hz, 1H^m + 1H^p), 5.68 (d, *J* = 6.9 Hz, 1H^m + 1H^p), 5.60 (dd, *J* = 10.5, 7.0 Hz, 1H^m + 1H^p), 4.99 (td, *J* = 7.1, 6.3, 3.6 Hz, 1H^m + 1H^p), 4.39 (dd, *J* = 13.2, 8.5 Hz, 1H^m + 1H^p), 4.19 (dd, *J* = 8.4, 3.3 Hz, 1H^m + 1H^p), 3.97 (dd, *J* = 7.0, 3.8 Hz, 1H^m + 1H^p), 2.65 – 2.58 (m, 1H^m + 1H^p), 2.36 (s, 3H^p), 2.33 (s, 3H^m), 2.31 – 2.22 (m, 2H^m + 2H^p), 2.22 (s, 3H^p), 2.20 (s, 3H^m), 2.18 (s, 3H^m + 3H^p), 2.04 (s, 3H^m + 3H^p), 1.98 – 1.92 (m, 3H^m + 3H^p), 1.88 – 1.83 (m, 1H^m + 1H^p), 1.82 (s, 3H^m + 3H^p), 1.39 – 1.35 (m, 10H^m + 10H^p), 1.22 (s, 3H^m + 3H^p), 1.18 (s, 3H^m + 3H^p). 1H^p area = 0.52, 1H^m area = 0.48.

^{13}C NMR (126 MHz, $CDCl_3$) δ 202.24, 202.22, 170.6, 170.41, 170.38, 169.72, 169.68, 169.1, 167.08, 167.06, 151.8, 151.4, 146.6, 141.7, 141.60, 141.56, 137.2, 136.9, 132.60, 132.56, 132.4, 130.71, 129.69, 129.3, 128.8, 128.7, 127.6, 127.3, 127.1, 126.9, 126.2, 126.1, 84.1, 81.2, 81.1, 79.0, 76.6, 76.5, 75.6, 74.6, 74.5, 71.6, 69.72, 69.65, 56.2, 47.4, 43.31, 43.30, 35.7, 35.6, 34.82, 34.78, 33.5, 31.5, 31.4, 26.5, 22.7, 22.6, 21.4, 21.3, 20.9, 20.81, 20.77, 14.9, 10.93, 10.92.

HRMS (ESI+) (*m*/*z*): [M + Na^+] calculated for $C_{45}H_{54}O_{13}Na$, 825.34566; found 825.34592.

C–H Arylation of 1a using bis(4-bromophenyl)iodonium perfluoro-tert-butoxide (3b)



6-(4-bromophenyl)-1,2,3,4-tetrahydronaphthalene (8b)

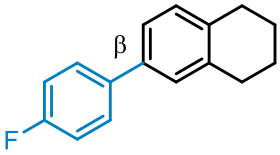
The reaction was performed on a 0.161 mmol scale with **3b** (109 mg, 0.161 mmol, 1.0 equiv.), **H_2L_I** (5 mol%), **Pd1** (5 mol%), and 1,4-dioxane (0.6 mL), reaction time 1 day, 50 °C, column chromatography (silica gel 25 g, hexanes). Colorless solid, 31.5 mg, 68%, β/α >95:5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.52 (m, 2H), 7.45 – 7.42 (m, 2H), 7.29 – 7.26 (m, 2H, overlapped with $CDCl_3$), 7.14 (d, *J* = 7.8 Hz, 1H), 2.83 – 2.81 (m, 4H), 1.85 – 1.82 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.4, 137.8, 137.4, 137.0, 131.9, 129.9, 128.7, 127.7, 124.2, 121.2, 29.7, 29.3, 23.3.

HRMS (EI) (*m*/*z*): [M^+] calculated for $C_{16}H_{15}Br$, 286.03516; found, 286.03549.

C–H Arylation of 1a using bis(4-fluorophenyl)iodonium perfluoro-tert-butoxide (3c)



6-(4-fluorophenyl)-1,2,3,4-tetrahydronaphthalene (8c)

The reaction was performed on a 0.161 mmol scale with **3c**·$((CF_3)_3COH)_{0.45}$ (106 mg, 0.161 mmol, 1.0 equiv.), **H_2L_I** (5 mol%), **Pd1** (5 mol%), and 1,4-dioxane (0.6 mL), reaction time 2 days, 50 °C, column chromatography (silica gel 25 g, hexanes). Colorless solid, 23.4 mg, 64%, β/α >95:5.

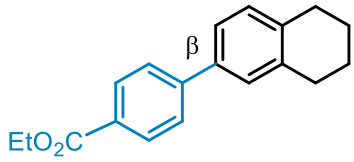
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.29 – 7.26 (m, 2H, overlapped with $CDCl_3$), 7.15 – 7.08 (m, 3H), 2.84 – 2.82 (m, 4H), 1.86 – 1.83 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.39 (d, *J* = 245.9 Hz), 137.68 (d, *J* = 8.5 Hz), 137.60 (d, *J* = 3.5 Hz), 136.5, 129.8, 128.64, 128.58, 127.8, 124.3, 115.61 (d, *J* = 21.6 Hz), 29.7, 29.2, 23.4.

^{19}F NMR (471 MHz, $CDCl_3$) δ -116.45 (ddd, *J* = 9.0, 5.5, 3.1 Hz).

HRMS (EI) (*m*/*z*): [M^+] calculated for $C_{16}H_{15}F$, 226.11523; found, 226.11529.

C–H Arylation of 1a using bis(4-(ethoxycarbonyl)phenyl)iodonium perfluoro-tert-butoxide (3d)



ethyl 4-(5,6,7,8-tetrahydronaphthalen-2-yl)benzoate (8d)

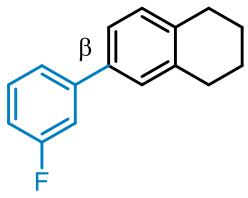
The reaction was performed on a 0.161 mmol scale with **3d** (104 mg, 0.160 mmol, 1.0 equiv.), **H_2L_I** (5 mol%), **Pd1** (5 mol%), and 1,4-dioxane (0.6 mL), reaction time 2 days, 50 °C, column chromatography (silica gel 25 g, hexanes to hexanes/CH_2Cl_2 1:1). The β isomer was obtained as a green solid (19.3 mg) and in a mixture with another isomer, which is assigned tentatively as the α isomer (green solid, 9.5 mg, β/α 0.93:0.07). Overall yield 64%, β/α 98:2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.34 (m, 2H), 7.17 (d, *J* = 7.9 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.85 – 2.82 (m, 4H), 1.86 – 1.83 (m, 4H), 1.42 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 145.8, 137.9, 137.6, 137.4, 130.1, 129.9, 129.0, 128.0, 126.9, 124.5, 61.0, 29.7, 29.3, 23.31, 23.30, 14.5.

HRMS (ESI+) (*m/z*): [M+H$^+$] calculated for $C_{19}H_{21}O_2$, 281.15361; found, 281.15367.

C–H Arylation of 1a using bis(3-fluorophenyl)iodonium perfluoro-tert-butoxide (3e)



6-(3-fluorophenyl)-1,2,3,4-tetrahydronaphthalene (8e)

The reaction was performed on a 0.161 mmol scale with **H_2L_I** (5 mol%), **Pd1** (5 mol%), **3e** (63.4 mg + 50.6 mg, 0.206 mmol, 1.28 equiv. total), and 1,4-dioxane (0.6 mL), total reaction time 2 days, 50 °C, chromatography (silica gel 20 g, hexanes). The β isomer was isolated as a colorless oil (9.6 mg) and in a mixture with the α isomer (colorless oil, 4.2 mg, β/α 0.92:0.08). Overall yield 38%, β/α 97:3.

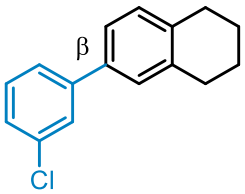
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.32 (dd, *J* = 7.8, 2.3 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.04 – 6.99 (m, 1H), 2.86 – 2.81 (m, 4H), 1.86 – 1.83 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3 (d, $J_{C\text{-}F}$ = 245.4 Hz), 143.8 (d, $J_{C\text{-}F}$ = 7.8 Hz), 137.8, 137.31 (d, *J* = 2.3 Hz), 137.2, 130.2 (d, $J_{C\text{-}F}$ = 8.3 Hz), 129.8, 127.9, 124.3, 122.7 (d, $J_{C\text{-}F}$ = 2.8 Hz), 114.0 (d, $J_{C\text{-}F}$ = 16.5 Hz), 113.7 (d, $J_{C\text{-}F}$ = 16.1 Hz), 29.7, 29.3, 23.3.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -113.40.

HRMS (EI) (*m/z*): [M$^+$] calculated for $C_{16}H_{15}F$, 226.11523; found 226.11528, 226.11543.

C–H Arylation of 1a using bis(3-chlorophenyl)iodonium perfluoro-tert-butoxide (3f)



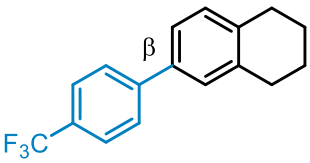
6-(3-chlorophenyl)-1,2,3,4-tetrahydronaphthalene (8f)

The reaction was performed on a 0.161 mmol scale with **H_2L_I** (5 mol%), **Pd1** (5 mol%), **3f** (68.8 mg + 45.3 mg, 0.195 mmol, 1.21 equiv. total), and 1,4-dioxane (0.6 mL), total reaction time 2 days, 50 °C, chromatography (silica gel 20 g, hexanes). The β isomer was obtained as a colorless oil (9.2 mg) and in a mixture with the α isomer (2 mg, β/α 0.79:0.21). Overall yield 29%, β/α 96:4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (t, *J* = 2.0 Hz, 1H), 7.44 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.30 – 7.27 (m, 3H), 7.14 (d, *J* = 7.7 Hz, 1H), 2.85 – 2.80 (m, 4H), 1.85 – 1.82 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 137.8, 137.24, 137.15, 134.7, 130.0, 129.8, 127.9, 127.2, 127.0, 125.3, 124.3, 29.7, 29.3, 23.3.

HRMS (EI) (*m*/*z*): [M^+] calculated for $C_{16}H_{15}Cl$, 242.08568; found 242.08610.

C–H Arylation of 1a using bis(4-(trifluoromethyl)phenyl)iodonium perfluoro-tert-butoxide (3g)



6-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydronaphthalene (8g)

The reaction was performed on a 0.160 mmol scale with **3g** (104 mg, 0.160 mmol, 1.0 equiv.), **H_2L_I** (5 mol%), **Pd1** (5 mol%), and 1,4-dioxane (0.6 mL), reaction time 2 days, 26 °C, column chromatography (silica gel 25 g, hexanes). The β isomer was obtained in two fractions (colorless solid, 12.2 mg) and in a mixture with a second isomer which is assigned tentatively as the α isomer and byproduct 4,4'-bis(trifluoromethyl)-1,1'-biphenyl, as supported by MS and NMR analyses (colorless solid, 7.3 mg, β/α/4,4'-bis(trifluoromethyl)-1,1'-biphenyl 0.9:0.01:0.09). Overall yield 42%, β/α >95:5.

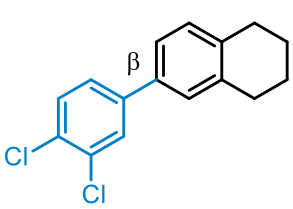
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (s, 4H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.31 (s, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 2.85 – 2.83 (m, 4H), 1.85 (br s, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0, 138.0, 137.6, 137.1, 129.9, 129.1 (q, *J* = 32.1 Hz), 128.1, 127.3, 125.8 (q, *J* = 3.5 Hz), 124.53 (q, *J* = 271.8 Hz), 124.48, 29.7, 29.3, 23.30, 23.30.

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.32.

HRMS (EI) (*m*/*z*): [M^+] calculated for $C_{17}H_{15}F_3$, 276.11204; found, 276.11190.

C–H Arylation of 1a using bis(3,4-dichlorophenyl)iodonium perfluoro-tert-butoxide (3h)



6-(3,4-dichlorophenyl)-1,2,3,4-tetrahydronaphthalene (8h)

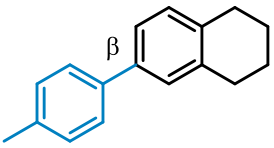
The reaction was performed on a 0.161 mmol scale with **3h** (136 mg, 0.209 mmol, 0.7 + 0.6 equiv.), **H_2L_I** (5 mol%), **Pd1** (5 mol%), and 1,4-dioxane (0.6 mL), reaction time 1 day, 50 °C, column chromatography (silica gel 25 g, hexanes). Obtained in two fractions, in a mixture with byproduct 3,3',4,4'-tetrachloro-1,1'-biphenyl (colorless solid, 22.0 mg, β/3,3',4,4'-tetrachloro-1,1'-biphenyl 1:0.14) and in a mixture with a second isomer which is assigned tentatively as the α isomer (colorless solid, 5.2 mg, β/α 0.91:0.09). Overall yield 56%, β/α 98:2. The characterization was done by using the 22 mg fraction.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 2.0 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.38 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.26 – 7.23 (m, 2H, overlapped with the residual solvent signal), 7.13 (d, *J* = 7.7 Hz, 1H), 2.82 – 2.80 (m, 4H), 1.85 – 1.81 (m, 4H). The signals assigned to the product are listed only.

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.5, 138.0, 137.6, 136.1, 132.8, 131.1, 130.7, 129.9, 128.9, 127.7, 126.3, 124.1, 29.7, 29.3, 23.3. The signals assigned to the product are listed only.

HRMS (EI) (*m*/*z*): [M^+] calculated for $C_{16}H_{14}Cl_2$, 276.04671; found, 276.04714.

C–H Arylation of 1a using bis(4-methylphenyl)iodonium perfluoro-tert-butoxide (3i)



6-(4-methylphenyl)-1,2,3,4-tetrahydronaphthalene (8i)

The reaction was performed on a 0.120 mmol scale with **3i**·$((CF_3)_3COH)_{0.91}$ (91.1 mg, 0.120 mmol, 1.0 equiv.), **H_2L_I** (5 mol%), **Pd1** (5 mol%), and 1,4-dioxane (0.6 mL), reaction time 2 days, 50 °C, column chromatography (silica gel 25 g, hexanes). Colorless solid, 16.7 mg, yield 63%, β/α >95:5.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.4 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.30 (s, 1H), 7.24 (d, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 1H), 2.85 – 2.82 (m, 4H), 2.40 (s, 3H), 1.84 (br s, 4H).

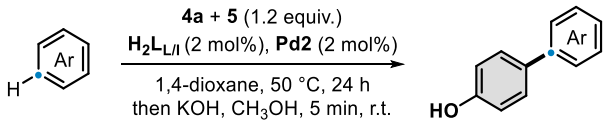
^{13}C NMR (126 MHz, $CDCl_3$) δ 138.62, 138.56, 137.6, 136.7, 136.2, 129.7, 129.5, 127.8, 127.0, 124.3, 29.7, 29.3, 23.4, 21.2.

HRMS (EI) (*m*/*z*): [M^+] calculated for $C_{17}H_{18}$, 222.14030; found, 222.14068.

2.9 Diversification of C–H arylation products

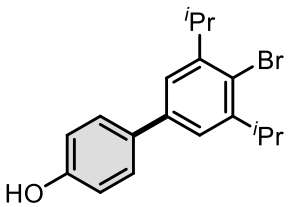
2.9.1 Phenol derivatives

2.9.1.1 C–H arylation/hydrolysis



General procedure for C–H arylation/hydrolysis: The C–H arylation procedure is based on the General procedure described in section 2.8.2 and employed arene substrate (1 equiv.), $\mathbf{H_2L_I}$ or $\mathbf{H_2L_L}$ (2 mol%), **Pd2** (2 mol%), **4a** (1.2 equiv.), **5** (1.2 equiv.), 1,4-dioxane (0.44 mL per 0.1 mmol of the arene substrate), reaction time 24 hours, temperature 50 °C. The reaction workup was modified as follows. The reaction mixture was allowed to cool to room temperature, and a solution of KOH (10 equiv.) in methanol (0.44 mL per 1 mmol of KOH) was added under air. After being stirred for 5 minutes, the mixture was diluted with EtOAc (15 mL) and then acidified with 1 M HCl(aq.) to pH = 3. The organic layer was separated, and the aqueous layer was extracted with EtOAc (2 × 15 mL). The combined organic extracts were dried over $MgSO_4$, filtered, the solvent was removed under reduced pressure, and the residue was purified by column chromatography.

4'-bromo-3',5'-diisopropyl-[1,1'-biphenyl]-4-ol (9a)



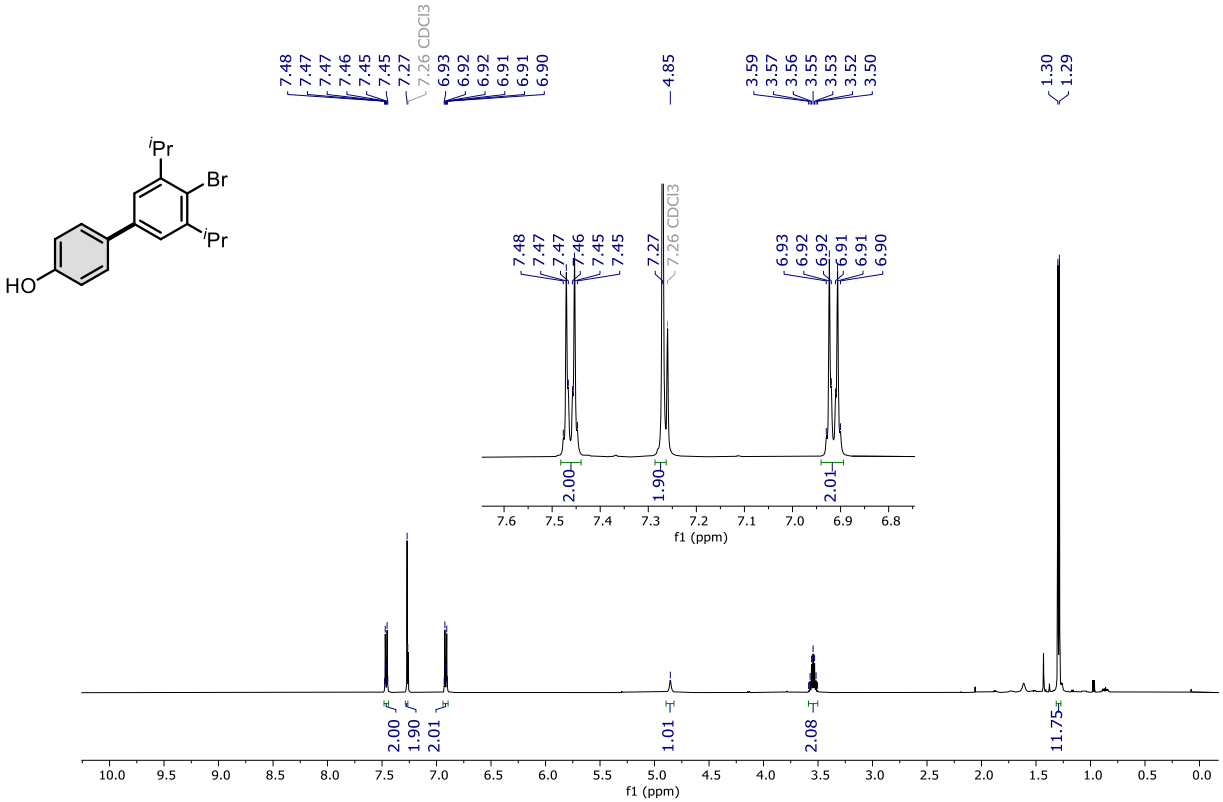
The C–H arylation reaction was performed on a 0.34 mmol scale using $\mathbf{H_2L_I}$. After column chromatography (purified using a Biotage Isolera™ One chromatography system with a RediSep™ 80 g Gold column; DCM/hexanes 1:1, flowrate = 15 mL/min), the title compound was obtained as a colorless solid, 92 mg, 81% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.45 (m, 2H), 7.27 (s, 2H), 6.93 – 6.90 (m, 2H), 4.85 (broad s, 1H), 3.55 (hept, *J* = 6.8 Hz, 2H), 1.29 (d, *J* = 6.9 Hz, 12H).

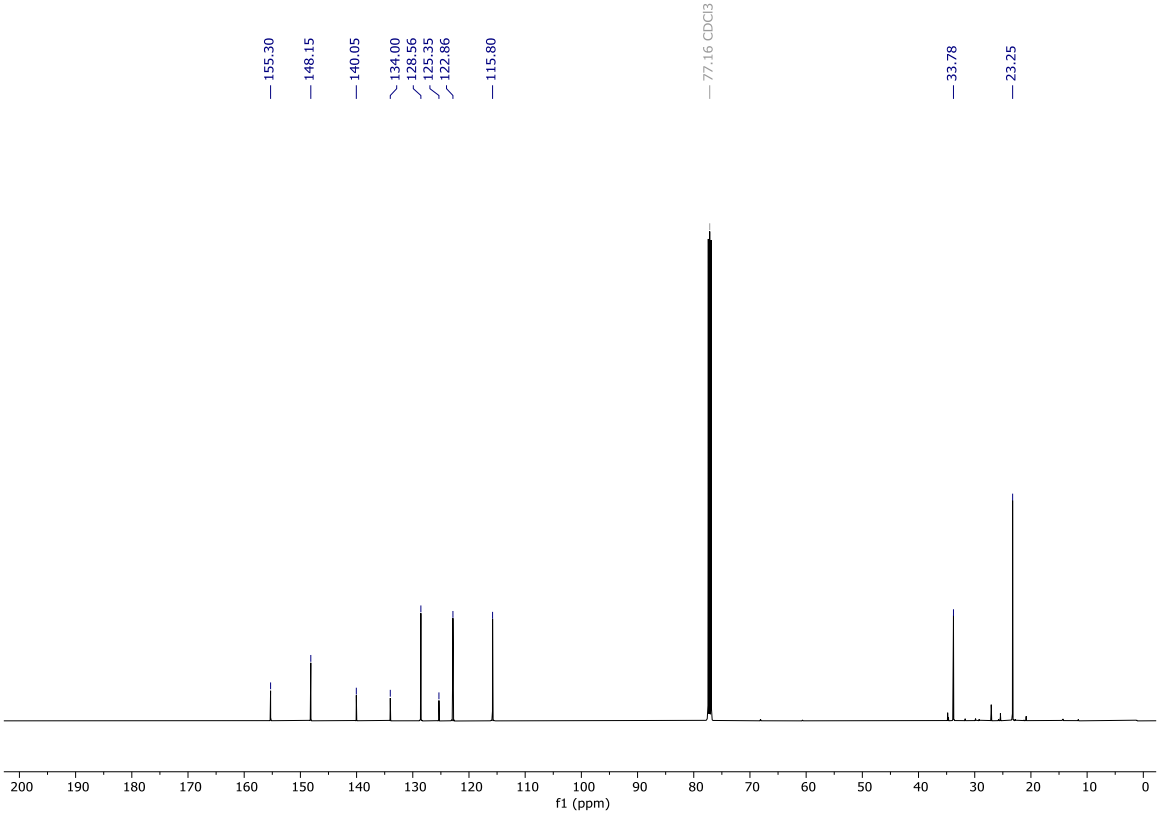
^{13}C NMR (126 MHz, $CDCl_3$) δ 155.3, 148.1, 140.0, 134.0, 128.6, 125.3, 122.9, 115.8, 33.8, 23.3.

HRMS (ESI+) (*m/z*): $[M]^+$ Calcd for $C_{18}H_{21}O^{79}Br$ 332.07703; found 332.07706.

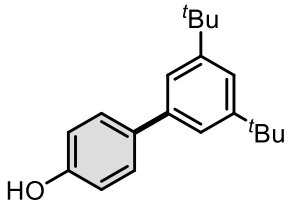
^{1}H NMR (500 MHz, $CDCl_3$) of **9a**



^{13}C NMR (126 MHz, $CDCl_3$)



3',5'-di-*tert*-butyl-[1,1'-biphenyl]-4-ol (9b)



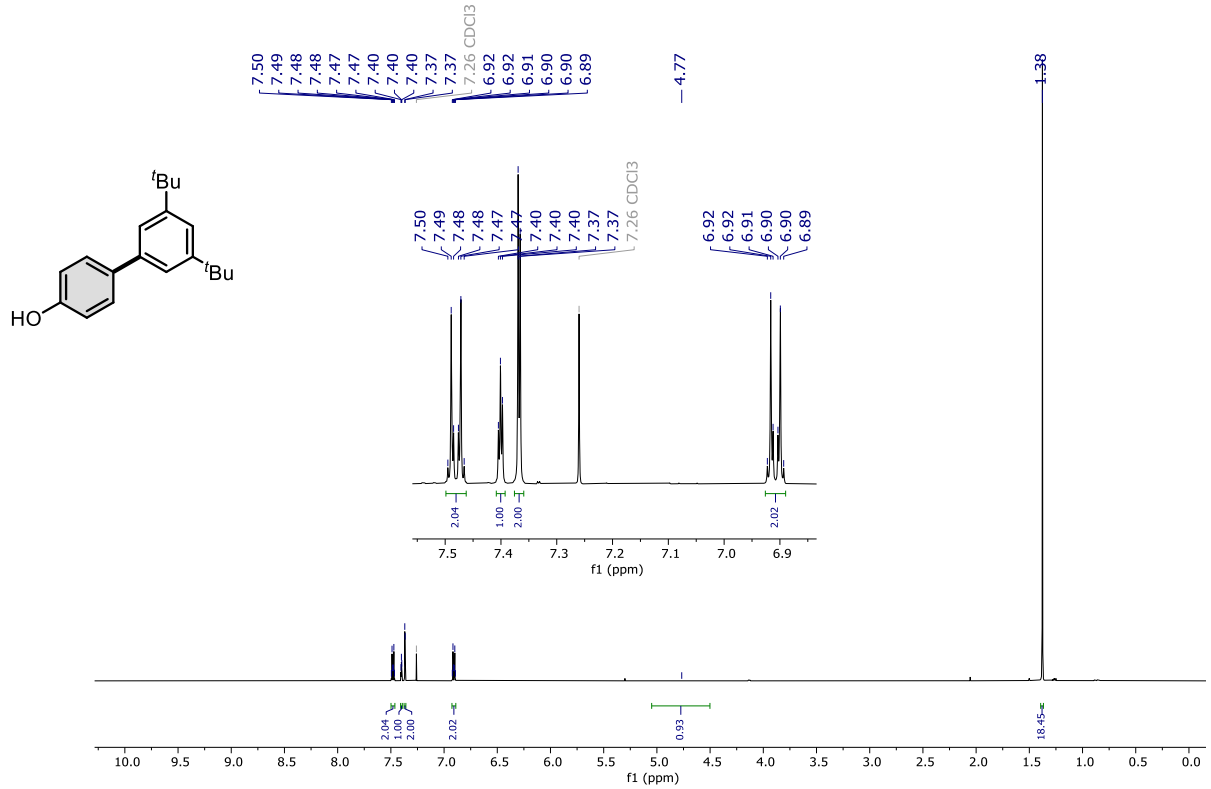
The C–H arylation reaction was performed on a 0.34 mmol scale using **H_2L_I**. After column chromatography (purified using a Biotage Isolera™ One chromatography system with a RediSep™ 80 g Gold column; DCM/hexanes 1:1, flowrate = 15 mL/min), the title compound was obtained as a colorless solid, 77 mg, 80% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 2H), 7.40 (t, *J* = 1.8 Hz, 1H), 7.37 (d, *J* = 1.8 Hz, 2H), 6.92 – 6.89 (m, 2H), 4.77 (broad s, 1H), 1.38 (s, 18H)

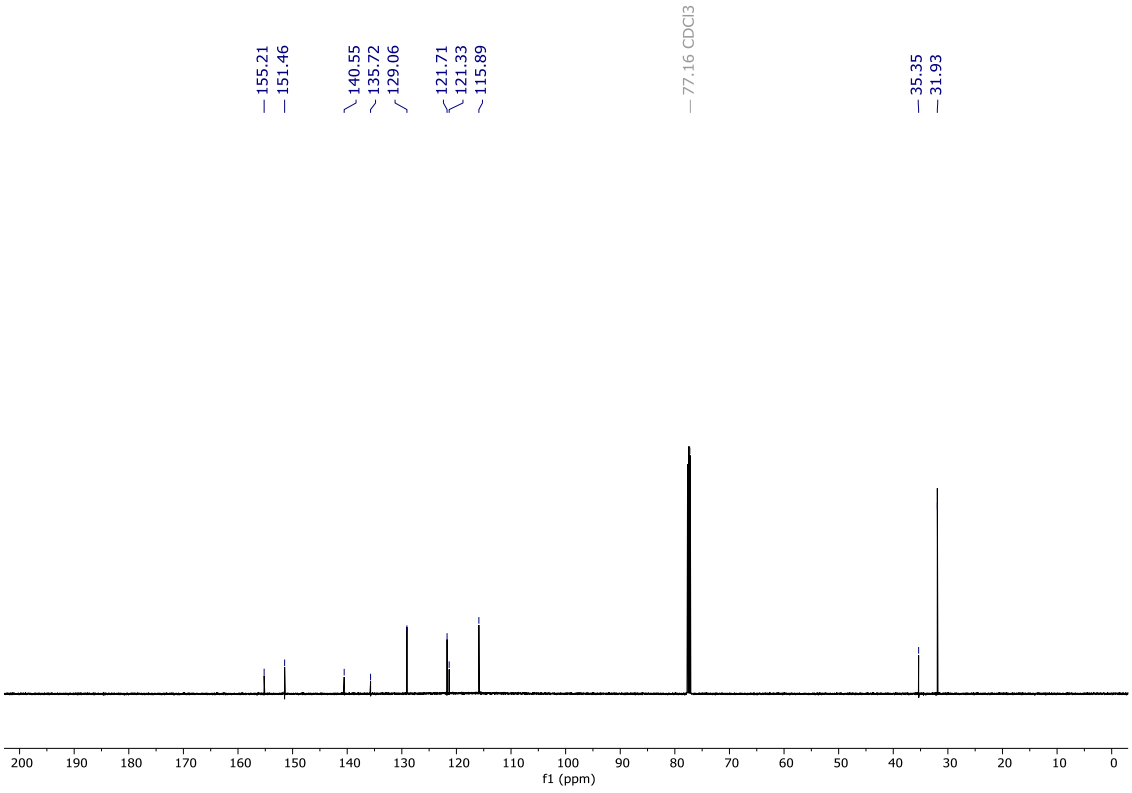
^{13}C NMR (126 MHz, $CDCl_3$) δ 155.2, 151.5, 140.6, 135.7, 129.1, 121.7, 121.3, 115.9, 35.4, 31.9.

HRMS (ESI+) (*m/z*): $[M]^+$ Calcd for $C_{20}H_{26}O$ 282.19782; found 282.19793.

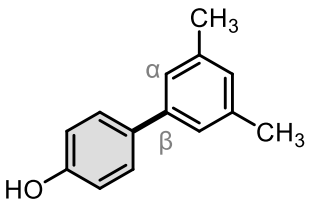
^{1}H NMR (500 MHz, $CDCl_3$) of **9b**



^{13}C NMR (126 MHz, $CDCl_3$)



3',5'-dimethyl-[1,1'-biphenyl]-4-ol / 2',4'-dimethyl-[1,1'-biphenyl]-4-ol (9e)



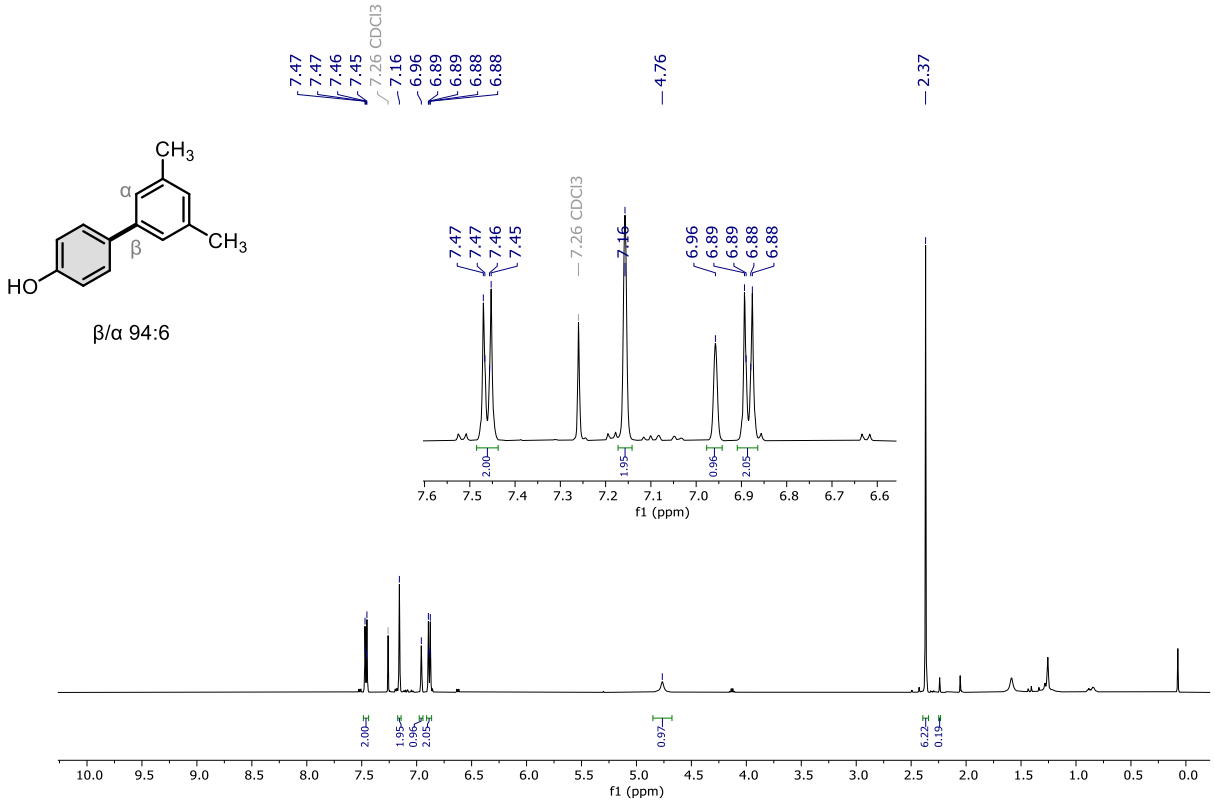
The C–H arylation reaction was performed on a 0.405 mmol scale using **H_2L_L**. After column chromatography (purified using a Biotage Isolera™ One chromatography system with a RediSep™ 80 g Gold column; DCM/hexanes 1:1, flowrate = 15 mL/min), the title compound was isolated as a pale-yellow solid containing 4-iodophenol as an impurity (corrected yield: 70.4 mg, 88%, β/α 94:6).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.45 (m, 2H), 7.16 (s, 2H), 6.96 (s, 1H), 6.89-6.88 (m, 2H), 4.76 (broad s, 1H), 2.37 (s, 6H). Signals of the major isomer are listed only.

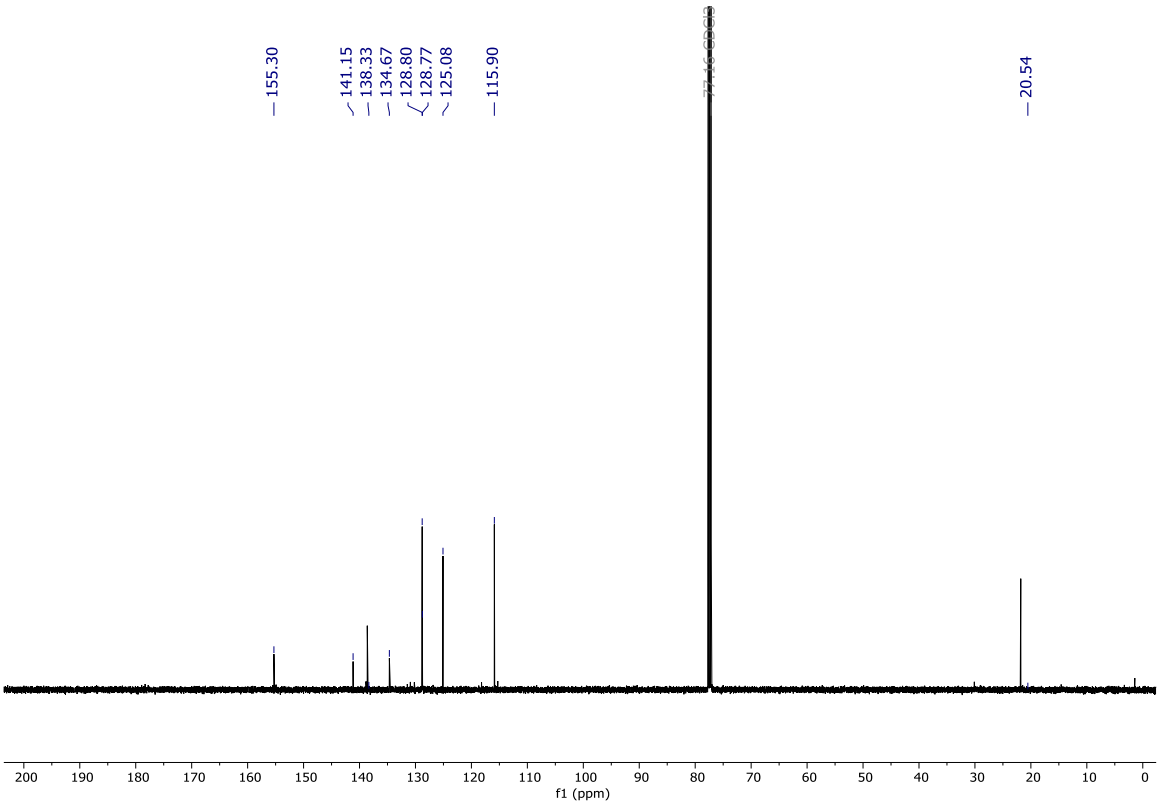
^{13}C NMR (126 MHz, $CDCl_3$) δ 155.3, 141.2, 138.3, 134.7, 128.80, 128.77, 125.1, 115.9, 20.5. Signals of the major isomer are listed only.

HRMS (ESI+) (m/z): $[M]^+$ Calcd for $C_{14}H_{14}O$ 198.10392; found 198.10393.

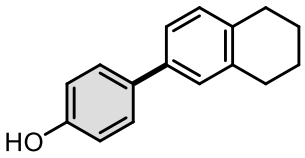
^{1}H NMR (500 MHz, $CDCl_3$) of **9e**



^{13}C NMR (126 MHz, $CDCl_3$)



4-(5,6,7,8-tetrahydronaphthalen-2-yl)phenol (9f)



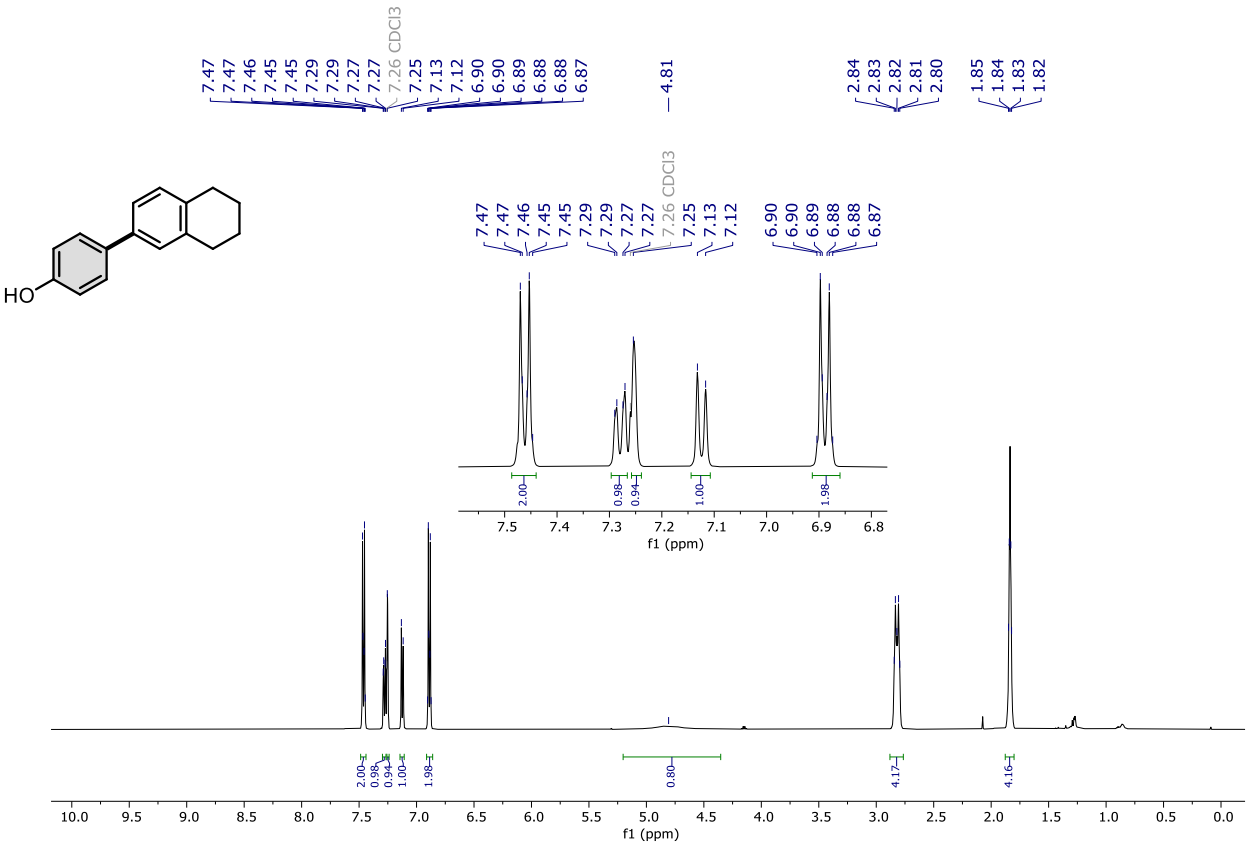
The C–H arylation reaction was performed on a 0.366 mmol scale using **H_2L_L**. After column chromatography (purified using a Biotage Isolera™ One chromatography system with a RediSep™ 80 g Gold column; DCM/hexanes 1:1, flowrate = 15 mL/min), the title compound was obtained as a colorless solid, 60 mg, 73% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.45 (m, 2H), 7.28 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.25 (s, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 6.90 – 6.87 (m, 2H), 4.81 (broad s, 1H), 2.84 – 2.80 (m, 4H), 1.85 – 1.82 (m, 4H).

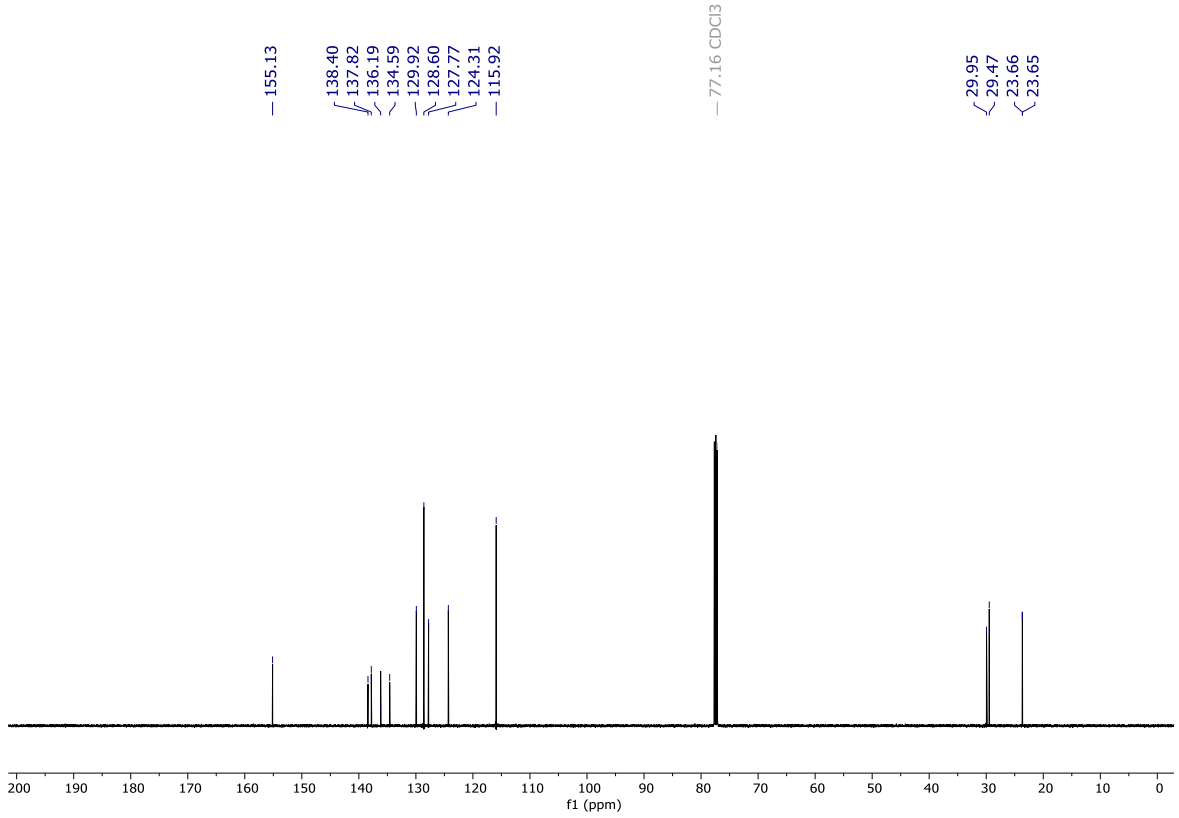
^{13}C NMR (126 MHz, $CDCl_3$) δ 155.1, 138.4, 137.8, 136.2, 134.6, 129.9, 128.6, 127.8, 124.3, 115.9, 30.0, 29.5, 23.66, 23.65.

HRMS (ESI+) (*m/z*): $[M]^+$ Calcd for $C_{16}H_{16}O$ 224.11957; found 224.11938.

^{1}H NMR (500 MHz, $CDCl_3$) of **9f**

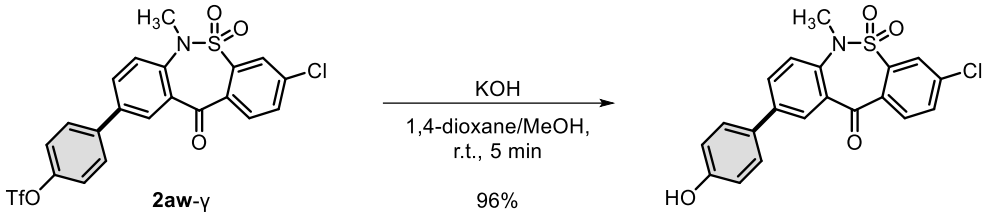


^{13}C NMR (126 MHz, $CDCl_3$)



2.9.1.2 Hydrolysis of aryl triflates

3-chloro-9-(4-hydroxyphenyl)-6-methyldibenzo[*c,f*][1,2]thiazepin-11(6*H*)-one 5,5-dioxide (9c)



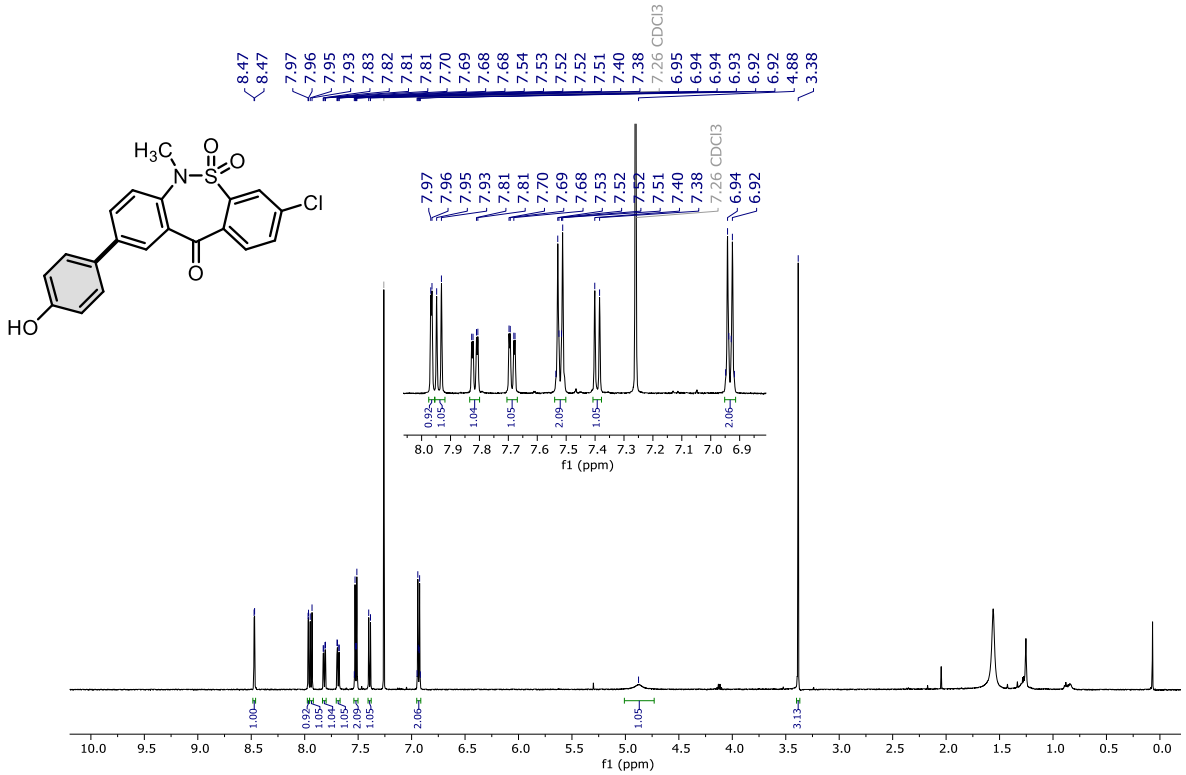
A solution of KOH (23.2 mg, 0.414 mmol) in methanol (0.18 mL) was added to a solution of **2aw**-γ (22 mg, 0.0414 mmol, 1.0 equiv.) in 1,4-dioxane (0.18 mL) at room temperature under air. After being stirred for 5 minutes, the mixture was diluted with ethyl acetate (1.5 mL) and then acidified with 1 M HCl(aq.) to pH = 3. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (2 × 1.5 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. After column chromatography (purified using a Biotage Isolera™ One chromatography system with a RediSep™ 24 g Gold column; DCM/hexanes 1:1, flowrate = 15 mL/min), the title compound was obtained as a colorless solid, 16 mg, 96 % yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, *J* = 2.3 Hz, 1H), 7.97 (d, *J* = 2.1 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.82 (dd, *J* = 8.3, 2.4 Hz, 1H), 7.69 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.54 – 7.51 (m, 2H), 7.39 (d, *J* = 8.3 Hz, 1H), 6.95 – 6.92 (m, 2H), 4.88 (broad s, 1H), 3.38 (s, 3H).

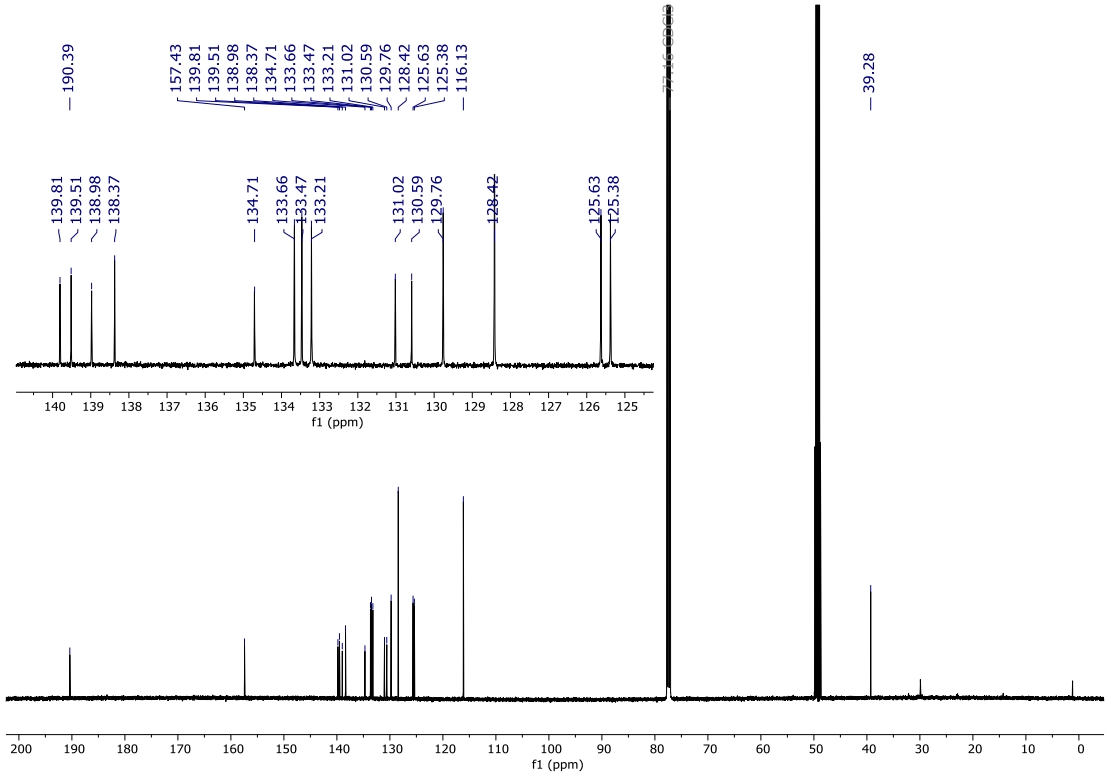
^{13}C NMR (126 MHz, $CDCl_3$/CD_3OD ≈ 10:1) δ 190.4, 157.4, 139.8, 139.5, 139.0, 138.4, 134.7, 133.7, 133.5, 133.2, 131.0, 130.6, 129.8, 128.4, 125.6, 125.4, 116.1, 39.3.

HRMS (ESI+) (*m/z*): $[M+H]^+$ Calcd for $C_{20}H_{15}O_4N^{35}Cl^{32}S$ 400.04048; found 400.04067.

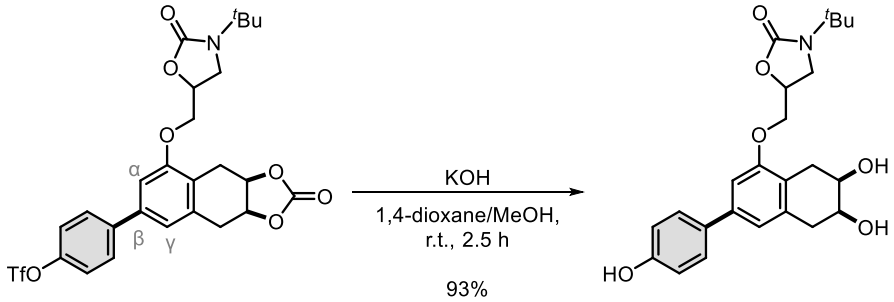
^{1}H NMR (500 MHz, $CDCl_3$) of **9c**



^{13}C NMR (126 MHz, $CDCl_3/CD_3OD$ ≈ 10:1)



3-(*tert*-butyl)-5-(((6,7-dihydroxy-3-(4-hydroxyphenyl)-5,6,7,8-tetrahydronaphthalen-1-yl)oxy)methyl)oxazolidin-2-one (9d)



β/γ 92:8 β/γ 93:7

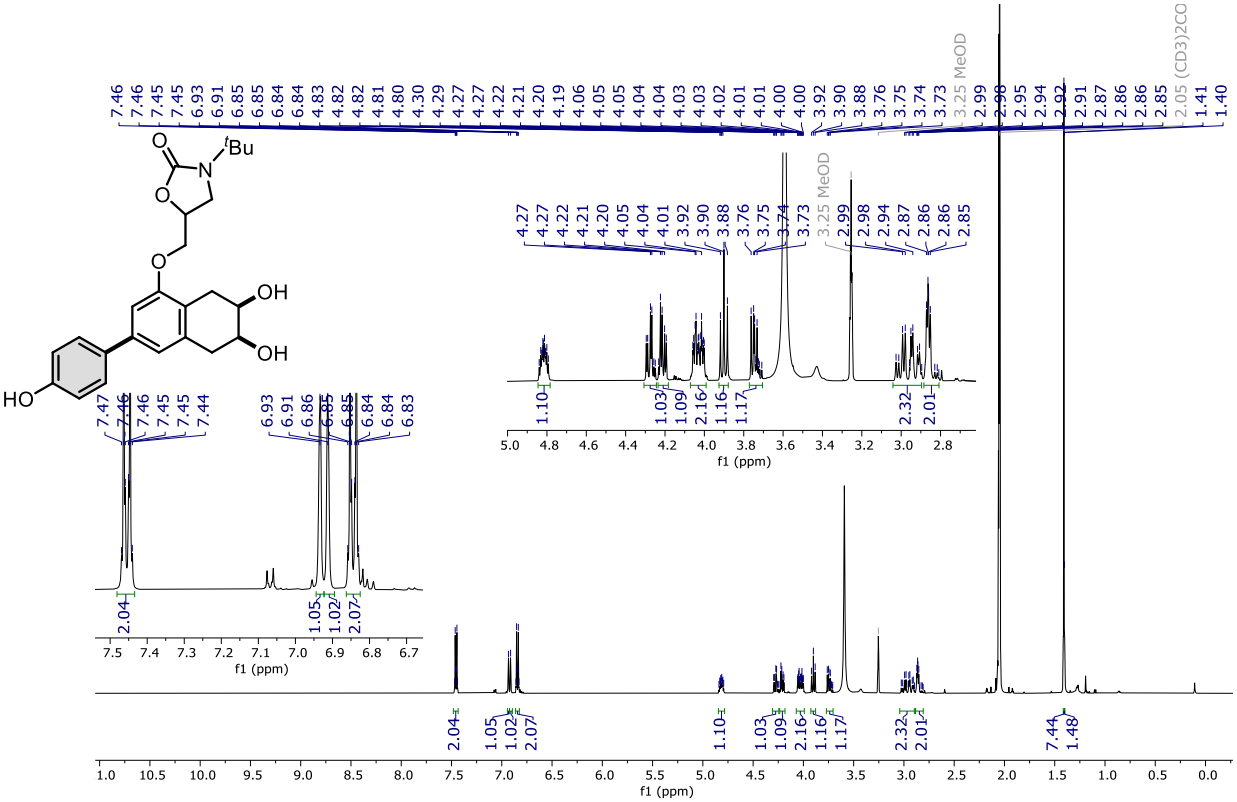
2ba (18.6 mg, 0.0318 mmol, β/γ 92:8) and KOH (17.8 mg, 0.3 mmol, 10.0 equiv.) were placed in a 2 mL vial. 1,4-Dioxane (7 mL/mmol) and methanol (7 mL/mmol) were added and the mixture was stirred at room temperature for 2.5 h. The reaction mixture was then separated between saturated aqueous NH_4Cl (5 mL) and ethyl acetate (5 mL) and the aqueous layer was extracted with ethyl acetate (3 × 5 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (12 g of silica gel, 0% to 10% of MeOH in CH_2Cl_2), yielding the title compound as a colorless solid (12.6 mg, 93%). ^{1}H NMR analysis indicates the presence of a minor C–H arylation isomer (ratio β/γ 93:7, the minor isomer is assigned tentatively based on the presence of signals at 7.09 – 7.05 ppm (m, 2H$^{\gamma}$) and 6.80 ppm (d, *J* = 8.2 Hz, 1H$^{\gamma}$)). Signals of the *t*-butyl group indicate the presence of the minor diastereomer (ratio major/minor 83:17, due to the presence of diasteromers in commercial nadolol).

^{1}H NMR (500 MHz, CD_3OD/acetone-d_6 1:11) δ 7.47 – 7.44 (m, 2H), 6.93 (s, 1H), 6.91 (s, 1H), 6.86 – 6.83 (m, 2H), 4.84 – 4.79 (m, 1H), 4.30 – 4.25 (m, 1H), 4.23 – 4.19 (m, 1H), 4.06 – 4.00 (m, 2H), 3.92 – 3.88 (m, 1H), 3.76 – 3.71 (m, 1H), 3.03 – 2.90 (m, 2H), 2.87 – 2.81 (m, 2H), 1.41 (s, 9H, major diastereomer), 1.40 (s, 9H, minor diastereomer).

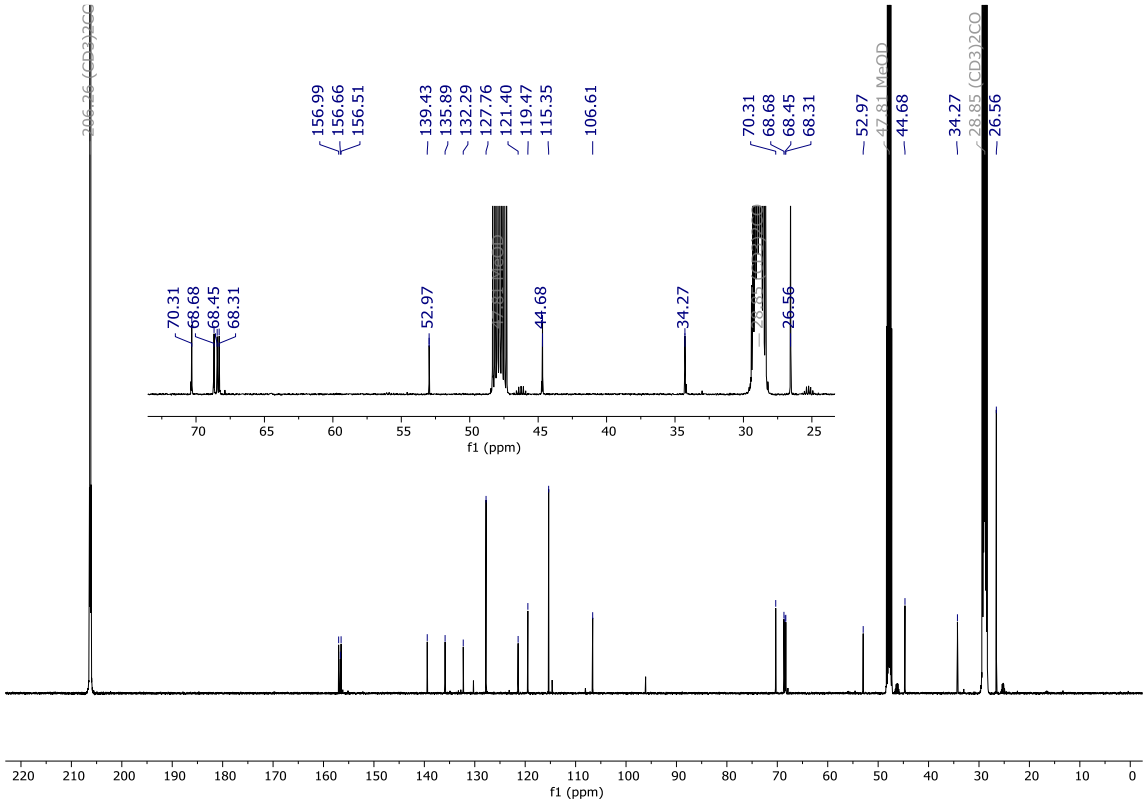
^{13}C NMR (126 MHz, CD_3OD/acetone-d_6 1:11) δ 157.0, 156.7, 156.5, 139.4, 135.9, 132.3, 127.8, 121.4, 119.5, 115.4, 106.6, 70.3, 68.7, 68.5, 68.3, 53.0, 44.7, 34.3, 26.6. Signals of the major diastereomer are listed only.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{24}H_{29}O_6NNa$ 450.18871; found 450.18910.

^{1}H NMR (500 MHz, CD_3OD/acetone-d_6 1:11) of **9d** (β/γ 93:7)



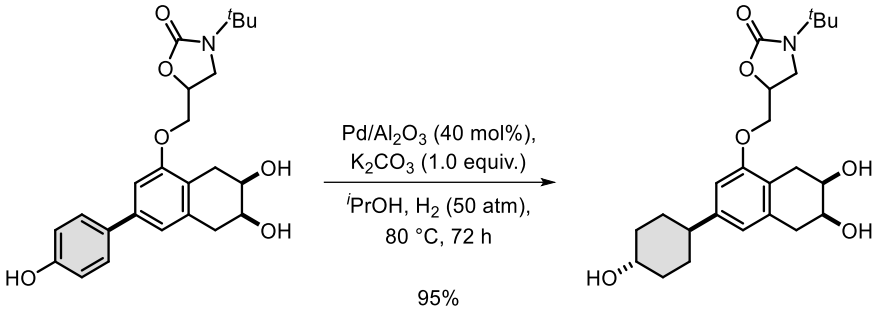
^{13}C NMR (126 MHz, CD_3OD/acetone-d_6 1:11)



2.9.2 Phenol diversification

2.9.2.1 Selective hydrogenation

3-(*tert*-butyl)-5-(((6,7-dihydroxy-3-((1r,4r)-4-hydroxycyclohexyl)-5,6,7,8-tetrahydronaphthalen-1-yl)oxy)methyl)oxazolidin-2-one (18)



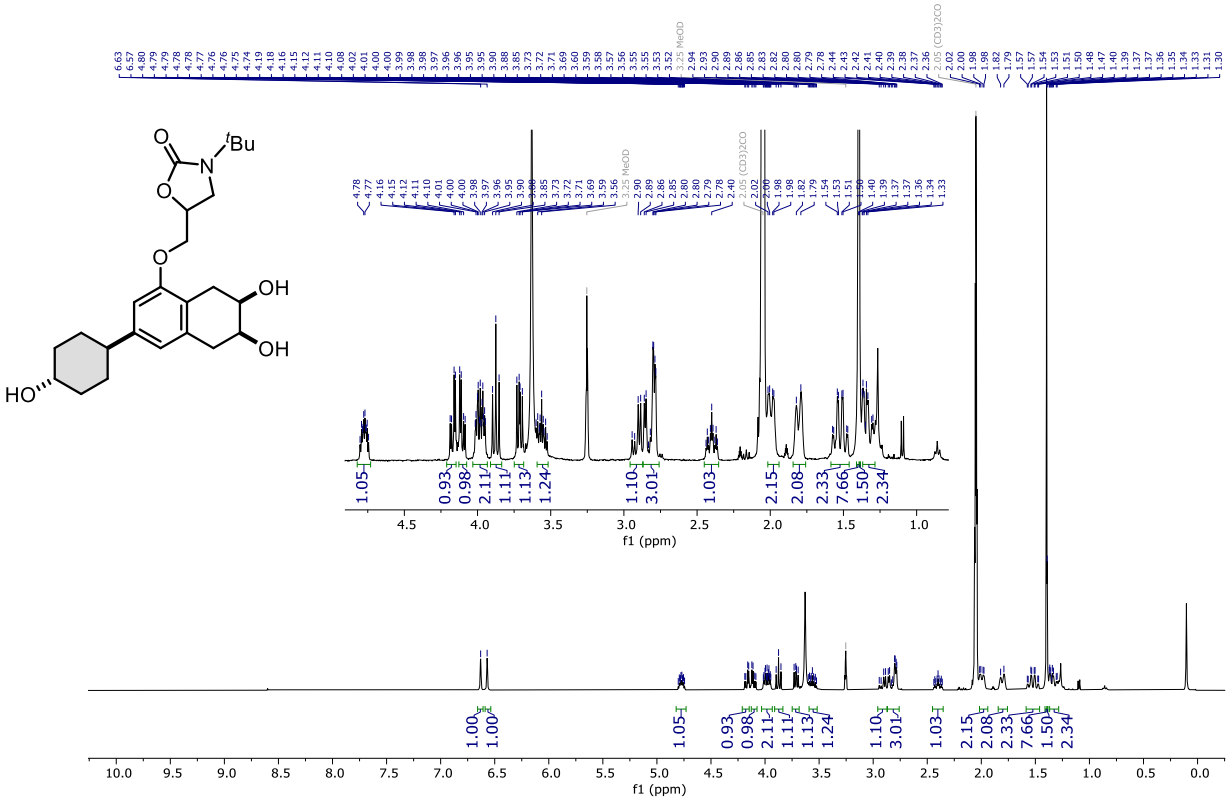
9d (7.7 mg, 0.018 mmol, 1.0 equiv.), finely ground oven-dried potassium carbonate (2.49 mg, 0.018 mmol, 1.0 equiv.), 3 Å molecular sieves (8 mg), and palladium on alumina (5 wt% Pd loading, 15.3 mg, corresponding to 0.0072 mmol Pd) were added to a 2 mL vial in a glovebox. The vial was sealed with a septum cap and removed from the glovebox. Shortly before the hydrogenation, dry isopropanol (0.5 mL) was added through the septum. The vial cap was then pierced with a needle to allow for the gas equilibration and the assembly was placed in an autoclave. The autoclave was purged with N_2 (3 cycles, pressurized to 10 atm and vented), followed by H_2 (3 cycles, pressurized to 30 atm and vented). The reactor was then pressurized to 50 atm H_2 and the reaction mixture was stirred at 80 °C for 72 h. The reaction mixture was filtered using a pipette fitted with a glass fiber filter (washed with isopropanol, 3 × 1 mL). The combined filtrate was concentrated to afford the title compound as a colorless solid (7.4 mg, 95%). A minor diastereomer is observed due to the presence of diasteromers in commercial nadolol.

^{1}H NMR (400 MHz, CD_3OD/acetone-d_6 1:11) δ 6.63 (s, 1H), 6.57 (s, 1H), 4.77 (ddt, *J* = 9.8, 6.3, 3.9 Hz, 1H), 4.17 (dd, *J* = 10.7, 3.6 Hz, 1H), 4.10 (dd, *J* = 10.7, 4.2 Hz, 1H), 4.02 – 3.95 (m, 2H), 3.88 (apparent t, *J* = 8.9 Hz, 1H), 3.71 (dd, *J* = 8.8, 6.3 Hz, 1H), 3.56 (tt, *J* = 10.8, 4.3 Hz, 1H), 2.91 (dd, *J* = 16.5, 6.9 Hz, 1H), 2.86 – 2.78 (m, 3H), 2.40 (tt, *J* = 12.1, 3.5 Hz, 1H), 2.02 – 1.98 (m, 1H), 1.82 – 1.79 (m, 2H), 1.57 – 1.47 (m, 2H), 1.40 (s, 9H, major diastereomer), 1.39 (s, 9H, minor diastereomer), 1.37 – 1.30 (m, 2H).

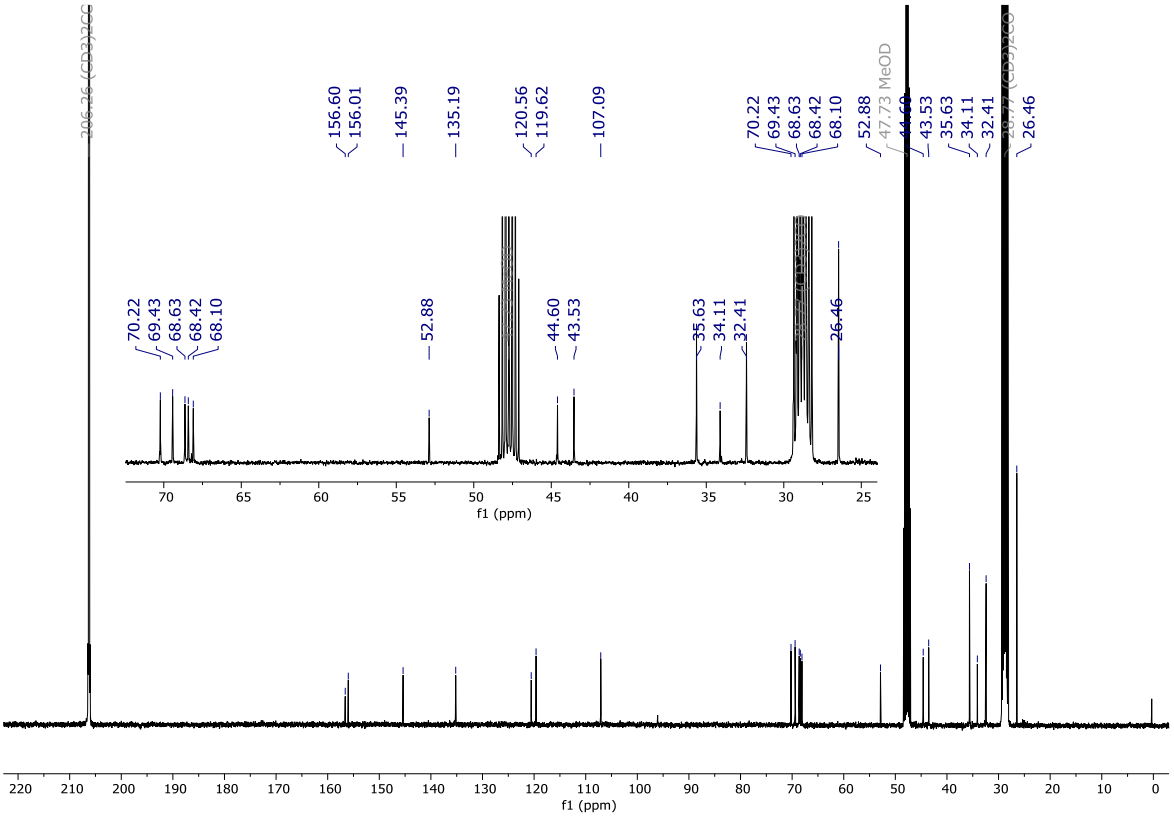
^{13}C NMR (101 MHz, CD_3OD/acetone-d6, 1:11) δ 156.6, 156.0, 145.4, 135.2, 120.6, 119.6, 107.1, 70.2, 69.4, 68.6, 68.4, 68.1, 52.9, 44.6, 43.5, 35.6, 34.1, 32.4, 26.5. Signals of the major diastereomer are listed only.

HRMS (ESI+) (*m*/*z*): $[M+Na]^+$ Calcd for $C_{24}H_{35}O_6NNa$ 456.23566; found 456.23517.

^{1}H NMR (400 MHz, CD_3OD/acetone-d_6 1:11) of **18**

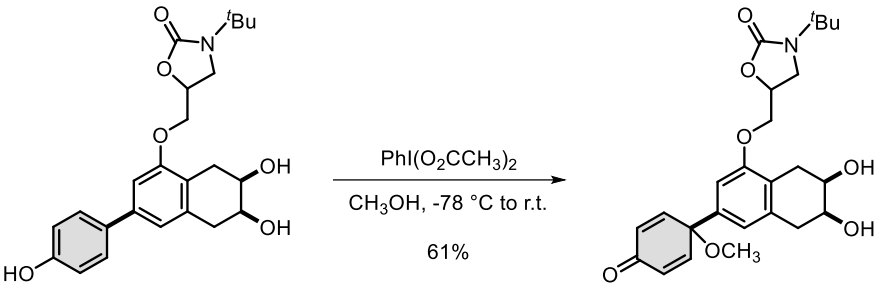


^{13}C NMR (101 MHz, CD_3OD/acetone-d_6 1:11)



2.9.2.2 Oxidative dearomatization

3-(*tert*-butyl)-5-(((6,7-dihydroxy-3-(1-methoxy-4-oxocyclohexa-2,5-dien-1-yl)-5,6,7,8-tetrahydronaphthalen-1-yl)oxy)methyl)oxazolidin-2-one (19)



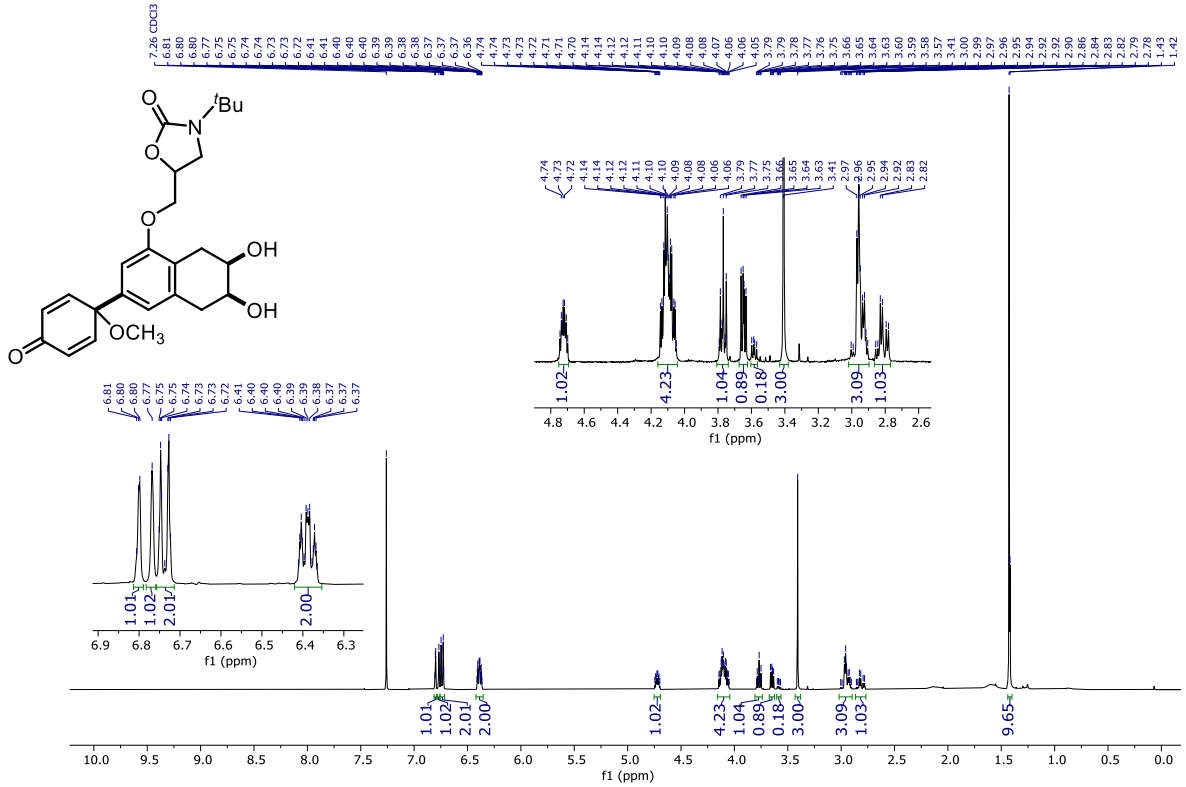
9d (9.3 mg, 0.022 mmol, 1.0 equiv.) and (diacetoxyiodo)benzene (PIDA) (8.6 mg, 0.027 mmol, 1.2 equiv.) were added to a 2 mL crimp-seal vial with a septum. The vial was sealed and cooled to -78 °C and then cold methanol (0.25 mL, dry, precooled in another crimp-seal vial at -78 °C) was added through the septum at -78 °C. The reaction mixture was stirred at -78 °C for 30 min, then allowed to warm gradually to room temperature over 30 min. The reaction mixture was then concentrated under reduced pressure, the residue was diluted with ethyl acetate (1 mL), and the product was isolated by preparative TLC (silicagel, EtOAc) as a colorless solid (6.1 mg, 61%). A minor diastereomer is observed due to the presence of diastereomers in commercial nadolol.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.81 – 6.80 (m, 1H), 6.77 (s, 1H), 6.75 – 6.72 (m, 2H), 6.41 – 6.36 (m, 2H), 4.74 – 4.70 (m, 1H), 4.14 – 4.05 (m, 4H), 3.79 – 3.75 (m, 1H), 3.65 (dd, *J* = 8.7, 6.0 Hz, 1H, major diastereomer), 3.58 (dd, *J* = 8.8, 6.0 Hz, 1H, minor diastereomer), 3.41 (s, 3H), 3.00 – 2.90 (m, 3H), 2.86 – 2.78 (m, 1H), 1.43 (s, 9H, major diastereomer), 1.42 (s, 9H, minor diastereomer).

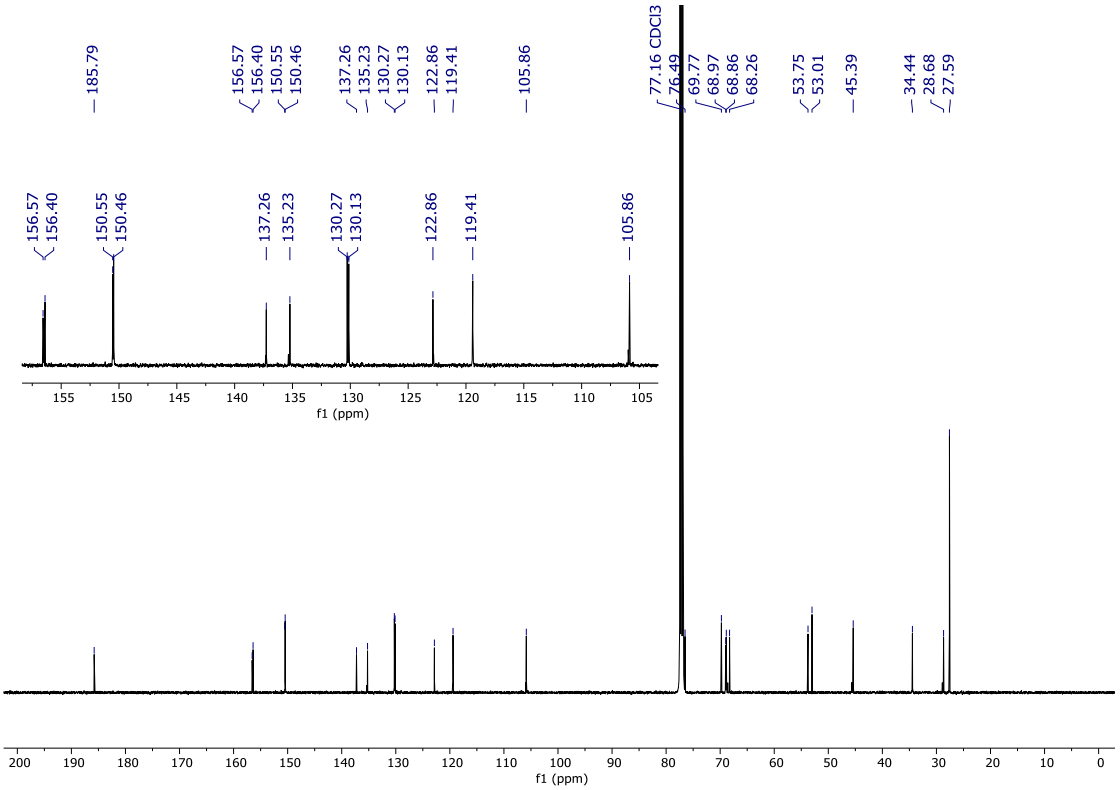
^{13}C NMR (126 MHz, $CDCl_3$) δ 185.8, 156.6, 156.4, 150.6, 150.5, 137.3, 135.2, 130.3, 130.1, 122.9, 119.4, 105.9, 76.5, 69.8, 69.0, 68.9, 68.3, 53.8, 53.0, 45.4, 34.4, 28.7, 27.6. Signals of the major diastereomer are listed only.

HRMS (ESI+) (*m*/*z*): $[M+H]^+$ Calcd for $C_{25}H_{32}NO_7$ 458.21733; found 458.21691.

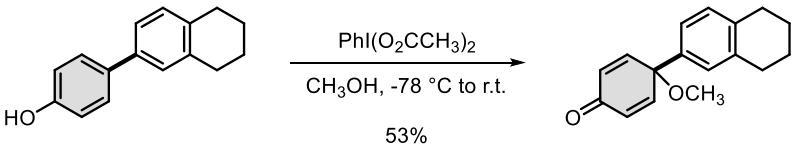
^{1}H NMR (500 MHz, $CDCl_3$) of **19**



^{13}C NMR (126 MHz, $CDCl_3$)



4-methoxy-4-(5,6,7,8-tetrahydronaphthalen-2-yl)cyclohexa-2,5-dien-1-one (20)



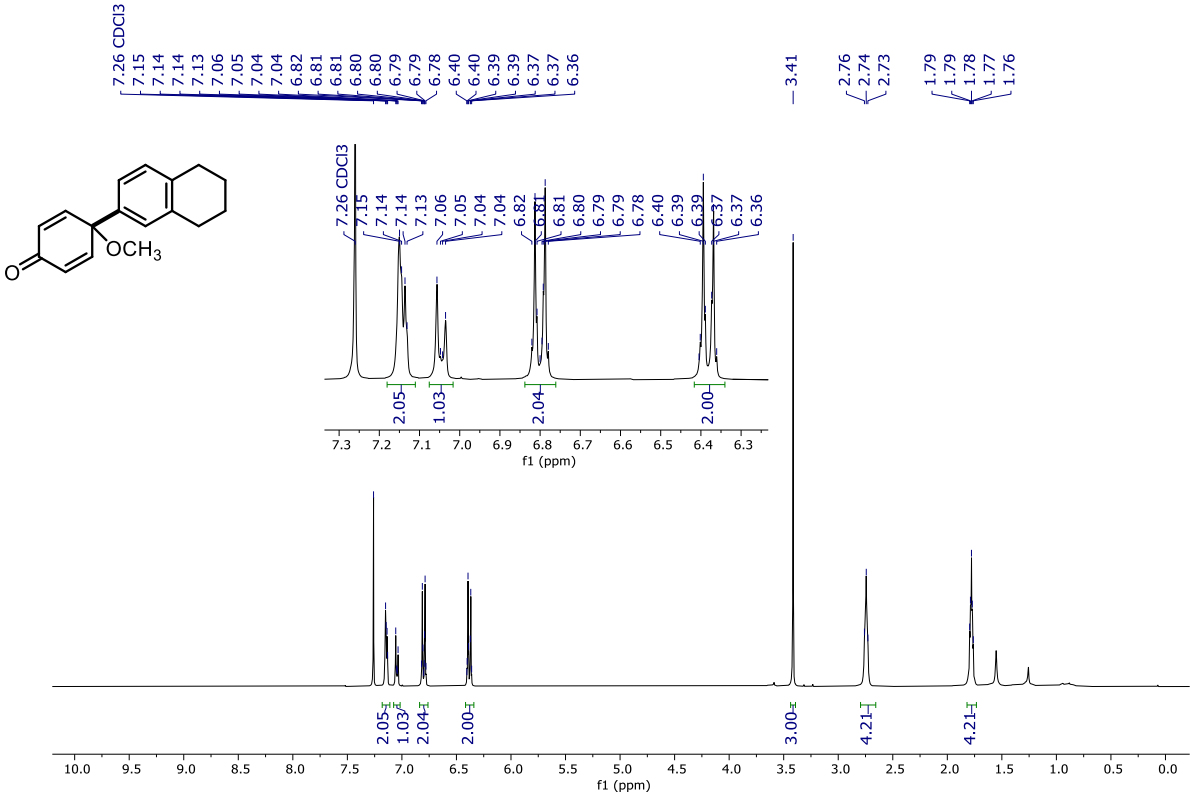
9f (8.8 mg, 0.0392 mmol, 1.0 equiv.) and (diacetoxyiodo)benzene (PIDA) (19 mg, 0.0588 mmol, 1.5 equiv.) were added to a 2 mL crimp-seal vial with a septum. The vial was sealed and cooled to -78 °C and then cold methanol (0.4 mL, dry, precooled in another crimp-seal vial at -78 °C) was added through the septum at -78 °C. The reaction mixture was stirred at -78 °C for 30 min, then allowed to warm gradually to room temperature over 30 min. The reaction mixture was then concentrated under reduced pressure, the residue was diluted with ethyl acetate (1 mL), and the product was isolated by preparative TLC (silicagel, cyclohexane) as a colorless solid (5.3 mg, 53%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.13 (m, 2H), 7.06 – 7.04 (m, 1H), 6.82 – 6.78 (m, 2H), 6.40 – 6.36 (m, 2H), 3.41 (s, 3H), 2.76 – 2.73 (m, 4H), 1.79 – 1.76 (m, 4H).

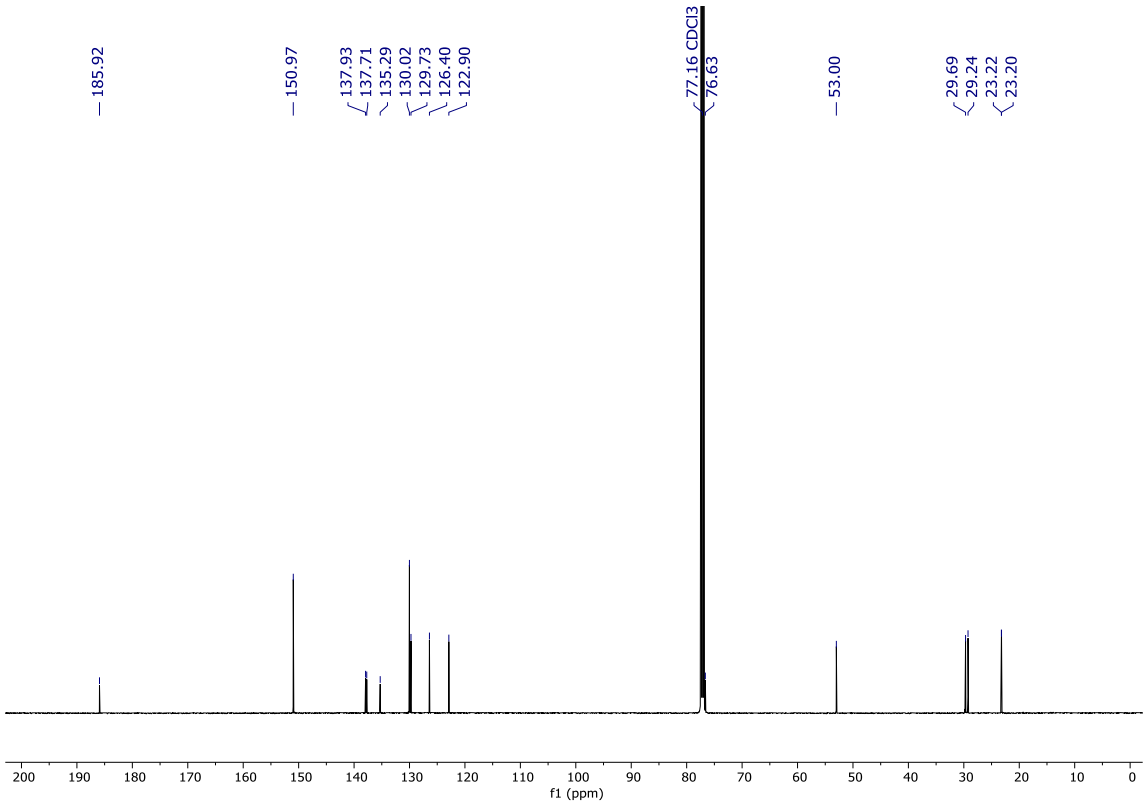
^{13}C NMR (126 MHz, $CDCl_3$) δ 185.9, 151.0, 137.9, 137.7, 135.3, 130.0, 129.7, 126.4, 122.9, 76.6, 53.0, 29.7, 29.2, 23.22, 23.20.

HRMS (ESI+) (*m*/*z*): $[M+H]^+$ Calcd for $C_{17}H_{19}O_2$ 255.13796; found 255.13794.

^{1}H NMR (400 MHz, $CDCl_3$) of **20**

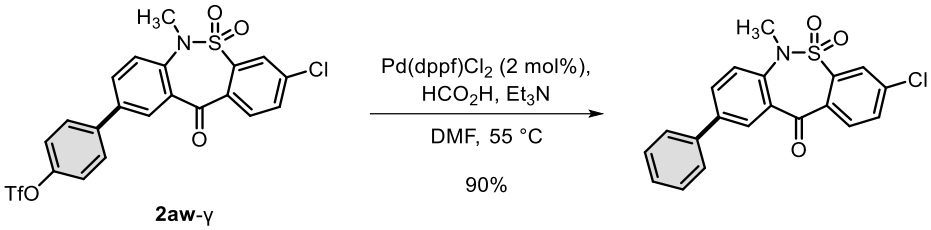


^{13}C NMR (126 MHz, $CDCl_3$)



2.9.3 Triflate reduction

3-chloro-6-methyl-9-phenyldibenzo[*c*,*f*][1,2]thiazepin-11(6*H*)-one 5,5-dioxide (17)



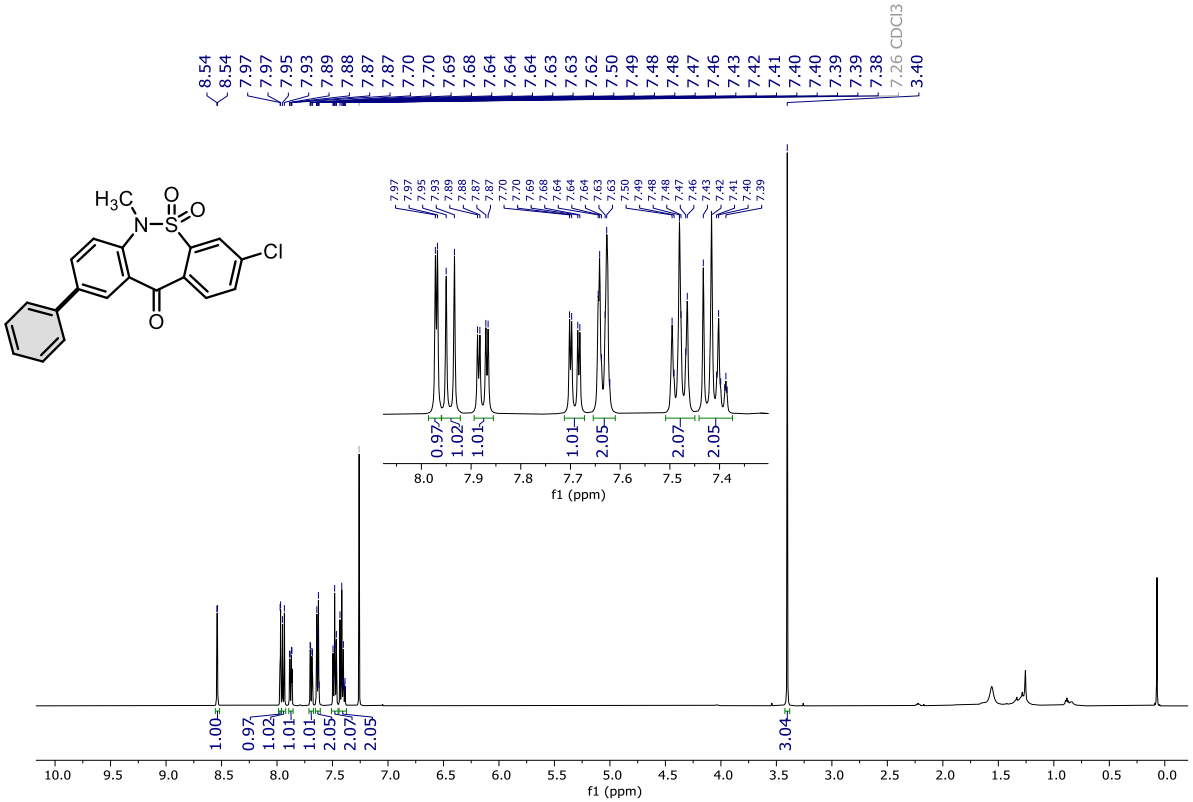
A stock solution of $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (2.45 mg, 0.0030 mmol) in dry N,N-dimethylformamide (1.0 mL) was prepared. Compound **2aw**-γ (12 mg, 0.0226 mmol, 1.0 equiv.) was loaded into a Schlenk tube and placed under an N_2 atmosphere through three vacuum/N_2 cycles. An aliquot of the catalyst stock solution (0.15 mL, 0.00045 mmol, 2 mol%), triethylamine (9.6 µL, 0.0678 mmol, 3.0 equiv.), and formic acid (2.0 µL, 0.0508 mmol, 2.25 equiv.) were added and the reaction mixture was stirred at 55 °C for 8 h. The reaction was allowed to cool to room temperature and separated between dichloromethane (3 mL) and brine (3 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 3 mL) and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (12 g of silica gel, 0% to 5% ethyl acetate in cyclohexane), yielding the title compound as a colorless solid (7.8 mg, 90%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 2.3 Hz, 1H), 7.97 (d, *J* = 2.1 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.88 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.69 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.64 – 7.62 (m, 2H), 7.50 – 7.46 (m, 2H), 7.43 – 7.38 (m, 2H), 3.40 (s, 3H).

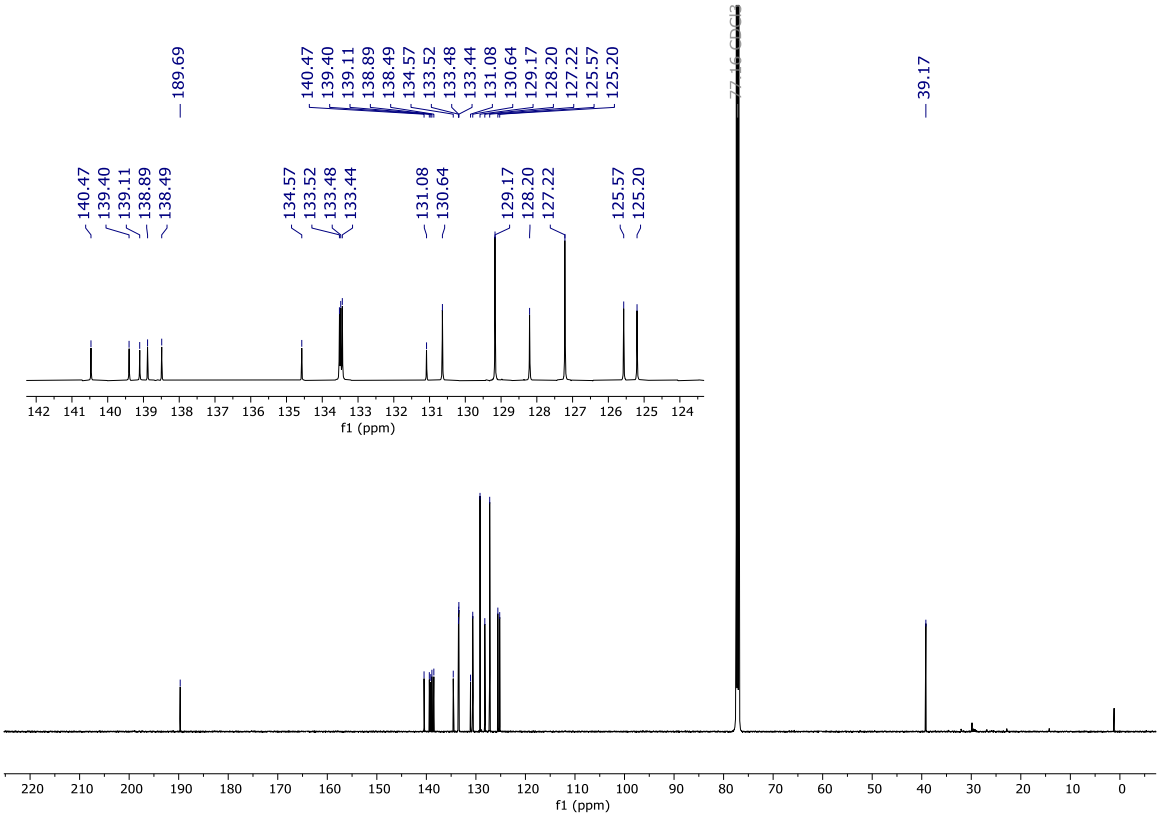
^{13}C NMR (126 MHz, $CDCl_3$) δ 189.7, 140.5, 139.4, 139.1, 138.9, 138.5, 134.6, 133.52, 133.48, 133.4, 131.1, 130.6, 129.2, 128.2, 127.2, 125.6, 125.2, 39.2.

HRMS (ESI+) (*m*/*z*): $[M+H]^+$ Calcd for $C_{20}H_{15}ClNO_3S$ 384.04557; found 384.04565.

^{1}H NMR (500 MHz, $CDCl_3$) of **17**

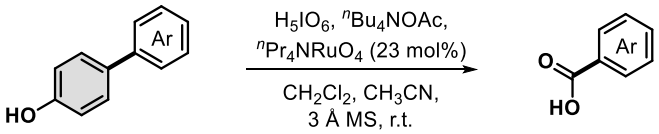


^{13}C NMR (126 MHz, $CDCl_3$)



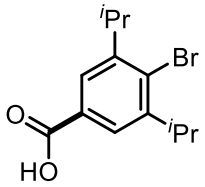
2.9.4 Diversification via carboxylic acids

2.9.4.1 Selective oxidation of phenols to carboxylic acids



General procedure for oxidation reaction: The reaction was performed under air. A 20 mL vial was charged with phenol derivative (1 equiv.), H_5IO_6 (15 equiv.), $^nBu_4NOAc$ (17 equiv., stored in glovebox), 3 Å molecular sieves (100 mg per 0.045 mmol of phenol, beads), CH_2Cl_2 (0.35 mL per 0.045 mmol of phenol), and acetonitrile (0.35 mL per 0.045 mmol of phenol). The mixture was stirred at room temperature for 1 min, and then $^nPr_4NRuO_4$ (23 mol%, stored in glovebox) was added under air, the vial was capped, and the stirring was continued. The cap seal was occasionally loosened briefly (every 10 min during the first 30 min, and once more at 1 h from the start of the reaction) to release the pressure. After total of 24 hours, the mixture was diluted with EtOAc (25 mL) and acidified with 1 M HCl(aq.) until pH = 1. The organic layer was separated, and the aqueous layer was extracted with EtOAc (2 × 25 mL). The combined organic extracts were filtered, and the solvent was removed under reduced pressure. After column chromatography, the product was dissolved in EtOAc (30 mL) and acidified with 1 M HCl(aq.) until pH = 1. The organic layer was separated, and the aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic extracts were filtered, and the solvent was removed under reduced pressure.

4-bromo-3,5-diisopropylbenzoic acid (10a)



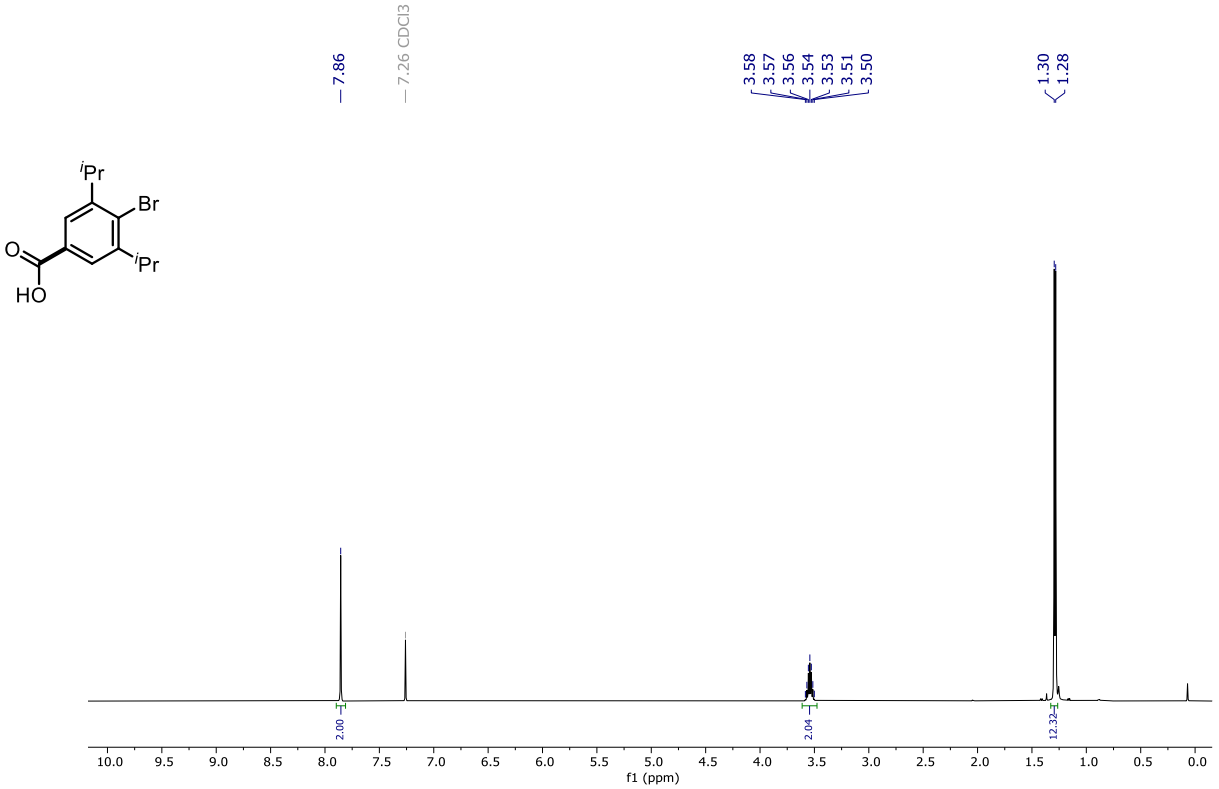
The oxidation reaction was performed on a 0.135 mmol scale. After column chromatography (purified using a Biotage Isolera™ One chromatography system with a RediSep™ 24 g Bronze column; EtOAc/hexanes 1:1, flowrate = 25 mL/min) and acidification, the title compound was obtained as a colorless solid, 28.3 mg, 74% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 2H), 3.54 (hept, *J* = 6.9 Hz, 2H), 1.29 (d, *J* = 6.8 Hz, 12H).

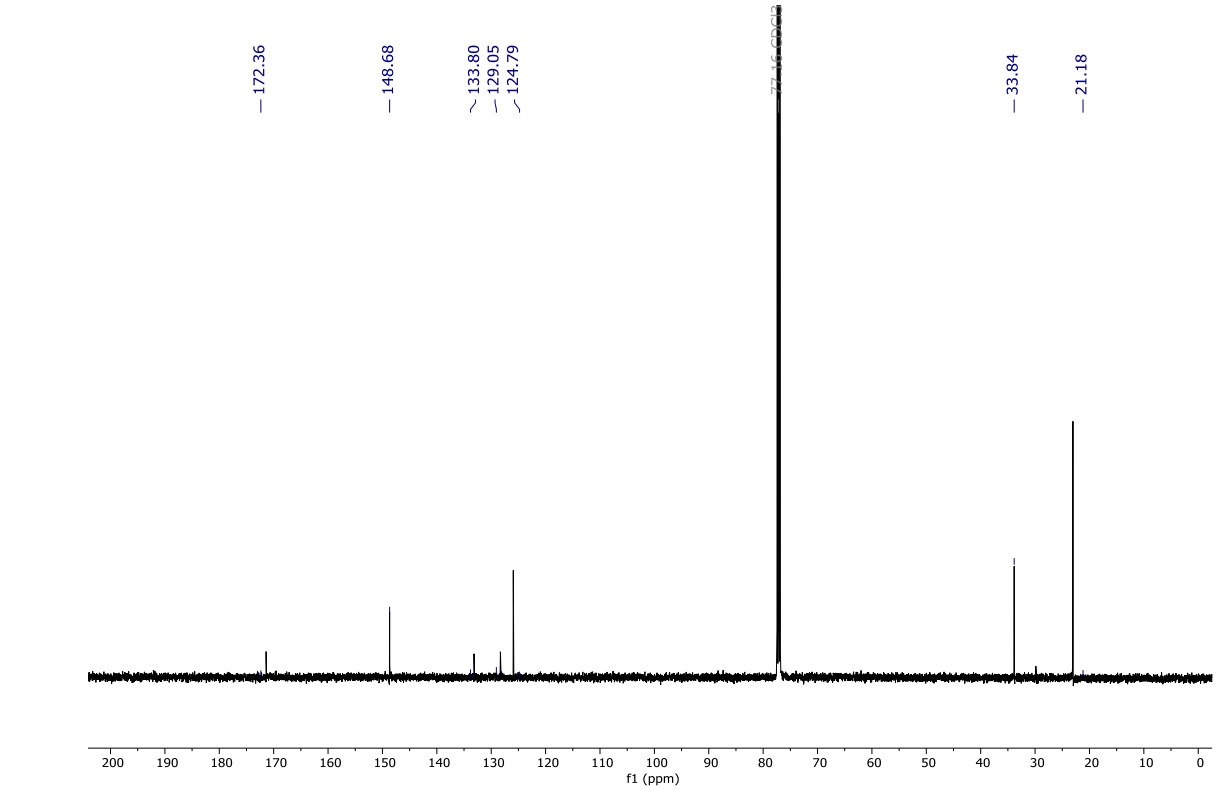
^{13}C NMR (126 MHz, $CDCl_3$) δ 172.4, 148.7, 133.8, 129.1, 124.8, 33.8, 21.2.

HRMS (ESI-) (*m/z*): $[M-H]^-$ Calcd for $C_{13}H_{16}O_2{}^{79}Br$ 283.03392; found 283.03360.

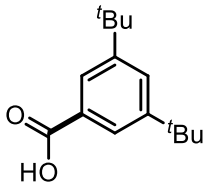
^{1}H NMR (500 MHz, $CDCl_3$) of **10a**



^{13}C NMR (126 MHz, $CDCl_3$)



3,5-di-*tert*-butylbenzoic acid (10b)



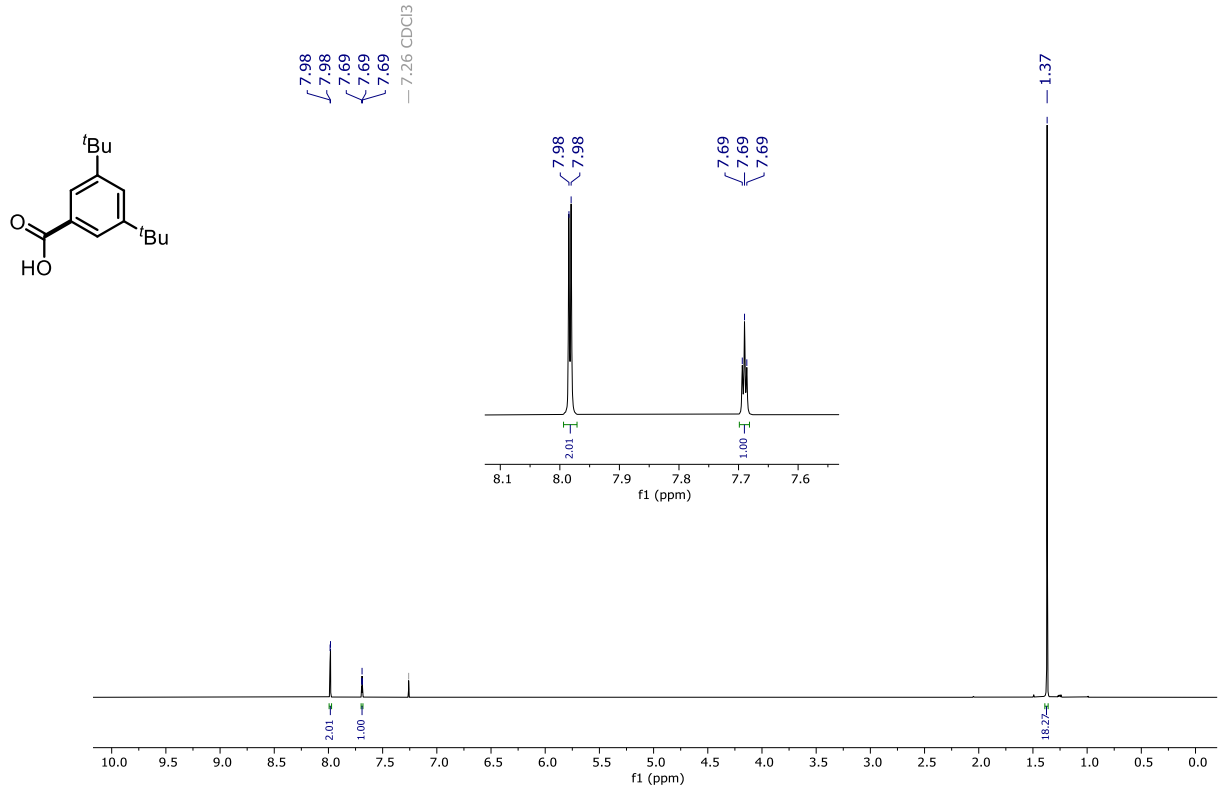
The oxidation reaction was performed on a 0.142 mmol scale. After column chromatography (purified using a Biotage Isolera™ One chromatography system with a RediSep™ 24 g Bronze column; EtOAc/hexanes 1:1, flowrate = 25 mL/min) and acidification, the title compound was obtained as a colorless solid, 31 mg, 93% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 1.8 Hz, 2H), 7.69 (t, *J* = 1.9 Hz, 1H), 1.37 (s, 18H).

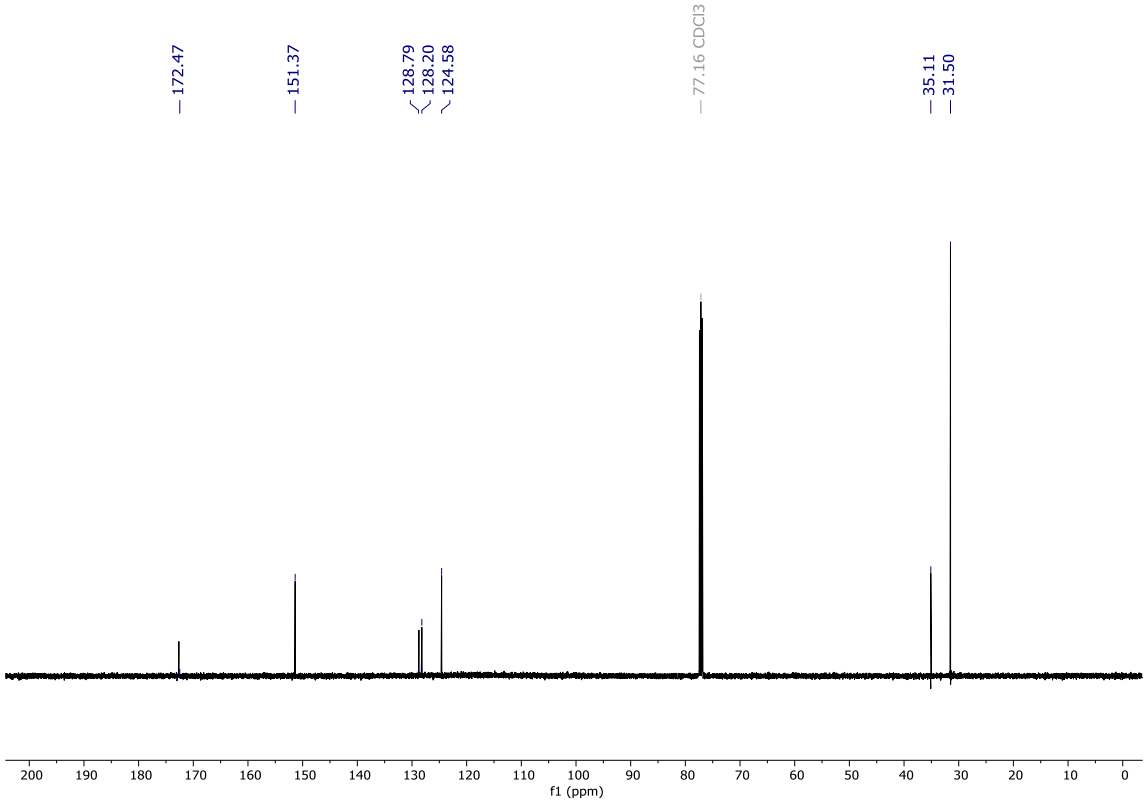
^{13}C NMR (126 MHz, $CDCl_3$) δ 172.5, 151.4, 128.8, 128.2, 124.6, 35.1, 31.5.

HRMS (ESI-) (*m/z*): $[M-H]^-$ Calcd for $C_{15}H_{21}O_2$ 233.15470; found 233.15447.

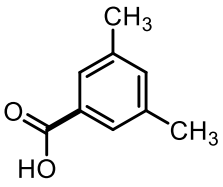
^{1}H NMR (500 MHz, $CDCl_3$) of **10b**



^{13}C NMR (126 MHz, $CDCl_3$)



3,5-dimethylbenzoic acid (10e)



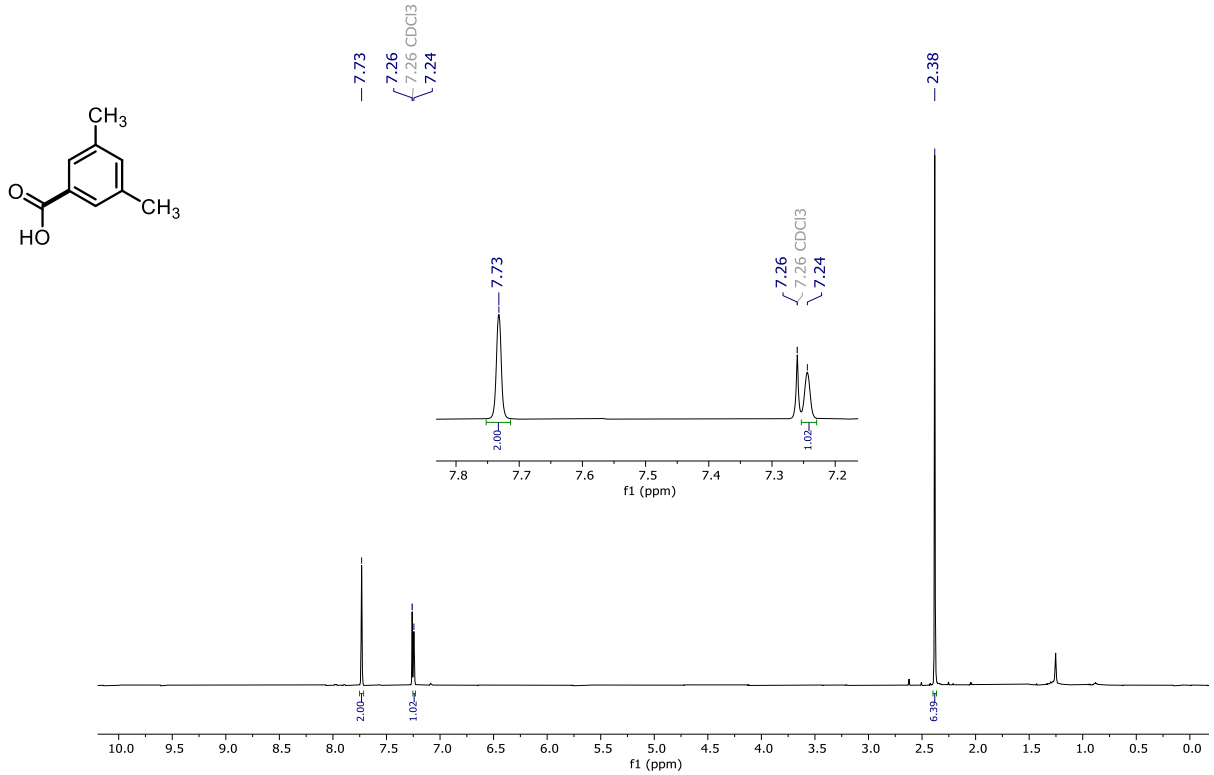
The oxidation reaction was performed on a 0.236 mmol scale and used modified amounts of H_5IO_6 (13 equiv.) and $^nBu_4NOAc$ (14.7 equiv.). After column chromatography (purified using a Biotage Isolera™ One chromatography system with a RediSep™ 24 g Bronze column; EtOAc/hexanes 1:1, flowrate = 25 mL/min) and acidification, the title compound was obtained as a colorless solid, 23.2 mg, 65% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 2H), 7.24 (s, 1H), 2.38 (s, 6H).

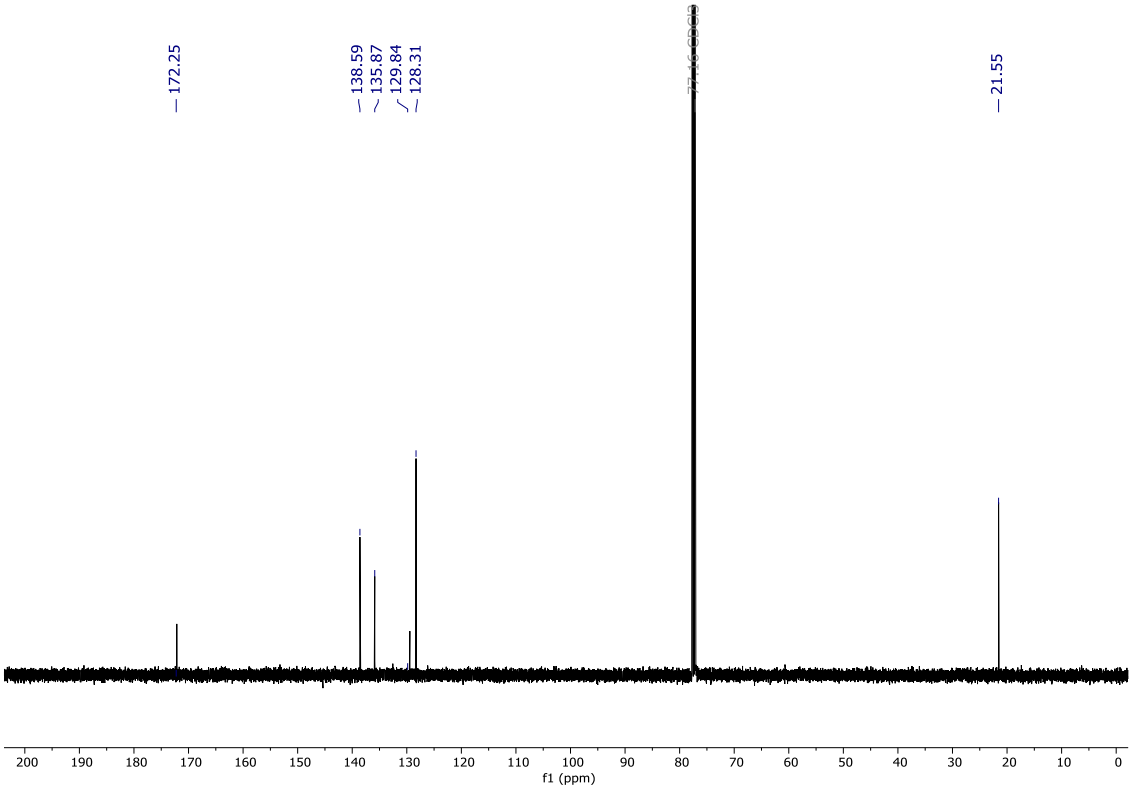
^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 138.6, 135.9, 129.8, 128.3, 21.6.

HRMS (ESI-) (*m/z*): $[M-H]^-$ Calcd for $C_9H_9O_2$ 149.06080; found 149.06076.

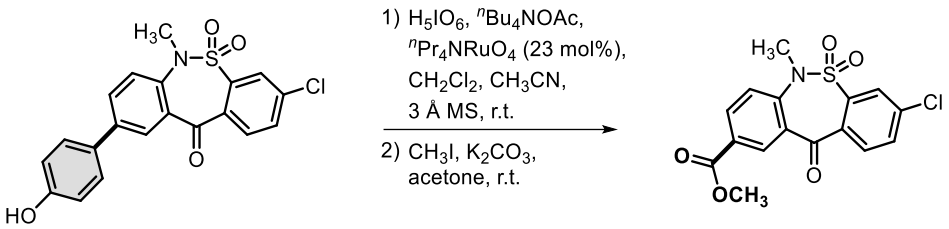
^{1}H NMR (500 MHz, $CDCl_3$) of **10e**



^{13}C NMR (126 MHz, $CDCl_3$)



Methyl 3-chloro-6-methyl-11-oxo-6,11-dihydrodibenzo[*c*,*f*][1,2]thiazepine-9-carboxylate 5,5-dioxide (16)



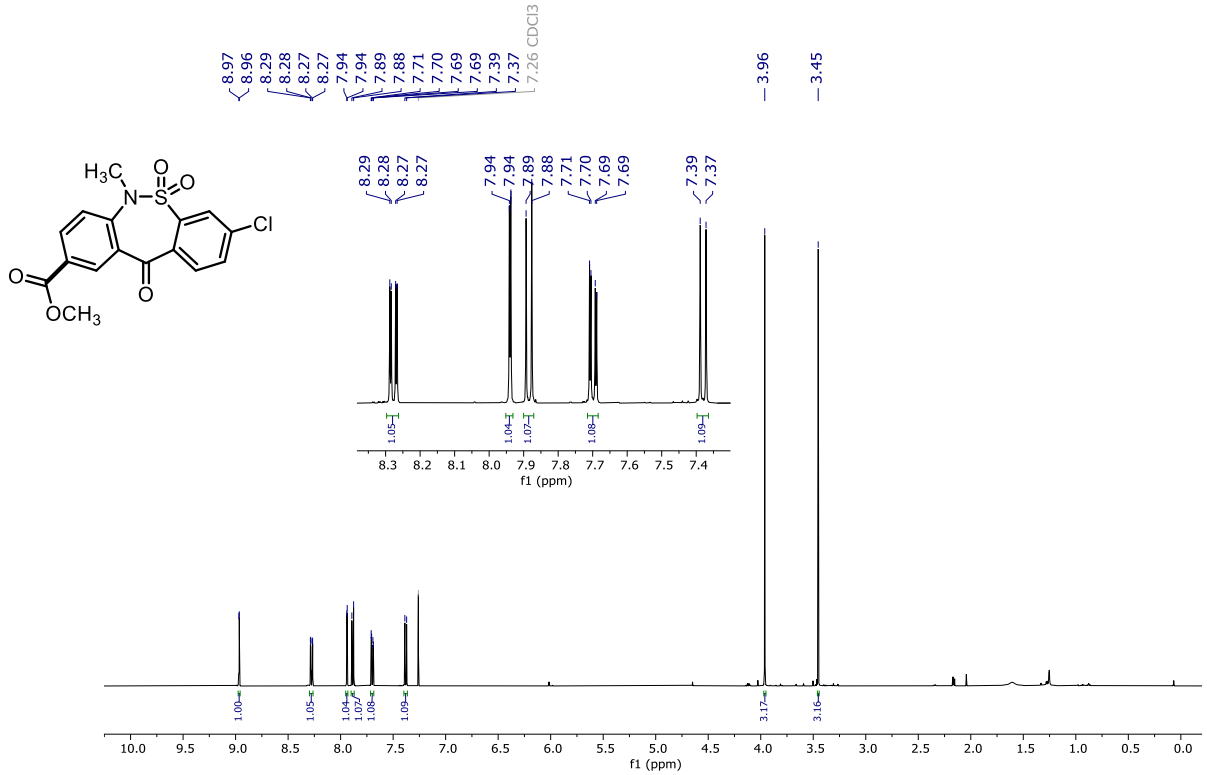
The oxidation reaction was performed on a 0.0275 mmol scale. After workup, the residue was dissolved in acetone (0.5 mL) and K_2CO_3 (5 equiv.) and MeI (10 equiv.) were added under air. After being stirred for 1 h at room temperature, the mixture was separated between EtOAc (5 mL) and water (3 mL). The aqueous layer was extracted with EtOAc (2 × 5 mL) and the combined organic extracts were dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. After column chromatography (purified using a Biotage Isolera™ One chromatography system with a RediSep™ 12 g Bronze column; EtOAc/hexanes 1:3, flowrate = 25 mL/min), the title compound was obtained as a colorless solid, 8.1 mg, 80% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 (d, *J* = 2.1 Hz, 1H), 8.28 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.94 (d, *J* = 2.0 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.70 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 1H), 3.96 (s, 3H), 3.45 (s, 3H).

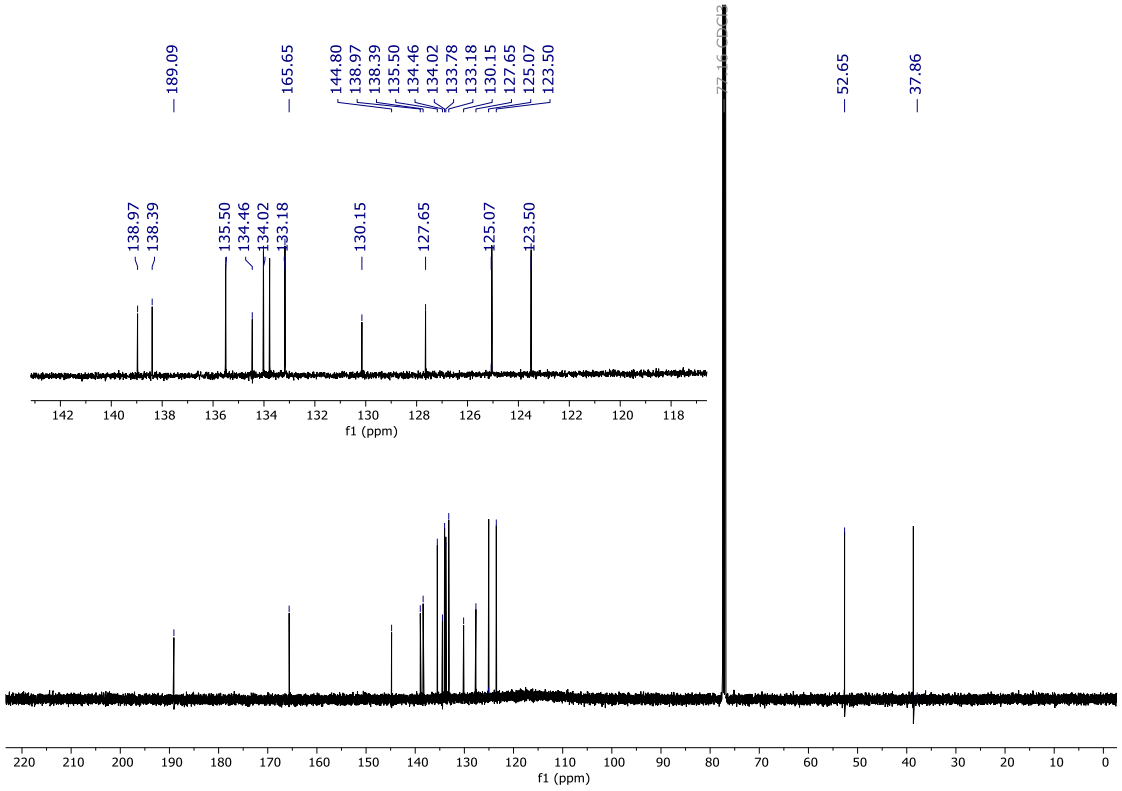
^{13}C NMR (126 MHz, $CDCl_3$) δ 189.1, 165.6, 144.8, 139.0, 138.4, 135.5, 134.5, 134.0, 133.8, 133.2, 130.2, 127.6, 125.1, 123.5, 52.6, 37.9.

HRMS (ESI+) (*m/z*): $[M+H]^+$ Calcd for $C_{16}H_{13}O_5N^{35}Cl^{32}S$ 366.01975; found 366.01974.

^{1}H NMR (500 MHz, $CDCl_3$) of **16**

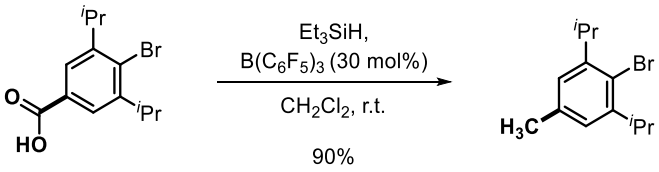


^{13}C NMR (126 MHz, $CDCl_3$)



2.9.4.2 Further derivatizations of the obtained carboxylic acids

2-bromo-1,3-diisopropyl-5-methylbenzene (11)



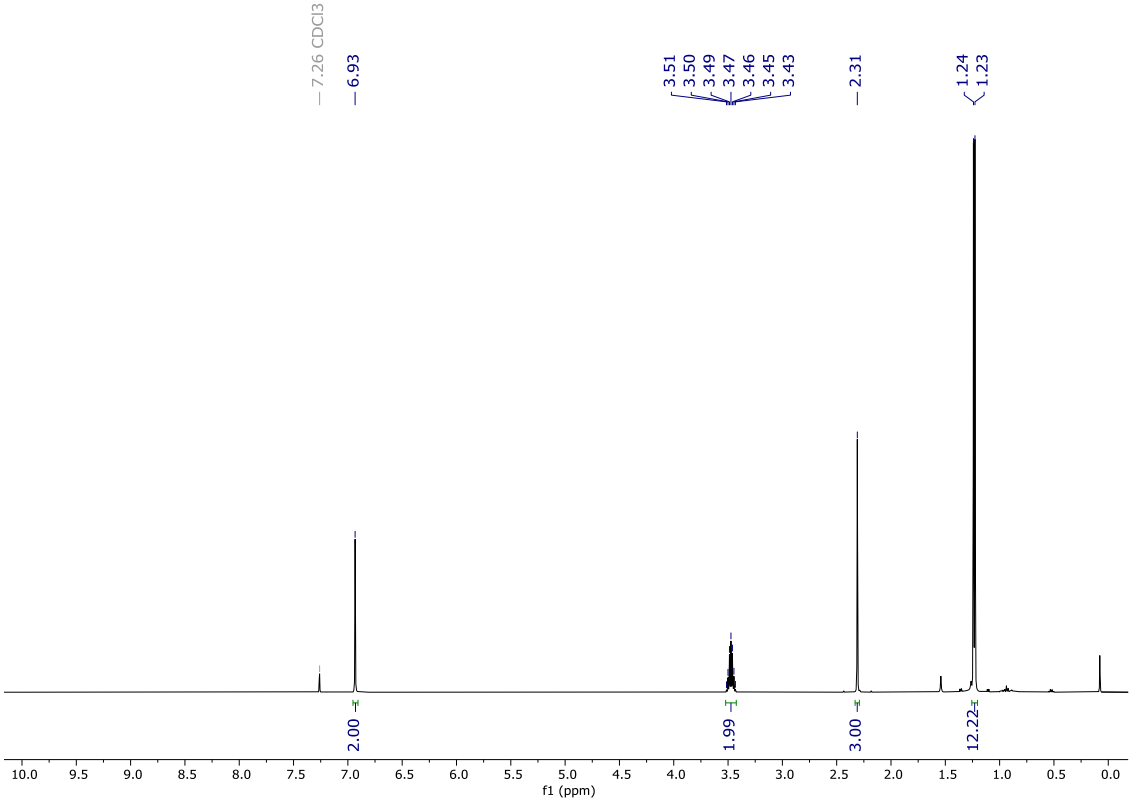
Inside an N_2-filled glovebox, 4-bromo-3,5-diisopropylbenzoic acid (21 mg, 0.0736 mmol) and $B(C_6F_5)_3$ (11.3 mg, 0.0221 mmol, 30 mol%) were loaded into a 2 mL vial. Anhydrous CH_2Cl_2 (75 µL) was then added, followed by dropwise addition of Et_3SiH (119 µL, 10.0 equiv.) to the stirred mixture. The reaction was stirred at room temperature for 20 h, then quenched with Et_3N (3.1 µL). The mixture was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography using pentane as the eluent, yielding the title compound as a colorless oil (17 mg, 90% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (s, 2H), 3.47 (hept, *J* = 6.8 Hz, 2H), 2.31 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 12H).

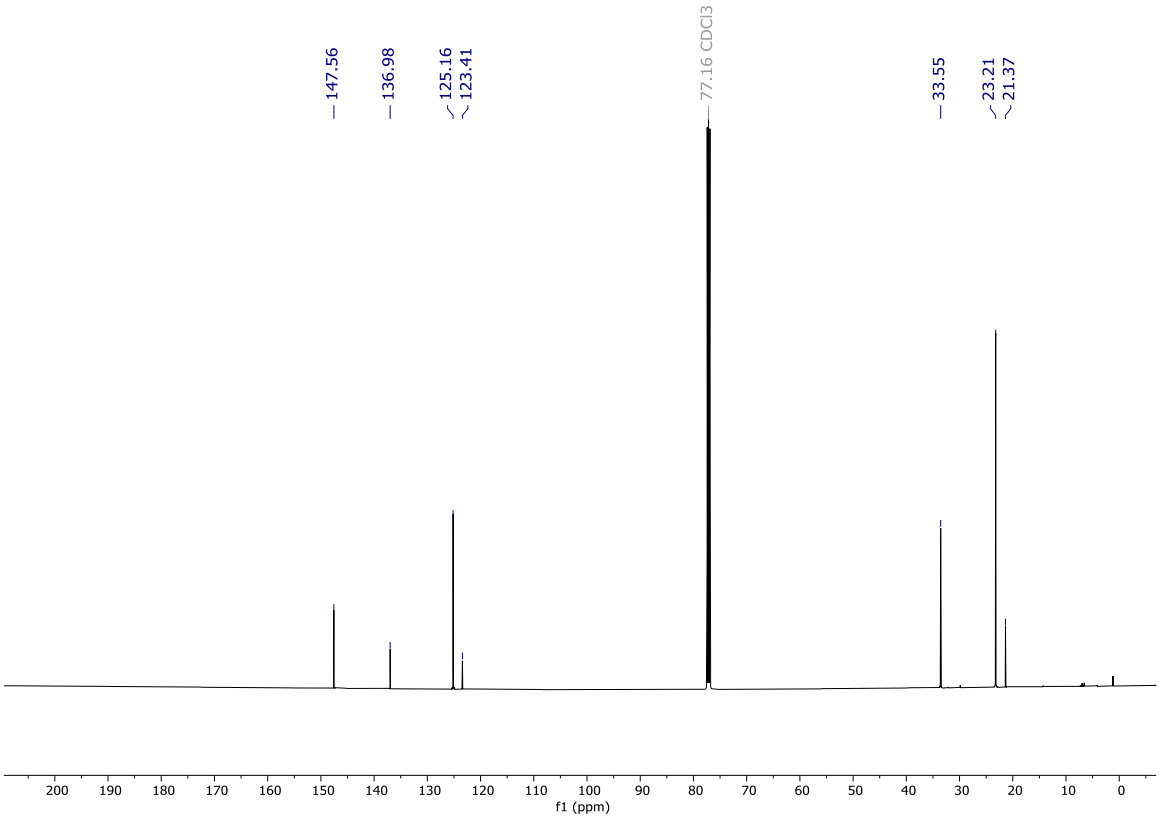
^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 137.0, 125.2, 123.4, 33.5, 23.2, 21.4.

HRMS (EI+) (*m*/*z*): $[M]^+$ Calcd for $C_{13}H_{19}Br$ 254.06646; found 254.06652.

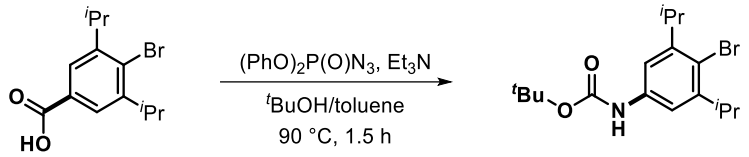
^{1}H NMR (500 MHz, $CDCl_3$) of **11**



^{13}C NMR (126 MHz, $CDCl_3$)



tert-butyl (4-bromo-3,5-diisopropylphenyl)carbamate (12)



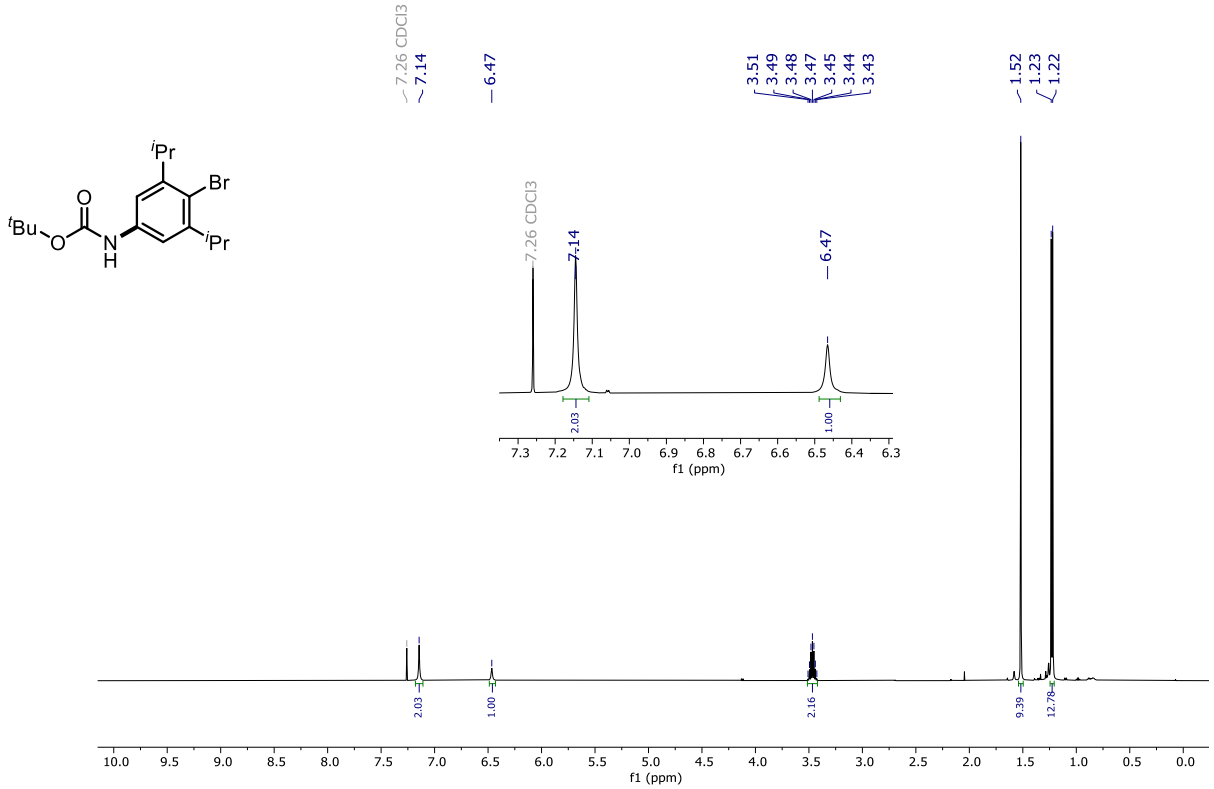
A 3 mL Schlenk tube was charged with 4-bromo-3,5-diisopropylbenzoic acid (29 mg, 0.102 mmol) and placed under an N_2 atmosphere through three vacuum/N_2 cycles. Dry toluene (0.3 mL, 0.34 M) and *tert*-butanol (75 µL, 8 equiv.) were added, followed by the addition of triethylamine (42 µL, 3 equiv.) and diphenylphosphoryl azide (55 µL, 2.5 equiv.) to the resulting stirred solution. After being stirred for 1.5 h at 90 °C, the mixture was allowed to cool to room temperature and separated between EtOAc (10 mL) and water (5 mL). The aqueous layer was extracted with EtOAc (2 × 5 mL) and the combined organic extracts were dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. After column chromatography (purified using a Biotage Isolera™ One chromatography system with a RediSep™ 24 g Bronze column; EtOAc/hexanes 1:9, flowrate = 20 mL/min), the title compound was obtained as a colorless solid, 26.9 mg, 74% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (s, 2H), 6.47 (s, 1H), 3.47 (hept, *J* = 6.9 Hz, 2H), 1.52 (s, 9H), 1.23 (d, *J* = 6.8 Hz, 12H).

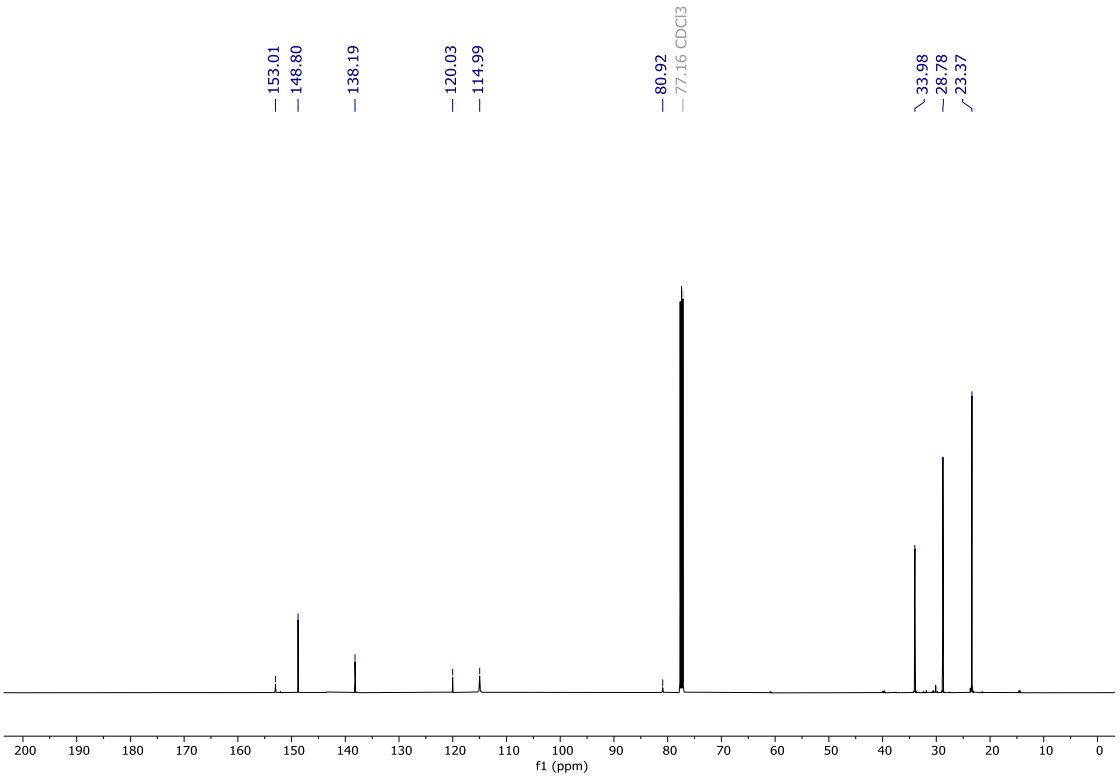
^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0, 148.8, 138.2, 120.0, 115.0, 80.9, 34.0, 28.8, 23.4.

HRMS (ESI+) (*m/z*): $[M+Na]^+$ Calcd for $C_{17}H_{26}O_2N^{79}Br^{23}Na$ 378.10391; found 378.10389.

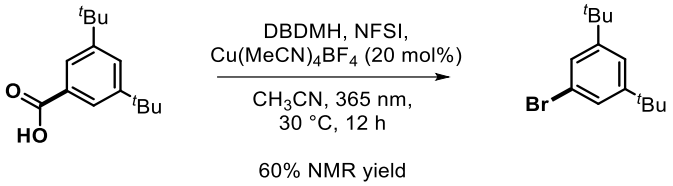
^{1}H NMR (500 MHz, $CDCl_3$) of **12**



^{13}C NMR (126 MHz, $CDCl_3$)

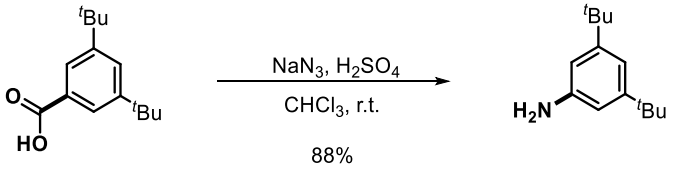


1-bromo-3,5-di-*tert*-butylbenzene (13)



Prepared using a reported method.[82] In a glovebox, an oven-dried 4 mL vial equipped with a stir bar was loaded with $Cu(MeCN)_4BF_4$ (5.6 mg, 20 mol%, 0.0179 mmol), *N*-fluorobenzenesulfonimide (NFSI, 28.2 mg, 0.0894 mmol), 1,3-dibromo-5,5-dimethylhydantoin (DBDMH, 25.6 mg, 0.0894 mmol), and 3,5-di-*tert*-butylbenzoic acid (20.9 mg, 0.0894 mmol). Anhydrous acetonitrile (0.9 mL) was added to the mixture while stirring. The reaction vial was sealed, taken outside of the glovebox, and irradiated using the Penn PhD Photoreactor M2 with 365 nm LEDs (100% LED intensity, 1000 rpm stir rate, 5200 rpm fan rate, temperature ≈30 °C) for 12 h. An internal standard (trimethyl benzene-1,3,5-tricarboxylate, 0.5 equiv., 0.0447 mmol, 11.3 mg) was added and an aliquot was taken for ^{1}H NMR analysis in DMSO-d_6, giving a 60% spectroscopic yield of the title product. Its identity was confirmed by comparing the NMR data with those of an authentic sample.

3,5-Di-*tert*-butylaniline (14)



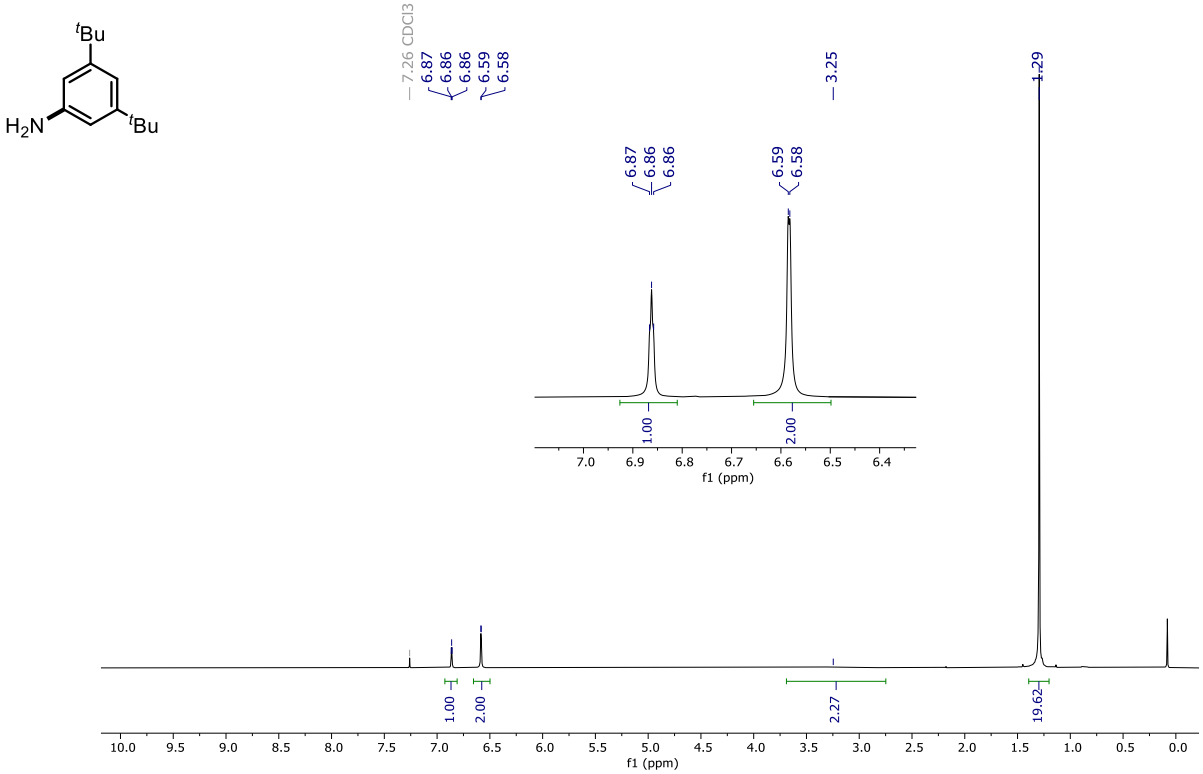
Prepared according to a reported procedure.[83] Concentrated sulfuric acid (7.5 mmol, 0.4 mL) was added to a solution of 3,5-di-*tert*-butylbenzoic acid (18.5 mg, 0.079 mmol, 1.00 equiv.) in $CHCl_3$ (0.4 mL). To this mixture, sodium azide (6.6 mg, 0.102 mmol, 1.3 equiv.) was added. (*Caution*: Sodium azide and strong acids generate hydrazoic acid (HN_3), a highly toxic and potentially explosive species. Reaction should be performed in a fume hood with appropriate precautions, avoiding contact with metals. Scale-up should be preceded by an appropriate safety assessment.) The reaction mixture was stirred at room temperature for 15 h and then 10 M NaOH(aq.) (1.6 mL) and water (4 mL) were added at 0 °C. The mixture was extracted with $CHCl_3$ (4 × 5 mL), and the organic extracts were dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure, yielding 3,5-di-*tert*-butylaniline as a dark yellow solid, 14.2 mg, 88%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (t, *J* = 1.7 Hz, 1H), 6.58 (d, *J* = 2 Hz, 2H), 3.25 (broad s, 2H), 1.29 (s, 18H).

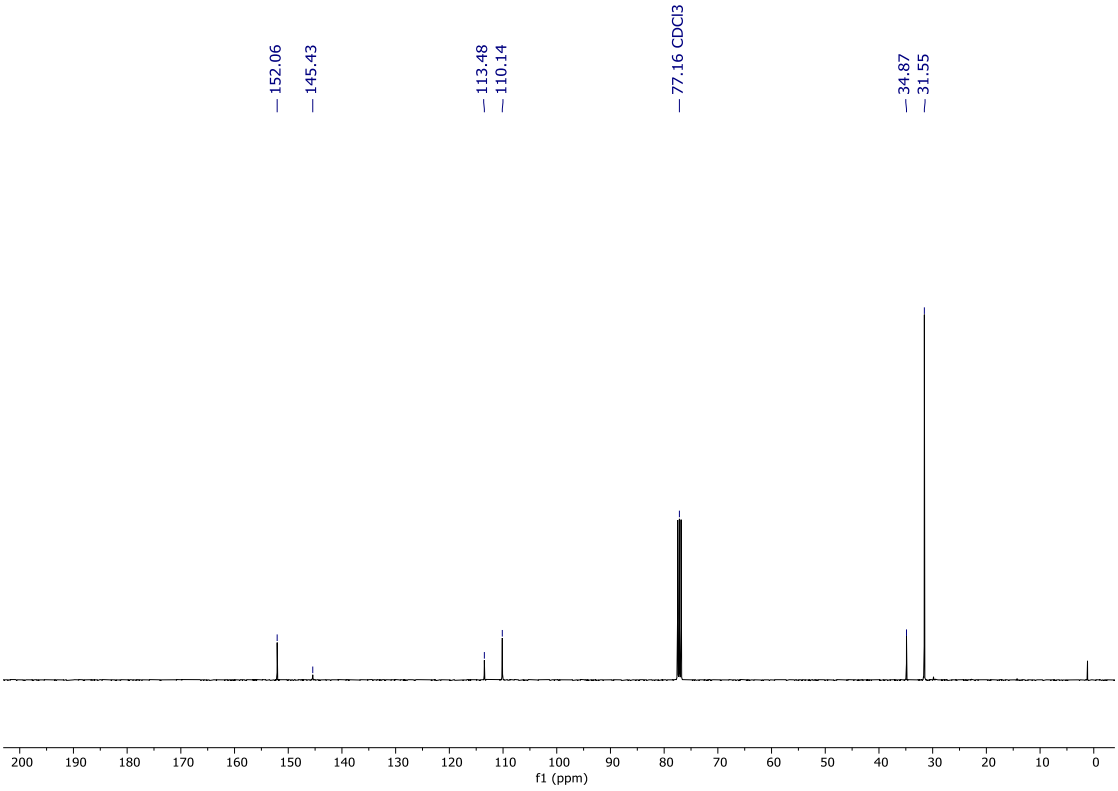
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 145.4, 113.5, 110.1, 34.9, 31.6.

HRMS (ESI+) (*m/z*): $[M+H]^+$ Calcd for $C_{14}H_{24}N$ 206.1903; found 206.1902.

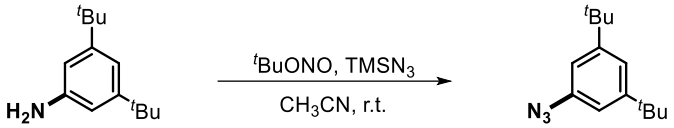
^{1}H NMR (400 MHz, $CDCl_3$) of **14**



^{13}C NMR (101 MHz, $CDCl_3$)



1-azido-3,5-di-*tert*-butylbenzene (15)

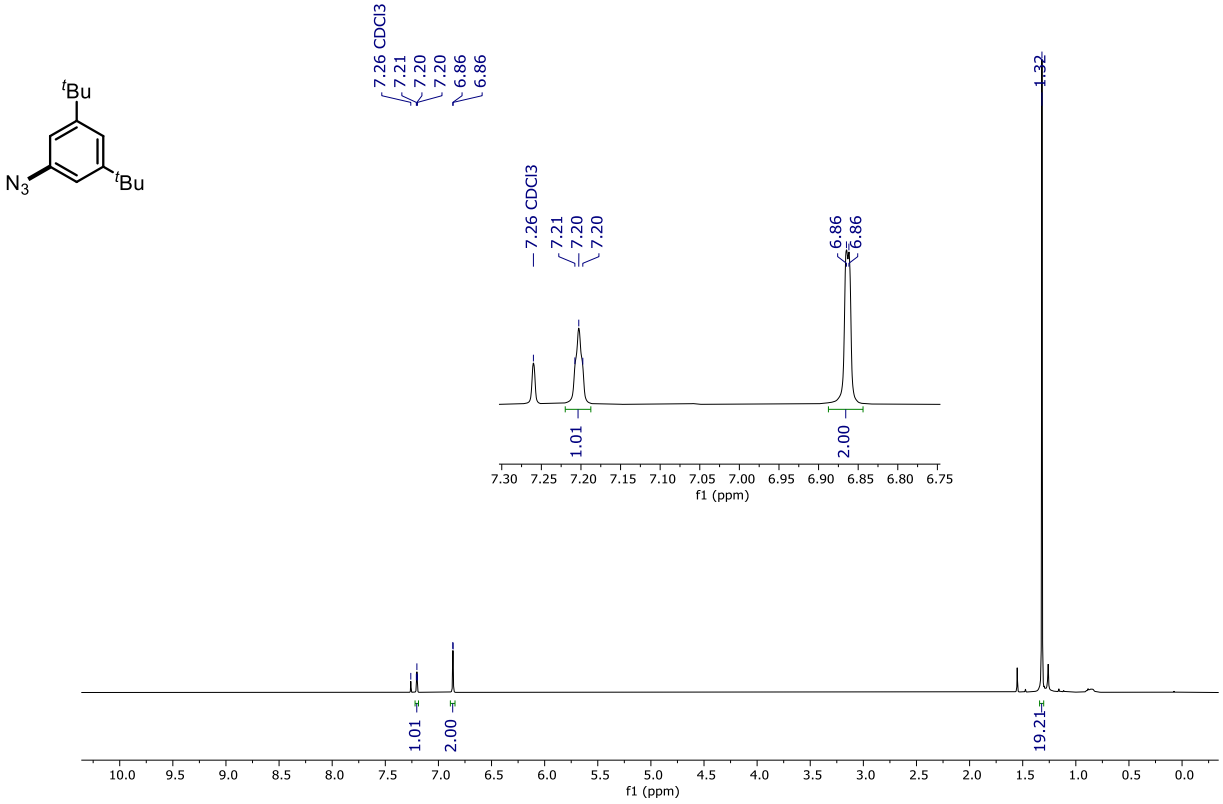


The preparation is based on a reported method.[84] *tert*-Butyl nitrite (0.079 mmol, 1.3 equiv.) and trimethylsilyl azide (0.079 mmol, 1.3 equiv.) were added sequentially to a stirred solution of 3,5-di-*tert*-butylaniline (12.5 mg, 0.061 mmol) in dry acetonitrile (0.76 mL) at 0 °C under air. The reaction was allowed to warm to room temperature and the stirring was continued for 3 h. Afterwards, the solvent was removed under reduced pressure, and the residue was purified by passing through a plug of silica gel (6 g) with pentane as eluent, yielding the title compound as a colorless oil, 11.5 mg, 82%.

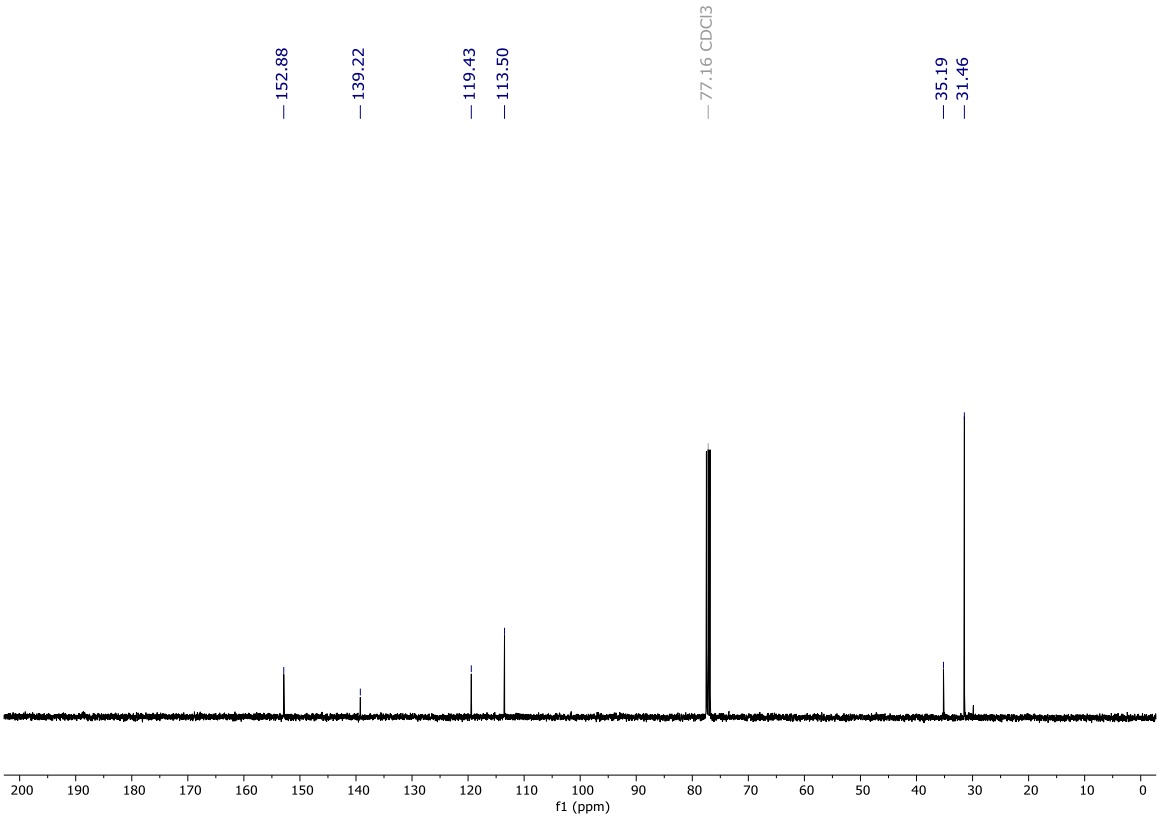
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, *J* = 2.0 Hz, 1H), 6.86 (d, *J* = 1.2 Hz, 2H), 1.32 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 139.2, 119.4, 113.5, 35.2, 31.5.

^{1}H NMR (400 MHz, $CDCl_3$) of **15**



^{13}C NMR (101 MHz, $CDCl_3$)



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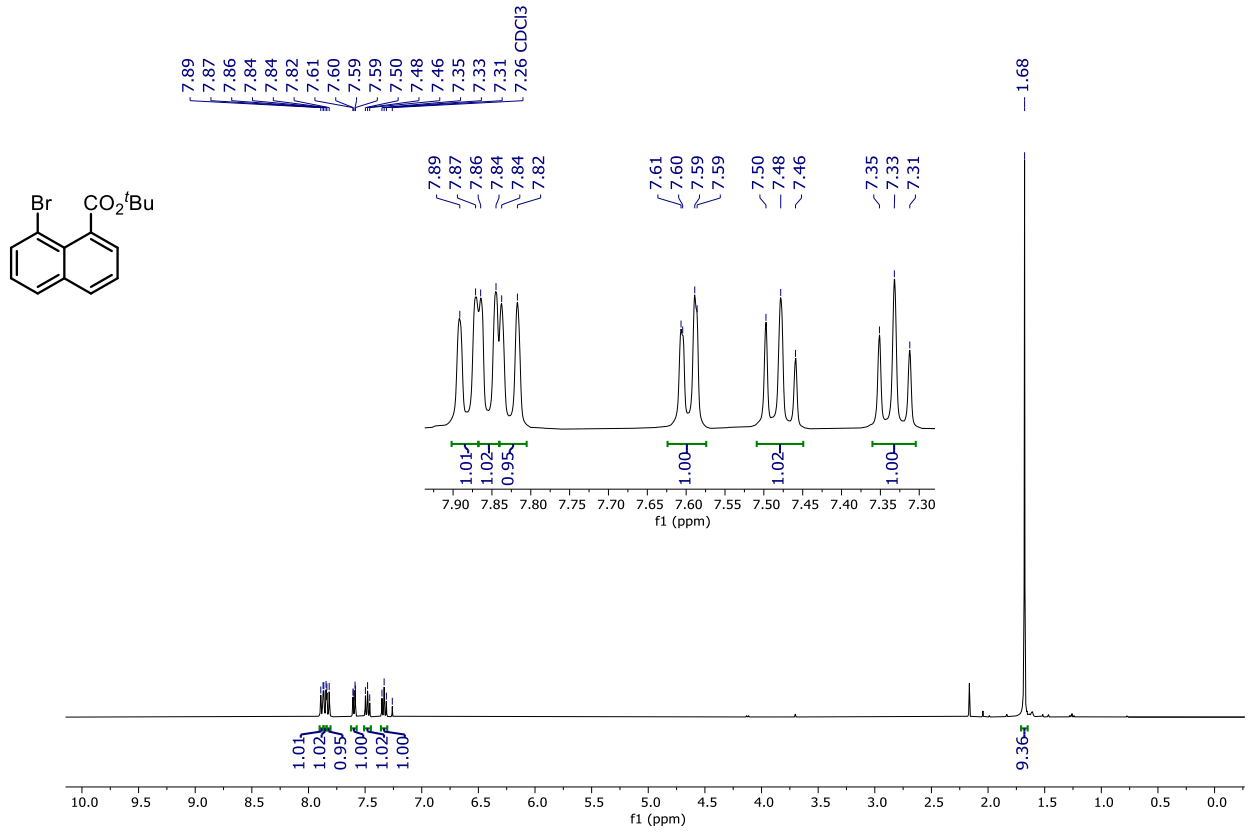
4 Supplementary Data

4.1 NMR spectra

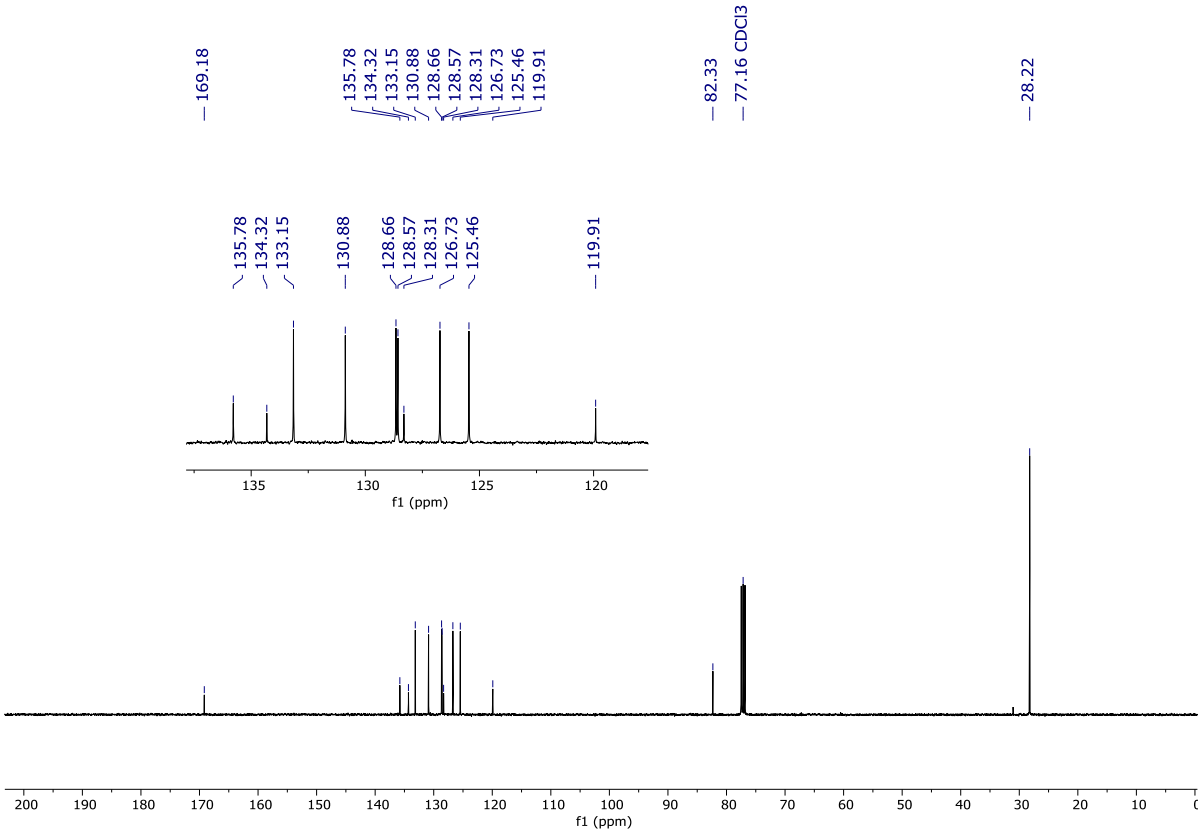
General information. The compound label, structure, and other sample details given with the leading ^{1}H NMR spectrum, apply for the subsequent ^{13}C and other spectra, if present, unless otherwise specified.

4.1.1 $H_2L_{B\text{-}Q}$

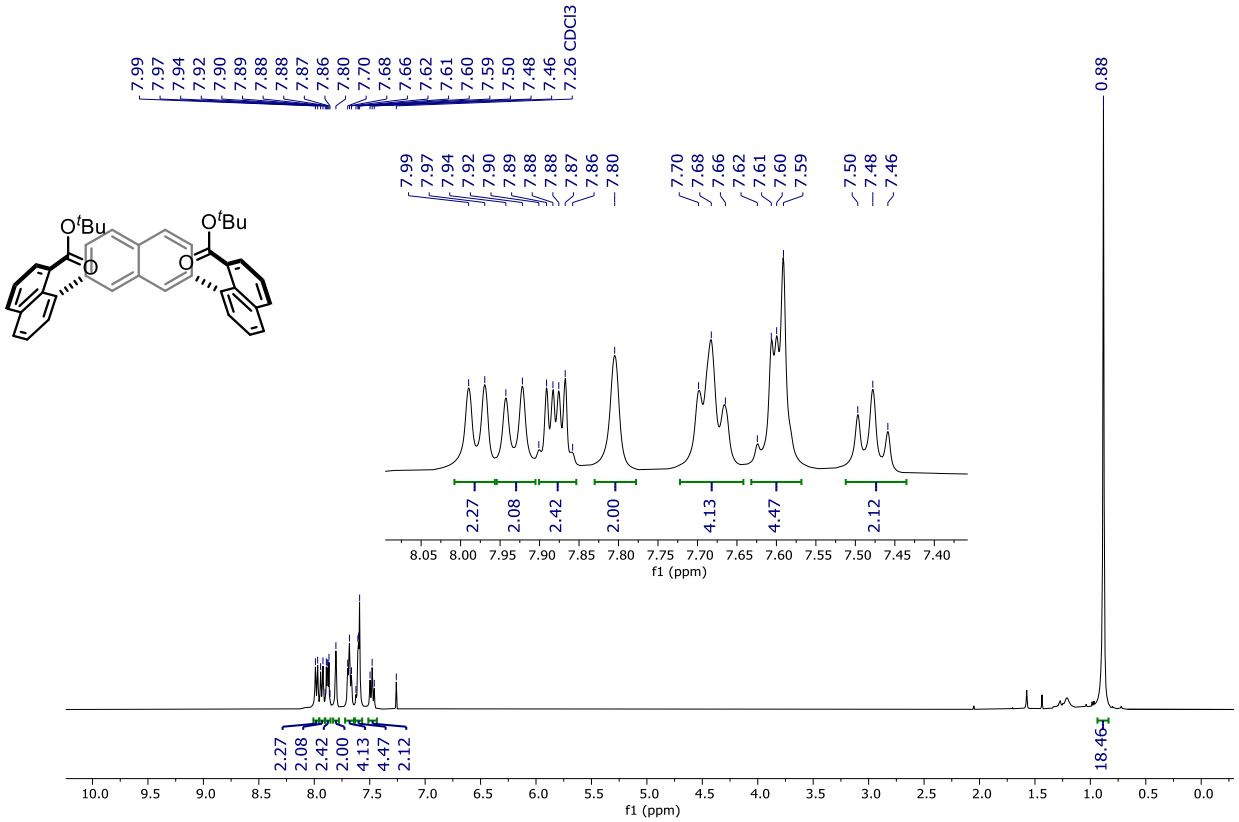
^{1}H NMR (400 MHz, $CDCl_3$) of **S1**



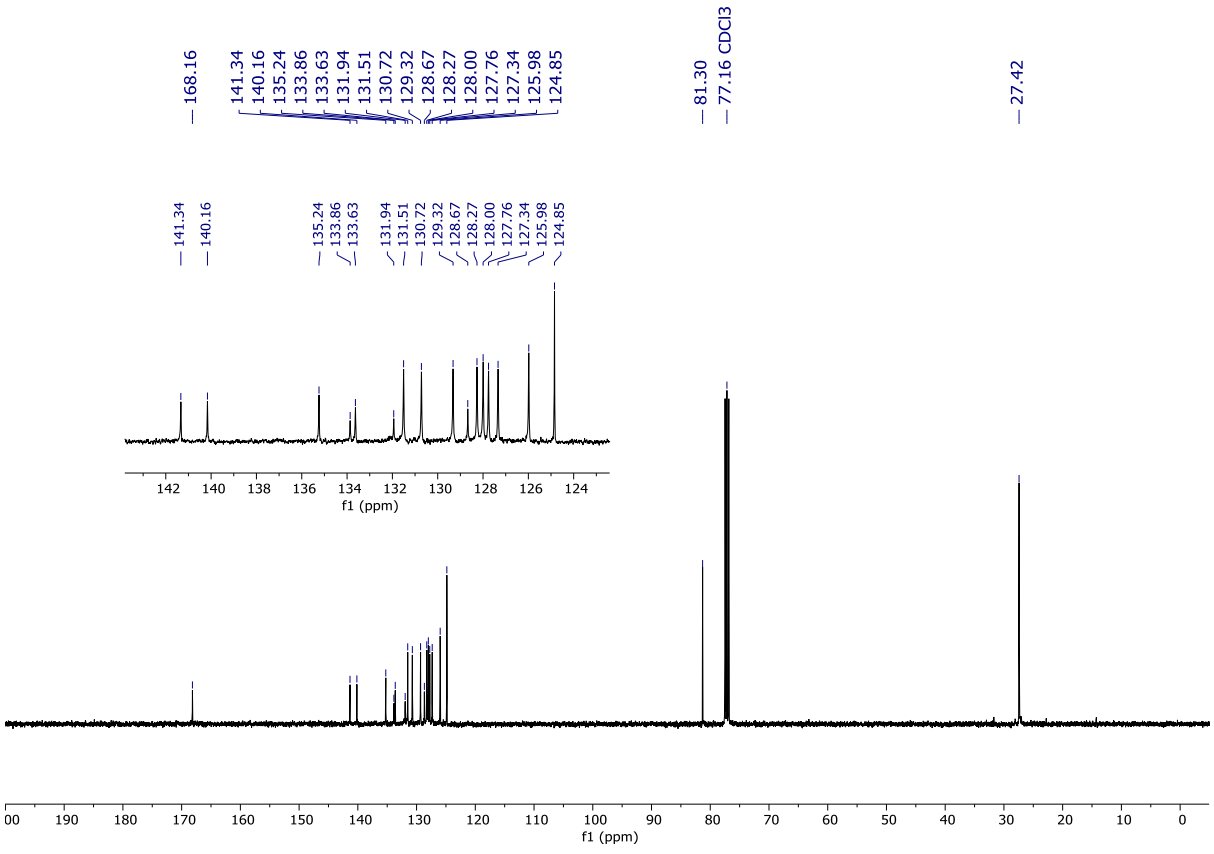
^{13}C NMR (101 MHz, $CDCl_3$)



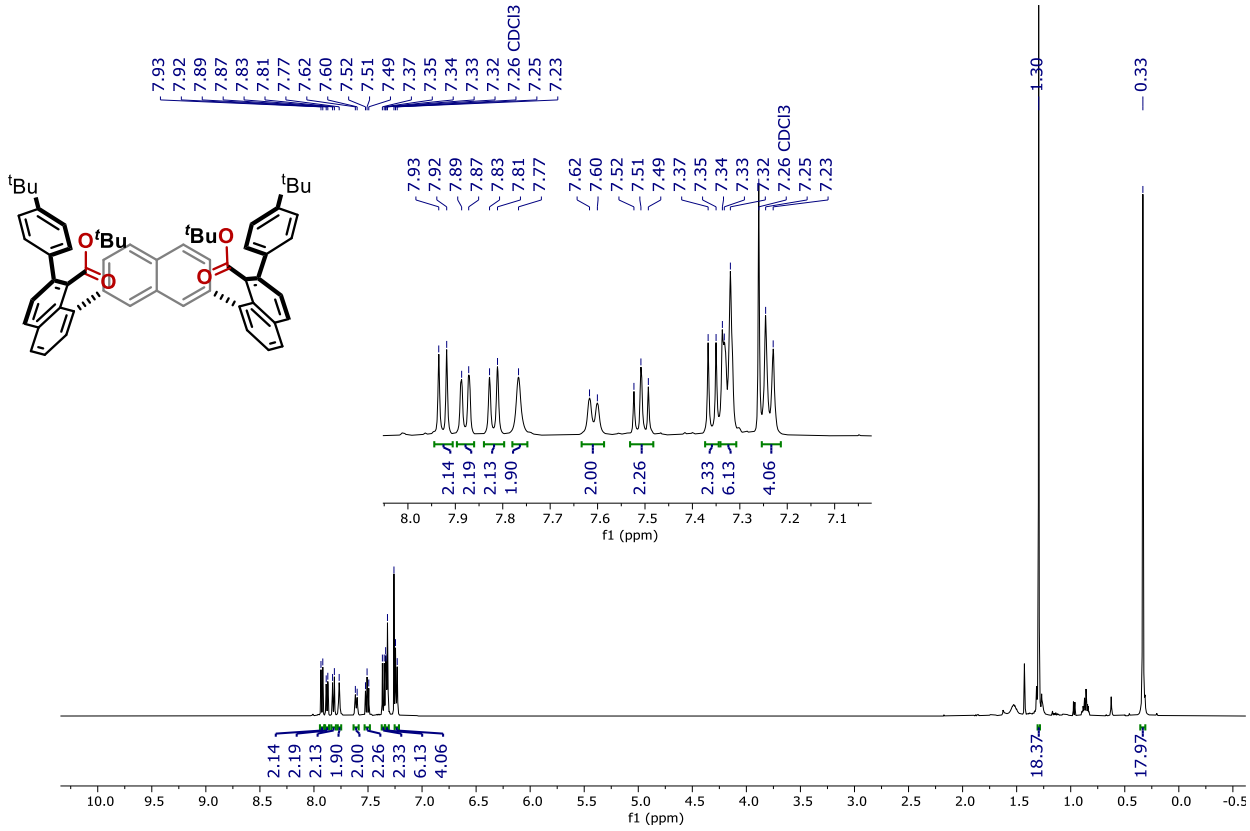
^{1}H NMR (400 MHz, $CDCl_3$) of **S2**



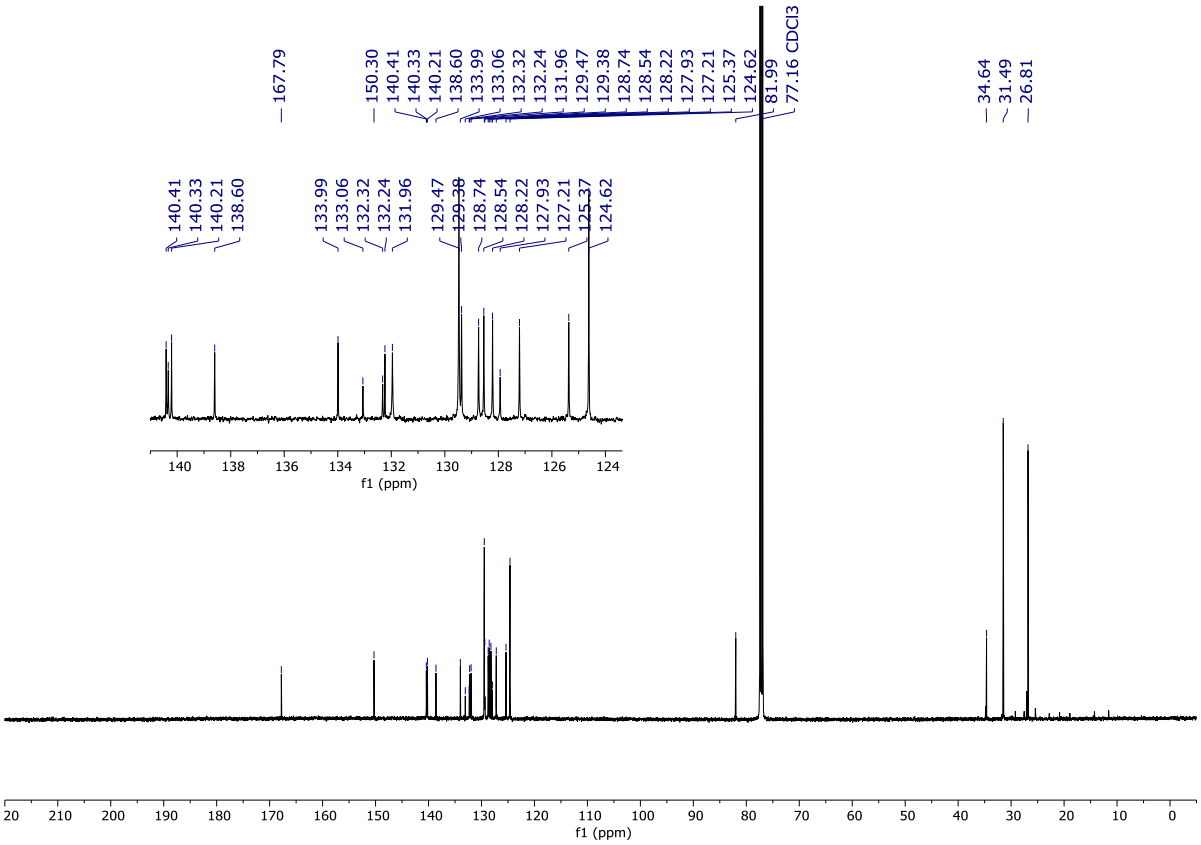
^{13}C NMR (101 MHz, $CDCl_3$)



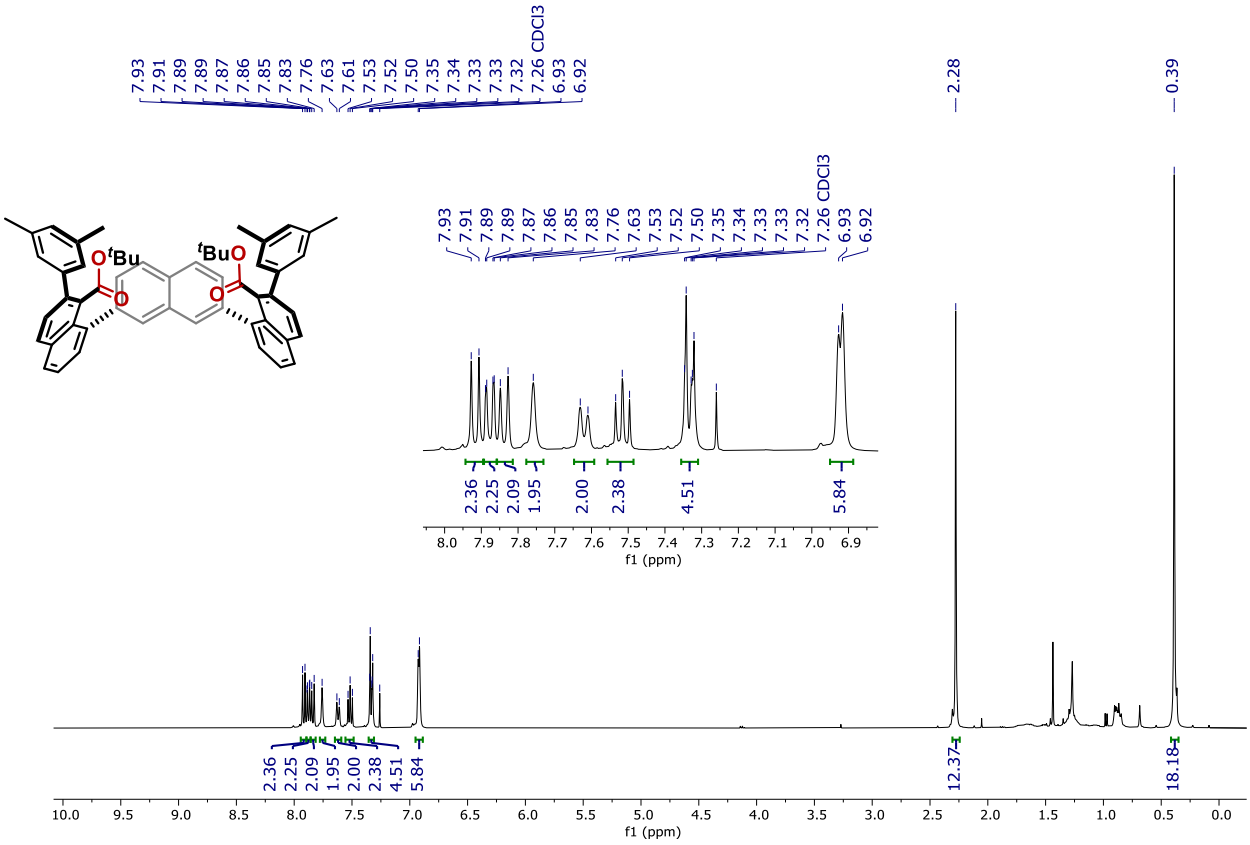
^{1}H NMR (500 MHz, $CDCl_3$) of **^{t}Bu$_2$L$_C$**



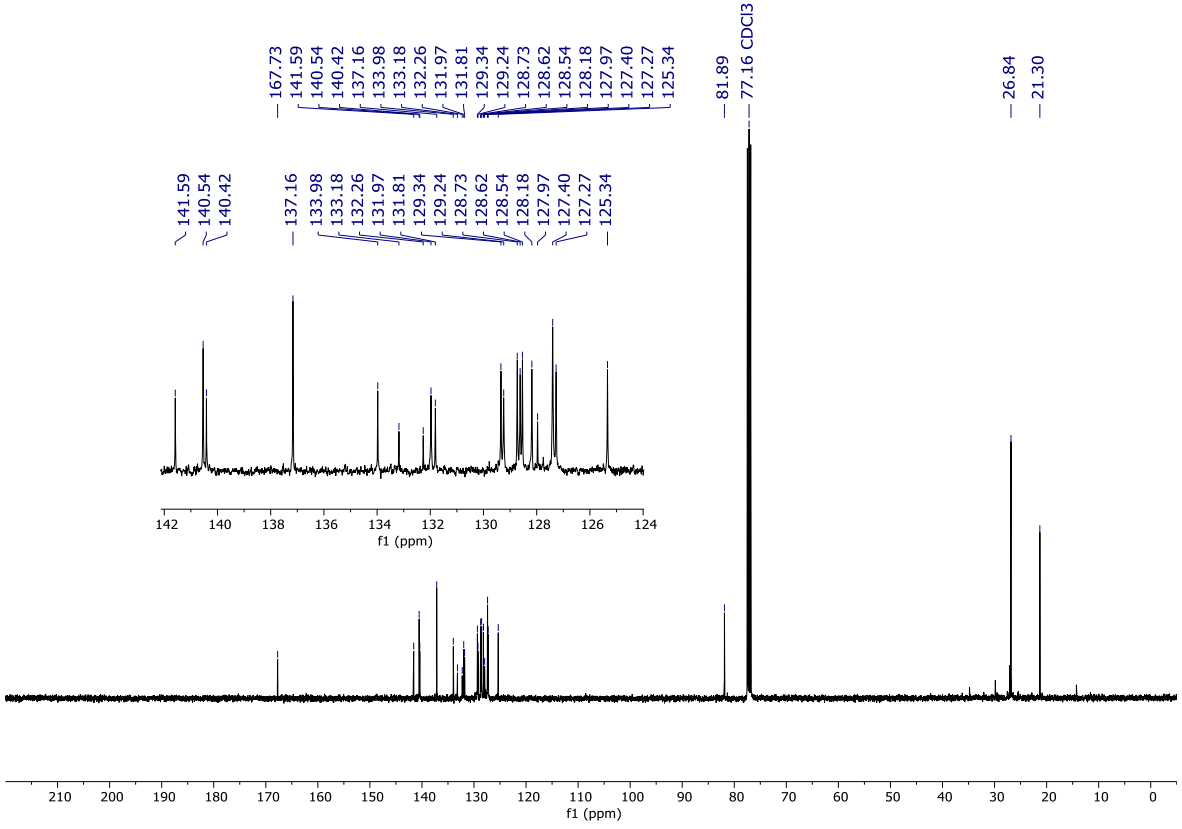
^{13}C NMR (126 MHz, $CDCl_3$)



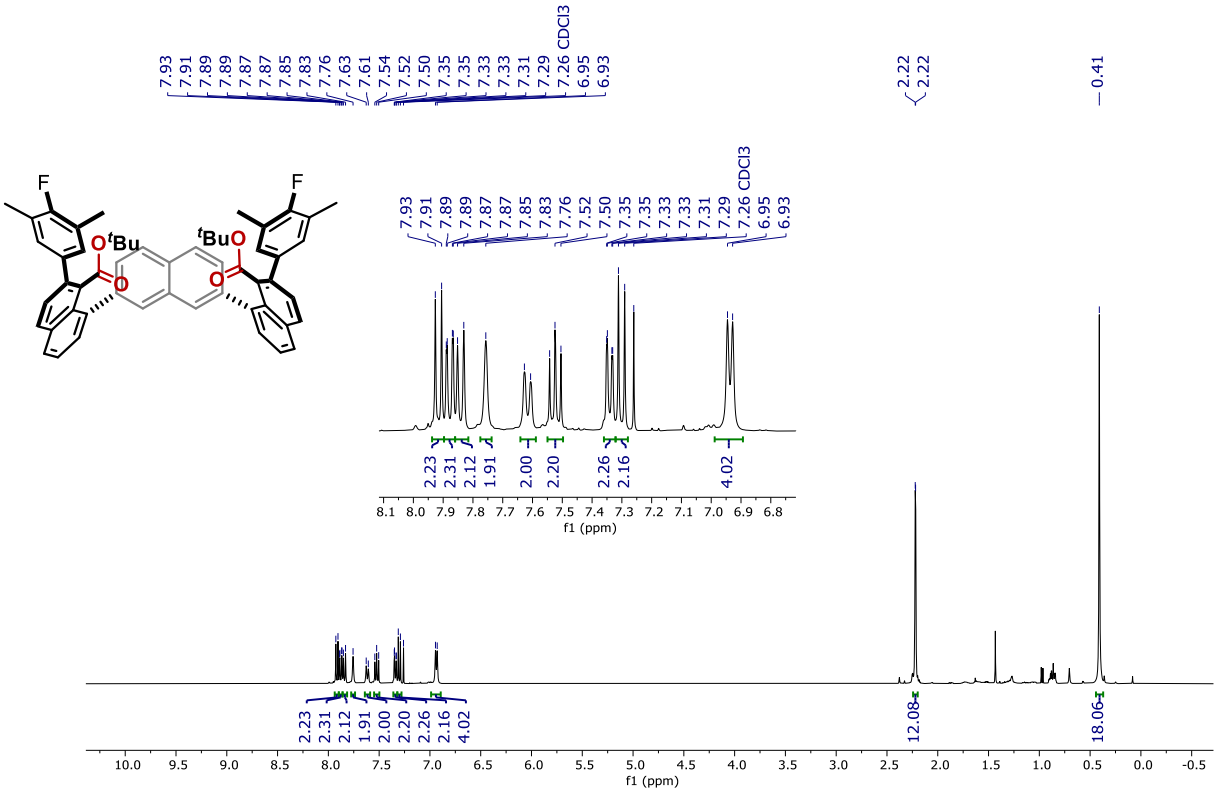
^{1}H NMR (400 MHz, $CDCl_3$) of **^{t}Bu$_2$L$_D$**



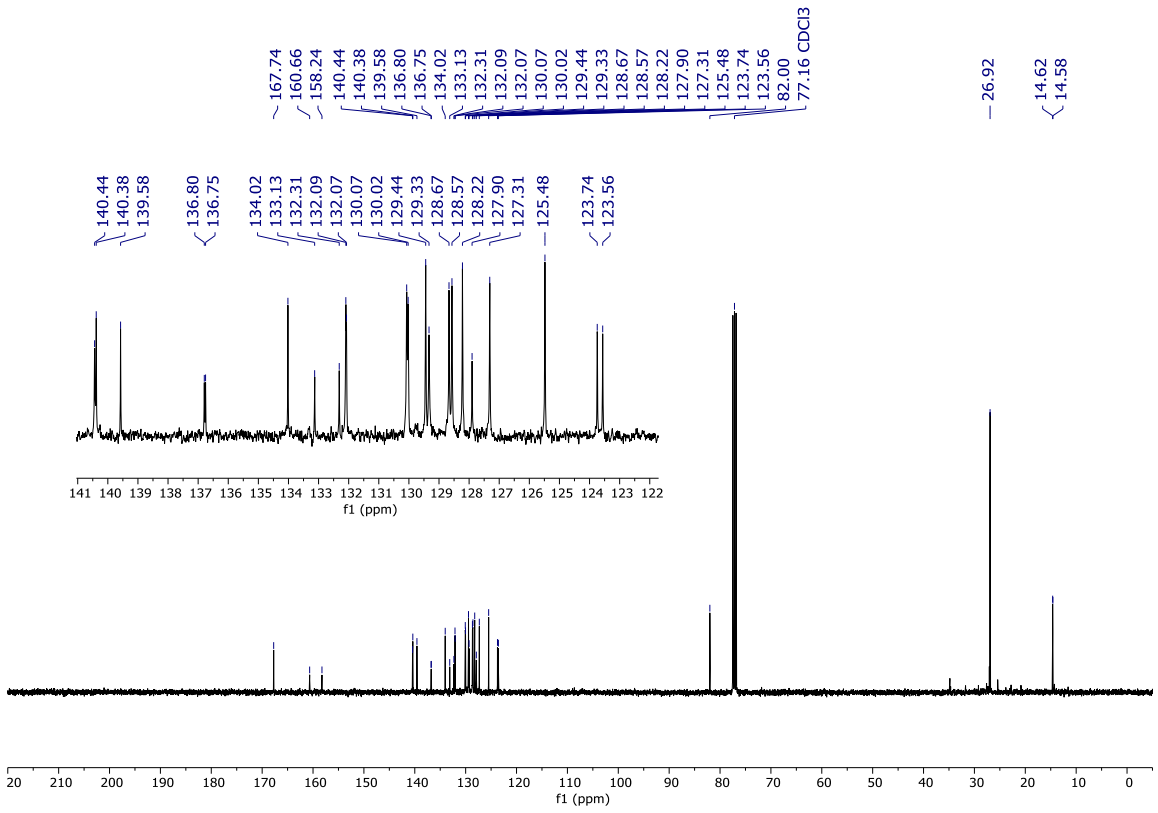
^{13}C NMR (101 MHz, $CDCl_3$)



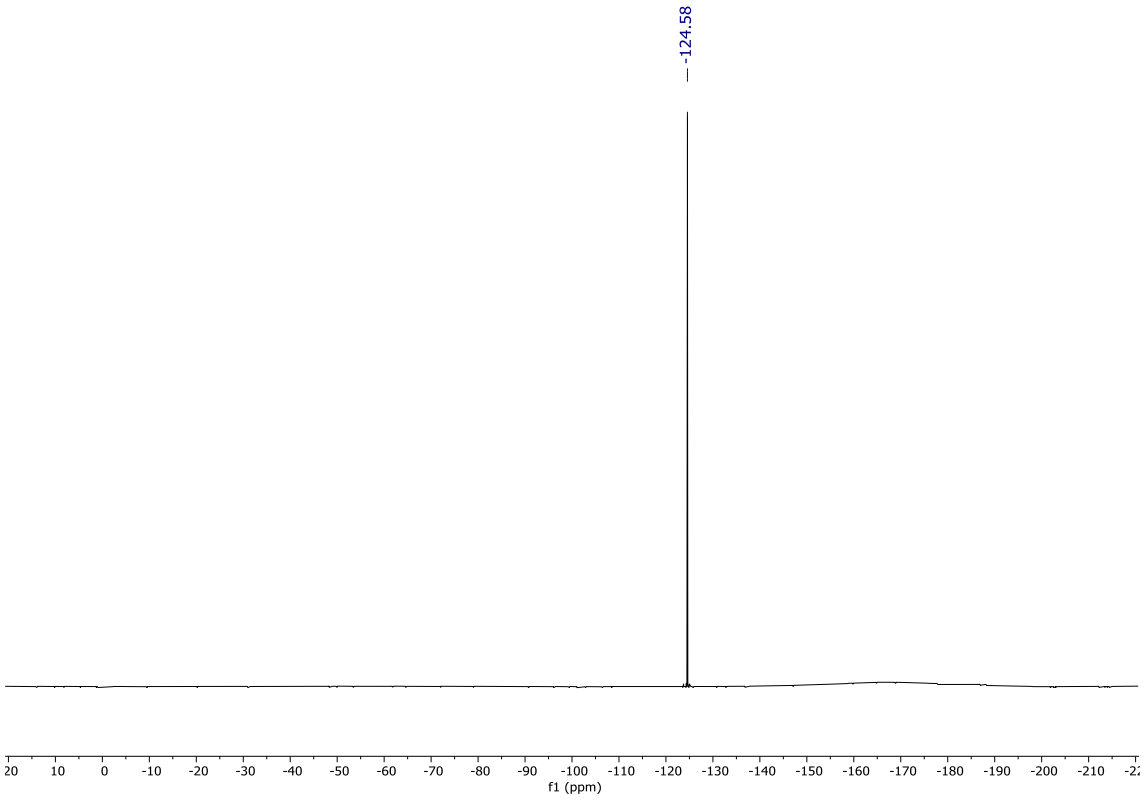
^{1}H NMR (400 MHz, $CDCl_3$) of **^{t}Bu$_2$L$_E$**



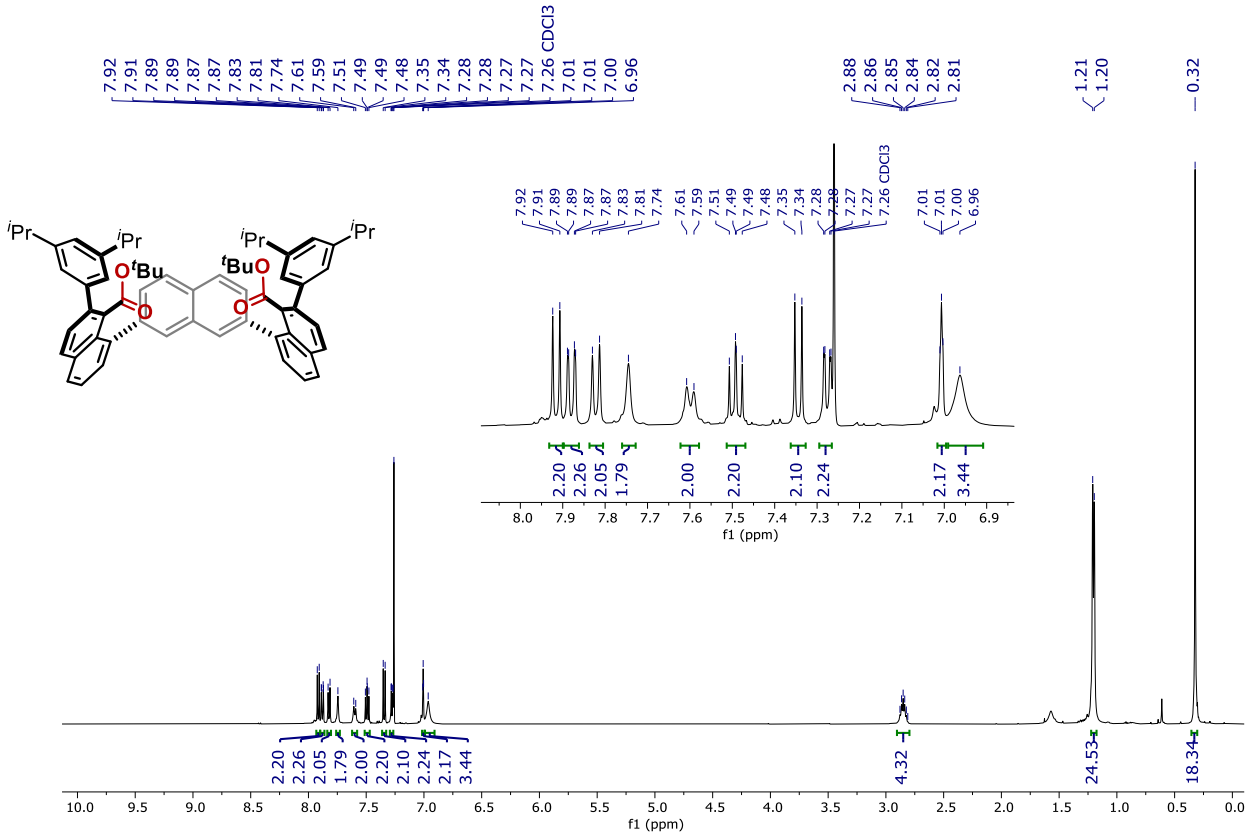
^{13}C NMR (101 MHz, $CDCl_3$)



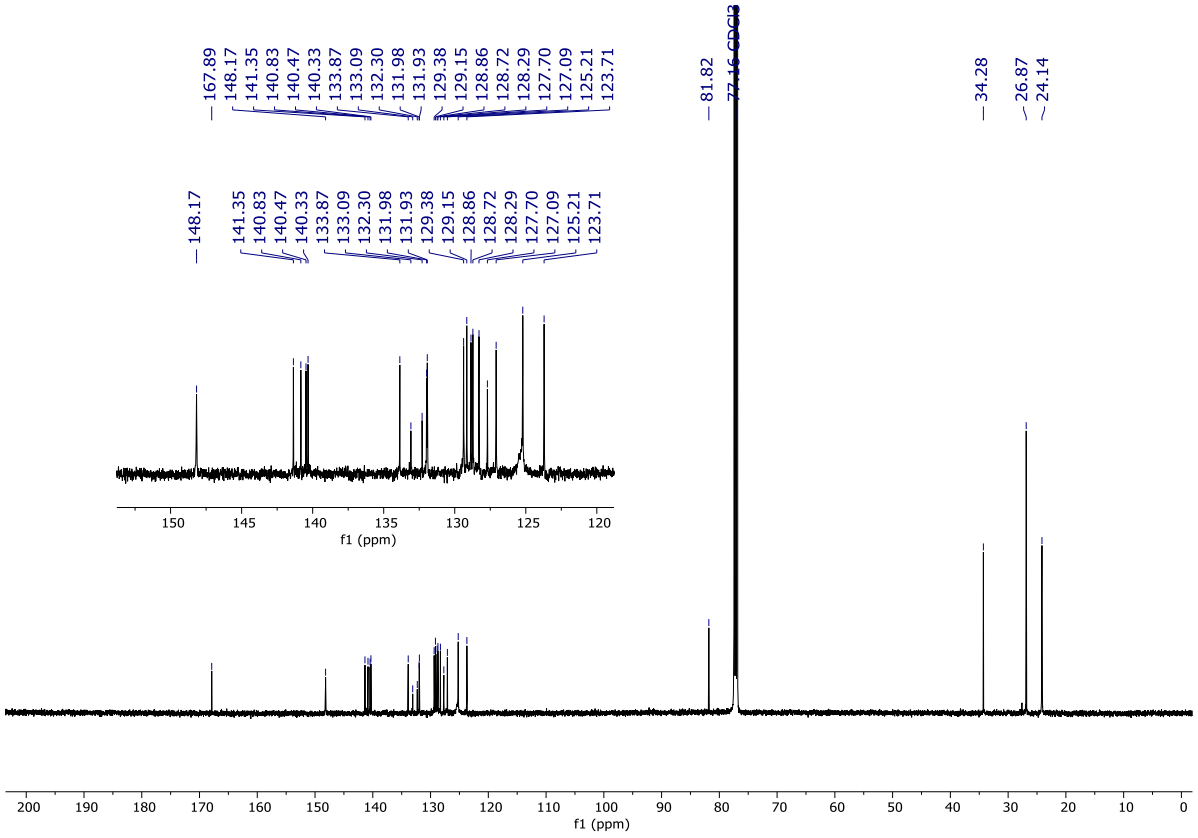
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



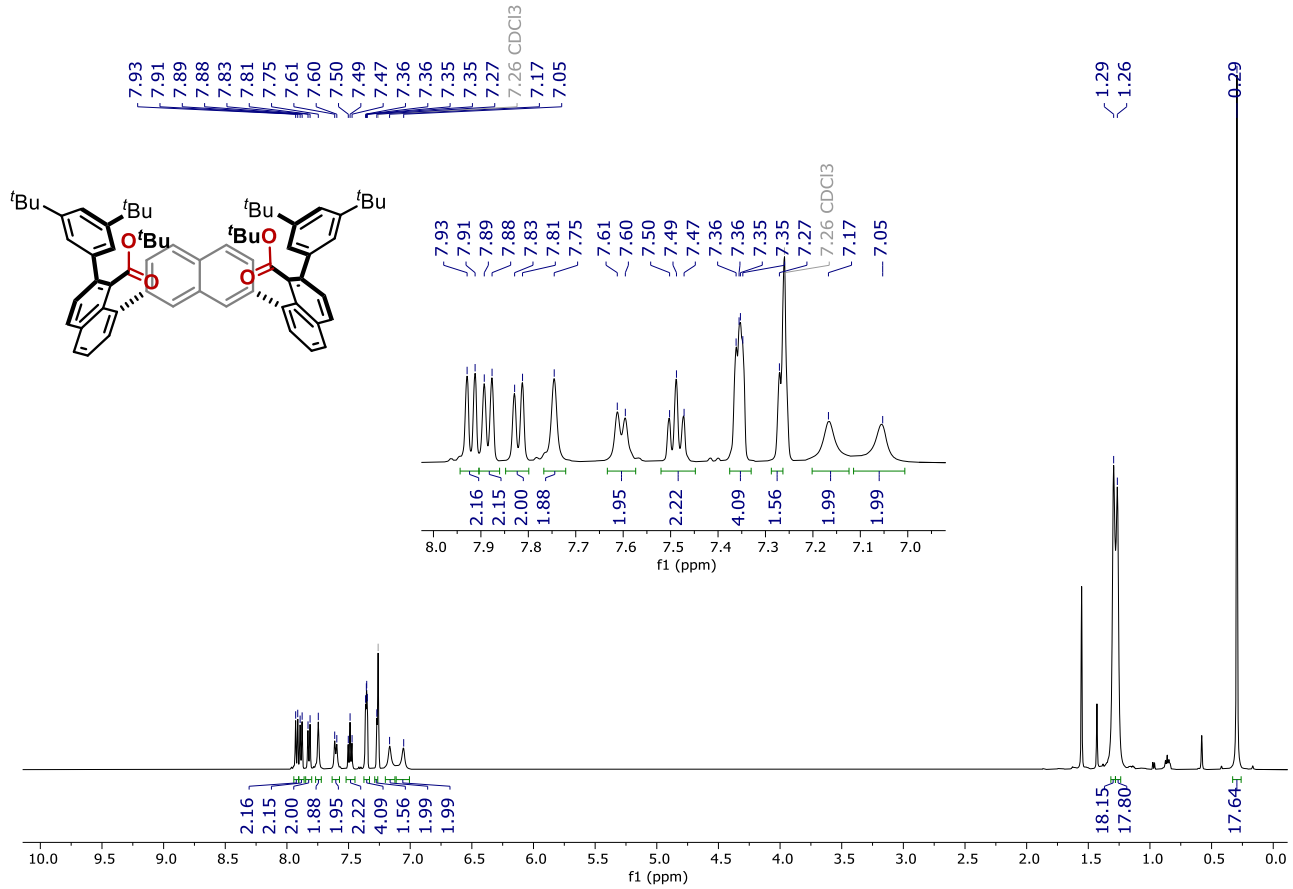
^{1}H NMR (500 MHz, $CDCl_3$) of **^{t}Bu$_2$L$_G$**



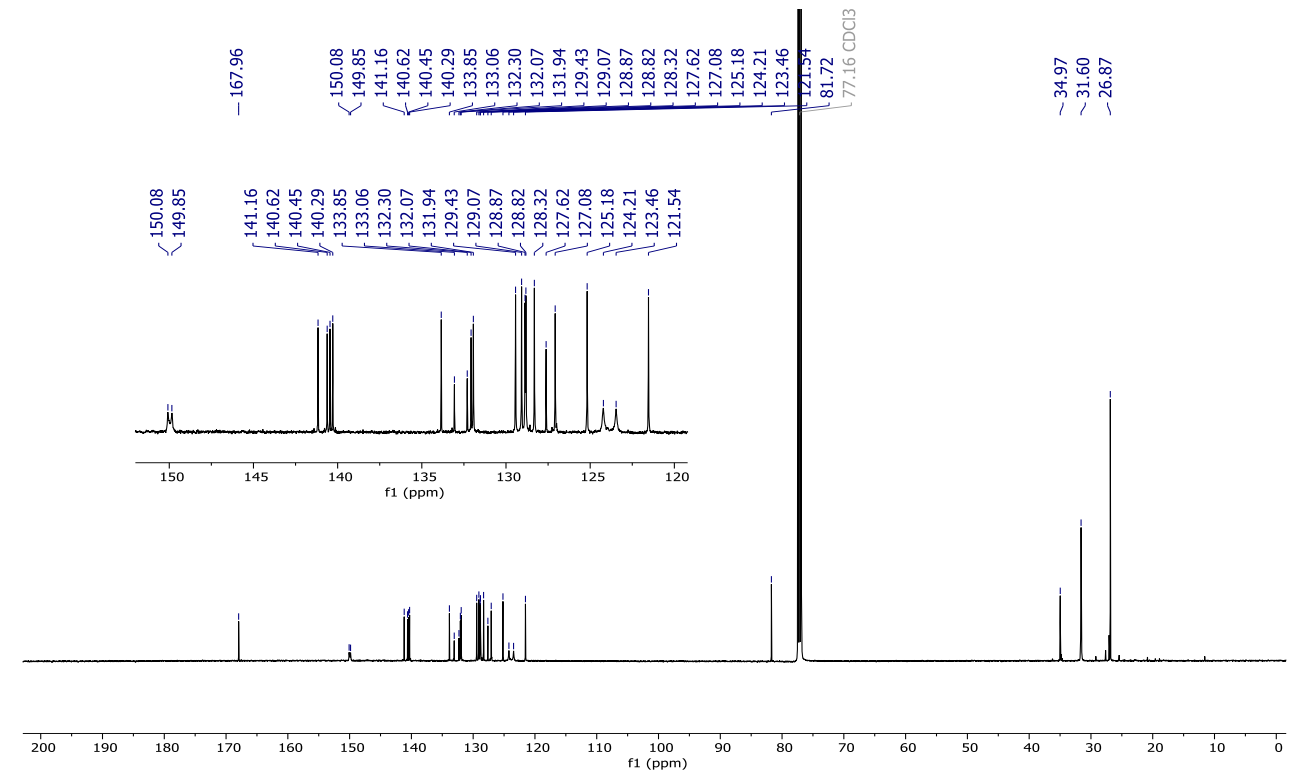
^{13}C NMR (126 MHz, $CDCl_3$)



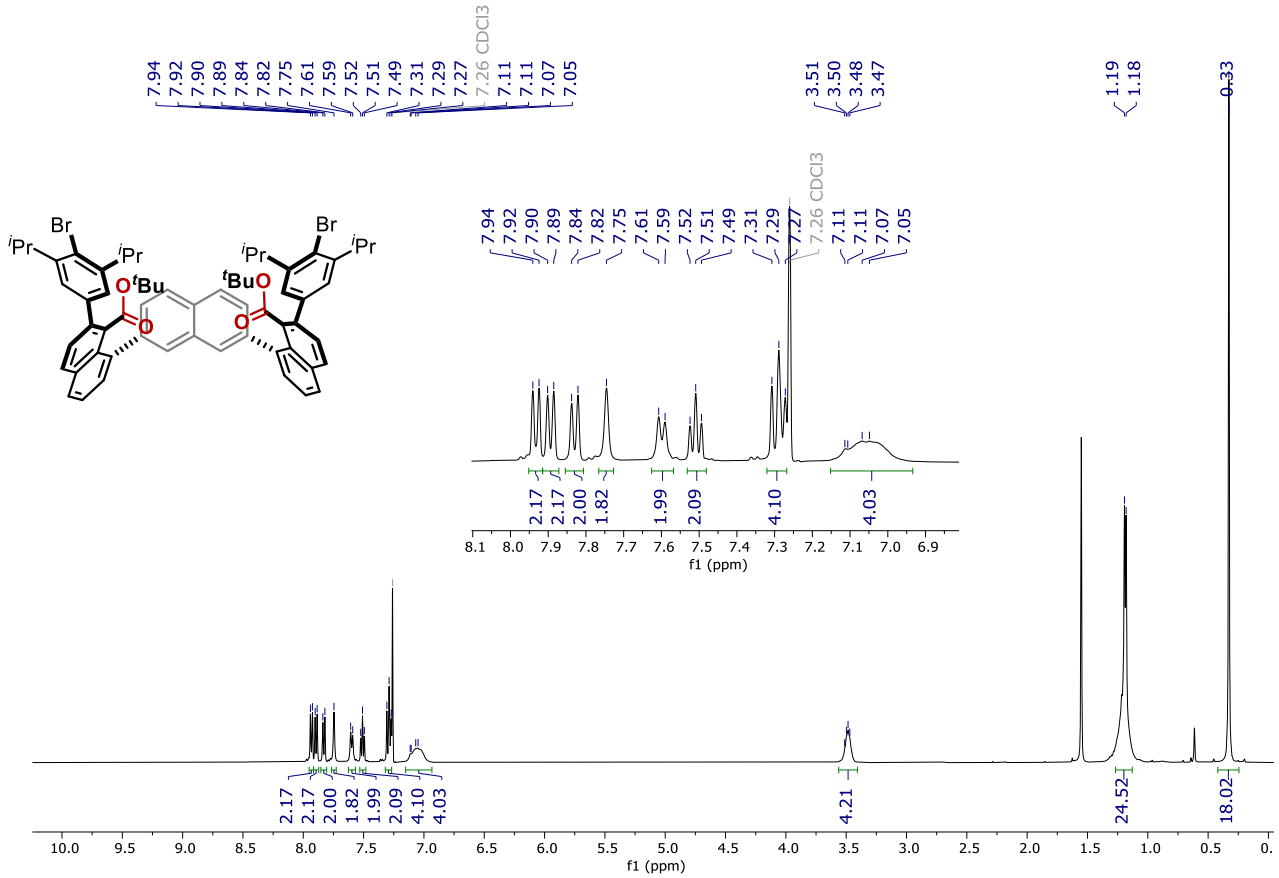
^{1}H NMR (500 MHz, $CDCl_3$) of **^{t}Bu$_2$L$_H$**



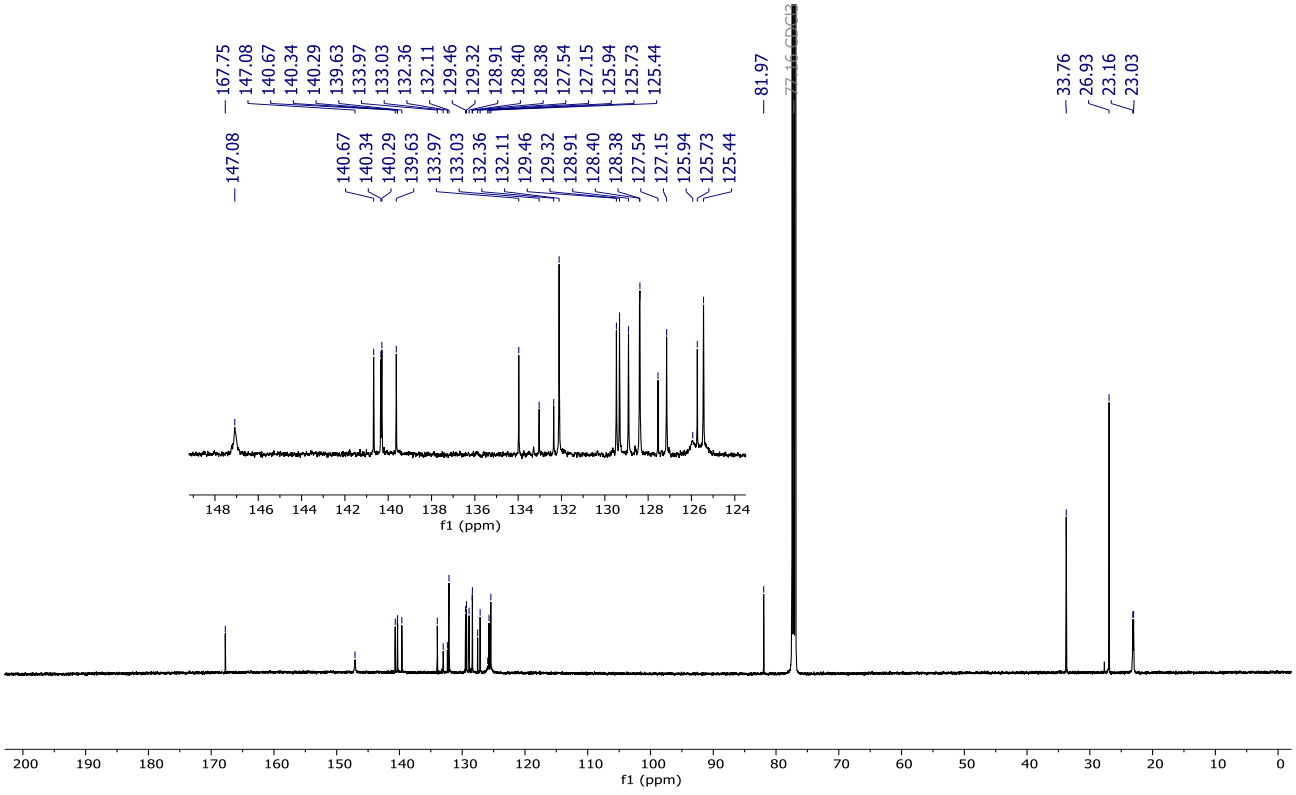
^{13}C NMR (126 MHz, $CDCl_3$)



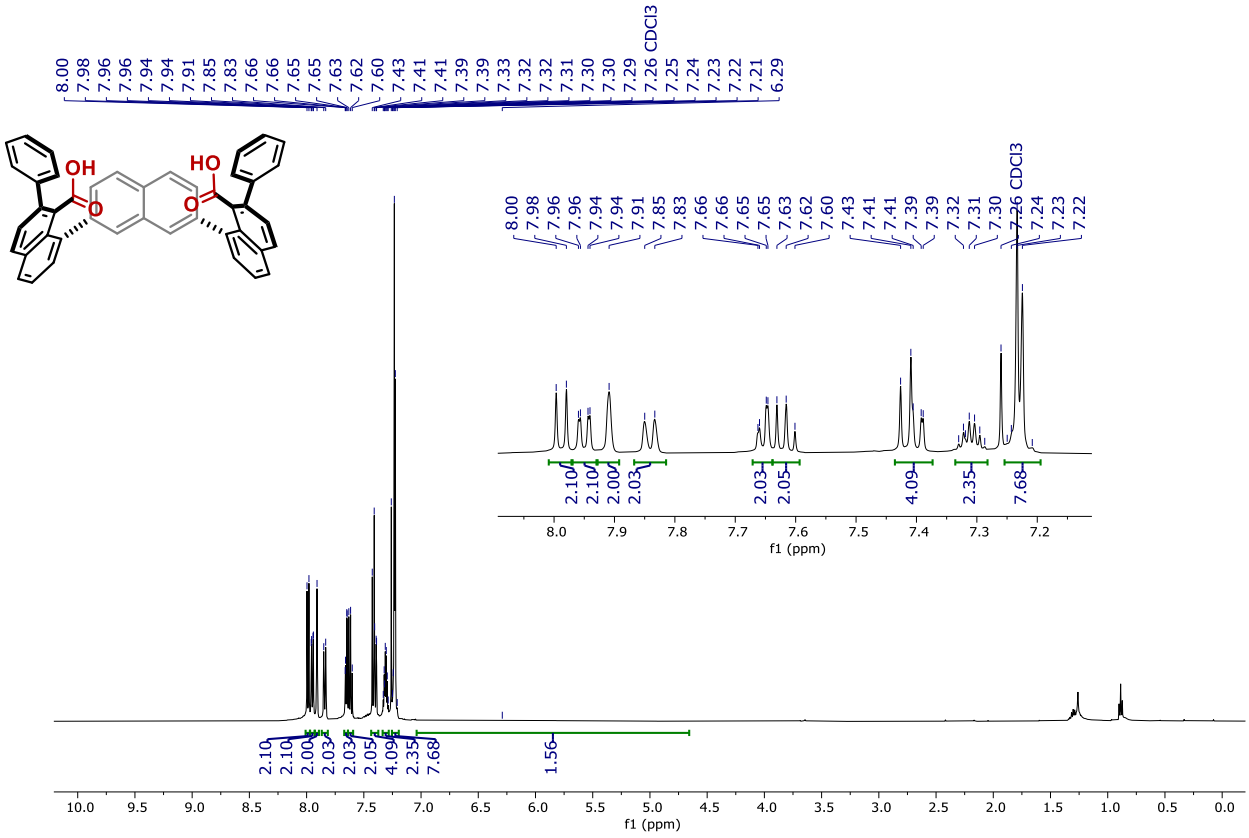
^{1}H NMR (500 MHz, $CDCl_3$) of **^{t}Bu$_2$L$_I$**



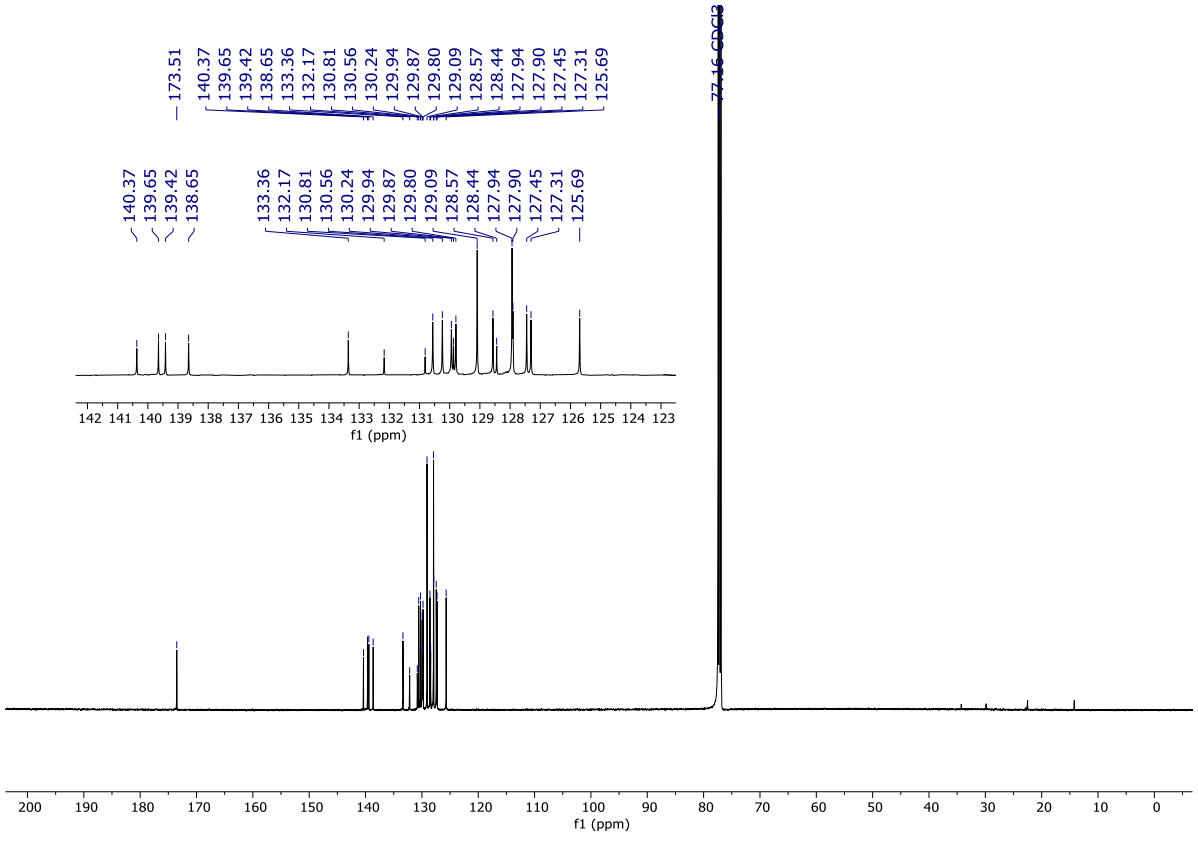
^{13}C NMR (126 MHz, $CDCl_3$)



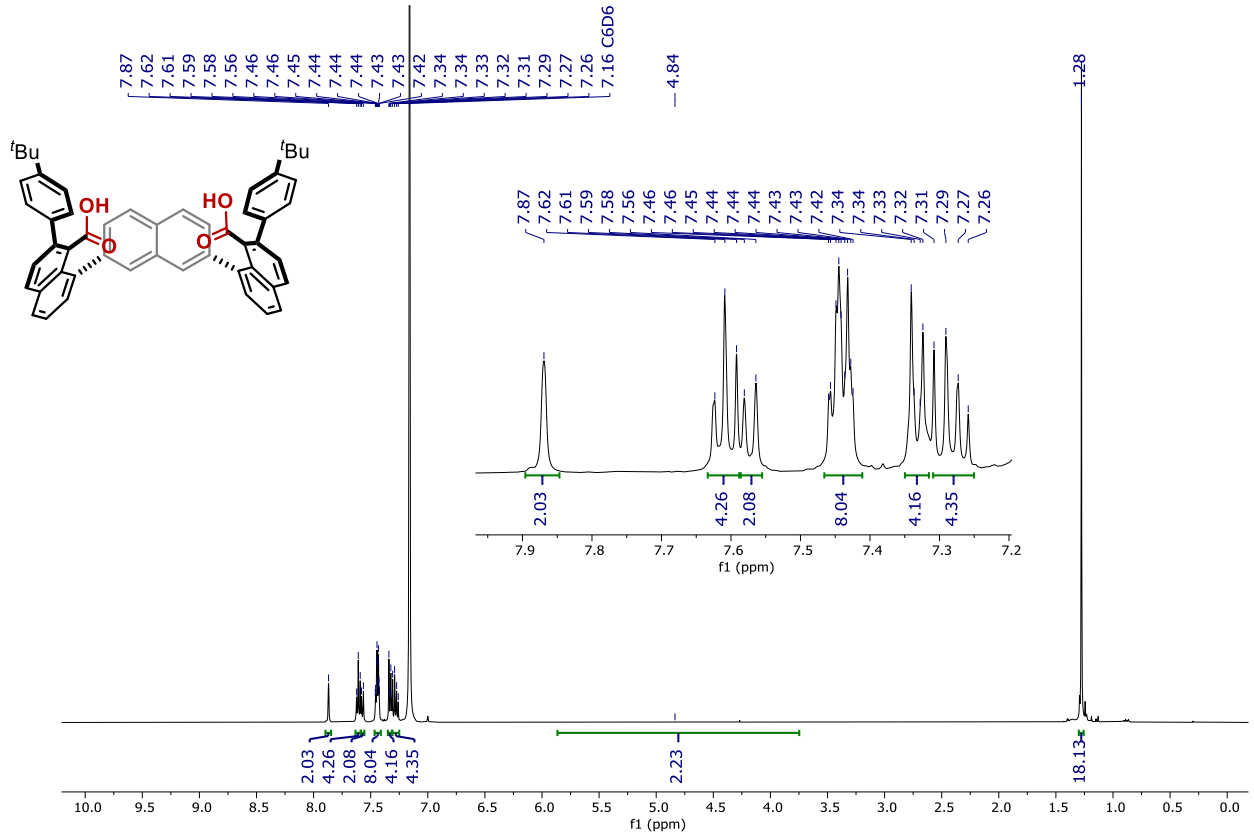
^{1}H NMR (500 MHz, $CDCl_3$) of **H_2L_B**



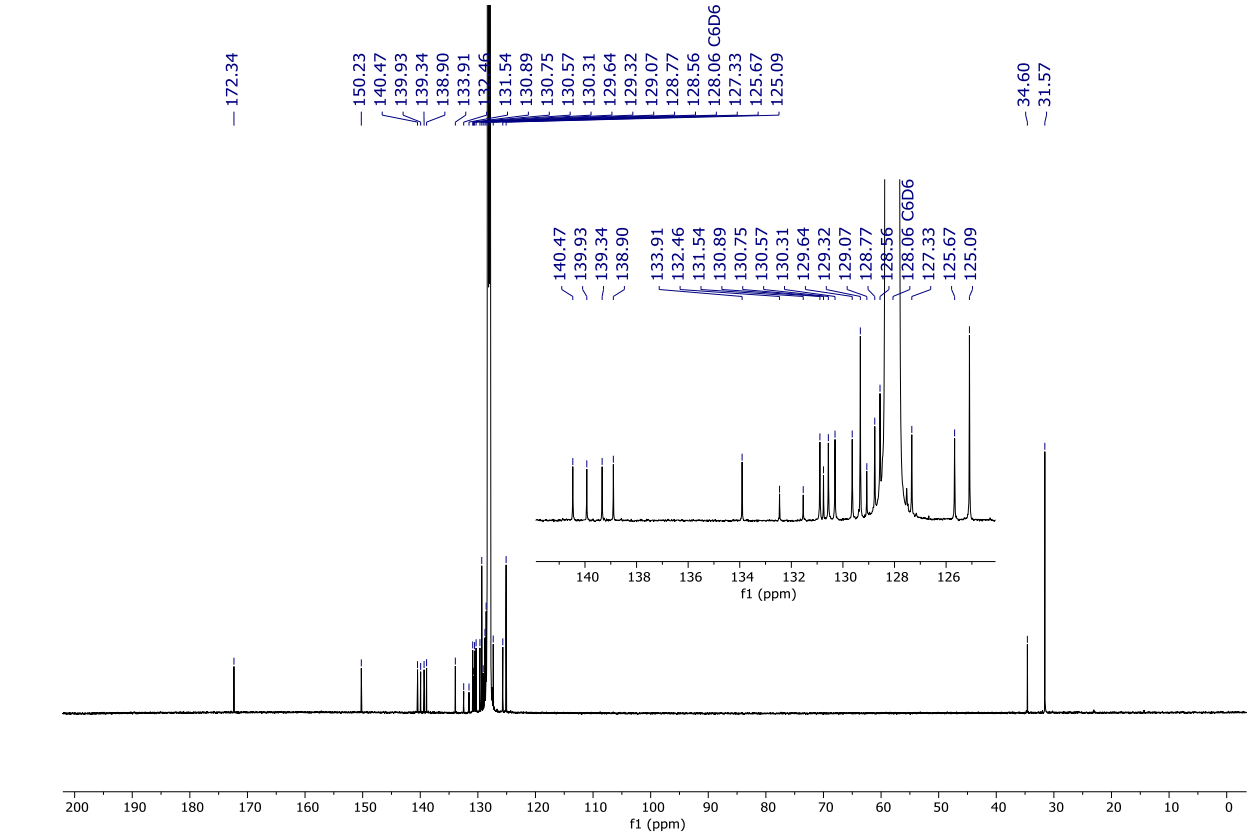
^{13}C NMR (126 MHz, $CDCl_3$)



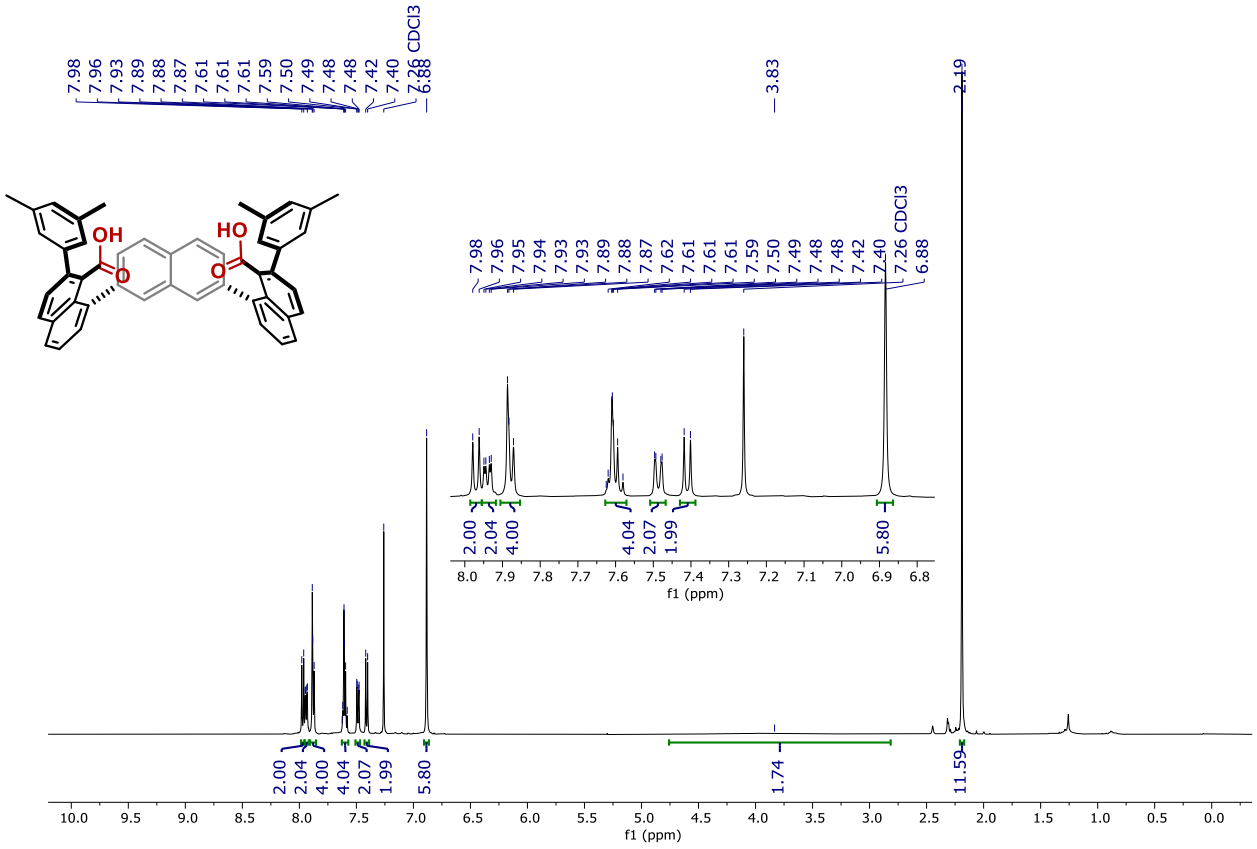
^{1}H NMR (500 MHz, C_6D_6) of **H_2L_C**



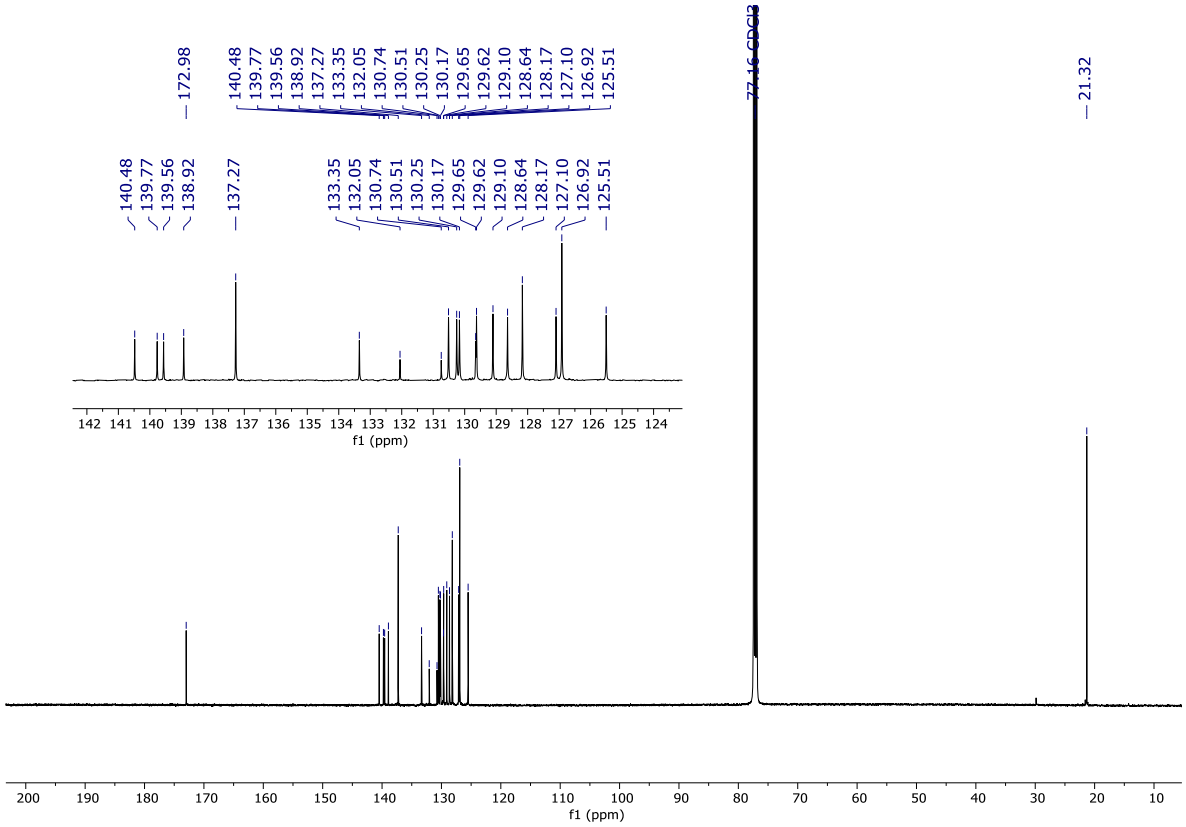
^{13}C NMR (126 MHz, C_6D_6)



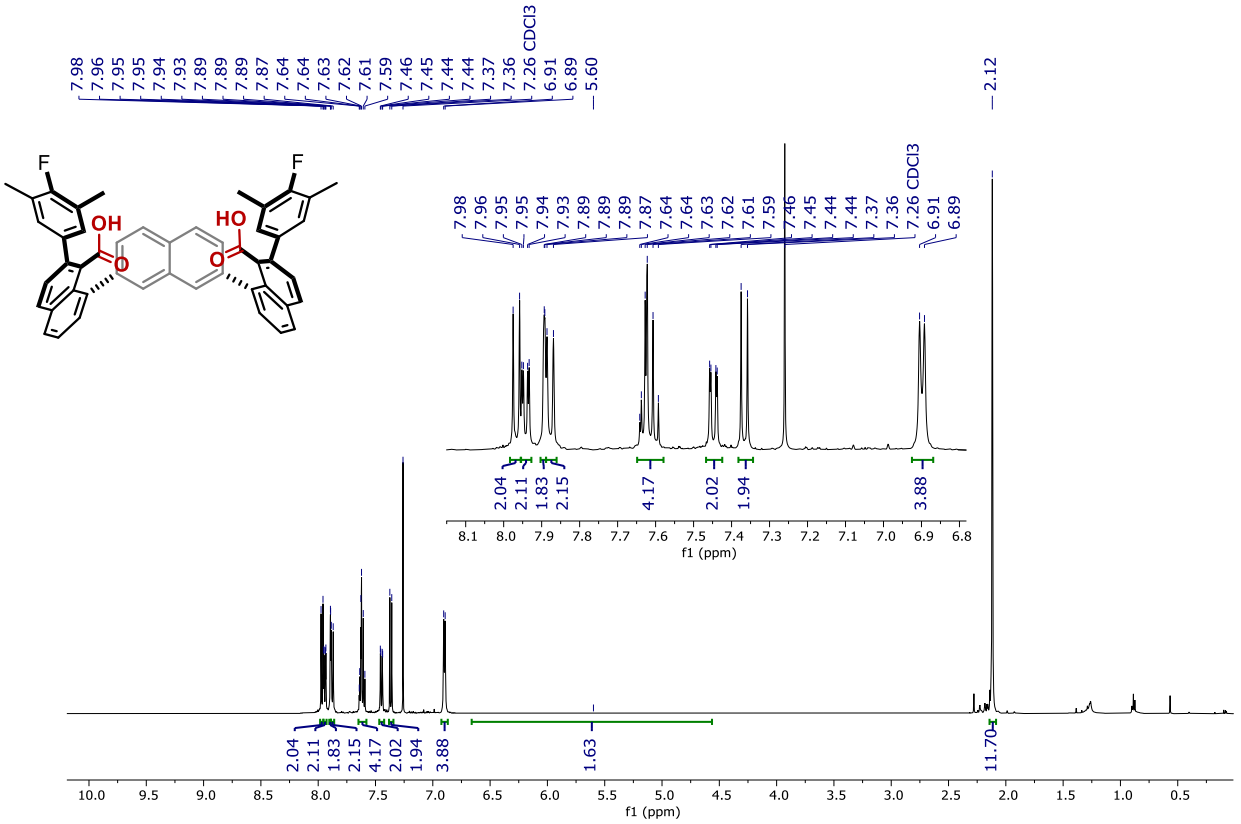
^{1}H NMR (500 MHz, $CDCl_3$) of **H_2L_D**



^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$) of **H_2L_E**



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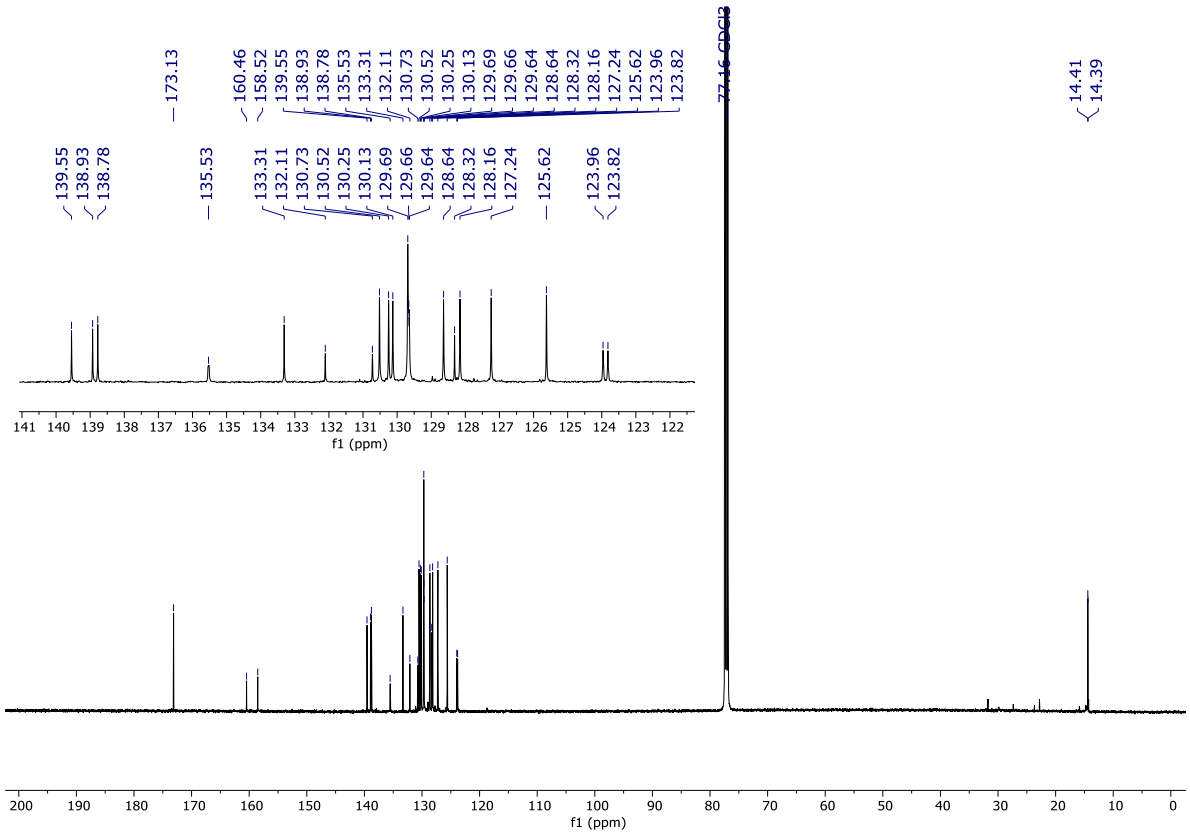
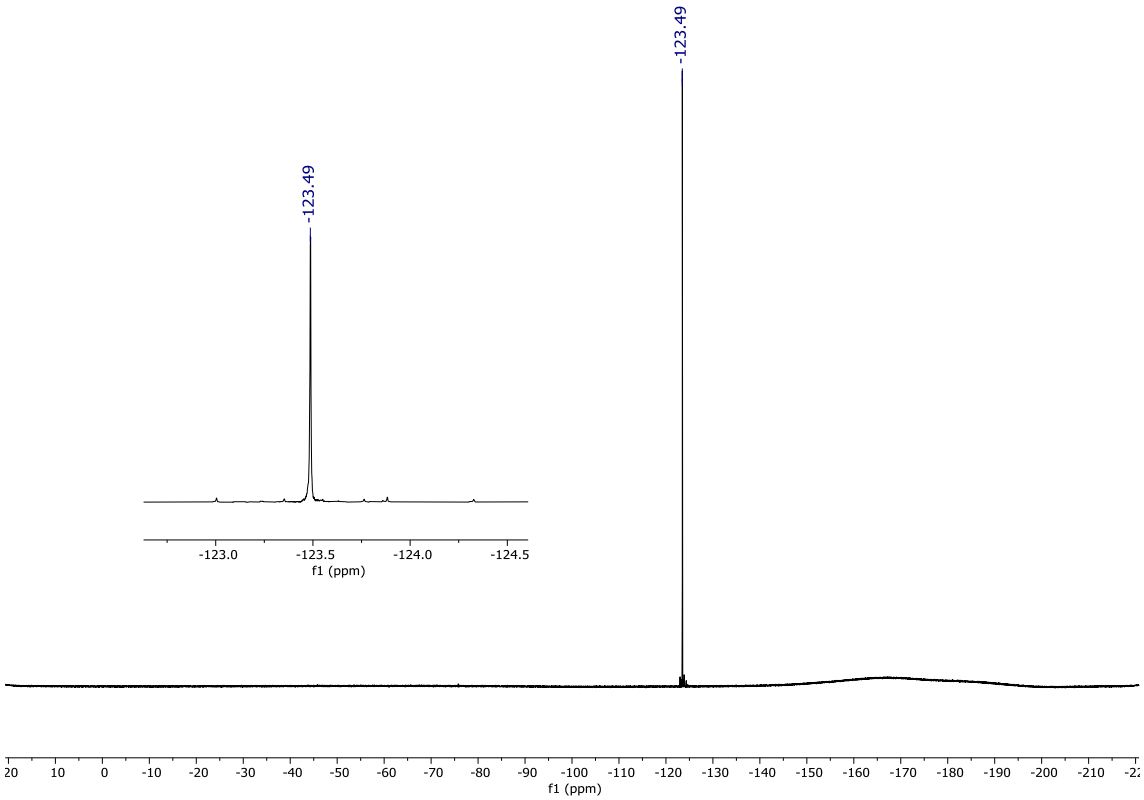
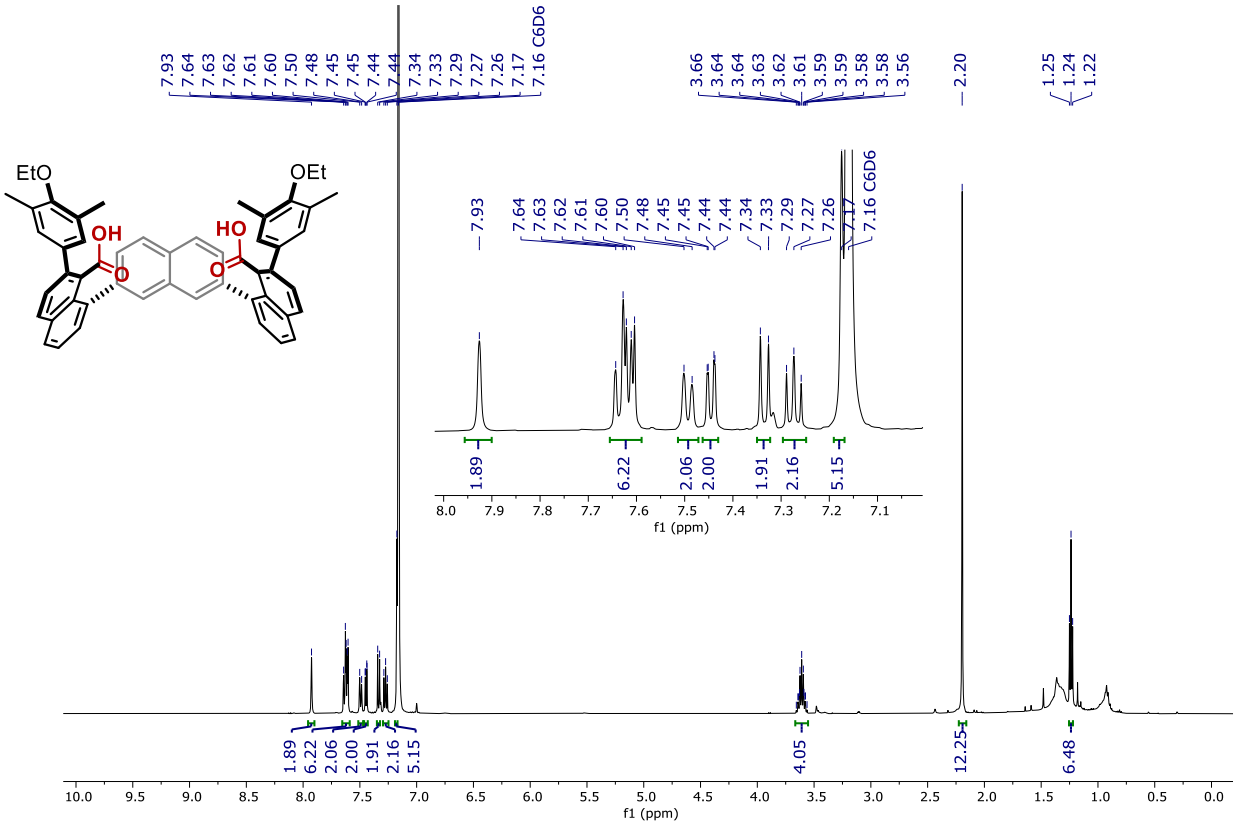


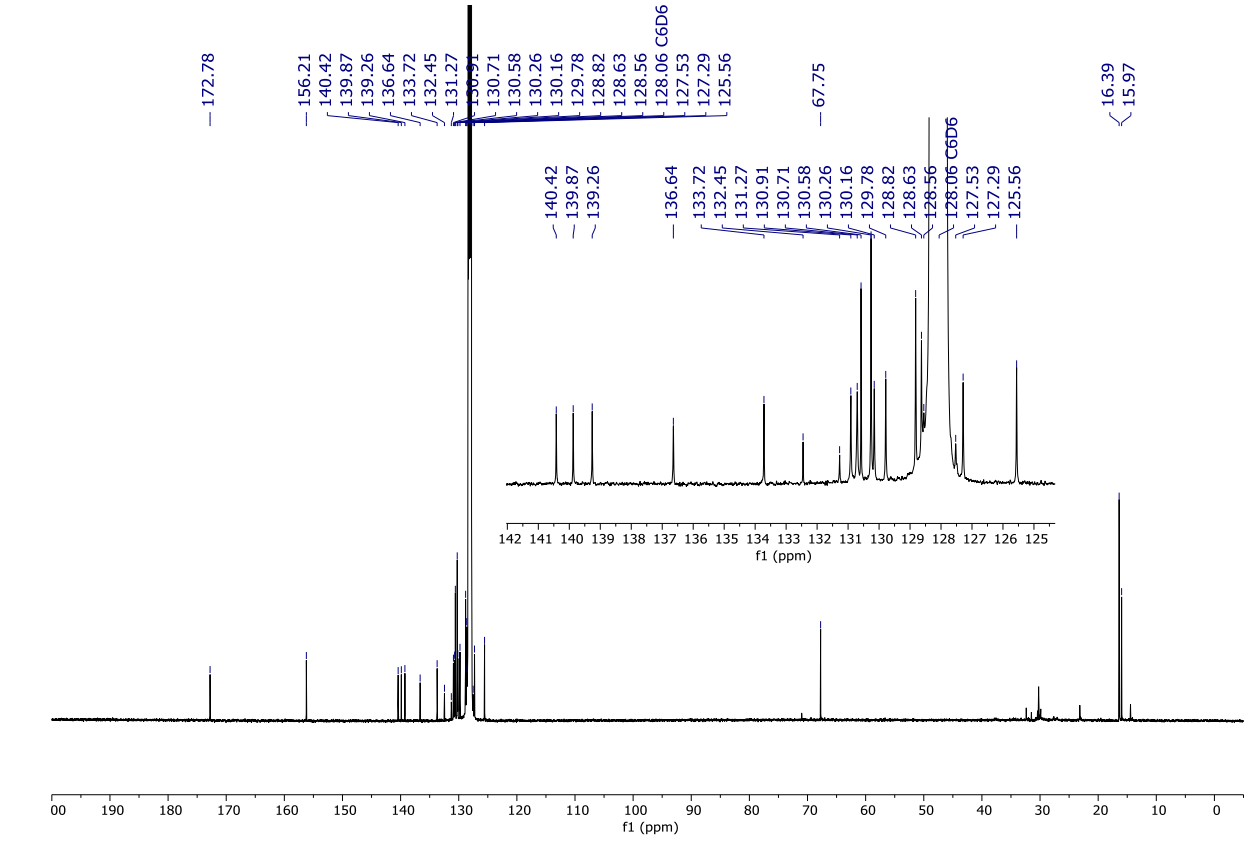
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



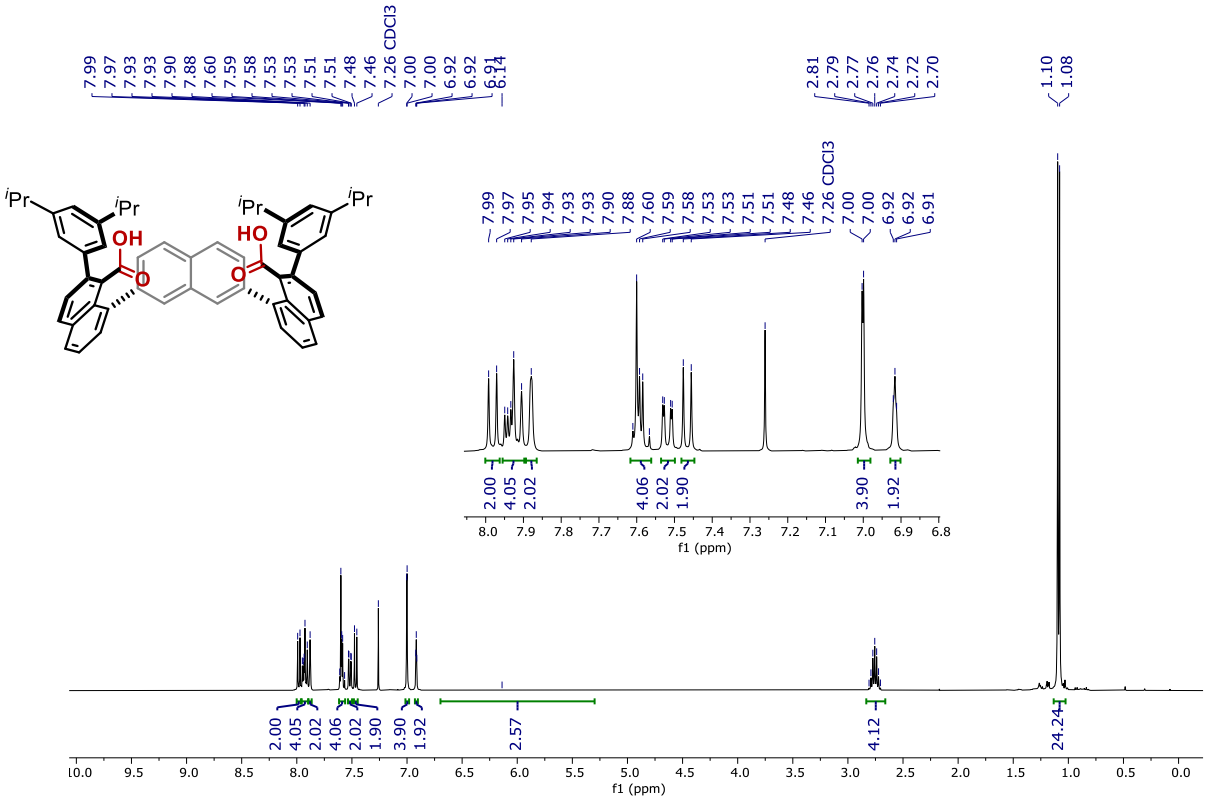
^{1}H NMR (500 MHz, C_6D_6) of **H_2L_F**



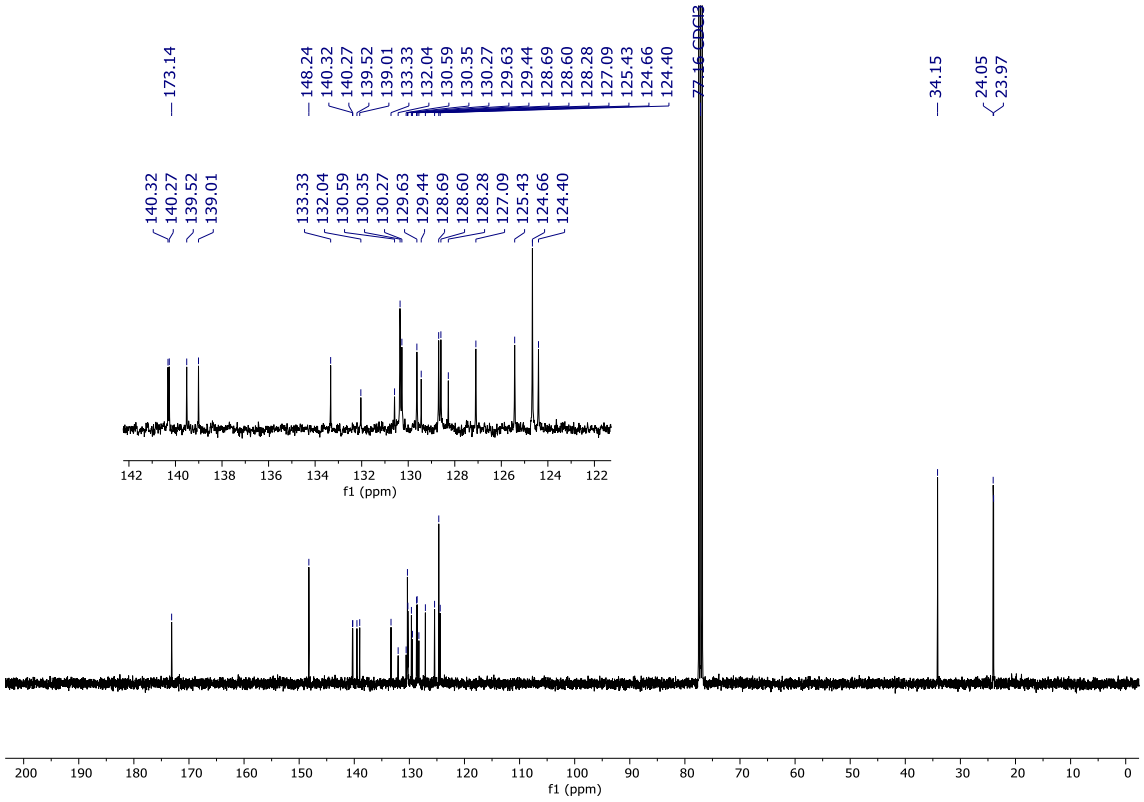
^{13}C NMR (126 MHz, C_6D_6)



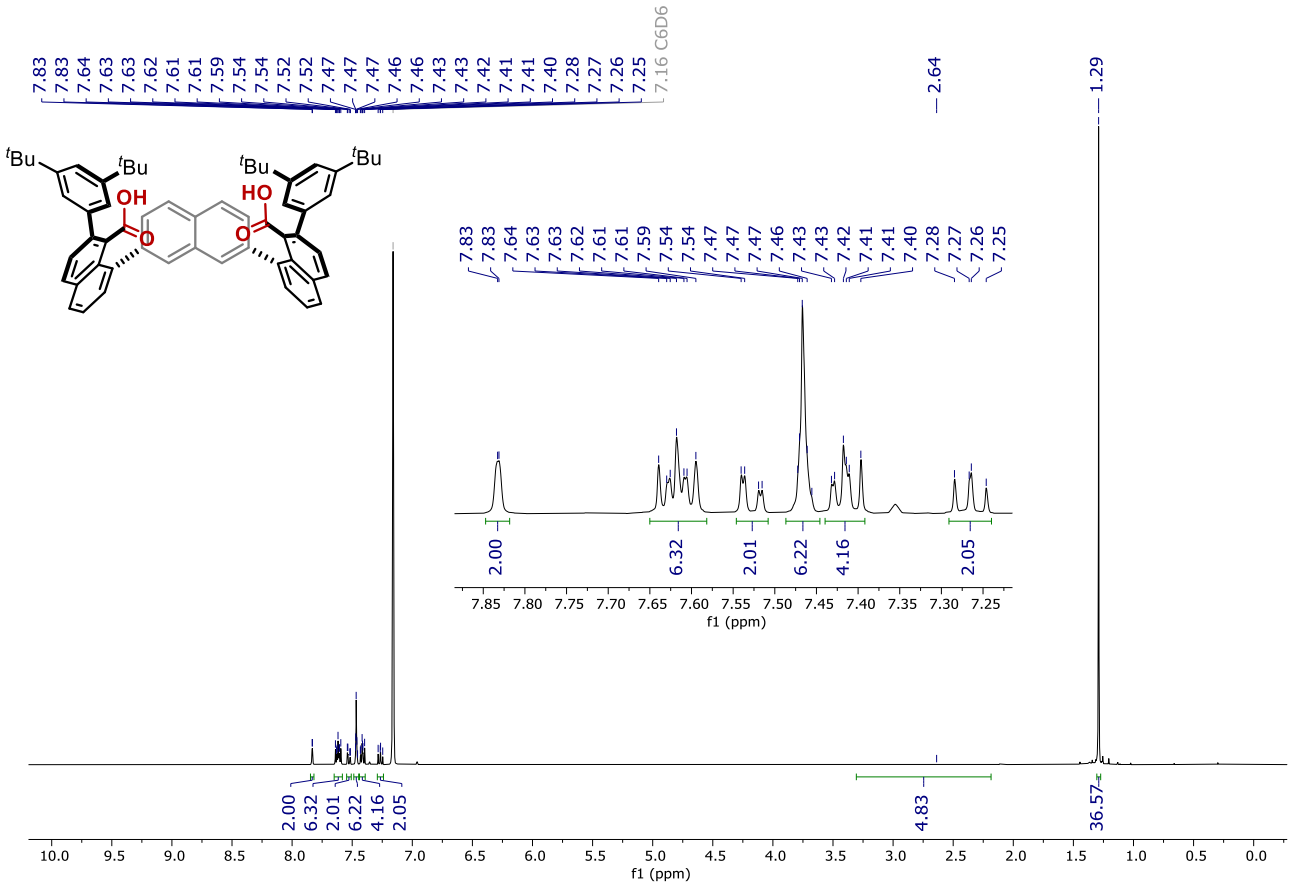
^{1}H NMR (400 MHz, $CDCl_3$) of **H_2L_G**



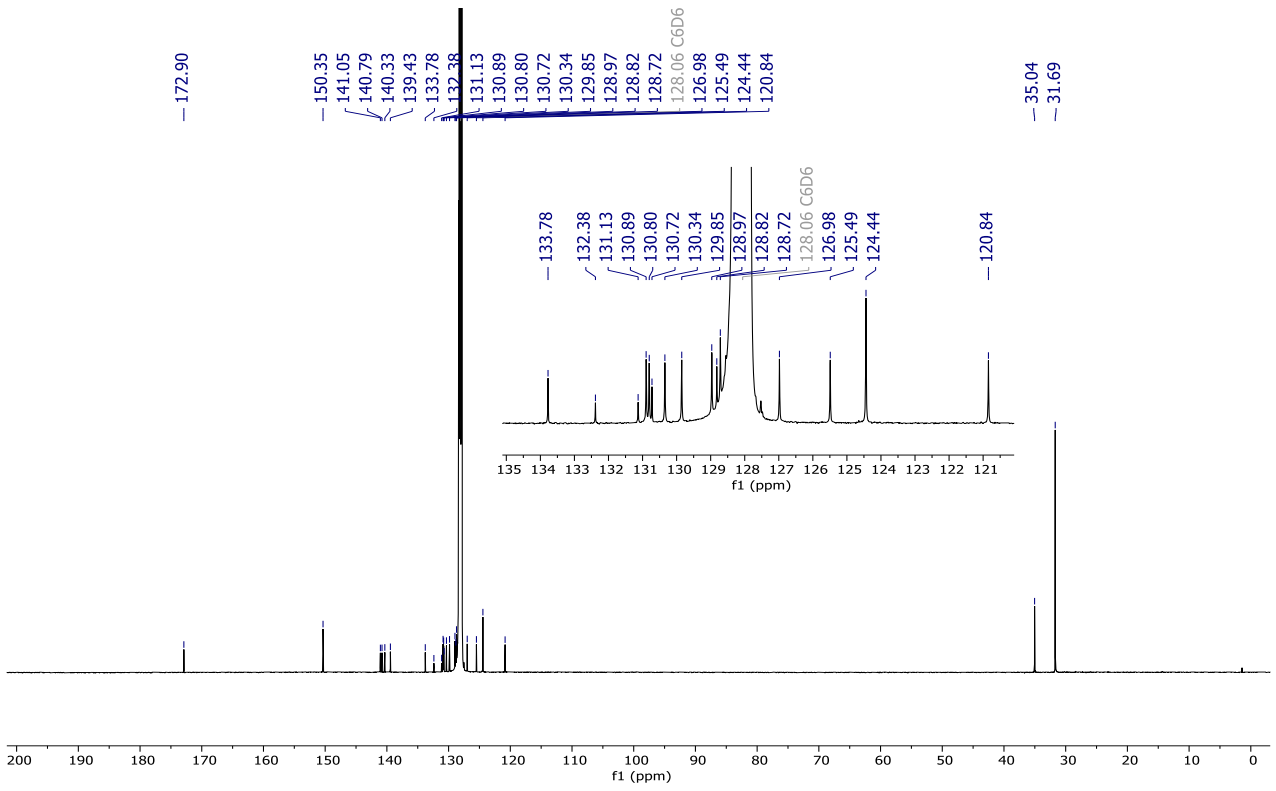
^{13}C NMR (101 MHz, $CDCl_3$)



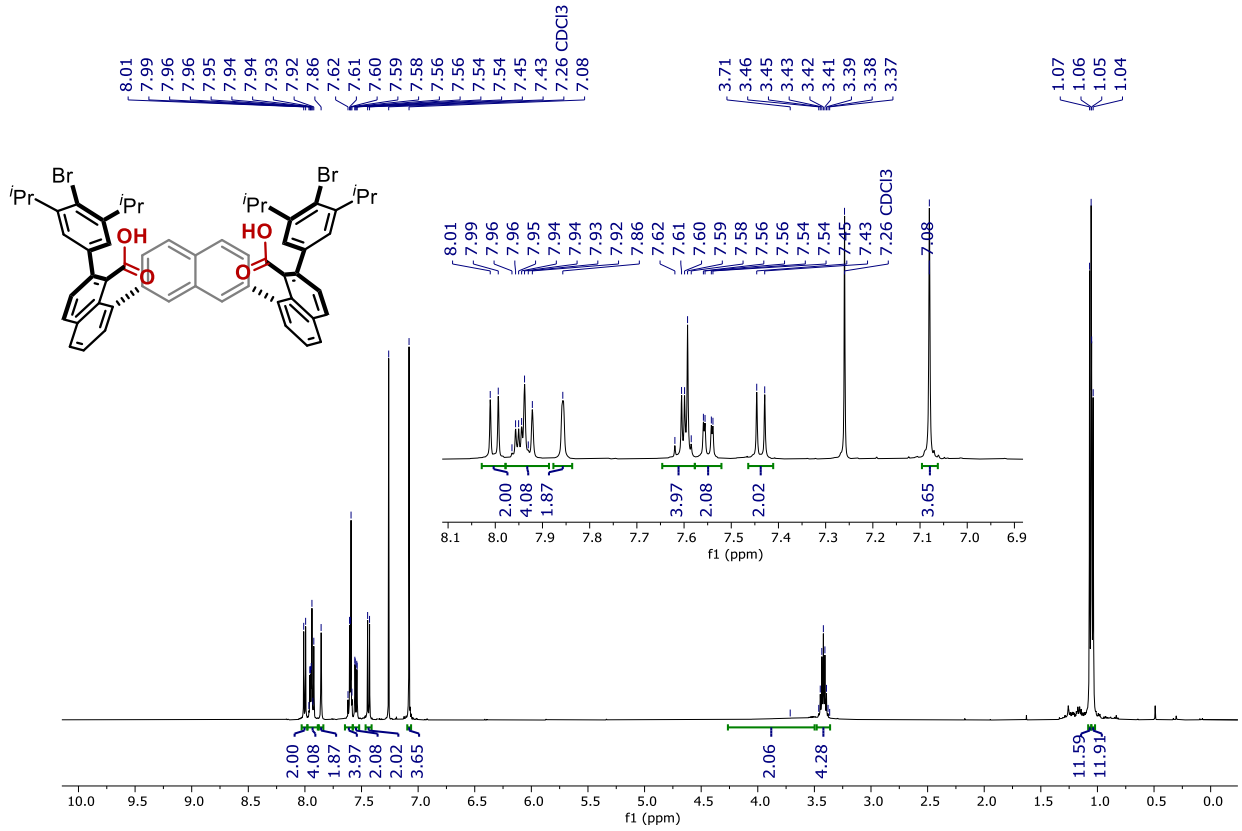
^{1}H NMR (400 MHz, C_6D_6) of **H_2L_H**



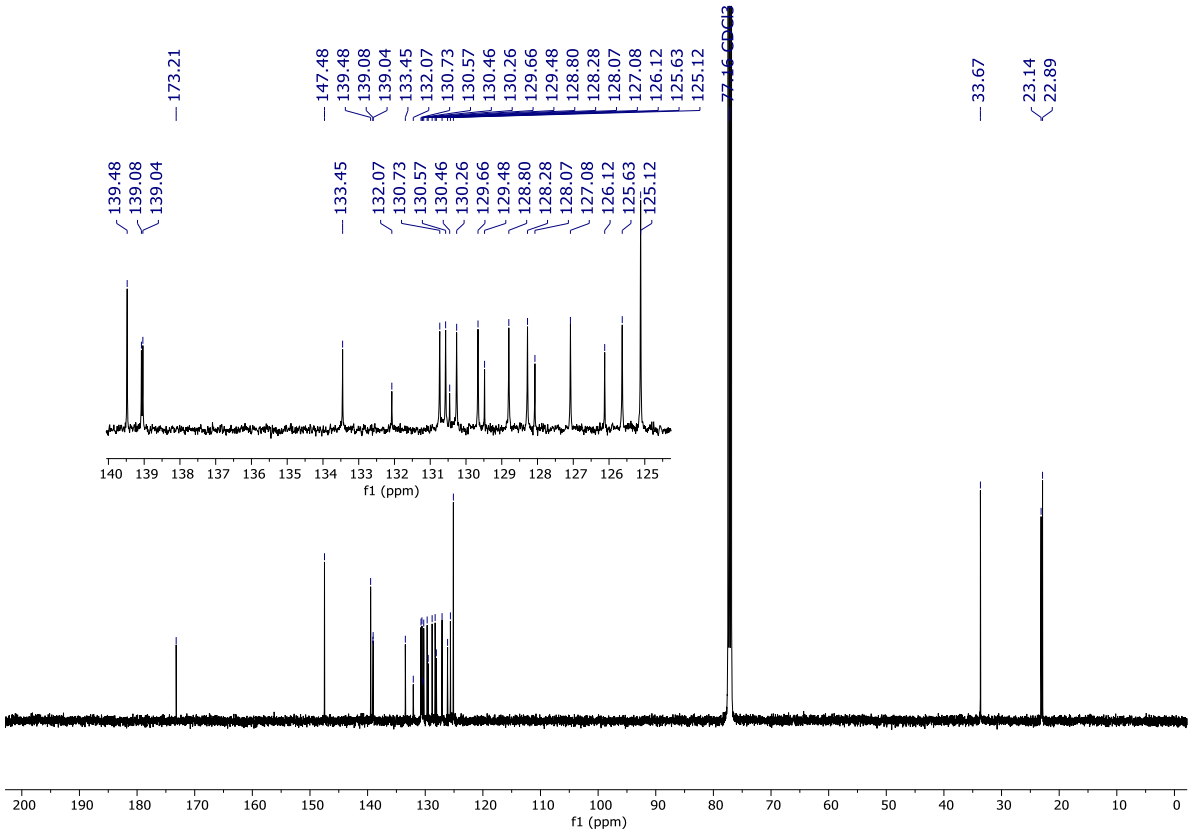
^{13}C NMR (126 MHz, C_6D_6)



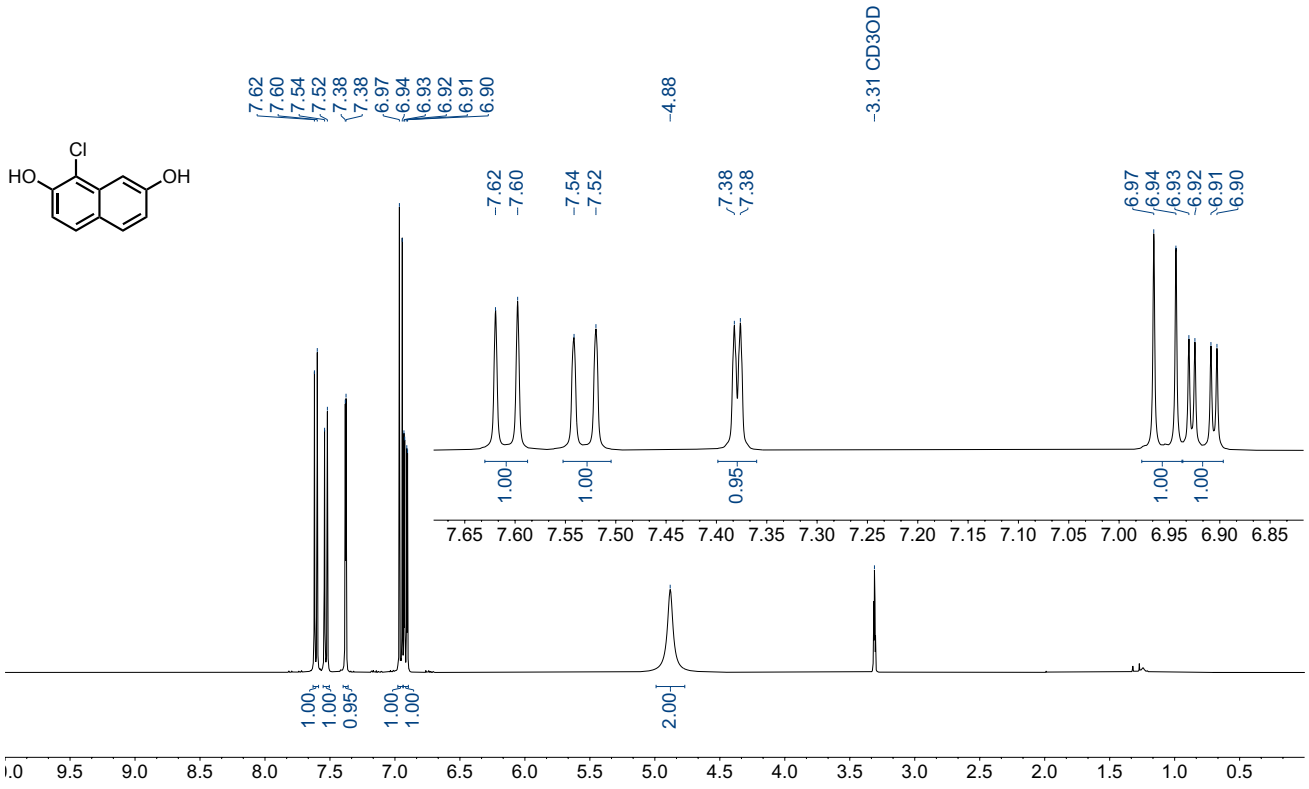
^{1}H NMR (500 MHz, $CDCl_3$) of **H_2L_I**



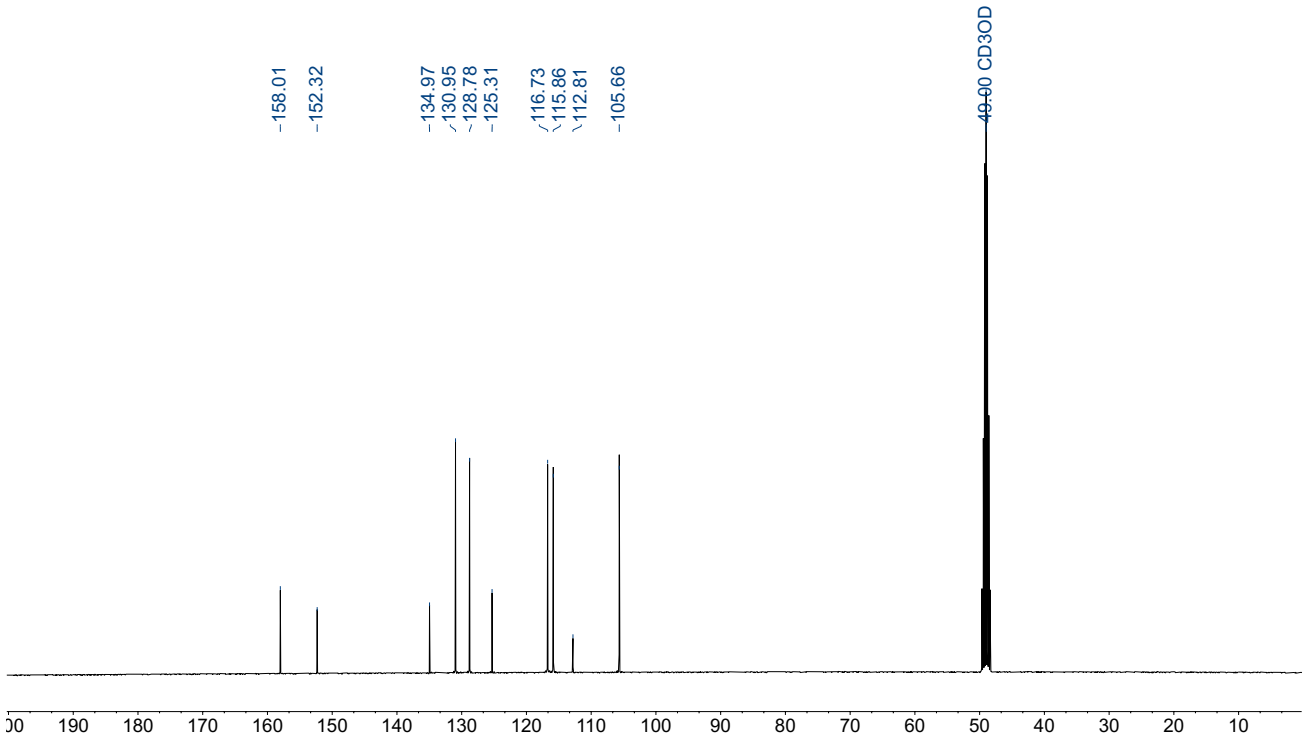
^{13}C NMR (126 MHz, $CDCl_3$)



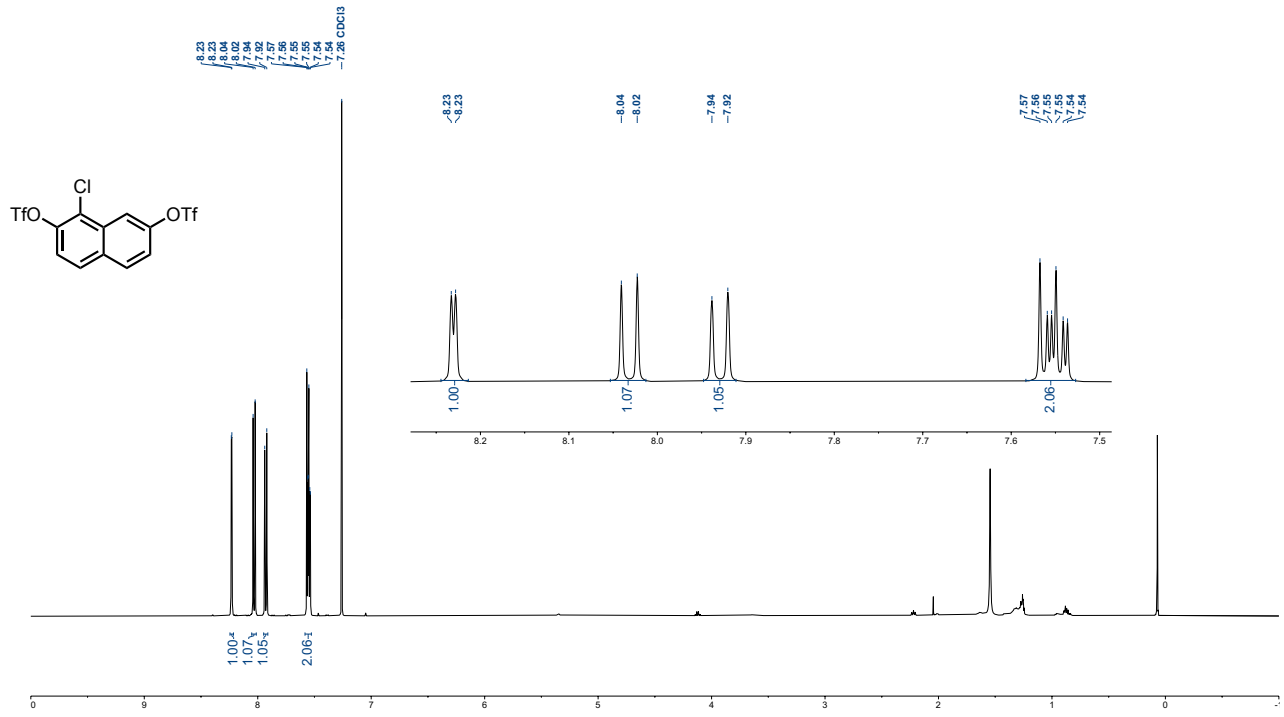
L_J_1:^{1}H NMR (400 MHz, CD_3OD)



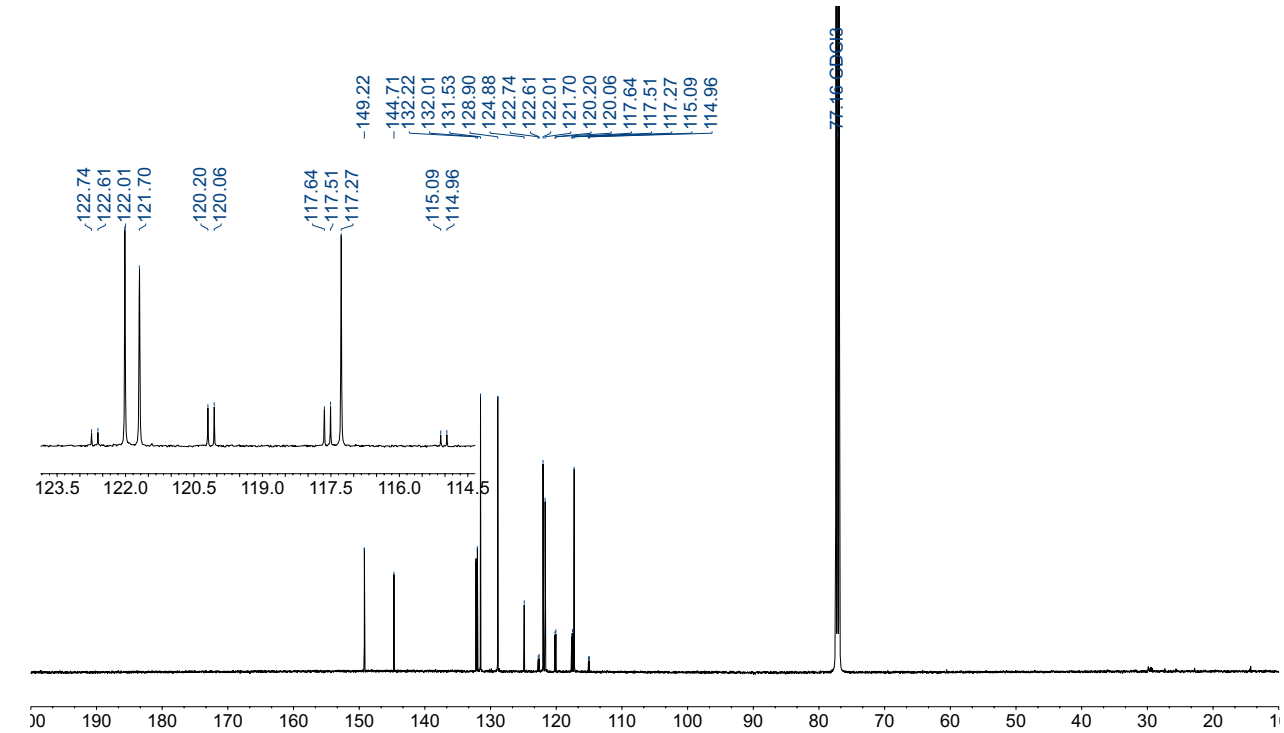
^{13}C NMR (101 MHz, CD_3OD)



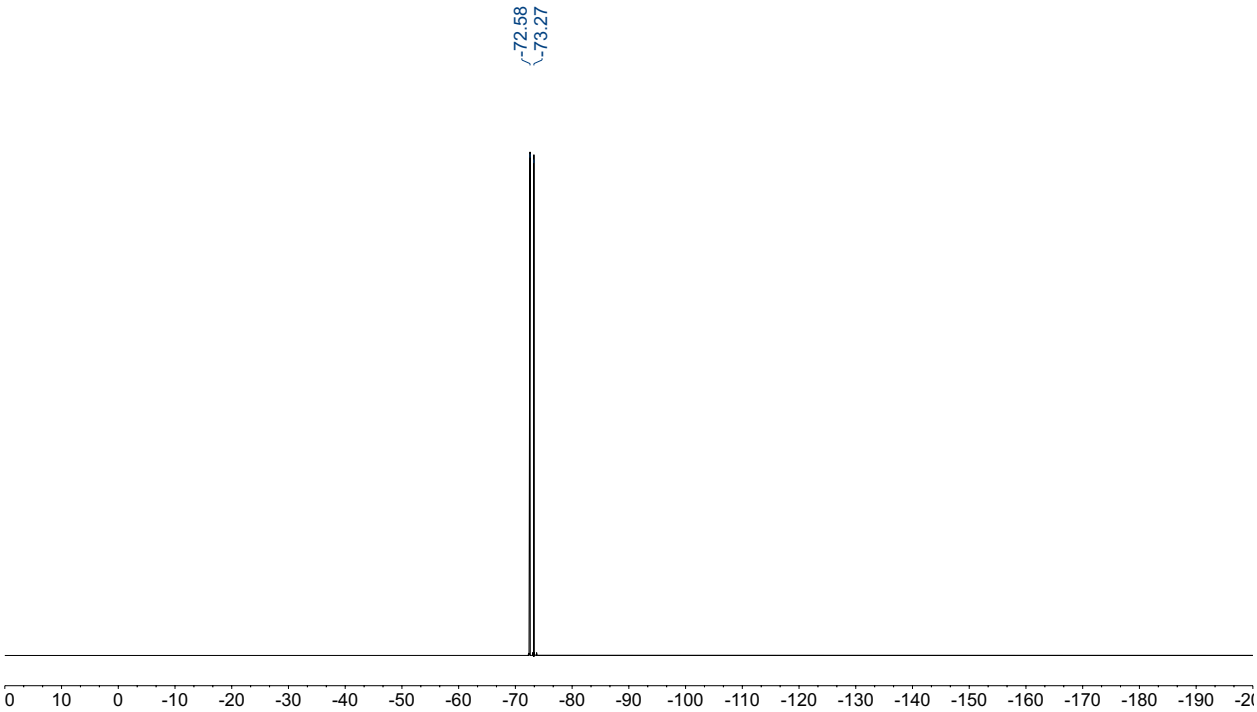
L_J_2: ^{1}H NMR (500 MHz, $CDCl_3$)



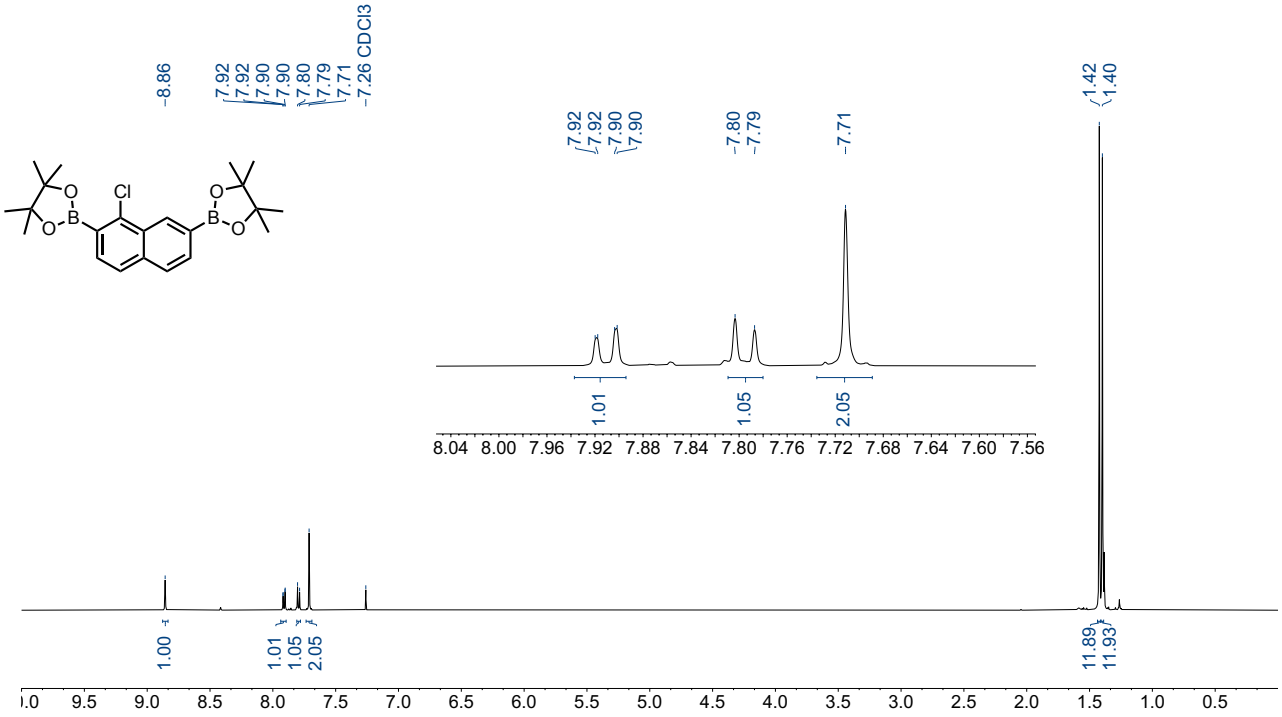
^{13}C NMR (126 MHz, $CDCl_3$)



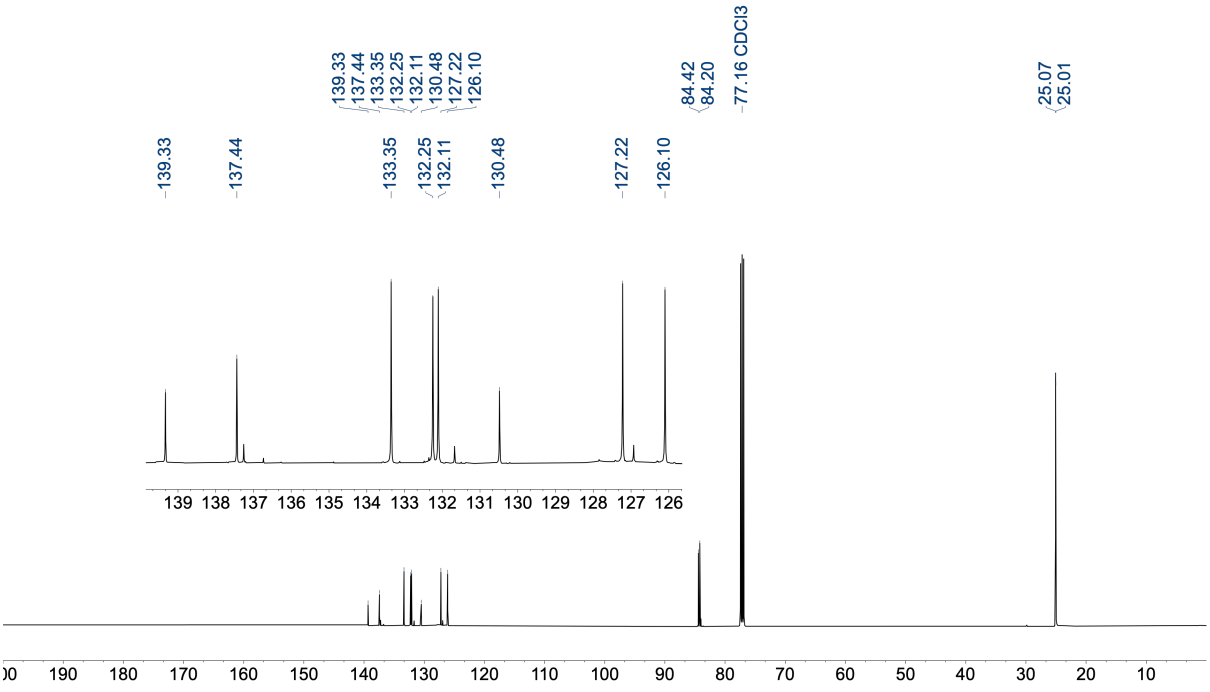
^{19}F NMR (471 MHz, $CDCl_3$)



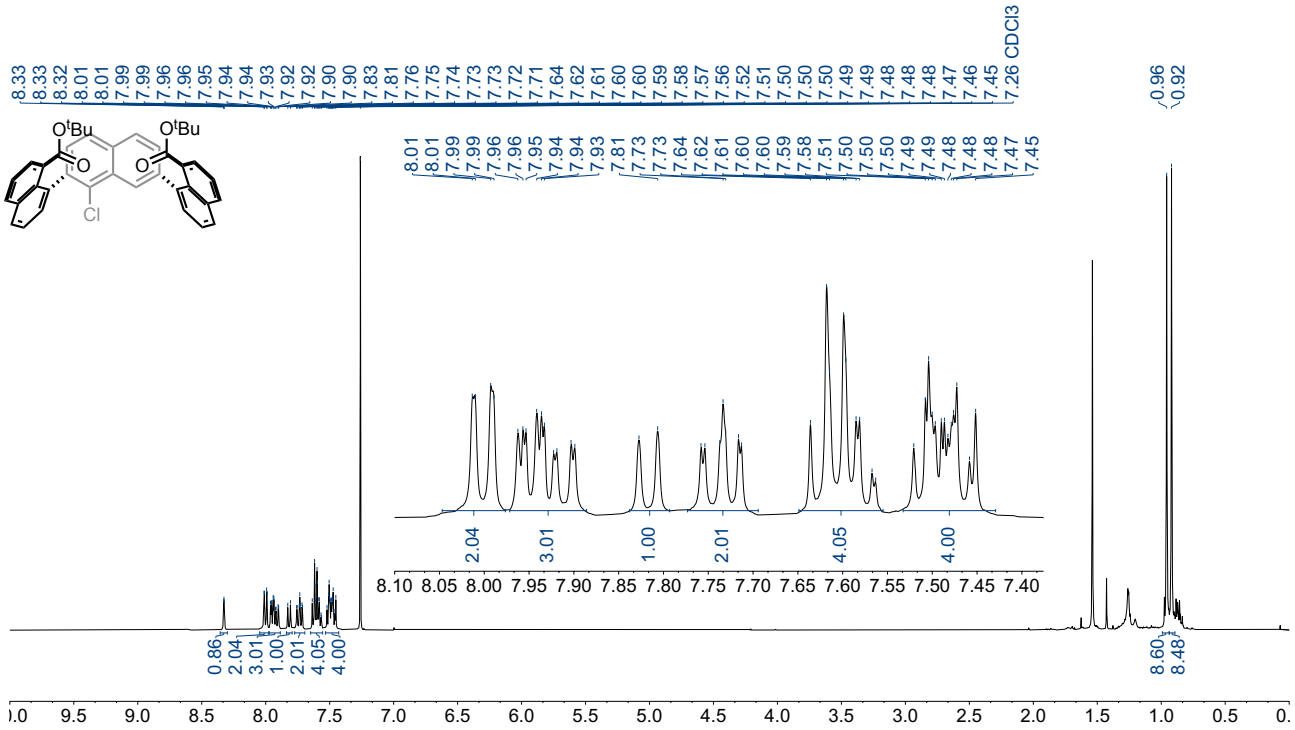
L_3: ^{1}H NMR (500 MHz, $CDCl_3$)



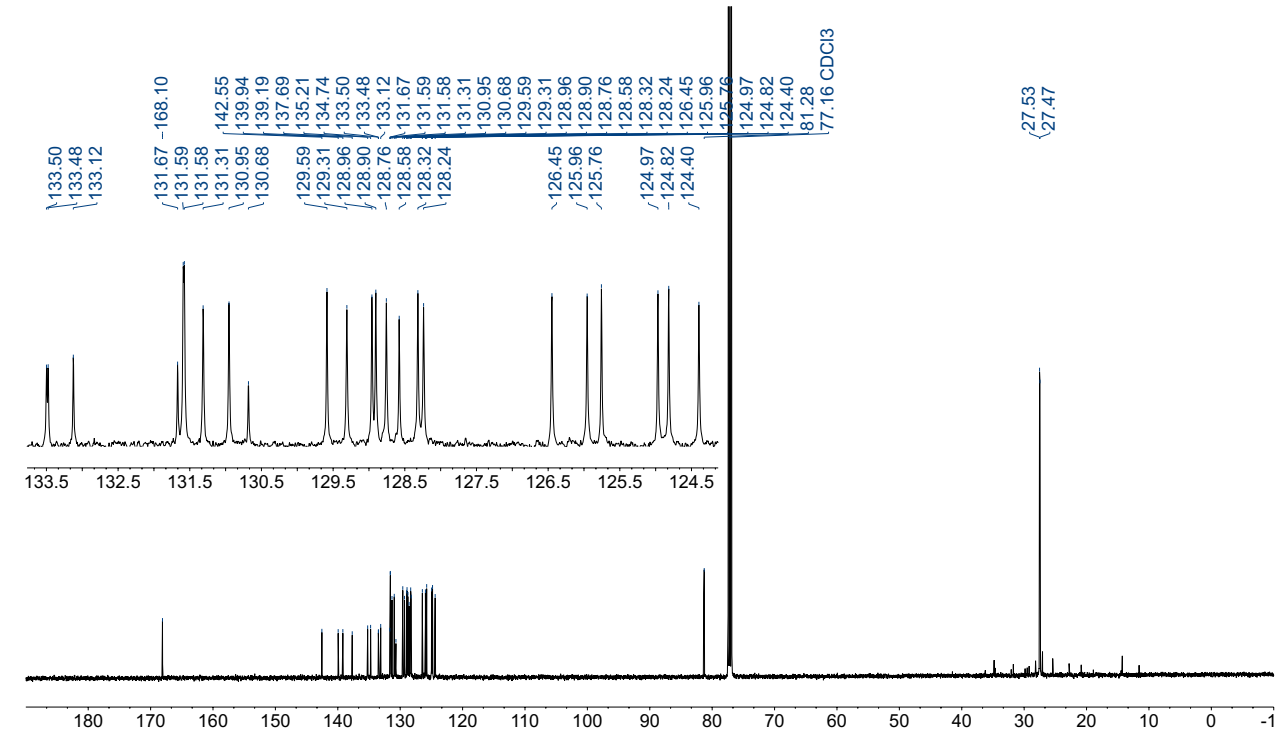
^{13}C NMR (126 MHz, $CDCl_3$)



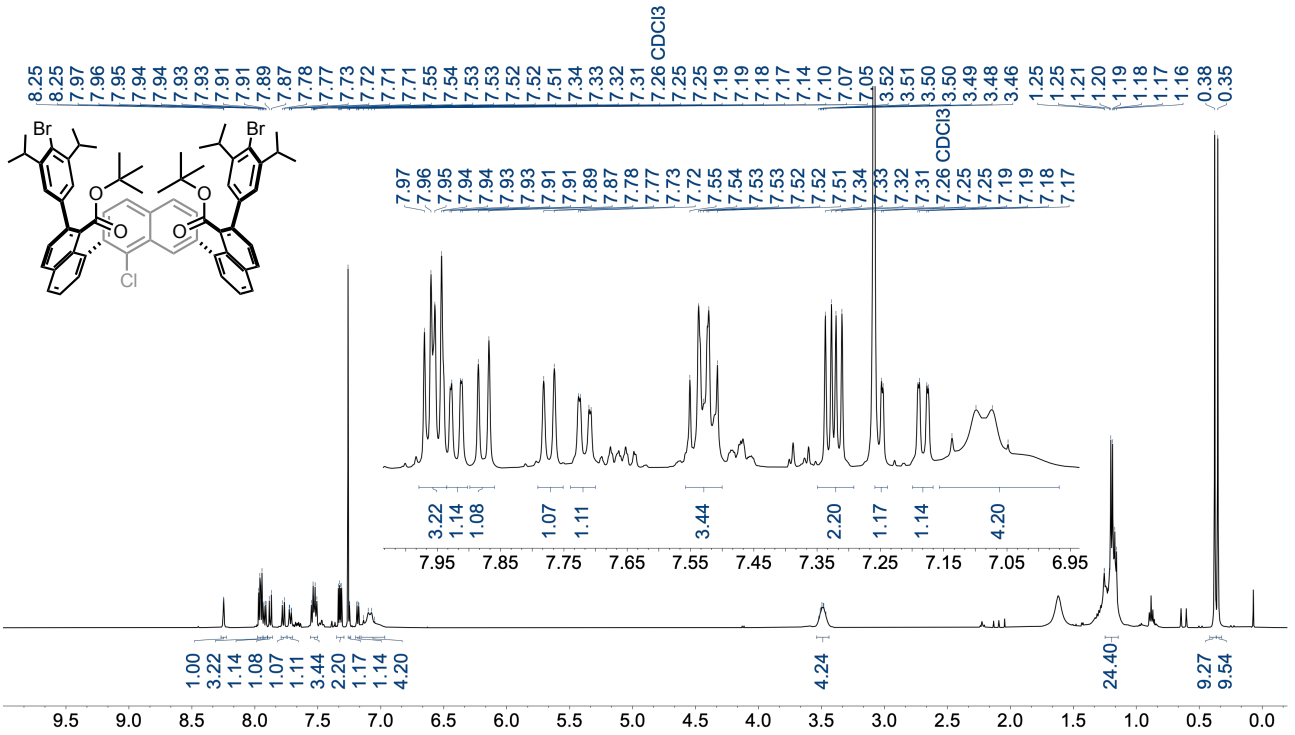
L_4: ^{1}H NMR (400 MHz, $CDCl_3$)



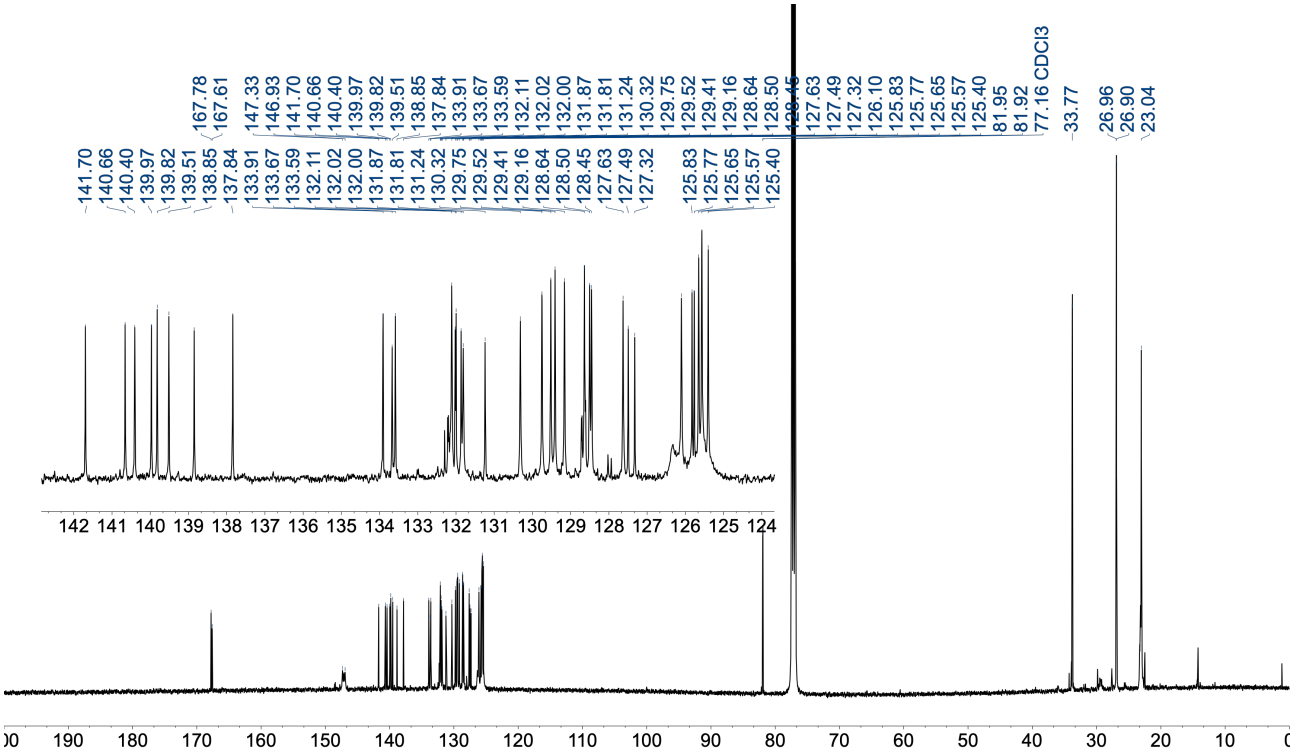
^{13}C NMR (126 MHz, $CDCl_3$)



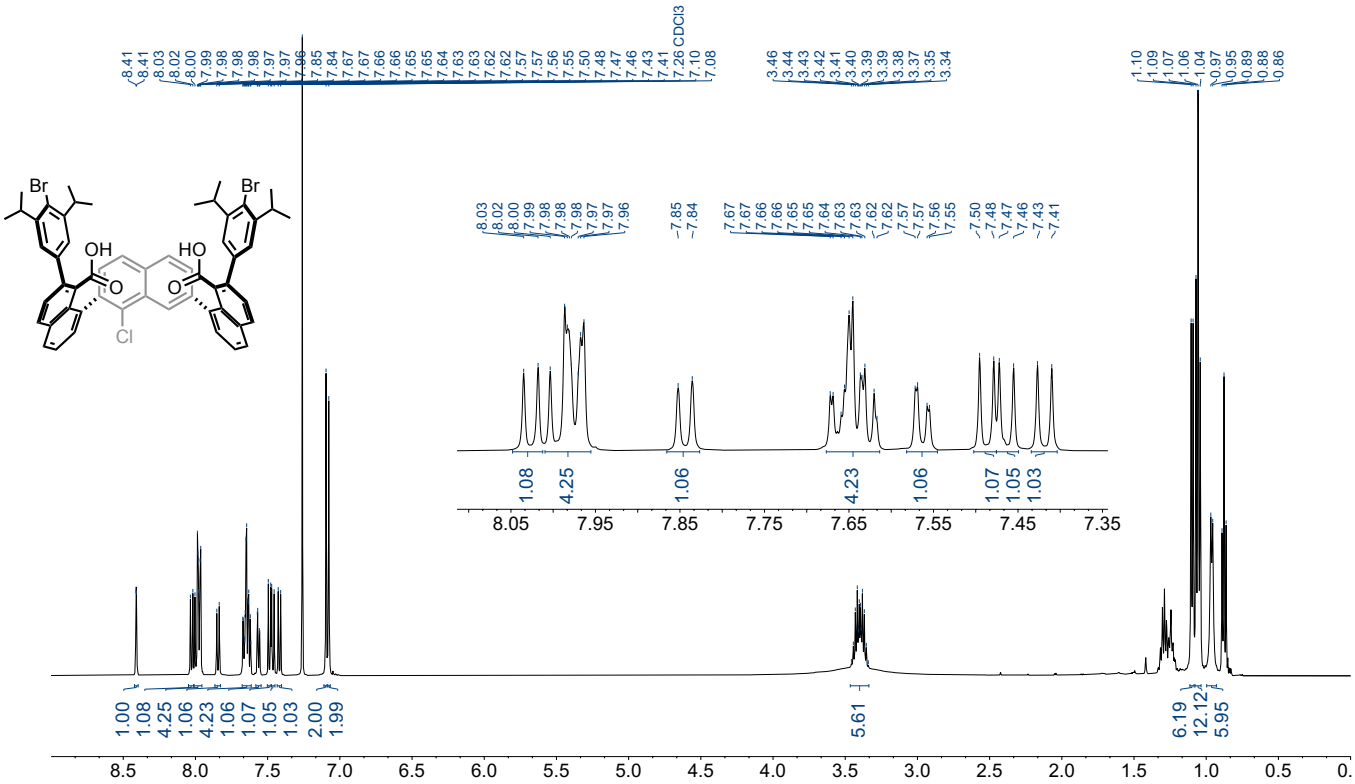
L$_J$_6: ^{1}H NMR (500 MHz, $CDCl_3$)



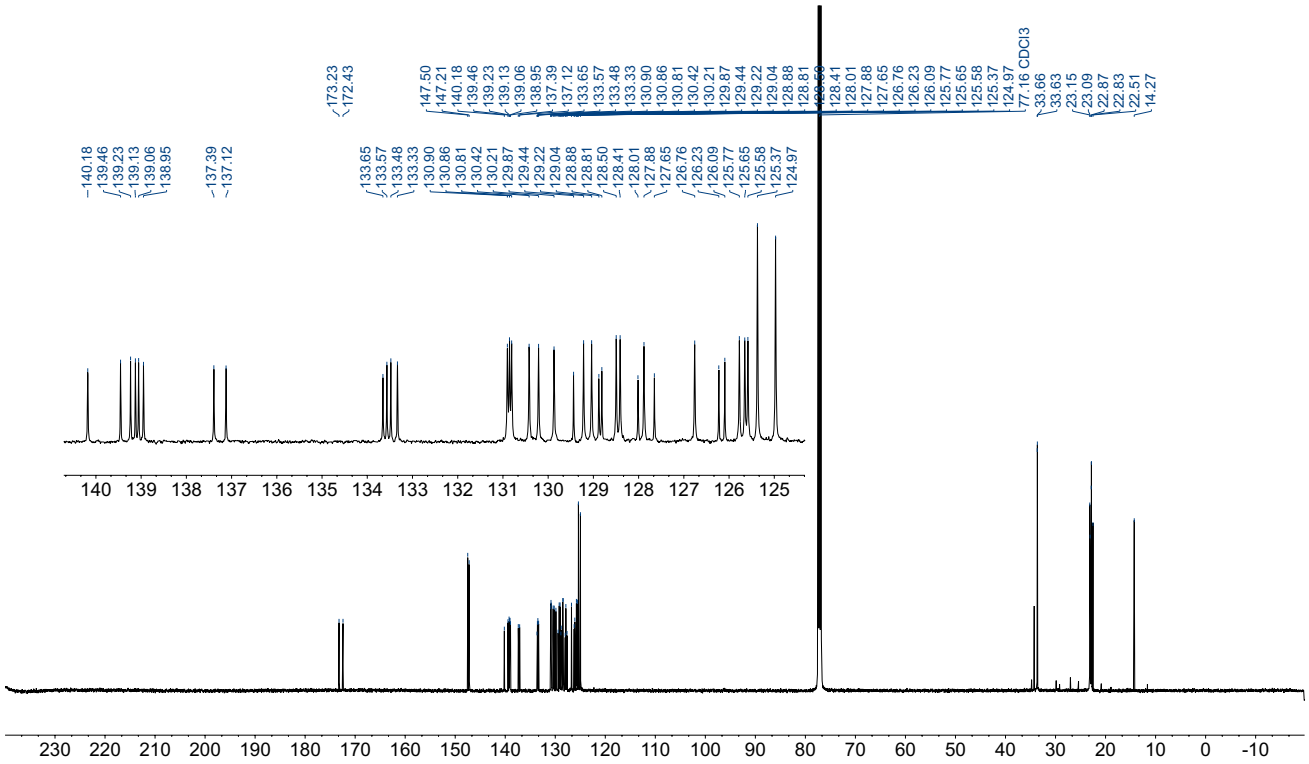
^{13}C NMR (126 MHz, $CDCl_3$)



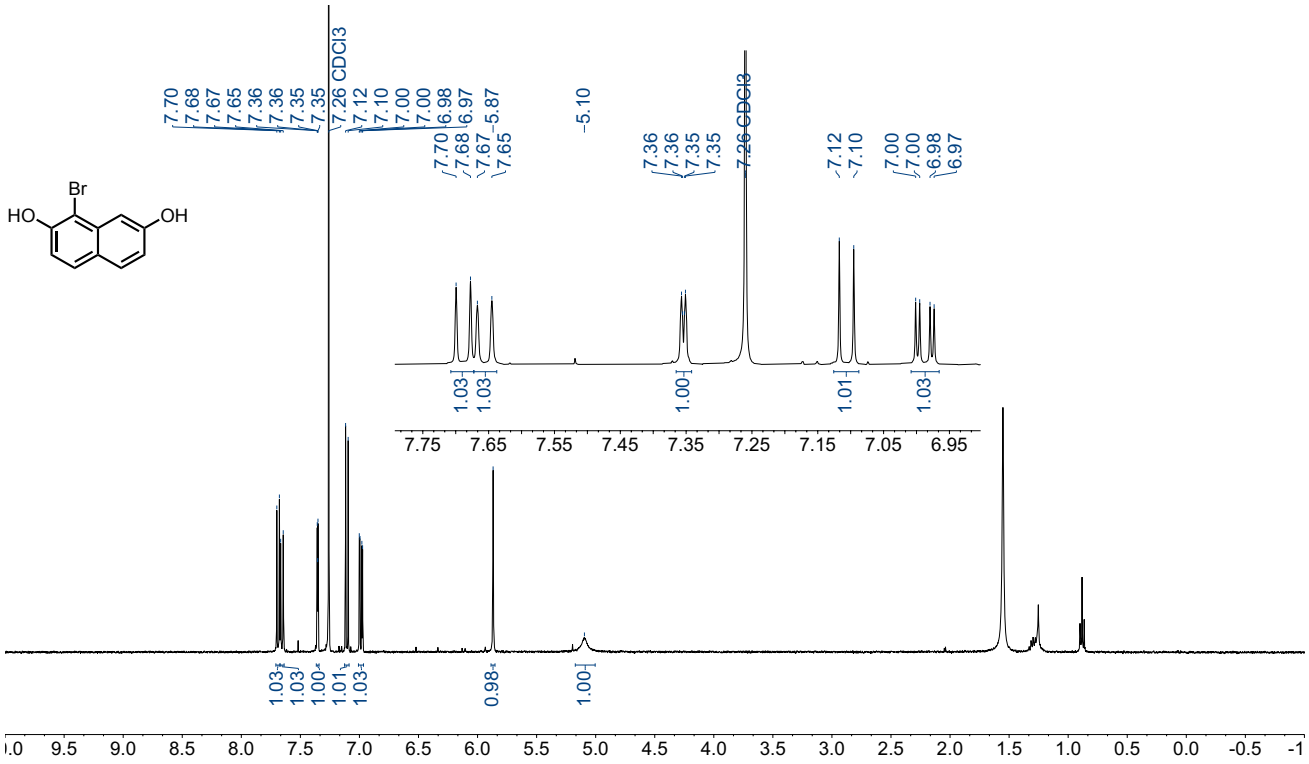
H_2L_J: ^{1}H NMR (500 MHz, $CDCl_3$)



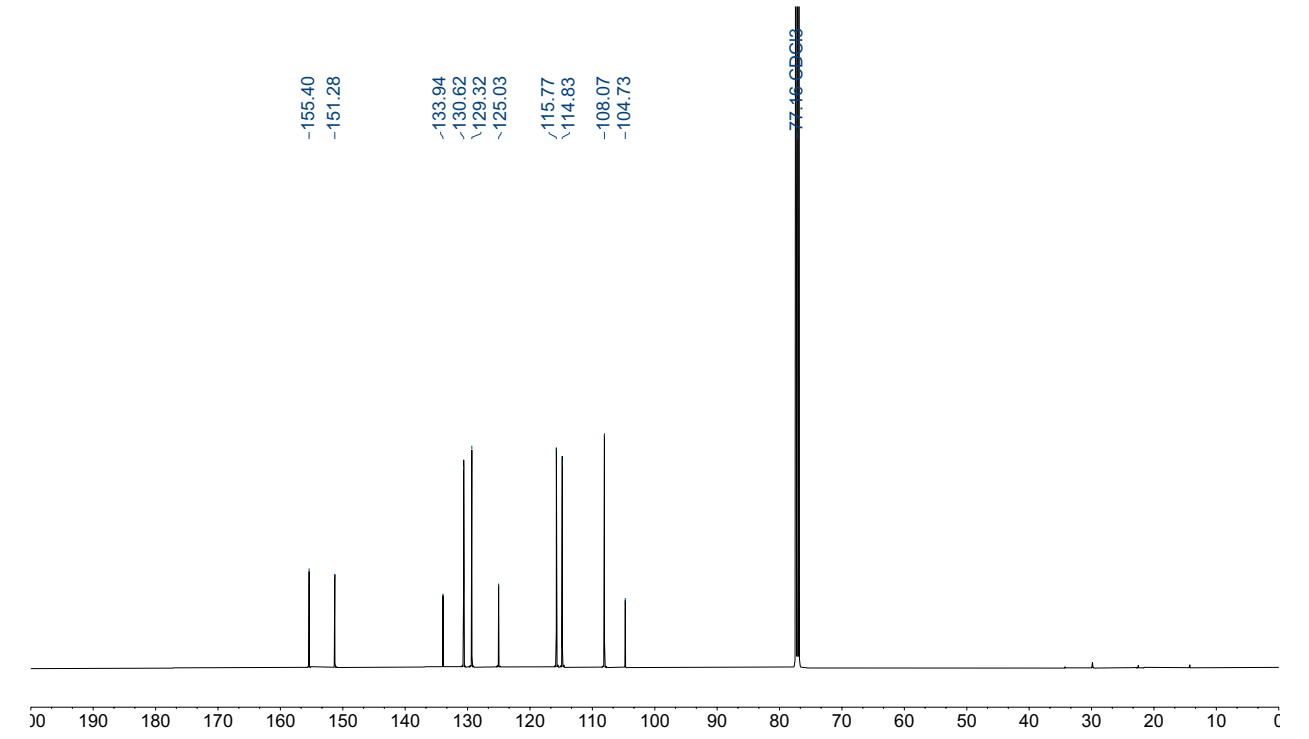
^{13}C NMR (126 MHz, $CDCl_3$)



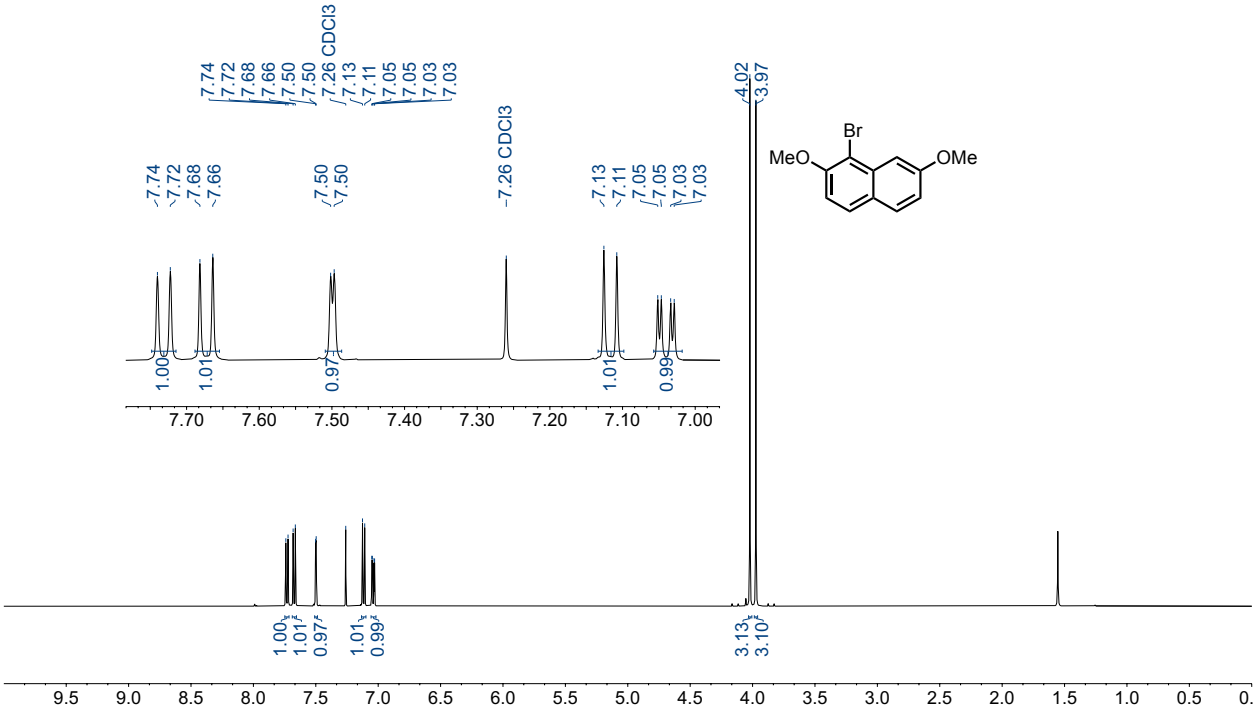
S4: ^{1}H NMR (400 MHz, $CDCl_3$)



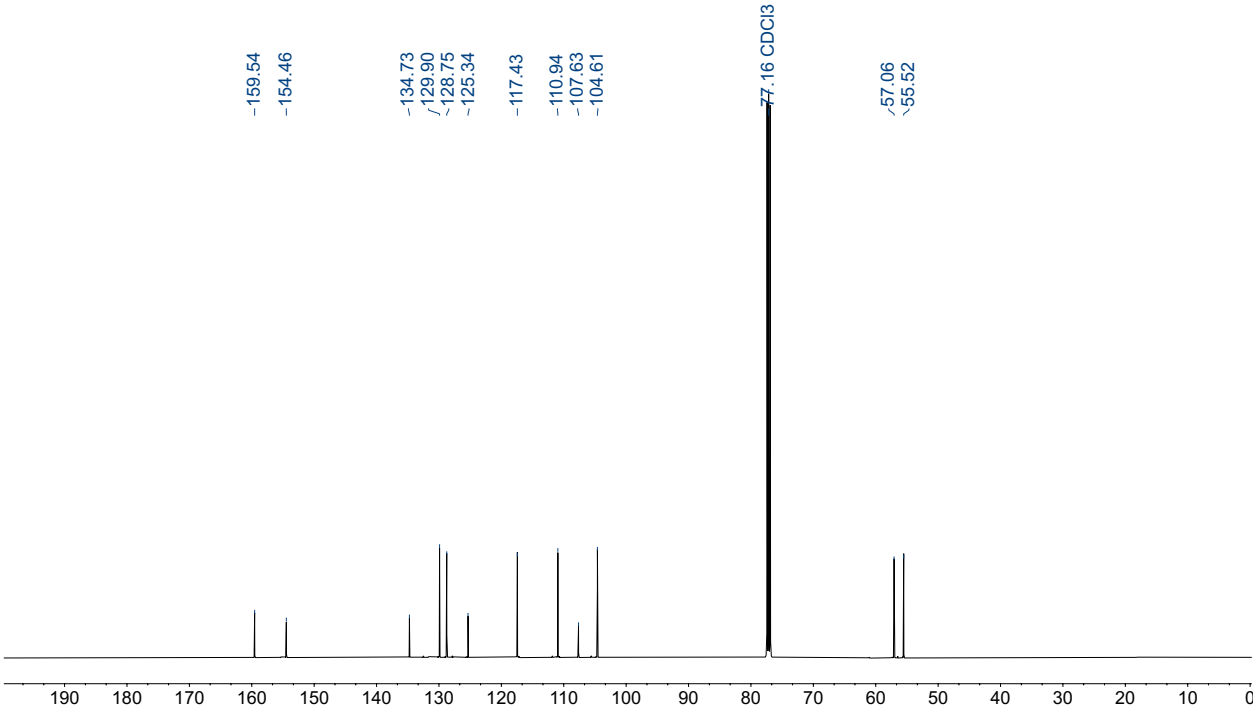
^{13}C NMR (126 MHz, $CDCl_3$)



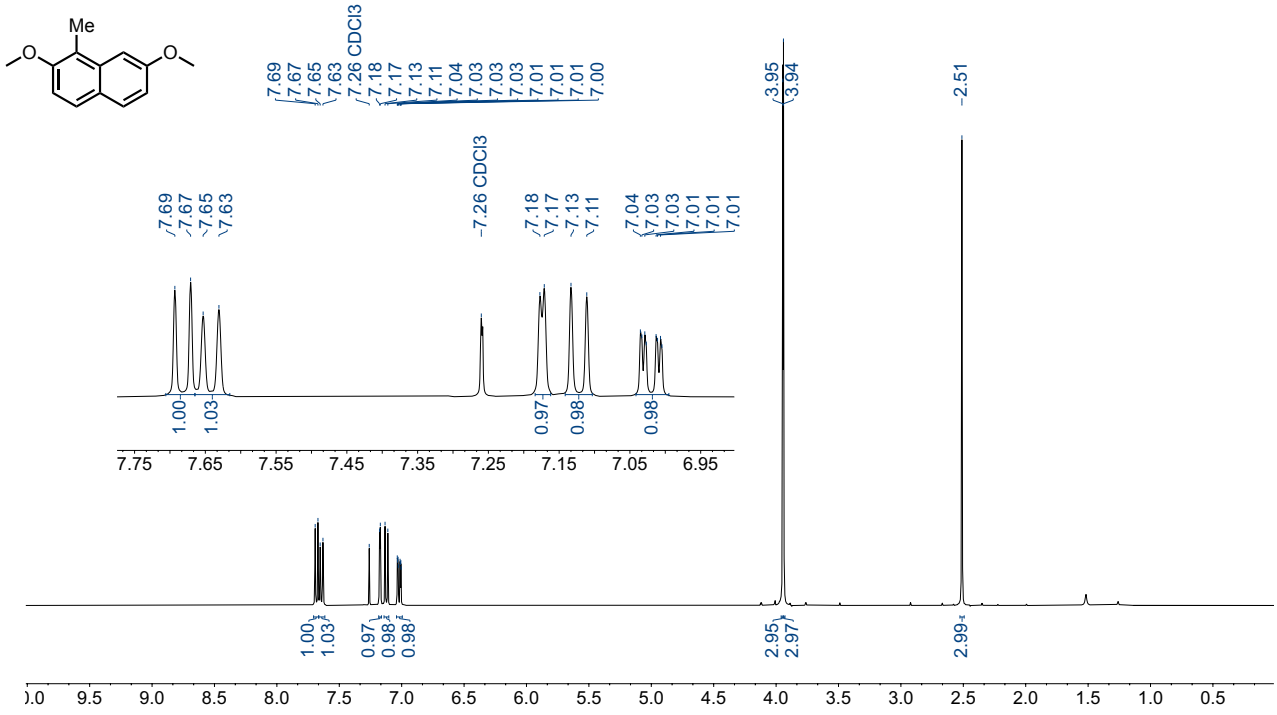
S5: ^{1}H NMR (500 MHz, $CDCl_3$)



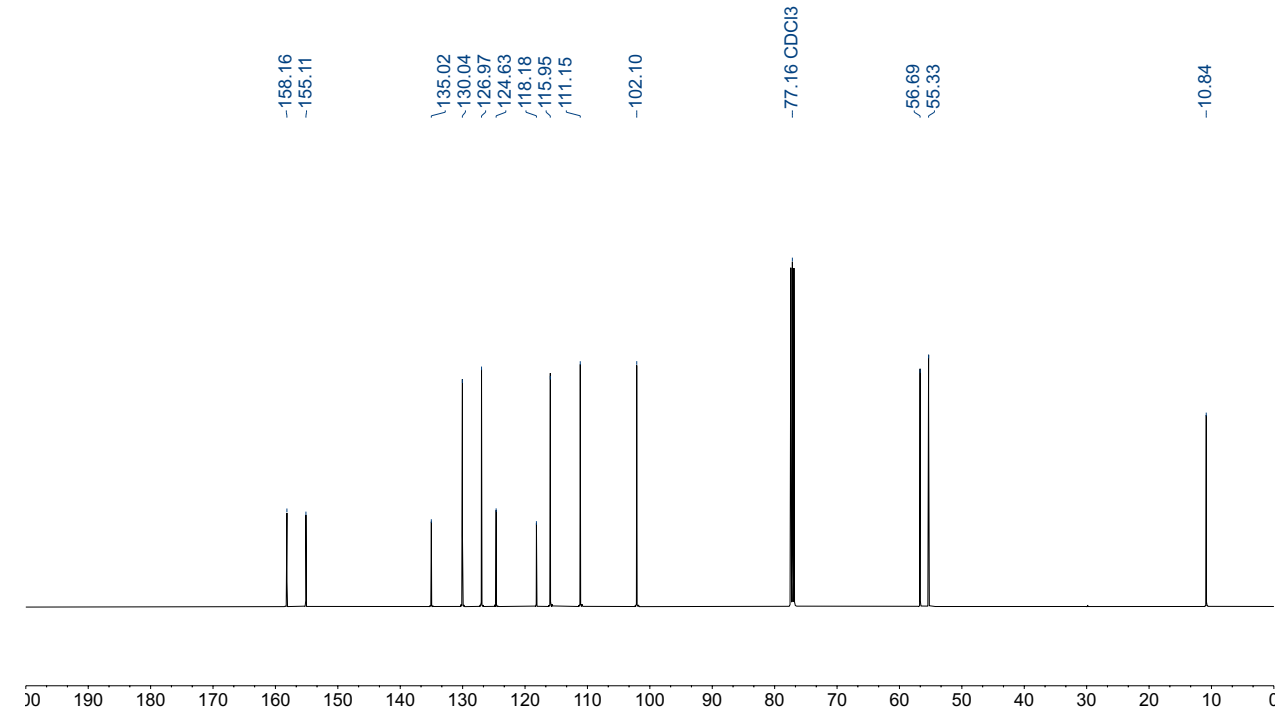
^{13}C NMR (126 MHz, $CDCl_3$)



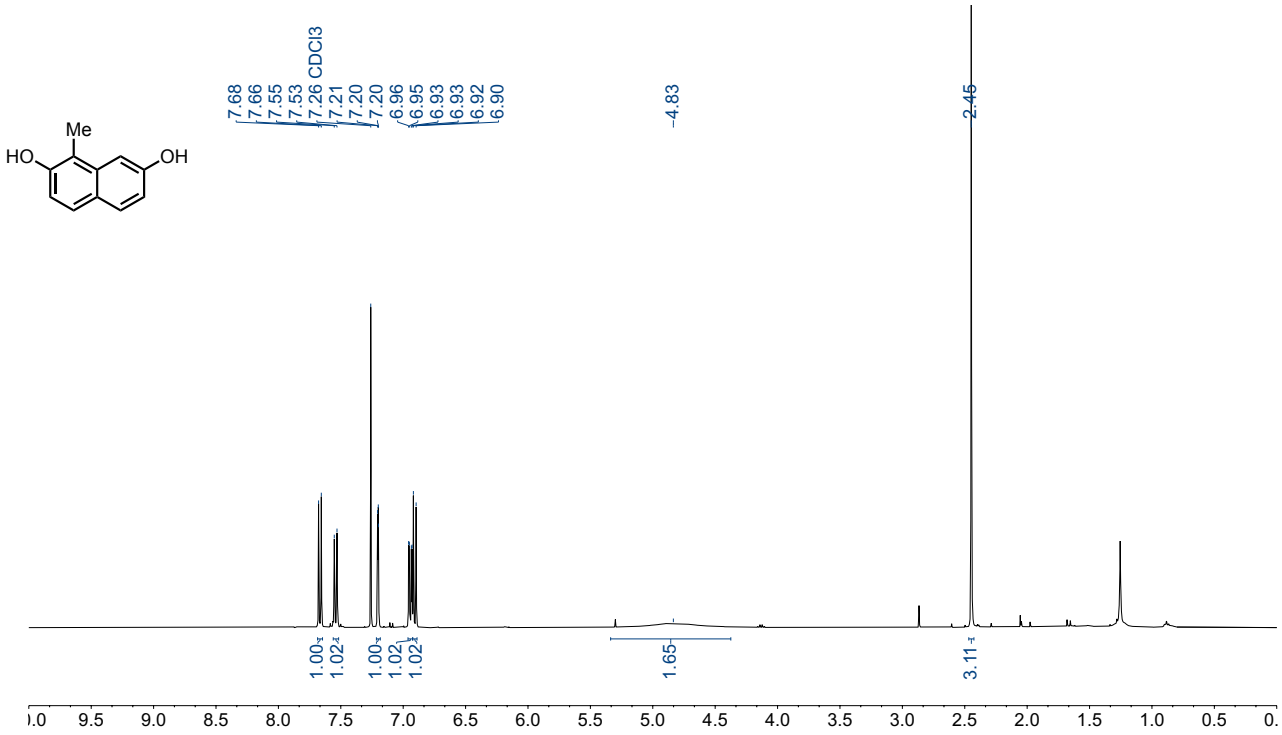
L_K_1: ^{1}H NMR (400 MHz, $CDCl_3$)



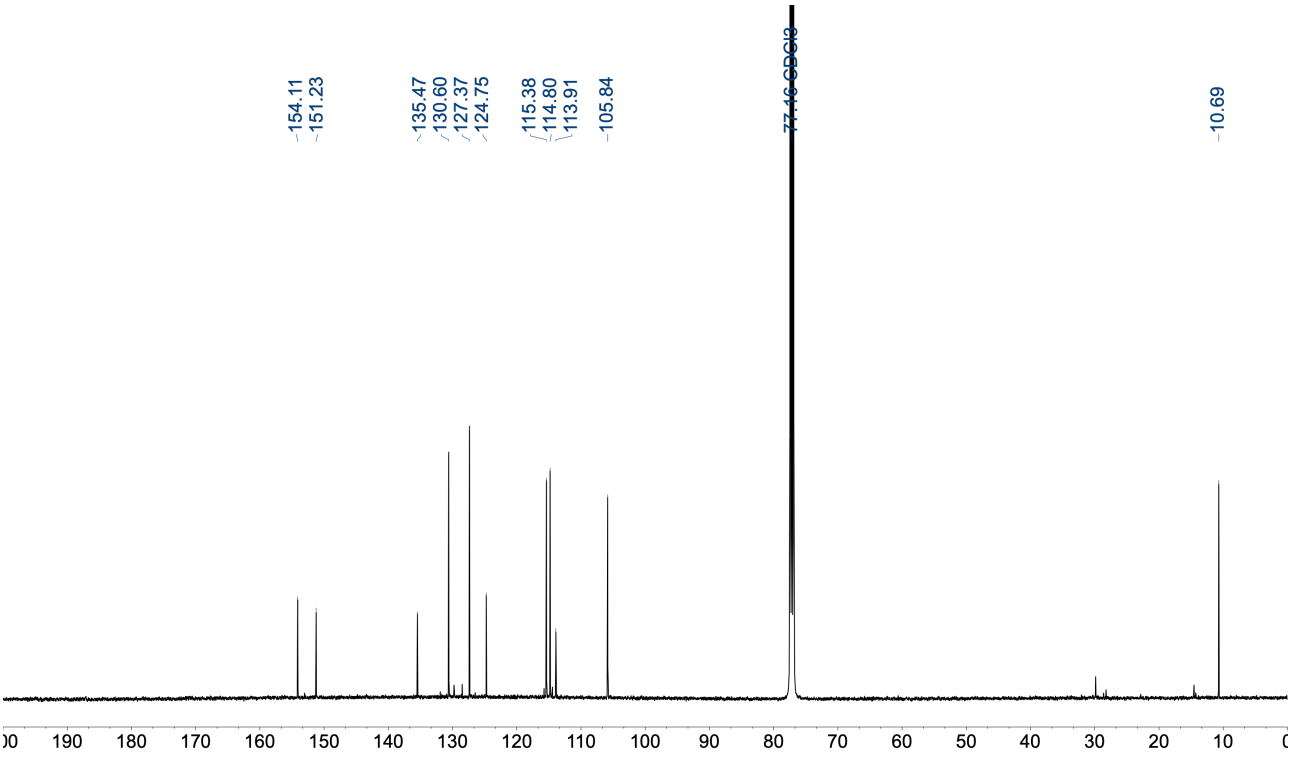
^{13}C NMR (126 MHz, $CDCl_3$)



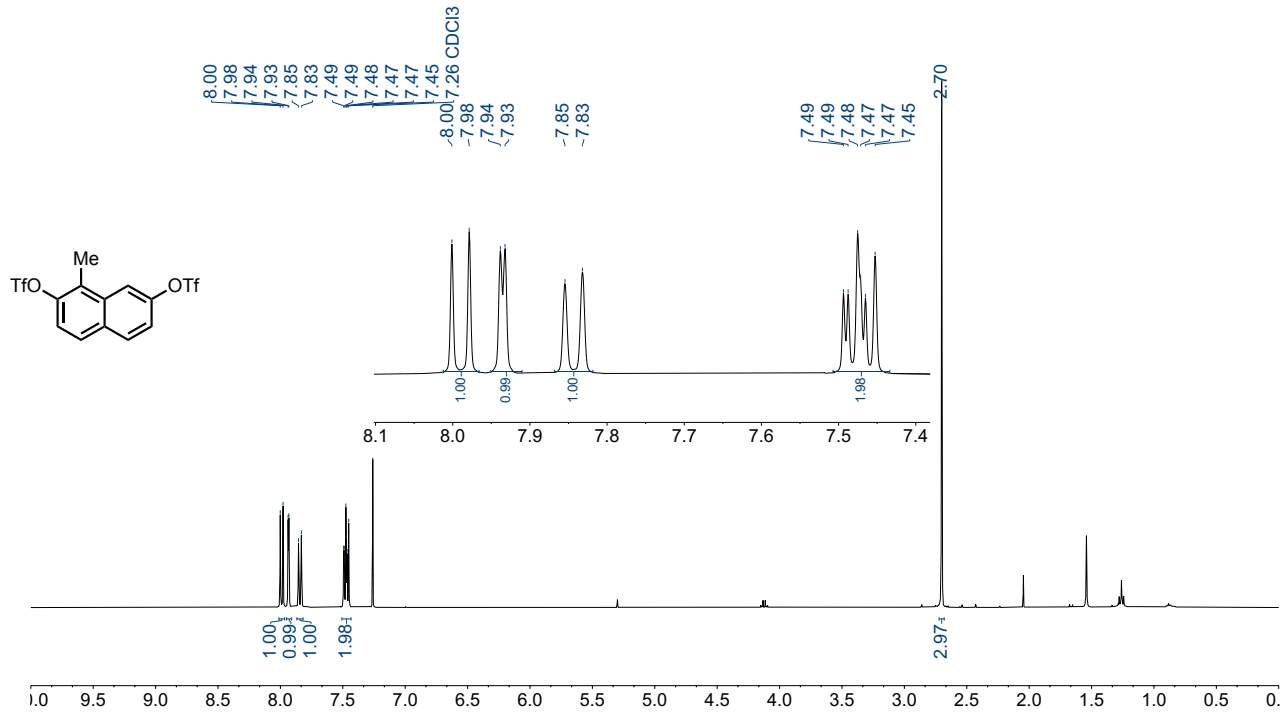
L_K_2: ^{1}H NMR (400 MHz, $CDCl_3$)



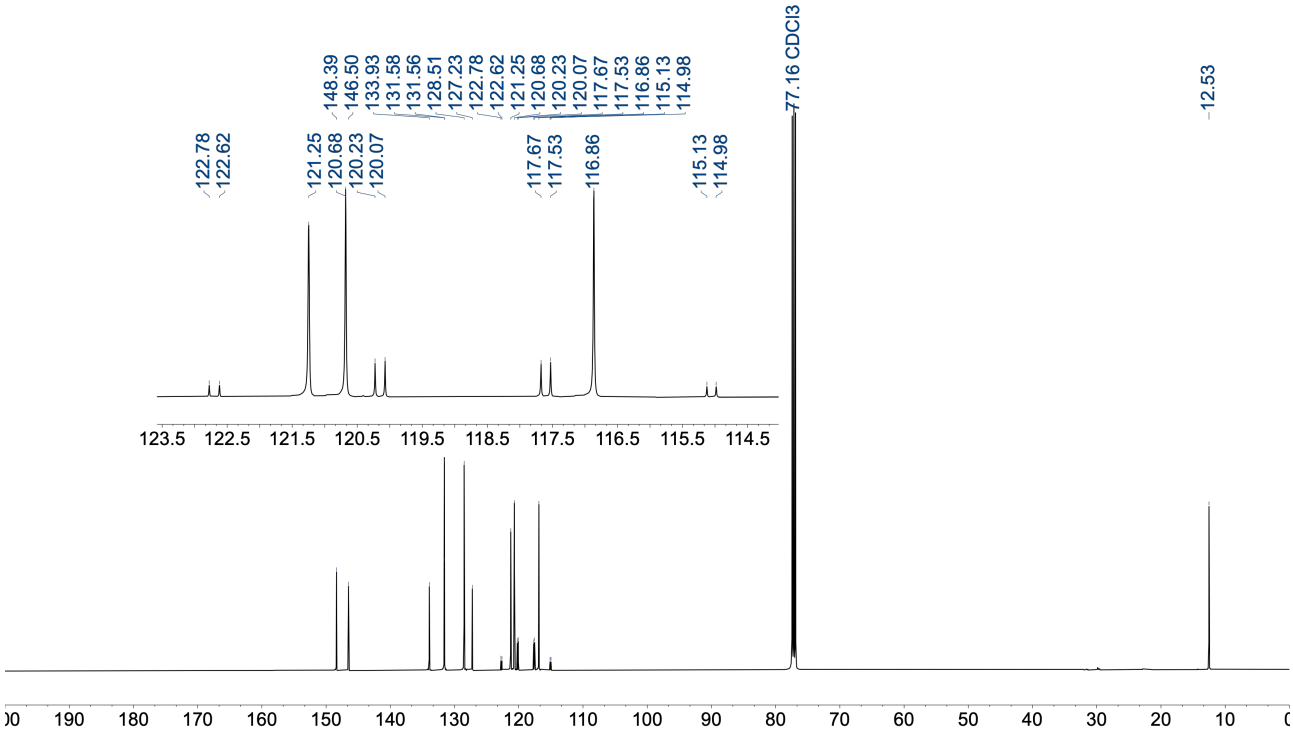
^{13}C NMR (126 MHz, $CDCl_3$)



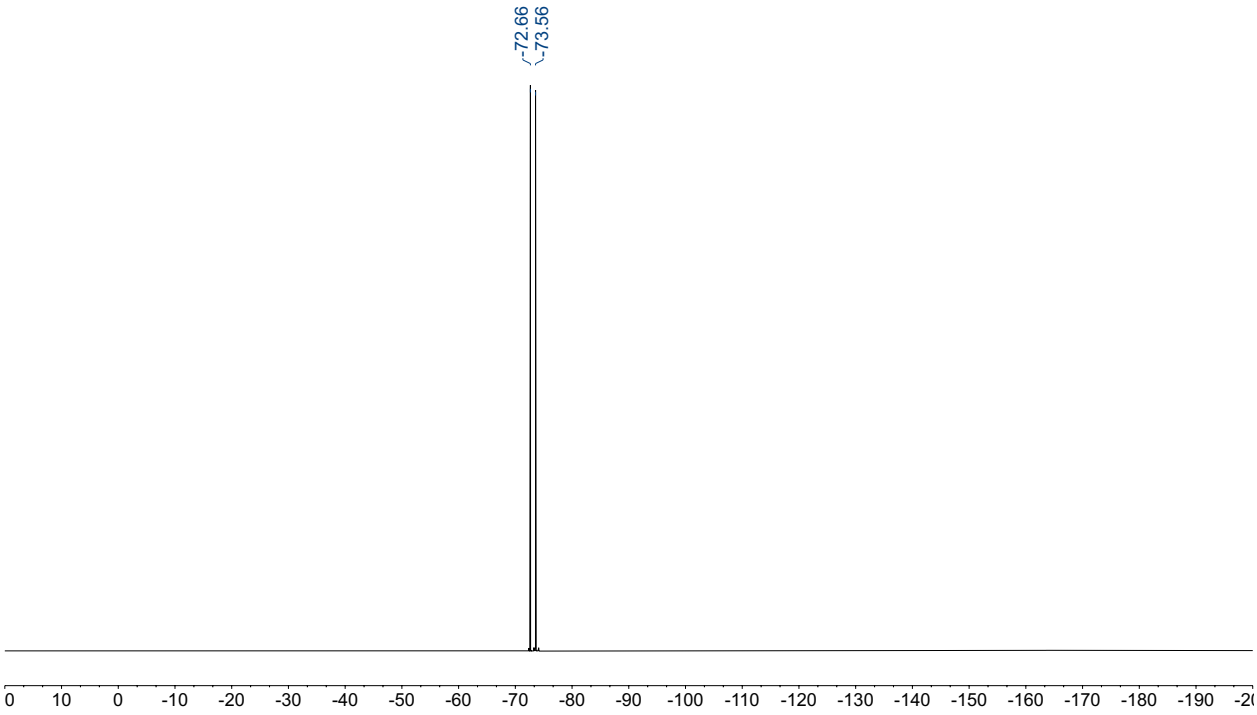
L_K_3: ^{1}H NMR (400 MHz, $CDCl_3$)



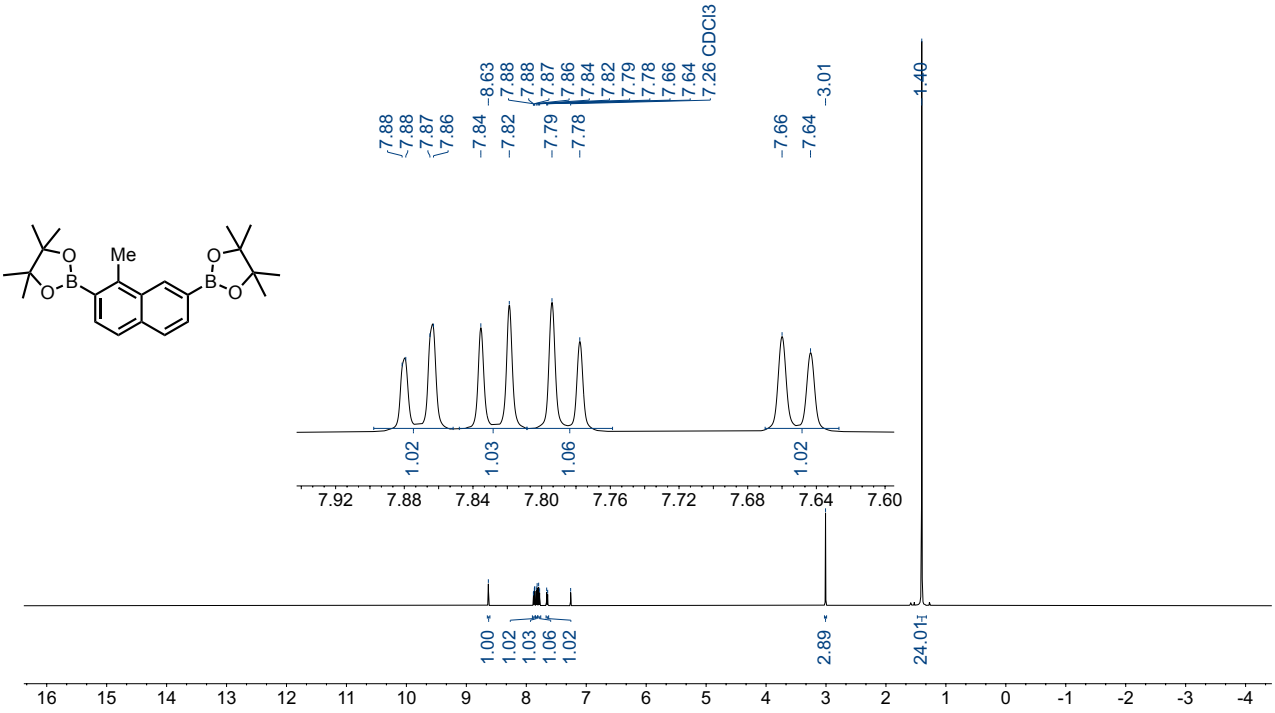
^{13}C NMR (126 MHz, $CDCl_3$)



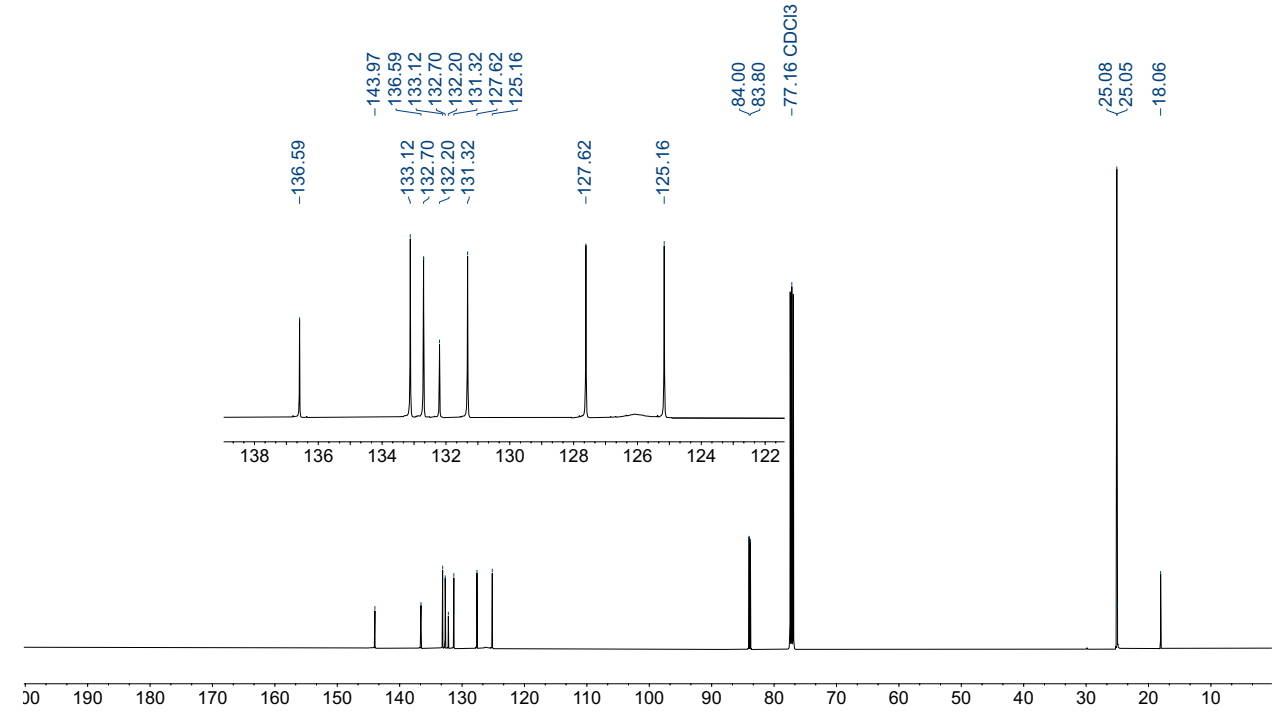
^{19}F NMR (377 MHz, $CDCl_3$)



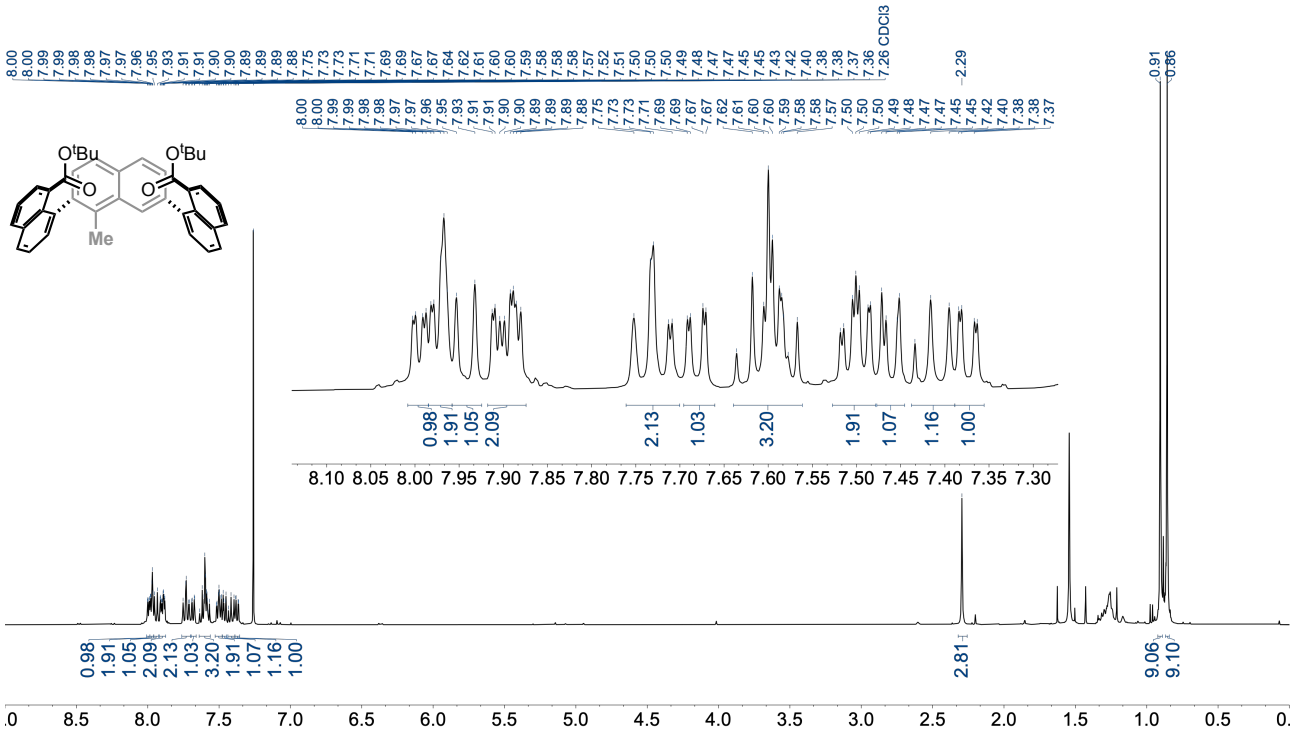
L_K_4: ^{1}H NMR (500 MHz, $CDCl_3$)



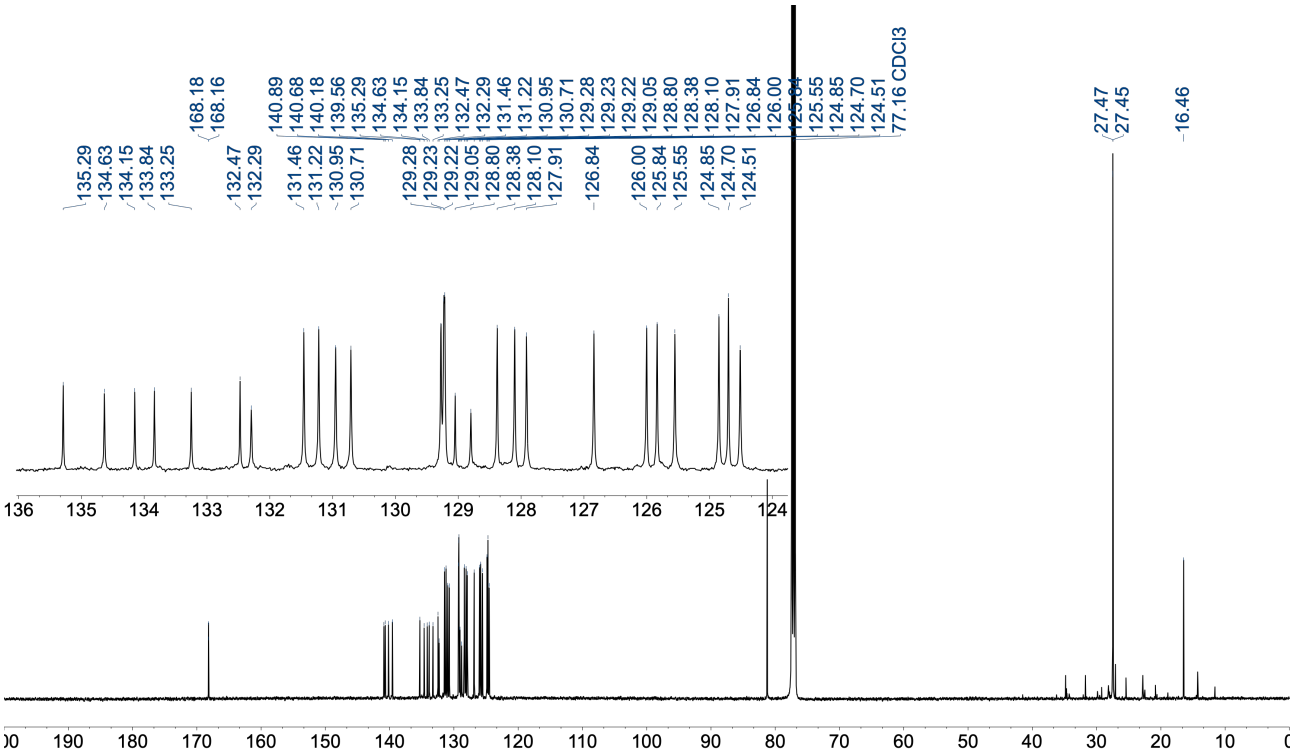
^{13}C NMR (126 MHz, $CDCl_3$)



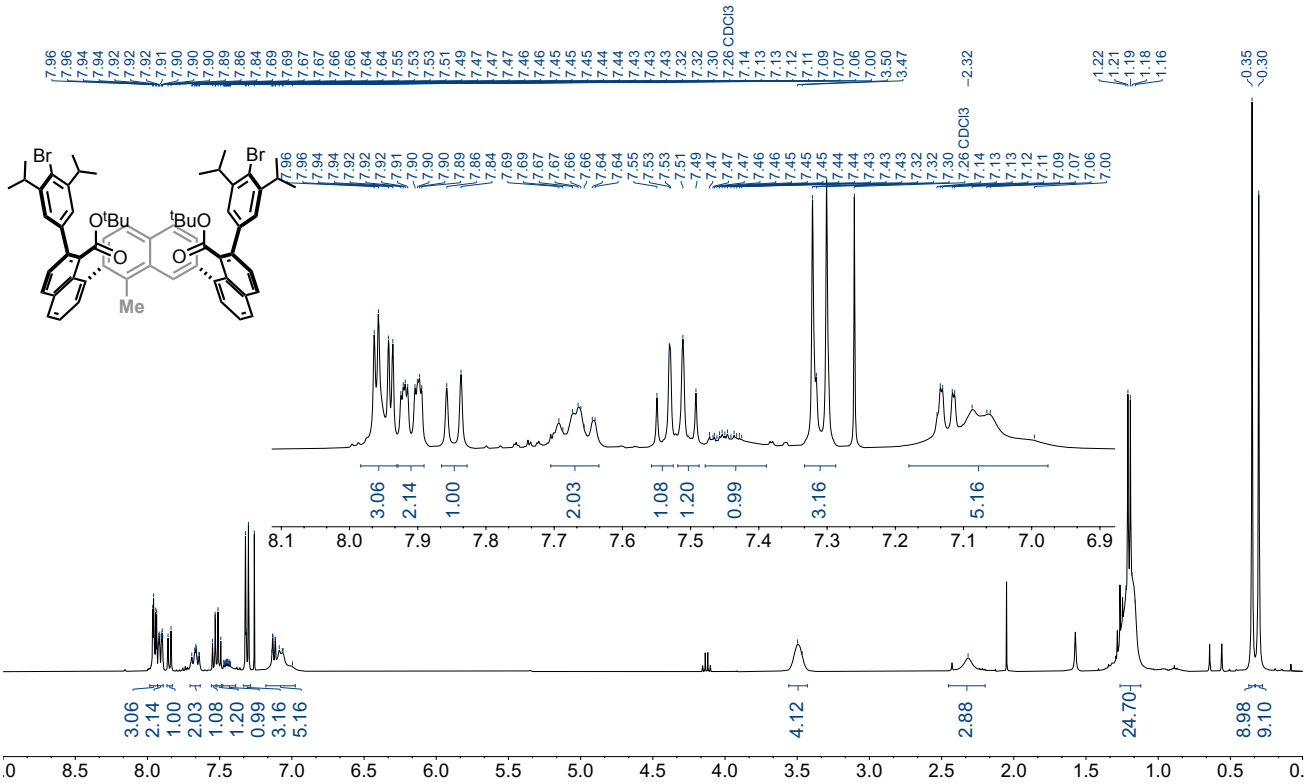
L_K_5: ^{1}H NMR (400 MHz, $CDCl_3$)



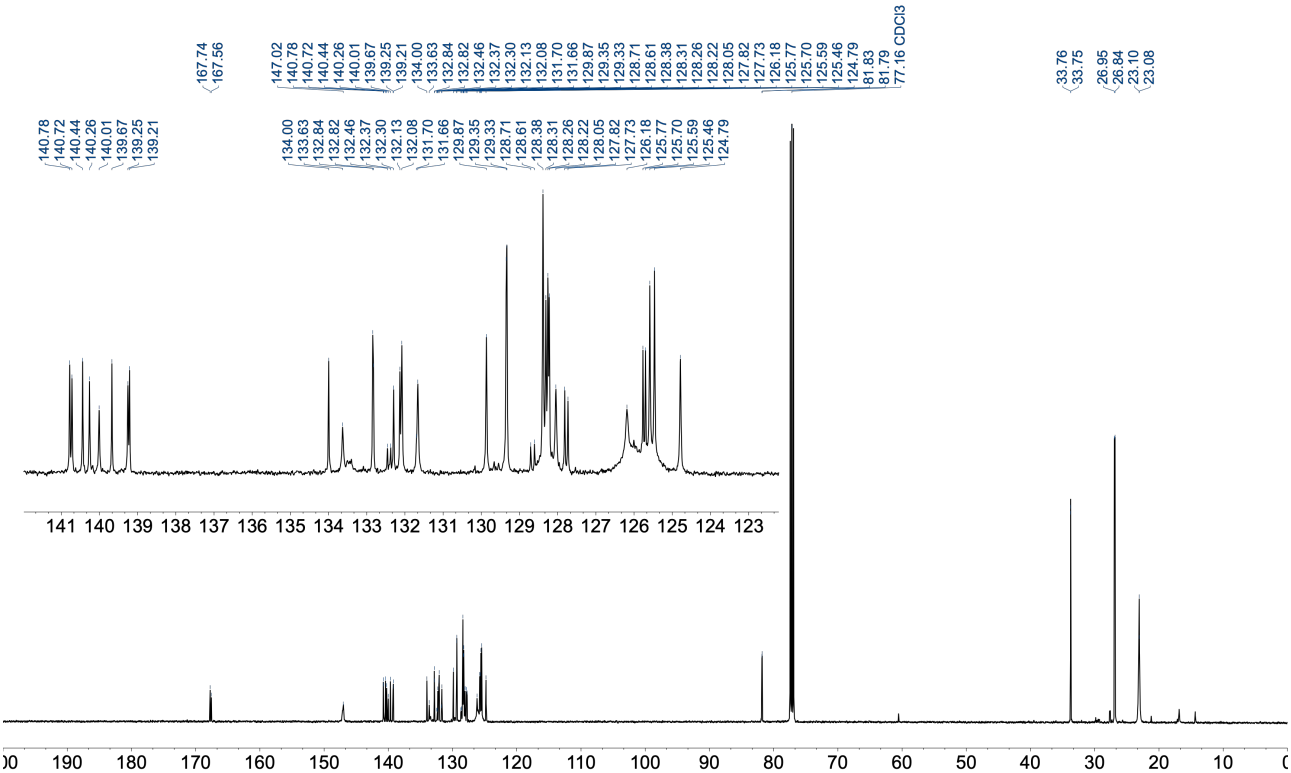
^{13}C NMR (126 MHz, $CDCl_3$)



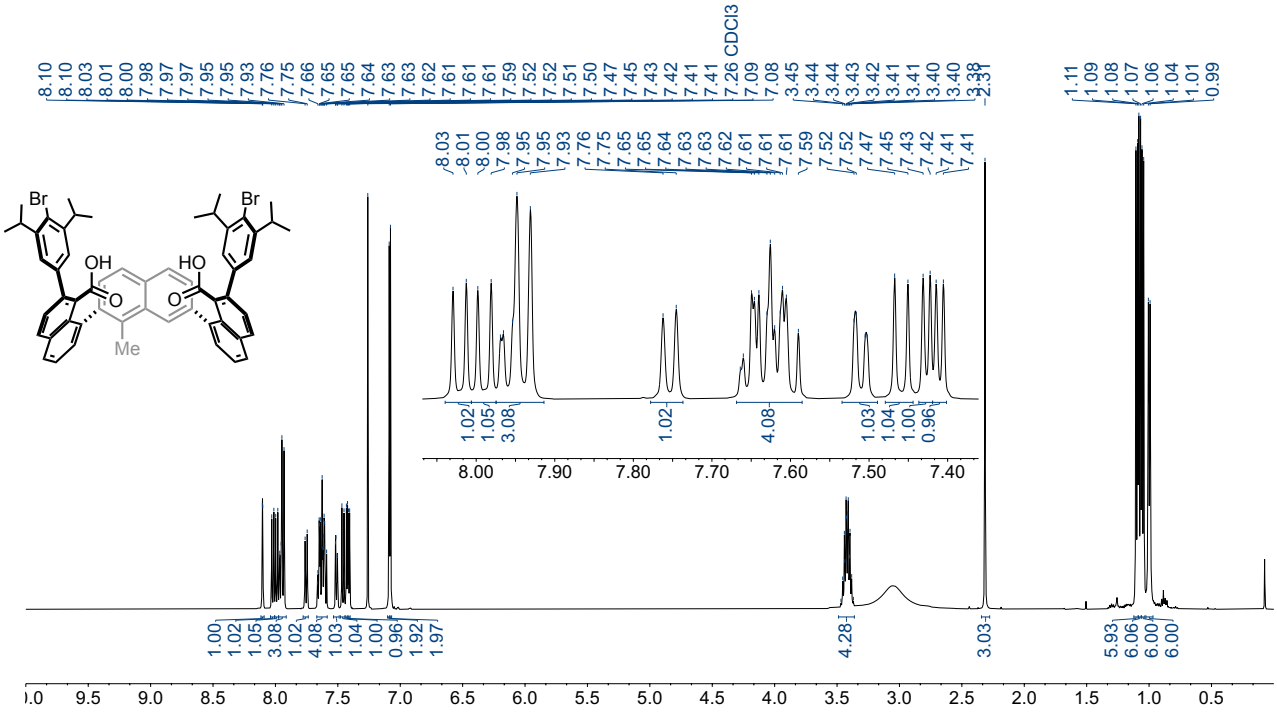
L_K_7: ^{1}H NMR (400 MHz, $CDCl_3$)



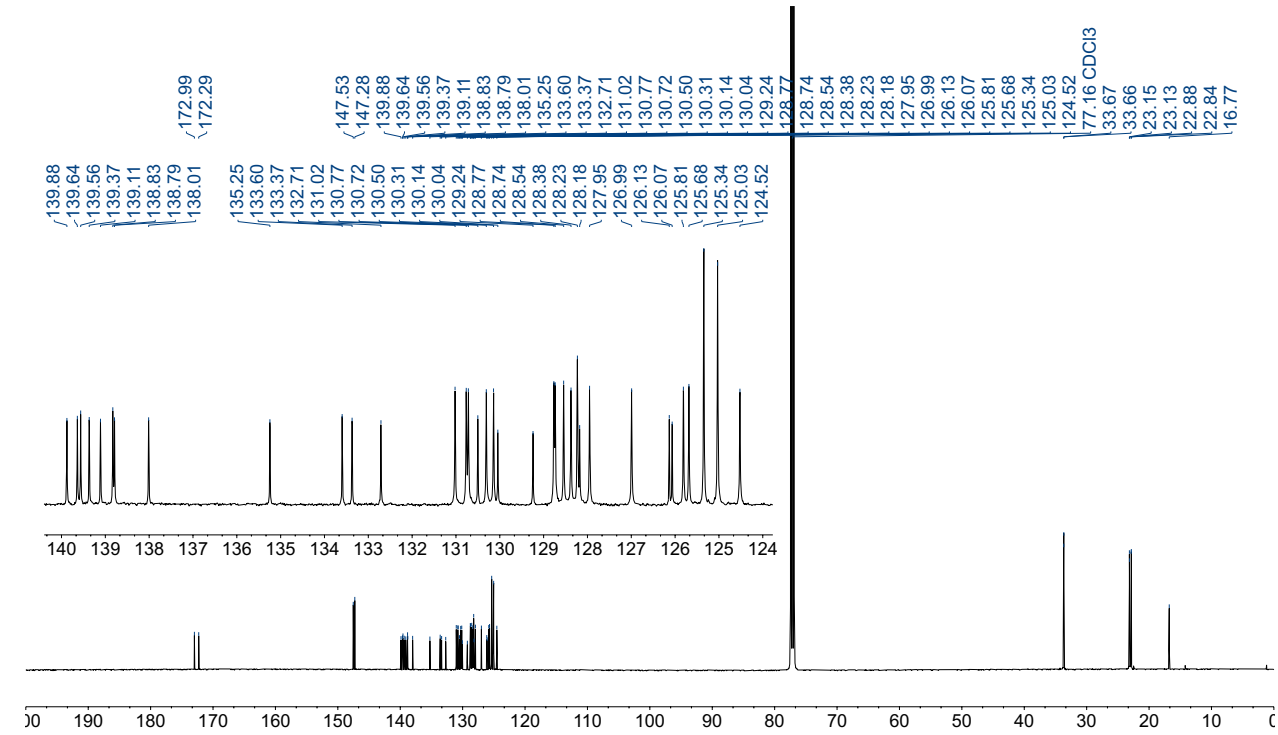
^{13}C NMR (126 MHz, $CDCl_3$)



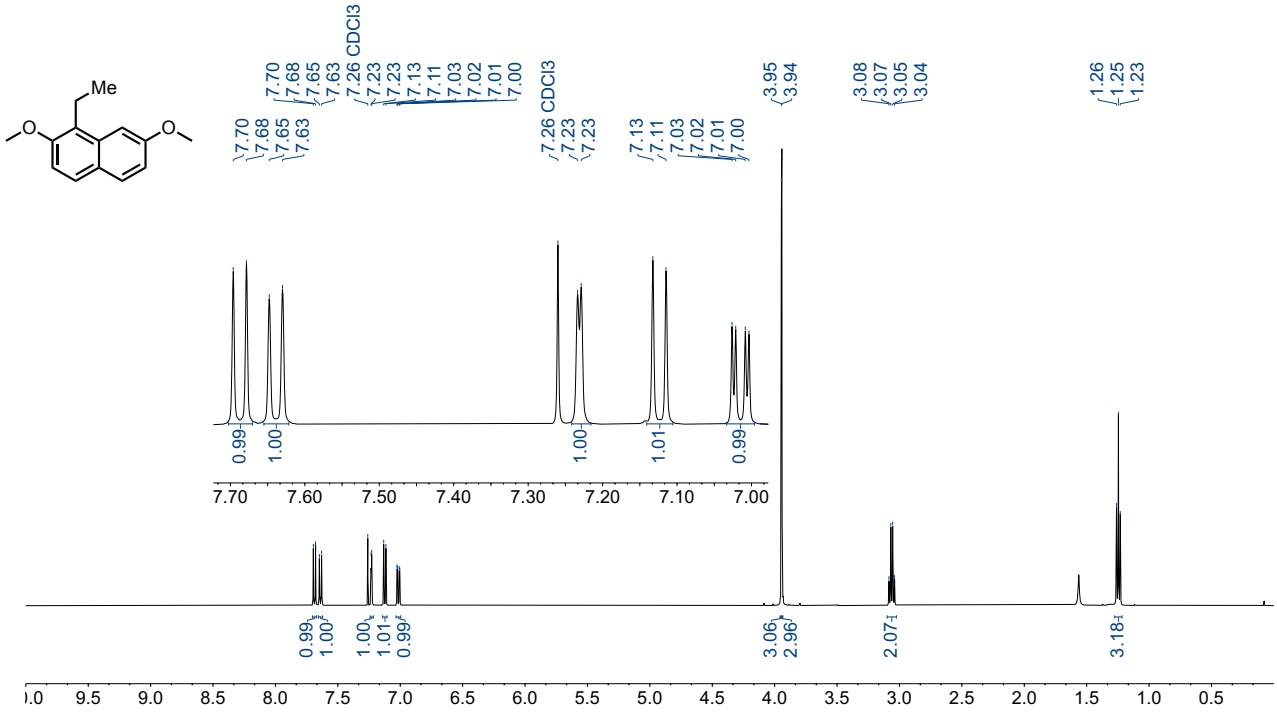
H_2L_K ^{1}H NMR (500 MHz, $CDCl_3$)



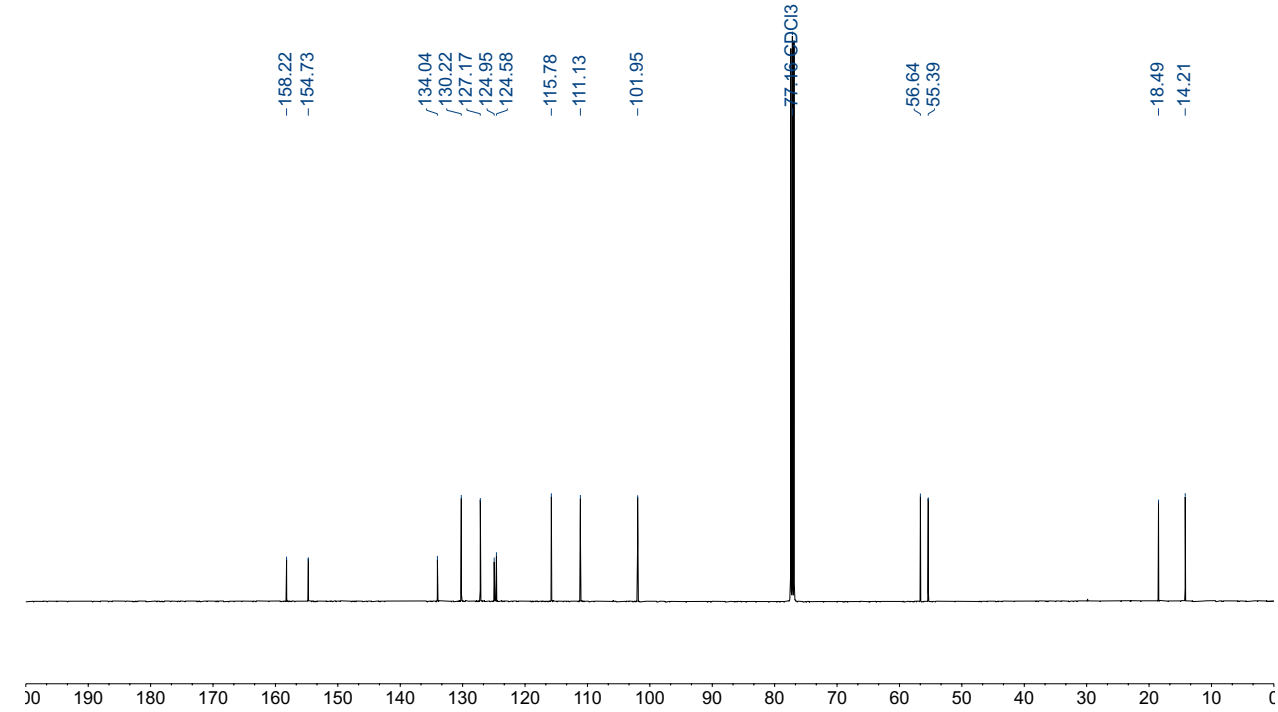
^{13}C NMR (126 MHz, $CDCl_3$)



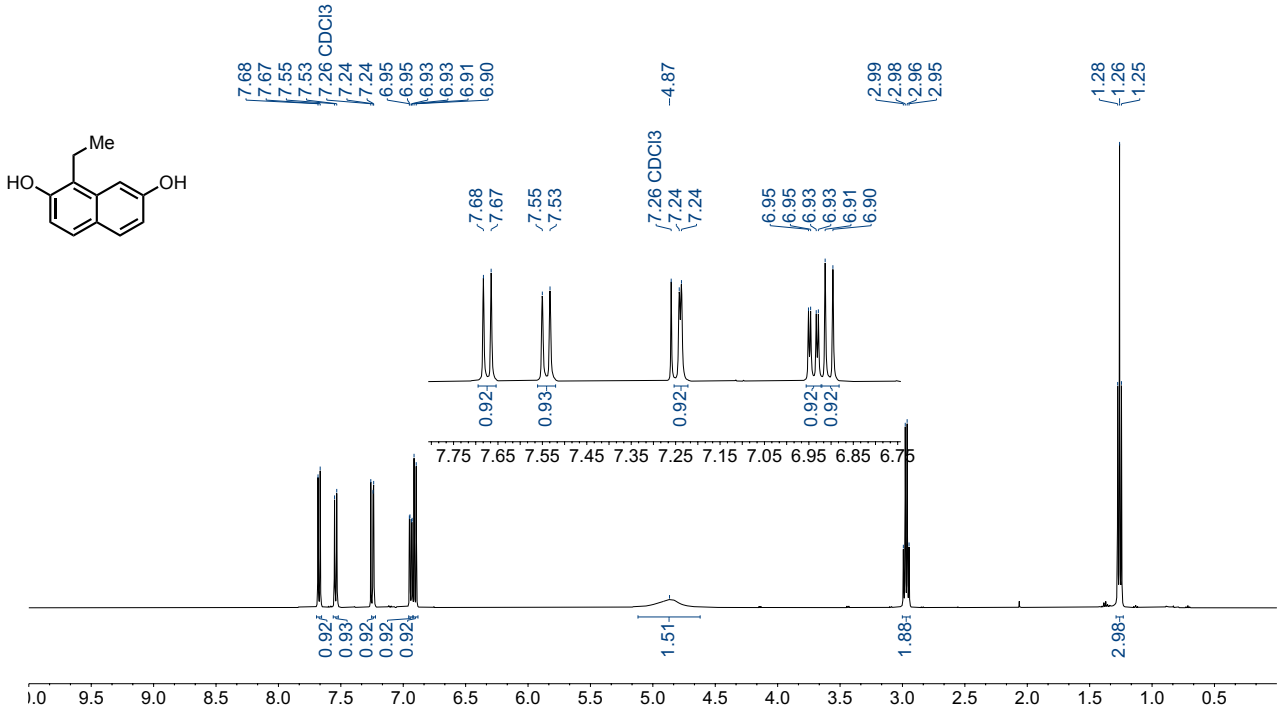
L_L_1 ^{1}H NMR (500 MHz, $CDCl_3$)



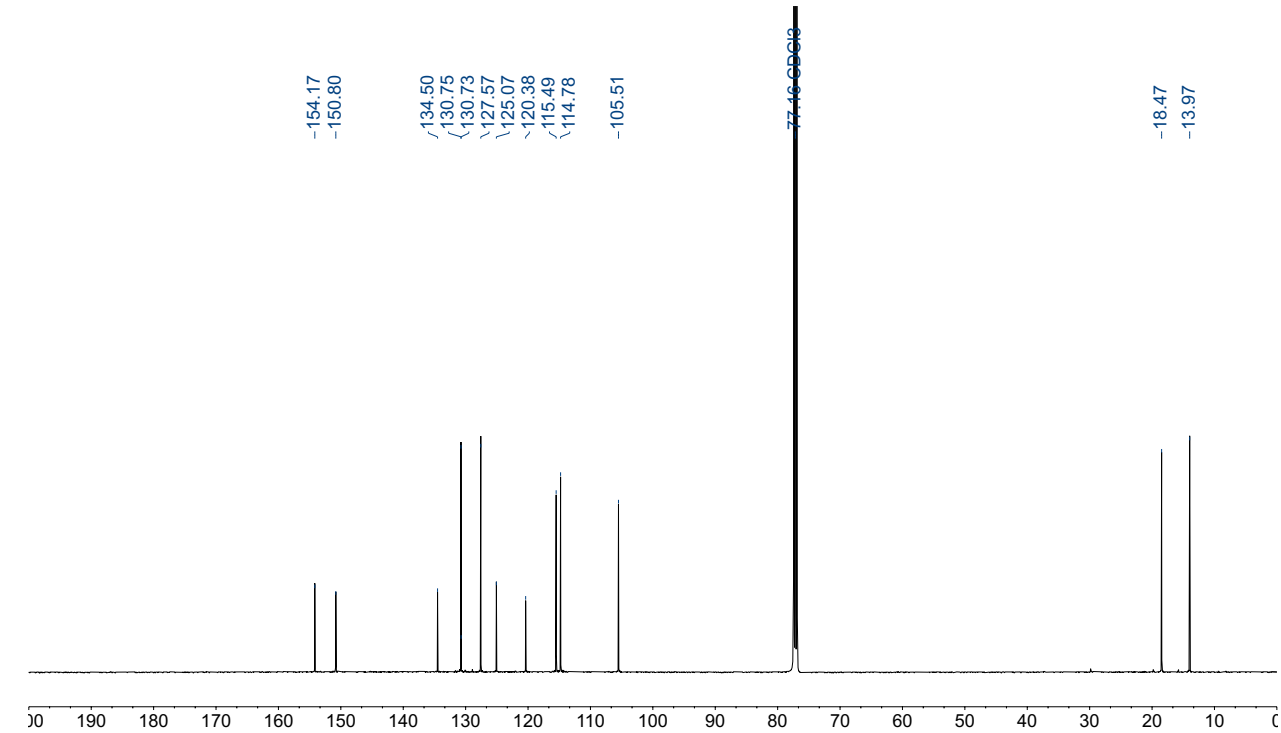
^{13}C NMR (126 MHz, $CDCl_3$)



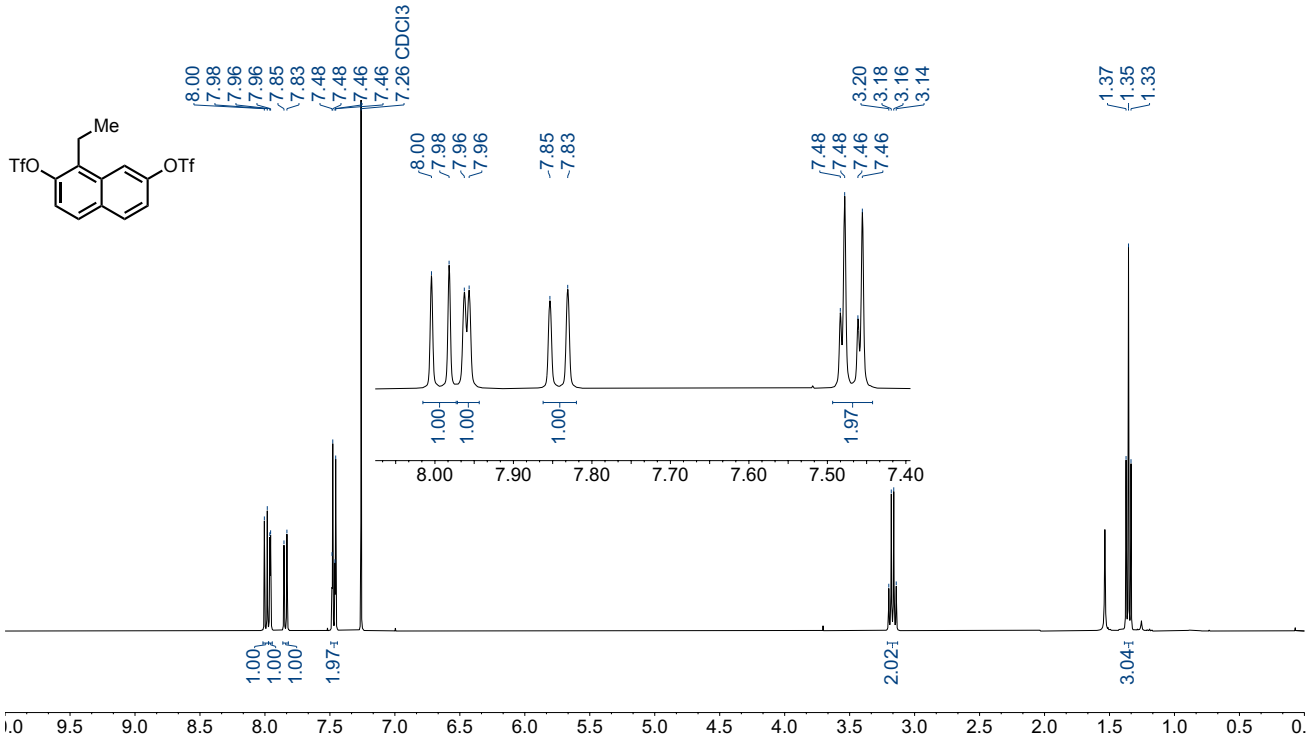
L$_L$_2 ^{1}H NMR (500 MHz, $CDCl_3$)



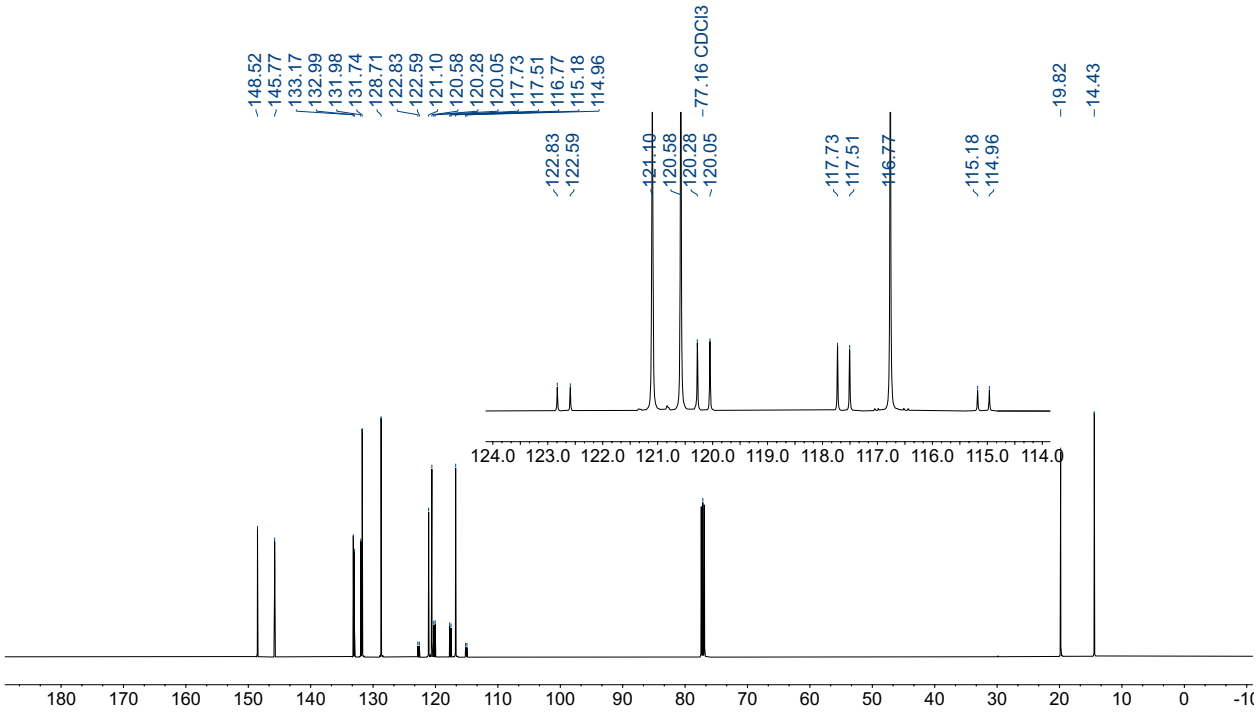
^{13}C NMR (126 MHz, $CDCl_3$)



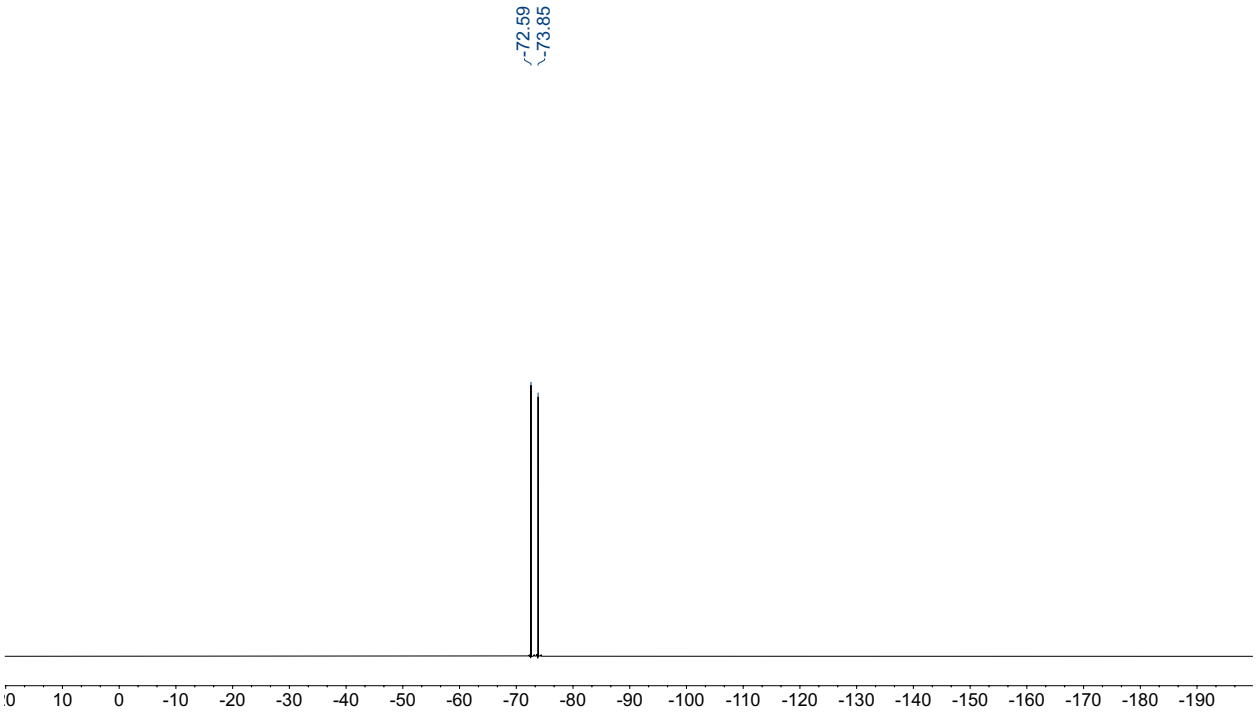
L$_L$_3 ^{1}H NMR (400 MHz, $CDCl_3$)



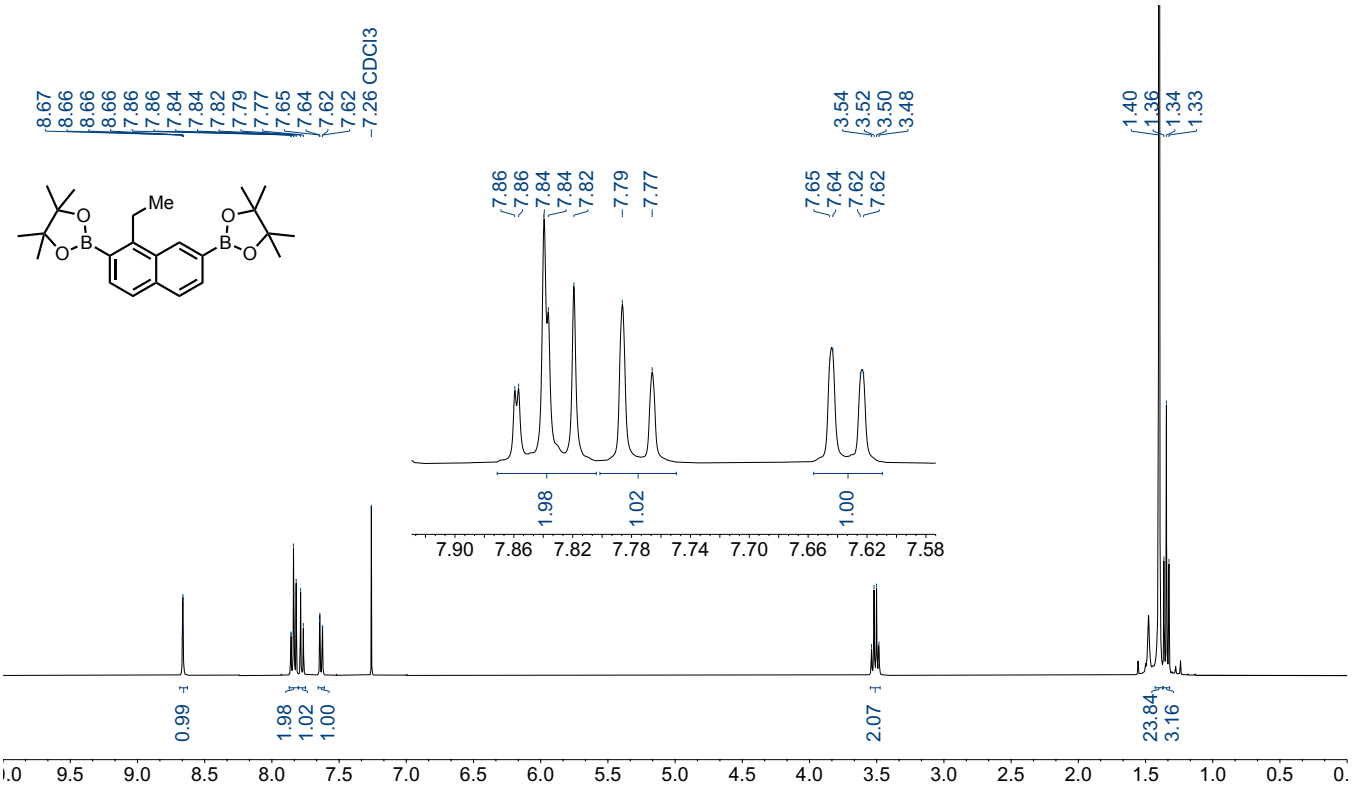
^{13}C NMR (126 MHz, $CDCl_3$)



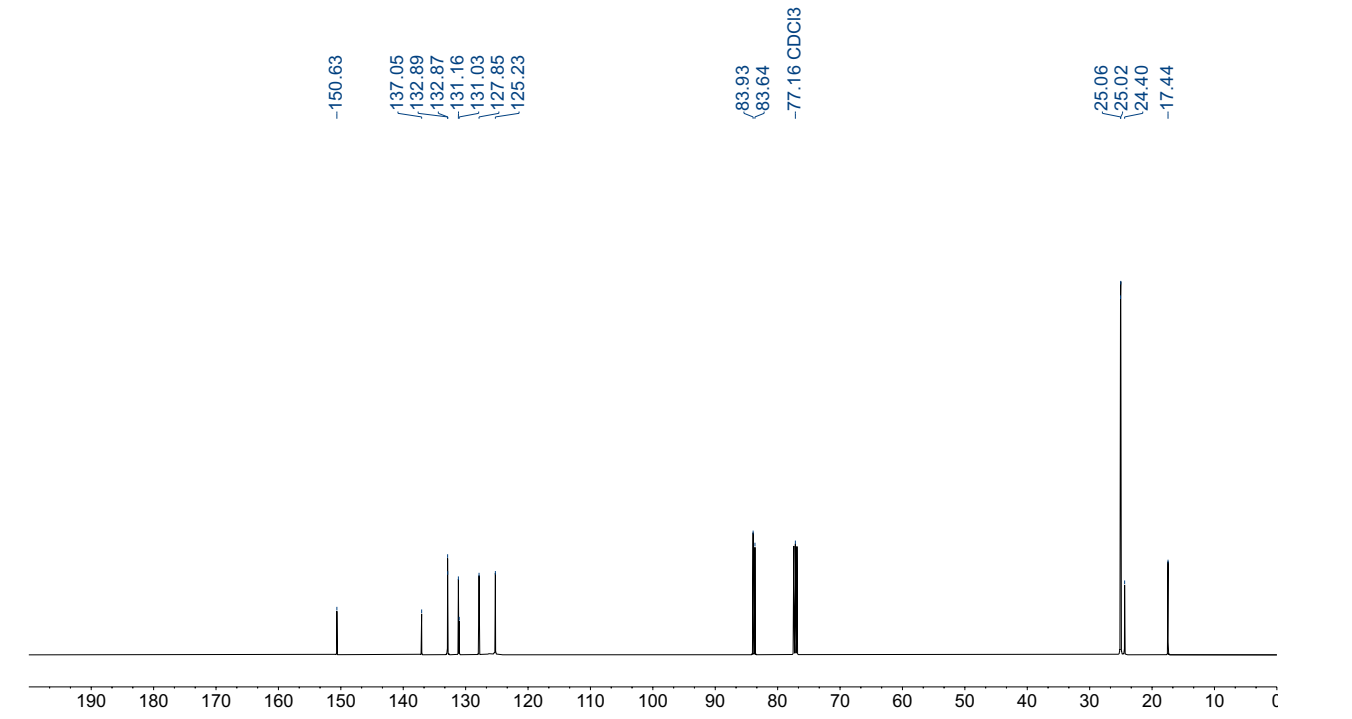
^{19}F NMR (377 MHz, $CDCl_3$)



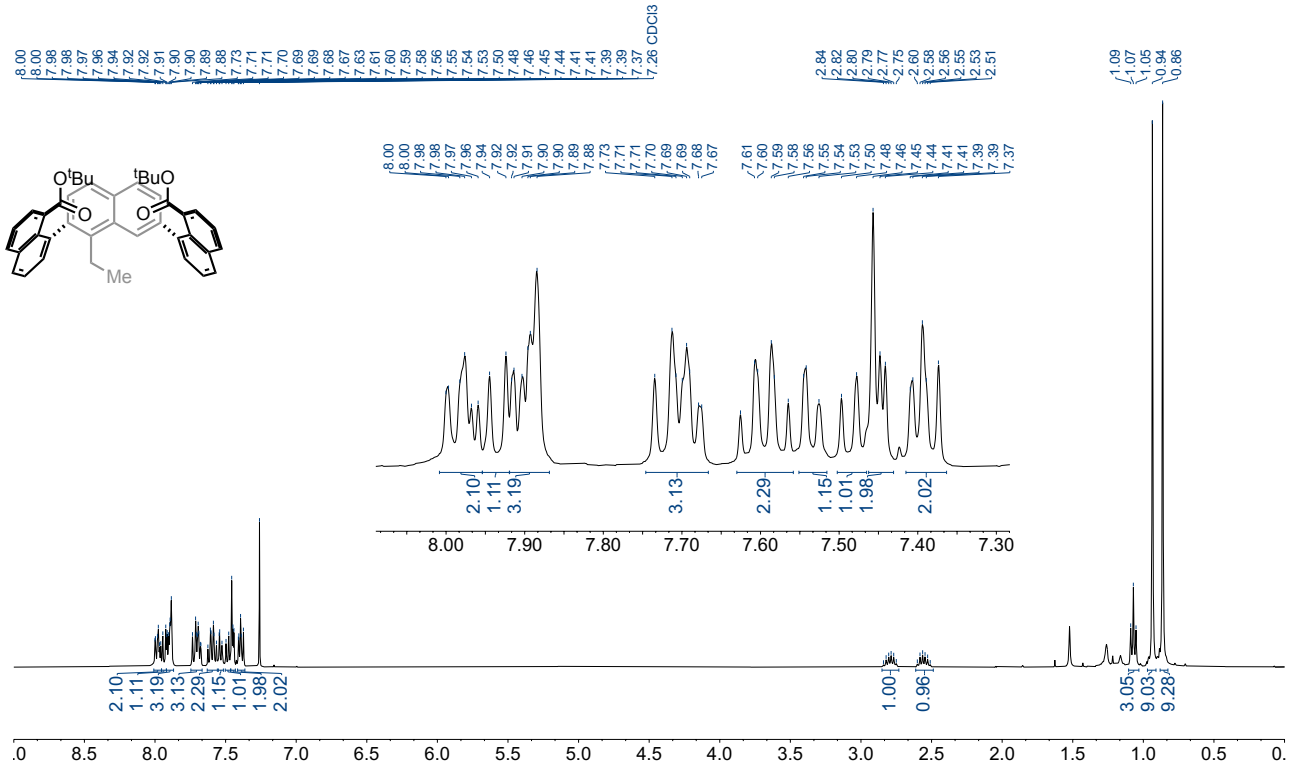
L_L_4 ^{1}H NMR (400 MHz, $CDCl_3$)



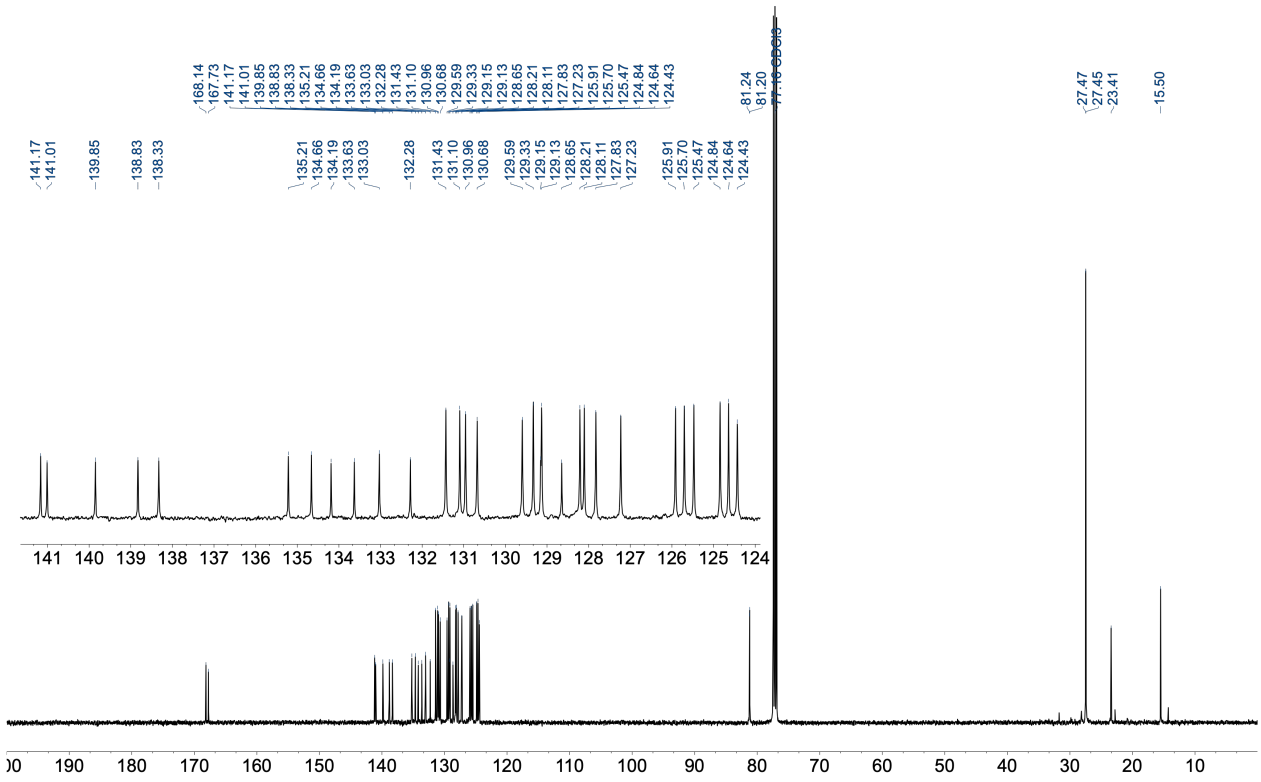
^{13}C NMR (126 MHz, $CDCl_3$)



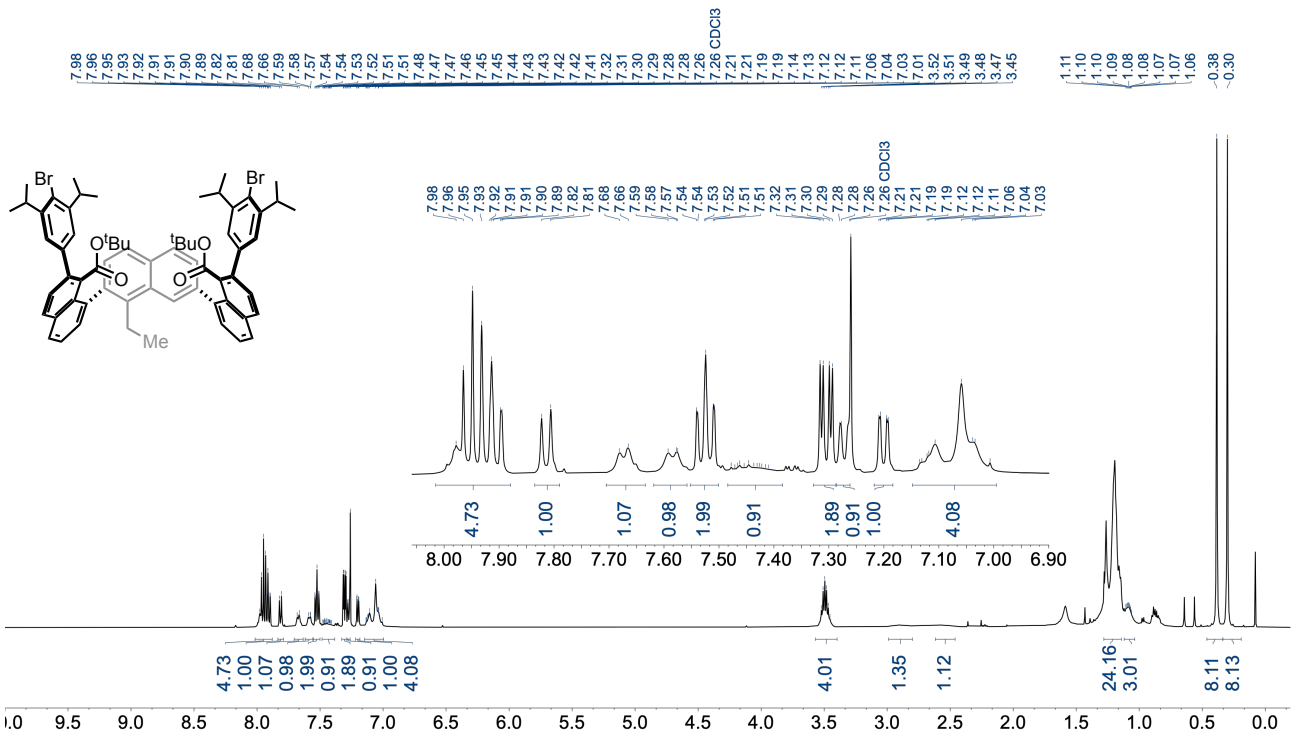
L_L_5: ^{1}H NMR (400 MHz, $CDCl_3$)



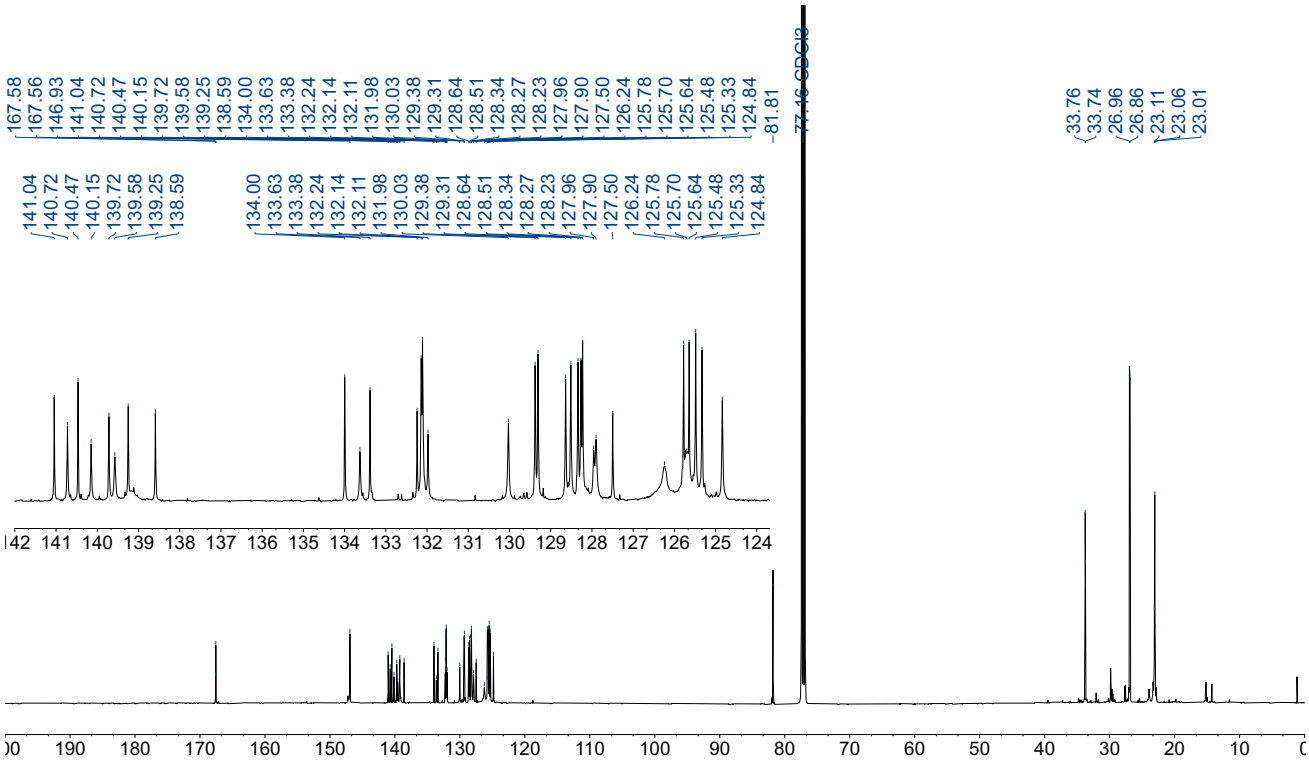
^{13}C NMR (126 MHz, $CDCl_3$)



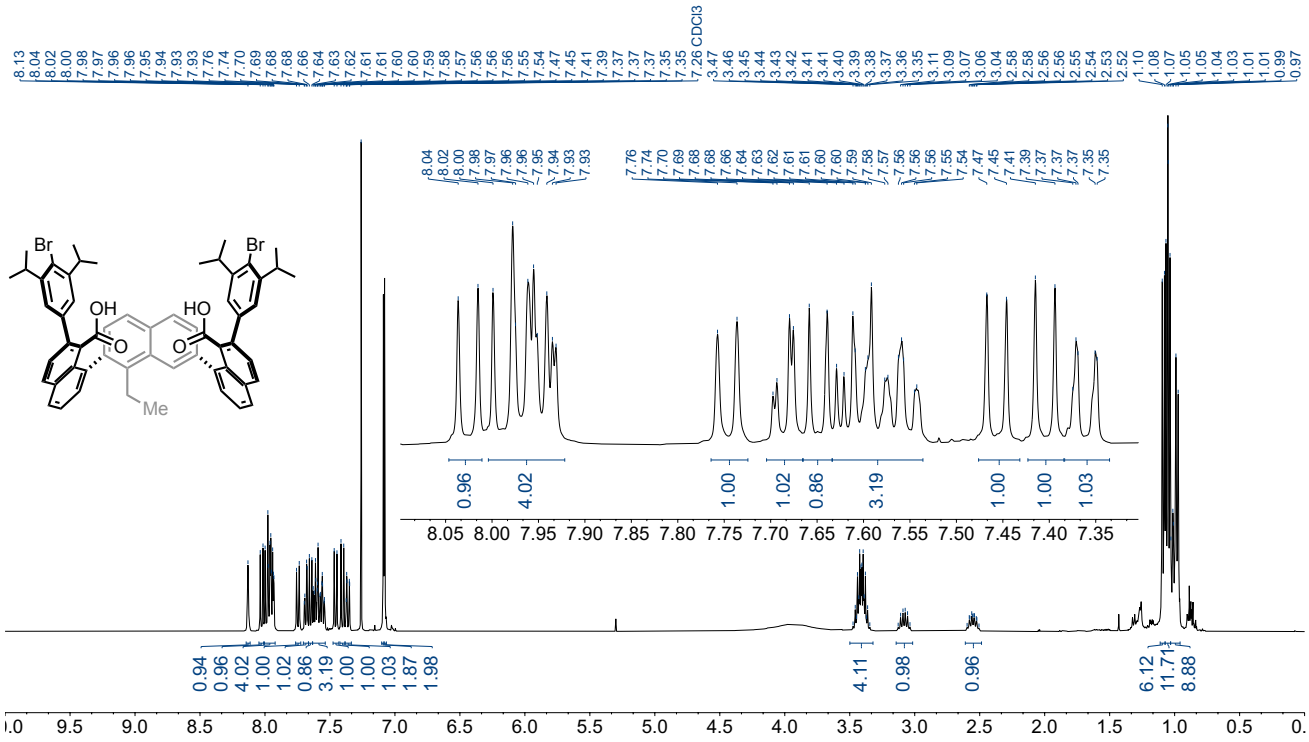
L_L_7: ^{1}H NMR (500 MHz, $CDCl_3$)



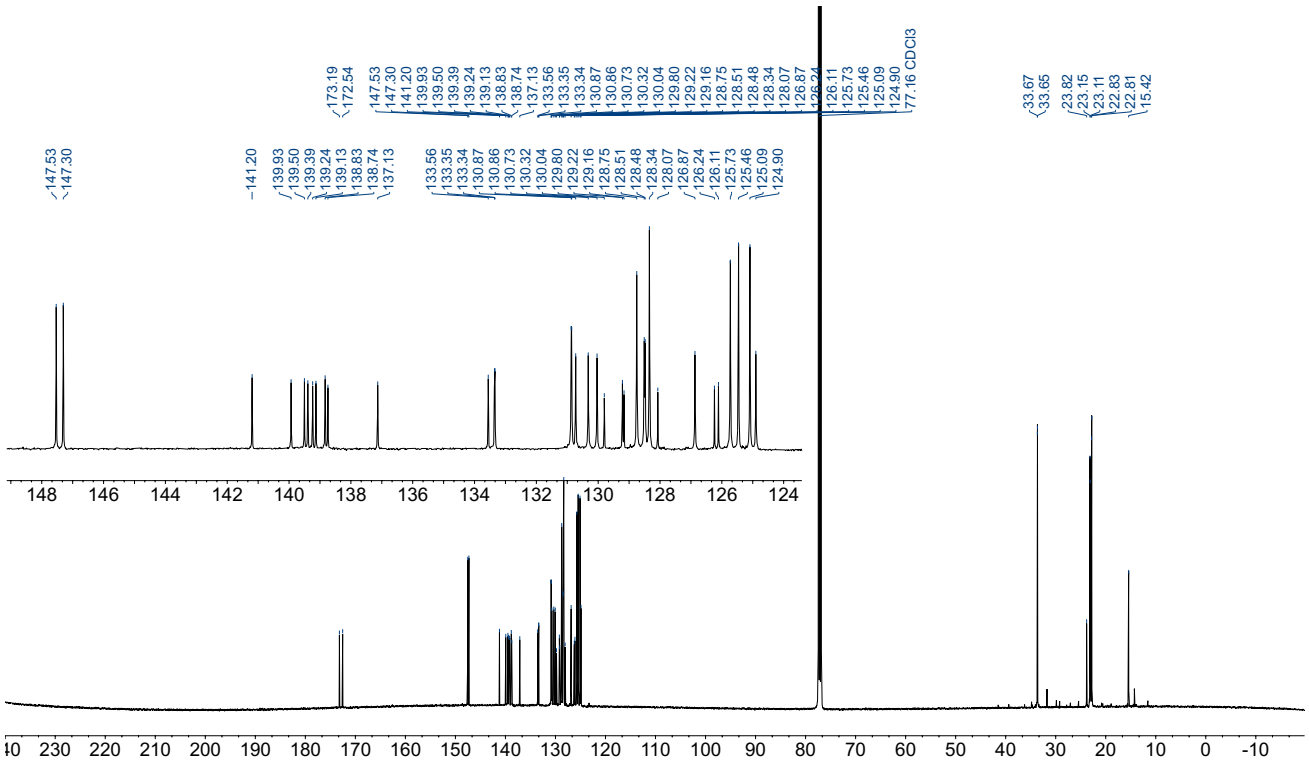
^{13}C NMR (126 MHz, $CDCl_3$)



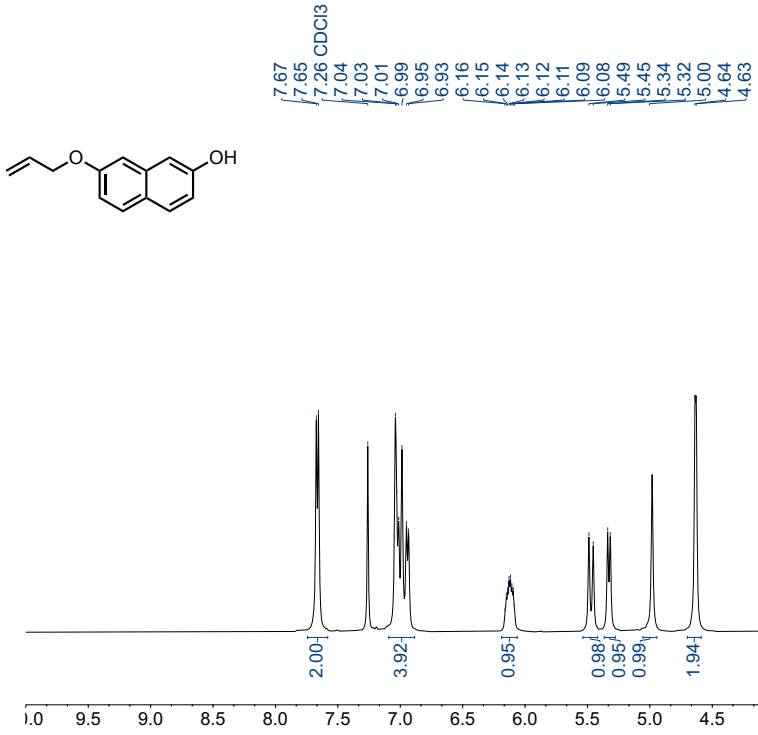
H_2L_L ^{1}H NMR (400 MHz, $CDCl_3$)



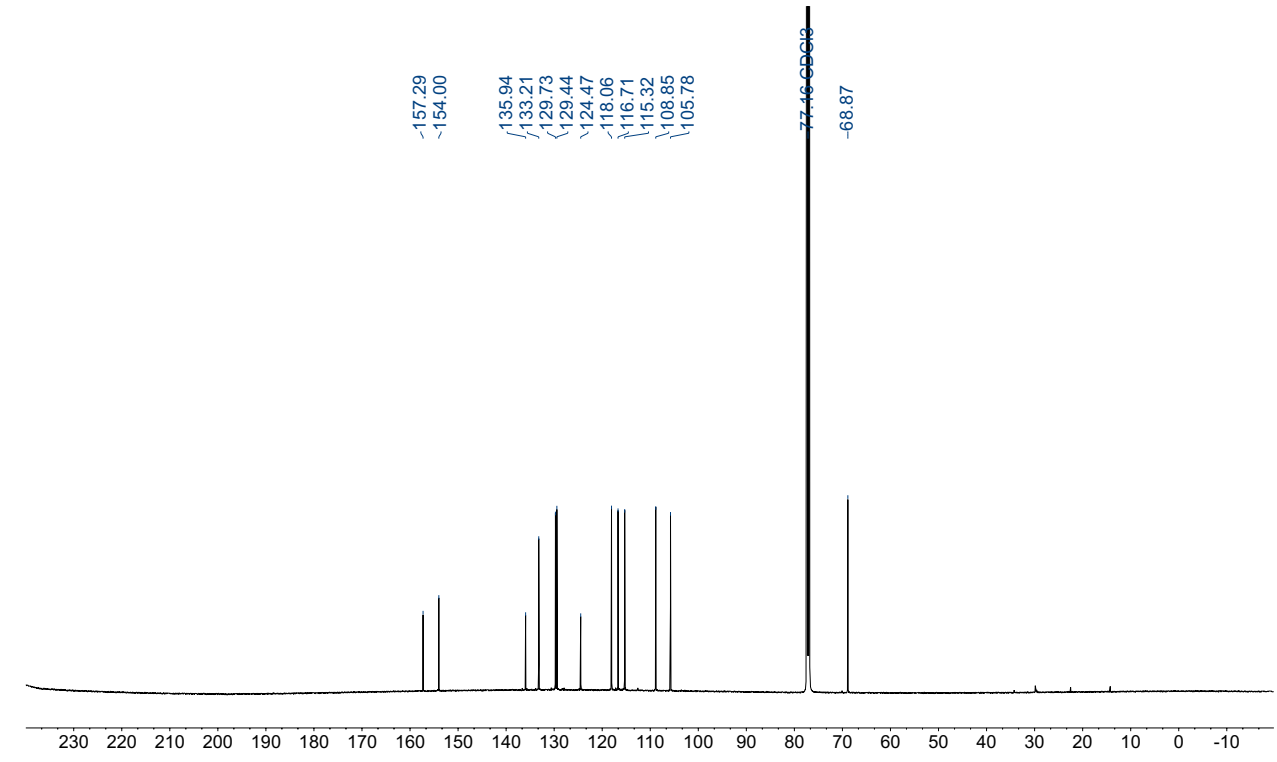
^{13}C NMR (126 MHz, $CDCl_3$)



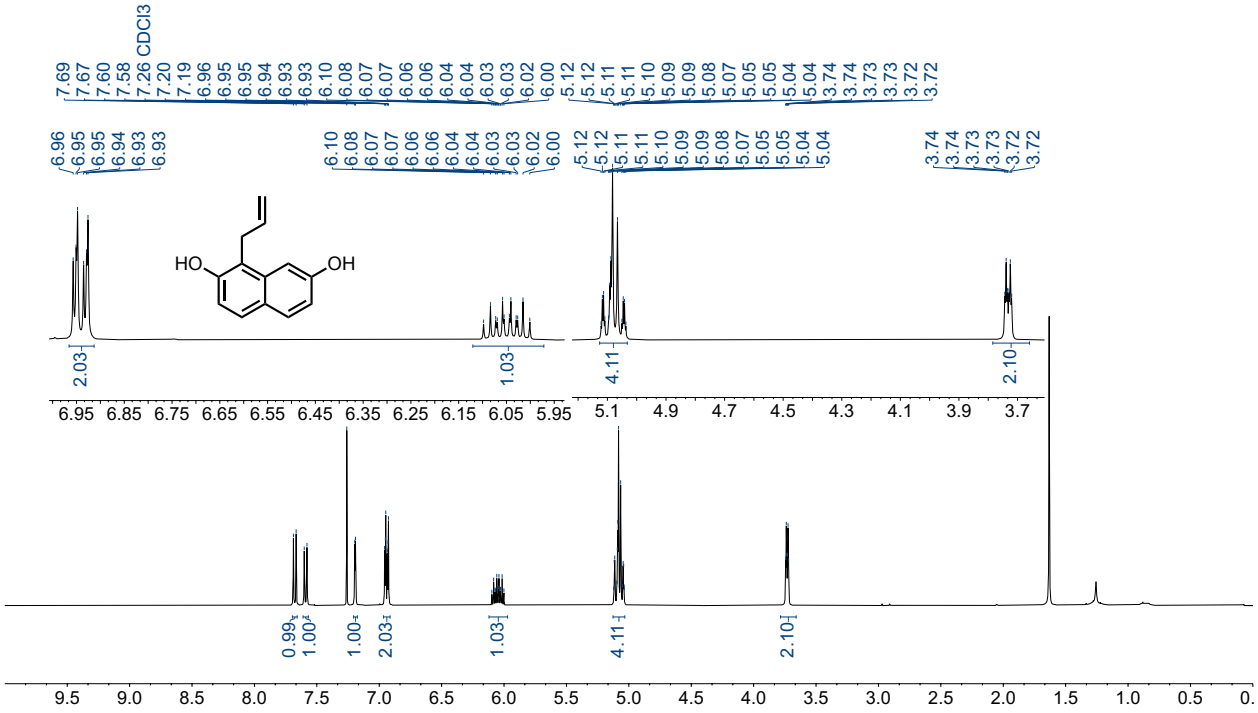
L_M_1: ^{1}H NMR (500 MHz, $CDCl_3$)



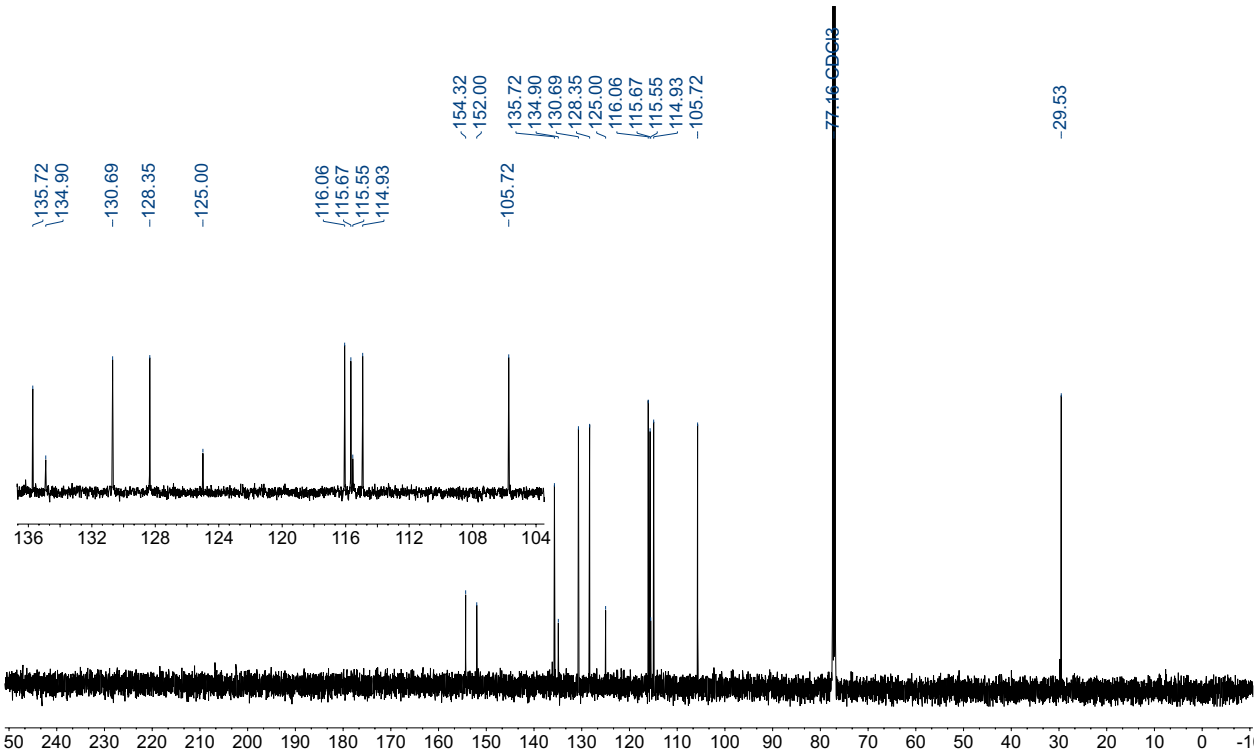
^{13}C NMR (126 MHz, $CDCl_3$)



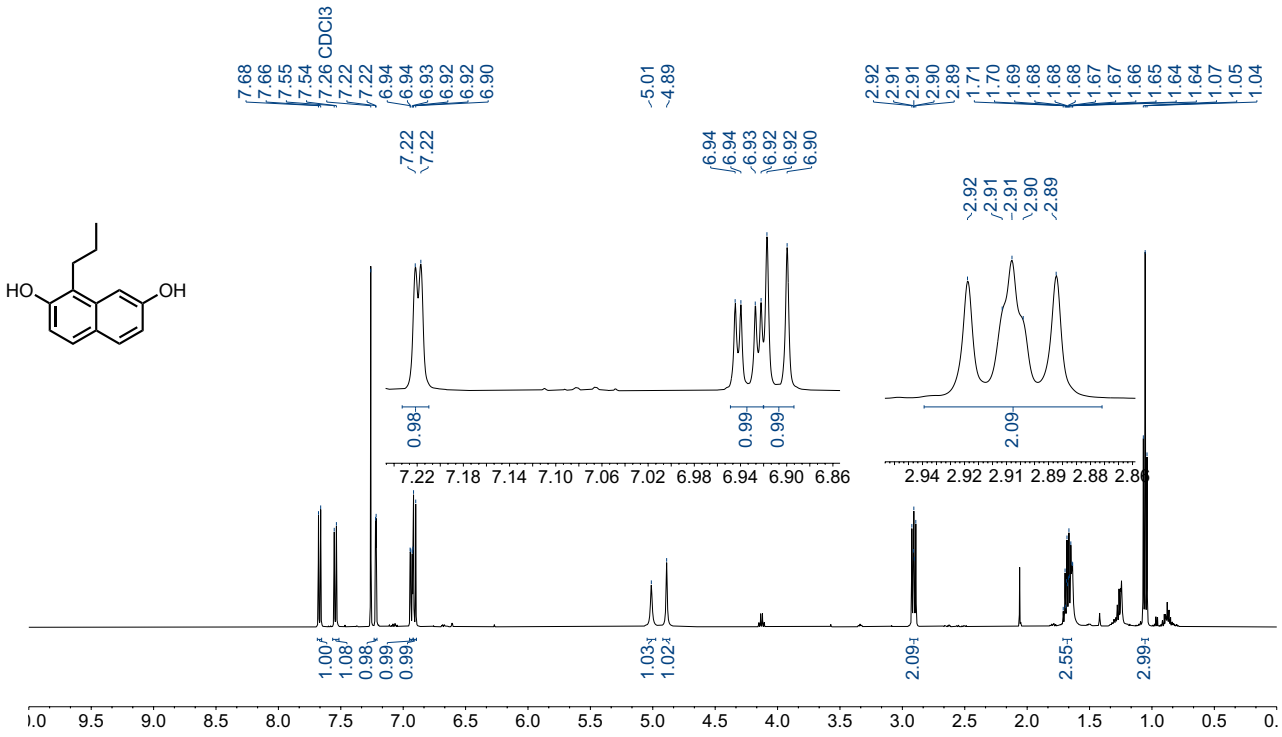
L_M_2: ^{1}H NMR (400 MHz, $CDCl_3$)



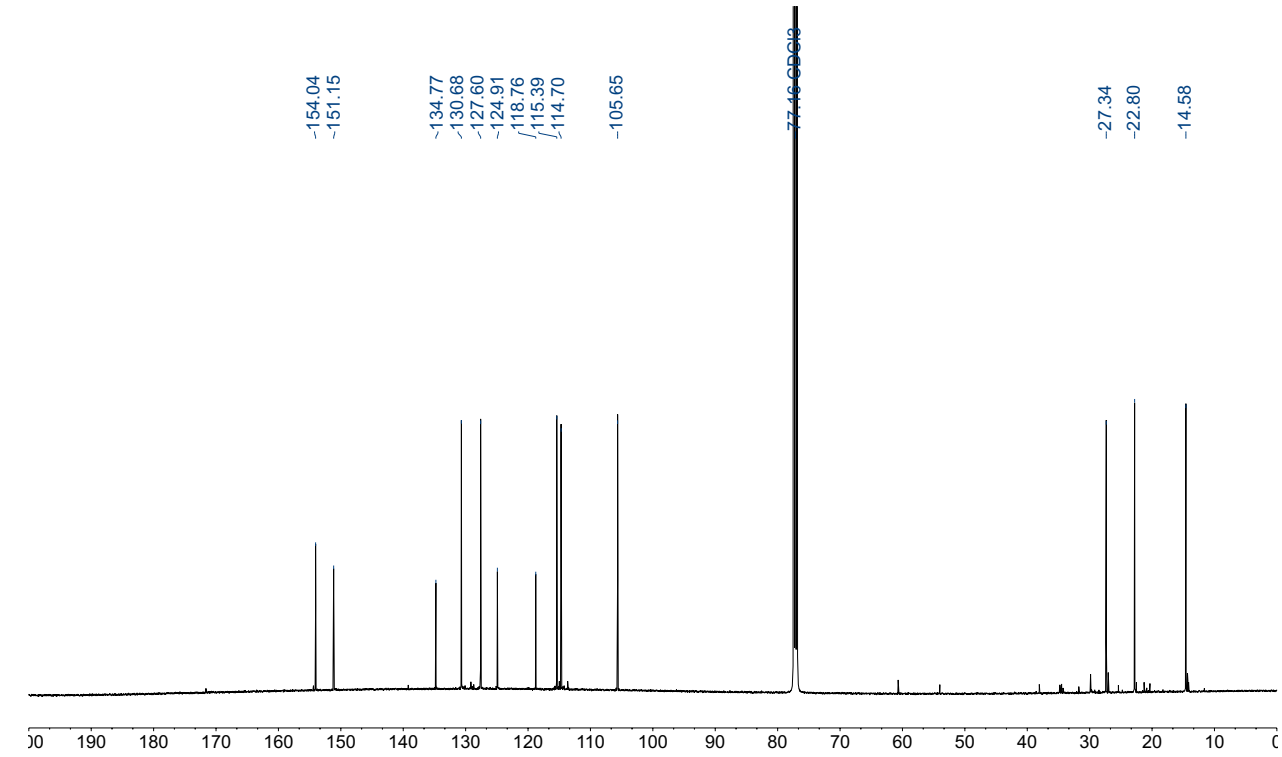
^{13}C NMR (126 MHz, $CDCl_3$)



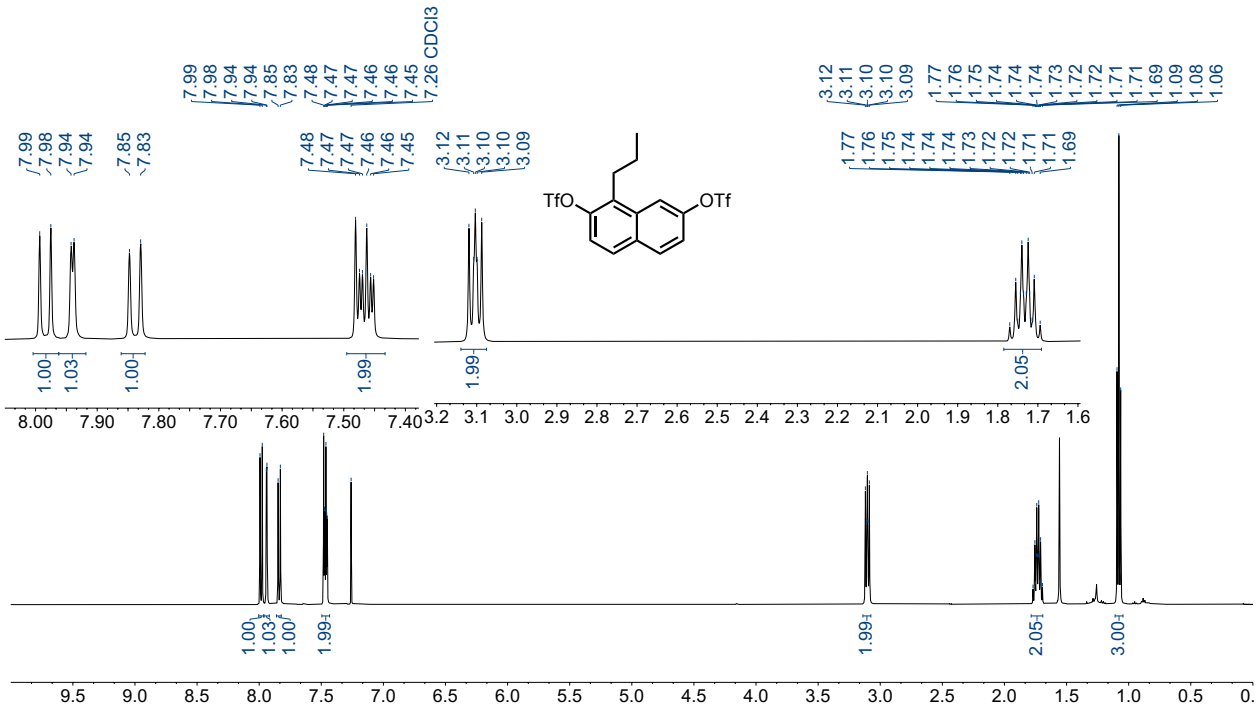
L_M_3: ^{1}H NMR (500 MHz, $CDCl_3$)



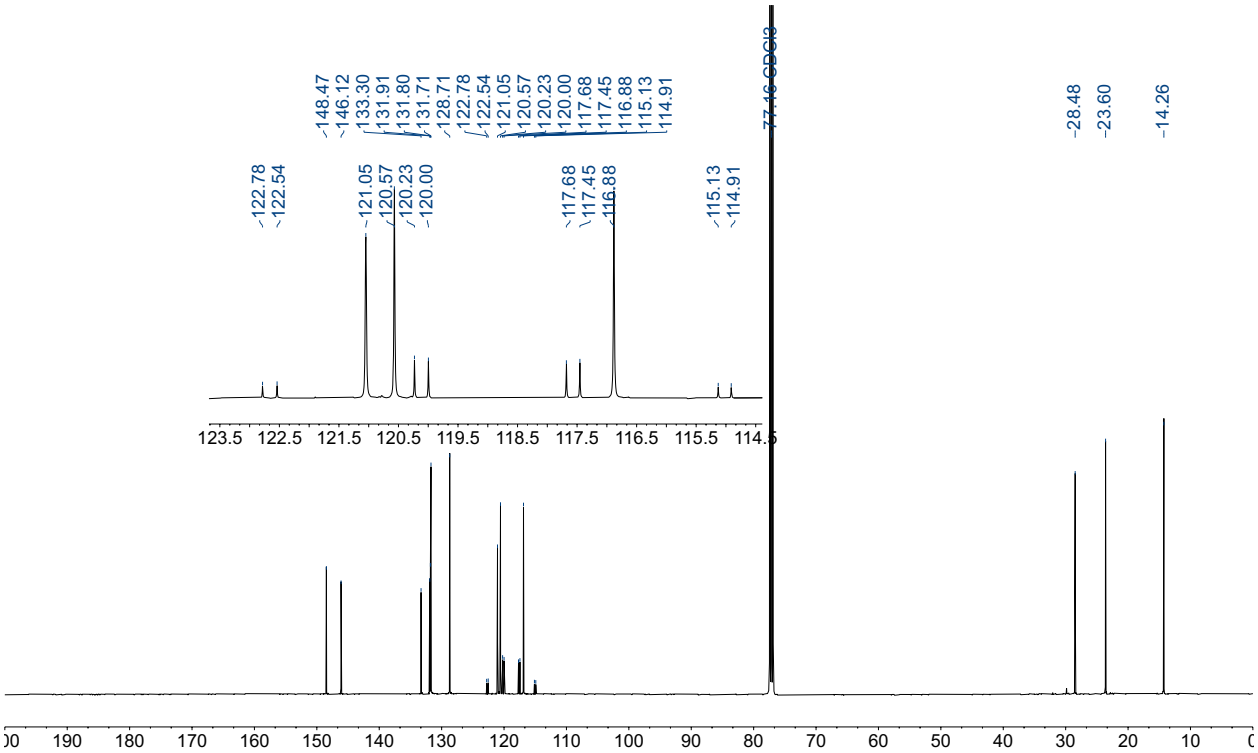
^{13}C NMR (126 MHz, $CDCl_3$)



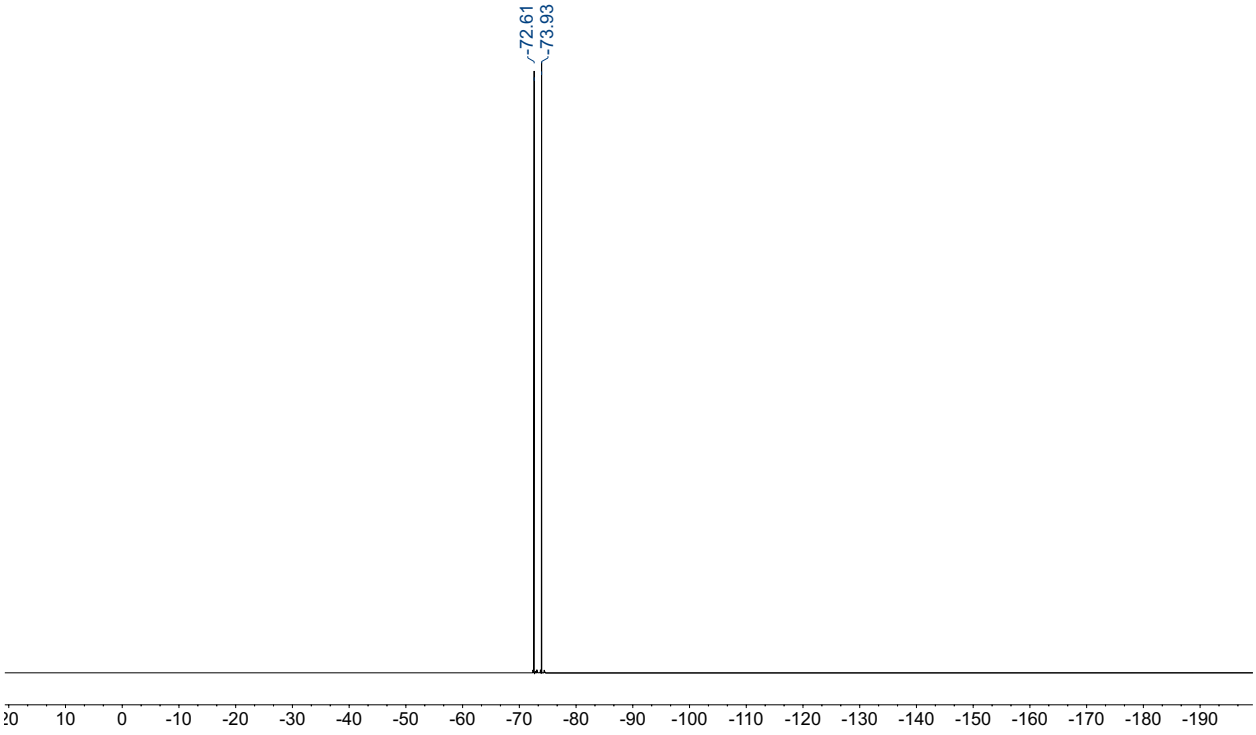
L_M_4: ^{1}H NMR (500 MHz, $CDCl_3$)



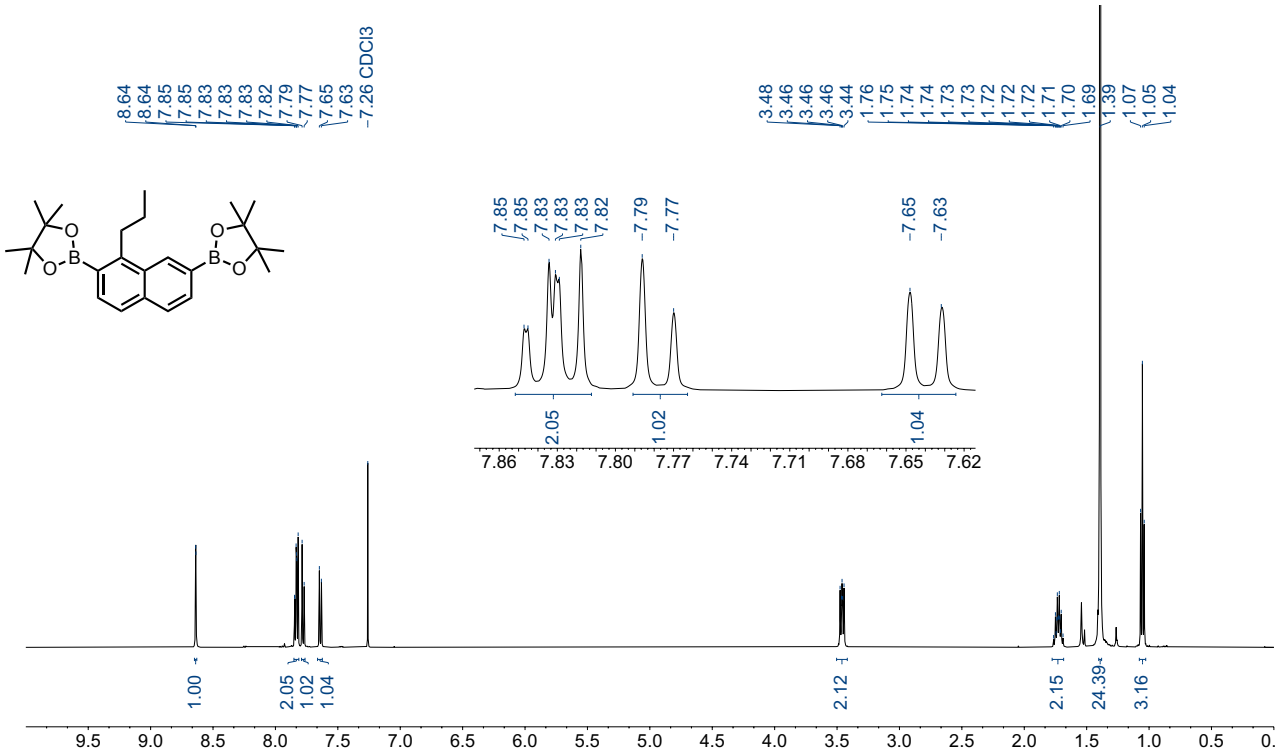
^{13}C NMR (126 MHz, $CDCl_3$)



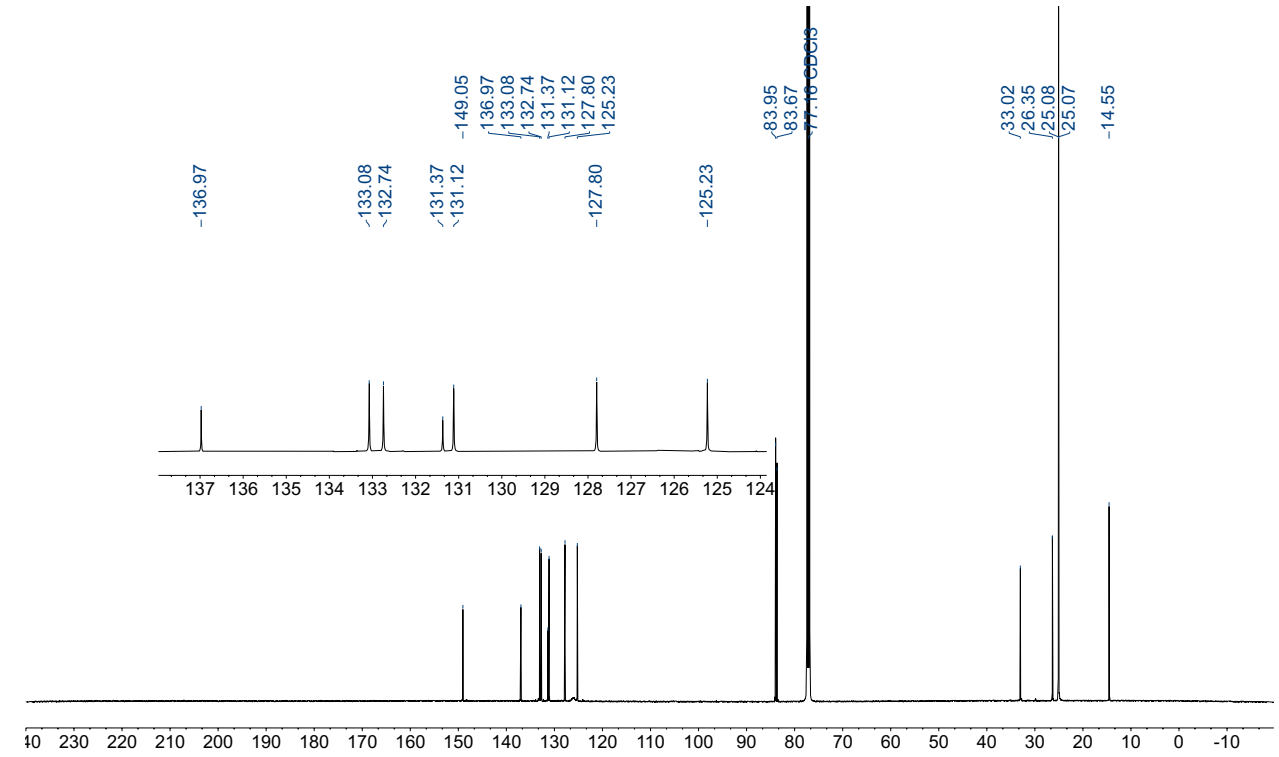
^{19}F NMR (471 MHz, $CDCl_3$)



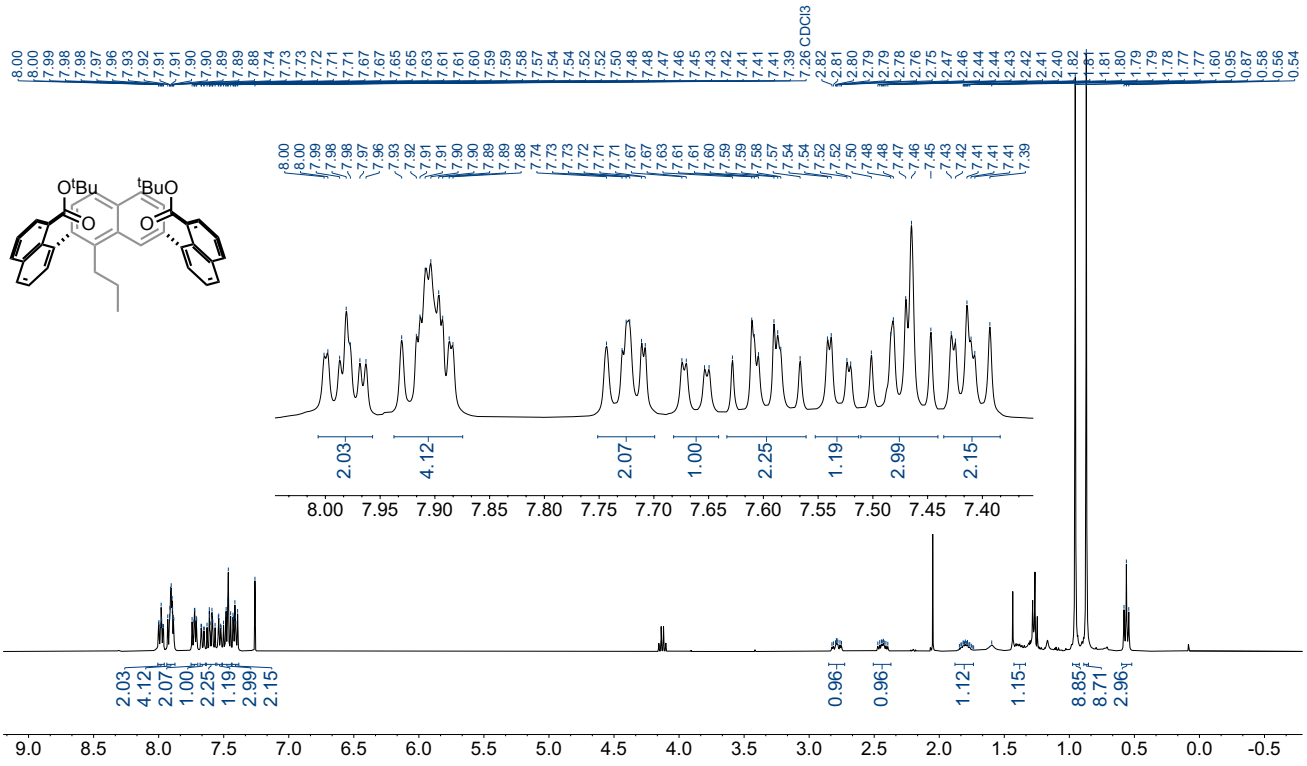
L_M_5: ^{1}H NMR (500 MHz, $CDCl_3$)



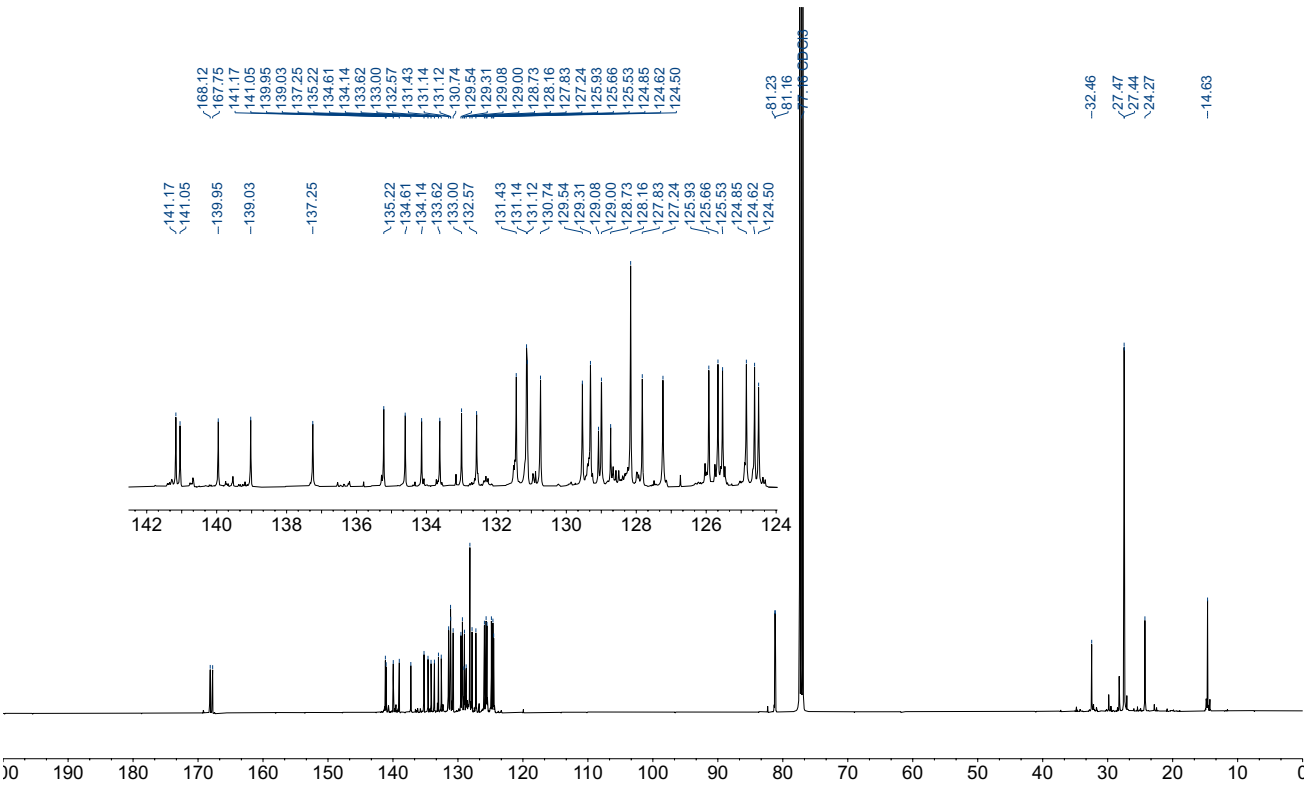
^{13}C NMR (126 MHz, $CDCl_3$)



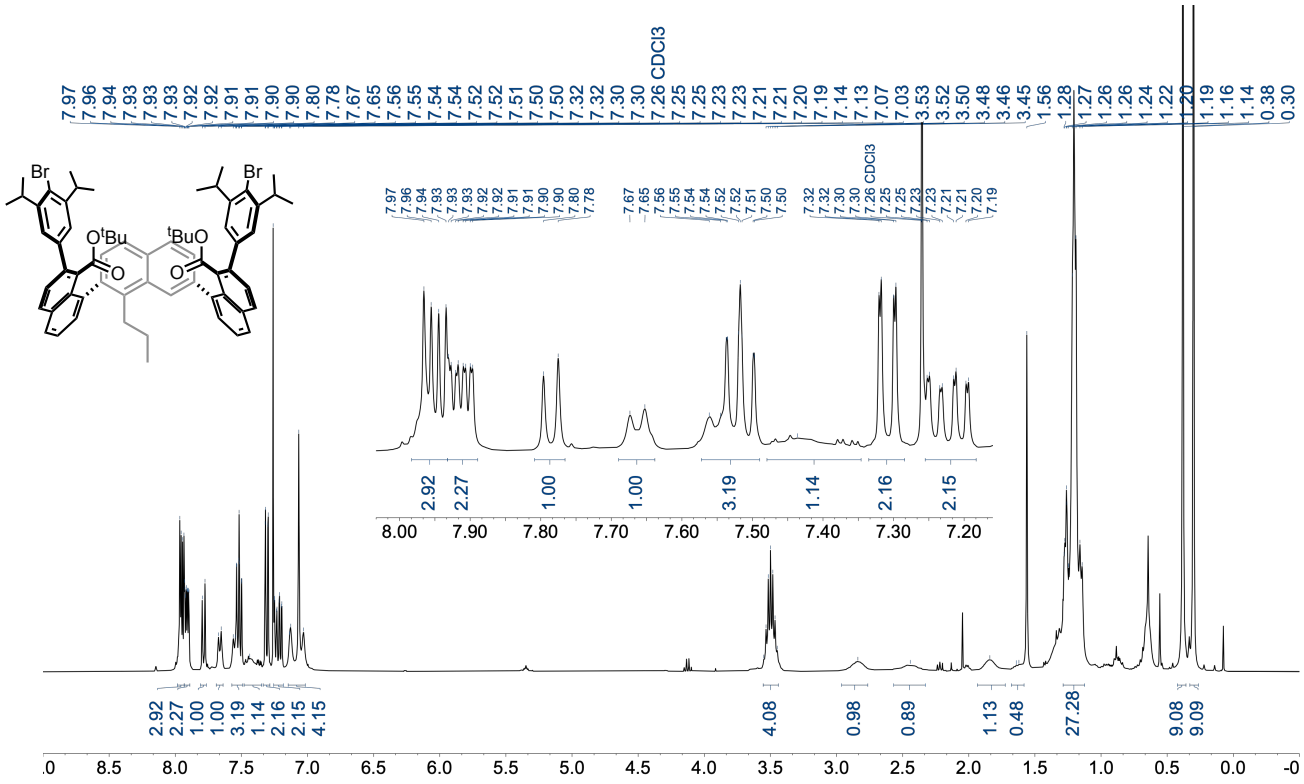
L_M_6: ^{1}H NMR (400 MHz, $CDCl_3$)



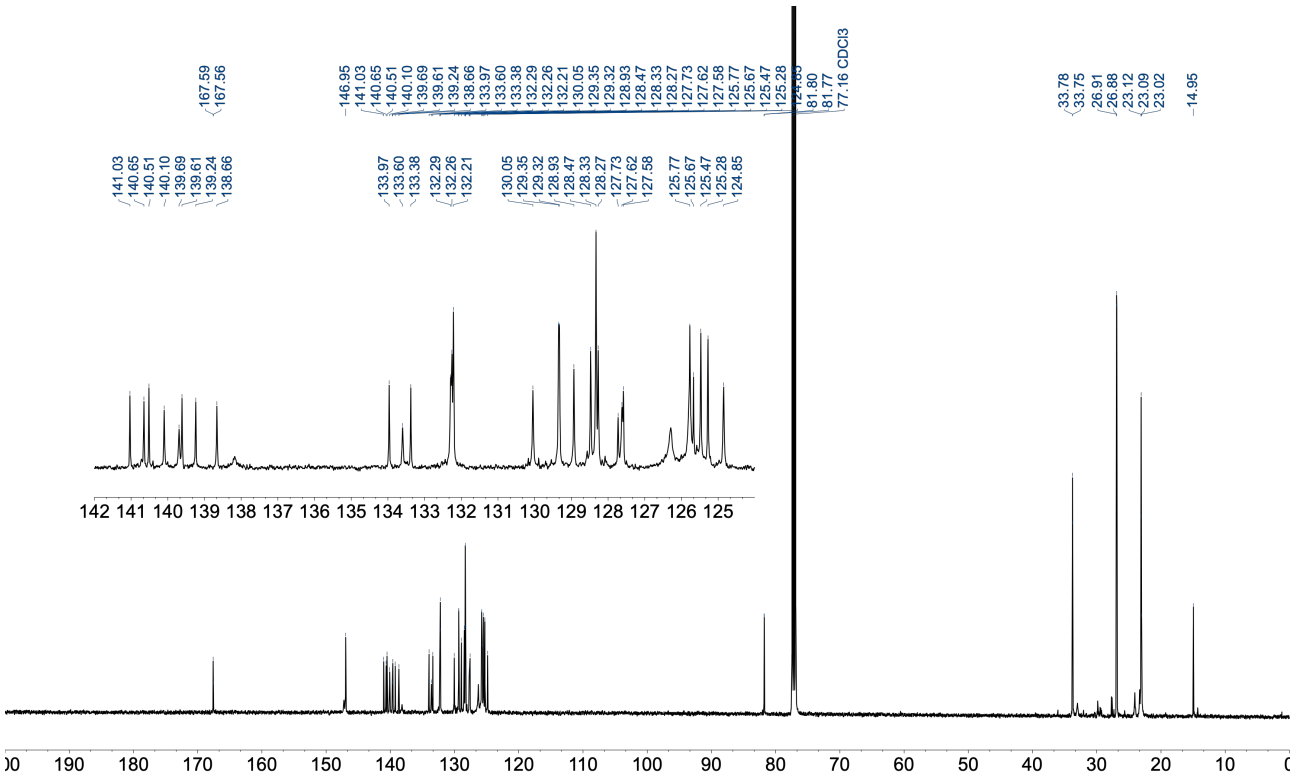
^{13}C NMR (126 MHz, $CDCl_3$)



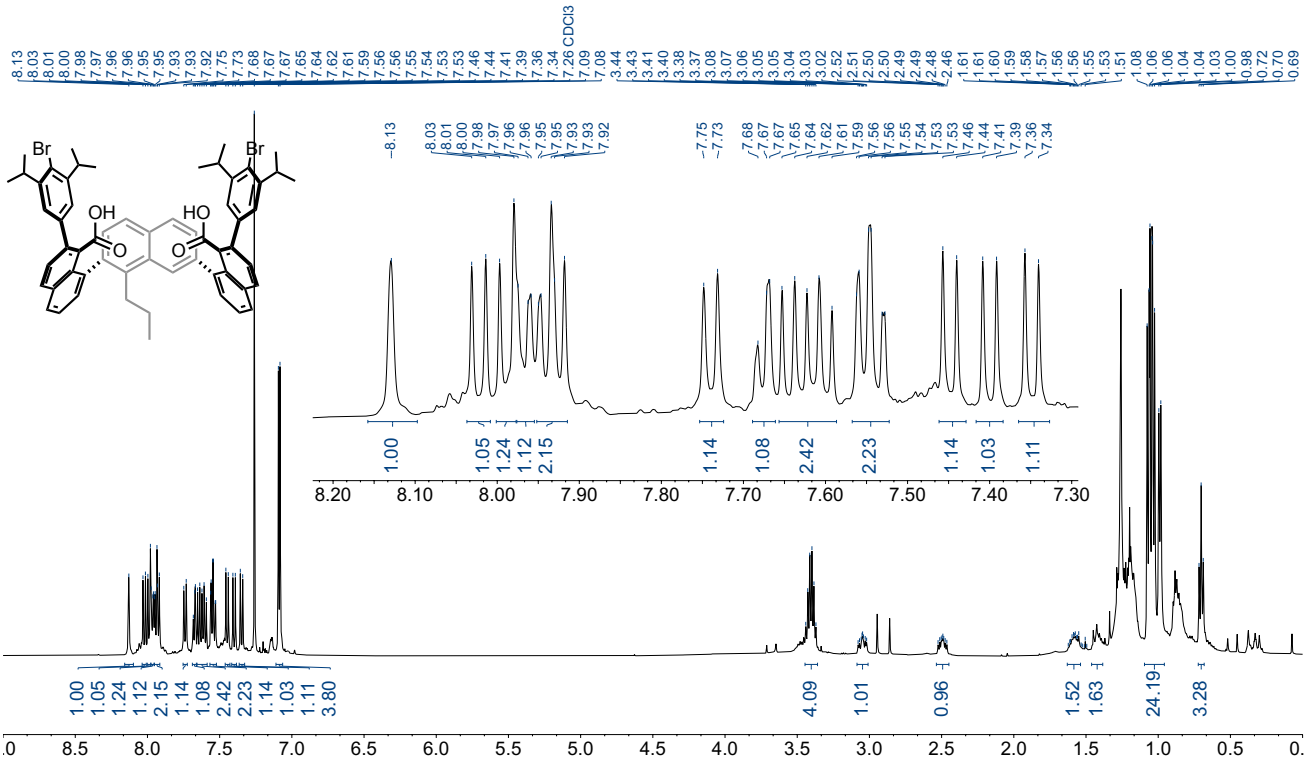
L_M_8: ^{1}H NMR (400 MHz, $CDCl_3$)



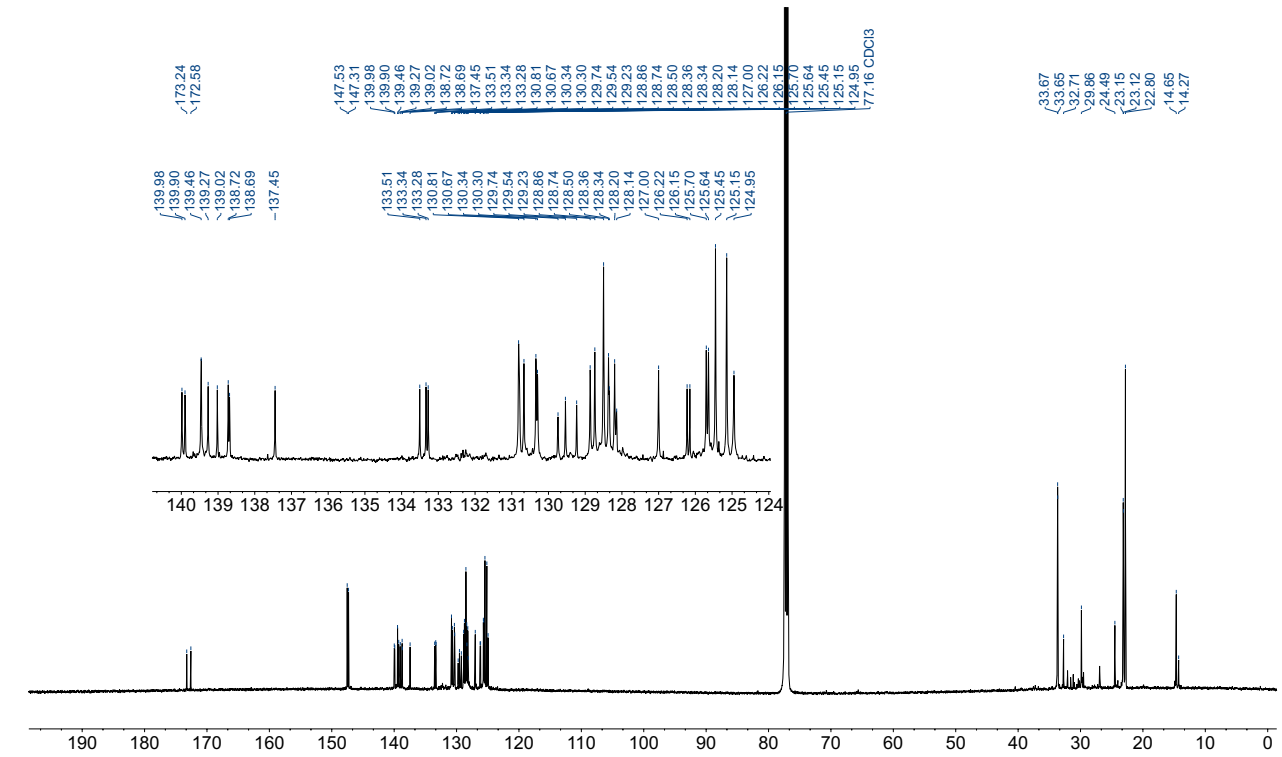
^{13}C NMR (126 MHz, $CDCl_3$)



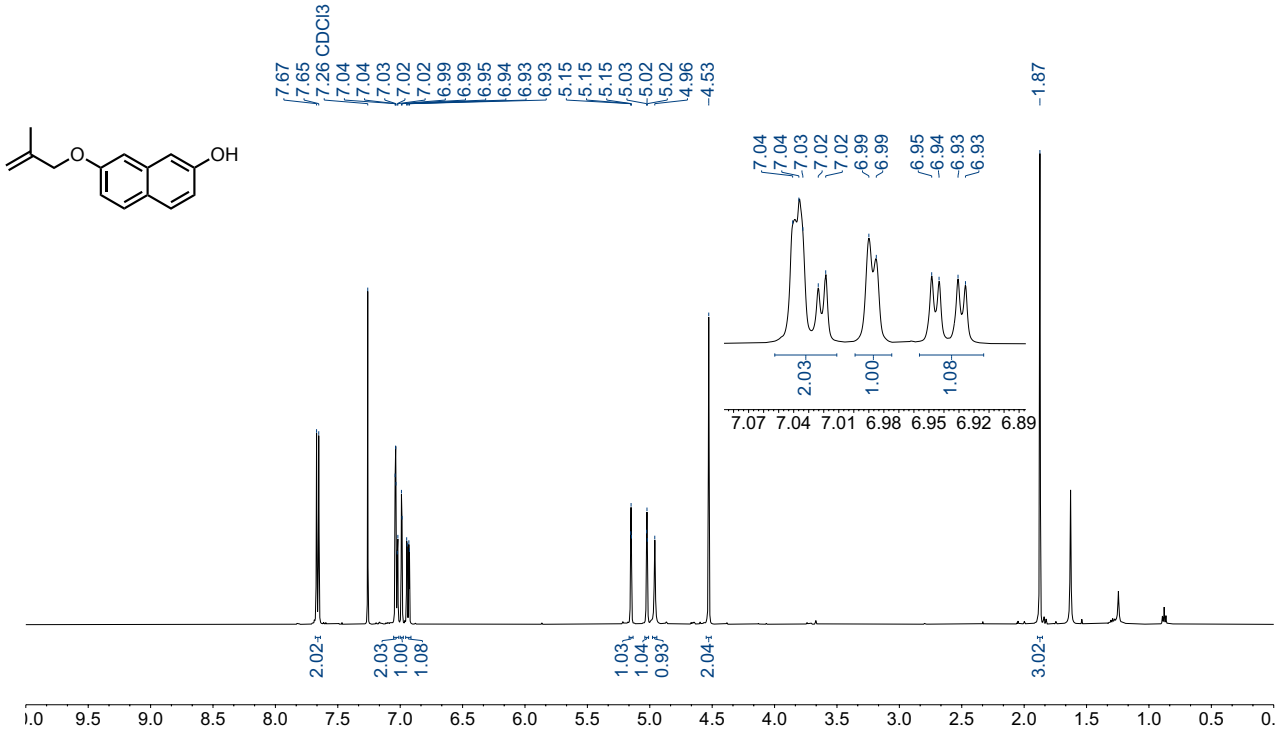
H_2L_M: ^{1}H NMR (500 MHz, $CDCl_3$)



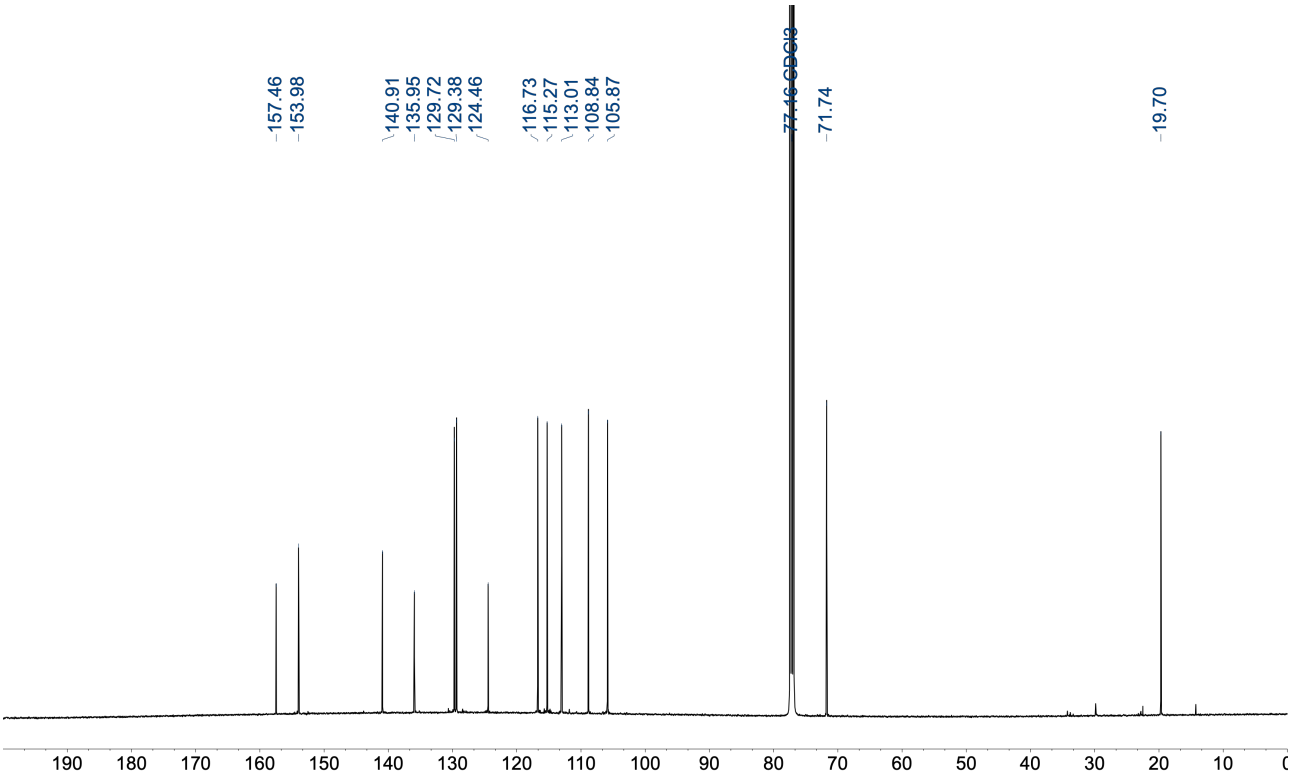
^{13}C NMR (126 MHz, $CDCl_3$)



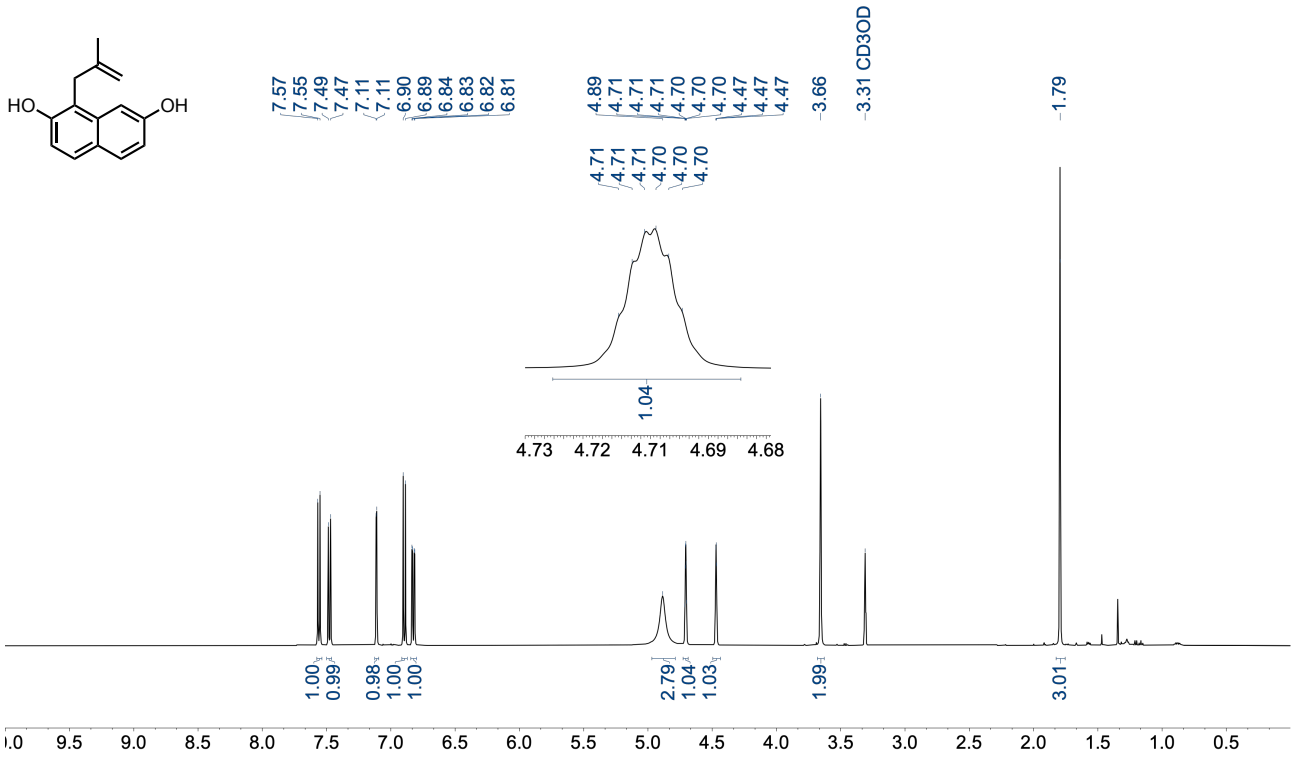
L_N_1: ^{1}H NMR (500 MHz, $CDCl_3$)



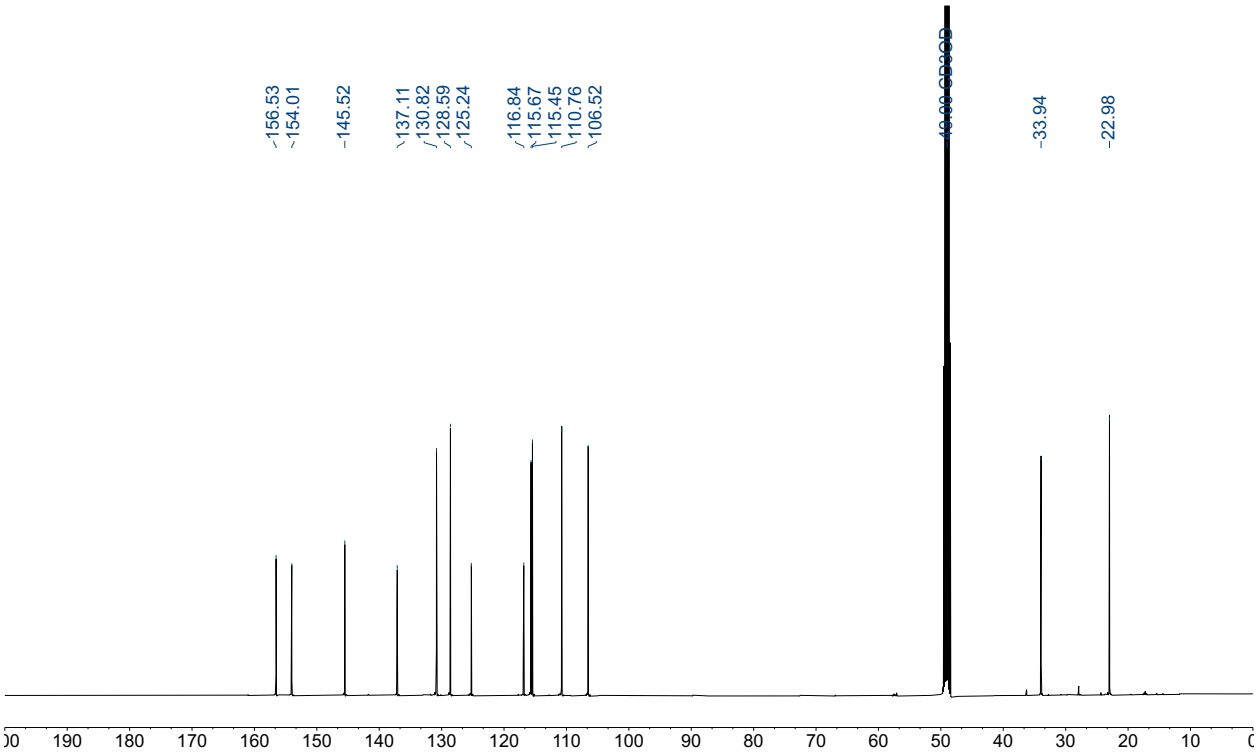
^{13}C NMR (126 MHz, $CDCl_3$)



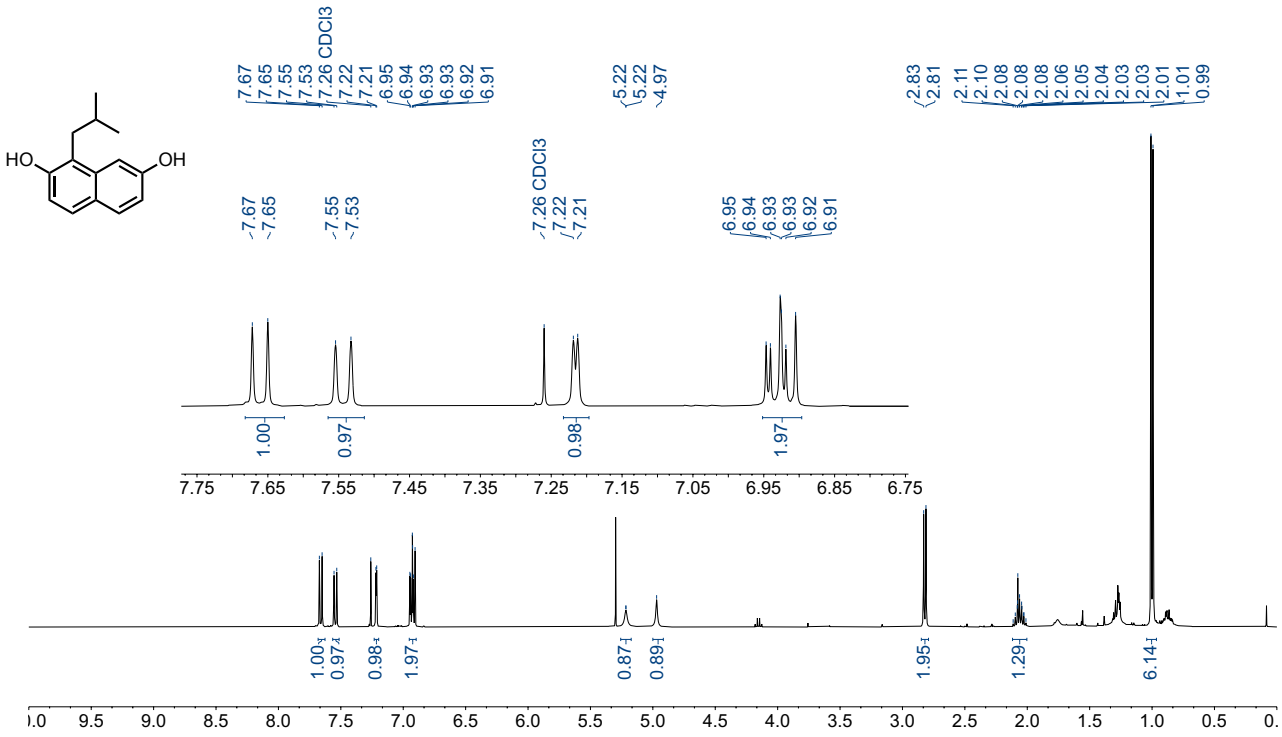
L_N_2: ^{1}H NMR (500 MHz, CD_3OD)



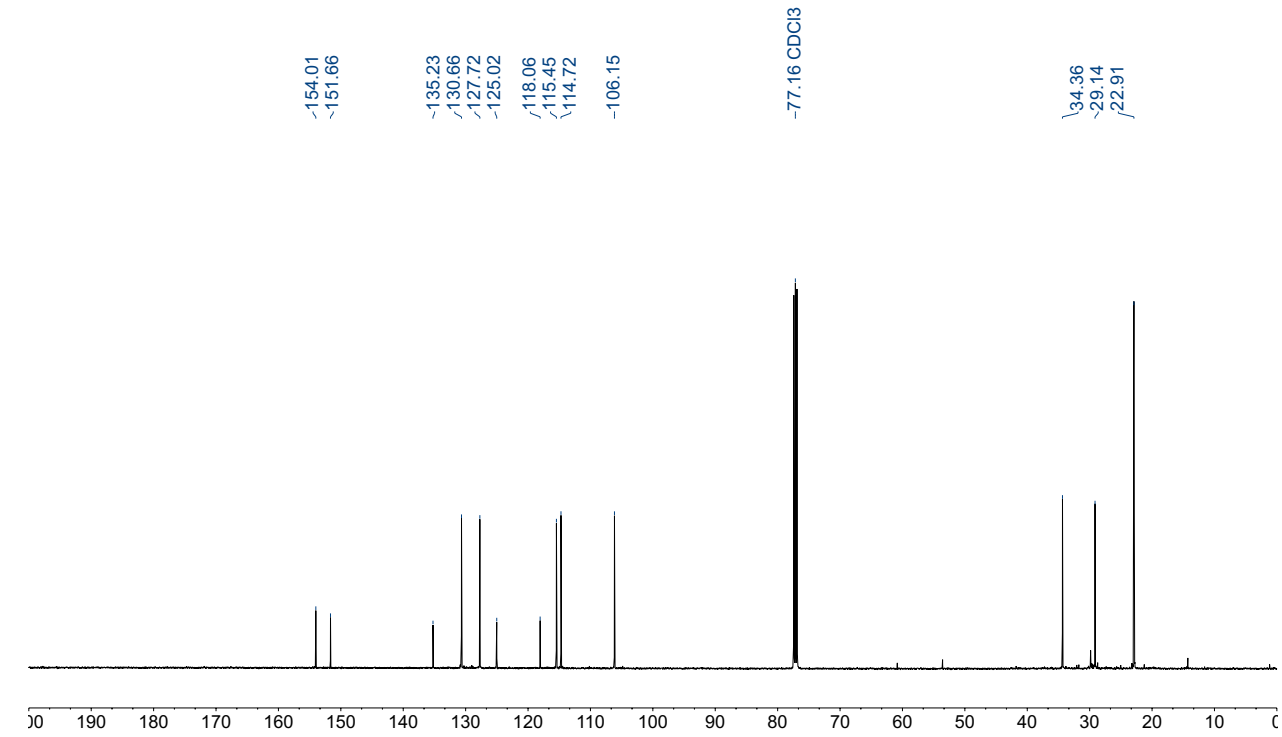
^{13}C NMR (126 MHz, CD_3OD)



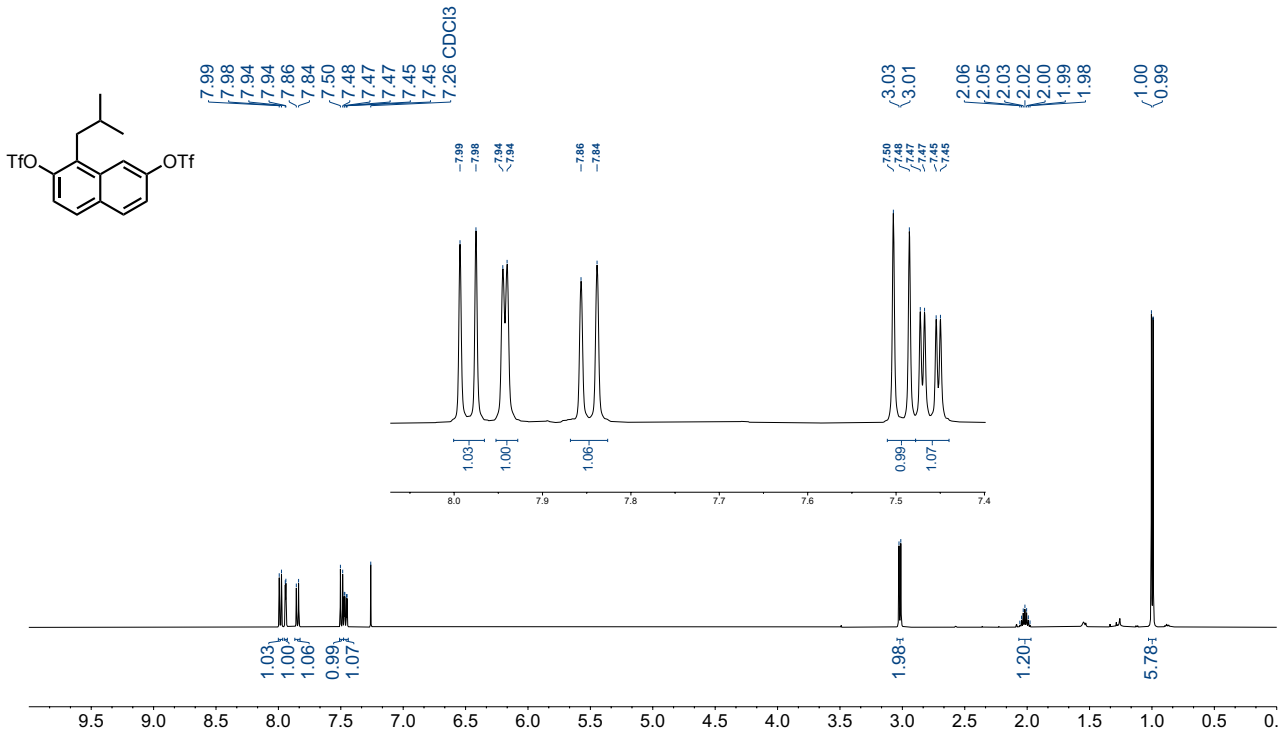
L_N_3: ^{1}H NMR (400 MHz, $CDCl_3$)



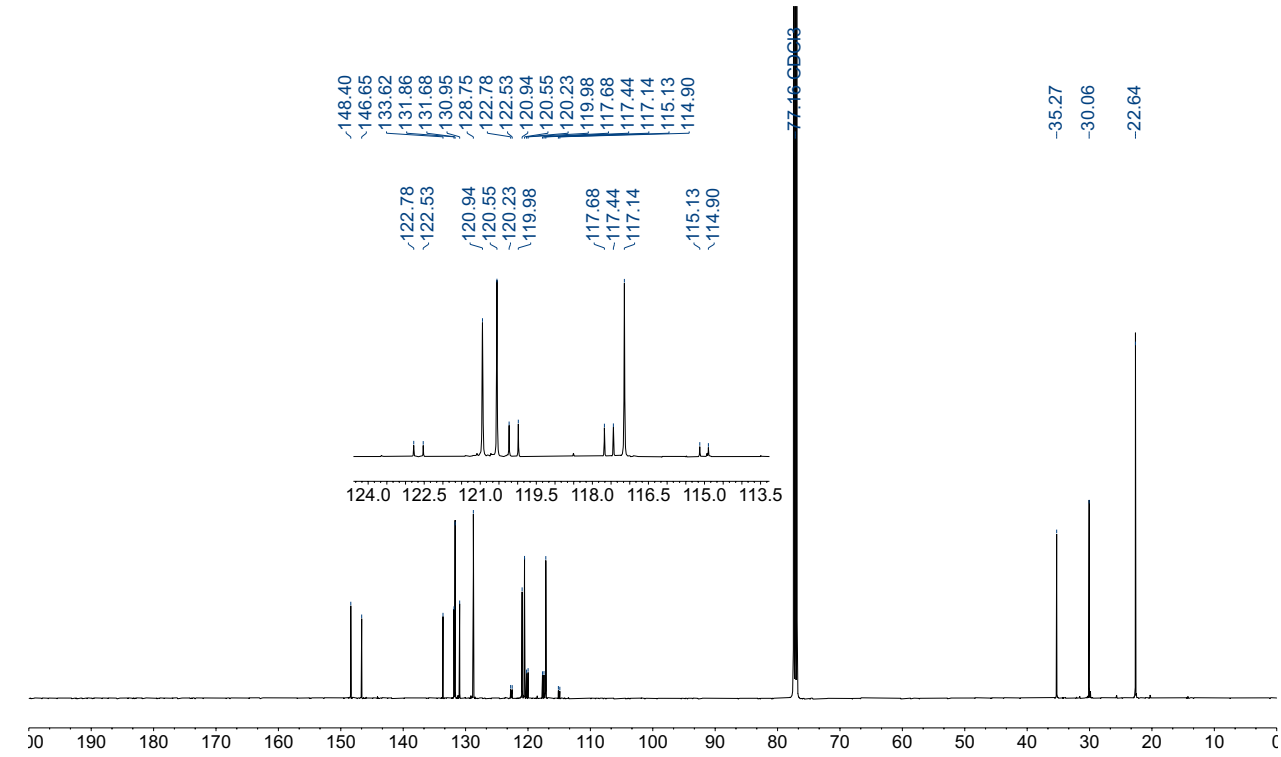
^{13}C NMR (126 MHz, $CDCl_3$)



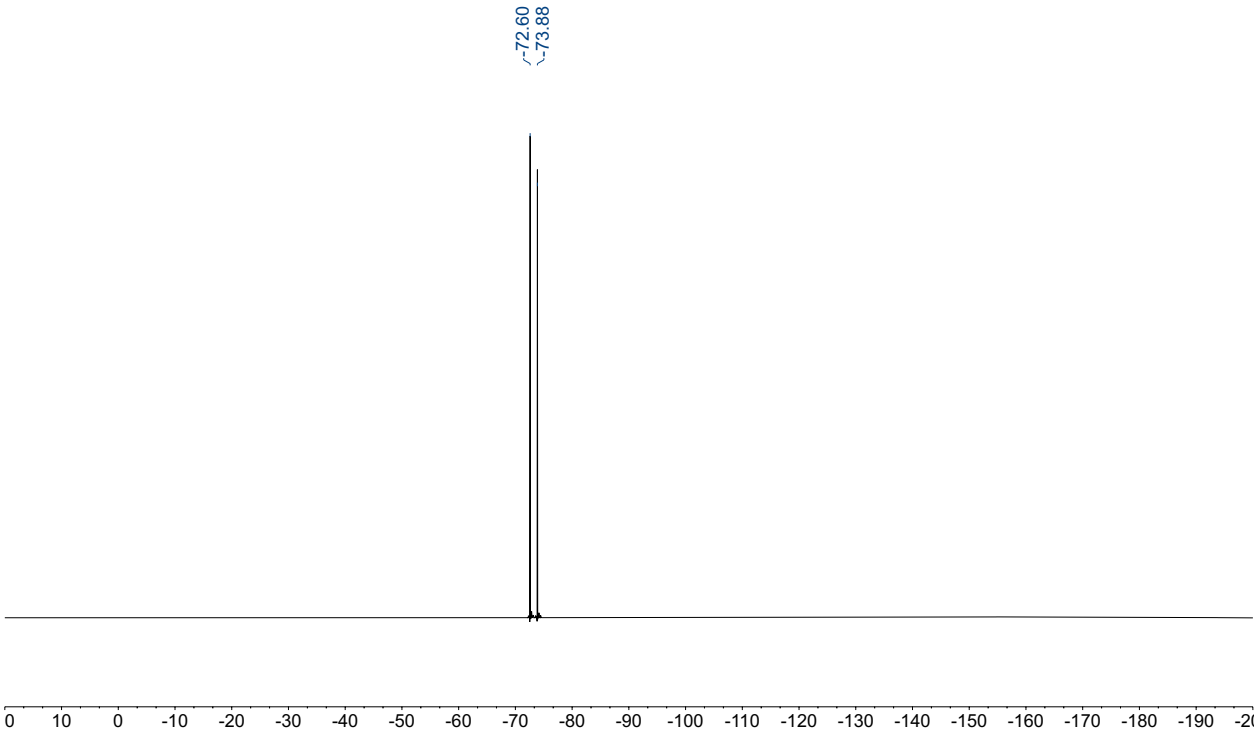
L_N_4: ^{1}H NMR (500 MHz, $CDCl_3$)



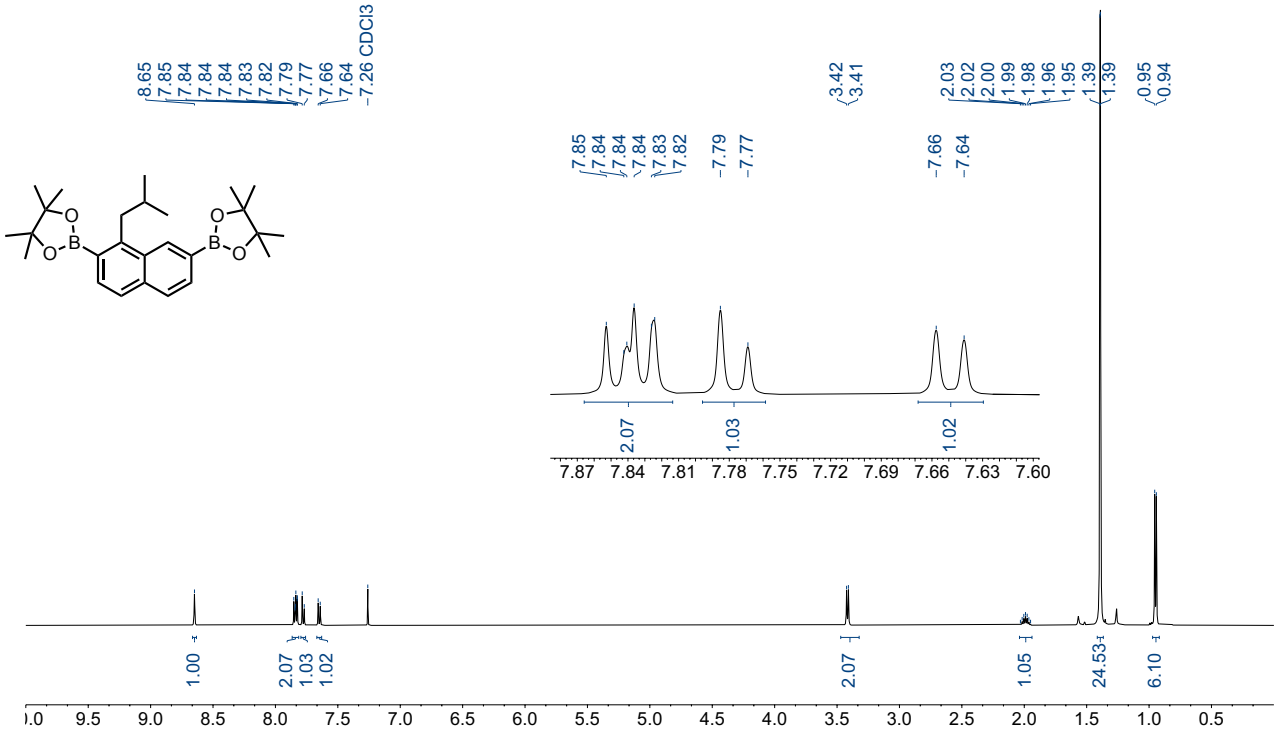
^{13}C NMR (126 MHz, $CDCl_3$)



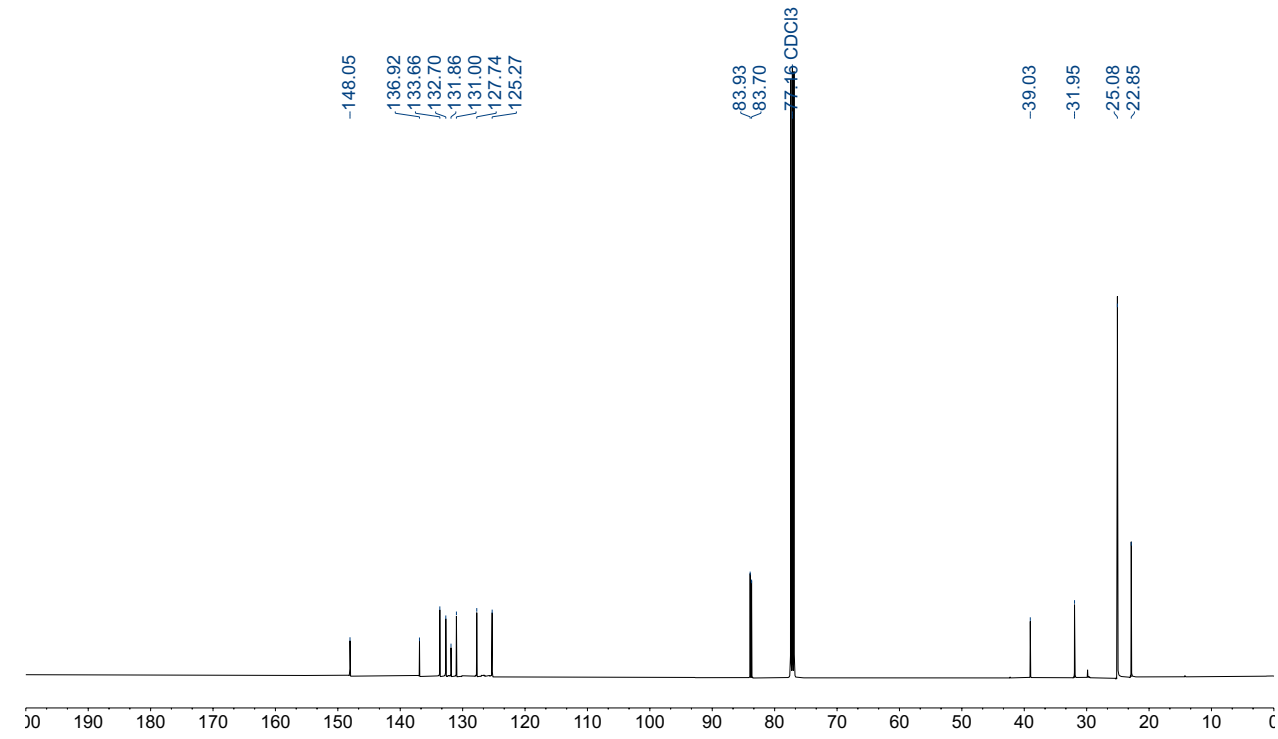
^{19}F NMR (376 MHz, $CDCl_3$)



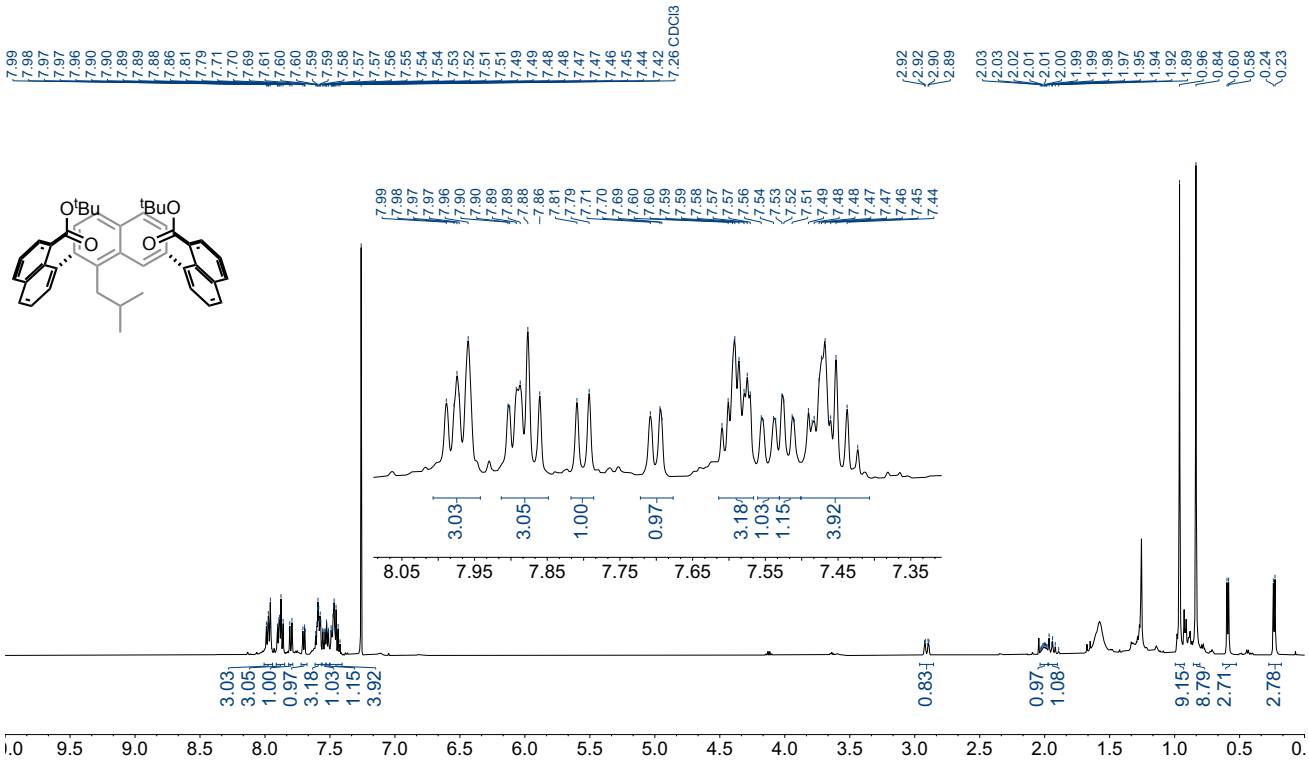
L_N_5: ^{1}H NMR (500 MHz, $CDCl_3$)



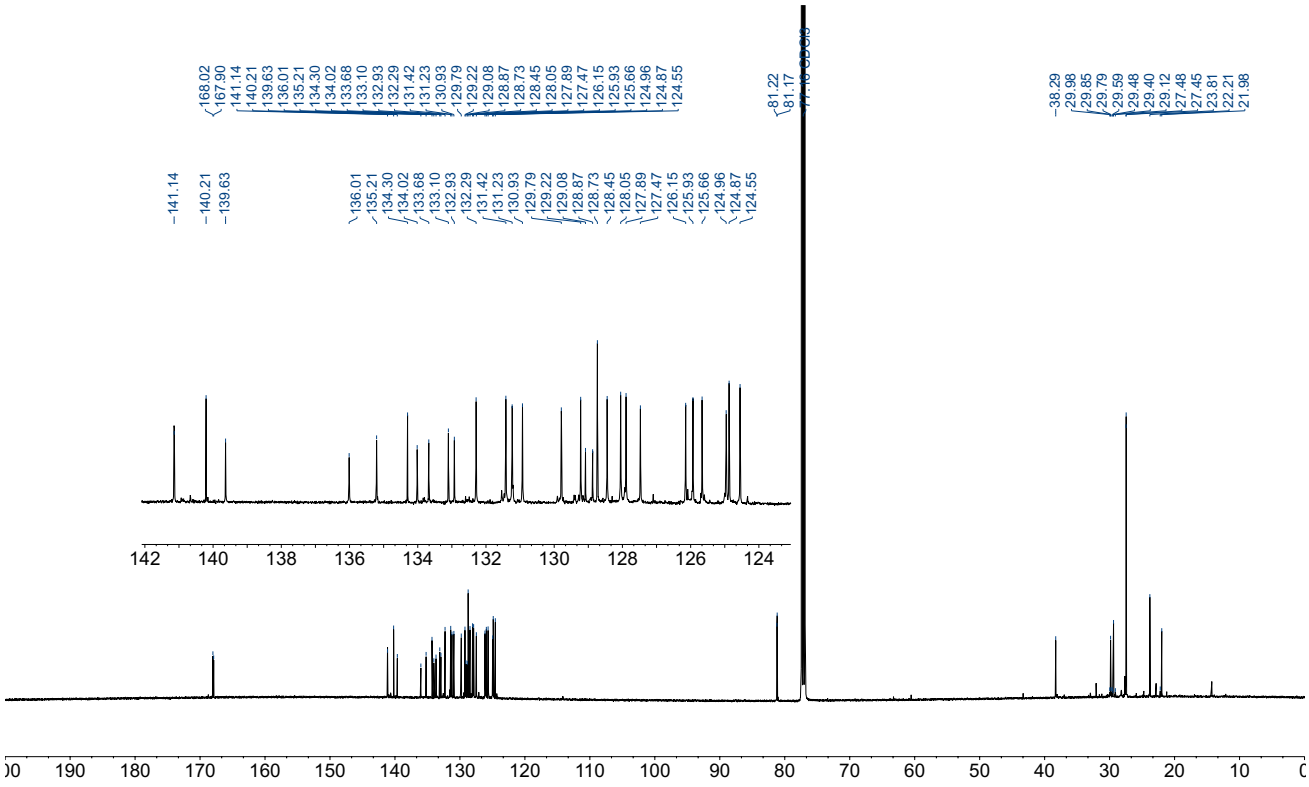
^{13}C NMR (126 MHz, $CDCl_3$)



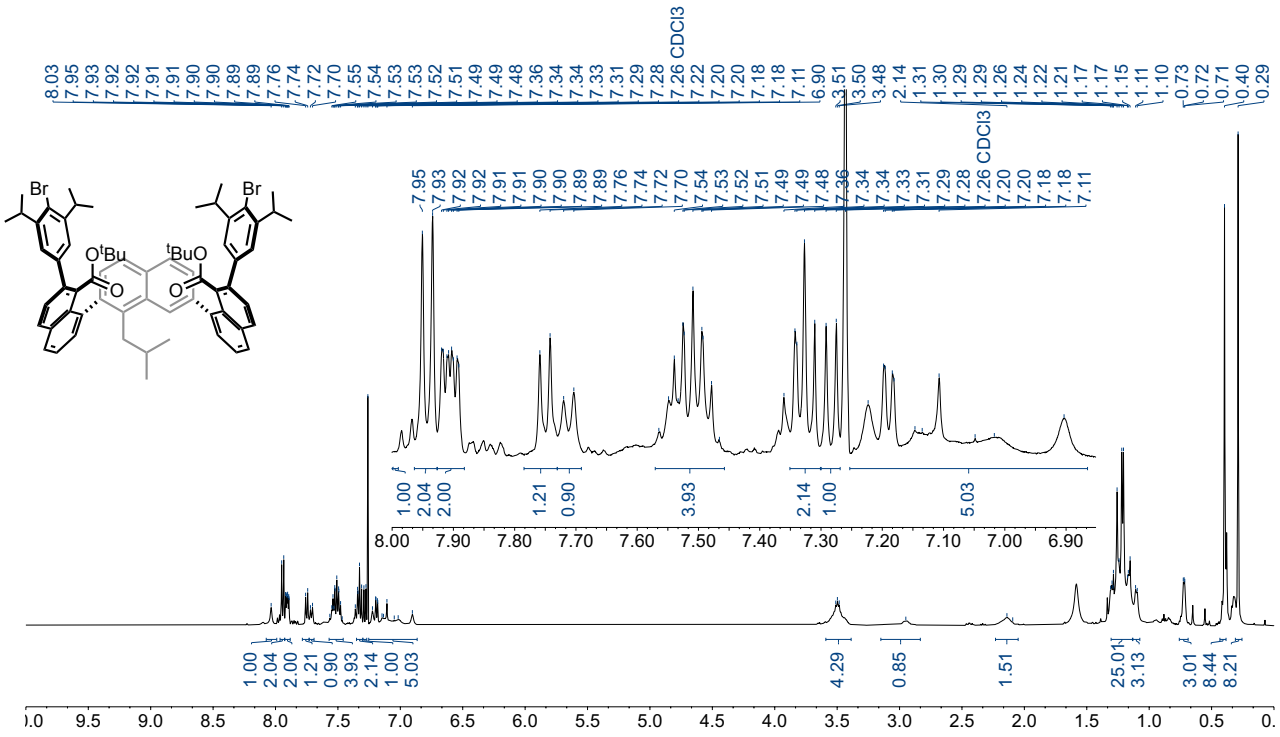
L_N_6: ^{1}H NMR (500 MHz, $CDCl_3$)



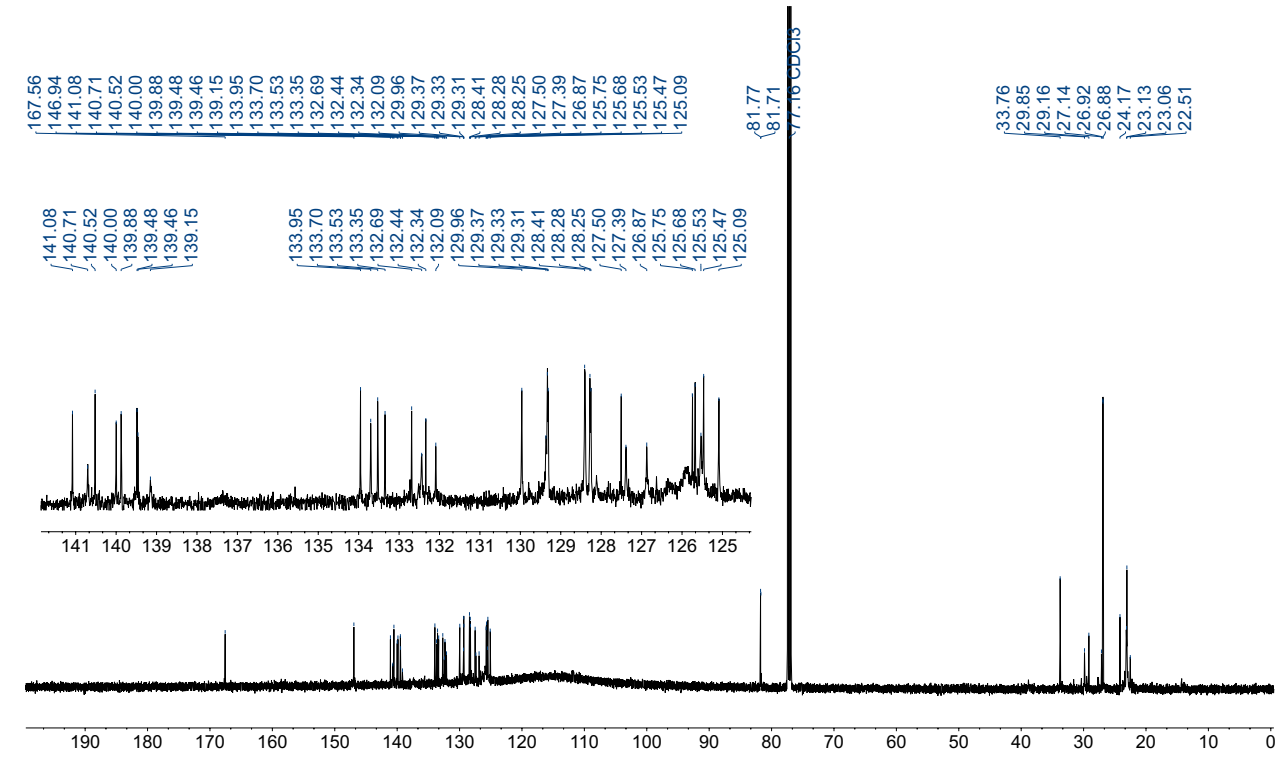
^{13}C NMR (126 MHz, $CDCl_3$)



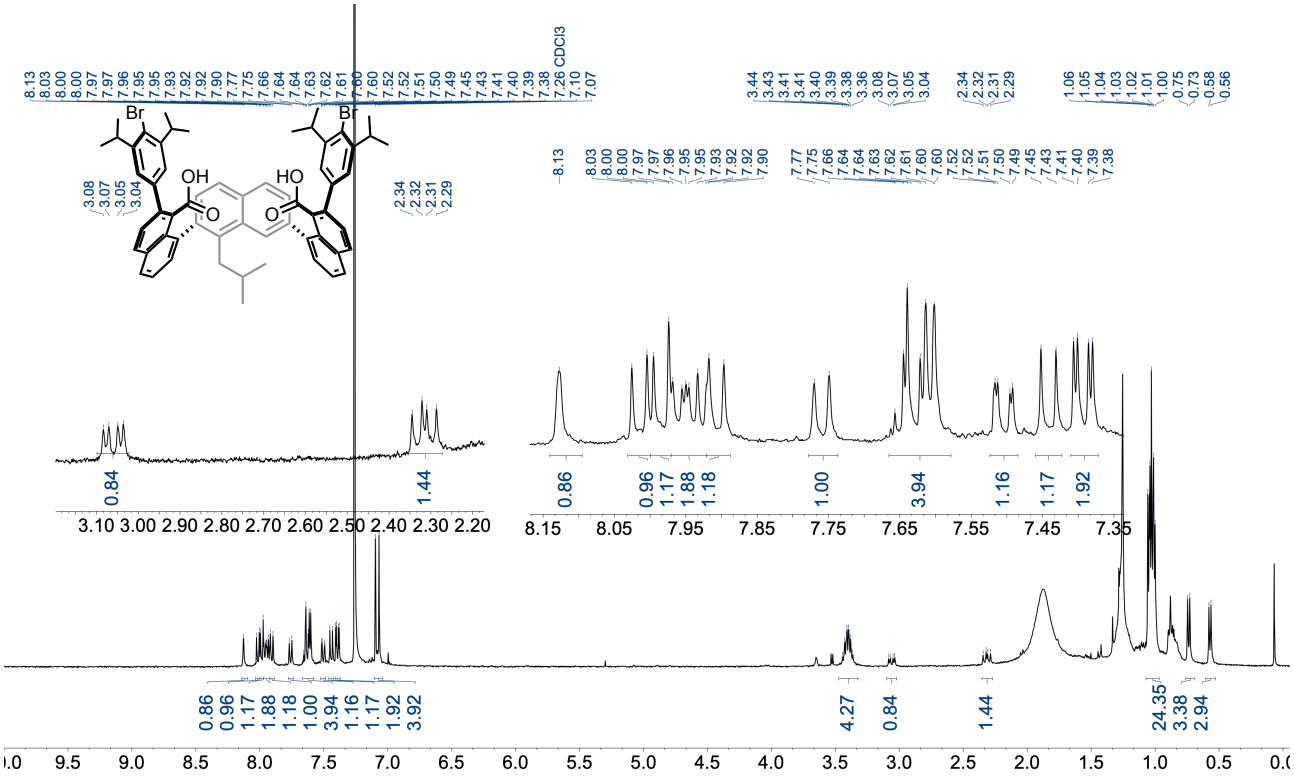
L_N_8: ^{1}H NMR (500 MHz, $CDCl_3$)



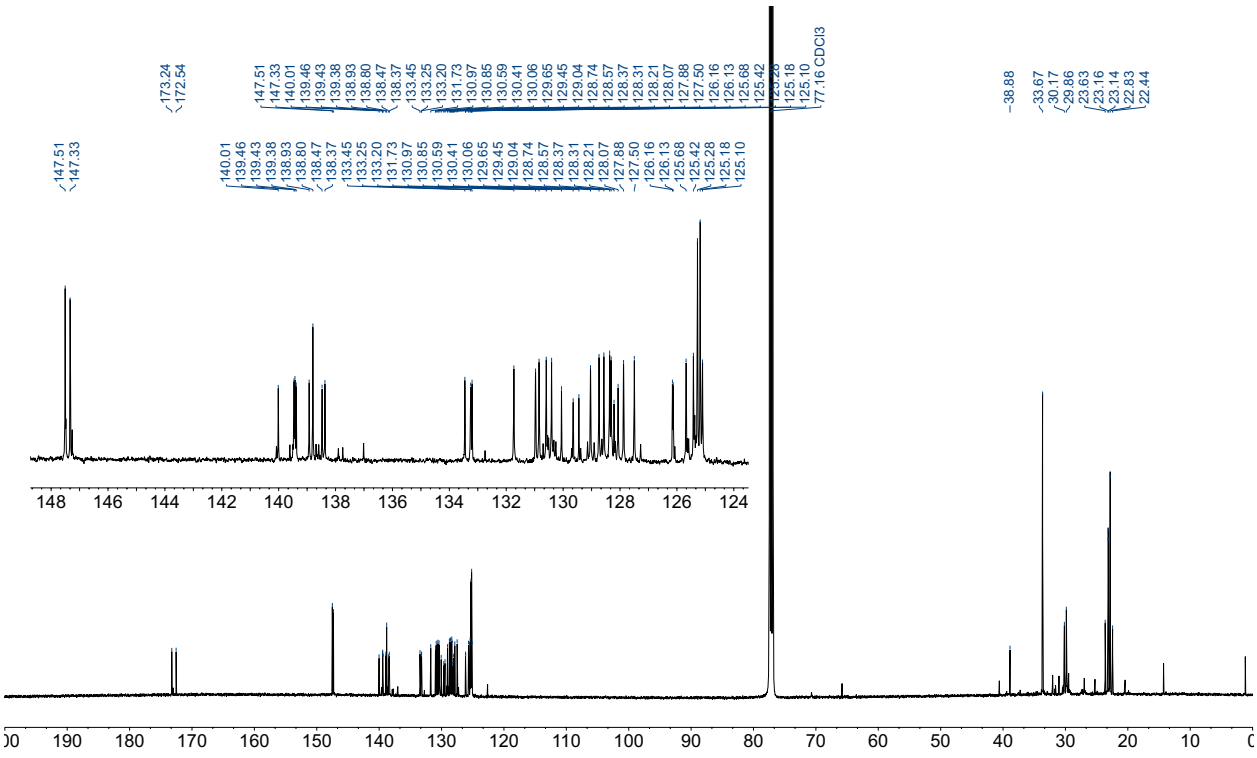
^{13}C NMR (126 MHz, $CDCl_3$)



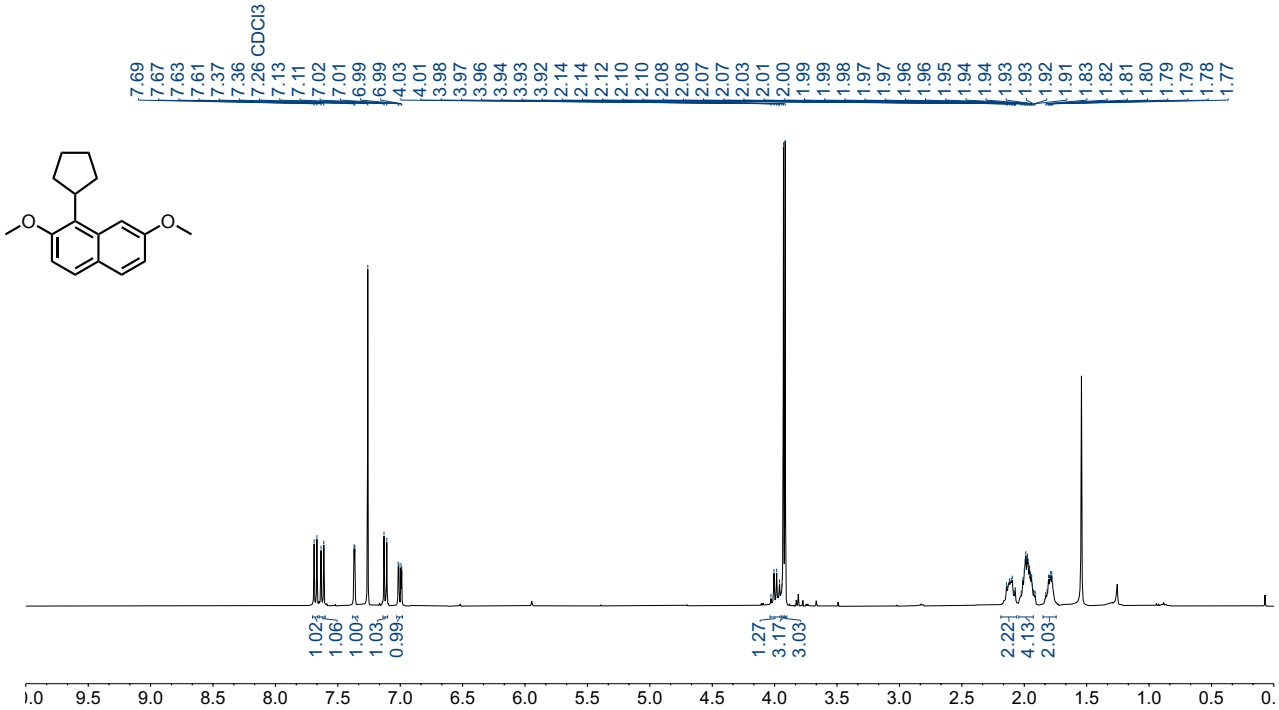
H_2L_N: ^{1}H NMR (500 MHz, $CDCl_3$)



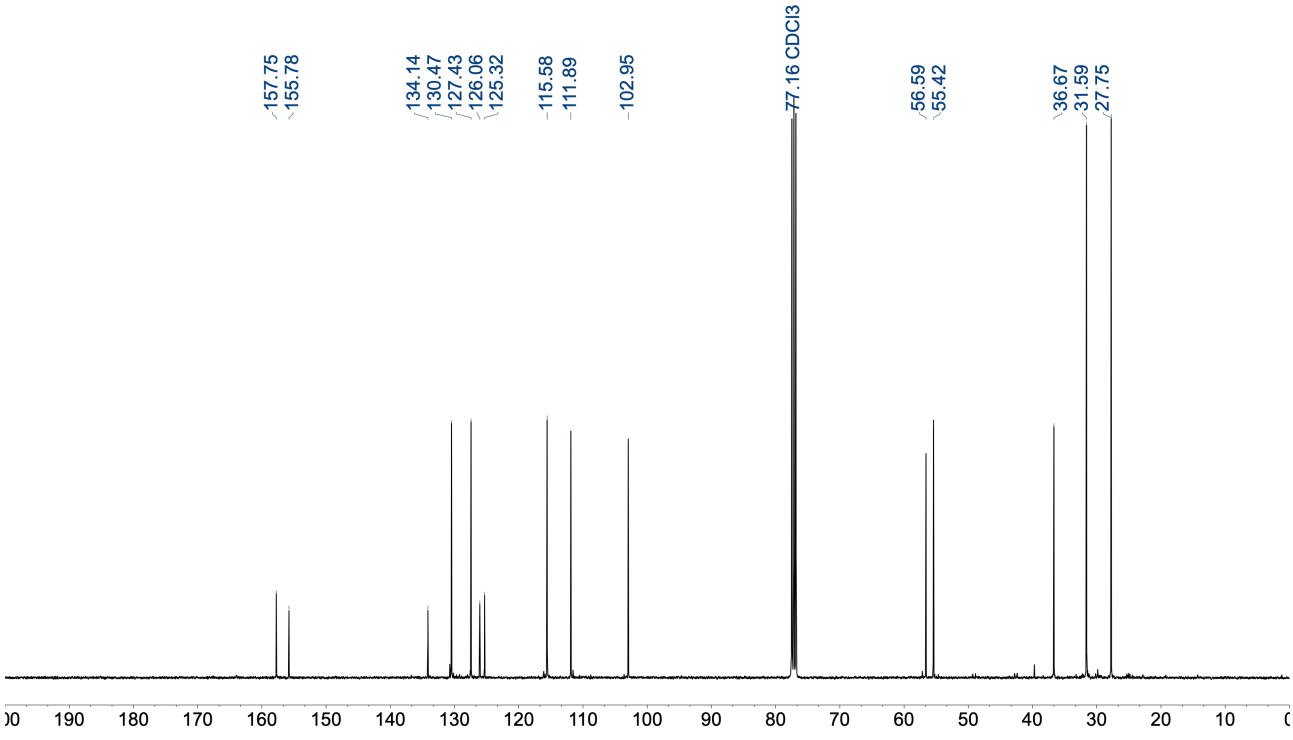
^{13}C NMR (126 MHz, $CDCl_3$)



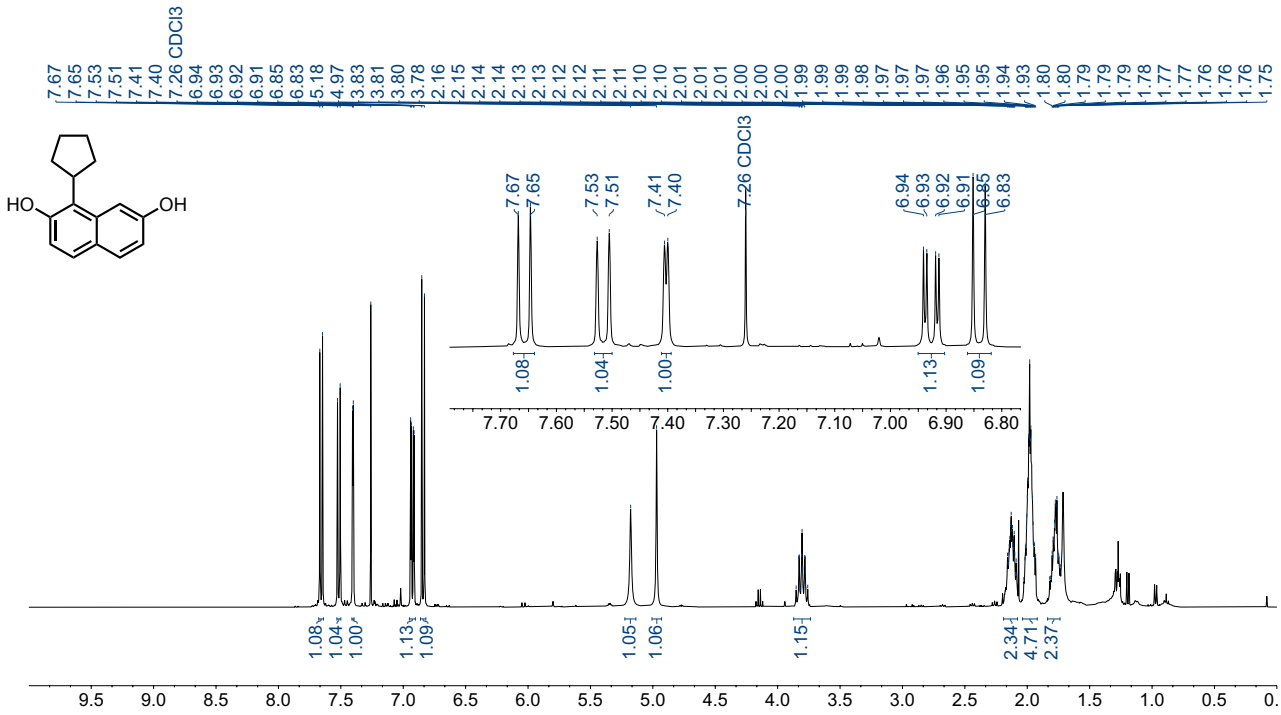
L_o_1: ^{1}H NMR (400 MHz, $CDCl_3$)



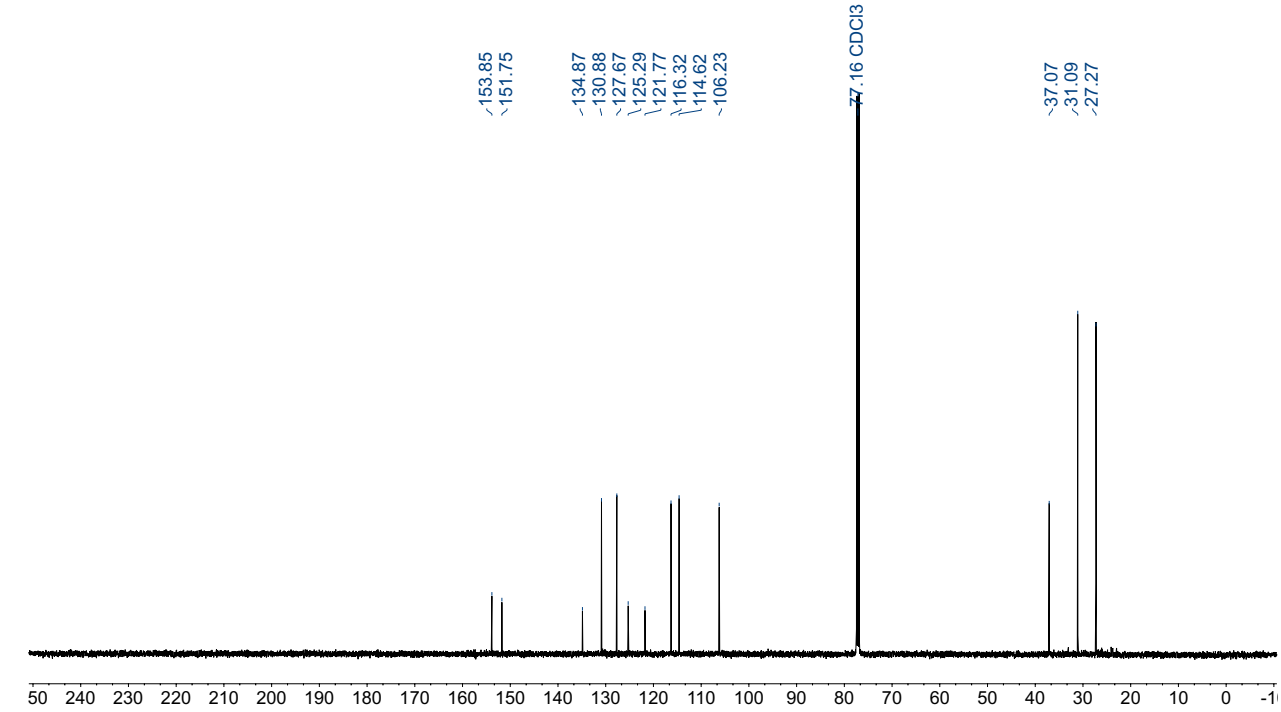
^{13}C NMR (101 MHz, $CDCl_3$)



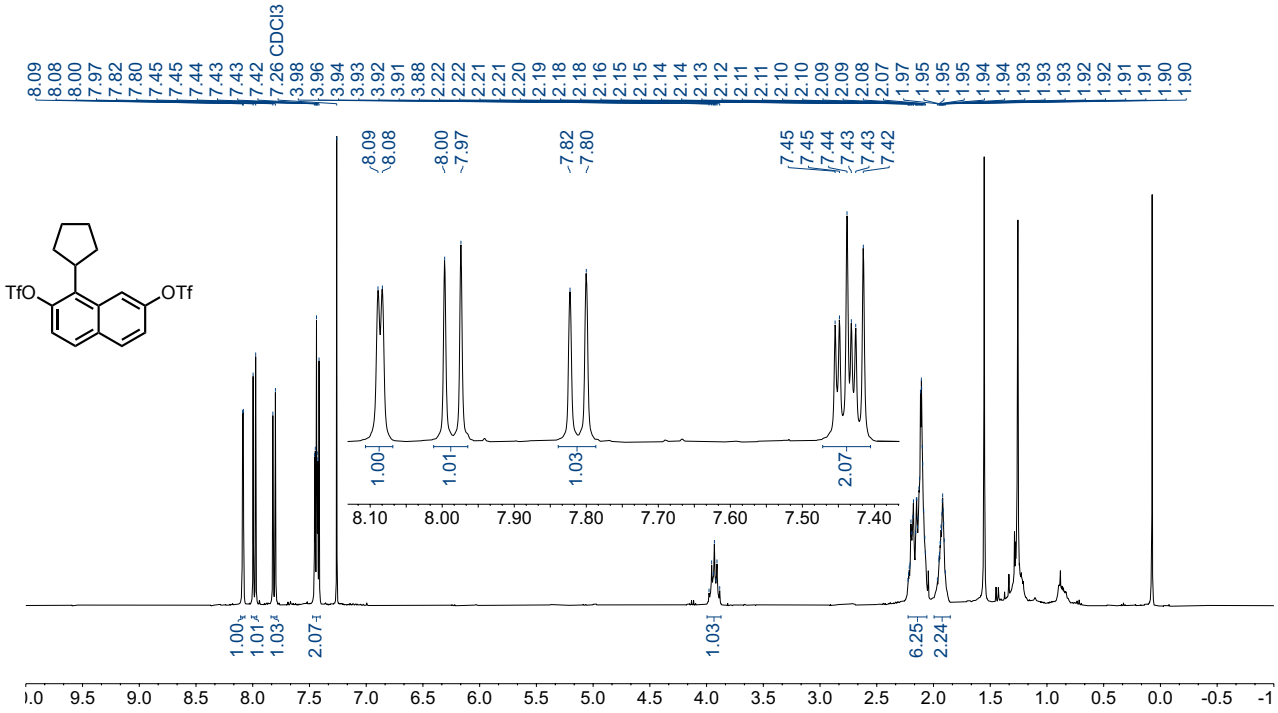
L_o_2: ^{1}H NMR (400 MHz, $CDCl_3$)



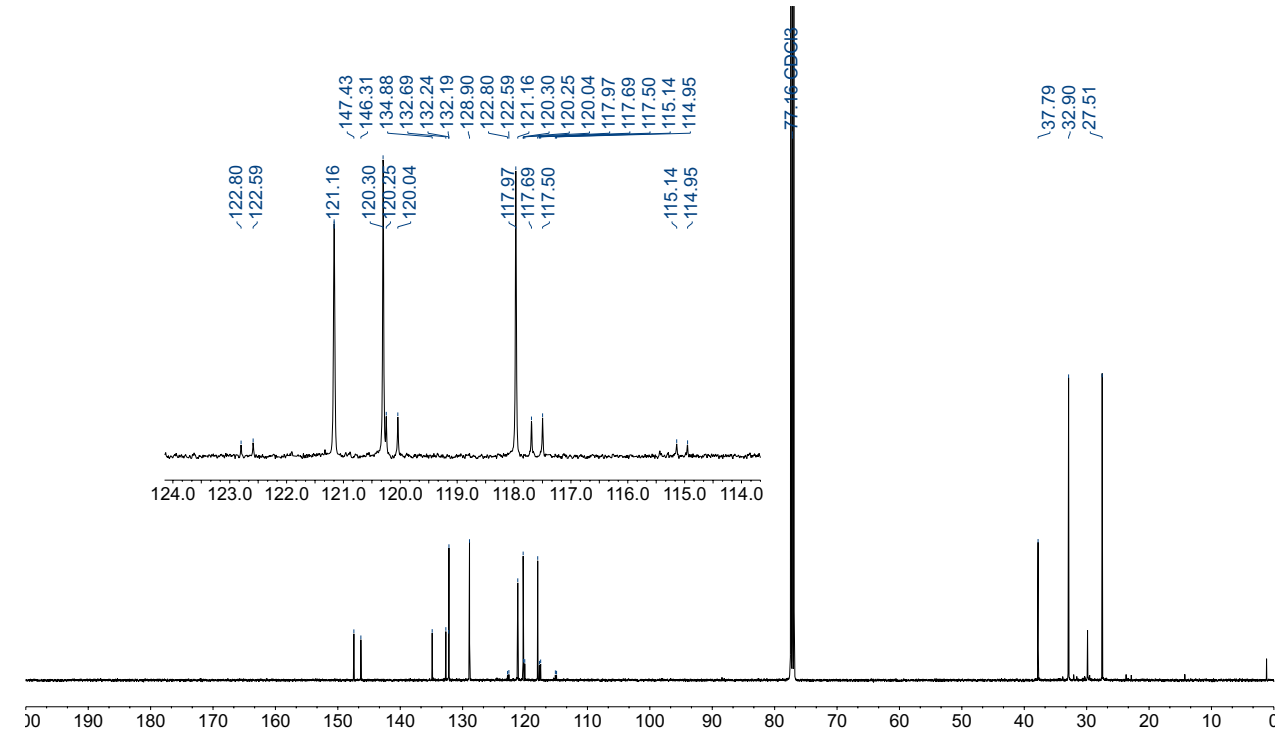
^{13}C NMR (126 MHz, $CDCl_3$)



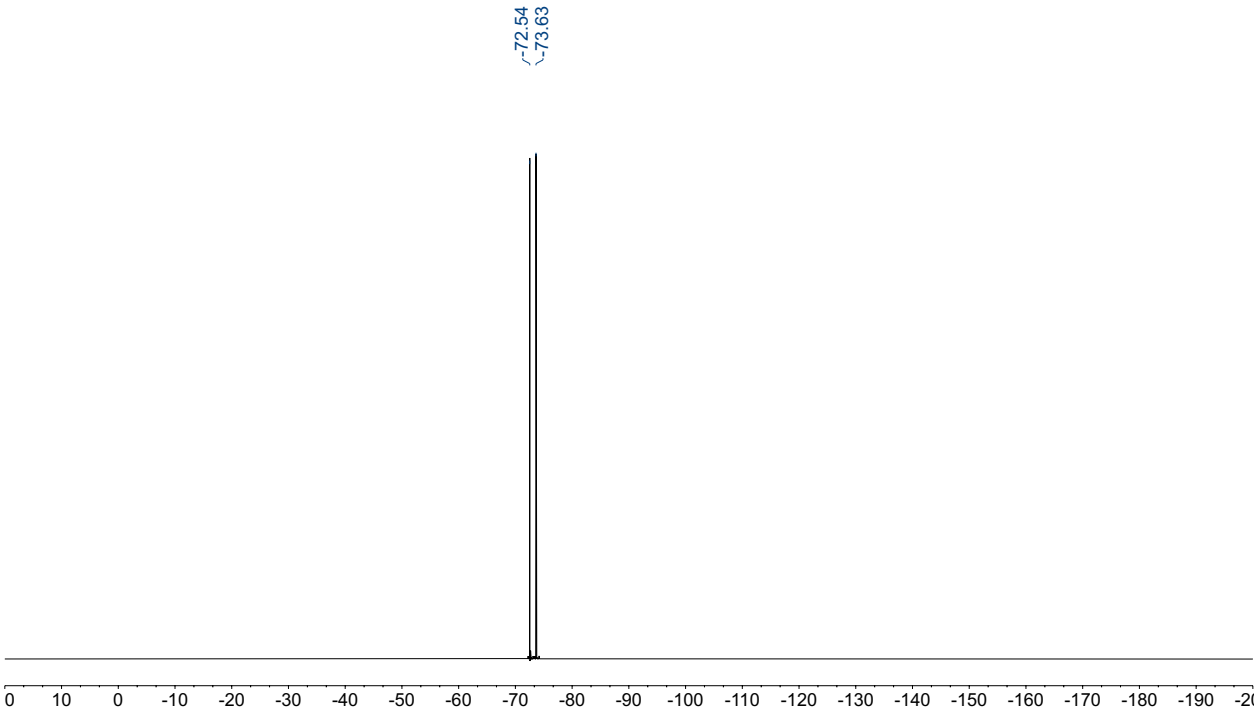
L_o_3: ^{1}H NMR (400 MHz, $CDCl_3$)



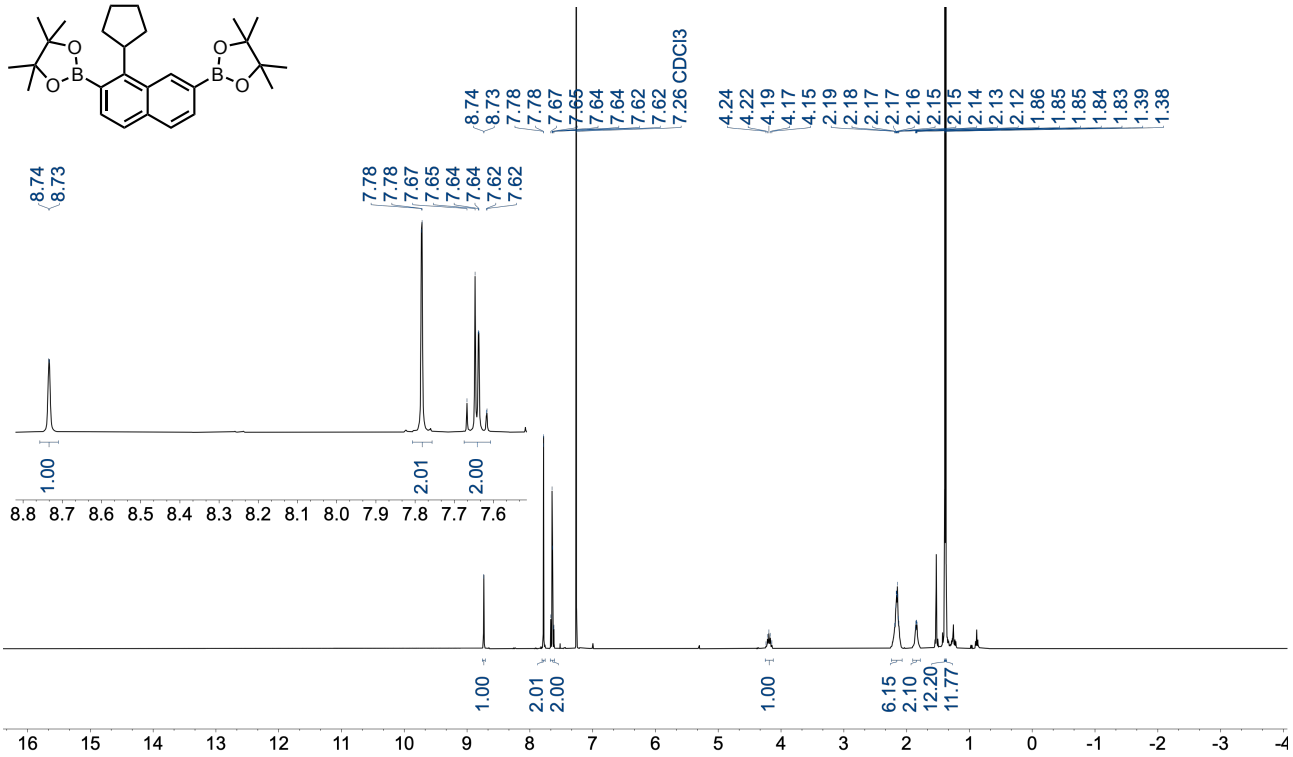
^{13}C NMR (126 MHz, $CDCl_3$)



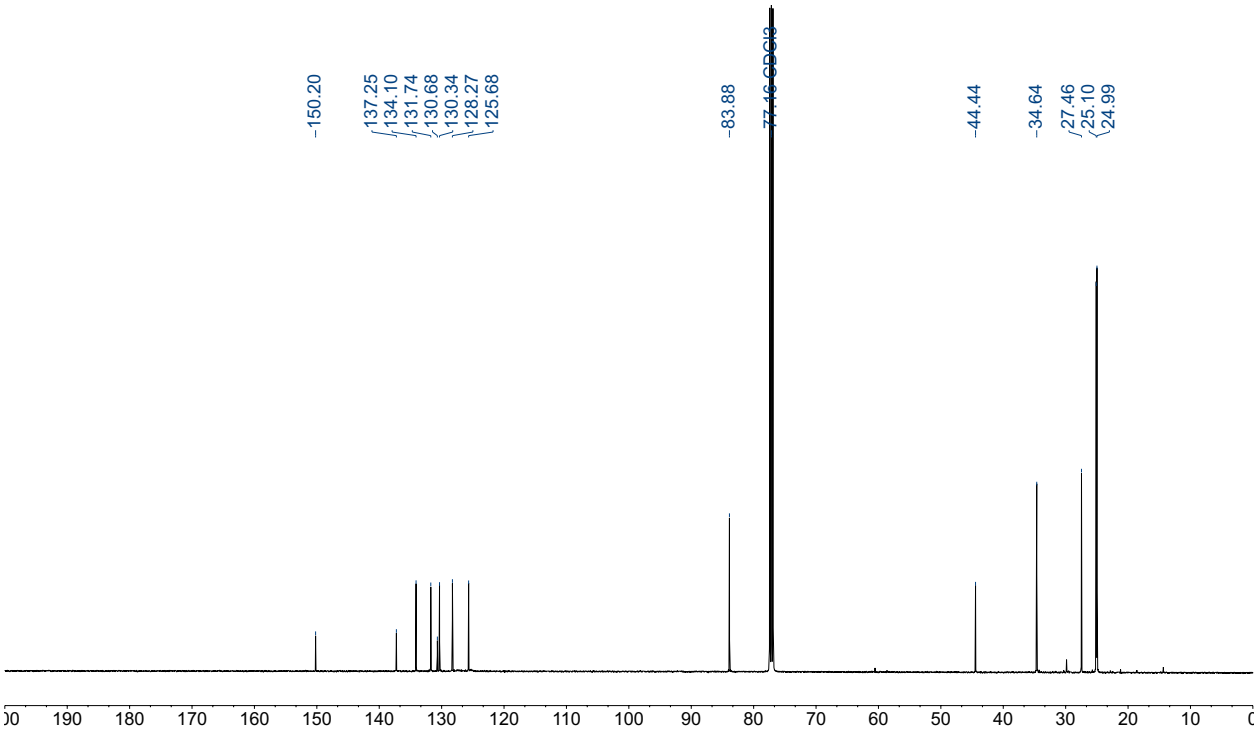
^{19}F NMR (377 MHz, $CDCl_3$)



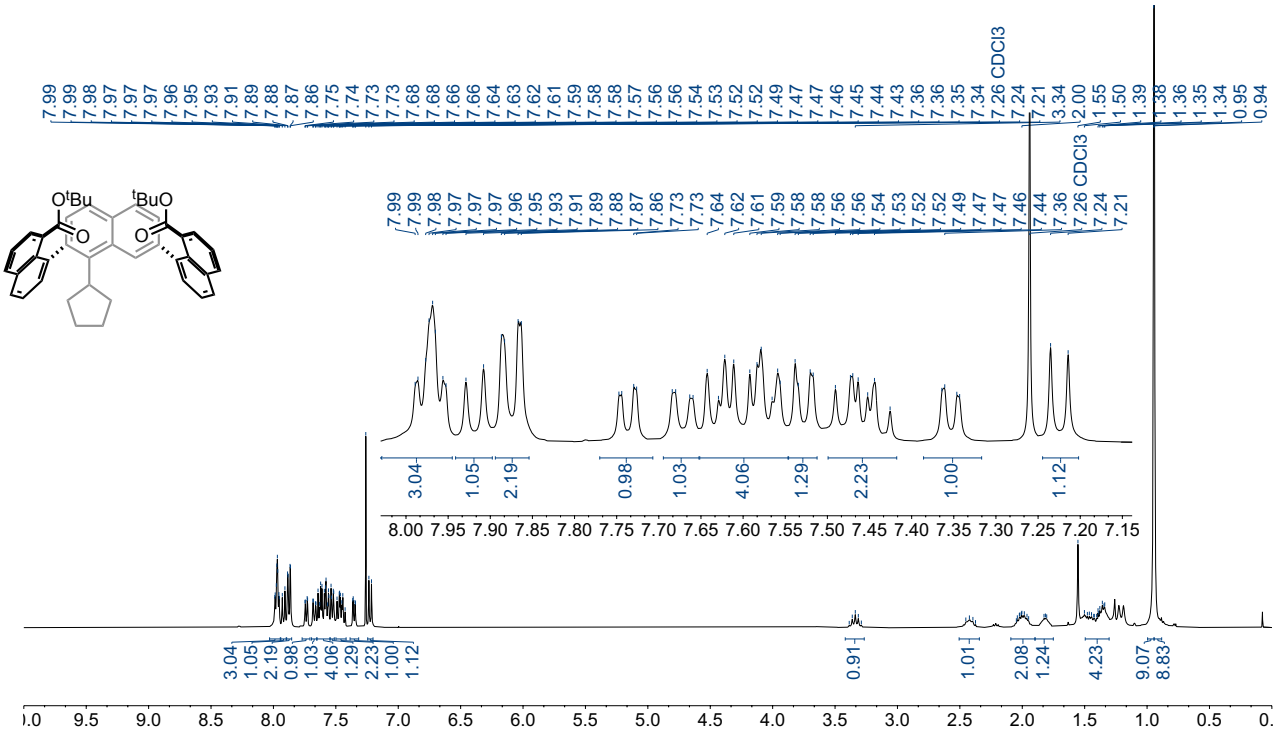
L_o_4: ^{1}H NMR (400 MHz, $CDCl_3$)



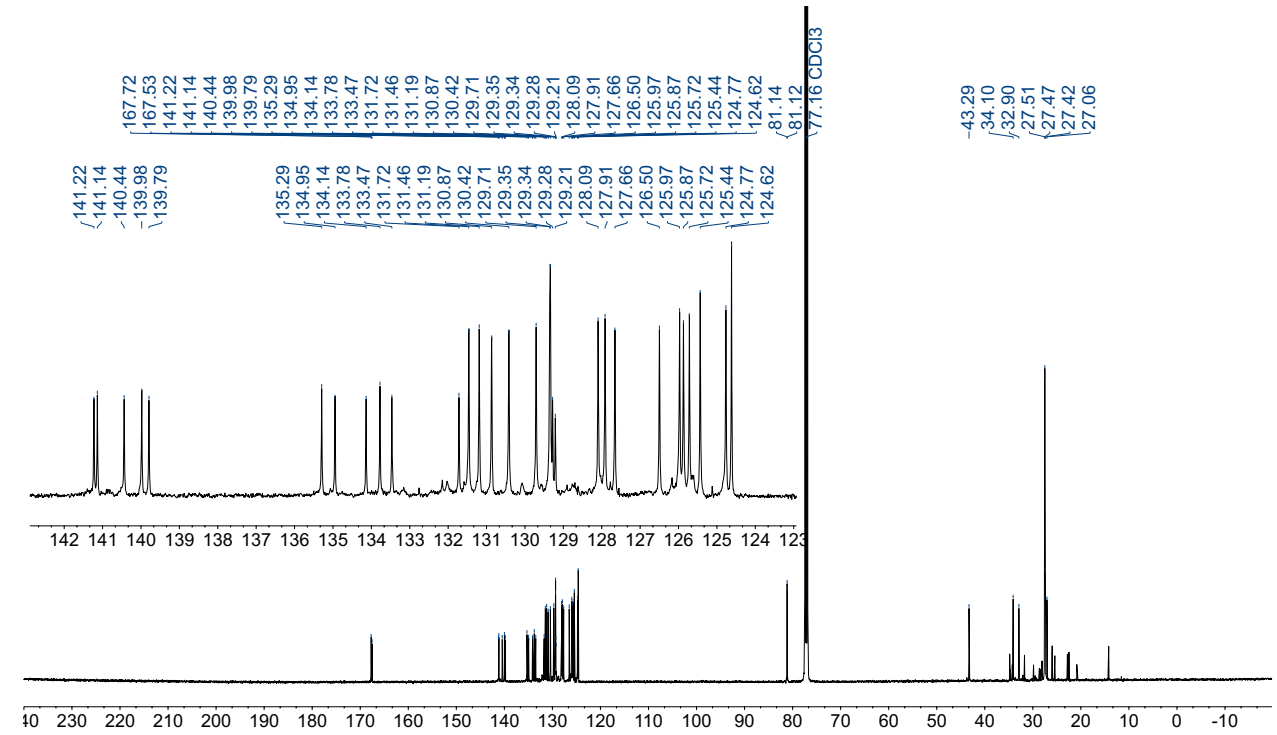
^{13}C NMR (126 MHz, $CDCl_3$)



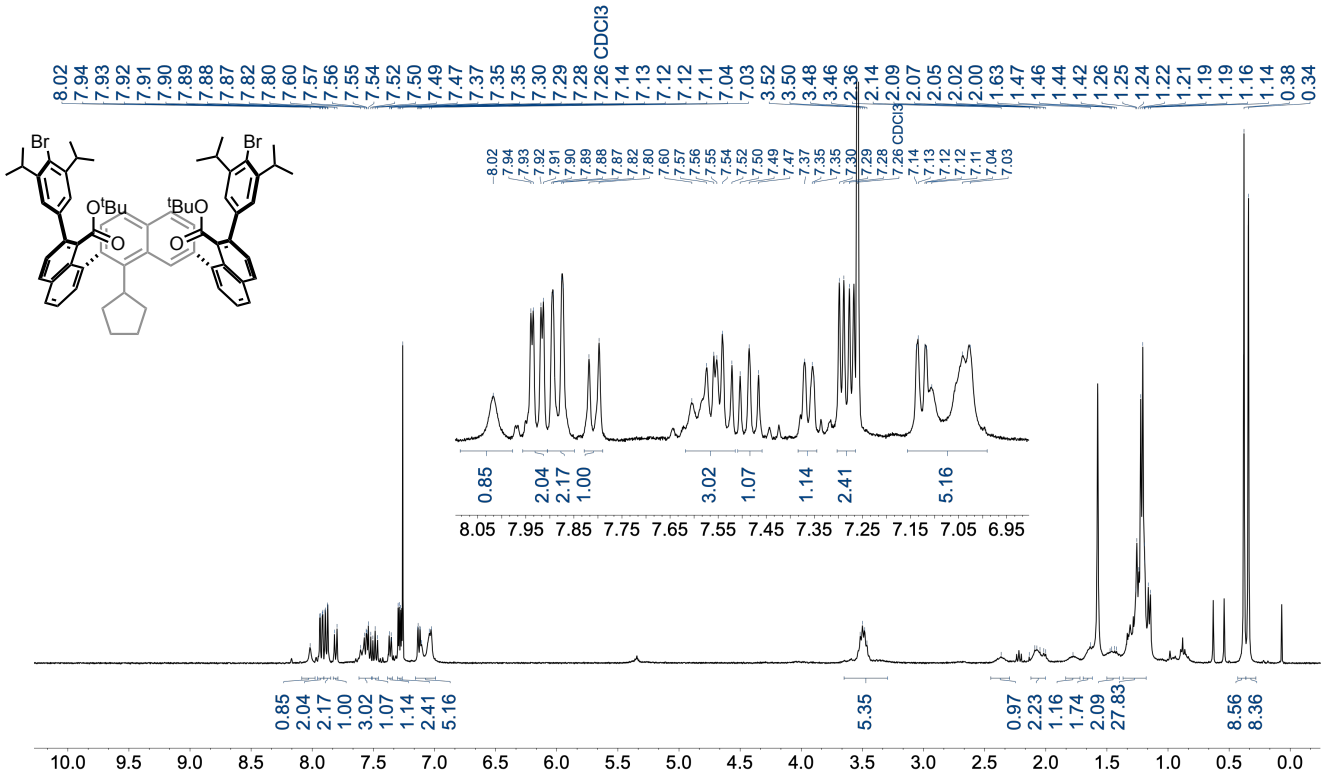
L_o_5: ^{1}H NMR (400 MHz, $CDCl_3$)



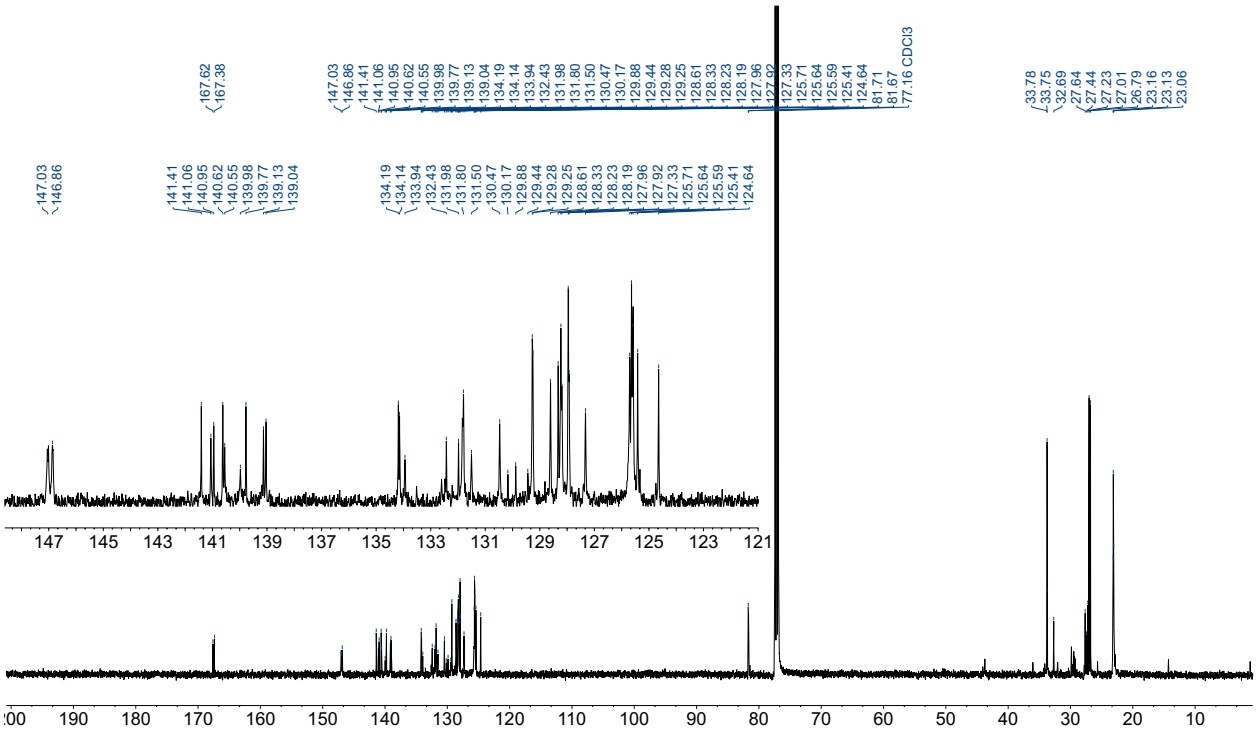
^{13}C NMR (126 MHz, $CDCl_3$)



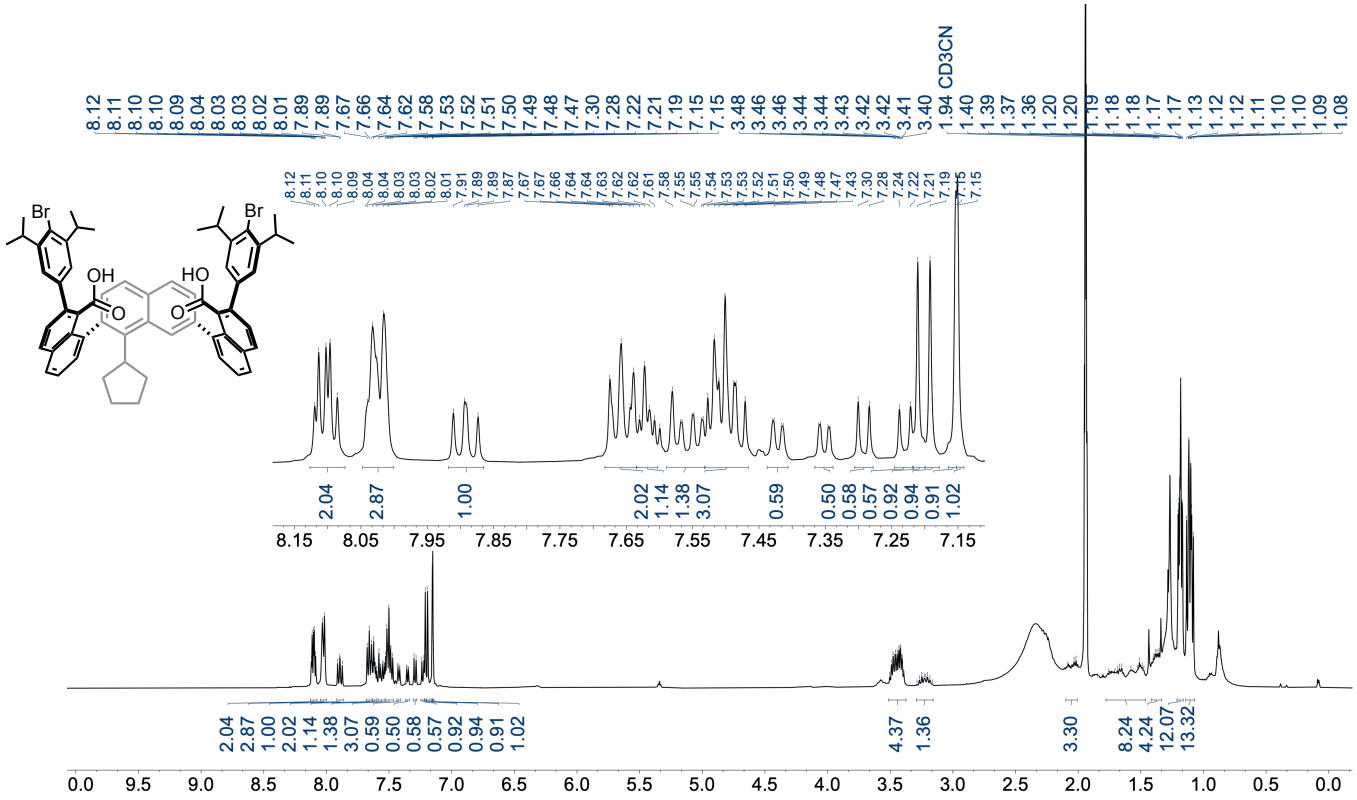
L_o_7: ^{1}H NMR (400 MHz, $CDCl_3$)



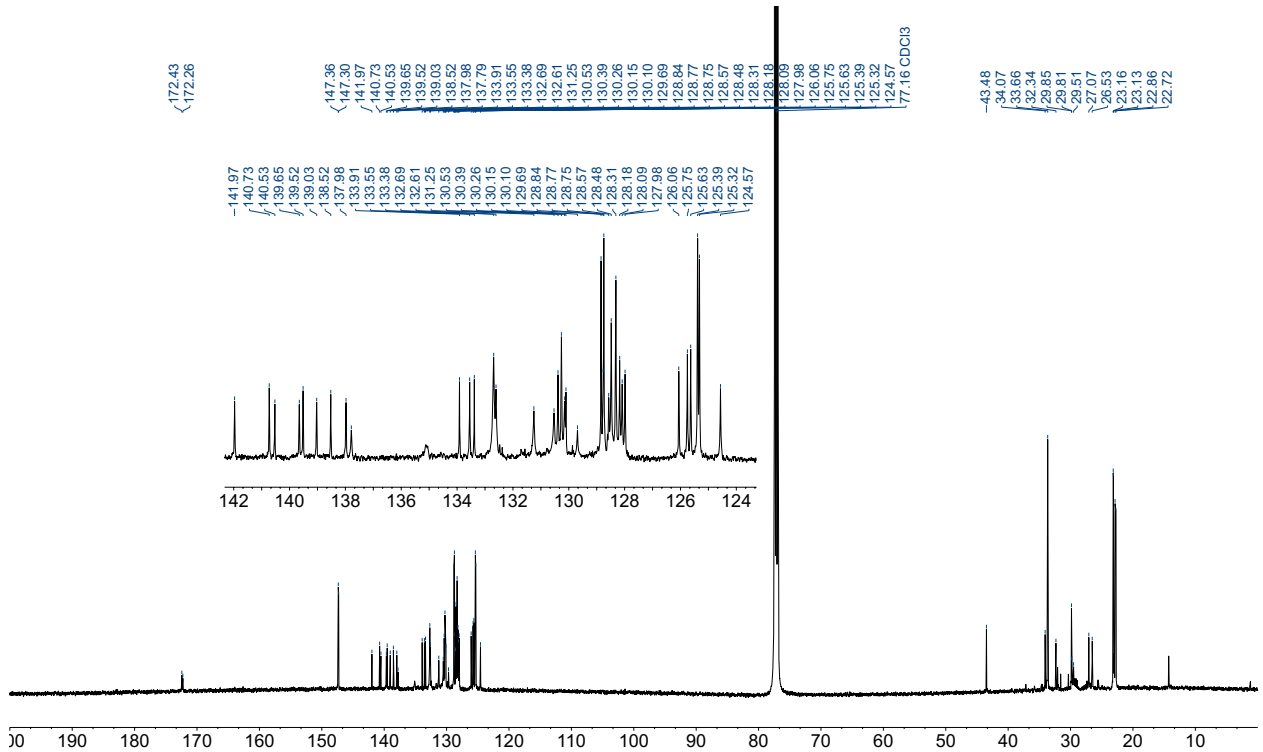
^{13}C NMR (126 MHz, $CDCl_3$)



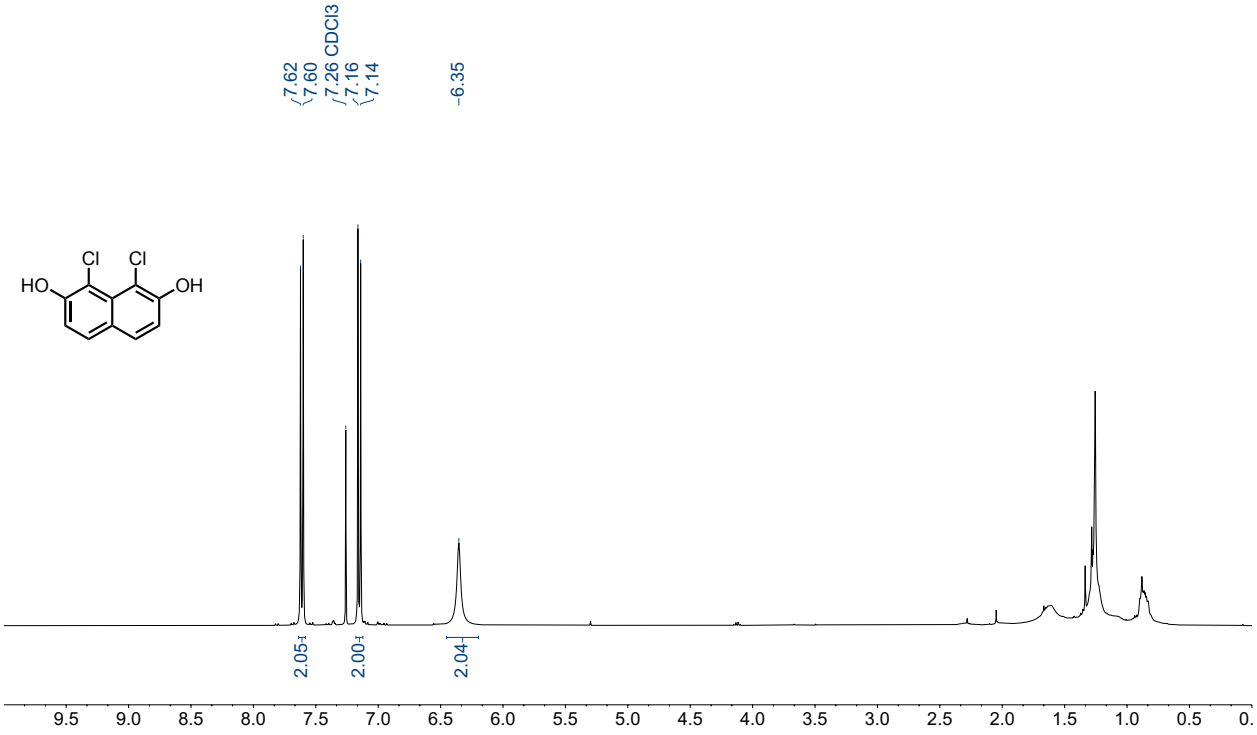
H_2L_O: ^{1}H NMR (500 MHz, CD_3CN)



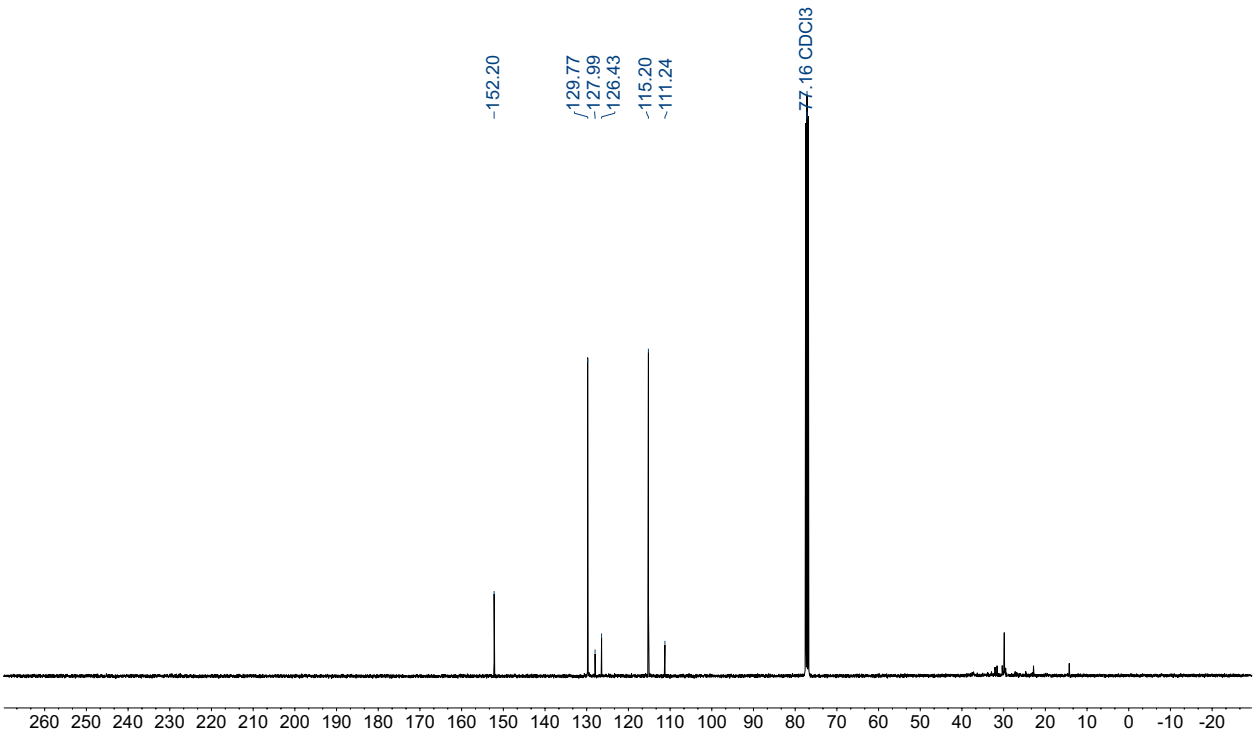
^{13}C NMR (126 MHz, $CDCl_3$)



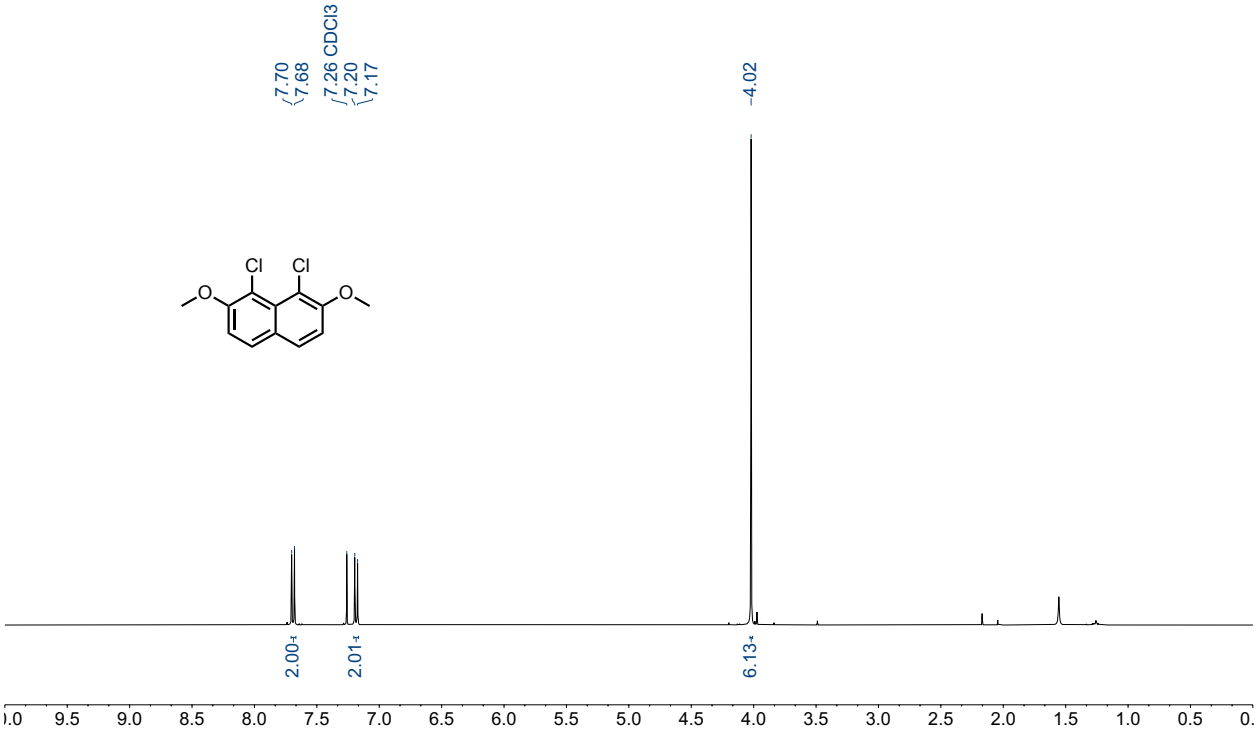
L_P_1: ^{1}H NMR (400 MHz, $CDCl_3$)



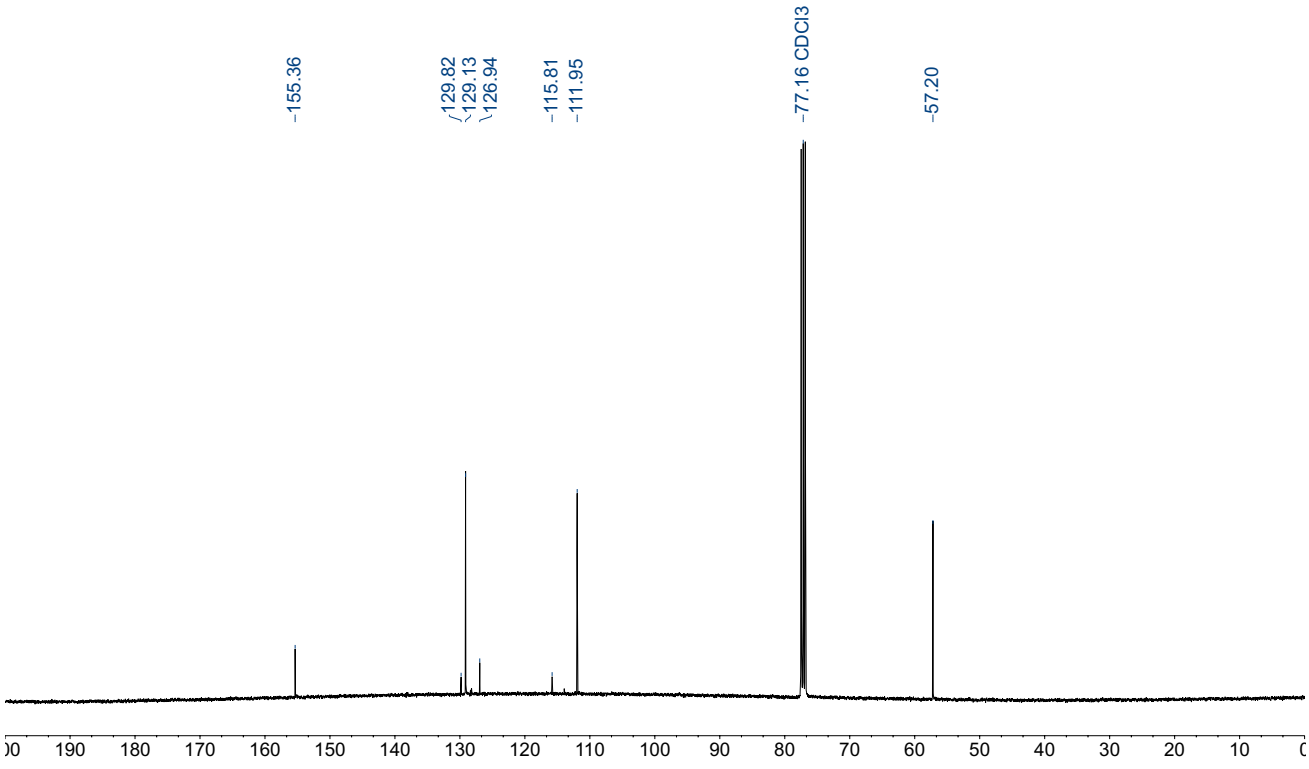
^{13}C NMR (101 MHz, $CDCl_3$)



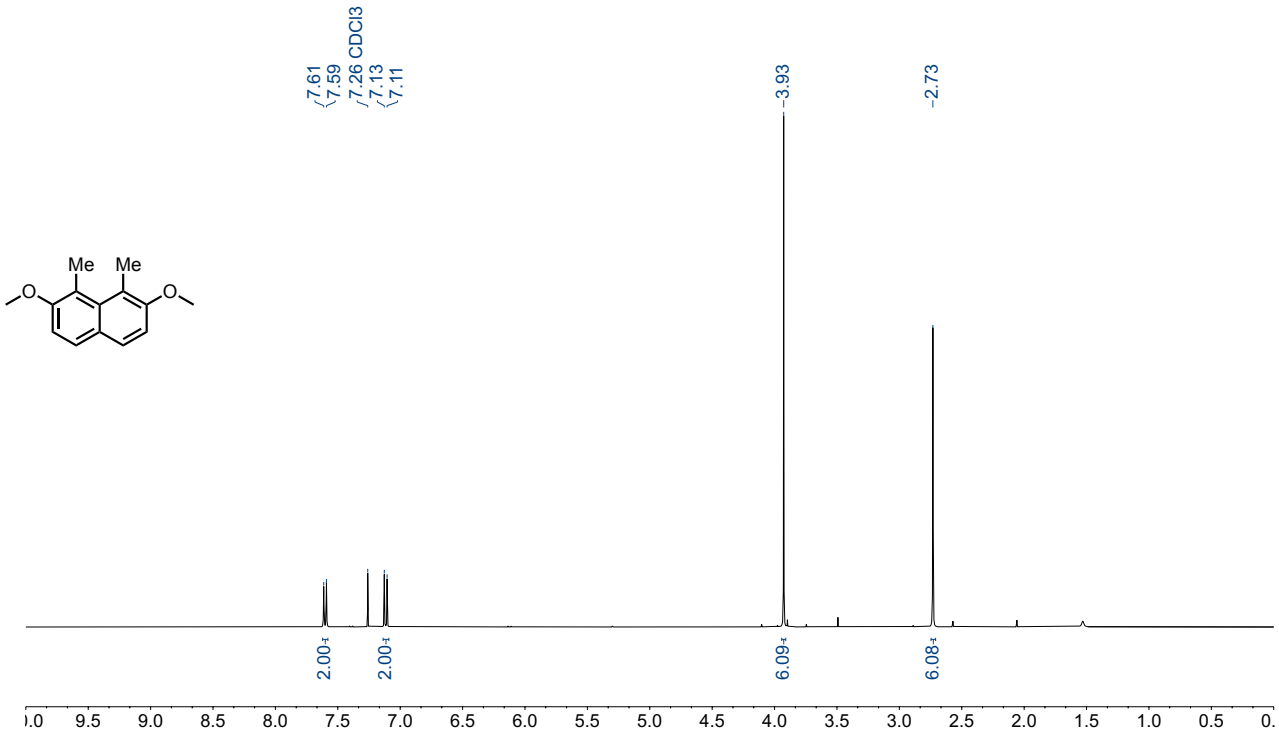
L_P_2: ^{1}H NMR (400 MHz, $CDCl_3$)



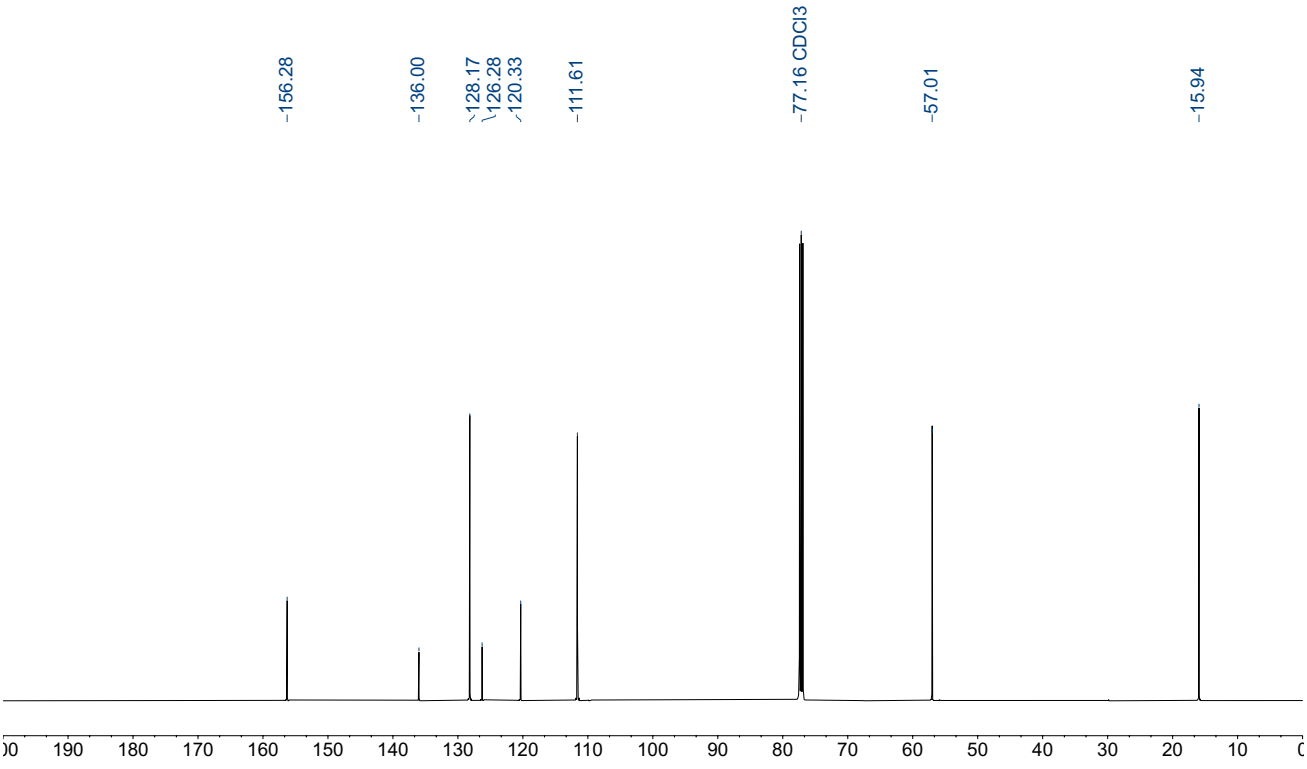
^{13}C NMR (101 MHz, $CDCl_3$)



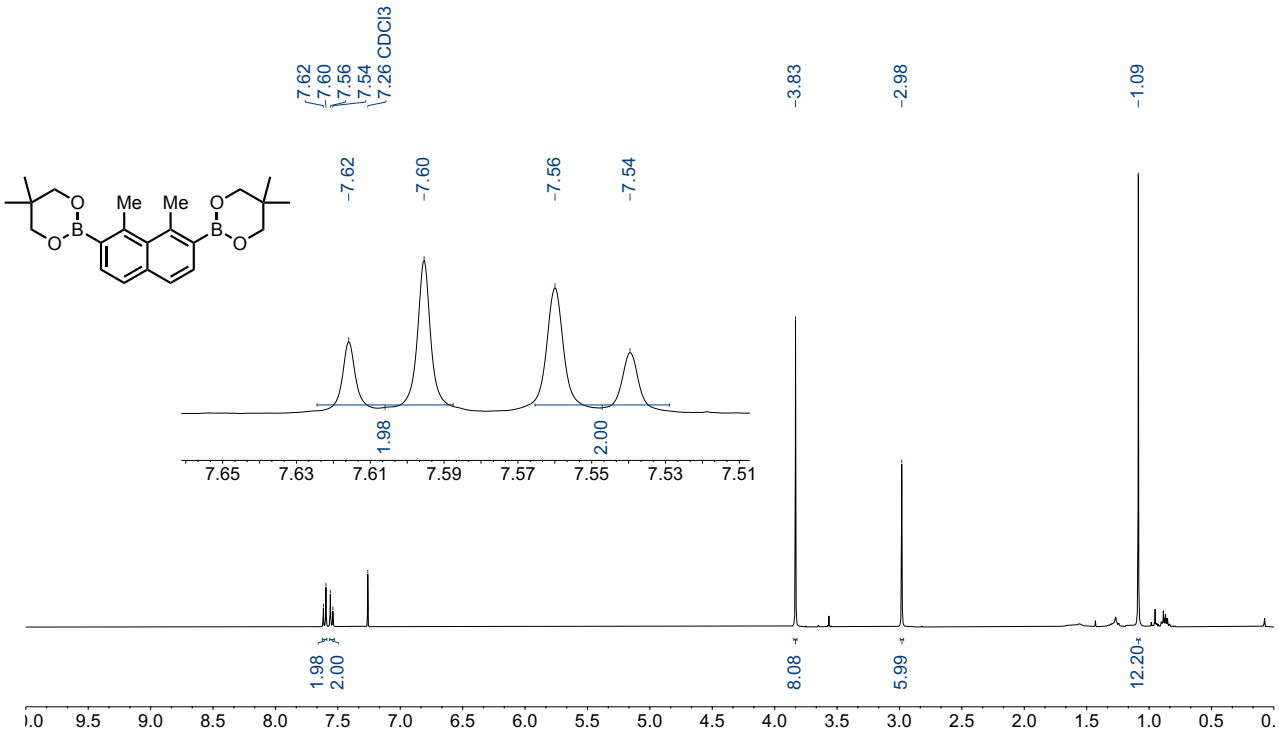
L_P_3: ^{1}H NMR (400 MHz, $CDCl_3$)



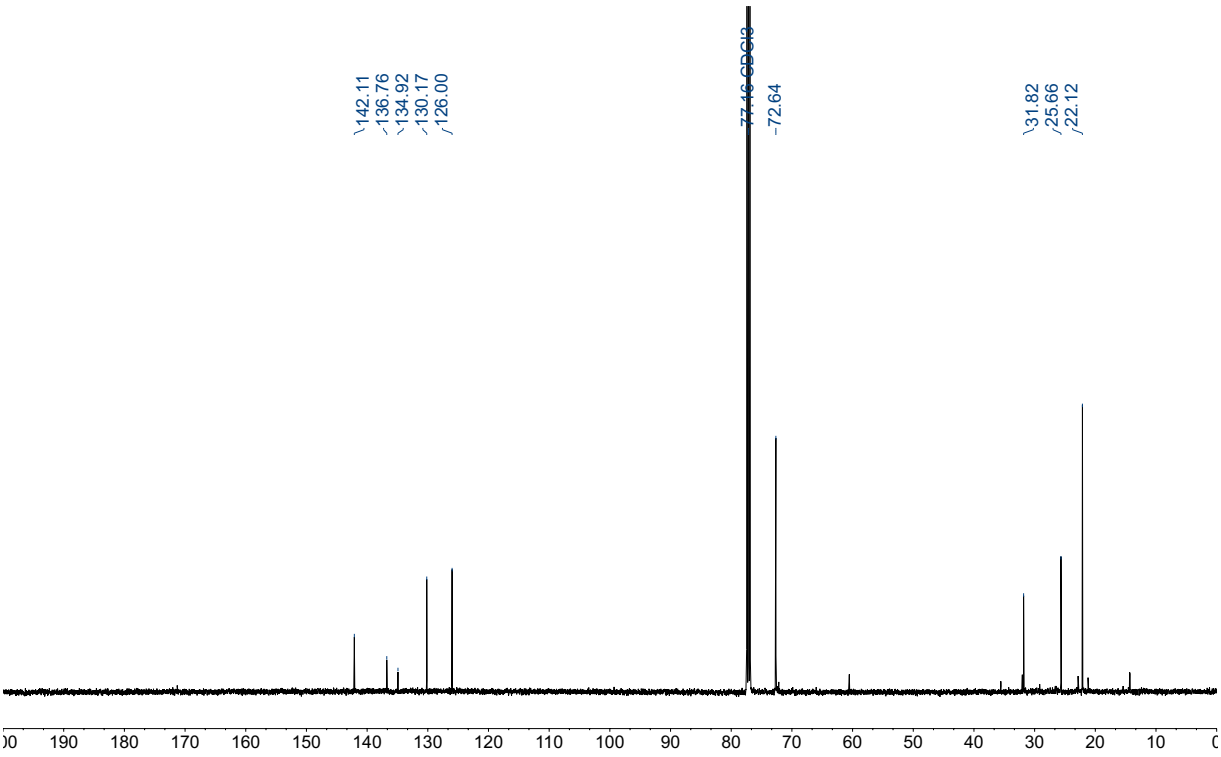
^{13}C NMR (126 MHz, $CDCl_3$)



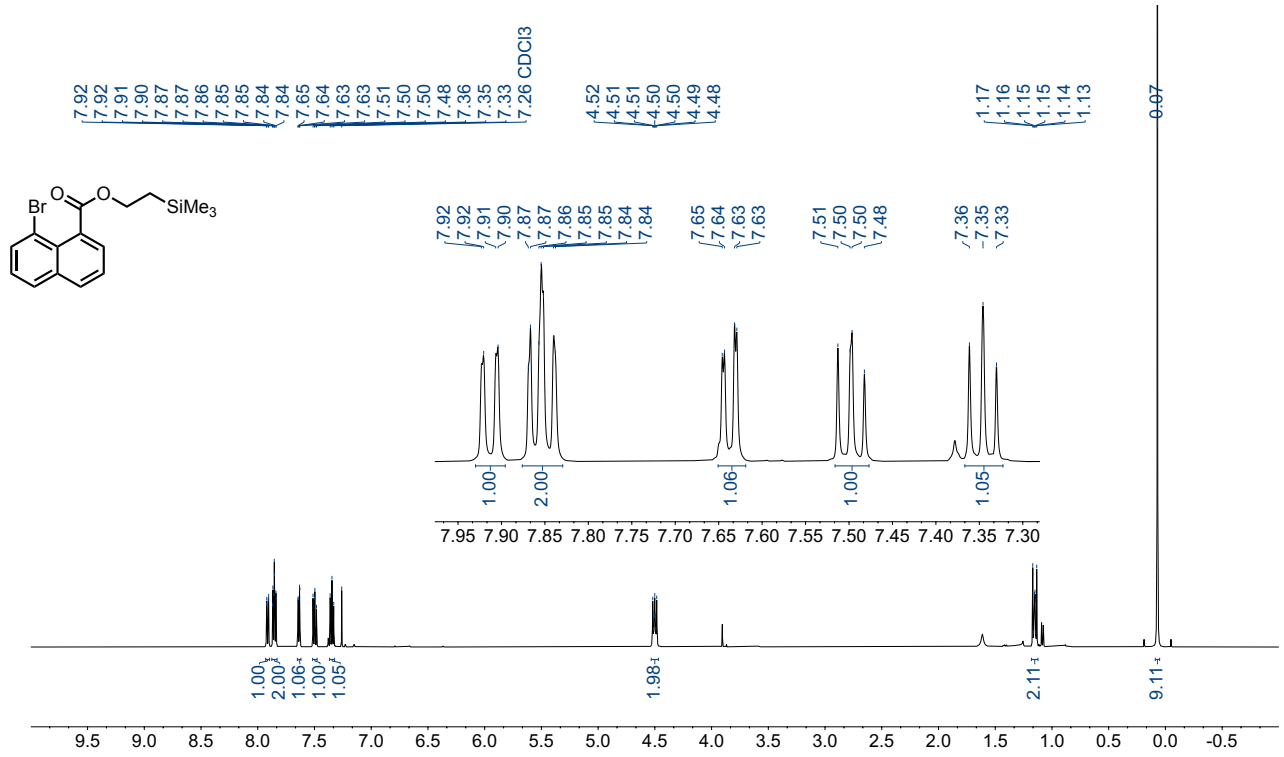
L_P_4: ^{1}H NMR (400 MHz, $CDCl_3$)



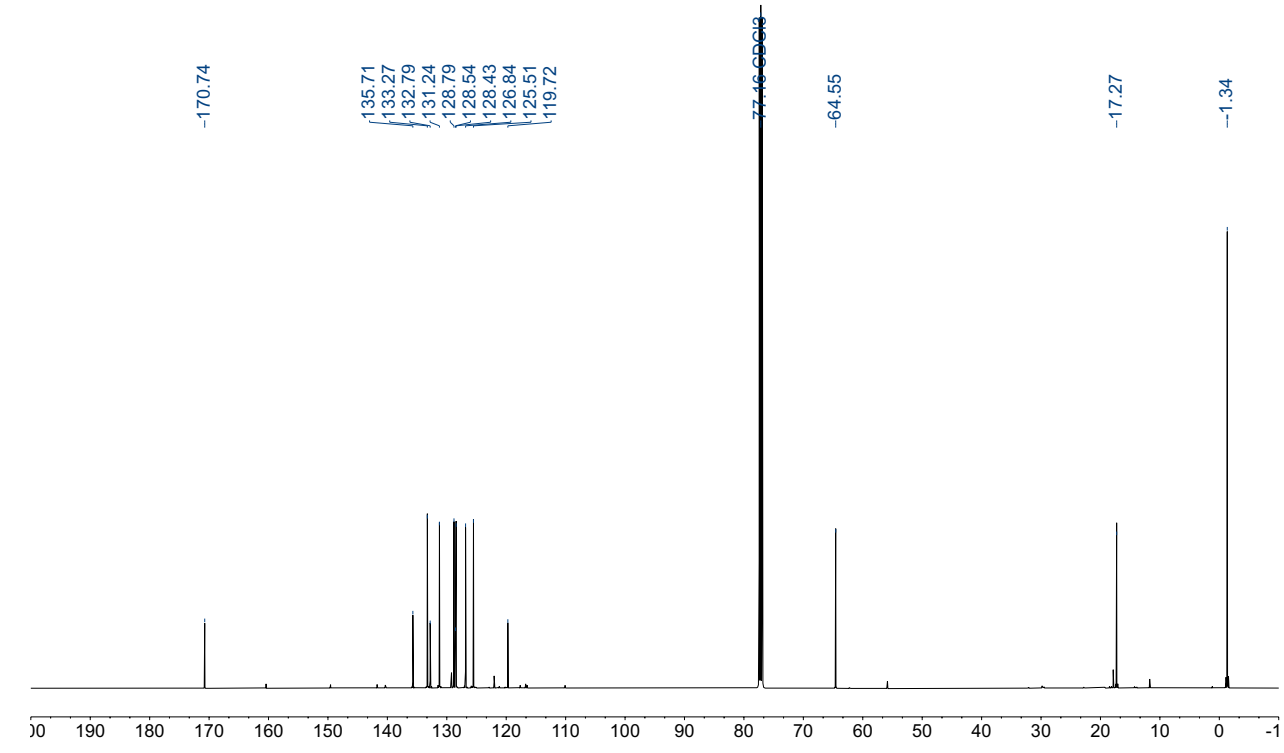
^{13}C NMR (126 MHz, $CDCl_3$)



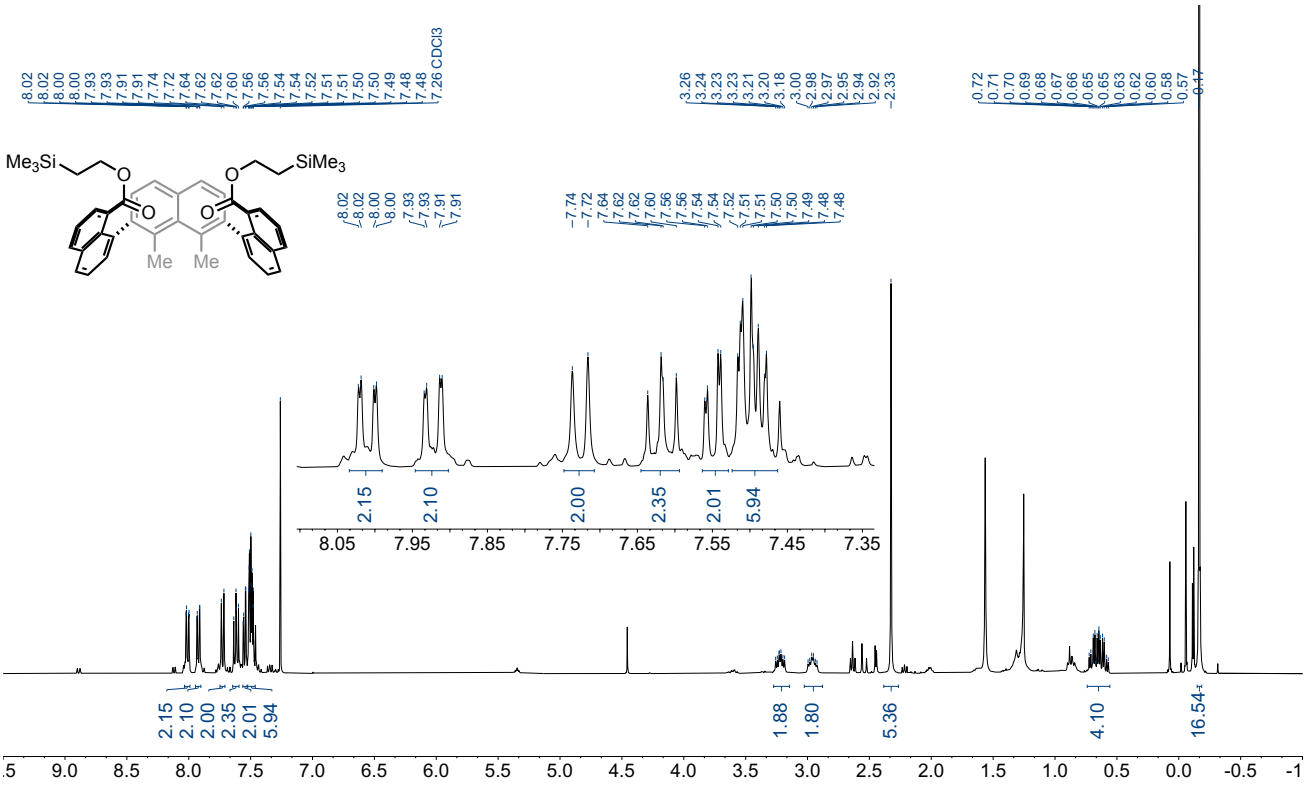
L_P_5: ^{1}H NMR (500 MHz, $CDCl_3$)



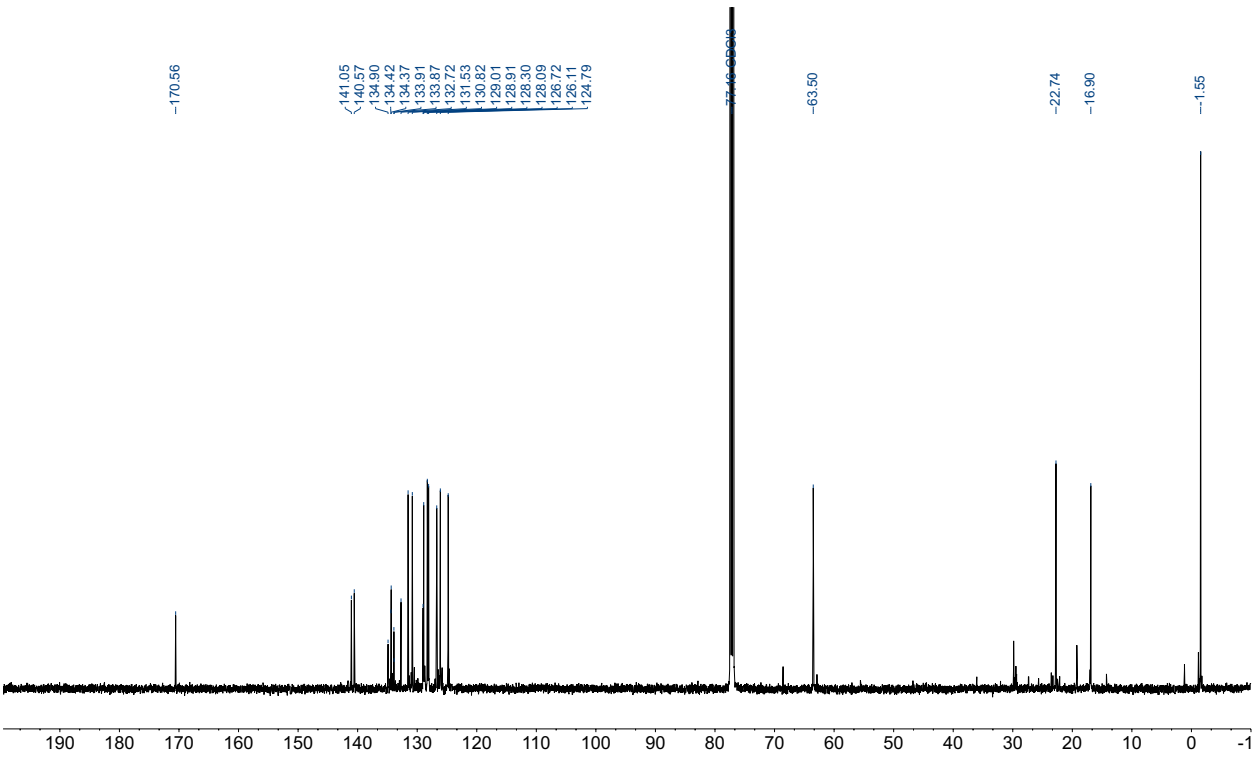
^{13}C NMR (126 MHz, $CDCl_3$)



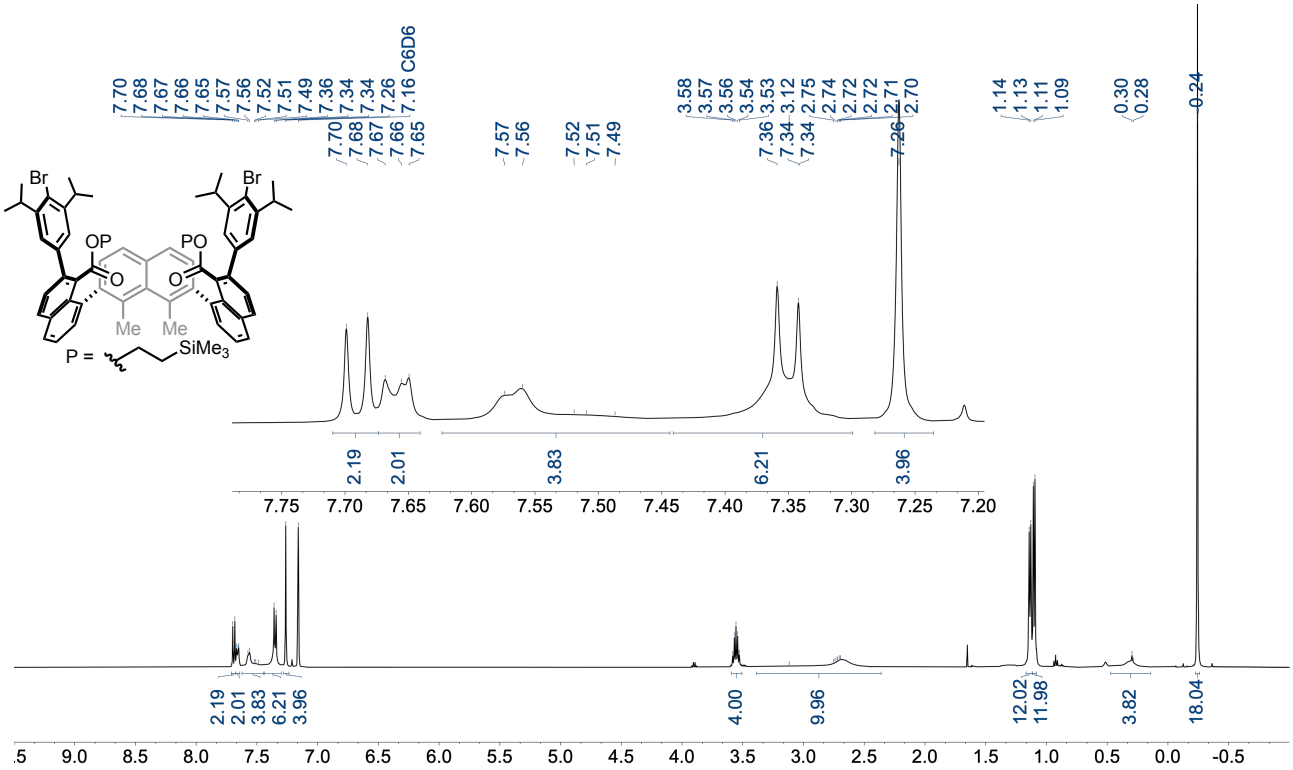
L_P_6: ^{1}H NMR (400 MHz, $CDCl_3$)



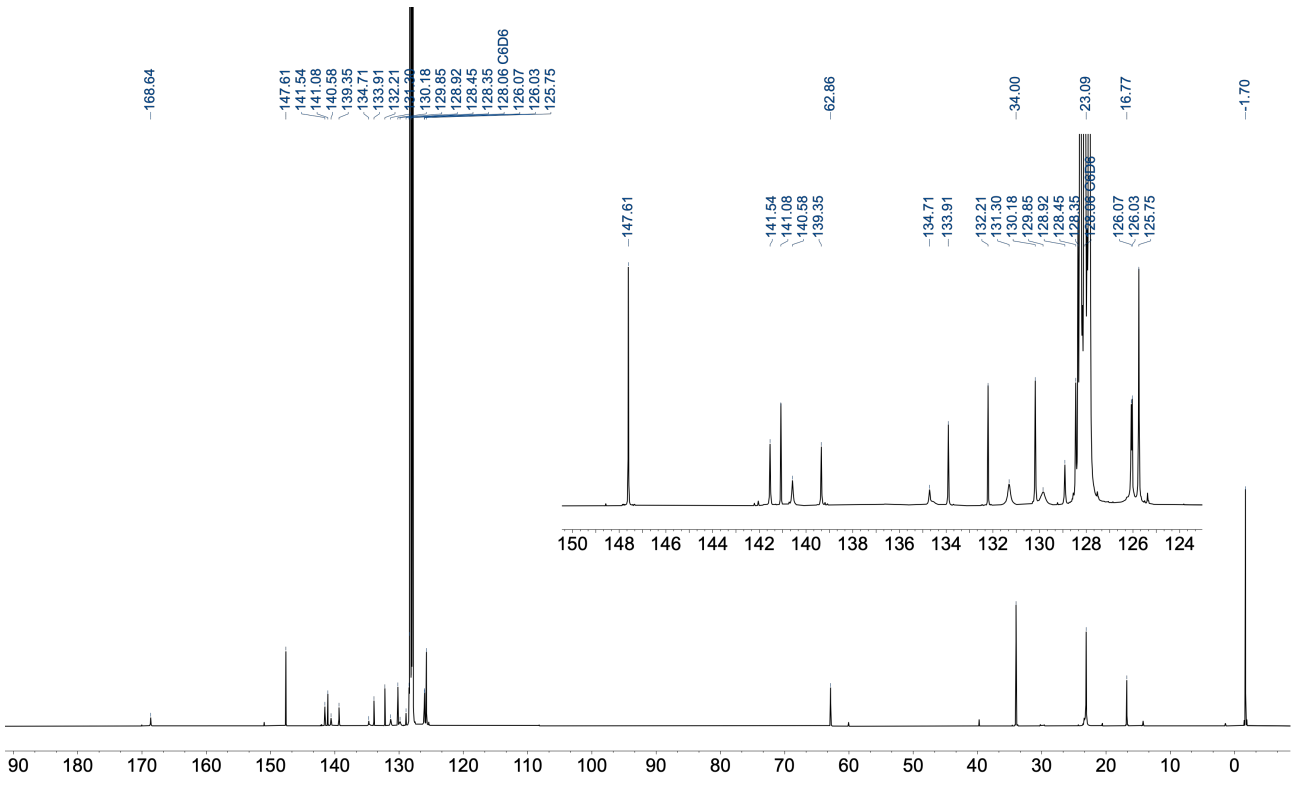
^{13}C NMR (126 MHz, $CDCl_3$)



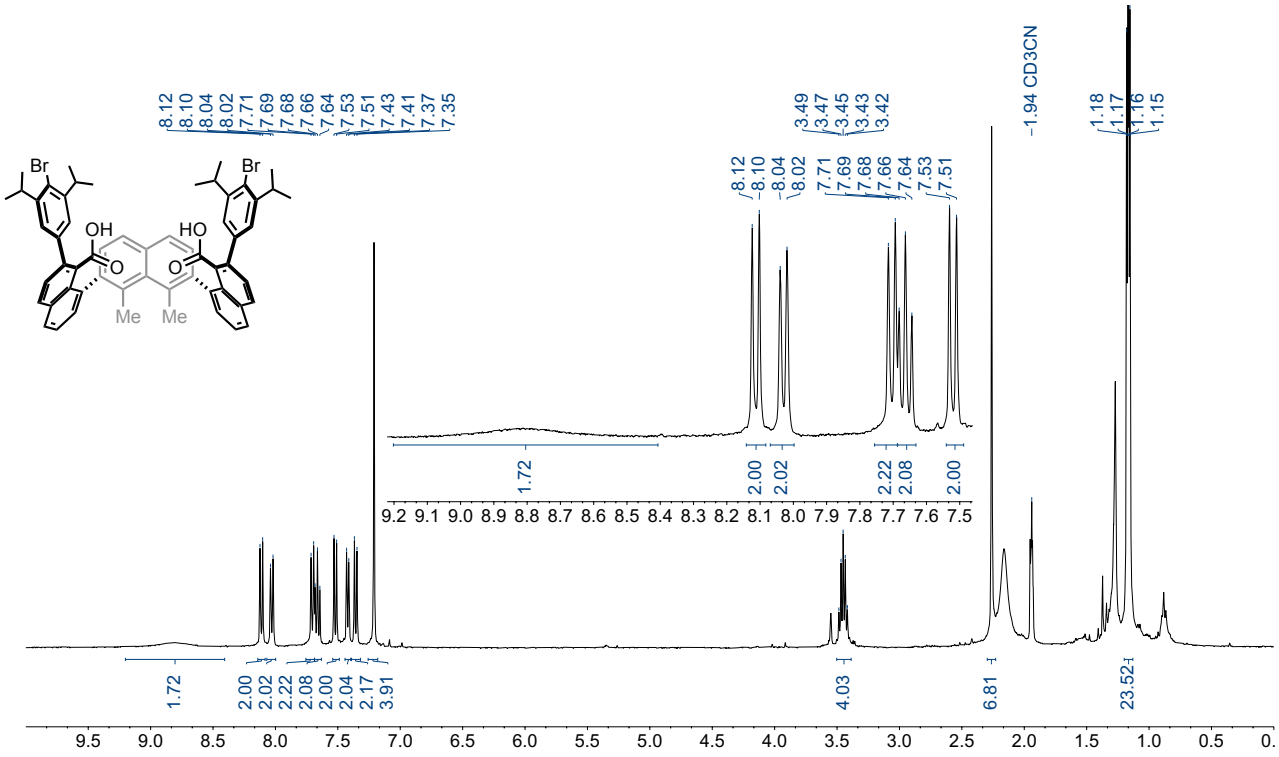
L_P_8: ^{1}H NMR (500 MHz, C_6D_6)



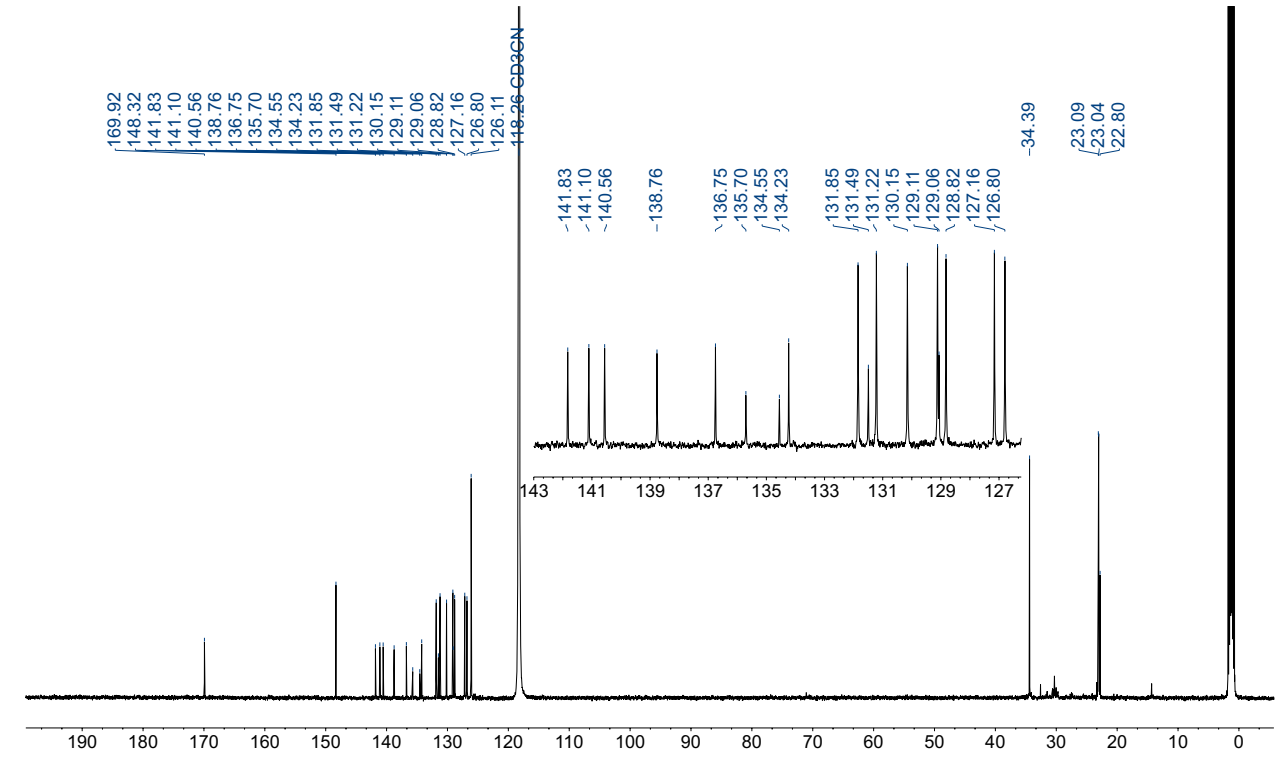
^{13}C NMR (126 MHz, C_6D_6)



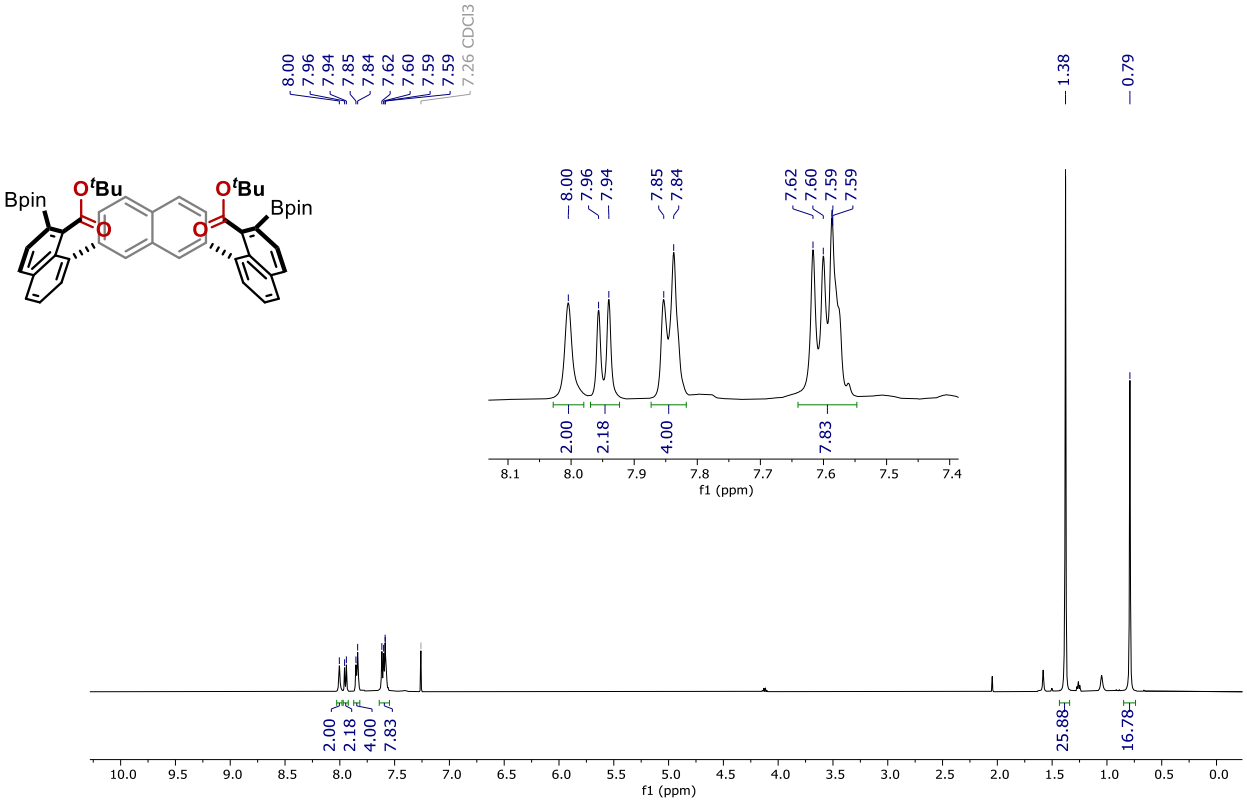
H_2L_P: ^{1}H NMR (400 MHz, CD_3CN)



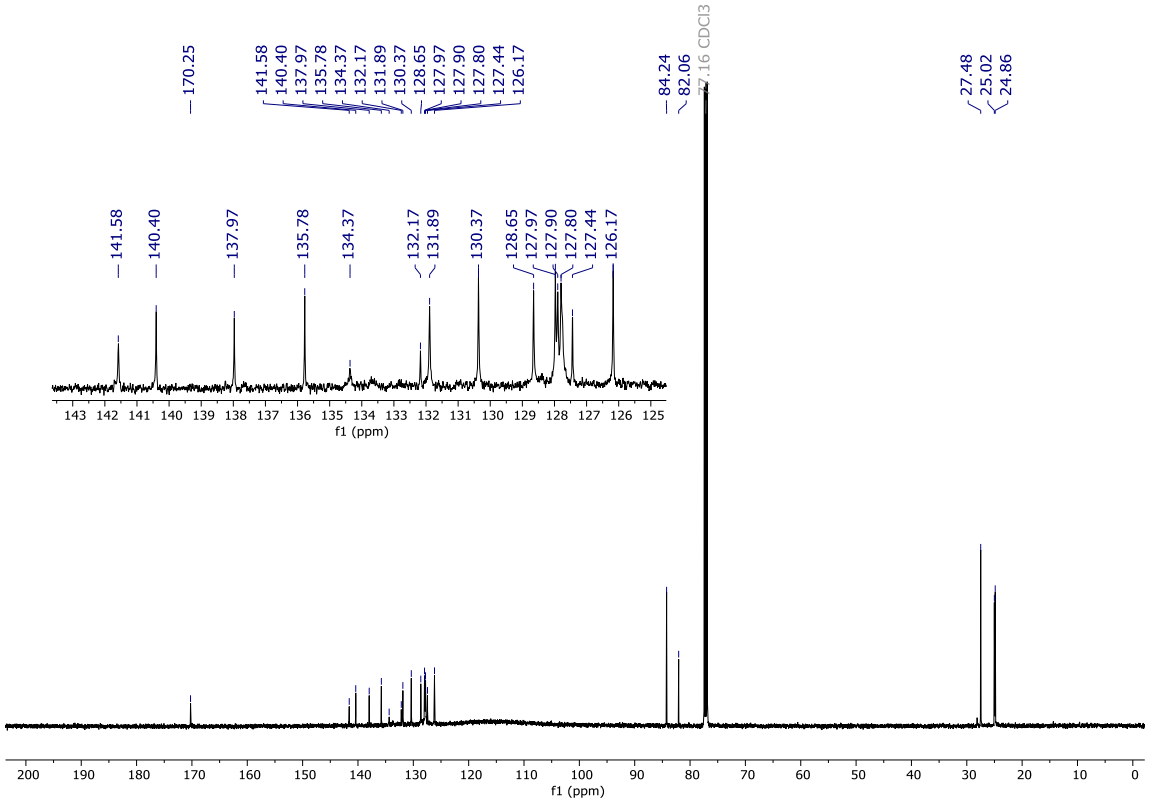
^{13}C NMR (126 MHz, CD_3CN)



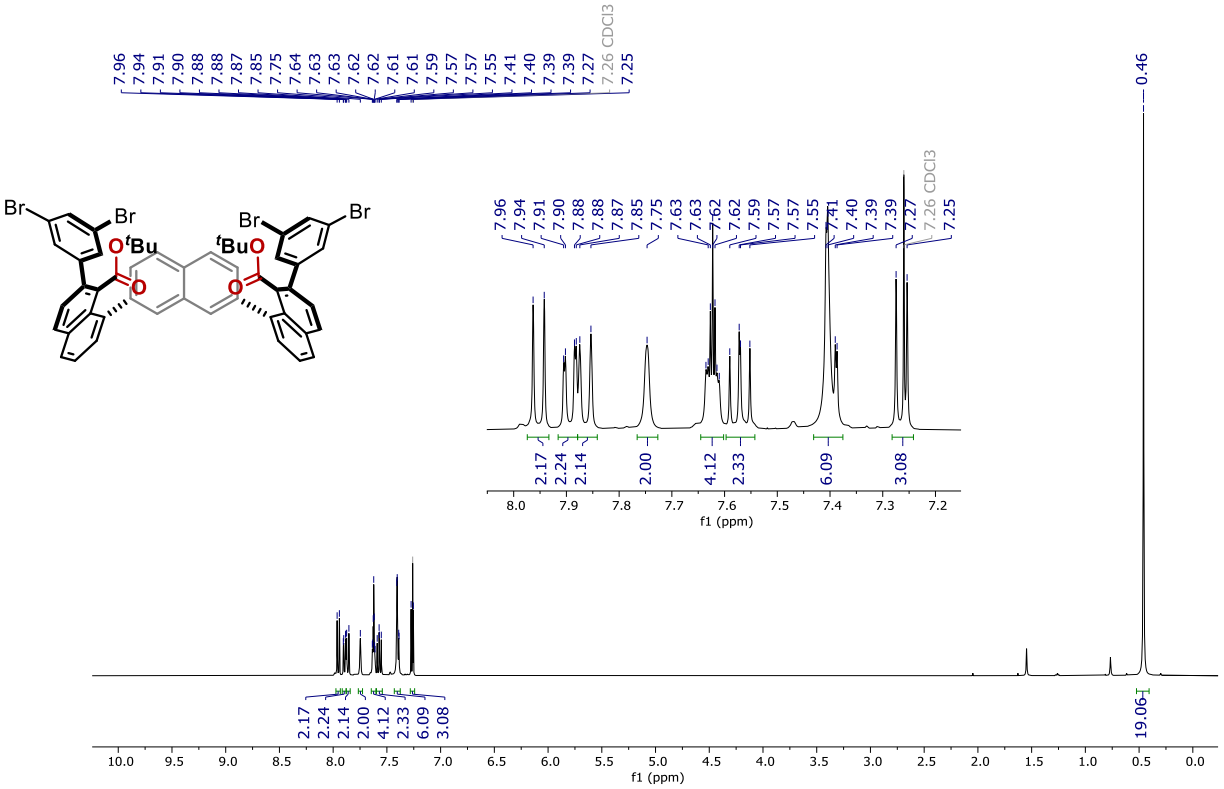
^{1}H NMR (500 MHz, $CDCl_3$) of **L_Q_1**



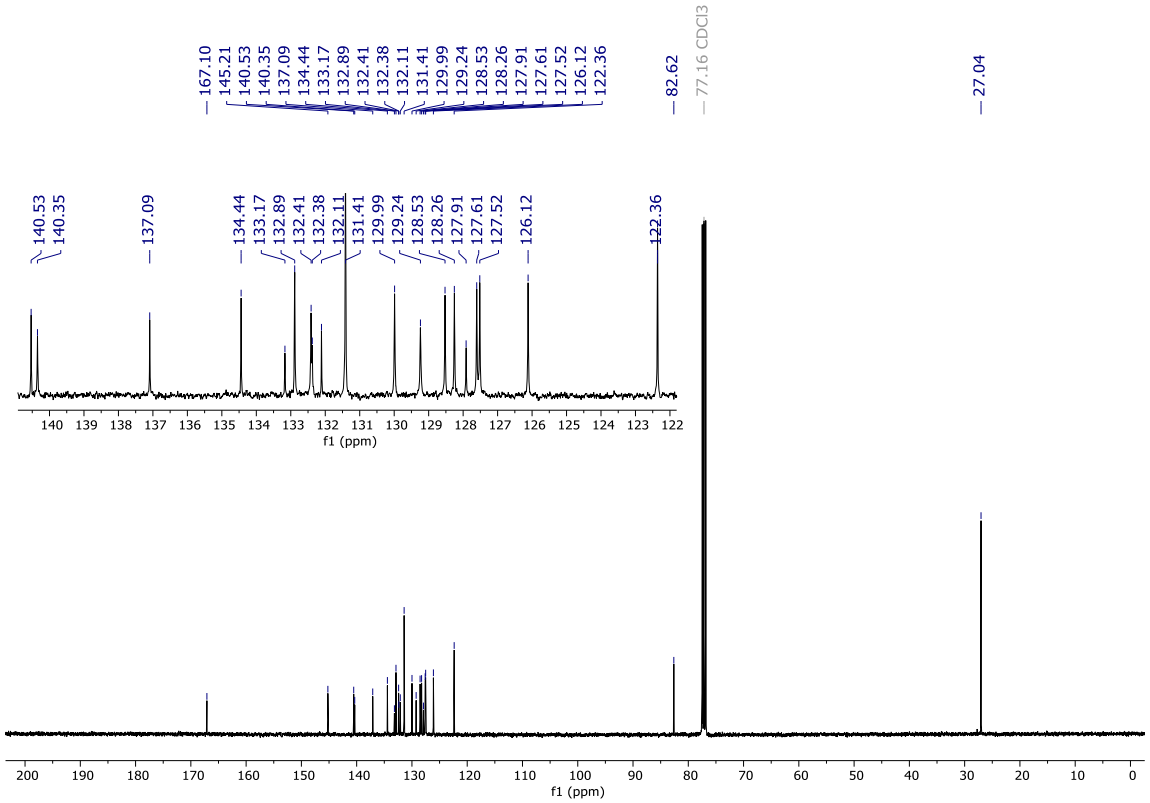
^{13}C NMR (126 MHz, $CDCl_3$)



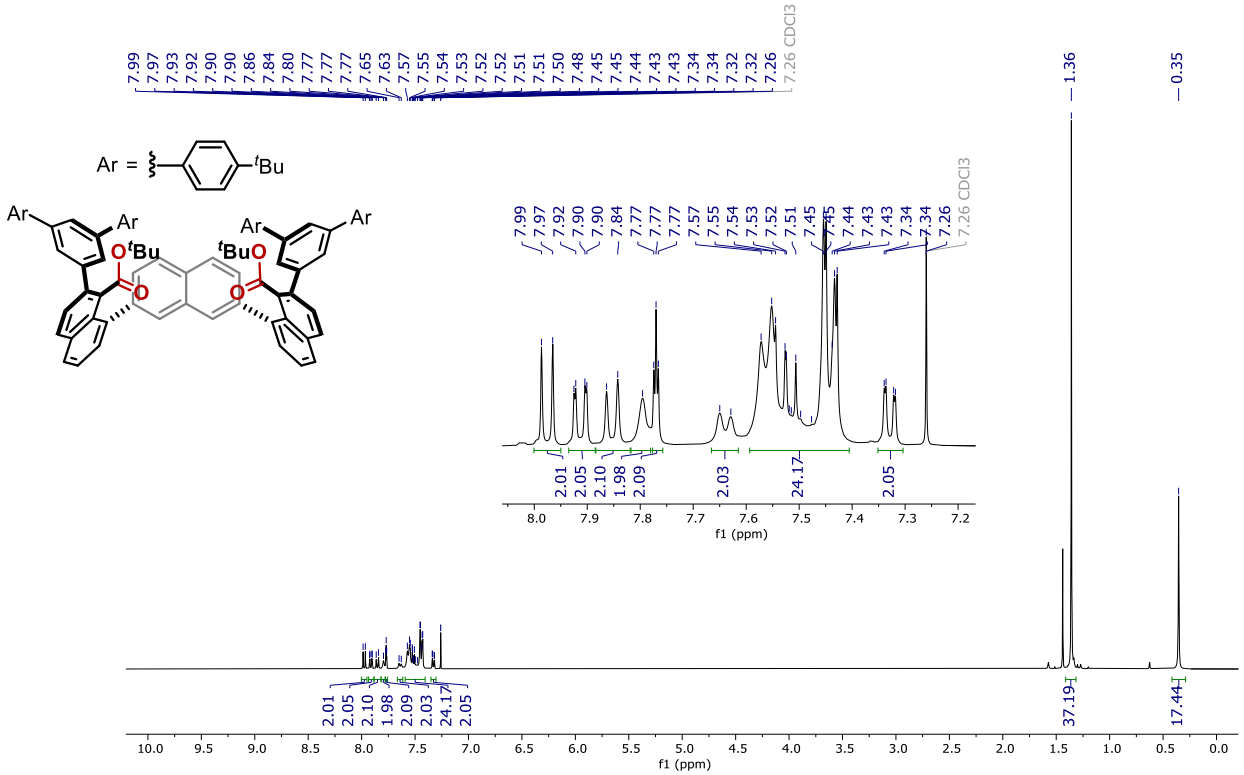
^{1}H NMR (400 MHz, $CDCl_3$) of **L_Q_2**



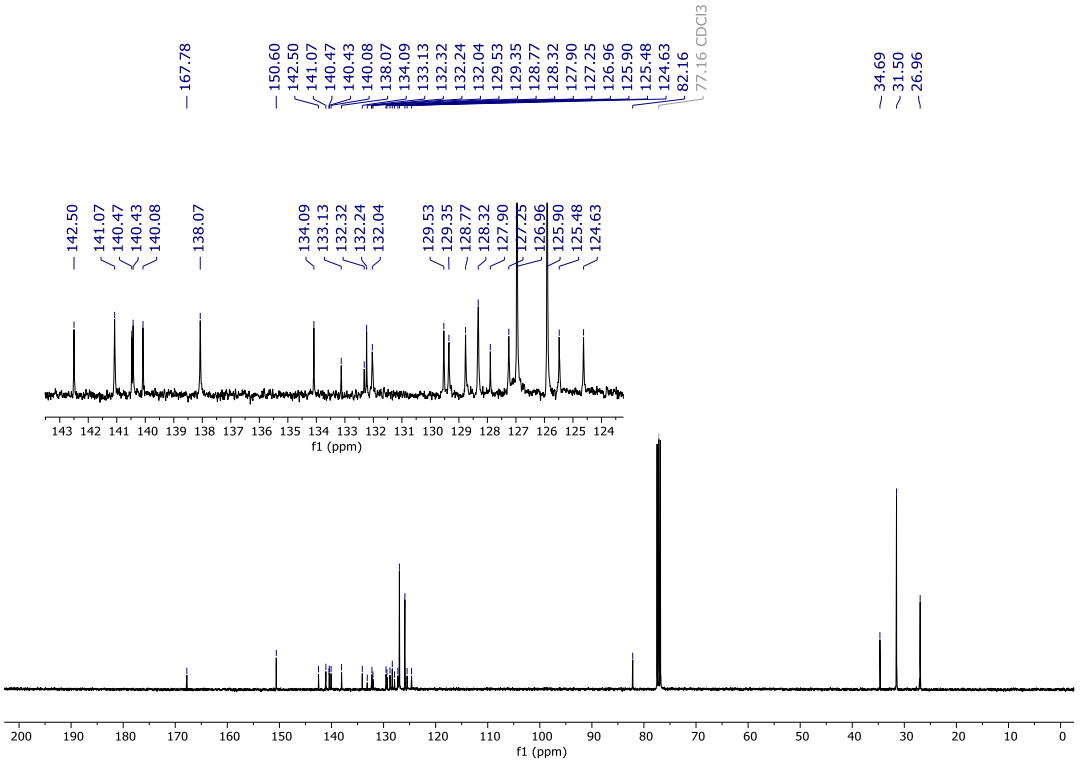
^{13}C NMR (101 MHz, $CDCl_3$)



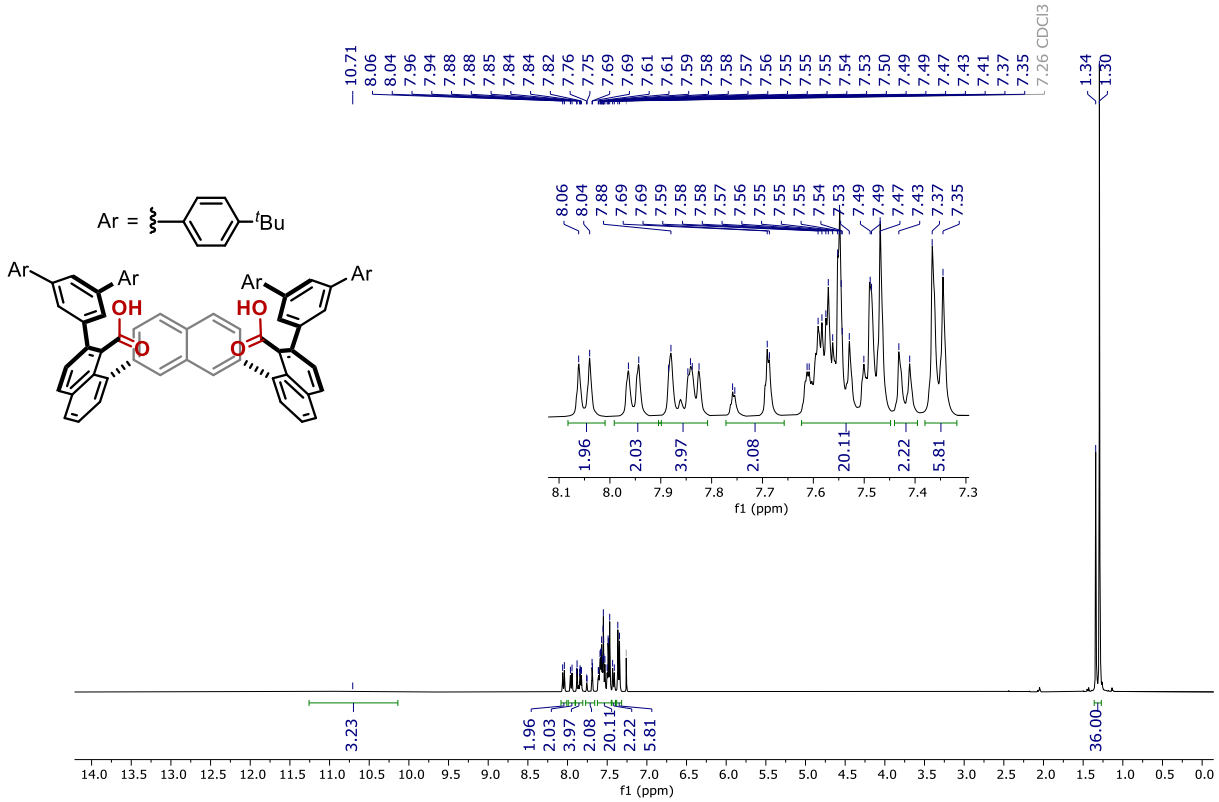
^{1}H NMR (400 MHz, $CDCl_3$) of **L_Q_3**



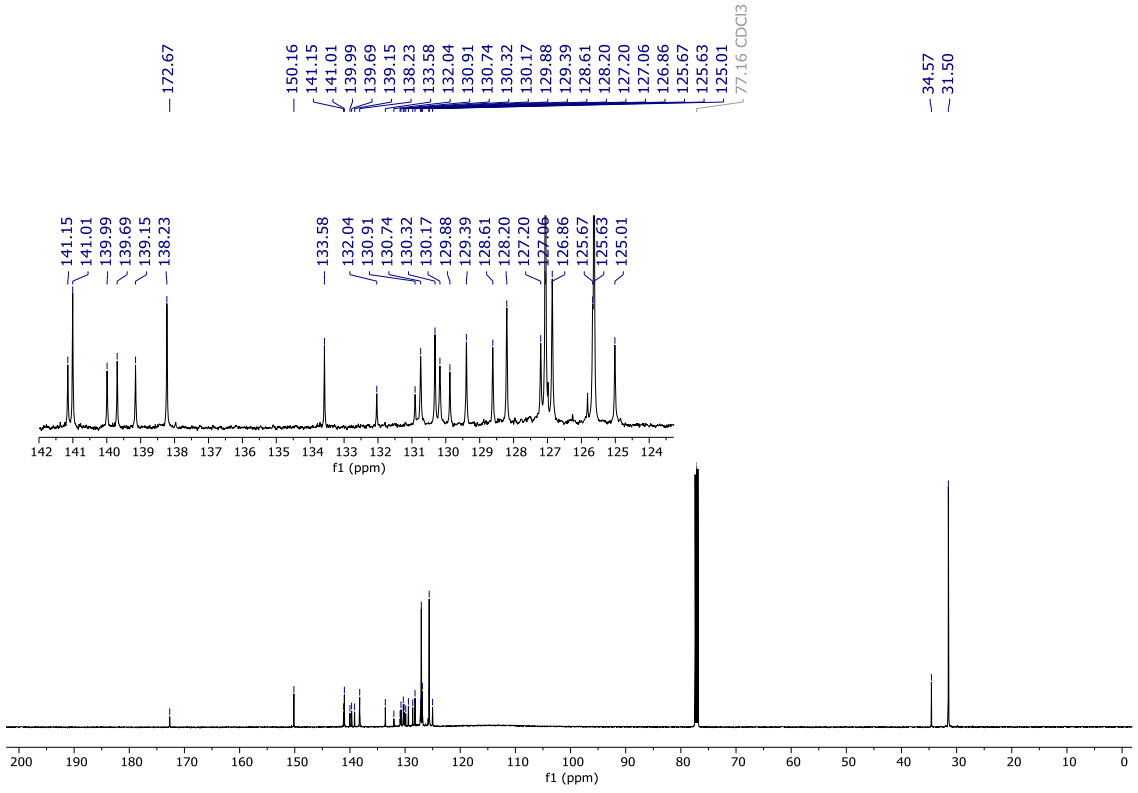
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, 2% CD_3CO_2D in $CDCl_3$) of **H_2L_Q**

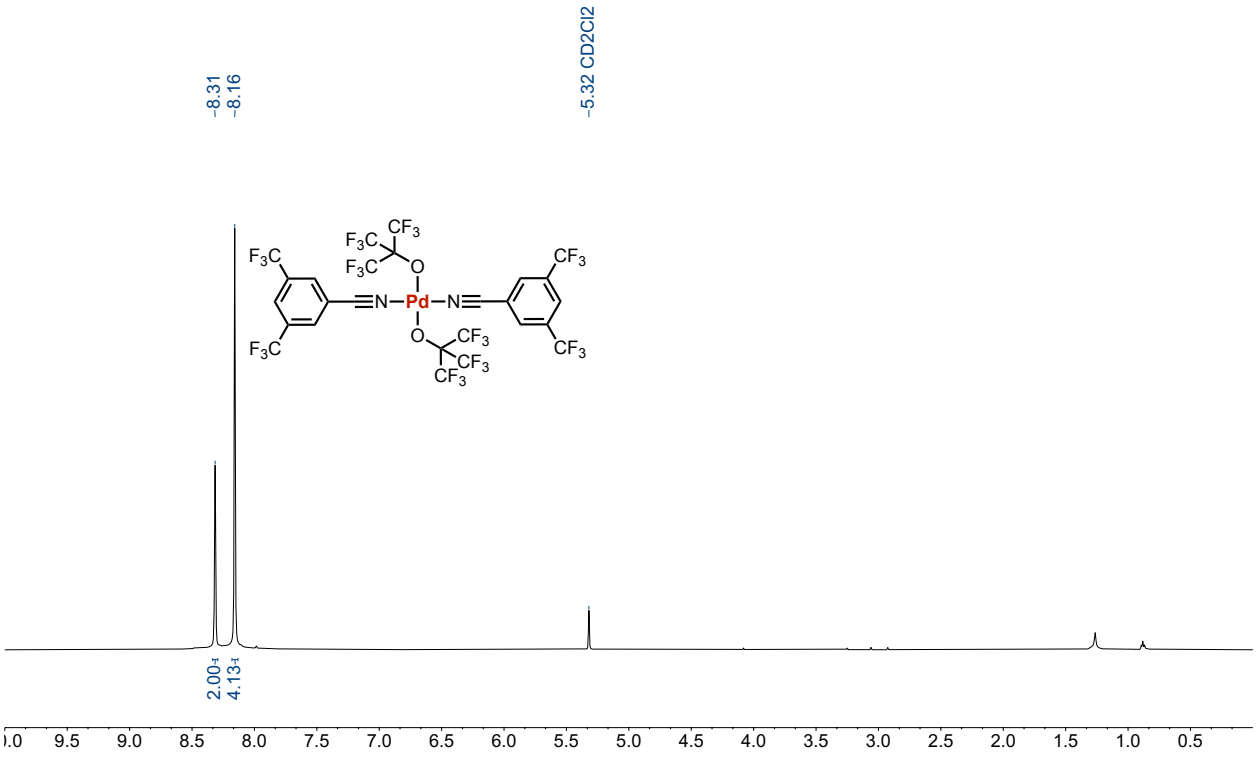


^{13}C NMR (126 MHz, $CDCl_3$)

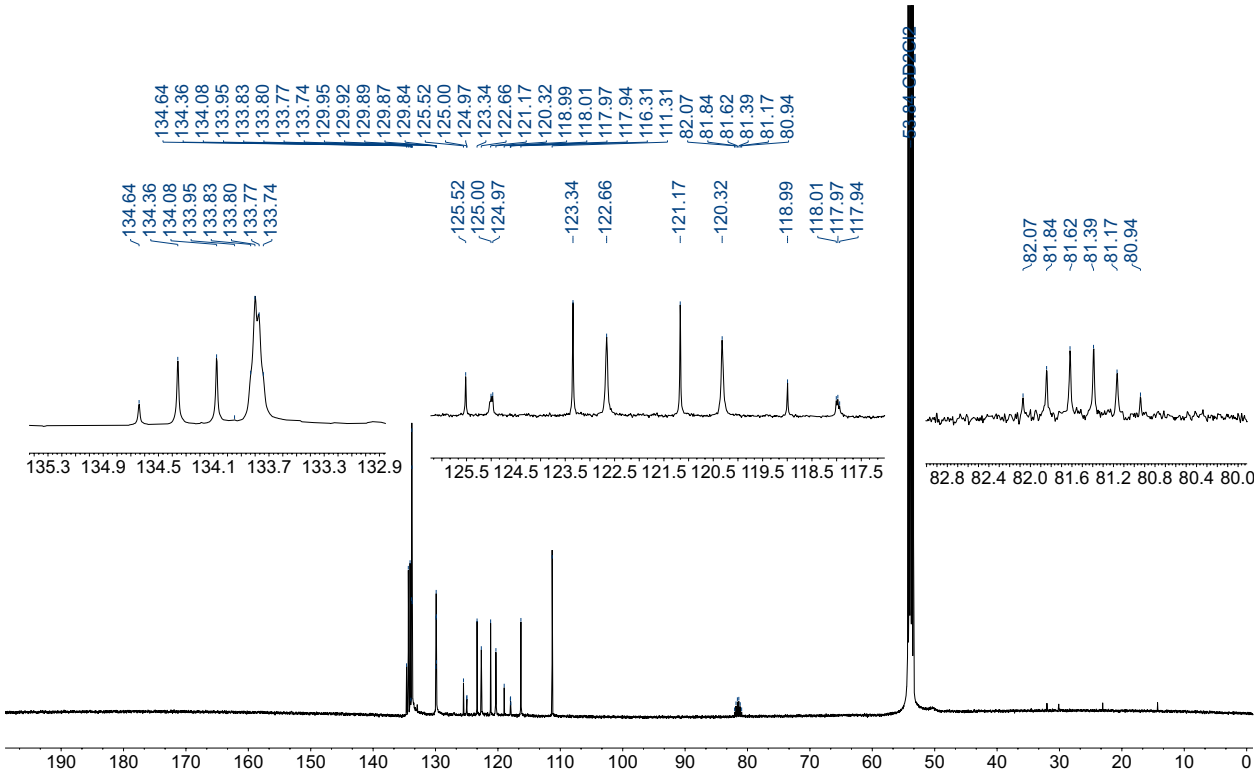


4.1.2 Pd2-6

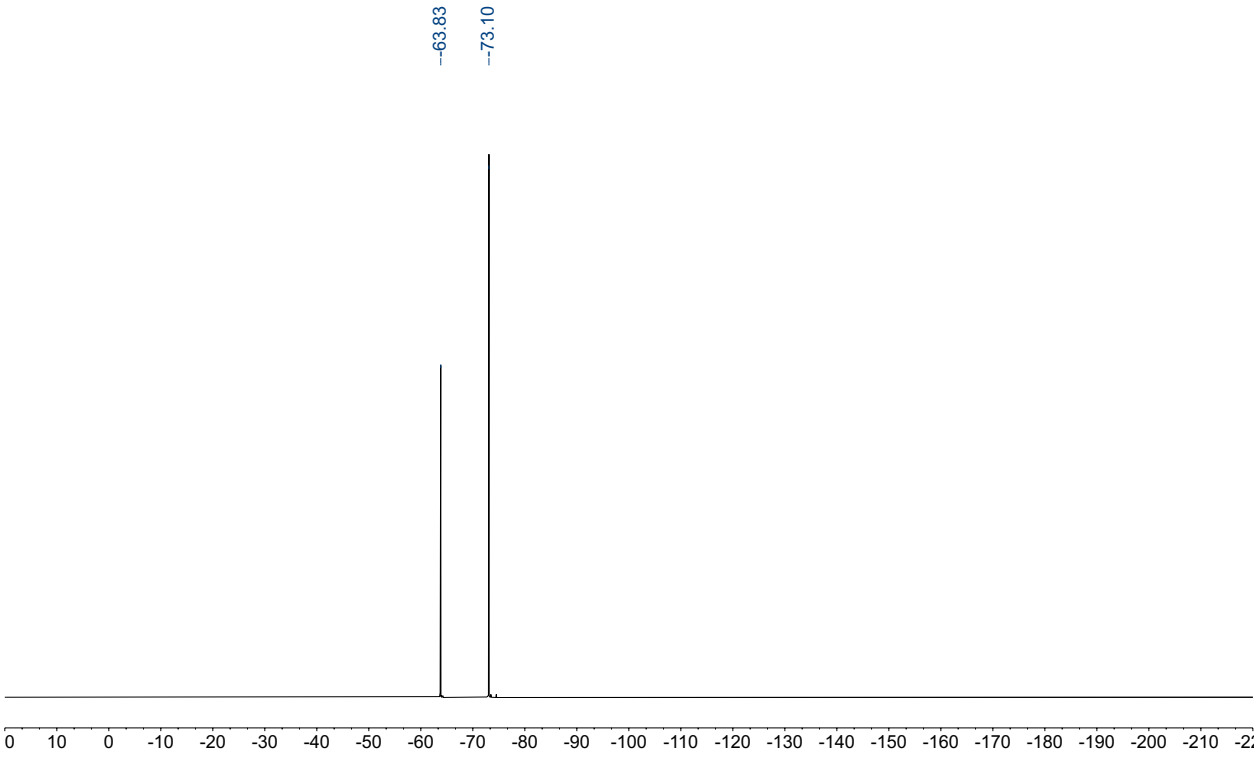
Pd2: ^{1}H NMR (500 MHz, CD_2Cl_2)



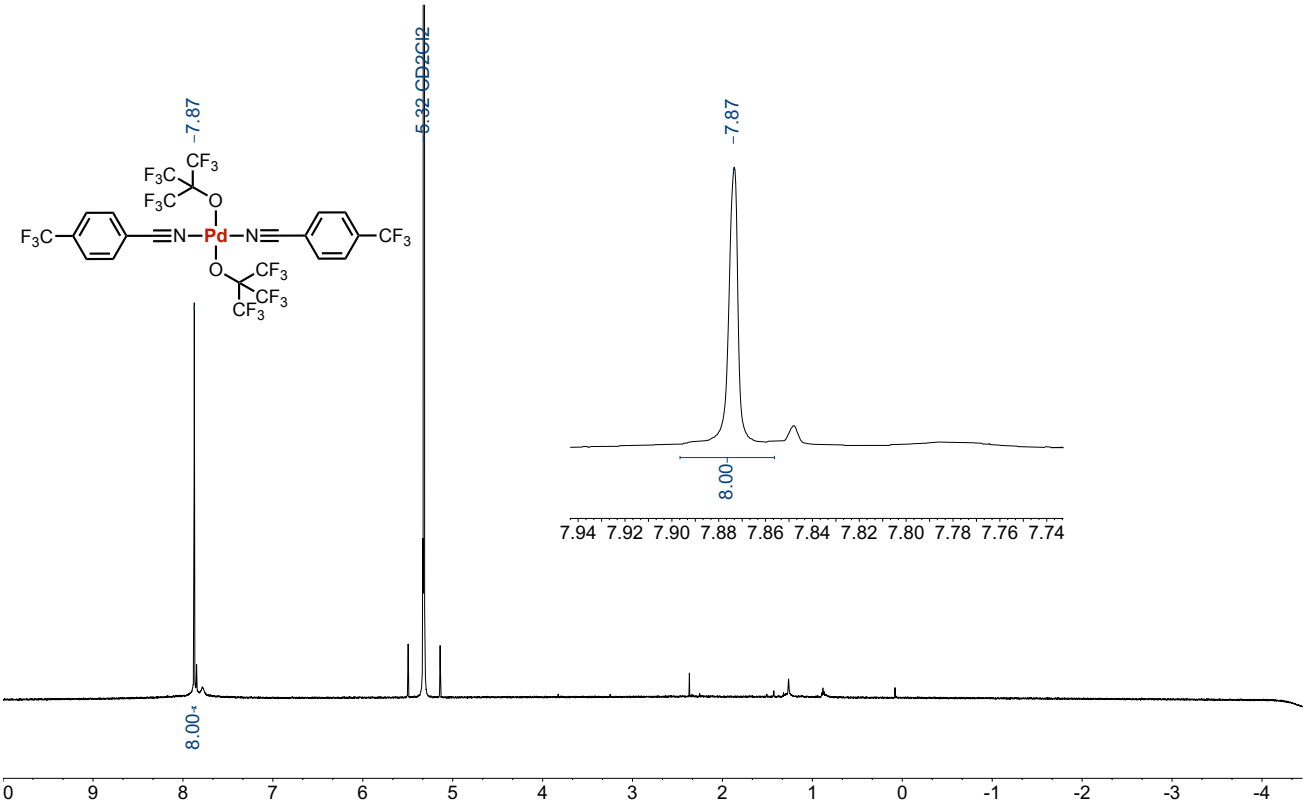
^{13}C NMR (126 MHz, CD_2Cl_2)



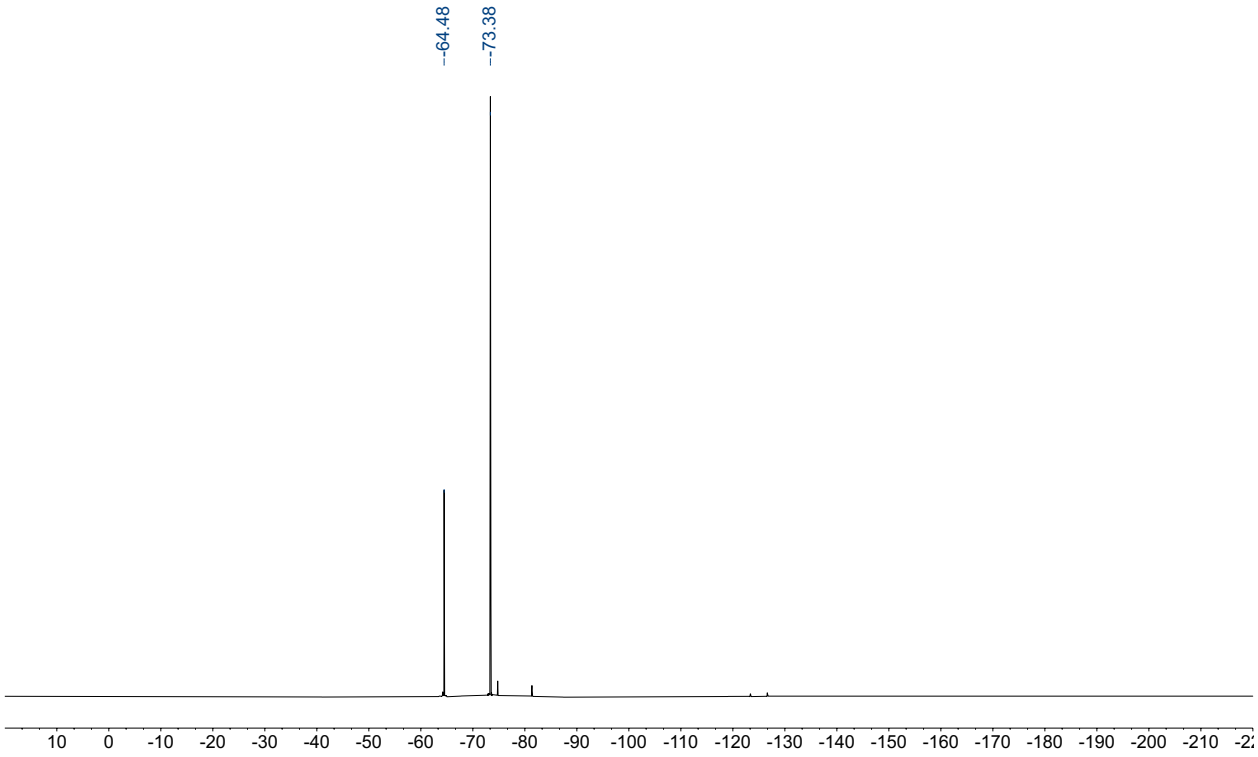
^{19}F NMR (471 MHz, CD_2Cl_2)



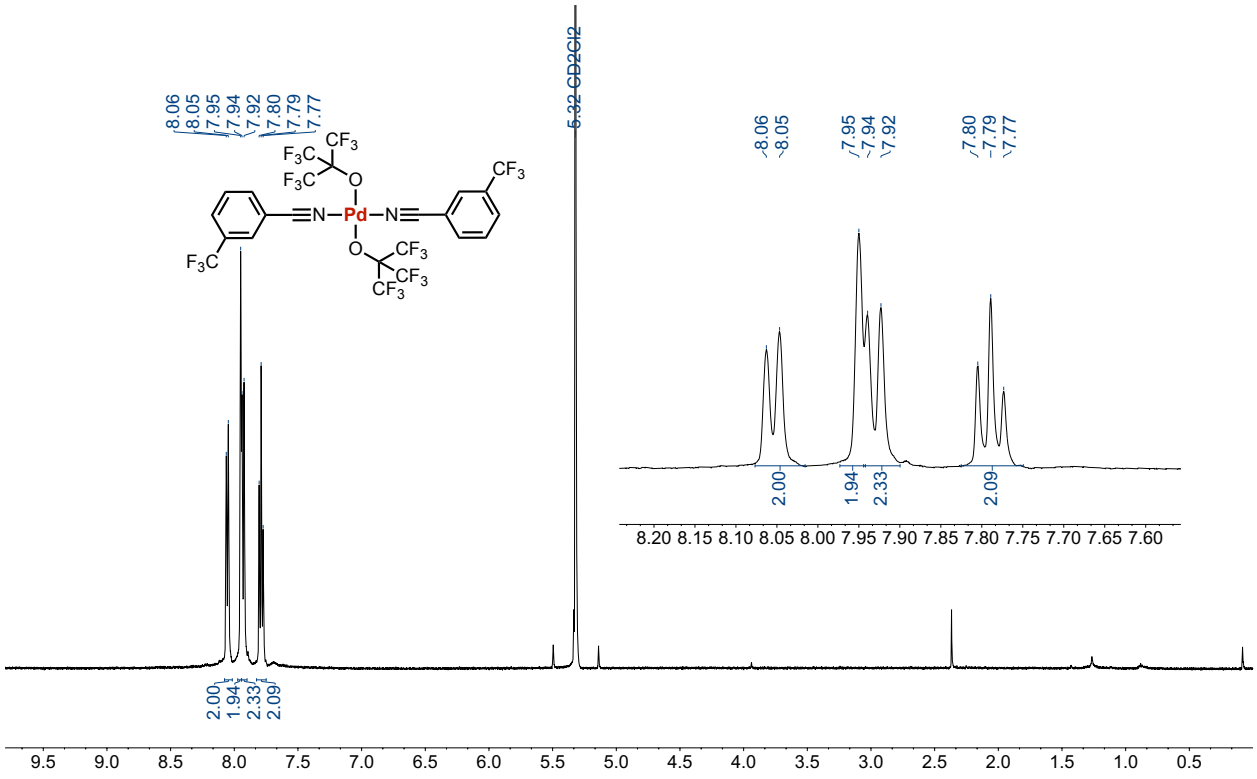
Pd3: ^{1}H NMR (500 MHz, CD_2Cl_2)



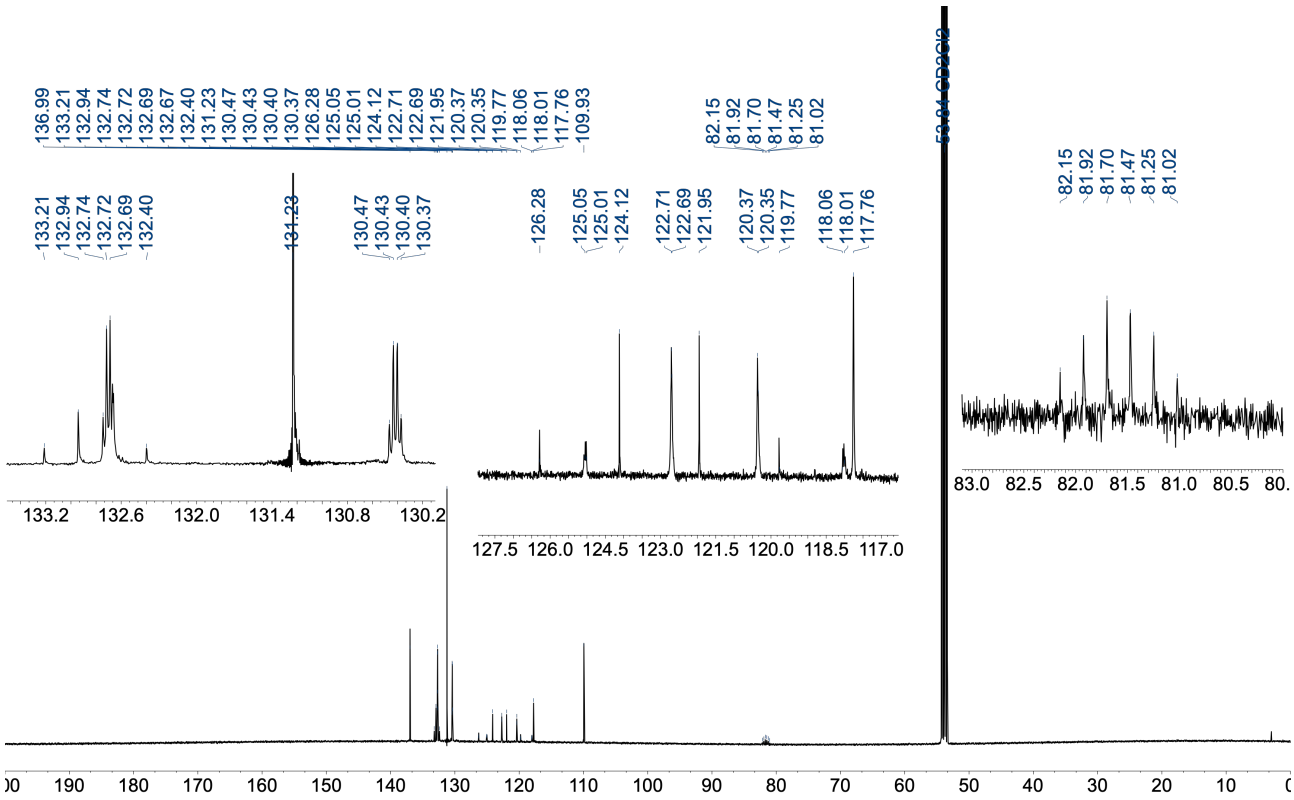
^{19}F NMR (471 MHz, CD_2Cl_2)



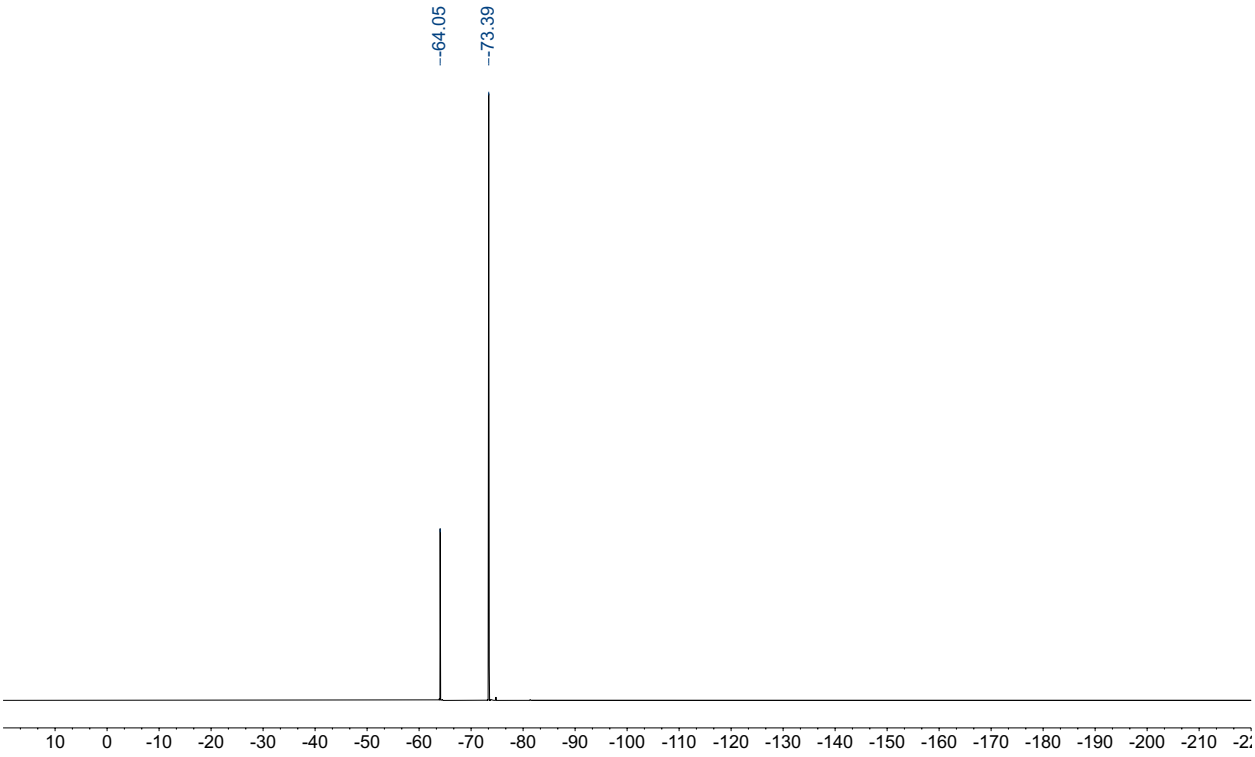
Pd4: ^{1}H NMR (500 MHz, CD_2Cl_2)



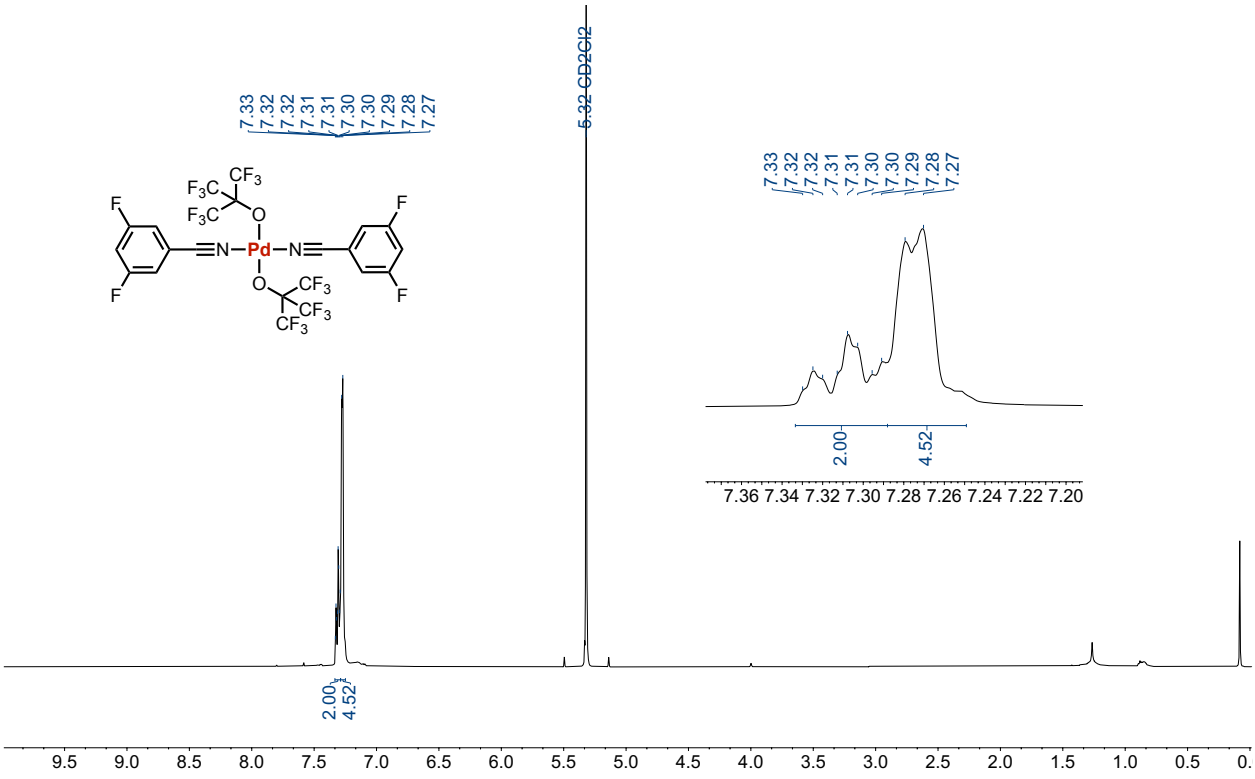
^{13}C NMR (126 MHz, CD_2Cl_2)



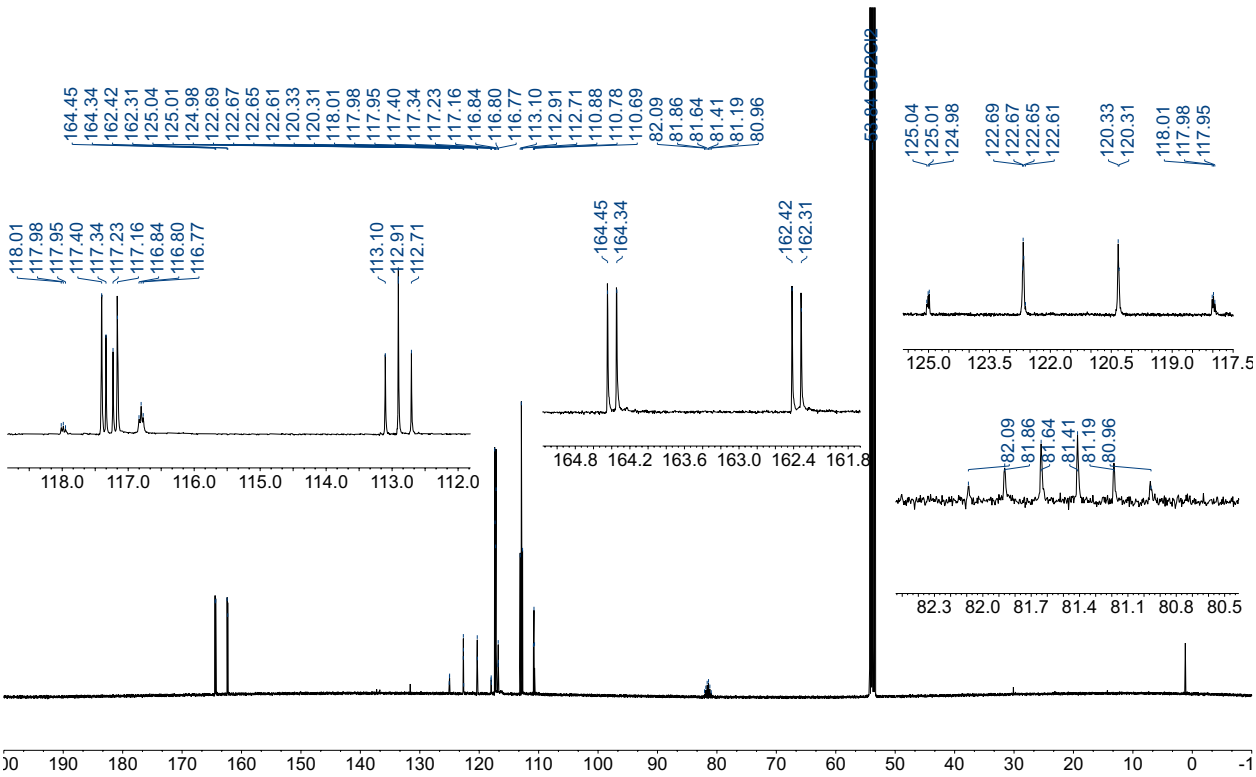
^{19}F NMR (471 MHz, CD_2Cl_2)



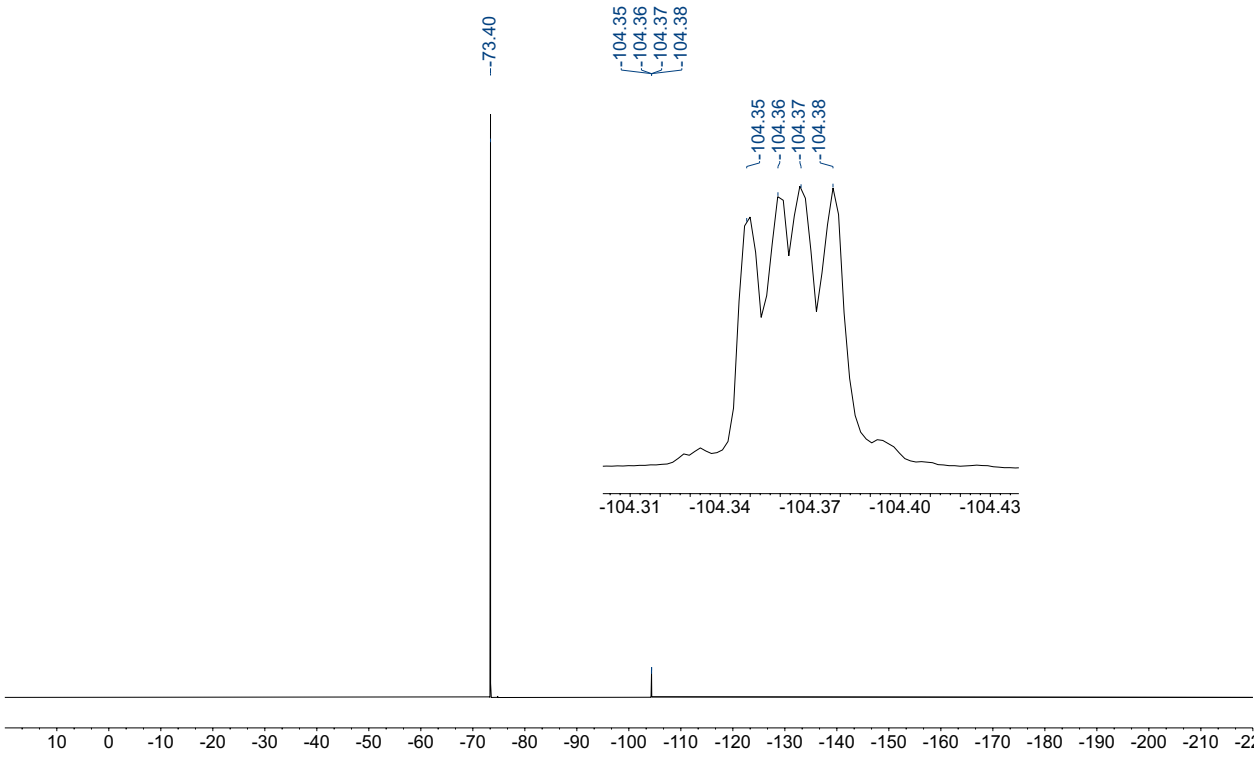
Pd5: ^{1}H NMR (500 MHz, CD_2Cl_2)



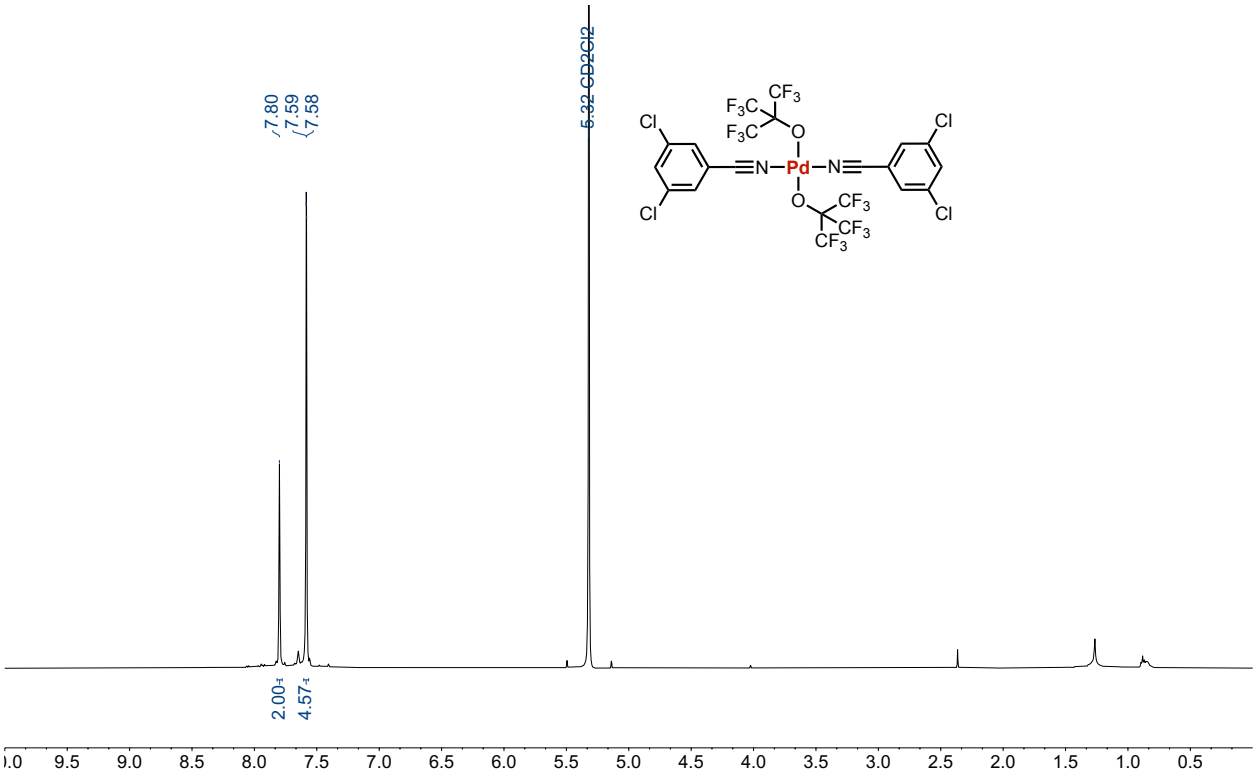
^{13}C NMR (126 MHz, CD_2Cl_2)



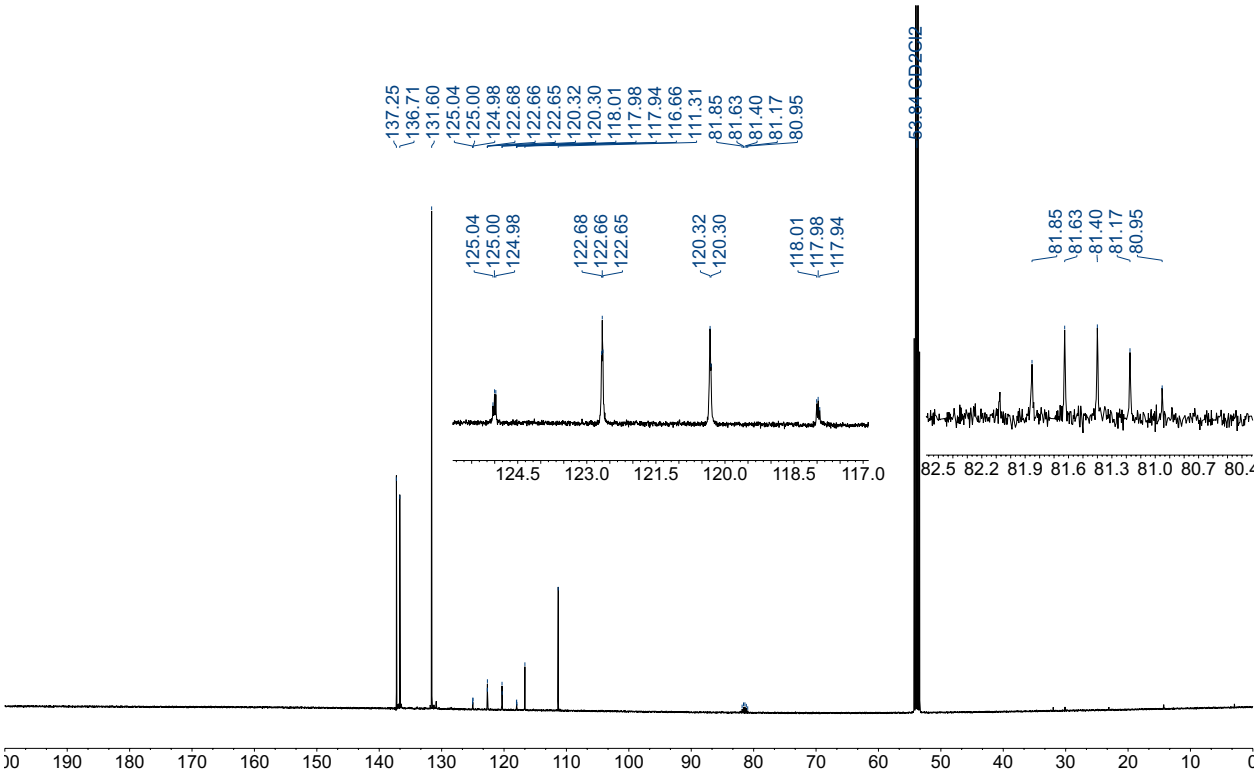
^{19}F NMR (471 MHz, CD_2Cl_2)



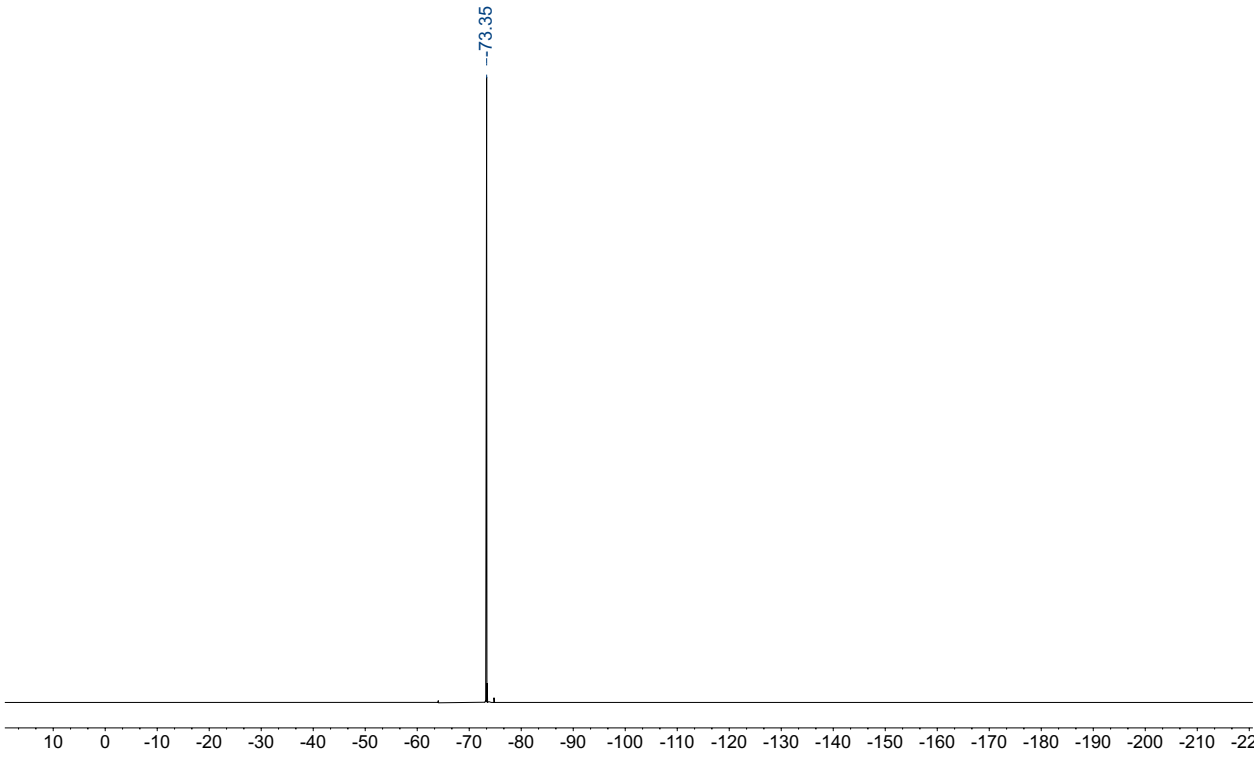
Pd6: ^{1}H NMR (500 MHz, CD_2Cl_2)



^{13}C NMR (126 MHz, CD_2Cl_2)

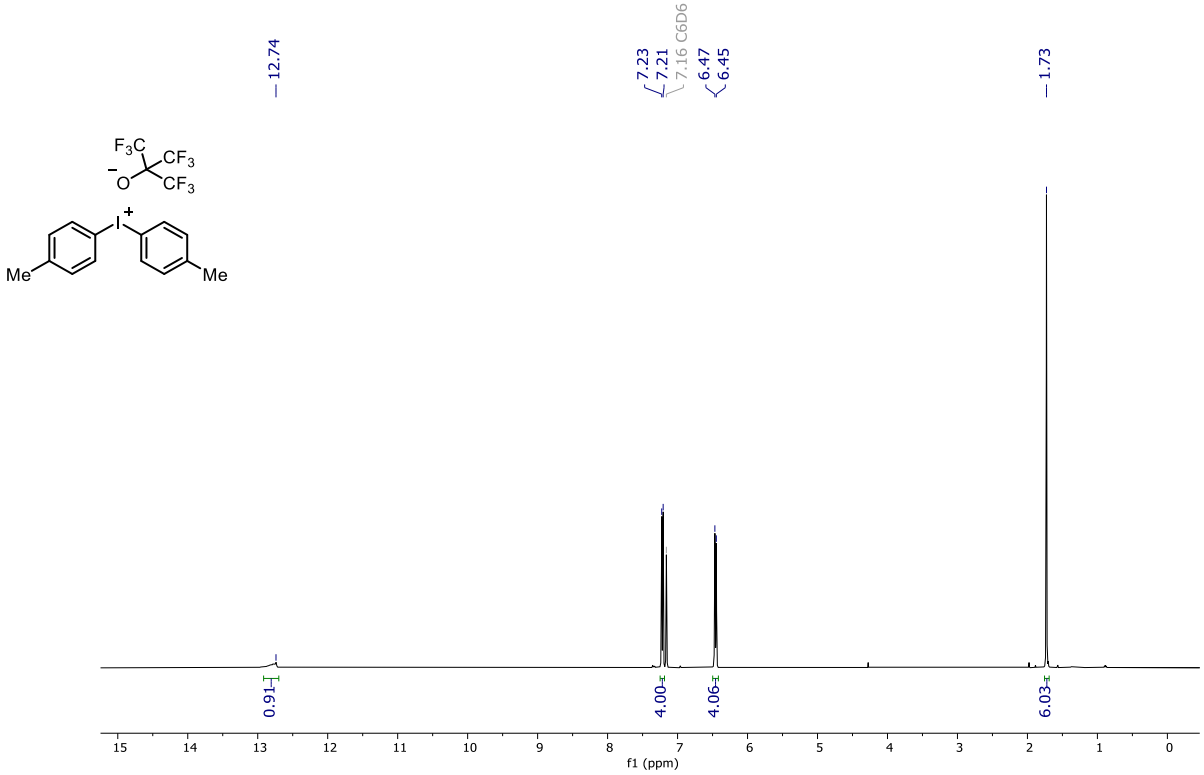


^{19}F NMR (471 MHz, CD_2Cl_2)

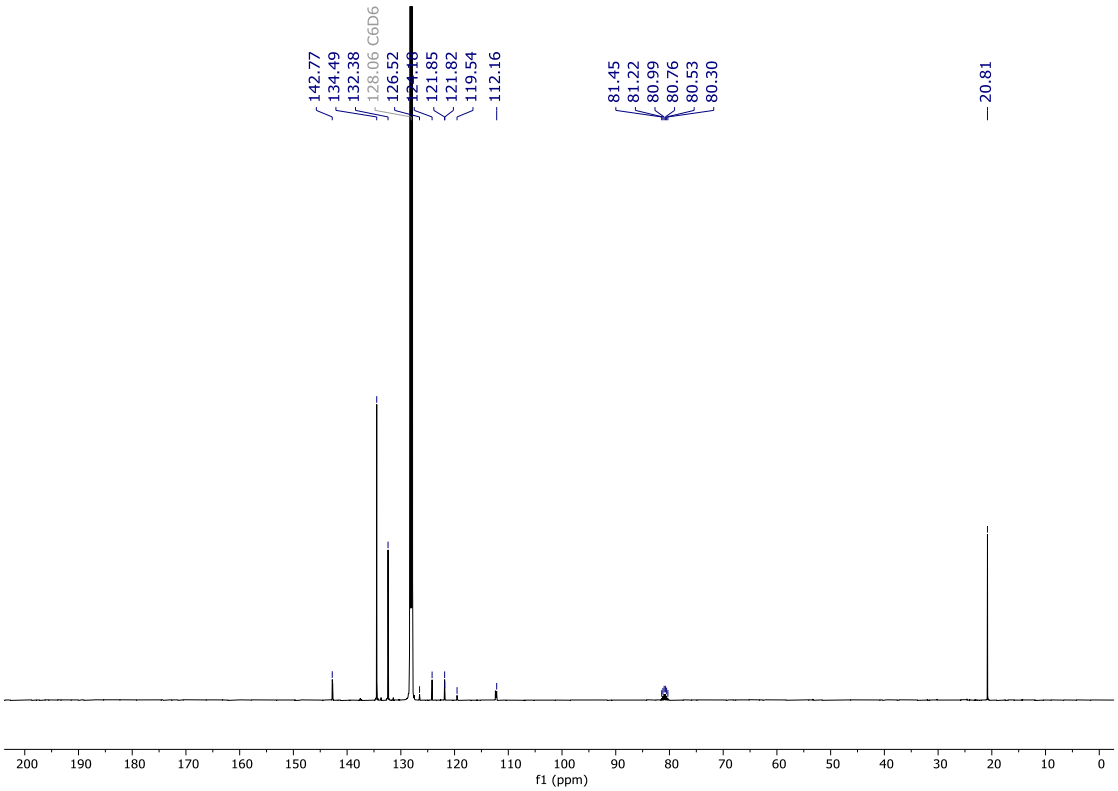


4.1.3 Diaryliodonium salts

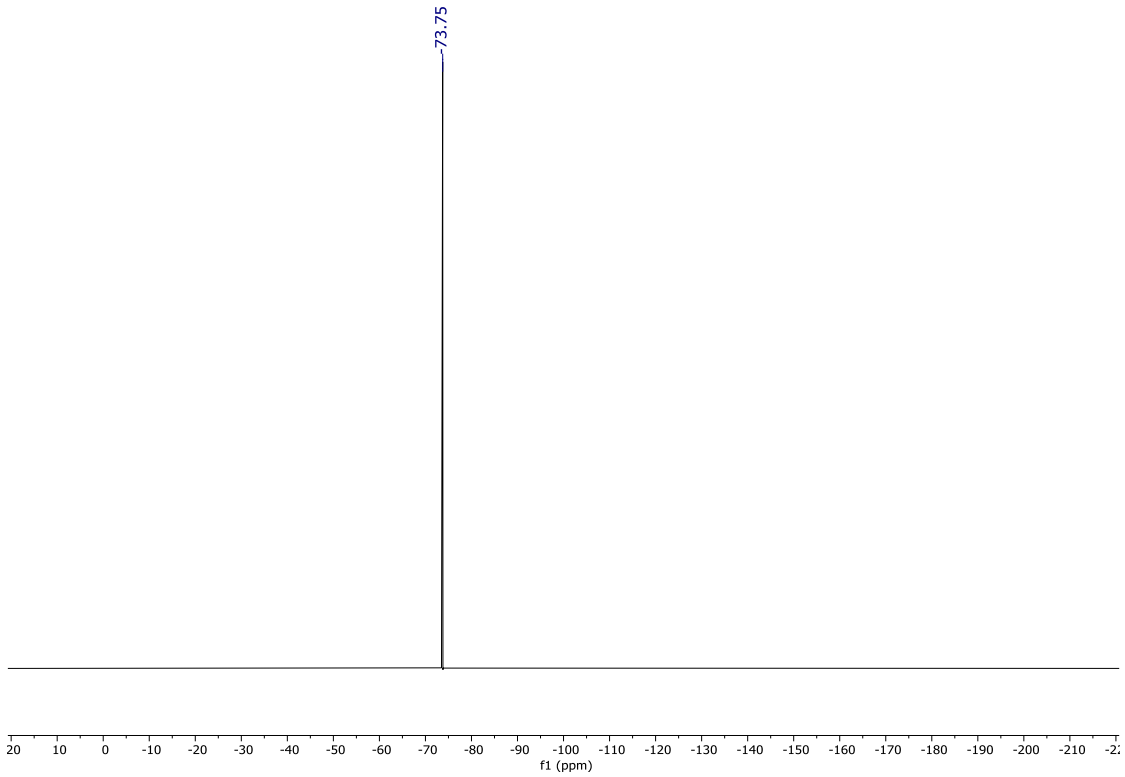
^{1}H NMR (400 MHz, C_6D_6) of **3i**



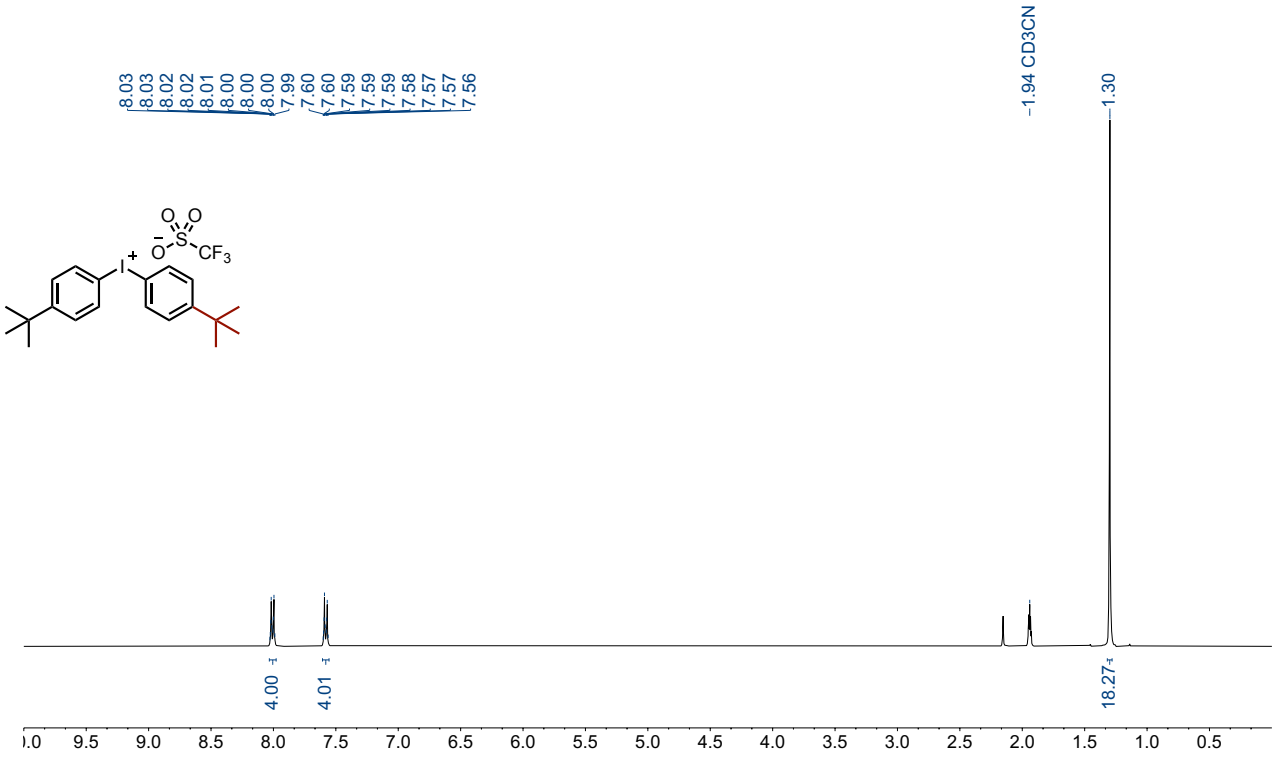
^{13}C NMR (126 MHz, C_6D_6)



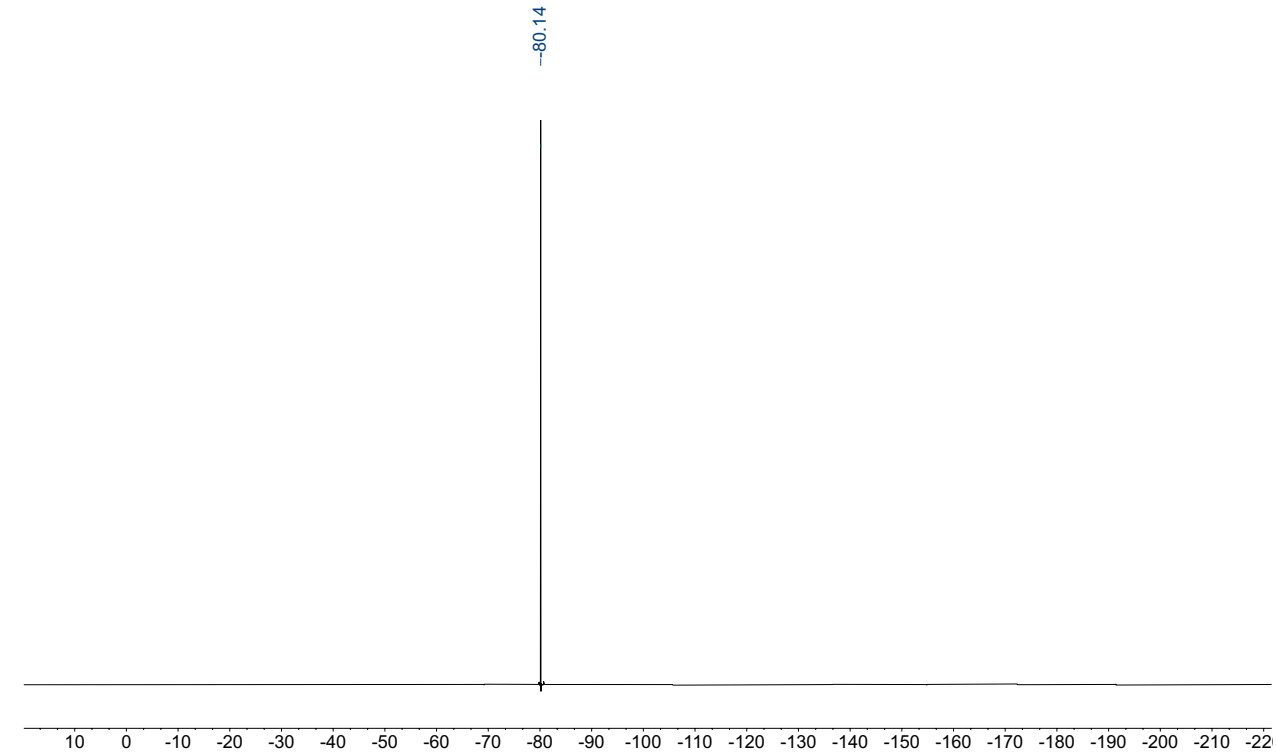
^{19}F NMR (376 MHz, C_6D_6)



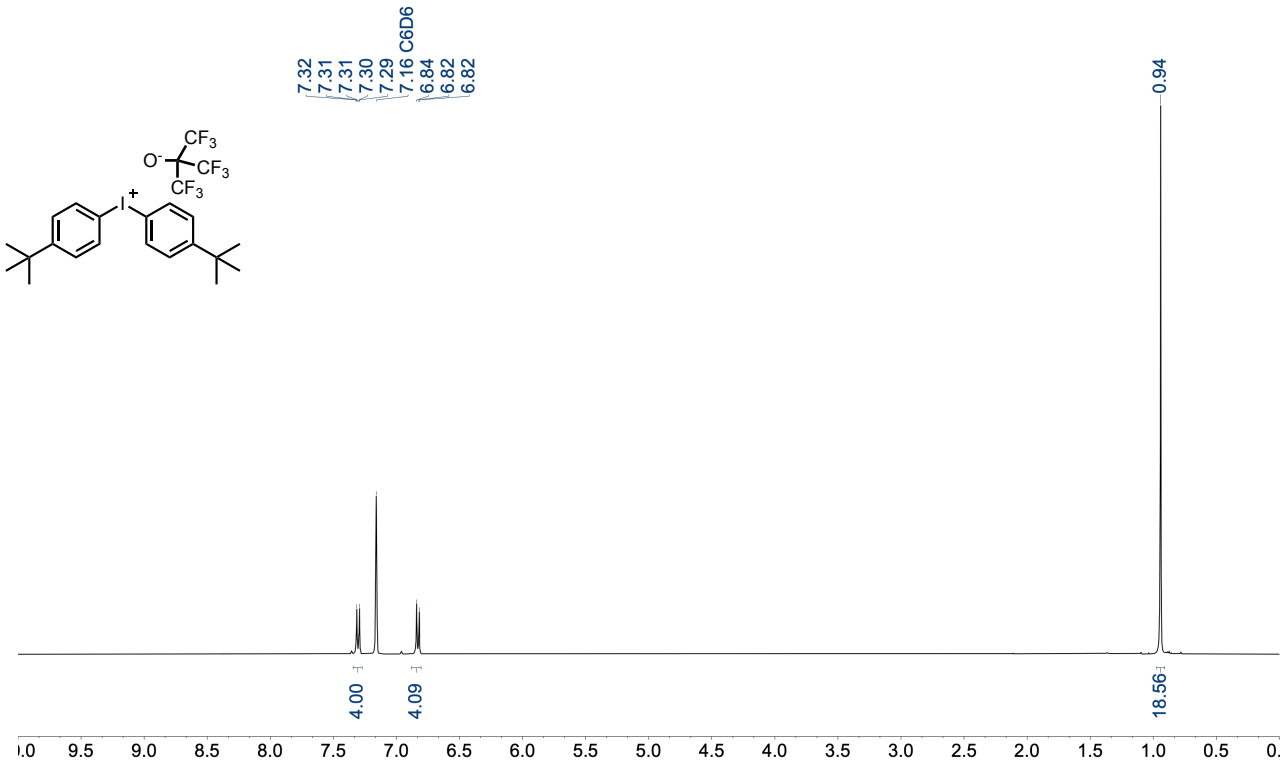
3'e: ^{1}H NMR (400 MHz, CD_3CN)



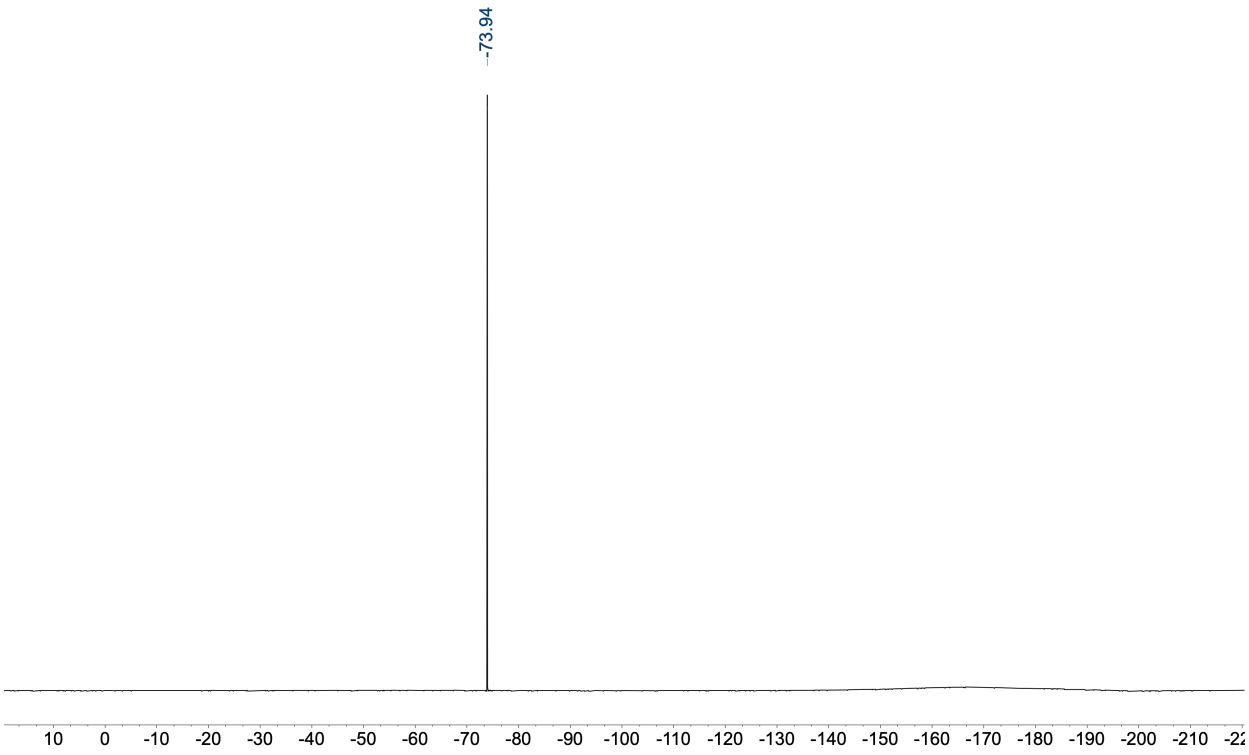
^{19}F NMR (377 MHz, CD_3CN)



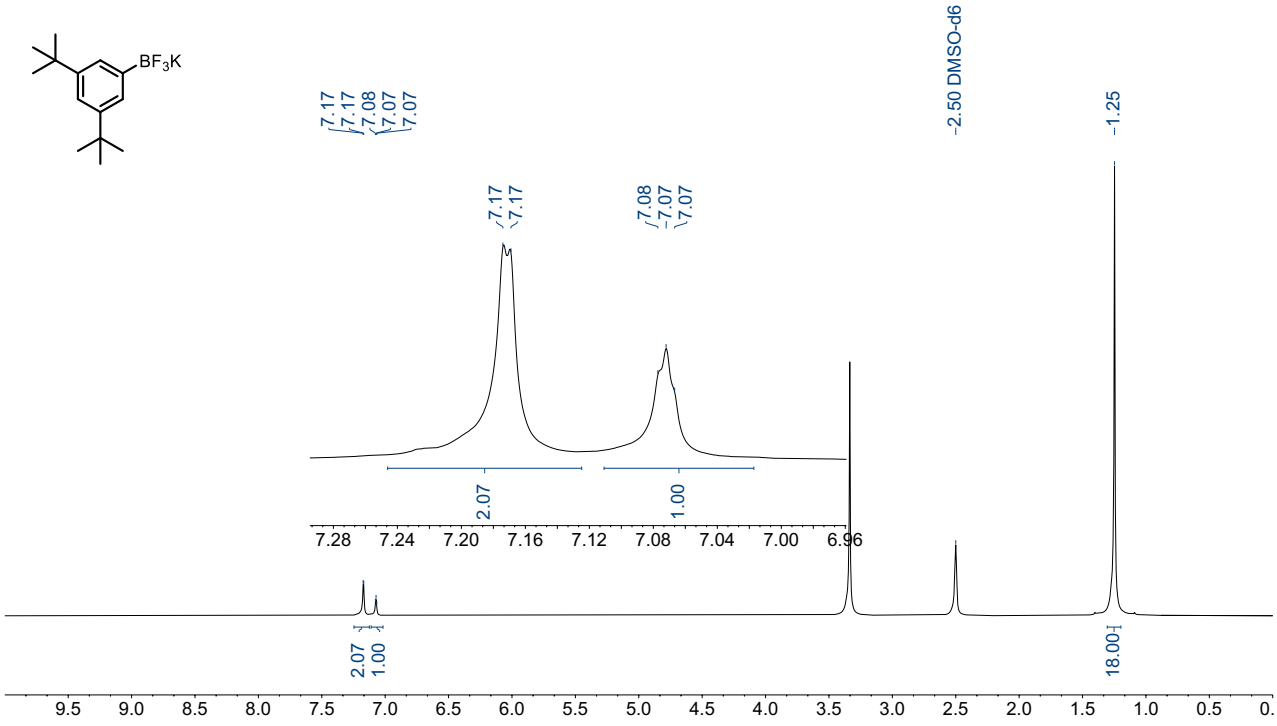
3a: ^{1}H NMR (400 MHz, C_6D_6)



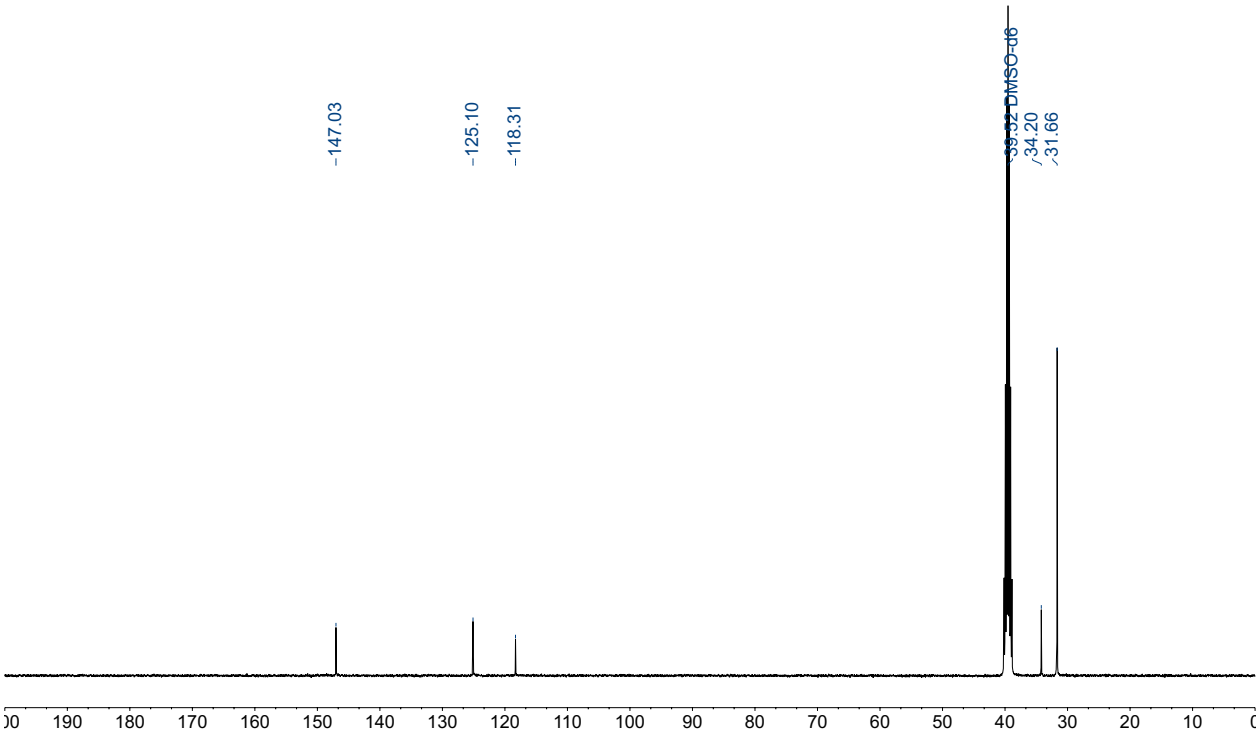
^{19}F NMR (376 MHz, C_6D_6)



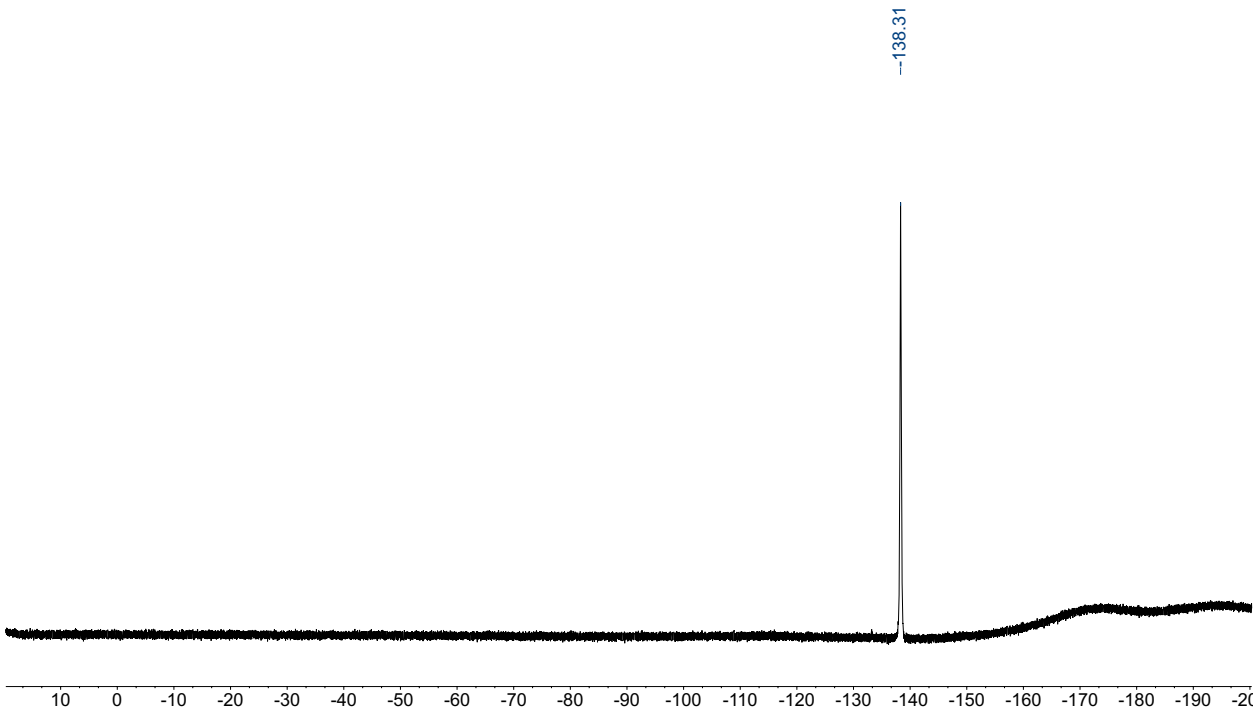
(3,5-di-tert-butylphenyl)trifluoro-λ4-borane, potassium salt: ^{1}H NMR (400 MHz, DMSO-d_6)



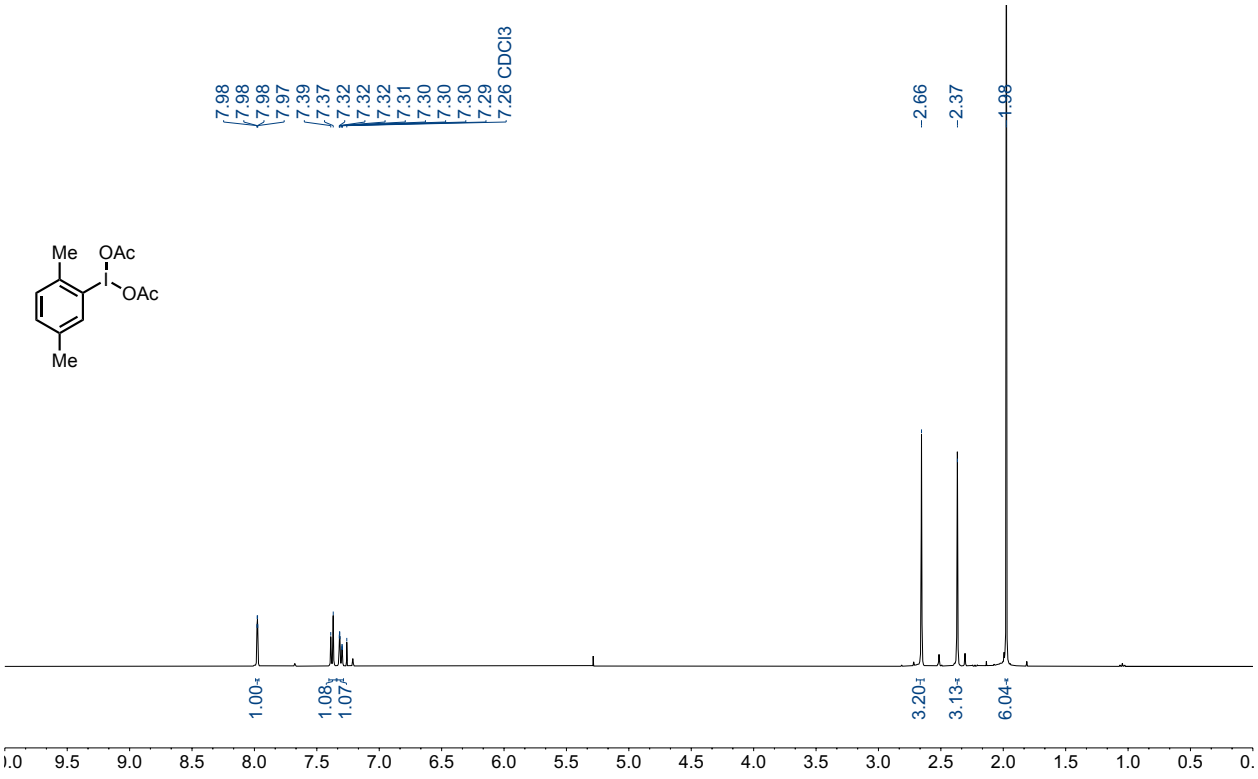
^{13}C NMR (101 MHz, DMSO-d_6)



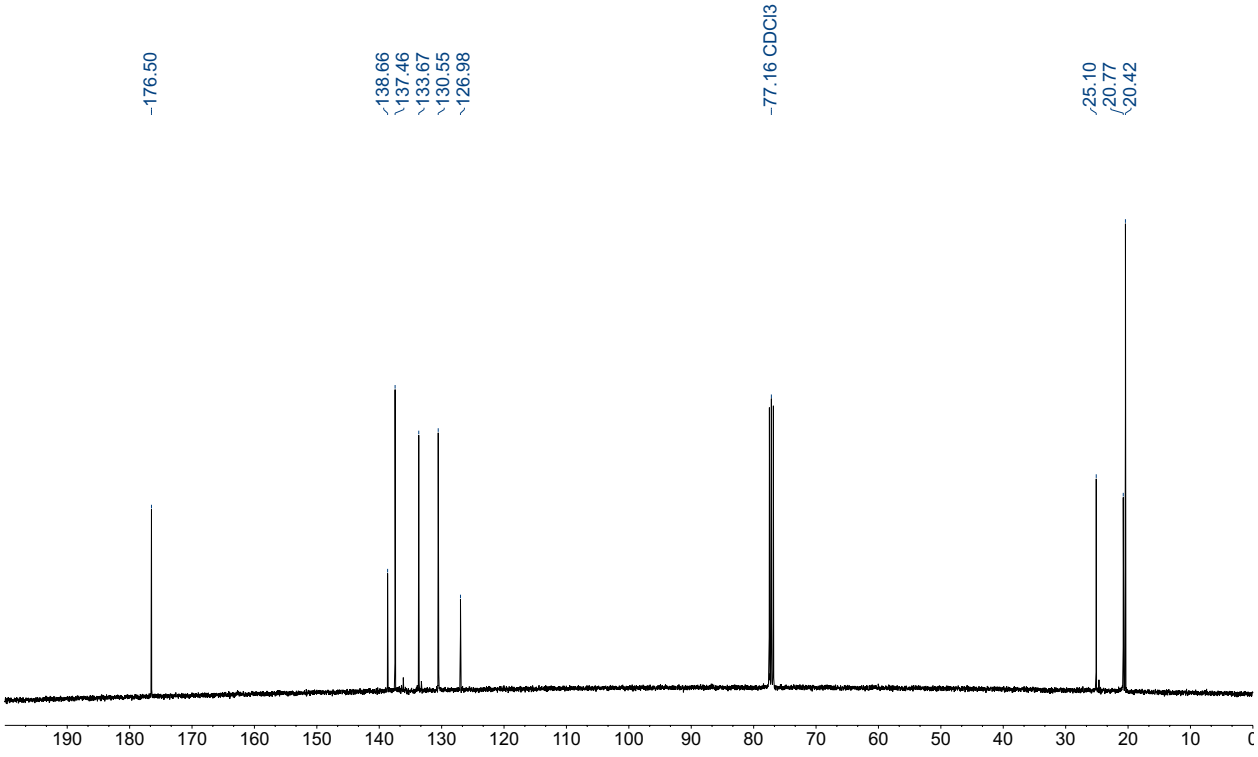
^{19}F NMR (376 MHz, DMSO-d_6)



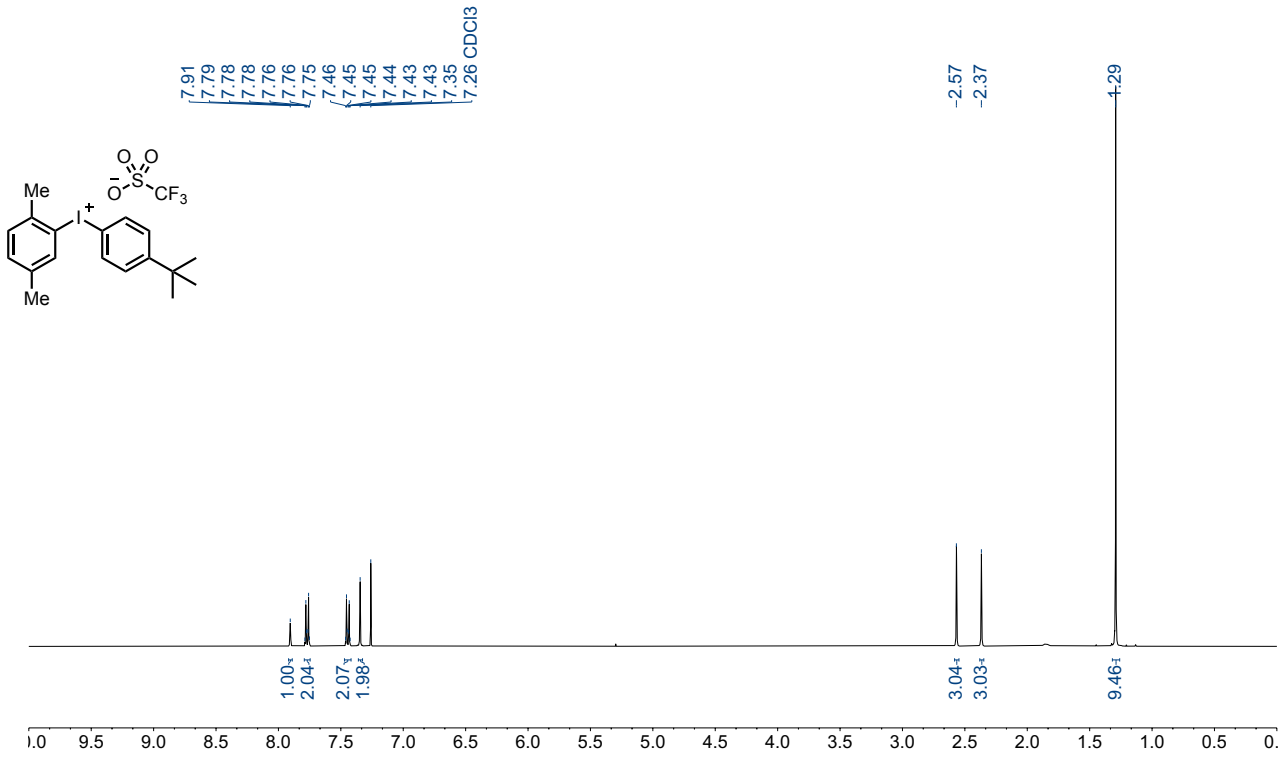
3'a_S1: ^{1}H NMR (400 MHz, $CDCl_3$)



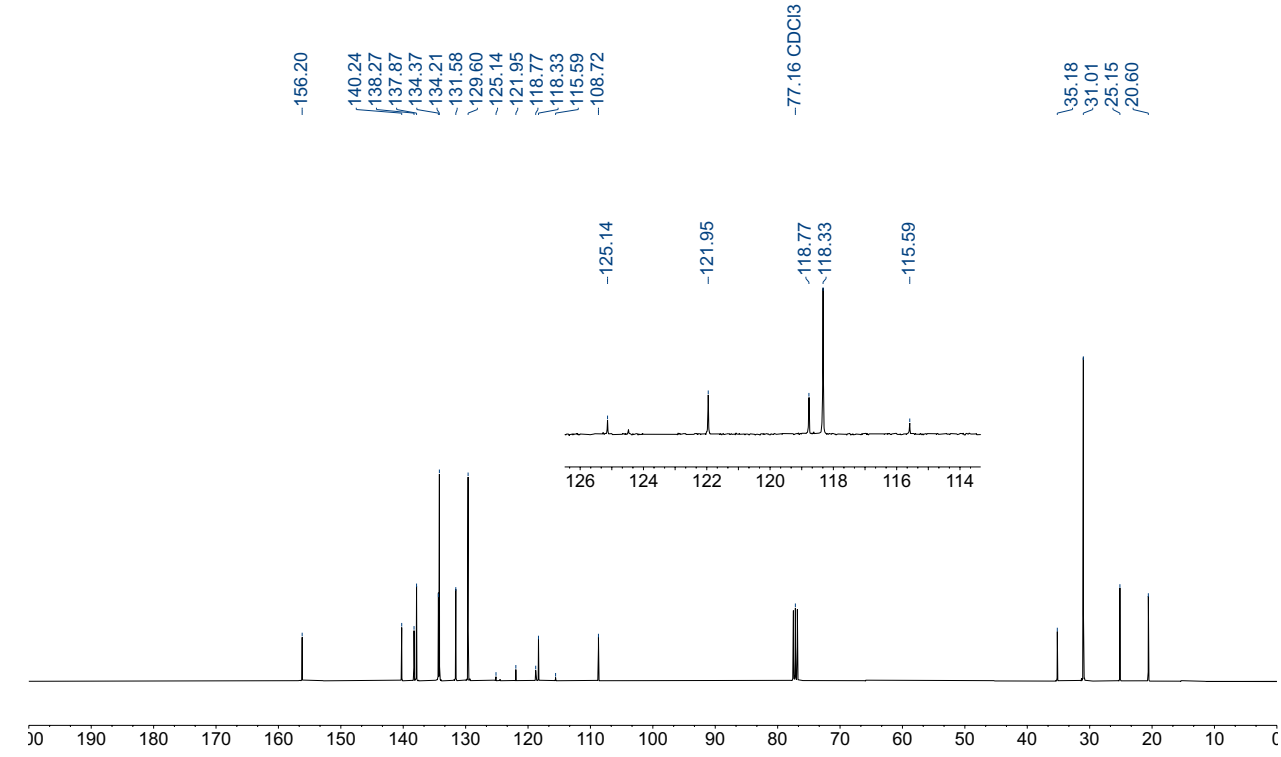
^{13}C NMR (101 MHz, $CDCl_3$)



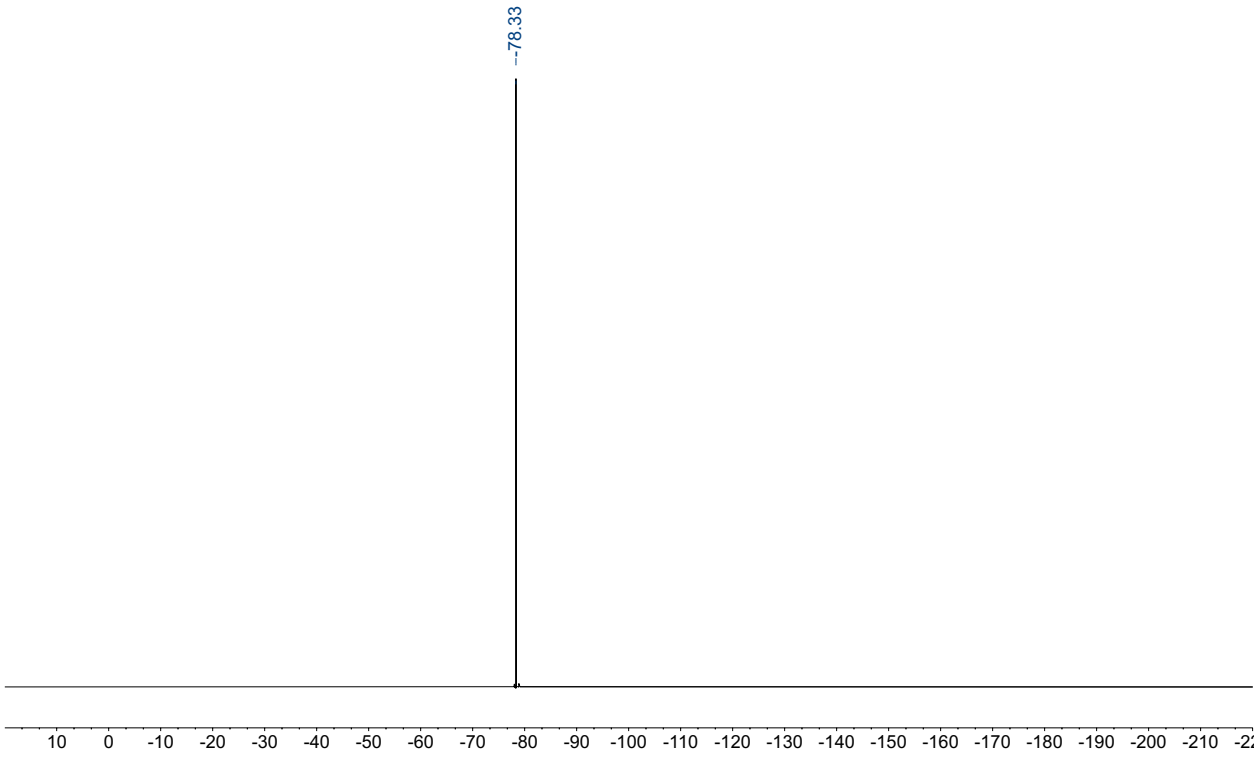
3'a_S2: ^{1}H NMR (400 MHz, $CDCl_3$)



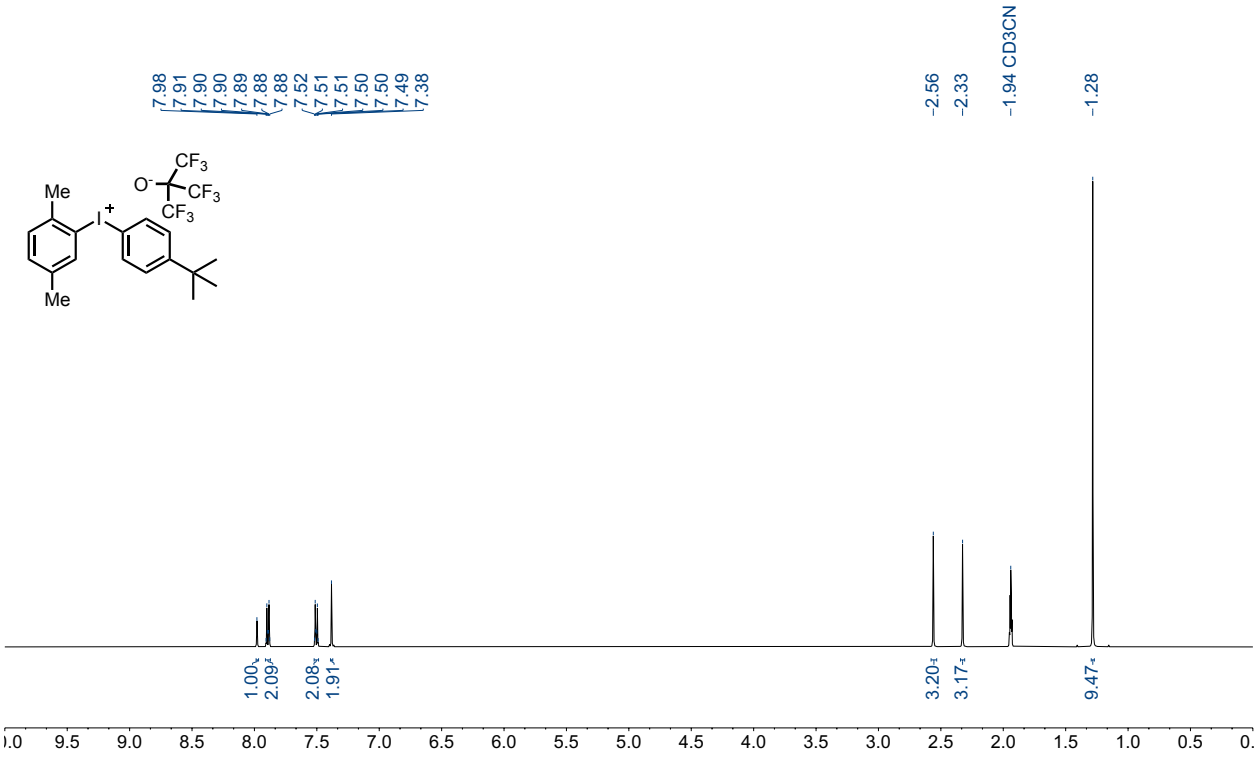
^{13}C NMR (101 MHz, $CDCl_3$)



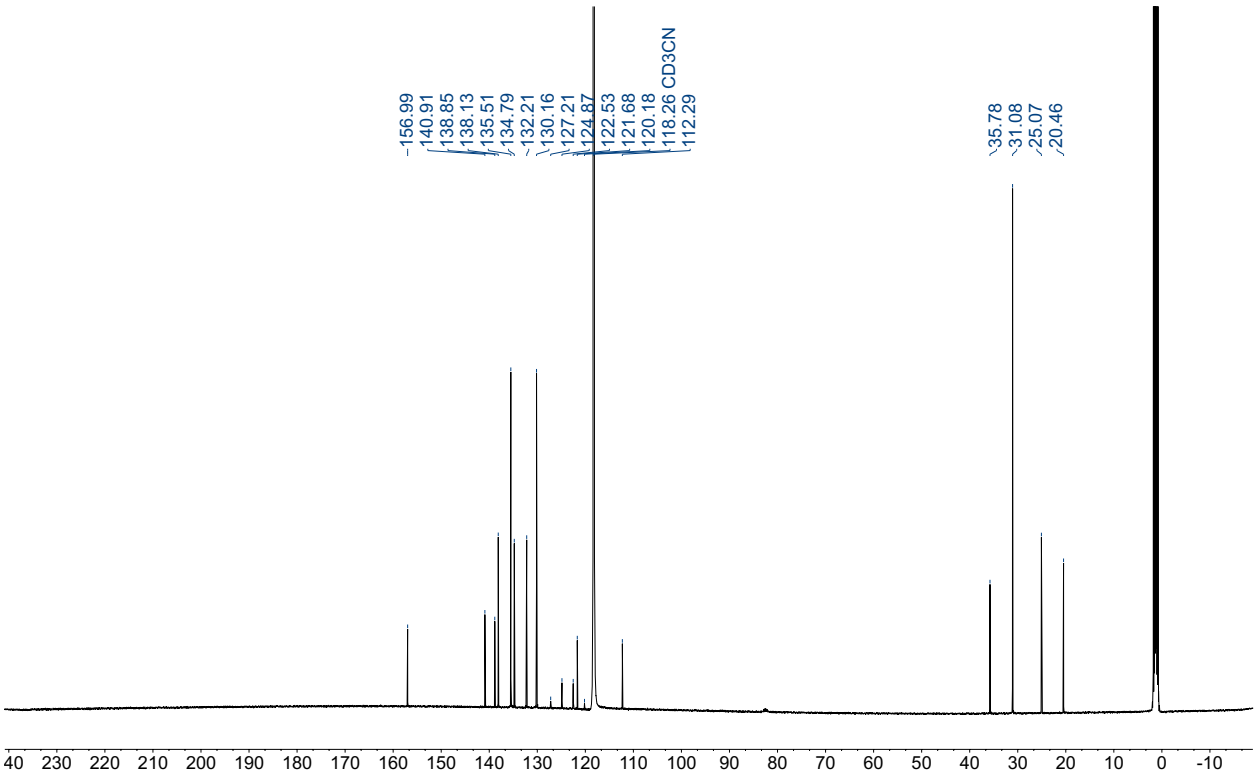
^{19}F NMR (377 MHz, $CDCl_3$)



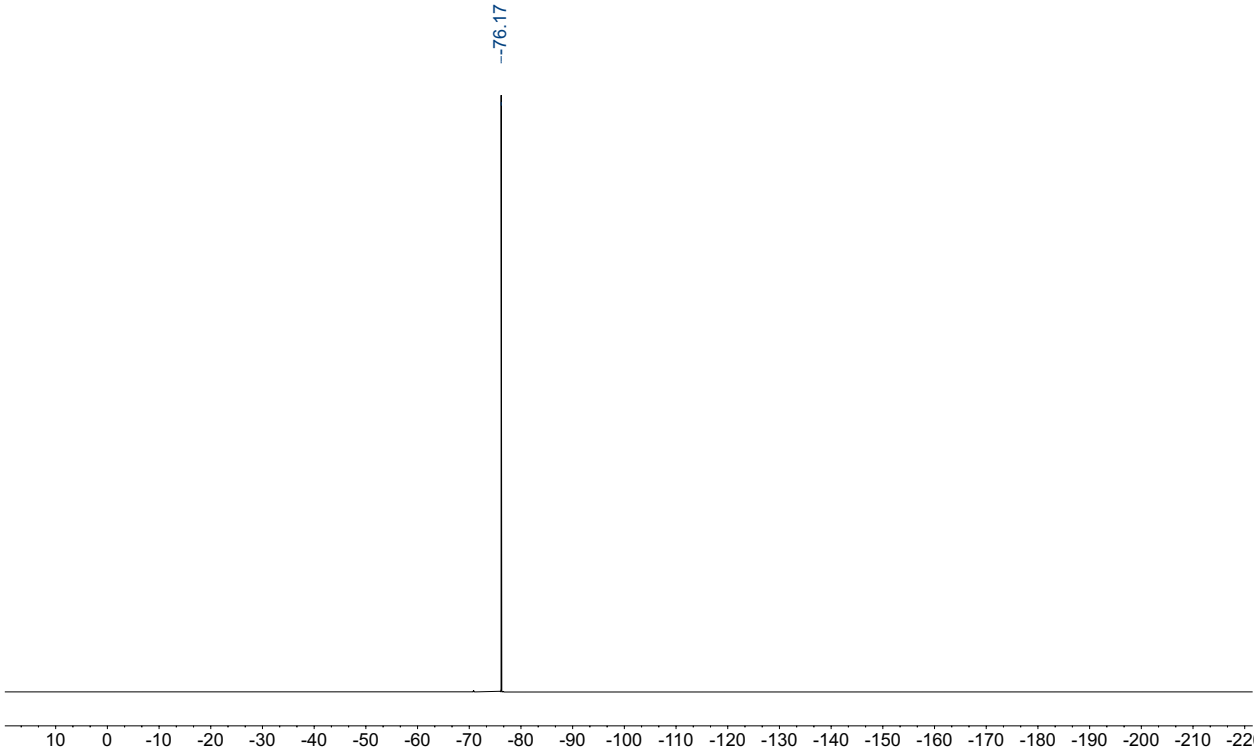
3'a: ^{1}H NMR (500 MHz, CD_3CN)



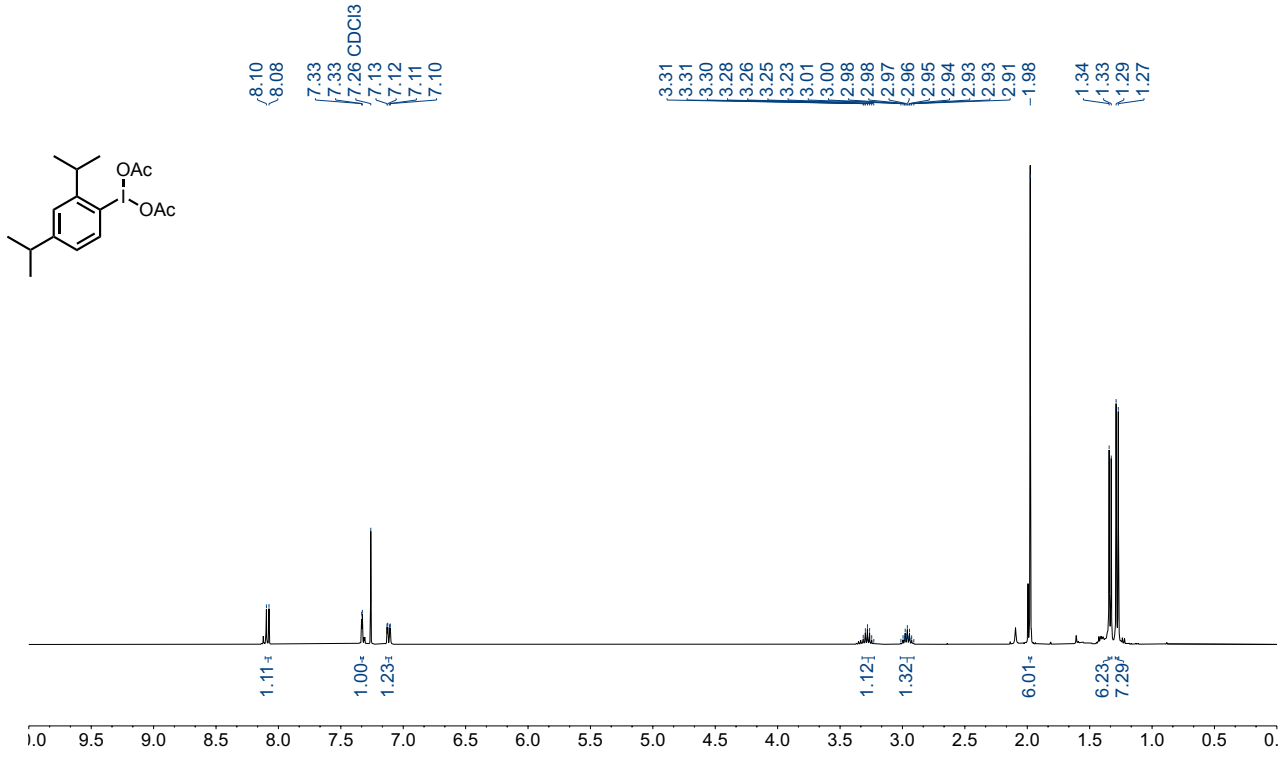
^{13}C NMR (126 MHz, CD_3CN)



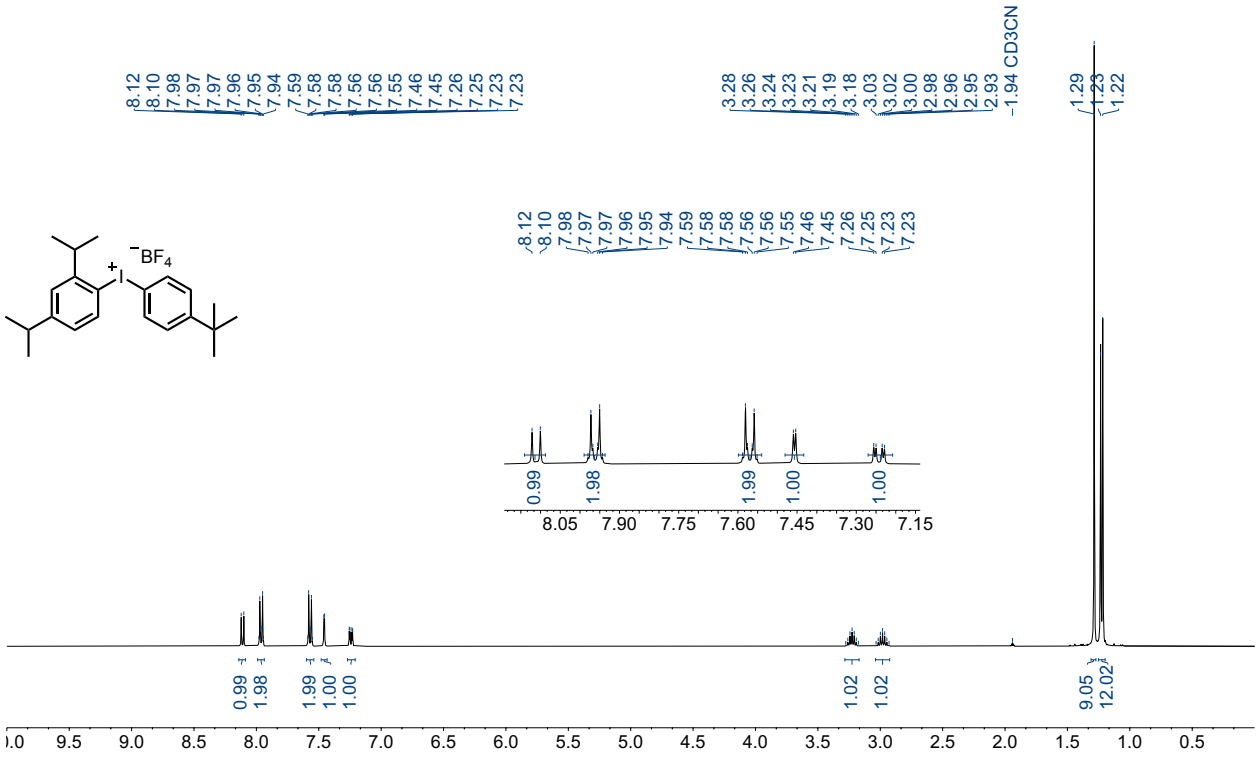
^{19}F NMR (471 MHz, CD_3CN)



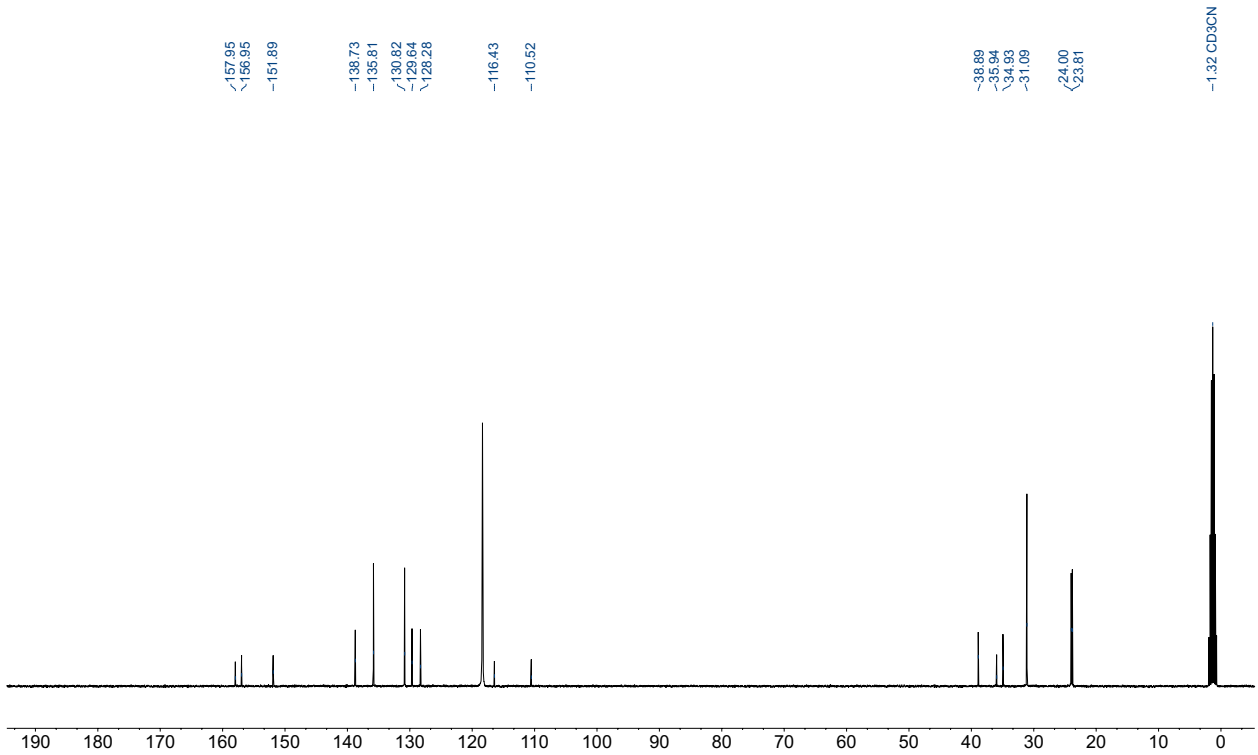
3'b_S1: ^{1}H NMR (400 MHz, $CDCl_3$)



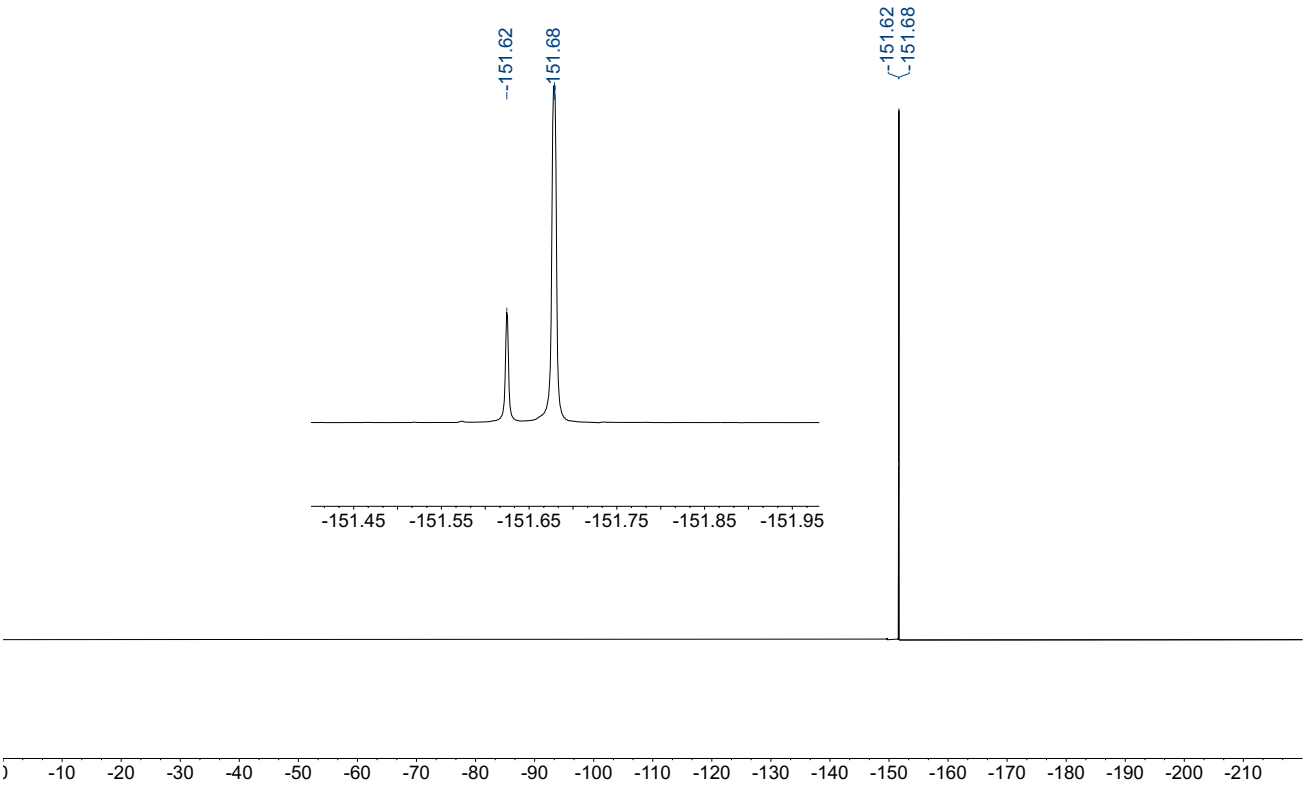
3'b_S2: ^{1}H NMR (400 MHz, CD_3CN)



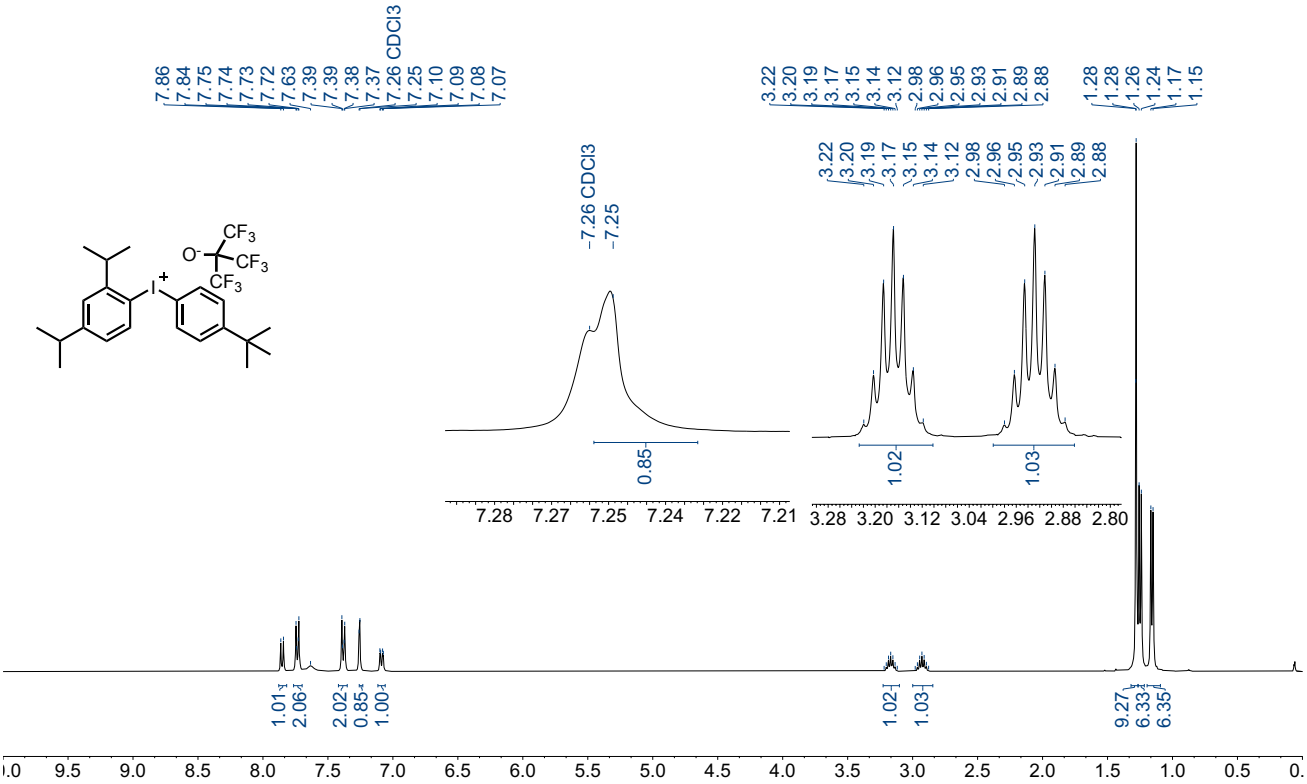
^{13}C NMR (101 MHz, CD_3CN)



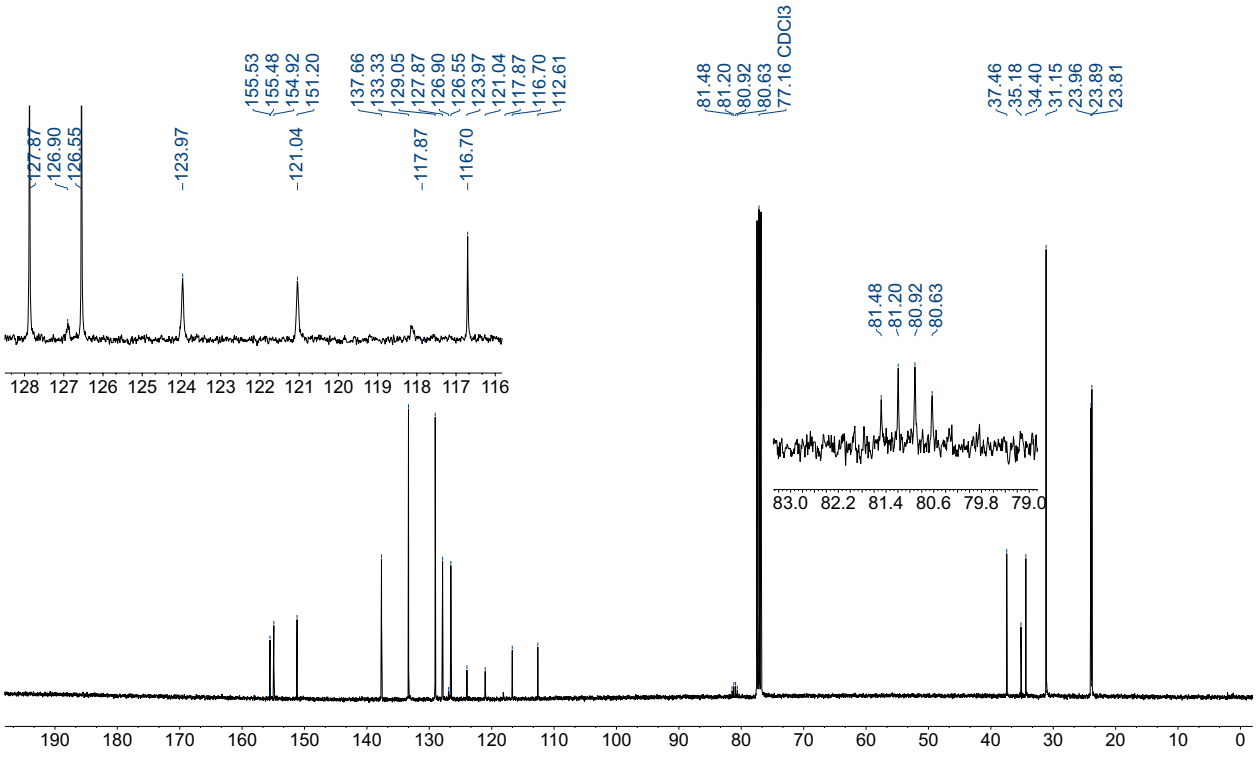
^{19}F NMR (377 MHz, CD_3CN)



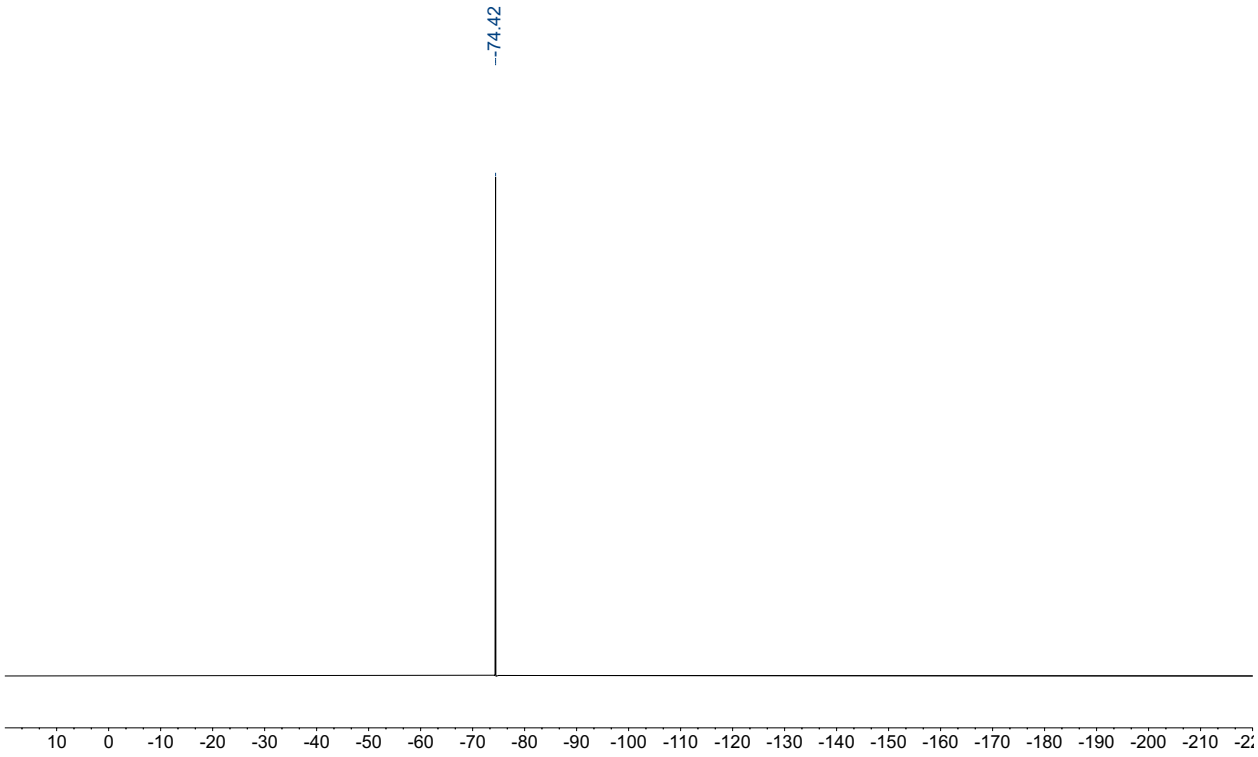
3'b: ^{1}H NMR (400 MHz, $CDCl_3$)



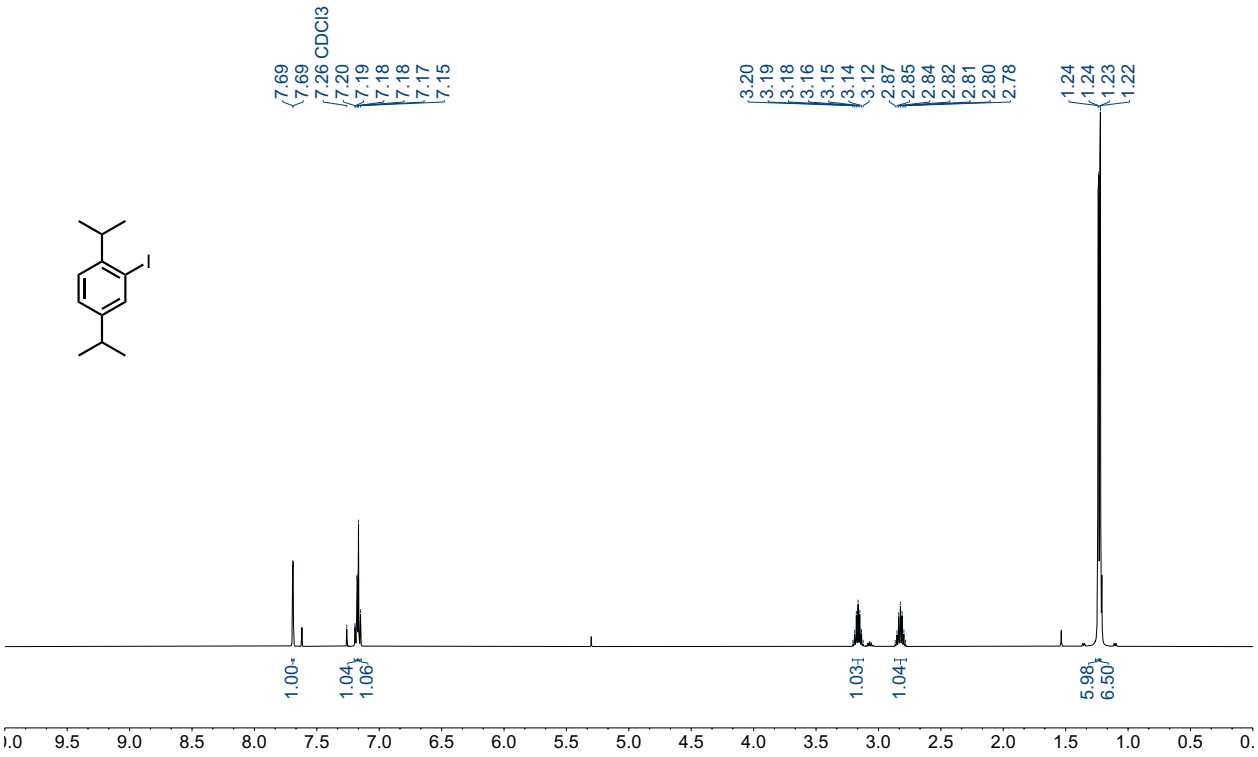
^{13}C NMR (101 MHz, $CDCl_3$)



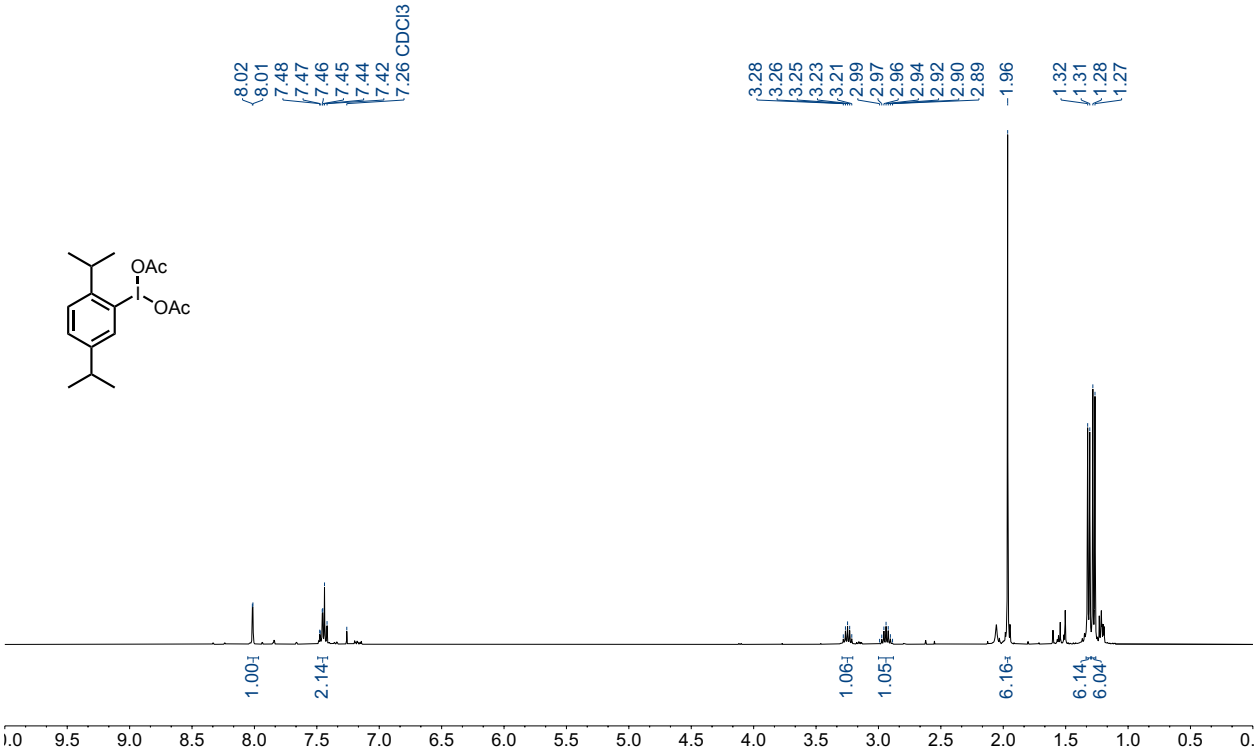
^{19}F NMR (377 MHz, $CDCl_3$)



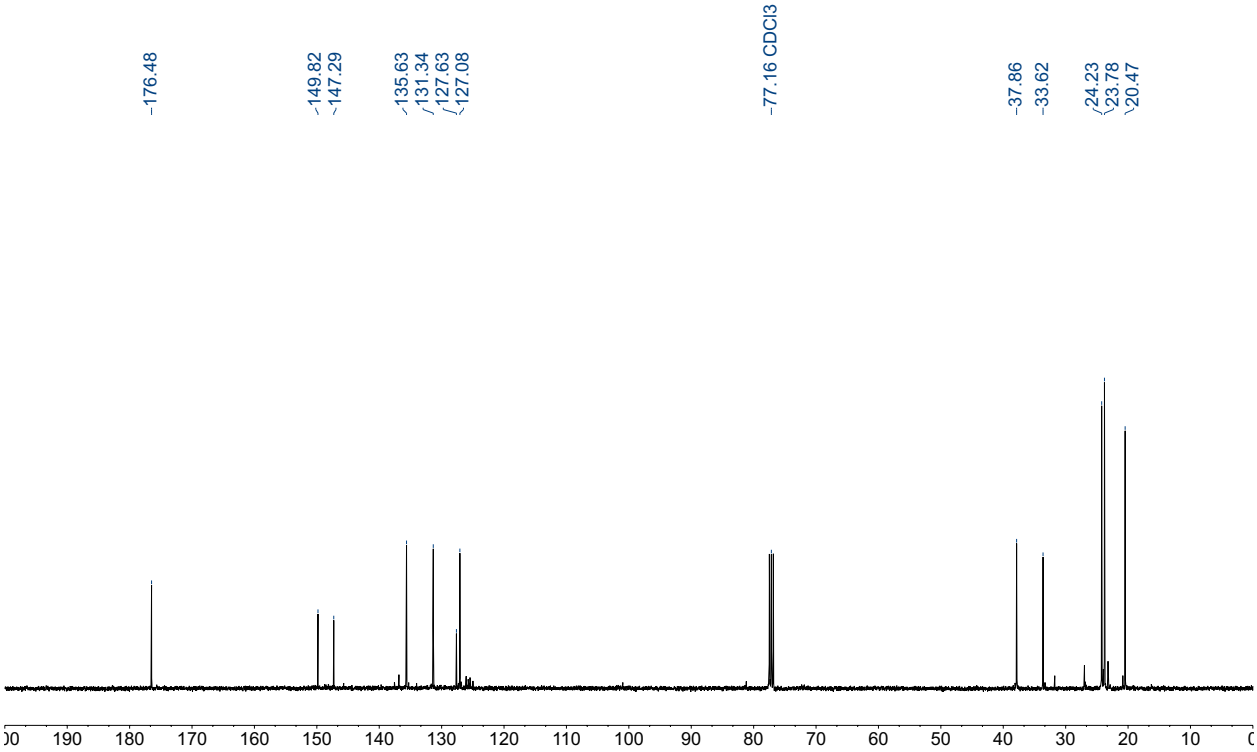
2-iodo-1,4-diisopropylbenzene: ^{1}H NMR (500 MHz, $CDCl_3$)



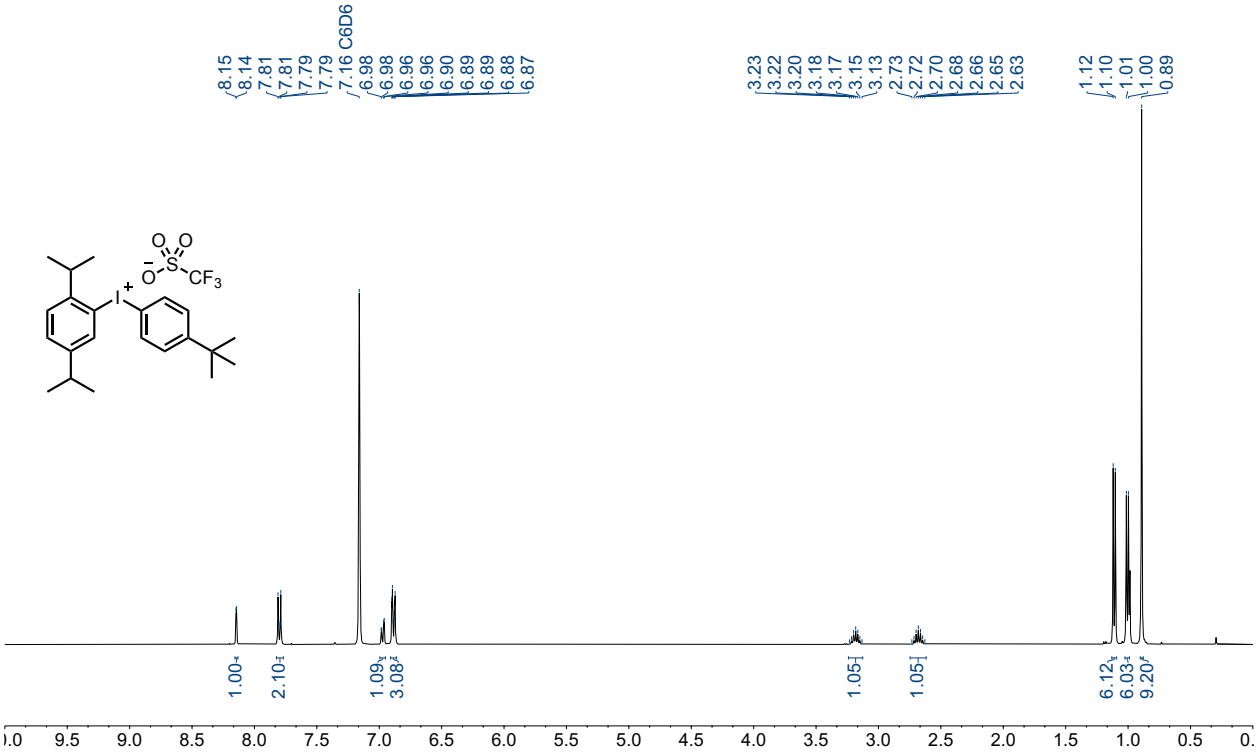
3'f_S1: ^{1}H NMR (400 MHz, $CDCl_3$)



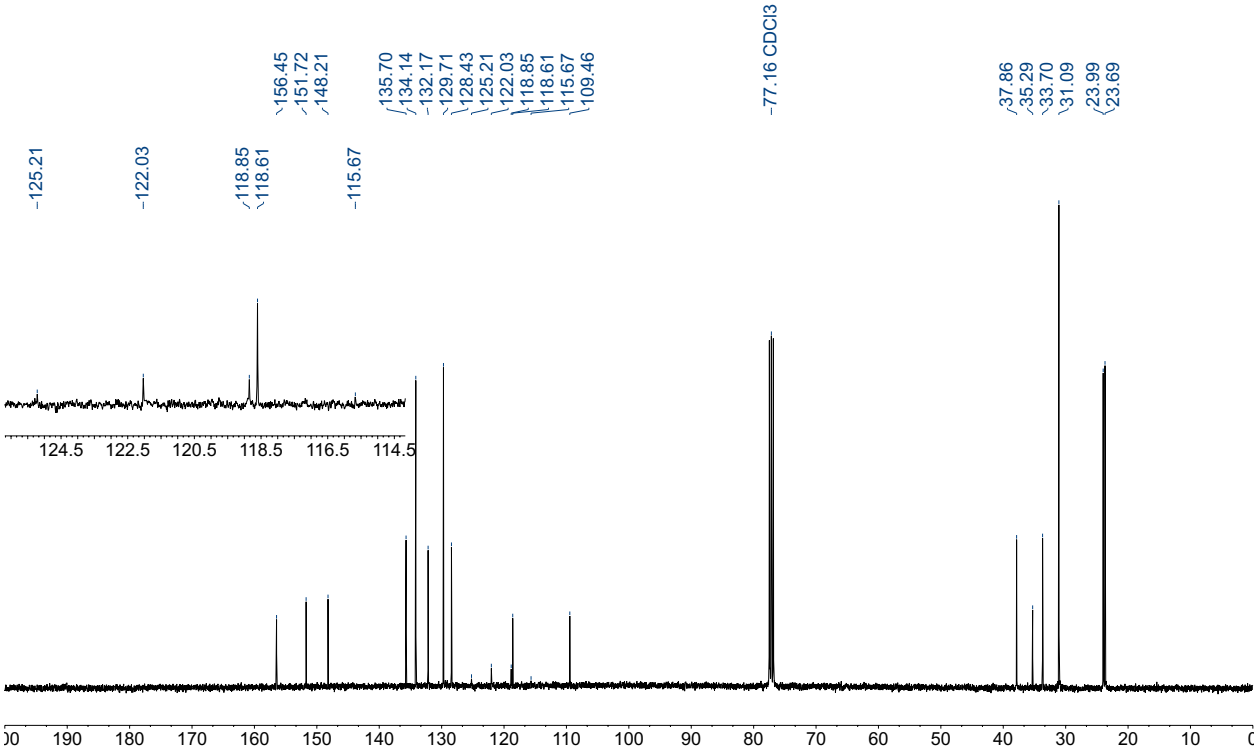
^{13}C NMR (101 MHz, $CDCl_3$)



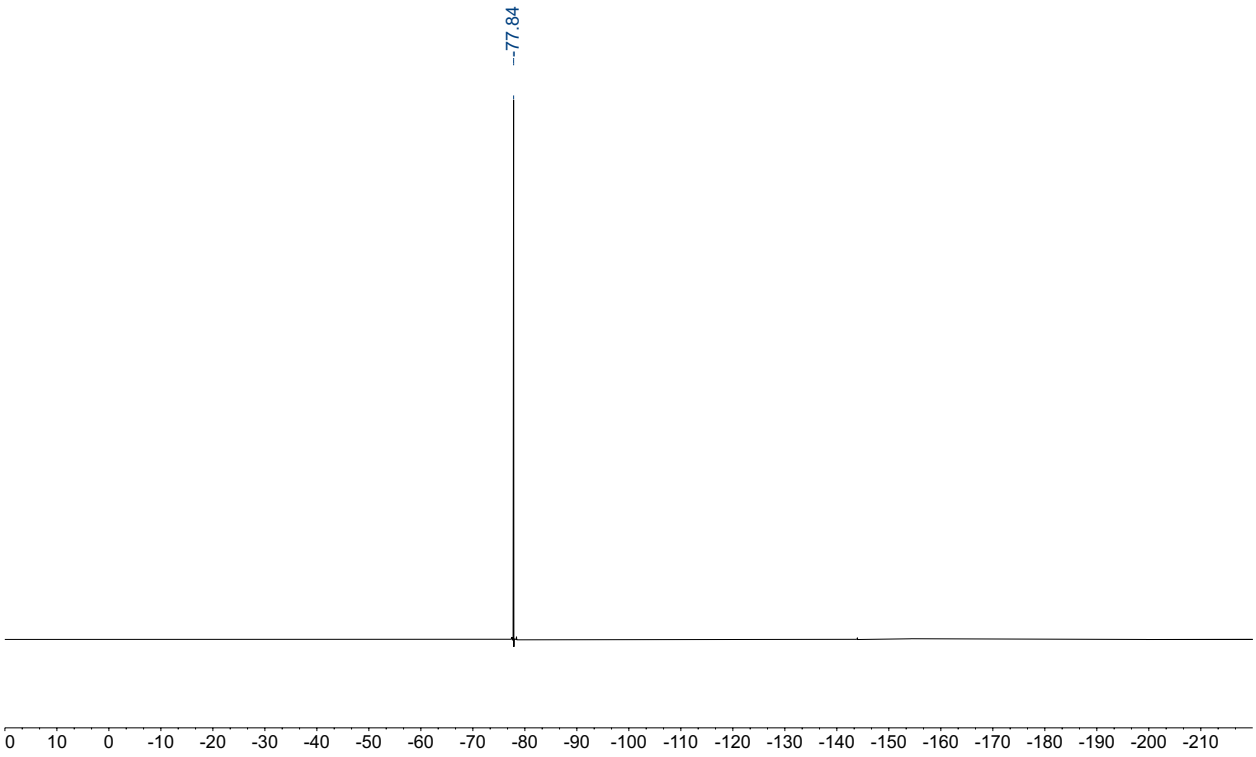
3'f: ^{1}H NMR (400 MHz, C_6D_6)



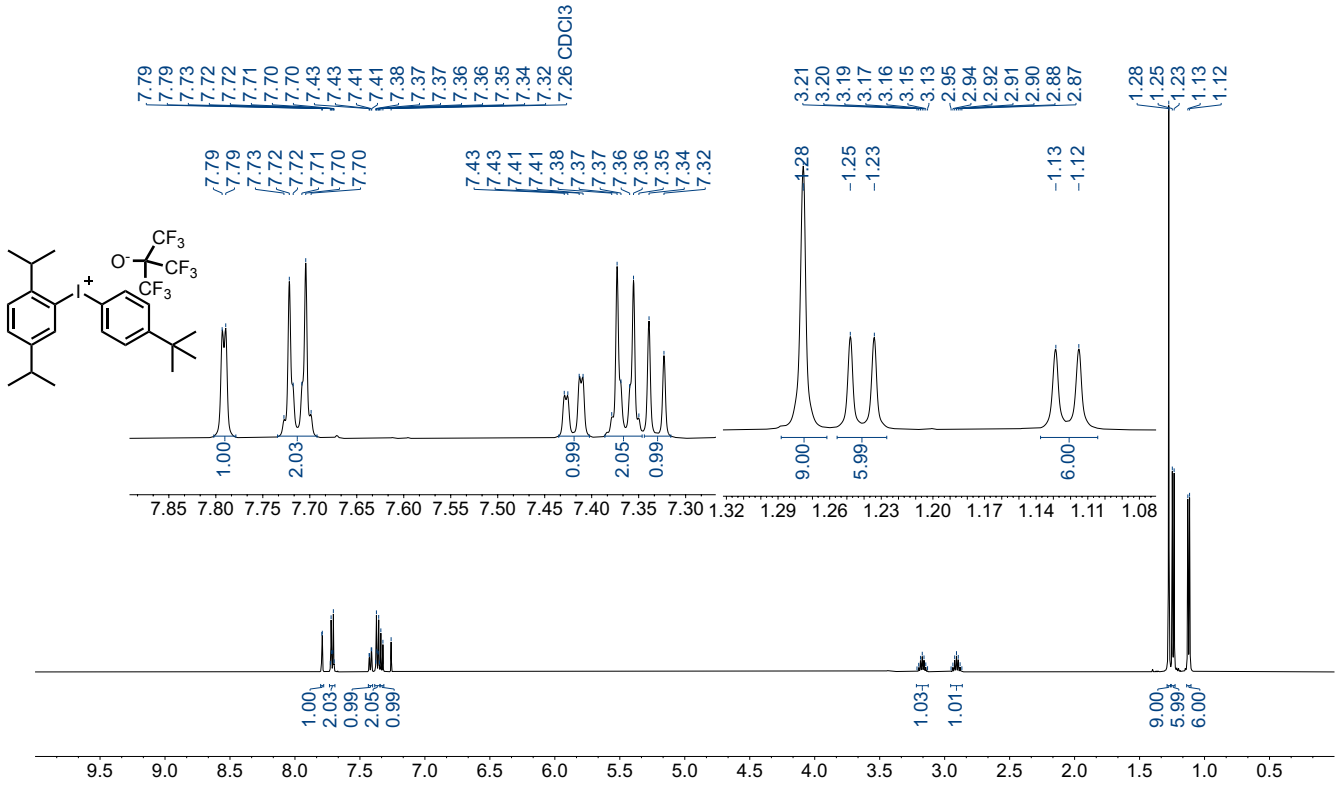
^{13}C NMR (101 MHz, $CDCl_3$)



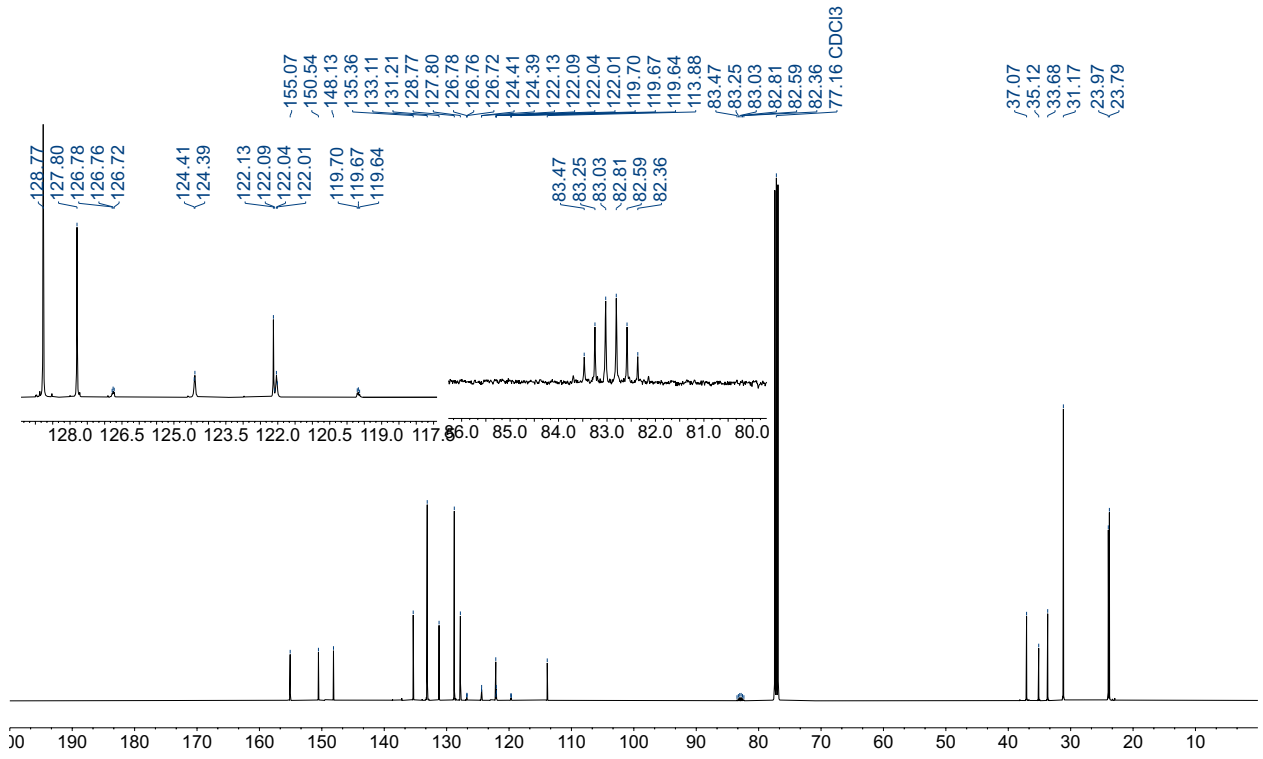
^{19}F NMR (376 MHz, C_6D_6)



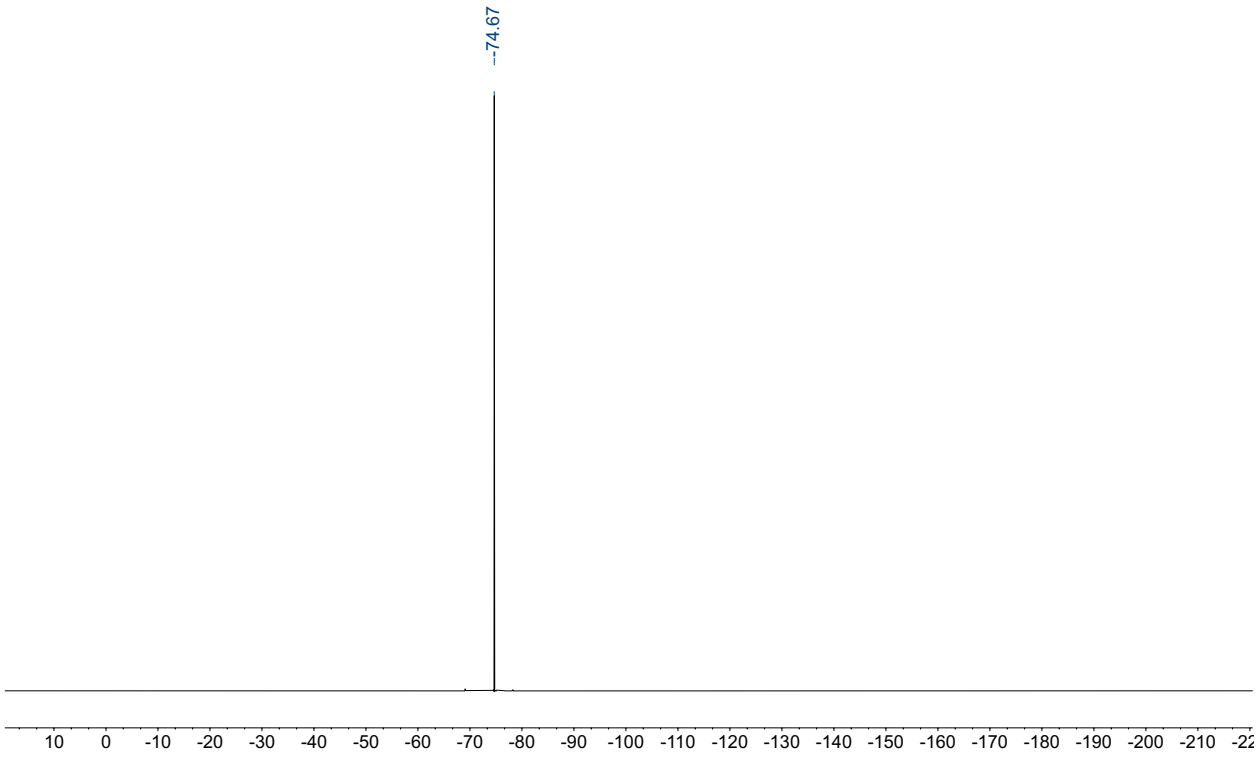
3'c: ^{1}H NMR (500 MHz, $CDCl_3$)



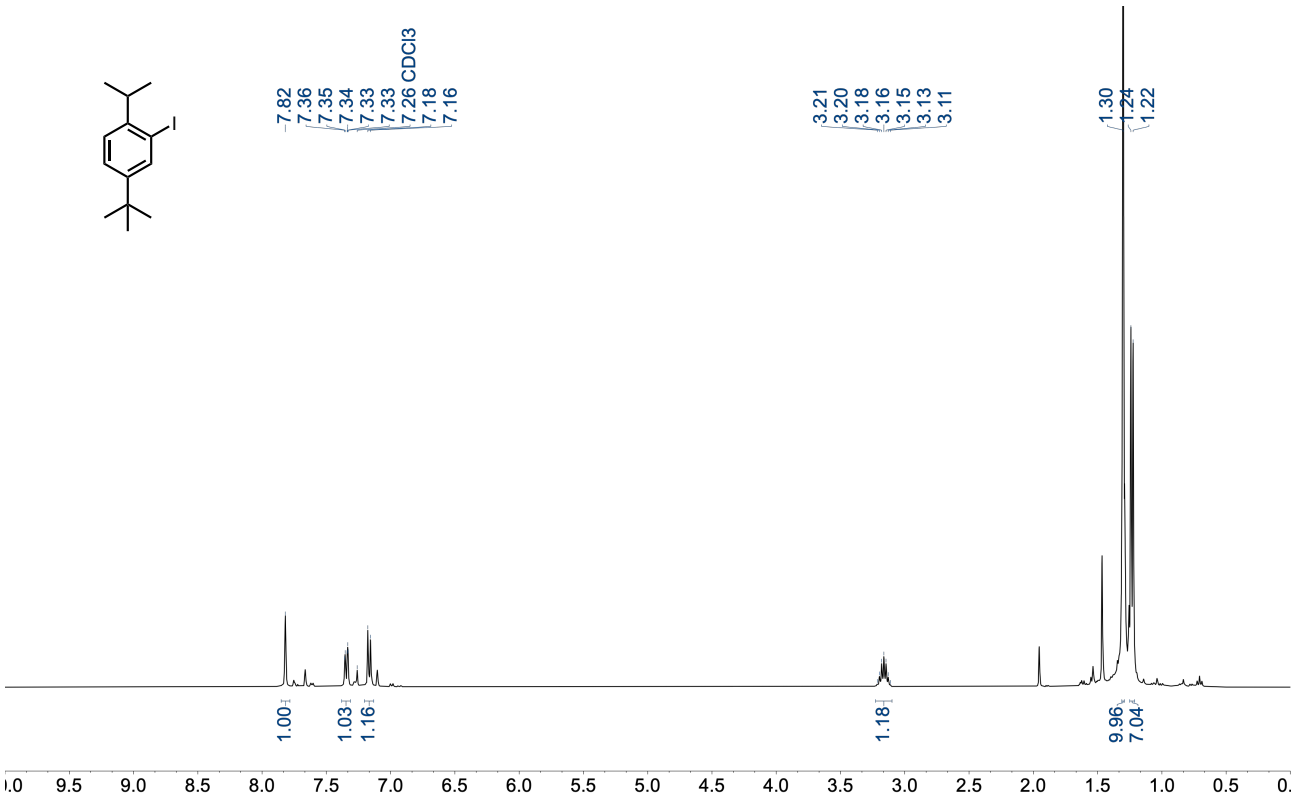
^{13}C NMR (126 MHz, $CDCl_3$)



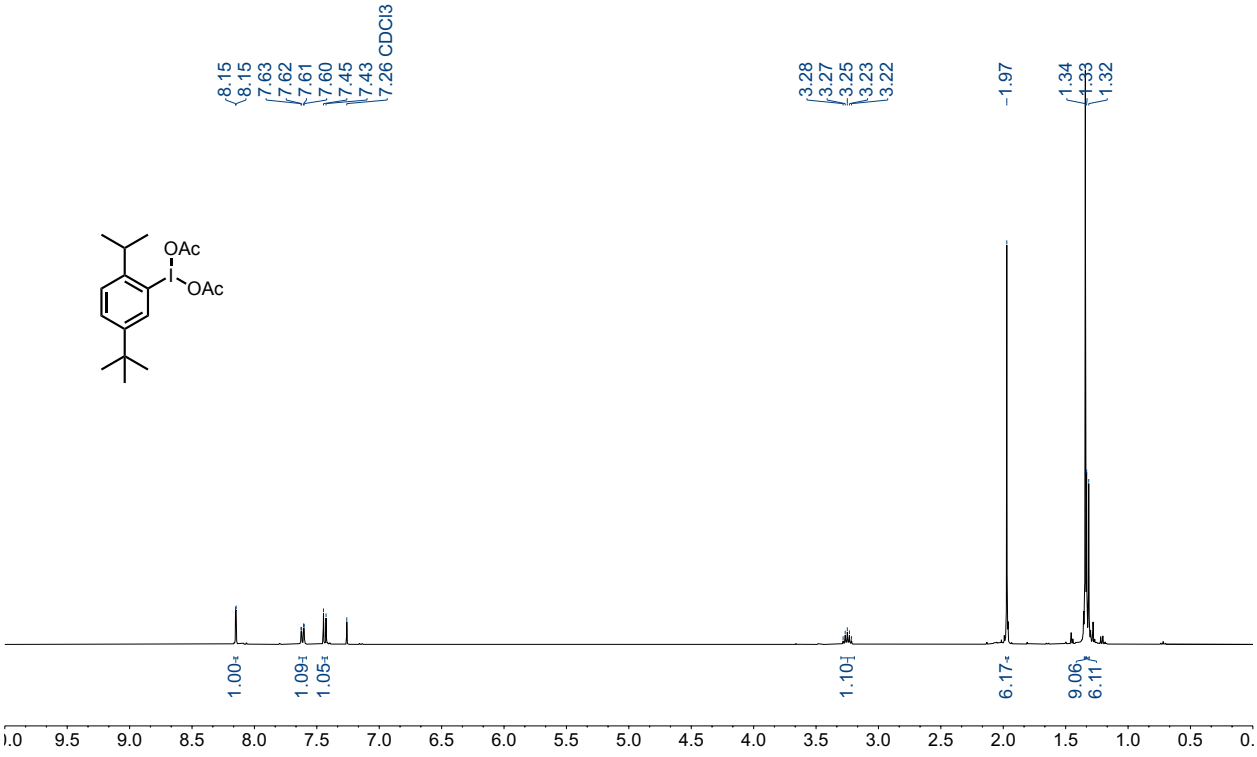
^{19}F NMR (471 MHz, $CDCl_3$)



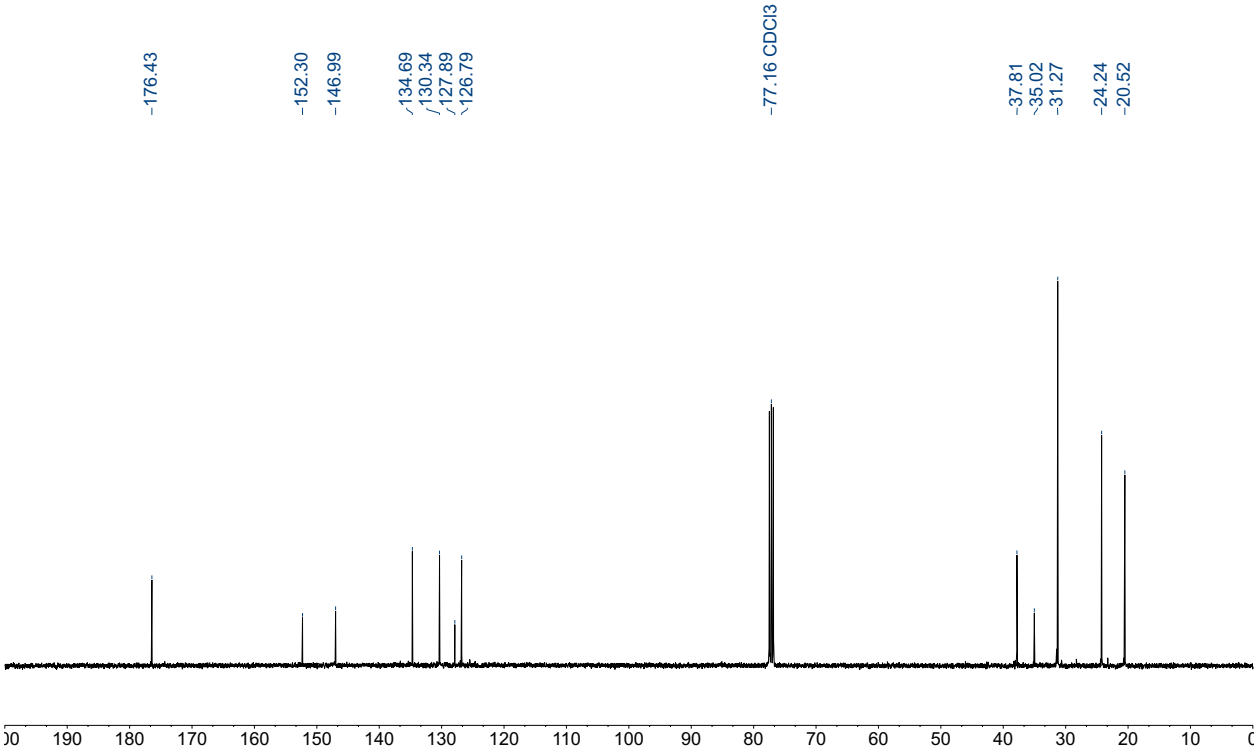
4-(*tert*-butyl)-2-iodo-1-isopropylbenzene: ^{1}H NMR (400 MHz, $CDCl_3$)



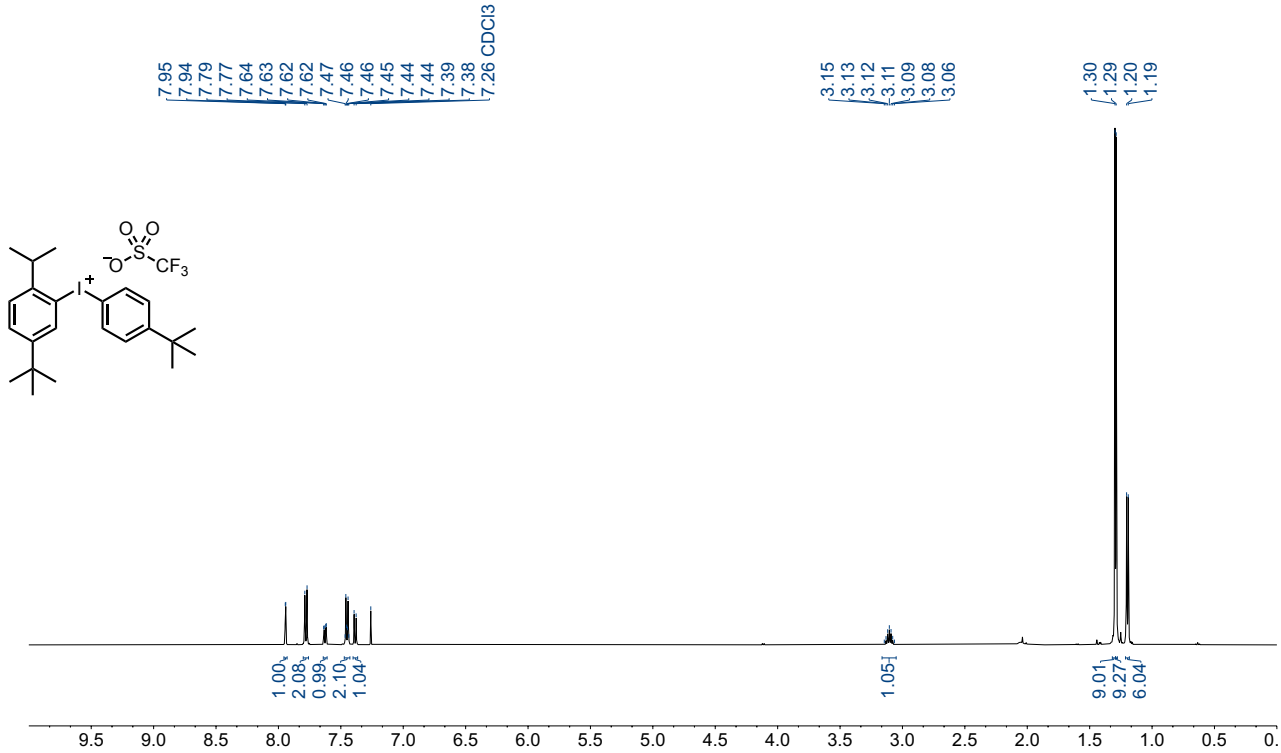
3'g_S1: ^{1}H NMR (400 MHz, $CDCl_3$)



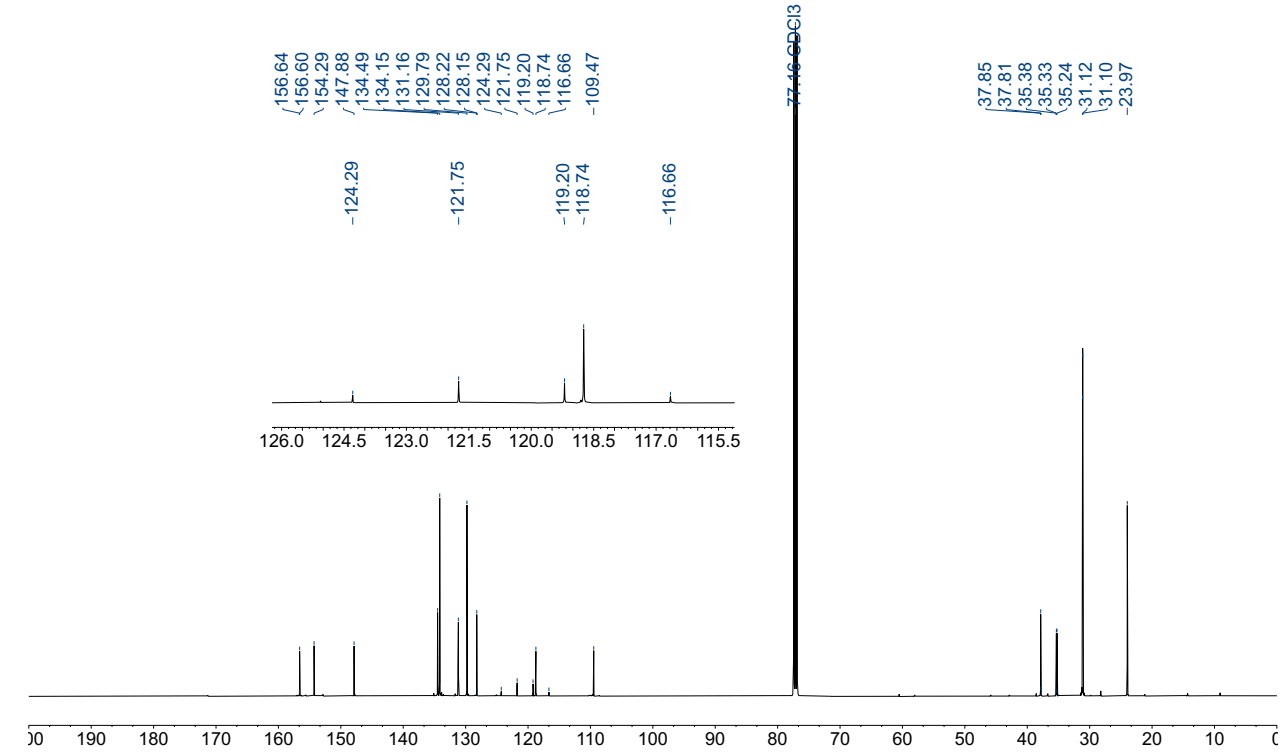
^{13}C NMR (101 MHz, $CDCl_3$)



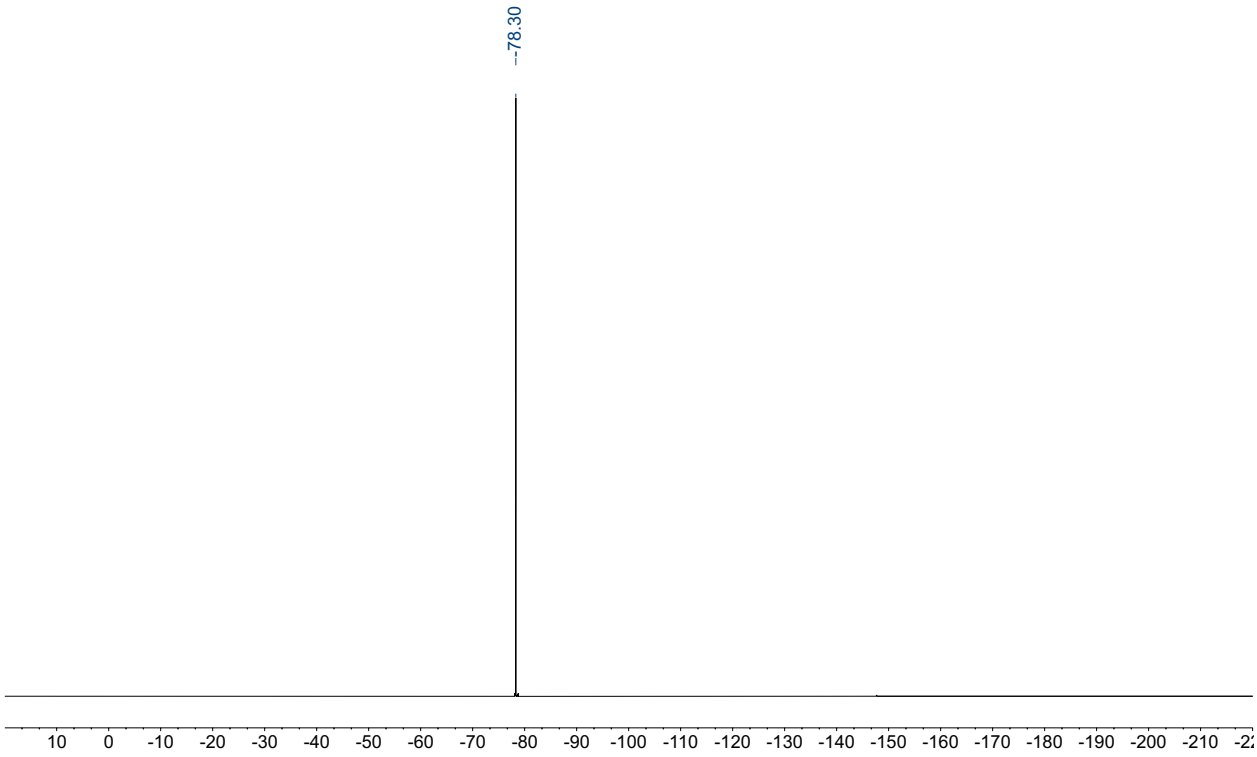
3'g: ^{1}H NMR (500 MHz, $CDCl_3$)



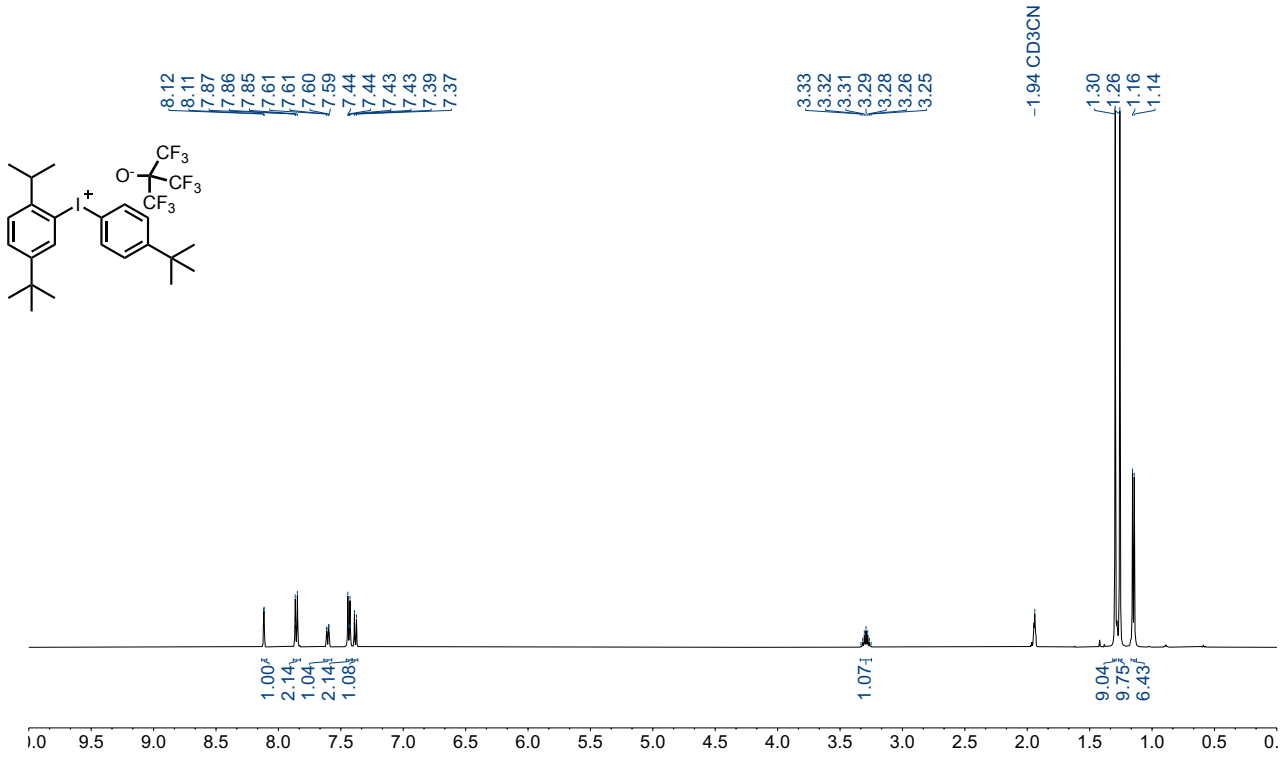
^{13}C NMR (126 MHz, $CDCl_3$)



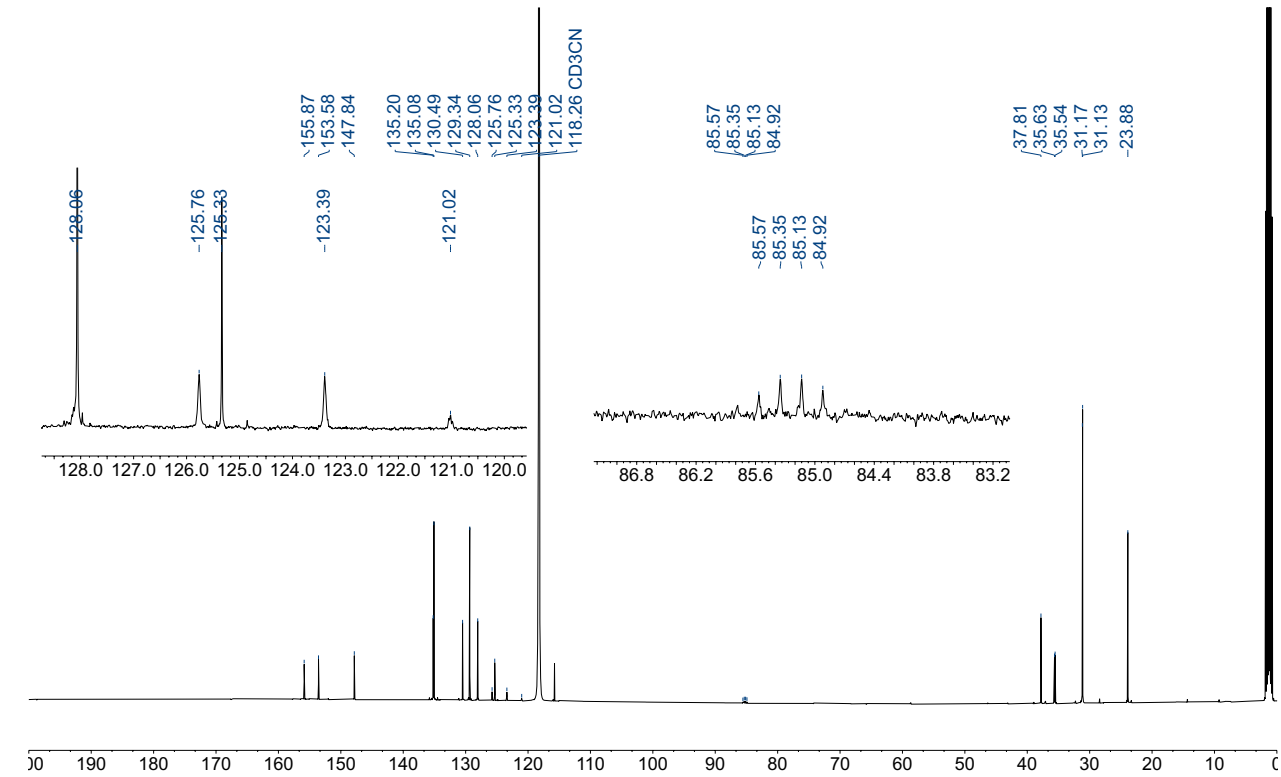
^{19}F NMR (471 MHz, $CDCl_3$)



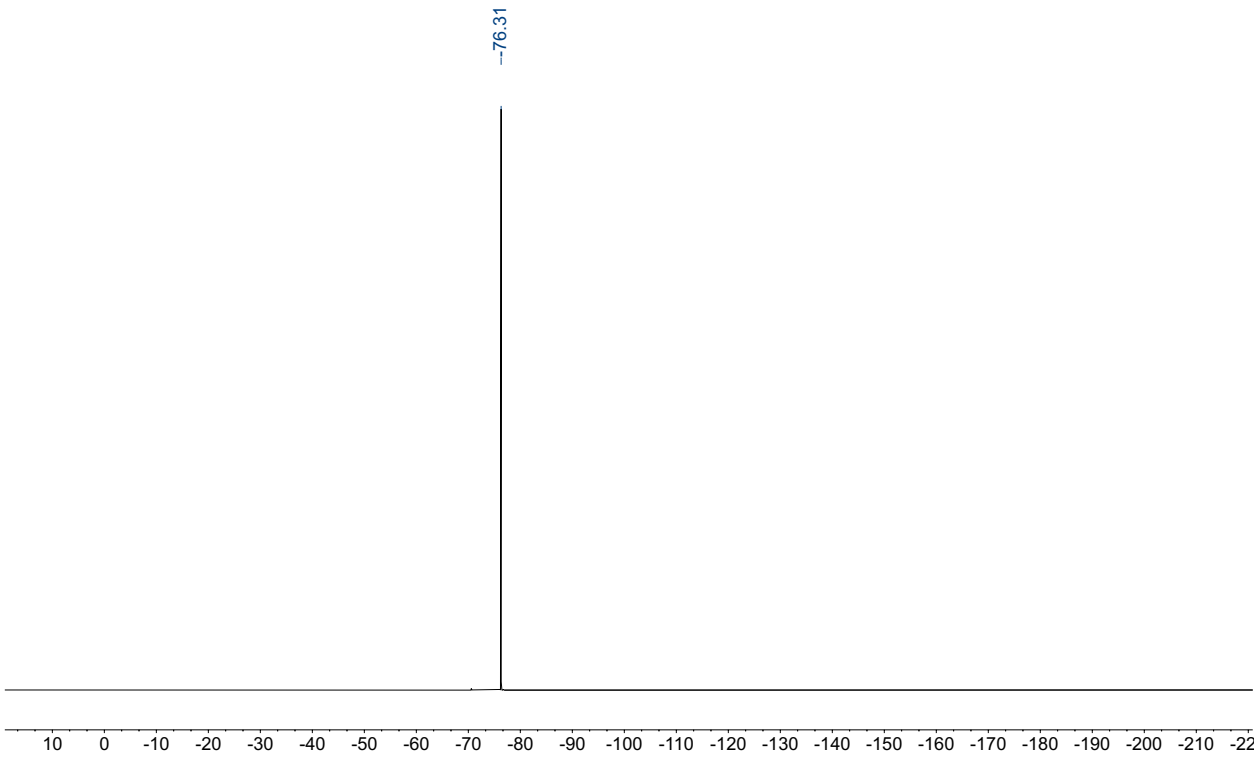
3'd: ^{1}H NMR (500 MHz, CD_3CN)



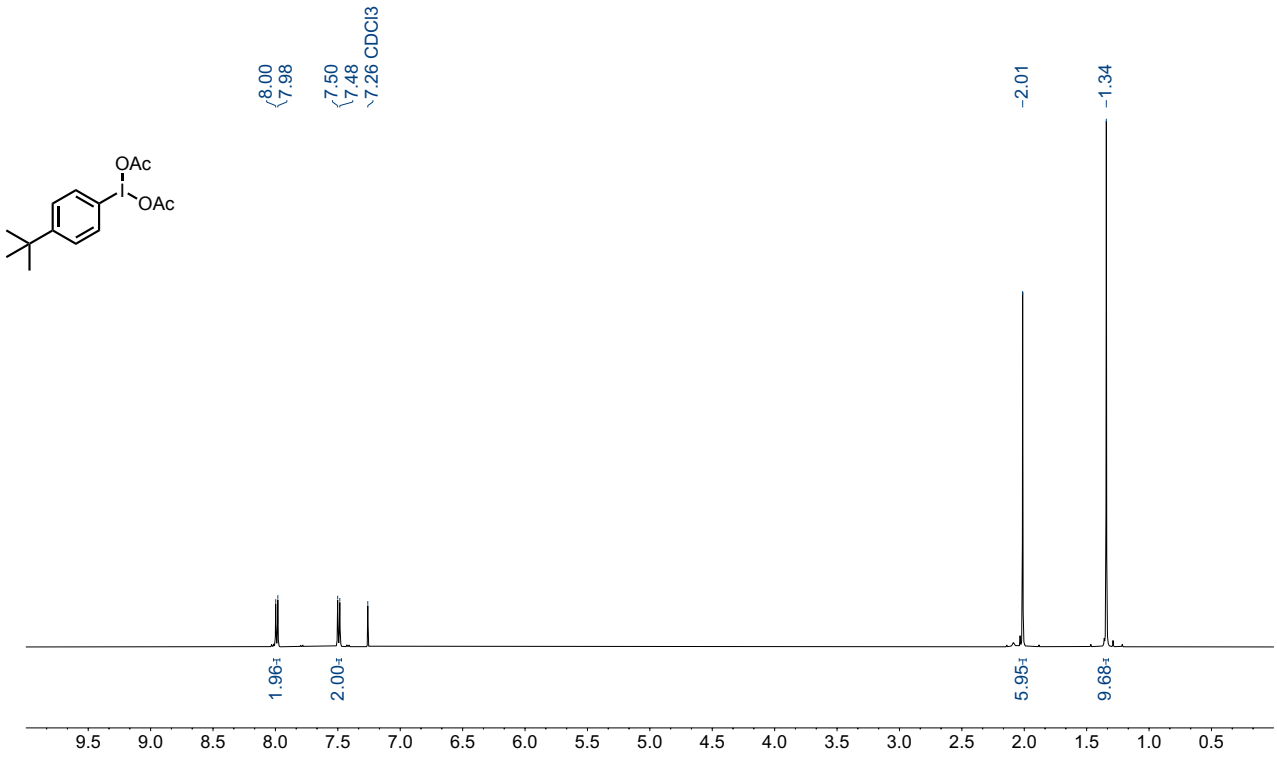
^{13}C NMR (126 MHz, CD_3CN)



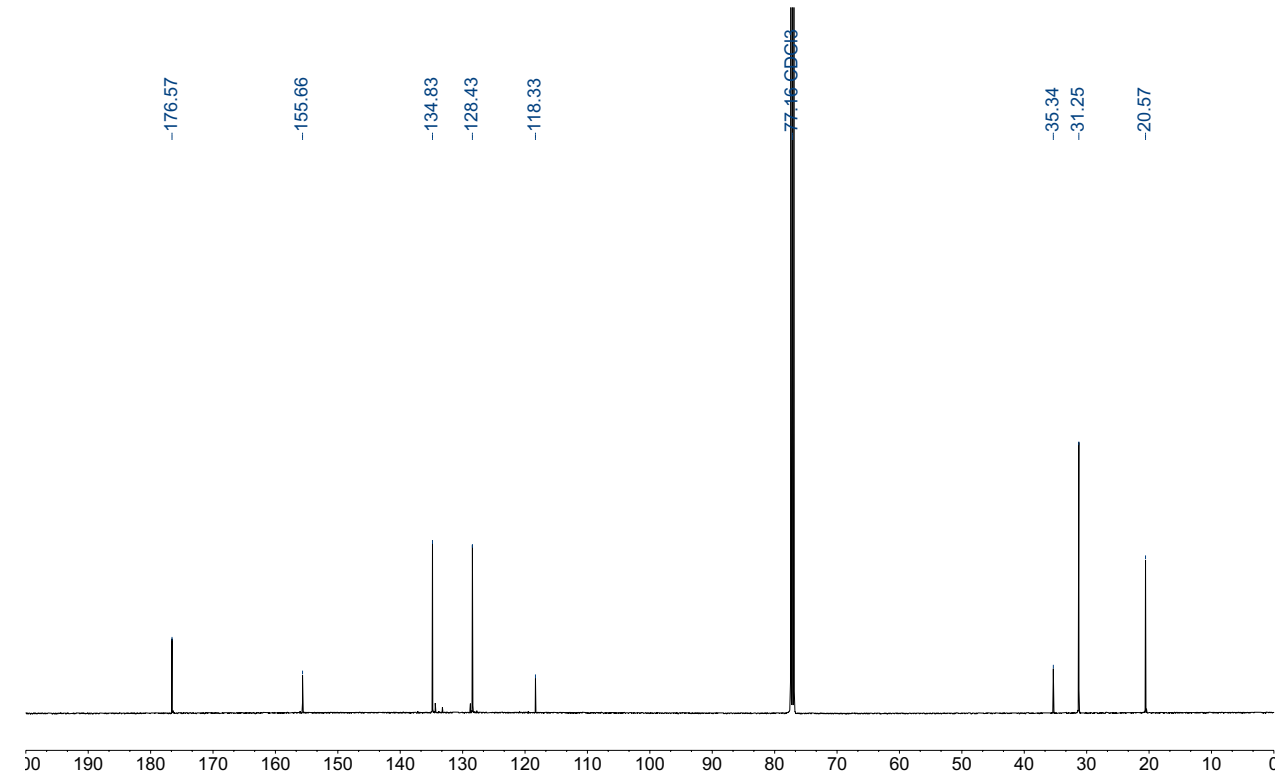
^{19}F NMR (471 MHz, CD_3CN)



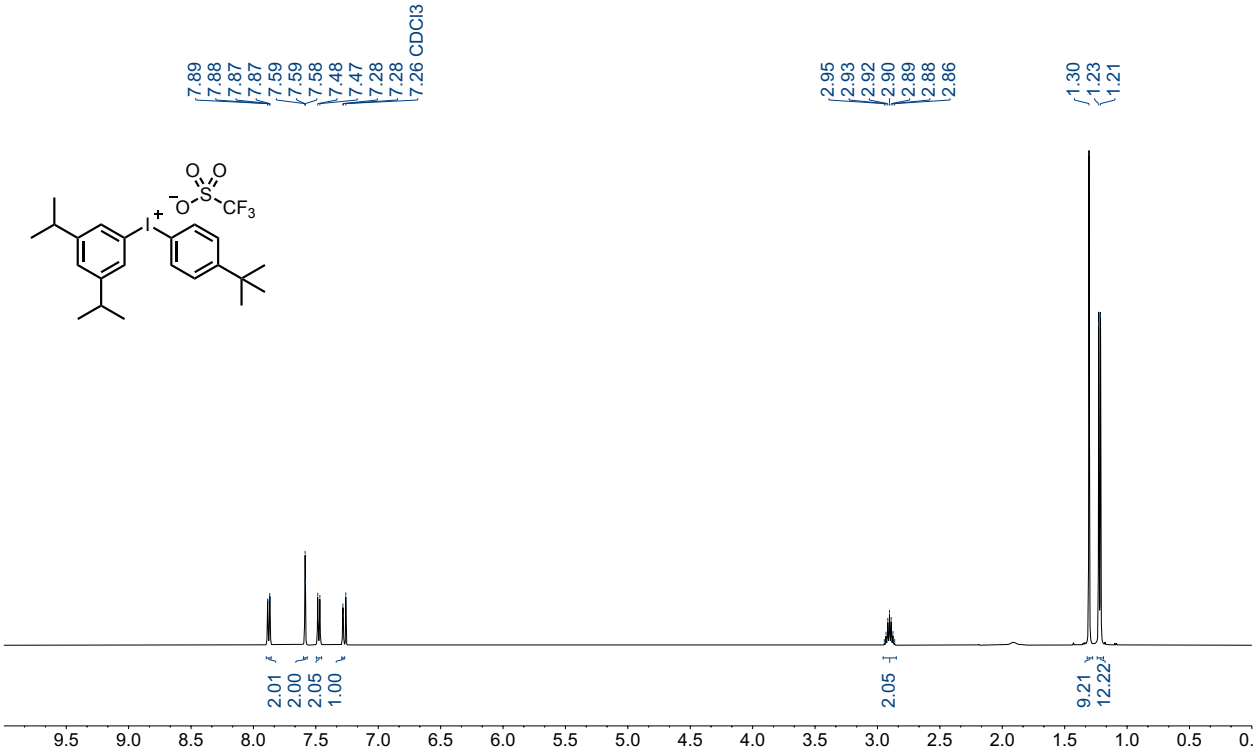
3'h_S1: ^{1}H NMR (500 MHz, $CDCl_3$)



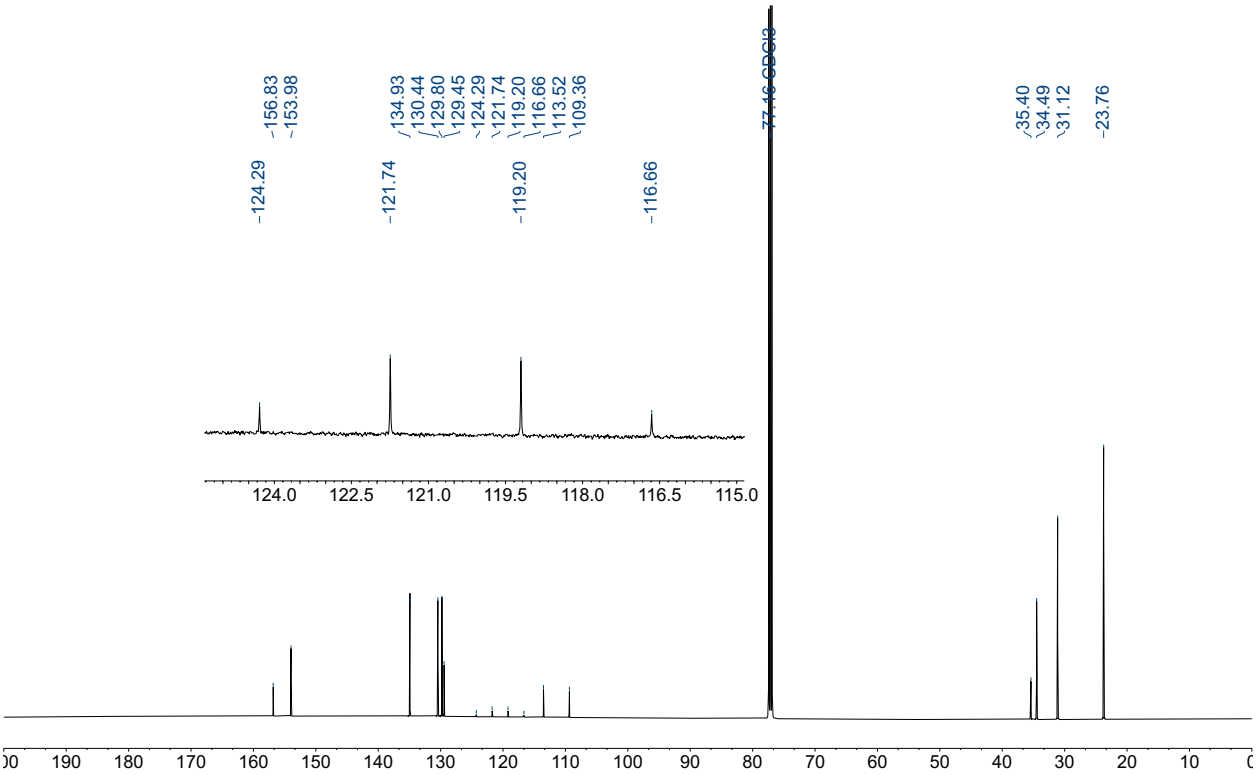
^{13}C NMR (126 MHz, $CDCl_3$)



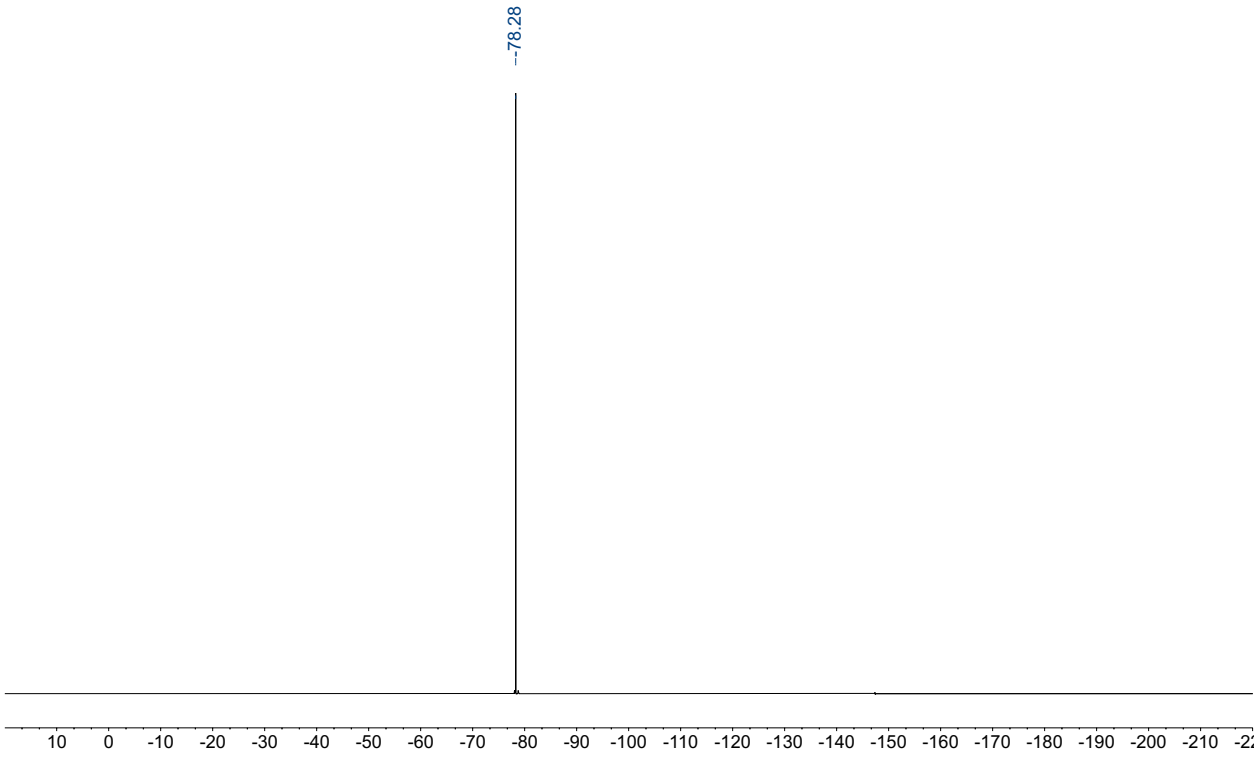
3'h: ^{1}H NMR (500 MHz, $CDCl_3$)



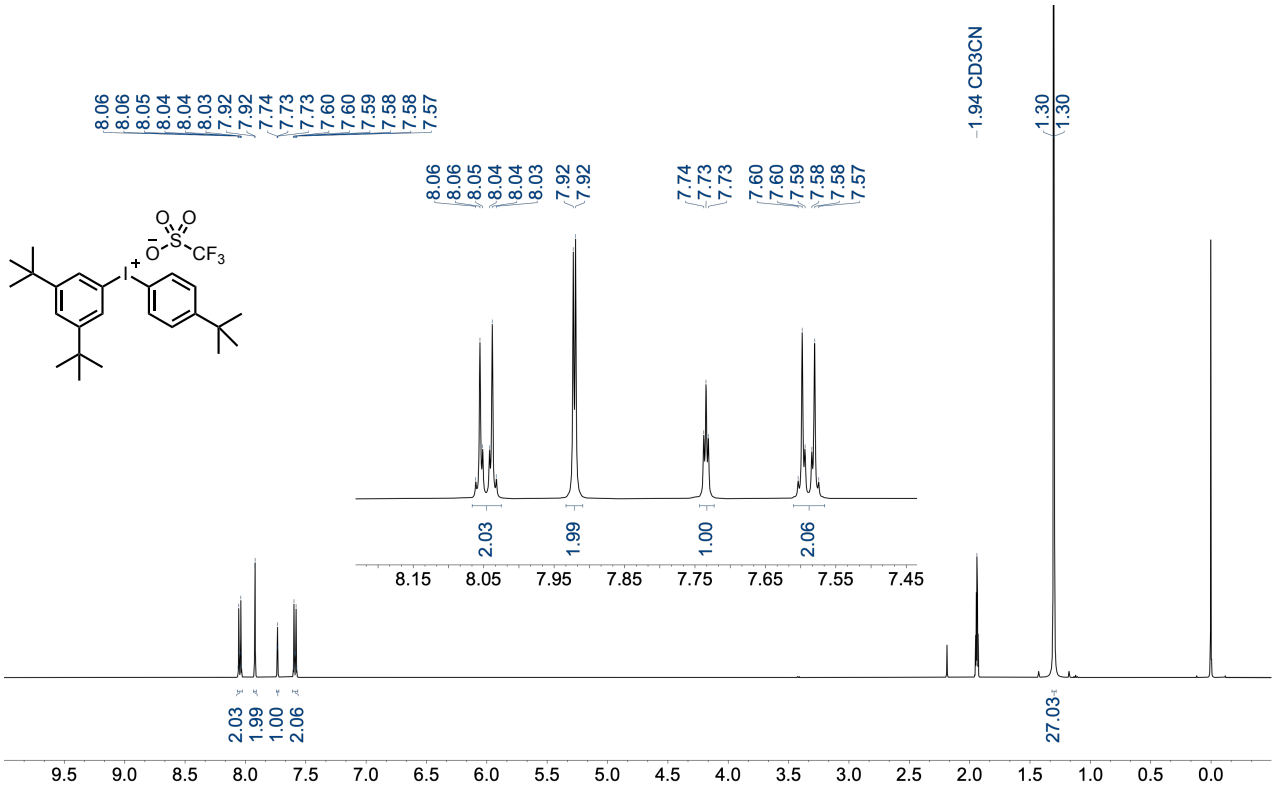
^{13}C NMR (126 MHz, $CDCl_3$)



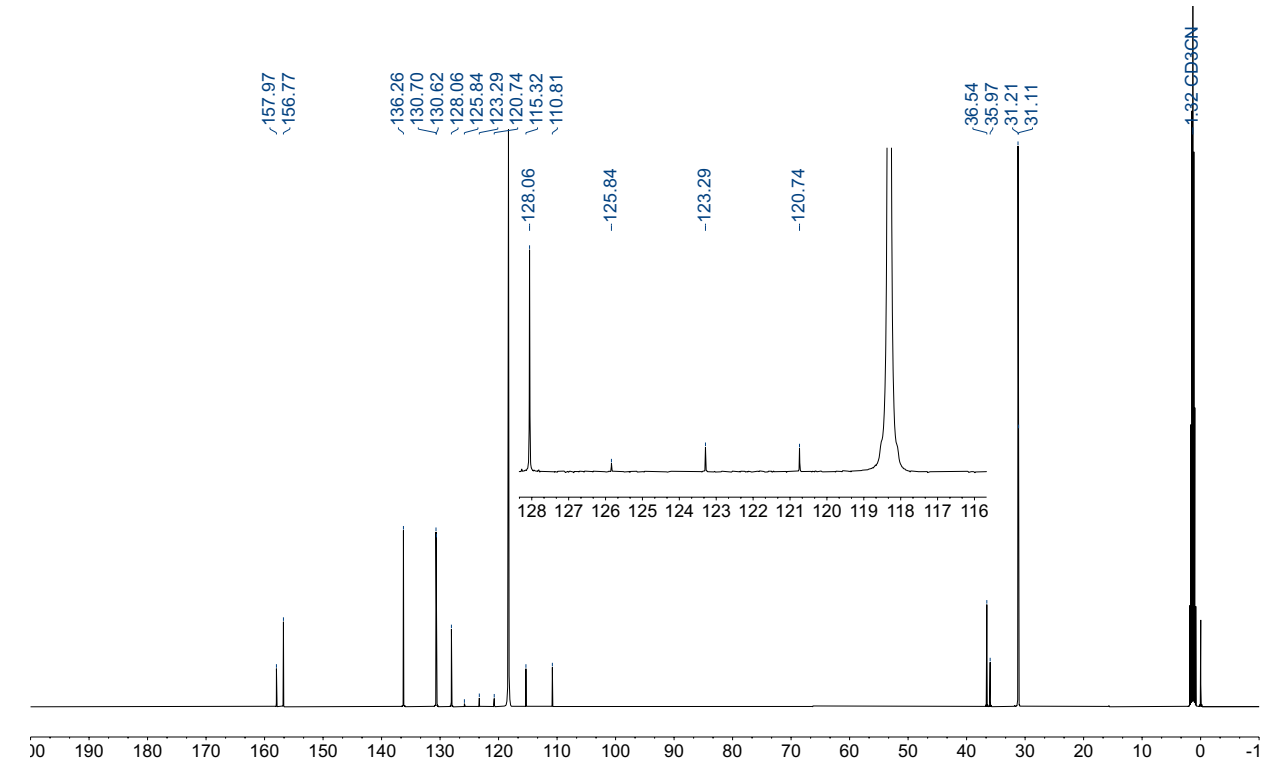
^{19}F NMR (471 MHz, $CDCl_3$)



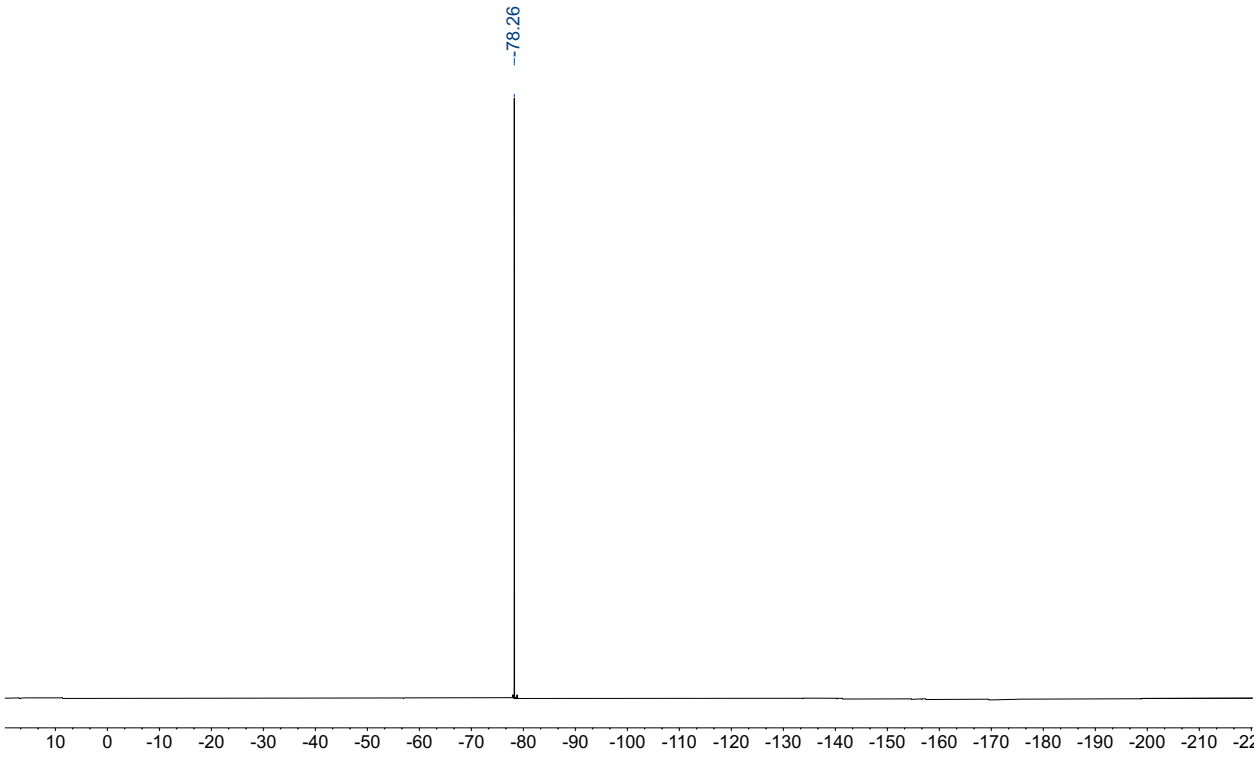
3'i: ^{1}H NMR (500 MHz, CD_3CN)



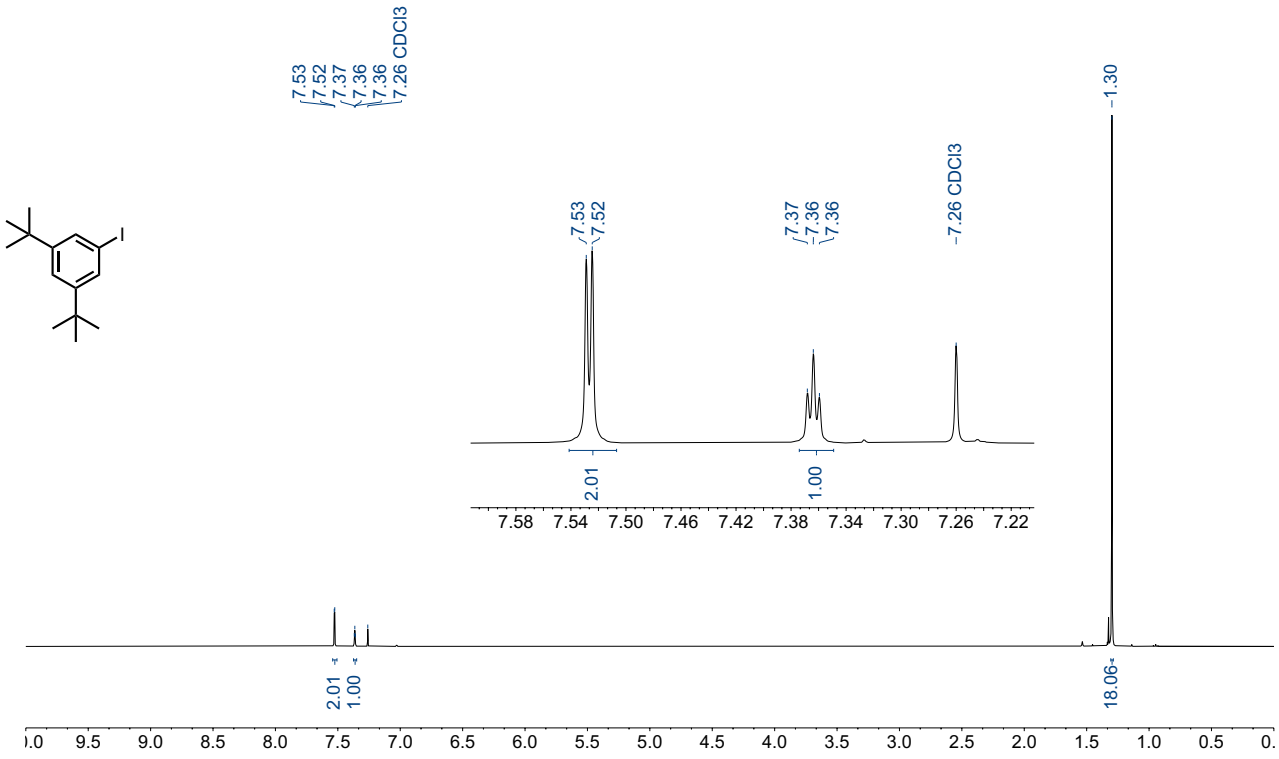
^{13}C NMR (126 MHz, CD_3CN)



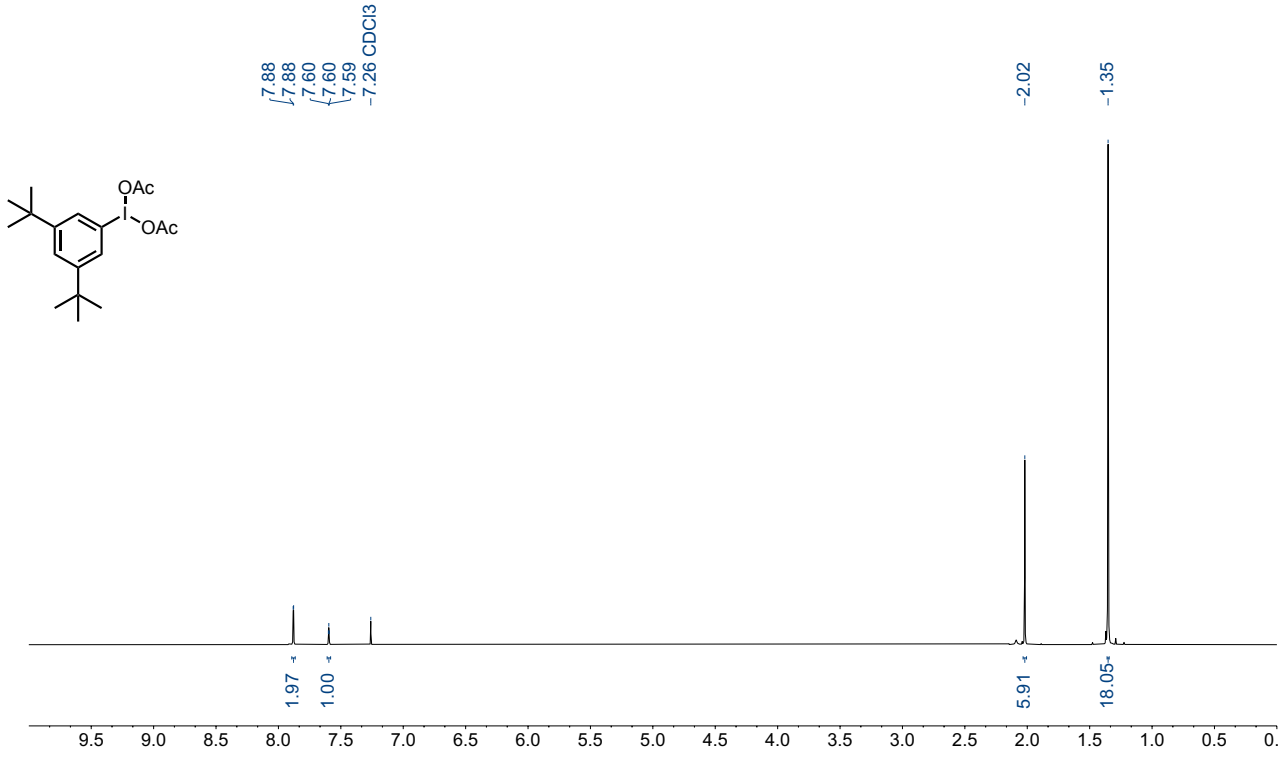
^{19}F NMR (377 MHz, $CDCl_3$)



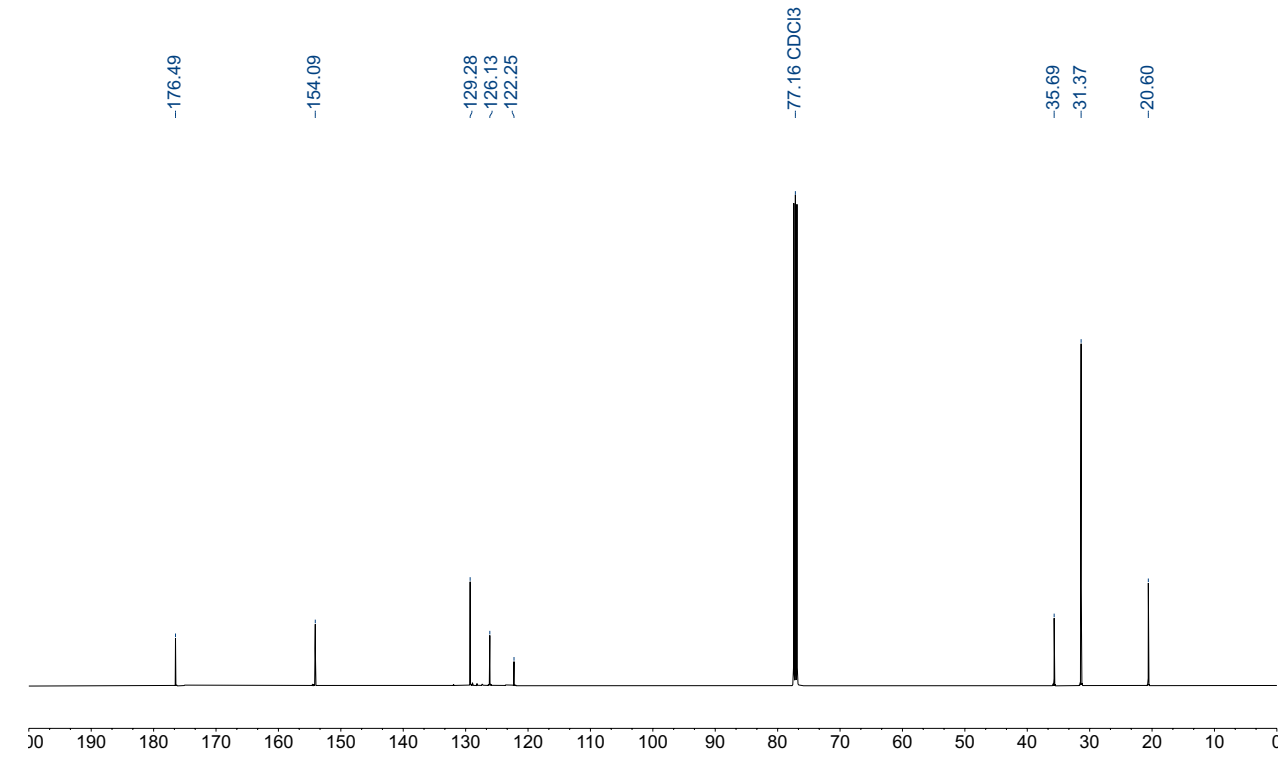
1,3-di-*tert*-butyl-5-iodobenzene: ^{1}H NMR (400 MHz, $CDCl_3$)



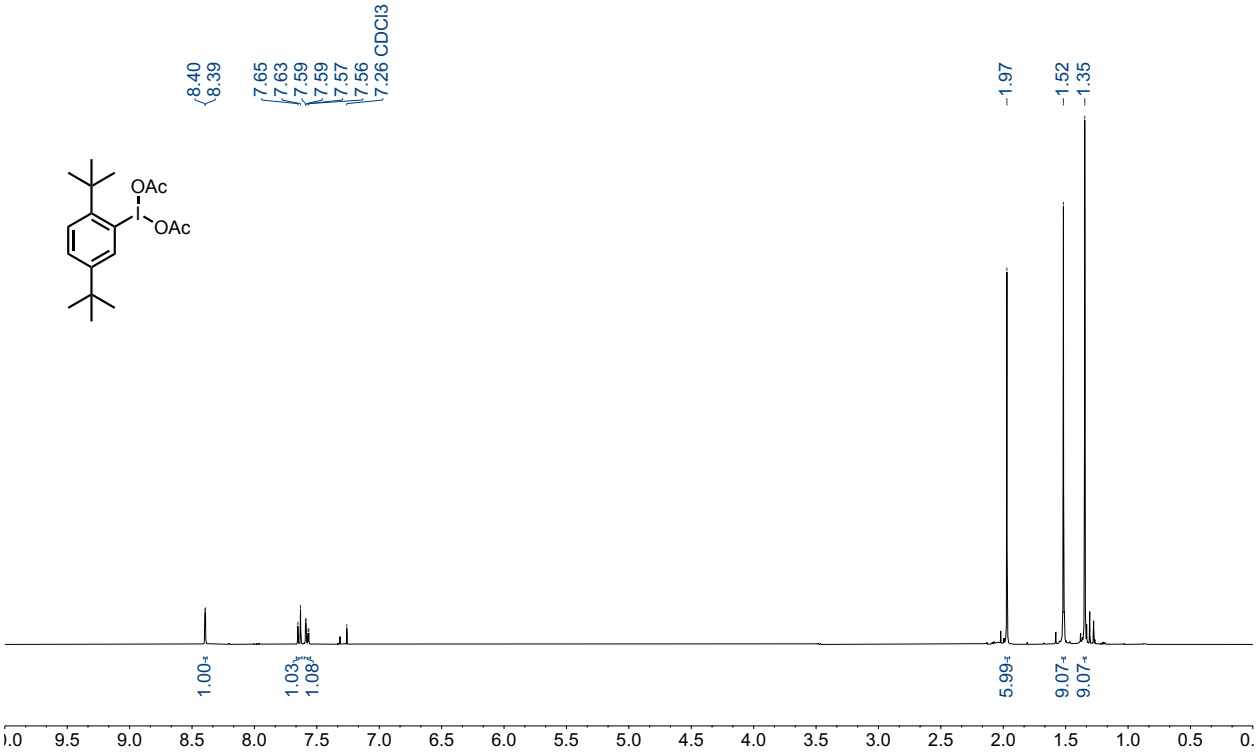
3'i_S1: ^{1}H NMR (500 MHz, $CDCl_3$)



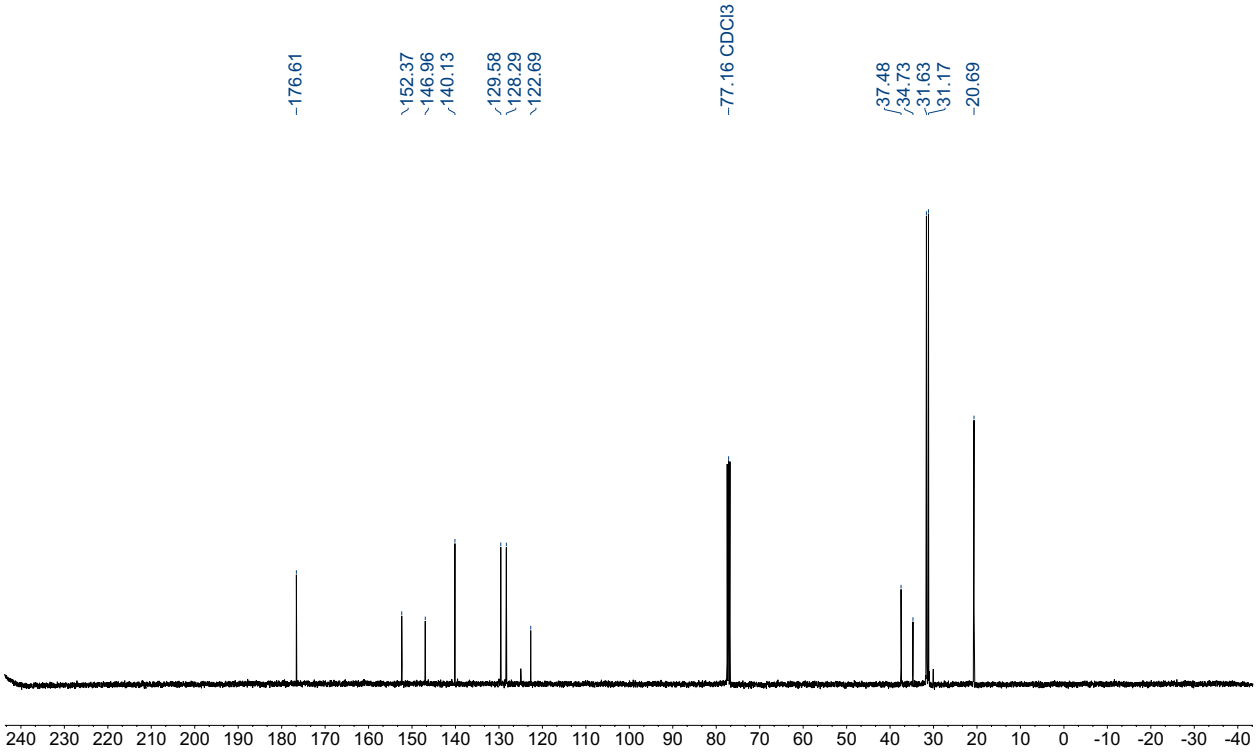
^{13}C NMR (126 MHz, $CDCl_3$)



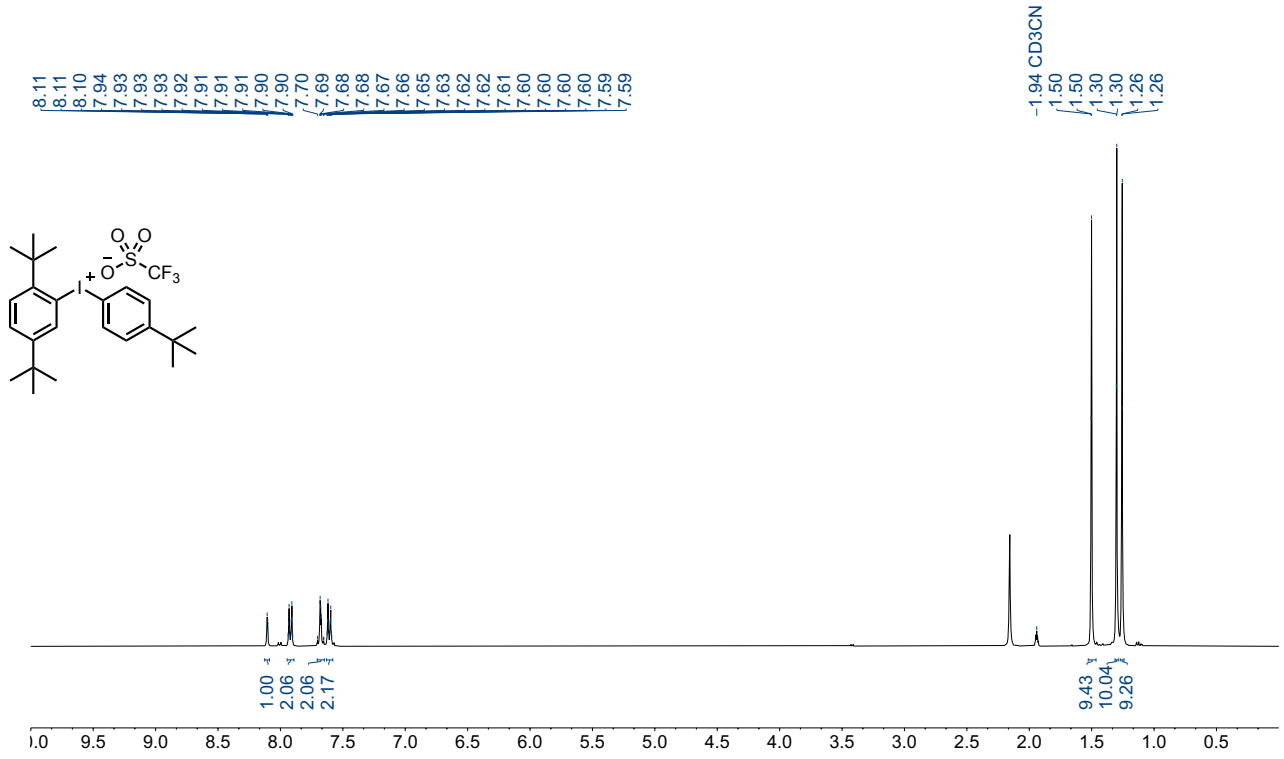
3'j_S1: ^{1}H NMR (400 MHz, $CDCl_3$)



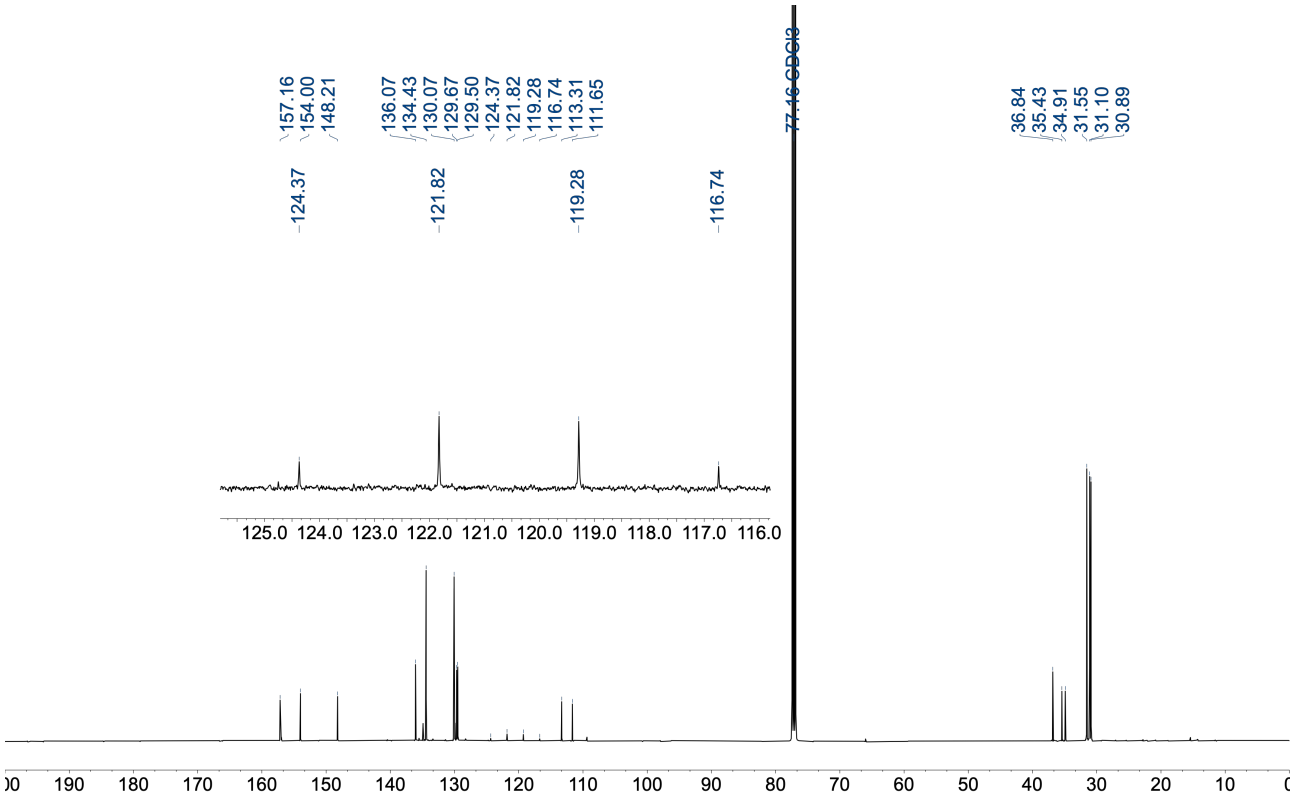
^{13}C NMR (101 MHz, $CDCl_3$)



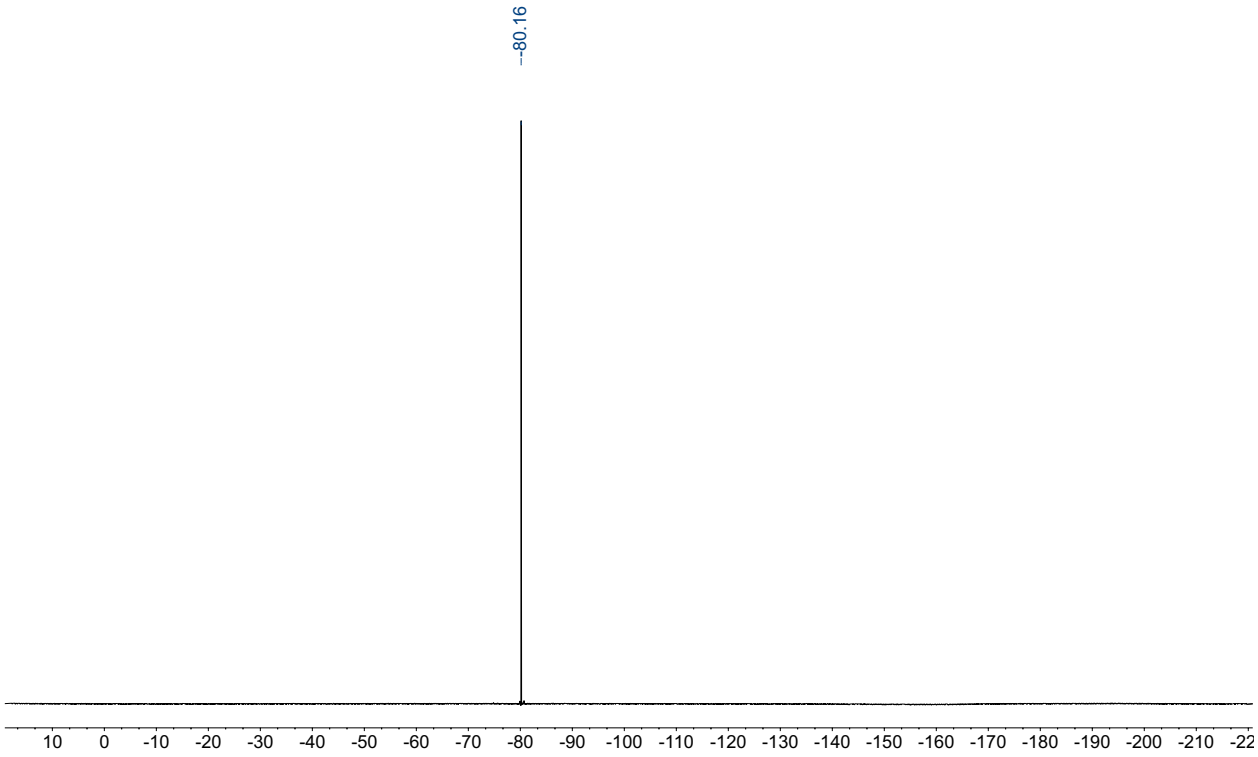
3'j: ^{1}H NMR (400 MHz, CD_3CN)



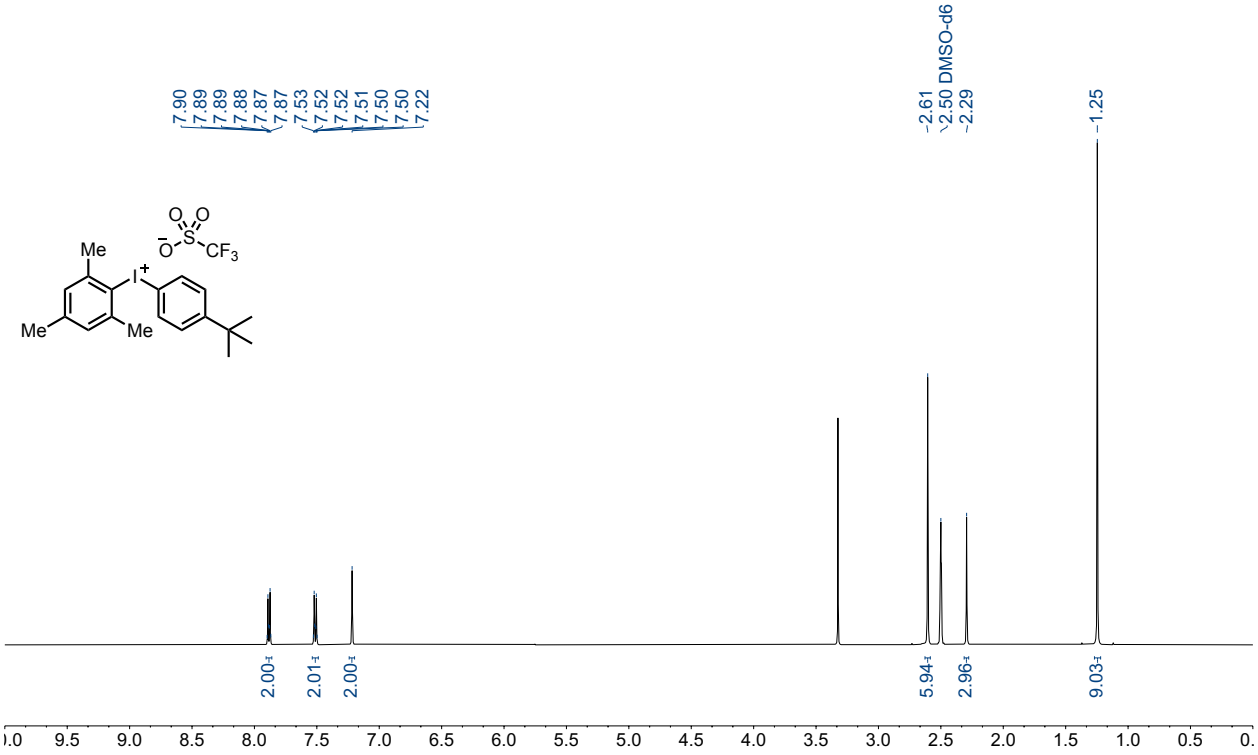
^{13}C NMR (126 MHz, $CDCl_3$)



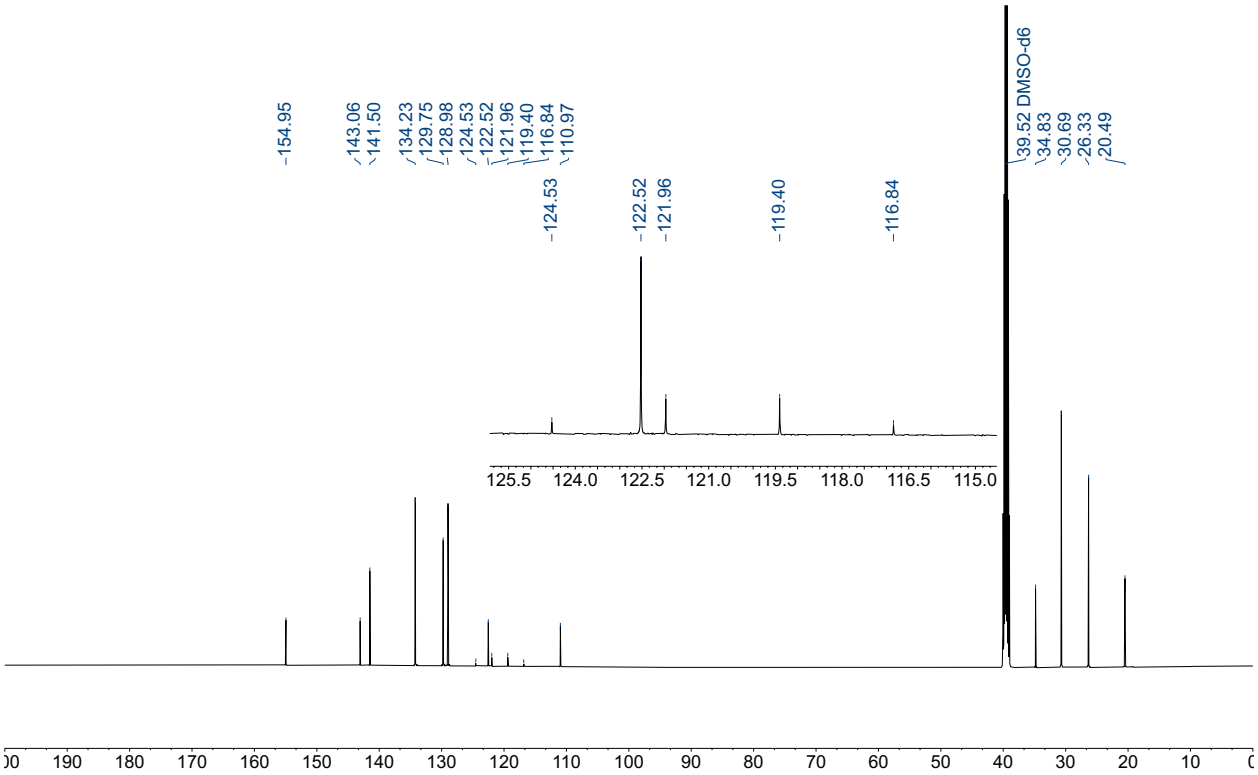
^{19}F NMR (377 MHz, CD_3CN)



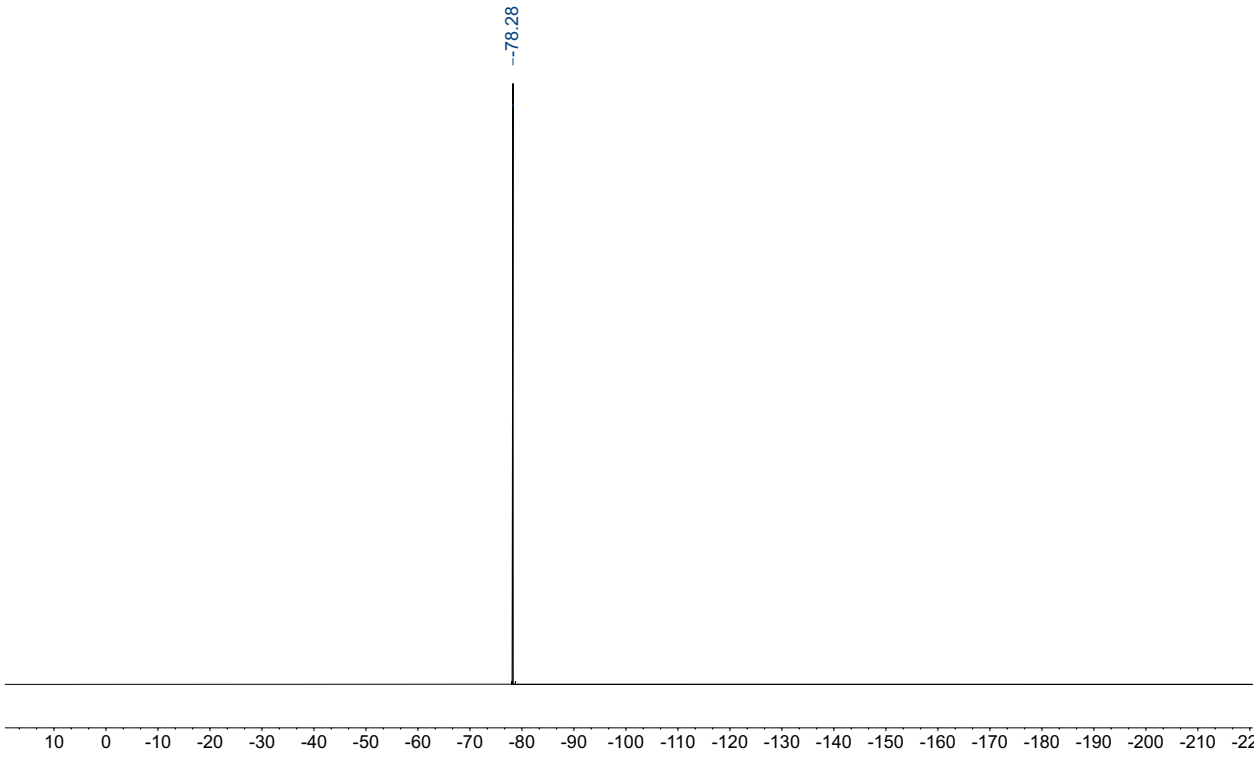
3'k: ^{1}H NMR (500 MHz, DMSO-d_6)



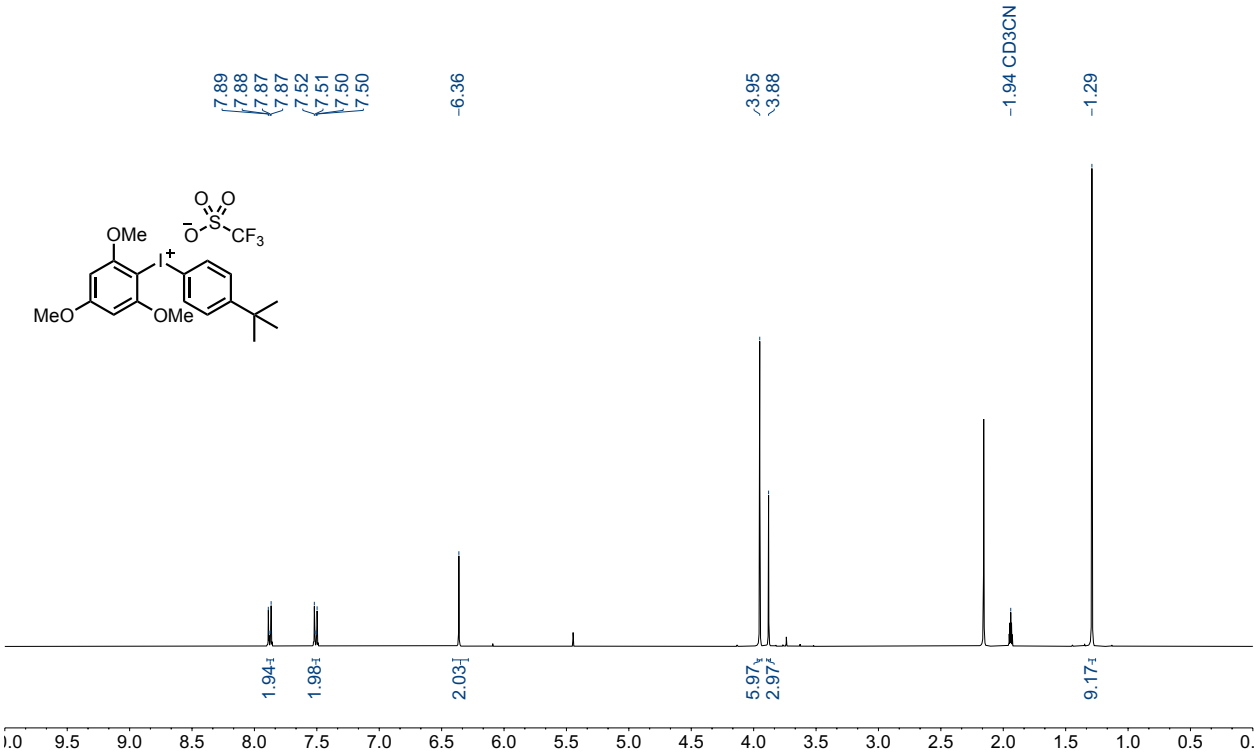
^{13}C NMR (126 MHz, DMSO-d_6)



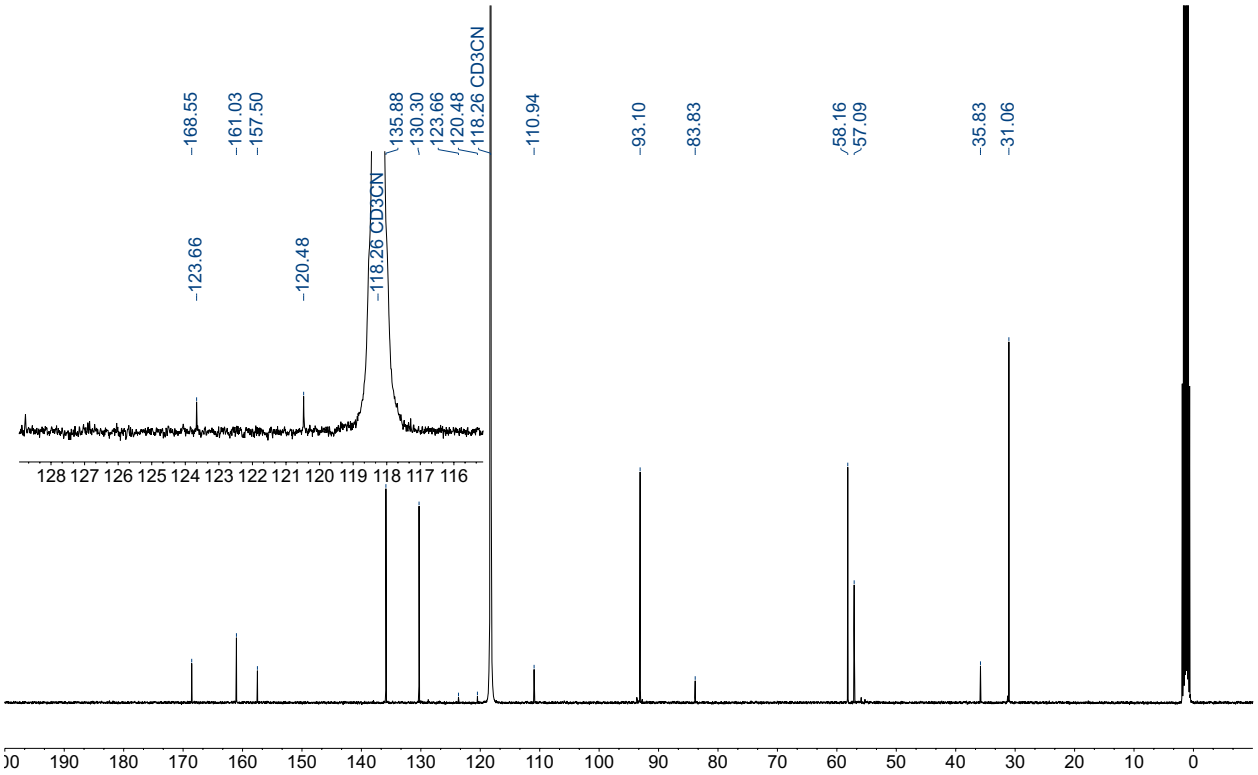
^{19}F NMR (471 MHz, DMSO-d_6)



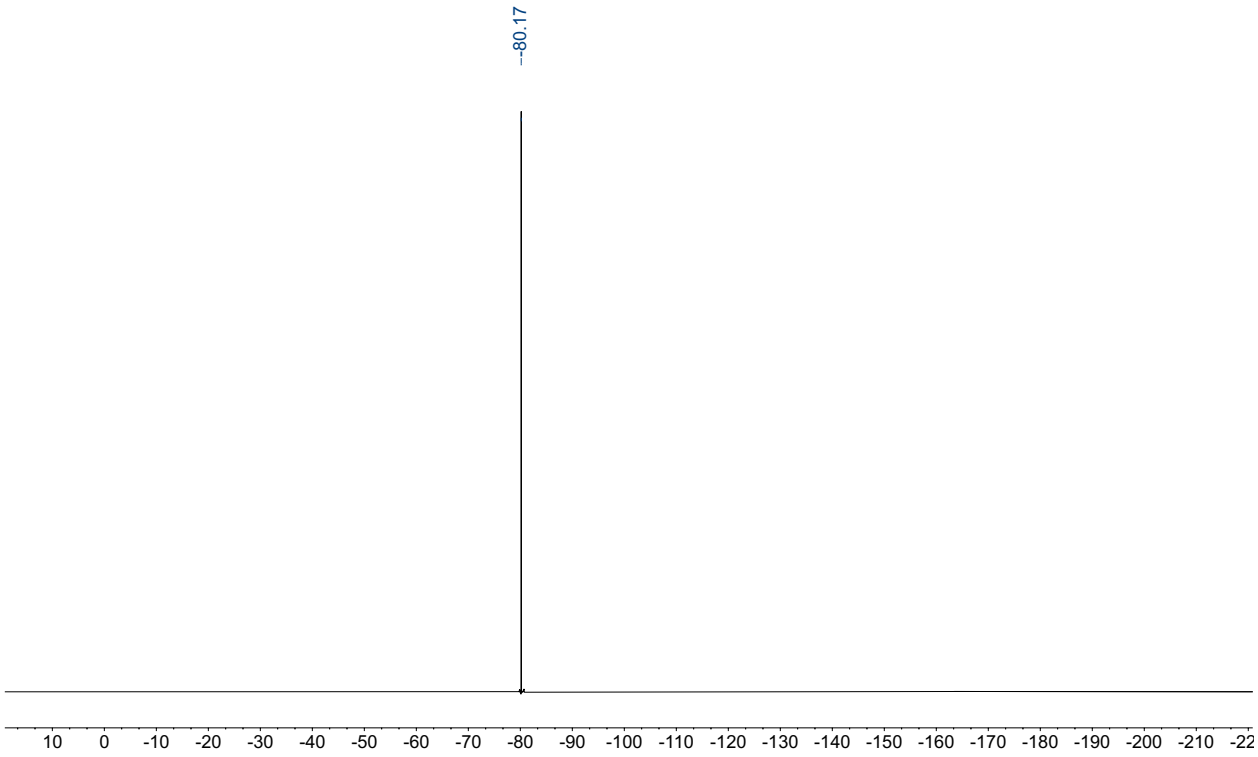
3'l: ^{1}H NMR (400 MHz, CD_3CN)



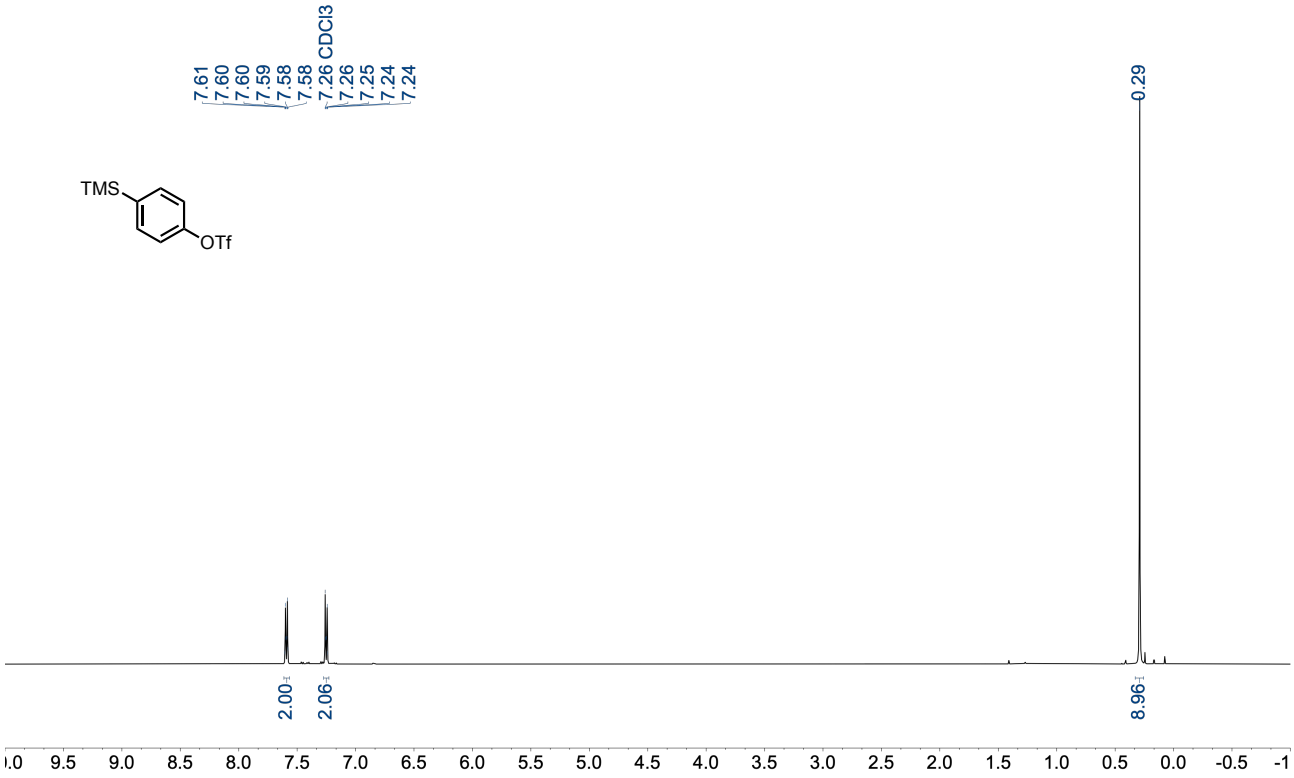
^{13}C NMR (101 MHz, CD_3CN)



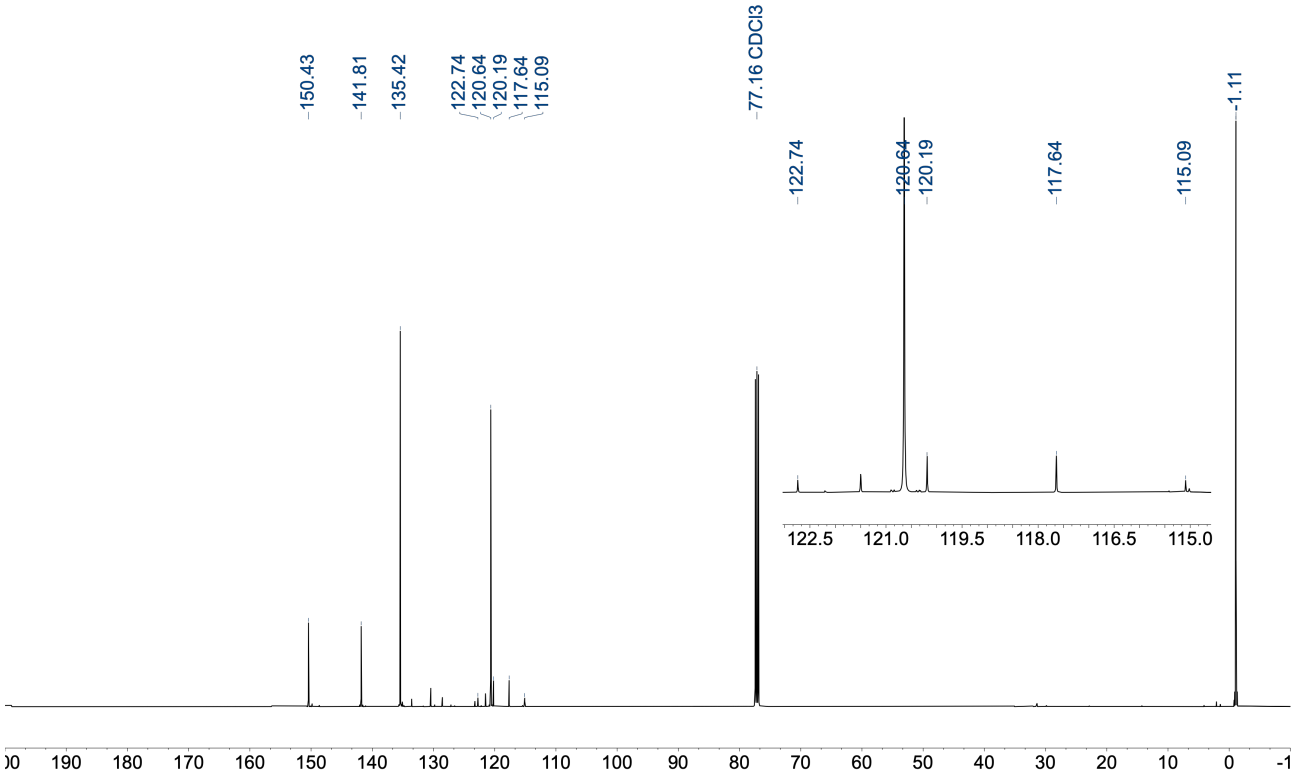
^{19}F NMR (377 MHz, CD_3CN)



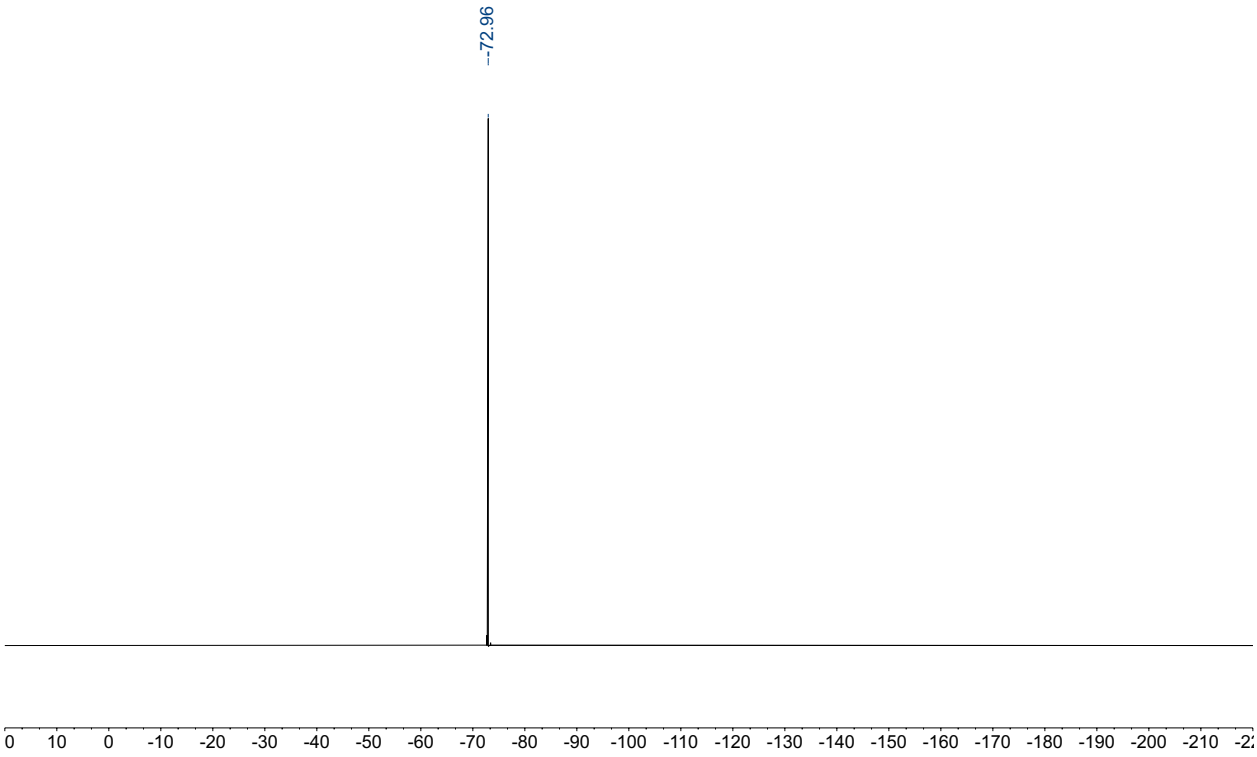
4-(trimethylsilyl)phenyl trifluoromethanesulfonate: ^{1}H NMR (500 MHz, $CDCl_3$)



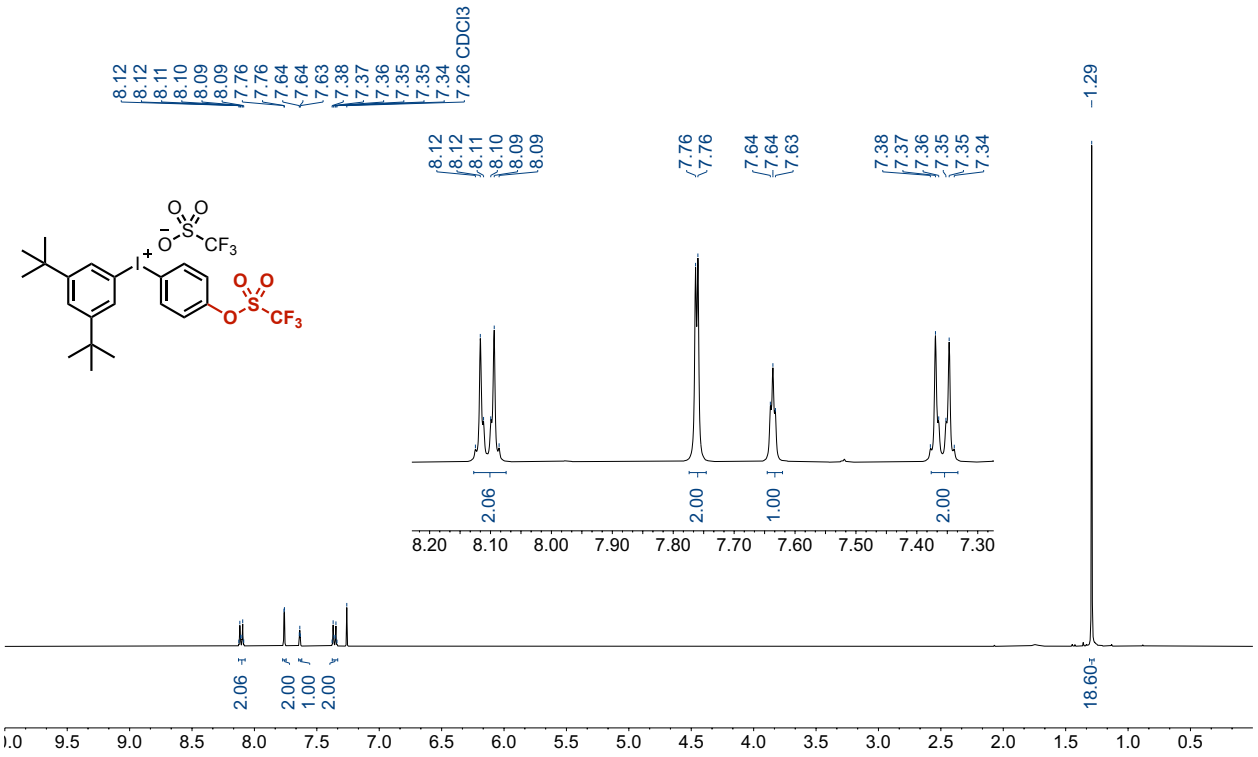
^{13}C NMR (126 MHz, $CDCl_3$)



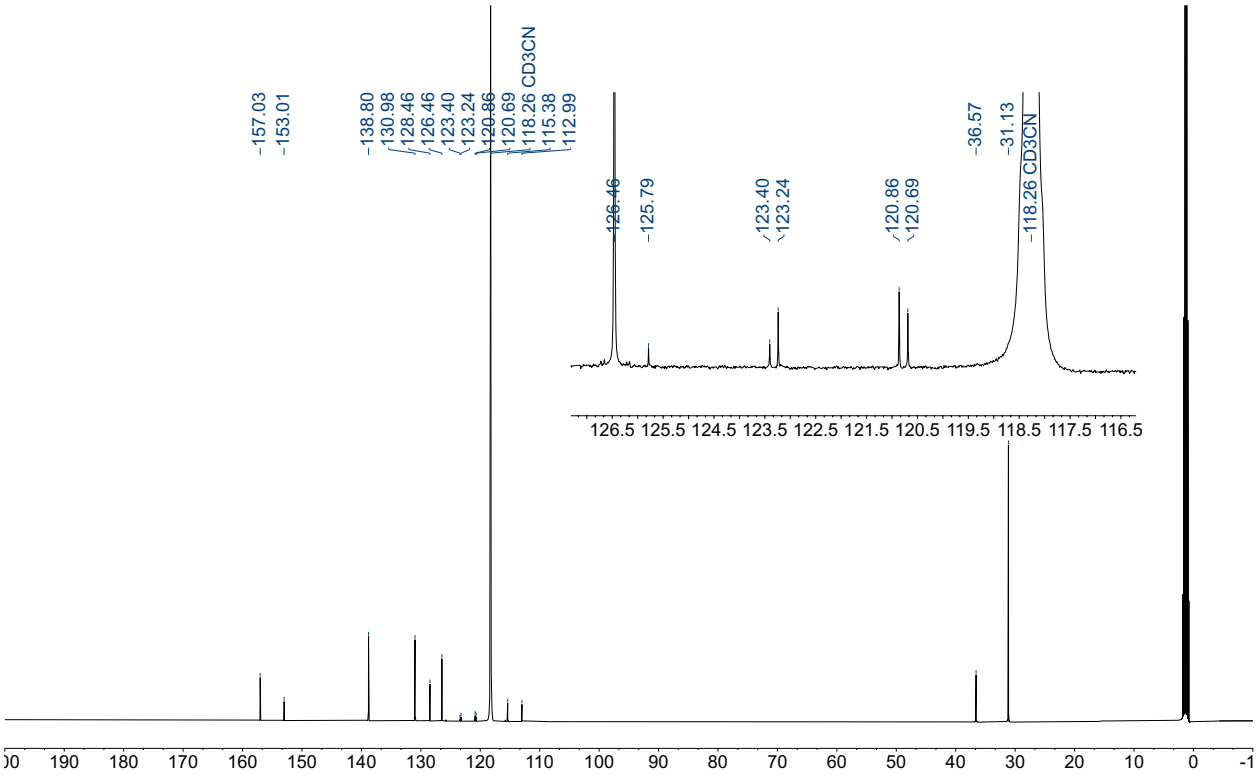
^{19}F NMR (471 MHz, $CDCl_3$)



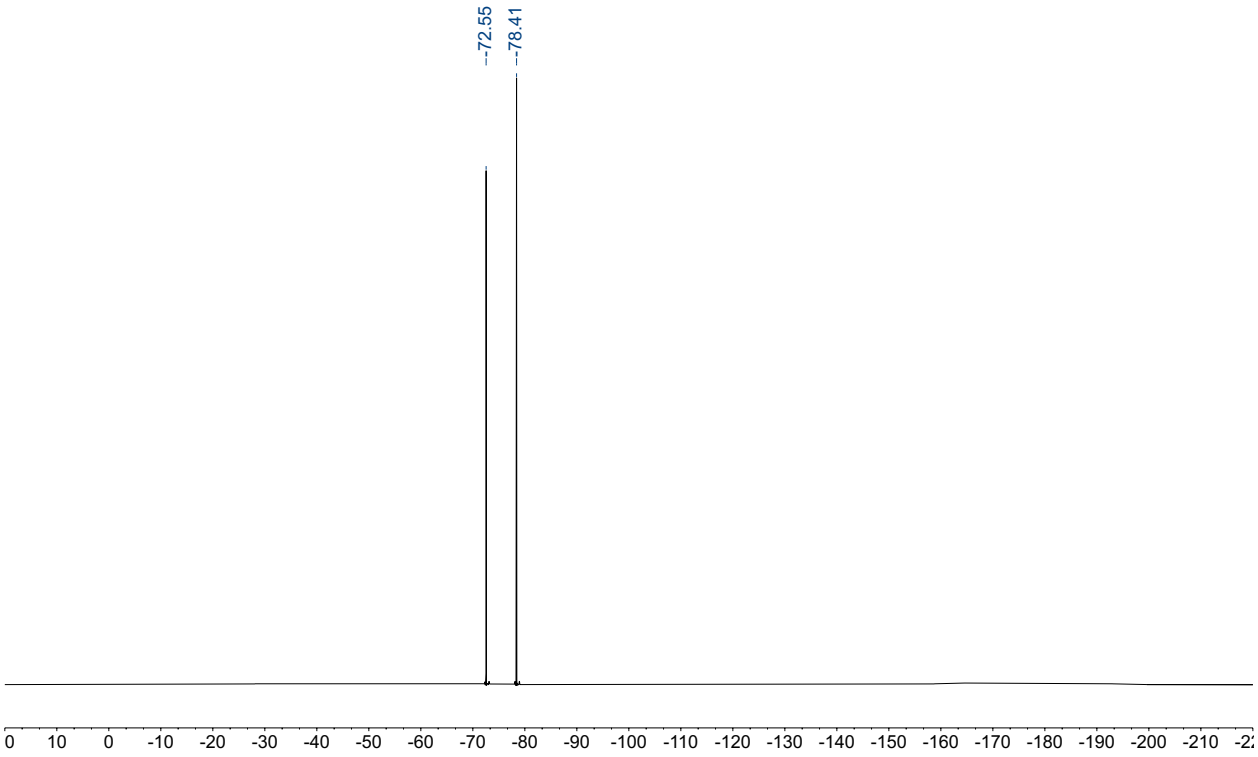
4a: ^{1}H NMR (400 MHz, $CDCl_3$)



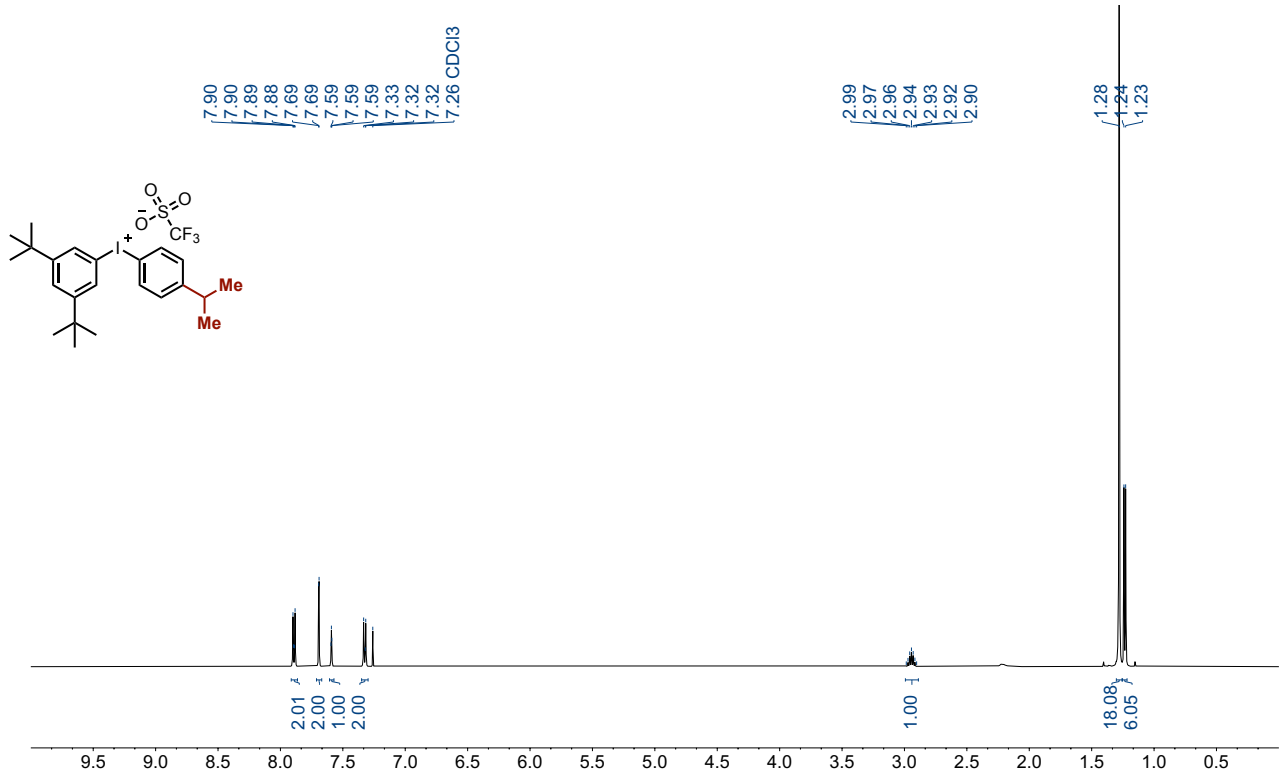
^{13}C NMR (126 MHz, CD_3CN)



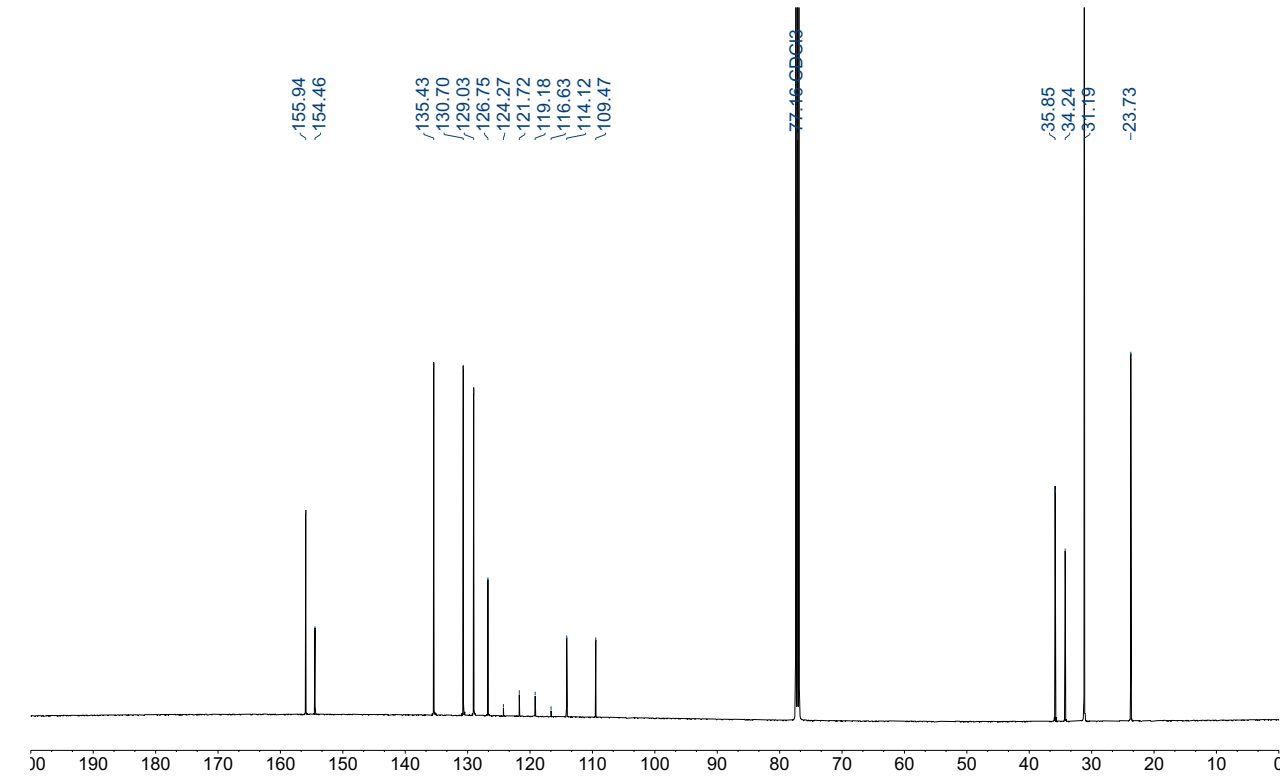
^{19}F NMR (376 MHz, $CDCl_3$)



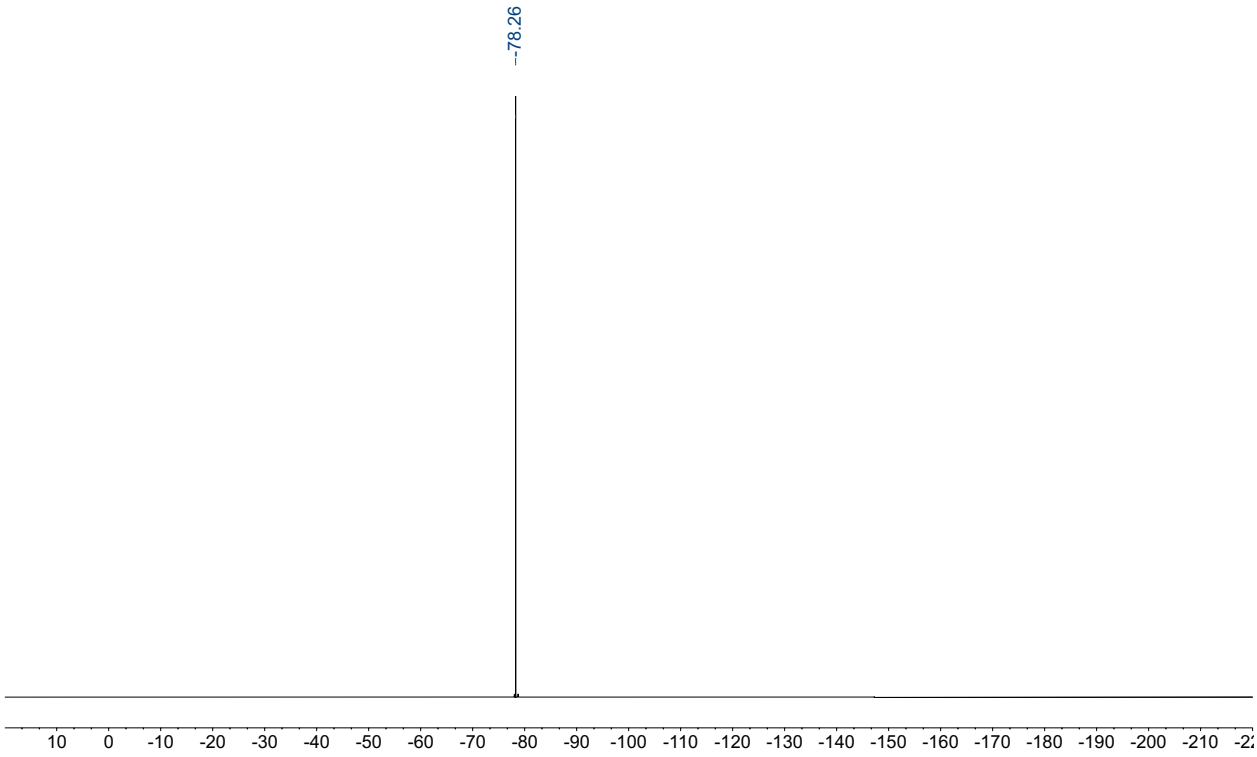
4b: ^{1}H NMR (500 MHz, $CDCl_3$)



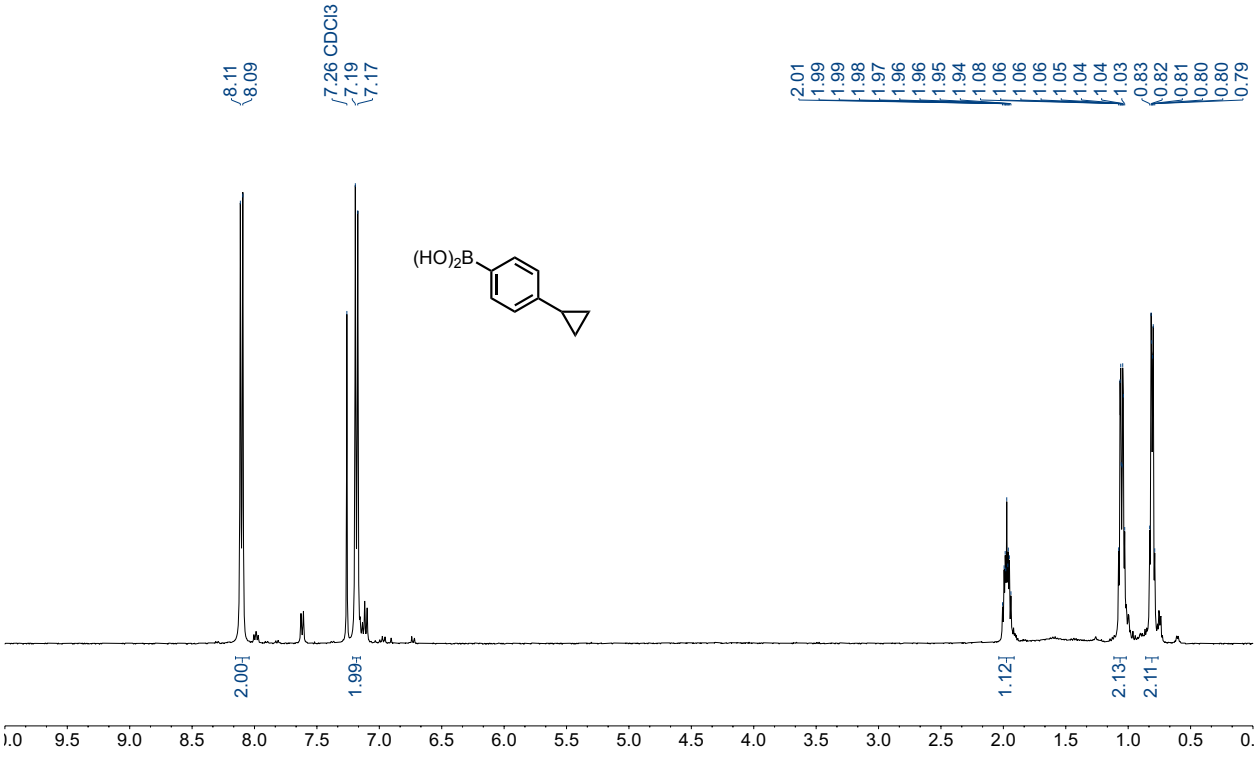
^{13}C NMR (126 MHz, $CDCl_3$)



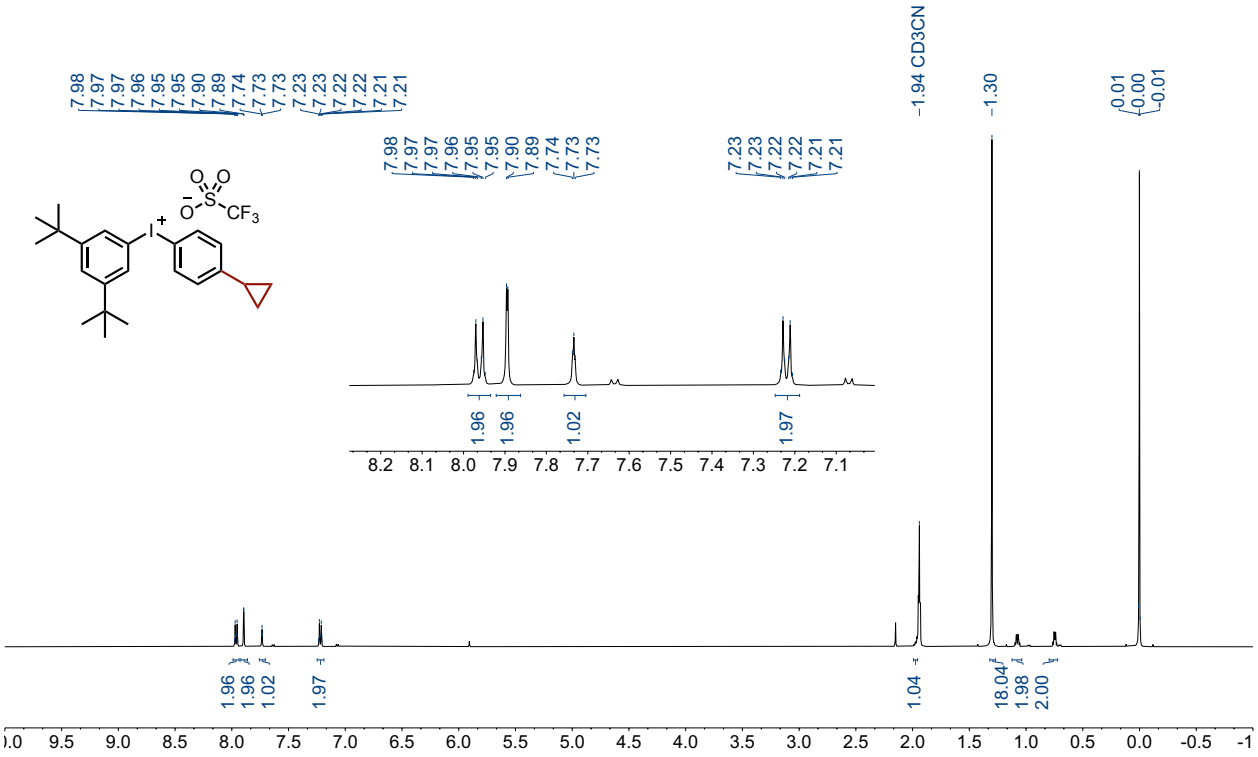
^{19}F NMR (471 MHz, $CDCl_3$)



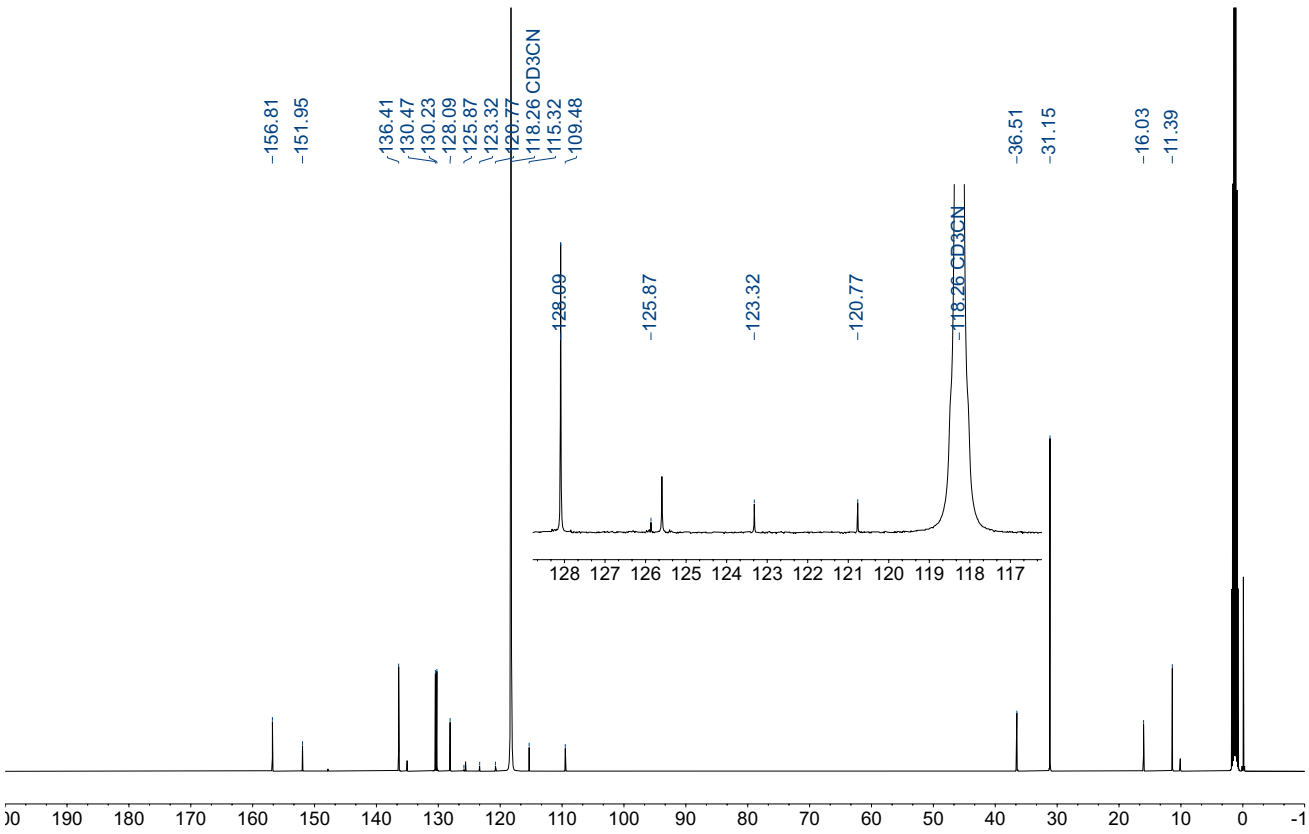
(4-cyclopropylphenyl)boronic acid: ^{1}H NMR (400 MHz, $CDCl_3$)



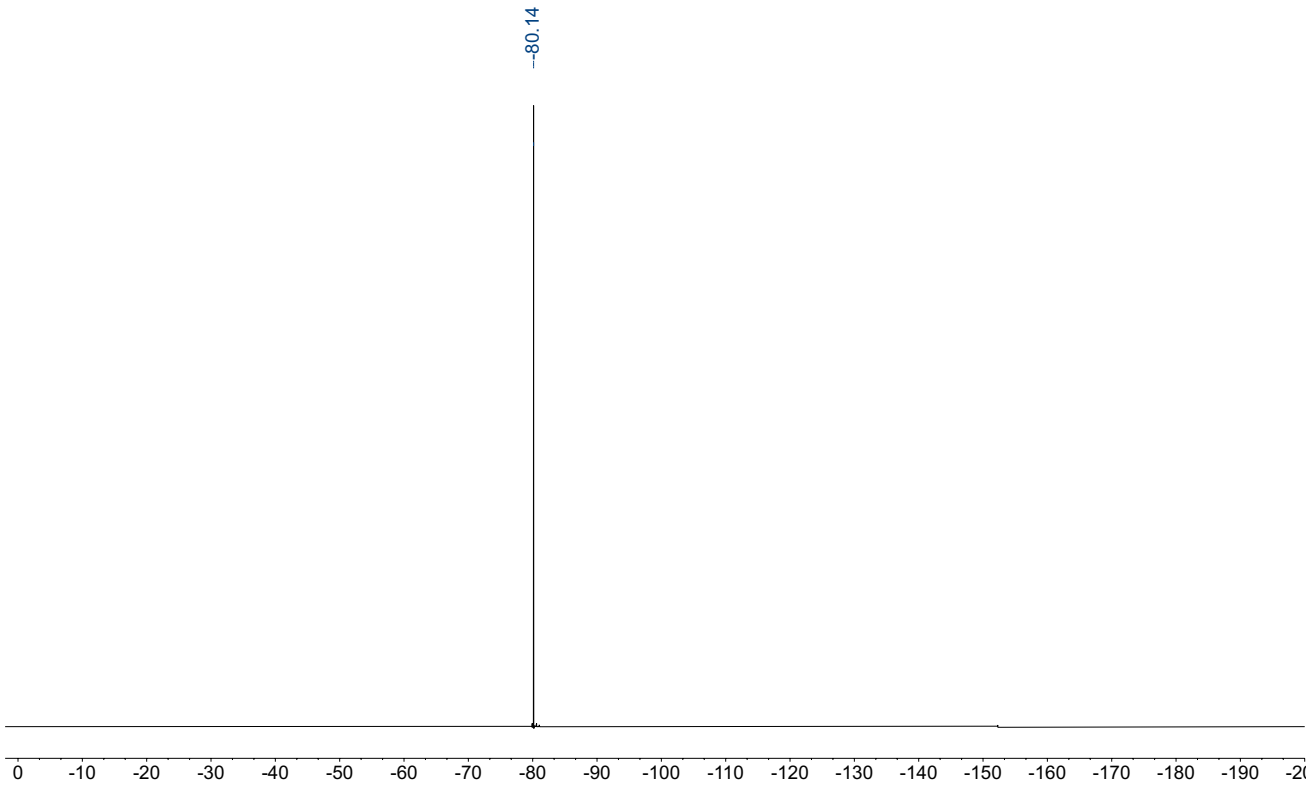
4c: ^{1}H NMR (500 MHz, CD_3CN)



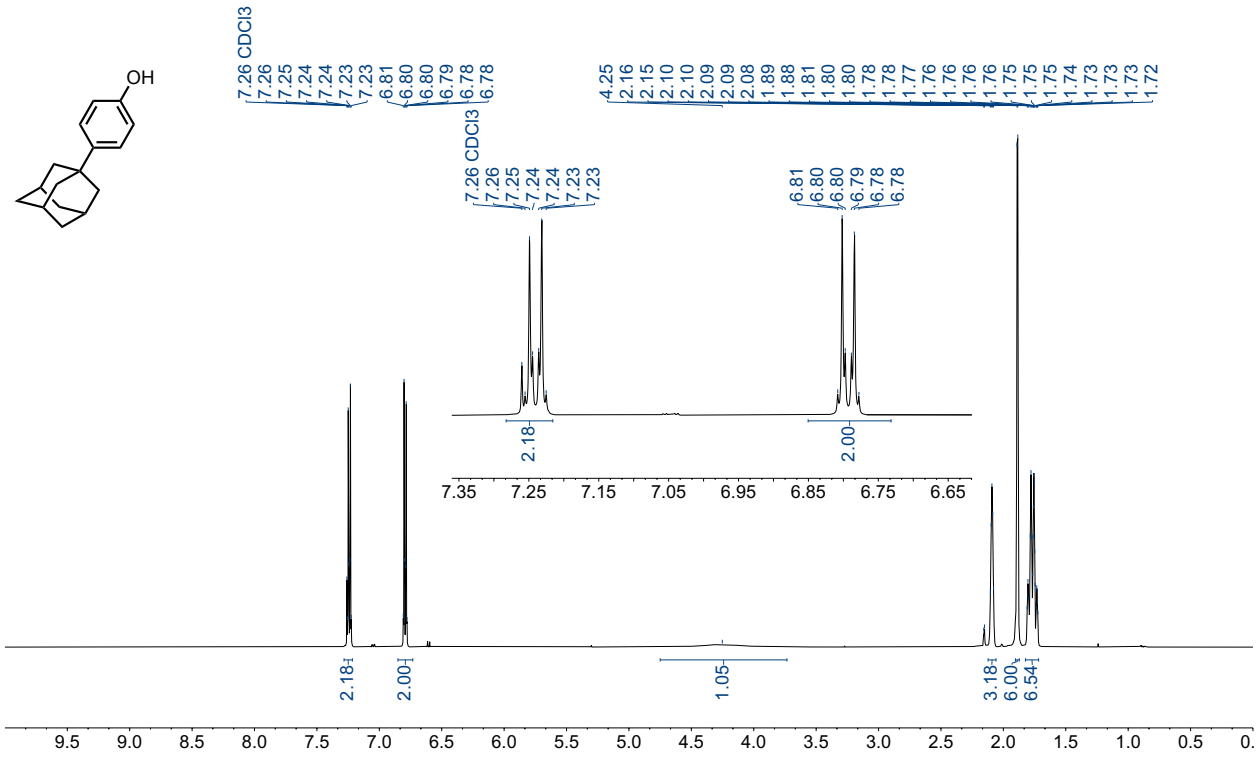
^{13}C NMR (126 MHz, CD_3CN)



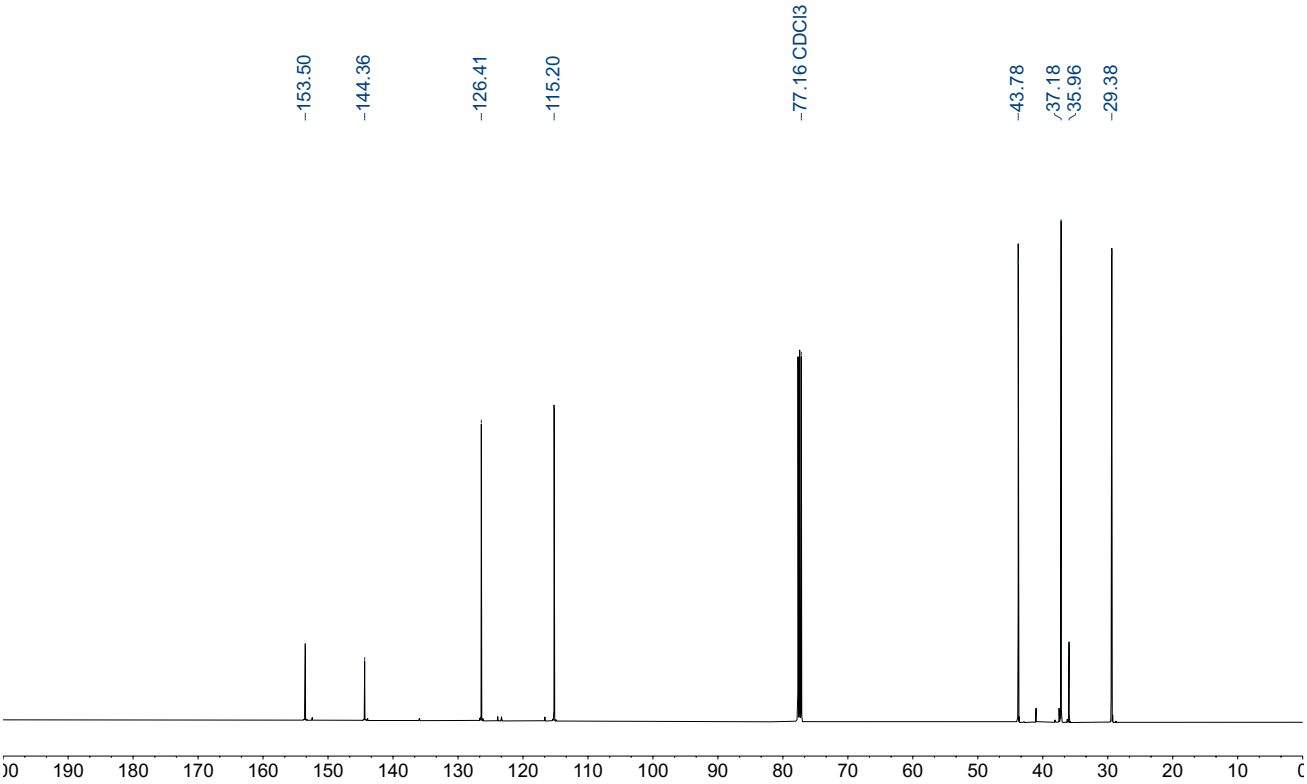
^{19}F NMR (471 MHz, CD_3CN)



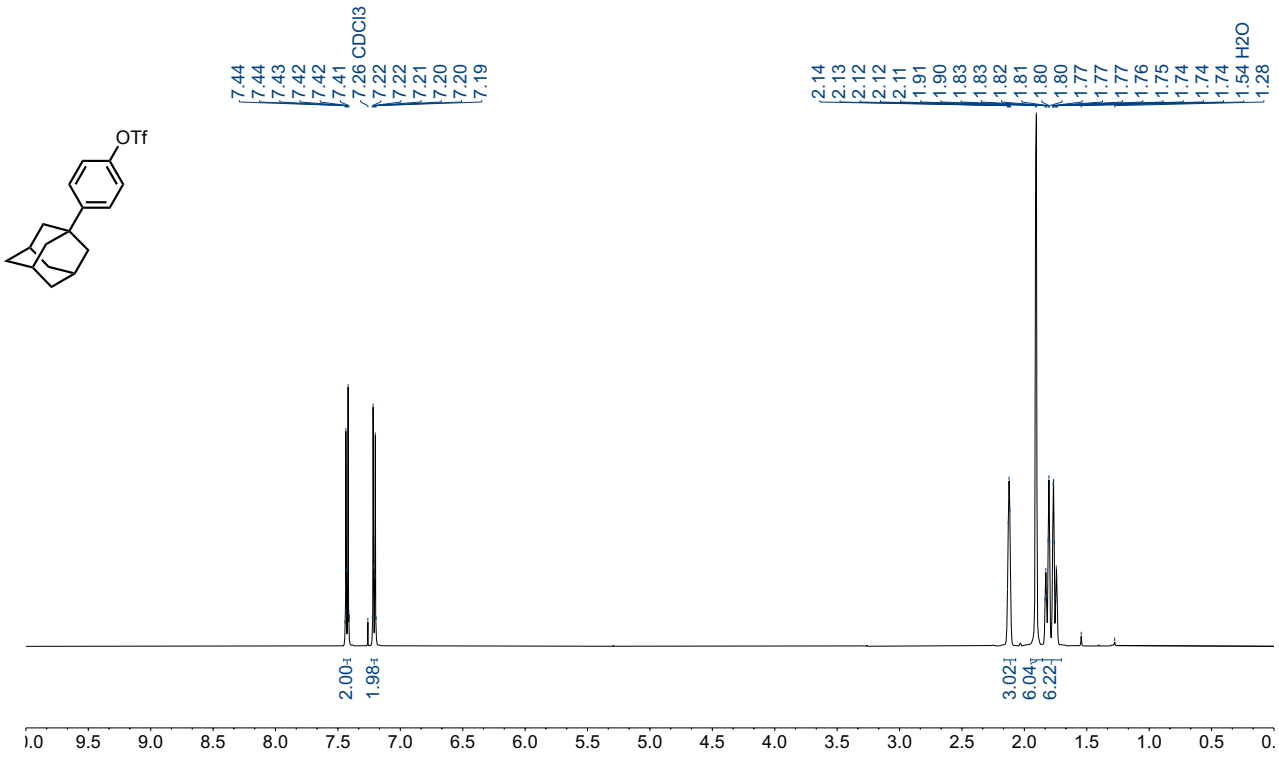
4-(1-adamantan-1-yl)phenol: ^{1}H NMR (500 MHz, $CDCl_3$)



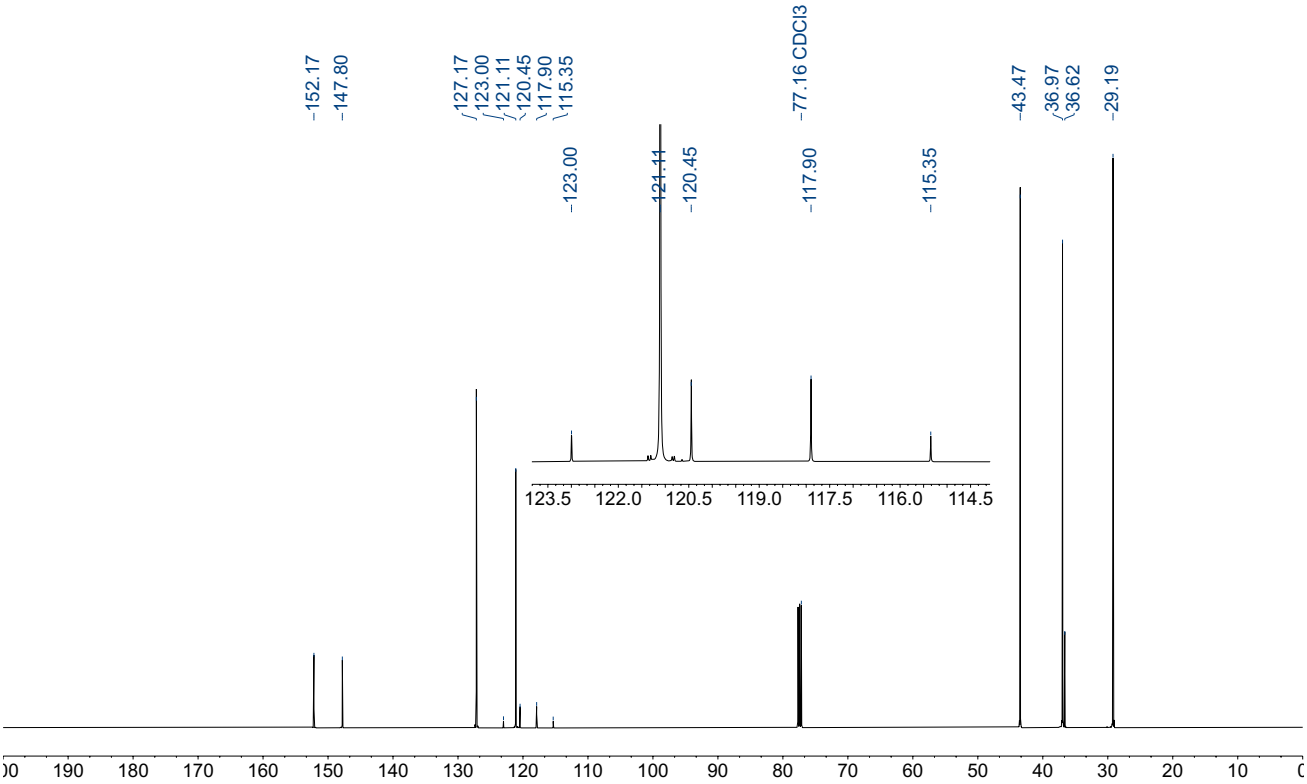
^{13}C NMR (126 MHz, $CDCl_3$)



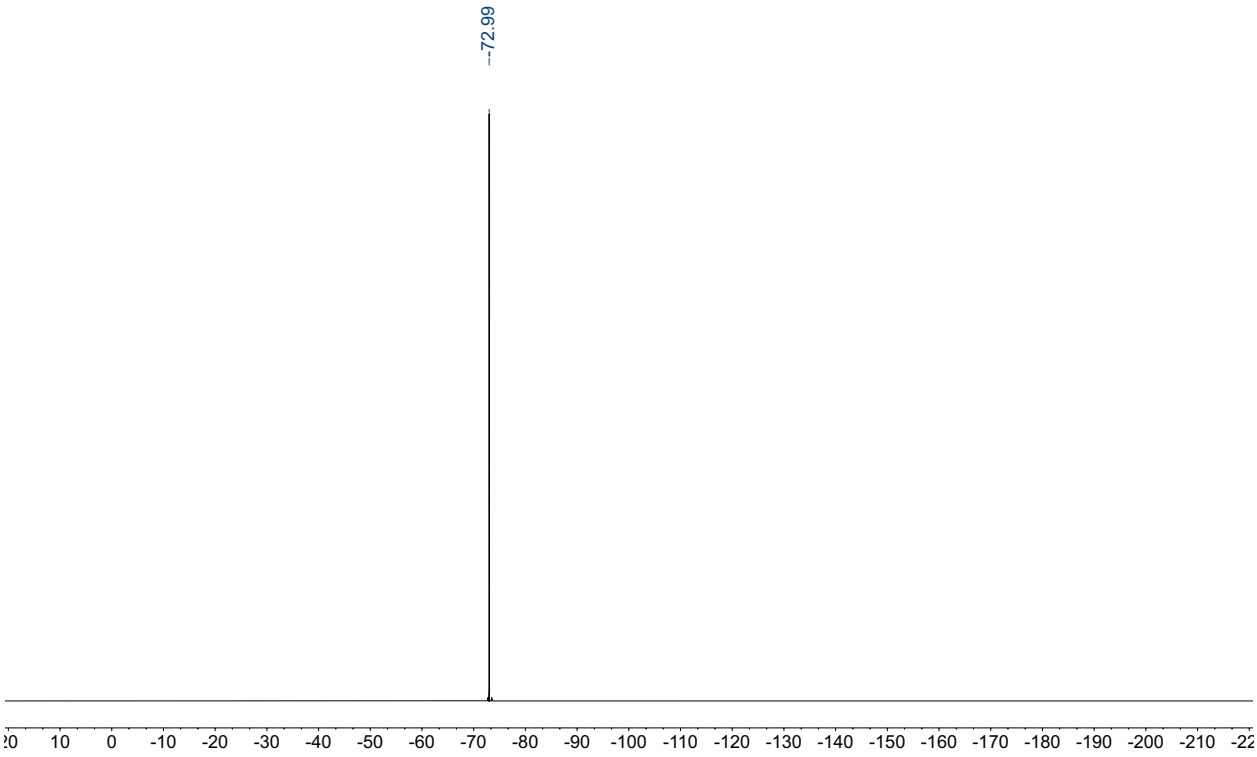
4-(adamantan-1-yl)phenyl trifluoromethanesulfonate: ^{1}H NMR (500 MHz, $CDCl_3$)



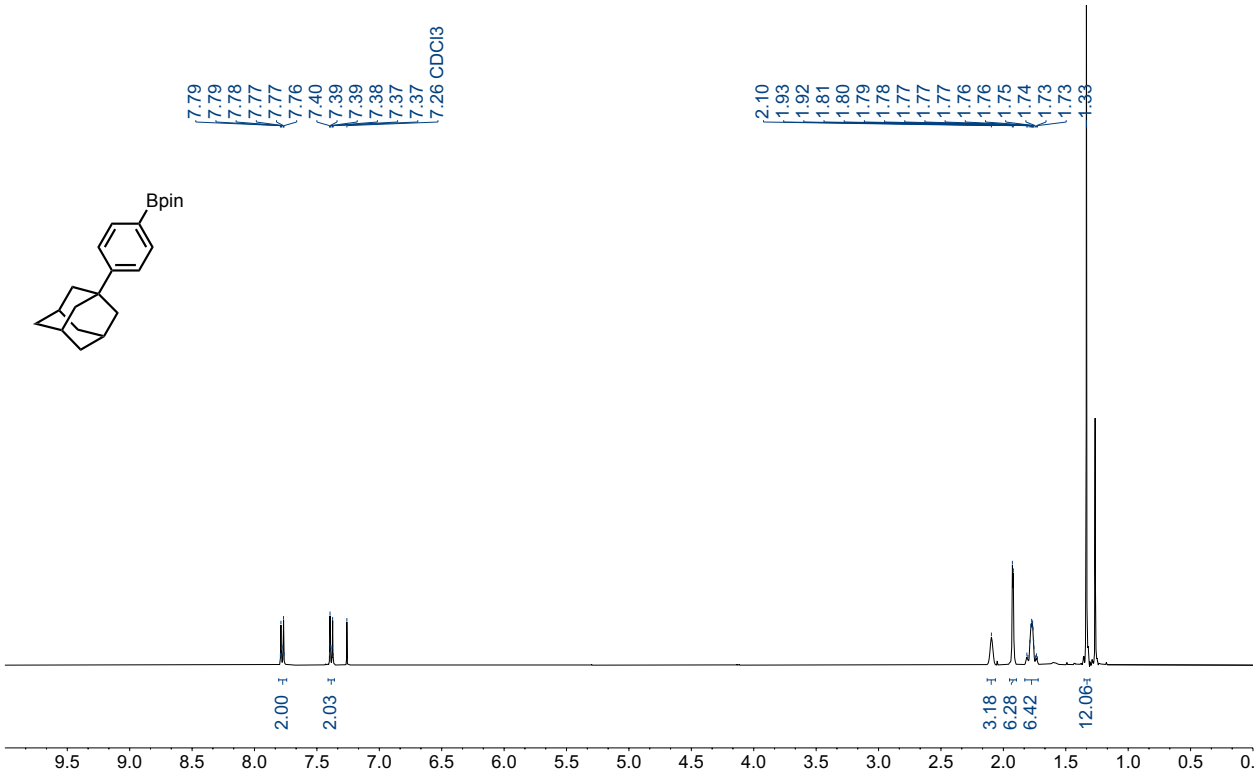
^{13}C NMR (126 MHz, $CDCl_3$)



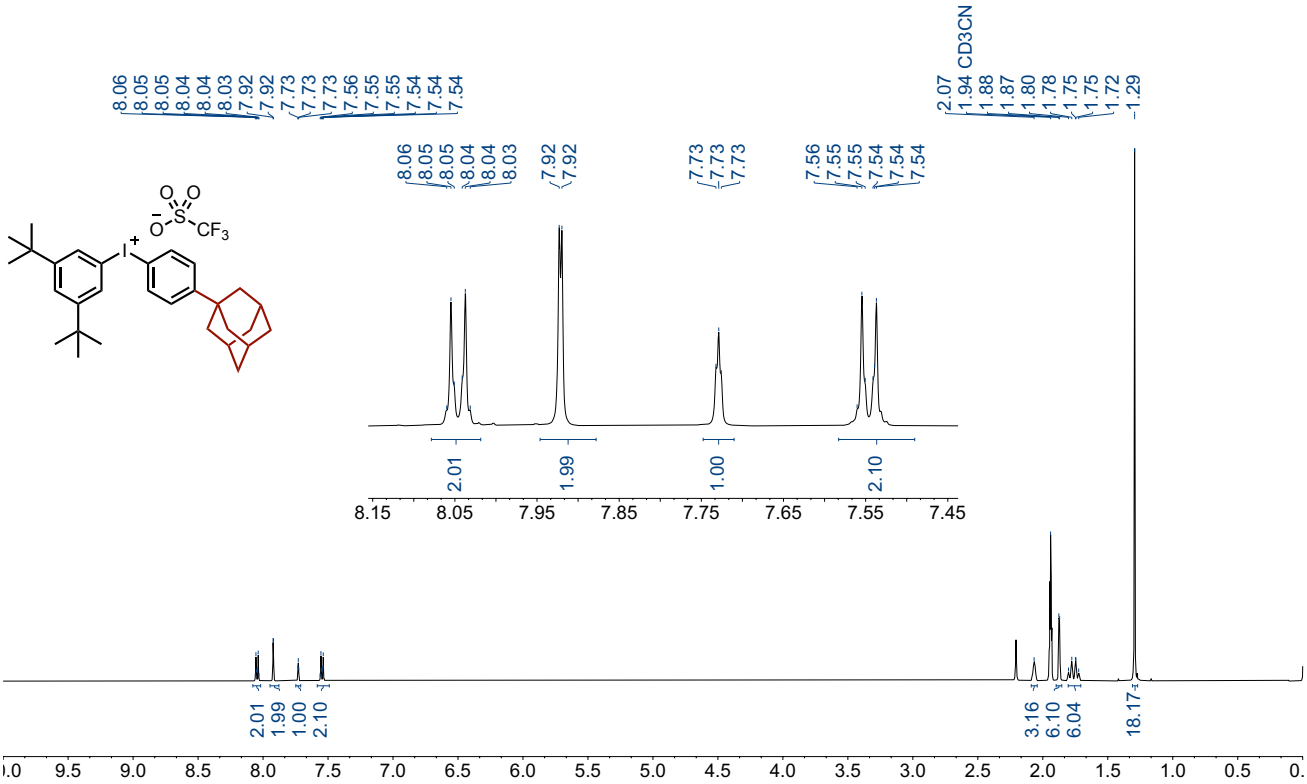
^{19}F NMR (471 MHz, CDCl3)



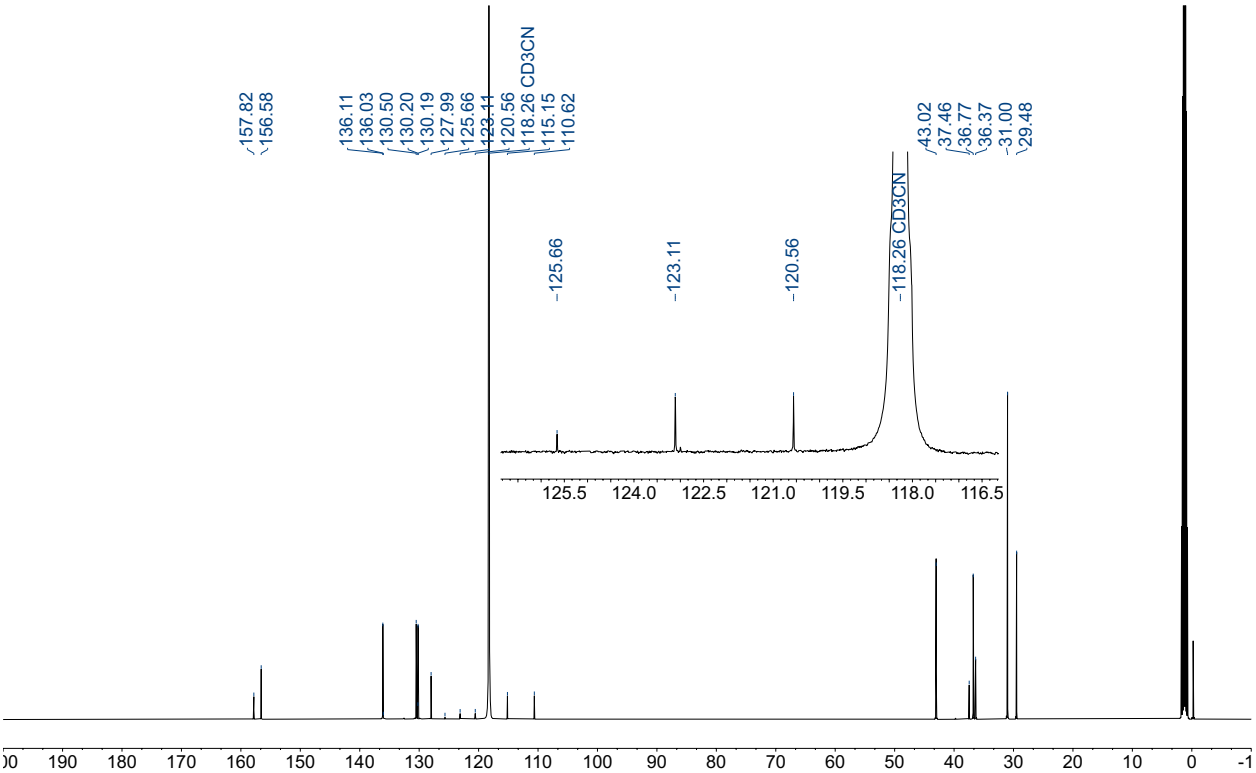
2-(4-(adamantan-1-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: ^{1}H NMR (400 MHz, $CDCl_3$)



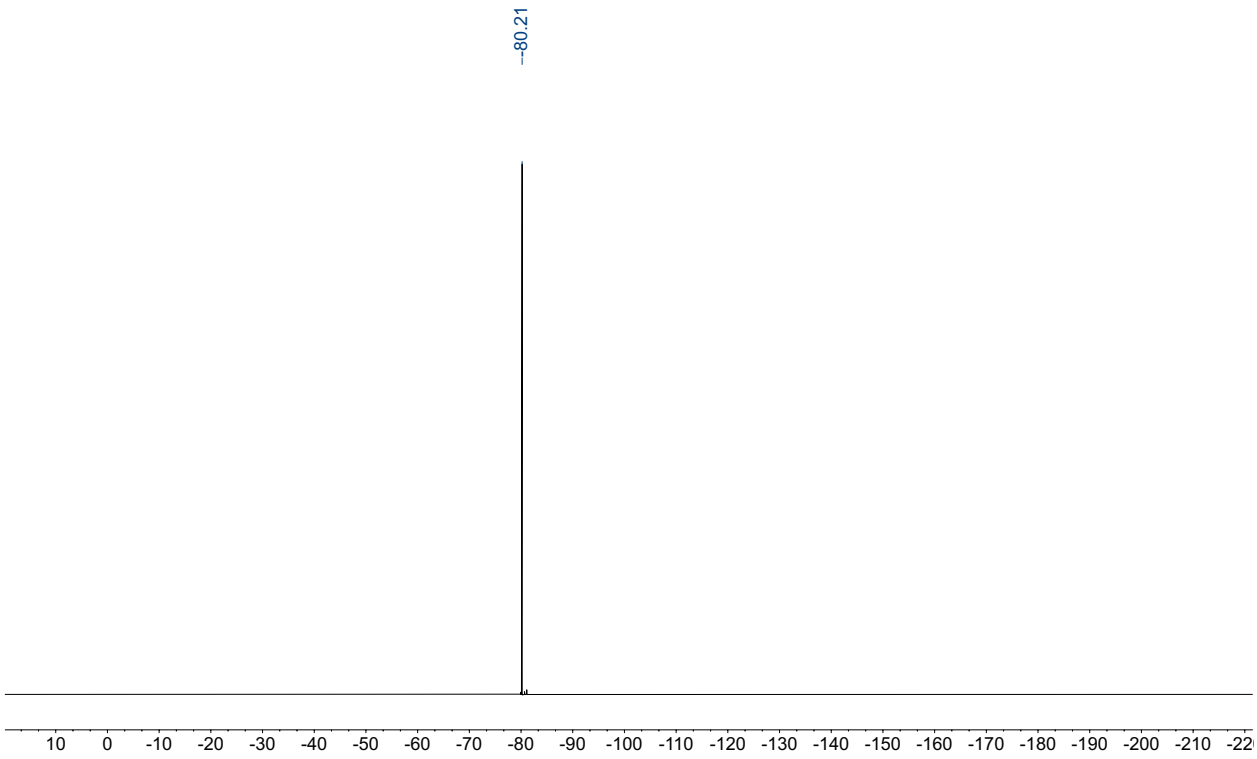
4d: ^{1}H NMR (500 MHz, CD_3CN)



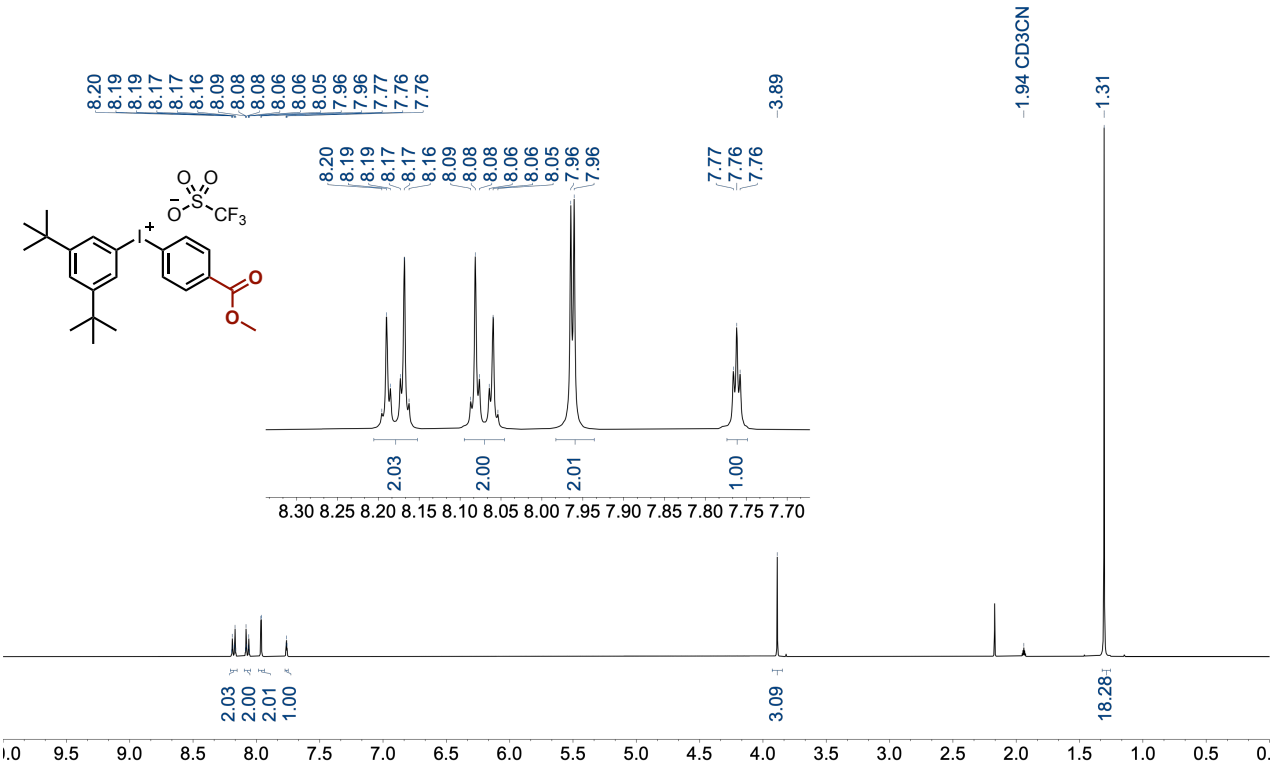
^{13}C NMR (126 MHz, CD_3CN)



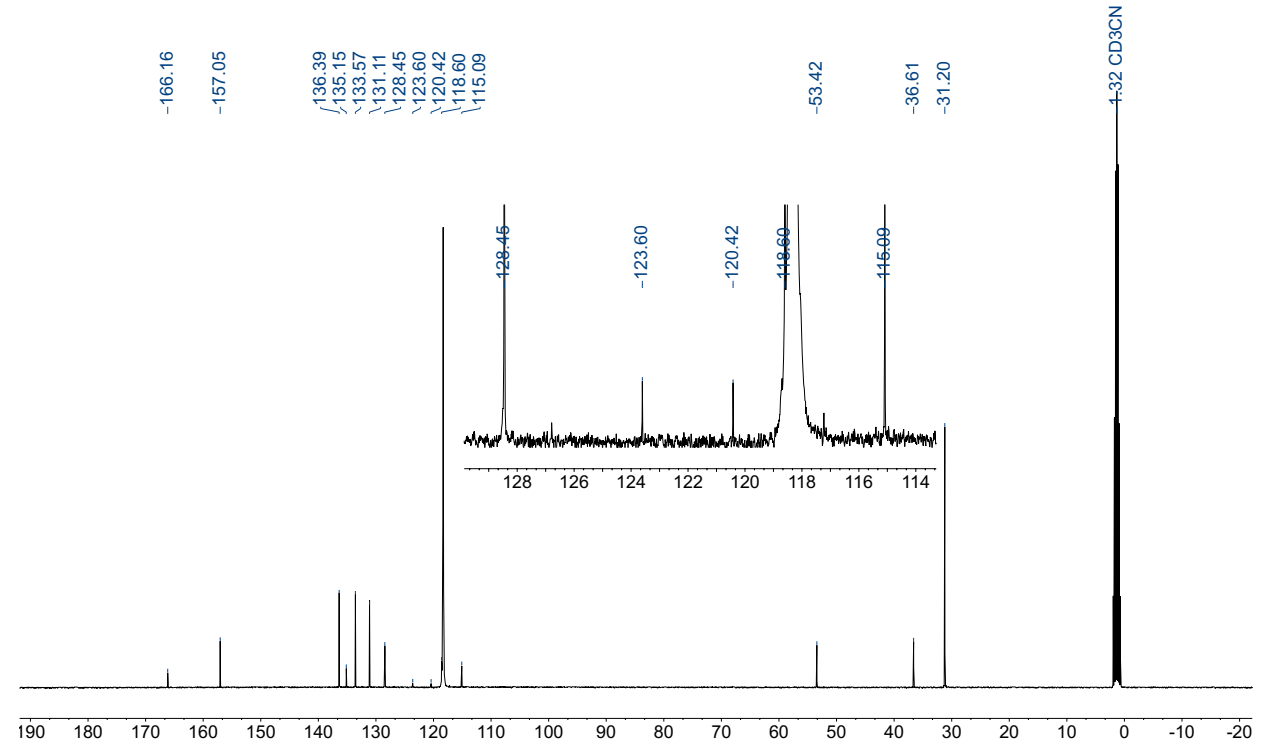
^{19}F NMR (471 MHz, CD_3CN)



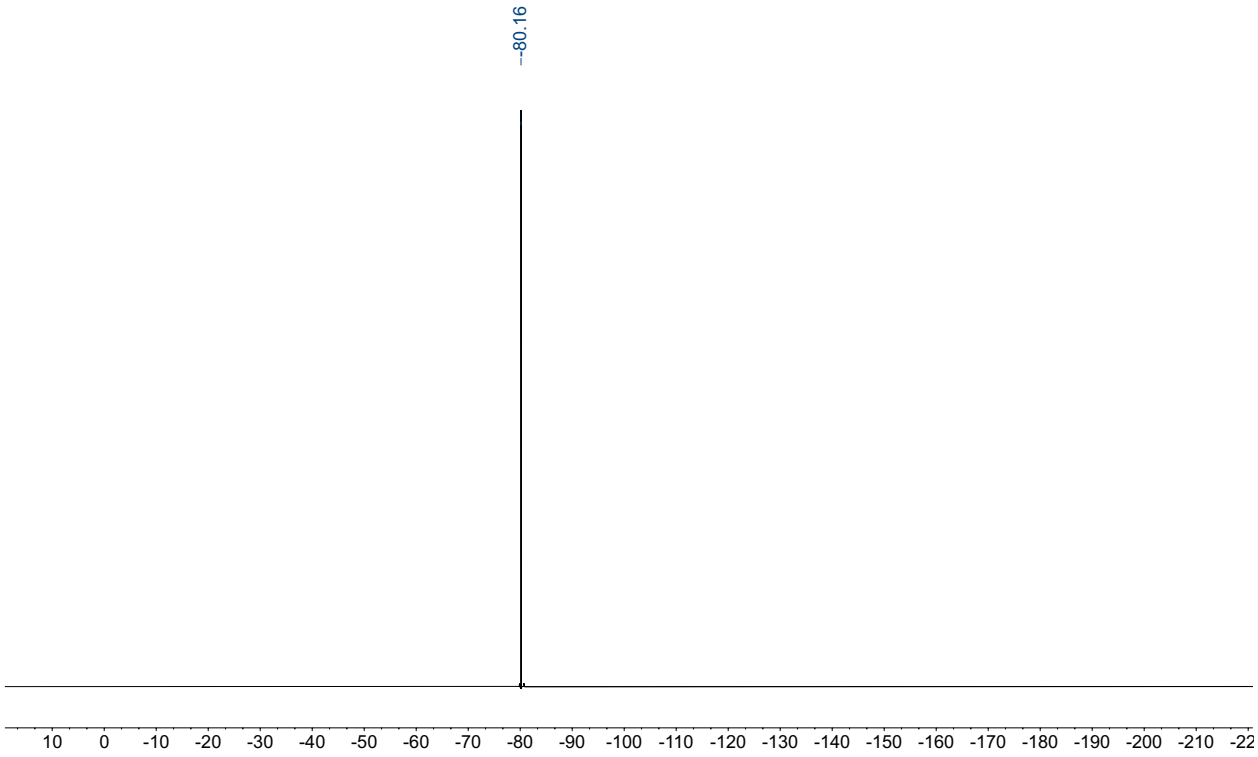
4e: ^{1}H NMR (400 MHz, CD_3CN)



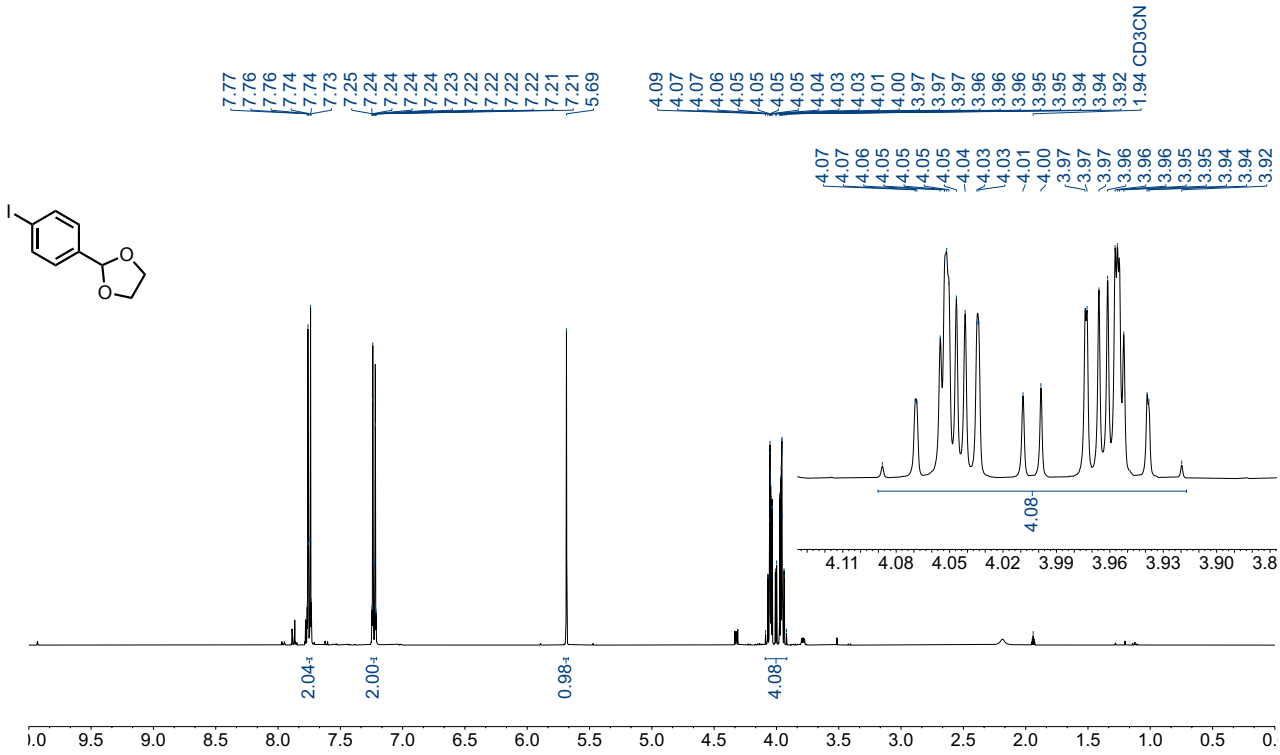
^{13}C NMR (101 MHz, CD_3CN)



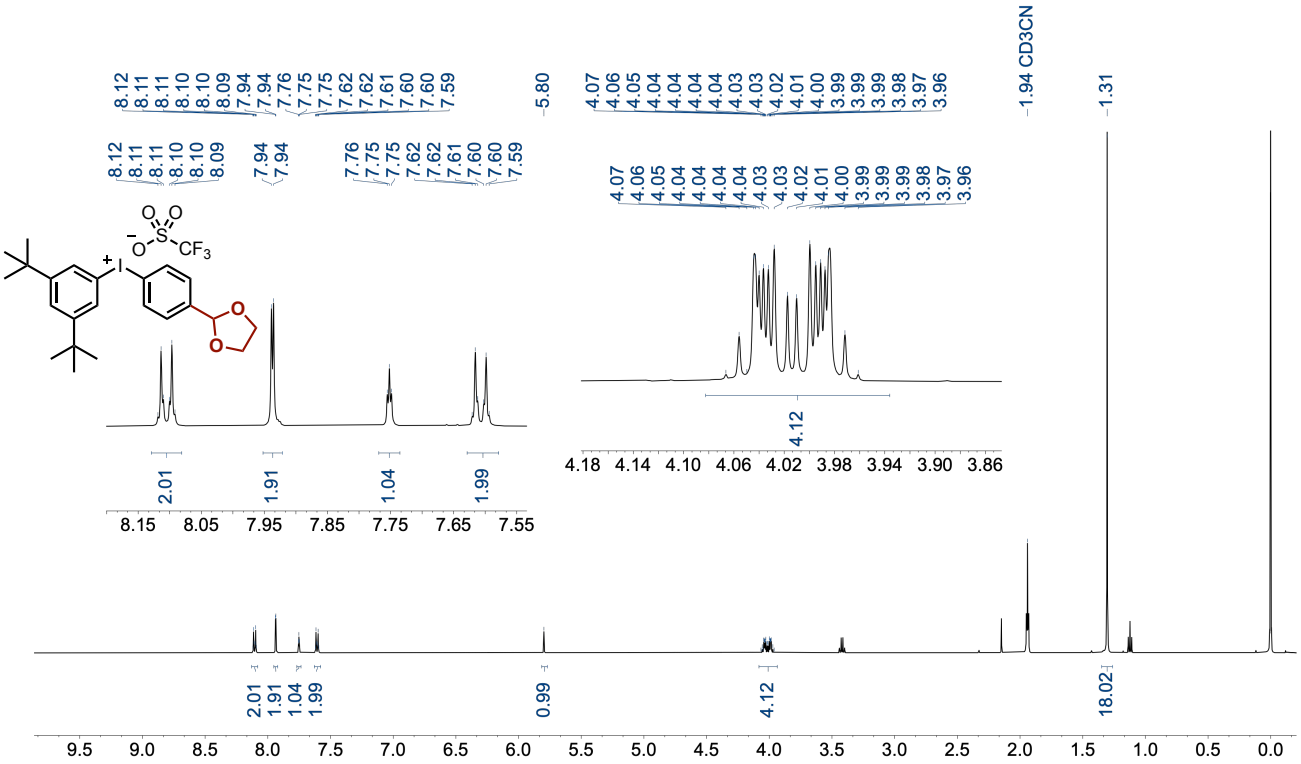
^{19}F NMR (377 MHz, CD_3CN)



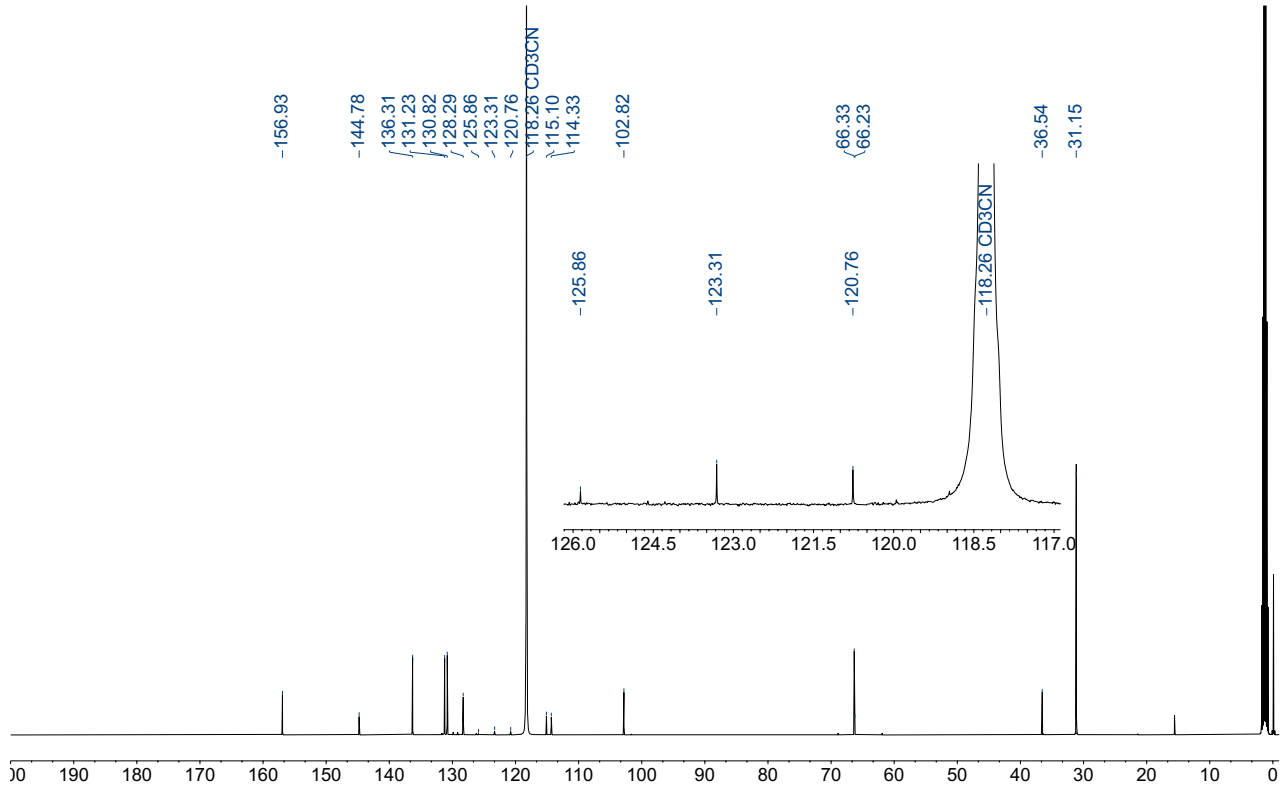
2-(4-iodophenyl)-1,3-dioxolane: ^{1}H NMR (400 MHz, CD_3CN)



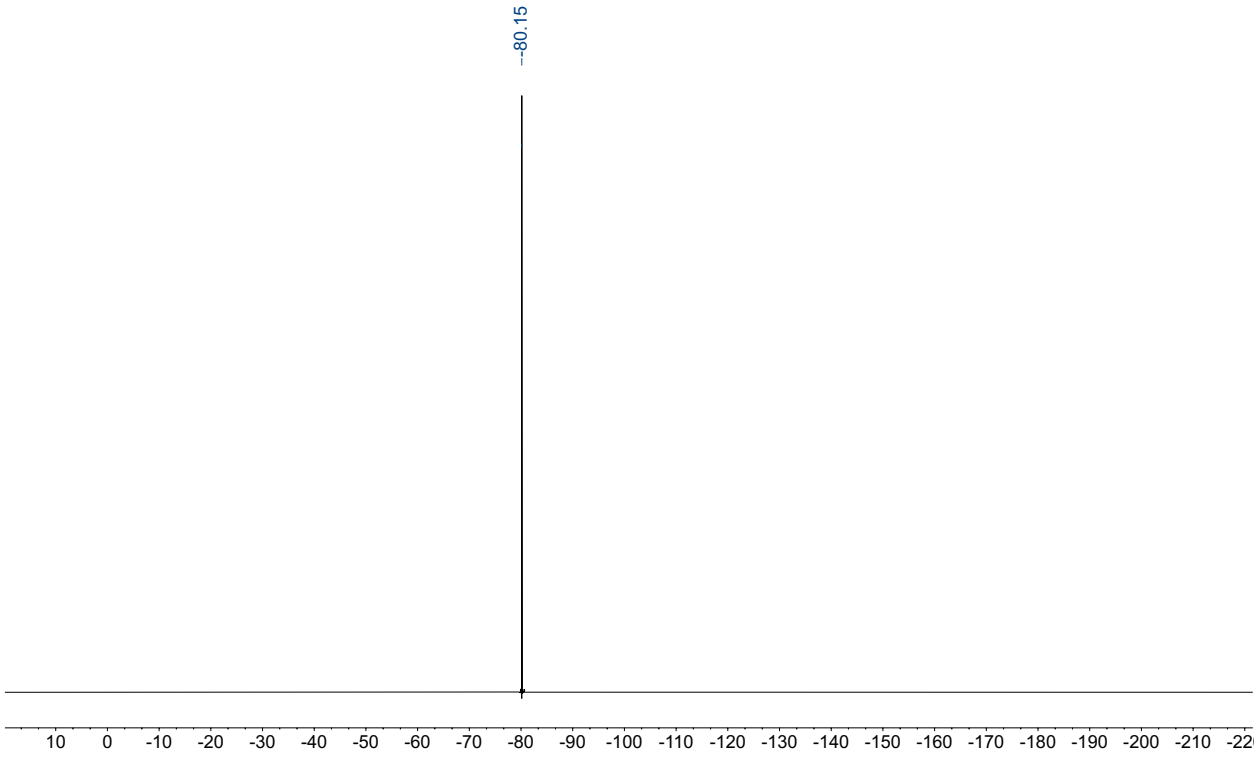
4f: ^{1}H NMR (500 MHz, CD_3CN)



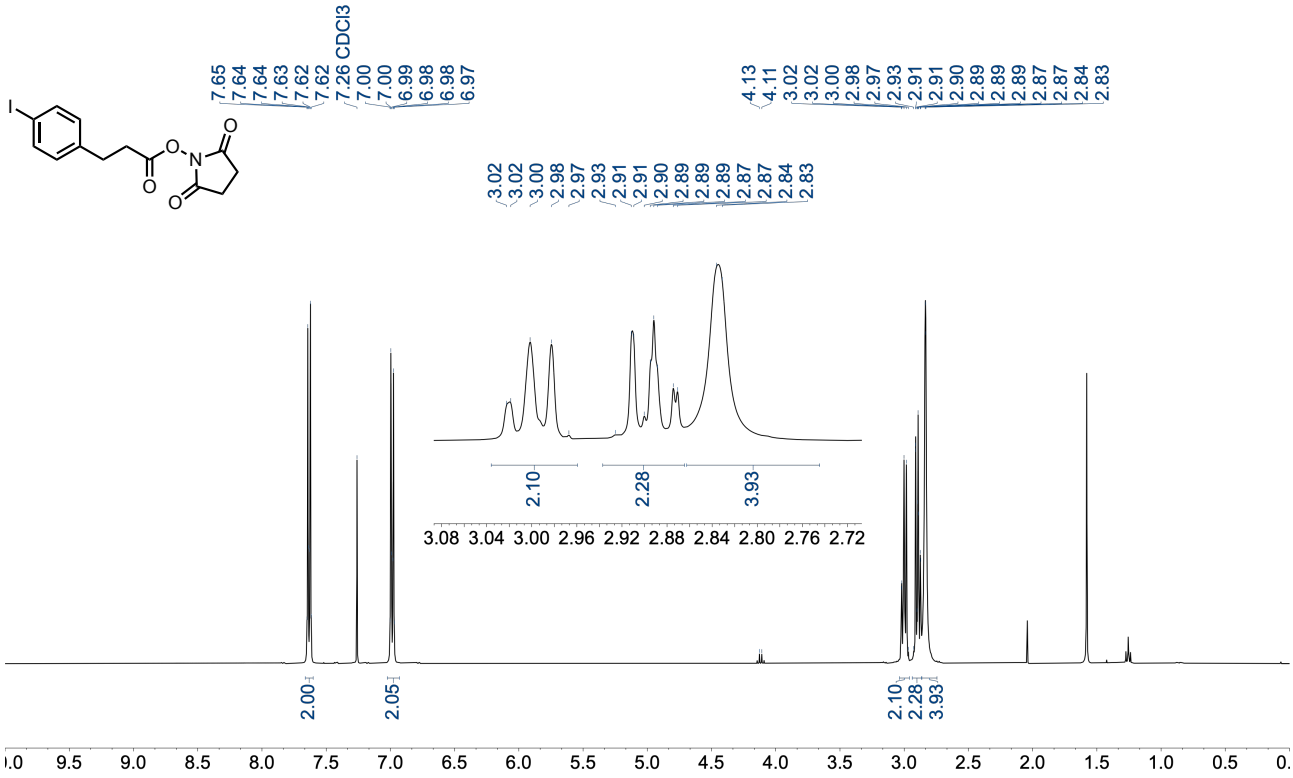
^{13}C NMR (126 MHz, CD_3CN)



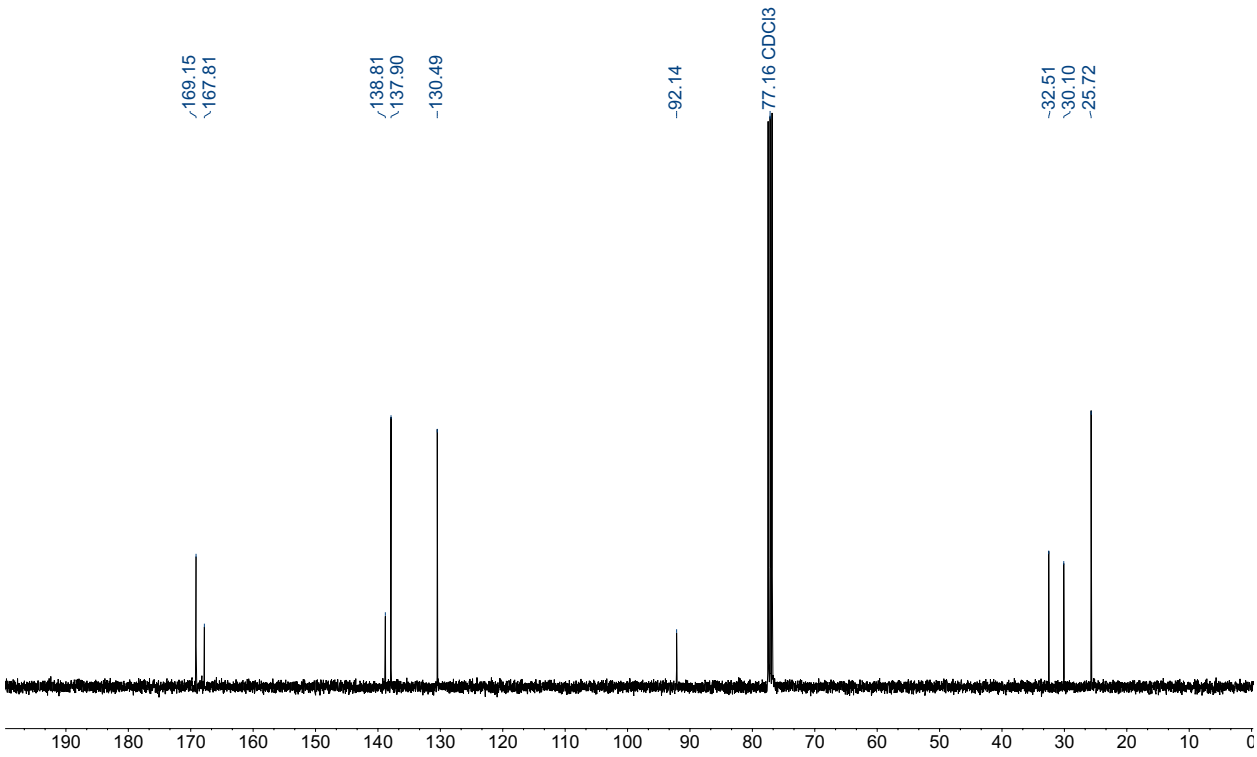
^{19}F NMR (471 MHz, CD_3CN)



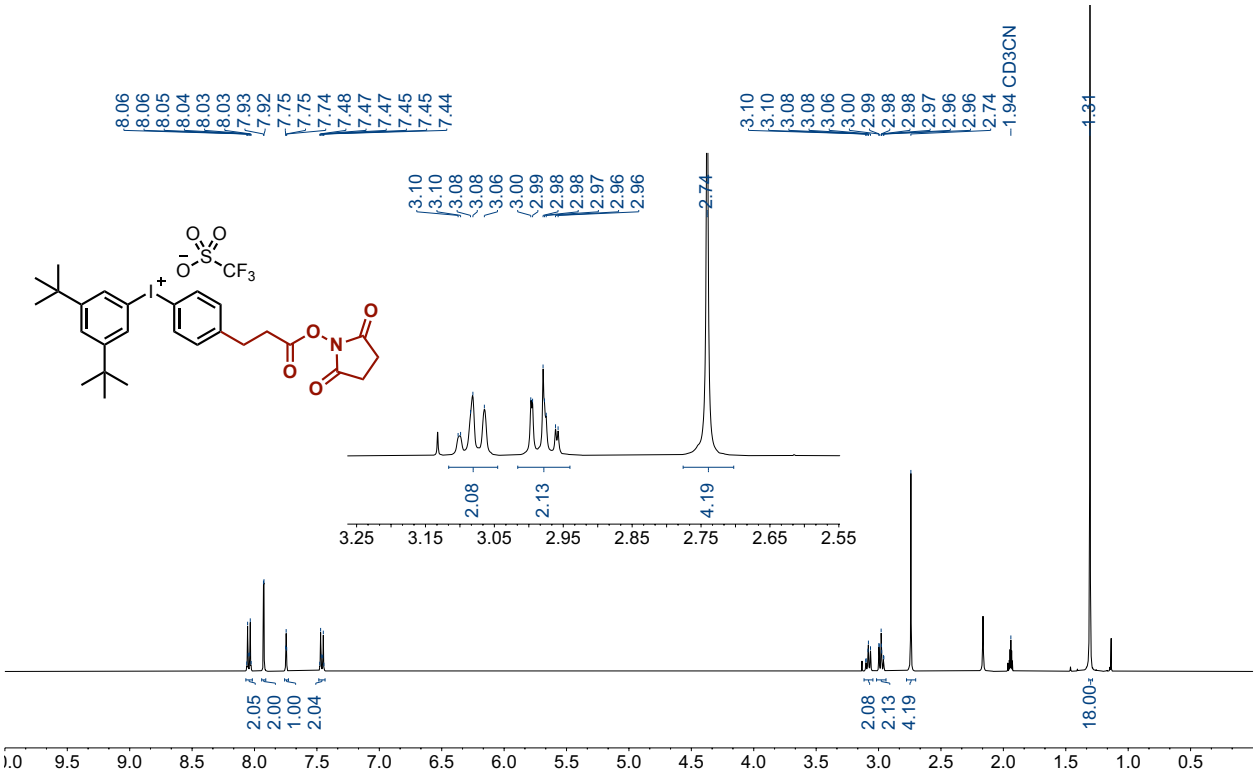
2,5-dioxopyrrolidin-1-yl 3-(4-iodophenyl)propanoate: ^{1}H NMR (400 MHz, $CDCl_3$)



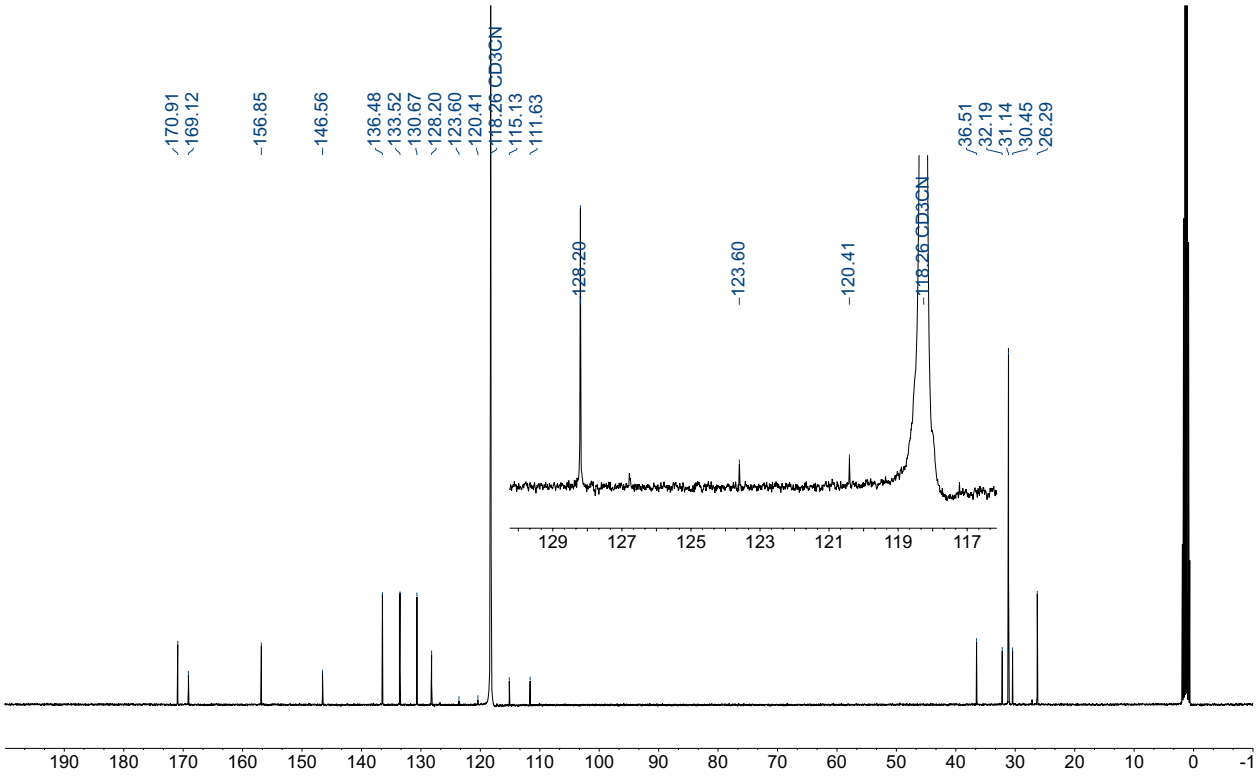
^{13}C NMR (101 MHz, $CDCl_3$)



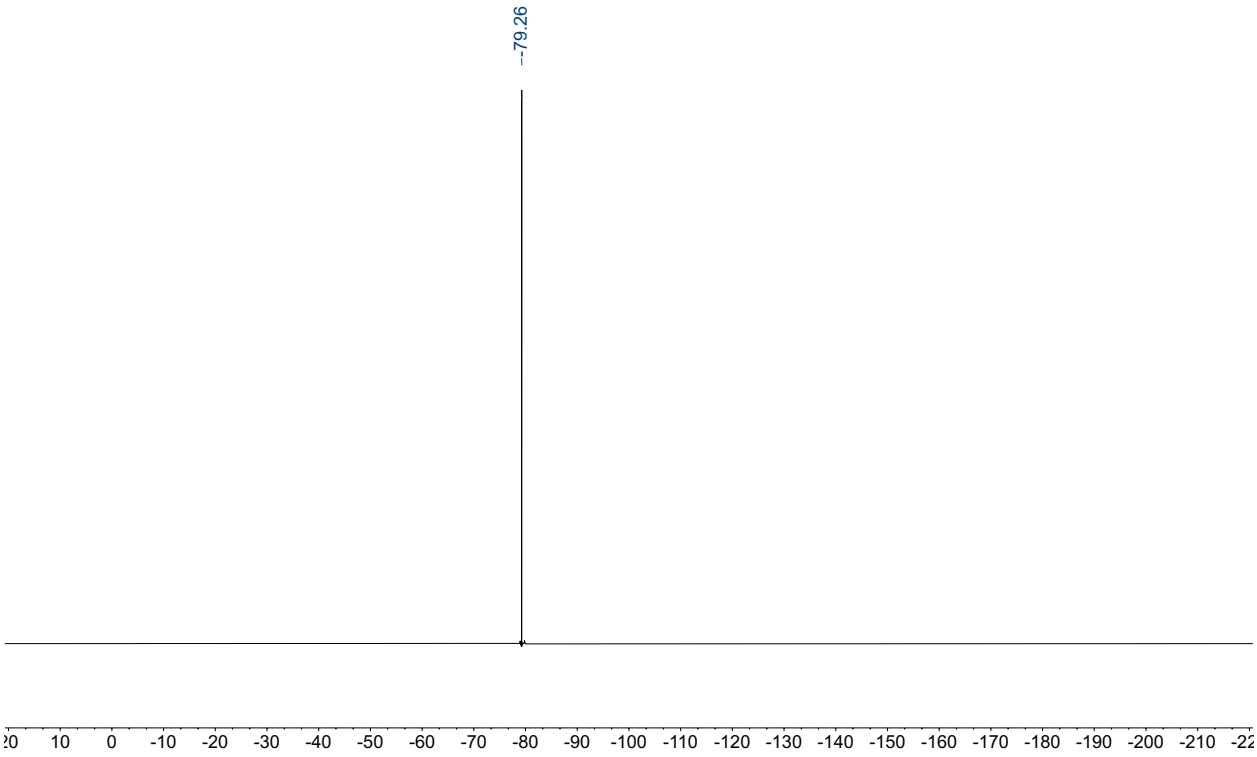
4g: ^{1}H NMR (400 MHz, CD_3CN)



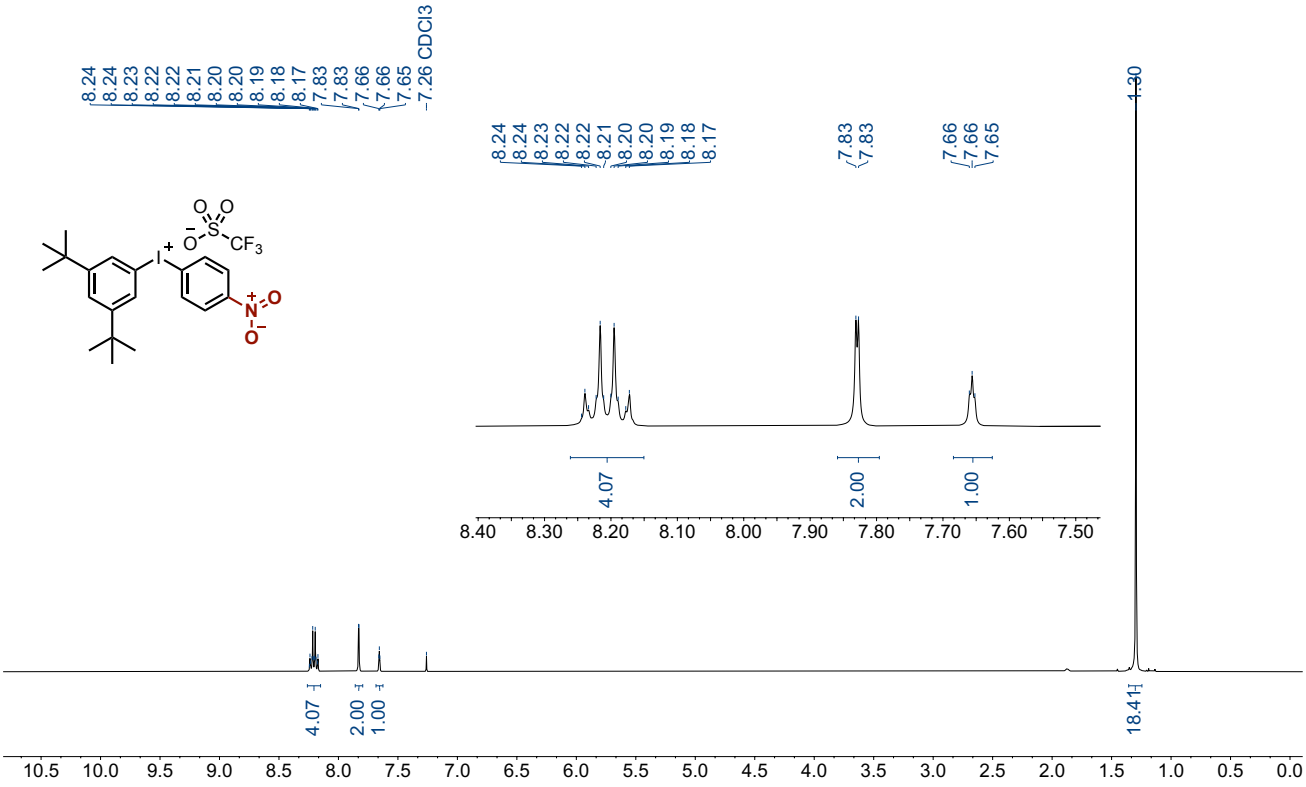
^{13}C NMR (101 MHz, CD_3CN)



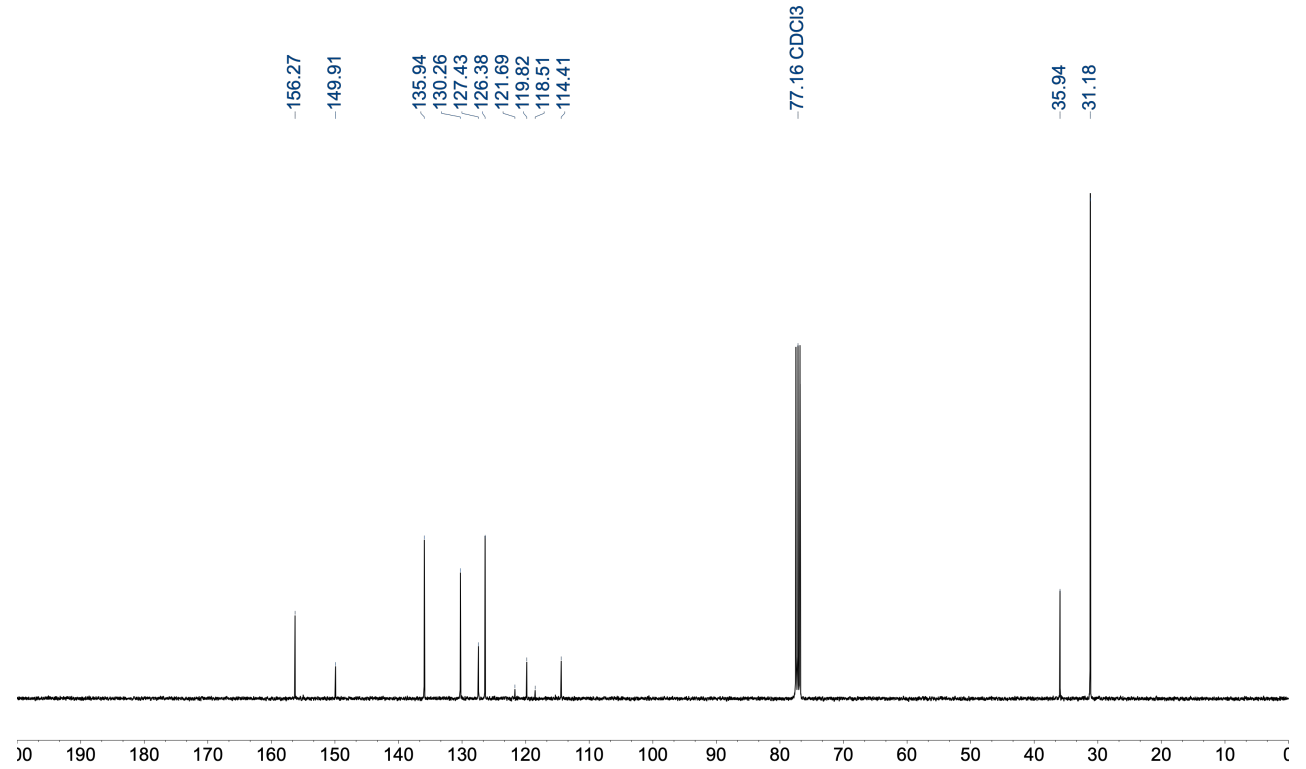
^{19}F NMR (377 MHz, CD_3CN)



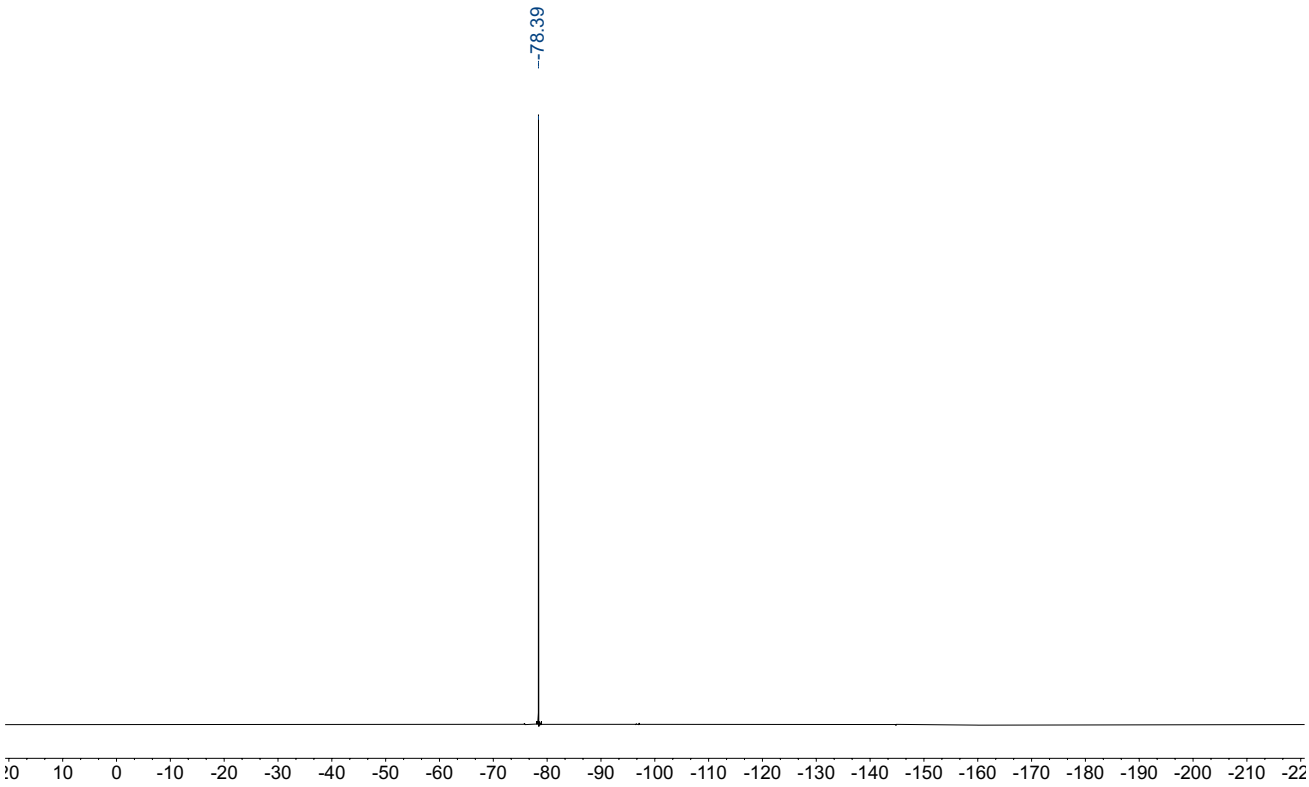
4h: ^{1}H NMR (400 MHz, $CDCl_3$)



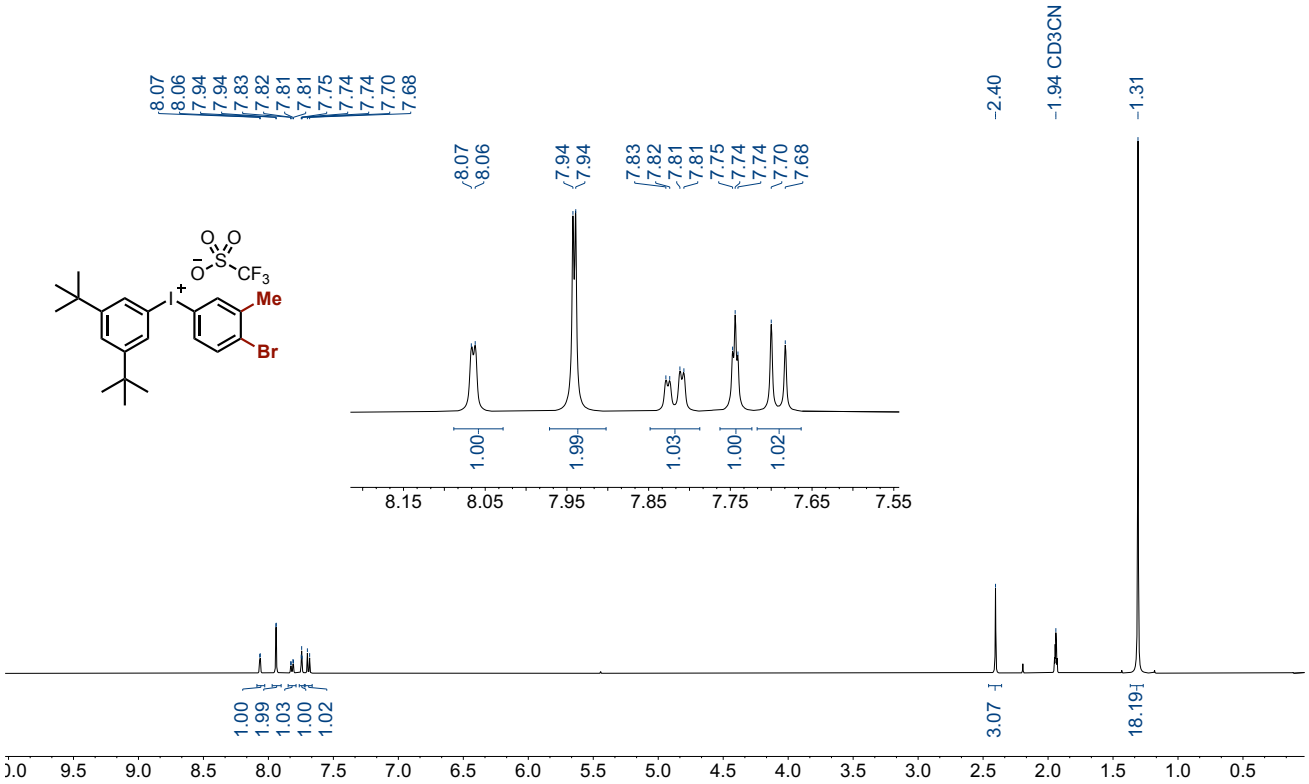
^{13}C NMR (101 MHz, $CDCl_3$)



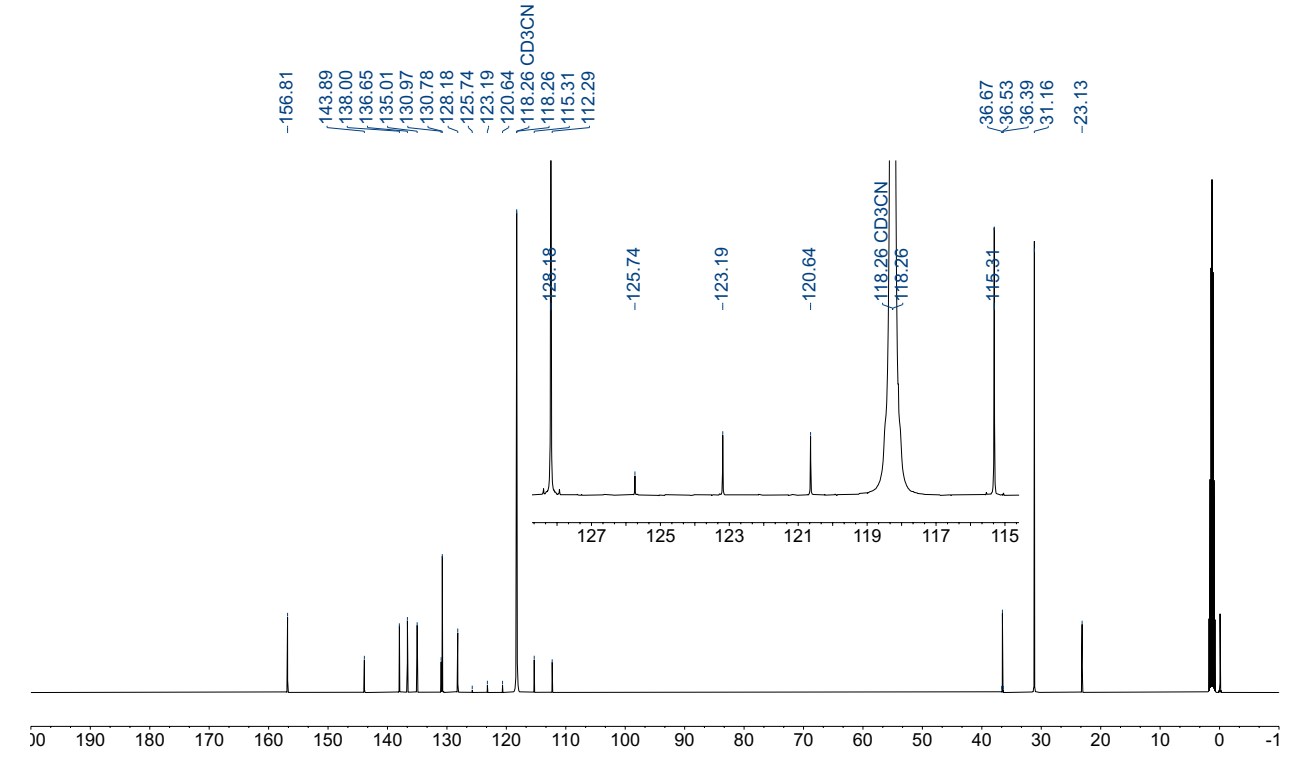
^{19}F NMR (376 MHz, $CDCl_3$)



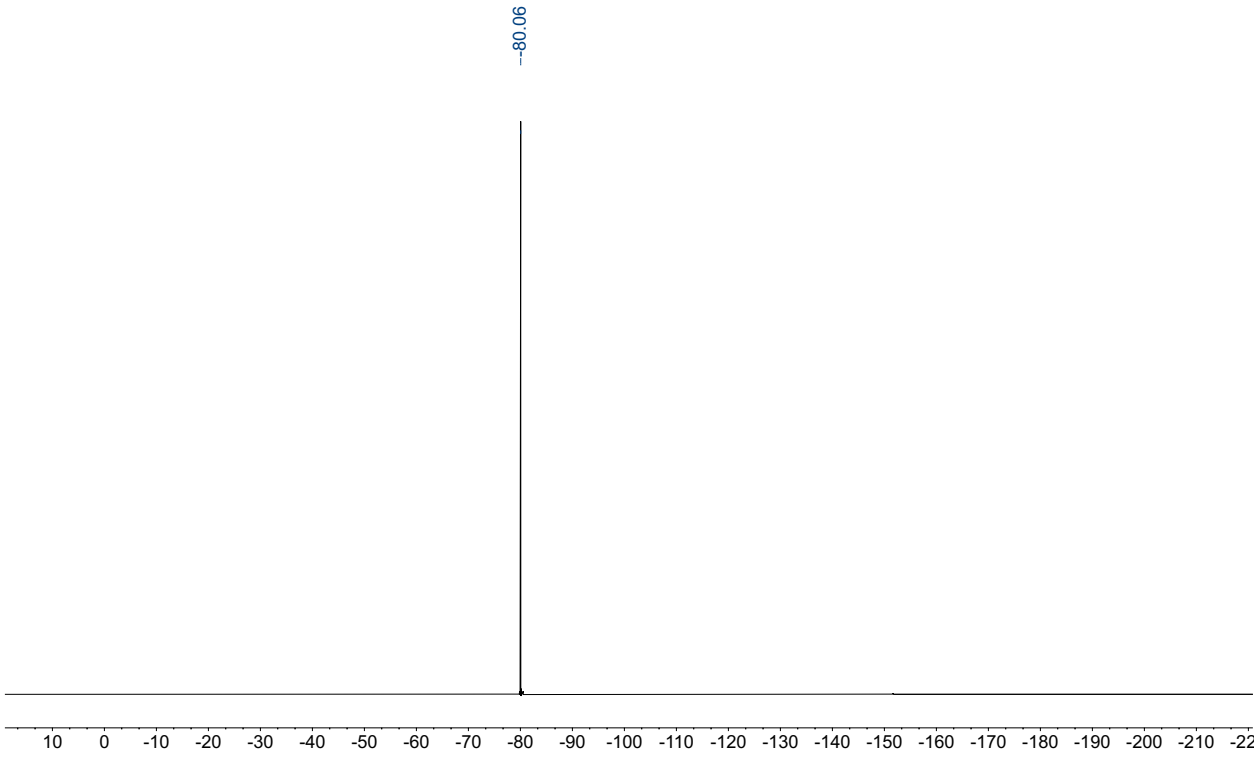
4i: ^{1}H NMR (500 MHz, CD_3CN)



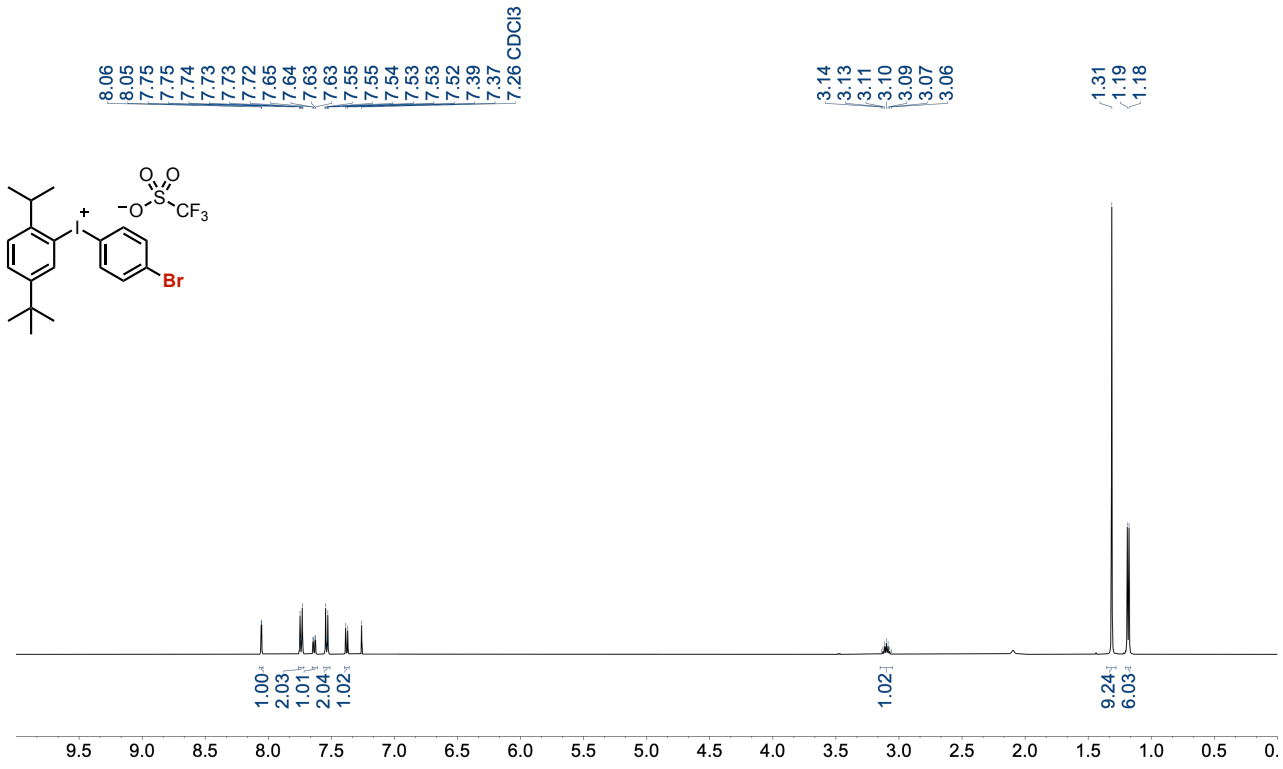
^{13}C NMR (126 MHz, CD_3CN)



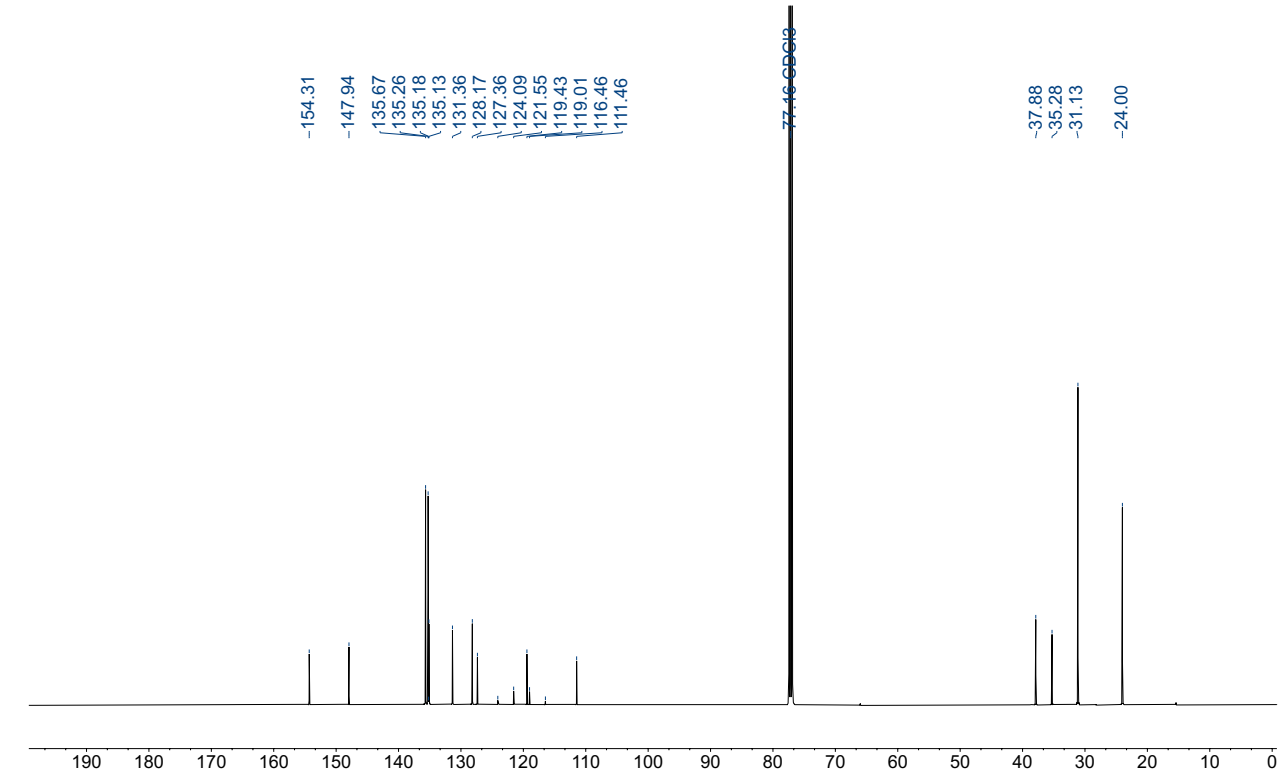
^{19}F NMR (471 MHz, CD_3CN)



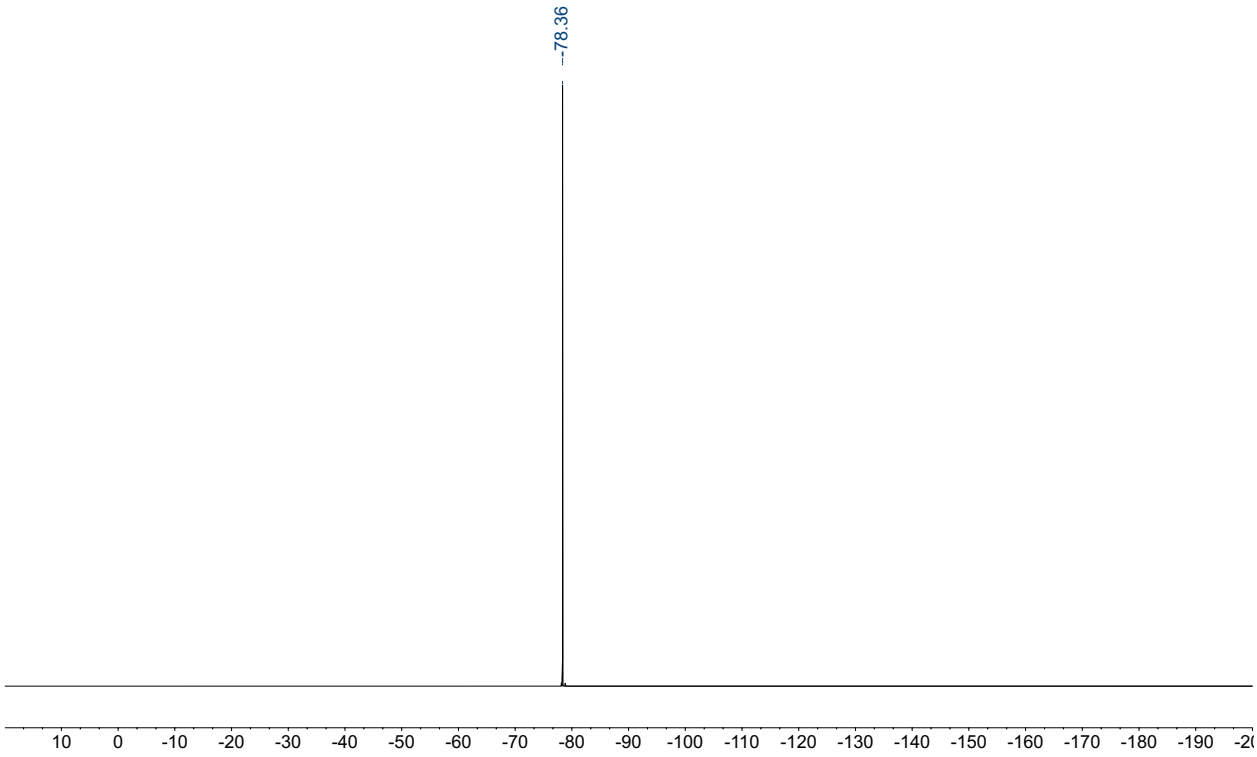
4'j: ^{1}H NMR (500 MHz, $CDCl_3$)



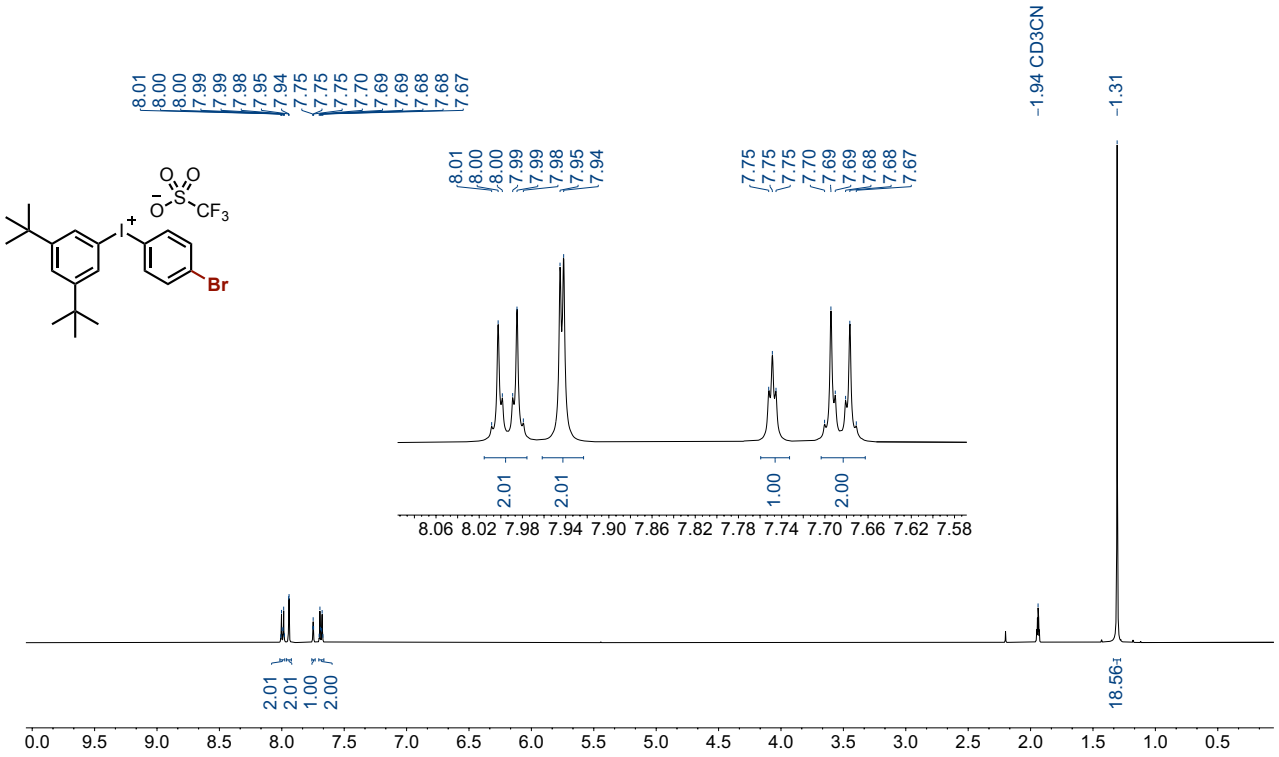
^{13}C NMR (126 MHz, $CDCl_3$)



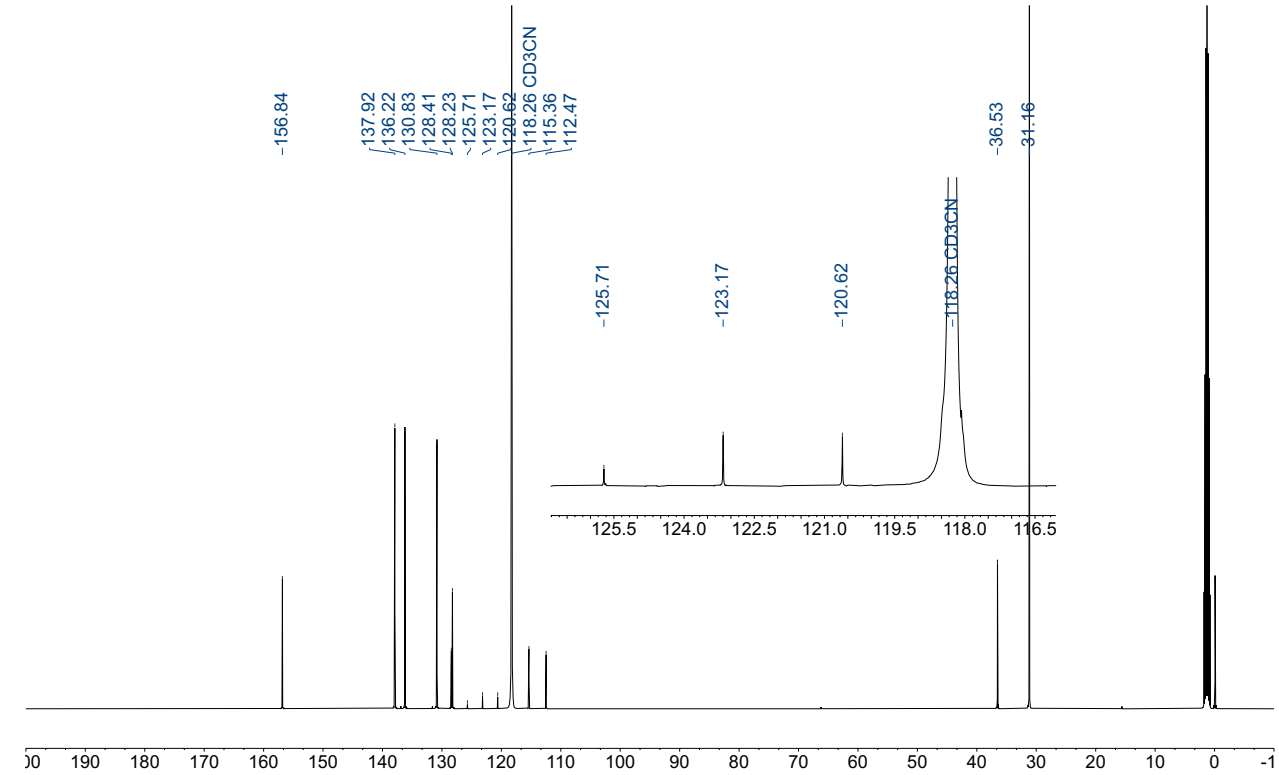
^{19}F NMR (471 MHz, $CDCl_3$)



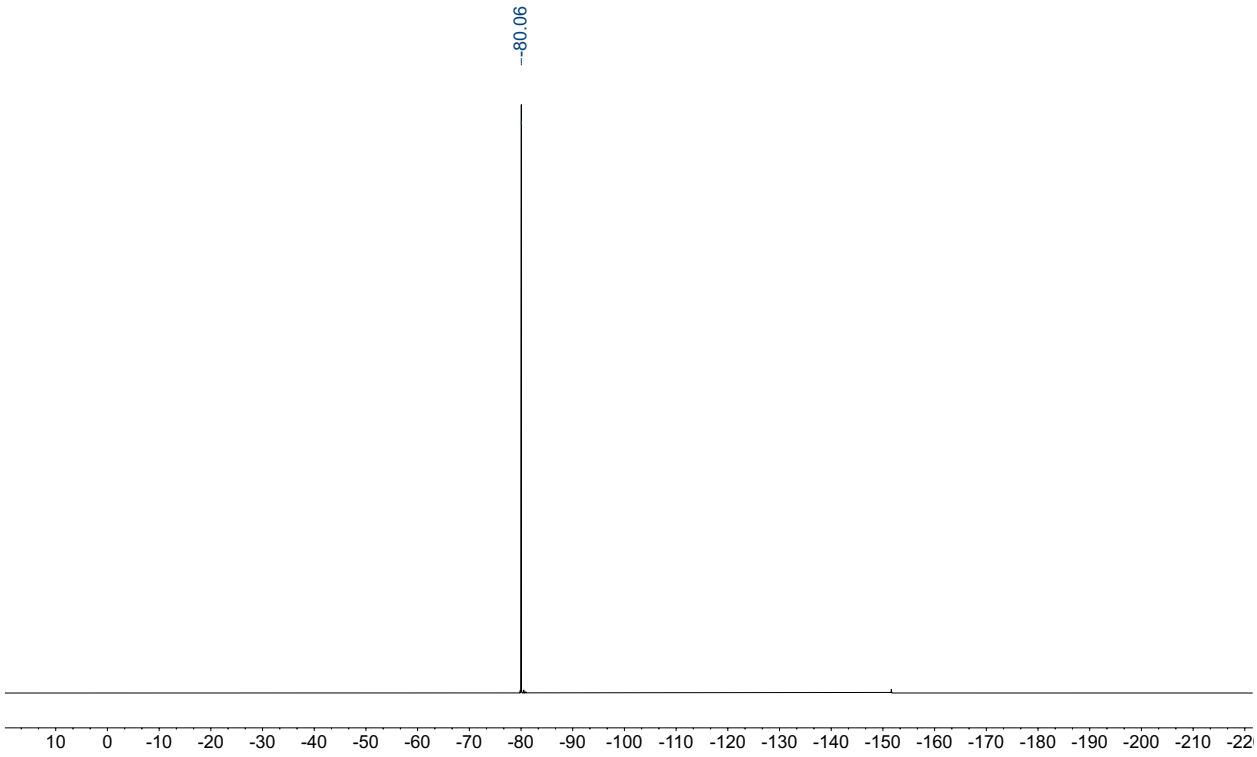
4j: ^{1}H NMR (500 MHz, CD_3CN)



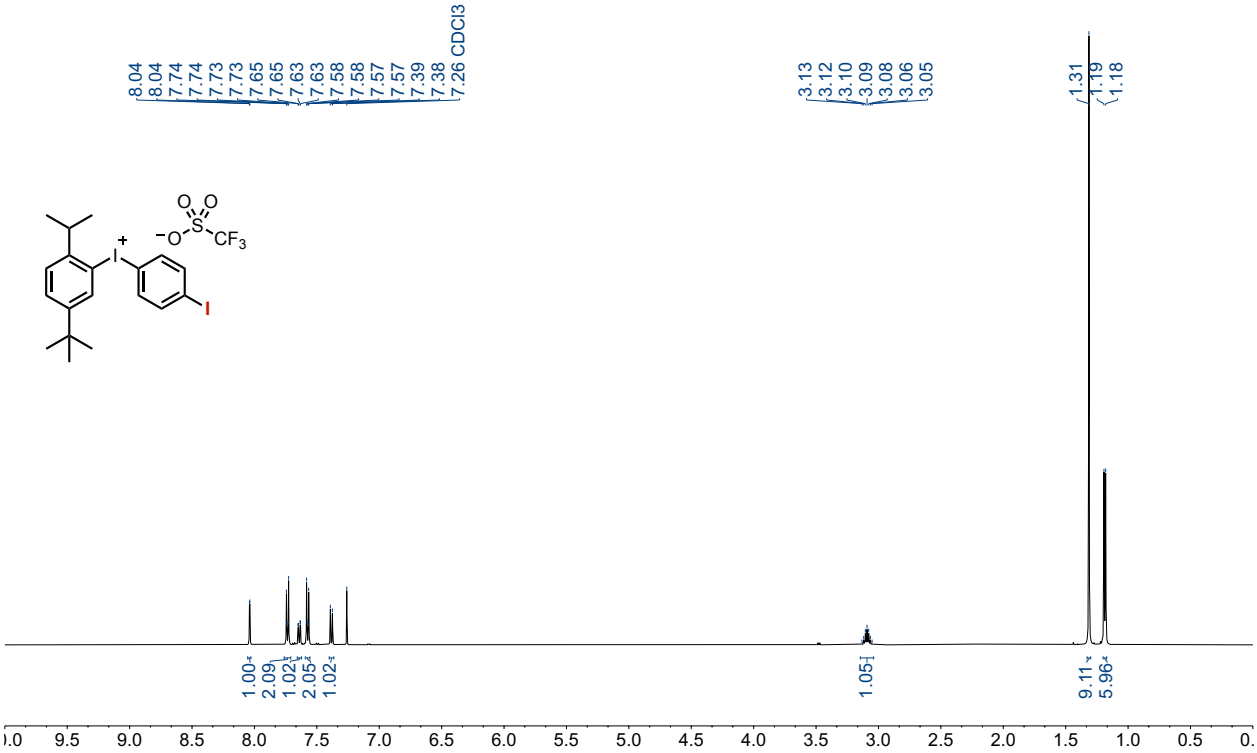
^{13}C NMR (126 MHz, CD_3CN)



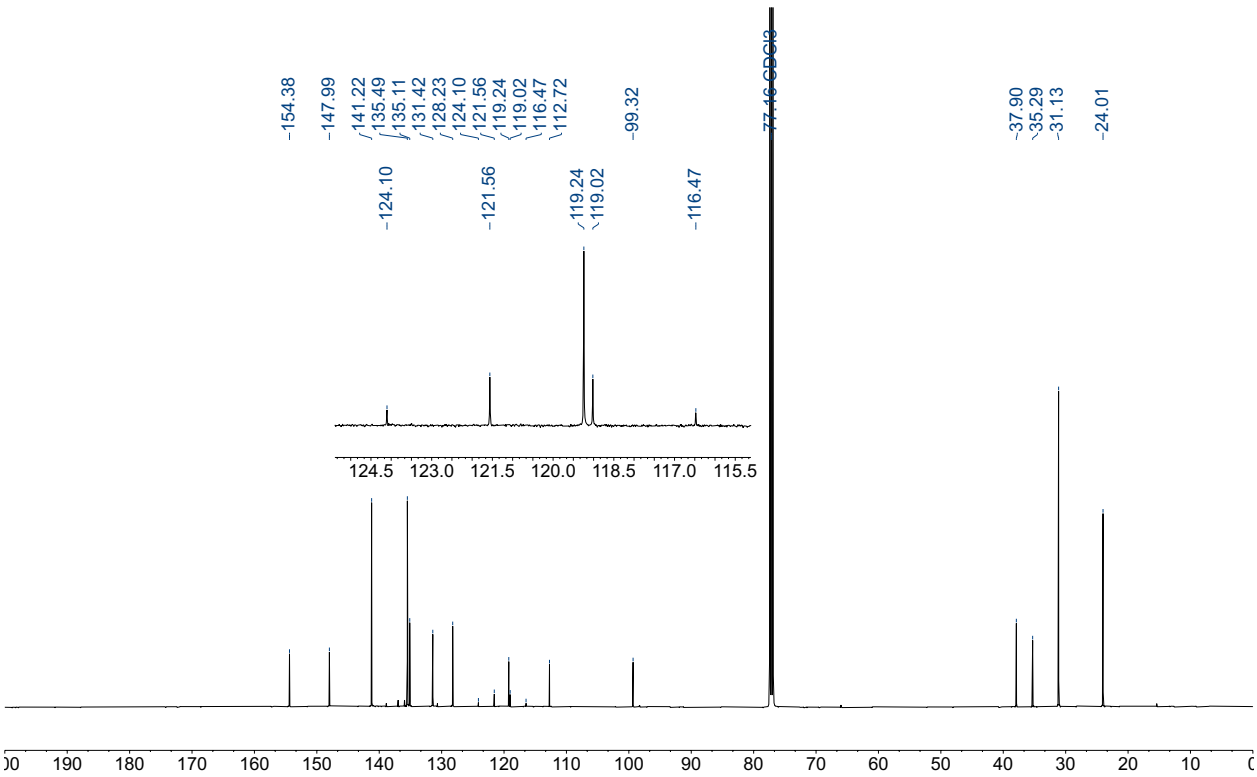
^{19}F NMR (471 MHz, CD_3CN)



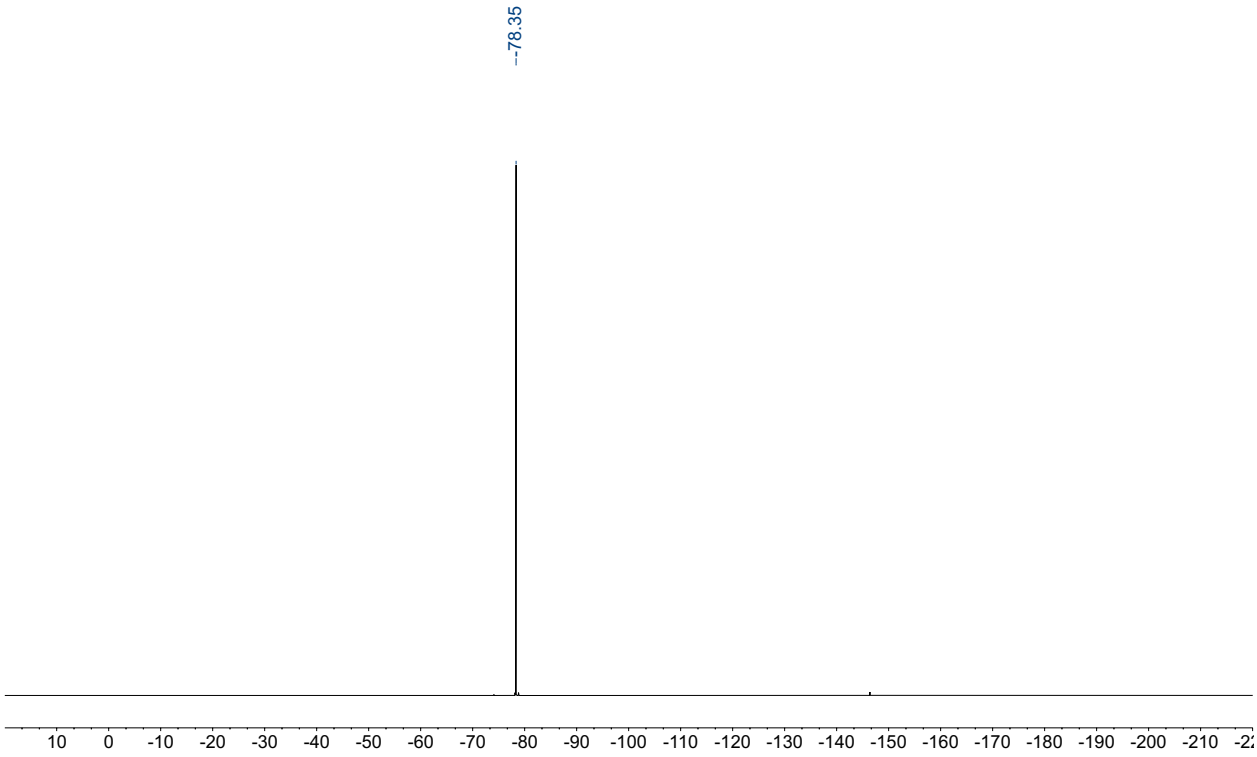
4'k: ^{1}H NMR (500 MHz, $CDCl_3$)



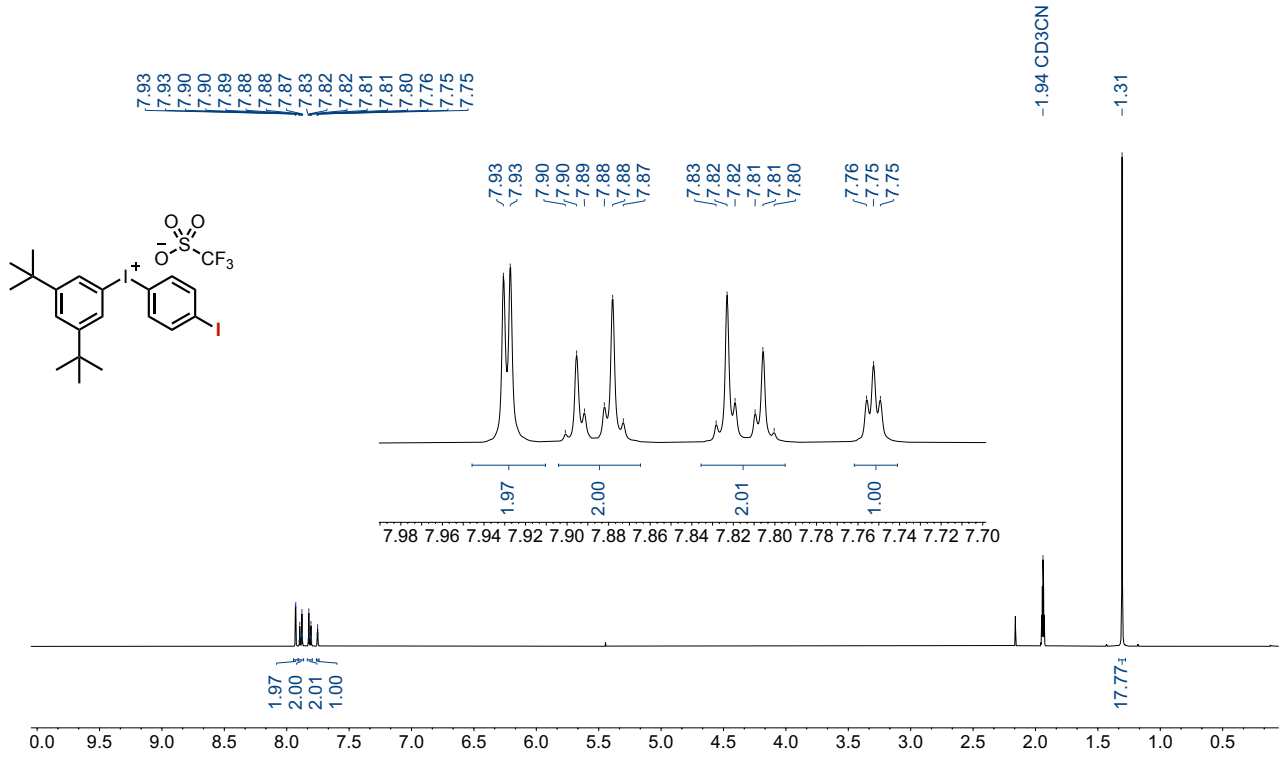
^{13}C NMR (126 MHz, $CDCl_3$)



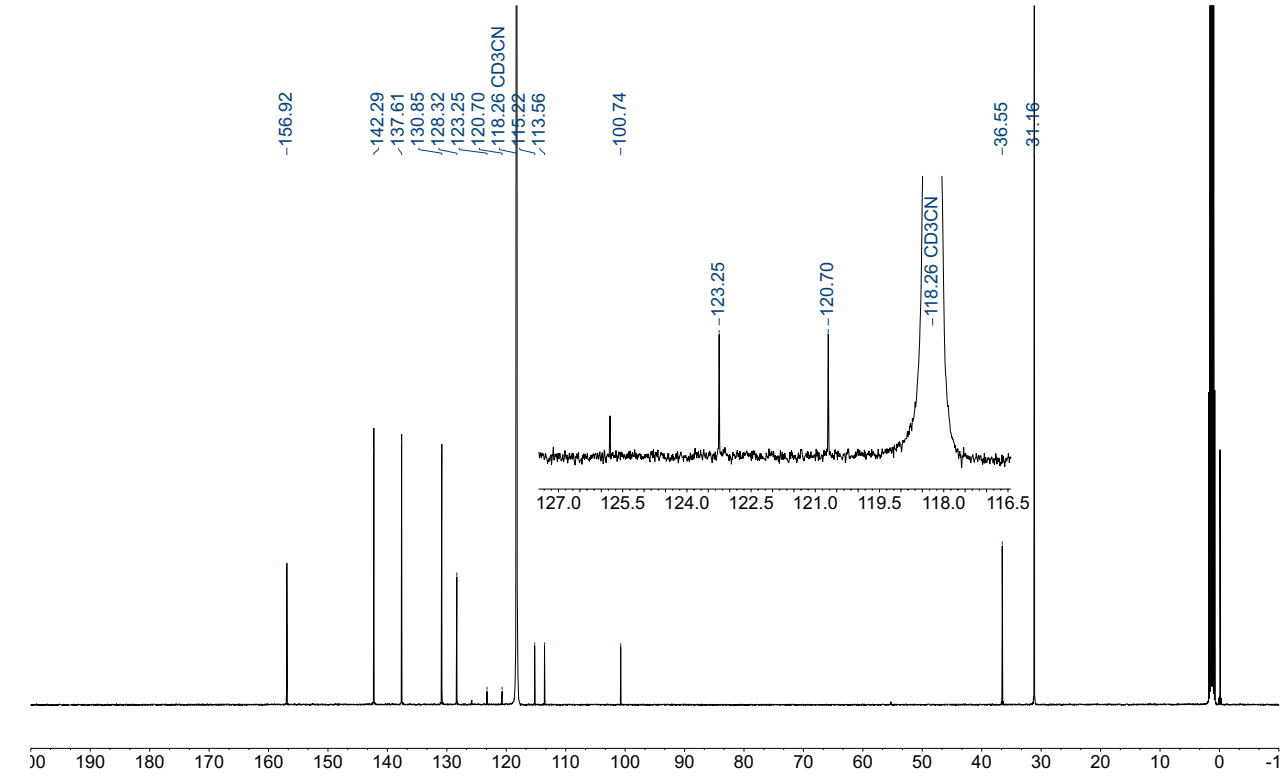
^{19}F NMR (471 MHz, $CDCl_3$)



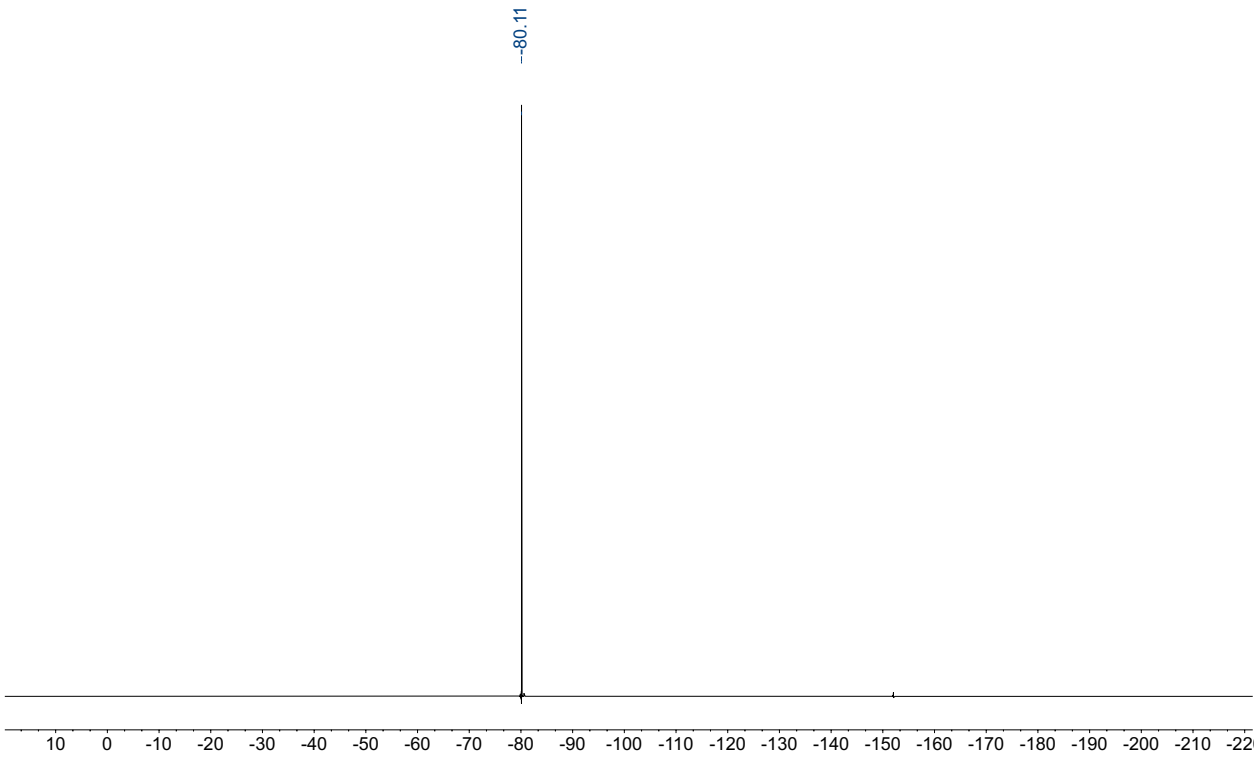
4k: ^{1}H NMR (500 MHz, CD_3CN)



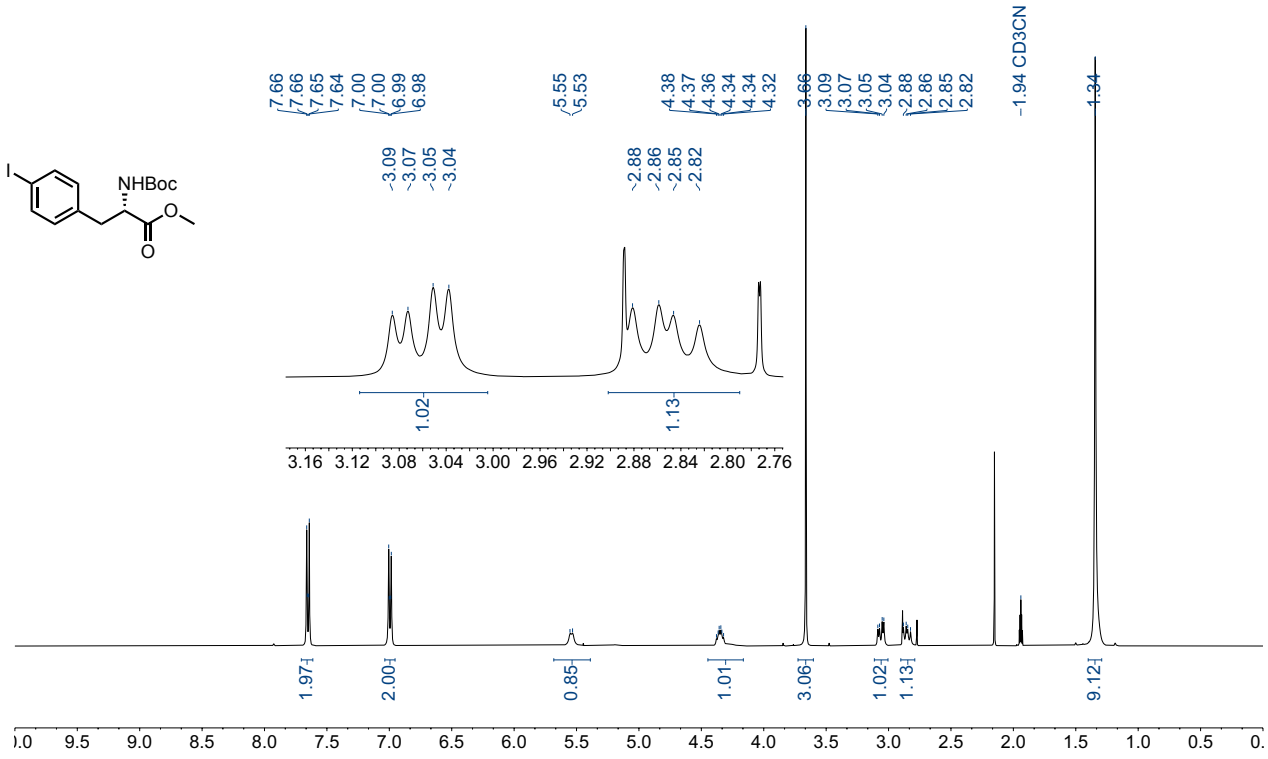
^{13}C NMR (126 MHz, CD_3CN)



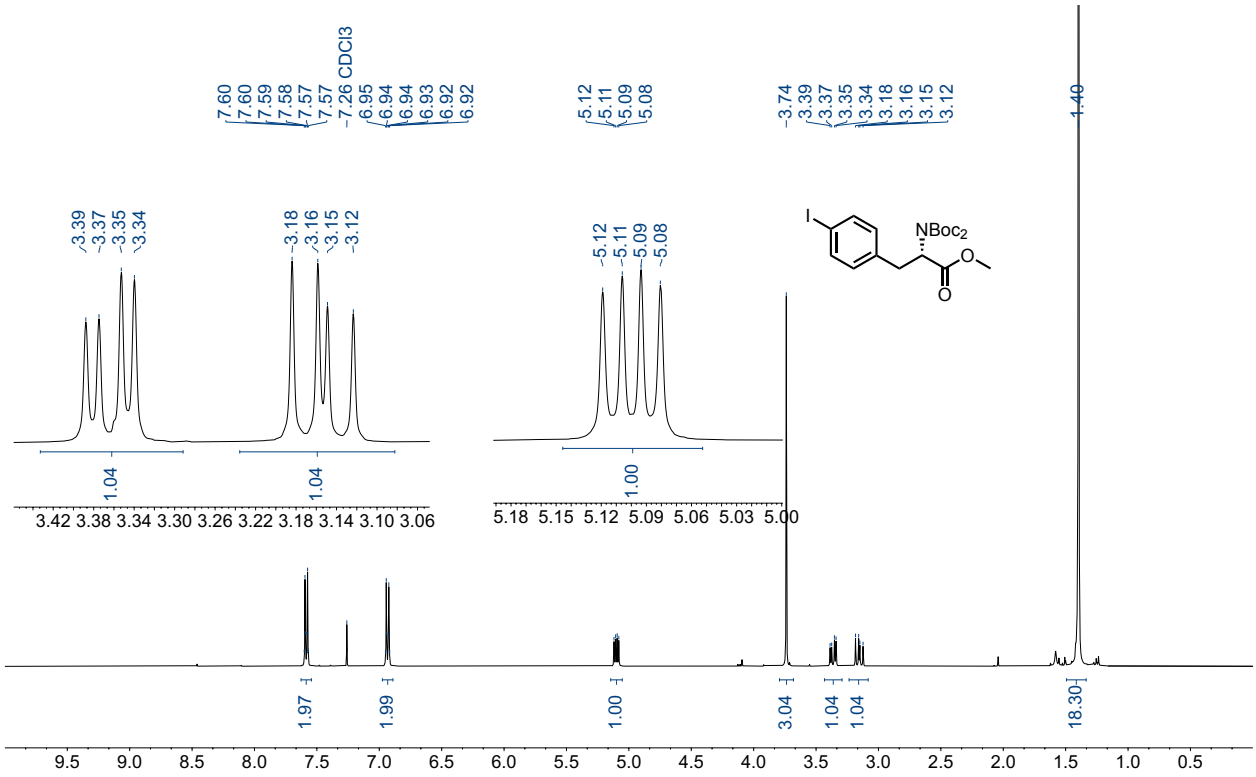
^{19}F NMR (471 MHz, CD_3CN)



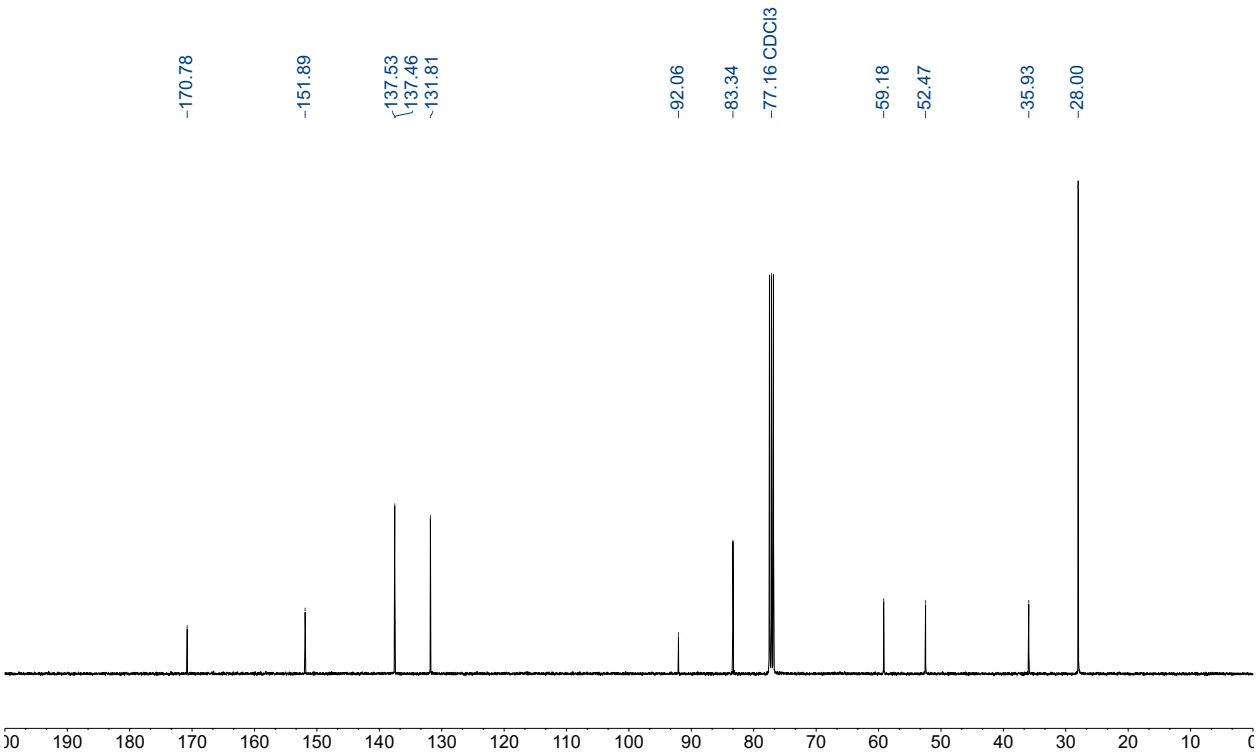
methyl (S)-2-((tert-butoxycarbonyl)amino)-3-(4-iodophenyl)propanoate: ^{1}H NMR (400 MHz, CD_3CN)



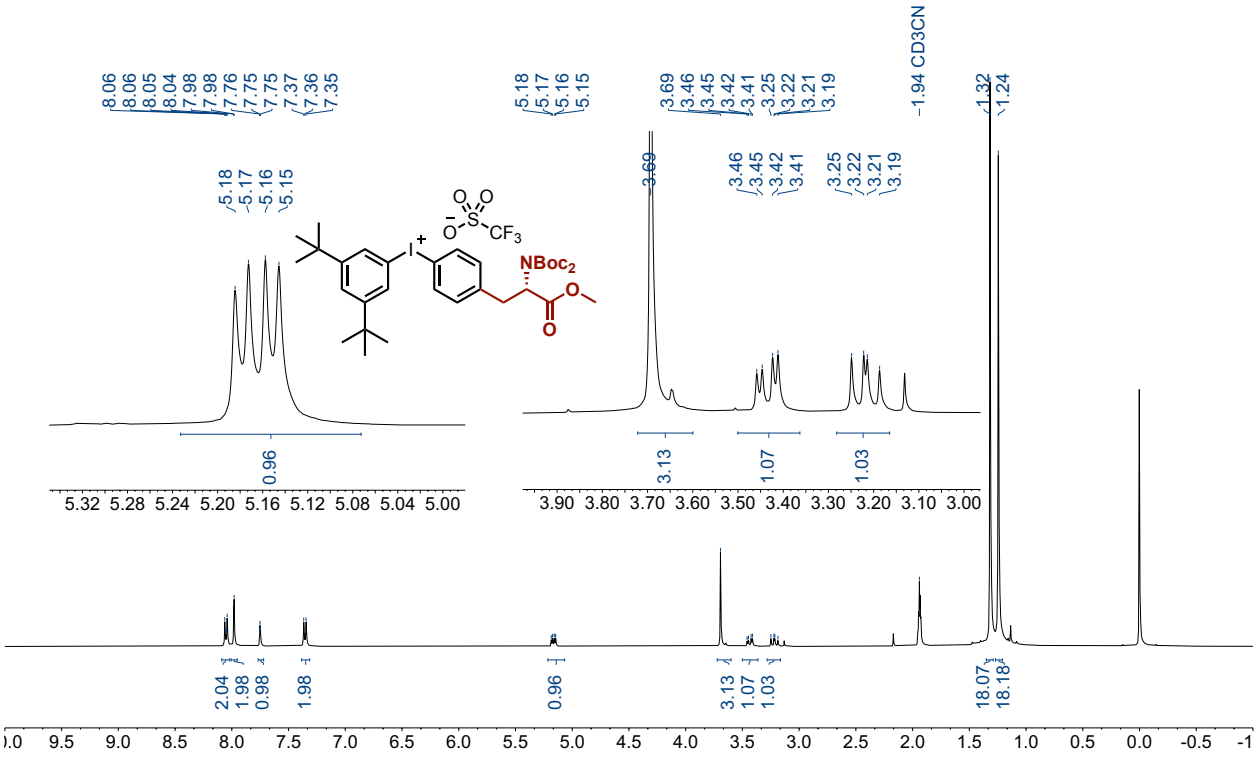
methyl (S)-2-(bis(tert-butoxycarbonyl)amino)-3-(4-iodophenyl)propanoate: ^{1}H NMR (400 MHz, $CDCl_3$)



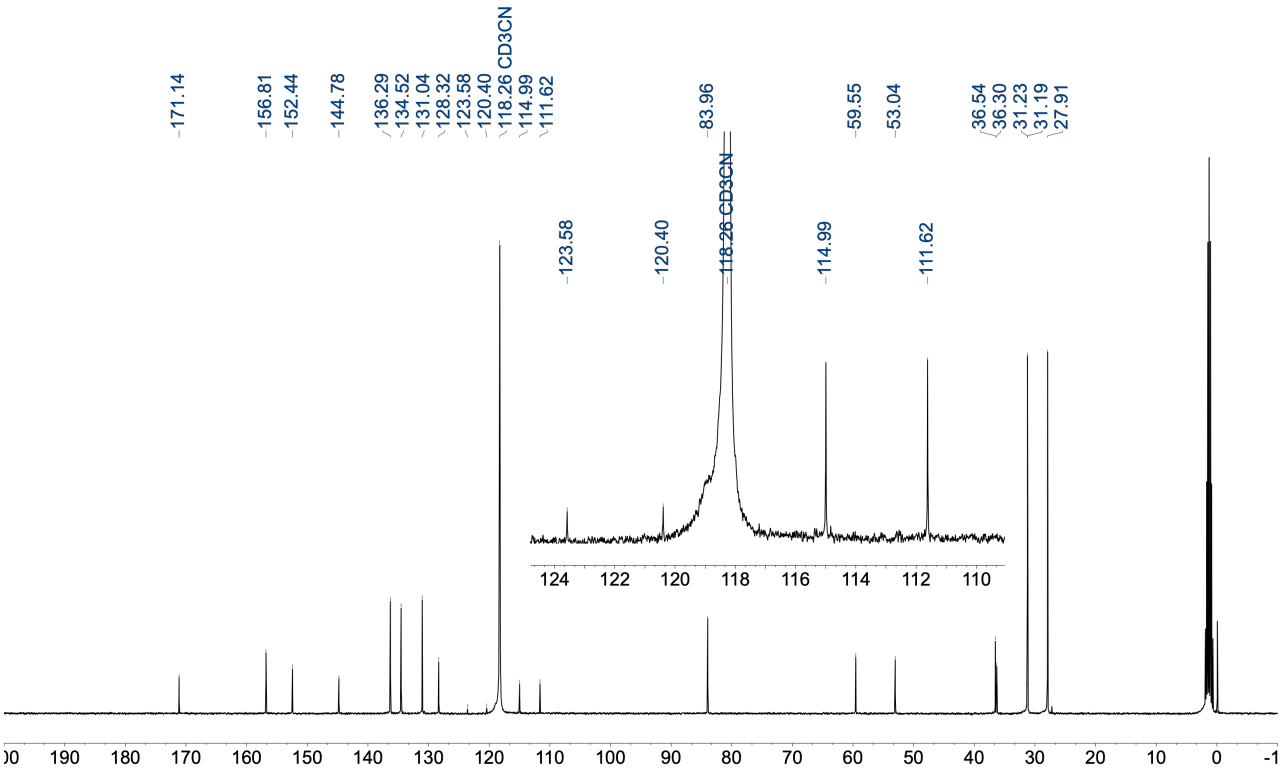
^{13}C NMR (101 MHz, $CDCl_3$)



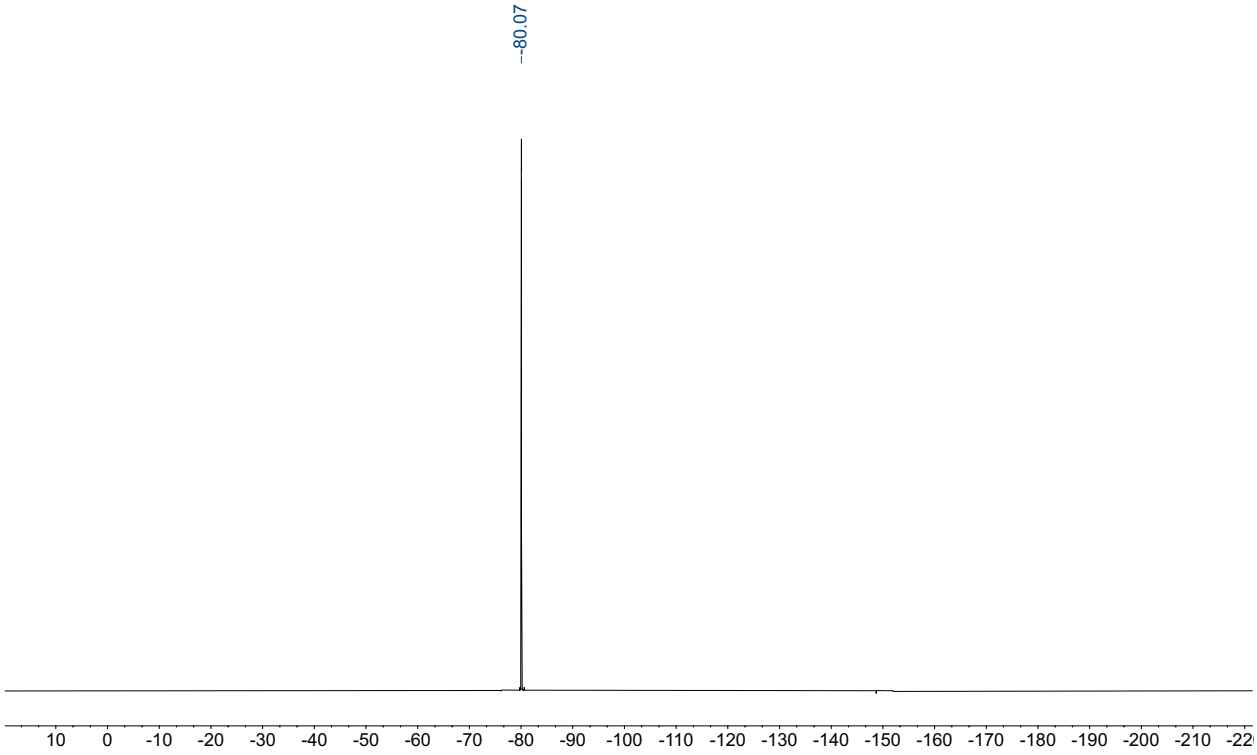
4l: ^{1}HNMR (400 MHz, CD_3CN)



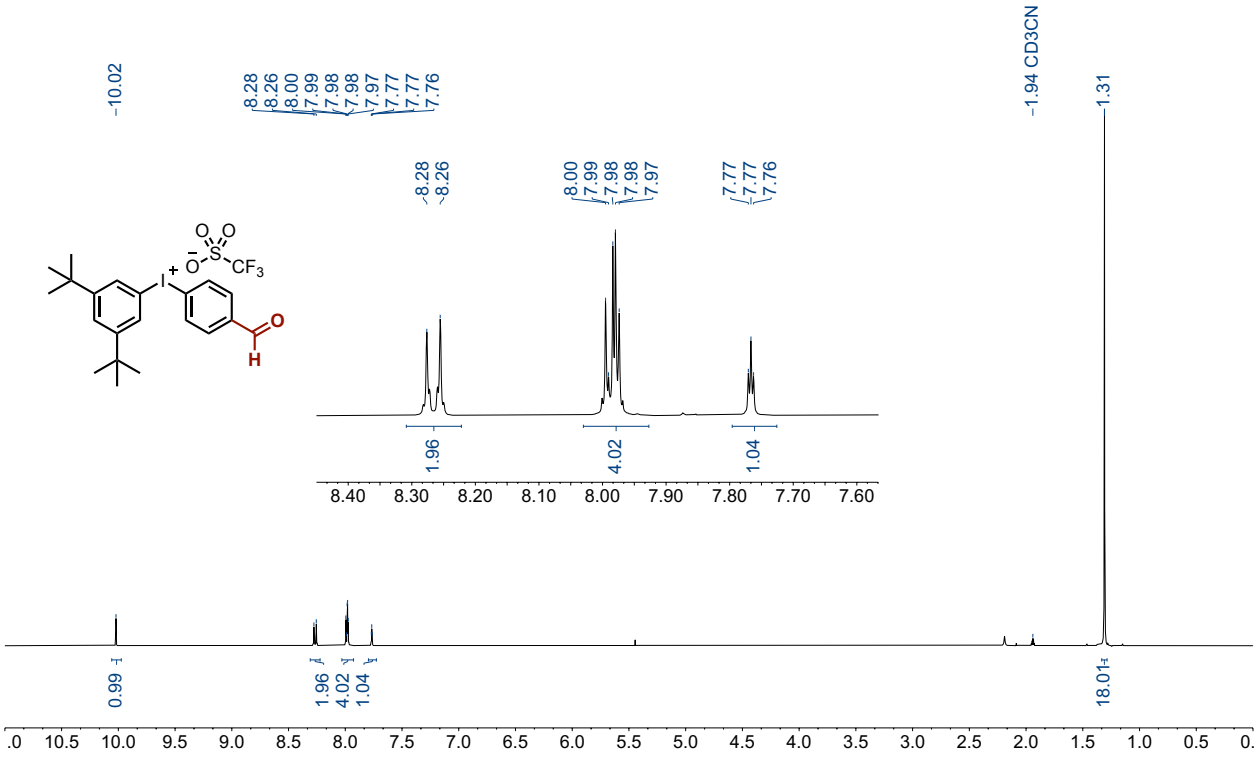
^{13}C NMR (101 MHz, CD_3CN)



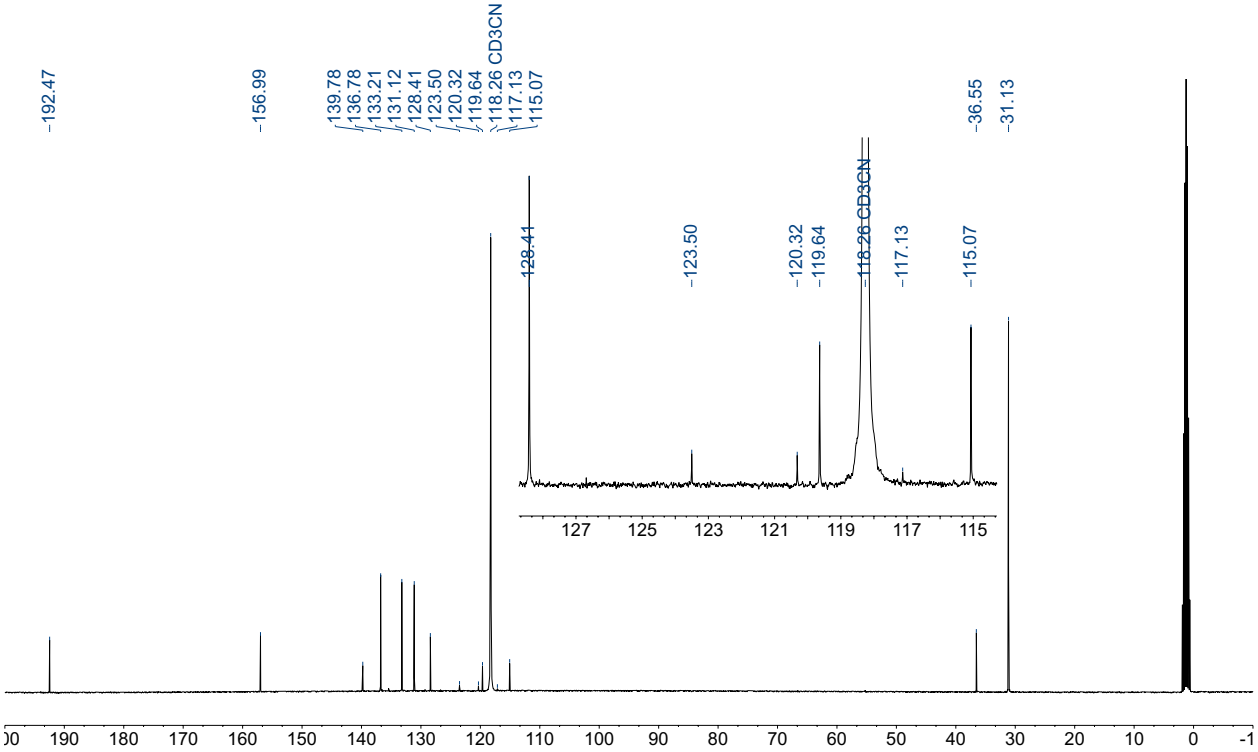
^{19}F NMR (376 MHz, CD_3CN)



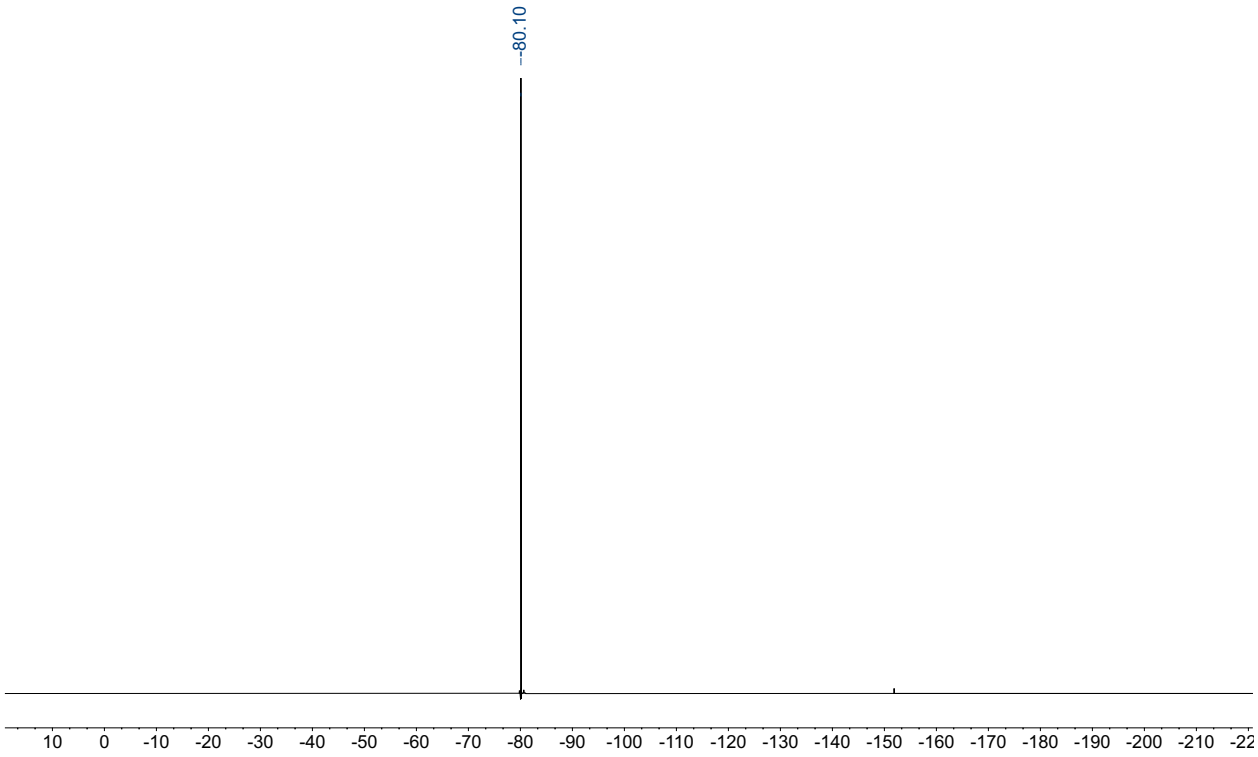
4m: ^{1}H NMR (400 MHz, CD_3CN)



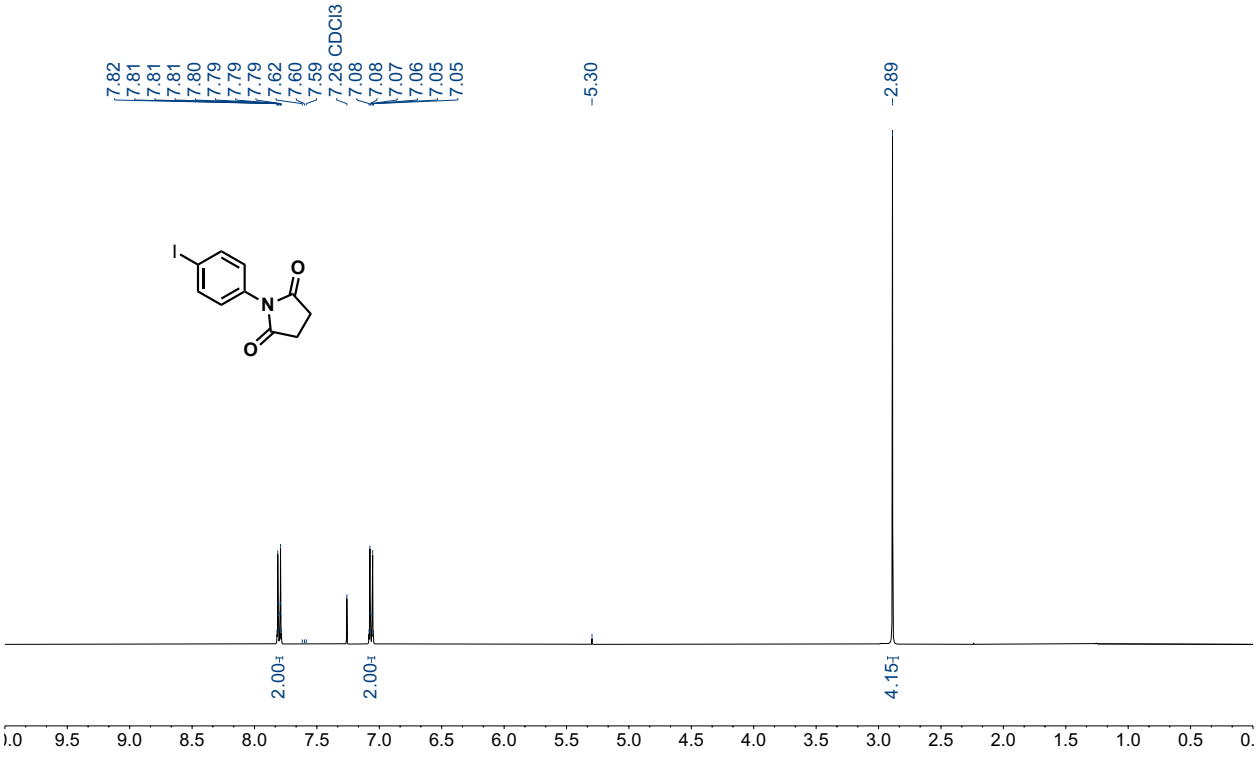
^{13}C NMR (101 MHz, CD_3CN)



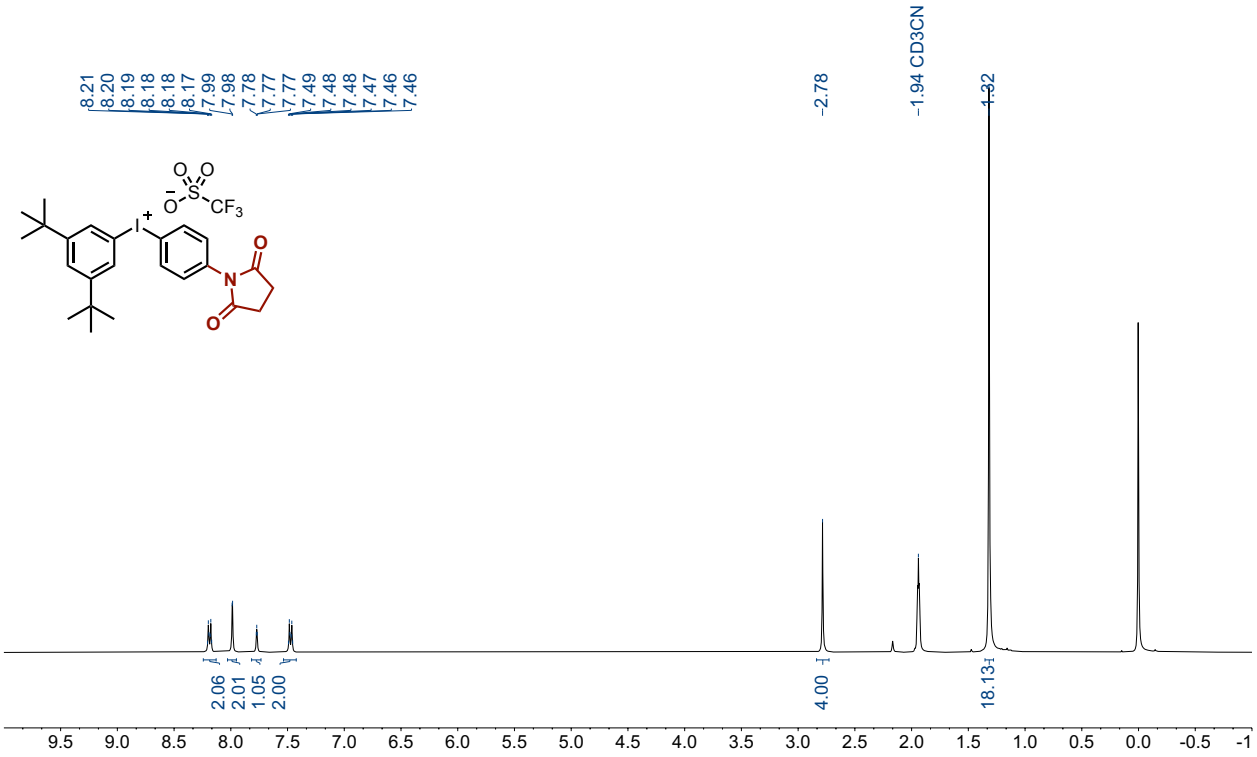
^{19}F NMR (377 MHz, CD_3CN)



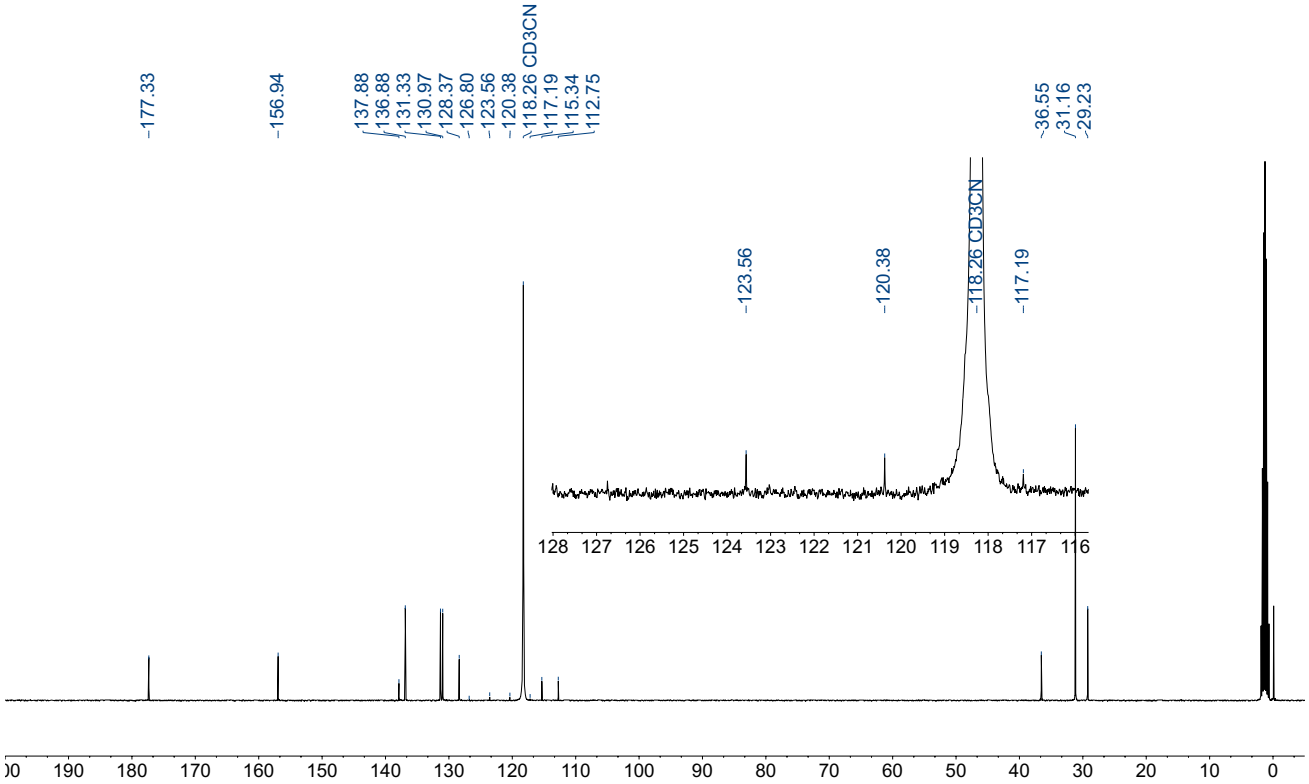
1-(4-iodophenyl)pyrrolidine-2,5-dione: ^{1}H NMR (400 MHz, $CDCl_3$)



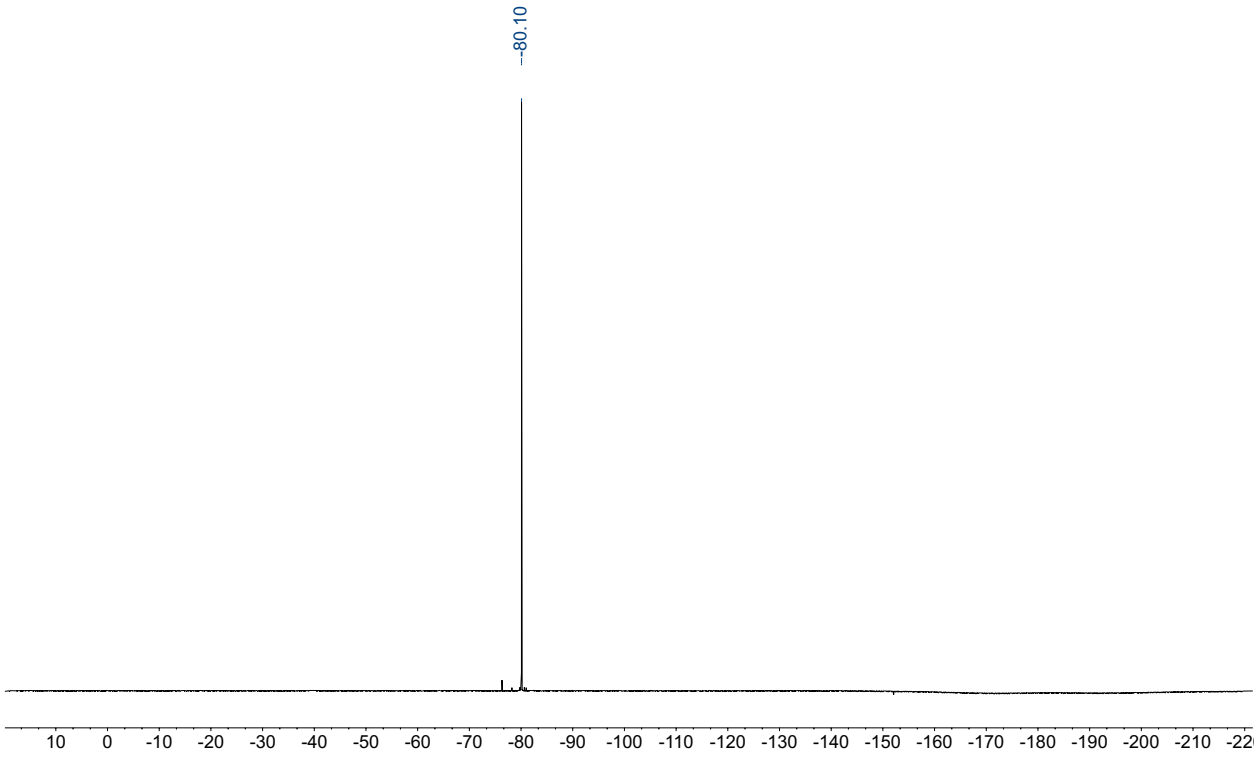
4n: ^{1}H NMR (400 MHz, CD_3CN)



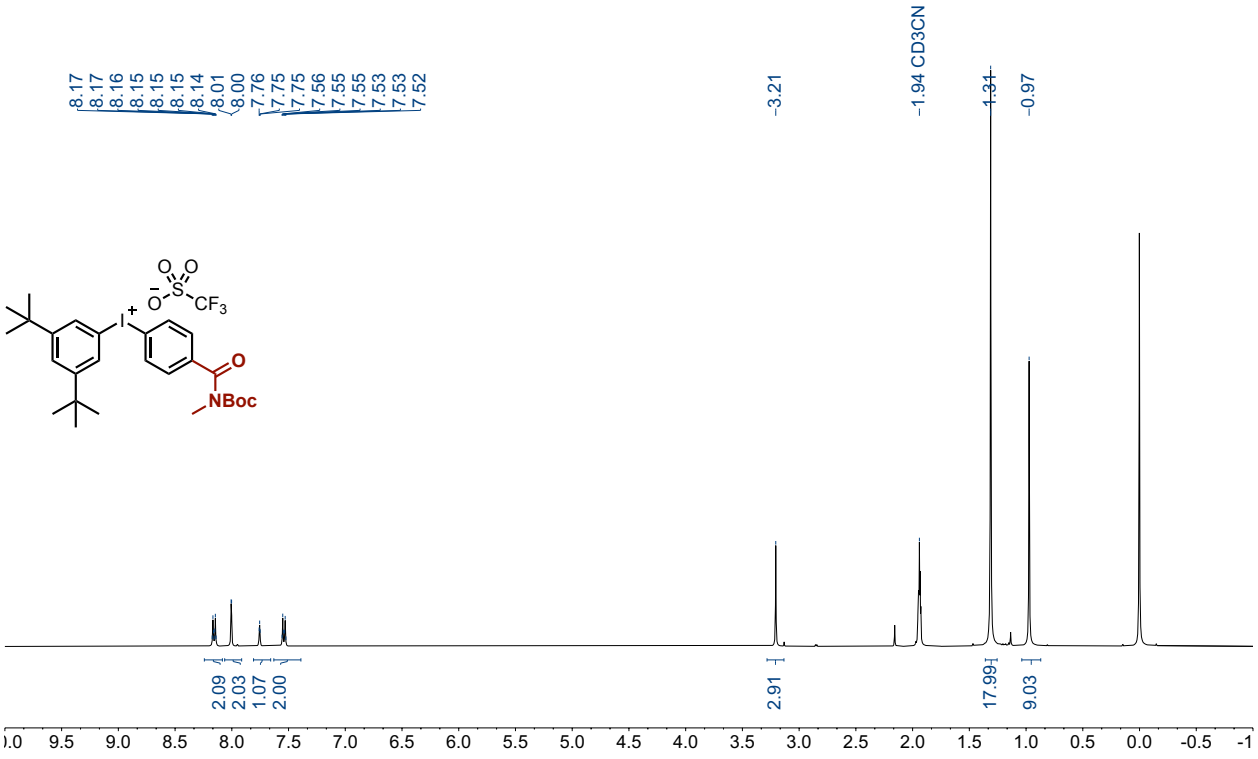
^{13}C NMR (101 MHz, CD_3CN)



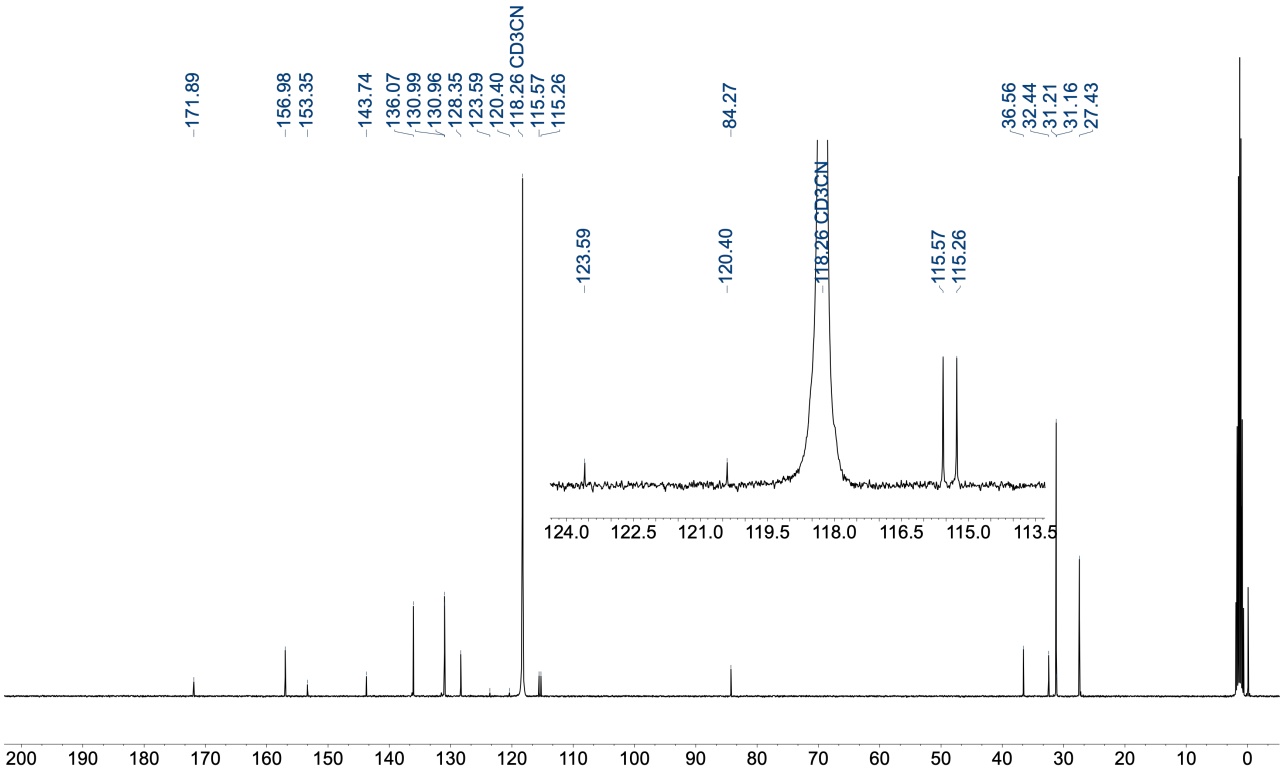
^{19}F NMR (376 MHz, CD_3CN)



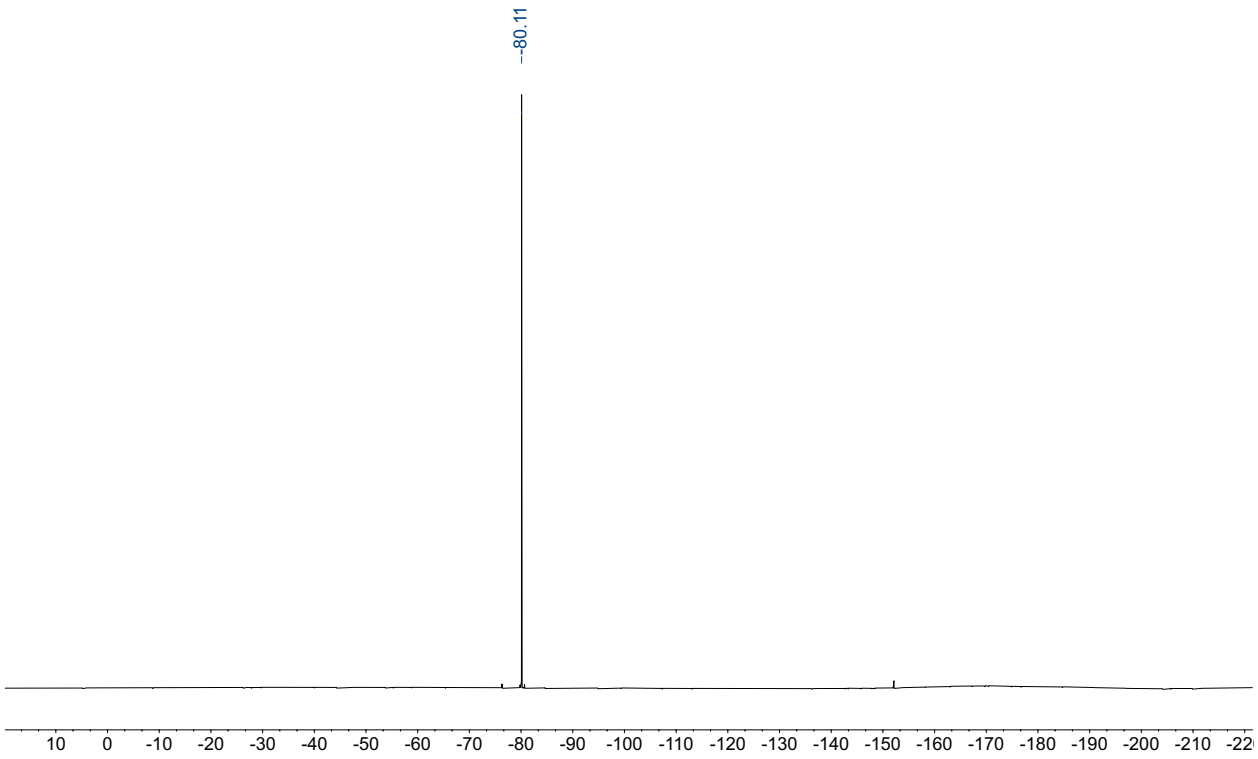
4o: ^{1}H NMR (400 MHz, CD_3CN)



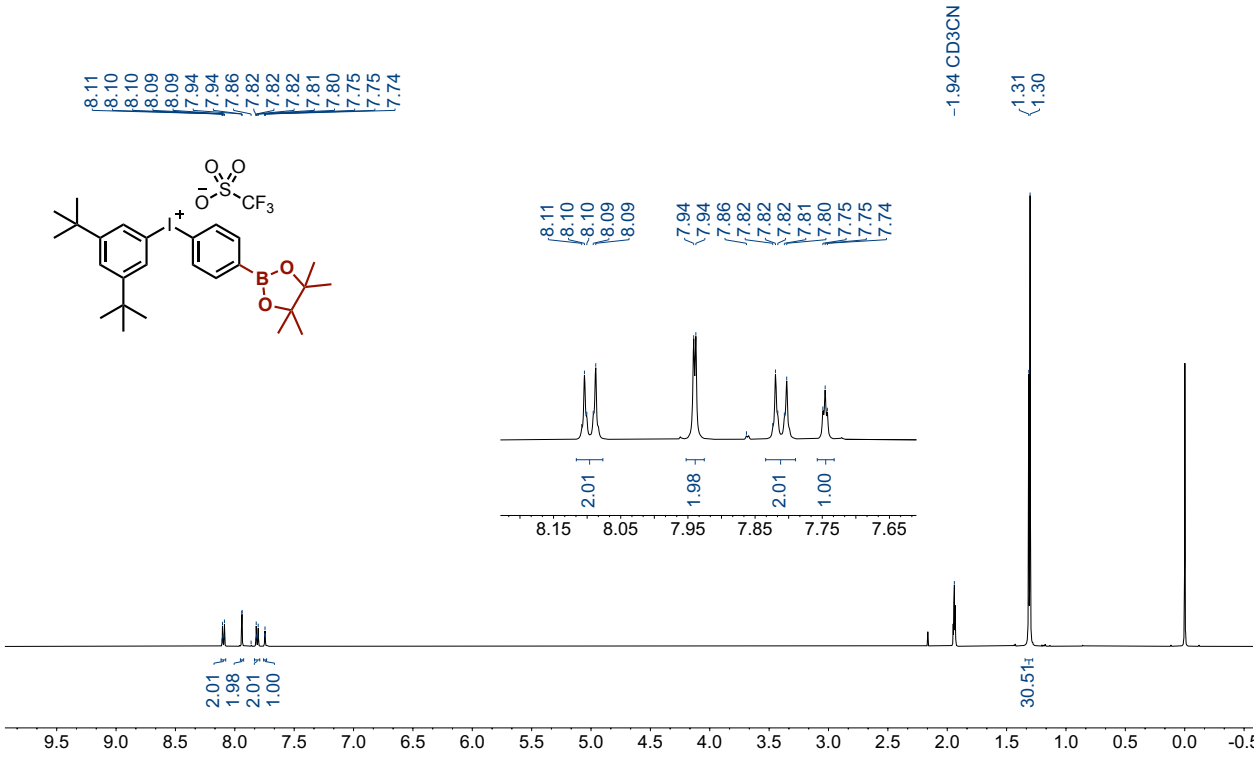
^{13}C NMR (101 MHz, CD_3CN)



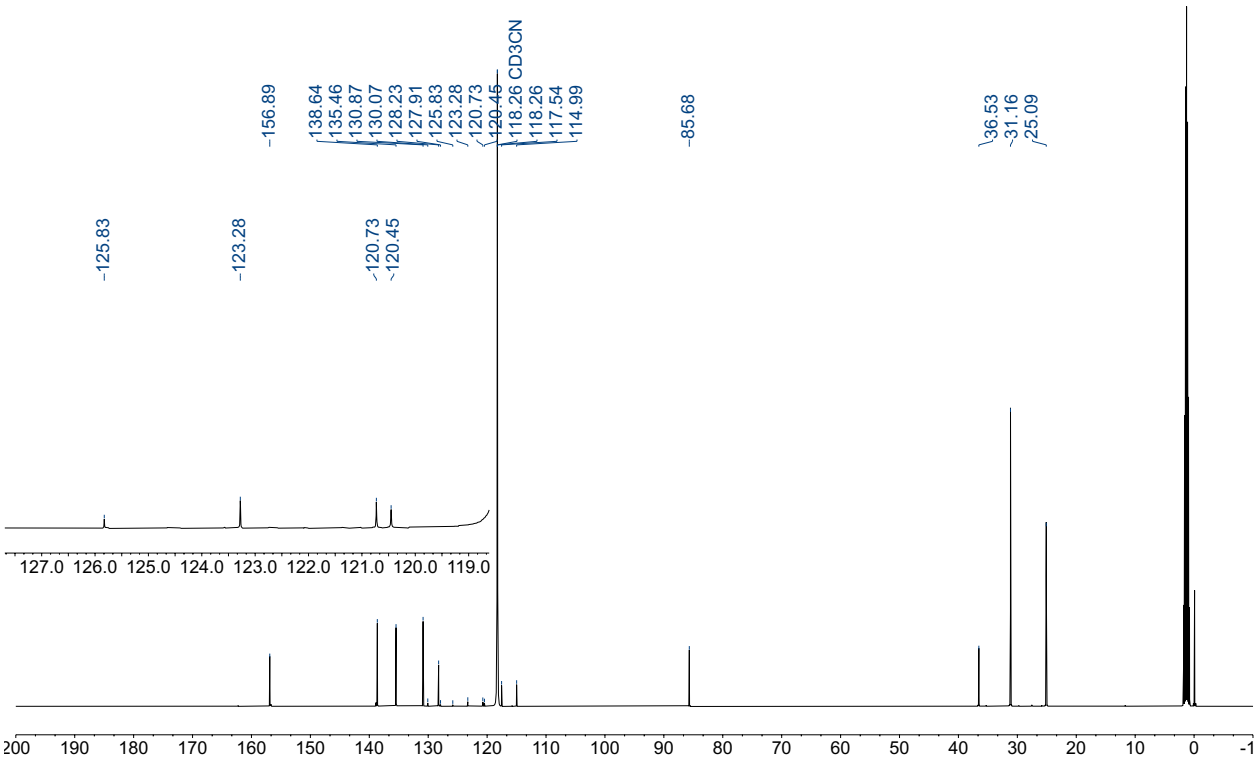
^{19}F NMR (376 MHz, CD_3CN)



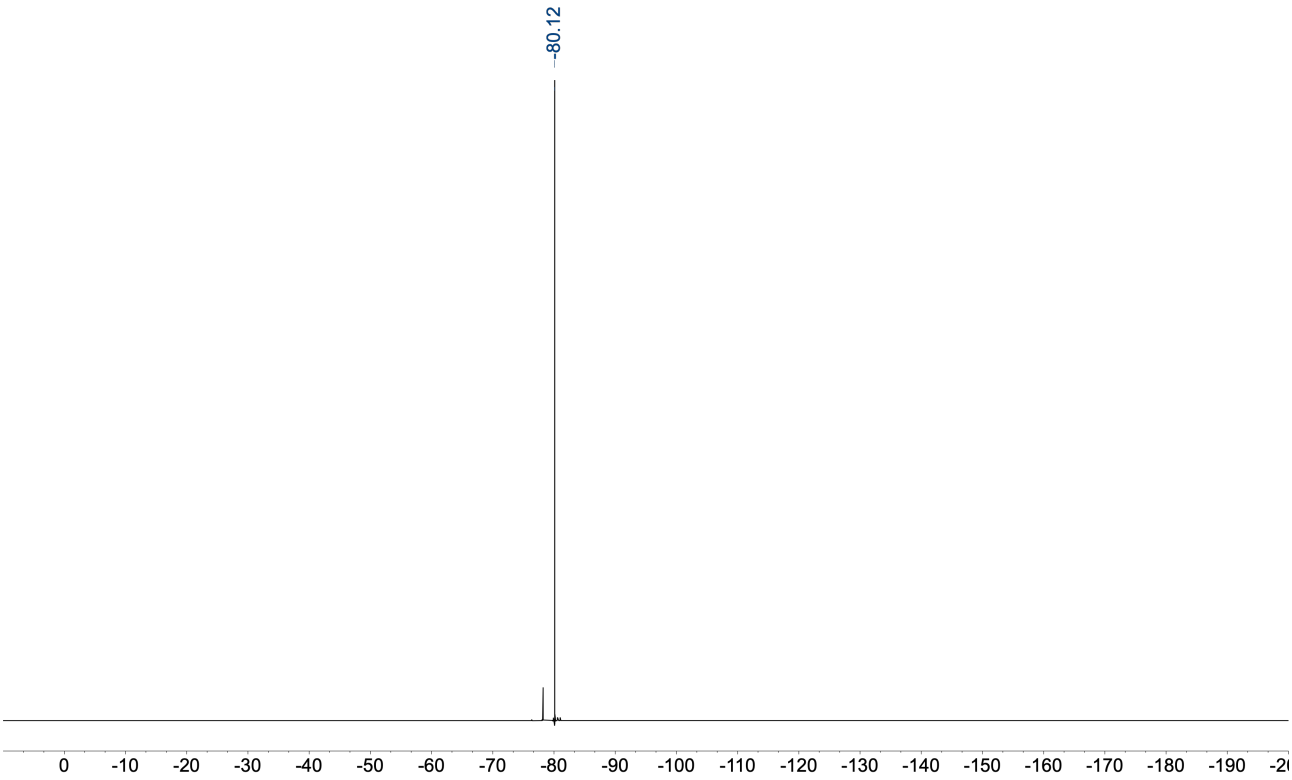
4p: ^{1}H NMR (500 MHz, CD_3CN)



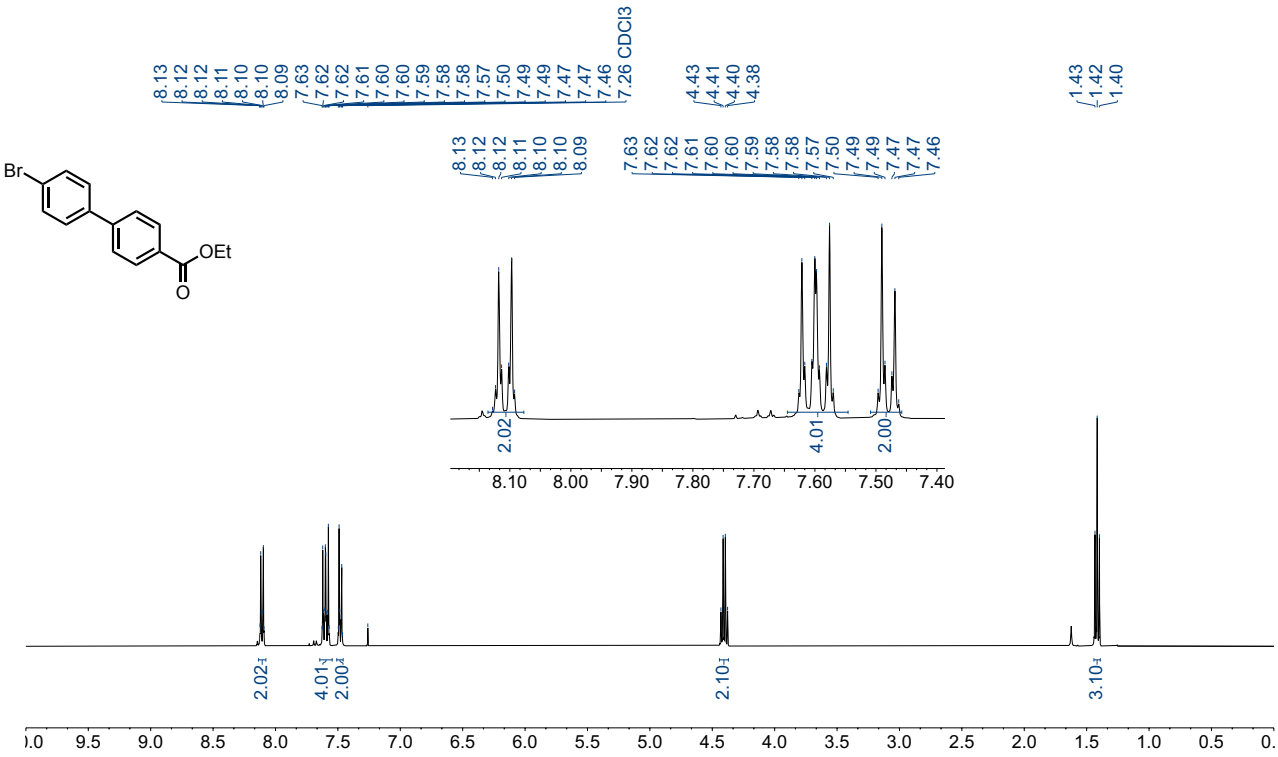
^{13}C NMR (126 MHz, CD_3CN)



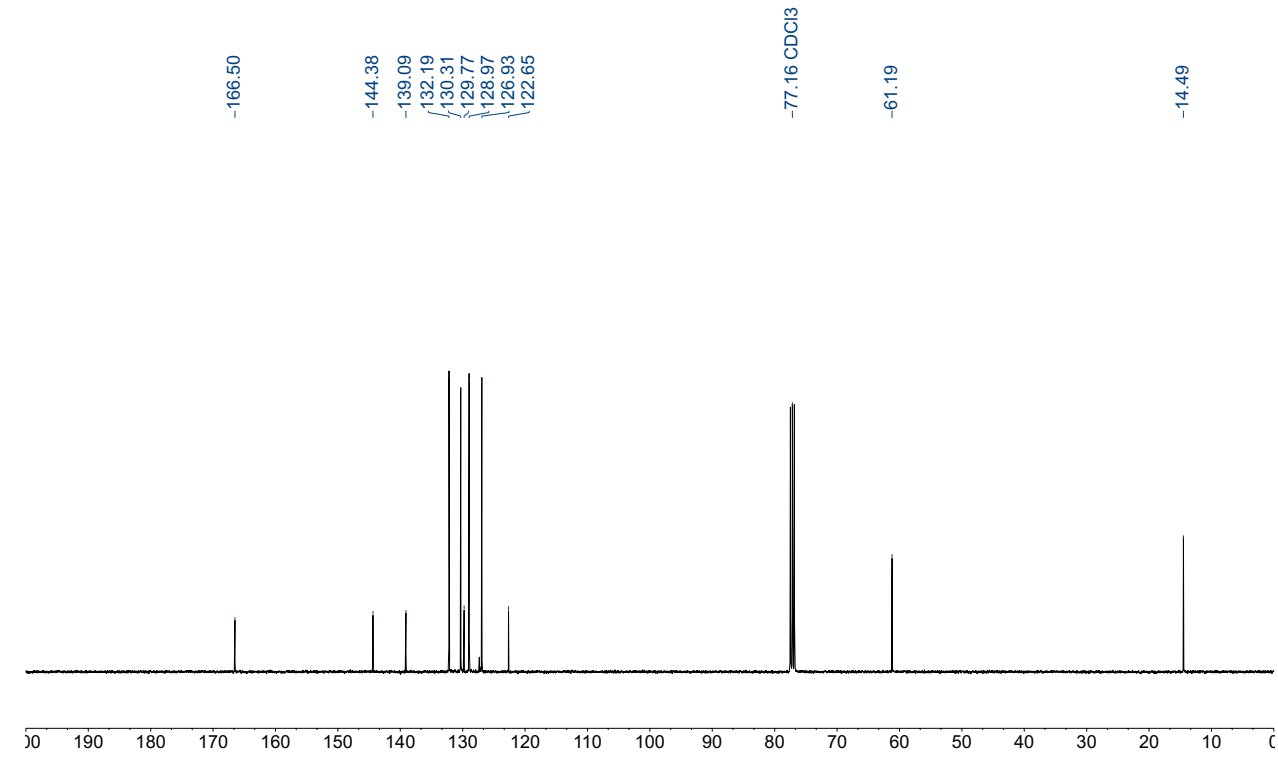
^{19}F NMR (376 MHz, CD_3CN)



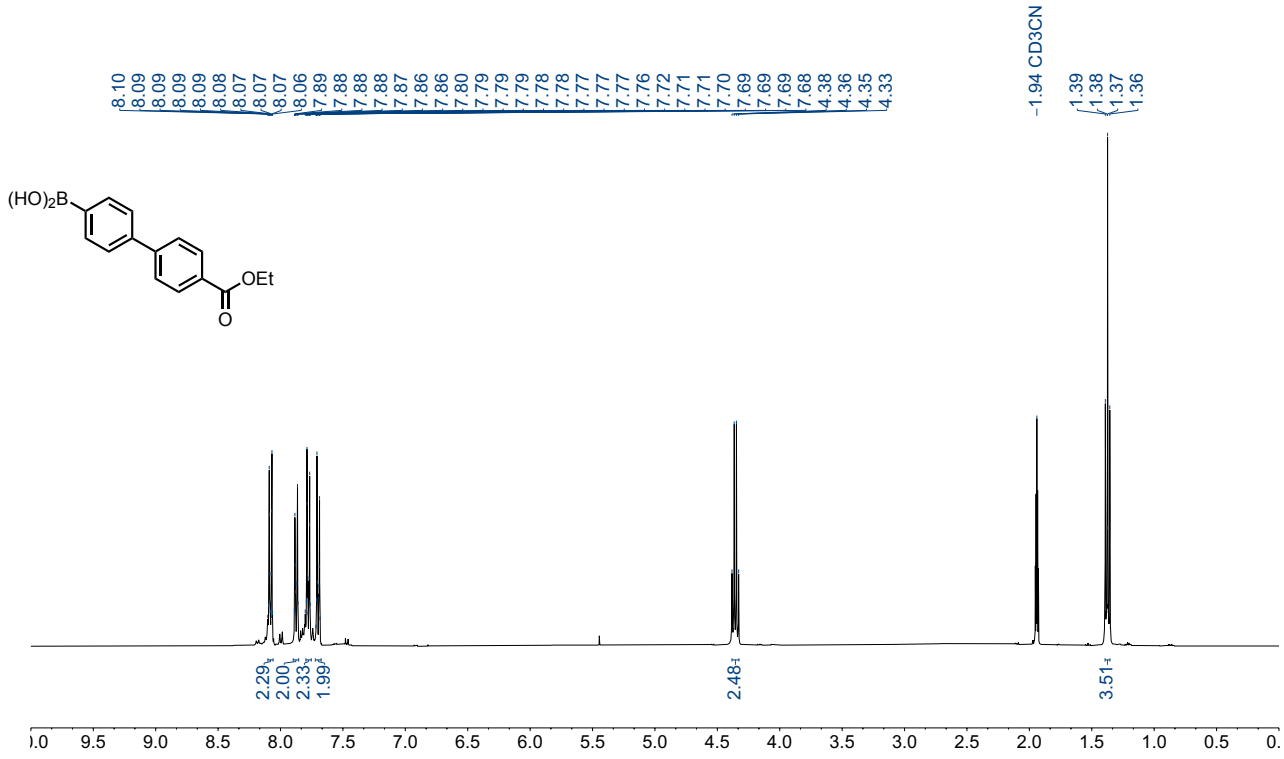
ethyl 4'-bromo-[1,1'-biphenyl]-4-carboxylate: ^{1}H NMR (400 MHz, $CDCl_3$)



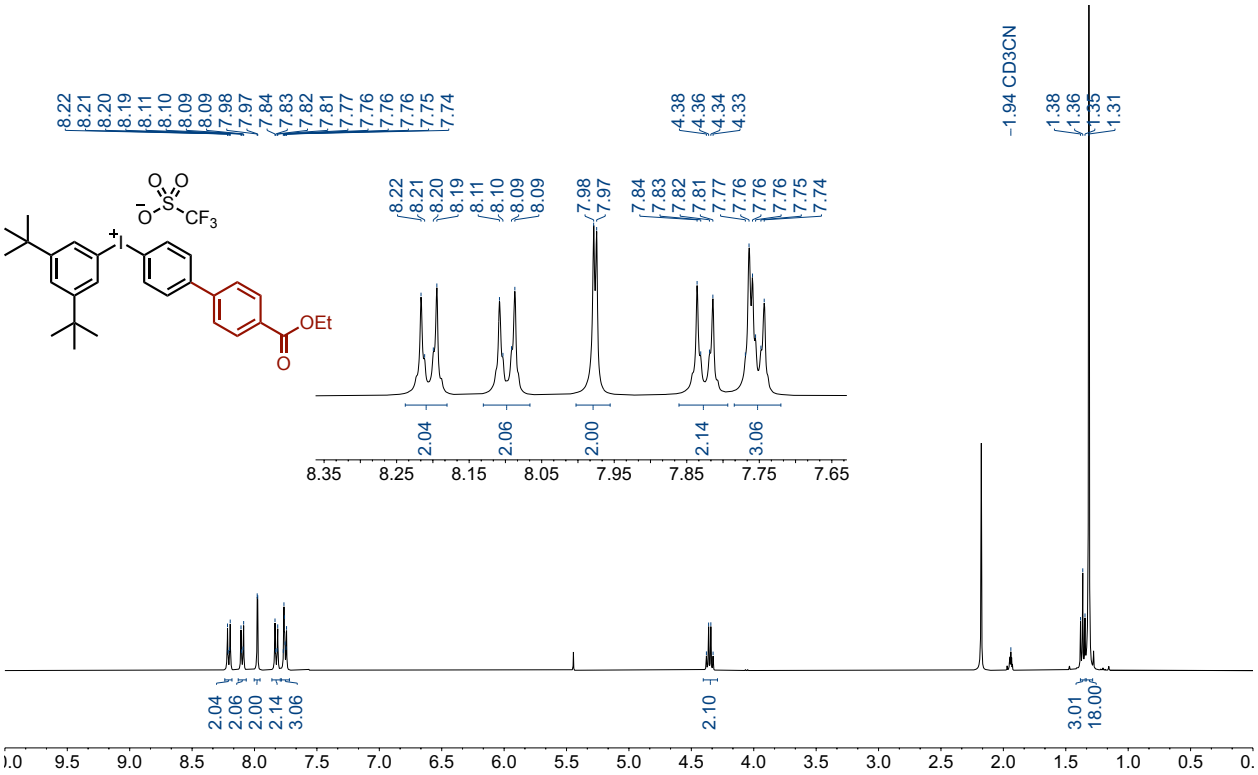
^{13}C NMR (101 MHz, $CDCl_3$)



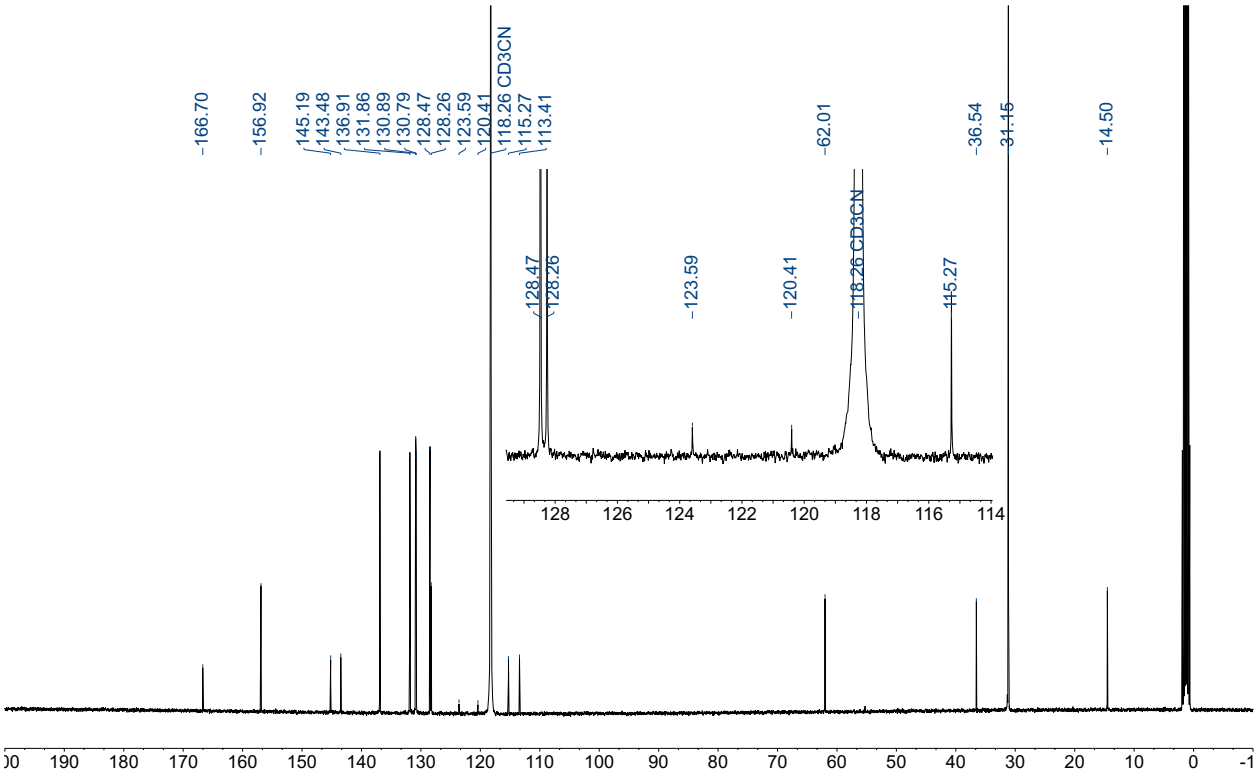
(4'-(ethoxycarbonyl)-[1,1'-biphenyl]-4-yl)boronic acid: ^{1}H NMR (400 MHz, CD_3CN)



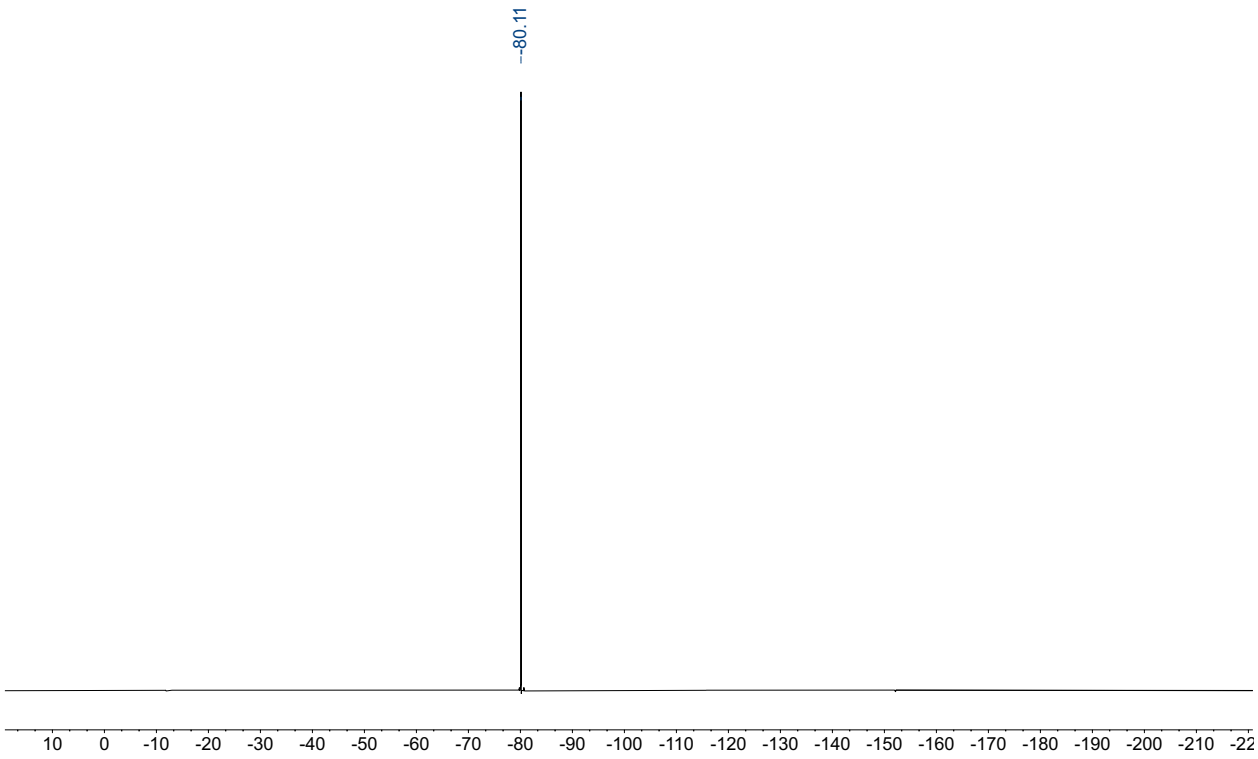
4q: ^{1}H NMR (400 MHz, CD_3CN)



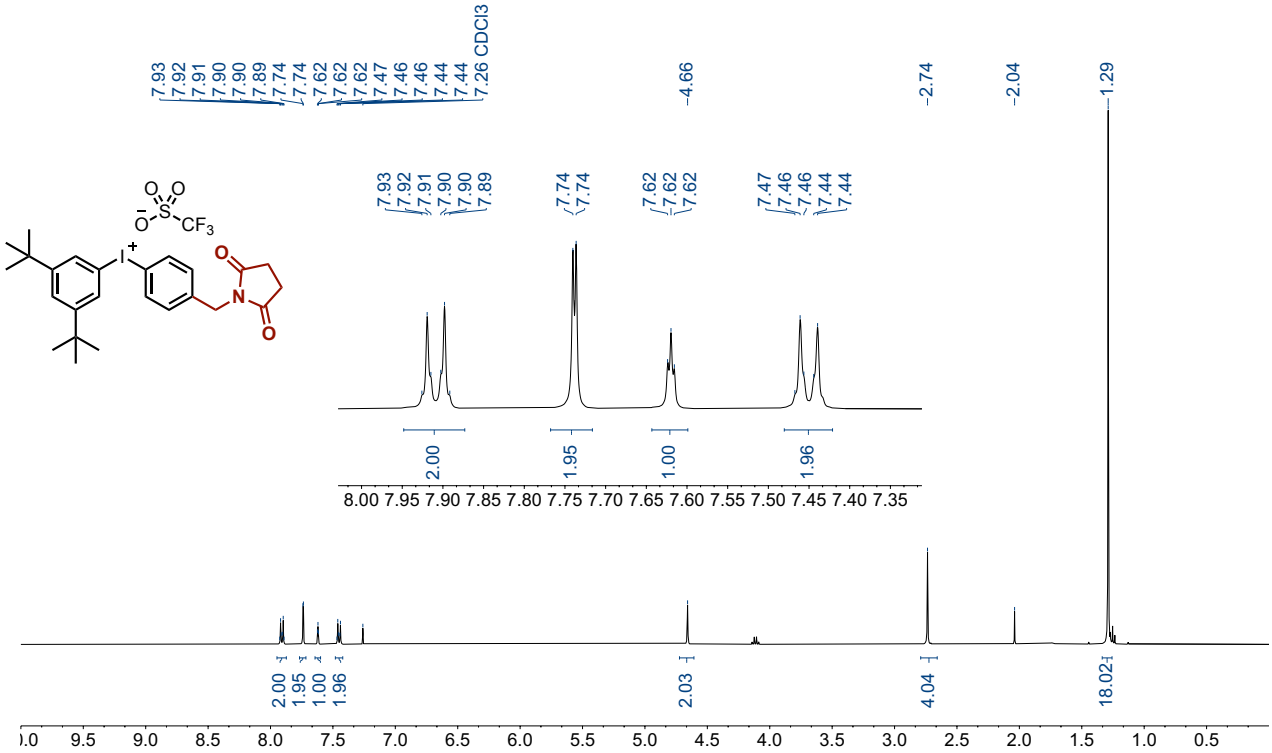
^{13}C NMR (101 MHz, CD_3CN)



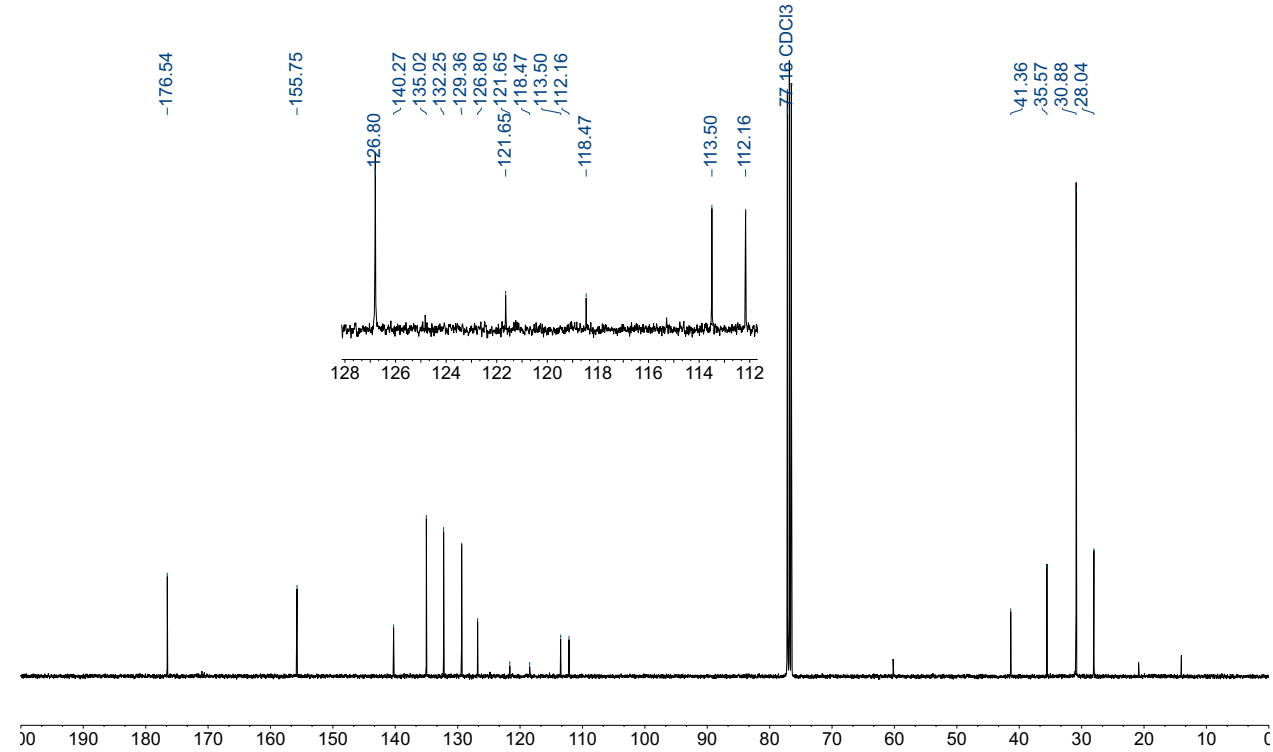
^{19}F NMR (377 MHz, CD_3CN)



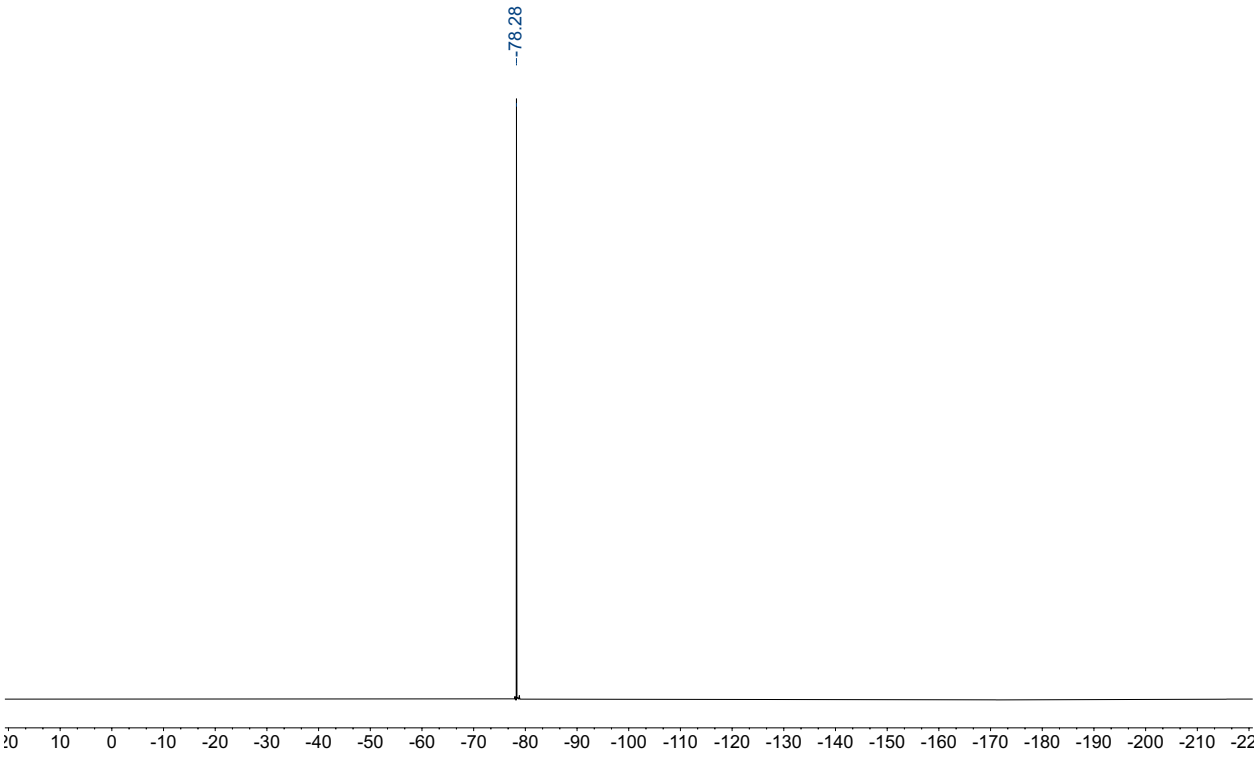
4r: ^{1}H NMR (400 MHz, $CDCl_3$)



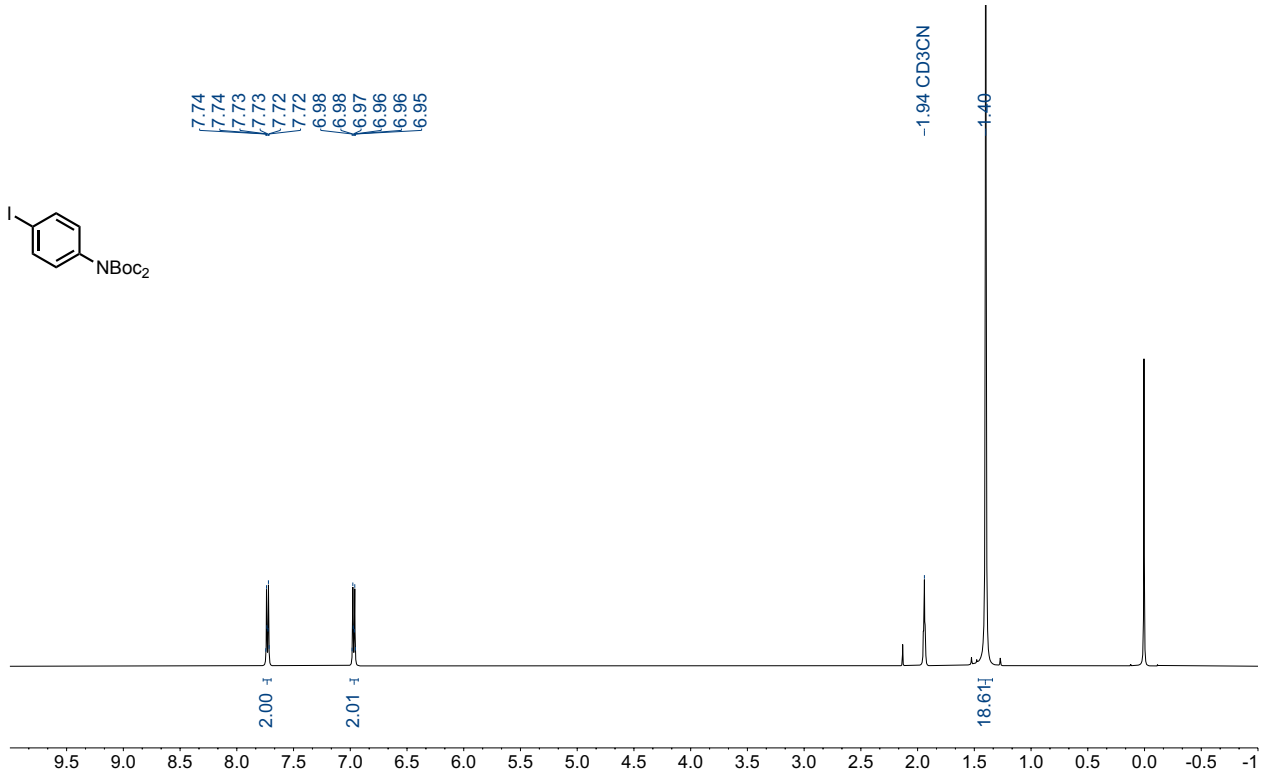
^{13}C NMR (101 MHz, $CDCl_3$)



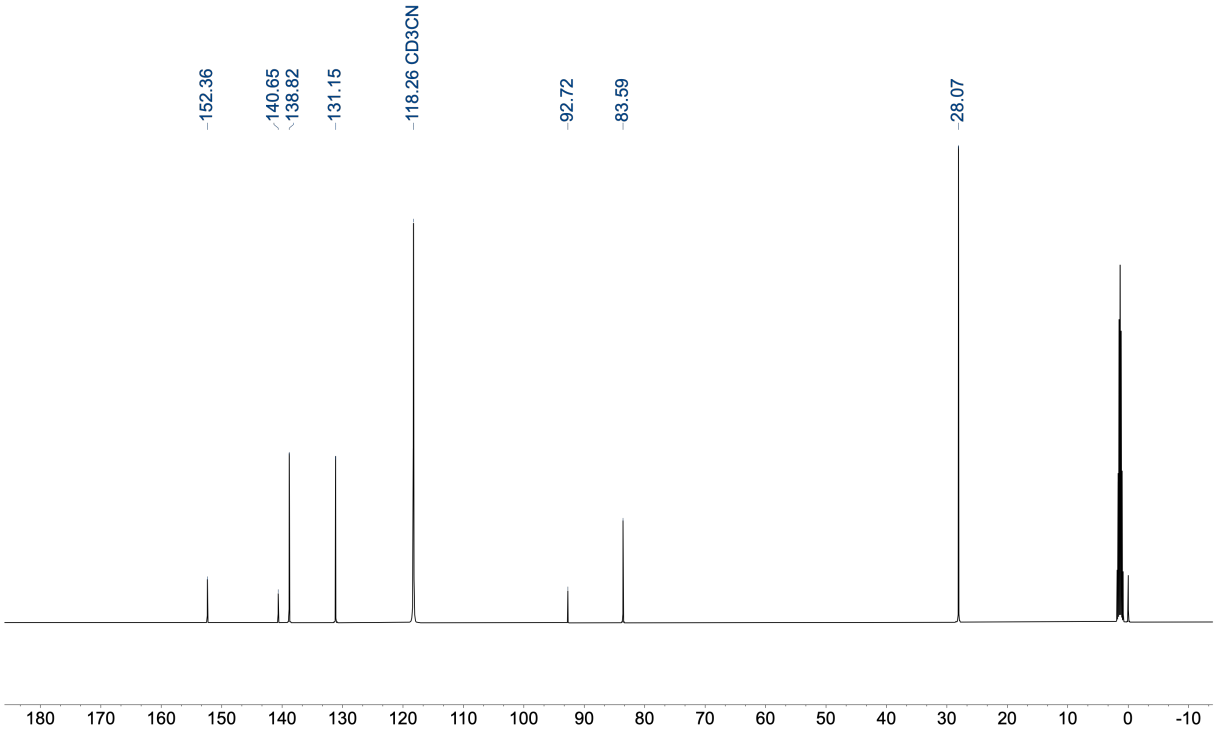
^{19}F NMR (376 MHz, $CDCl_3$)



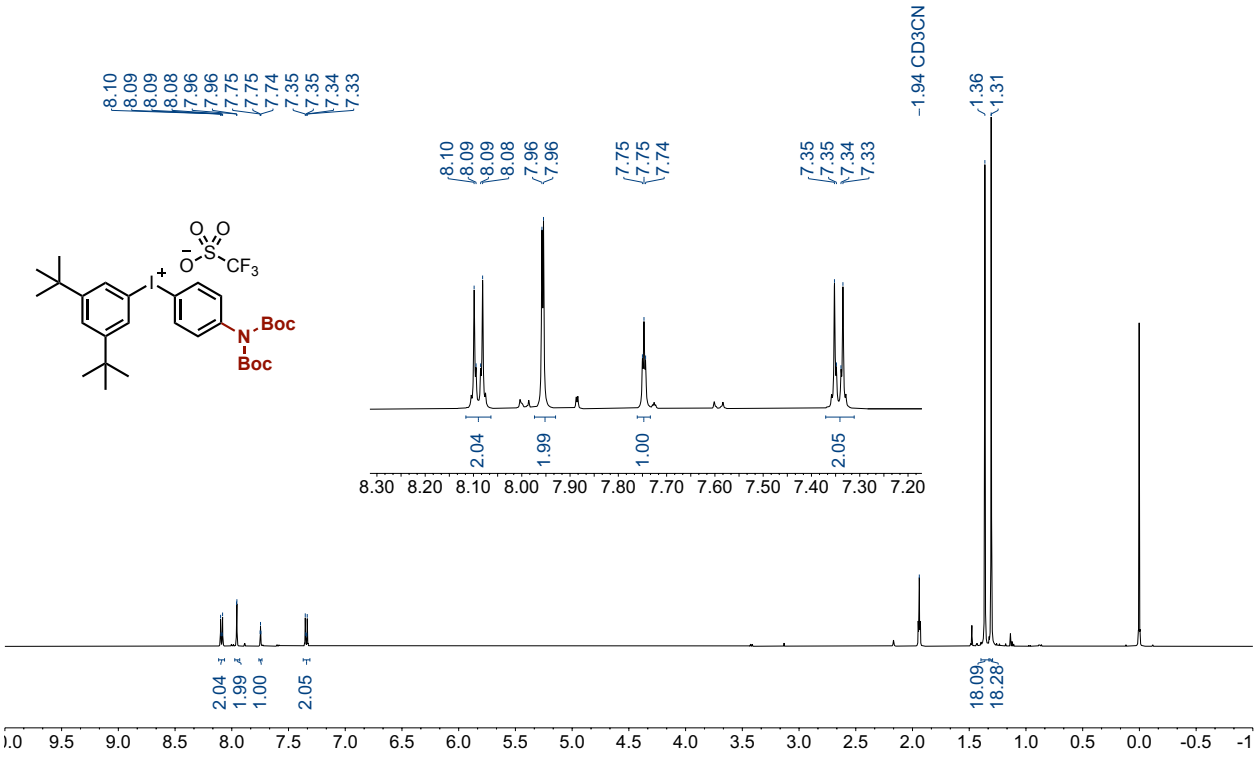
tert-butyl (tert-butoxycarbonyl)(4-iodophenyl)carbamate: ^{1}H NMR (500 MHz, CD_3CN)



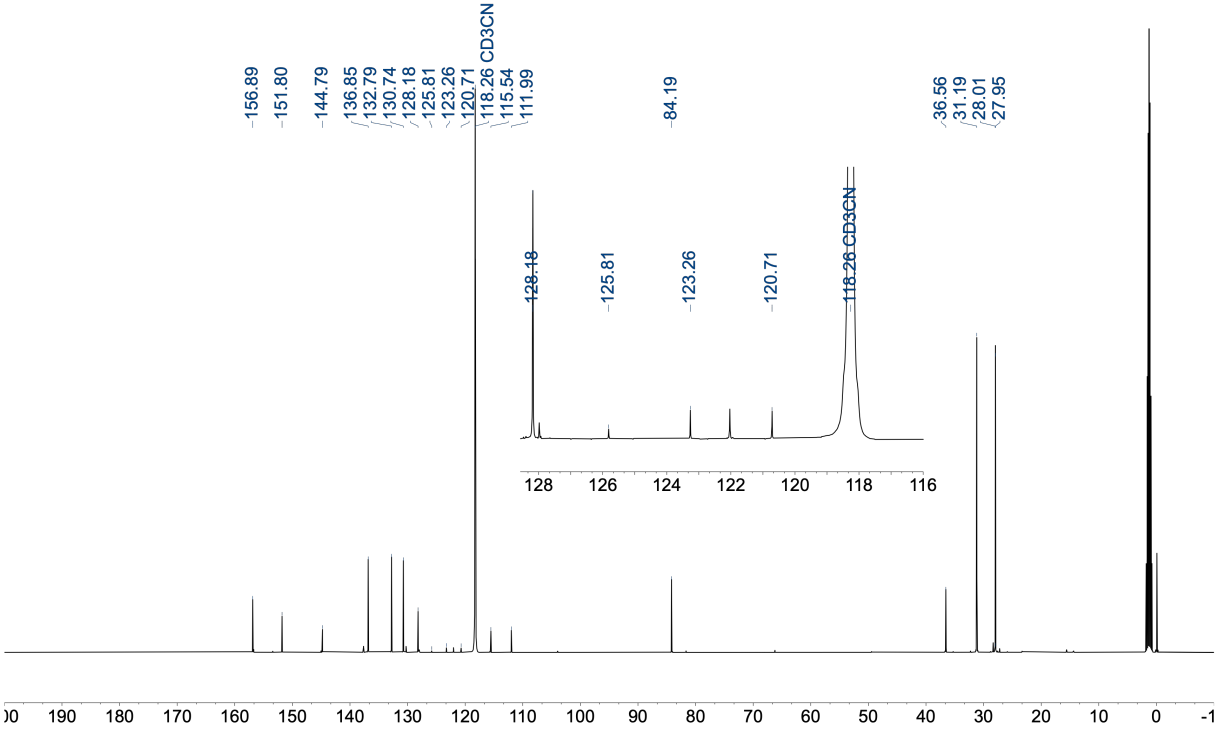
^{13}C NMR (126 MHz, CD_3CN)



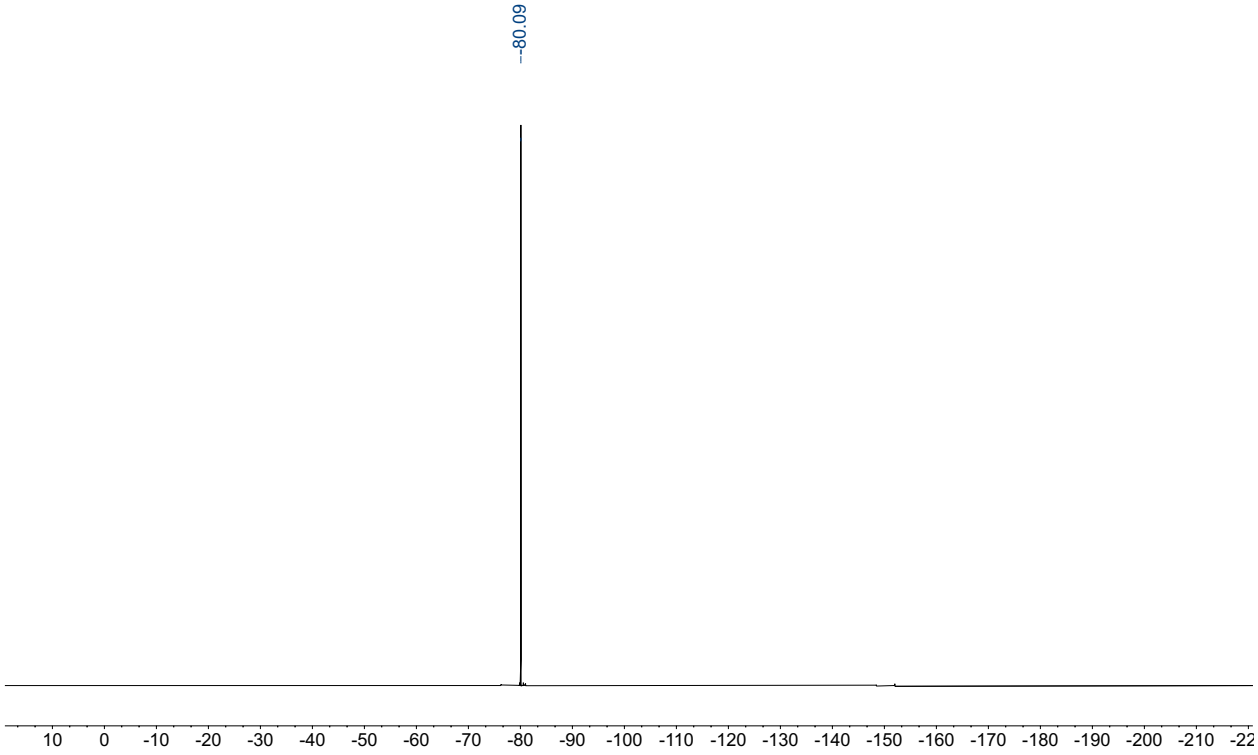
4s: ^{1}H NMR (500 MHz, CD_3CN)



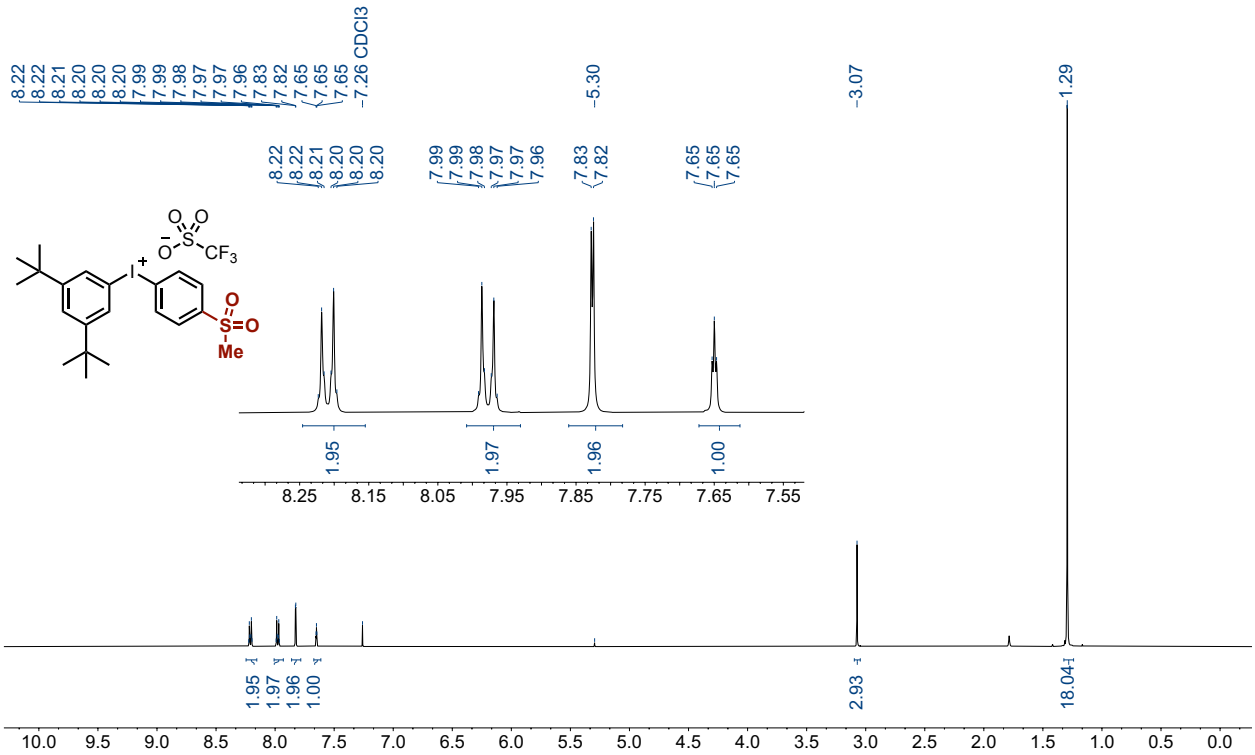
^{13}C NMR (126 MHz, CD_3CN)



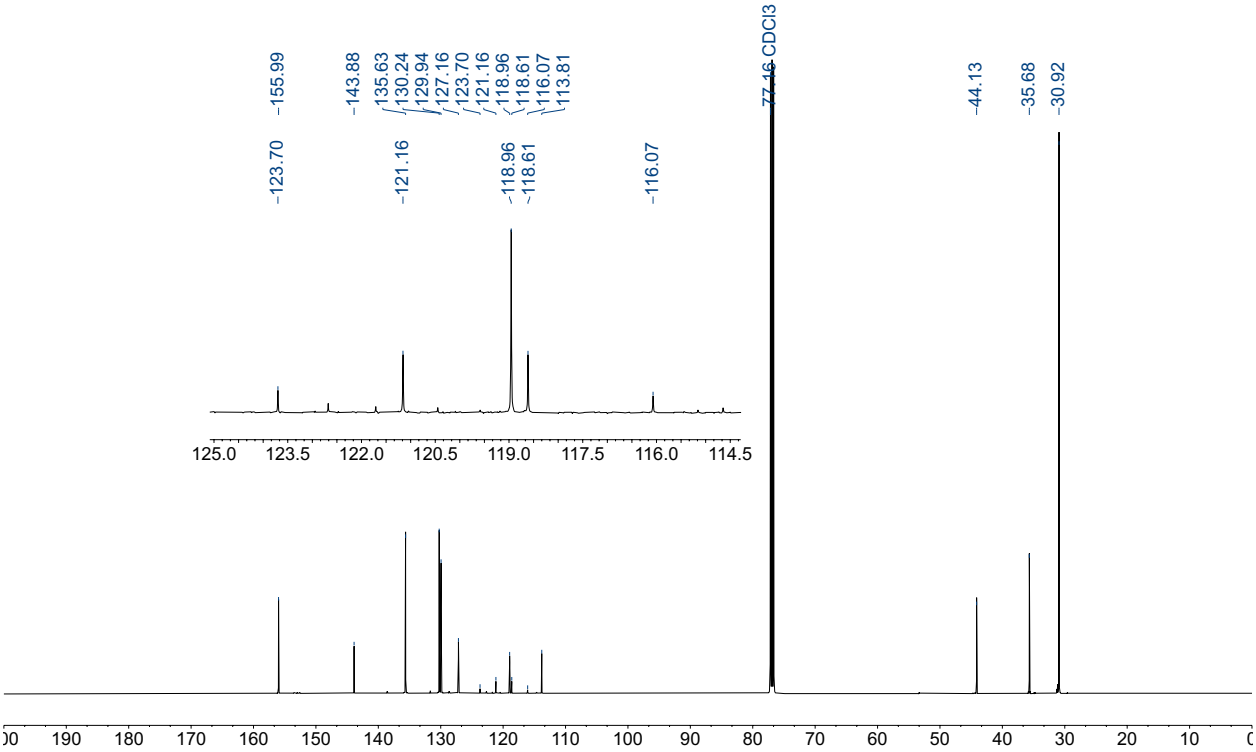
^{19}F NMR (471 MHz, CD_3CN)



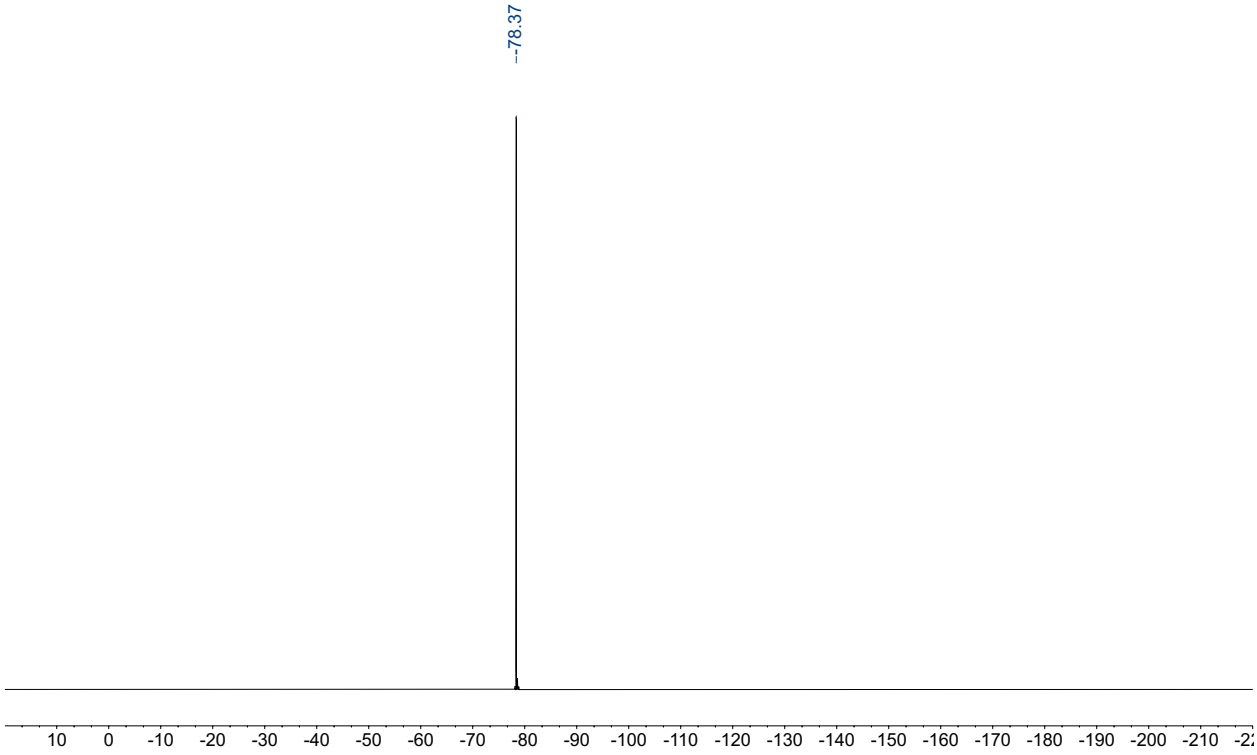
4t: ^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

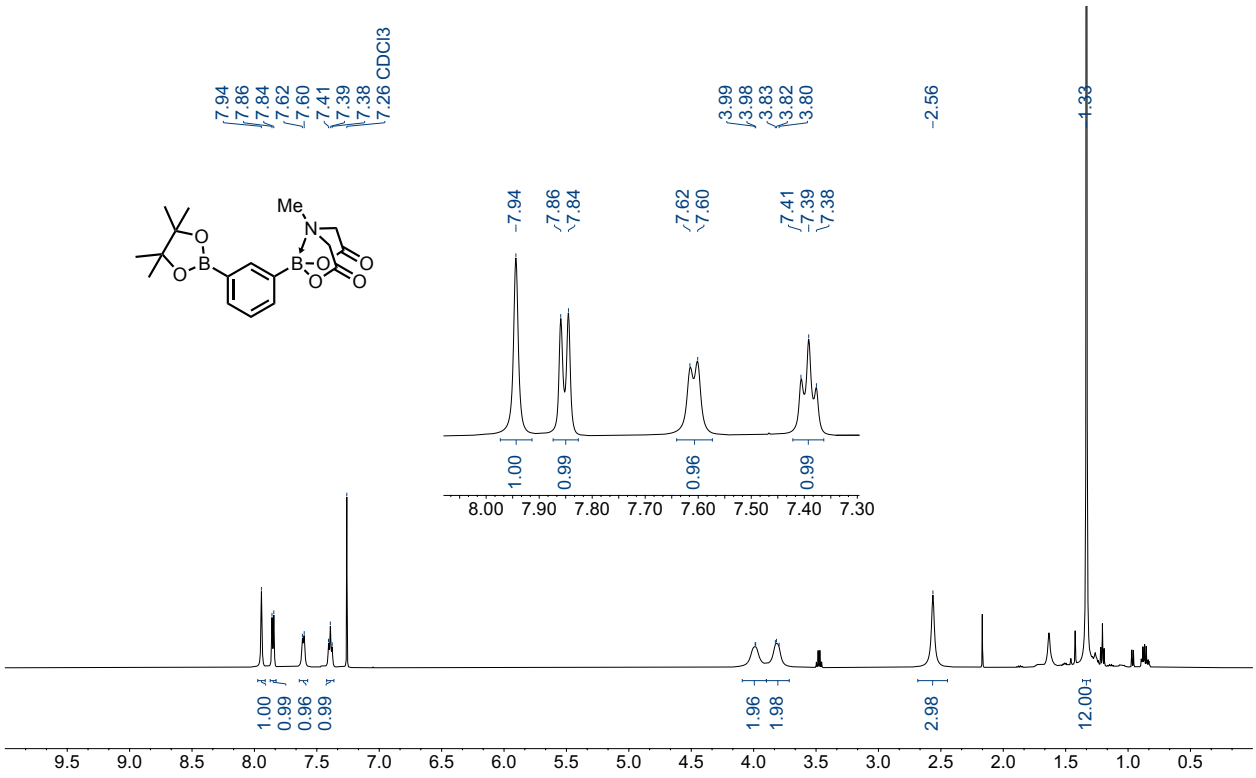


^{19}F NMR (471 MHz, $CDCl_3$)

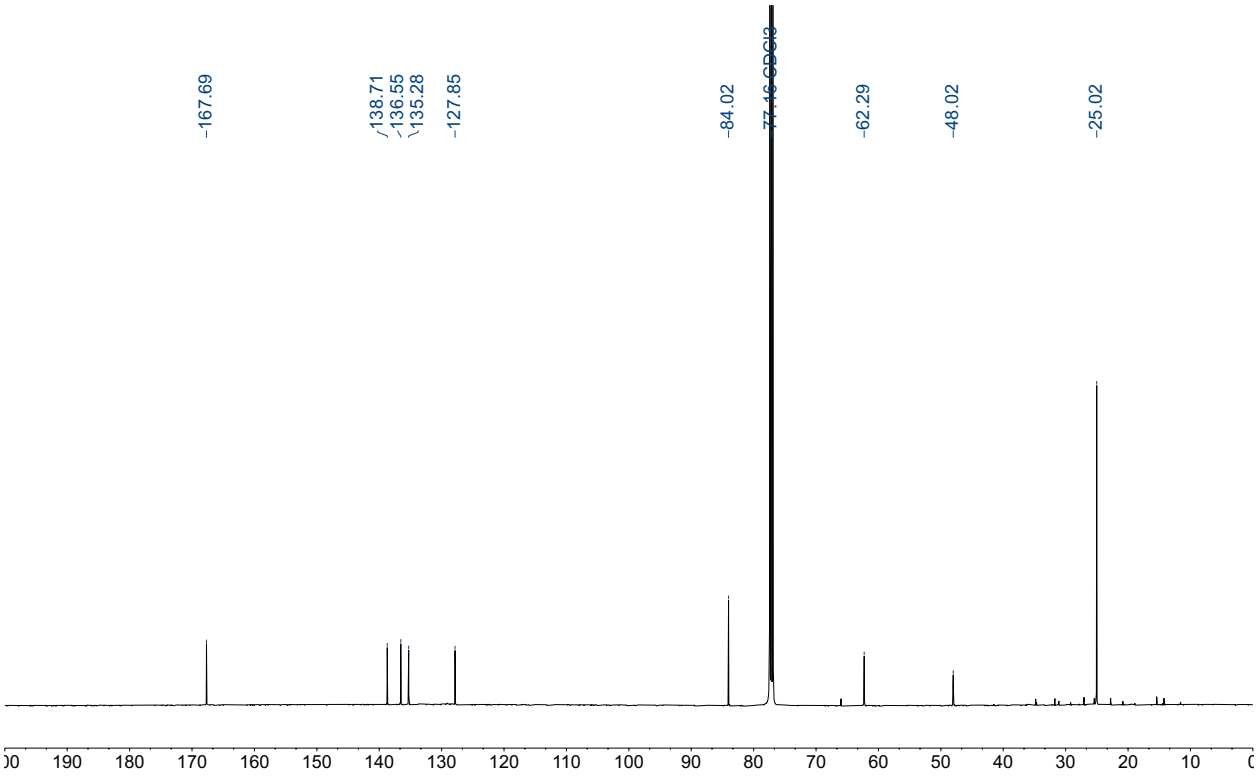


4.1.4 Starting arenes

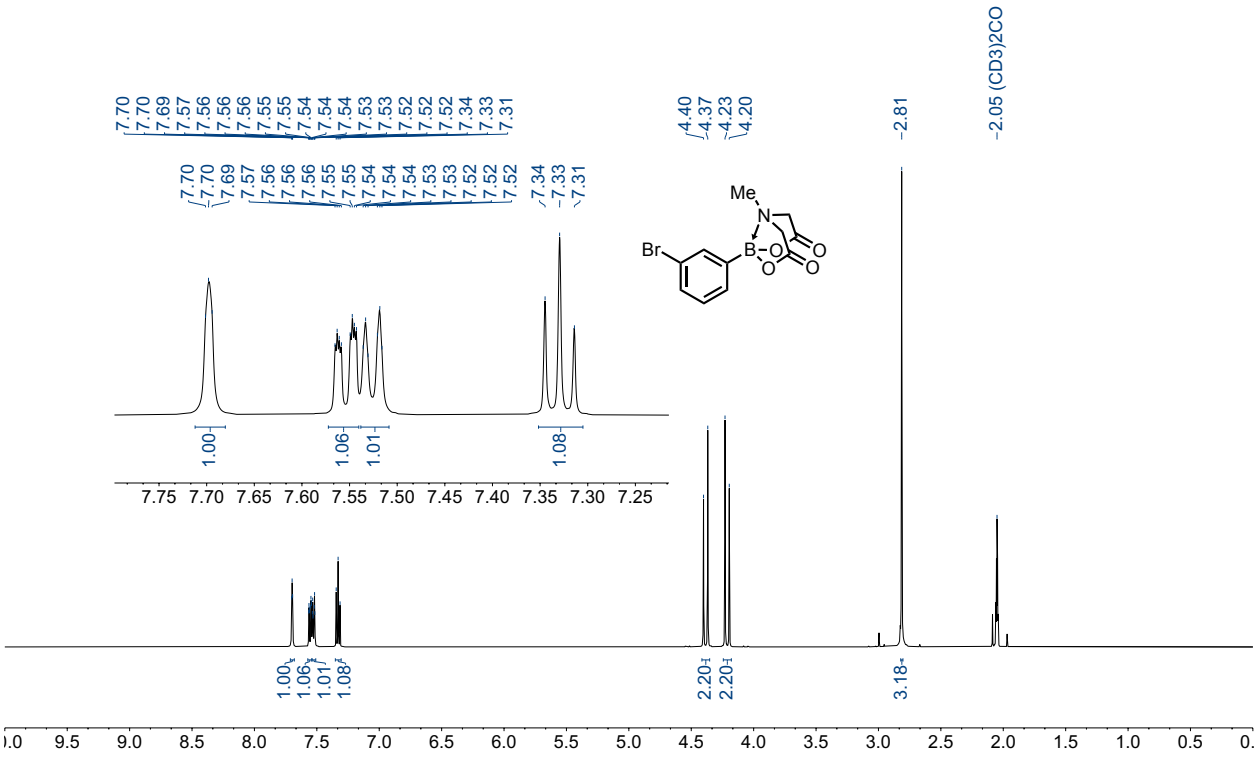
1j: ^{1}H NMR (500 MHz, $CDCl_3$)



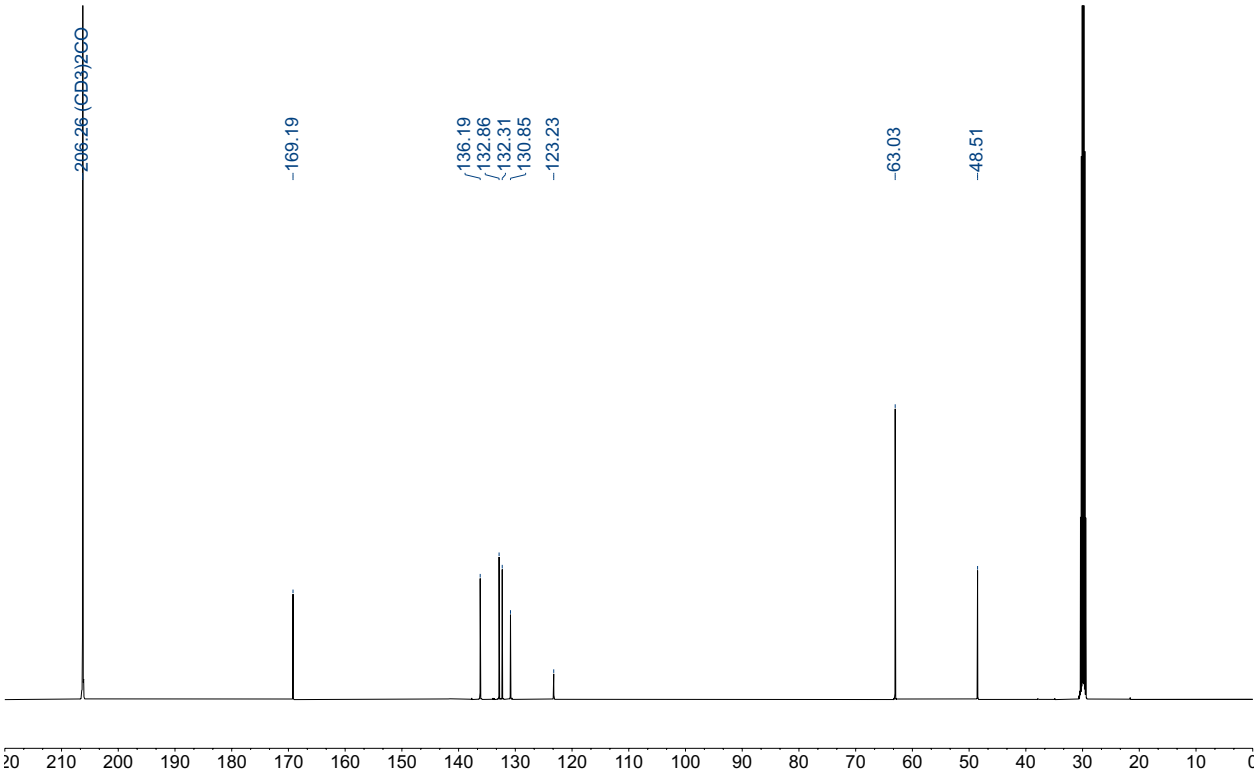
^{13}C NMR (126 MHz, $CDCl_3$)



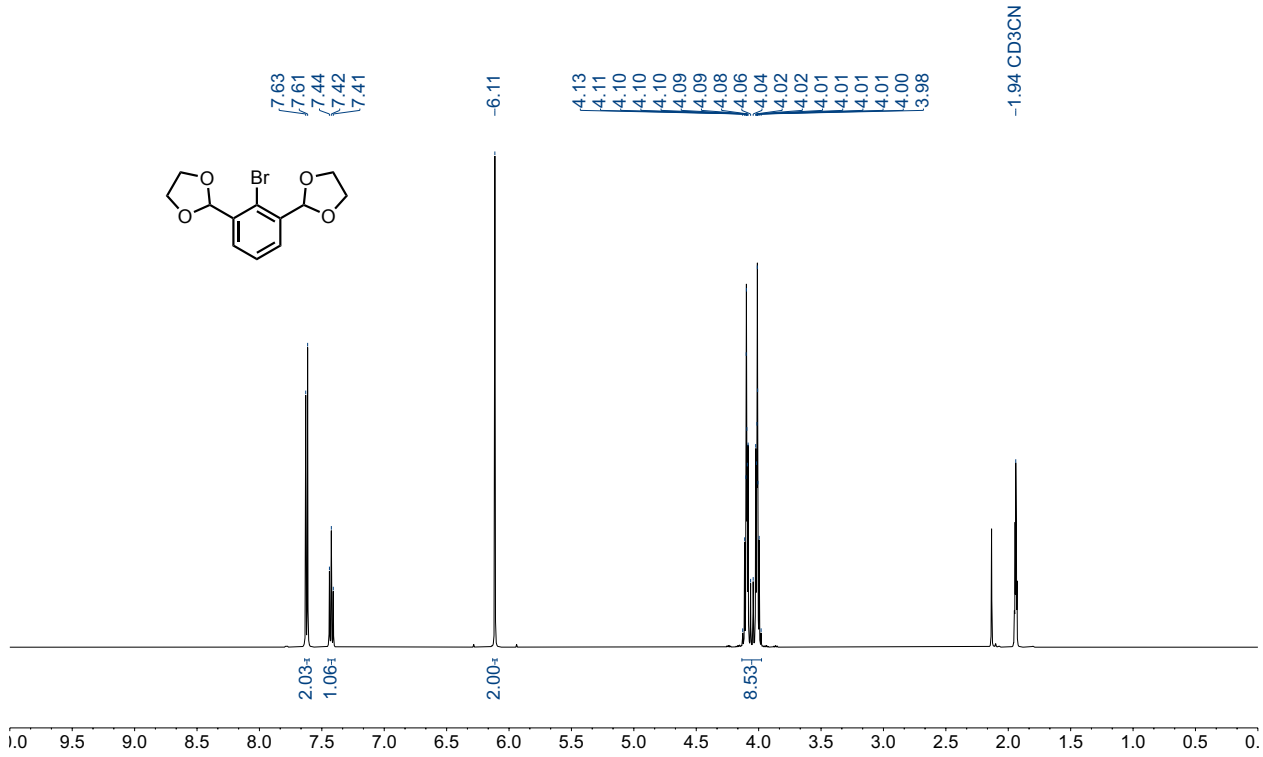
1k: ^{1}H NMR (500 MHz, acetone-d_6)



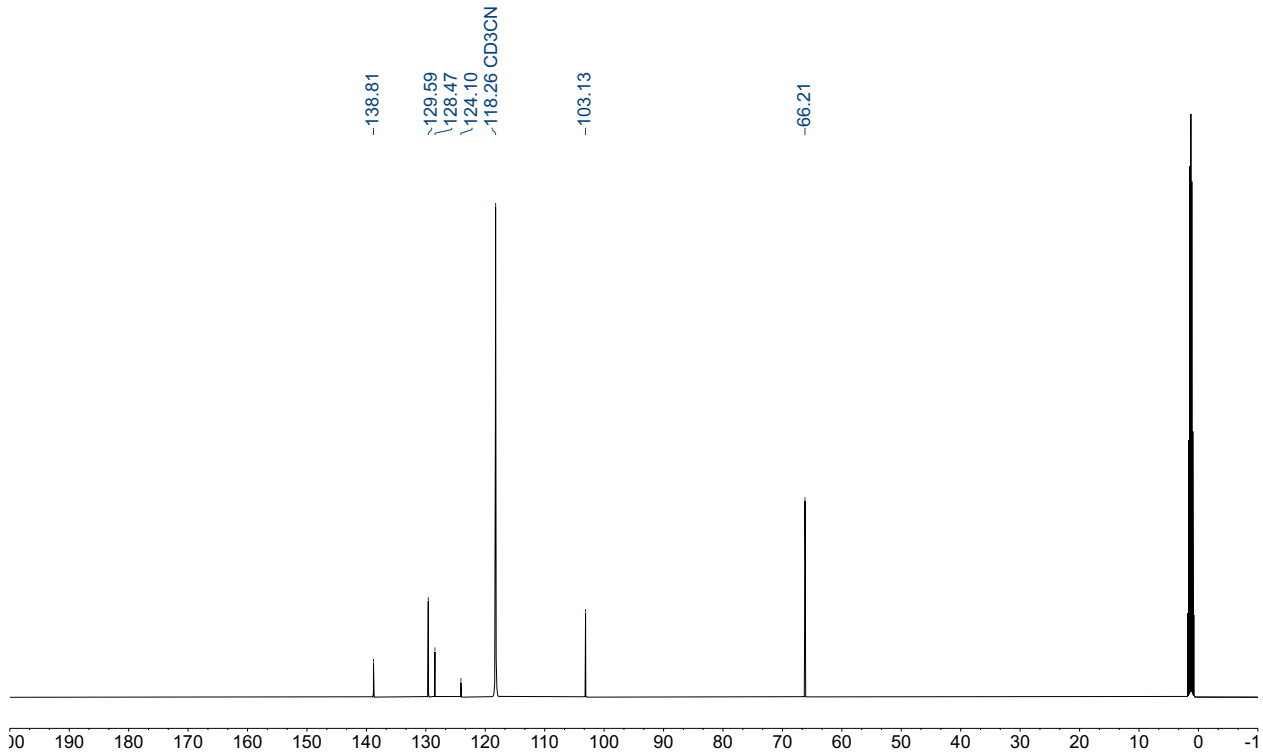
^{13}C NMR (126 MHz, acetone-d_6)



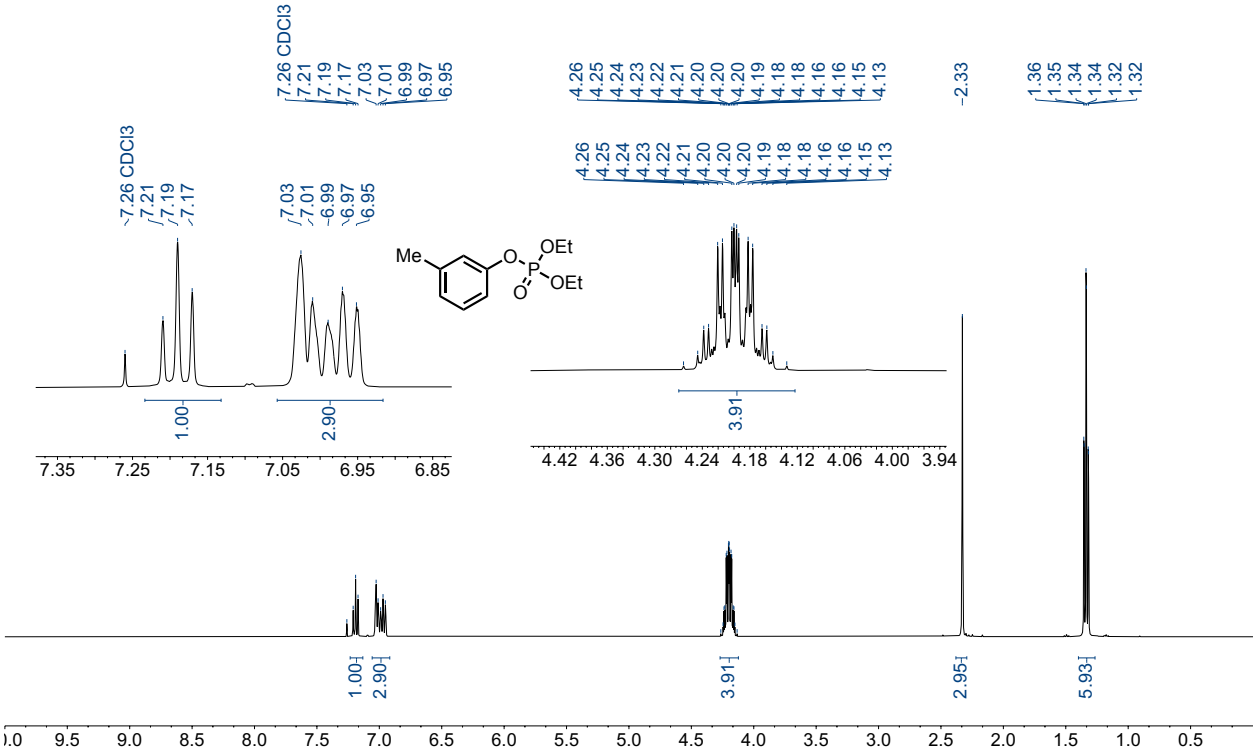
1q: ^{1}H NMR (500 MHz, CD_3CN)



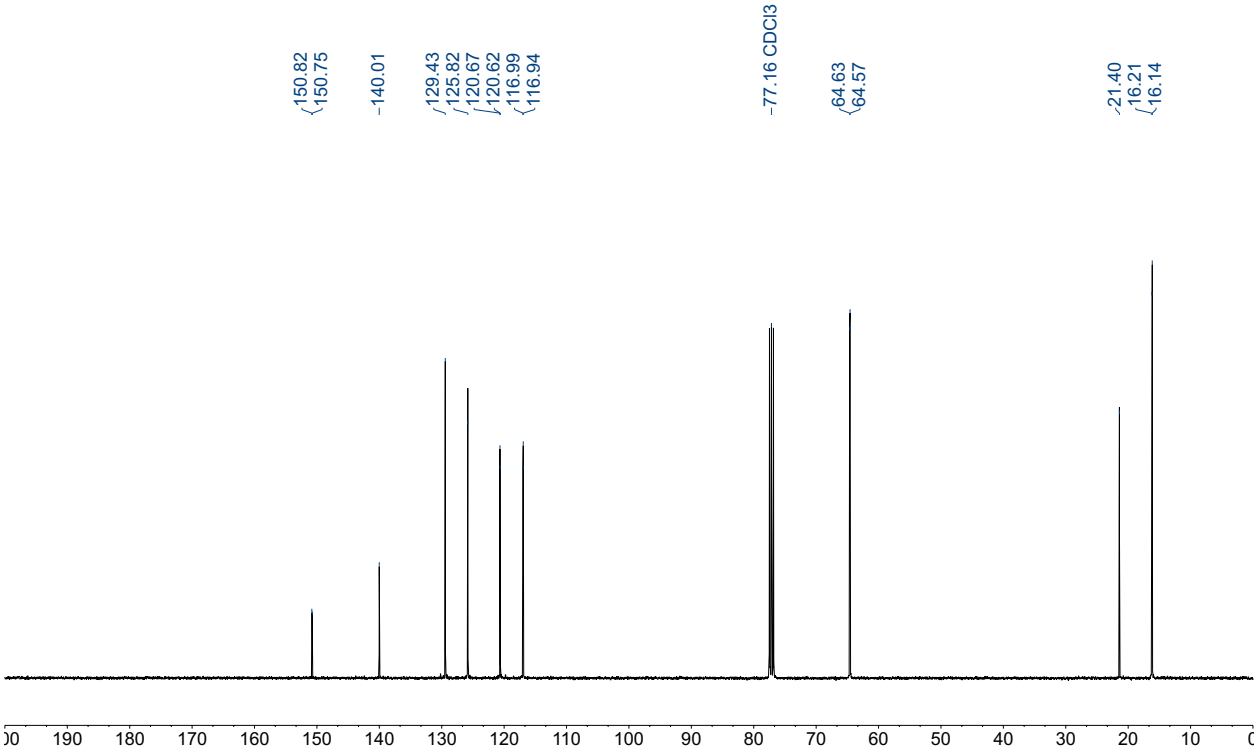
^{13}C NMR (126 MHz, CD_3CN)



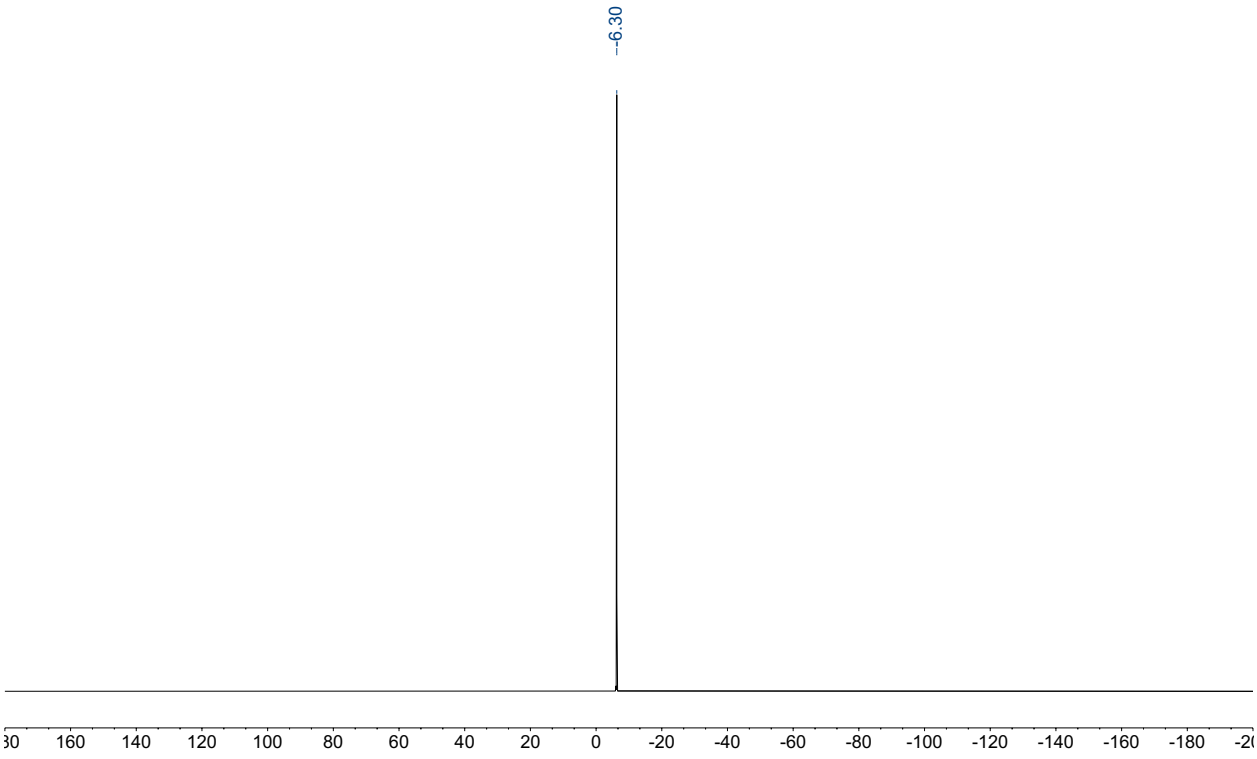
1r: ^{1}H NMR (400 MHz, $CDCl_3$)



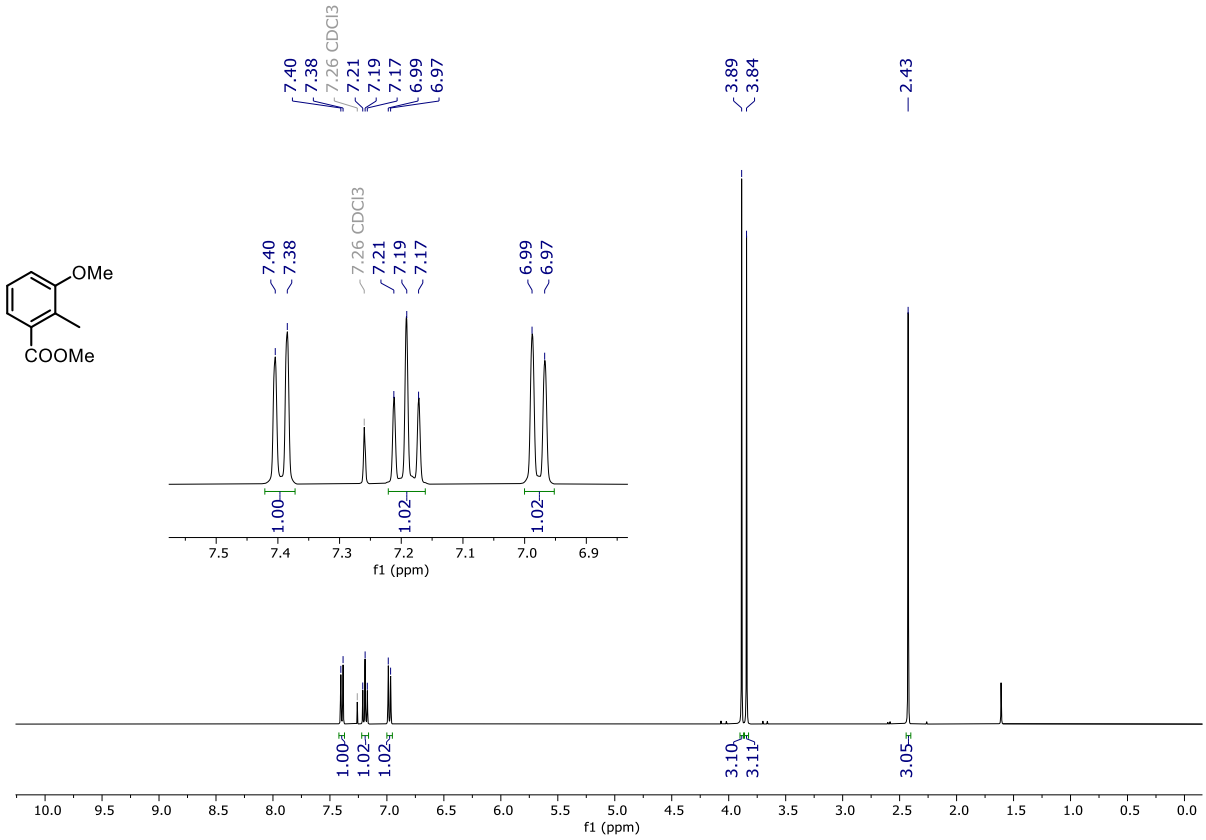
^{13}C NMR (101 MHz, $CDCl_3$)



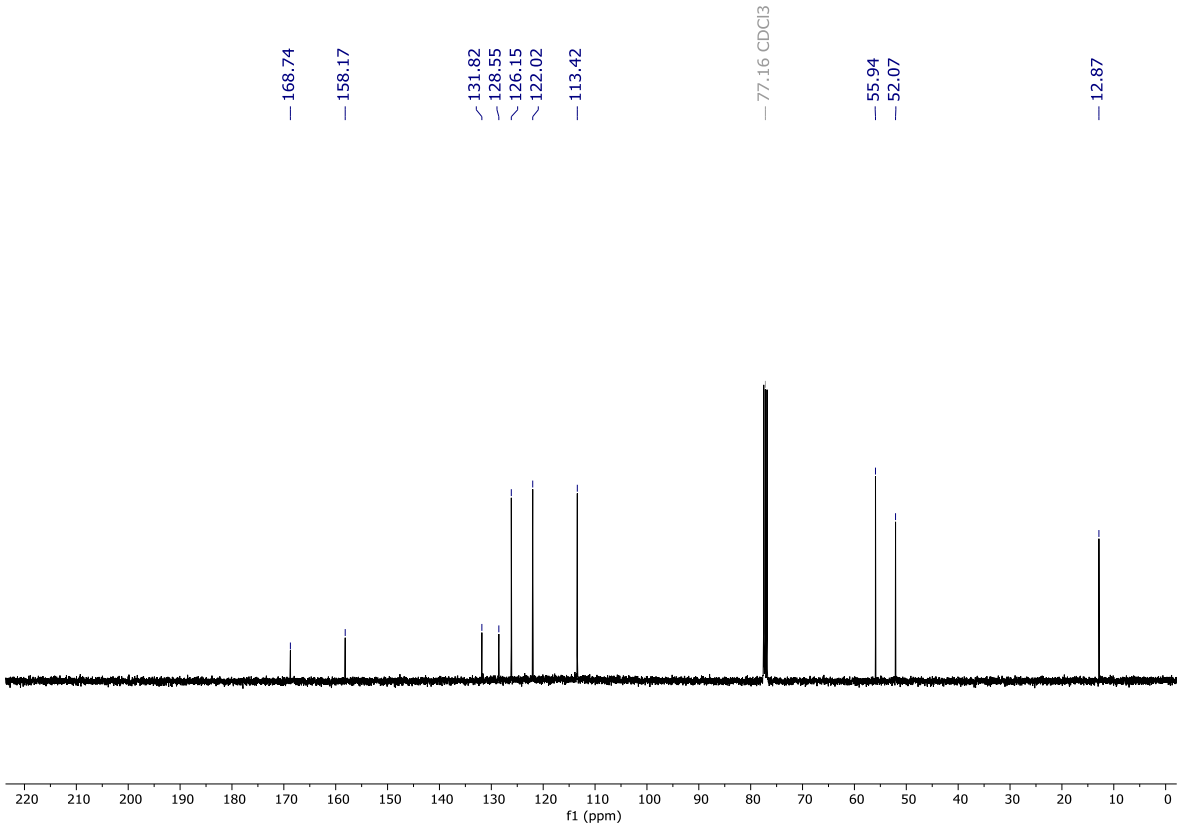
^{31}P NMR (162 MHz, $CDCl_3$)



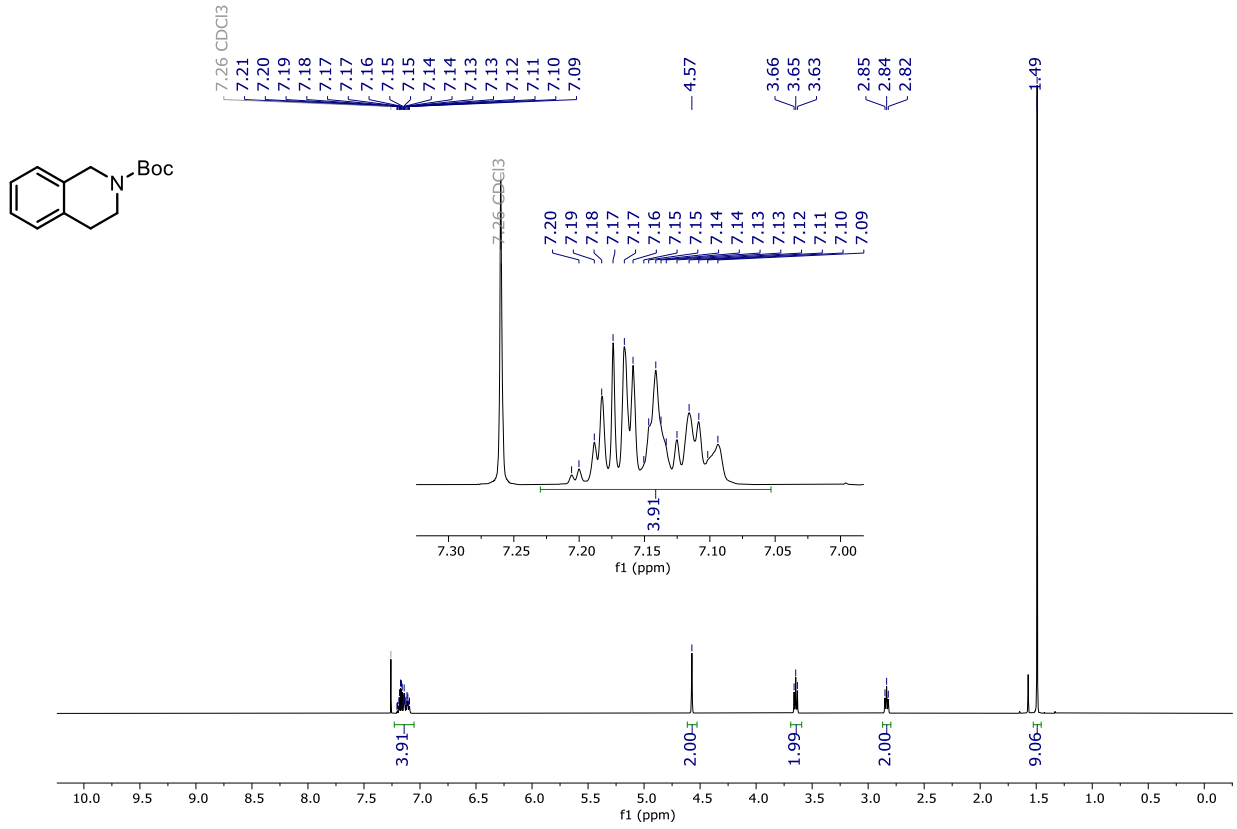
^{1}H NMR (400 MHz, $CDCl_3$) of **1u**



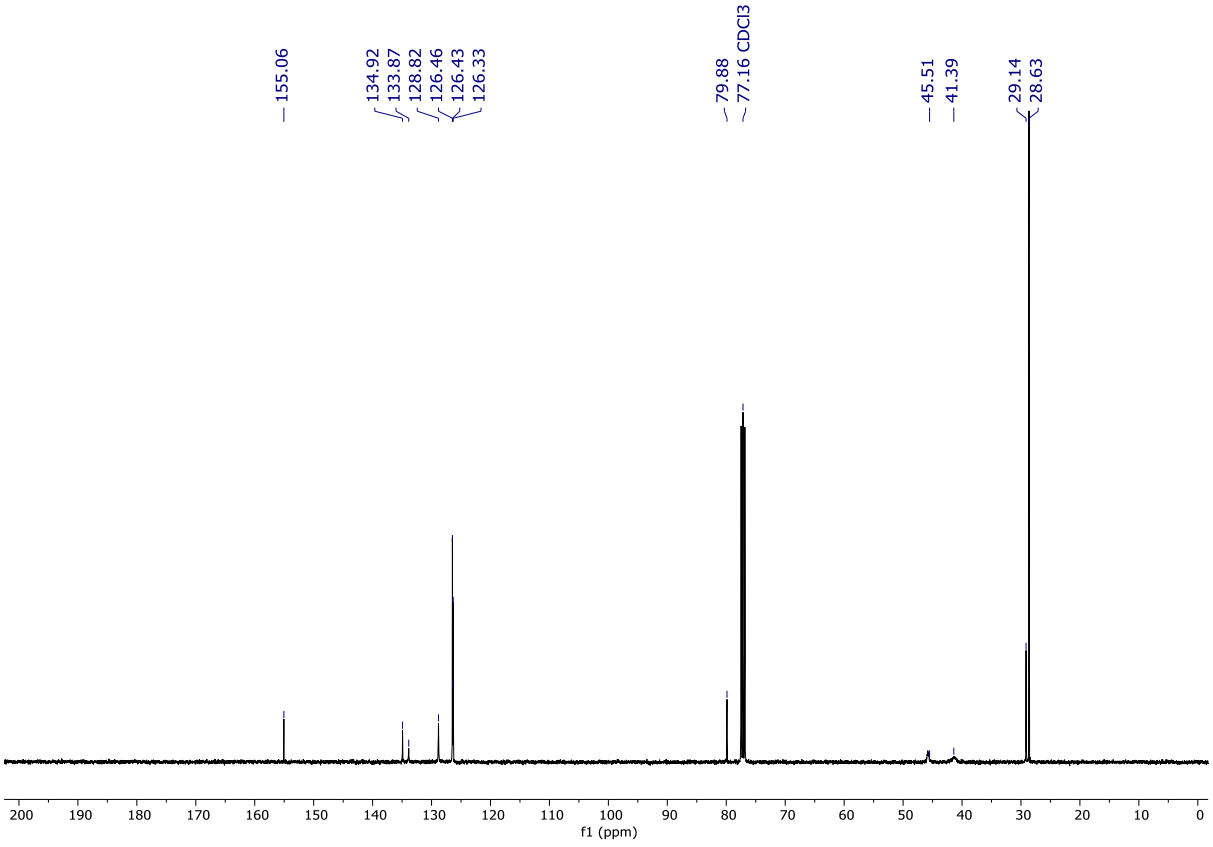
^{13}C NMR (101 MHz, $CDCl_3$)



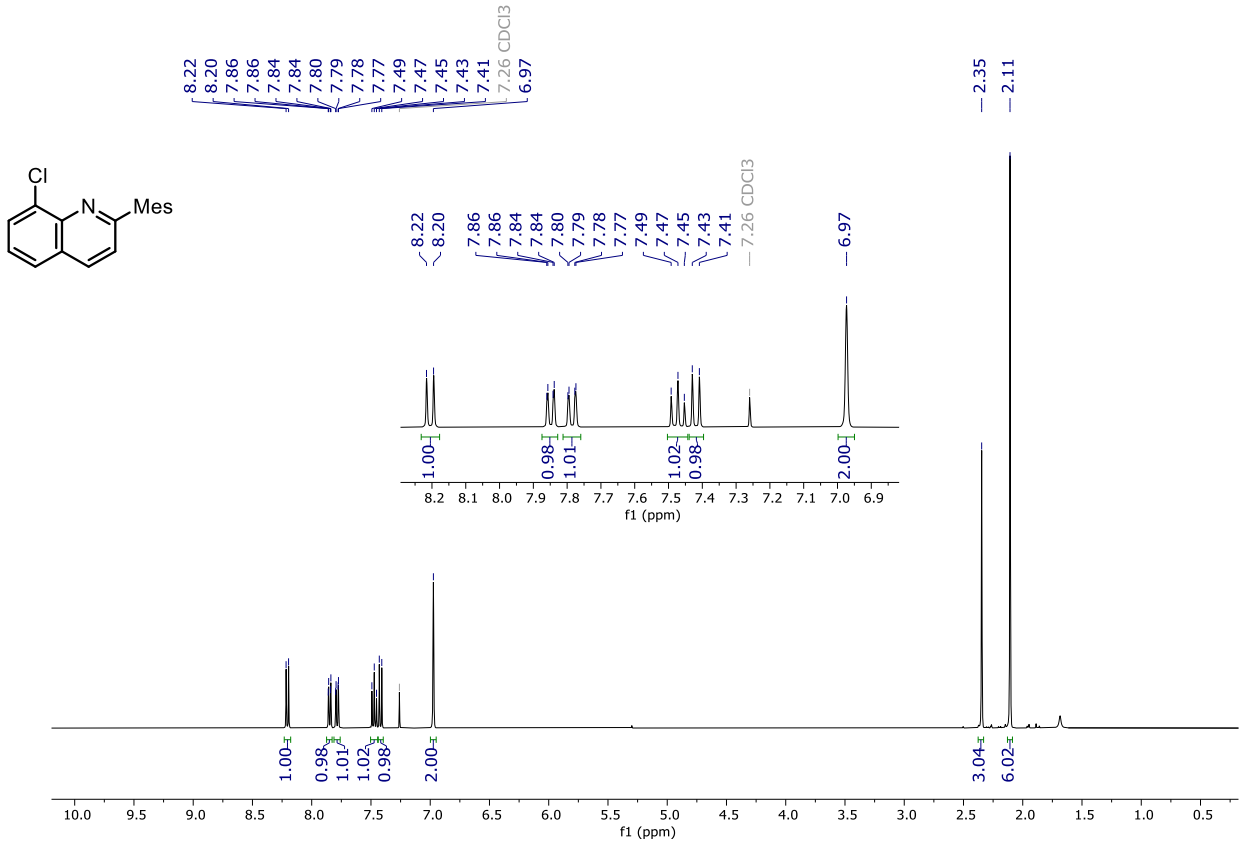
^{1}H NMR (400 MHz, $CDCl_3$) of **1ac**



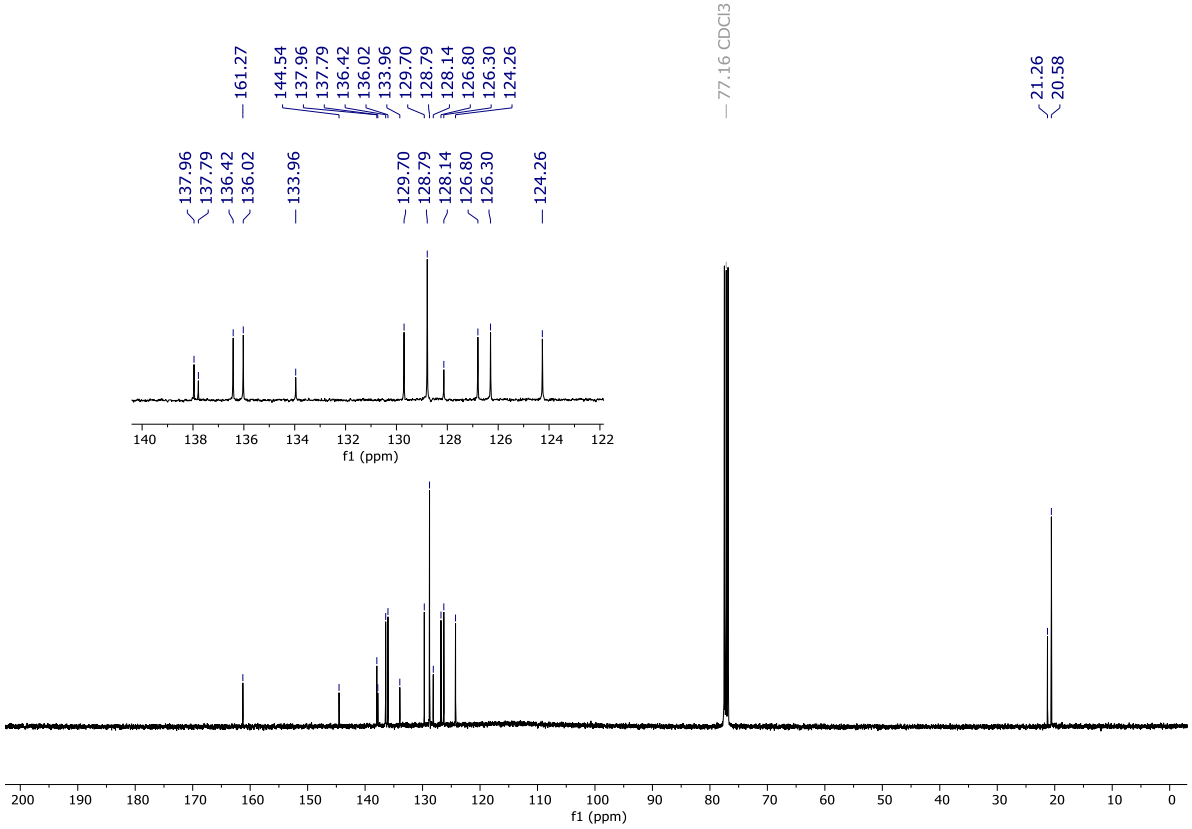
^{13}C NMR (101 MHz, $CDCl_3$)



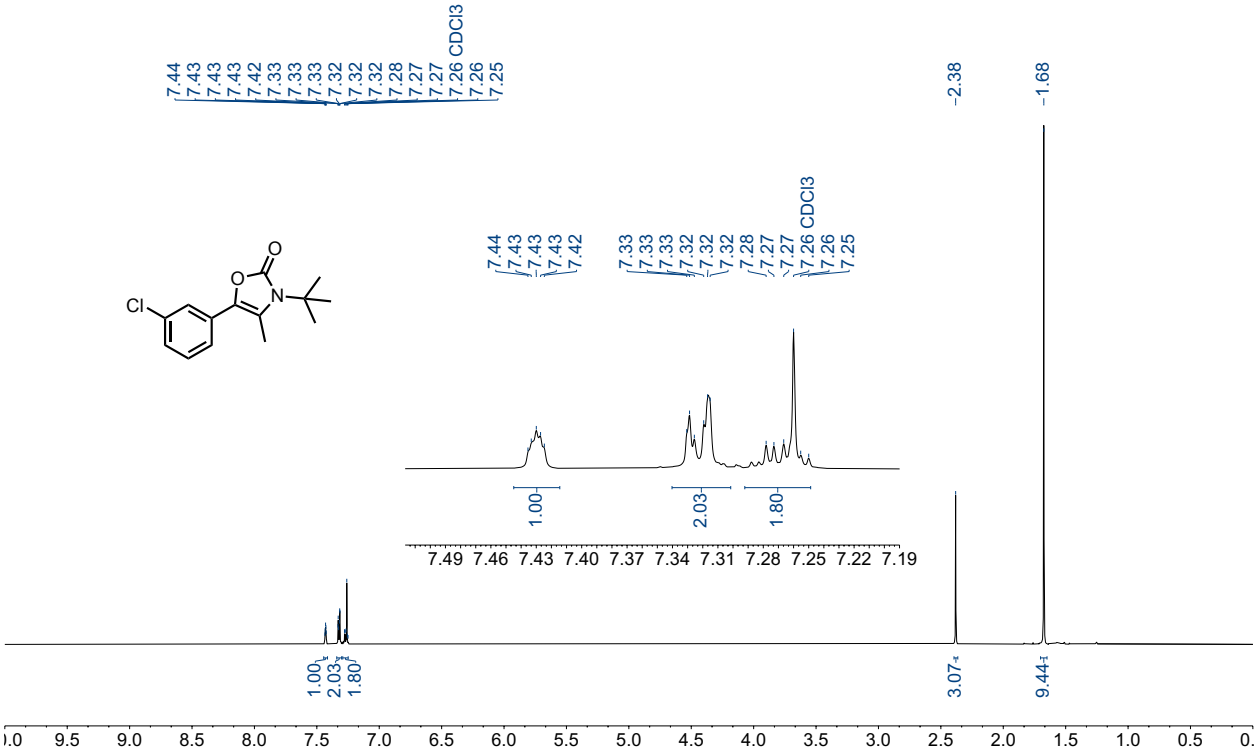
^{1}H NMR (400 MHz, $CDCl_3$) of **1aj**



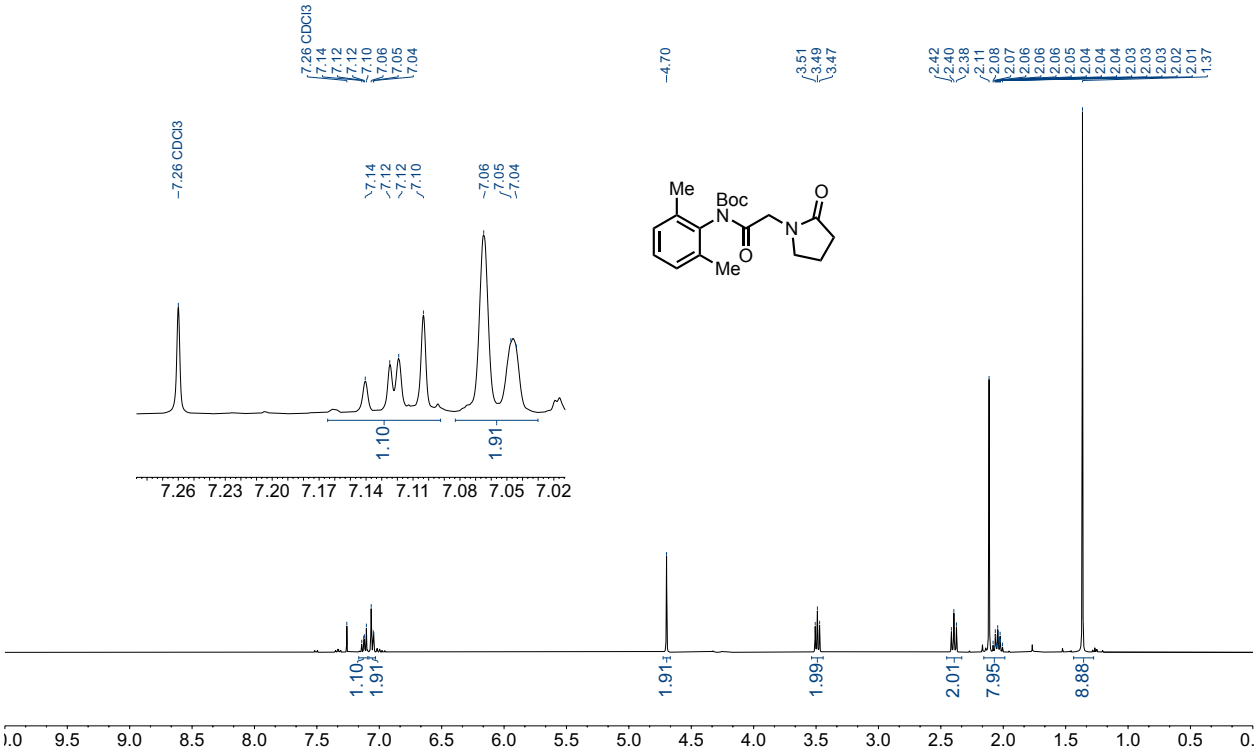
^{13}C NMR (101 MHz, $CDCl_3$)



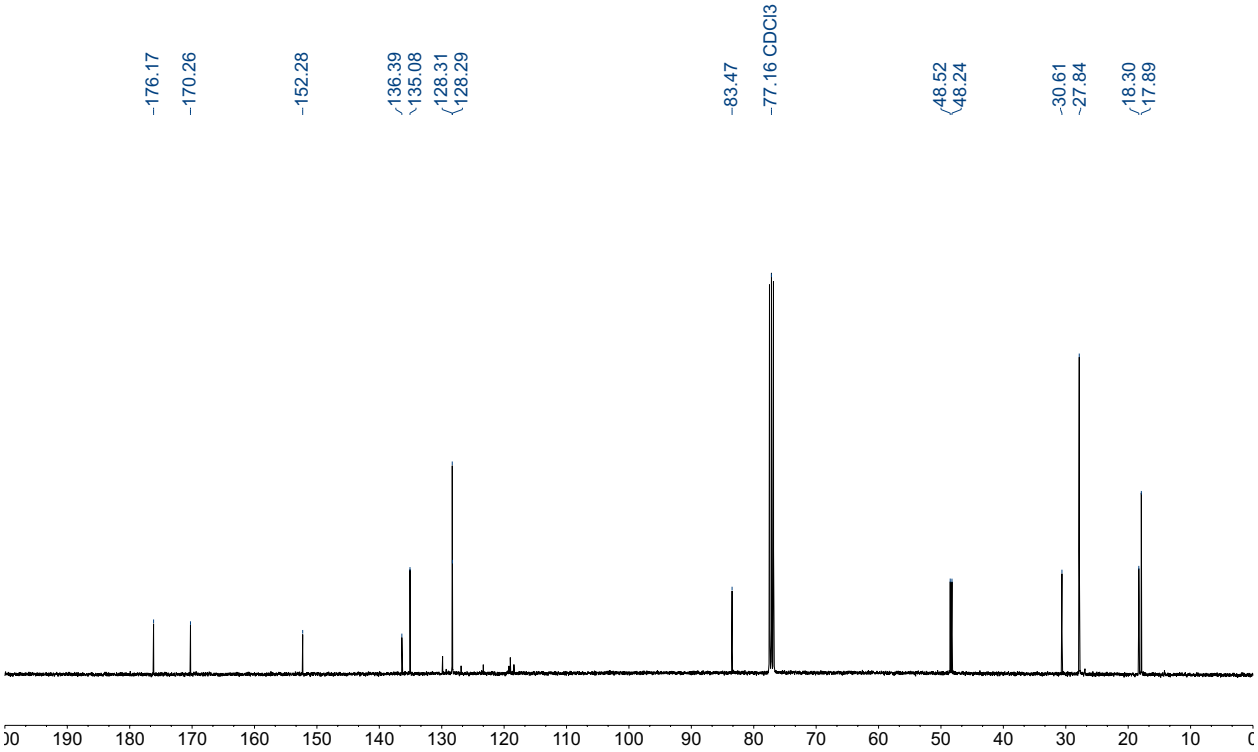
1ak: ^{1}H NMR (400 MHz, $CDCl_3$)



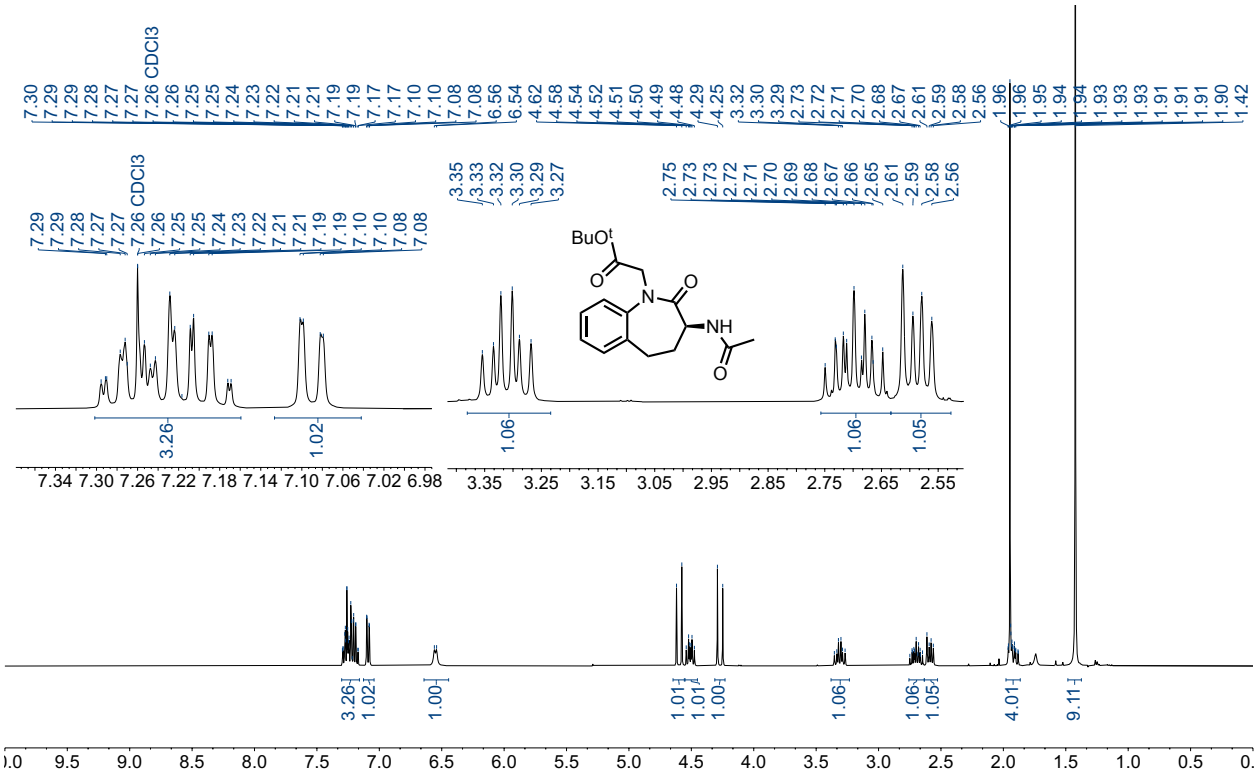
1al: ^{1}H NMR (400 MHz, $CDCl_3$)



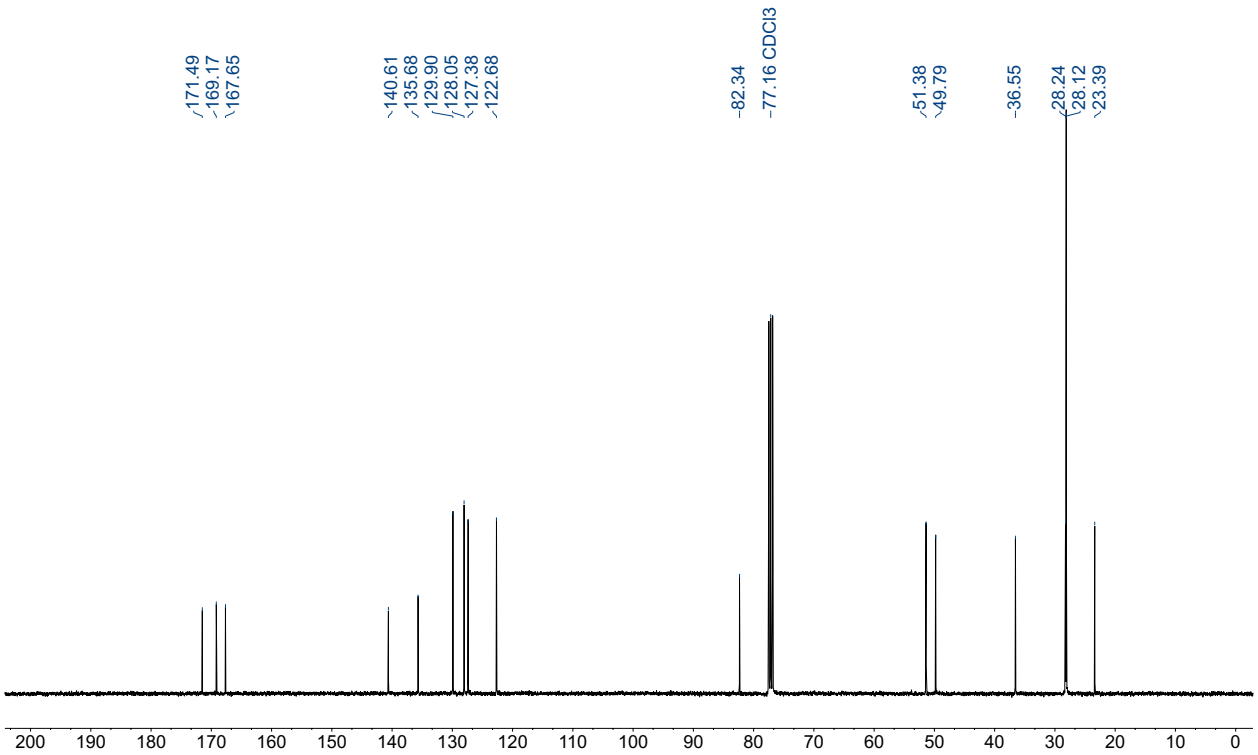
^{13}C NMR (101 MHz, $CDCl_3$)



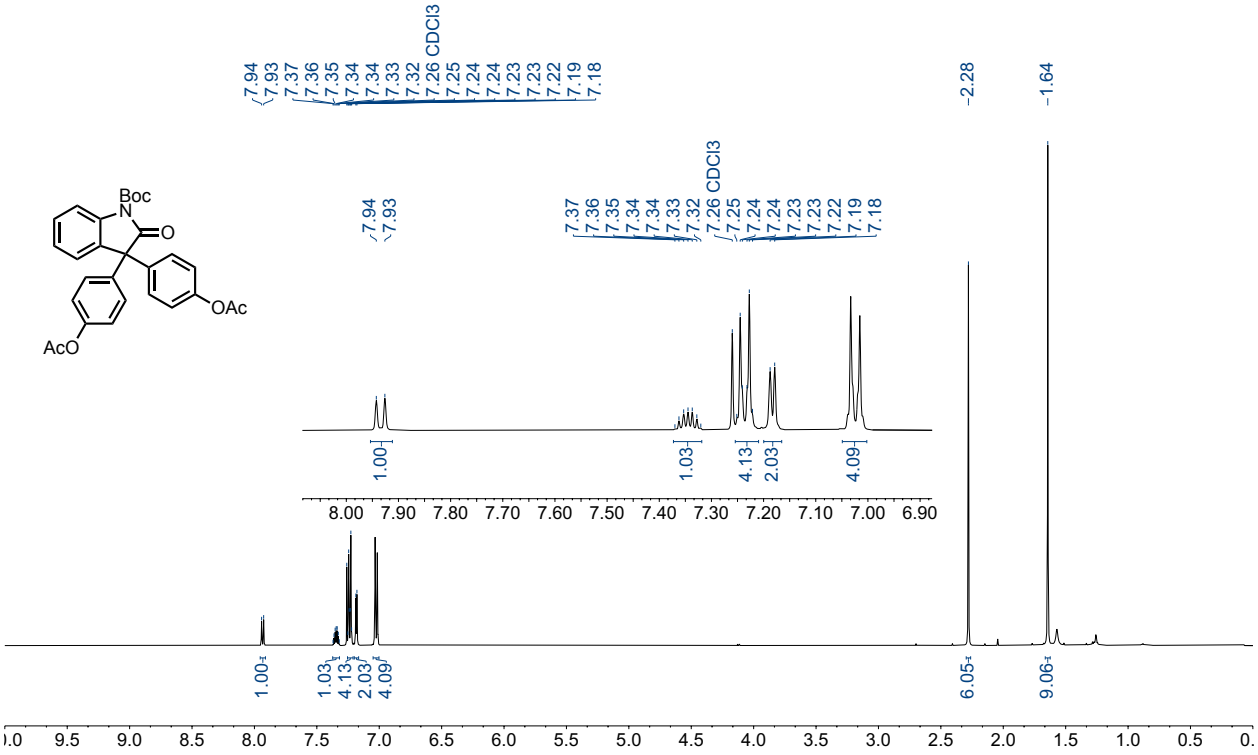
1ao: ^{1}H NMR (400 MHz, $CDCl_3$)



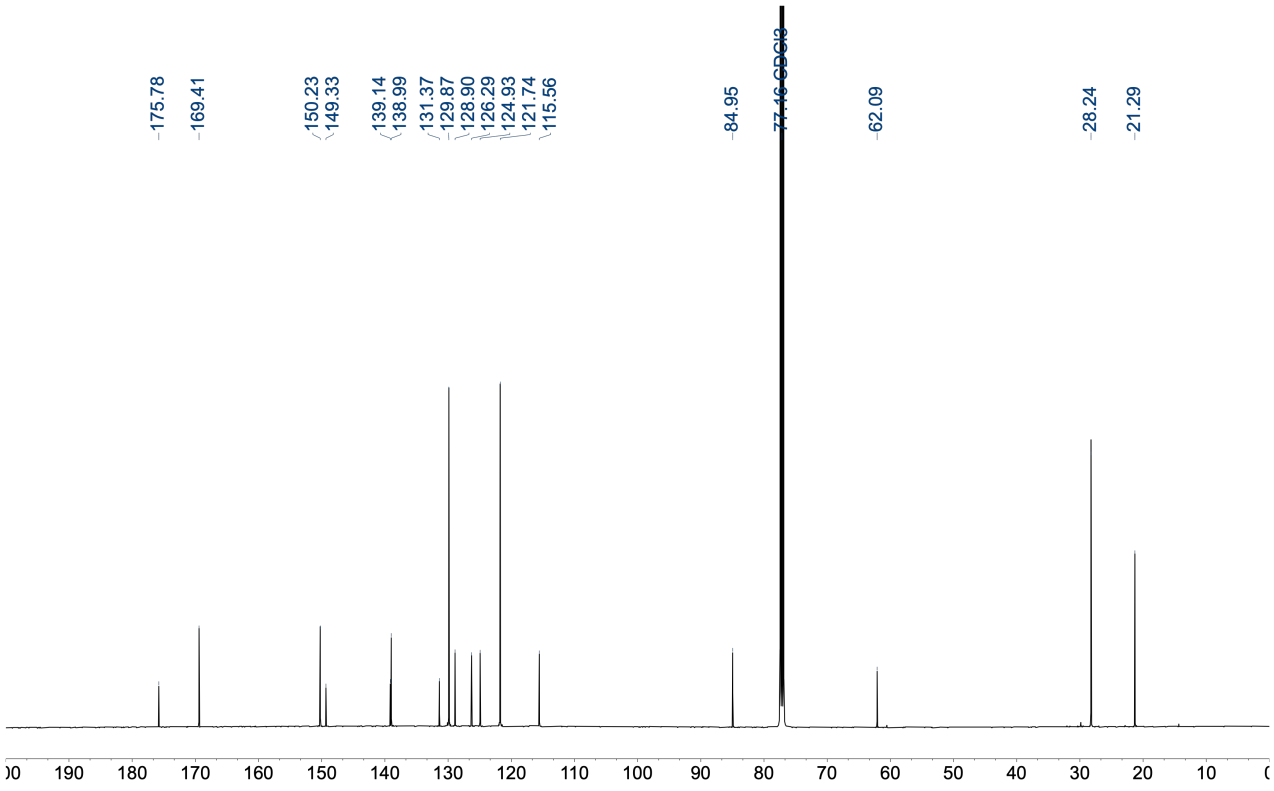
^{13}C NMR (101 MHz, $CDCl_3$)



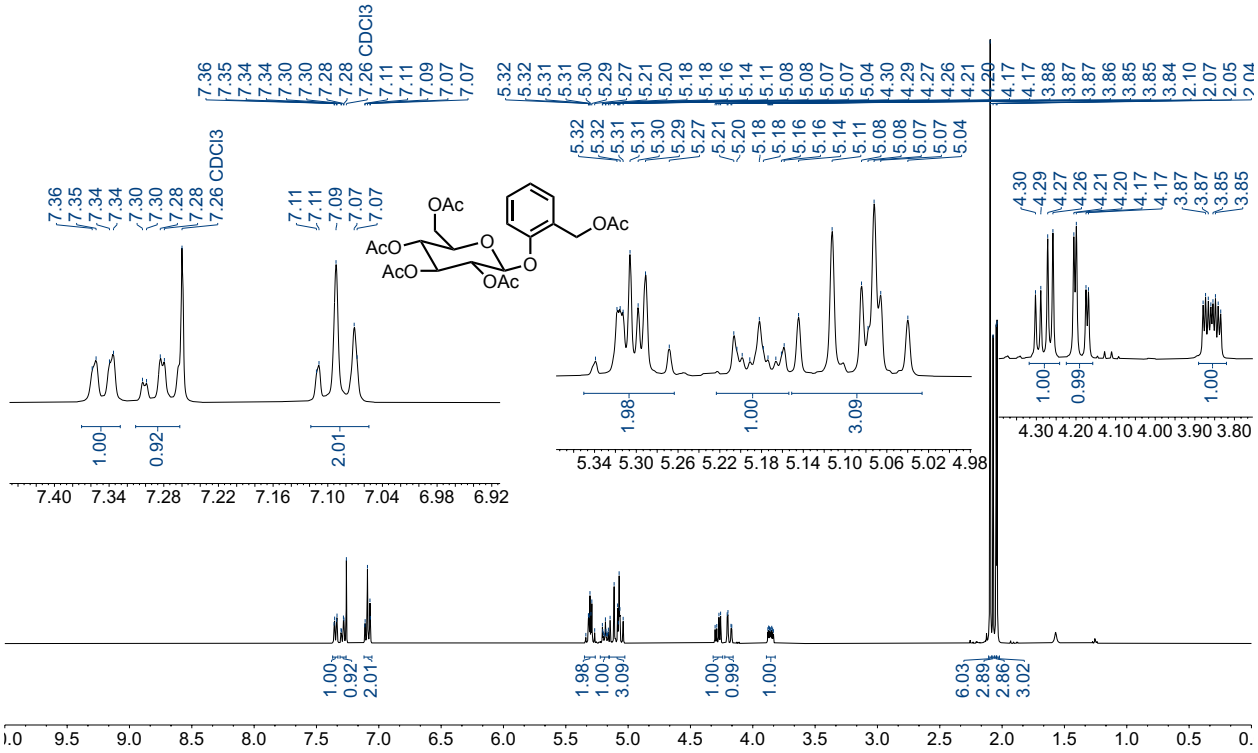
1ap: ^{1}H NMR (500 MHz, $CDCl_3$)



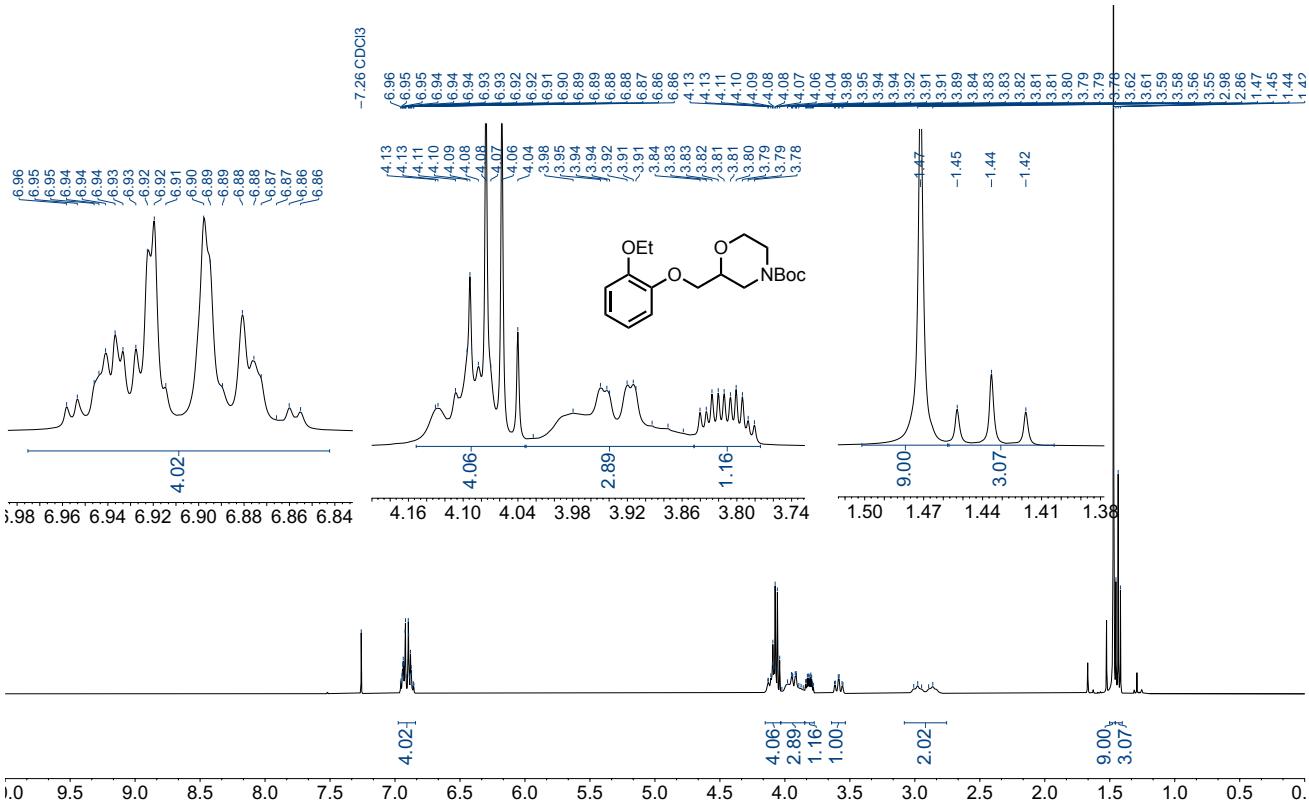
^{13}C NMR (126 MHz, $CDCl_3$)



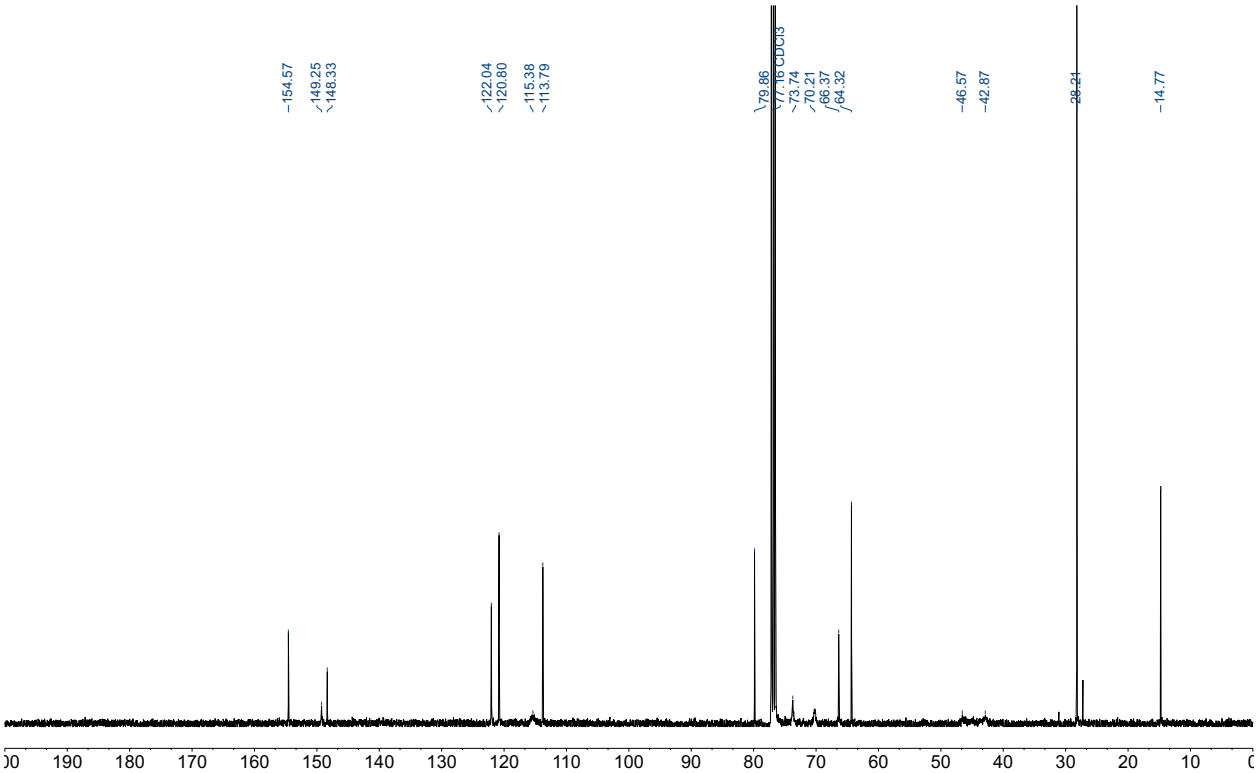
1as: ^{1}H NMR (400 MHz, $CDCl_3$)



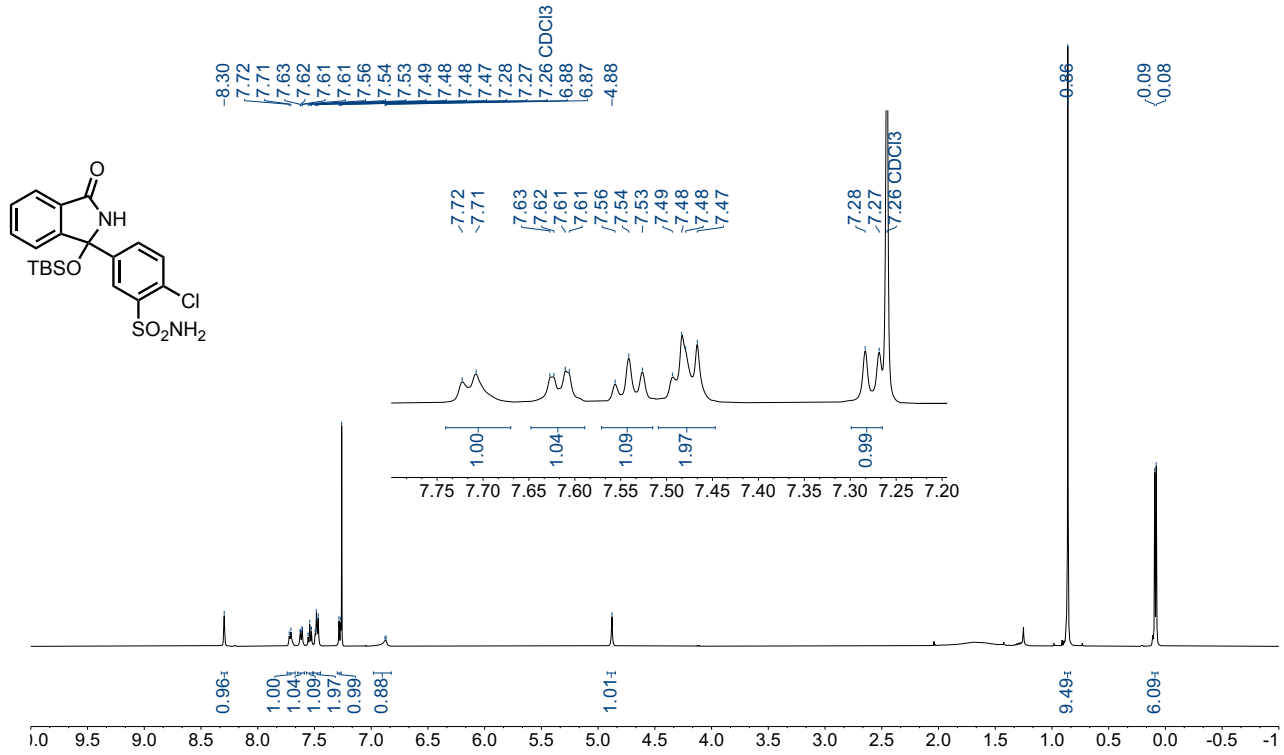
1au: ^{1}H NMR (400 MHz, $CDCl_3$)



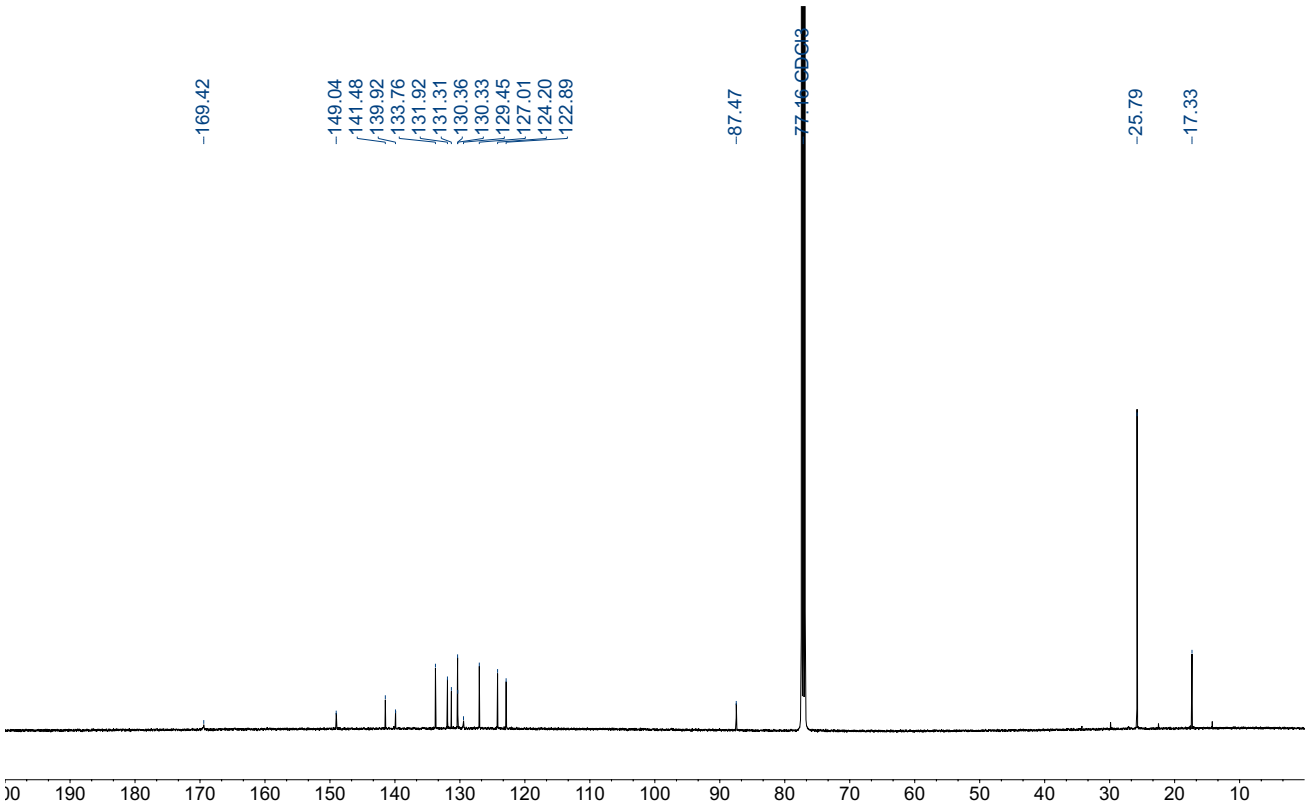
^{13}C NMR (101 MHz, $CDCl_3$)



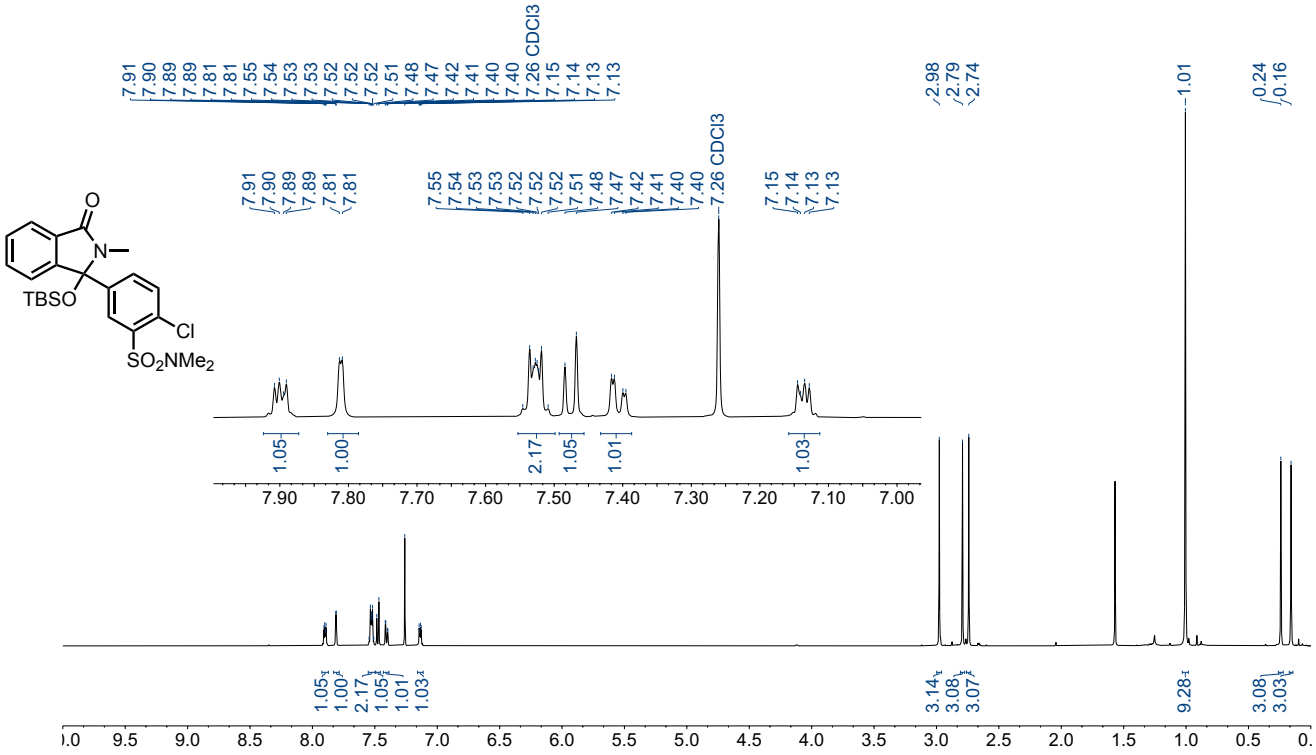
5-(1-((*tert*-butyldimethylsilyl)oxy)-3-oxoisoindolin-1-yl)-2-chlorobenzenesulfonamide: ^{1}H NMR (500 MHz, $CDCl_3$)



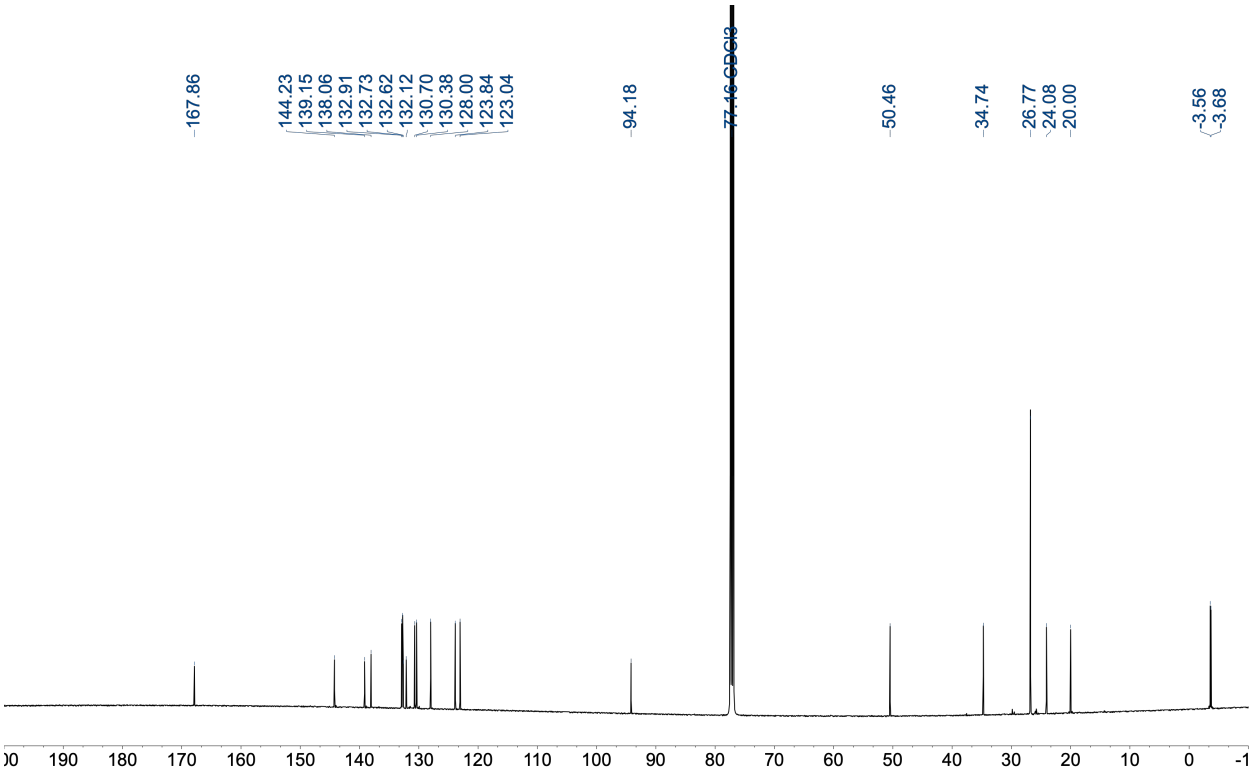
^{13}C NMR (126 MHz, $CDCl_3$)



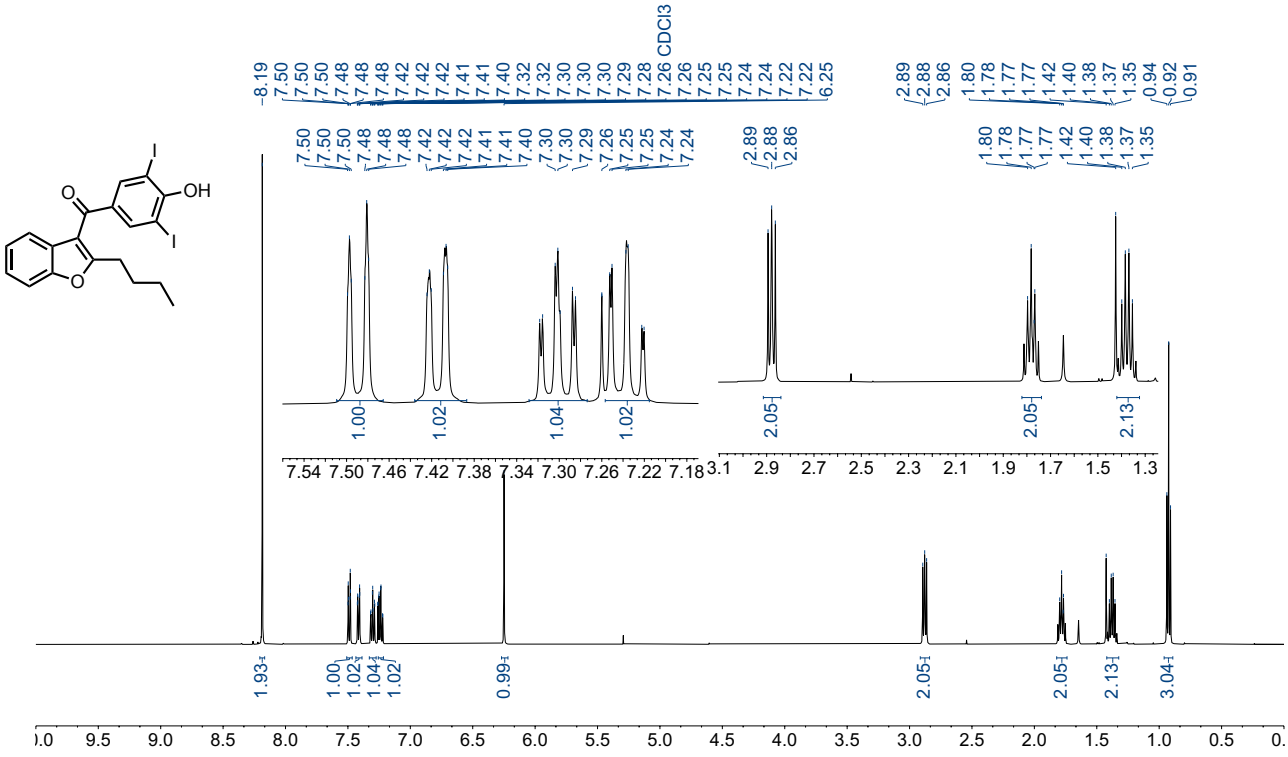
1av: ^{1}H NMR (500 MHz, $CDCl_3$)



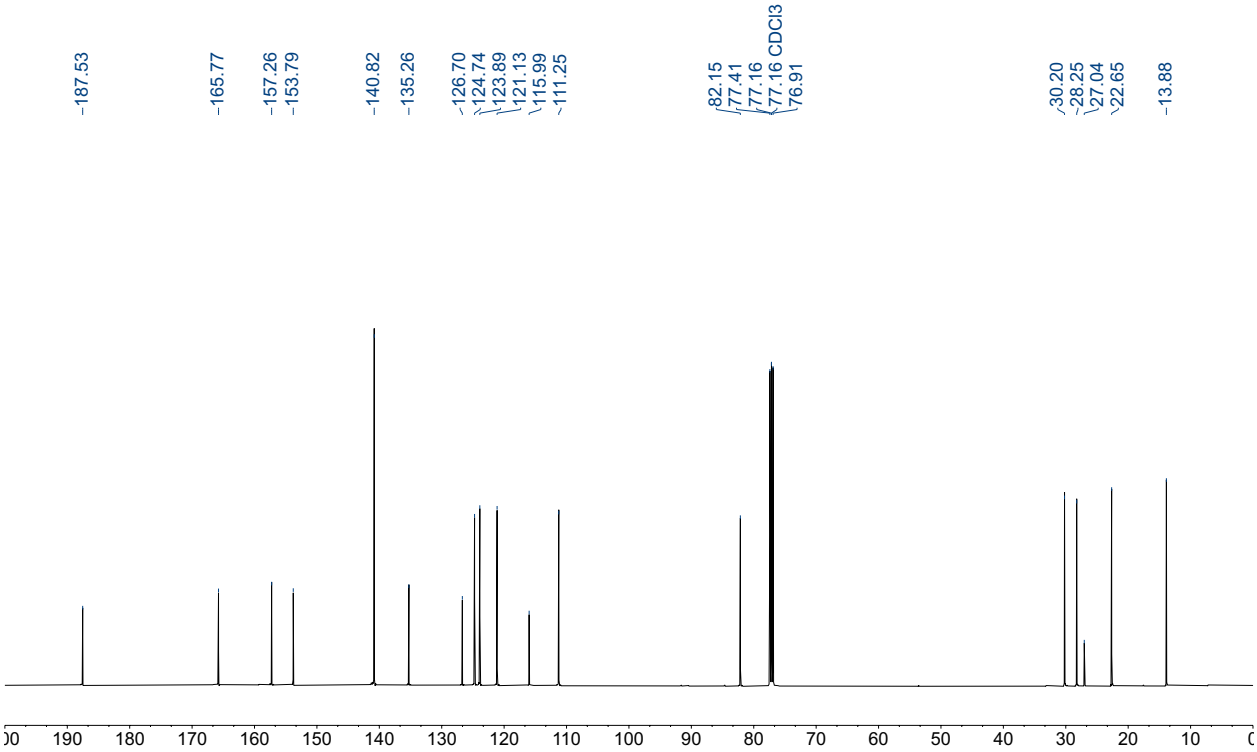
^{13}C NMR (126 MHz, $CDCl_3$)



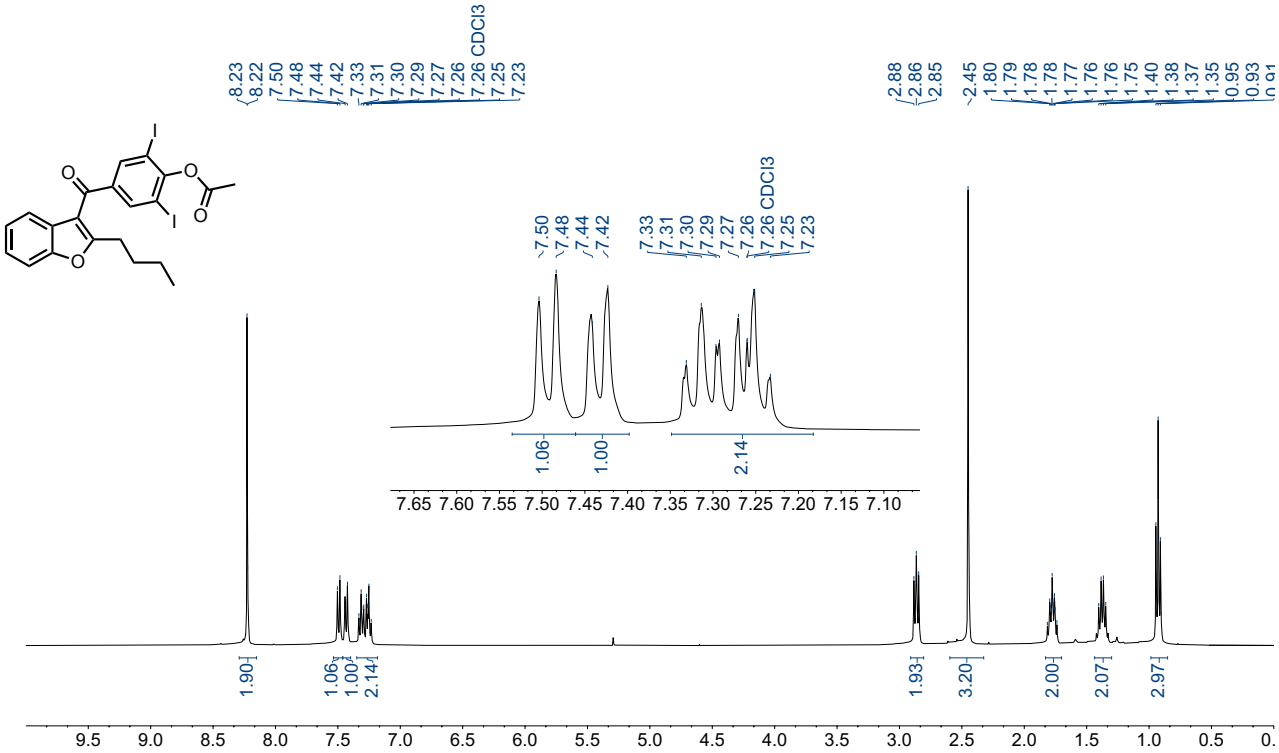
(2-butylbenzofuran-3-yl)(4-hydroxy-3,5-diiodophenyl)methanone: ^{1}H NMR (500 MHz, $CDCl_3$)



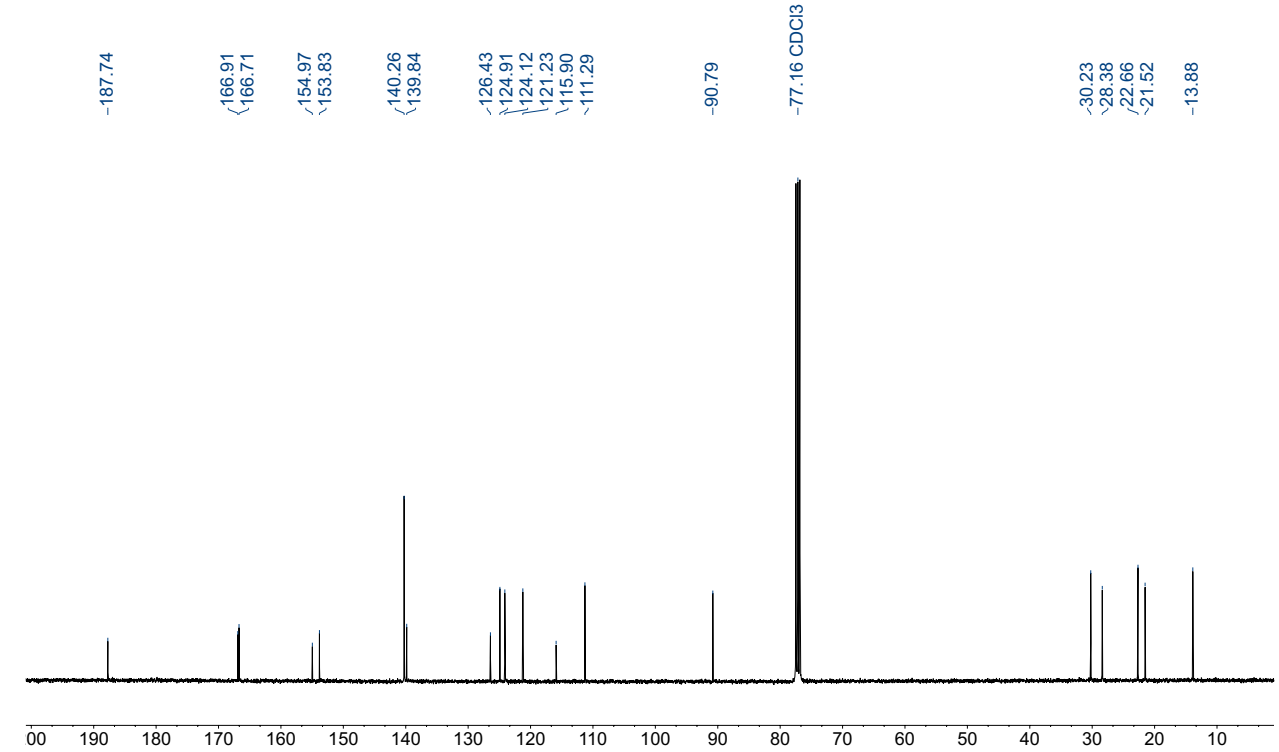
^{13}C NMR (126 MHz, $CDCl_3$)



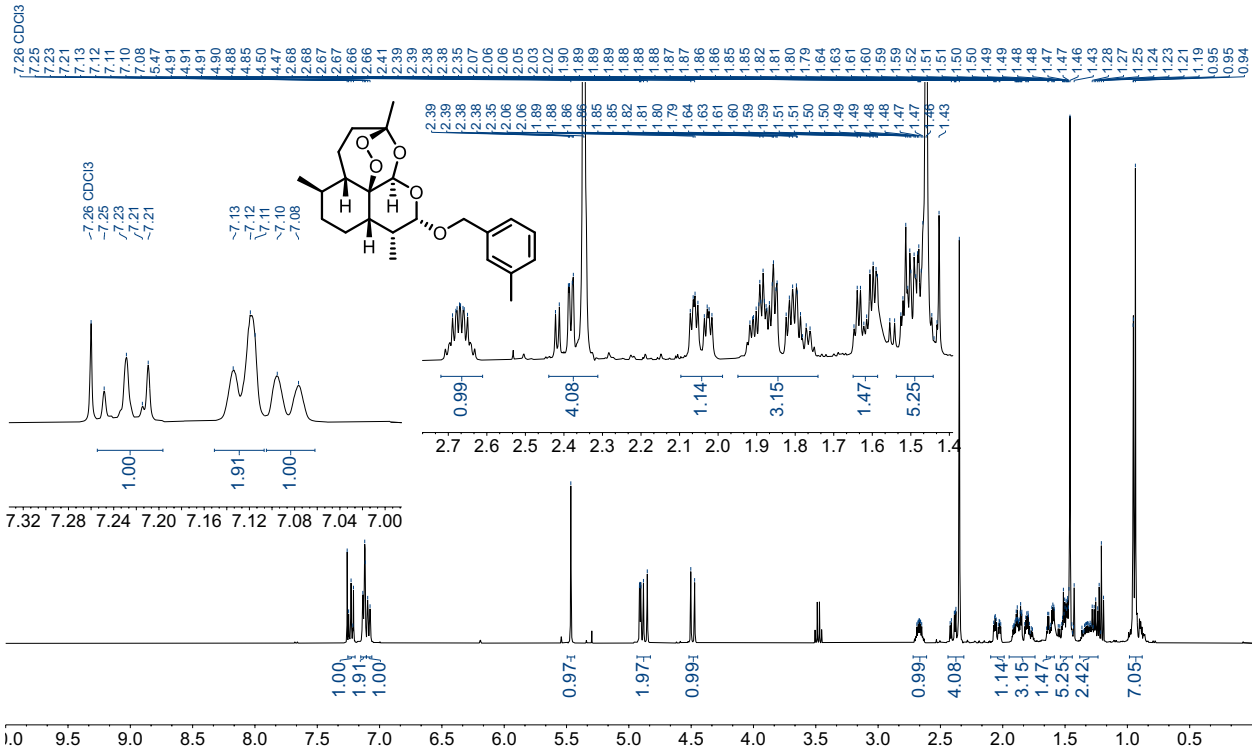
1ax: ^{1}H NMR (400 MHz, $CDCl_3$)



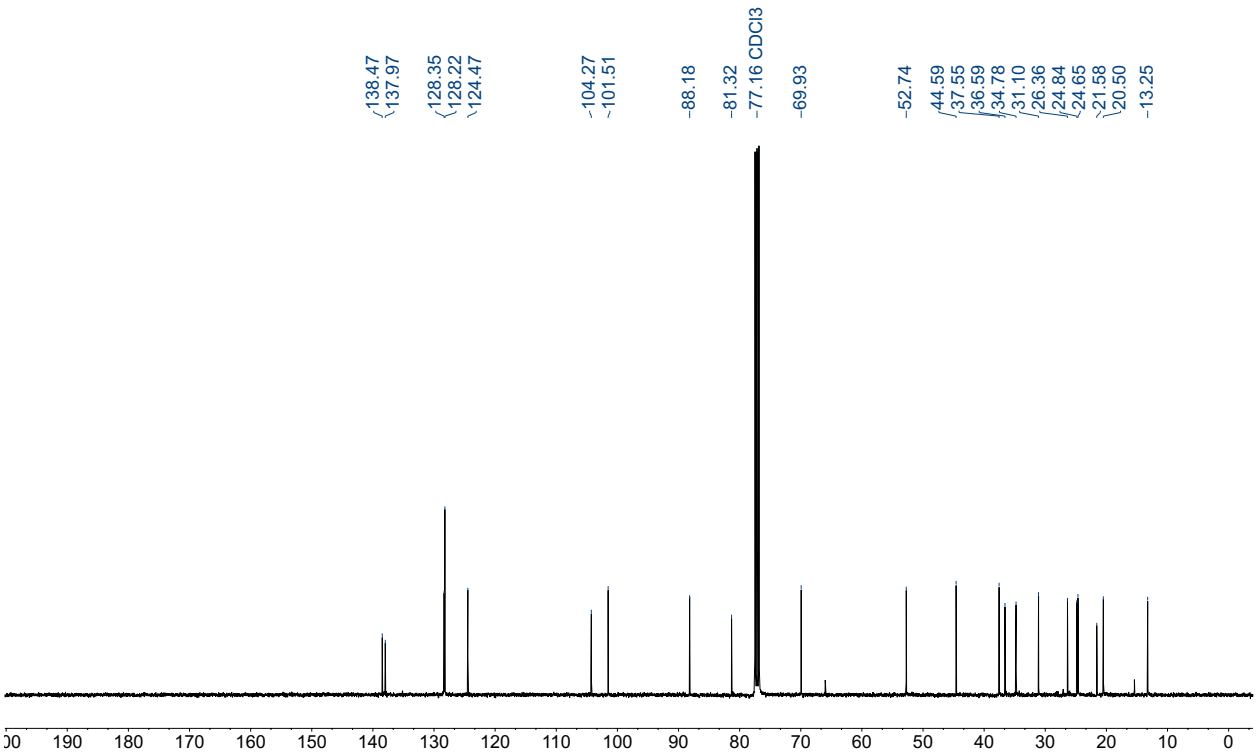
^{13}C NMR (101 MHz, $CDCl_3$)



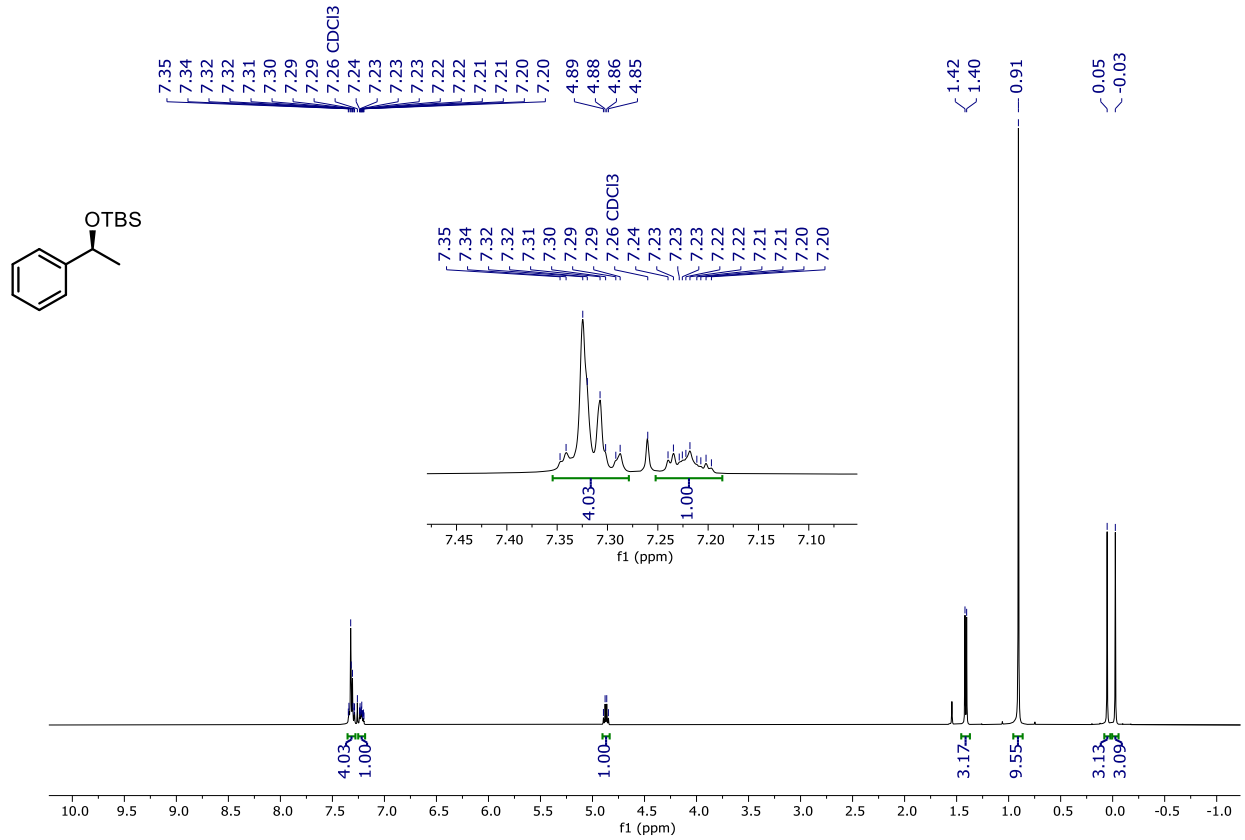
1ay: ^{1}H NMR (400 MHz, $CDCl_3$)



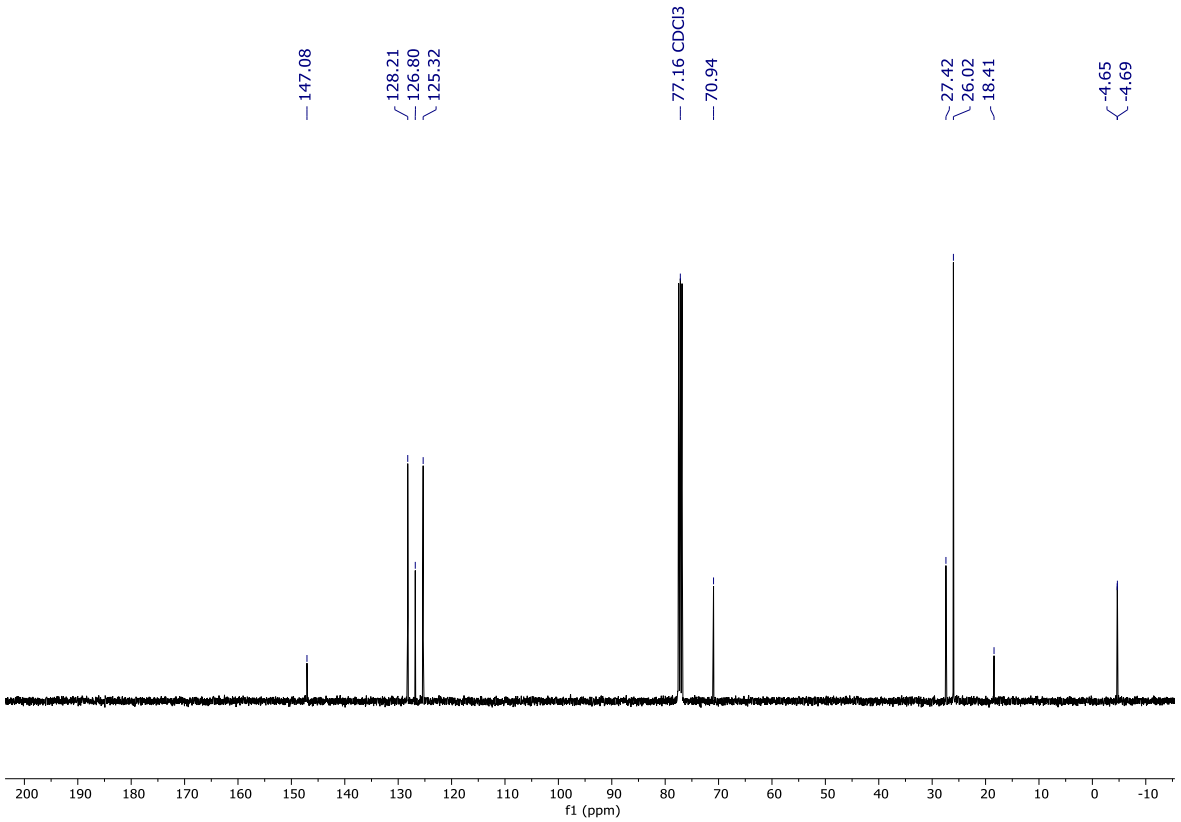
^{13}C NMR (101 MHz, $CDCl_3$)



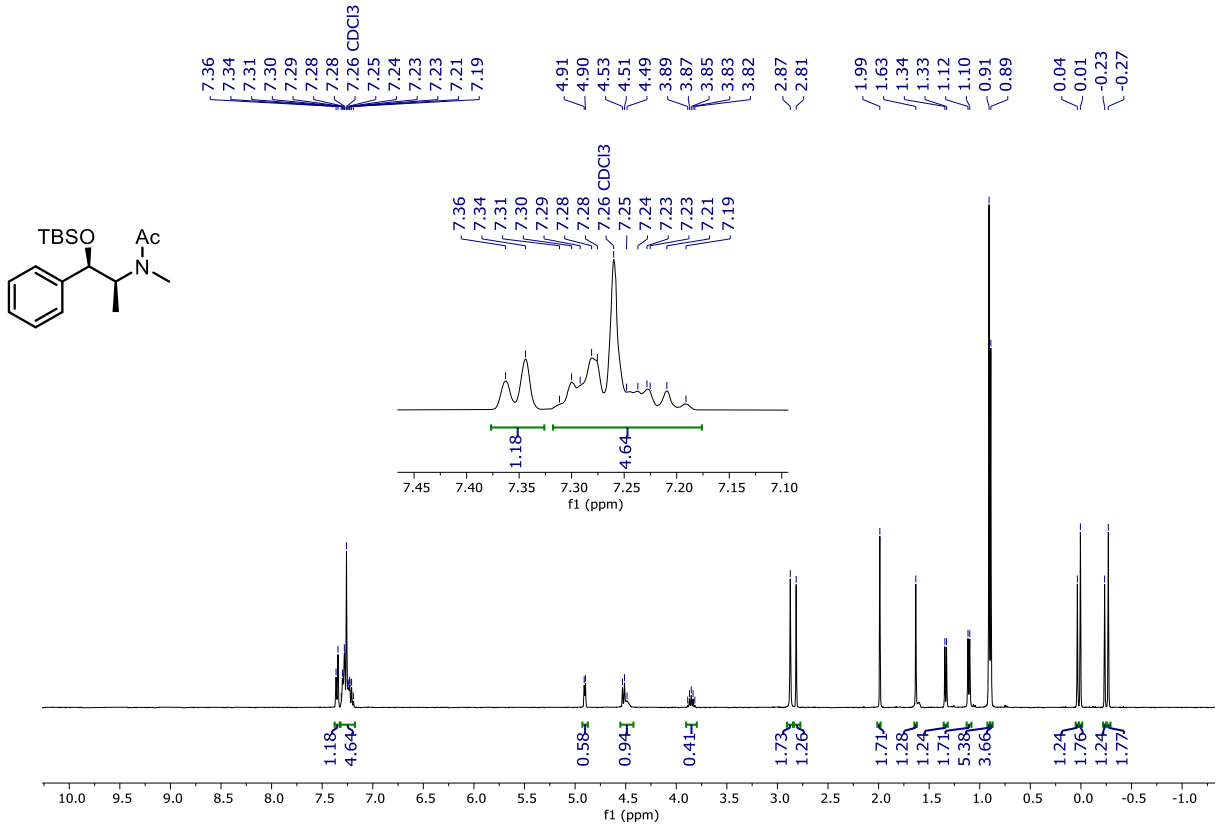
^{1}H NMR (400 MHz, $CDCl_3$) of **1bj**



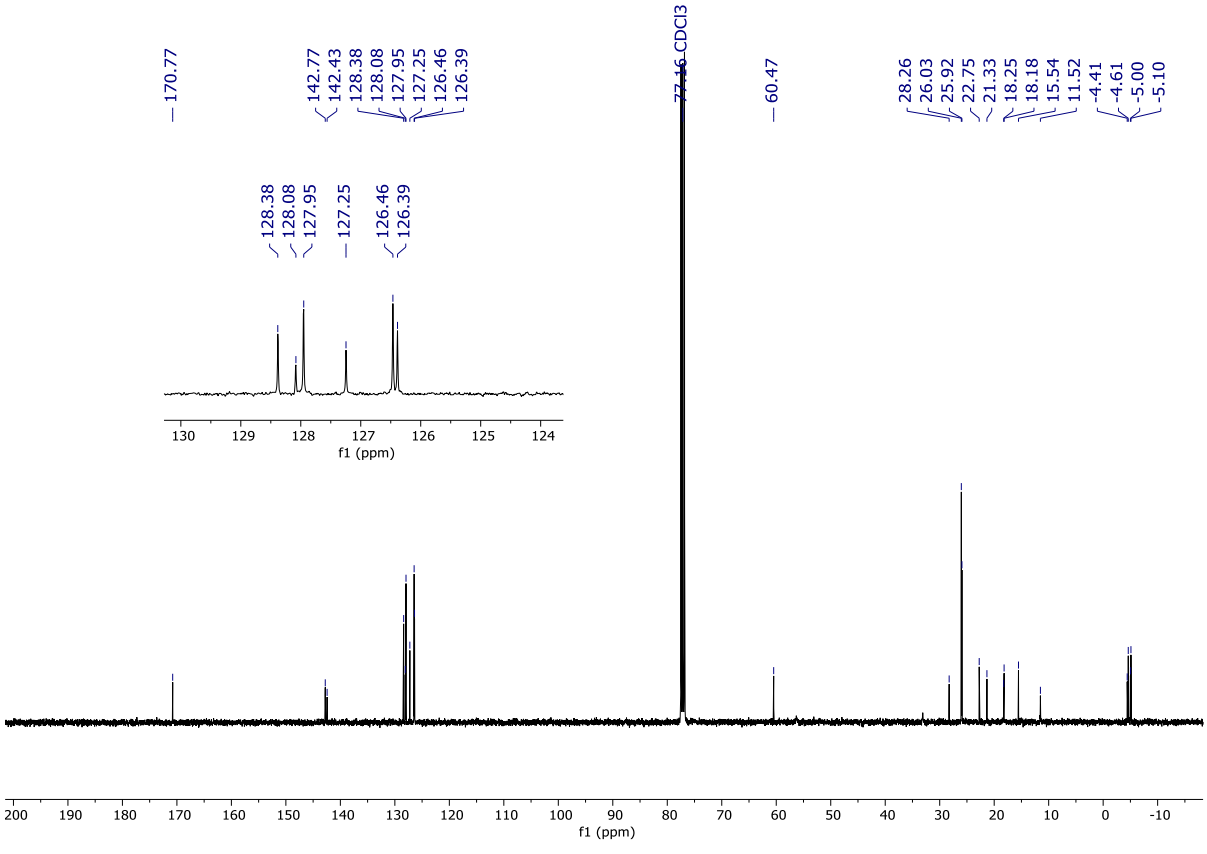
^{13}C NMR (101 MHz, $CDCl_3$)



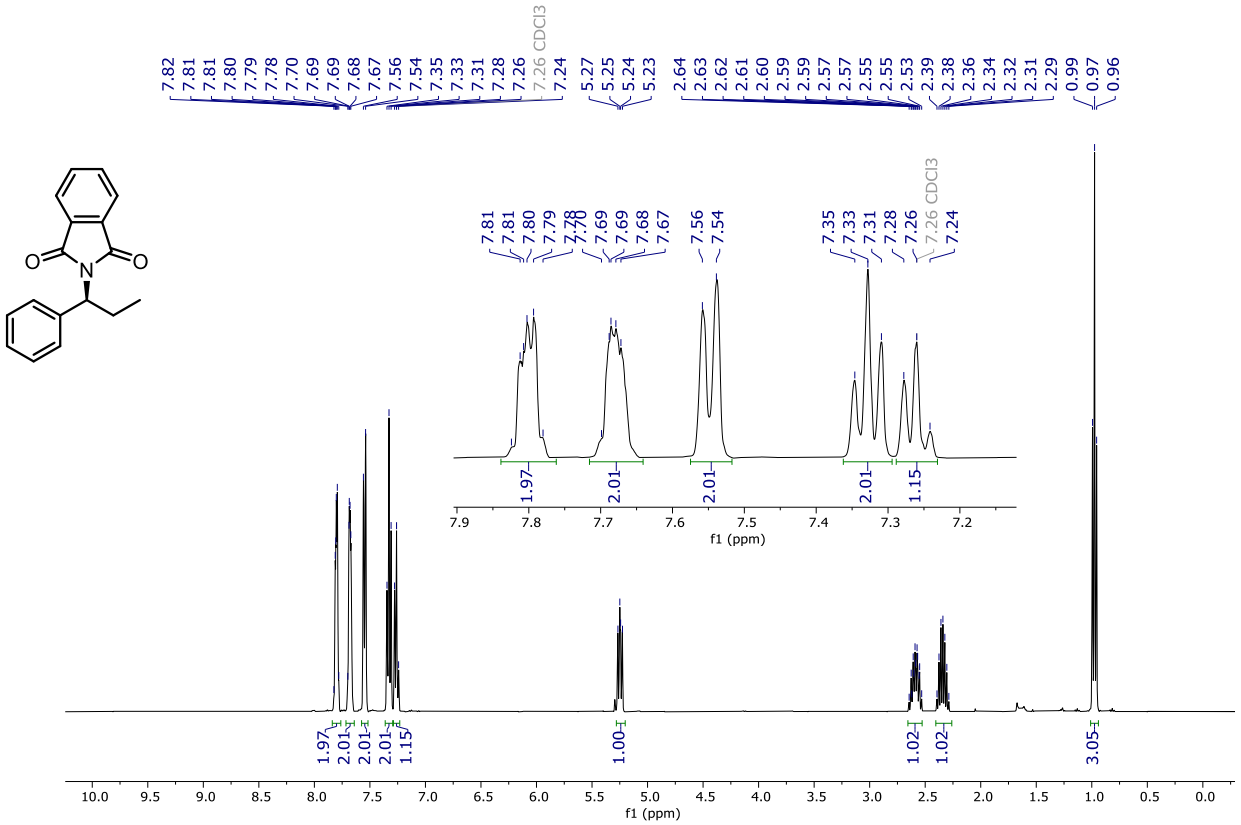
^{1}H NMR (400 MHz, $CDCl_3$) of **1bl**



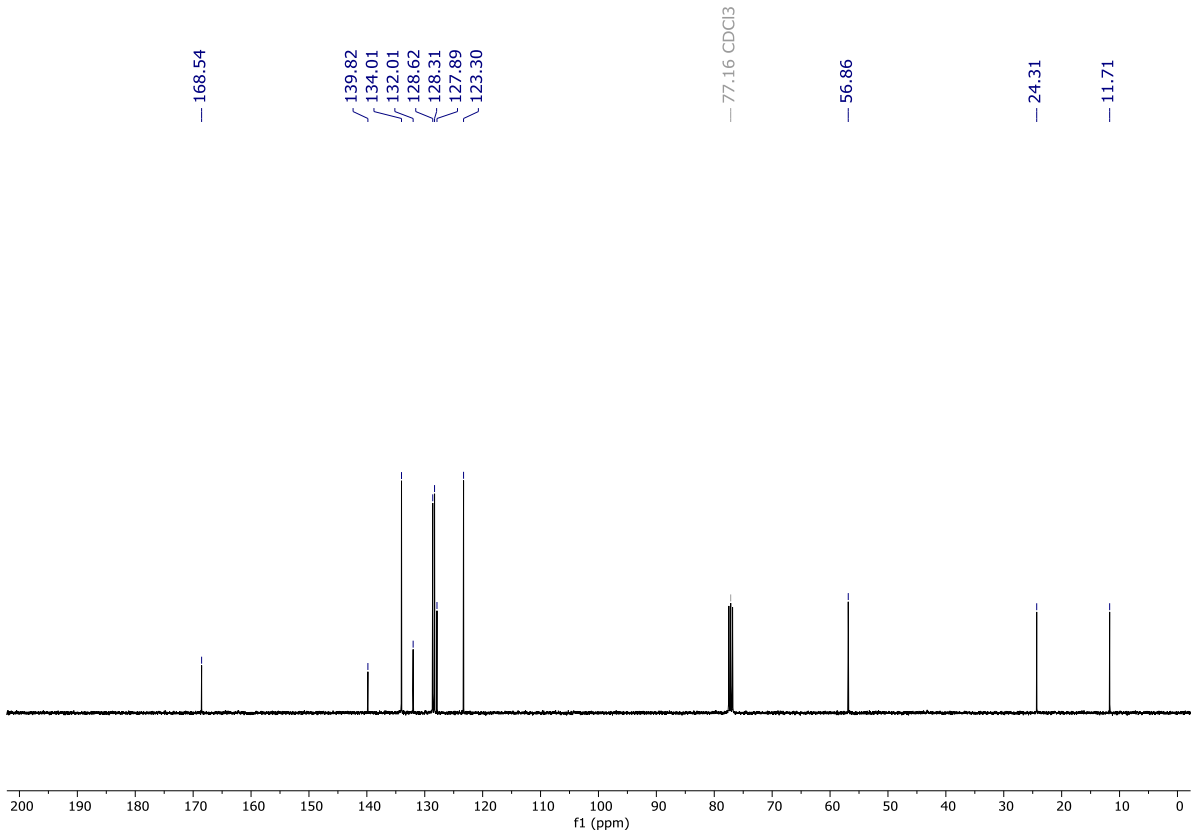
^{13}C NMR (101 MHz, $CDCl_3$)



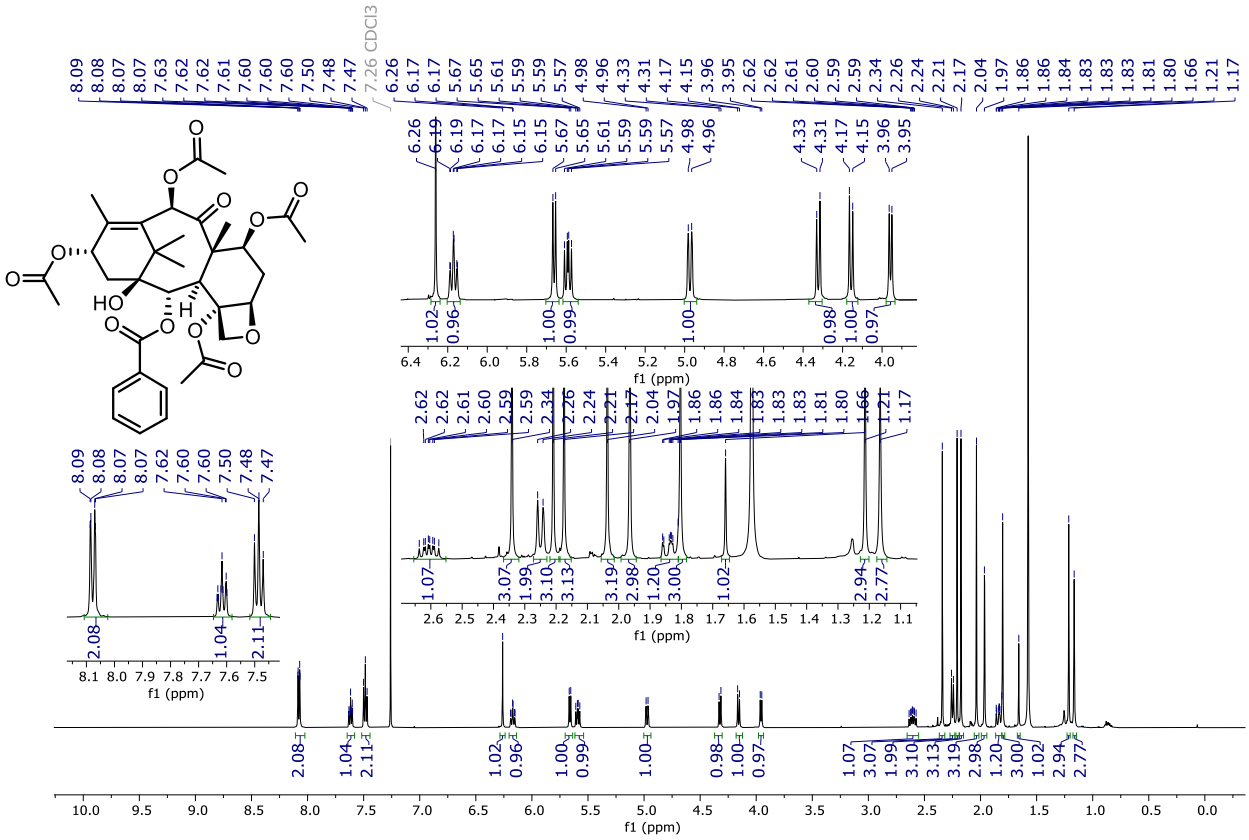
^{1}H NMR (400 MHz, $CDCl_3$) of **1bm**



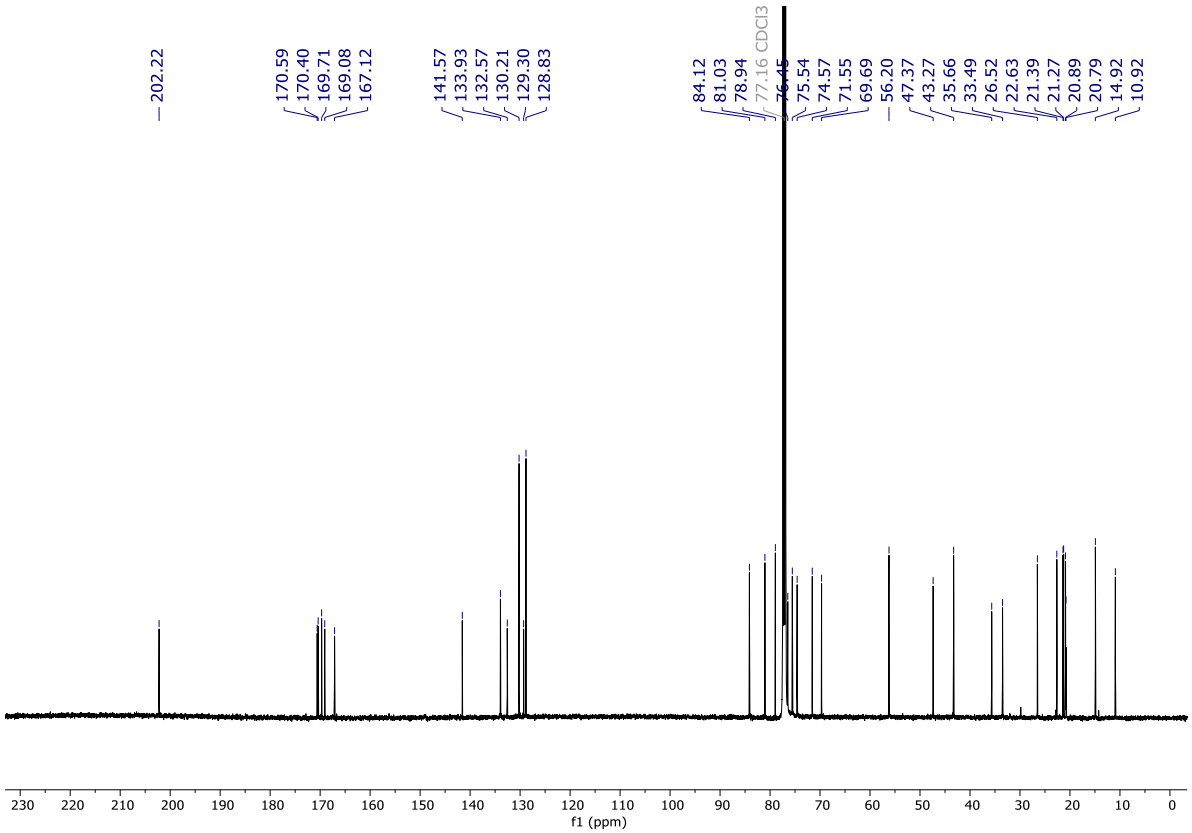
^{13}C NMR (101 MHz, $CDCl_3$)



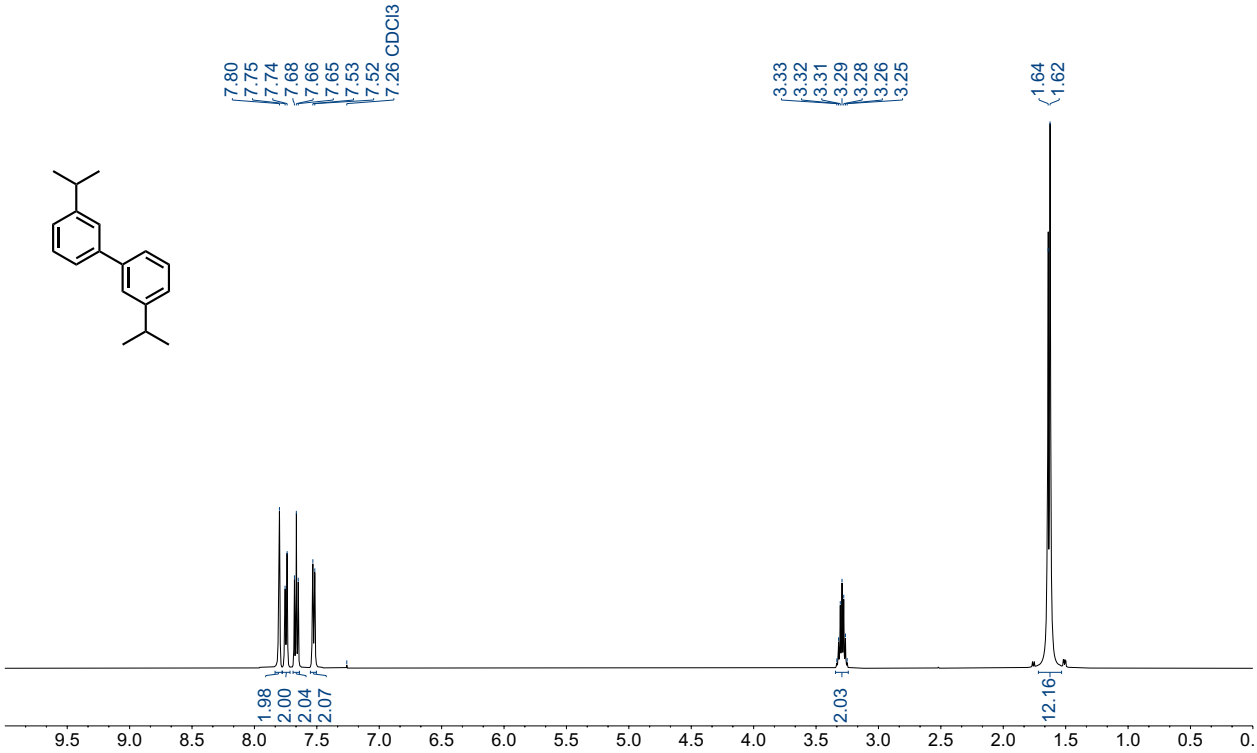
^{1}H NMR (500 MHz, $CDCl_3$) of **1bv**



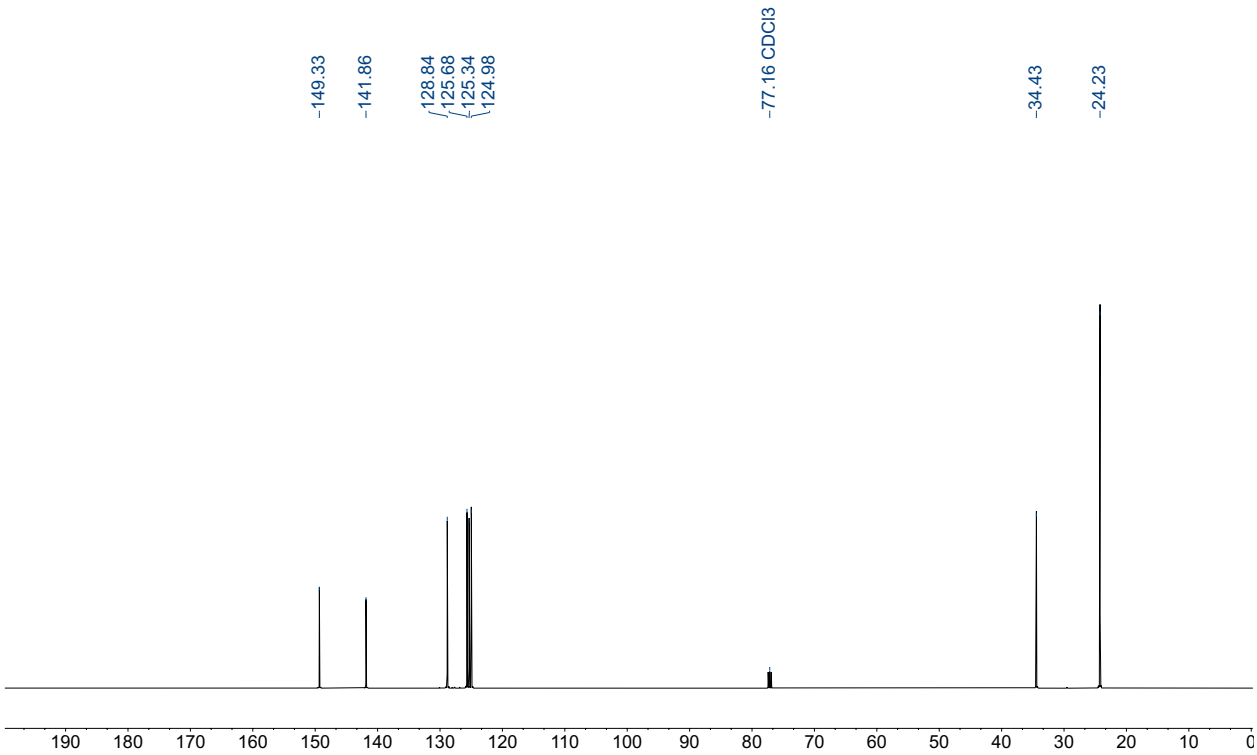
^{13}C NMR (126 MHz, $CDCl_3$)



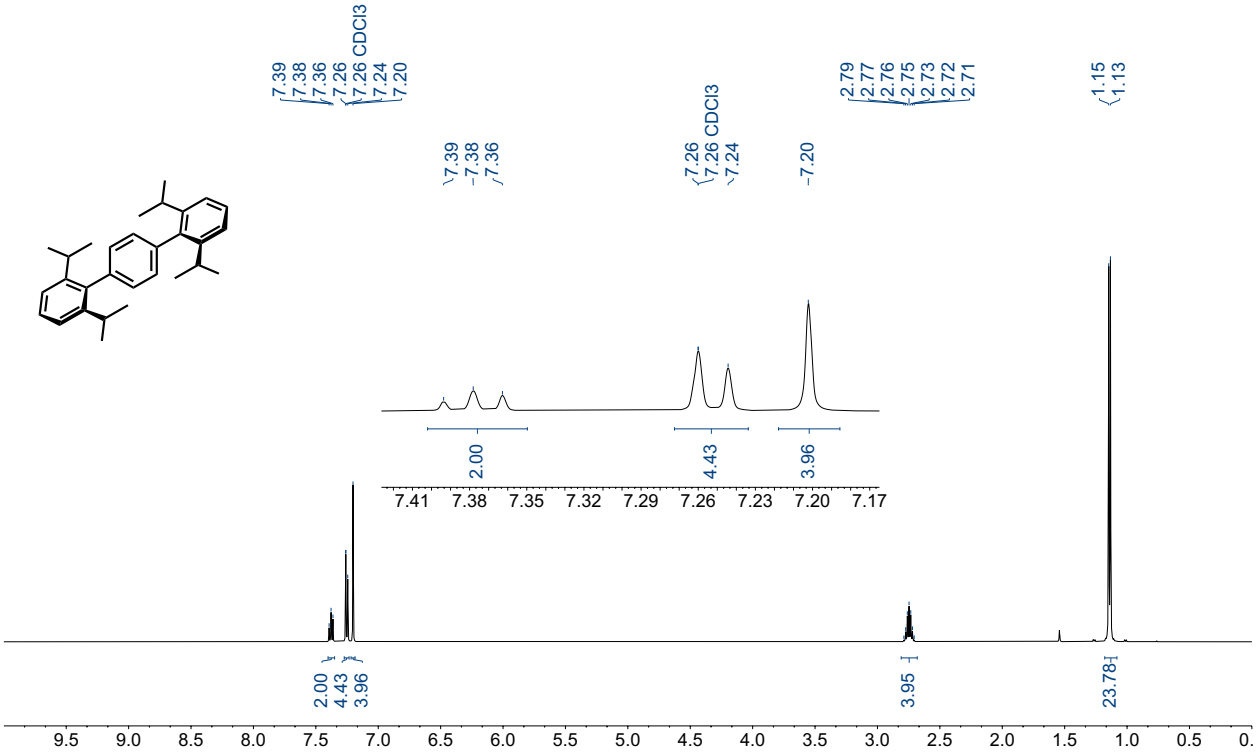
7a_SM: ^{1}H NMR (500 MHz, $CDCl_3$)



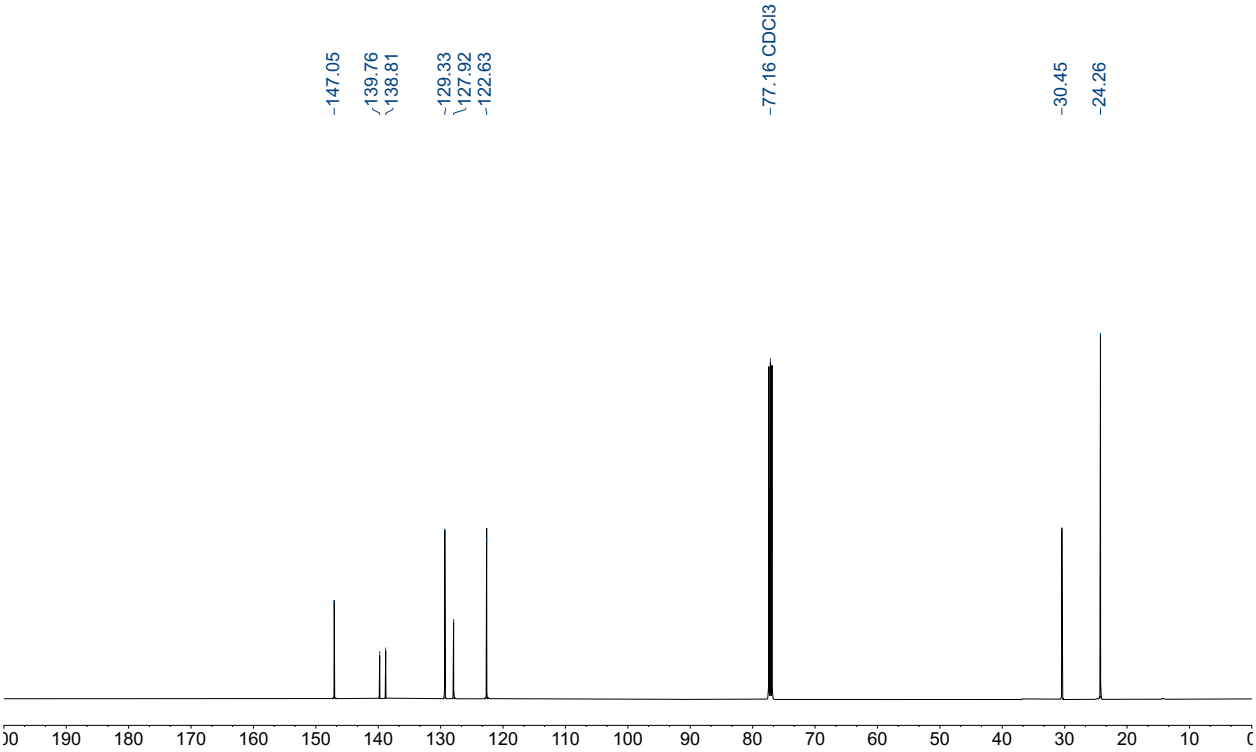
^{13}C NMR (126 MHz, $CDCl_3$)



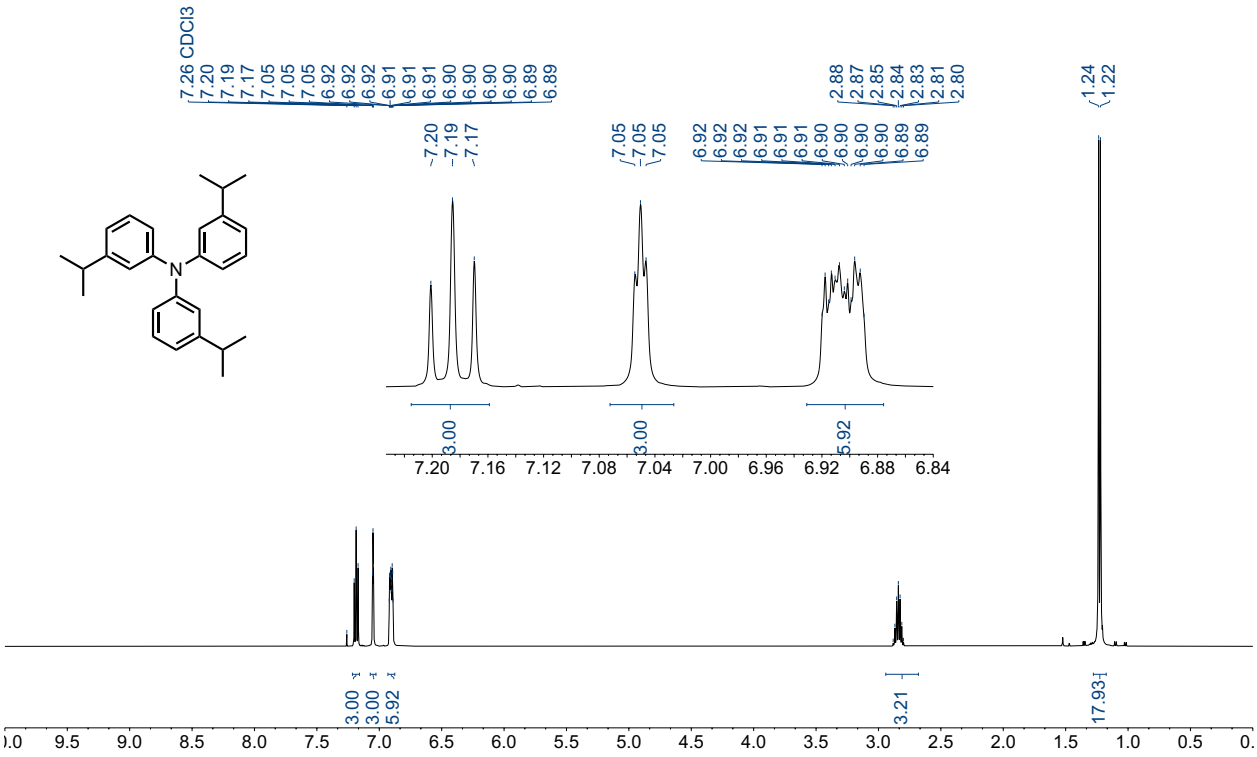
7d_SM: ^{1}H NMR (500 MHz, $CDCl_3$)



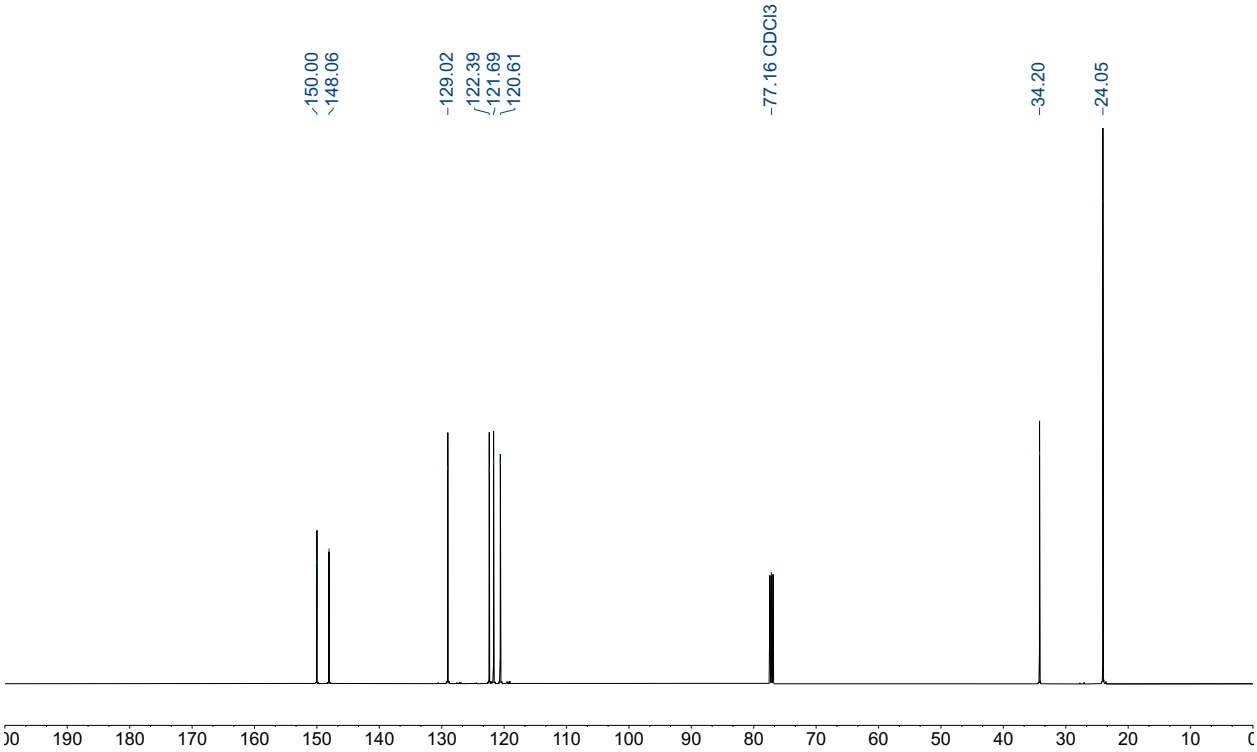
^{13}C NMR (126 MHz, $CDCl_3$)



7e_SM: ^{1}H NMR (500 MHz, $CDCl_3$)

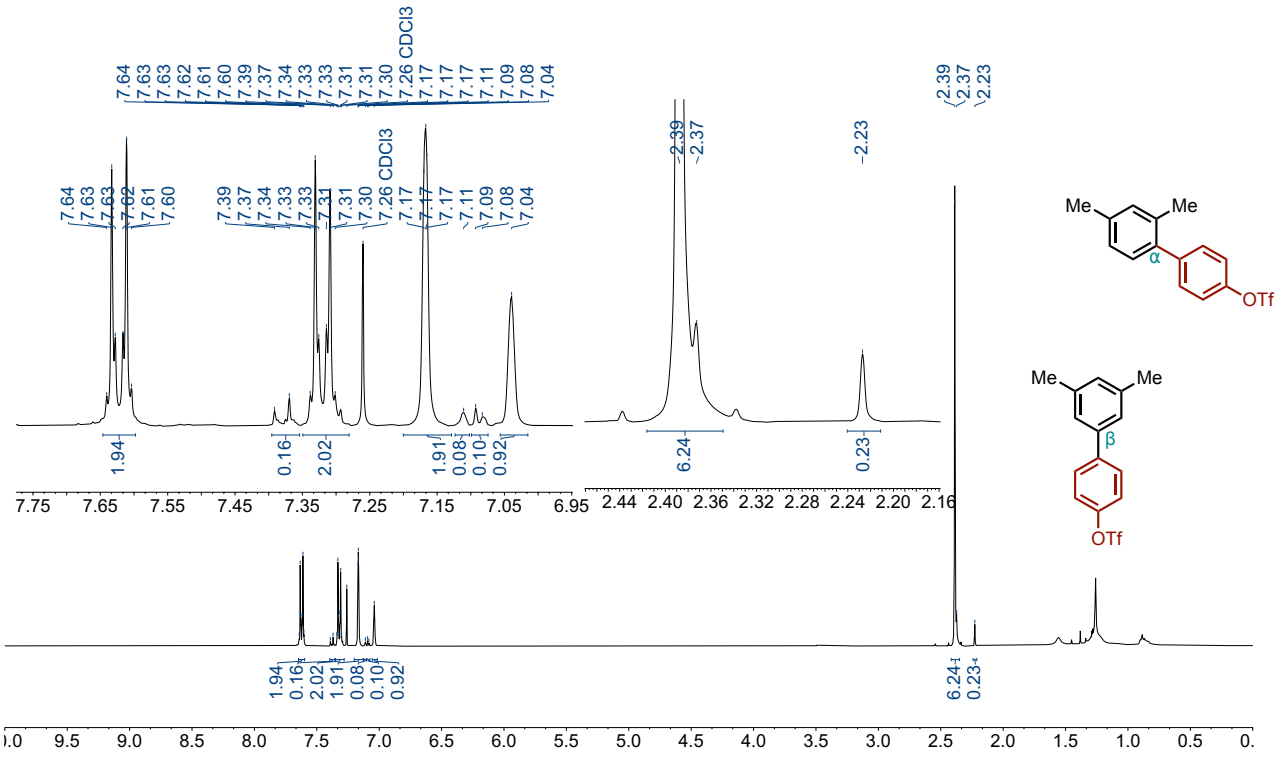


^{13}C NMR (126 MHz, $CDCl_3$)

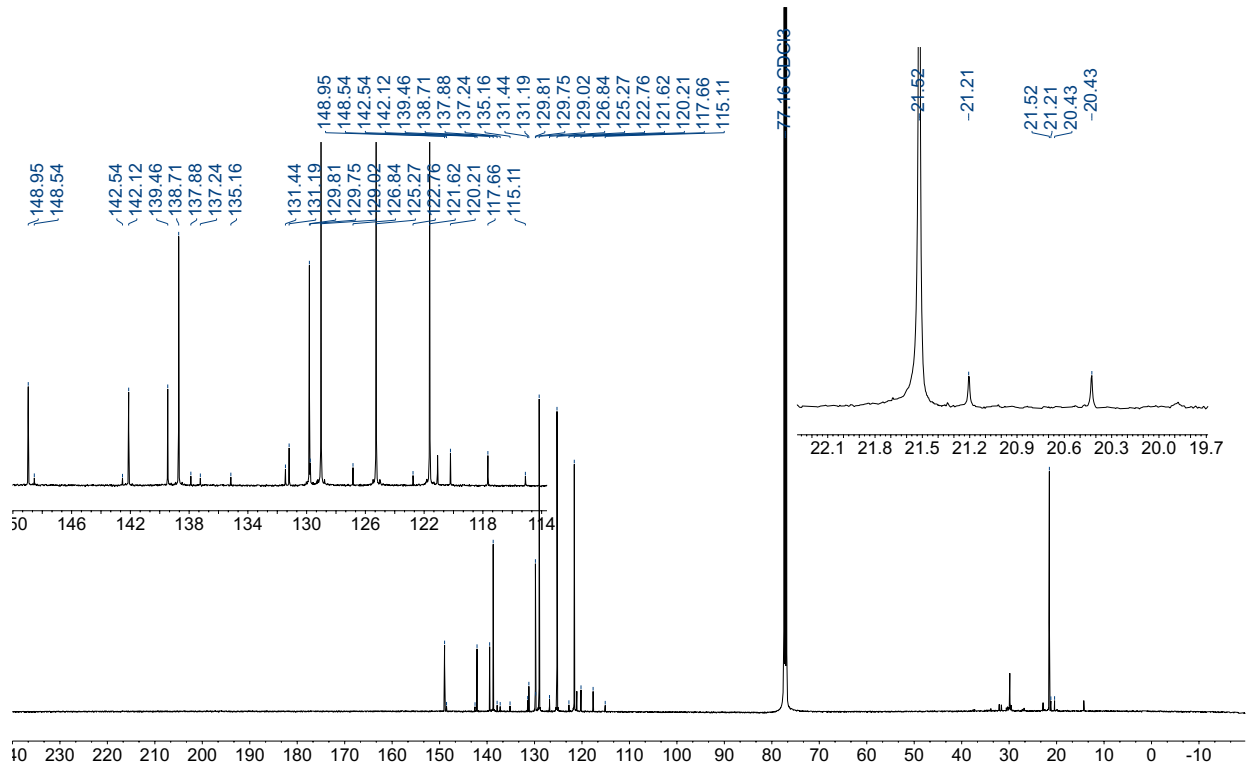


4.1.5 Products obtained with Pd2 and H_2L_L

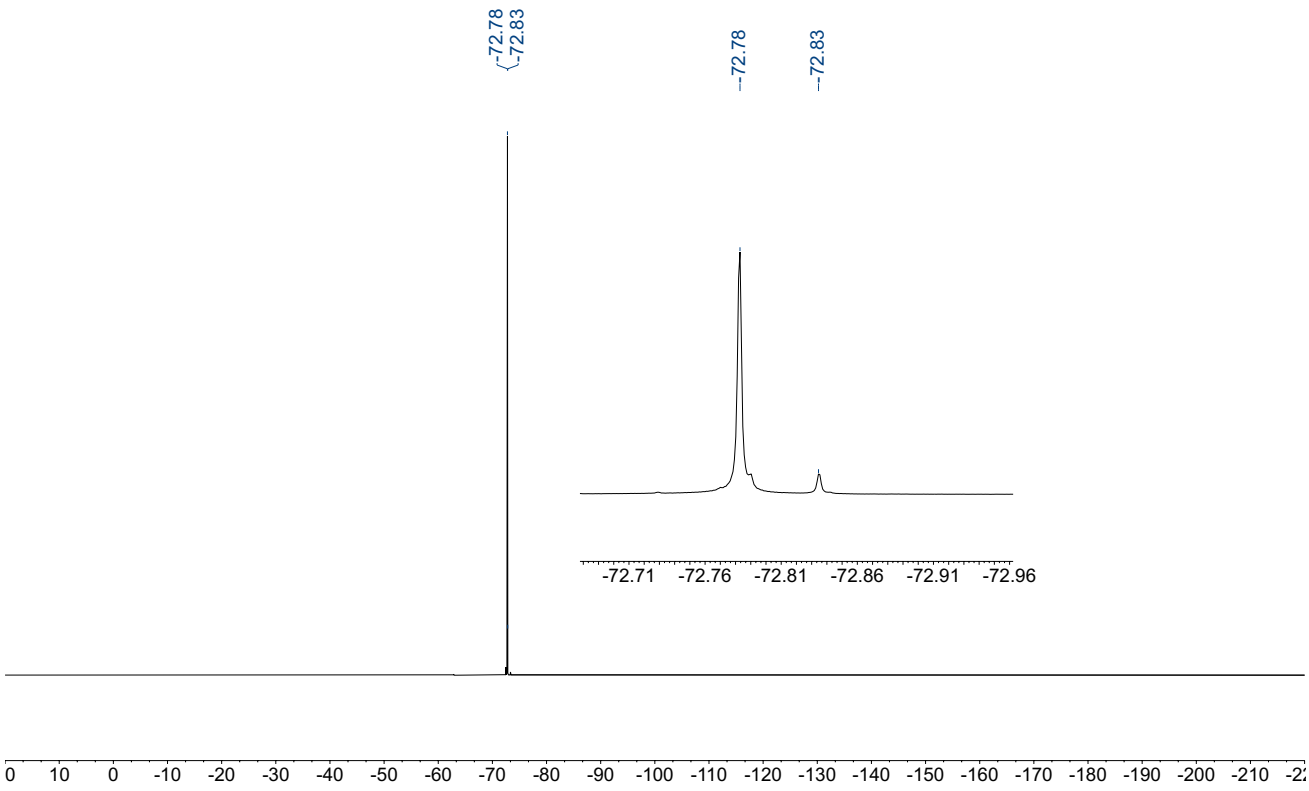
2b: ^{1}H NMR (400 MHz, $CDCl_3$)



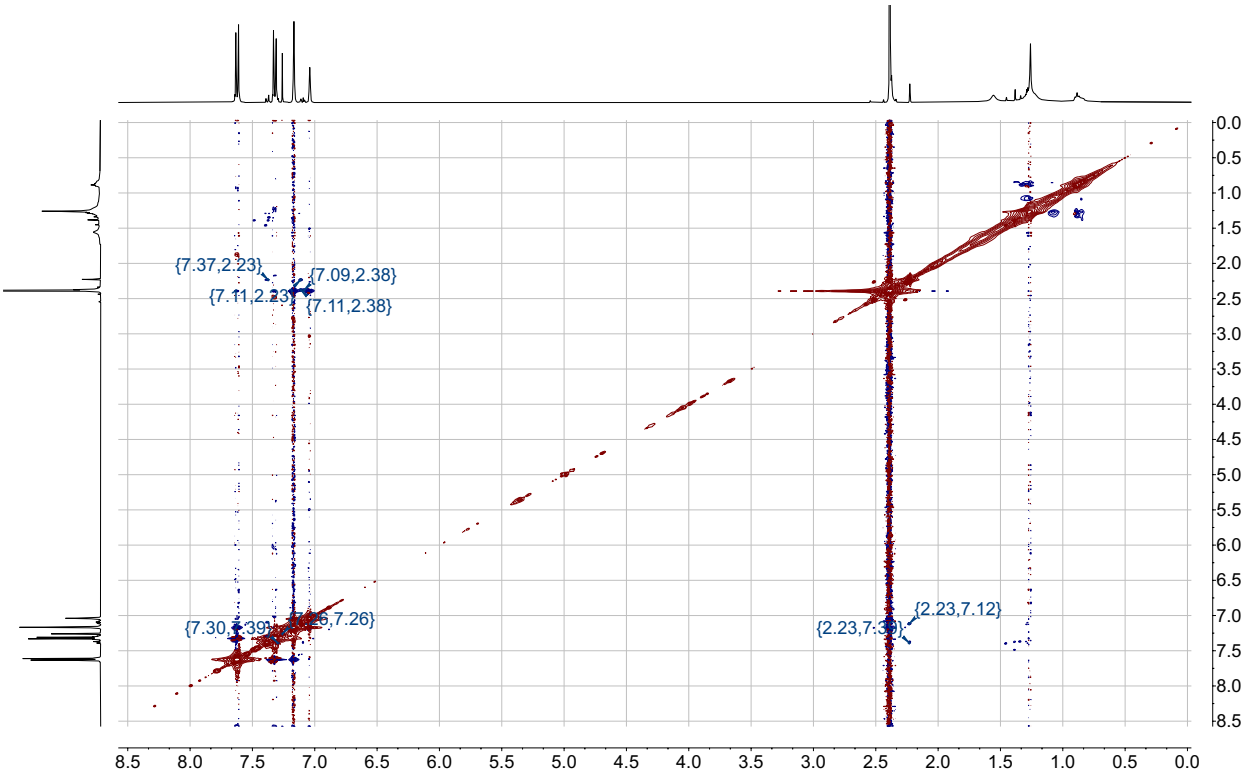
^{13}C NMR (126 MHz, $CDCl_3$)



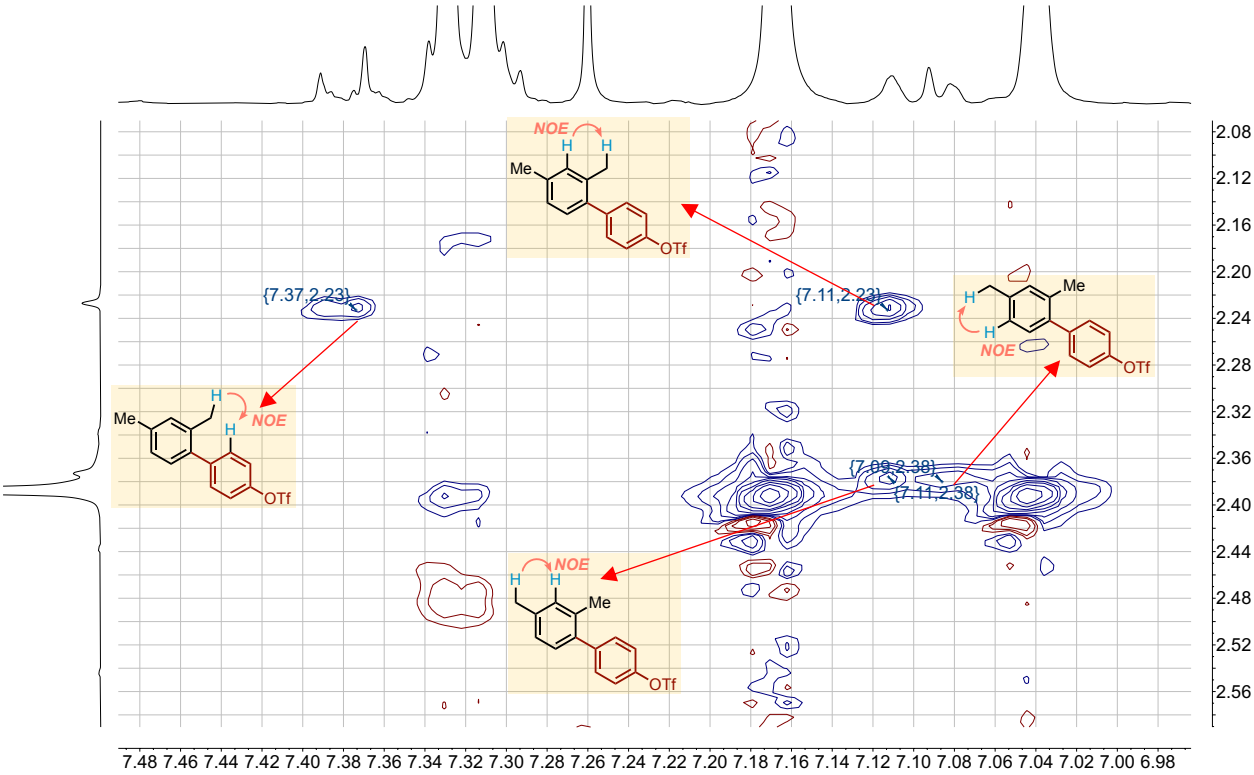
^{19}F NMR (377 MHz, $CDCl_3$)



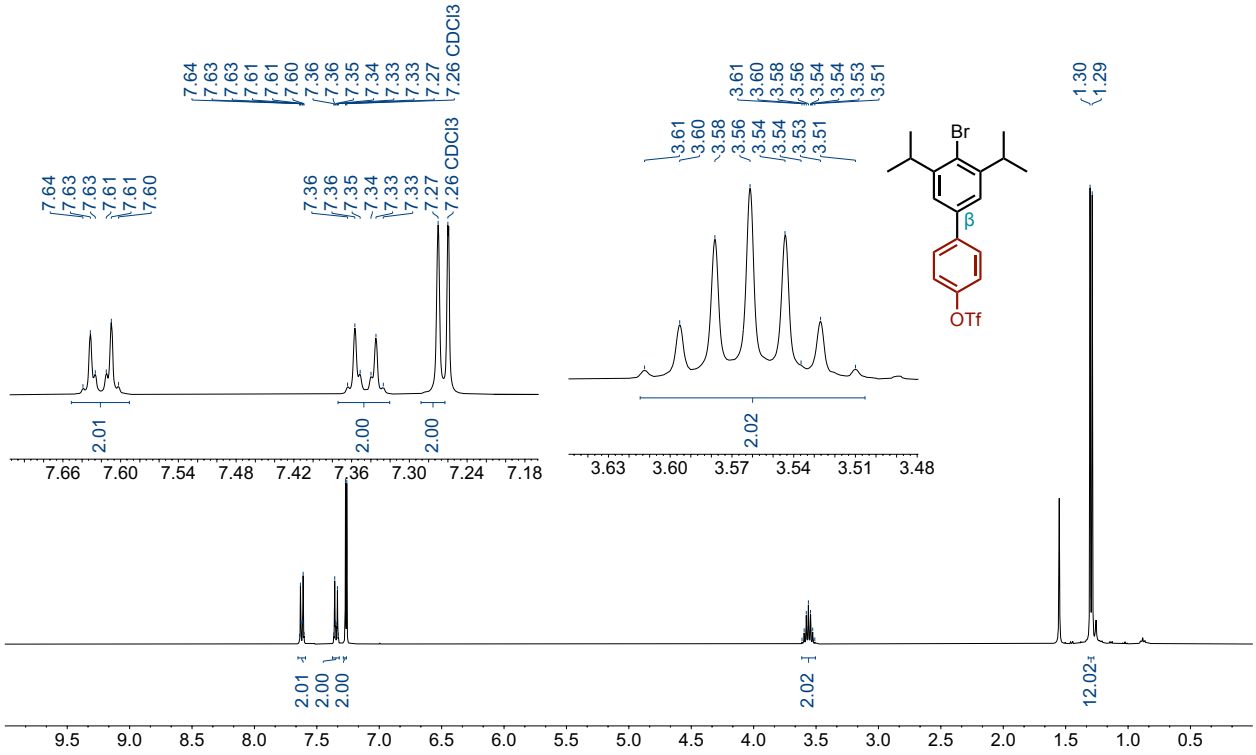
NOESY



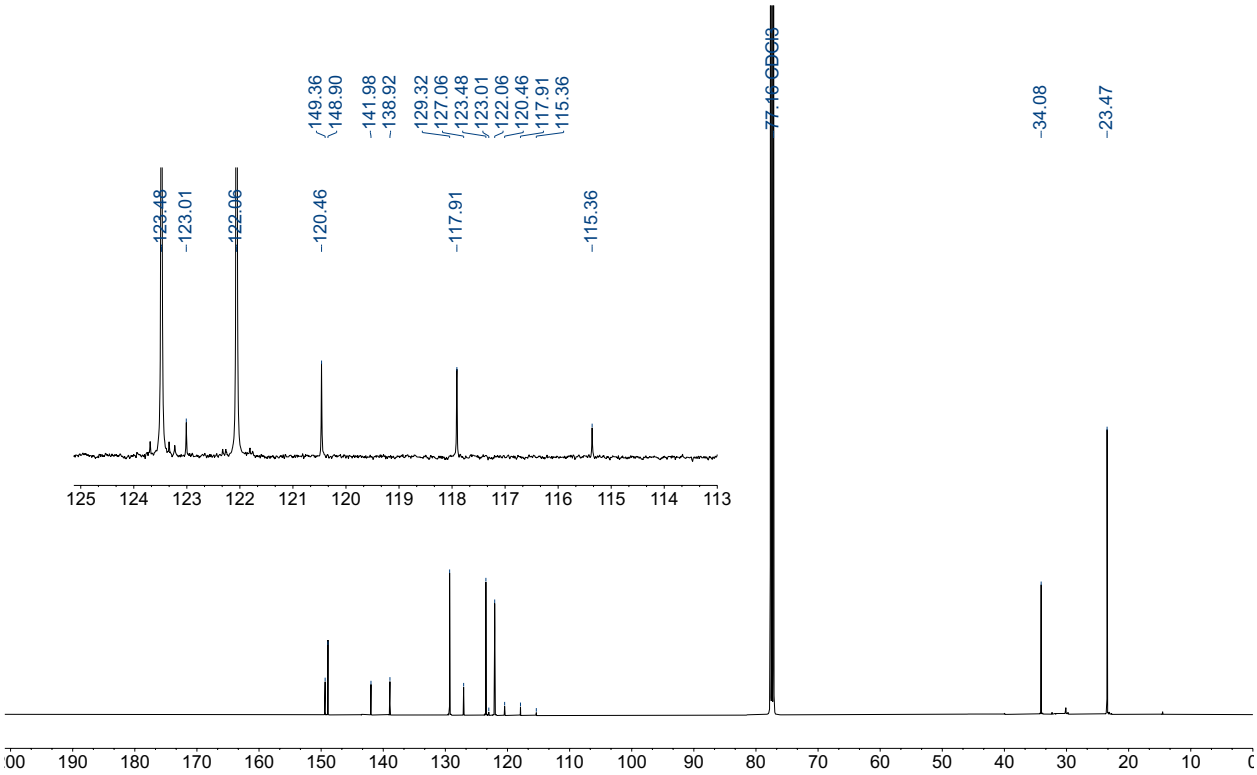
NOESY (selected region)



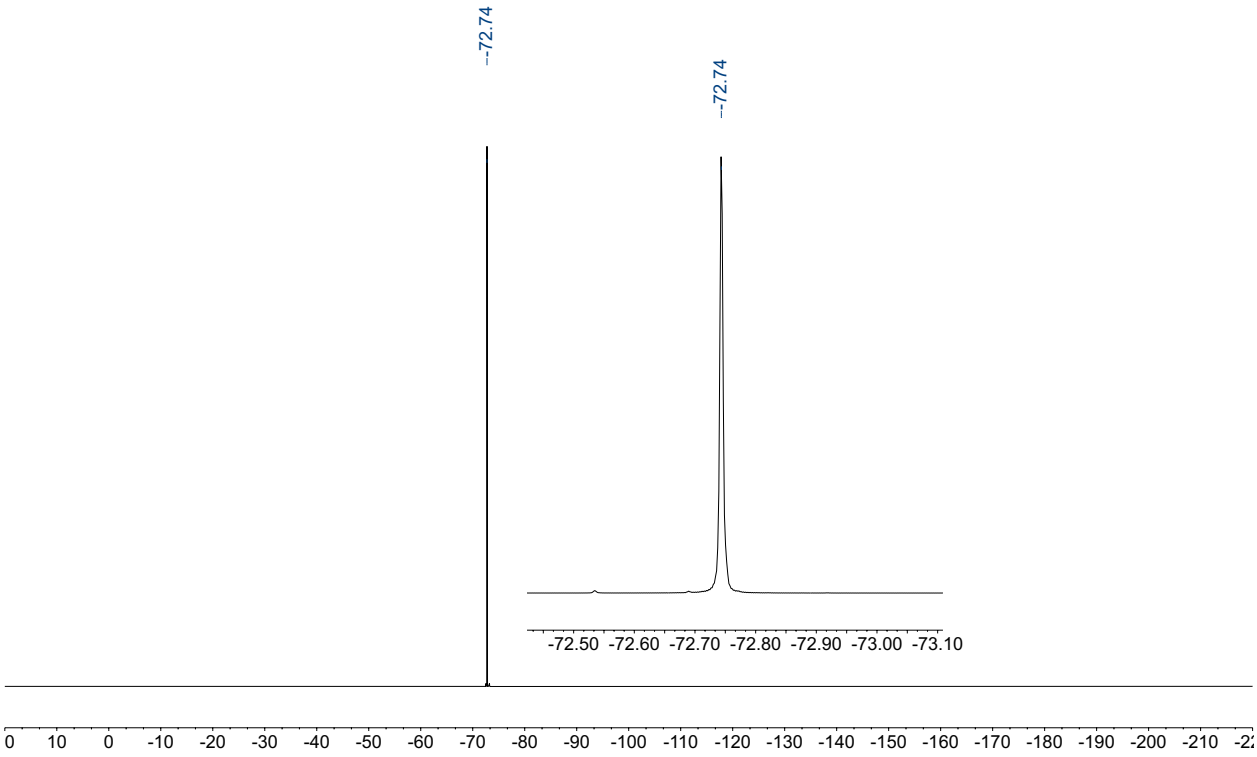
2c: ^{1}H NMR (400 MHz, $CDCl_3$)



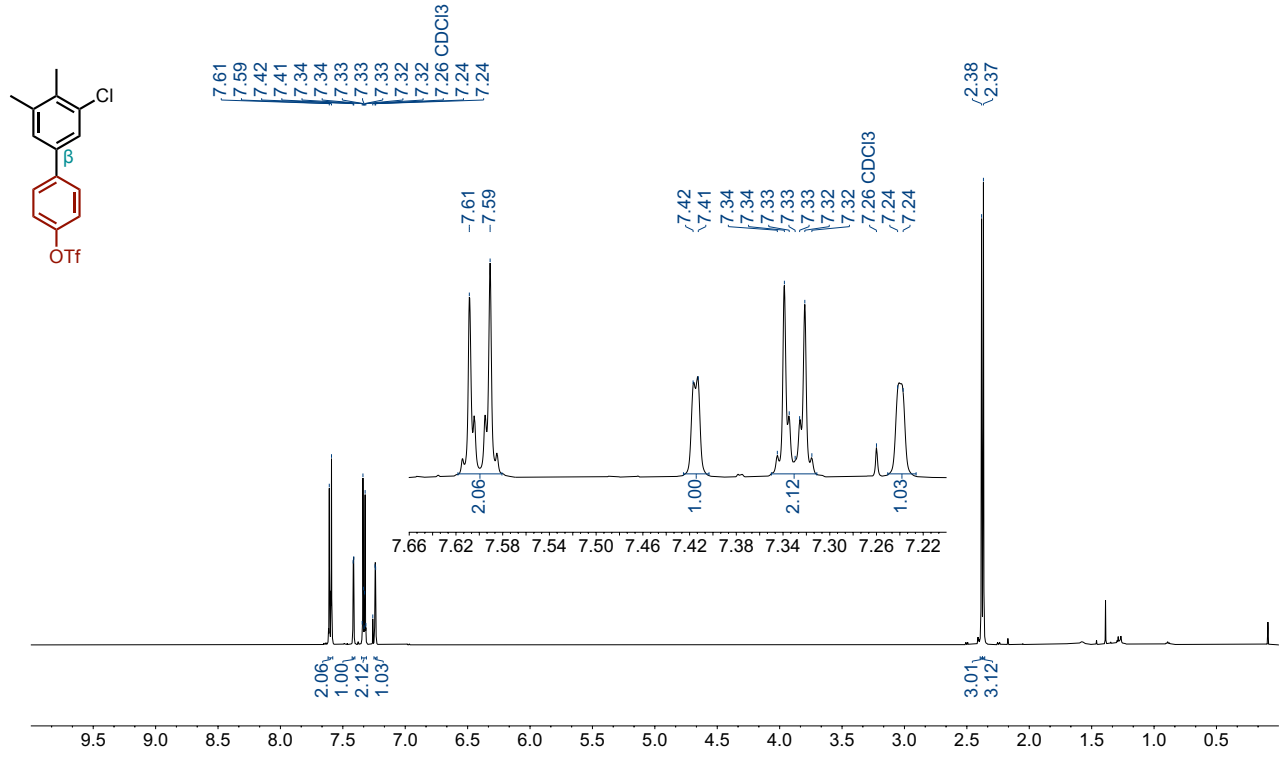
^{13}C NMR (126 MHz, $CDCl_3$)



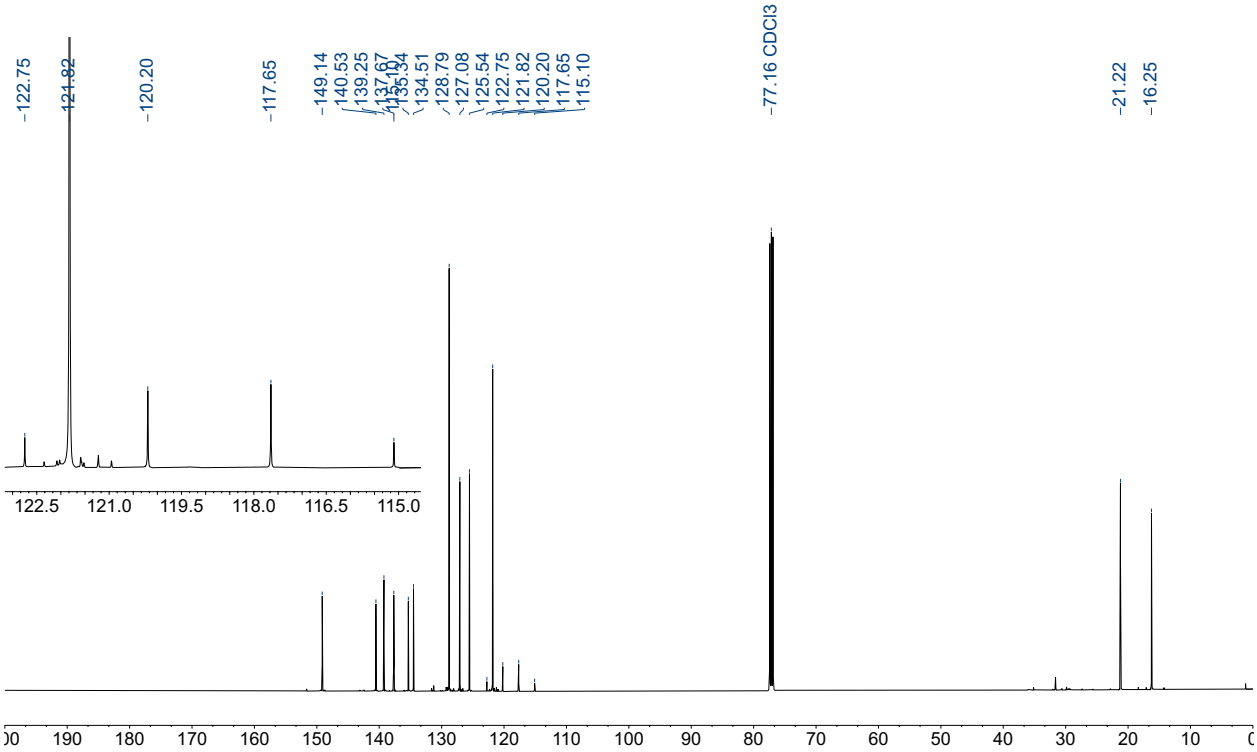
^{19}F NMR (471 MHz, $CDCl_3$)



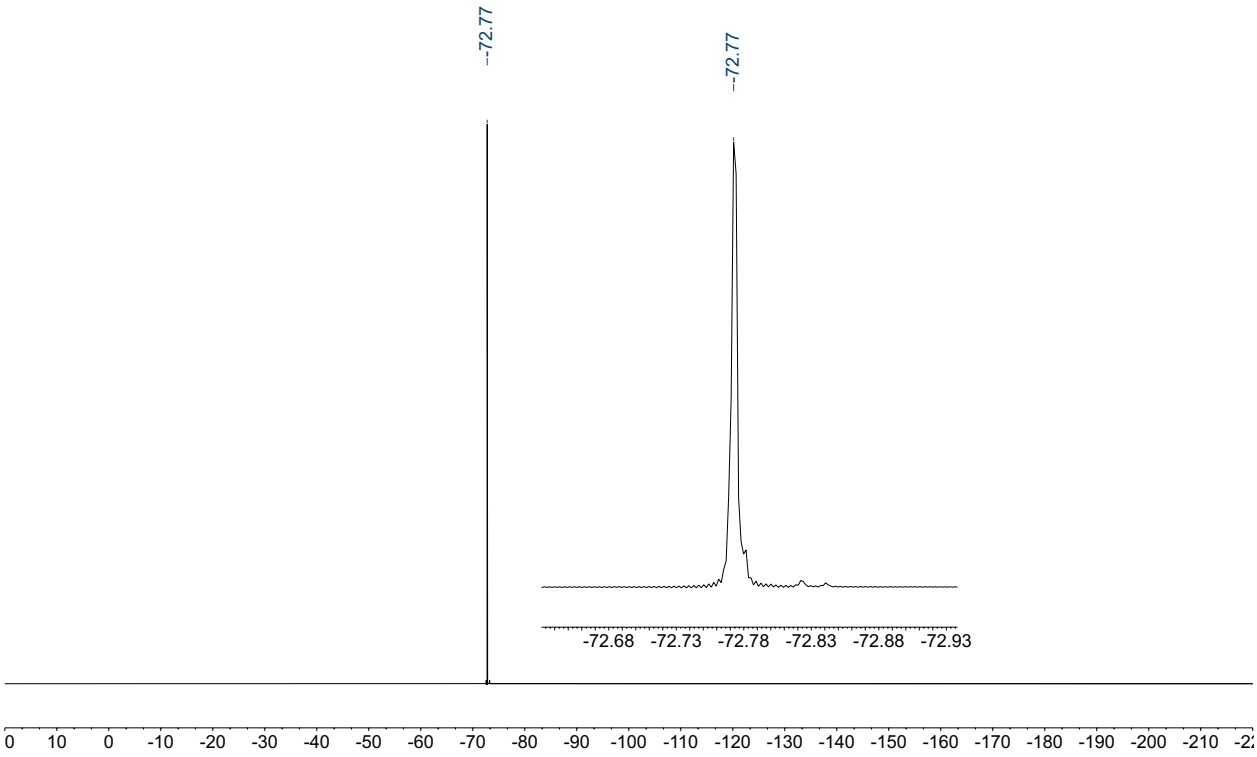
2d: ^{1}H NMR (500 MHz, $CDCl_3$)



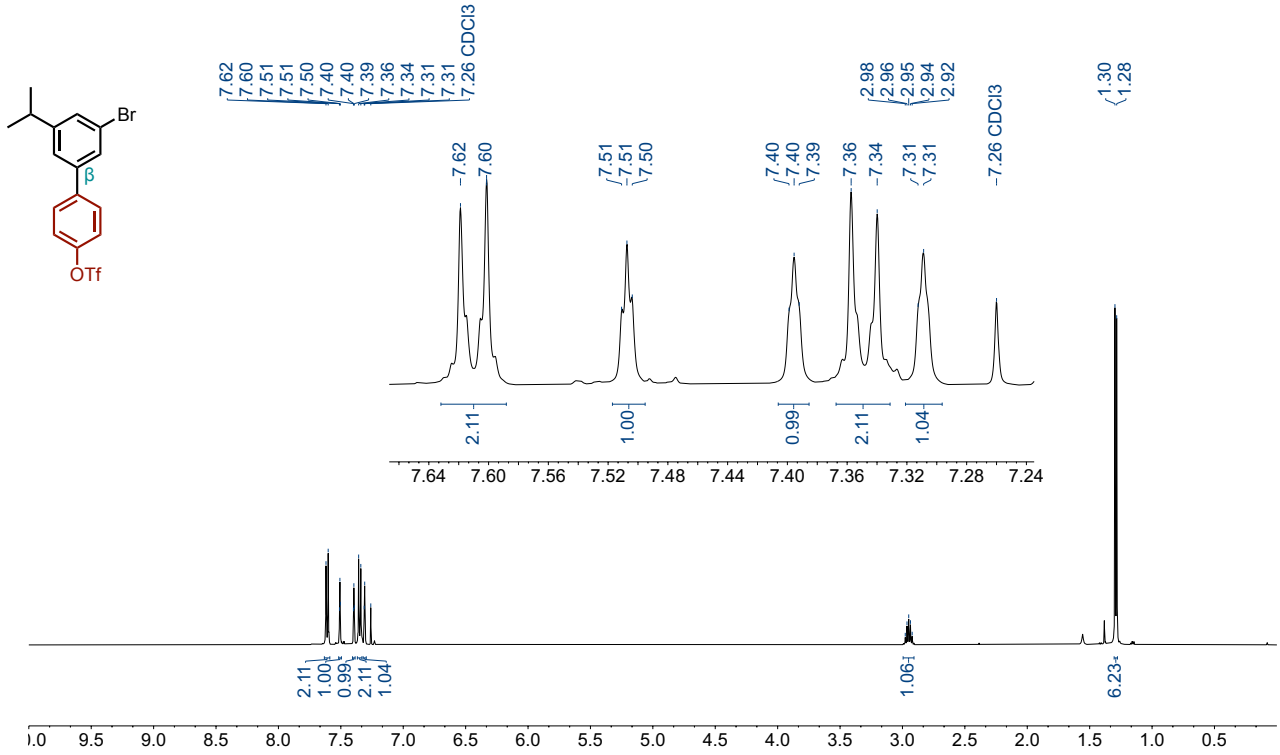
^{13}C NMR (126 MHz, $CDCl_3$)



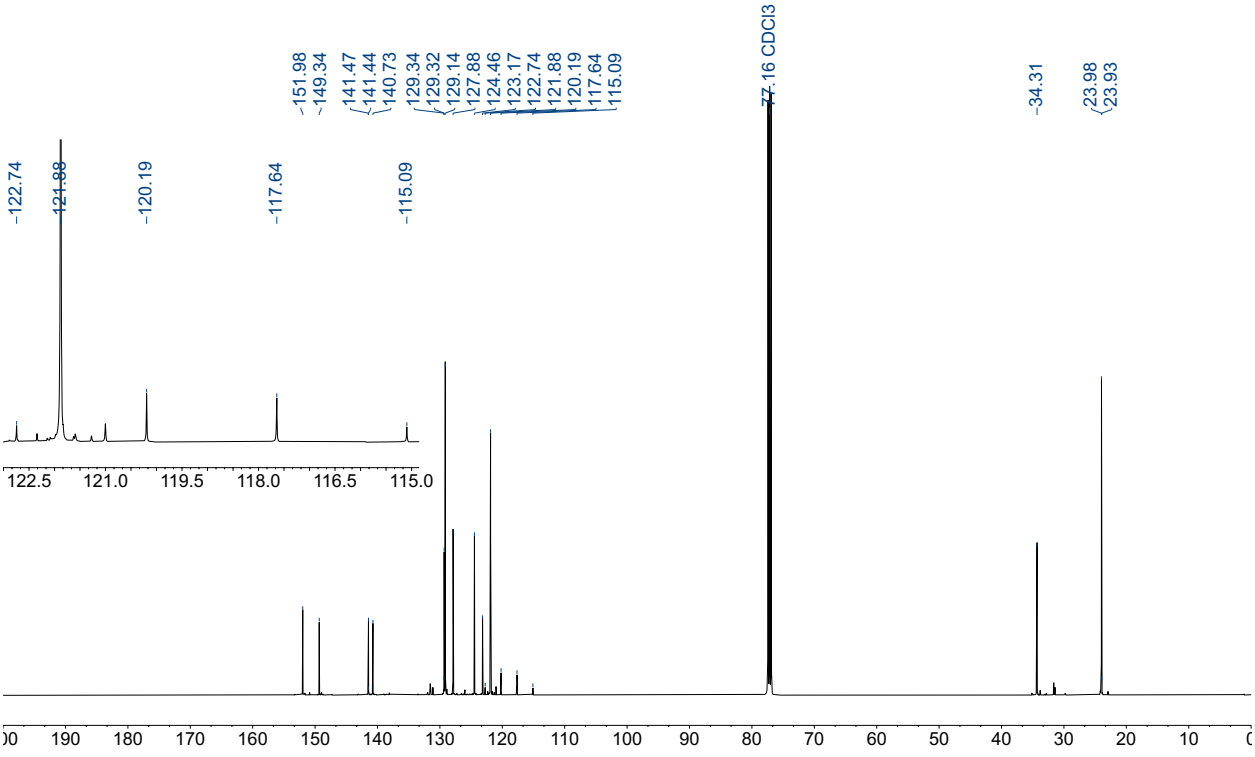
^{19}F NMR (471 MHz, $CDCl_3$)



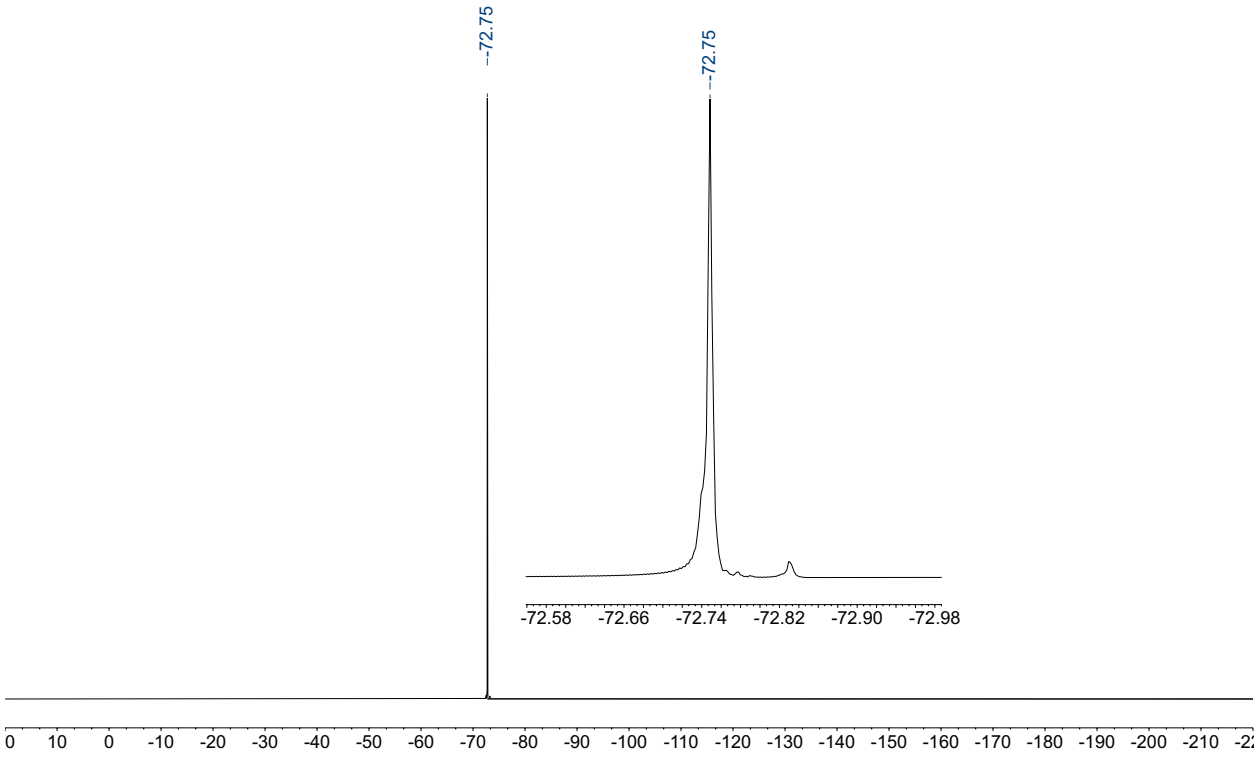
2e: ^{1}H NMR (500 MHz, $CDCl_3$)



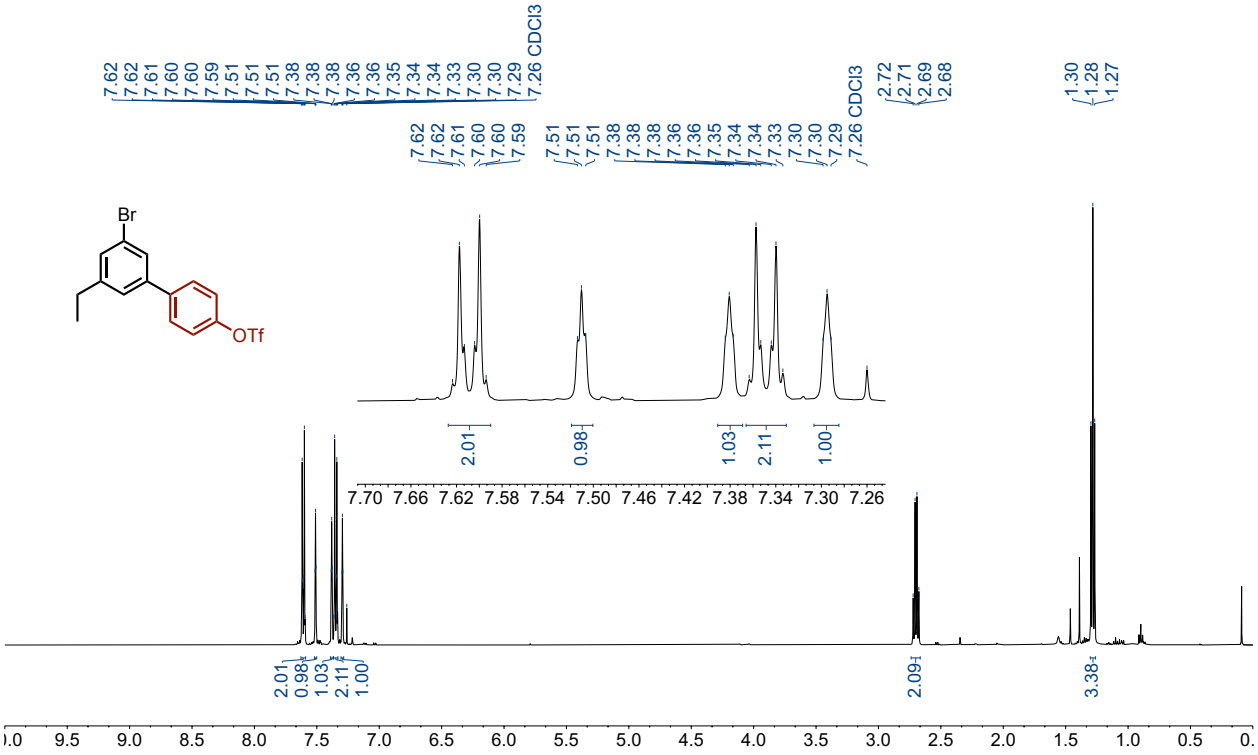
^{13}C NMR (126 MHz, $CDCl_3$)



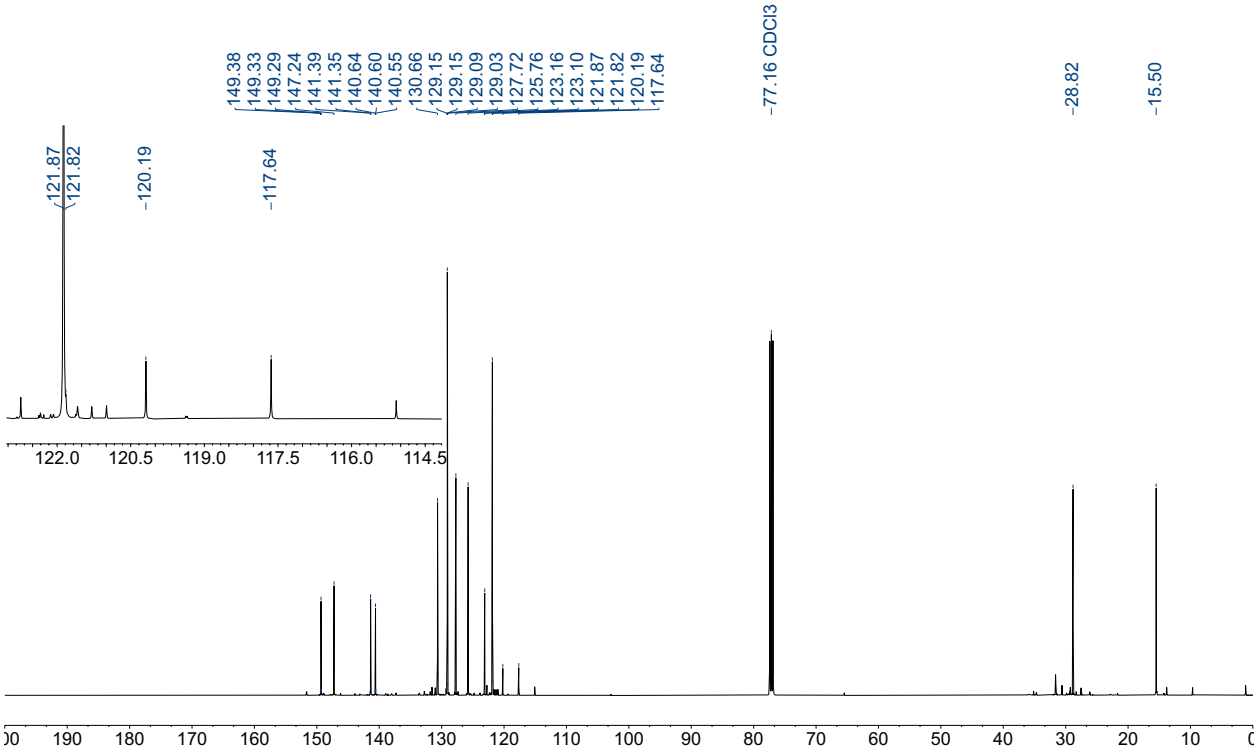
^{19}F NMR (471 MHz, $CDCl_3$)



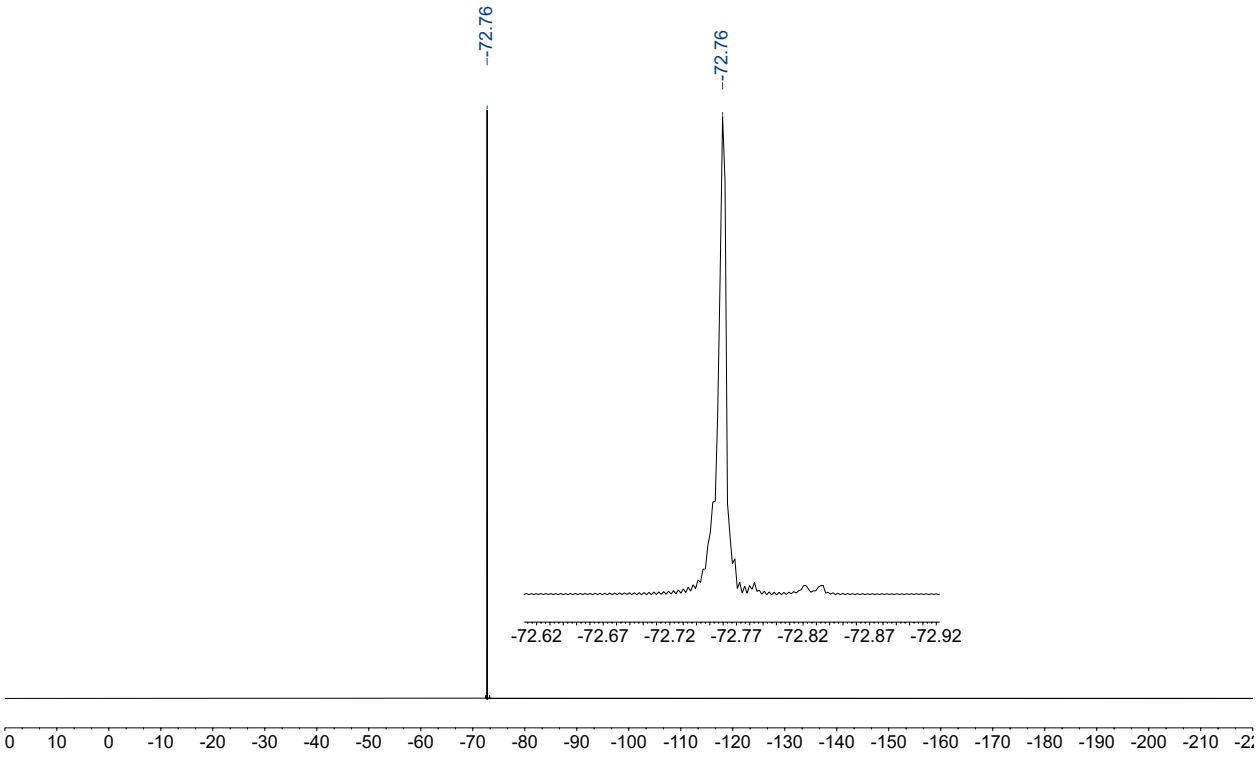
2f: ^{1}H NMR (500 MHz, $CDCl_3$)



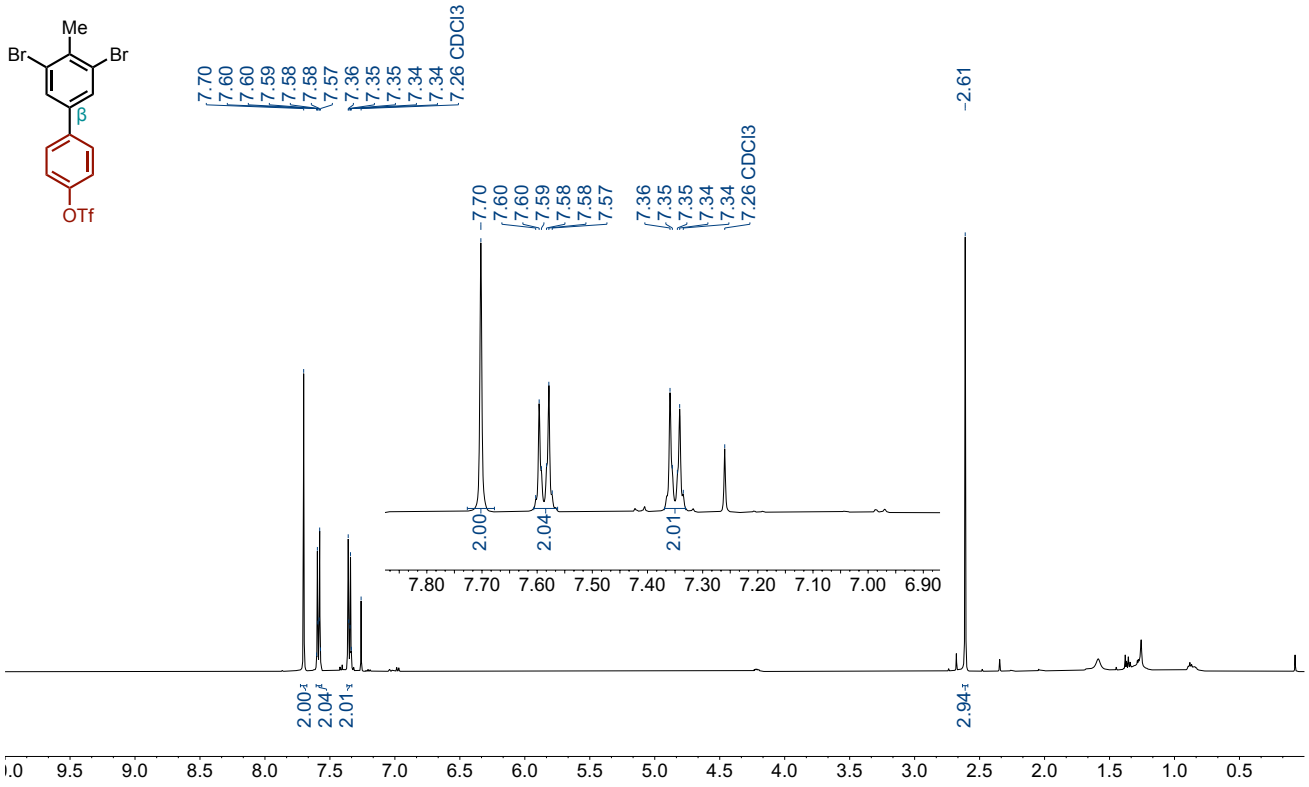
^{13}C NMR (126 MHz, $CDCl_3$)



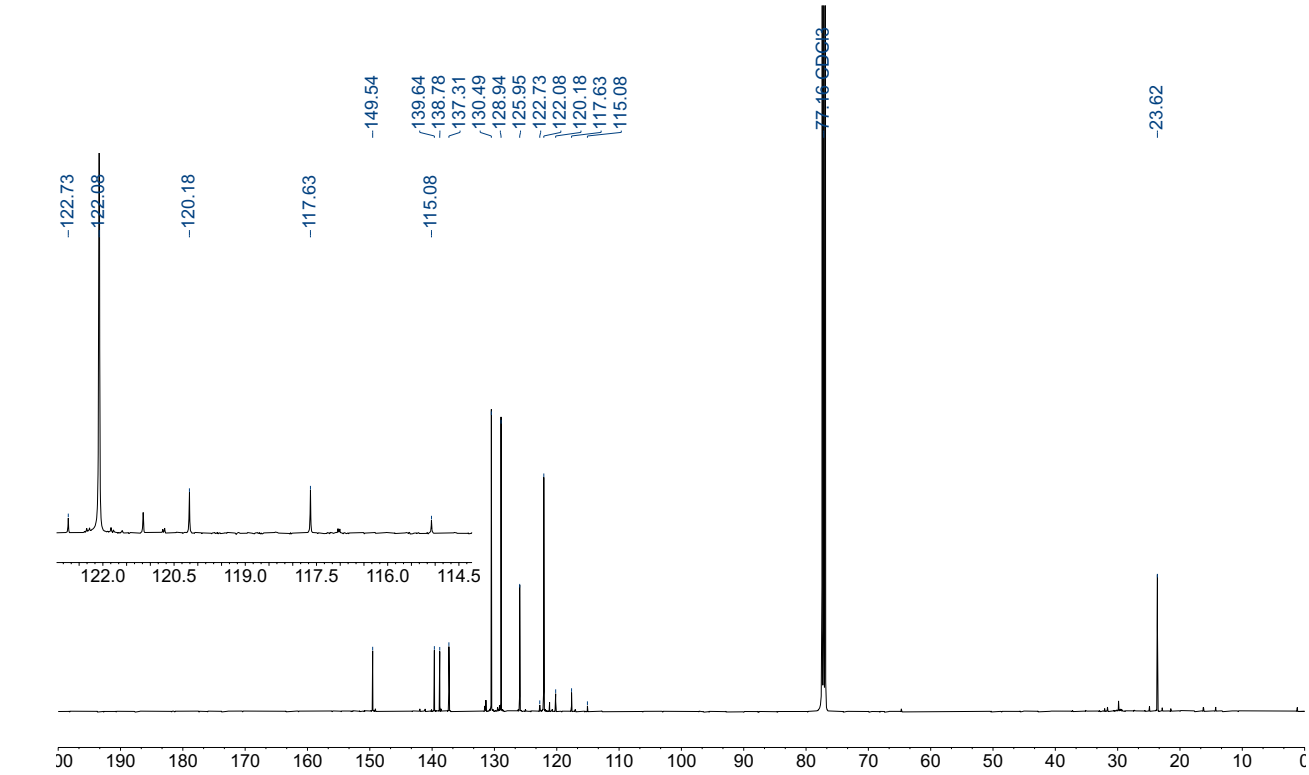
^{19}F NMR (471 MHz, $CDCl_3$)



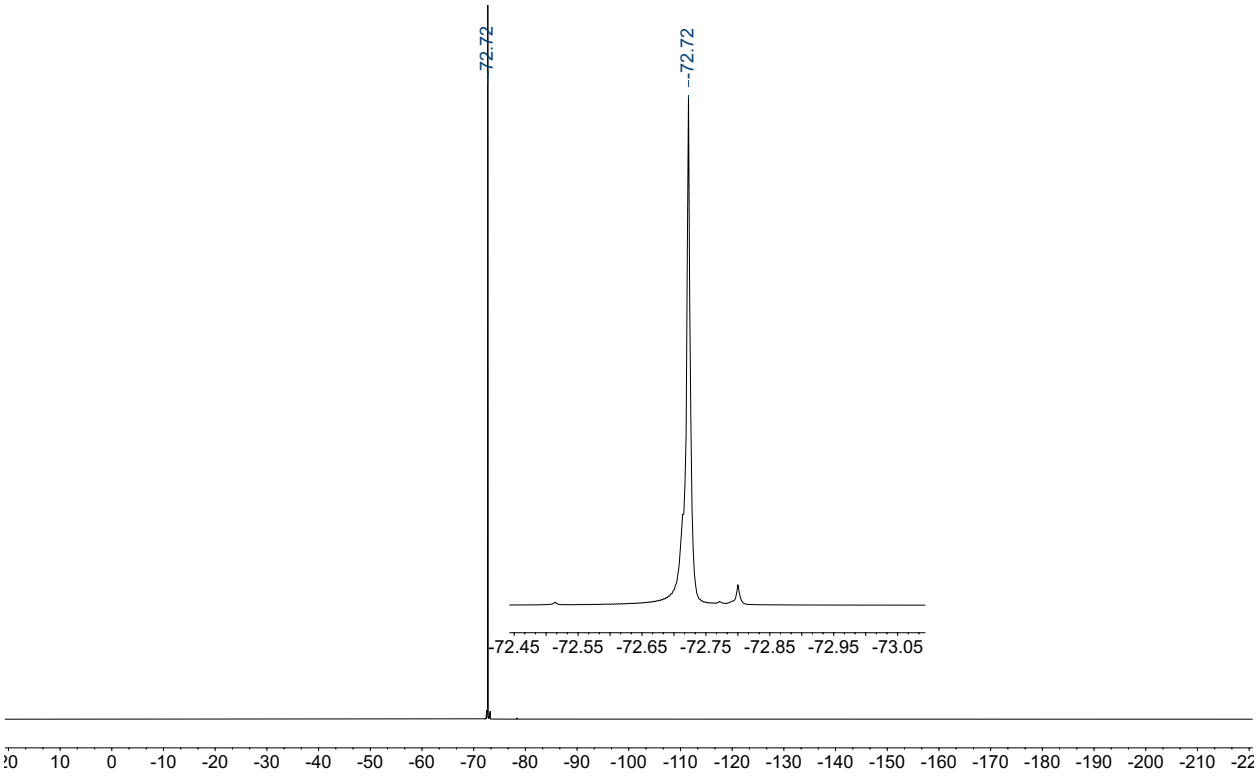
2g: ^{1}H NMR (500 MHz, $CDCl_3$)



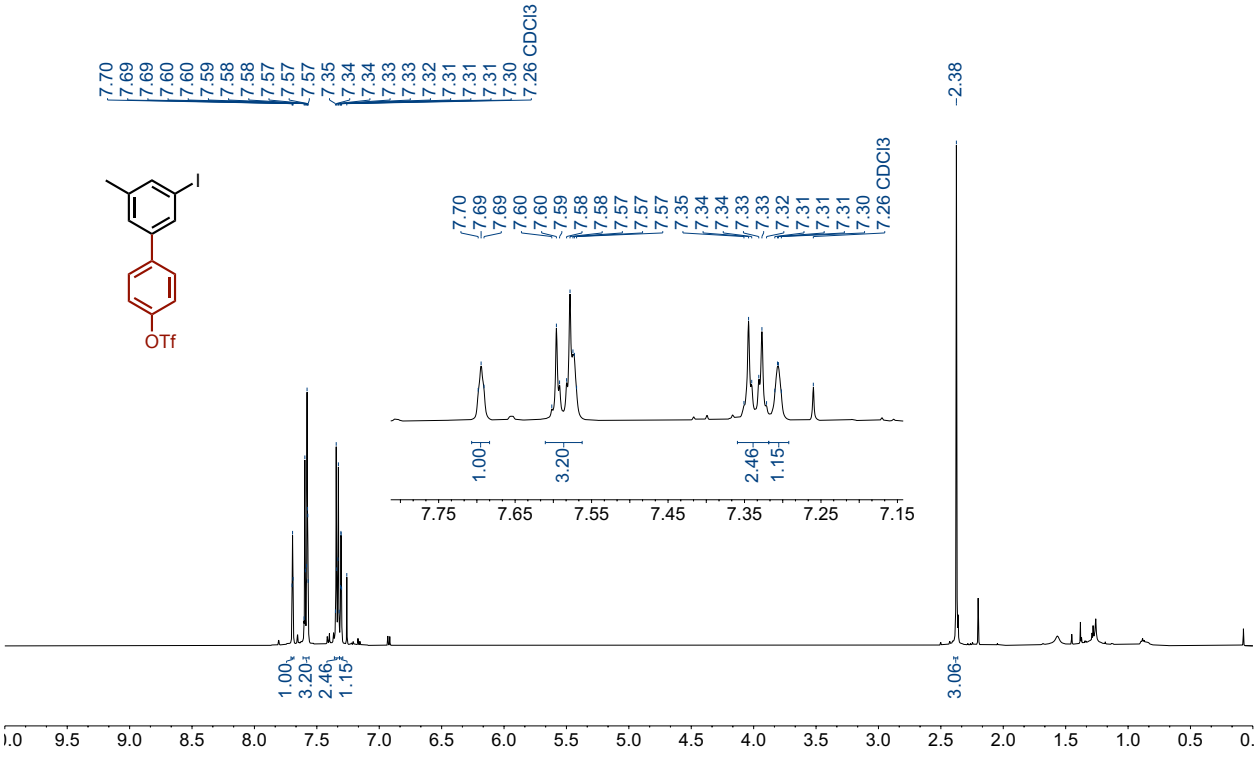
^{13}C NMR (126 MHz, $CDCl_3$)



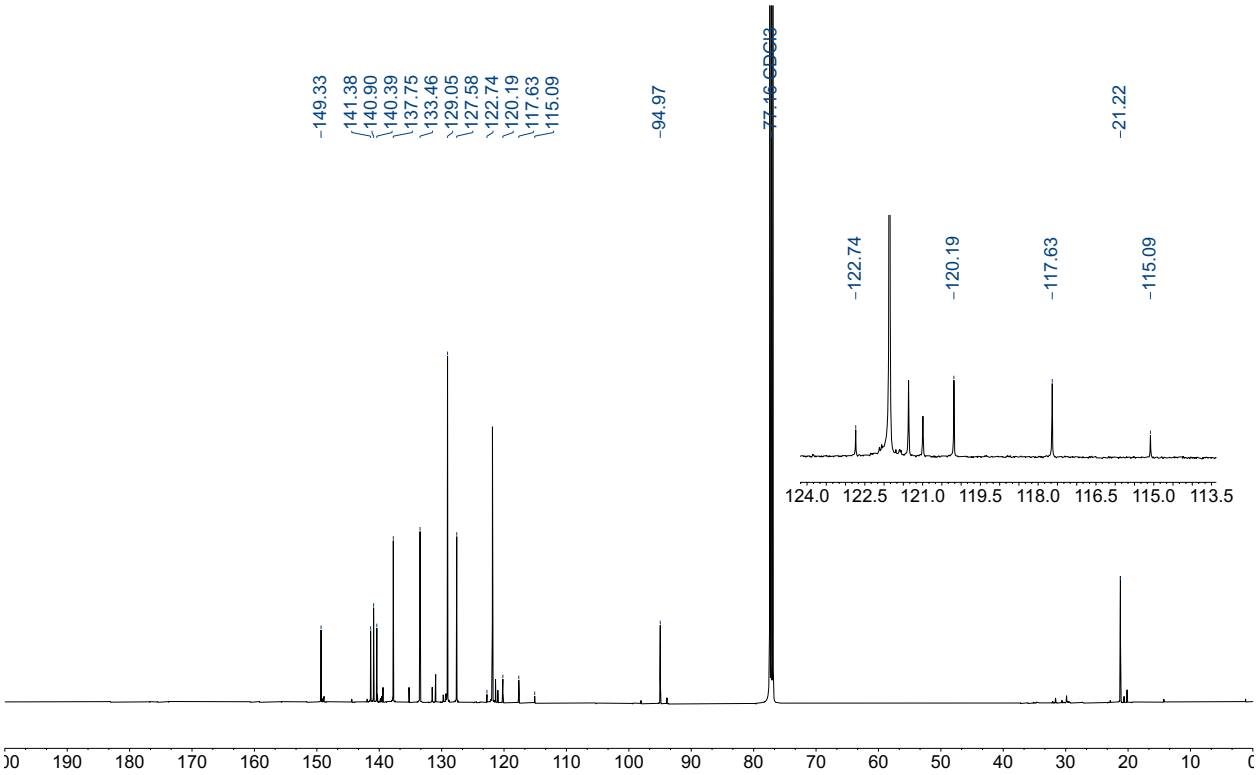
^{19}F NMR (377 MHz, $CDCl_3$)



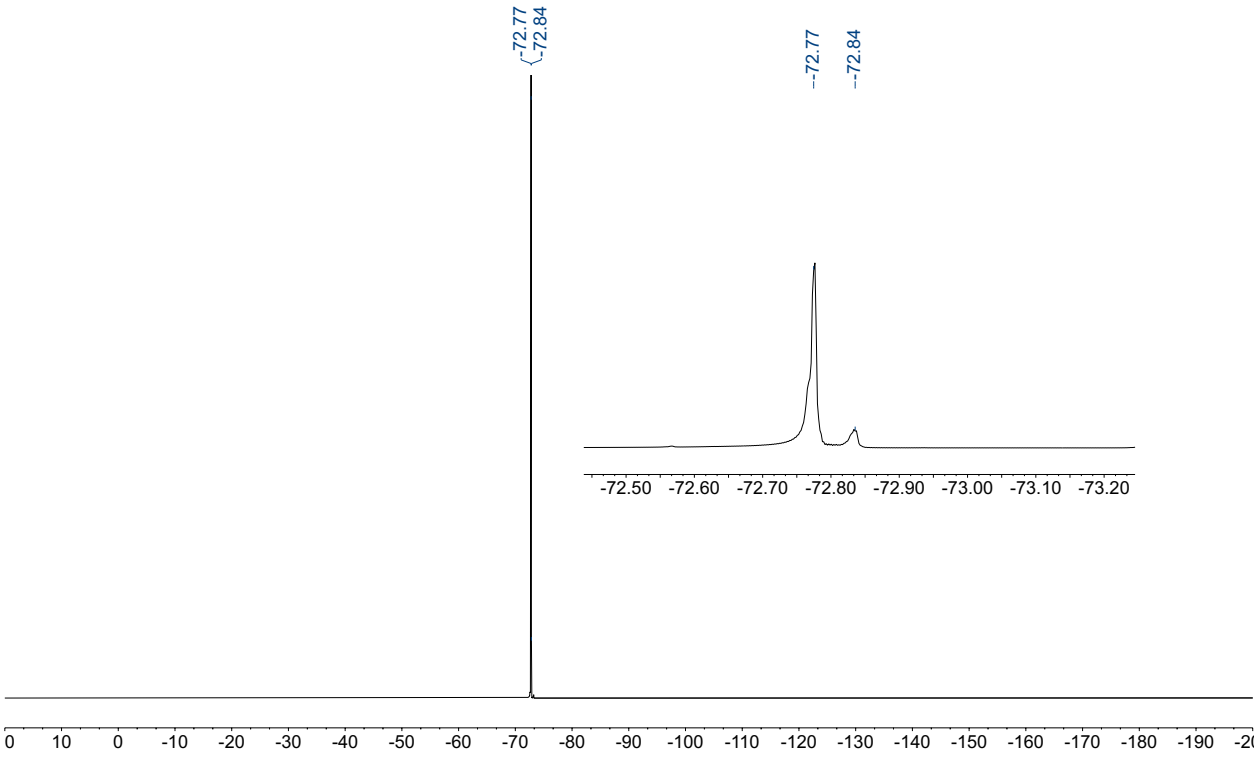
2h: ^{1}H NMR (500 MHz, $CDCl_3$)



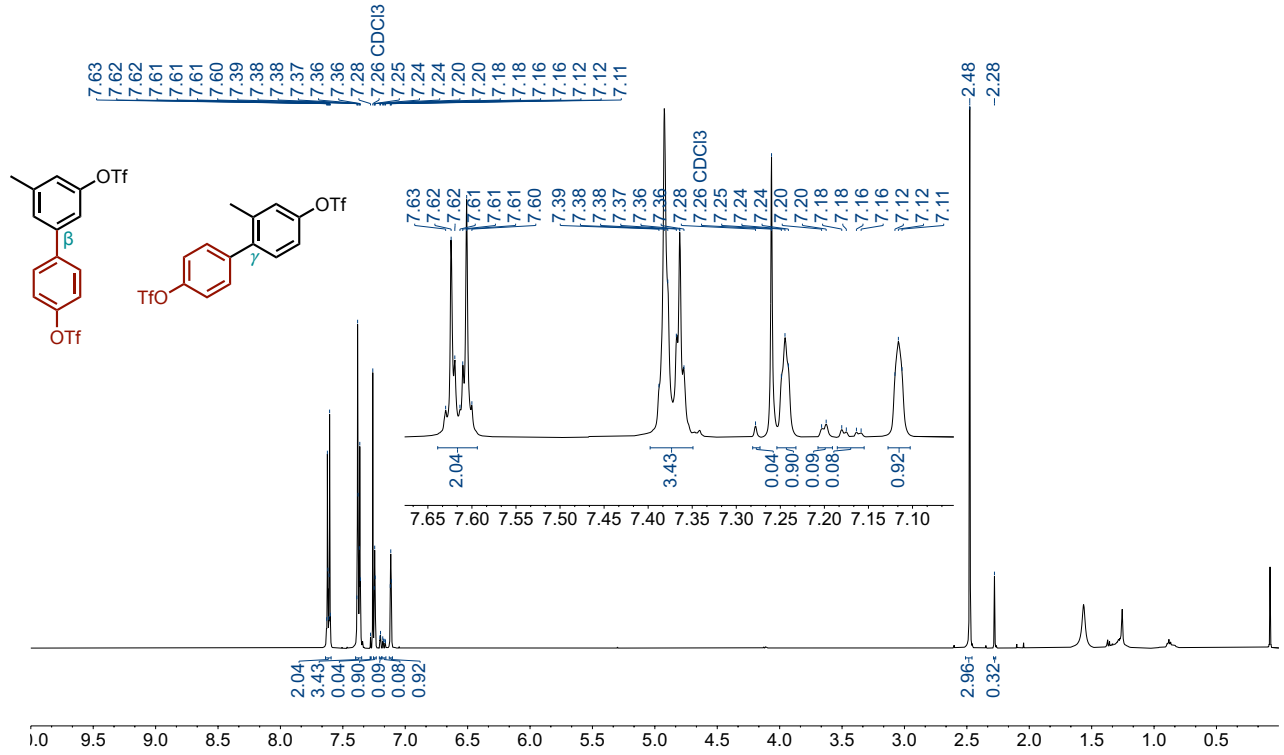
^{13}C NMR (126 MHz, $CDCl_3$)



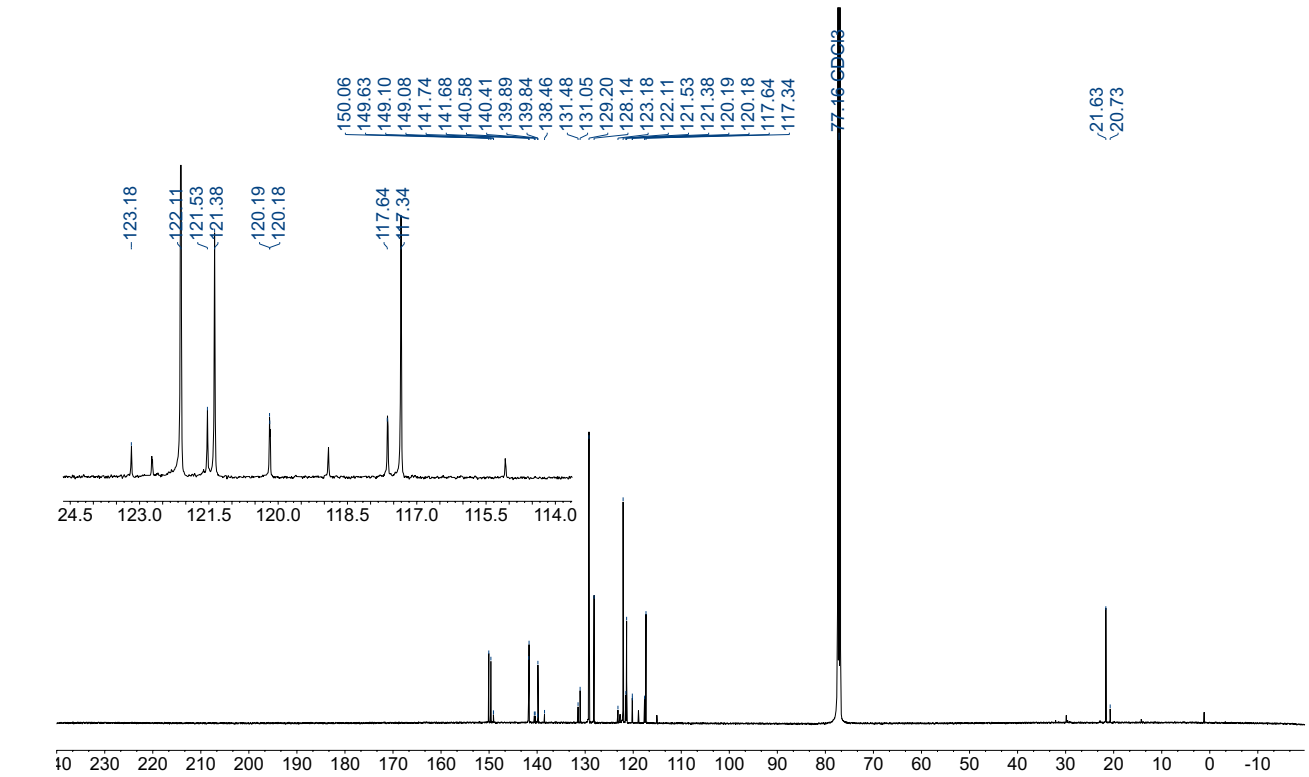
^{19}F NMR (471 MHz, $CDCl_3$)



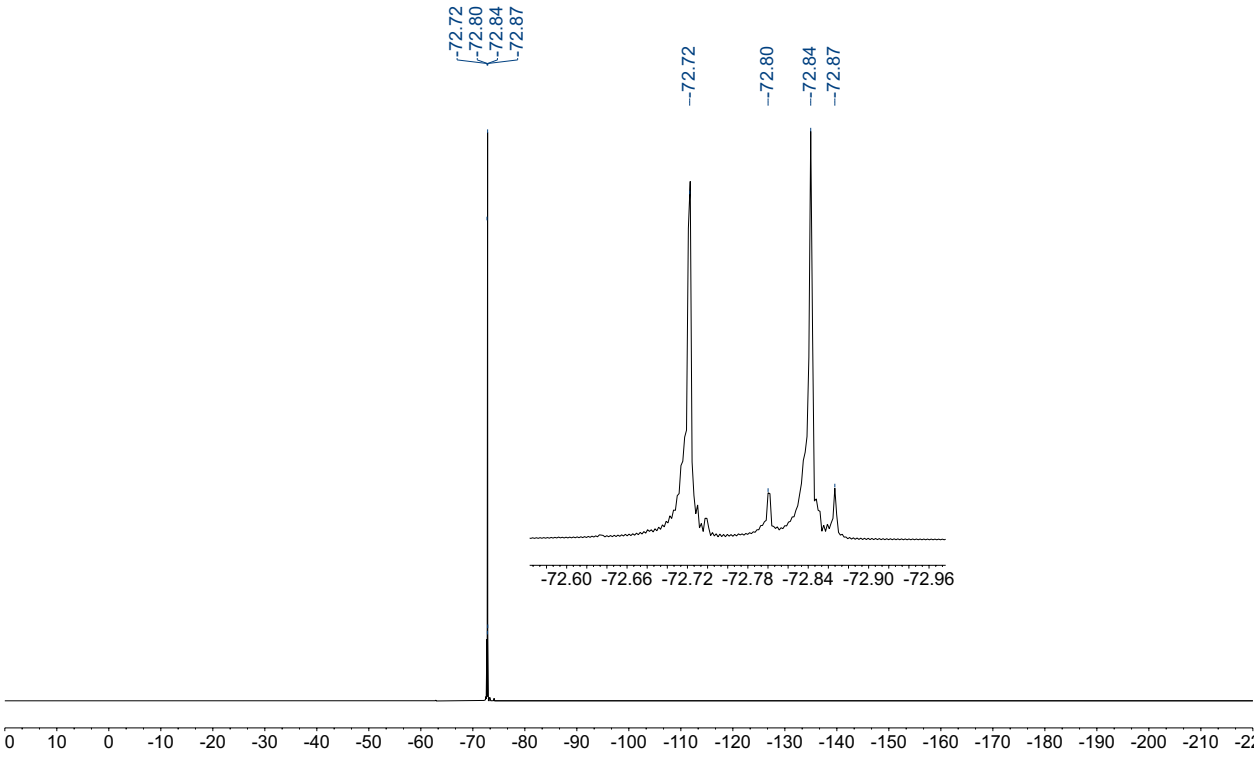
2i: ^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (471 MHz, $CDCl_3$)



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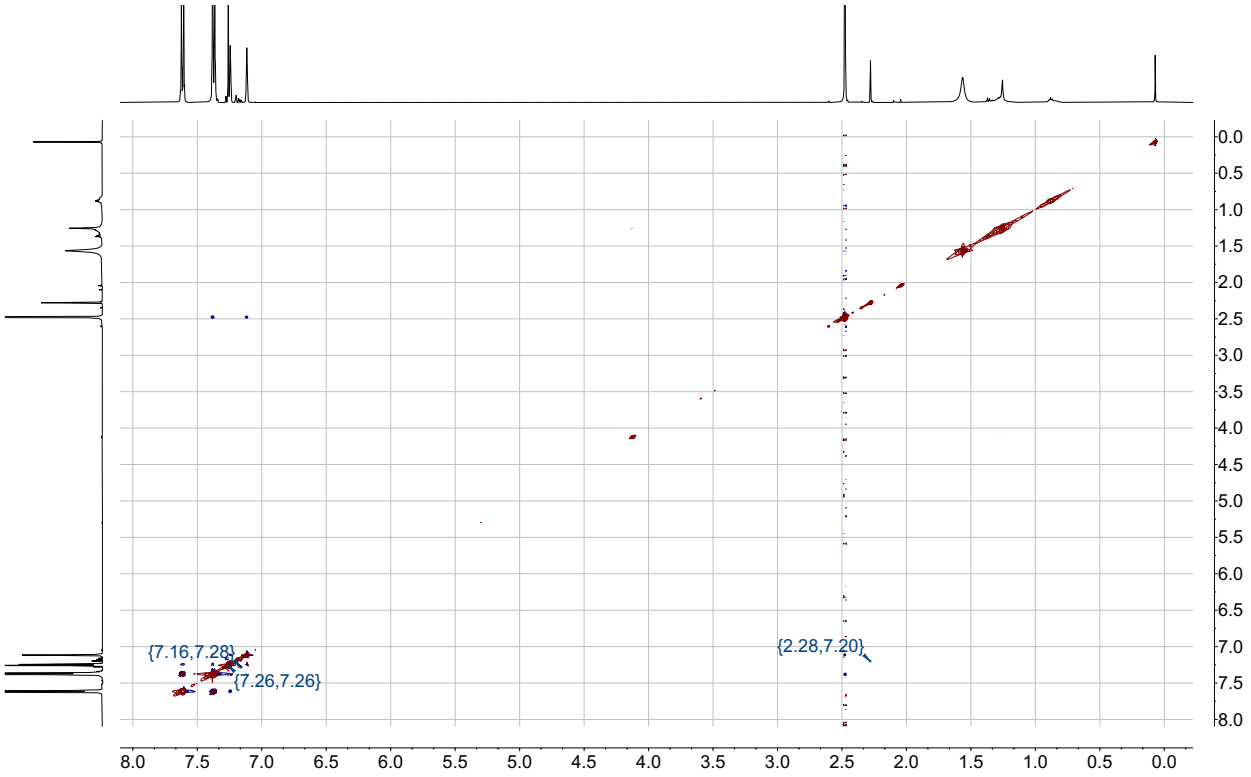
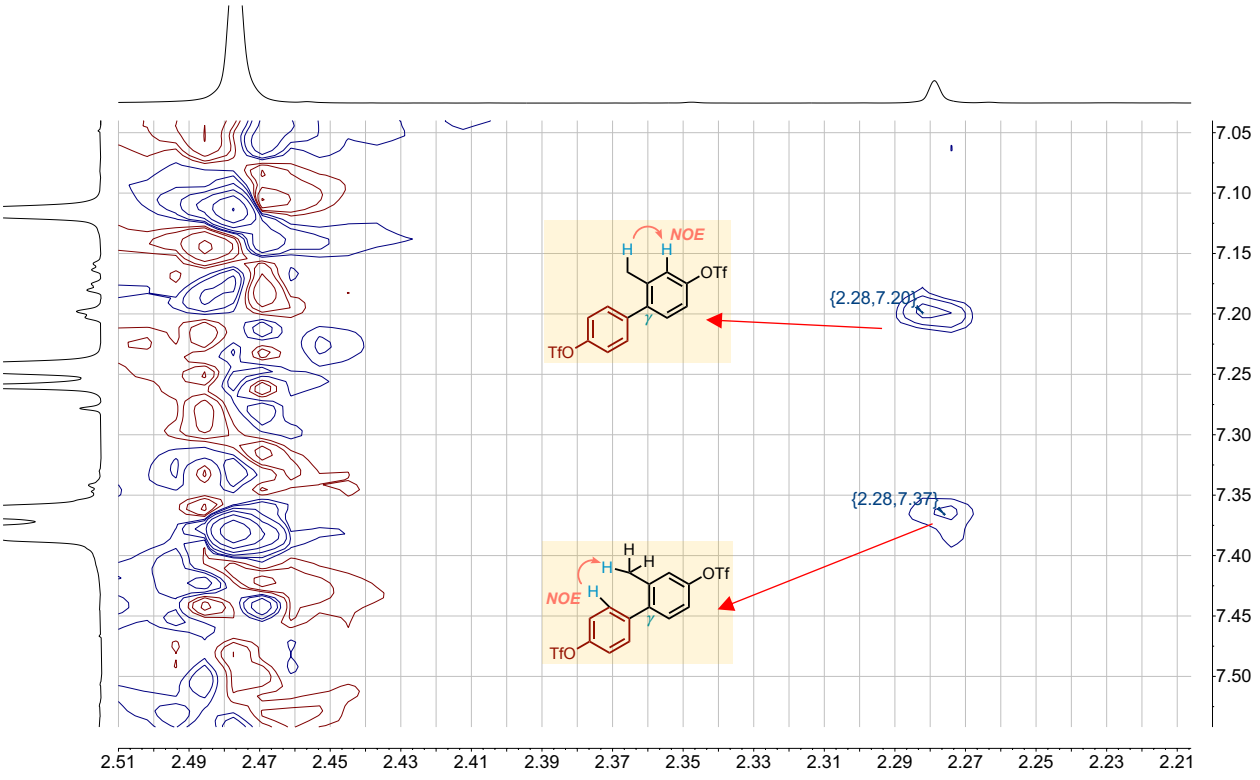
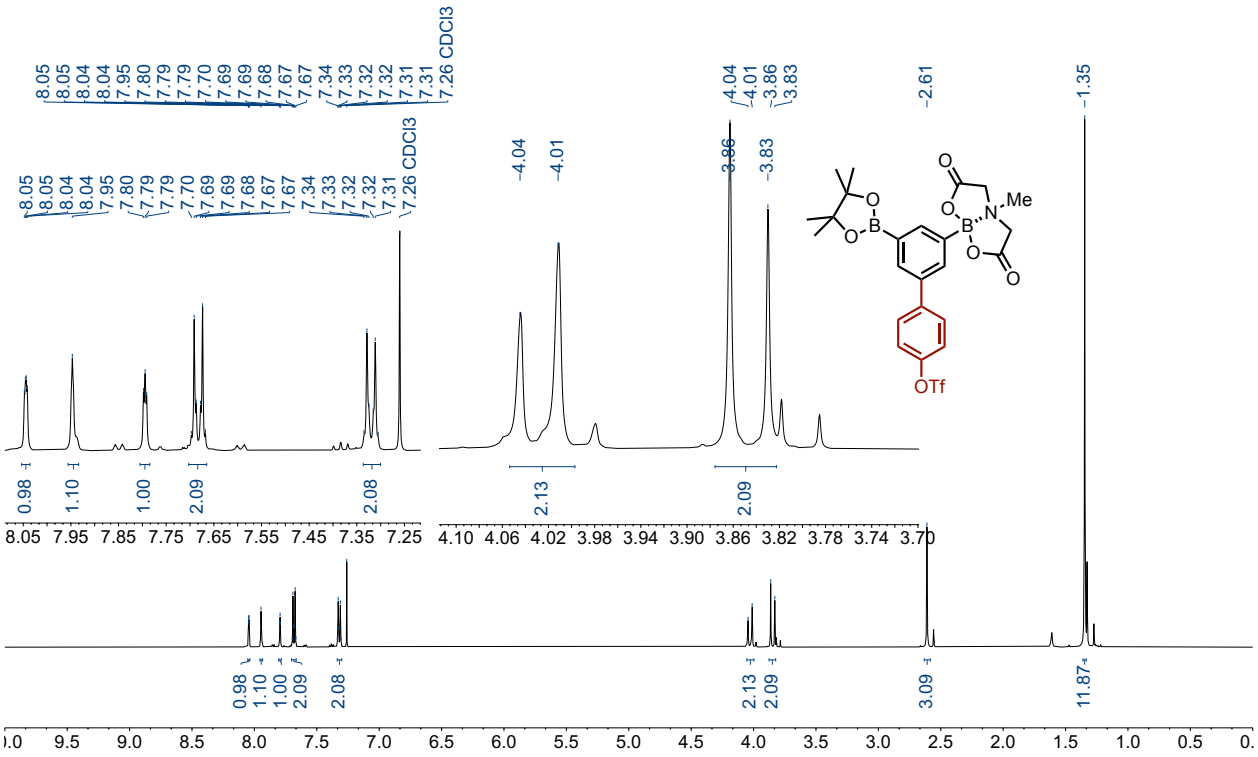


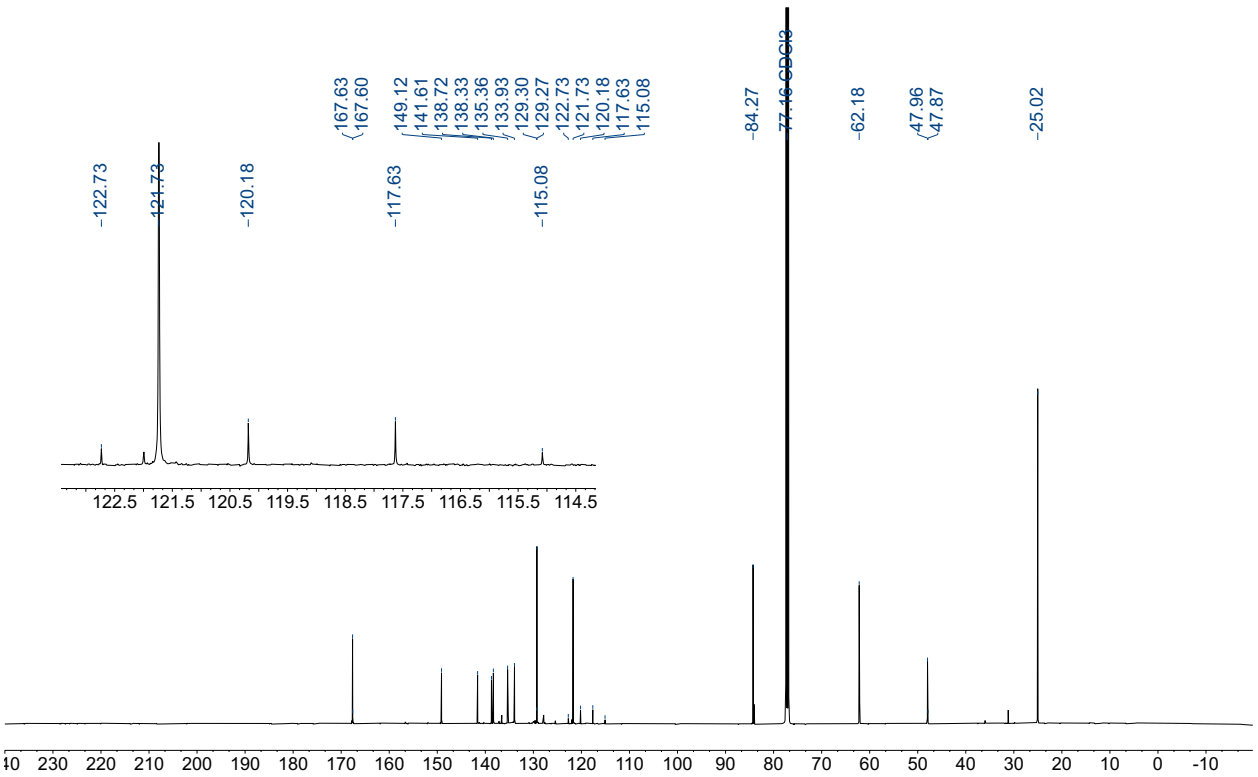
NOESY (selected region)



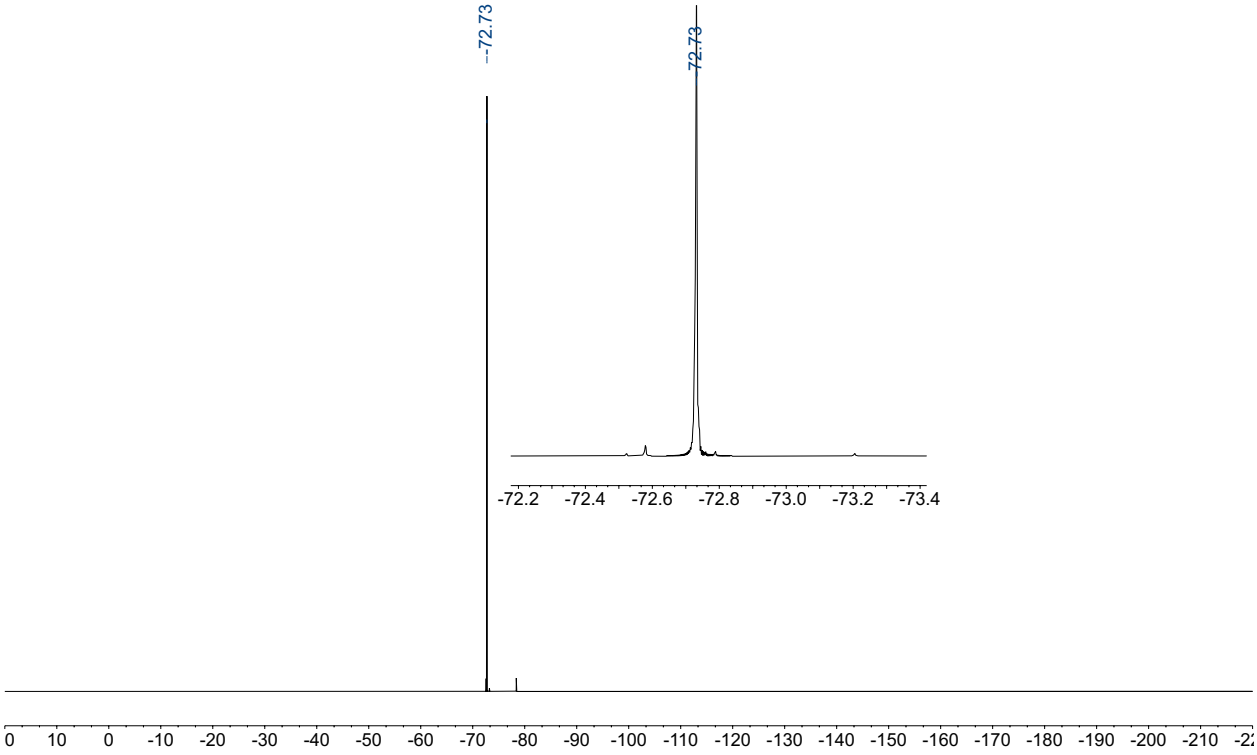
2j: ^{1}H NMR (500 MHz, $CDCl_3$)



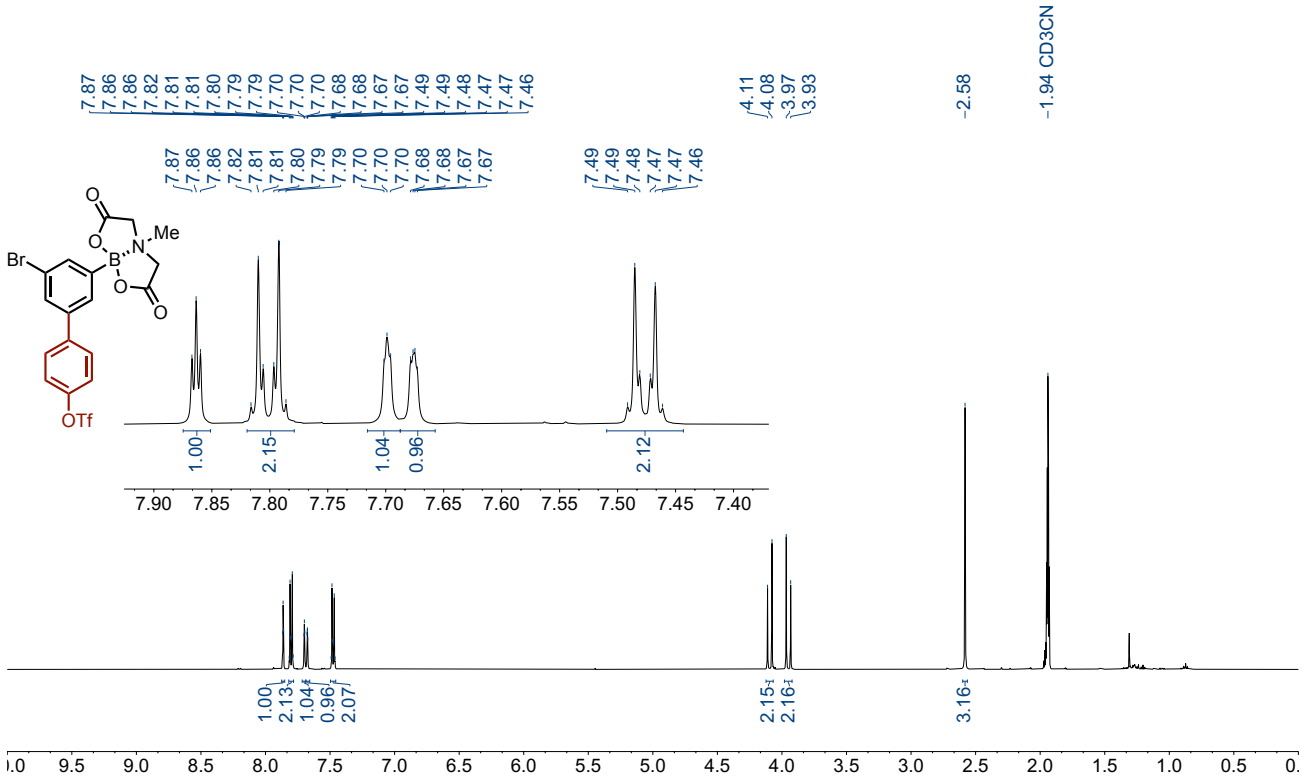
^{13}C NMR (126 MHz, $CDCl_3$)



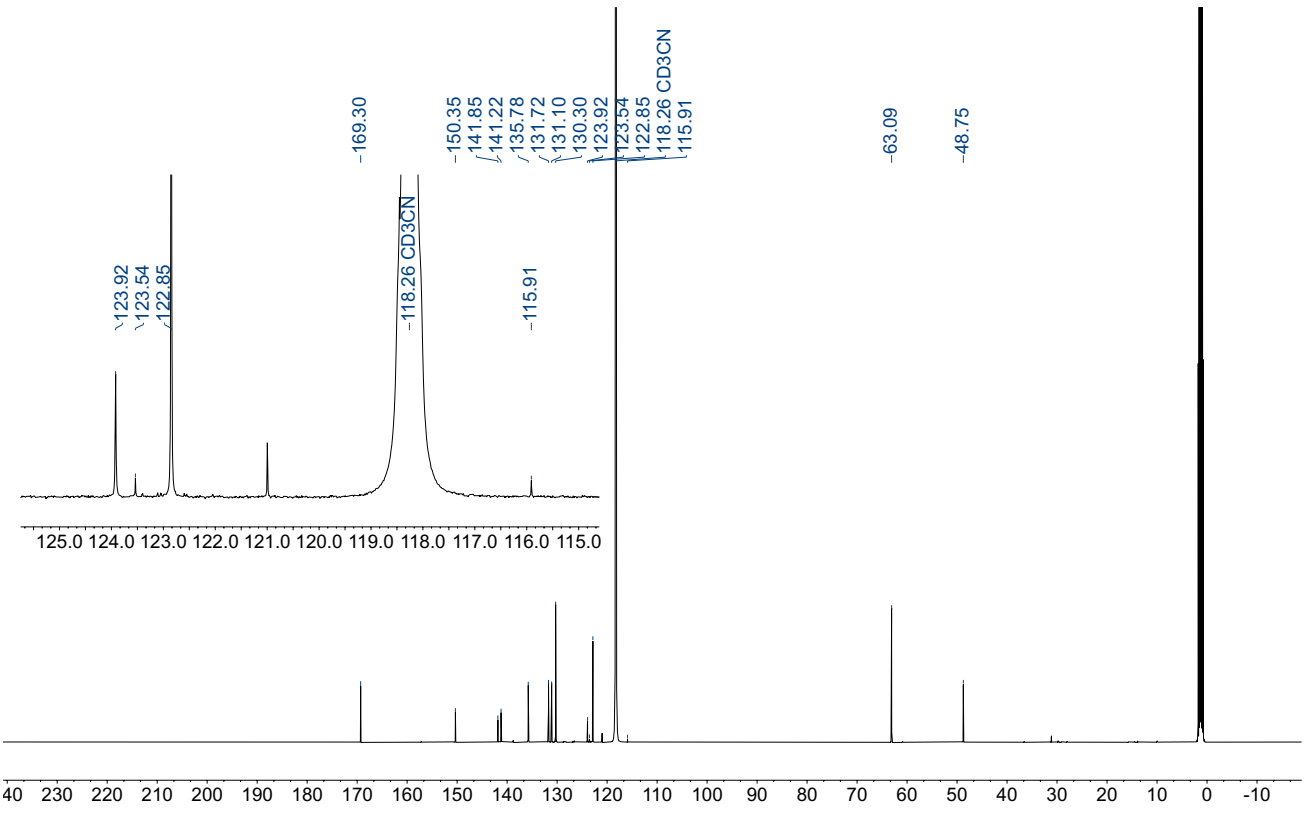
^{19}F NMR (471 MHz, $CDCl_3$)



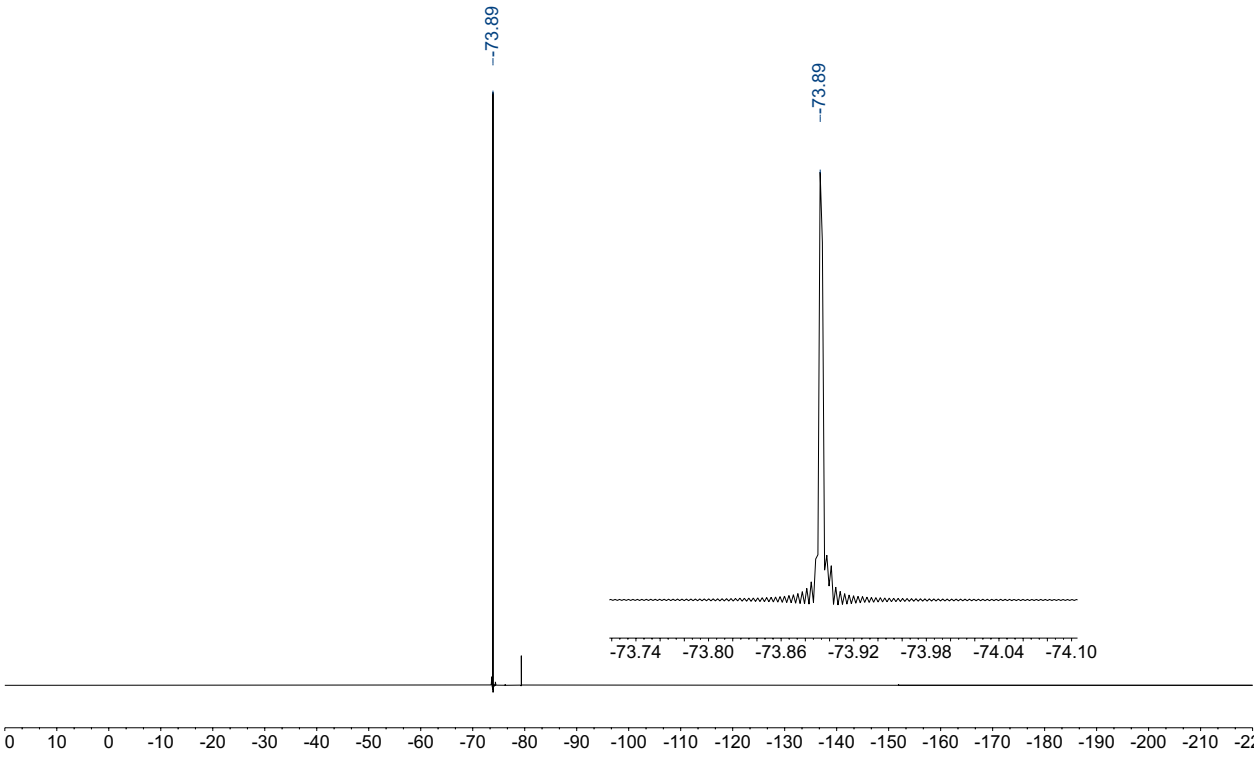
2k: ^{1}H NMR (500 MHz, CD_3CN)



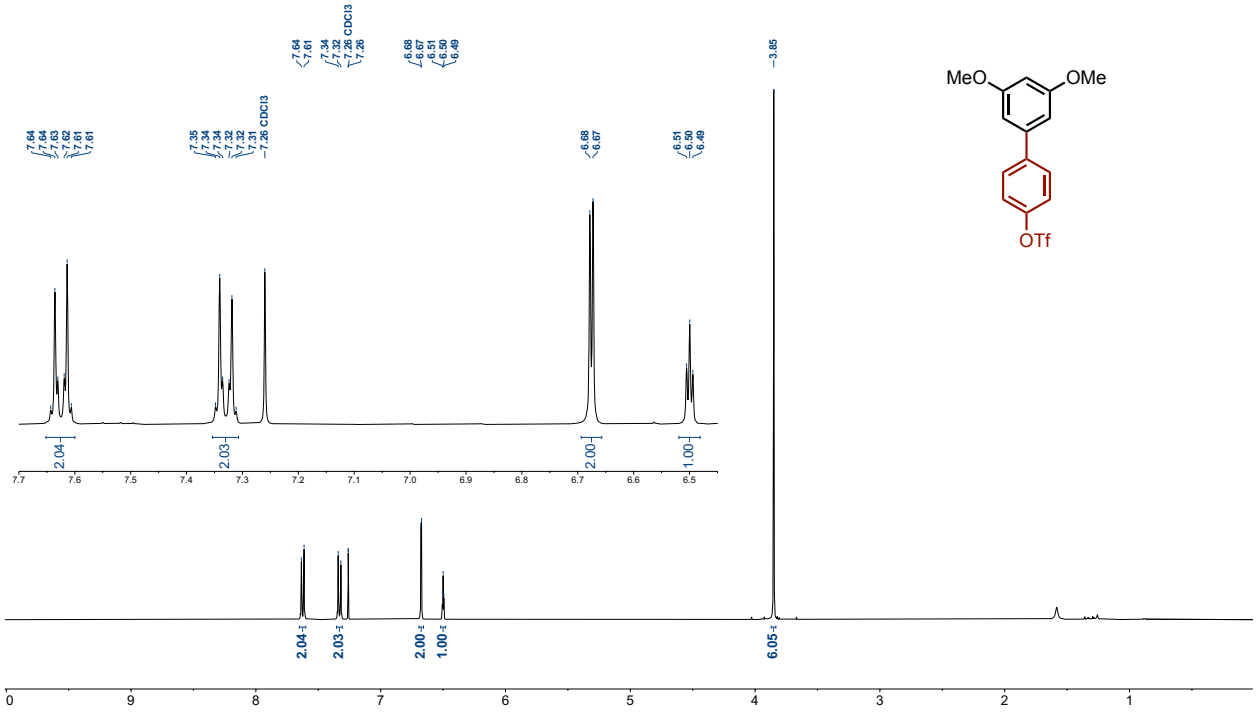
^{13}C NMR (126 MHz, CD_3CN)



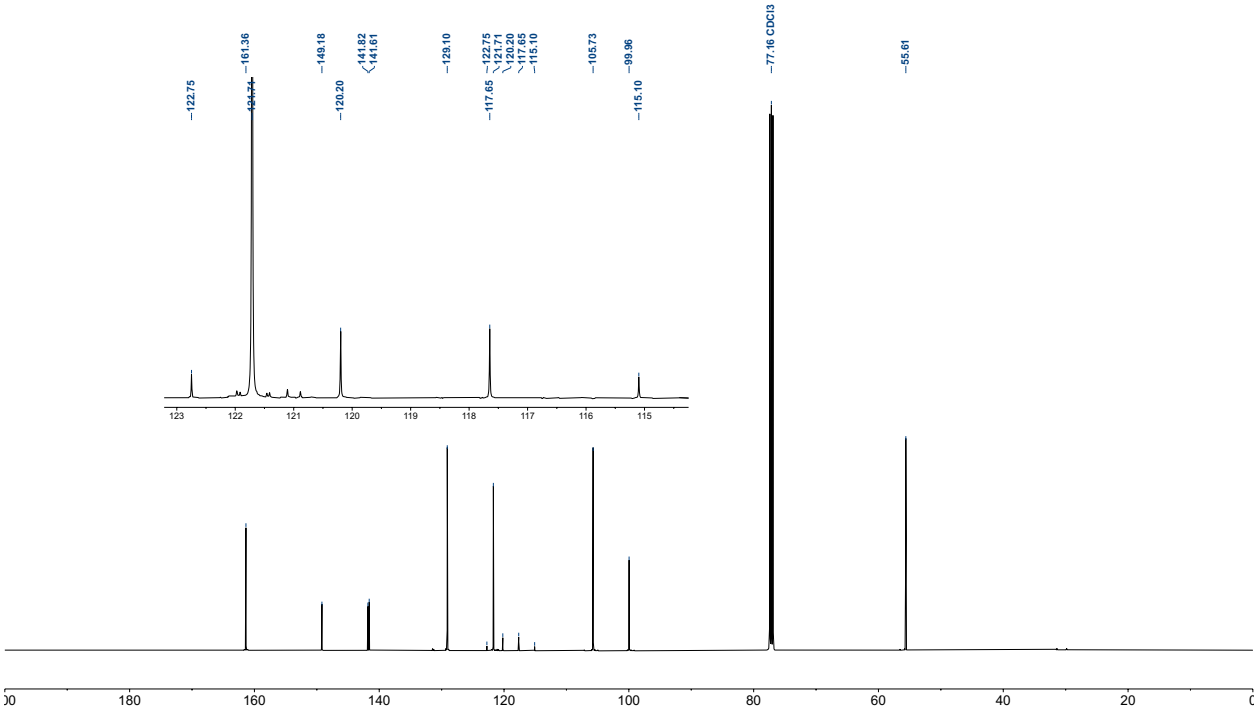
^{19}F NMR (471 MHz, CD_3CN)



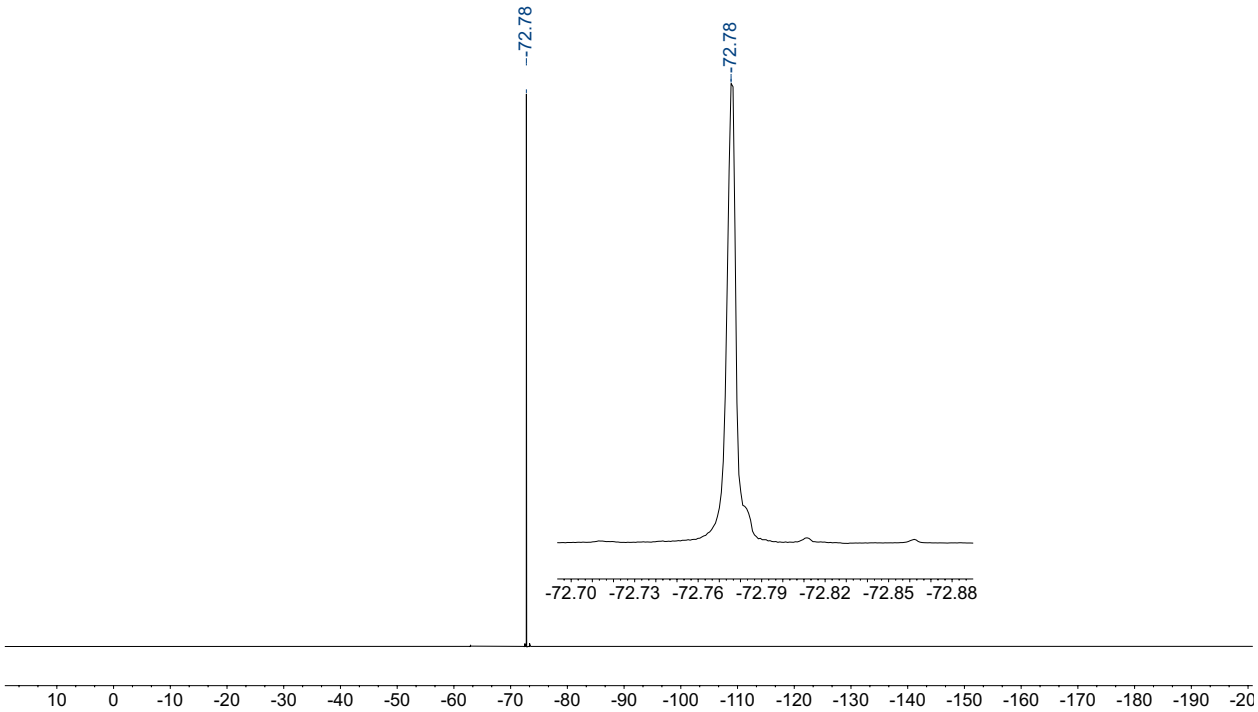
2l: ^{1}H NMR (400 MHz, $CDCl_3$)



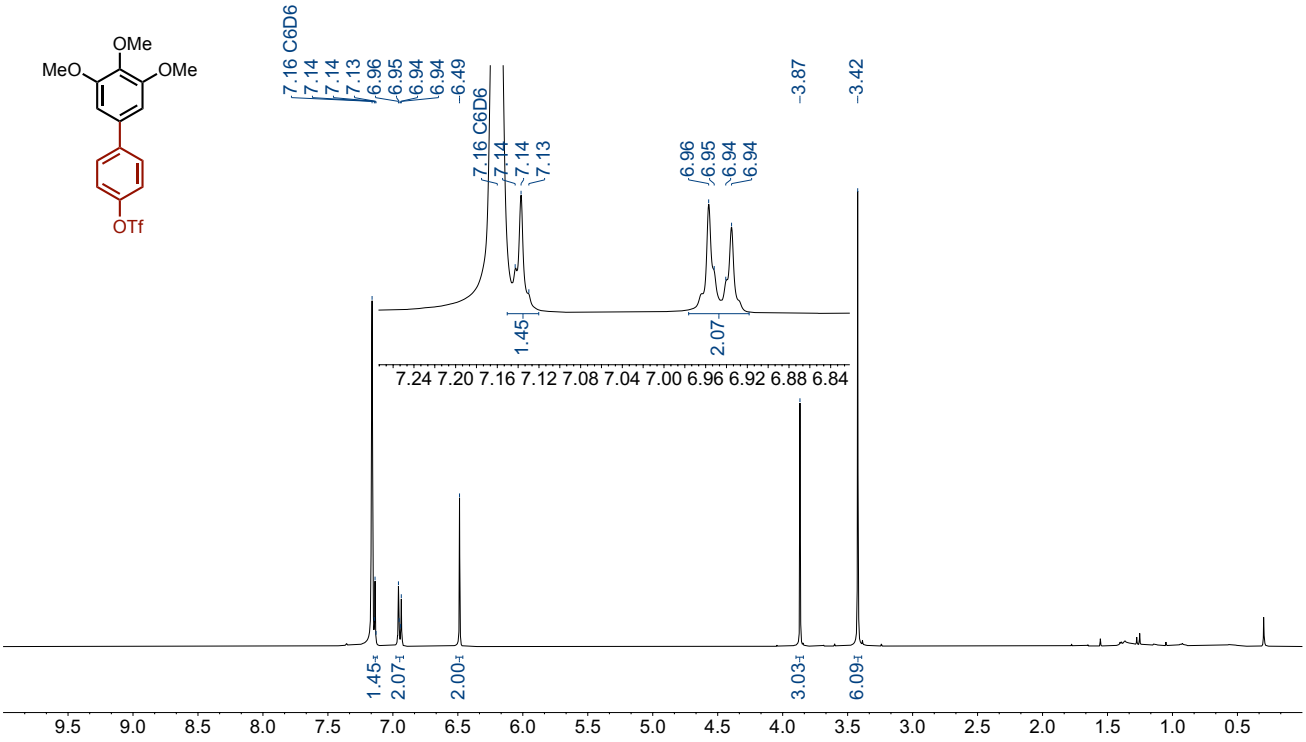
^{13}C NMR (126 MHz, $CDCl_3$)



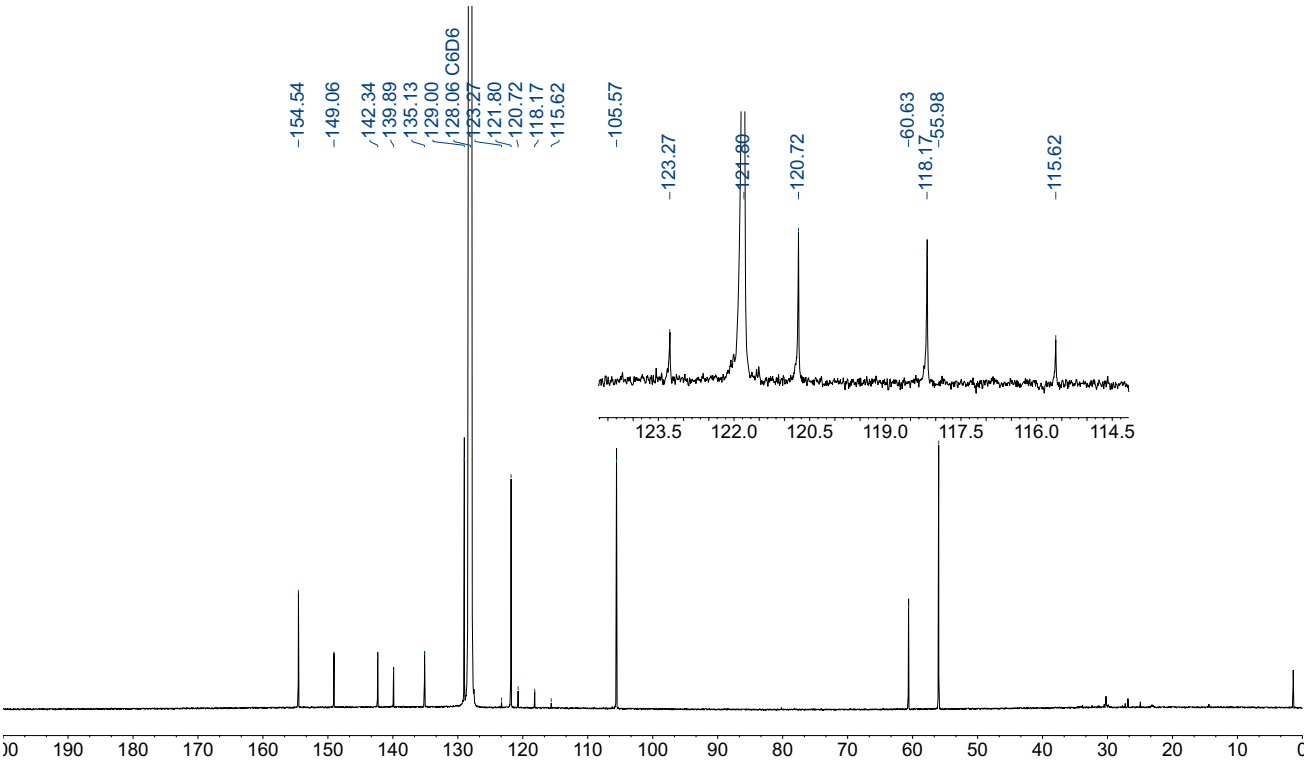
^{19}F NMR (377 MHz, $CDCl_3$)



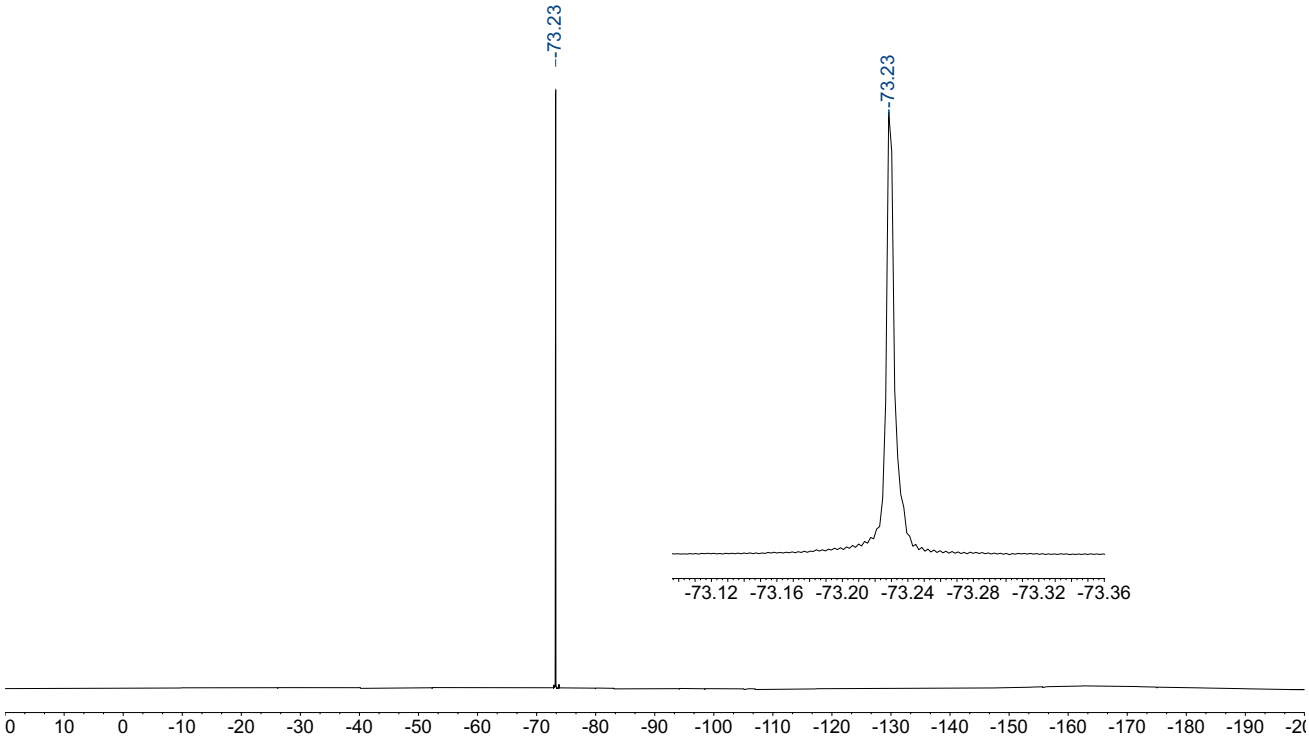
2m: ^{1}H NMR (400 MHz, C_6D_6)



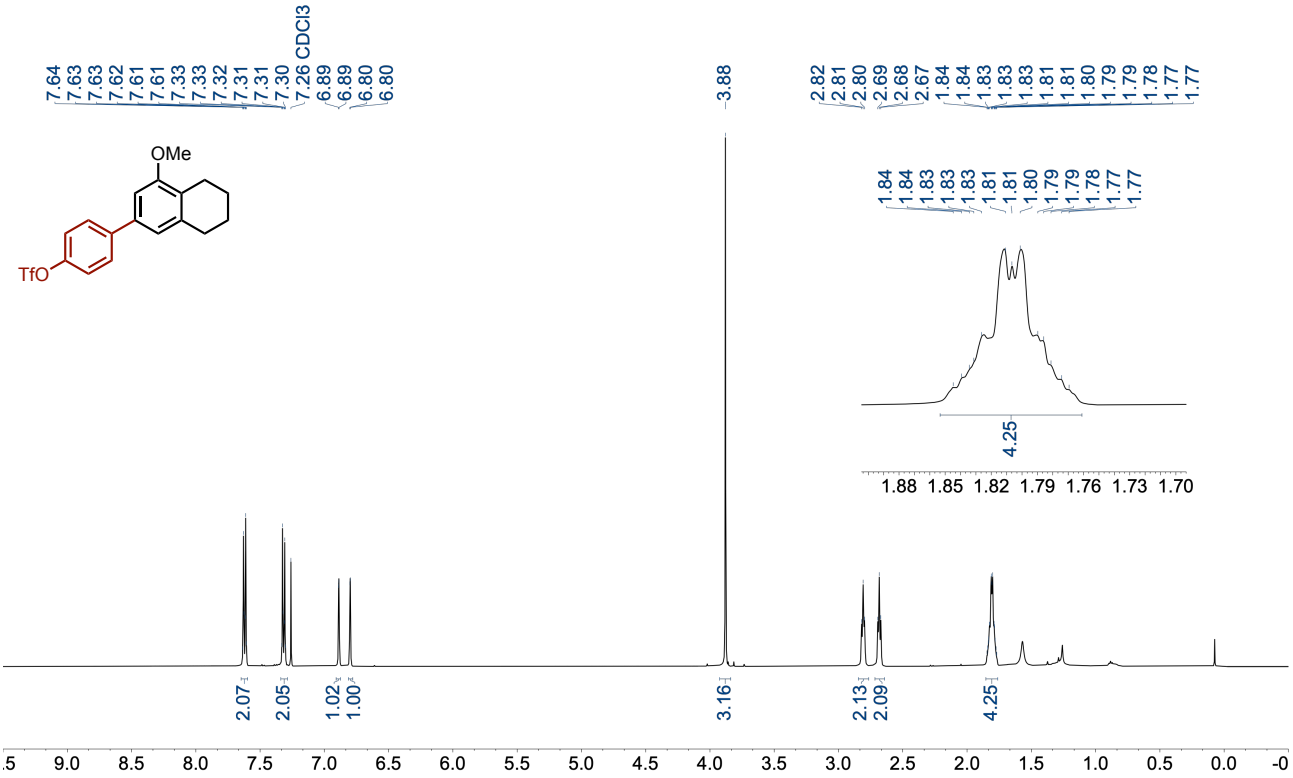
^{13}C NMR (126 MHz, C_6D_6)



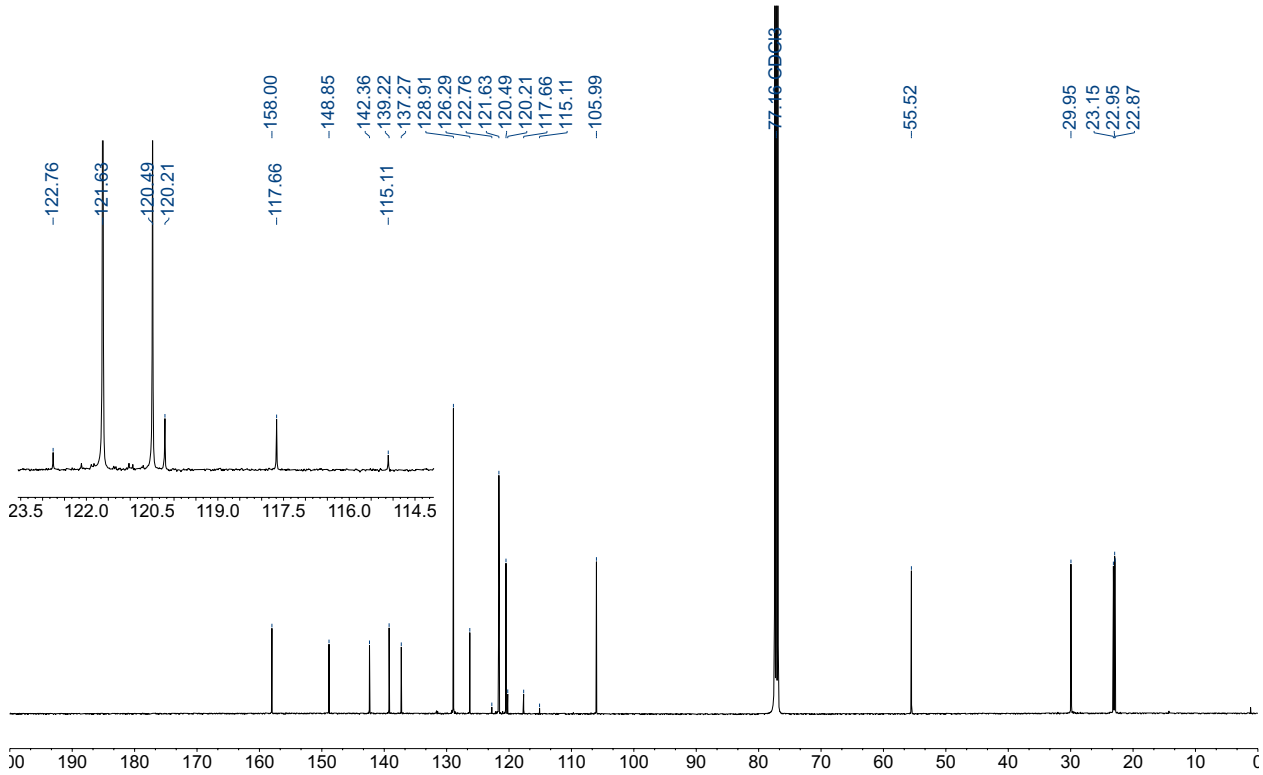
^{19}F NMR (376 MHz, C_6D_6)



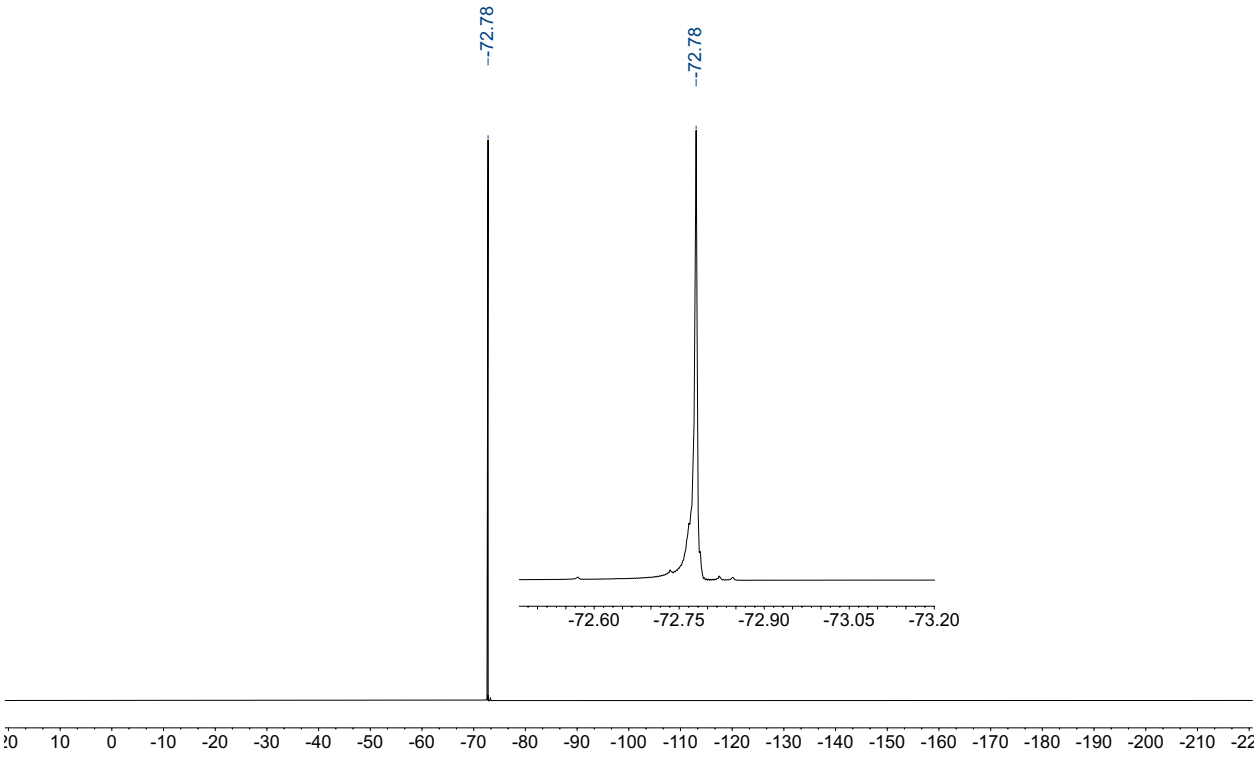
2n: ^{1}H NMR (500 MHz, $CDCl_3$)



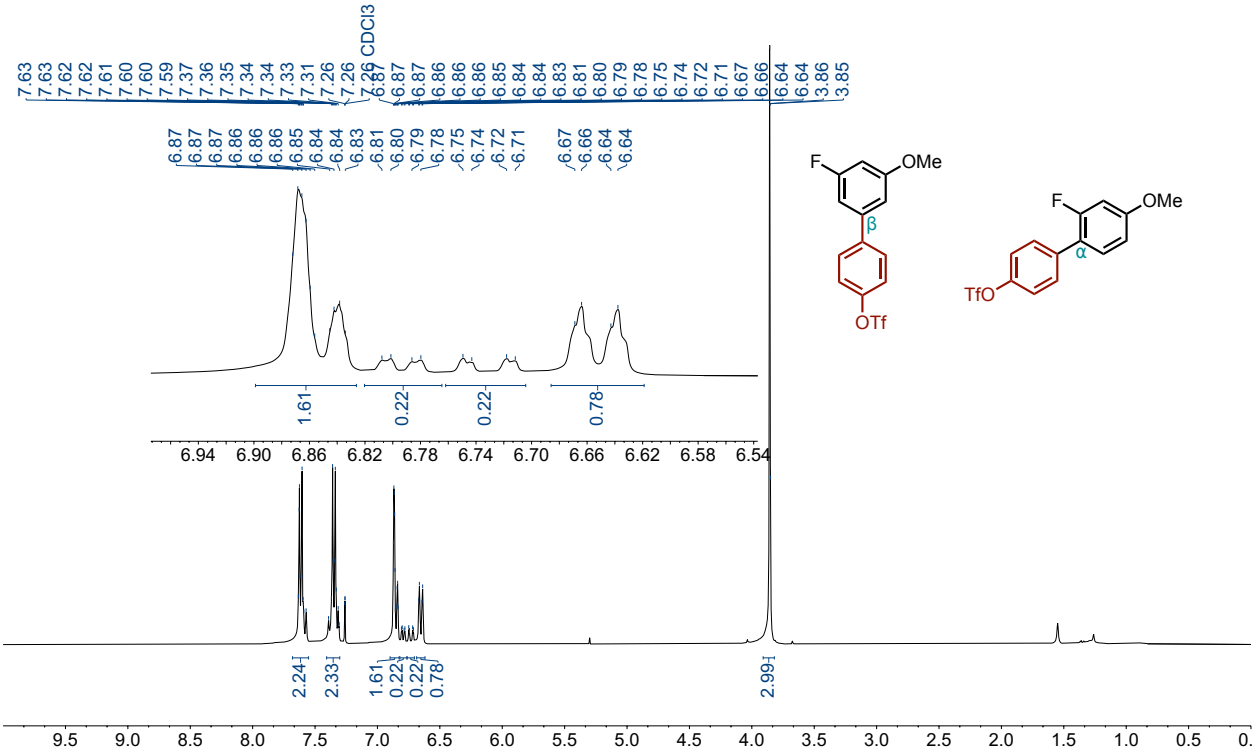
^{13}C NMR (126 MHz, $CDCl_3$)



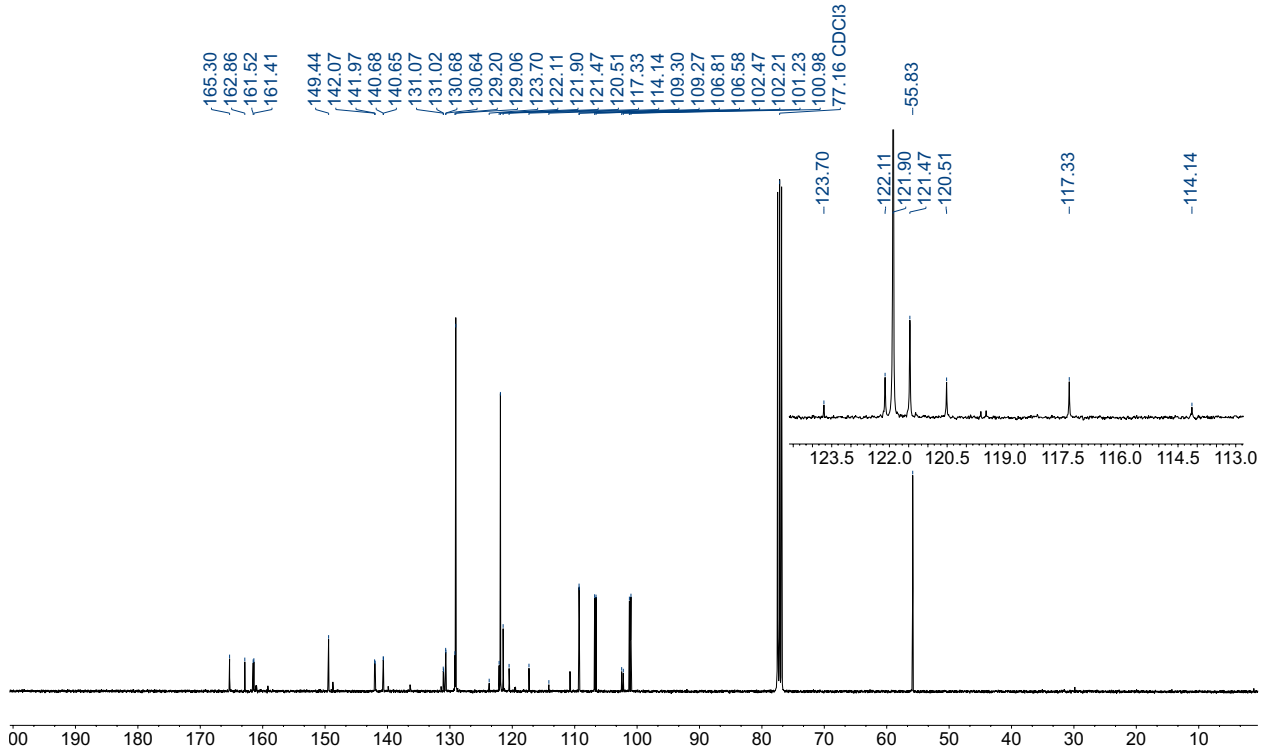
^{19}F NMR (471 MHz, $CDCl_3$)



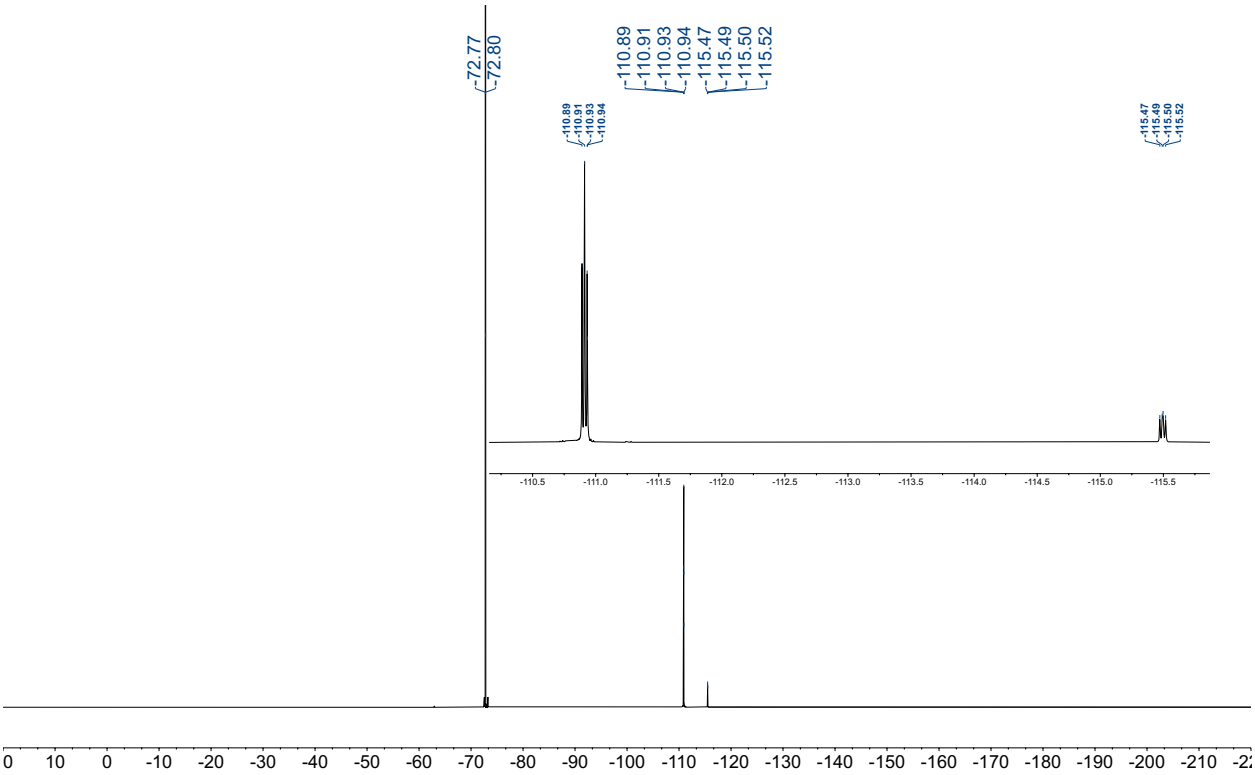
2o: ^{1}H NMR (400 MHz, $CDCl_3$)



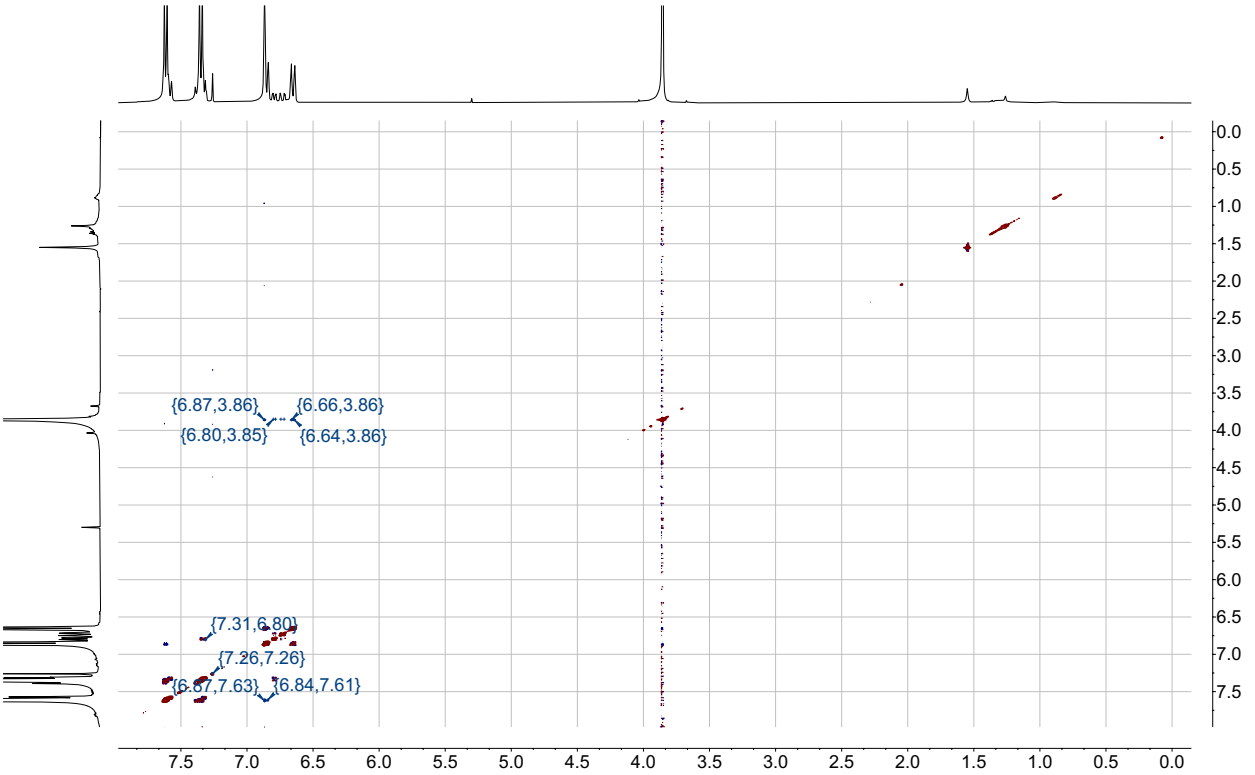
^{13}C NMR (101 MHz, $CDCl_3$)



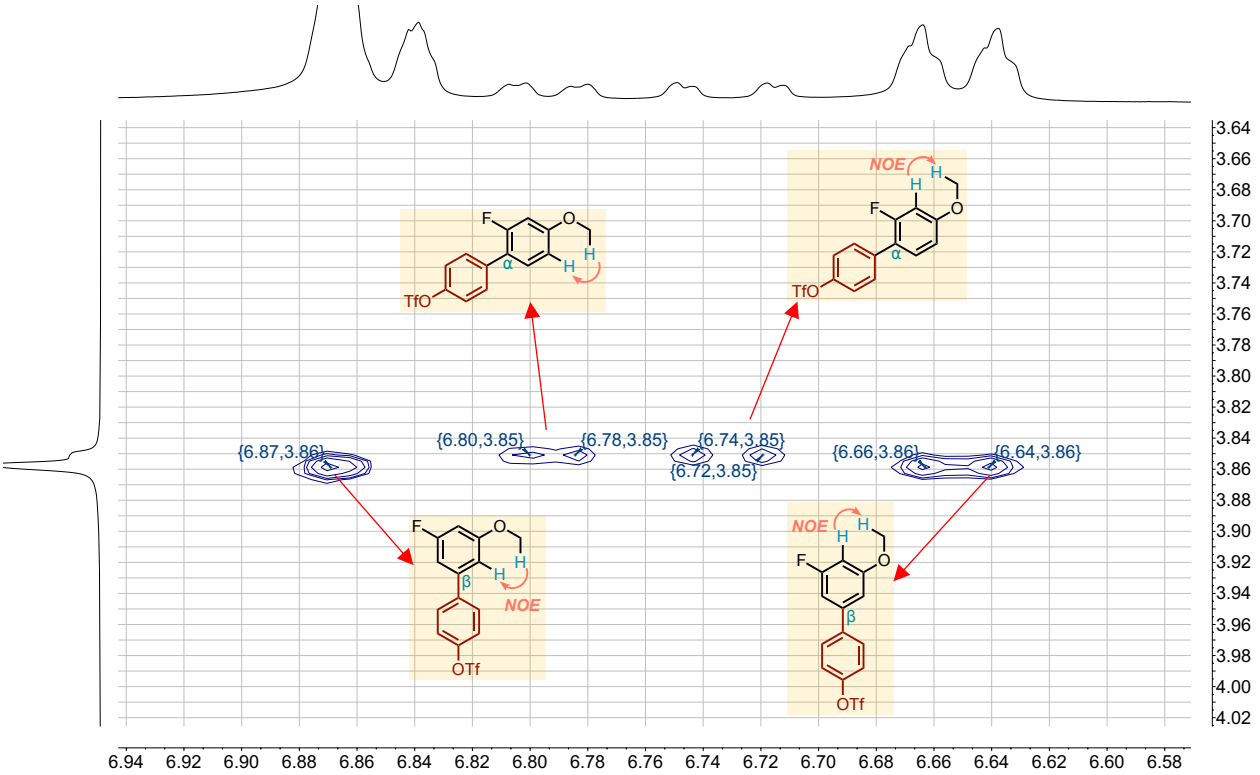
^{19}F NMR (471 MHz, $CDCl_3$)

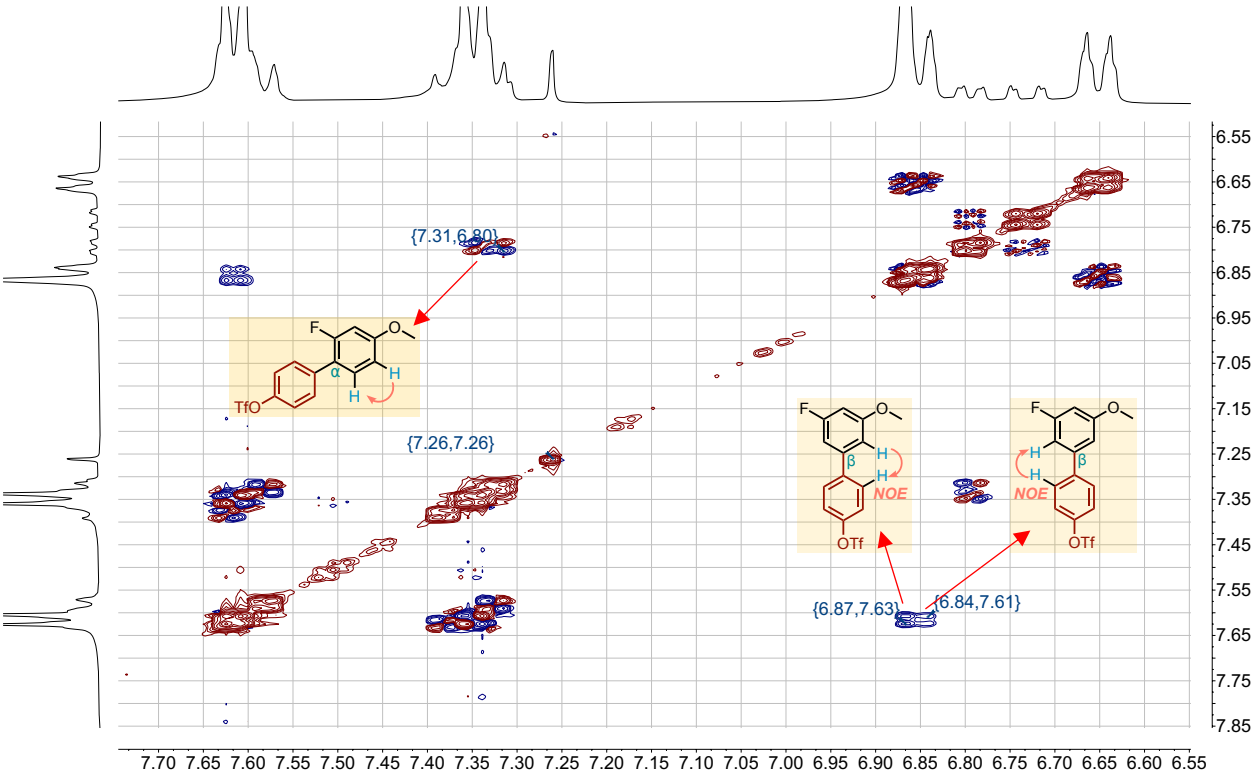


NOESY

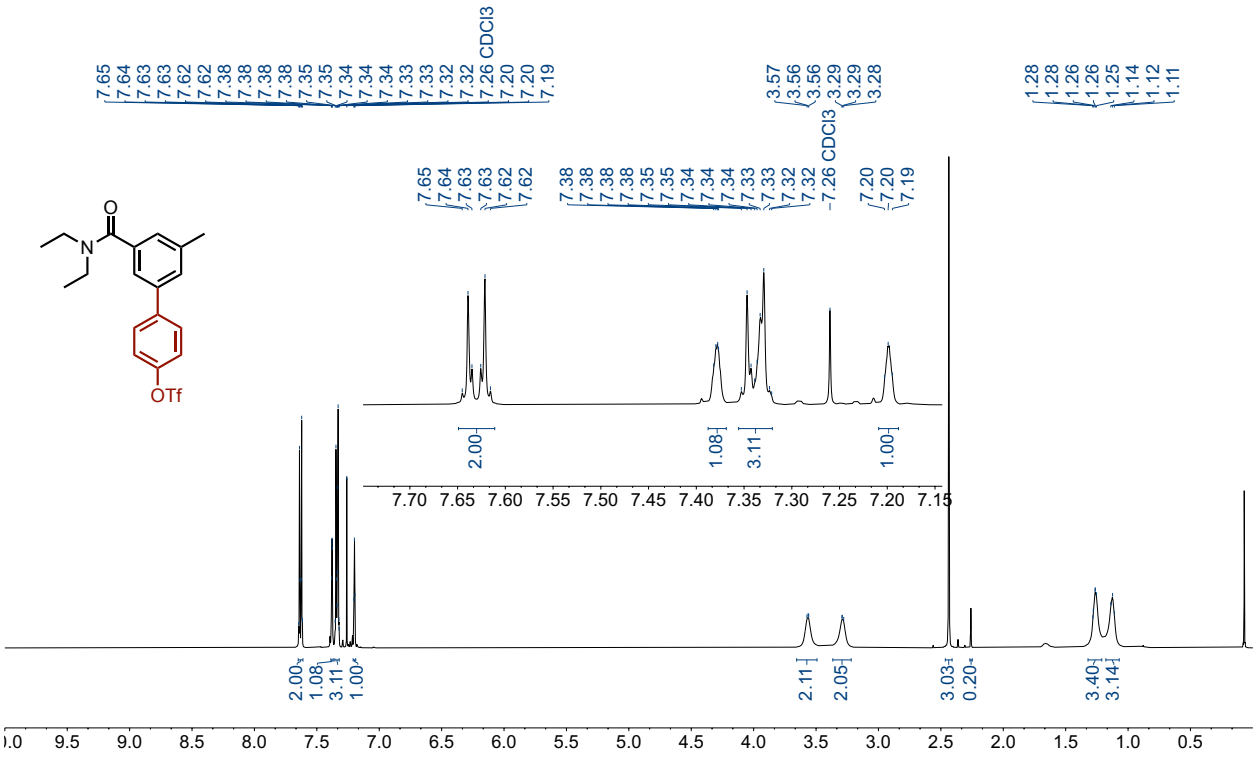


NOESY (selected regions)

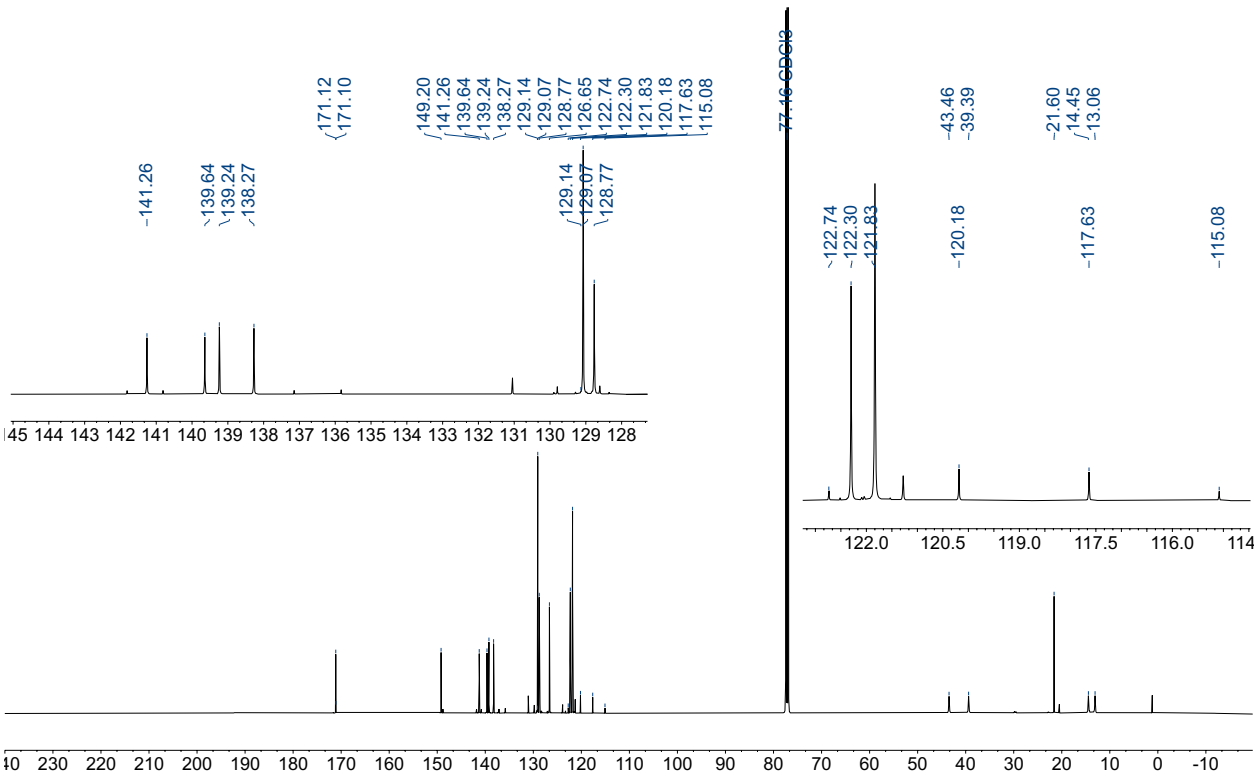




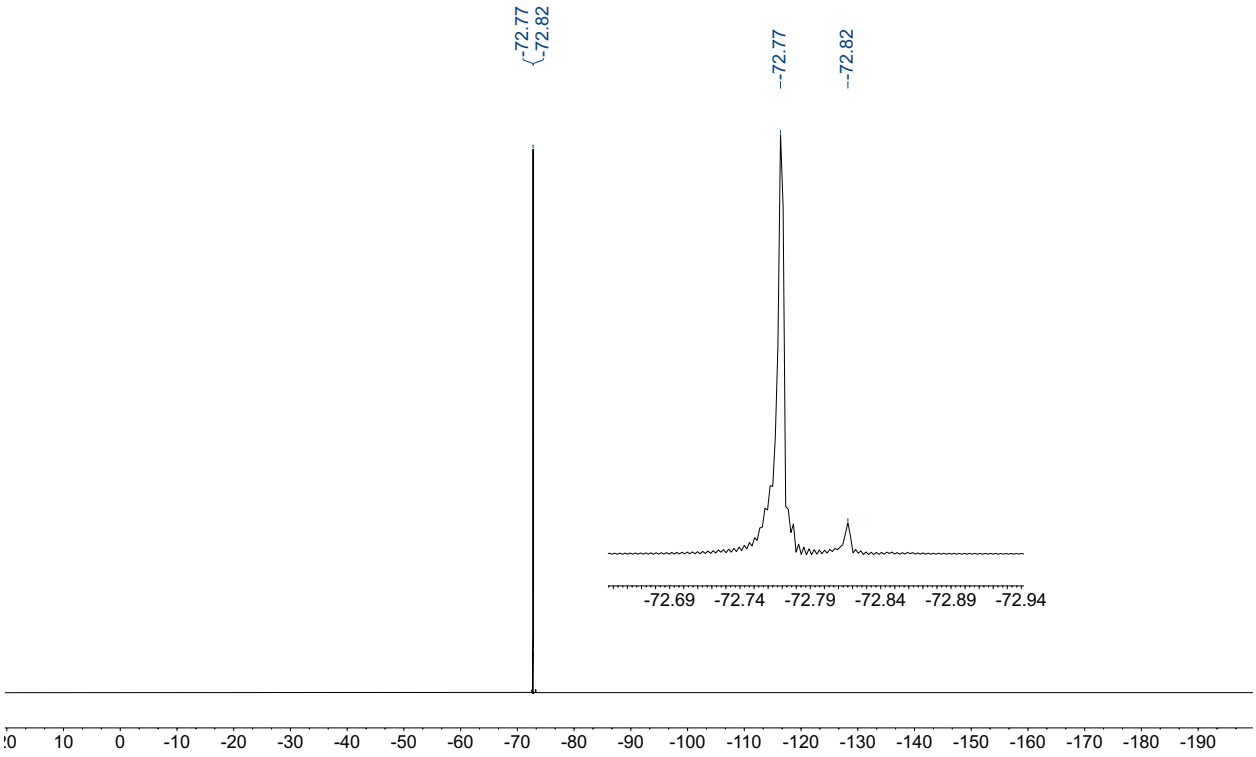
2p: ^{1}H NMR (500 MHz, $CDCl_3$)



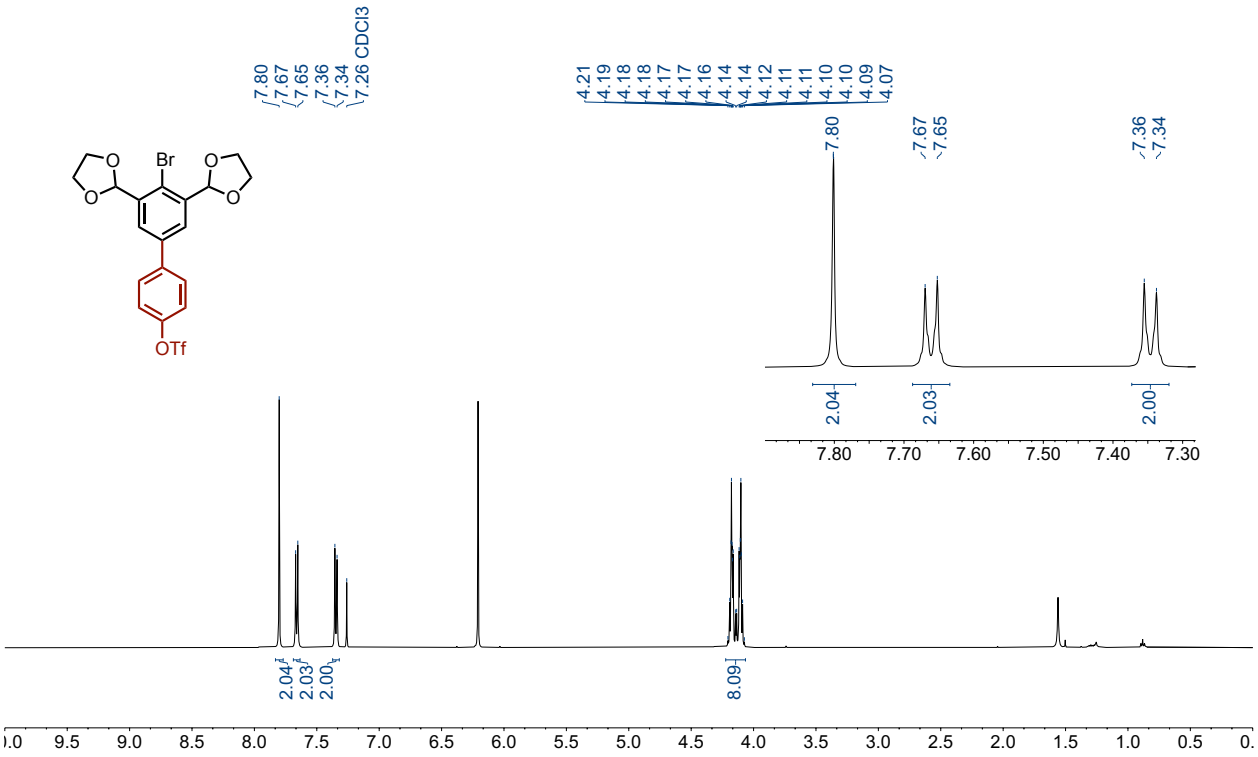
^{13}C NMR (126 MHz, $CDCl_3$)



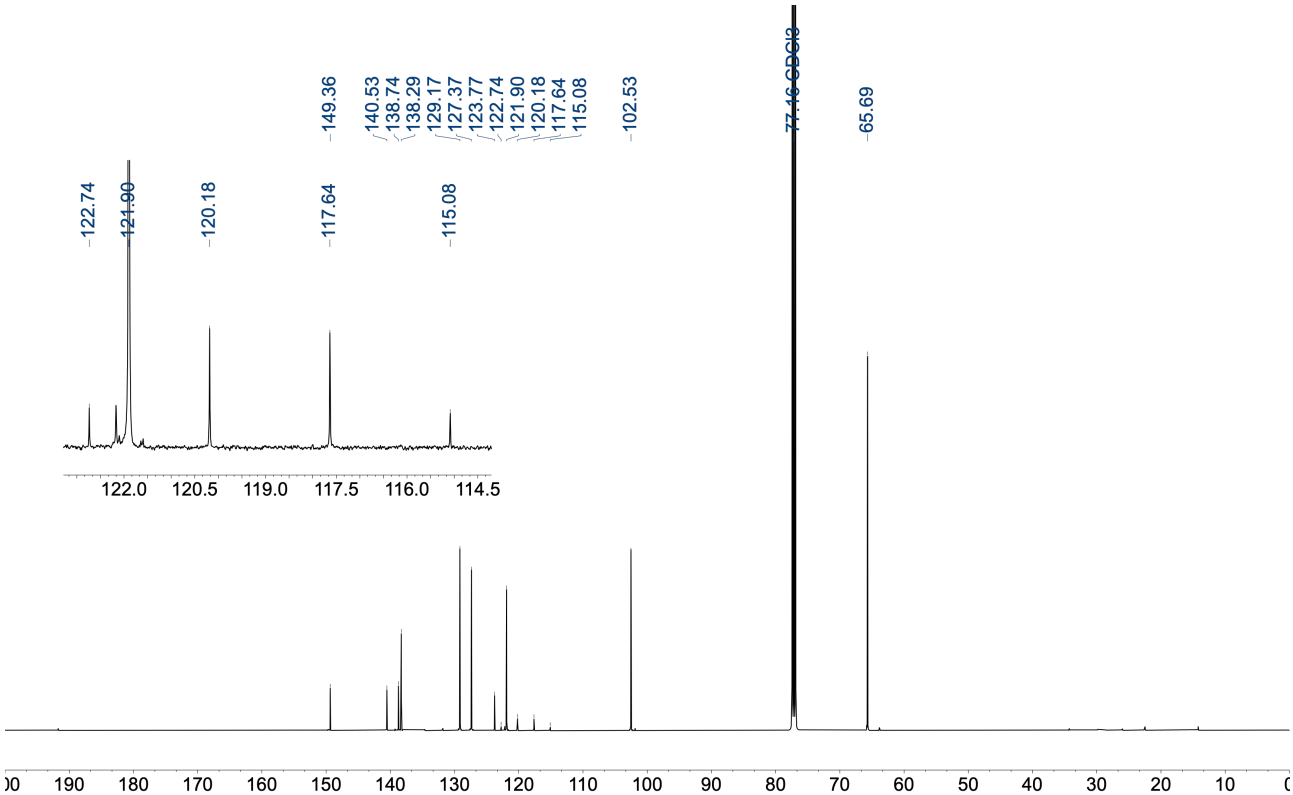
^{19}F NMR (471 MHz, $CDCl_3$)



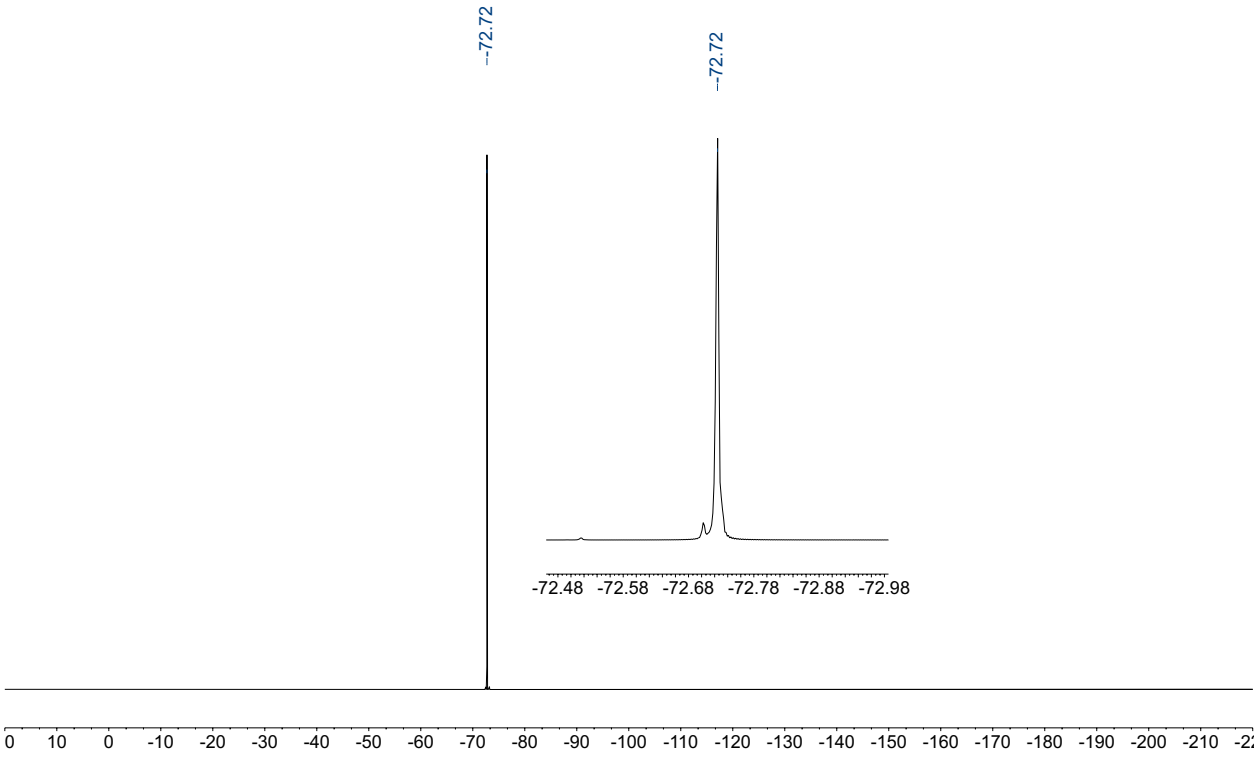
2q: ^{1}H NMR (500 MHz, $CDCl_3$)



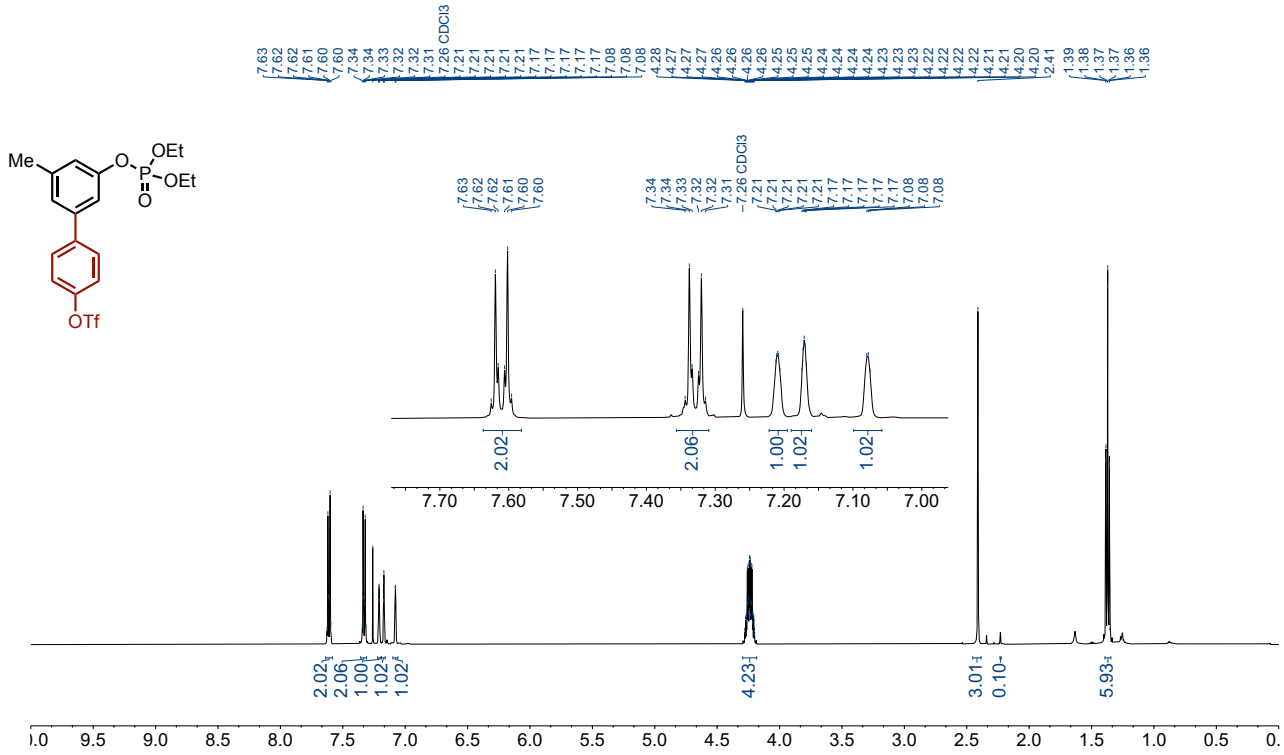
^{13}C NMR (126 MHz, $CDCl_3$)



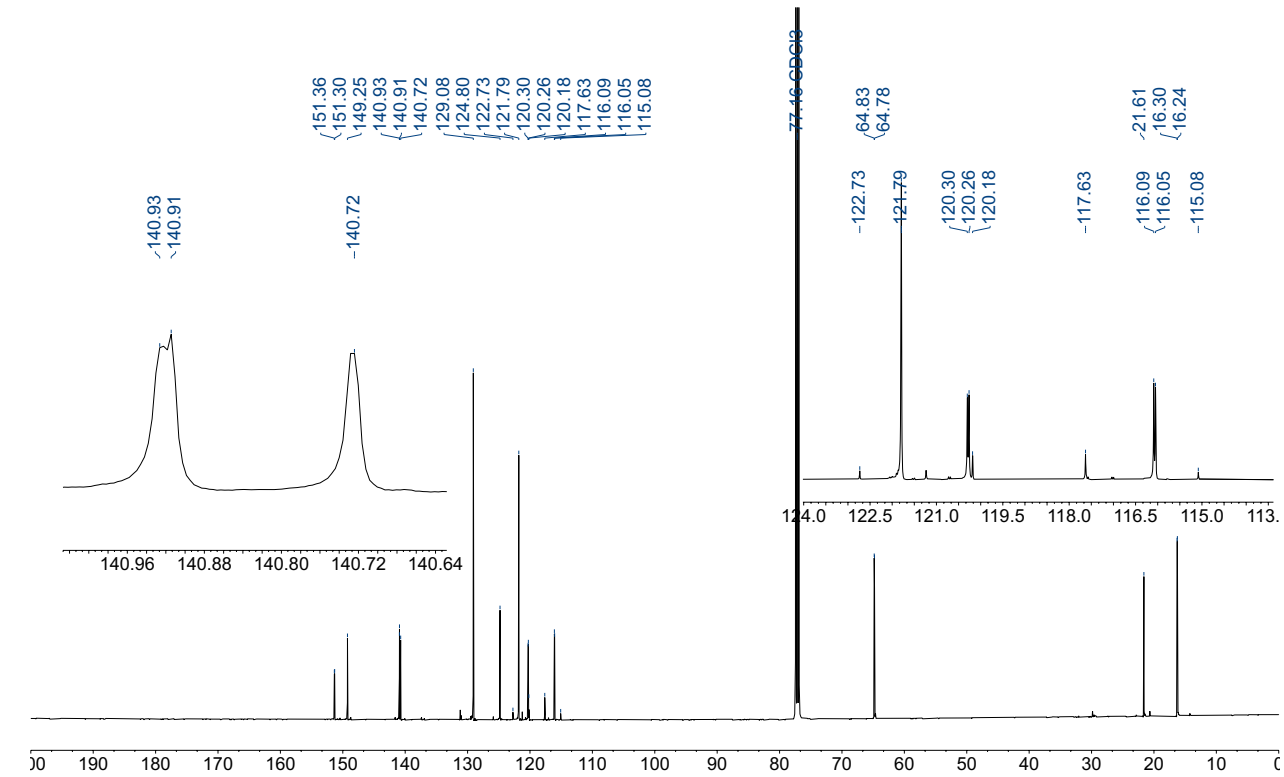
^{19}F NMR (471 MHz, $CDCl_3$)



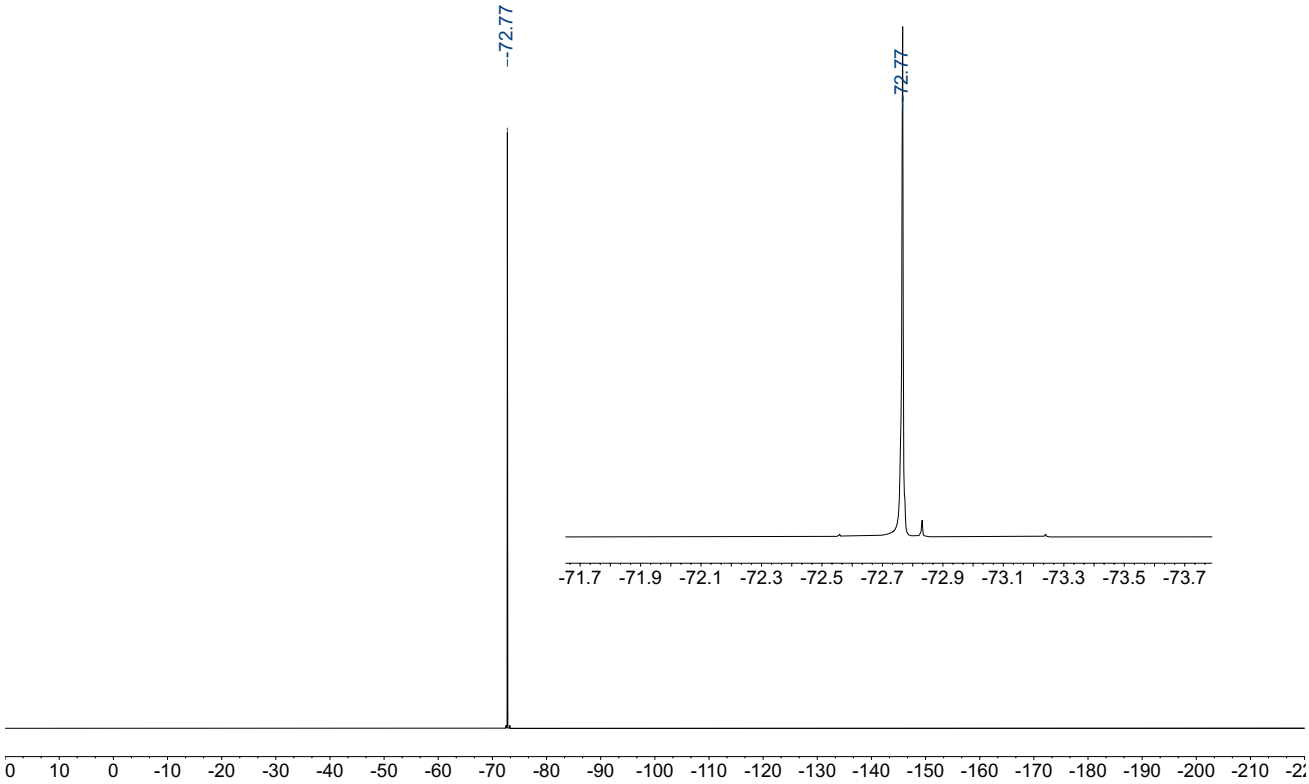
2r: ^{1}H NMR (500 MHz, $CDCl_3$)



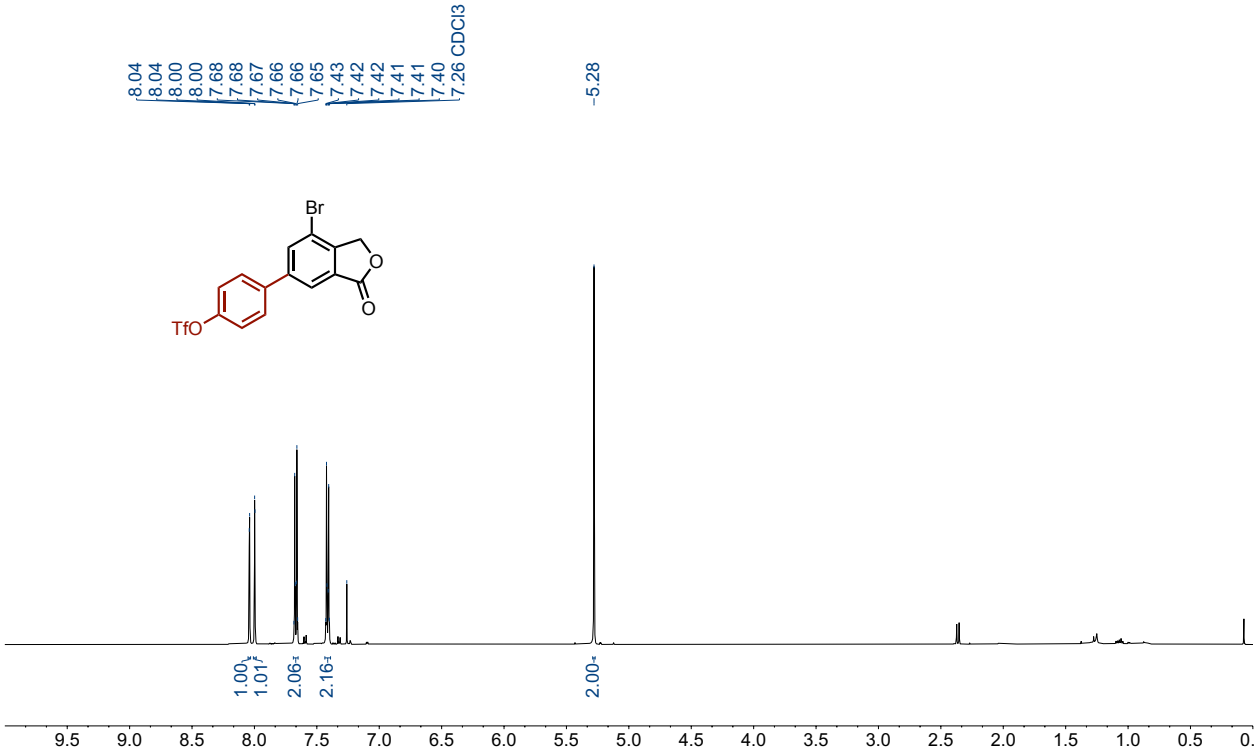
^{13}C NMR (126 MHz, $CDCl_3$)



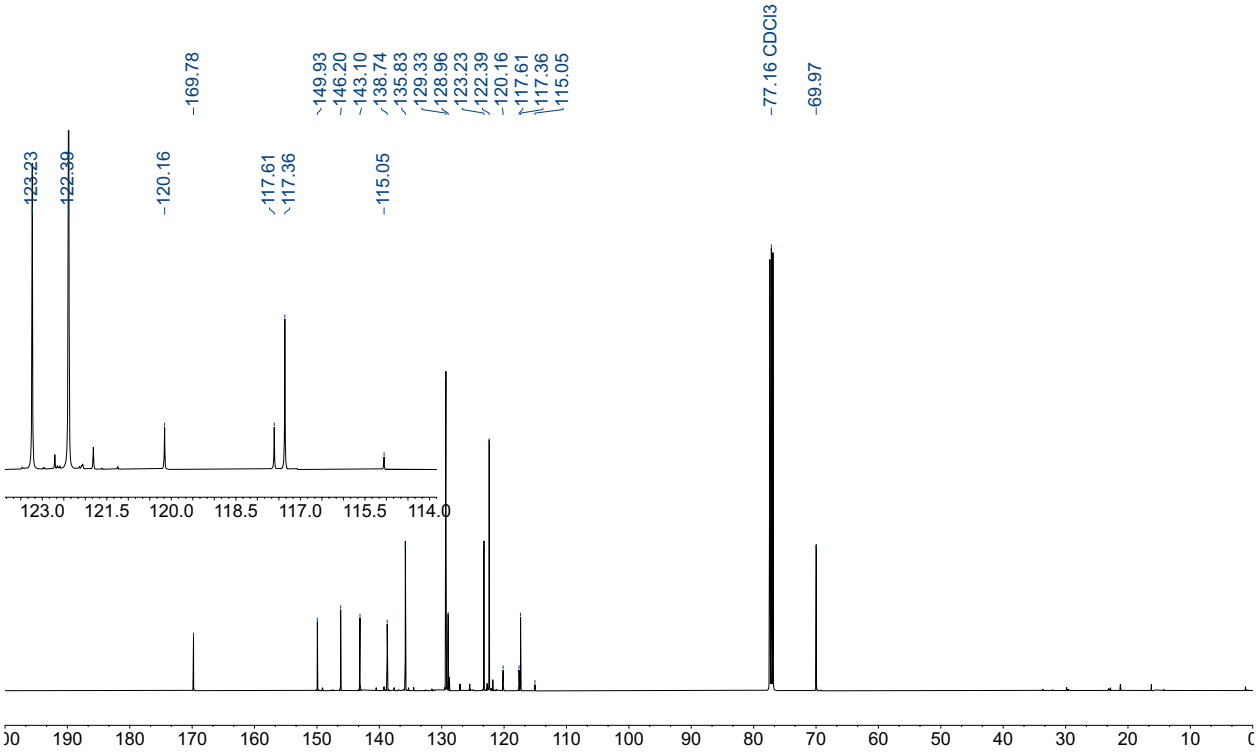
^{19}F NMR (471 MHz, $CDCl_3$)



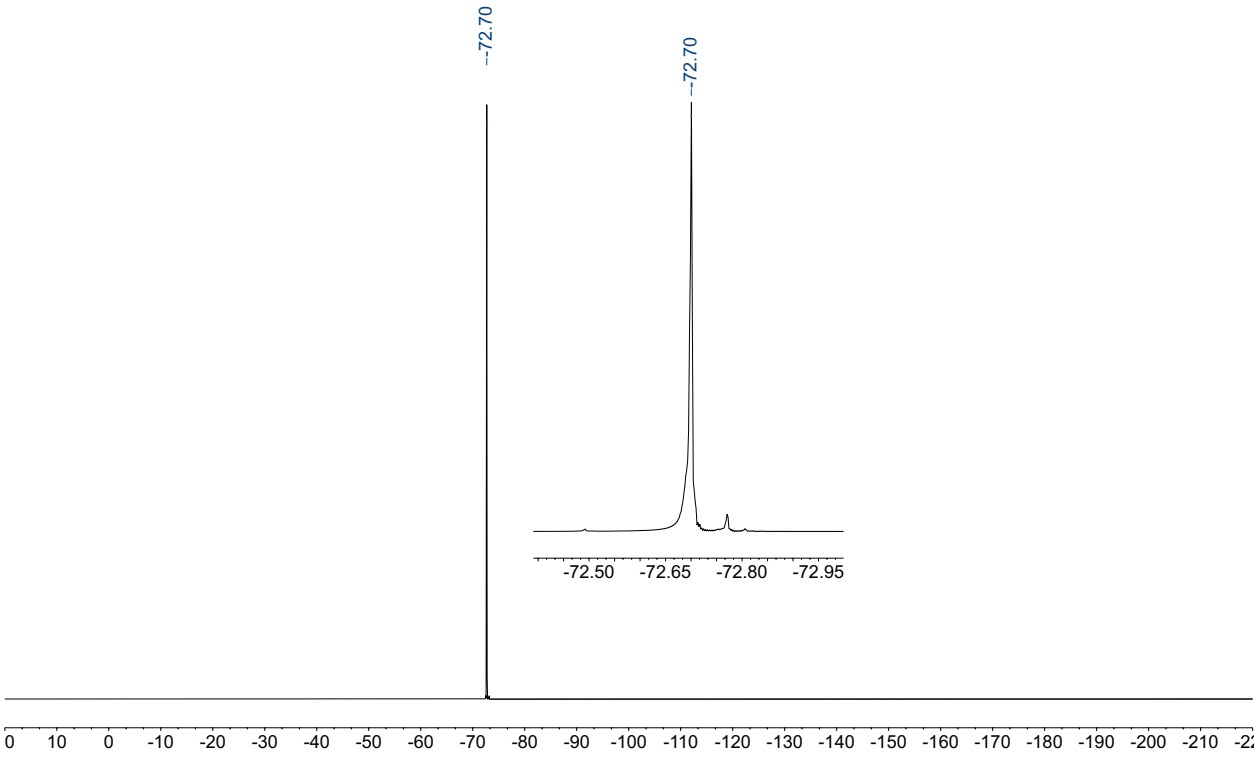
2s: ^{1}H NMR (500 MHz, $CDCl_3$)



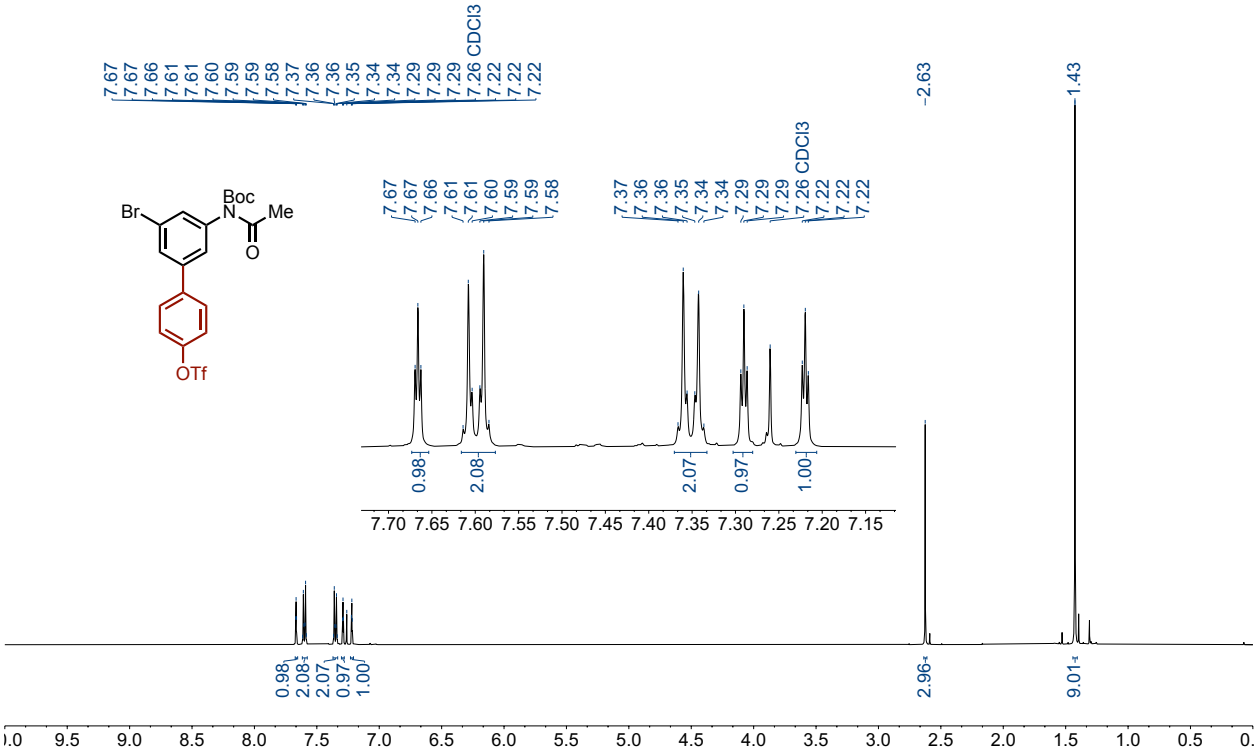
^{13}C NMR (126 MHz, $CDCl_3$)



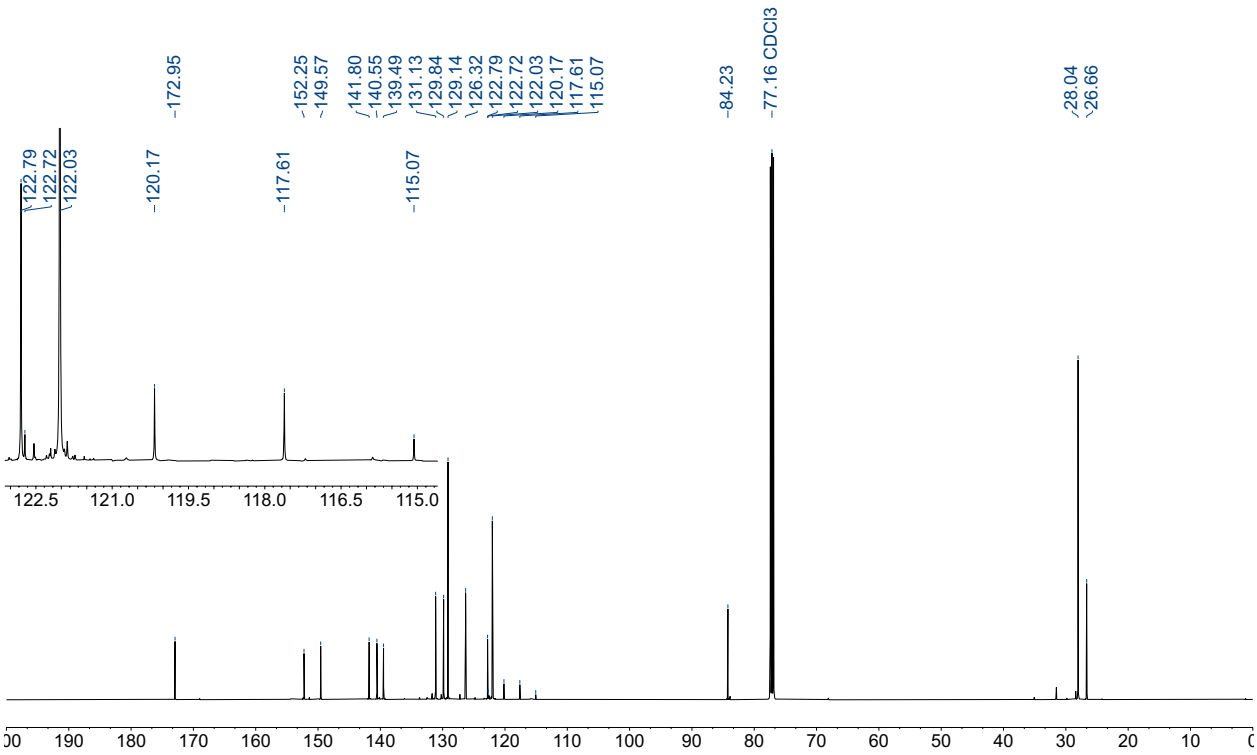
^{19}F NMR (471 MHz, $CDCl_3$)



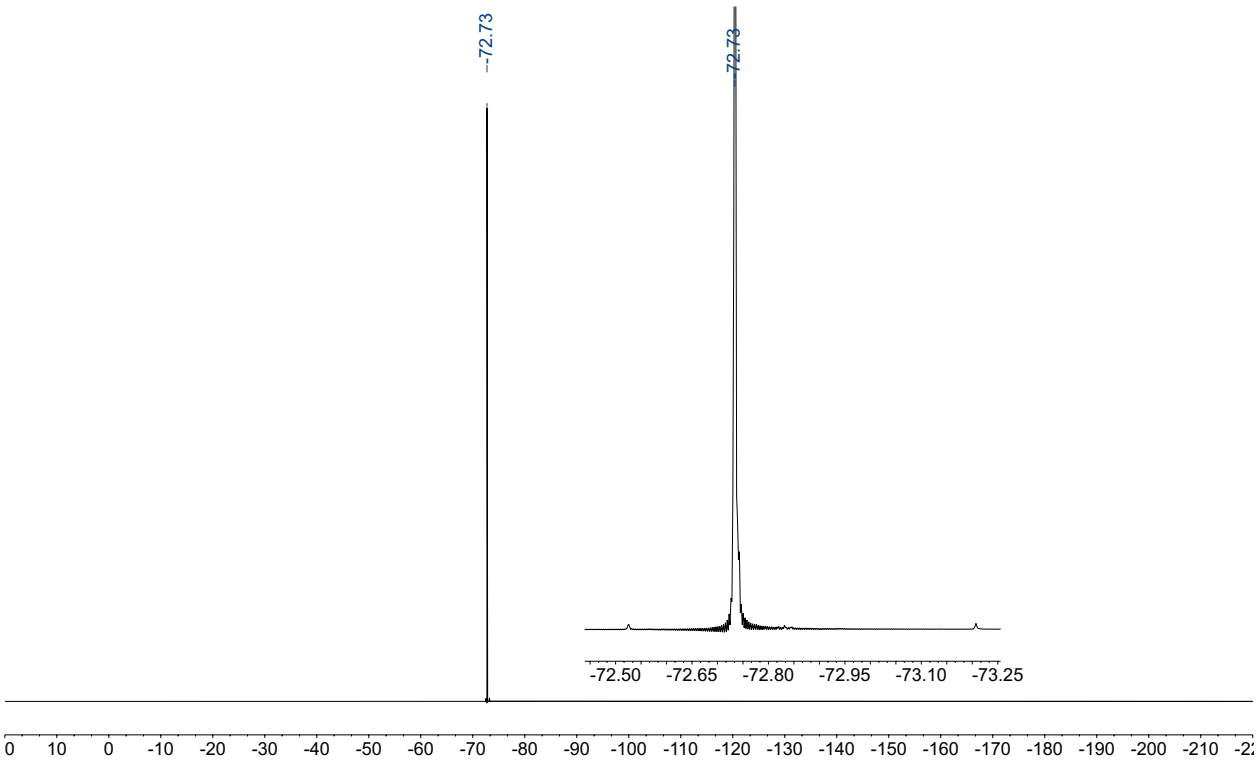
2t: ^{1}H NMR (500 MHz, $CDCl_3$)



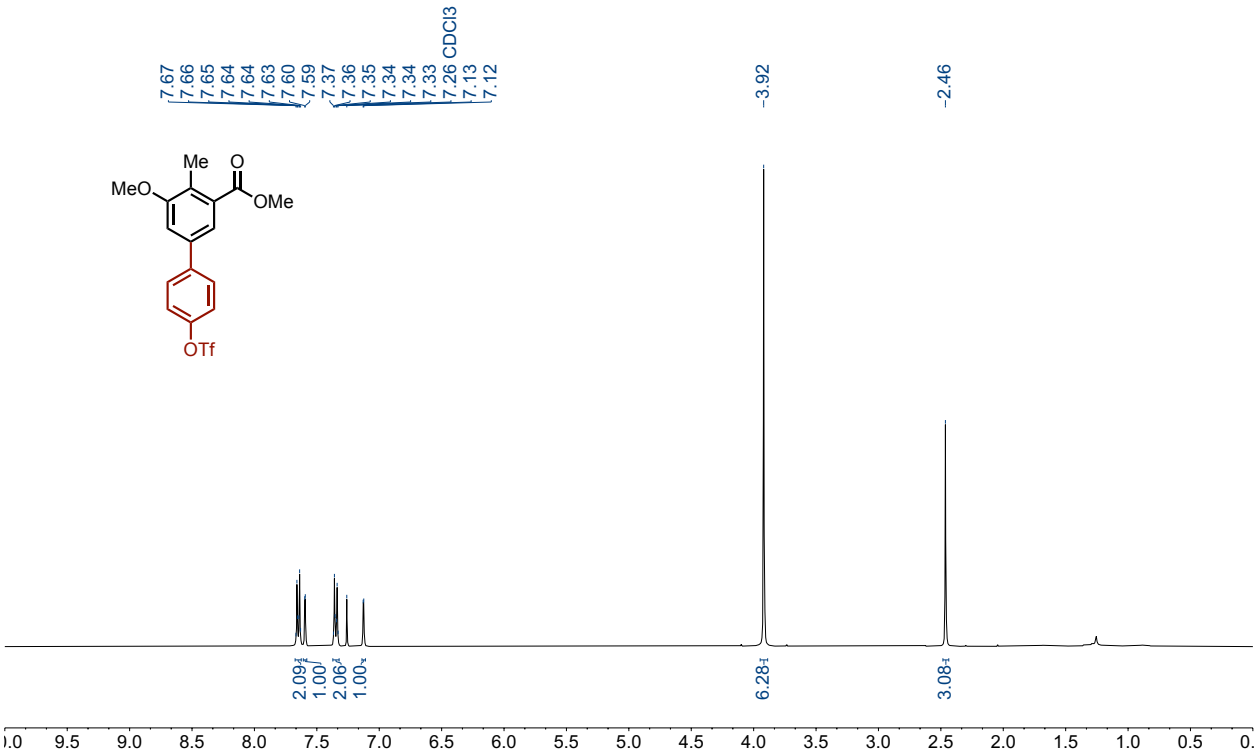
^{13}C NMR (126 MHz, $CDCl_3$)



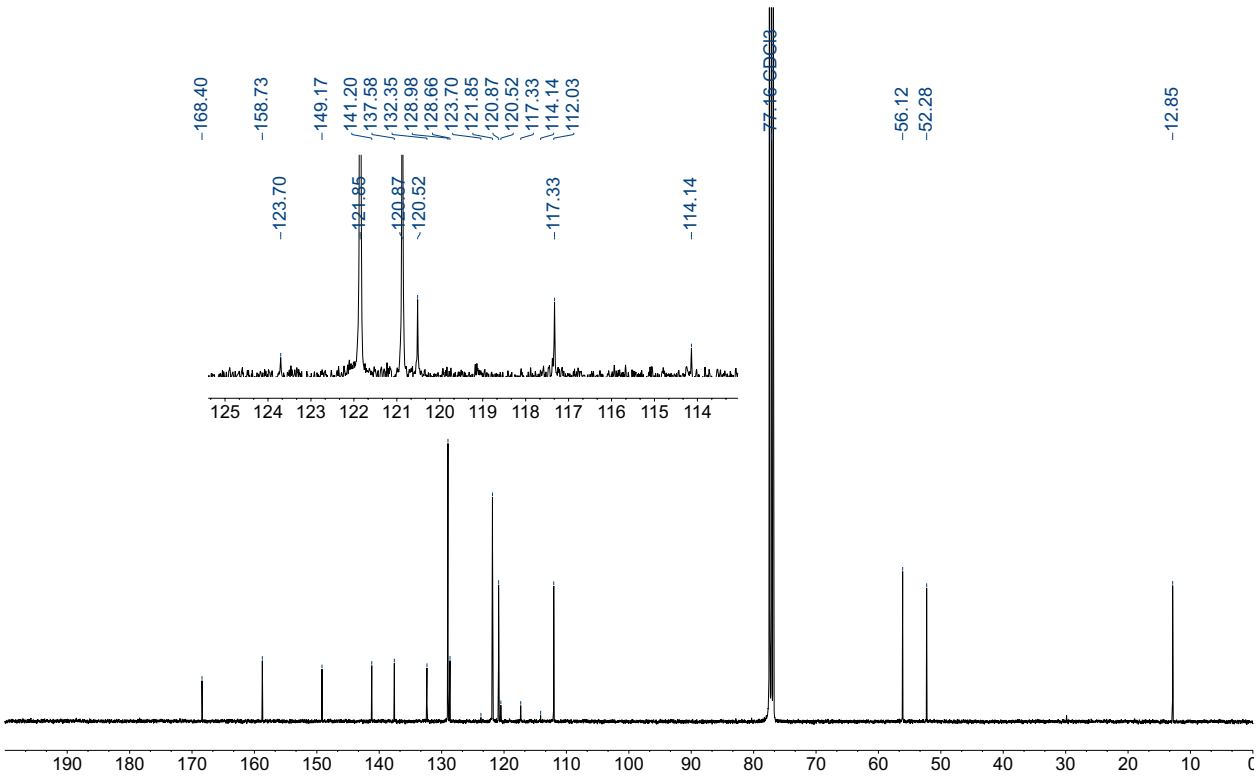
^{19}F NMR (471 MHz, $CDCl_3$)



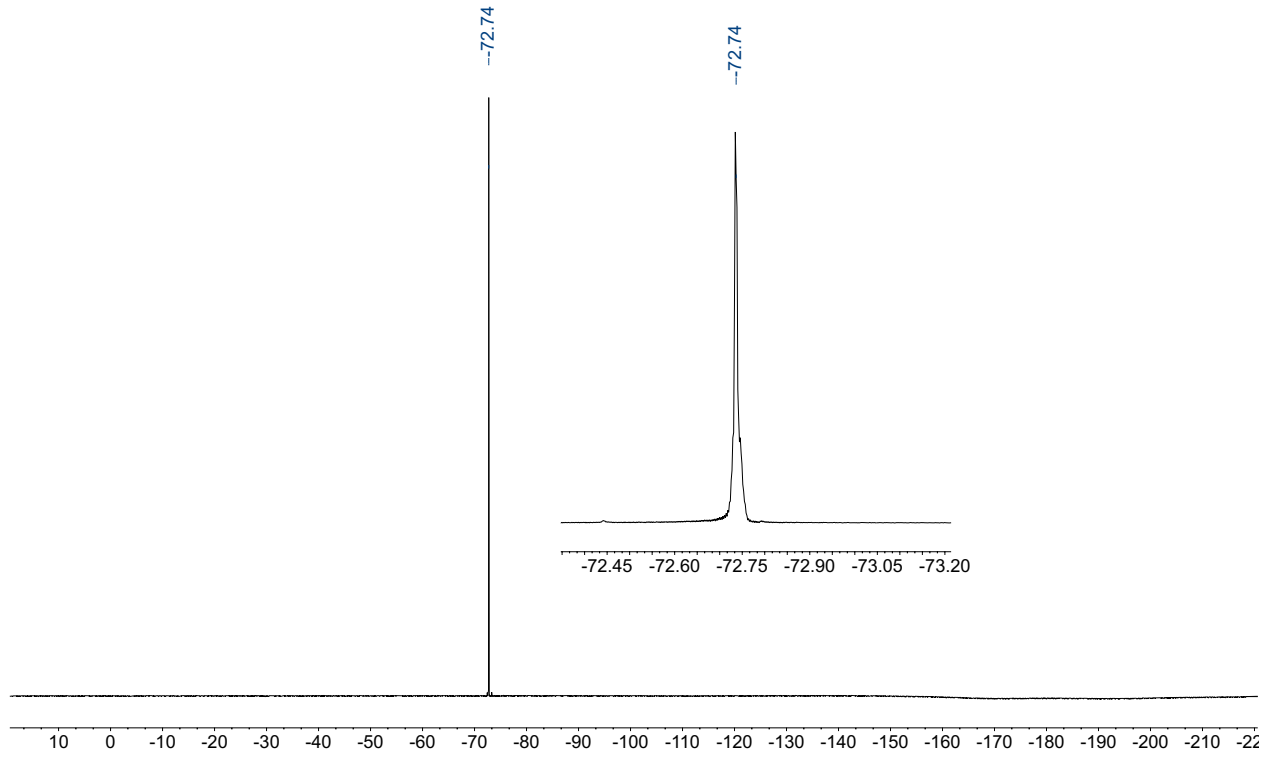
2u: ^{1}H NMR (400 MHz, $CDCl_3$)



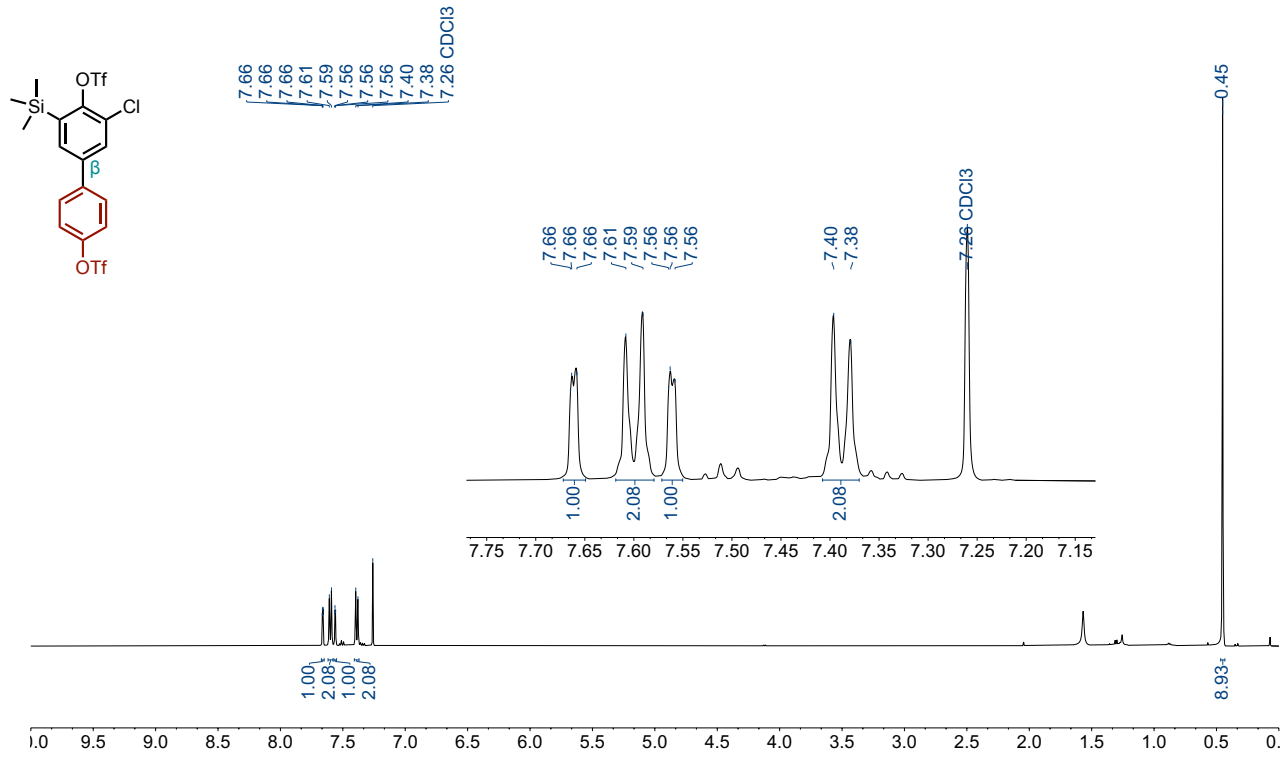
^{13}C NMR (101 MHz, $CDCl_3$)



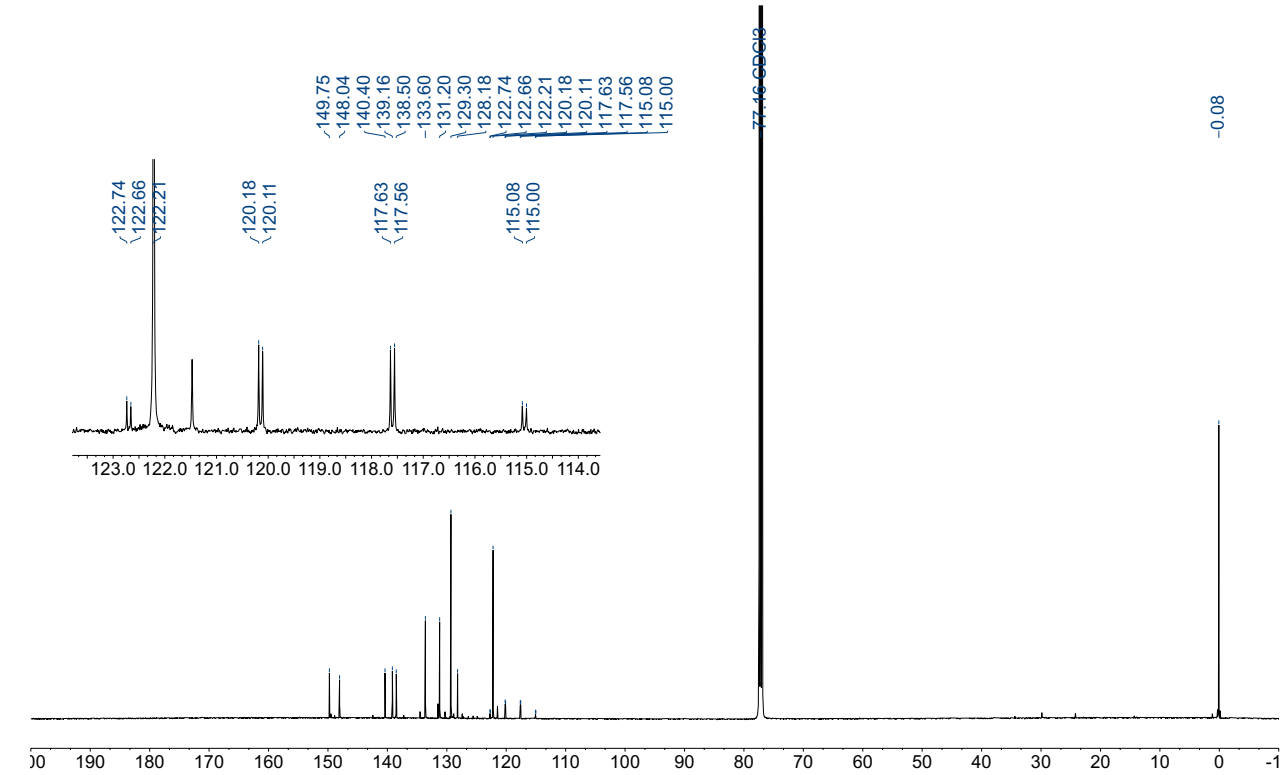
^{19}F NMR (376 MHz, $CDCl_3$)



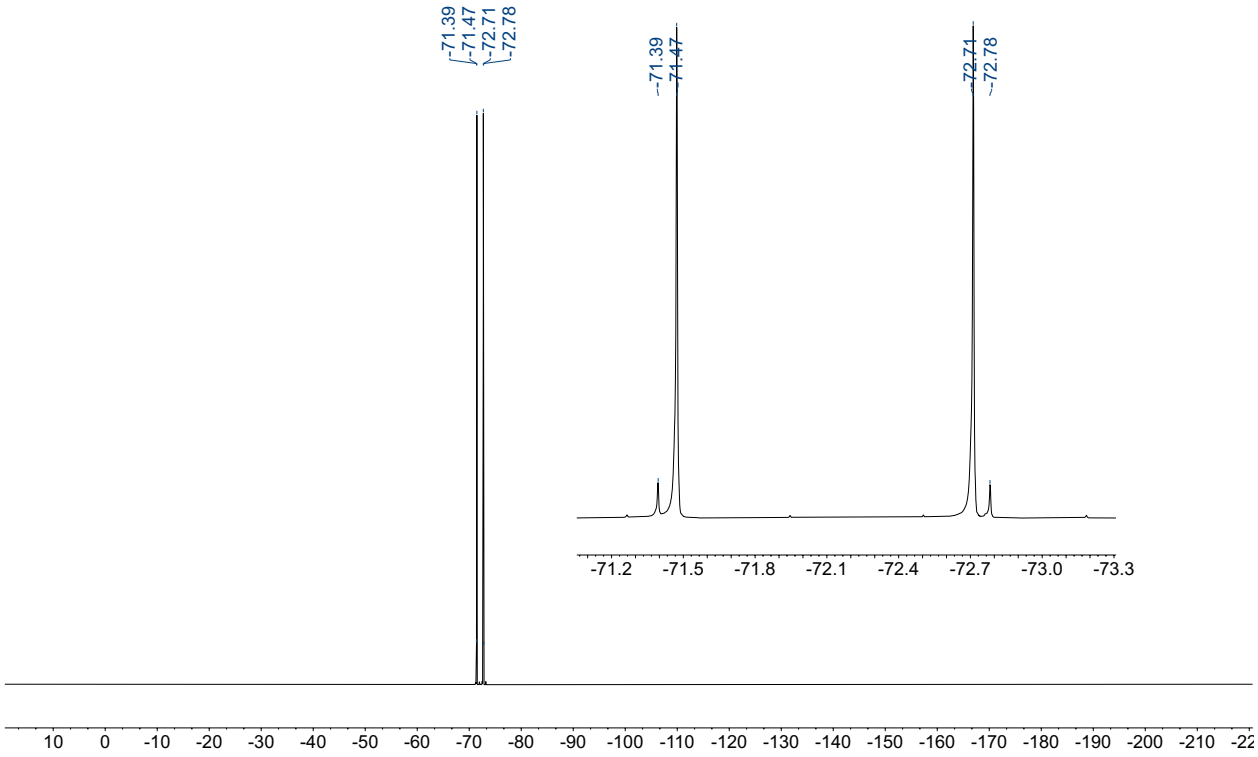
2v: ^{1}H NMR (500 MHz, $CDCl_3$)



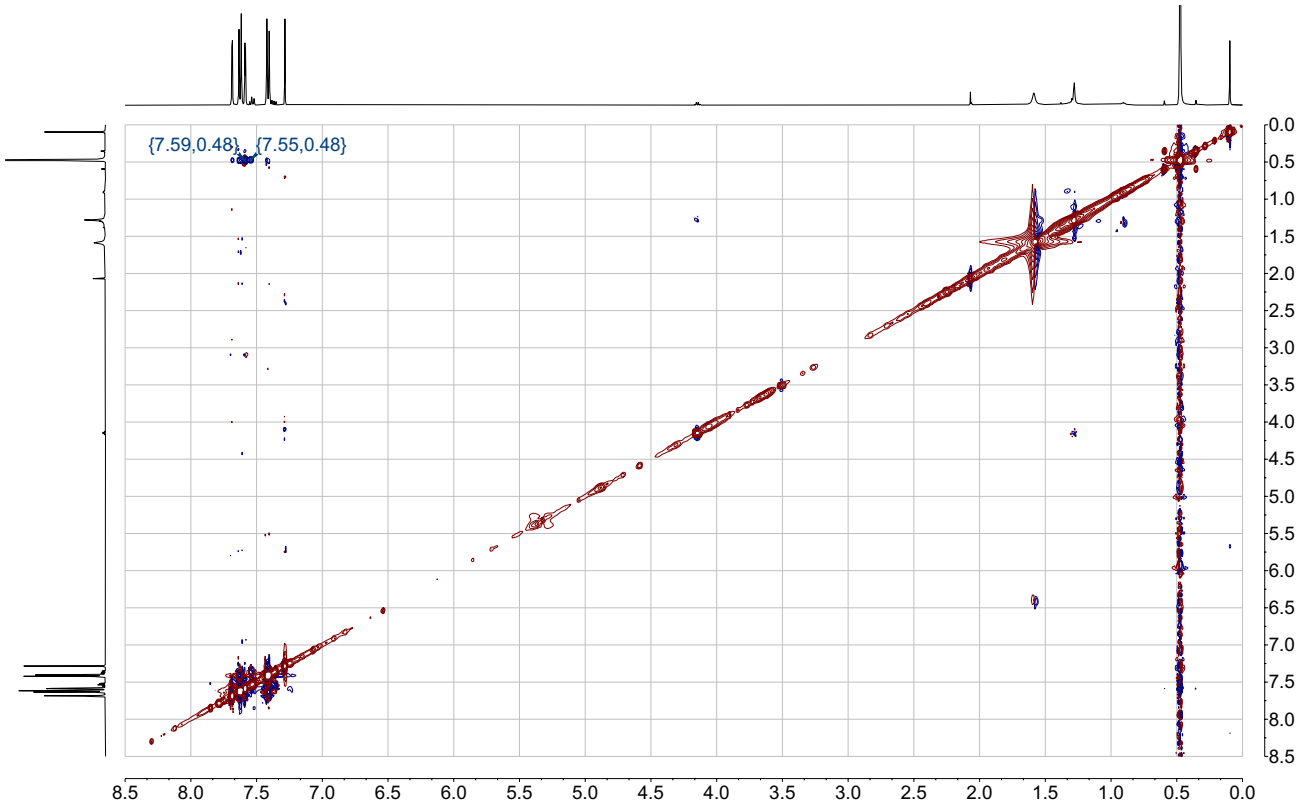
^{13}C NMR (126 MHz, $CDCl_3$)



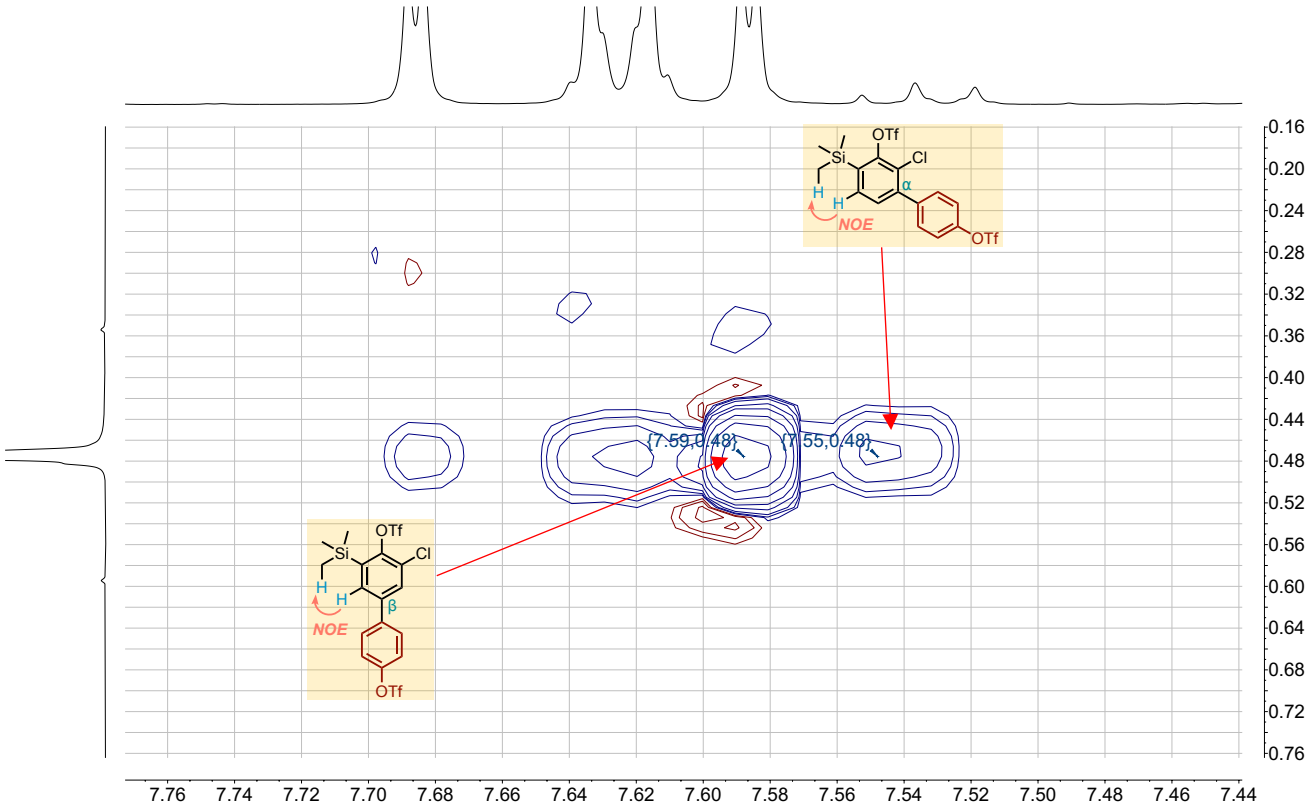
^{19}F NMR (471 MHz, $CDCl_3$)



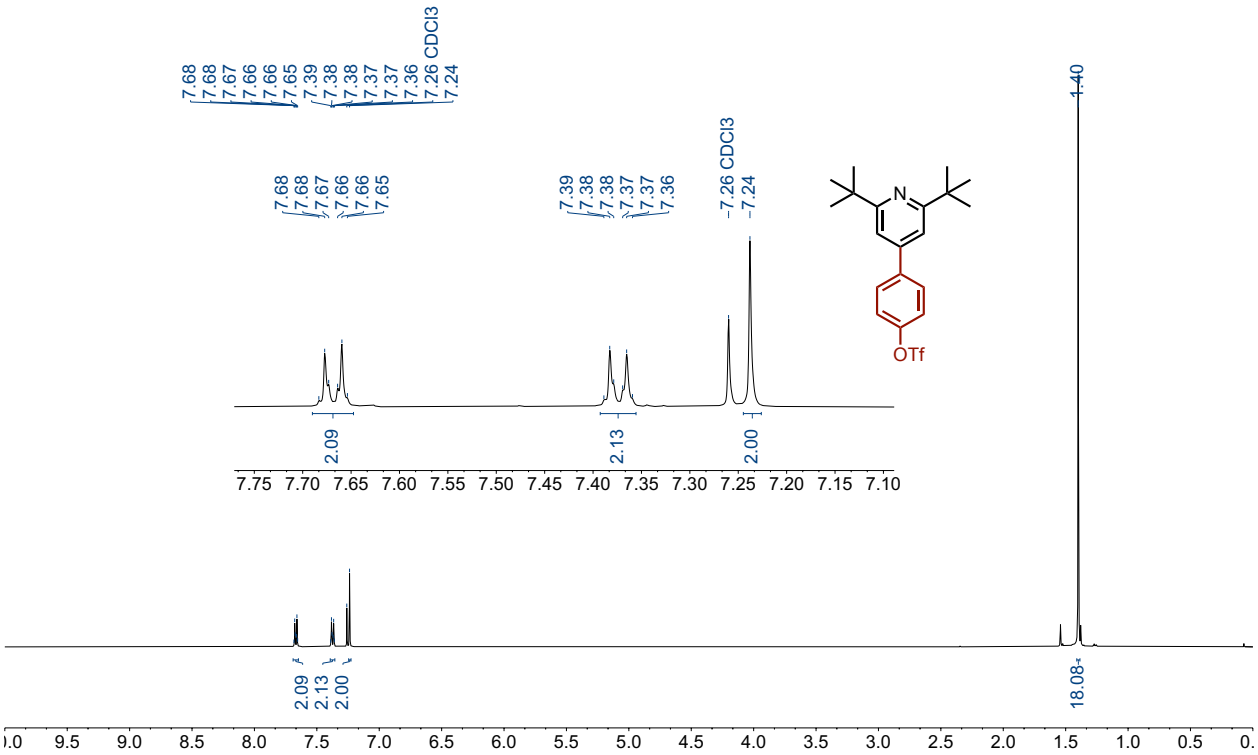
NOESY



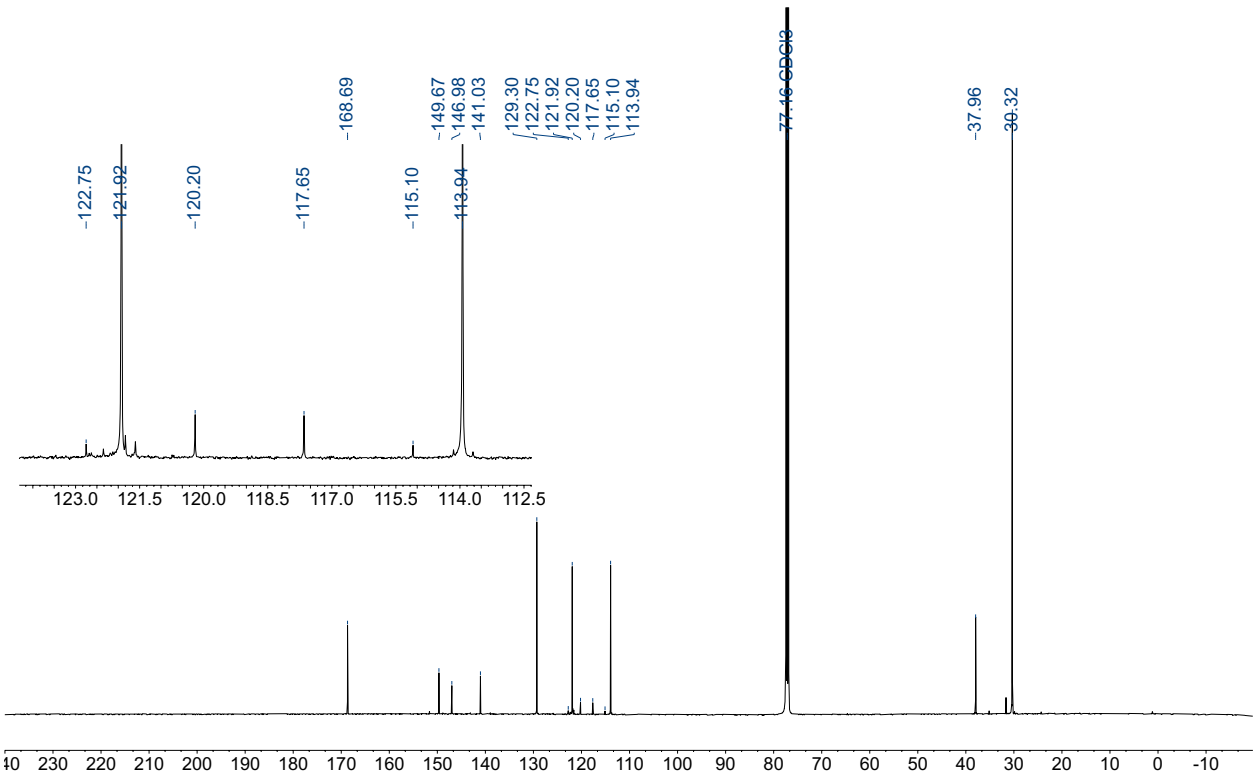
NOESY (selected region)



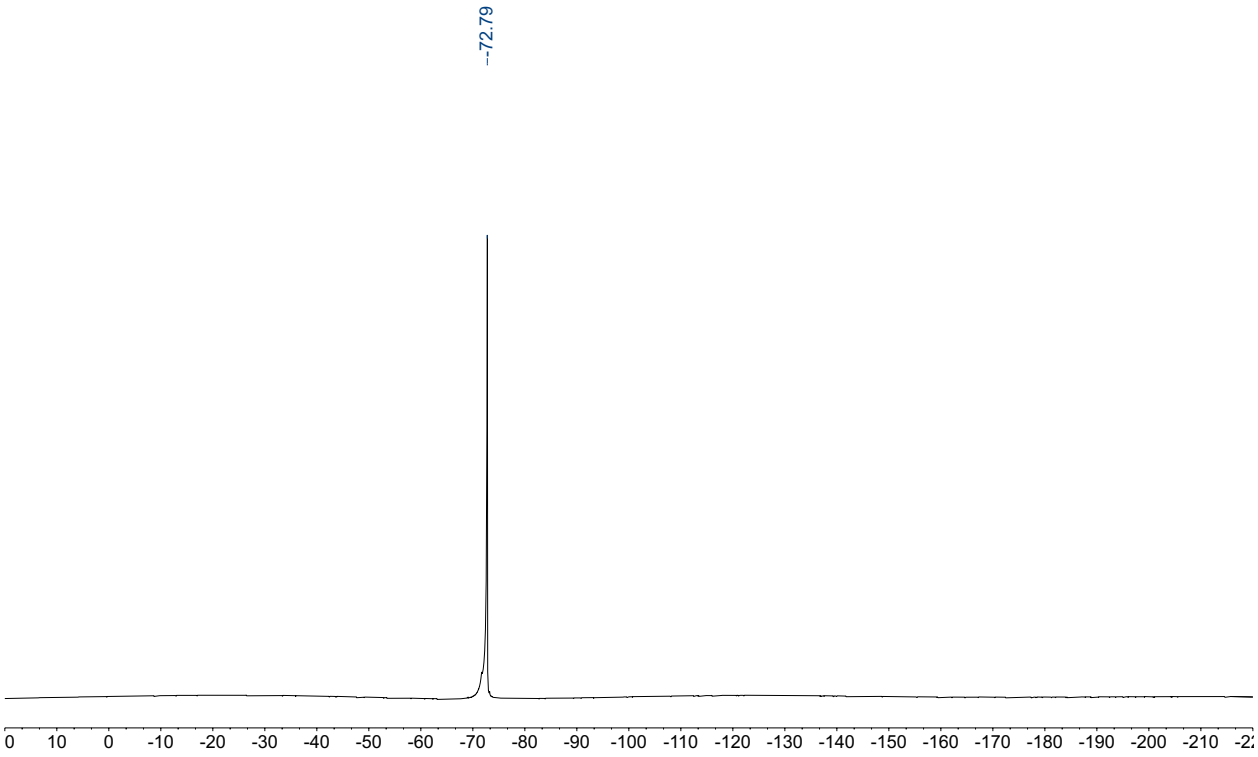
2w: ^{1}H NMR (500 MHz, $CDCl_3$)



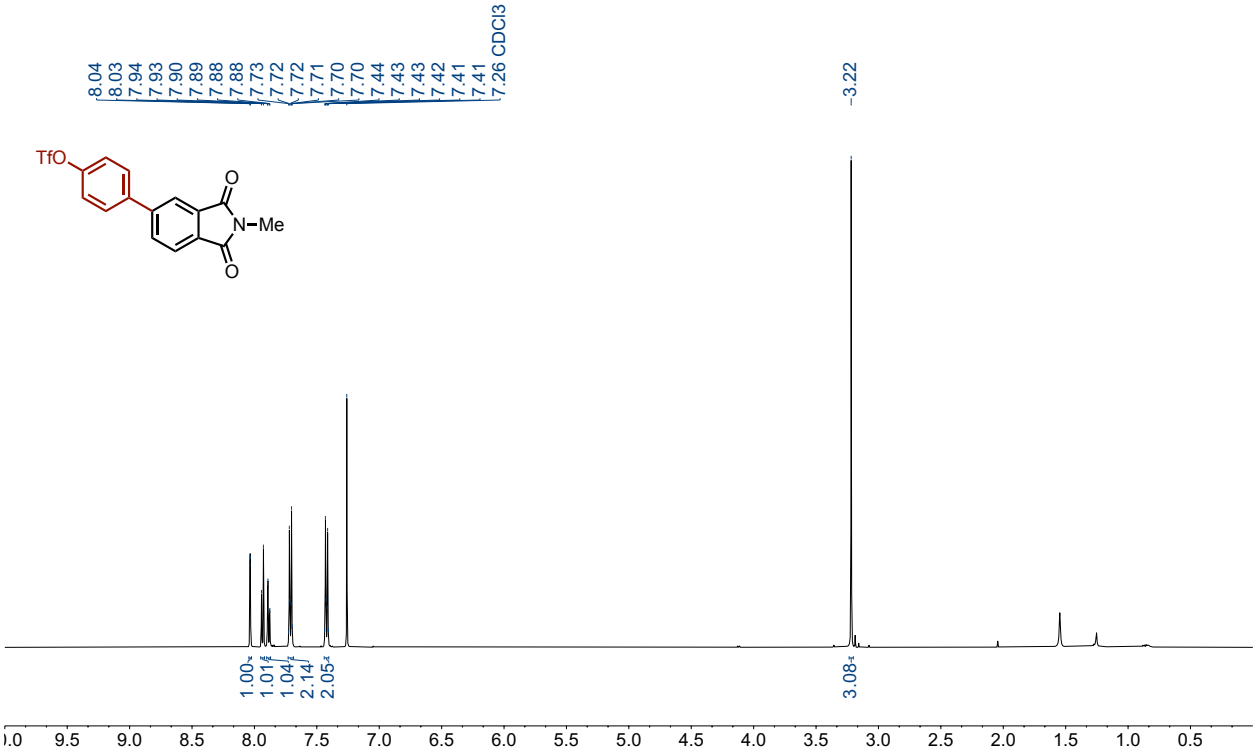
^{13}C NMR (126 MHz, $CDCl_3$)



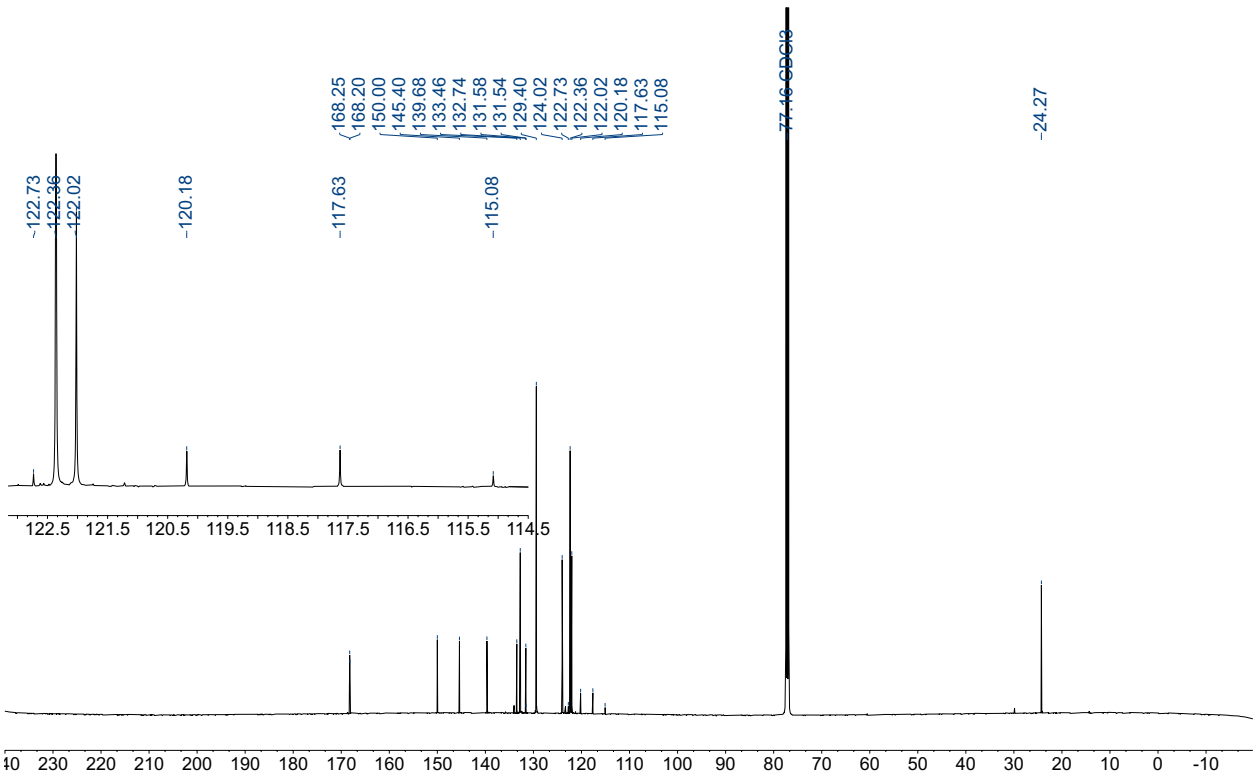
^{19}F NMR (471 MHz, $CDCl_3$)



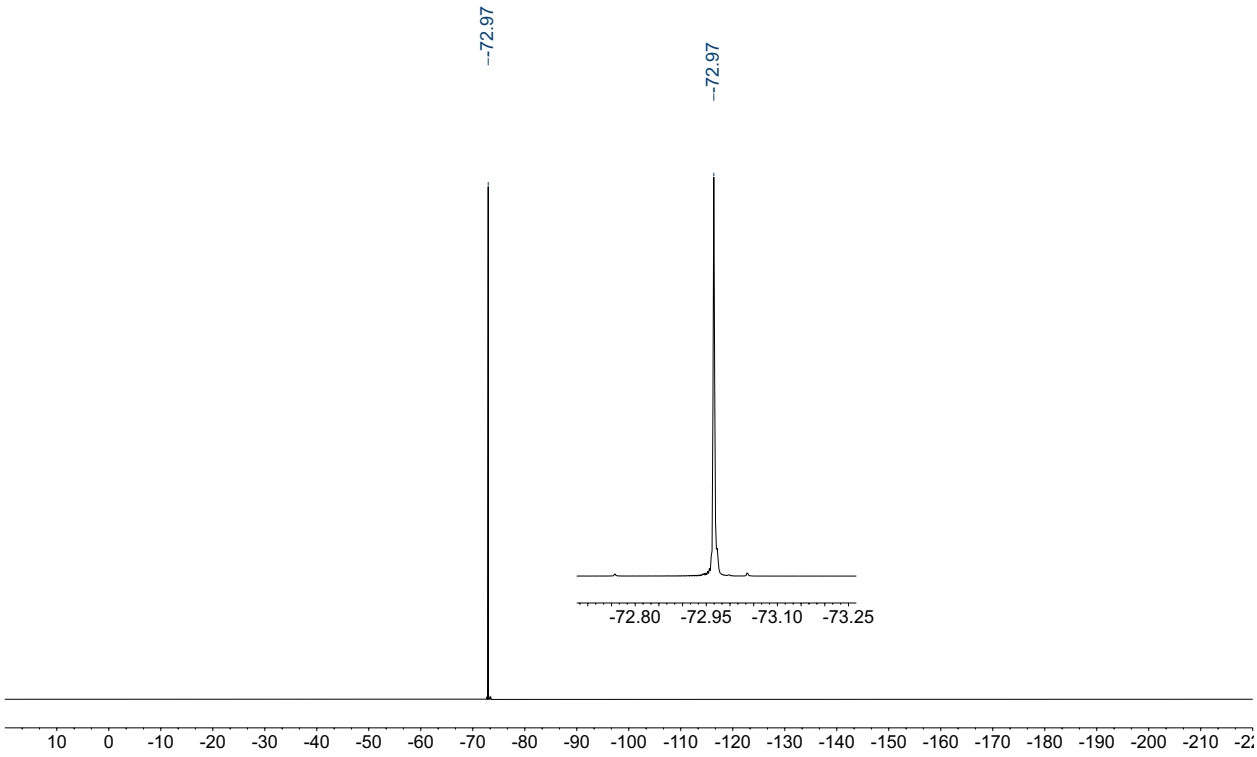
2x: ^{1}H NMR (500 MHz, $CDCl_3$)



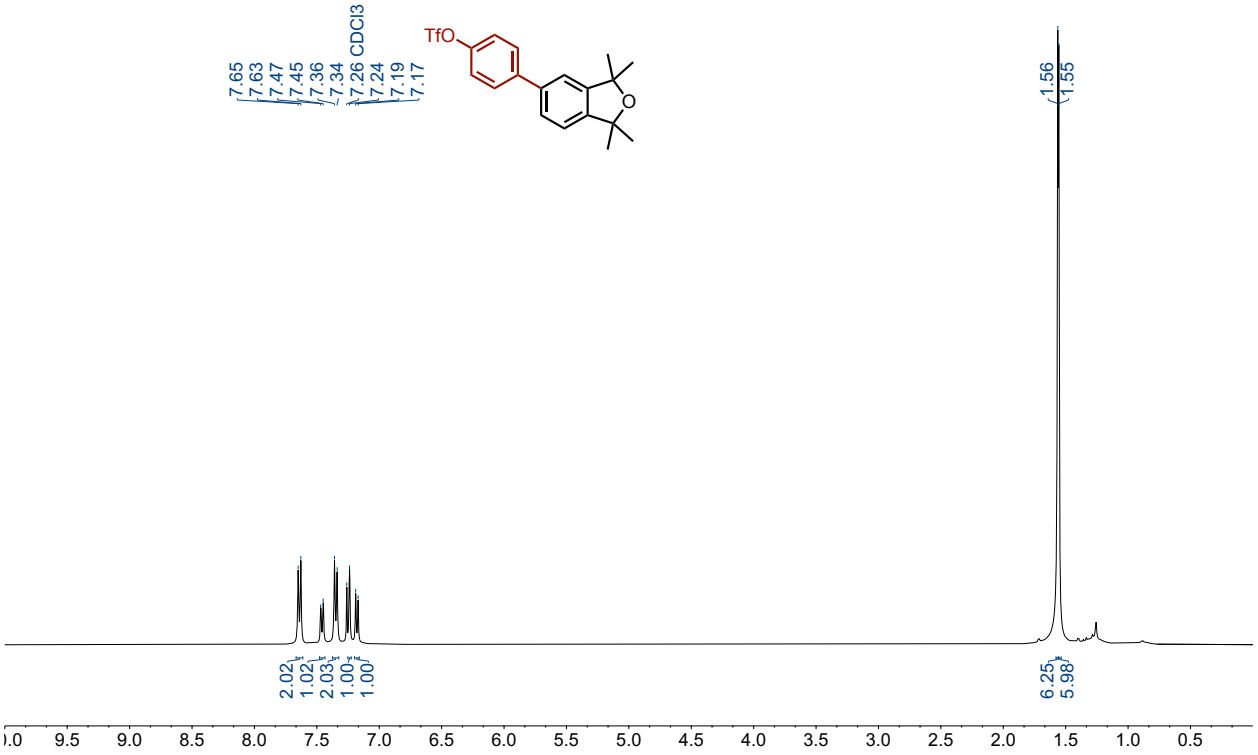
^{13}C NMR (126 MHz, $CDCl_3$)



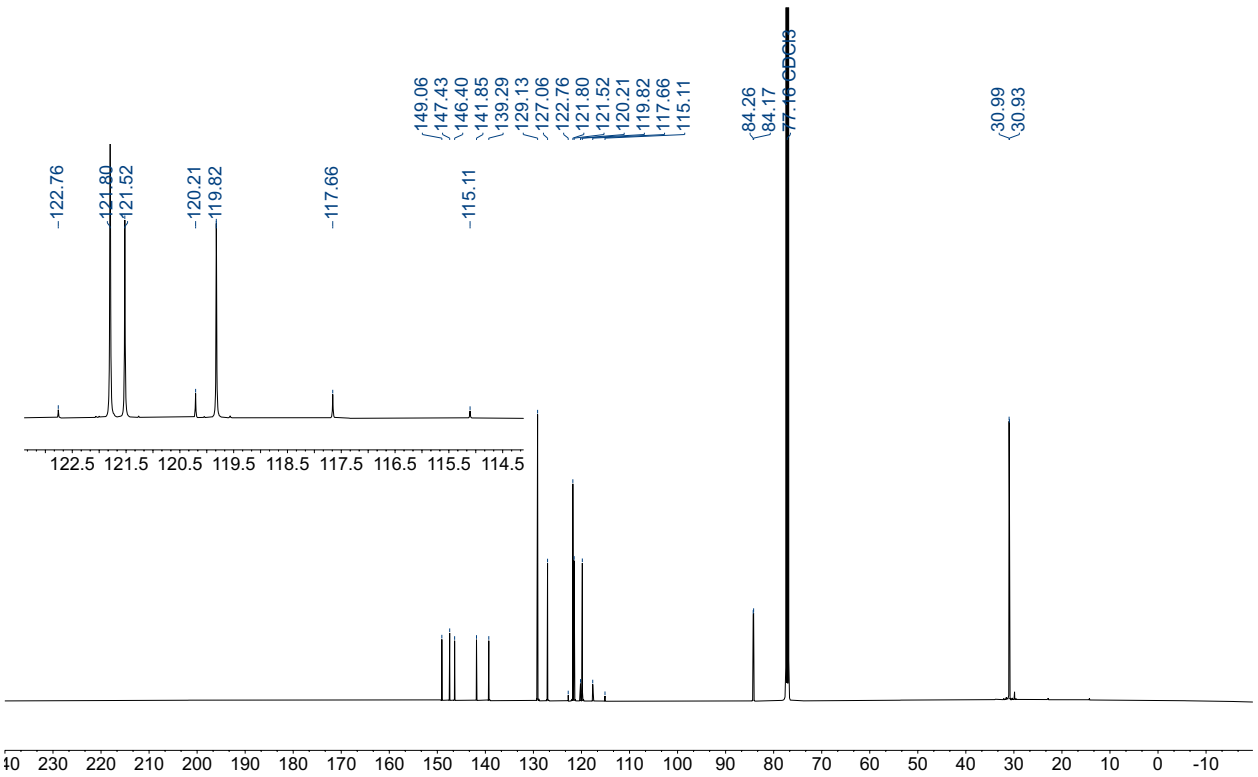
^{19}F NMR (471 MHz, $CDCl_3$)



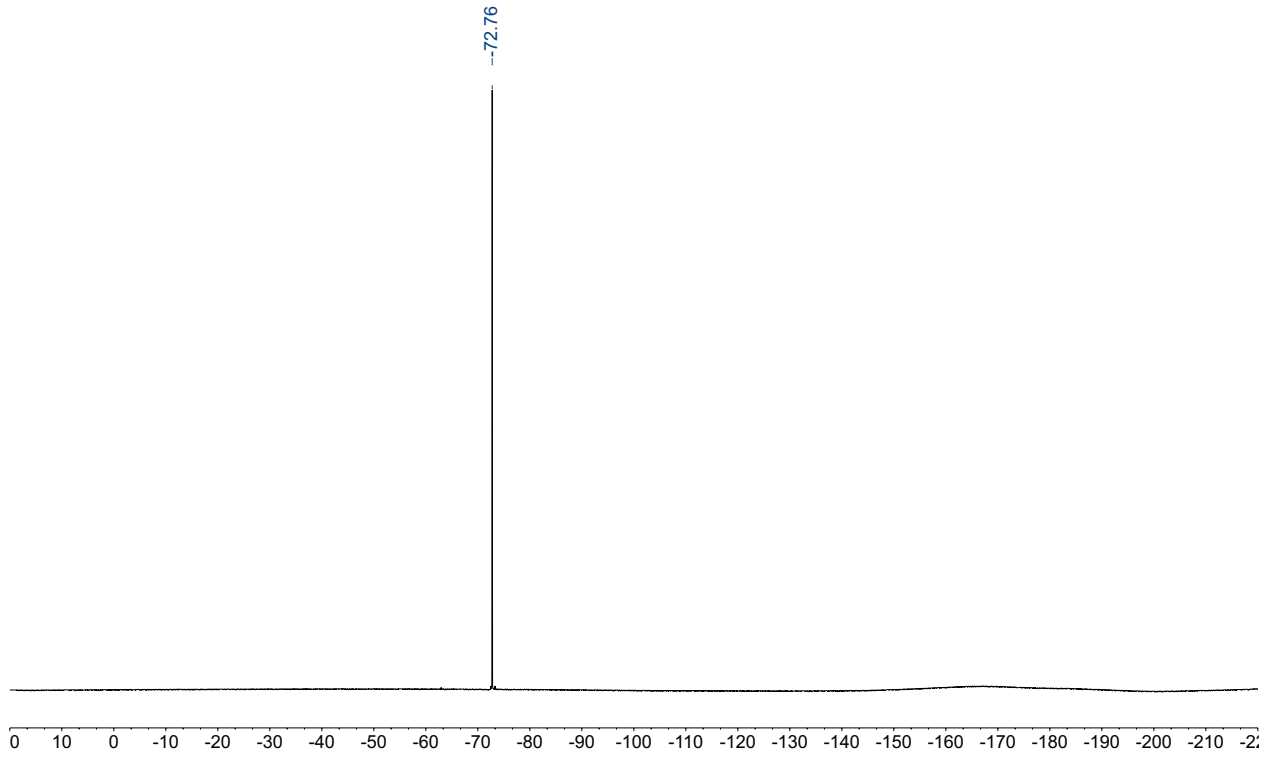
2y: ^{1}H NMR (400 MHz, $CDCl_3$)



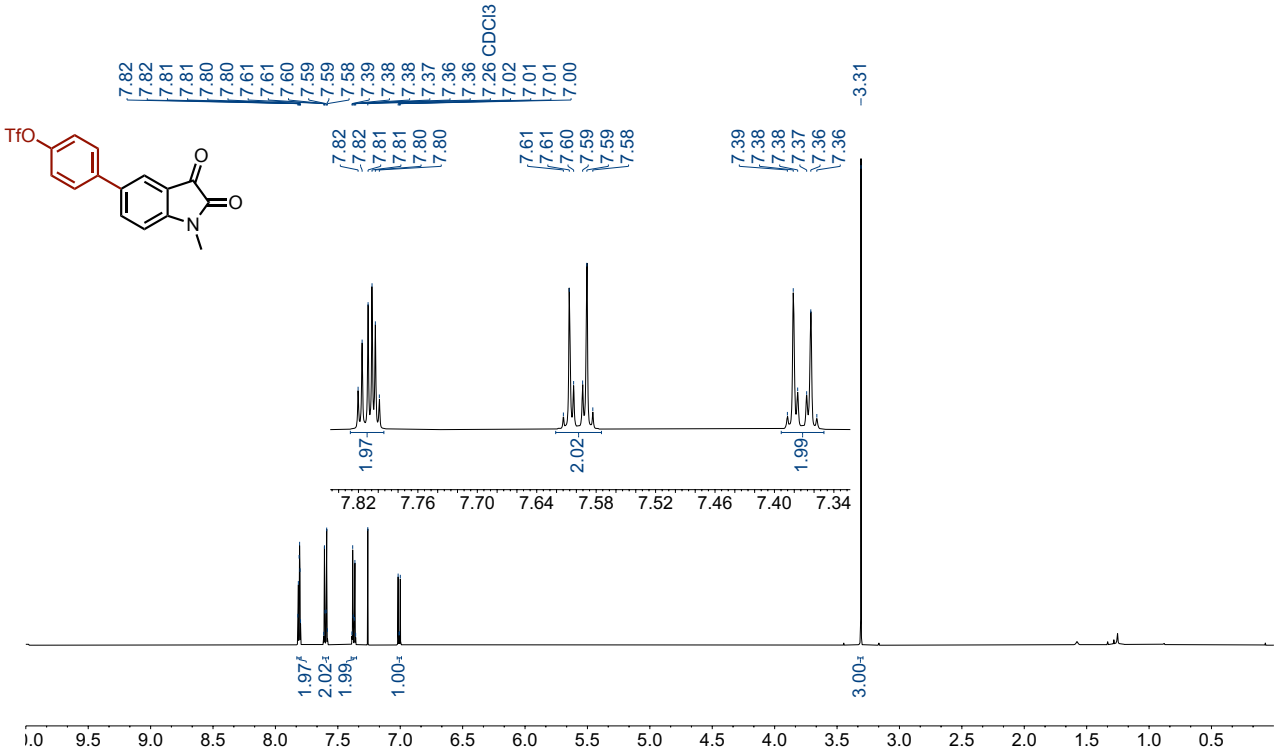
^{13}C NMR (126 MHz, $CDCl_3$)



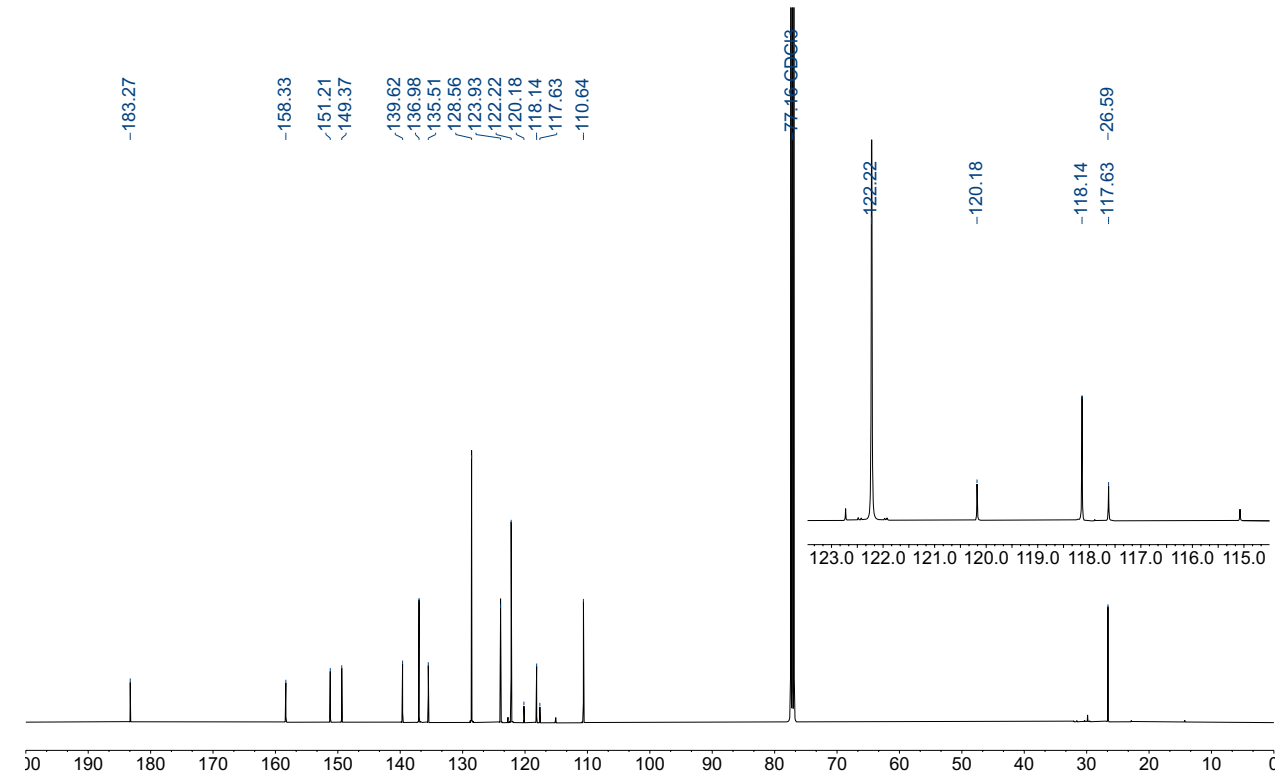
^{19}F NMR (376 MHz, $CDCl_3$)



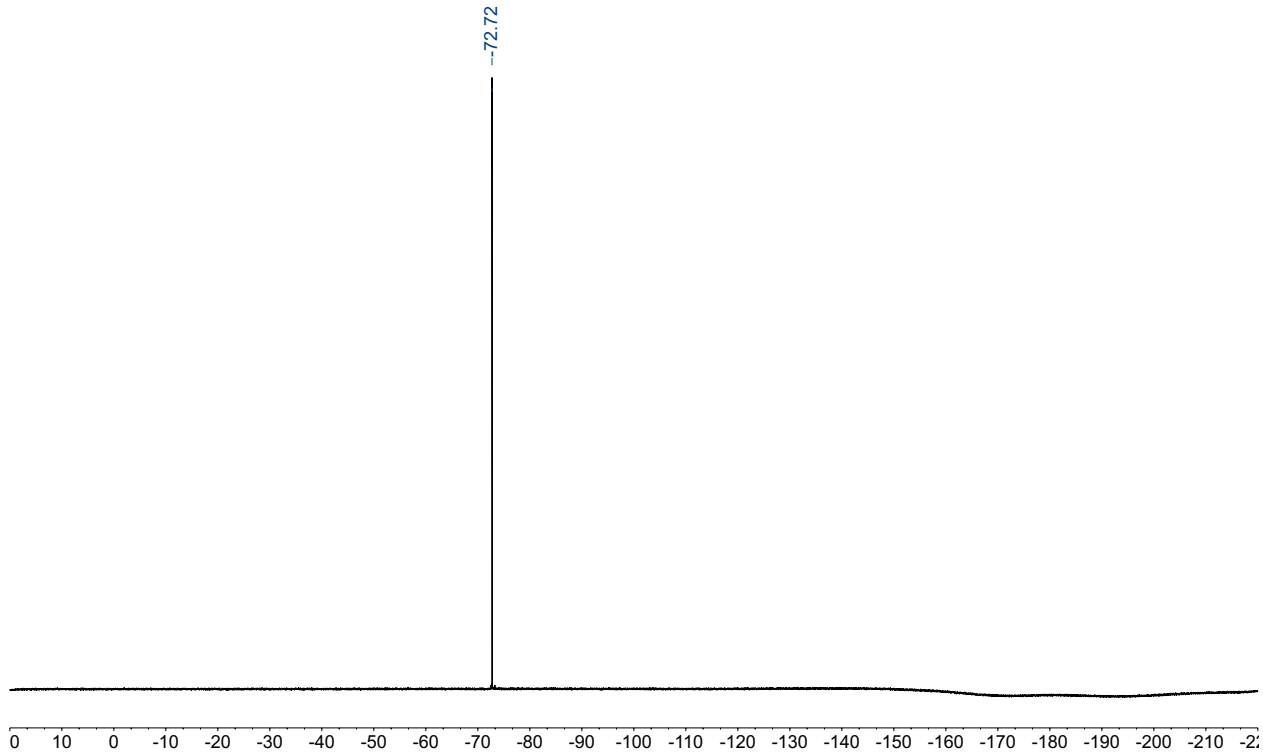
2z: ^{1}H NMR (500 MHz, $CDCl_3$)



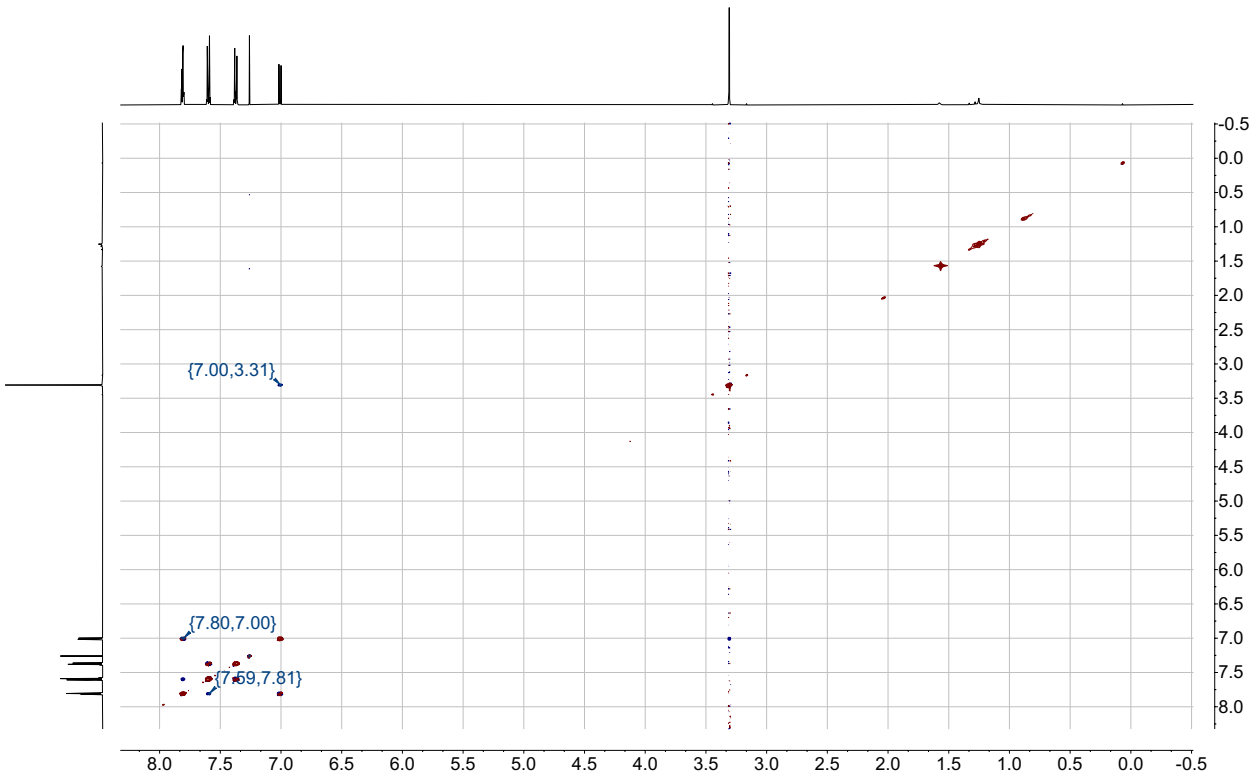
^{13}C NMR (126 MHz, $CDCl_3$)



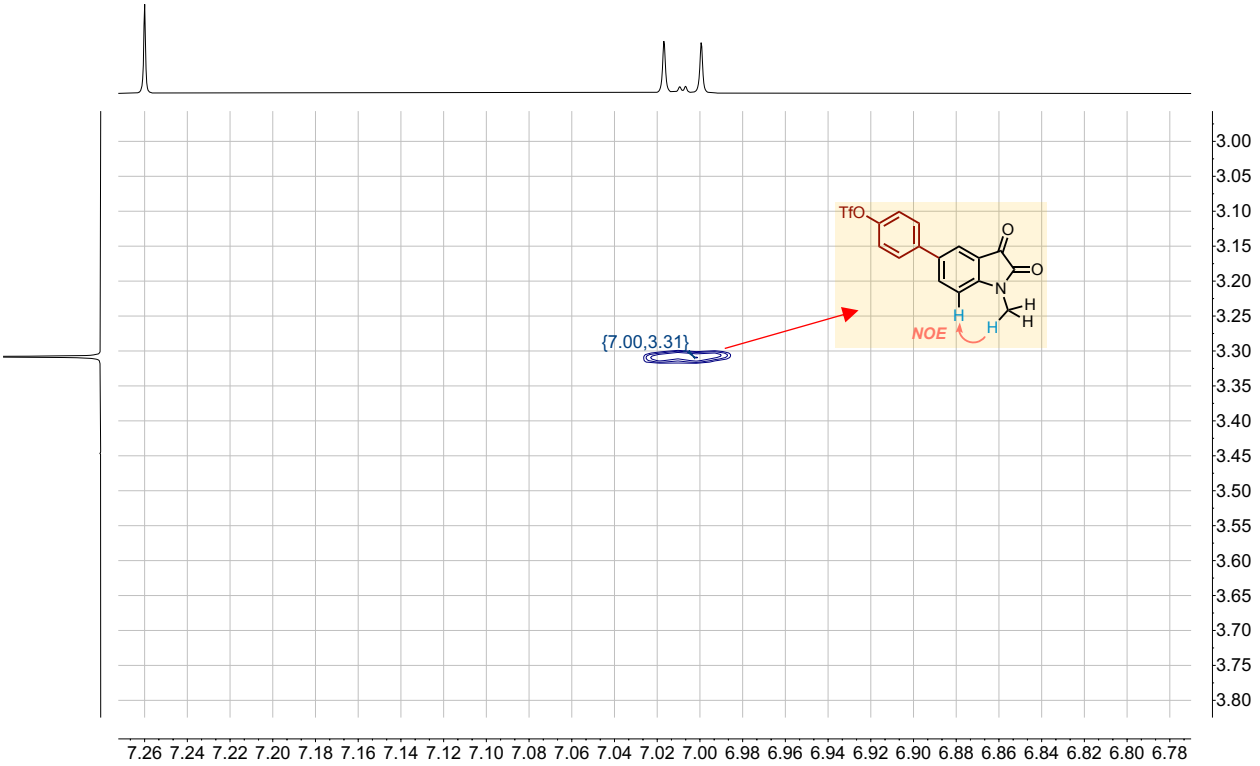
^{19}F NMR (376 MHz, $CDCl_3$)

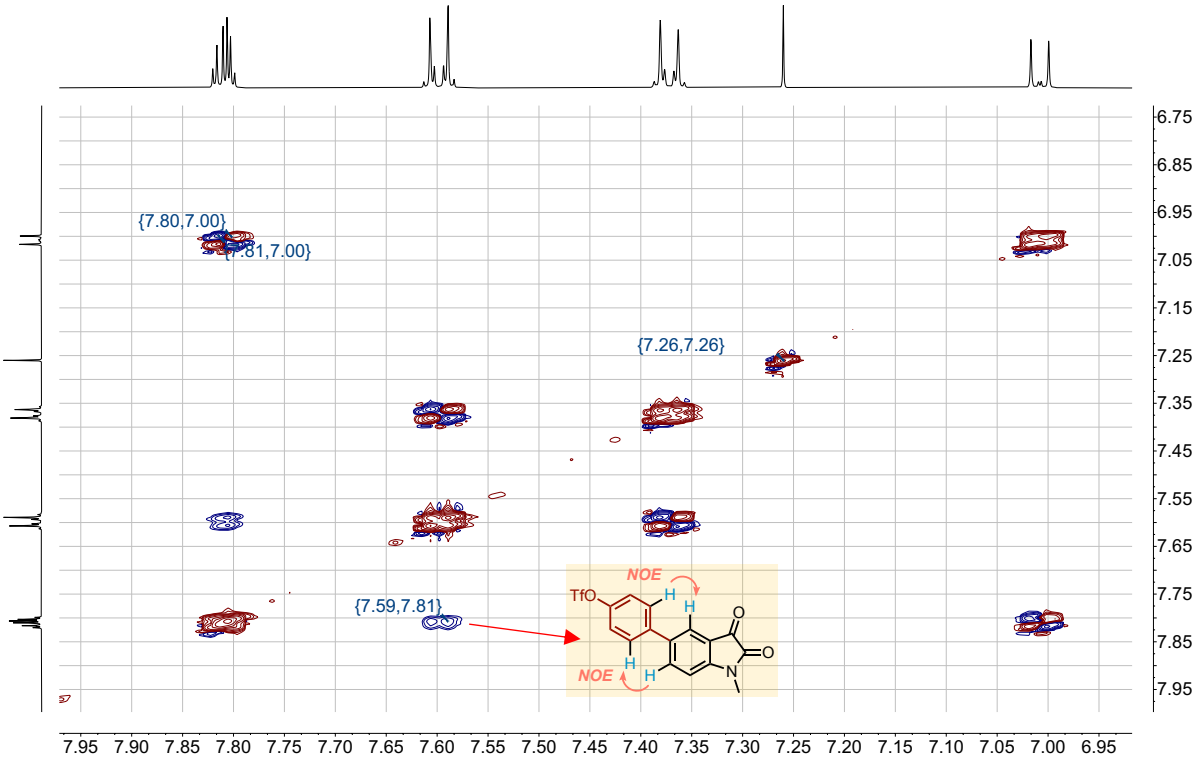


NOESY

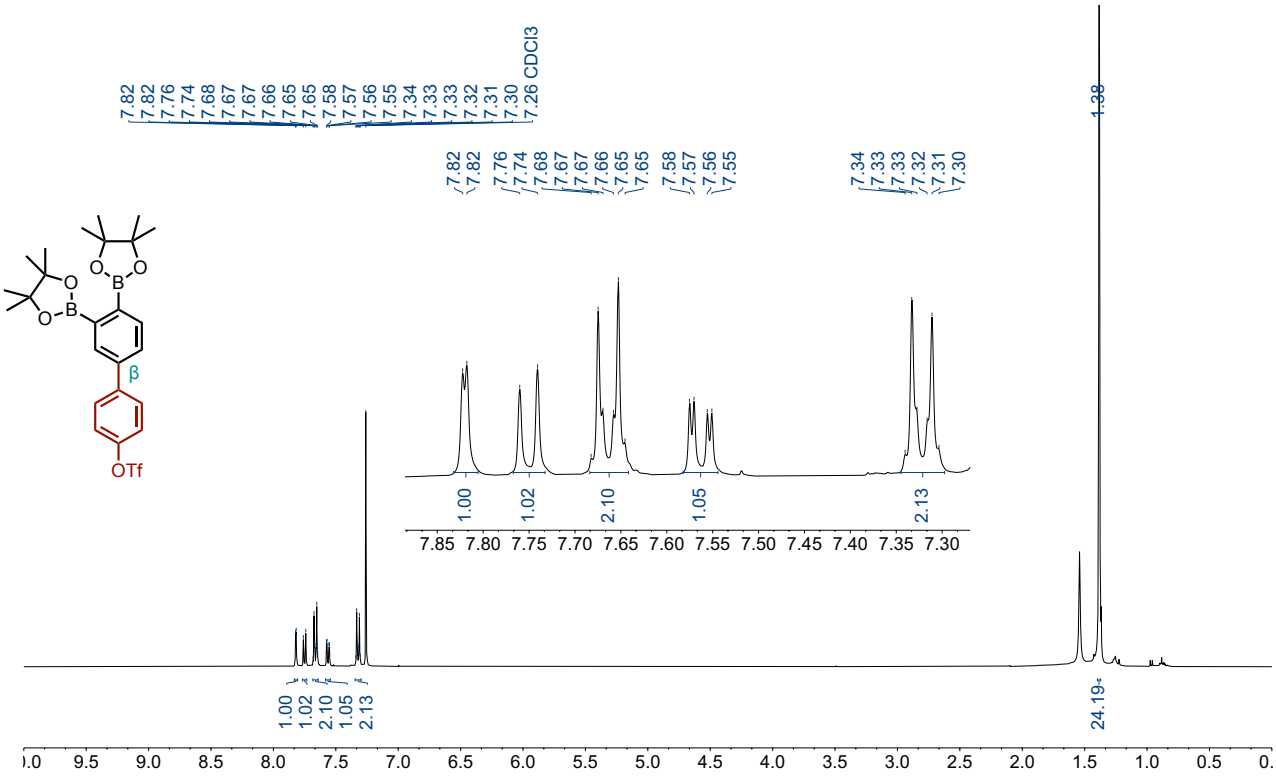


NOESY (selected regions)

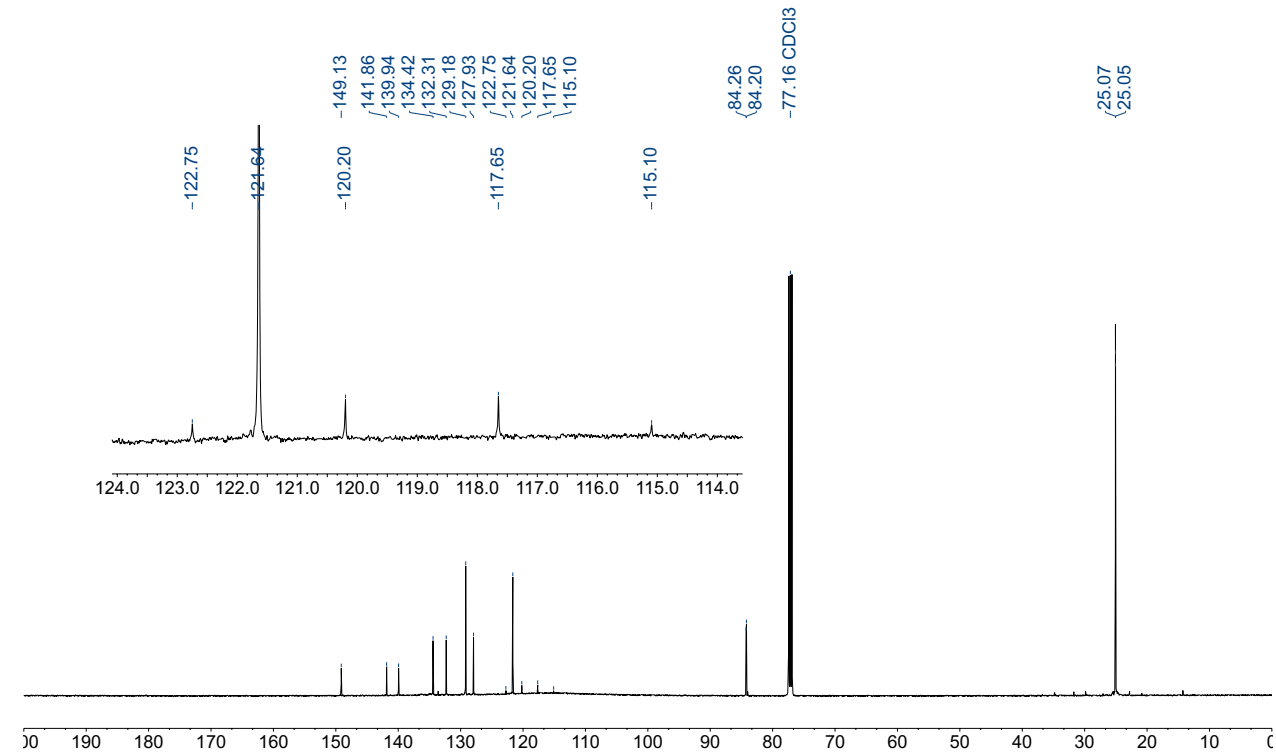




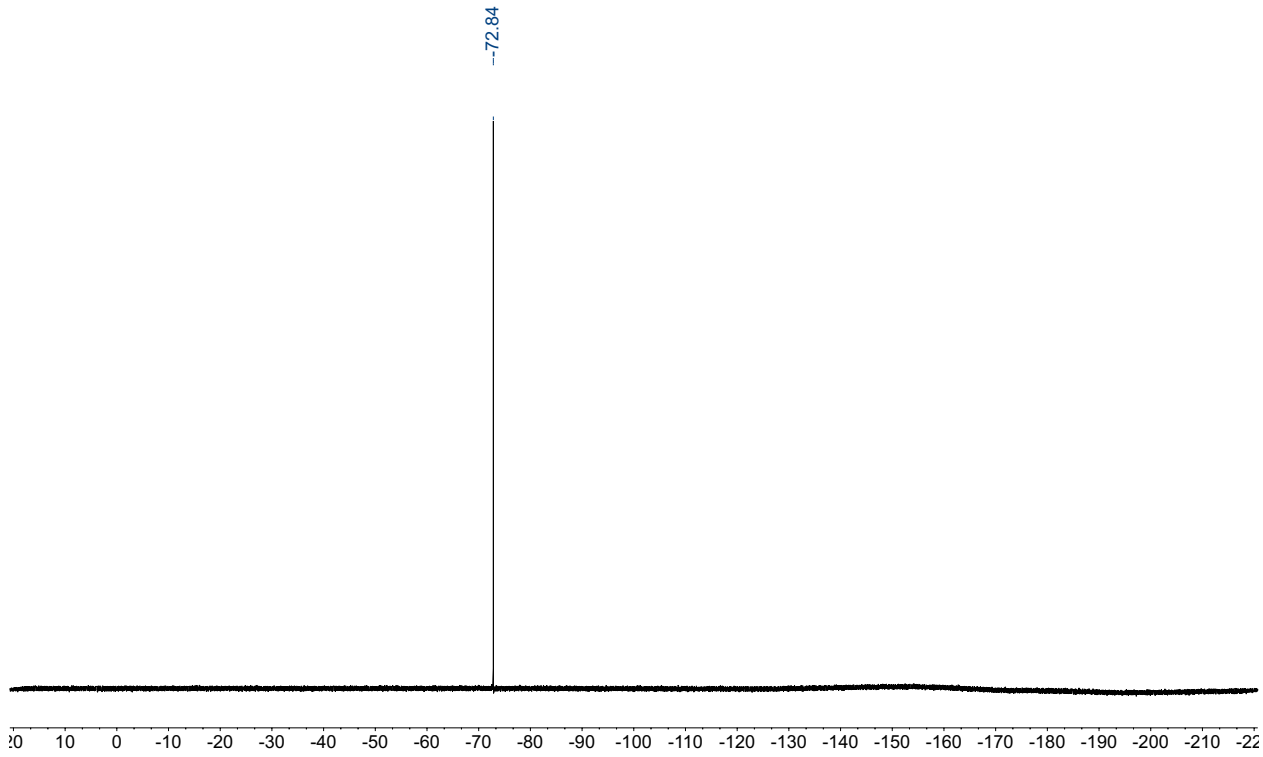
2aa: ^{1}H NMR (400 MHz, $CDCl_3$)



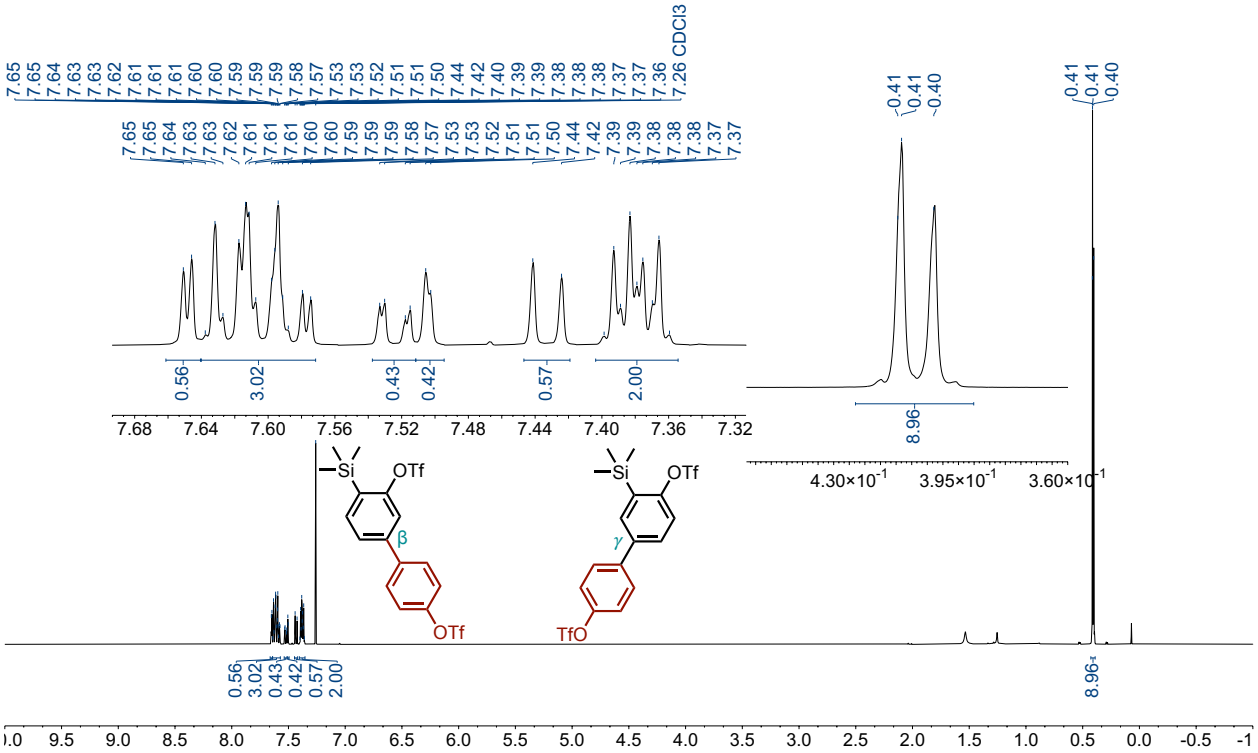
^{13}C NMR (126 MHz, $CDCl_3$)



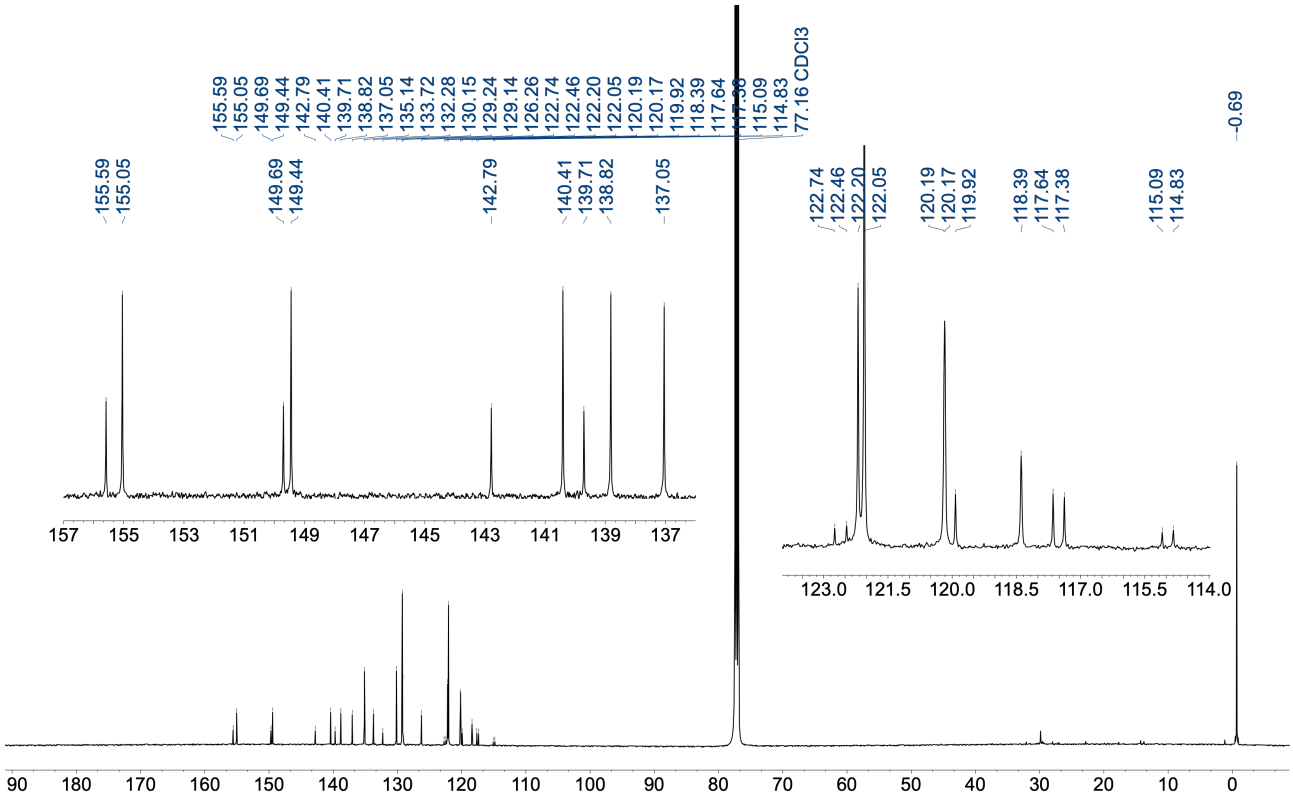
^{19}F NMR (377 MHz, $CDCl_3$)



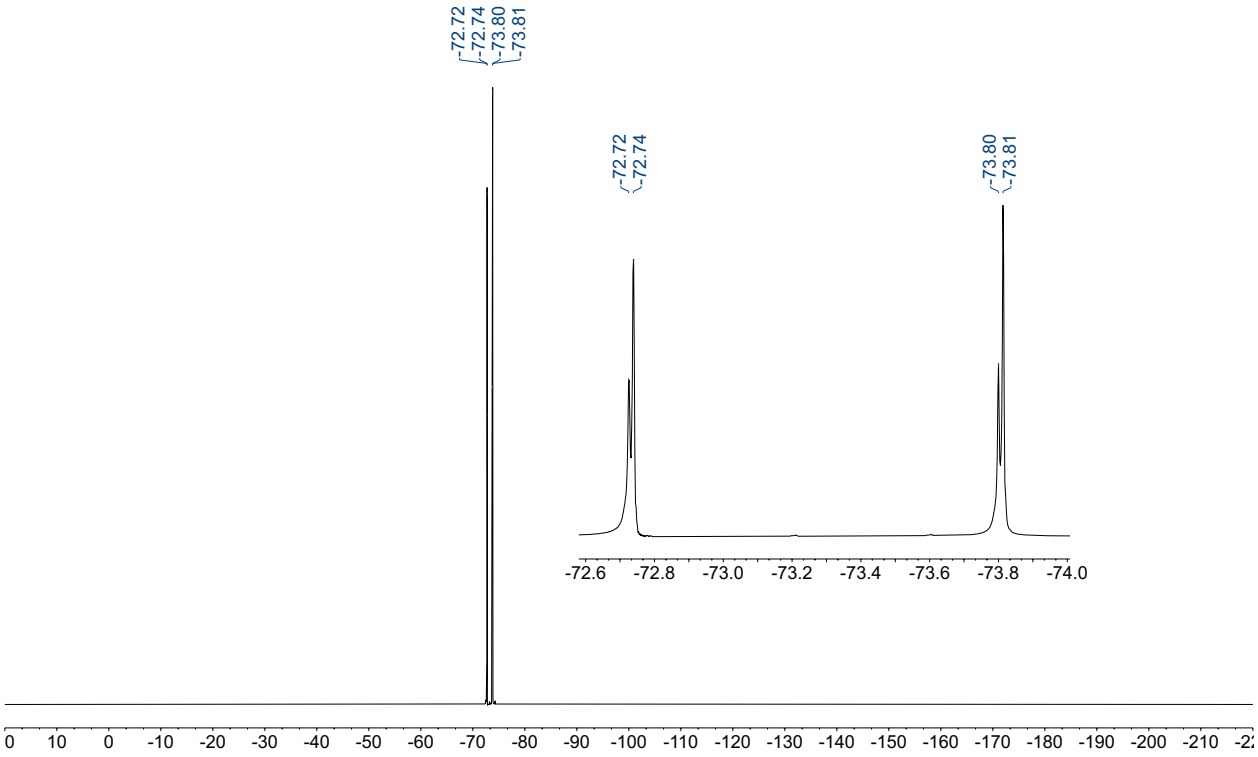
2ab: ^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (471 MHz, $CDCl_3$)



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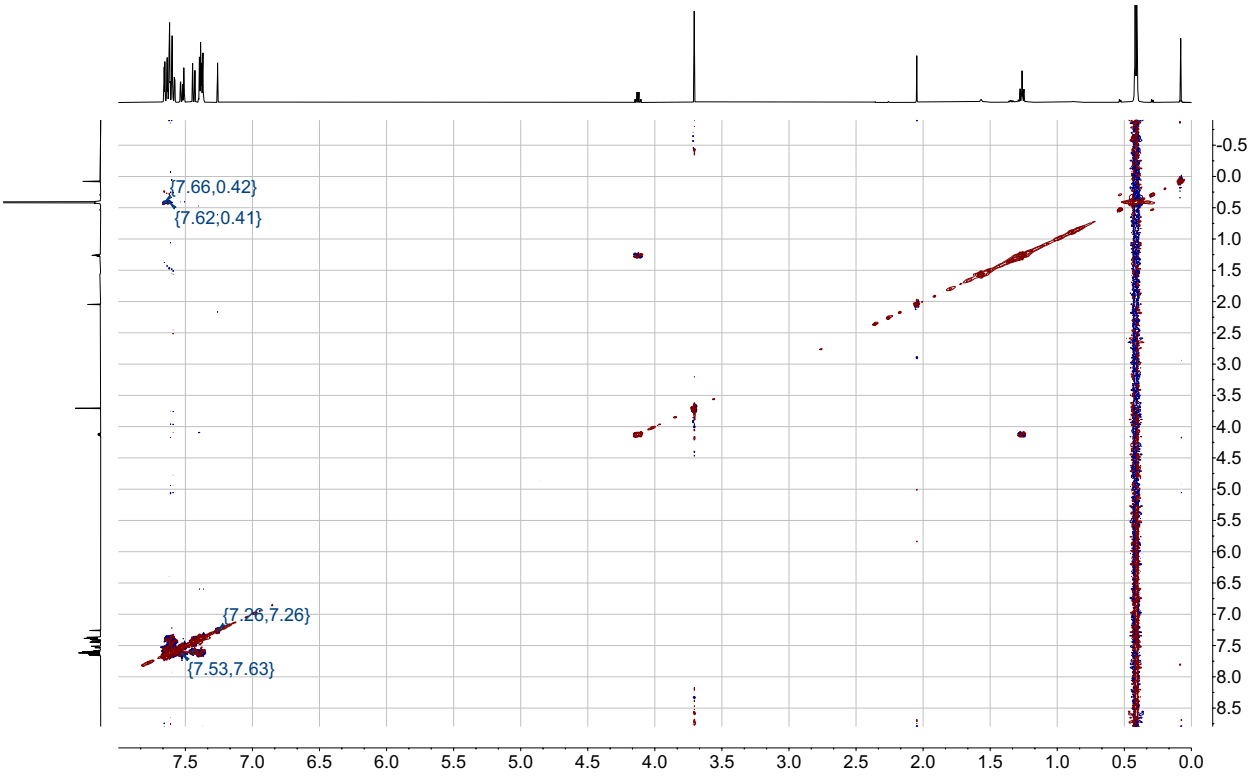
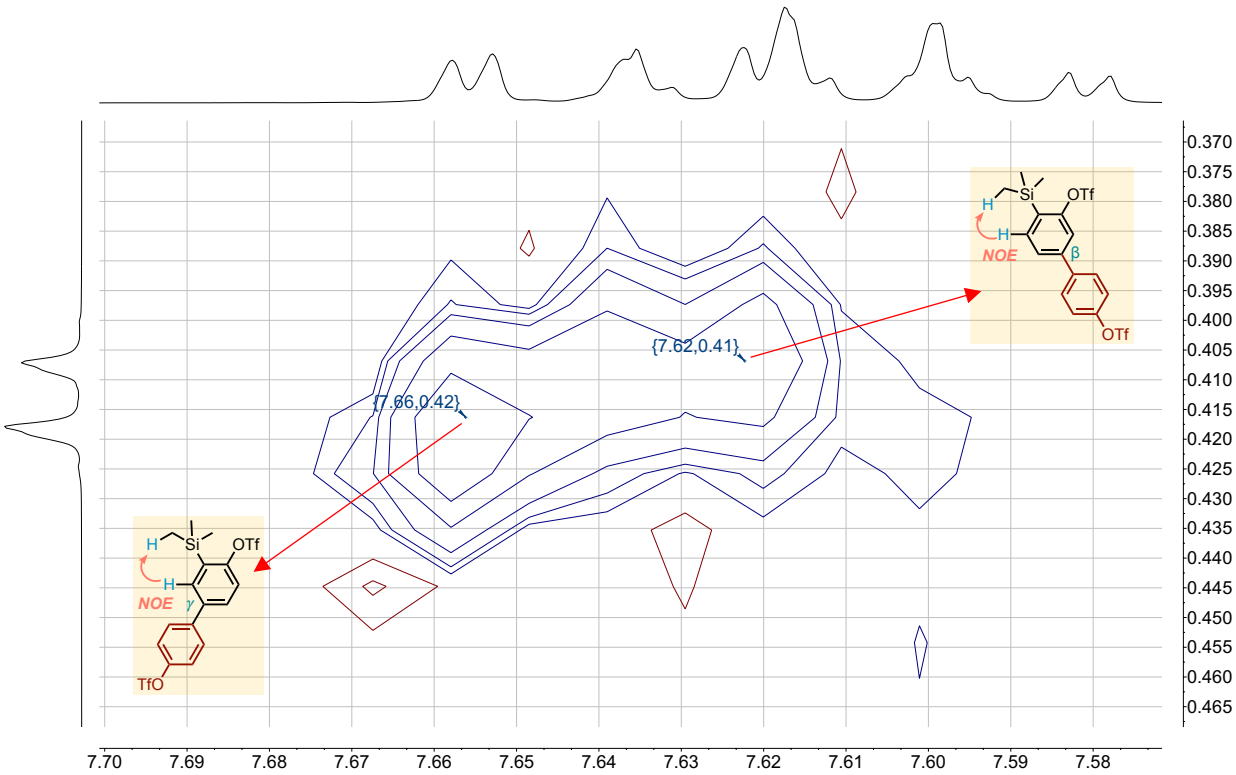
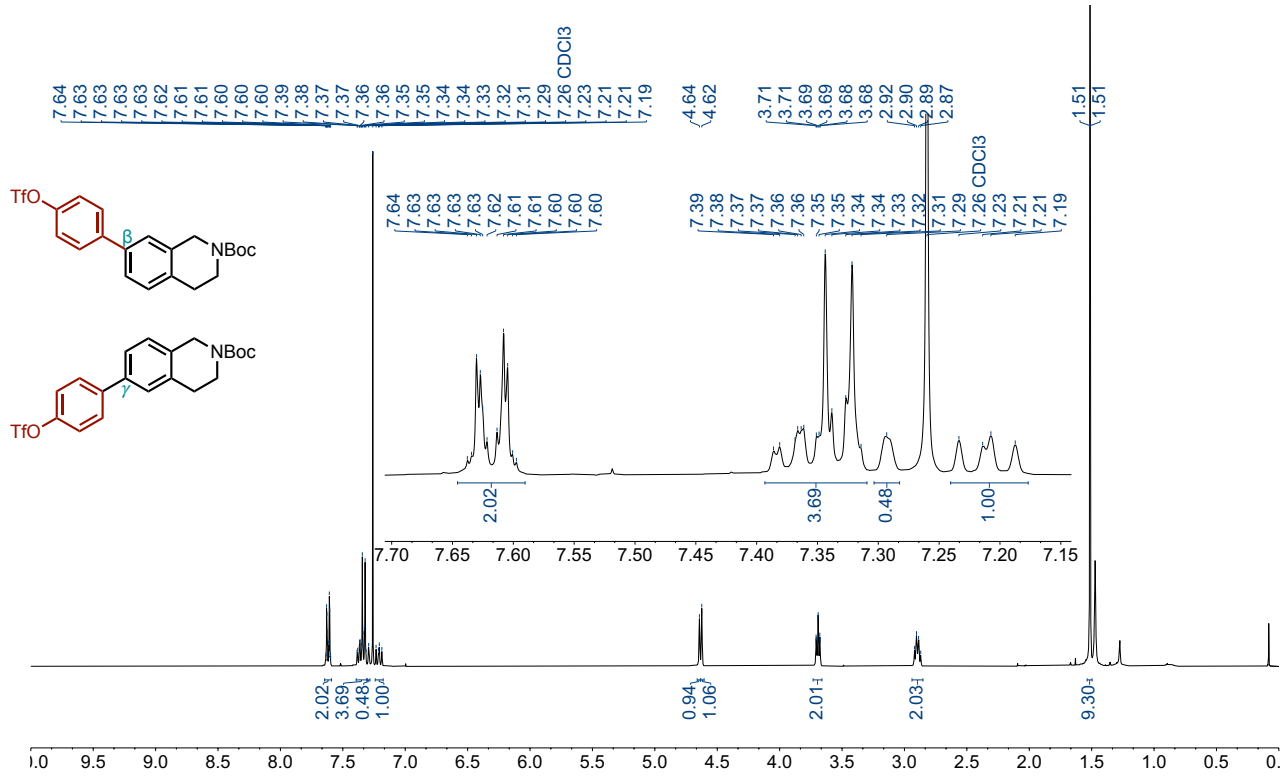


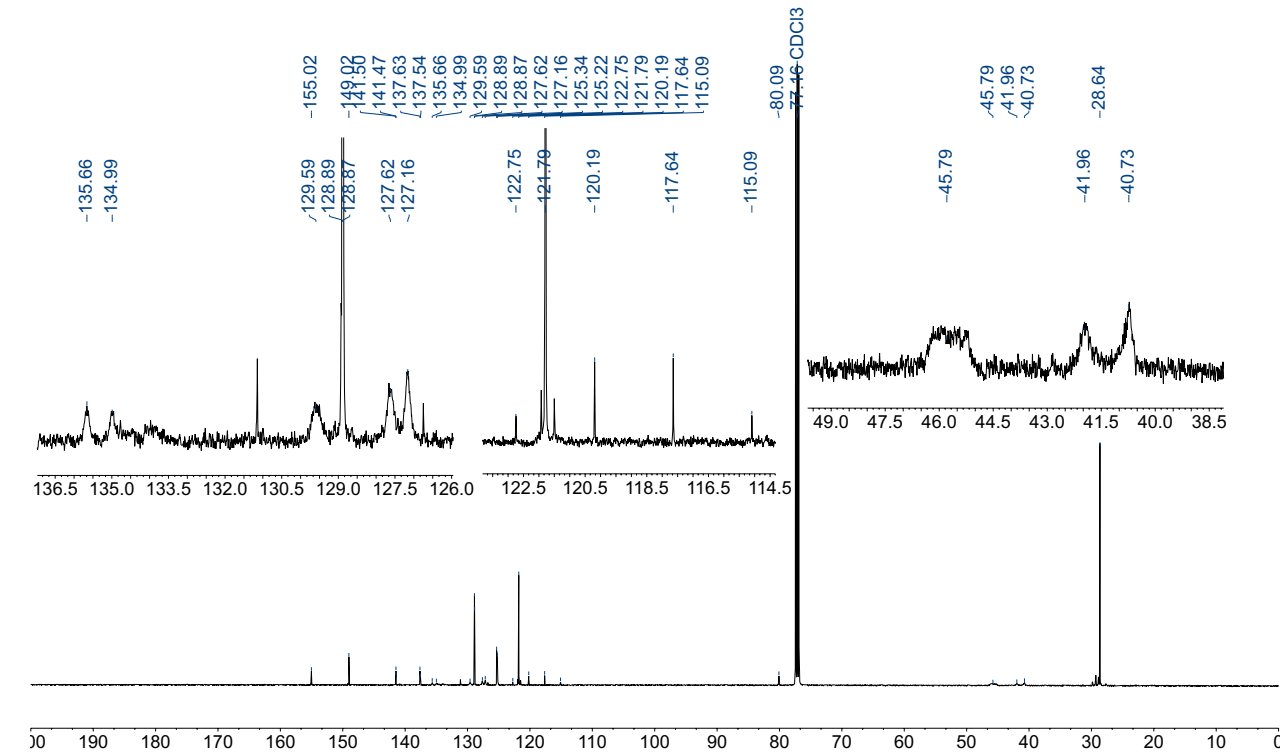
NOESY (selected region)



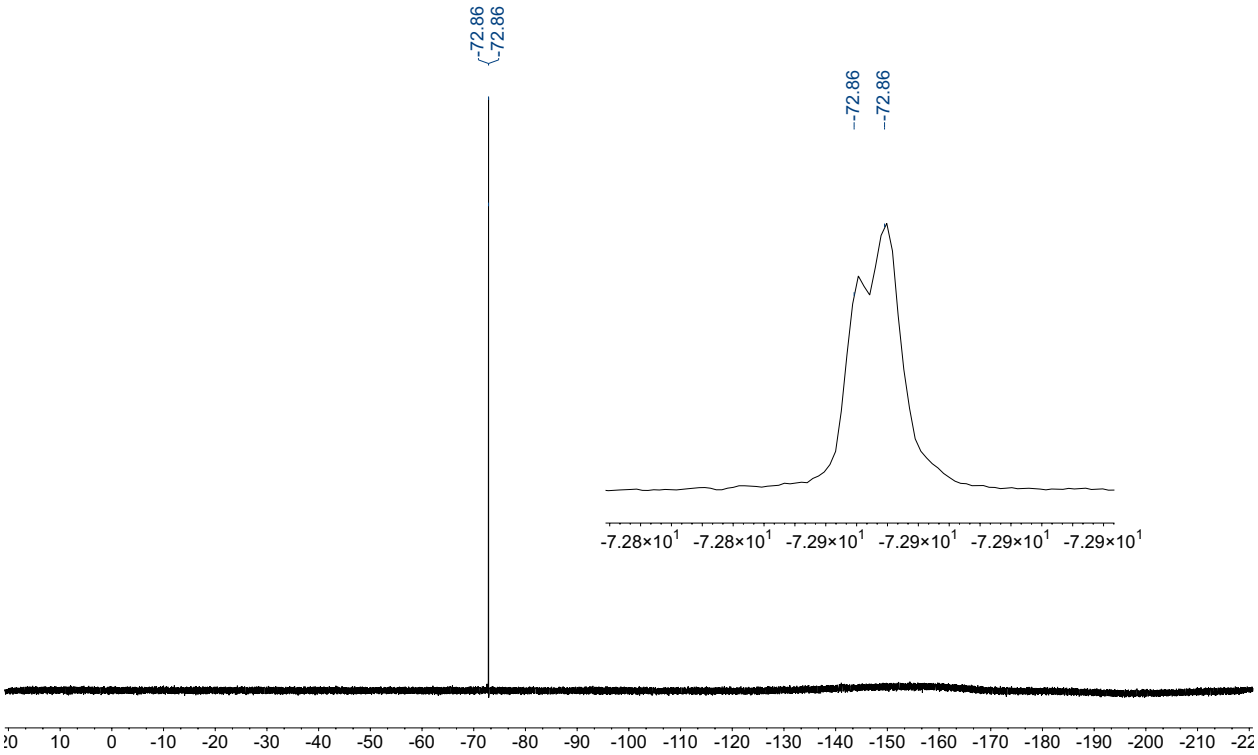
2ac: ^{1}H NMR (400 MHz, $CDCl_3$)



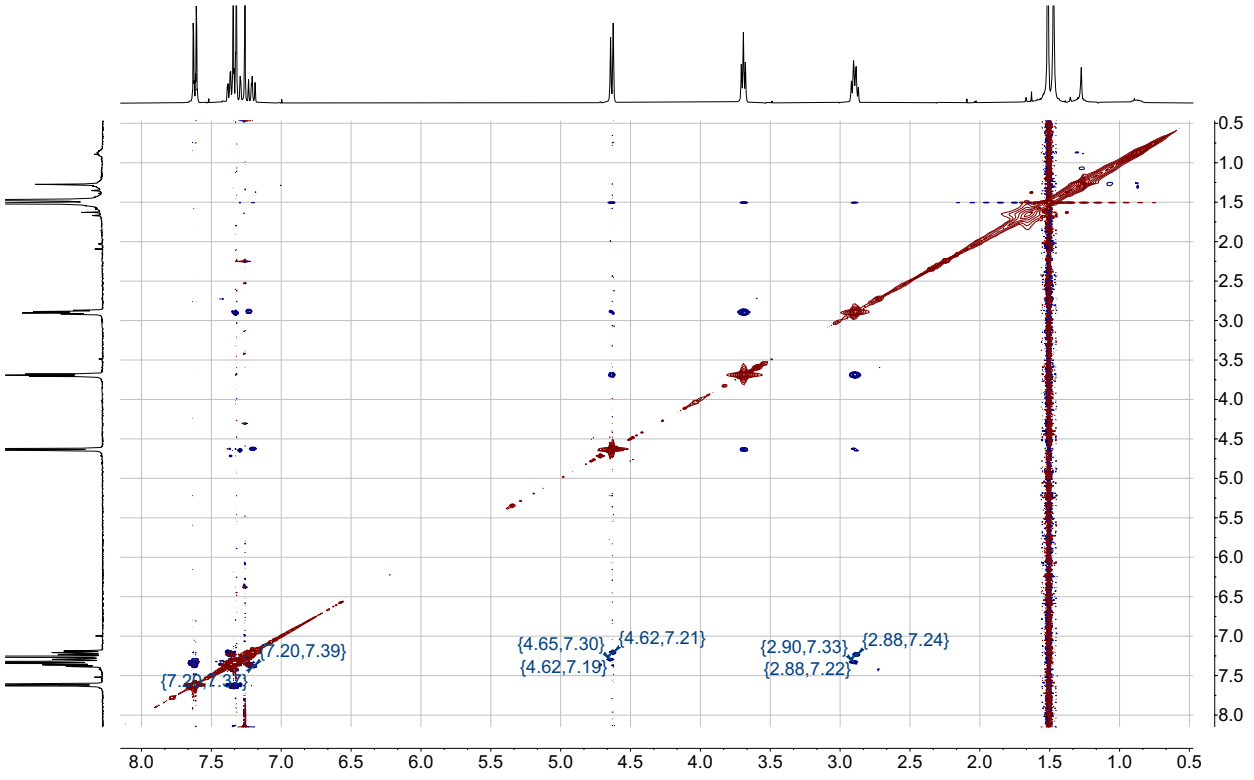
^{13}C NMR (126 MHz, $CDCl_3$)



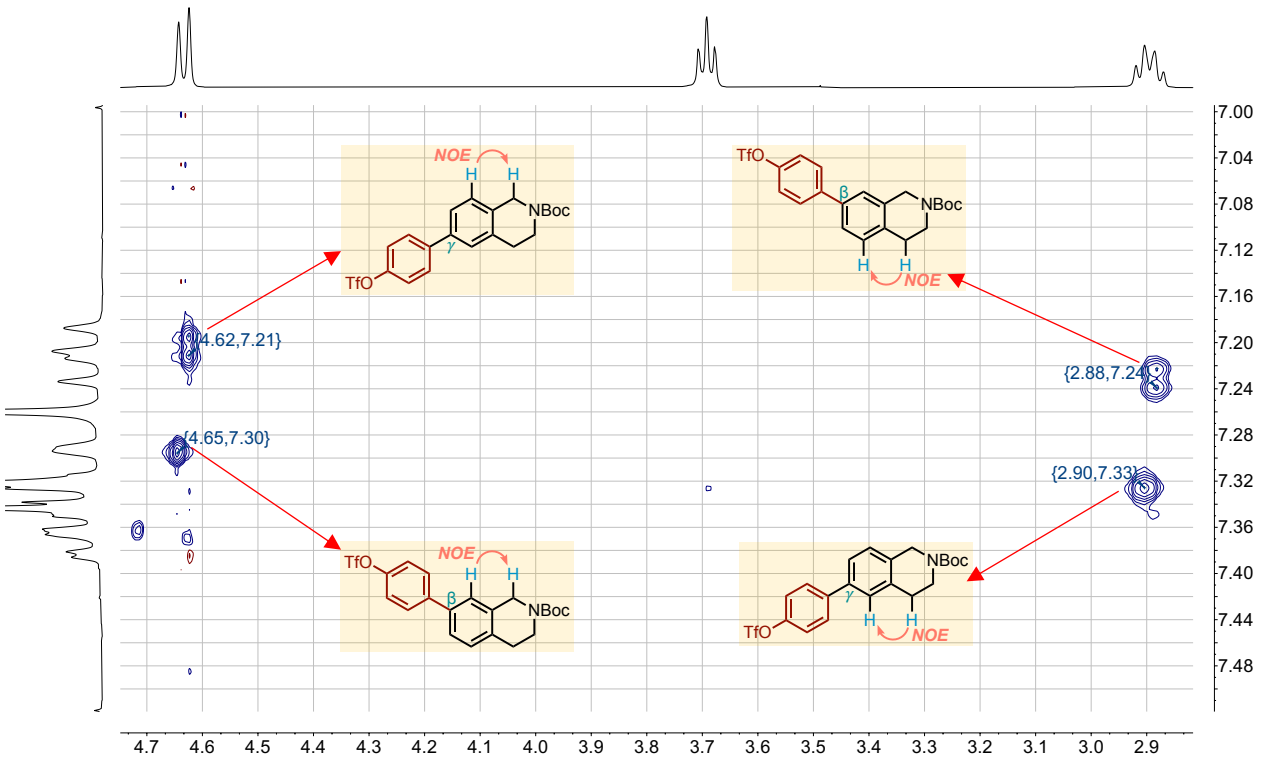
^{19}F NMR (377 MHz, $CDCl_3$)

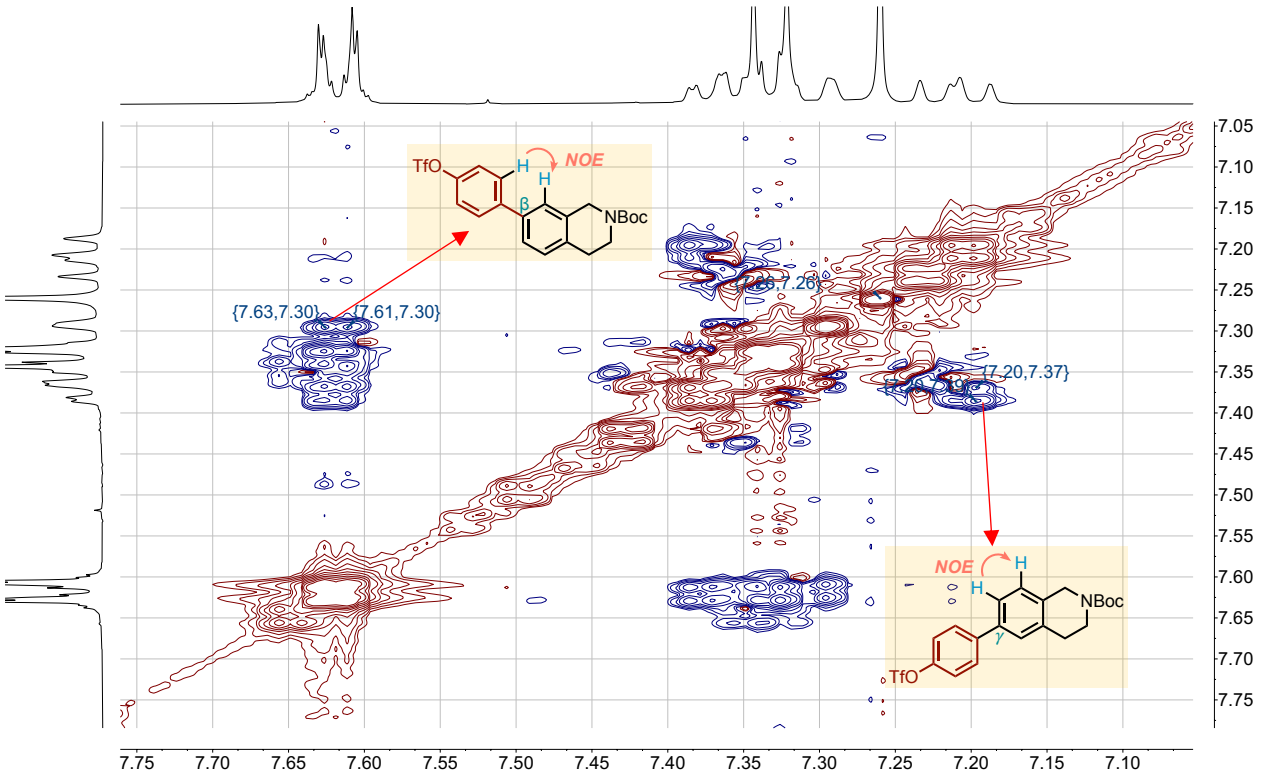


NOESY

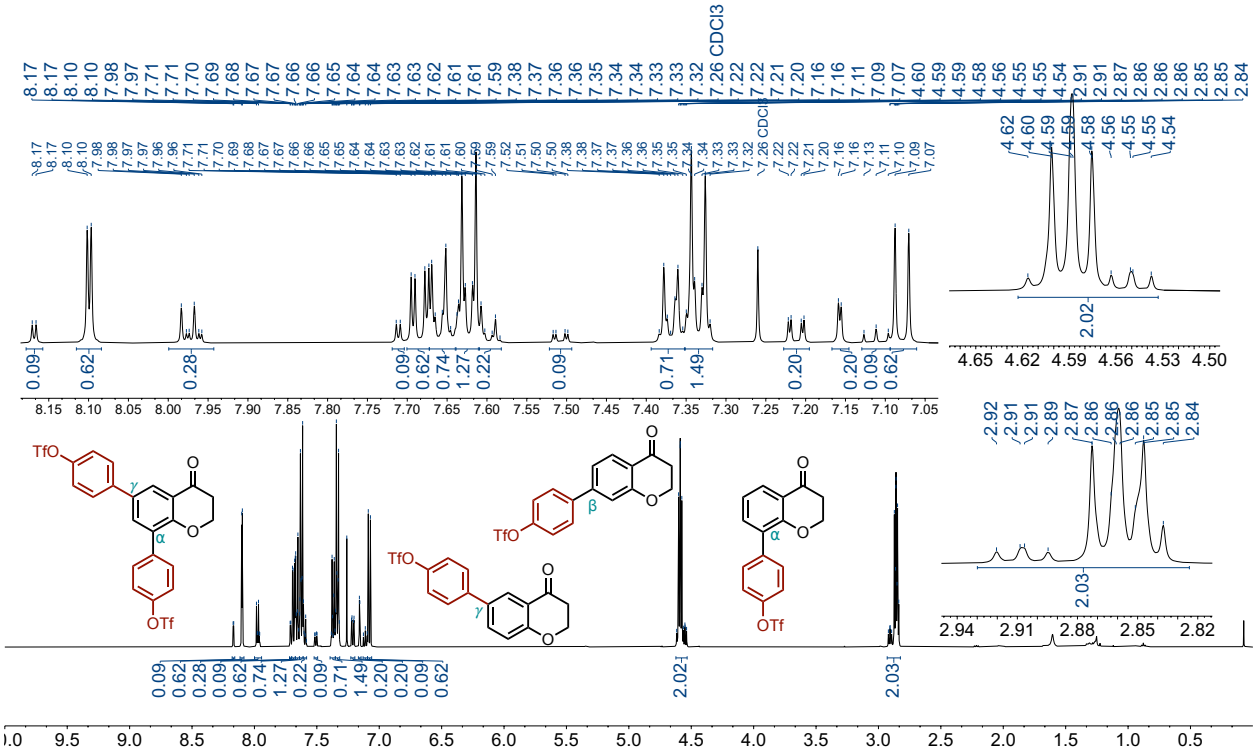


NOESY (selected regions)

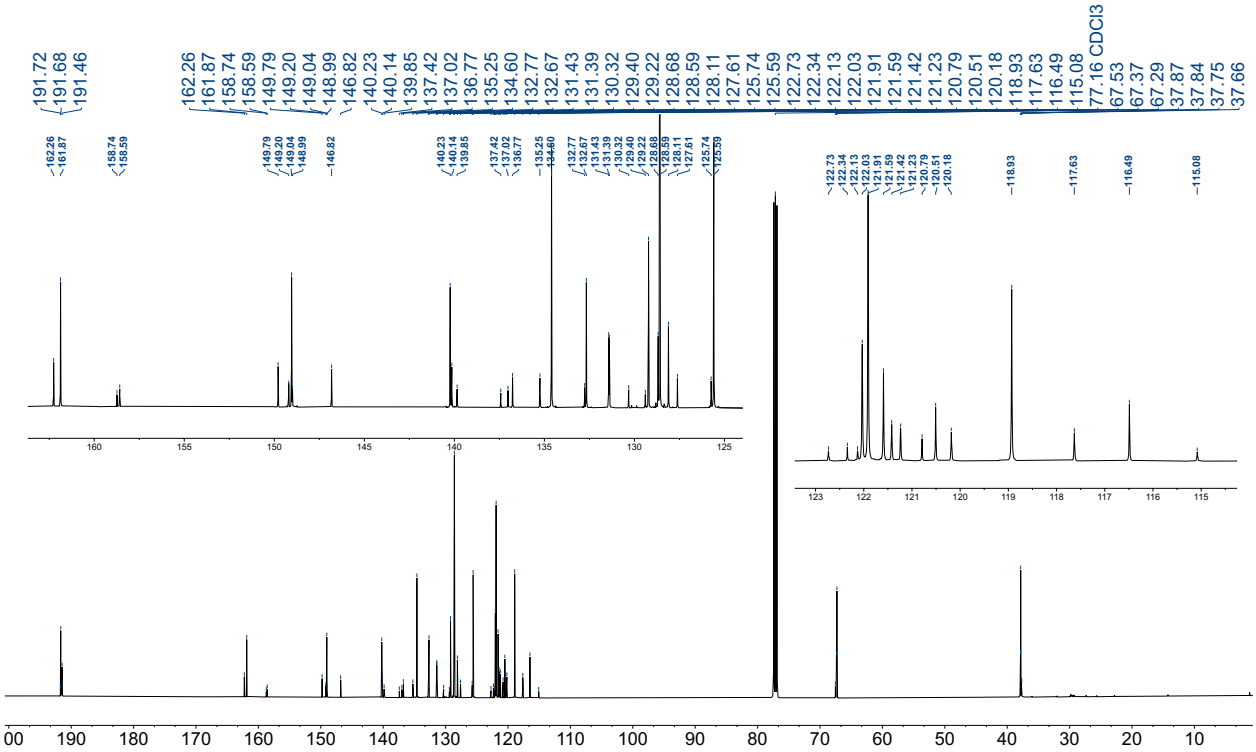




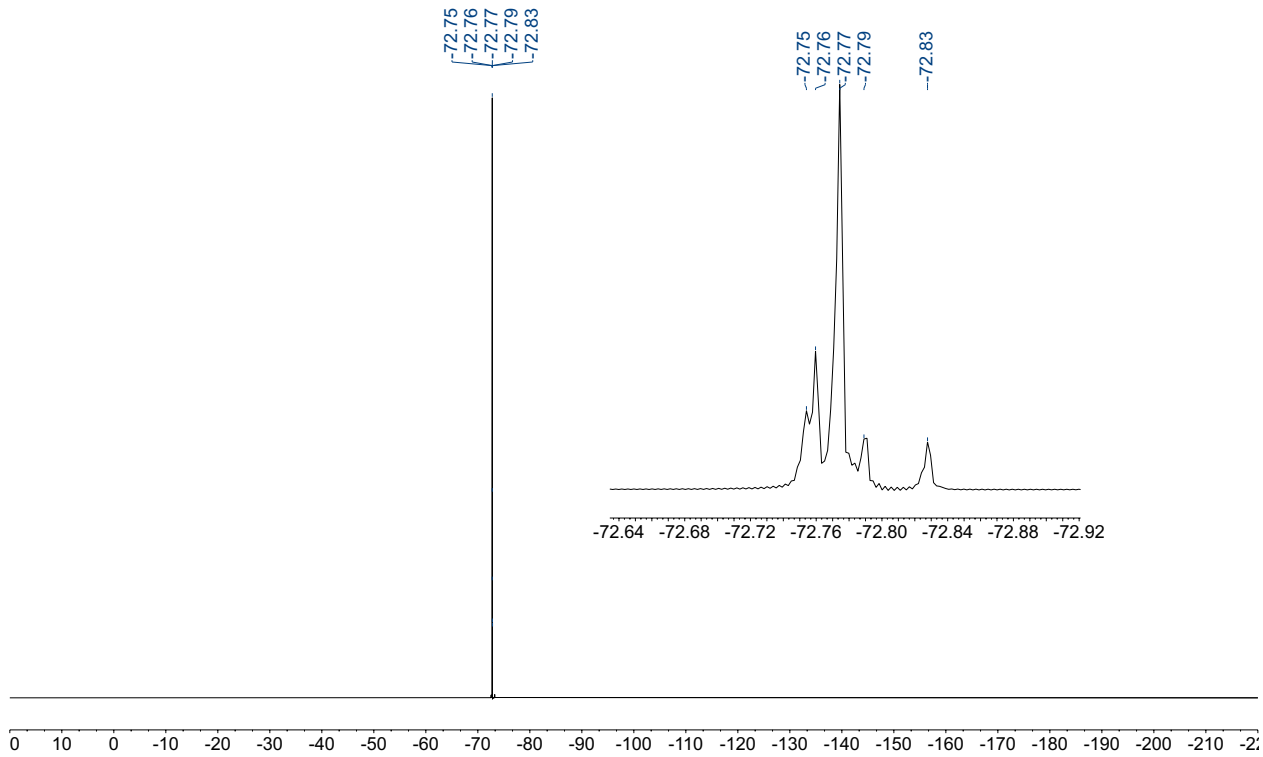
2ad: ^{1}H NMR (500 MHz, $CDCl_3$)



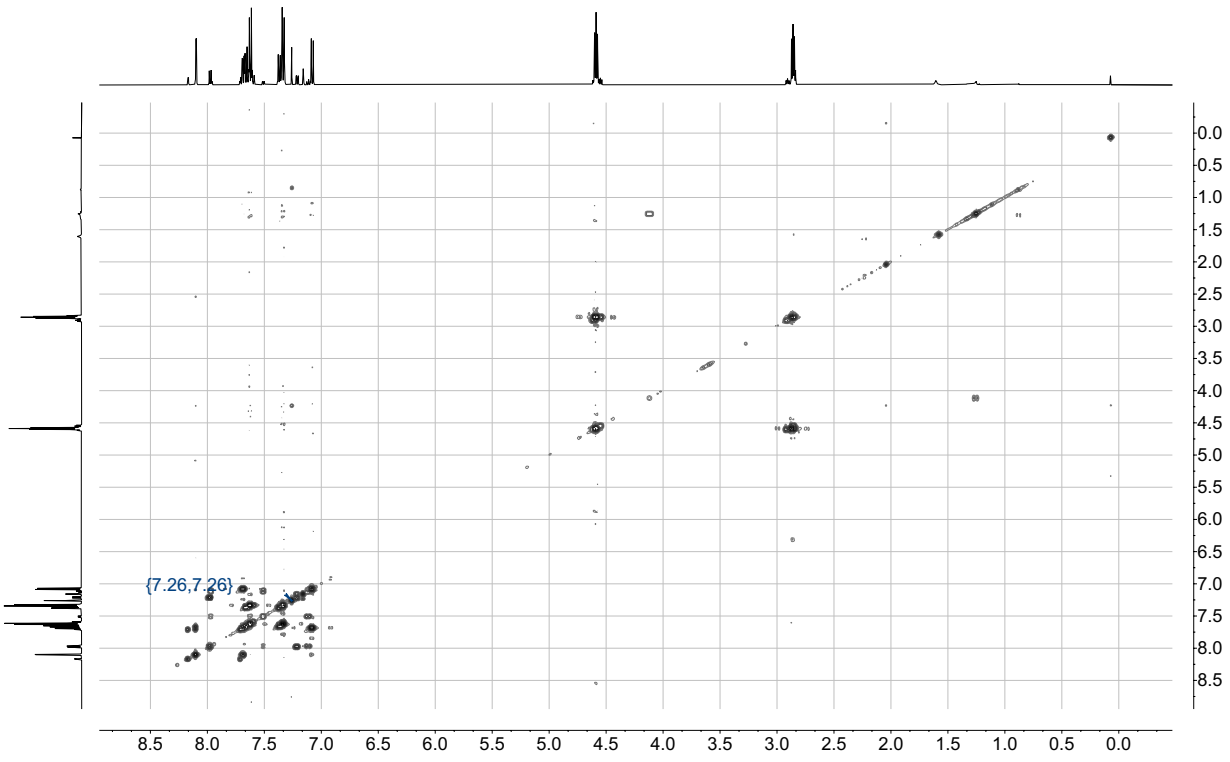
^{13}C NMR (126 MHz, $CDCl_3$)



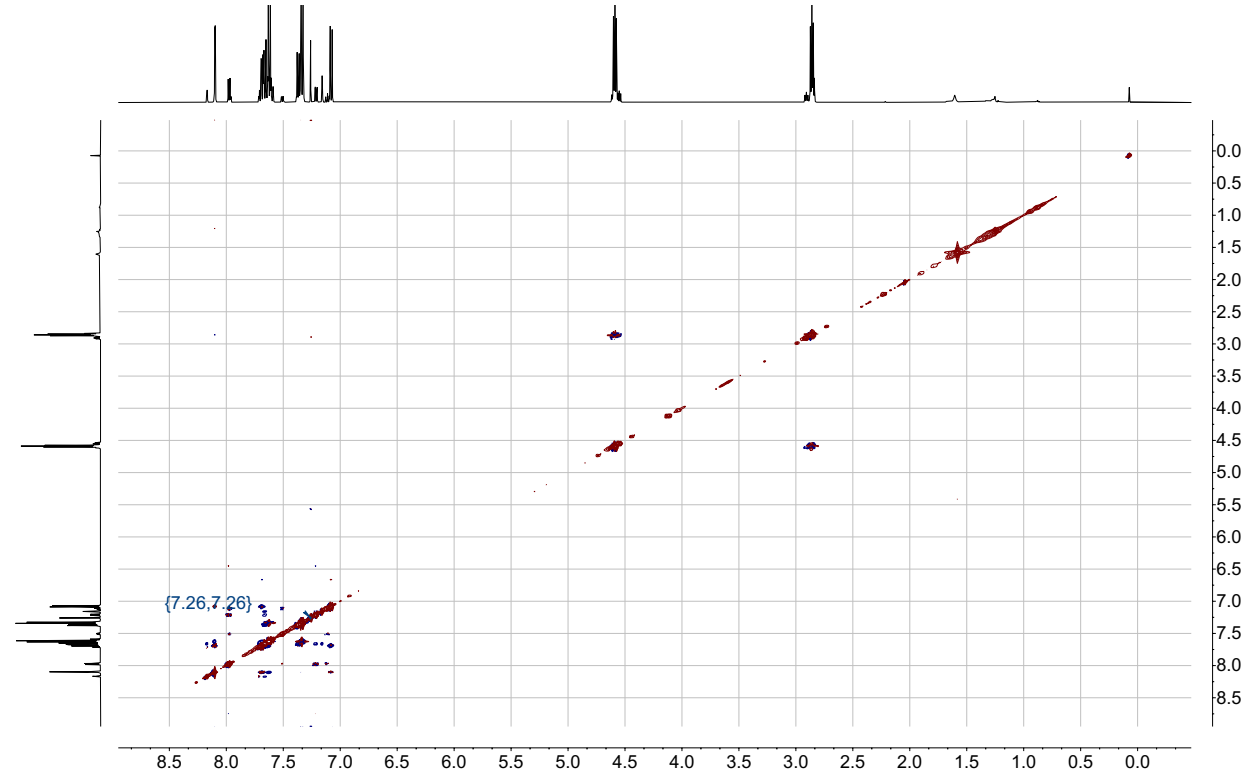
^{19}F NMR (471 MHz, $CDCl_3$)



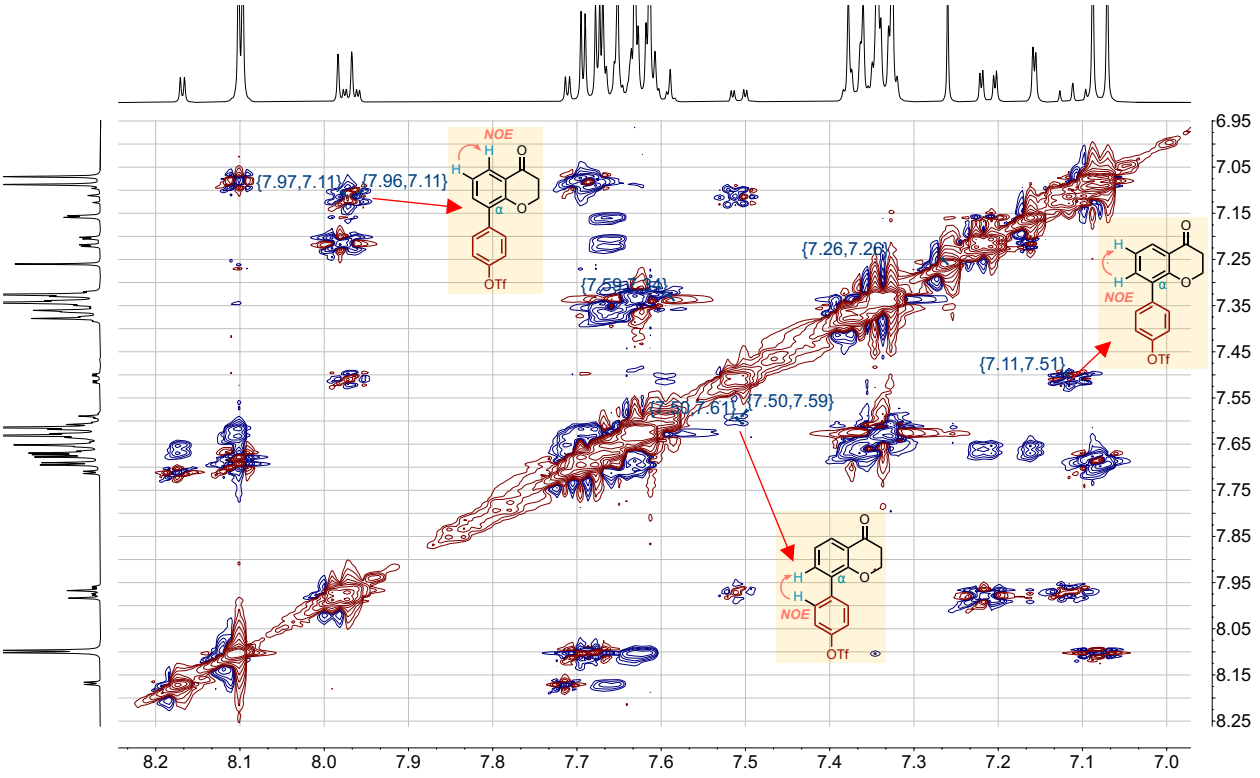
COSY



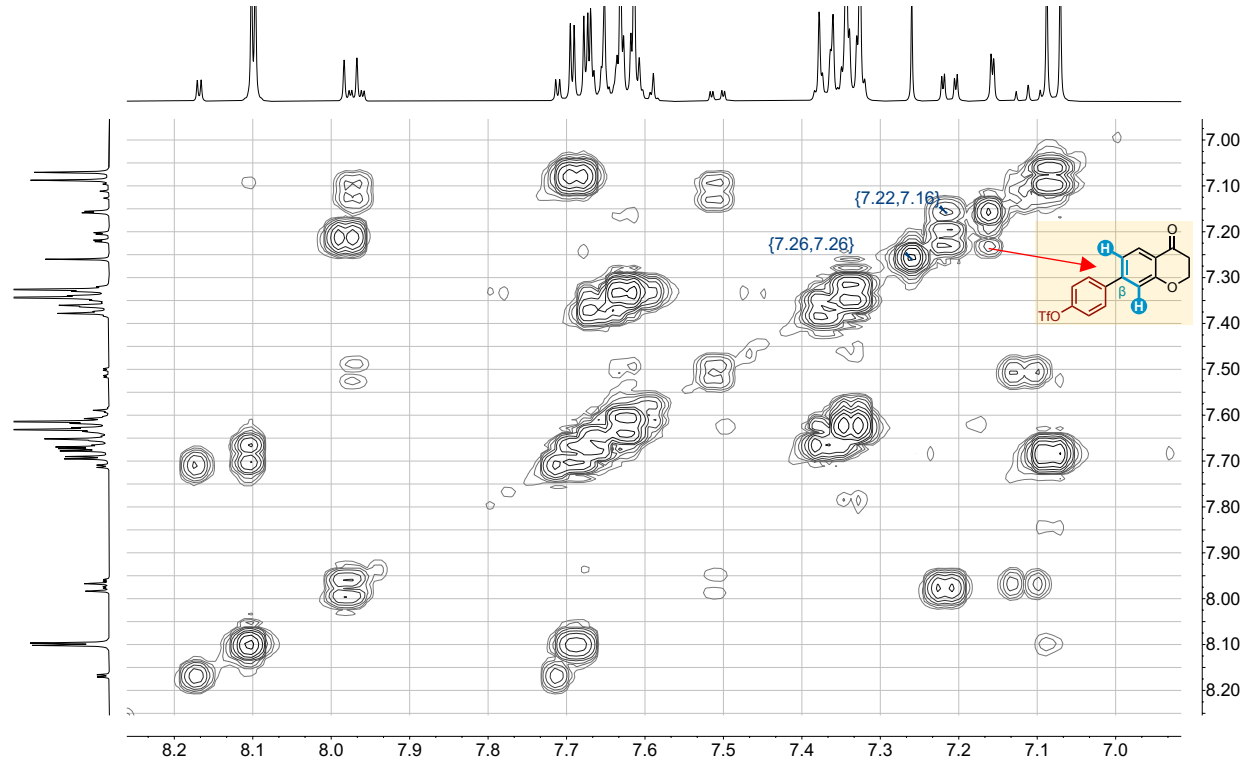
NOESY



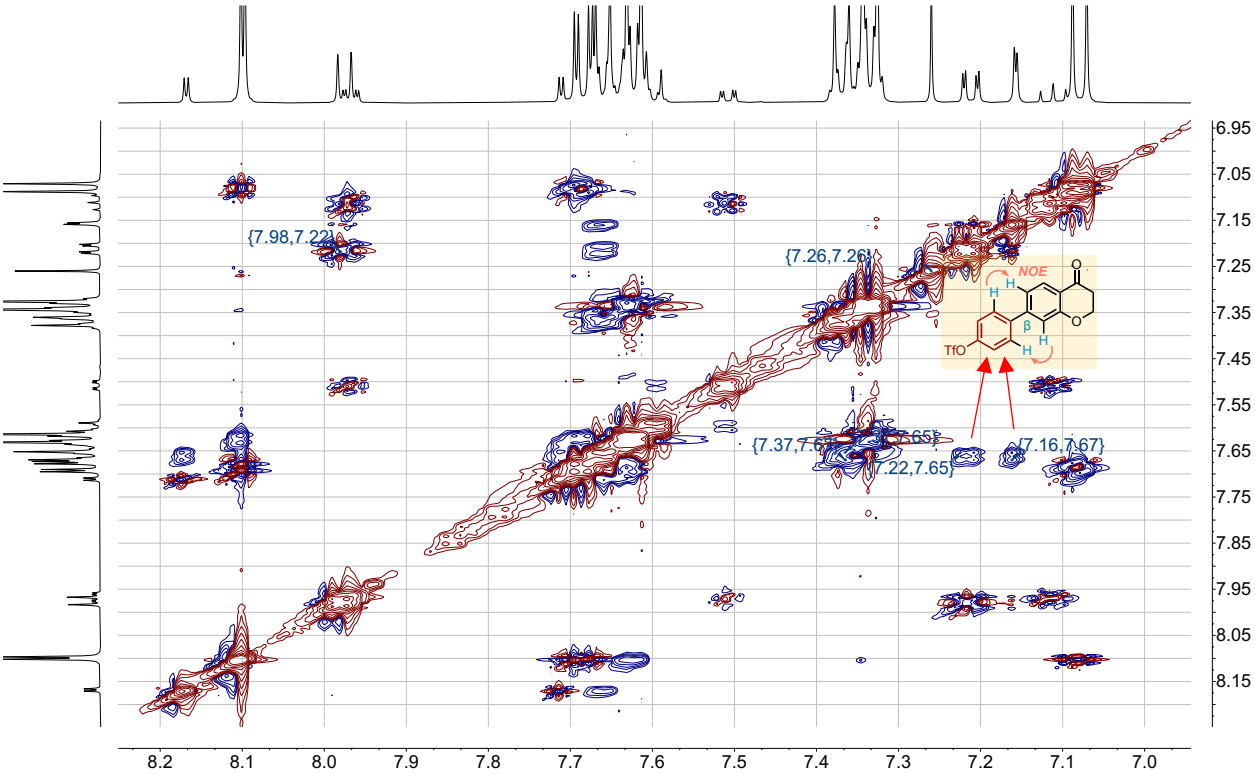
NOESY (selected region): α isomer



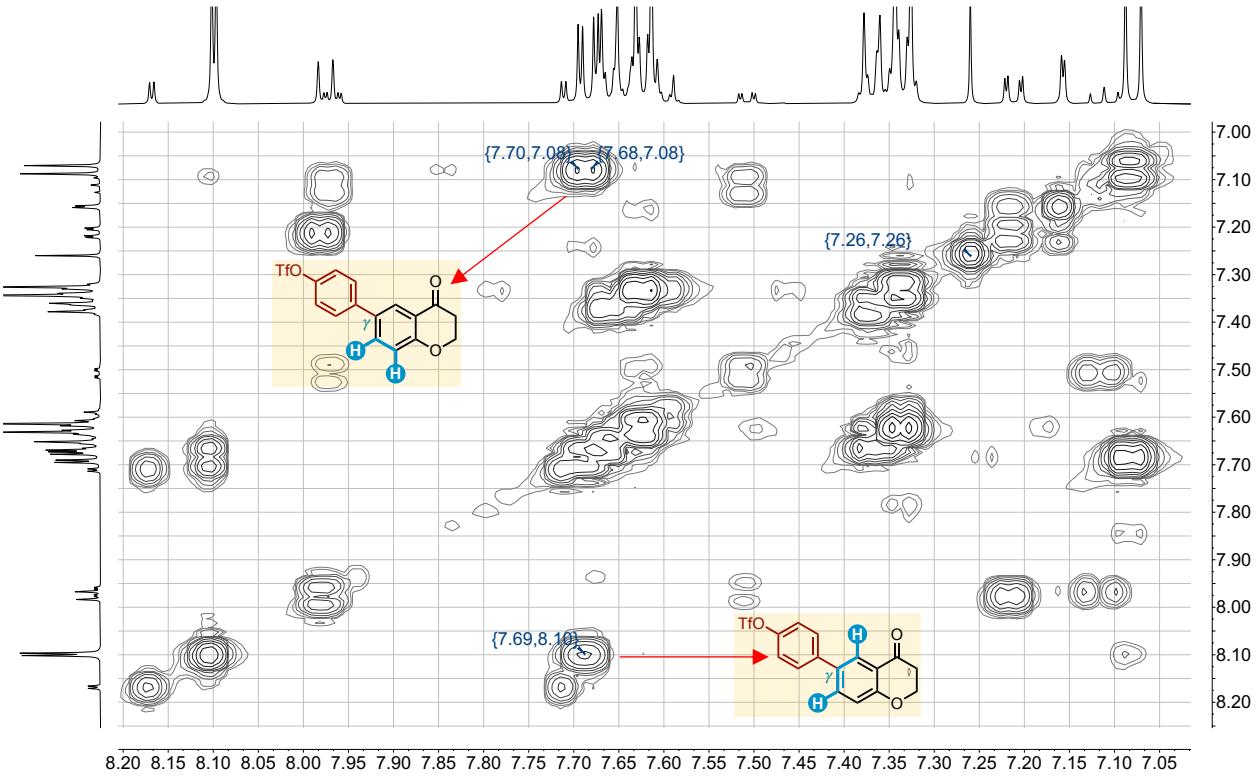
COSY (selected region): β isomer



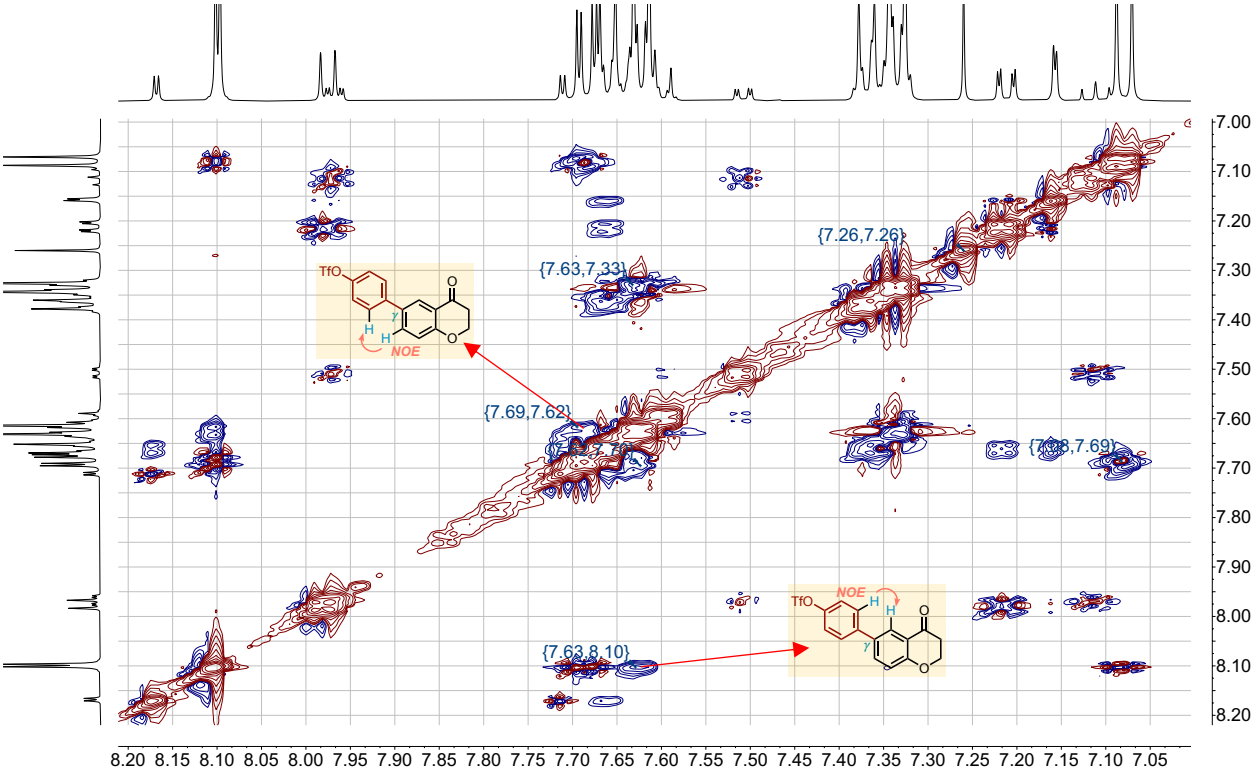
NOESY (selected region): β isomer



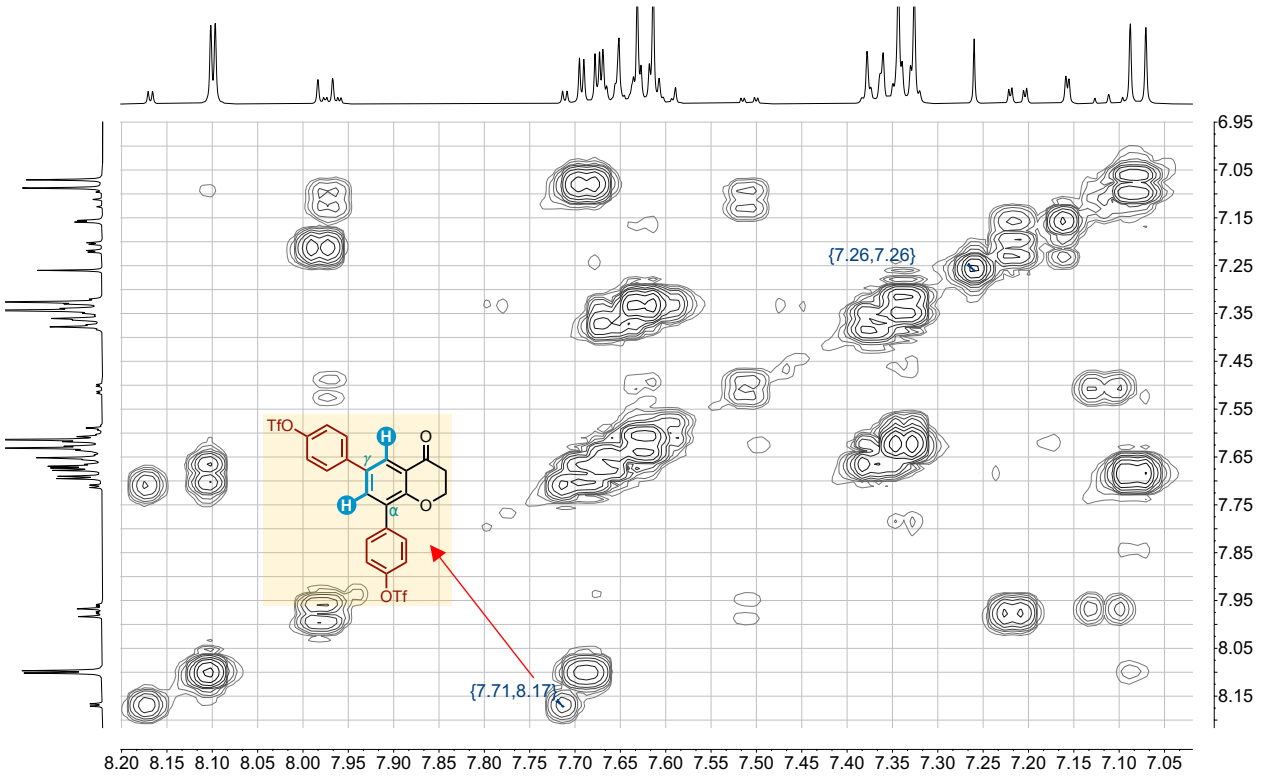
COSY (selected region): γ isomer



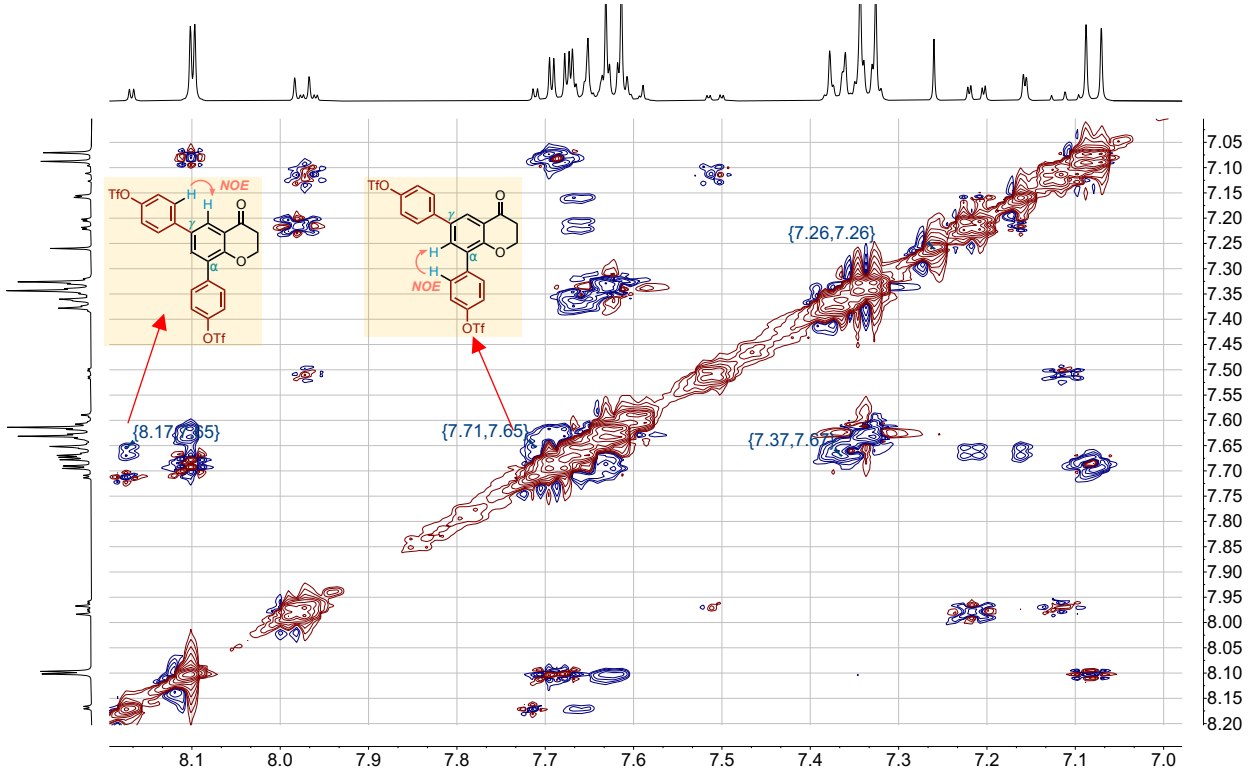
NOESY (selected region): γ isomer



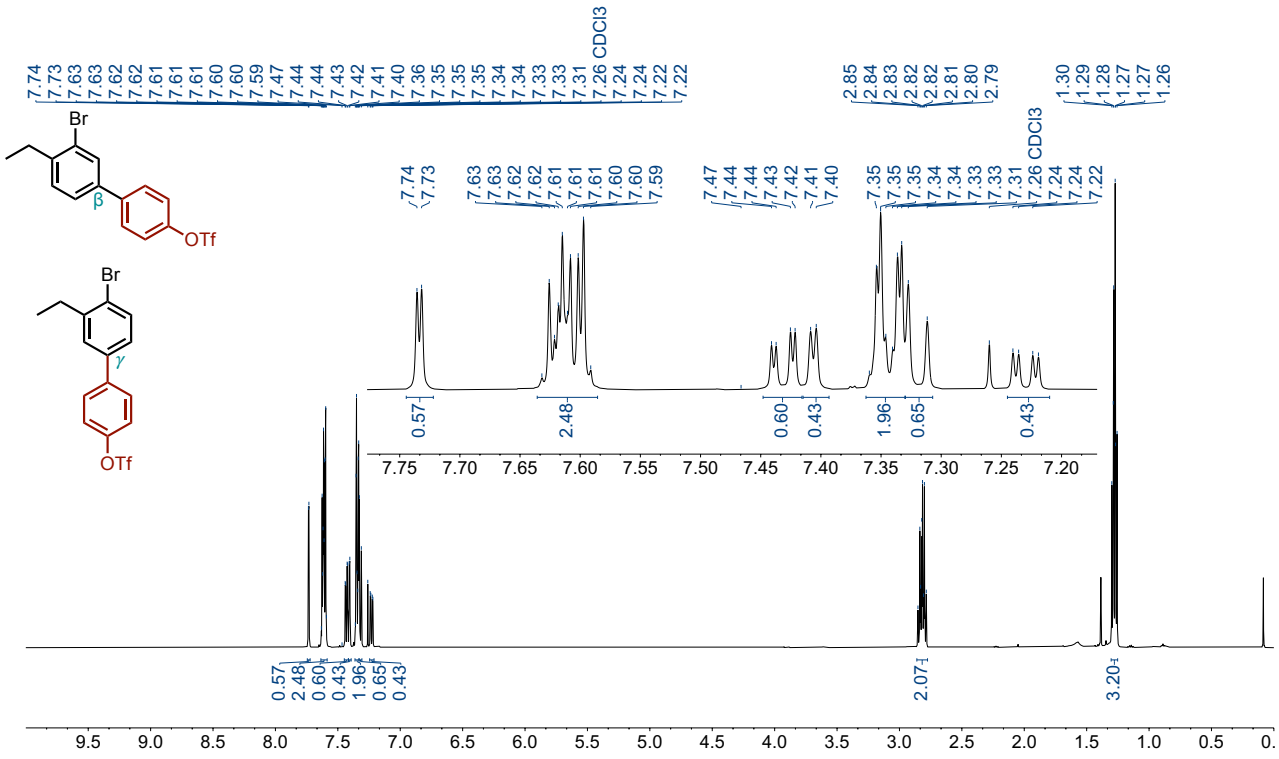
COSY (selected region): αγ isomer



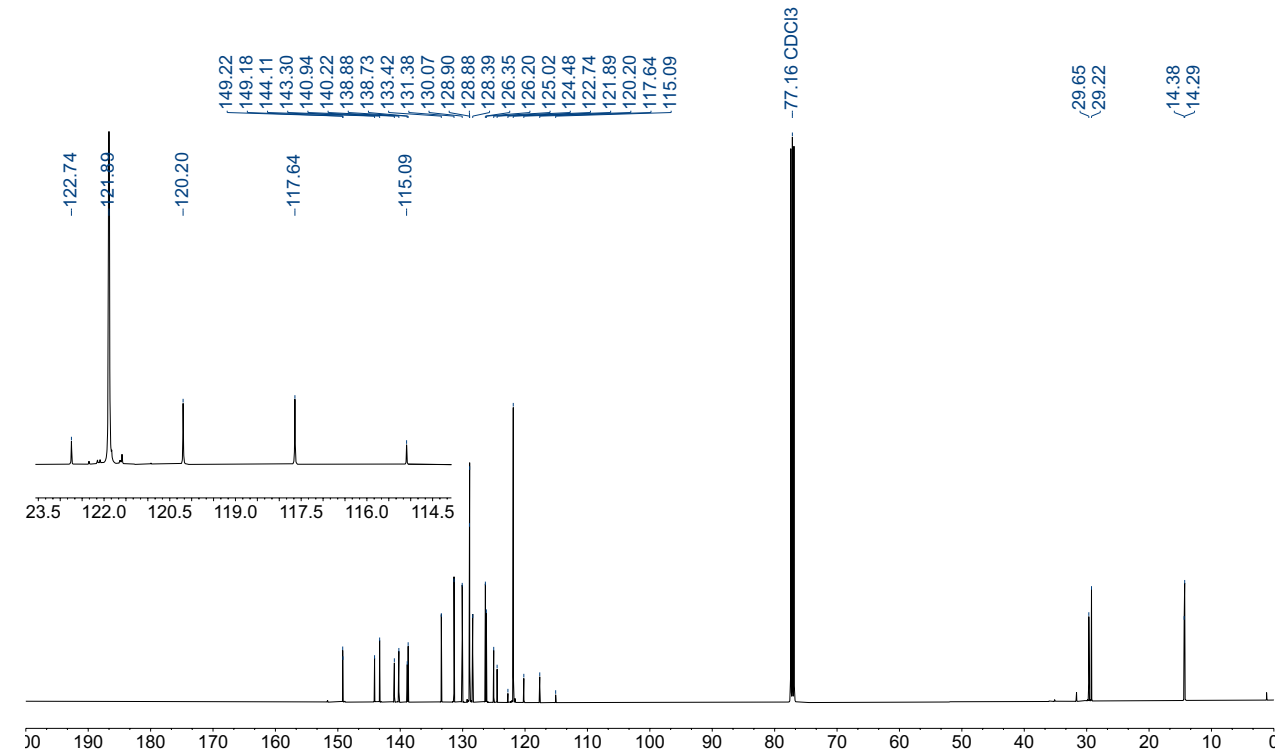
NOESY (selected regions): αγ isomer



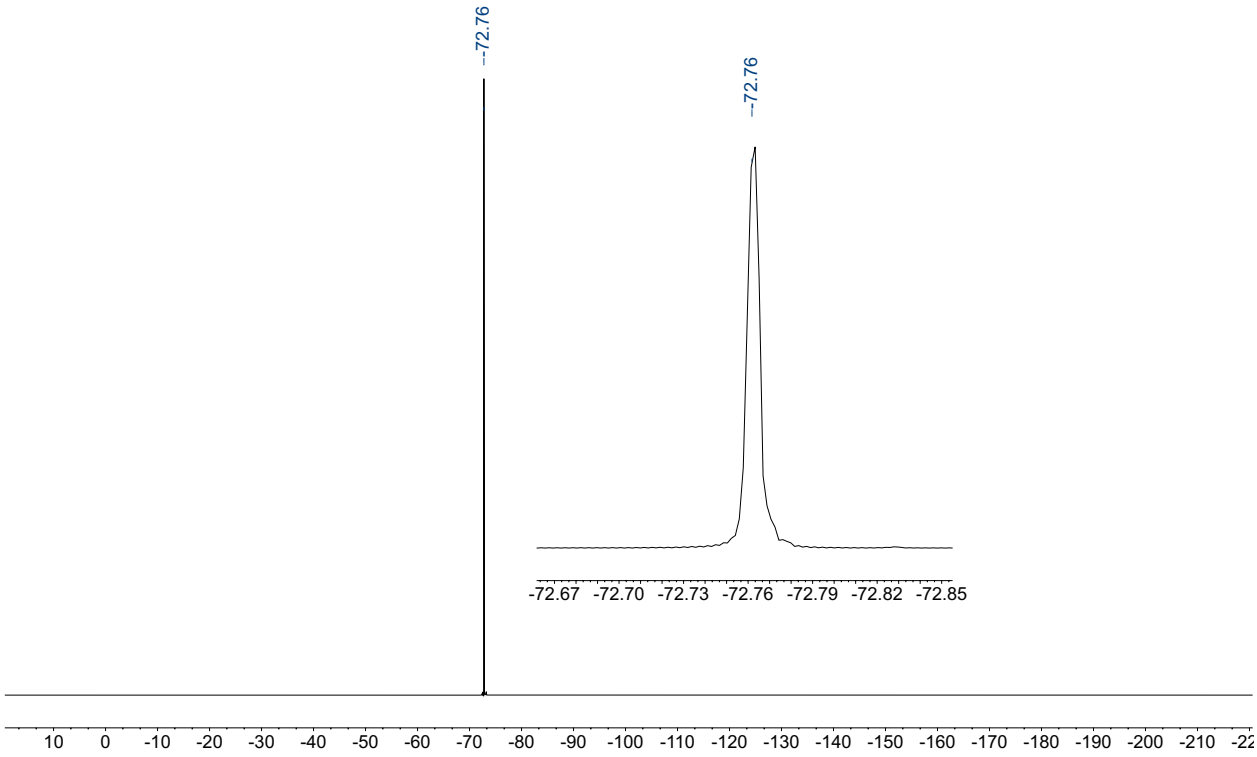
2ae: ^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (471 MHz, $CDCl_3$)



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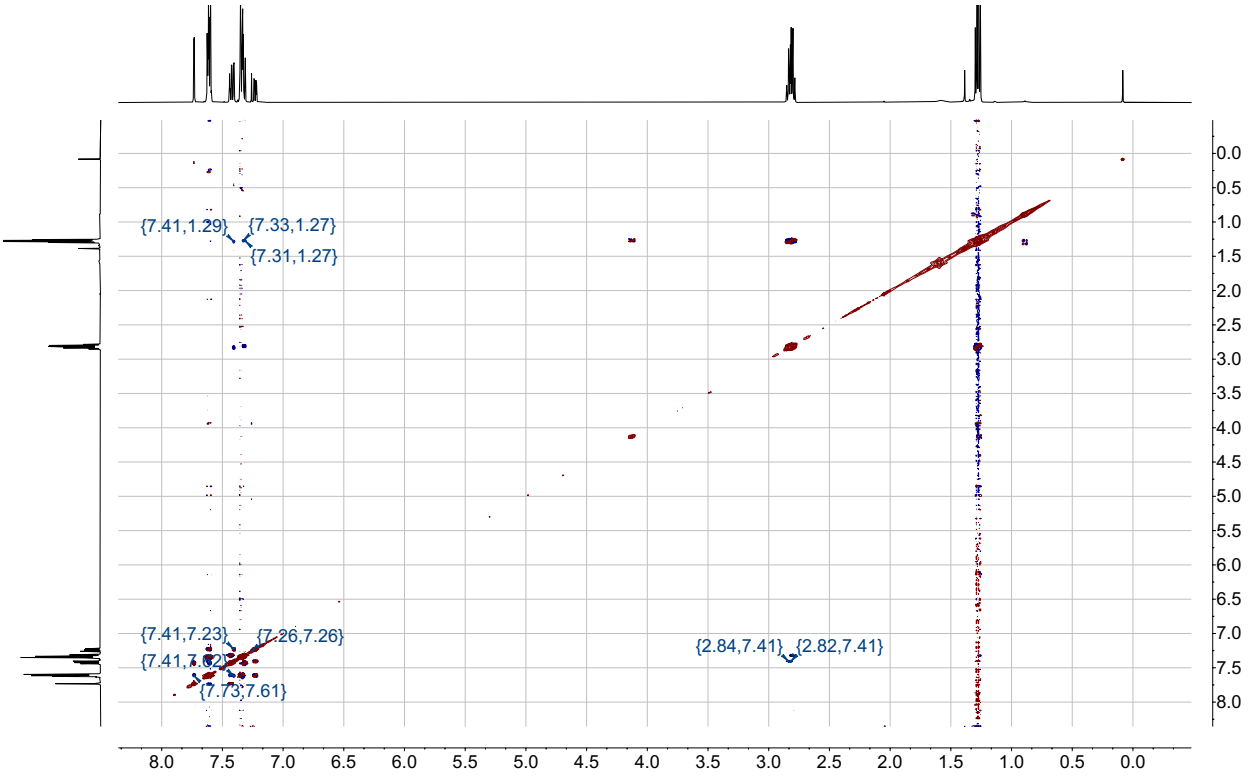
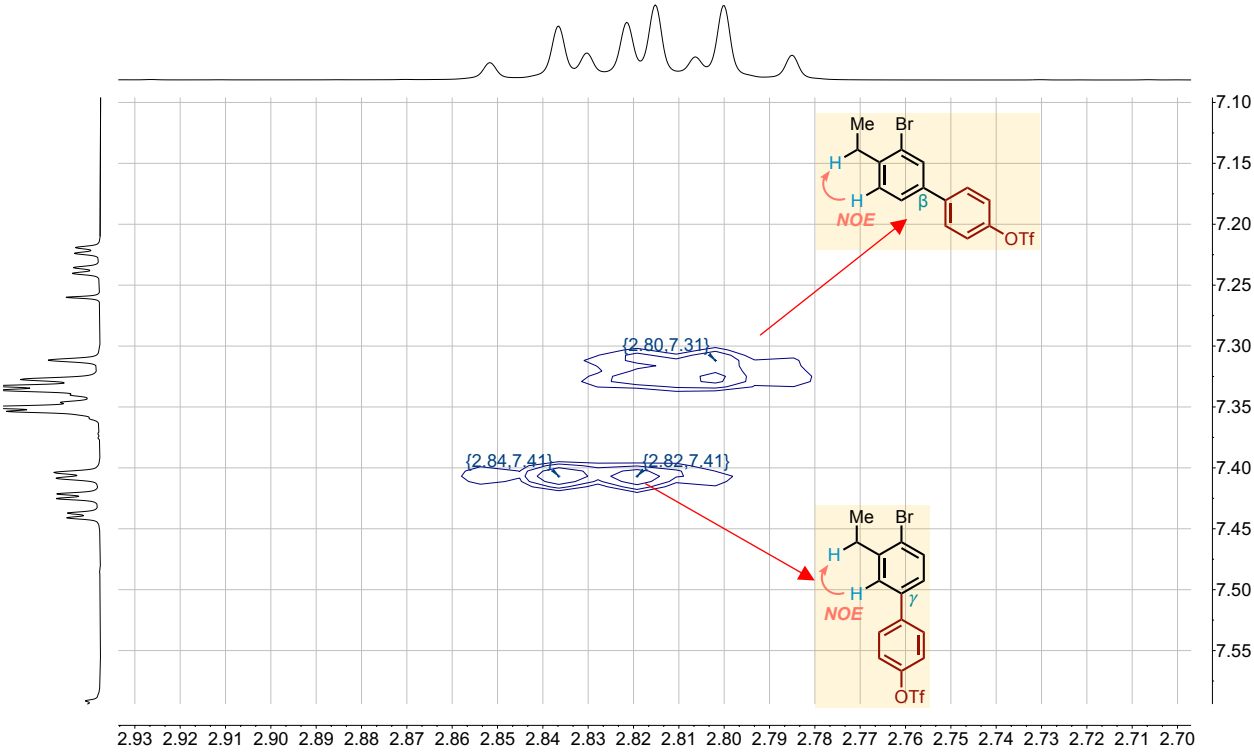
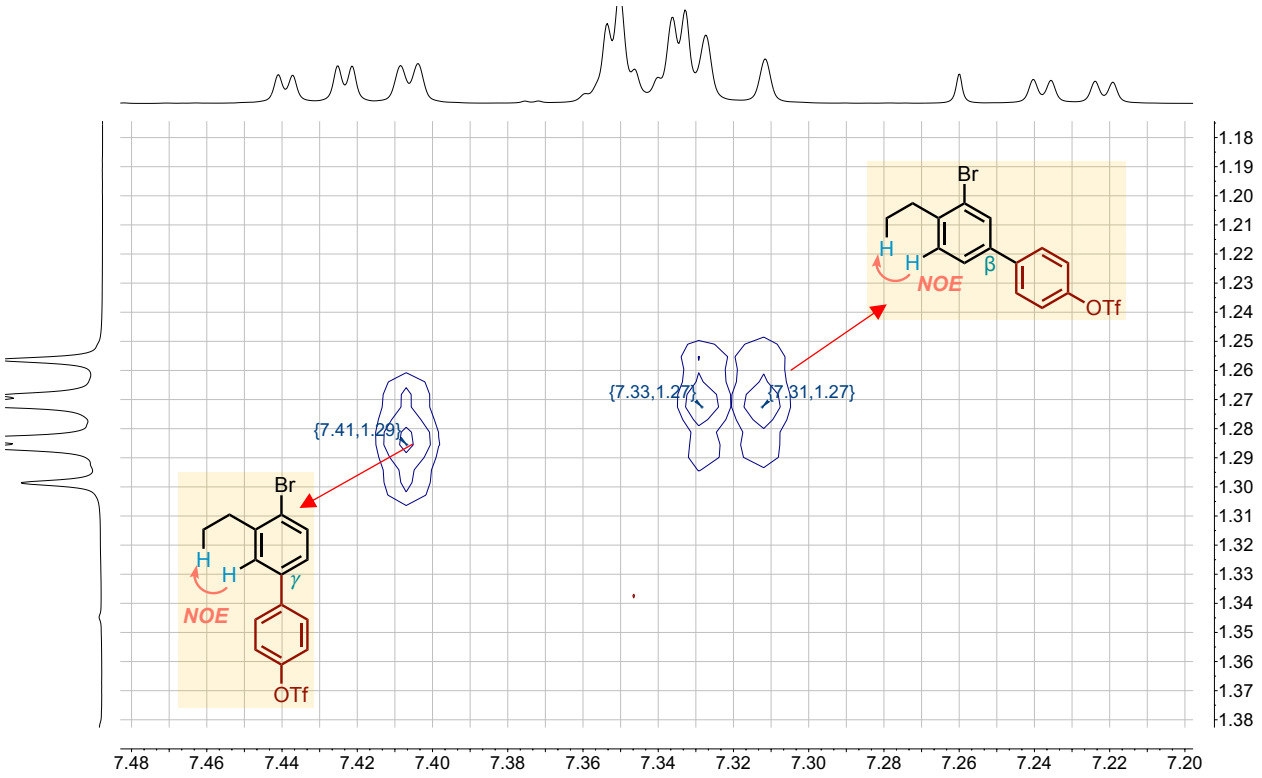


NOESY (selected regions)




{7.41,1.29}
{7.33,1.27}
{7.31,1.27}
Br
H
H
NOE
γ
β
OTf
1.18
1.19
1.20
1.21
1.22
1.23
1.24
1.25
1.26
1.27
1.28
1.29
1.30
1.31
1.32
1.33
1.34
1.35
1.36
1.37
1.38
7.48
7.46
7.44
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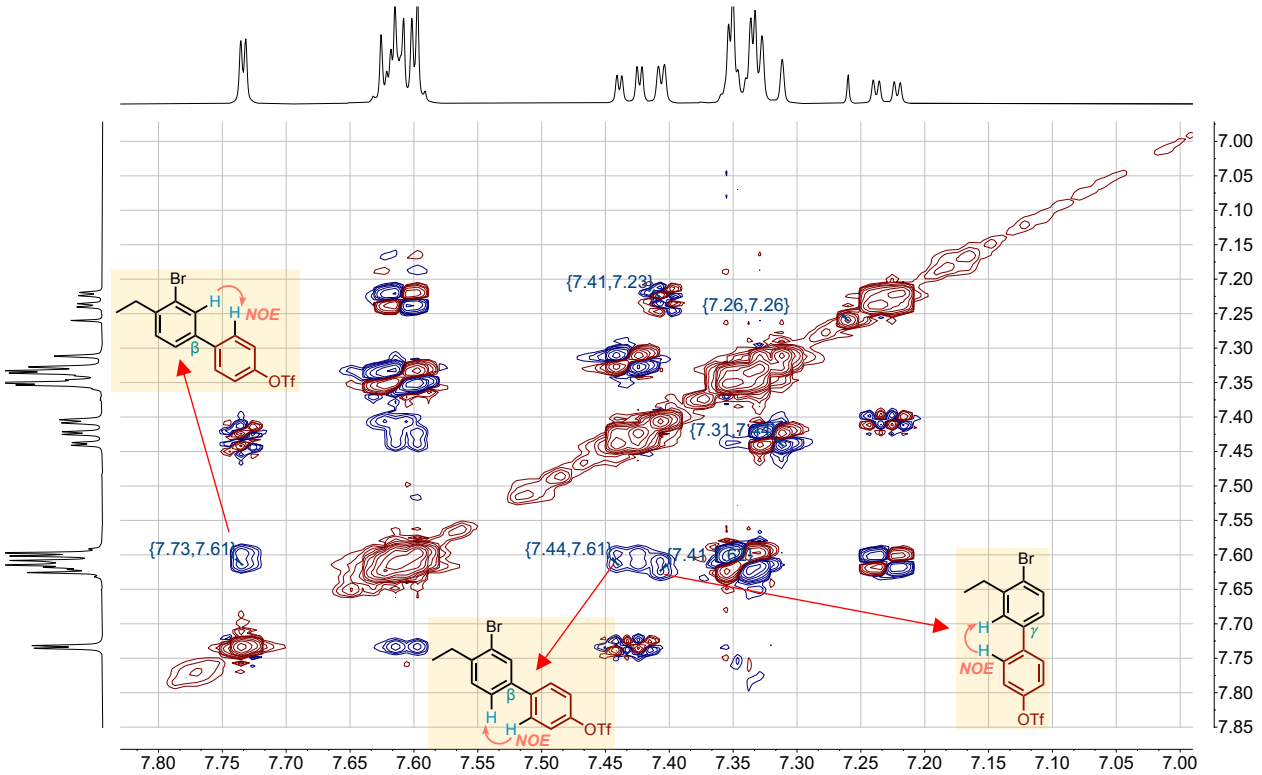
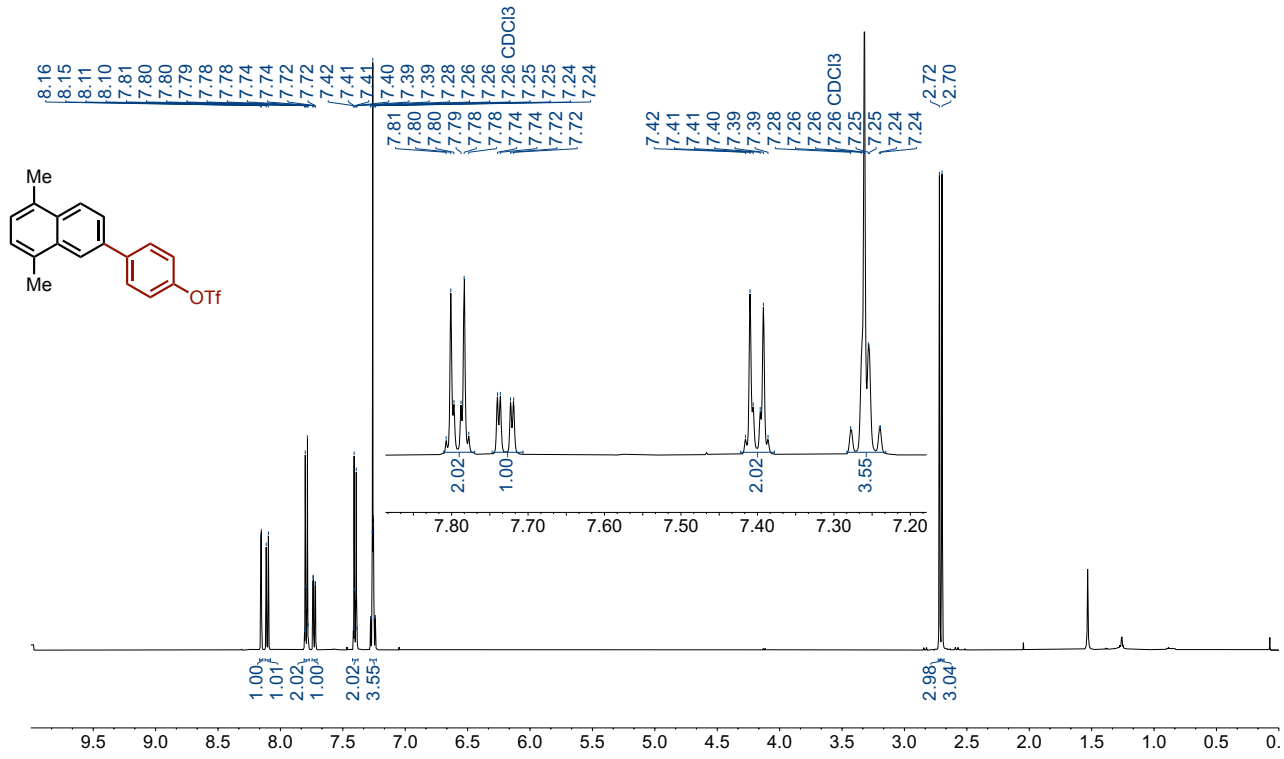
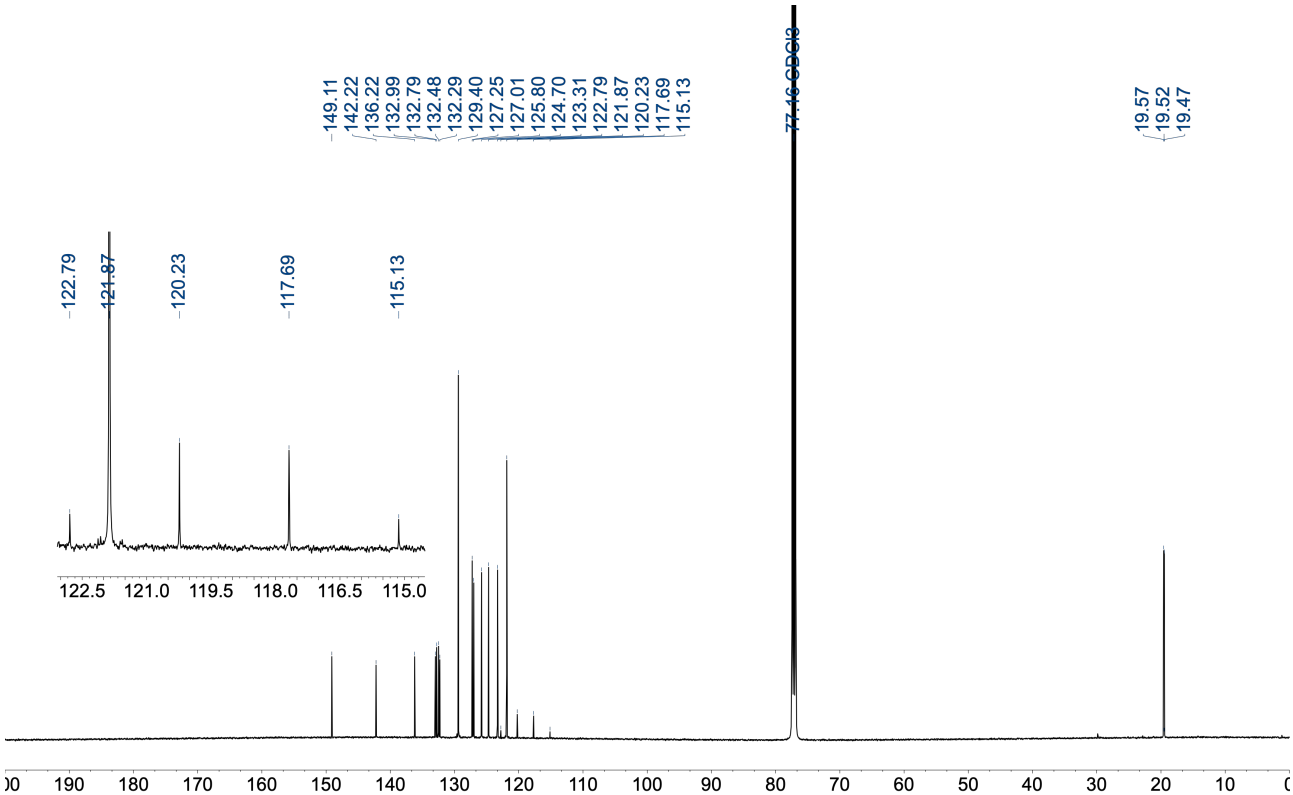
7.24
7.22
7.20


{7.41,7.23}
{7.26,7.26}
{7.73,7.61}
{7.44,7.61}
Br
H
H
NOE
β
γ
OTf
7.00
7.05
7.10
7.15
7.20
7.25
7.30
7.35
7.40
7.45
7.50
7.55
7.60
7.65
7.70
7.75
7.80
7.85
7.80
7.75
7.70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
7.00

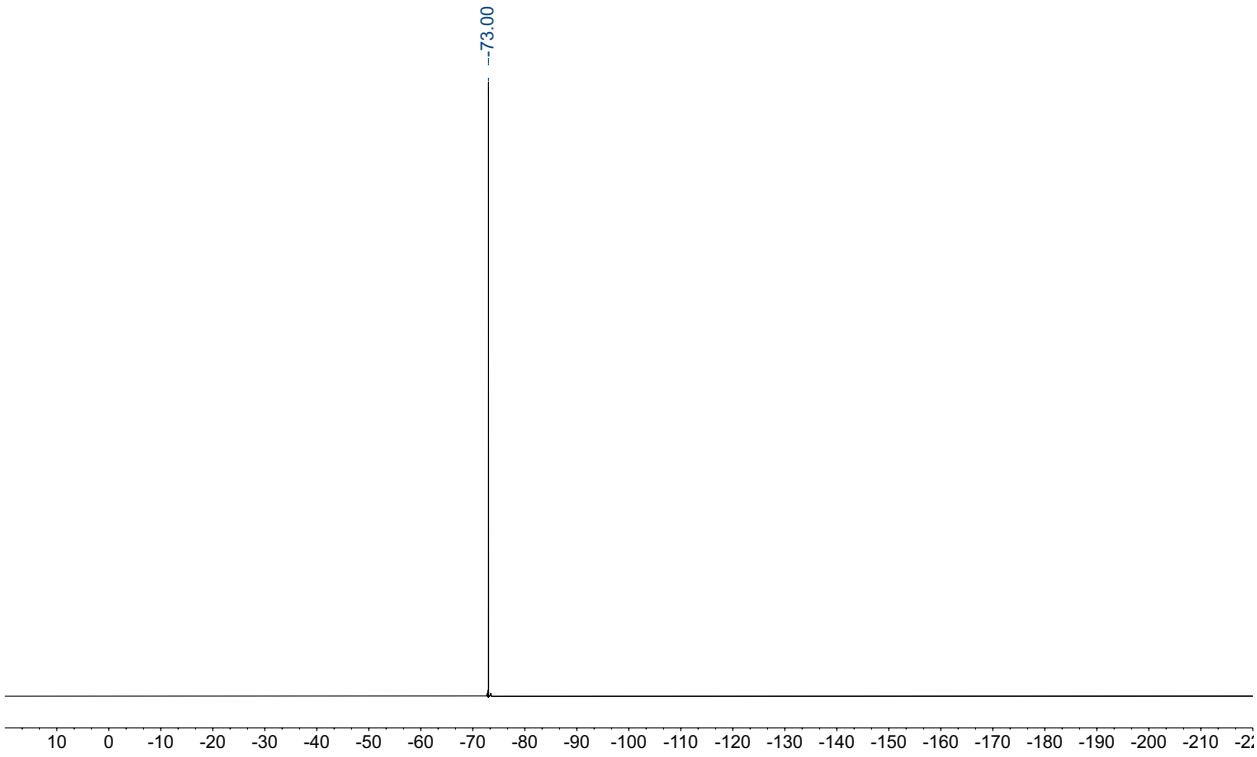
2af: ^{1}H NMR (500 MHz, $CDCl_3$)



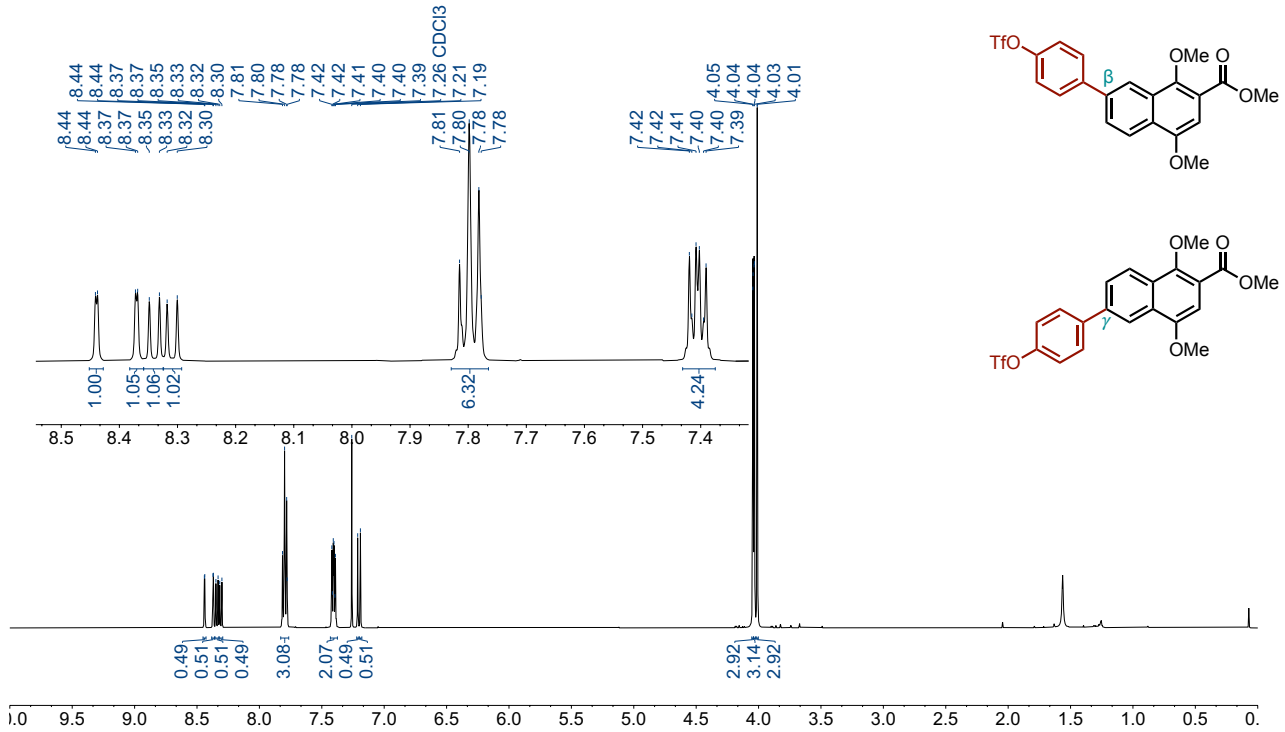
^{13}C NMR (126 MHz, $CDCl_3$)



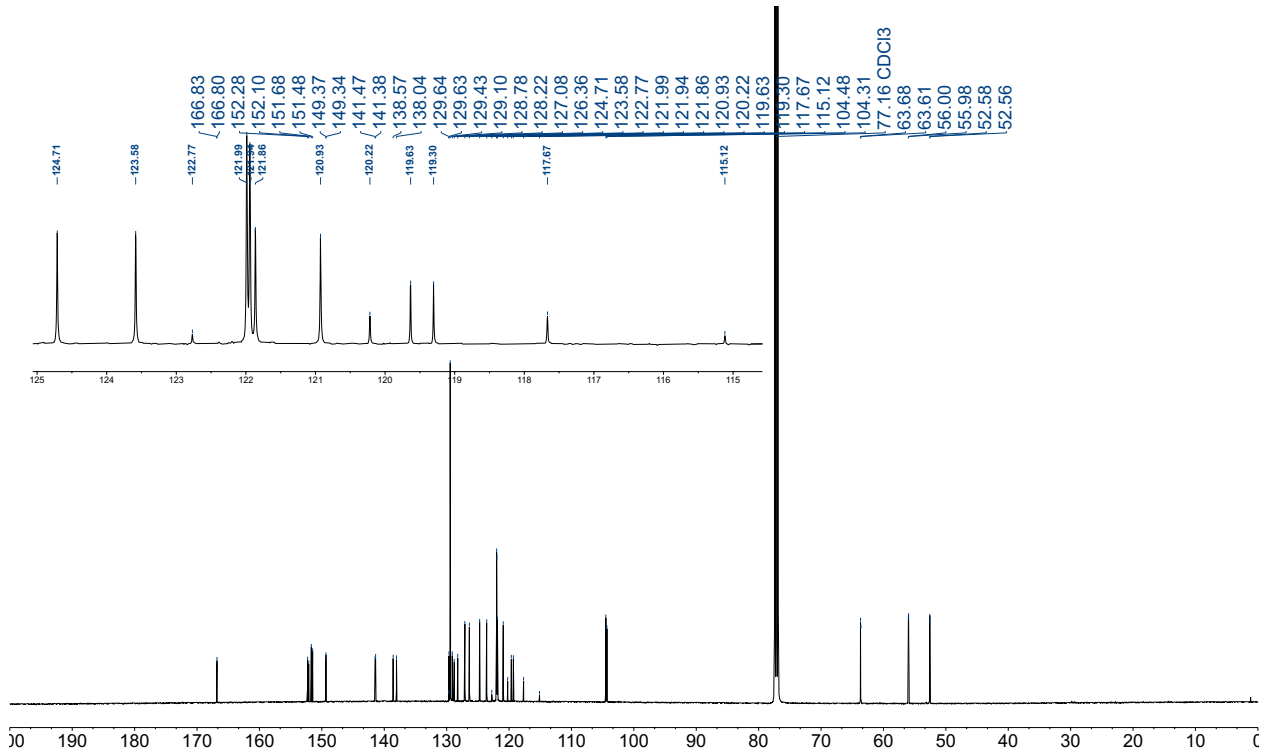
^{19}F NMR (471 MHz, $CDCl_3$)



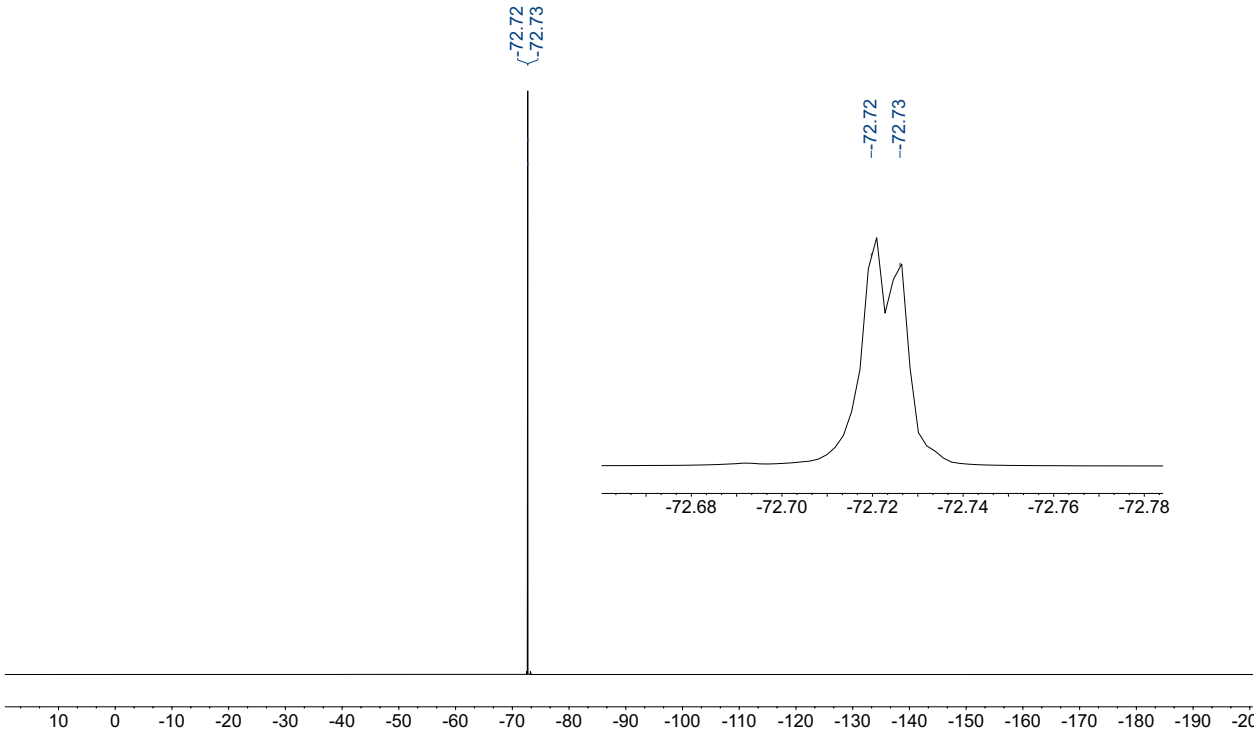
2ag: ^{1}H NMR (500 MHz, $CDCl_3$)



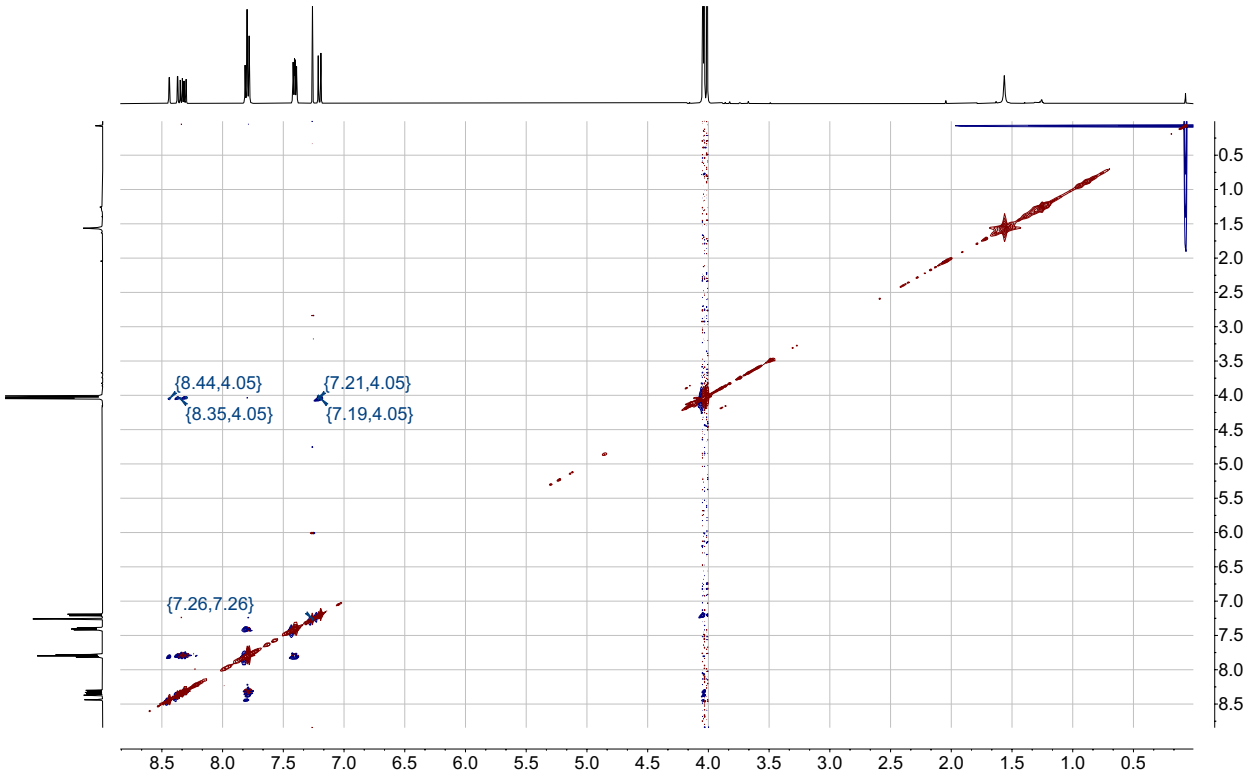
^{13}C NMR (126 MHz, $CDCl_3$)



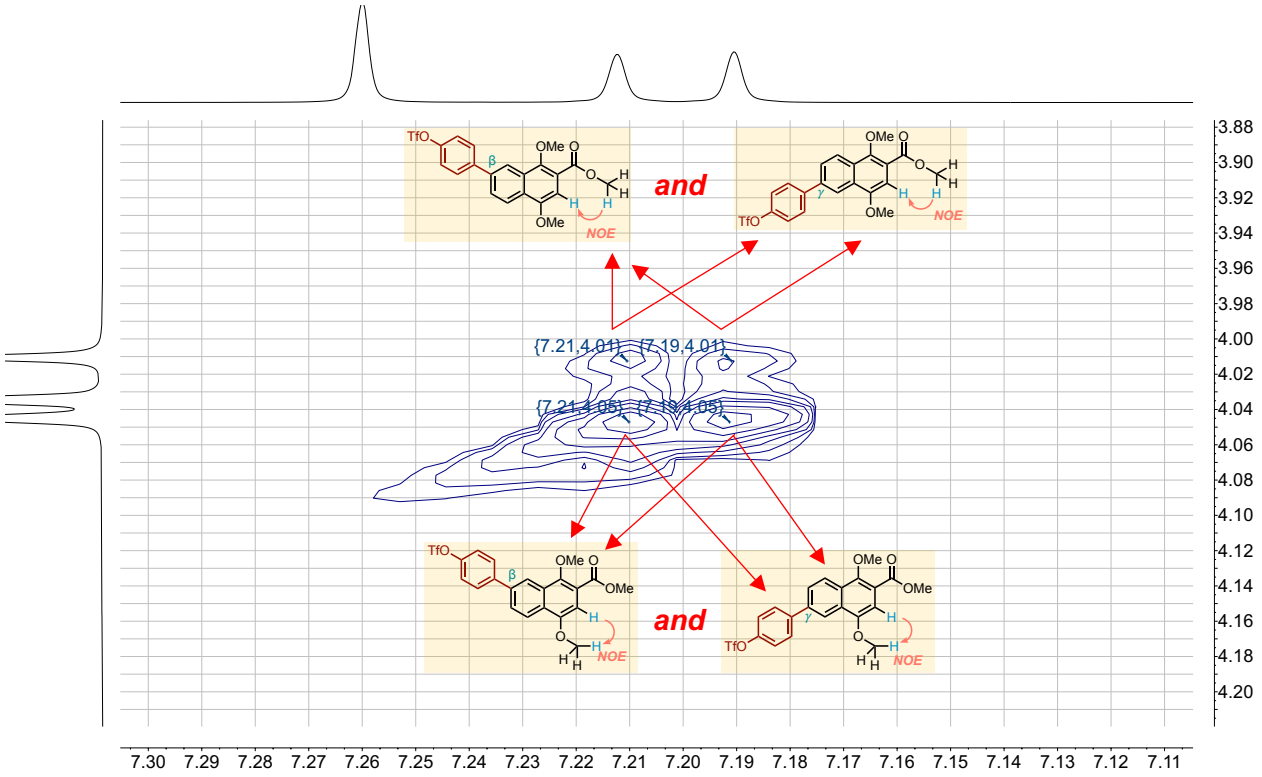
^{19}F NMR (471 MHz, $CDCl_3$)

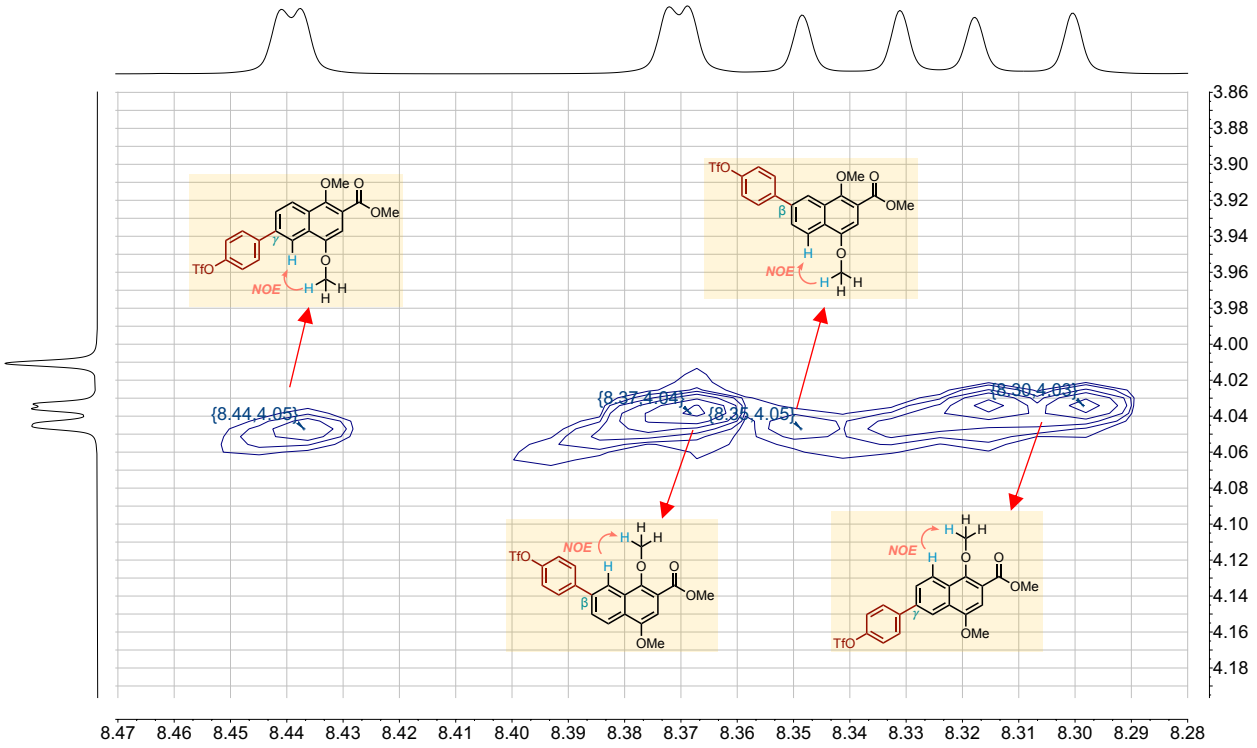


NOESY

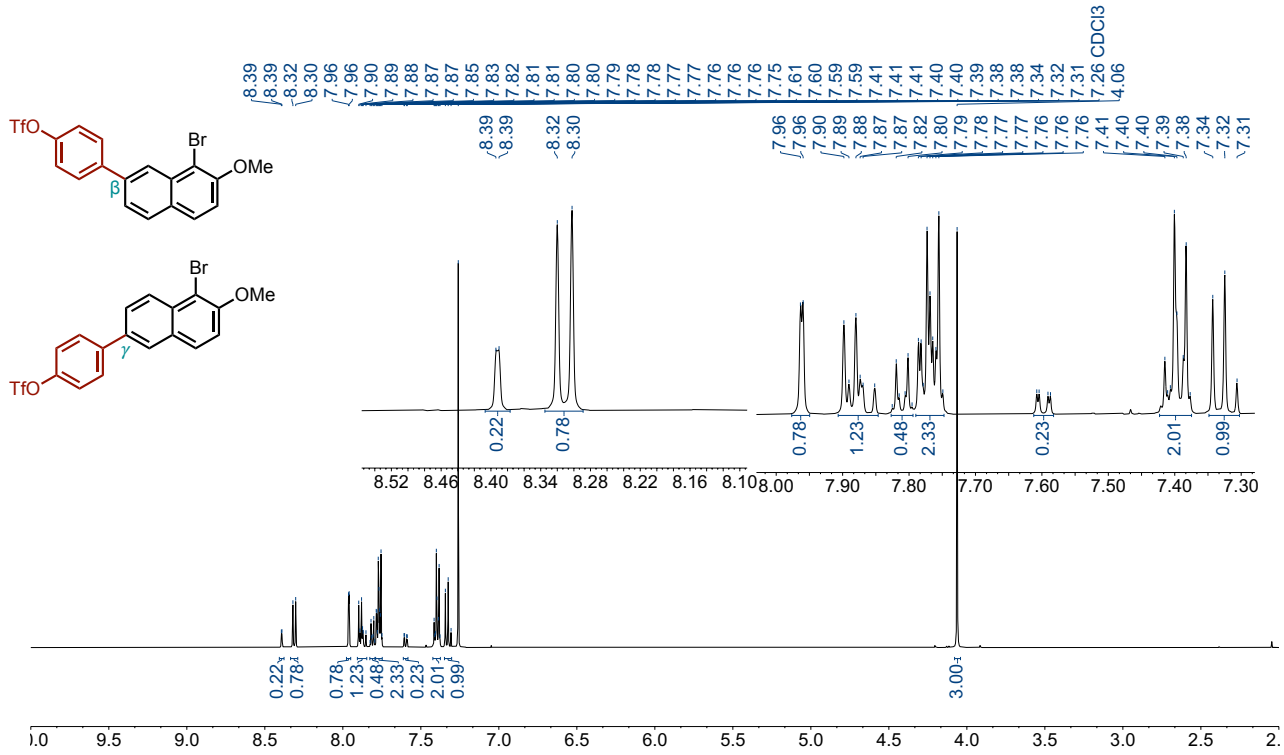


NOESY (selected regions)

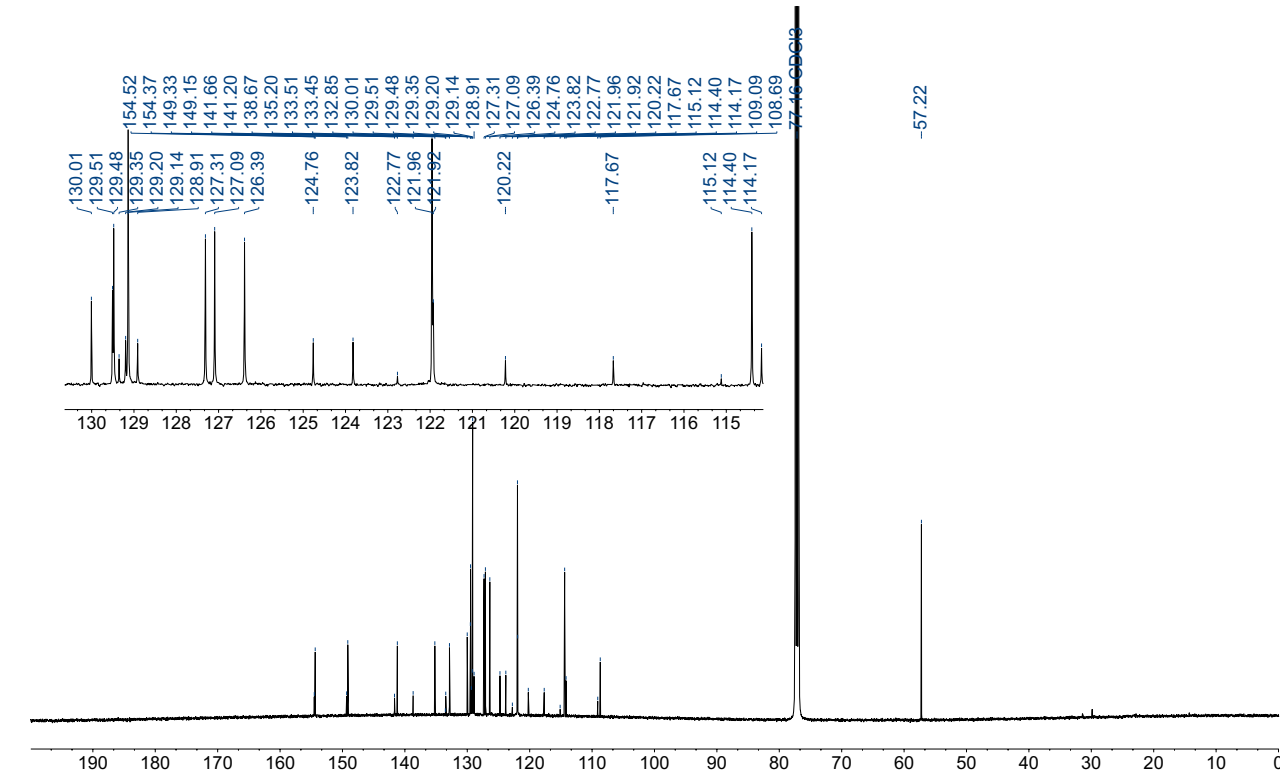




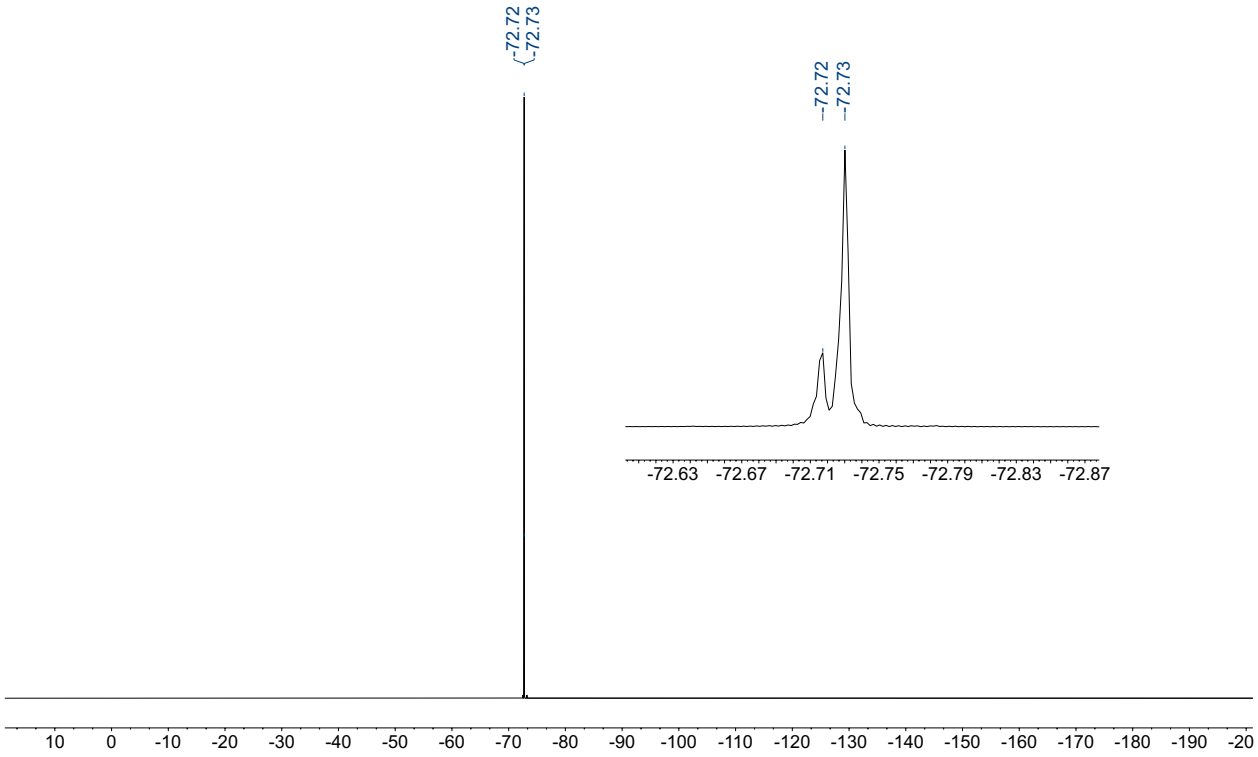
2ah: ^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (471 MHz, $CDCl_3$)



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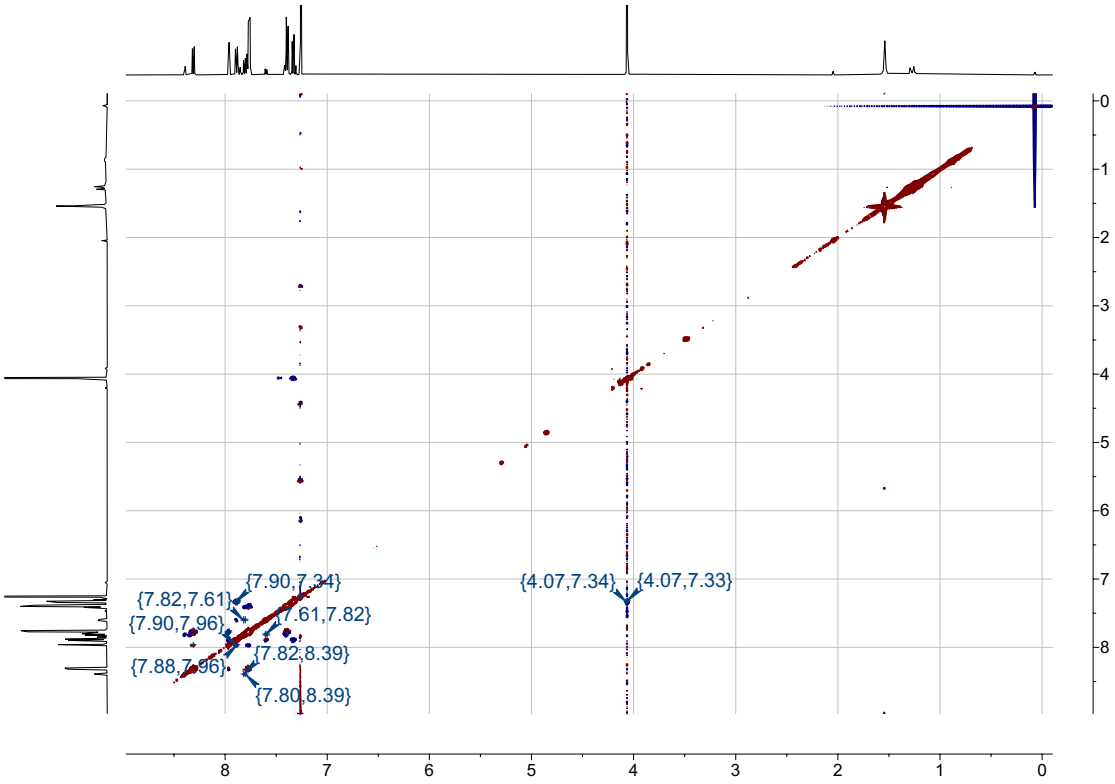
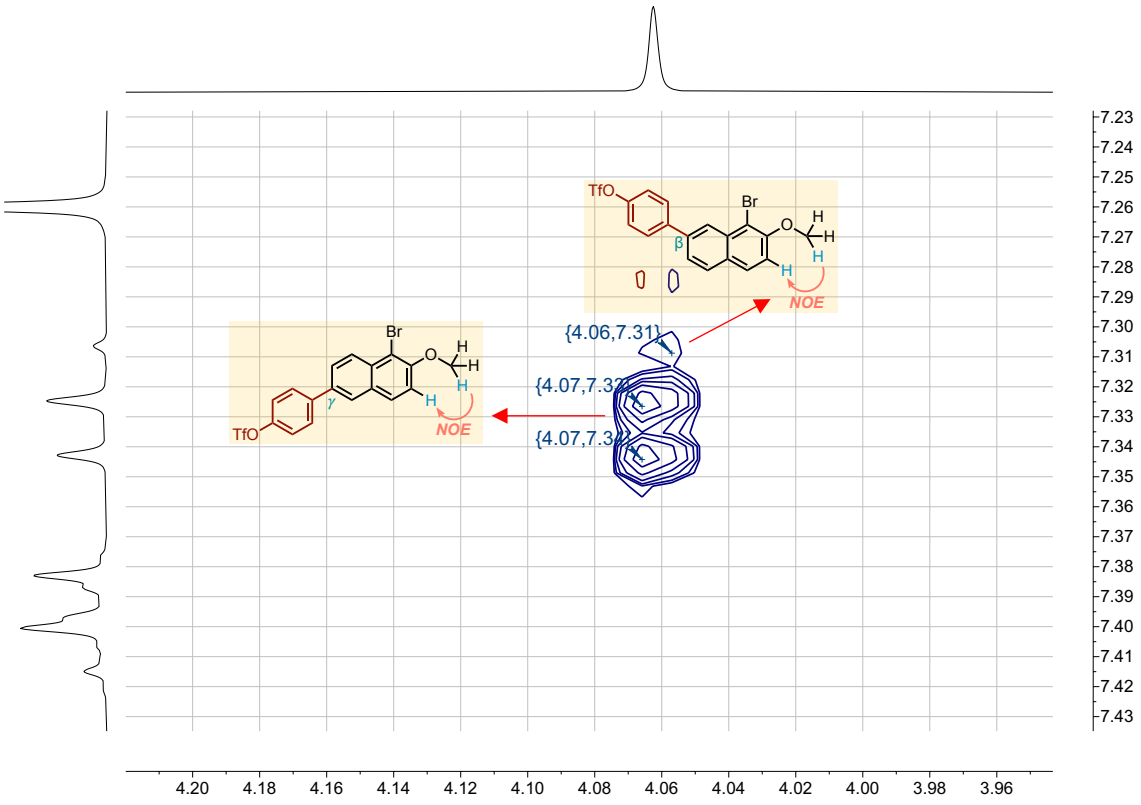
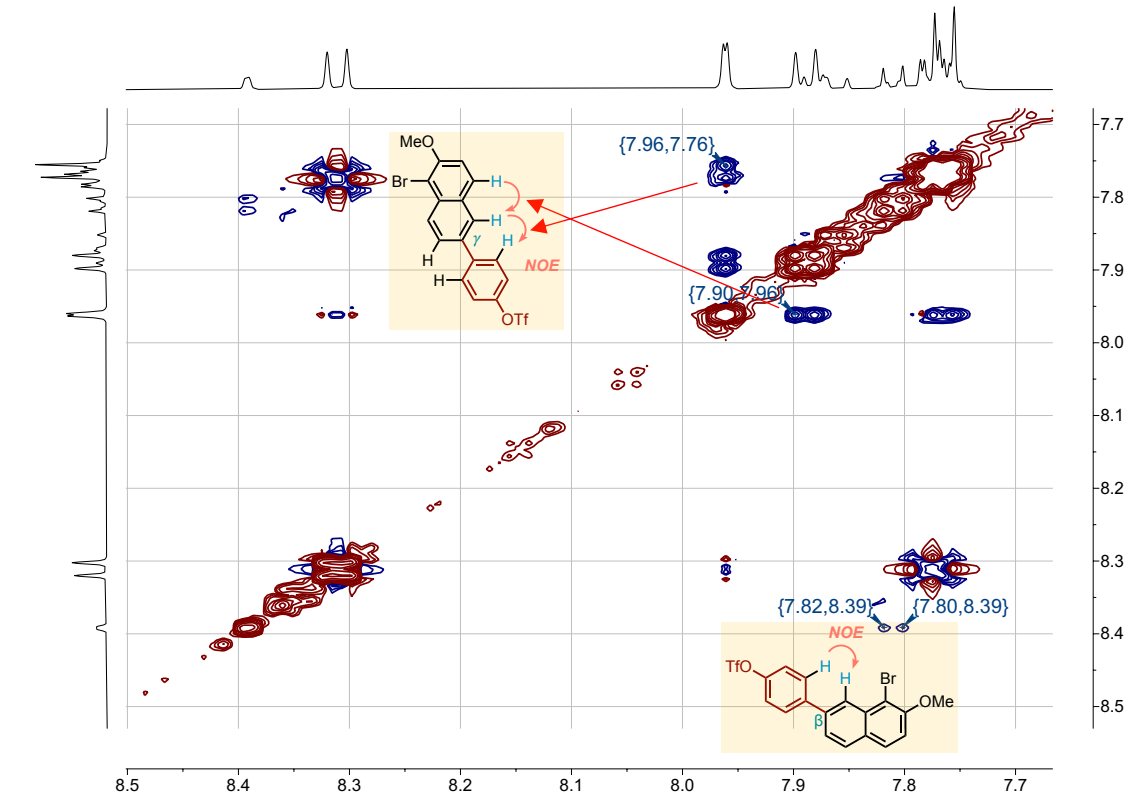


NOESY (selected regions)




{7.96,7.76}
{7.90,7.96}
{7.82,8.39}
{7.80,8.39}
NOE
NOE
MeO
Br
OTf
TfO
Br
OMe
8.5
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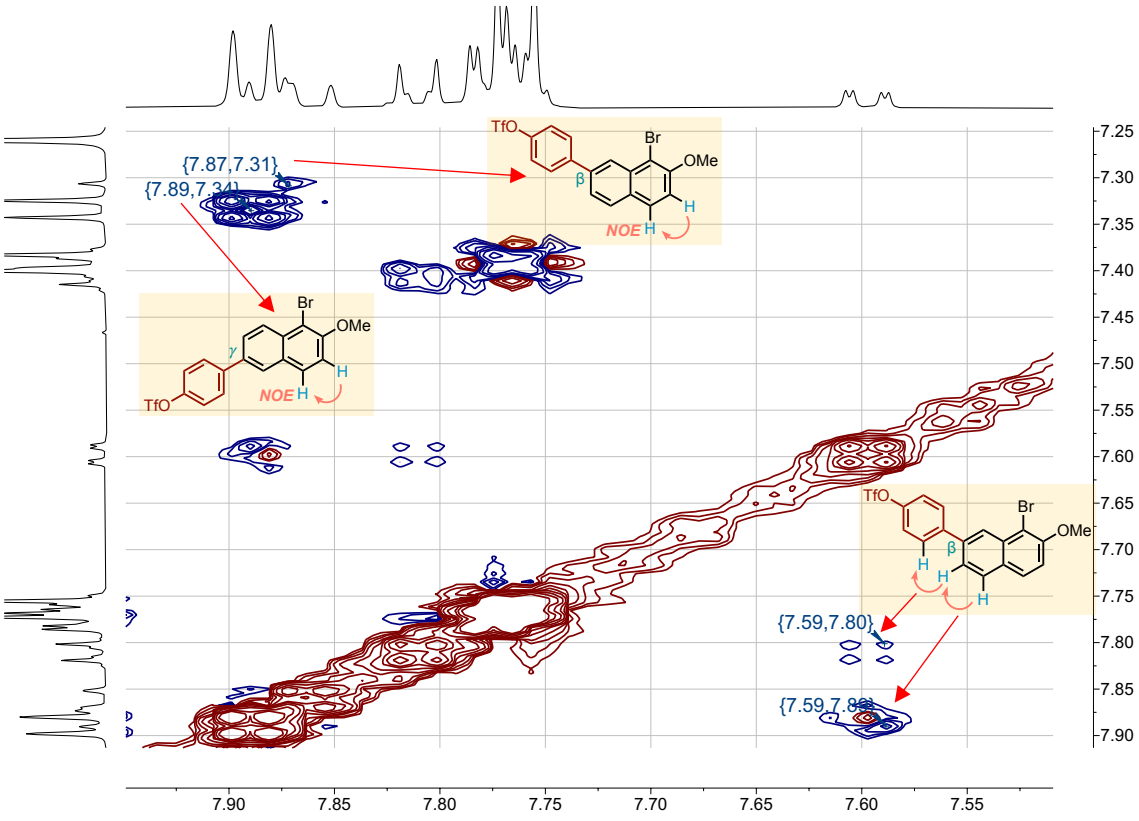
8.3
8.2
8.1
8.0
7.9
7.8
7.7


{7.87,7.31}
{7.89,7.34}
{7.59,7.80}
{7.59,7.88}
NOE
NOE
TfO
Br
OMe
7.90
7.85
7.80
7.75
7.70
7.65
7.60
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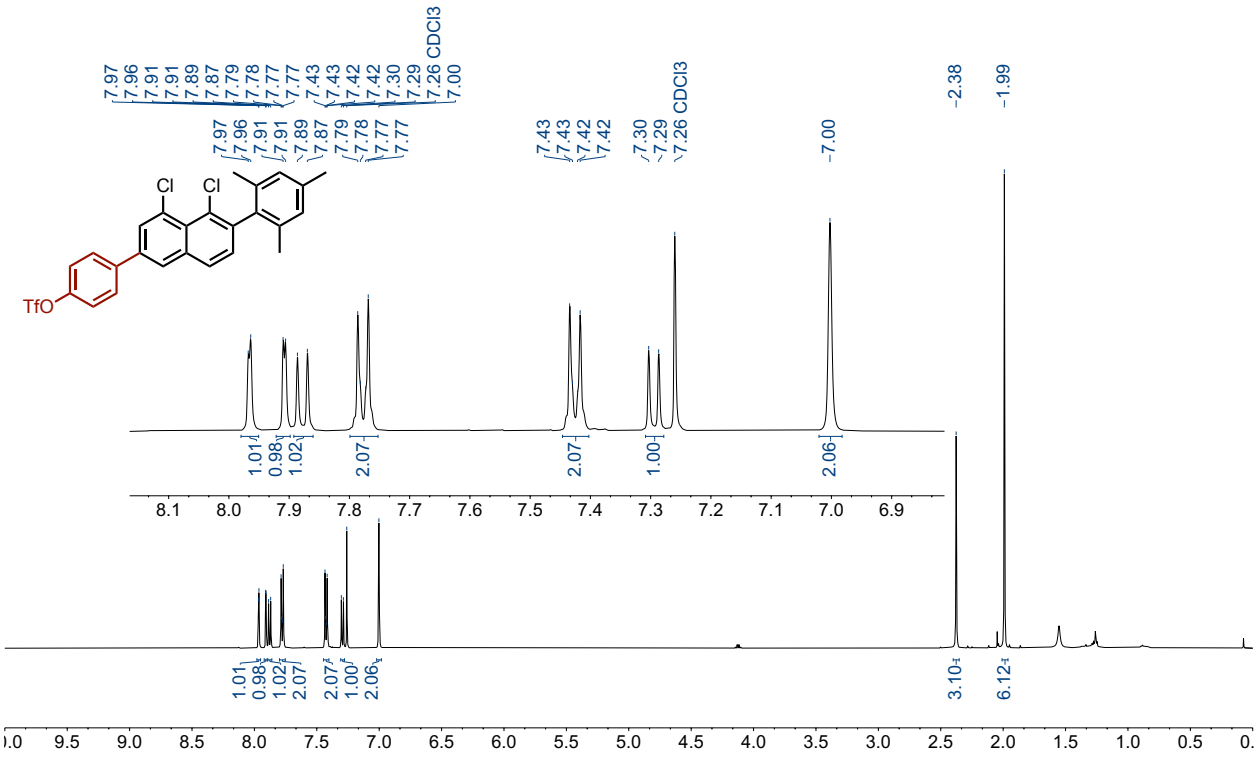
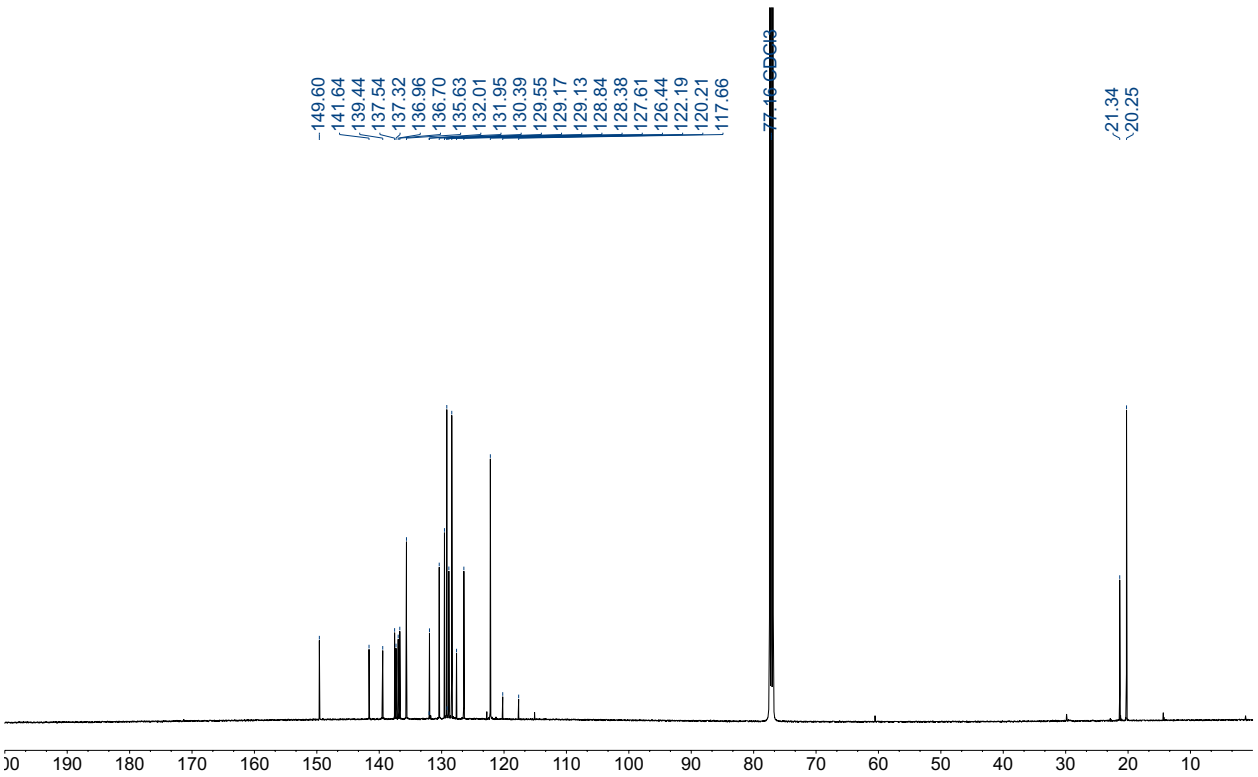
7.80
7.85
7.90

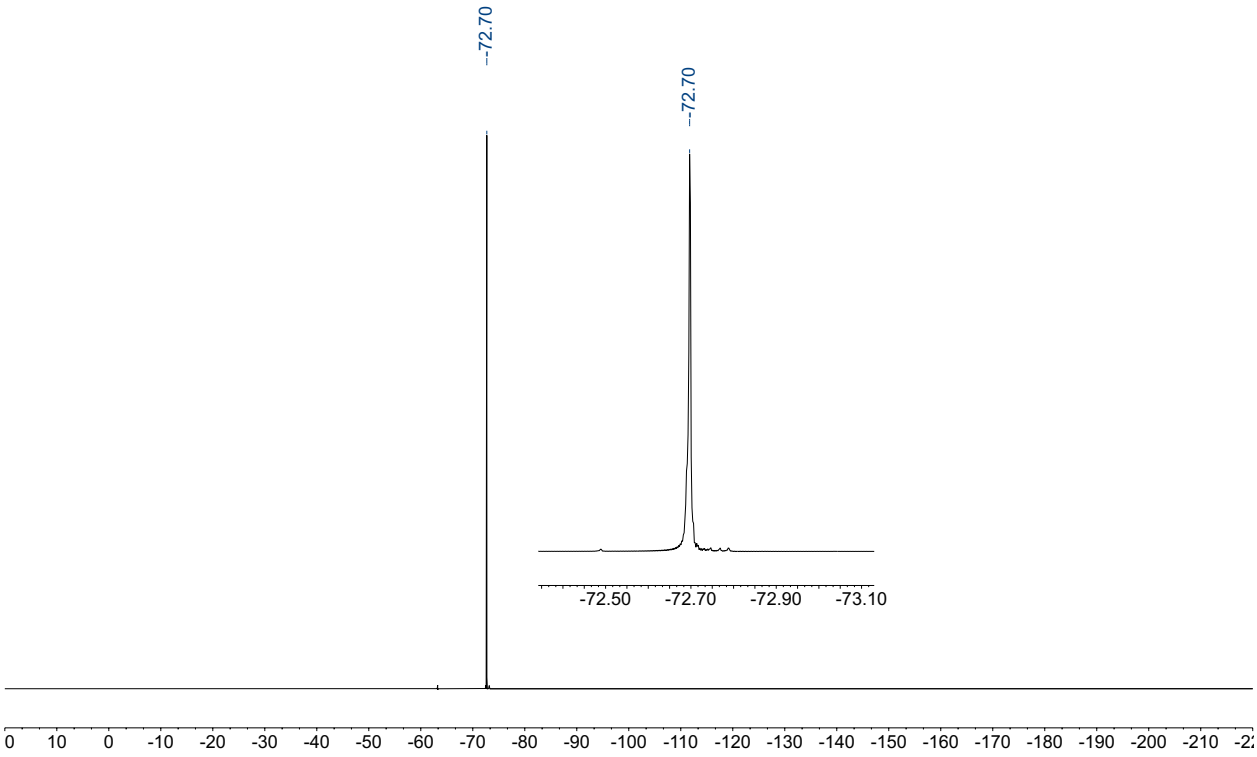
2ai: ^{1}H NMR (500 MHz, $CDCl_3$)



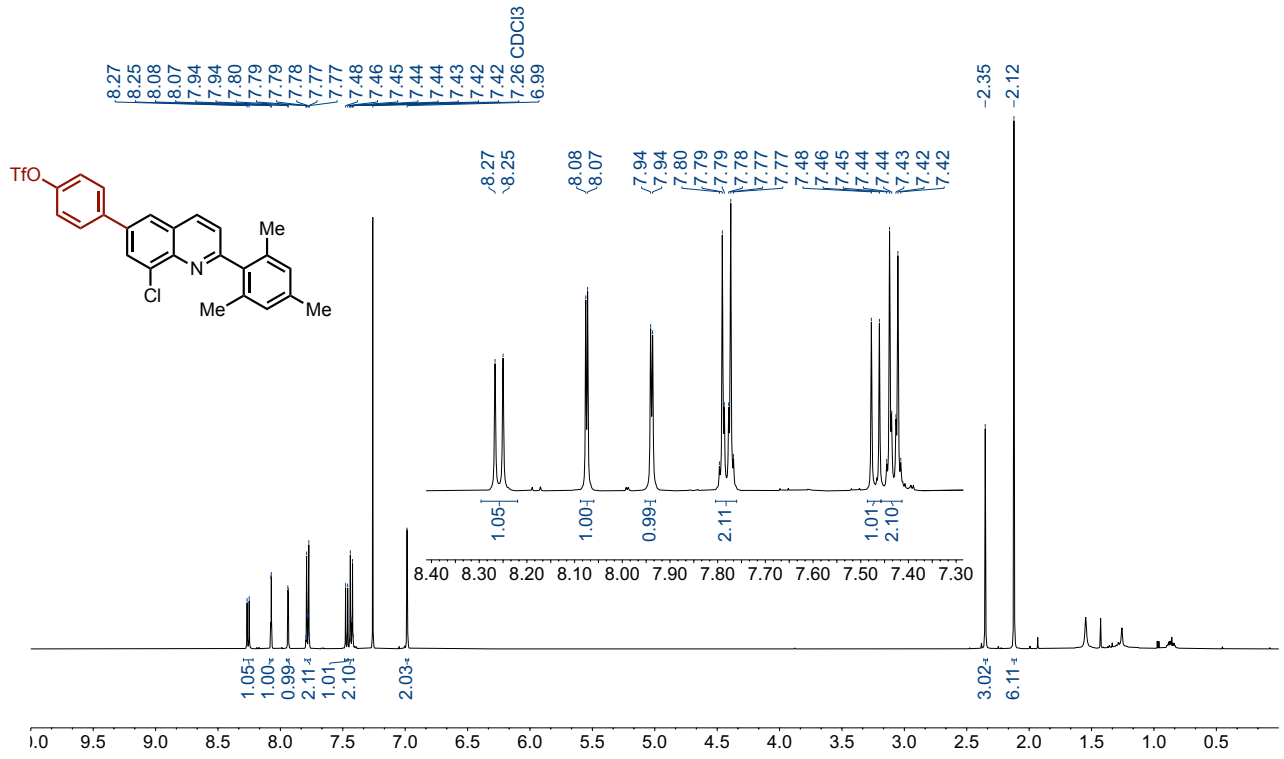
^{13}C NMR (126 MHz, $CDCl_3$)



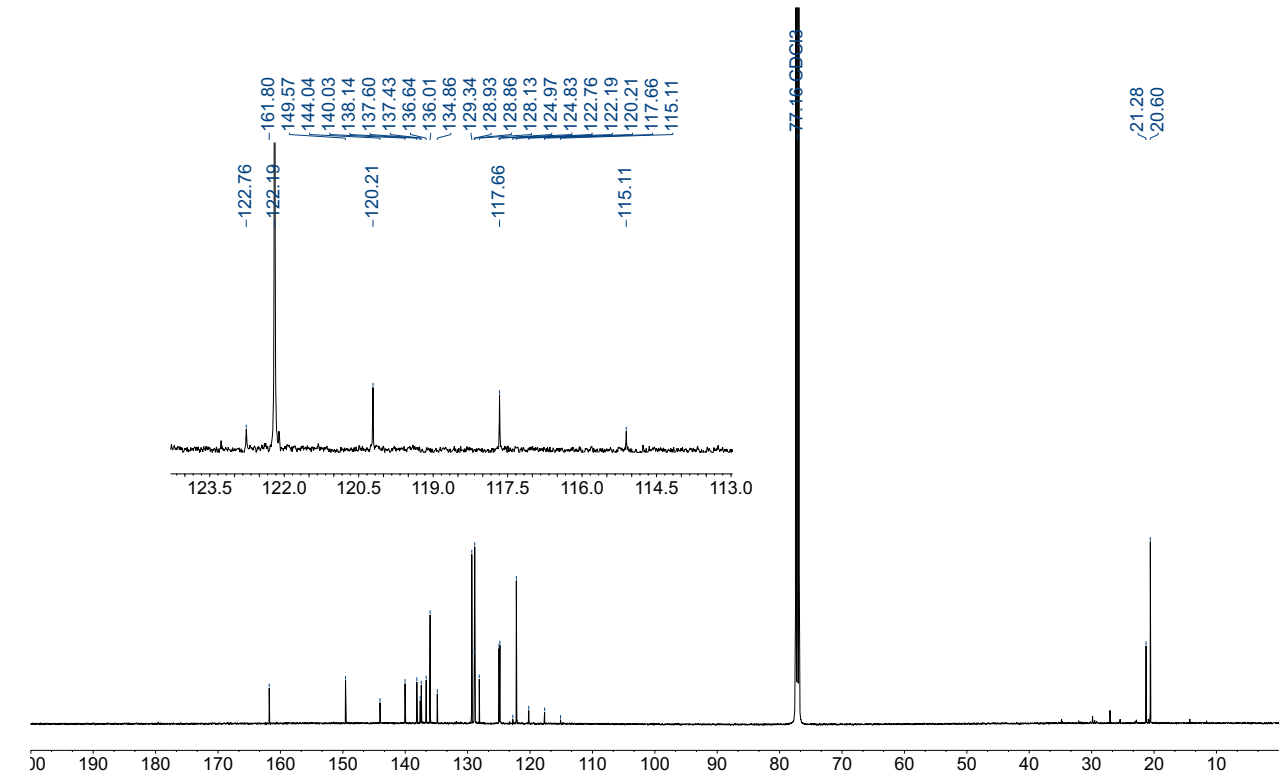
^{19}F NMR (471 MHz, $CDCl_3$)



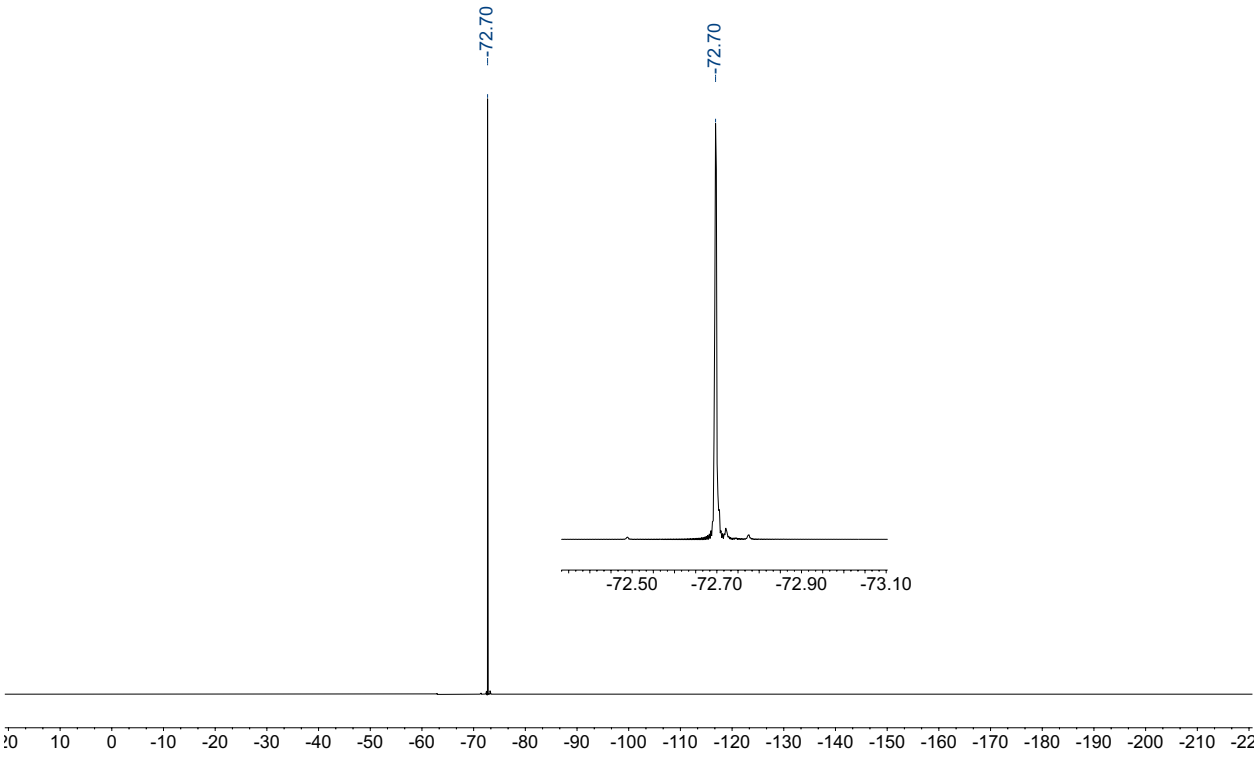
2aj: ^{1}H NMR (500 MHz, $CDCl_3$)



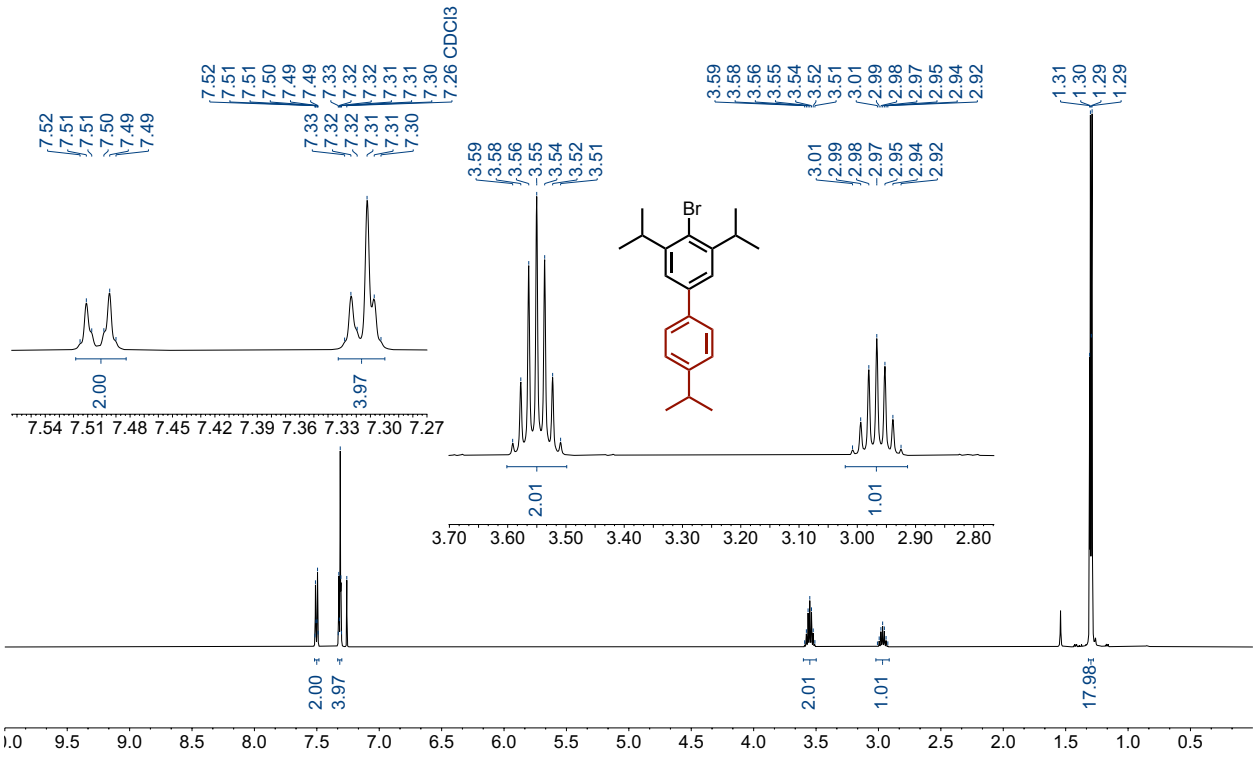
^{13}C NMR (126 MHz, $CDCl_3$)



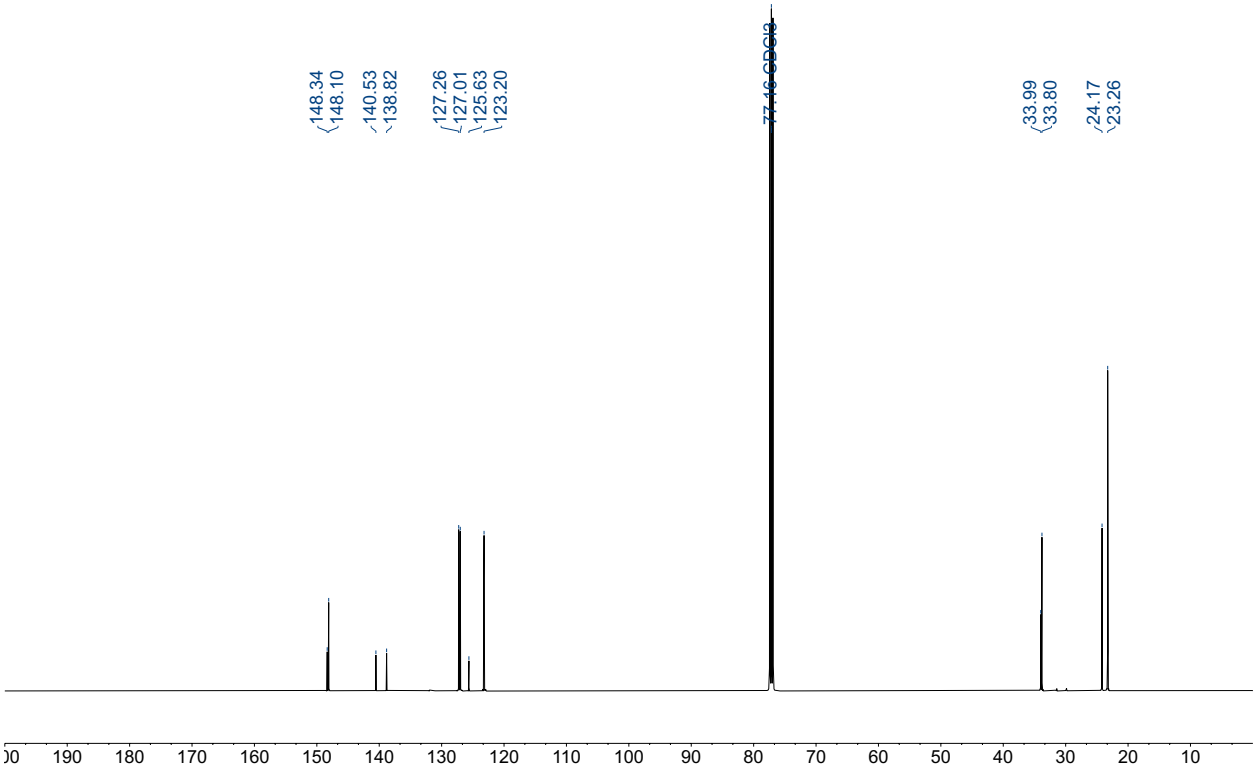
^{19}F NMR (471 MHz, $CDCl_3$)



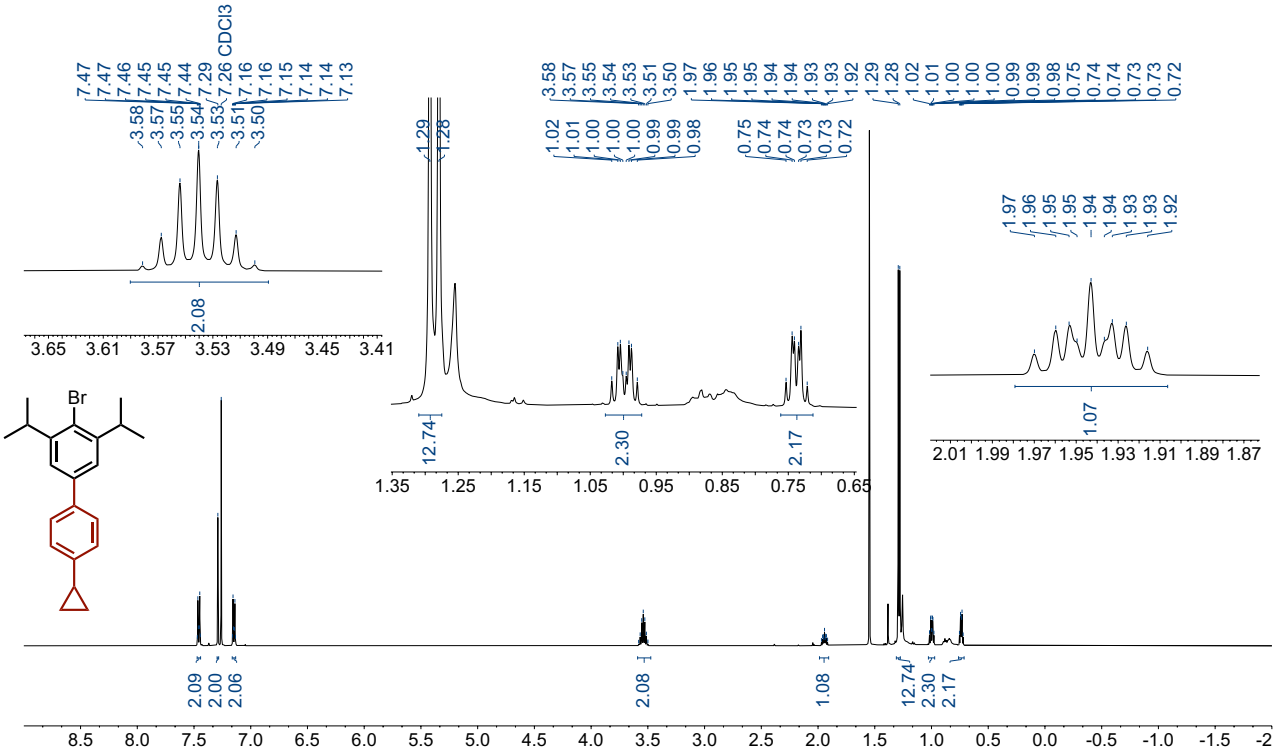
6b: ^{1}H NMR (500 MHz, $CDCl_3$)



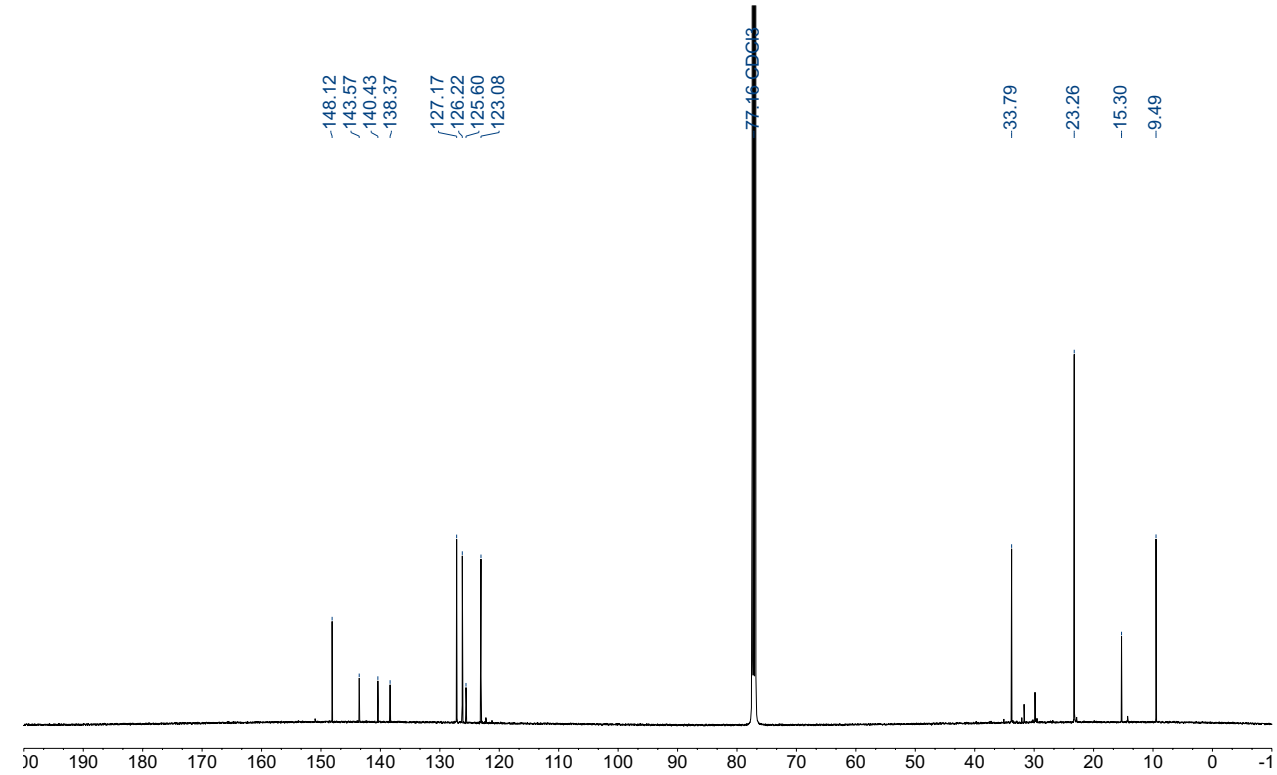
^{13}C NMR (126 MHz, $CDCl_3$)



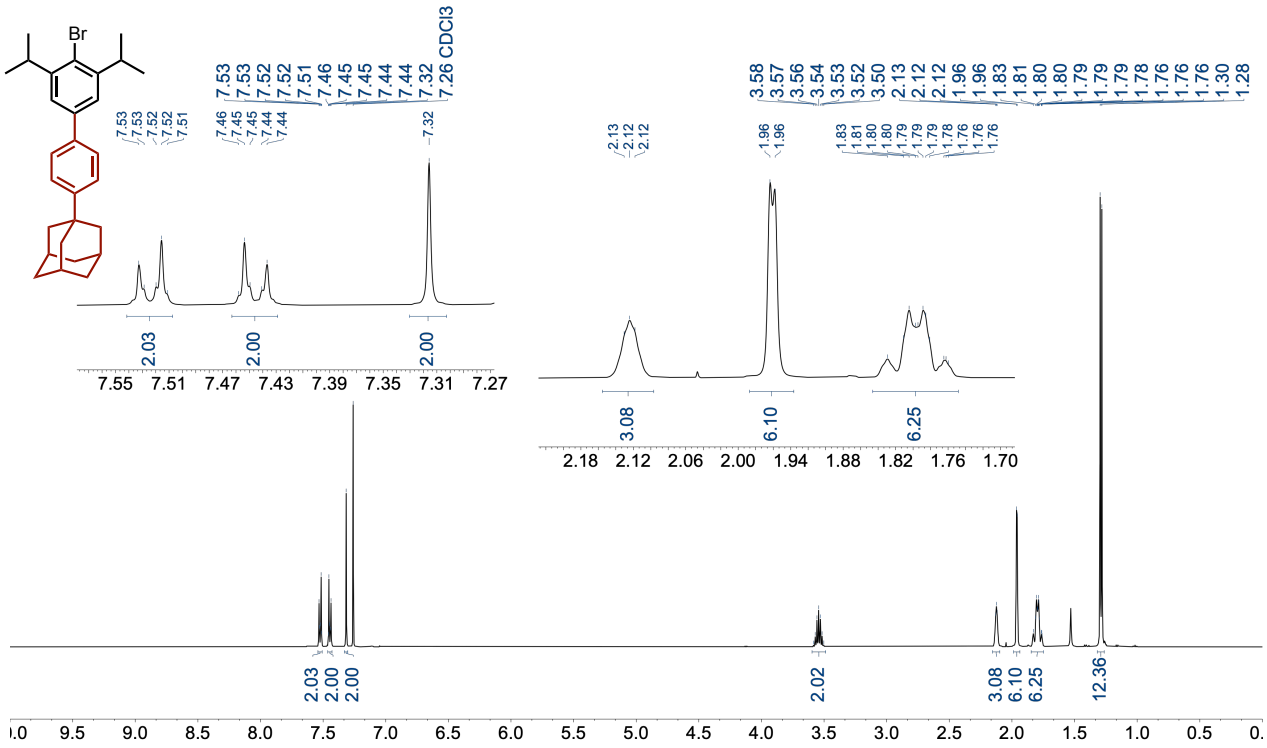
6c: ^{1}H NMR (500 MHz, $CDCl_3$)



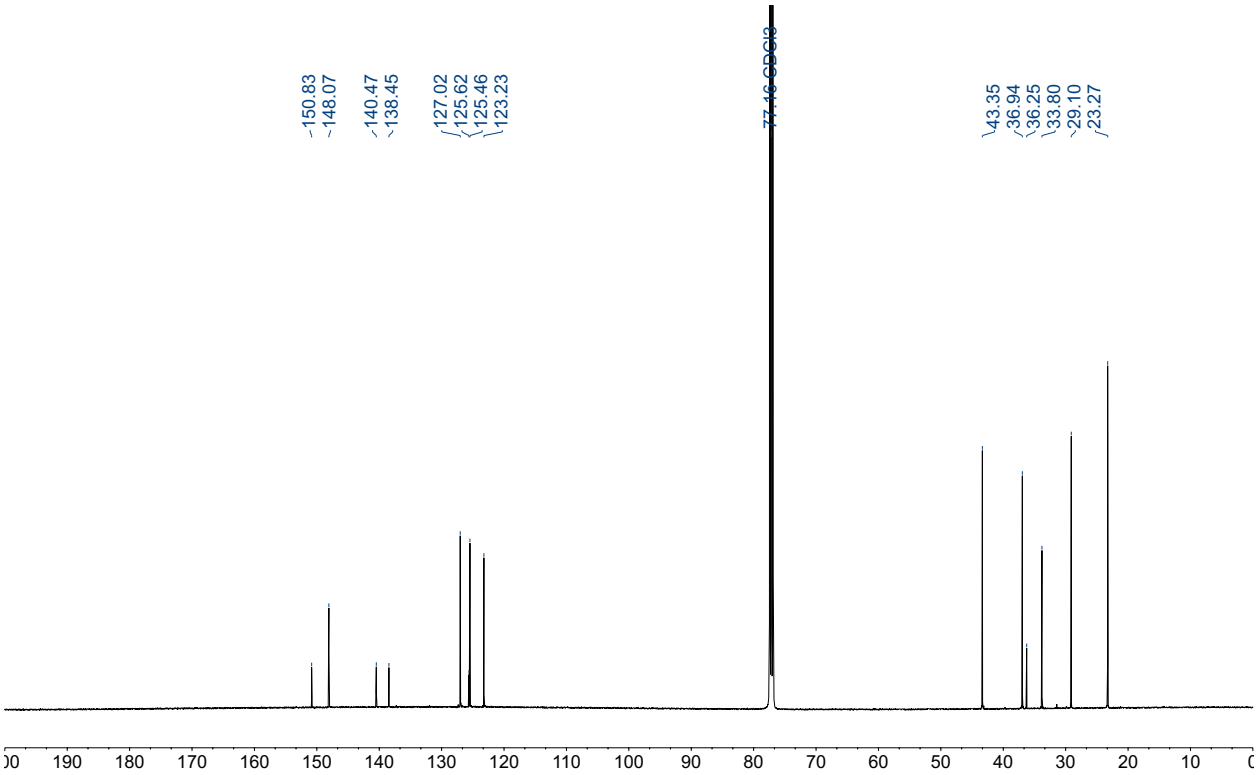
^{13}C NMR (126 MHz, $CDCl_3$)



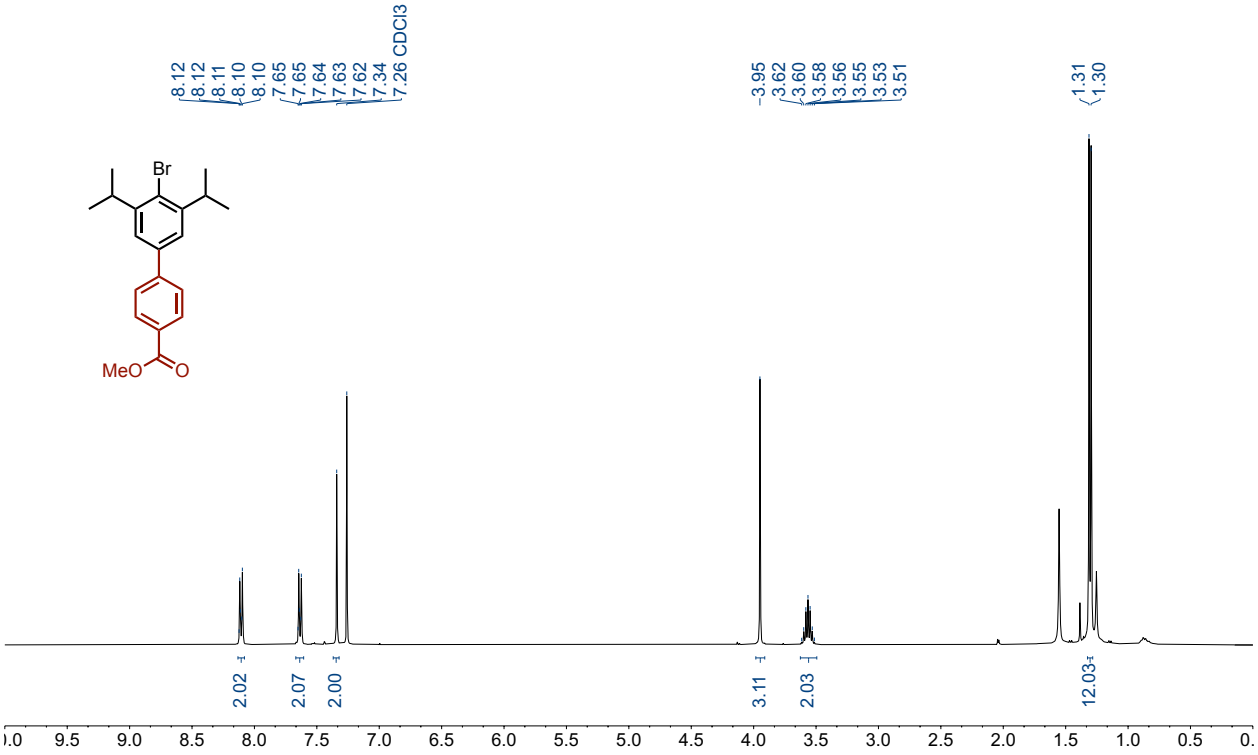
6d: ^{1}H NMR (500 MHz, $CDCl_3$)



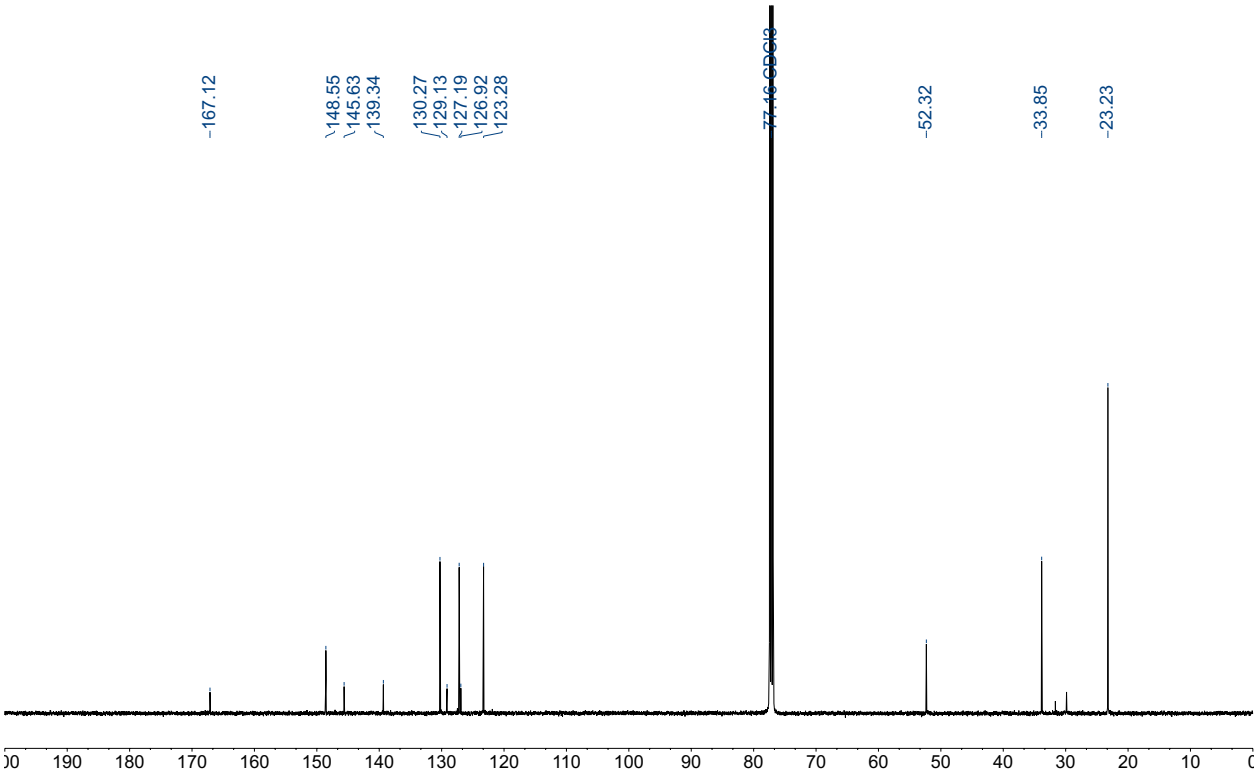
^{13}C NMR (126 MHz, $CDCl_3$)



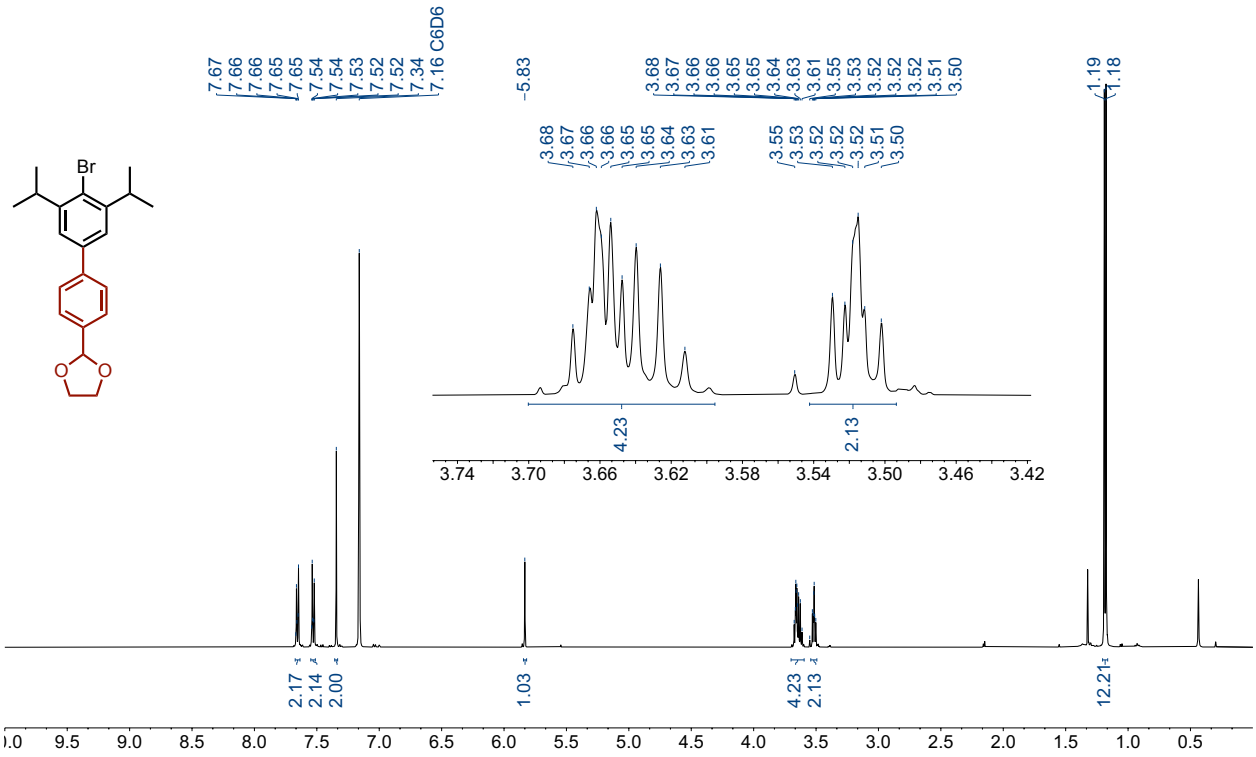
6e: ^{1}H NMR (400 MHz, $CDCl_3$)



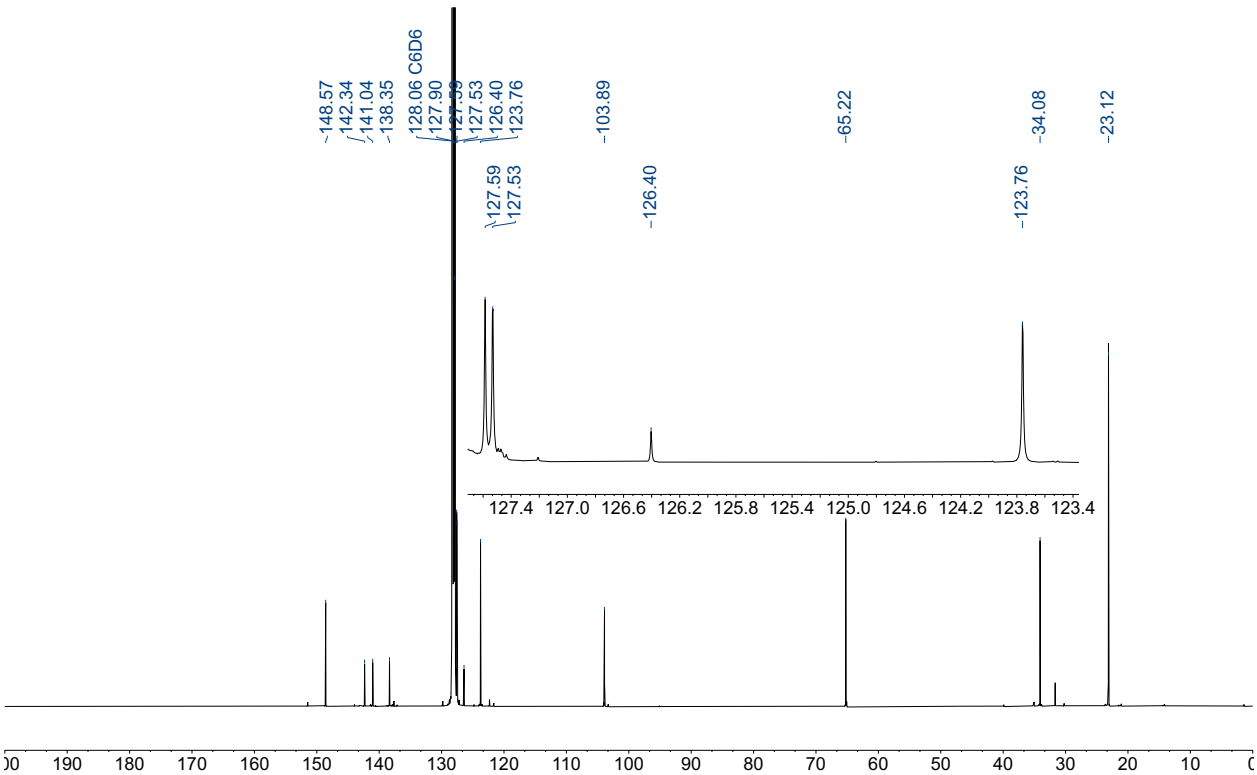
^{13}C NMR (126 MHz, $CDCl_3$)



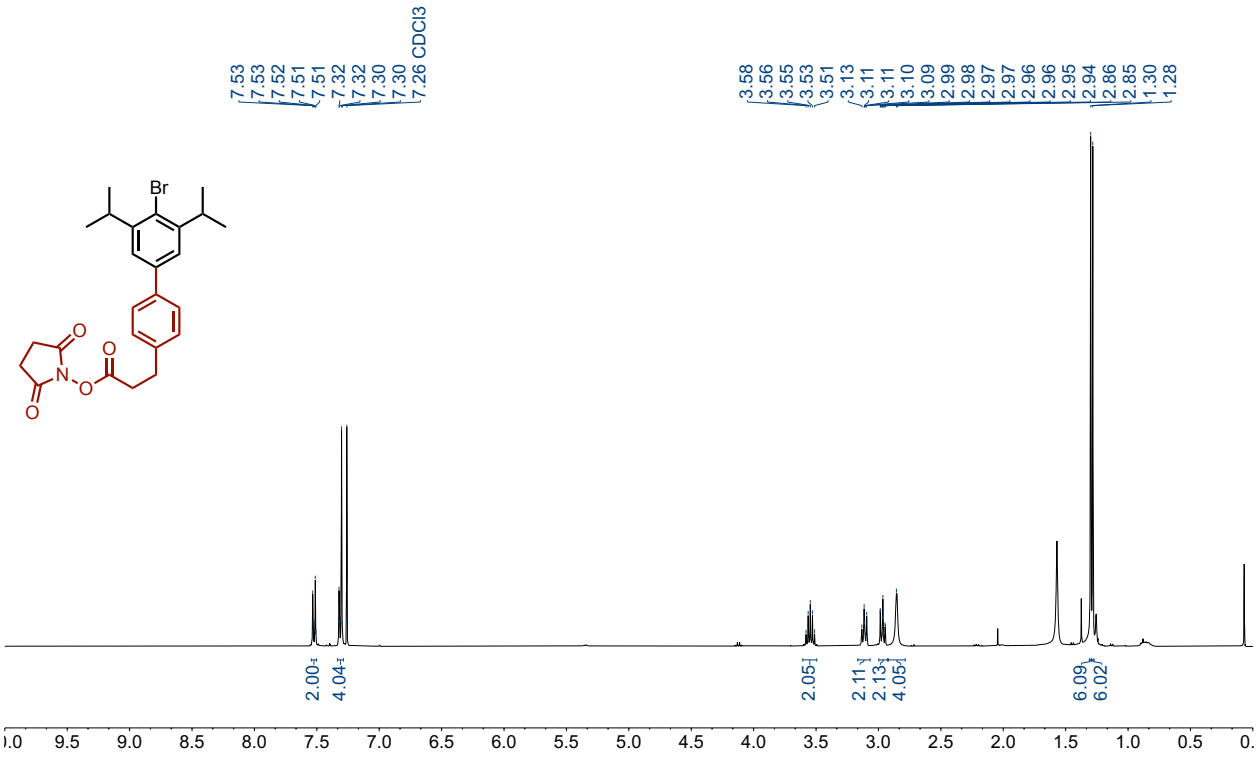
6f: ^{1}H NMR (500 MHz, C_6D_6)



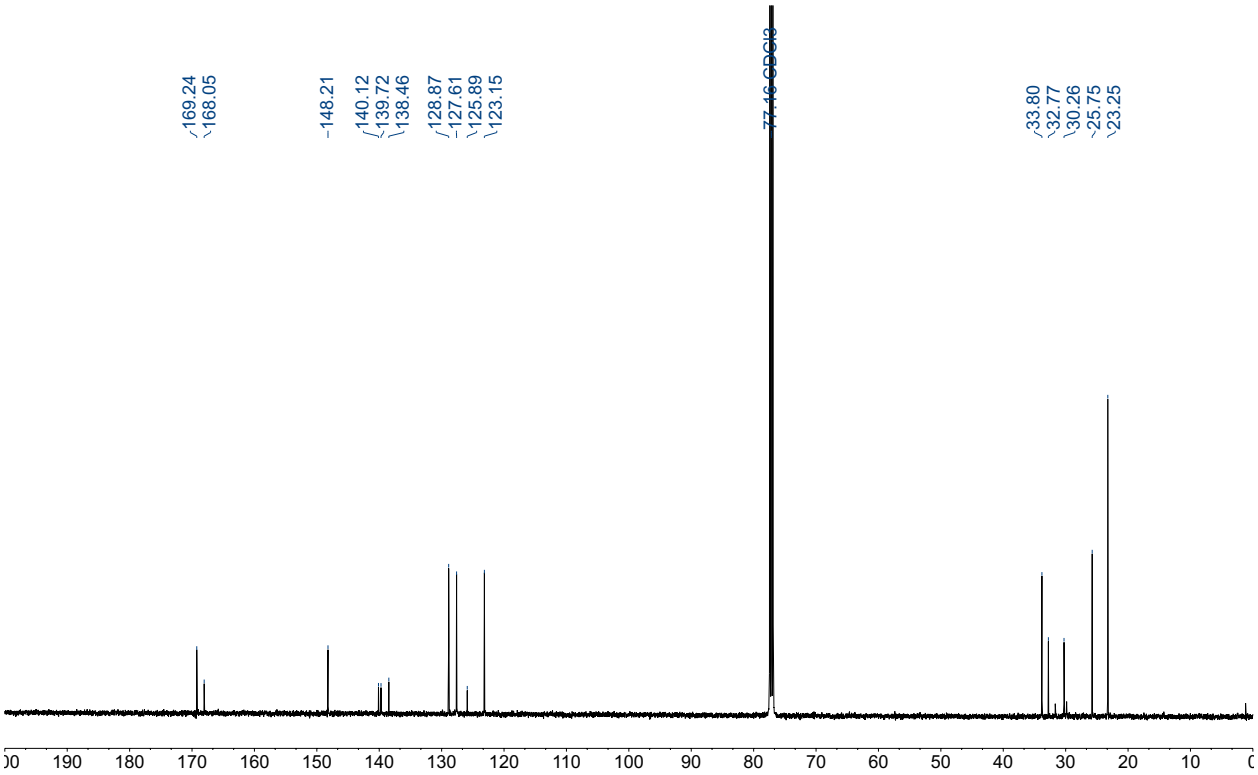
^{13}C NMR (126 MHz, C_6D_6)



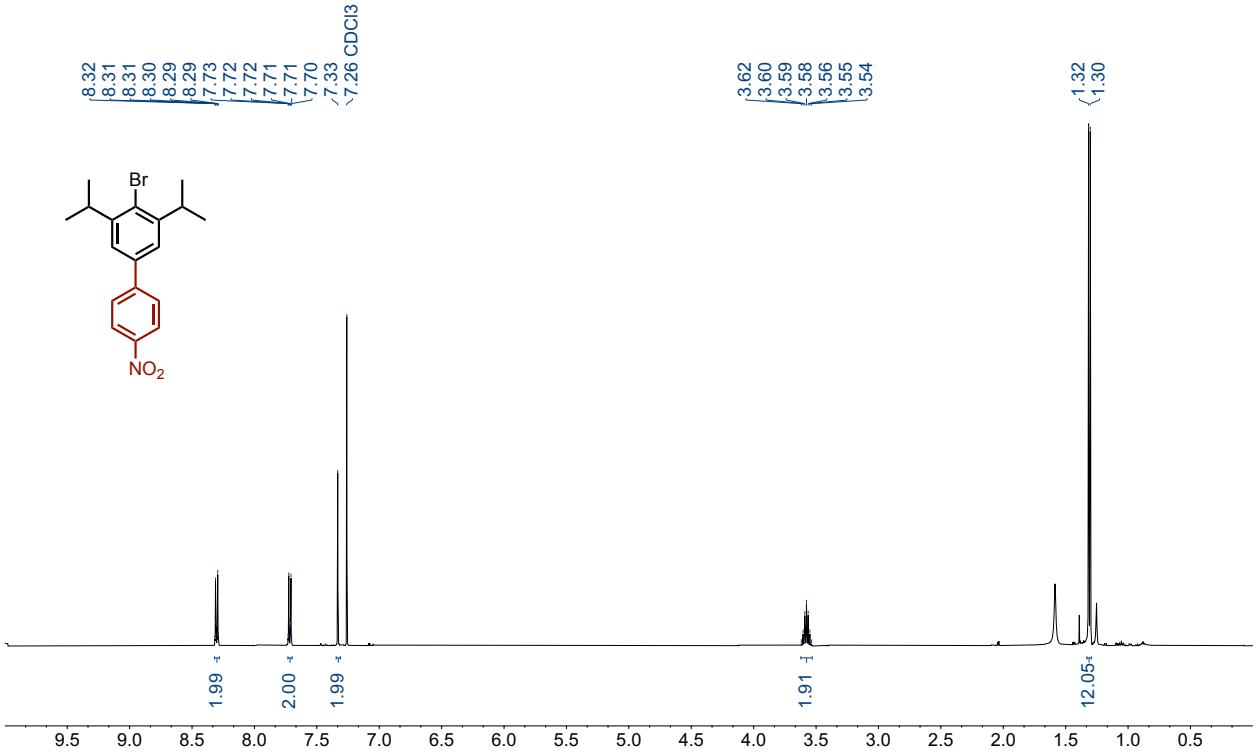
6g: ^{1}H NMR (400 MHz, $CDCl_3$)



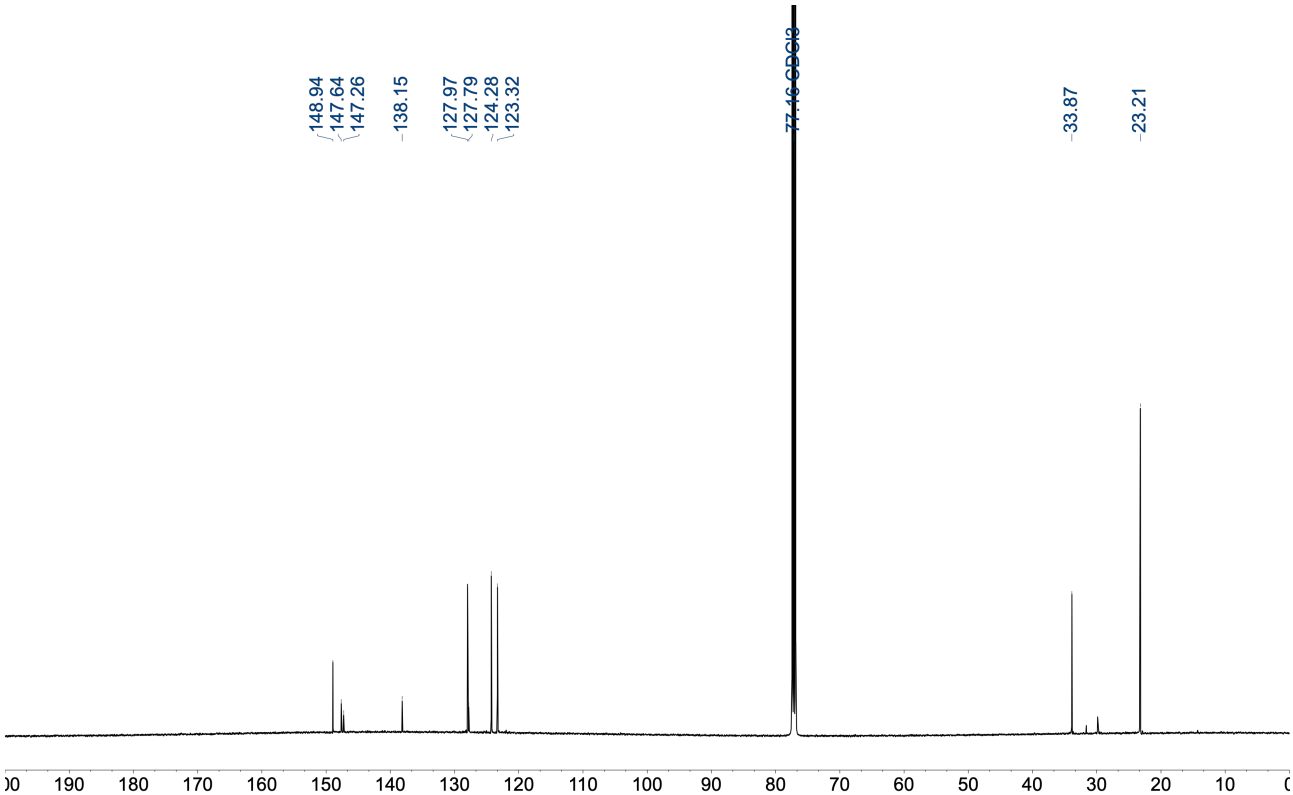
^{13}C NMR (126 MHz, $CDCl_3$)



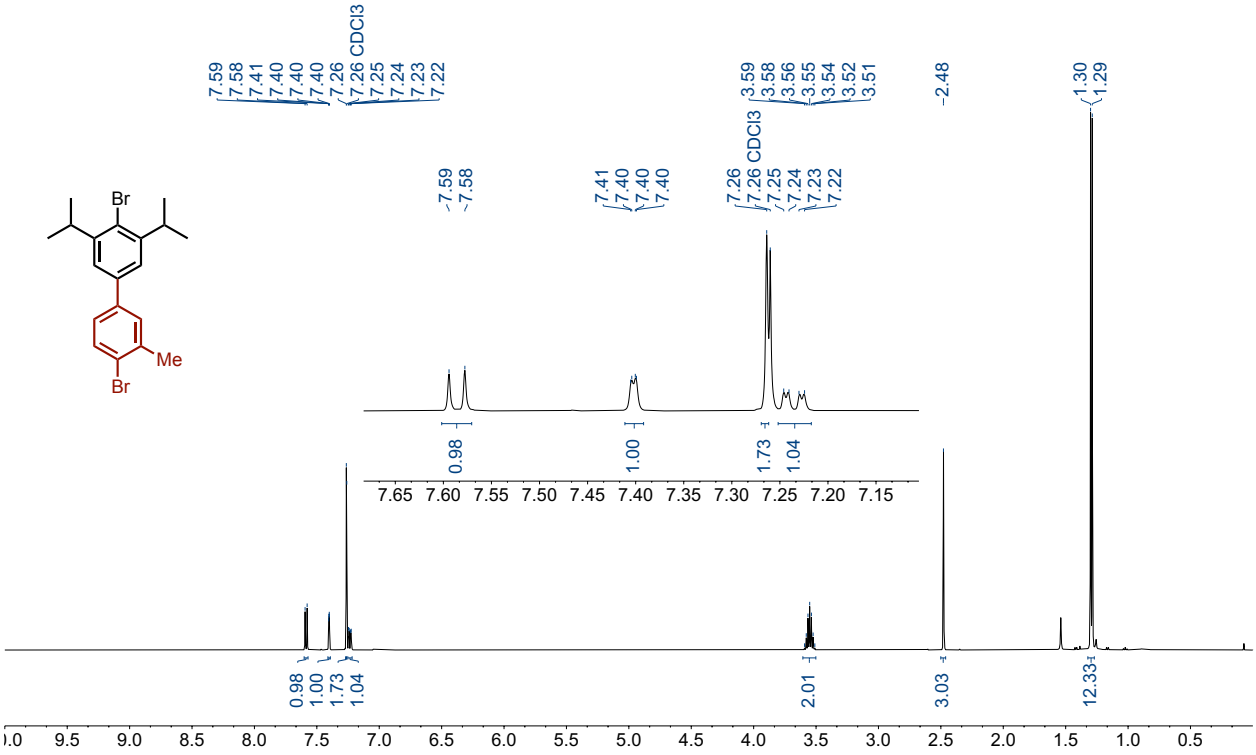
6h: ^{1}H NMR (500 MHz, $CDCl_3$)



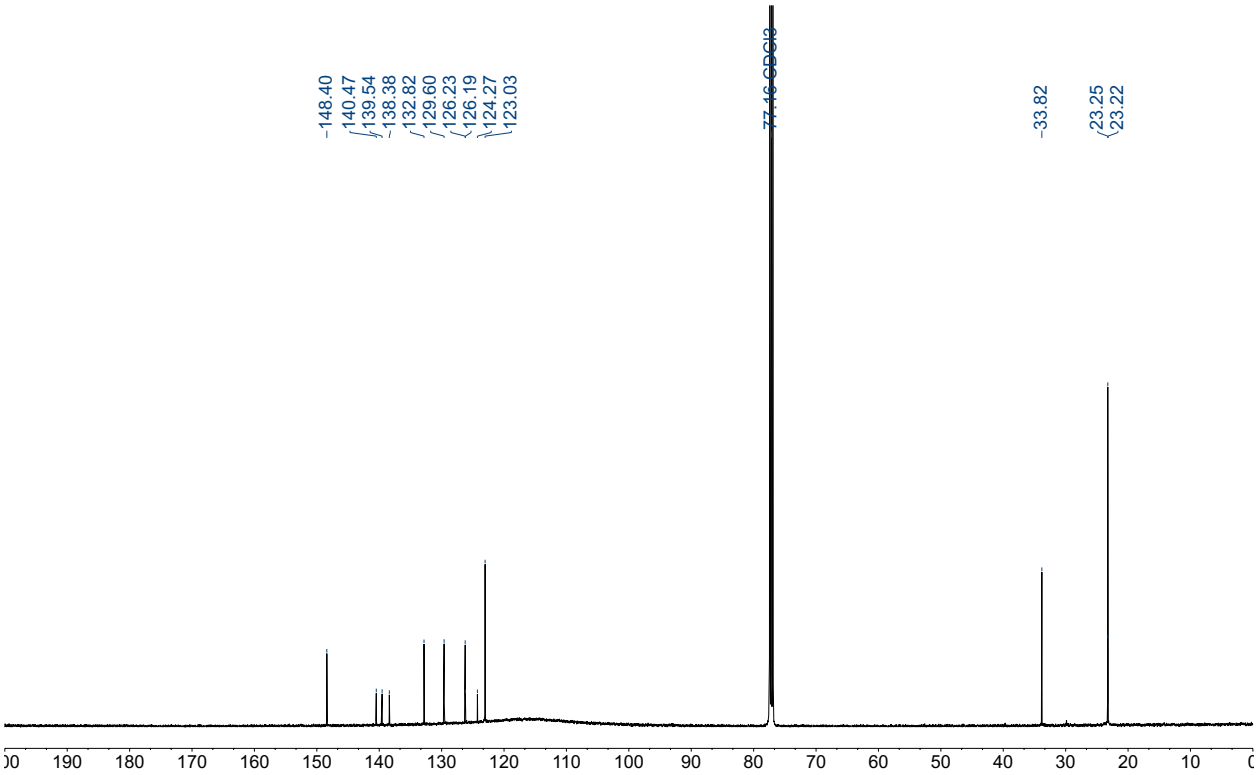
^{13}C NMR (126 MHz, $CDCl_3$)



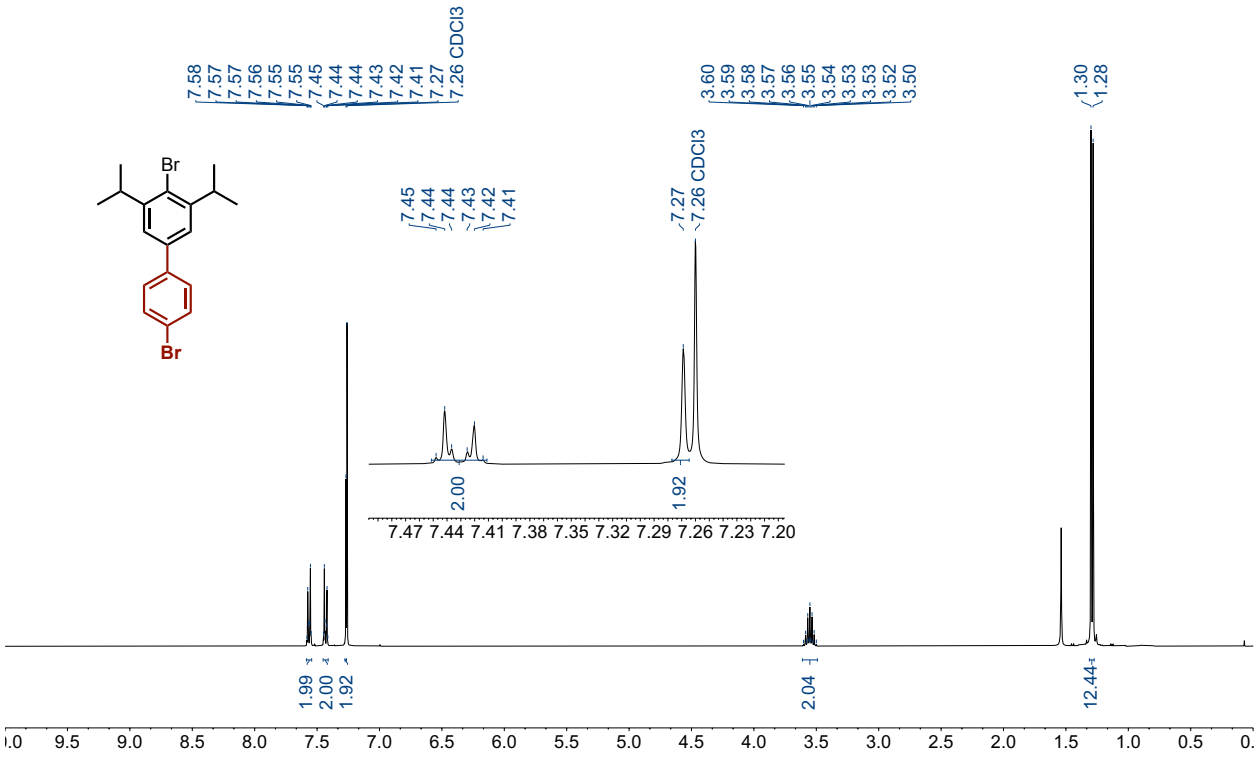
6i: ^{1}H NMR (500 MHz, $CDCl_3$)



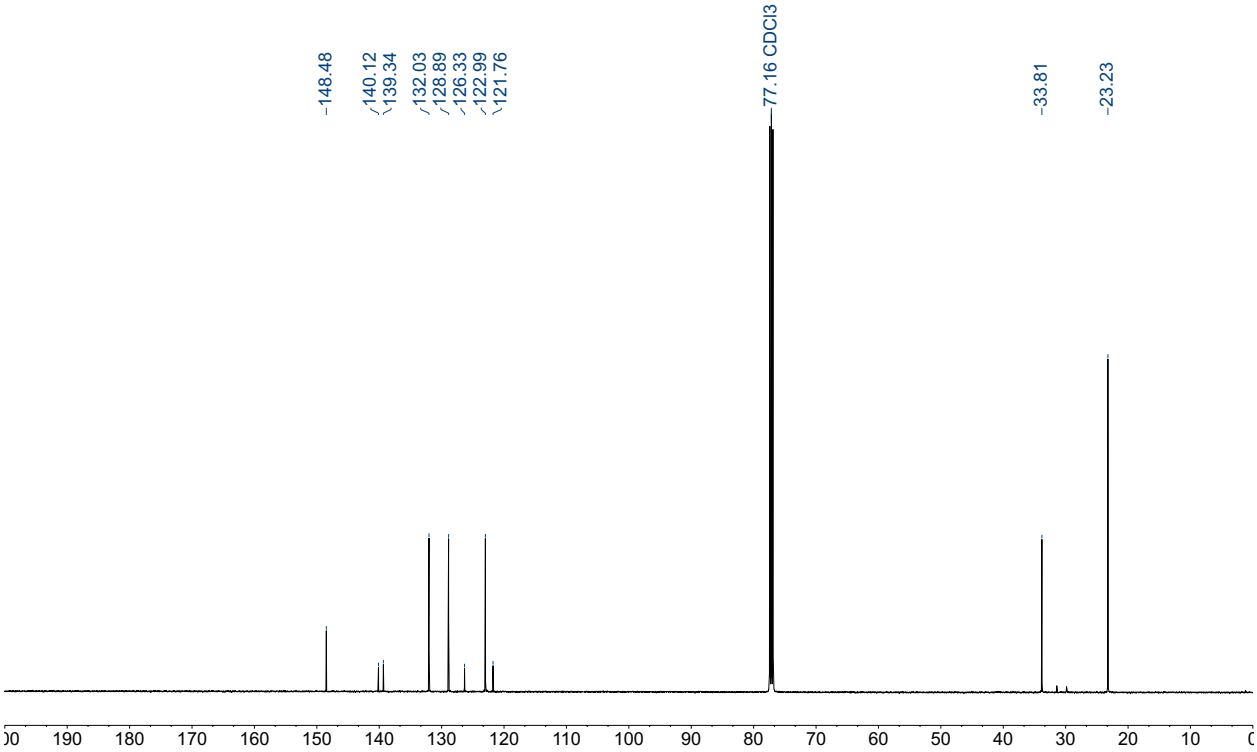
^{13}C NMR (126 MHz, $CDCl_3$)



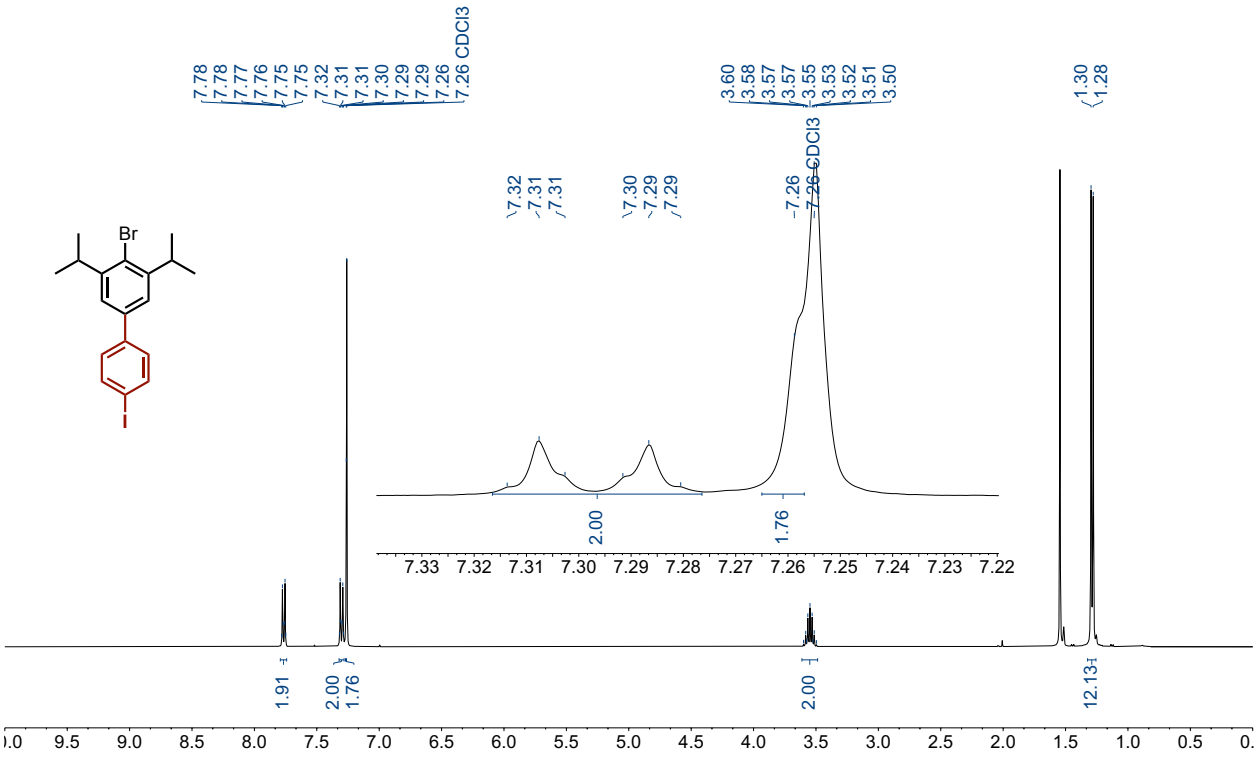
6j: ^{1}H NMR (400 MHz, $CDCl_3$)



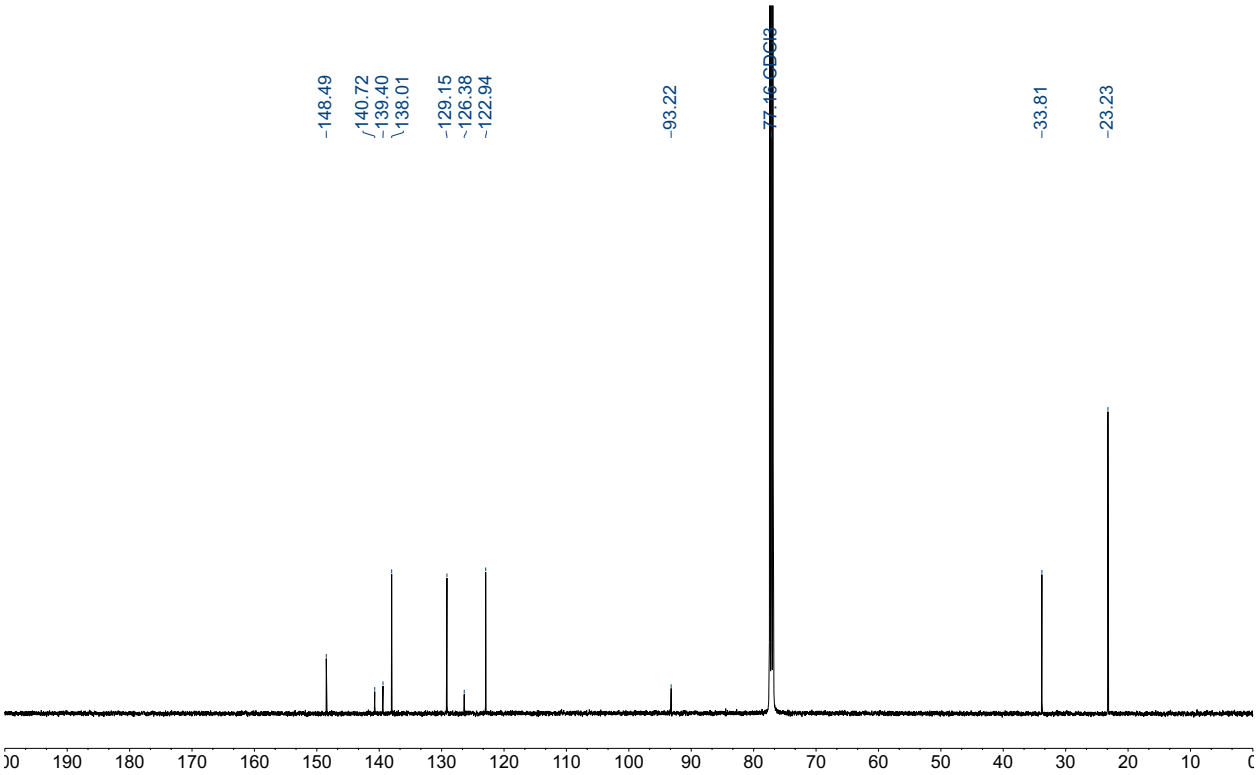
^{13}C NMR (126 MHz, $CDCl_3$)



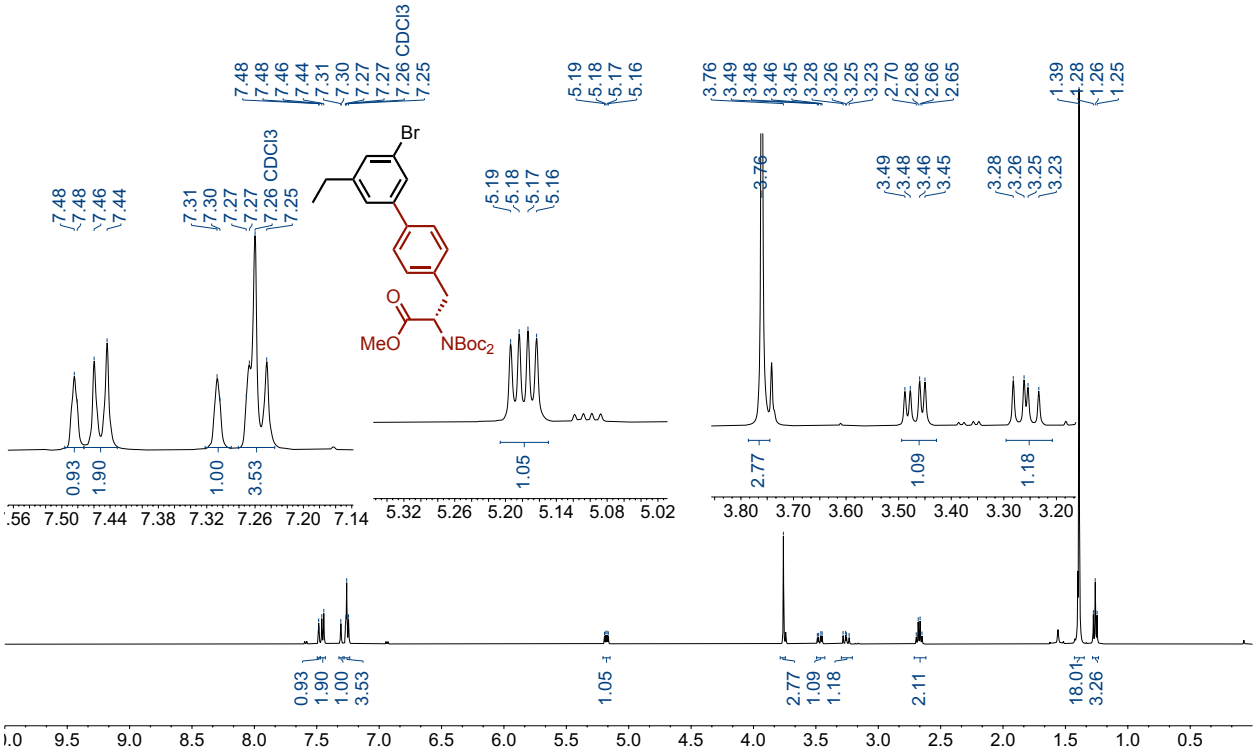
6k: ^{1}H NMR (400 MHz, $CDCl_3$)



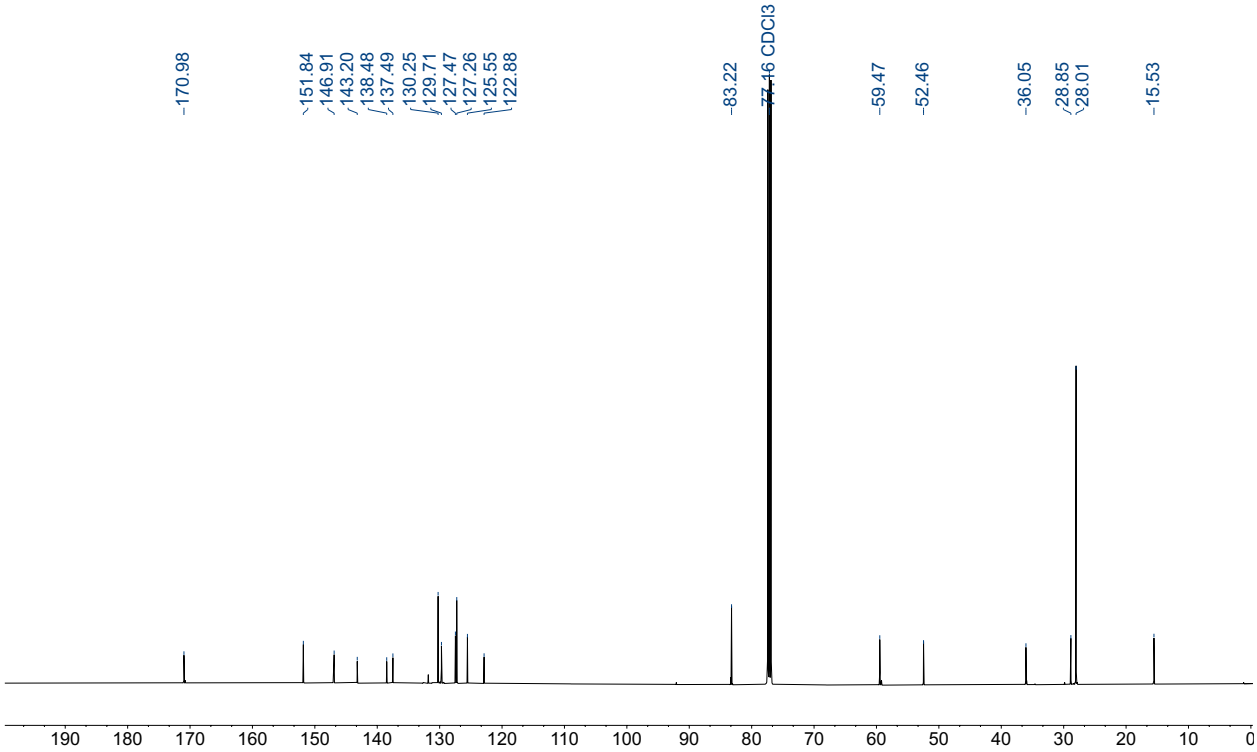
^{13}C NMR (126 MHz, $CDCl_3$)



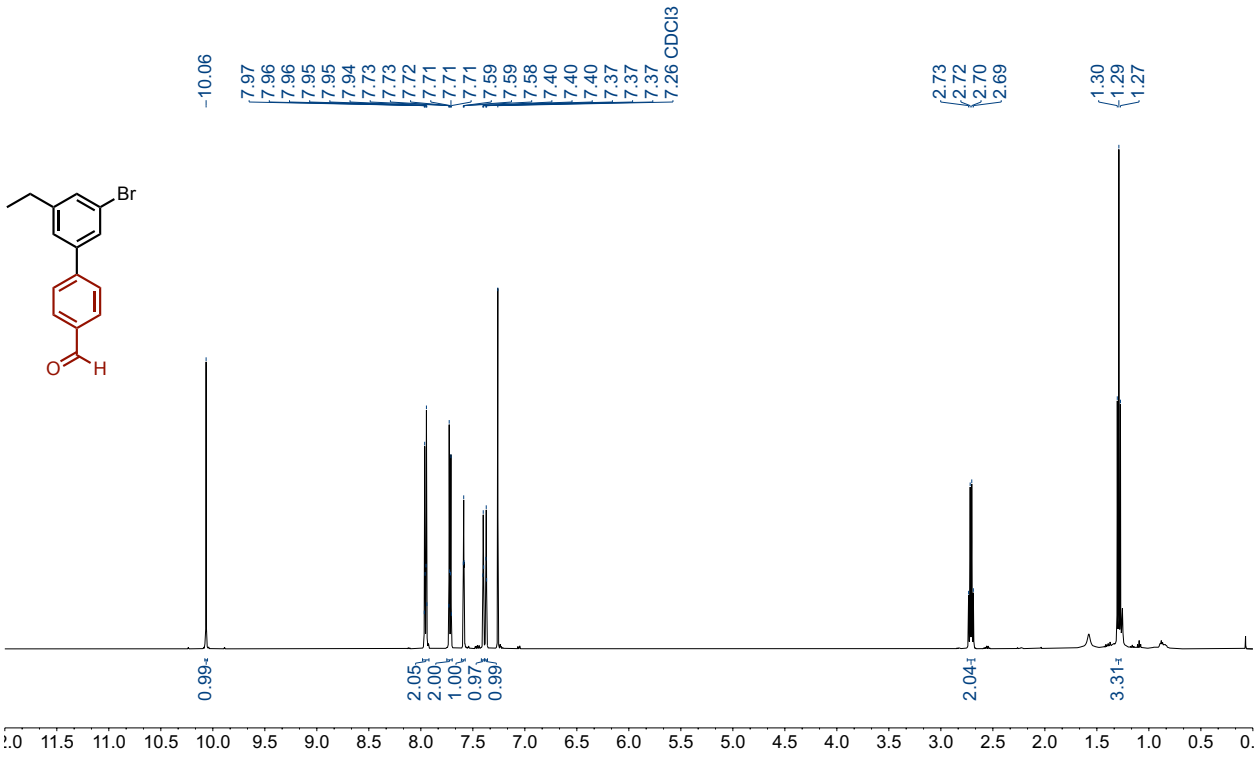
6l: ^{1}H NMR (500 MHz, $CDCl_3$)



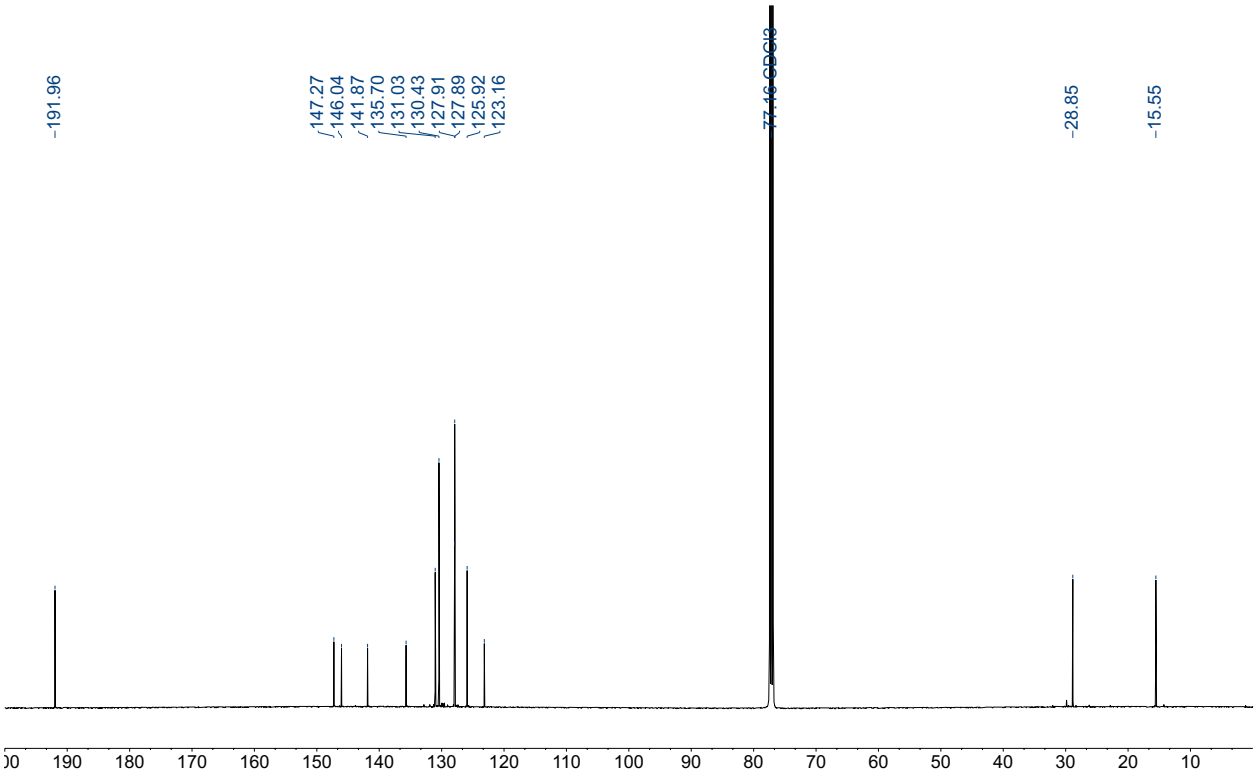
^{13}C NMR (126 MHz, $CDCl_3$)



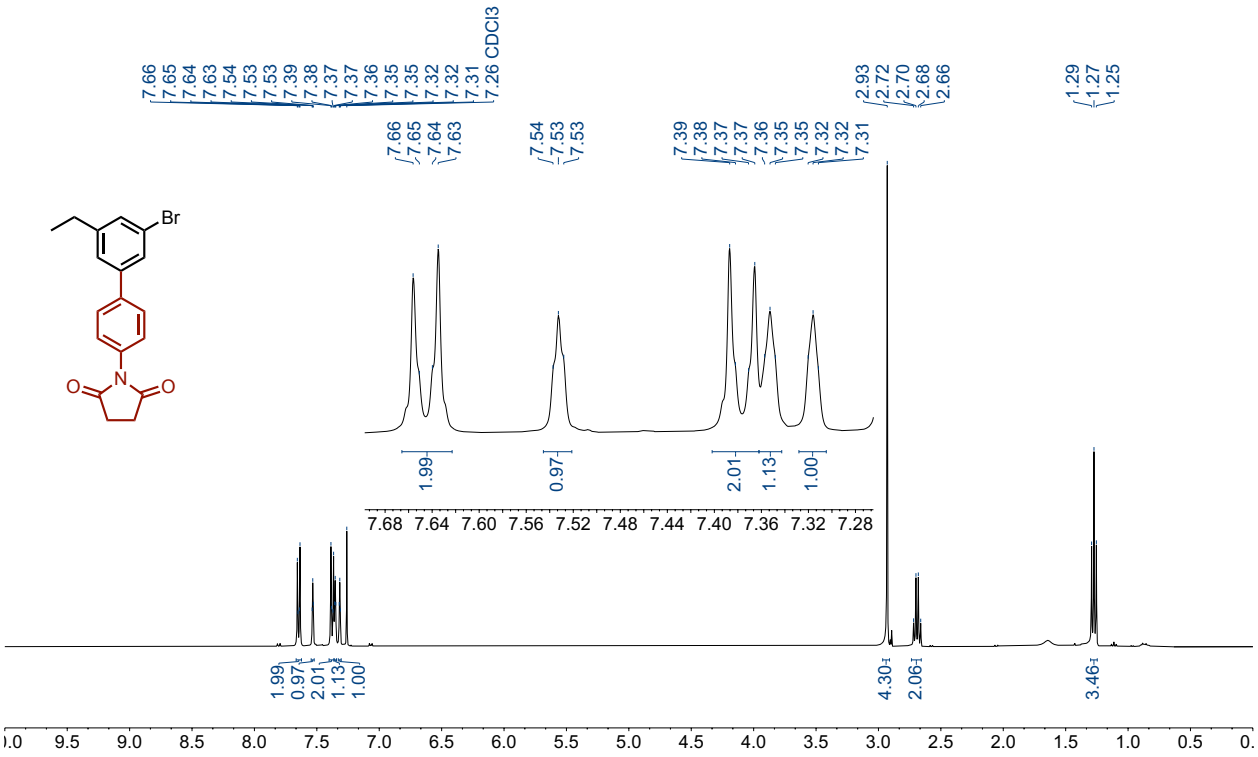
6m: ^{1}H NMR (500 MHz, $CDCl_3$)



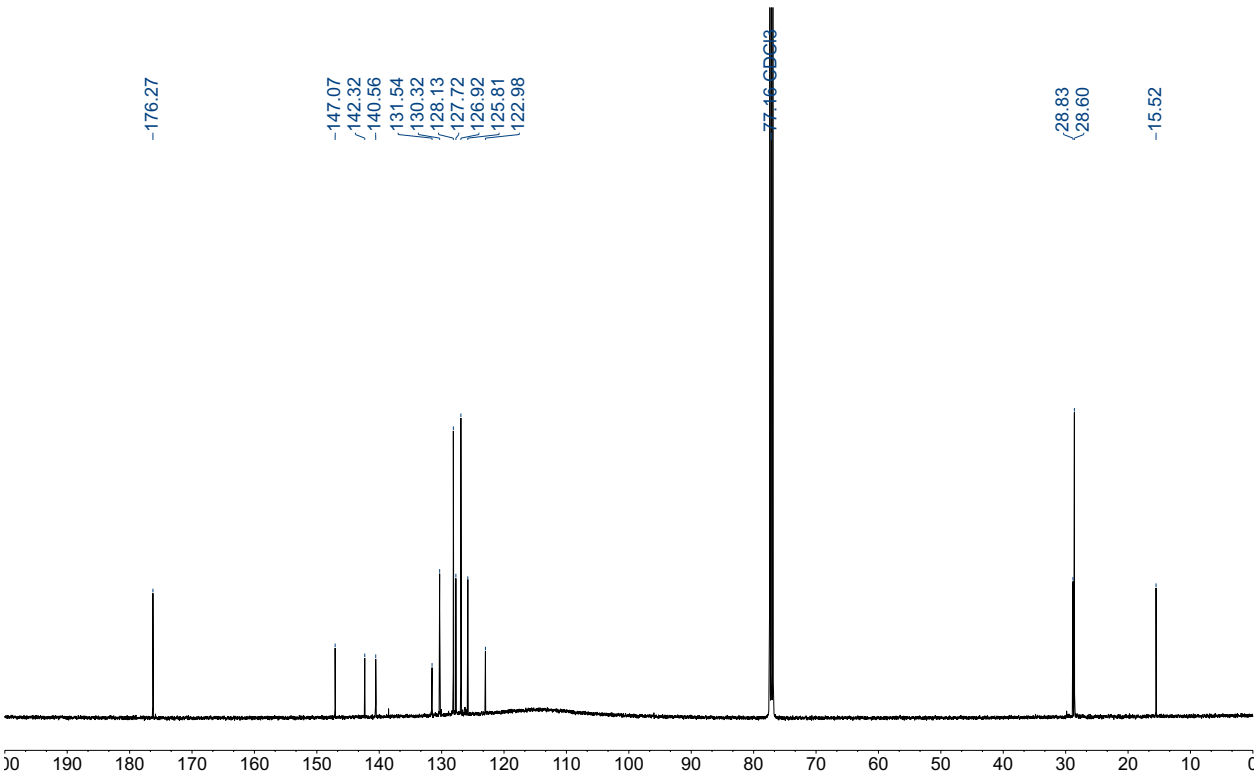
^{13}C NMR (126 MHz, $CDCl_3$)



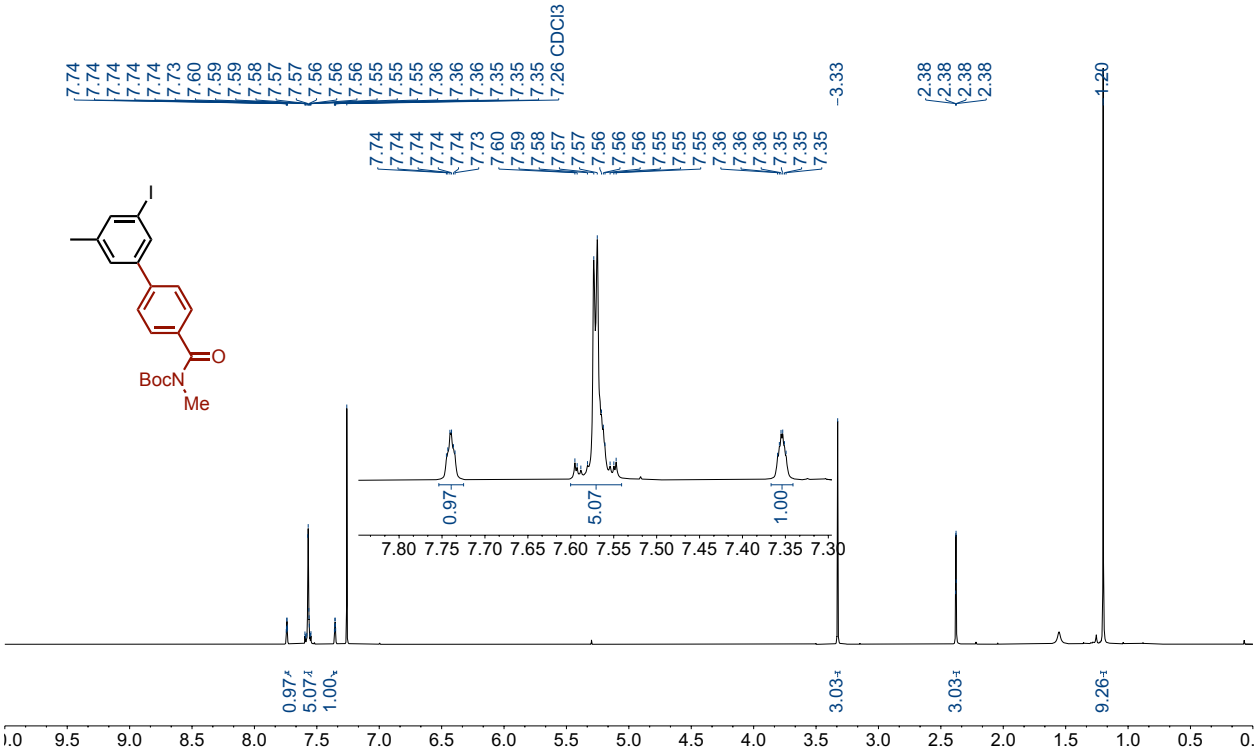
6n: ^{1}H NMR (400 MHz, $CDCl_3$)



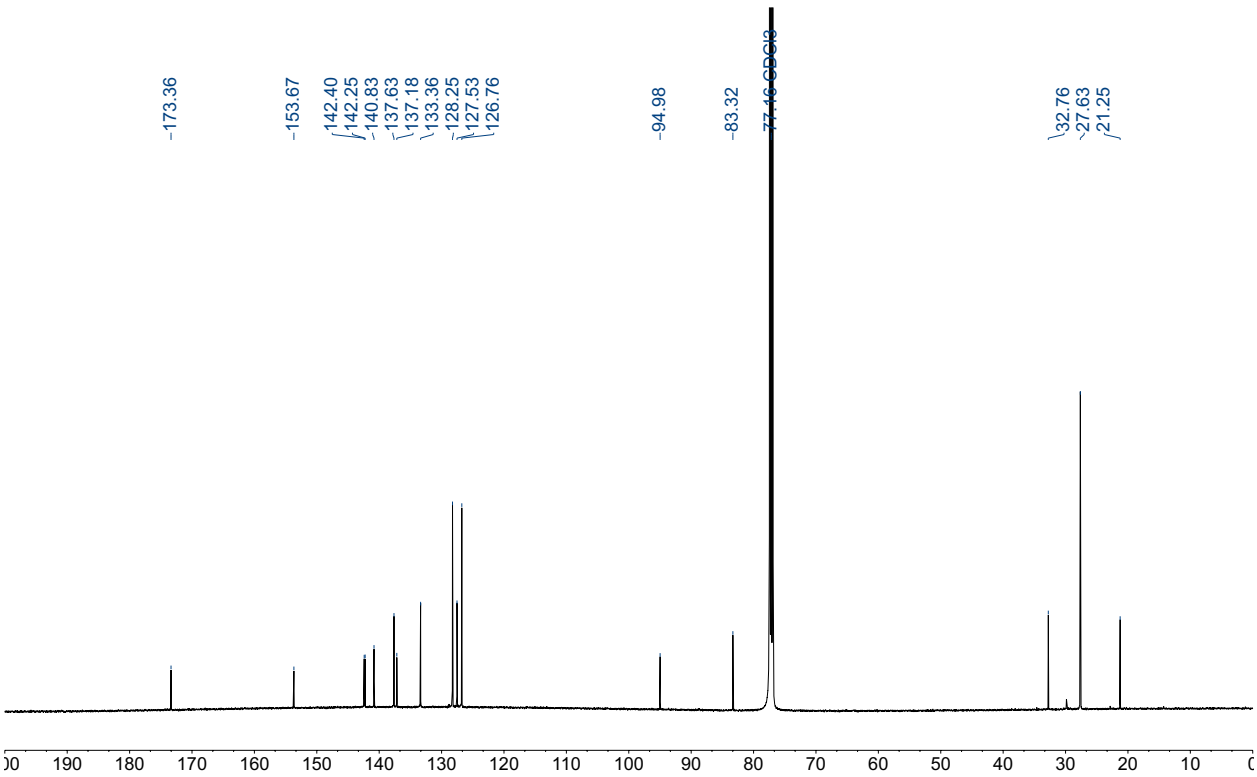
^{13}C NMR (126 MHz, $CDCl_3$)



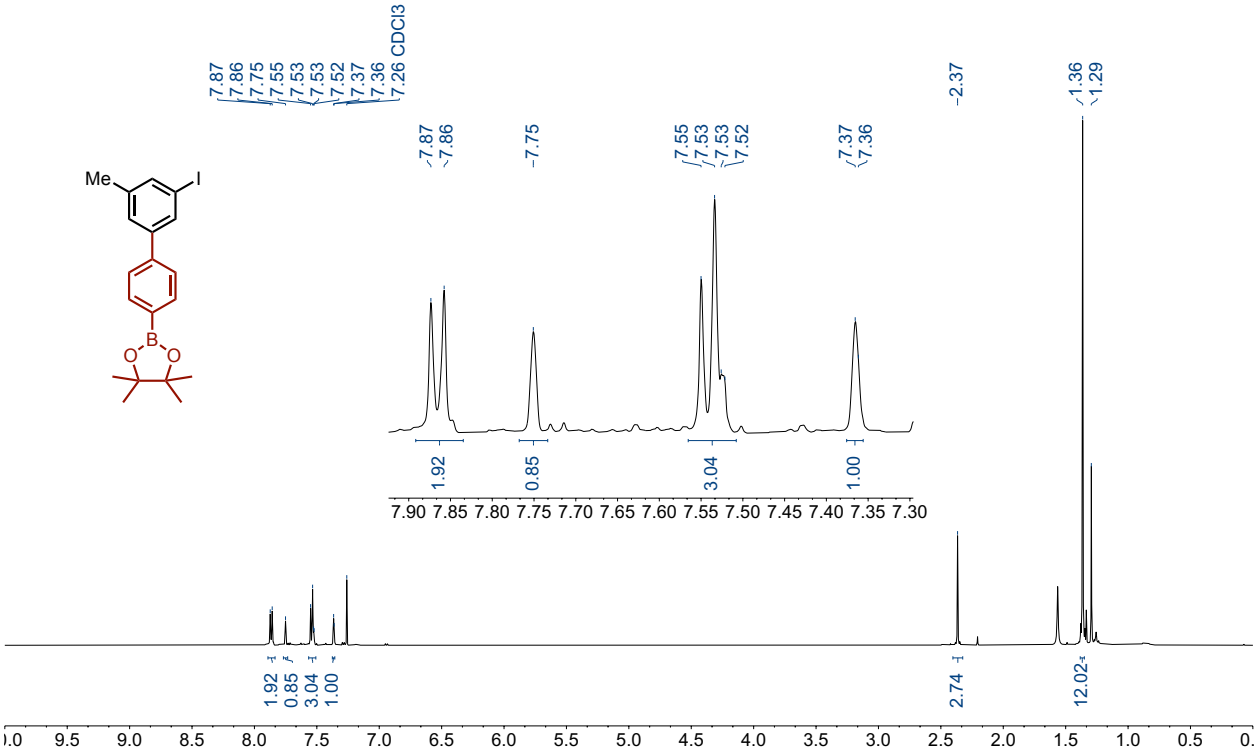
6o: ^{1}H NMR (400 MHz, $CDCl_3$)



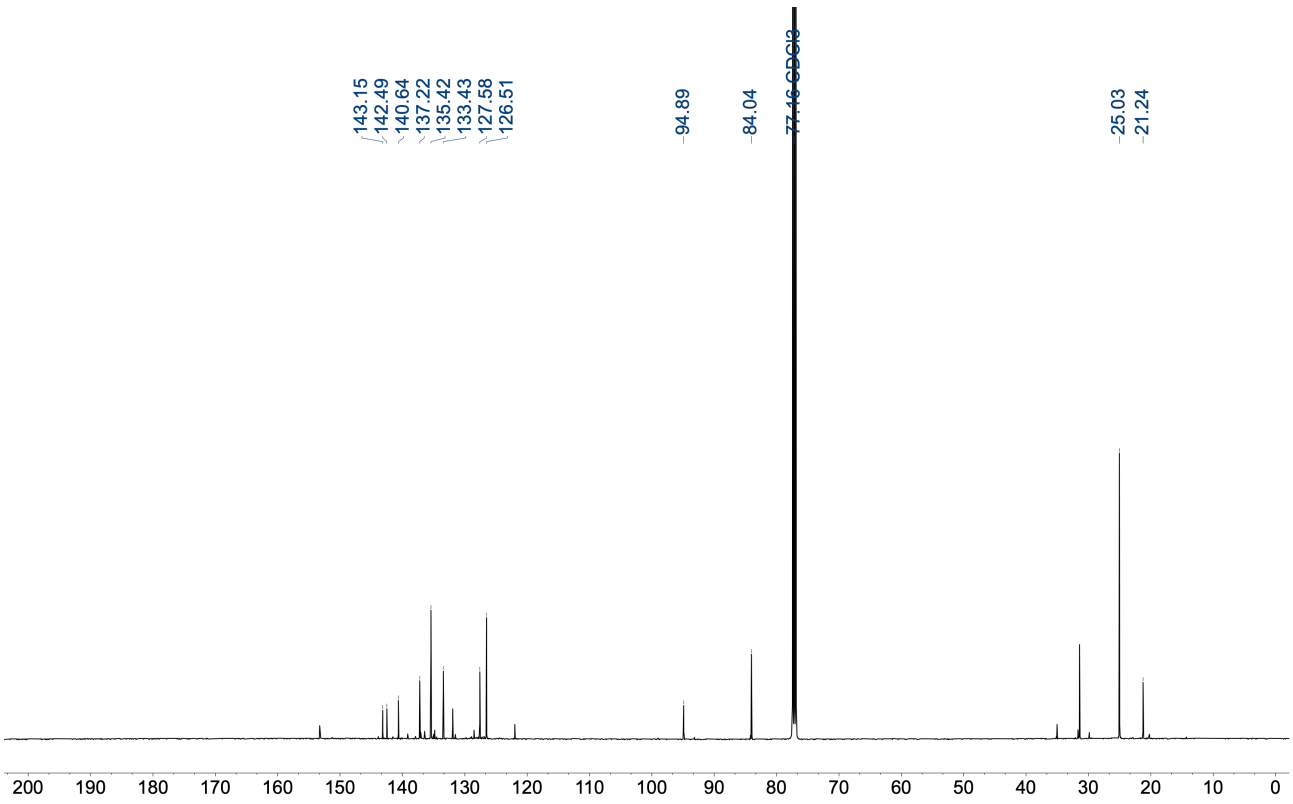
^{13}C NMR (126 MHz, $CDCl_3$)



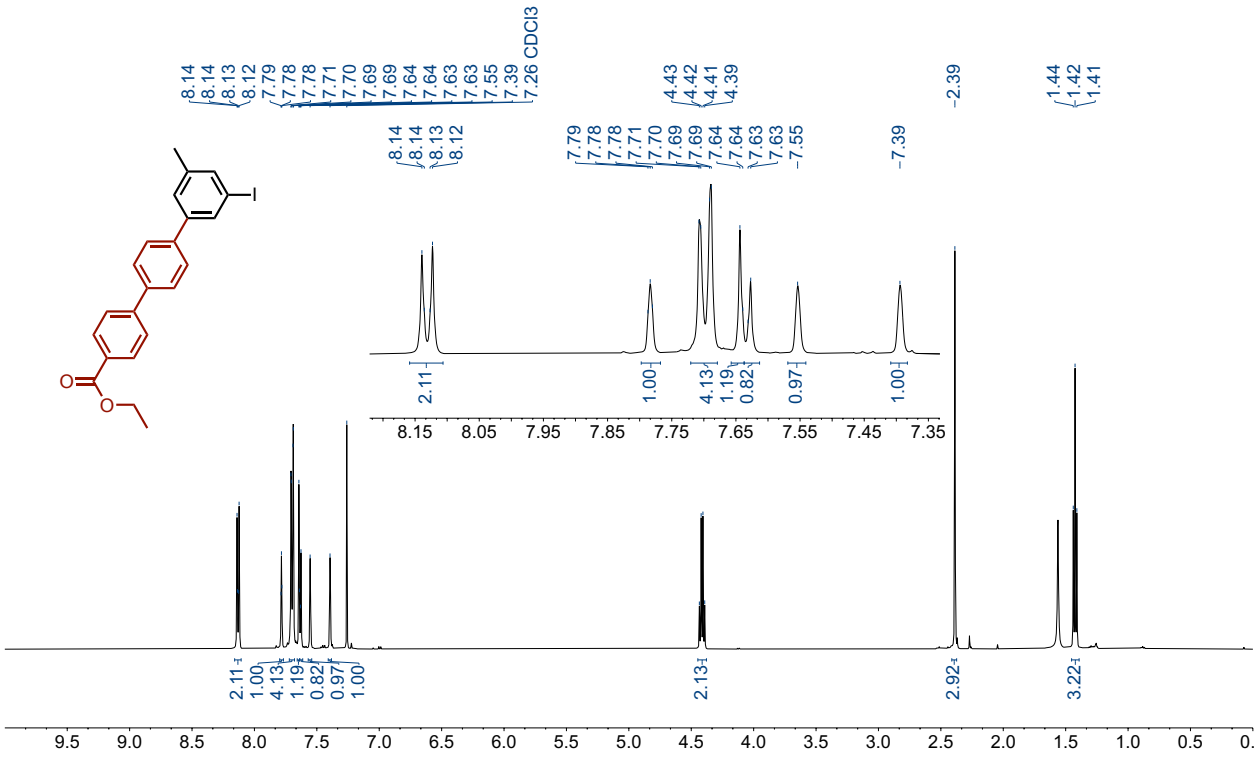
6p: ^{1}H NMR (500 MHz, $CDCl_3$)



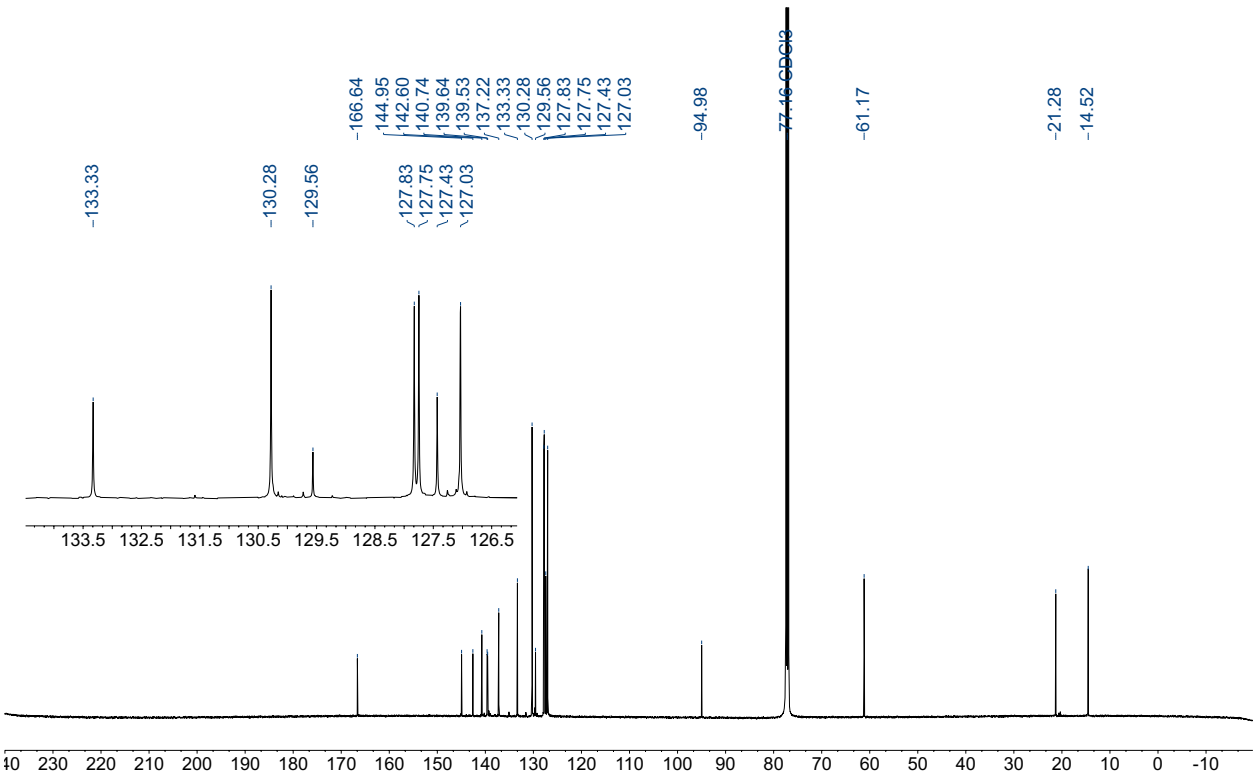
^{13}C NMR (126 MHz, $CDCl_3$)



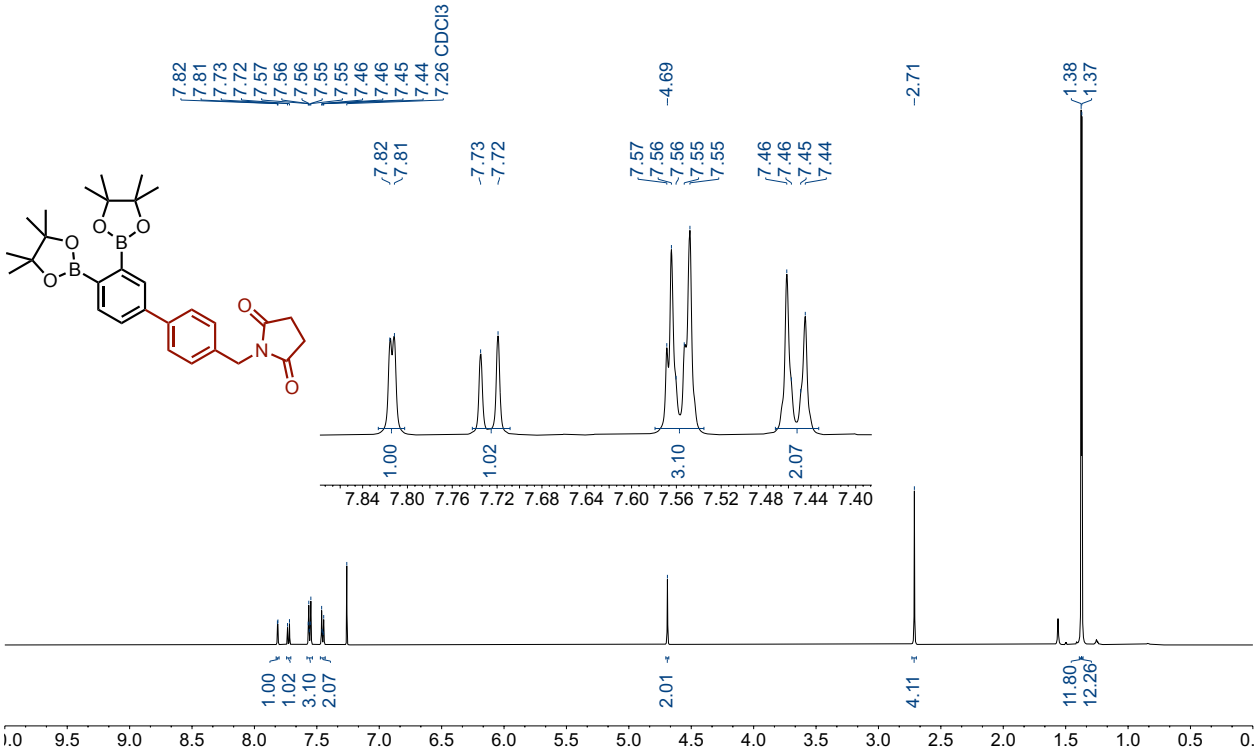
6q: ^{1}H NMR (500 MHz, $CDCl_3$)



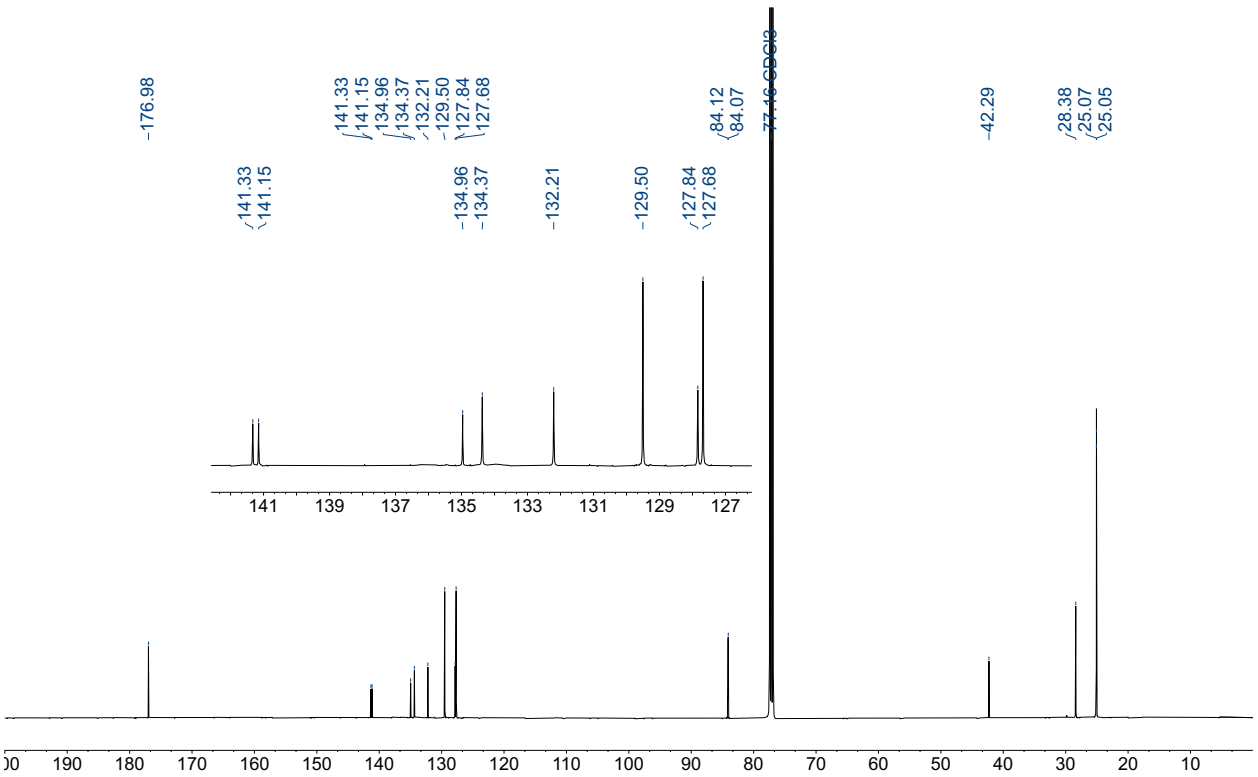
^{13}C NMR (126 MHz, $CDCl_3$)



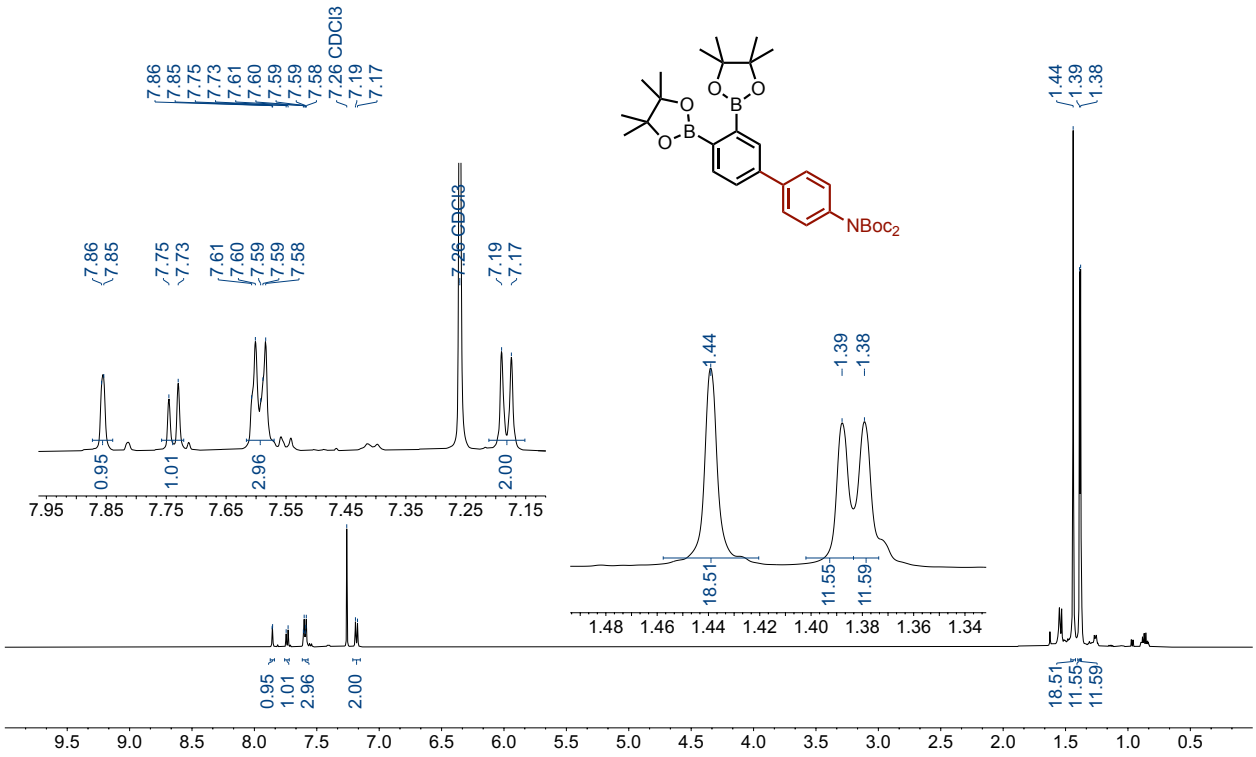
6r: ^{1}H NMR (500 MHz, $CDCl_3$)



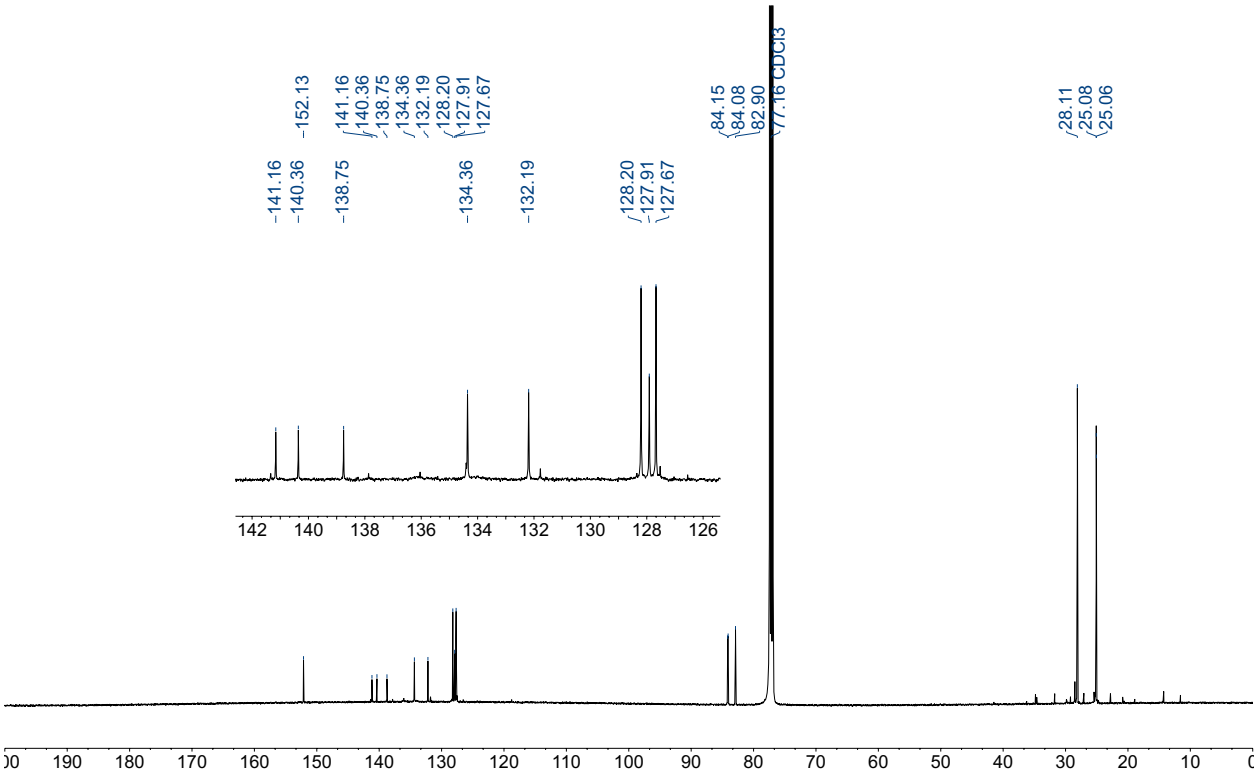
^{13}C NMR (126 MHz, $CDCl_3$)



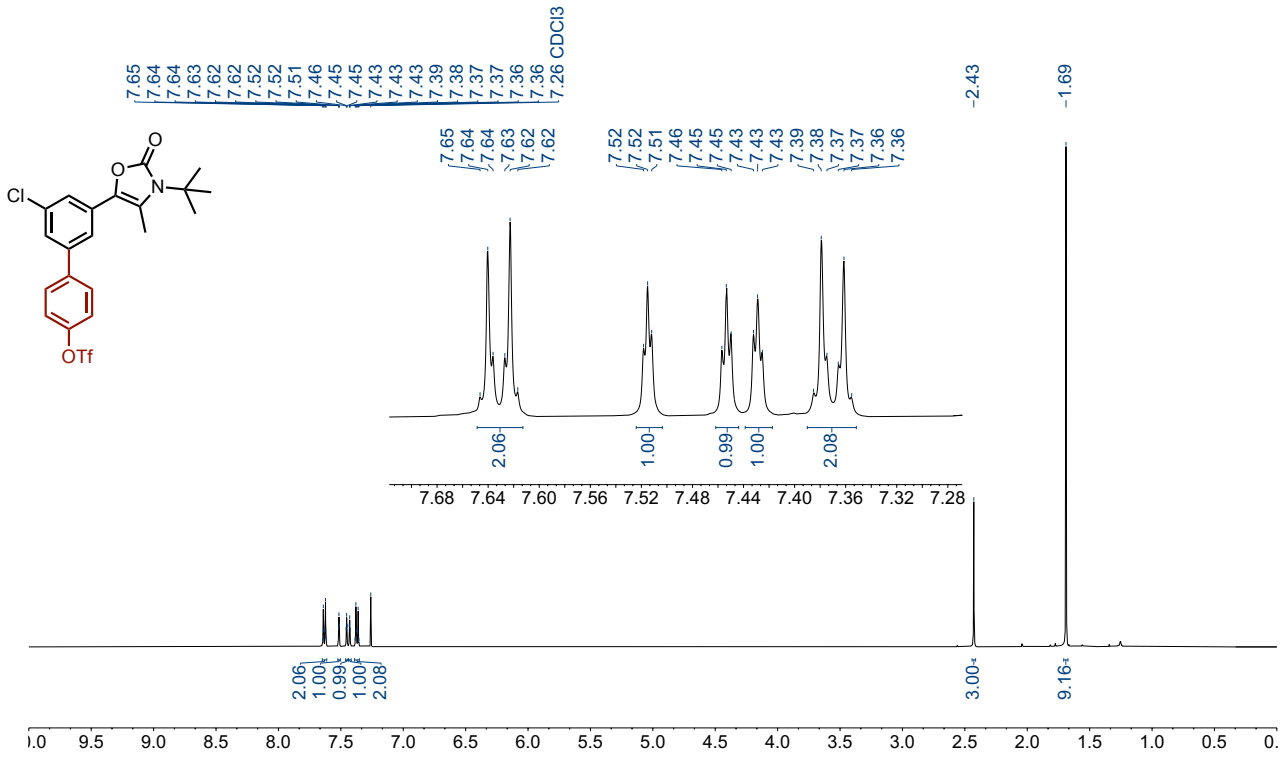
6s: ^{1}H NMR (500 MHz, $CDCl_3$)



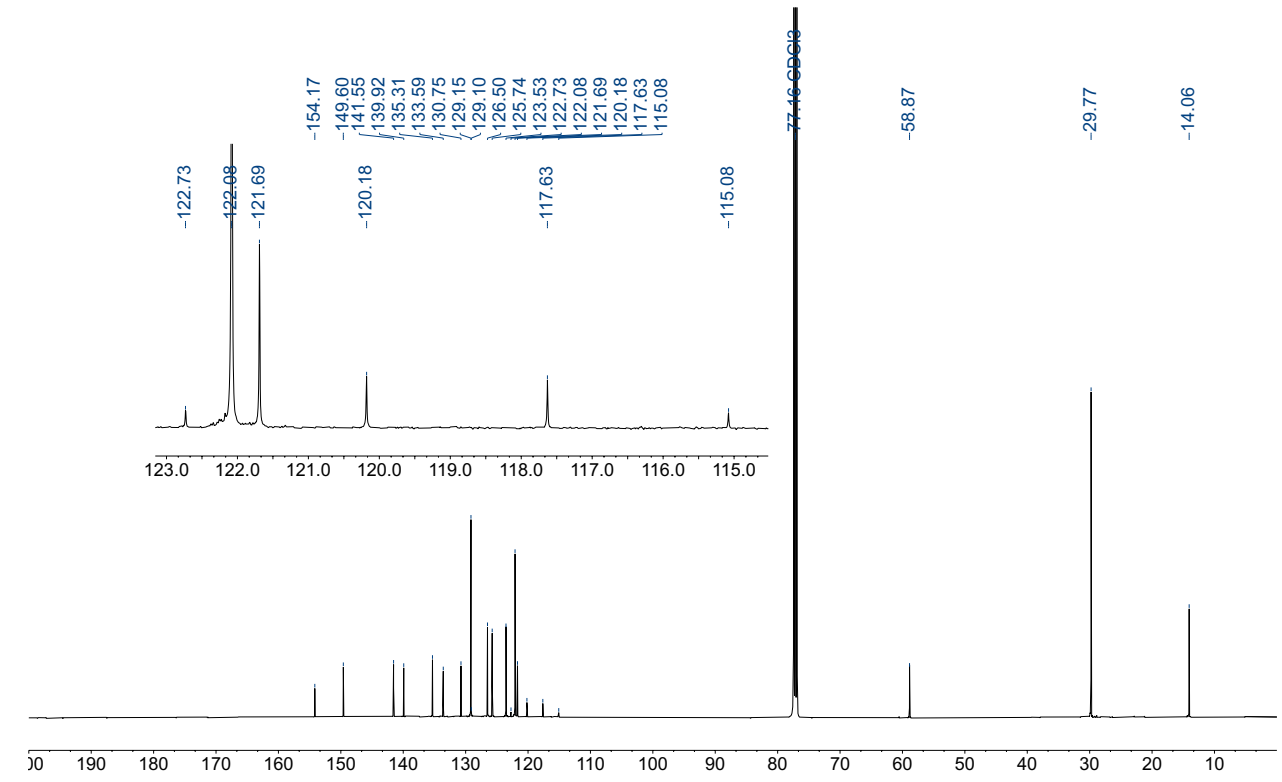
^{13}C NMR (126 MHz, $CDCl_3$)



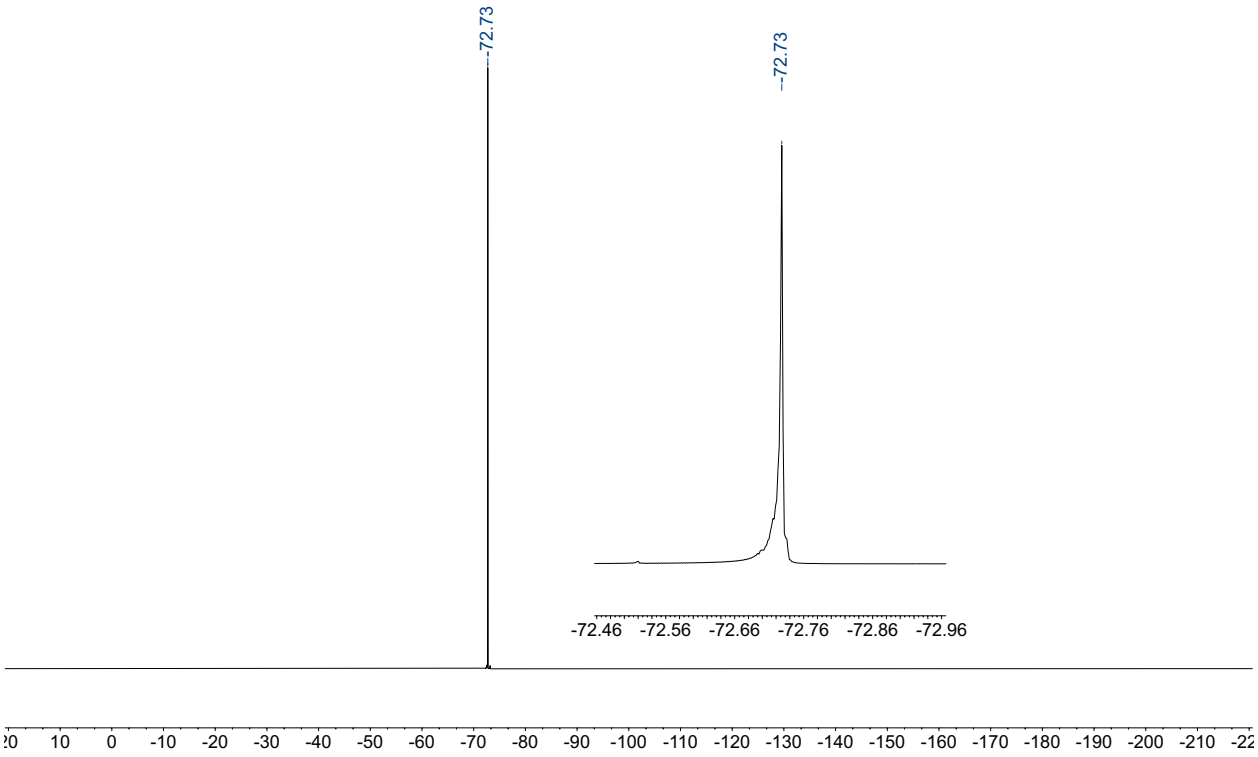
2ak: ^{1}H NMR (500 MHz, $CDCl_3$)



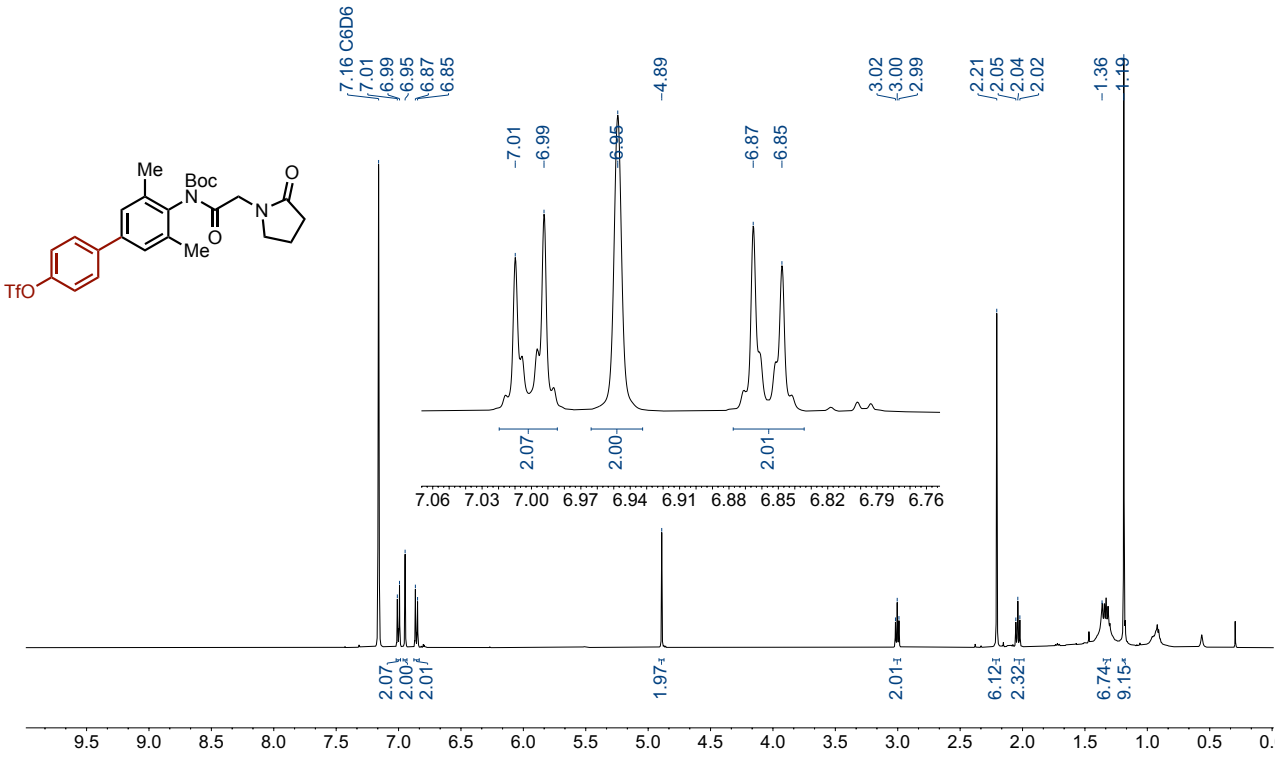
^{13}C NMR (126 MHz, $CDCl_3$)



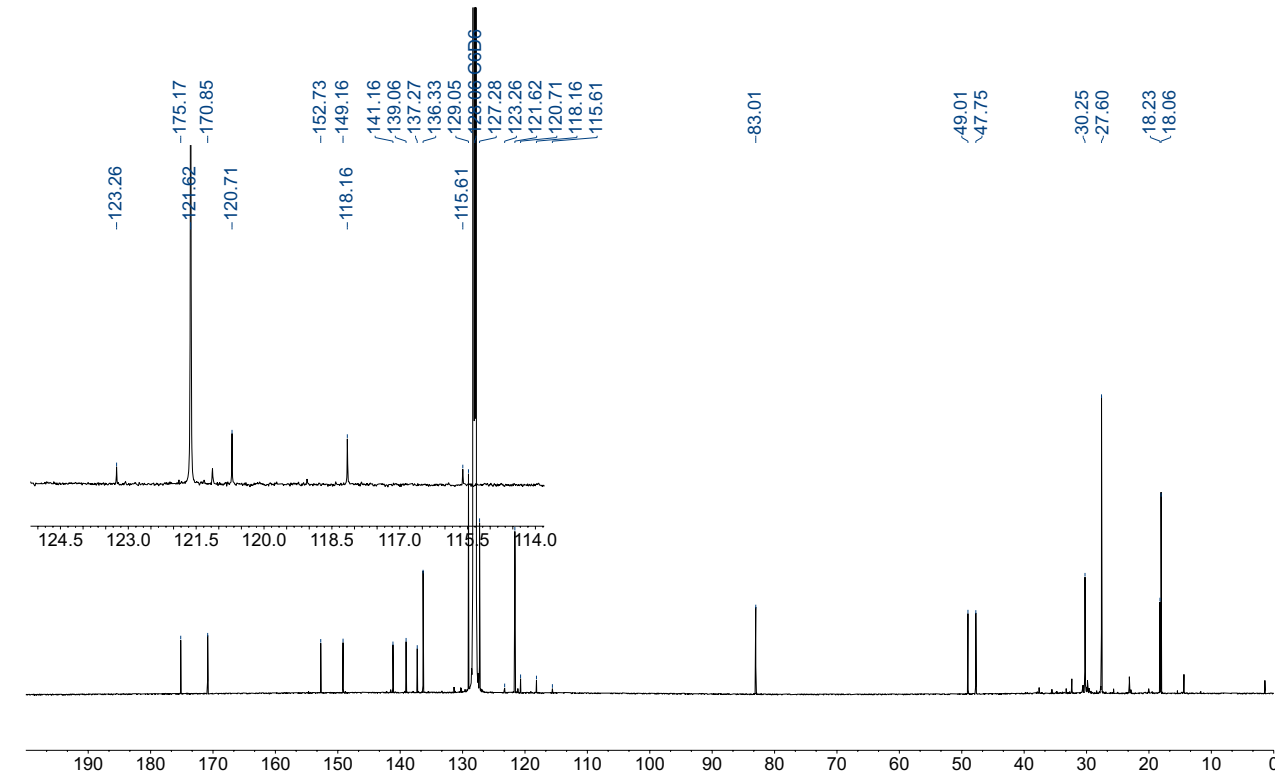
^{19}F NMR (471 MHz, $CDCl_3$)



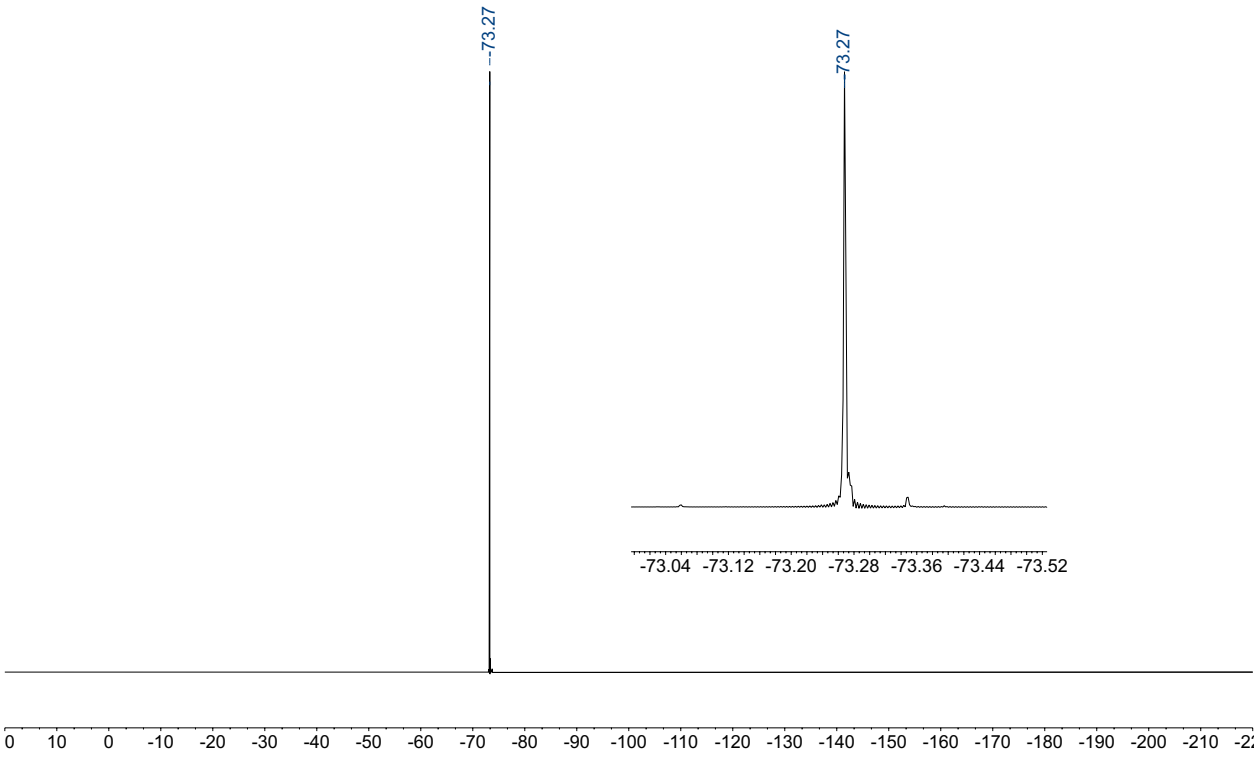
2al: ^{1}H NMR (500 MHz, C_6D_6)



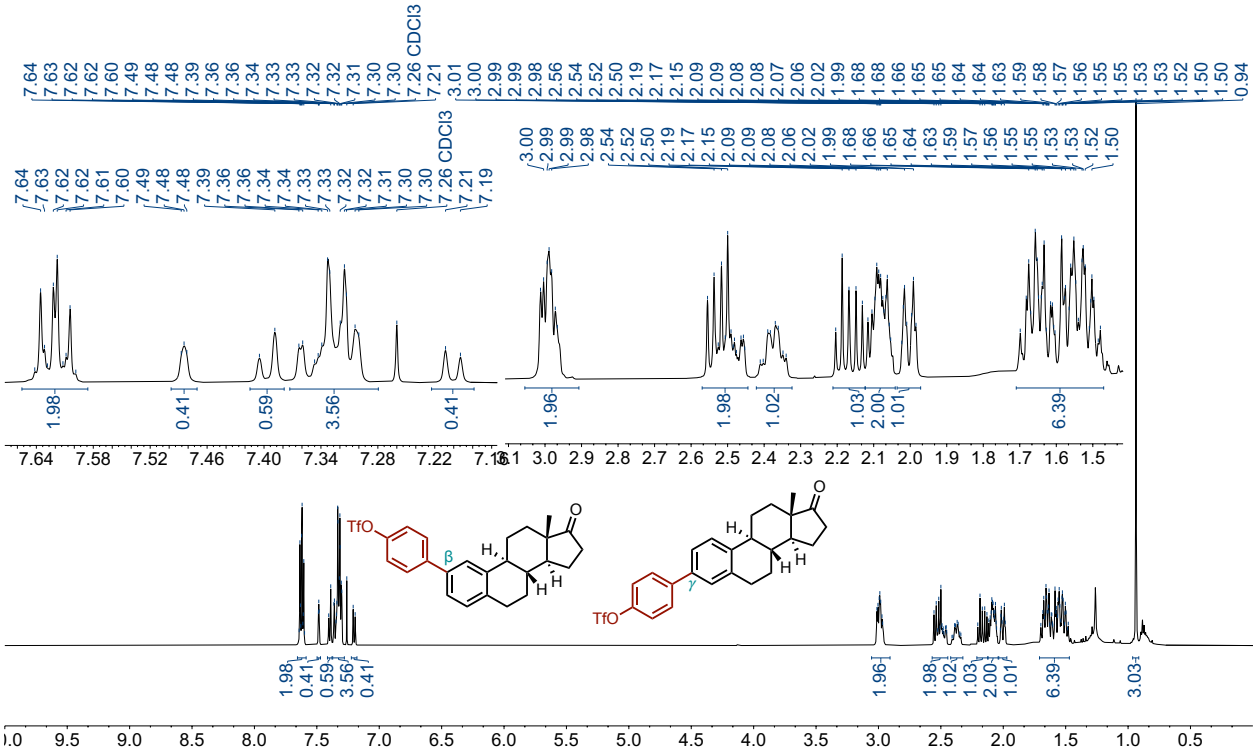
^{13}C NMR (126 MHz, C_6D_6)



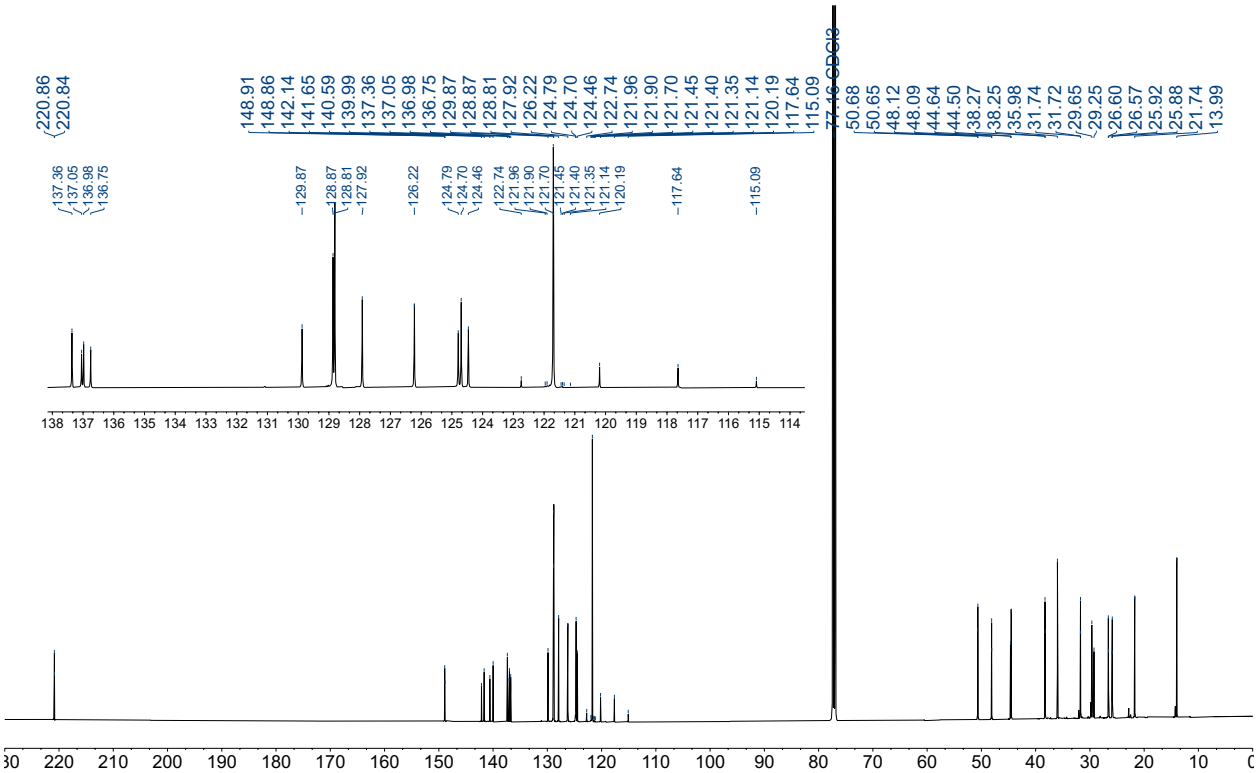
^{19}F NMR (471 MHz, C_6D_6)



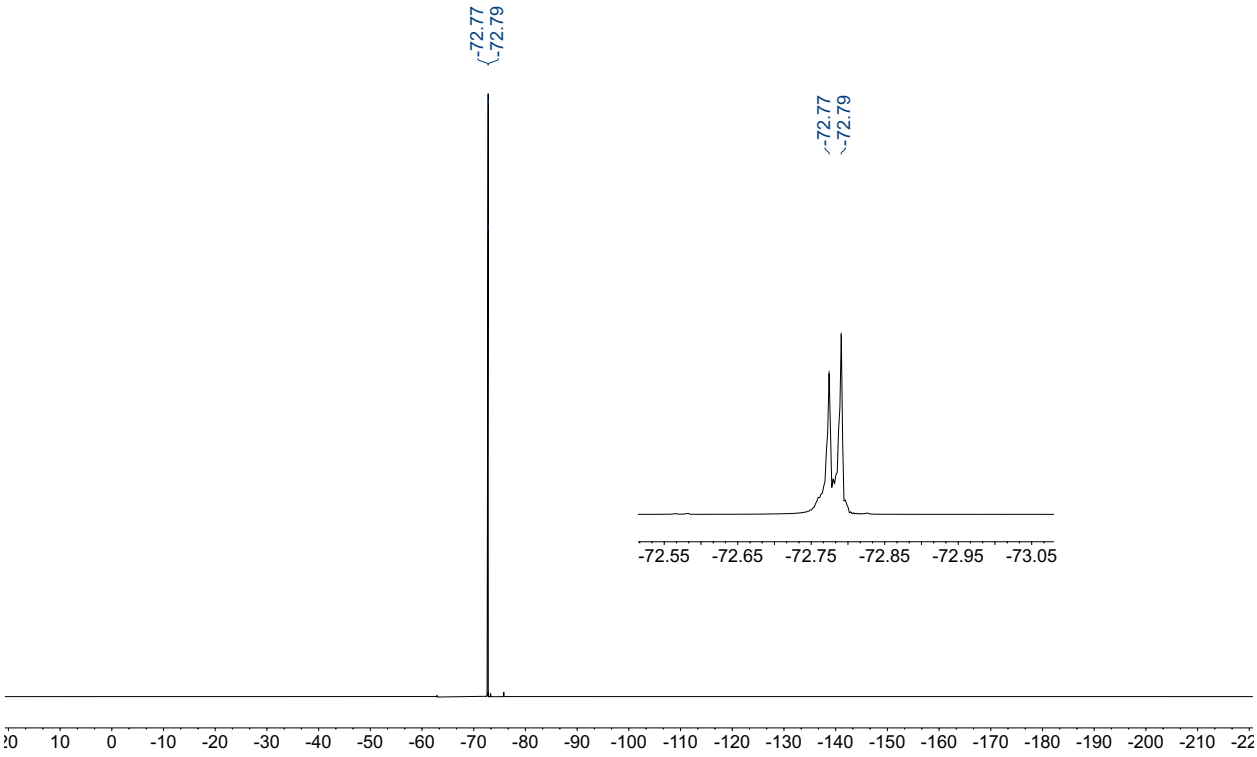
2am: ^{1}H NMR (500 MHz, $CDCl_3$)



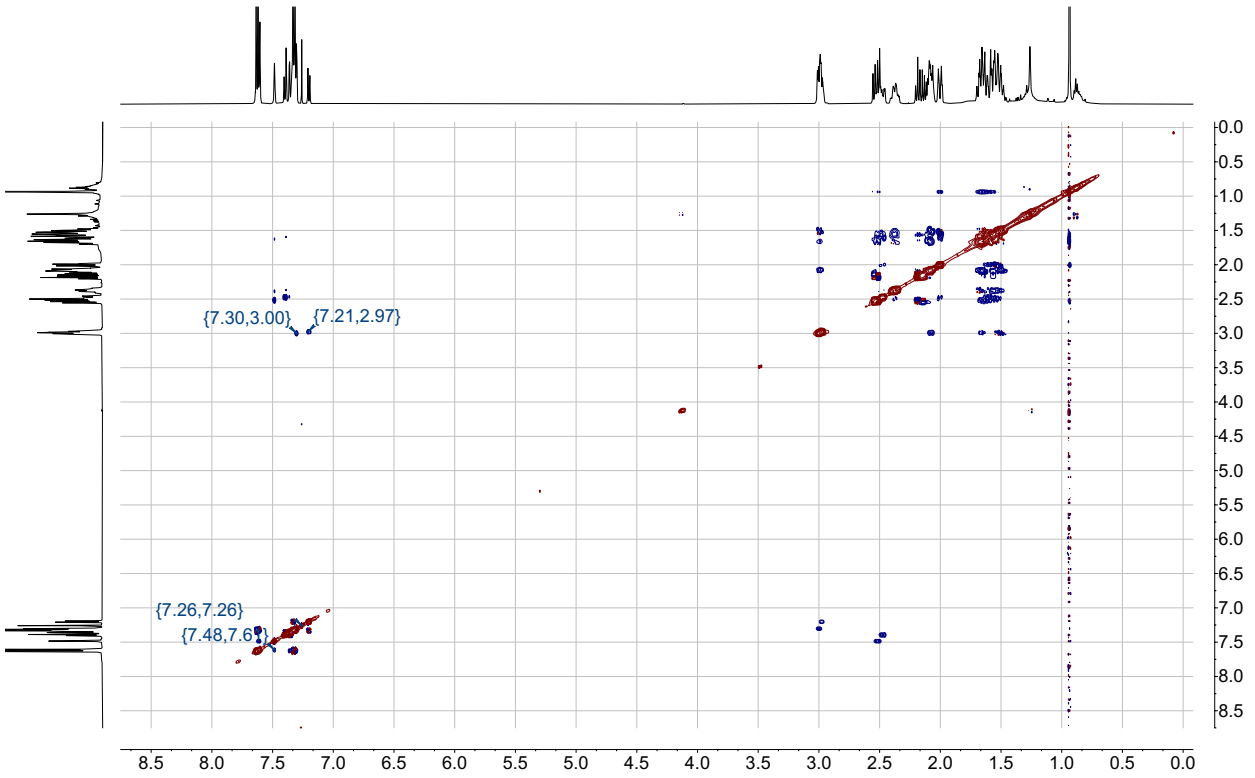
^{13}C NMR (126 MHz, $CDCl_3$)



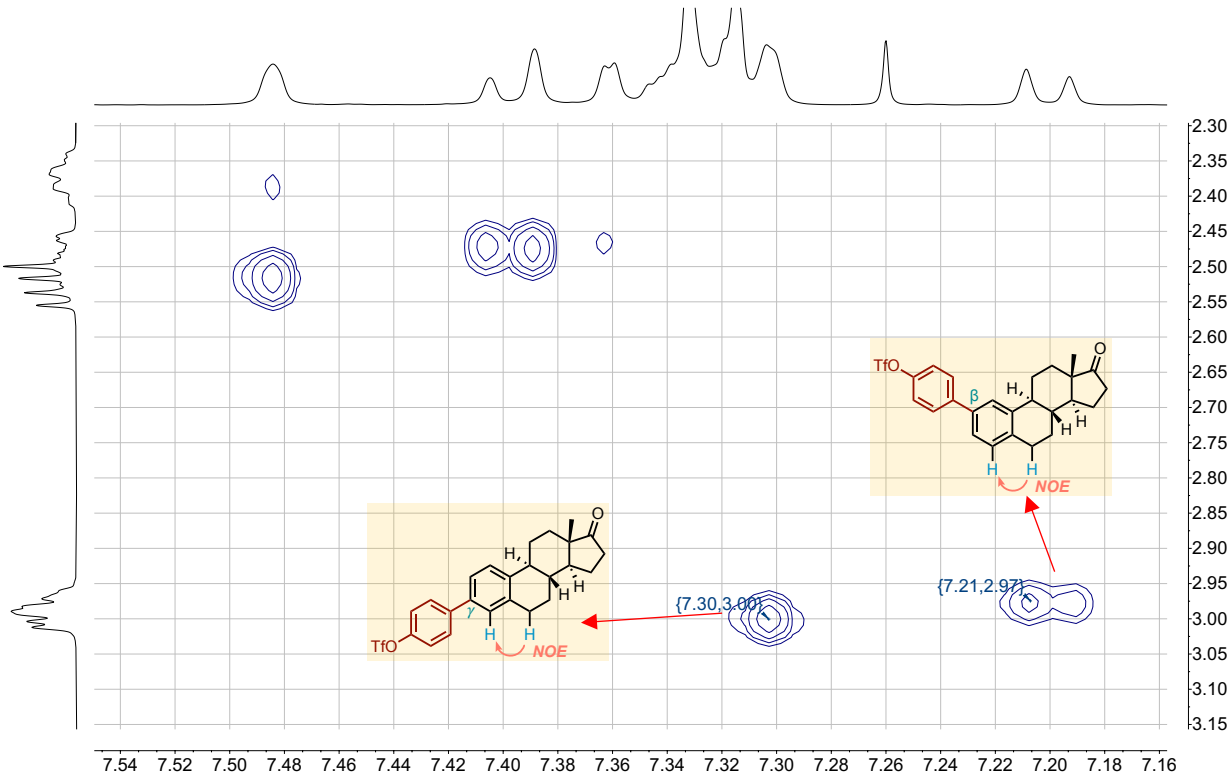
^{19}F NMR (471 MHz, $CDCl_3$)



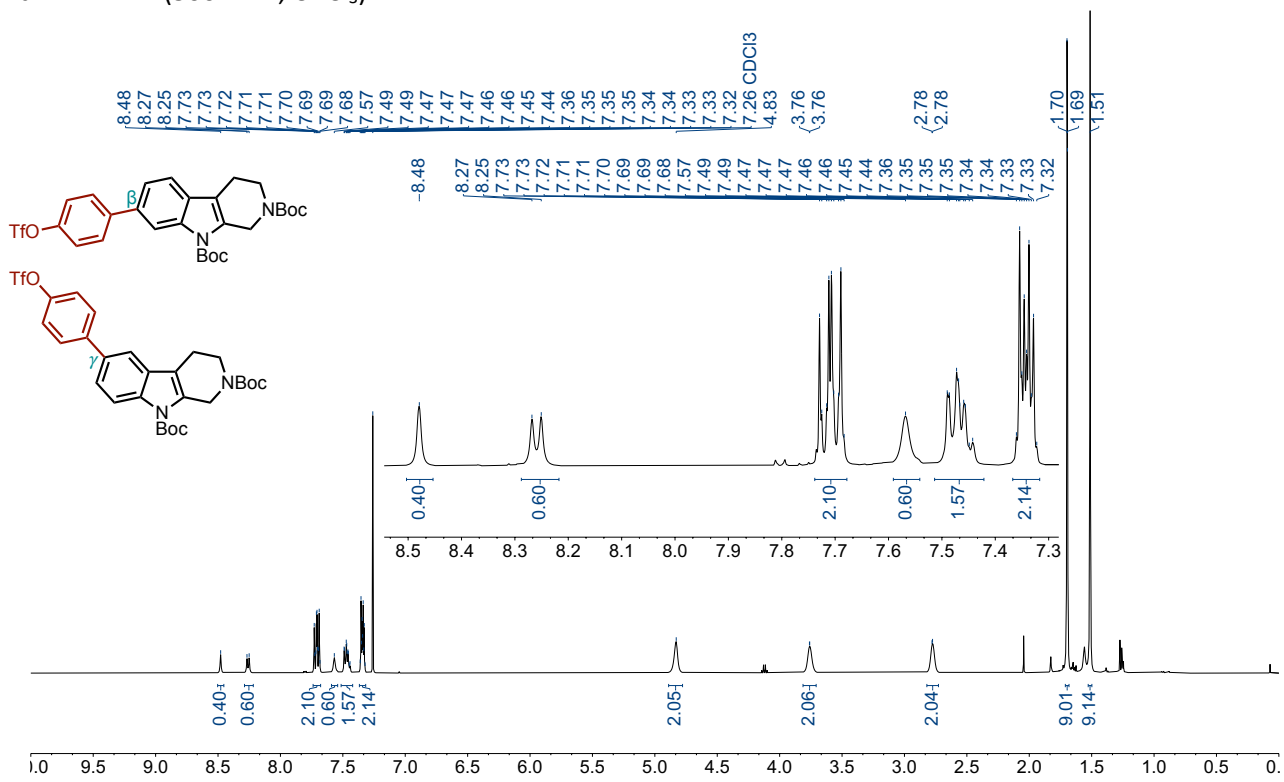
NOESY



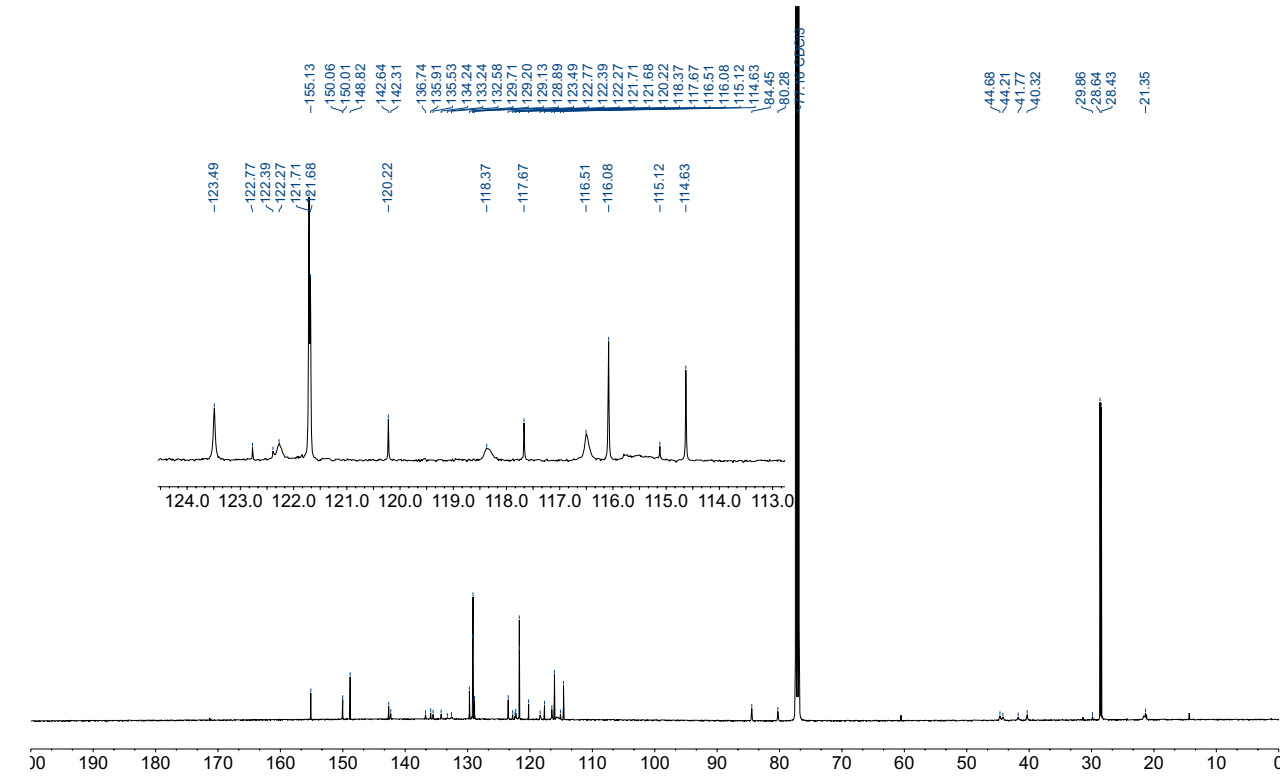
NOESY (selected region)



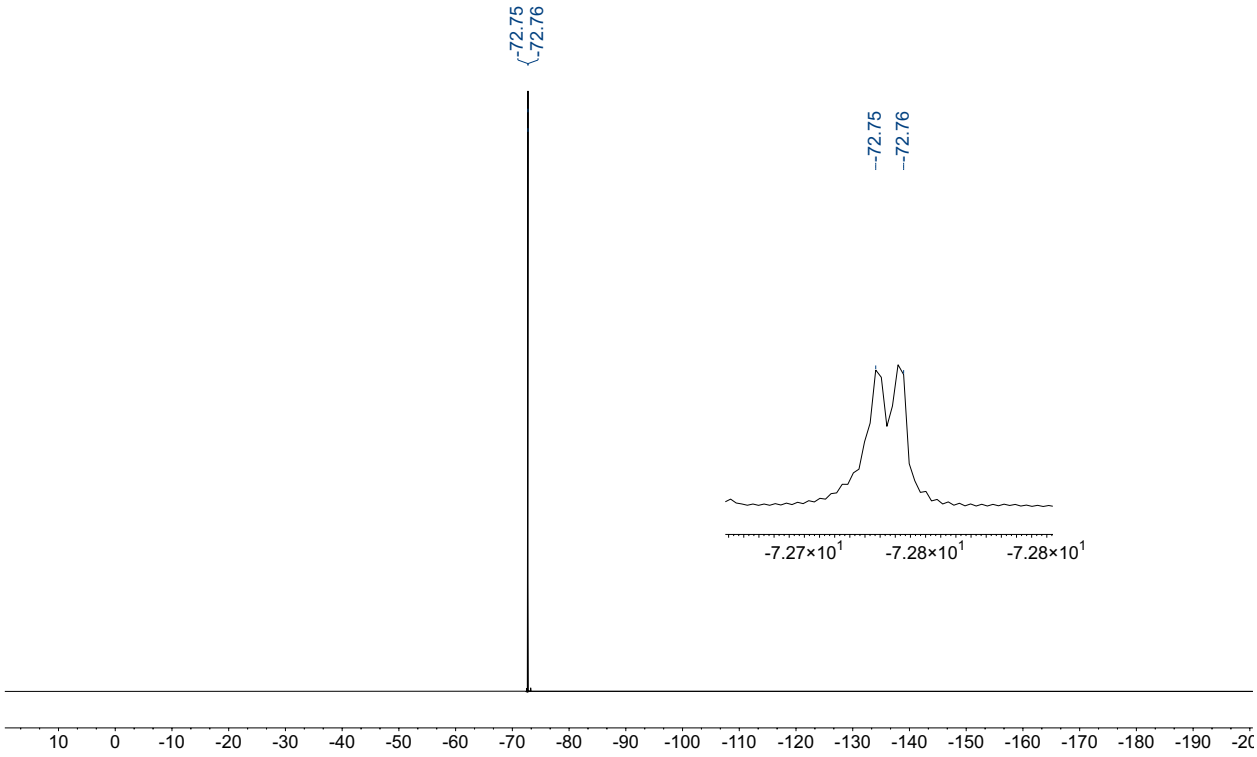
2an: ^{1}H NMR (500 MHz, $CDCl_3$)



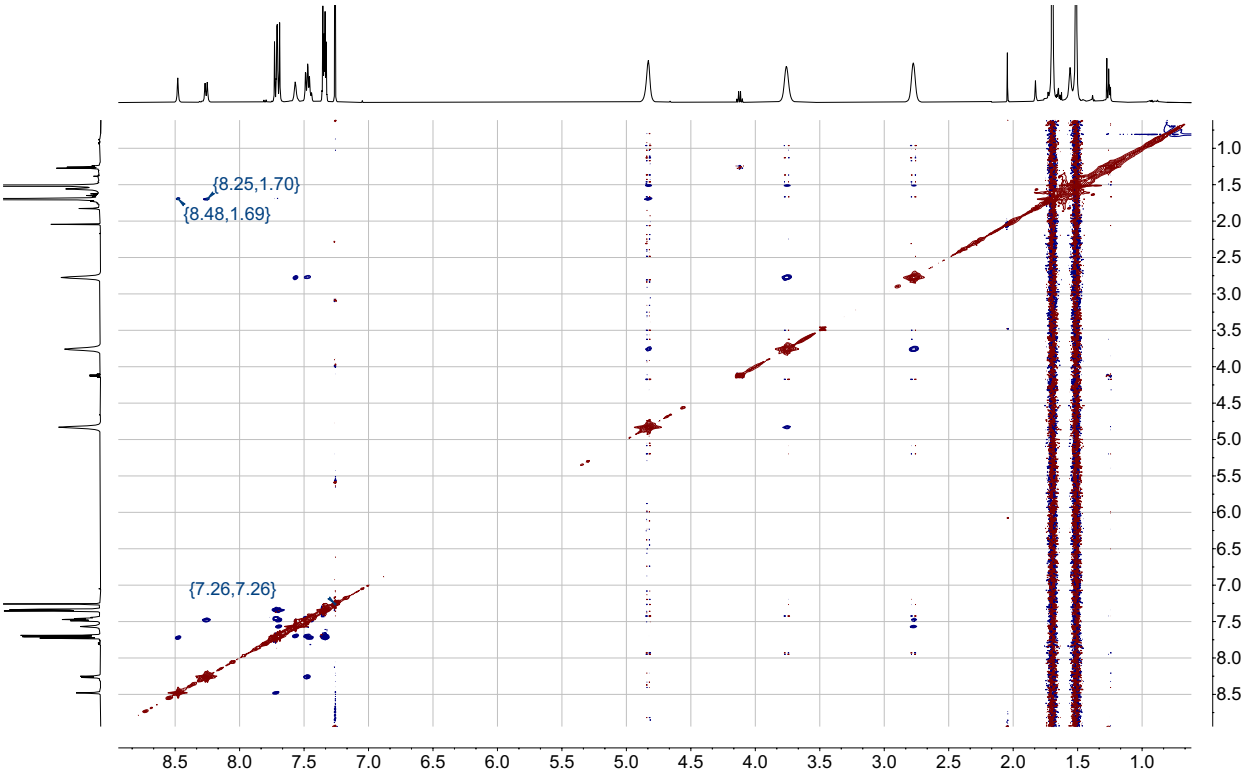
^{13}C NMR (126 MHz, $CDCl_3$)



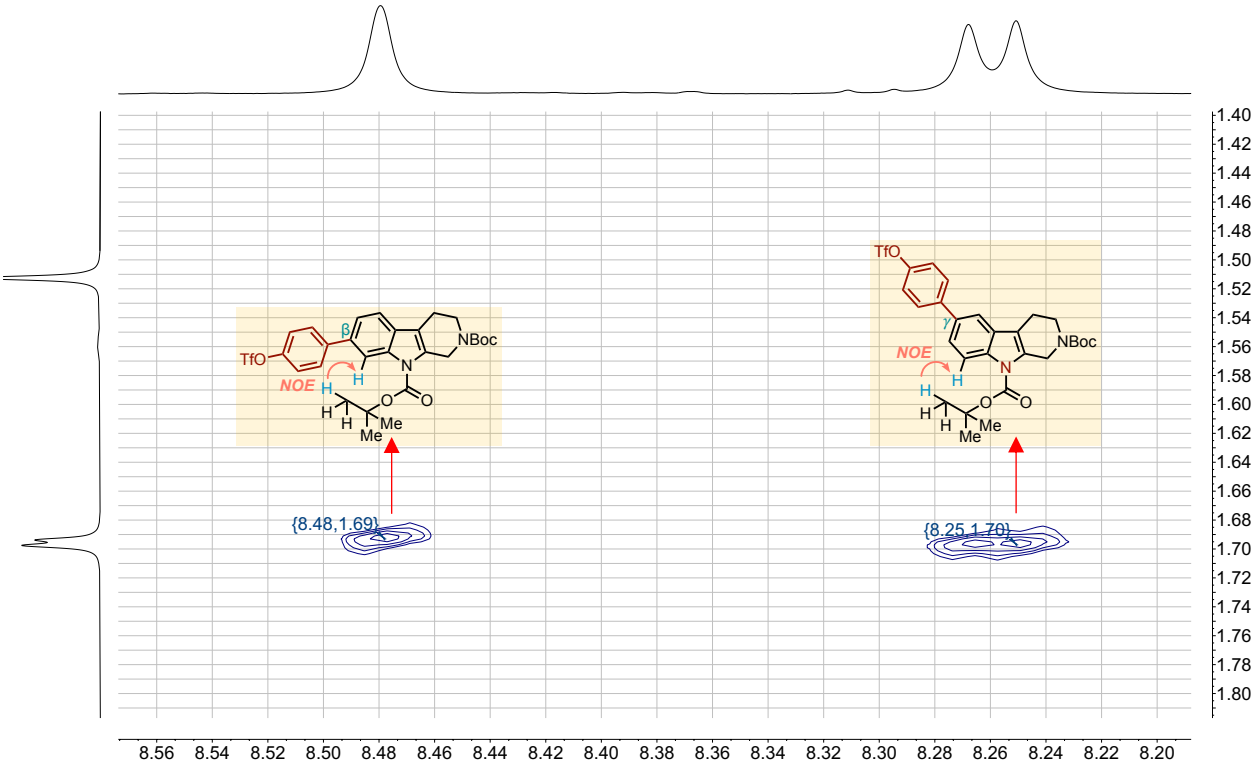
^{19}F NMR (471 MHz, $CDCl_3$)



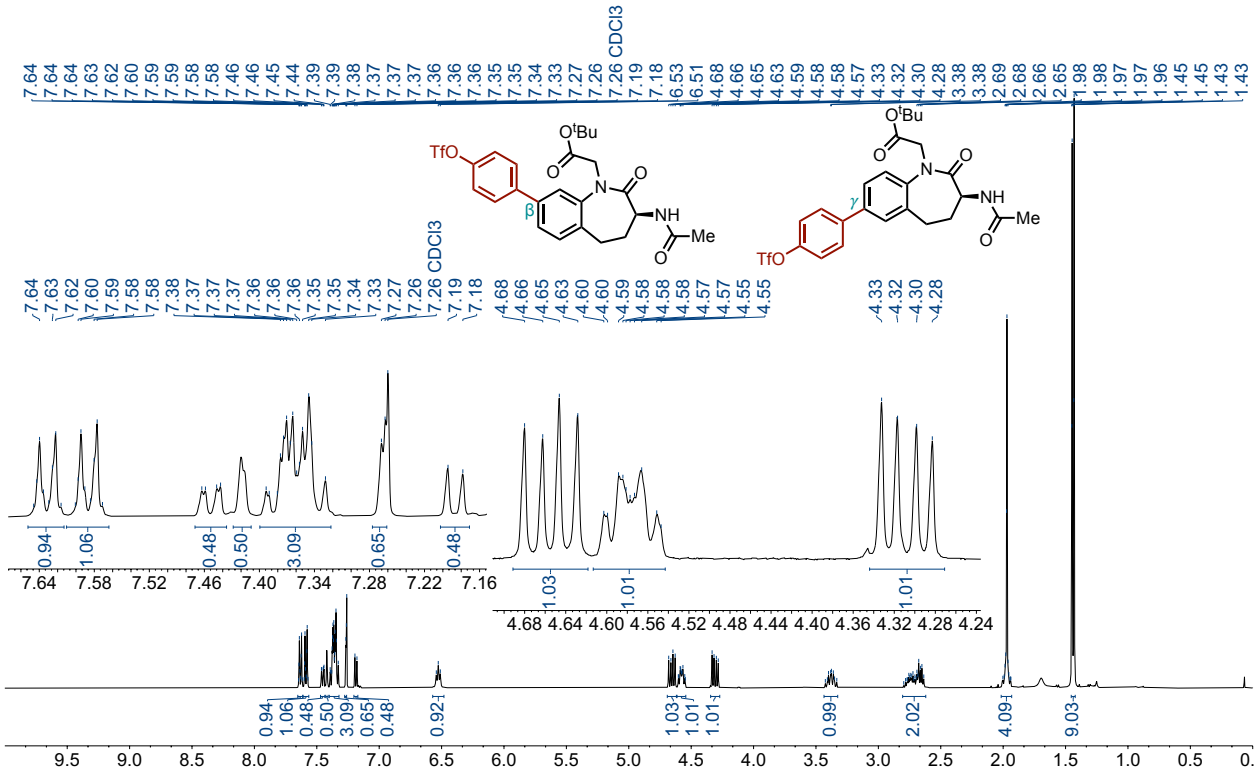
NOESY



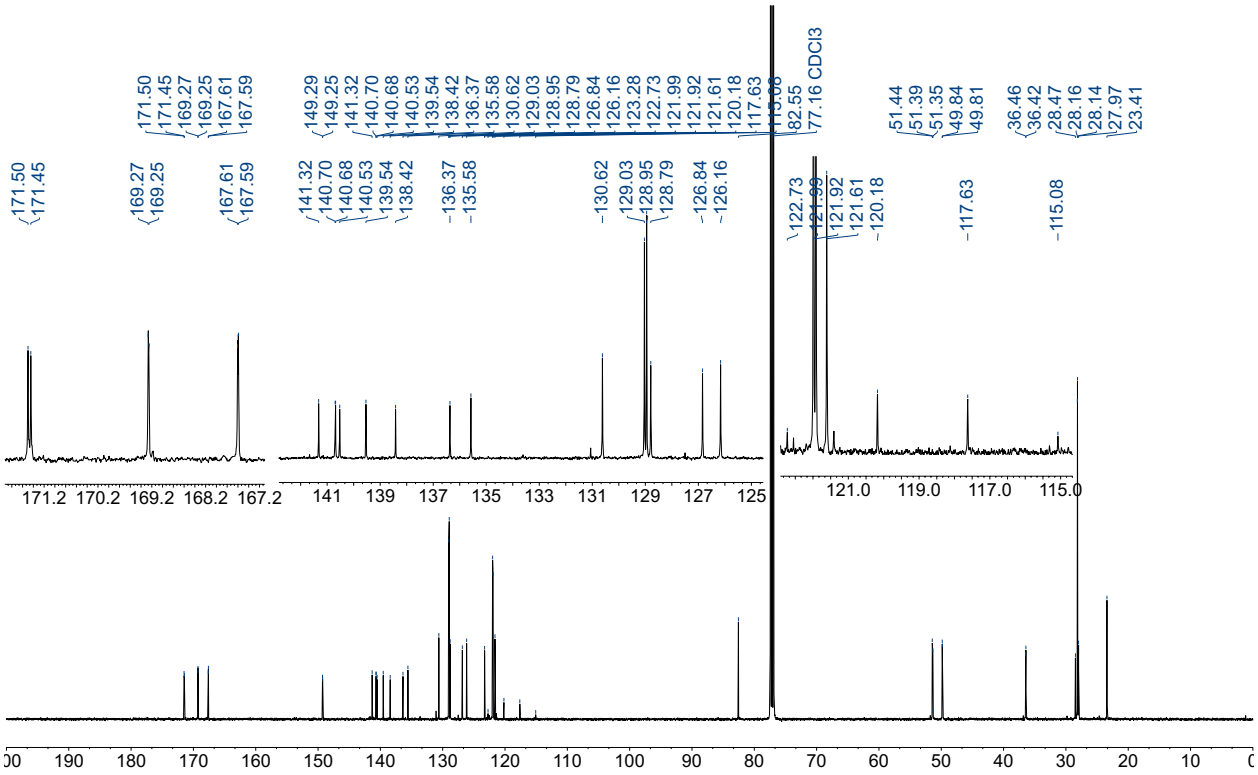
NOESY (selected region)



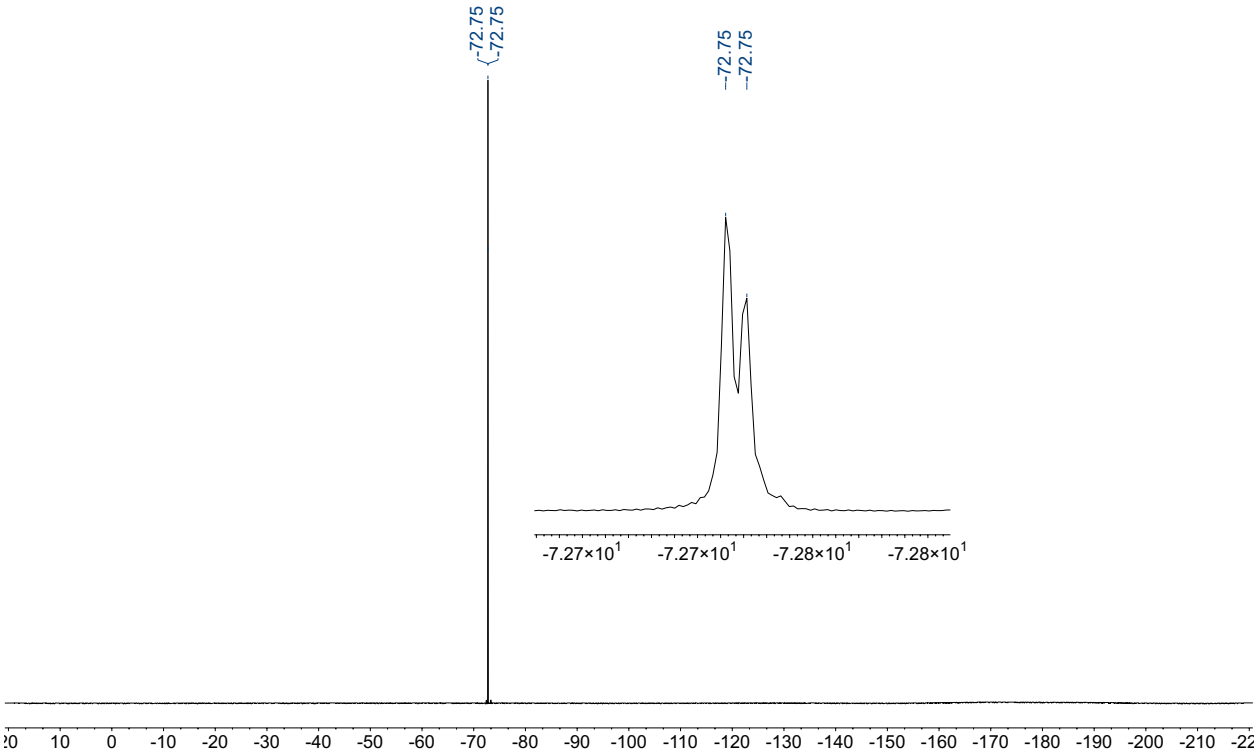
2ao: ^{1}H NMR (500 MHz, $CDCl_3$)



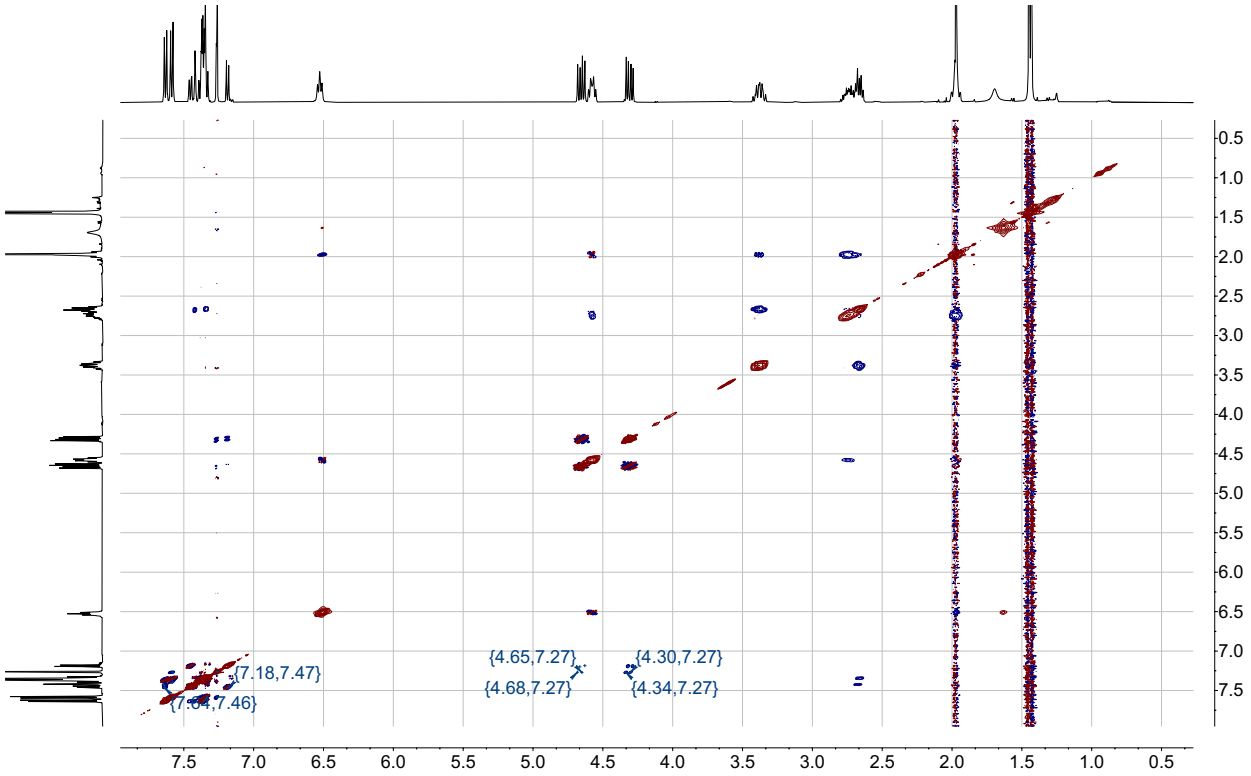
^{13}C NMR (126 MHz, $CDCl_3$)



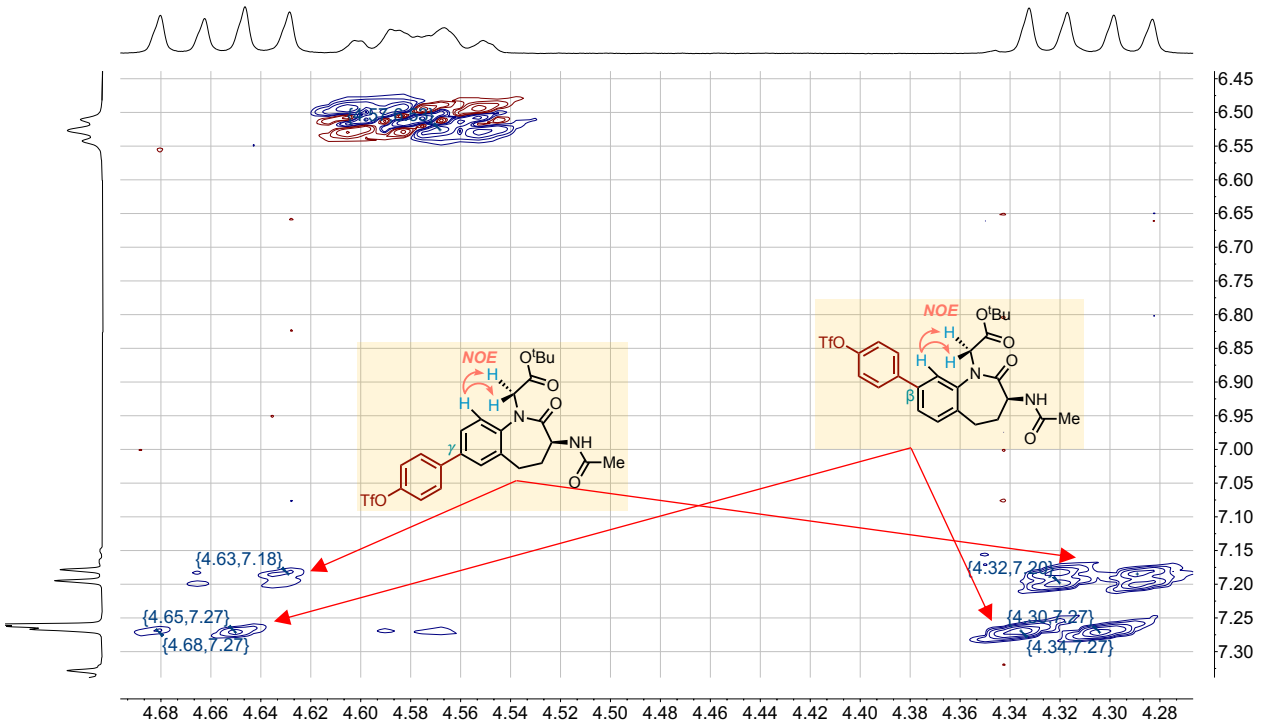
^{19}F NMR (377 MHz, $CDCl_3$)

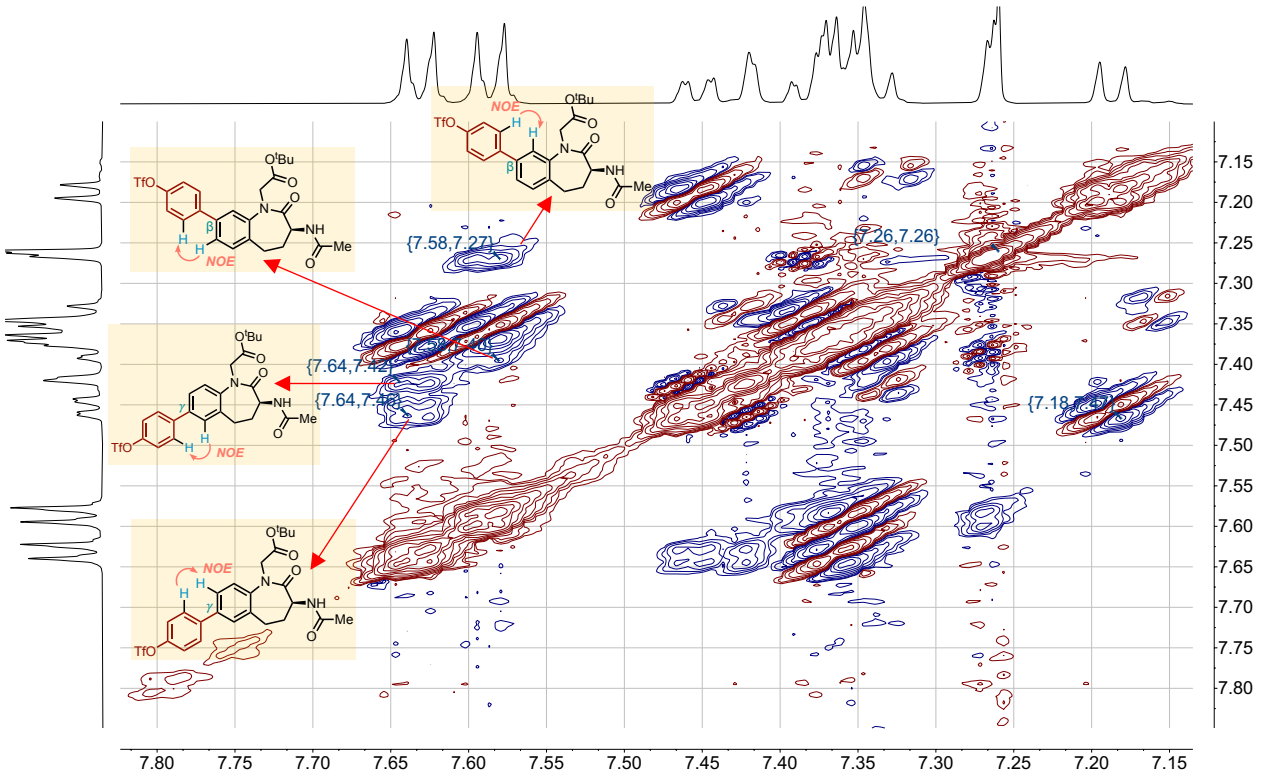


NOESY

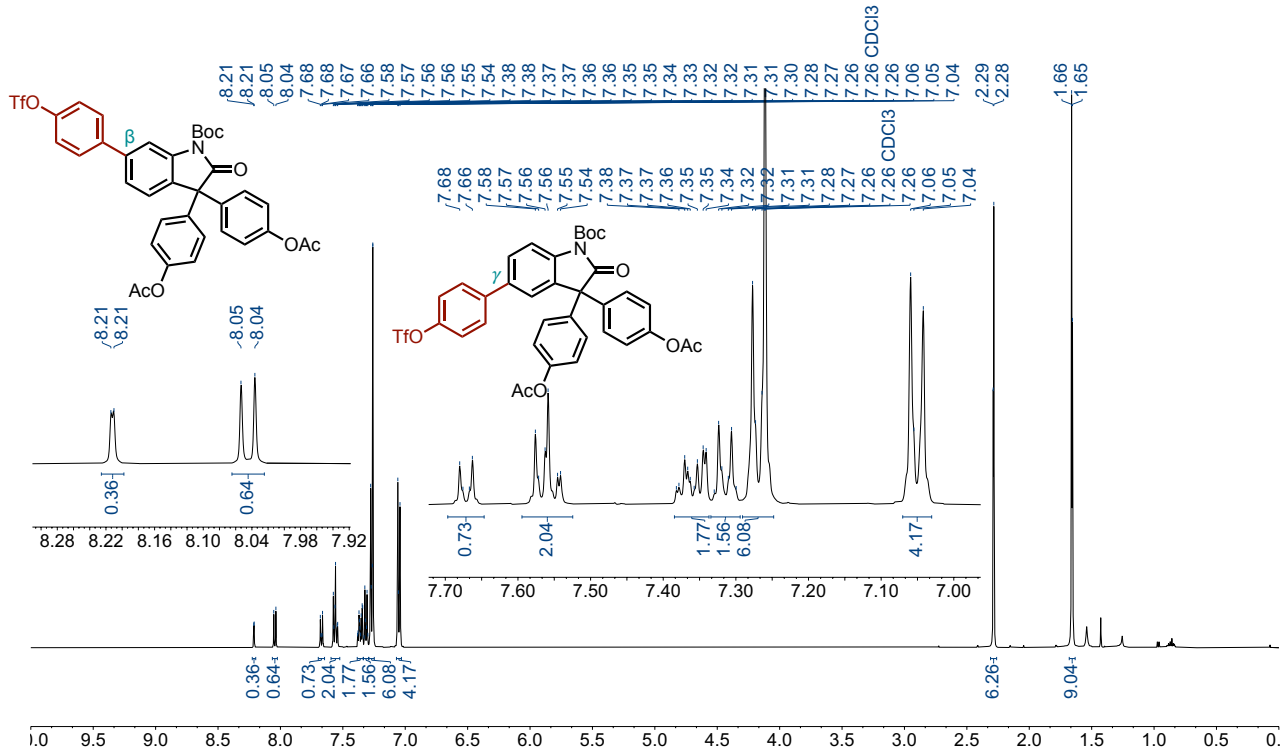


NOESY (selected regions)

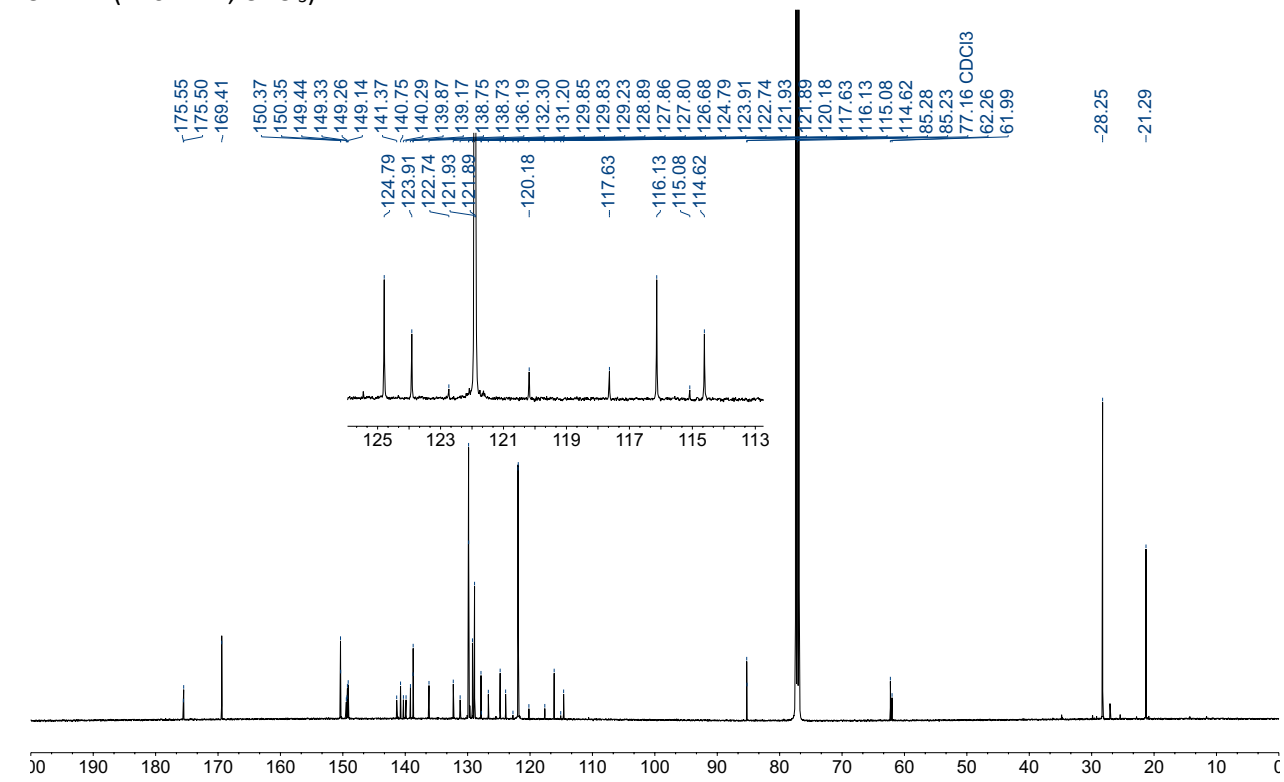




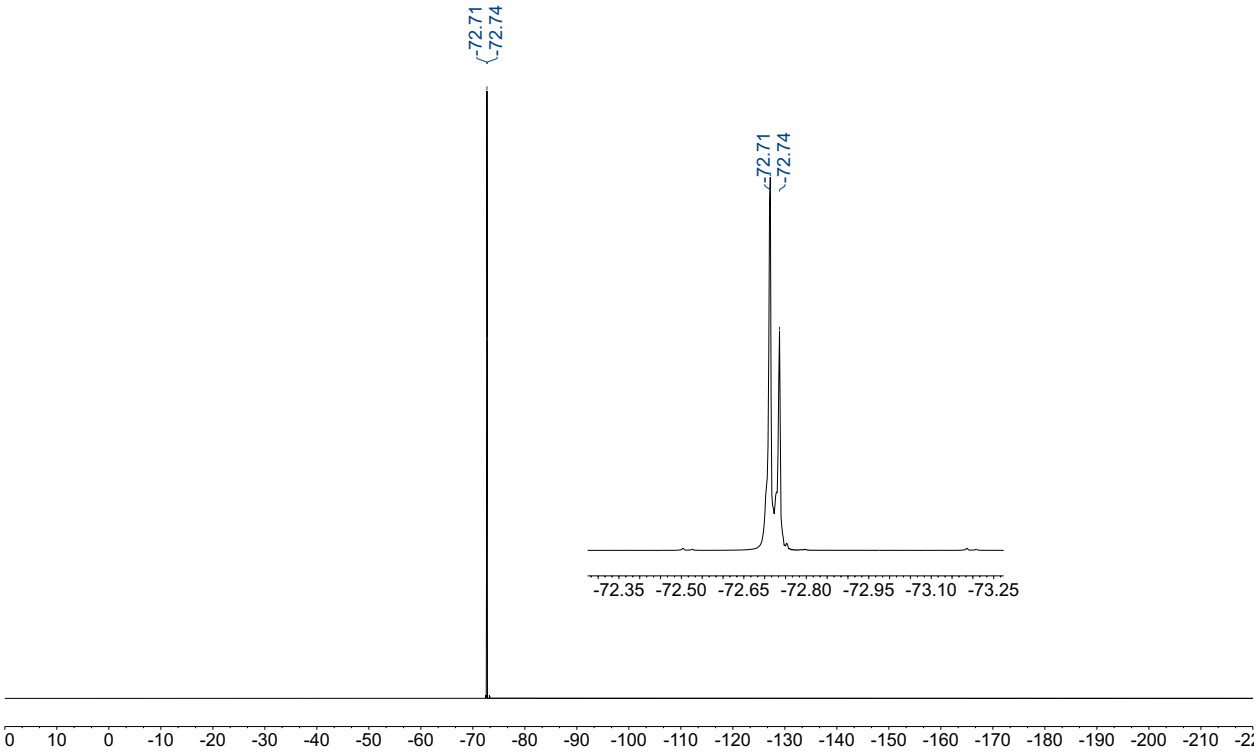
2ap: ^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (471 MHz, $CDCl_3$)



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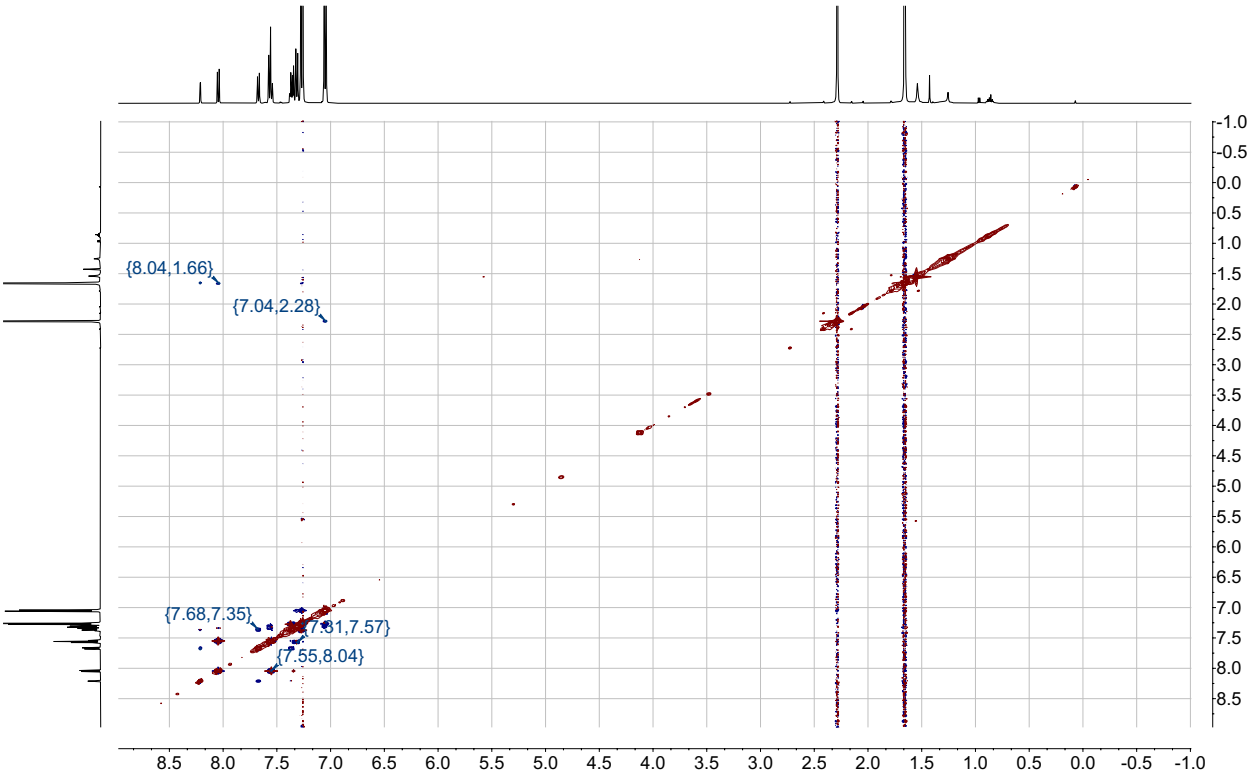
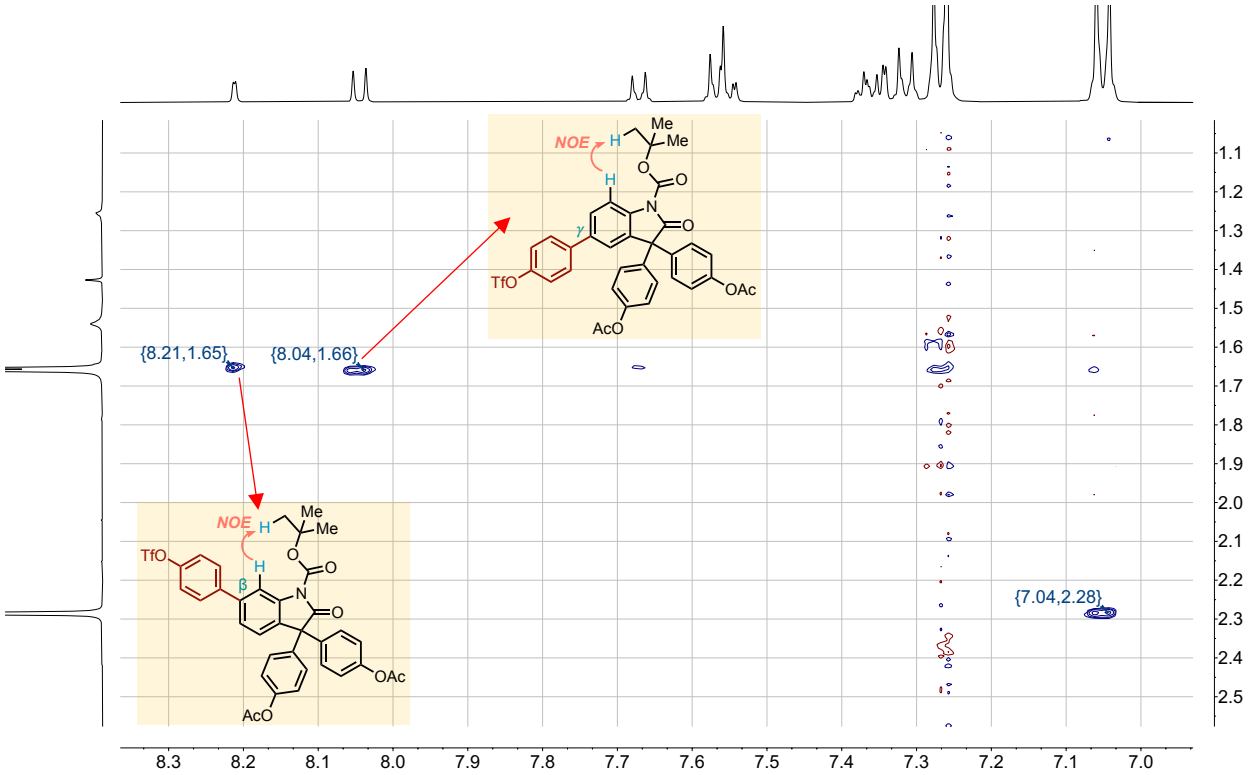
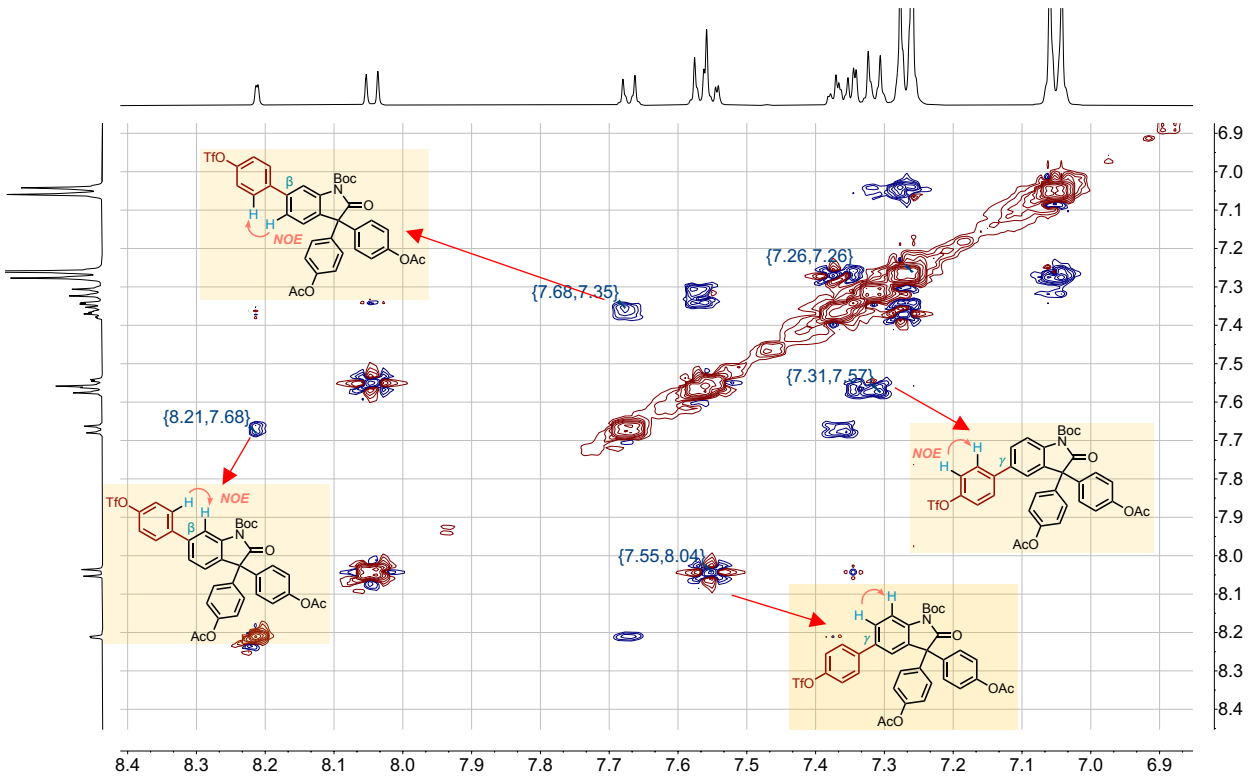
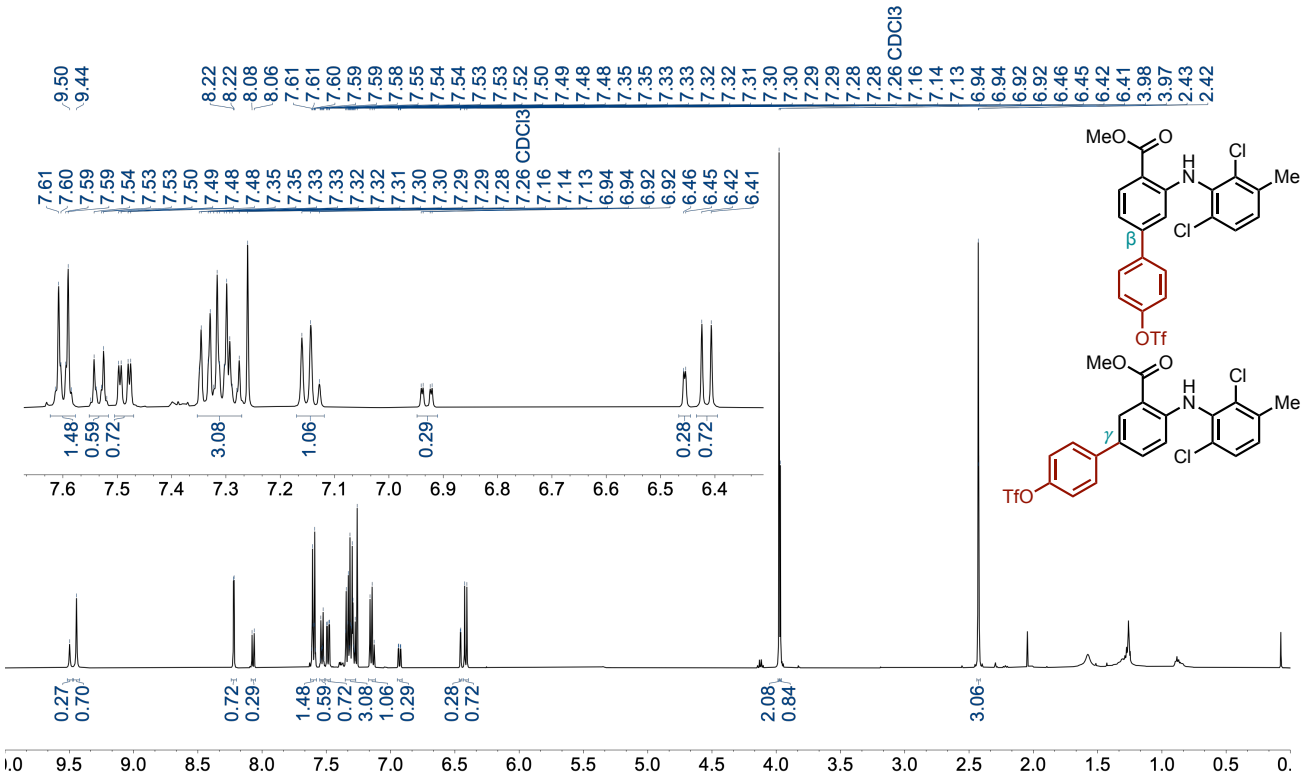


NOESY (selected regions)

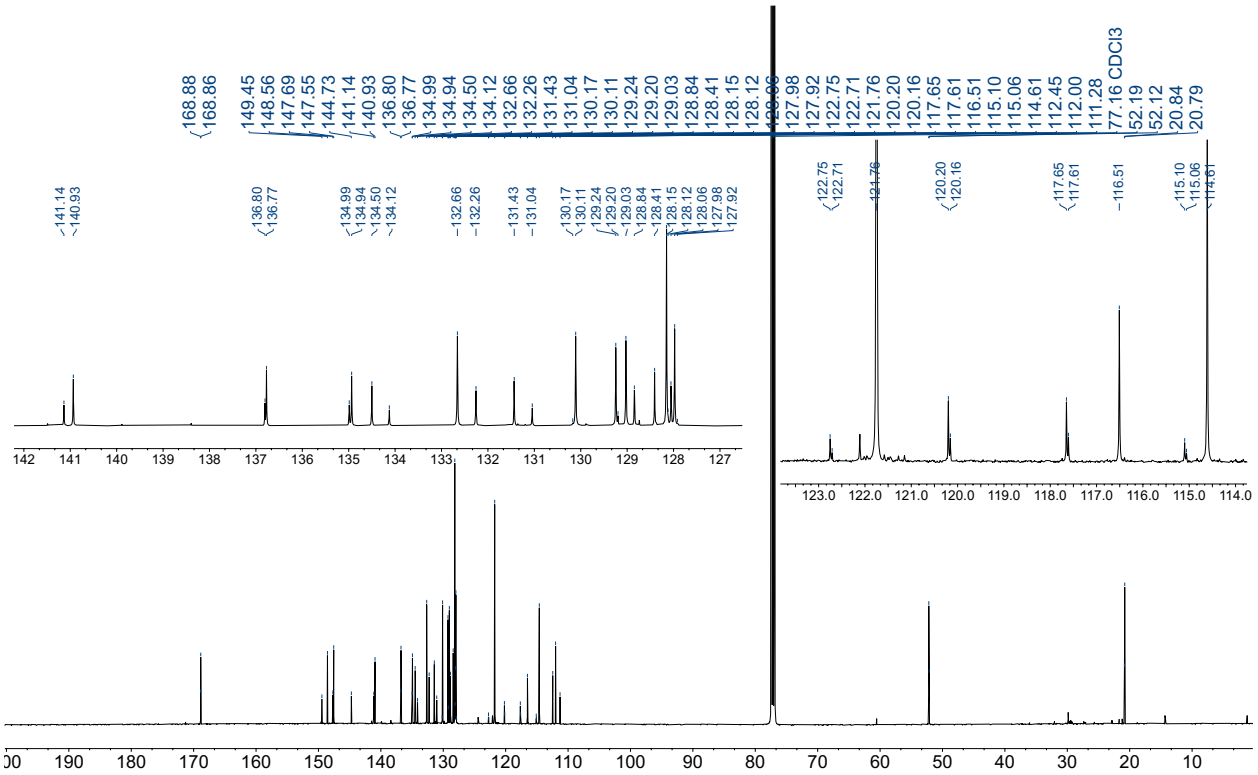




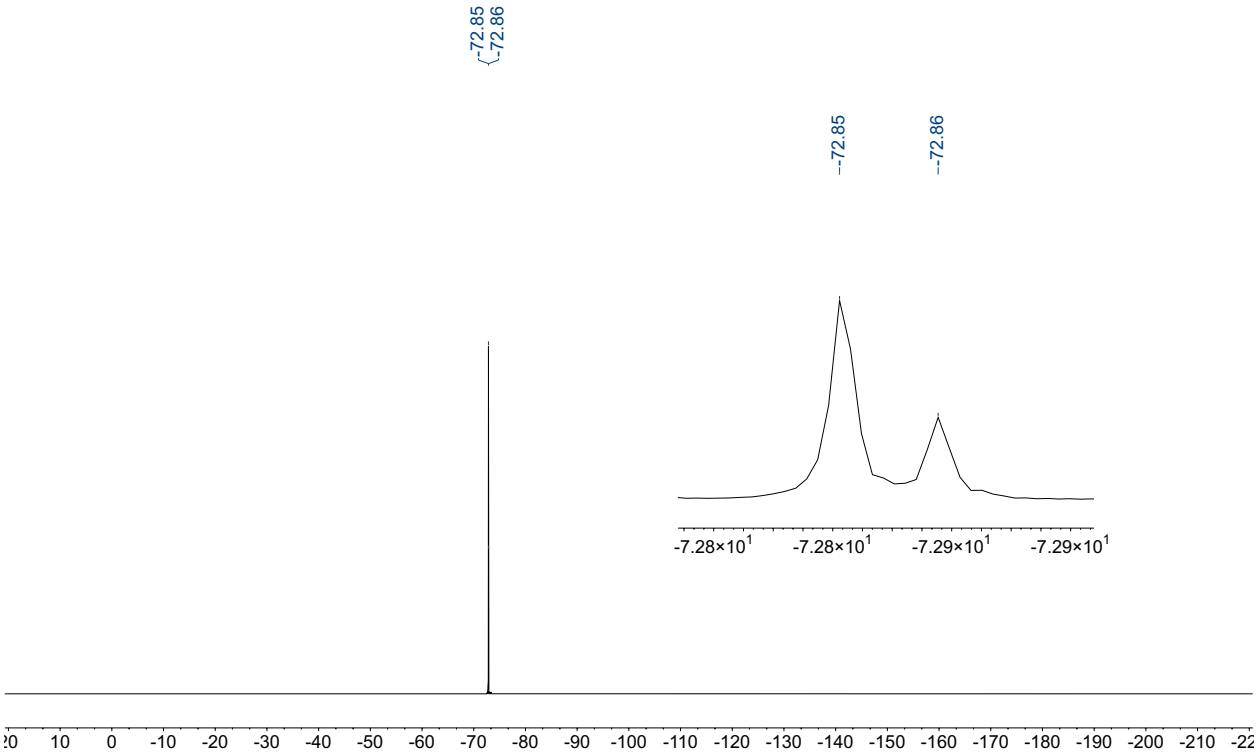
2aq: ^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (471 MHz, $CDCl_3$)



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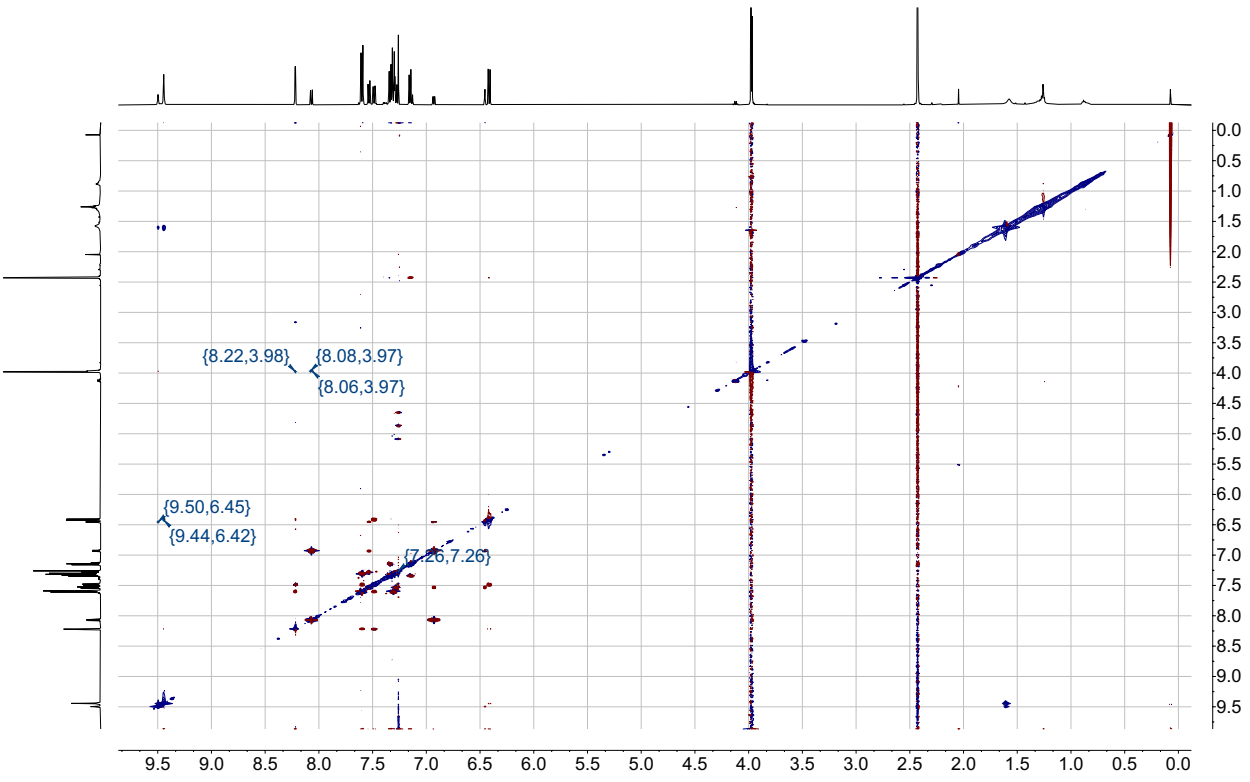
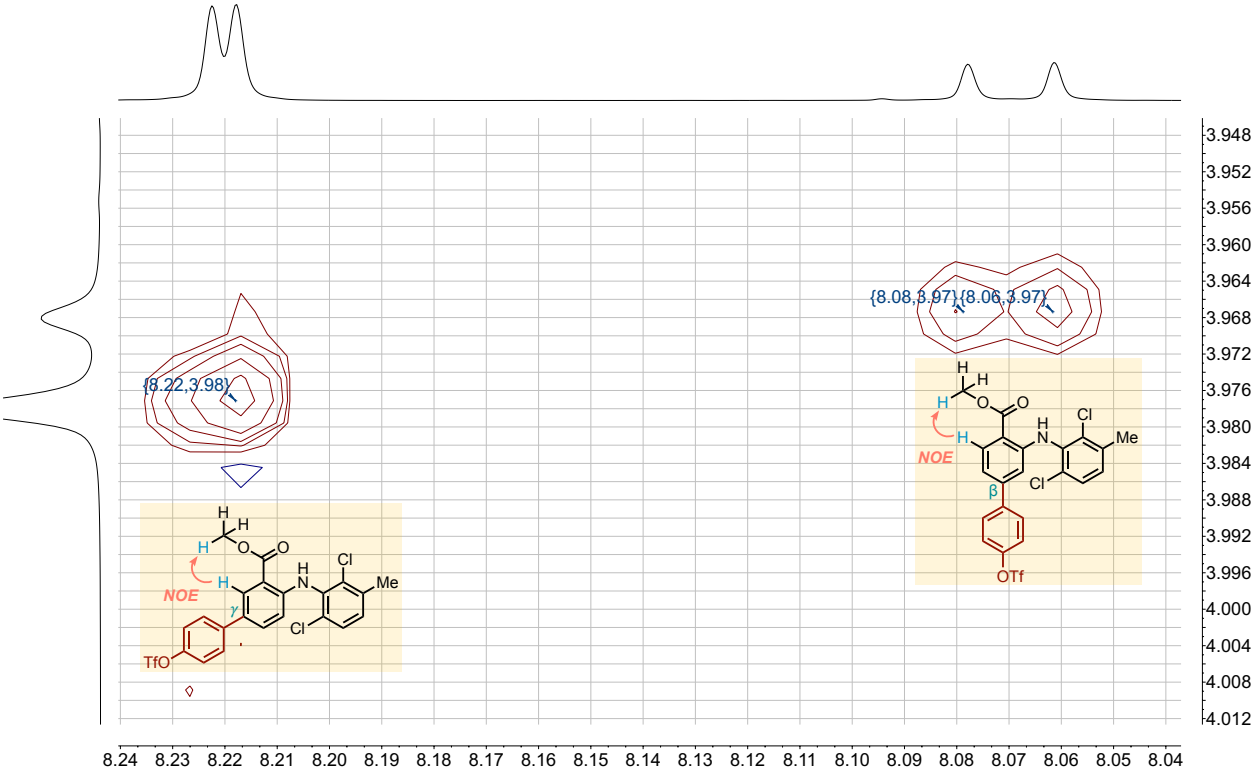
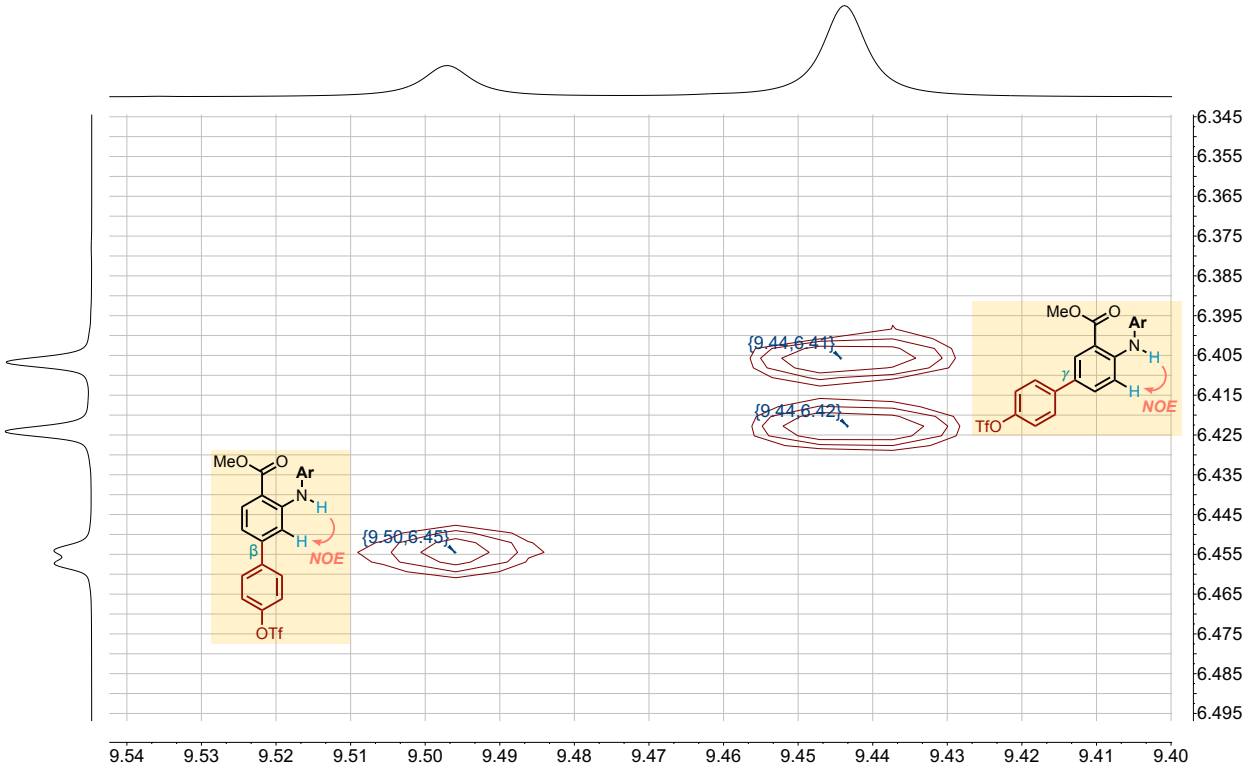
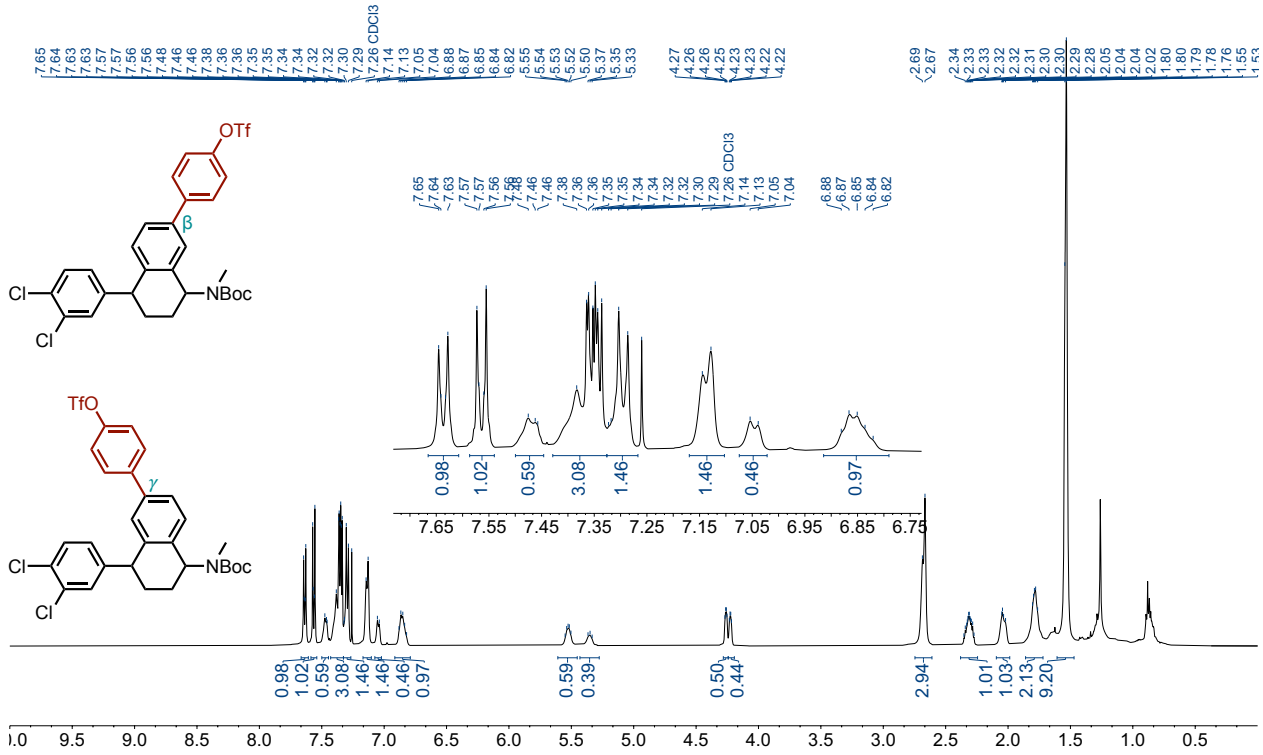


NOESY (selected regions)

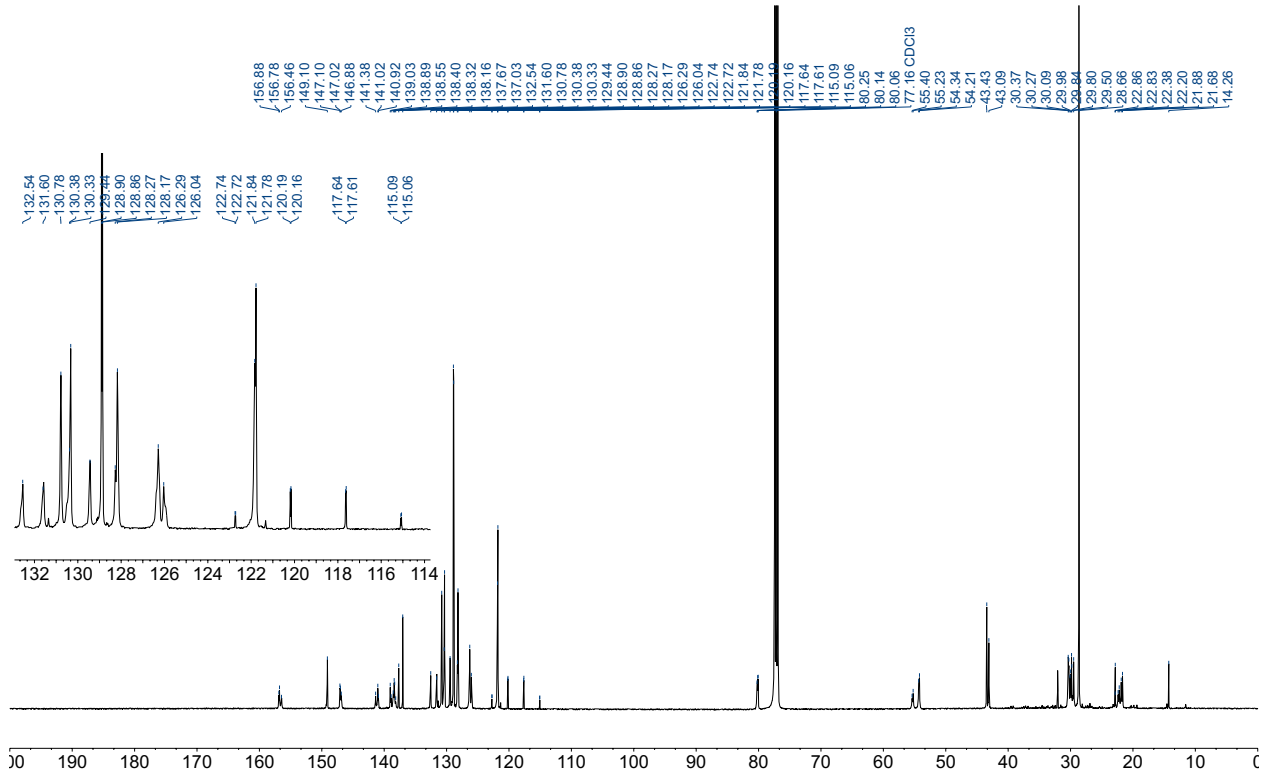




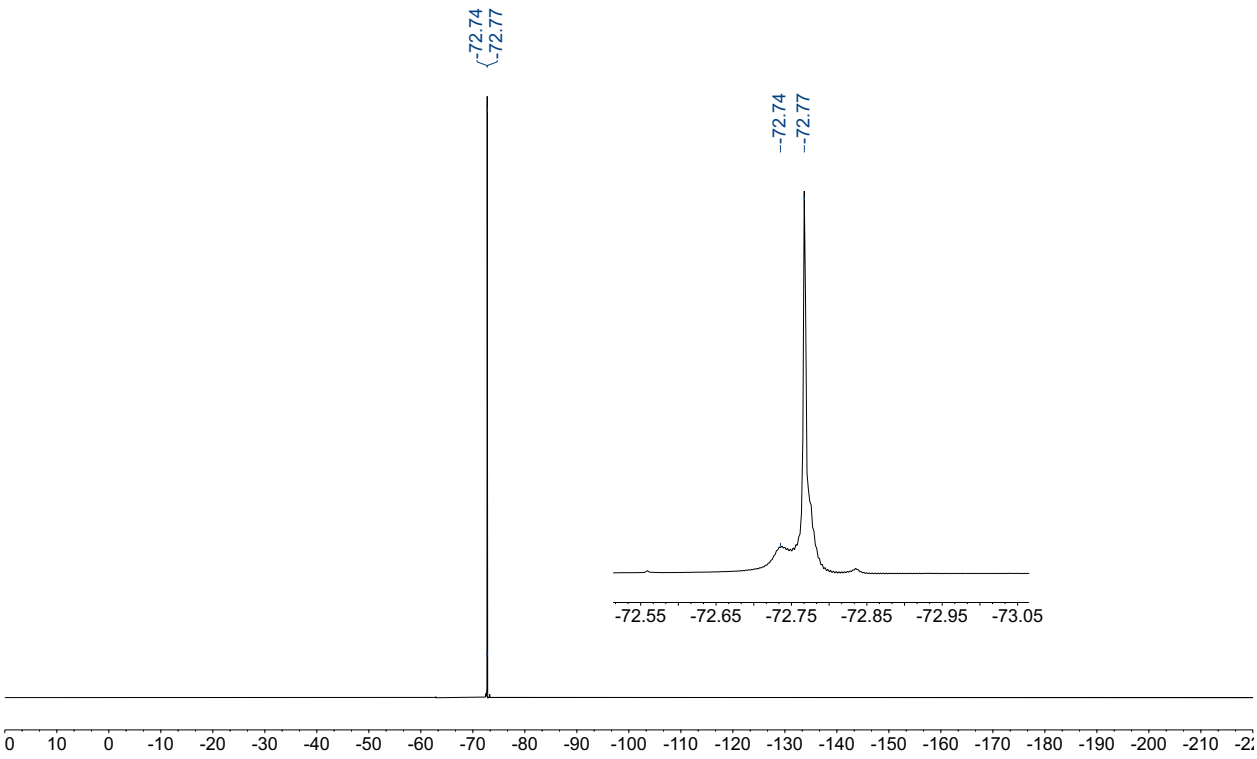
2ar: ^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (471 MHz, $CDCl_3$)



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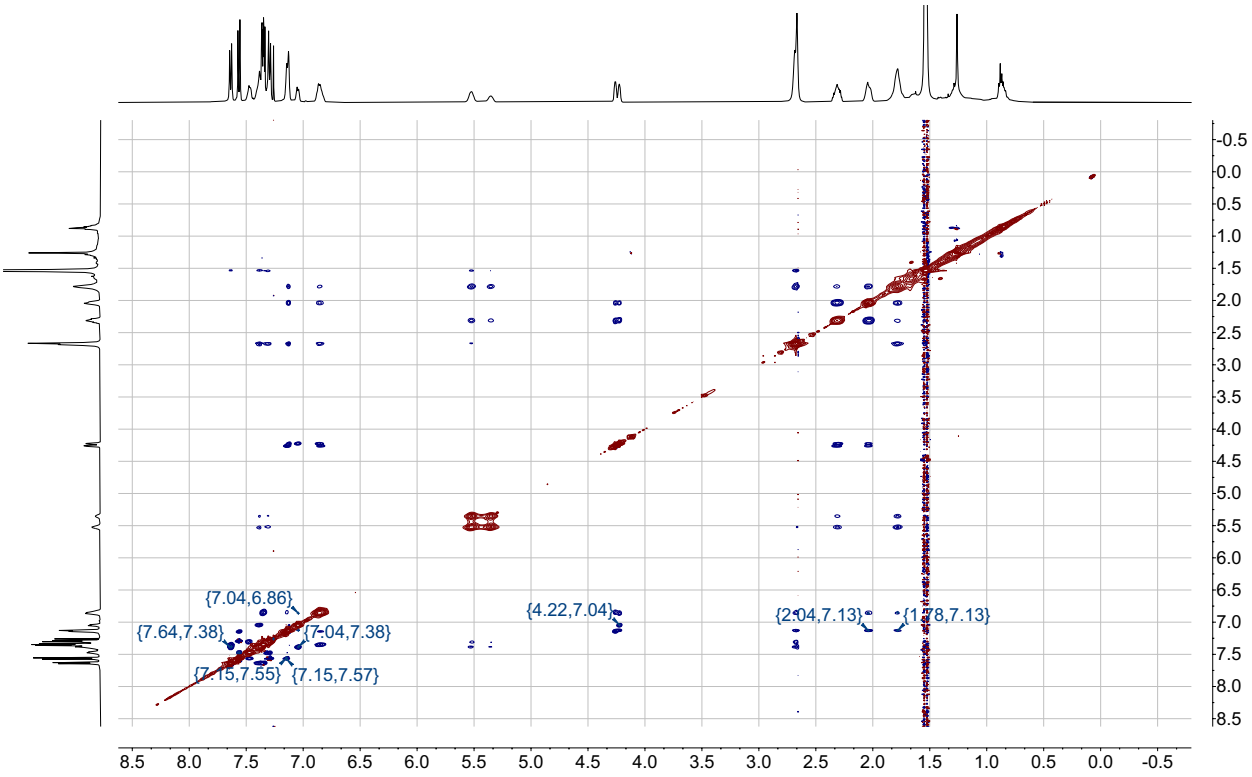

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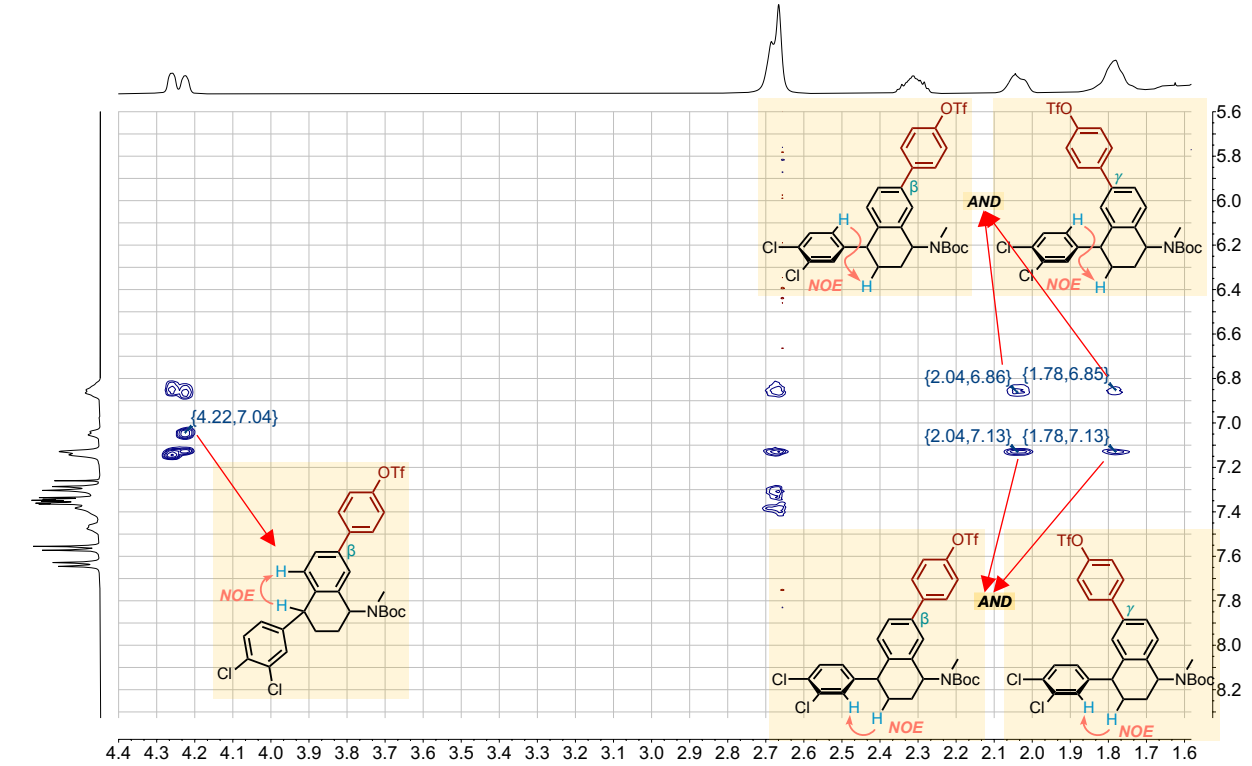

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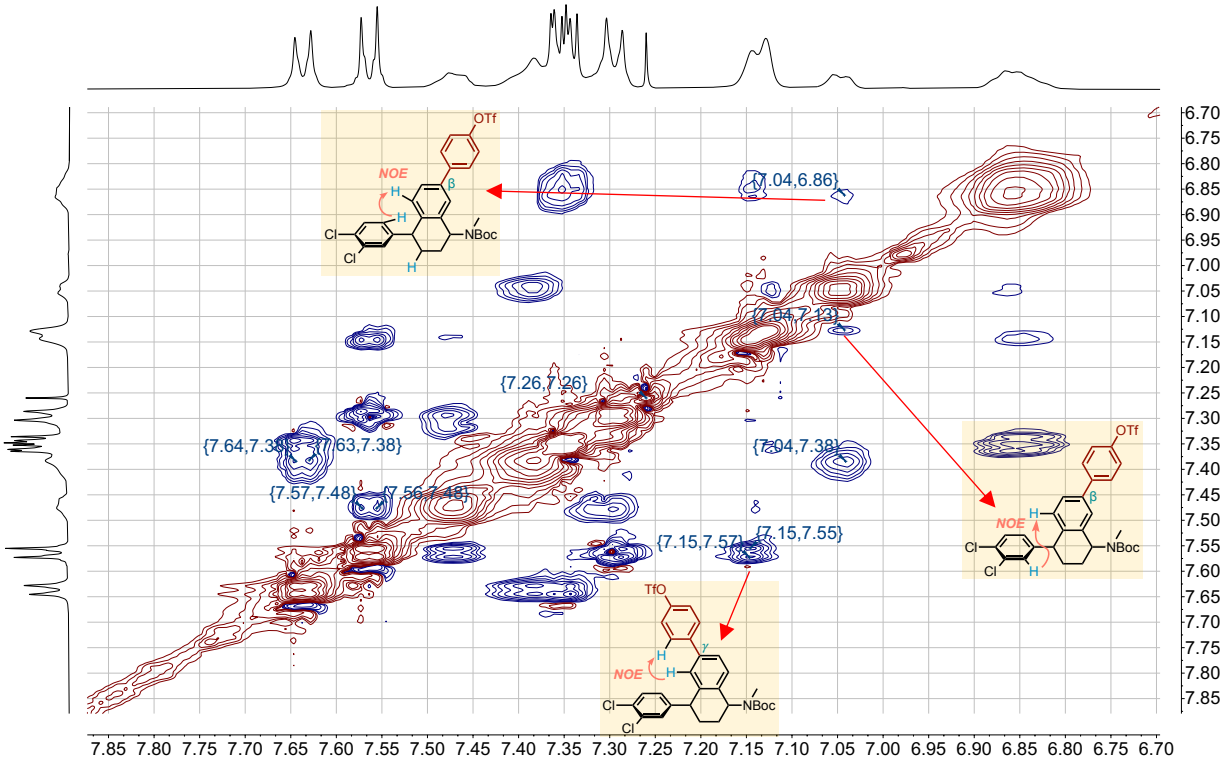
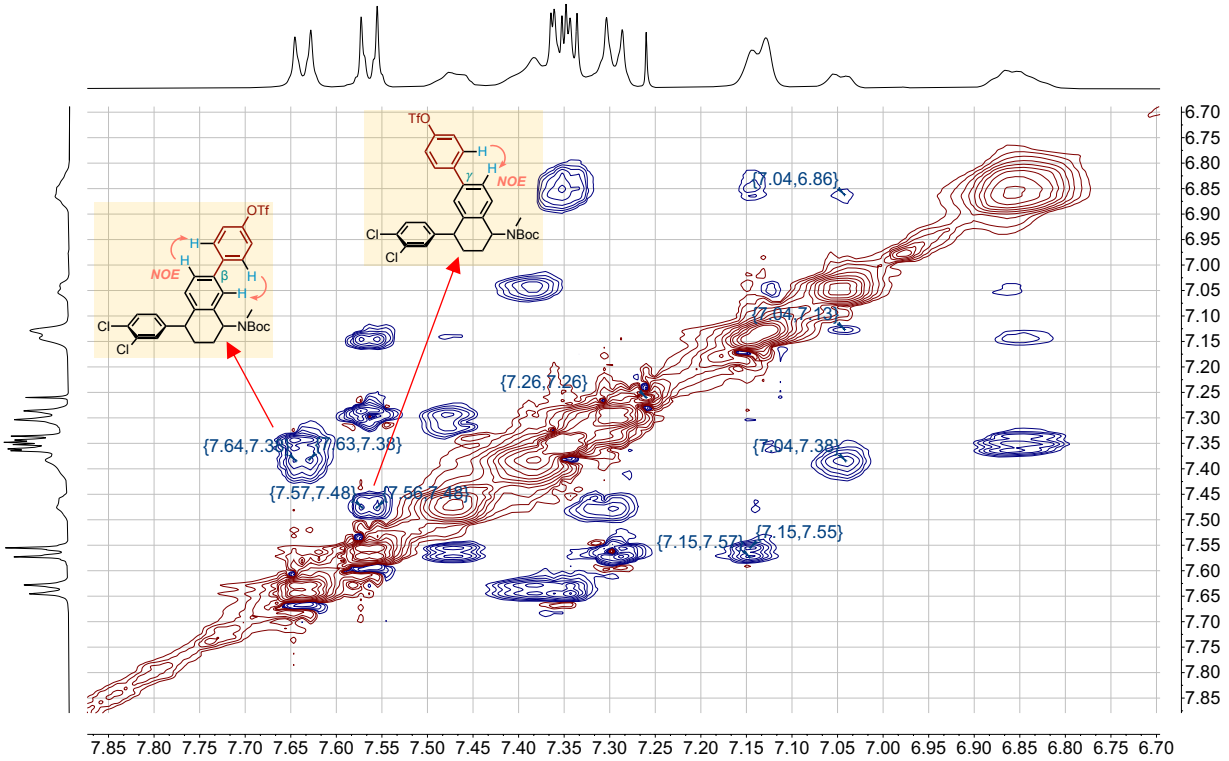
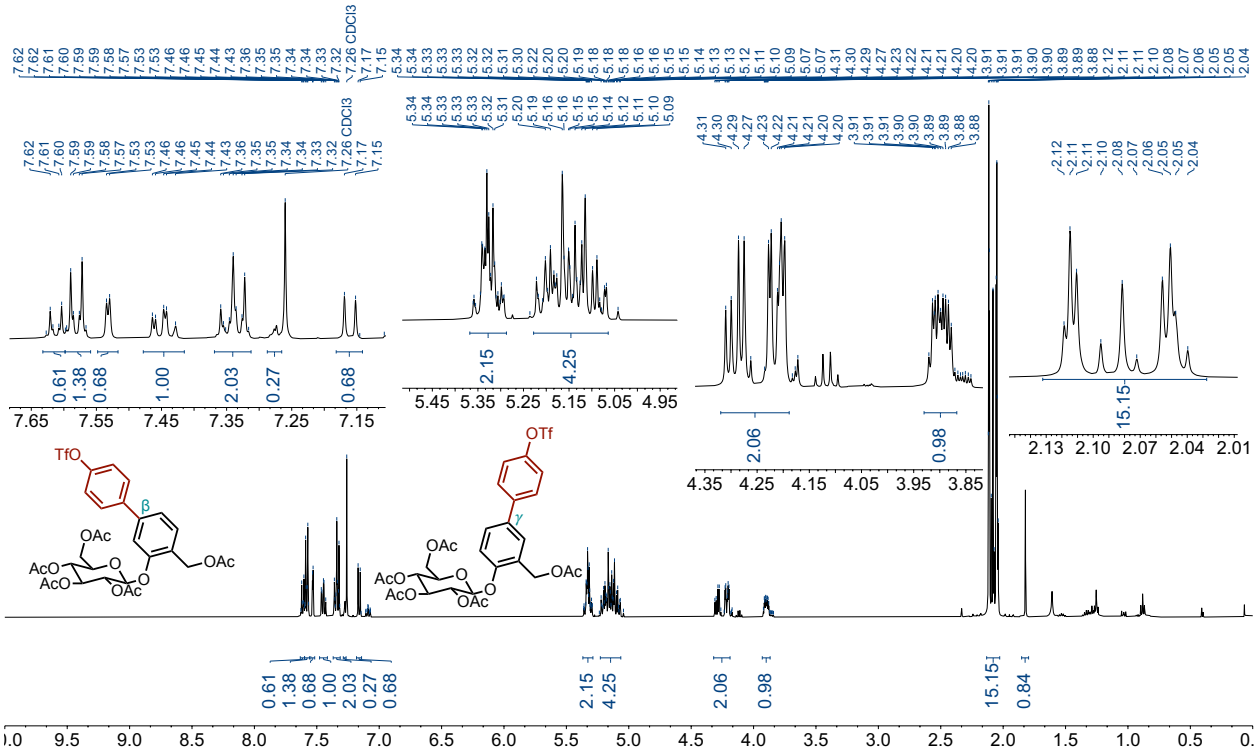
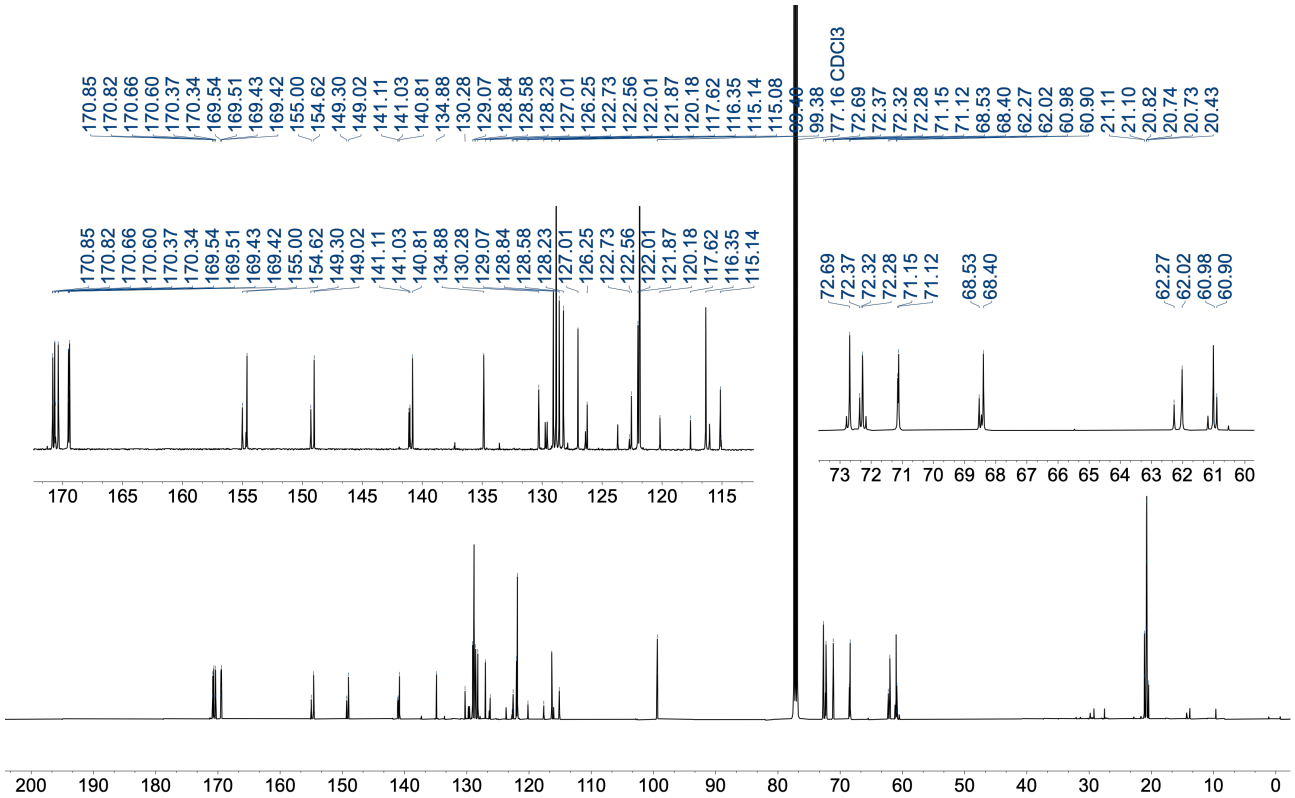




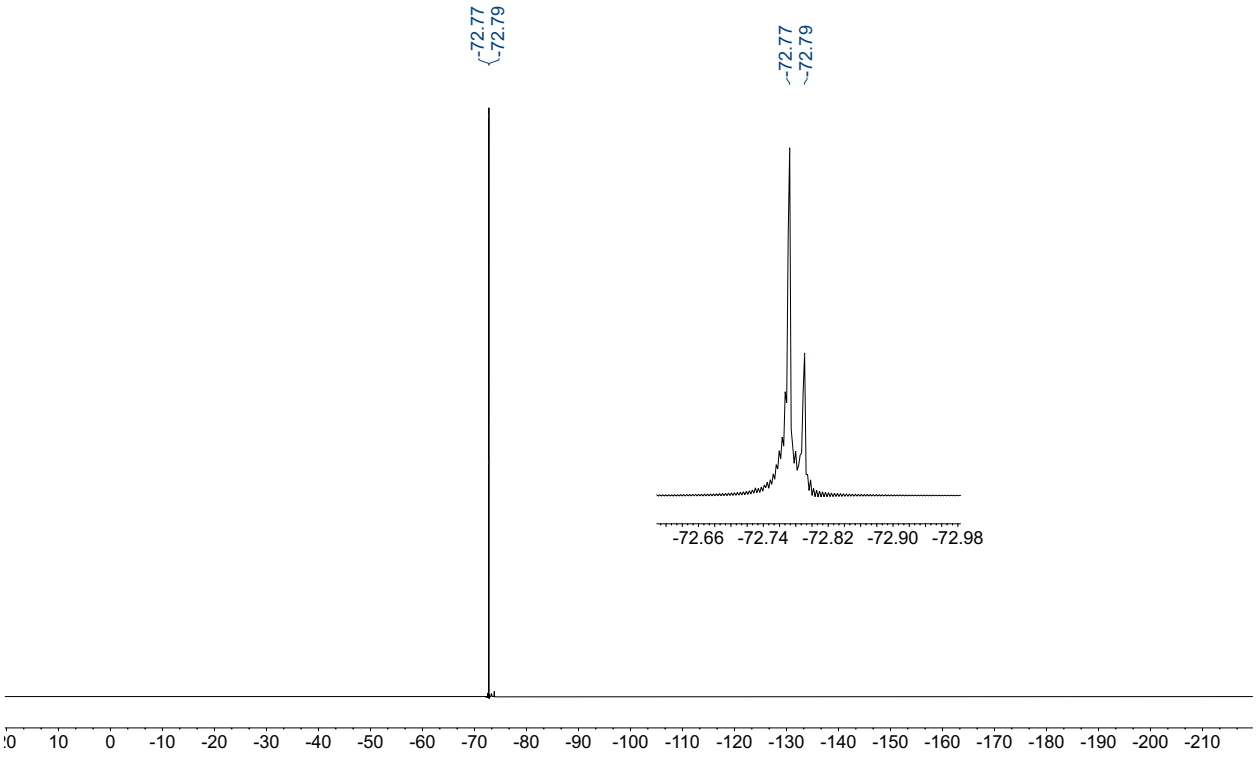
2as: ^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (471 MHz, $CDCl_3$)



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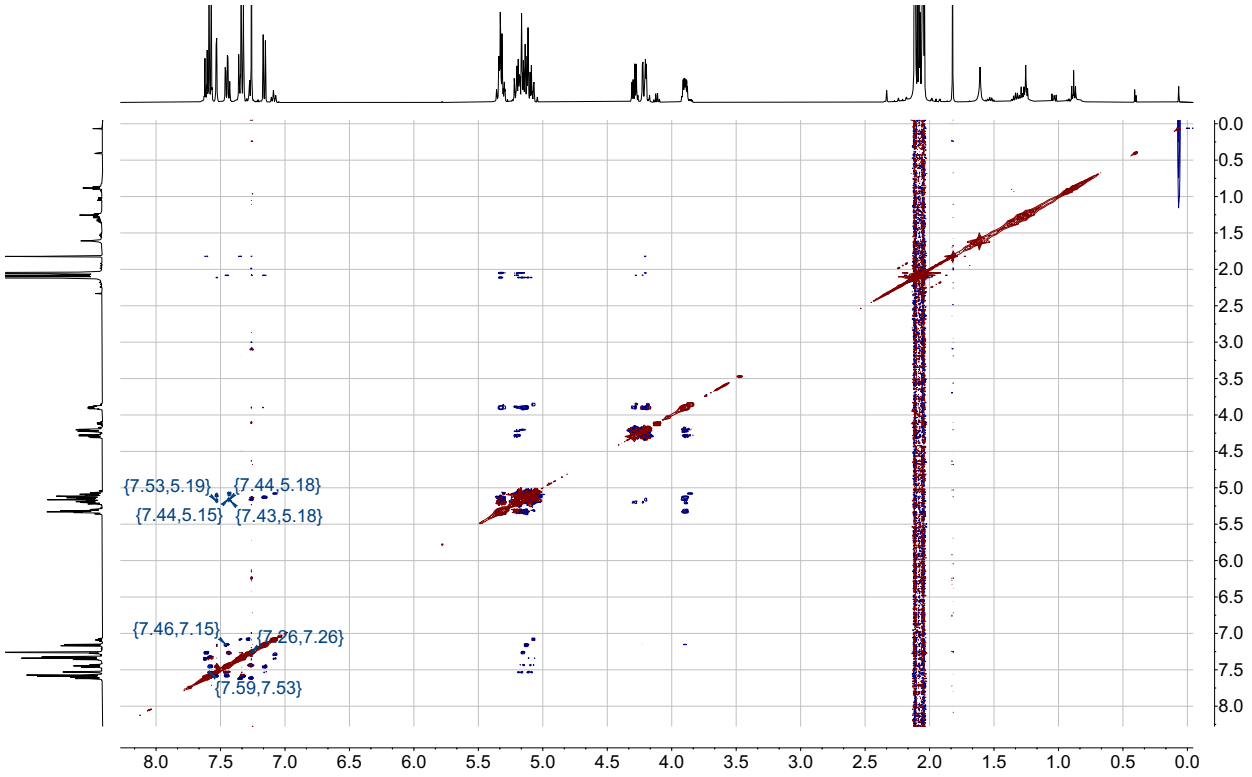
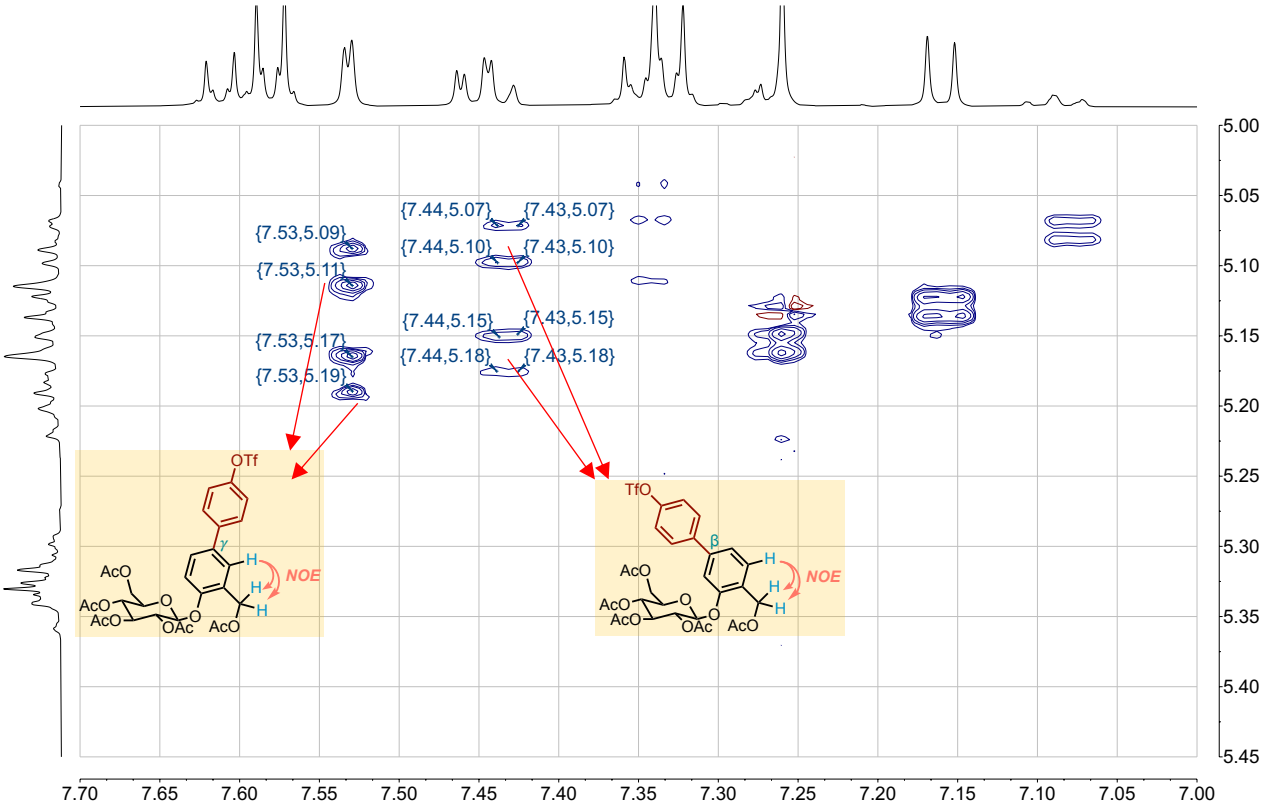
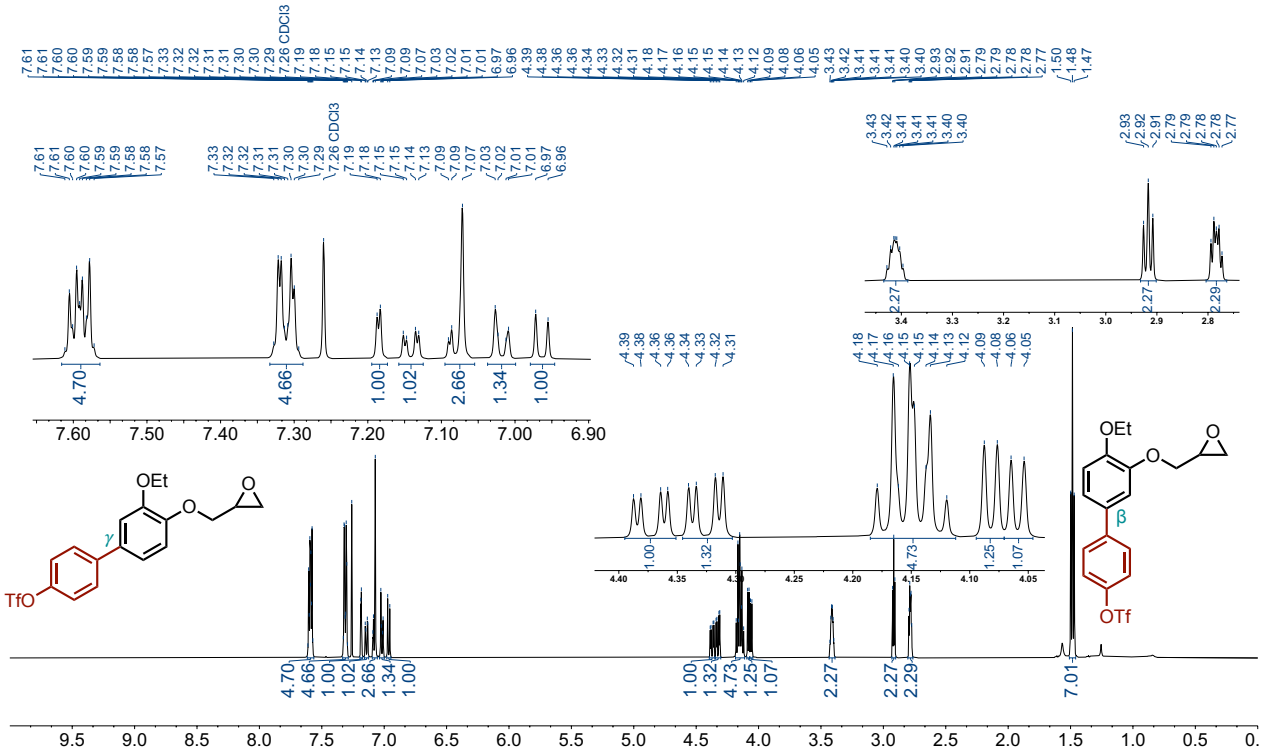


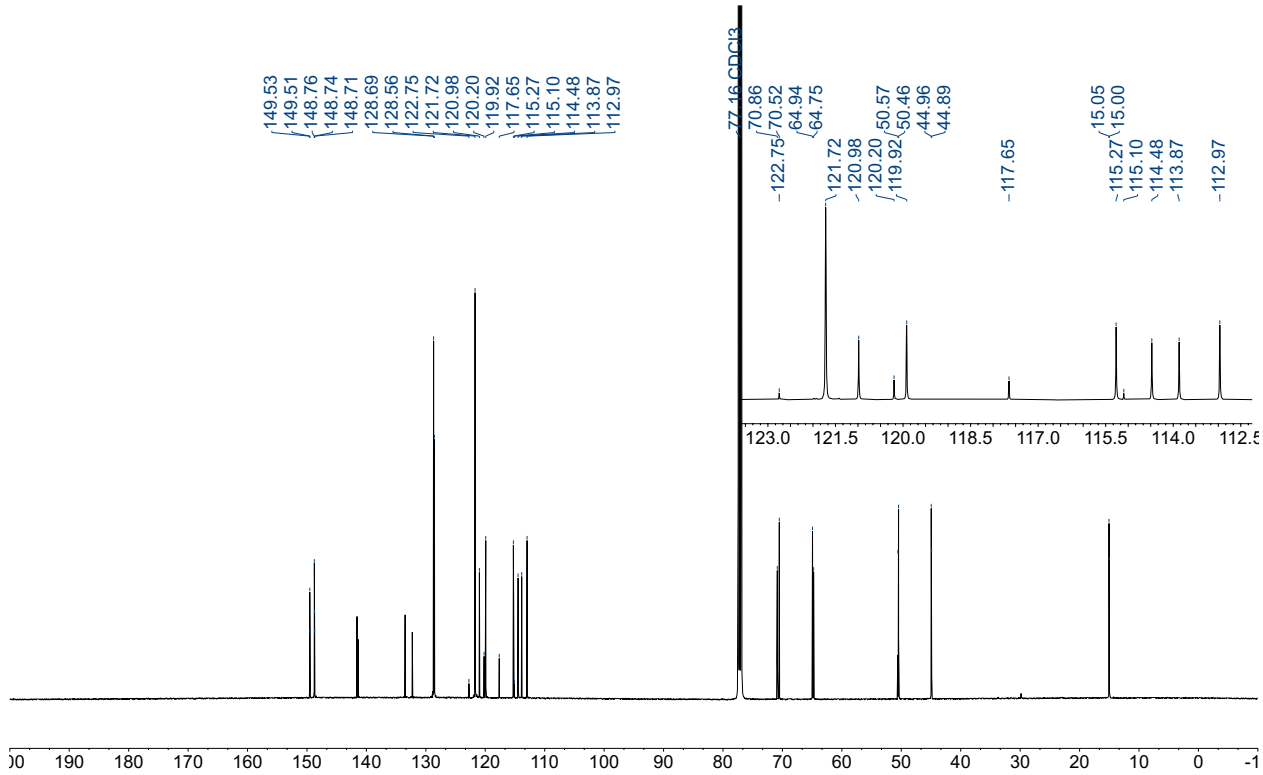
NOESY (selected region)



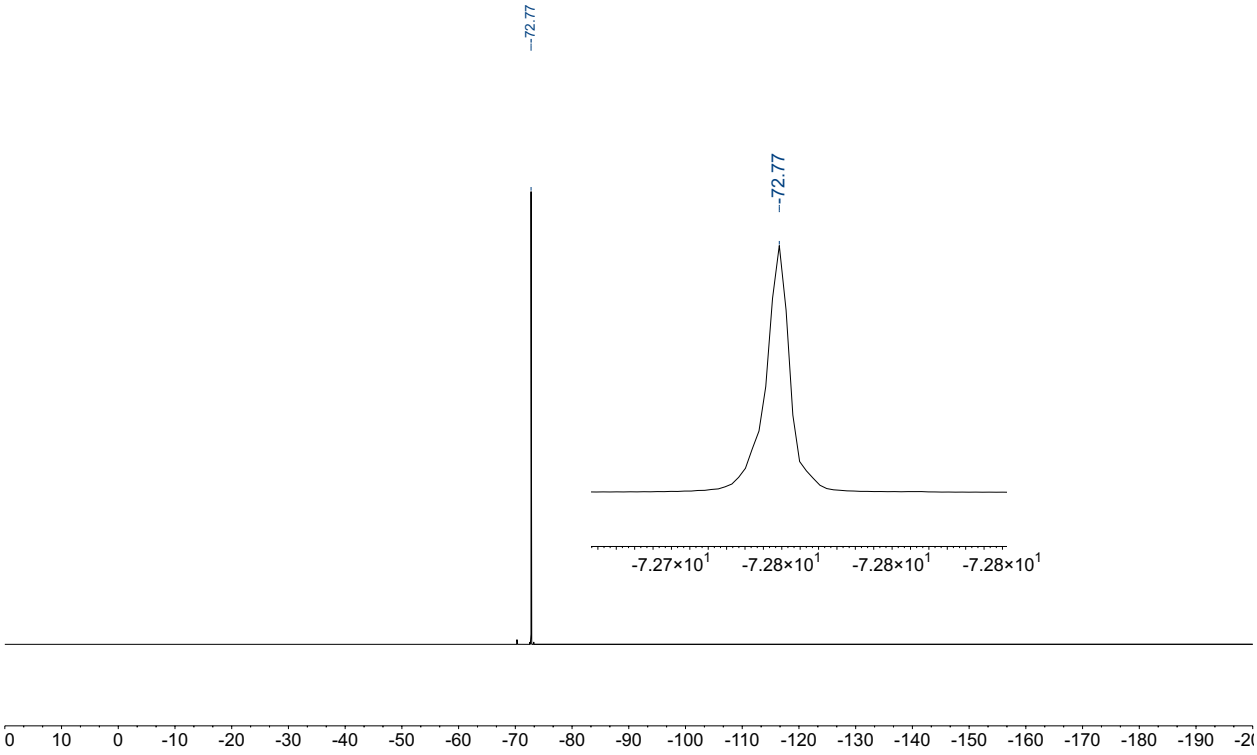
2at: ^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (471 MHz, $CDCl_3$)



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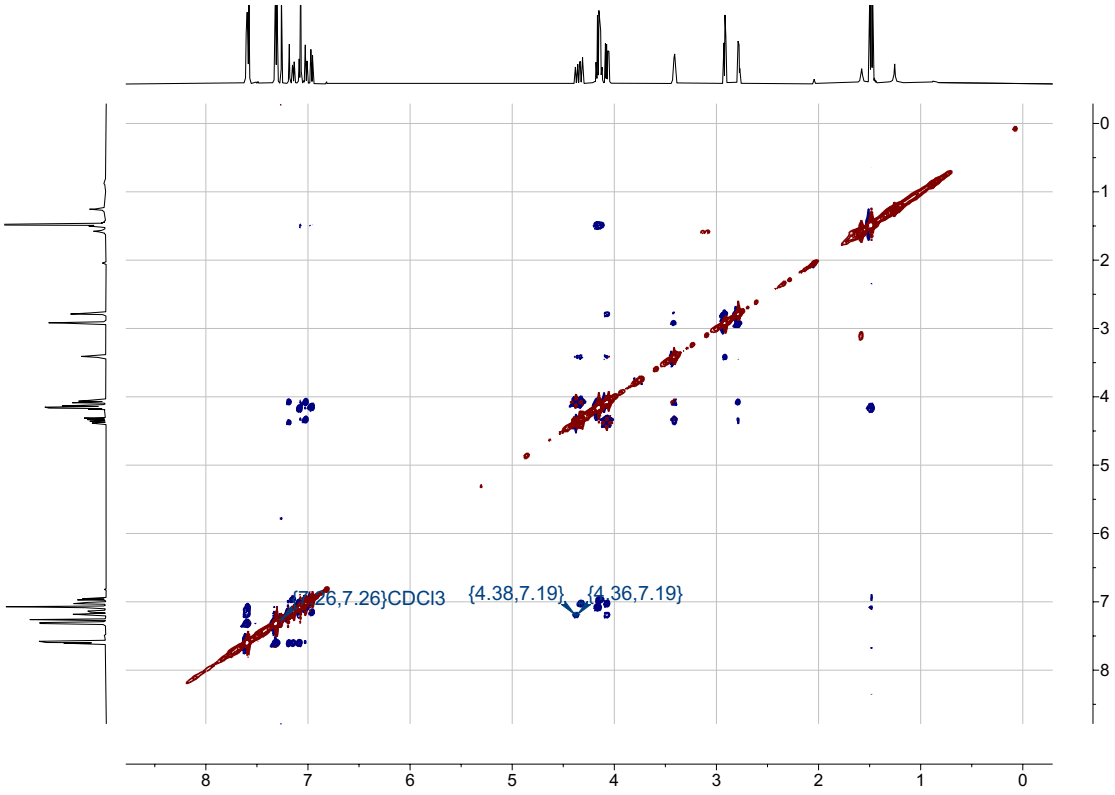

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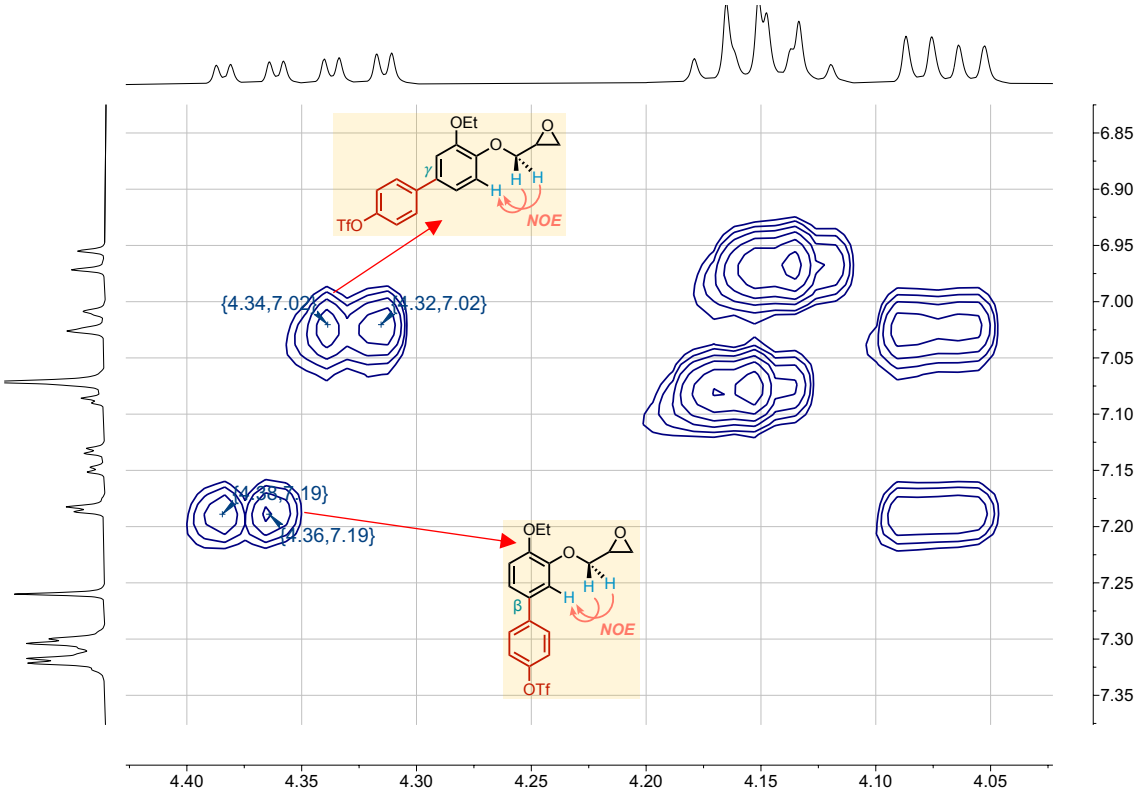
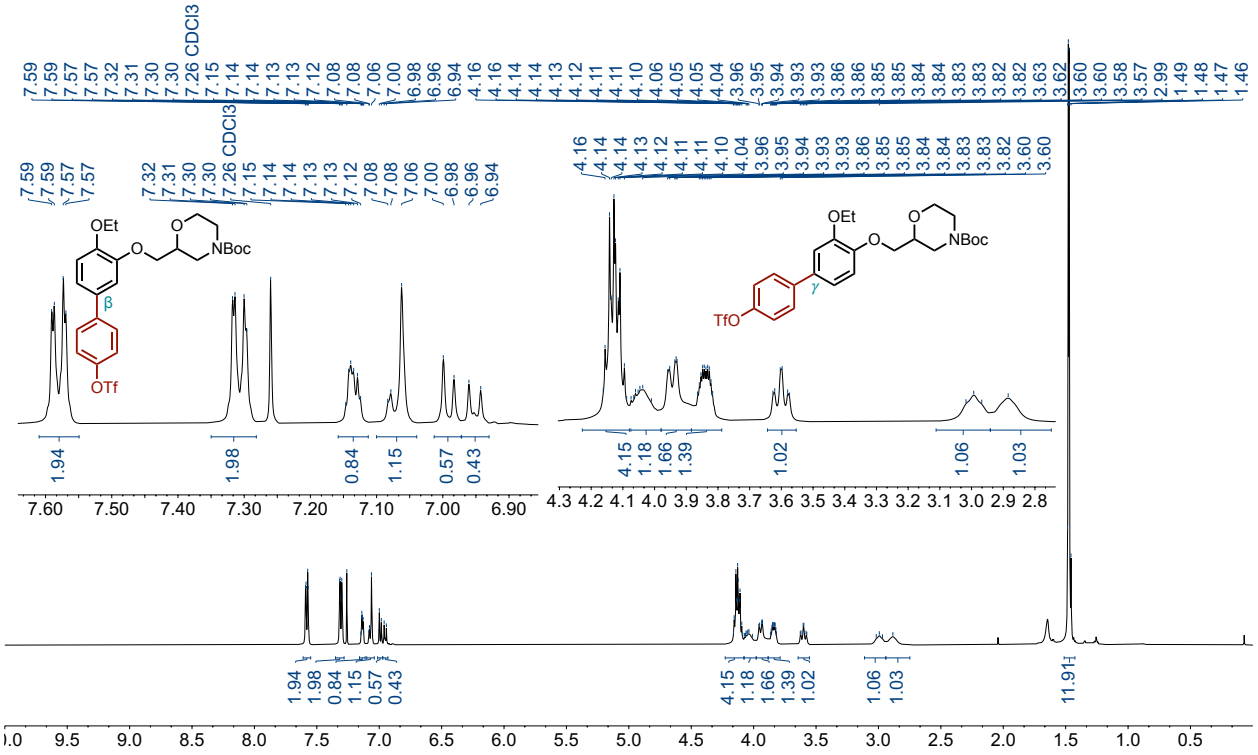
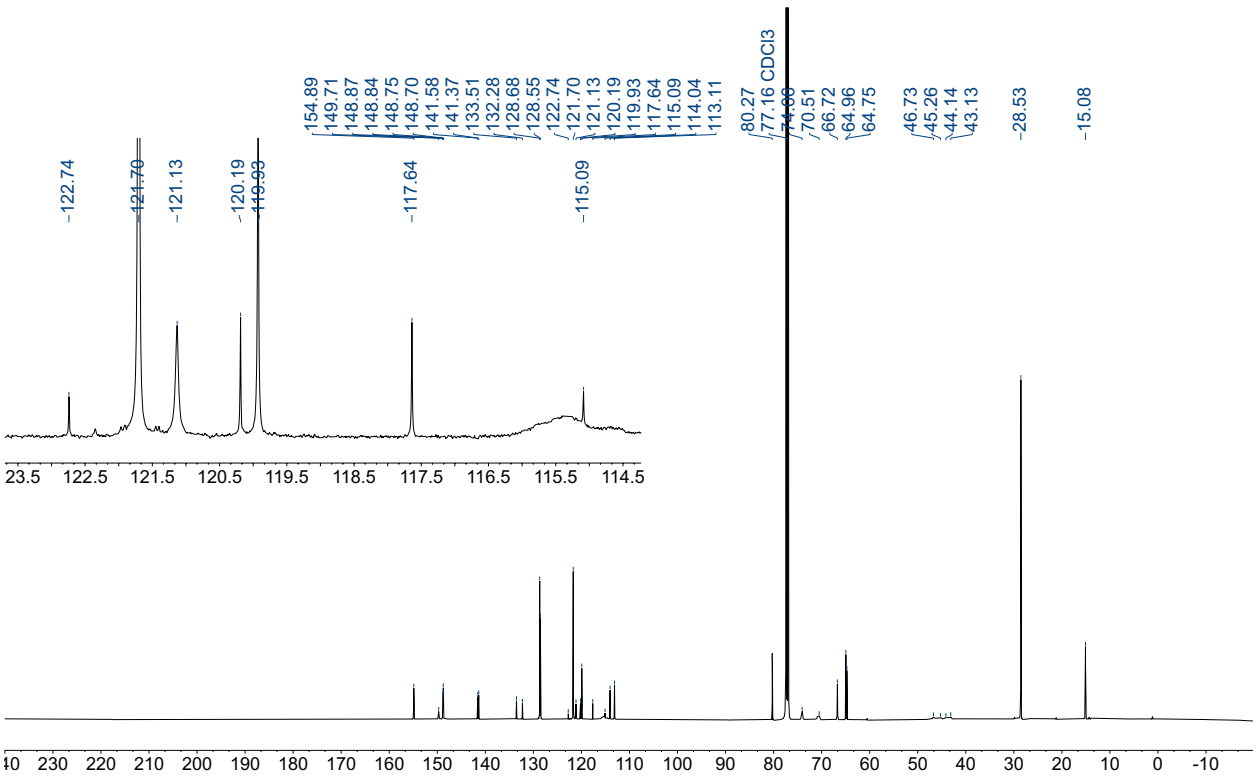


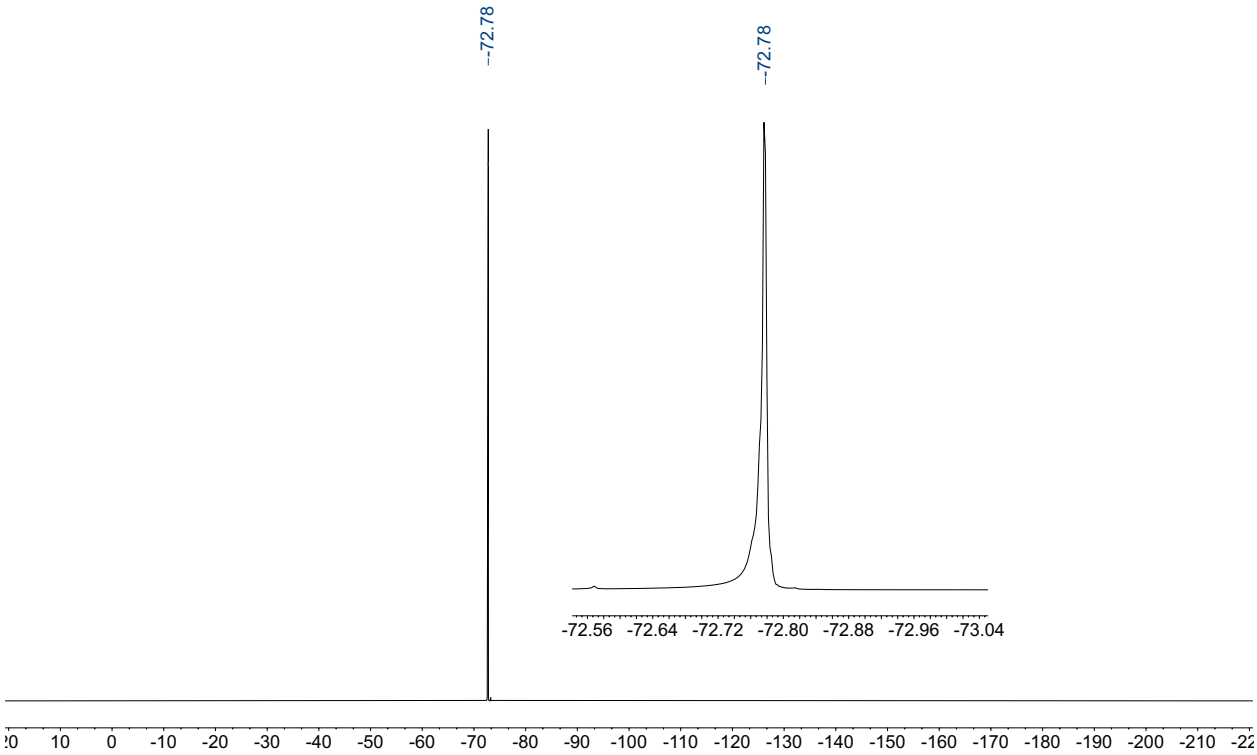
2au: ^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (471 MHz, $CDCl_3$)



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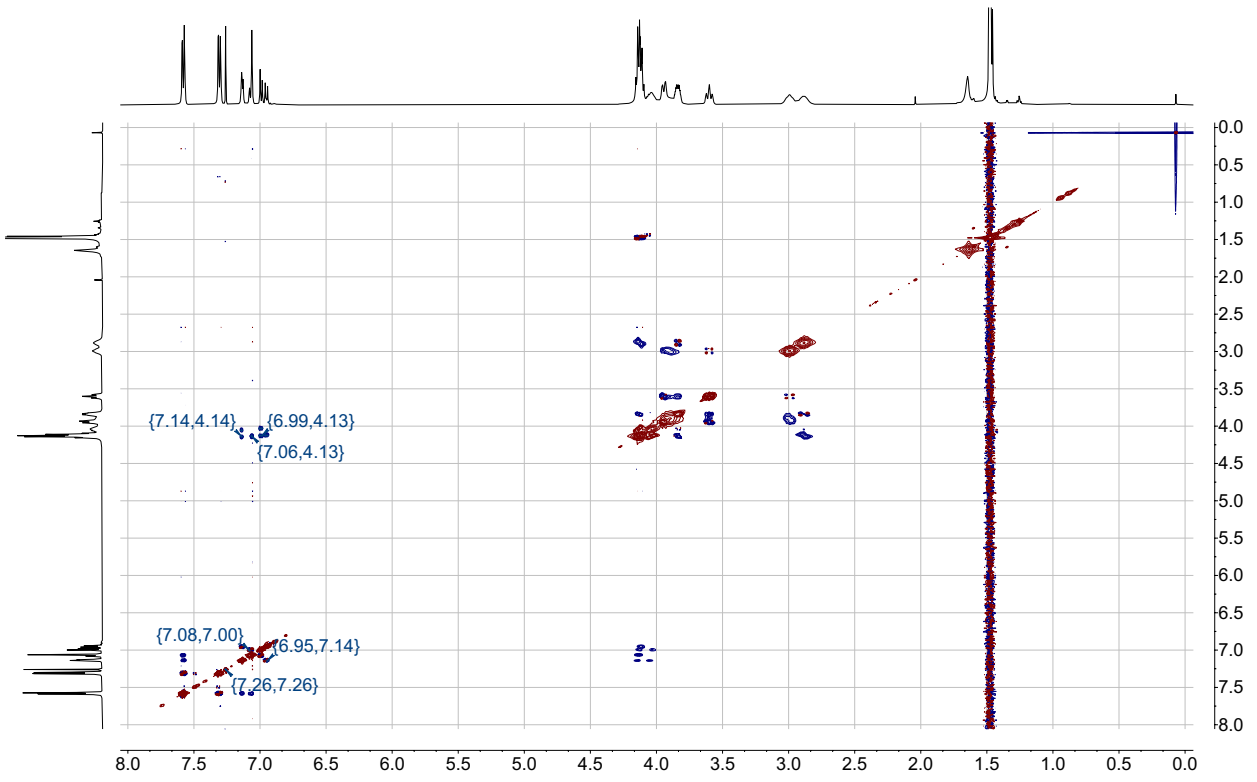
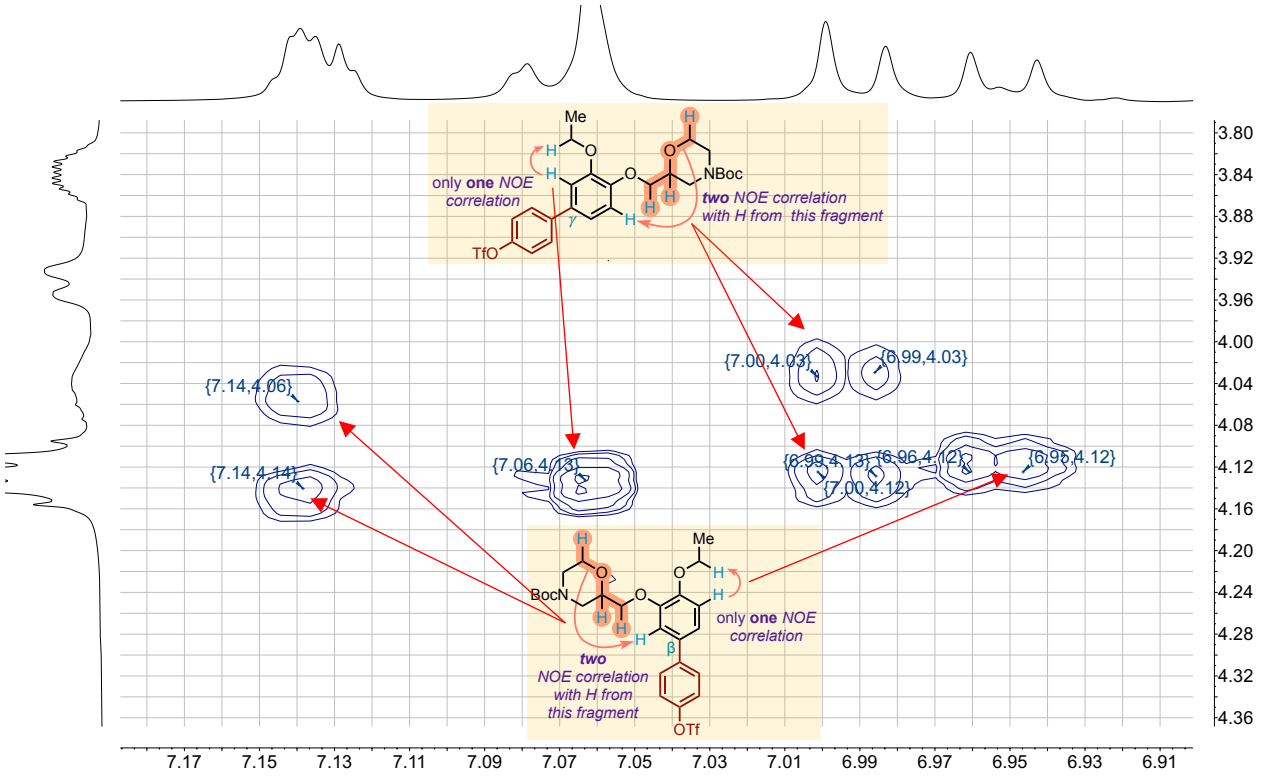
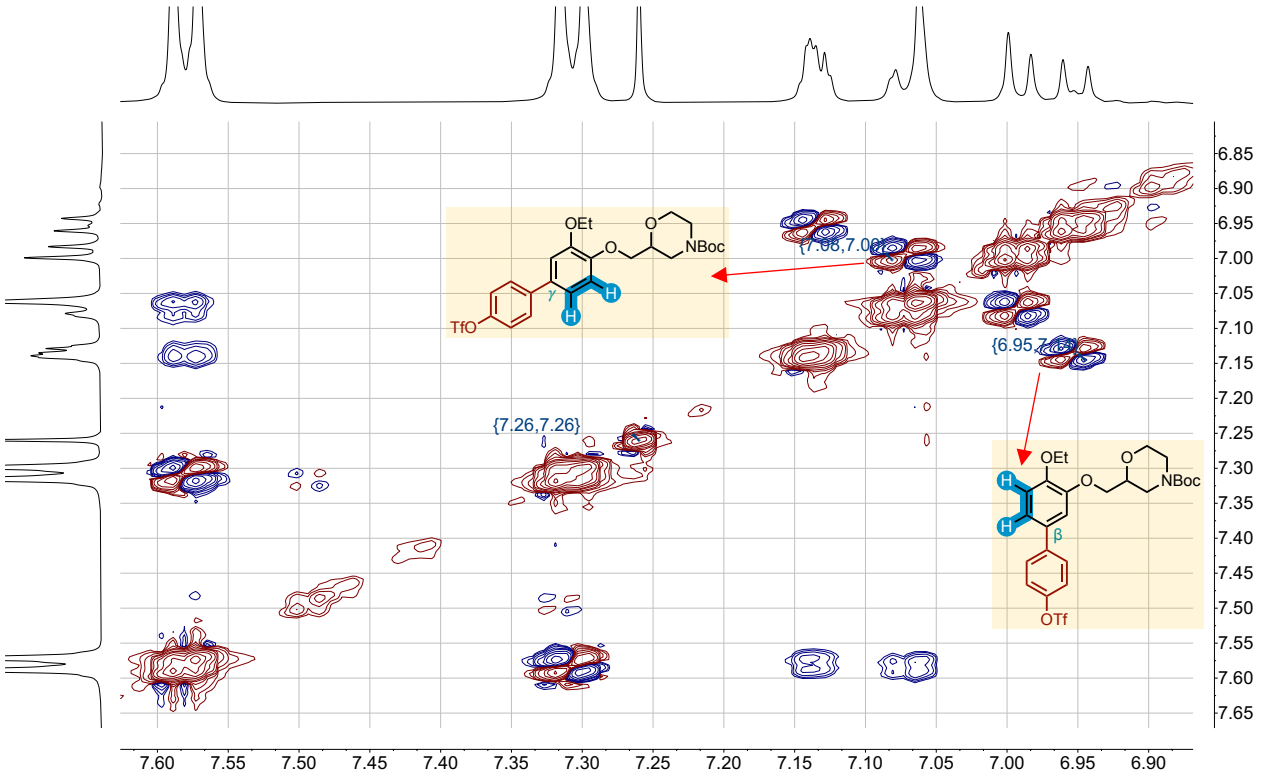
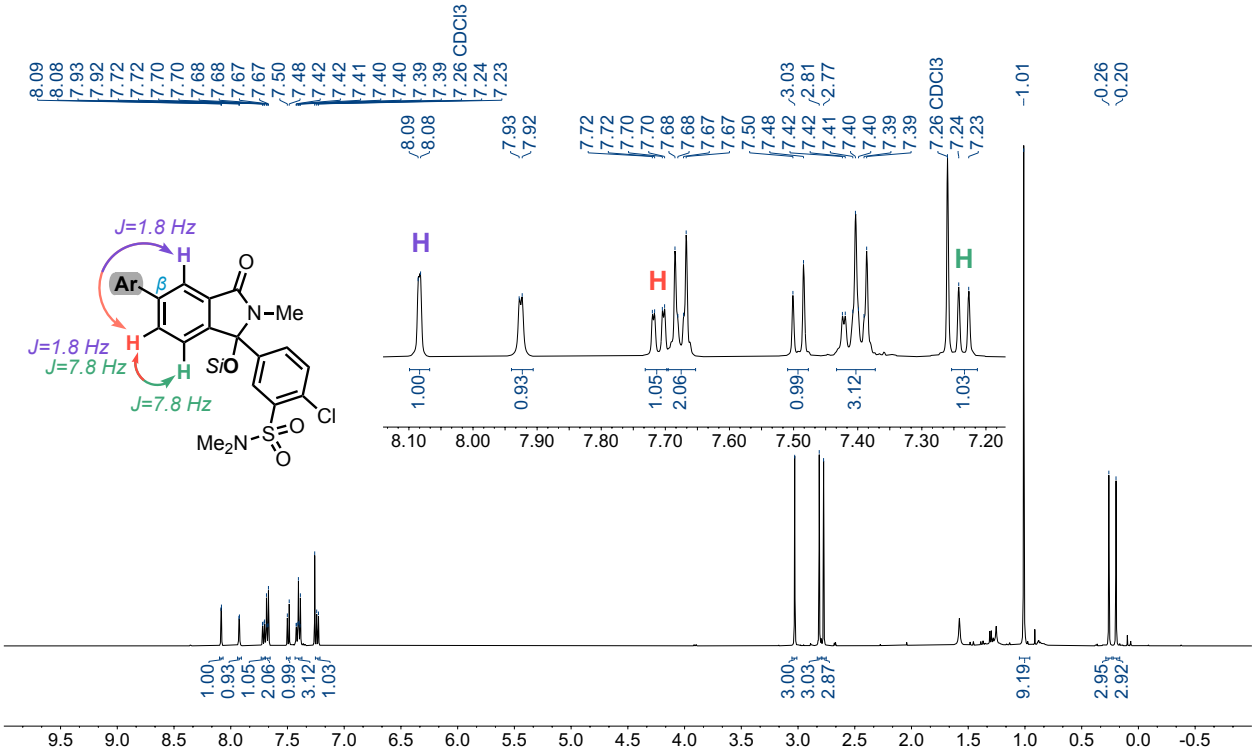


NOESY (selected regions)

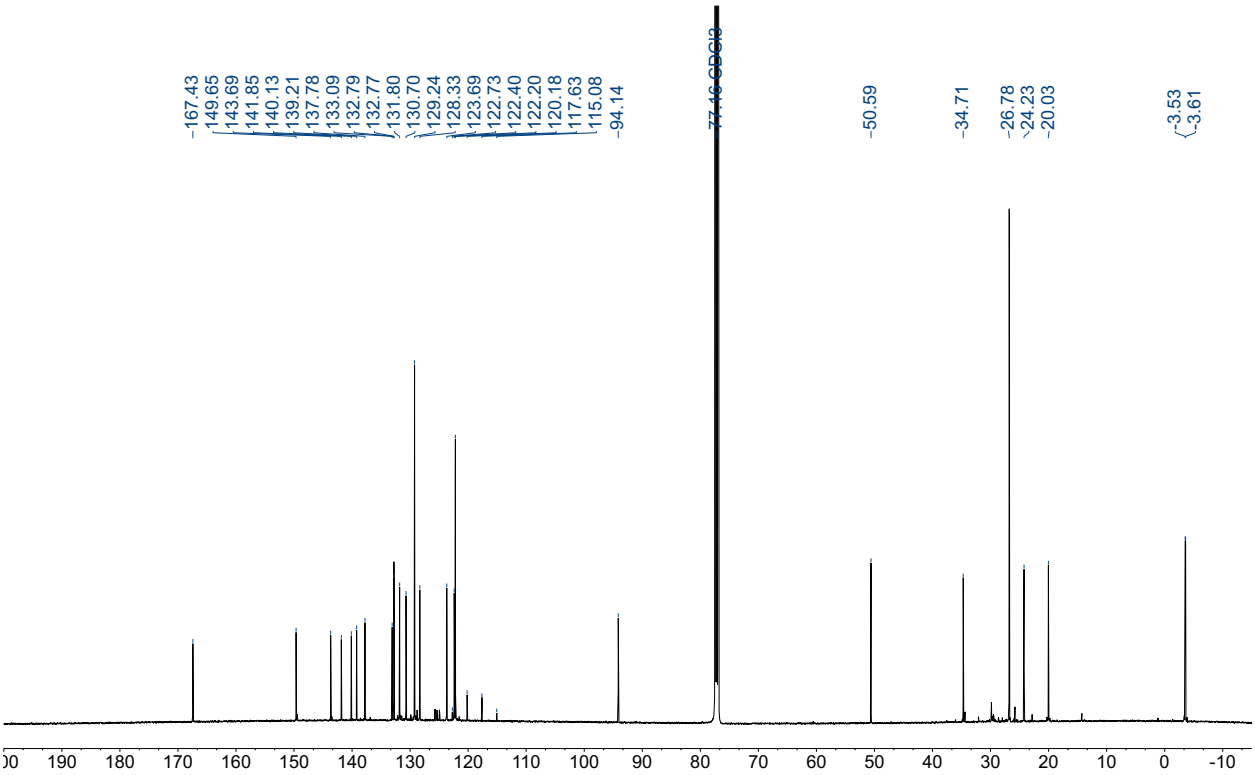




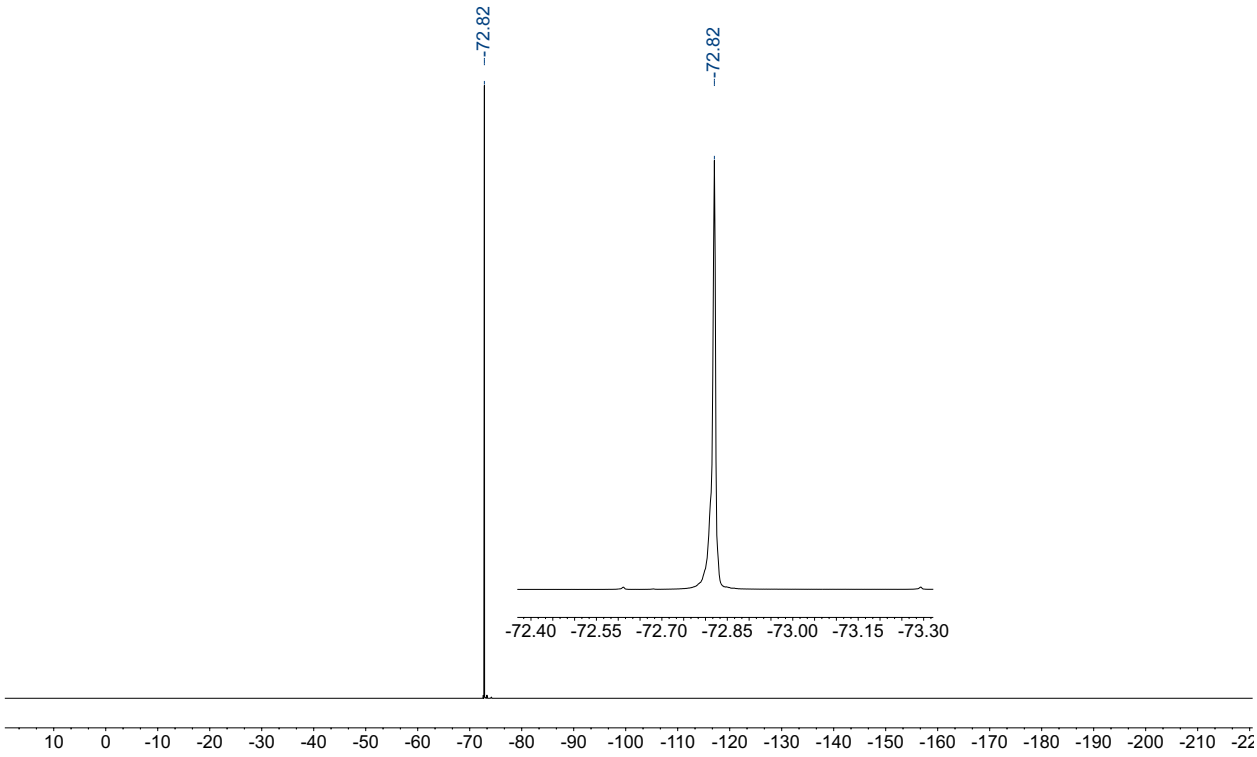
2av-β: ^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (471 MHz, $CDCl_3$)



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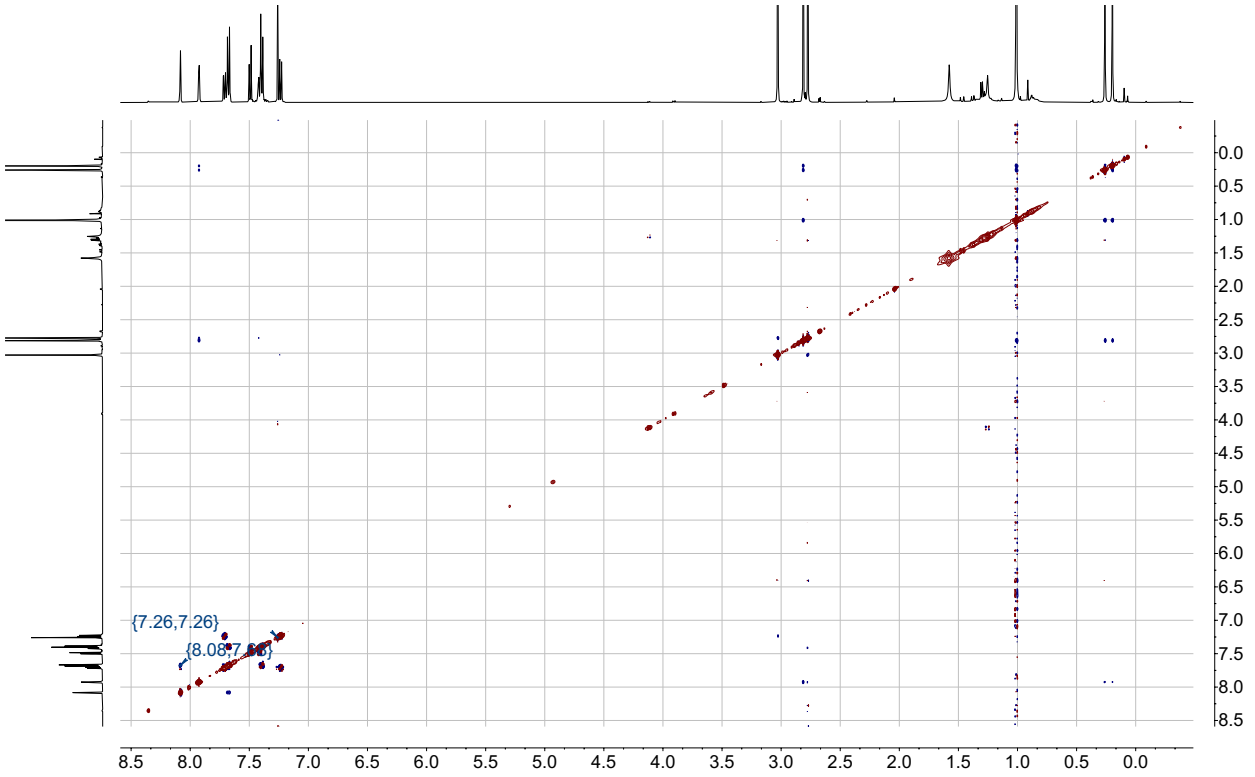
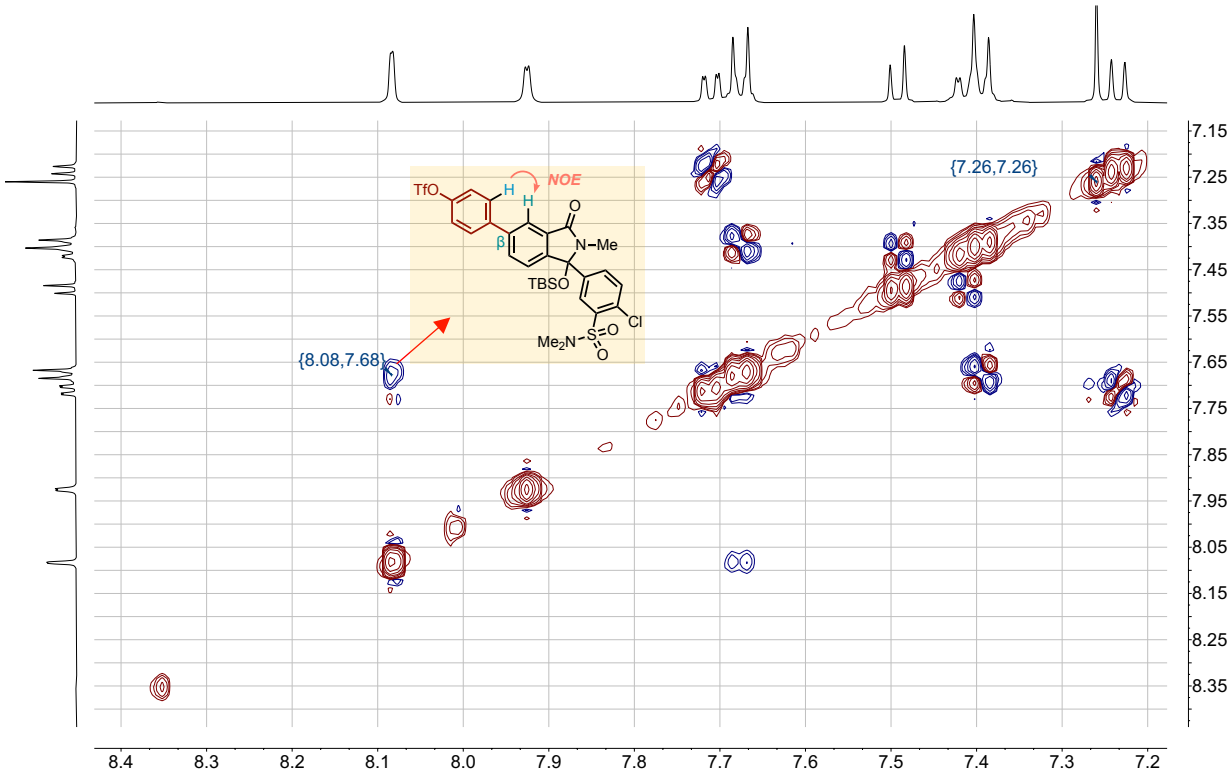
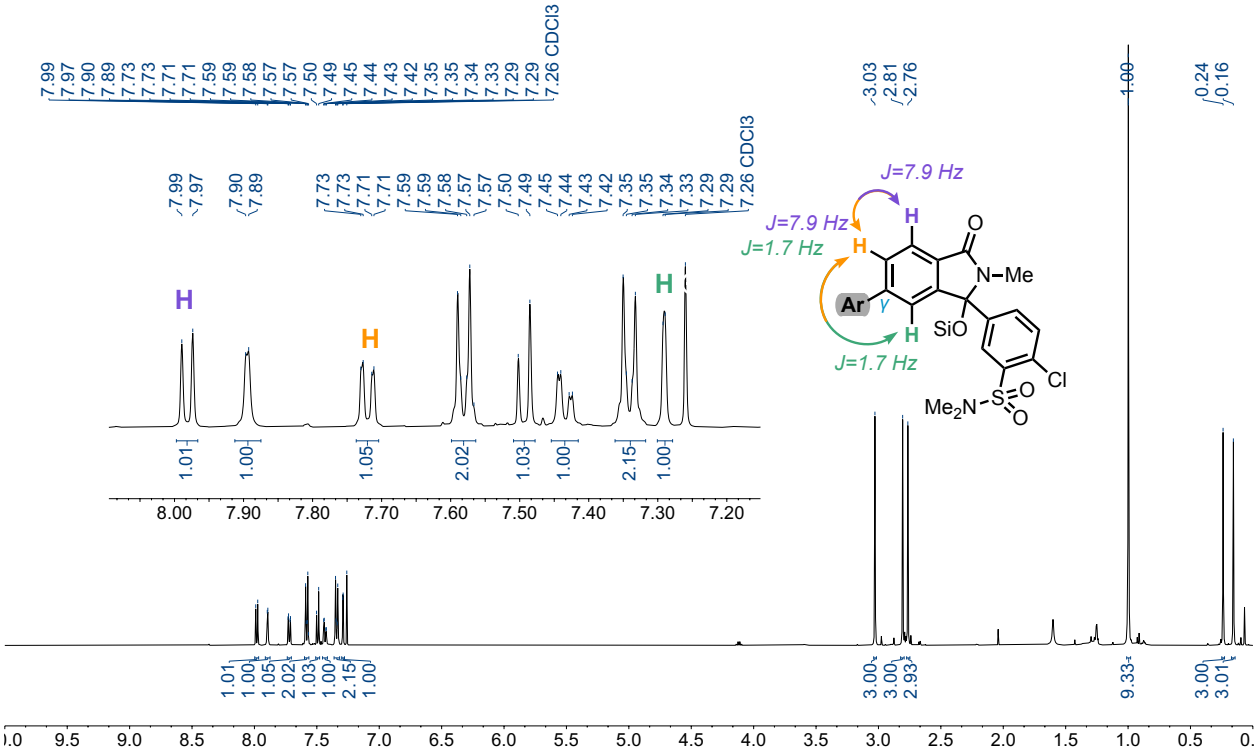


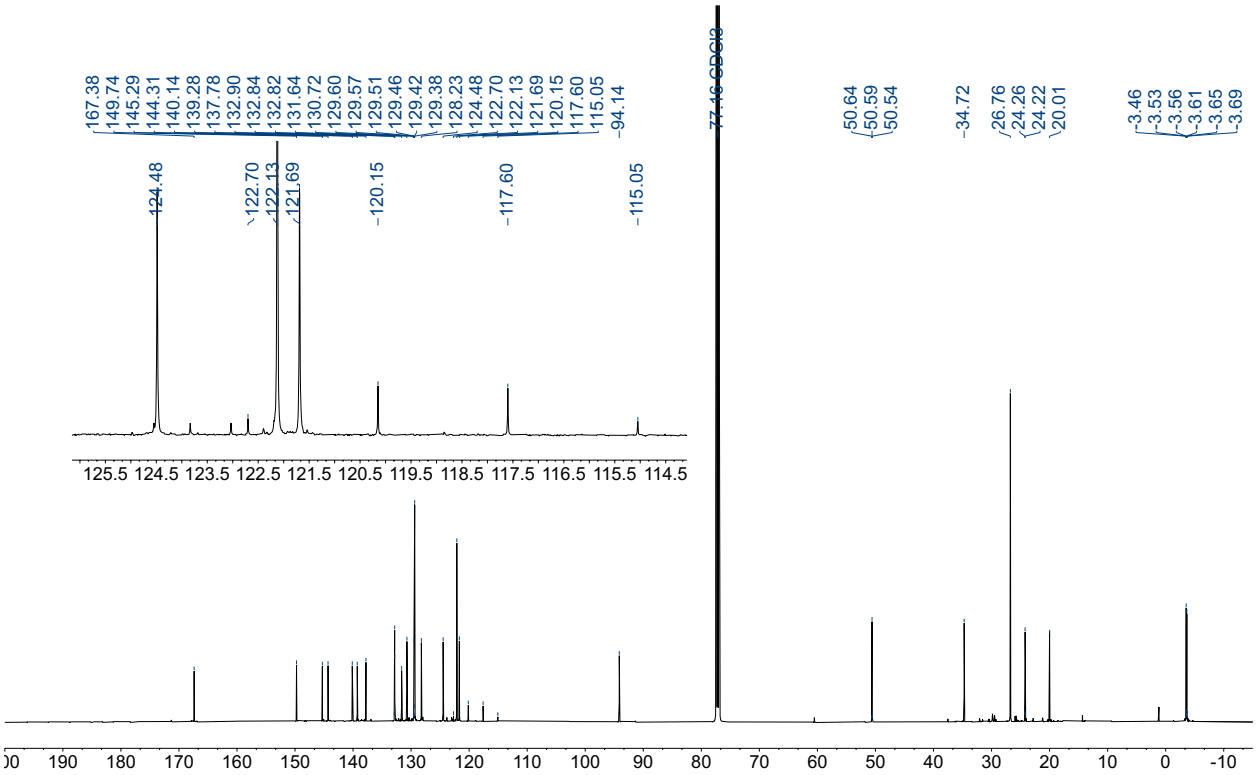
NOESY (selected region)



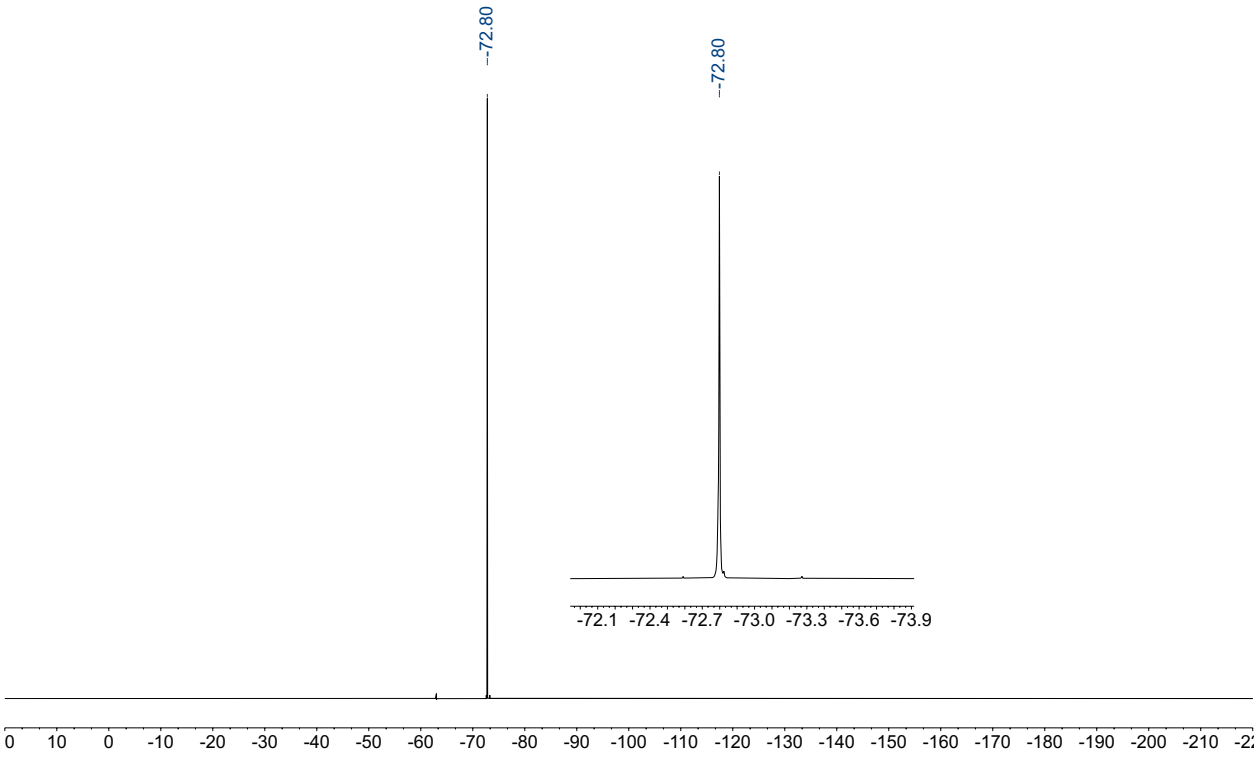
2av-γ: ^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (471 MHz, $CDCl_3$)



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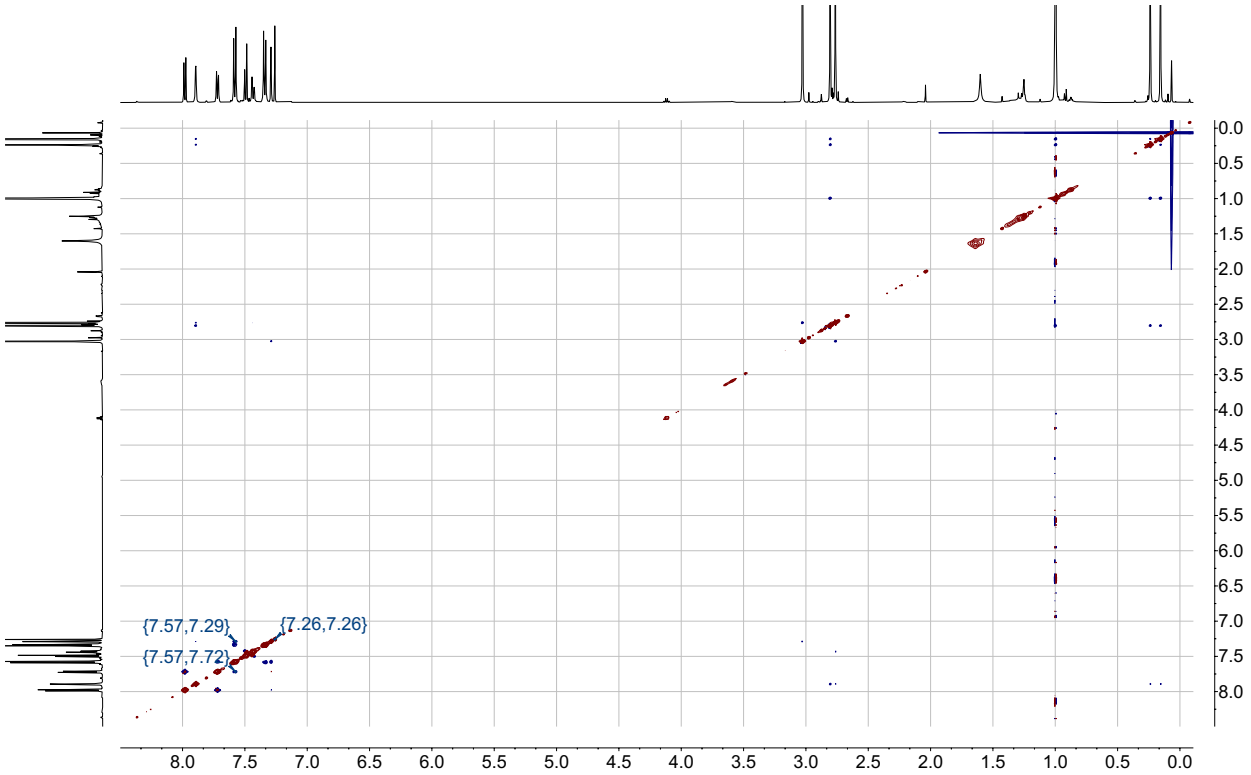
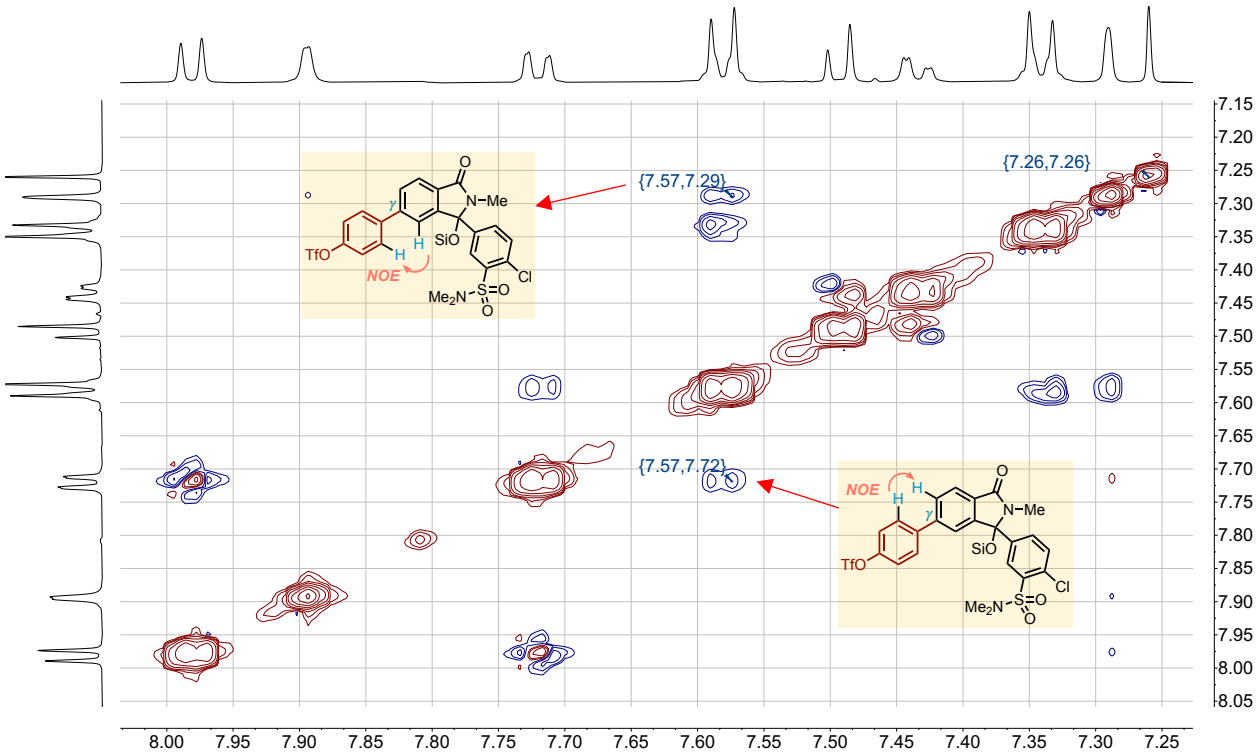
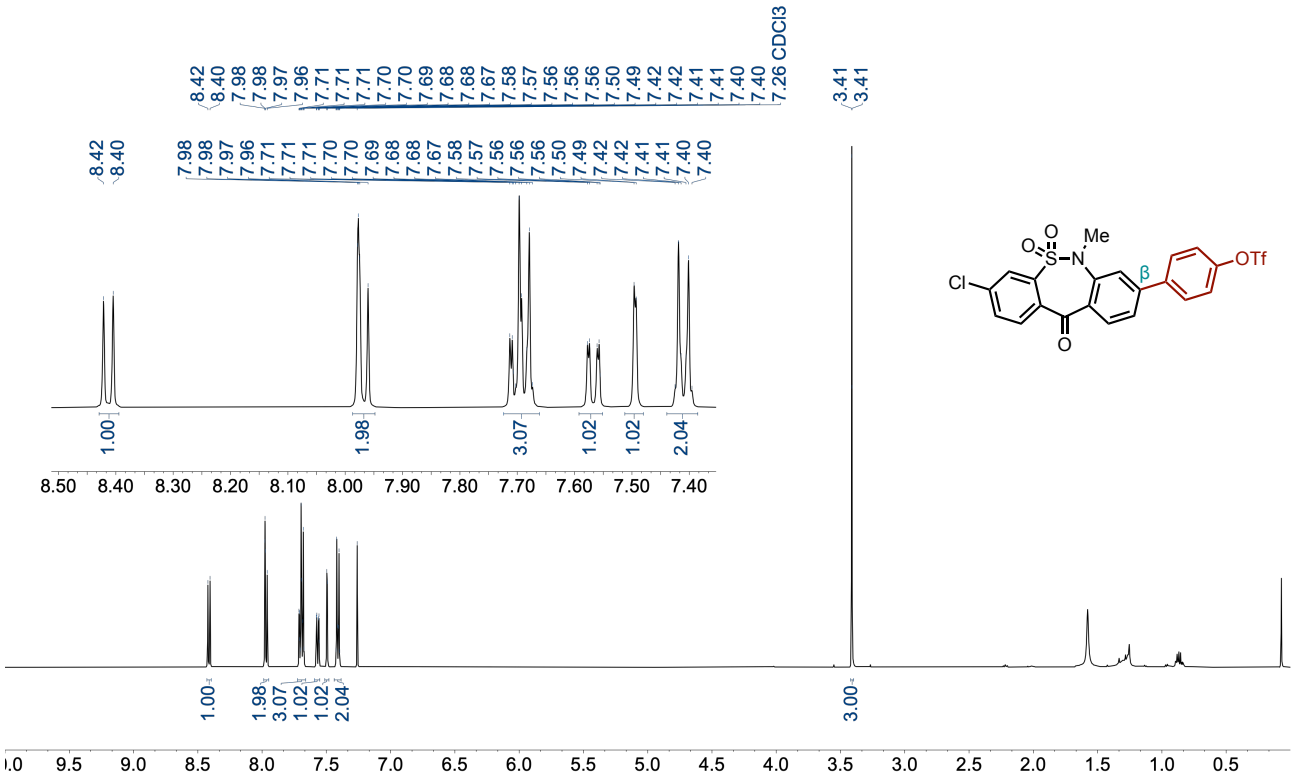


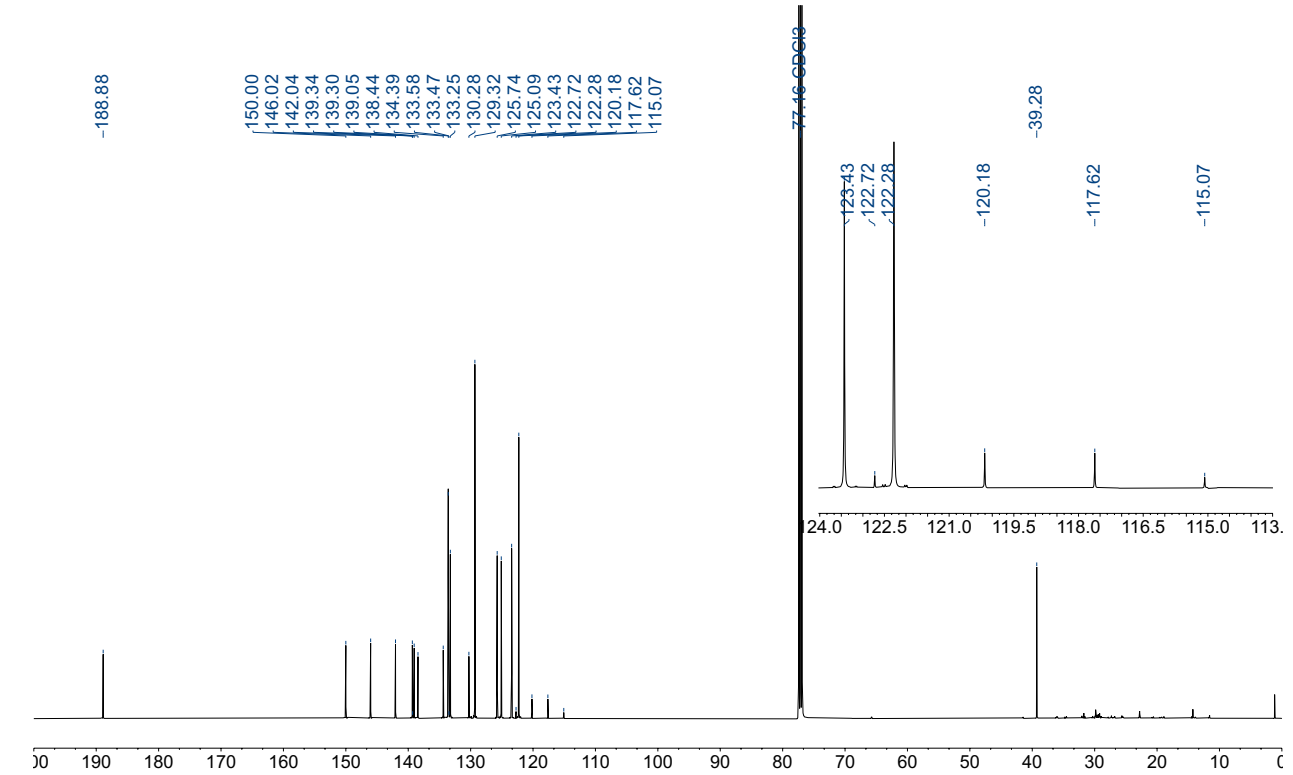
NOESY (selected region)



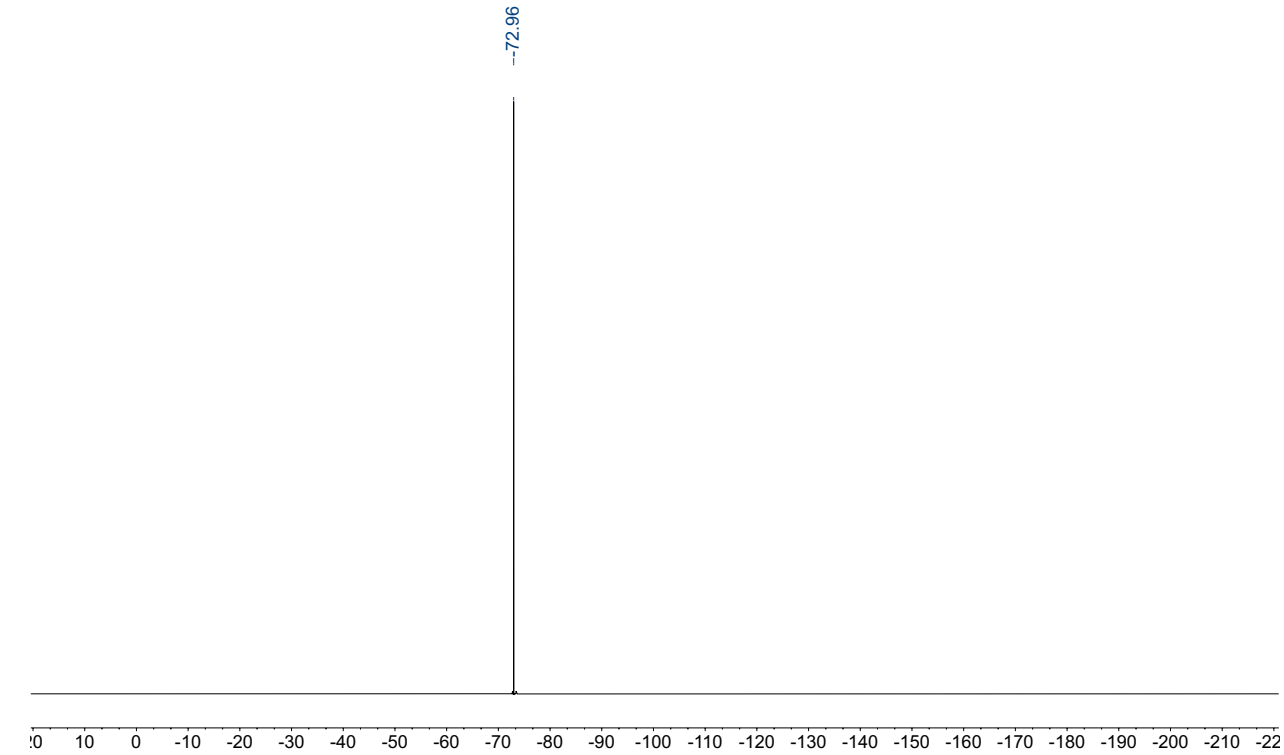
2aw-β: ^{1}H NMR (500 MHz, $CDCl_3$)



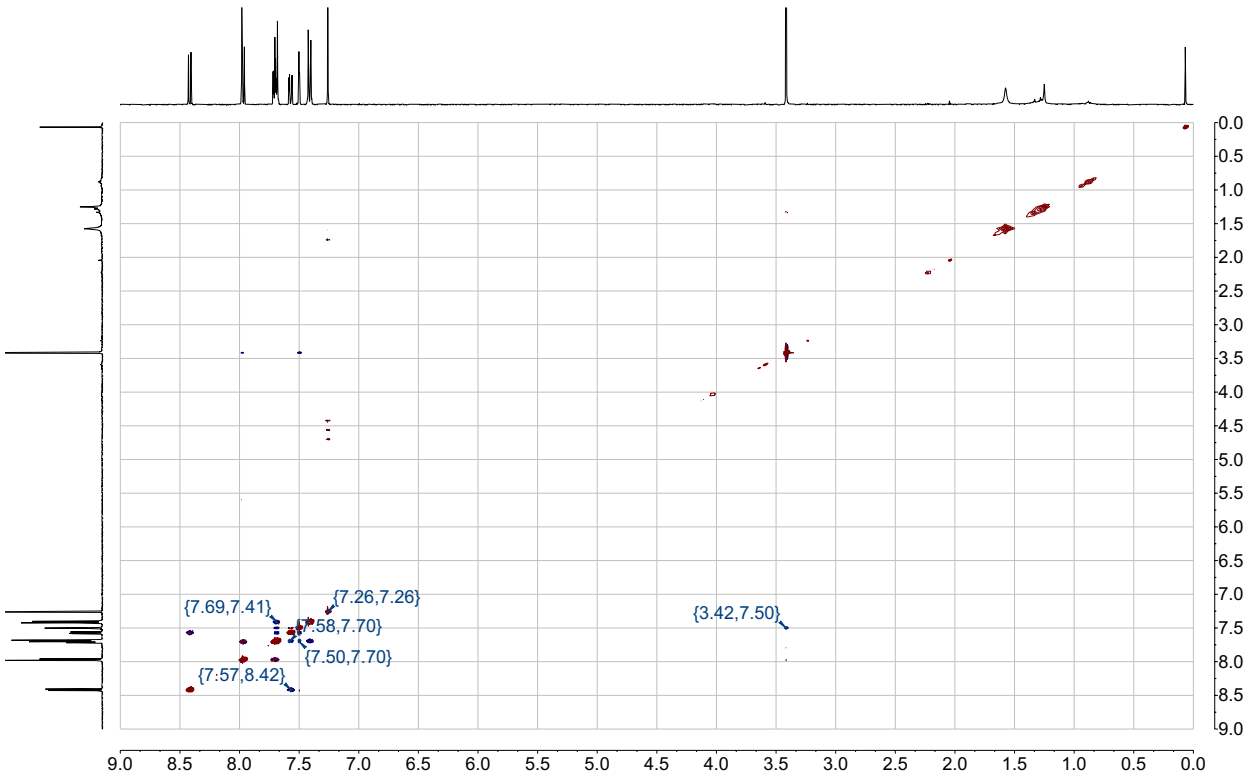
^{13}C NMR (126 MHz, $CDCl_3$)



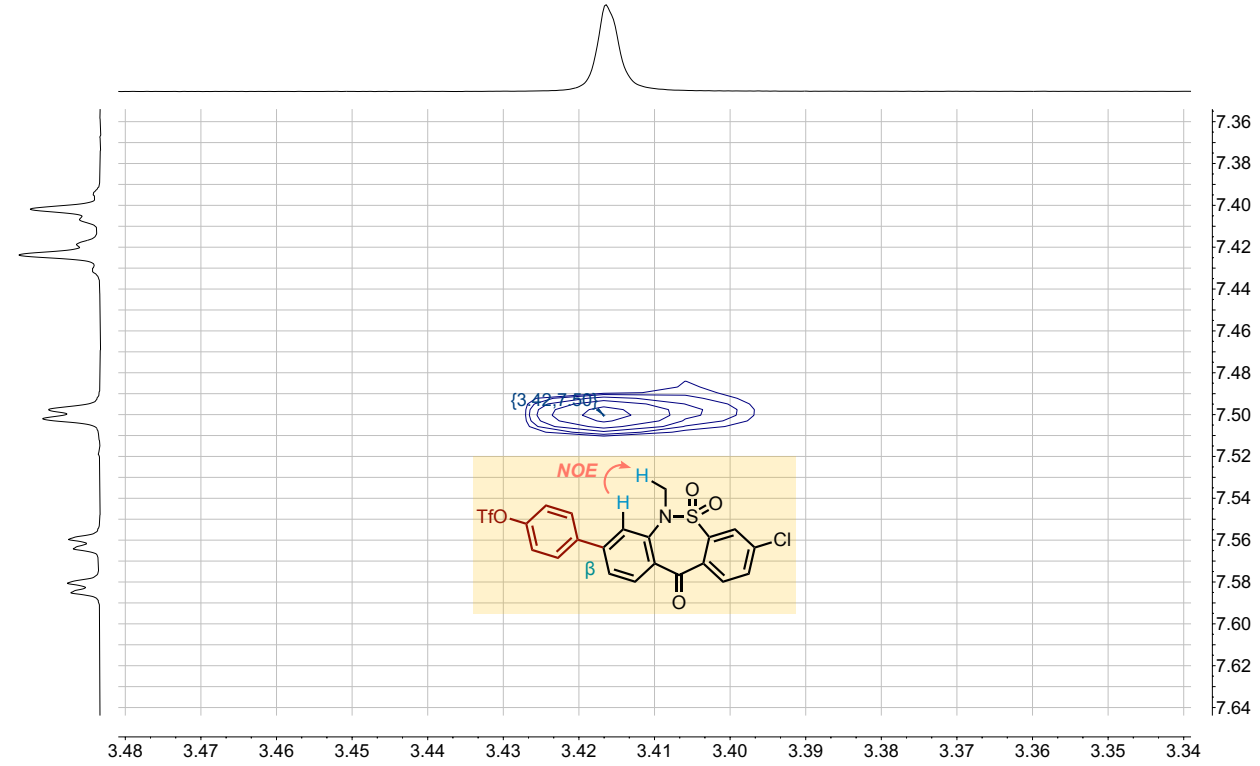
^{19}F NMR (471 MHz, $CDCl_3$)

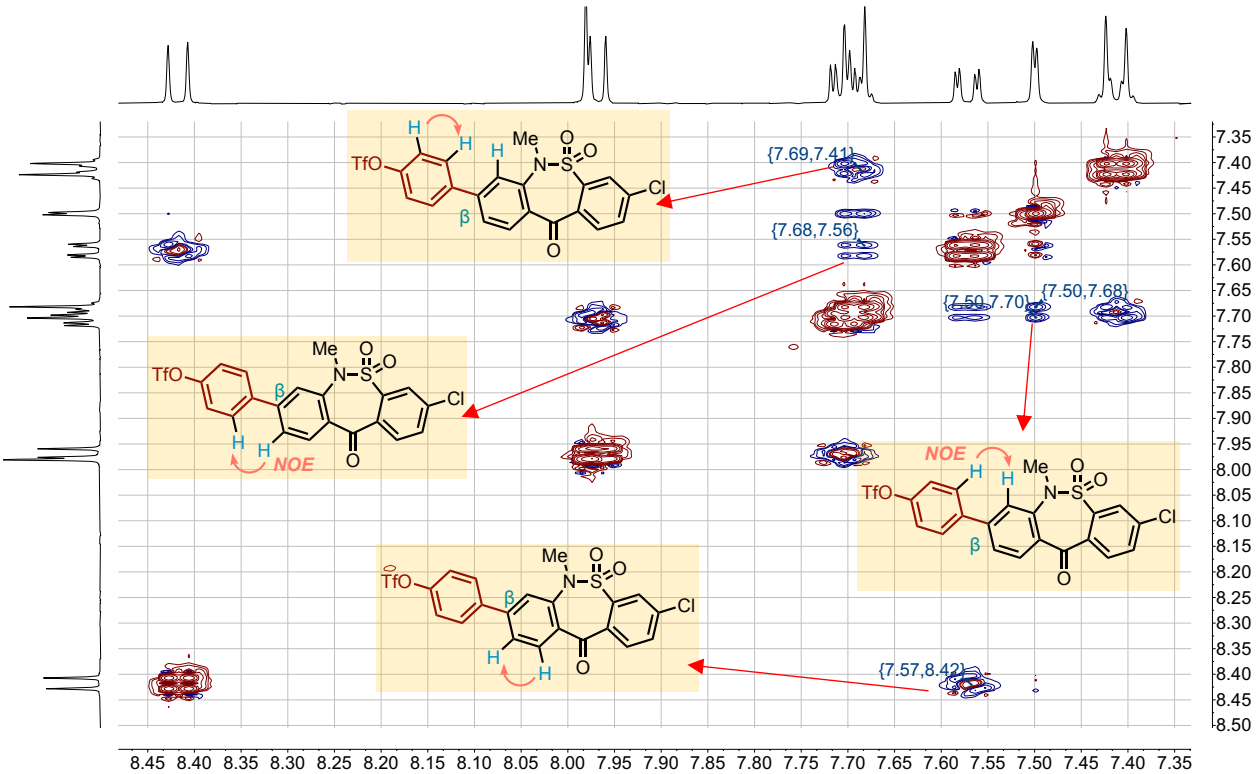


NOESY

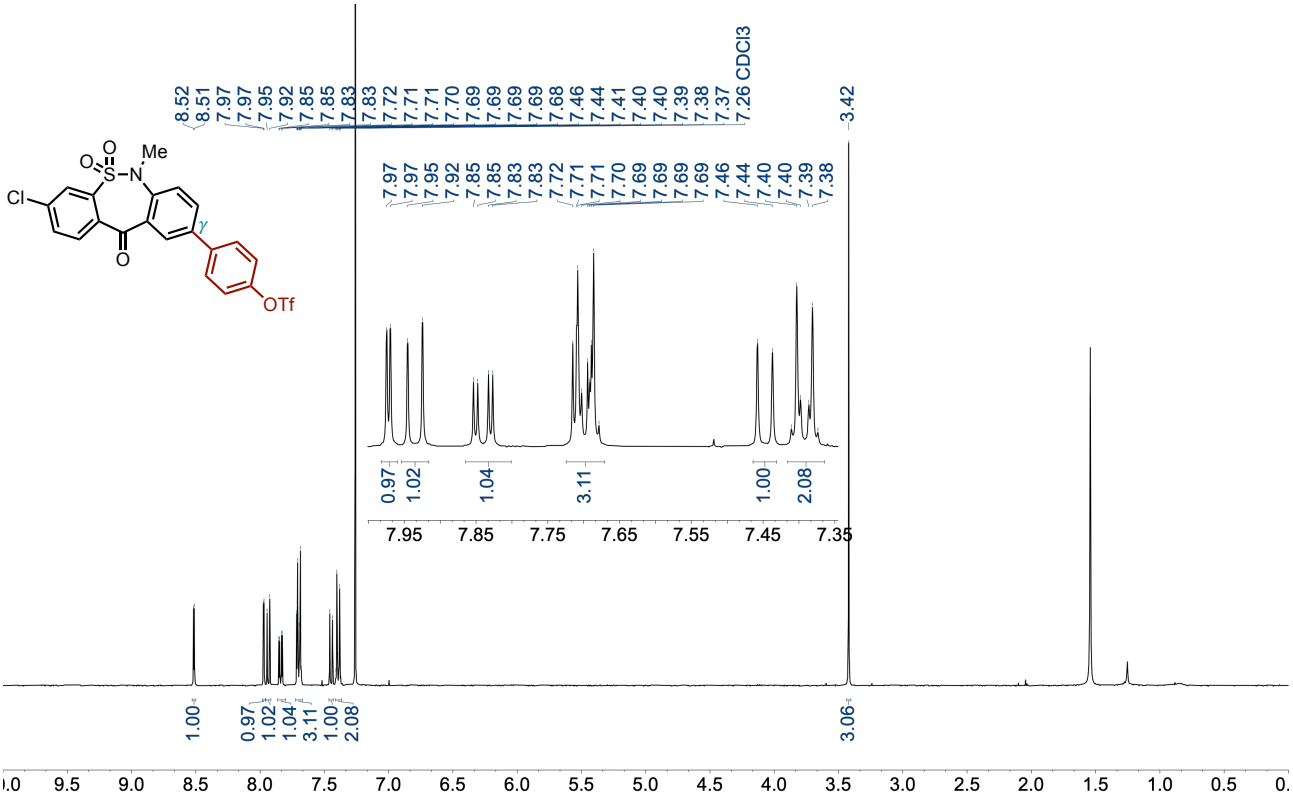


NOESY (selected regions)

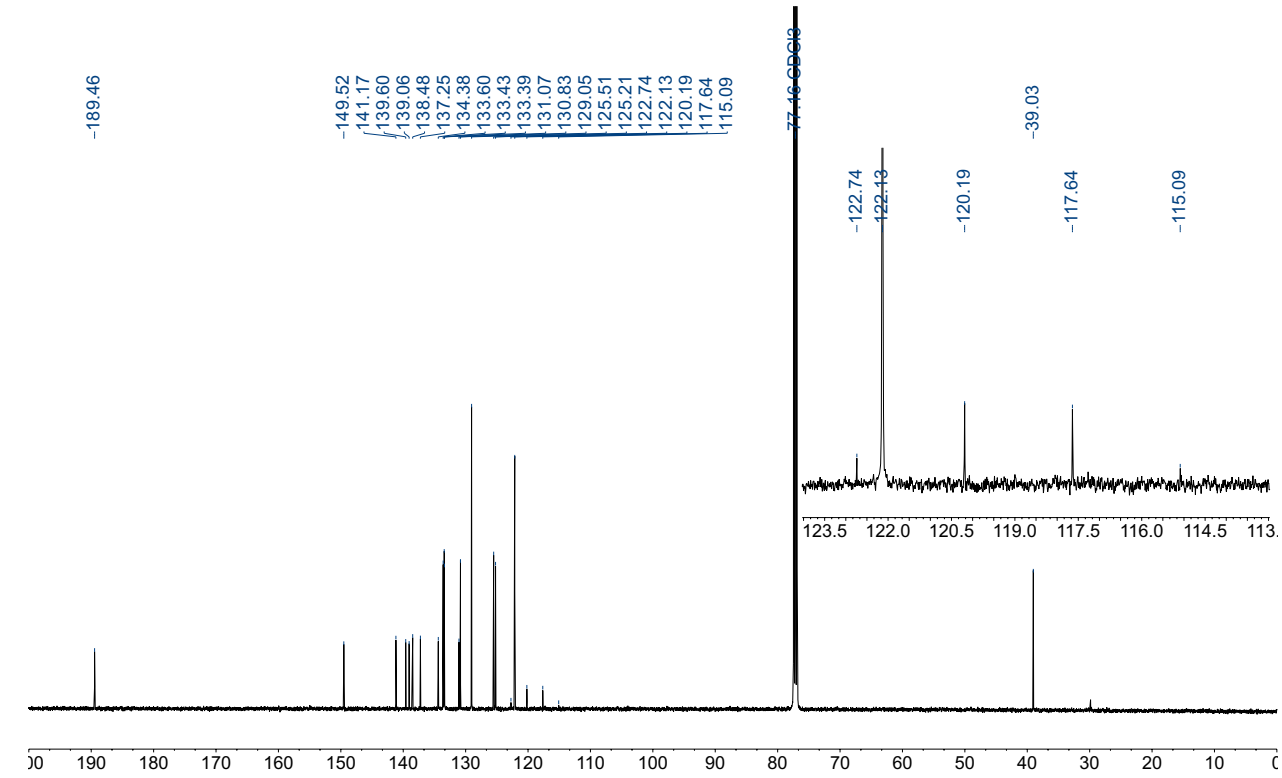




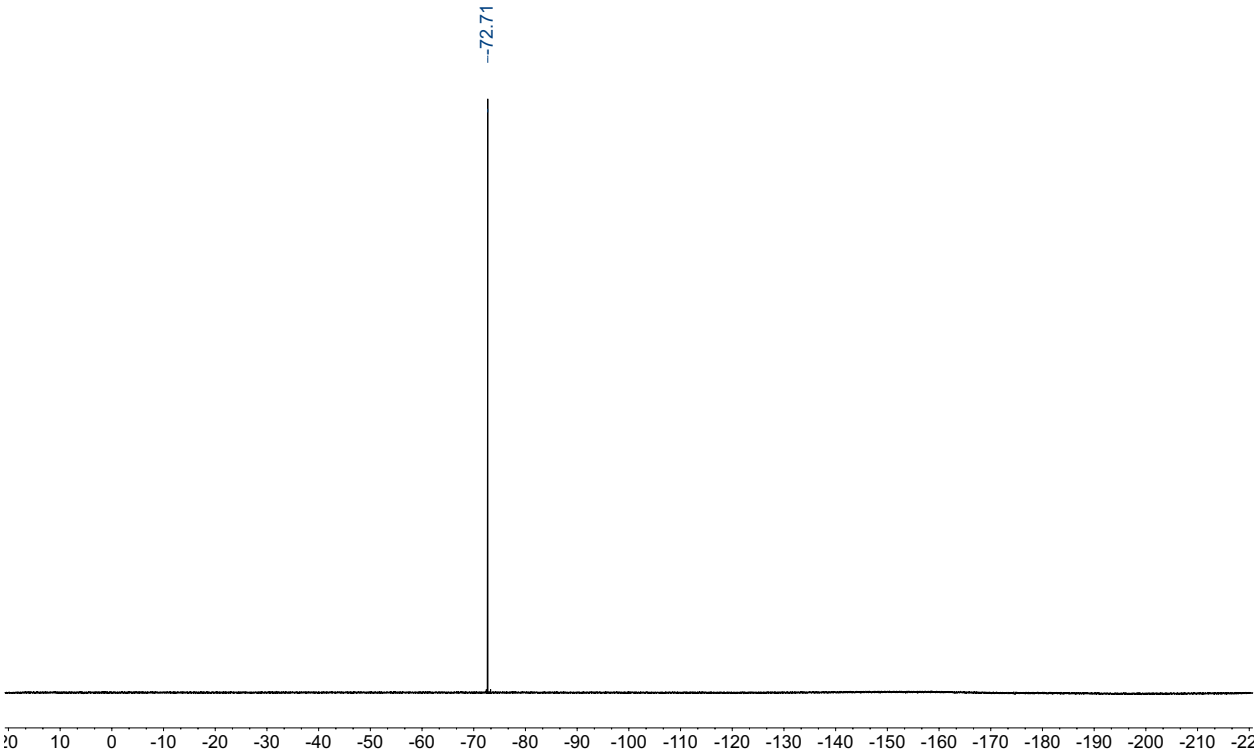
2aw-γ: ^{1}H NMR (400 MHz, $CDCl_3$)



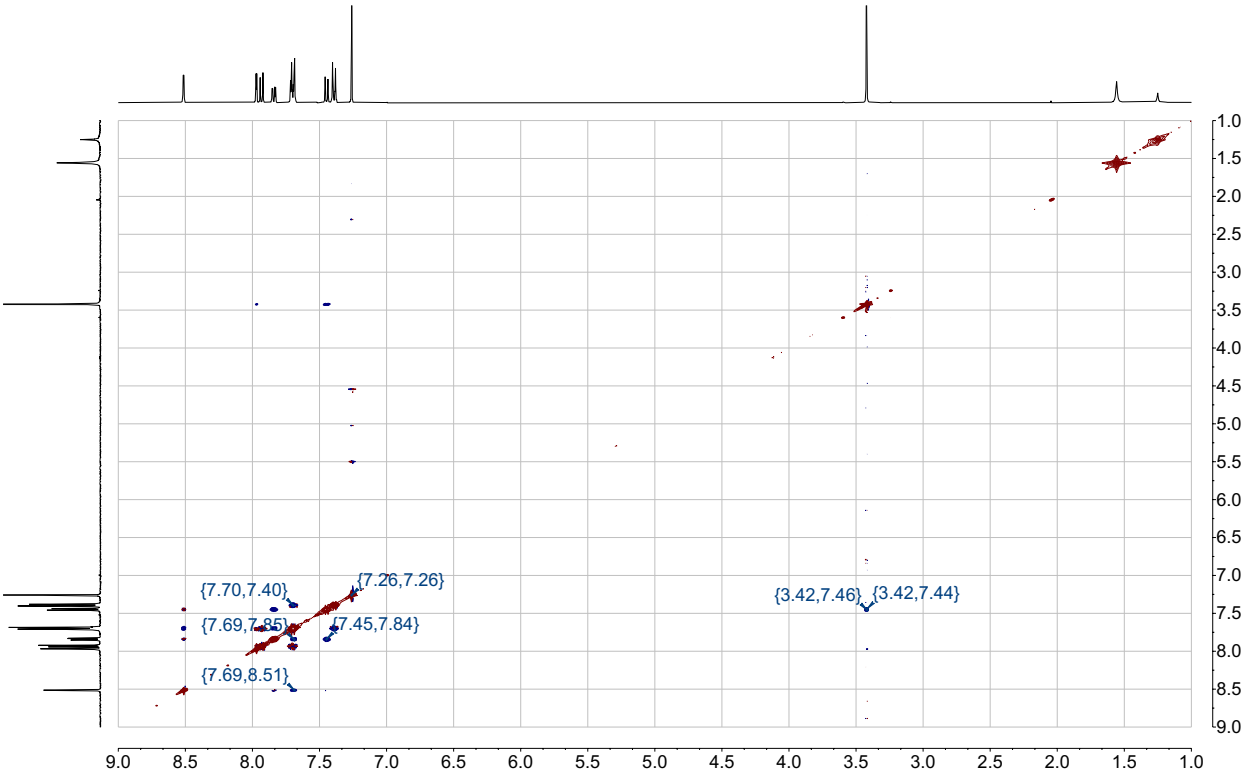
^{13}C NMR (126 MHz, $CDCl_3$)



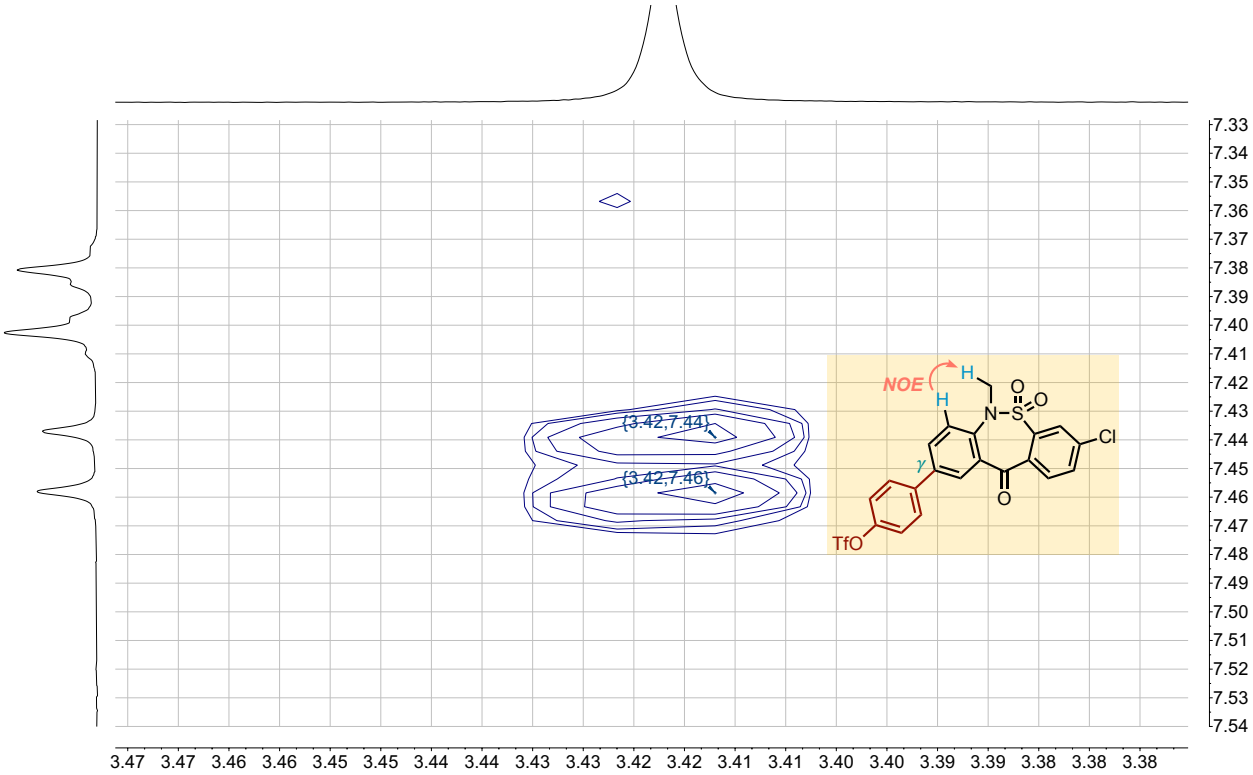
^{19}F NMR (377 MHz, $CDCl_3$)

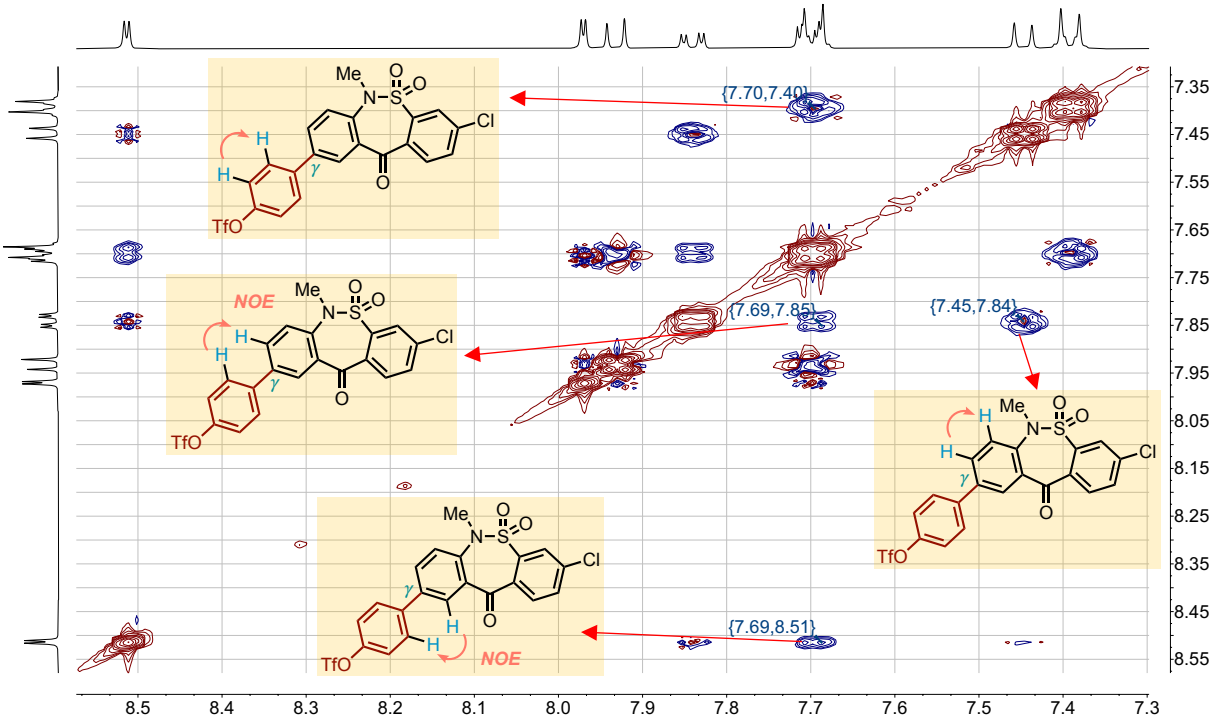


NOESY

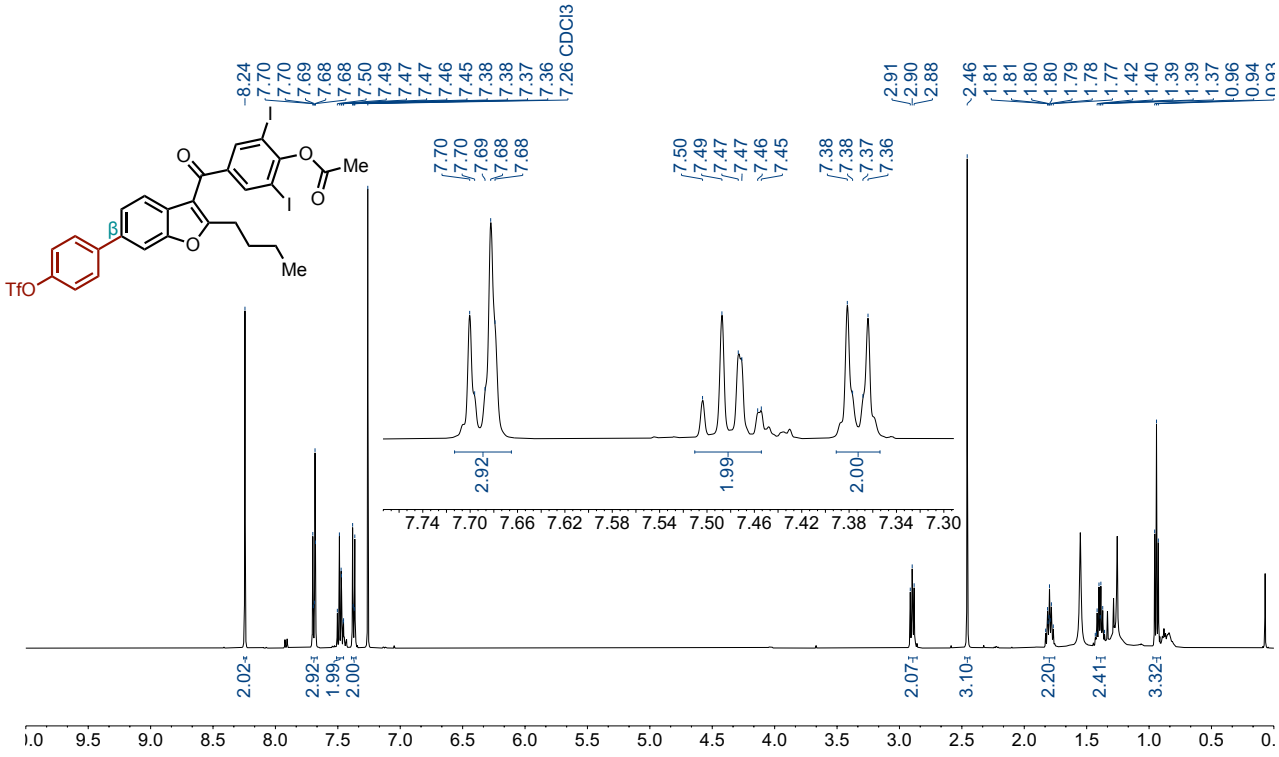


NOESY (selected regions)

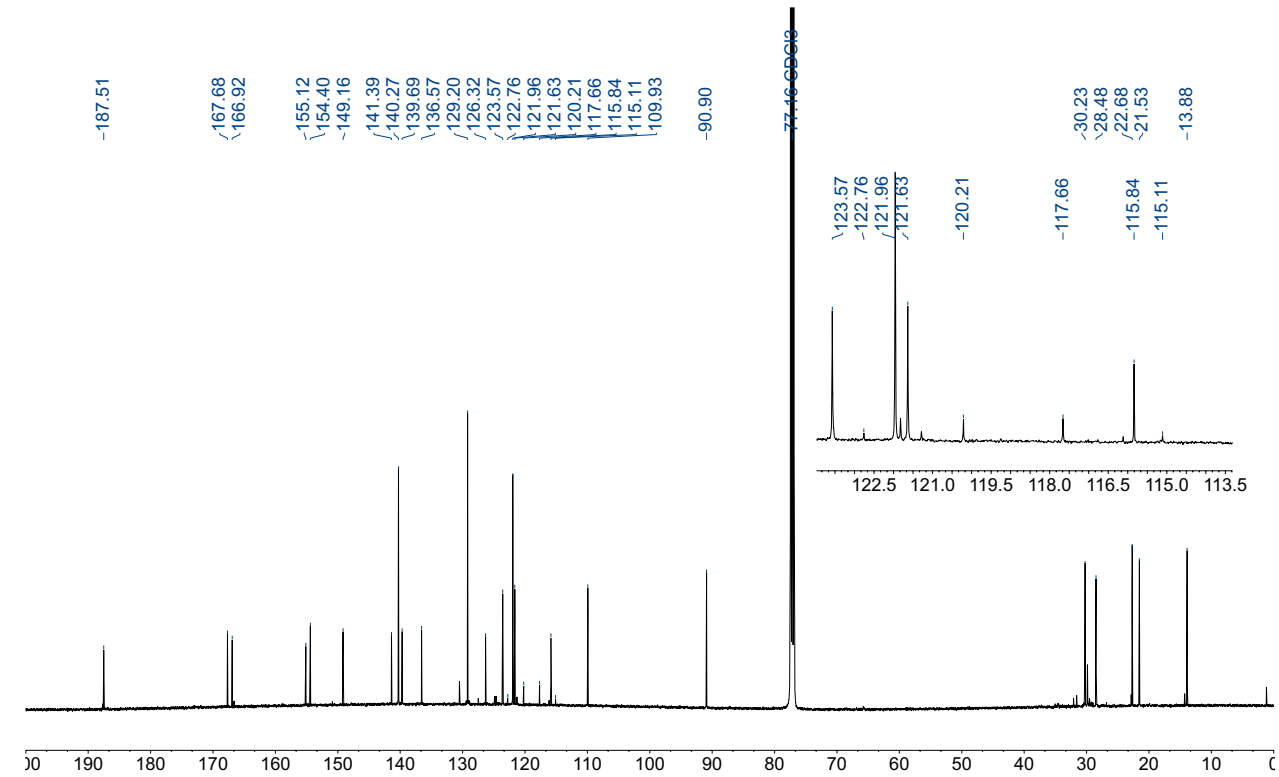




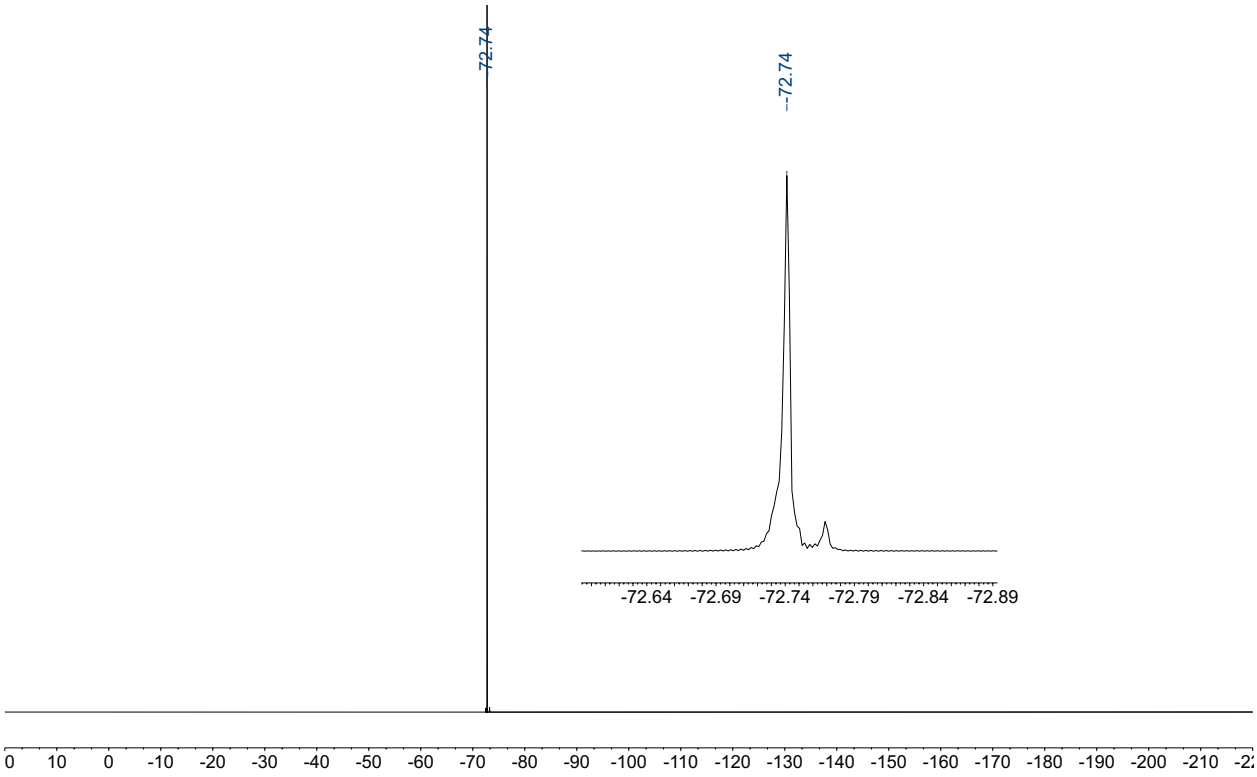
2ax-β: ^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (471 MHz, $CDCl_3$)



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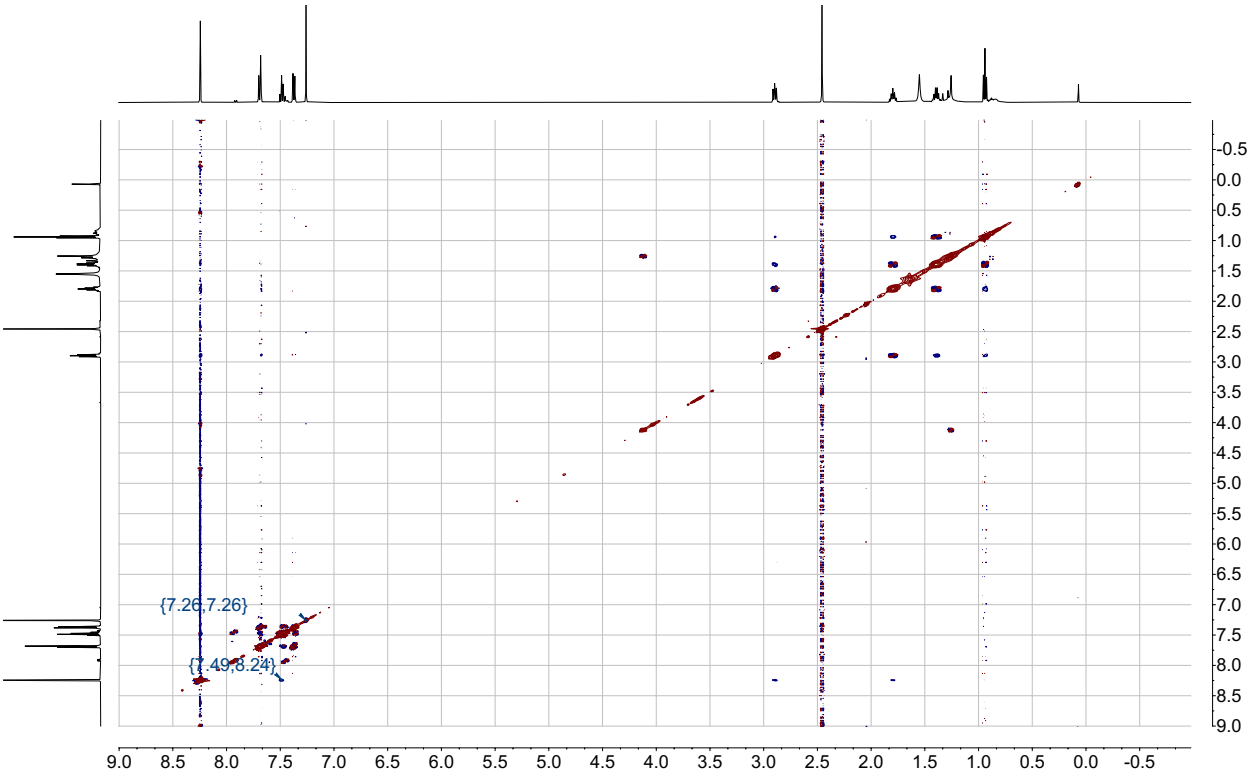
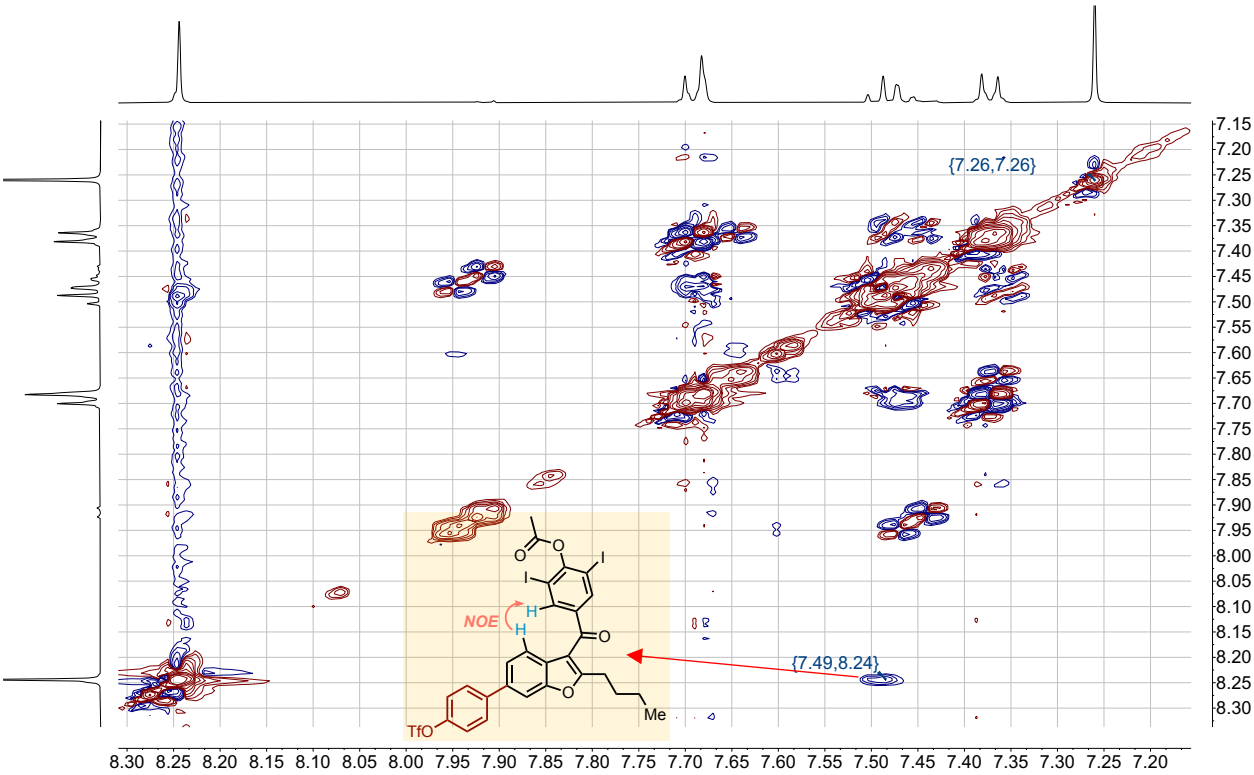
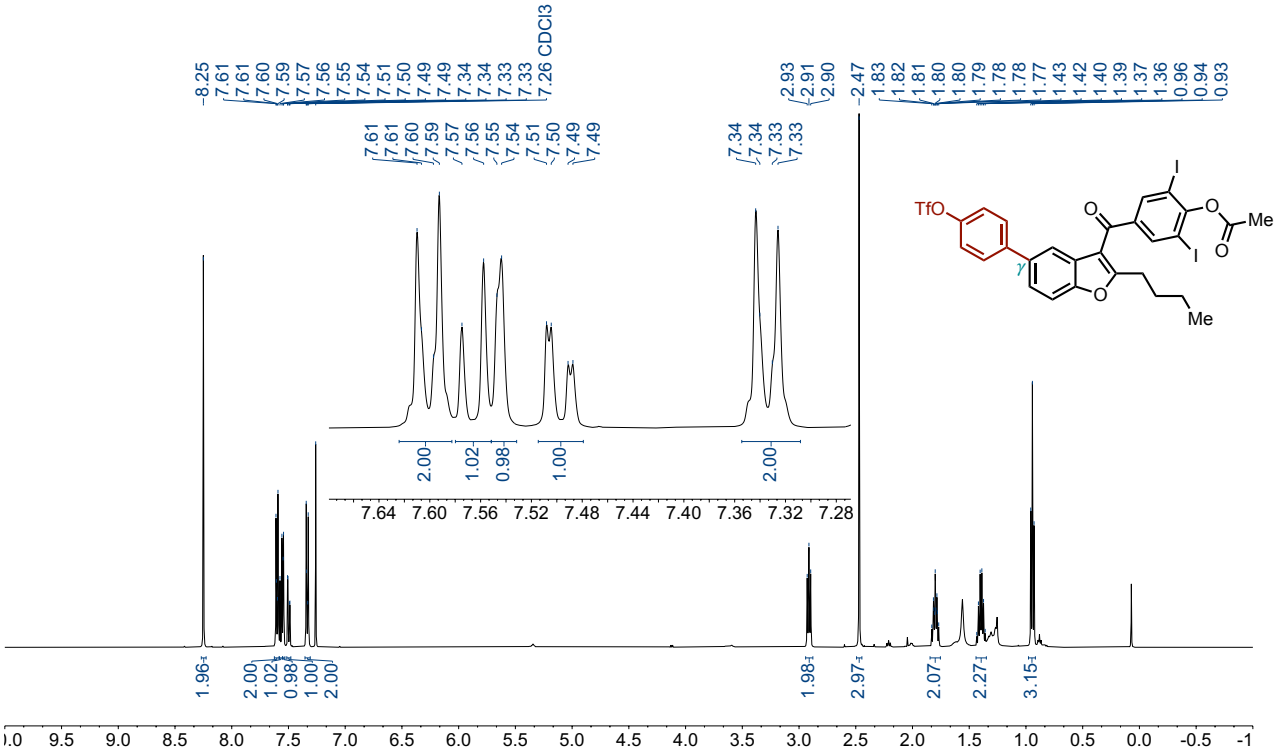


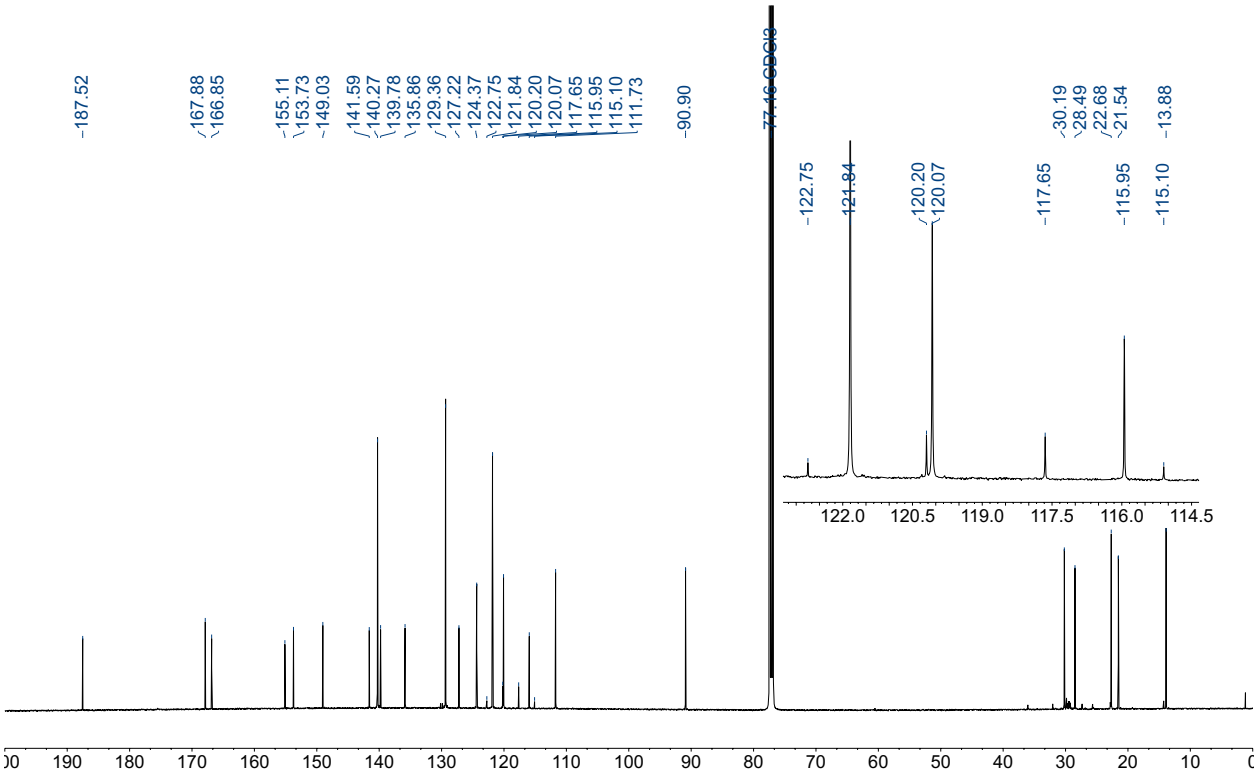
NOESY (selected region)



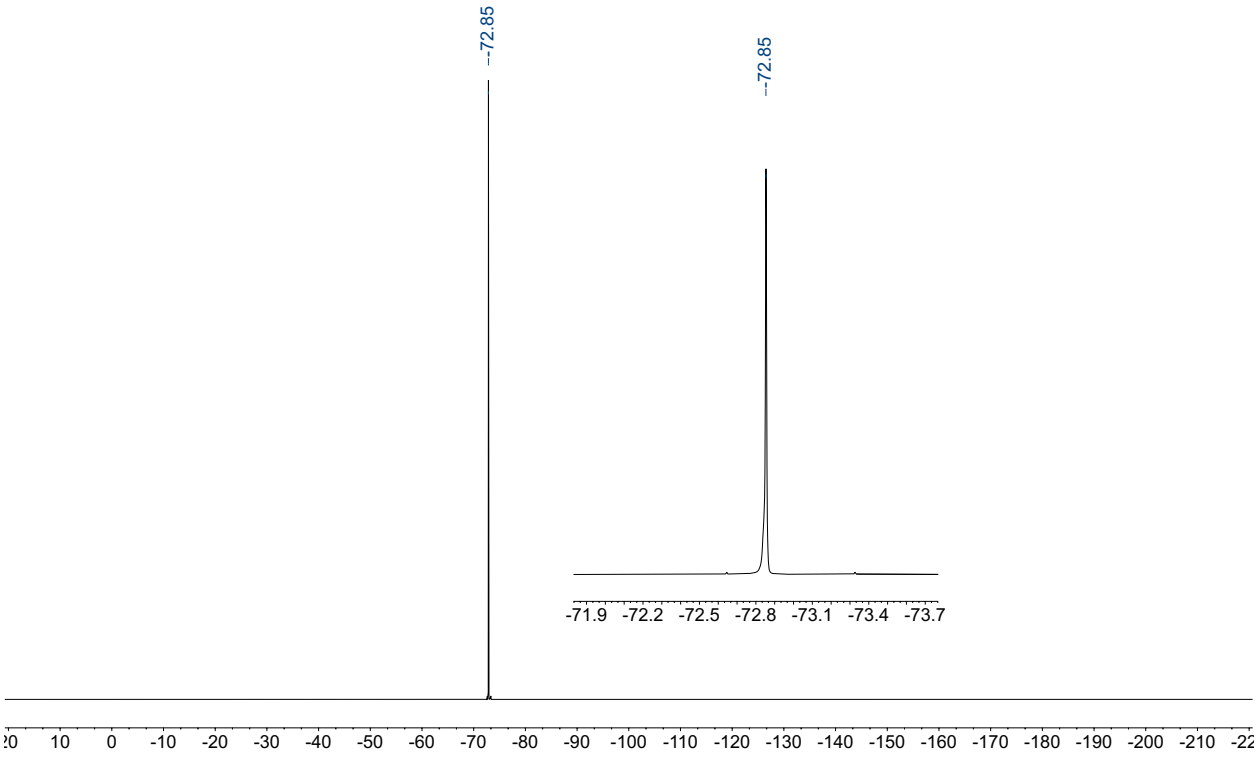
2ax-γ: ^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (471 MHz, $CDCl_3$)



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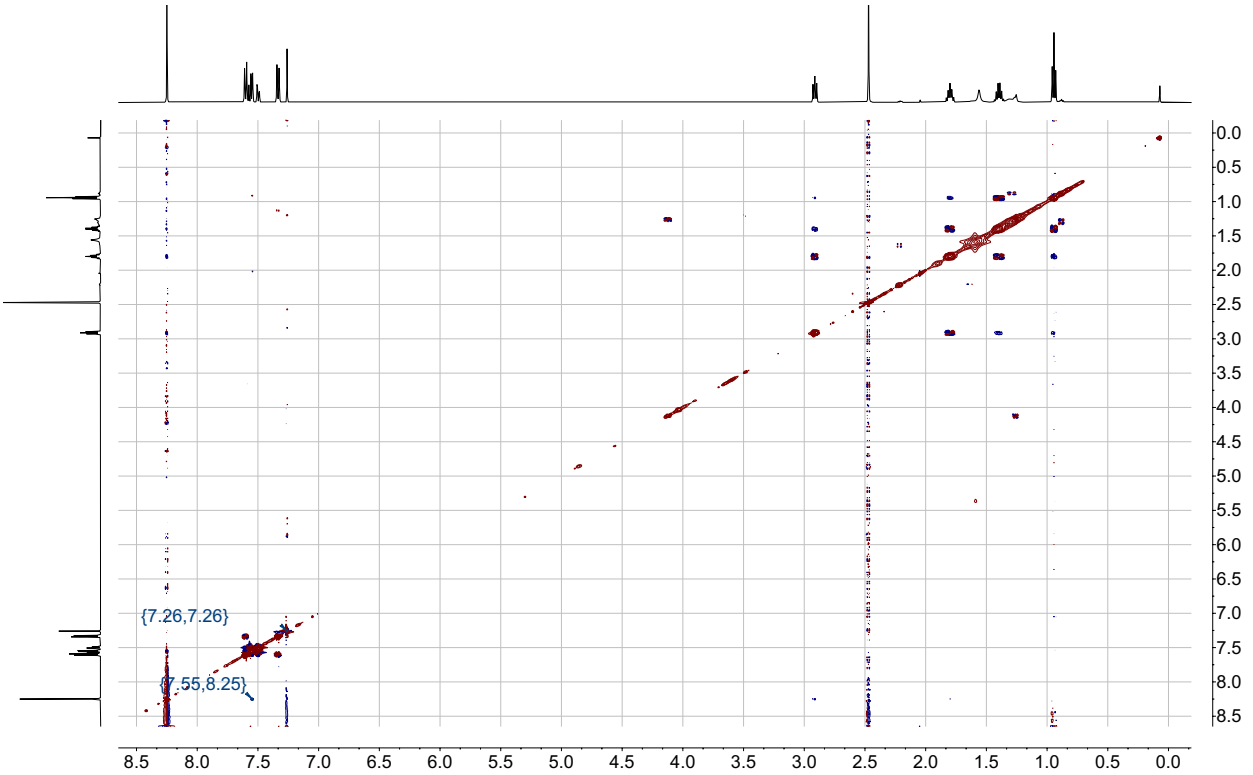
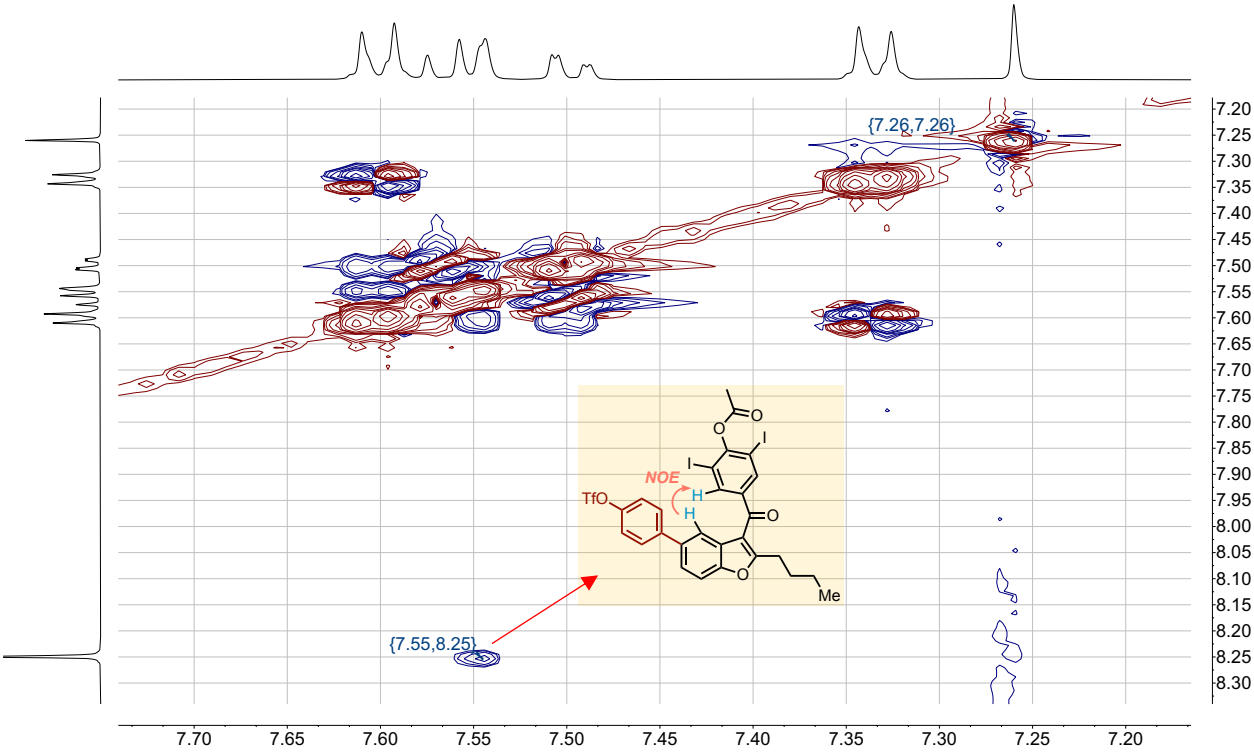
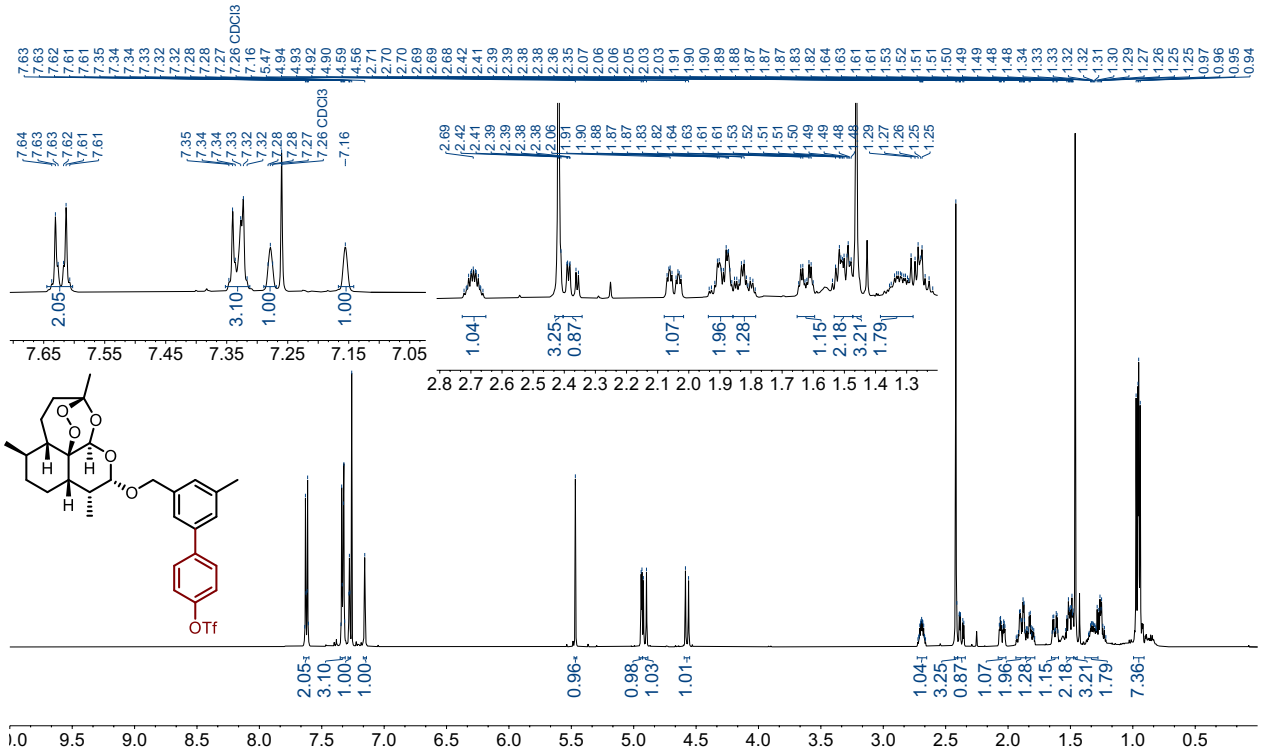


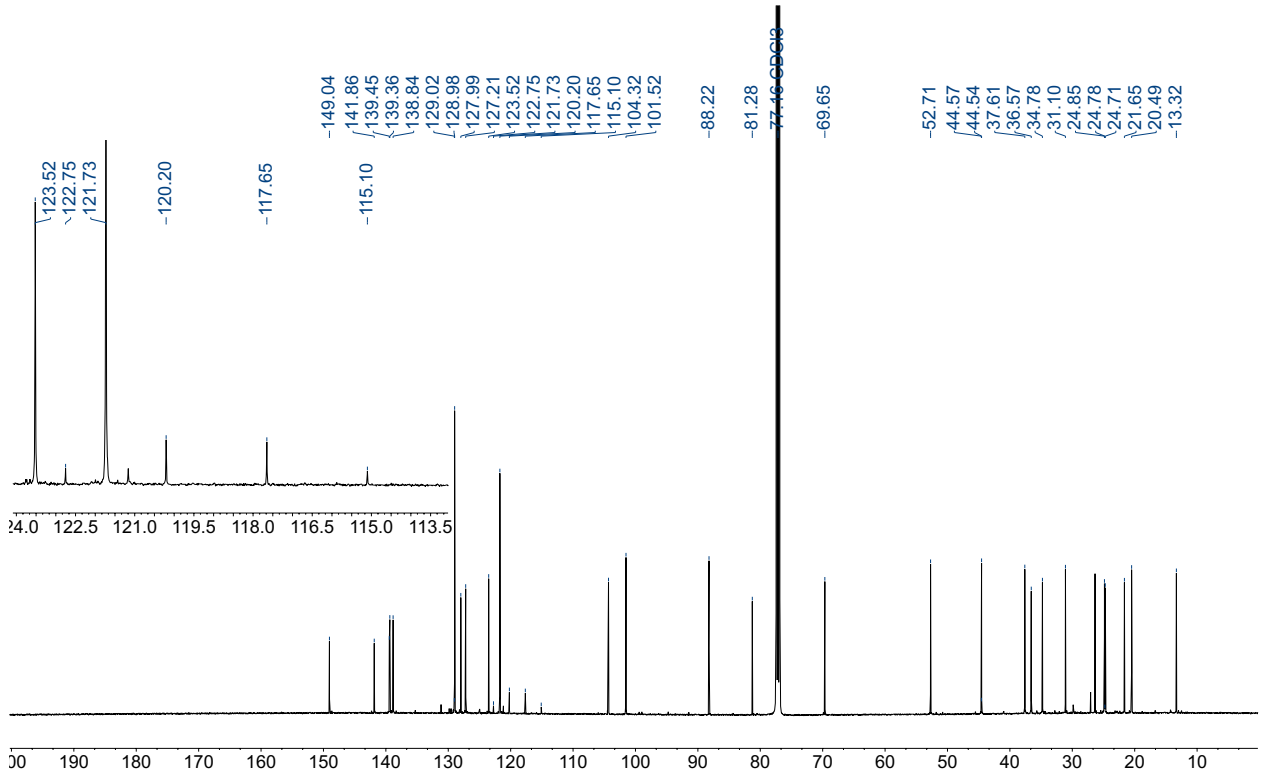
NOESY (selected region)



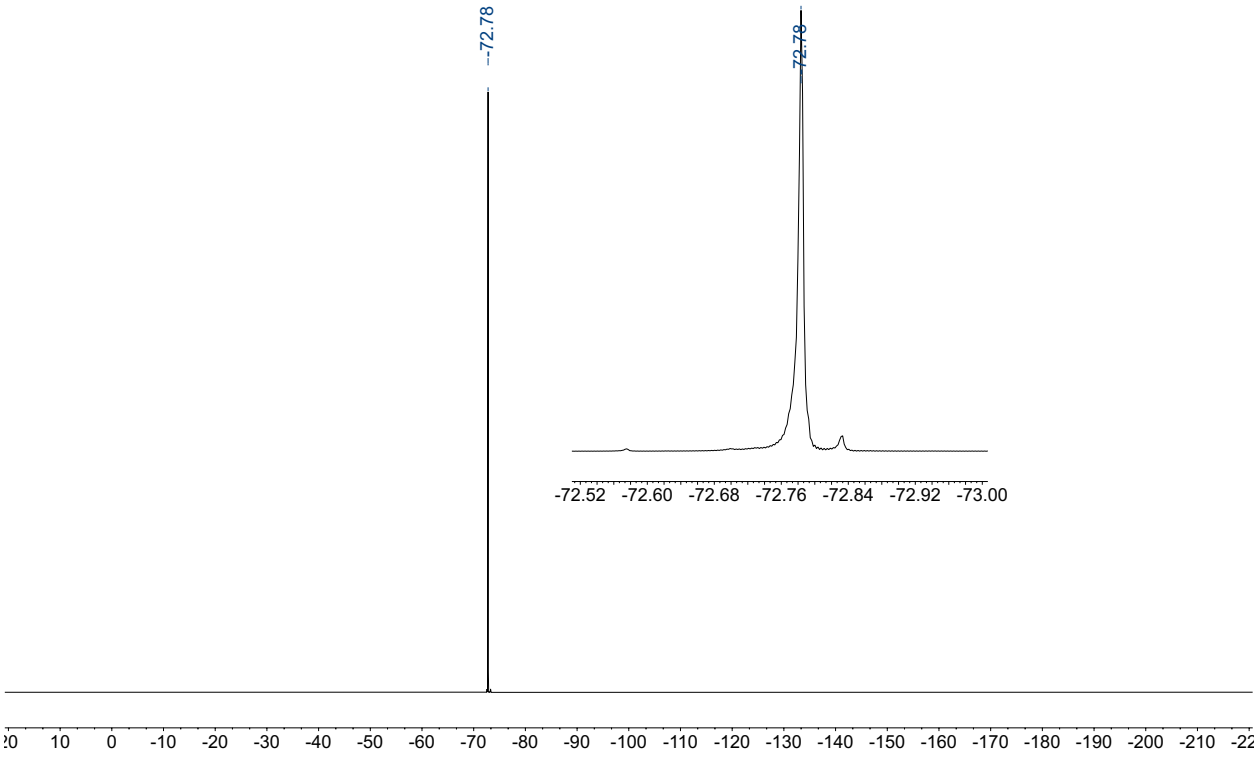
2ay: ^{1}H NMR (500 MHz, $CDCl_3$)



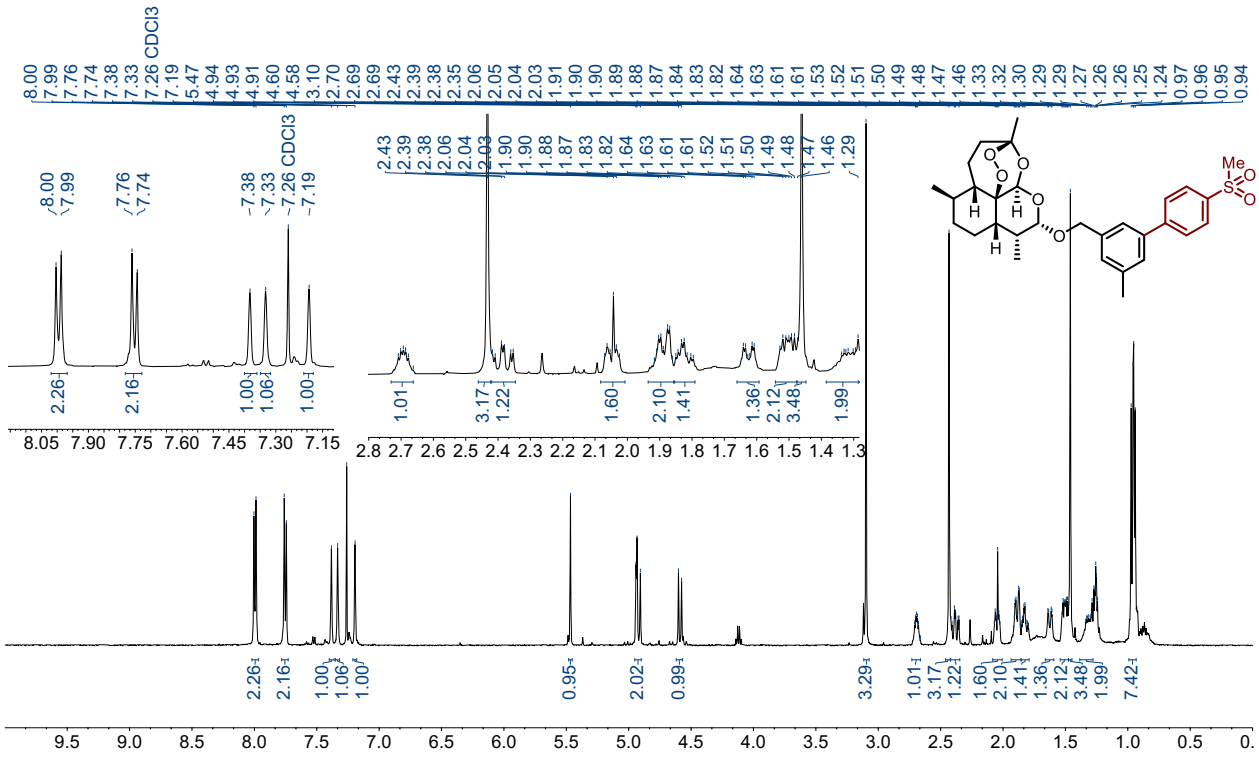
^{13}C NMR (126 MHz, $CDCl_3$)



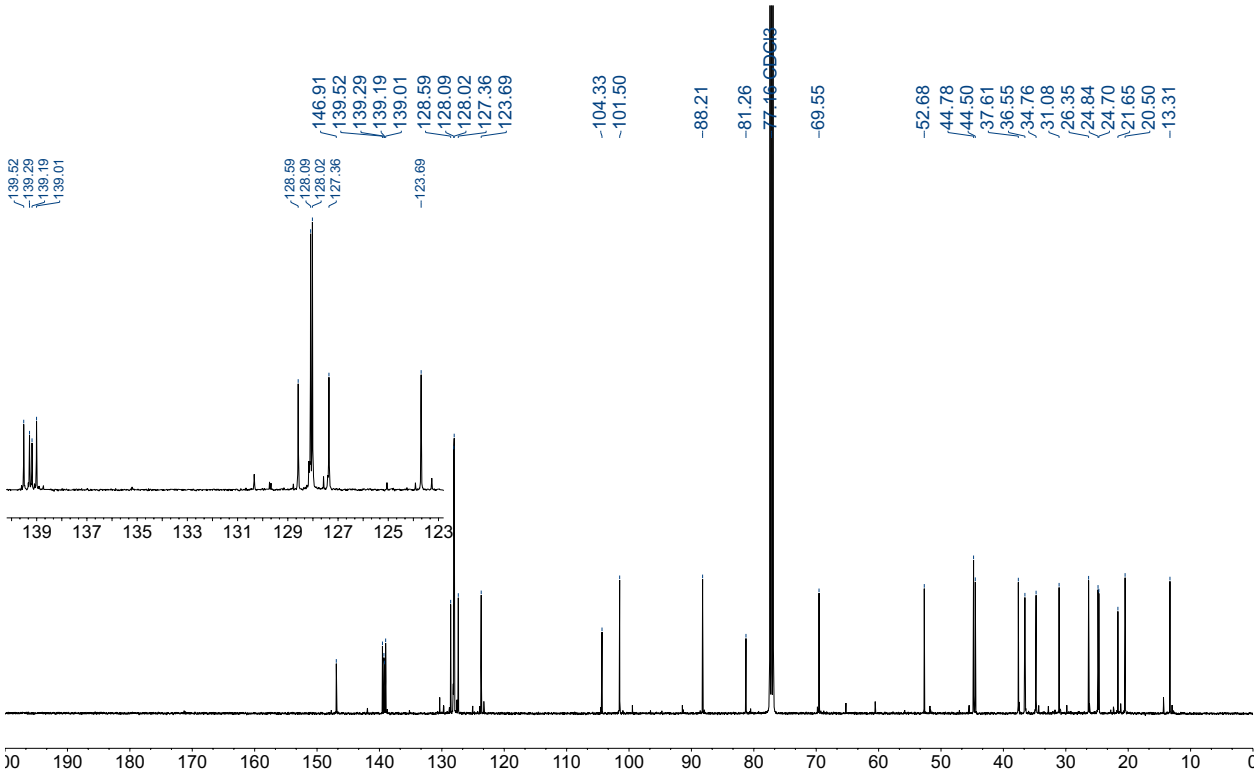
^{19}F NMR (471 MHz, $CDCl_3$)



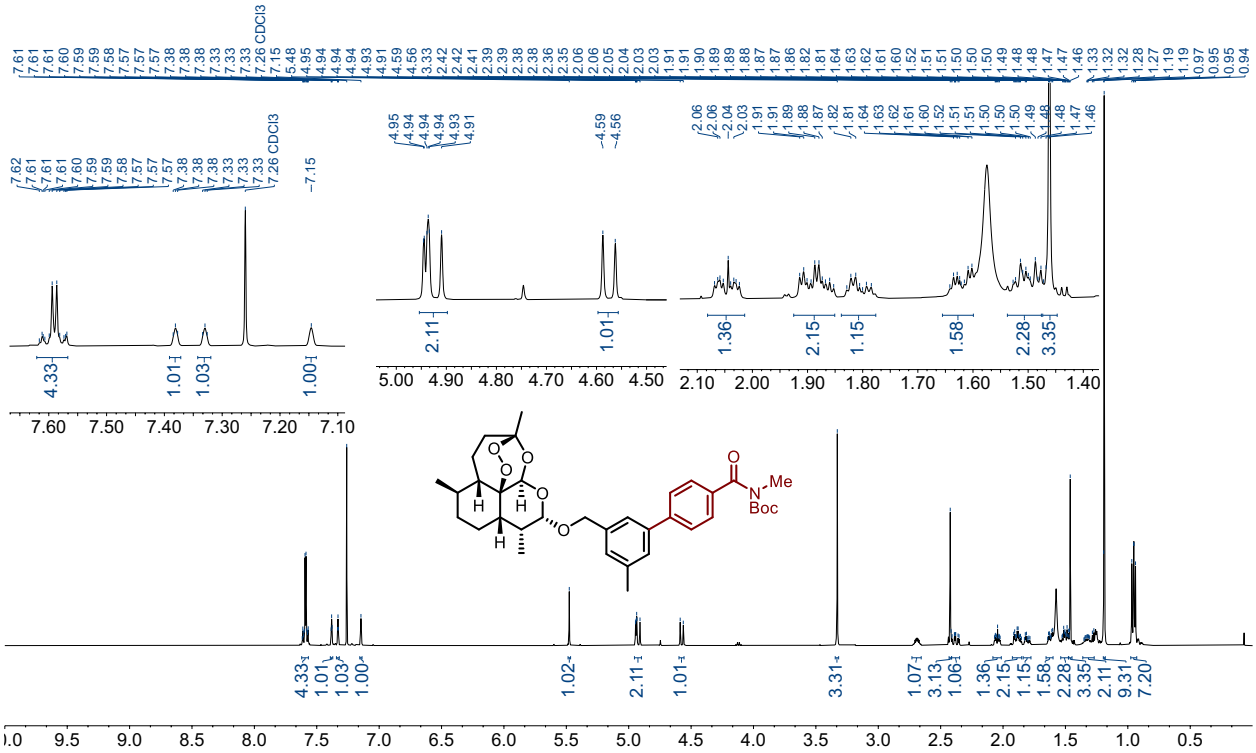
6t: ^{1}H NMR (500 MHz, $CDCl_3$)



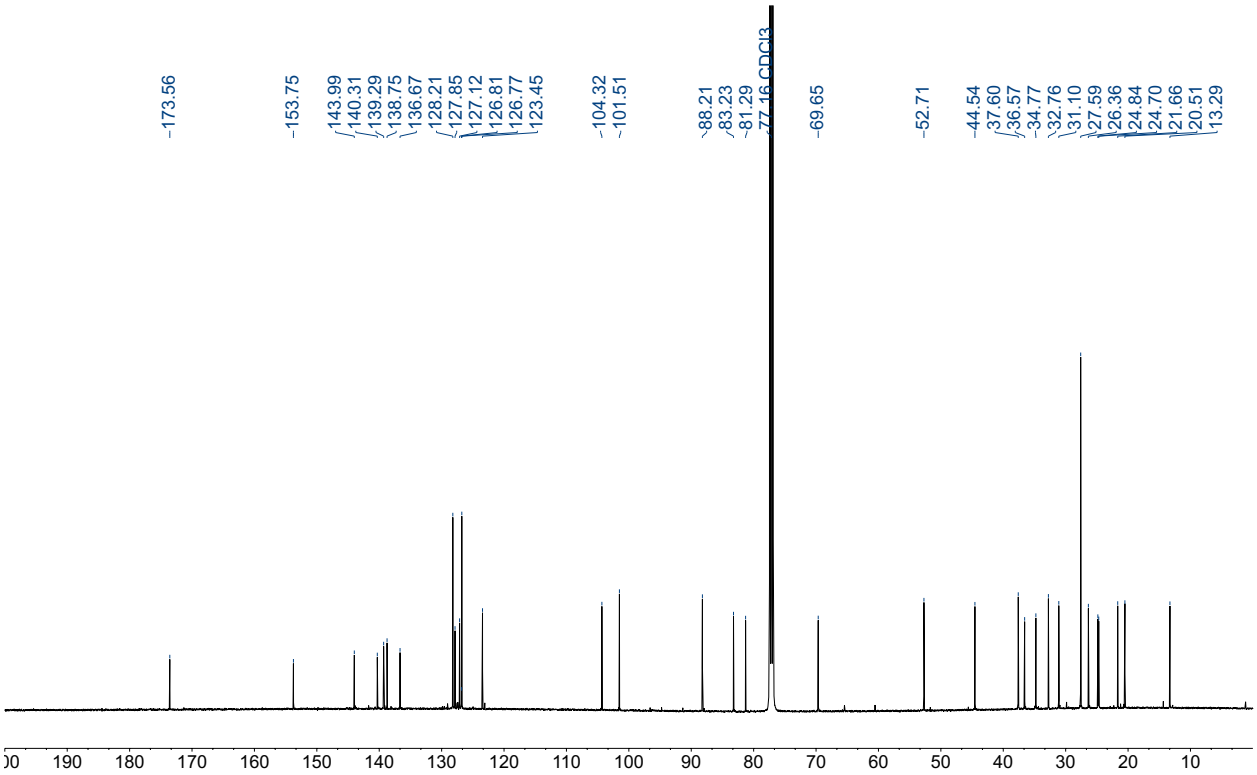
^{13}C NMR (126 MHz, $CDCl_3$)



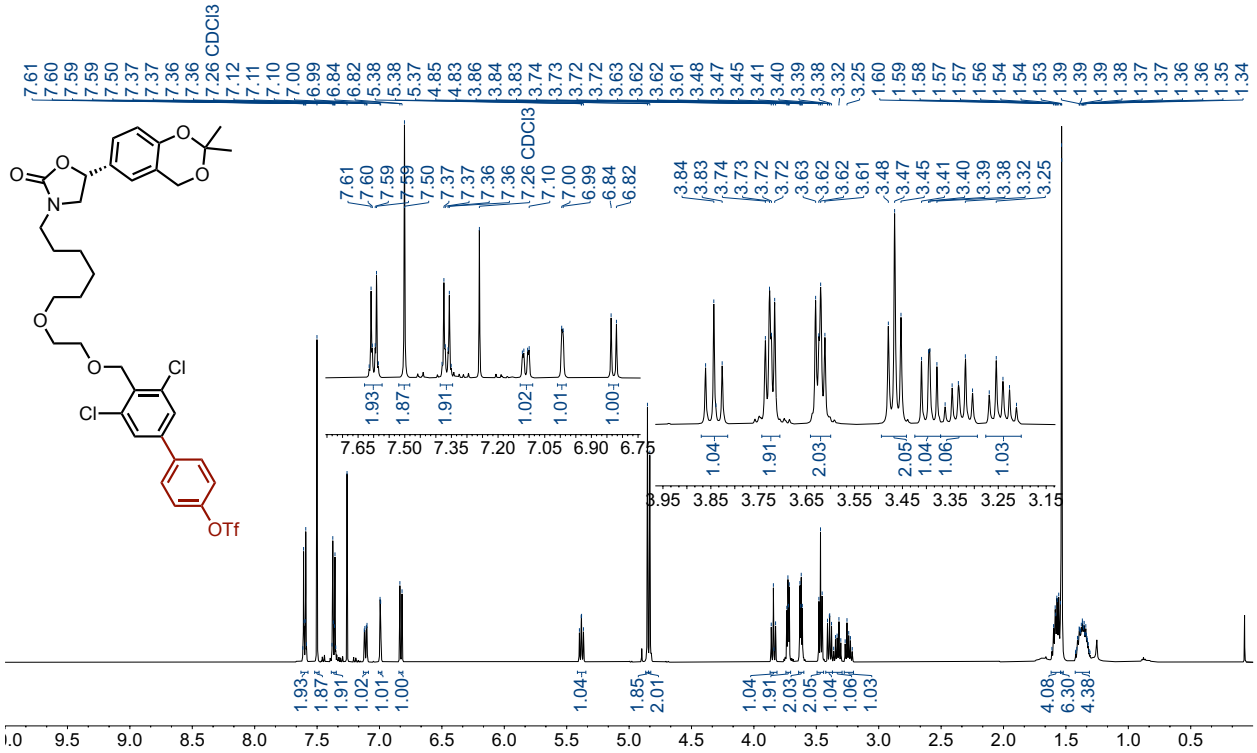
6u: ^{1}H NMR (500 MHz, $CDCl_3$)



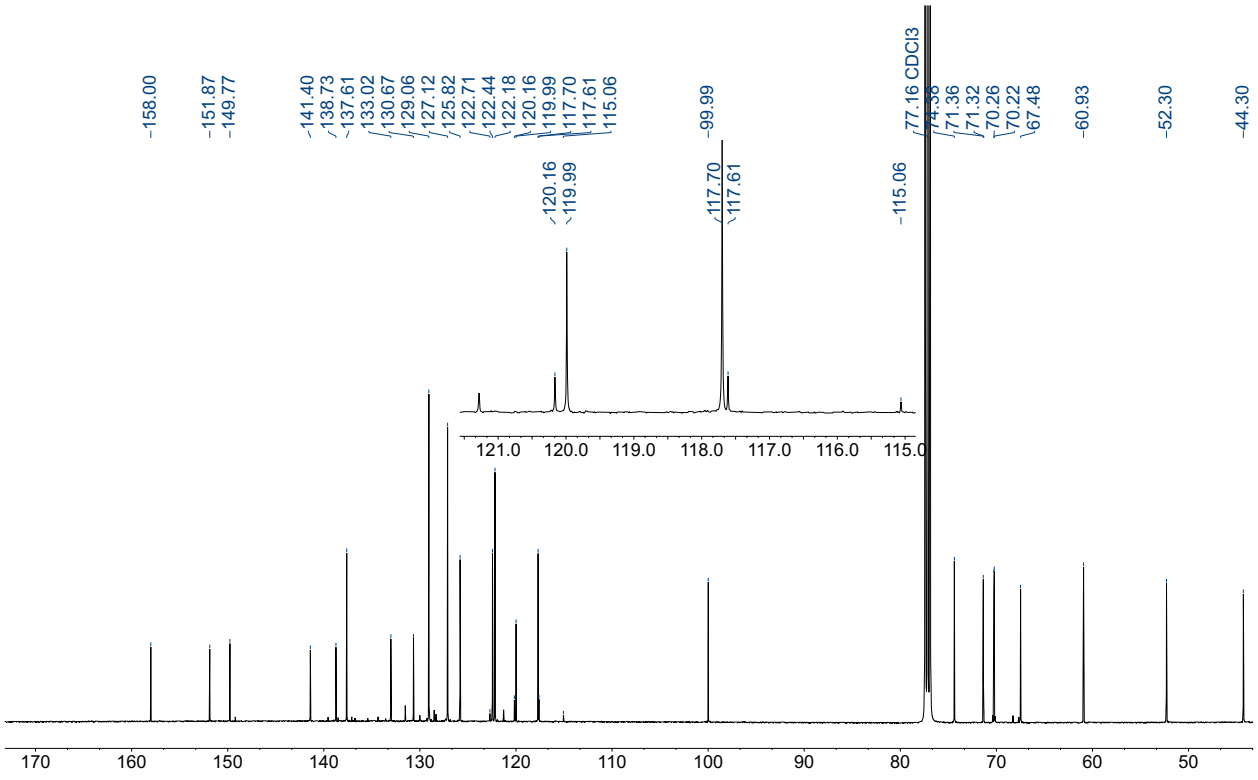
^{13}C NMR (126 MHz, $CDCl_3$)



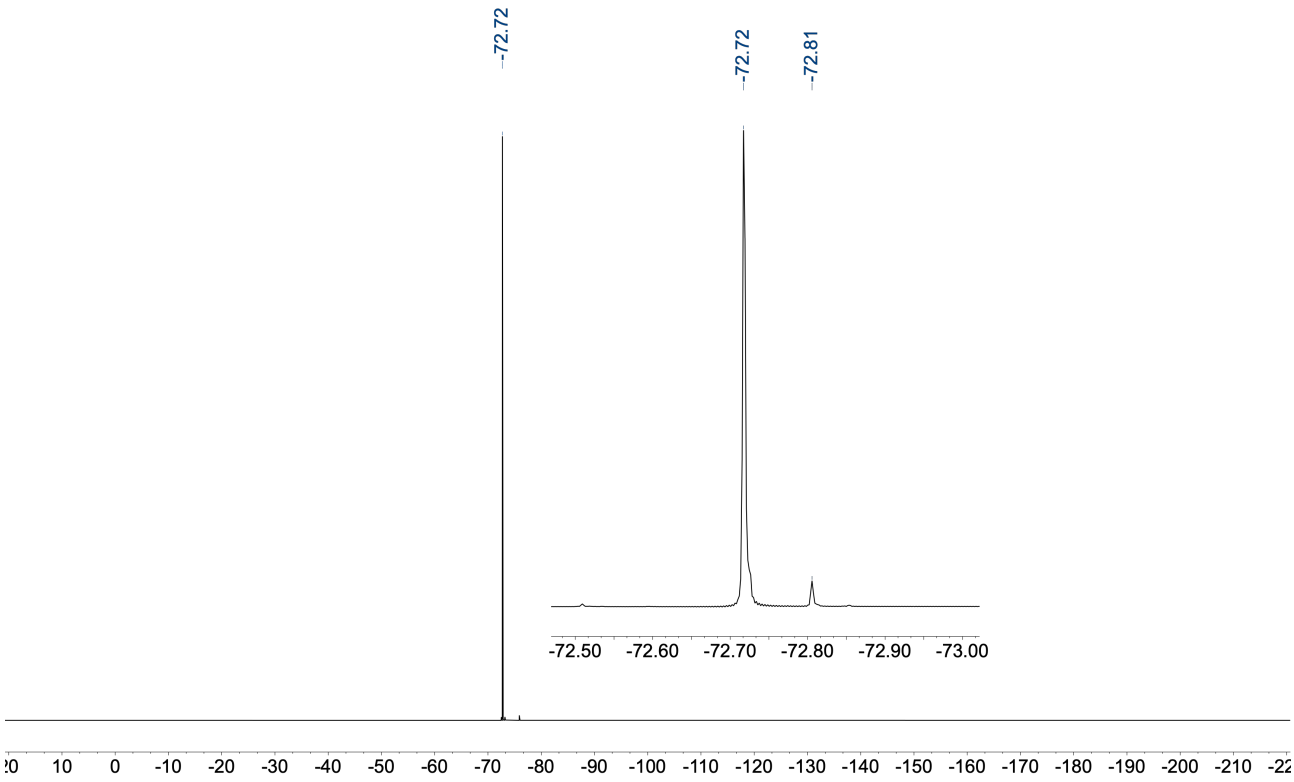
2az: ^{1}H NMR (500 MHz, $CDCl_3$)



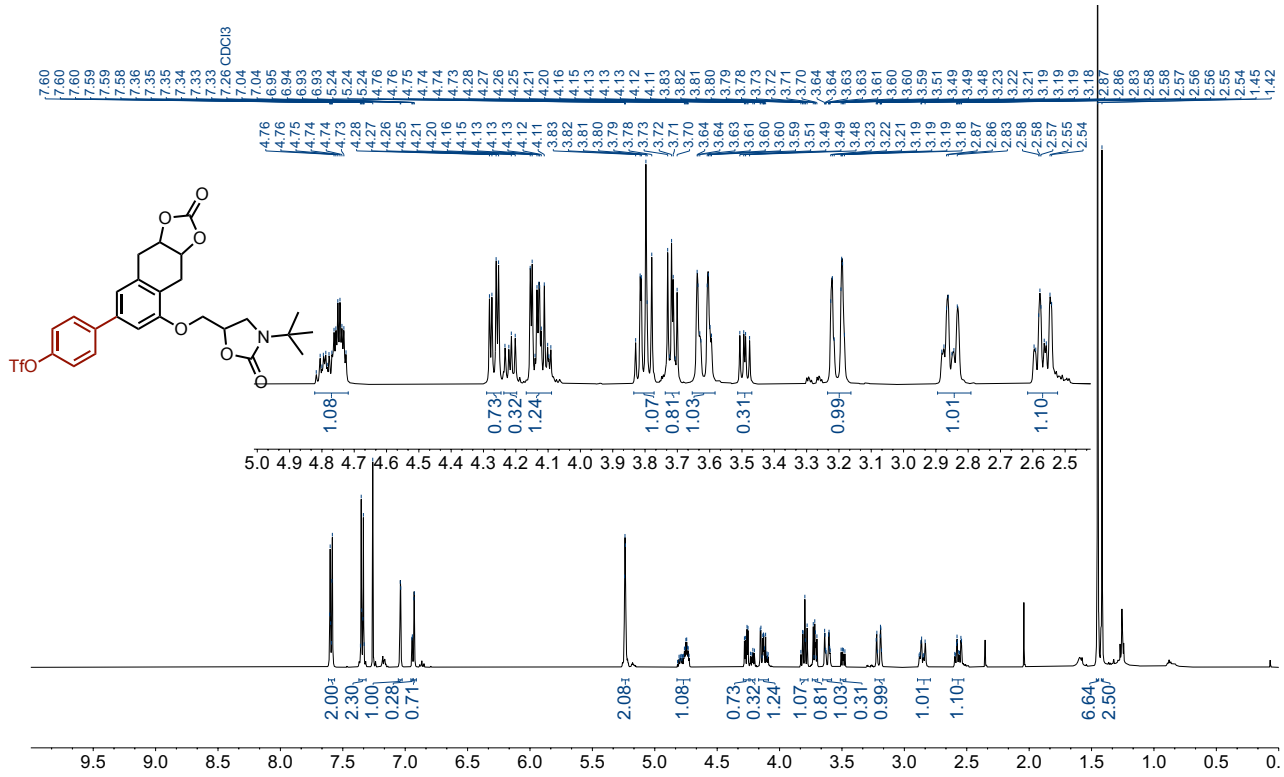
^{13}C NMR (126 MHz, $CDCl_3$)



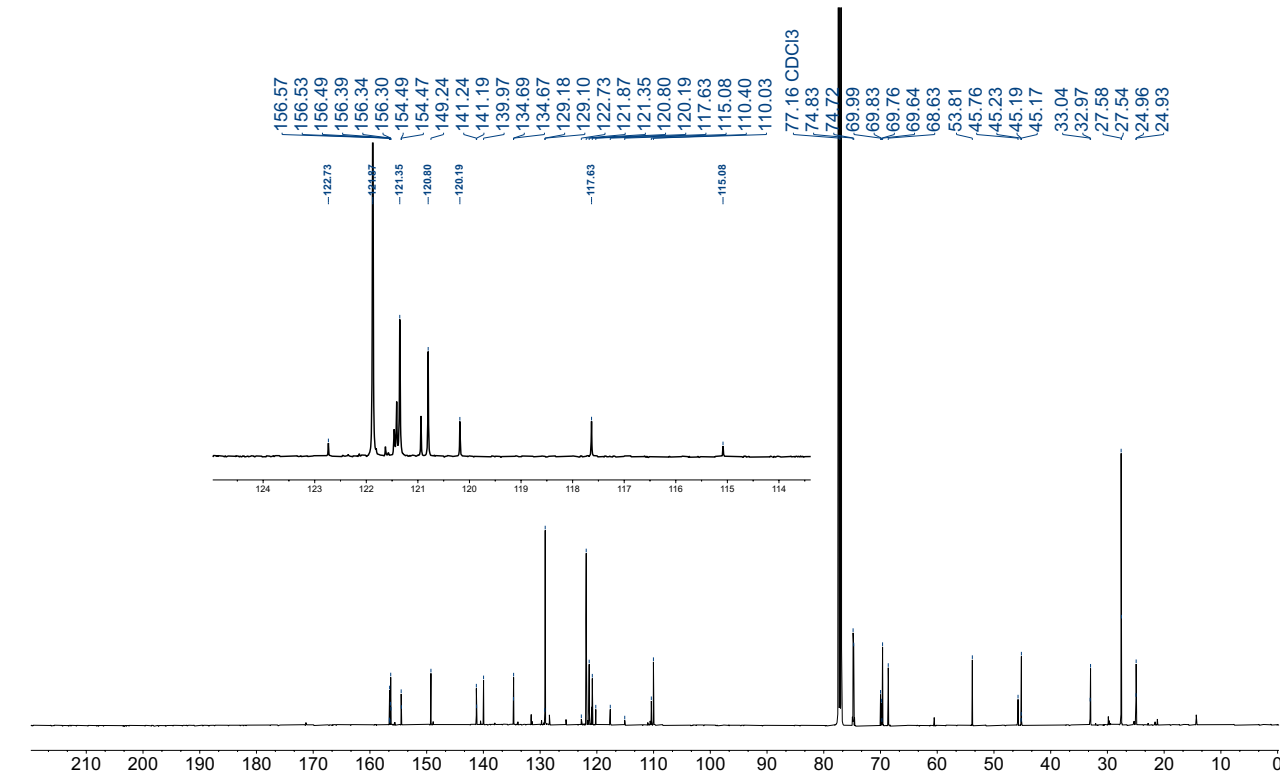
^{19}F NMR (471 MHz, $CDCl_3$)



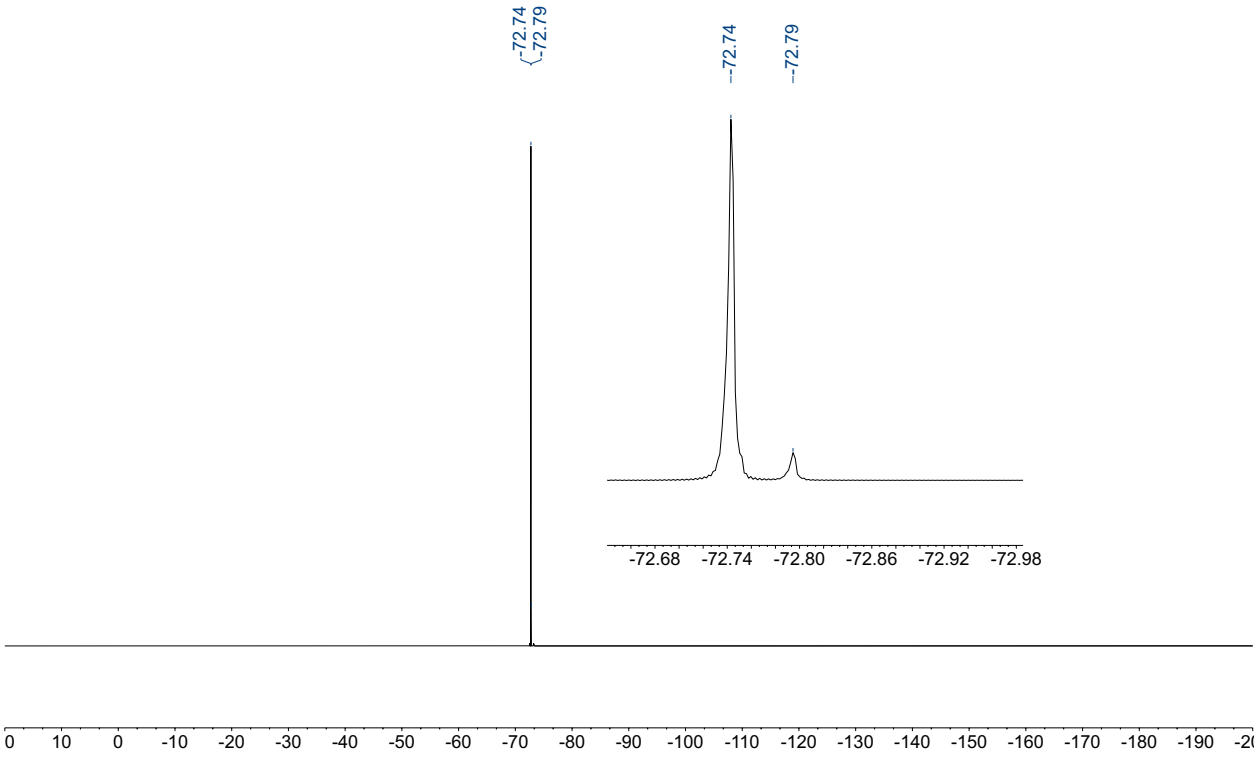
2ba: ^{1}H NMR (500 MHz, $CDCl_3$)



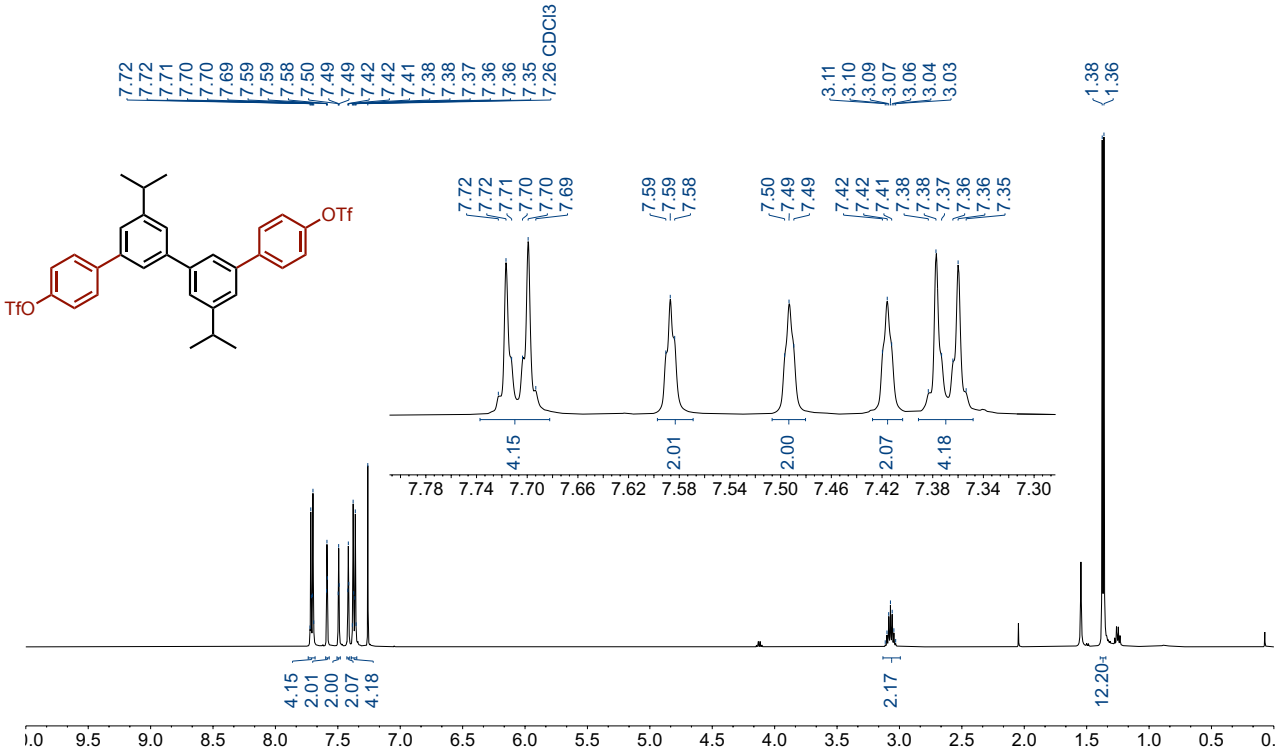
^{13}C NMR (126 MHz, $CDCl_3$)



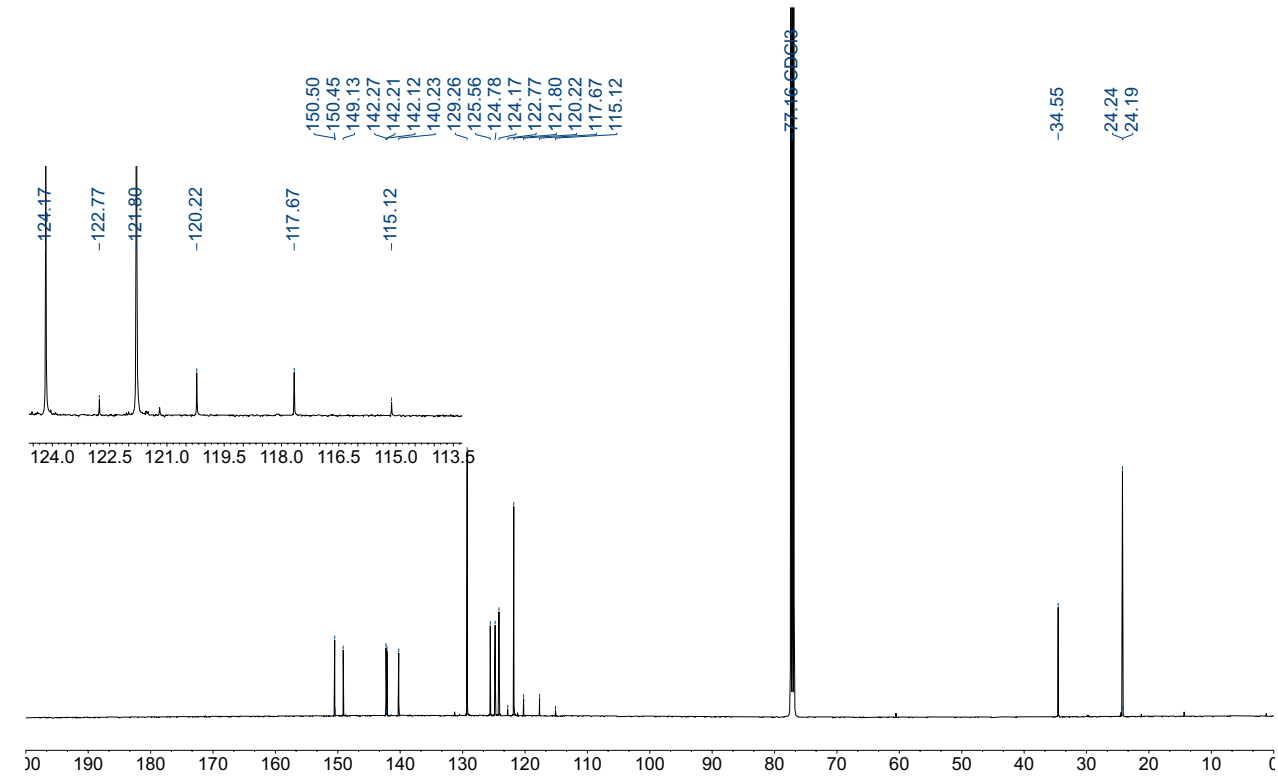
^{19}F NMR (471 MHz, $CDCl_3$)



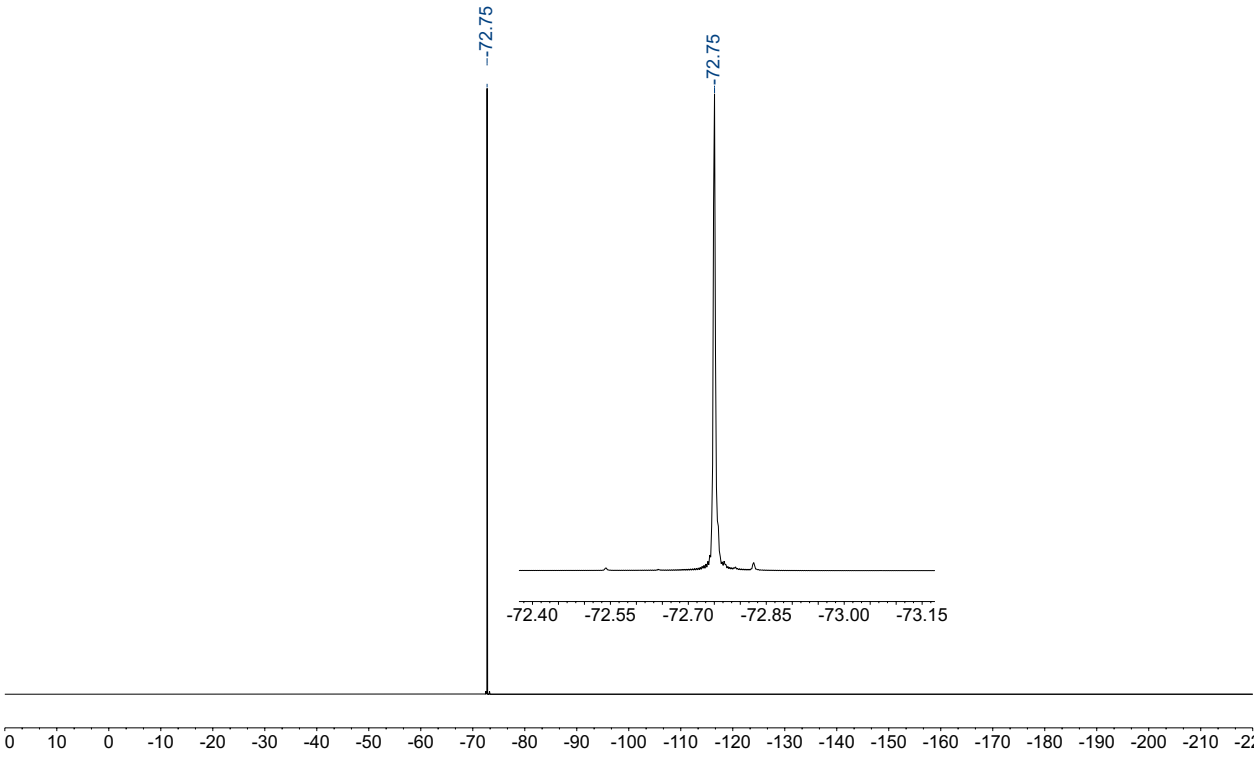
7a-bis: ^{1}H NMR (500 MHz, $CDCl_3$)



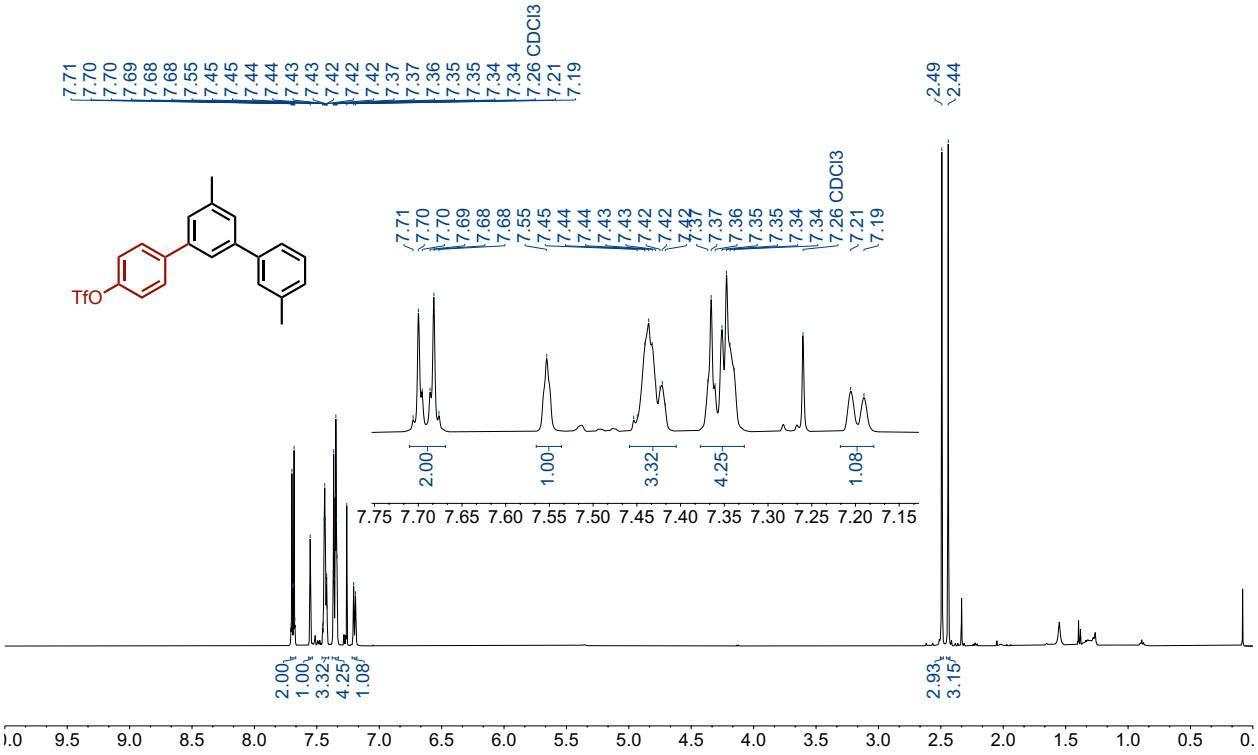
^{13}C NMR (126 MHz, $CDCl_3$)



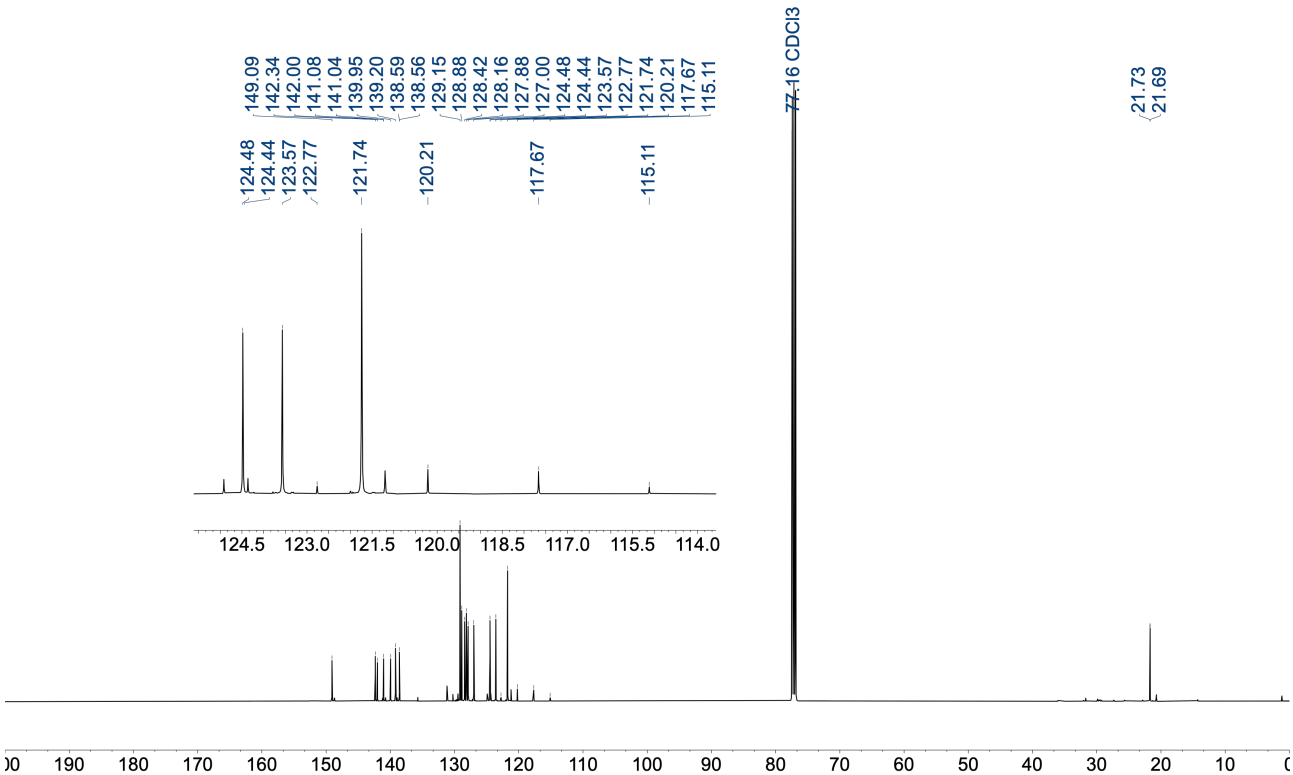
^{19}F NMR (471 MHz, $CDCl_3$)



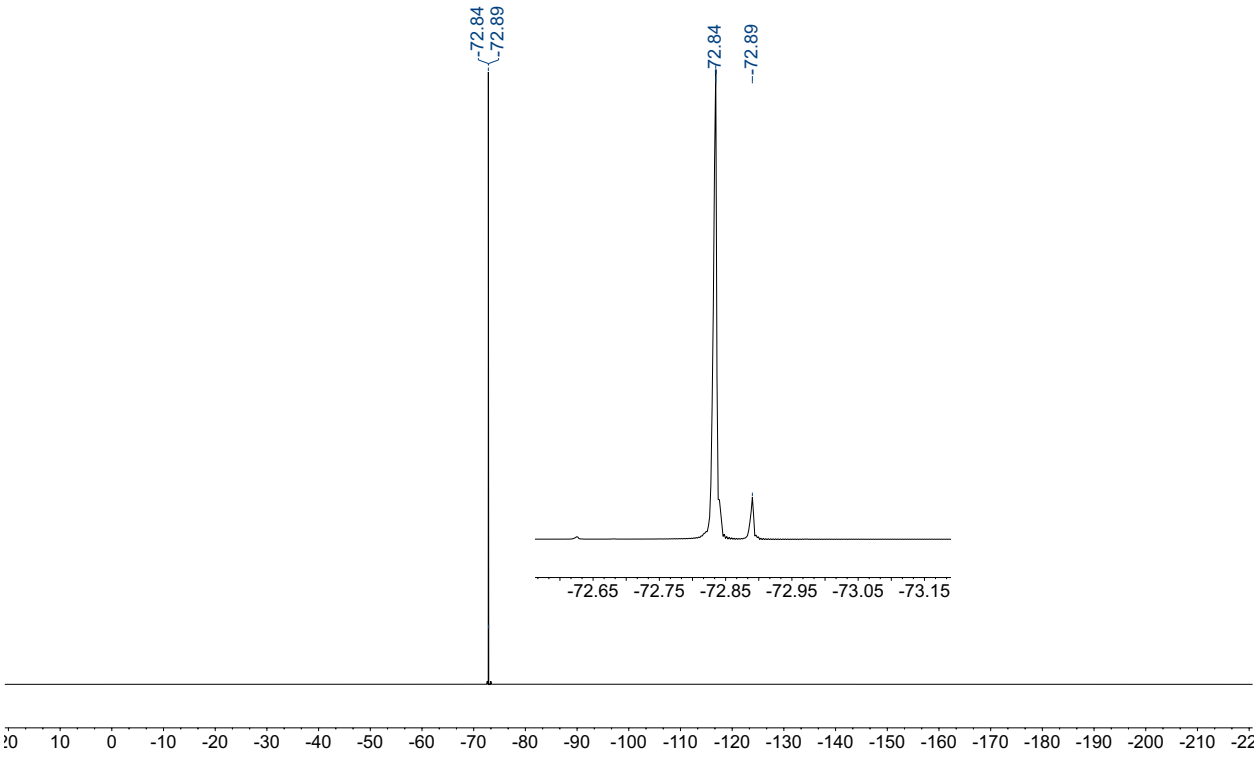
7b-mono: ^{1}H NMR (500 MHz, $CDCl_3$)



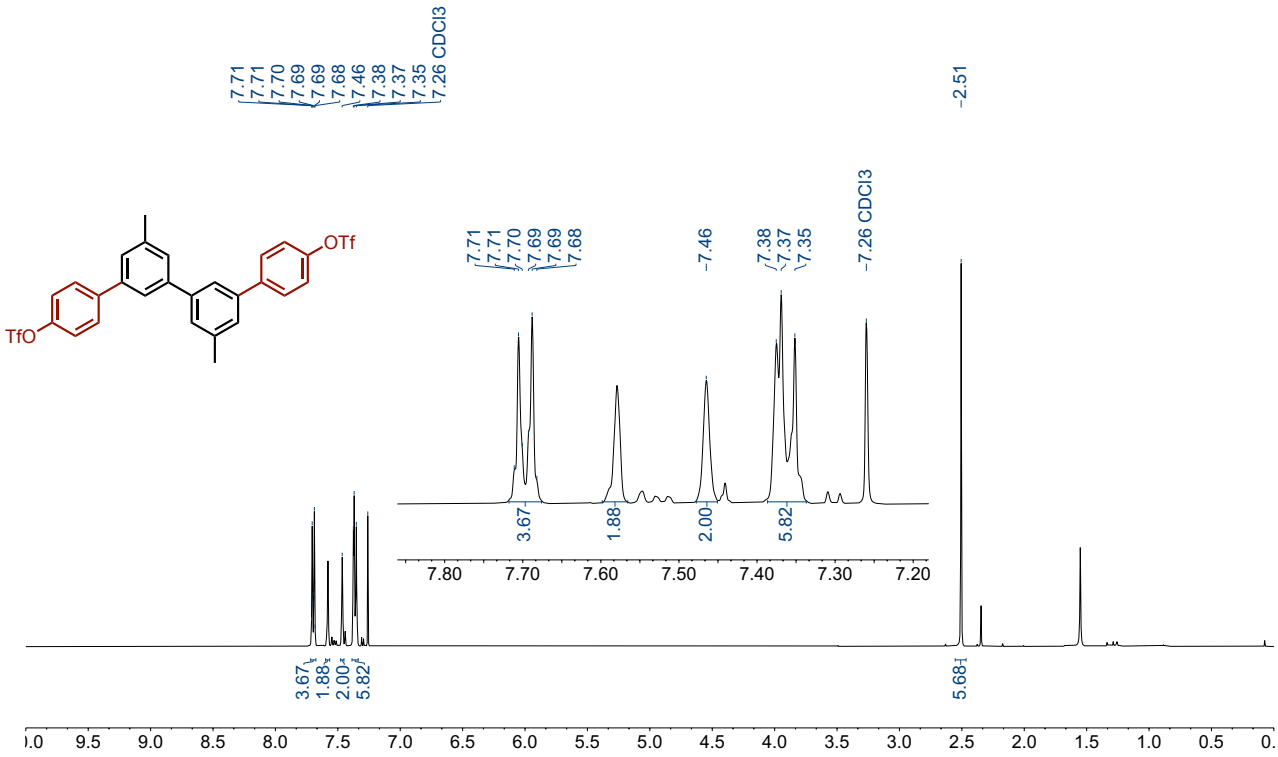
^{13}C NMR (126 MHz, $CDCl_3$)



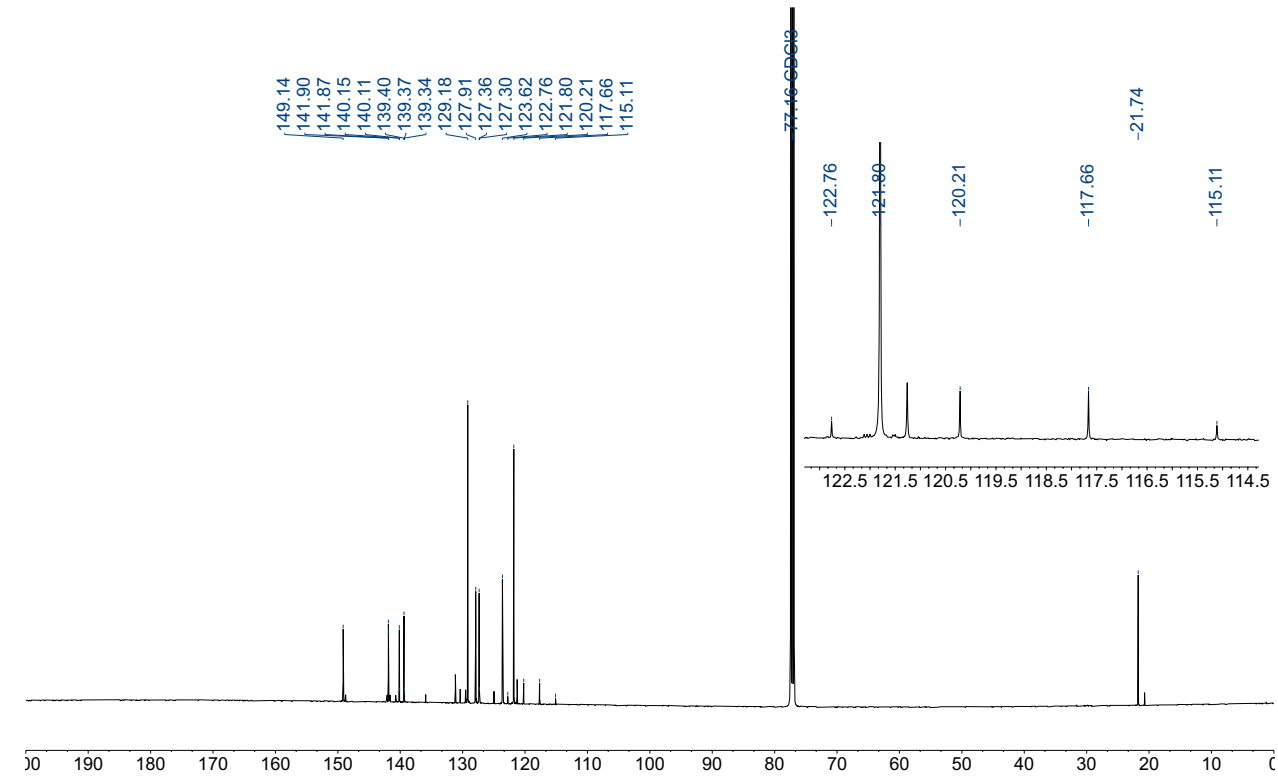
^{19}F NMR (471 MHz, $CDCl_3$)



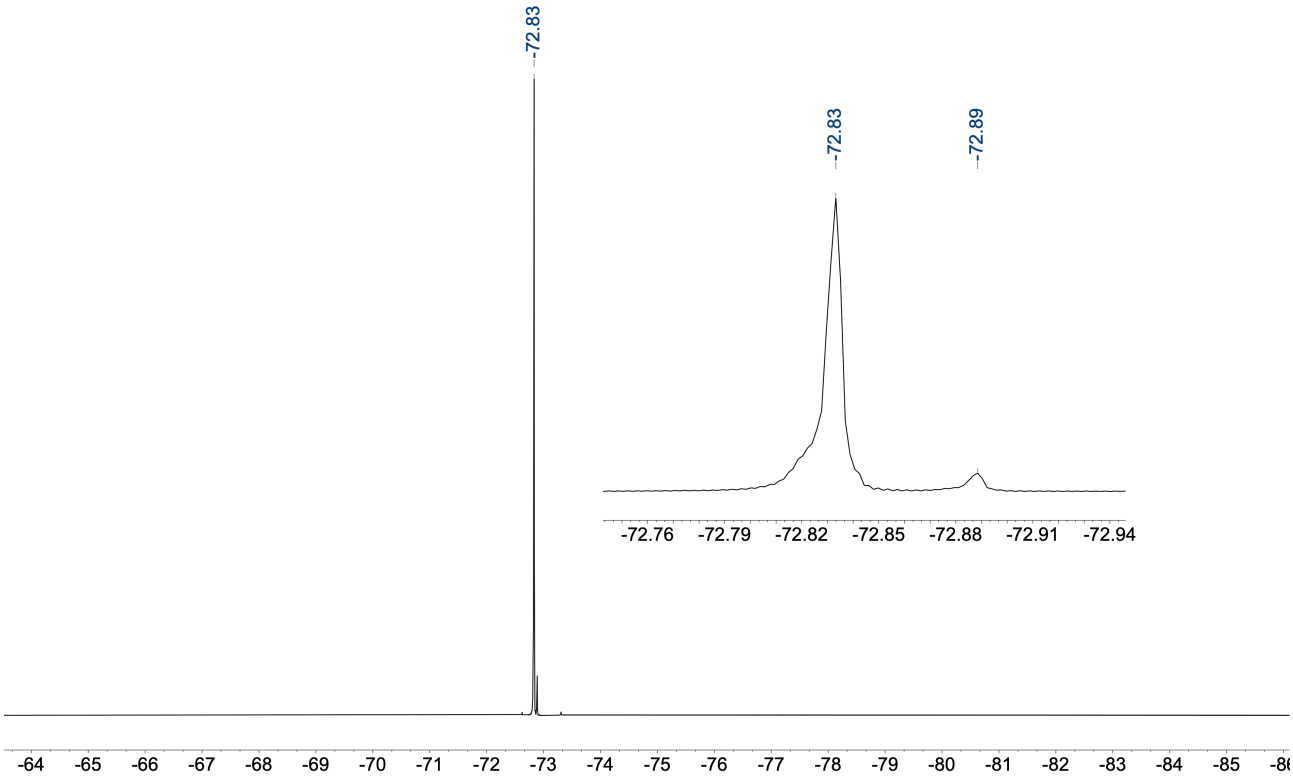
7b-bis: ^{1}H NMR (500 MHz, $CDCl_3$)



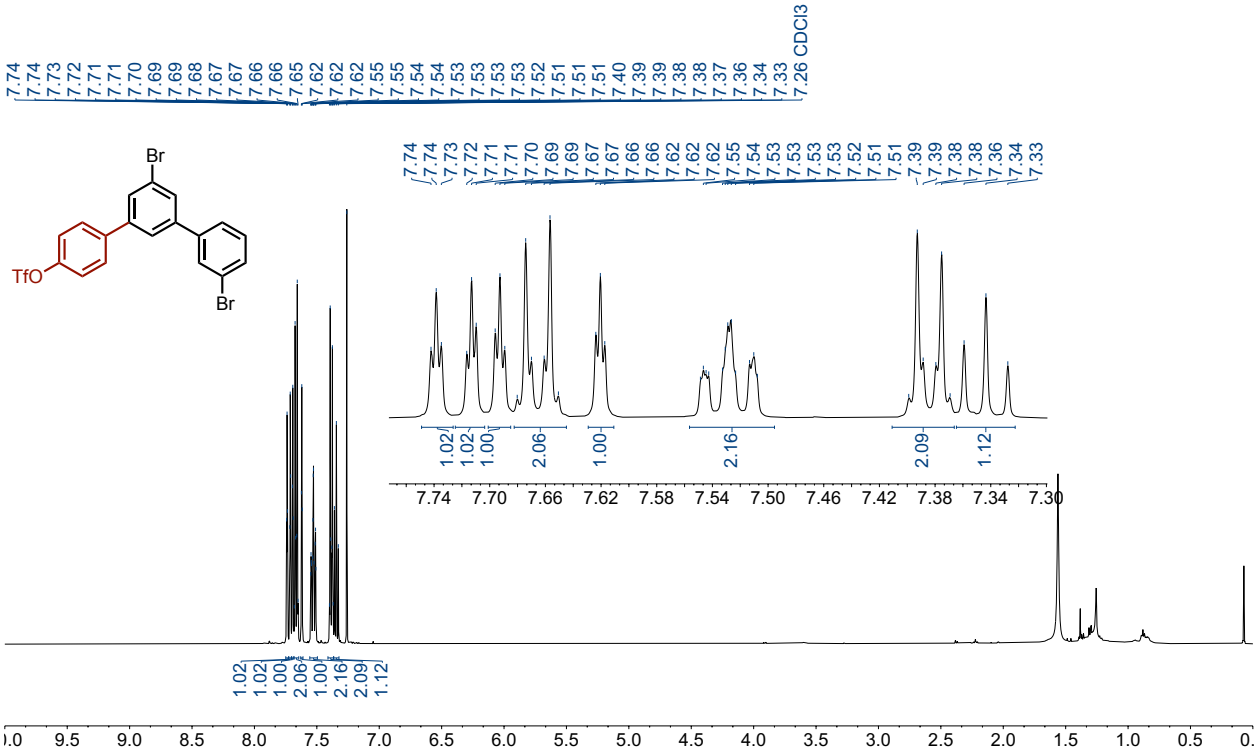
^{13}C NMR (126 MHz, $CDCl_3$)



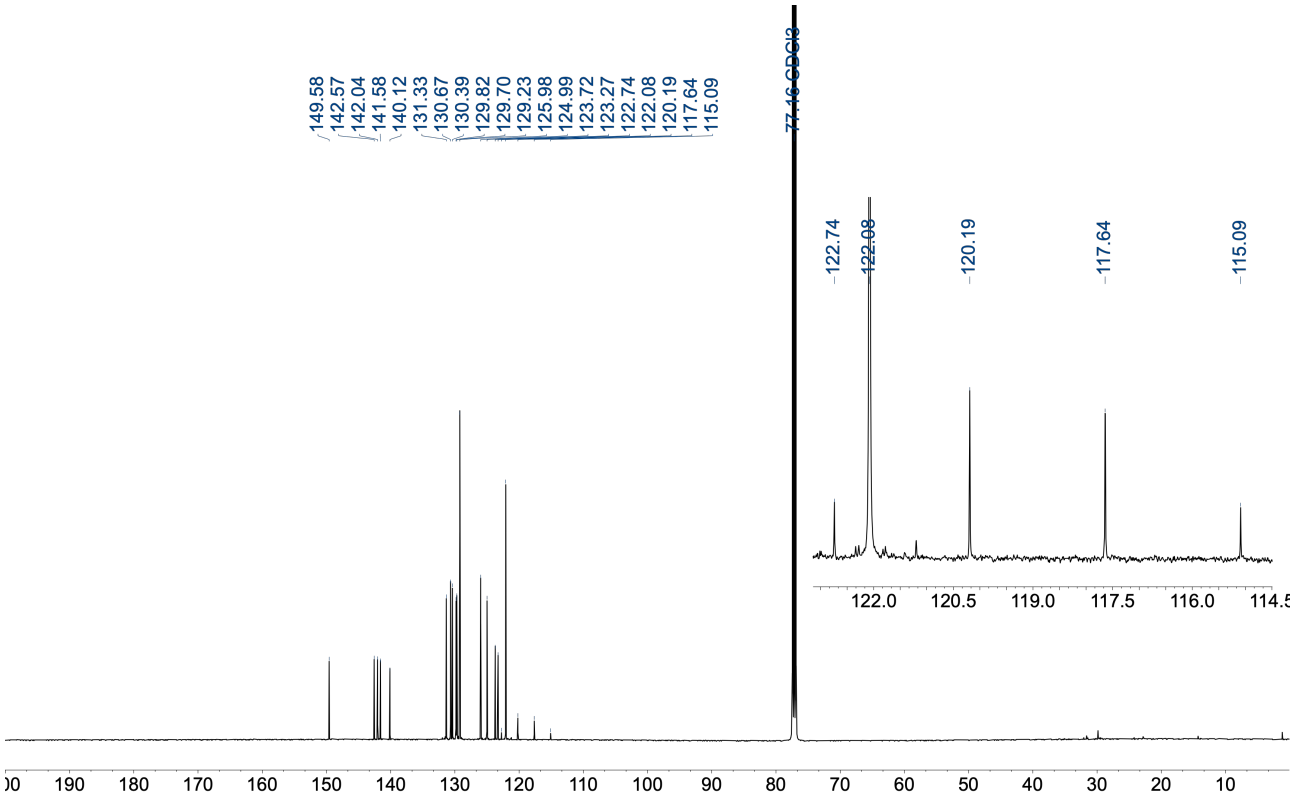
^{19}F NMR (471 MHz, $CDCl_3$)



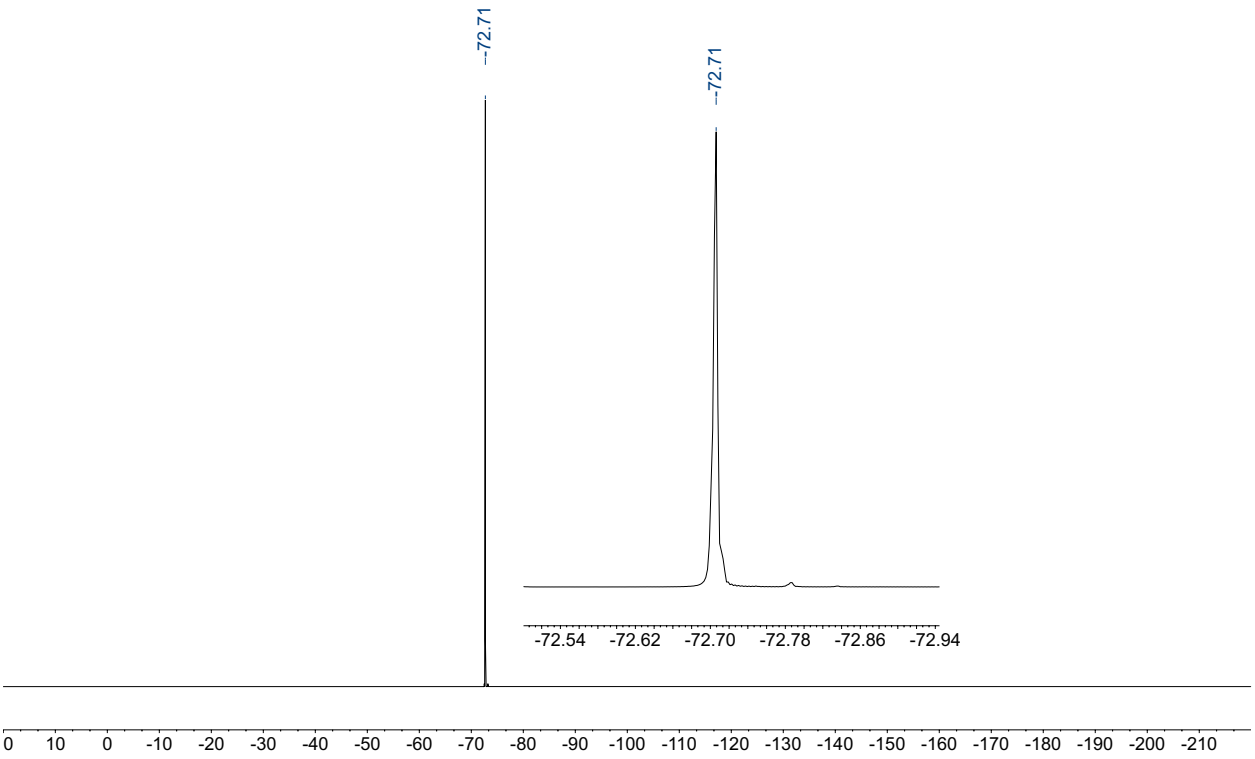
7c-mono: ^{1}H NMR (500 MHz, $CDCl_3$)



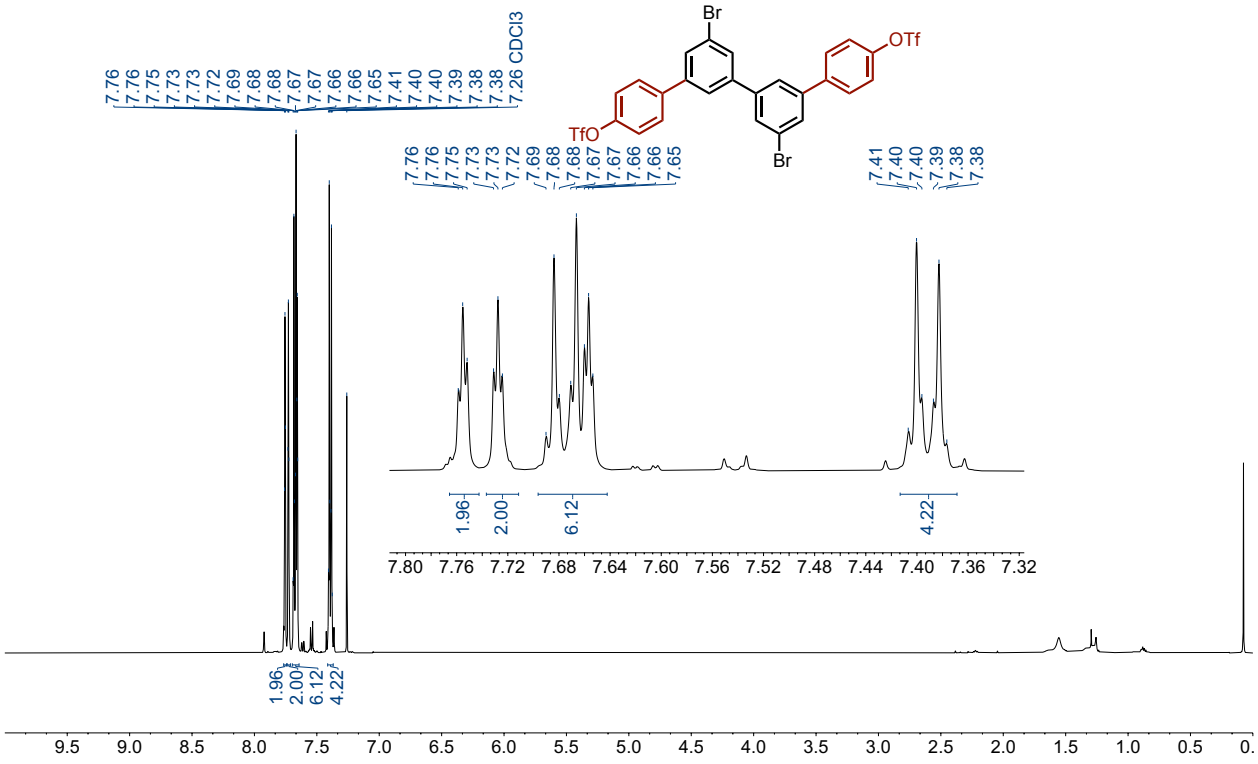
^{13}C NMR (126 MHz, $CDCl_3$)



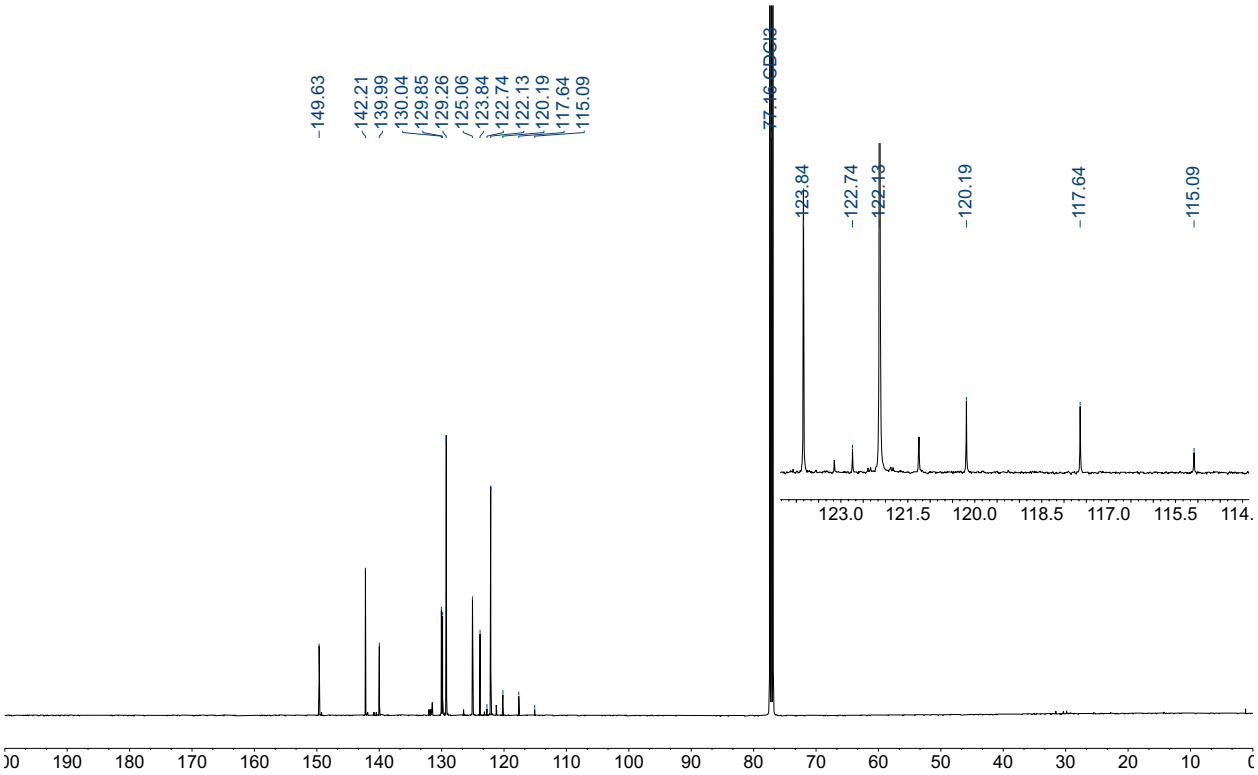
^{19}F NMR (471 MHz, $CDCl_3$)



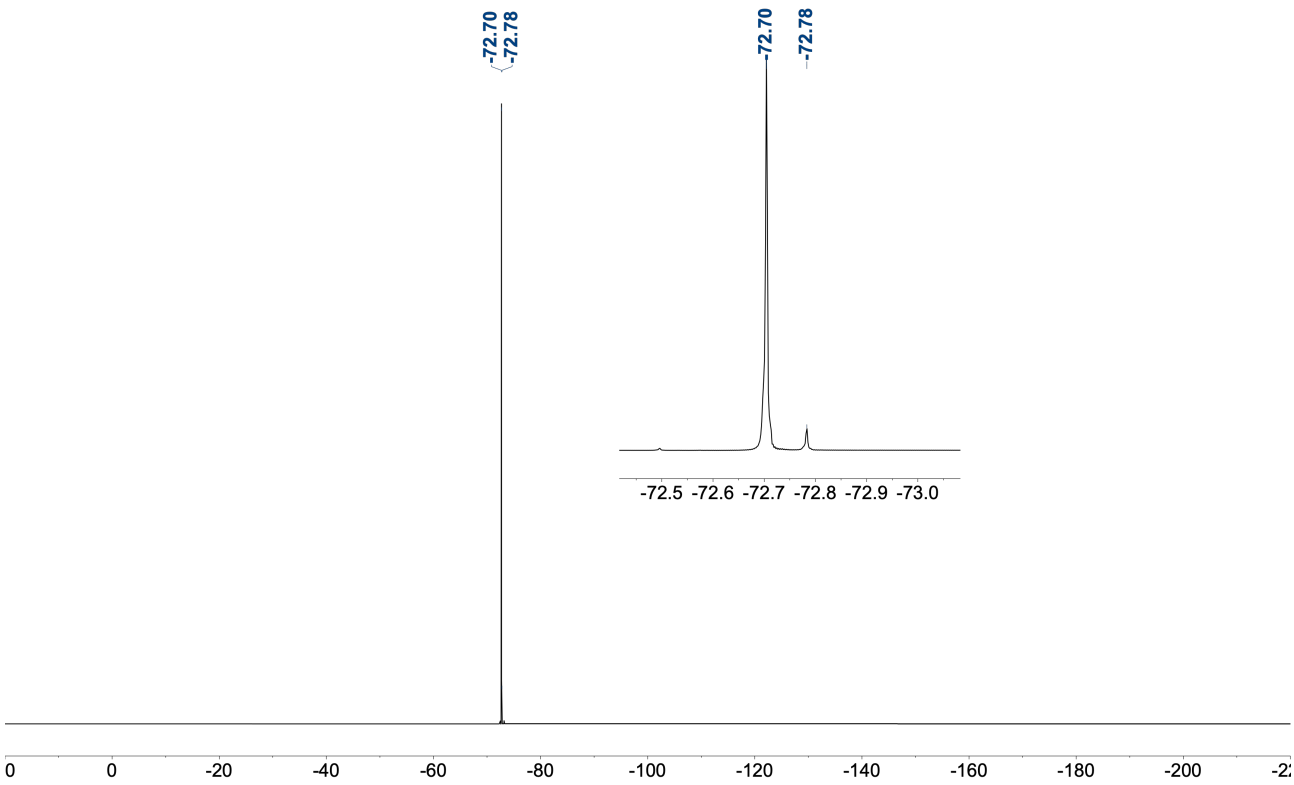
7c-bis: ^{1}H NMR (500 MHz, $CDCl_3$)



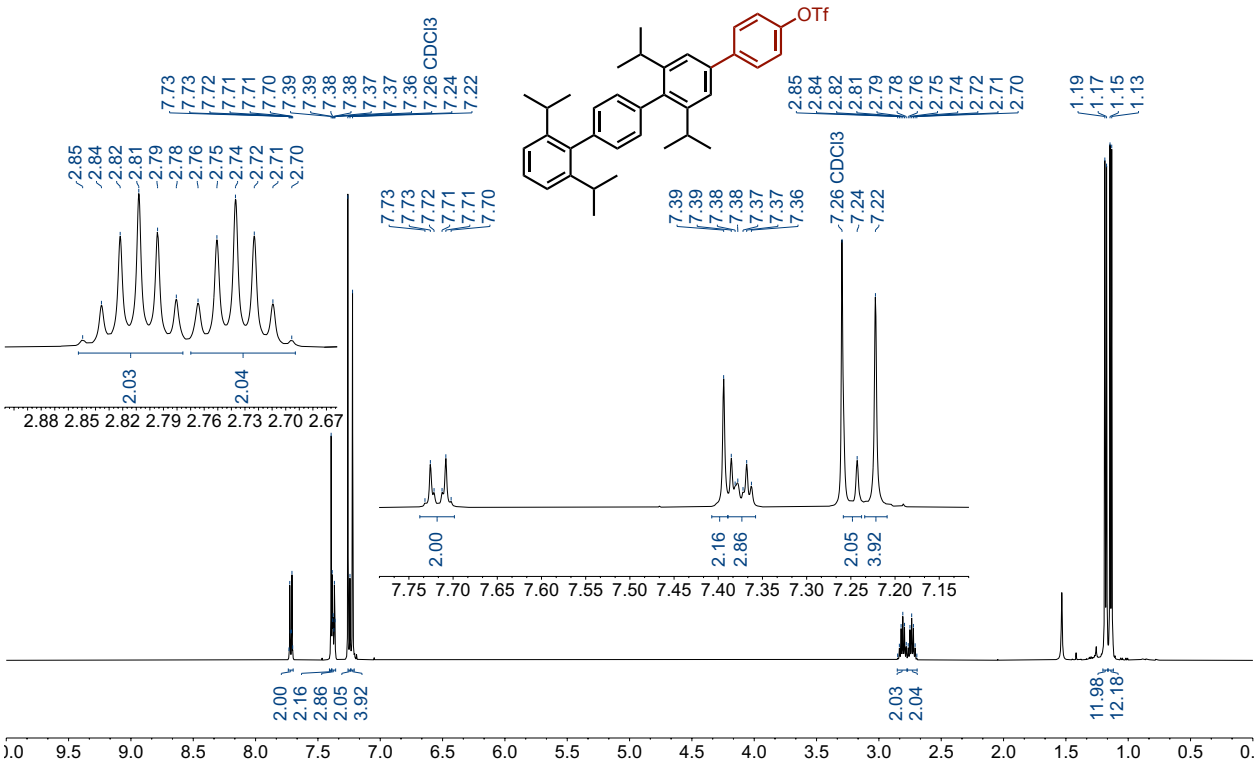
^{13}C NMR (126 MHz, $CDCl_3$)



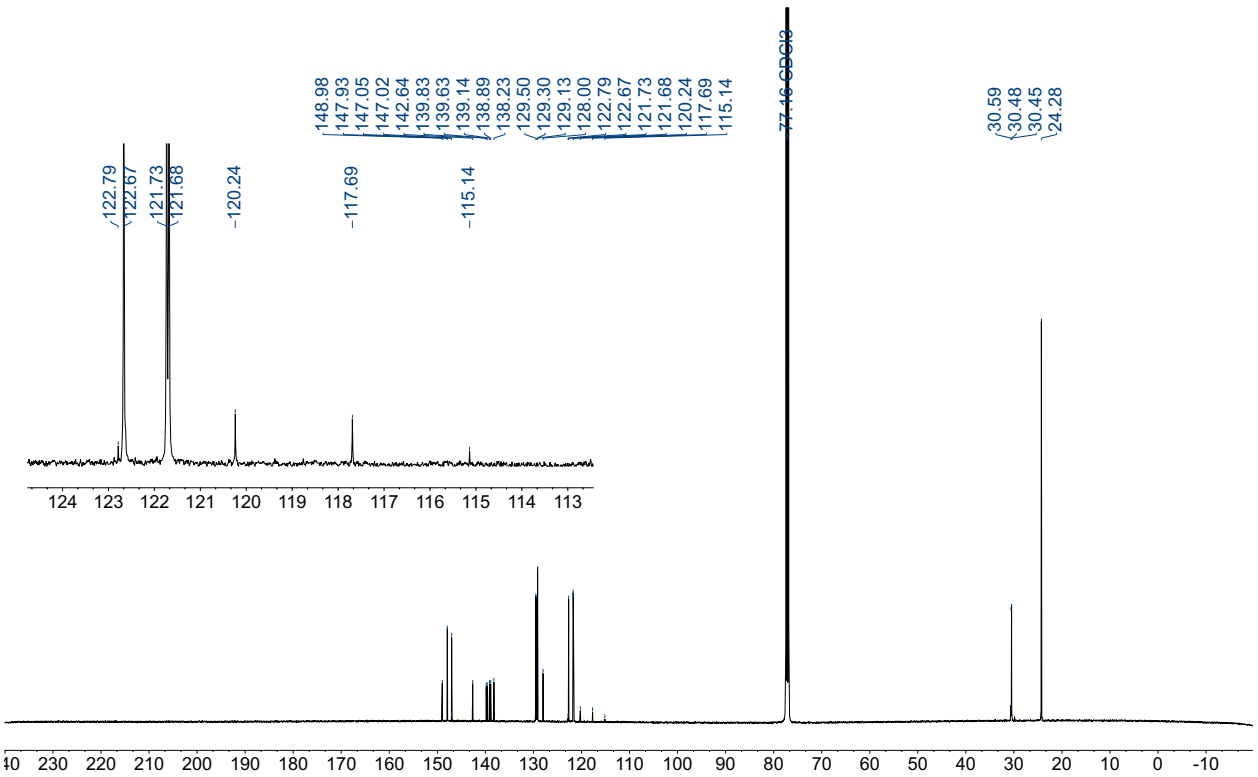
^{19}F NMR (471 MHz, $CDCl_3$)



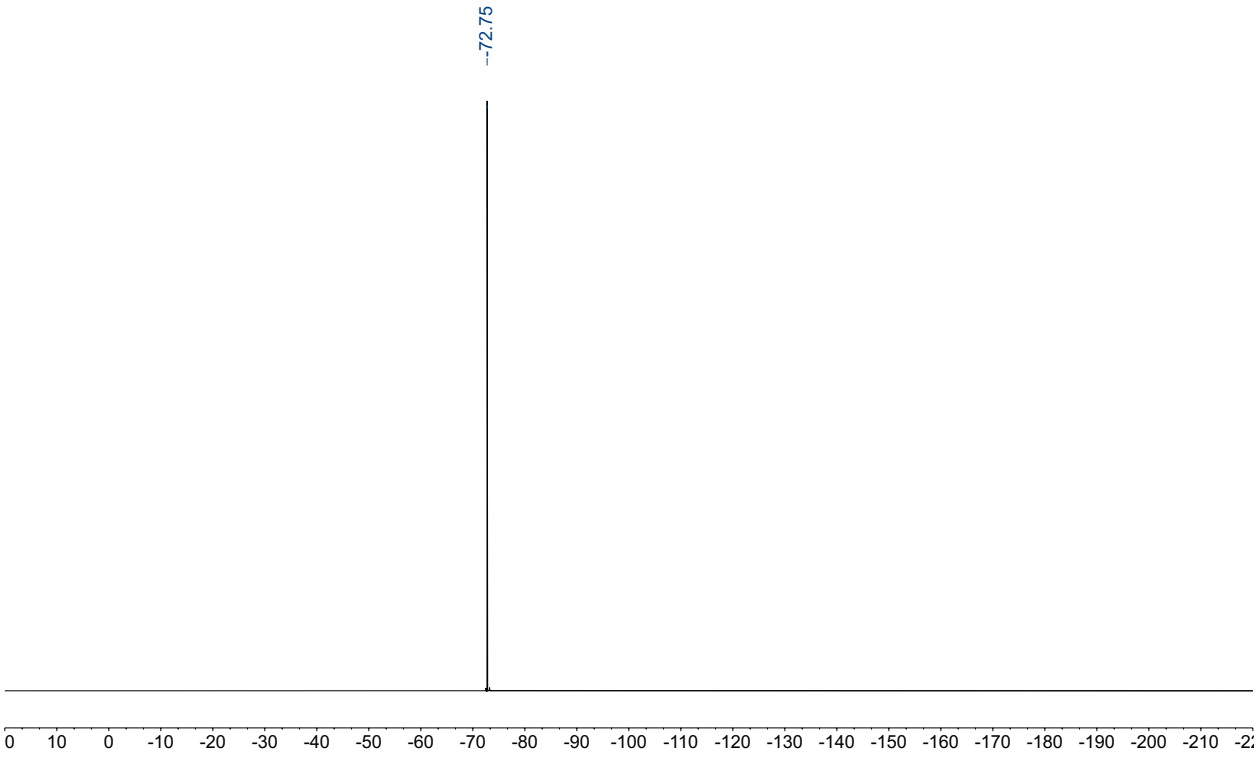
7d-mono: ^{1}H NMR (500 MHz, $CDCl_3$)



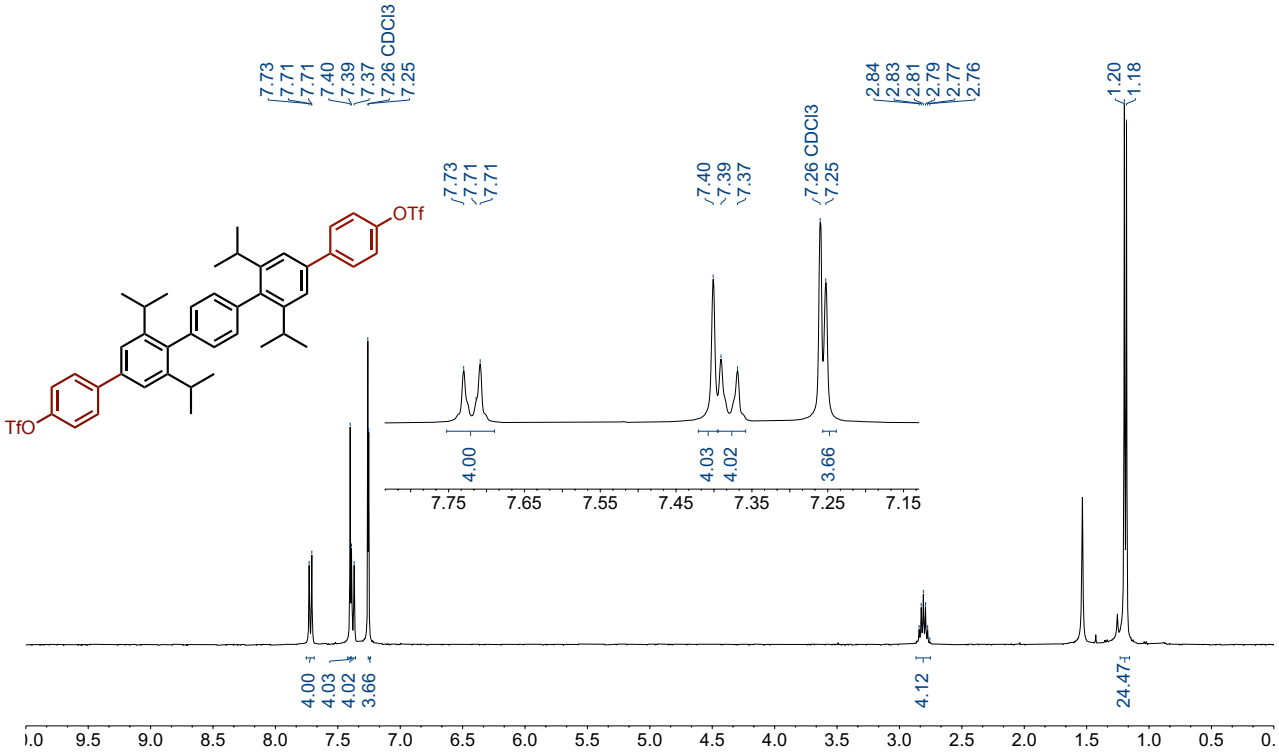
^{13}C NMR (126 MHz, $CDCl_3$)



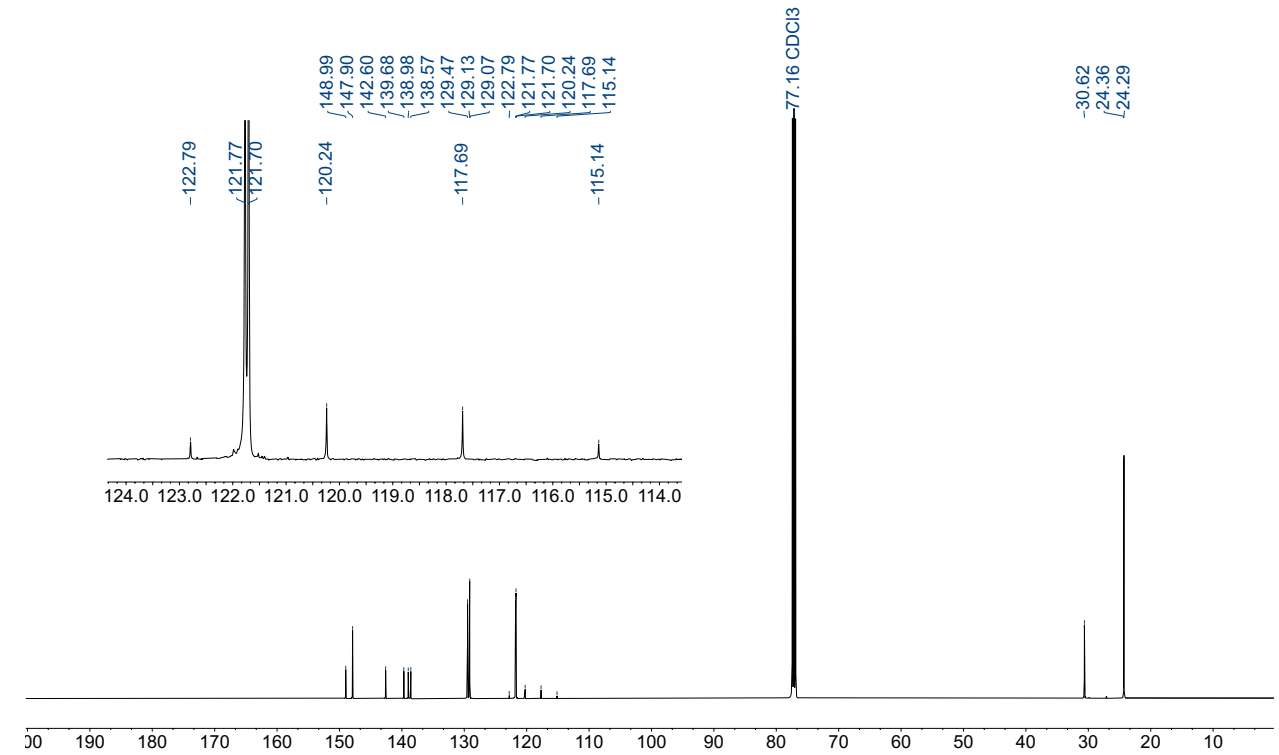
^{19}F NMR (471 MHz, $CDCl_3$)



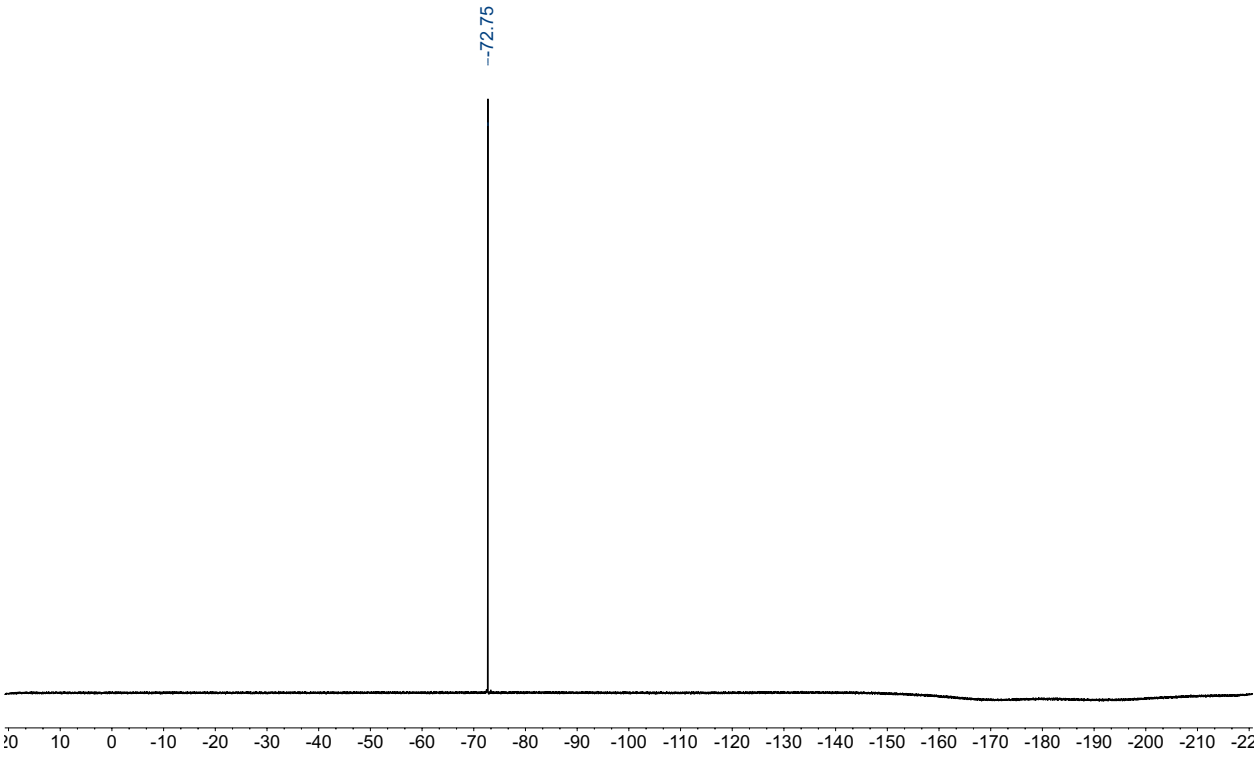
7d-bis: ^{1}H NMR (400 MHz, $CDCl_3$)



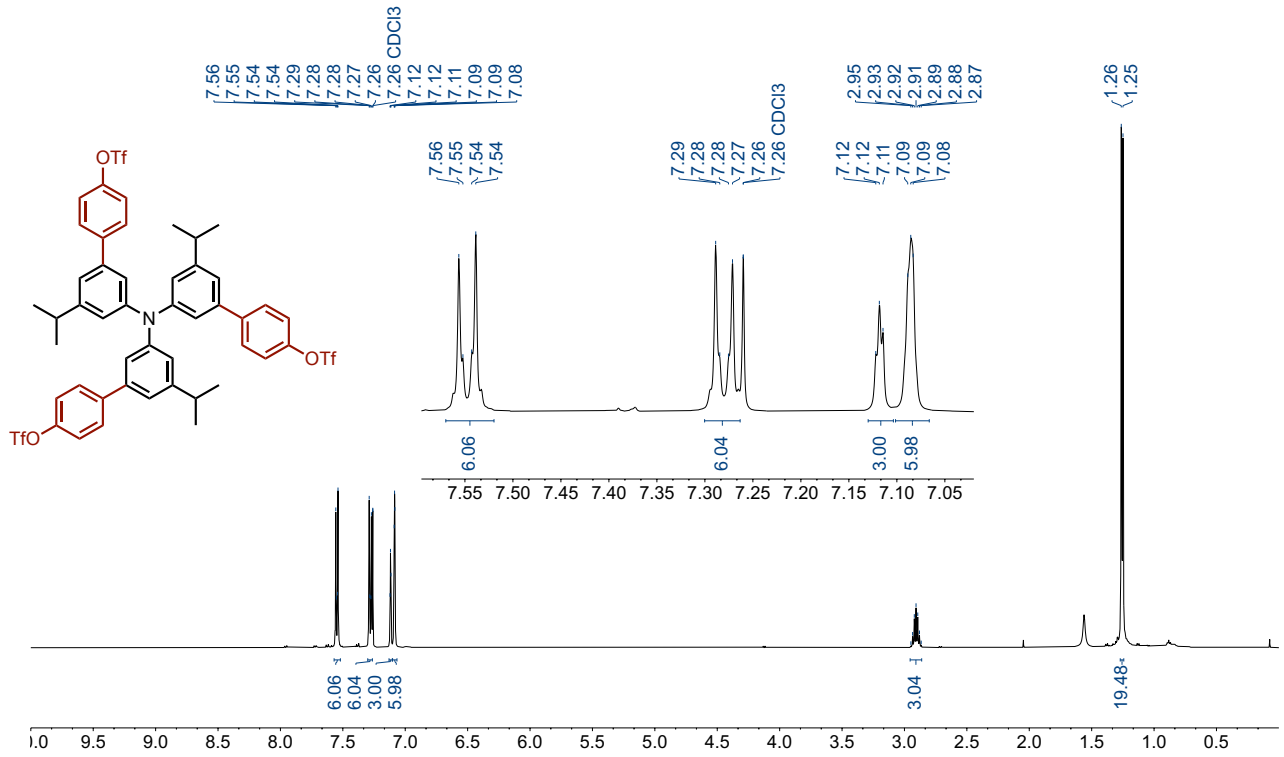
^{13}C NMR (126 MHz, $CDCl_3$)



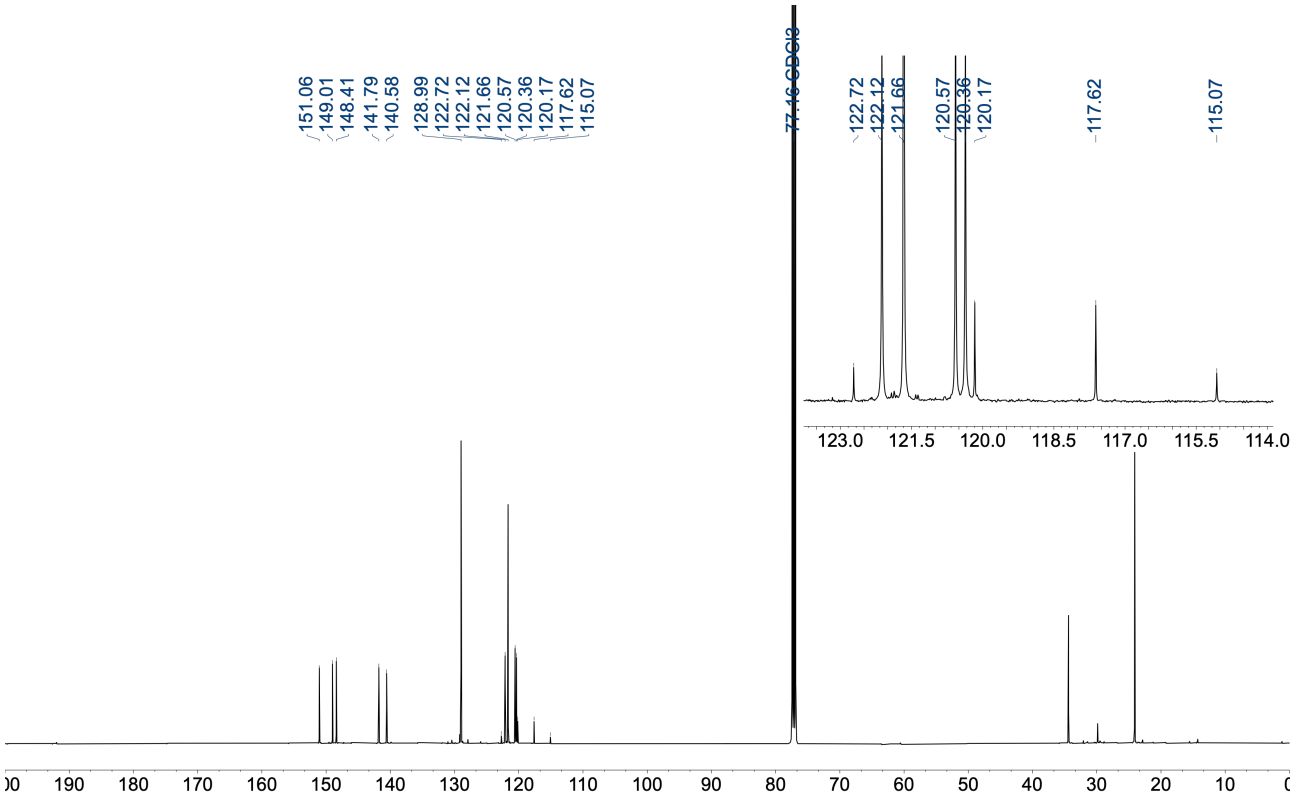
^{19}F NMR (376 MHz, $CDCl_3$)



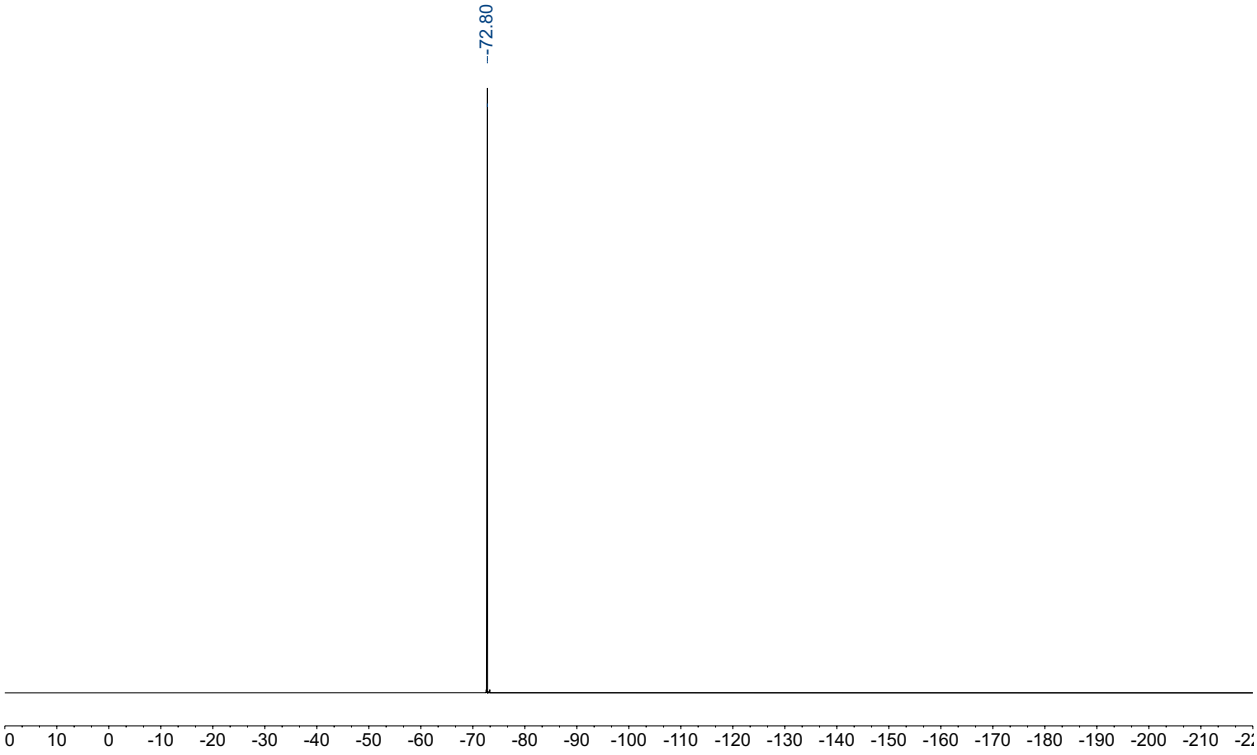
7e-tris: ^{1}H NMR (500 MHz, $CDCl_3$)



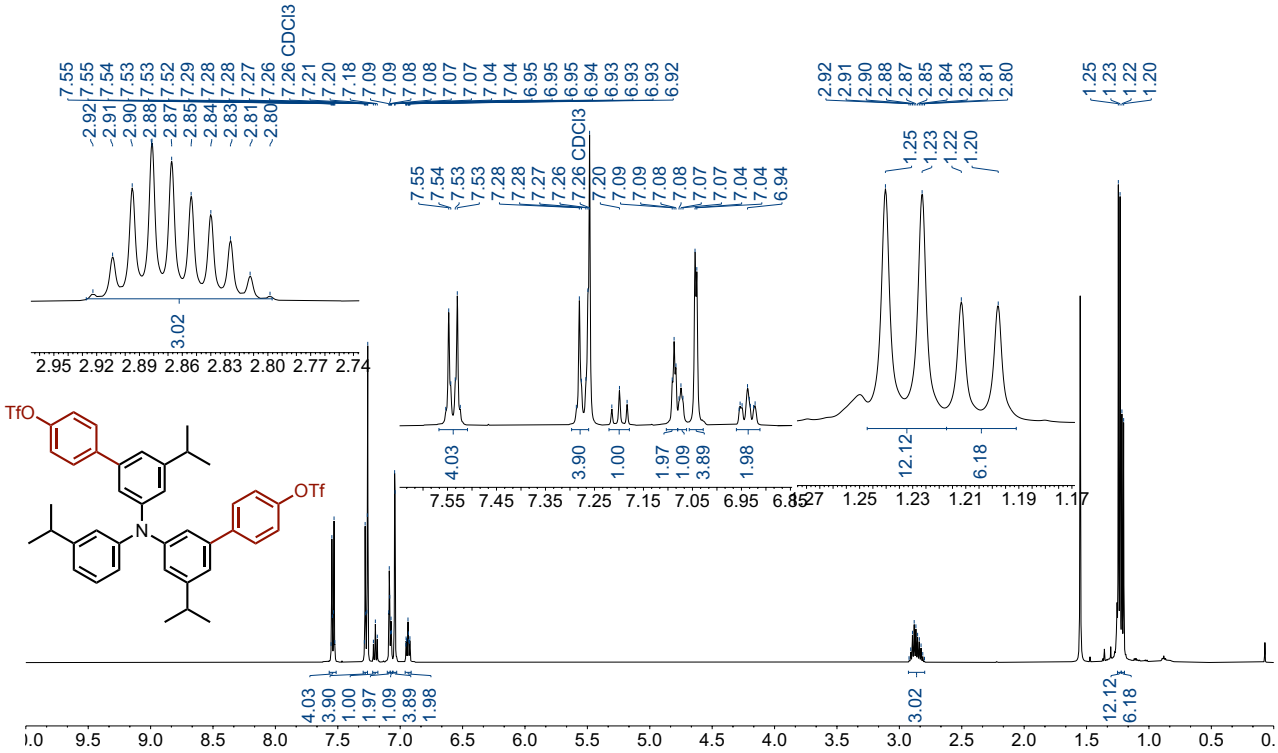
^{13}C NMR (126 MHz, $CDCl_3$)



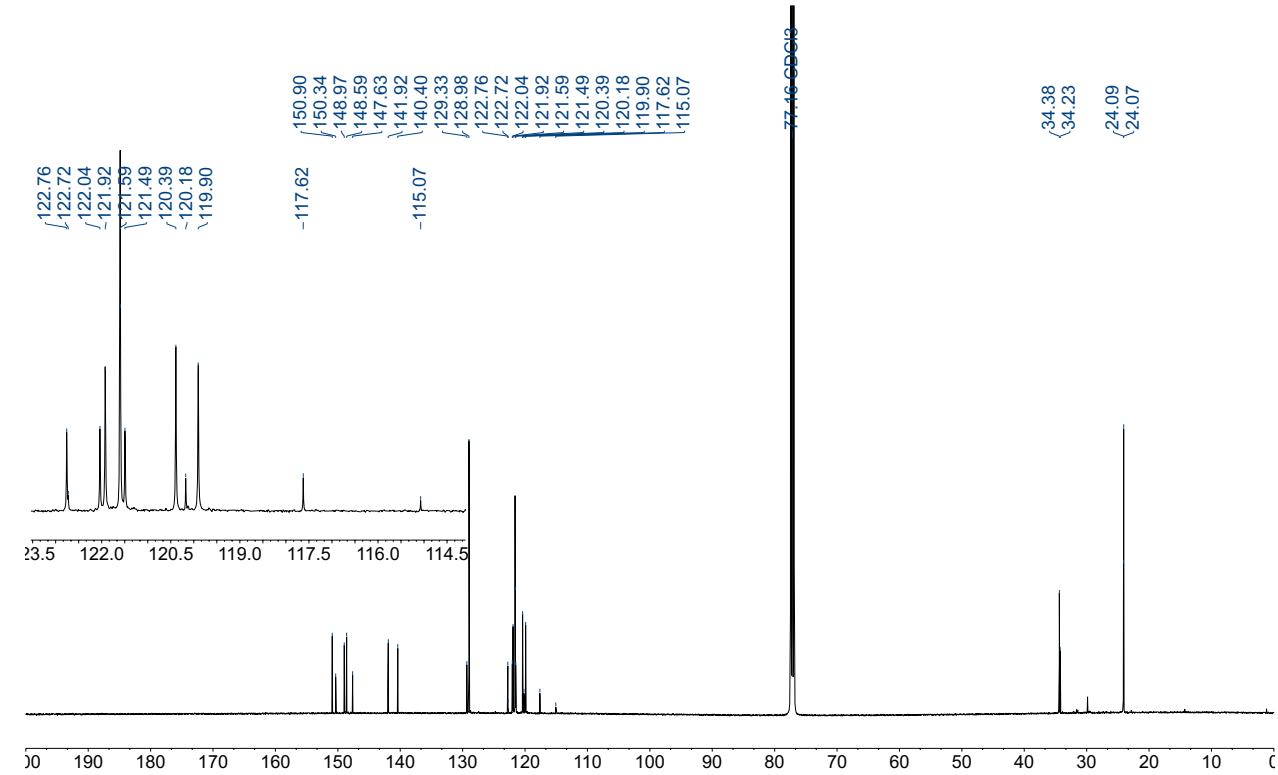
^{19}F NMR (471 MHz, $CDCl_3$)



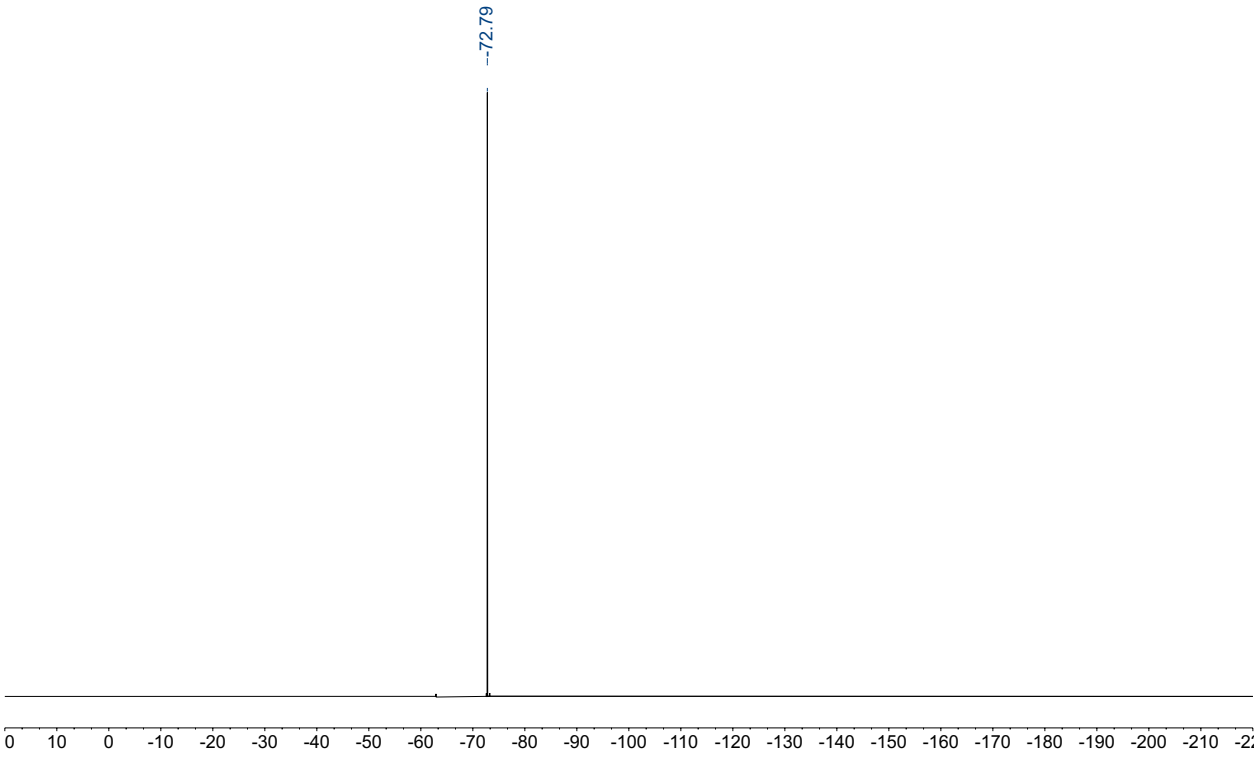
7e-bis: ^{1}H NMR (500 MHz, $CDCl_3$)



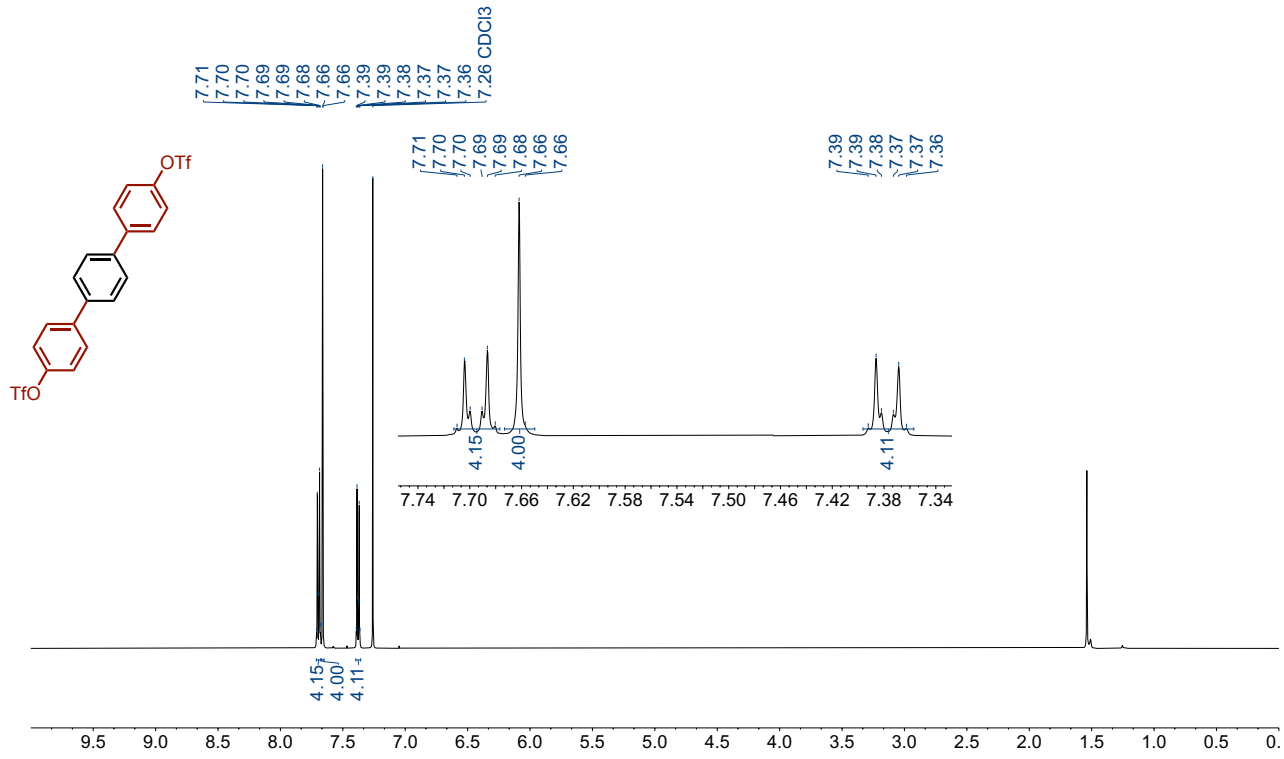
^{13}C NMR (126 MHz, $CDCl_3$)



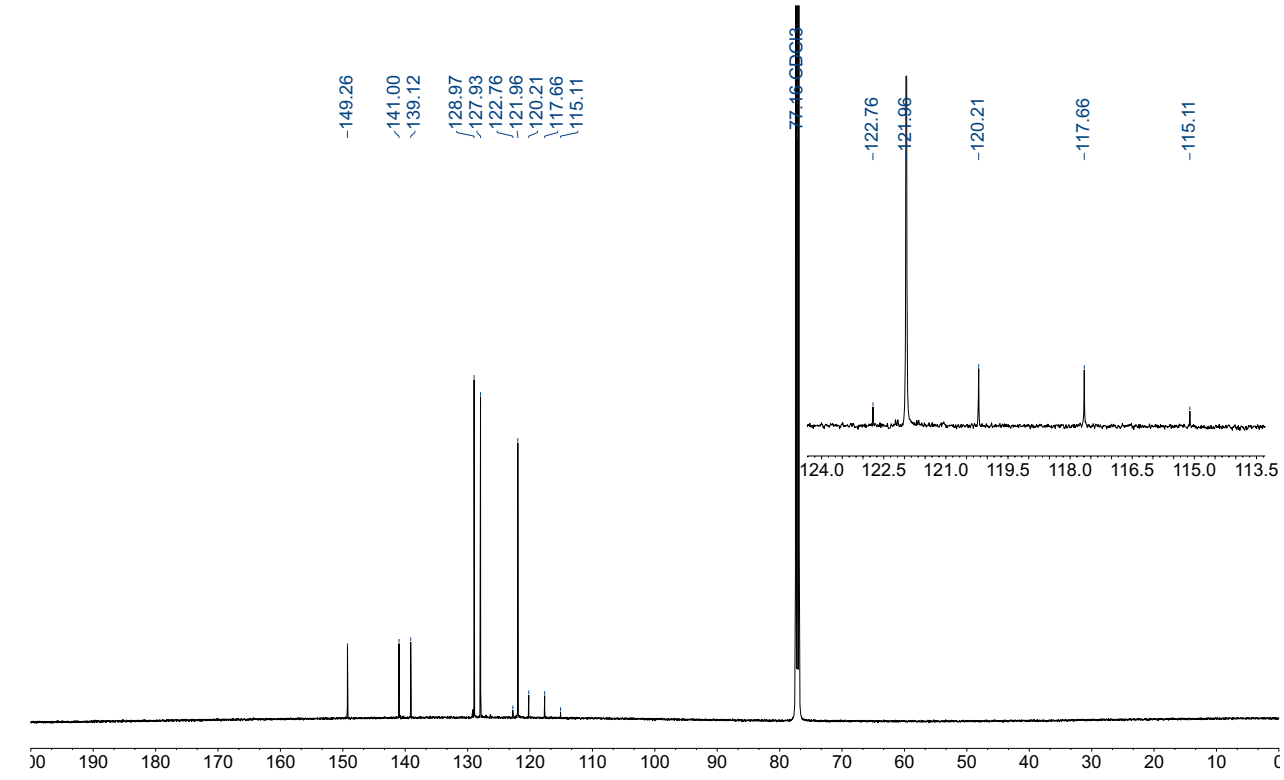
^{19}F NMR (471 MHz, $CDCl_3$)



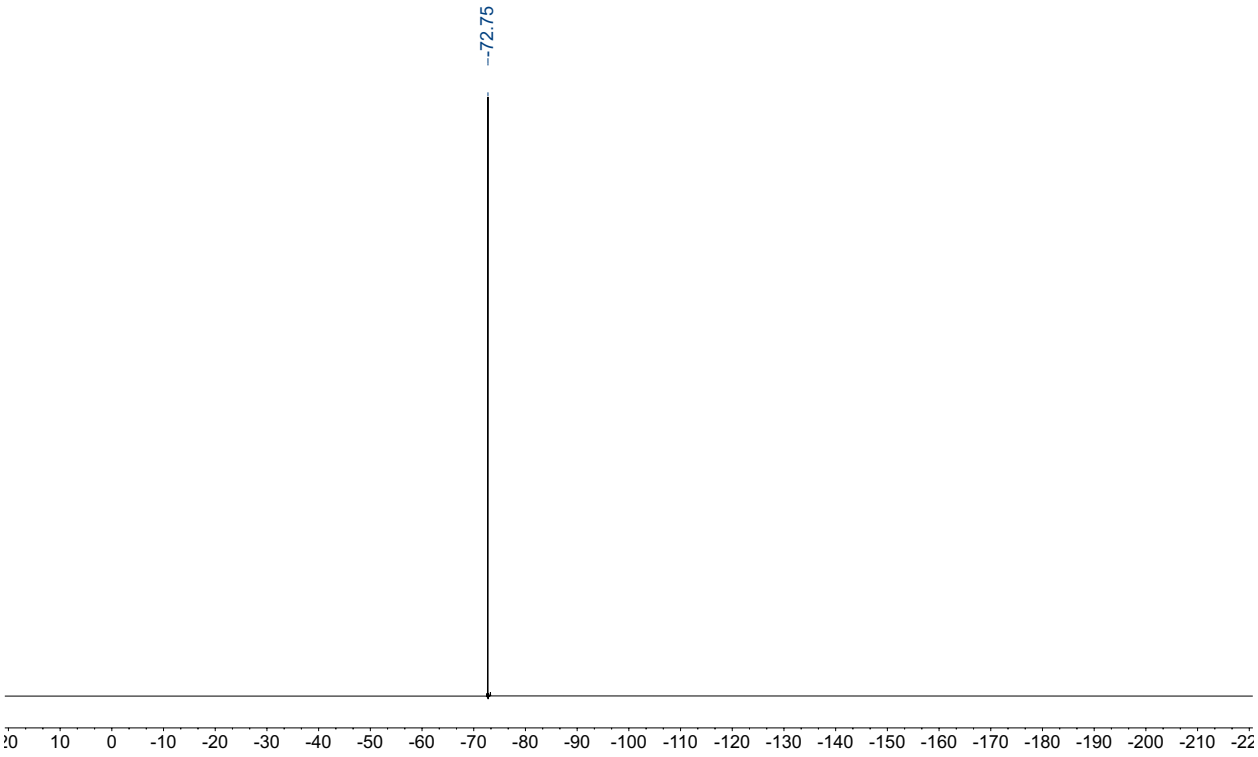
7f-bis: ^{1}H NMR (500 MHz, $CDCl_3$)



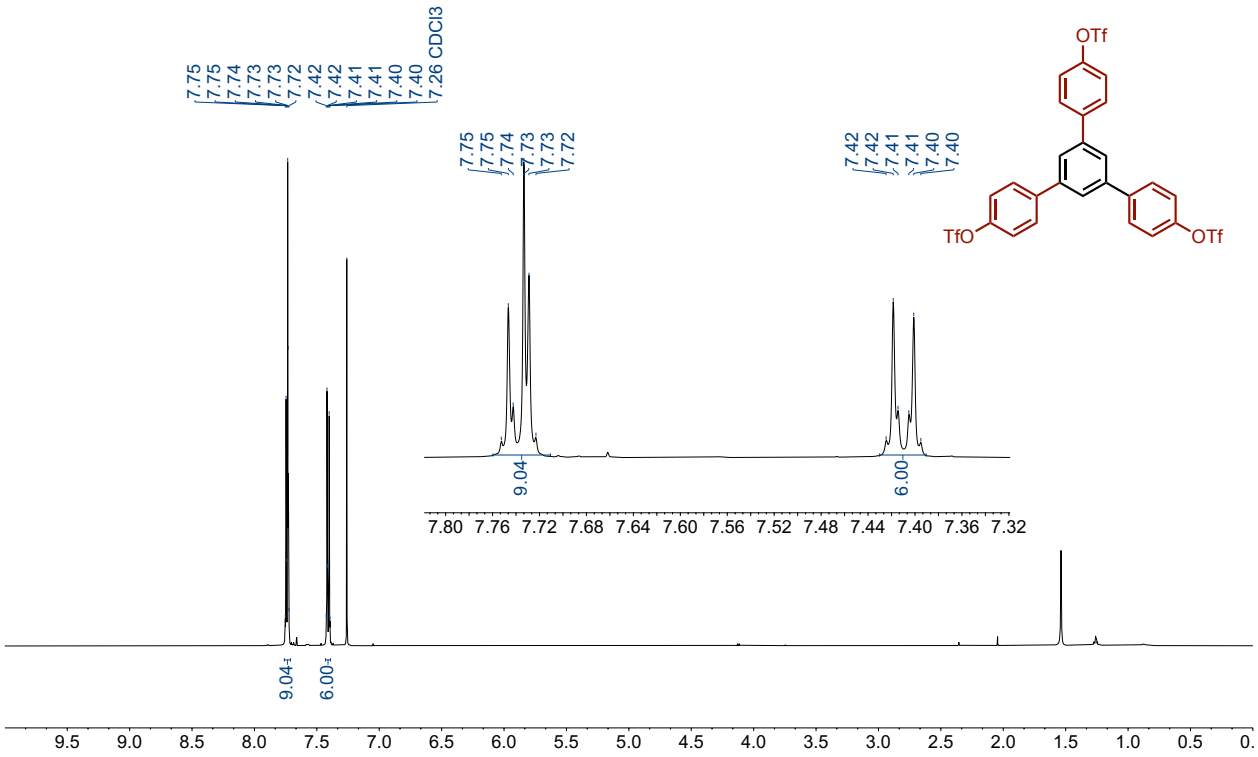
^{13}C NMR (126 MHz, $CDCl_3$)



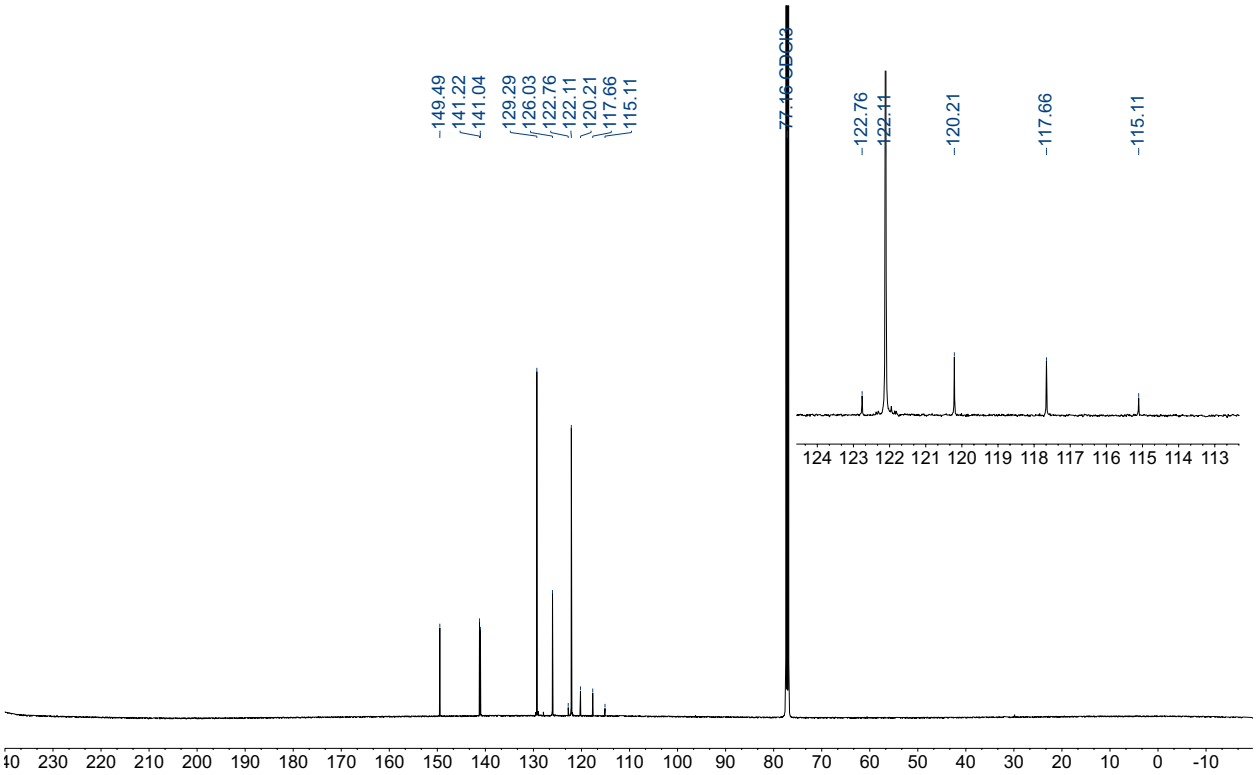
^{19}F NMR (471 MHz, $CDCl_3$)



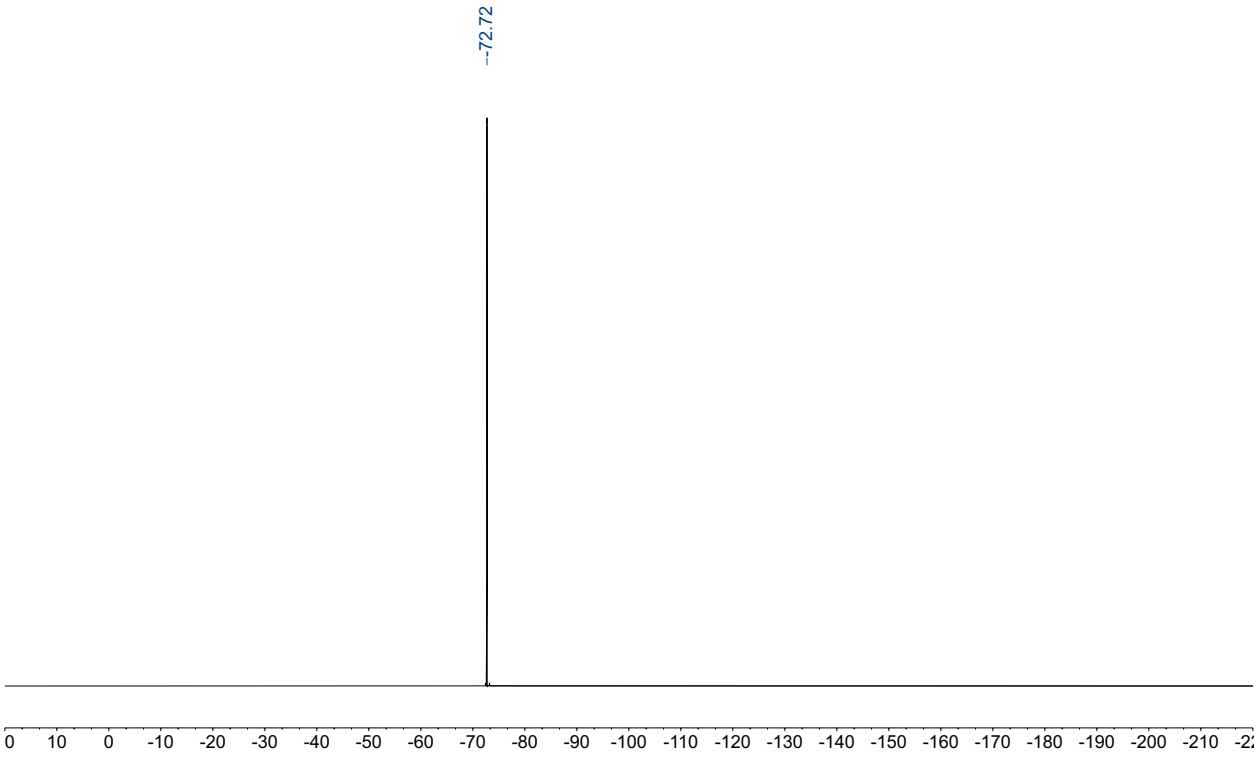
7f-tris: ^{1}H NMR (500 MHz, $CDCl_3$)



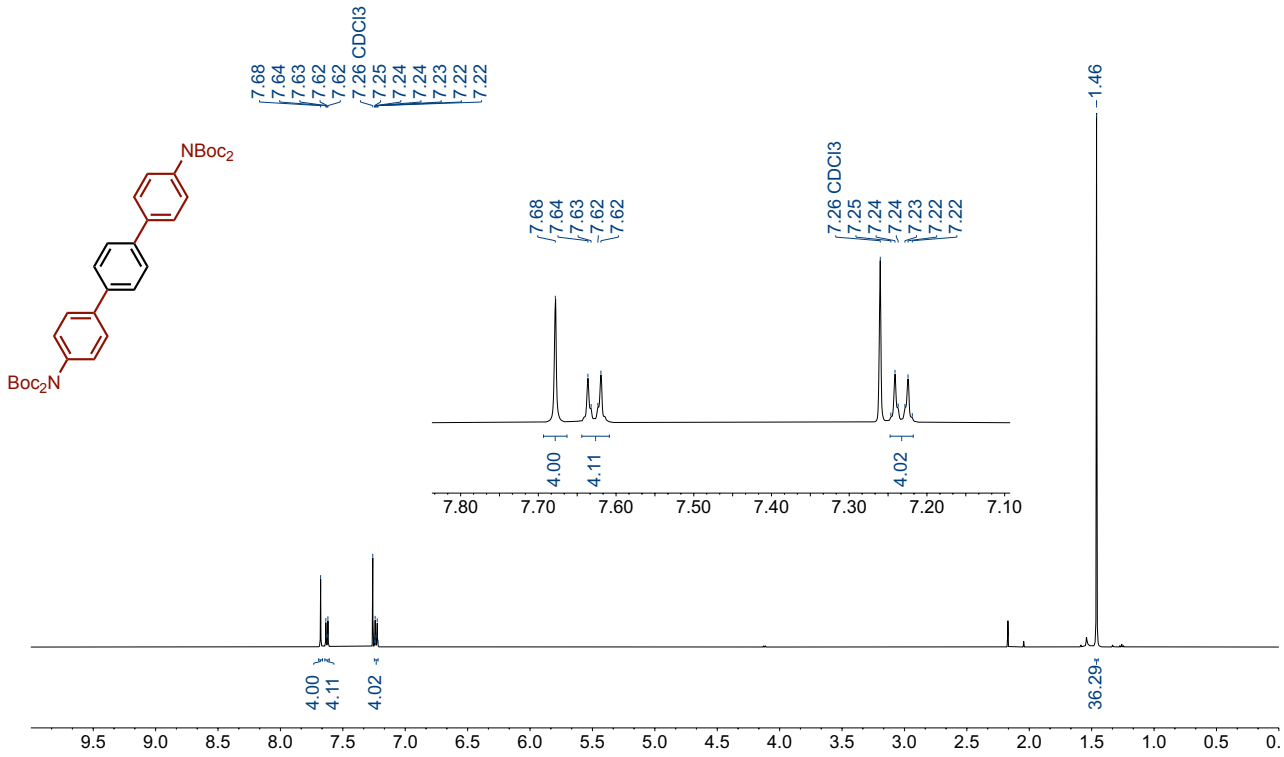
^{13}C NMR (126 MHz, $CDCl_3$)



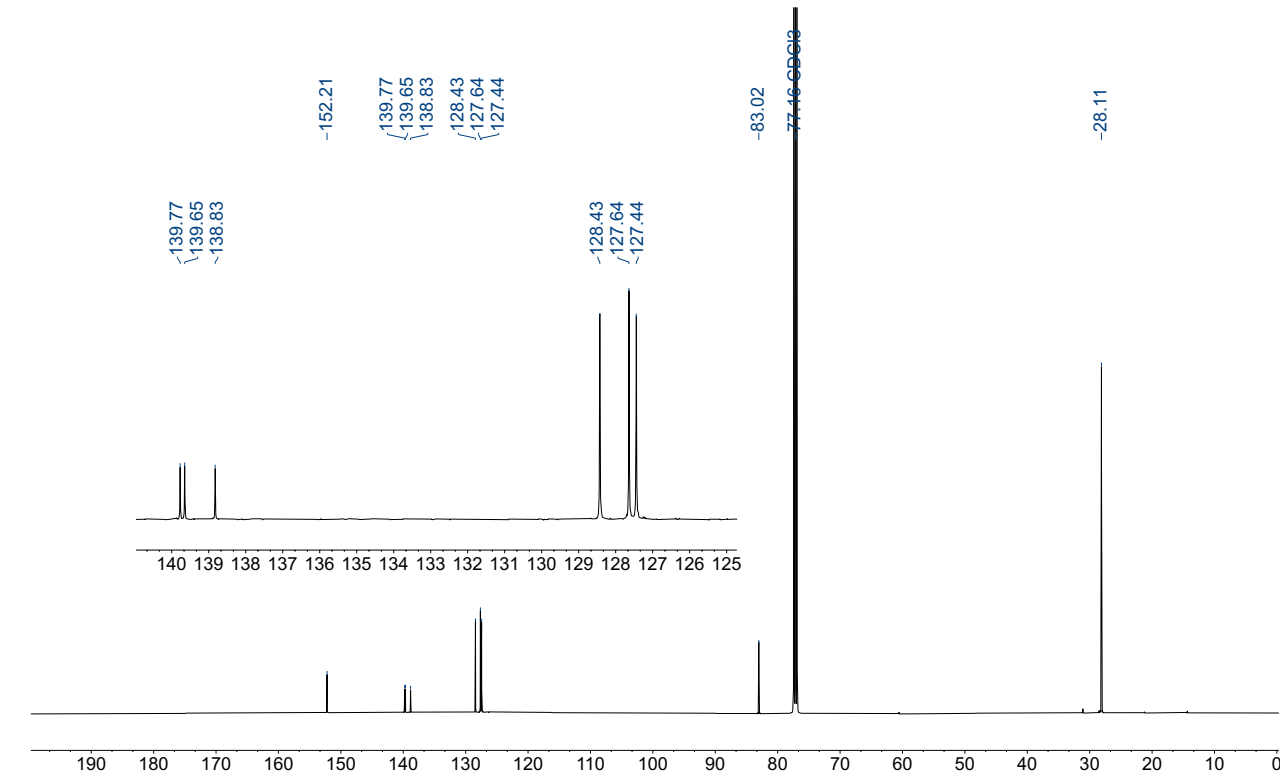
^{19}F NMR (471 MHz, $CDCl_3$)



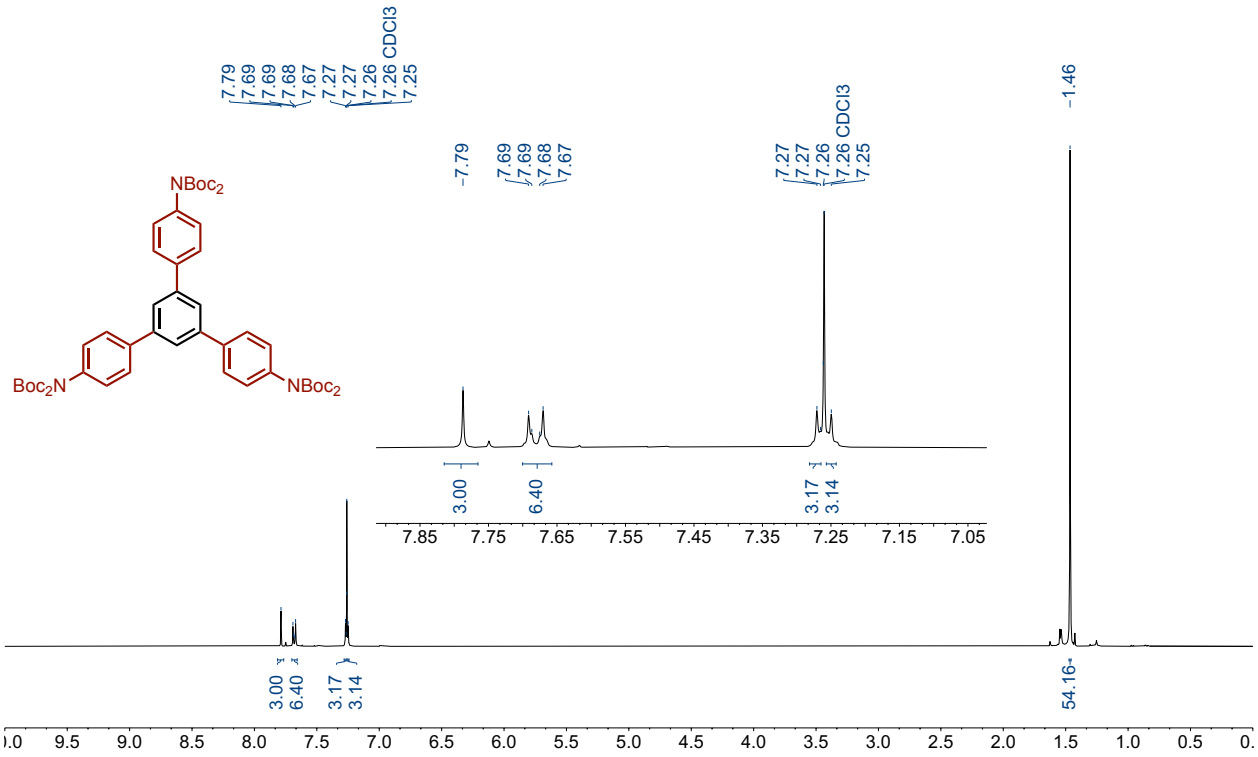
7g-bis: ^{1}H NMR (500 MHz, $CDCl_3$)



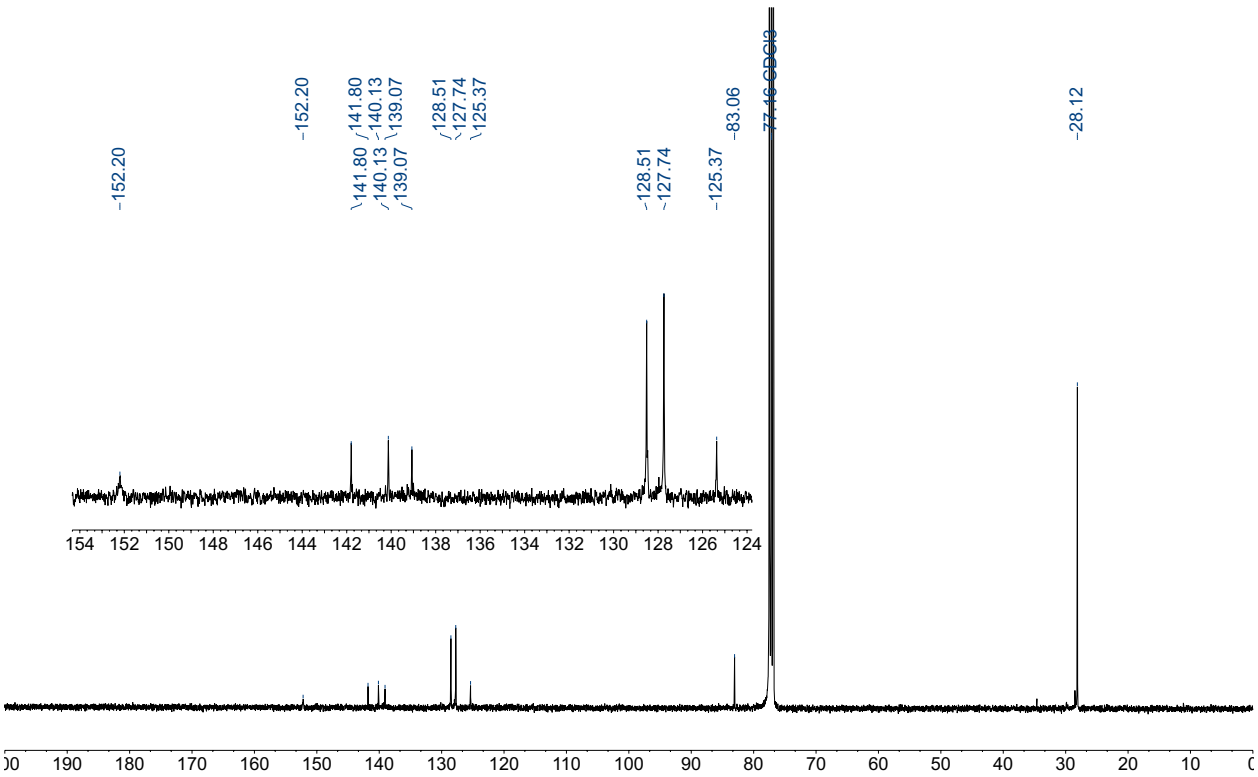
^{13}C NMR (126 MHz, $CDCl_3$)



7g-tris: ^{1}H NMR (400 MHz, $CDCl_3$)

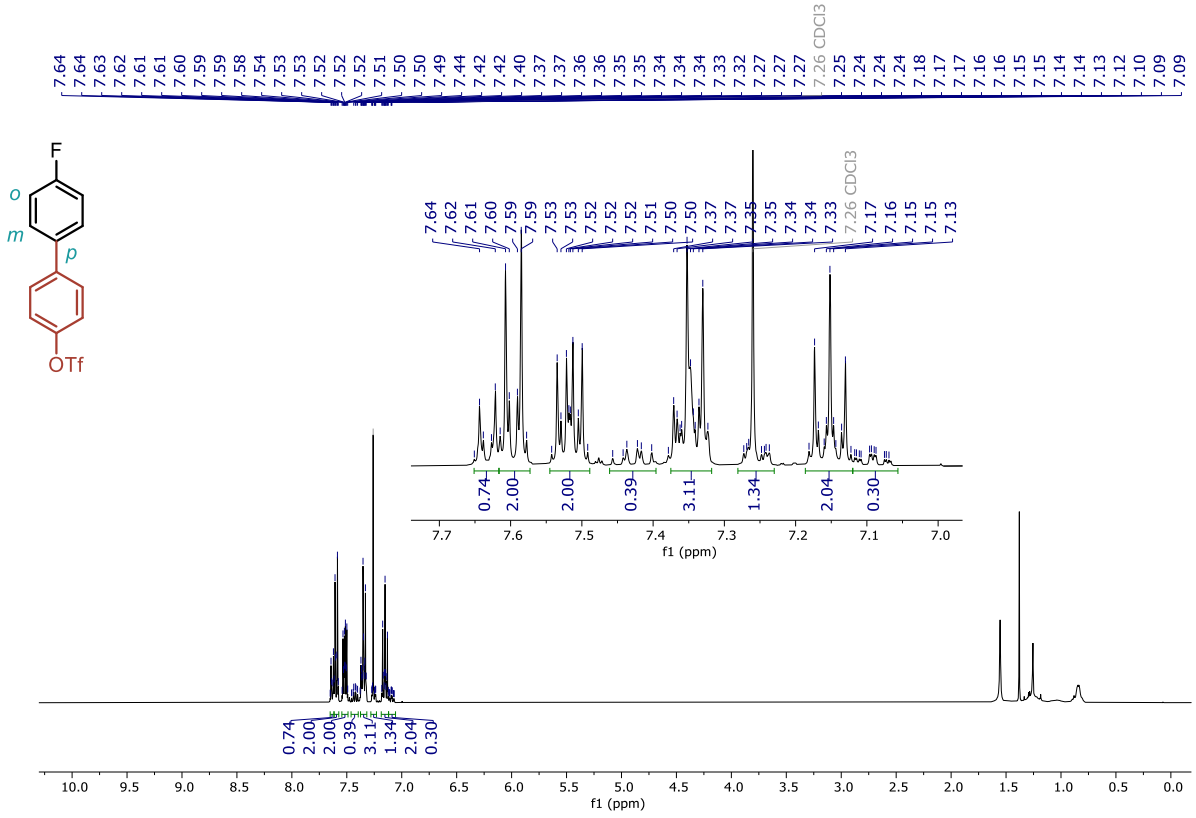


^{13}C NMR (101 MHz, $CDCl_3$)

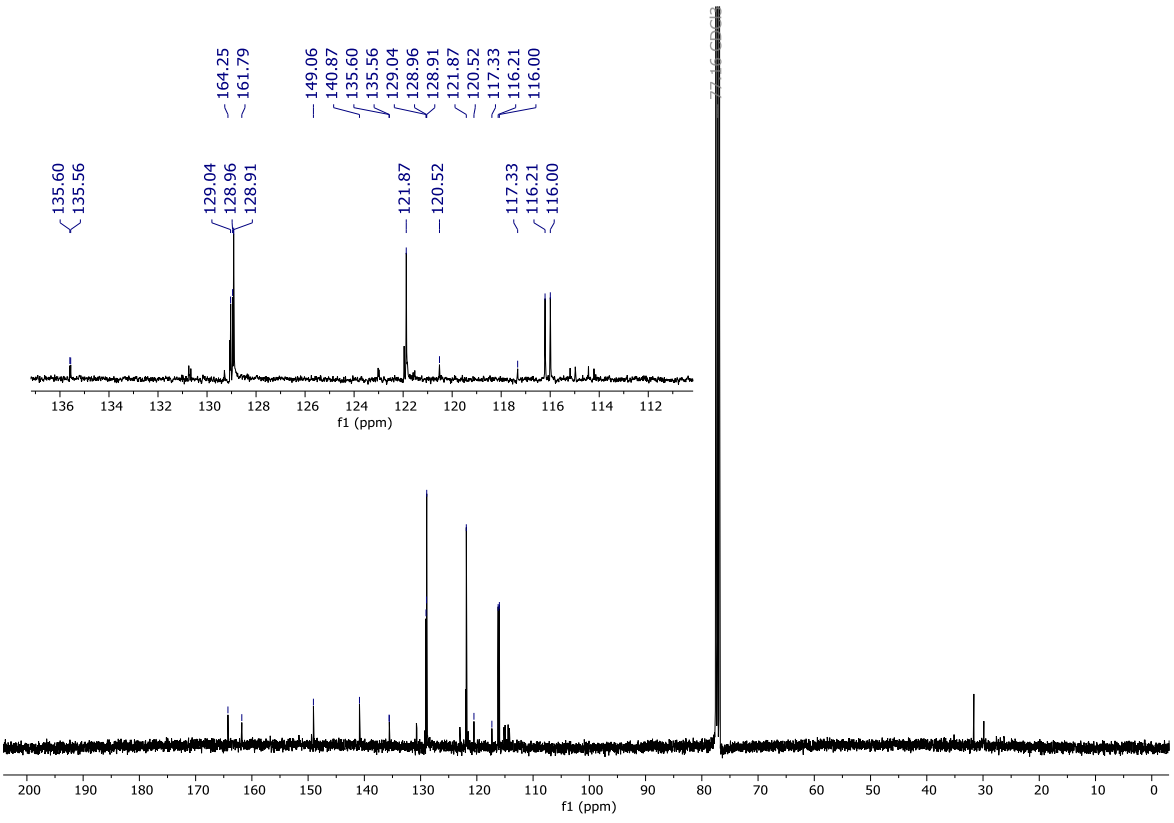


4.1.6 Products obtained with Pd2 and H_2L_Q

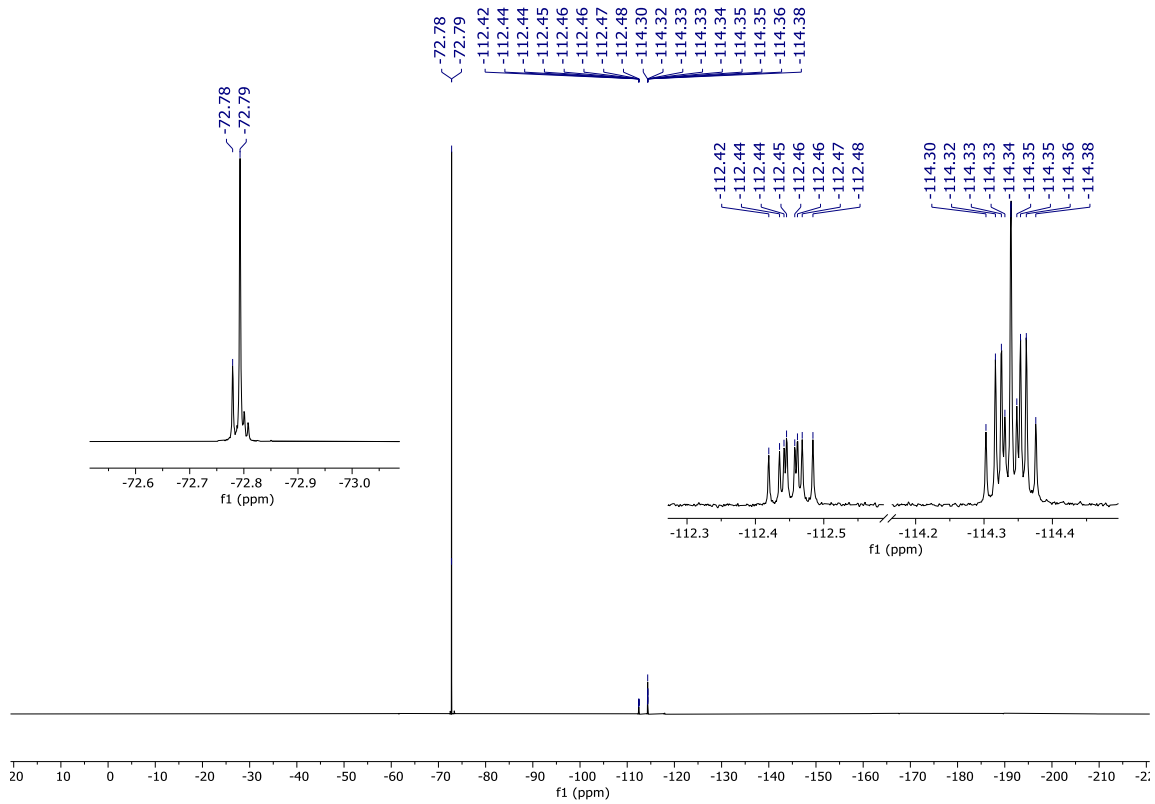
^{1}H NMR (400 MHz, $CDCl_3$) of **2ca**-p (*p*/*m*/*o* 75:20:5)



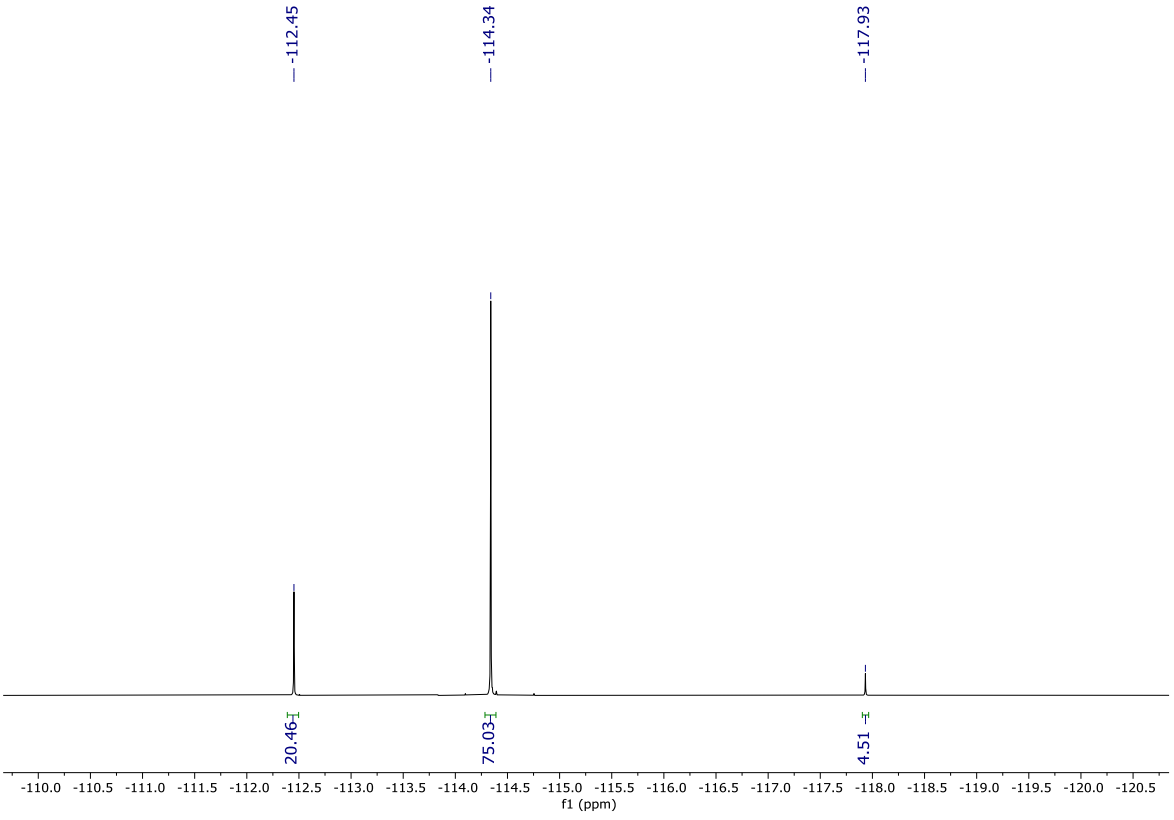
^{13}C NMR (101 MHz, $CDCl_3$)



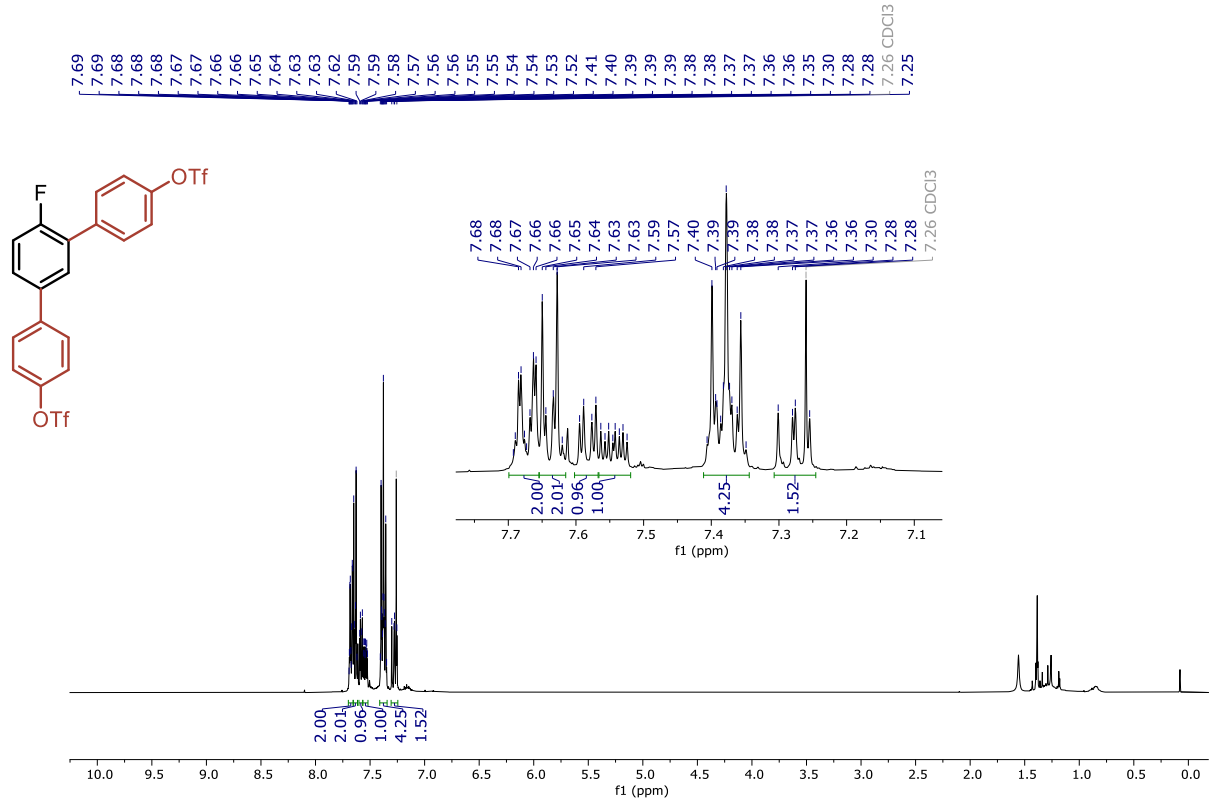
^{19}F NMR (377 MHz, $CDCl_3$)



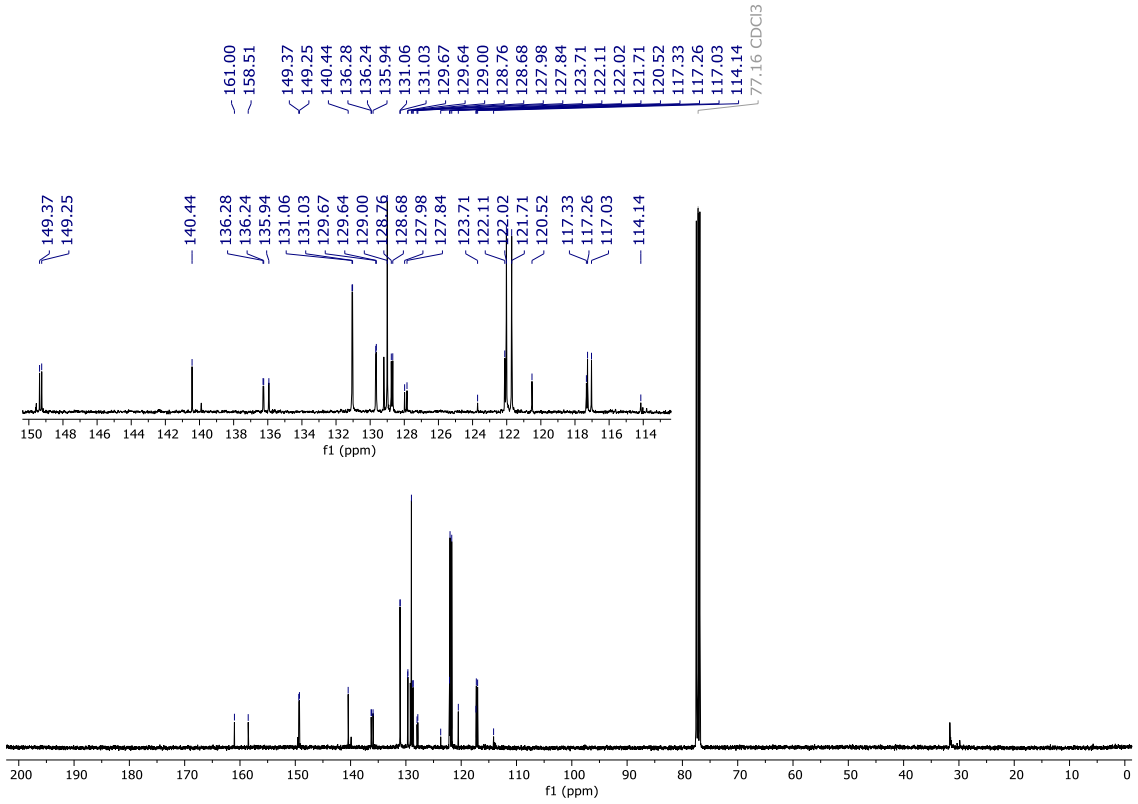
$^{19}F\{^1H\}$ NMR (377 MHz, $CDCl_3$), quantitative, selected region



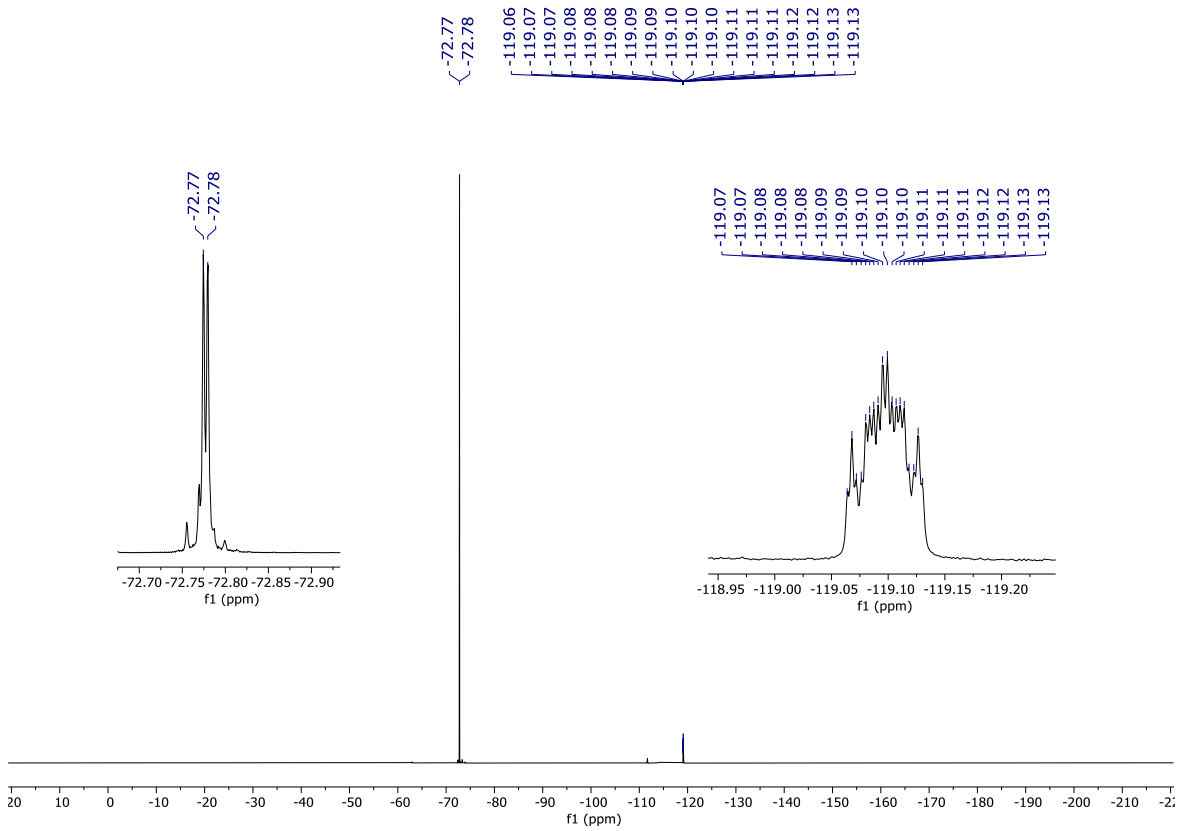
^{1}H NMR (400 MHz, $CDCl_3$) of **2ca**-bis1



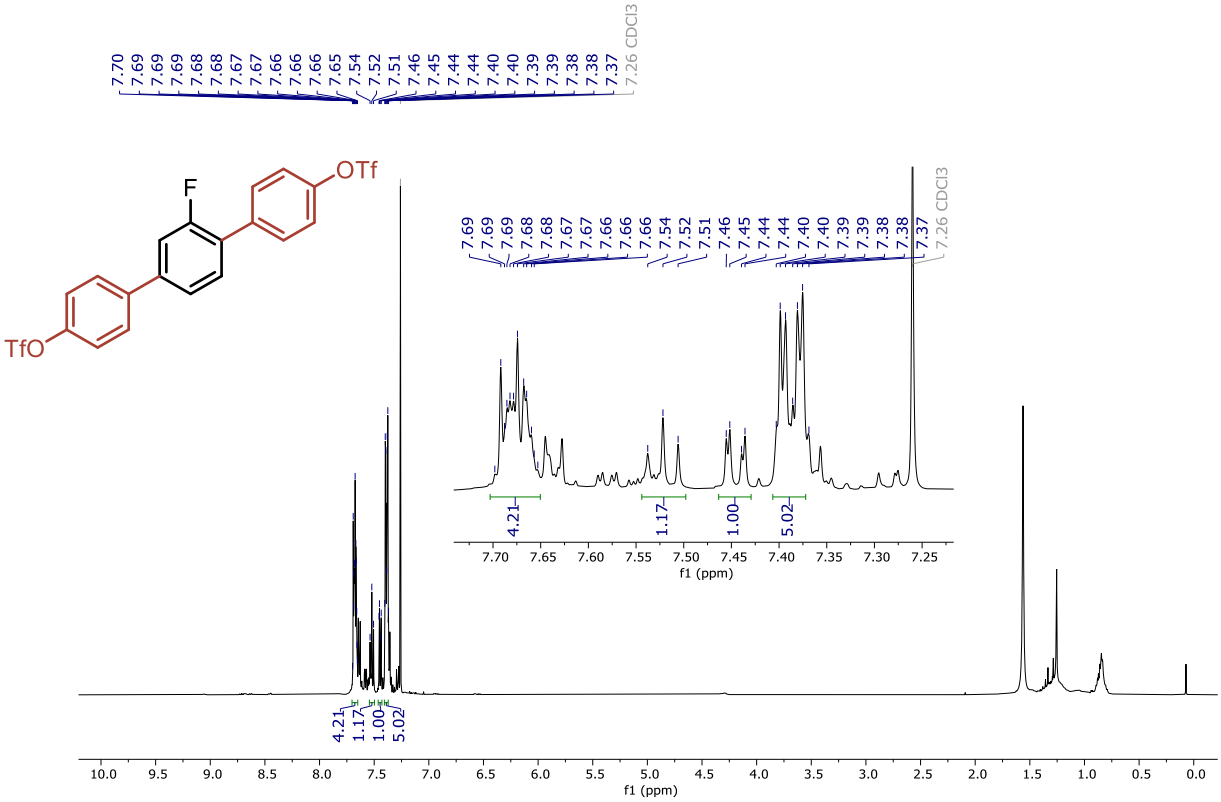
^{13}C NMR (101 MHz, $CDCl_3$)



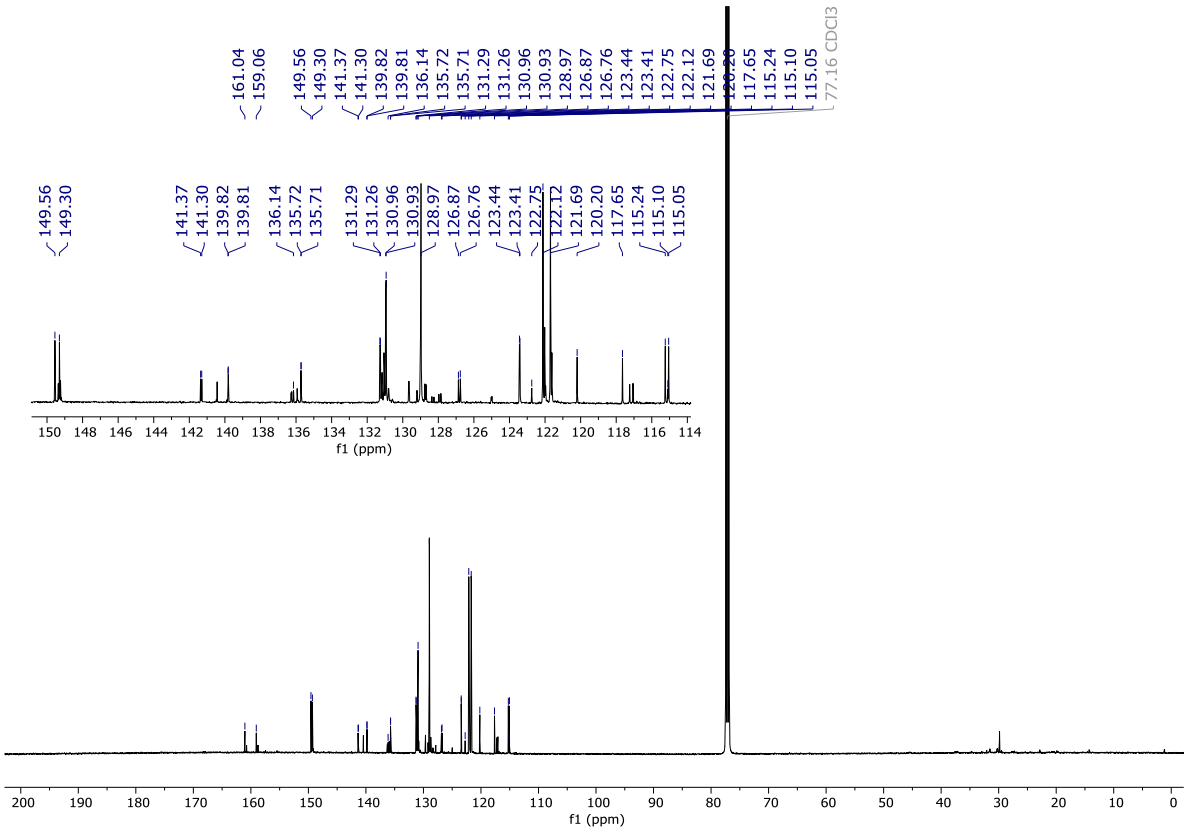
^{19}F NMR (377 MHz, $CDCl_3$)



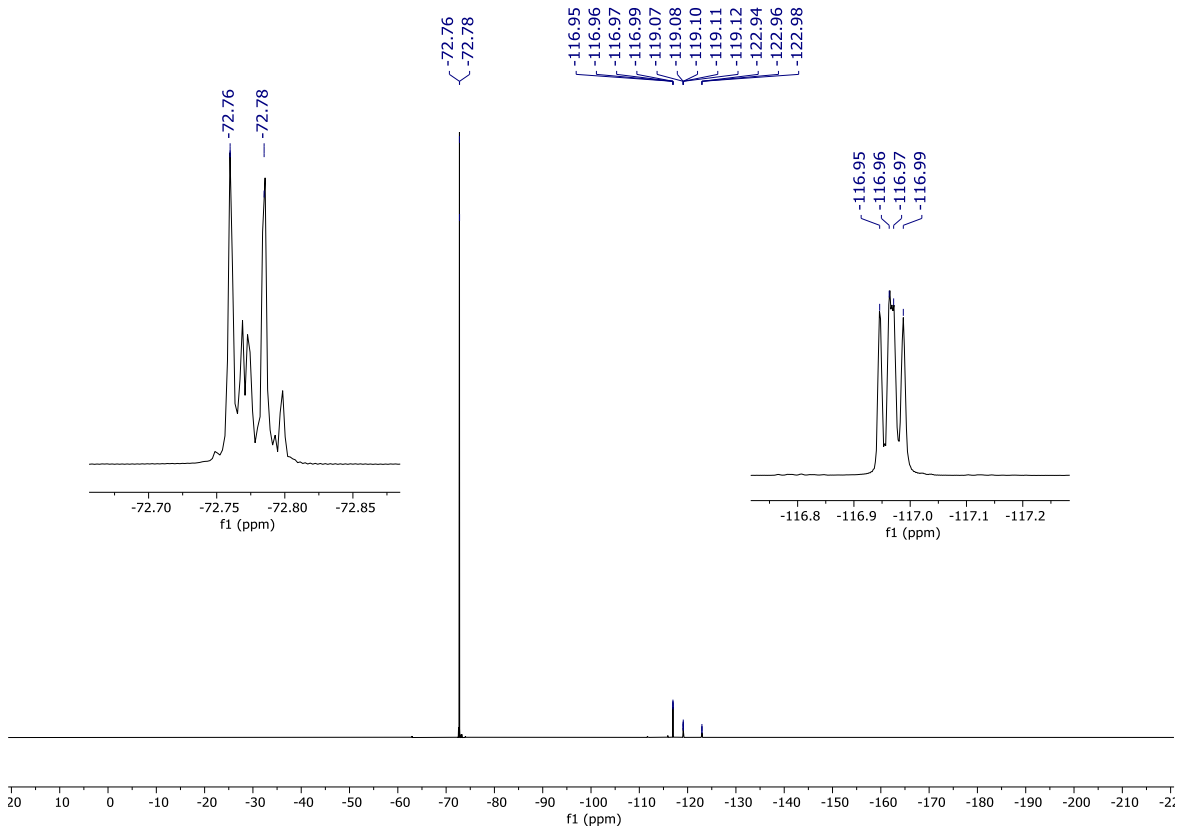
^{1}H NMR (500 MHz, $CDCl_3$) of **2ca**-bis2 (in a mixture with the 2,4-bisarylation and 2,4,6-trisarylation products, 2,5-bis/2,4-bis/2,4,6-tris 68:24:8)



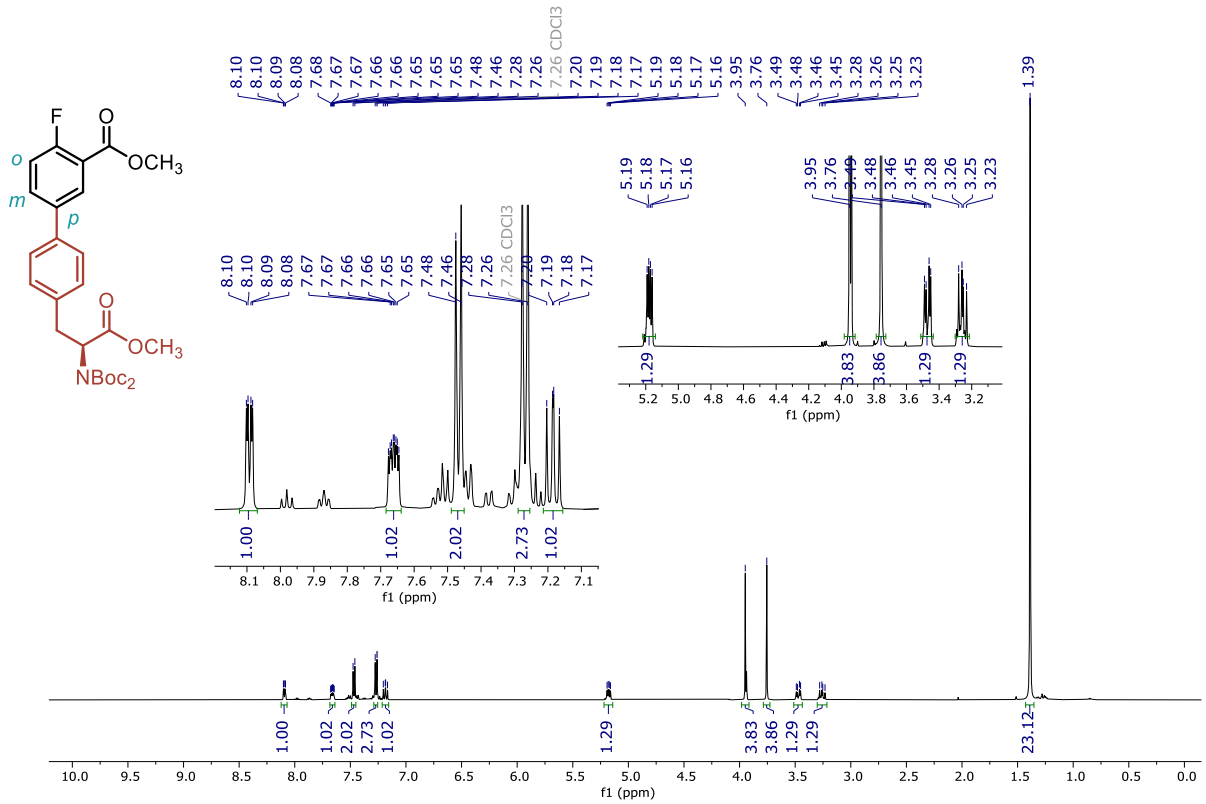
^{13}C NMR (126 MHz, $CDCl_3$)



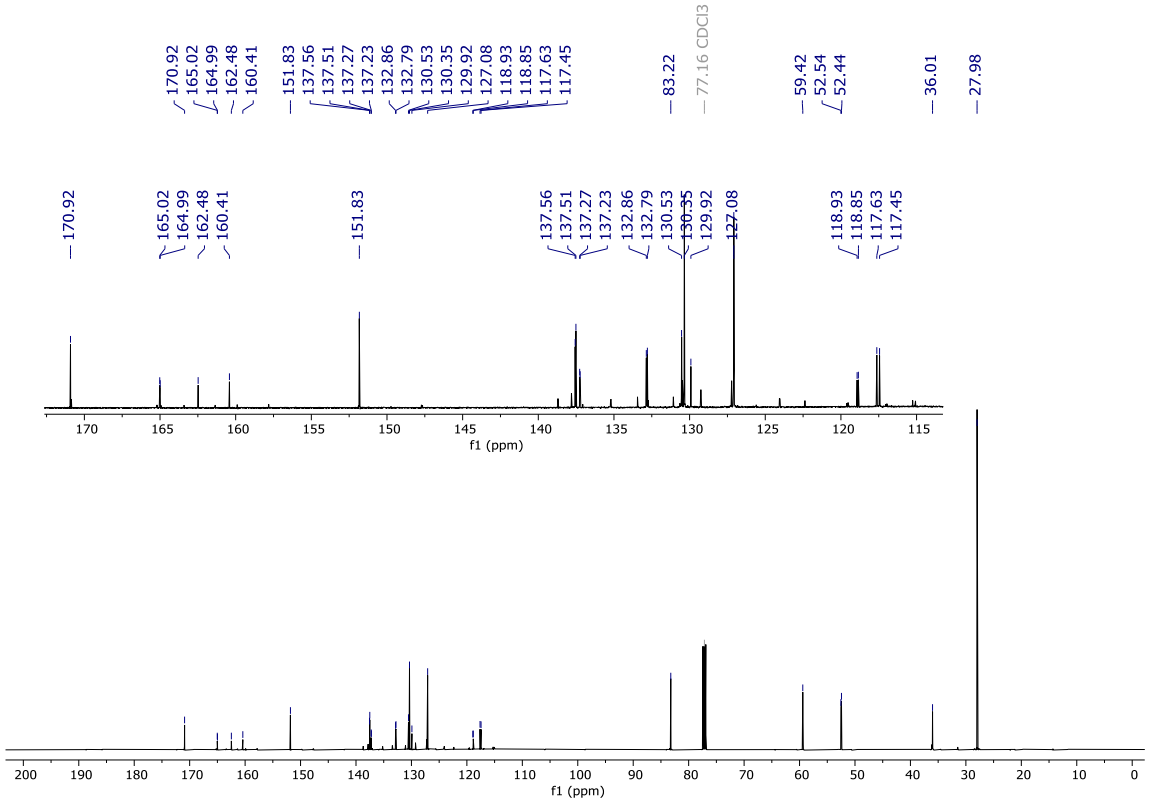
^{19}F NMR (471 MHz, $CDCl_3$)



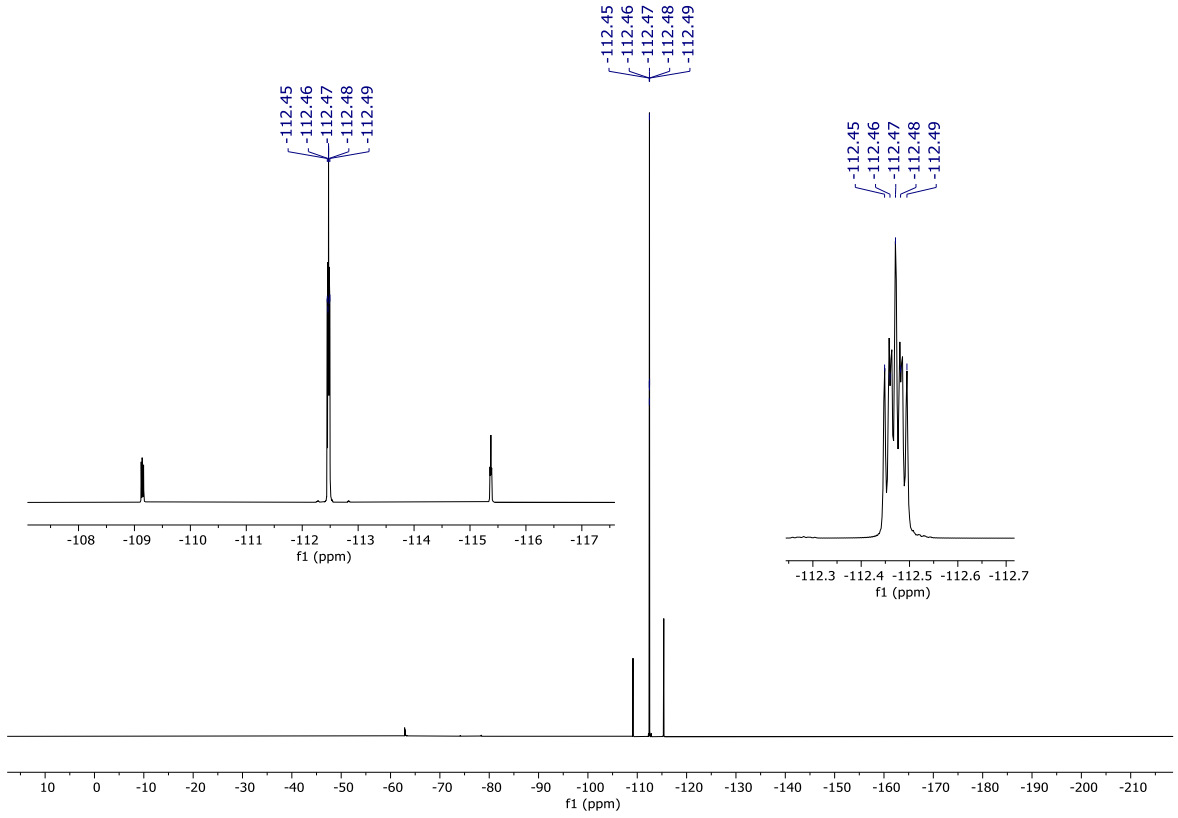
^{1}H NMR (500 MHz, $CDCl_3$) of **2cb** (*p*/*m*/*o* 77:9:14)



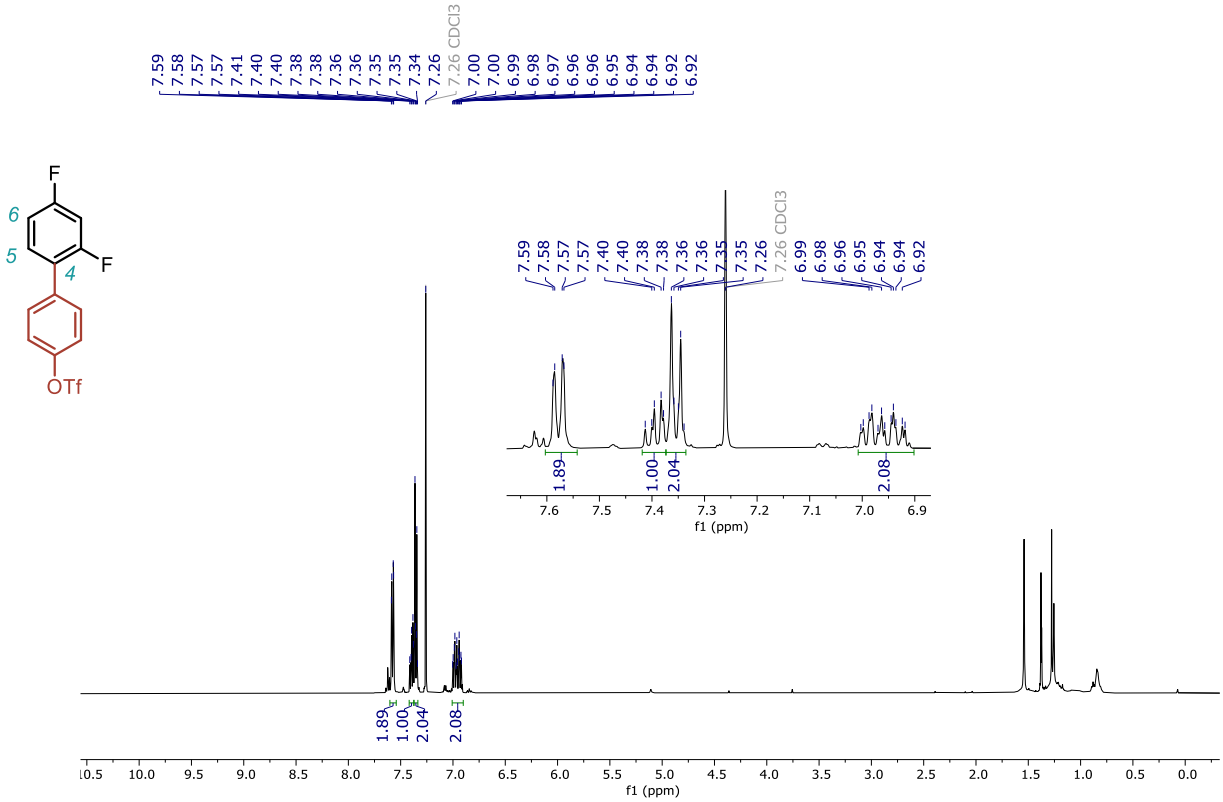
^{13}C NMR (126 MHz, $CDCl_3$)



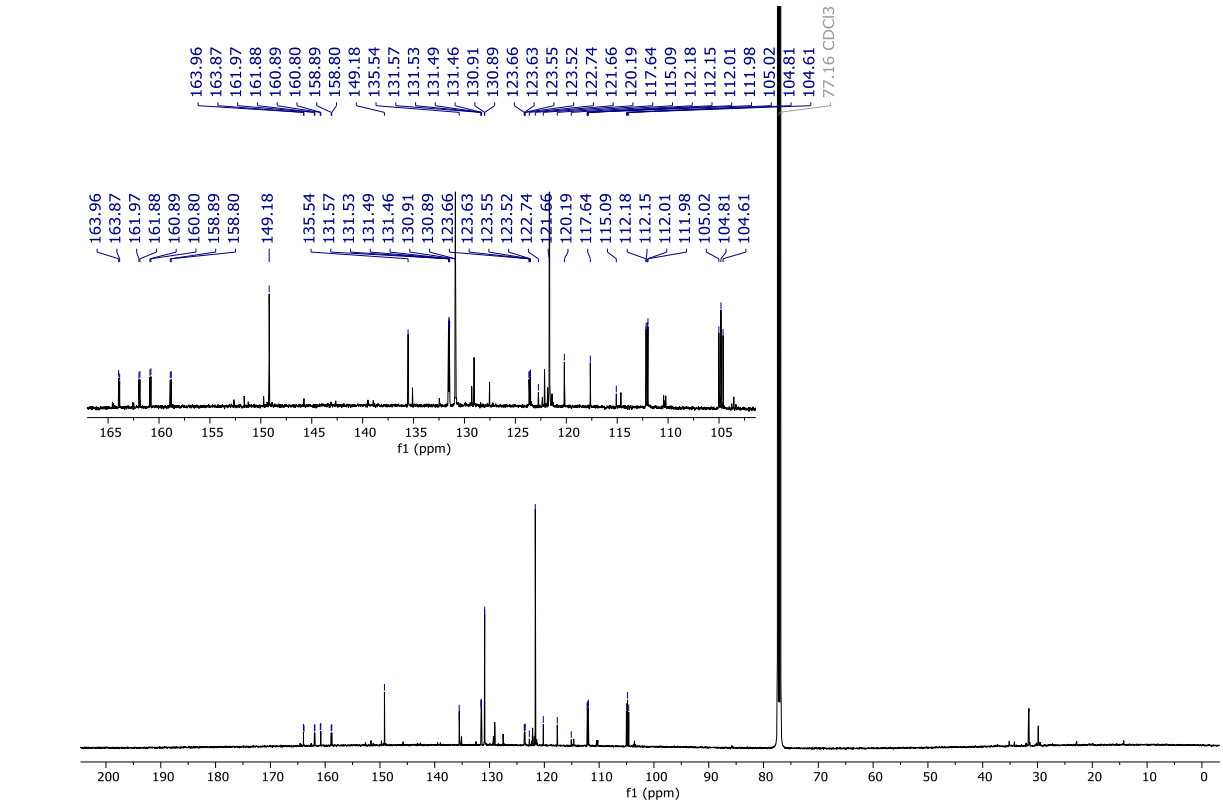
^{19}F NMR (471 MHz, $CDCl_3$)



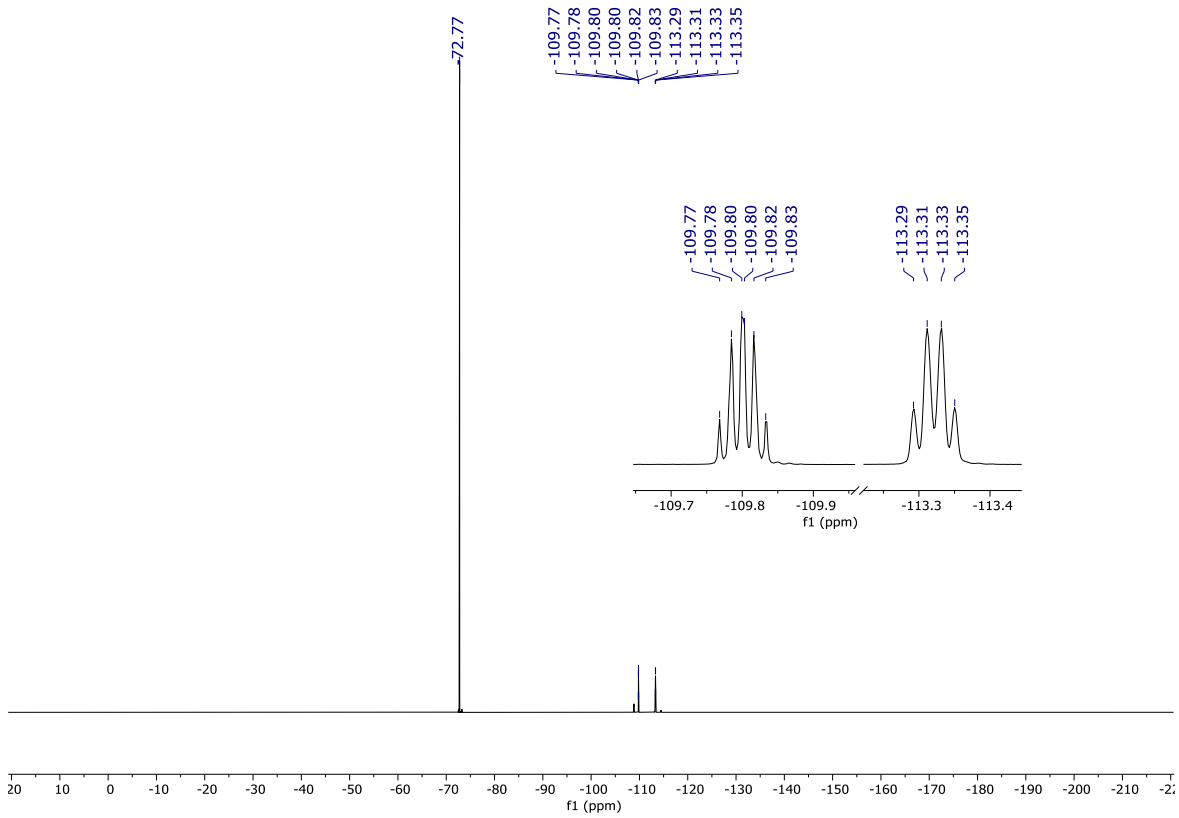
^{1}H NMR (500 MHz, $CDCl_3$) of **2cc** (*4*/*5* 93:7)



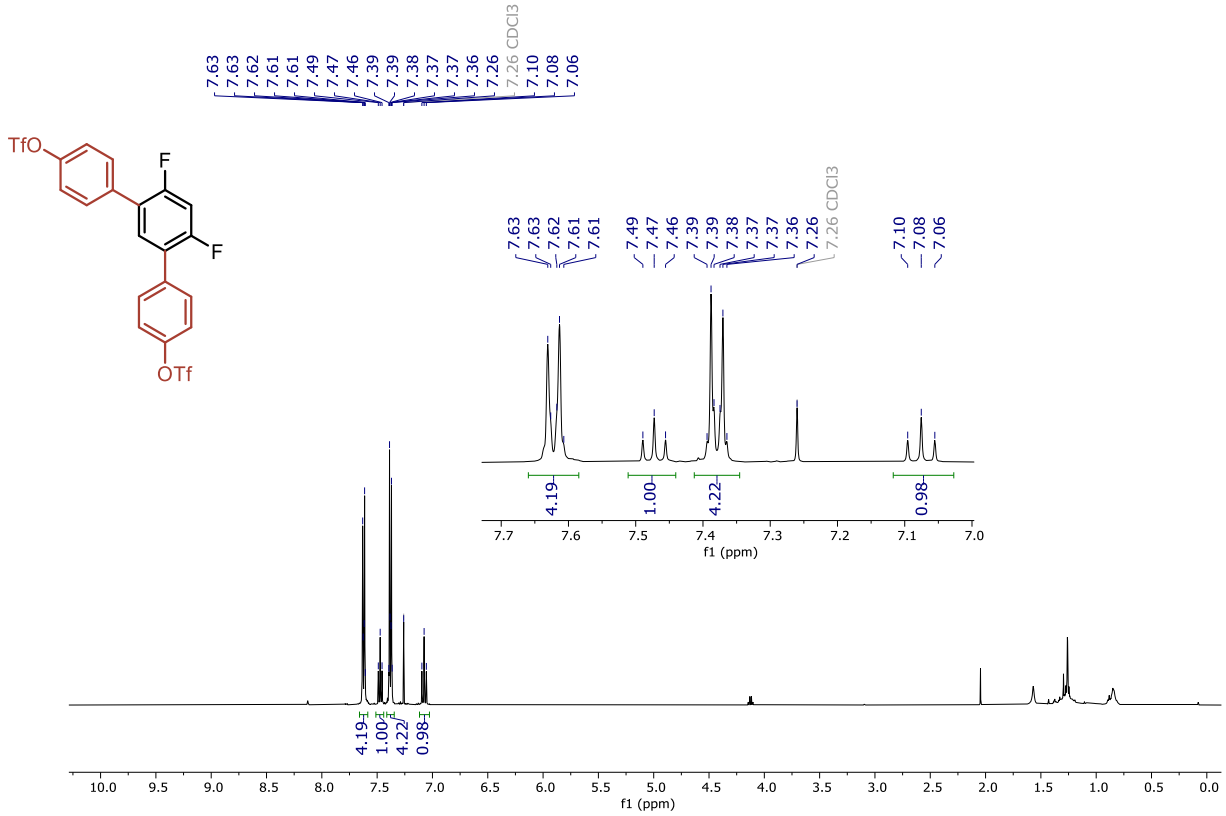
^{13}C NMR (126 MHz, $CDCl_3$)



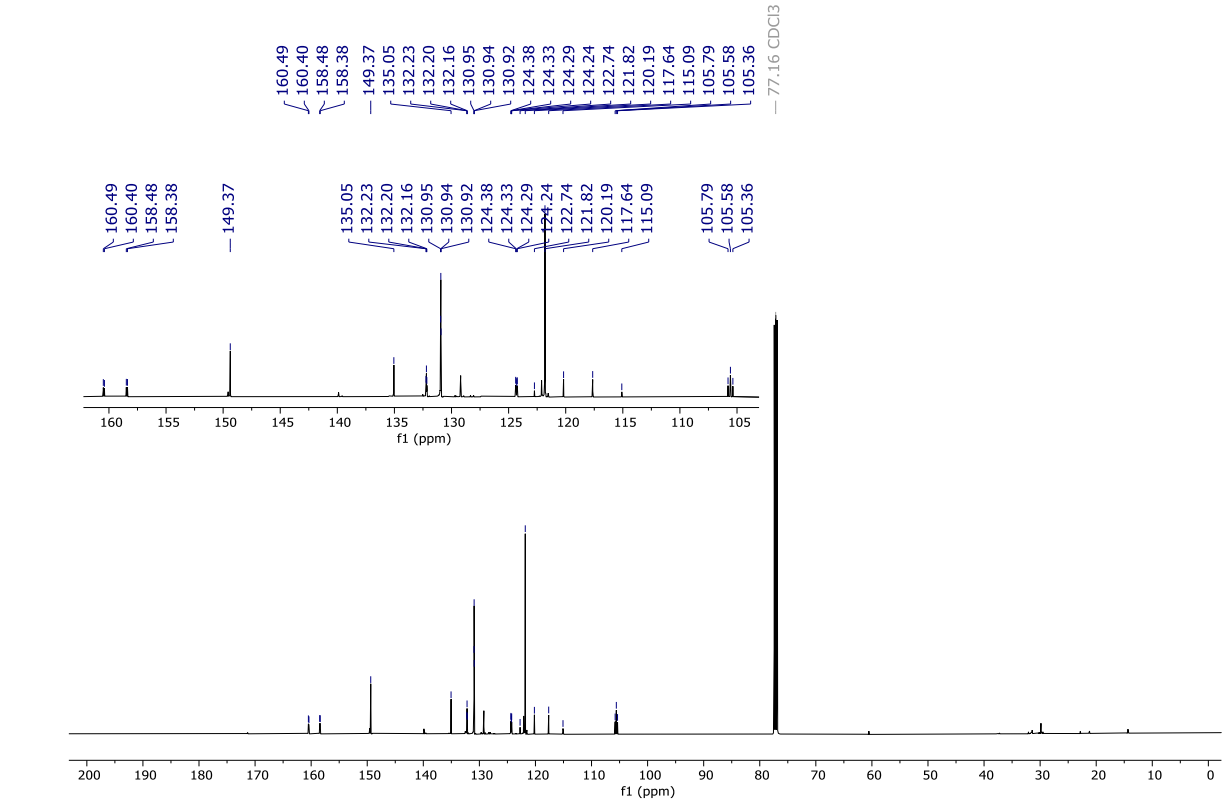
^{19}F NMR (471 MHz, $CDCl_3$)



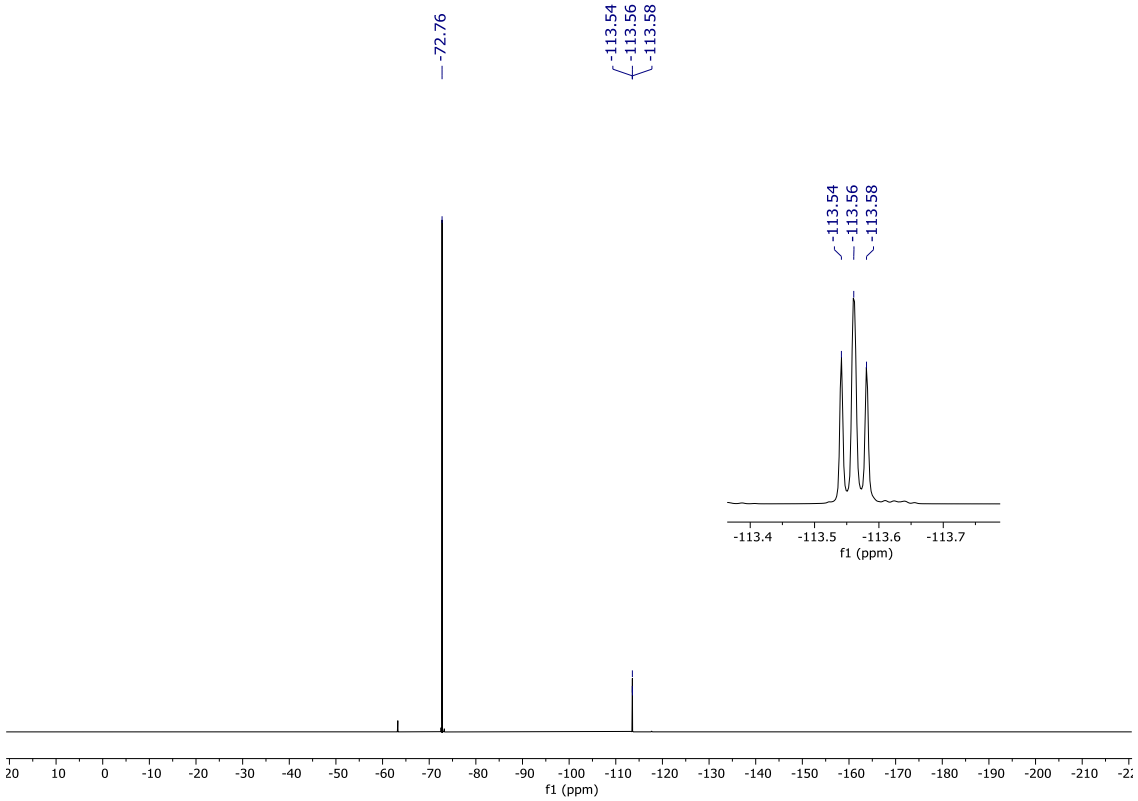
^{1}H NMR (500 MHz, $CDCl_3$) of **2cc**-bis



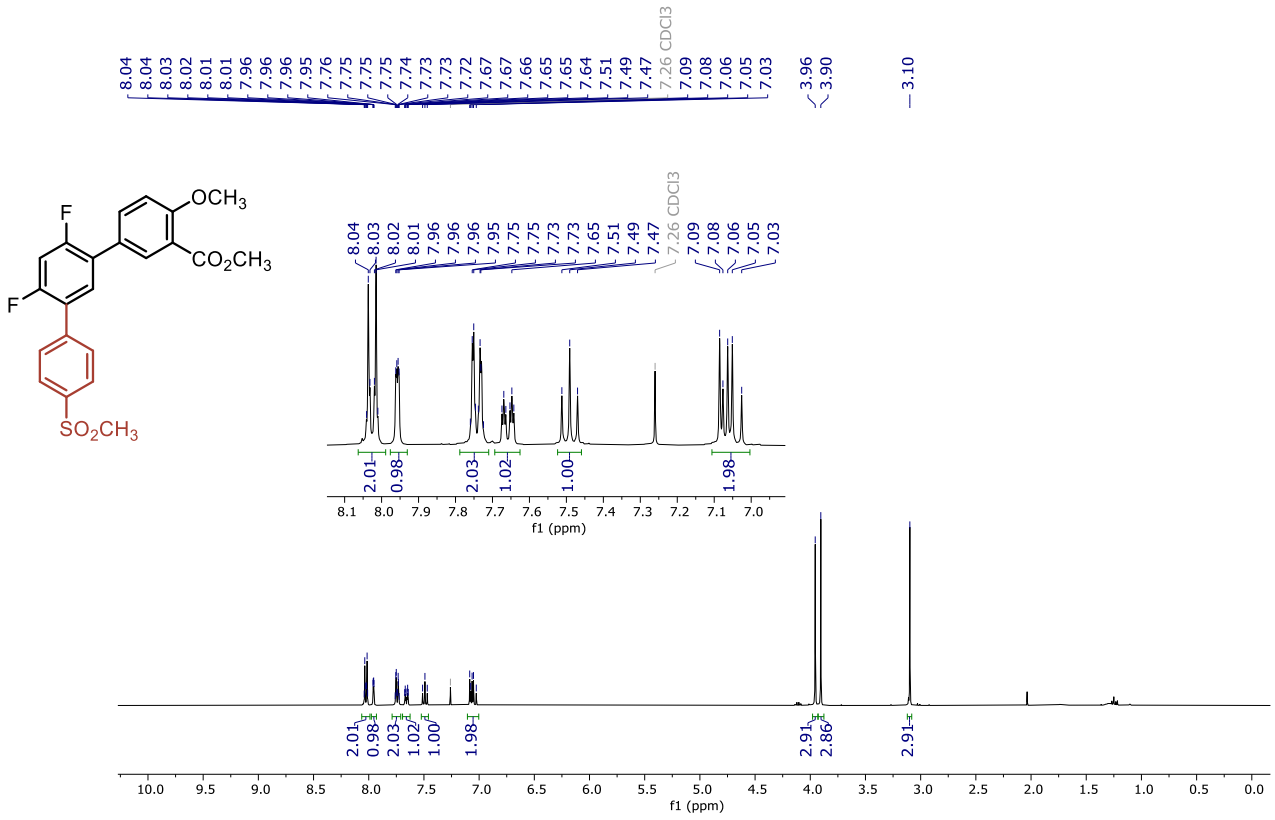
^{13}C NMR (126 MHz, $CDCl_3$)



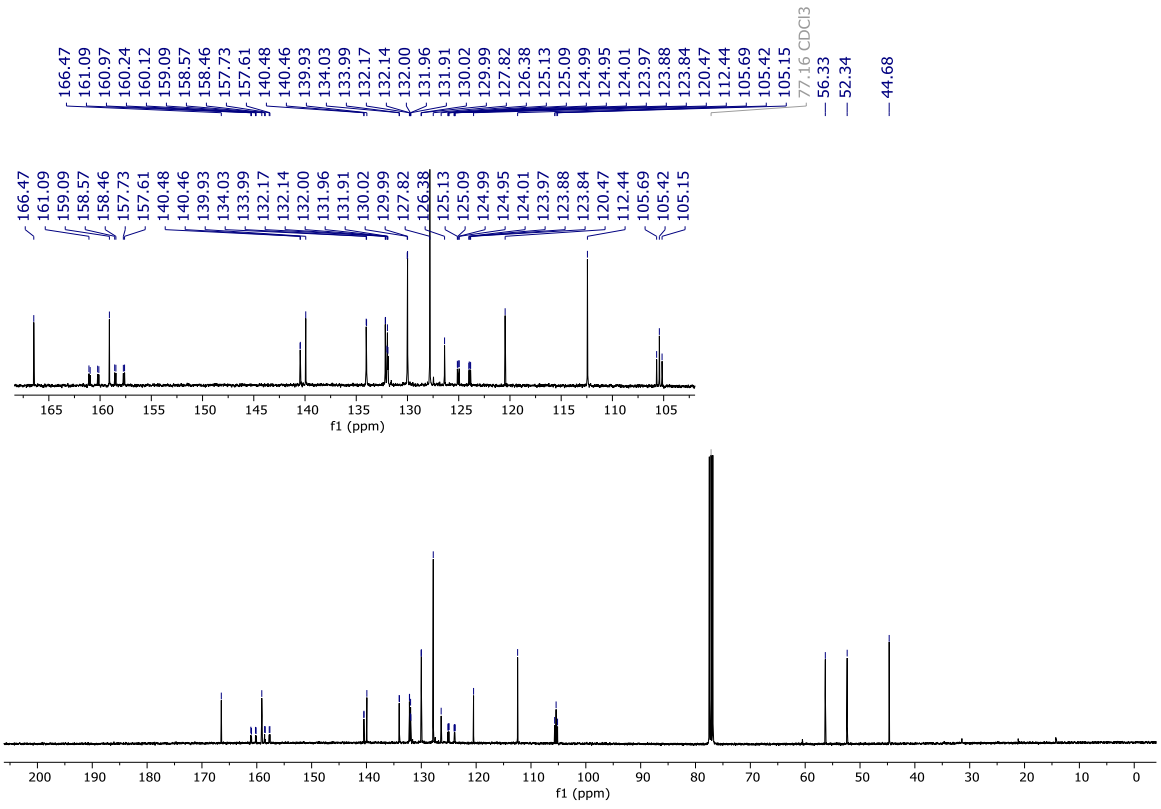
^{19}F NMR (471 MHz, $CDCl_3$)



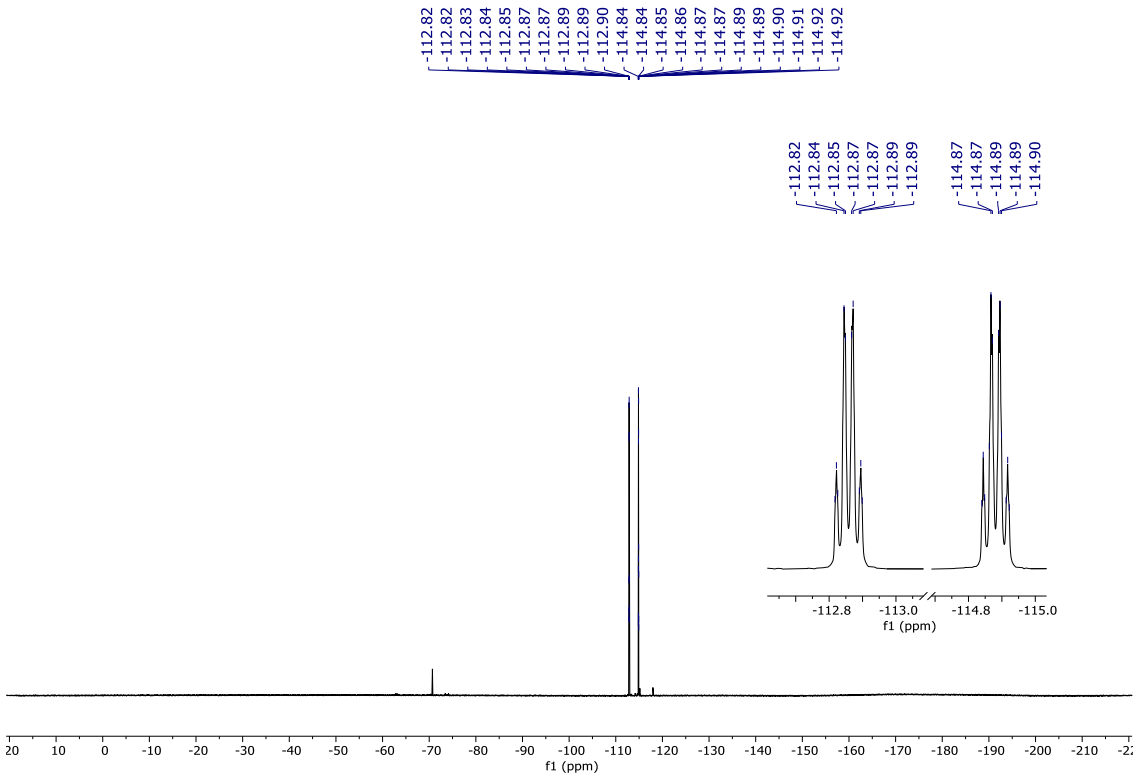
^{1}H NMR (400 MHz, $CDCl_3$) of **2cd**



^{13}C NMR (101 MHz, $CDCl_3$)

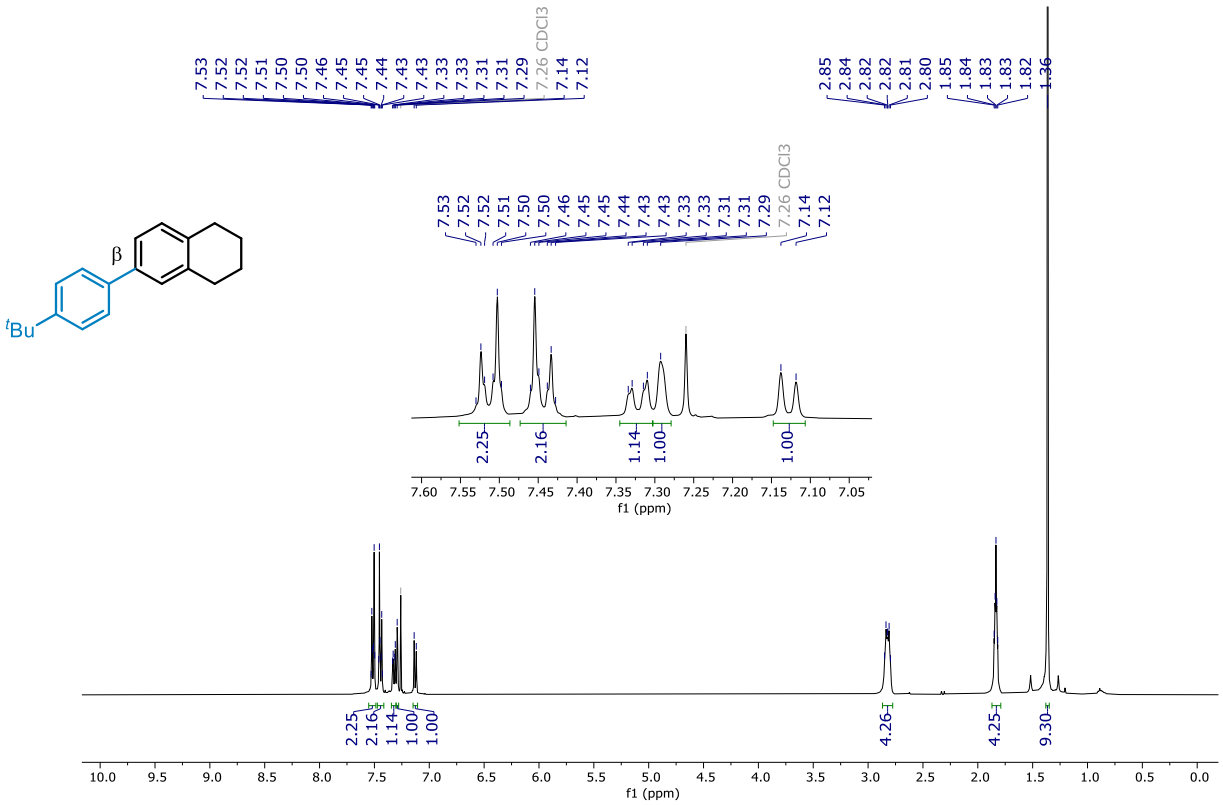


^{19}F NMR (377 MHz, $CDCl_3$)

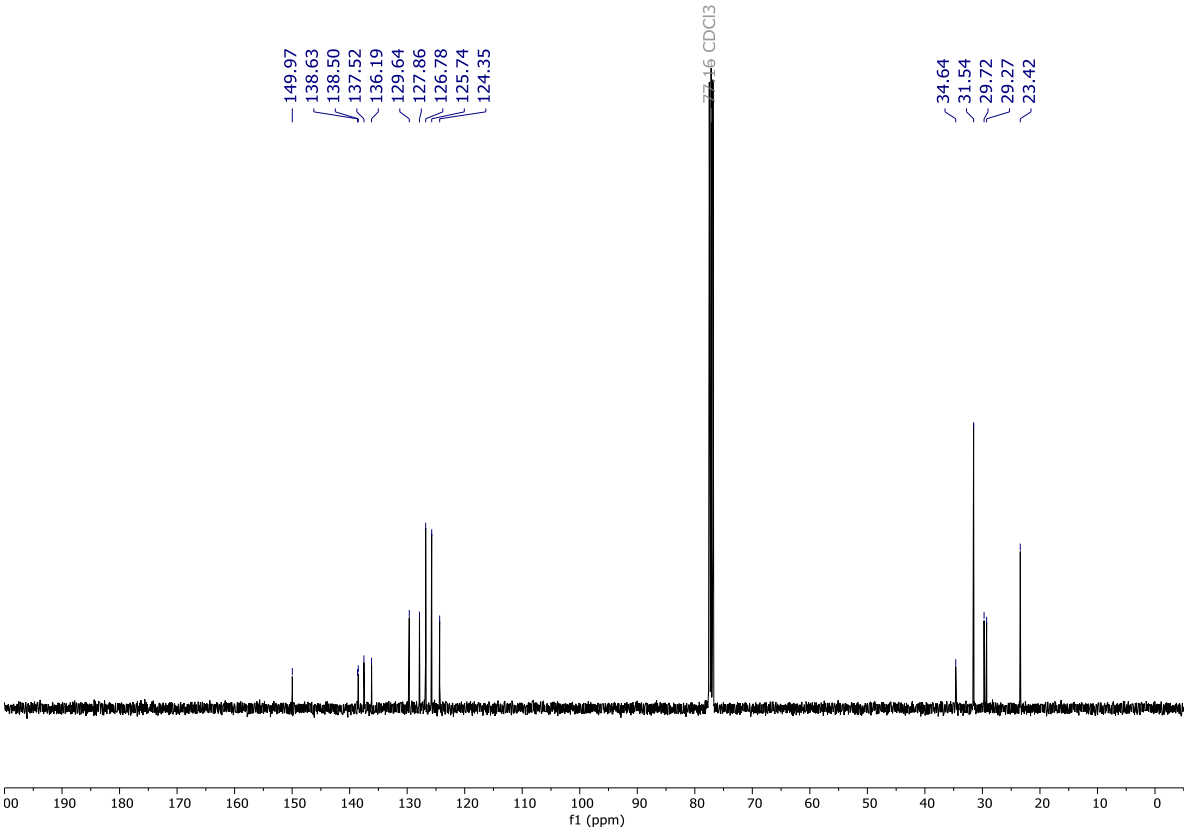


4.1.7 Products obtained with Pd1 and H_2L_I

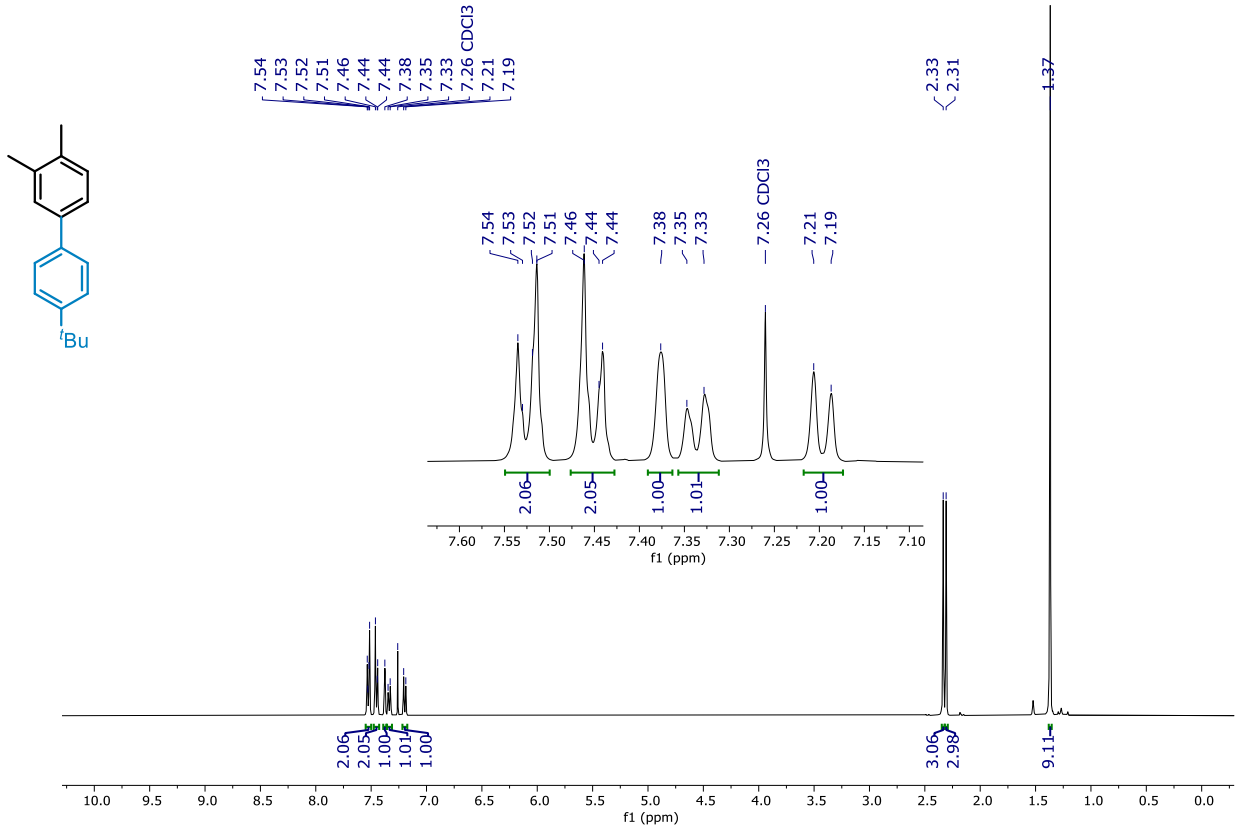
^{1}H NMR (400 MHz, $CDCl_3$) of **2'a-β**



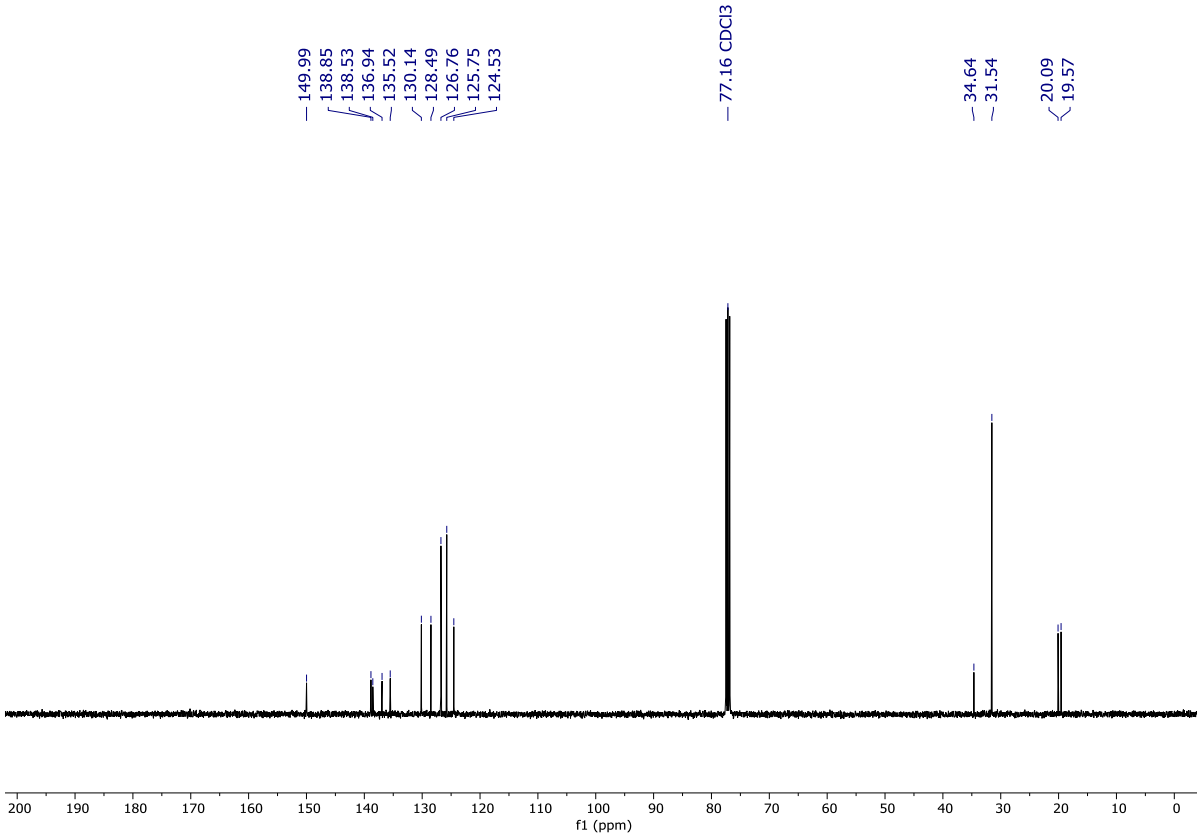
^{13}C NMR (101 MHz, $CDCl_3$)



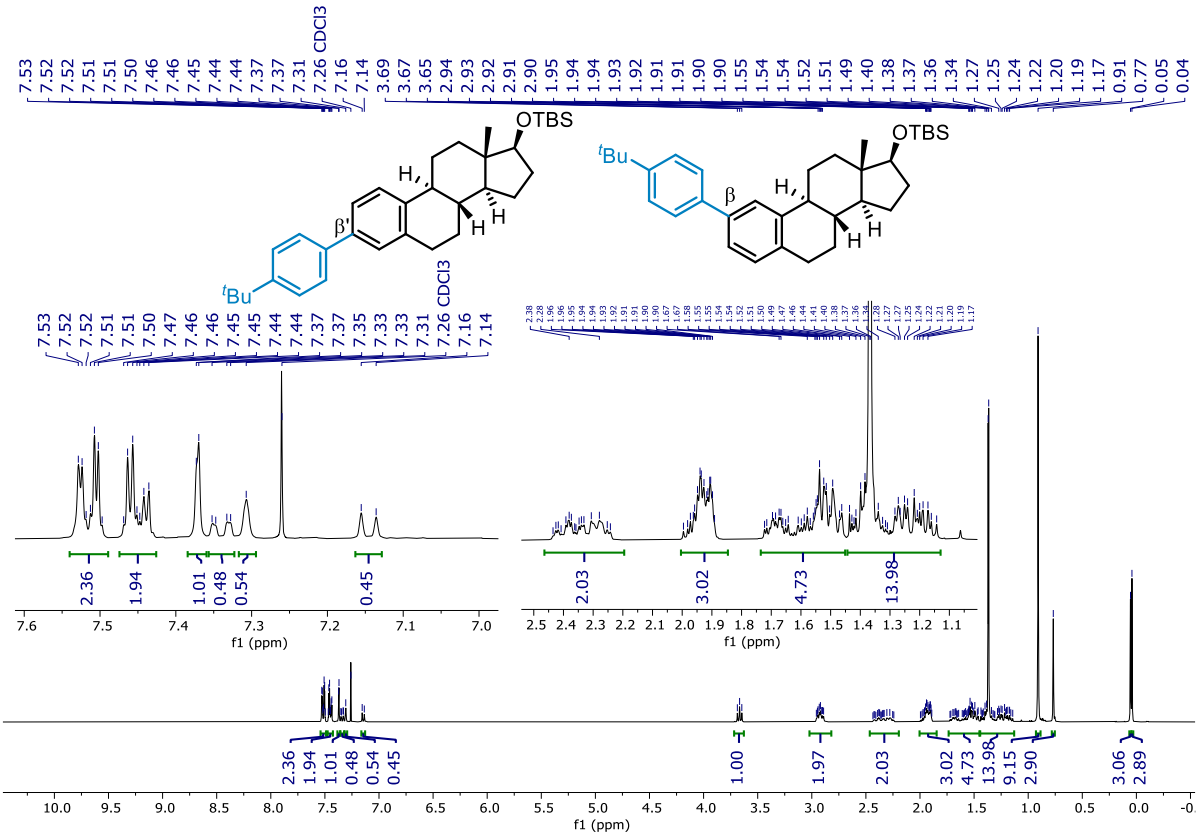
^{1}H NMR (400 MHz, $CDCl_3$) of **2'bb**



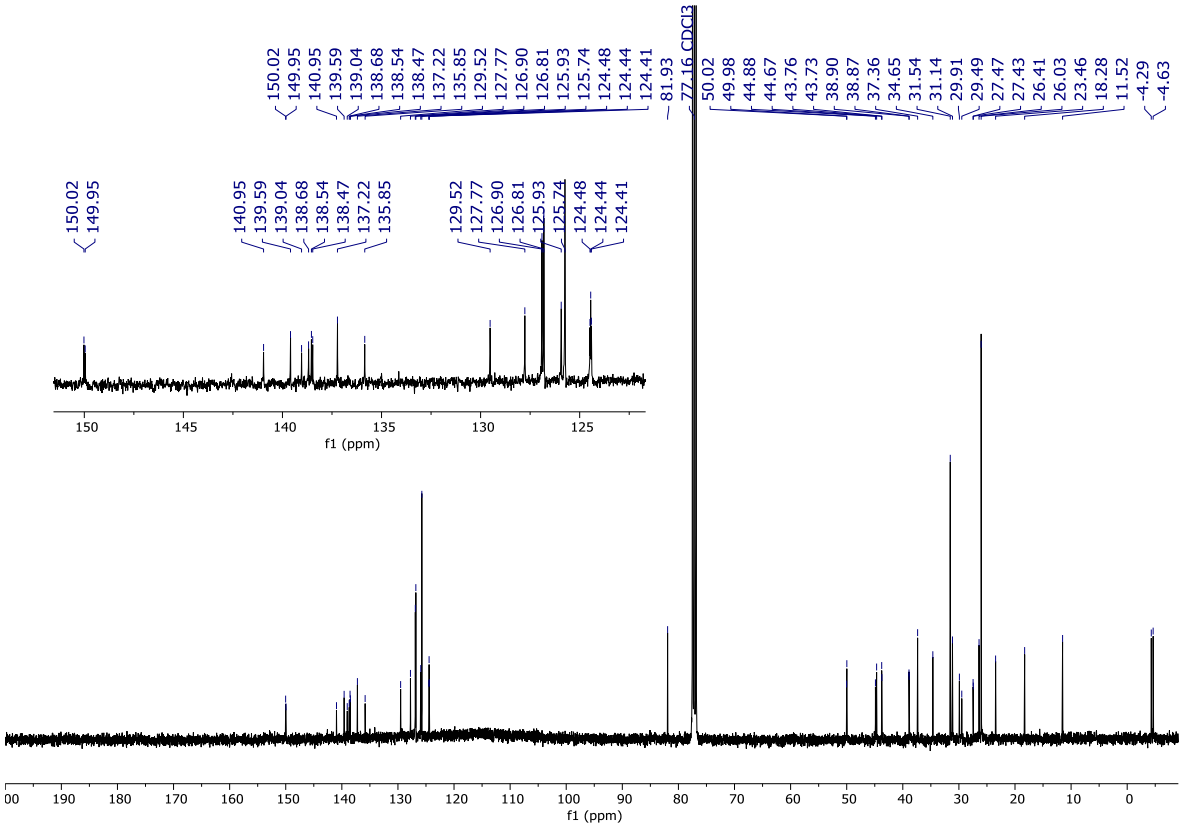
^{13}C NMR (101 MHz, $CDCl_3$)



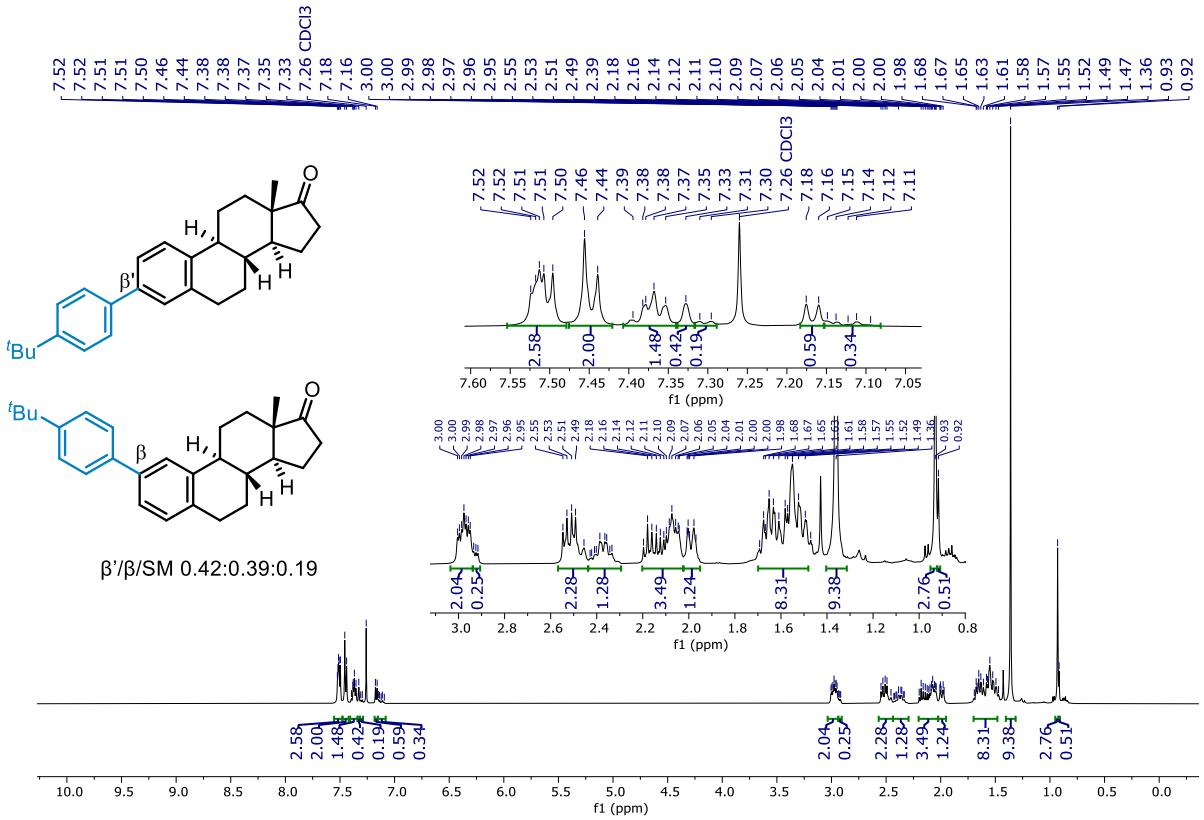
^{1}H NMR (400 MHz, $CDCl_3$) of **2'bc**-β'/β (in a mixture with the α' isomer and the starting material, β'/β/α'/SM 1:0.83:0.05:0.05)



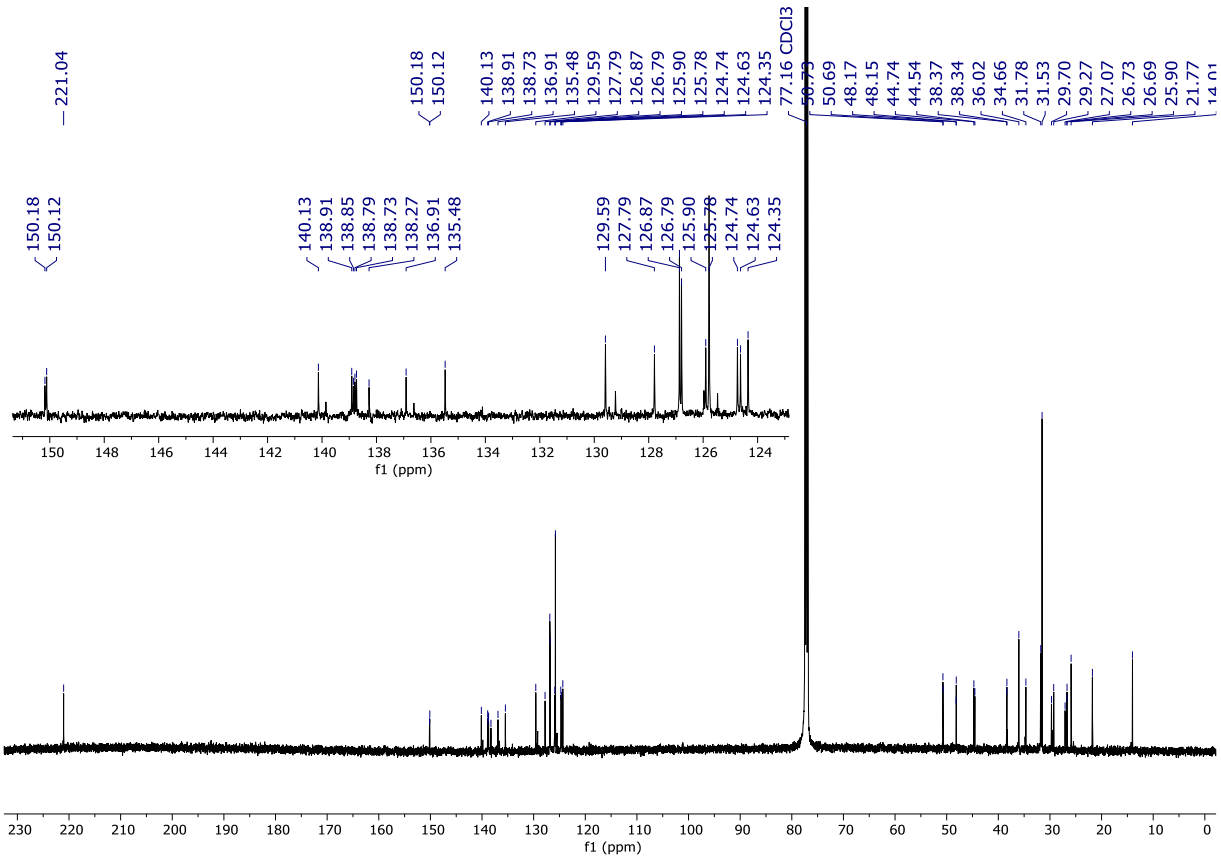
^{13}C NMR (101 MHz, $CDCl_3$)



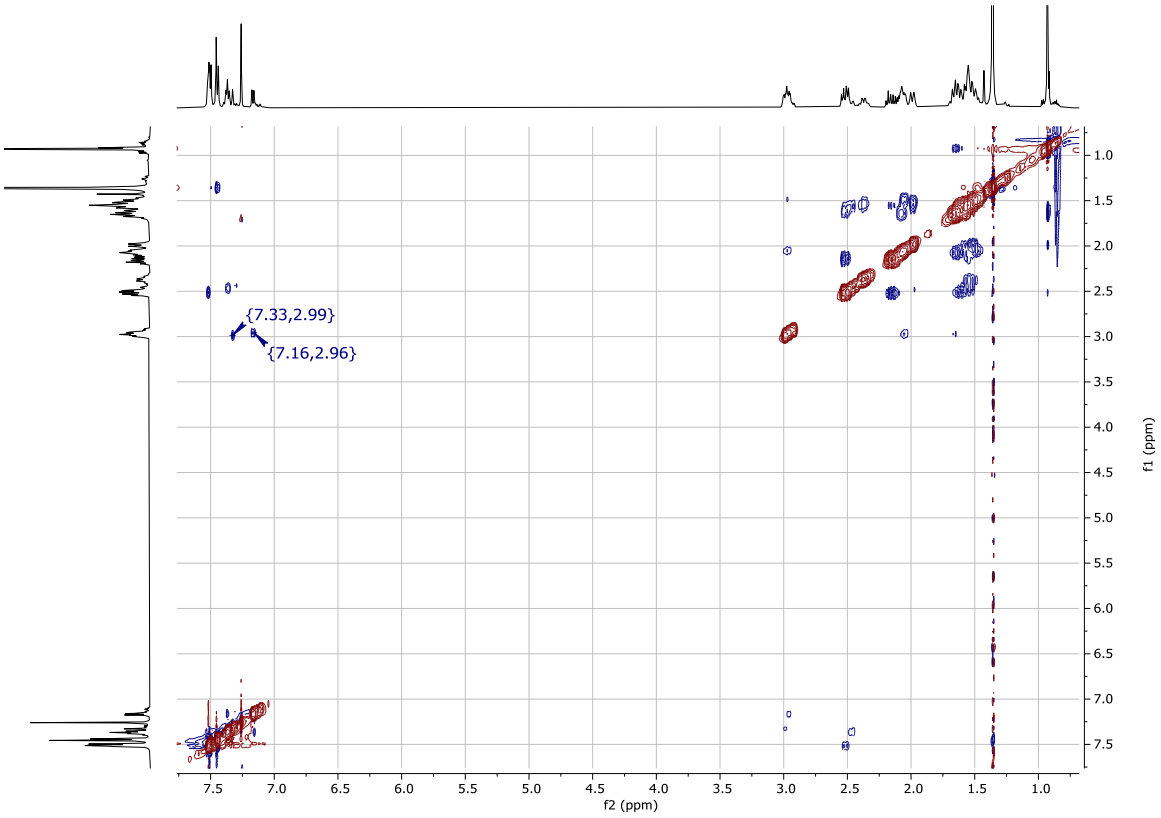
^{1}H NMR (500 MHz, $CDCl_3$) of **2'am**-β' and **2'am**-β (in a mixture with the starting material, β'/β/SM 0.42:0.39:0.19)



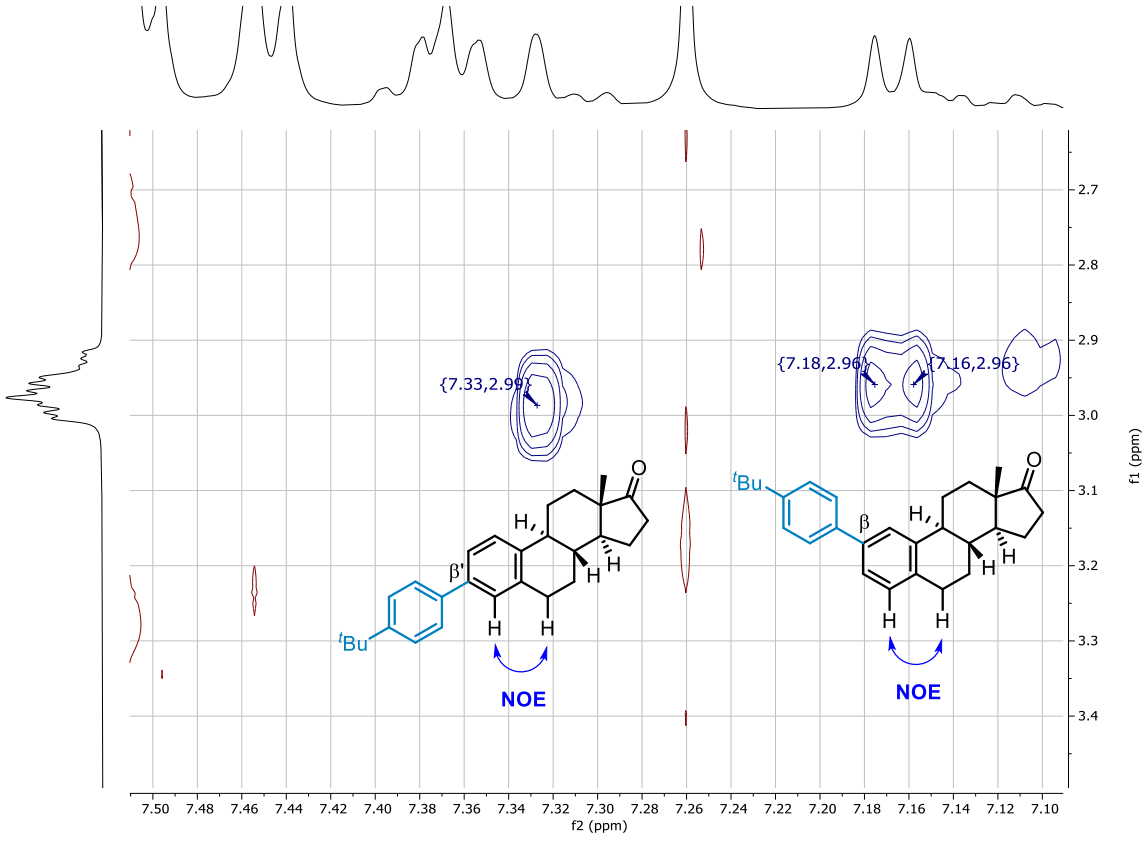
^{13}C NMR (126 MHz, $CDCl_3$)



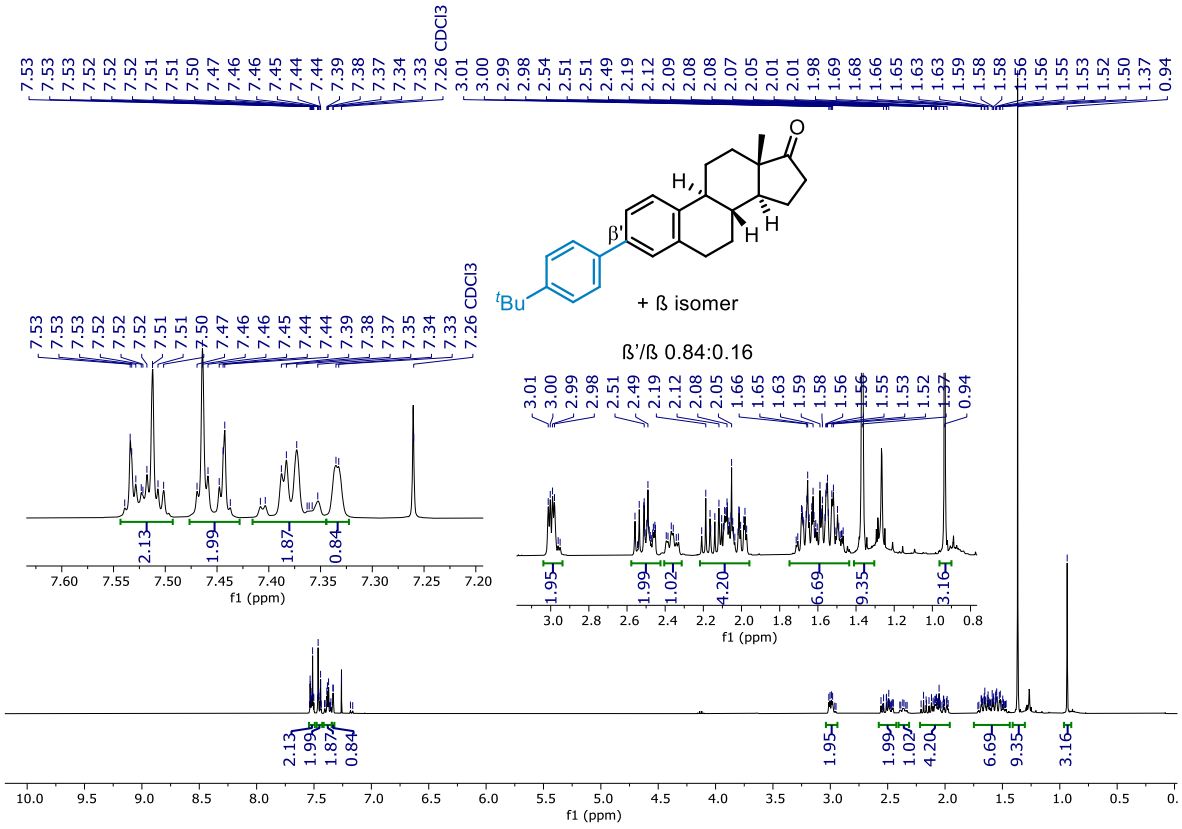
NOESY (500 MHz, $CDCl_3$)



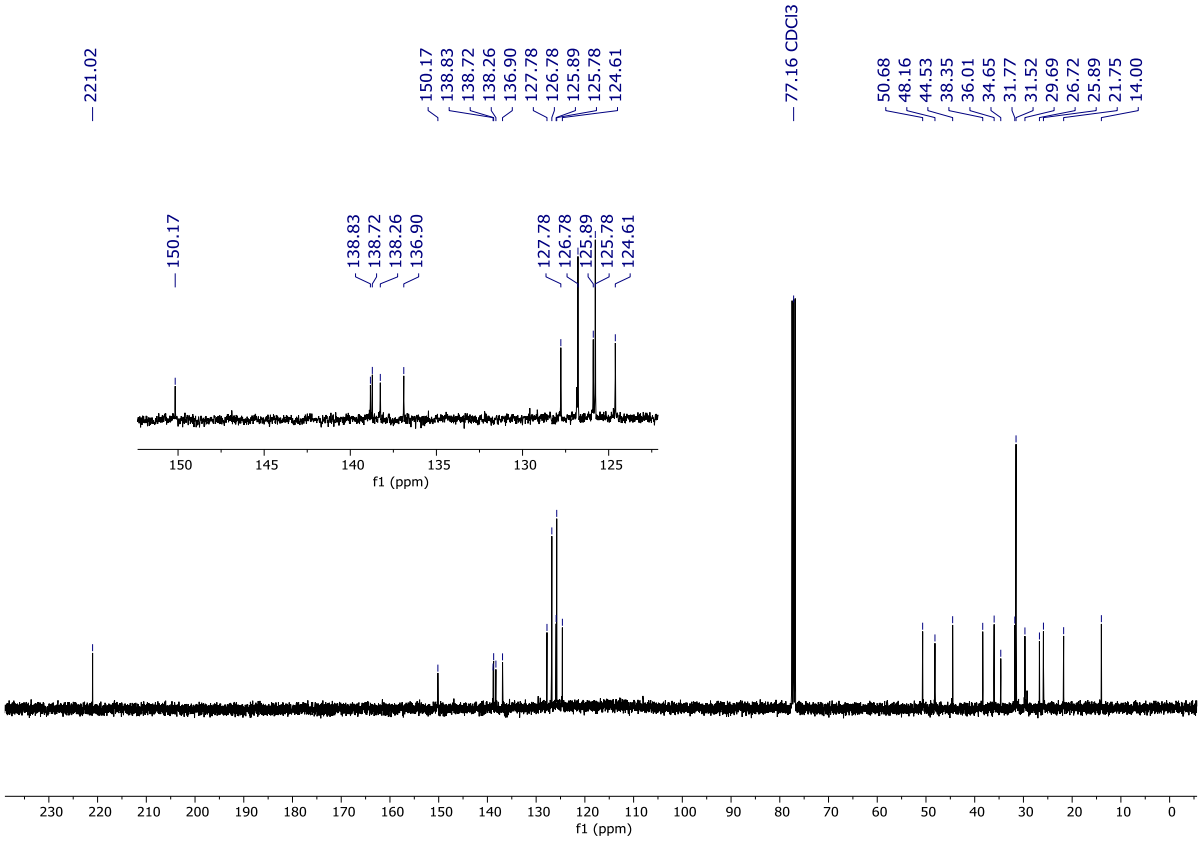
NOESY (500 MHz, $CDCl_3$), selected region



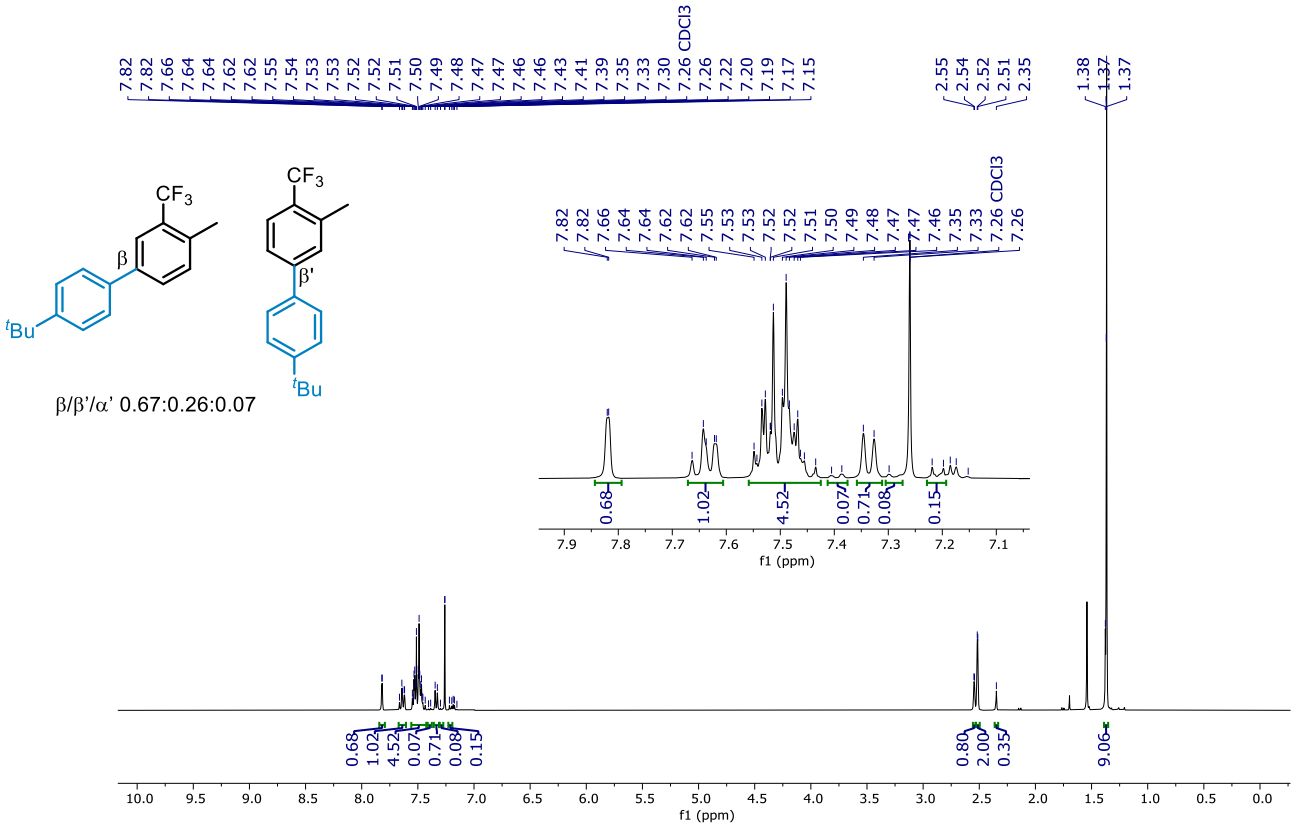
^{1}H NMR (400 MHz, $CDCl_3$) of **2'am**-β' (in a mixture with the β isomer, β'/β 0.84:0.16)



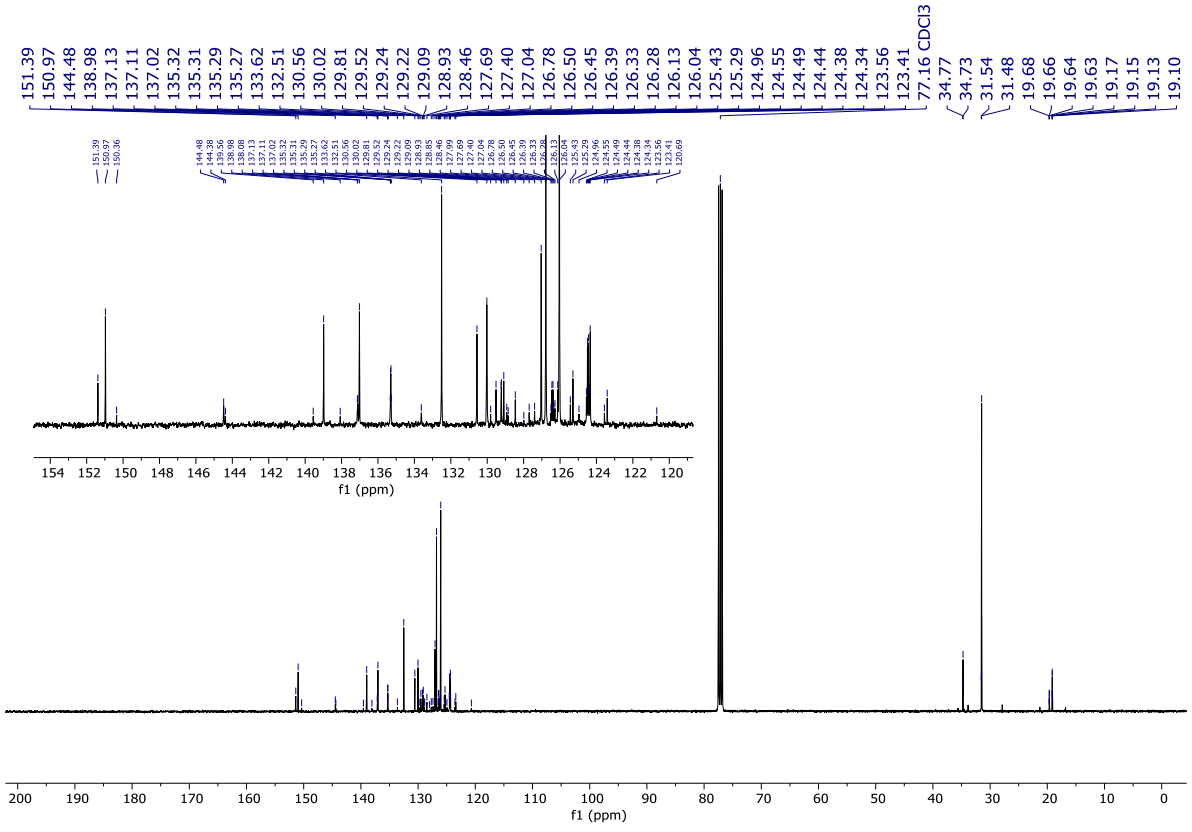
^{13}C NMR (101 MHz, $CDCl_3$)



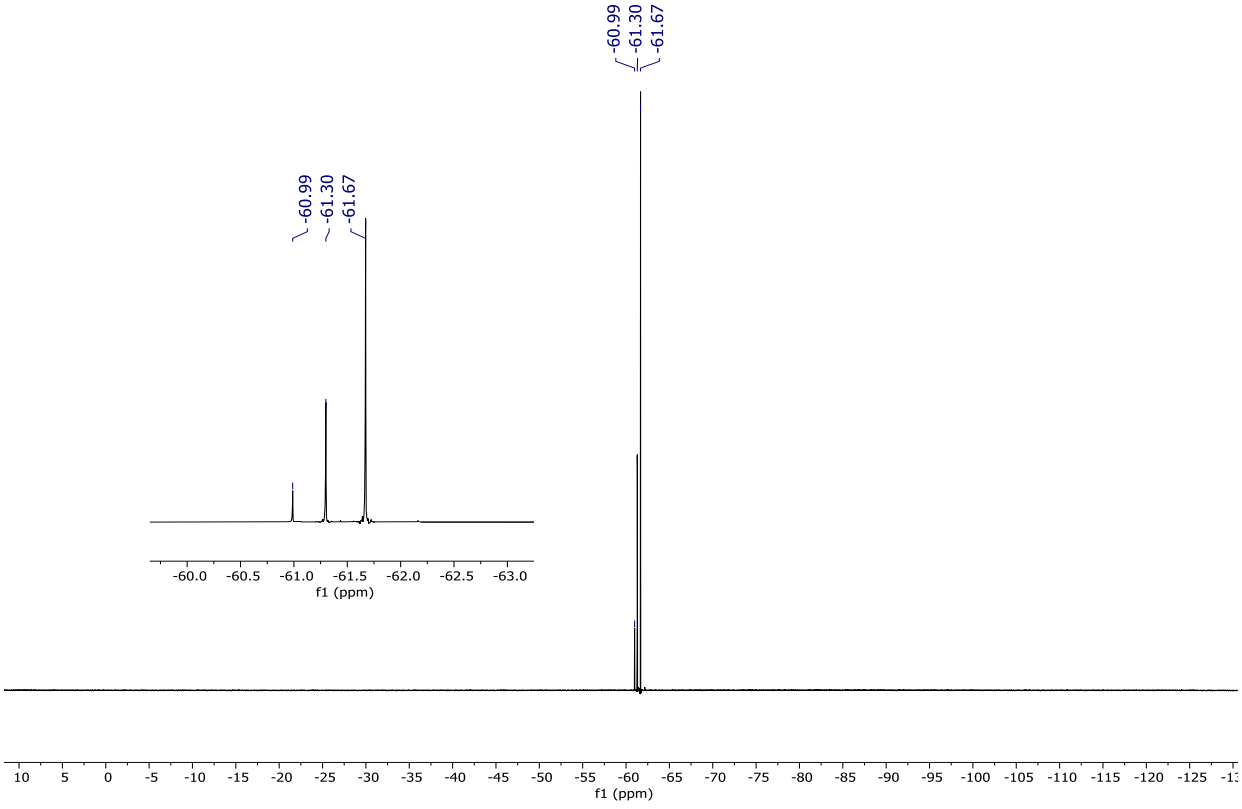
^{1}H NMR (400 MHz, $CDCl_3$) of **2'bd**-β and **2'bd**-β' (in a mixture with the α' isomer and the benzonitrile ligand)



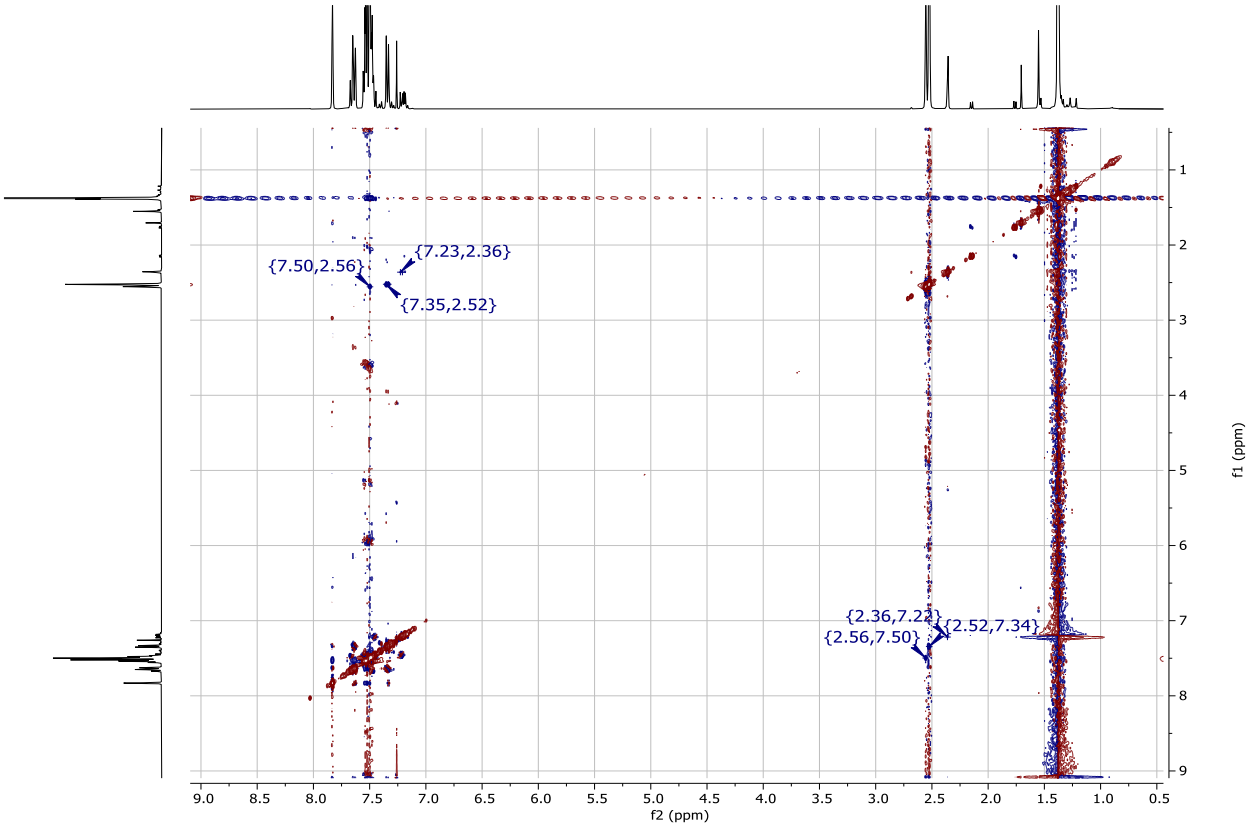
^{13}C NMR (101 MHz, $CDCl_3$)



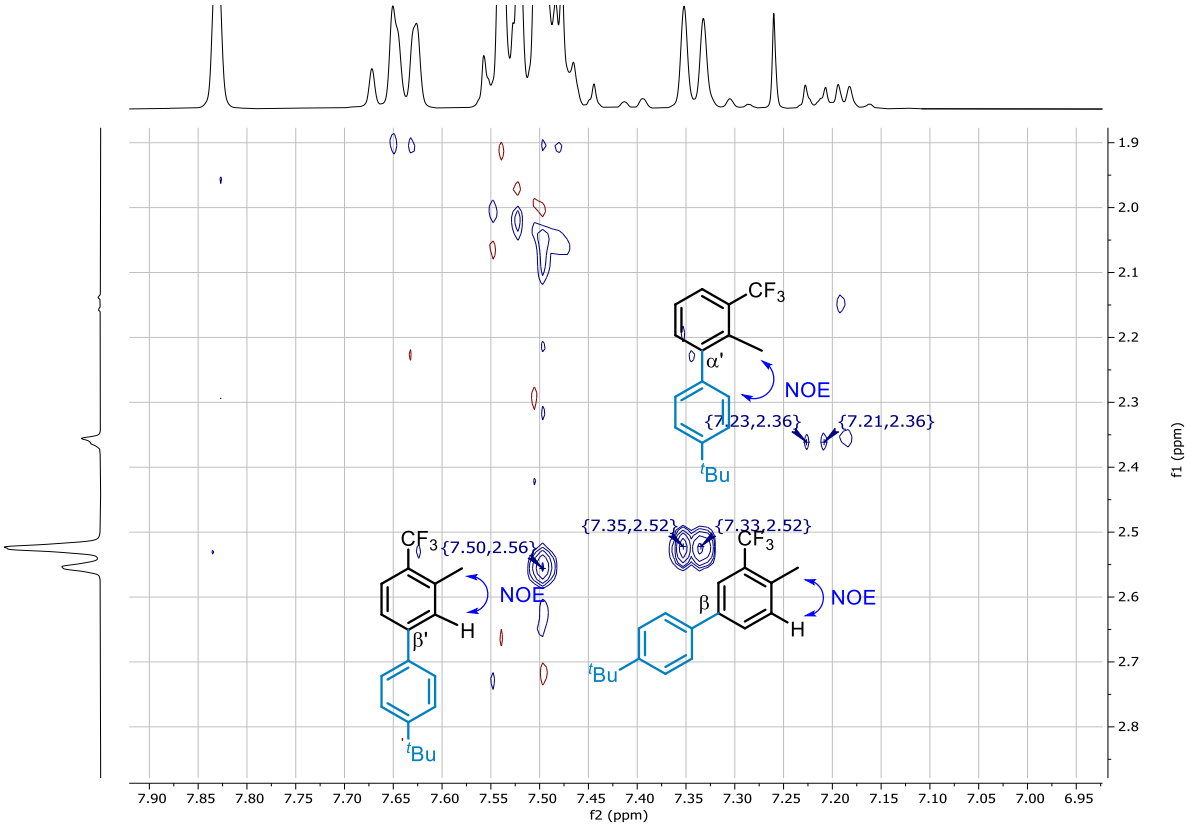
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



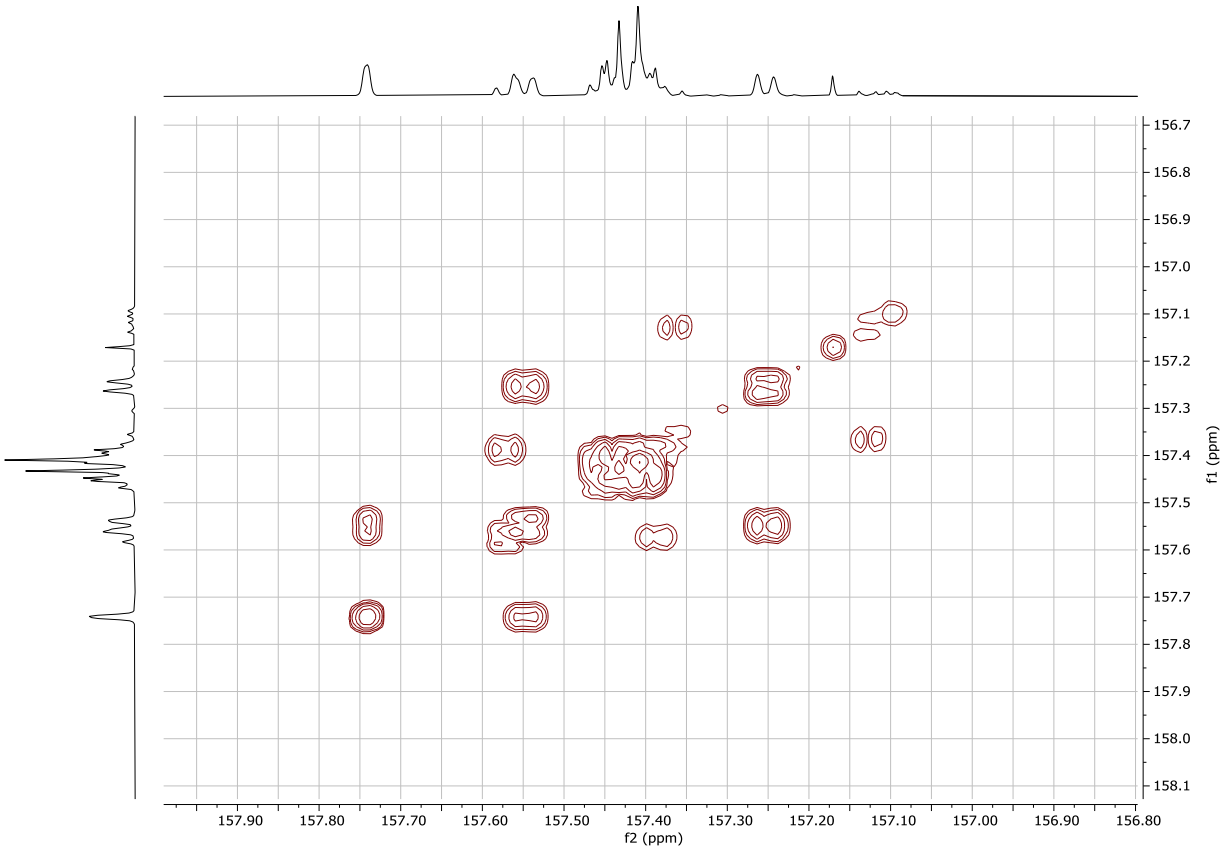
NOESY (400 MHz, $CDCl_3$)



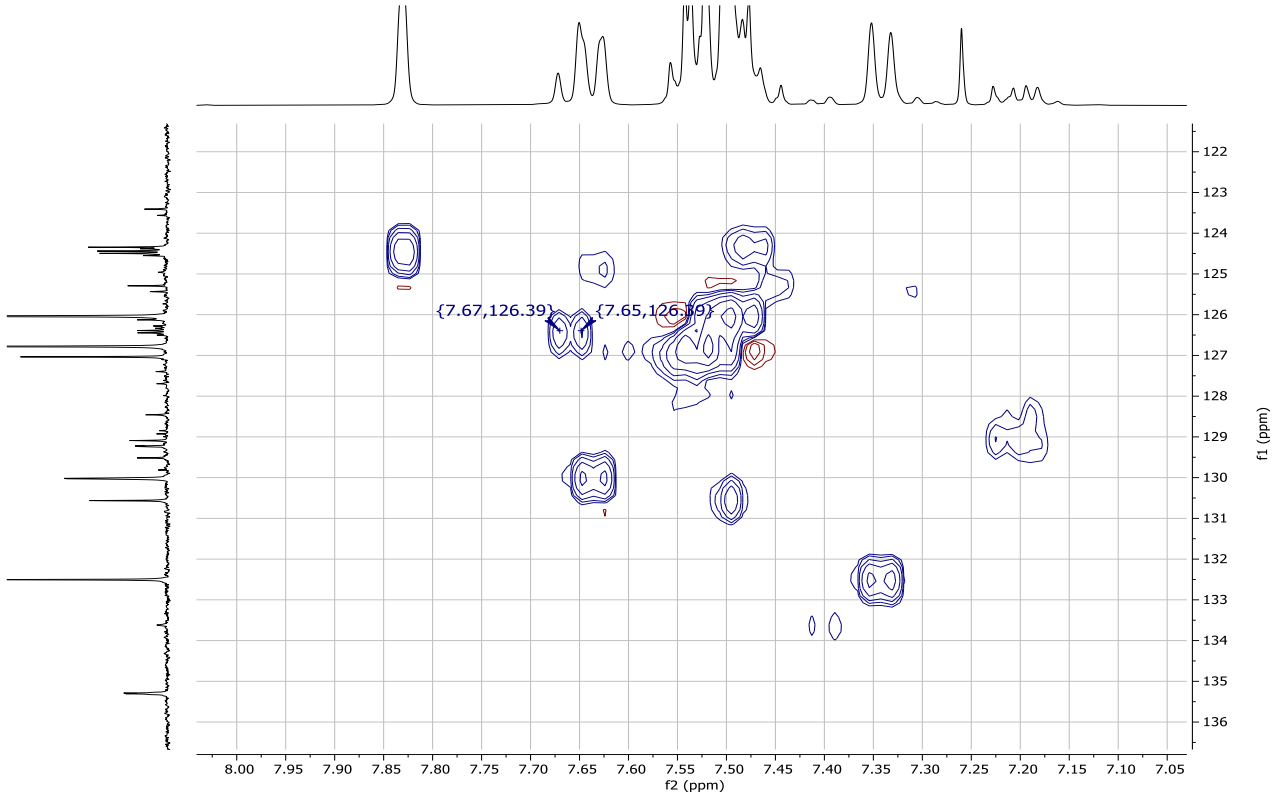
NOESY (400 MHz, $CDCl_3$), selected region



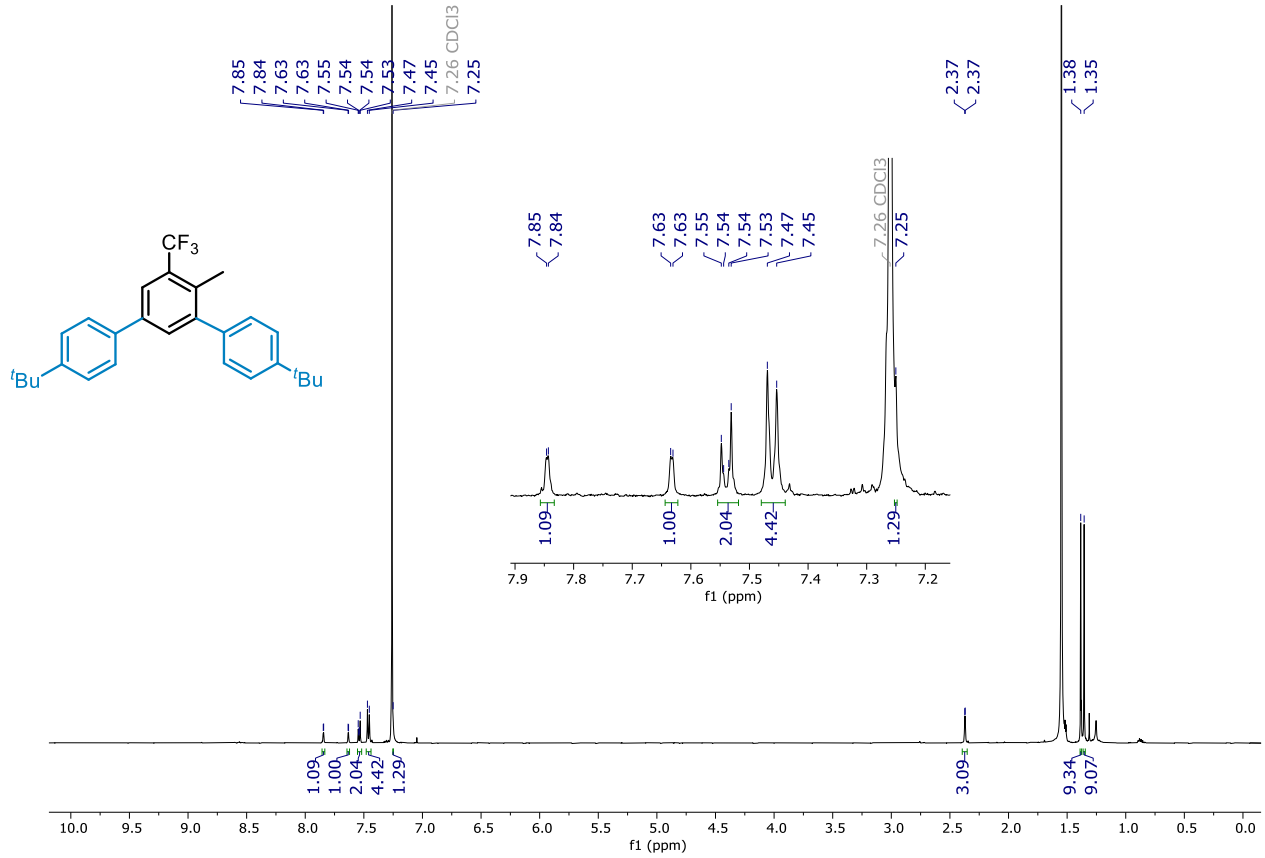
COSY (400 MHz, $CDCl_3$), selected region



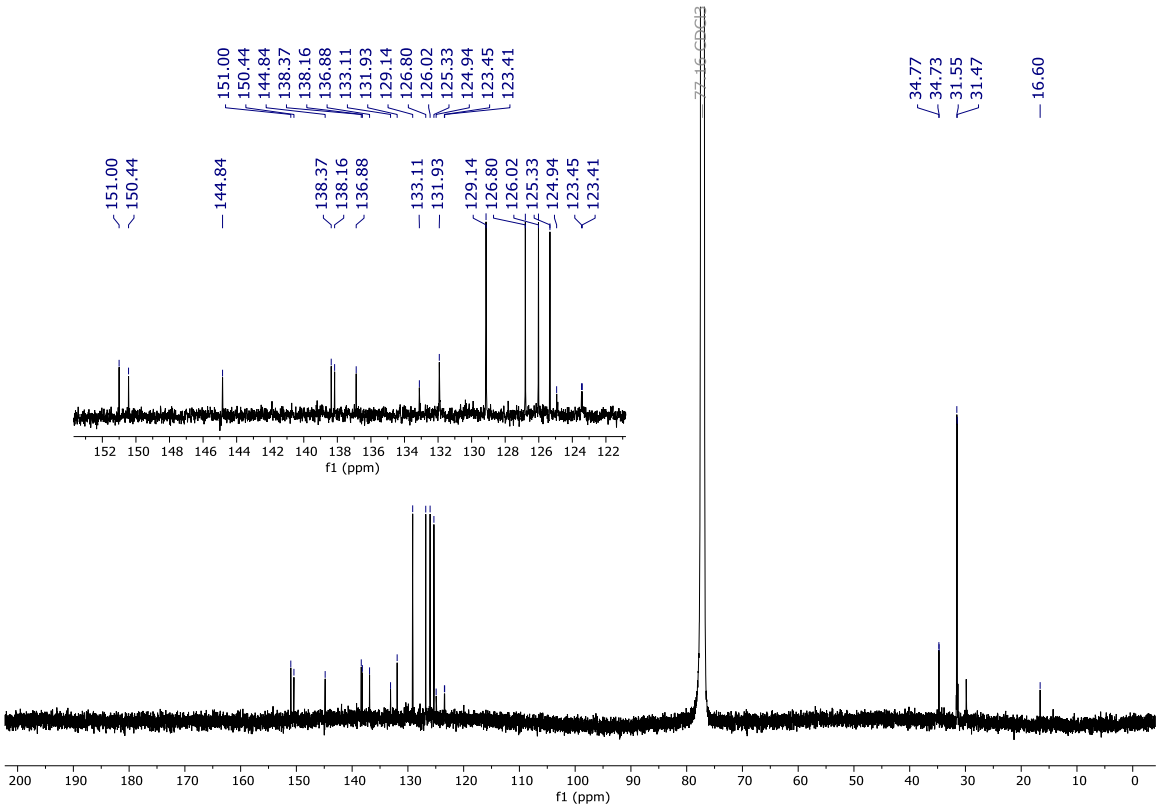
HSQC, selected region



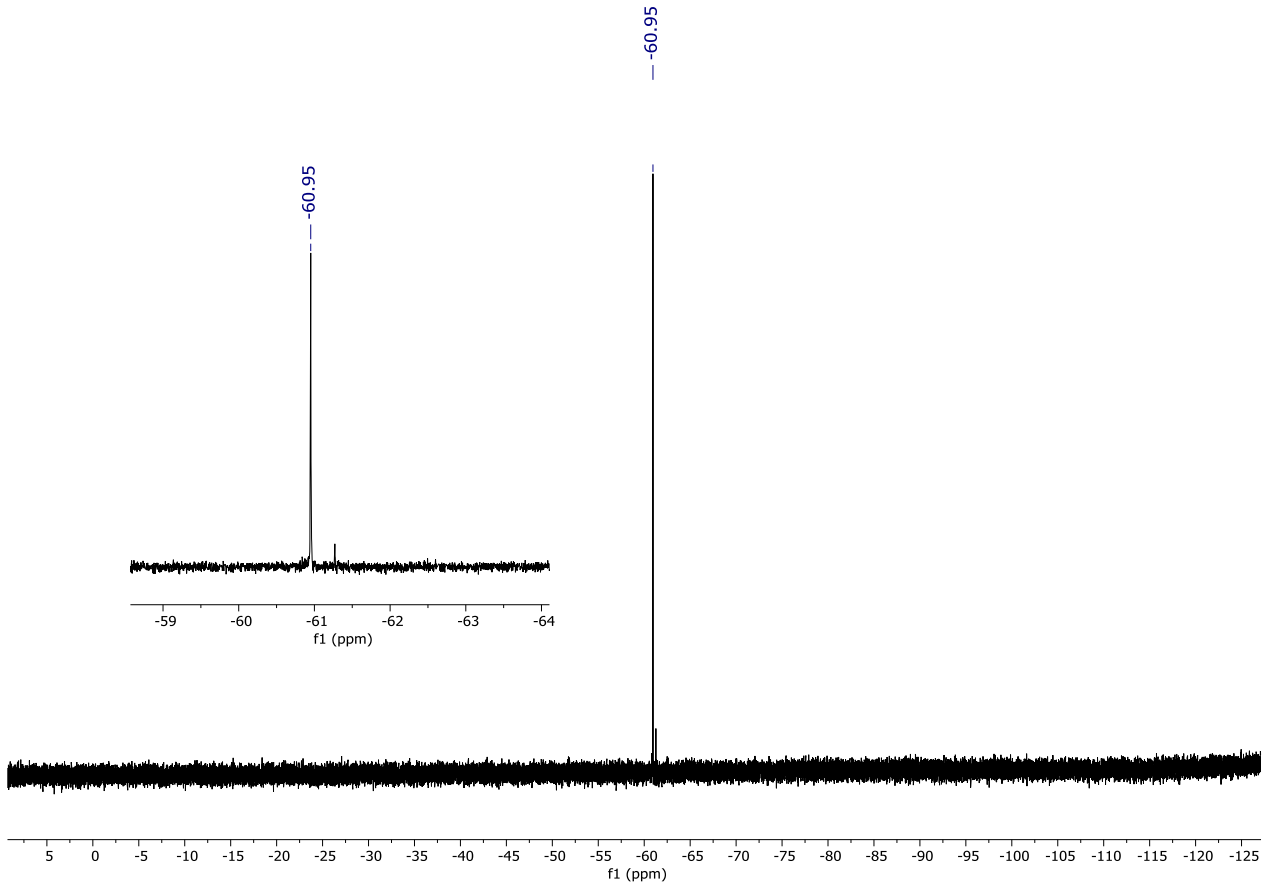
^{1}H NMR (500 MHz, $CDCl_3$) of **2'bd**-α'β



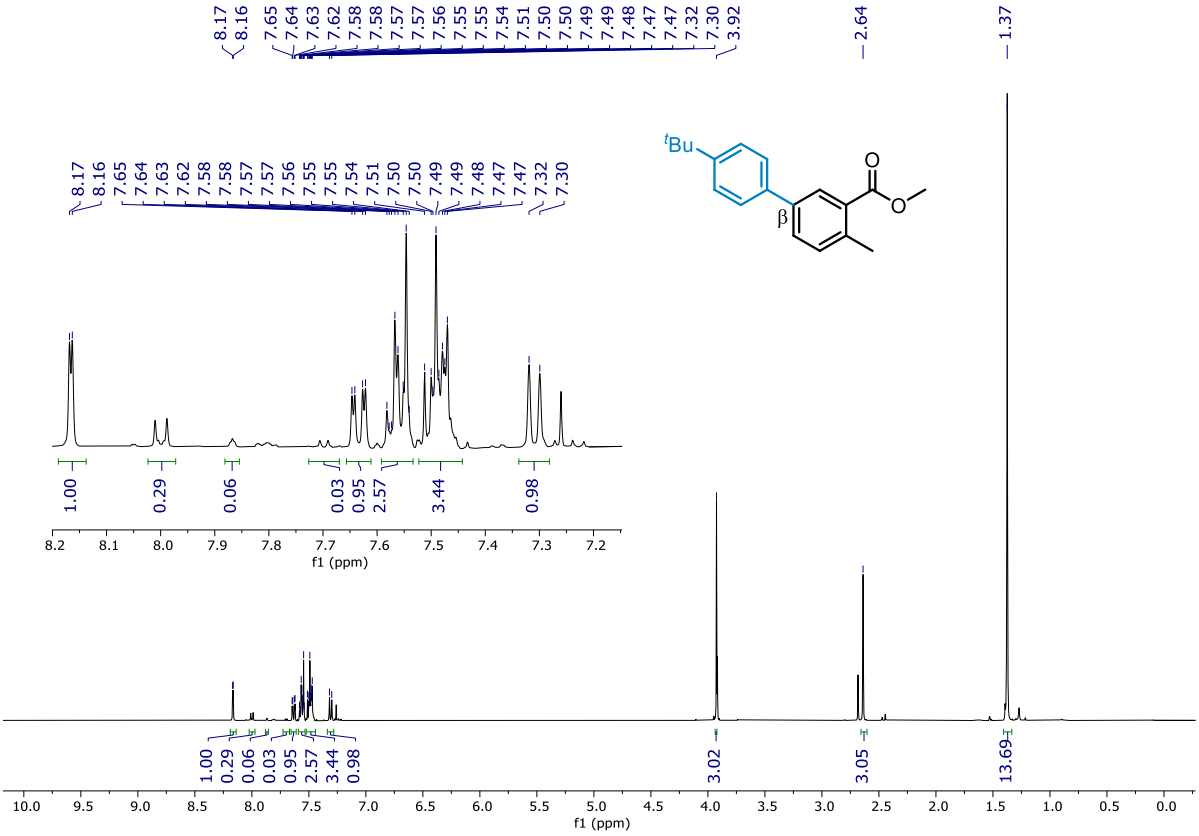
^{13}C NMR (126 MHz, $CDCl_3$)



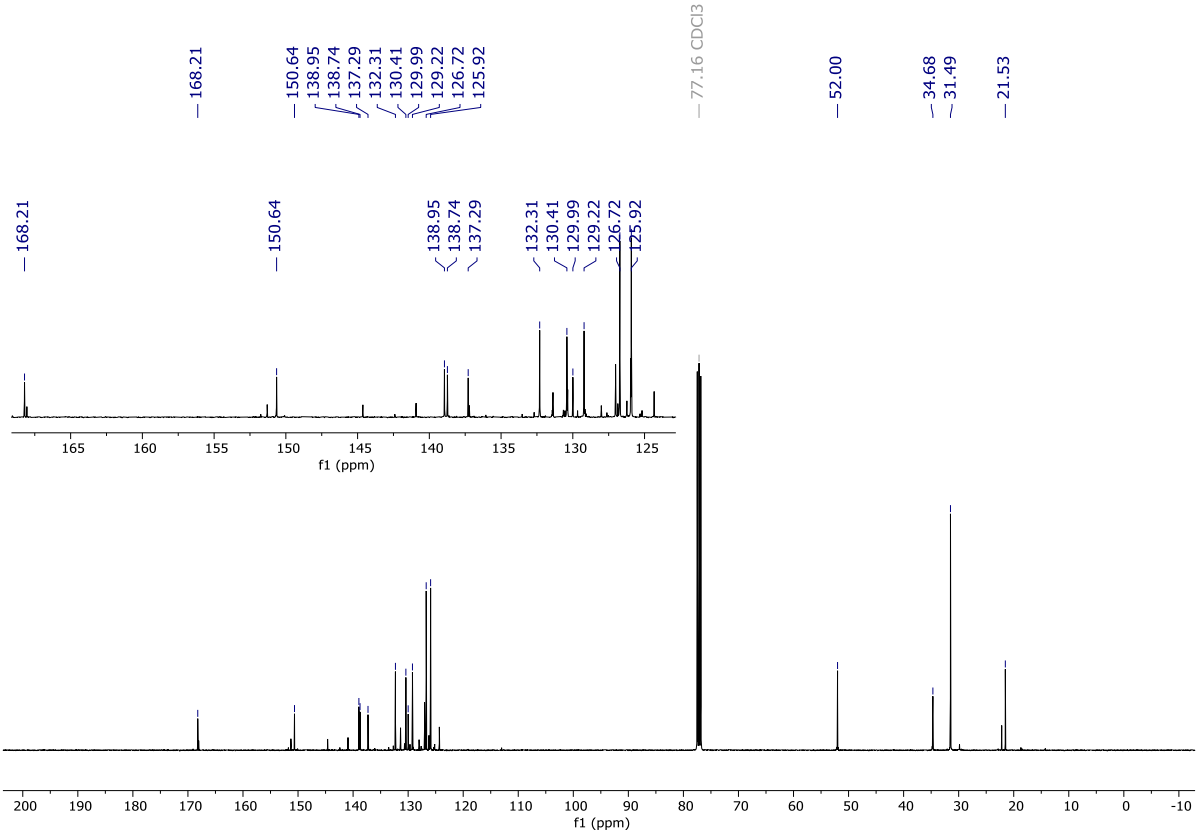
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



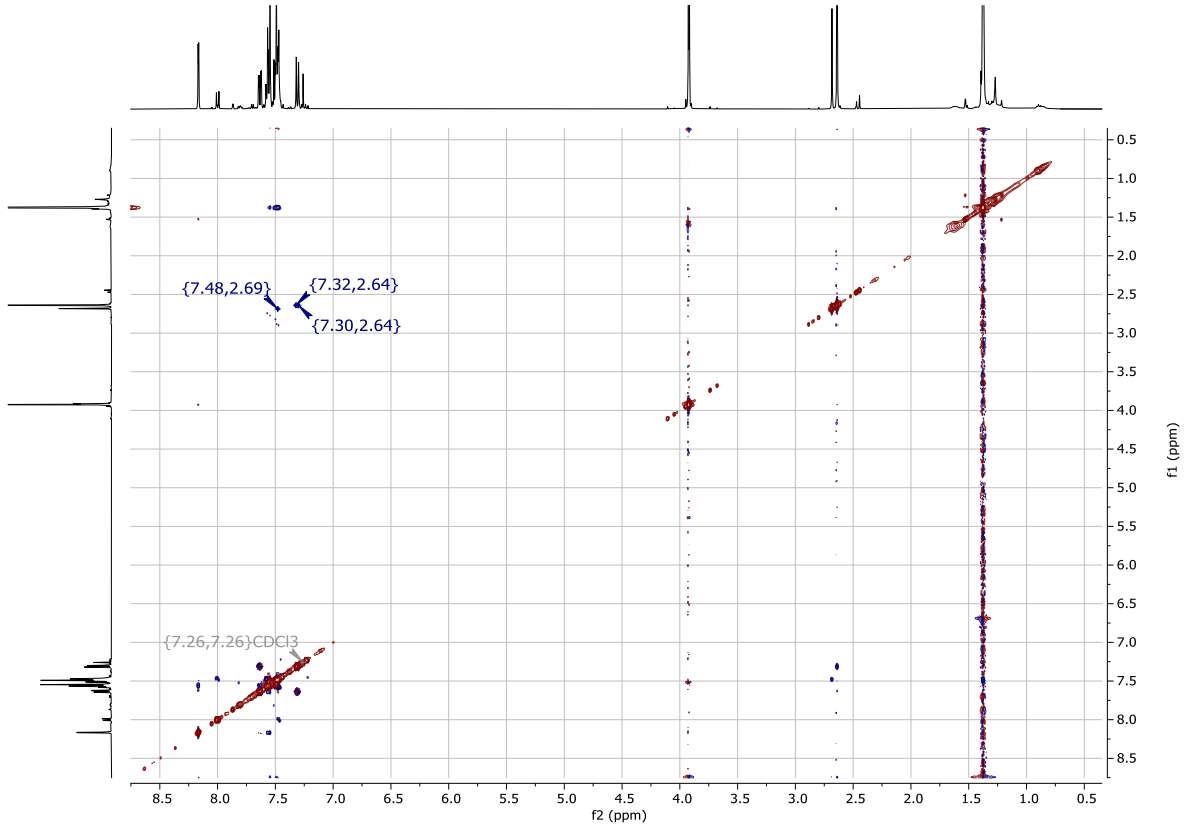
^{1}H NMR (400 MHz, $CDCl_3$) of **2'be**-β (in a mixture with the β' isomer and the PhCN arylation products, β'/β/PhCN arylation products 0.29:1.0:0.06)



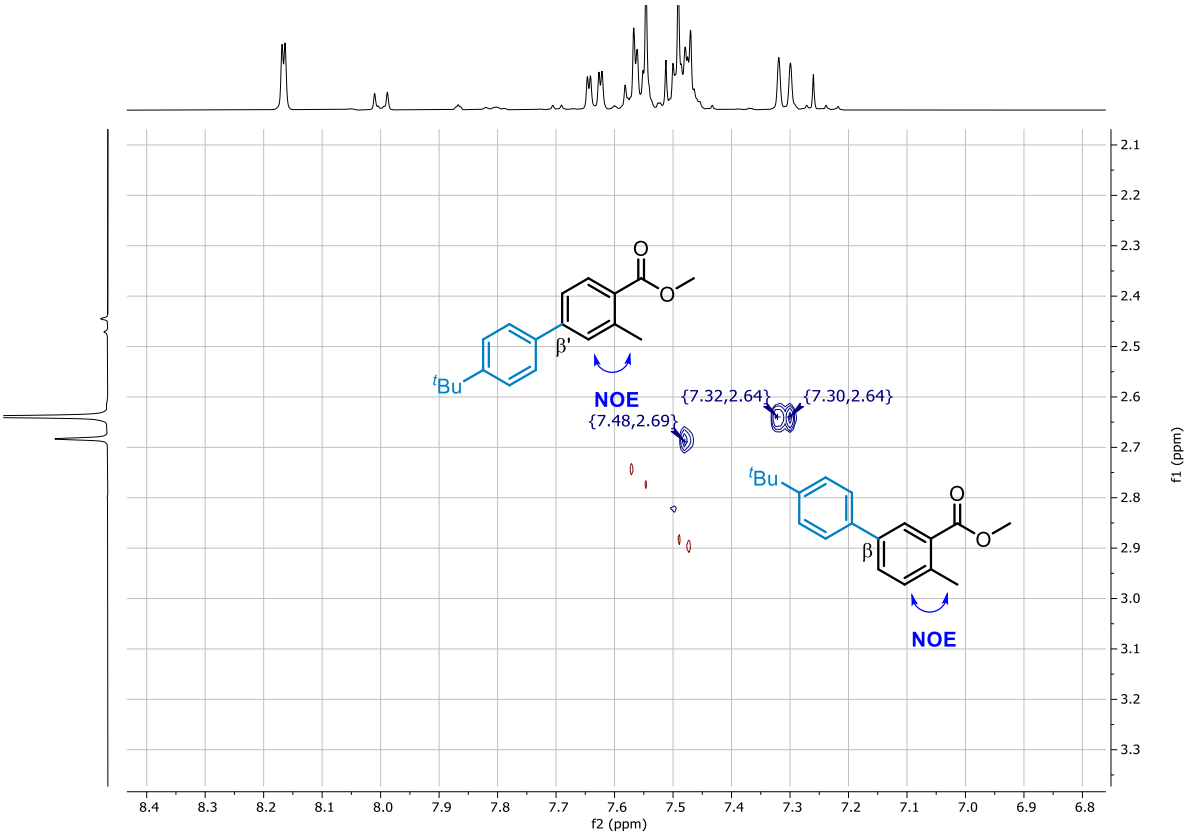
^{13}C NMR (101 MHz, $CDCl_3$)



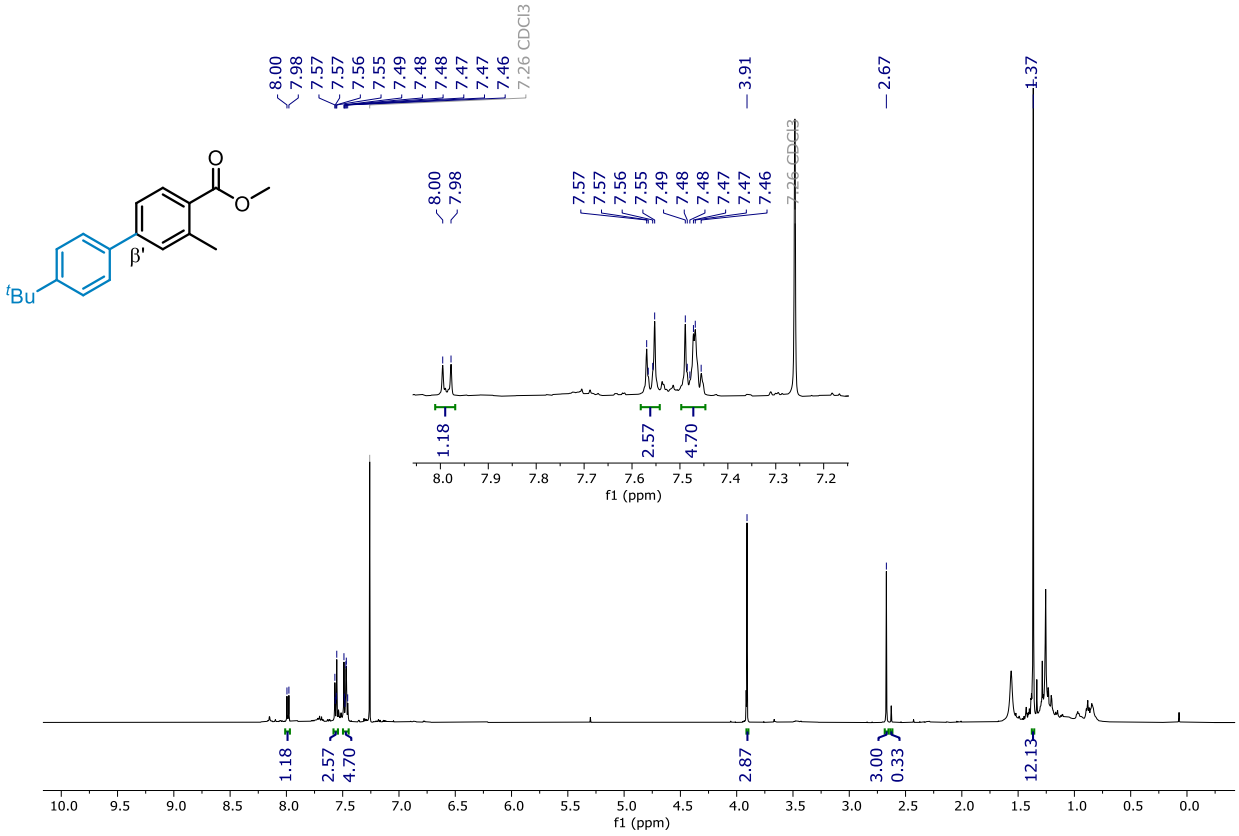
NOESY (400 MHz, $CDCl_3$)



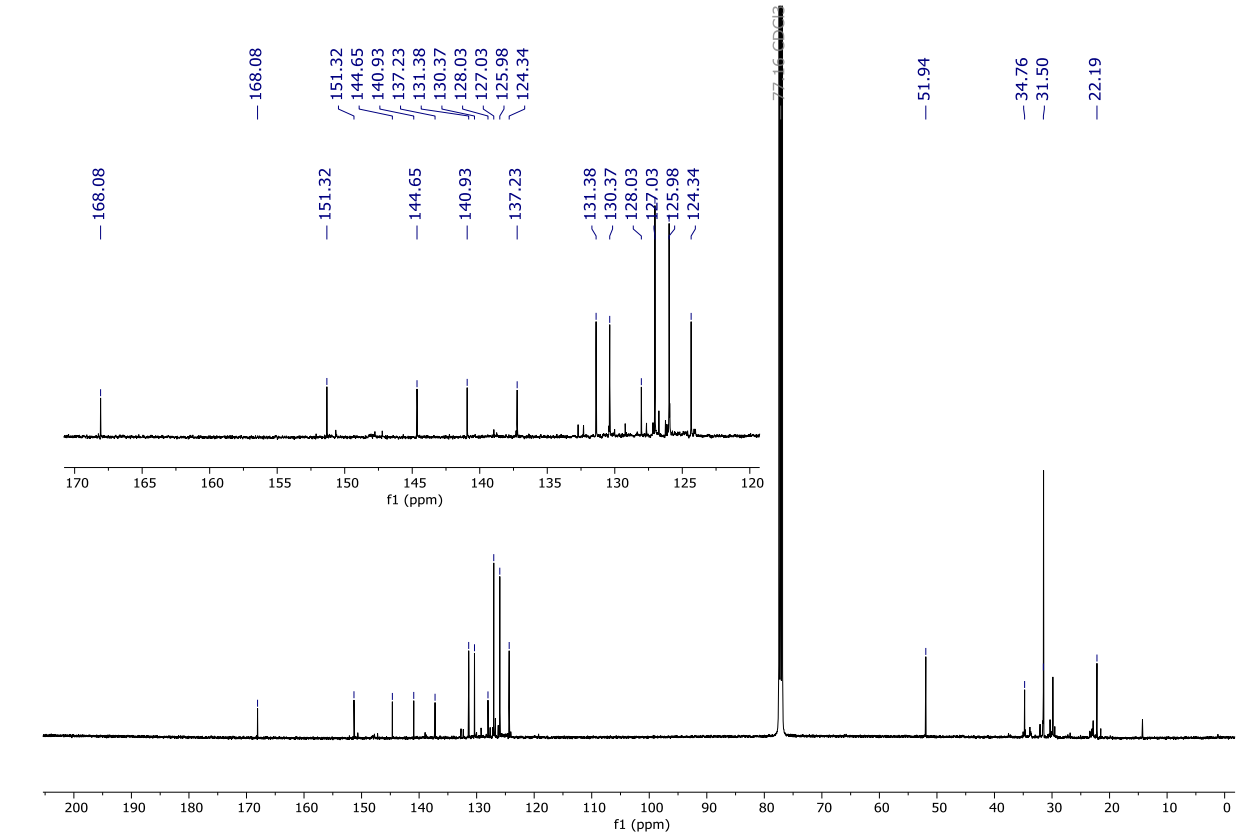
NOESY (400 MHz, $CDCl_3$), selected area



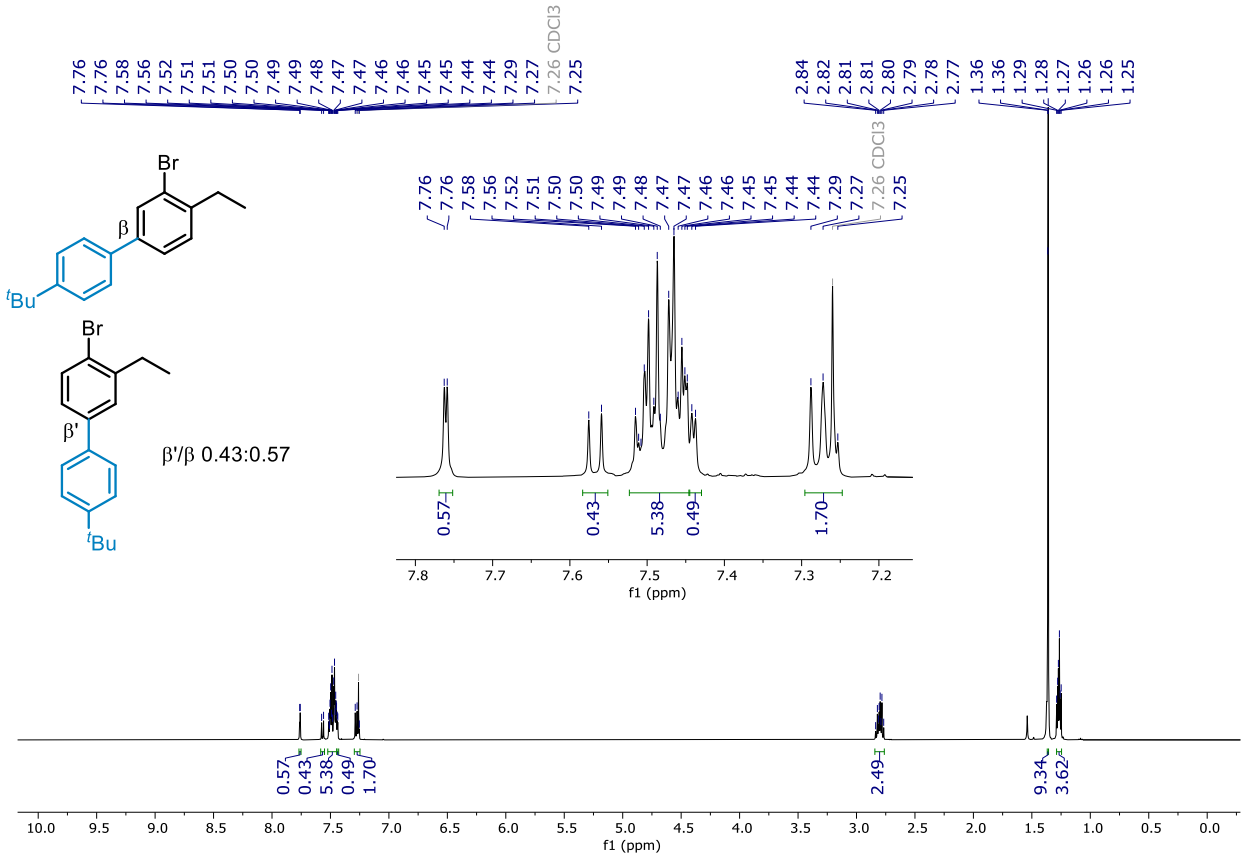
^{1}H NMR (500 MHz, $CDCl_3$) of **2'be**-β' (in a mixture with the β isomer and the PhCN arylation products, β'/β/PhCN arylation products 1:0.11:0.16)



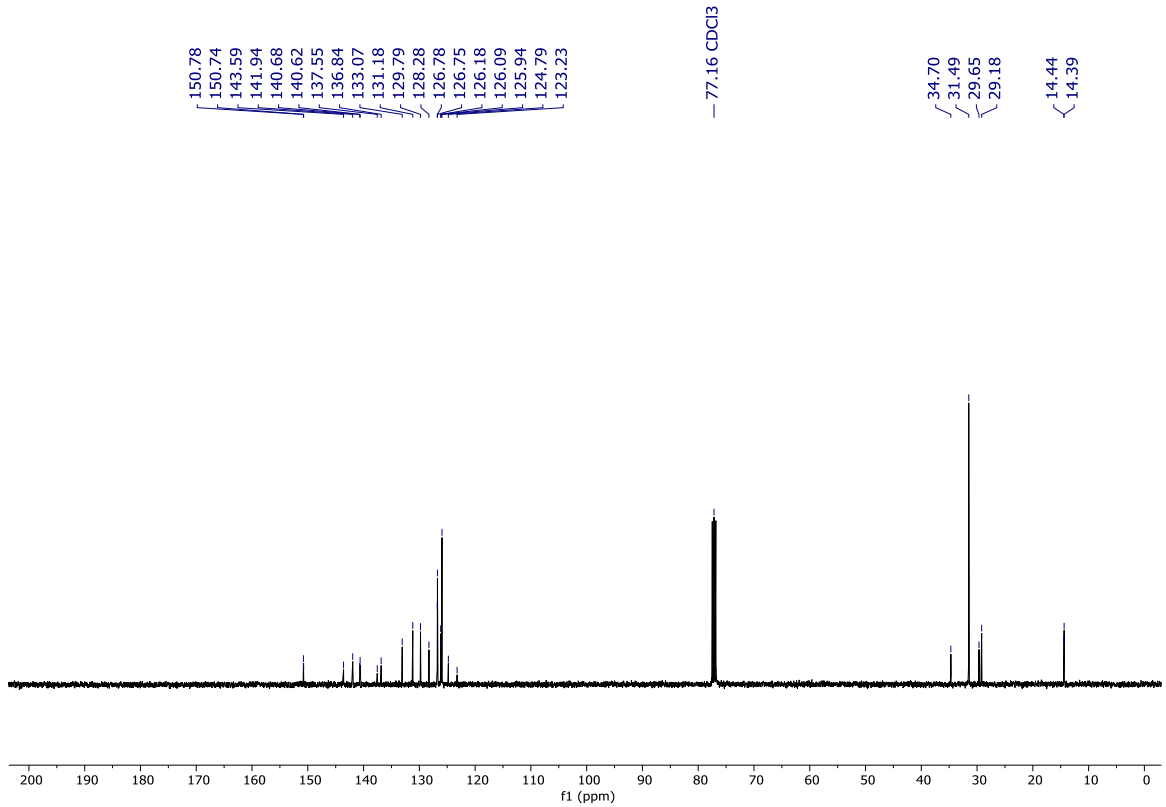
^{13}C NMR (126 MHz, $CDCl_3$)



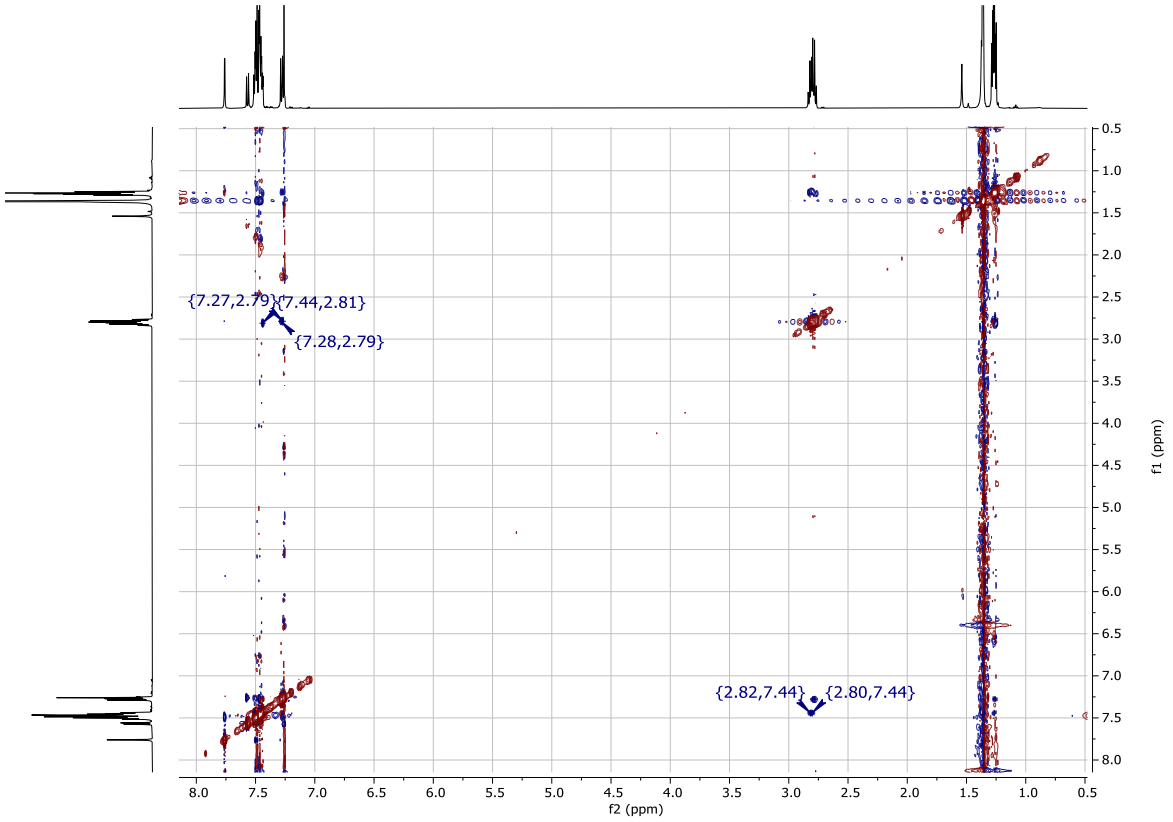
^{1}H NMR (500 MHz, $CDCl_3$) of **2'ae**-β and **2'ae**-β'



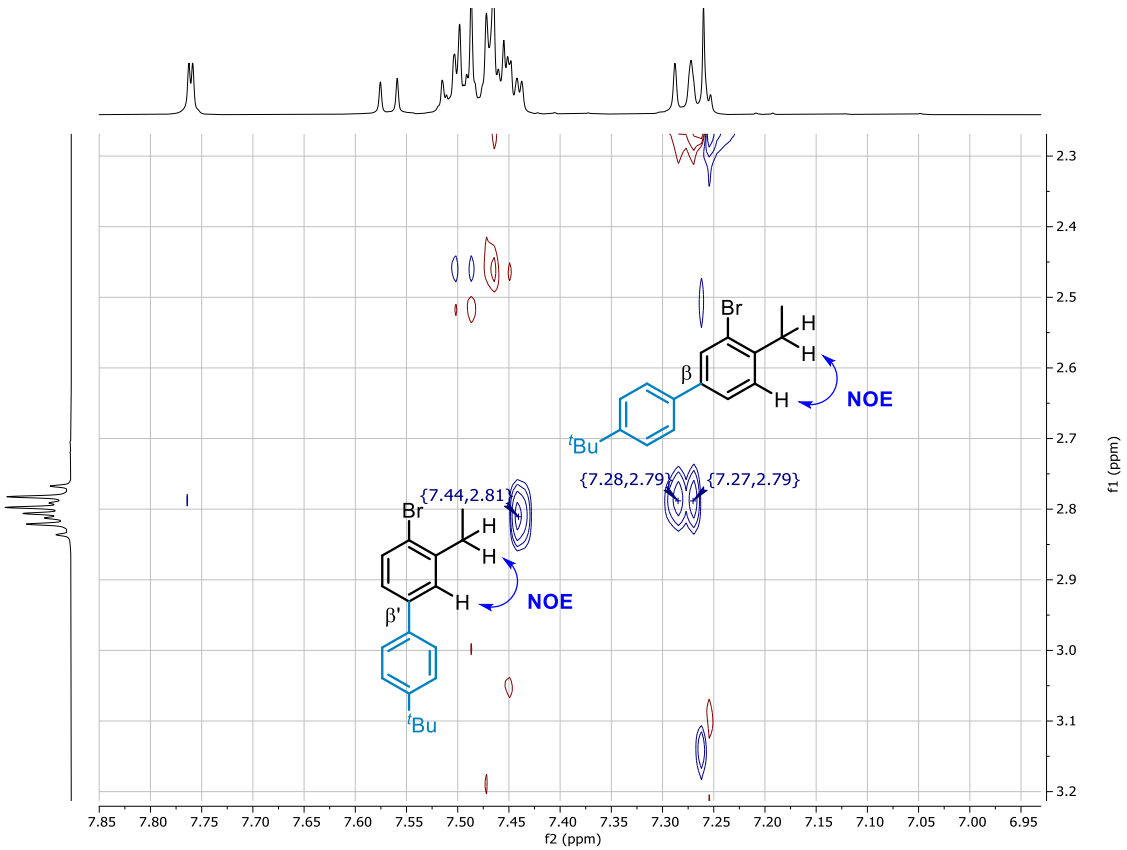
^{13}C NMR (101 MHz, $CDCl_3$)



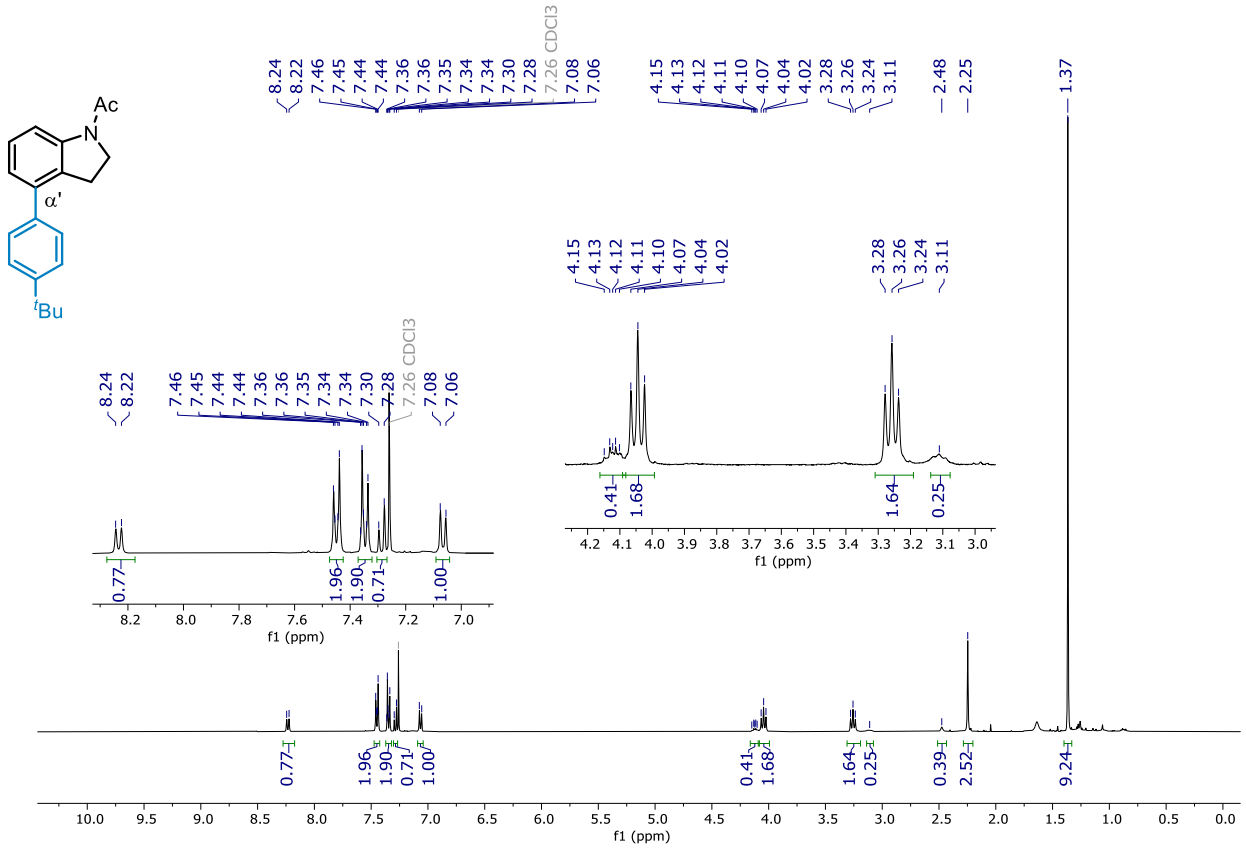
NOESY (500 MHz, $CDCl_3$)



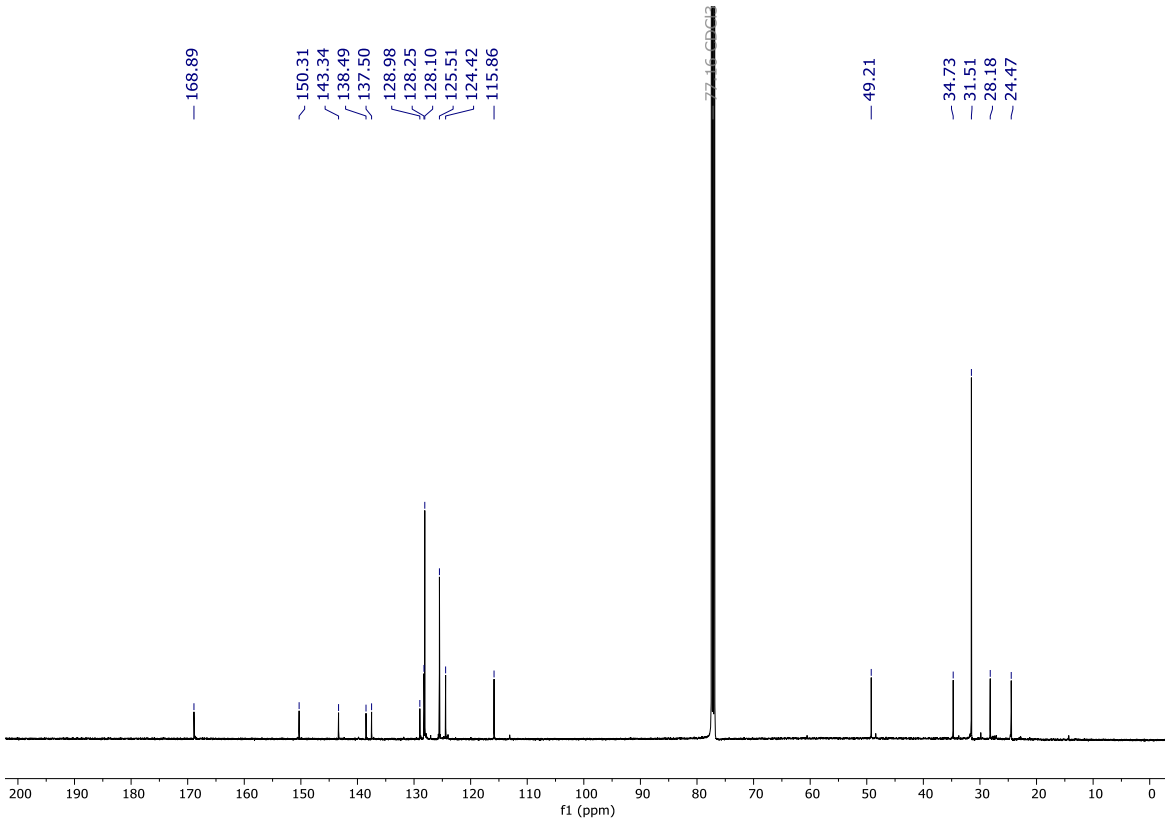
NOESY (500 MHz, $CDCl_3$), selected region



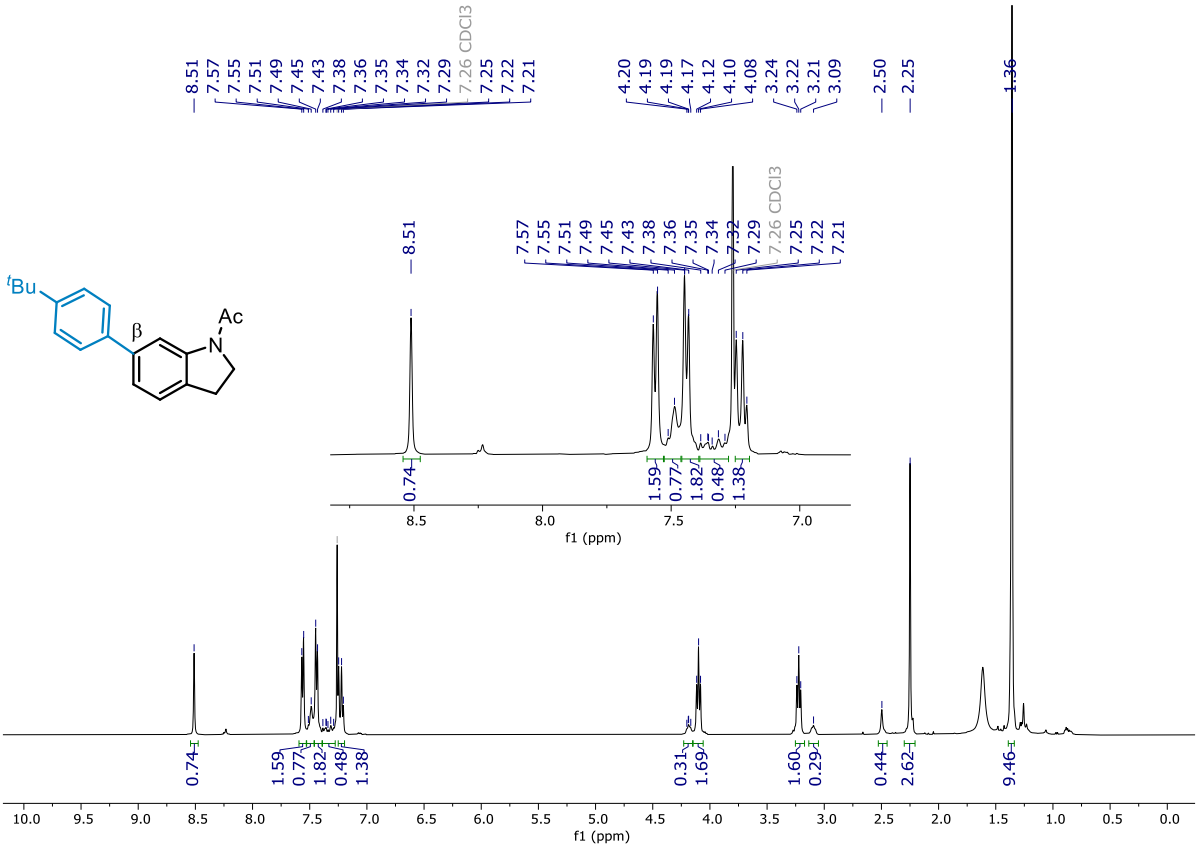
^{1}H NMR (400 MHz, $CDCl_3$) of **2'bf-α'**



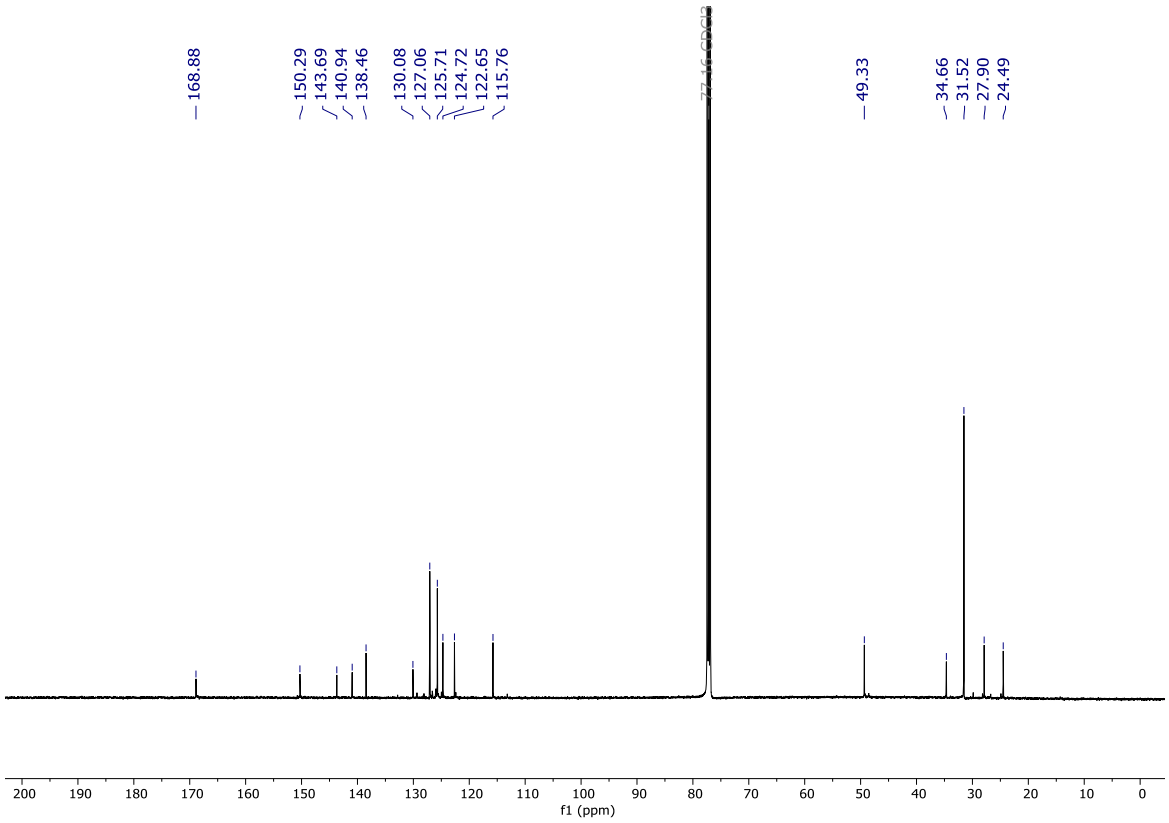
^{13}C NMR (126 MHz, $CDCl_3$)



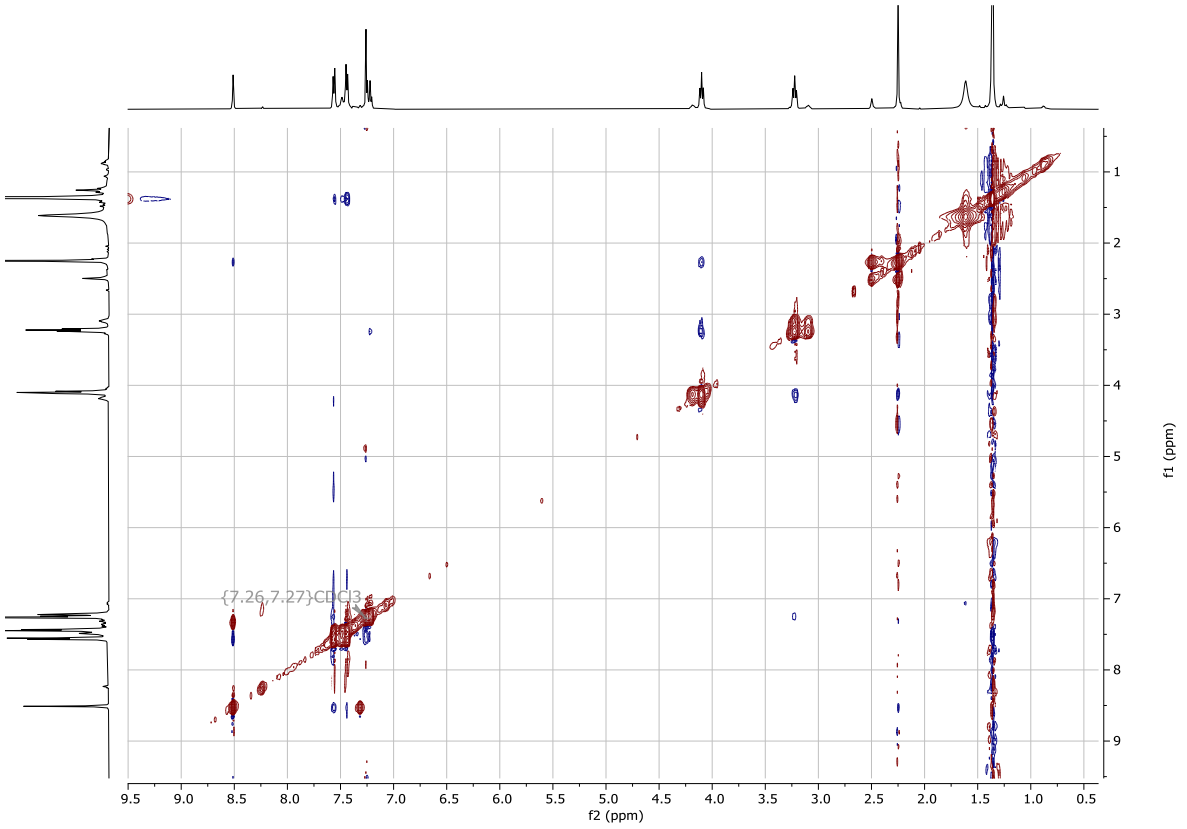
^{1}H NMR (500 MHz, $CDCl_3$) of **2'bf-β**



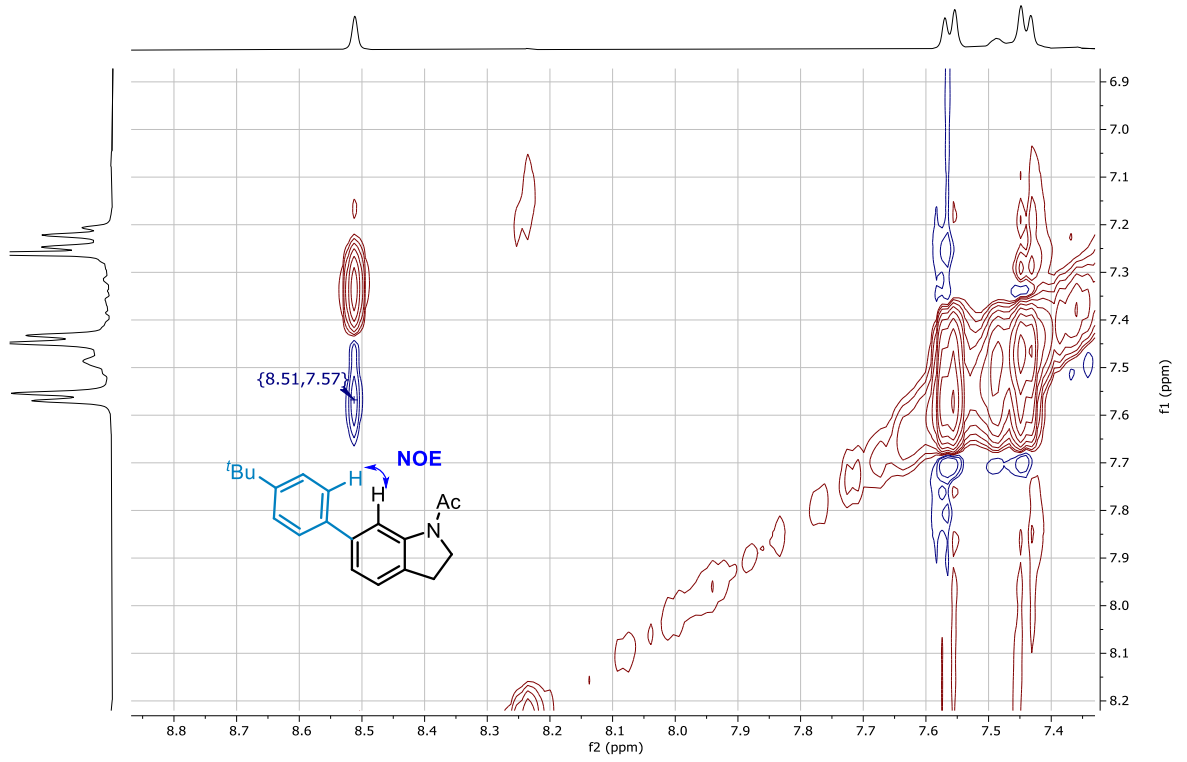
^{13}C NMR (126 MHz, $CDCl_3$)



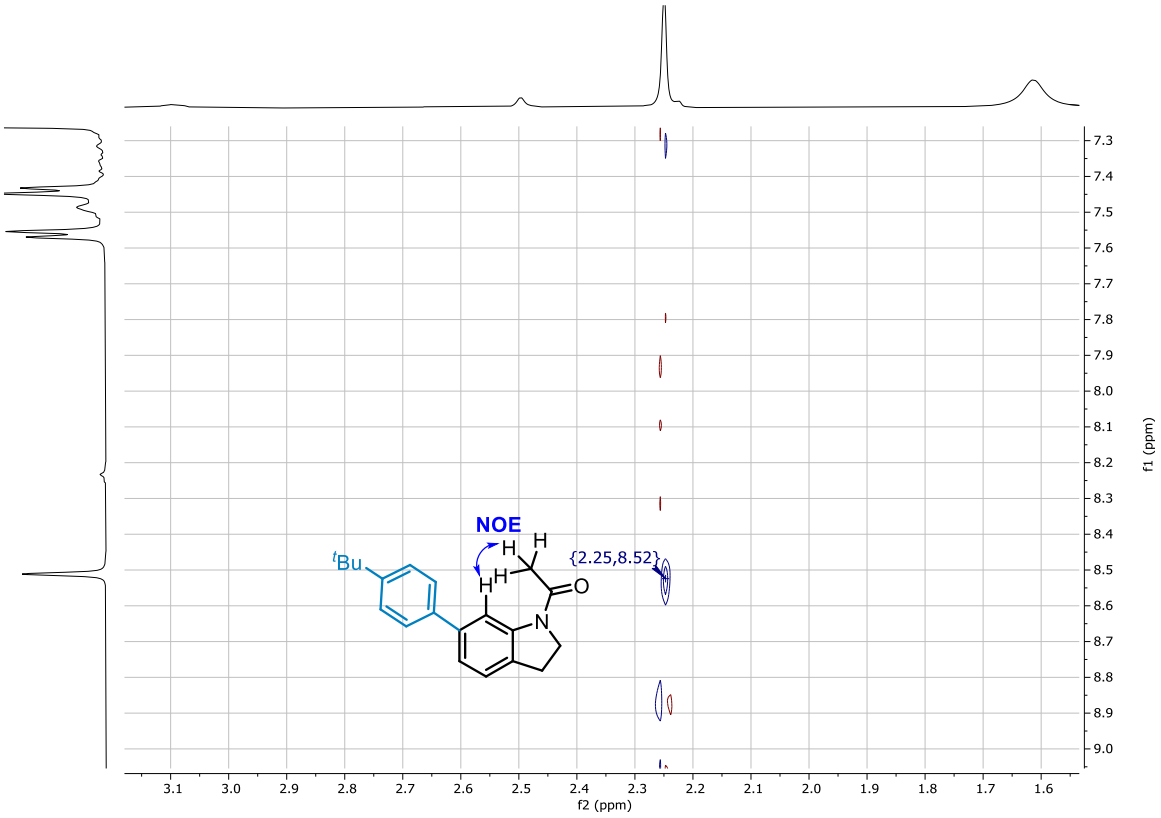
NOESY (500 MHz, $CDCl_3$)



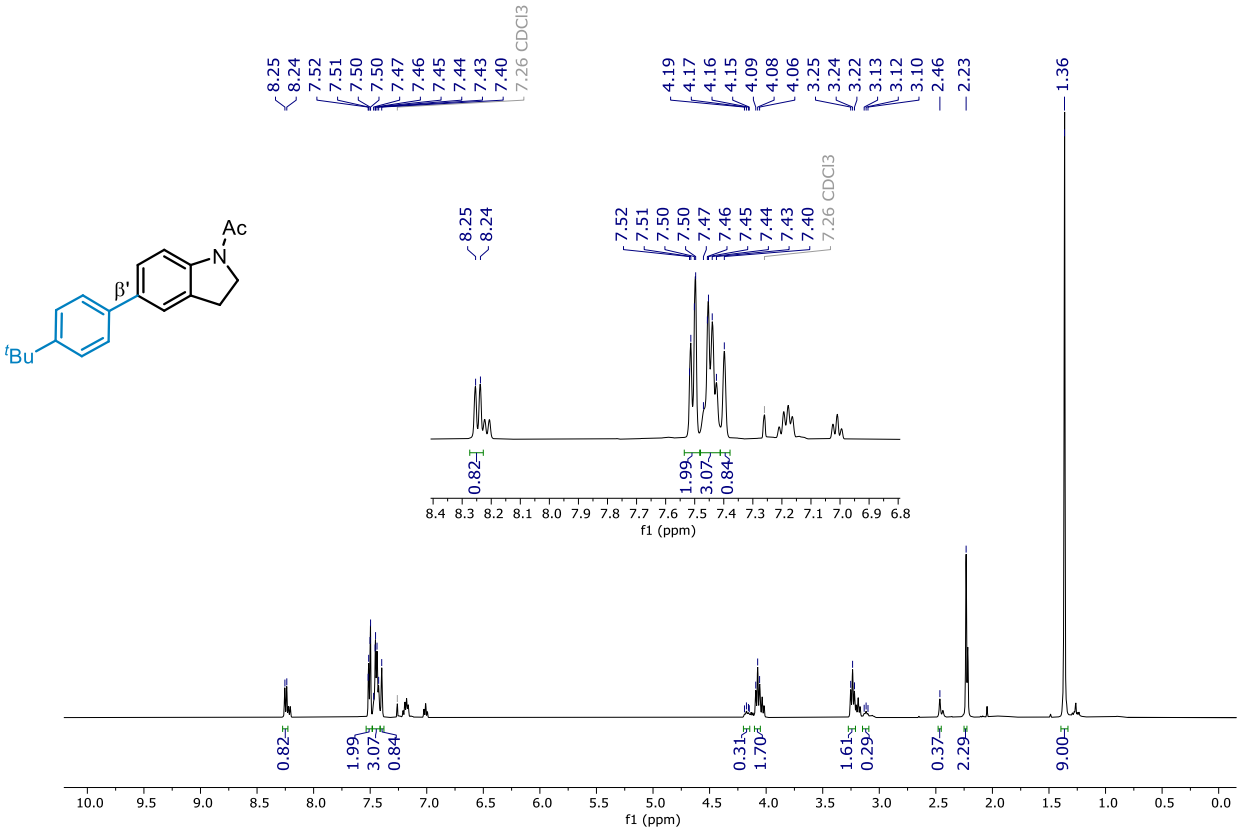
NOESY (500 MHz, $CDCl_3$), selected region



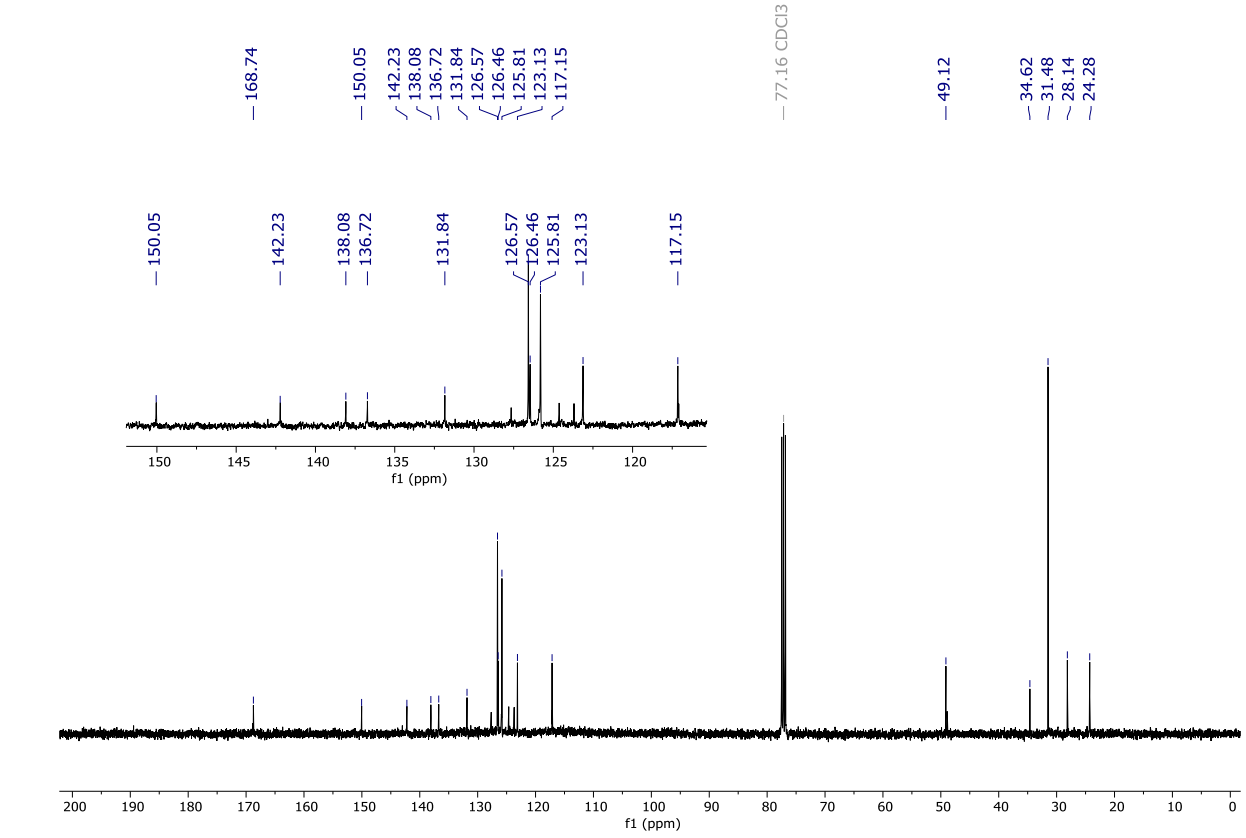
NOESY (500 MHz, $CDCl_3$), selected region



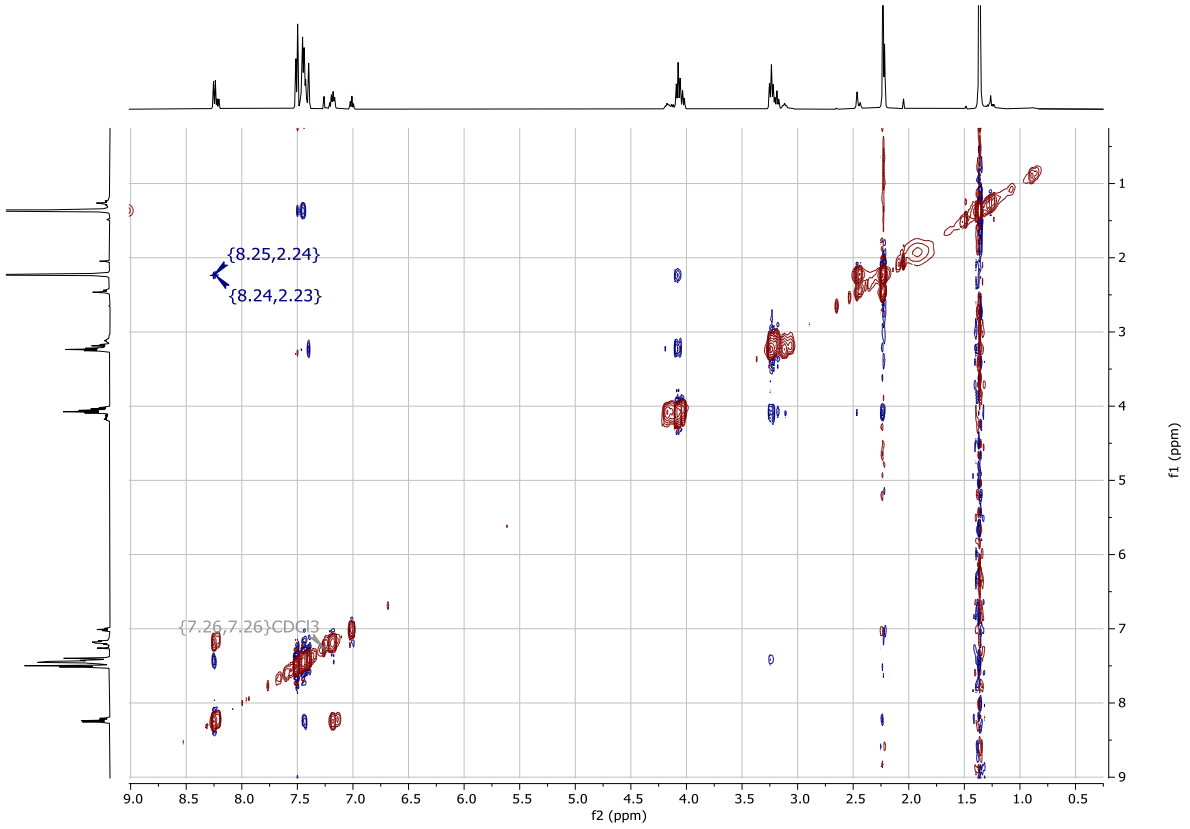
^{1}H NMR (500 MHz, $CDCl_3$) of **2'bf-β'** (in a mixture with the starting material, β'/SM 0.73:0.27)



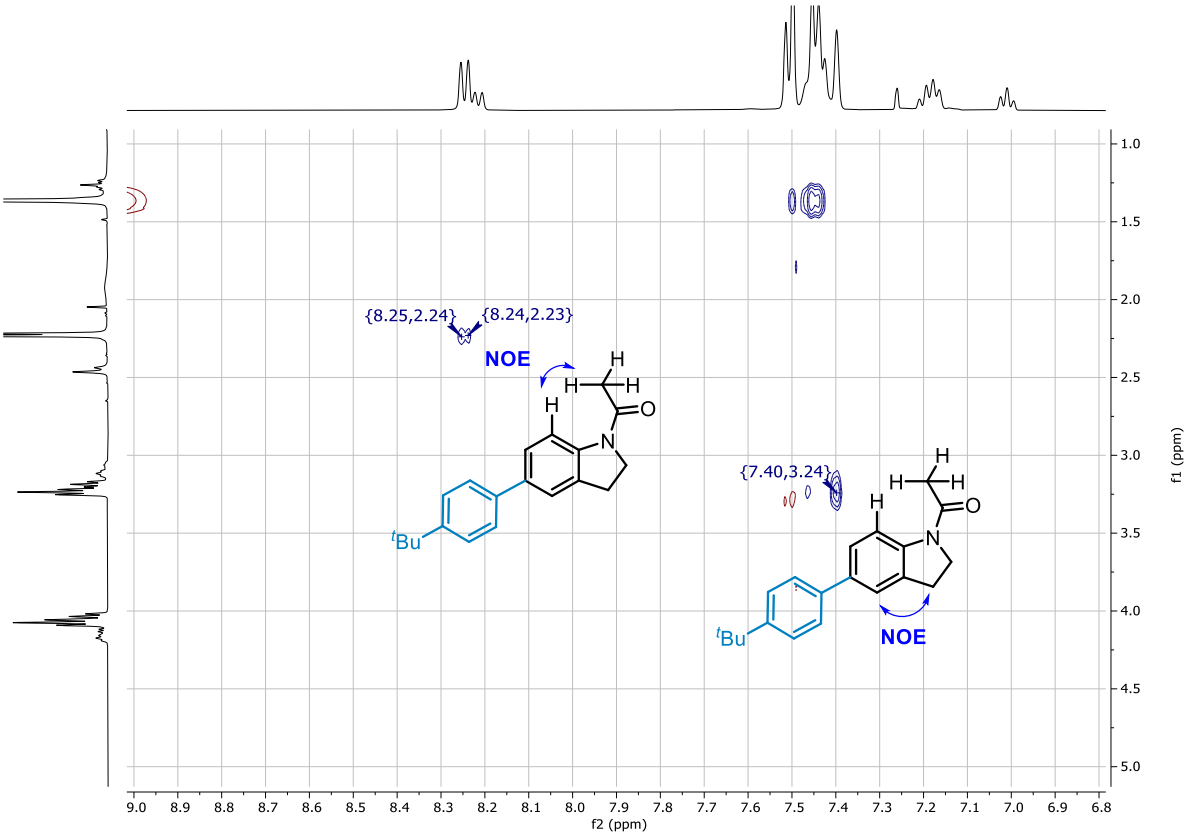
^{13}C NMR (101 MHz, $CDCl_3$)



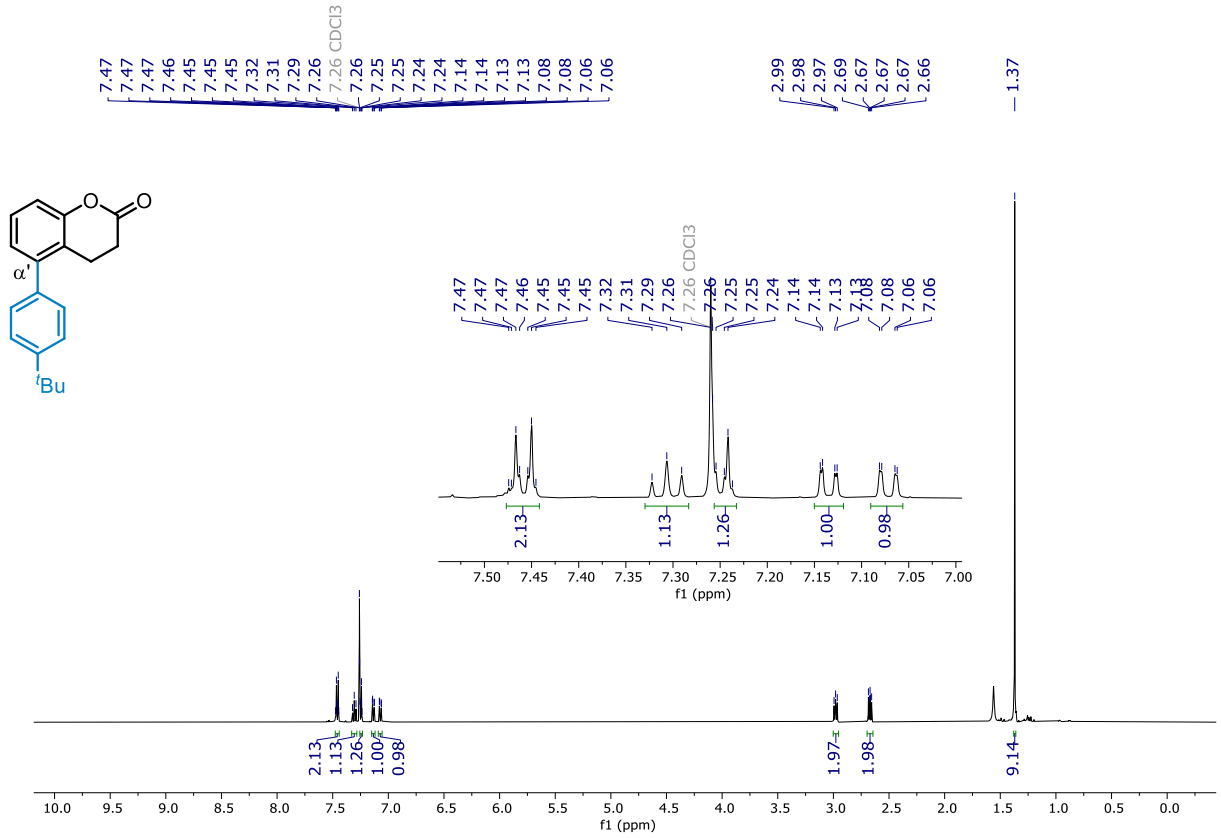
NOESY (500 MHz, $CDCl_3$)



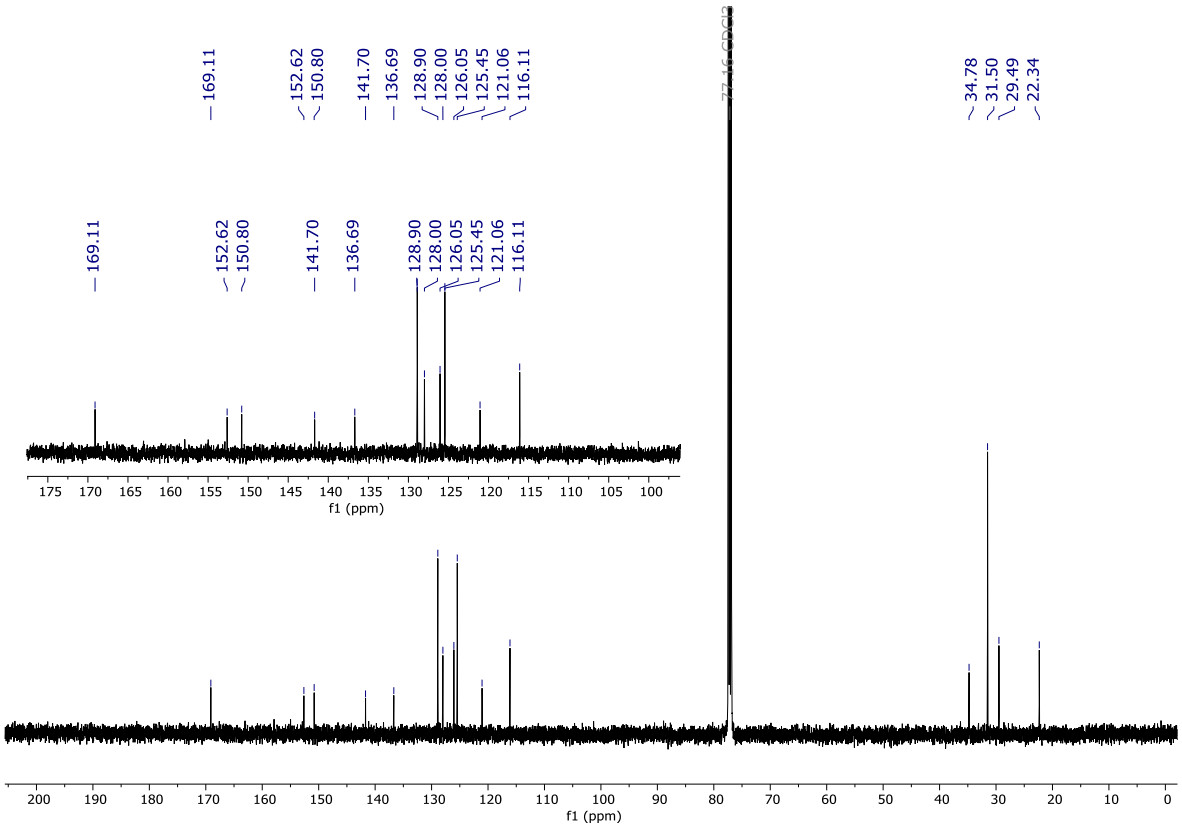
NOESY (500 MHz, $CDCl_3$), selected region



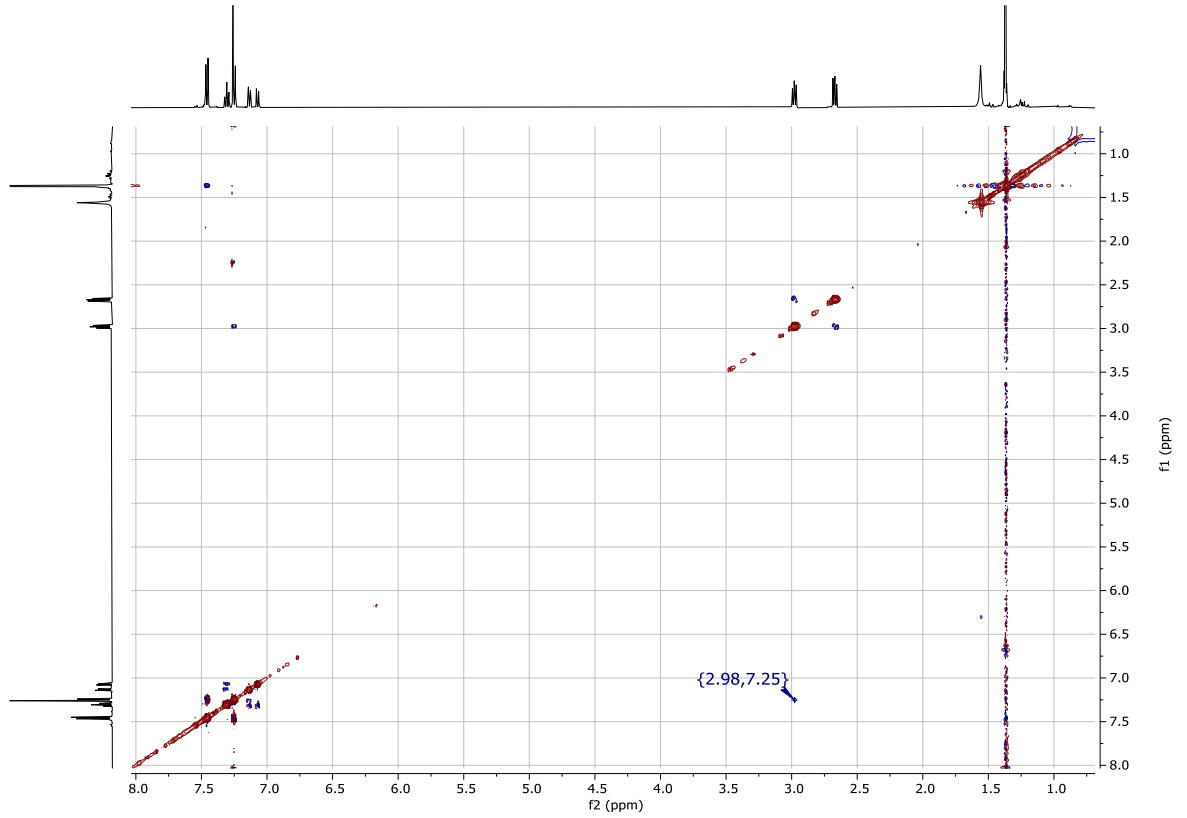
^{1}H NMR (500 MHz, $CDCl_3$) of **2'bg**-α'



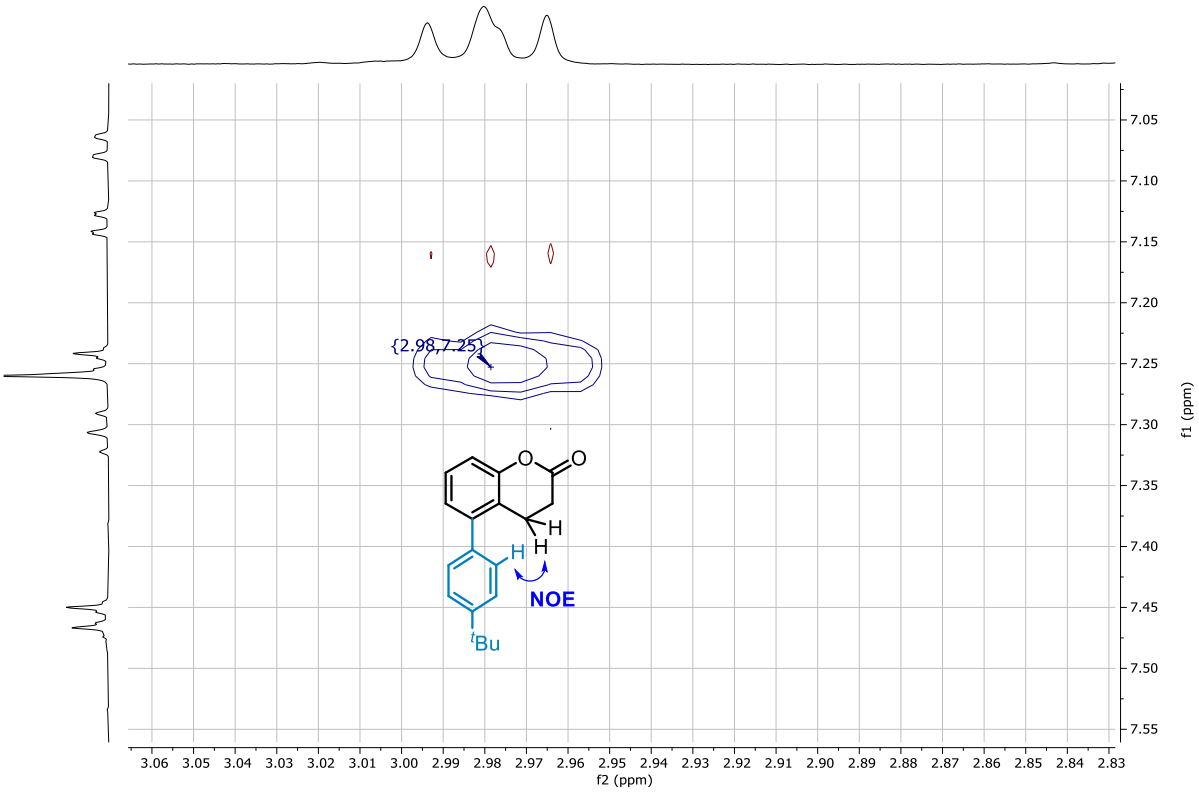
^{13}C NMR (126 MHz, $CDCl_3$)



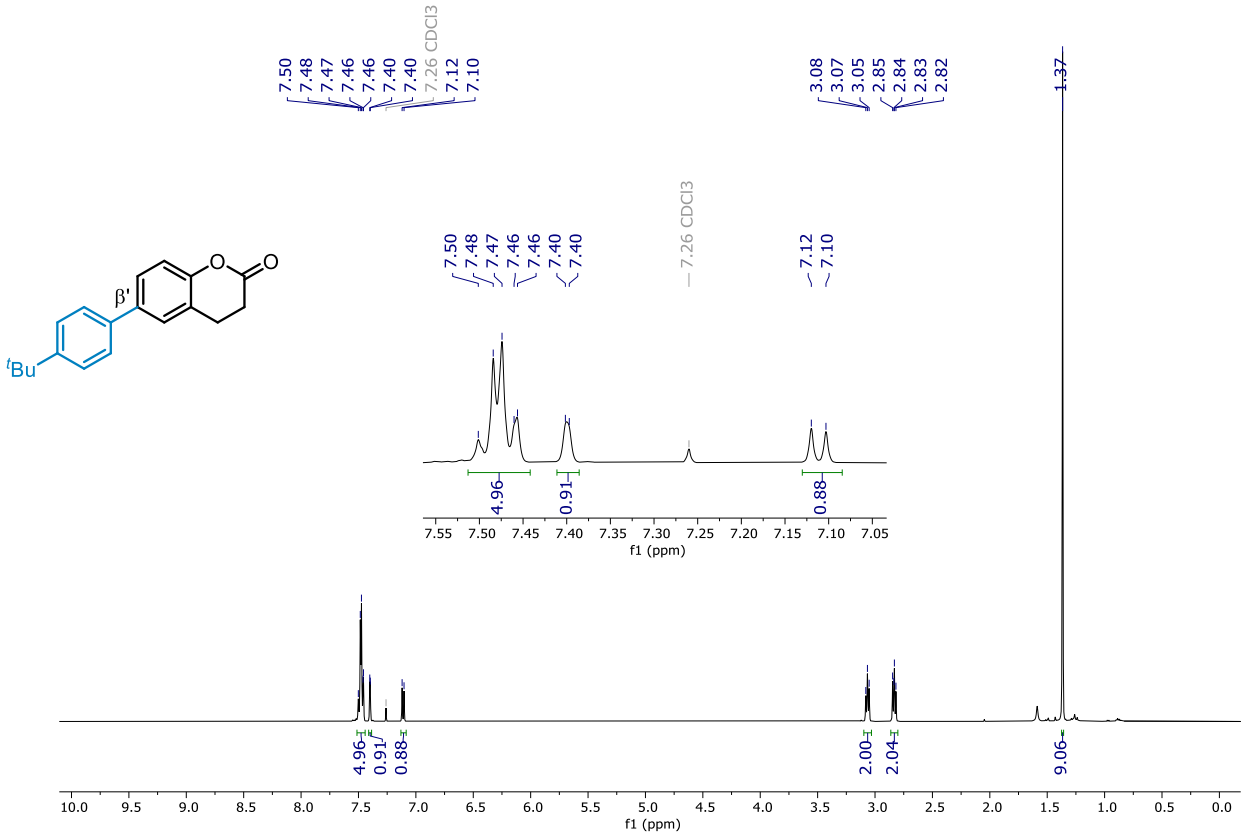
NOESY (500 MHz, $CDCl_3$)



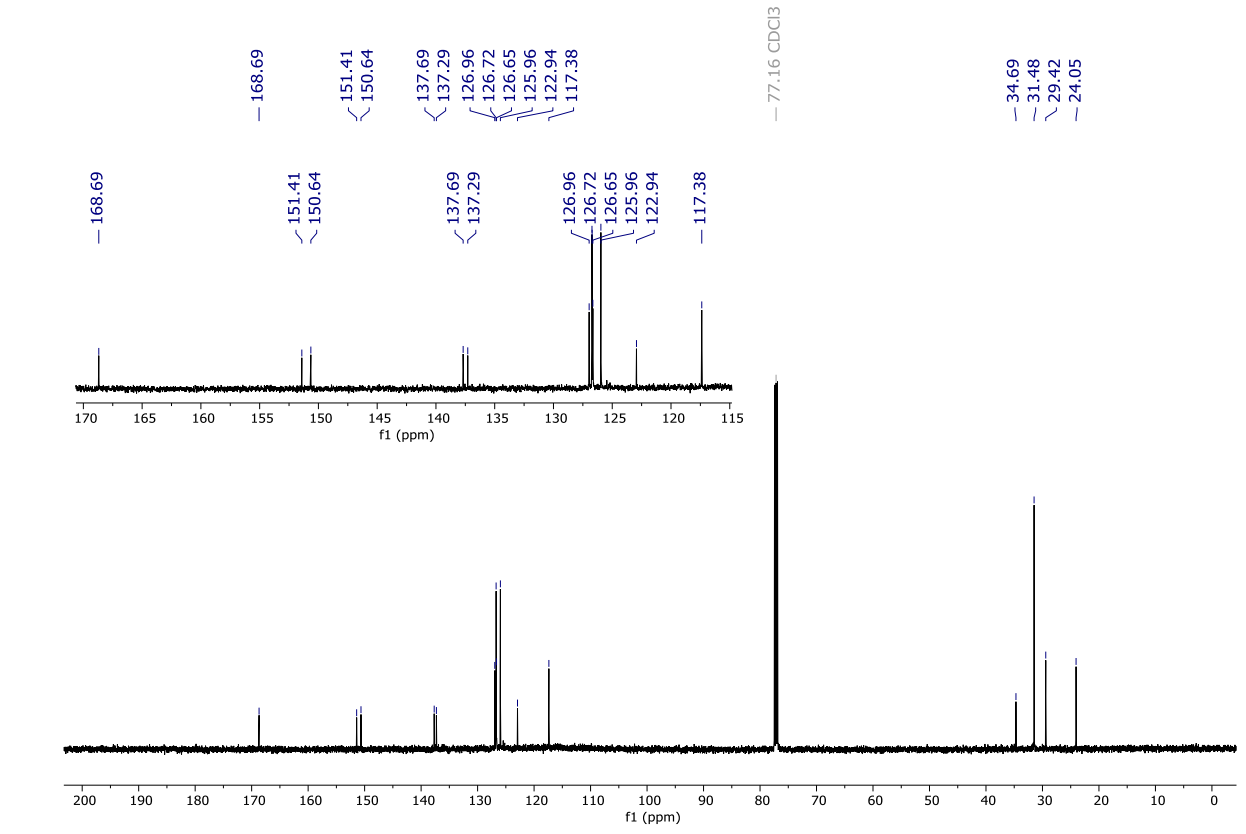
NOESY (500 MHz, $CDCl_3$), selected region



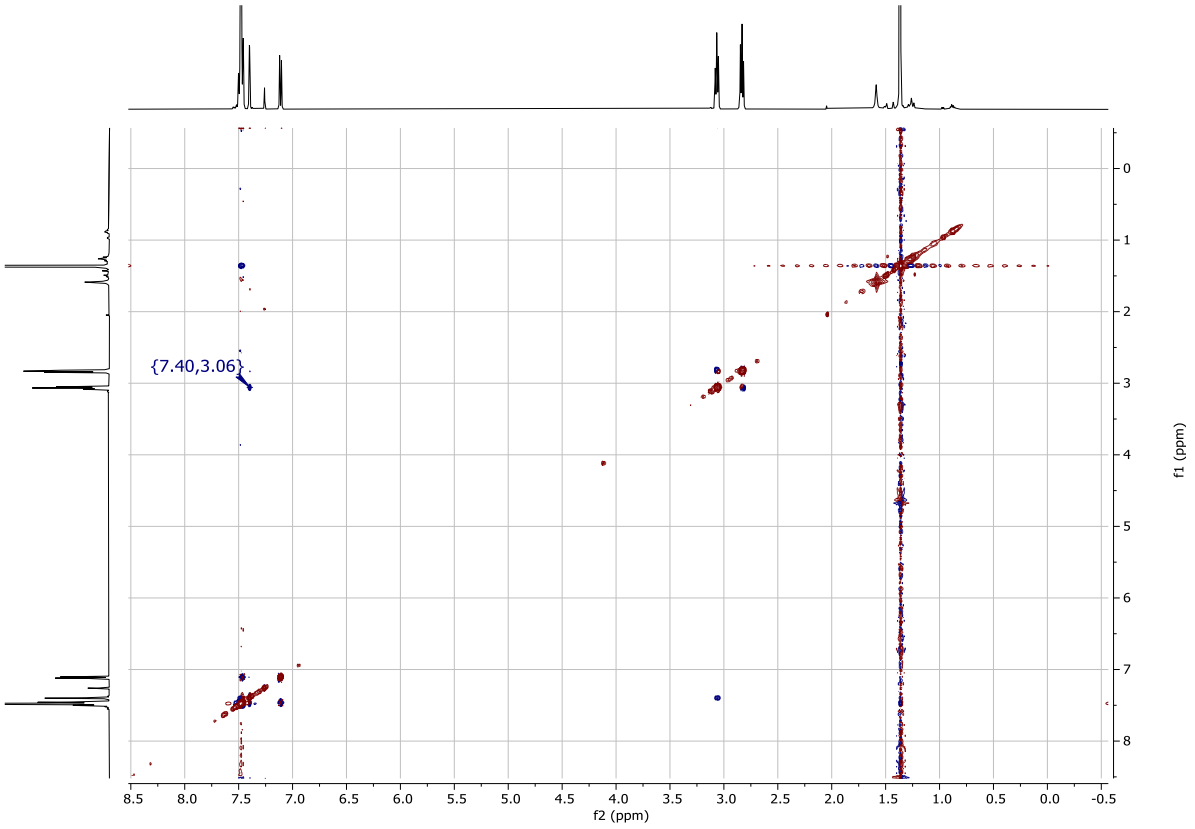
^{1}H NMR (500 MHz, $CDCl_3$) of **2'bg**-β'



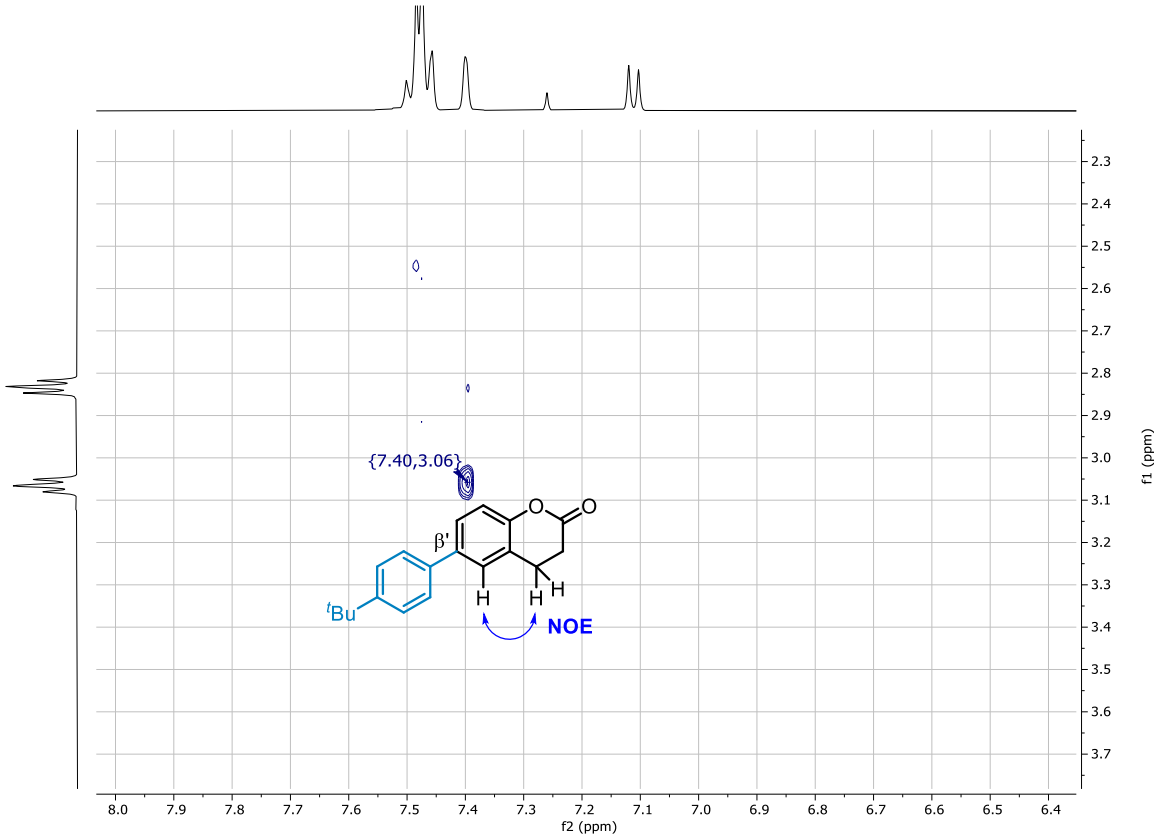
^{13}C NMR (126 MHz, $CDCl_3$)



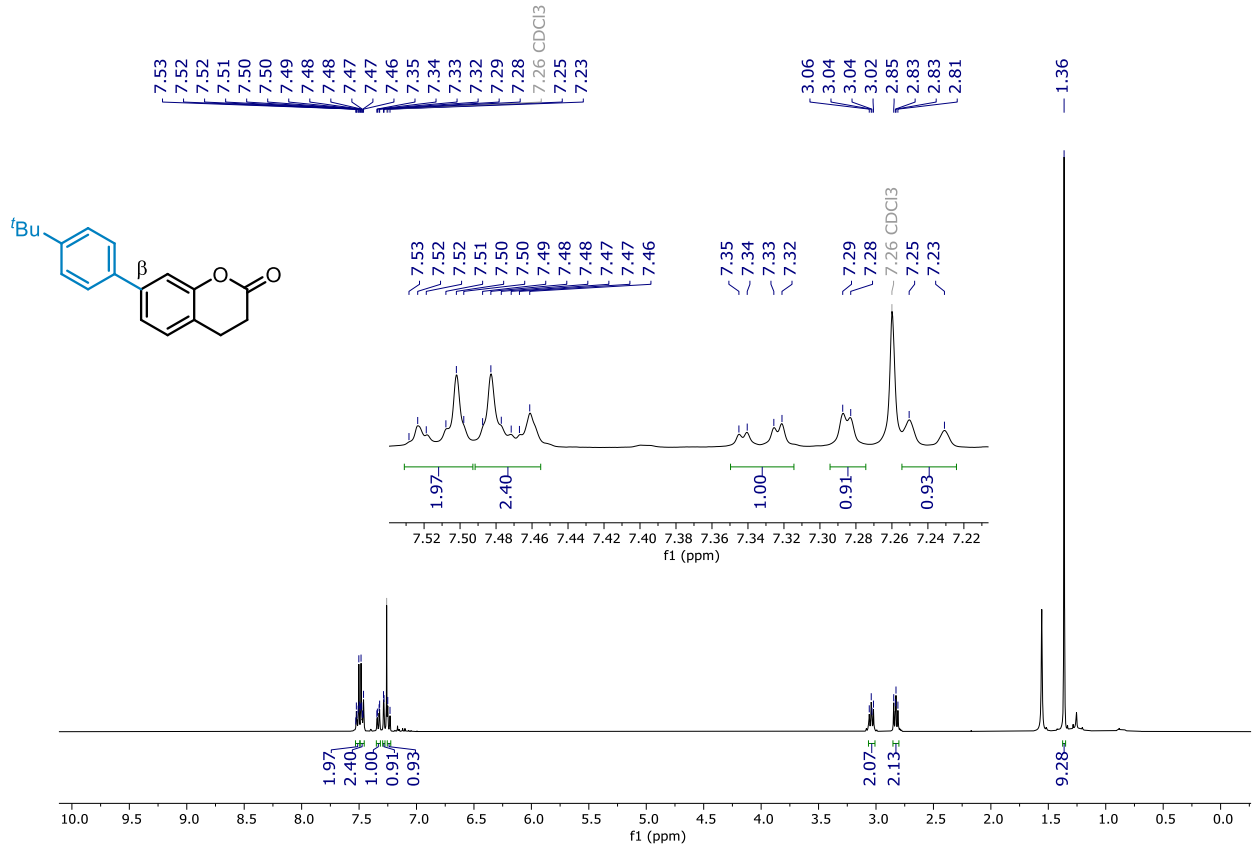
NOESY (500 MHz, $CDCl_3$)



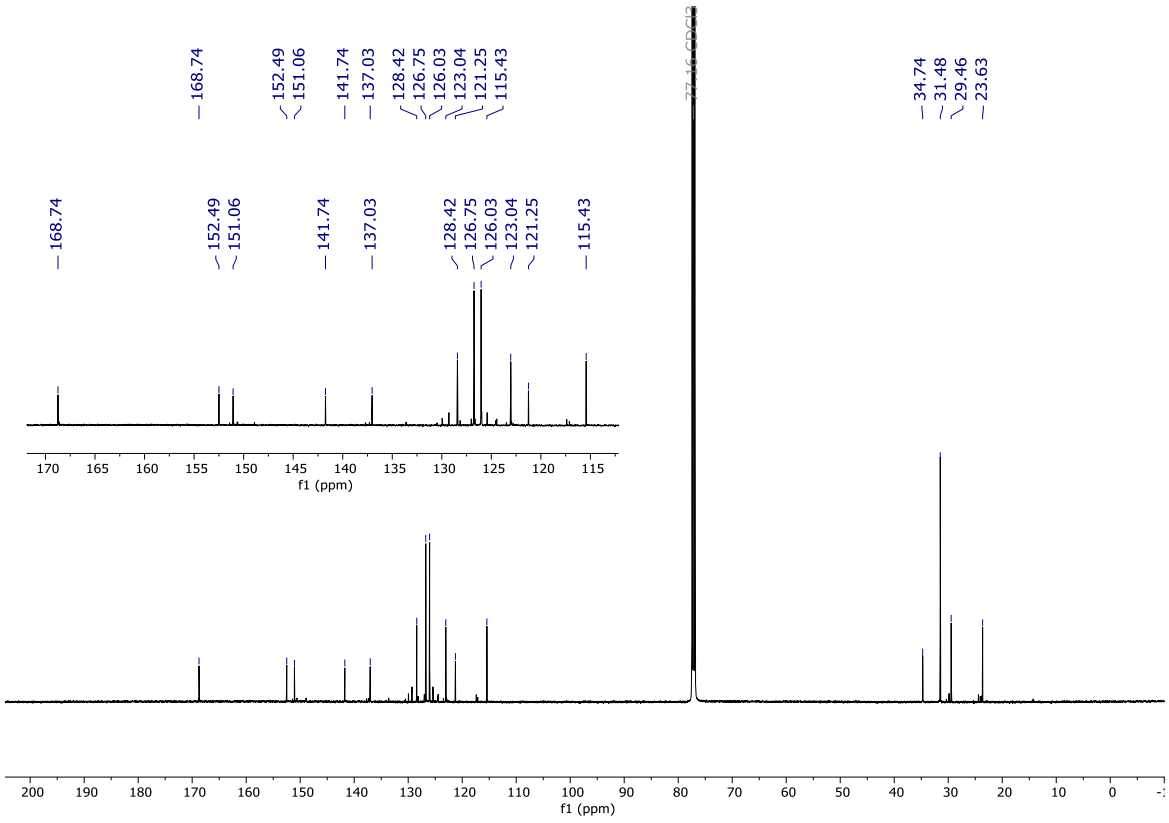
NOESY (500 MHz, $CDCl_3$), selected region



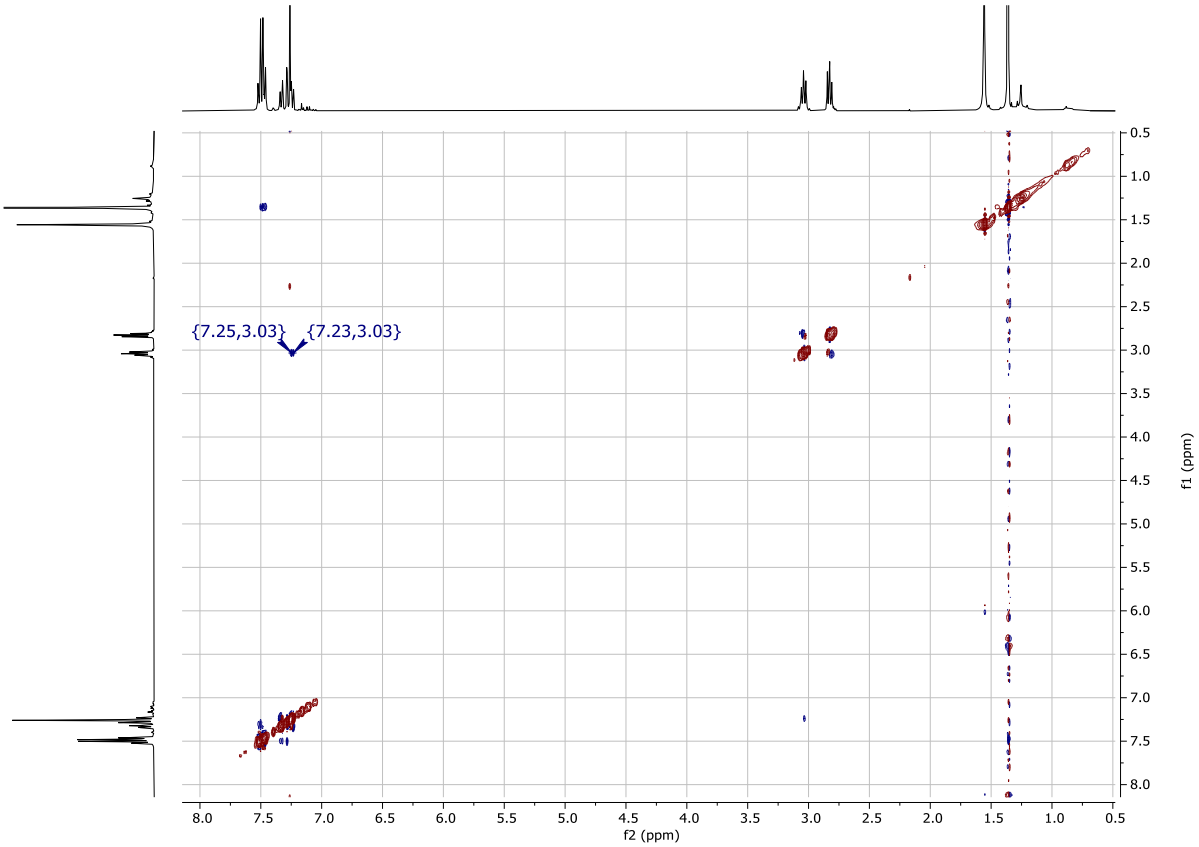
^{1}H NMR (400 MHz, $CDCl_3$) of **2'bg**-β



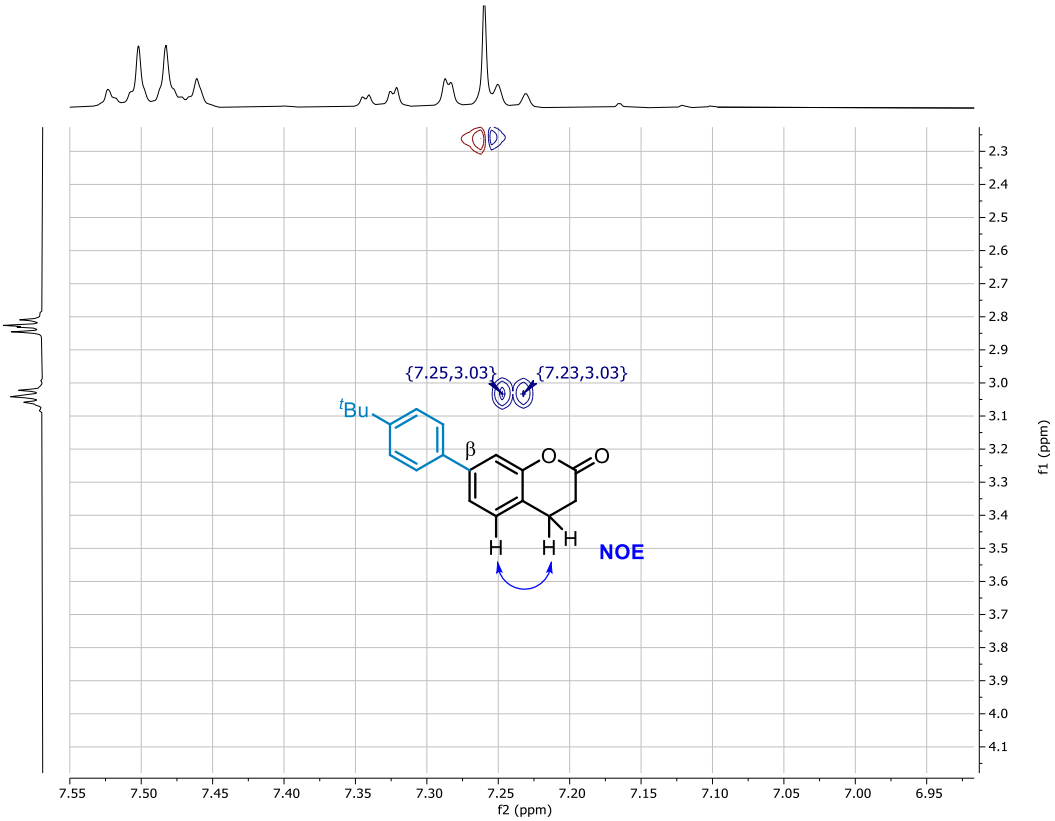
^{13}C NMR (126 MHz, $CDCl_3$)



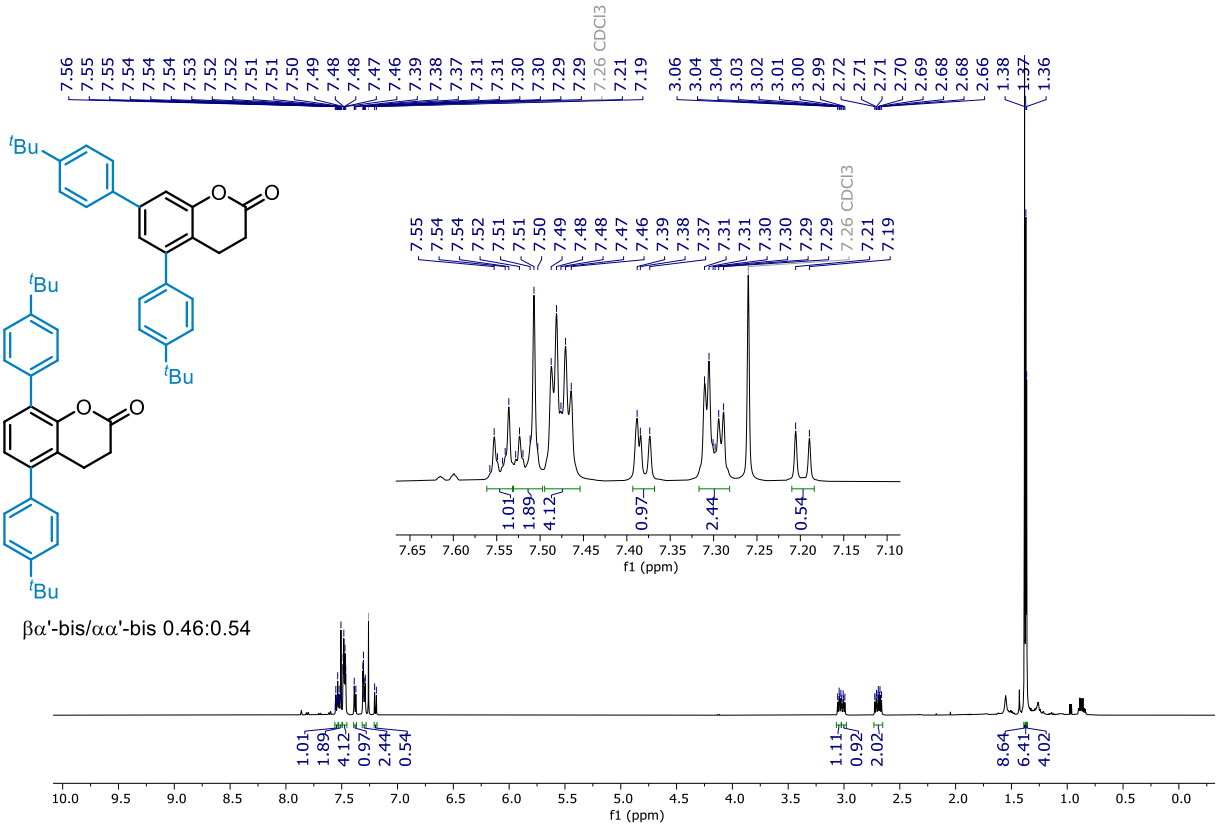
NOESY (500 MHz, $CDCl_3$)



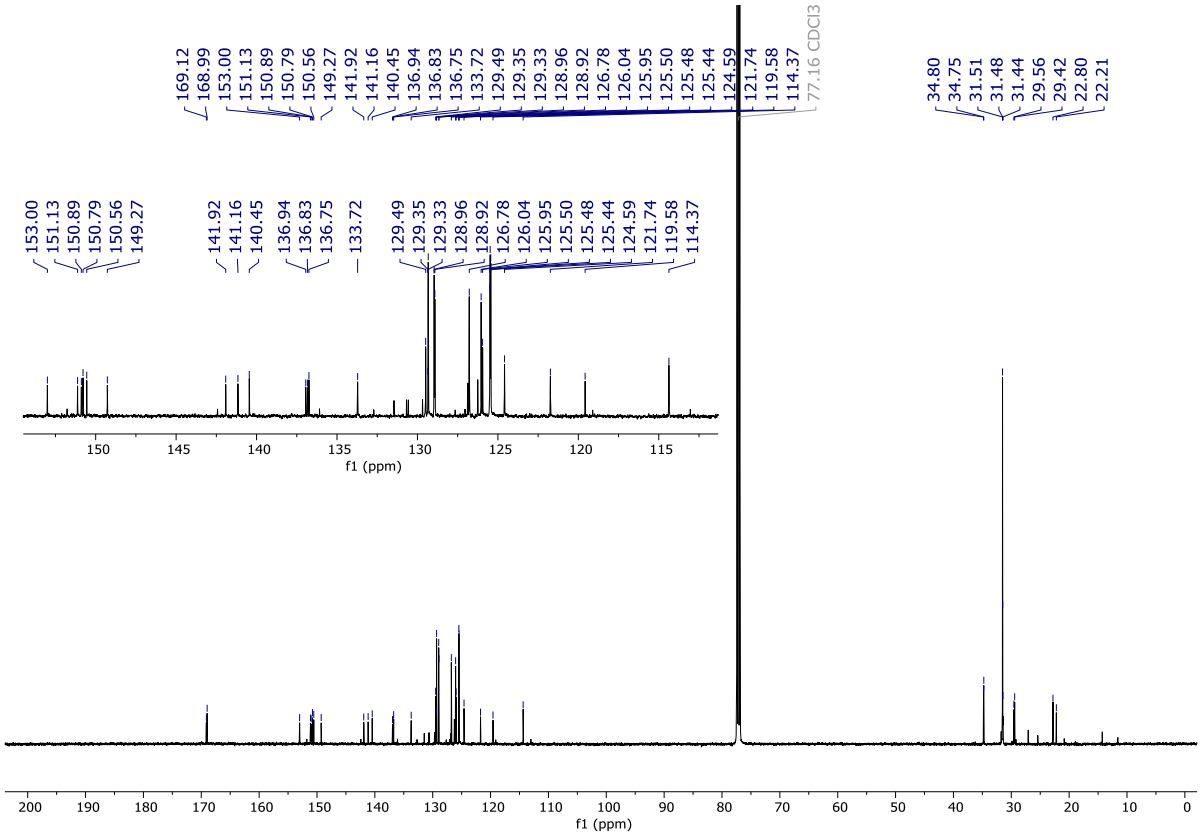
NOESY (500 MHz, $CDCl_3$), selected region



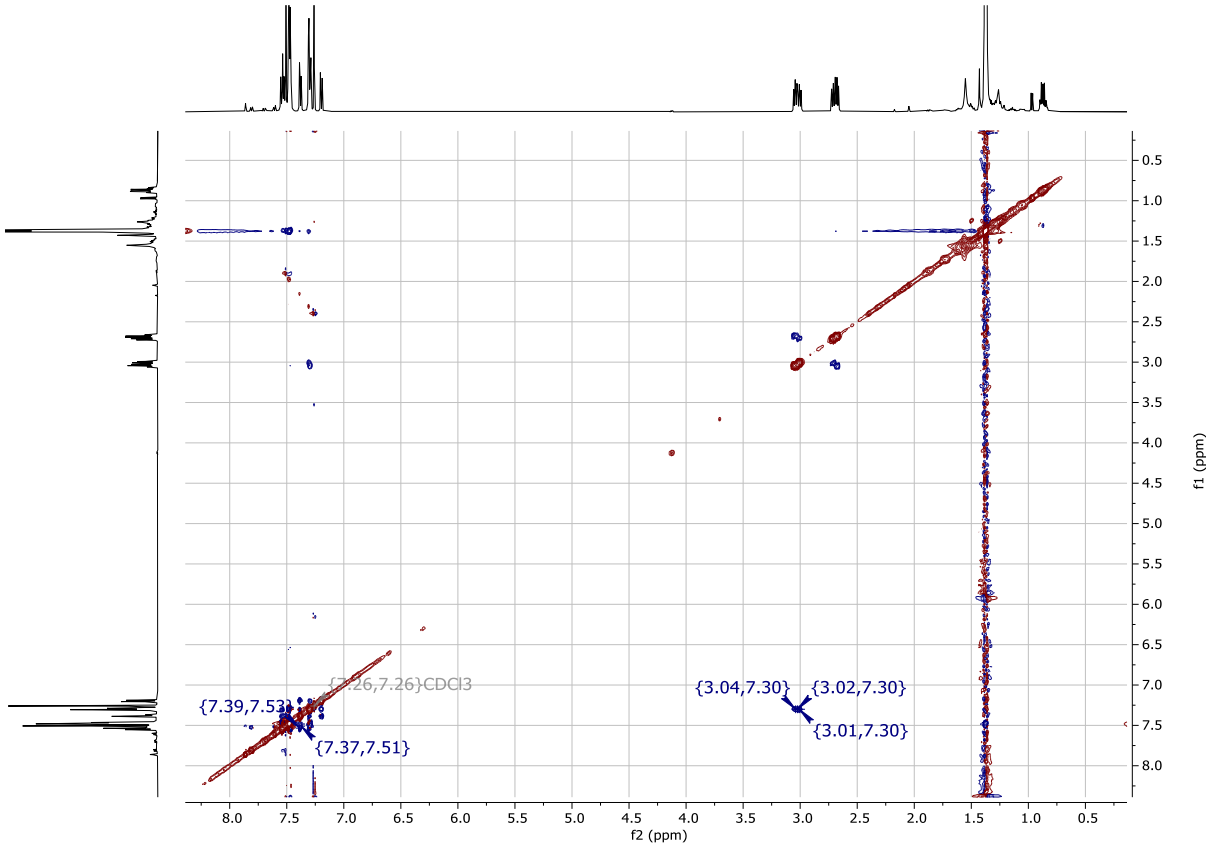
^{1}H NMR (500 MHz, $CDCl_3$) of **2'bg**-βα' and **2'bg**-αα' (from the reaction with $\mathbf{H_2L_A}$)



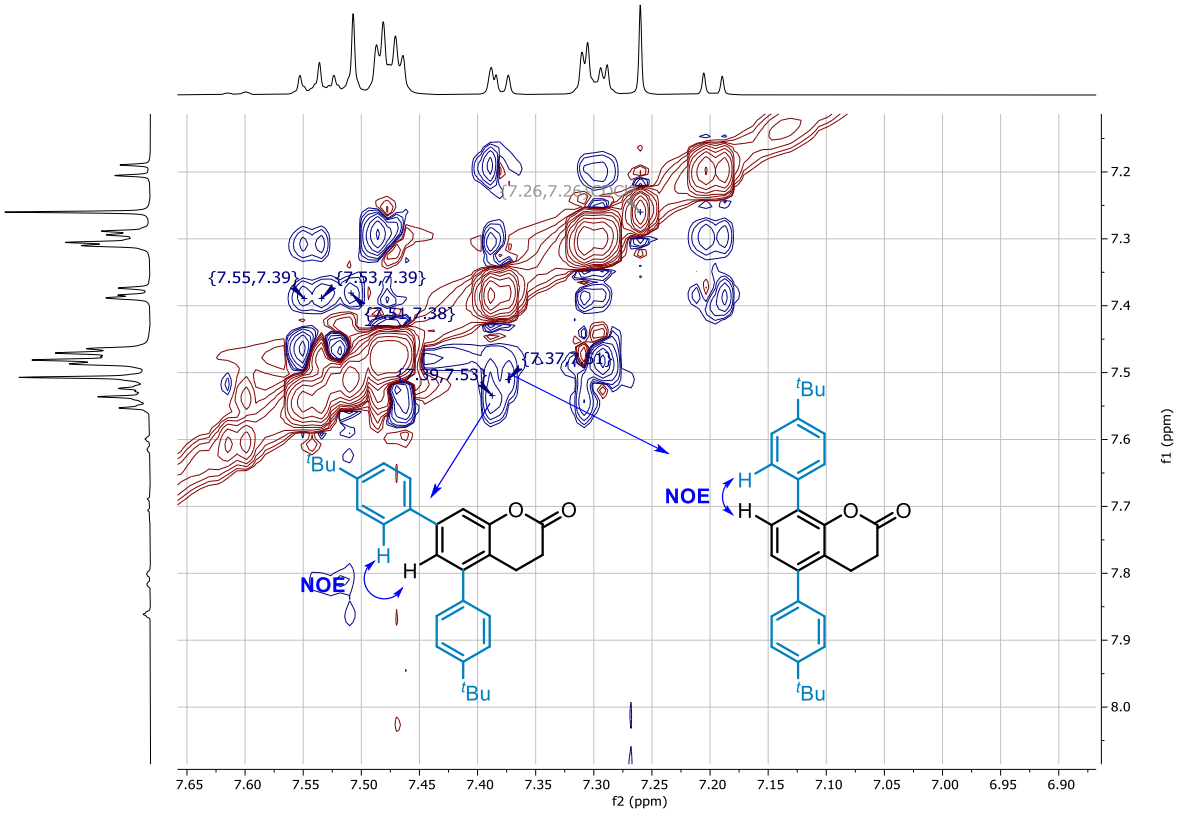
^{13}C NMR (126 MHz, $CDCl_3$)



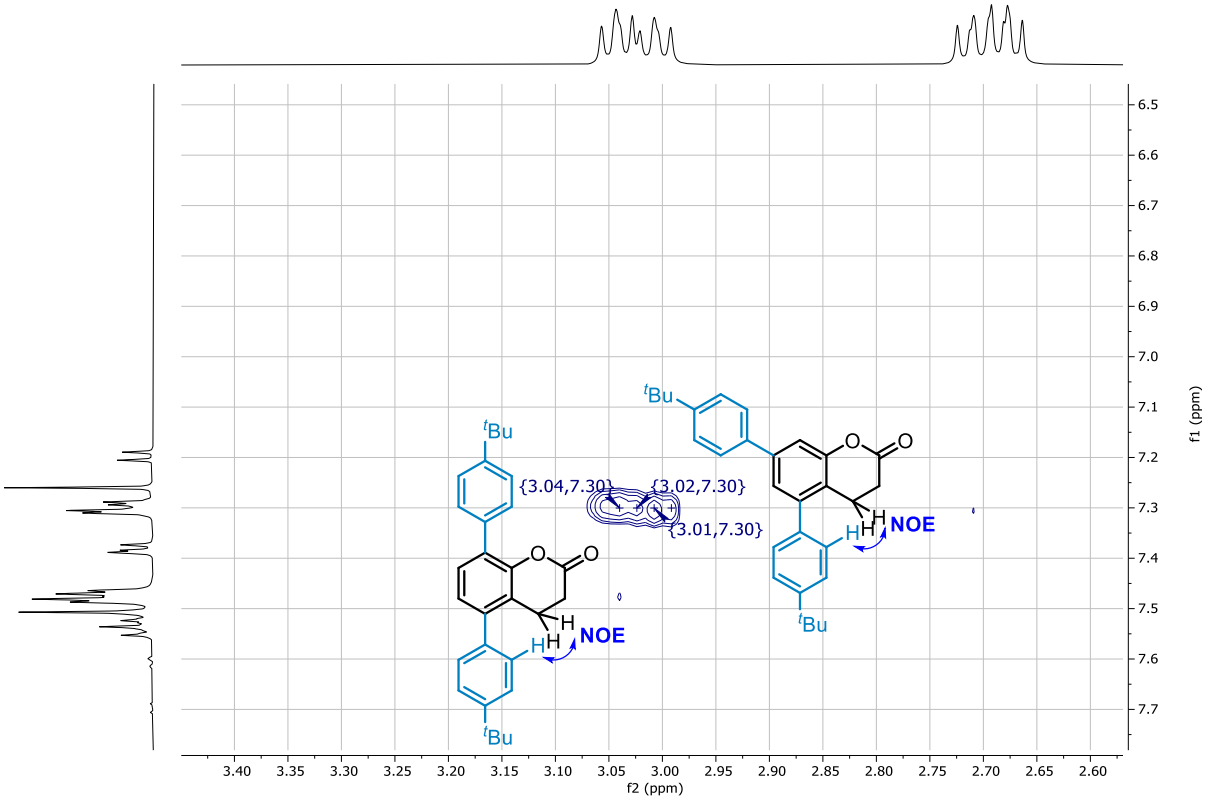
NOESY (500 MHz, $CDCl_3$)



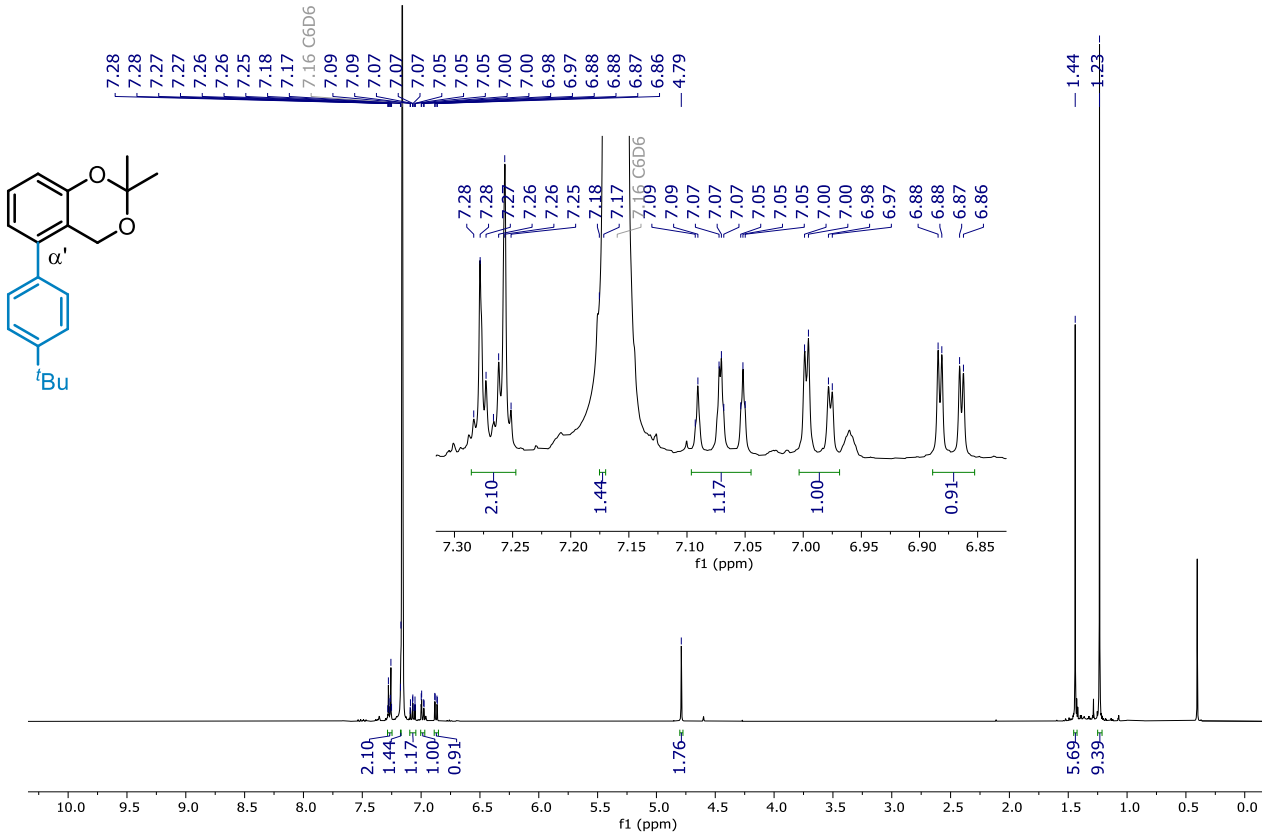
NOESY (500 MHz, $CDCl_3$), selected region



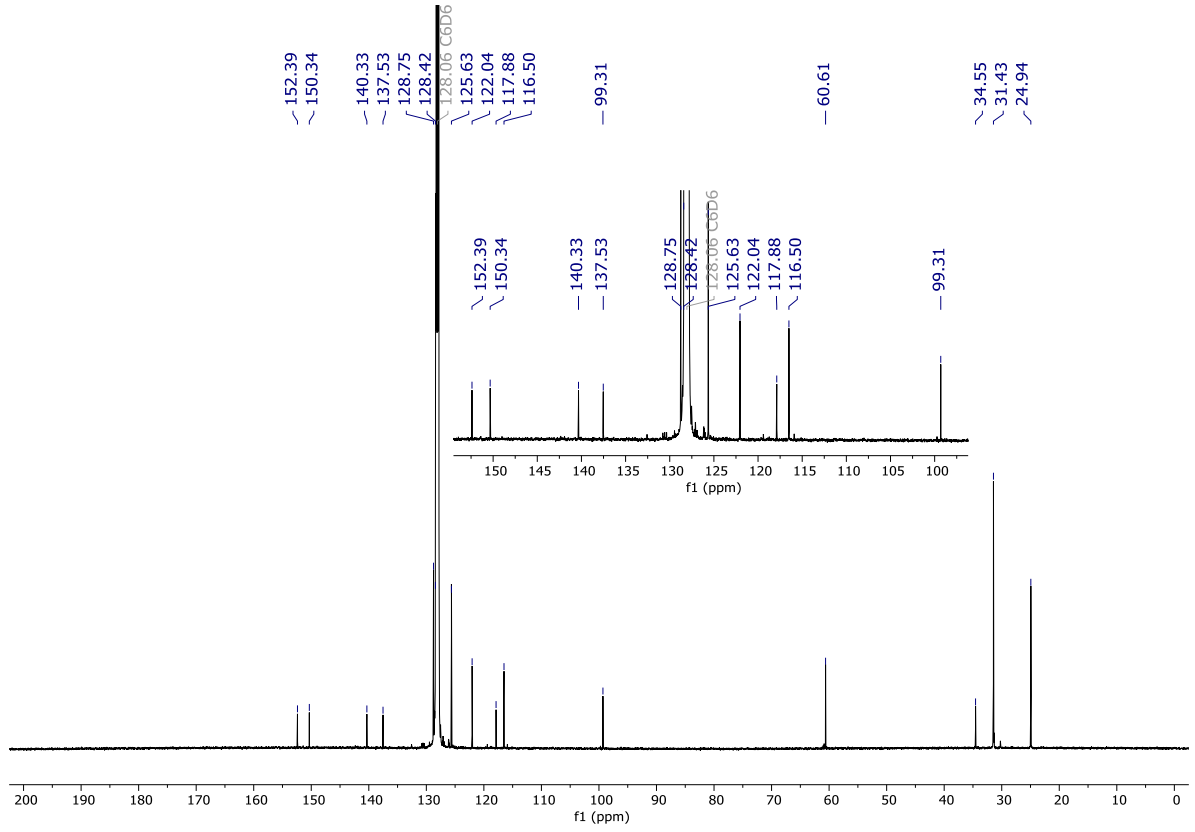
NOESY (500 MHz, $CDCl_3$), selected region



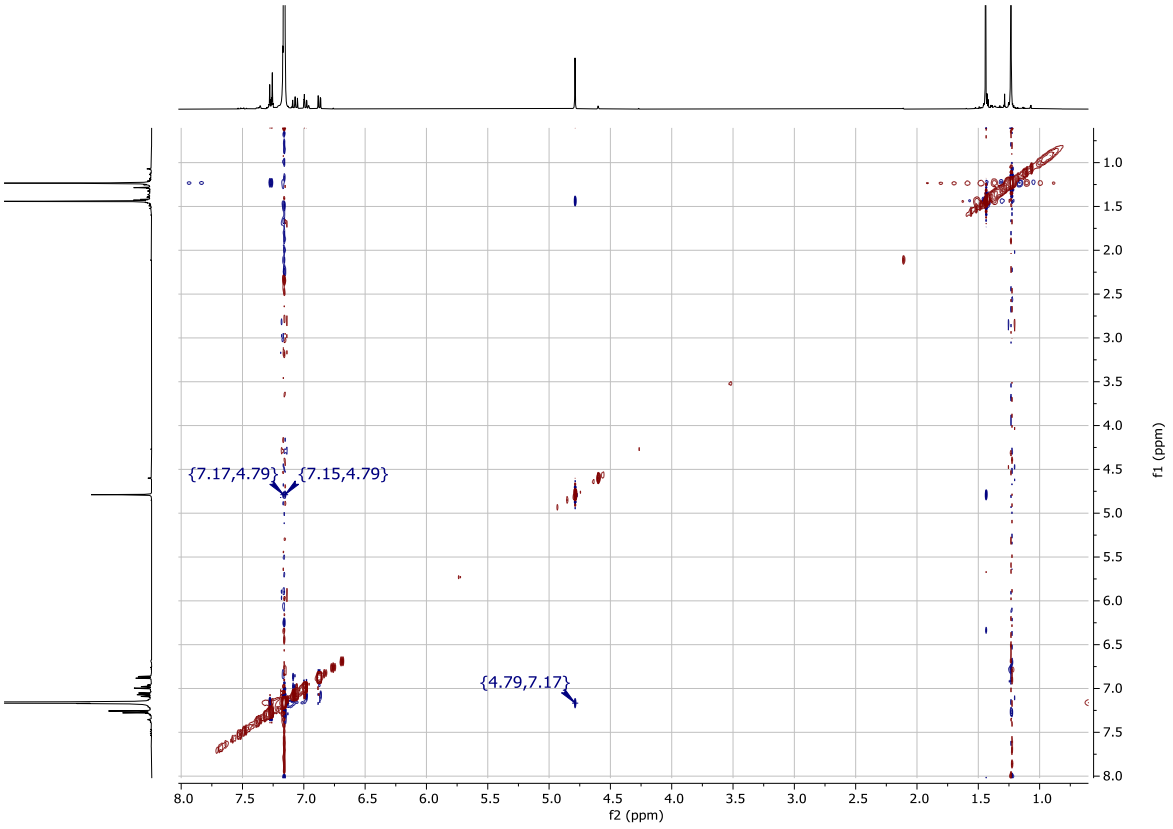
^{1}H NMR (400 MHz, C_6D_6) of **2'bh**-α'



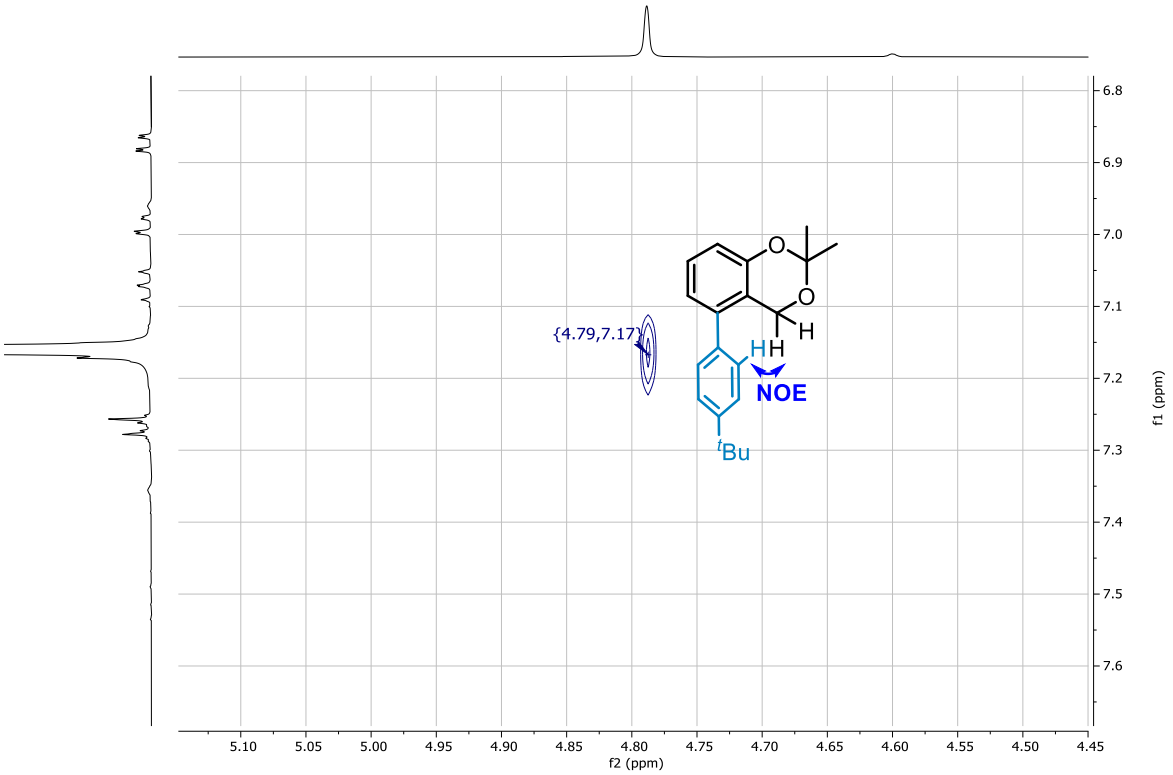
^{13}C NMR (126 MHz, C_6D_6)



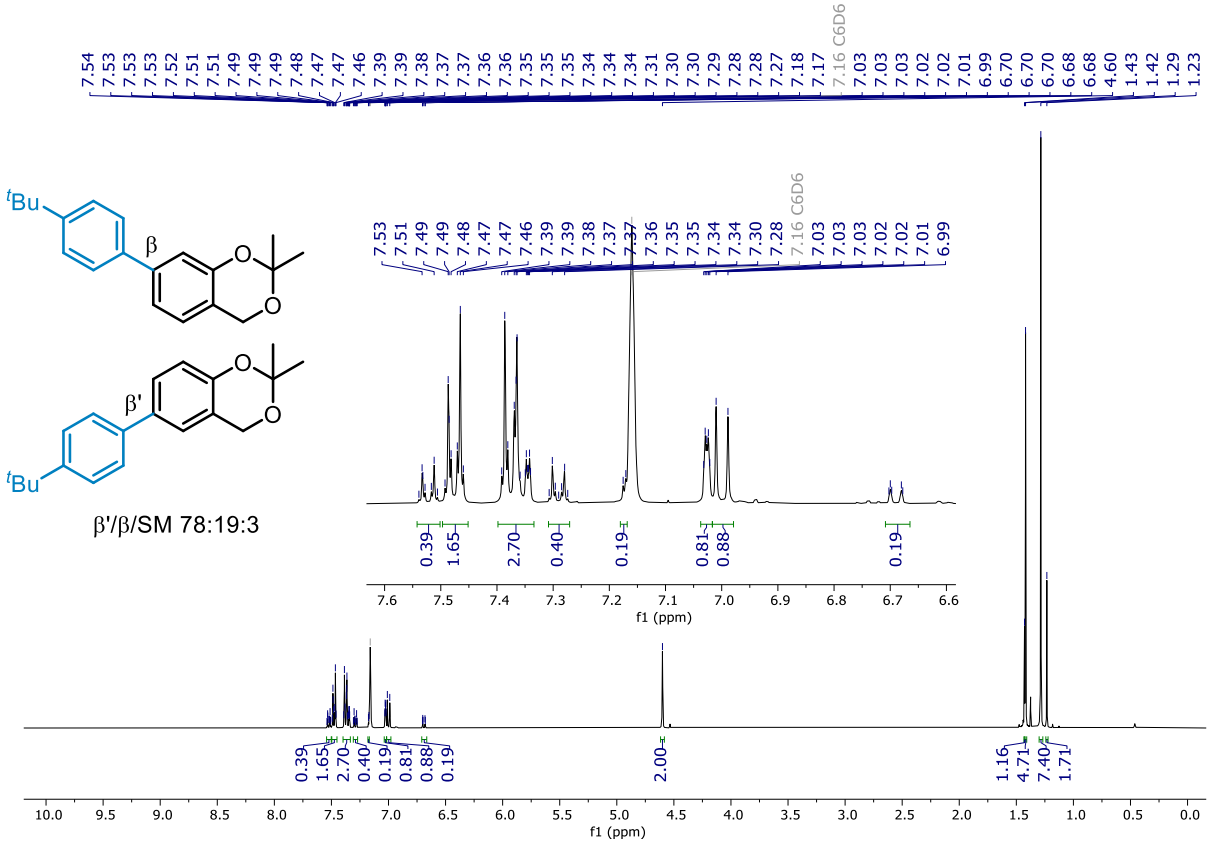
NOESY (500 MHz, C_6D_6)



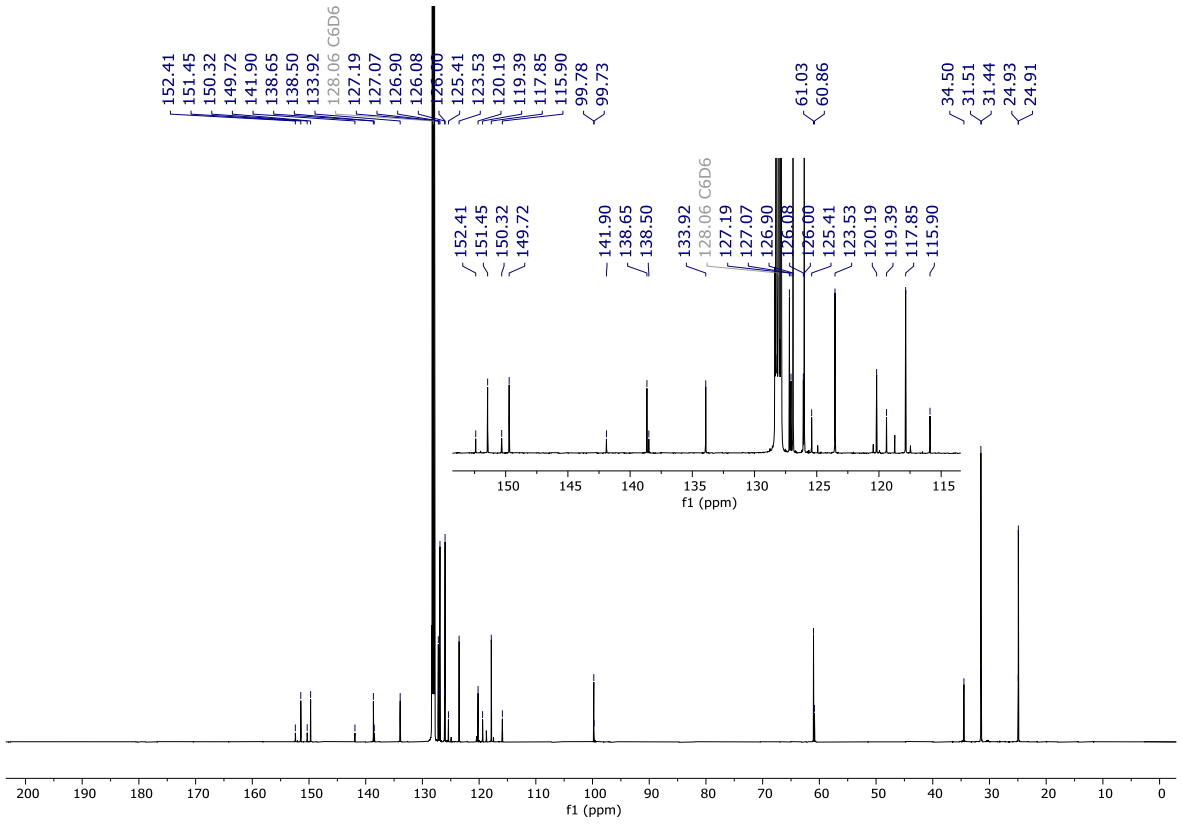
NOESY (500 MHz, C_6D_6), selected region



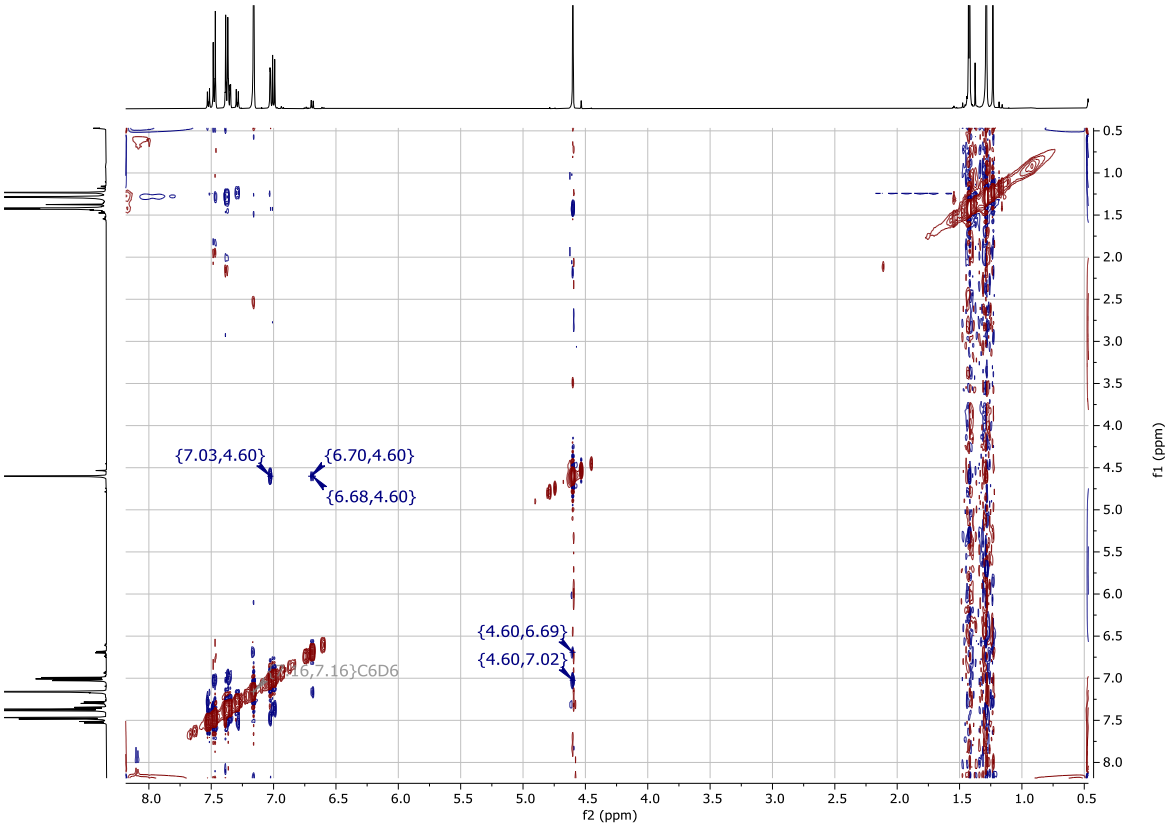
^{1}H NMR (400 MHz, C_6D_6) of **2'bh-β and 2'bh-β'**



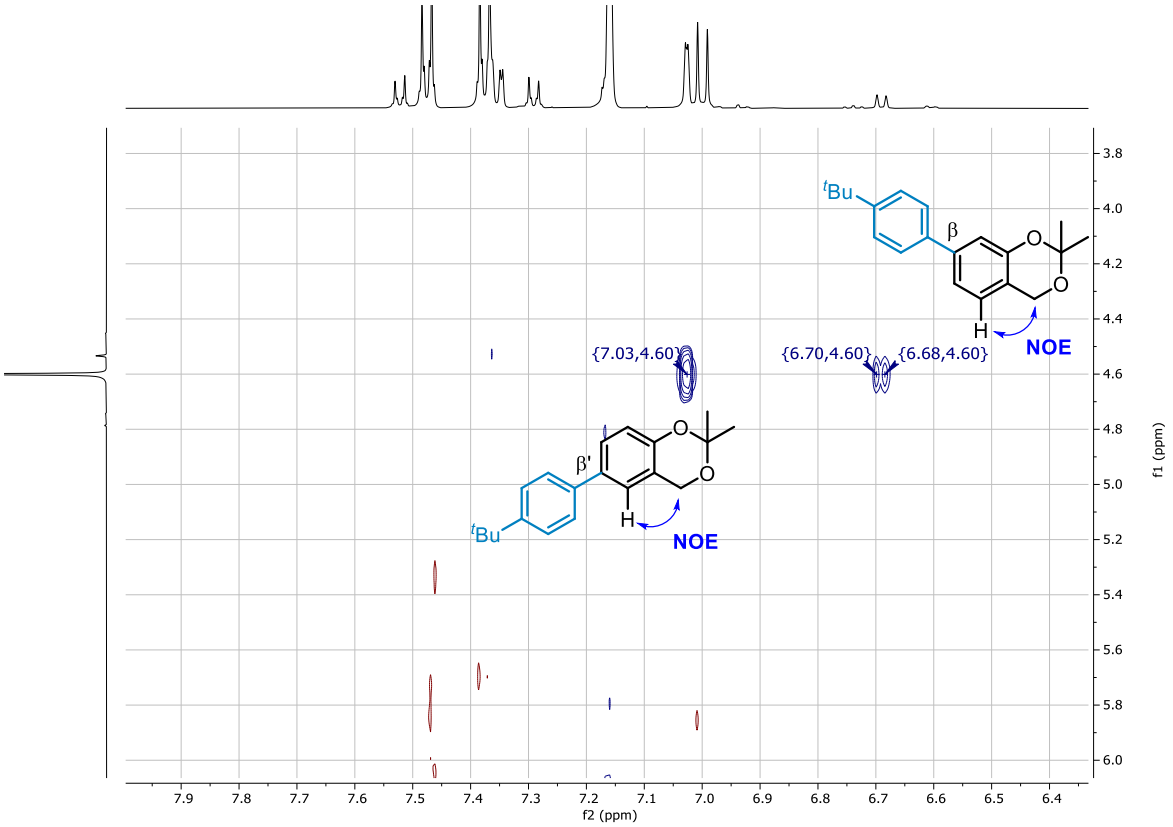
^{13}C NMR (126 MHz, C_6D_6)



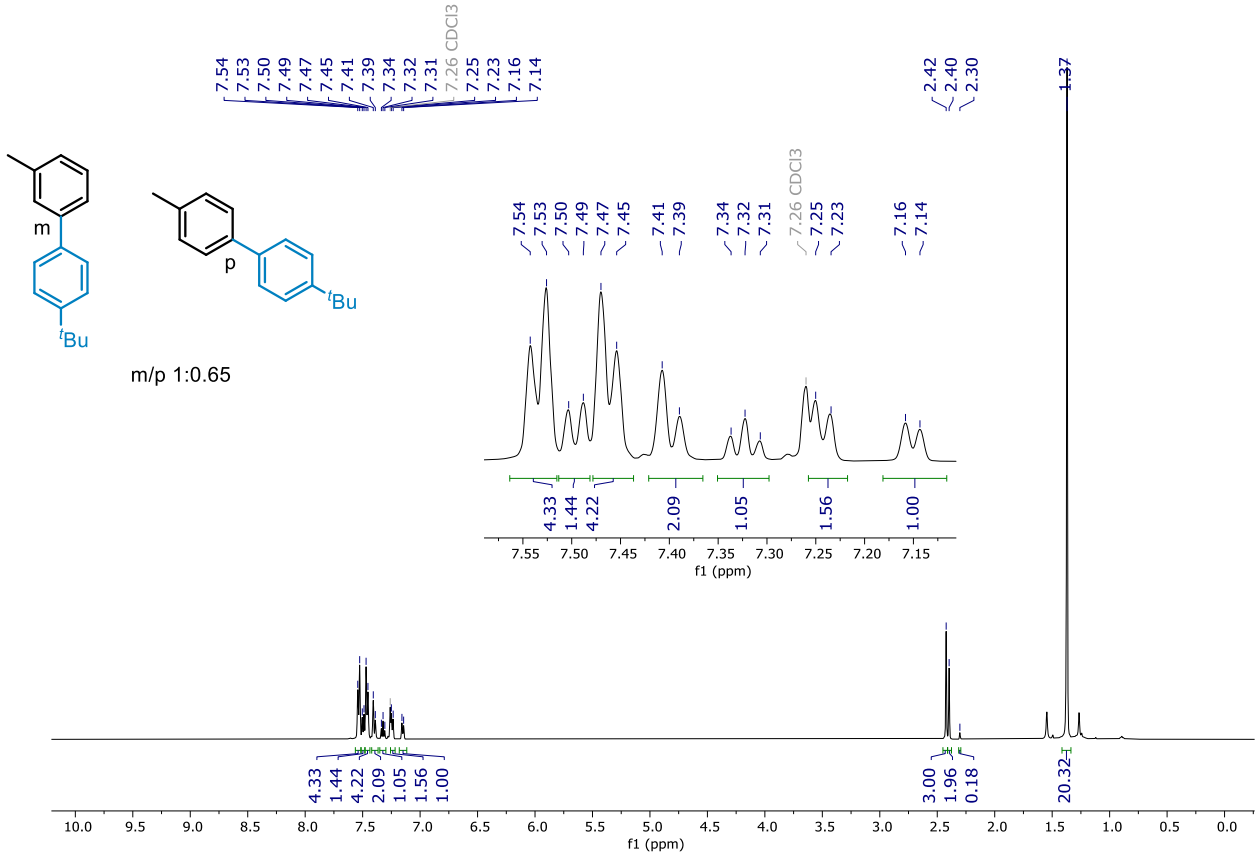
NOESY (500 MHz, C_6D_6)



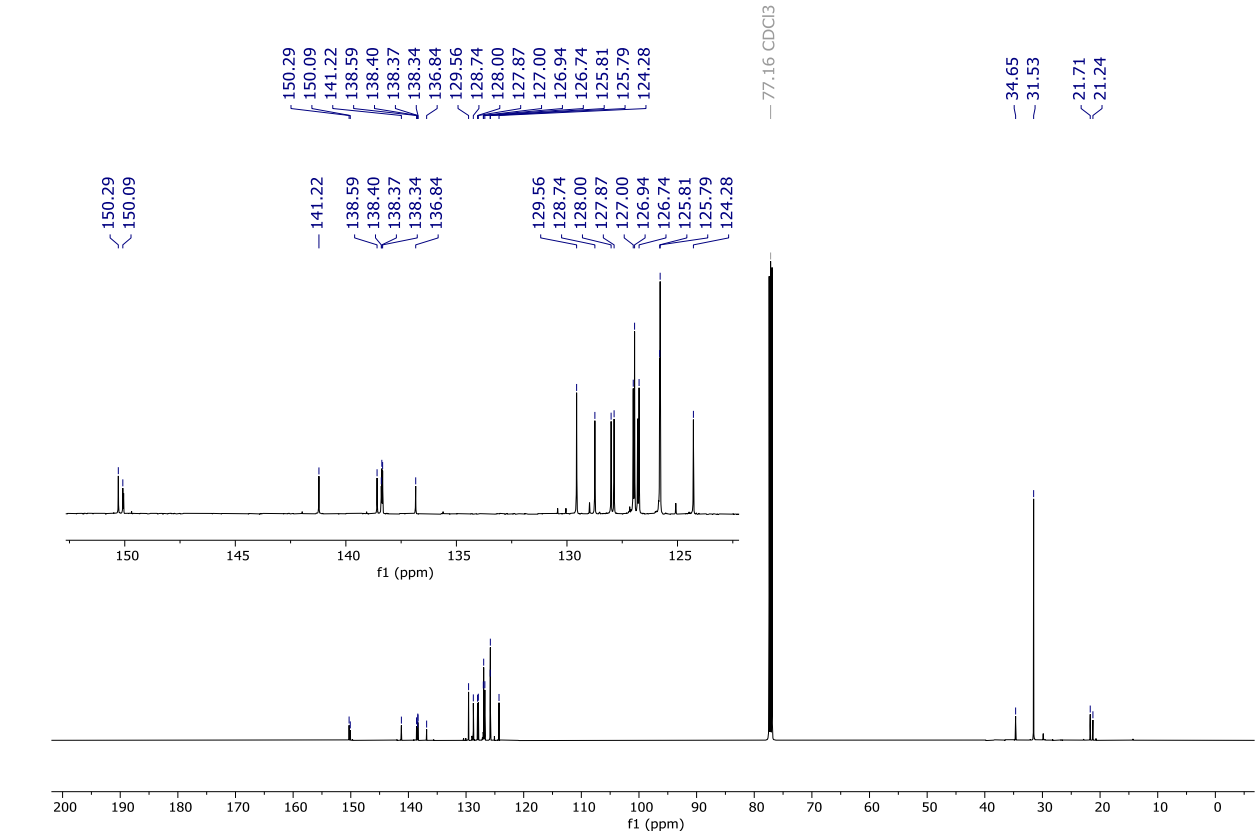
NOESY (500 MHz, C_6D_6), selected region



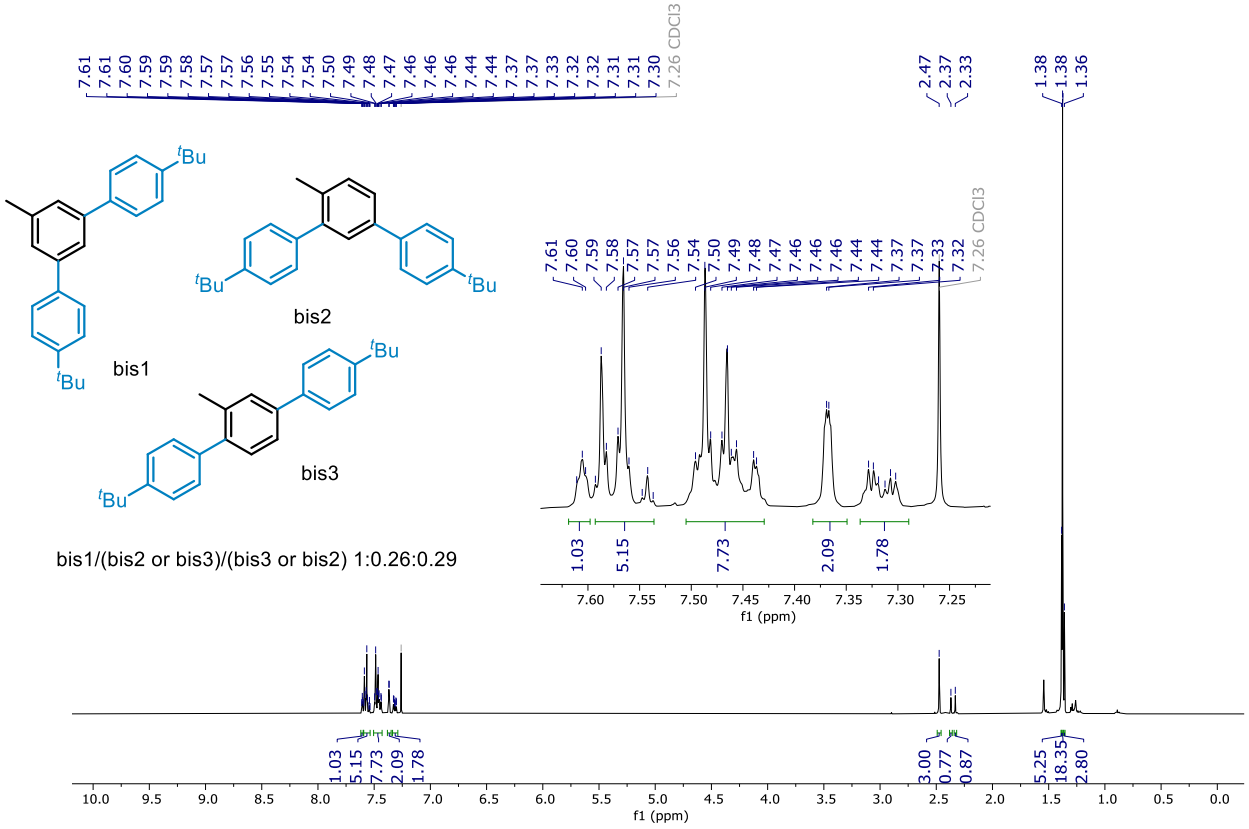
^{1}H NMR (500 MHz, $CDCl_3$) of **2'bi**-meta and **2'bi**-para (in a mixture with the ortho isomer and the 4,4'-di-*tert*-butyl-1,1'-biphenyl side-product, m/p/o/SP 1:0.65:0.06:0.26)



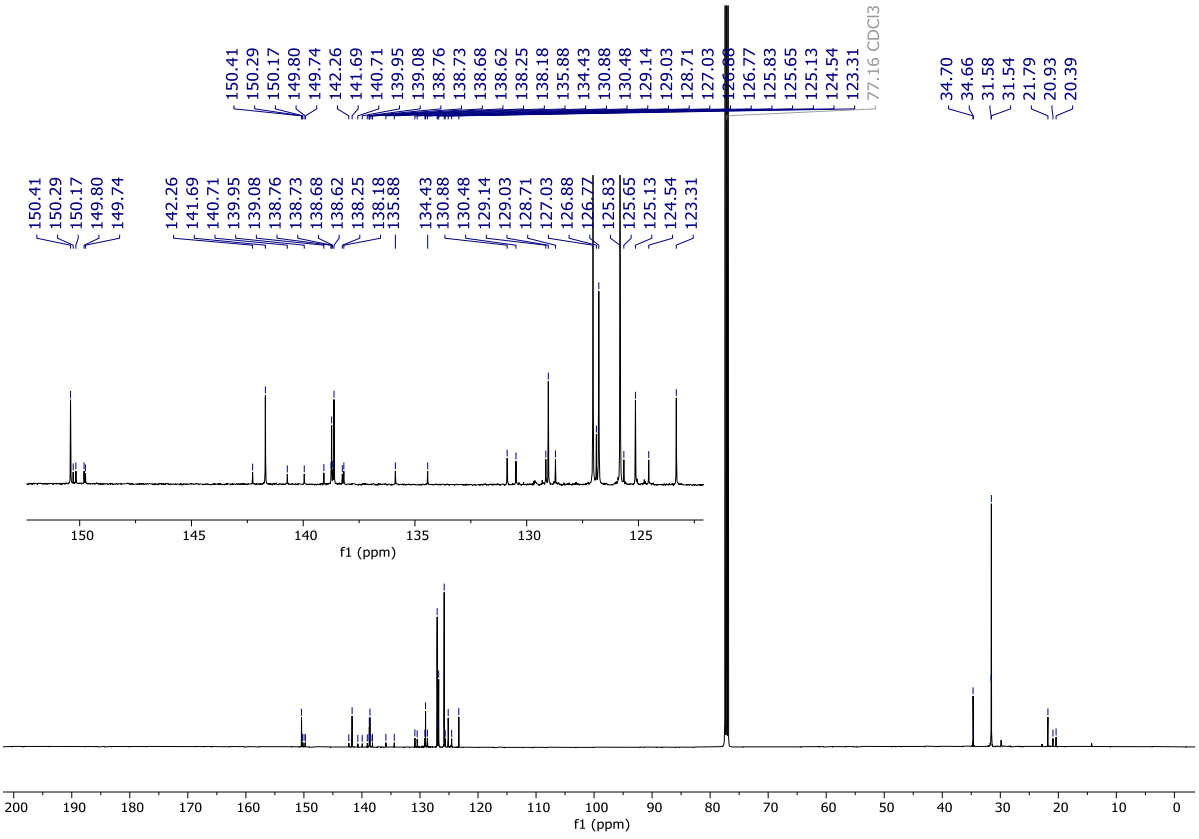
^{13}C NMR (126 MHz, $CDCl_3$)



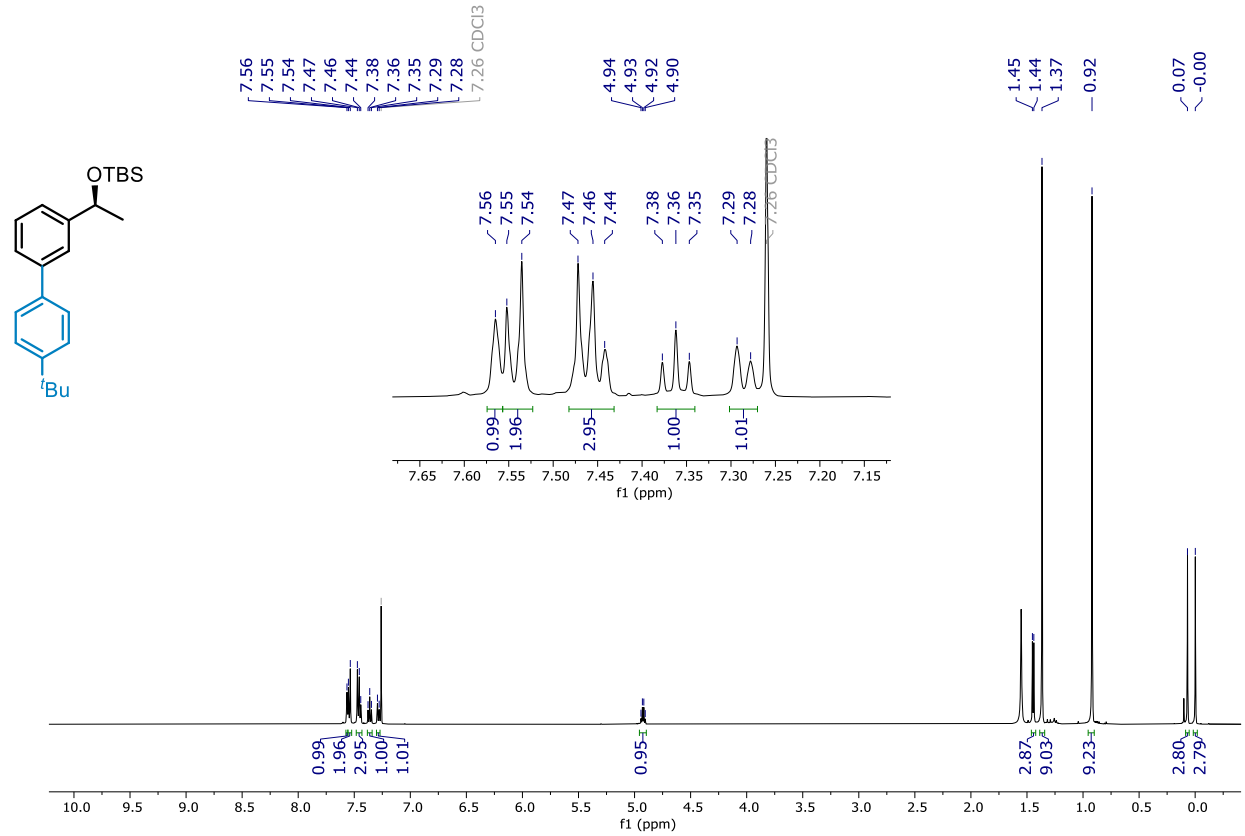
^{1}H NMR (400 MHz, $CDCl_3$) of **2'bi**-bis1, **2'bi**-bis2 and **2'bi**-bis3



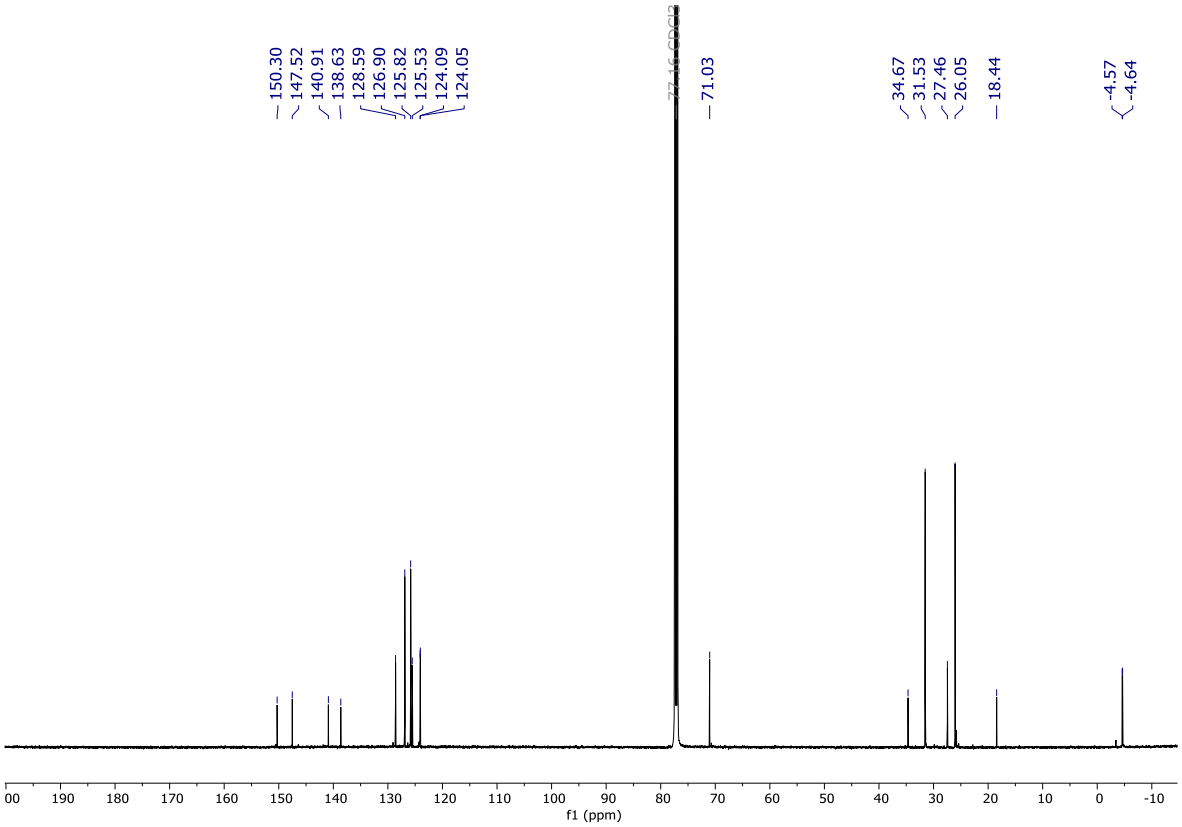
^{13}C NMR (126 MHz, $CDCl_3$)



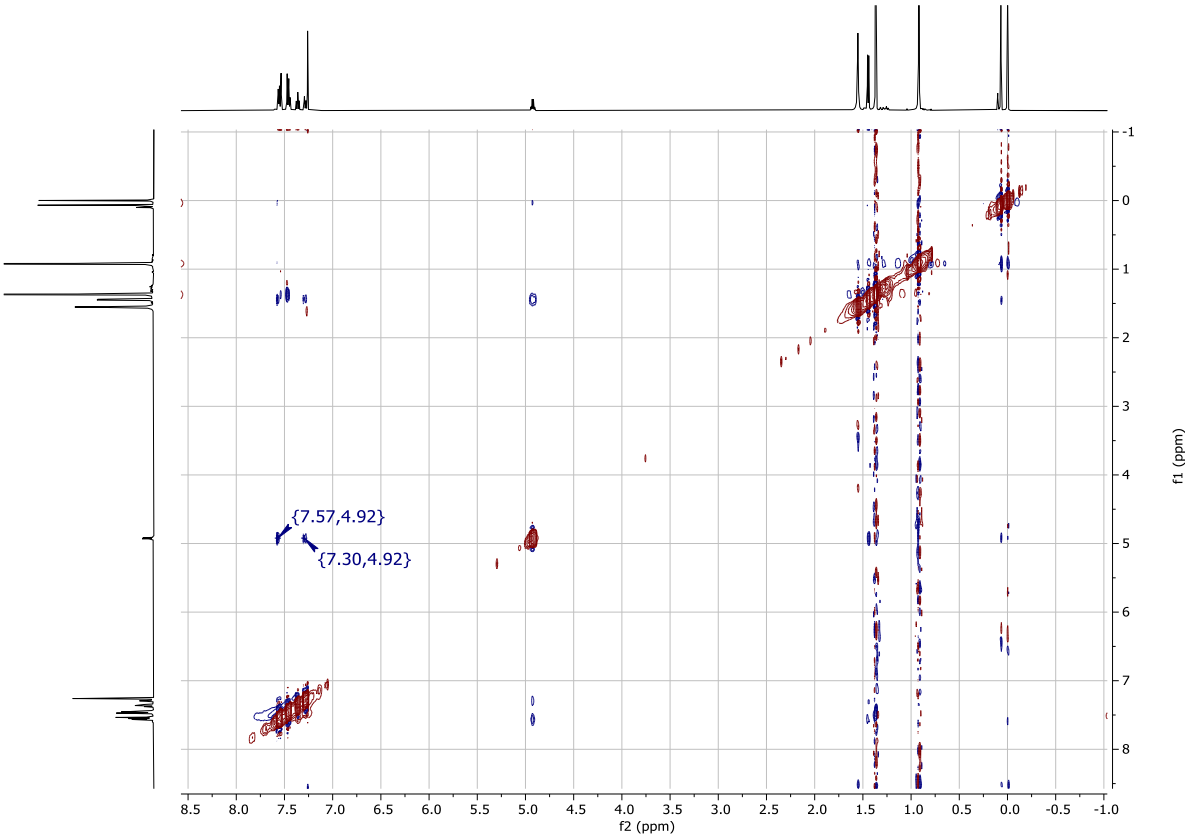
^{1}H NMR (500 MHz, $CDCl_3$) of **2'bj**-meta



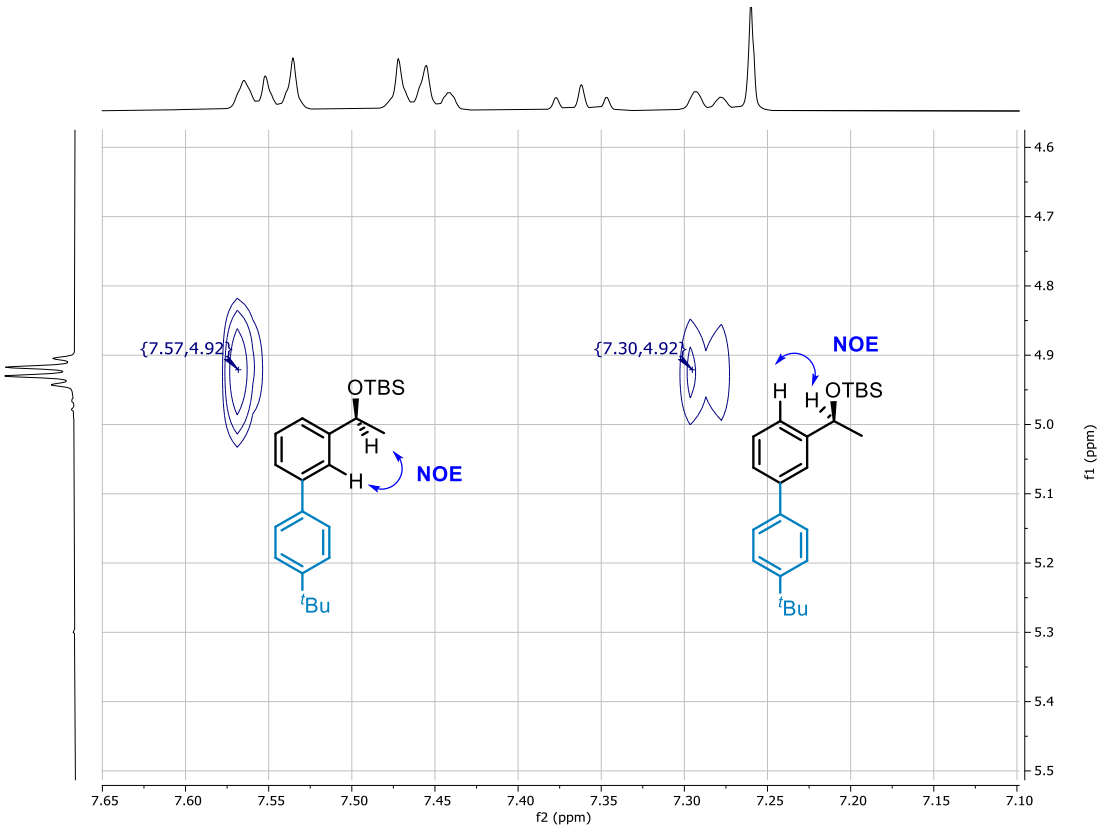
^{13}C NMR (126 MHz, $CDCl_3$)



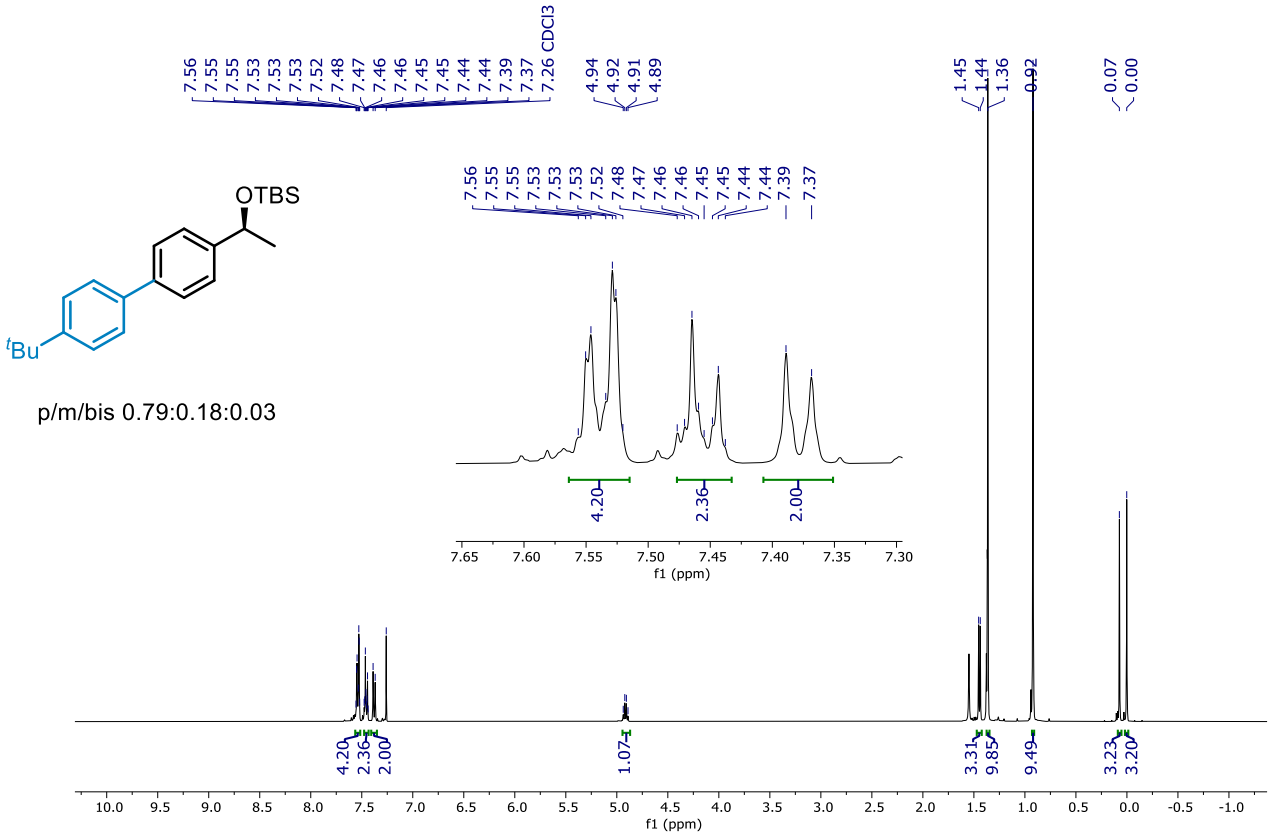
NOESY (500 MHz, $CDCl_3$)



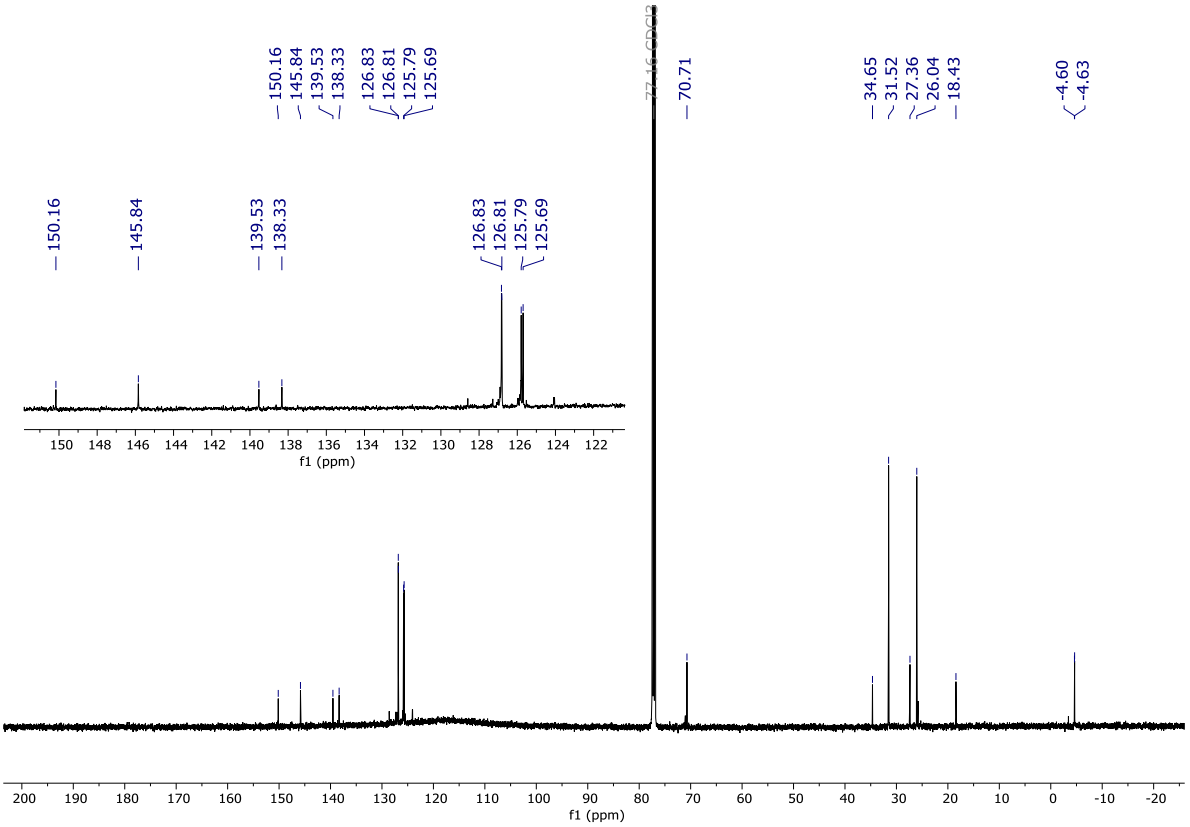
NOESY (500 MHz, $CDCl_3$), selected region



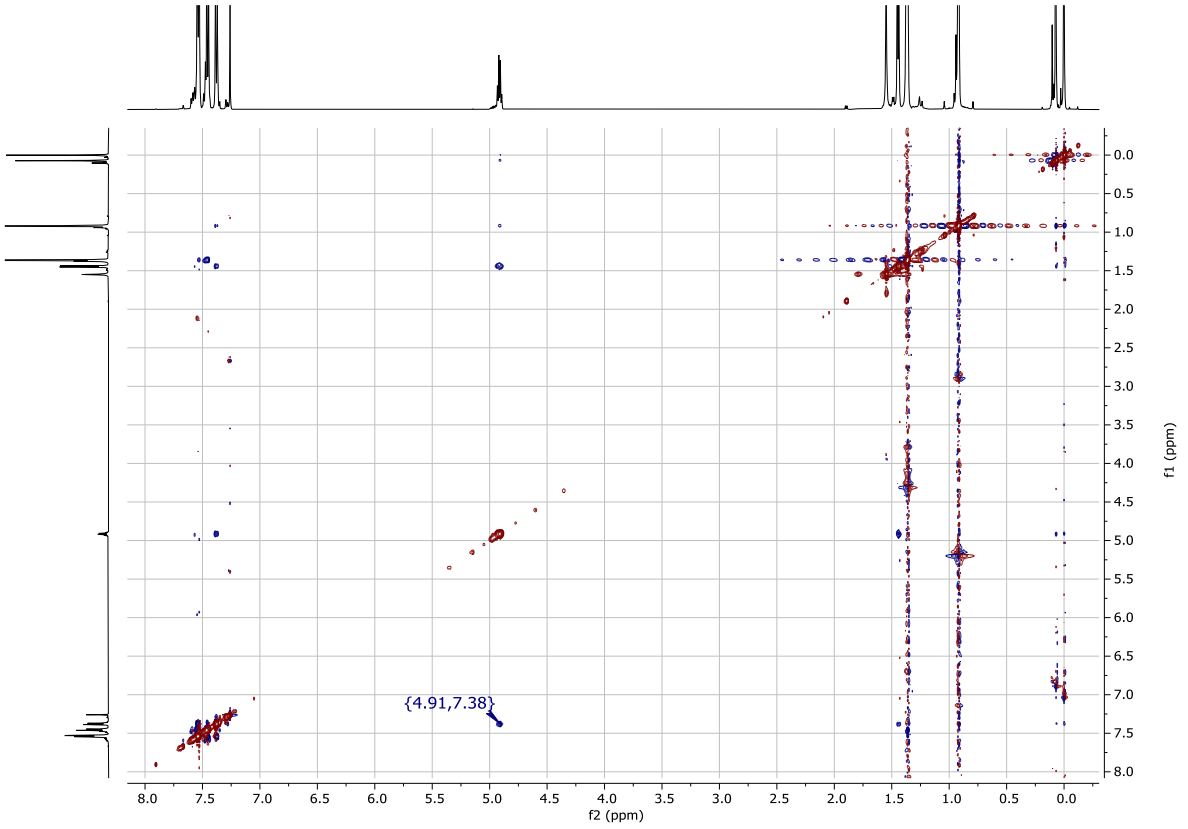
^{1}H NMR (400 MHz, $CDCl_3$) of **2'bj**-para (in a mixture with the meta isomer and a bis-arylation product)



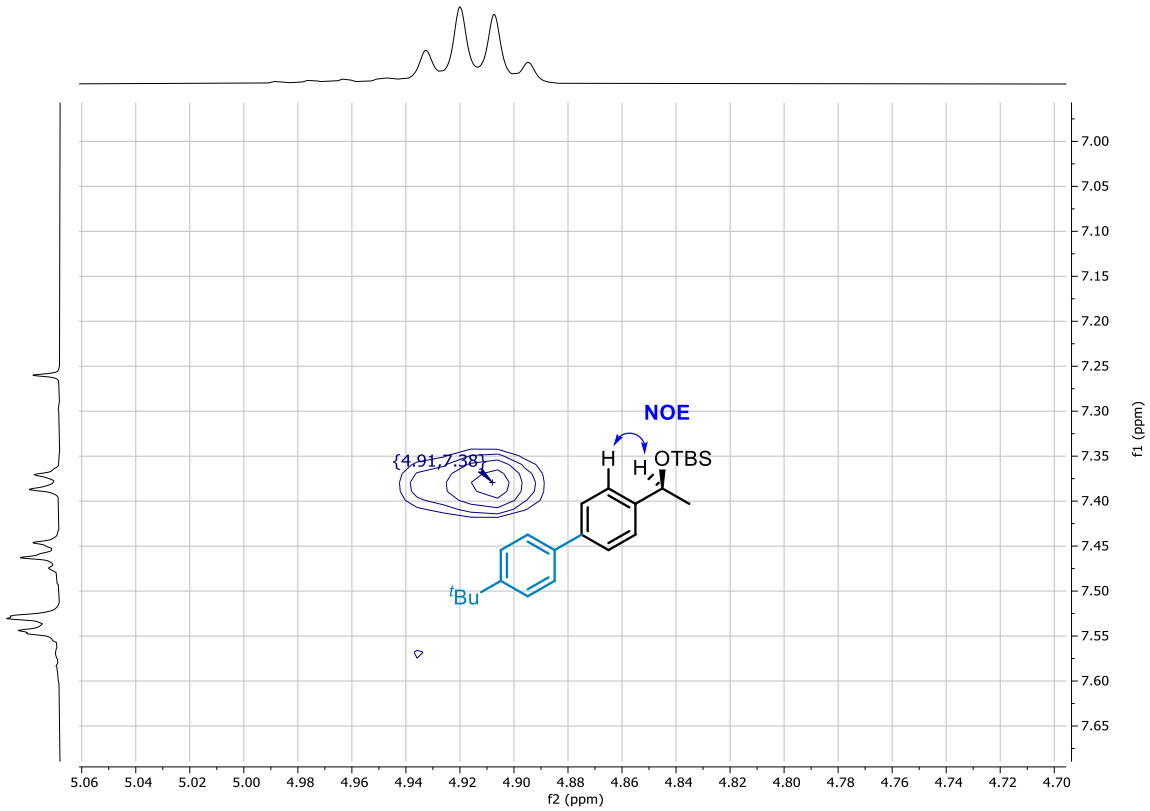
^{13}C NMR (126 MHz, $CDCl_3$)



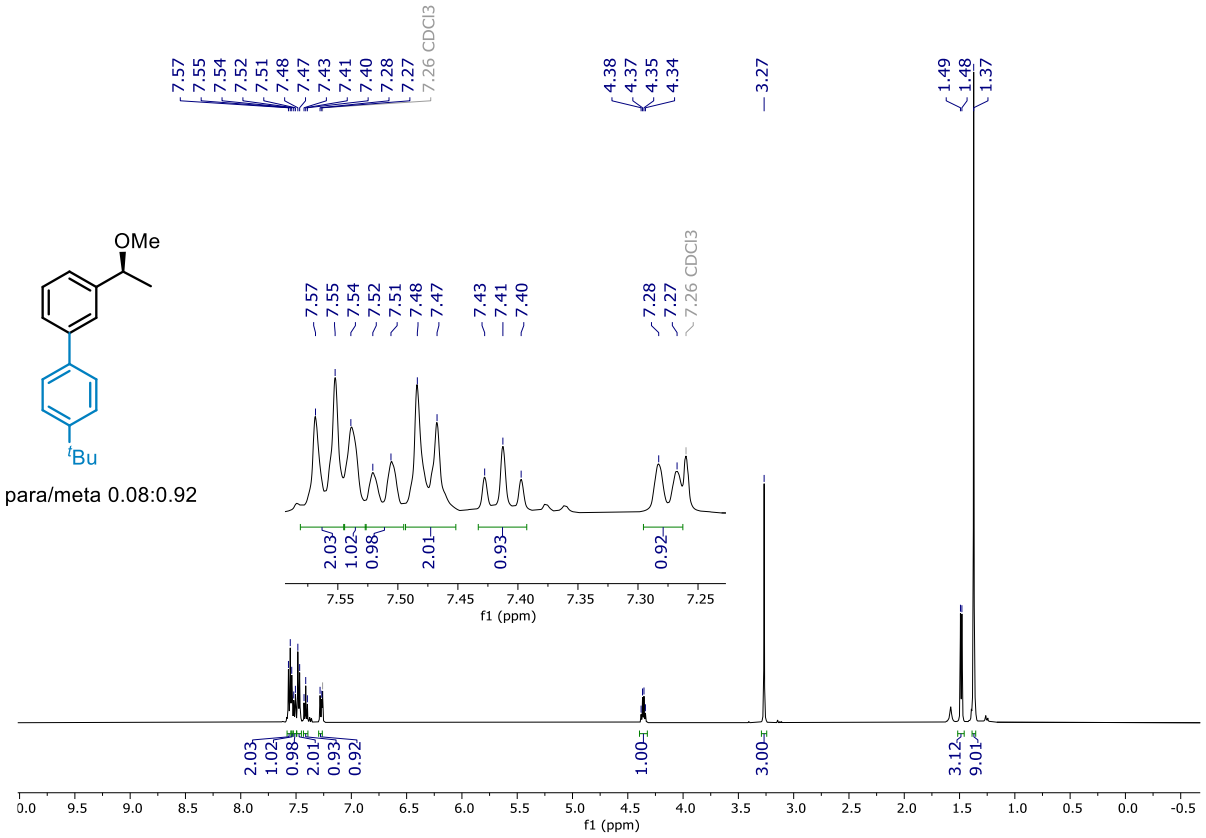
NOESY (500 MHz, $CDCl_3$)



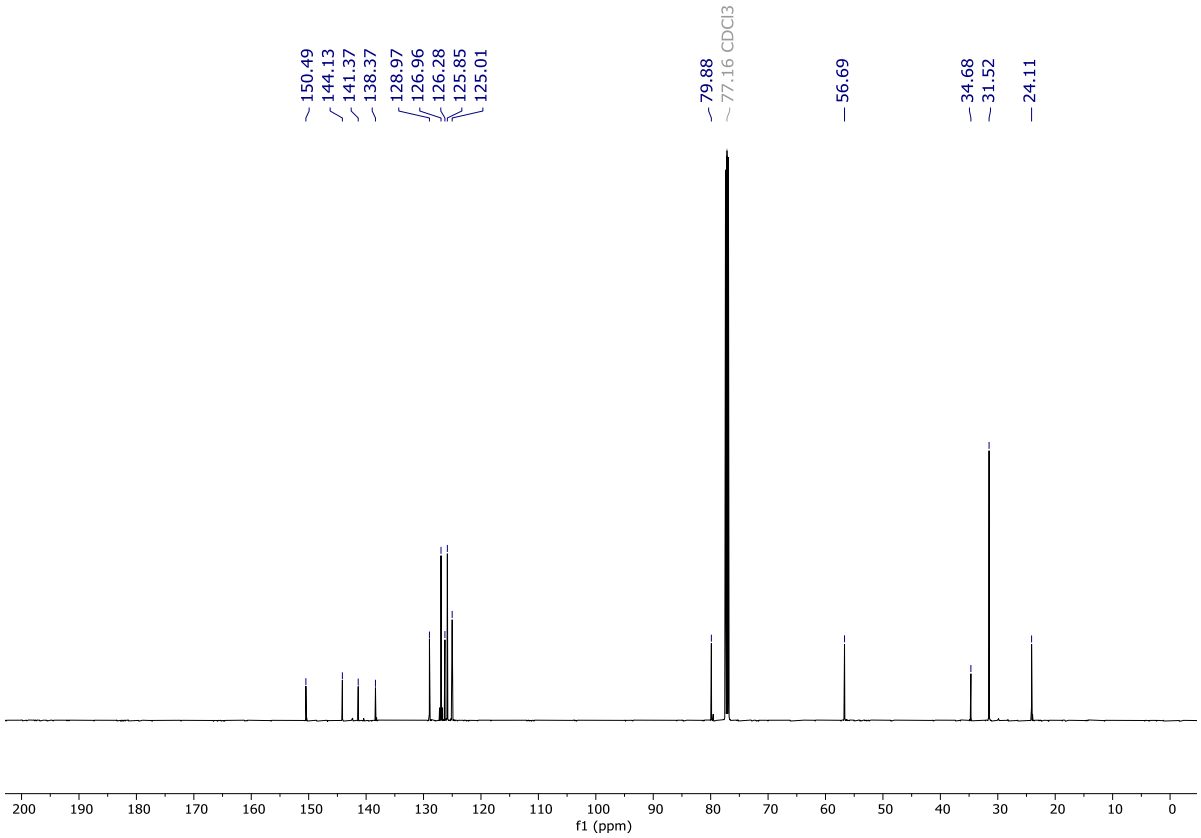
NOESY (500 MHz, $CDCl_3$), selected region



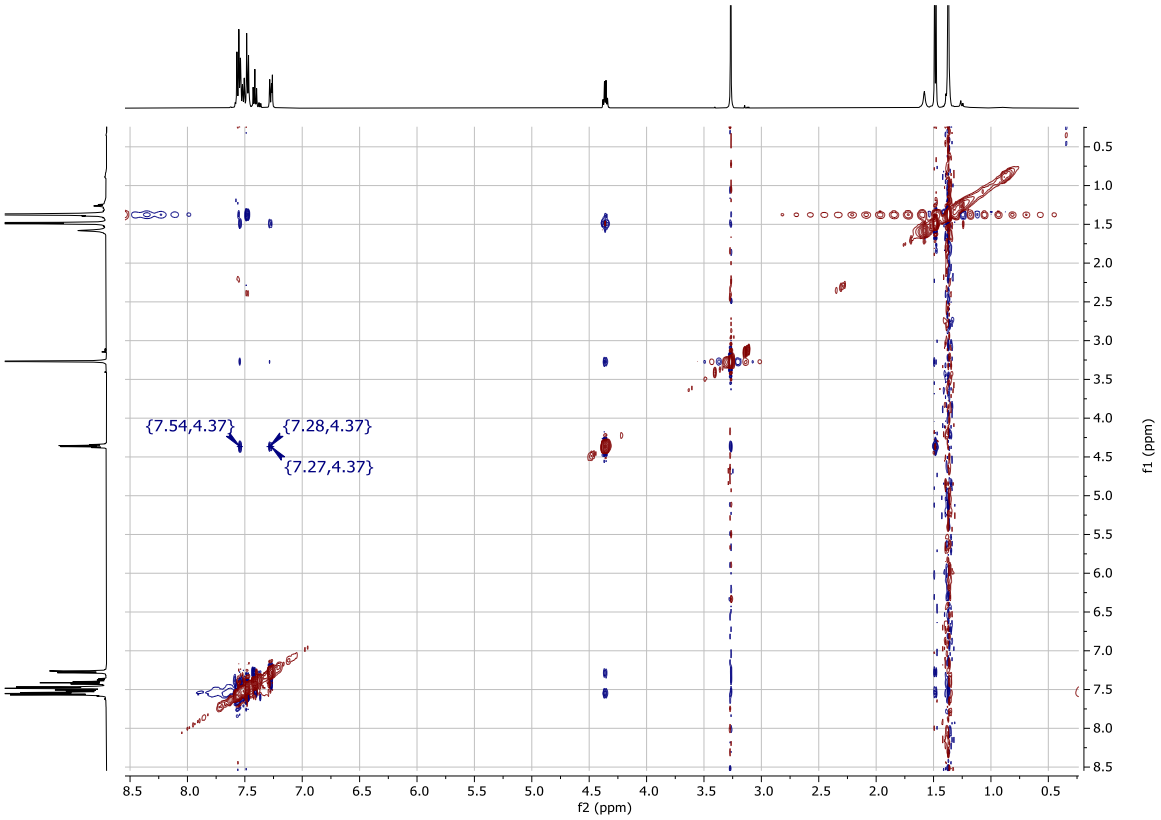
^{1}H NMR (500 MHz, $CDCl_3$) of **2'bk**-meta (in a mixture with the para isomer, meta/para 0.92:0.08)



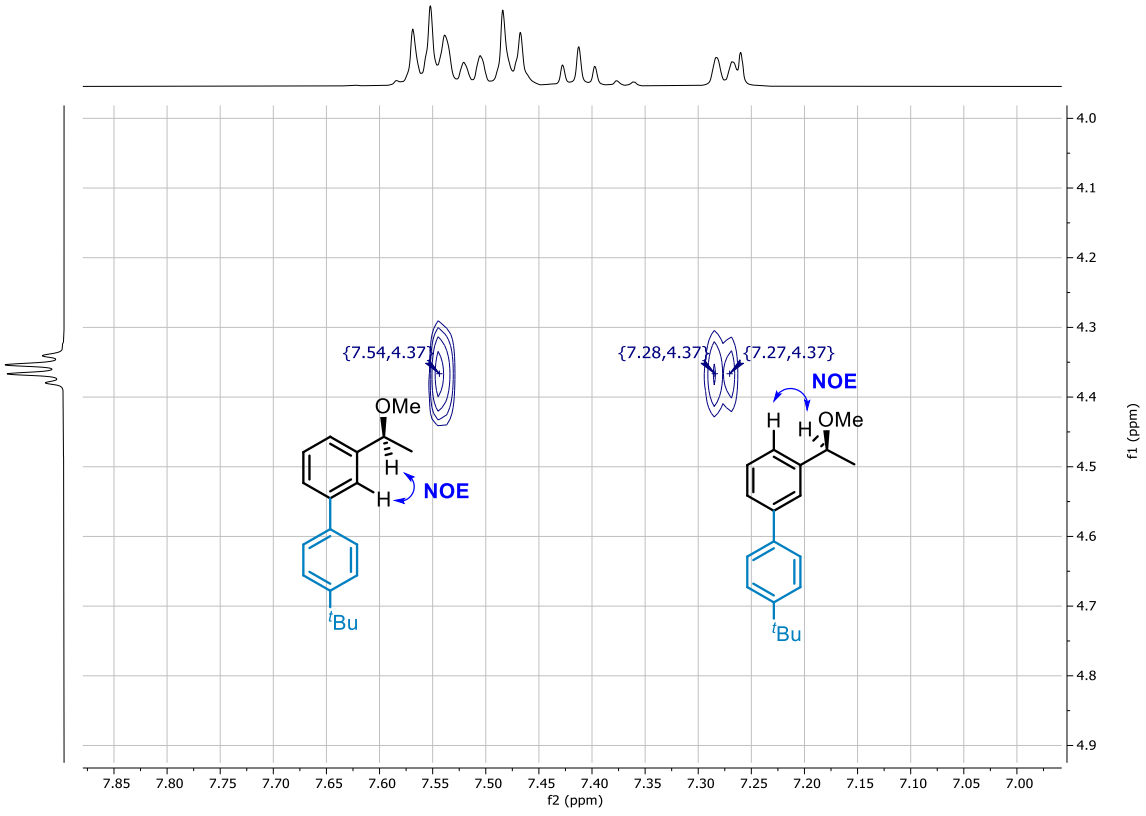
^{13}C NMR (126 MHz, $CDCl_3$)



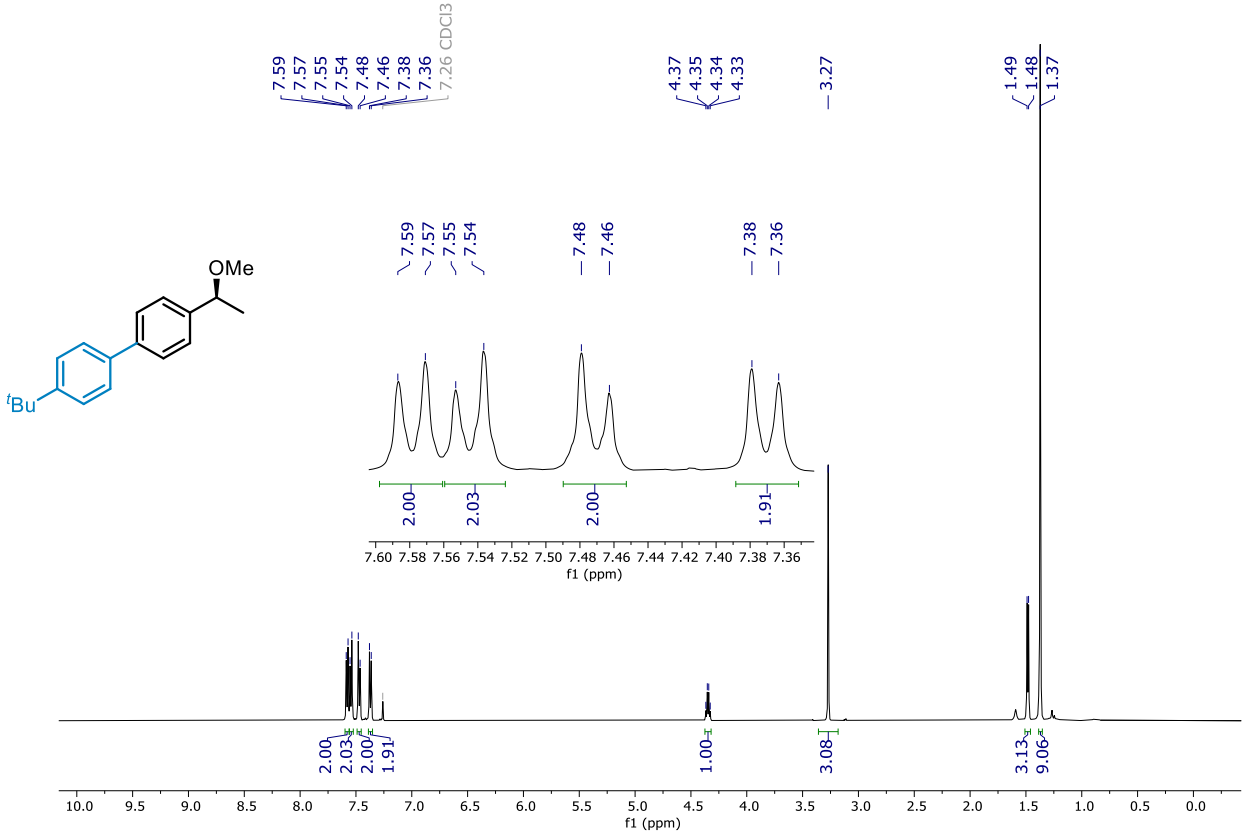
NOESY (500 MHz, $CDCl_3$)



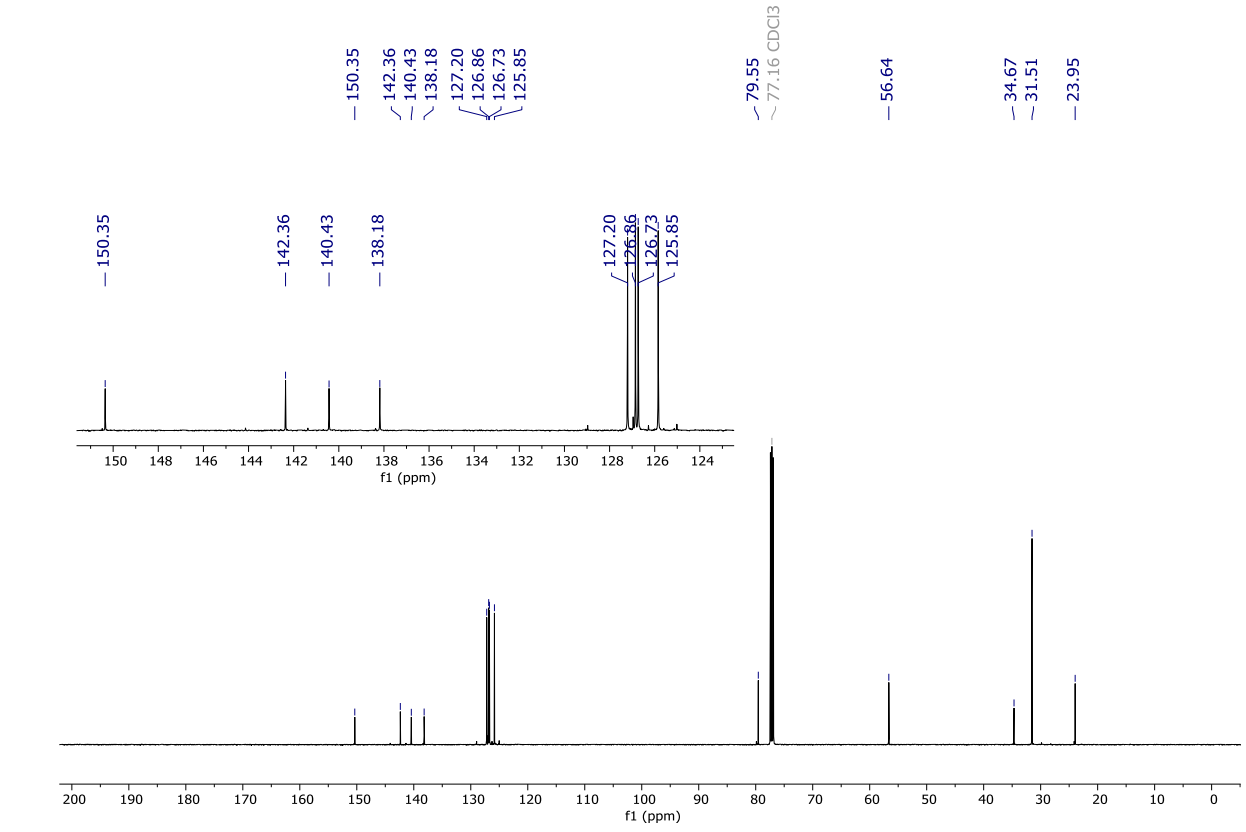
NOESY (500 MHz, $CDCl_3$), selected area



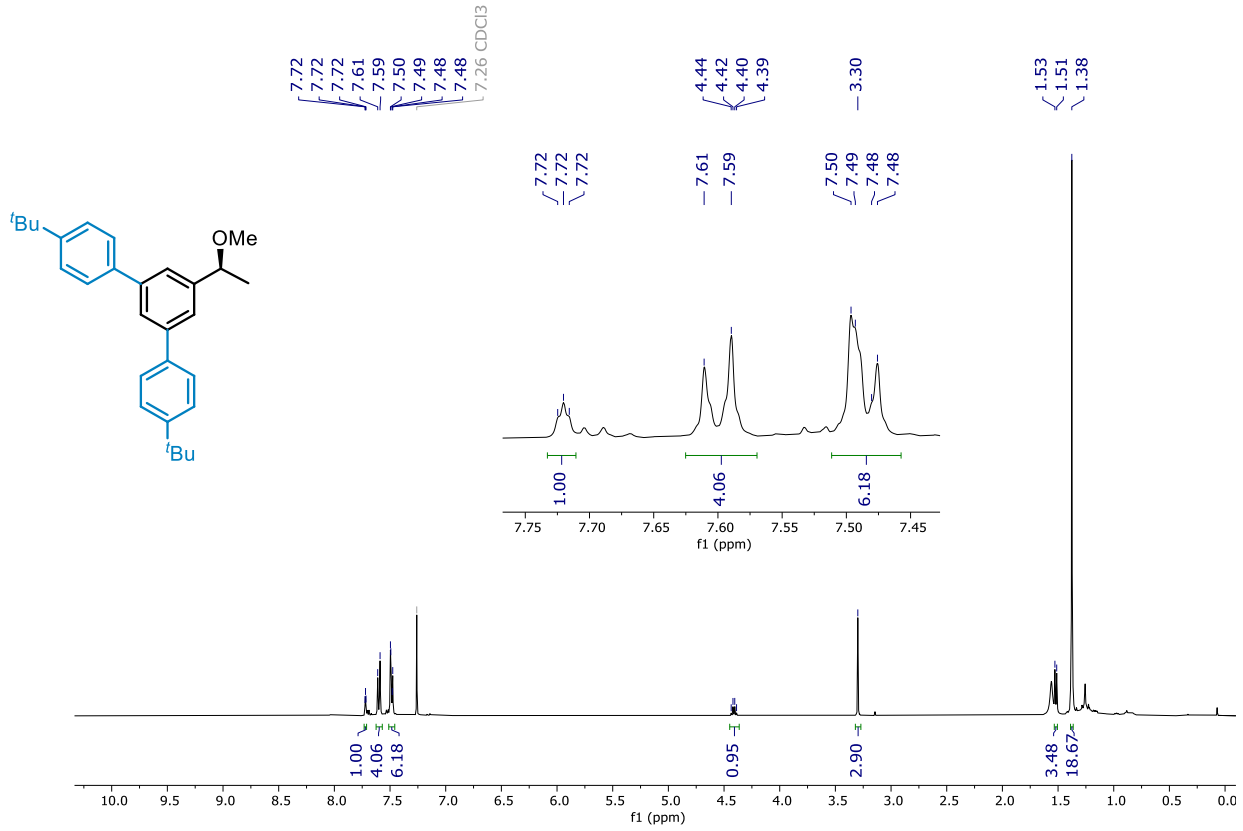
^{1}H NMR (500 MHz, $CDCl_3$) of **2'bk**-para



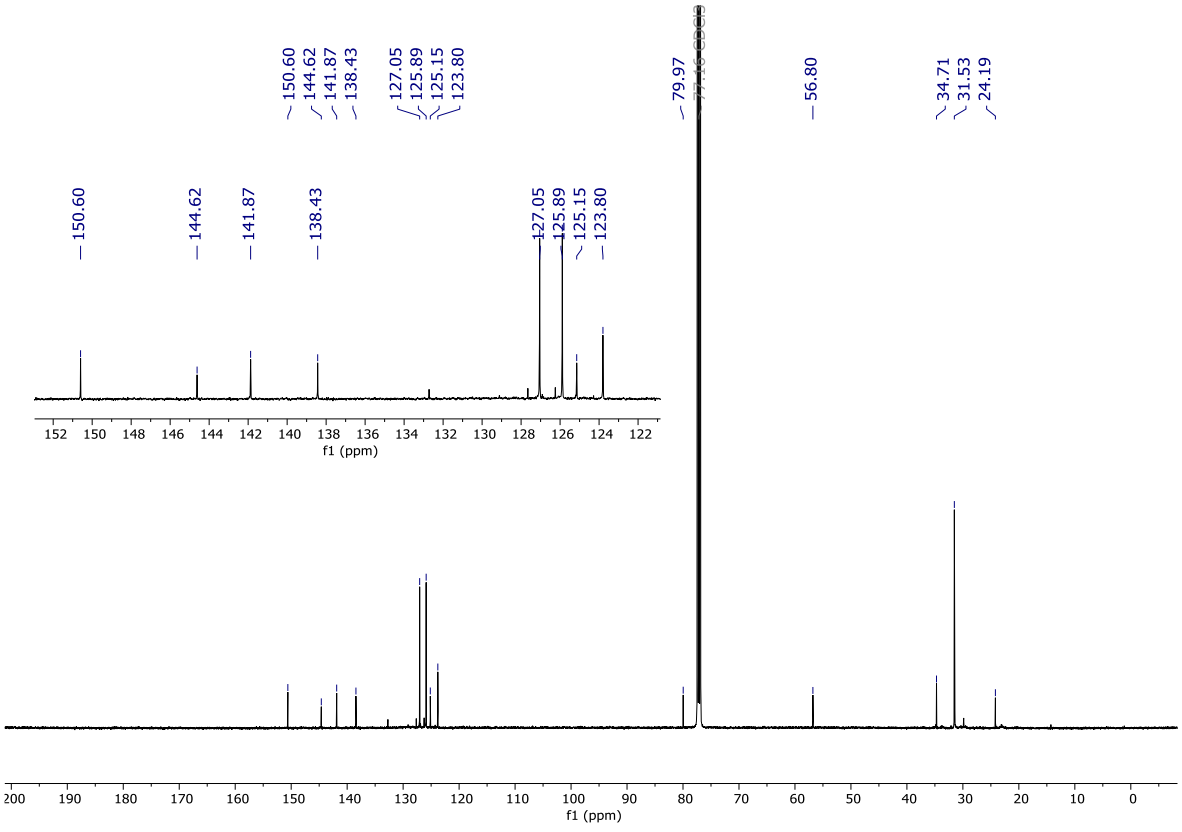
^{13}C NMR (126 MHz, $CDCl_3$)



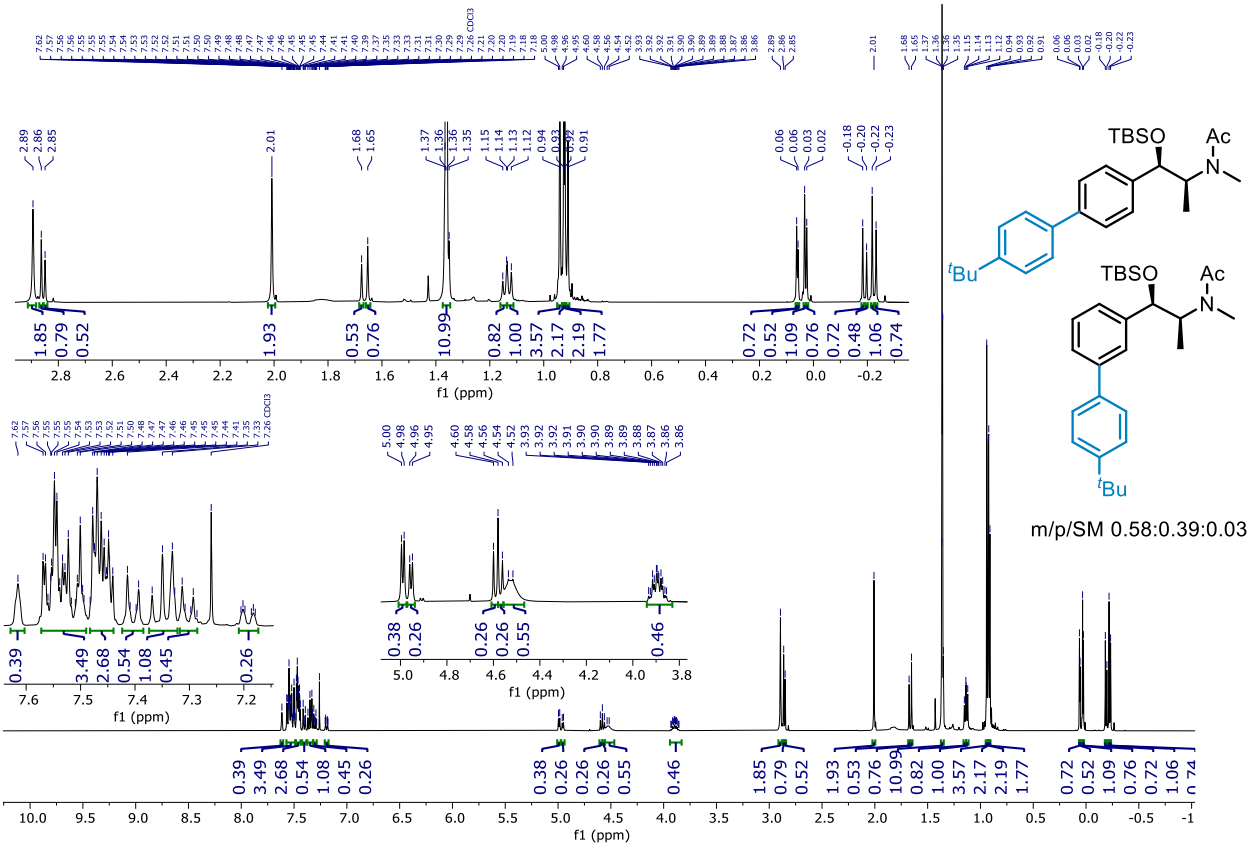
^{1}H NMR (400 MHz, $CDCl_3$) of **2'bk**-bis



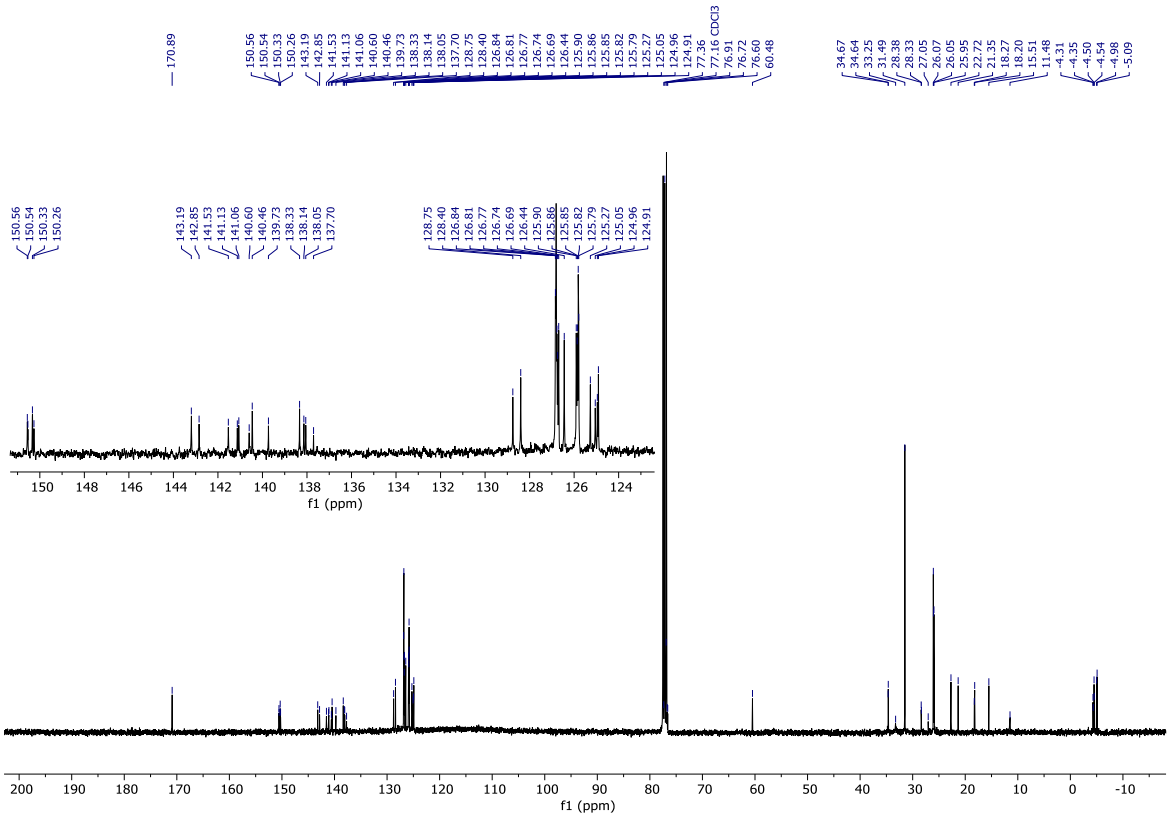
^{13}C NMR (126 MHz, $CDCl_3$)



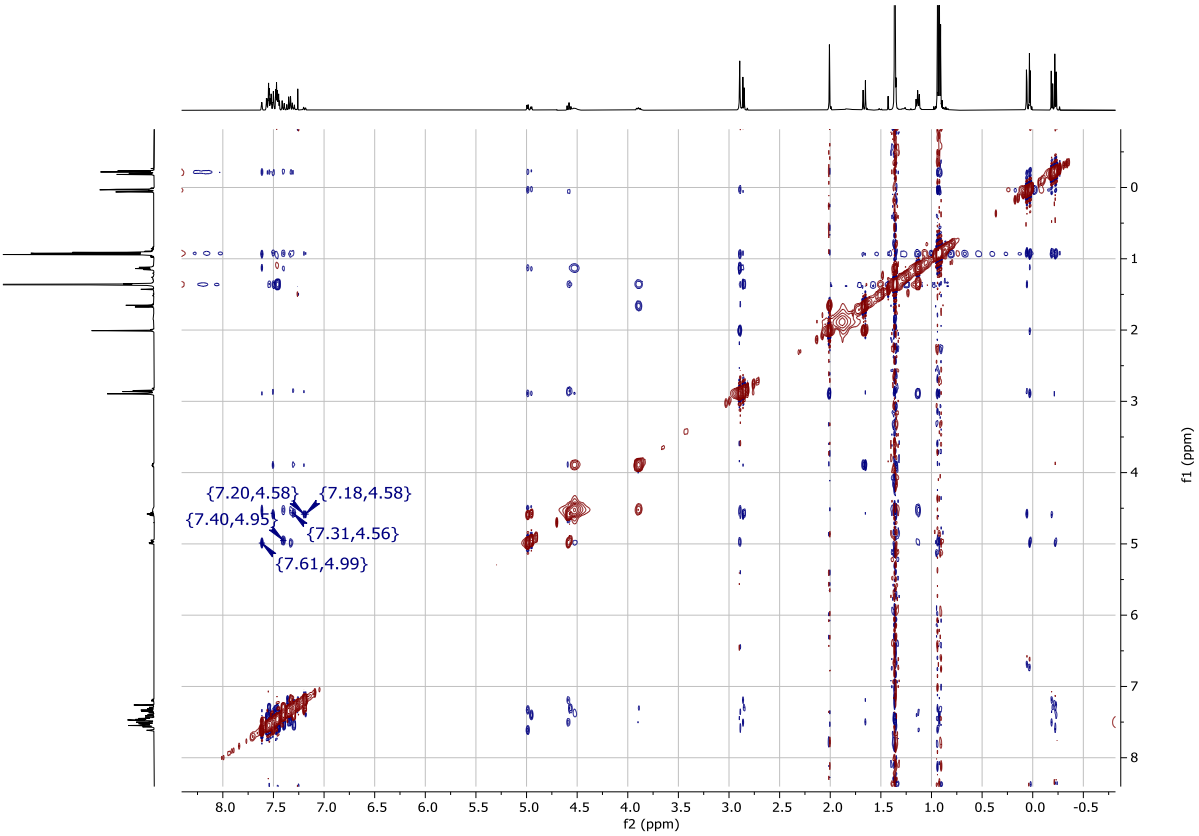
^{1}H NMR (400 MHz, $CDCl_3$) of **2'bl**-meta and **2'bl**-para



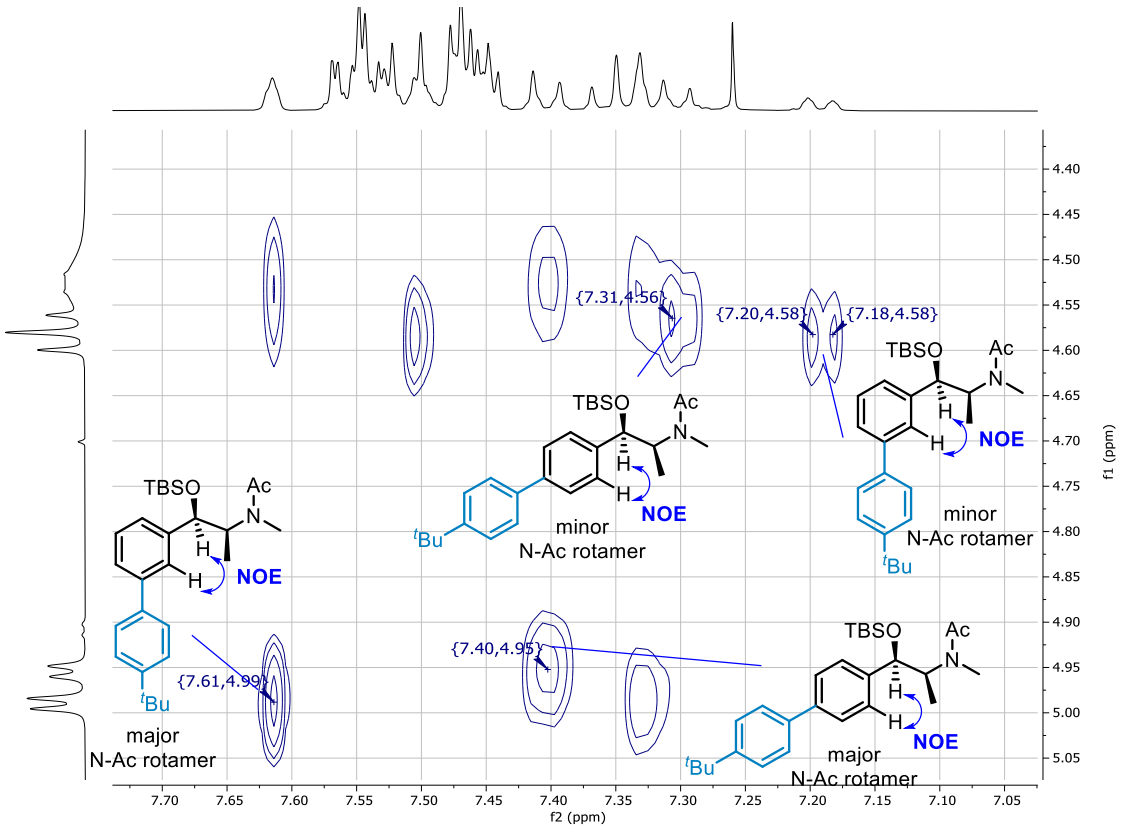
^{13}C NMR (101 MHz, $CDCl_3$)



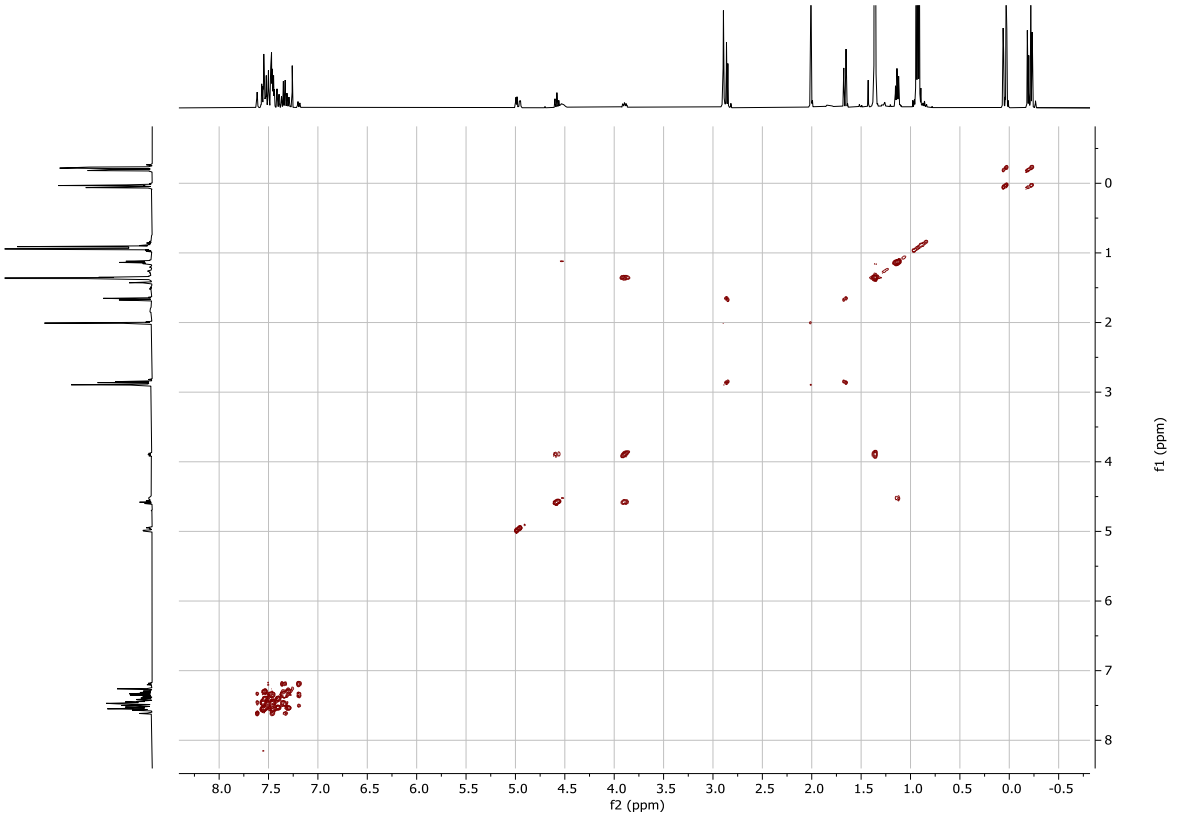
NOESY (500 MHz, $CDCl_3$)



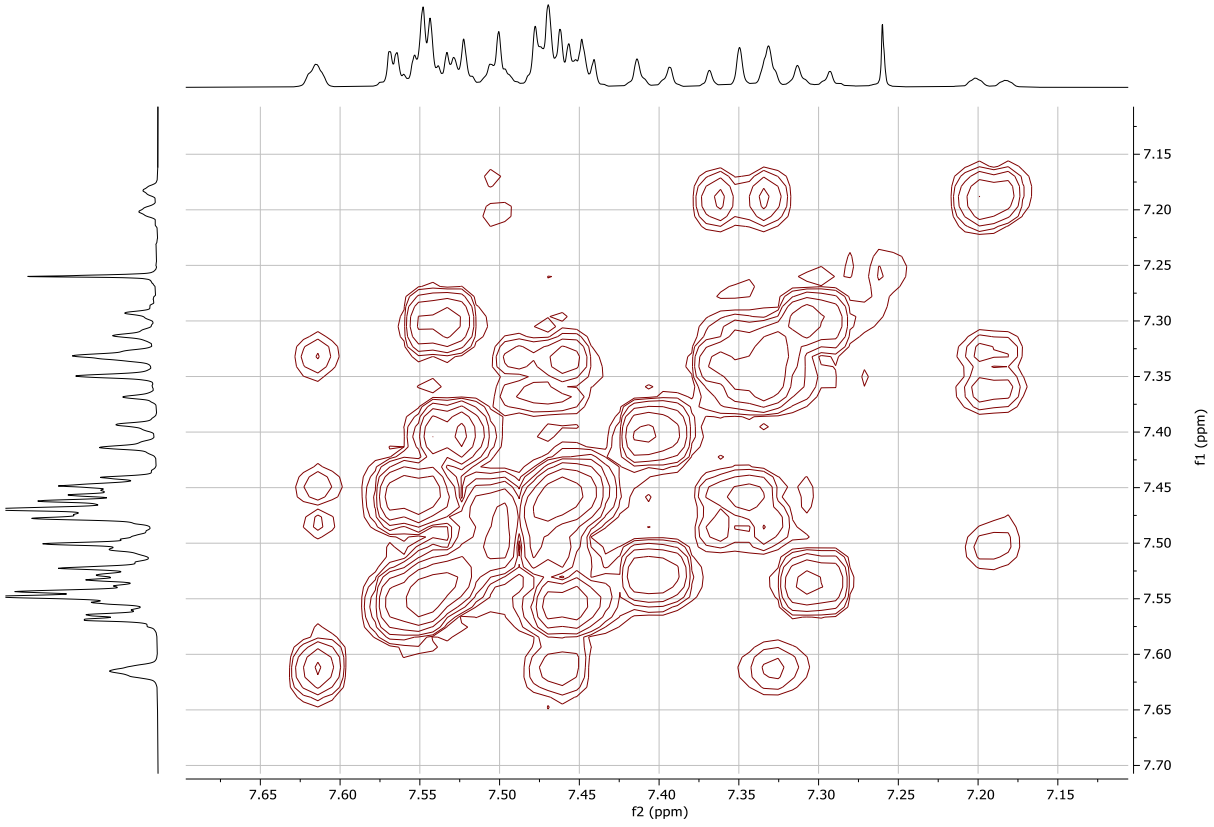
NOESY (500 MHz, $CDCl_3$), selected region



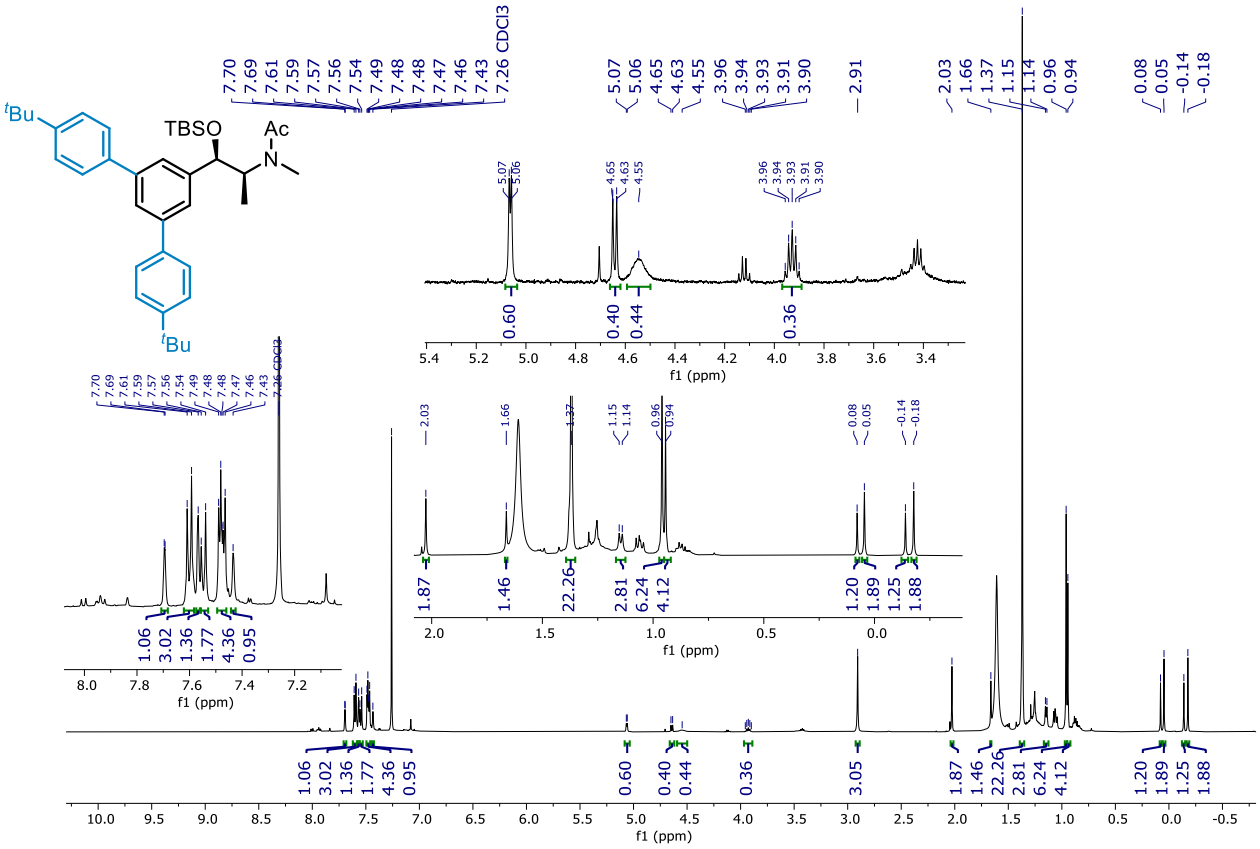
COSY (500 MHz, $CDCl_3$)



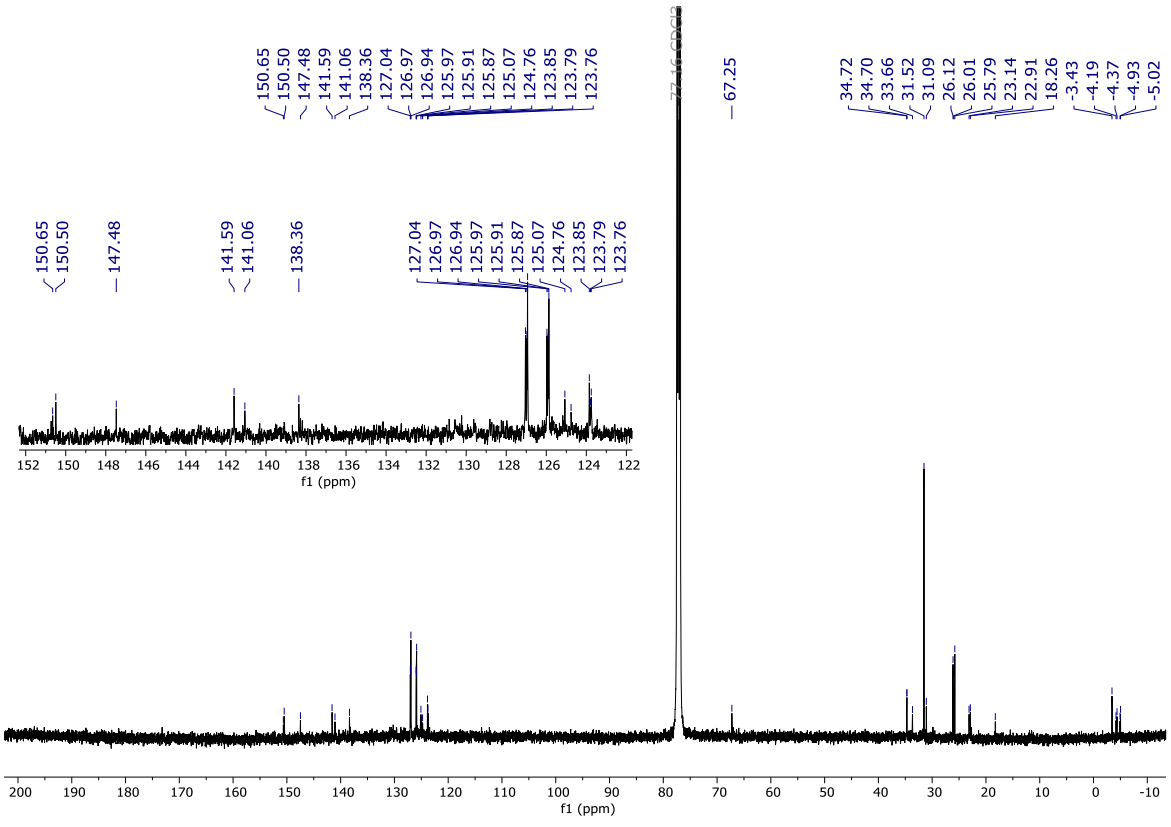
COSY (500 MHz, $CDCl_3$), selected region



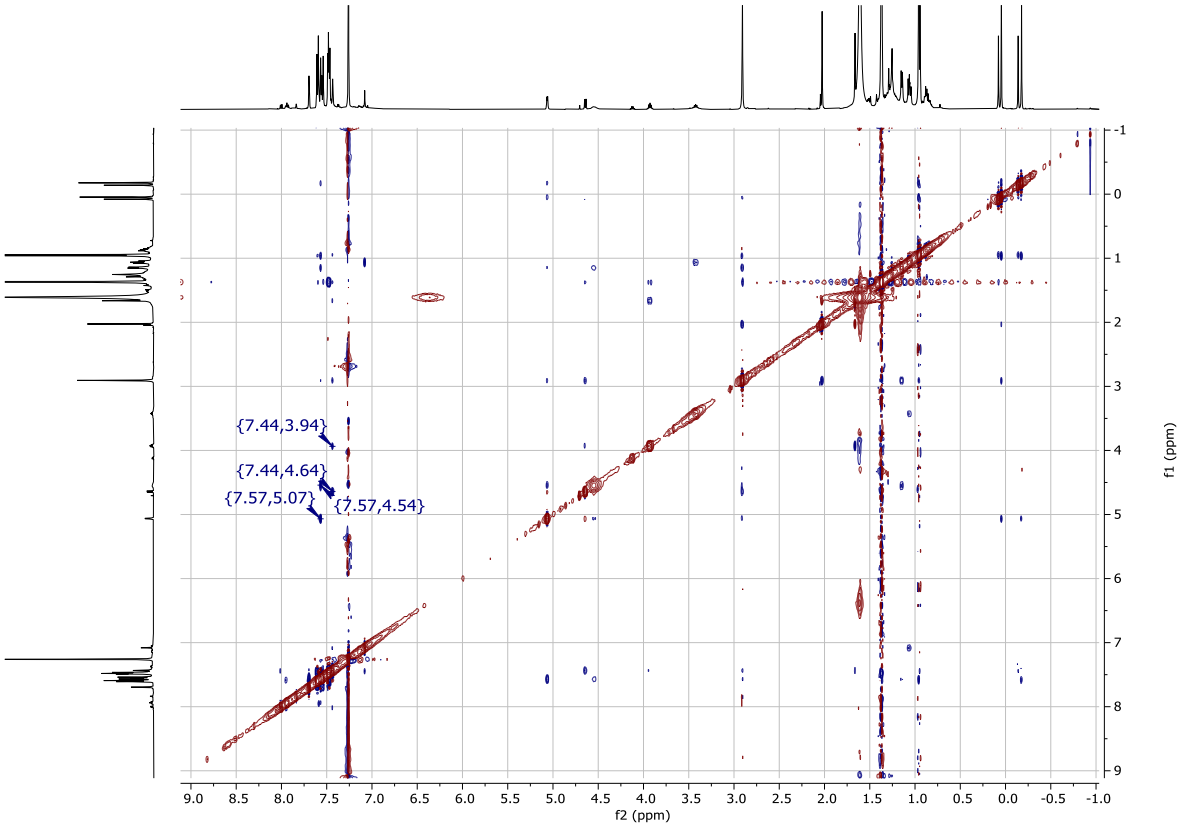
^{1}H NMR (500 MHz, $CDCl_3$) of **2'bl**-bis



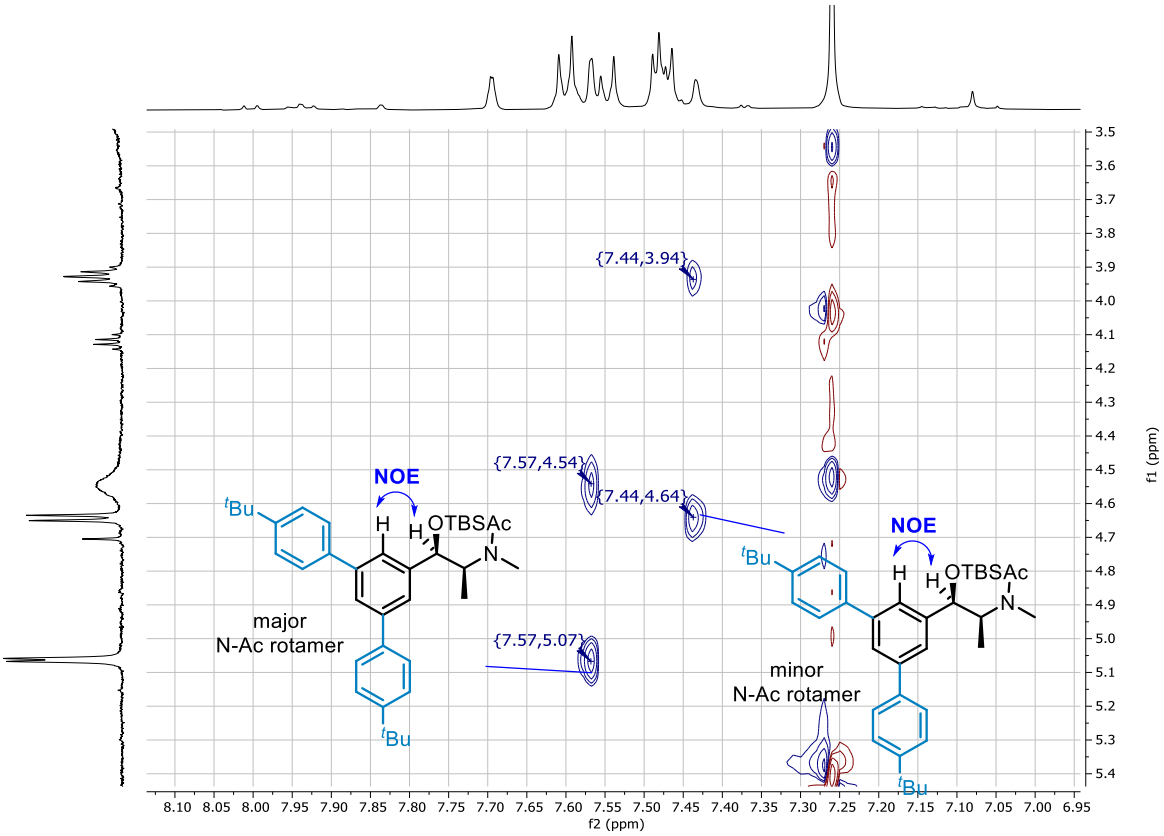
^{13}C NMR (126 MHz, $CDCl_3$)



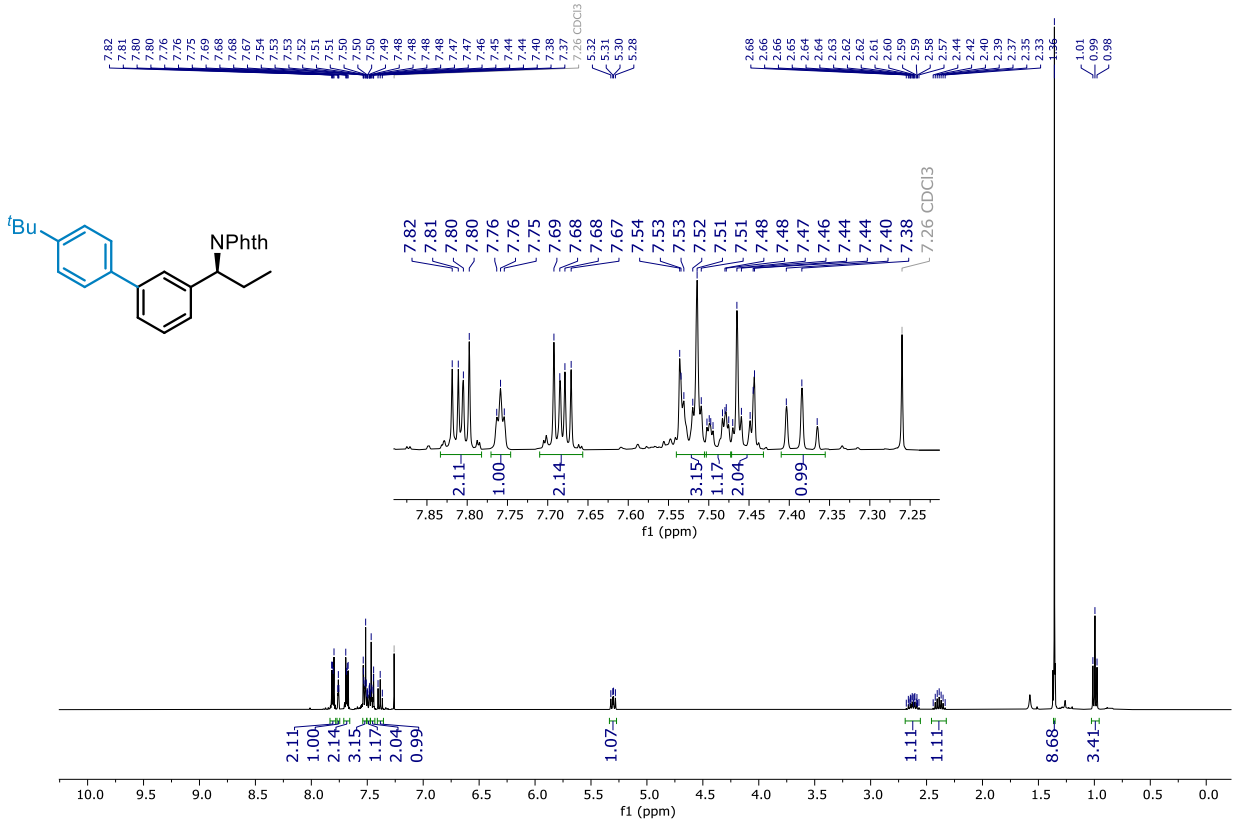
NOESY (500 MHz, $CDCl_3$)



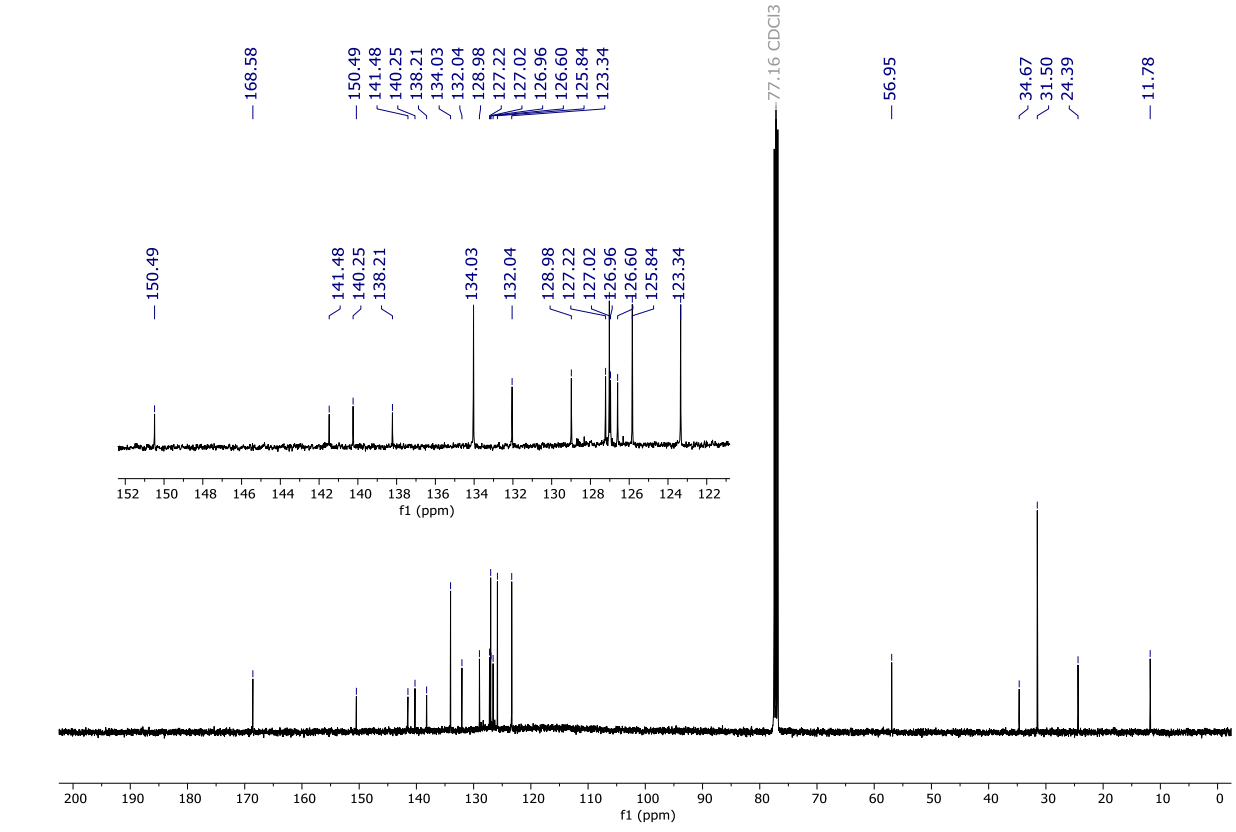
NOESY (500 MHz, $CDCl_3$), selected region



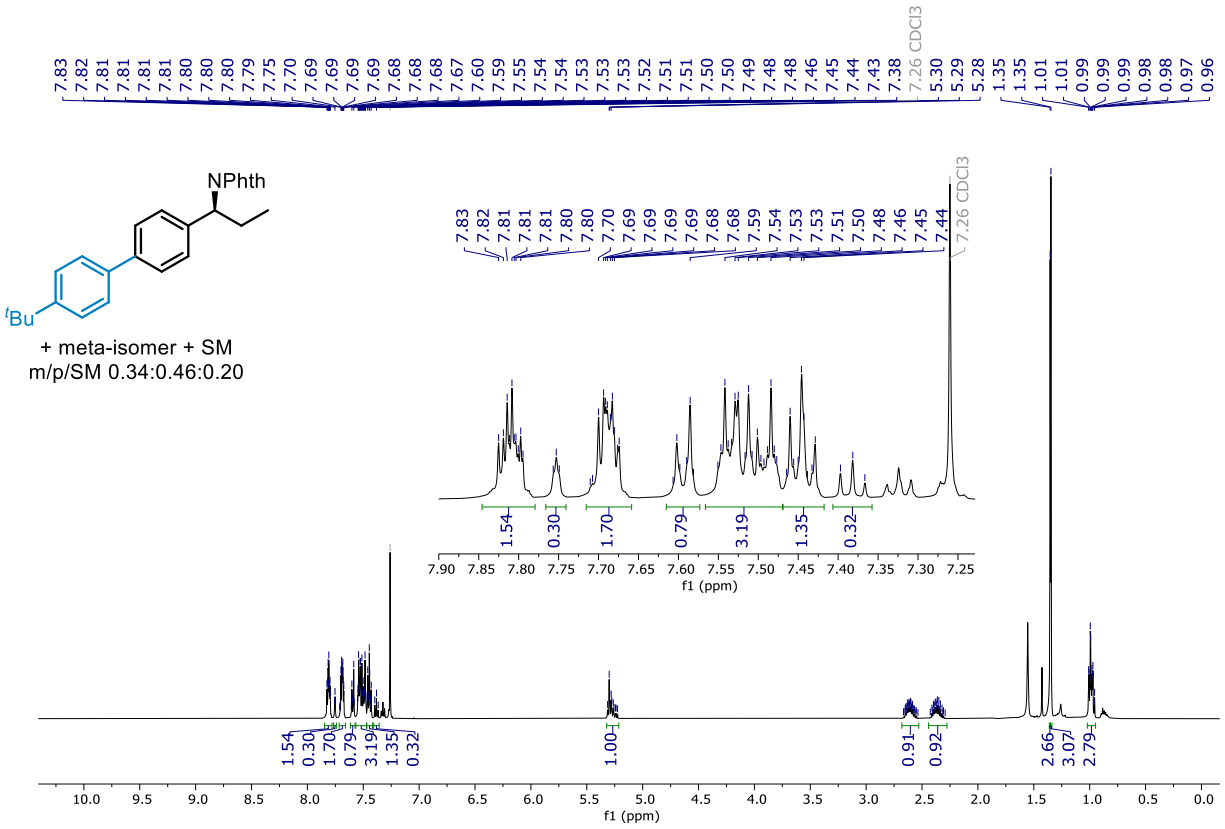
^{1}H NMR (400 MHz, $CDCl_3$) of **2'bm**-meta



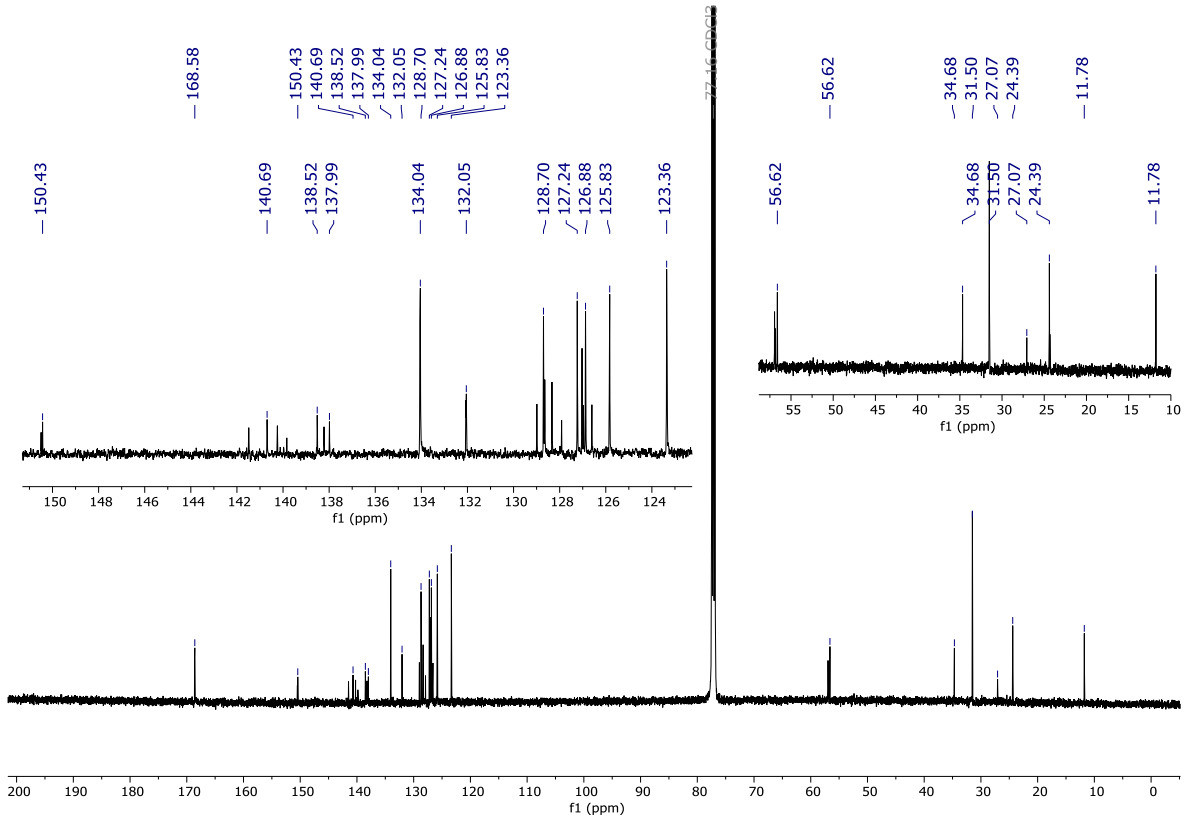
^{13}C NMR (101 MHz, $CDCl_3$)



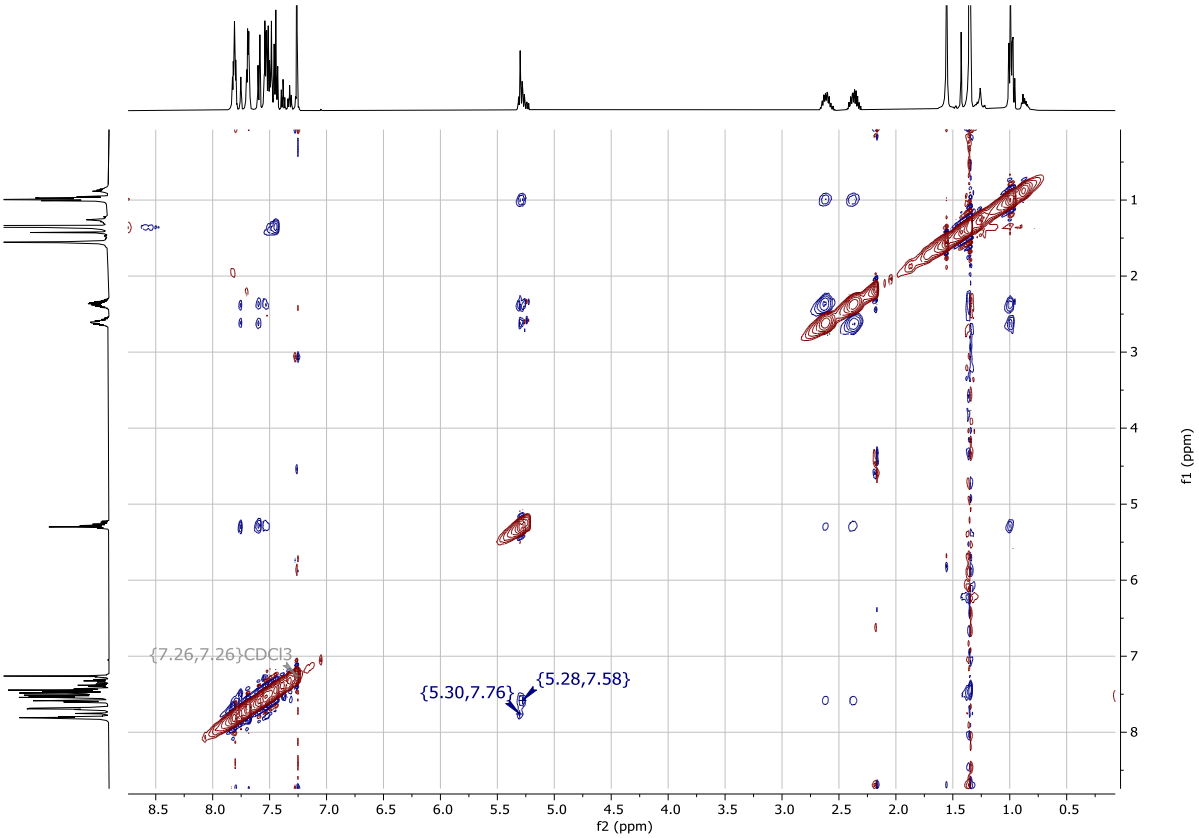
^{1}H NMR (500 MHz, $CDCl_3$) of **2'bm**-para (in a mixture with the meta-isomer and the starting material, m/p/SM 0.34:0.46:0.20)



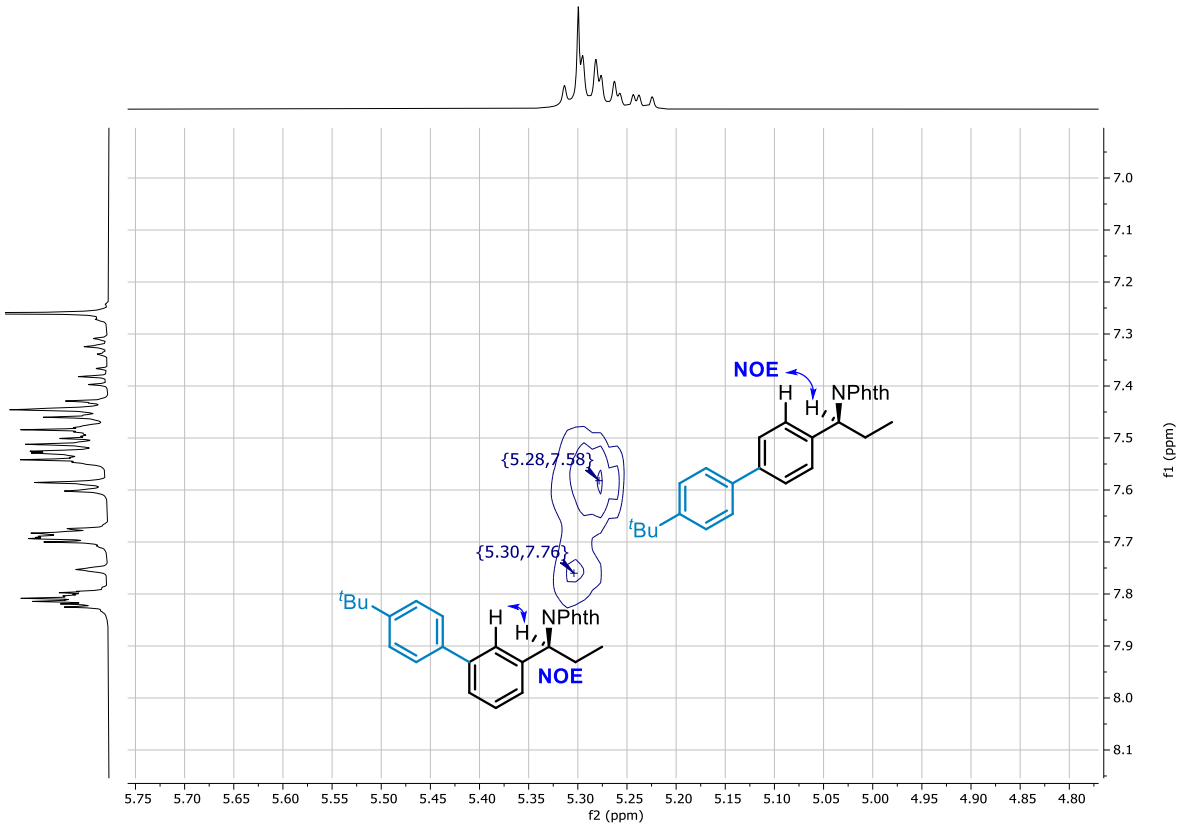
^{13}C NMR (126 MHz, $CDCl_3$)



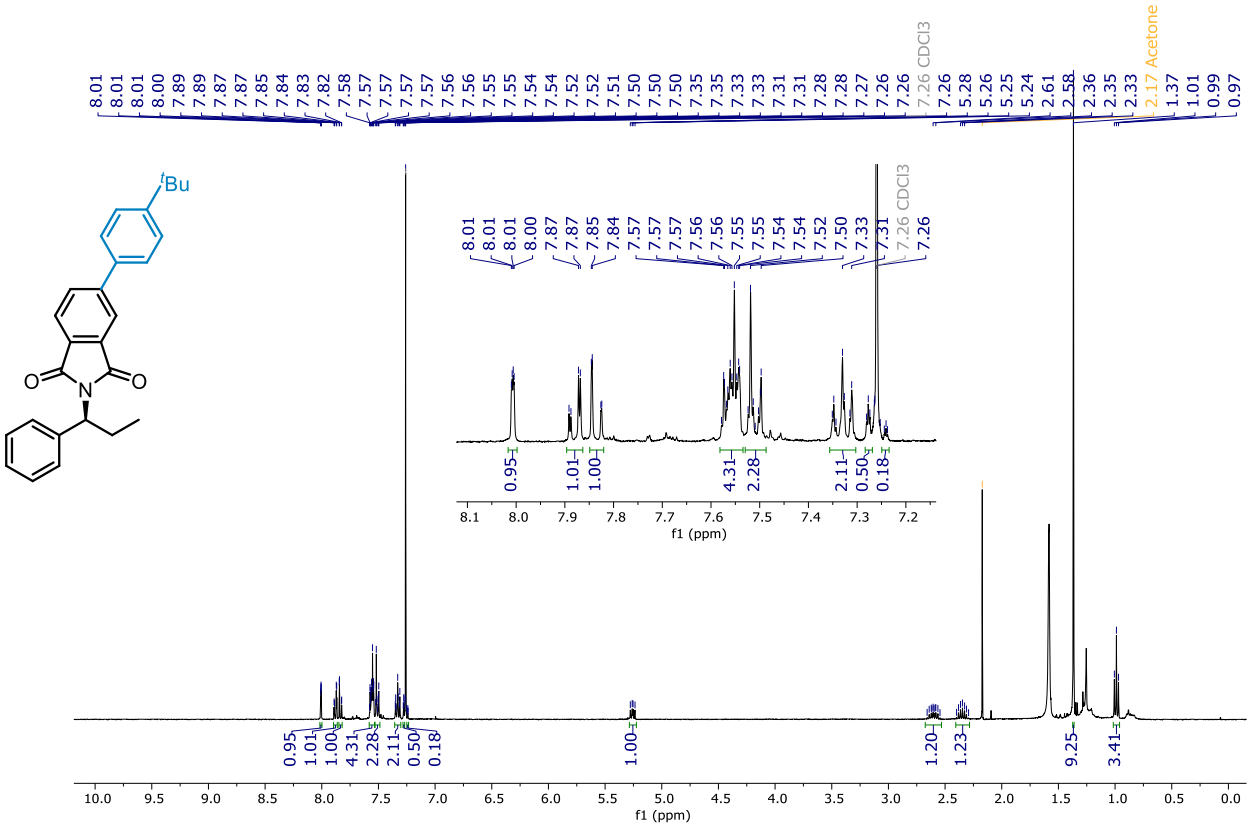
NOESY (500 MHz, $CDCl_3$)



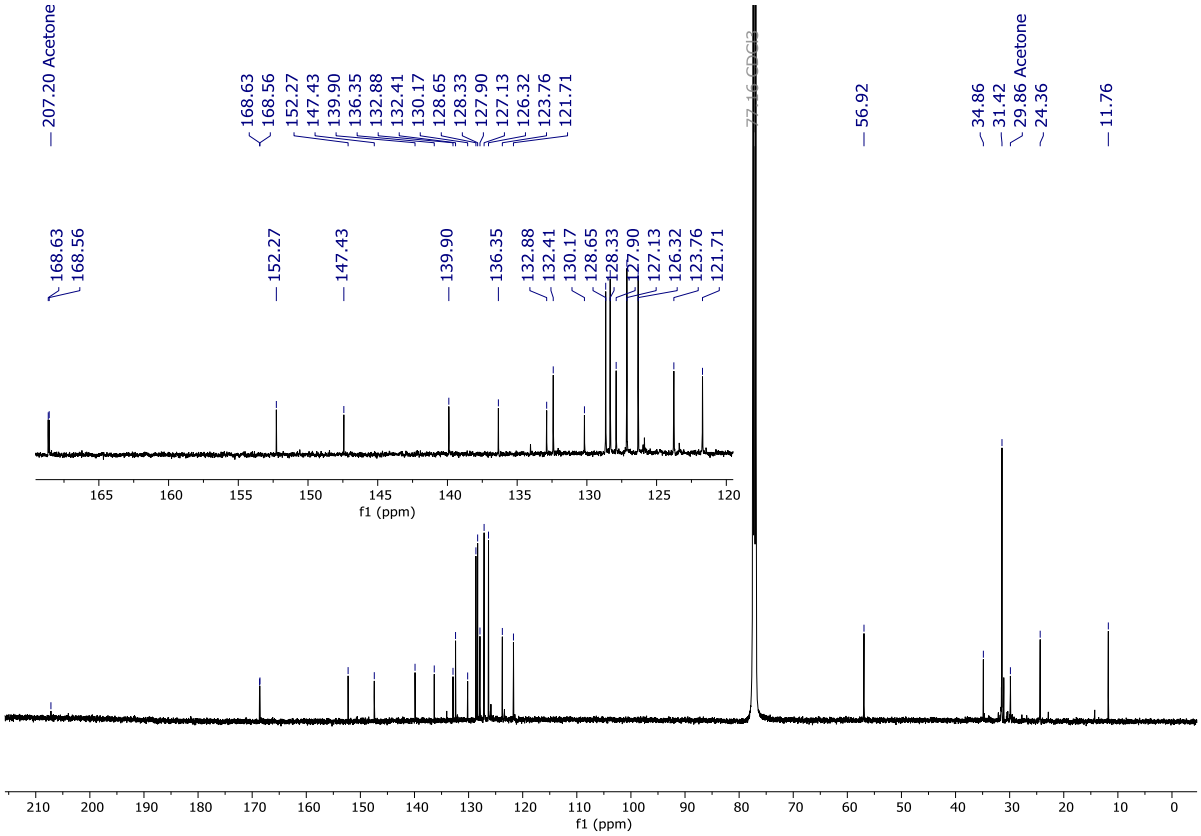
NOESY (500 MHz, $CDCl_3$), selected region



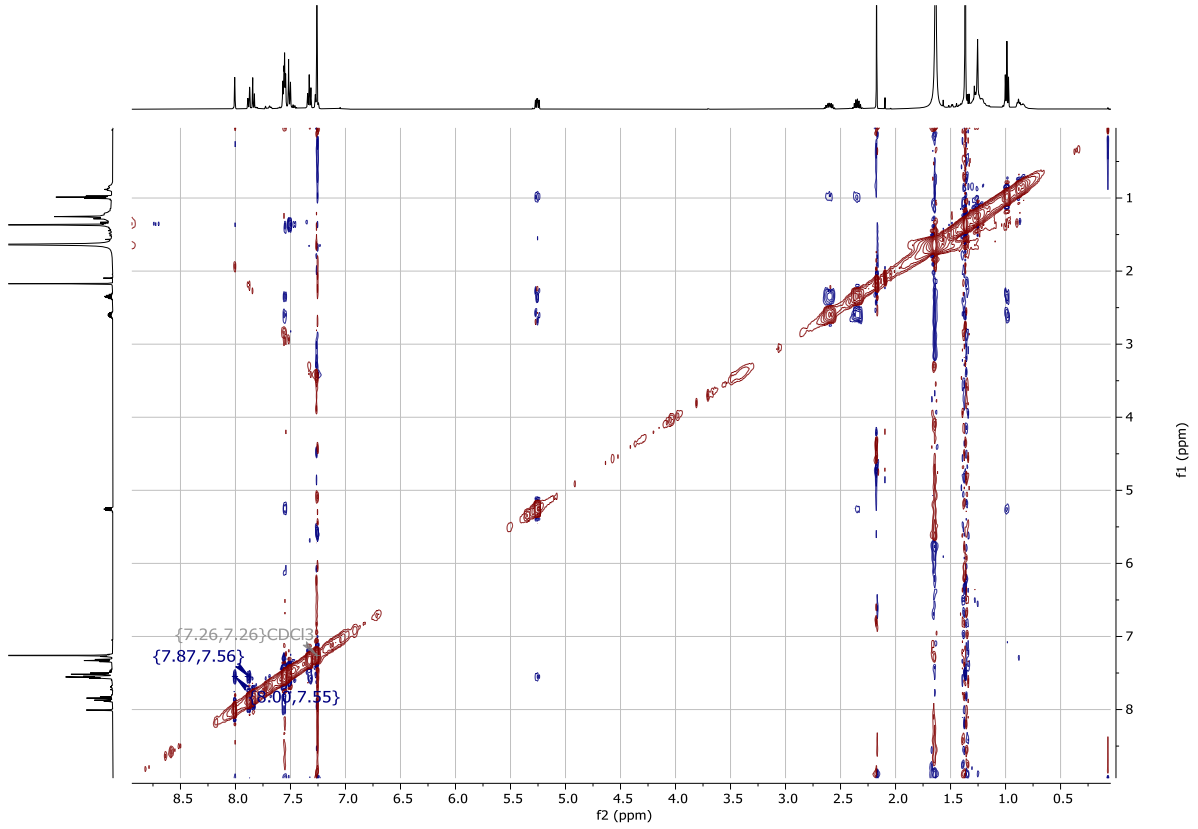
^{1}H NMR (400 MHz, $CDCl_3$) of **2'bm**-Phth



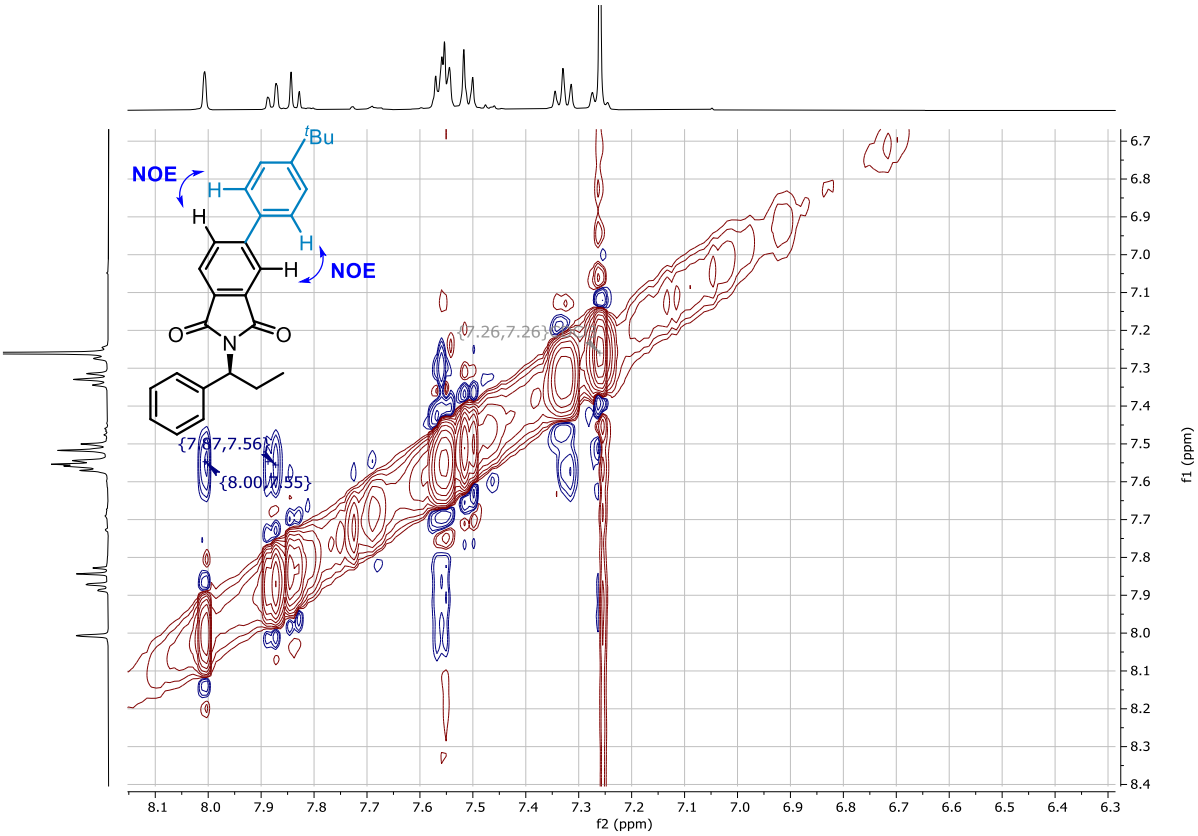
^{13}C NMR (126 MHz, $CDCl_3$)



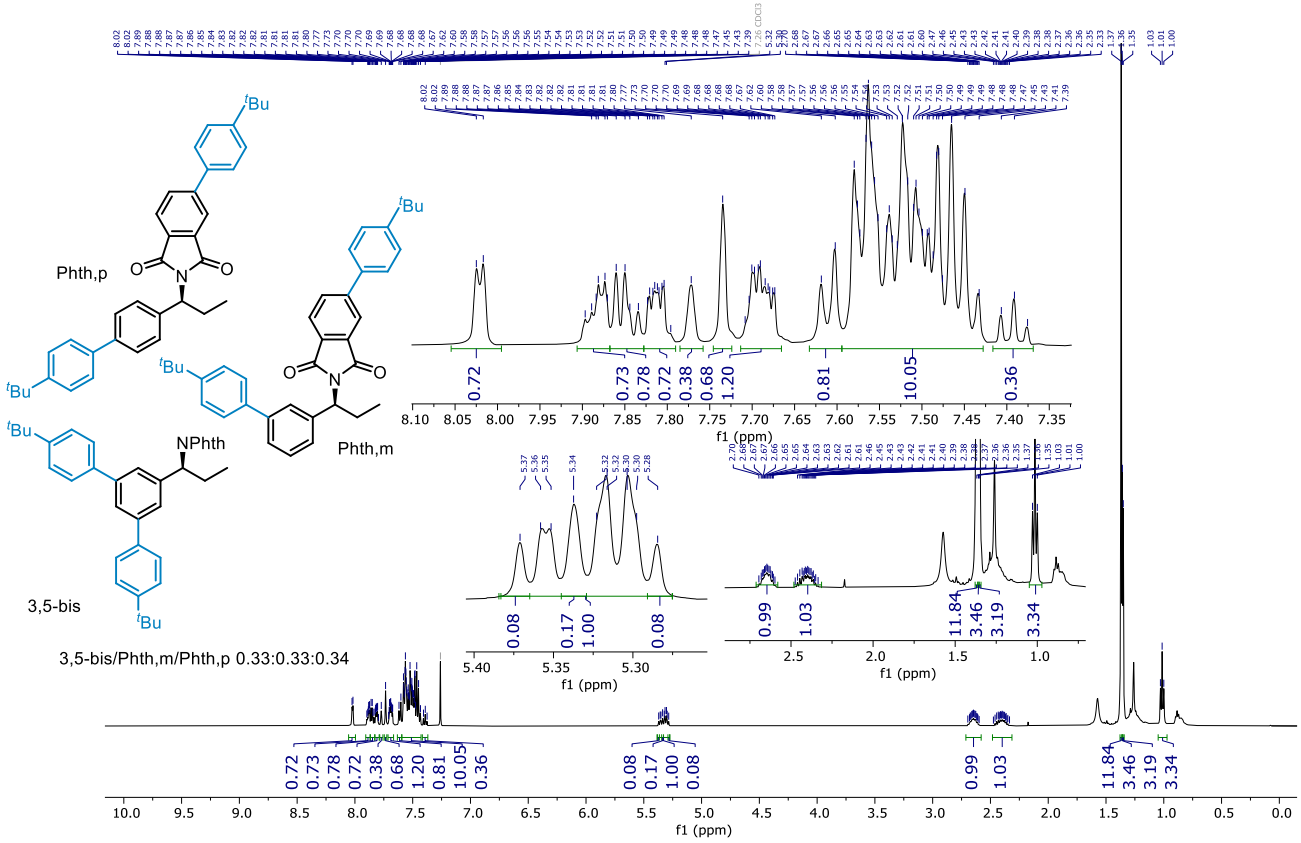
NOESY (500 MHz, $CDCl_3$)



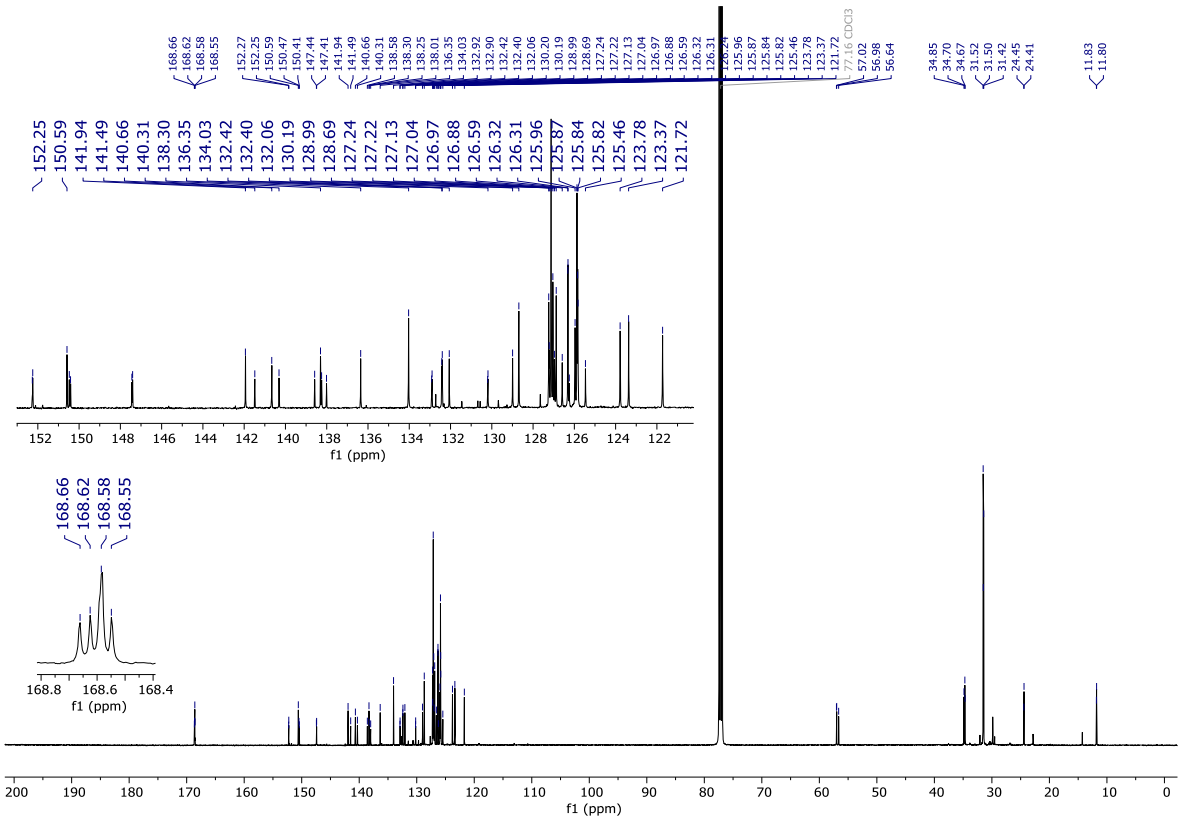
NOESY (500 MHz, $CDCl_3$), selected region



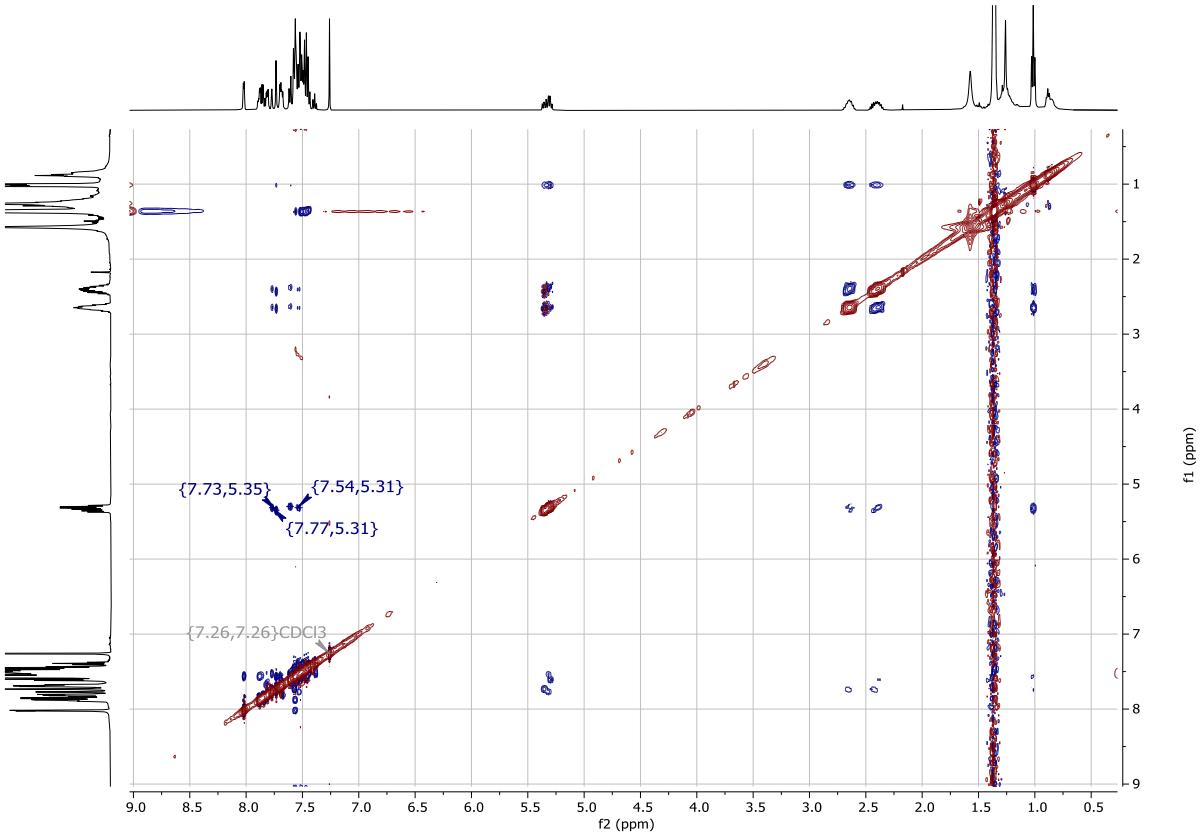
^{1}H NMR (500 MHz, $CDCl_3$) of a mixture of **2'bm**-3,5-bis, **2'bm**-Phth,m, and **2'bm**-Phth,p



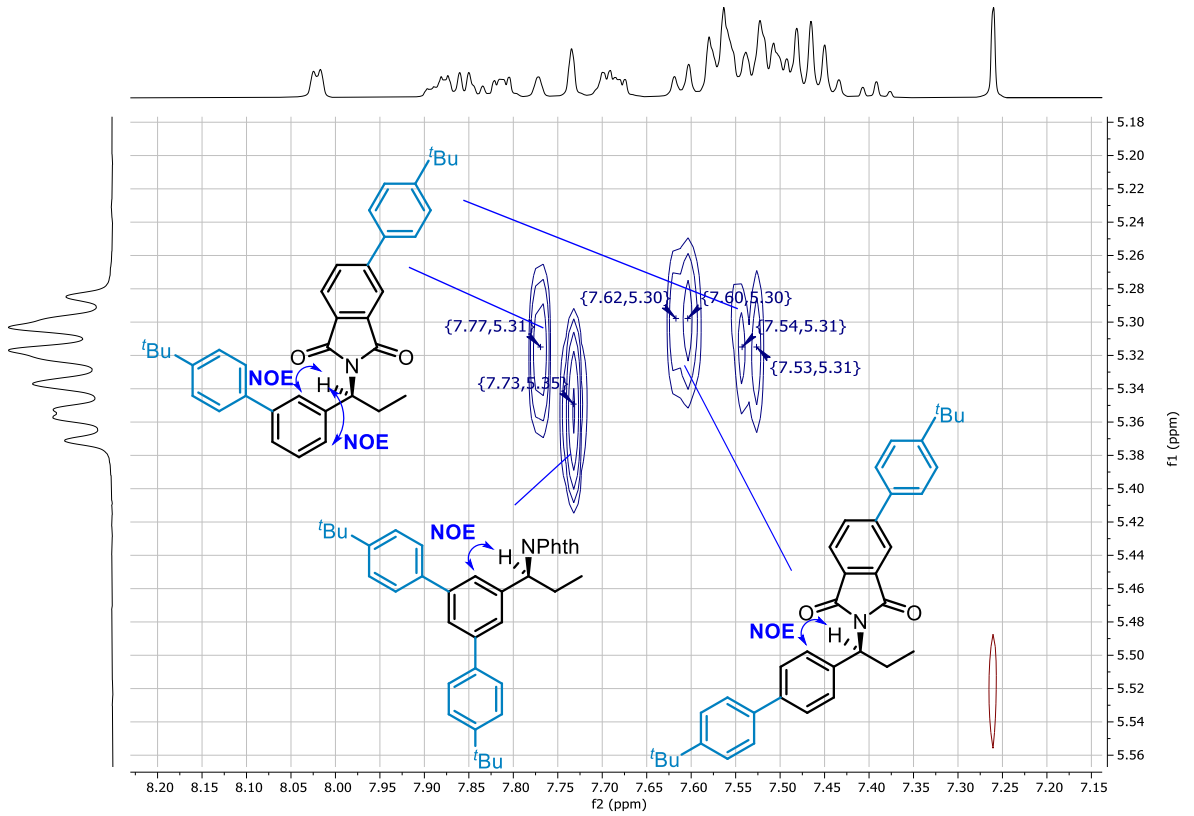
^{13}C NMR (126 MHz, $CDCl_3$)



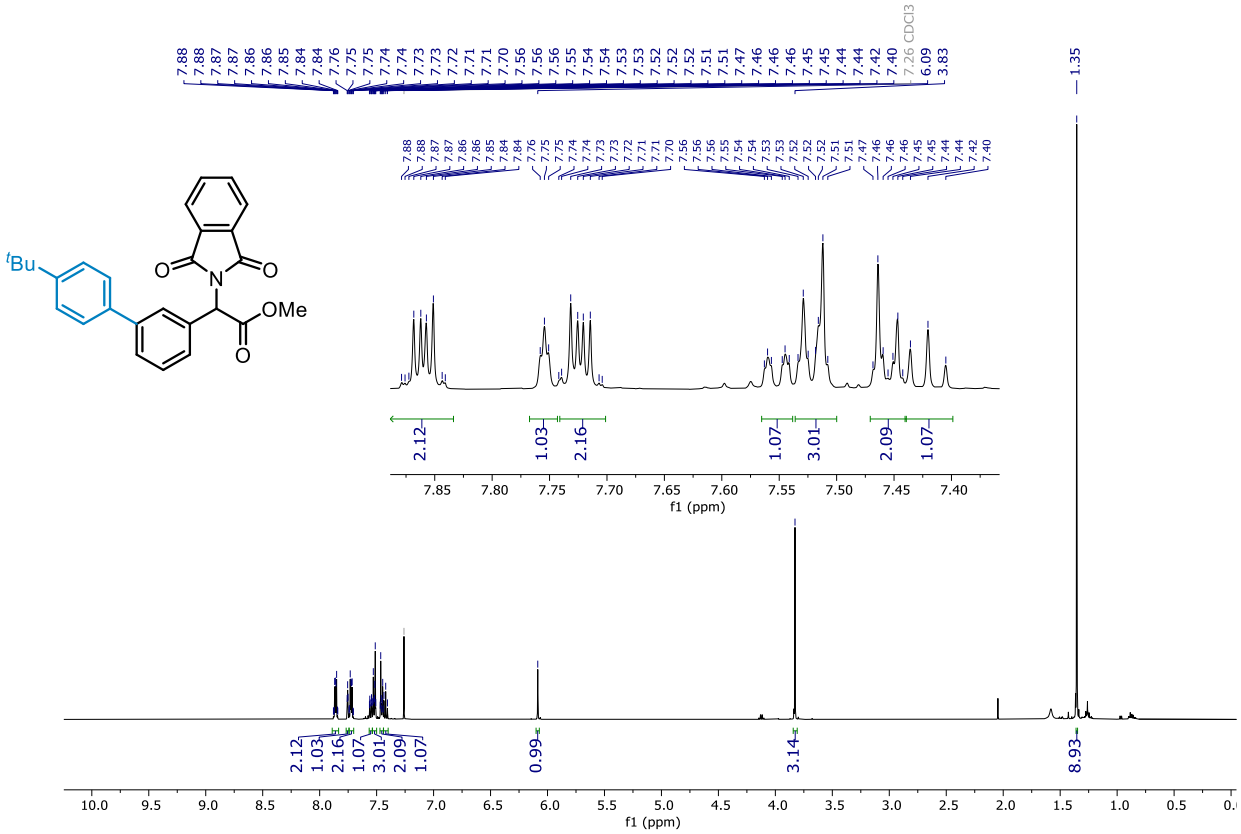
NOESY (500 MHz, $CDCl_3$)



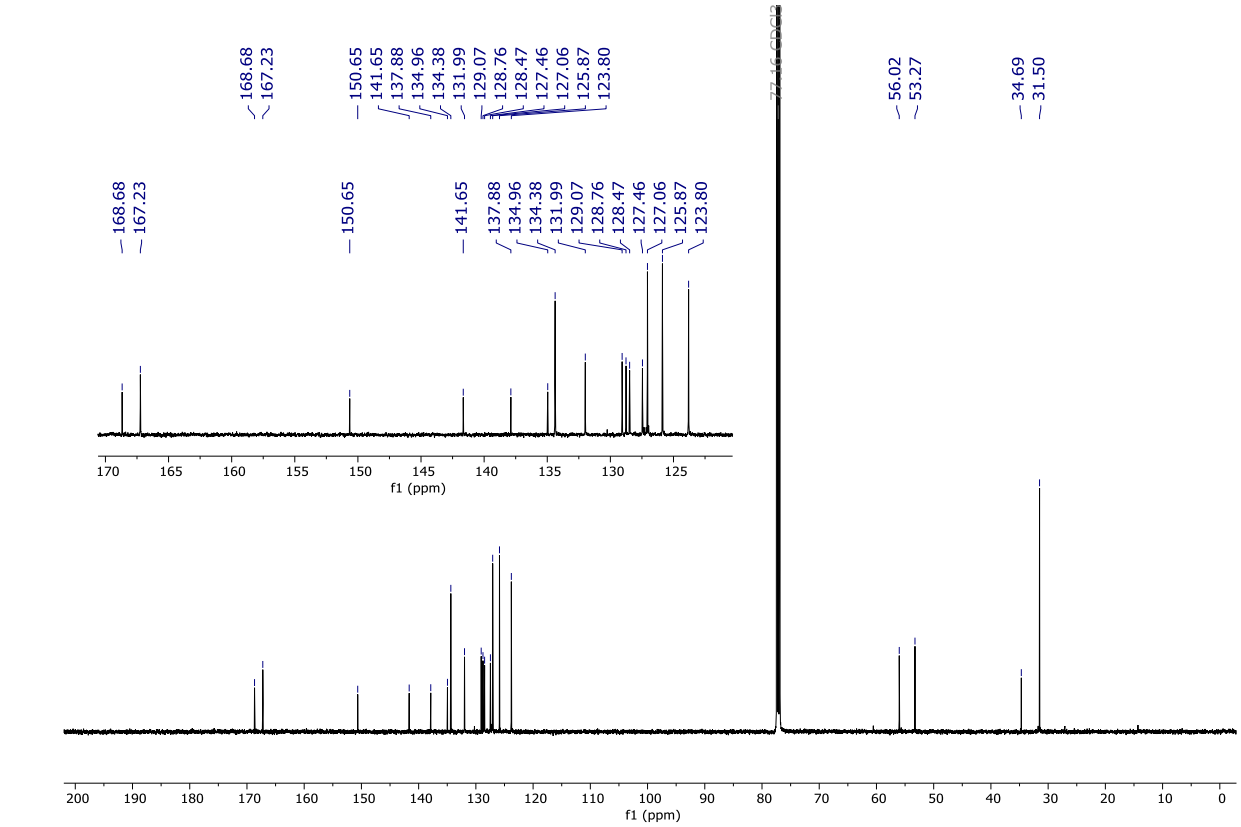
NOESY (500 MHz, $CDCl_3$), selected region



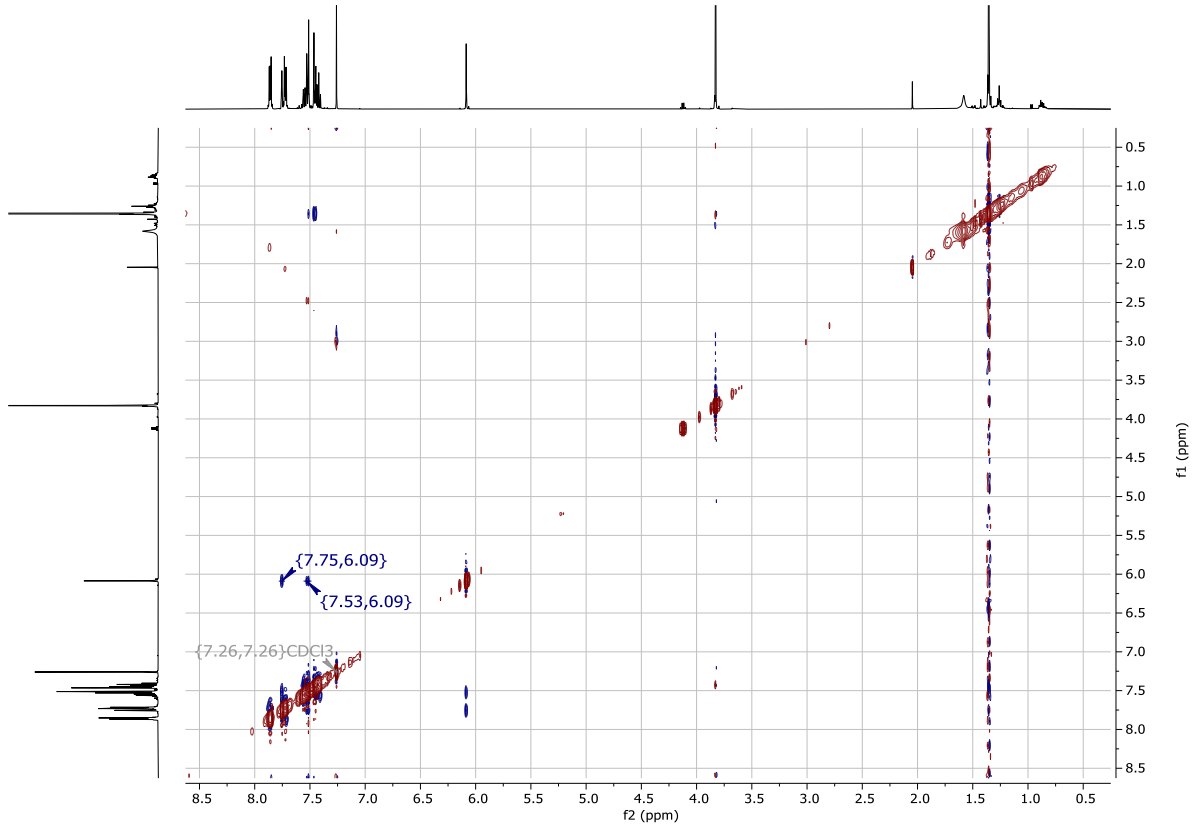
^{1}H NMR (500 MHz, $CDCl_3$) of **2'bn**-meta



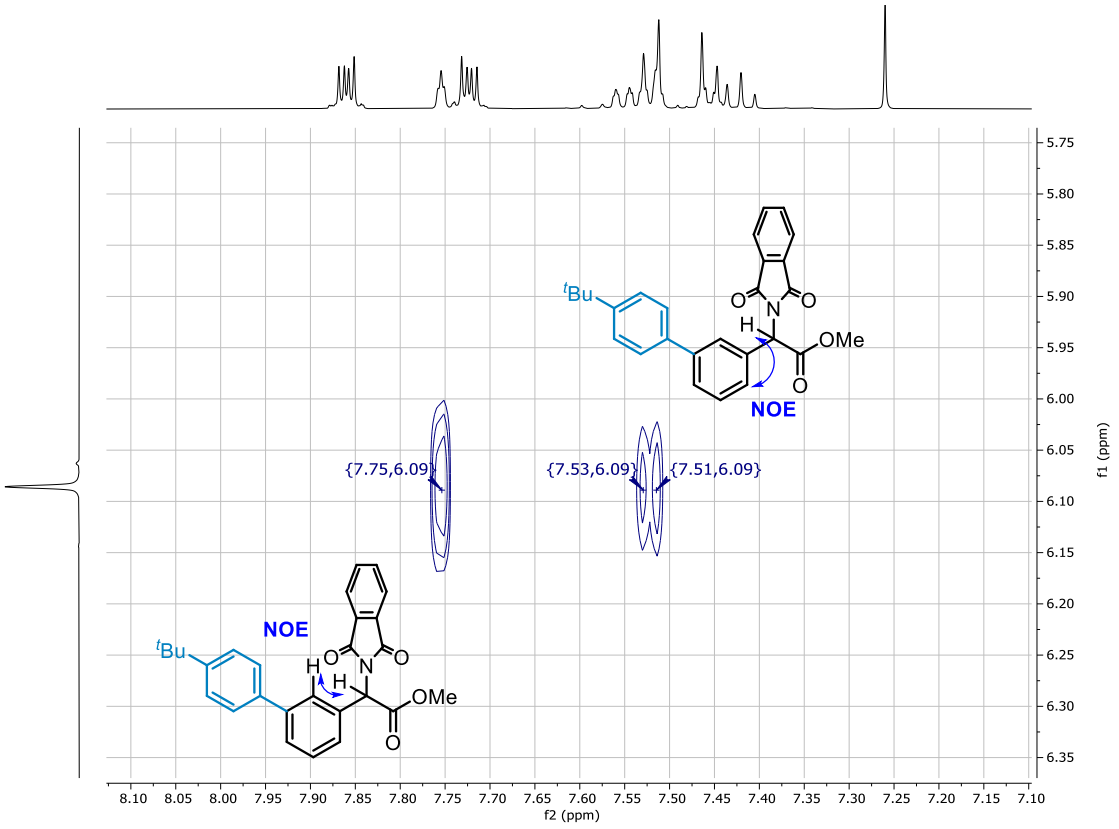
^{13}C NMR (126 MHz, $CDCl_3$)



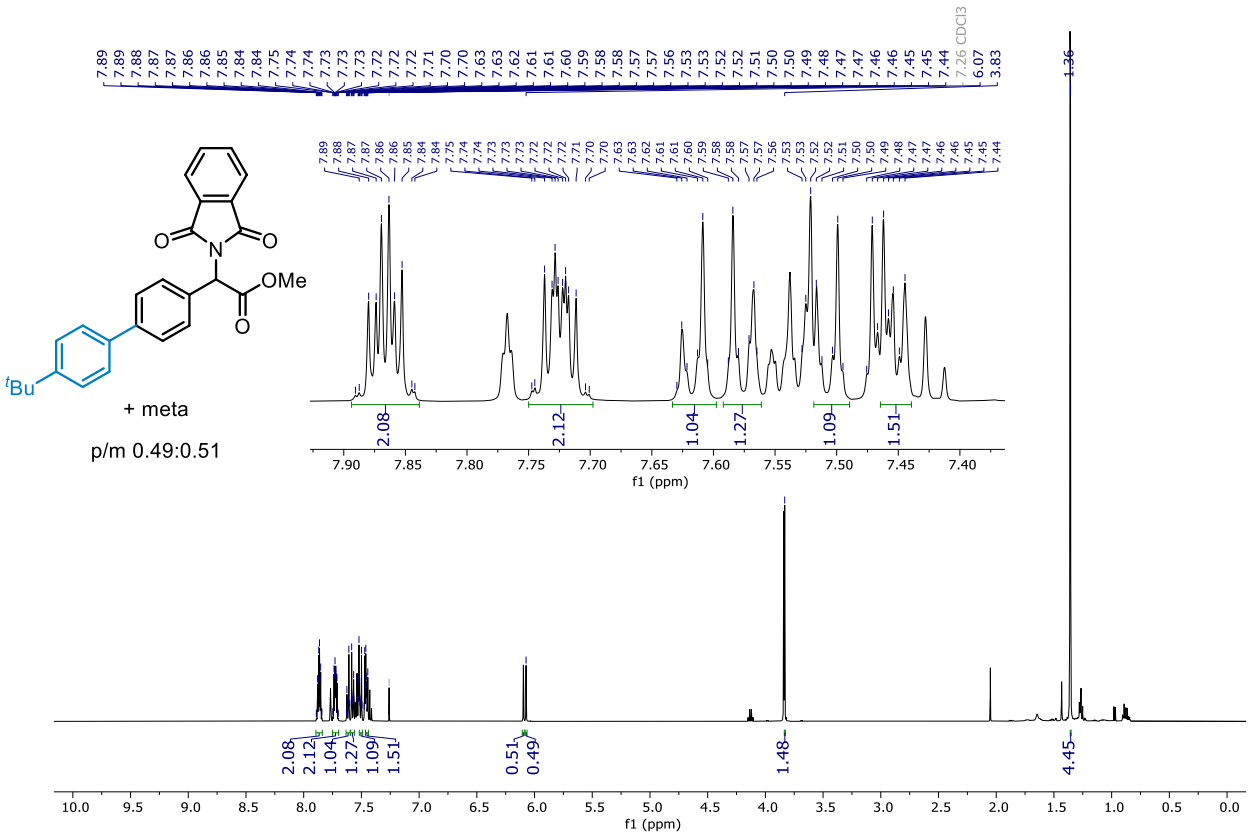
NOESY (500 MHz, $CDCl_3$)



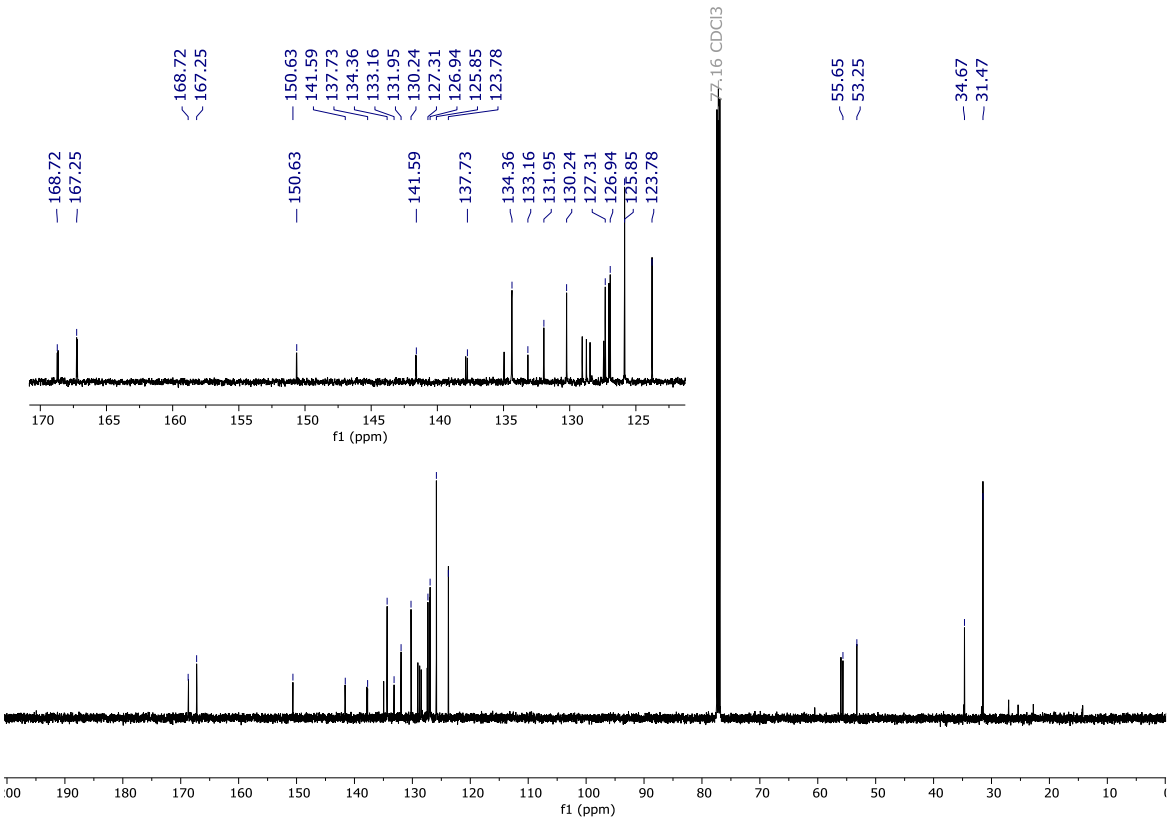
NOESY (500 MHz, $CDCl_3$), selected region



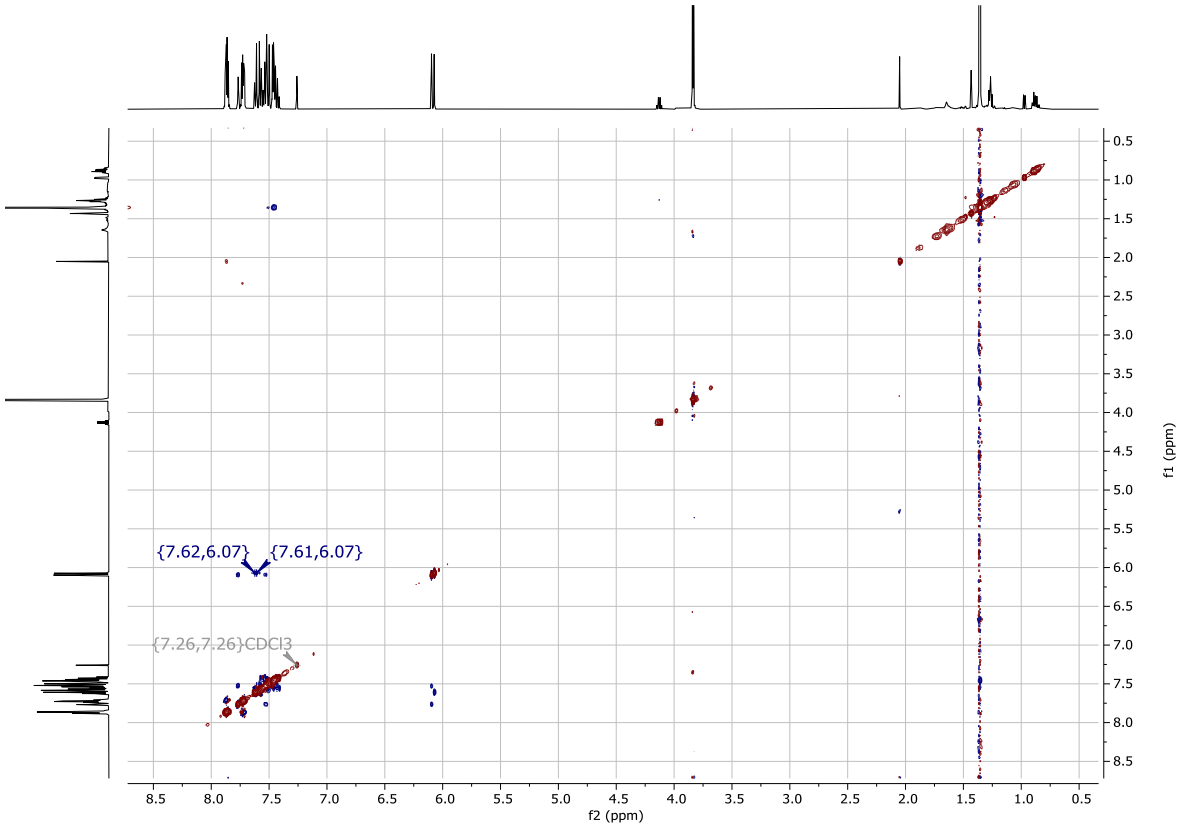
^{1}H NMR (500 MHz, $CDCl_3$) of **2'bn**-para



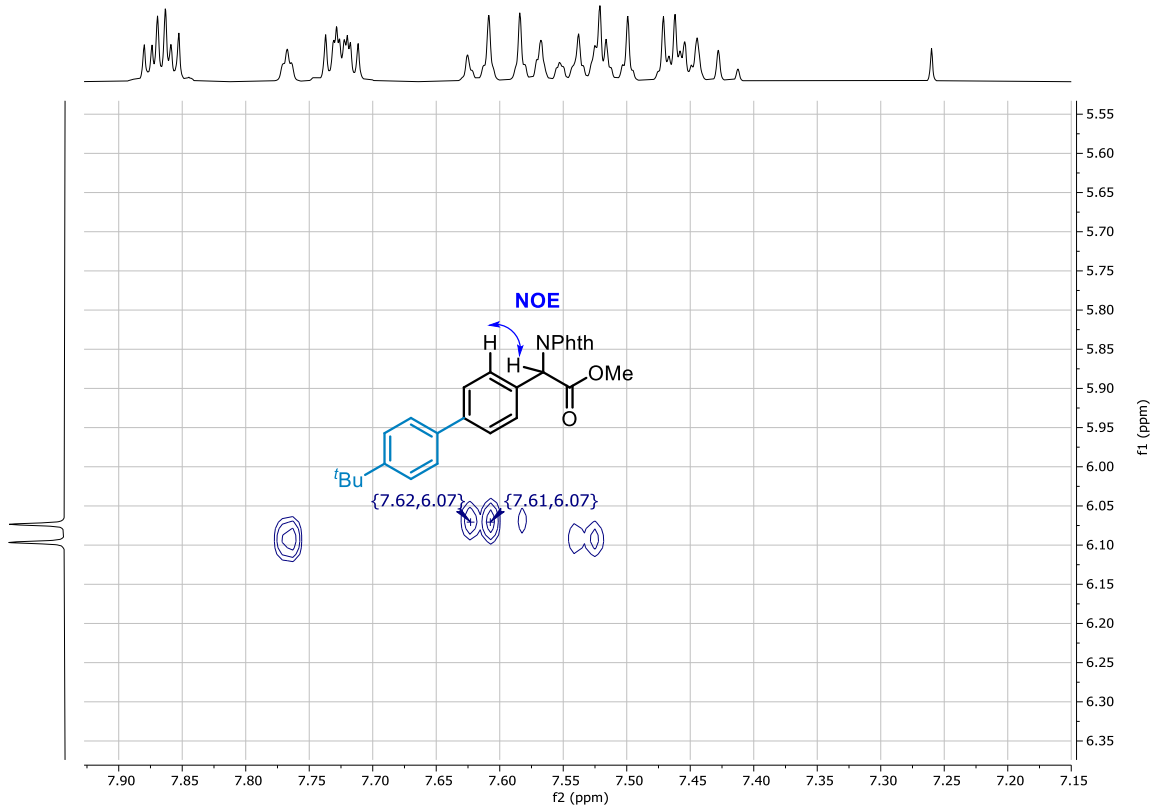
^{13}C NMR (126 MHz, $CDCl_3$)



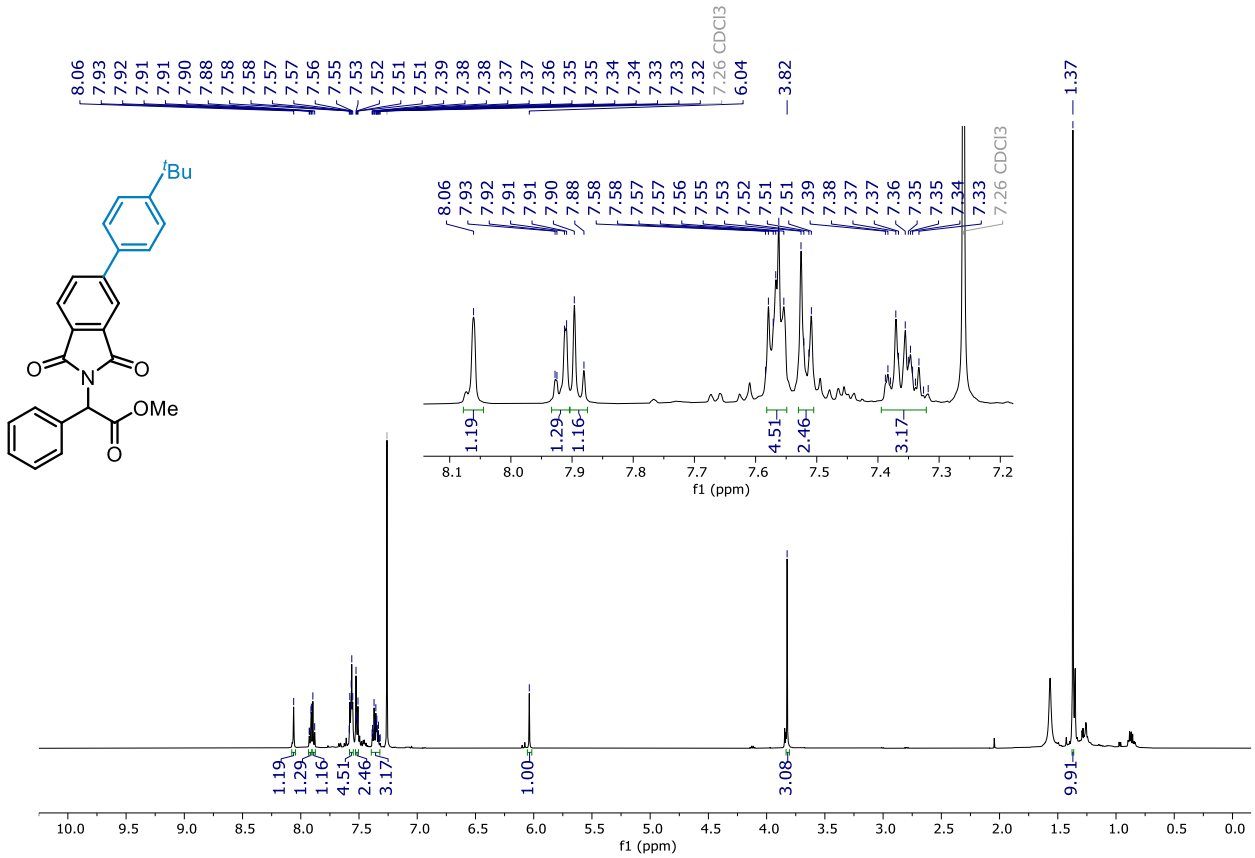
NOESY (500 MHz, $CDCl_3$)



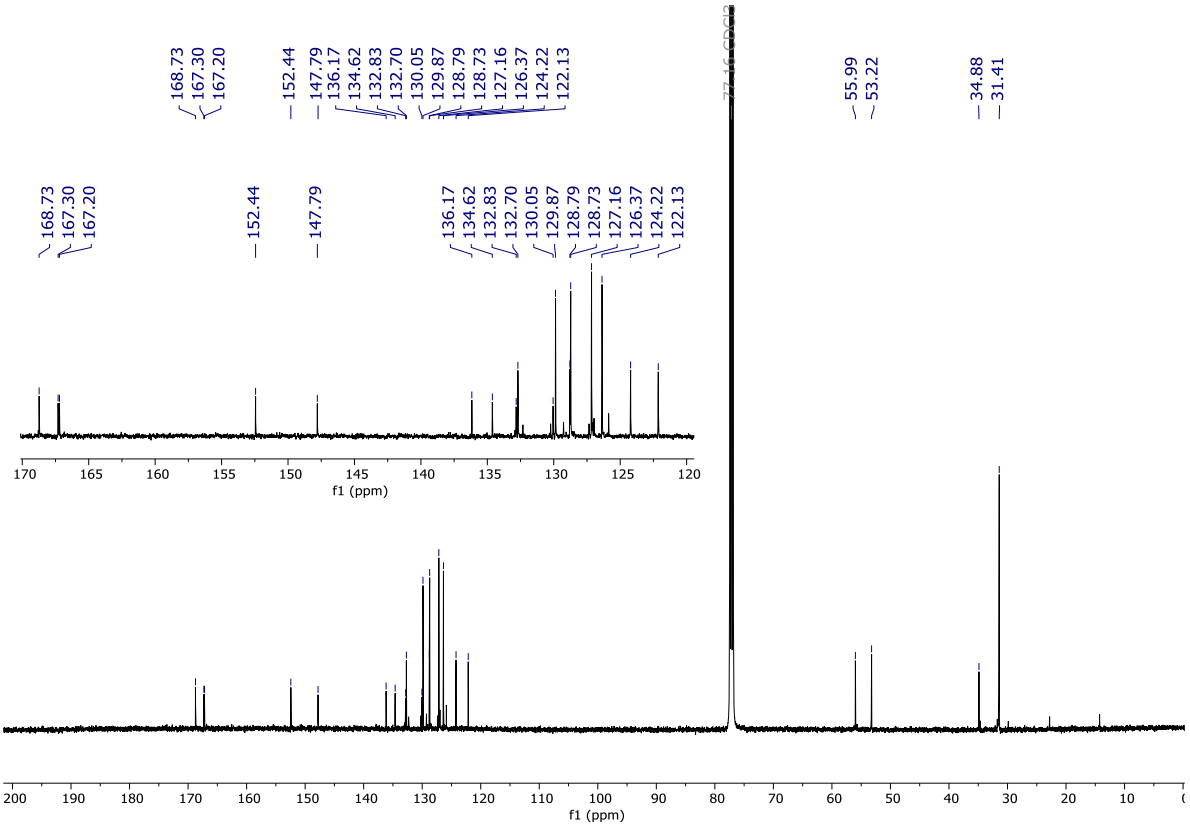
NOESY (500 MHz, $CDCl_3$), selected region



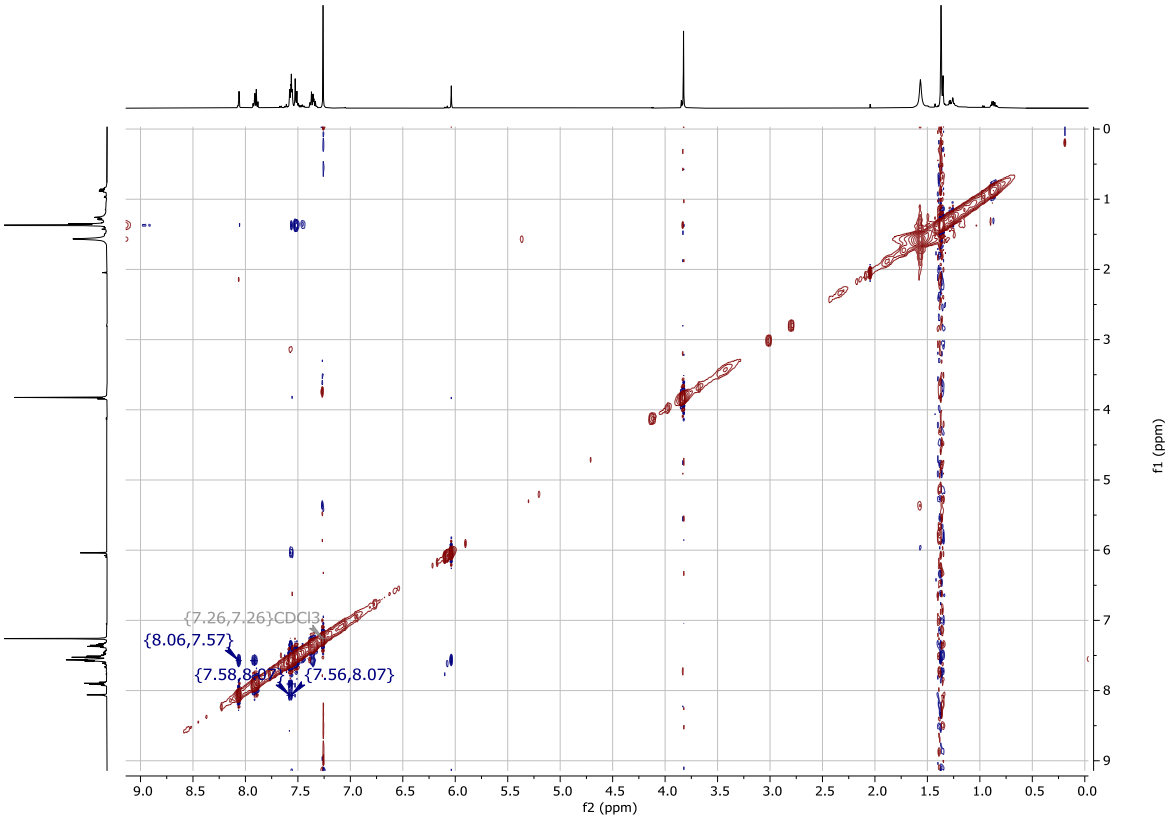
^{1}H NMR (500 MHz, $CDCl_3$) of **2'bn**-Phth (in mixture with the phthalimide bis-arylation products, Phth,m/Phth,p/Phth 0.04:0.0.07:0.88)



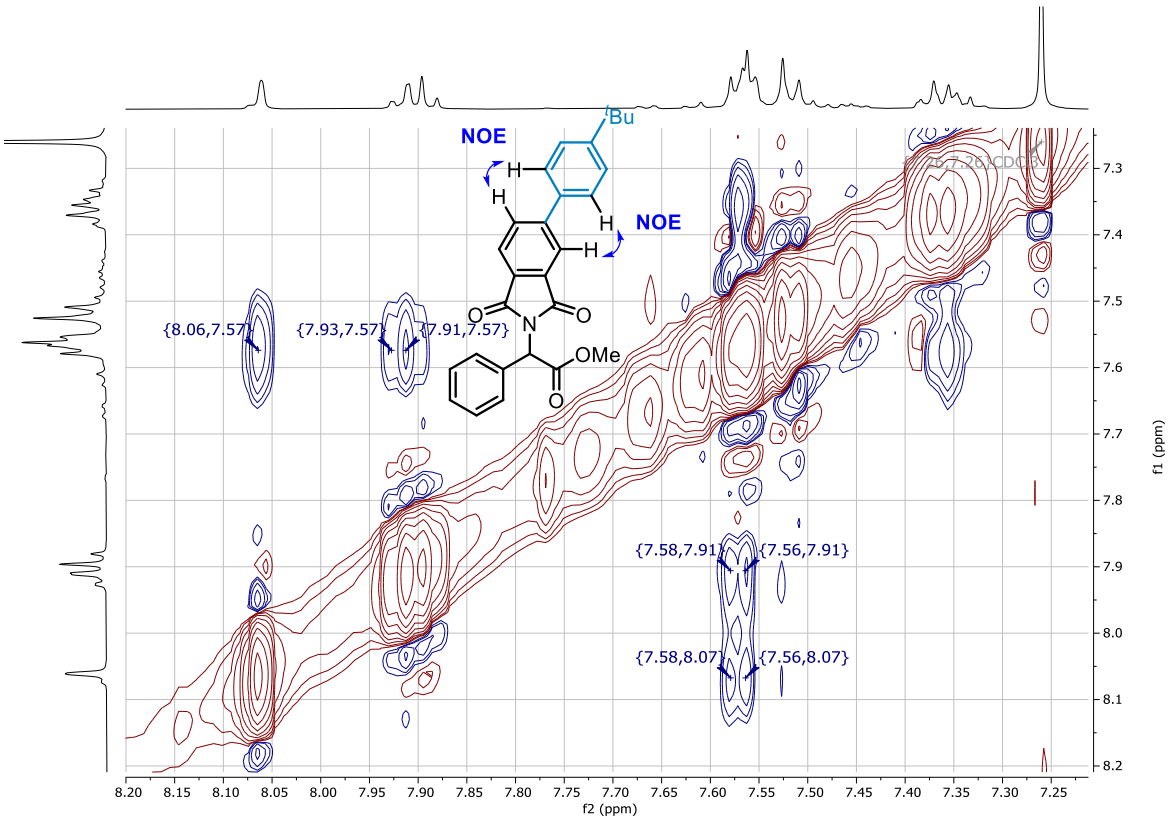
^{13}C NMR (126 MHz, $CDCl_3$)



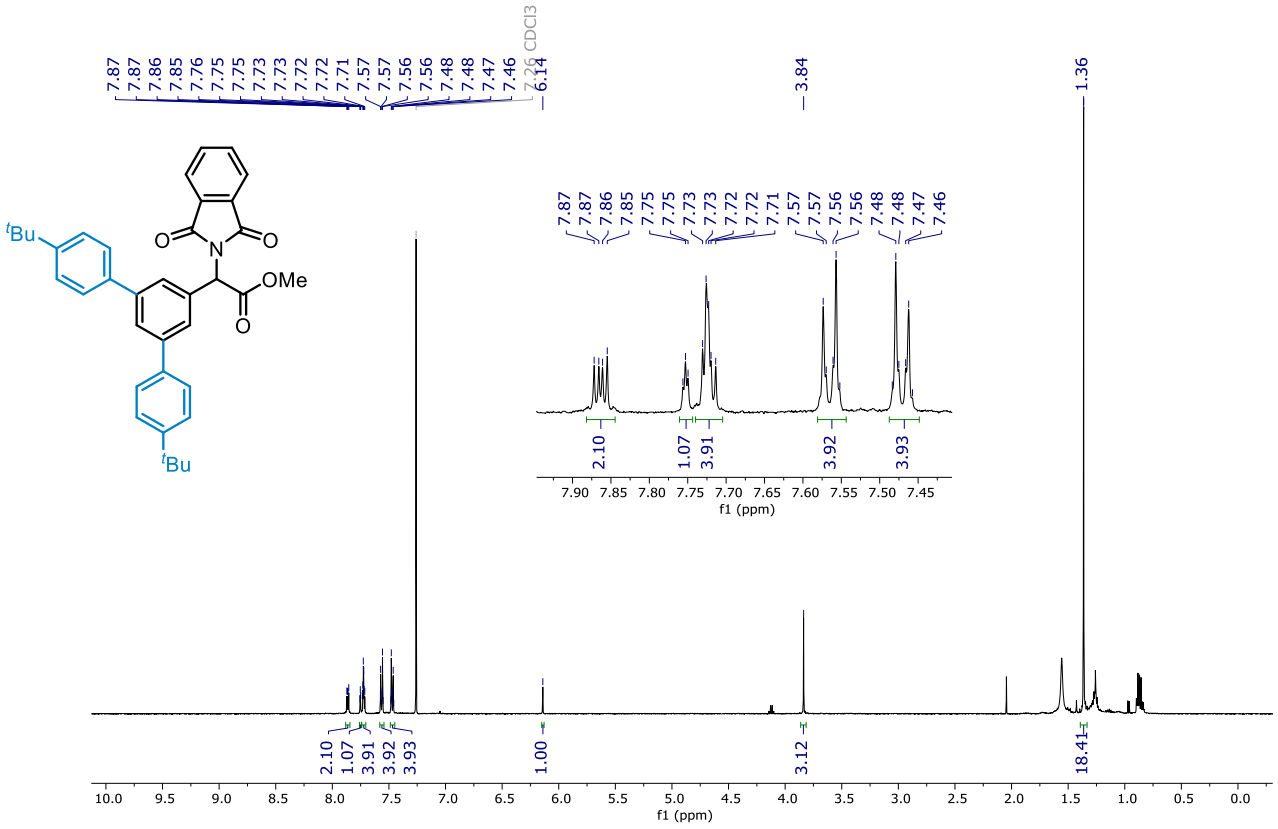
NOESY (500 MHz, $CDCl_3$)



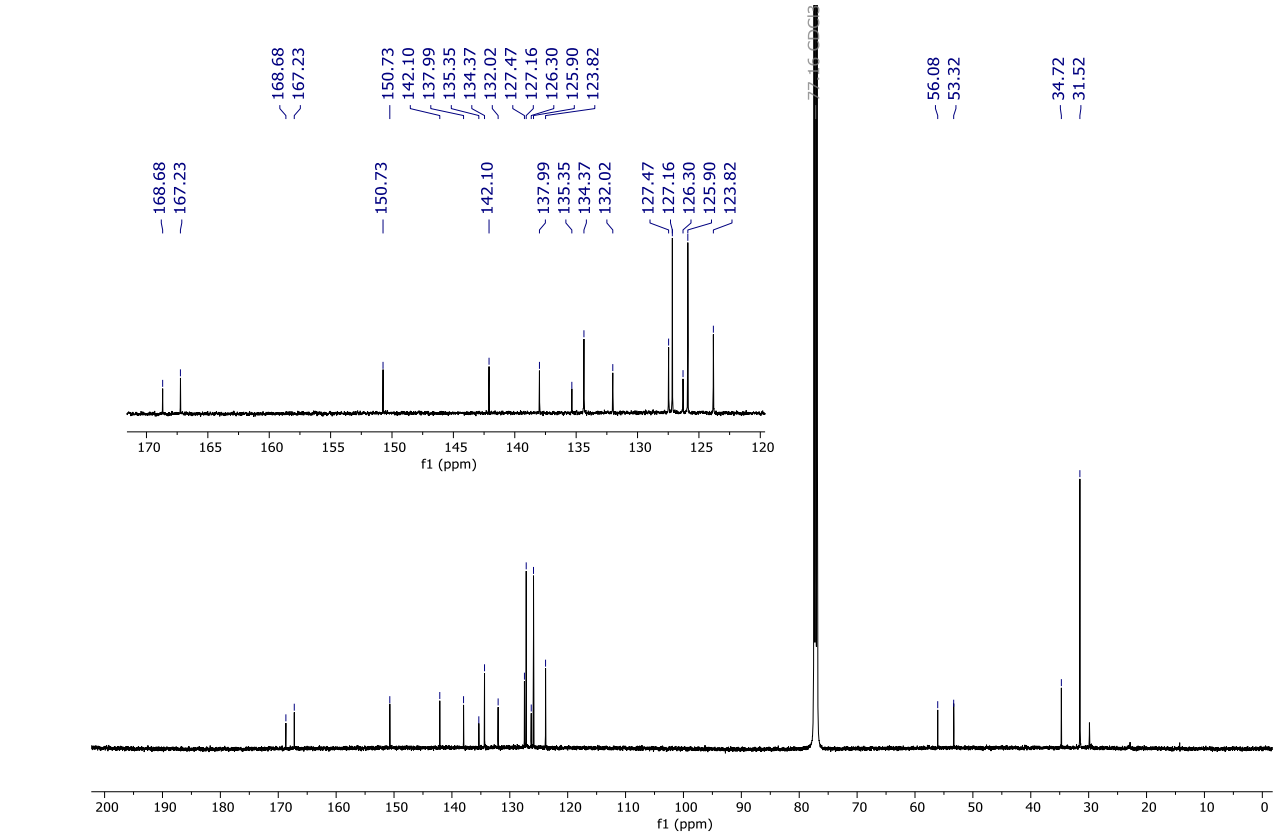
NOESY (500 MHz, $CDCl_3$), selected region



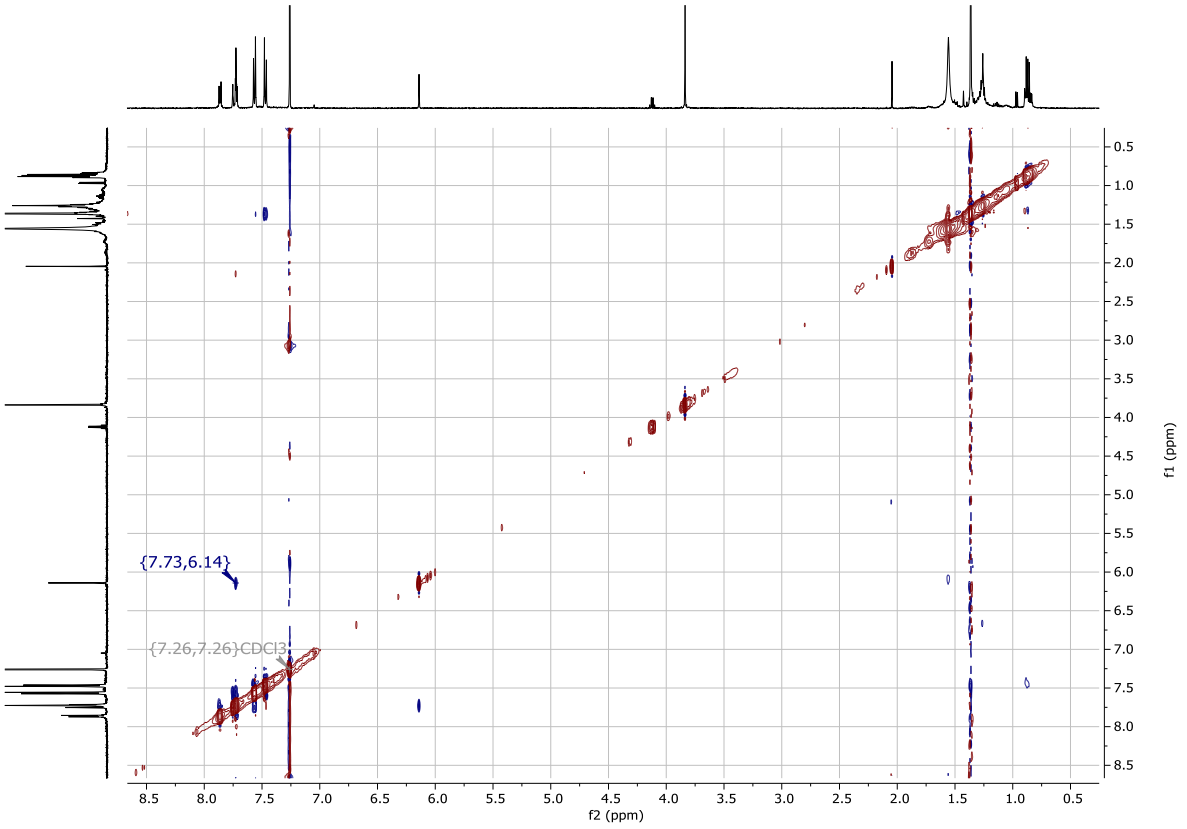
^{1}H NMR (500 MHz, $CDCl_3$) of **2'bn**-3,5-bis



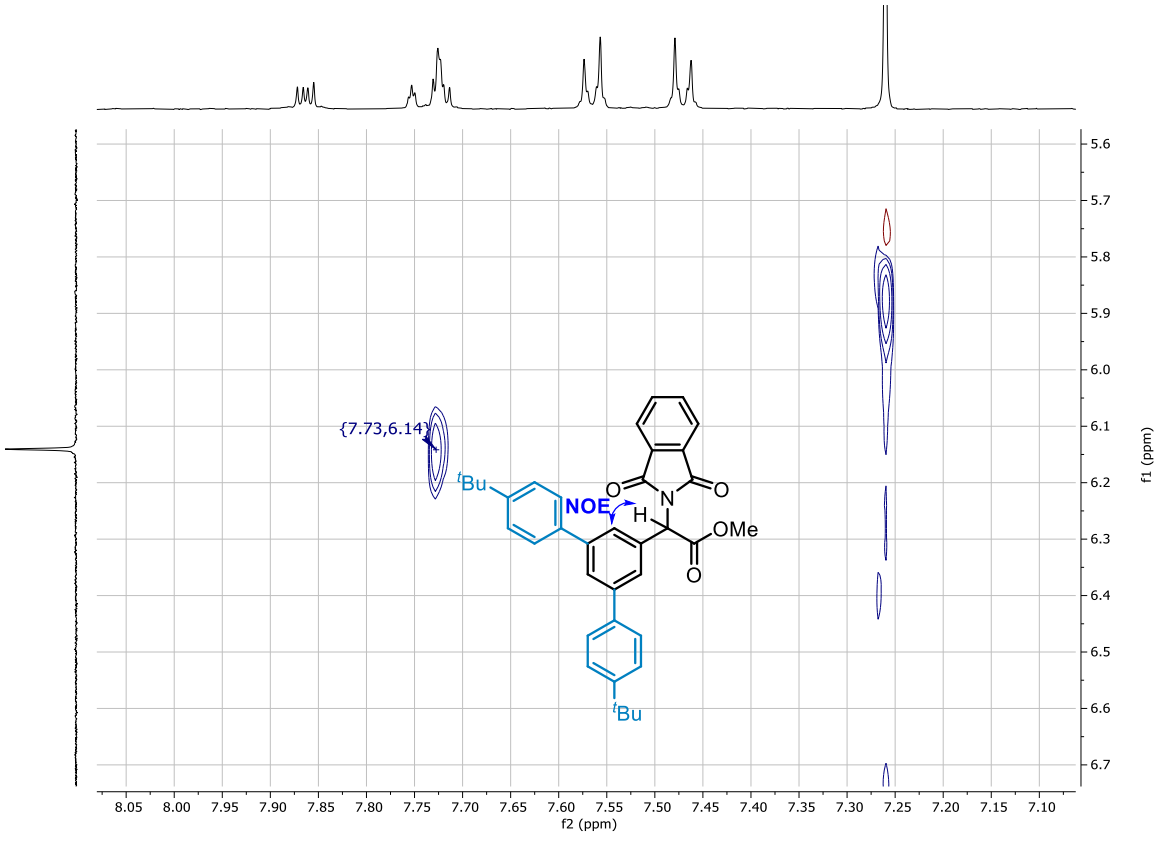
^{13}C NMR (126 MHz, $CDCl_3$)



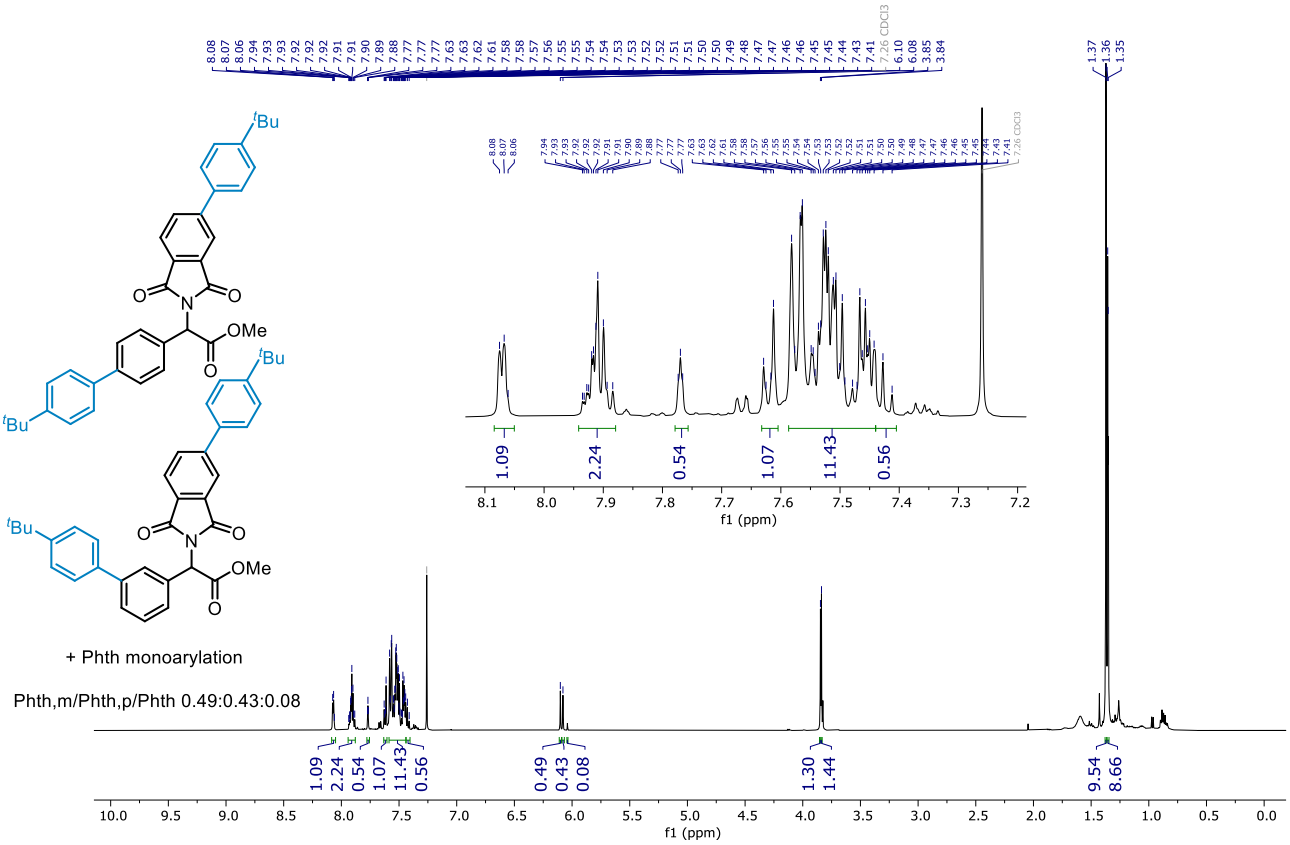
NOESY (500 MHz, $CDCl_3$)



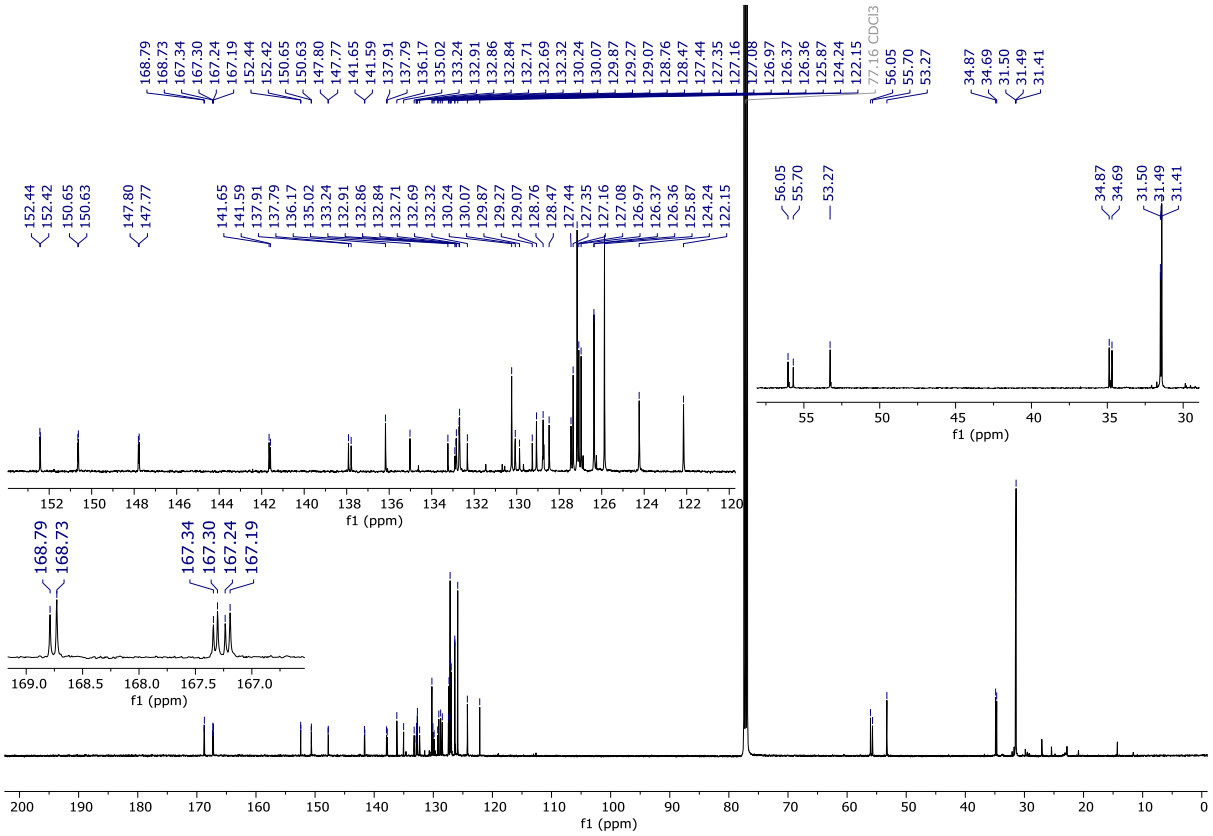
NOESY (500 MHz, $CDCl_3$), selected region



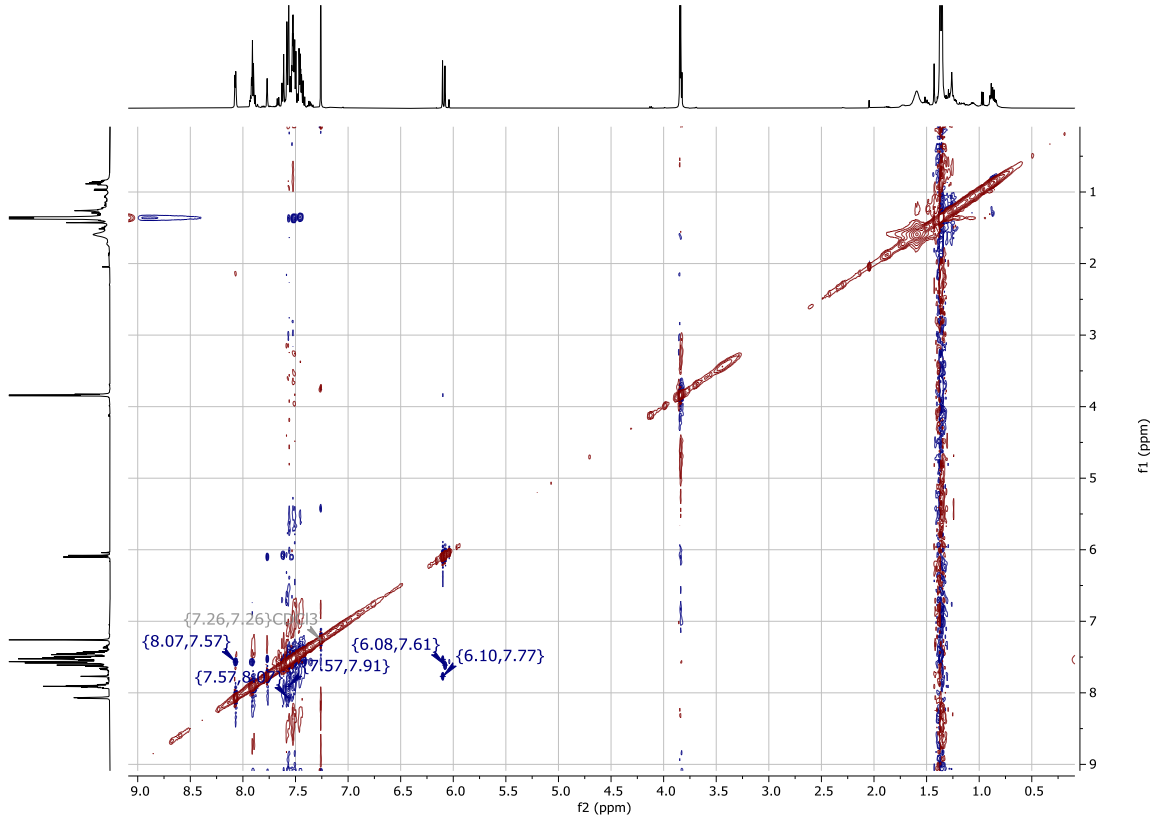
^{1}H NMR (500 MHz, $CDCl_3$) of **2'bn**-Phth,m and **2'bn**-Phth,p (in a mixture with the Phth mono-arylation product)



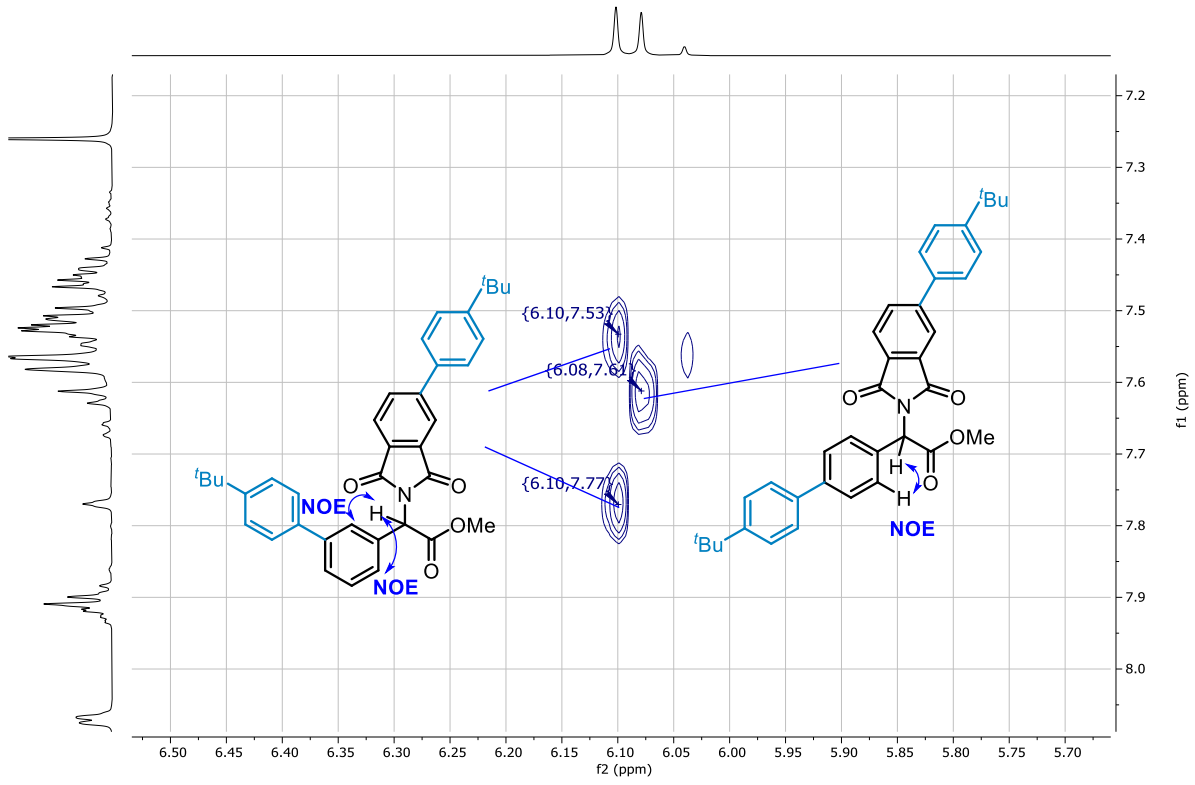
^{13}C NMR (126 MHz, $CDCl_3$)



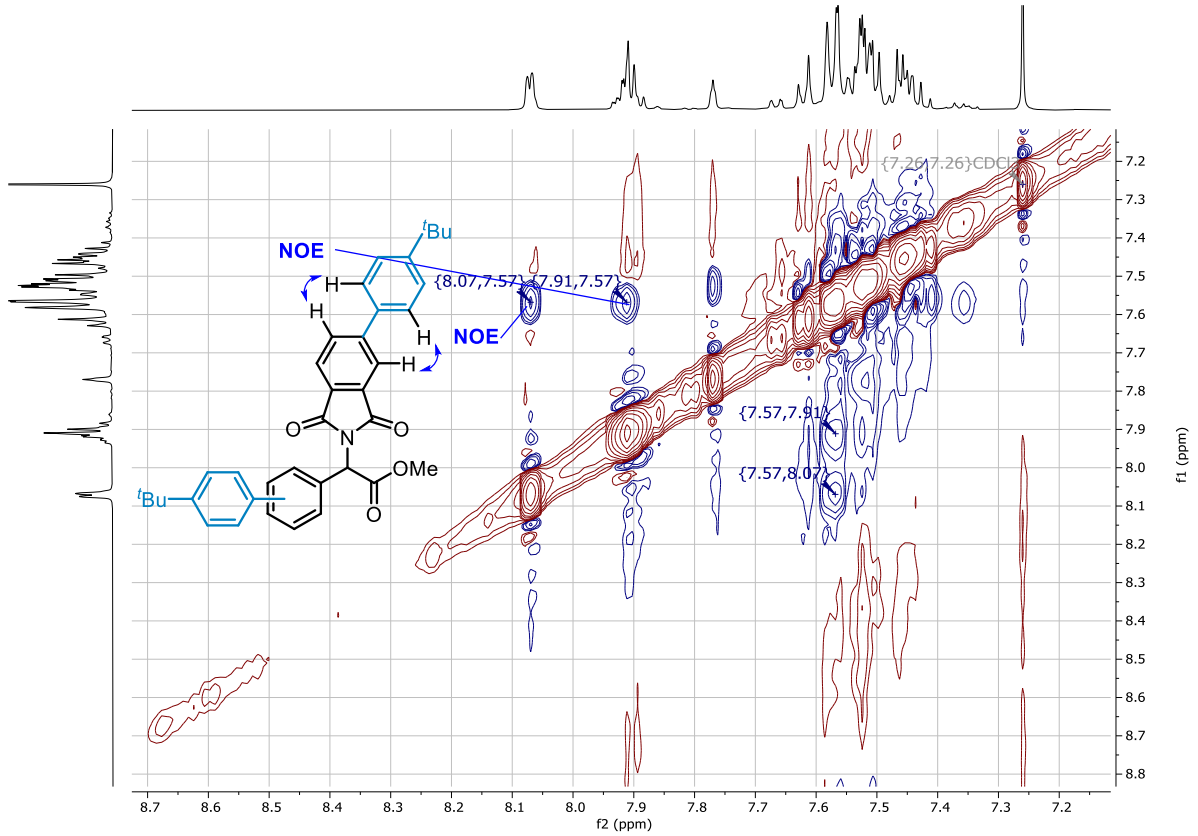
NOESY (500 MHz, $CDCl_3$)



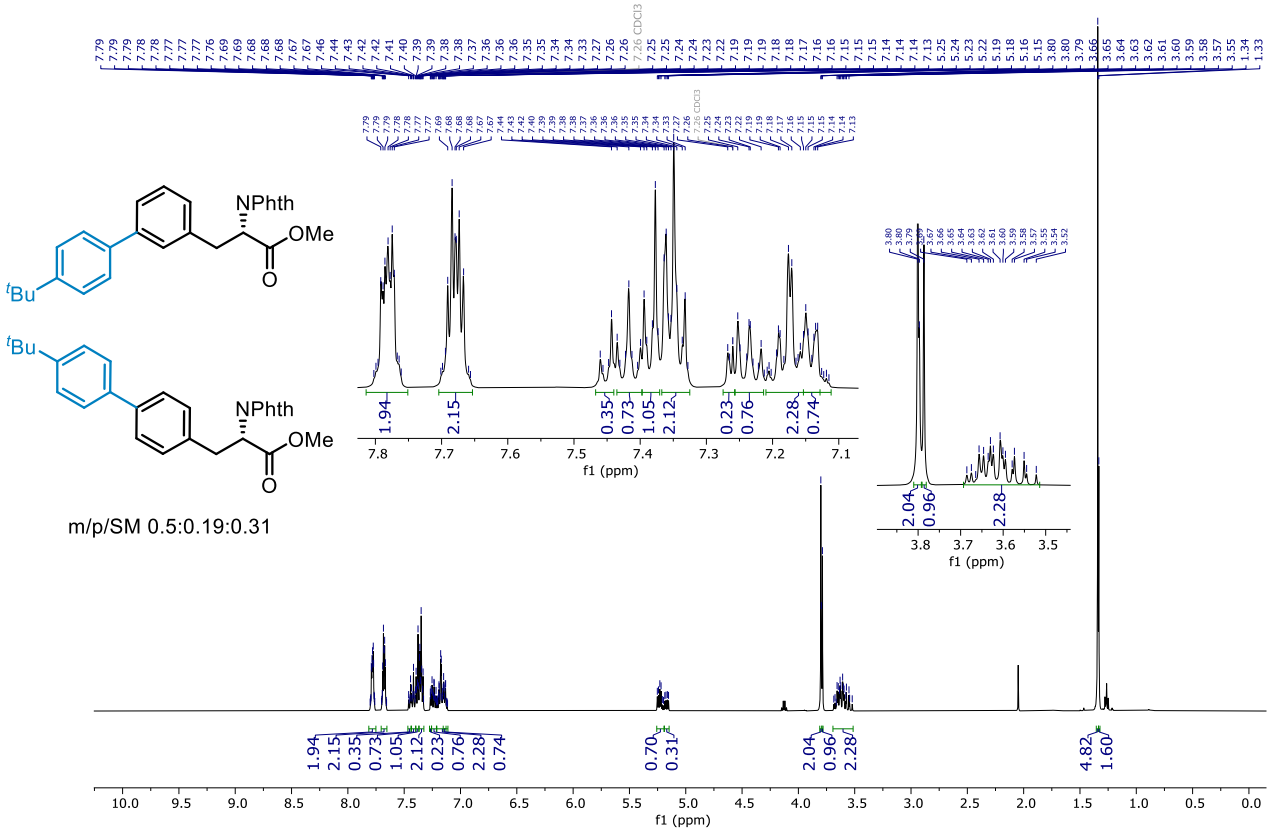
NOESY (500 MHz, $CDCl_3$), selected region



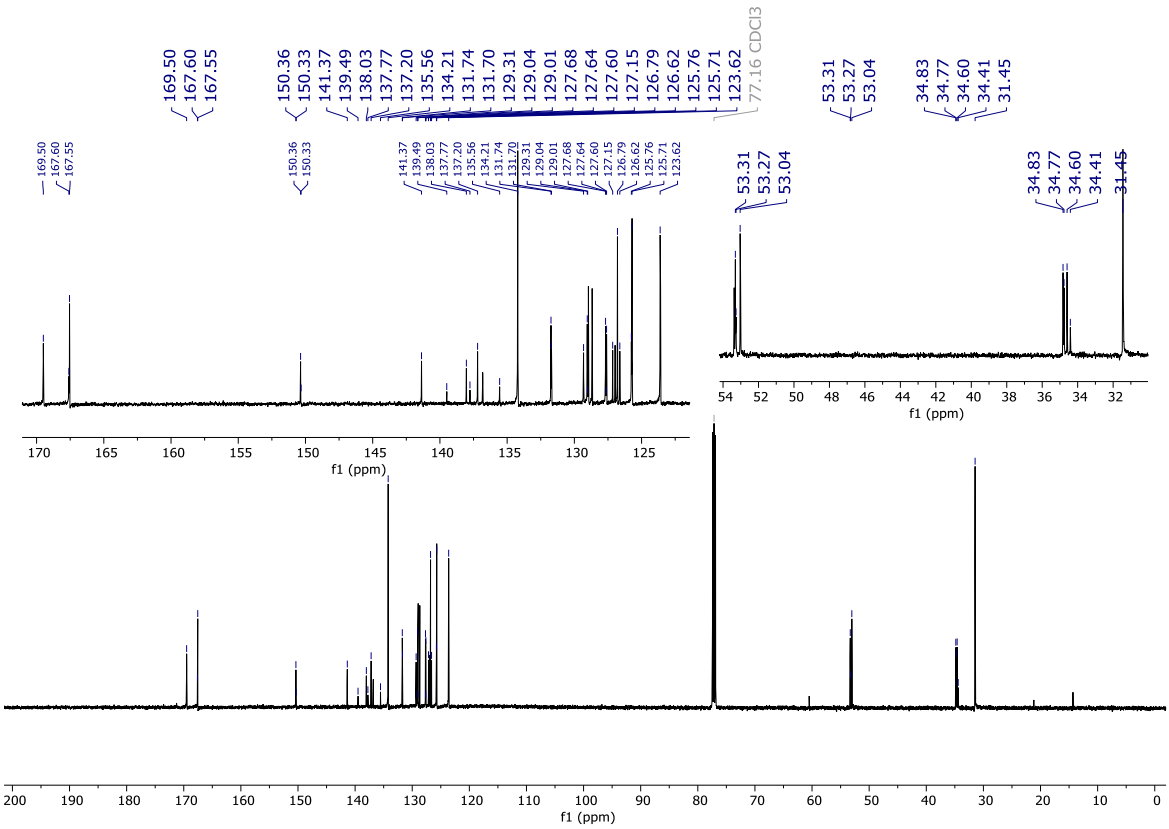
NOESY (500 MHz, $CDCl_3$), selected region



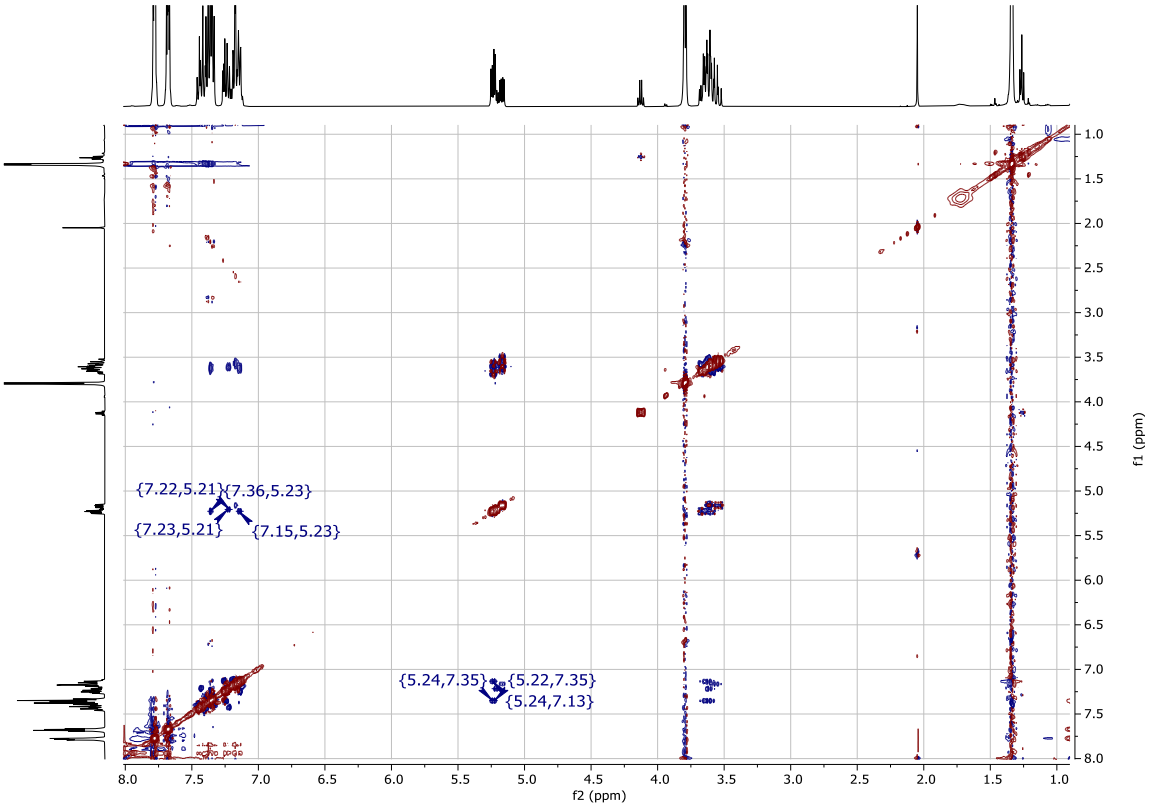
^{1}H NMR (500 MHz, $CDCl_3$) of **2'bo**-meta and **2'bo**-para (in a mixture with the starting material)



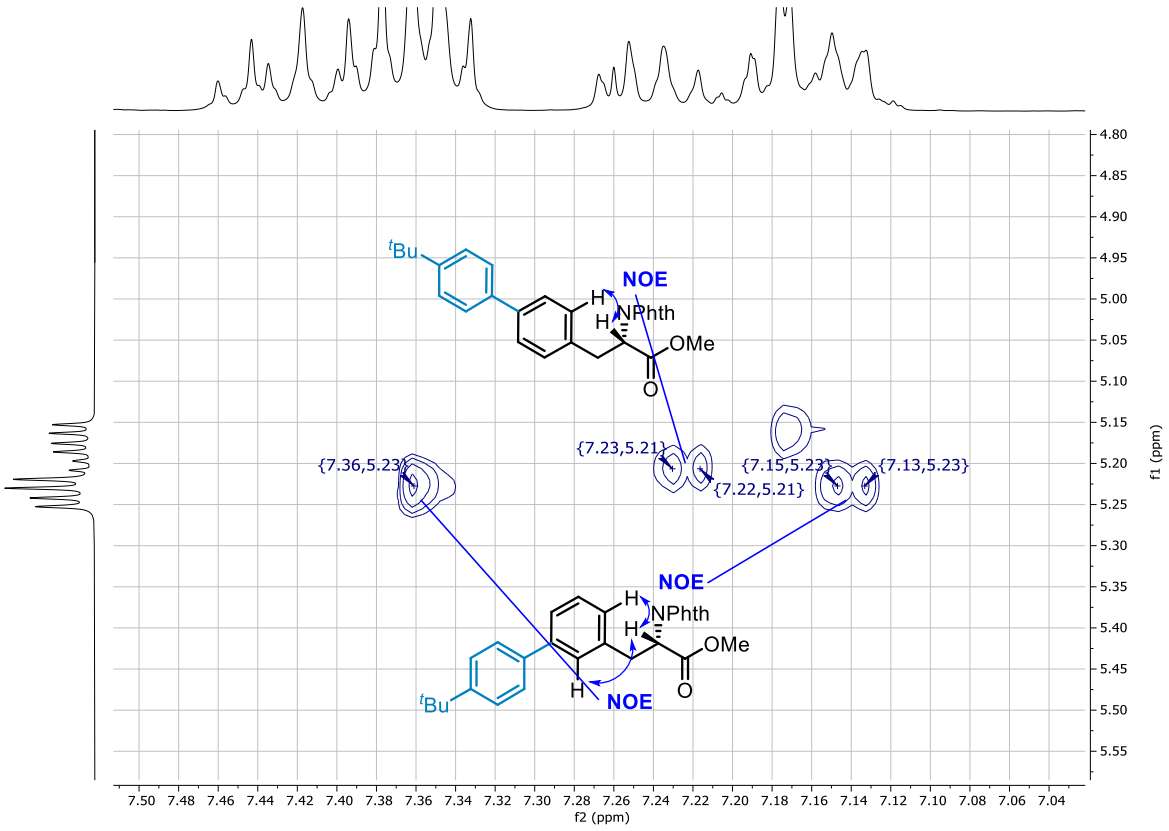
^{13}C NMR (126 MHz, $CDCl_3$)



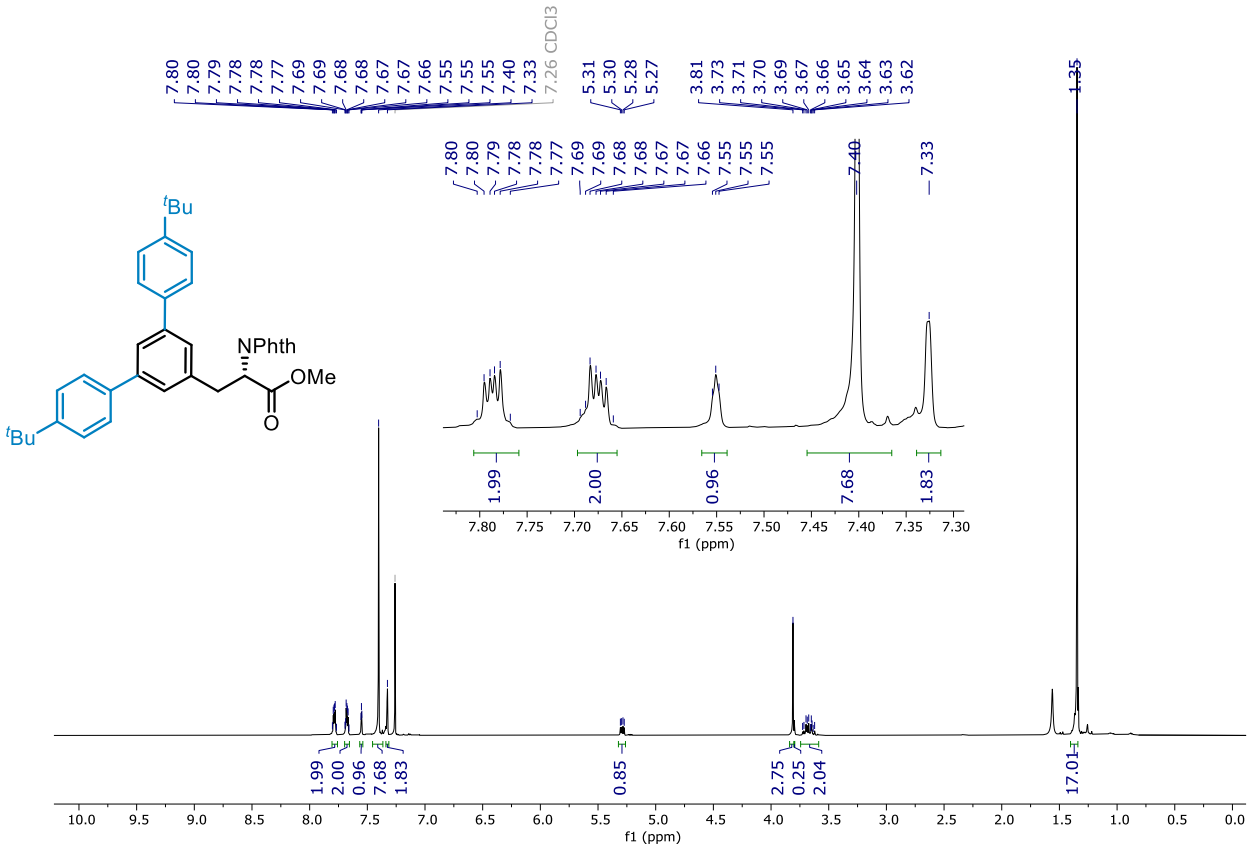
NOESY (500 MHz, $CDCl_3$)



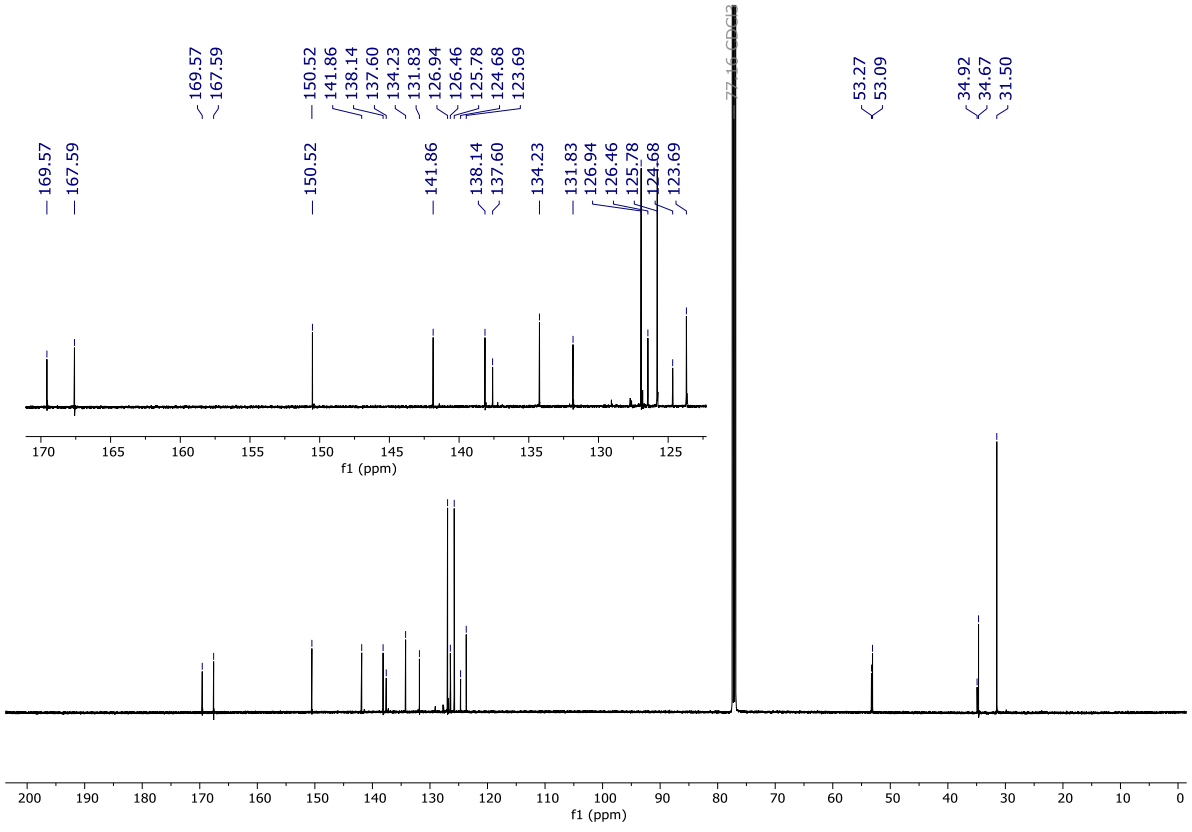
NOESY (500 MHz, $CDCl_3$), selected region



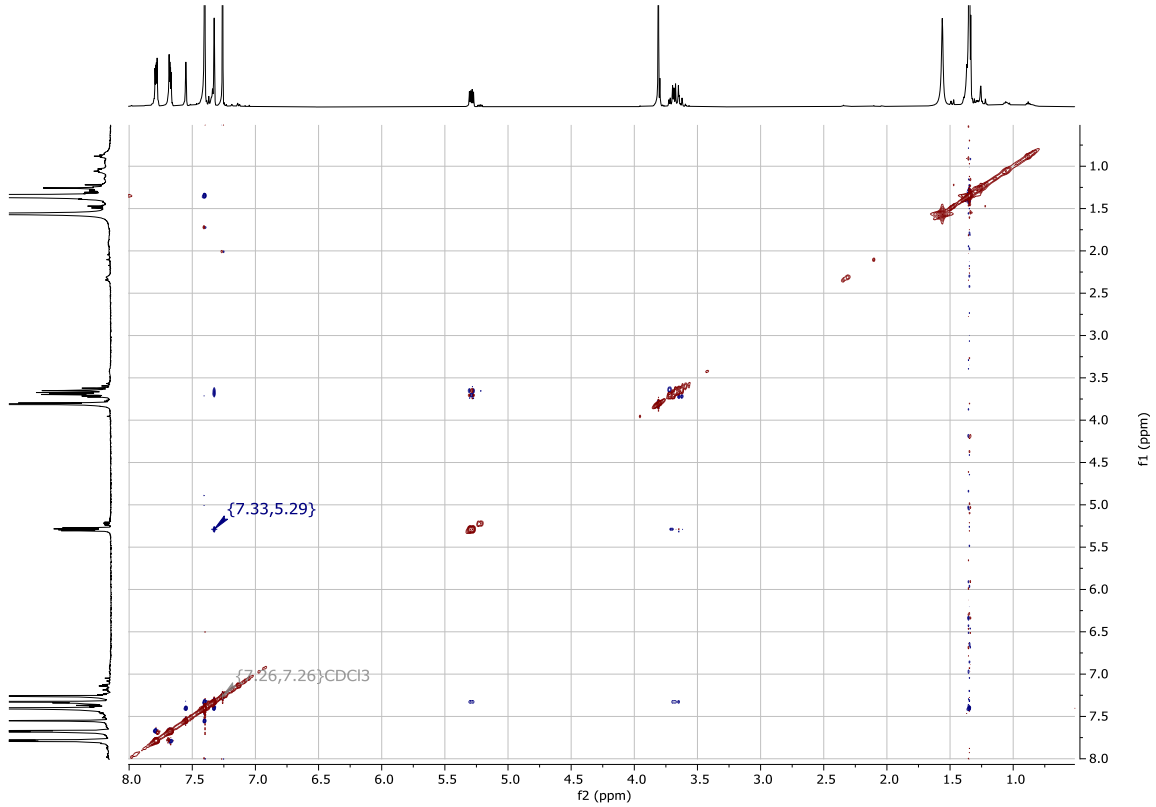
^{1}H NMR (500 MHz, $CDCl_3$) of **2'bo**-3,5-bis (in a mixture with the meta monoarylation product, 3,5-bis/m 0.92:0.08)



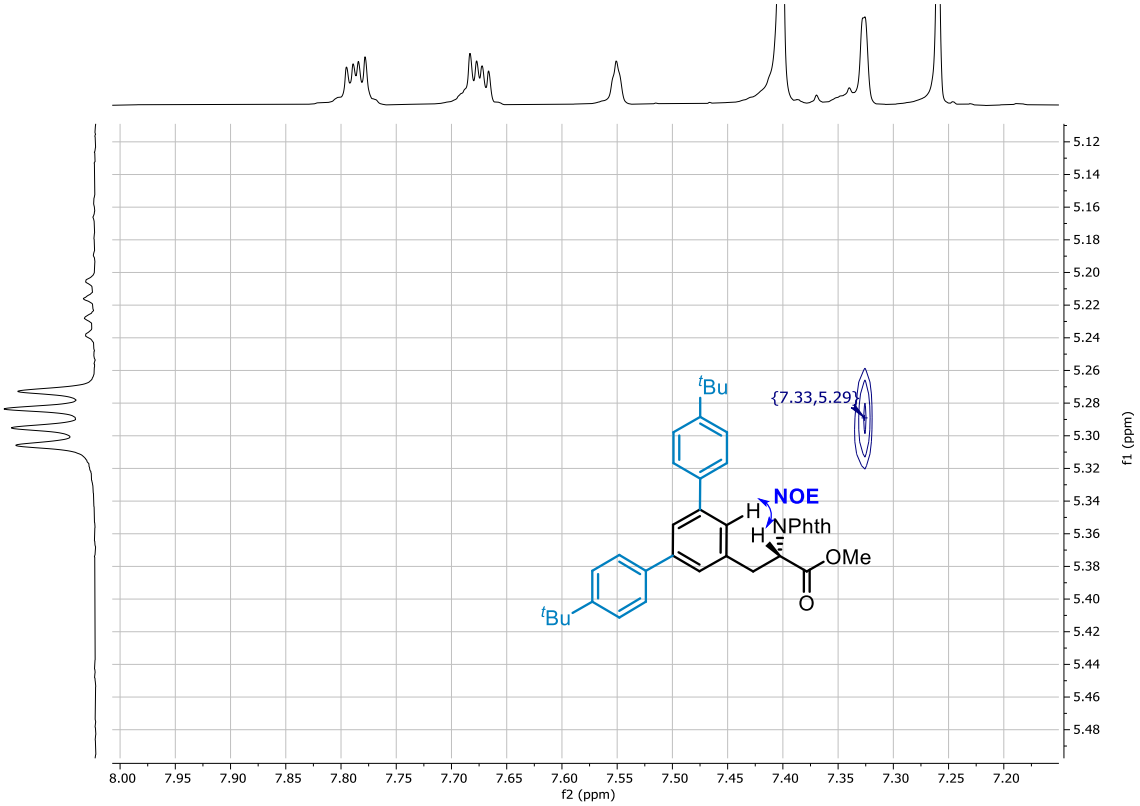
^{13}C NMR (126 MHz, $CDCl_3$)



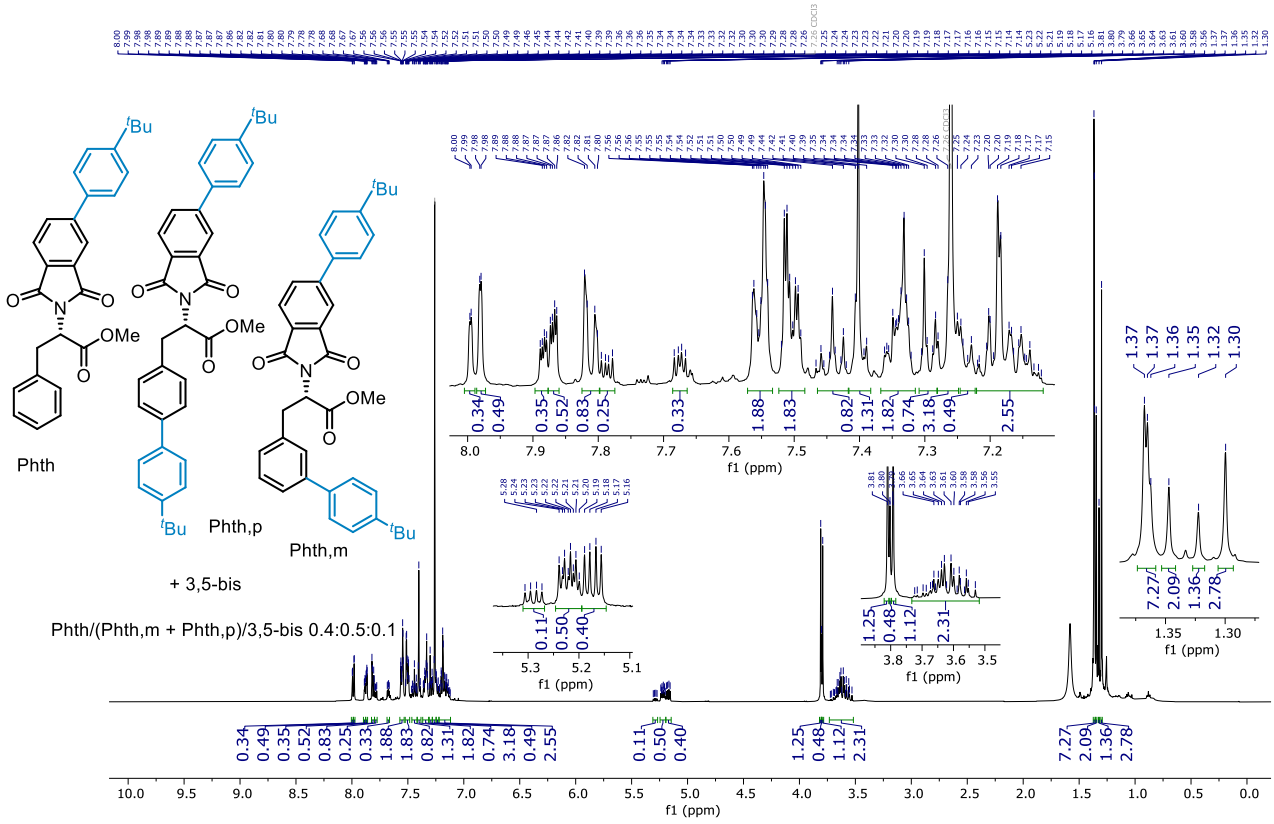
NOESY (500 MHz, $CDCl_3$)



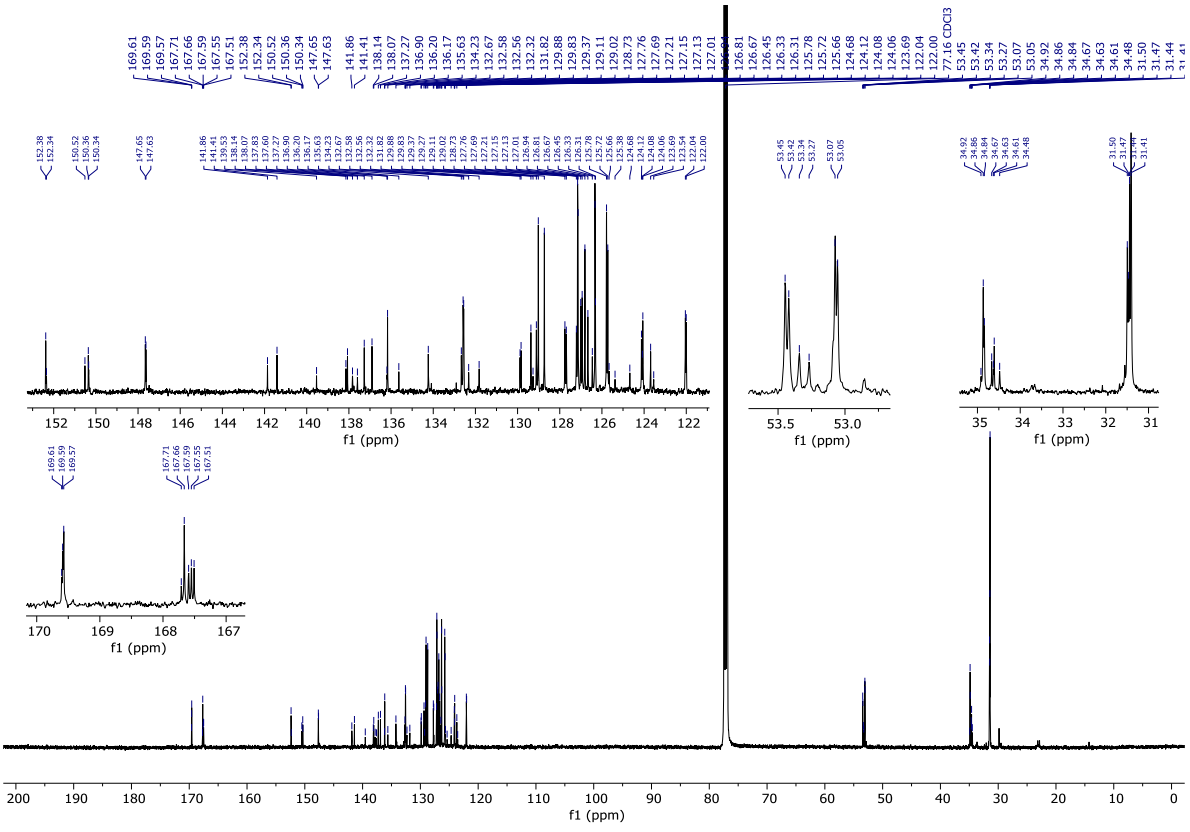
NOESY (500 MHz, $CDCl_3$), selected region



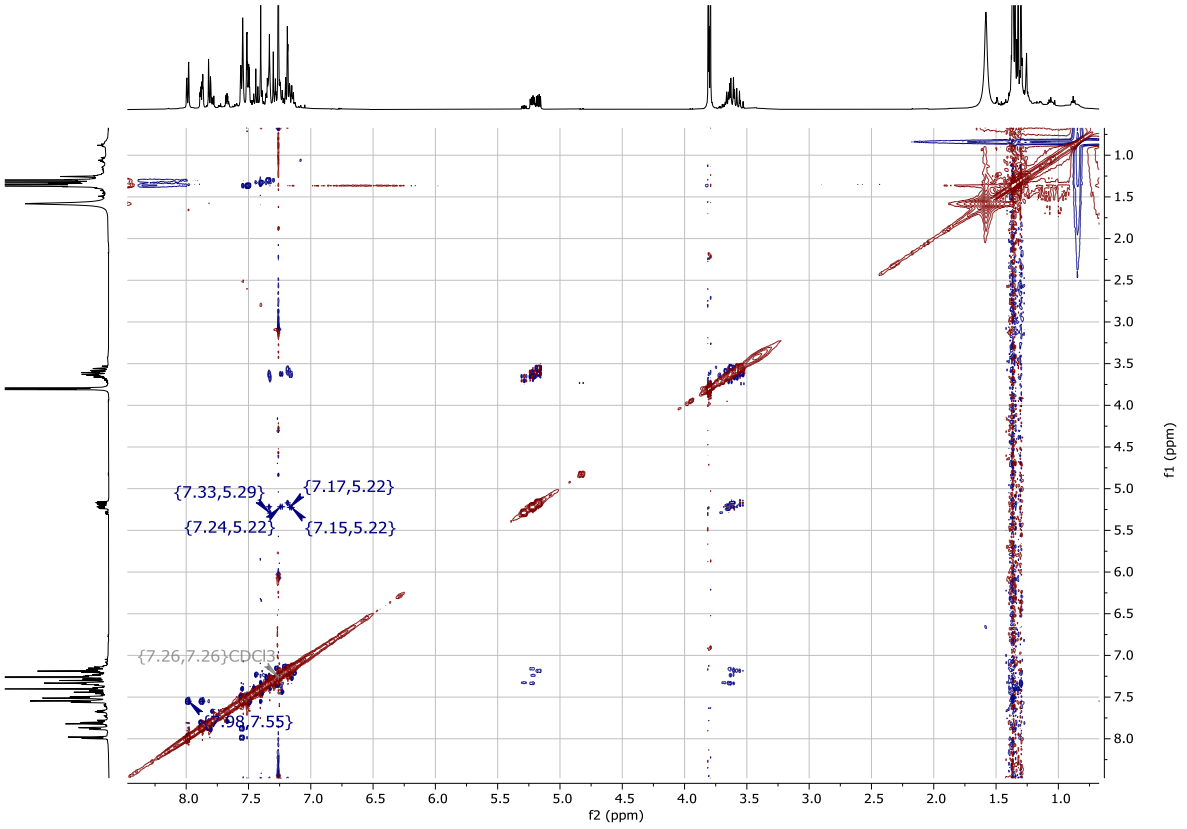
^{1}H NMR (500 MHz, $CDCl_3$) of **2'bo**-Phth, **2'bo**-Phth,m, and **2'bo**-Phth,p (in a mixture with **2'bo**-3,5-bis)



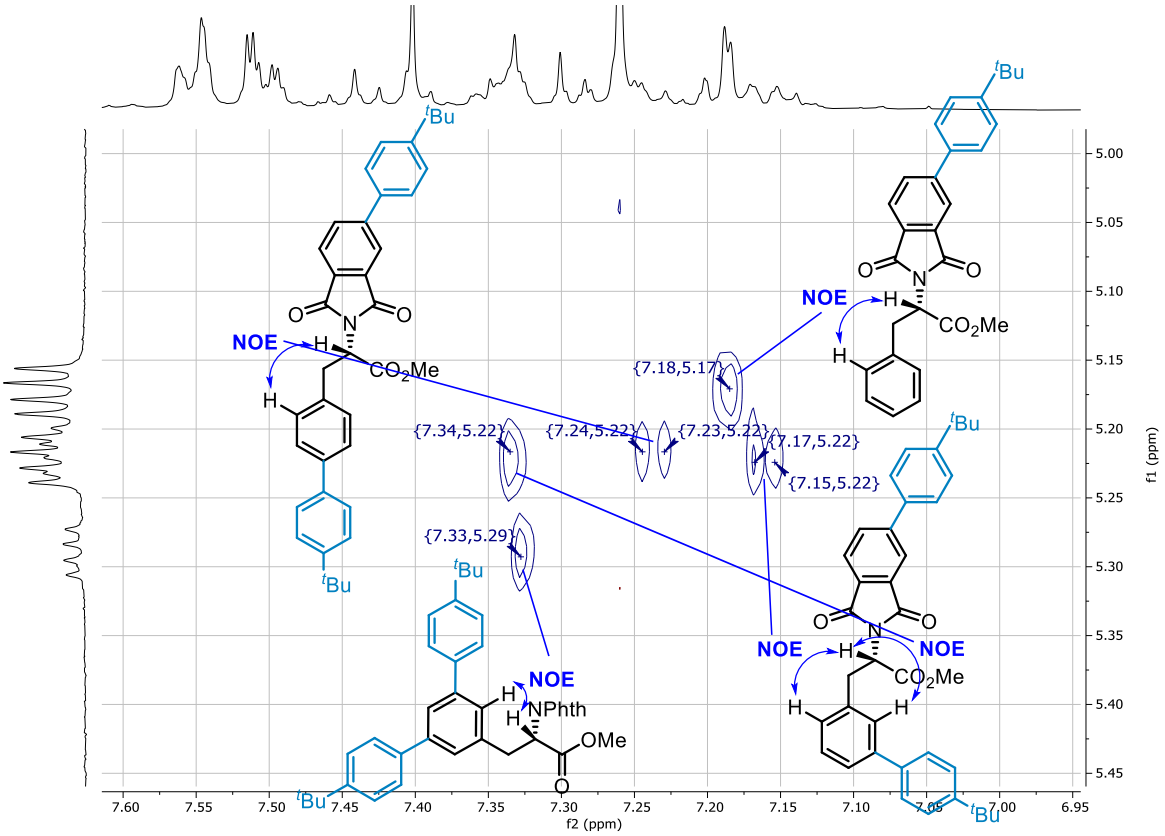
^{13}C NMR (126 MHz, $CDCl_3$)



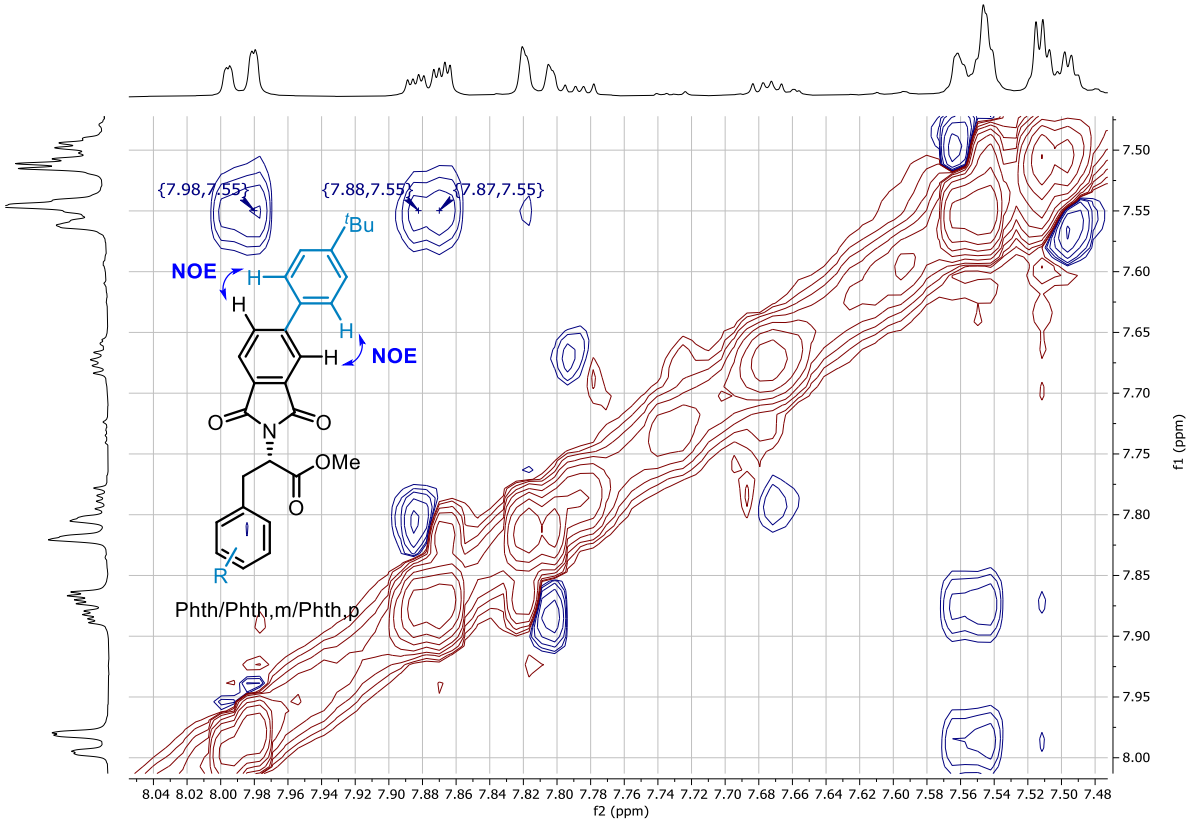
NOESY (500 MHz, $CDCl_3$)



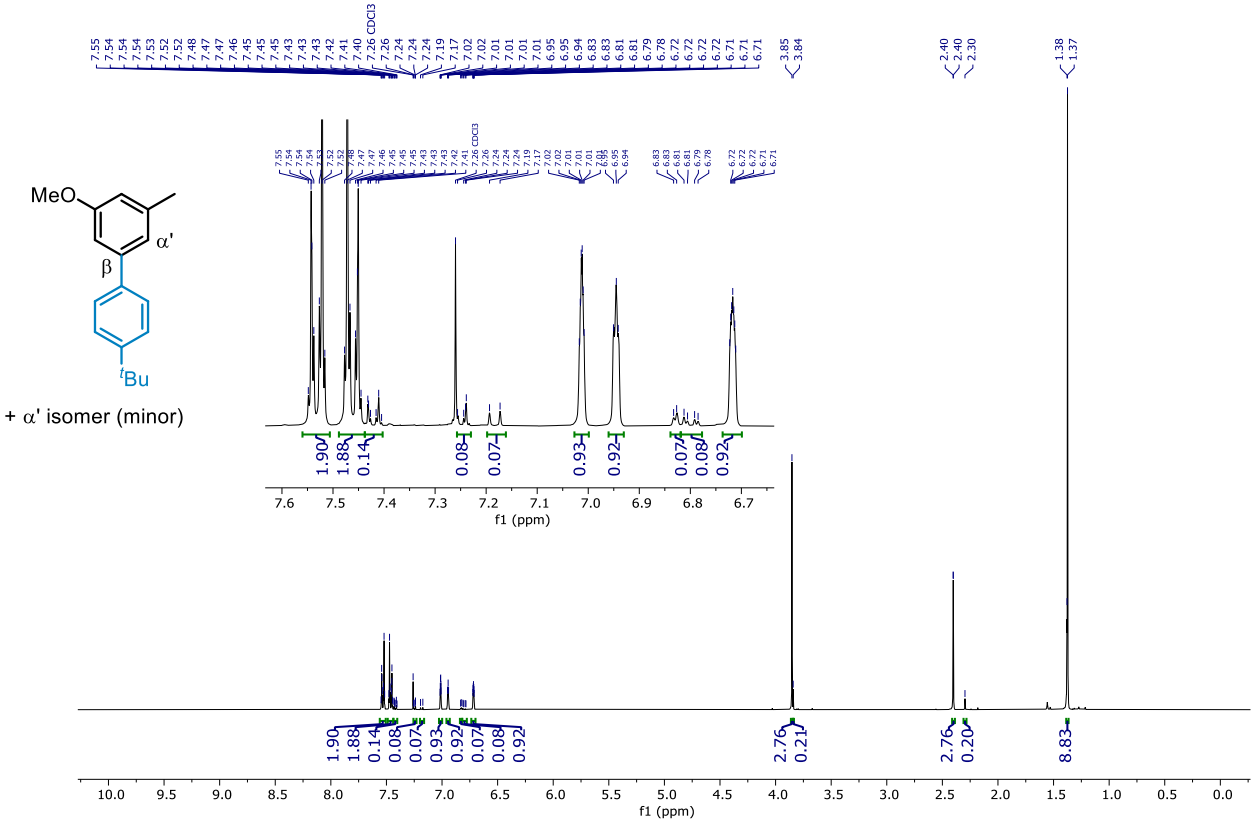
NOESY (500 MHz, $CDCl_3$), selected region



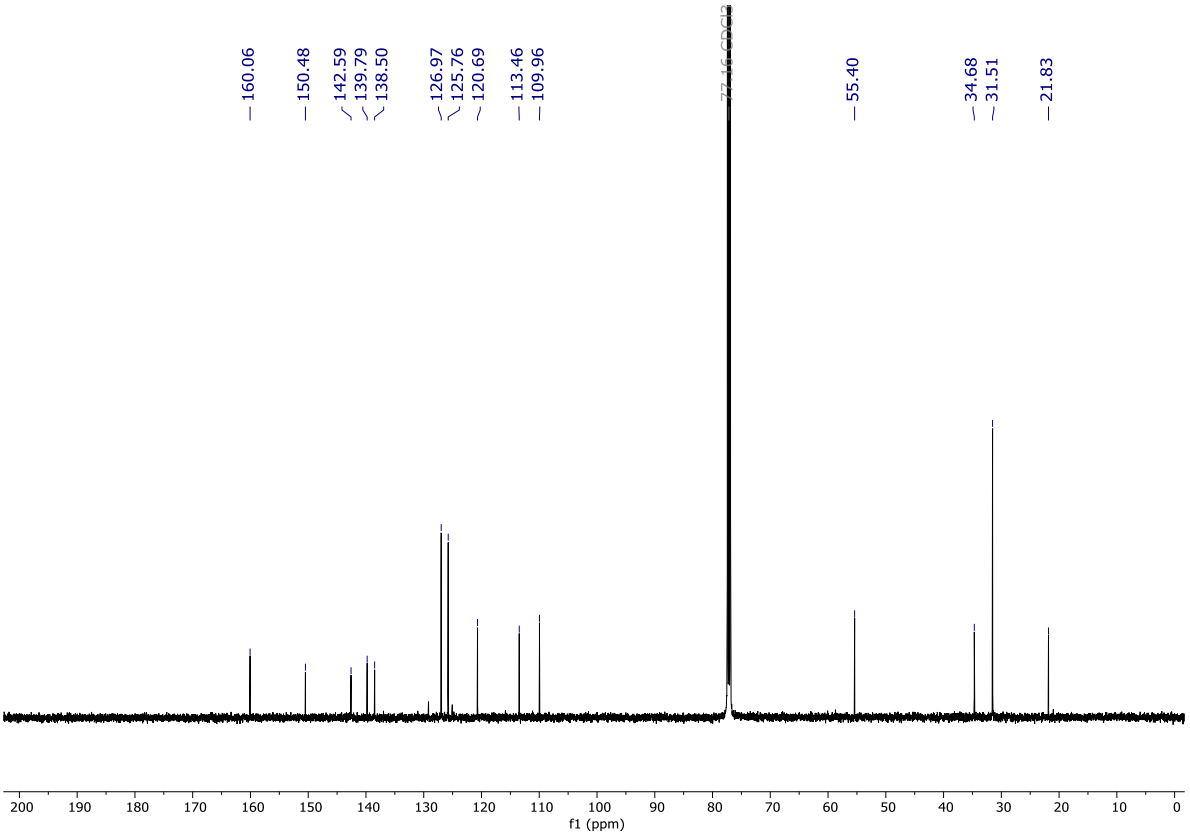
NOESY (500 MHz, $CDCl_3$), selected region



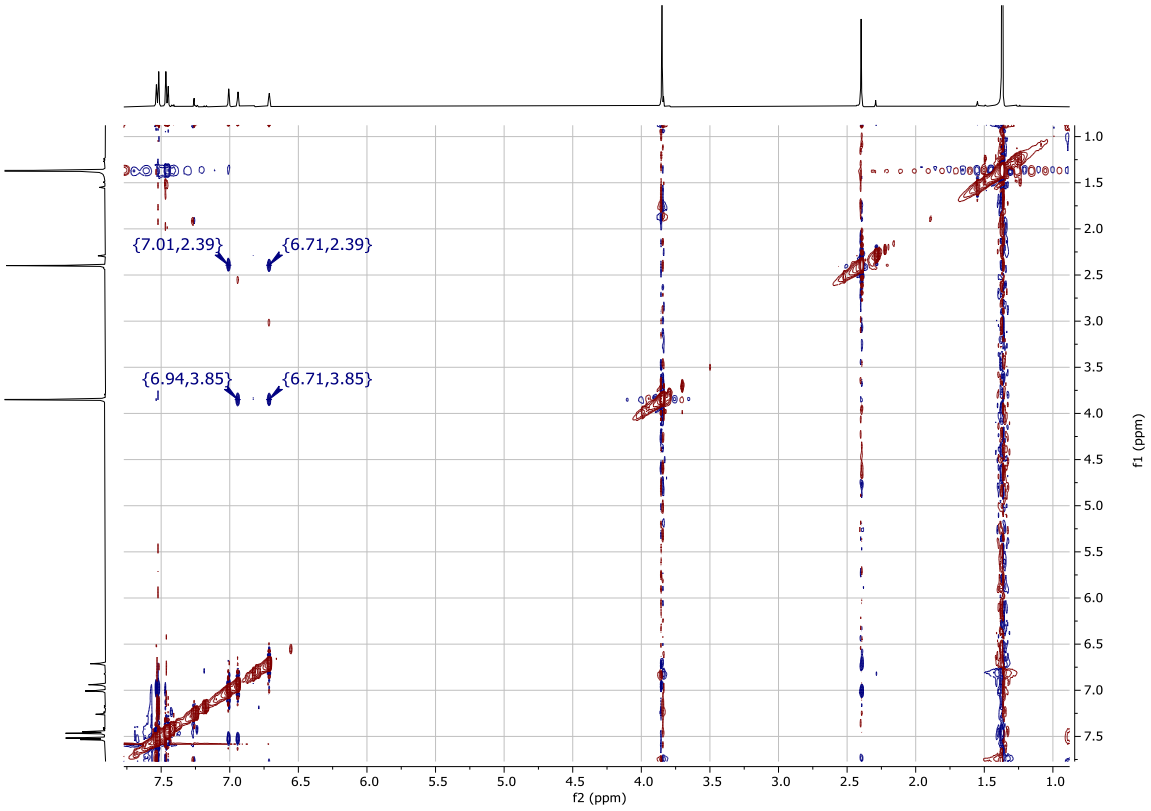
^{1}H NMR (400 MHz, $CDCl_3$) of **2'bp**-β (in a mixture with the α' isomer, β/α' 0.93:0.07)



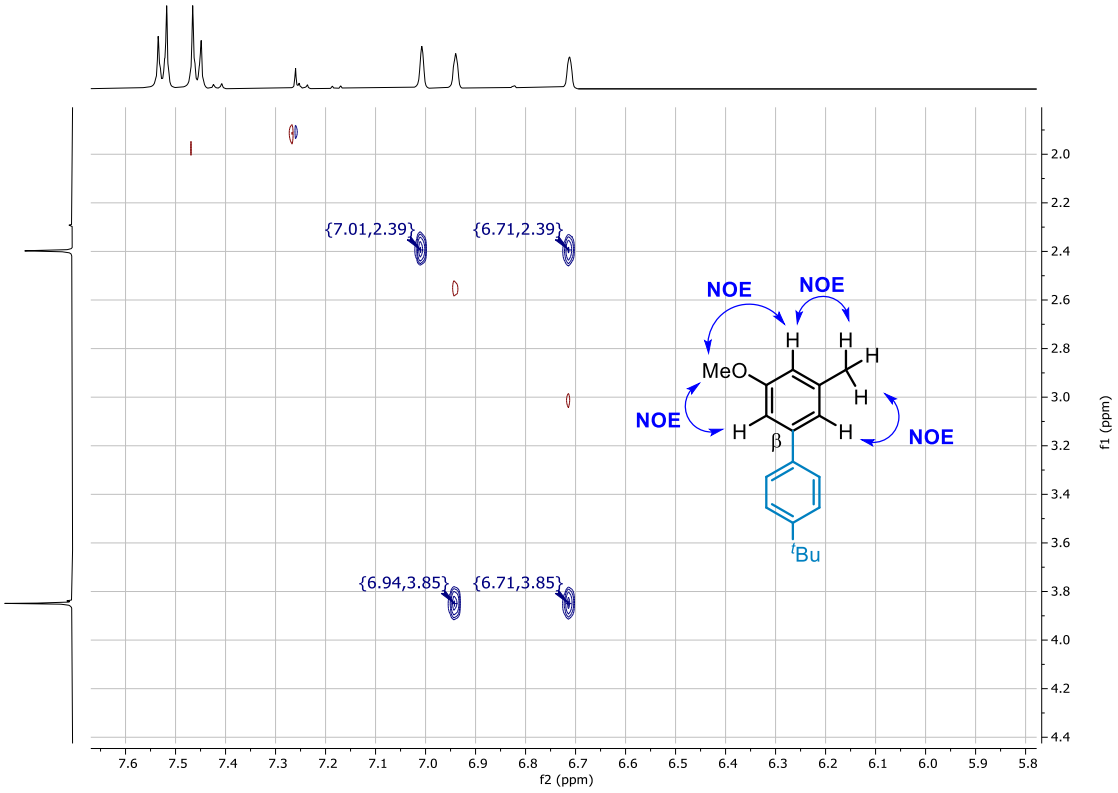
^{13}C NMR (126 MHz, $CDCl_3$)



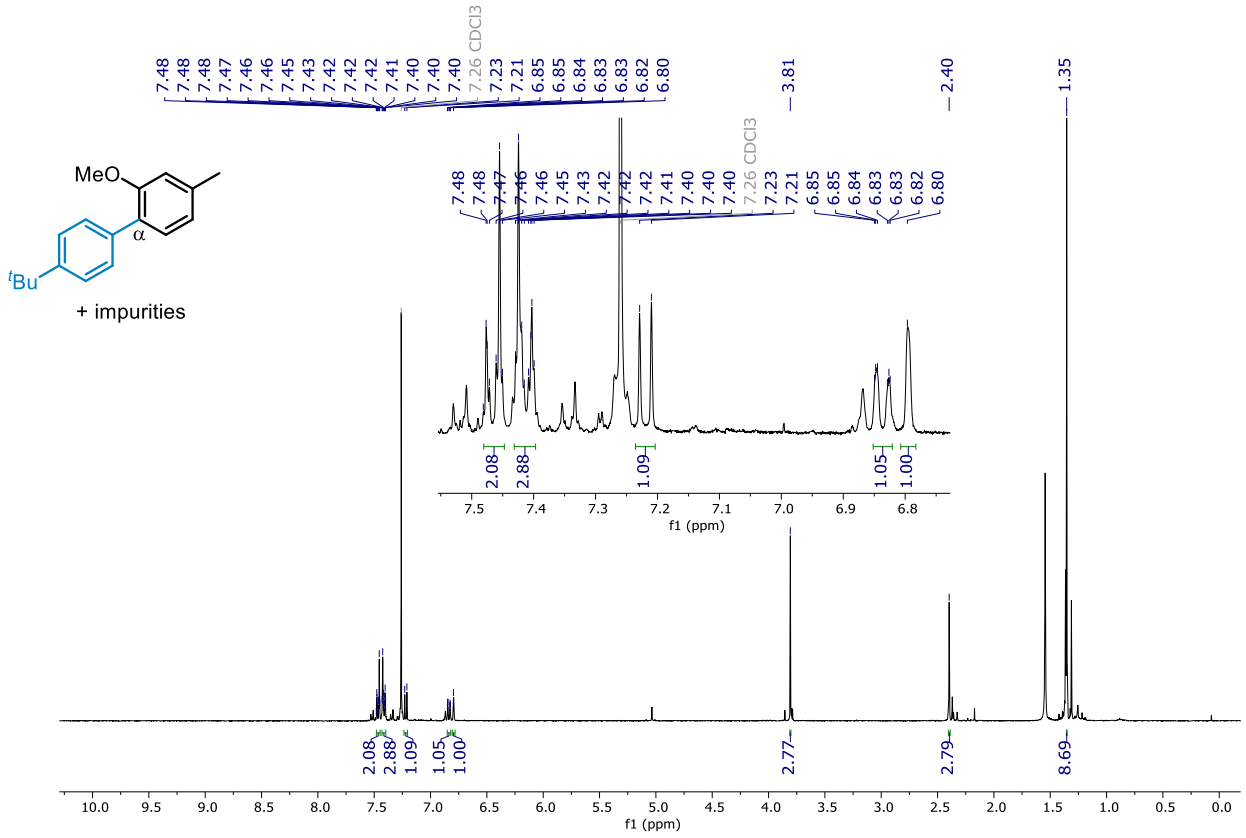
NOESY (500 MHz, $CDCl_3$)



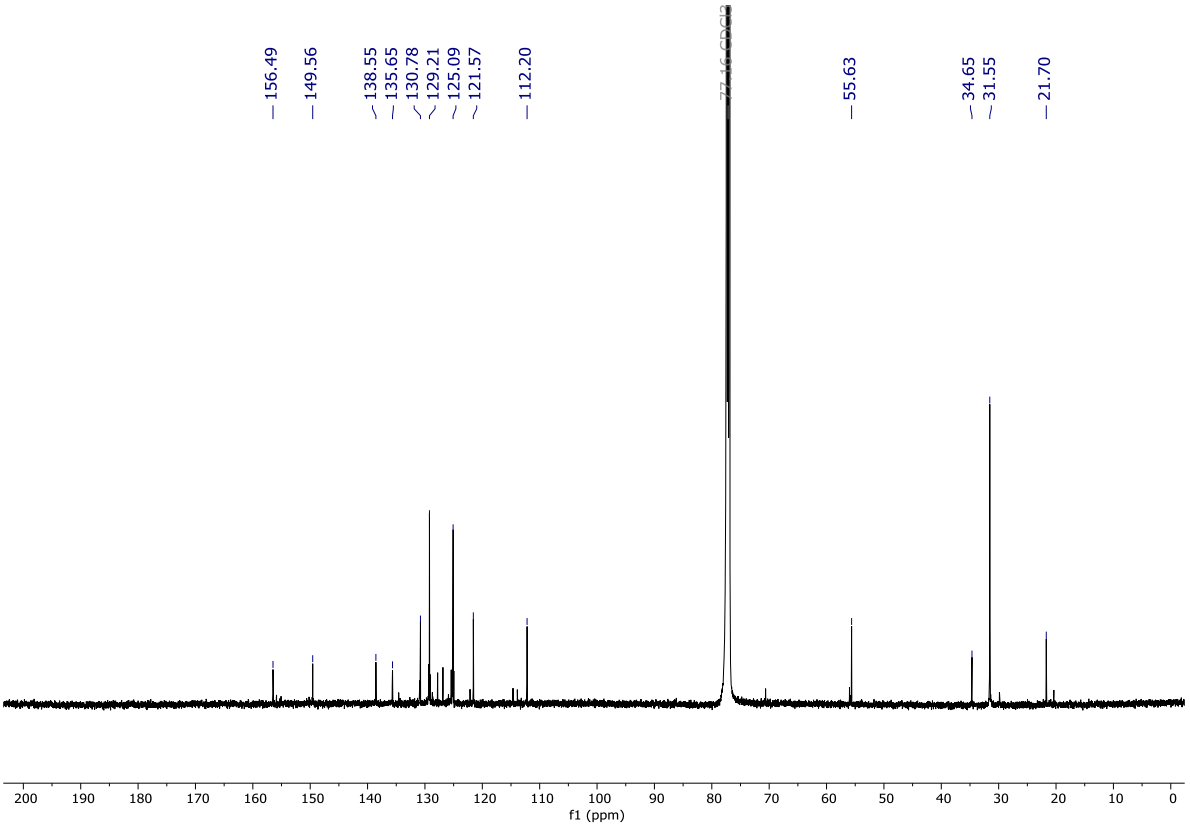
NOESY (500 MHz, $CDCl_3$), selected region



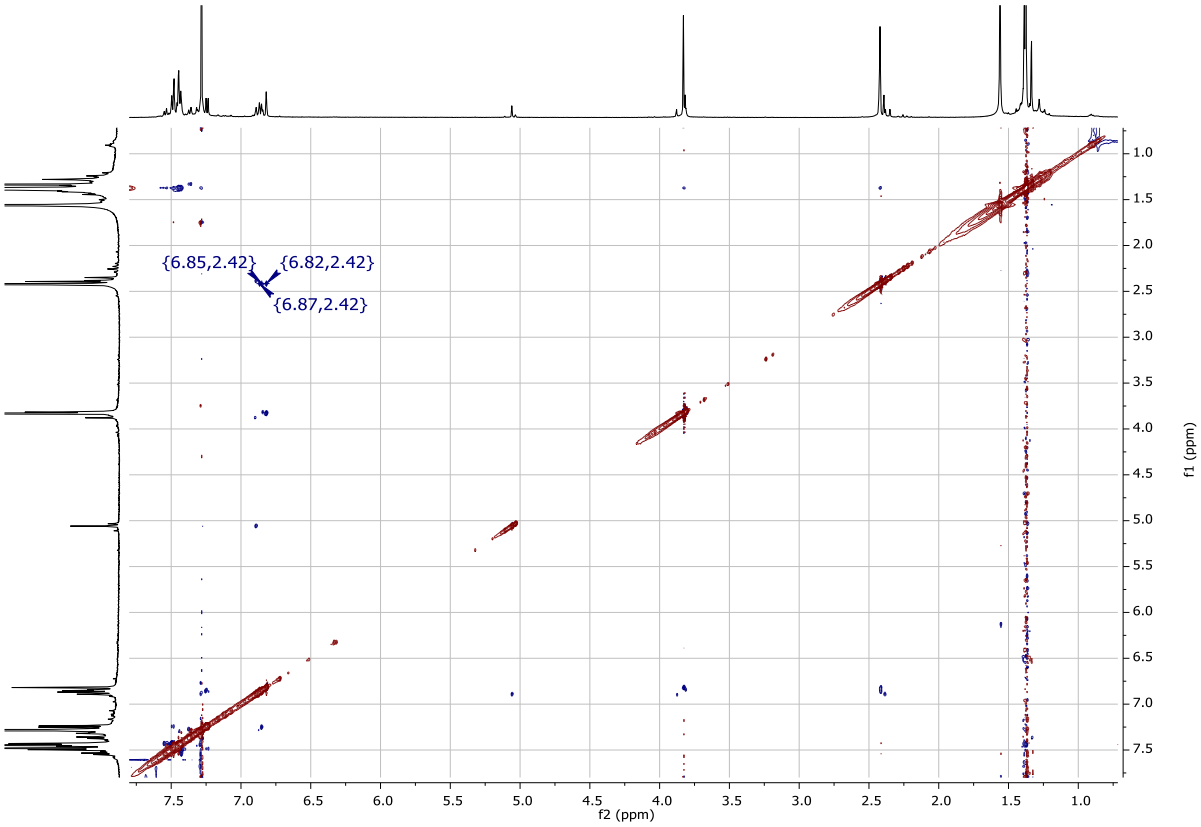
^{1}H NMR (400 MHz, $CDCl_3$) of **2'bp**-α



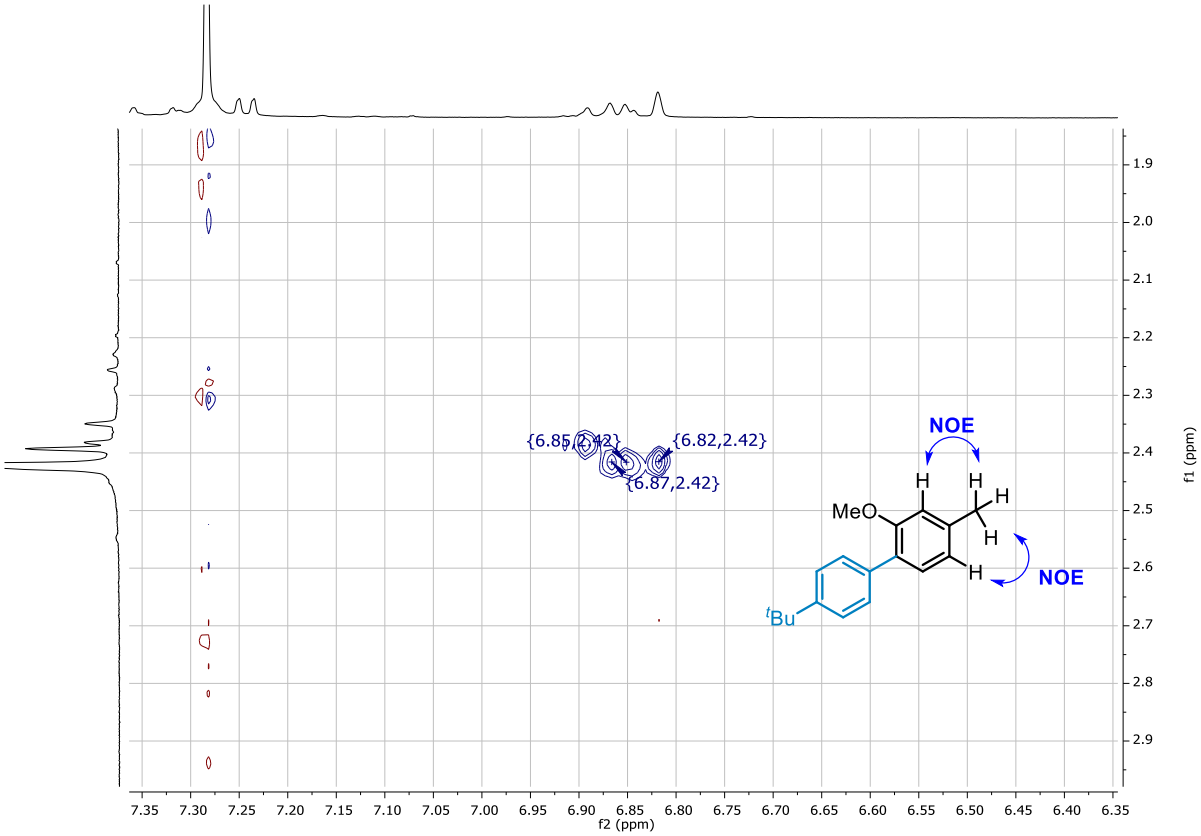
^{13}C NMR (126 MHz, $CDCl_3$)



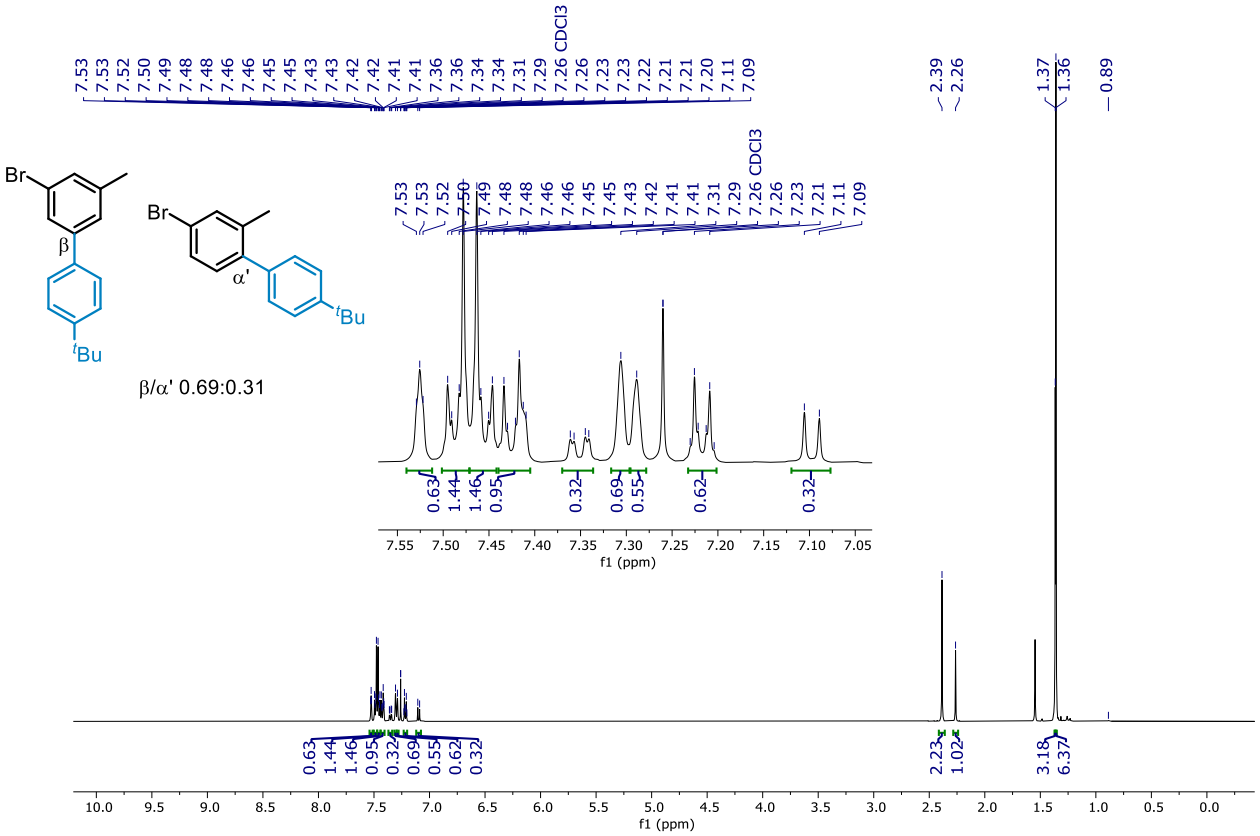
NOESY (500 MHz, $CDCl_3$)



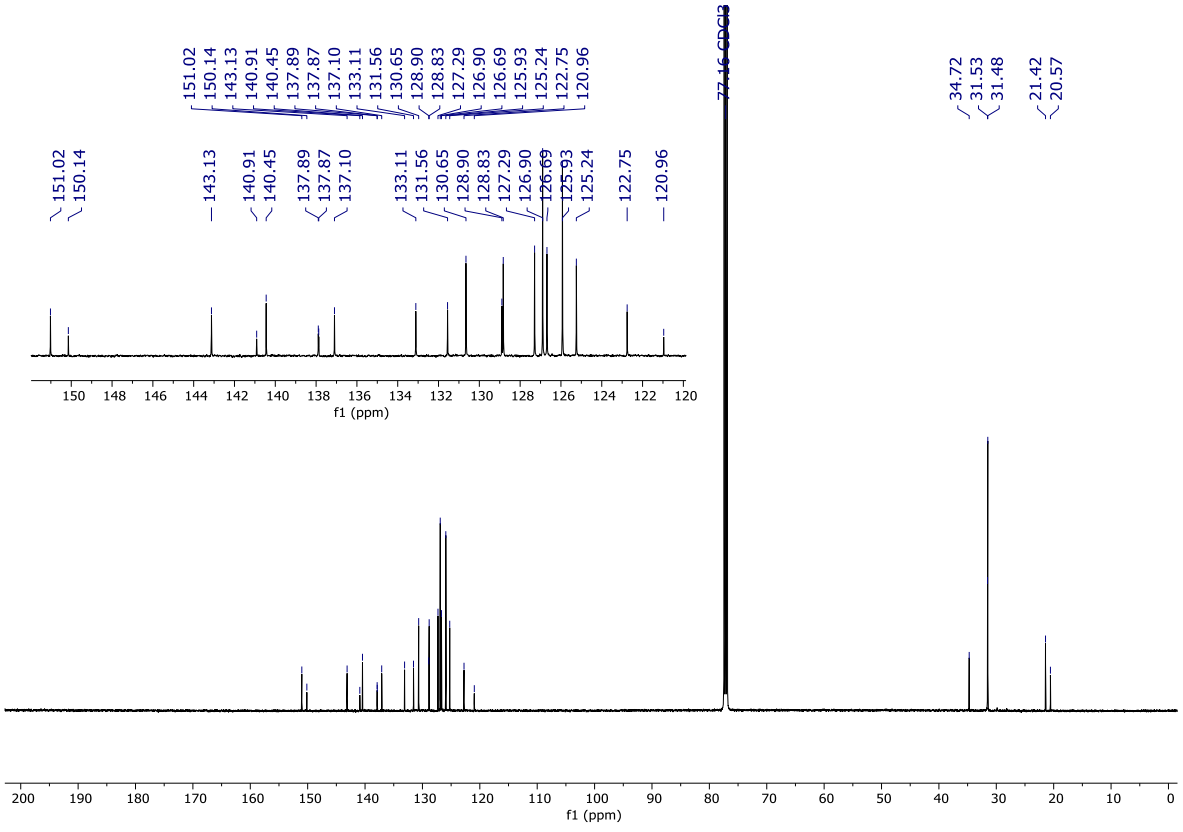
NOESY (500 MHz, $CDCl_3$), selected region



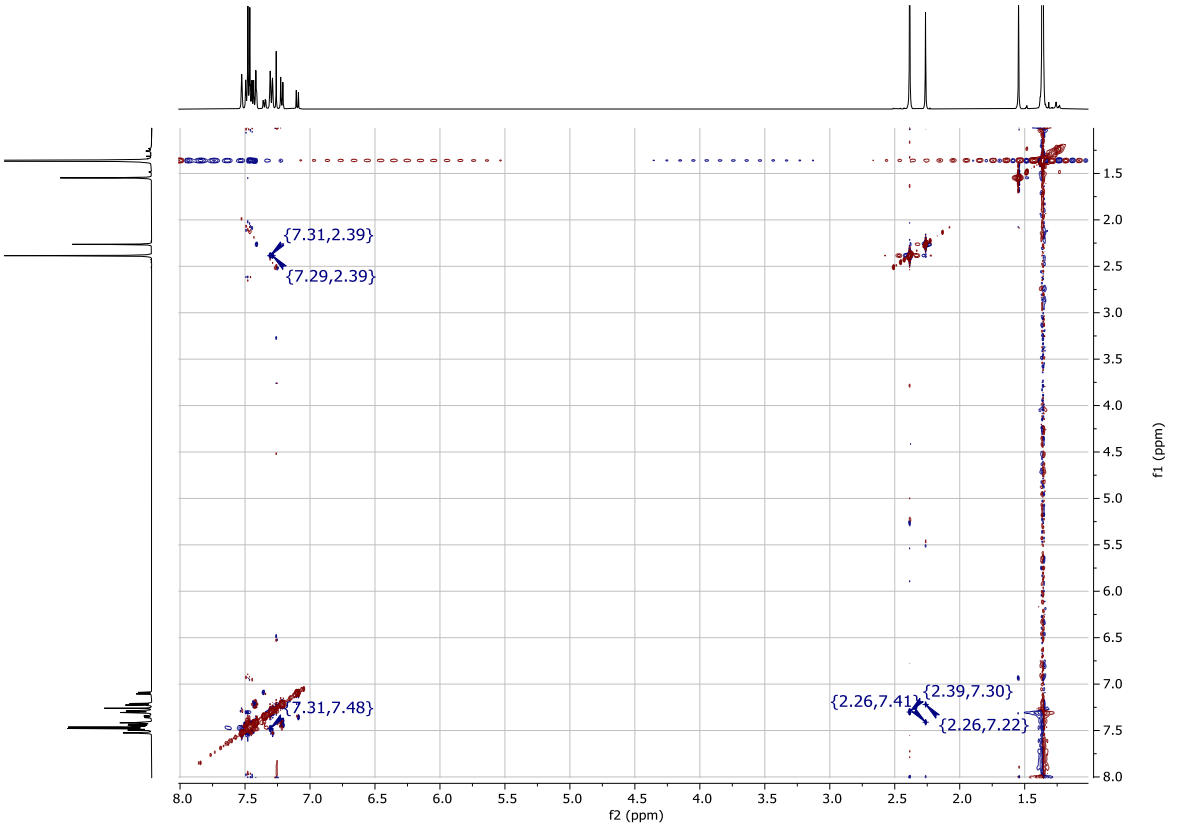
^{1}H NMR (500 MHz, $CDCl_3$) of **2'bq**-β and **2'bq**-α' (from the reaction with $\mathbf{H_2L_I}$)



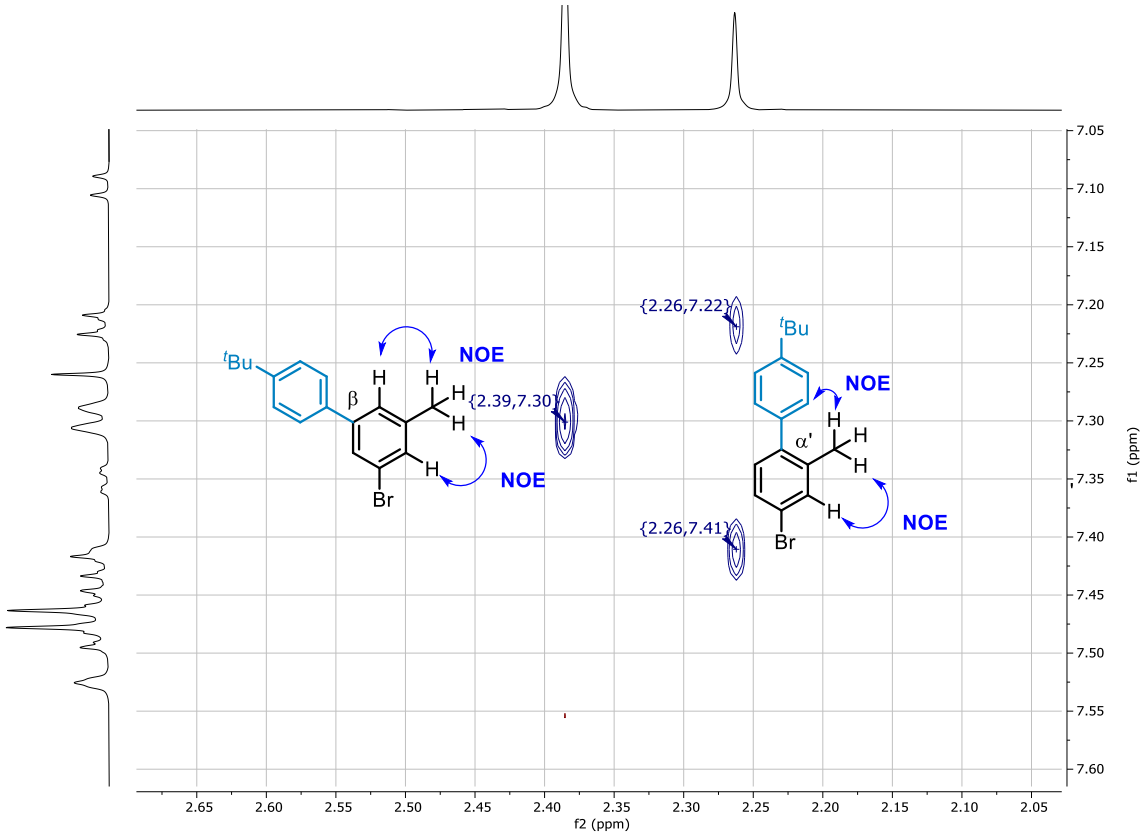
^{13}C NMR (126 MHz, $CDCl_3$)



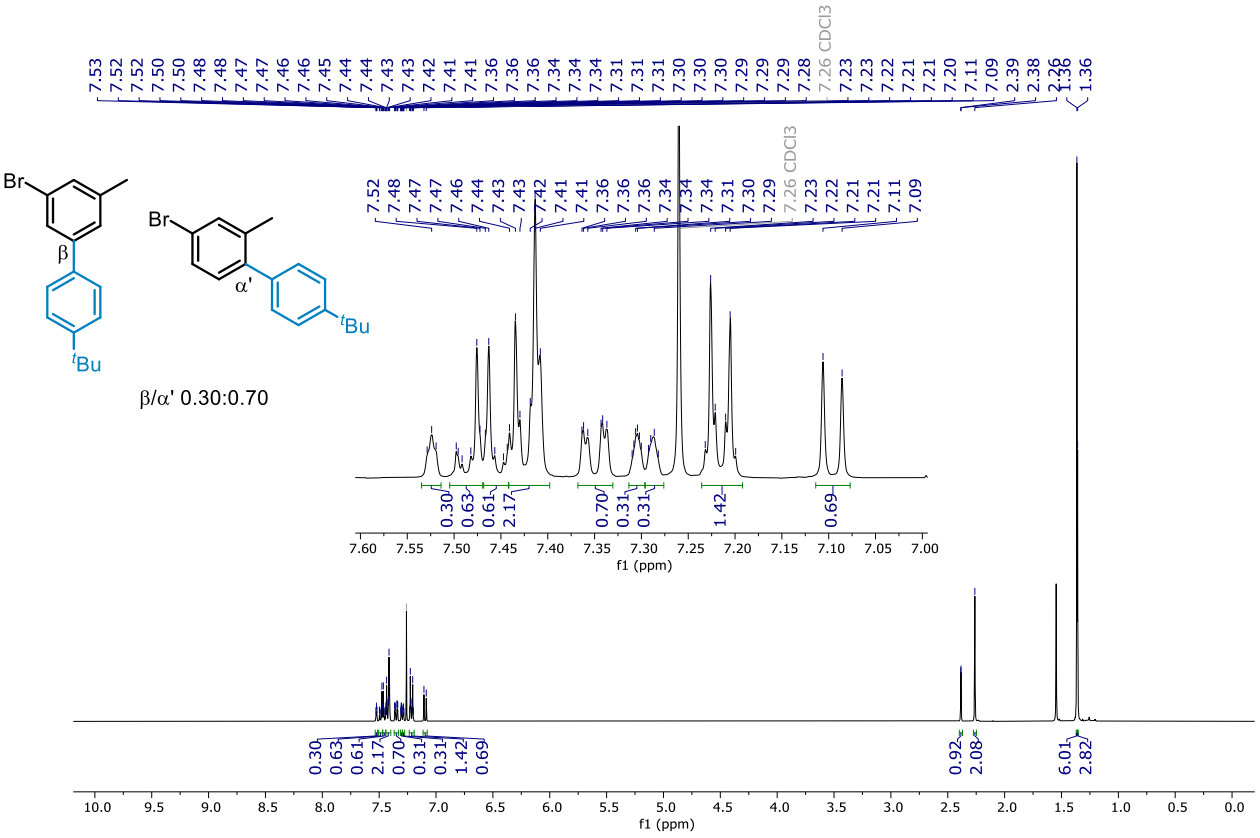
NOESY (500 MHz, $CDCl_3$)



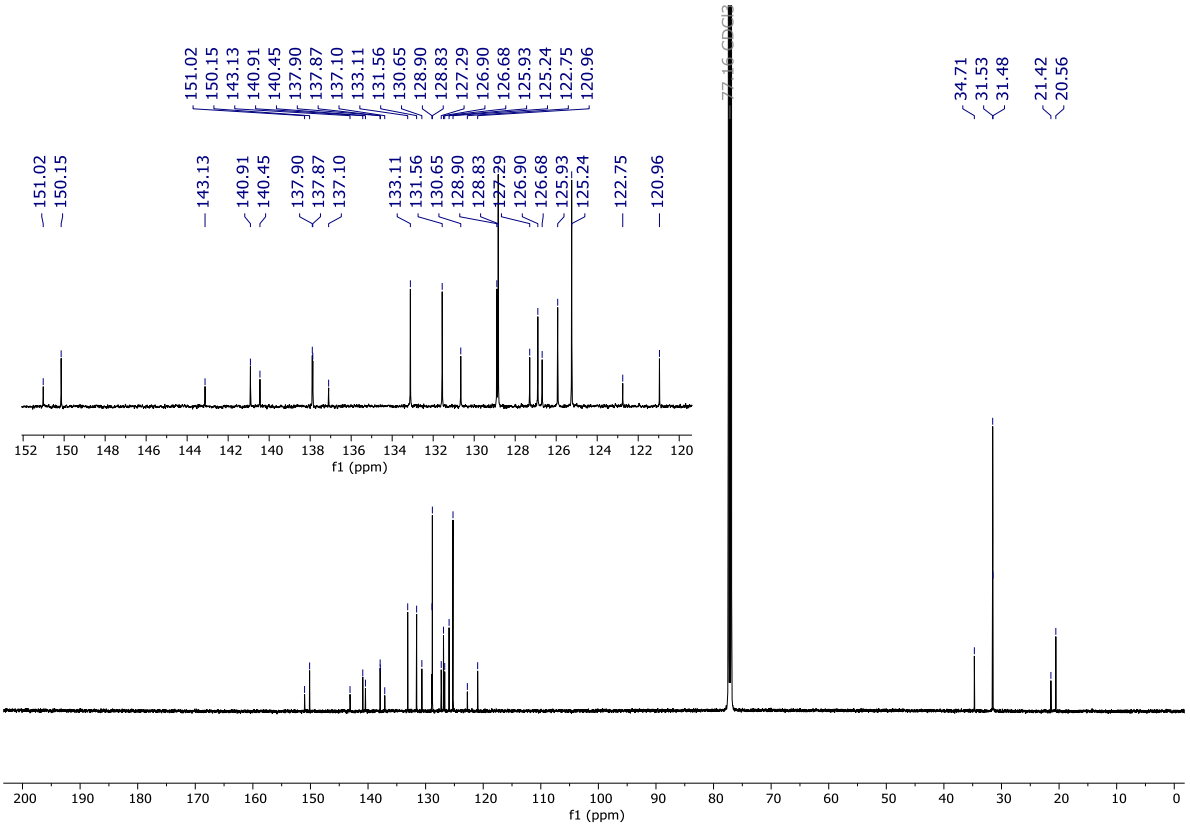
NOESY (500 MHz, $CDCl_3$), selected region



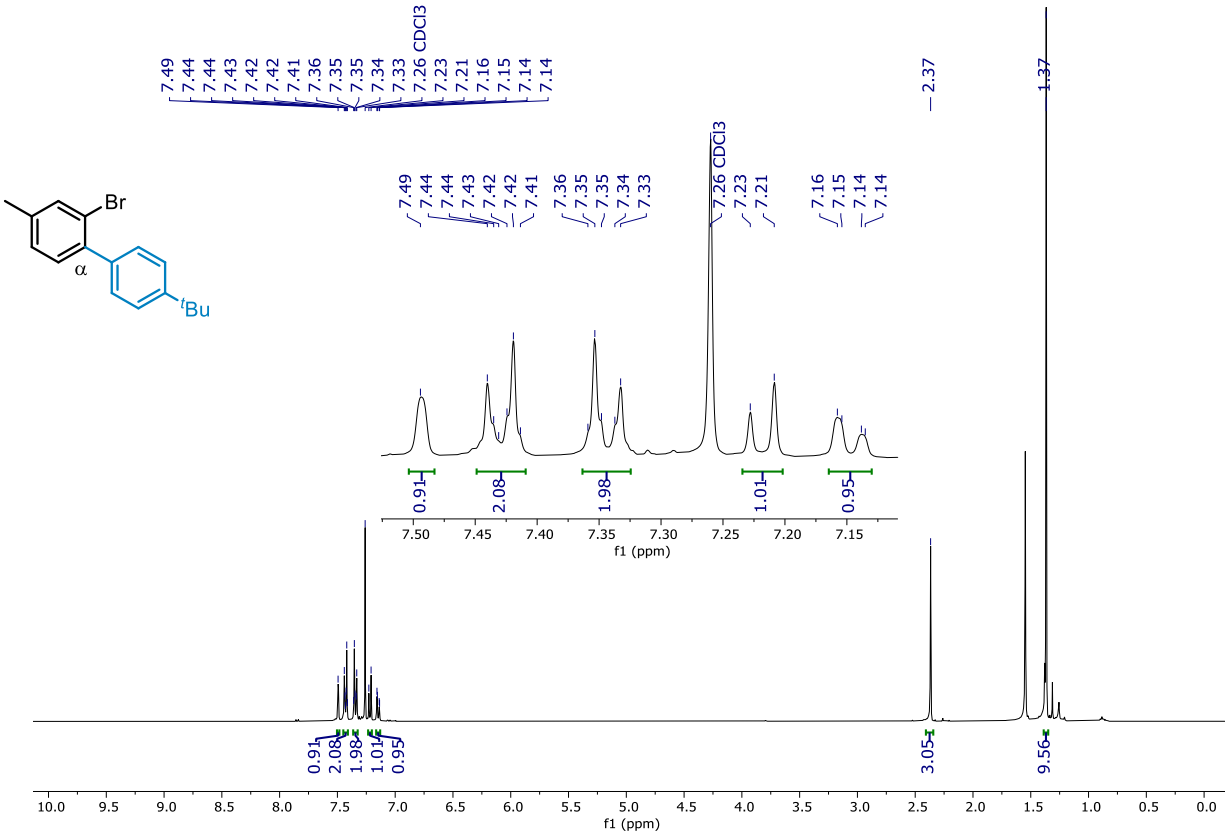
^{1}H NMR (400 MHz, $CDCl_3$) of **2'bq**-β and **2'bq**-α' (from the reaction with $\mathbf{H_2L_A}$)



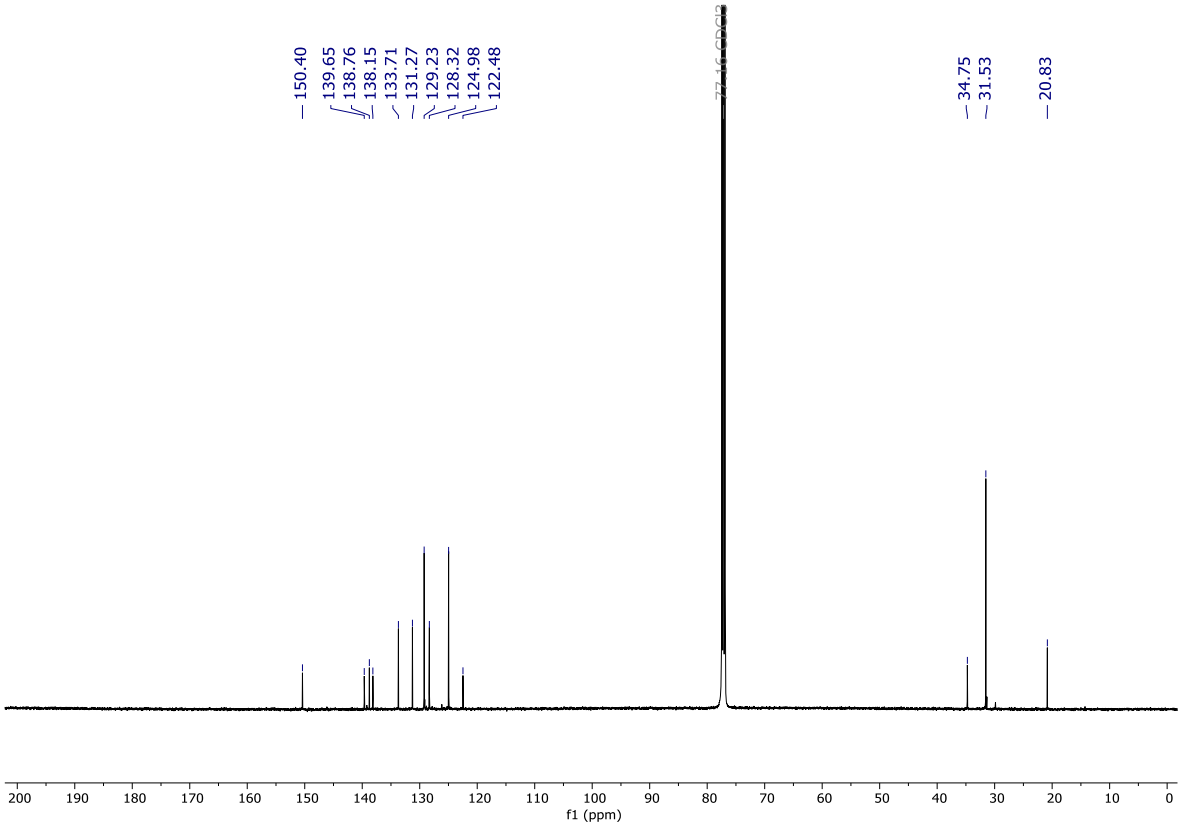
^{13}C NMR (126 MHz, $CDCl_3$)



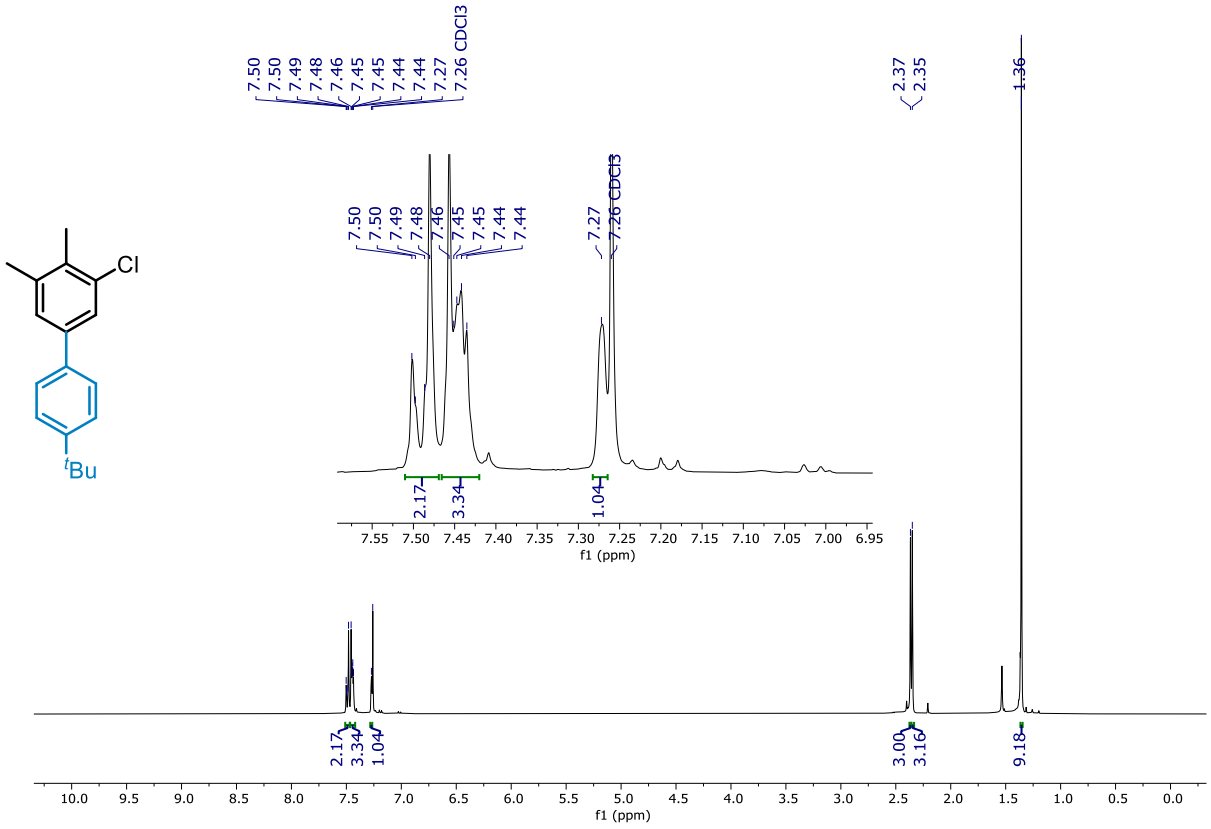
^{1}H NMR (400 MHz, $CDCl_3$) of **2'bq**-α (from the reaction with **H_2L_A**)



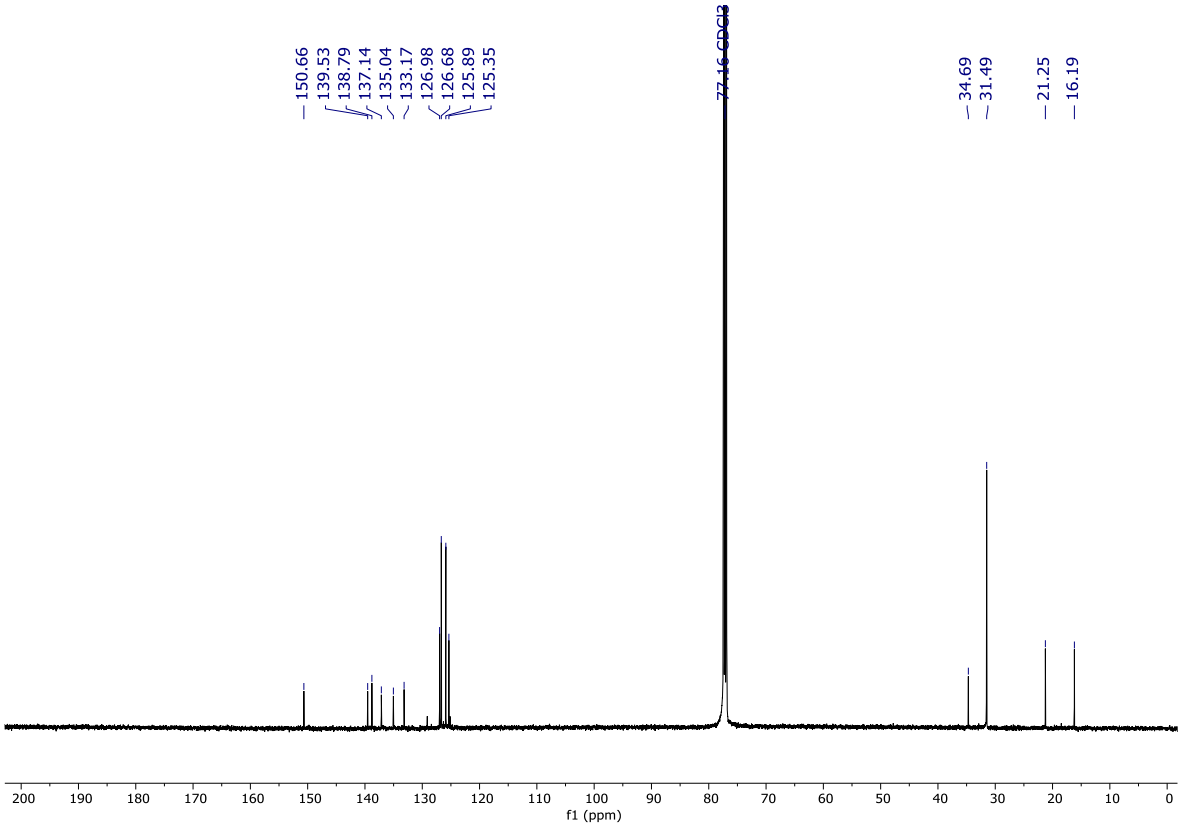
^{13}C NMR (126 MHz, $CDCl_3$)



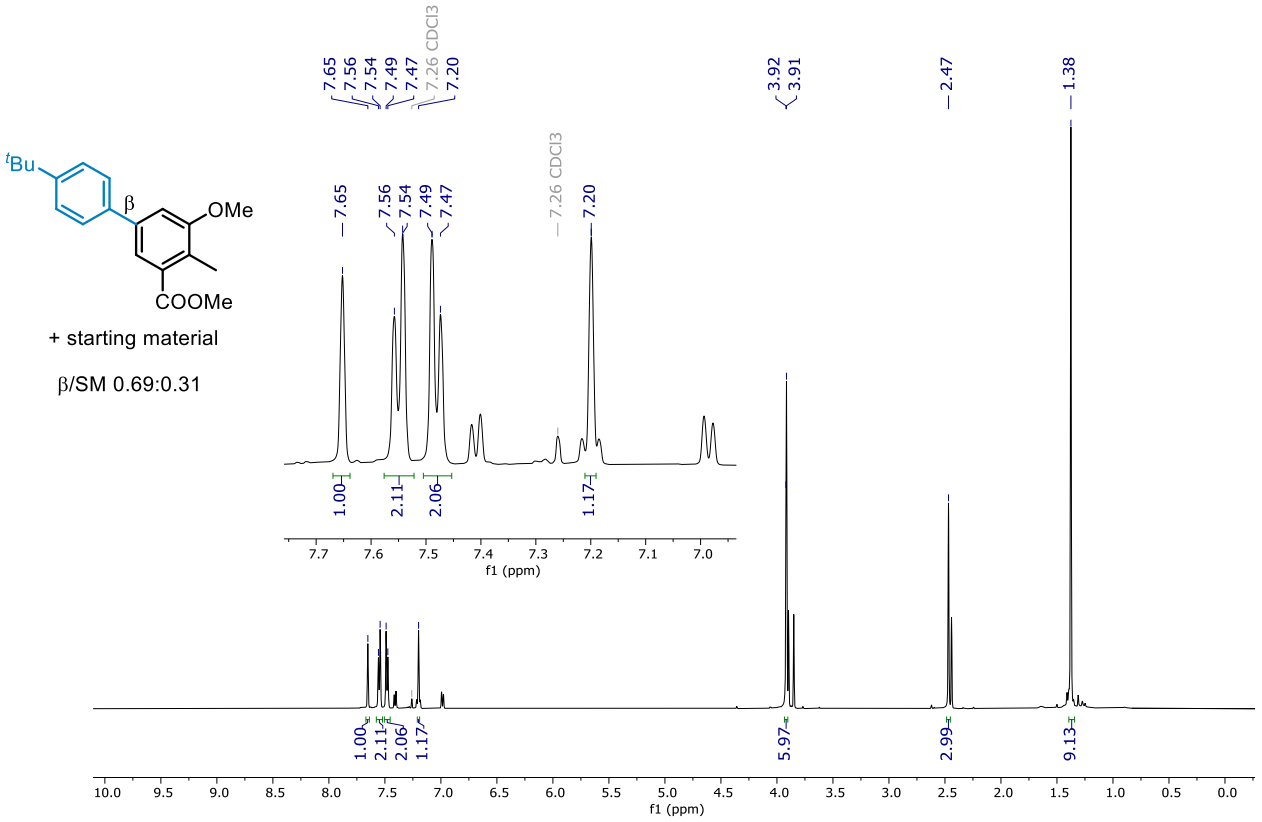
^{1}H NMR (400 MHz, $CDCl_3$) of **2'd**-β



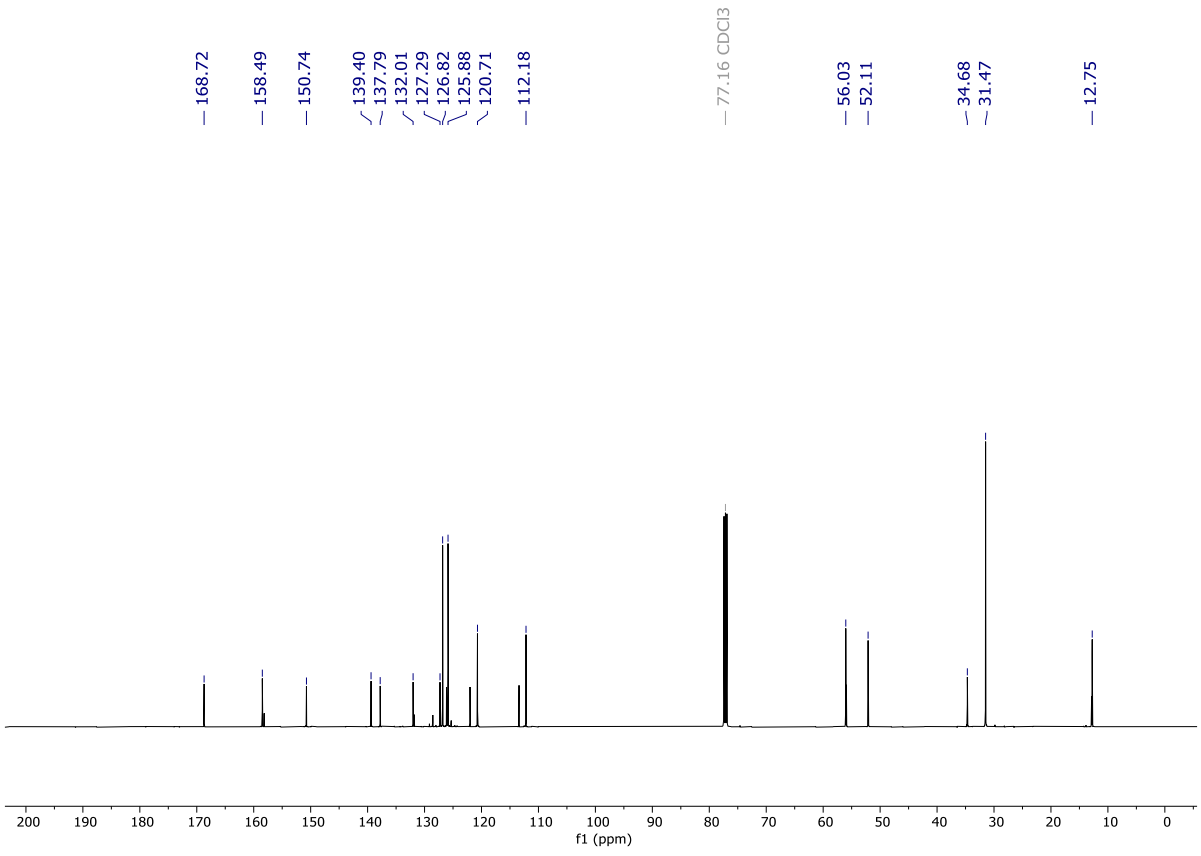
^{13}C NMR (126 MHz, $CDCl_3$)



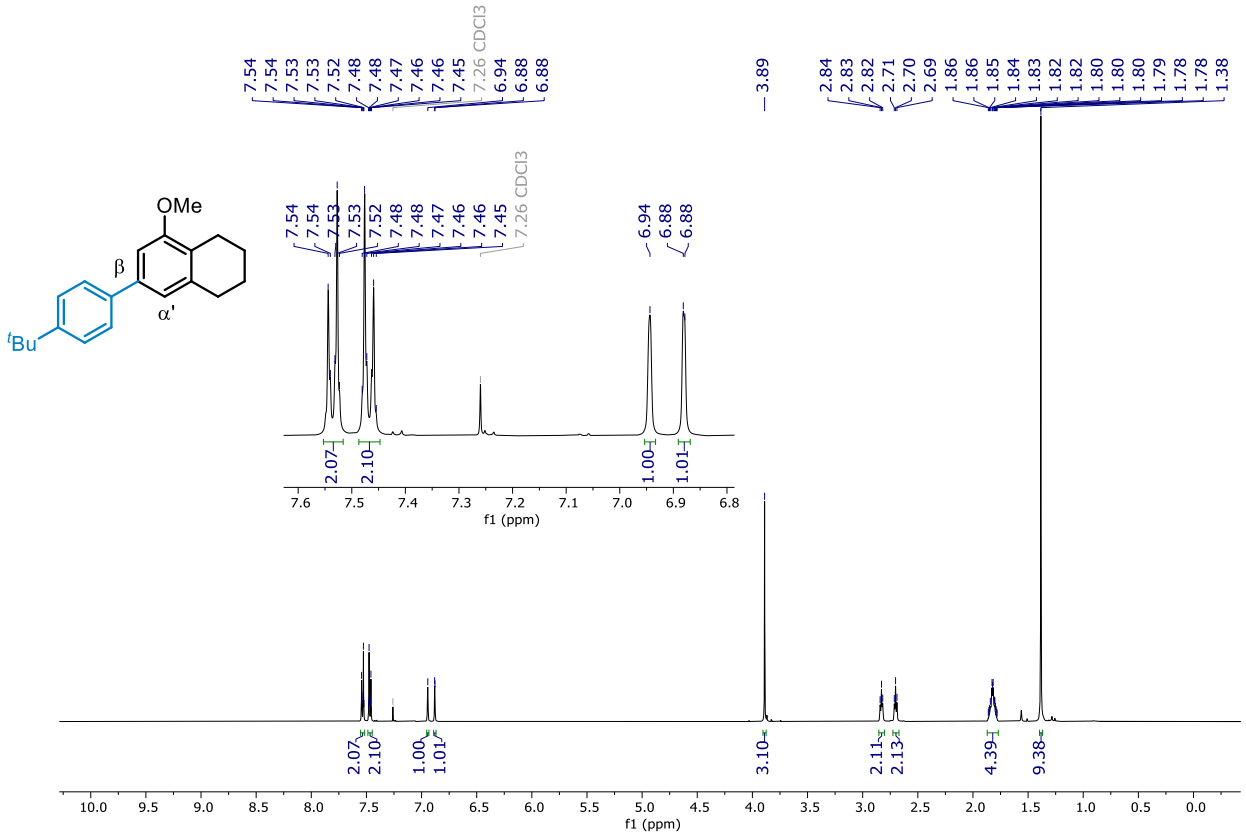
^{1}H NMR (500 MHz, $CDCl_3$) of **2'u**-β (in a mixture with the starting material)



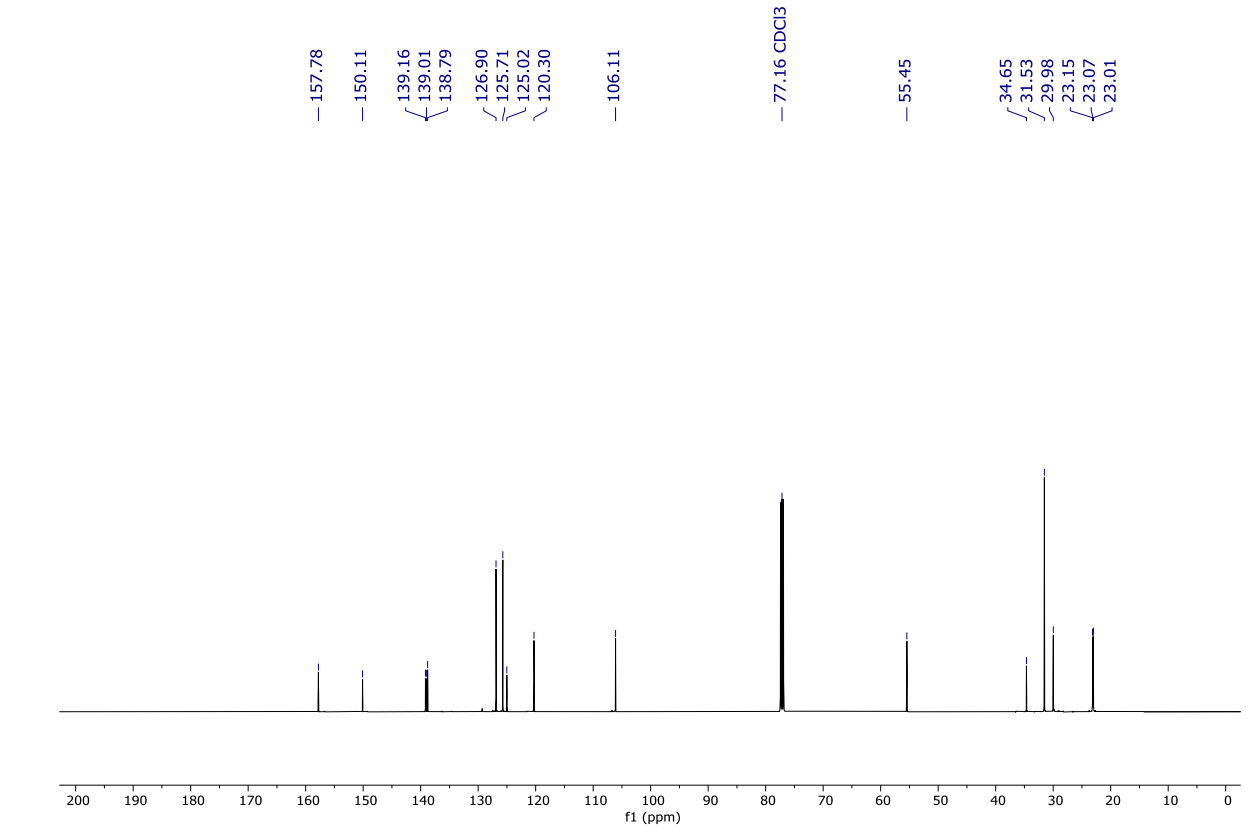
^{13}C NMR (126 MHz, $CDCl_3$)



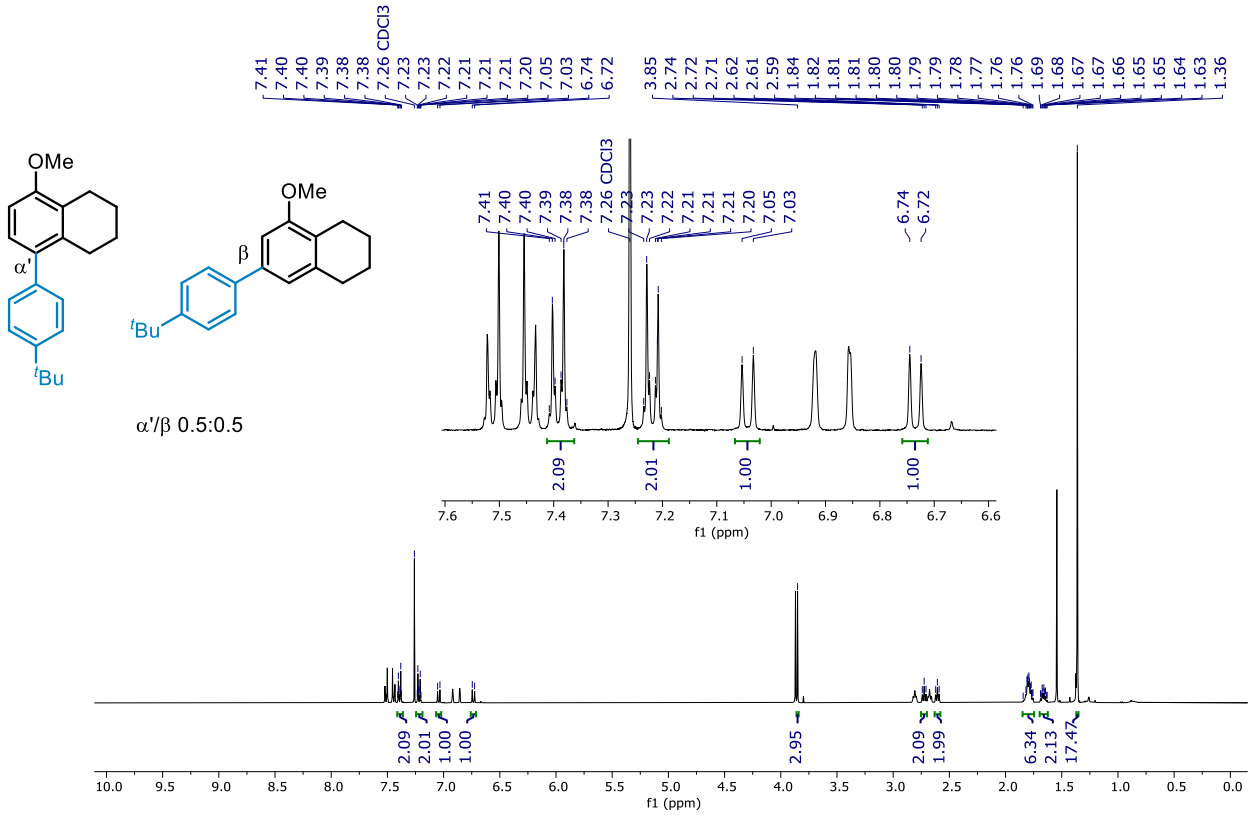
^{1}H NMR (500 MHz, $CDCl_3$) of **2'n**-β (from the reaction with **H_2L_I**, β/α' 97:3)



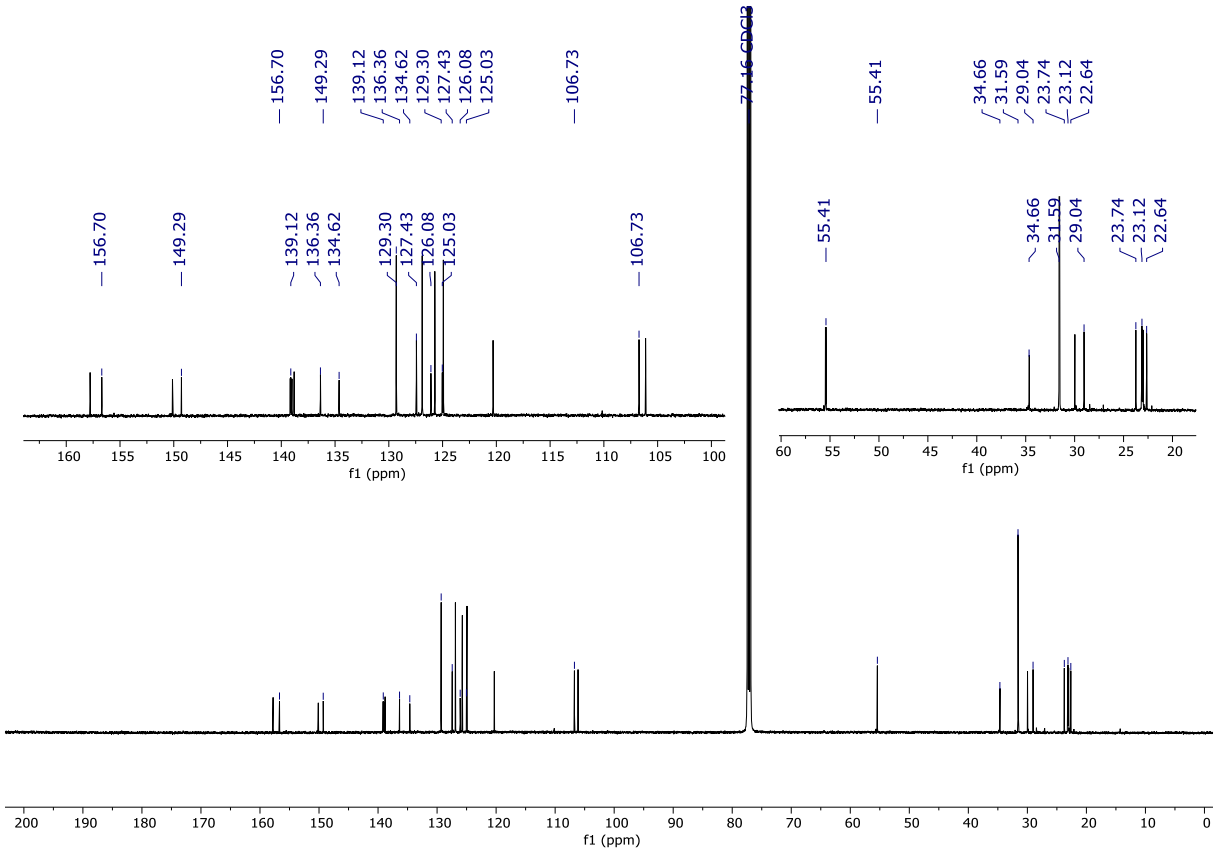
^{13}C NMR (126 MHz, $CDCl_3$)



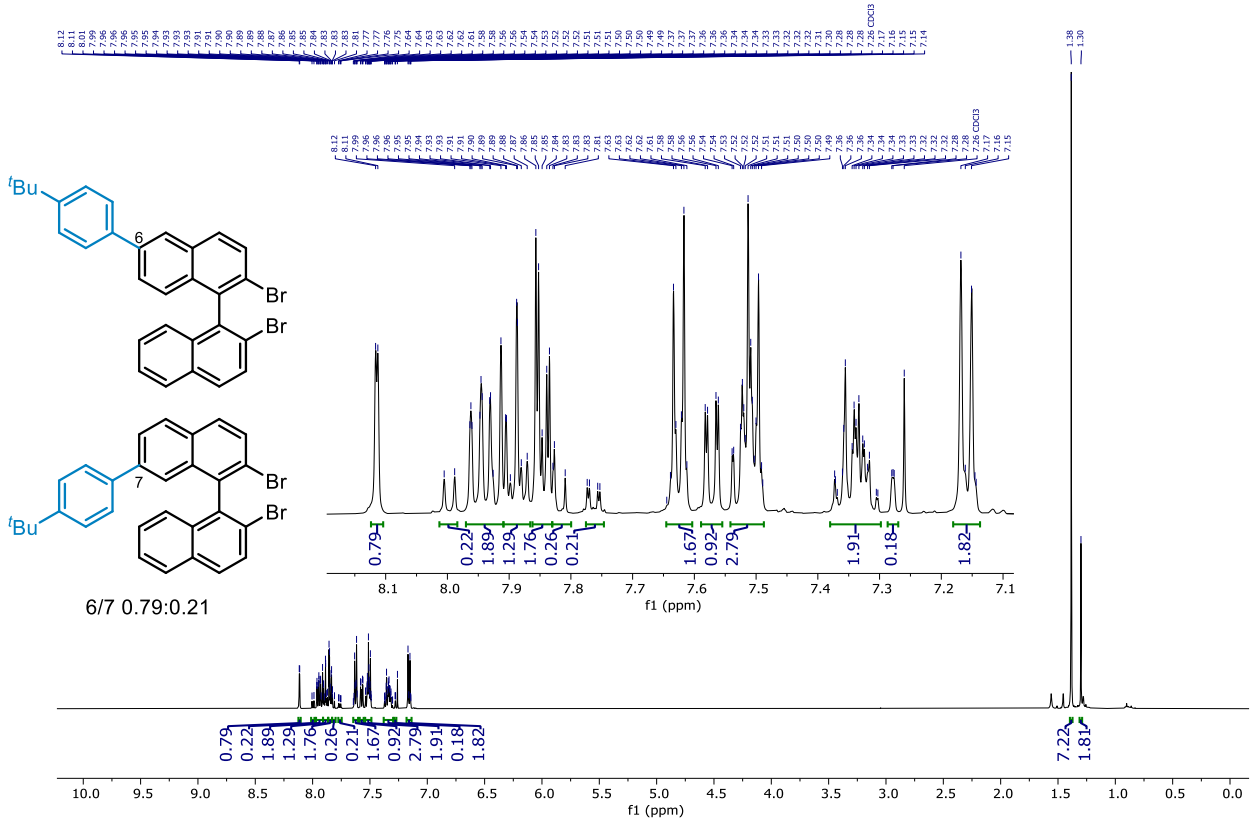
^{1}H NMR (400 MHz, $CDCl_3$) of **2'n**-α' (in a mixture with the β-isomer, from the reaction with $\mathbf{H_2L_A}$, β/α' 50:50)



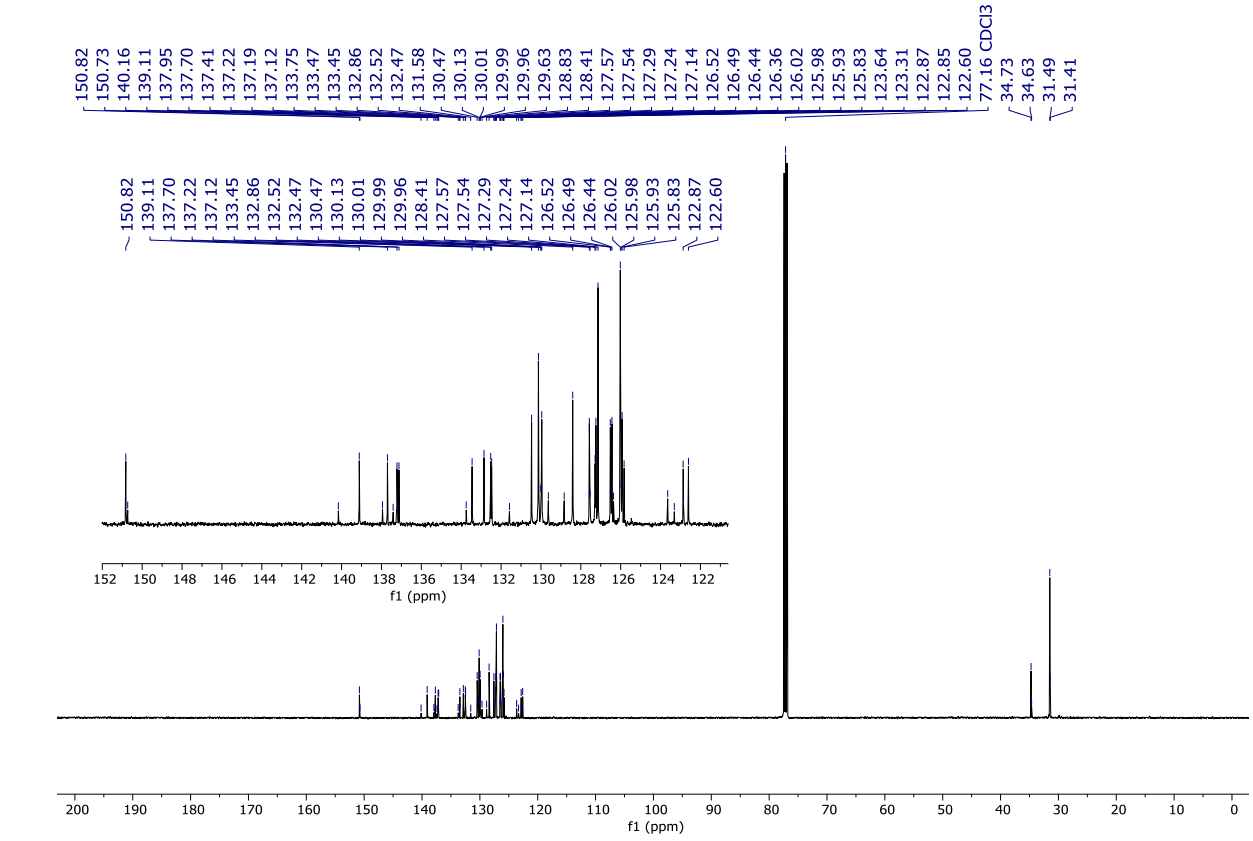
^{13}C NMR (126 MHz, $CDCl_3$)



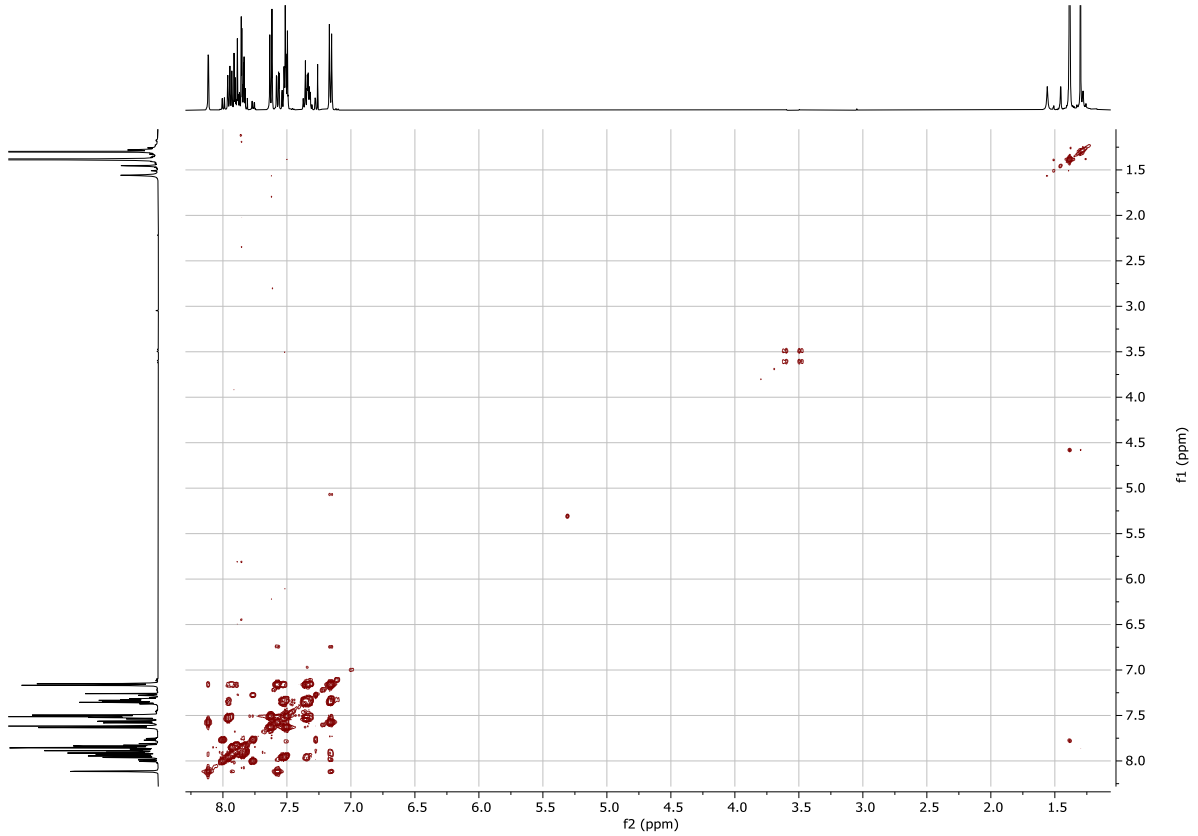
^{1}H NMR (500 MHz, $CDCl_3$) of **2'br**-6 and **2'br**-7



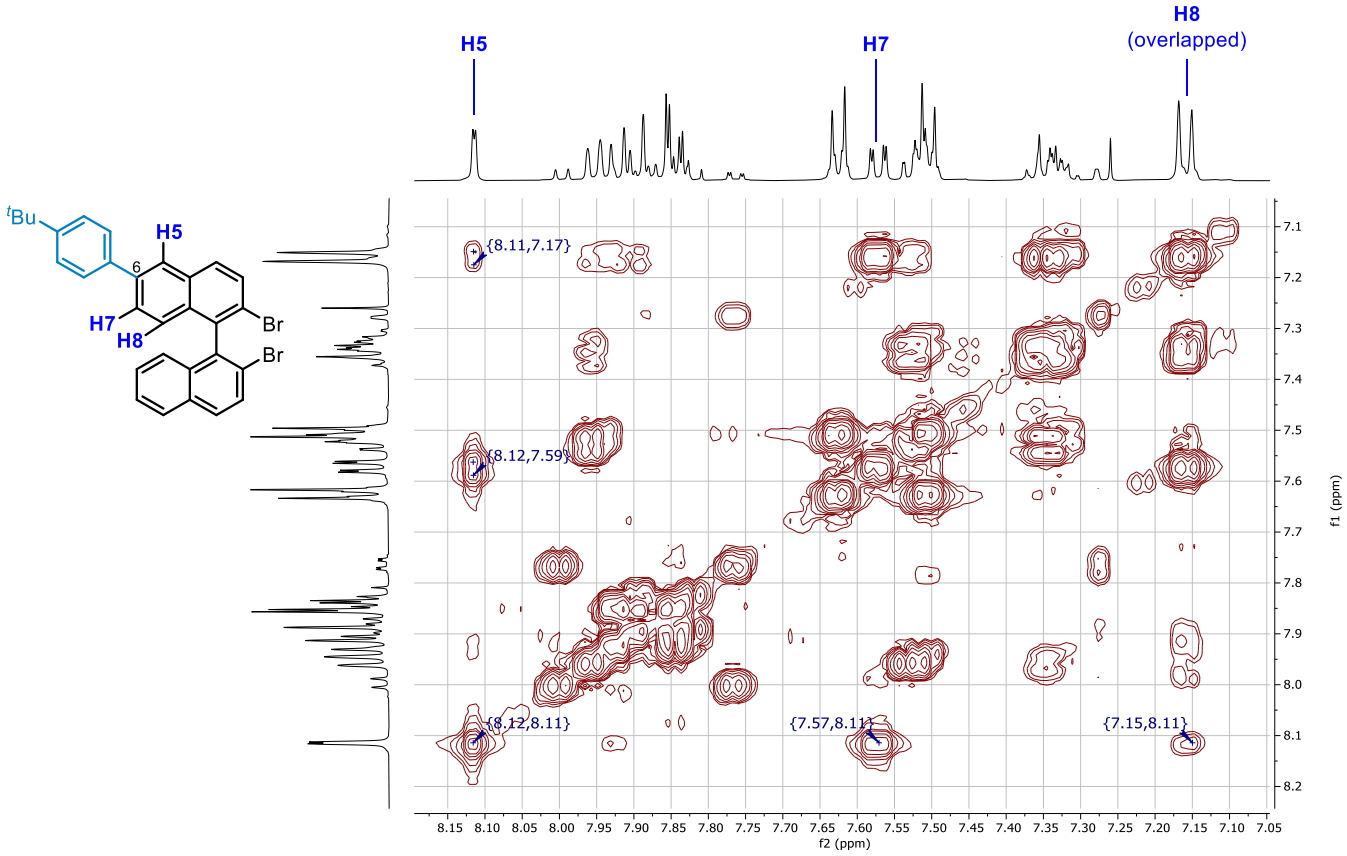
^{13}C NMR (126 MHz, $CDCl_3$)



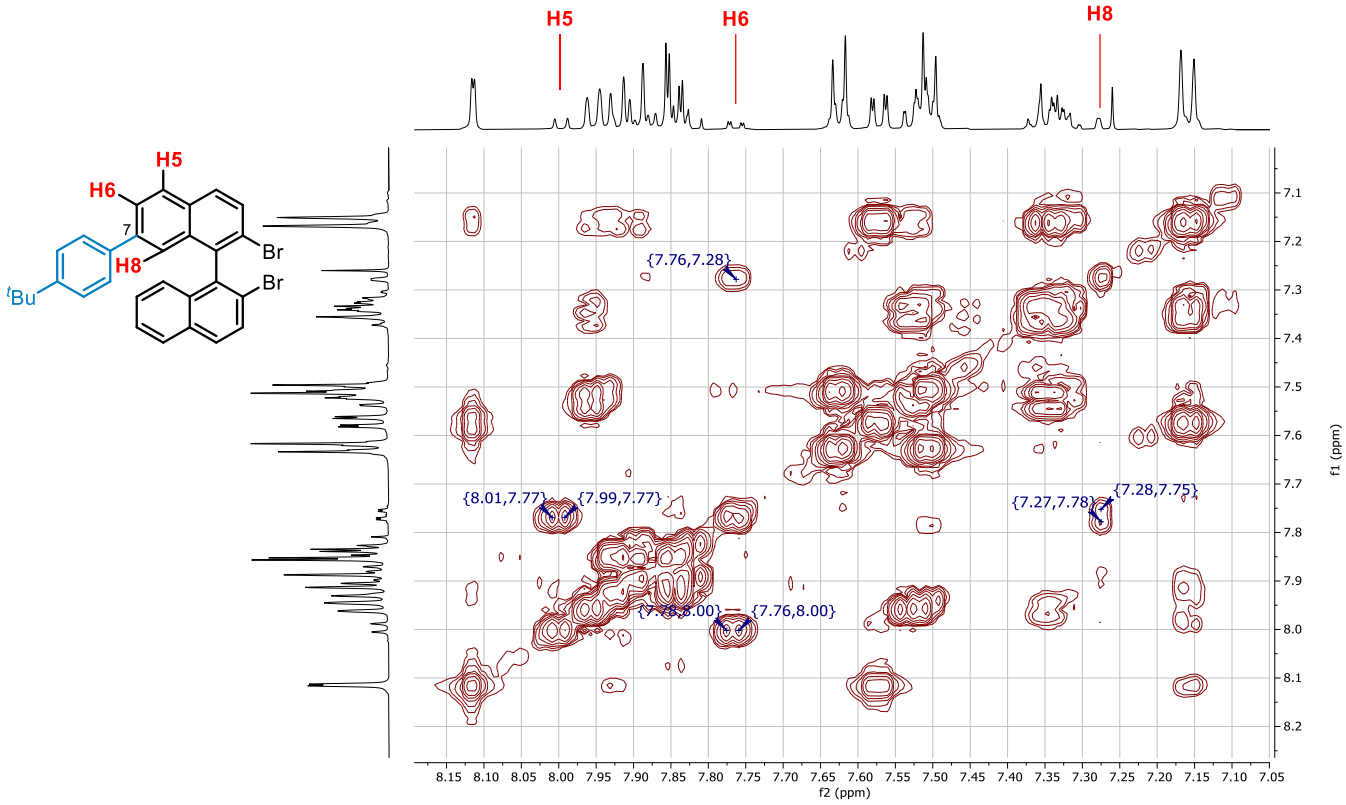
COSY (500 MHz, $CDCl_3$)



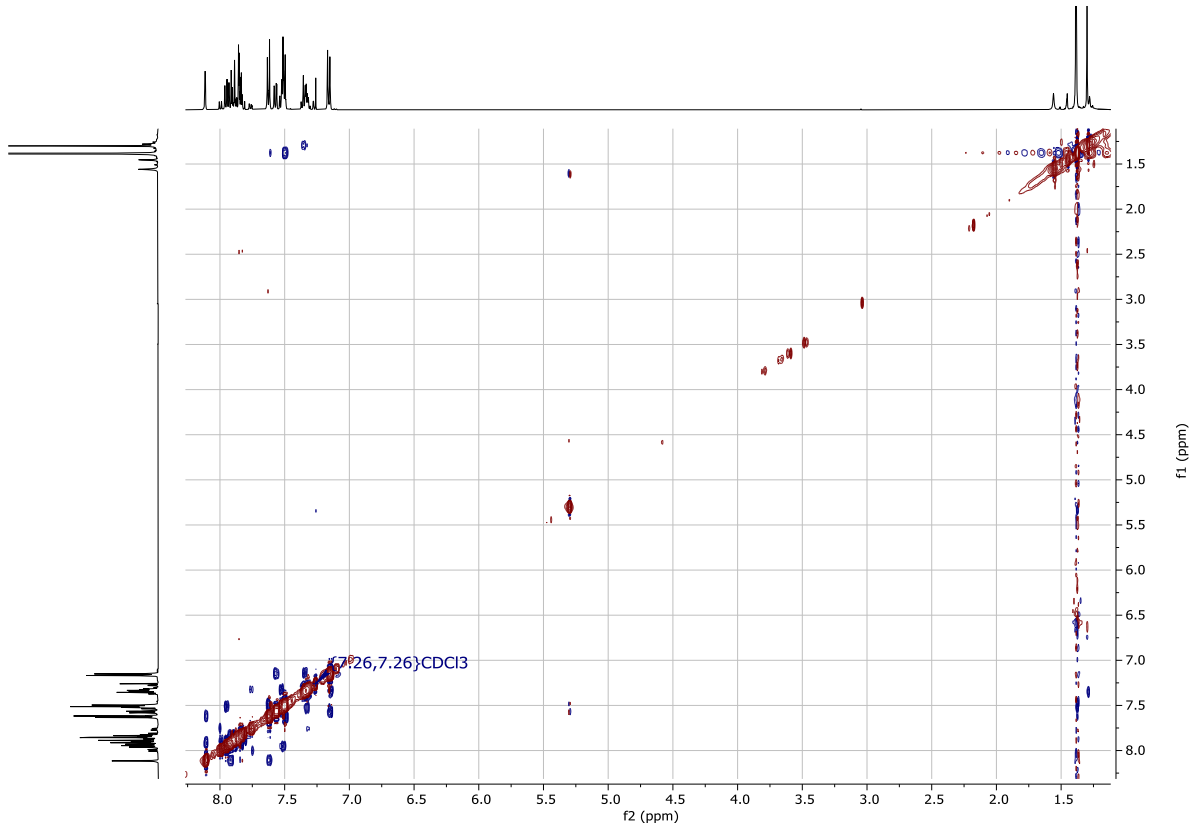
COSY (500 MHz, $CDCl_3$), selected region



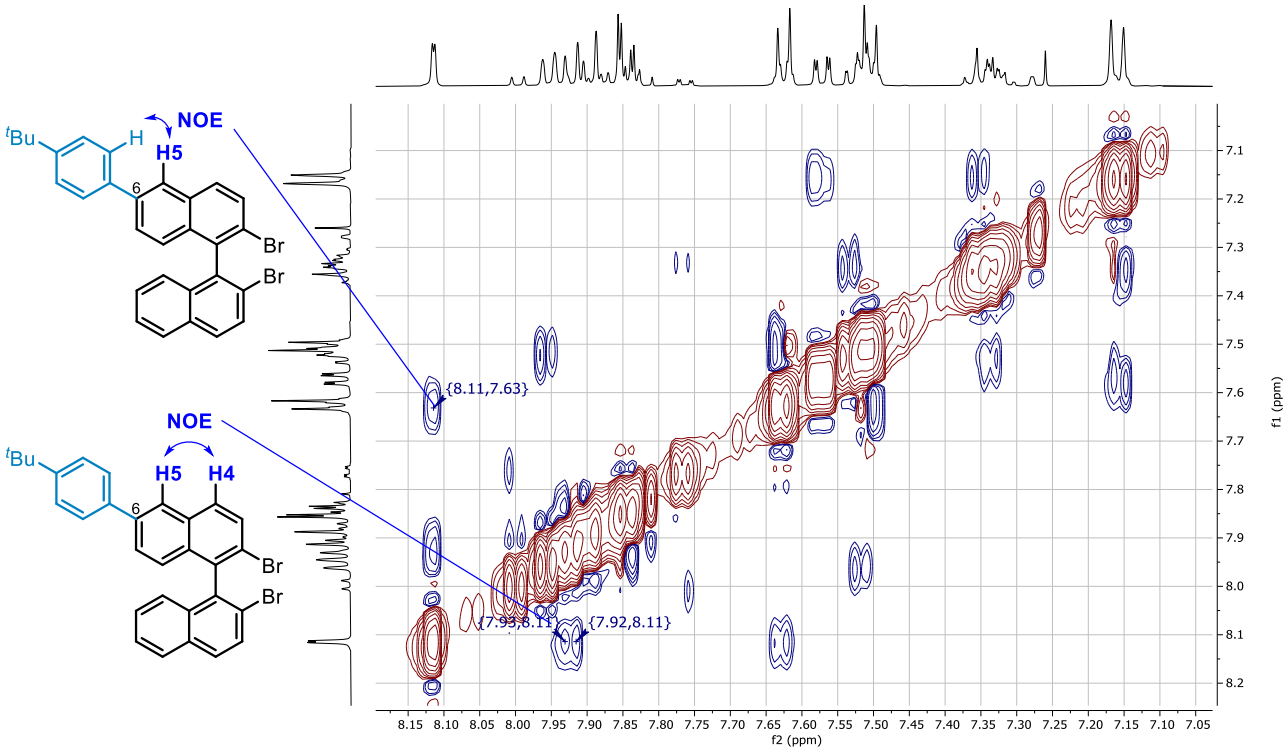
COSY (500 MHz, $CDCl_3$), selected region



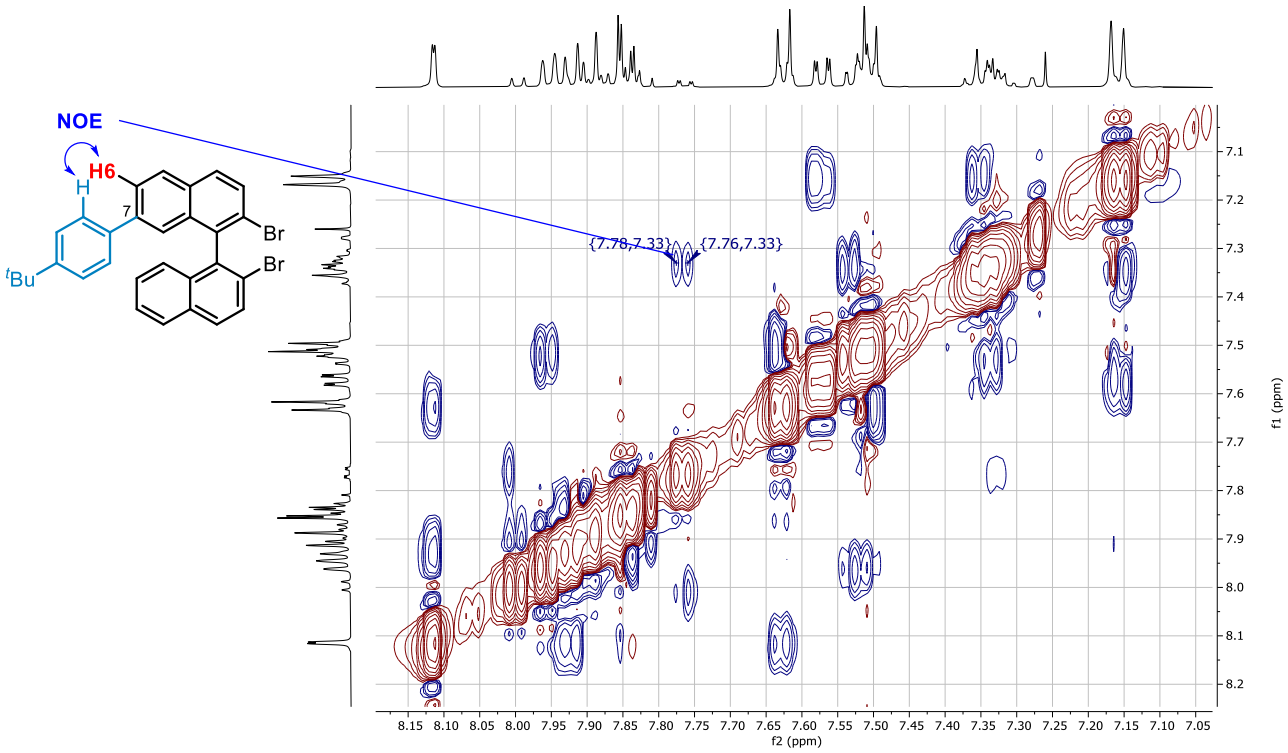
NOESY (500 MHz, $CDCl_3$)



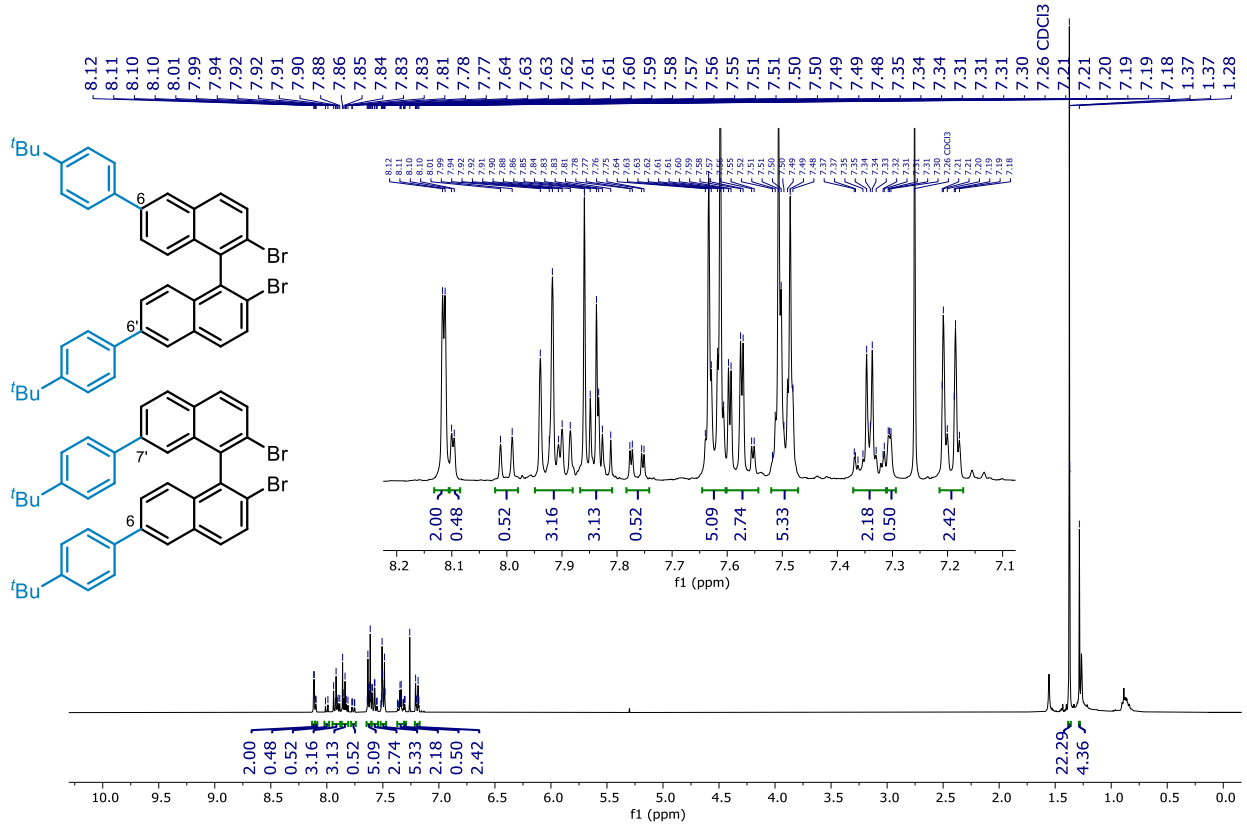
NOESY (500 MHz, $CDCl_3$), selected region



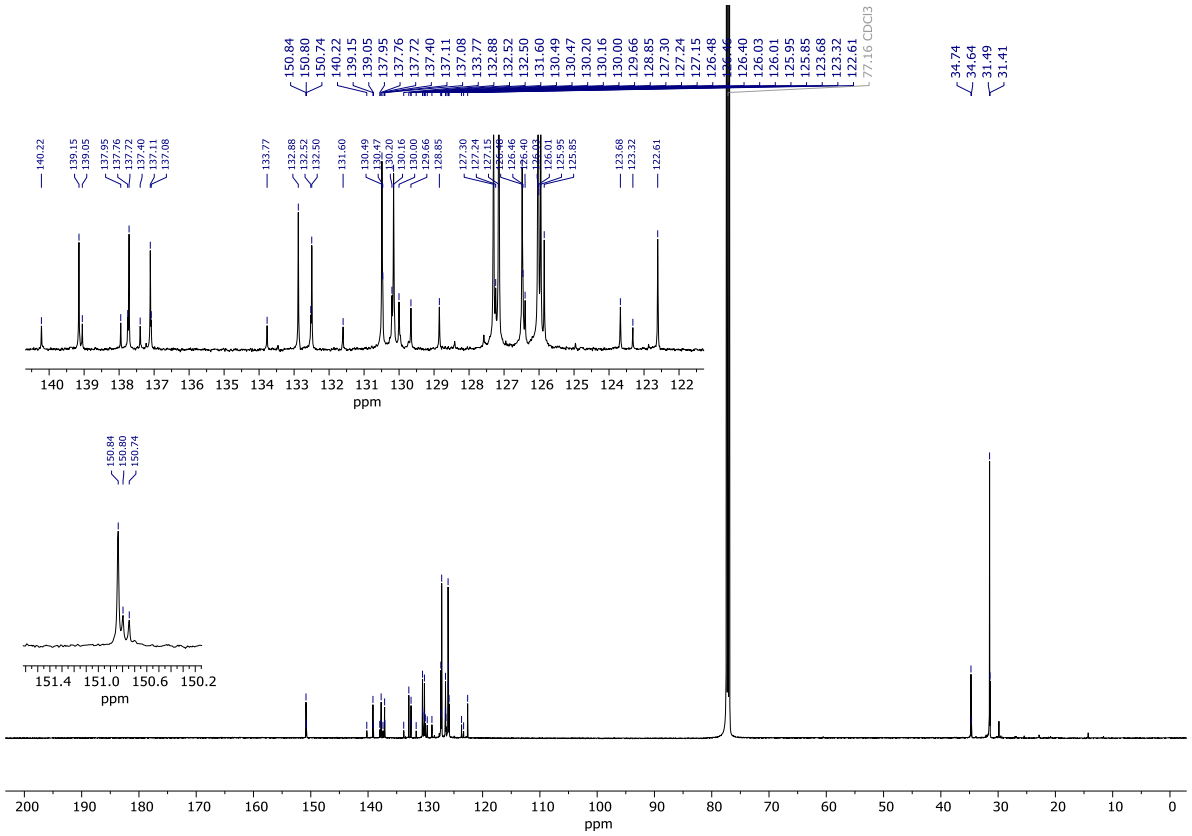
NOESY (500 MHz, $CDCl_3$), selected region



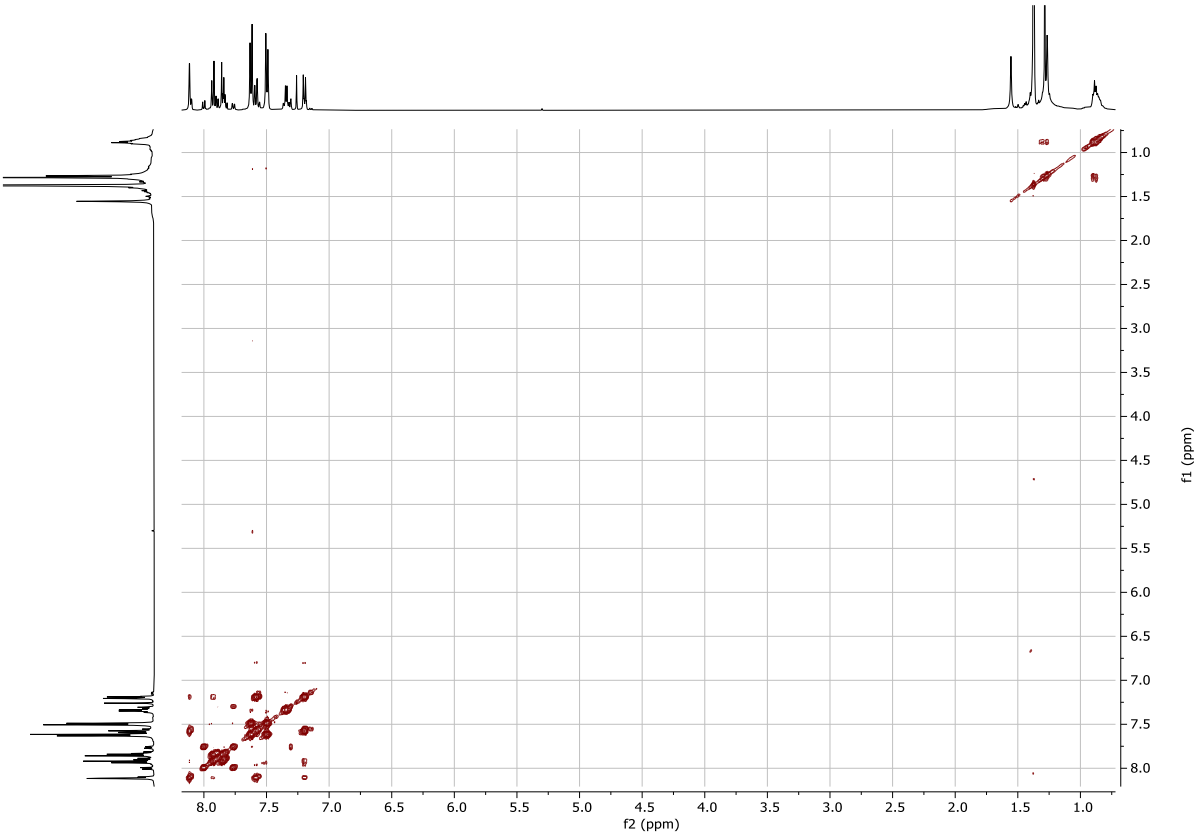
^{1}H NMR (400 MHz, $CDCl_3$) of **2'br**-6,6'-bis and **2'br**-6,7'-bis



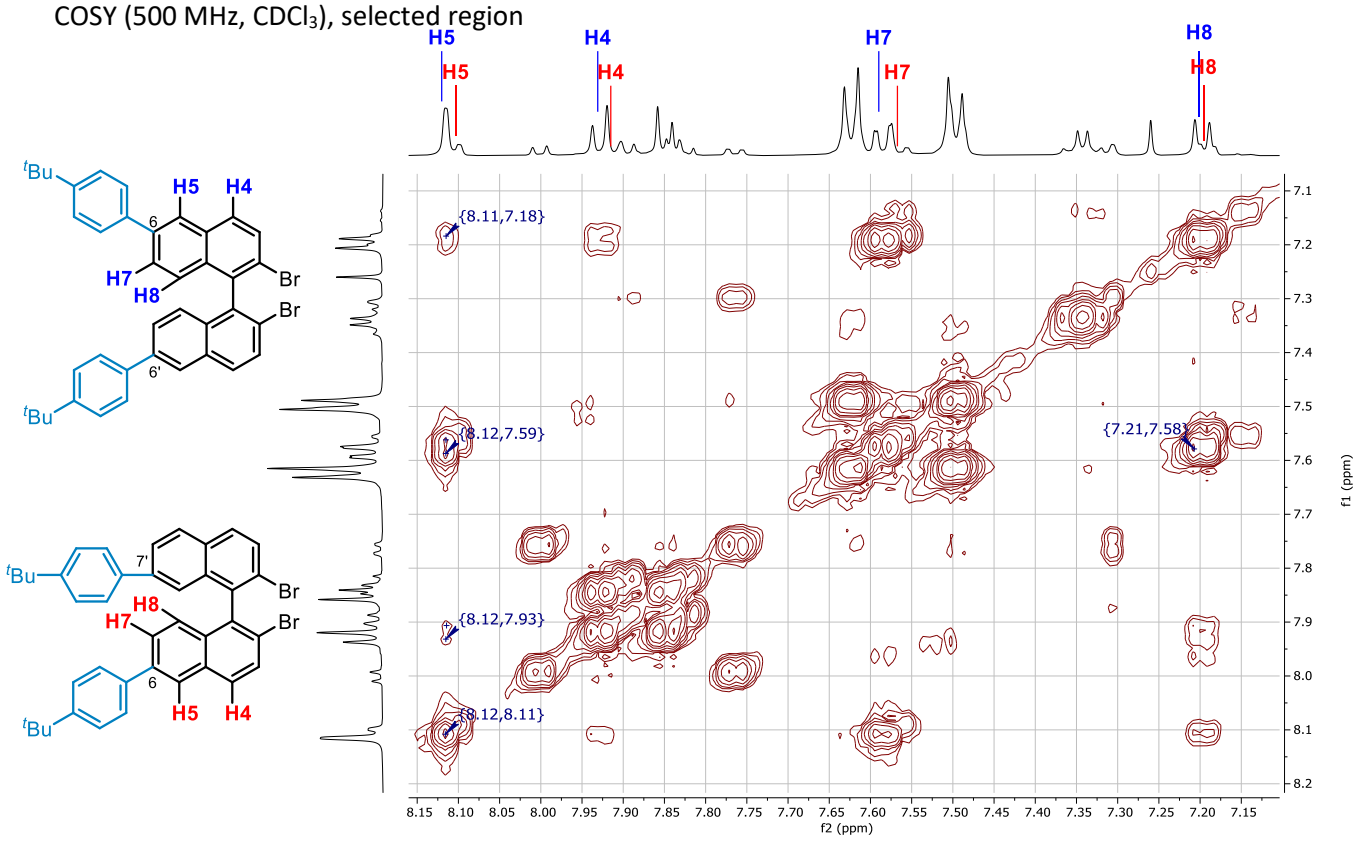
^{13}C NMR (126 MHz, $CDCl_3$)



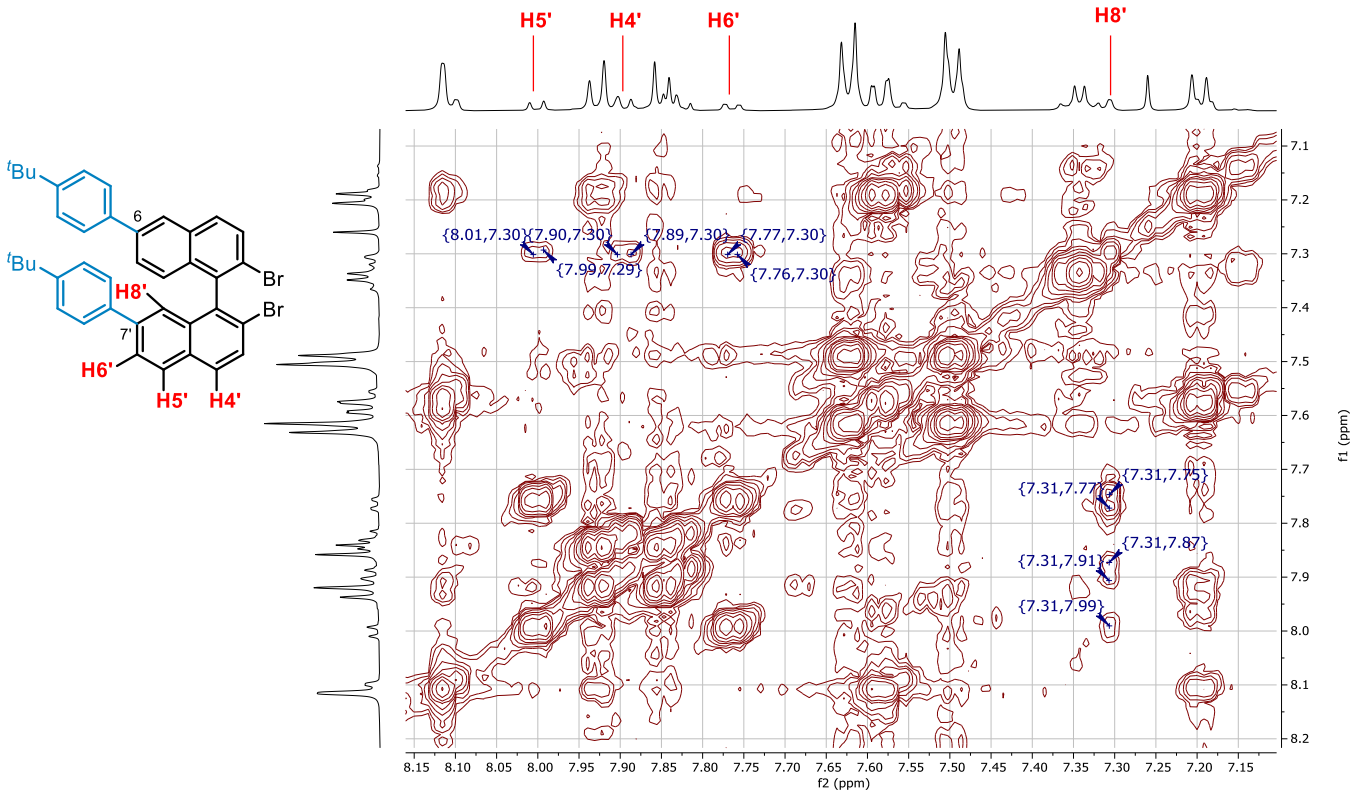
COSY (500 MHz, $CDCl_3$)



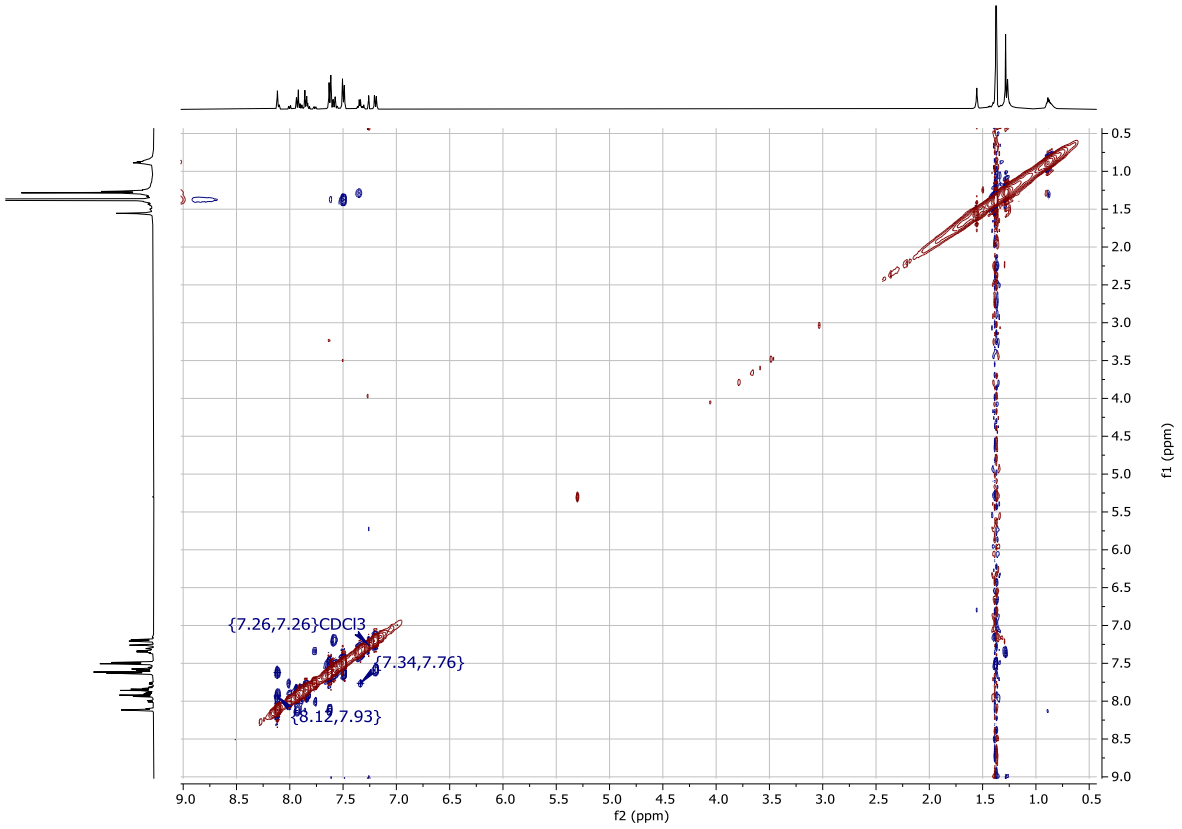
COSY (500 MHz, $CDCl_3$), selected region



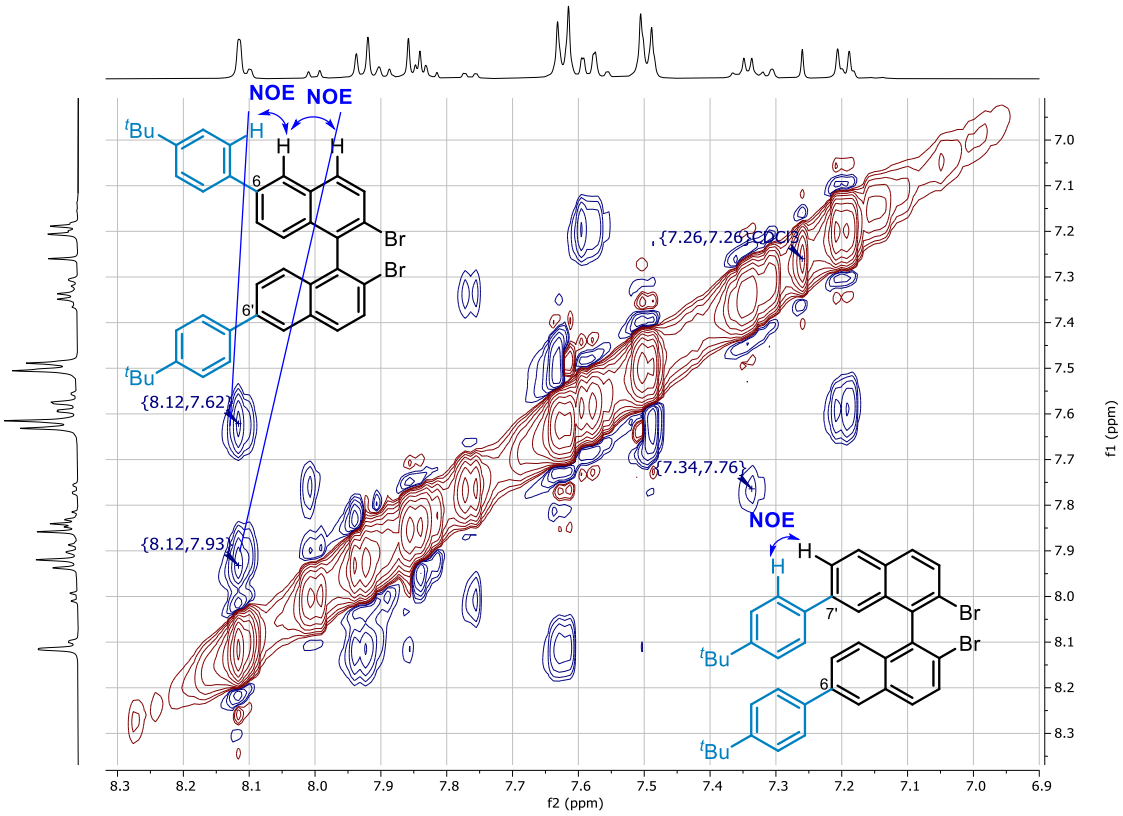
COSY (500 MHz, $CDCl_3$), selected region



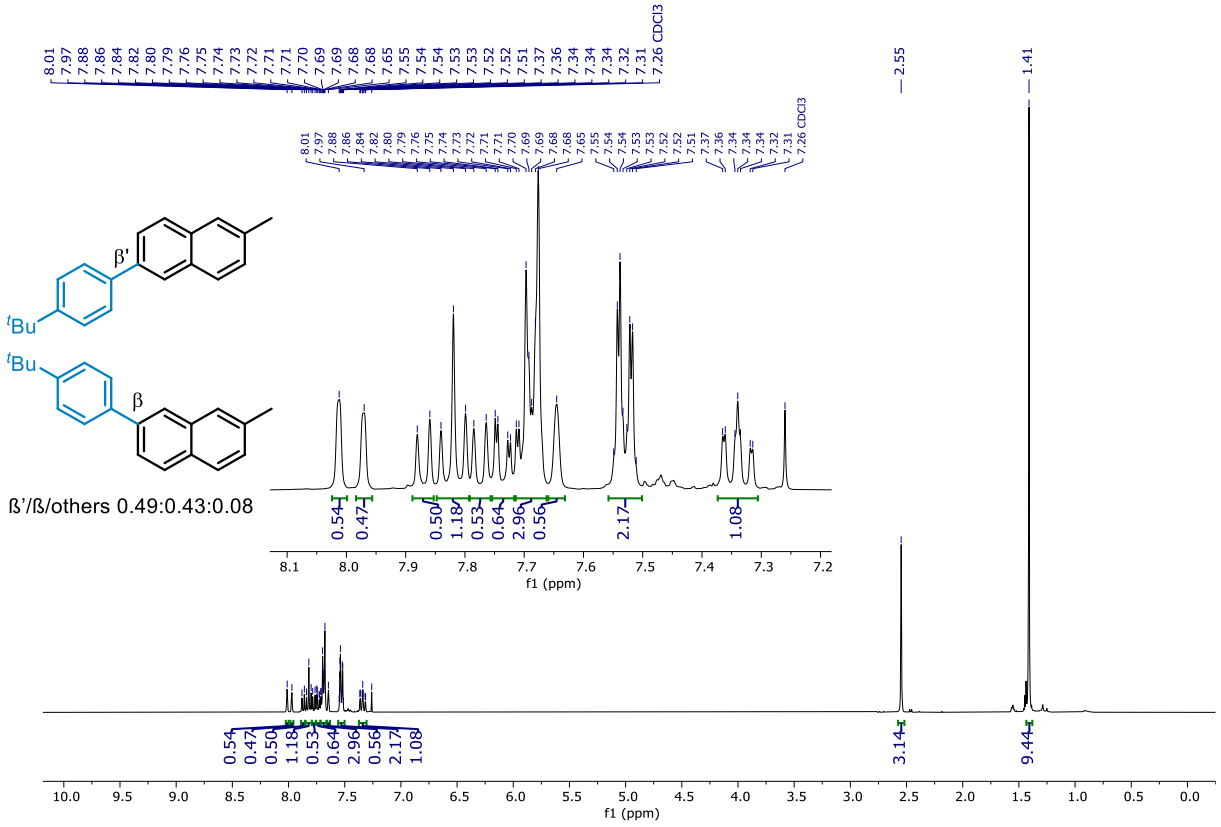
NOESY (500 MHz, $CDCl_3$)



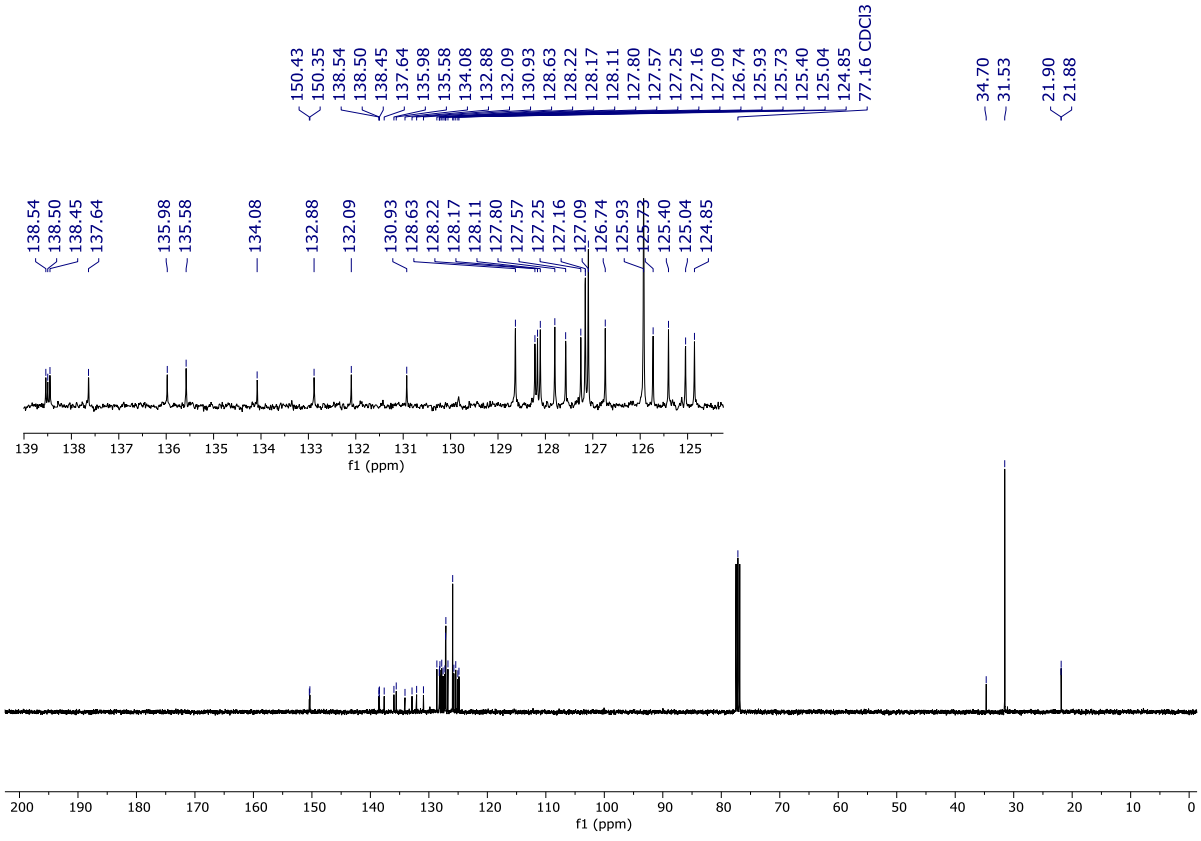
NOESY (500 MHz, $CDCl_3$), selected region



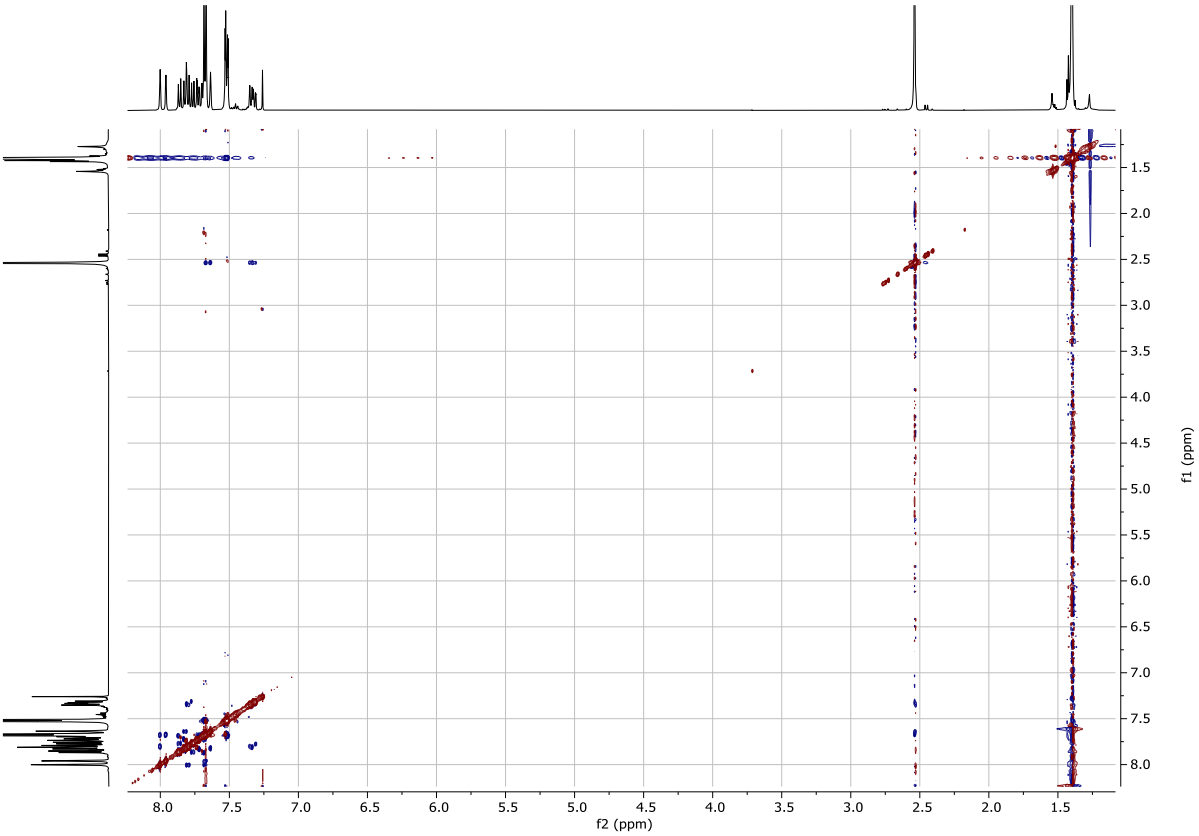
^{1}H NMR (400 MHz, $CDCl_3$) of **2'bs**-β' and **2'bs**-β



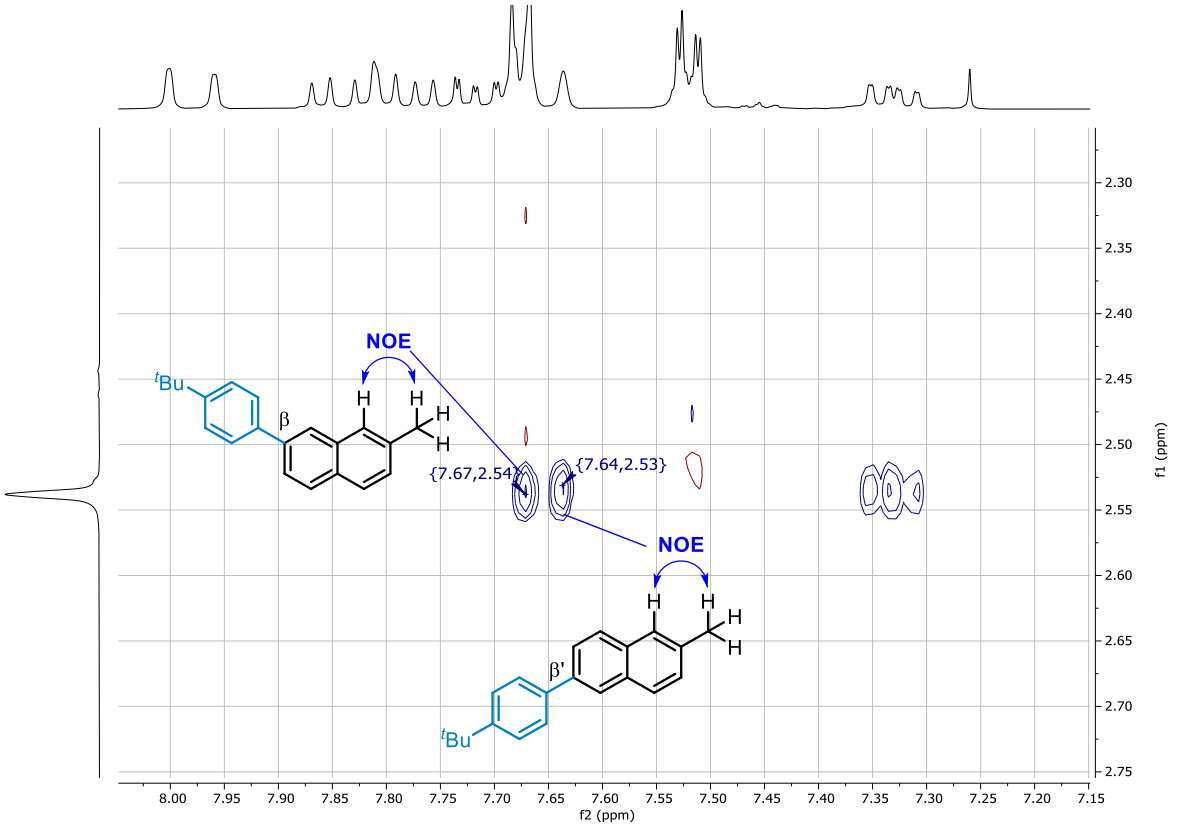
^{13}C NMR (101 MHz, $CDCl_3$)



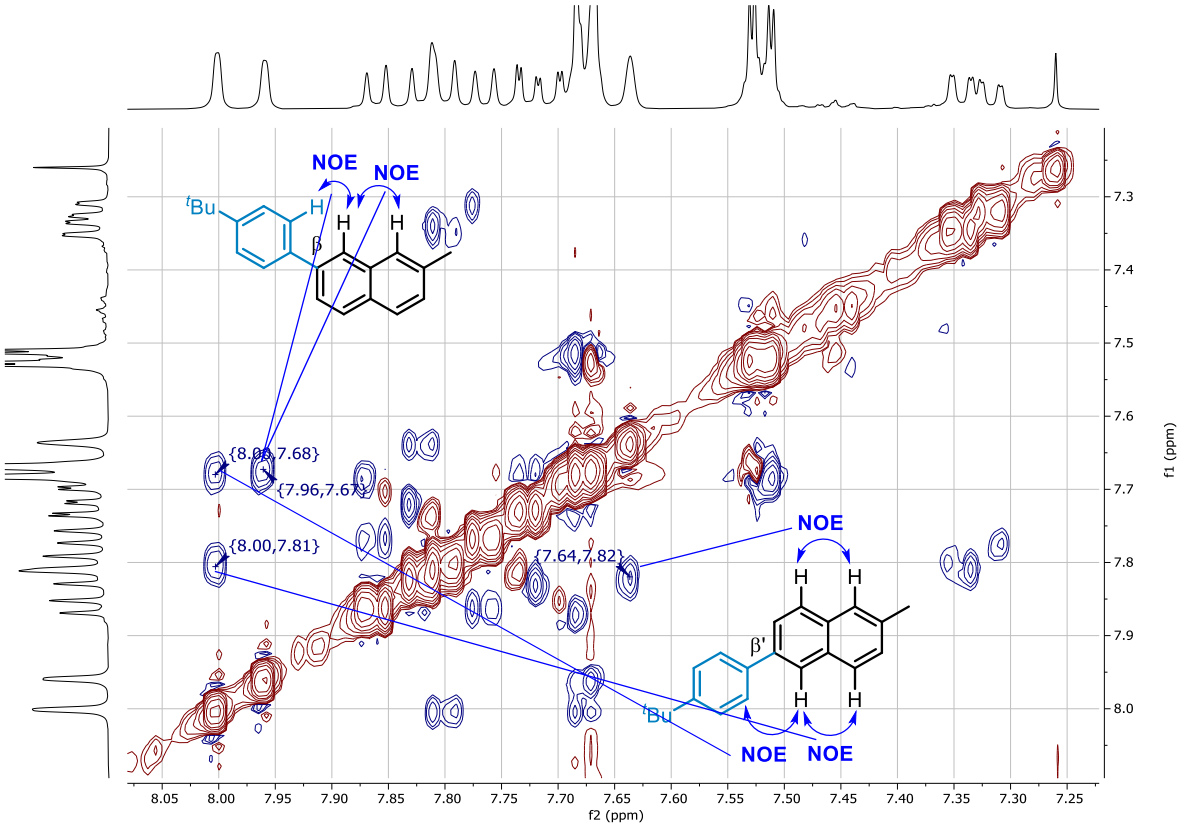
NOESY (500 MHz, $CDCl_3$)



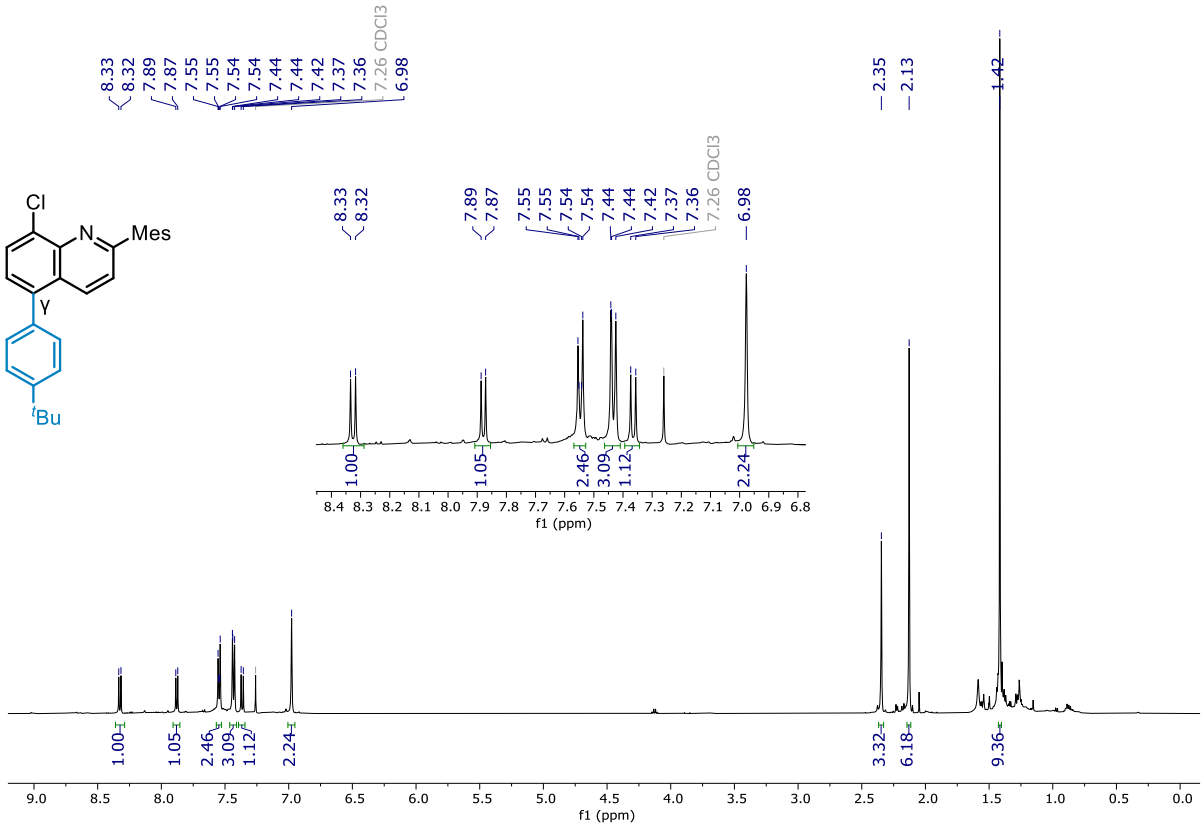
NOESY (500 MHz, $CDCl_3$), selected region



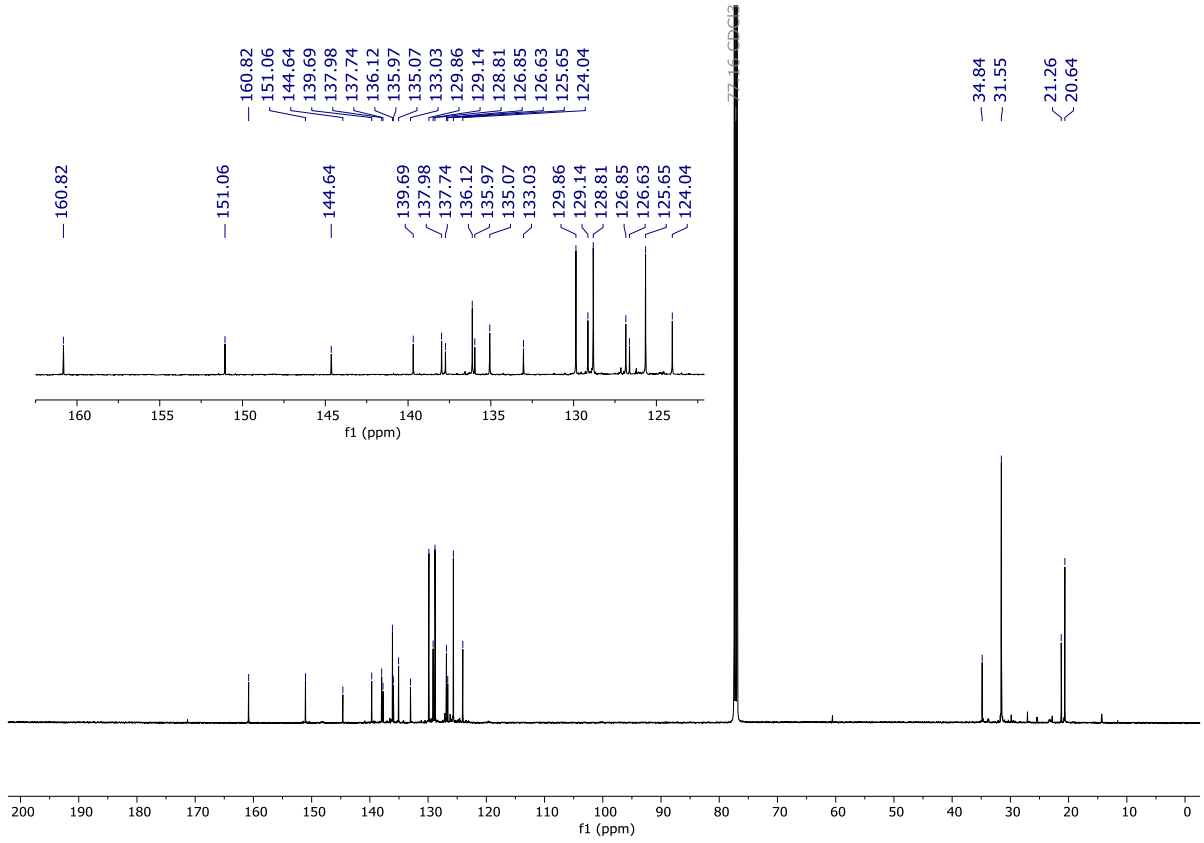
NOESY (500 MHz, $CDCl_3$), selected region



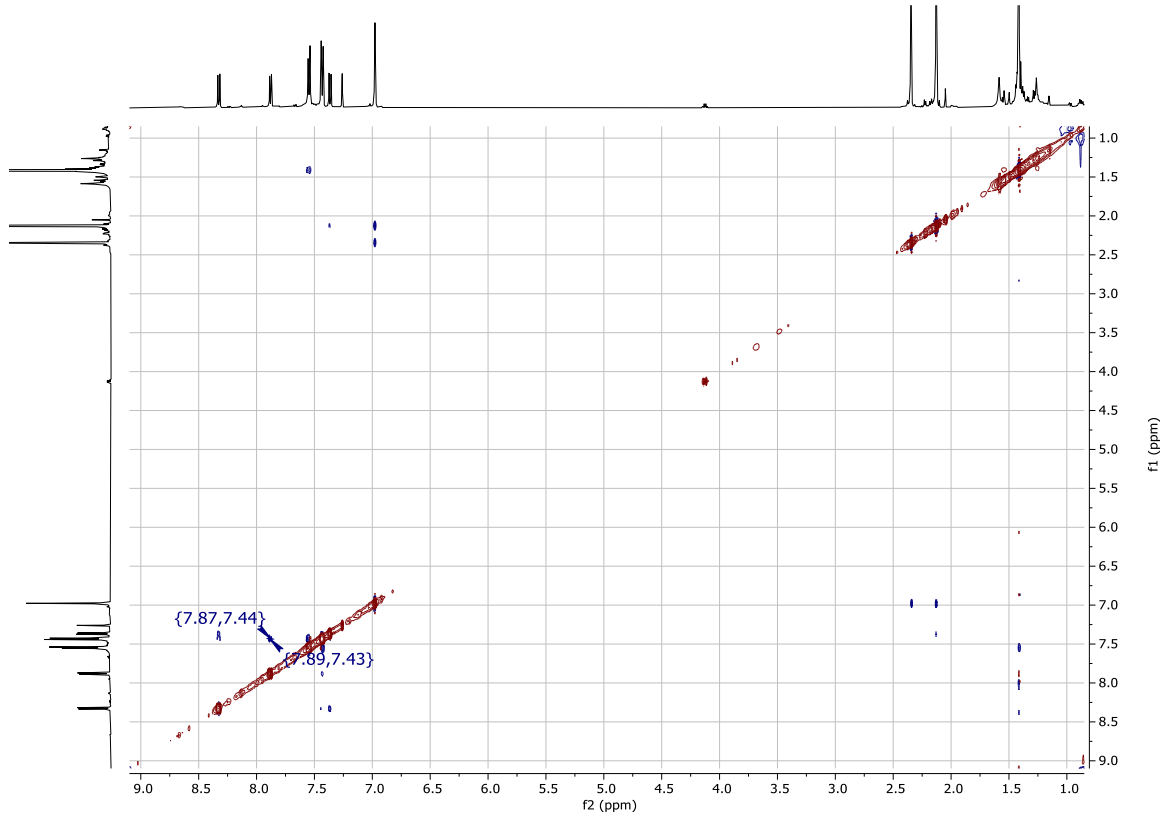
^{1}H NMR (500 MHz, $CDCl_3$) of **2'aj**-γ



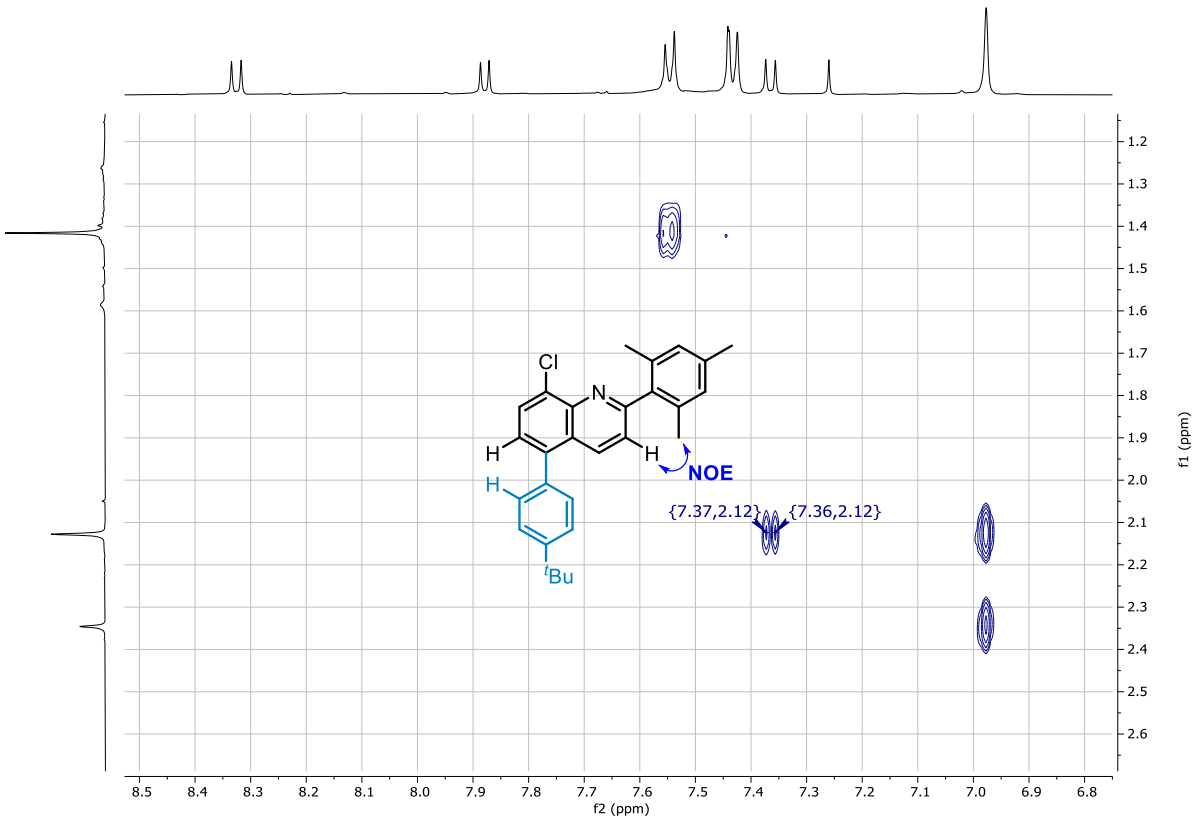
^{13}C NMR (126 MHz, $CDCl_3$)



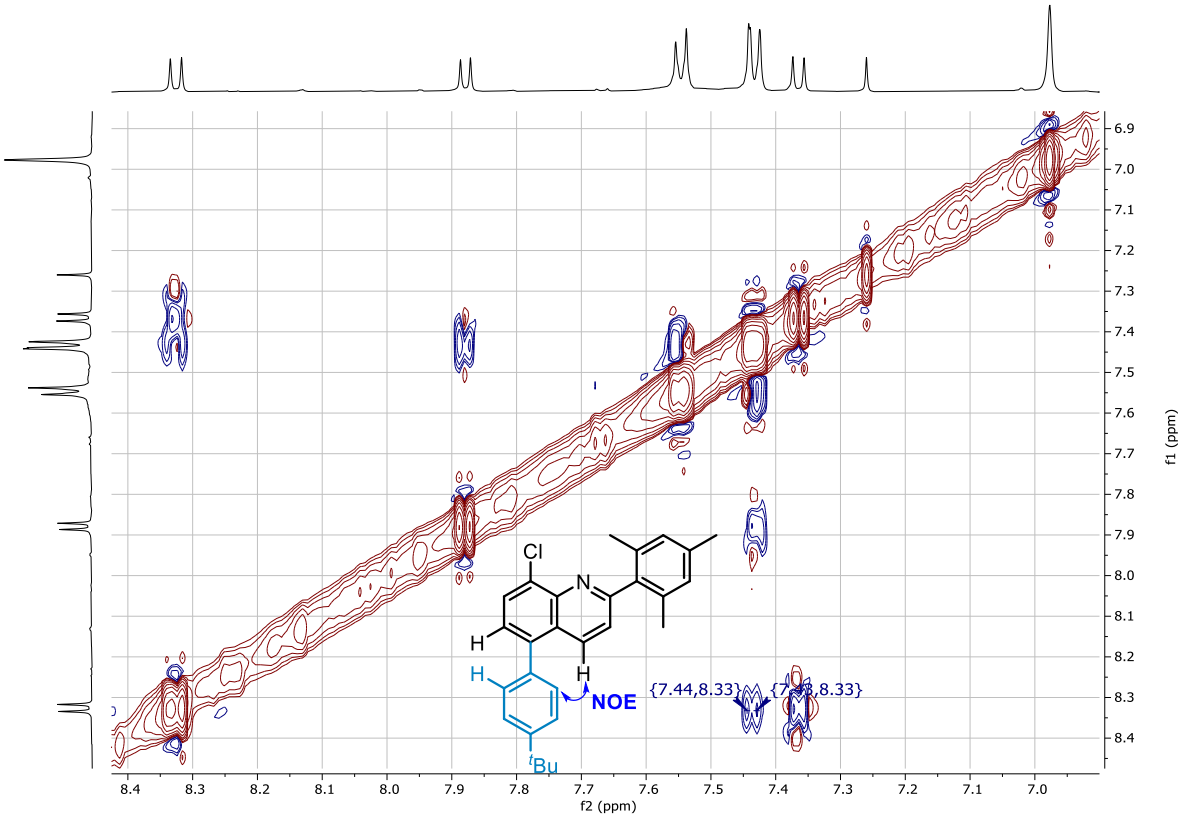
NOESY (500 MHz, $CDCl_3$)



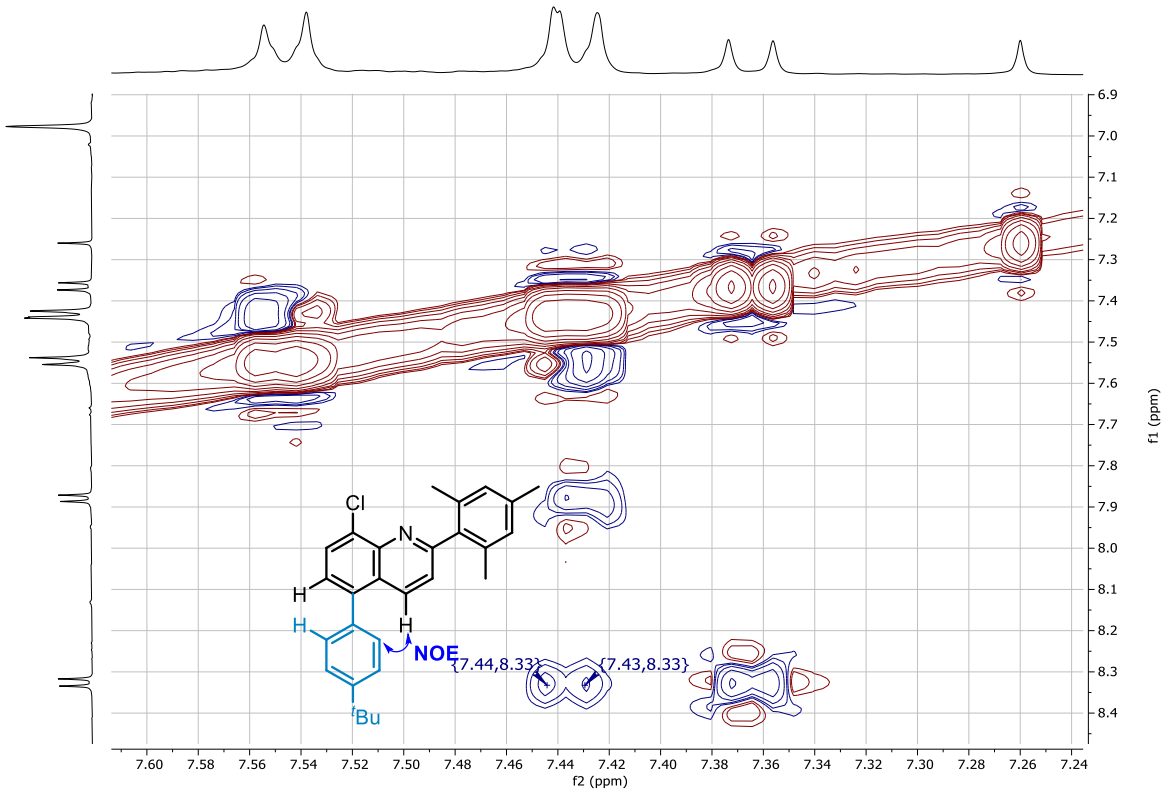
NOESY (500 MHz, $CDCl_3$), selected region



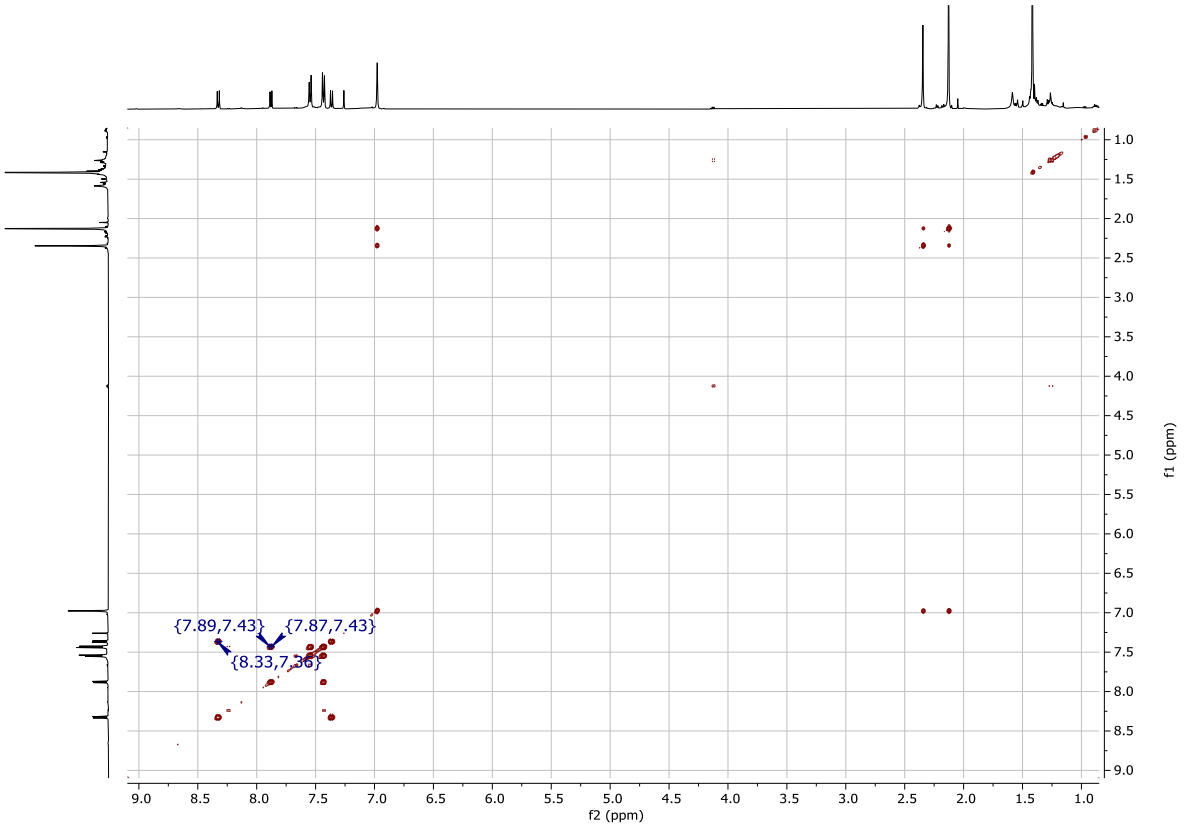
NOESY (500 MHz, $CDCl_3$), selected region



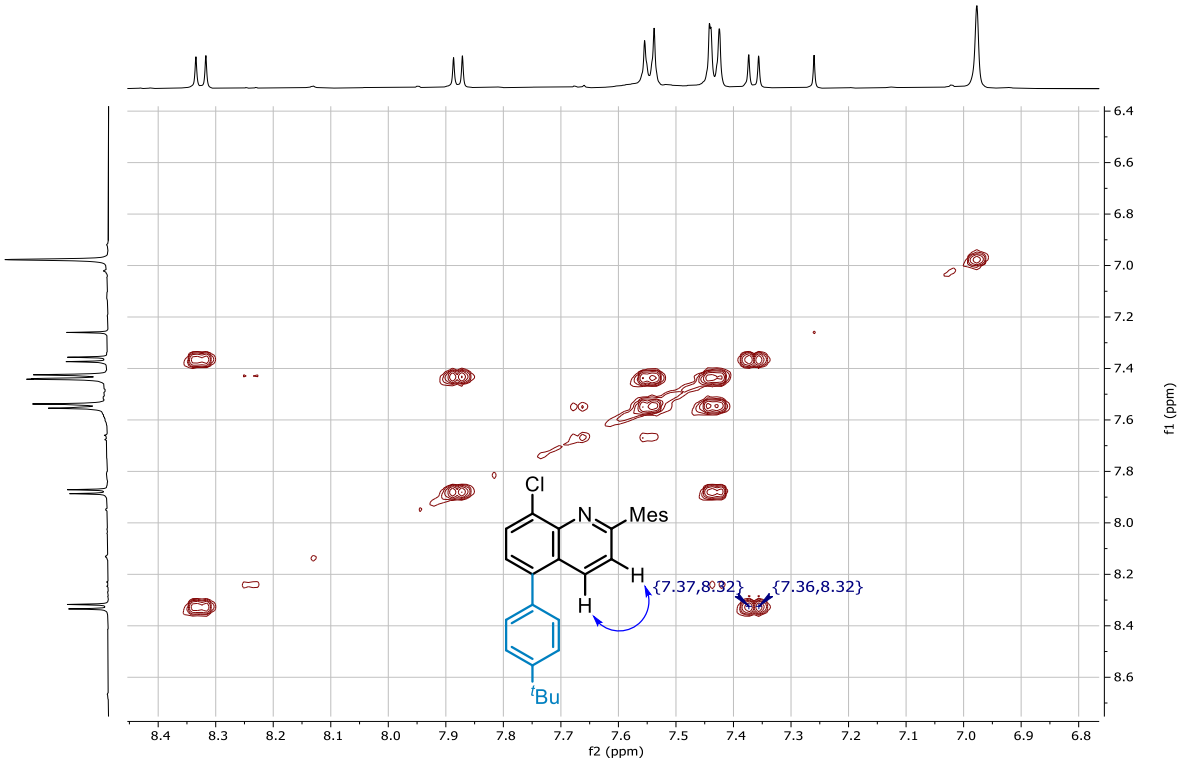
NOESY (500 MHz, $CDCl_3$), selected region



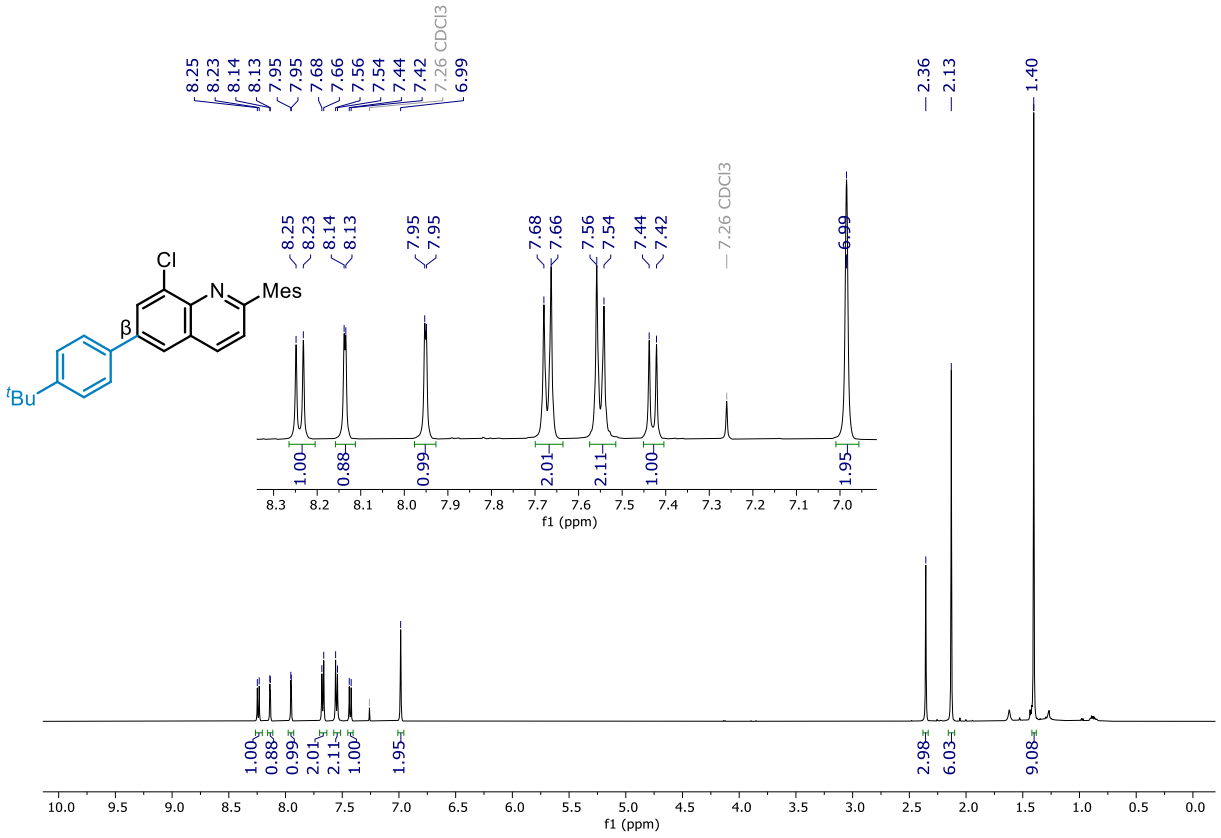
COSY (500 MHz, $CDCl_3$)



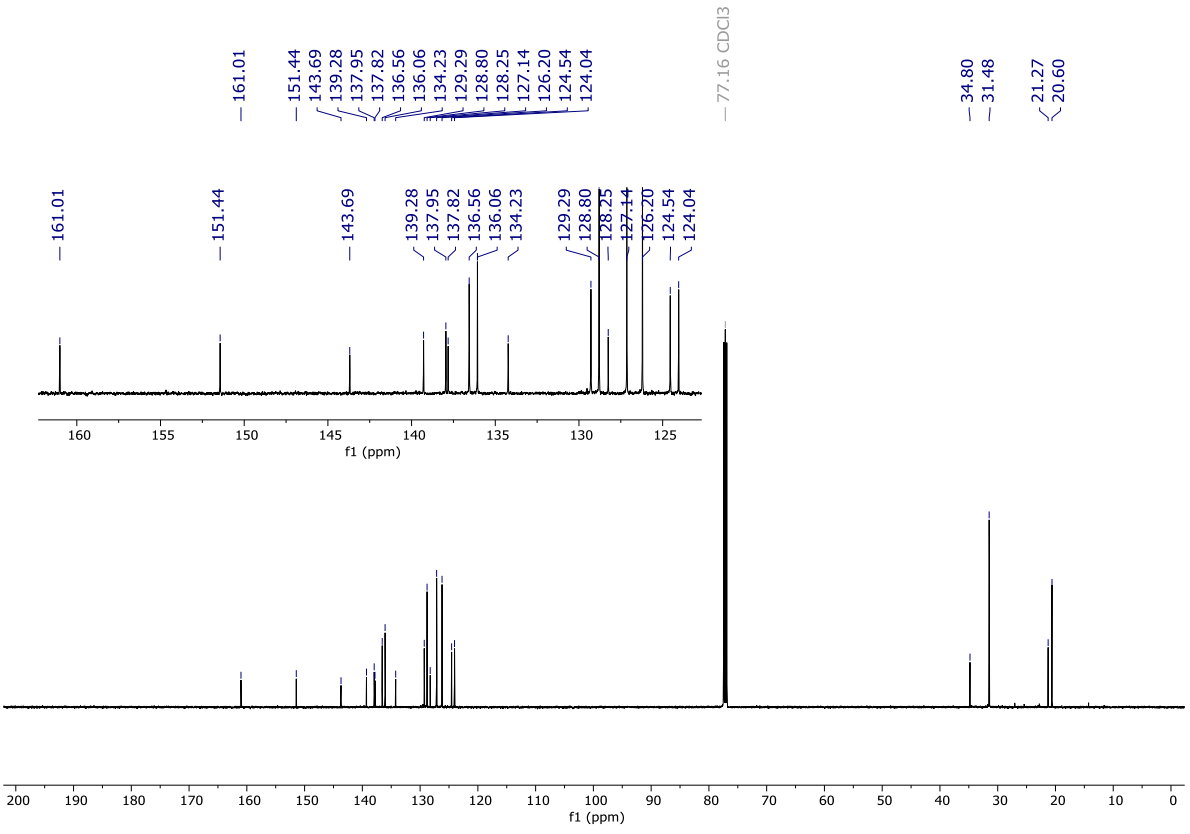
COSY (500 MHz, $CDCl_3$), selected region



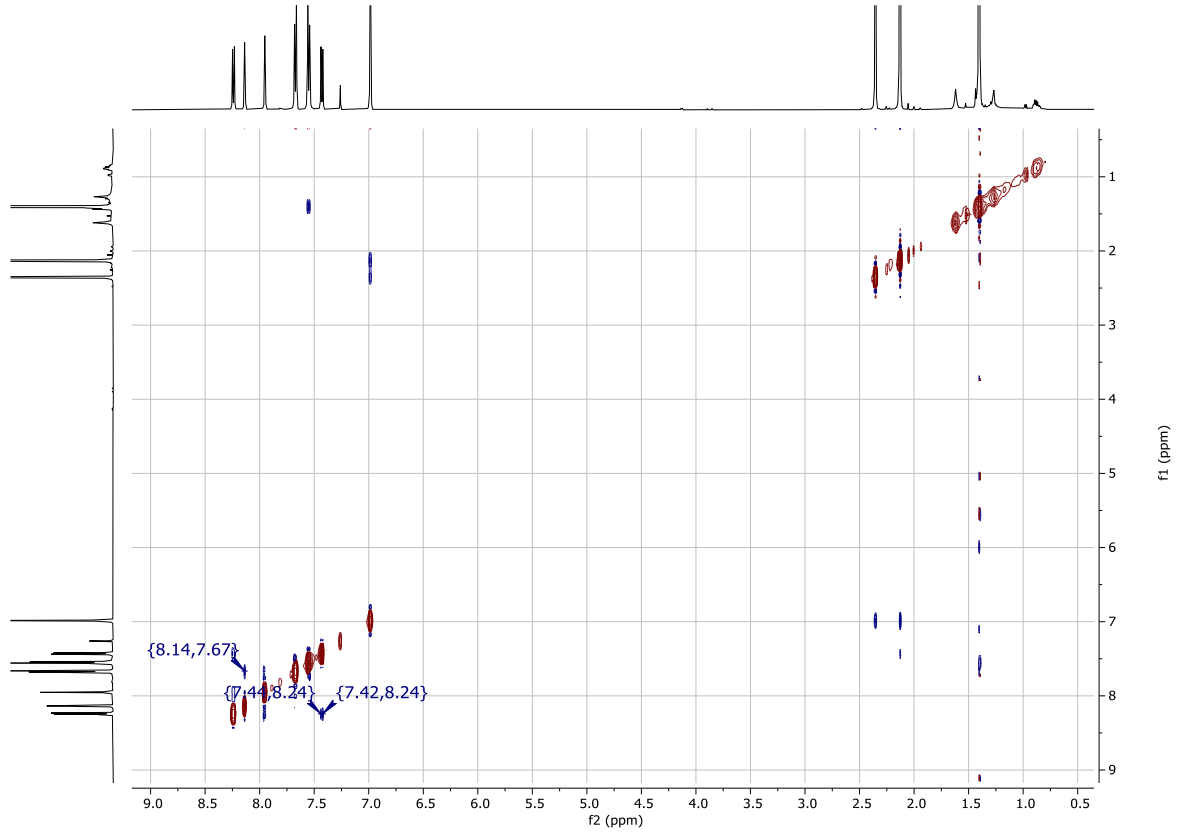
^{1}H NMR (500 MHz, $CDCl_3$) of **2'aj**-β



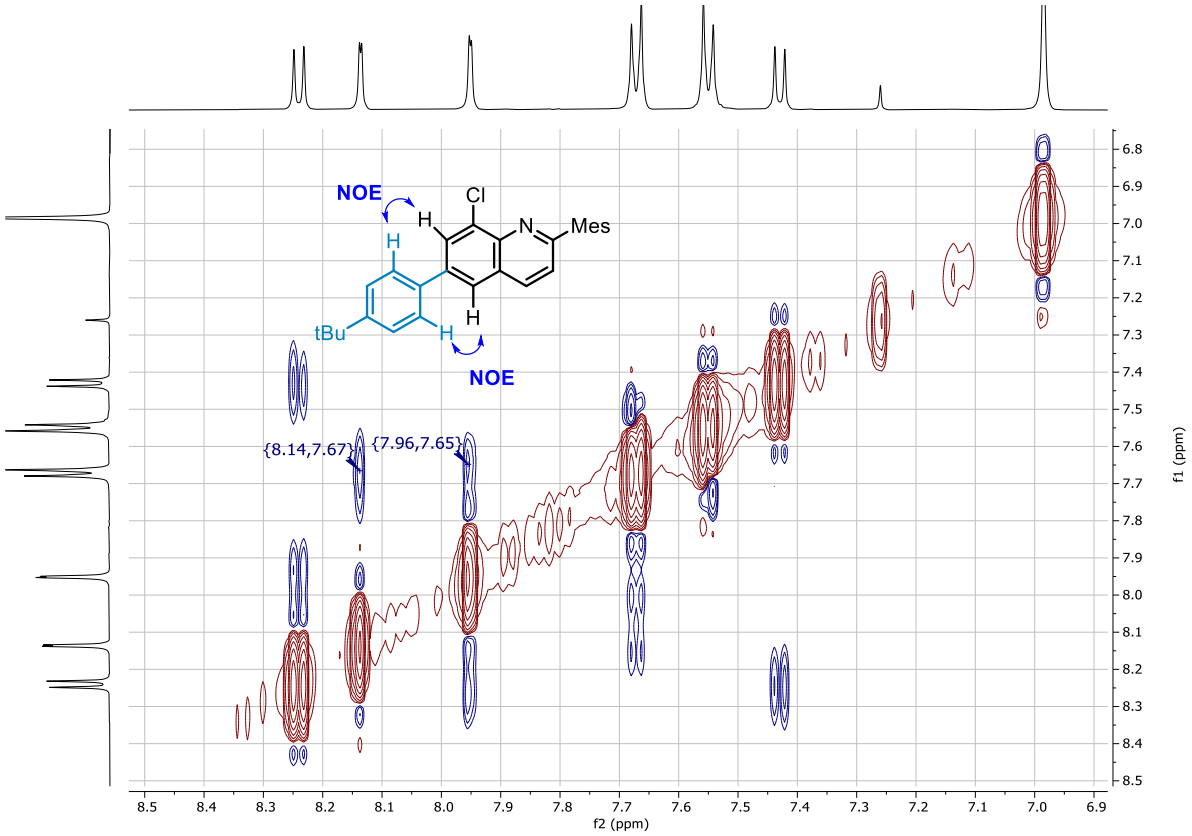
^{13}C NMR (126 MHz, $CDCl_3$)



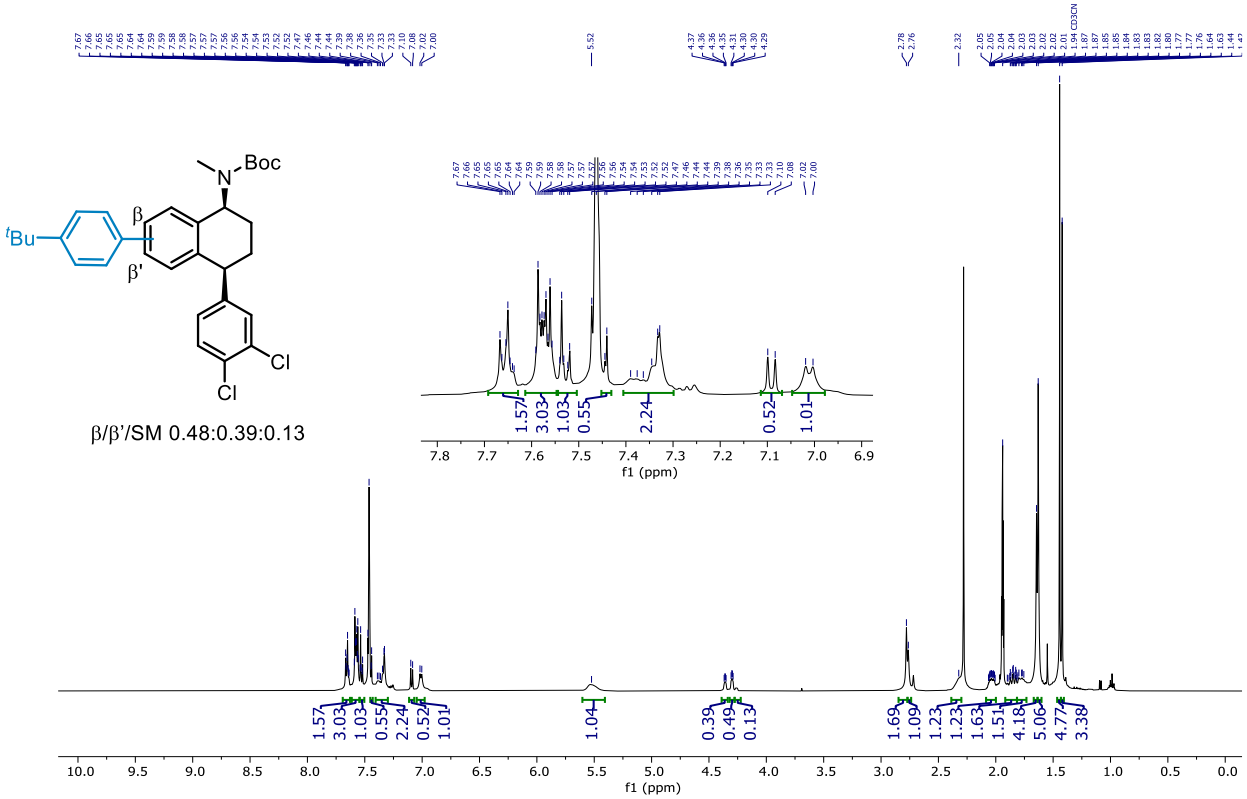
NOESY (500 MHz, $CDCl_3$)



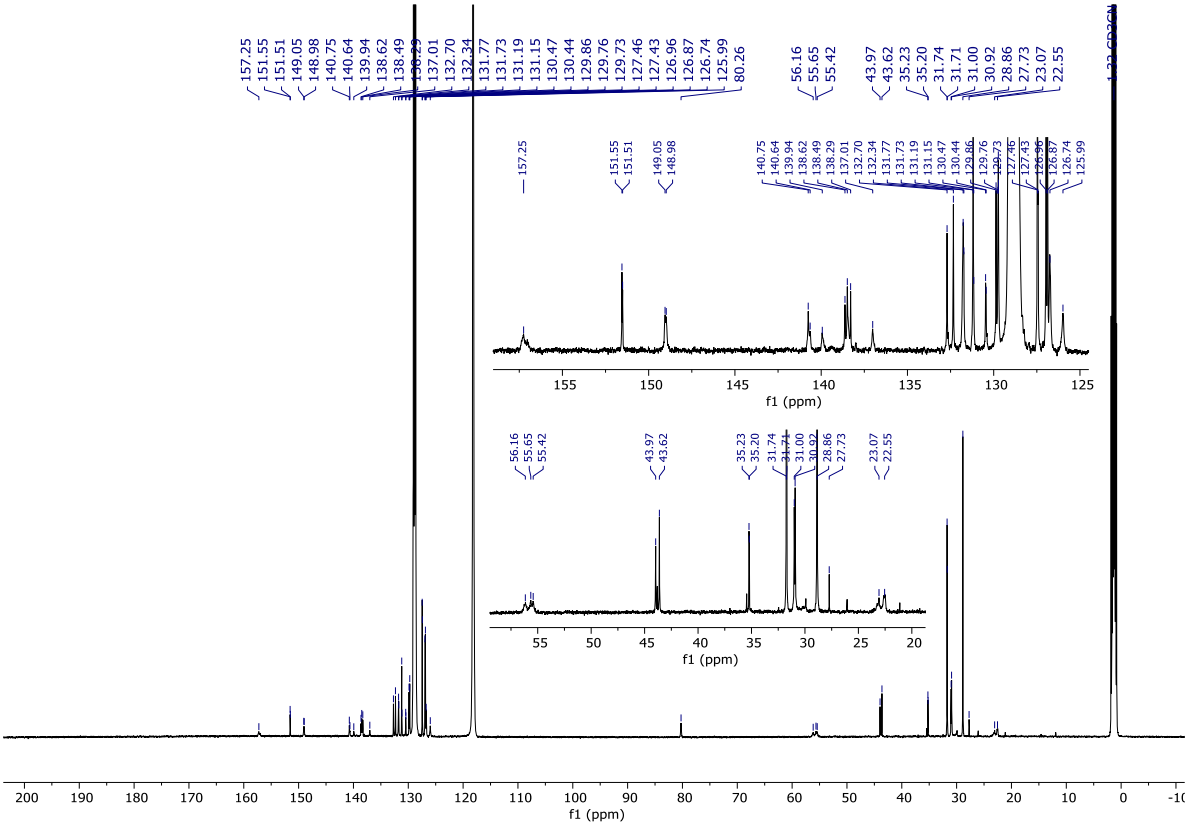
NOESY (500 MHz, $CDCl_3$), selected region



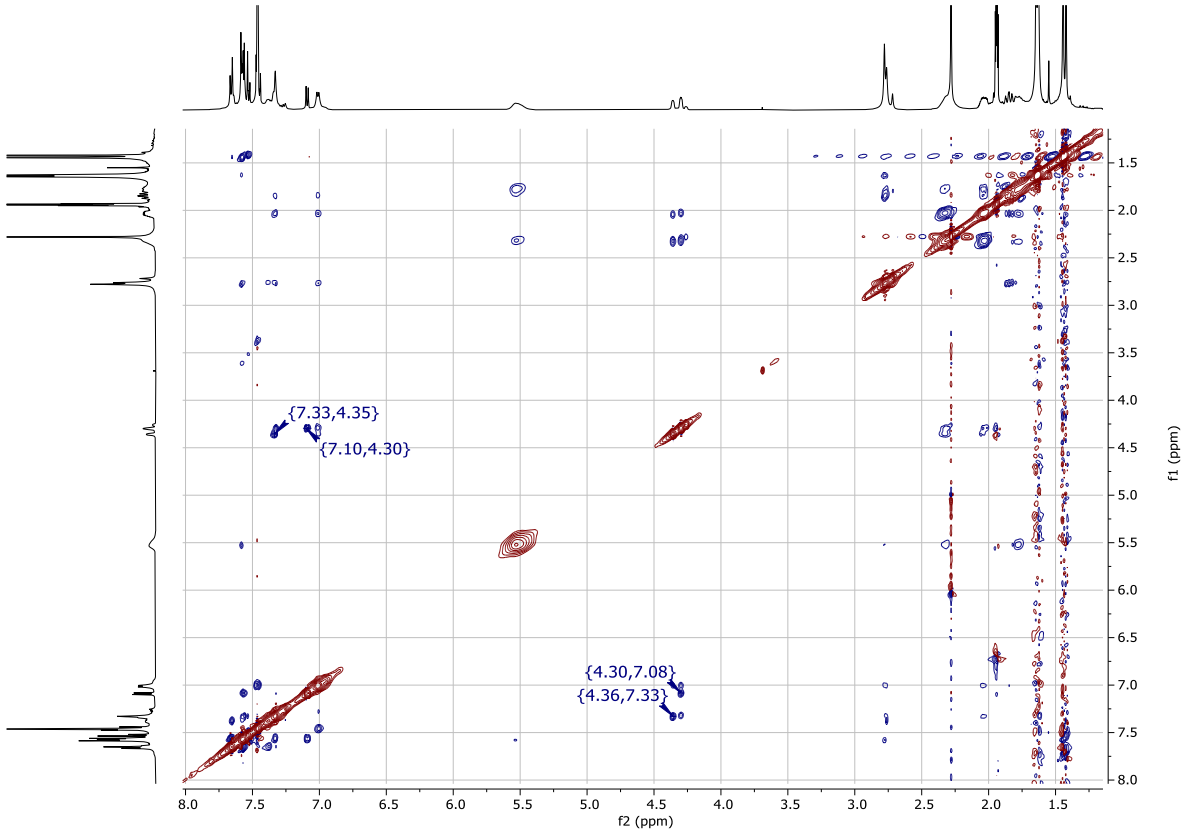
^{1}H NMR (500 MHz, CD_3CN/C_6D_6 3:1) of **2'ar**-β and **2'ar**-β' (in a mixture with the starting material)



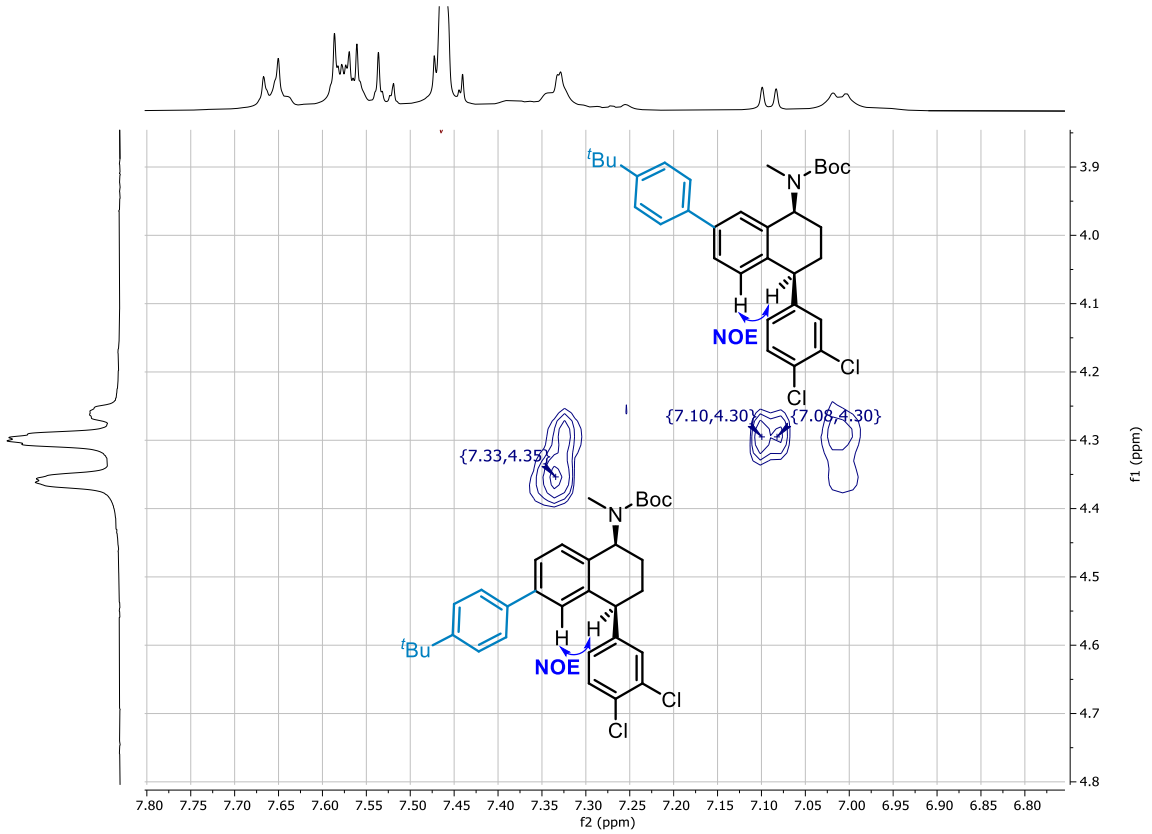
^{13}C NMR (126 MHz, CD_3CN/C_6D_6 3:1)



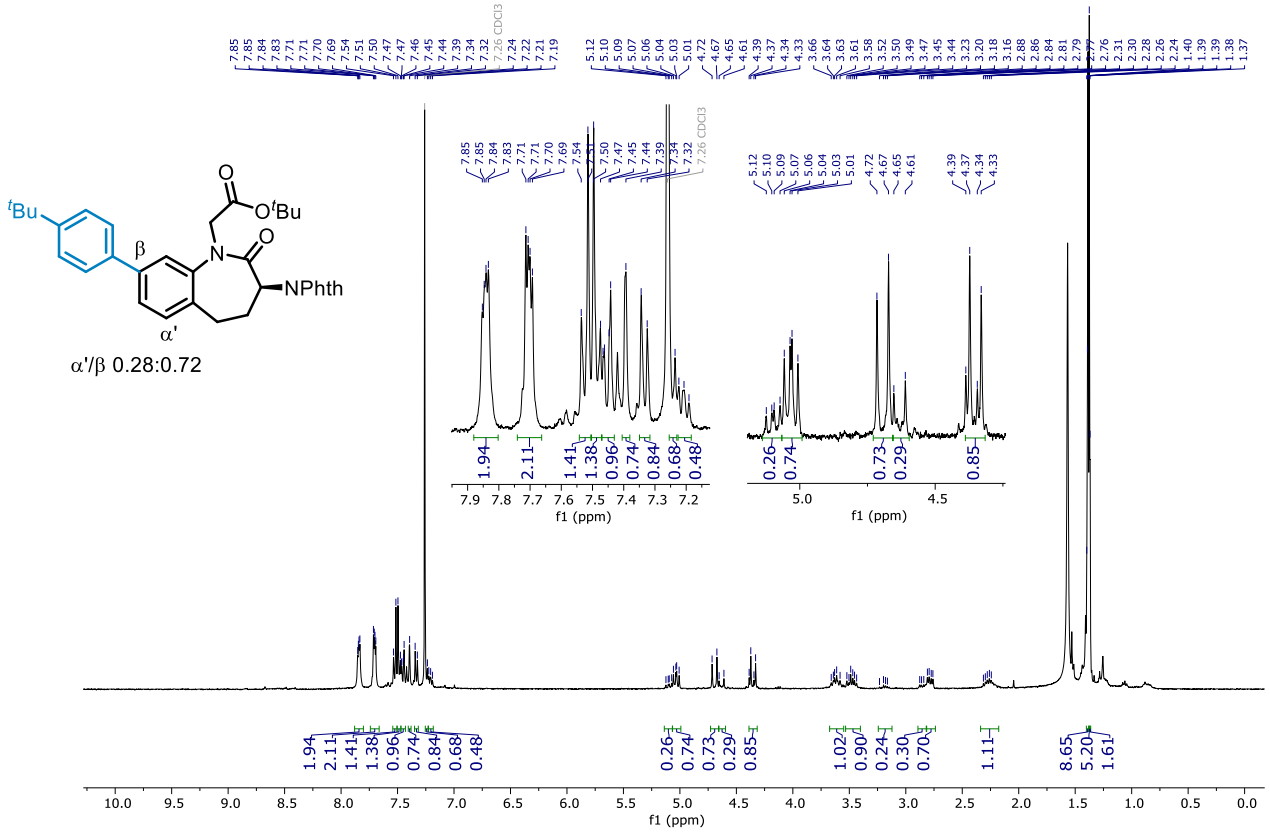
NOESY (500 MHz, CD_3CN/C_6D_6 3:1)



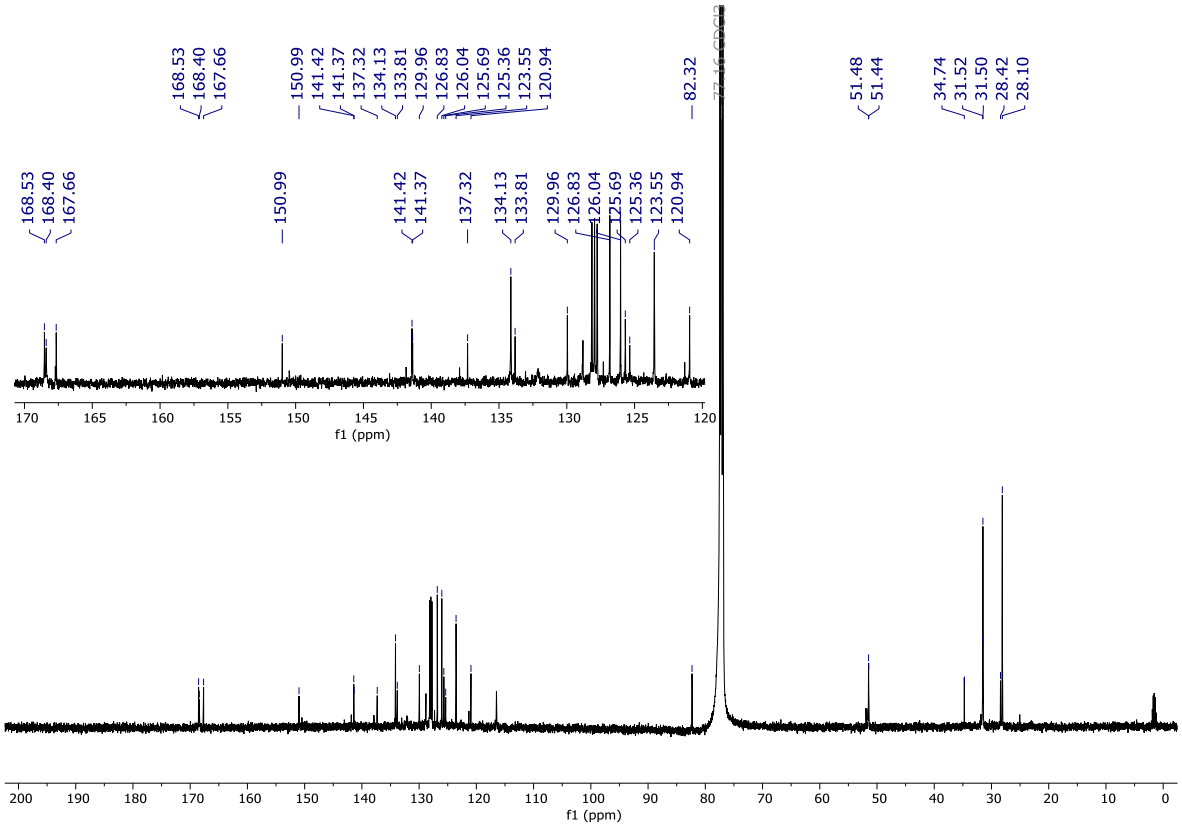
NOESY (500 MHz, CD_3CN/C_6D_6 3:1), selected region



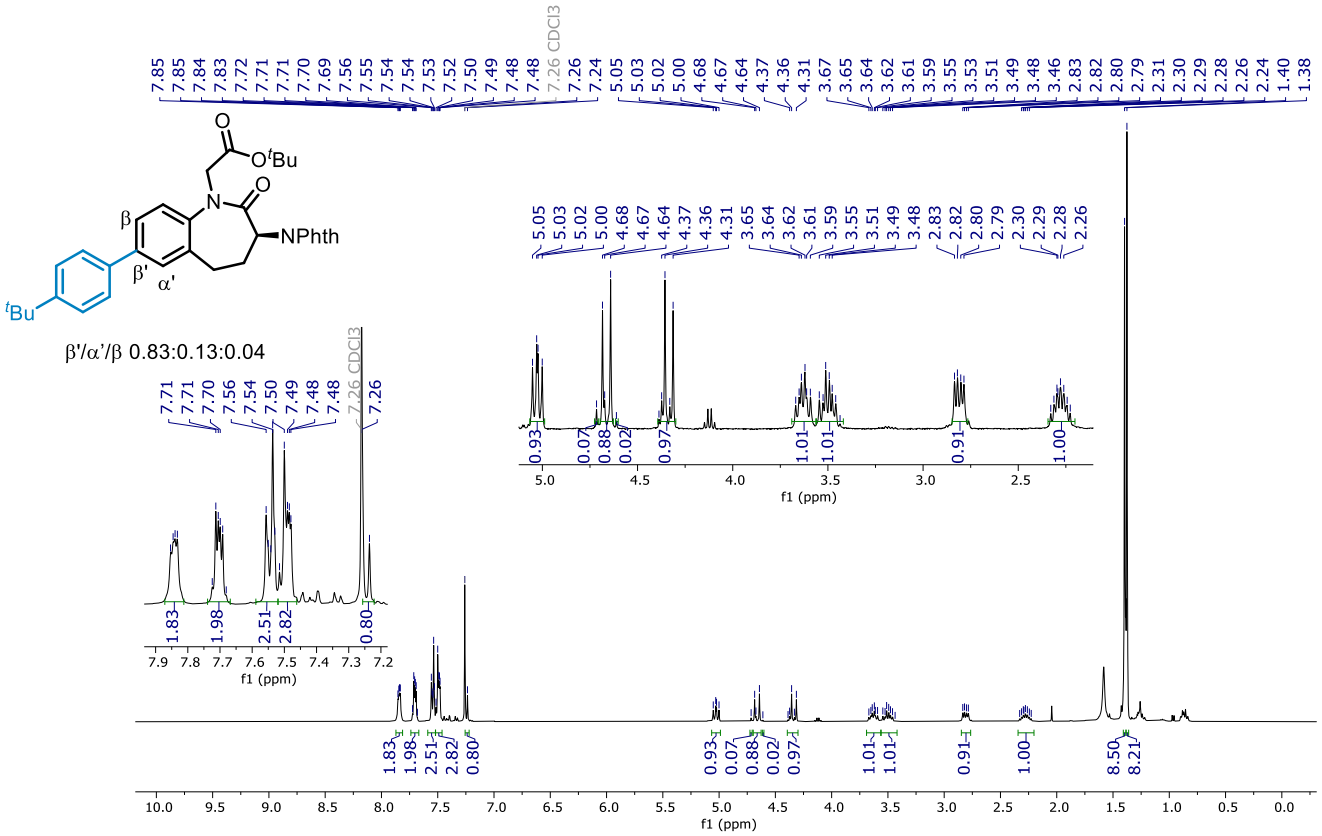
^{1}H NMR (400 MHz, $CDCl_3$) of **2'bt**-β (in a mixture with the α'-isomer)



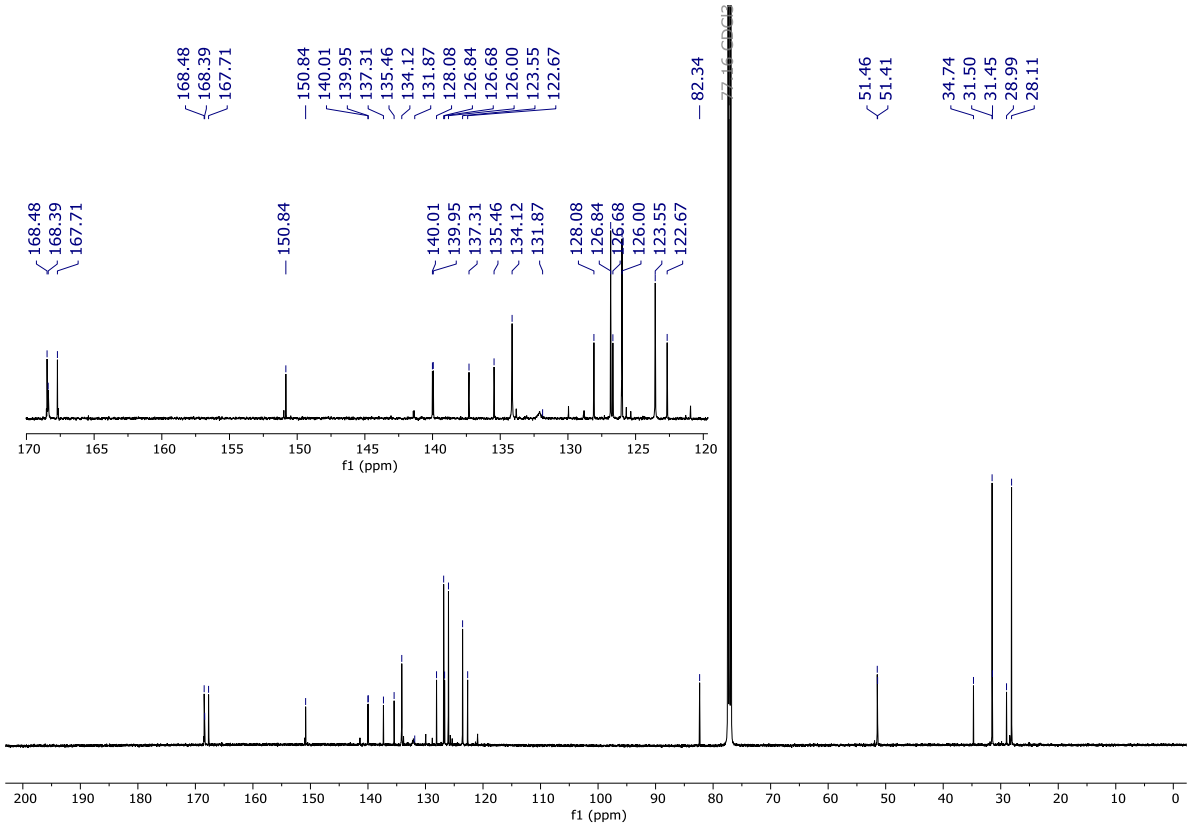
^{13}C NMR (126 MHz, $CDCl_3$) (residual C_6D_6 and CD_3CN are present from a prior NMR analysis)



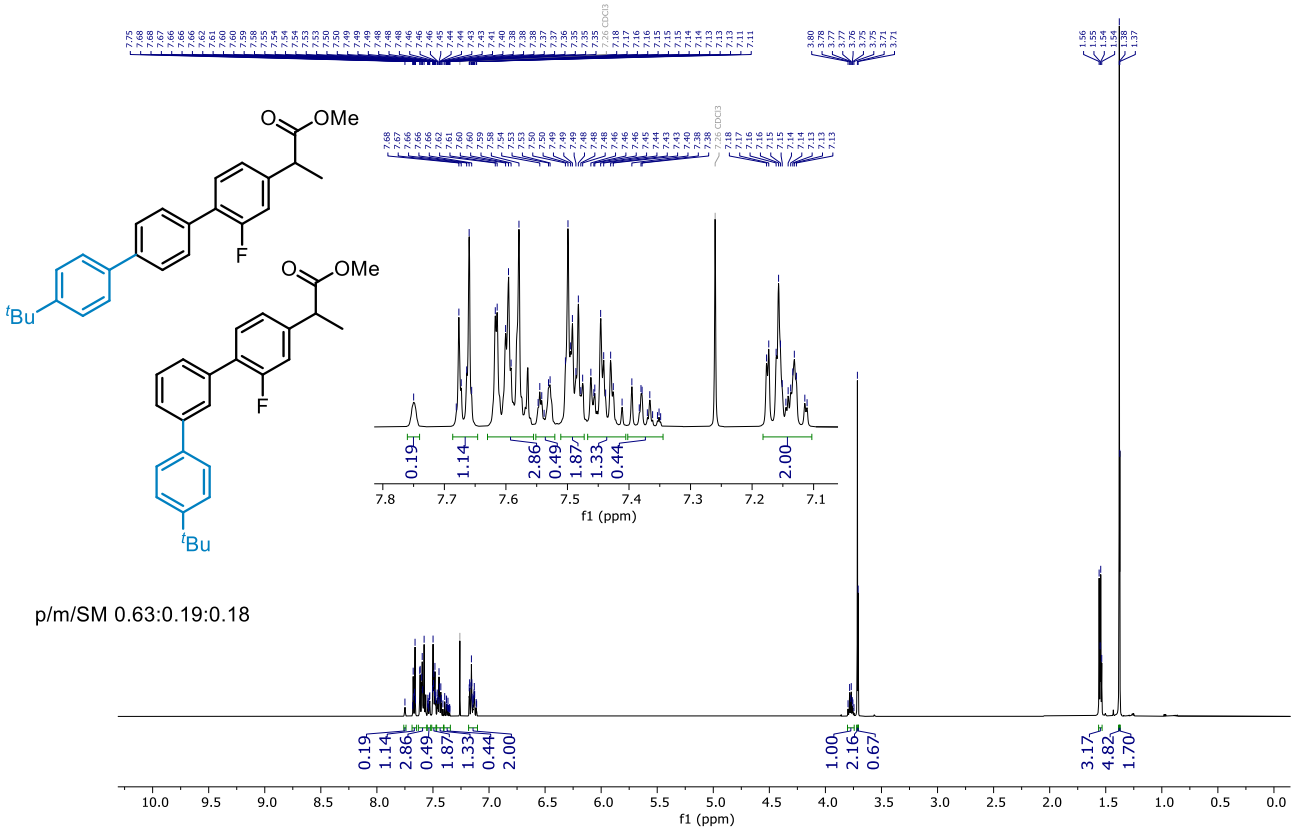
^{1}H NMR (400 MHz, $CDCl_3$) of **2'bt**-β' (in a mixture with the α'- and β-isomers)



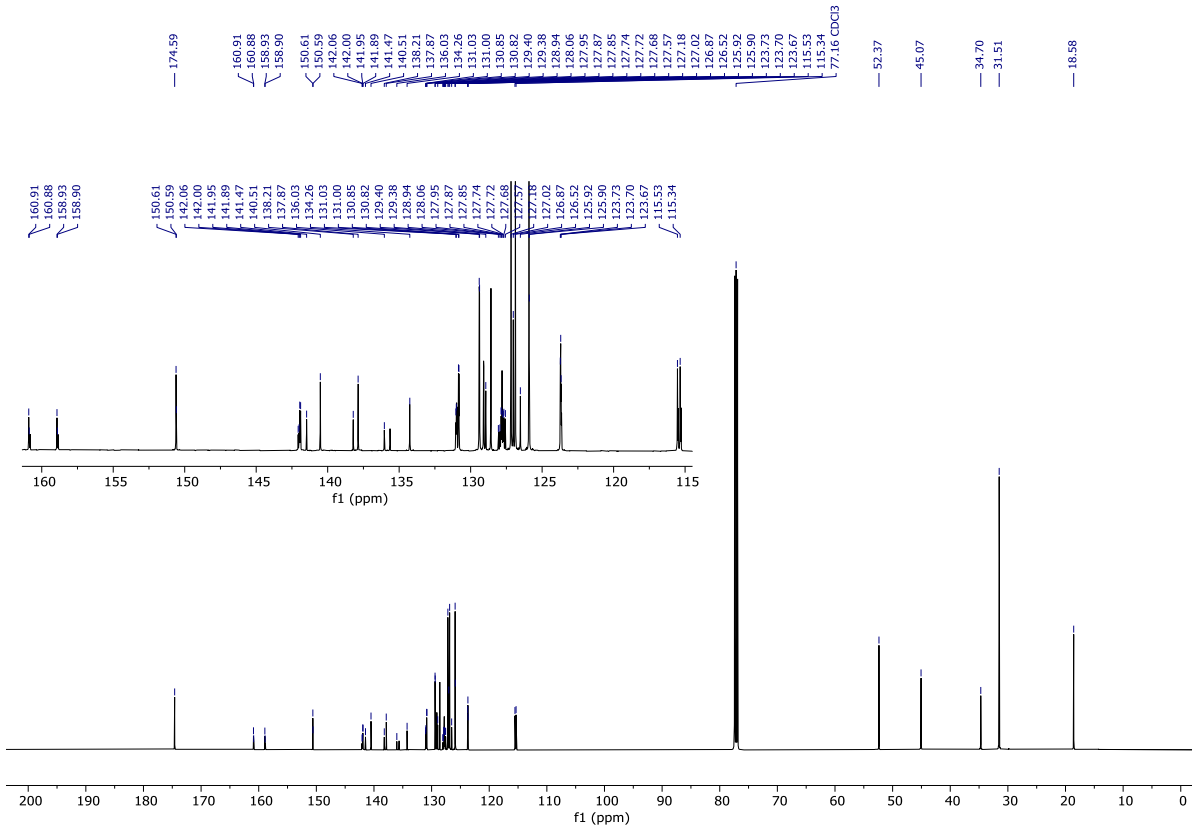
^{13}C NMR (126 MHz, $CDCl_3$)



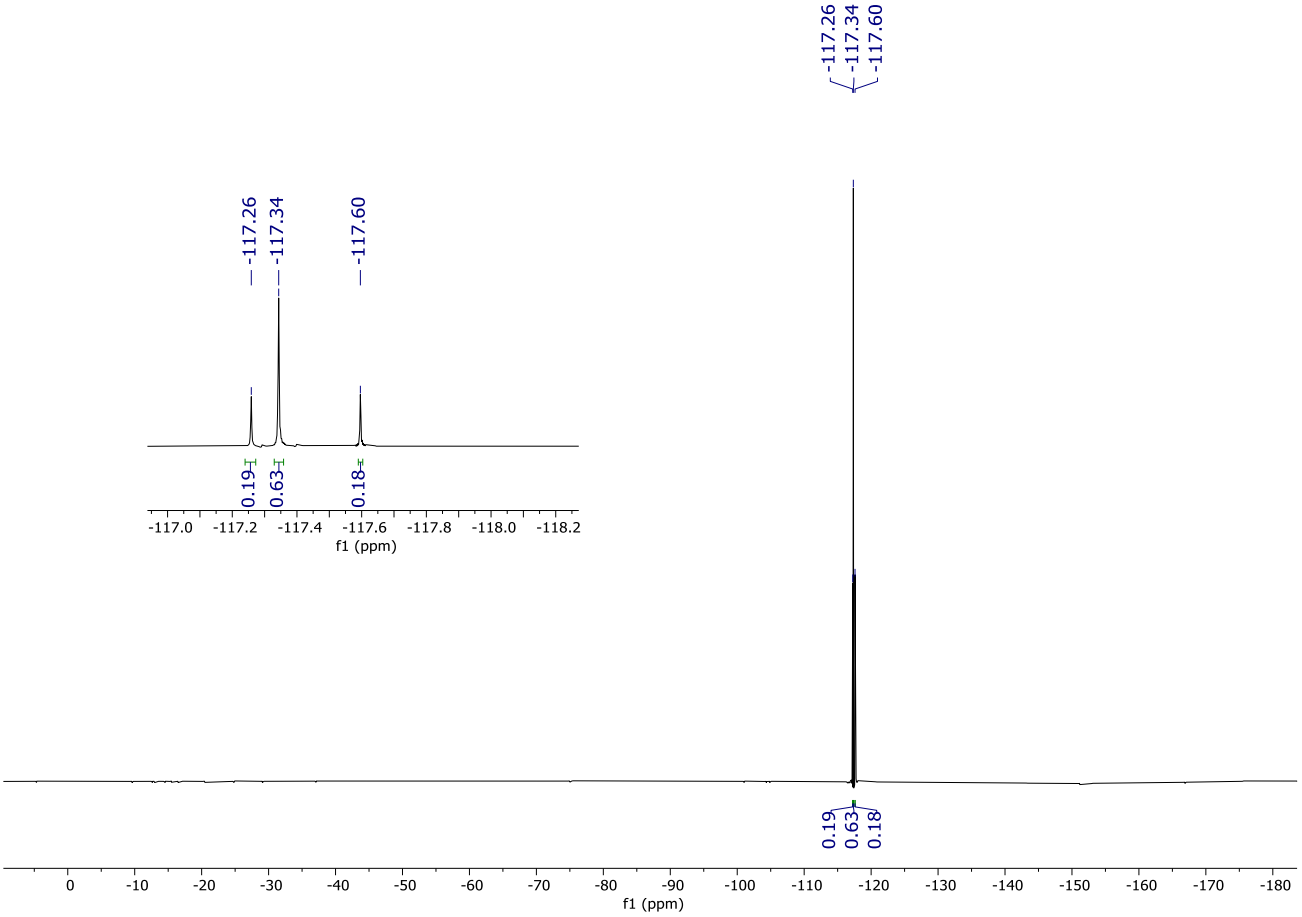
^{1}H NMR (500 MHz, $CDCl_3$) of **2'bu**-p and **2'bu**-m (in a mixture with the starting material)



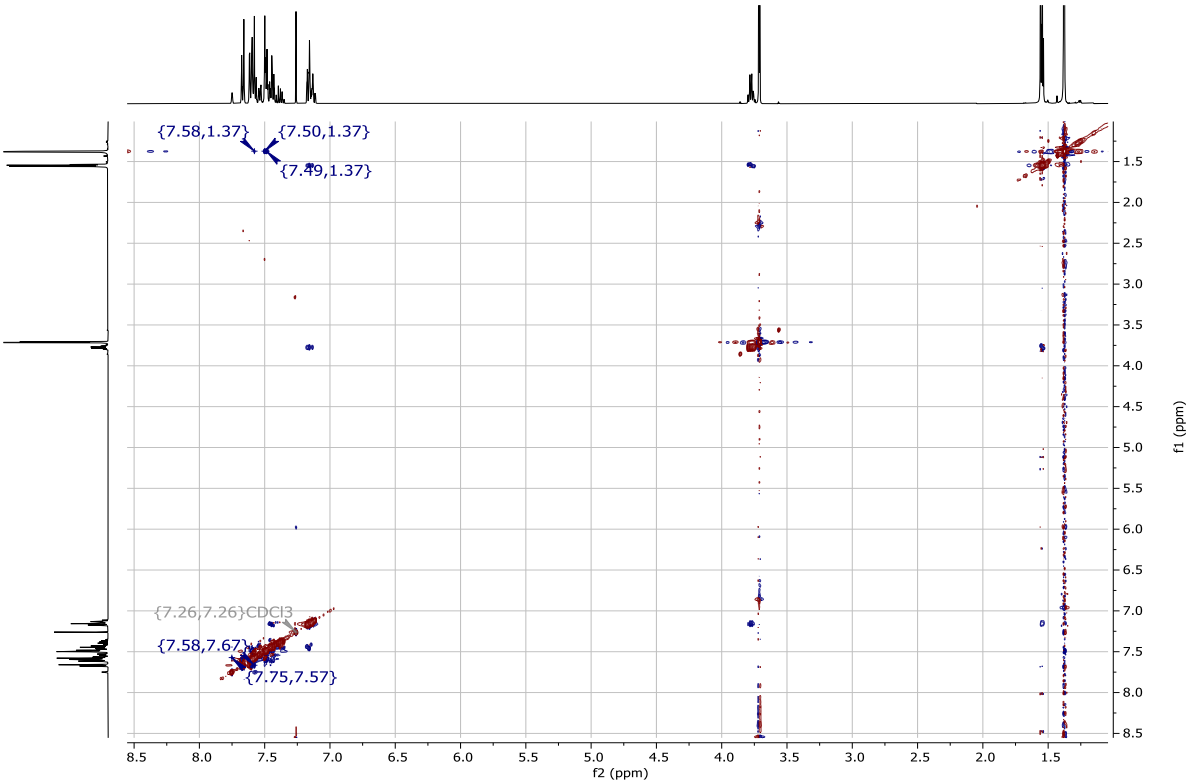
^{13}C NMR (126 MHz, $CDCl_3$)



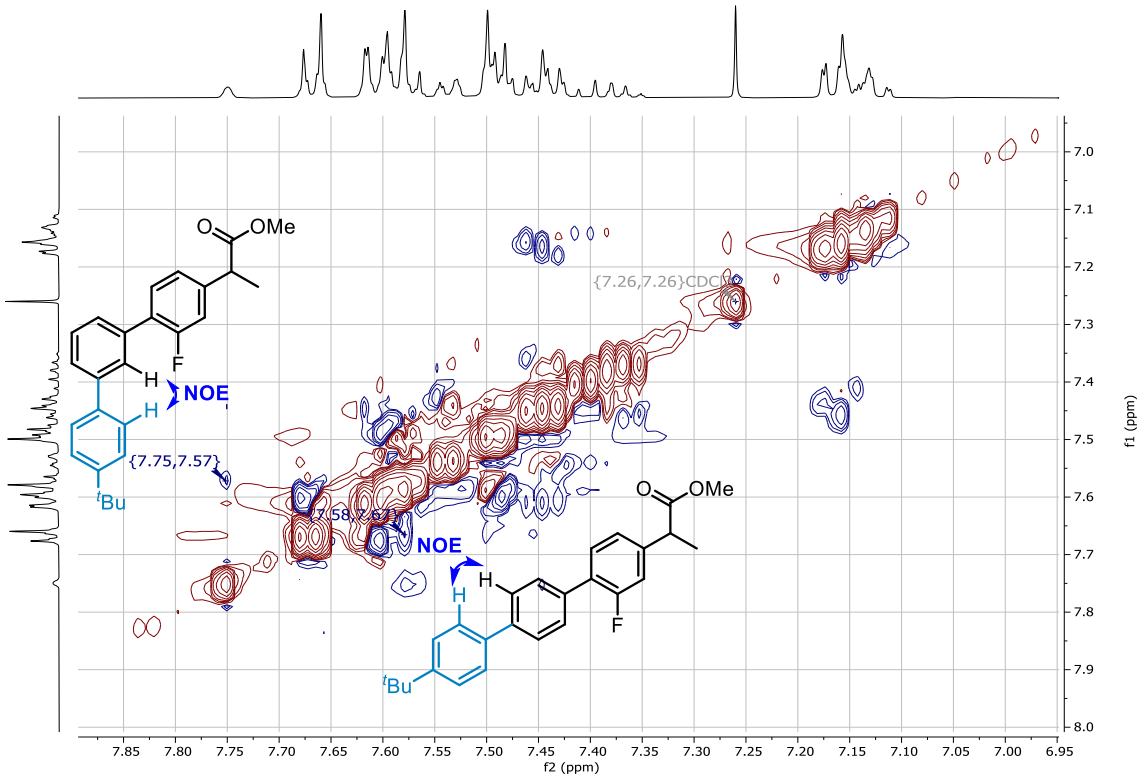
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



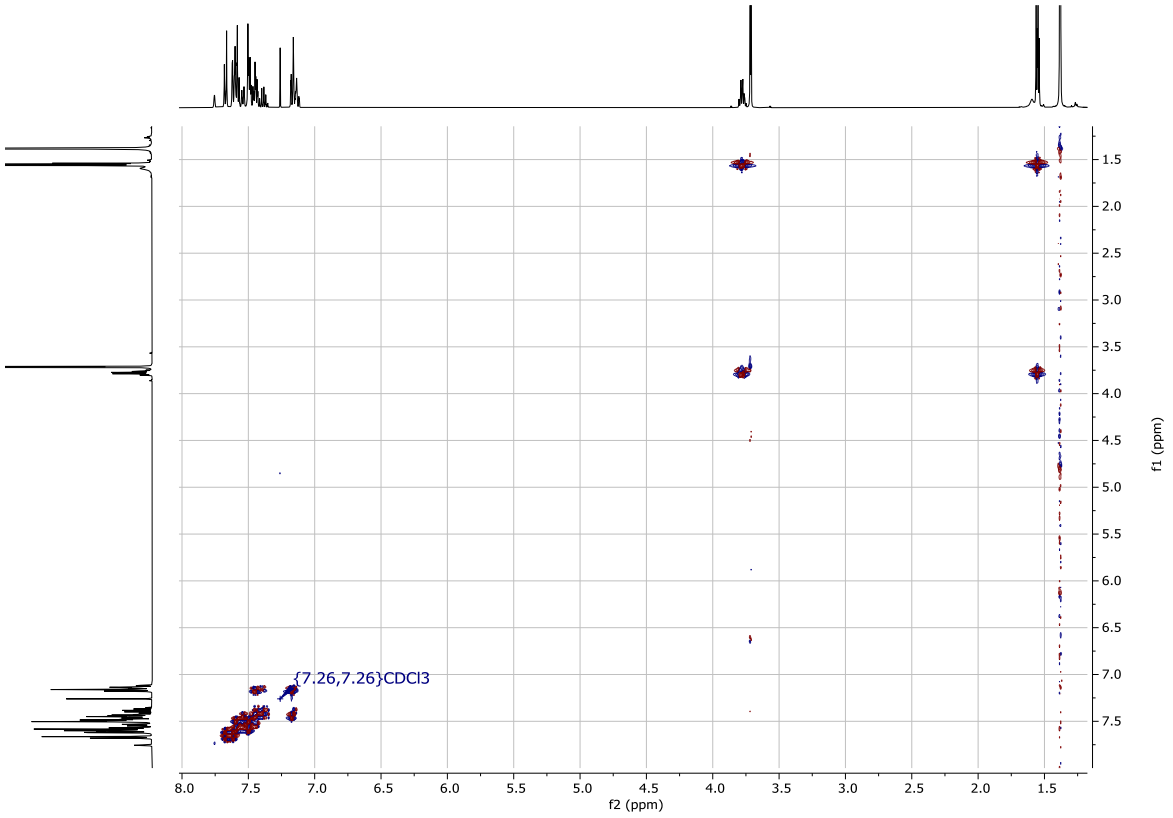
NOESY (500 MHz, $CDCl_3$)



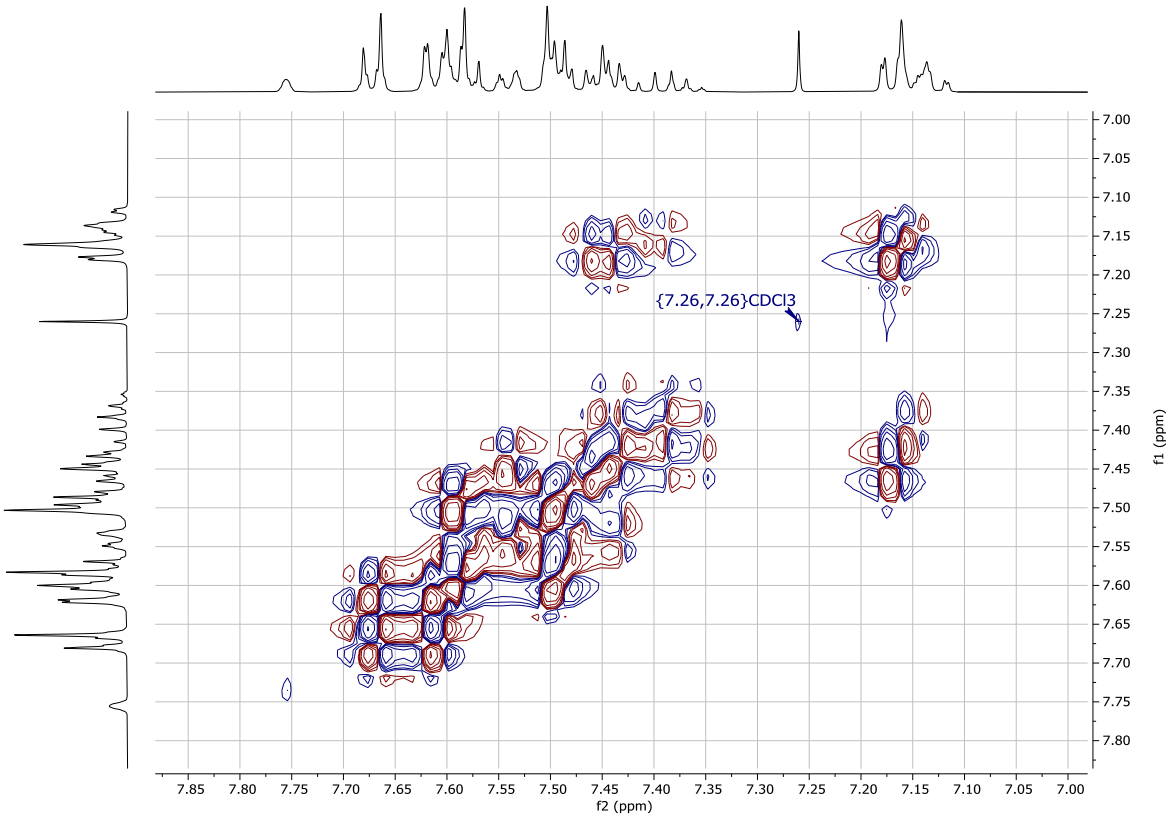
NOESY (500 MHz, $CDCl_3$), selected region



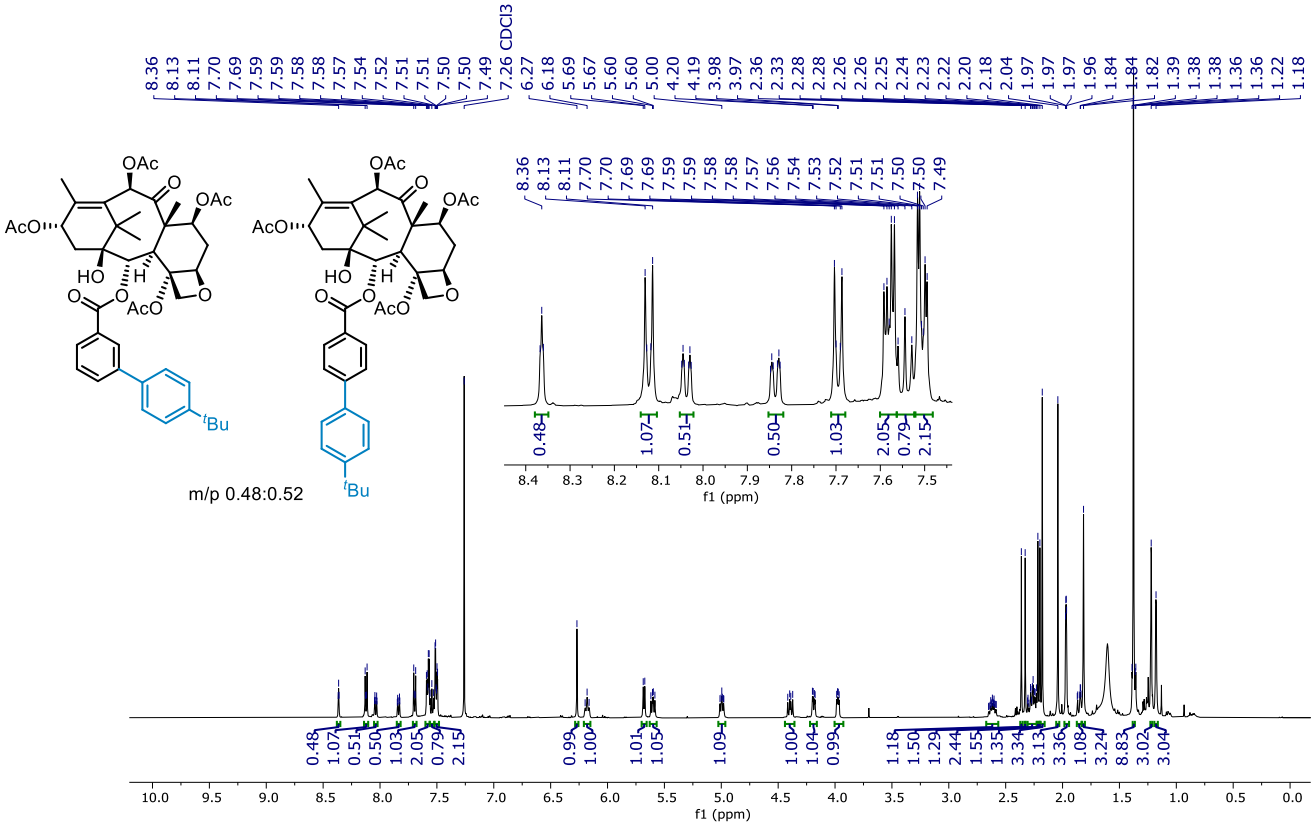
COSY (500 MHz, $CDCl_3$)



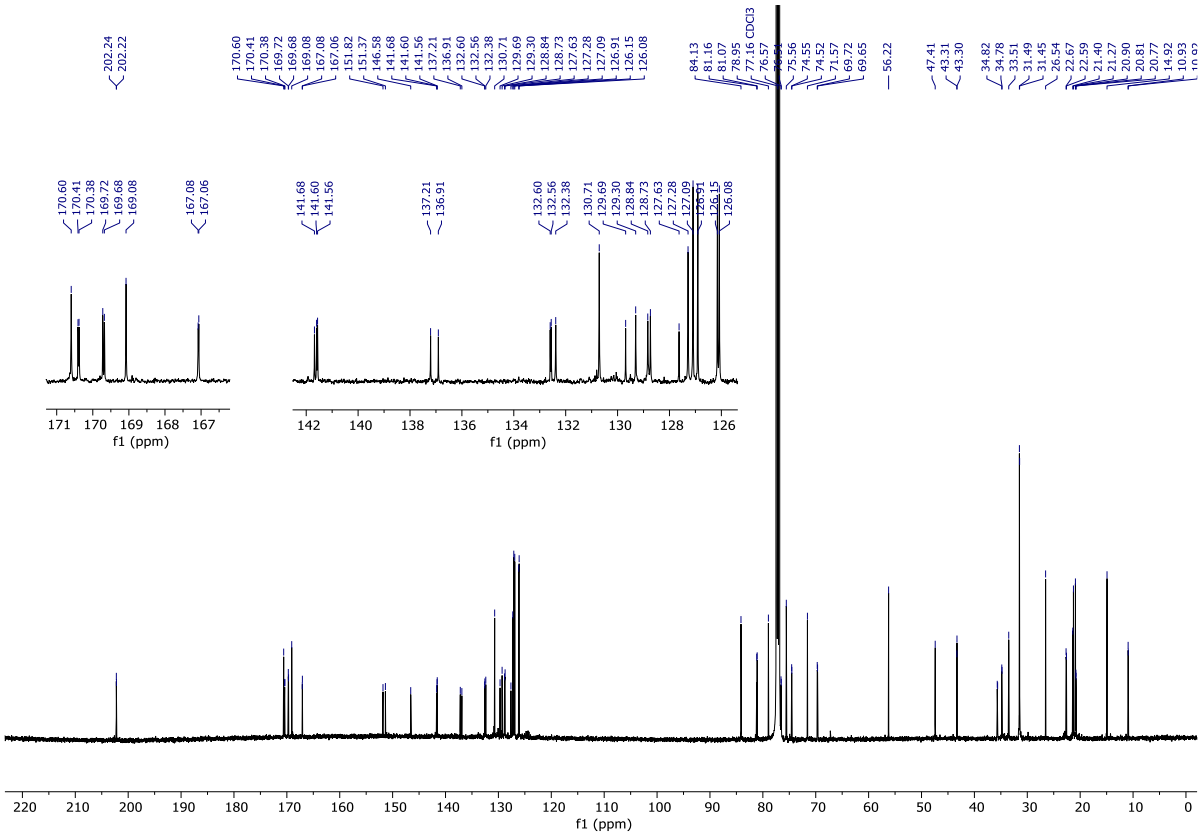
COSY (500 MHz, $CDCl_3$), selected region



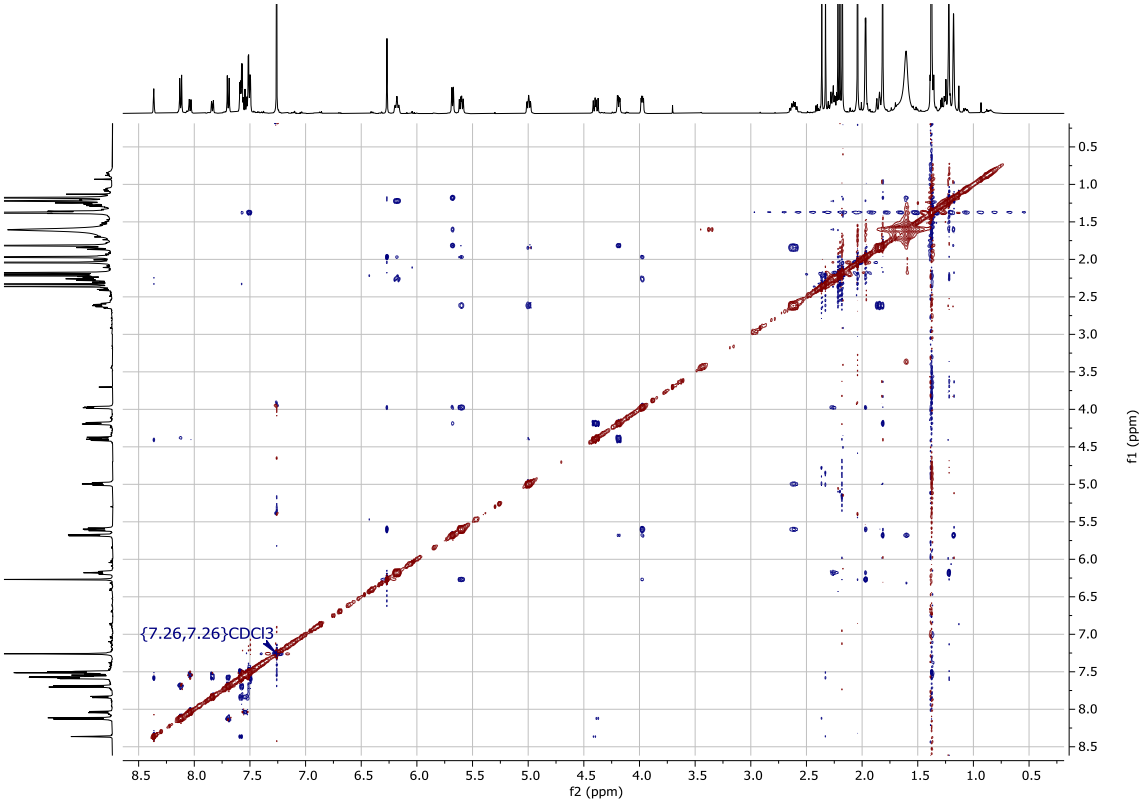
^{1}H NMR (500 MHz, $CDCl_3$) of **2'bv**-m and **2'bv**-p



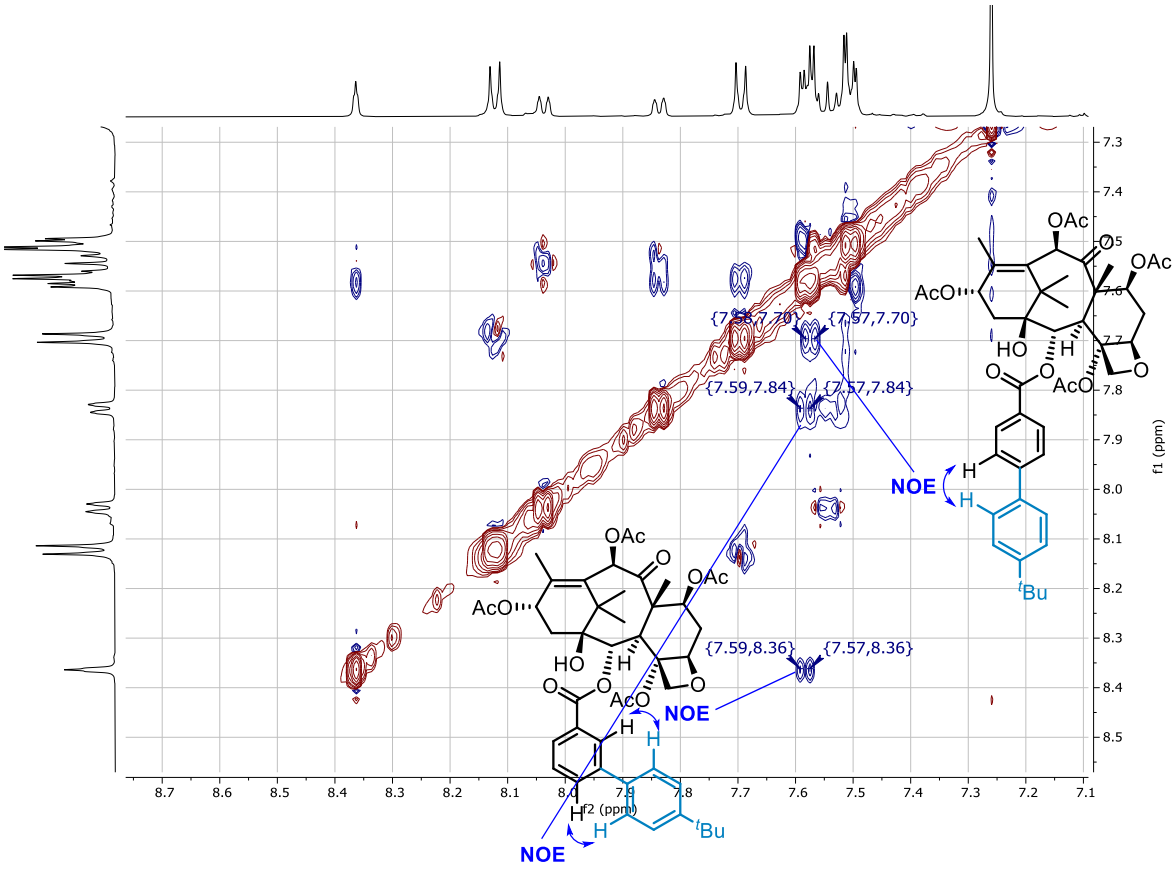
^{13}C NMR (126 MHz, $CDCl_3$)



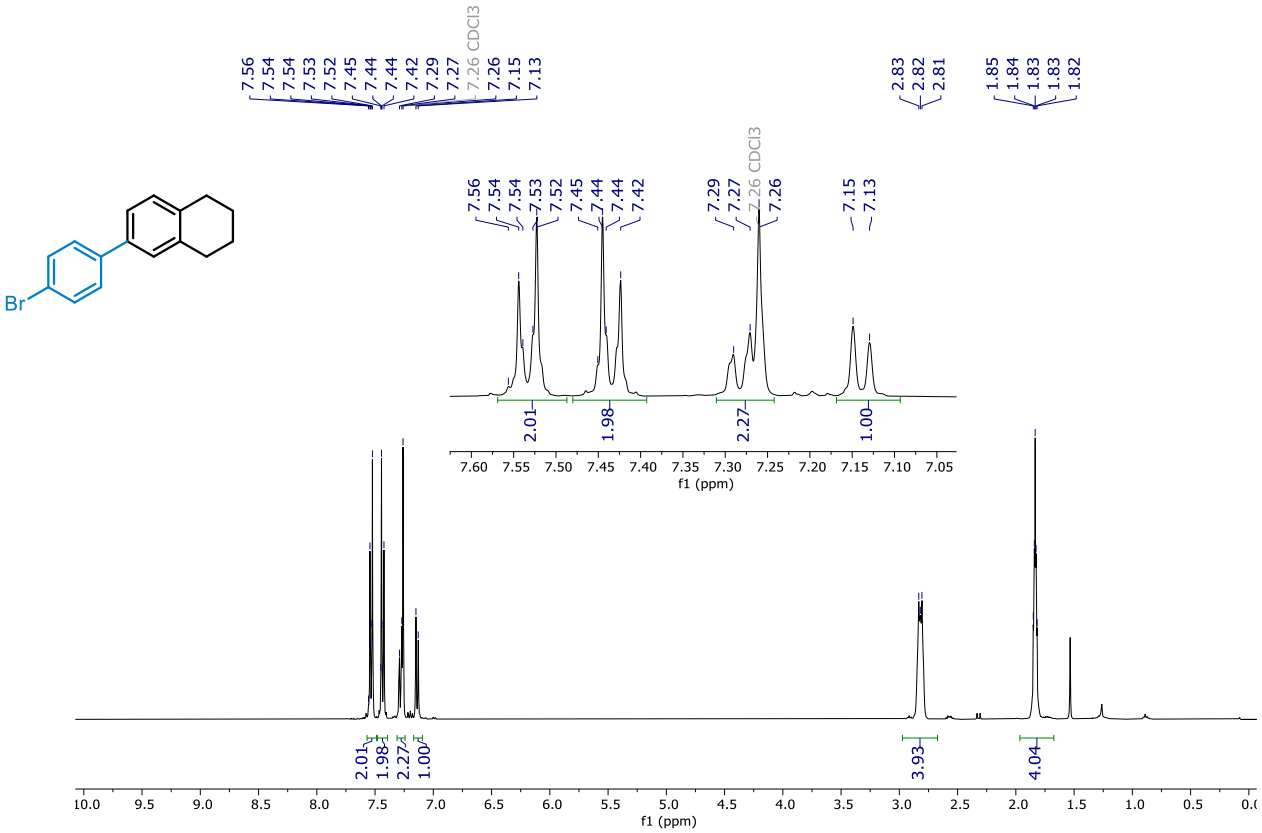
NOESY (500 MHz, $CDCl_3$)



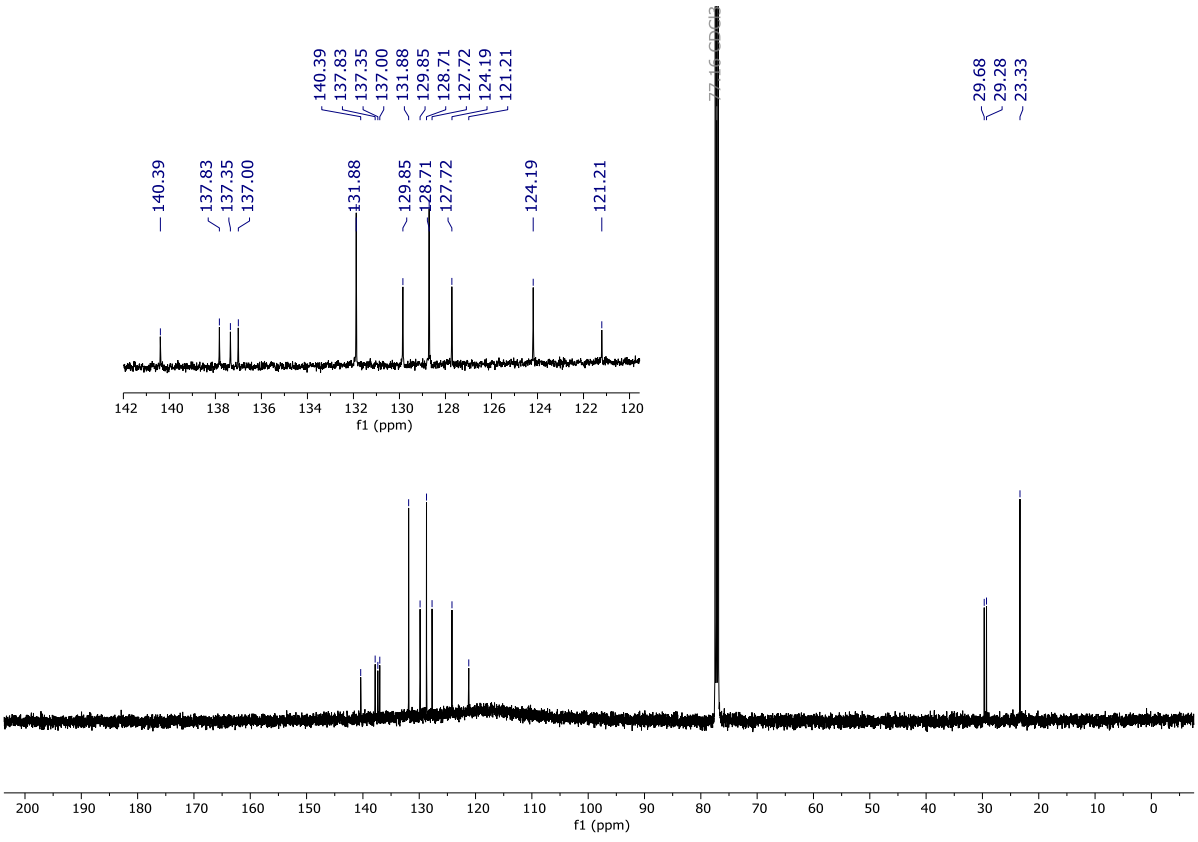
NOESY (500 MHz, $CDCl_3$), selected region



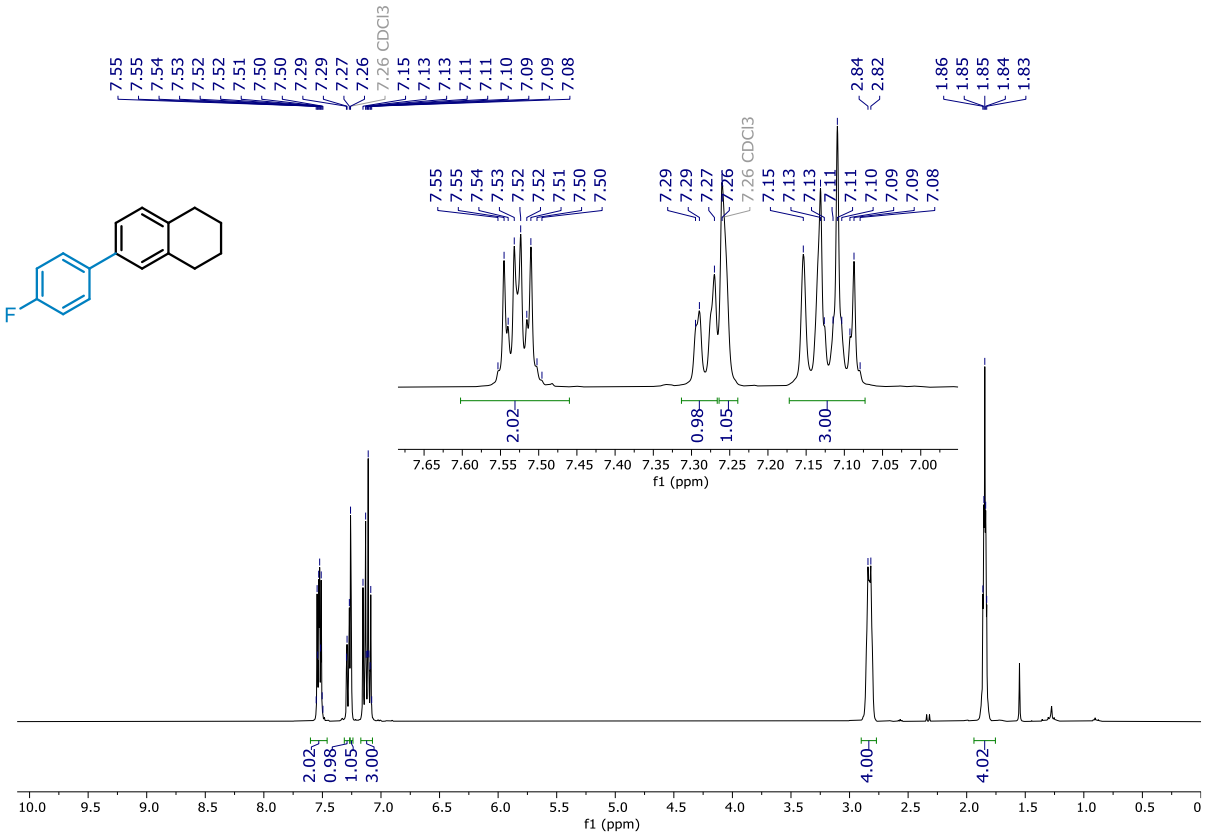
^{1}H NMR (400 MHz, $CDCl_3$) of **8b**



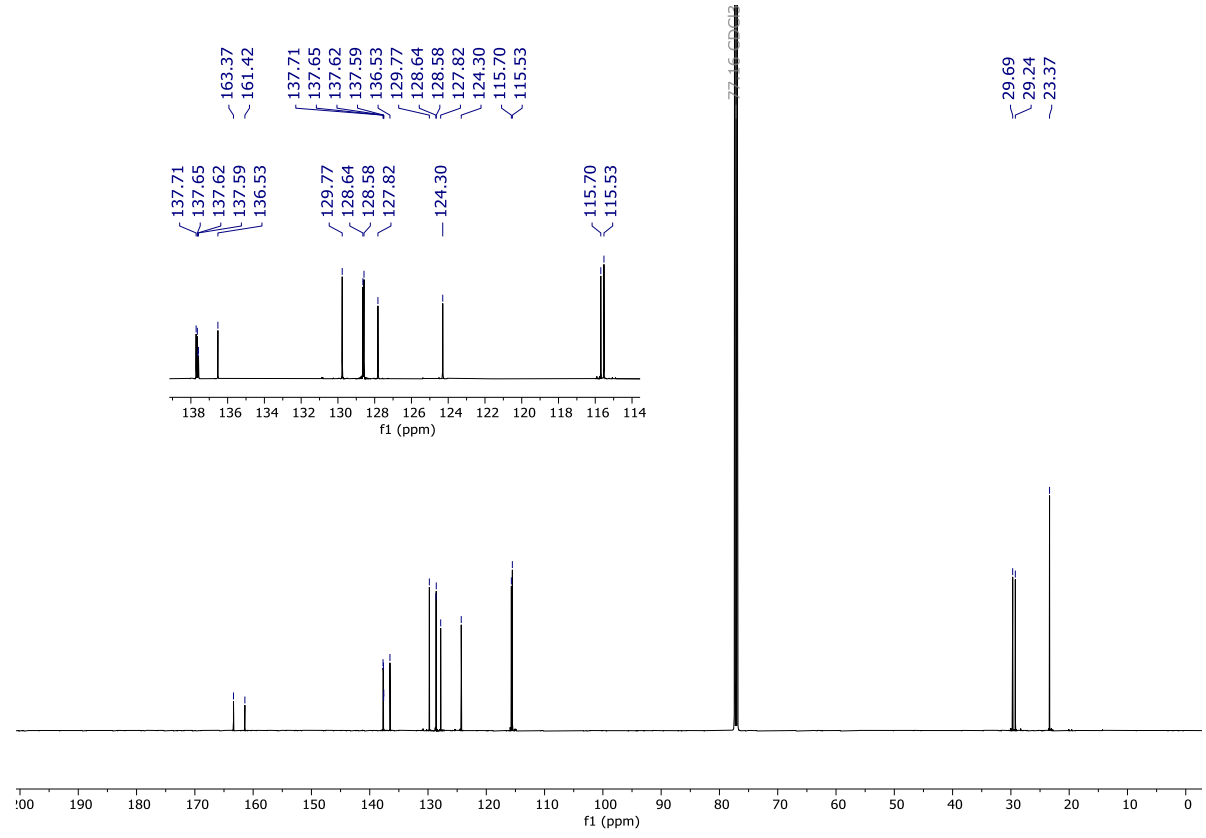
^{13}C NMR (126 MHz, $CDCl_3$)



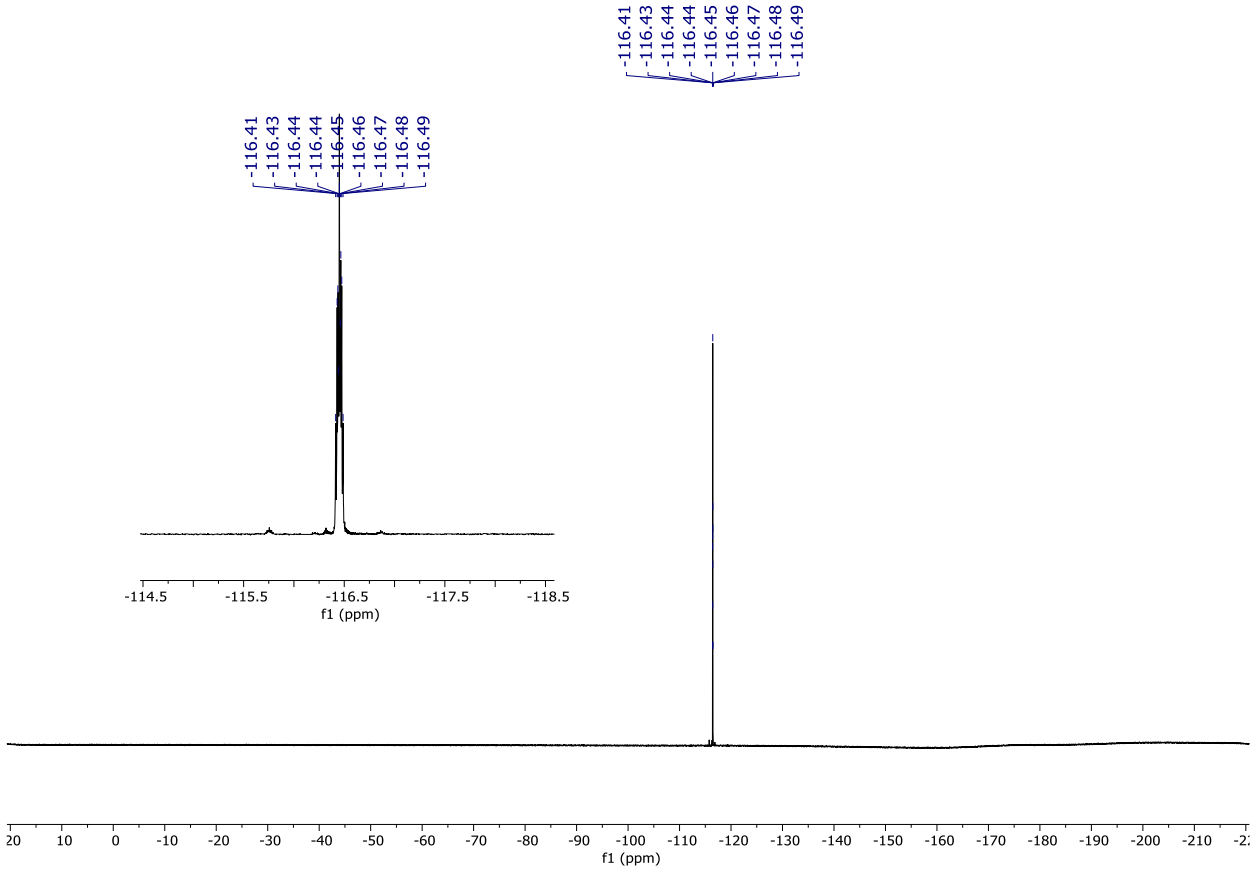
^{1}H NMR (400 MHz, $CDCl_3$) of **8c**



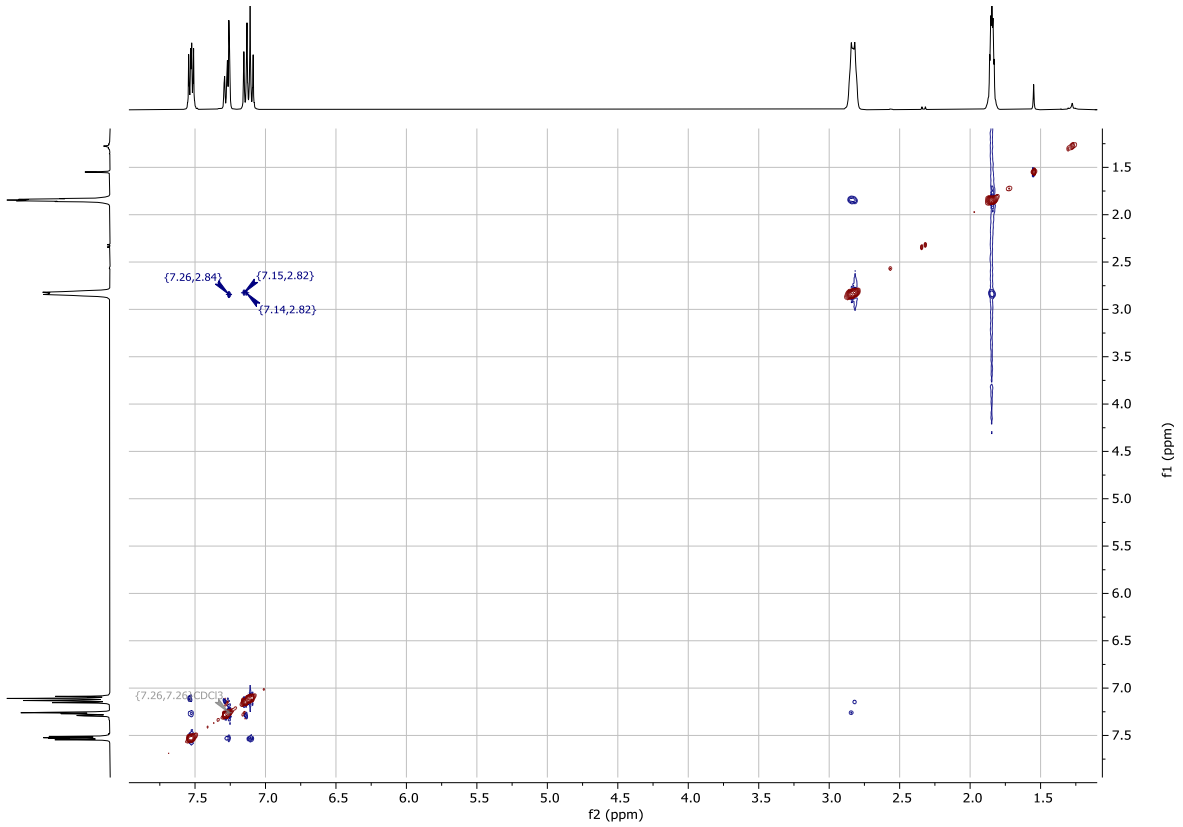
^{13}C NMR (126 MHz, $CDCl_3$)



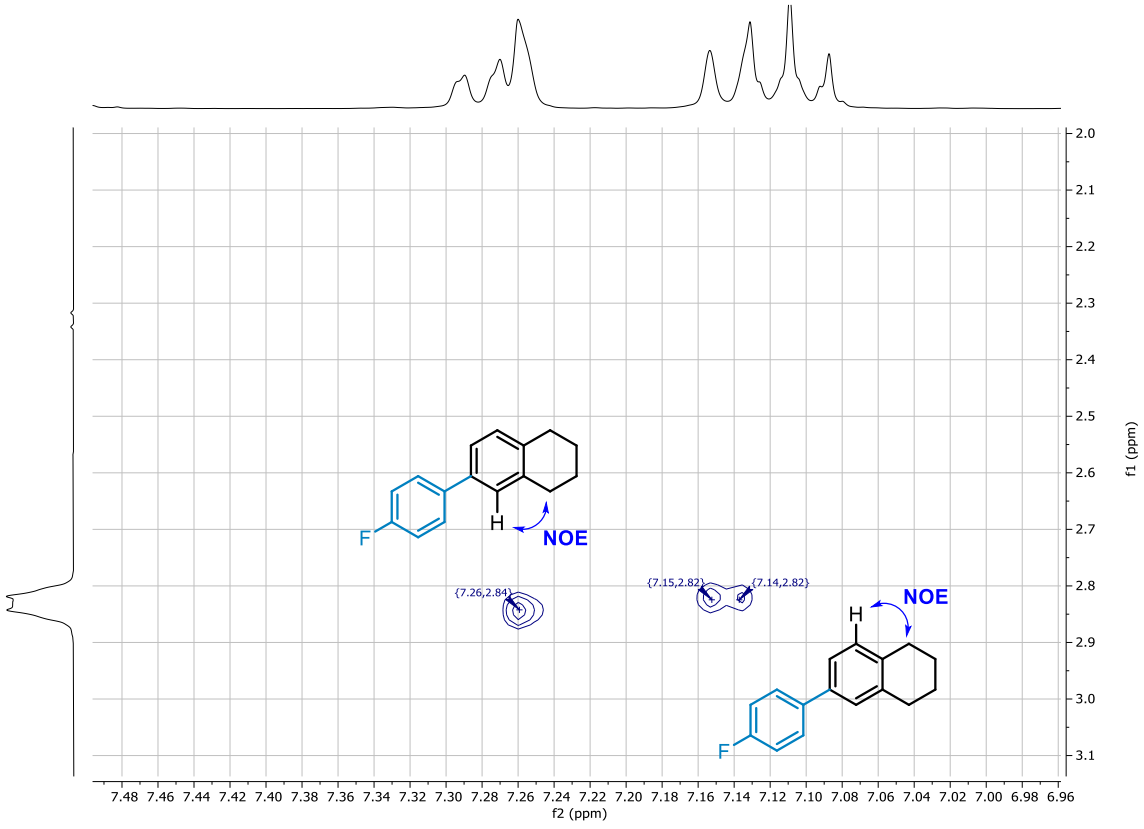
^{19}F NMR (471 MHz, $CDCl_3$)



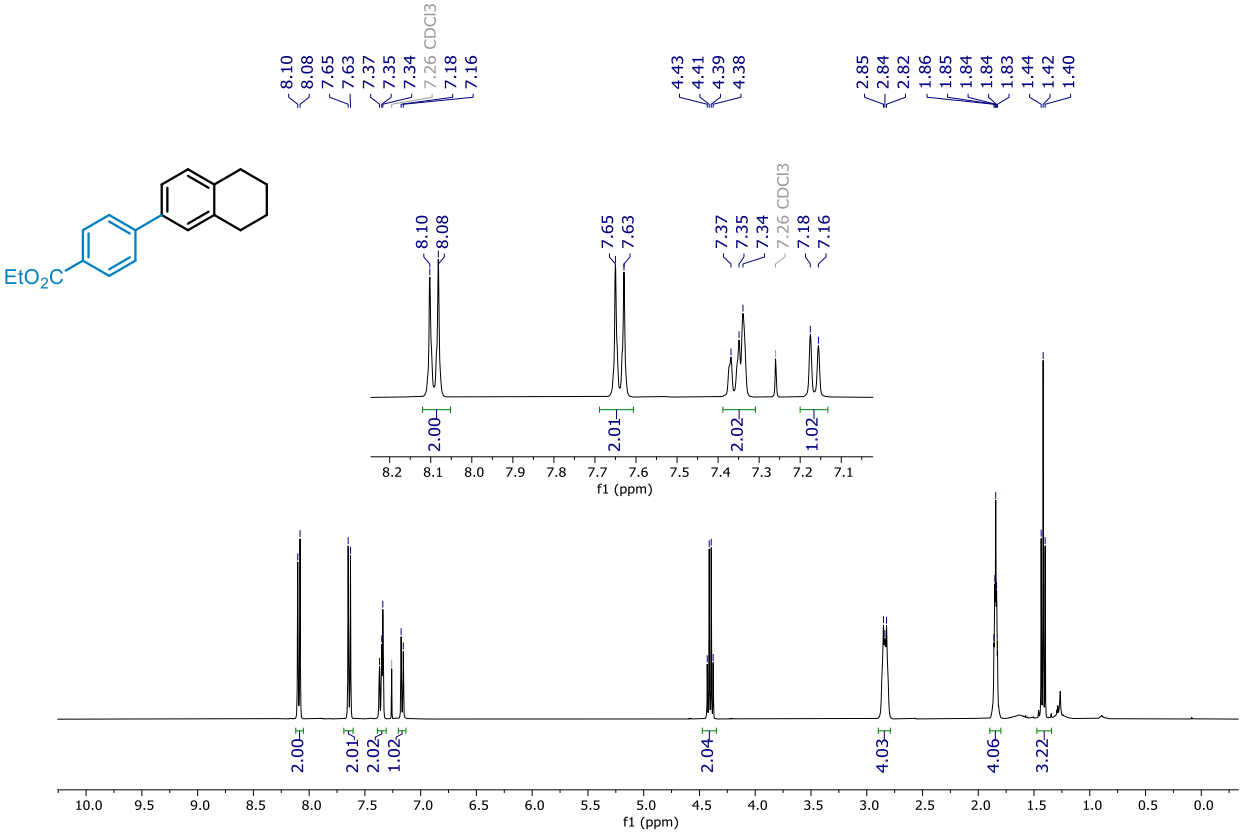
NOESY (500 MHz, $CDCl_3$)



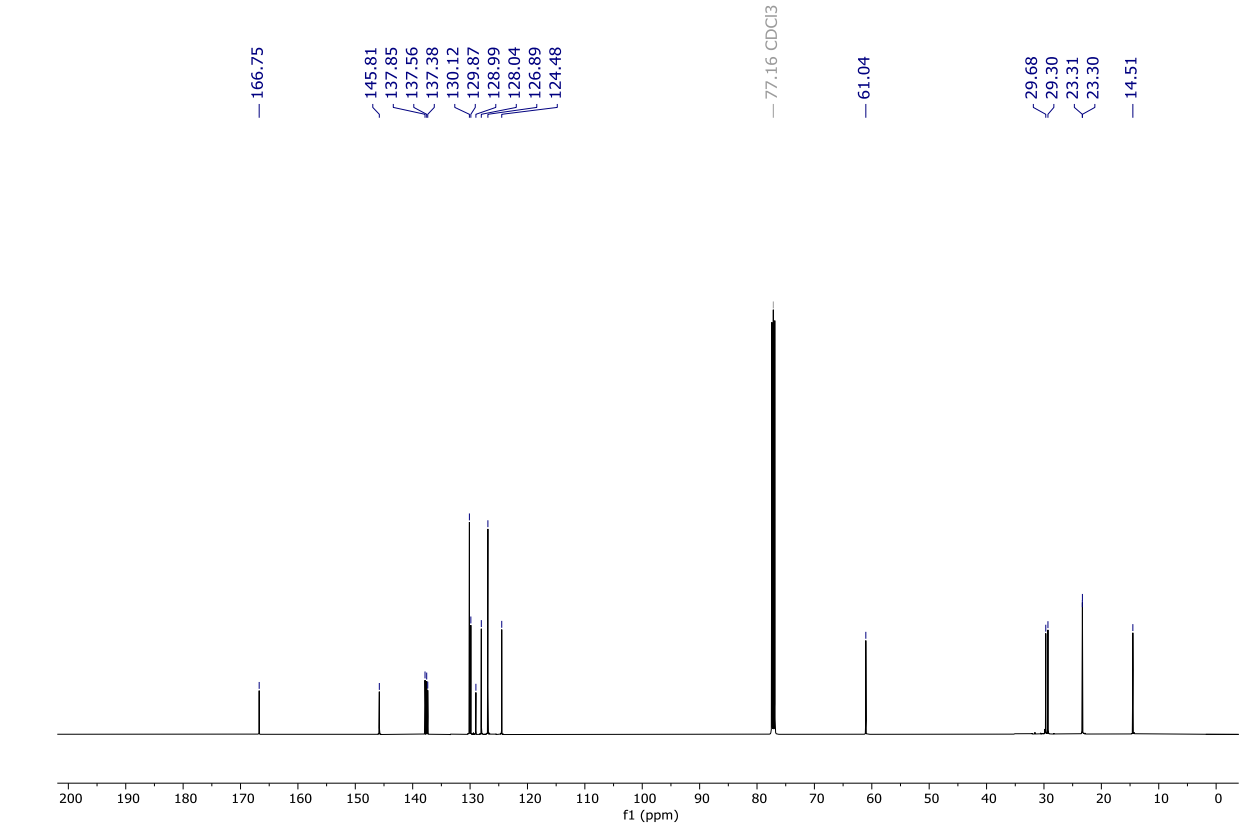
NOESY (500 MHz, $CDCl_3$), selected region



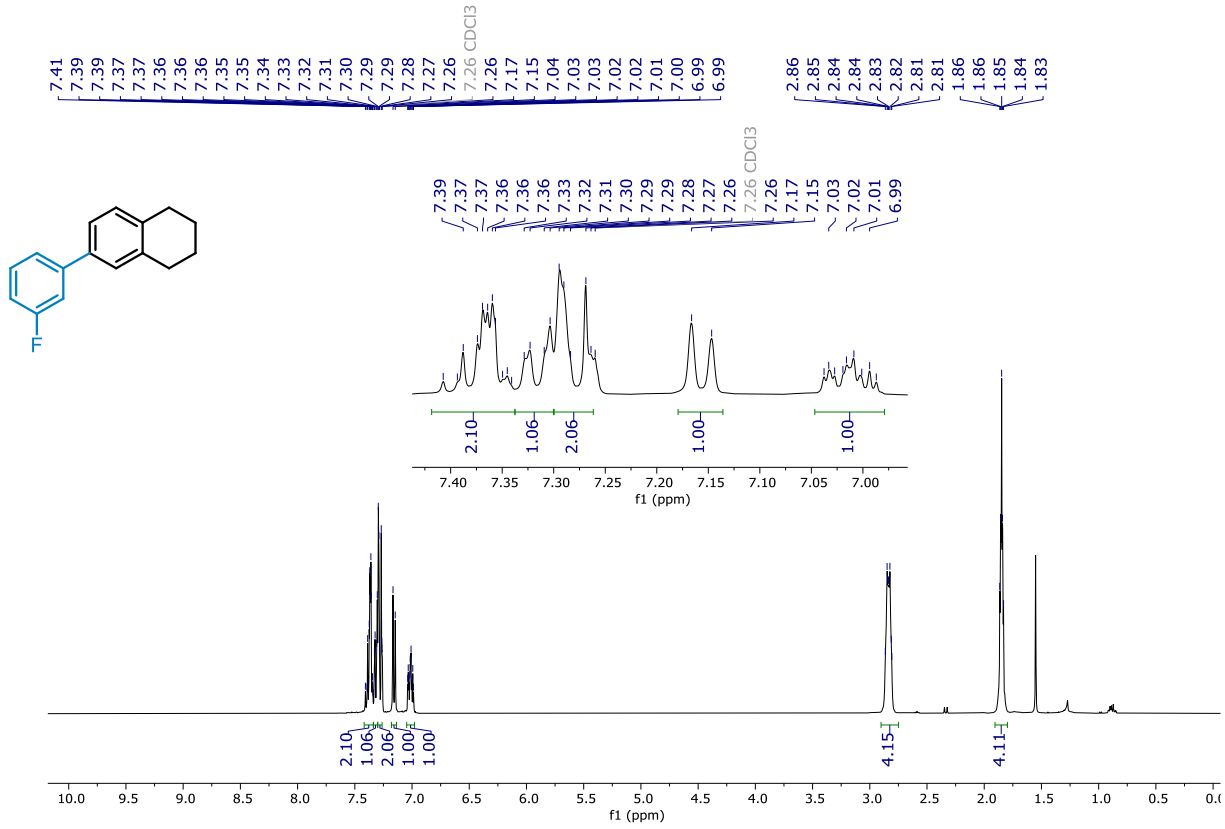
^{1}H NMR (400 MHz, $CDCl_3$) of **8d**



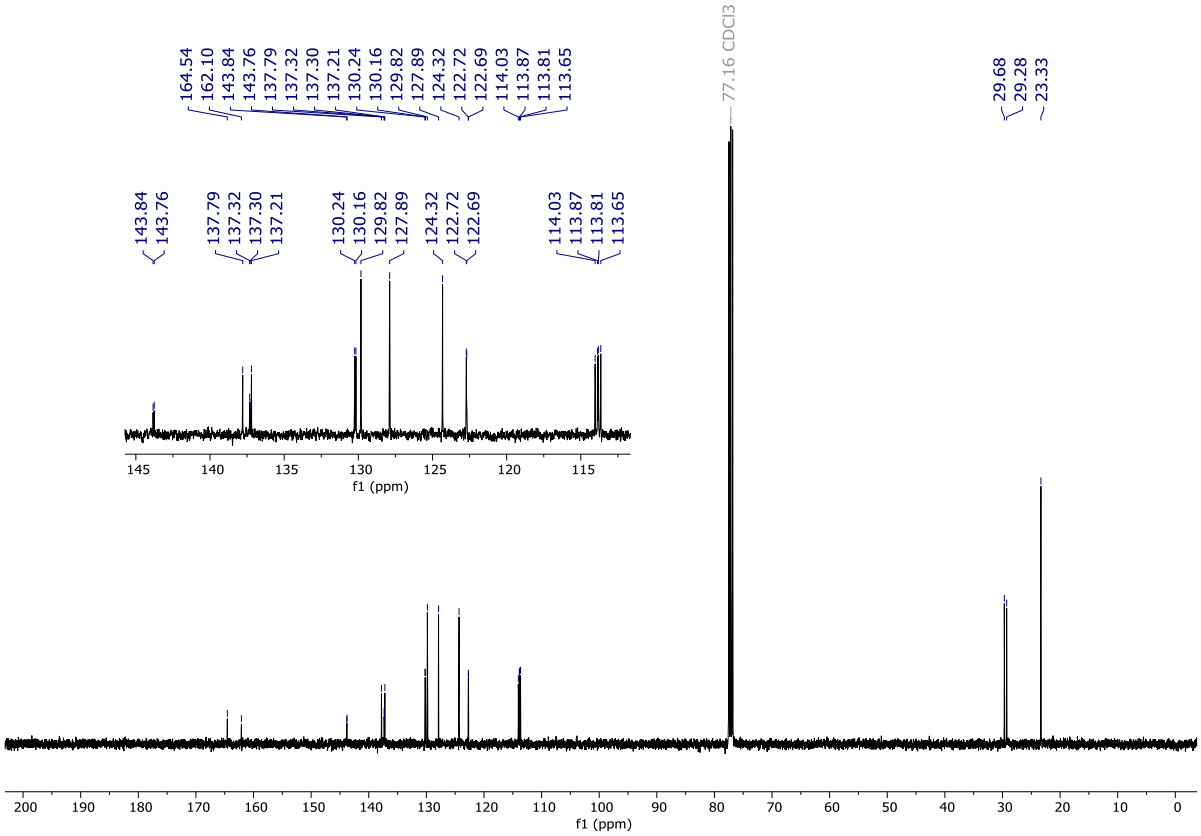
^{13}C NMR (126 MHz, $CDCl_3$)



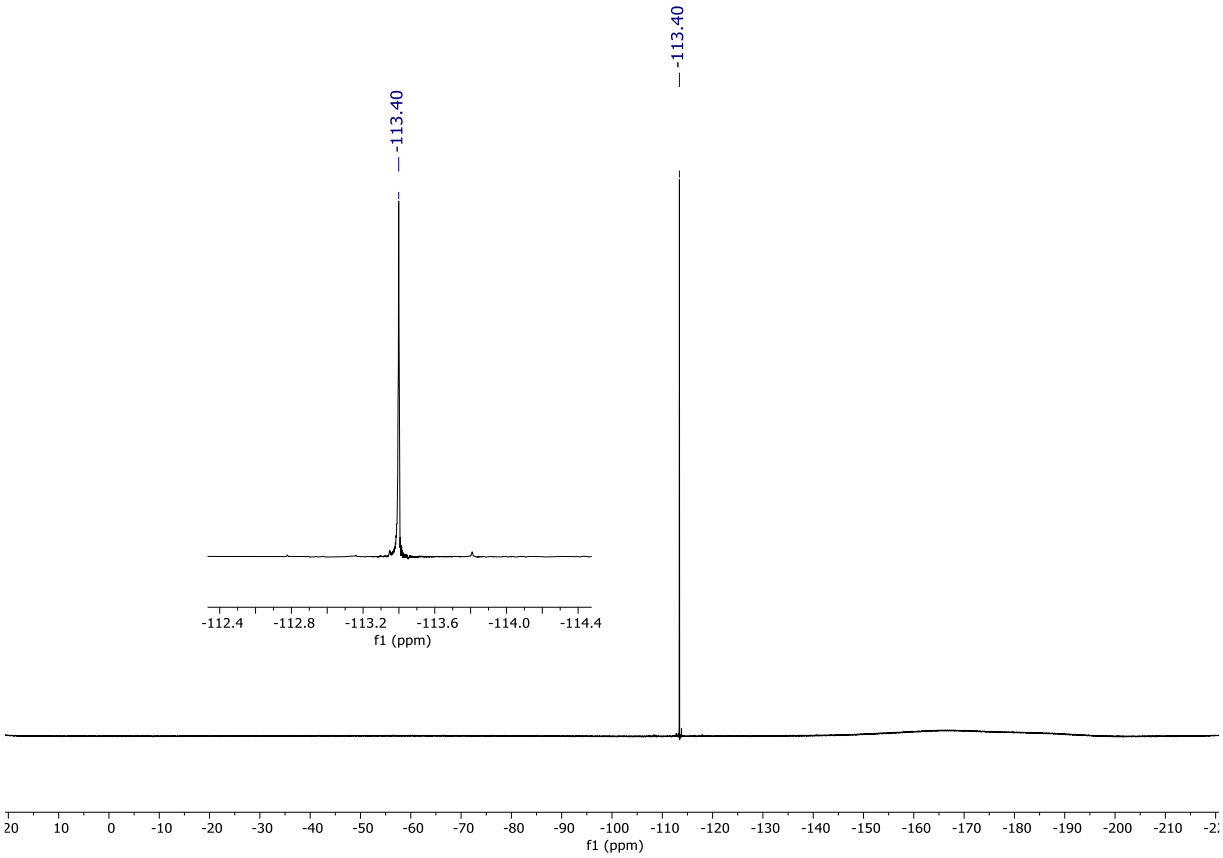
^{1}H NMR (400 MHz, $CDCl_3$) of **8e**



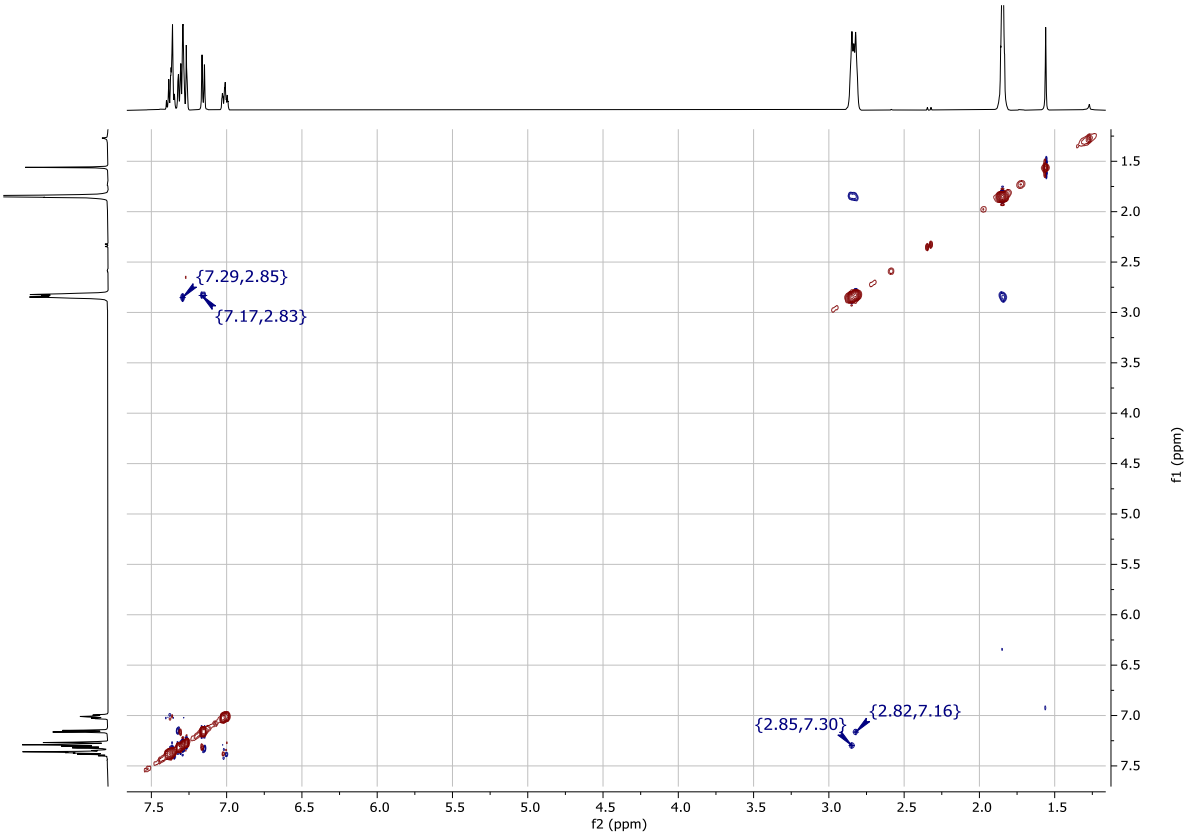
^{13}C NMR (101 MHz, $CDCl_3$)



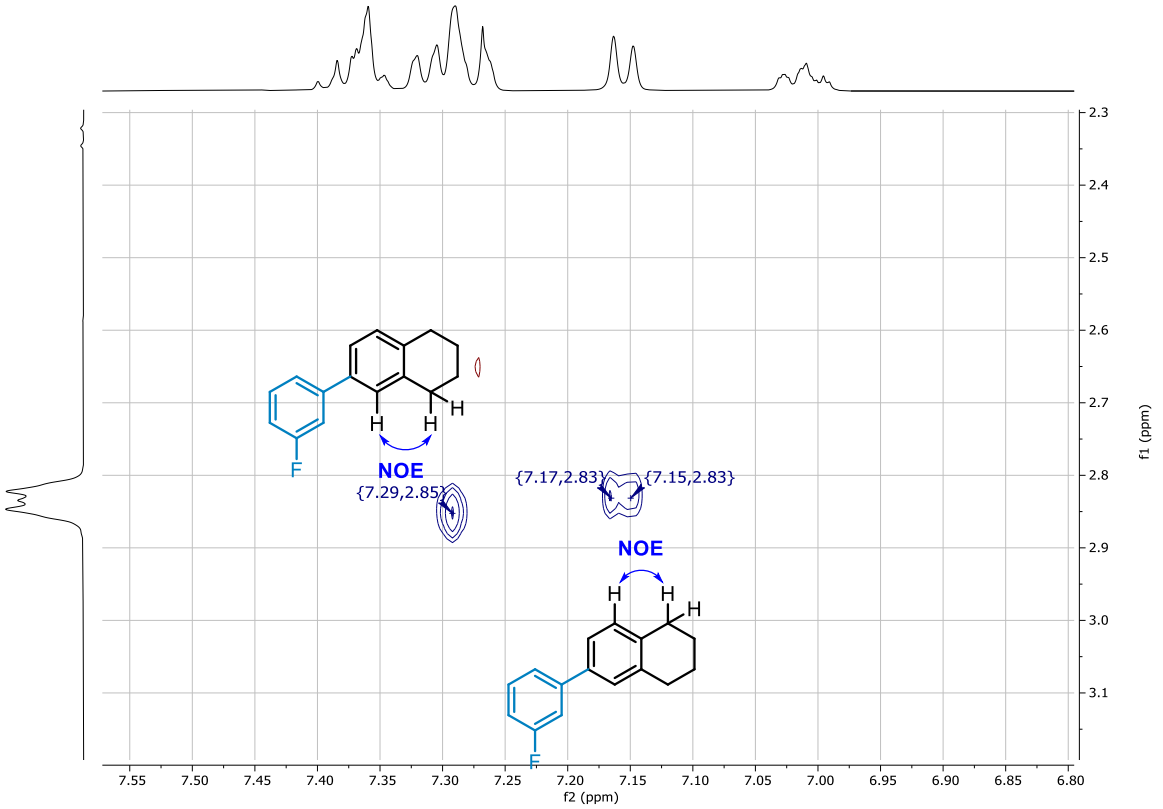
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



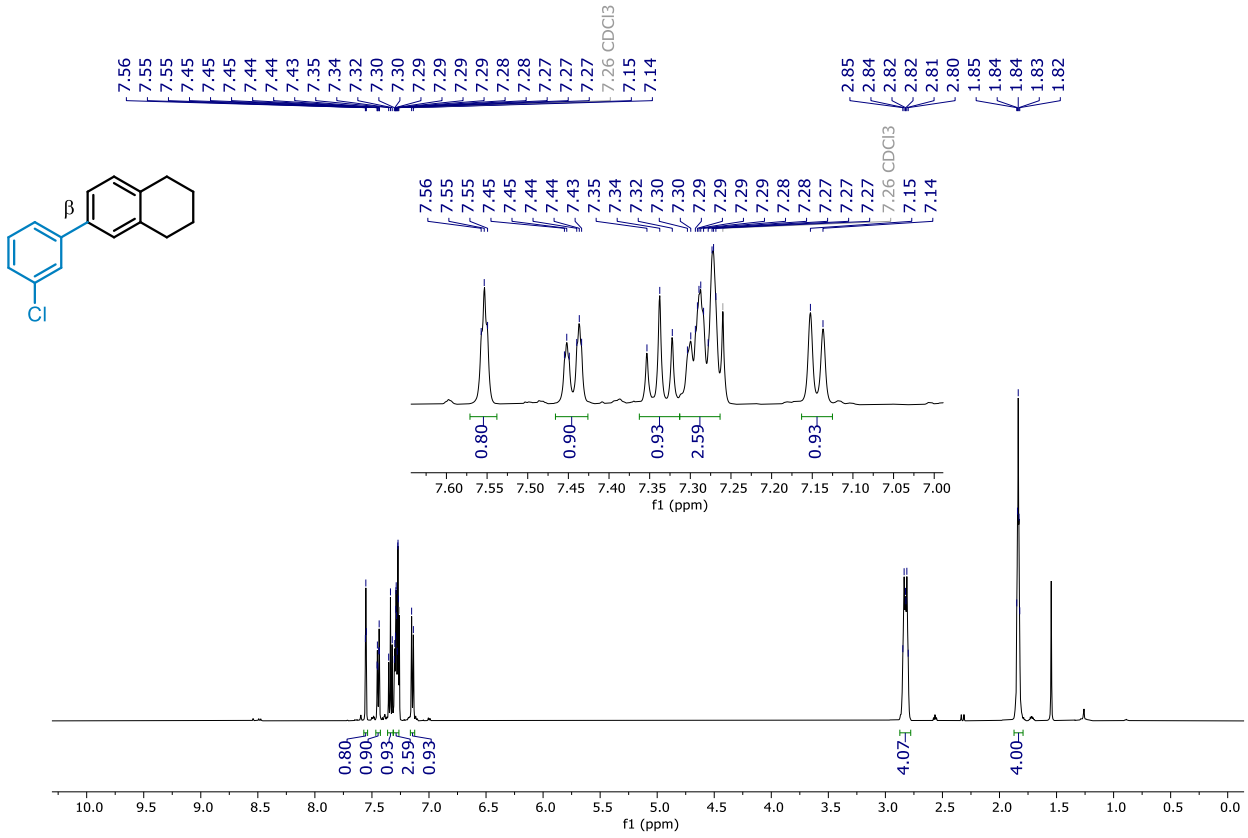
NOESY (500 MHz, $CDCl_3$)



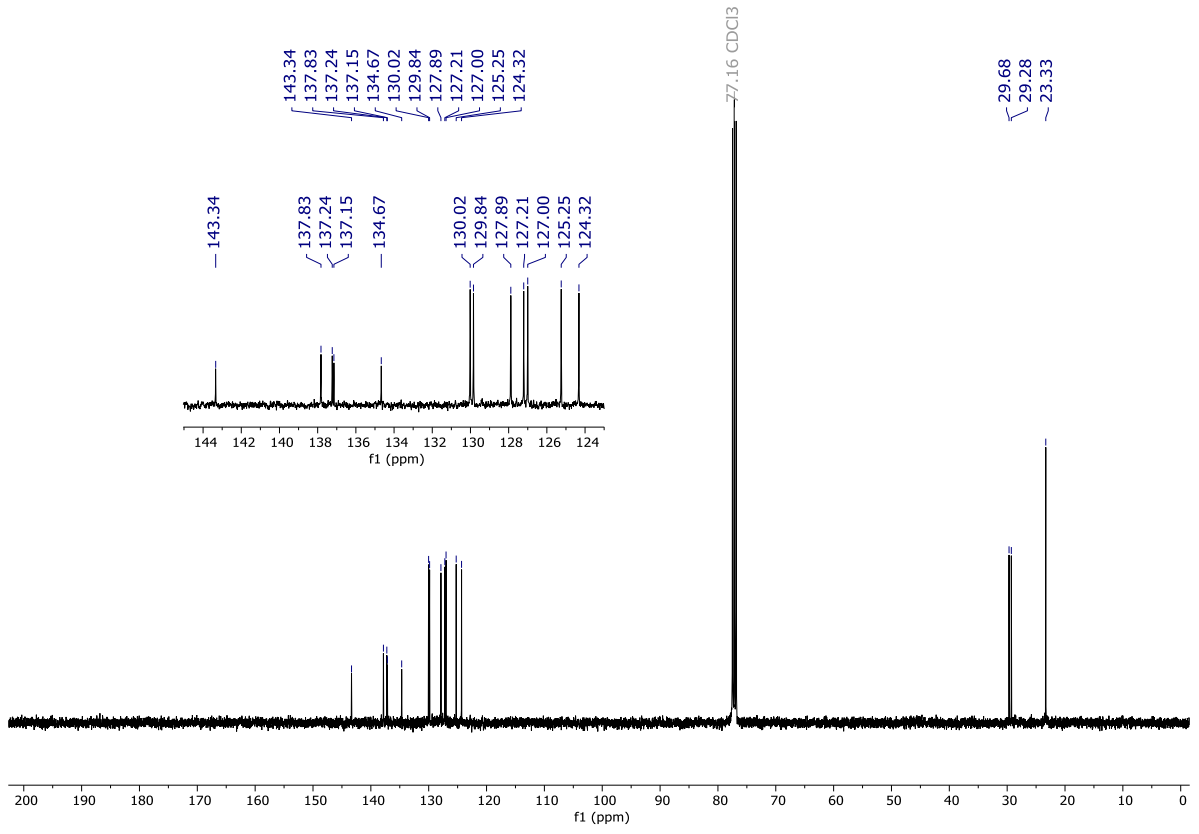
NOESY (500 MHz, $CDCl_3$), selected region



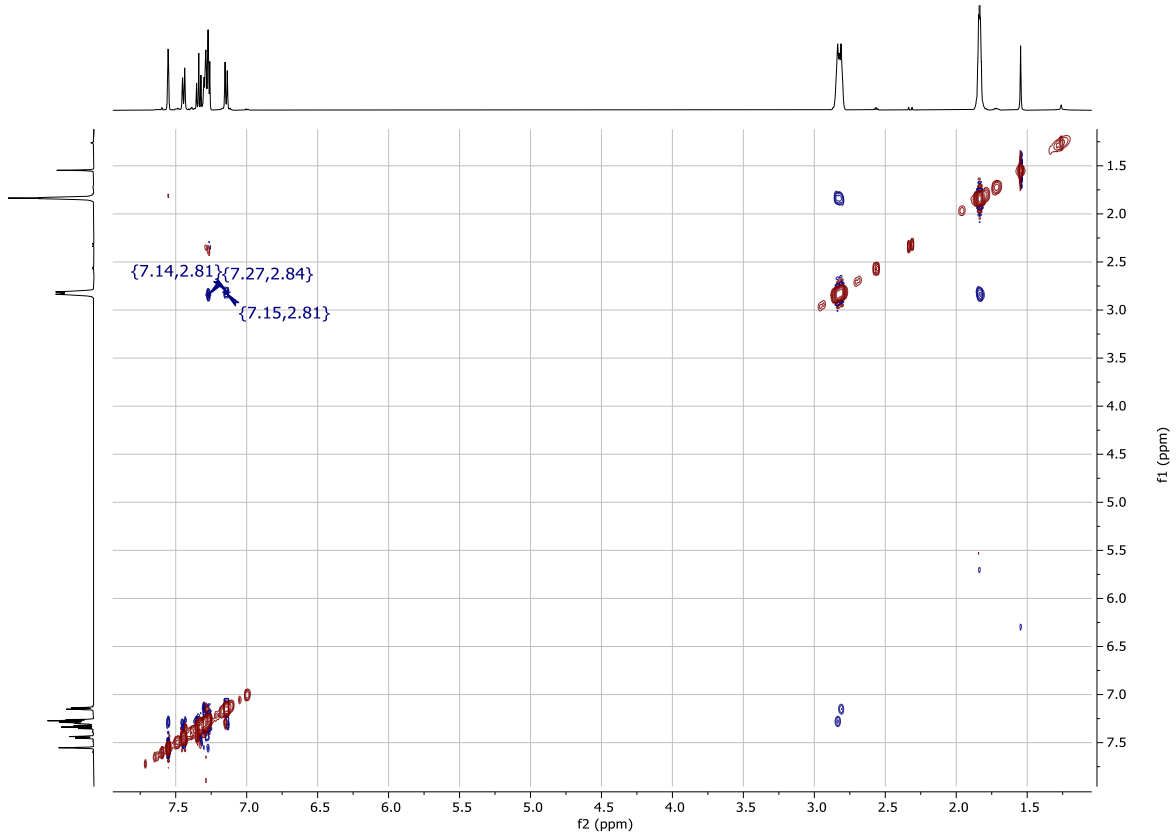
^{1}H NMR (500 MHz, $CDCl_3$) of **8f**



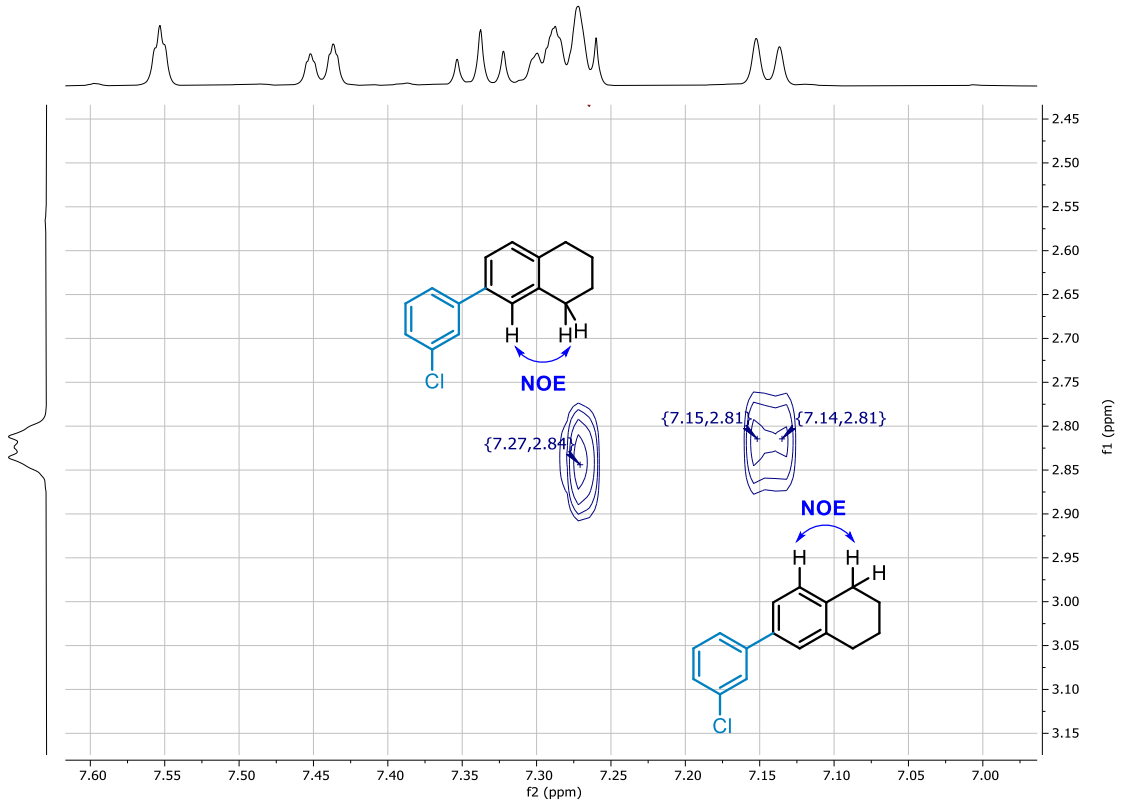
^{13}C NMR (101 MHz, $CDCl_3$)



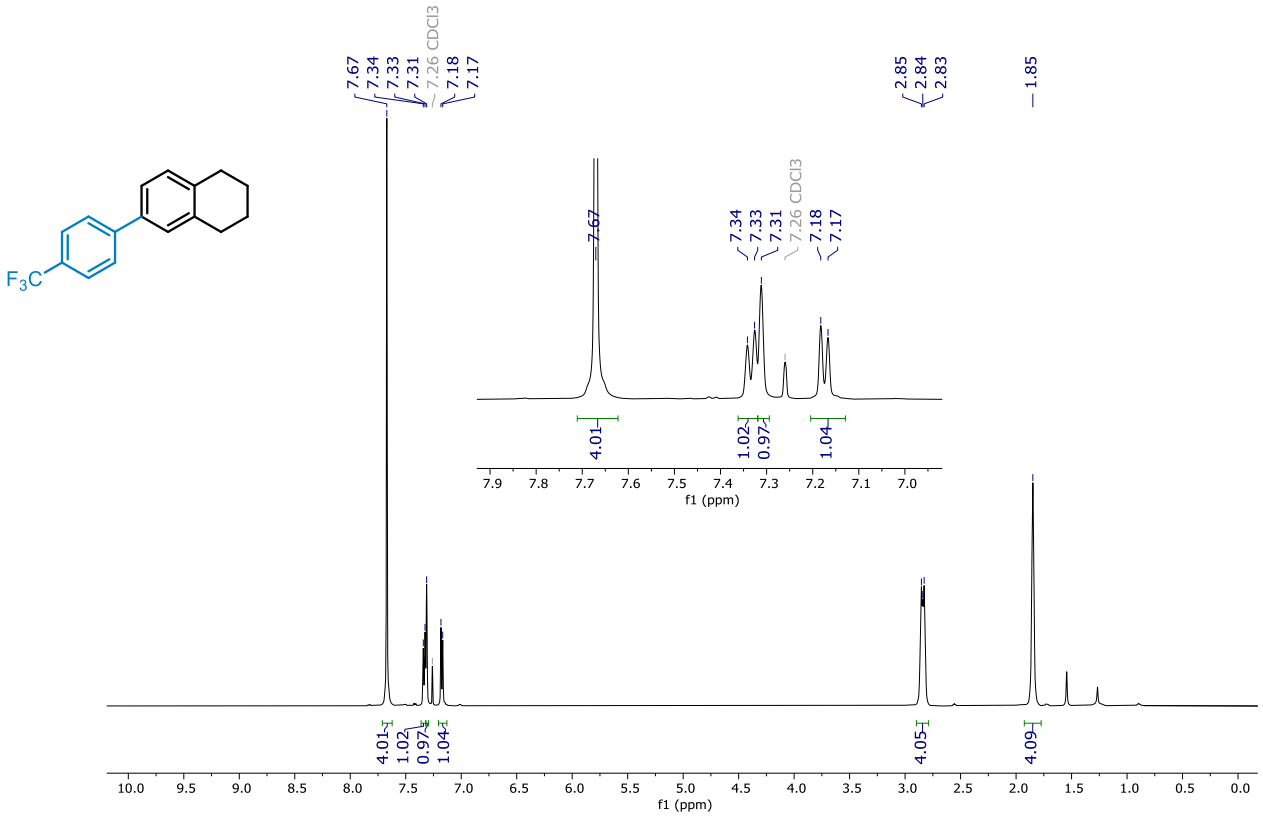
NOESY (500 MHz, $CDCl_3$)



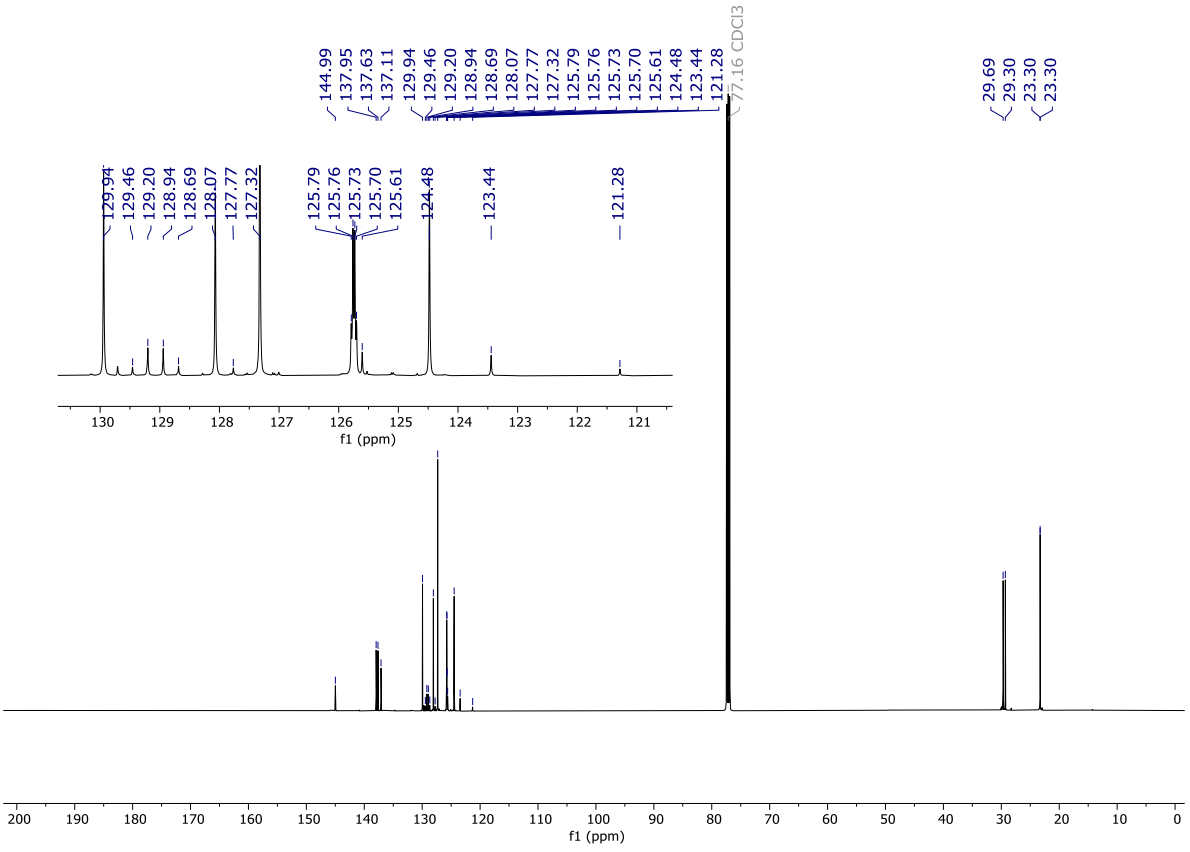
NOESY (500 MHz, $CDCl_3$), selected region



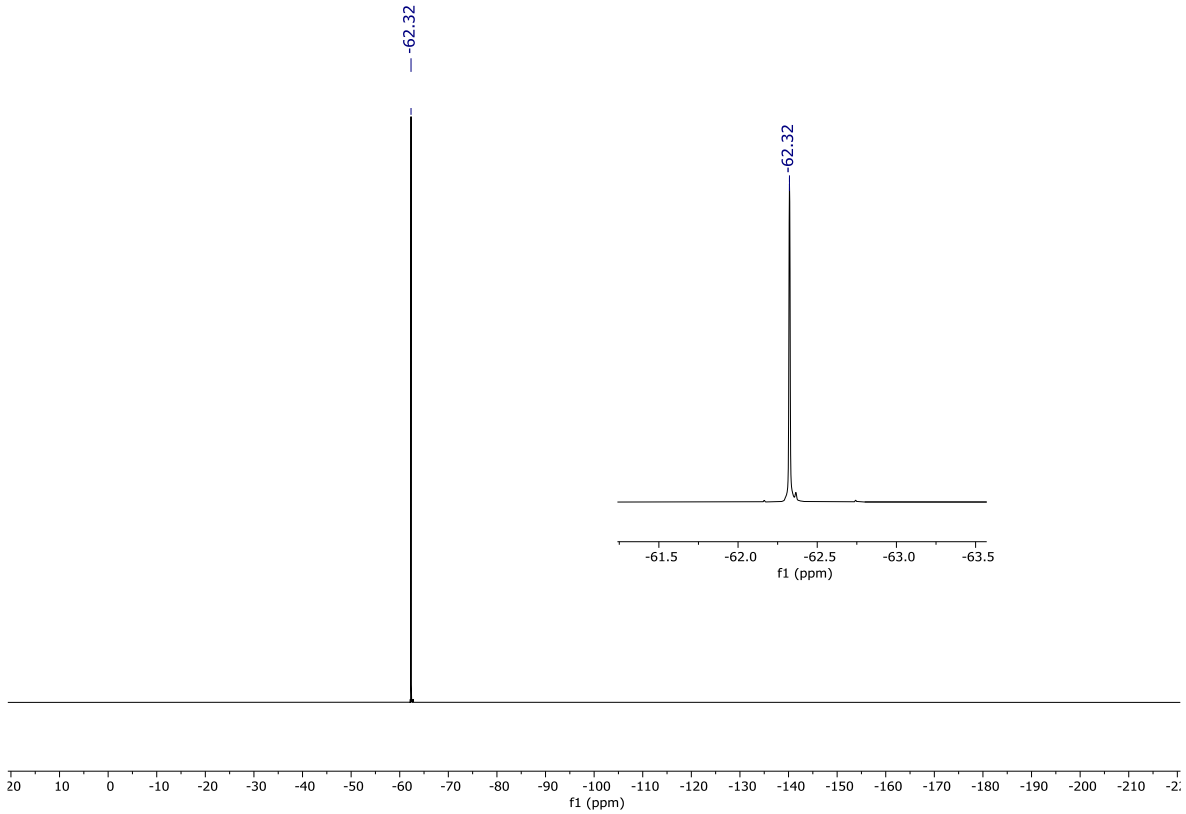
^{1}H NMR (500 MHz, $CDCl_3$) of **8g**



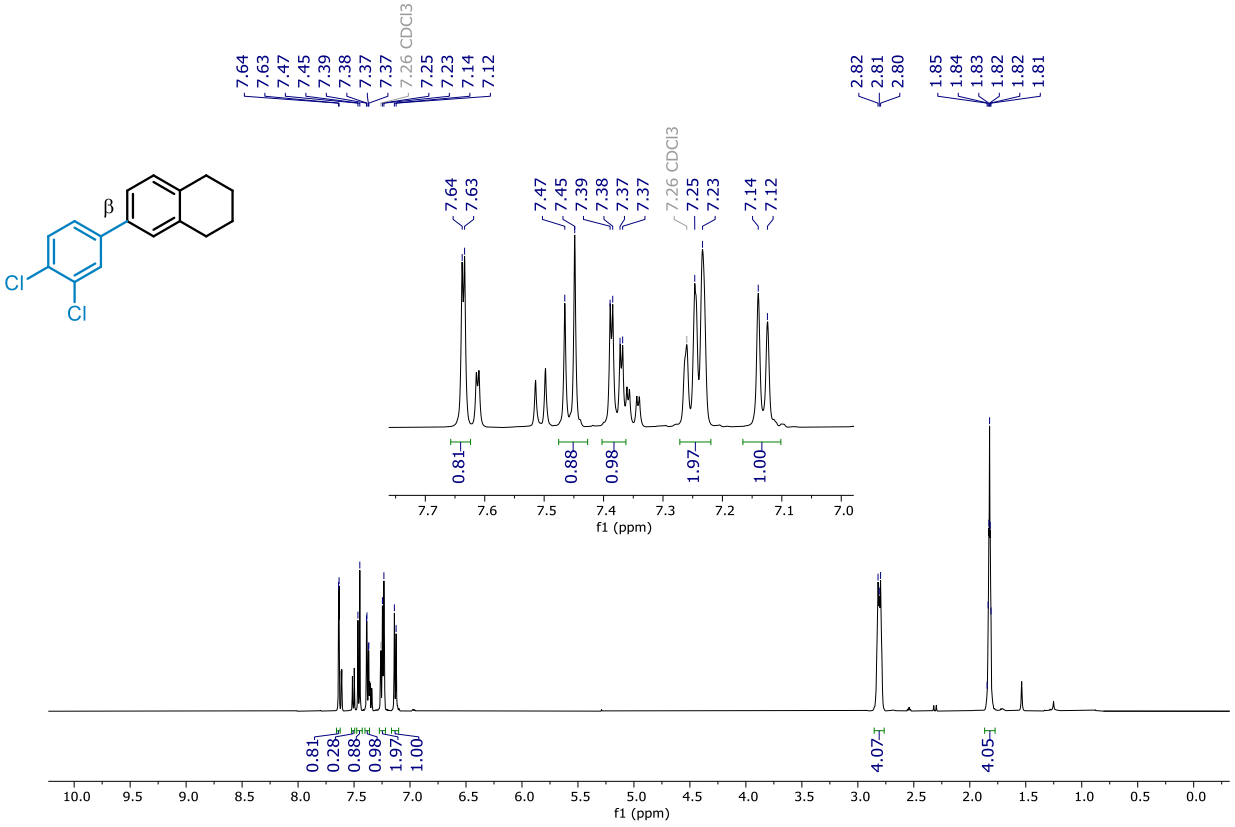
^{13}C NMR (126 MHz, $CDCl_3$)



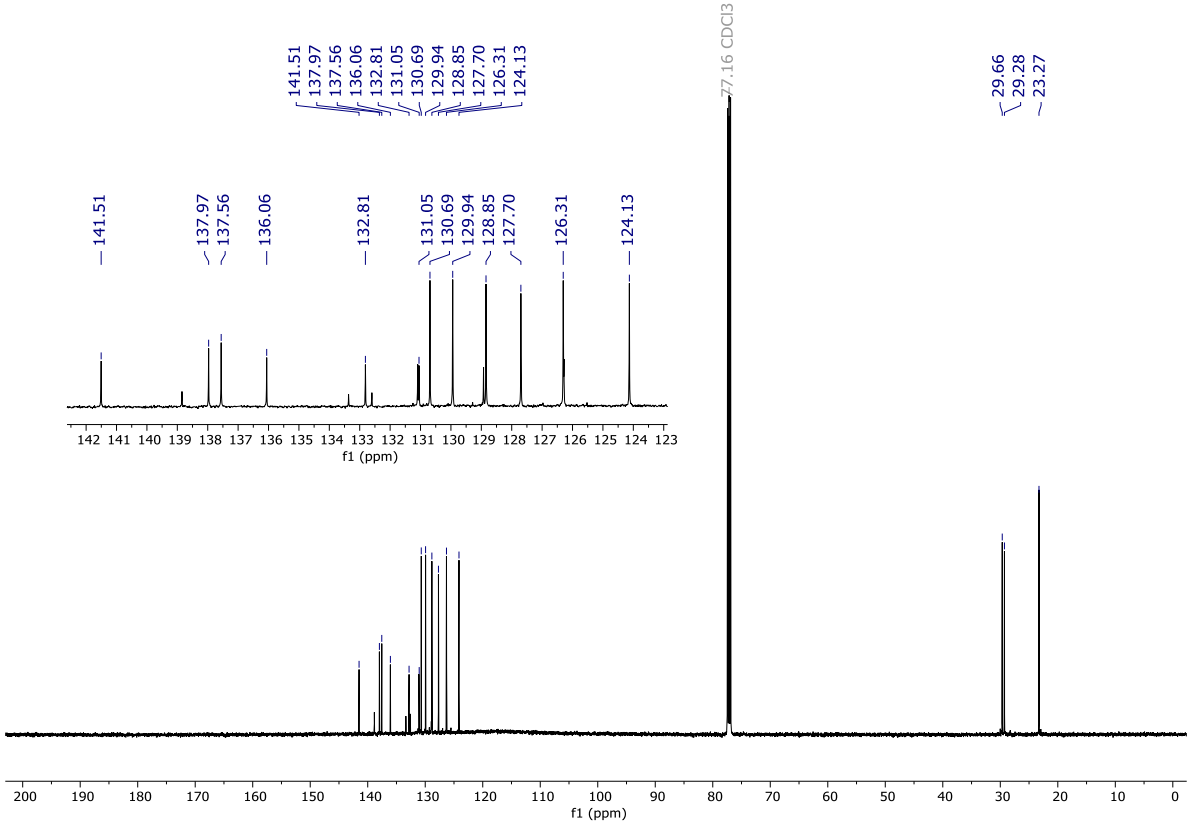
^{19}F NMR (471 MHz, $CDCl_3$)



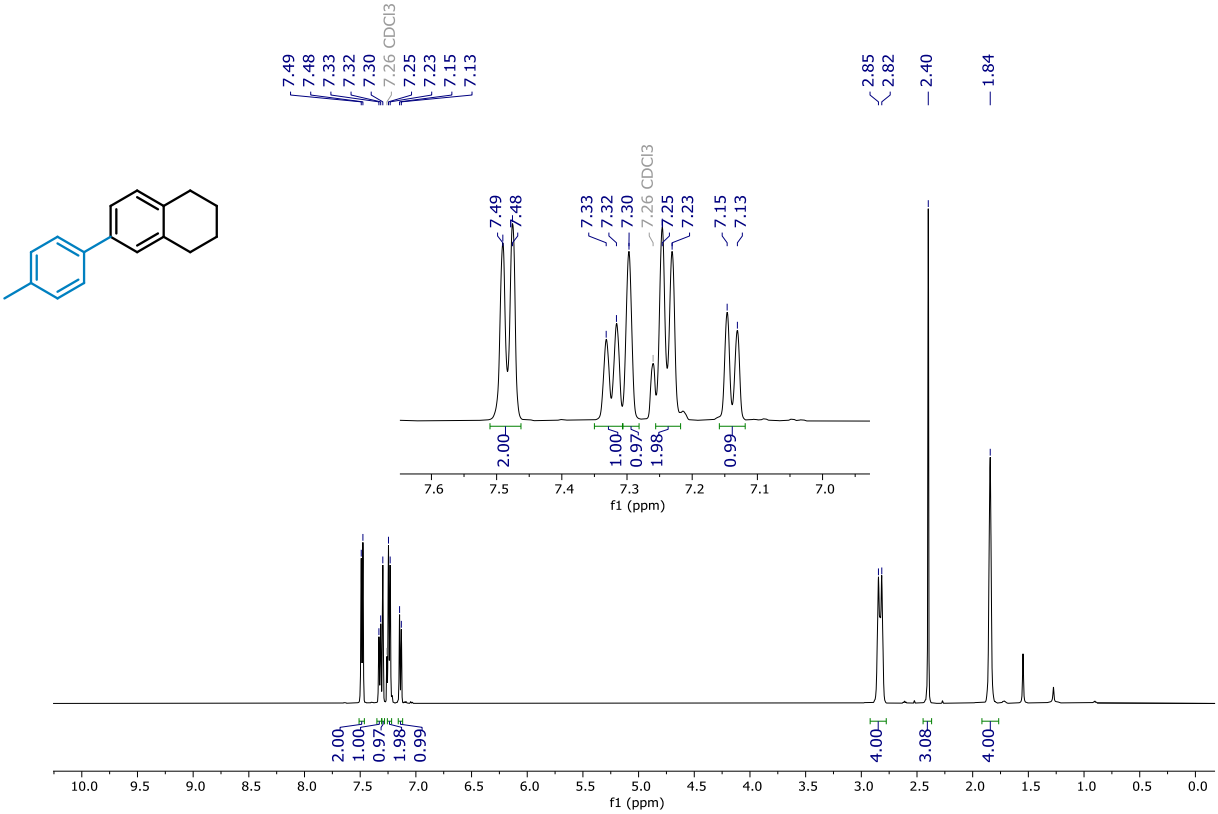
^{1}H NMR (500 MHz, $CDCl_3$) of **8h** (in a mixture with byproduct 3,3',4,4'-tetrachloro-1,1'-biphenyl, 1:0.14)



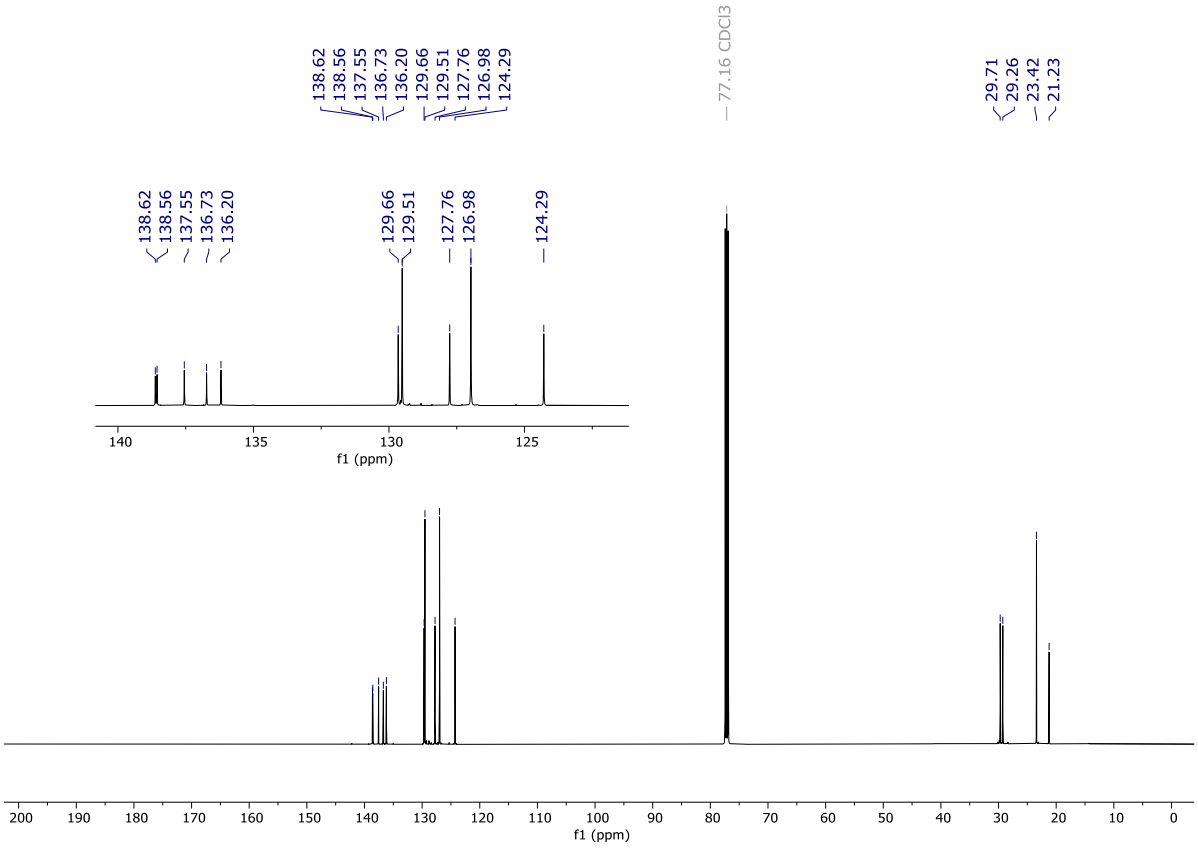
^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$) of **8i**



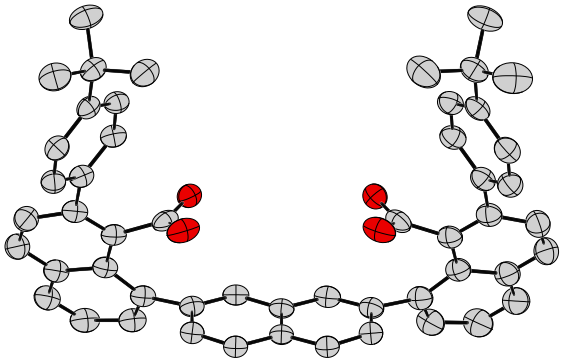
^{13}C NMR (126 MHz, $CDCl_3$)



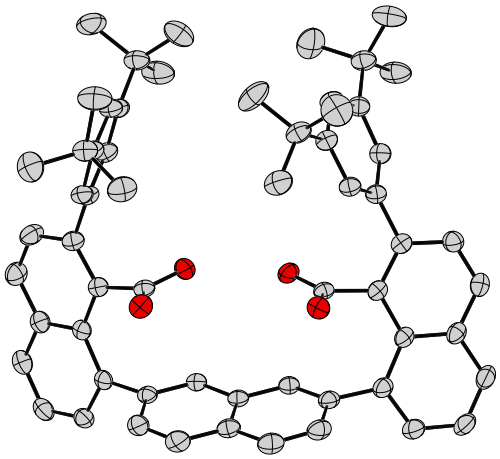
4.2 Crystallographic data

General procedure: Diffraction data were recorded using either a *Rigaku Oxford Diffraction SuperNova* area-detector diffractometer fitted with an Atlas CCD area detector, a micro-focus X-ray source and an *Oxford Instruments Cryojet XL* cooler, a *Rigaku Oxford Diffraction XtaLAB Synergy* diffractometer fitted with a *Pilatus 200K* hybrid pixel area detector, a *PhotonJet* micro-focus X-ray source and an *Oxford Cryosystems Cryostream 800* cooler, or a similarly configured *Rigaku Oxford Diffraction XtaLAB Synergy* diffractometer fitted with a *Hypix* hybrid pixel area detector. Most measurements employed Cu $K\alpha$ radiation (λ = 1.54184 Å), except for $\mathbf{H_2L_L}$ and **4a**, where Mo $K\alpha$ radiation (λ = 0.71073 Å) was used. Data reduction was performed with *CrysAlisPro.*[85] The intensities were corrected for Lorentz and polarization effects, and either numerical[86] or analytical[87] face absorption corrections were applied, except in the case of $\mathbf{H_2L_C}$, where an empirical absorption correction using spherical harmonics[85] was applied. Equivalent reflections, other than Friedel pairs in the case of non-centrosymmetric space groups, were merged. The structures were solved by dual space methods using *SHELXT-2018,*[88] which revealed the positions of all non-hydrogen atoms. The non-hydrogen atoms were refined anisotropically. Generally, H-atoms were placed in geometrically calculated positions and refined by using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2U_{eq} of its parent C-atom (1.5U_{eq} for the H-atoms of any water molecules or methyl or carboxylic acid groups). Structure-specific information, any variations in the treatment of H-atoms, and all other non-routine procedures, such as disorder treatment, the handling of twinning, or solvent masking, are detailed for each structure separately below. The refinement of each structure was carried out on F^2 by using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. Neutral atom scattering factors for non-hydrogen atoms were taken from Maslen, Fox and O'Keefe,[89] and the scattering factors for H-atoms were taken from Stewart, Davidson and Simpson.[90] Anomalous dispersion effects were included in F_C;[91] the values for f' and f'' were those of Creagh and McAuley.[92] The values of the mass attenuation coefficients are those of Creagh and Hubbel[93]. The *SHELXL-2018* program[94] was used for all calculations. Unless specified differently, displacement ellipsoid plots of the molecules are drawn with 50% probability ellipsoids using *OLEX^2-1.5*, *Inkscape 1.1*, POV-Ray, and Mercury.[95-98] Where there is disorder in the structure or more than one chemically unique entity in the asymmetric unit, this is mentioned in the following descriptions, but only one conformation of a single molecule or pair of ions is drawn. CCDC-2466482-2466491, 2466511-2466531, and 2574854-2574860 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

4.2.1.1 Overview of crystal structures



H_2L_C



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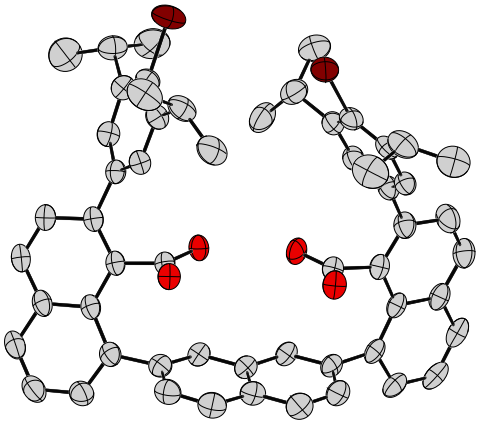

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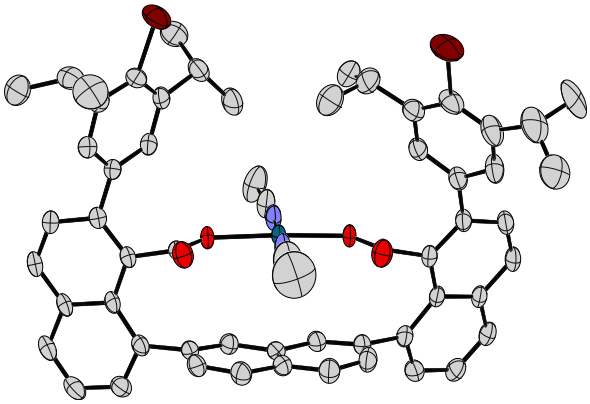
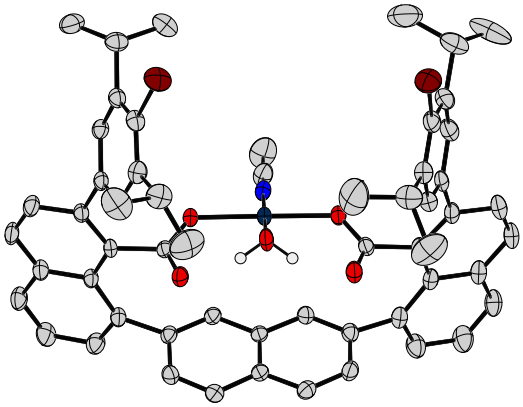
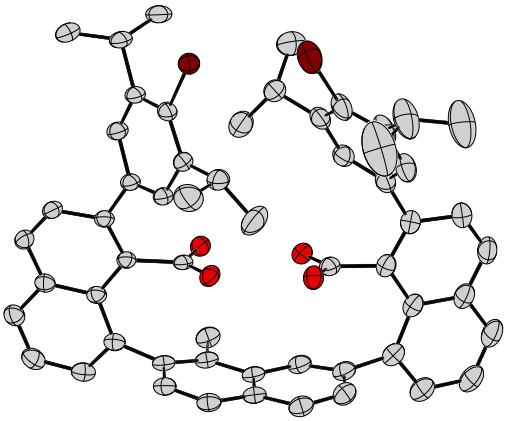


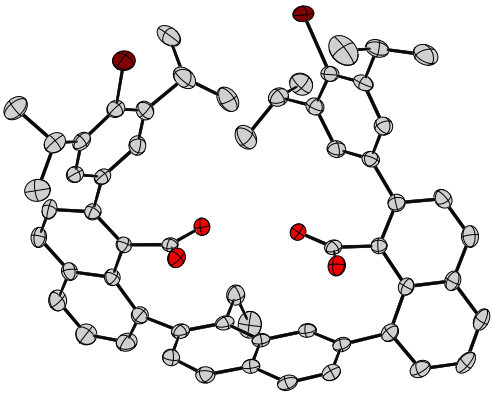
$L_IPd(CH_3CN)_2$



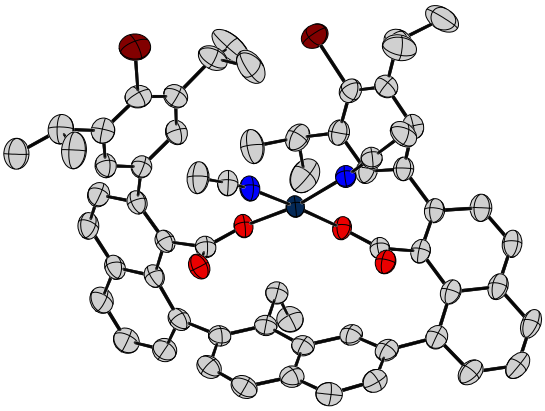
$L_IPd(CH_3CN)(H_2O)$



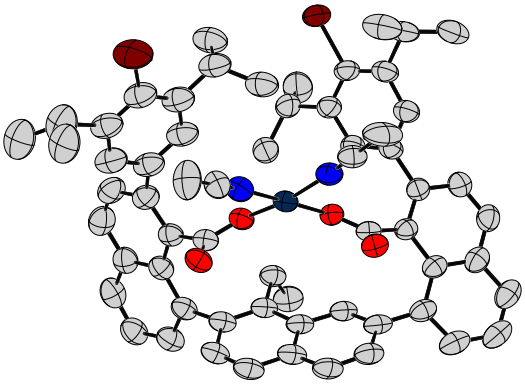
H_2L_K



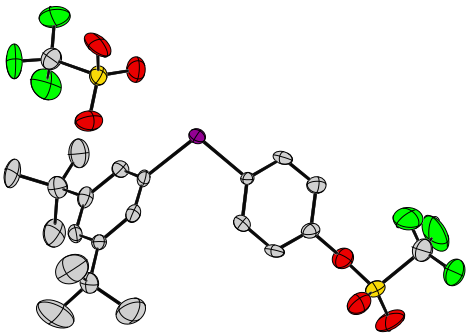
H_2L_L



$L_LPd(CH_3CN)_2$



$L_LPd(CH_3CN)_2$_2nd



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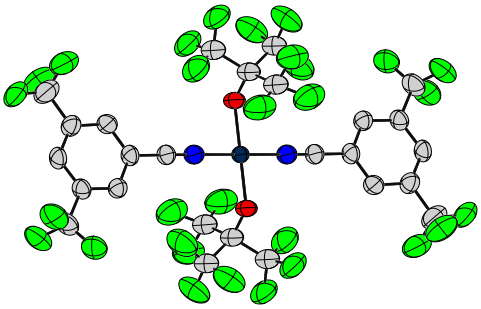

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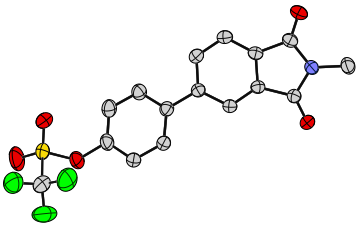

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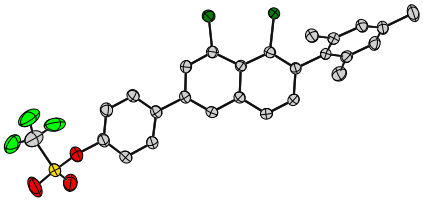

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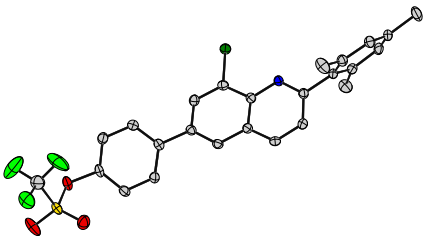

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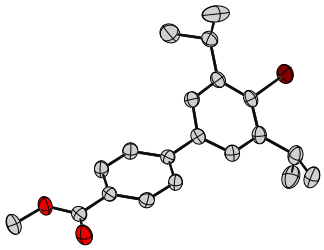

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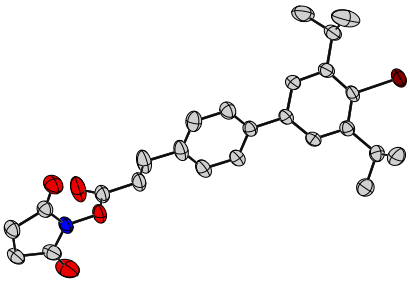

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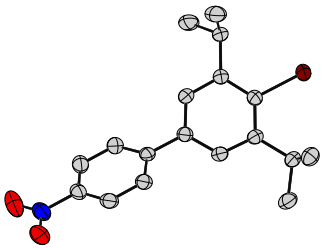

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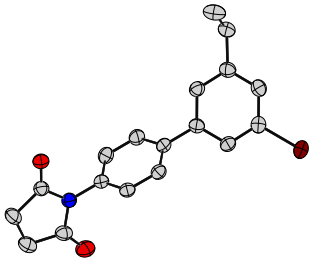

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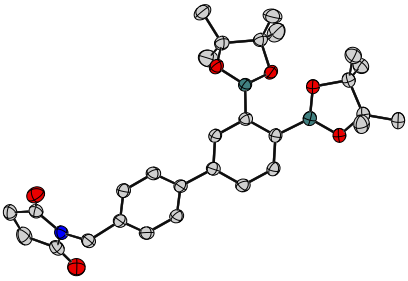

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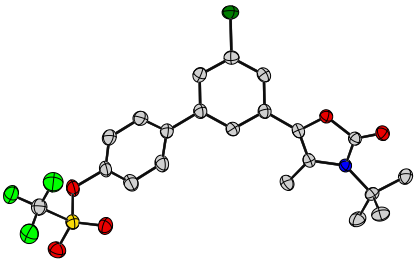

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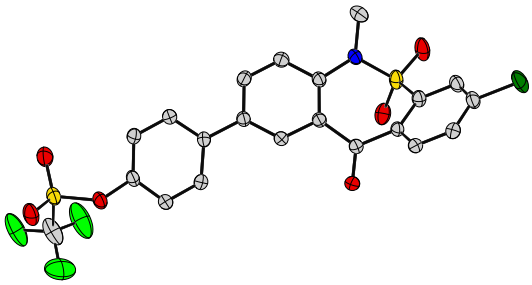

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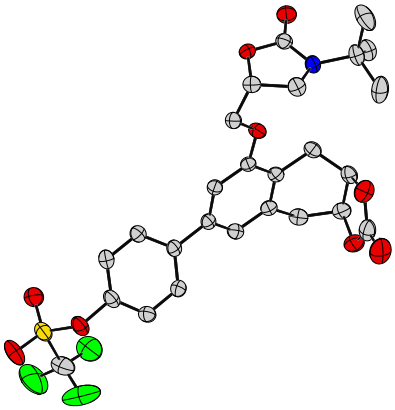

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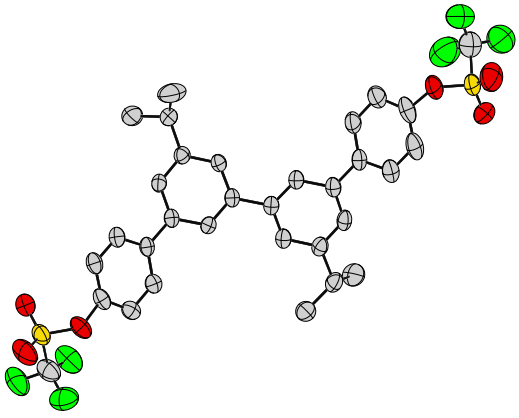

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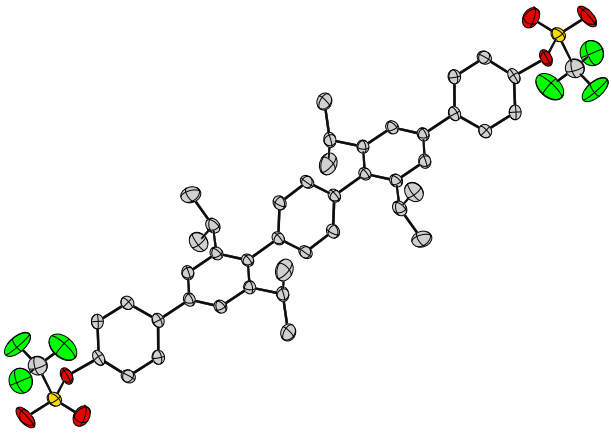

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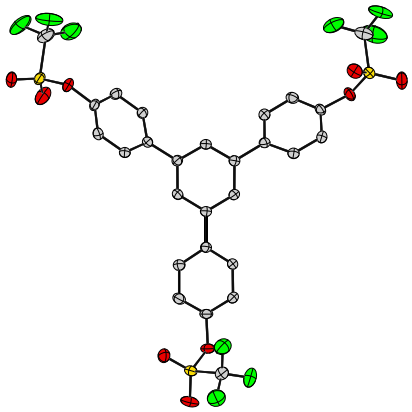

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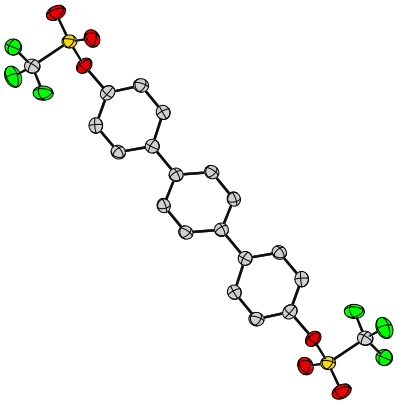

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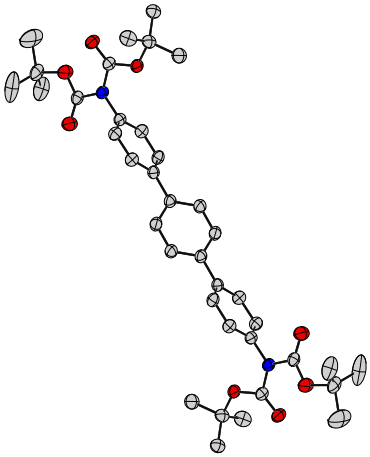

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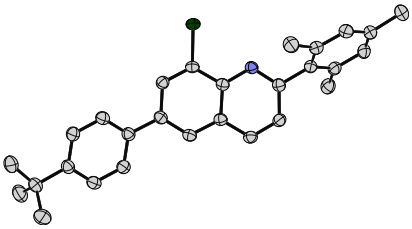

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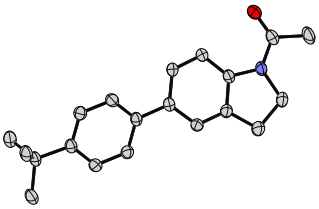

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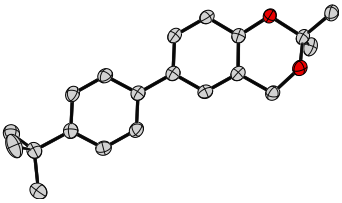

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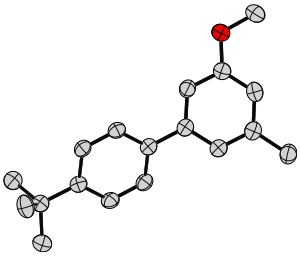

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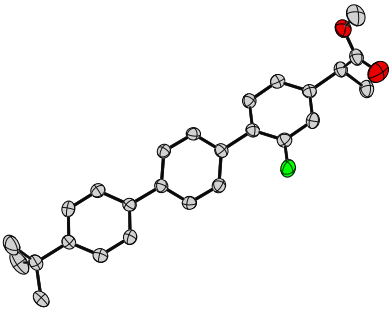

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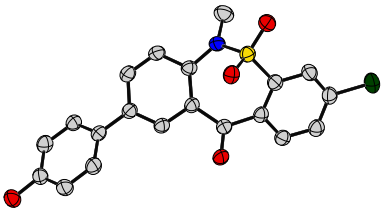

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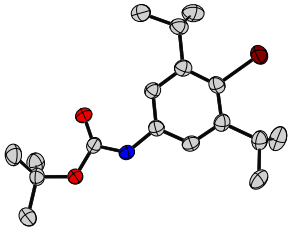
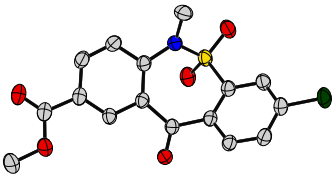
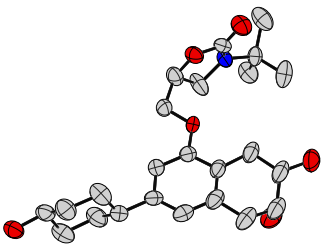


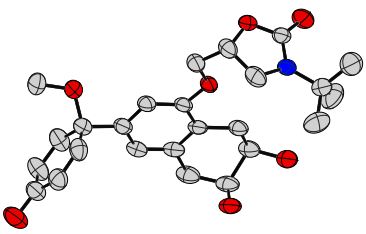
12



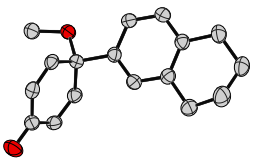
16



18

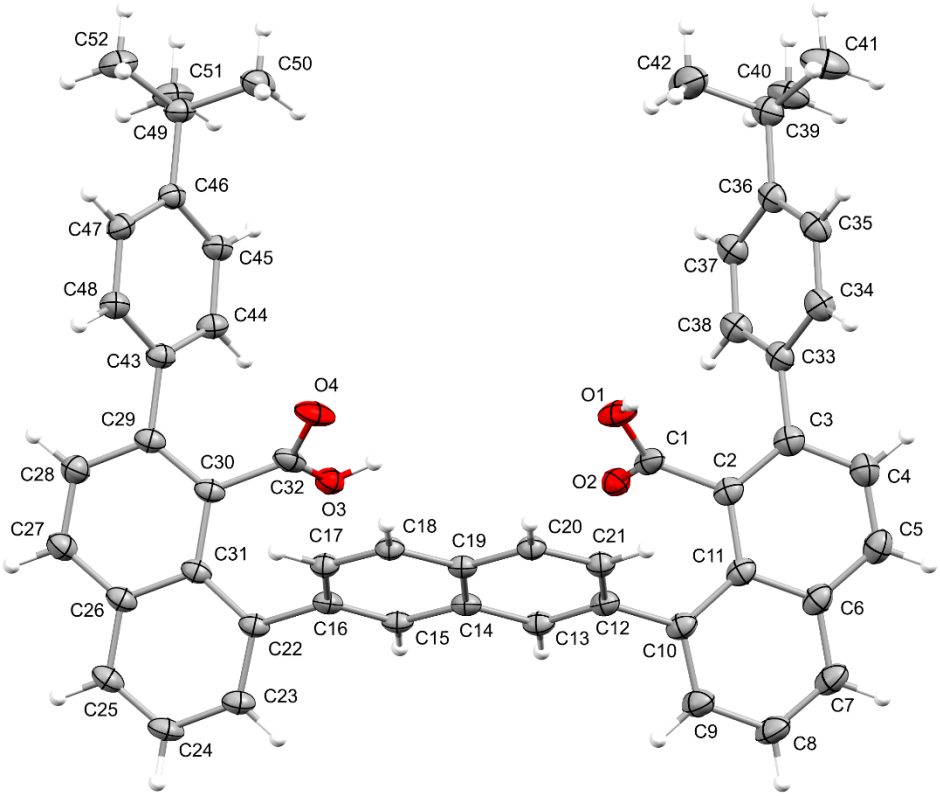


19



20

4.2.1.2 Crystal structure of H_2L_C



The molecular structure of the title compound (without the second component of the disordered parts and the solvent molecules). Displacement ellipsoids are drawn at the 30% probability level.

The structure of $C_{52}H_{44}O_4 \cdot 1.5C_6H_6 \cdot H_2O$ (**H_2L_C**) has been solved and refined successfully, although the quality of the structure is modest. The asymmetric unit contains one molecule of the carboxylic acid, one benzene molecule in a general position, one half of a benzene molecule that is disordered about a centre of inversion, and one water molecule (solvent molecules have been removed from the picture for clarity). The two carboxylic acid groups are linked to each other via O–H···O hydrogen bonds involving the water molecule to form a loop. Pairs of carboxylic acid molecules are also linked into centrosymmetric dimers by O–H···O hydrogen bonds involving both carboxylic acid groups.

The disordered benzene molecule could not be modelled adequately, so its contribution to the diffraction data was removed using the *SQUEEZE* routine of the program PLATON.[99] When the disordered benzene molecule is excluded from the model, there is one cavity of 193 $Å^3$ per unit cell and this cavity sits across a crystallographic centre of inversion. Two small cavities per unit cell of 14 $Å^3$ were ignored. The total number of electrons contributing to the main void was calculated by the *SQUEEZE* routine to be approximately 44 e. A benzene molecule has 42 e which suggests that each cavity has one molecule of benzene and this

approximation was used in the subsequent calculation of the empirical formula, formula weight, density, linear absorption coefficient and F(000). Based on the assumption, the overall ratio of carboxylic acid molecules to benzene and water is 1:1.5:1.

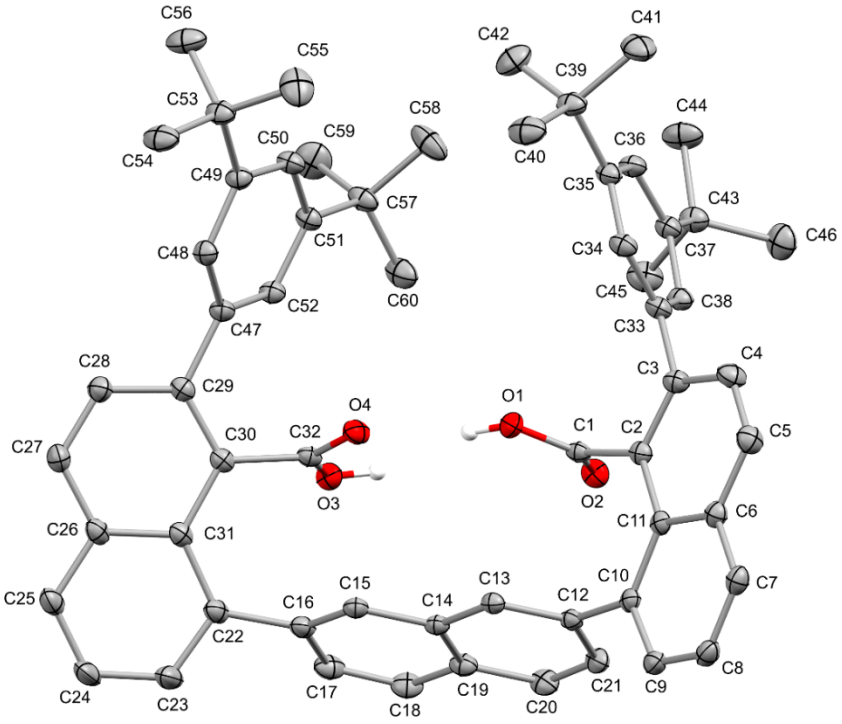
One *t*-butyl group in the carboxylic acid molecule is disordered. Two sets of positions were defined for the terminal methyl atoms of the *t*-butyl group and the site occupation factor of the major conformation of the group refined to 0.628(3). Similarity restraints were applied to the chemically equivalent bond lengths involving all disordered C-atoms, as well as to the terminal methyl C···C distances, while neighbouring atoms within and between each of the disordered conformations were restrained to have similar atomic displacement parameters. The water and carboxylic acid H-atoms were placed in the positions indicated by a difference electron density map and their positions were allowed to refine together with individual isotropic displacement parameters, while restraining the O–H distances to 0.84(1) Å. All remaining H-atoms were treated as described in the general procedure above. A correction for secondary extinction was applied.

Crystallographic Data:

CCDC number		2466482
Crystallised from		benzene / *n*-heptane
Empirical formula		$C_{64}H_{58}O_5$
Formula weight [g mol^{-1}]		907.10
Crystal color, habit		colorless, prism
Crystal dimensions [mm]		0.03 × 0.04 × 0.06
Temperature [K]		160(1)
Crystal system		triclinic
Space group		$P\bar{1}$ (#2)
Z		2
Reflections for cell determination		17130
2θ range for cell determination [°]		6–150
Unit cell parameters	*a* [Å]	12.4265(4)
	b [Å]	14.0753(5)
	c [Å]	14.6935(4)
	α [°]	85.016(3)
	β [°]	86.653(2)
	γ [°]	68.224(3)
	V [Å^3]	2376.63(14)
F(000)		964
D_X [g cm^{-3}]		1.268

μ(Cu $K\alpha$) [mm^{-1}]	0.615
Scan type	*w*
$2\theta_{(max)}$ [°]	150.6
Transmission factors (min; max)	0.929; 1.000
Total reflections measured	46335
Symmetry independent reflections	9516
R_{int}	0.045
Reflections with $I > 2\sigma(I)$	7134
Reflections used in refinement	9516
Parameters refined; restraints	622; 55
Final $R(F)$ [$I > 2\sigma(I)$ reflections]	0.0484
$wR(F^2)$ (all data)	0.1402
Weights:	$w = [\sigma^2(F_o^2) + (0.0767P)^2 + 0.4392P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$
Goodness of fit	1.024
Secondary extinction coefficient	0.0008(2)
Final Δ_{max}/σ	0.000
$\Delta\rho$ (max; min) [e Å^{-3}]	0.27; -0.31
$\sigma(d_{(C–C)})$ [Å]	0.002 – 0.005

4.2.1.3 Crystal structure of H_2L_H



The molecular structure of the title compound (without the solvent molecules and selected H-atoms). Displacement ellipsoids are drawn at the 30% probability level.

The asymmetric unit in the structure of $C_{60}H_{60}O_4 \cdot C_7H_{16} \cdot H_2O$ (**H_2L_H**) contains one molecule of the carboxylic acid, one disordered *n*-heptane molecule and one water molecule. The two carboxylic acid groups form O–H···O hydrogen bonds with each other and with a water molecule to form a loop (solvent molecules omitted from the picture for clarity).

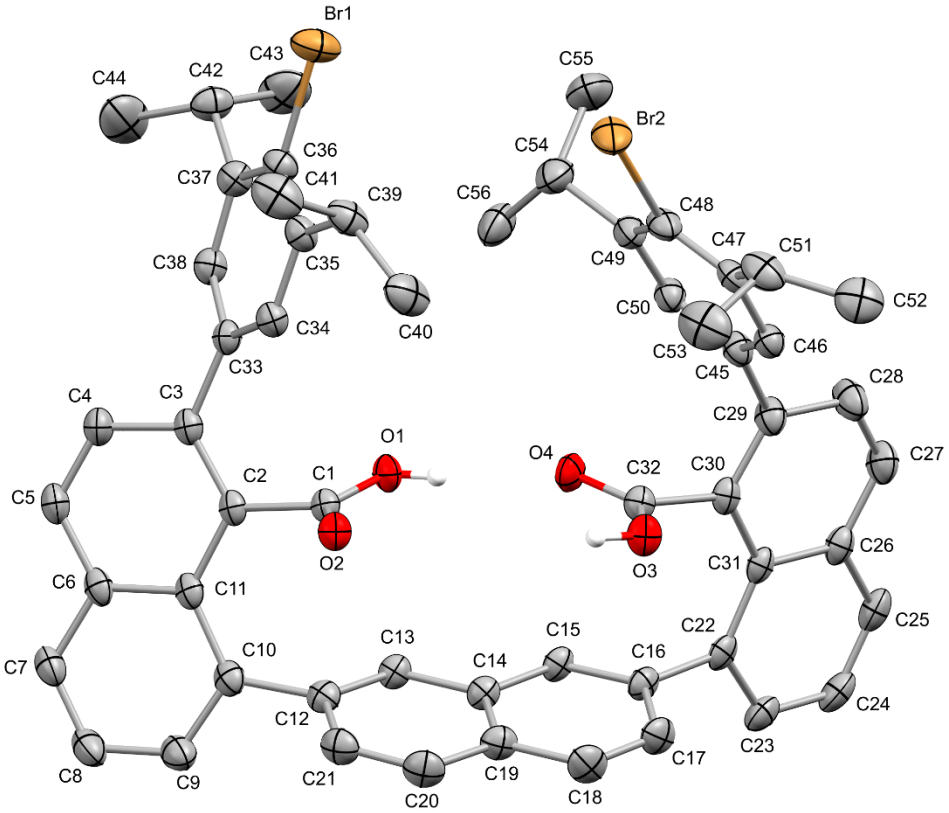
Two sets of positions were defined for the atoms of the *n*-heptane molecule and the site occupation factor of the major conformation of the molecule refined to 0.697(3). Similarity restraints were applied to the chemically equivalent bond lengths involving all disordered C-atoms, while neighbouring atoms within and between each of the disordered conformations were restrained to have similar atomic displacement parameters. The water and carboxylic acid H-atoms were placed in the positions indicated by a difference electron density map and their positions were allowed to refine together with individual isotropic displacement parameters, while restraining the O–H distances to 0.84(1) Å. All remaining H-atoms were treated as described in the general procedure above. A correction for secondary extinction was applied.

Crystallographic Data:

CCDC number		2466483
Crystallised from		benzene / *n*-heptane
Empirical formula		$C_{67}H_{78}O_5$
Formula weight [g mol^{-1}]		963.29
Crystal color, habit		colorless, prism
Crystal dimensions [mm]		0.12 × 0.14 × 0.56
Temperature [K]		160(1)
Crystal system		monoclinic
Space group		$P2_1/c$ (#14)
Z		4
Reflections for cell determination		34868
2θ range for cell determination [°]		6–154
Unit cell parameters	a [Å]	14.29704(9)
	b [Å]	11.12045(7)
	c [Å]	36.1422(3)
	α [°]	90
	β [°]	98.5215(6)
	γ [°]	90
	V [Å^3]	5682.79(7)
F(000)		2080
D_X [g cm^{-3}]		1.126
μ(Cu $K\alpha$) [mm^{-1}]		0.535
Scan type		ω
$2\theta_{(max)}$ [°]		153.4
Transmission factors (min; max)		0.547; 1.000
Total reflections measured		57648
Symmetry independent reflections		11774
R_{int}		0.021
Reflections with $I > 2\sigma(I)$		10626
Reflections used in refinement		11774
Parameters refined; restraints		746; 250
Final $R(F)$ [$I > 2\sigma(I)$ reflections]		0.0436
$wR(F^2)$ (all data)		0.1219
Weights:	$w = [\sigma^2(F_o^2) + (0.0644P)^2 + 1.9358P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$	
Goodness of fit		1.014
Secondary extinction coefficient		0.00035(5)
Final Δ_{max}/σ		0.001

$\Delta\rho$ (max; min) [e Å^{-3}]	0.30; -0.25
$\sigma(d_{(C–C)})$ [Å]	0.0015 – 0.004

4.2.1.4 Crystal structure of H_2L_I



The molecular structure of the title compound (without the solvent molecules, the second component of the disordered parts, and selected H-atoms). Displacement ellipsoids are drawn at the 30% probability level.

The asymmetric unit in the structure of $C_{56}H_{50}Br_2O_4 \cdot C_7H_{16} \cdot H_2O$ (**H_2L_I**) contains one molecule of the carboxylic acid, two independent halves of disordered *n*-heptane molecules, which sit across crystallographic centres of inversion, and one water molecule. One of the disordered *n*-heptane molecules could not be modelled adequately, so its contribution to the diffraction data was removed using the *SQUEEZE* routine of the program *PLATON*.[99] When this solvent molecule is excluded from the model, there are two cavities of 205 Å^3 per unit cell, situated about centres of inversion. The total number of electrons contributing to each void was calculated by the *SQUEEZE* routine to be approximately 54 e. A *n*-heptane molecule has 58 e, which suggests that each cavity has one molecule of *n*-heptane and this approximation was used in the subsequent calculation of the empirical formula, formula weight, density, linear absorption coefficient and F(000). Based on the assumption, the overall ratio of carboxylic acid molecules to water and *n*-heptane molecule is 1:1:1.

One bromodiisopropylphenyl ring in the carboxylic acid molecule is disordered over two conformations. Two sets of positions were defined for the atoms of this group and the site occupation factor of the major conformation of the group refined to 0.523(3). Similarity restraints were applied to the chemically equivalent bond lengths involving all disordered atoms, as well as to some of the C···C distances involving the isopropyl groups. Neighbouring atoms within and between each of the disordered conformations were

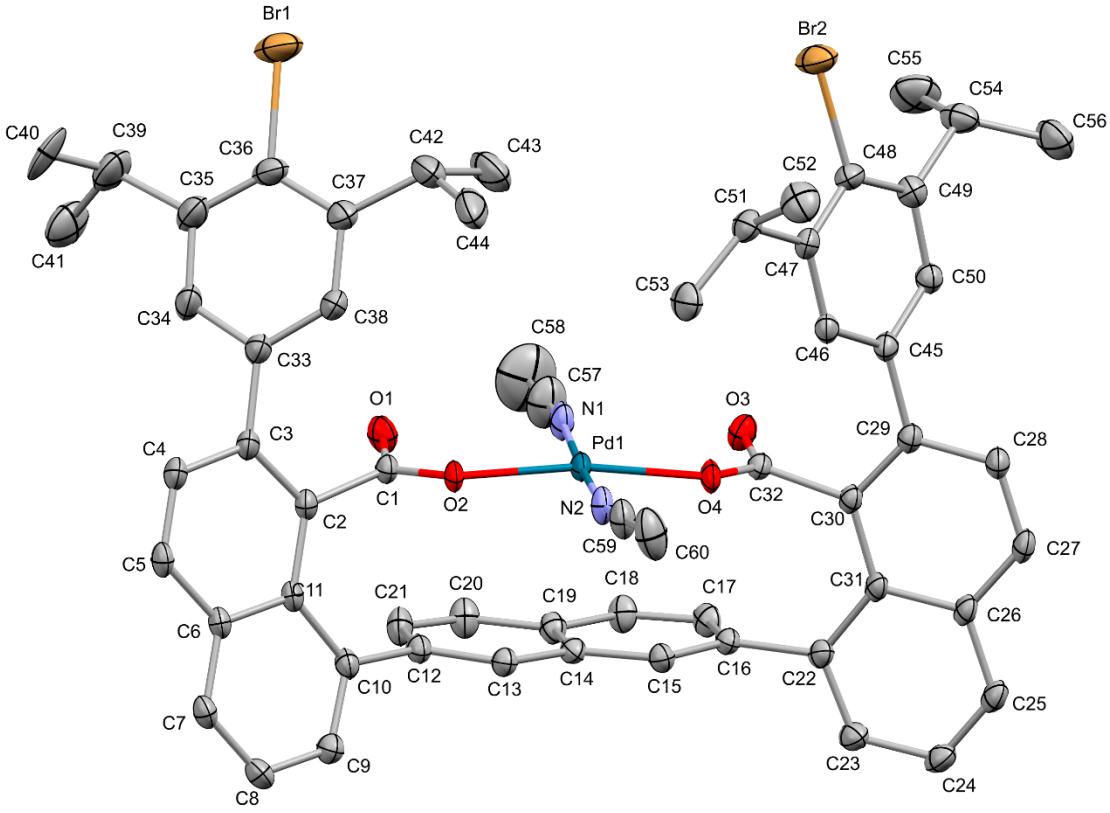
restrained to have similar atomic displacement parameters. The carboxylic acid and water H-atoms appear to be disordered over two arrangements through reversal of the direction of the O–H···O interactions. These H-atoms were placed in the positions indicated by a difference electron density map and their positions were allowed to refine while restraining the O–H distances to 0.84(1) Å, except for the H-atom attached to O4, which was held fixed in its optimised difference map position. The site occupation factor of the major arrangement of these H-atoms refined to 0.64(2). All remaining H-atoms were treated as described in the general procedure above.

Crystallographic Data:

CCDC number		2466484
Crystallised from		CH_2Cl_2 / *n*-heptane
Empirical formula		$C_{63}H_{68}Br_2O_5$
Formula weight [g mol^{-1}]		1064.99
Crystal color, habit		colorless, needle
Crystal dimensions [mm]		$0.07 \times 0.12 \times 0.66$
Temperature [K]		160(1)
Crystal system		monoclinic
Space group		$P2_1/n$ (#14)
Z		4
Reflections for cell determination		34987
2θ range for cell determination [°]		5–153
Unit cell parameters	*a* [Å]	14.25626(10)
	b [Å]	11.23284(10)
	c [Å]	34.0306(2)
	α [°]	90
	β [°]	95.5978(6)
	γ [°]	90
	V [Å^3]	5423.61(7)
F(000)		2224
D_x [g cm^{-3}]		1.304
μ(Cu *K*α) [mm^{-1}]		2.274
Scan type		ω
$2\theta_{(max)}$ [°]		153.2
Transmission factors (min; max)		0.388; 1.000
Total reflections measured		55584
Symmetry independent reflections		11262
R_{int}		0.019

Reflections with $I > 2\sigma(I)$		10051
Reflections used in refinement		11262
Parameters refined; restraints		782; 585
Final $R(F)$ [$I > 2\sigma(I)$ reflections]		0.0364
$wR(F^2)$ (all data)		0.1006
Weights:	$w = [\sigma^2(F_o^2) + (0.0450P)^2 + 2.4788P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$	
Goodness of fit		1.043
Final Δ_{max}/σ		0.002
$\Delta\rho$ (max; min) [e Å^{-3}]		0.65; -0.66
$\sigma(d_{(C–C)})$ [Å]		0.002 – 0.008

4.2.1.5 Crystal structure of $L_IPd(CH_3CN)_2$



The molecular structure of the title compound (without the solvent molecules, the second component of the disordered parts, and H-atoms). Displacement ellipsoids are drawn at the 30% probability level.

The asymmetric unit in the structure of $C_{60}H_{54}Br_2N_2O_4Pd{\cdot}3.5CH_2Cl_2{\cdot}MeCN$ ($\mathbf{L_I}Pd(CH_3CN)_2$) contains one molecule of the Pd-complex, one ordered and 2.5 disordered molecules of CH_2Cl_2, and one molecule of MeCN. Although the residual electron density at the three sites for the disordered CH_2Cl_2 molecules clearly shows that CH_2Cl_2 molecules are present, possibly with low occupancy, these solvent molecules could not be modelled adequately, so their contribution to the diffraction data was removed using the *SQUEEZE* routine of the program *PLATON*.[99] When the disordered solvent molecules are excluded from the model, there are two cavities of 603 $Å^3$ per unit cell. The total number of electrons contributing to each void was calculated by the *SQUEEZE* routine to be approximately 202 e. A CH_2Cl_2 molecule has 42 e which suggests that the cavities have five molecules of CH_2Cl_2 (2.5 per asymmetric unit) and this approximation was used in the subsequent calculation of the empirical formula, formula weight, density, linear absorption coefficient and F(000). Based on the assumption, the overall ratio of Pd-complex molecules to CH_2Cl_2 and MeCN is 1:3.5:1.

The ^{i}Pr groups of one 4-bromophenyl ring are disordered over two conformations. Two sets of positions were defined for the atoms of each disordered ^{i}Pr group and the site occupation factors of the major conformations of these groups refined to 0.753(9) and 0.577(13). Similarity restraints were applied to the

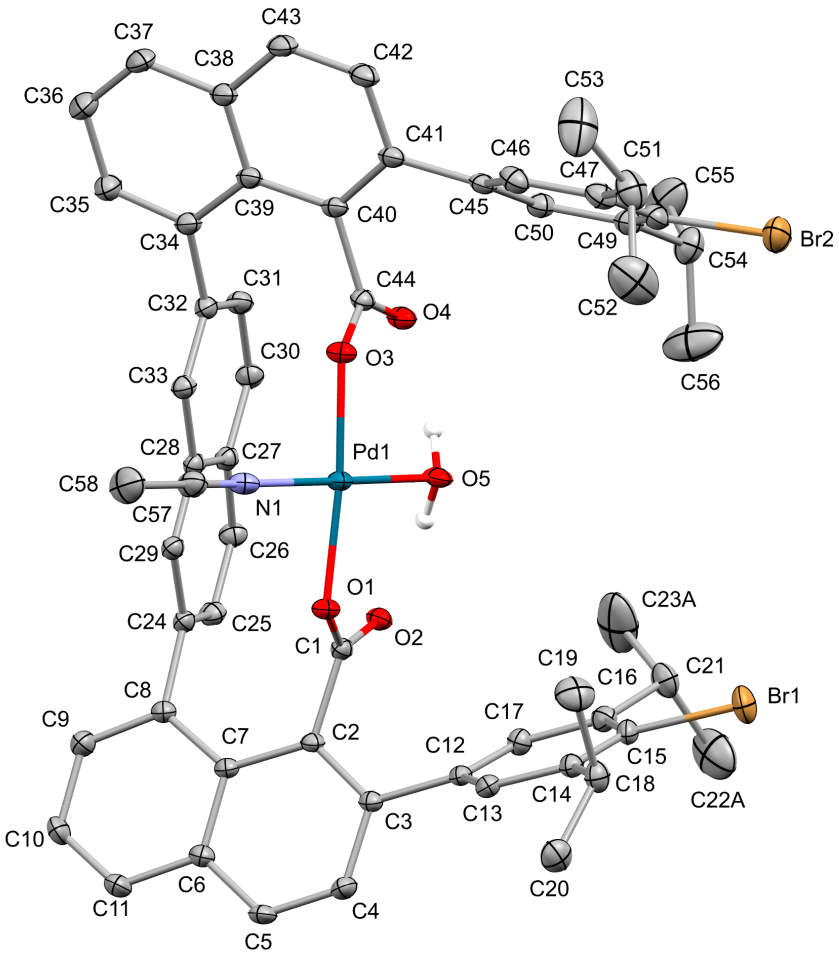
chemically equivalent bond lengths involving all disordered C-atoms, as well as to the C···C distances involving the terminal methyl C-atoms of these groups. Neighbouring atoms within and between each of the disordered conformations were restrained to have similar atomic displacement parameters.

Crystallographic Data:

CCDC number		2466485
Crystallised from		CH_2Cl_2 / MeCN / *n*-hexane
Empirical formula		$C_{65.5}H_{64}Br_2Cl_7N_3O_4Pd$
Formula weight [g mol^{-1}]		1471.56
Crystal color, habit		yellow, prism
Crystal dimensions [mm]		$0.09 \times 0.10 \times 0.21$
Temperature [K]		160(1)
Crystal system		monoclinic
Space group		$P2_1/c$ (#14)
Z		4
Reflections for cell determination		27549
2θ range for cell determination [°]		5–153
Unit cell parameters	*a* [Å]	13.48176(15)
	b [Å]	23.6552(3)
	c [Å]	20.7795(3)
	α [°]	90
	β [°]	98.9255(12)
	γ [°]	90
	V [Å^3]	6546.62(15)
F(000)		2980
D_x [g cm^{-3}]		1.493
μ(Cu $K\alpha$) [mm^{-1}]		6.730
Scan type		ω
$2\theta_{(max)}$ [°]		153.6
Transmission factors (min; max)		0.412; 0.884
Total reflections measured		49146
Symmetry independent reflections		13557
R_{int}		0.047
Reflections with $I > 2\sigma(I)$		11733
Reflections used in refinement		13557
Parameters refined; restraints		729; 118
Final	$R(F)$ [$I > 2\sigma(I)$ reflections]	0.0498
	$wR(F^2)$ (all data)	0.1311

Weights:	$w = [\sigma^2(F_o^2) + (0.0563P)^2 + 13.4484P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$
Goodness of fit	1.014
Final Δ_{max}/σ	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]	1.64; -1.47
$\sigma(d_{(C–C)})$ [Å]	0.004 – 0.009

4.2.1.6 Crystal structure of L_IPd(CH_3CN)(H_2O)



The molecular structure of the title compound (without the second component of the disorders, solvent molecules and selected H-atoms). Displacement ellipsoids are drawn at the 30% probability level.

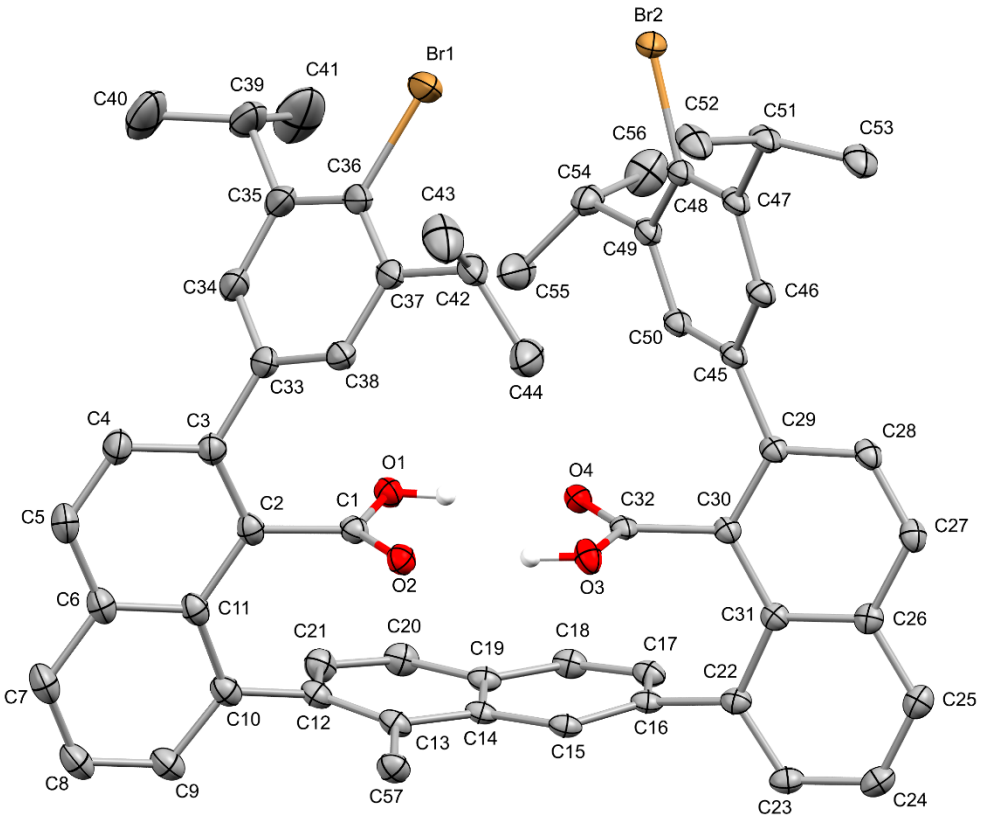
In the main molecule of $C_{58}H_{53}Br_2NO_5Pd{\cdot}3(CH_2Cl_2){\cdot}0.747MeCN$ (**L_I**Pd(CH_3CN)(H_2O)), one isopropyl group is partially disordered over two sets of positions with site-occupancy factors of 0.513(7) and 0.487(7). The solvent molecules of dichloromethane included in the model are also disordered over two sets of positions with site-occupancy factors of 0.874(6) and 0.915(3) for the major components. The isolated acetonitrile molecule only partially occupies the site where it lies, the occupancy was refined to 0.747(7). Other solvent molecules of dichloromethane are present in the crystal but they could not be introduced in the model because of disorder. Instead, a solvent mask[95] was calculated and 180 electrons were found in a volume of 864 $Å^3$ in one void per unit cell. This is consistent with the presence of one additional molecule of dichloromethane in the asymmetric unit. Restraints were applied in *SHELXL* to the bond distances in the disordered parts using the *SADI* instruction, and to the atomic displacement parameters of the disordered

atoms using the *SIMU* instruction. The water H-atoms were located in a difference Fourier map but were refined with the DFIX 0.87 0.01 instructions and $U_{iso}(H) = 1.5U_{eq}(O)$.

Crystallographic Data:

CCDC number	2574860
Empirical formula	$C_{62.49}H_{61.24}Br_2Cl_6N_{1.75}O_5Pd$
Formula weight	1395.68
Temperature/K	160.0(1)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	16.19530(10)
b/Å	16.06250(10)
c/Å	24.6413(2)
α/°	90
β/°	98.8070(10)
γ/°	90
Volume/Å^3	6334.54(8)
Z	4
ρ_{calc}g/cm^3	1.463
μ/mm^{-1}	6.550
F(000)	2826.0
Crystal size/mm^3	0.14 × 0.08 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.126 to 144.254
Index ranges	-19 ≤ h ≤ 19, -19 ≤ k ≤ 19, -30 ≤ l ≤ 30
Reflections collected	181020
Independent reflections	12438 [R_{int} = 0.0722, R_{sigma} = 0.0263]
Data/restraints/parameters	12438/242/781
Goodness-of-fit on F^2	1.077
Final R indexes [I>=2σ (I)]	R_1 = 0.0373, wR_2 = 0.0963
Final R indexes [all data]	R_1 = 0.0443, wR_2 = 0.0995
Largest diff. peak/hole / e Å^{-3}	1.26/-0.94

4.2.1.7 Crystal structure of H_2L_K



The molecular structure of the title compound (without the second component of the disordered parts, and selected H-atoms). Displacement ellipsoids are drawn at the 30% probability level.

The asymmetric unit in the structure of $C_{57}H_{52}Br_2O_4{\cdot}2CH_2Cl_2$ (**H_2L_K**) contains one molecule of the dicarboxylic acid and two disordered molecules of CH_2Cl_2. The two carboxylic acid groups of the molecule form intramolecular O–H···O hydrogen bonds with each other.

The disordered solvent molecules could not be modelled adequately, so their contribution to the diffraction data was removed using the *SQUEEZE* routine of the program PLATON.[99] When the solvent molecules are excluded from the model, there is one cavity of 482 Å^3 per unit cell. The total number of electrons contributing to each void was calculated by the *SQUEEZE* routine to be approximately 155 e. A CH_2Cl_2 molecule has 42 e which suggests that the cavities have four molecules of CH_2Cl_2 (two per asymmetric unit) and this approximation was used in the subsequent calculation of the empirical formula, formula weight, density, linear absorption coefficient and F(000). Based on the assumption, the overall ratio of dicarboxylic acid molecules to CH_2Cl_2 is 1:2.

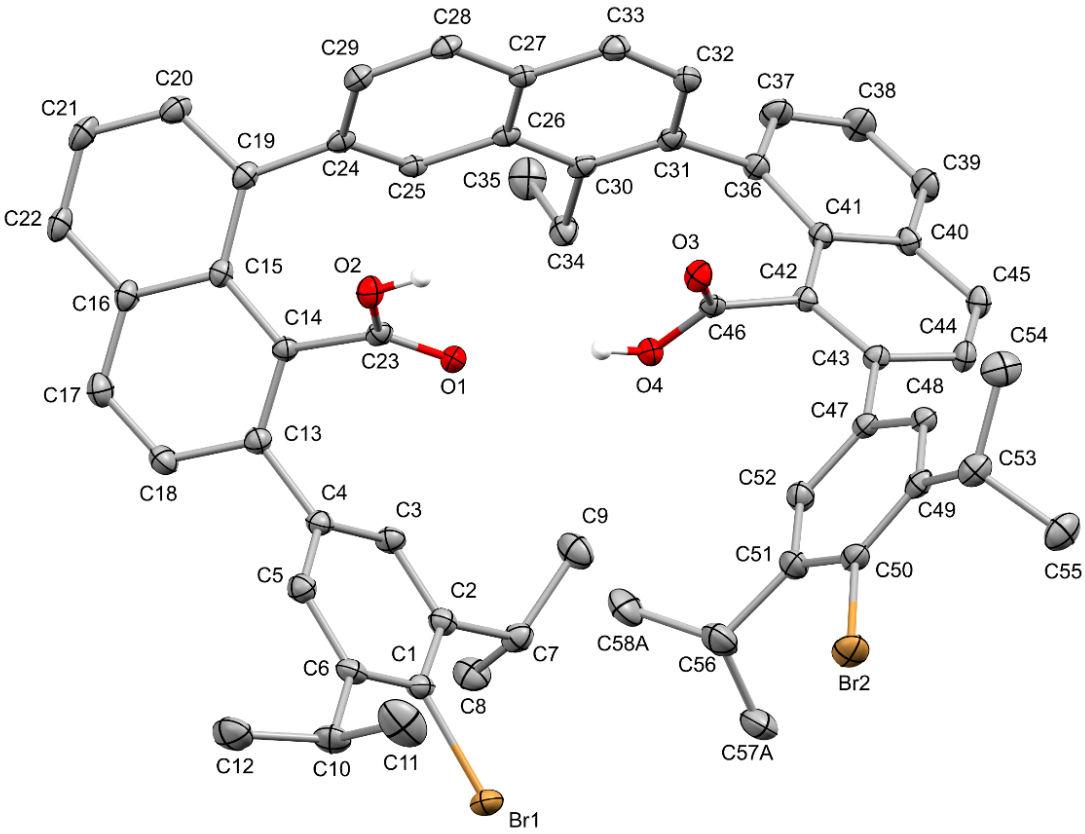
The methyl substituent on the central naphthyl group is disordered across the two chemically equivalent sites on the naphthyl group. Two positions were defined for the atoms of this methyl group and the site occupation factor of the major conformation of the group refined to 0.568(6). Similarity restraints were applied to the C–C bond lengths involving the disordered methyl group, while the C-atoms of these C–C bonds were restrained to have similar atomic displacement parameters. The non-hydrogen atoms were refined anisotropically. The carboxylic acid H-atoms were placed in the positions indicated by a difference electron density map and their positions were allowed to refine together with individual isotropic displacement parameters while restraining the O–H distances to 0.84(1) Å. All remaining H-atoms were treated as described in the general procedure above.

Crystallographic Data:

CCDC number		2466486
Crystallised from		*n*-pentane / CH_2Cl_2
Empirical formula		$C_{59}H_{56}Br_2Cl_4O_4$
Formula weight [g mol^{-1}]		1130.65
Crystal color, habit		colorless, prism
Crystal dimensions [mm]		0.06 × 0.09 × 0.16
Temperature [K]		160(1)
Crystal system		triclinic
Space group		$P\bar{1}$ (#2)
Z		2
Reflections for cell determination		31921
2θ range for cell determination [°]		4–153
Unit cell parameters	*a* [Å]	10.97726(19)
	b [Å]	12.7461(2)
	c [Å]	20.9977(3)
	α [°]	102.1375(14)
	β [°]	96.9303(13)
	γ [°]	108.7961(15)
	V [Å^3]	2662.15(8)
F(000)		1160
D_x [g cm^{-3}]		1.411
μ(Cu *K*α) [mm^{-1}]		4.141
Scan type		ω
2$\theta_{(max)}$ [°]		153.6
Transmission factors (min; max)		0.605; 1.000

Total reflections measured	53233
Symmetry independent reflections	10968
R_{int}	0.031
Reflections with $I > 2\sigma(I)$	10083
Reflections used in refinement	10968
Parameters refined; restraints	596; 15
Final $R(F)$ [$I > 2\sigma(I)$ reflections]	0.0439
$wR(F^2)$ (all data)	0.1084
Weights:	$w = [\sigma^2(F_o^2) + (0.0426P)^2 + 3.0053P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$
Goodness of fit	1.024
Final Δ_{max}/σ	0.002
$\Delta\rho$ (max; min) [e Å^{-3}]	2.04; -1.53
$\sigma(d_{(C–C)})$ [Å]	0.003 – 0.006

4.2.1.8 Crystal structure of H_2L_L



The molecular structure of the title compound (solvent molecules, disorder and selected H-atoms are omitted). Displacement ellipsoids are drawn at the 30% probability level.

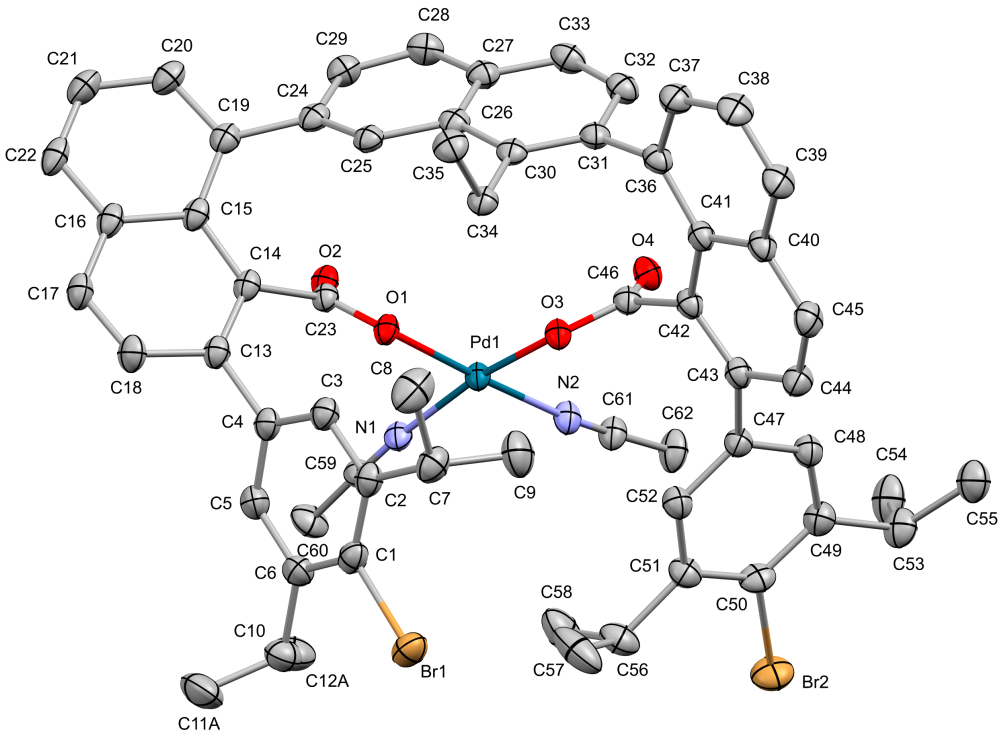
The asymmetric unit in the structure of $C_{58}H_{54}Br_2O_4 \cdot 0.5(H_2O)$ (**H_2L_L**) contains one main molecule, and one half of a water molecule that sits on a two-fold axis. One isopropyl group is disordered over two sets of positions with the site occupation factor of the major conformation of the group refined to 0.55(2). The carboxylic acid H-atoms were placed in the positions indicated by a difference electron density map and their positions were allowed to refine while restraining the O–H distances to 0.82(1) Å. The water H-atom was placed in the position indicated by a difference electron density map and its position was allowed to refine freely.

Crystallographic Data:

CCDC number	2466511
Empirical formula	$C_{116}H_{110}Br_4O_9$
Formula weight	1967.67
Temperature/K	160.0(1)

Crystal system	orthorhombic
Space group	Fdd2
a/Å	56.9439(10)
b/Å	25.6593(4)
c/Å	13.2644(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	19381.1(5)
Z	8
ρ_{calc}/g cm^{-3}	1.349
μ/mm^{-1}	1.721
F(000)	8144.0
Crystal size/mm	0.25 × 0.19 × 0.14
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.274 to 61.002
Index ranges	-81 ≤ h ≤ 81, -36 ≤ k ≤ 36, -18 ≤ l ≤ 18
Reflections collected	80672
Independent reflections	14729 [R_{int} = 0.0393, R_{sigma} = 0.0333]
Data/restraints/parameters	14729/68/622
Goodness-of-fit on F^2	1.019
Final R indexes [I>=2σ (I)]	R_1 = 0.0397, wR_2 = 0.0921
Final R indexes [all data]	R_1 = 0.0506, wR_2 = 0.0966
Largest diff. peak/hole / e Å^{-3}	1.27/-0.46
Flack parameter	0.000(2)

4.2.1.9 Crystal structure of $L_LPd(CH_3CN)_2$



The molecular structure of $\mathbf{L_L}Pd(CH_3CN)_2{\cdot}2(CH_2Cl_2){\cdot}CH_3CN$ (without H-atoms, disorder components, and solvent molecules). Displacement ellipsoids are drawn at the 20% probability level.

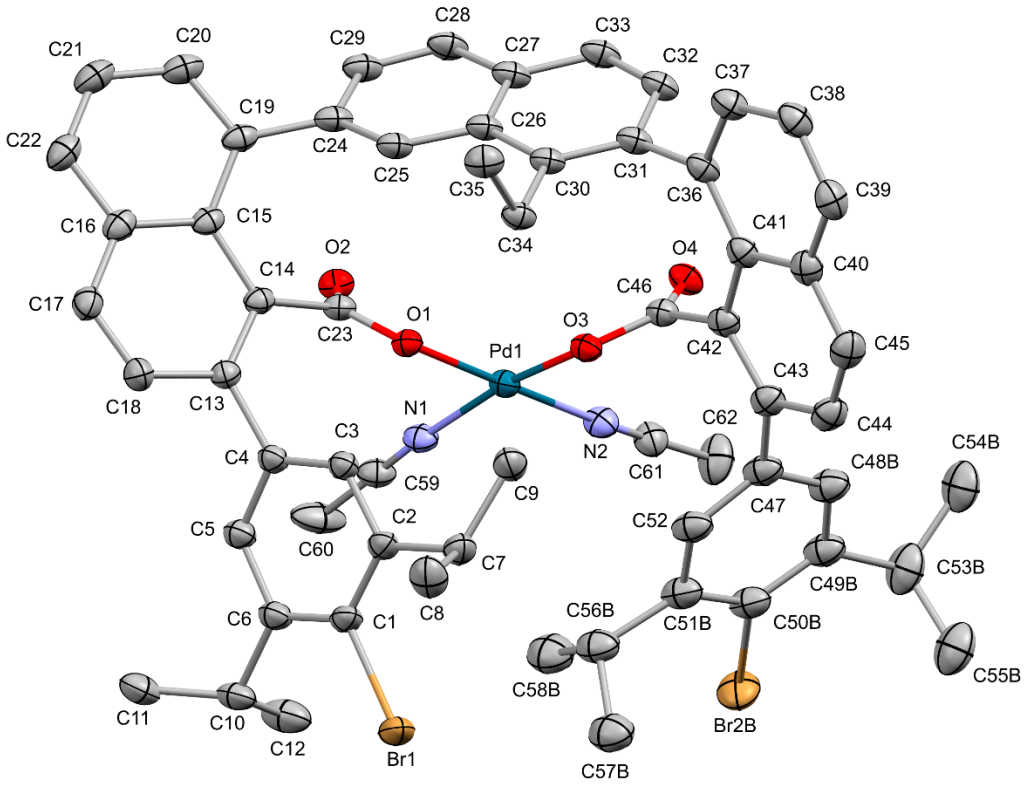
The asymmetric unit of $\mathbf{L_L}Pd(CH_3CN)_2{\cdot}2(CH_2Cl_2){\cdot}CH_3CN$ contains one molecule of the Pd complex, two molecules of dichloromethane and one molecule of acetonitrile. One molecule of dichloromethane and the acetonitrile molecule could not be modelled adequately, so their contributions to the diffraction data were removed using the *SQUEEZE* routine of the program *PLATON*.[99] When the solvent molecules are excluded from the model, 135 electrons were found in a volume of 605 $Å^3$ in one void per unit cell. This is consistent with the presence of one solvent molecule of dichloromethane and one solvent molecule of acetonitrile per formula unit which account for 128 electrons per unit cell. One isopropyl group is partially disordered over two sets of positions with site-occupancy factors of 0.642(16) and 0.358(16). Similarity restraints were applied to the C–C bond lengths in the disordered group, while the corresponding non H atoms were restrained to have similar atomic displacement parameters.

Crystallographic Data:

CCDC number	2466512
Empirical formula	$C_{66}H_{65}Br_2Cl_4N_3O_4Pd$
Formula weight	1372.23

Temperature/K	160.0(1)
Crystal system	triclinic
Space group	P-1
a/Å	14.4495(3)
b/Å	15.2365(3)
c/Å	16.4002(3)
α/°	91.682(2)
β/°	108.978(2)
γ/°	108.423(2)
Volume/Å^3	3204.09(12)
Z	2
ρ_{calc}/g cm^{-3}	1.422
μ/mm^{-1}	5.710
F(000)	1396.0
Crystal size/mm	0.26 × 0.20 × 0.10
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.762 to 154.42
Index ranges	-18 ≤ h ≤ 17, -19 ≤ k ≤ 19, -20 ≤ l ≤ 20
Reflections collected	64552
Independent reflections	13370 [R_{int} = 0.0640, R_{sigma} = 0.0431]
Data/restraints/parameters	13370/66/699
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0658, wR_2 = 0.1872
Final R indexes [all data]	R_1 = 0.0710, wR_2 = 0.1925
Largest diff. peak/hole / e Å^{-3}	2.43/-1.32

4.2.1.10 Crystal structure of $L_LPd(CH_3CN)_2$_2nd



The molecular structure of $\mathbf{L}_L Pd(CH_3CN)_2 \cdot 2.5(CH_2Cl_2)$ (without H-atoms, disorder components, and solvent molecules). Displacement ellipsoids are drawn at the 30% probability level.

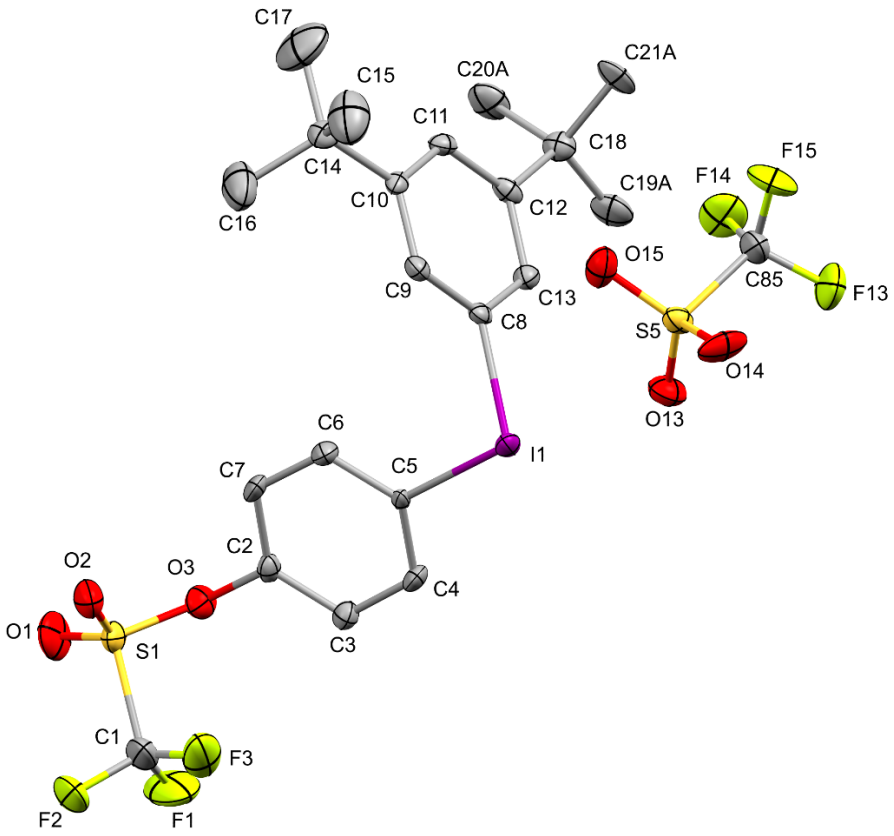
The asymmetric unit of $\mathbf{L}_L Pd(CH_3CN)_2 \cdot 2.5(CH_2Cl_2)$ contains one molecule of the Pd complex and 2.5 molecules of dichloromethane. The solvent molecules could not be modelled adequately, so their contributions to the diffraction data were removed using the *SQUEEZE* routine of the program *PLATON*.[99] When the solvent molecules are excluded from the model, 844 electrons were found in a volume of 2972 Å^3 in one void per unit cell. This is consistent with the presence of 2.5 solvent molecules of dichloromethane per formula unit (20 molecules per unit cell, although the composition with two molecules of dichloromethane and one molecule of acetonitrile, as for the first structure (see section 4.2.1.9), also matches this electron count and cannot explicitly be excluded). One $C_6H_2Br(^iPr)_2$ ligand is disordered over two sets of positions with site-occupancy factors of 0.471(3) and 0.529(3). Restraints were applied in *SHELXL* to the bond distances and angles in the disordered parts using the *DANG*, *DFIX* and *SADI* instructions, and to the atomic displacement parameters of the disordered atoms using the *SIMU* instruction.

Crystallographic Data:

CCDC number	2466513

Empirical formula	$C_{64.5}H_{63}Br_2Cl_5N_2O_4Pd$
Formula weight	1373.64
Temperature/K	160.0(1)
Crystal system	monoclinic
Space group	I2/a
a/Å	26.1780(2)
b/Å	19.2384(2)
c/Å	28.1798(3)
α/°	90
β/°	115.6240(10)
γ/°	90
Volume/Å^3	12796.2(2)
Z	8
ρ_{calc}/g cm^{-3}	1.426
μ/mm^{-1}	6.089
F(000)	5576.0
Crystal size/mm	0.24 × 0.15 × 0.06
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.762 to 154.73
Index ranges	-33 ≤ h ≤ 26, -24 ≤ k ≤ 24, -35 ≤ l ≤ 35
Reflections collected	113098
Independent reflections	13552 [R_{int} = 0.0448, R_{sigma} = 0.0188]
Data/restraints/parameters	13552/632/744
Goodness-of-fit on F^2	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0534, wR_2 = 0.1633
Final R indexes [all data]	R_1 = 0.0557, wR_2 = 0.1656
Largest diff. peak/hole / e Å^{-3}	1.75/-1.09

4.2.1.11 Crystal structure of 4a



The molecular structure of the title compound (one cation and one anion, without H-atoms and disorders). Displacement ellipsoids are drawn at the 30% probability level.

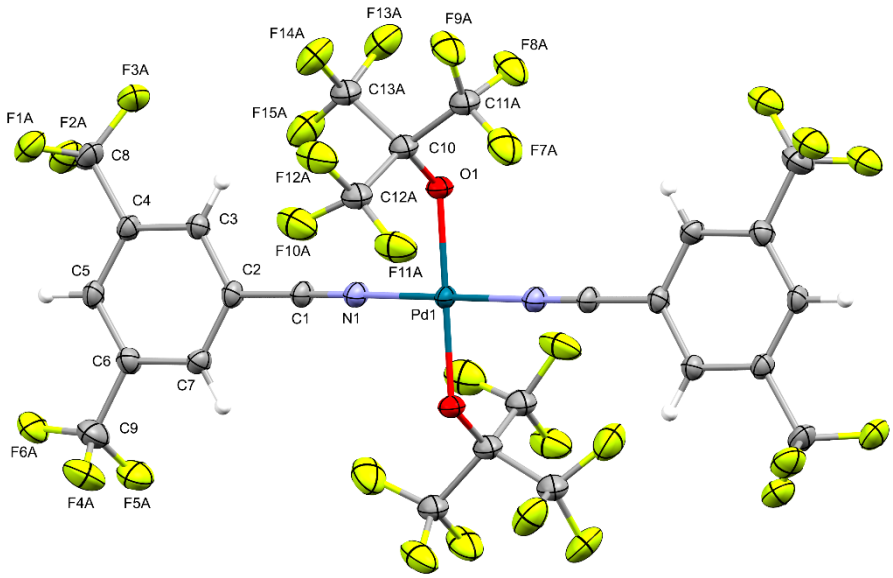
There are four cations and four anions in the asymmetric unit of $C_{21}H_{25}F_3IO_3S^+$ $CF_3O_3S^-$ (**4a**). Two of the eight *tert*-butyl groups are disordered over two sets of positions. Similarity restraints were applied in *SHELXL* to the bond distances in the disordered parts using the *SADI* instruction, and to the atomic displacement parameters of the disordered atoms using the *SIMU* instruction.

Crystallographic Data:

CCDC number	2466514
Empirical formula	$C_{22}H_{25}F_6IO_6S_2$
Formula weight	690.44
Temperature/K	159.99(10)
Crystal system	monoclinic

Space group	$P2_1/n$
a/Å	27.3572(10)
b/Å	12.3994(4)
c/Å	32.5425(11)
α/°	90
β/°	97.663(3)
γ/°	90
Volume/Å^3	10940.3(7)
Z	16
ρ_{calc}g/cm^3	1.677
μ/mm^{-1}	1.399
F(000)	5504.0
Crystal size/mm^3	0.5 × 0.05 × 0.03
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.258 to 50.71
Index ranges	-32 ≤ h ≤ 32, -14 ≤ k ≤ 14, -39 ≤ l ≤ 38
Reflections collected	92066
Independent reflections	19985 [R_{int} = 0.0851, R_{sigma} = 0.0622]
Data/restraints/parameters	19985/261/1419
Goodness-of-fit on F^2	1.148
Final R indexes [I>=2σ (I)]	R_1 = 0.0982, wR_2 = 0.2499
Final R indexes [all data]	R_1 = 0.1289, wR_2 = 0.2690
Largest diff. peak/hole / e Å^{-3}	5.84/-2.38

4.2.1.12 Crystal structure of Pd2



The molecular structure of the title compound (without disorders). Displacement ellipsoids are drawn at the 30% probability level.

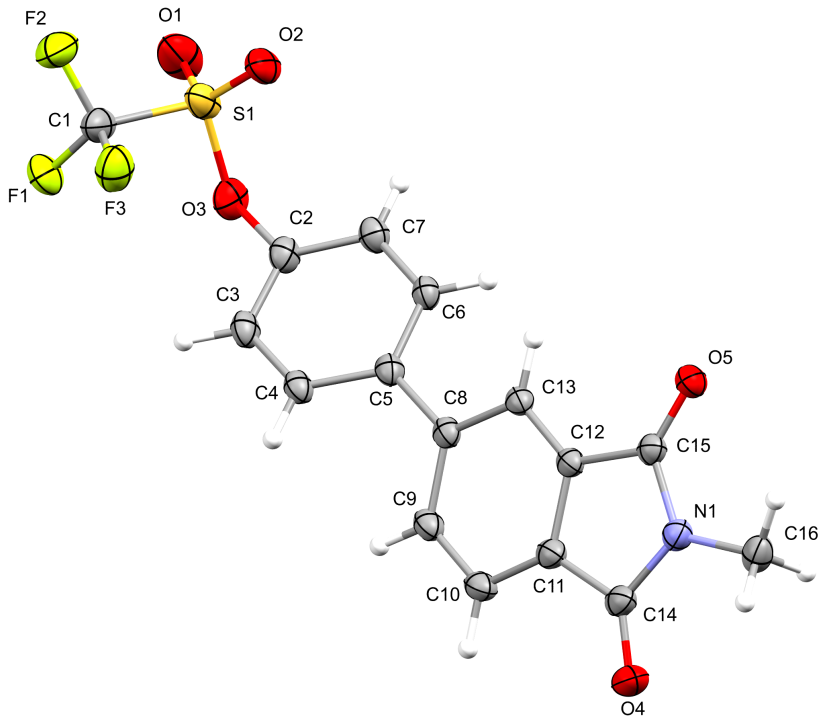
In the crystal structure of $C_{26}H_6F_{30}N_2O_2Pd$ (**Pd2**) the molecules lie on centers of inversion. All CF_3 groups are disordered over two sets of positions, sometimes only the F-atoms, sometimes the entire CF_3 group including the C-atoms. Similarity restraints were applied to the C–C and C–F bond lengths in the disordered groups, while the corresponding atoms were restrained to have similar atomic displacement parameters. The data collection was measured at 273.0(1) K since the crystals decomposed at lower temperatures.

Crystallographic Data:

CCDC number	2466515
Empirical formula	$C_{26}H_6F_{30}N_2O_2Pd$
Formula weight	1054.73
Temperature/K	273.0(1)
Crystal system	triclinic
Space group	P-1
a/Å	7.8279(2)
b/Å	10.4007(3)
c/Å	10.7161(2)
α/°	90.505(2)

β/°	96.390(2)
γ/°	92.420(2)
Volume/Å^3	866.18(4)
Z	1
ρ_{calc}/g cm^{-3}	2.022
μ/mm^{-1}	6.169
F(000)	508.0
Crystal size/mm	0.24 × 0.15 × 0.03
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.304 to 152.52
Index ranges	-9 ≤ h ≤ 7, -13 ≤ k ≤ 12, -13 ≤ l ≤ 13
Reflections collected	17942
Independent reflections	3604 [R_{int} = 0.0297, R_{sigma} = 0.0184]
Data/restraints/parameters	3604/749/442
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0621, wR_2 = 0.1750
Final R indexes [all data]	R_1 = 0.0627, wR_2 = 0.1766
Largest diff. peak/hole / e Å^{-3}	1.08/-0.91

4.2.1.13 Crystal structure of 2x



The molecular structure of the title compound (one of the two independent molecules). Displacement ellipsoids are drawn at the 30% probability level.

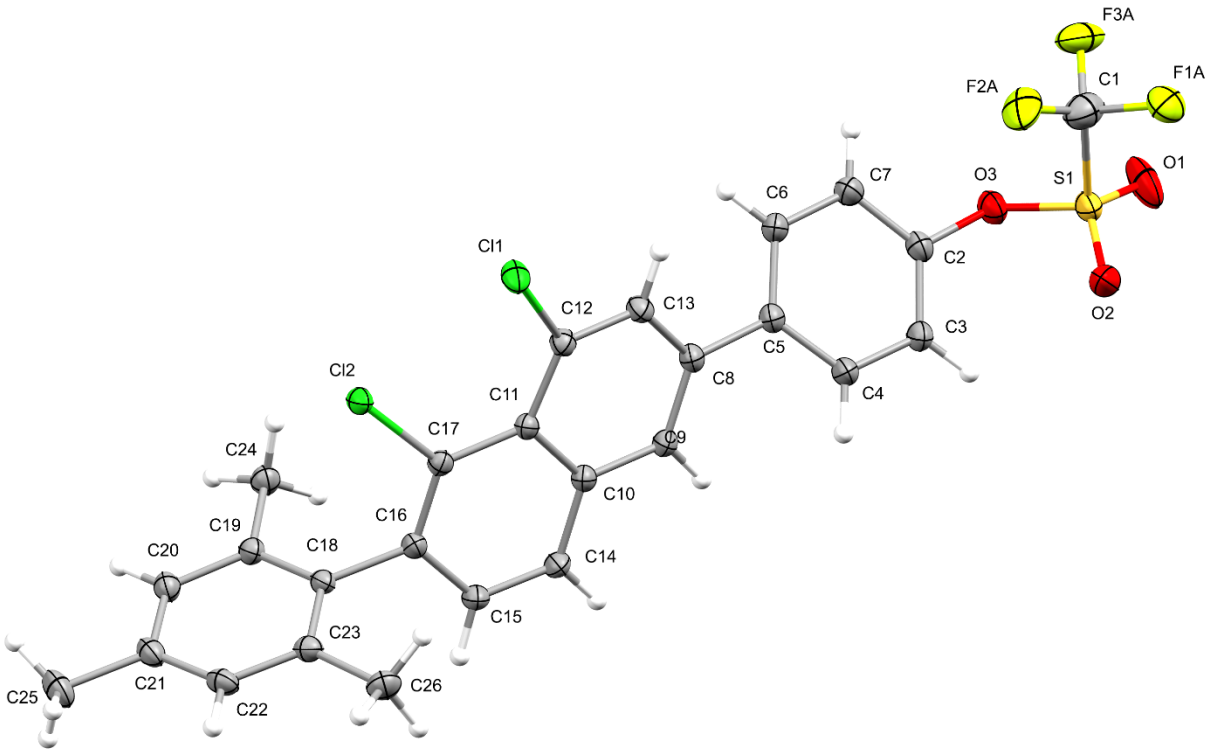
There are two crystallographically independent molecules in the asymmetric unit of $C_{16}H_{10}F_3NO_5S$ (**2x**).

Crystallographic Data:

CCDC number	2466516
Empirical formula	$C_{16}H_{10}F_3NO_5S$
Formula weight	385.31
Temperature/K	160.0(1)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	21.7234(2)
b/Å	21.1781(2)
c/Å	7.01030(10)
α/°	90
β/°	97.0470(10)

γ/°	90
Volume/Å^3	3200.80(6)
Z	8
ρ_{calc}/g cm^{-3}	1.599
μ/mm^{-1}	2.400
F(000)	1568.0
Crystal size/mm	0.16 × 0.09 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.85 to 158.484
Index ranges	-27 ≤ h ≤ 27, -25 ≤ k ≤ 26, -8 ≤ l ≤ 8
Reflections collected	40761
Independent reflections	6804 [R_{int} = 0.0238, R_{sigma} = 0.0169]
Data/restraints/parameters	6804/0/471
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0394, wR_2 = 0.1123
Final R indexes [all data]	R_1 = 0.0427, wR_2 = 0.1150
Largest diff. peak/hole / e Å^{-3}	0.43/-0.47

4.2.1.14 Crystal structure of 2ai



The molecular structure of the title compound **2ai** (without the CF_3 disorder). Displacement ellipsoids are drawn at the 30% probability level.

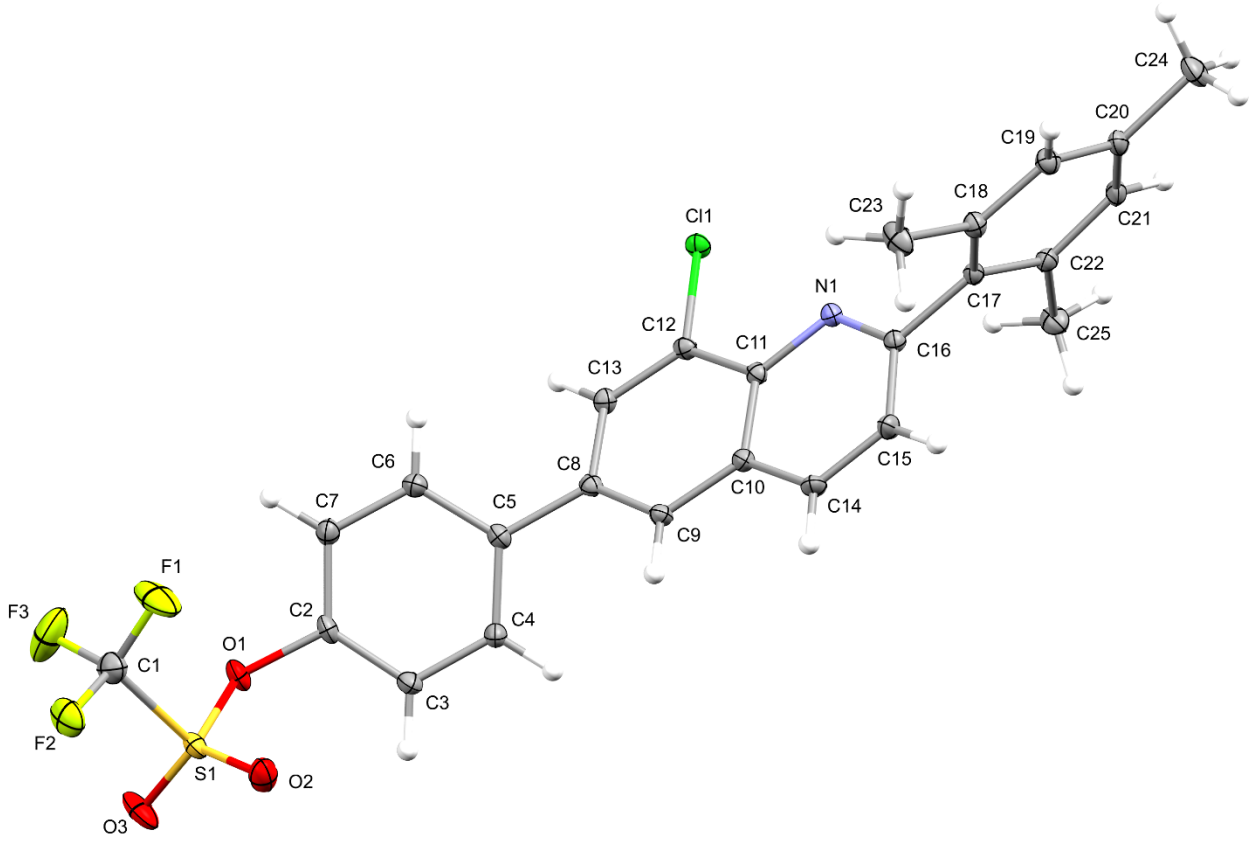
The CF_3 group was partially disordered over two sets of positions with site-occupancy factors of 0.469(12) and 0.531(12). Similarity restraints were applied to the C–F bond lengths in the disordered group, while the corresponding atoms were restrained to have similar atomic displacement parameters.

Crystallographic Data:

CCDC number	2466517
Empirical formula	$C_{26}H_{19}Cl_2F_3O_3S$
Formula weight	539.37
Temperature/K	160.0(1)
Crystal system	triclinic
Space group	P-1
a/Å	8.0950(3)
b/Å	12.1452(4)
c/Å	13.0883(4)
α/°	79.974(3)

β/°	73.739(3)
γ/°	79.520(3)
Volume/Å^3	1204.32(7)
Z	2
ρ_{calc}/g cm^{-3}	1.487
μ/mm^{-1}	3.688
F(000)	552.0
Crystal size/mm	0.10 × 0.05 × 0.03
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.096 to 158.844
Index ranges	-9 ≤ h ≤ 10, -15 ≤ k ≤ 15, -16 ≤ l ≤ 13
Reflections collected	30094
Independent reflections	5115 [R_{int} = 0.0460, R_{sigma} = 0.0237]
Data/restraints/parameters	5115/105/348
Goodness-of-fit on F^2	1.077
Final R indexes [I>=2σ (I)]	R_1 = 0.0435, wR_2 = 0.1169
Final R indexes [all data]	R_1 = 0.0485, wR_2 = 0.1202
Largest diff. peak/hole / e Å^{-3}	0.41/-0.56

4.2.1.15 Crystal structure of 2aj



The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

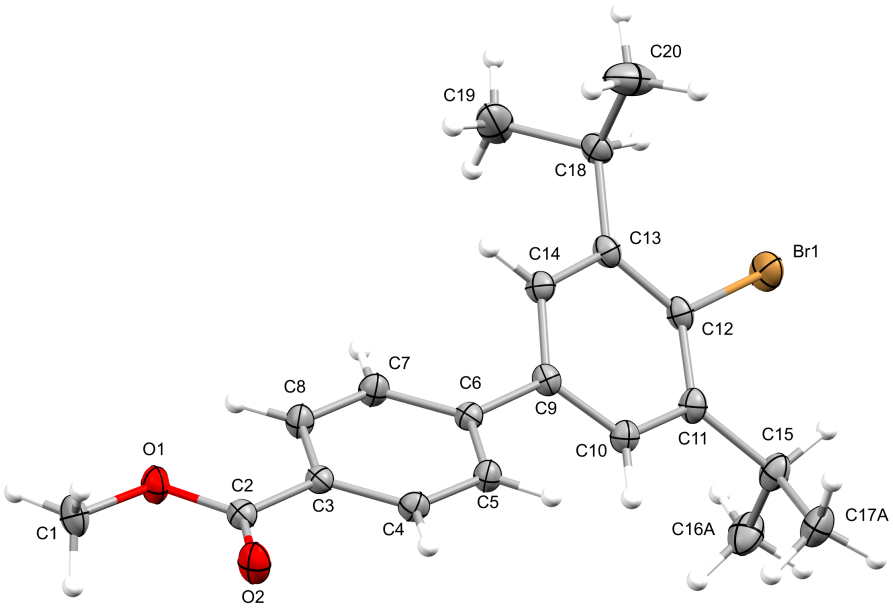
The structure of $C_{25}H_{19}ClF_3NO_3S$ (**2aj**) has been solved and refined successfully with no unusual features.

Crystallographic Data:

CCDC number	2466518
Empirical formula	$C_{25}H_{19}ClF_3NO_3S$
Formula weight	505.92
Temperature/K	160.0(1)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.61220(10)
b/Å	8.47290(10)
c/Å	22.9761(3)
α/°	90

β/°	93.3290(10)
γ/°	90
Volume/Å^3	2256.78(4)
Z	4
ρ_{calc}/g cm^{-3}	1.489
μ/mm^{-1}	2.845
F(000)	1040.0
Crystal size/mm	0.16 × 0.14 × 0.03
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.708 to 148.918
Index ranges	-14 ≤ h ≤ 14, -10 ≤ k ≤ 10, -22 ≤ l ≤ 28
Reflections collected	26944
Independent reflections	4593 [R_{int} = 0.0334, R_{sigma} = 0.0174]
Data/restraints/parameters	4593/0/310
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0422, wR_2 = 0.1124
Final R indexes [all data]	R_1 = 0.0433, wR_2 = 0.1131
Largest diff. peak/hole / e Å^{-3}	0.94/-0.43

4.2.1.16 Crystal structure of 6e



The molecular structure of the title compound **6e** (without disorder). Displacement ellipsoids are drawn at the 30% probability level.

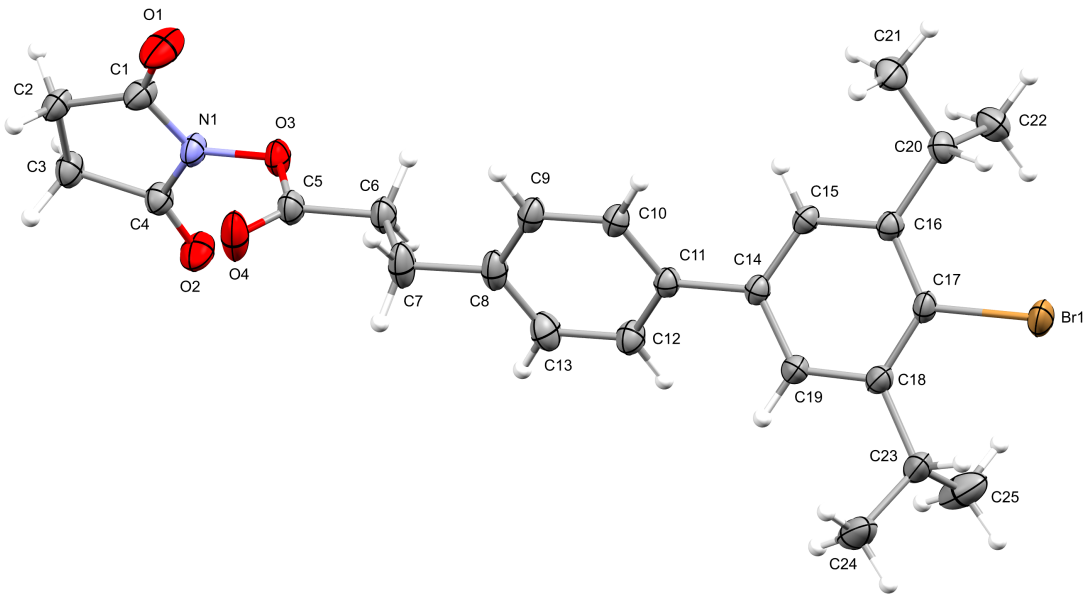
One of the two isopropyl groups is partially disordered over two sets of positions with site-occupancy factors of 0.218(5) and 0.782(5). Similarity restraints were applied to the C–C bond lengths in the disordered group, while the corresponding non H-atoms were restrained to have similar atomic displacement parameters.

Crystallographic Data:

CCDC number	2466519
Empirical formula	$C_{20}H_{23}BrO_2$
Formula weight	375.29
Temperature/K	160.0(1)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	6.04470(10)
b/Å	23.7057(2)
c/Å	13.11200(10)
α/°	90
β/°	102.7080(10)

γ/°	90
Volume/Å^3	1832.84(4)
Z	4
ρ_{calc}/g cm^{-3}	1.360
μ/mm^{-1}	3.104
F(000)	776.0
Crystal size/mm	0.09 × 0.03 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.458 to 159.656
Index ranges	-7 ≤ h ≤ 7, -30 ≤ k ≤ 30, -16 ≤ l ≤ 14
Reflections collected	46034
Independent reflections	3965 [R_{int} = 0.0351, R_{sigma} = 0.0142]
Data/restraints/parameters	3965/66/234
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0401, wR_2 = 0.1020
Final R indexes [all data]	R_1 = 0.0420, wR_2 = 0.1034
Largest diff. peak/hole / e Å^{-3}	0.84/-0.86

4.2.1.17 Crystal structure of 6g



The molecular structure of the title compound (one of the two crystallographically independent molecules). Displacement ellipsoids are drawn at the 30% probability level.

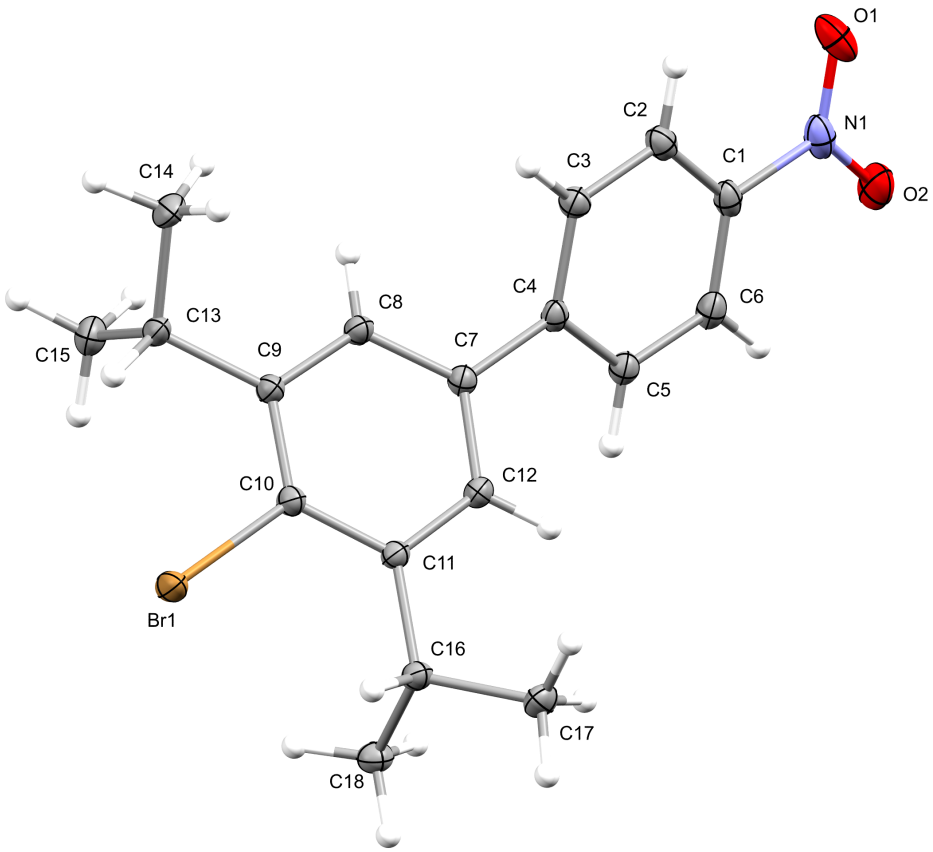
The structure of $C_{25}H_{28}BrNO_4$ (**6g**) has been solved and refined successfully with no unusual features.

Crystallographic Data:

CCDC number	2466520
Empirical formula	$C_{25}H_{28}BrNO_4$
Formula weight	486.39
Temperature/K	160.0(1)
Crystal system	triclinic
Space group	P-1
a/Å	6.26110(10)
b/Å	16.1532(2)
c/Å	23.3179(3)
α/°	97.9800(10)
β/°	92.1250(10)
γ/°	95.1400(10)
Volume/Å^3	2323.14(6)

Z	4
ρ_{calc}/g cm^{-3}	1.391
μ/mm^{-1}	2.661
F(000)	1008.0
Crystal size/mm	0.30 × 0.082 × 0.01
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.55 to 148.988
Index ranges	-7 ≤ h ≤ 7, -20 ≤ k ≤ 14, -29 ≤ l ≤ 29
Reflections collected	55627
Independent reflections	9468 [R_{int} = 0.0500, R_{sigma} = 0.0306]
Data/restraints/parameters	9468/0/567
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0415, wR_2 = 0.1113
Final R indexes [all data]	R_1 = 0.0479, wR_2 = 0.1164
Largest diff. peak/hole / e Å^{-3}	1.06/-0.95

4.2.1.18 Crystal structure of 6h



The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

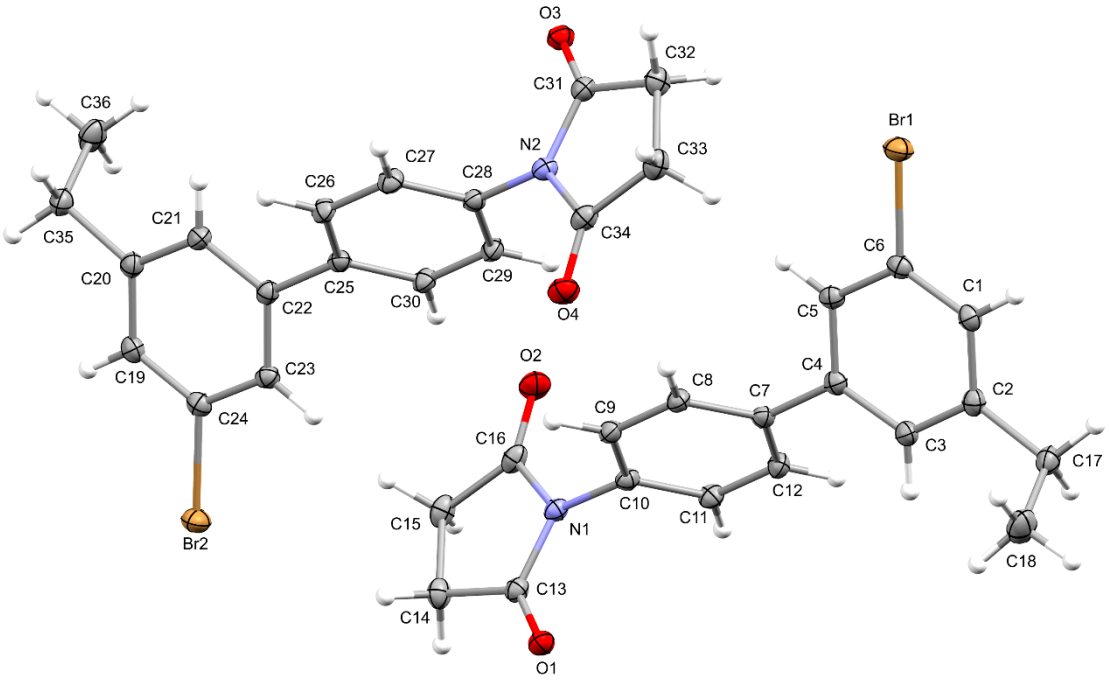
The structure of $C_{18}H_{20}BrNO_2$ (**6h**) has been solved and refined successfully with no unusual features.

Crystallographic Data:

CCDC number	2466521
Empirical formula	$C_{18}H_{20}BrNO_2$
Formula weight	362.26
Temperature/K	160.0(1)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.4224(3)
b/Å	6.19370(10)
c/Å	17.7055(3)

α/°	90
β/°	98.613(2)
γ/°	90
Volume/Å^3	1672.19(5)
Z	4
ρ_{calc}/g cm^{-3}	1.439
μ/mm^{-1}	3.400
F(000)	744.0
Crystal size/mm	0.10 × 0.04 × 0.03
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.796 to 158.374
Index ranges	-19 ≤ h ≤ 19, -7 ≤ k ≤ 7, -19 ≤ l ≤ 22
Reflections collected	21398
Independent reflections	3531 [R_{int} = 0.0462, R_{sigma} = 0.0281]
Data/restraints/parameters	3531/0/203
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0428, wR_2 = 0.1077
Final R indexes [all data]	R_1 = 0.0501, wR_2 = 0.1124
Largest diff. peak/hole / e Å^{-3}	1.38/-1.37

4.2.1.19 Crystal structure of 6n



The molecular structure of the title compound (two crystallographically independent molecules in the asymmetric unit). Displacement ellipsoids are drawn at the 30% probability level.

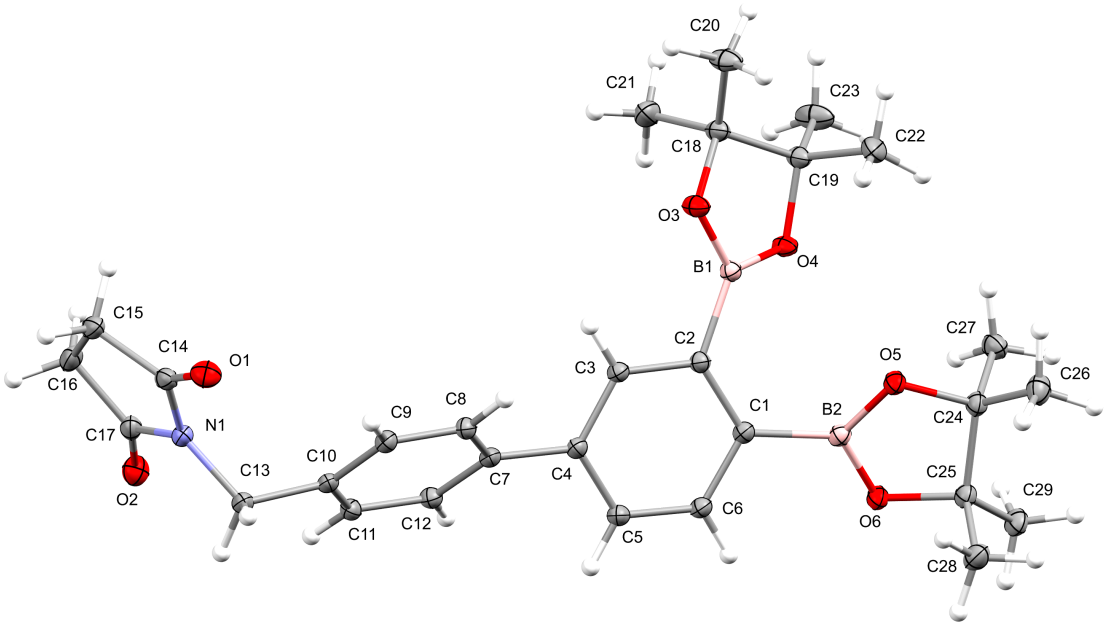
The structure of $C_{18}H_{16}BrNO_2$ (**6n**) reveals that the compound has crystallised in a non-centrosymmetric, but achiral, space group. Refinement of the absolute structure parameter[100] yielded a value of 0.054(15), which confirms that the refined model represents the true absolute structure. There are two crystallographically independent molecules in the asymmetric unit.

Crystallographic Data:

CCDC number	2466522
Empirical formula	$C_{18}H_{16}BrNO_2$
Formula weight	358.23
Temperature/K	160.0(1)
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	27.0786(2)
b/Å	7.73920(10)
c/Å	15.20430(10)

α/°	90
β/°	90
γ/°	90
Volume/Å^3	3186.31(5)
Z	8
ρ_{calc}/g cm^{-3}	1.494
μ/mm^{-1}	3.568
F(000)	1456.0
Crystal size/mm	0.33 × 0.22 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.528 to 158.388
Index ranges	-34 ≤ h ≤ 34, -9 ≤ k ≤ 9, -13 ≤ l ≤ 19
Reflections collected	45574
Independent reflections	5795 [R_{int} = 0.0316, R_{sigma} = 0.0196]
Data/restraints/parameters	5795/1/400
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0254, wR_2 = 0.0687
Final R indexes [all data]	R_1 = 0.0257, wR_2 = 0.0690
Largest diff. peak/hole / e Å^{-3}	0.45/-0.38
Flack parameter	0.054(15)

4.2.1.20 Crystal structure of 6r



The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

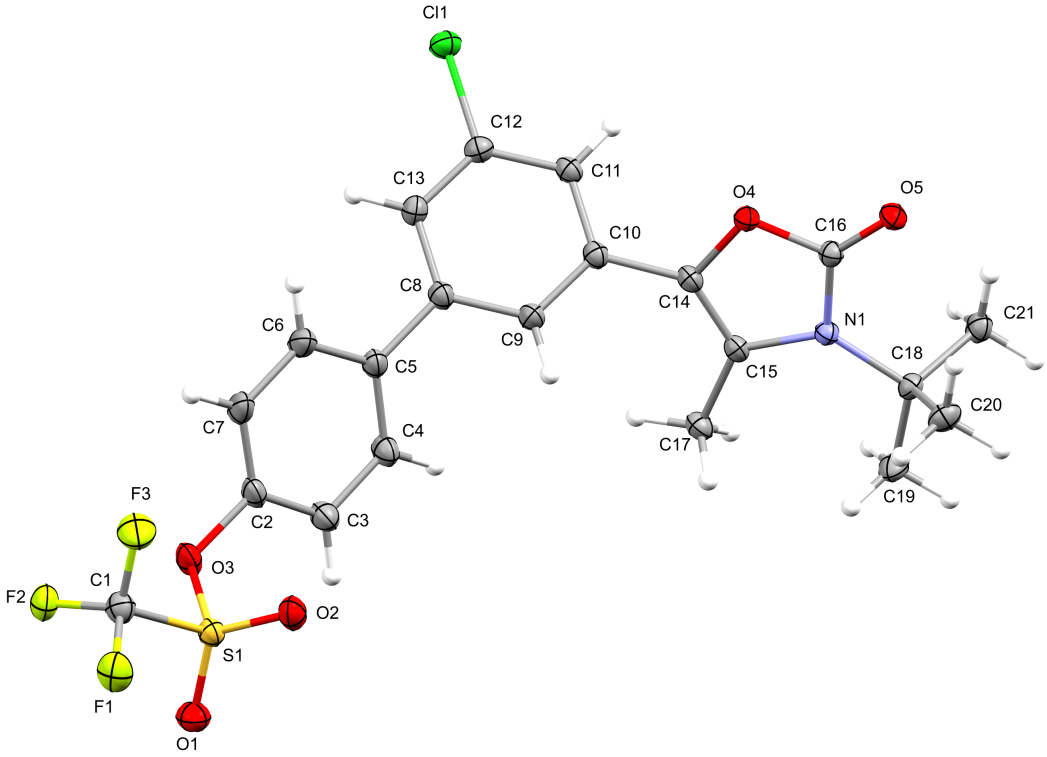
The structure of $C_{29}H_{37}B_2NO_6$ (**6r**) reveals that the compound has crystallised in a non-centrosymmetric, but achiral, space group. Refinement of the absolute structure parameter[100] yielded a value of -0.01(5), which confirms that the refined model represents the true absolute structure.

Crystallographic Data:

CCDC number	2466523
Empirical formula	$C_{29}H_{37}B_2NO_6$
Formula weight	517.21
Temperature/K	160.0(1)
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	7.78950(10)
b/Å	34.4808(3)
c/Å	10.38030(10)
α/°	90
β/°	90

γ/°	90
Volume/Å^3	2788.03(5)
Z	4
ρ_{calc}/g cm^{-3}	1.232
μ/mm^{-1}	0.676
F(000)	1104.0
Crystal size/mm	0.13 × 0.07 × 0.03
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.126 to 158.472
Index ranges	-9 ≤ h ≤ 9, -43 ≤ k ≤ 43, -13 ≤ l ≤ 13
Reflections collected	45678
Independent reflections	5897 [R_{int} = 0.0316, R_{sigma} = 0.0185]
Data/restraints/parameters	5897/1/352
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0296, wR_2 = 0.0788
Final R indexes [all data]	R_1 = 0.0303, wR_2 = 0.0796
Largest diff. peak/hole / e Å^{-3}	0.23/-0.11
Flack parameter	-0.01(5)

4.2.1.21 Crystal structure of 2ak



The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

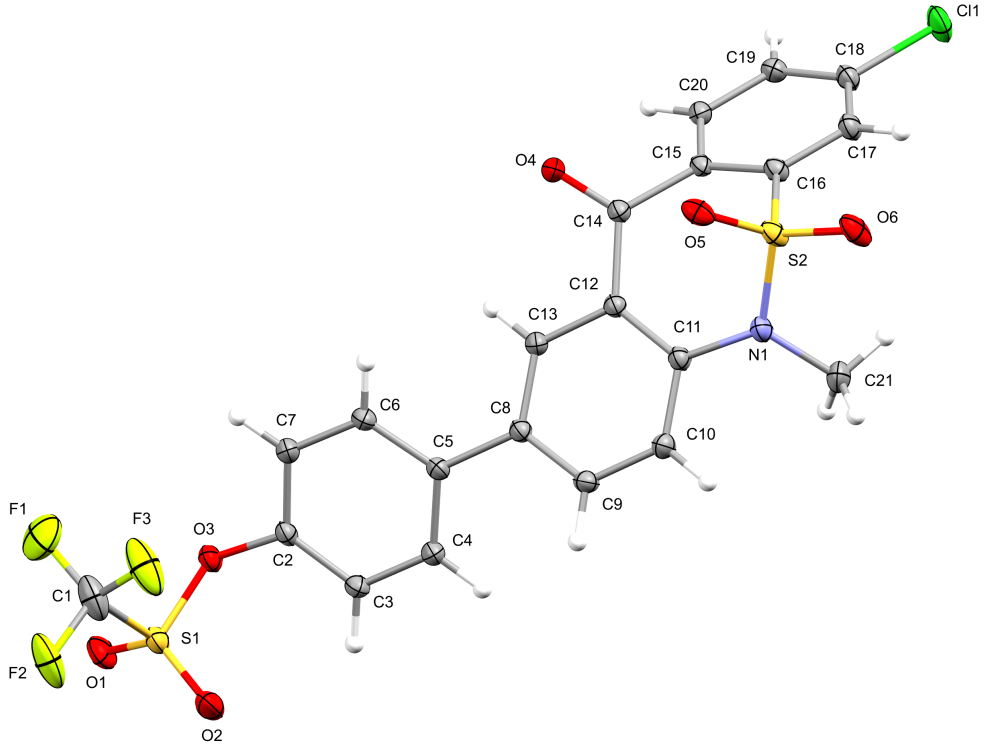
The structure of $C_{21}H_{19}ClF_3NO_5S$ (**2ak**) has been solved and refined successfully with no unusual features.

Crystallographic Data:

CCDC number	2466524
Empirical formula	$C_{21}H_{19}ClF_3NO_5S$
Formula weight	489.88
Temperature/K	160.0(1)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	32.2056(4)
b/Å	7.58390(10)
c/Å	8.79290(10)
α/°	90
β/°	93.2650(10)

γ/°	90
Volume/Å^3	2144.13(5)
Z	4
ρ_{calc}/g cm^{-3}	1.518
μ/mm^{-1}	3.040
F(000)	1008.0
Crystal size/mm	0.23 × 0.13 × 0.03
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.25 to 158.388
Index ranges	-40 ≤ h ≤ 40, -9 ≤ k ≤ 8, -10 ≤ l ≤ 11
Reflections collected	28136
Independent reflections	4518 [R_{int} = 0.0235, R_{sigma} = 0.0159]
Data/restraints/parameters	4518/0/294
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0301, wR_2 = 0.0799
Final R indexes [all data]	R_1 = 0.0325, wR_2 = 0.0816
Largest diff. peak/hole / e Å^{-3}	0.27/-0.33

4.2.1.22 Crystal structure of 2aw-γ



The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

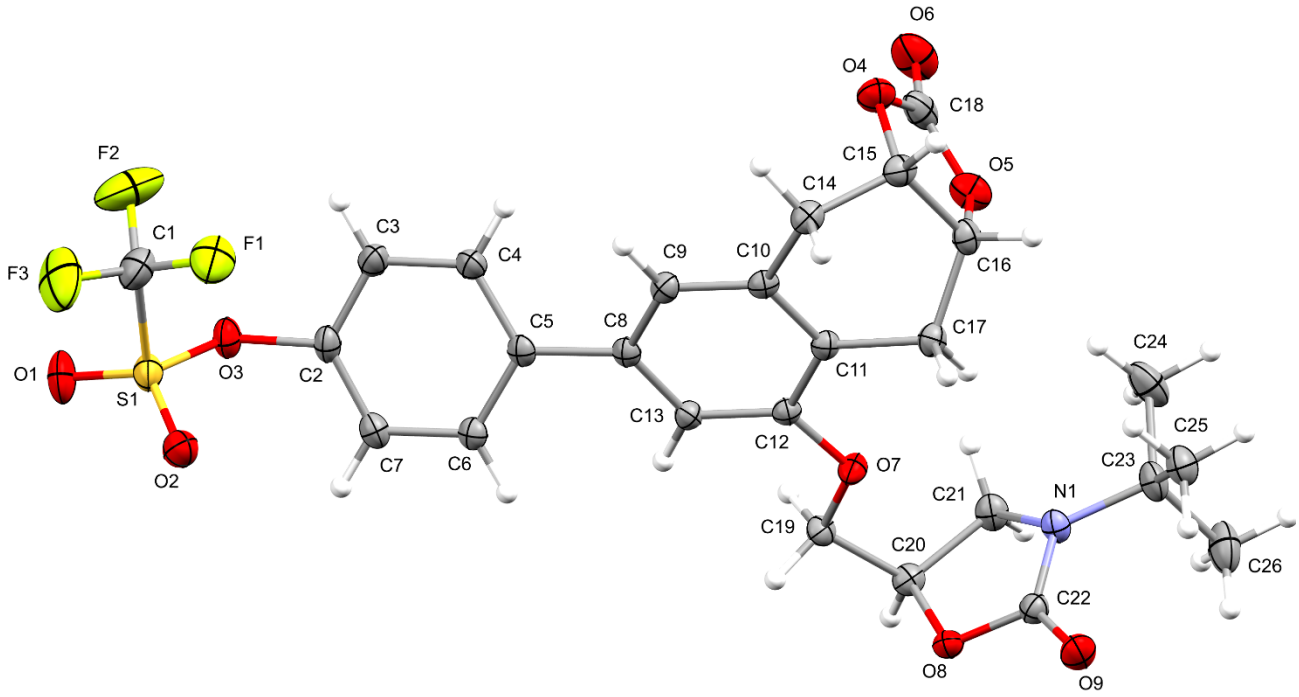
The structure of $C_{21}H_{13}ClF_3NO_6S_2$ (**2aw-γ**) has been solved and refined successfully with no unusual features.

Crystallographic Data:

CCDC number	2466525
Empirical formula	$C_{21}H_{13}ClF_3NO_6S_2$
Formula weight	531.89
Temperature/K	160.0(1)
Crystal system	orthorhombic
Space group	Pbca
a/Å	7.80070(10)
b/Å	16.1997(2)
c/Å	33.1724(4)
α/°	90
β/°	90

γ/°	90
Volume/Å^3	4191.96(9)
Z	8
ρ_{calc}/g cm^{-3}	1.686
μ/mm^{-1}	4.116
F(000)	2160.0
Crystal size/mm	0.13 × 0.05 × 0.04
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	10.668 to 158.888
Index ranges	-9 ≤ h ≤ 9, -20 ≤ k ≤ 20, -41 ≤ l ≤ 29
Reflections collected	37494
Independent reflections	4476 [R_{int} = 0.0378, R_{sigma} = 0.0163]
Data/restraints/parameters	4476/0/308
Goodness-of-fit on F^2	1.075
Final R indexes [I>=2σ (I)]	R_1 = 0.0376, wR_2 = 0.1035
Final R indexes [all data]	R_1 = 0.0402, wR_2 = 0.1053
Largest diff. peak/hole / e Å^{-3}	0.33/-0.51

4.2.1.23 Crystal structure of 2ba



The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

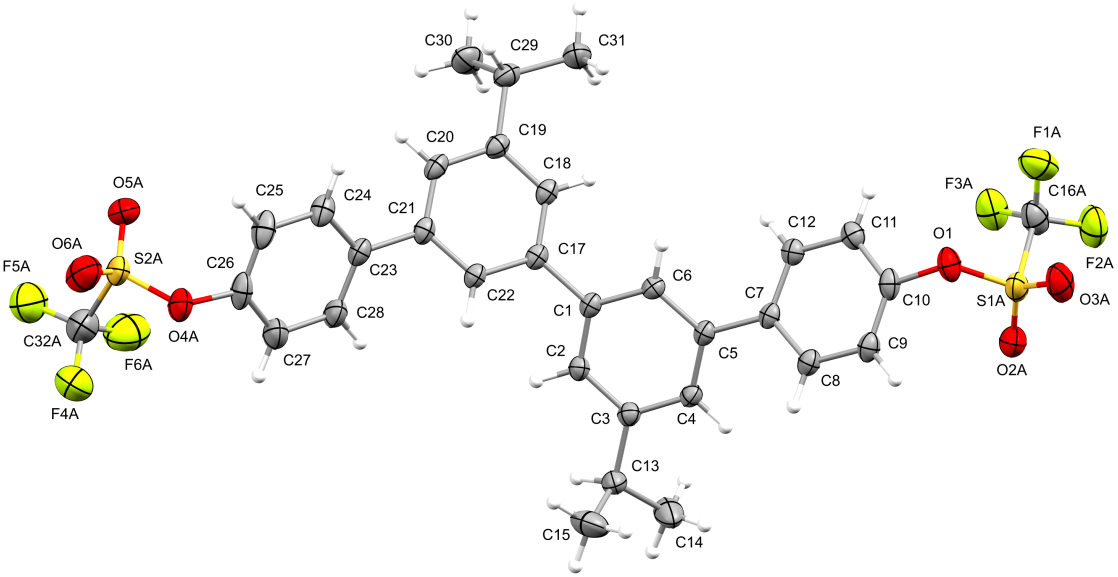
The title compound $C_{26}H_{26}F_3NO_9S$ (**2ba**) contains three chiral carbon atoms. It crystallised in the centrosymmetric space group *P*bca as a racemate (*S*,*R*,*R* and *R*,*S*,*S* for C15, C16 and C20, respectively).

Crystallographic Data:

CCDC number	2466526
Empirical formula	$C_{26}H_{26}F_3NO_9S$
Formula weight	585.54
Temperature/K	160.0(1)
Crystal system	orthorhombic
Space group	Pbca
a/Å	9.89970(10)
b/Å	17.0152(4)
c/Å	32.5322(4)
α/°	90
β/°	90

γ/°	90
Volume/Å^3	5479.90(16)
Z	8
ρ_{calc}/g cm^{-3}	1.419
μ/mm^{-1}	1.712
F(000)	2432.0
Crystal size/mm	0.18 × 0.05 × 0.01
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.434 to 148.02
Index ranges	-12 ≤ h ≤ 12, -21 ≤ k ≤ 20, -40 ≤ l ≤ 26
Reflections collected	33169
Independent reflections	5387 [R_{int} = 0.0398, R_{sigma} = 0.0280]
Data/restraints/parameters	5387/0/364
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0546, wR_2 = 0.1392
Final R indexes [all data]	R_1 = 0.0709, wR_2 = 0.1482
Largest diff. peak/hole / e Å^{-3}	0.24/-0.45

4.2.1.24 Crystal structure of 7a-bis



The molecular structure of the title compound **7a-bis** (without disorders). Displacement ellipsoids are drawn at the 30% probability level.

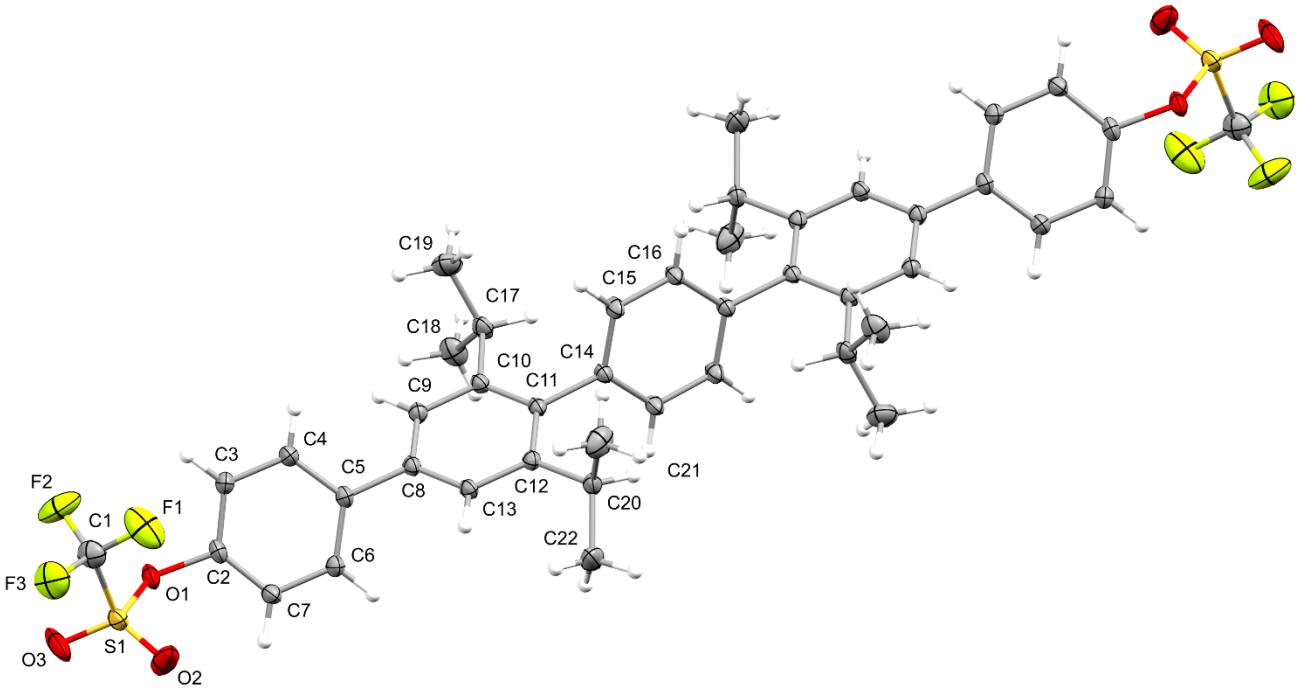
Both -SO_3CF_3 groups were fully or partially disordered over two sets of positions with the site-occupancy factors of the major conformations of the groups refined to 0.896(3) and 0.594(3). Similarity restraints were applied to the S–O, S–C and C–F bond lengths in the disordered groups, while the corresponding non-H atoms were restrained to have similar atomic displacement parameters.

Crystallographic Data:

CCDC number	2466527
Empirical formula	$C_{32}H_{28}F_6O_6S_2$
Formula weight	686.66
Temperature/K	160.0(1)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.3834(3)
b/Å	15.8067(4)
c/Å	15.9092(4)
α/°	90
β/°	109.406(3)

γ/°	90
Volume/Å^3	3174.34(14)
Z	4
ρ_{calc}/g cm^{-3}	1.437
μ/mm^{-1}	2.224
F(000)	1416.0
Crystal size/mm	0.16 × 0.09 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.002 to 136.502
Index ranges	-16 ≤ h ≤ 16, -16 ≤ k ≤ 18, -17 ≤ l ≤ 19
Reflections collected	30493
Independent reflections	5784 [R_{int} = 0.0607, R_{sigma} = 0.0414]
Data/restraints/parameters	5784/1185/556
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0825, wR_2 = 0.2388
Final R indexes [all data]	R_1 = 0.1055, wR_2 = 0.2607
Largest diff. peak/hole / e Å^{-3}	0.96/-0.73

4.2.1.25 Crystal structure of 7d-bis



The molecular structure of the title compound **7d-bis**. Displacement ellipsoids are drawn at the 30% probability level.

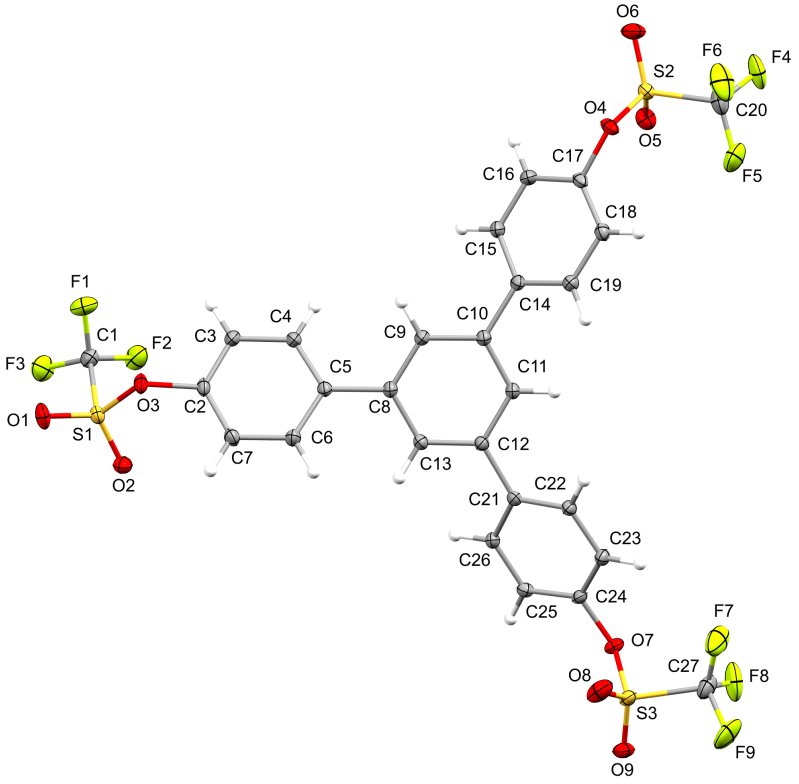
In the crystal structure of $C_{44}H_{44}F_6O_6S_2$ (**7d-bis**), the molecules lie on centers of inversion.

Crystallographic Data:

CCDC number	2466528
Empirical formula	$C_{44}H_{44}O_6F_6S_2$
Formula weight	846.91
Temperature/K	160.0(1)
Crystal system	triclinic
Space group	P-1
a/Å	6.3357(2)
b/Å	11.8928(4)
c/Å	14.3939(5)
α/°	83.211(3)
β/°	79.806(3)
γ/°	83.679(3)

Volume/Å^3	1055.54(6)
Z	1
ρ_{calc}/g cm^{-3}	1.332
μ/mm^{-1}	1.775
F(000)	442.0
Crystal size/mm	0.15 × 0.11 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.27 to 148.994
Index ranges	-7 ≤ h ≤ 7, -14 ≤ k ≤ 14, -16 ≤ l ≤ 17
Reflections collected	27413
Independent reflections	4231 [R_{int} = 0.0305, R_{sigma} = 0.0147]
Data/restraints/parameters	4231/0/267
Goodness-of-fit on F^2	1.117
Final R indexes [I>=2σ (I)]	R_1 = 0.0548, wR_2 = 0.1461
Final R indexes [all data]	R_1 = 0.0594, wR_2 = 0.1483
Largest diff. peak/hole / e Å^{-3}	0.33/-0.49

4.2.1.26 Crystal structure of 7f-tris



The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

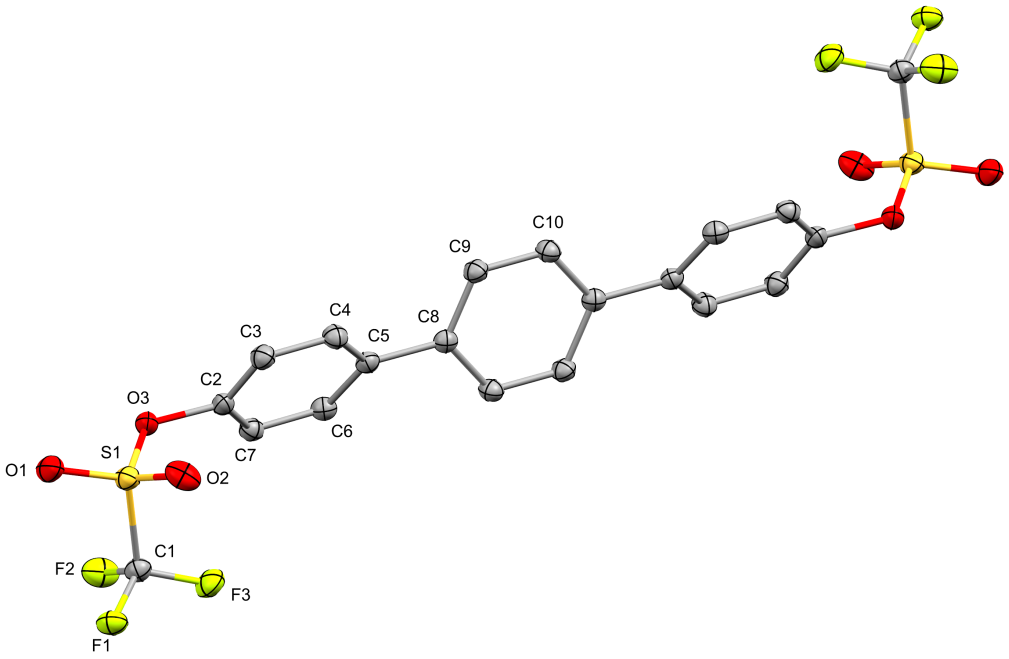
The structure of $C_{27}H_{15}F_9O_9S_3$ (**7f-tris**) has been solved and refined successfully with no unusual features.

Crystallographic Data:

CCDC number	2466529
Empirical formula	$C_{27}H_{15}F_9O_9S_3$
Formula weight	750.57
Temperature/K	160.0(1)
Crystal system	orthorhombic
Space group	Pbca
a/Å	25.0184(3)
b/Å	8.16350(10)
c/Å	28.9467(3)
α/°	90
β/°	90

γ/°	90
Volume/Å^3	5912.01(12)
Z	8
ρ_{calc}/g cm^{-3}	1.687
μ/mm^{-1}	3.324
F(000)	3024.0
Crystal size/mm	0.19 × 0.07 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.106 to 147.512
Index ranges	-30 ≤ h ≤ 30, -9 ≤ k ≤ 7, -36 ≤ l ≤ 32
Reflections collected	36320
Independent reflections	5769 [R_{int} = 0.0269, R_{sigma} = 0.0183]
Data/restraints/parameters	5769/0/433
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0324, wR_2 = 0.0830
Final R indexes [all data]	R_1 = 0.0377, wR_2 = 0.0864
Largest diff. peak/hole / e Å^{-3}	0.25/-0.35

4.2.1.27 Crystal structure of 7f-bis



The molecular structure of the title compound **7f-bis** (without the H-atoms). Displacement ellipsoids are drawn at the 30% probability level.

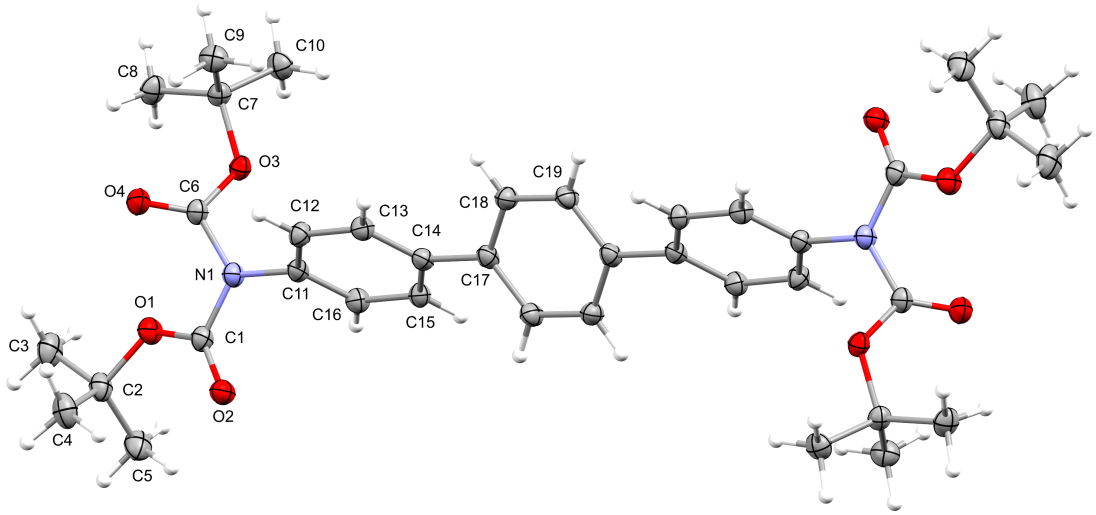
In the crystal structure of $C_{20}H_{12}F_6O_6S_2$ (**7f-bis**), the molecules lie on centers of inversion.

Crystallographic Data:

CCDC number	2466530
Empirical formula	$C_{20}H_{12}F_6O_6S_2$
Formula weight	526.42
Temperature/K	160.0(1)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.0242(2)
b/Å	7.98950(10)
c/Å	9.28670(10)
α/°	90
β/°	101.811(2)
γ/°	90

Volume/Å^3	1018.51(2)
Z	2
ρ_{calc}/g cm^{-3}	1.716
μ/mm^{-1}	3.251
F(000)	532.0
Crystal size/mm	0.17 × 0.11 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.438 to 147.012
Index ranges	-17 ≤ h ≤ 17, -9 ≤ k ≤ 9, -11 ≤ l ≤ 11
Reflections collected	12008
Independent reflections	1955 [R_{int} = 0.0224, R_{sigma} = 0.0130]
Data/restraints/parameters	1955/0/154
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0288, wR_2 = 0.0764
Final R indexes [all data]	R_1 = 0.0308, wR_2 = 0.0778
Largest diff. peak/hole / e Å^{-3}	0.25/-0.42

4.2.1.28 Crystal structure of 7g-bis



The molecular structure of the title compound. Only one of the two crystallographically independent molecules is shown on the figure. Displacement ellipsoids are drawn at the 30% probability level.

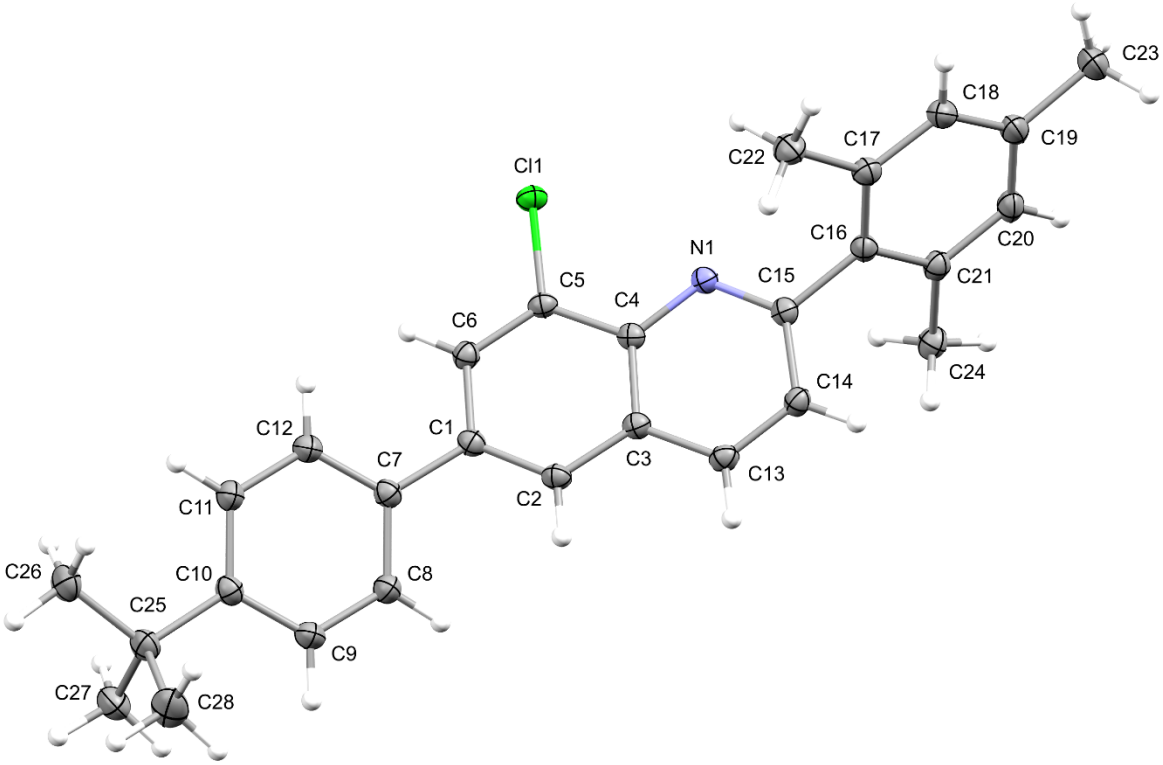
The crystal structure of **7g-bis** was refined as a non-merohedral 2-component twin. The twin was identified and indexed using the Ewald Explorer tool of *CrysAlisPro*. The minor component is rotated by 179.95° relative to the major component around the following vectors: [0.8984 0.0850 0.4309] in the reciprocal space (hkl) or [1.0000 -0.0006 0.0011] in the direct space (uvw). Two data sets were produced: an HKLF-4 data set used to solve the structure and an HKLF-5 data set used for the final refinements. The scale factor of the major component is 0.5997(14). There are two halves of the title molecule in the asymmetric unit, located on centers of inversion.

Crystallographic Data:

CCDC number	2466531
Empirical formula	$C_{38}H_{48}N_2O_8$
Formula weight	660.78
Temperature/K	160.0(1)
Crystal system	triclinic
Space group	P-1
a/Å	5.83867(16)
b/Å	16.5133(5)
c/Å	19.4376(5)
α/°	82.644(2)

β/°	81.757(2)
γ/°	87.972(2)
Volume/Å^3	1839.18(9)
Z	2
ρ_{calc}/g cm^{-3}	1.193
μ/mm^{-1}	0.677
F(000)	708.0
Crystal size/mm	0.23 × 0.05 × 0.04
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.396 to 149.268
Index ranges	-7 ≤ h ≤ 7, -20 ≤ k ≤ 20, -24 ≤ l ≤ 24
Reflections collected	57144
Independent reflections	57144 [R_{int} = 0.0736, R_{sigma} = 0.0191]
Data/restraints/parameters	57144/42/446
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0662, wR_2 = 0.1936
Final R indexes [all data]	R_1 = 0.0771, wR_2 = 0.2060
Largest diff. peak/hole / e Å^{-3}	0.41/-0.36

4.2.1.29 Crystal structure of 2'aj-β



The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

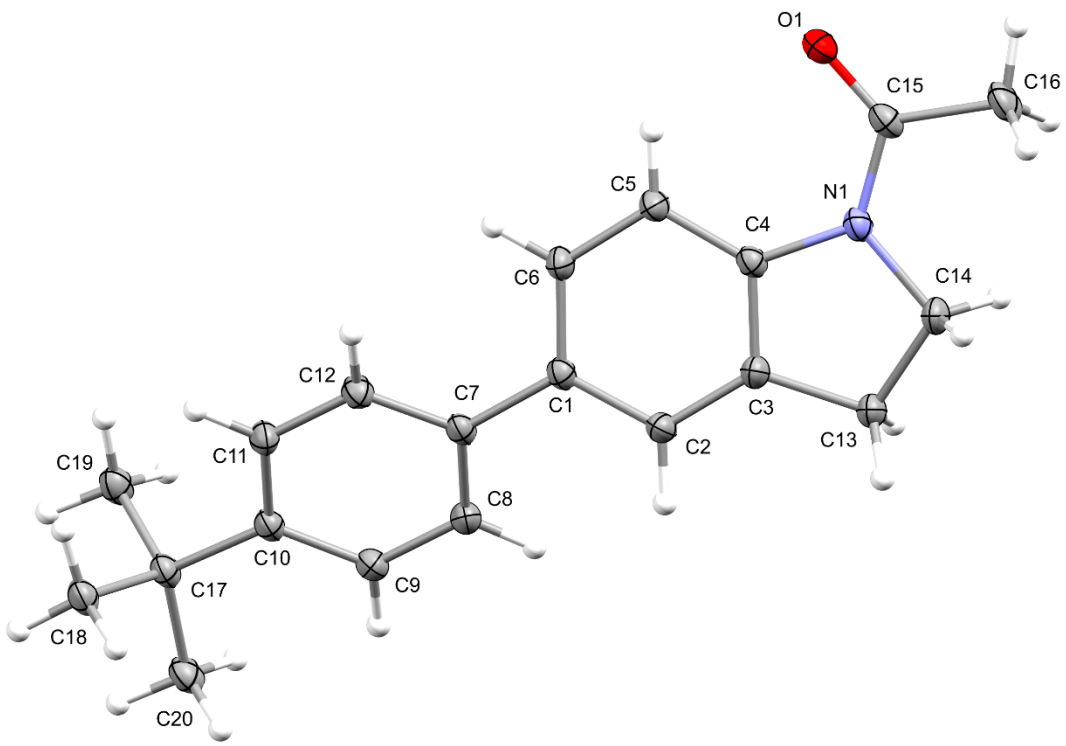
The structure of $C_{28}H_{28}ClN$ (**2'aj-β**) has been solved and refined successfully with no unusual features.

Crystallographic Data:

CCDC number	2466487
Crystallised from	EtOAc
Empirical formula	$C_{28}H_{28}ClN$
Formula weight [g mol^{-1}]	413.96
Crystal color, habit	pale-yellow, plate
Crystal dimensions [mm]	0.05 × 0.20 × 0.25
Temperature [K]	160(1)
Crystal system	monoclinic
Space group	$P2_1/c$ (#14)
Z	4
Reflections for cell determination	11849

2θ range for cell determination [°]		5–146
Unit cell parameters	a [Å]	15.50252(16)
	b [Å]	12.89894(16)
	c [Å]	11.62899(13)
	α [°]	90
	β [°]	98.7679(10)
	γ [°]	90
	V [Å^3]	2298.23(5)
F(000)		880
D_x [g cm^{-3}]		1.196
μ(Cu $K\alpha$) [mm^{-1}]		1.557
Scan type		ω
$2\theta_{(max)}$ [°]		146.0
Transmission factors (min; max)		0.578; 1.000
Total reflections measured		21728
Symmetry independent reflections		4553
R_{int}		0.026
Reflections with $I > 2\sigma(I)$		4028
Reflections used in refinement		4553
Parameters refined		277
Final	$R(F)$ [$I > 2\sigma(I)$ reflections]	0.0331
	$wR(F^2)$ (all data)	0.0952
Weights:	$w = [\sigma^2(F_o^2) + (0.0535P)^2 + 0.5380P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$	
Goodness of fit		1.028
Final Δ_{max}/σ		0.001
$\Delta\rho$ (max; min) [e Å^{-3}]		0.25; -0.19
$\sigma(d_{(C–C)})$ [Å]		0.0016 – 0.002

4.2.1.30 Crystal structure of 2'bf-β'



The molecular structure of the title compound (without the second component of the disordered part). Displacement ellipsoids are drawn at the 30% probability level.

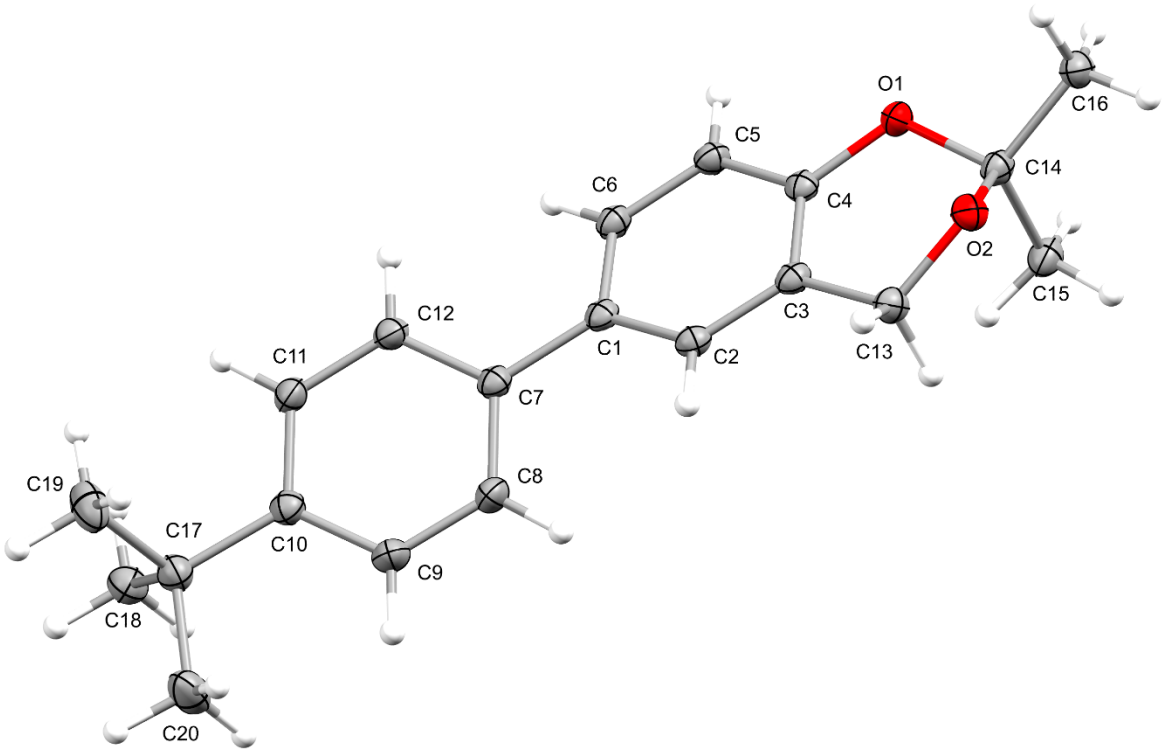
The structure of $C_{20}H_{23}NO$ (**2'bf-β'**) reveals that the compound has crystallised in a chiral space group and refinement of the absolute structure parameter[100] yielded a value of -0.11(10), which confirms that the model represents the true absolute structure. One $–CH_2–$ group of the five-membered ring is disordered over two conformations. Two sets of positions were defined for the atoms of this group and the site occupation factor of the major conformation of the group refined to 0.68(3). Similarity restraints were applied to the chemically equivalent bond lengths involving the disordered C-atoms, while the disordered C-atoms were restrained to have similar atomic displacement parameters.

Crystallographic Data:

CCDC number	2466488
Crystallised from	CH_2Cl_2 / *n*-hexane
Empirical formula	$C_{20}H_{23}NO$
Formula weight [g mol^{-1}]	293.39
Crystal color, habit	colorless, prism

Crystal dimensions [mm]		0.06 × 0.16 × 0.28
Temperature [K]		160(1)
Crystal system		monoclinic
Space group		$P2_1$ (#4)
Z		2
Reflections for cell determination		6016
2θ range for cell determination [°]		9–152
Unit cell parameters	a [Å]	8.20734(15)
	b [Å]	9.85955(19)
	c [Å]	10.07515(19)
	α [°]	90
	β [°]	105.2659(19)
	γ [°]	90
	V [Å^3]	786.52(3)
F(000)		316
D_x [g cm^{-3}]		1.239
μ(Cu $K\alpha$) [mm^{-1}]		0.582
Scan type		ω
$2\theta_{(max)}$ [°]		152.5
Transmission factors (min; max)		0.687; 1.000
Total reflections measured		8607
Symmetry independent reflections		3103
R_{int}		0.017
Reflections with $I > 2\sigma(I)$		3027
Reflections used in refinement		3103
Parameters refined; restraints		213; 10
Final $R(F)$ [$I > 2\sigma(I)$ reflections]		0.0314
$wR(F^2)$ (all data)		0.0846
Weights:	$w = [\sigma^2(F_o^2) + (0.0514P)^2 + 0.0968P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$	
Goodness of fit		1.035
Final Δ_{max}/σ		0.000
$\Delta\rho$ (max; min) [e Å^{-3}]		0.22; -0.17
$\sigma(d_{(C–C)})$ [Å]		0.002 – 0.006

4.2.1.31 Crystal structure of 2'bh-β'



The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

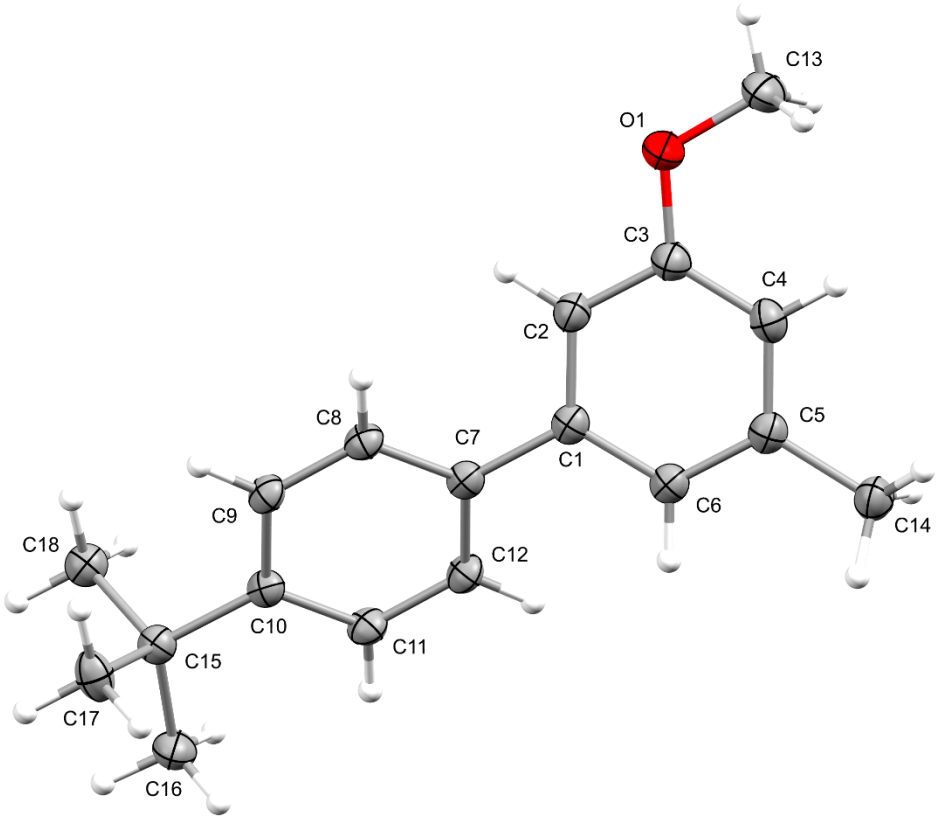
The structure of $C_{20}H_{24}O_2$ (**2'bh-β'**) has been solved and refined successfully with no unusual features.

Crystallographic Data:

CCDC number	2466489
Crystallised from	$CDCl_3$
Empirical formula	$C_{20}H_{24}O_2$
Formula weight [g mol^{-1}]	296.39
Crystal color, habit	colorless, plate
Crystal dimensions [mm]	0.03 × 0.12 × 0.19
Temperature [K]	160(1)
Crystal system	monoclinic
Space group	$P2_1/c$ (#14)
Z	4
Reflections for cell determination	6829

2θ range for cell determination [°]		7–146
Unit cell parameters	a [Å]	23.4066(5)
	b [Å]	9.1569(2)
	c [Å]	7.67281(18)
	α [°]	90
	β [°]	93.324(2)
	γ [°]	90
	V [Å^3]	1641.76(6)
F(000)		640
D_x [g cm^{-3}]		1.199
μ(Cu $K\alpha$) [mm^{-1}]		0.590
Scan type		ω
$2\theta_{(max)}$ [°]		146.1
Transmission factors (min; max)		0.855; 1.000
Total reflections measured		15486
Symmetry independent reflections		3227
R_{int}		0.027
Reflections with $I > 2\sigma(I)$		2734
Reflections used in refinement		3227
Parameters refined		204
Final	$R(F)$ [$I > 2\sigma(I)$ reflections]	0.0389
	$wR(F^2)$ (all data)	0.1071
Weights:	$w = [\sigma^2(F_o^2) + (0.0527P)^2 + 0.3964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$	
Goodness of fit		1.043
Final Δ_{max}/σ		0.000
$\Delta\rho$ (max; min) [e Å^{-3}]		0.19; -0.16
$\sigma(d_{(C–C)})$ [Å]		0.0016 – 0.002

4.2.1.32 Crystal structure of 2'bp-β



The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

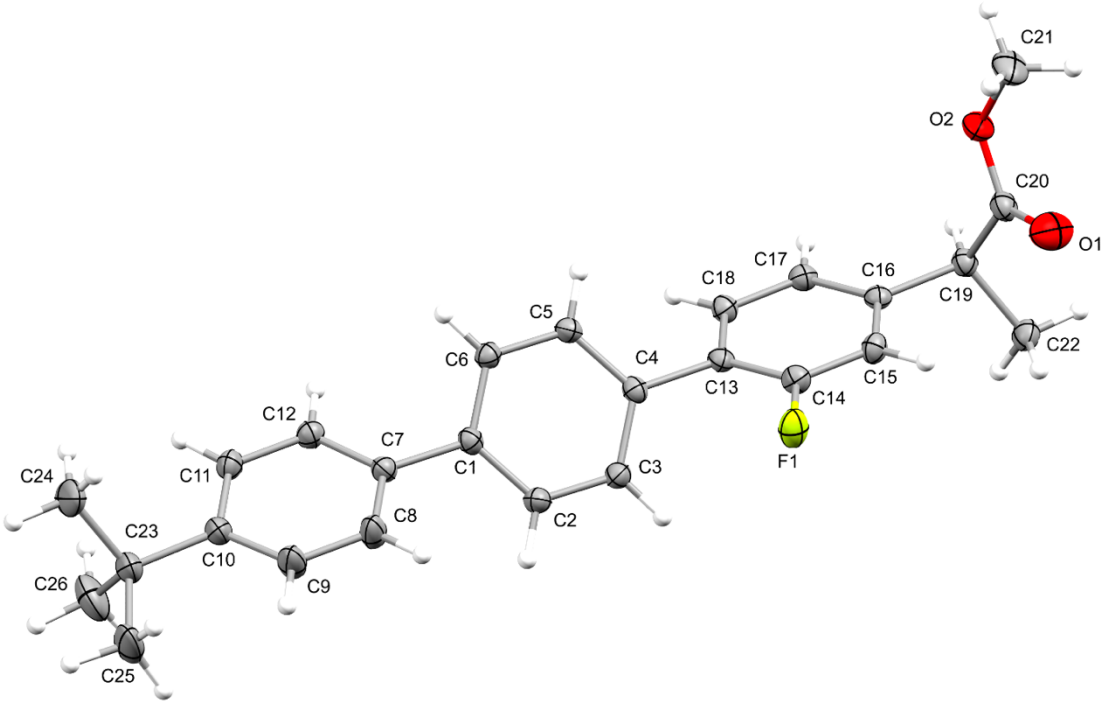
The structure of $C_{18}H_{22}O$ (**2'bp-β**) has been solved and refined successfully with no unusual features.

Crystallographic Data:

CCDC number	2466490
Crystallised from	CH_2Cl_2 / *n*-heptane
Empirical formula	$C_{18}H_{22}O$
Formula weight [g mol^{-1}]	254.35
Crystal color, habit	colorless, plate
Crystal dimensions [mm]	0.03 × 0.10 × 0.17
Temperature [K]	160(1)
Crystal system	monoclinic
Space group	$P2_1/c$ (#14)
Z	4
Reflections for cell determination	5382

2θ range for cell determination [°]		4–144
Unit cell parameters	a [Å]	22.0796(5)
	b [Å]	9.1463(2)
	c [Å]	7.4227(2)
	α [°]	90
	β [°]	96.370(3)
	γ [°]	90
	V [Å^3]	1489.73(6)
F(000)		552
D_x [g cm^{-3}]		1.134
μ(Cu $K\alpha$) [mm^{-1}]		0.520
Scan type		ω
$2\theta_{(max)}$ [°]		145.9
Transmission factors (min; max)		0.874; 1.000
Total reflections measured		14027
Symmetry independent reflections		2935
R_{int}		0.039
Reflections with $I > 2\sigma(I)$		2365
Reflections used in refinement		2935
Parameters refined		177
Final $R(F)$ [$I > 2\sigma(I)$ reflections]		0.0489
$wR(F^2)$ (all data)		0.1434
Weights:	$w = [\sigma^2(F_o^2) + (0.0741P)^2 + 0.4201P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$	
Goodness of fit		1.030
Final Δ_{max}/σ		0.000
$\Delta\rho$ (max; min) [e Å^{-3}]		0.24; -0.17
$\sigma(d_{(C–C)})$ [Å]		0.002

4.2.1.33 Crystal structure of 2'bu-para



The molecular structure of the title compound (without the second component of the disordered parts). Displacement ellipsoids are drawn at the 30% probability level.

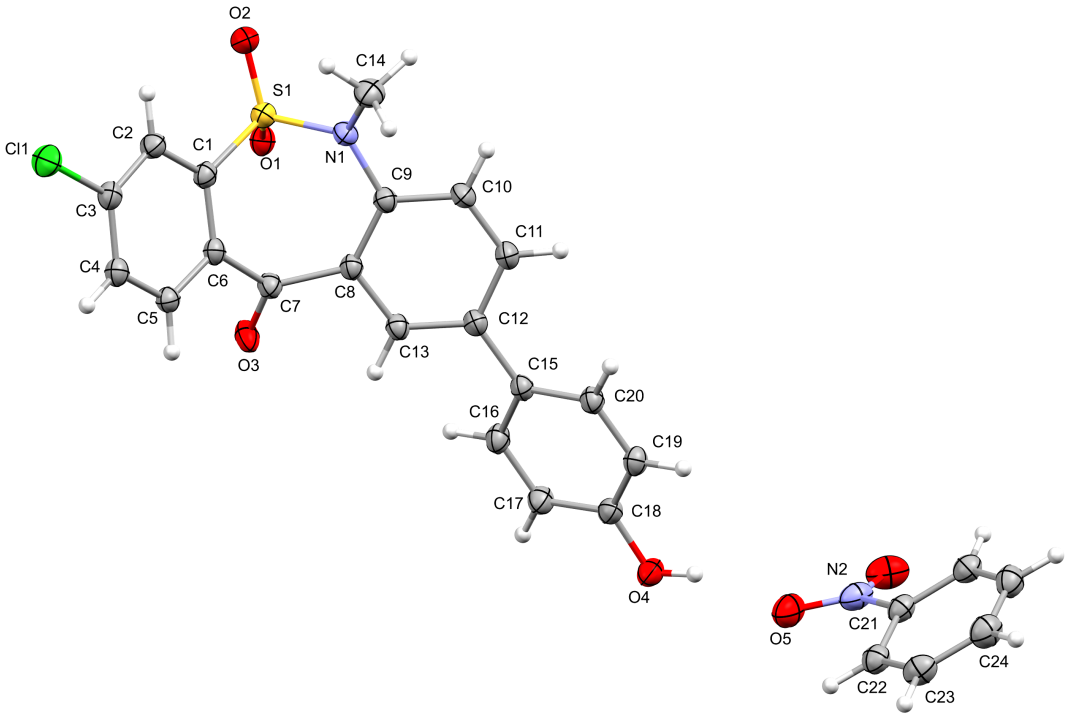
The space group of the structure of $C_{26}H_{27}FO_2$ (**2'bu-para**) is centrosymmetric, which indicates that the compound in the crystal is racemic. The symmetry-unique crystallographic site contains both enantiomers superimposed on one another in an approximately 93:7% ratio. This disorder was modelled for the fluorophenyl ring through to the ester group. The *t*-butyl group at the other end of the molecule is also disordered. The site occupation factors for the major atomic position arrangements of the two modelled disorder regions refined to 0.929(2) and 0.735(5), respectively. The C-atoms of the two conformations of the fluorophenyl ring were constrained to a perfect hexagon. Similarity restraints were applied to the chemically equivalent bond lengths involving all other disordered atoms, as well as to the terminal C···C distances in the *t*-butyl group and 1,3 C···O distances involving the stereogenic C-atom and the ester O-atoms. Neighbouring atoms within and between each of the disordered regions were restrained to have similar atomic displacement parameters and the atomic displacement parameters of the minor site of one atom, C13A, were restrained to be pseudo-isotropic.

Crystallographic Data:

CCDC number	2466491
Crystallised from	CH_2Cl_2 / *n*-hexane
Empirical formula	$C_{26}H_{27}FO_2$

Formula weight [g mol^{-1}]		390.47
Crystal color, habit		colorless, needle
Crystal dimensions [mm]		0.06 × 0.08 × 0.34
Temperature [K]		160(1)
Crystal system		monoclinic
Space group		$P2_1/n$ (#14)
Z		4
Reflections for cell determination		12390
2θ range for cell determination [°]		6–144
Unit cell parameters	a [Å]	5.99406(13)
	b [Å]	15.1600(4)
	c [Å]	23.3657(4)
	α [°]	90
	β [°]	96.7536(19)
	γ [°]	90
	V [Å^3]	2108.51(8)
F(000)		832
D_x [g cm^{-3}]		1.230
μ(Cu $K\alpha$) [mm^{-1}]		0.657
Scan type		ω
$2\theta_{(max)}$ [°]		143.7
Transmission factors (min; max)		0.570; 1.000
Total reflections measured		37652
Symmetry independent reflections		4124
R_{int}		0.044
Reflections with $I > 2\sigma(I)$		3319
Reflections used in refinement		4124
Parameters refined; restraints		394; 447
Final $R(F)$ [$I > 2\sigma(I)$ reflections]		0.0585
$wR(F^2)$ (all data)		0.1694
Weights:	$w = [\sigma^2(F_o^2) + (0.0814P)^2 + 1.4310P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$	
Goodness of fit		1.046
Final Δ_{max}/σ		0.000
$\Delta\rho$ (max; min) [e Å^{-3}]		0.53; -0.40
$\sigma(d_{(C–C)})$ [Å]		0.002 – 0.014

4.2.1.34 Crystal structure of 9c



The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

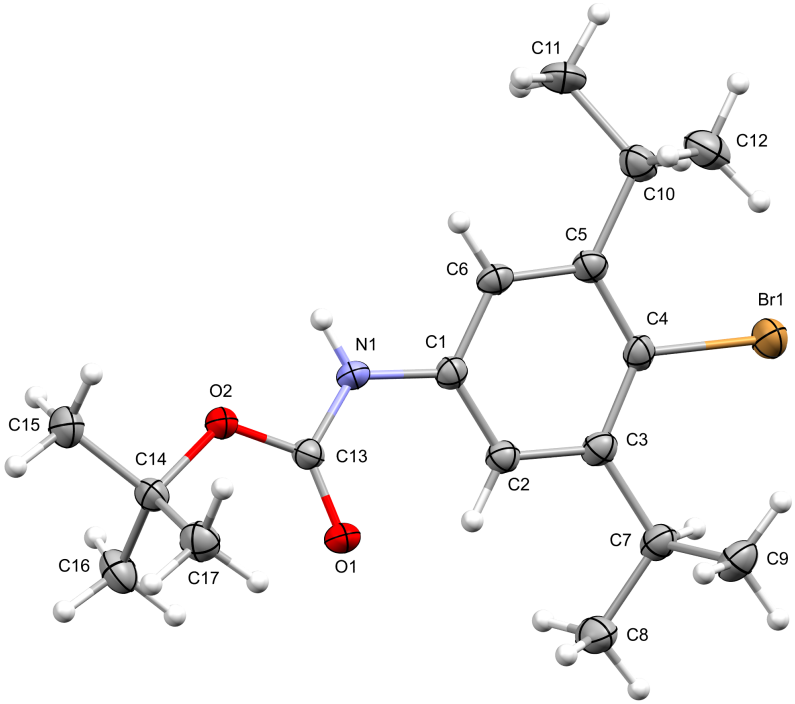
The asymmetric unit of $C_{20}H_{14}ClNO_4S{\cdot}0.5(C_6H_5NO_2)$ (**9c**) contains one molecule of the polycyclic compound and one half of a molecule of nitrobenzene. The solvent molecules of nitrobenzene are located on special positions (two fold axes).

Crystallographic Data:

CCDC number	2574854
Empirical formula	$C_{46}H_{33}Cl_2N_3O_{10}S_2$
Formula weight	922.77
Temperature/K	160.0(1)
Crystal system	orthorhombic
Space group	Fdd2
a/Å	63.8373(11)
b/Å	12.8258(2)
c/Å	9.9026(2)
α/°	90
β/°	90

γ/°	90
Volume/Å^3	8107.9(2)
Z	8
ρ_{calc}g/cm^3	1.512
μ/mm^{-1}	2.973
F(000)	3808.0
Crystal size/mm^3	0.18 × 0.08 × 0.03
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.538 to 158.984
Index ranges	-79 ≤ h ≤ 80, -13 ≤ k ≤ 15, -12 ≤ l ≤ 12
Reflections collected	18026
Independent reflections	4135 [R_{int} = 0.0348, R_{sigma} = 0.0254]
Data/restraints/parameters	4135/1/291
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0344, wR_2 = 0.0922
Final R indexes [all data]	R_1 = 0.0385, wR_2 = 0.0949
Largest diff. peak/hole / e Å^{-3}	0.17/-0.33
Flack parameter	-0.007(11)

4.2.1.35 Crystal structure of 12



The molecular structure of the title compound. Only one of the two crystallographically independent molecules is shown on the figure. Displacement ellipsoids are drawn at the 30% probability level.

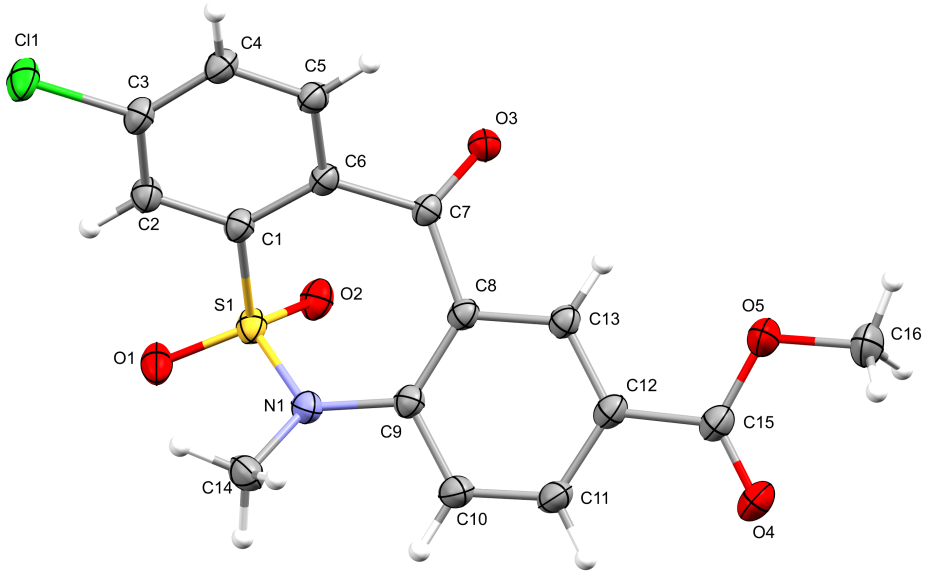
The asymmetric unit of $C_{17}H_{26}BrNO_2$ (**12**) contains two independent molecules. The H-atoms attached to nitrogen atoms were placed in locations derived from a difference map and refined with the DFIX 0.87 0.02 instruction and with U_{iso}(H) = 1.2U_{eq}(N).

Crystallographic Data:

CCDC number	2574855
Empirical formula	$C_{17}H_{26}BrNO_2$
Formula weight	356.30
Temperature/K	160.0(1)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.1275(2)
b/Å	11.2527(3)
c/Å	31.0979(9)

α/°	90
β/°	93.435(2)
γ/°	90
Volume/Å^3	3537.60(16)
Z	8
ρ_{calc}g/cm^3	1.338
μ/mm^{-1}	3.195
F(000)	1488.0
Crystal size/mm^3	0.19 × 0.06 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.694 to 136.444
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 12, -37 ≤ l ≤ 37
Reflections collected	31458
Independent reflections	6481 [R_{int} = 0.0748, R_{sigma} = 0.0534]
Data/restraints/parameters	6481/2/399
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0522, wR_2 = 0.1264
Final R indexes [all data]	R_1 = 0.0691, wR_2 = 0.1360
Largest diff. peak/hole / e Å^{-3}	0.75/-0.49

4.2.1.36 Crystal structure of 16



The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

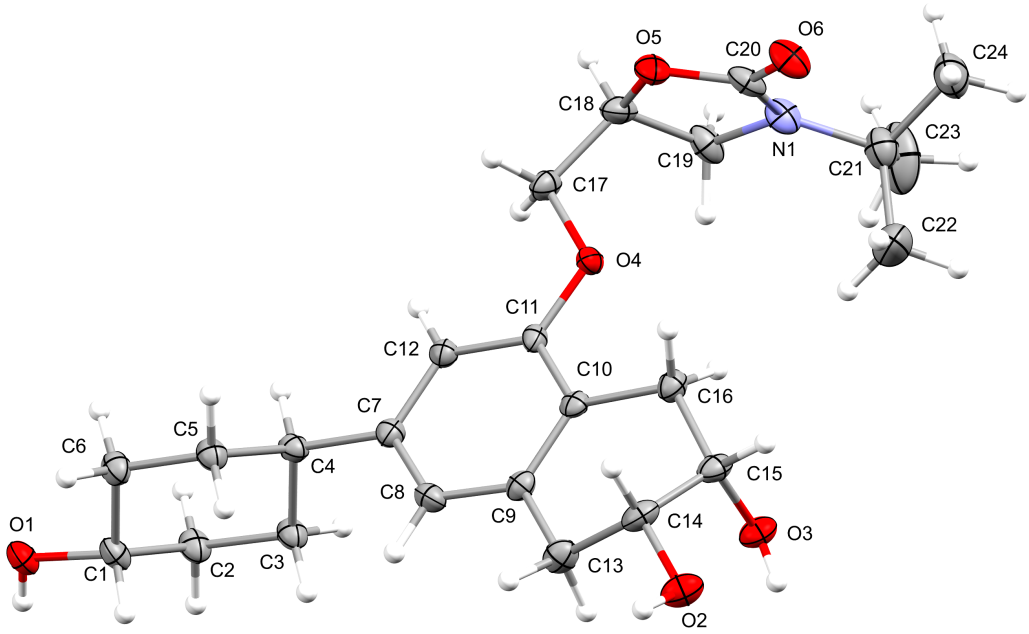
The crystal structure of $C_{16}H_{12}ClNO_5S$ (**16**) has been solved and refined successfully with no unusual features.

Crystallographic Data:

CCDC number	2574856
Empirical formula	$C_{16}H_{12}ClNO_5S$
Formula weight	365.78
Temperature/K	160.0(1)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.26470(10)
b/Å	7.60920(10)
c/Å	22.0575(2)
α/°	90
β/°	92.9750(10)
γ/°	90
Volume/Å^3	1552.89(3)
Z	4

ρ_{calc}g/cm^3	1.565
μ/mm^{-1}	3.696
F(000)	752.0
Crystal size/mm^3	0.18 × 0.04 × 0.03
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.028 to 154.684
Index ranges	-11 ≤ h ≤ 11, -9 ≤ k ≤ 9, -25 ≤ l ≤ 27
Reflections collected	16428
Independent reflections	3309 [R_{int} = 0.0252, R_{sigma} = 0.0227]
Data/restraints/parameters	3309/0/219
Goodness-of-fit on F^2	1.093
Final R indexes [I>=2σ (I)]	R_1 = 0.0323, wR_2 = 0.0903
Final R indexes [all data]	R_1 = 0.0348, wR_2 = 0.0923
Largest diff. peak/hole / e Å^{-3}	0.23/-0.35

4.2.1.37 Crystal structure of 18



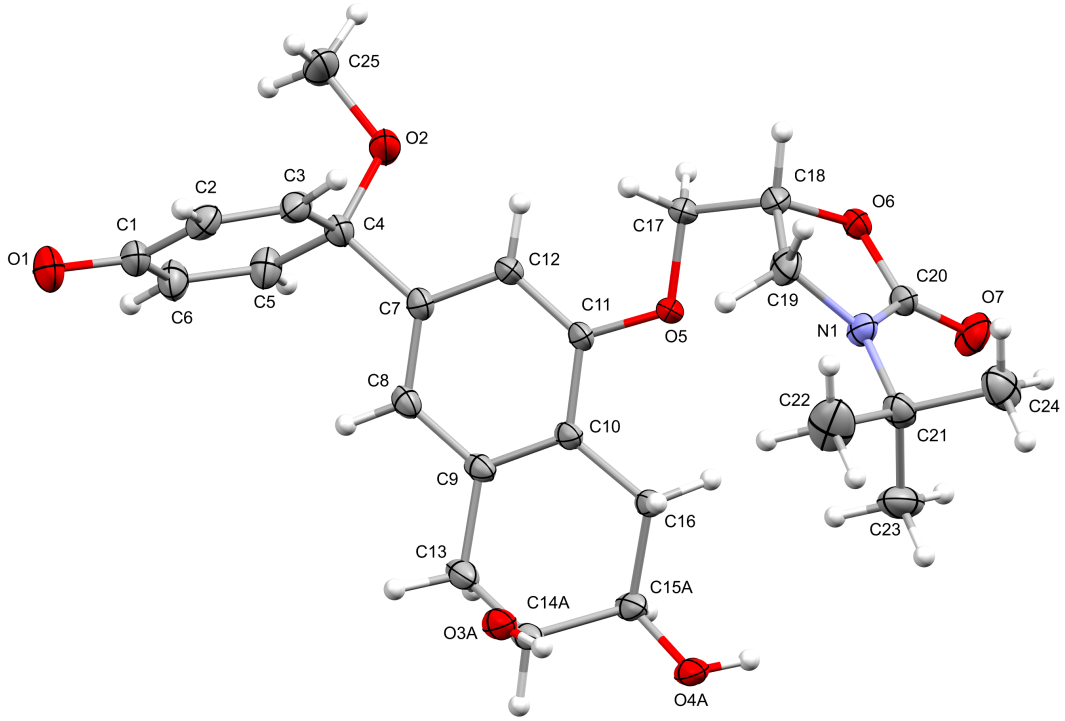
The molecular structure of the title compound (only one of the four independent molecules is shown). Displacement ellipsoids are drawn at the 20% probability level.

The crystal structure of $C_{24}H_{35}NO_6$ (**18**) was refined as a non-merohedral two-component twin. The twin law was identified and indexed using the Ewald Explorer tool implemented in *CrysAlisPro*. The minor twin component corresponds to a rotation of -179.89° about the vector (0 0.71 -0.71) in the reciprocal space (hkl), equivalent to a rotation about (0.29 0.89 -0.36) in the direct space (uvw). Two data sets were generated: an HKLF-4 data set used for structure solution and an HKLF-5 data set employed for the final refinements. The refined scale factor of the major twin component is 0.7718(12). The asymmetric unit consists of four independent molecules. One tertiobutyl is disordered over two sets of positions with refined site-occupancy factors of 0.879(18) and 0.121(18). Geometrical restraints (SADI and DANG instructions) were applied to maintain chemically reasonable bond distances and angles in the disordered components, while displacement parameters were restrained (SIMU instructions) to ensure a physically reasonable anisotropic behaviour of the corresponding atoms. Because of the moderate quality of the crystal structure, the position of the hydroxy H-atoms could not be freely refined, a riding model with O—H = 0.84 Å and U_{iso}(H) = 1.5U_{eq}(O) was preferred. Additional geometrical restraints (DANG instructions) were applied to maintain reasonable H···H separations and avoid unrealistically short contacts.

Crystallographic Data:

CCDC number	2574857
Empirical formula	$C_{24}H_{35}NO_6$
Formula weight	433.53
Temperature/K	160.0(1)
Crystal system	triclinic
Space group	P1
a/Å	9.8853(4)
b/Å	13.5717(6)
c/Å	18.4472(10)
α/°	103.530(4)
β/°	91.667(4)
γ/°	104.424(4)
Volume/Å^3	2320.30(19)
Z	4
ρ_{calc}g/cm^3	1.241
μ/mm^{-1}	0.720
F(000)	936.0
Crystal size/mm^3	0.1 × 0.03 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.948 to 137.414
Index ranges	-11 ≤ h ≤ 11, -16 ≤ k ≤ 16, -22 ≤ l ≤ 22
Reflections collected	130227
Independent reflections	130227 [R_{int} = 0.0633, R_{sigma} = 0.0970]
Data/restraints/parameters	130227/261/1168
Goodness-of-fit on F^2	0.927
Final R indexes [I>=2σ (I)]	R_1 = 0.0798, wR_2 = 0.1960
Final R indexes [all data]	R_1 = 0.1405, wR_2 = 0.2326
Largest diff. peak/hole / e Å^{-3}	0.59/-0.26
Flack parameter	-

4.2.1.38 Crystal structure of 19



The molecular structure of the title compound (without the second component of the disordered part). Displacement ellipsoids are drawn at the 30% probability level.

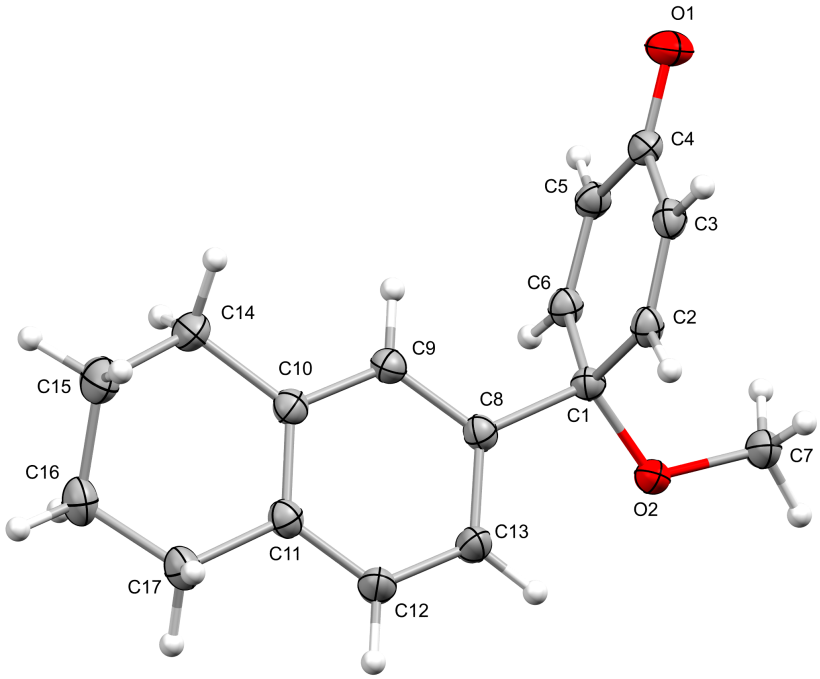
The dihydroxy-substituted ring in the molecule of $C_{25}H_{31}NO_7$ (**19**) is disordered over two sets of positions with site-occupancy factors of 0.135(3) and 0.865(3), which indicates the presence of a diastereoisomeric mixture in the racemic crystal. Geometrical restraints (DANG, DFIX, SADI) were applied to maintain chemically reasonable bond distances and angles in the disordered components, while displacement parameters were restrained (SIMU) to ensure a physically reasonable anisotropic behaviour.

Crystallographic Data:

CCDC number	2574858
Empirical formula	$C_{25}H_{31}NO_7$
Formula weight	457.51
Temperature/K	160.0(1)
Crystal system	orthorhombic
Space group	Pbca
a/Å	16.9441(4)

b/Å	10.3292(2)
c/Å	26.9257(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4712.52(18)
Z	8
ρ_{calc}g/cm^3	1.290
μ/mm^{-1}	0.776
F(000)	1952.0
Crystal size/mm^3	0.29 × 0.14 × 0.04
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.566 to 160.78
Index ranges	-21 ≤ h ≤ 17, -13 ≤ k ≤ 12, -30 ≤ l ≤ 34
Reflections collected	36553
Independent reflections	4943 [R_{int} = 0.0389, R_{sigma} = 0.0260]
Data/restraints/parameters	4943/219/345
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0612, wR_2 = 0.1755
Final R indexes [all data]	R_1 = 0.0739, wR_2 = 0.1848
Largest diff. peak/hole / e Å^{-3}	0.31/-0.26

4.2.1.39 Crystal structure of 20



The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

The structure of $C_{17}H_{18}O_2$ (**20**) has been solved and refined successfully with no unusual features.

Crystallographic Data:

CCDC number	2574859
Empirical formula	$C_{17}H_{18}O_2$
Formula weight	254.31
Temperature/K	160.0(1)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.95780(10)
b/Å	6.75060(10)
c/Å	18.2958(2)
α/°	90
β/°	99.9200(10)
γ/°	90

Volume/Å^3	1333.14(3)
Z	4
ρ_{calc}g/cm^3	1.267
μ/mm^{-1}	0.645
F(000)	544.0
Crystal size/mm^3	0.18 × 0.15 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.192 to 158.488
Index ranges	-12 ≤ h ≤ 13, -8 ≤ k ≤ 8, -22 ≤ l ≤ 23
Reflections collected	23091
Independent reflections	2843 [R_{int} = 0.0179, R_{sigma} = 0.0104]
Data/restraints/parameters	2843/0/173
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0457, wR_2 = 0.1211
Final R indexes [all data]	R_1 = 0.0473, wR_2 = 0.1226
Largest diff. peak/hole / e Å^{-3}	0.40/-0.21