Electronic Supplementary Material (ESI) for ChemComm.

A Site-selective and Stereospecific Cascade Suzuki-Miyaura Annulation of Alkyl 1,2-Bisboronic Esters and 2,2'-Dihalo 1,1'-Biaryls

Suzanne Willems,[a] Georgios Toupalas,[b] Julia C. Reisenbauer,[b] and Bill Morandi [*ab]

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1. General Information

Chemicals All reagents were purchased from commercial suppliers and used without further purification unless noted otherwise. Dry argon was purchased from Air Liquide with >99.5% purity. Anhydrous solvents were distilled under argon from an appropriate drying agent by the facilities of the institute: DCM (CaH_2), THF (Mg/anthracene), toluene (Na/K), or purchased from a commercial supplier (Acros, Sigma Aldrich). All solvents for extraction and column chromatography were distilled before use by facilities of the MPI für Kohlenforschung.

General Methods Unless otherwise stated, all air- and moisture sensitive reactions were performed using Schlenk techniques under inert gas or in an MBraun LabMaster Pro SP dry box under argon atmosphere in oven-dried (100 °C) vials, Schlenk flasks or round-bottom flasks flame-dried under vacuum with a teflon-coated magnetic stir bar. For the reactions carried out at elevated temperatures, an aluminum heating block or an oil bath was used. After the reaction work-up the solvents were removed under reduced pressure at 40 °C using a Büchi R-210 rotary evaporator and the compounds were dried under high vacuum.

Chromatography Thin-layer chromatography (TLC) was performed using silica gel pre-coated plastic sheets (Polygram SIL G/UV254, 0.2 mm, with fluorescent indicator; Macherey-Nagel), which were visualized with a UV lamp (254 or 366 nm) or detected by staining with acidic cerium-ammonium-molybdate or vaniline or basic $KMnO_4$ solution. Preparative thin-layer chromatography (PrepTLC) was performed on silica gel pre-coated glass plates SIL G-25 UV254 with 0.25 mm and SIL G-100 UV254 with 1.0 mm SiO_2 layers (Macherey-Nagel). Flash column chromatography was performed on Merck silica gel (60, particle size 0.040–0.063 mm) at room temperature under elevated pressure. Gas chromatography was performed on a Shimadzu GC-2025 using a Macherey-Nagel Optima 5 (30.0 m x 0.25 mm x 0.25 µm) column. The following program was applied 50 °C (2 min); 15 °C/min to 320 °C; 320 °C (10 min), injection volume 1 µL. The purification of enantiomers and determination of enantiomeric excess was performed by the chromatography department using high-performance liquid chromatography (HPLC), and GC employing a chiral stationary phase and is specified in the individual experiment.

NMR Spectroscopy NMR-Spectra were recorded on Bruker DPX-300, AV-500, AVIII-600 in solvents indicated. Chemical shifts were referenced to the corresponding solvent residual peak ($CDCl_3$: δ_C = 77.16 ppm, residual $CHCl_3$ in $CDCl_3$ δ_H 7.26 ppm)[1] and were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, p = pentet, hept = heptet, m = multiplet and br = broad signal), coupling constants (*J* values) in Hz

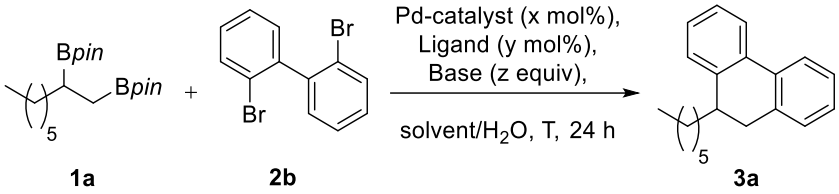
and integration. ^{13}C NMR, ^{11}B NMR, and ^{19}F NMR were recorded in [^{1}H]-decoupled mode and the values of the chemical shifts are rounded to one decimal point. The NMR department at the MPI für Kohlenforschung acquired all spectra from 600 MHz. The Spectra were processed with MestReNova 11.0.2 and coupling constants are reported as observed.

High Resolution Mass Spectrometry (HRMS) The HRMS data was obtained by the department of the MPI für Kohlenforschung by electron ionization (EI) or electron spray ionization (ESI) using a Finnigan MAT 95 (EI), Bruker APEX II FTMS (7T magnet, ESI) or Bruker maXis ESI-Qq-TOF-MS and are reported in m/z. The ionization method and mode of detection employed is indicated for the corresponding experiment. All published data ware within a range of m/z ±3 ppm of theoretical values.

X-Ray X-ray single-crystal structure analysis was performed by the Small Molecule Crystallography Center (SMoCC) of the Department of Chemistry and Applied Biosciences at ETH Zürich. Single crystalline samples were measured on the following instrument: Rigaku Oxford Diffraction XtaLAB Synergy-S Dualflex kappa diffractometer equipped with a Dectris Pilatus 300 HPAD detector and using microfocus sealed tube Cu-Kα radiation with mirror optics (λ = 1.54178 Å).

2. Reaction Development

2.1 General Procedure for the reaction development

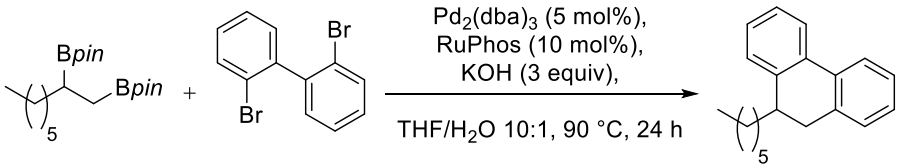


1a **2b** **3a**

An oven-dried 8 mL vial with a magnetic stir bar was taken into a dry box, and Pd-catalyst (x mol%), and ligand (y mol%) were added and solubilized in an organic solvent (0.3 mL). After stirring in the dry box for 30 min at room temperature, the pre-stirred catalytic system was added to a solution of 2,2'-(octane-1,2-diyl)bis(pinacolatoborolane) **1a** (0.1 mmol, 1 equiv), dibromide **2b** (1 equiv) and base (z equiv) in organic solvent/H_2O (0.1 mmol/L with resp. to **1a**) via syringe at once. The mixture was closed with a screw cap, removed from the dry box, and stirred at indicated temperature and time. Then, water (1 mL) and the internal standard *n*-tetradecane (26 µL, 0.762 g/mL, 0.1 mmol, 1 equiv) were added to the mixture. The organic phase was separated, collected, and filtered over a Na_2SO_4/silica plug. The aqueous phase was extracted twice with MTBE (1 mL), and the organic phases were combined after filtration over the Na_2SO_4/silica plug. An aliquot was taken to analyze by GC.

2.1 Optimization details for the annulation reaction with 2,2'-dibromobiphenyl 2b

Table S1: Optimization of base, equiv of dihalide and ligand ratio[a]

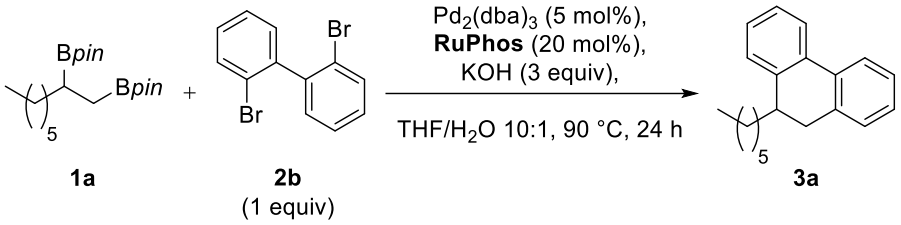


1a **2b** (1 equiv) **3a**

Entry	Deviation from standard conditions	3a [%][b]
1	none	18
2	Cs_2CO_3 instead of KOH	2
3	K_2CO_3 instead of KOH	2
4	CsF instead of KOH	3
5	KO*t*Bu instead of KOH	16
6	K_3PO_4 instead of KOH	2
7	1.1 equiv of **1a**	14
8	1.5 equiv of **1a**	18
9	***RuPhos 20 mol%***	***26***

[a] Reaction conditions: **1a** (0.1 mmol), **2b** (0.1 mmol), $Pd_2(dba)_3$ (0.005 mmol), RuPhos (0.01 mmol), KOH (0.3 mmol), THF/H_2O (0.9 mL:0.1 mL), 90 °C, 24 h. [b] GC yield using *n*-tetradecane as internal standard

Table S2: Optimization of solvent, base and ligands.[a]



Entry	Deviation from standard conditions	3a [%][b]
1	none	26
2	Toluene/THF /H_2O 4.5:4.5:1	16
3	2-MeTHF instead of THF	26
4	2,5-MeTHF instead of THF	10
5	K_2CO_3 and DMF instead of KOH and THF	14
6	KOH (6 equiv)	16
7	SPhos instead of RuPhos	13
8	CyJohnPhos instead of RuPhos	9
9	dcype (10 mol%) instead of RuPhos	7
10	Xantphos instead of RuPhos	6
11	bbbpy instead of RuPhos	8
12	IMes · HCl instead of RuPhos	3
13	ICy · HCl instead of RuPhos	2
14	IAd · HCl instead of RuPhos	3
15	IPr carbene instead of RuPhosl	32
16	SPr · HCl instead of RuPhos	36
17	***IPr · HCl instead of RuPhos***	***35***

[a] Reaction conditions: **1a** (0.1 mmol), **2b** (0.1 mmol), $Pd_2(dba)_3$ (0.005 mmol), RuPhos (0.02 mmol), KOH (0.3 mmol), THF/H_2O (0.9 mL:0.1 mL), 90 °C, 24 h. [b] GC yield using *n*-tetradecane as internal standard

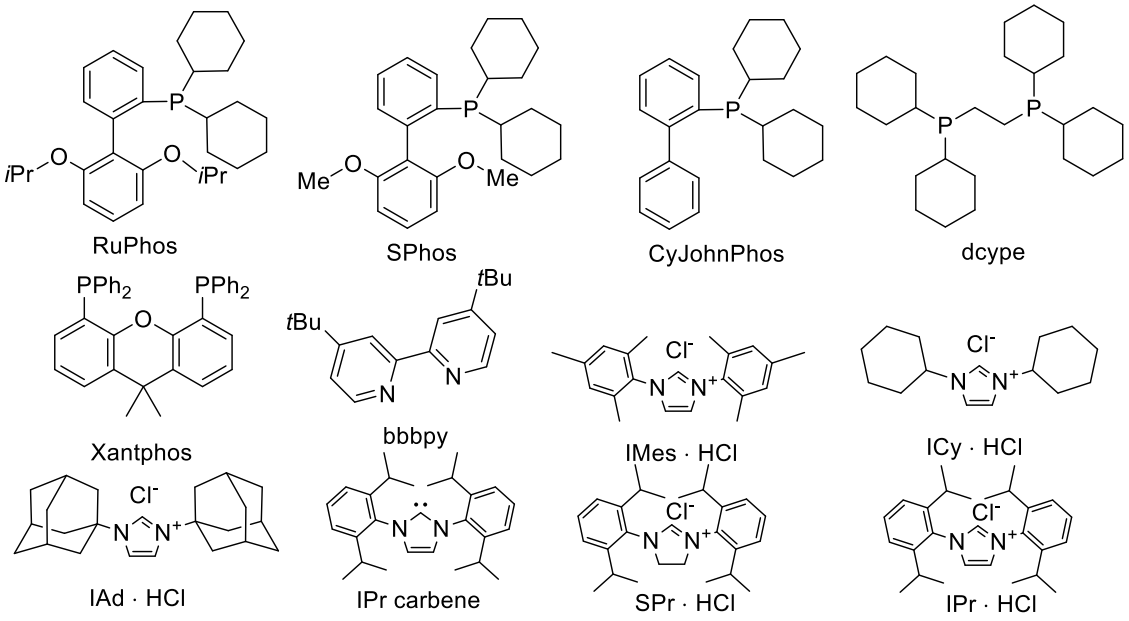
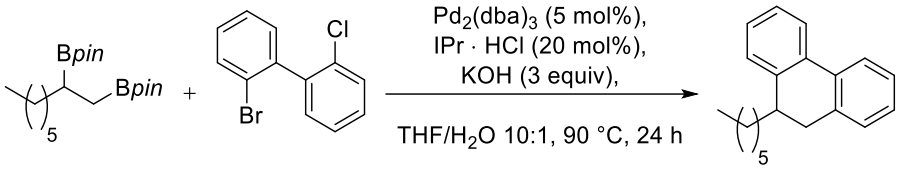


Figure S1: Ligands tested in the optimization.

2.2 Optimization details for the annulation with 2-bromo-2'-chloro-biphenyl 2a

Table S3: Optimization of Pd-source, solvent, and base.[a]

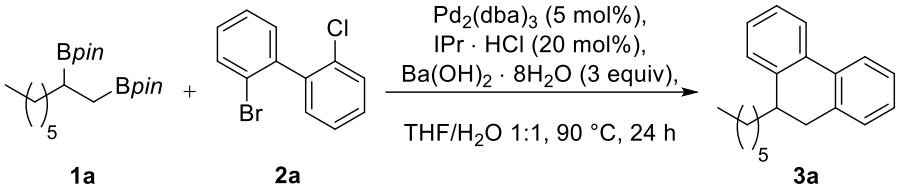


1a **2a** **3a**

Entry	Deviation from standard conditions	3a [%][b]
1	none	48
2	$Pd(PCy)_4$ instead of $Pd_2(dba)_3$	24
3	$Pd(OAc)_2$ instead of $Pd_2(dba)_3$	28
4	SingaCycle A1 instead of $Pd_2(dba)_3$	24
5	DMF instead of THF	16
6	Dioxane instead of THF	31
7	MeCN instead of THF	2
8	K_2CO_3 and DMF instead of KOH and THF	11
9	KO*t*Bu and DMF instead of KOH and THF	9
10	Cs_2CO_3 and DMF instead of KOH and THF	12
11	K_2CO_3 instead of KOH	29
12	K_3PO_4 instead of KOH	36
13	KOtBu instead of KOH	30
14	NaOH instead of KOH	43
15	$CsOH_{aq.}$ instead of KOH	63
16	$Ba(OH)_2 \cdot 8H_2O$ instead of KOH	32
17	***$Ba(OH)_2 \cdot 8H_2O$ instead of KOH***[c]	***67***

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), $Pd_2(dba)_3$ (0.005 mmol), IPr · HCl (0.02 mmol), KOH (0.3 mmol), THF/H_2O (0.9 mL:0.1 mL), 90 °C, 24 h. [b] GC yield using *n*-tetradecane as internal standard. [c] THF/H_2O 1:1 (0.5 mL:0.5 mL)

Table S4: Optimization of equiv of base and temperature.[a]

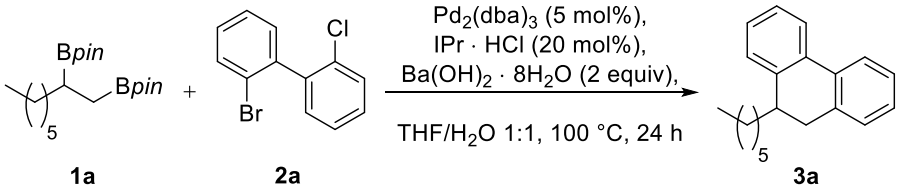


1a **2a** **3a**

Entry	Deviation from standard conditions	3a [%][b]
1	none	67
2	$Ba(OH)_2 \cdot 8H_2O$ (1 equiv)	19
3	***$Ba(OH)_2 \cdot 8H_2O$ (2 equiv)***	***73***
4	$Ba(OH)_2 \cdot 8H_2O$ (4 equiv)	62
5	$Ba(OH)_2 \cdot 8H_2O$ (5 equiv)	65
6	$Ba(OH)_2 \cdot 8H_2O$ (6 equiv)	50
7	70 °C instead of 90 °C	54
8	80 °C instead of 90 °C	61
9	***100 °C instead of 90 °C***	***67***
10	110 °C instead of 90 °C	70
11	120 °C instead of 90 °C	47

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), $Pd_2(dba)_3$ (0.005 mmol), IPr · HCl (0.02 mmol), $Ba(OH)_2 \cdot 8H_2O$ (0.3 mmol), THF/H_2O (0.5 mL:0.5 mL), 90 °C, 24 h. [b] GC yield using *n*-tetradecane as internal standard.

Table S5: Optimization of catalyst loading and concentration.[a]



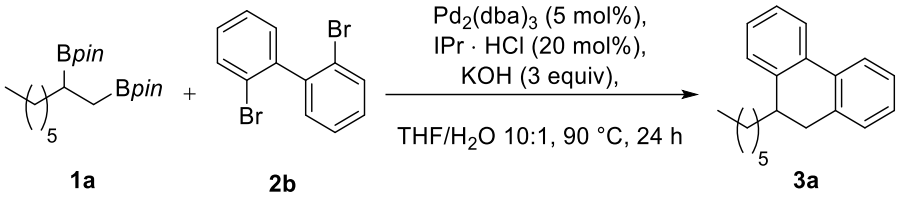
1a **2a** **3a**

Entry	Deviation from standard conditions	3a [%][b]
1	none	70
2	$Pd_2(dba)_3$ (0.5 mol%), IPr · HCl (2 mol%)	7
3	$Pd_2(dba)_3$ (1.75 mol%), IPr · HCl (5 mol%)	22
4	$Pd_2(dba)_3$ (2.5 mol%), IPr · HCl (5 mol%)	42
5	90 °C instead of 100 °C	68
6	Only H_2O	53
7	THF/H_2O (0.2 mL:0.5 mL)	69
8	***THF/H_2O (2 mL:0.5 mL)***	***76***
9	THF/H_2O (10 mL:0.5 mL)	34

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), $Pd_2(dba)_3$ (0.005 mmol), IPr · HCl (0.02 mmol), $Ba(OH)_2 \cdot 8H_2O$ (0.2 mmol), THF/H_2O (0.5 mL:0.5 mL), 90 °C, 24 h. [b] GC yield using *n*-tetradecane as internal standard.

2.3 Control Reactions

Table S6: Control reactions with 2,2'-dibromobiphenyl **2b** after optimization.

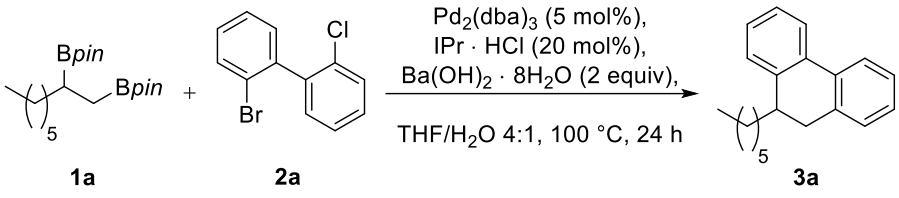


1a **2b** **3a**

Entry	Deviation from standard conditions	3a [%][b]
1	none	35
2	No base	0
3	No IPr · HCl	0
4	No Pd-precatalyst	0
5	No Pd-precatalyst and base	0
6	No Pd-precatalyst and ligand	0
7	No ligand and base	0
8	No Pd-precatalyst, ligand and base	0

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), $Pd_2(dba)_3$ (0.005 mmol), IPr · HCl (0.02 mmol), KOH (0.3 mmol), THF/H_2O (0.9 mL:0.1 mL), 90 °C, 24 h. [b] GC yield using n-tetradecane as internal standard.

Table S7: Control reactions for optimized reaction conditions.



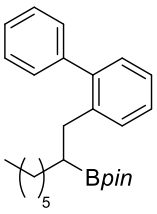
1a **2a** **3a**

Entry	Deviation from standard conditions	3 [%][b]
1	none	76
2	No base	0
3	No IPr · HCl	0
4	No Pd-precatalyst	0
5	No Pd-precatalyst and base	0
6	No Pd-precatalyst and ligand	0
7	No ligand and base	0
8	No Pd-precatalyst, ligand and base	0

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), $Pd_2(dba)_3$ (0.005 mmol), IPr · HCl (0.02 mmol), $Ba(OH)_2 \cdot 8H_2O$ (0.2 mmol), THF/H_2O (2 mL:0.5 mL), 100 °C, 24 h. [b] GC yield using n-tetradecane as internal standard.

2.4 Side Product Isolation

2-(1-([1,1'-biphenyl]-2-yl)octan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



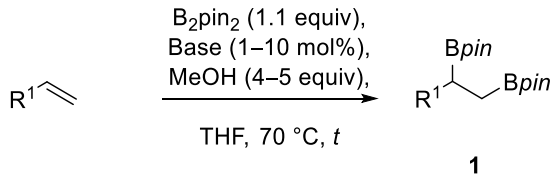
Prepared from 2,2'-(octane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **1a** (183.1 mg, 0.5 mmol, 1 equiv), 2-bromo-1,1'-biphenyl (115.6 mg, 0.5 mmol, 1 equiv), $Pd_2(dba)_3$ (22.9 mg, 0.025 mmol, 5 mol%), RuPhos (23.3 mg, 0.05 mmol, 10 mol%) and KOH (84.2 mg, 1.5 mmol, 1.5 equiv) following general procedure for the reaction development. The product was purified by flash column chromatography (SiO_2, MTBE/pentane 1:10) to afford **SP** as colorless oil (14%, 23 mg, 0.07 mmol).

^{1}H NMR (501 MHz, $CDCl_3$) δ = 7.40 – 7.35 (m, 3H), 7.34 – 7.30 (m, 3H), 7.26 – 7.22 (m, 1H), 7.20 (td, *J*=7.3, 1.4, 1H), 7.16 (dd, *J*=7.4, 1.8, 1H), 2.71 – 2.63 (m, 2H), 1.26 – 1.10 (m, 23H), 0.84 (t, *J*=7.2, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 142.30, 142.25, 140.16, 130.08, 129.60, 129.54, 128.05, 127.12, 126.72, 125.60, 82.97, 34.37, 31.88, 31.55, 29.54, 28.98, 24.88, 24.79, 22.72, 14.24. **^{11}B NMR** (161 MHz, $CDCl_3$) δ = 34.77. **HRMS-ESIpos** (m/z): $[M+Na]^+$ calcd. for $C_{26}H_{37}O_2B_1Na^+$, 415.2778; found 415.2774.

3. Starting Material Synthesis

3.1 General Procedure for the synthesis of alkyl 1,2-bisboronic pinacol esters 1

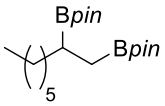
The synthesis was set up according to Fernandez *et al*.[2]



1

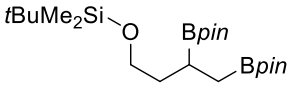
Base (1-10 mol%) and bis(pinacolato)diboron) (1.1 equiv) were transferred into an oven-dried 2-neck round bottom flask, containing a stir bar under argon. The flask was evacuated and flushed with argon thrice. THF (0.25 mol/L) was added to dissolve the mixture. After that, methanol (4-5 equiv) and olefin (1 equiv) were added, and the reaction mixture was allowed to stir in a pre-heated oil bath at 70 °C for at least 6 h. The reaction mixture was cooled to room temperature and after gently concentrated on a rotary evaporator, it was made sure that MeOH was completely removed. The sample was purified via flash column chromatography on deactivated silica (1% TEA). The product-containing fractions were identified after staining with CAM and collected to afford the bisborylated product **1**.

2,2'-(octane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1a)



Prepared from 1-octen (2.8 mL, 0.715 g/mL, 17.82 mmol), bis(pinacolato)diboron (4.979 g, 19.61 mmol), methanol (2.9 mL, 0.791 g/mL, 71.3 mmol) and caesium carbonate (58 mg, 0.178 mmol, 1 mol%) according to the general procedure. The crude product was purified by flash column columnchromatography (MTBE/pentane 1:5) to afford the product **1a** as a colorless oil (71%, 4.6 g, 12.57 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 1.46 – 1.41 (m, 1H), 1.32 – 1.20 (m, 33H), 1.14 – 1.06 (m, 1H), 0.89 – 0.77 (m, 5H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ = 82.94, 82.87, 33.99, 32.00, 29.70, 28.99, 25.06, 24.99, 24.93, 24.90, 22.79, 18.54, 14.26, 12.80. **^{11}B NMR** (161 MHz, $CDCl_3$) δ = 34.29. **HRMS-ESIpos** (m/z): $[M+Na]^+$ calcd. for $C_{20}H_{40}O_4B_2Na^+$, 389.3004; found 389.3003. Analytical data are consistent with the literature.[2]

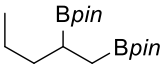
(3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butoxy)(tert-butyl)dimethylsilane (1b)



Prepared from 3-buten-1-ol (0.86 mL, 0.838 g/mL, 10 mmol), bis(pinacolato)diboron (5.079 g, 20 mmol, 2 equiv), methanol (1.6 mL, 0.791 g/mL, 40 mmol) and caesium carbonate (978 mg, 3 mmol, 30 mol%) at 70°C for 16 h according to the general procedure. The crude product was used without purification and taken up in DCM (46 mL). Subsequently imidazole (6 g, 88 mmol, 8.8 equiv) was added. The mixture was cooled to 0 °C and *tert*-butylchlorodimethylsilane (4.522 g, 30 mmol, 3 equiv) in toluene (10 mL) was added. The cooling bath was removed and the mixture was allowed to stir at room temperature for 16 h. Then saturated, aqueous NH_4Cl-solutuion (30 mL) was added, and the organic phase was collected. The aqueous phase was extracted thrice with DCM (15 mL) and the combined organic phases were dried over Na_2SO_4, filtered, and concentrated at reduced pressure at 40 °C. The crude material was purified by flash column chromatography (MTBE/pentane 1:5) to afford the product **1b** as a colorless oil (64% over 2 steps, 2.8 g, 6.36 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 3.62 (qdd, *J*=9.9, 8.7, 6.0, 2H), 1.72 (dddd, *J*=12.8, 8.8, 7.8, 6.2, 1H), 1.58 – 1.51 (m, 1H), 1.22 (s, 12H), 1.22 (s, 12H), 1.19 – 1.13 (m, 1H), 0.88 (s, 9H), 0.85 – 0.80 (m, 1H), 0.04 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 83.00, 82.97, 63.03, 36.73, 26.22, 25.05, 25.00, 24.96, 24.91, 18.58, 14.58, 12.53, -5.03. **^{11}B NMR** (161 MHz, $CDCl_3$) δ = 34.45. **HRMS-ESIpos** (m/z): $[M+Na]^+$ calcd. for

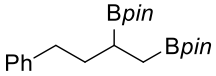
$C_{22}H_{46}O_5B_2SiNa^+$, 463.3192; found 463.3192. Analytical data are consistent with the literature.[3]

2,2'-(pentane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1c)



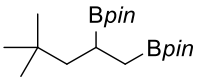
Prepared from 1-penten (2.19 mL, 0.641 g/mL, 20 mmol), bis(pinacolato)diboron (5.59 g, 22 mmol), methanol (3.24mL, 0.791 g/mL, 80 mmol) and caesium carbonate (65.2 mg, 0.2 mmol, 1 mol%) and stirred at 45 °C over 2 days according to the general procedure. The crude product was purified by flash column chromatography (MTBE/pentane 1:10) to afford the product **1c** as a colorless oil (31%, 2.03 g, 6.28 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 1.46 – 1.41 (m, 1H), 1.35 – 1.24 (m, 3H), 1.23 (s, 12H), 1.22 (s, 12H), 1.16 – 1.08 (m, 1H), 0.91 – 0.83 (m, 4H), 0.79 (dd, *J*=15.8, 5.8, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 82.94, 82.88, 36.30, 29.86, 25.06, 25.00, 24.99, 24.93, 24.89, 14.54. **^{11}B NMR** (161 MHz, $CDCl_3$) δ = 34.22. **HRMS-ESIpos** (m/z): $[M+Na]^+$ calcd. for $C_{17}H_{34}O_4B_2Na^+$, 347.2535; found 347.2535.[4]

2,2'-(4-phenylbutane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1d)



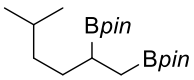
Prepared from 4-phenyl-1-buten (1.5 mL, 0.88 g/mL, 10 mmol), bis(pinacolato)diboron (2.793 g, 11 mmol), methanol (1.6 mL, 0.791 g/mL, 40 mmol) and caesium carbonate (325.8 mg, 1 mmol, 10 mol%) according to the general procedure. The crude product was purified by flash column chromatography (MTBE/pentane 1:5) to afford the product **1d** as a colorless, viscous oil (71%, 4.6 g, 12.57 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.24 (d, *J*=7.5, 2H), 7.20 – 7.13 (m, 3H), 2.61 (t, *J*=8.3, 2H), 1.82 – 1.75 (m, 1H), 1.63 (m, 1H), 1.26 (s, 12H), 1.23 (s, 12H), 0.97 – 0.81 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 143.48, 128.59, 128.31, 125.56, 83.03, 36.10, 35.50, 25.07, 25.04, 24.95, 24.93. **^{11}B NMR** (161 MHz, $CDCl_3$) δ = 34.19. **HRMS-ESIpos** (m/z): $[M+Na]^+$ calcd. for $C_{22}H_{36}O_4B_2Na^+$, 409.2691; found 409.2692. Analytical data are consistent with the literature.[5]

2,2'-(4,4-dimethylpentane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1e)



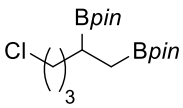
Prepared from 4,4-dimethyl-1-penten (1.66 g, 10 mmol), bis(pinacolato)diboron (2.79 g, 11 mmol), methanol (1.6 mL, 0.791 g/mL, 40 mmol) and caesium carbonate (32.6 mg, 0.1 mmol, 1 mol%) according to the general procedure. The crude product was purified by flash column chromatography (MTBE/pentane 1:10) to afford the product as a colorless oil **1e** (40%, 1.42 g, 4.03 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 1.58 (dd, *J*=13.1, 10.2, 2H), 1.23 (s, 12H), 1.22 (s, 12H), 1.18 – 1.08 (m, 2H), 0.87 (s, 9H), 0.74 (dd, *J*=15.6, 7.9, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 82.85, 82.68, 48.37, 31.16, 29.77, 24.97, 24.82, 24.72. **^{11}B NMR** (161 MHz, $CDCl_3$) δ = 34.07. **HRMS-ESIpos** (m/z): $[M+Na]^+$ calcd. for $C_{19}H_{38}O_4B_2Na^+$, 375.2848; found 375.2848. Analytical data are consistent with the literature.[5]

2,2'-(5-methylhexane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1f)



Prepared from 5-methyl-1-hexen (1.42 mL, 0.691 g/mL, 10 mmol), bis(pinacolato)diboron (2.79 g, 11 mmol), methanol (1.6 mL, 0.791 g/mL, 40 mmol) and cesium carbonate (32.6 mg, 0.1 mmol, 1 mol%) according to the general procedure. The crude product was purified by flash column chromatography (MTBE/pentane 1:10) to afford the product **1f** as a colorless oil (11%, 390 mg, 1.1 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 1.55 – 1.38 (m, 2H), 1.36 – 1.28 (m, 1H), 1.23 (s, 12H), 1.22 (s, 12H), 1.17 (m, 2H), 1.11 – 1.03 (m, 1H), 0.92 – 0.75 (m, 8H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 82.94, 82.87, 38.40, 31.68, 28.32, 25.06, 24.99, 24.92, 24.89, 22.86, 22.78, 18.80, 12.89. **^{11}B NMR** (161 MHz, $CDCl_3$) δ = 34.04. **HRMS-ESIpos** (m/z): $[M+Na]^+$ calcd. for $C_{19}H_{38}O_4B_2Na^+$, 375.2848; found 375.2852.

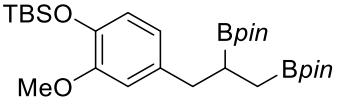
2,2'-(6-chlorohexane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1g)



Prepared from 6-chlor-1-hexen (1.3 mL, 0.896 g/mL, 10 mmol), bis(pinacolato)diboron (2.8 g, 11 mmol), methanol (1.6 mL, 0.791 g/mL, 40 mmol) and caesium carbonate (325.8 mg, 1 mmol, 10 mol%) according to the general procedure. The crude product was purified by flash column chromatography (MTBE/pentane 1:10) to afford the product **1g** as a colorless oil (52%, 1.955 g, 5.25 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 3.52 (t, *J*=6.8, 2H), 1.75 (p, *J*=6.9, 2H), 1.50 – 1.41 (m, 3H),

1.37 – 1.31 (m, 1H), 1.23 (s, 12H), 1.23 (s, 12H), 1.17 – 1.07 (m, 1H), 0.88 (dd, *J*=15.8, 9.5, 1H), 0.79 (dd, *J*=15.8, 5.9, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 83.02, 45.31, 33.03, 33.00, 26.30, 25.06, 25.01, 24.95, 24.94, 24.91. **^{11}B NMR** (161 MHz, $CDCl_3$) δ = 33.91. **HRMS-ESIpos** (m/z): $[M+Na]^+$ calcd. for $C_{18}H_{35}O_4B_2ClNa^+$, 395.2302; found 395.2303. Analytical data are consistent with the literature.[4]

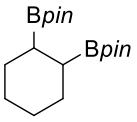
(4-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-2-methoxyphenyl)(tert-butyl)dimethylsilane (**1h)**



Following a procedure by Piva *et al.*[6], Eugenol (1.55 mL, 10 mmol, 1.0 eq.) was added to a solution of DMAP (183 mg, 1.5 mmol, 0.15 eq.) and imidazole (749 mg, 11 mmol, 1.1 eq.) in DCM (1.5 mL). The resulting mixture was cooled to 0 °C and TBSCl (1658 mg, 11 mmol, 1.1 eq.) was added. Thereafter the cooling bath was removed and the reaction was stirred for 7 h while warming to r.t.. The reaction was quenched by the addition of an aq. sat. solution of NH_4Cl. DCM was added and the layers were separated. The aq. layer was extracted three times with DCM and the combined organic layers were dried over $MgSO_4$. Filtration and removal of the solvent under reduced pressure afforded the crude product as an oil, which was used without further purification.

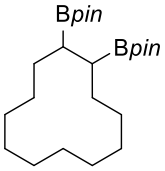
Subsequently according to the general procedure, crude TBS-protected Eugenol was dissolved in THF (10 mL) and added to a suspension of B_2pin_2 (2930 mg, 11.0 mmol, 1.1 eq.) and Cs_2CO_3 (520 mg, 1.6 mmol, 0.15 eq.) in THF (30 mL). Afterwards, MeOH (2.1 mL, 50 mmol, 5.0 eq.) was added and the reaction was stirred at 70 °C for 20 h. Upon completion, the reaction mixture was concentrated under reduced pressure and purified via column chromatography (SiO_2; ^{n}Hex / EtOAc, 10 / 1 + 1% NEt_3) to afford the bisborylated product as a white solid **1h** (58% over 2 steps, 3063 mg, 5.75 mmol,) **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 6.71 – 6.69 (m, 2H), 6.64 (dd, *J*=8.0, 2.0 Hz, 1H), 3.76 (s, 3H), 2.69 (dd, *J*=13.5, 8.0 Hz, 1H), 2.55 (dd, *J*=13.5, 8.0 Hz, 1H), 1.49 – 1.37 (m, 1H), 1.23 (s, 12H), 1.16 (d, *J*=7.8 Hz, 12H), 0.97 (s, 9H), 0.83 (d, *J*=7.8 Hz, 2H), 0.12 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 150.45, 142.84, 136.04, 121.36, 120.45, 113.24, 83.01, 55.51, 39.54, 25.91, 25.05, 24.98, 24.93, 24.92, 21.00, 18.59, 12.61, -4.53, -4.54. **11B NMR (128 MHz, $CDCl_3$)** δ = 34.23. **HRMS (ESI)** (m/z)**:** $[M]^+$ calcd. for $C_{28}H_{51}B_2O_6Si^+$, 533.3646; found: 533.3642.

1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane (S1a)



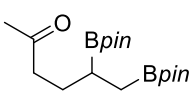
Prepared from cyclohexene (0.50 mL, 0.811 g/mL, 5 mmol), bis(pinacolato)diboron (1.397 g, 5.5 mmol), methanol (0.8 mL, 0.791 g/mL, 20 mmol) and sodium *tert*-butoxide (7.2 mg, 0.075 mmol, 1.5 mol%) at 70°C for 16 h according to the general procedure. The crude product was purified by flash column chromatography (MTBE/pentane 1:10) to afford the product **S1a** as a white solid (39%, 655 mg, 1.95 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 1.62 (m, 2H), 1.55 (m, 2H), 1.48 – 1.33 (m, 4H), 1.24 (s, 12H), 1.23 – 1.14 (m, 14H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ = 82.90, 28.23, 27.01, 25.06, 24.99, 23.50. **^{11}B NMR** (161 MHz, $CDCl_3$) δ = 34.27. **HRMS-ESIpos** (m/z): $[M+Na]^+$ calcd. for $C_{18}H_{34}O_4B_2Na^+$, 359.2535; found 359.2534. Analytical data are consistent with the literature.[2]

1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclododecane (S1b)



Prepared from cyclododecene (1.93 mL, 0.863 g/mL, 10 mmol), bis(pinacolato)diboron (2.793 g, 11 mmol), methanol (1.6 mL, 0.791 g/mL, 40 mmol) and caesium carbonate (32.6 mg, 0.1 mmol, 1 mol%) at 70°C for 16 h according to the general procedure. The crude product was purified by flash column chromatography (MTBE/pentane 1:10) to afford the product **S1b** as a colorless, viscous oil (8%, 344 mg, 0.819 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 1.57 – 1.25 (m, 18H), 1.23 (s, 12H), 1.23 (s, 12H), 1.20 – 1.08 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 82.84, 25.26, 25.17, 24.82, 24.81, 22.39. **^{11}B NMR** (161 MHz, $CDCl_3$) δ = 34.35. **HRMS-ESIpos** (m/z): $[M+Na]^+$ calcd. for $C_{24}H_{46}O_4B_2Na^+$, 443.3474; found 443.3475.

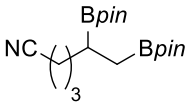
5,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-one (S1c)



Prepared from 5-hexen-2-on (2.36 mL, 0.847 g/mL, 20.39 mmol), bis(pinacolato)diboron (5.692 g, 22.42 mmol), methanol (3.3 mL, 0.791 g/mL, 81.5 mmol) and cesium carbonate (66.4 mg, 0.204 mmol, 1 mol%) at 70°C for 16 h according to the general procedure. The crude product was purified by flash column chromatography (MTBE/pentane 1:5) to afford the product **S1c** as a colorless, viscous oil (3%, 250 mg, 0.71 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 2.44 (dd, *J*=8.5, 7.3, 2H), 2.12 (s, 3H), 1.76 – 1.66 (m, 1H), 1.66 – 1.58 (m, 1H), 1.23 (s, 12H), 1.22 (s, 12H), 1.13 – 1.05 (m, 1H),

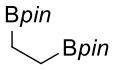
0.88 (dd, *J*=15.9, 9.6, 1H), 0.79 (dd, *J*=15.9, 5.7, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 209.60, 82.98, 82.94, 43.32, 29.77, 27.78, 25.03, 24.90, 24.89, 24.81, 24.75. **^{11}B NMR** (161 MHz, $CDCl_3$) δ = 34.02, 30.61. **HRMS-ESIpos** (m/z): $[M+Na]^+$ calcd. for $C_{18}H_{34}O_5B_2Na^+$, 375.2484; found 375.2484. Analytical data are consistent with the literature.[7]

6,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptanenitrile (S1d)



Prepared from 6-heptennitril (0.546 g, 5 mmol), bis(pinacolato)diboron (1.4 g, 5.5 mmol), methanol (0.8 mL, 0.791 g/mL, 20 mmol) and caesium carbonate (16.3 mg, 0.05 mmol, 1 mol%) according to the general procedure. The crude product **S1d** was purified by flash column chromatography (MTBE/pentane 1:10) to afford the product as a colorless oil (22%, 403 mg, 1.109 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 2.32 (t, *J*=7.2, 2H), 1.68 – 1.62 (m, 2H), 1.48 – 1.44 (m, 2H), 1.39 – 1.30 (m, 2H), 1.23 (s, 12H), 1.23 (s, 12H), 1.15 – 1.08 (m, 1H), 0.88 – 0.86 (m, 1H), 0.79 (dd, *J*=15.8, 5.9, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 120.03, 83.10, 83.06, 32.77, 28.02, 25.67, 25.03, 24.99, 24.93, 24.88, 18.17, 17.14, 12.73. **^{11}B NMR** (161 MHz, $CDCl_3$) δ = 34.07. **HRMS-ESIpos** (m/z): $[M+Na]^+$ calcd. for $C_{19}H_{35}O_4B_2NNa^+$, 386.2644; found 38f6.2644. Analytical data are consistent with the literature.[5]

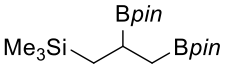
1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane (S1e)



Bis(pinacolato)diboron (7.73 g, 30.5 mmol), methanol (3.3 mL, 0.791 g/mL, 81.2 mmol), and cesium carbonate (99.2 mg, 0.3 mmol, 1.5 mol%) were added into a pressure tube equipped with a stir bar according to the general procedure. Ethylene was transferred from a cylinder by bubbling through a needle, passing through a septum, into the pressure tube at -78°C for 10 min. After bubbling, the septum was exchanged for a cap, and the mixture was heated to 60 °C and stirred overnight. The charging of ethylene and heating was iterated over a period of 20 days until bis(pinacolato)diboron was fully consumed. Aliquots were taken from the reaction mixture, and the product formation was monitored by ^{11}B NMR. The crude product was purified by flash column chromatography (EtOAc/pentane 1:5) to afford the product **S1e** as a colorless liquid (64%, 3.2 g, 11.35 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 1.23 (s, 24H), 0.84 (s, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 82.97, 24.95,

4.55. **^{11}B NMR** (161 MHz, $CDCl_3$) δ = 34.27. **HRMS-ESIpos** (m/z): $[M+Na]^+$ calcd. for $C_{14}H_{28}O_4B_2Na^+$, 305.2065; found 305.2068. Analytical data are consistent with the literature.[4]

(2,3-di(1,3,2-dioxaborolan-2-yl)propyl)trimethylsilane (**S1f**)



Prepared from allyltrimethylsilane (1.93 mL, 0.863 g/mL, 10 mmol), bis(pinacolato)diboron (2.793 g, 11 mmol), methanol (1.6 mL, 0.791 g/mL, 40 mmol) and caesium carbonate (32.6 mg, 0.1 mmol, 1 mol%) at 70°C for 16 h according to the general procedure. The crude product was purified by flash column chromatography (MTBE/pentane 1:10) to afford the product **S1f** as a colorless, viscous oil (8%, 344 mg, 0.819 mzmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 1.23 (s, 12H), 1.23 (s, 12H), 0.96 – 0.75 (m, 3H), 0.49 (dd, *J*=14.6, 6.6, 1H), -0.01 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 82.94, 82.89, 25.09, 25.03, 24.95, 24.93, 20.51, 16.60, 13.42, -0.62. **^{11}B NMR** (161 MHz, $CDCl_3$) δ = 34.14. **HRMS-ESIpos** (m/z): $[M+Na]^+$ calcd. for $C_{18}H_{38}O_4B_2SiNa^+$, 391.2617; found 391.2616.

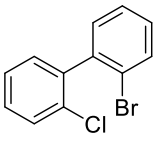
Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (S1g)

Prepared according to Marder *et al.*[8]

In a round-bottom flask equipped with a magnetic stirring bar, $CuCl_2$ (5.4 mg, 0.04 mmol, 4 mol%), 1,3-bis-(2,6-diisopropylphenyl)imidazol-2- ylidene (15.5 mg, 0.04 mmol, 4 mol %) and THF (2 mL) were added. After stirring for 10 min, bis(pinacolato)diboron (558.7 mg, 2.2 mmol, 2.2 equiv) and KOMe (154.3 mg, 2.2 mmol, 2.2 equiv) were added and the reaction was stirred for an additional 10 min. To this reaction mixture, DCM (64 µL, 1.325 g/mL, 1.0 mmol, 1 equiv) was added. The resulting reaction mixture was stirred vigorously at 60 °C for the indicated amount of time. The reaction mixture was then diluted with MTBE (4 mL) and filtered through a plug of celite and rinsed with MTBE. The solvents were removed in vacuo, and the residue was purified by flash chromatography on silica (MTBE/pentane 1:20) to afford the pure product **S1g** as a white solid (77%, 207 mg, 0.772 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 1.23 (s, 24H), 0.35 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 83.15, 24.87. **^{11}B NMR** (161 MHz, $CDCl_3$) δ = 33.41. **HRMS-ESIpos** (m/z): $[M]^+$ calcd. for $C_{13}H_{27}O_4B_2^+$, 269.2089; found 269.2090. Analytical data are consistent with the literature.[8]

3.2 Substrate Synthesis Table 1

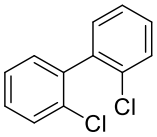
2-bromo-2'-chloro-1,1'-biphenyl (2a)



The synthesis was performed according to Itami *et al.*[9]

To an oven-dried, 200-mL two-necked round bottom flask filled with argon 1-bromo-2-chlorobenzene (4.7 mL, 1.638 g/mL, 40 mmol, 2 equiv) and THF (80 mL) were added. A hexane solution of n-butyllithium (12.5 mL, 1.6 M, 20 mmol, 1 equiv) was slowly added to the solution at –78 °C. The reaction mixture was stirred at room temperature for 4 h. The reaction was quenched by aqueous HCl solution (50 mL, 2 mol/L). The organic layer was extracted with DCM, washed with brine, dried over Na_2SO_4, filtrated, and then concentrated *in vacuo* at 40 °C. The crude material was purified by flash column chromatography (SiO_2, pentane), and product **2a** is obtained as a white solid. **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.67 (dd, *J*=8.4, 1.3, 1H), 7.48 – 7.46 (m, 1H), 7.36 (td, *J*=7.6, 1.3, 1H), 7.34 – 7.29 (m, 2H), 7.26 – 7.22 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 140.56, 140.16, 133.50, 132.74, 131.23, 131.21, 129.57, 129.52, 129.39, 127.26, 126.64, 123.77. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{12}H_8BrCl^+$, 265.9498; found 265.9502. Analytical data are consistent with the literature.[10]

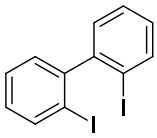
2,2'-dichloro-1,1'-biphenyl (2c)



The reaction was adapted from Wanner *et al.*[11]

A mixture of toluene/ethanol/Na_2CO_3 (2 mol/L in H_2O) (1:1:1 v/v/v, 15 mL) was flushed with argon for 10 min. 1-bromo-2-chlorobenzene (610.5 µL, 1.638 g/mL, 5.2 mmol, 1 equiv), (2-chlorophenyl)boronic acid (816.8 mg, 5.2 mmol, 1 equiv) and tetrakis-(triphenylphosphine)-palladium (301.8 mg, 0.26 mmol, 5 mol%) were added to a two-neck round bottom flask under argon and evacuated and flushed thrice with argon. Then, the mixture was solubilized adding the flushed solvent mixture via syringe, the flask was sealed, and the mixture was stirred at 80 °C overnight. After completion of the reaction, the mixture was extracted thrice with MTBE (10 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated *in vacuo* at 40 °C to yield the crude product which was purified by flash column chromatography (SiO_2, pentane/MTBE 10:1). The product **2c** was obtained as a white solid (77%, 900 mg, 4.03 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.48 – 7.45 (m, 2H), 7.34 – 7.29 (m, 4H), 7.27 – 7.23 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 138.51, 133.67, 131.33, 129.59, 129.38, 126.65. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{12}H_8Cl_2^+$, 222.0003; found 222.0006. Analytical data are consistent with the literature.[12]

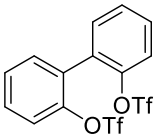
2,2'-diiodo-1,1'-biphenyl (**2d**)



The reaction was set up according to Hedberg *et al*.[13]

In an oven-dried round bottom flask *n*-butyllithium (5.641 mL, 2.5 mol/L in hexane, 14.1 mmol, 2.2 equiv) was added dropwise to a solution of 2,2'-dibromobiphenyl (2 g, 6.41 mmol, 1 equiv) in THF (6 mL, 1 mol/L) at 0 °C. The cooling bath was removed and the mixture was stirred at 25 °C for 2 h, cooled to 0 °C again, and treated with iodine (3.579 g, 14.1 mmol, 2.2 equiv) in THF (6 mL, 2.3 mol/L). In the end, the mixture acquired a brown tint, indicating a slight excess of iodine. The solution was allowed to stir for 16 hours at 25 °C before being washed with water (10 mL), aqueous sodium bisulfite (10 mL, 20% in H_2O), saturated sodium bicarbonate (10 mL), and then water (10 mL). The organic phase was separated, dried over Na_2SO_4, and concentrated *in vacuo* at 40 °C to a white solid mass. Recrystallization in methanol/EtOAc/PhMe (10:1:1, 12 mL) afforded the product **2d** as white crystals (9%, 222 mg, 0.547 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.95 (dd, *J*=8.0, 1.2, 2H), 7.42 (td, *J*=7.5, 1.2, 2H), 7.20 (dd, *J*=7.6, 1.7, 2H), 7.09 (ddd, *J*=7.9, 7.4, 1.7, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 149.09, 139.04, 130.05, 129.52, 128.18, 99.77. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{12}H_8I_2^+$, 405.8715; found 405.8716. Analytical data are consistent with the literature.[14]

[1,1'-biphenyl]-2,2'-diyl bis(trifluoromethanesulfonate) (**2e**)

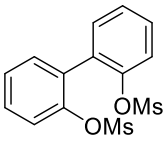


The synthesis was performed according to Yu *et al*.[15]

In a 100 mL two necked flame-dried round-bottom flask under argon 2,2'-biphenol (1.117 mg, 6 mmol, 1 equiv), dry DCM (20 mL, 0.3 mol/L) and pyridine (1.165 mL, 0.978 g/mL, 14.4 mmol, 2.4 equiv) were mixed. The solution was cooled to 0 °C using an ice bath, and triflic anhydride (5.079 g, 18 mmol, 3 equiv) was added dropwise. The resulting mixture was allowed to warm to room temperature and kept stirring for additional 2 hours. The mixture was diluted with MTBE, quenched with aqueous HCl (1 mol/L), and washed with aqueous, saturated $NaHCO_3$ and brine. The combined organic phases were dried over Na_2SO_4, filtrated, and concentrated *in vacuo* at 40 °C. The crude residue was purified by flash column chromatography (SiO_2, pentane) to afford the product **2e** as a white solid (81%, 2.2 g, 4.854 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.57 – 7.45 (m, 6H), 7.43 (dd, *J*=8.1, 1.3, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 146.93, 132.72, 130.89, 129.49, 128.65, 121.83, 119.71, 117.17. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -74.18. **HRMS-EI** (m/z):

$[M]^+$ calcd for $C_{14}H_8O_6S_2F_6^+$, 449.9666; found 449.9661. Analytical data are consistent with the literature.[15]

[1,1'-biphenyl]-2,2'-diyl dimethanesulfonate (**2f**)

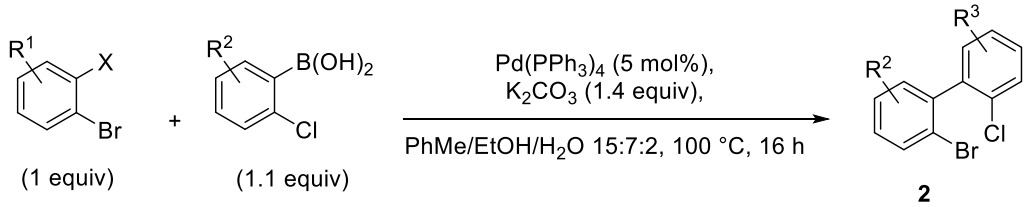


The reaction conditions were adapted from Procopio *et al.*[16]

To an oven-dried, two-neck round bottom flask a solution of 2,2'-biphenol (5 g, 26.85 mmol, 1 equiv) in DCM (100 mL, 0.2 mol/L) triethylamine (11.2 ml, 0.726 g/mL, 80.56 mmol, 3 equiv) was added. The solution was cooled to 0 °C, and mesylchloride (9.227 g, 80.56 mmol, 3 equiv) in DCM (35 mL) was slowly added via a dropping funnel. The mixture was allowed to warm to room temperature and stirred until no further conversion of the diol was detected by TLC. The mixture was quenched with saturated, aqueous NH_4Cl solution (50 mL) and extracted with DCM (30 mL). After combining the organic fractions, drying over Na_2SO_4, and filtration, the crude mixture was concentrated *in vacuo* at 40 °C. Recrystallization in DCM/hexane (1:20) afforded the product **2f** as white solid (32%, 2.95 g, 8.628 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.52 – 7.45 (m, 6H), 7.43 – 7.38 (m, 2H), 2.76 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 146.97, 132.59, 130.37, 130.30, 127.54, 123.34, 38.81. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{14}H_{14}O_6S_2^+$, 342.0231; found 342.0231.

3.3 General Procedure for the synthesis of dihalides 2

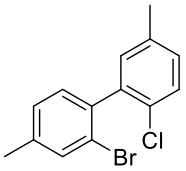
The synthesis was set up according to Oestreich *et al.*[17]



To an argon flushed two-neck round bottom flask was added boronic acid (2.2 mmol, 1.1 equiv), tetrakis-(triphenylphosphine)-palladium(0) (5 mol%), and potassium carbonate (1.4 equiv) and the solids were solubilized in toluene/ethanol/H_2O (15:7:2, 0.13 mol/L wrspt. aryl halide). To the resulting mixture the aryl halide (2 mmol, 1 equiv) was added in one shot while stirring. The flask was sealed with a rubber septum and heated to 100 °C overnight. The reaction was cooled and diluted with water and extracted with MTBE. The combined organic phases were dried over Na_2SO_4, and all volatiles were removed under reduced pressure at 40

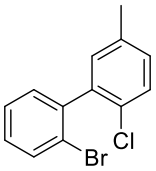
°C. The crude reaction products were purified by flash column chromatography (SiO_2), affording biaryls **2**.

2-bromo-2'-chloro-4,5'-dimethyl-1,1'-biphenyl (**2g**)



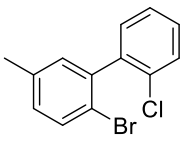
Prepared from (2-chloro-5-methylphenyl)boronic acid (375 mg) and 2-bromo-1-iodo-4-methylbenzene (257 µL) according to the general procedure. The crude product was purified by flash column chromatography (pentane) to afford the product **2g** as a white solid (75%, 441 mg, 1.49 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.51 (s, 1H), 7.35 (d, *J*=8.2, 1H), 7.19 – 7.13 (m, 3H), 7.08 – 7.06 (m, 1H), 2.40 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 139.75, 139.60, 137.73, 136.42, 133.12, 131.98, 130.85, 130.53, 129.98, 129.17, 128.05, 123.44, 21.01, 20.99. **HRMS-EI** (m/z): $[M]^+$ calcd. for $C_{14}H_{12}BrCl^+$, 293.9805; found 293.9804.

2'-bromo-2-chloro-5-methyl-1,1'-biphenyl (**2h**)



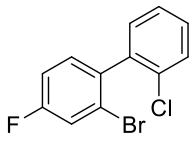
Prepared from (2-chloro-5-methylphenyl)boronic acid (375 mg) and 1-bromo-2-iodobenzene (257 µL, 2.203 g/mL) according to the general procedure. The crude product was purified by flash column chromatography (pentane) to afford the product **2h** as a white solid (80%, 452 mg, 1.6 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.68 – 7.66 (m, 1H), 7.39 – 7.34 (m, 2H), 7.27 – 7.23 (m, 2H), 7.15 (dd, *J*=8.2, 2.2, 1H), 7.06 (d, *J*=2.1, 1H), 2.37 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 140.72, 139.81, 136.50, 132.68, 131.77, 131.19, 130.36, 130.12, 129.40, 129.22, 127.22, 123.78, 21.01. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{13}H_{10}BrCl^+$, 279.9649; found 279.9649.

2-bromo-2'-chloro-5-methyl-1,1'-biphenyl (**2i**)



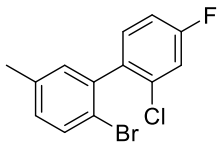
Prepared from (2-chlorophenyl)boronic acid (344 mg) and 1-bromo-2-iodo-4-methylbenzene (257 µL) according to the general procedure. The crude product was purified by flash column chromatography (pentane) to afford the product **2i** as a white solid (73%, 412 mg, 1.46 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.55 – 7.53 (m, 1H), 7.48 – 7.46 (m, 1H), 7.36 – 7.30 (m, 2H), 7.25 – 7.23 (m, 1H), 7.08 – 7.06 (m, 2H), 2.35 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 140.28, 140.25, 137.19, 133.49, 132.40, 131.85, 131.21, 130.36, 129.52, 129.27, 126.60, 120.32, 21.04. **HRMS-EI** (m/z): $[M]^+$ calcd. for $C_{13}H_{10}BrCl^+$, 279.9649; found 279.9648.

2-bromo-2'-chloro-4-fluoro-1,1'-biphenyl (**2j**)



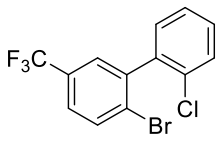
Prepared from (2-chlorophenyl)boronic acid (375 mg) and 2-bromo-4-fluoro-1-iodobenzene (241 µL) according to the general procedure. The crude product was purified by flash column chromatography (pentane) to afford the product **2j** as a clear, colorless oil (90%, 516mg, 1.807 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.52 – 7.47 (m, 1H), 7.43 (d, J=11.0, 1H), 7.31 – 7.29 (m, 2H), 7.26 – 7.23 (m, 2H), 7.10 (td, J=8.3, 2.6, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 162.07 (d, *J*=251.1), 139.22, 136.67 (d, *J*=3.7), 133.70, 132.11 (d, *J*=8.5), 131.41, 129.63 (d, *J*=4.9), 126.71, 124.01 (d, *J*=9.7), 120.01 (d, *J*=24.4), 114.56 (d, *J*=21.2). **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -112.22. **HRMS-EI** (m/z): $[M]^+$ calcd. for $C_{12}H_7FClBr^+$, 283.9398; found 283.9398. Analytical data are consistent with the literature.[18]

2'-bromo-2-chloro-4-fluoro-5'-methyl-1,1'-biphenyl (**2k**)



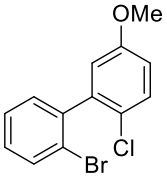
Prepared from (2-chloro-4-fluorophenyl)boronic acid (628 mg, 3.6 mmol) and 1-bromo-2-iodo-4-methylbenzene (412 µL, 3 mmol) according to the general procedure. The crude product was purified by flash column chromatography (pentane) to afford the product **2k** as a white solid (61%, 552 mg, 1.843 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.54 (d, *J*=8.1, 1H), 7.24 – 7.19 (m, 2H), 7.10 – 7.01 (m, 3H), 2.35 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 162.19 (d, *J*=250.1), 139.31, 137.31, 136.43 (d, *J*=3.5), 134.37 (d, *J*=10.3), 132.49, 132.21 (d, *J*=8.7), 132.03, 130.58, 120.54, 116.88 (d, *J*=24.9), 113.95 (d, *J*=21.1), 21.01. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -112.18. **HRMS-EI** (m/z): $[M]^+$ calcd. for $C_{13}H_9FClBr^+$, 297.9554; found 297.9559.

2-bromo-2'-chloro-5-(trifluoromethyl)-1,1'-biphenyl (**2l**)



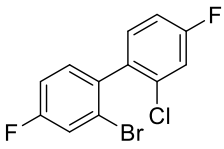
Prepared from (2-chlorophenyl)boronic acid (311 mg) and 1-bromo-2-iodo-4-(trifluoromethyl)benzene (257 µL) according to the general procedure. The crude product was purified by flash column chromatography (pentane) to afford the product **2l** as a clear, colorless oil (88%, 533 mg, 1.587 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.81 (d, *J*=8.2, 1H), 7.53 – 7.50 (m, 3H), 7.41 – 7.34 (m, 2H), 7.26 (dd, *J*=7.1, 2.2, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 141.37, 138.84, 133.43, 133.36, 131.03, 130.01, 129.78, 128.08 (q, *J*=4.0), 126.88, 126.21 (q, *J*=3.7), 124.96, 122.80. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -62.59.. **HRMS-EI** (m/z): $[M]^+$ calcd. for $C_{13}H_7F_3ClBr^+$, 333.9366; found 333.9371.

2'-bromo-2-chloro-5-methoxy-1,1'-biphenyl (**2m**)



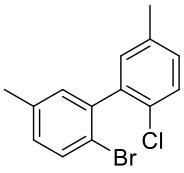
Prepared from (2-chloro-5-methoxyphenyl)boronic acid (410 mg) and 1-bromo-2-iodobenzene (257 µL) according to the general procedure. The crude product was purified by flash column chromatography (MTBE/pentane 40:1) to afford the product **2m** as white solid (42%, 247 mg, 0.845 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.68 – 7.66 (m, 1H), 7.39 – 7.36 (m, 2H), 7.26 (td, *J*=7.4, 1.5, 3H), 6.89 (dd, *J*=8.8, 3.0, 1H), 6.79 (d, *J*=3.0, 1H), 3.81 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 158.09, 140.84, 140.57, 132.76, 131.12, 130.22, 129.54, 127.26, 123.63, 116.43, 115.24, 55.74. **HRMS-EI** (m/z): $[M]^+$ calcd. for $C_{13}H_{10}OBrCl^+$, 295.9598; found 295.9601.

2-bromo-2'-chloro-4,4'-difluoro-1,1'-biphenyl (**2n**)



Prepared from (2-chloro-4-fluorophenyl)boronic acid (628 mg, 3.6 mmol) and 2-bromo-4-fluoro-1-iodobenzene (413 µL, 3 mmol) according to the general procedure. The crude product was purified by flash column chromatography (pentane) to afford the product **2n** as a clear colorless oil (81%, 748 mg, 2.427 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.42 (dd, *J*=8.3, 2.6, 1H), 7.25 – 7.19 (m, 3H), 7.10 (td, *J*=8.3, 2.6, 1H), 7.05 (td, *J*=8.3, 2.6, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 163.28 (d, *J*=23.8), 161.29 (d, *J*=24.9), 135.72 (d, *J*=3.5), 135.36 (d, *J*=3.7), 134.62 (d, *J*=10.3), 132.43 (d, *J*=8.9), 132.30 (d, *J*=8.5), 124.28 (d, *J*=9.8), 120.11 (d, *J*=24.4), 117.05 (d, *J*=24.8), 114.66 (d, *J*=21.1), 114.11 (d, *J*=21.2). **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -111.54, -111.76. **HRMS-EI** (m/z): $[M]^+$ calcd. for $C_{12}H_6F_2ClBr^+$, 301.9304; found 301.9306.

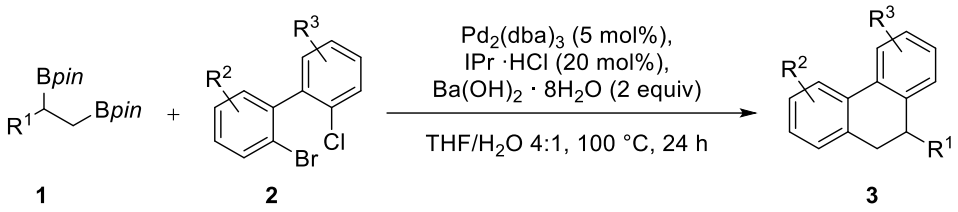
2-bromo-2'-chloro-5,5'-dimethyl-1,1'-biphenyl (**2o**)



Prepared from (2-chloro-5-methylphenyl)boronic acid (613 mg, 3.6 mmol) and 1-bromo-2-iodo-4-methylbenzene (413 µL, 3 mmol) according to the general procedure. The crude product was purified by flash column chromatography (pentane) to afford the product **2o** as a white solid (66%, 587 mg, 1.986 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.55 – 7.54 (m, 1H), 7.35 (d, *J*=8.1, 1H), 7.14 (dd, *J*=8.2, 2.2, 1H), 7.09 – 7.04 (m, 3H), 2.37 (s, 3H), 2.35 (s, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ = 140.41, 139.92, 137.14, 136.45, 132.35, 131.84, 131.76, 130.36, 130.25, 130.01, 129.17, 120.34, 21.03, 21.00.. **HRMS-EI** (m/z): $[M]^+$ calcd. for $C_{14}H_{12}BrCl^+$, 293.9805; found 293.9807.

4. Substrate Scope of the Annulation Reaction

4.1 General Procedure for the synthesis of 9,10-dihydrophenanthrenes 3

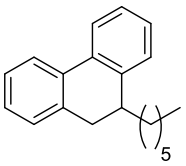


1 **2** **3**

In a 50 mL Schlenk flask purged with Ar or N_2, equipped with a magnetic stir bar and a generously greased joint, were added IPr ·HCl (0.1 mmol, 20 mol%), tris-(dibenzylidenaceton)-dipalladium (0.025 mmol, 5 mol%), barium hydroxide octahydrate (1 mmol, 2 equiv), dihalide **2** (0.5 mmol, 1 equiv), and alkyl 1,2-bisboronic pinacol ester **1** (0.5 mmol, 1 equiv) under Ar or N_2 flow. The Schlenk was sealed with a septum and evacuated/purged with Ar or N_2 three times over 10 min. The reagents inside the Schlenk were solubilized with THF (0.05 mol/L wrt starting material) and water (0.2 mol/L wrt staring material) and sealed with a glass stopcock with Teflon ring and secured with Teflon tape and a metal clamp. The joint was fixed until it was almost not rotatable anymore. The resulting mixture was installed into a pre-heated oil bath at 100 °C and stirred at 500-700 rpm for 24 hours. After the reaction period, the mixture was taken from the oil bath and cooled to room temperature, water (5-10 mL), and MTBE (10 mL) were added. The organic phase was collected, and the aqueous phase was extracted twice with MTBE (10 mL). The combined organic fractions were dried over Na_2SO_4 and concentrated *in vacuo* at 40 °C. The concentrate was taken up with deuterated chloroform (0.5 mL), and tetrachloroethane was added as an internal standard (26 µL, 0.25 mmol, 0.5 equiv). An aliquot (~0.1 mL) was analyzed by NMR. After rejoining the aliquot, the volatiles were removed under reduced pressure at 40 °C and purified by flash column chromatography on silica gel to yield the title compound **3**.

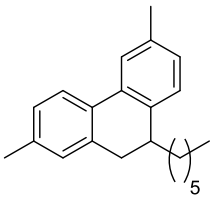
Since all reagents are bench-stable, the reaction can be set up in air. However, before initiation by addition of the catalytic system, aerial oxygen has to be completely removed. A [$Pd(IPr)_2$]-complex has been shown to bind to molecular oxygen, which potentially deactivates its catalytic activity.[19]

9-hexyl-9,10-dihydrophenanthrene (**3a**)



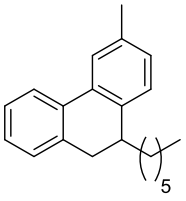
Prepared from 2,2'-(octane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **1a** (183.1 mg) and 2-bromo-2'-chloro-1,1'-biphenyl **2a** according to the general reaction procedure. The crude product was purified by flash column chromatography (pentane) and the product **3a** was obtained as a clear oil (61%, 81.2 mg, 0.307 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.76 (t, *J*=7.6, 2H), 7.33 – 7.28 (m, 2H), 7.25 – 7.21 (m, 4H), 3.09 (dd, *J*=14.9, 5.2, 1H), 2.84 (tdd, *J*=7.0, 7.0, 5.2, 3.4 1H), 2.78 (dd, *J*=14.9, 3.4, 1H), 1.41 – 1.20 (m, 10H), 0.85 (t, *J*=6.8, 3H).**^{13}C NMR** (151 MHz, $CDCl_3$) δ = 141.52, 135.75, 134.24, 133.64, 129.05, 128.31, 127.57, 127.43, 126.98, 126.95, 124.11, 123.52, 38.70, 34.13, 33.54, 31.98, 29.48, 27.72, 22.79, 14.23. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{20}H_{24}^+$, 264.1872; found 264.1877

9-hexyl-2,6-dimethyl-9,10-dihydrophenanthrene (**3b**)



Prepared from 2,2'-(octane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **1a** (183.1 mg) and 2-bromo-2'-chloro-4,5'-dimethyl-1,1'-biphenyl **2g** (147.8 mg) according to the general reaction procedure. The crude product was purified by flash column chromatography (pentane) and the product **3b** was obtained as a clear oil (52%, 75.6 mg, 0.258 mmol). An analytically pure sample was obtained after prep. TLC (pentane) purification. The isomer was assigned by 2D-NMR analysis, performed by the NMR-services. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.62 (d, *J*=7.8, 1H), 7.55 (s, 1H), 7.10 (d, *J*=7.8, 2H), 7.06 – 7.00 (m, 2H), 3.03 (dd, *J*=15.0, 5.4, 1H), 2.80 – 2.76 (m, 1H), 2.71 (dd, *J*=15.0, 3.5, 1H), 2.39 (s, 3H), 2.36 (s, 3H), 1.37 – 1.21 (m, 10H), 0.86 – 0.84 (m, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 138.31, 137.20, 136.27, 135.79, 133.53, 131.56, 129.82, 128.16, 127.75, 127.59, 124.51, 123.36, 38.35, 34.35, 33.69, 32.00, 29.49, 27.76, 22.80, 21.51, 21.35, 14.23. **HRMS-EI** (m/z): $[M]^+$ calcd. for $C_{22}H_{28}^+$, 292.2185; found 292.2185.

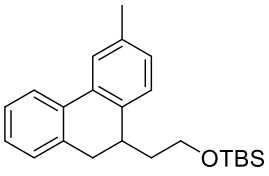
10-hexyl-3-methyl-9,10-dihydrophenanthrene (**3c**)



Prepared from 2,2'-(octane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **1a** (183.1 mg) and 2'-bromo-2-chloro-5-methyl-1,1'-biphenyl **2h** (140.8 mg) according to the general reaction procedure. The crude product was purified by flash column chromatography (pentane) and the product **3c** was obtained as a clear oil (52%, 71.8 mg, 0.258 mmol). The isomer was assigned by 2D-NMR

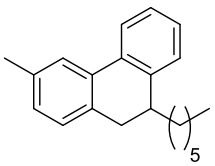
analysis, performed by the NMR-services. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.75 – 7.73 (m, 1H), 7.59 (m, 1H), 7.30 – 7.28 (m, 1H), 7.23 – 7.20 (m, 2H), 7.11 (d, *J*=7.6, 1H), 7.06 (ddd, *J*=7.6, 1.7, 0.7, 1H), 3.06 (dd, *J*=14.8, 5.2, 1H), 2.82 – 2.79 (m, 1H), 2.76 (dd, *J*=14.8, 3.6, 1H), 2.40 (s, 3H), 1.37 – 1.19 (m, 10H), 0.85 (t, *J*=7.0, 3H)..**^{13}C NMR** (151 MHz, $CDCl_3$) δ = 138.60, 136.34, 135.88, 134.30, 133.45, 129.03, 128.19, 128.17, 127.44, 126.88, 124.81, 123.46, 38.27, 34.34, 33.65, 31.98, 29.48, 27.74, 22.79, 21.50, 14.23. **HRMS-CI** (m/z): $[M]^+$ calcd for $C_{21}H_{27}^+$, 279.2107; found 279.2112.

***tert*-butyldimethyl(2-(6-methyl-9,10-dihydrophenanthren-9-yl)ethoxy)silane** (**3d**)



Prepared from (3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butoxy)(tert-butyl)dimethylsilane **1b** (183.7 mg, 0.417 mmol, 1 equiv) and 2'-bromo-2-chloro-5-methyl-1,1'-biphenyl **2h** (117.5 mg, 0.417 mmol, 1 equiv) according to the general reaction procedure. The crude product was purified by flash column chromatography (pentane) and **3d** was obtained as a white solid (48%, 69.9 mg, 0.198 mmol). The isomer was assigned by 2D-NMR analysis, performed by the NMR-services. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.73 (d, *J*=7.4, 1H), 7.60 – 7.55 (d, *J*=1.8, 1H), 7.30 – 7.27 (m, 1H), 7.23 – 7.20 (m, 2H), 7.14 (d, *J*=7.6, 1H), 7.07 (ddd, *J*=7.6, 1.8, 0.8, 1H), 3.59 – 3.53 (m, 2H), 3.12 – 3.08 (m, 2H), 2.78 – 2.75 (m, 1H), 2.40 (s, 3H), 1.60 – 1.52 (m, 2H), 0.91 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 137.92, 136.48, 135.70, 134.27, 133.52, 129.13, 128.37, 128.23, 127.49, 126.94, 124.83, 123.50, 60.91, 36.30, 34.29, 34.21, 26.13, 21.51, 18.45, -5.11, -5.15.. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd. for $C_{23}H_{32}OSiNa^+$, 375.2114; found 375.2119.

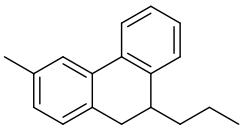
9-hexyl-3-methyl-9,10-dihydrophenanthrene (**3e**)



Prepared from 2,2'-(octane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **1a** (183.1 mg) and 2-bromo-2'-chloro-5-methyl-1,1'-biphenyl **2i** (140.8 mg) according to the general reaction procedure. The crude product was purified by flash column chromatography (pentane) and **3e** was obtained as a clear oil (74%, 74.42 mg, 0.372 mmol). The isomer was assigned by 2D-NMR analysis, performed by the NMR-services. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.76 (ddd, *J*=7.7, 1.3, 0.6, 1H), 7.57 (m, 1H), 7.30 (ddd, *J*=7.7, 7.1, 1.7, 1H), 7.25 – 7.20 (m, 2H), 7.11 (dd, *J*=7.6, 1.0, 1H), 7.05 (ddd, *J*=7.5, 1.8, 0.8, 1H), 3.04 (ddt, *J*=15.0, 5.4, 1.1, 1H), 2.82 (tdd, *J*= 5.4, 3.4, 1H), 2.76 (dd, *J*=15.0, 3.4, 1H), 2.40 (s, 3H), 1.40 – 1.20 (m, 10H), 0.85 (t, *J*=7.0, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 141.64, 136.27, 134.01, 133.72, 132.70, 128.92, 128.32,

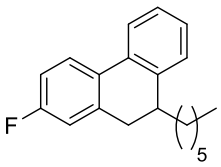
128.29, 127.29, 126.90, 124.26, 124.03, 38.83, 33.67, 33.53, 31.99, 29.47, 27.74, 22.79, 21.57, 14.23. **HRMS-CI** (m/z): $[M]^+$ calcd. for $C_{21}H_{27}^+$, 279.2107; found 279.2109.

3-methyl-9-propyl-9,10-dihydrophenanthrene (**3f**)



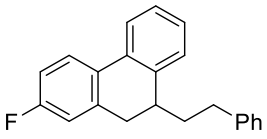
Prepared from 2,2'-(pentane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **1c** (100.4 mg, 0.31 mmol, 1 equiv) and 2'-bromo-2-chloro-5-methyl-1,1'-biphenyl **2i** (92 mg, 0.31 mmol, 1 equiv) according to the general reaction procedure. The crude product was purified by flash column chromatography (pentane) and **3f** was obtained as a clear oil (56%, 41.1 mg, 0.1742 mmol). The isomer was assigned by 2D-NMR analysis, performed by the NMR-services. **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.77 (d, *J*=7.7, 1H), 7.57 (s, 1H), 7.30 (td, *J*=7.4, 1.8, 1H), 7.25 – 7.20 (m, 2H), 7.11 (d, *J*=7.5, 1H), 7.05 (dd, *J*=7.5, 1.7, 1H), 3.06 (dd, *J*=15.0, 5.4, 1H), 2.87 – 2.82 (m, 1H), 2.76 (dd, J=15.0, 3.0, 1H), 2.41 (s, 3H), 1.43 – 1.30 (m, 3H), 1.29 – 1.22 (m, 1H), 0.85 (t, J=6.9, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 141.57, 136.28, 134.02, 133.73, 132.70, 128.92, 128.33, 128.30, 127.28, 126.91, 124.27, 124.04, 38.61, 35.81, 33.70, 21.57, 20.85, 14.25. **HRMS-EI** (m/z): $[M]^+$ calcd. for $C_{18}H_{20}^+$, 236.1559; found 236.1563.

2-fluoro-9-hexyl-9,10-dihydrophenanthrene (**3g**)



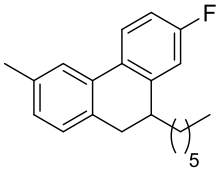
Prepared from 2,2'-(octane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **1a** (183.1 mg) and 2-bromo-2'-chloro-4-fluoro-1,1'-biphenyl **2j** (142.8 mg) according to the general reaction procedure. The crude product was purified by flash column chromatography (pentane) and the product **3g** was obtained as a clear oil (45%, 63.8 mg, 0.226 mmol). The isomer was assigned by 2D-NMR analysis, performed by the NMR-services. **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.70 – 7.68 (m, 2H), 7.32 – 7.28 (m, 1H) 7.24 (td, *J*=7.3, 1.3, 1H), 7.20 (dd, *J*=7.5, 1.5, 1H), 6.98 (tdd, *J*=8.7, 2.8, 0.9 1H), 6.93 (ddd, *J*=8.8, 2.9, 1.0 1H), 3.07 (dd, *J*=15.2, 5.3, 1H), 2.83 (tdd, *J*=7.0, 5.2, 3.2, 1H), 2.75 (dd, *J*=15.2, 3.3, 1H), 1.38 – 1.20 (m, 10H), 0.85 (t, *J*=6.9, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 162.43 (d, J=246.5), 140.91, 138.19 (d, J=7.6), 132.90, 130.41 (d, J=3.0), 128.39, 127.34, 127.11, 125.15 (d, J=8.4), 123.88, 115.79 (d, J=21.1), 113.68 (d, J=21.4), 38.56, 34.27, 34.26, 33.49, 31.94, 29.45, 27.66, 22.78, 14.22. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -115.47. **HRMS-EI** (m/z): $[M]^+$ calcd. for $C_{20}H_{23}F^+$, 282.1778; found 282.1778.

2-fluoro-9-phenethyl-9,10-dihydrophenanthrene (3h)



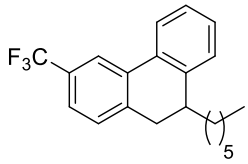
Prepared from 2,2'-(4-phenylbutane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **1d** (193.1 mg) and 2'-bromo-2-chloro-5-methyl-1,1'-biphenyl **2j** (142.8 mg) according to the general reaction procedure. The crude product was purified by flash column chromatography (pentane) and the product **3h** was obtained as a thick yellowish oil (68%, 102.7 mg, 0.34 mmol). The isomer was assigned by 2D-NMR analysis, performed by the NMR-services. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.72 (d, *J*=5.2, 1H), 7.71 – 7.69 (m, 1H), 7.32 (td, *J*=7.4, 1.7, 1H), 7.27 – 7.21 (m, 4H), 7.17 – 7.14 (m, 1H), 7.13 – 7.11 (m, 2H), 6.99 (td, *J*=8.7, 2.7, 0.9, 1H), 6.94 (dd, *J*=9.0, 2.8, 1.0, 1H), 3.13 (dd, *J*=15.3, 5.4, 1.1, 1H), 2.93 – 2.88 (m, 1H), 2.83 (dd, *J*=15.3, 3.1, 1H), 2.71 – 2.65 (m, 1H), 2.60 – 2.54 (m, 1H), 1.75 – 1.70 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 162.47 (d, *J*=246.8), 142.18, 140.31, 137.87 (d, *J*=7.7), 132.98, 130.35 (d, *J*=2.9), 128.46, 127.41, 127.32, 125.92, 125.24 (d, *J*=8.4), 124.00, 115.82 (d, *J*=21.0), 113.82 (d, *J*=21.4), 38.17, 35.04, 34.33, 33.81. **^{19}FNMR** (470 MHz, $CDCl_3$) δ = -115.27. **HRMS-EI** (m/z): $[M]^+$ calcd. for $C_{22}H_9F^+$, 302.1465; found 302.1471.

2-fluoro-10-hexyl-6-methyl-9,10-dihydrophenanthrene (**3i**)



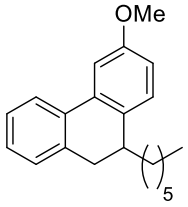
Prepared from 2,2'-(octane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **1a** (183.1 mg) and 2'-bromo-2-chloro-4-fluoro-5'-methyl-1,1'-biphenyl **2k** (149.8 mg) according to the general reaction procedure. The crude product was purified by flash column chromatography (pentane) and the product **3i** was obtained as a clear oil (44%, 65.6 mg, 0.221 mmol). The isomer was assigned by 2D-NMR analysis, performed by the NMR-services. **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.70 (dd, *J*=8.6, 5.6, 1H), 7.50 (d, *J*=1.8, 1H), 7.11 (d, *J*=7.6, 1H), 7.03 (dd, *J*=7.6, 1.7, 1H), 6.98 (td, *J*=8.5, 2.7, 1H), 6.91 (dd, *J*=9.4, 2.7, 1H), 3.01 (dd, *J*=15.0, 5.2, 1H), 2.81 – 2.76 (m, 1H), 2.71 (dd, *J*=14.9, 3.8, 1H), 2.40 (s, 3H), 1.39 – 1.20 (m, 10H), 0.85 (t, *J*=6.9, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 162.18 (d, J=246.1), 144.07 (d, J=7.0), 136.45, 133.33, 132.13, 129.93 (d, J=3.1), 128.94, 128.19, 125.66 (d, J=8.1), 124.04, 114.86 (d, J=21.1), 113.61 (d, J=21.5), 39.00 (2C), 33.49, 33.26, 31.95, 29.44, 27.63, 22.78, 21.55, 14.22.. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -115.51.**HRMS-EI** (m/z): $[M]^+$ calcd. for $C_{21}H_{26}F^+$, 297.2013; found 297.2015.

9-hexyl-3-(trifluoromethyl)-9,10-dihydrophenanthrene (**3j**)



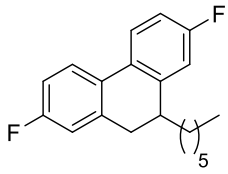
Prepared from 2,2'-(octane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **1a** (183.1 mg) and 2-bromo-2'-chloro-5-(trifluoromethyl)-1,1'-biphenyl **2l** (167.8 mg) according to the general reaction procedure. The crude product was purified by flash column chromatography (pentane) and the product **3j** was obtained as a clear oil (74%, 123.6 mg, 0.372 mmol). The isomer was assigned by 2D-NMR analysis, performed by the NMR-services. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.97 (s, 1H), 7.77 (dd, *J*=7.6, 1.5, 1H), 7.46 (dd, *J*=7.8, 1.8, 1H), 7.36 – 7.22 (m, 4H), 3.11 (dd, *J*=16.0, 6.0, 1H), 2.90 – 2.83 (m, 2H), 1.37 – 1.19 (m, 10H), 0.85 (t, *J*=6.8, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 141.48, 139.67, 134.95, 132.35, 129.41 (q, *J*=32.2), 128.65, 128.51, 128.33, 127.29, 124.30, 124.11 (q, *J*=272.1), 123.25 (q, *J*=3.8), 120.34 (q, *J*=3.8), 38.22, 33.93, 33.42, 31.77, 29.26, 27.49, 22.61, 14.05. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.34. **HRMS-EI** (m/z): $[M]^+$ calcd. for $C_{21}H_{23}F_3^+$, 332.1751; found 332.1748.

10-hexyl-3-methoxy-9,10-dihydrophenanthrene (**3k**)



Prepared from 2,2'-(octane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **1a** (183.1 mg) and 2'-bromo-2-chloro-5-methoxy-1,1'-biphenyl **2m** (142.8 mg) according to the general reaction procedure. The crude product was purified by flash column chromatography (pentane) and the product **3k** was obtained as a clear oil (30%, 44.6 mg, 0.151 mmol). An analytically pure sample was obtained after prep. TLC (pentane) purification. The isomer was assigned by 2D-NMR analysis, performed by the NMR-services. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.72 (d, *J*=7.7 1H), 7.32 (d, *J*=2.7, 1H), 7.31 (tdd, *J*=7.7, 2.3, 1.1, 1H), 7.25 – 7.21 (m, 2H), 7.14 (d, *J*=8.3, 1H), 6.81 (dd, *J*=8.3, 2.7, 1H), 3.87 (s, 3H), 3.08 (dd, *J*=14.7, 5.1, 1H), 2.81 – 2.74 (m, 2H), 1.36 – 1.19 (m, 10H), 0.85 (t, *J*=7.1, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 158.76, 136.03, 134.69, 134.14, 133.92, 129.13, 129.08, 127.69, 126.91, 123.54, 112.76, 109.74, 55.50, 37.88, 34.51, 33.76, 31.99, 29.49, 27.73, 22.79, 14.22. **HRMS-EI** (m/z): $[M]^+$ calcd. for $C_{21}H_{26}O^+$, 294.1978; found 294.1979.

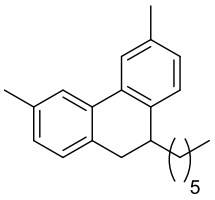
2,7-difluoro-9-hexyl-9,10-dihydrophenanthrene (**3l**)



Prepared from 2,2'-(octane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **1a** (183.1 mg) and 2-bromo-2'-chloro-4,4'-difluoro-1,1'-biphenyl **2n** (151.8 mg) according to the general reaction procedure. The crude product was purified by flash column chromatography (pentane) and

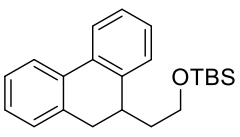
the product **3l** was obtained as a clear oil (53%, 79.3 mg, 0.264 mmol). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.63 (t, *J*=8.2, 1H), 7.62 (t, *J*=8.2, 1H), 6.98 (m, 2H), 6.92 (t, *J*=8.9, 1H), 6.91 (t, *J*=8.9, 1H), 3.05 (ddd, *J*=15.3, 5.2, 1.1, 1H), 2.82 – 2.78 (m, 1H), 2.73 (dd, *J*=15.2, 3.7, 1H), 1.38 – 1.21 (m, 10H), 0.85 (td, J=7.1, 0.7, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 163.05 (d, *J*=27.9), 161.41 (d, *J*=28.1), 143.33 (d, *J*=7.2), 137.60 (d, *J*=7.6), 129.74 (d, *J*=3.2), 129.14 (d, *J*=3.0), 125.52 (d, *J*=8.3), 124.92 (d, *J*=8.4), 115.82 (d, *J*=21.1), 114.96 (d, *J*=21.2), 113.85 (dd, *J*=21.5, 3.9), 38.74 (d, *J*=1.5), 34.09 (d, *J*=1.5), 33.21, 31.90, 29.41, 27.55, 22.77, 14.20. **^{19}F NMR** (565 MHz, $CDCl_3$) δ = -115.36 (tt, *J*=9.0, 5.4), -115.52 (tt, *J*=9.0, 5.2). **HRMS-EI** (m/z): $[M]^+$ calcd. for $C_{20}H_{22}F_2^+$, 300.1684; found 300.1684.

9-hexyl-3,6-dimethyl-9,10-dihydrophenanthrene (**3m**)



Prepared from 2,2'-(octane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **1a** (183.1 mg) and 2-bromo-2'-chloro-5,5'-dimethyl-1,1'-biphenyl **2o** (147.8 mg) according to the general reaction procedure. The crude product was purified by flash column chromatography (pentane) and the product **3m** was obtained as a clear oil (57%, 83.8 mg, 0.287 mmol). An analytically pure sample was obtained after prep. TLC (pentane) purification. **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.58 (s, 1H), 7.56 (s, 1H), 7.10 (d, *J*=7.6, 2H), 7.05 (d, *J*=1.8, 1H), 7.04 (d, *J*=1.7, 1H), 3.01 (dd, *J*=14.9, 5.3, 1H), 2.80 – 2.76 (m, 1H), 2.72 (dd, *J*=14.9, 3.4, 1H), 2.41 (s, 6H), 1.37 – 1.20 (m, 10H), 0.85 (t, *J*=6.9, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 138.73, 136.25, 136.19, 134.10, 133.55, 132.85, 128.89, 128.18, 128.17, 128.04, 124.73, 124.19, 38.42, 33.91, 33.66, 32.00, 29.49, 27.77, 22.80, 21.56, 21.50, 14.23. (151 MHz, $CDCl_3$) δ = 141.64, 136.27, 134.01, 133.72, 132.70, 128.92, 128.32, 128.29, 127.29, 126.90, 124.26, 124.03, 38.83, 33.67, 33.53, 31.99, 29.47, 27.74, 22.79, 21.57, 14.23. **HRMS-CI** (m/z): $[M]^+$ calcd. for $C_{22}H_{28}^+$, 292.2191; found 292.2190.

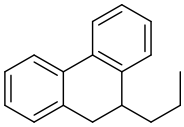
***tert*-butyl (2-(9,10-dihydrophenanthren-9-yl)ethoxy) dimethyl-silane** (**3n**)



Prepared from (3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butoxy)(tert-butyl)dimethylsilane **1b** (220.2 mg) and 2-bromo-2'-chloro-1,1'-biphenyl **2a** (134 mg) according to the general reaction procedure. The crude product was purified by flash column chromatography (pentane) and the product **3n** was obtained as a clear oil (56%, 94.9 mg, 0.28 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.77 – 7.73 (m, 2H), 7.32 – 7.28 (m, 2H), 7.25 – 7.24 (m, 2H), 7.23 – 7.21 (m, 2H), 3.60 – 3.52 (m, 2H), 3.15 – 3.11 (m, 2H), 2.80 – 2.76 (m, 1H), 1.61 – 1.54 (m, 2H), 0.91 (s,

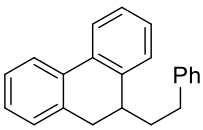
9H), 0.04 (s, 3H), 0.04 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 140.86, 135.59, 134.21, 133.72, 129.15, 128.51, 127.63, 127.49, 127.11, 127.02, 124.15, 123.57, 60.86, 36.20, 34.63, 34.08, 26.13, 18.45, -5.12, -5.16. **HRMS-EI** (m/z): $[M+Na^+]^+$ calcd. for $C_{22}H_{30}O_1SiNa^+$, 361.1958; found 361.1963.

9-propyl-9,10-dihydrophenanthrene (**3o**)



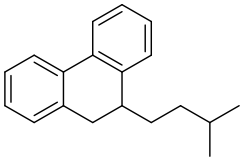
Prepared from 2,2'-(pentane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **1c** (162 mg) and 2-bromo-2'-chloro-1,1'-biphenyl **2a** (134 mg) according to the general reaction procedure. The crude product was purified by flash column chromatography (pentane) and the producte **3o** was obtained as a clear oil (62%, 69.2 mg, 0.311 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.80 (t, *J*=7.6, 2H), 7.38 – 7.32 (m, 2H), 7.29 – 7.24 (m, 4H), 3.16 (dd, *J*=15.0, 5.4, 1H), 2.90 (m, 1H), 2.81 (dd, *J*=15.1, 3.4, 1H), 1.46 – 1.37 (m, 3H), 1.34 – 1.26 (m, 1H), 0.89 (t, *J*=6.8, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 141.46, 135.75, 134.25, 133.65, 129.06, 128.34, 127.58, 127.42, 127.00, 126.97, 124.13, 123.53, 38.46, 35.80, 34.15, 20.83, 14.24. **HRMS-EI** (m/z): $[M]^+$ calcd. for $C_{17}H_{18}^+$, 222.1403; found 222.1406.

9-phenethyl-9,10-dihydrophenanthrene (**3p**)



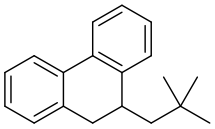
Prepared from 2,2'-(4-phenylbutane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **1d** (193.1 mg) and 2-bromo-2'-chloro-1,1'-biphenyl **2a** (134 mg) according to the general reaction procedure. The crude product was purified by flash column chromatography (pentane) and the product **3p** was obtained as a clear oil (70%, 99.1 mg, 0.348 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.81 – 7.75 (m, 2H), 7.36 – 7.28 (m, 2H), 7.25 – 7.21 (m, 5H), 7.17 – 7.11 (m, 3H), 3.15 (dd, *J*=14.9, 5.2, 1H), 2.91 (tdd, *J*=7.3, 5.0, 3.3, 1H), 2.84 (dd, *J*=15.0, 3.2, 1H), 2.69 (ddd, *J*= 13.9, 9.3, 6.8, 1H), 2.57 (ddd, *J*=13.9, 9.1, 7.0, 1H), 1.74 (dtd, *J*=9.2, 6.9, 2.0, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 142.36, 140.92, 135.42, 134.17, 133.72, 129.08, 128.49, 128.42, 127.68, 127.50, 127.19, 127.07, 125.84, 124.24, 123.60, 38.30, 35.11, 34.18, 33.87. **HRMS-EI** (m/z): $[M]^+$ calcd. for $C_{22}H_{20}$, 284.1559; found 284.1563.

9-isopentyl-9,10-dihydrophenanthrene (**3q**)



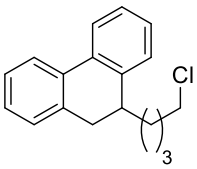
Prepared from 2,2'-(5-methylhexane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **1f** (176.1 mg) and 2-bromo-2'-chloro-1,1'-biphenyl **2a** (134 mg) according to the general reaction procedure. The crude product was purified by flash column chromatography (pentane) and the product **3q** was obtained as a clear oil (64%, 80.5 mg, 0.322 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.80 – 7.73 (m, 2H), 7.33 – 7.29 (m, 2H), 7.27 – 7.21 (m, 4H), 3.11 (dd, *J*=15.9, 6.2, 1H), 2.83 – 2.78 (m, 2H), 1.49 – 1.34 (m, 3H), 1.28 – 1.22 (m, 1H), 1.20 – 1.10 (m, 1H), 0.83 (d, *J*=2.9, 3H), 0.81 (d, *J*=2.9, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 141.57, 135.73, 134.24, 133.67, 129.05, 128.28, 127.58, 127.44, 126.99, 126.96, 124.12, 123.53, 38.95, 36.97, 34.08, 31.25, 28.15, 22.91, 22.60.. **HRMS-CI** (m/z): $[M]^+$ calcd. for $C_{17}H_{18}^+$, 250.1716; found 250.1716.

9-neopentyl-9,10-dihydrophenanthrene (**3r**)



Prepared from 2,2'-(4,4-dimethylpentane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **1e** (176.1 mg) and 2-bromo-2'-chloro-1,1'-biphenyl **2a** (134 mg) according to the general reaction procedure. The crude product was purified by flash column chromatography (pentane) and the product **3r** was obtained as a clear oil (51%, 64.1 mg, 0.256 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.78 – 7.75 (m, 2H), 7.35 – 7.28 (m, 3H), 7.27 – 7.22 (m, 3H), 3.14 (dd, *J*=14.7, 5.0, 1H), 3.08 – 3.04 (m, 1H), 2.89 (dd, *J*=14.9, 2.9, 1H), 1.48 (dd, *J*=14.4, 7.6, 1H), 1.29 (dd, *J*=14.3, 3.7, 1H), 0.97 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 143.60, 135.80, 134.72, 133.60, 129.40, 127.84, 127.73, 127.54, 127.01, 126.81, 124.16, 123.48, 46.75, 35.79, 35.44, 31.47, 30.12. **HRMS-EI** (m/z): $[M]^+$ calcd. for $C_{17}H_{18}^+$, 250.1716; found 250.1716.

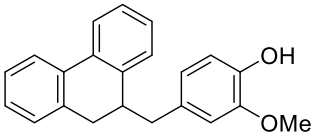
9-(4-chlorobutyl)-9,10-dihydrophenanthrene (**3s**)



Prepared from 2,2'-(6-chlorohexane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **1g** (162 mg) and 2-bromo-2'-chloro-1,1'-biphenyl **2a** (134 mg) according to the general reaction procedure. The crude product was purified by flash column chromatography (pentane) and the product **3s** was obtained as a clear oil (42%, 56.4 mg, 0.208 mmol). An analytically pure sample was obtained after prep. TLC (pentane) purification. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.78 – 7.74 (m, 2H), 7.34 – 7.29 (m, 2H), 7.27 – 7.20 (m, 4H), 3.47 (t, *J*=6.7, 2H), 3.13 (dd, *J*=15.1, 5.3, 1H), 2.88 – 2.83 (m, 1H), 2.79 (dd, *J*=15.1, 3.2, 1H), 1.69 (m, 2H), 1.57 – 1.47 (m, 1H), 1.45 – 1.33 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 140.92, 135.42, 134.13, 133.61, 129.09, 128.37, 127.68,

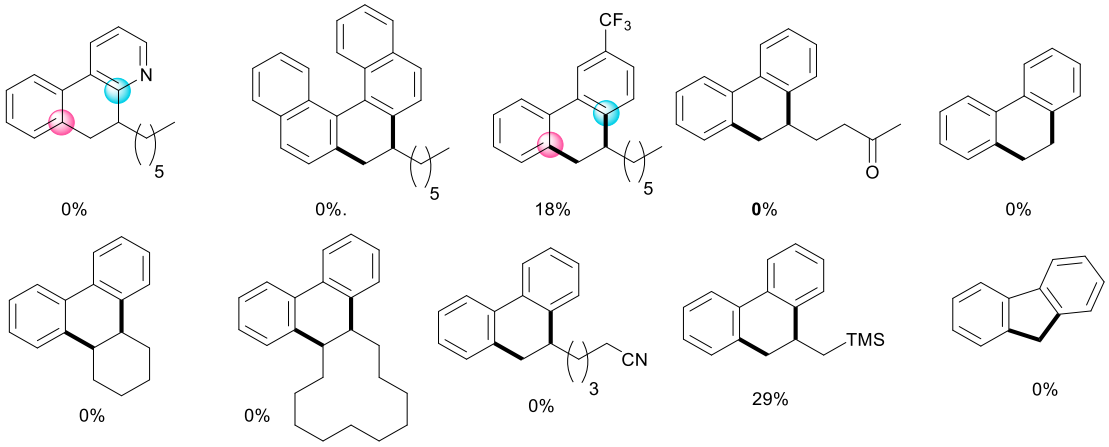
127.51, 127.20, 127.08, 124.22, 123.57, 45.13, 38.64, 34.14, 32.78, 32.74, 25.08. **HRMS-CI** (m/z): $[M]^+$ calcd. for $C_{18}H_{19}Cl^+$, 271.1248; found 271.1247.

4-((9,10-dihydrophenanthren-9-yl)methyl)-2-methoxyphenol (3t)



Prepared from 2-bromo-2'-chloro-1,1'-biphenyl **2a** (134 mg) and(4-(2,3 bis(4,4,5,5 tetramethyl-1,3,2-dioxaborolan-2-yl) propyl) -2-methoxyphenoxy) (tert-butyl)dimethylsilane **1h** (266 mg, 0.5 mmol, 1.0 eq.) according to the general procedure. Purification via flash column chromatography (^{n}Hex/EtOAc, 20:1) afforded the title compound **3t** as a yellow viscous liquid (35%, 55.3 mg, 0.18 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.83 – 7.81 (m, 2H), 7.38 – 7.30 (m, 2H), 7.28 (dd, *J*=7.4, 1.4 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.11 (dd, *J*=7.5, 1.4 Hz, 1H), 6.85 (d, *J*=8.0 Hz, 1H), 6.58 (dd, *J*=8.0, 1.9 Hz, 1H), 6.46 (d, *J*=1.9 Hz, 1H), 5.51 (s, 1H), 3.82 (s, 3H), 3.10 – 3.04 (m, 1H), 2.99 (dd, *J* = 15.1, 5.5 Hz, 1H), 2.73 (dd, *J* = 14.8, 2.4 Hz, 1H), 2.69 – 2.66 (m, 1H), 2.48 (dd, *J*=13.5, 9.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.26, 143.89, 140.60, 135.14, 134.19, 133.60, 132.42, 129.36, 128.48, 127.74, 127.57, 127.24, 127.10, 124.06, 123.64, 121.94, 114.21, 111.95, 55.96, 41.10, 39.72, 32.65. **HRMS (ESI)** (m/z)**:** $[M+Na]^+$: calc. for $C_{22}H_{20}NaO_2^+$ 339.1356; found 339.1361.

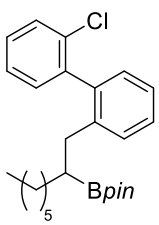
4.2 Unsuccessful examples



5. Mechanistic Experiments

5.1 Intramolecular Cross-Coupling

2-(1-(2'-chloro-[1,1'-biphenyl]-2-yl)octan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4)

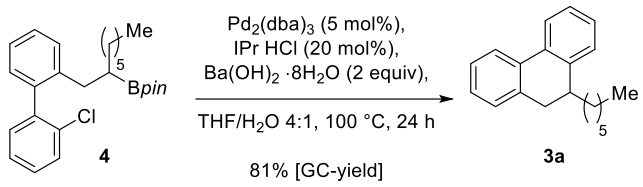


Prepared from 2,2'-(octane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **1a** (183.1 mg, 0.5 mmol, 1 equiv), 2-bromo-2'-chloro-1,1'-biphenyl **2a** (133.8 mg, 0.5 mmol, 1 equiv), $Pd_2(dba)_3$ (22.9 mg, 0.025 mmol, 5 mol%), IPr · HCl (42.5 mg, 0.1 mmol, 20 mol%) and $Ba(OH)_2 \cdot 8H_2O$ (473.2 mg, 1.5 mmol, 3 equiv) following the general procedure for the reaction development. The product was purified by flash column chromatography (SiO_2, MTBE/pentane 1:100) to afford **4** as a colorless oil (26%, 54 mg, 0.13 mmol). A double set of signals is observed: **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.46 – 7.42 (m, 2H), 7.39 – 7.38 (m, 1H), 7.38 – 7.37 (m, 1H), 7.30 – 7.27 (m, 8H), 7.21 (tt, *J*=7.5, 1.8, 2H), 7.11 (dd, *J*=7.5, 1.5, 1H), 7.08 (dd, *J*=7.4, 1.5, 1H), 2.61 – 2.56 (m, 2H), 2.50 – 2.41 (m, 2H), 1.29 – 0.97 (m, 22H), 1.17 (s, 6H), 1.12 (s, 6H), 1.11 (s, 6H), 1.10 (s, 6H), 0.84 (t, *J*=7.2, 3H), 0.84 (t, *J*=7.3, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 139.94, 139.67, 139.65, 139.61, 139.16, 138.50, 138.33, 132.82, 132.58, 130.83, 130.63, 128.90, 128.68, 128.54, 128.52, 128.35, 128.26, 127.56, 127.51, 126.78, 126.72, 125.48, 125.44, 124.61, 124.38, 82.02, 81.94, 33.83, 33.09, 30.90, 30.86, 30.54, 30.42, 28.56, 28.48, 28.06, 27.87, 24.02, 23.95, 23.85, 23.82, 23.75, 21.72, 21.70, 13.24. **^{11}B NMR** (161 MHz, $CDCl_3$) δ = 37.47. **HRMS-ESIpos** (m/z): $[M+Na]^+$ calcd. for $C_{26}H_{36}BO_2ClNa$, 449.2389; found 449.2394.

To obtain a higher quantity of the intermediate **4**, milder conditions according to Marder *et al.* were used.[20]

An oven-dried 16 mL vial with a magnetic stir bar containing 2,2'-(octane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **1a** (366.2 mg, 1 mmol, 1 equiv) and 2-bromo-2'-chloro-1,1'-biphenyl **2a** (267.5 mg, 1 mmol, 1 equiv) was taken into the dry box and KOH (168.3 mg, 3 mmol, 3 equiv) was added. The reagents were dissolved in a mixture of THF/toluene (2.8 mL:3.4 mL) and H_2O (1 mL) was added. In a separate vial $Pd_2(dba)_3$ (45.8 mg, 0.05 mmol, 5 mol%), and RuPhos (46.7 mg, 0.1 mol, 10 mol%) were solubilized in THF (1 mL) and toluene (1 mL). After solubilizing, the catalytic system was added to the reagents. The reaction mixture was mixted, seald with a cap and Teflon tape, removed from the dry box and stirred at

70 °C overnight. Then, an aqueous saturated solution of ammonium chloride (1 mL) was added to the mixture. The organic phase was separated, collected, and the aqueous phase was extracted twice with MTBE. The combined organic phases were dried over Na_2SO_4. After filtration the volatiles were removed at reduced pressure at 40 °C and the crude product was purified by flash column chromatography (SiO_2, MTBE/pentane 1:100). The intermediate **4** was obtained as a colorless oil (70%, 300 mg, 0.703 mmol).



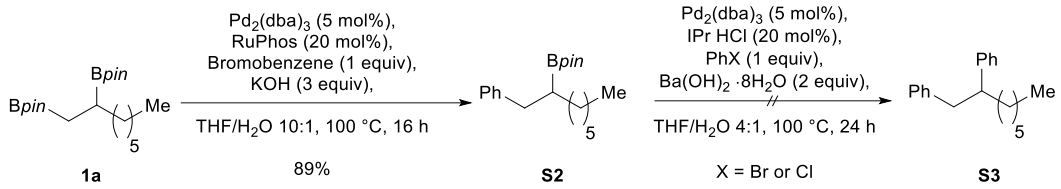
The reaction was setup following general procedure for the synthesis of 9,10-dihydrophenanthrenes: from 2-(1-(2'-chloro-[1,1'-biphenyl]-2-yl)octan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **4** (42.7 mg, 0.1 mmol, 1 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 5 mol%), IPr · HCl (8.5 mg, 0.02 mmol, 20 mol%) and $Ba(OH)_2{\cdot}8H_2O$ (63.1 mg, 0.2 mmol, 2 equiv). The product formation was observed after measuring an aliquot by GC using n-tetradecane (26 µL, 0.1 mol) as internal standard.

Table S8: Results of the intramolecular annulation reaction.

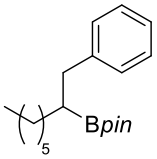
Entry	Deviation from standard conditions	4 [%][b]	3a [%][b]
1	none	0	81
2	KOH (3 equiv) instead of $Ba(OH)_2{\cdot}8H_2O$	0	77
3	No base	65	0
4	No pre-catalyst and ligand	86	0

[a] Reaction conditions: **4** (0.1 mmol), $Pd_2(dba)_3$ (0.005 mmol), IPr · HCl (0.02 mmol), $Ba(OH)_2$ $8H_2O$ (0.2 mmol), THF/H_2O (2 mL:0.5 mL), 100 °C, 24 h. [b] GC yield using *n*-tetreadecane as internal standard.

5.2 Intermolecular Cross-Coupling



4,4,5,5-tetramethyl-2-(1-phenyloctan-2-yl)-1,3,2-dioxaborolane (S2)



The reaction was setup following the general procedure for the synthesis of 9,10-dihydrophenanthrene using 2,2'-(octane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **1a** (183.1 mg, 0.5 mmol, 1 equiv), arylhalide (0.5 mmol, 1 equiv), $Pd_2(dba)_3$ (22.9 mg, 0.025 mmol, 5 mol%), IPr · HCl (42.5 mg, 0.1 mmol, 20 mol%) and $Ba(OH)_2{\cdot}8H_2O$ (315.5 mg, 1 mmol, 2 equiv). Tetrachloroethane (5.3 µL, 0.05 mmol, 0.5 equiv) was added and an aliquot (0.1 mL) was taken to determine the NMR-yield.

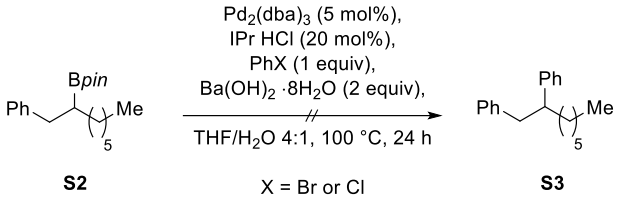
Table S9: Results of the intermolecular cross-coupling.

Entry	Arylhalide	S2 [%]
1	Bromobenzene	17
2	Chlorobenzene	62

To obtain a higher quantity of the intermediate **S2**, milder conditions according to Marder *et al.* were used. [20]

An oven-dried 16 mL vial with a magnetic stir bar containing 2,2'-(octane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **1a** (183.1 mg, 0.5 mmol, 1 equiv) and bromobenzene (53 µl, 1.491 g/mL, 0.5 mmol, 1 equiv) was taken into the dry box and KOH (84.2 mg, 1.5 mmol, 3 equiv) was added. The reagents were dissolved in a mixture of THF/H_2O (3.5 mL:0.5 mL). In a separate vial $Pd_2(dba)_3$ (22.9 mg, 0.025 mmol, 5 mol%), and RuPhos (46.7 mg, 0.1 mmol, 20 mol%) were solubilized in THF (1 mL). After solubilizing the catalytic system was added to the reagents. The reaction mixture was mixed, sealed with a cap and Teflon tape, removed from the dry box and stirred at 70 °C overnight. Then, an aqueous saturated solution of ammonium chloride (1 mL) was added to the mixture. The organic phase was separated, collected, and the aqueous phase was extracted twice with MTBE. The combined organic phases were dried over Na_2SO_4. After filtration the volatiles were removed at reduced pressure at 40 °C and the crude product was purified by flash column chromatography (SiO_2, MTBE/pentane 1:10). The boronic ester **S2** was obtained as a colorless oil (88%, 140 mg,

0.443 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 7.25 – 7.19 (m, 4H), 7.15 – 7.12 (m, 1H), 2.73 – 2.64 (m, 2H), 1.47 – 1.34 (m, 3H), 1.32 – 1.22 (m, 7H), 1.16 (s, 6H), 1.13 (s, 6H), 0.87 (t, *J*=6.9, 3H), 0.85 – 0.76 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 142.56, 129.00, 128.15, 125.66, 83.07, 37.55, 31.95, 31.39, 29.68, 29.28, 24.92, 24.85, 22.76, 14.24. **^{11}B NMR** (161 MHz, $CDCl_3$) δ = 34.60. **HRMS-ESIpos** (m/z): $[M+Na]^+$ calcd. for $C_{20}H_{33}O_2BNa^+$, 339.2465; found 339.2465. Analytical data are consistent with the literature.[21]



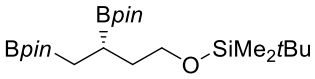
The reaction was setup following the general procedure for the synthesis of 9,10-dihydrophenanthrene using 4,4,5,5-tetramethyl-2-(1-phenyloctan-2-yl)-1,3,2-dioxaborolane **S2** (31.6 mg, 0.1 mmol, 1 equiv), arylhalide (0.1 mmol, 1 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 5 mol%), IPr · HCl (8.5 mg, 0.02 mmol, 20 mol%) and $Ba(OH)_2{\cdot}8H_2O$ (63.1 mg, 0.2 mmol, 2 equiv). Tetrachloroethane (5.3 µL, 0.05 mmol, 0.5 equiv) was added and an aliquot was taken to measure the ^{1}H NMR spectrum. The NMR-yield was determined.

Table S10: Results of the intermolecular cross-coupling.

Entry	Arylhalide	S2 [%]	S3 [%]
1	Bromobenzene	99	0
2	Chlorobenzene	93	0

5.3 Stereospecific Cross-Coupling

(*S*)-(3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butoxy)(tert-butyl)dimethylsilane ((*S*)-1b)



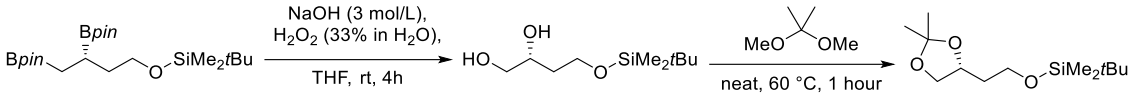
Prepared according to Morken *et al.*[22]

To a round-bottom flask equipped with a stir bar 3-buten-1-ol (1.3 mL, 0.838 g/mL, 15 mmol, 1 equiv) in DCM (30 mL) was added. Subsequently, imidazole (3.064 g, 45 mmol, 3 equiv) wasadded. The mixture was cooled to 0 °C and *tert*-butylchlorodimethylsilane (6.783 g, 45 mmol, 3 equiv) was added. Then the cooling bath was removed and the mixture was allowed to stir at room temperature for 3 days. Then saturated, aqueous NH_4Cl-solution (30 mL) was added, and the organic phase was collected. The aqueous phase was extracted thrice with DCM (15 mL) and the combined organic phases were dried over Na_2SO_4, filtered, and concentrated at reduced pressure at 40 °C. The crude material was purified by flash column chromatography (pentane). The silyl-protected alkenol was obtained as a colorless oil (89%, 2.5 g, 13.414 mmol) **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 5.82 (ddt, *J*=17.1, 10.2, 6.9, 1H), 5.10 – 4.99 (m, 2H), 3.66 (t, *J*=6.8, 2H), 2.28 (qt, *J*=6.7, 1.5, 2H), 0.89 (s, 9H), 0.05 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 135.58, 116.43, 62.96, 37.62, 26.09, 18.51, -5.11.

To an oven-dried vial equipped with a magnetic stir bar in air was added $Pt(dba)_3$ (34.1 mg, 38 µmol, 1 mol%), (*S*,*S*)-3,5-diisopropylphenyl-TADDOL-PPh (36.3 mg, 45.6 µmol, 1.2 mol%), and $B_2(pin)_2$ (1.062 g, 4.18 mmol, 1.1 equiv). The vial was sealed with a septum cap and purged with argon. Tetrahydrofuran (3.8 mL, 1.0 mol/L wrp. to alkene) was added via syringe, and the vial was heated to 60 °C in an oil bath for 1.5 hours. The vial was then cooled to room temperature and charged with deoxygenated silyl-protected alkene (708.2 mg, 3.8 mmol, 1 equiv). After purging once more with argon, the vial was stirred at 60 °C for 3 hours. The mixture was cooled to rt, filtered over a short silica plug and concentrated *in vacuo* at 40 °C. The crude material was purified by flash column chromatography (1% TEA, MTBE/pentane 1:5). The enantioenriched diboronate **(*S*)-1b** was obtained as a colorless liquid (63%, 1.055 g, 2.4 mmol). **^{1}H NMR** (501 MHz, $CDCl_3$) δ = 3.62 (qdd, *J*=9.9, 8.7, 6.0, 2H), 1.72 (dddd, *J*=12.8, 8.8, 7.8, 6.2, 1H), 1.60 – 1.49 (m, 1H), 1.22 (s, 12H), 1.22 (s, 12H), 1.19 – 1.13 (m, 1H), 0.88 (s, 9H), 0.85 – 0.80 (m, 1H), 0.04 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 83.00, 82.97, 63.03, 36.73, 26.22, 25.05, 25.00, 24.96, 24.91, 18.58, 14.58, 12.53, -5.03. **^{11}B NMR** (161 MHz, $CDCl_3$) δ = 34.45. **HRMS-ESIpos** (m/z): $[M+Na]^+$ calcd. for $C_{22}H_{46}O_5B_2SiNa$, 463.3192; found 463.3192.

Analysis of stereochemistry

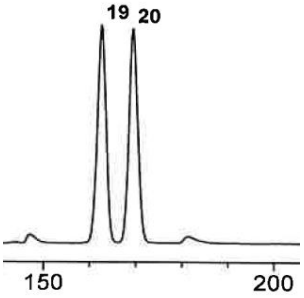
Performed according to Aggarwal *et al.*[23, 24]



An aliquot of racemic **1b** and enantioenriched **(*S*)-1b** was oxidized and protected as acetonide for analysis of enantiomeric purity by chiral-GC.

Chiral-GC: Hydrodex-*β*-TBDAc-CD, injector T = 220 °C, detector T = 350 °C. **Oven conditions:** 70 °C isotherm 180 min, 8 °C/min to 220 °C, 220 °C isotherm 3 min, He carrier gas at 0.5 bar.

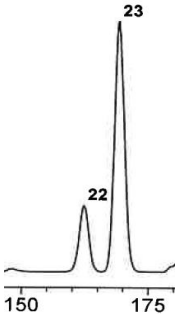
Racemic **1b**



50:50 e.r.

[t_R (19) = 162.7 min, t_R (20) = 169.5 min]

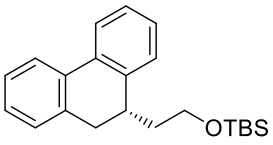
Enantioenriched **(*S*)-1b**



20.3:79.7 e.r.

[t_R (22) = 162.3 min, t_R (23) = 169.4 min]

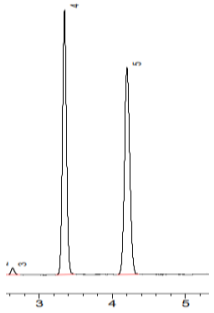
(*S*)-tert-butyl(2-(9,10-dihydrophenanthren-9-yl)ethoxy)dimethylsilane (**(*S*)-3n**)



Prepared from (3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butoxy)(tert-butyl)dimethylsilane **(*S*)-1b** (220.2 mg) and 2-bromo-2'-chloro-1,1'-biphenyl **2a** (134 mg) according to the general reaction procedure for the synthesis of 9,10-dihydrophenanthrene. The crude product was purified by flash column chromatography (pentane) and the product **(*S*)-3n** was obtained as a clear oil (56%, 94.9 mg, 0.28 mmol). The enantiopurity was determined by chiral HPLC.

Chiral HPLC: 150 mm Chiralpak OJ-3, 4.6 mm i.D., CO_2/Methanol = 90:10, flow rate = 1 mL/min, p = 17.5 MPa, T = 50 °C, λ = 210 nm

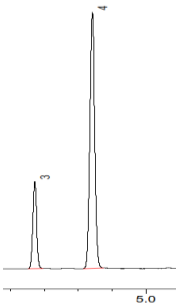
Racemic **3n**



50.2:49.8 e.r.

[t_R (4) = 3.35 min, t_R (5) =4.2 min]

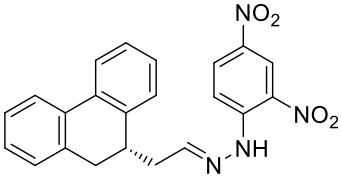
Enantioenriched **(*S*)-3n**



20.9:79.1 e.r.

[t_R (3) = 3.36 min, t_R (4) = 4.21 min]

(*S*)-1-(2-(9,10-dihydrophenanthren-9-yl)ethylidene)-2-(2,4-dinitrophenyl)hydrazine ((*S*)-5)



Set up according to Dong *et al.*[25]

In a screw cap vial equipped with a stir bar 9,10-dihyrophenanthrene **(*S*)-3n** (97 mg, 0.287 mmol, 1 equiv) was dissolved in dry THF (1.5 mL, 0.2 mol/L) and TBAF (0.6 mL, 1 mol/L in THF, 2 equiv) was added. The red solution was stirred for 3 h at room temperature and thereafter water was added. MTBE was added to the reaction mixture, the layers were separted. The aqueous layer was extracted with MTBE (3x). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo* at 40 °C. Analysis of an aliquot by ^{1}H NMR indicated the formation of alcohol. The deprotected alcohol was used without further purification.

The crude was taken up in DCM (3 mL, 0.1 mol/L) and transferred to a round-bottom flask equipped with a stir bar under argon. To the stirring solution was added a solution of Dess-Martin periodinane (151.9 mg, 0.36 mmol, 1.25 equiv) in DCM (1.5 mL, 5 mL/mmol wrst ***S*-3n**) at 0 °C in an ice/water bath. Then the ice bath was removed and the mixture was stirred at room temperature for 1.5 h. The reaction was quenched with NaOH solution (7 mL, 1 mol/L in H_2O). The aqueous layer was extracted thrice with MTBE (10 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated by reduced pressure at 40 °C. An aliquot was taken and analyzed by ^{1}H NMR to confirm the formation of the aldehyde. The product was used without further purification.

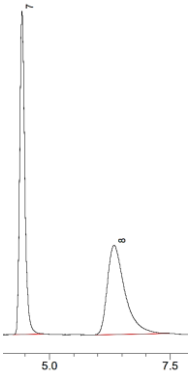
To an 8 mL vial equipped with a stir bar was added the aldehyde (0.29 mmol, 1 equiv) in methanol (7.2 mL, 0.04 mol/L) to give a pale yellow solution. To the solution of aldehyde was

added sequentially DNP (68.1 mg, 0.344 mmol 1.2 equiv) and hydrochloric acid (50 µL, 35-37% *w*/*w* in water, 2 equiv). The reaction was stirred at room temperature for 24 hours. The reaction was quenched with saturated, aqueous $NaHCO_3$ (15 mL). The organic layer was extracted thrice with EtOAc (10 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo* at 40 °C. The crude material was obtained as yellow solid and the major enantiomer **(*S*)-5** was separated by HLPC purification:

Chiral HPLC: 100 mm Chiralpak IA-3 (3.0 mm d) MeCN/H_2O = 90:10 (v/v), flow rate = 1 mL/min, T =25 °C, λ = 220 nm

p(racemic) = 9.5 MPa

Racemic **5**

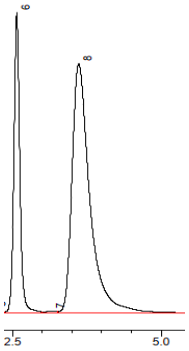


51.2:48.8 e.r.

[t_R (7) = 4.43 min, t_R (8) = 6.34 min]

p(enantioenriched) = 4.5 MPa

Enantioenriched **(*S*)-5**



28.5:71.5 e.r.

[t_R (6) = 2.57 min, t_R (8) = 3.61 min]

Single crystals of the major enantiomer of **(*S*)-5** were obtained by dissolving it in DCM (0.2 mL) and over-layering it with pentane (0.5 mL) in a closed NMR tube after 3 days of standing at room temperature. Notes on crystal structure: two symmetrically independent molecules yet with identical chirality which was determined to be of *(S)*-configuration according to the CIP priority rules.

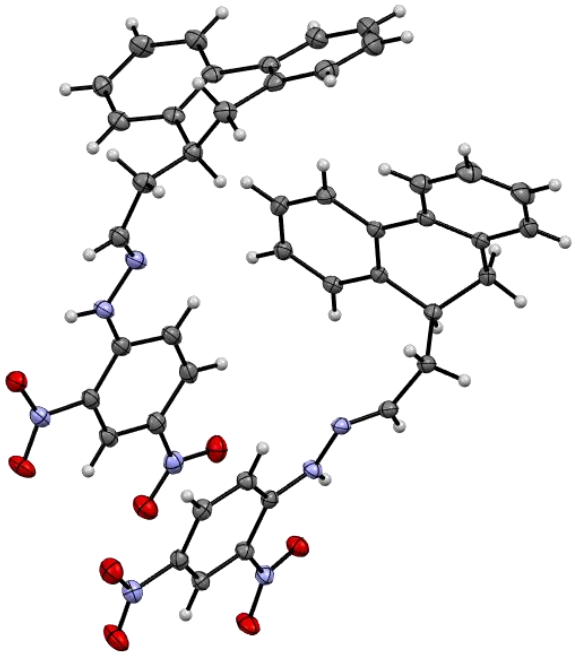


Figure S1: Asymmetric unit of the crystal structure of the major enantiomer of **(*S*)-5.**

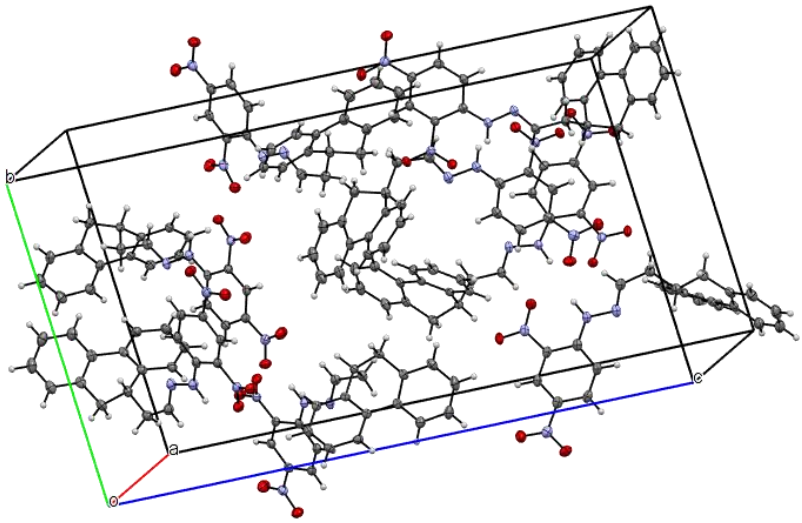


Figure S2: Packing of the crystal structure of the major enantiomer of **(*S*)-5.**

Structure Tables

	bm011120_1_1.cif
CCDC number	2054485
Empirical formula	$C_{22}H_{18}N_4O_4$
Formula weight	402.40
Temperature [K]	100.0(1)
Crystal system	orthorhombic
Space group (number)	$P2_12_12_1$ (19)
a [Å]	7.79890(10)
b [Å]	15.9461(2)
c [Å]	30.2933(3)
α [Å]	90
β [Å]	90
γ [Å]	90

Volume [Å^3]	3767.34(8)
Z	8
ρ_{calc} [g/cm^3]	1.419
μ [mm^{-1}]	0.828
F(000)	1680
Crystal size [mm^3]	0.255×0.153×0.094
Crystal colour	clear yellow
Crystal shape	block
Radiation	Cu K_α (λ=1.54184 Å)
2Θ range [°]	5.83 to 160.79 (0.78 Å)
Index ranges	-9 ≤ h ≤ 9 -18 ≤ k ≤ 20 -38 ≤ l ≤ 38
Reflections collected	107452
Independent reflections	8157 R_{int} = 0.0672 R_{sigma} = 0.0234
Completeness	100.0 %
Data / Restraints / Parameters	8157/2/547
Goodness-of-fit on F^2	1.039
Final R indexes [I≥2σ(I)]	R_1 = 0.0341 wR_2 = 0.0834
Final R indexes [all data]	R_1 = 0.0352 wR_2 = 0.0844
Largest peak/hole [eÅ^3]	0.37/-0.22
Flack X parameter	-0.01(6)

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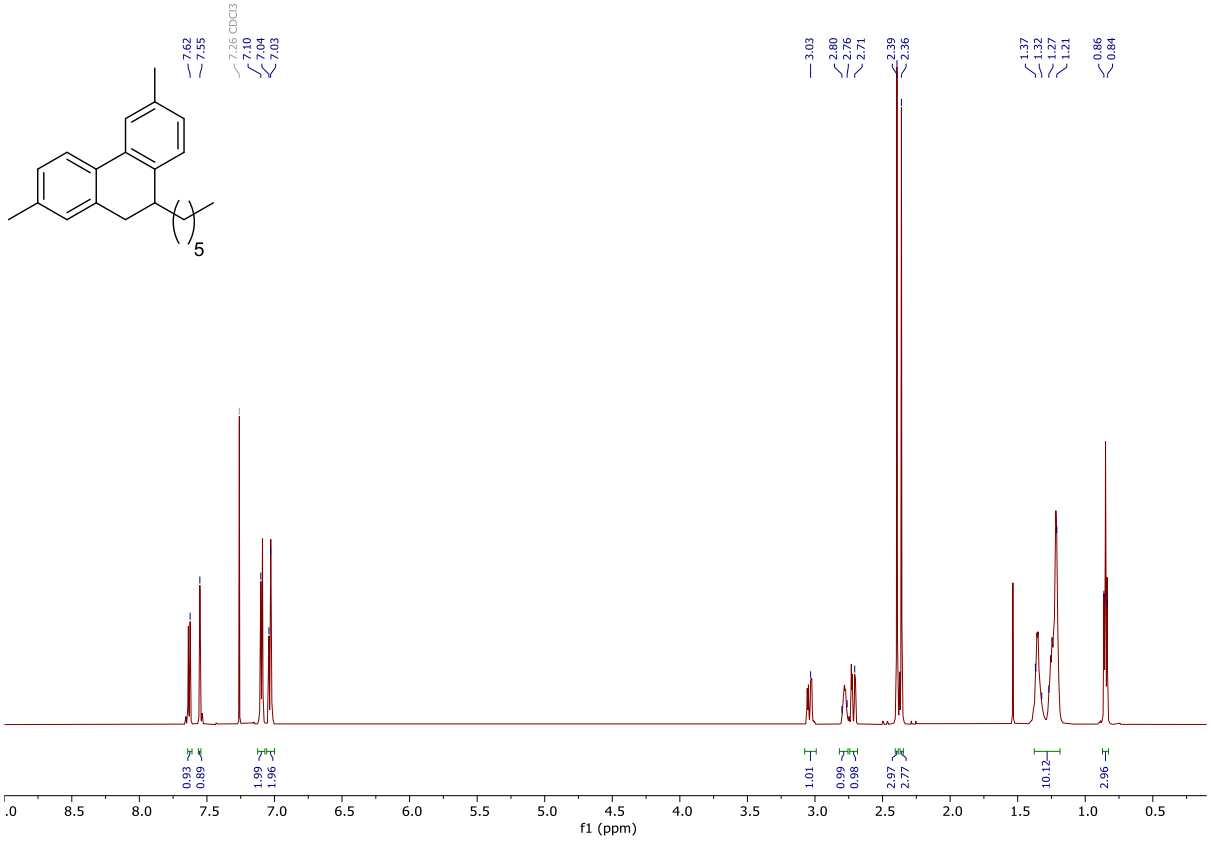
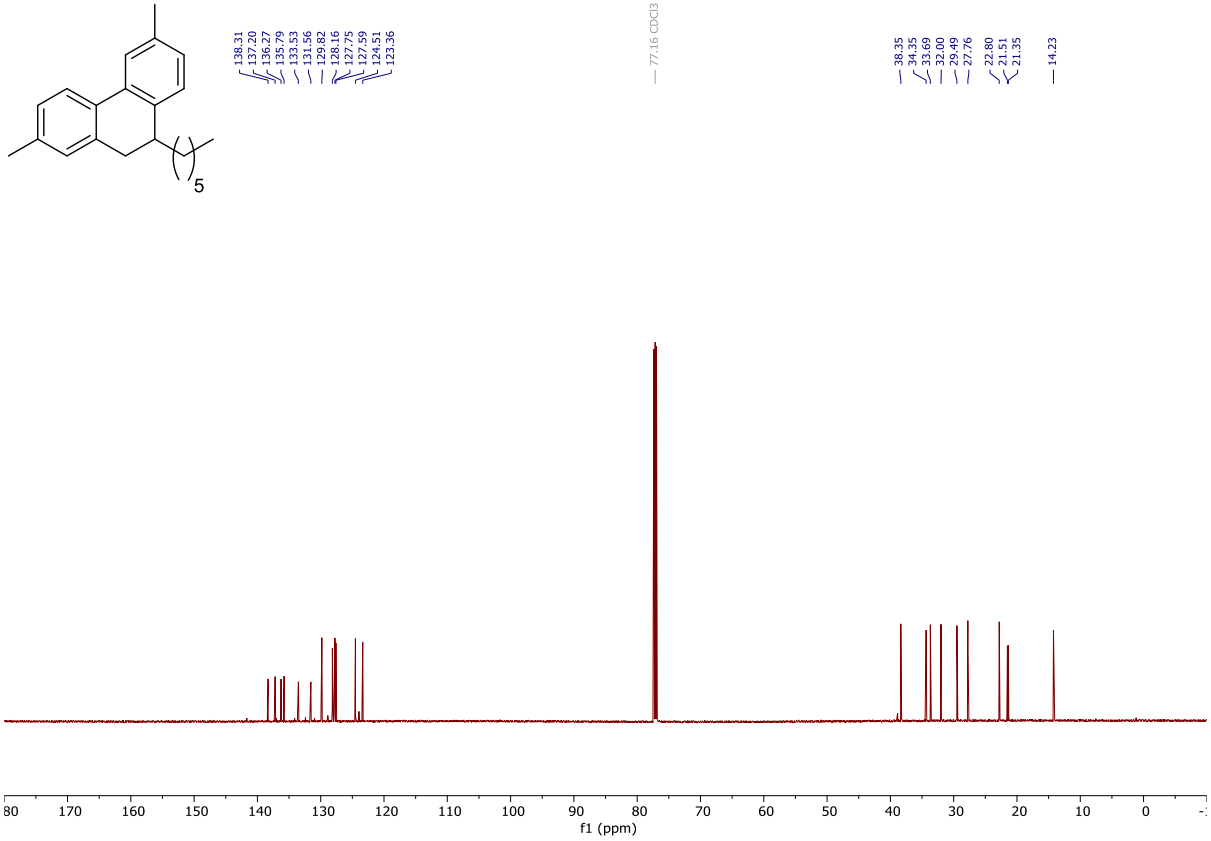
NMR spectra

^{1}H NMR, $CDCl_3$, 600 MHz, 9-hexyl-2,6-dimethyl-9,10-dihydrophenanthrene (**3a**)



^{13}C NMR, $CDCl_3$, 151 MHz, 9-hexyl-2,6-dimethyl-9,10-dihydrophenanthrene (**3a**)



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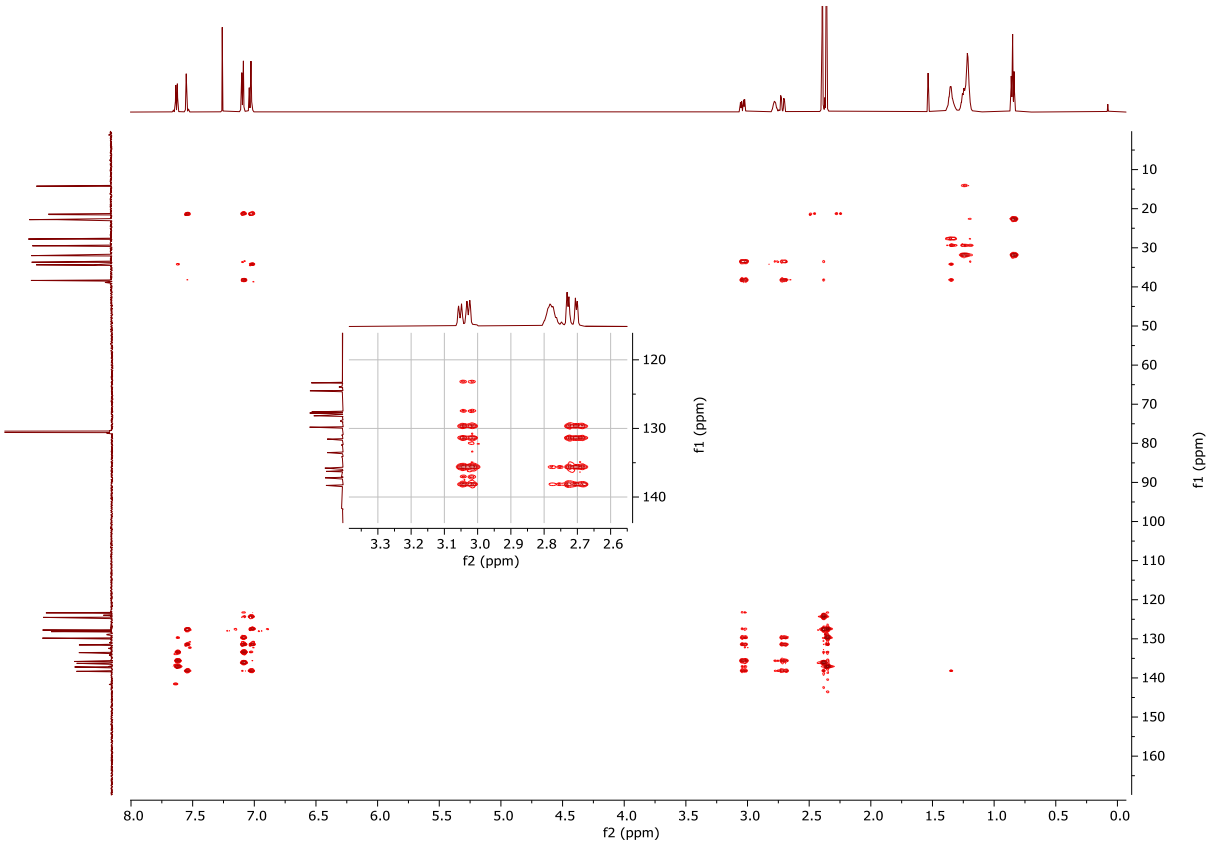
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140

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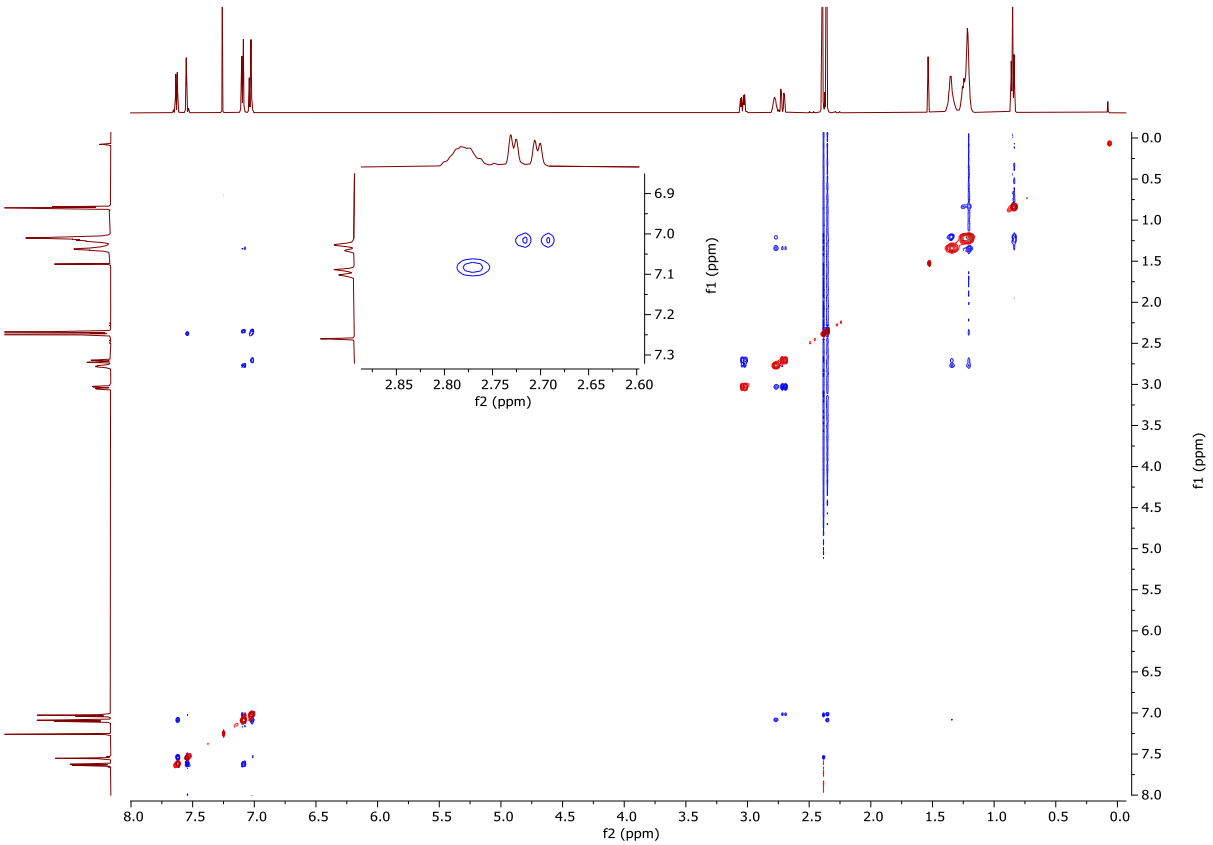
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6.9
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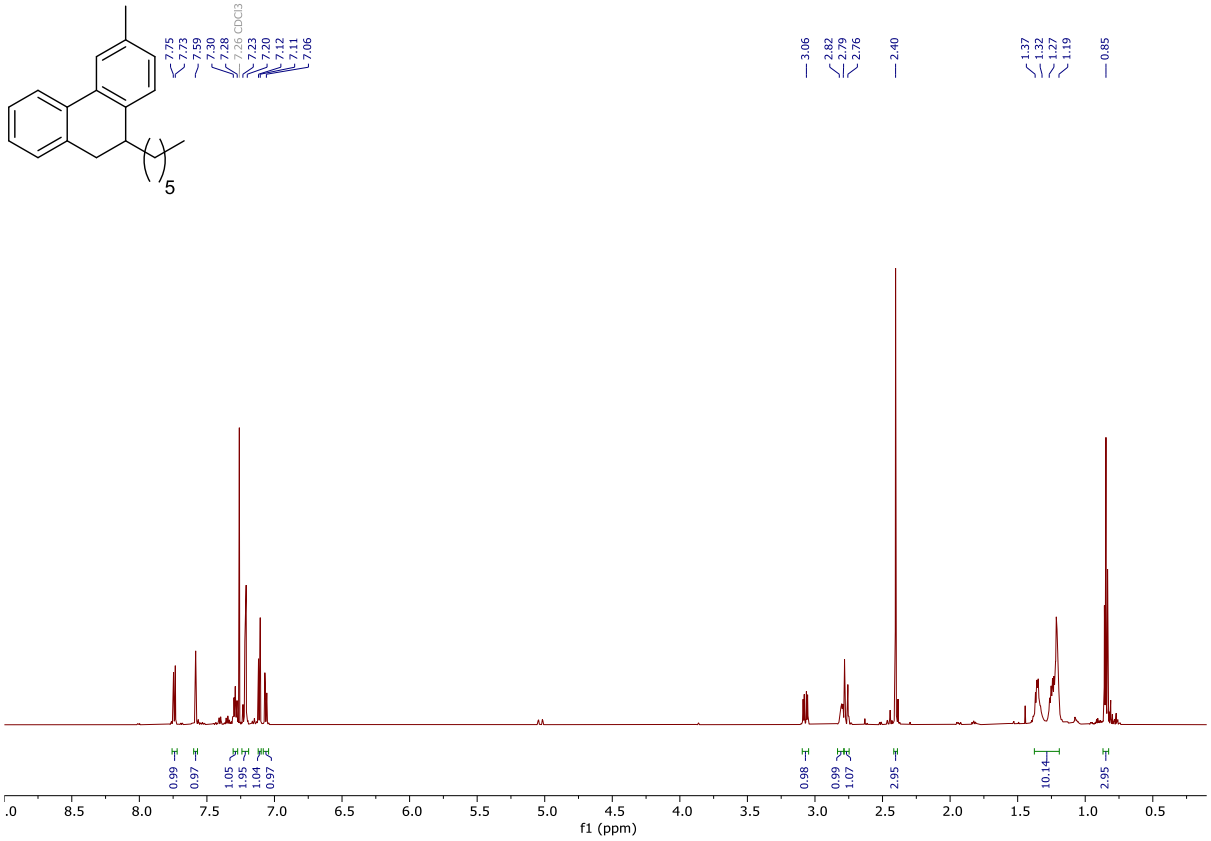
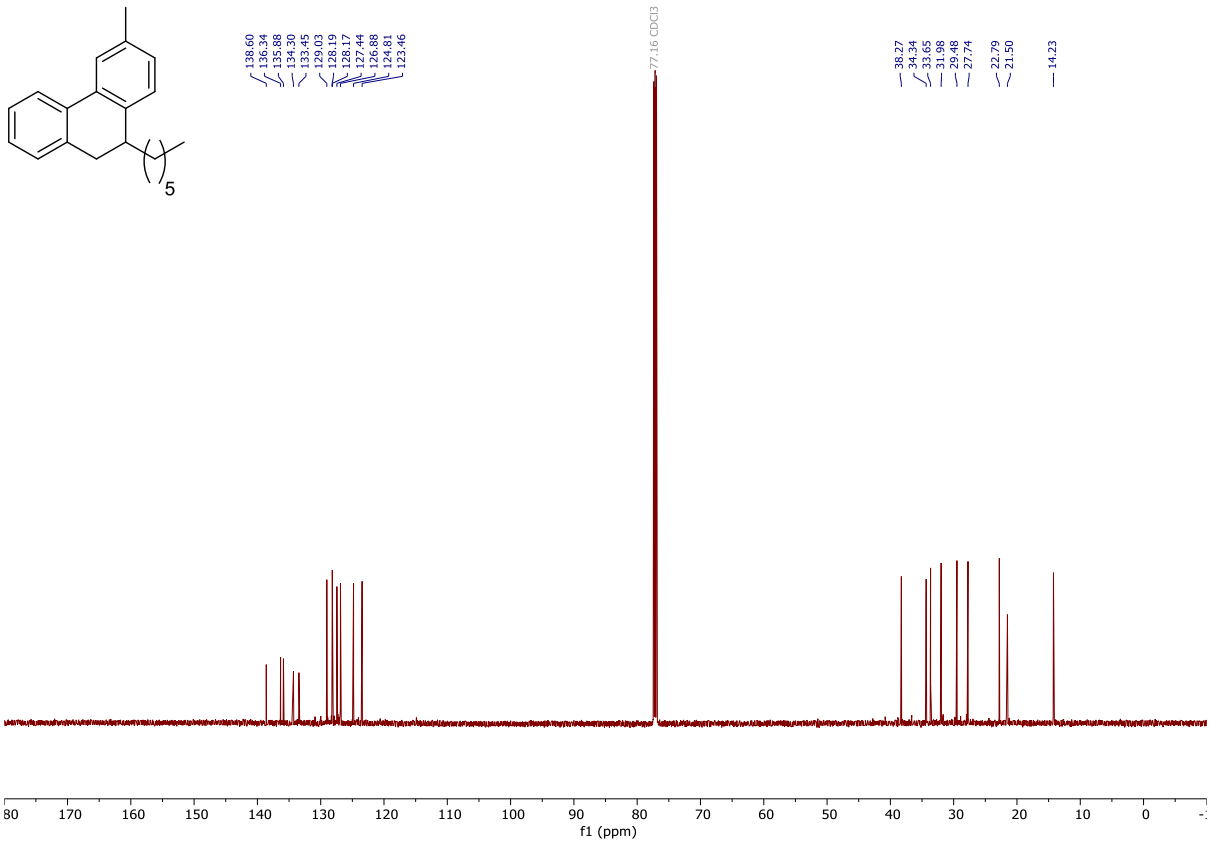
7.1
7.2
7.3

^{1}H NMR, $CDCl_3$, 600 MHz, 10-hexyl-3-methyl-9,10-dihydrophenanthrene (**3b**)



^{13}C NMR, $CDCl_3$, 151 MHz, 10-hexyl-3-methyl-9,10-dihydrophenanthrene (**3b**)



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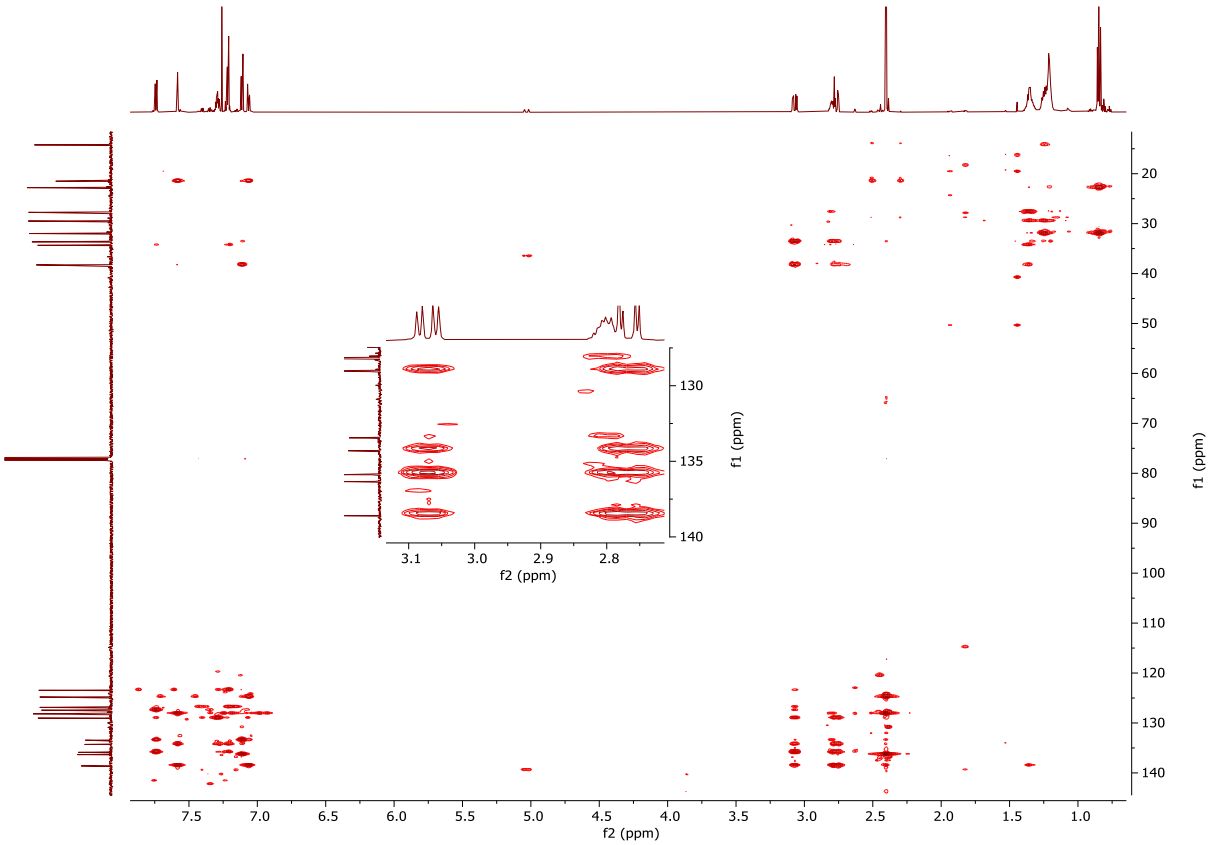
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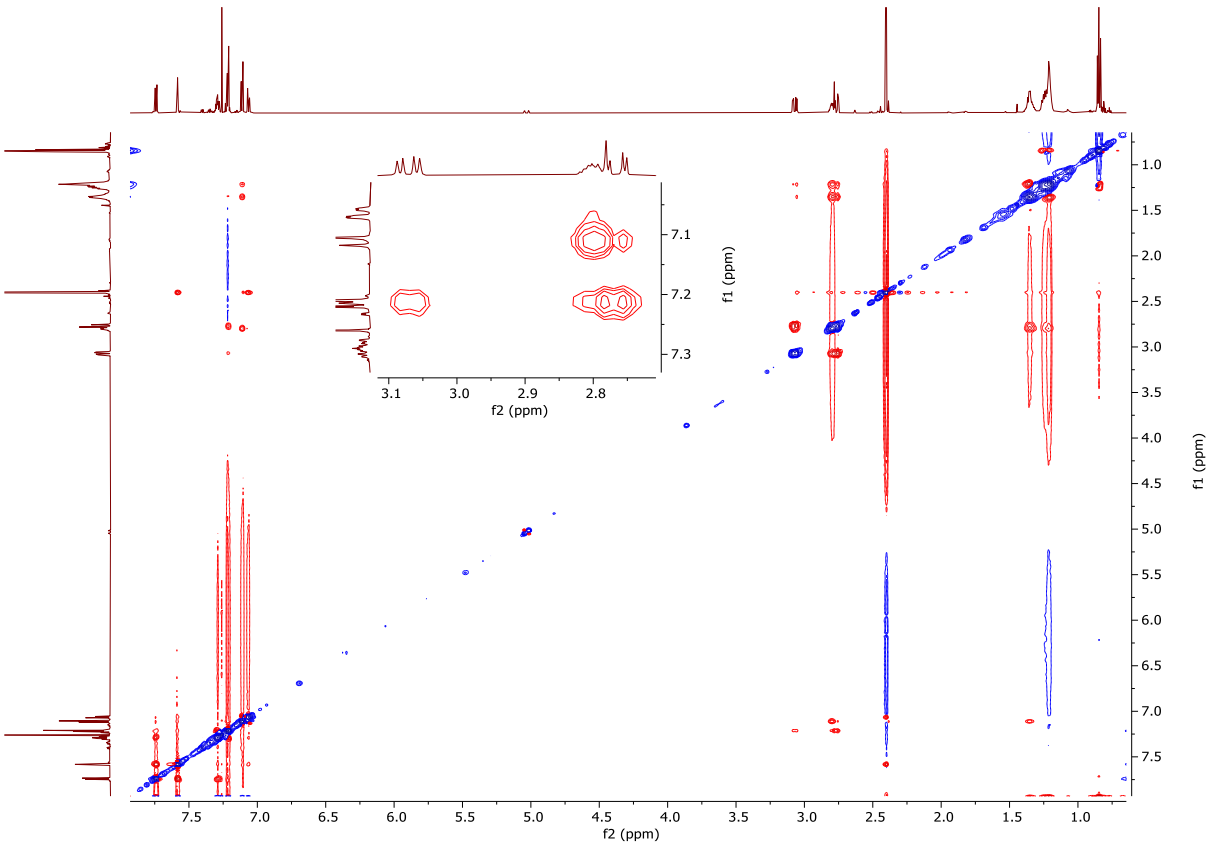
3.1 3.0 2.9 2.8
130 135 140

NOESY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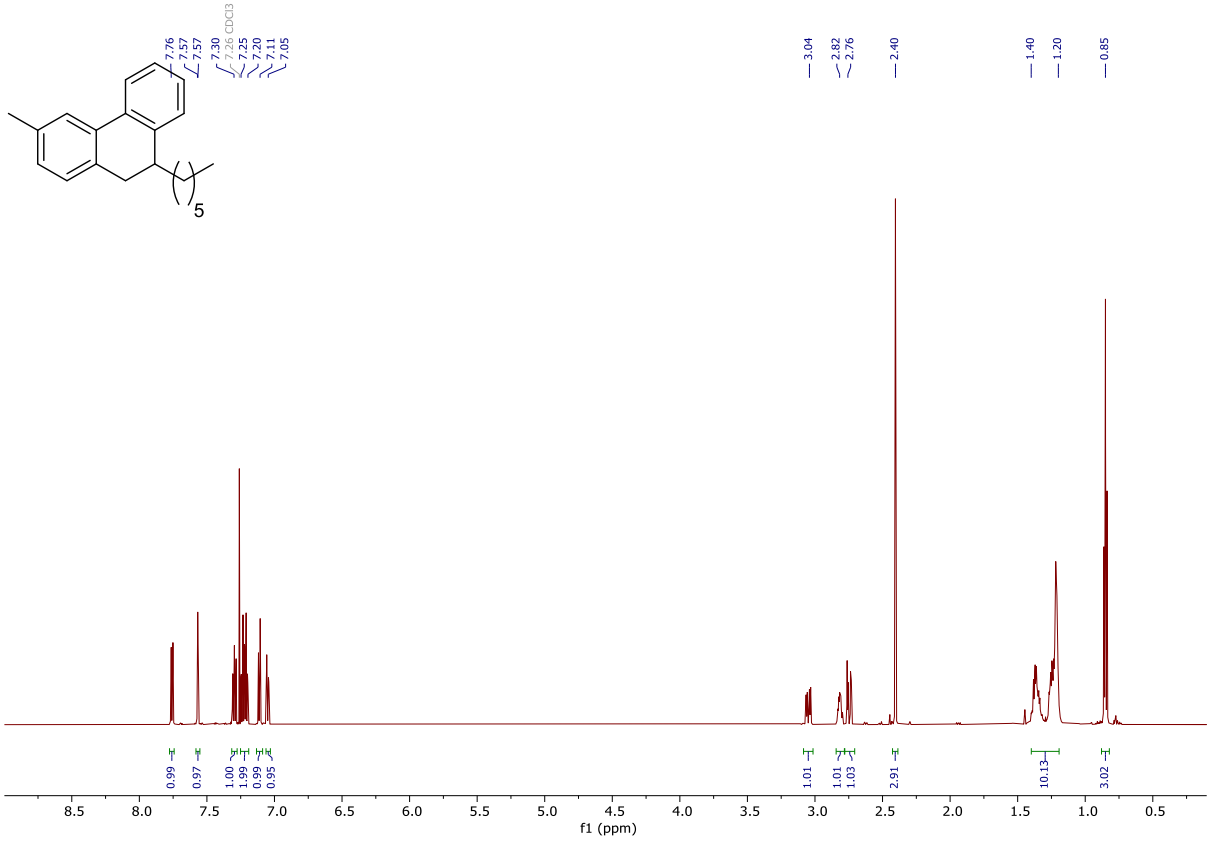
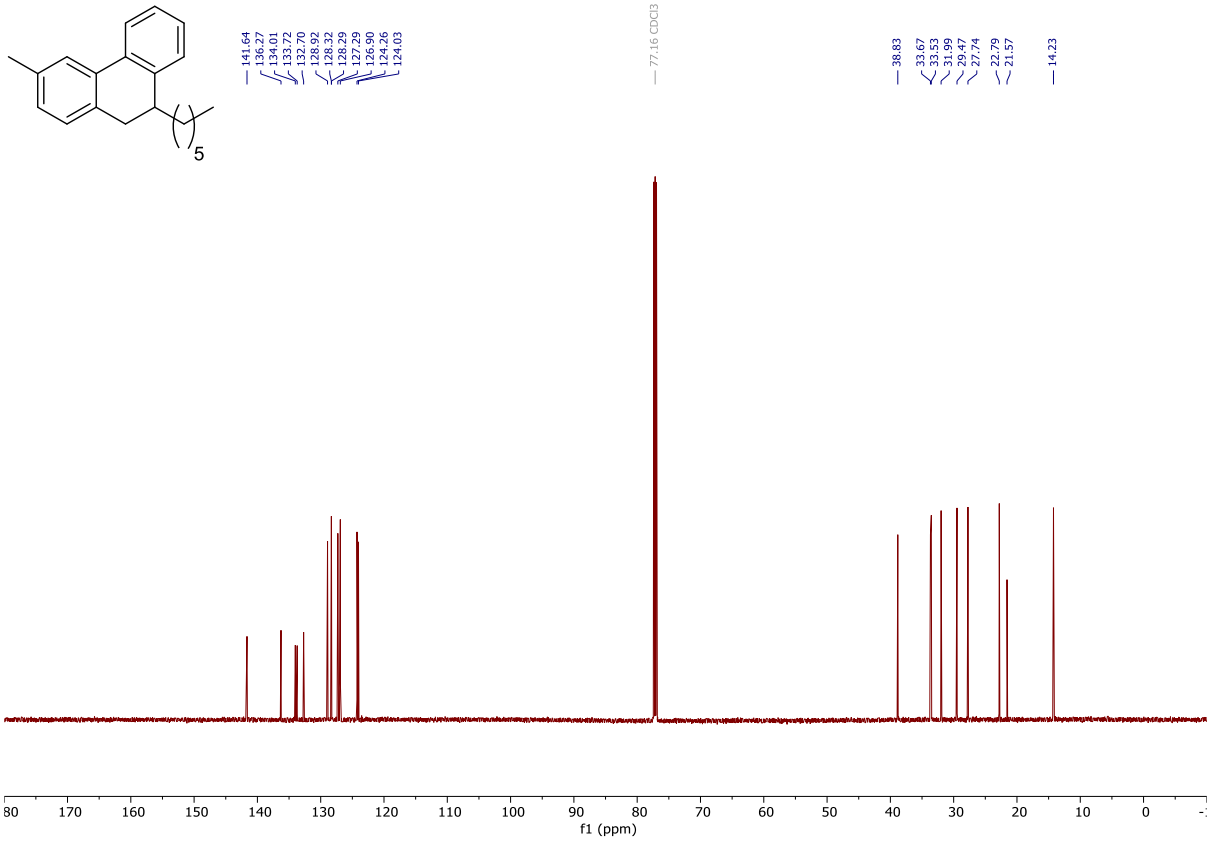
3.1 3.0 2.9 2.8
7.1 7.2 7.3

^{1}H NMR, $CDCl_3$, 600 MHz, 9-hexyl-3-methyl-9,10-dihydrophenanthrene (**3c**)



^{13}C NMR, $CDCl_3$, 151 MHz, 9-hexyl-3-methyl-9,10-dihydrophenanthrene (**3c**)



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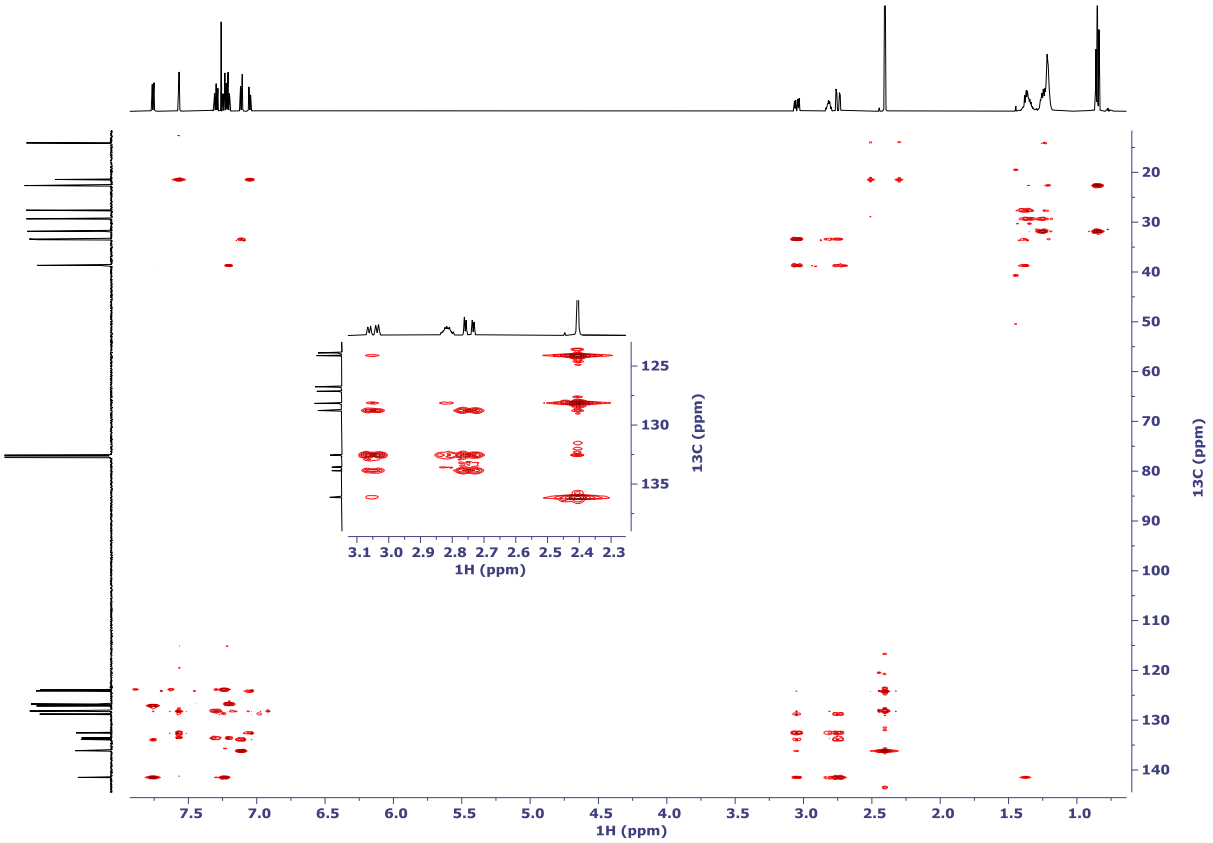

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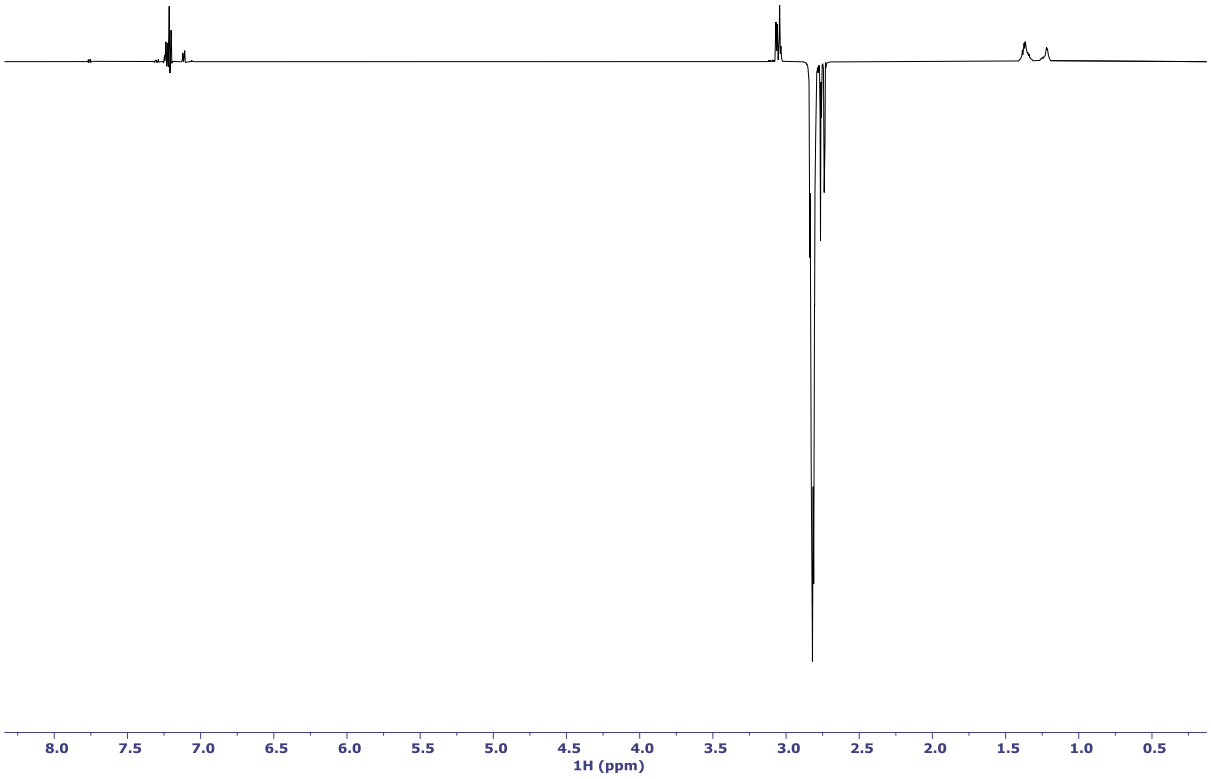
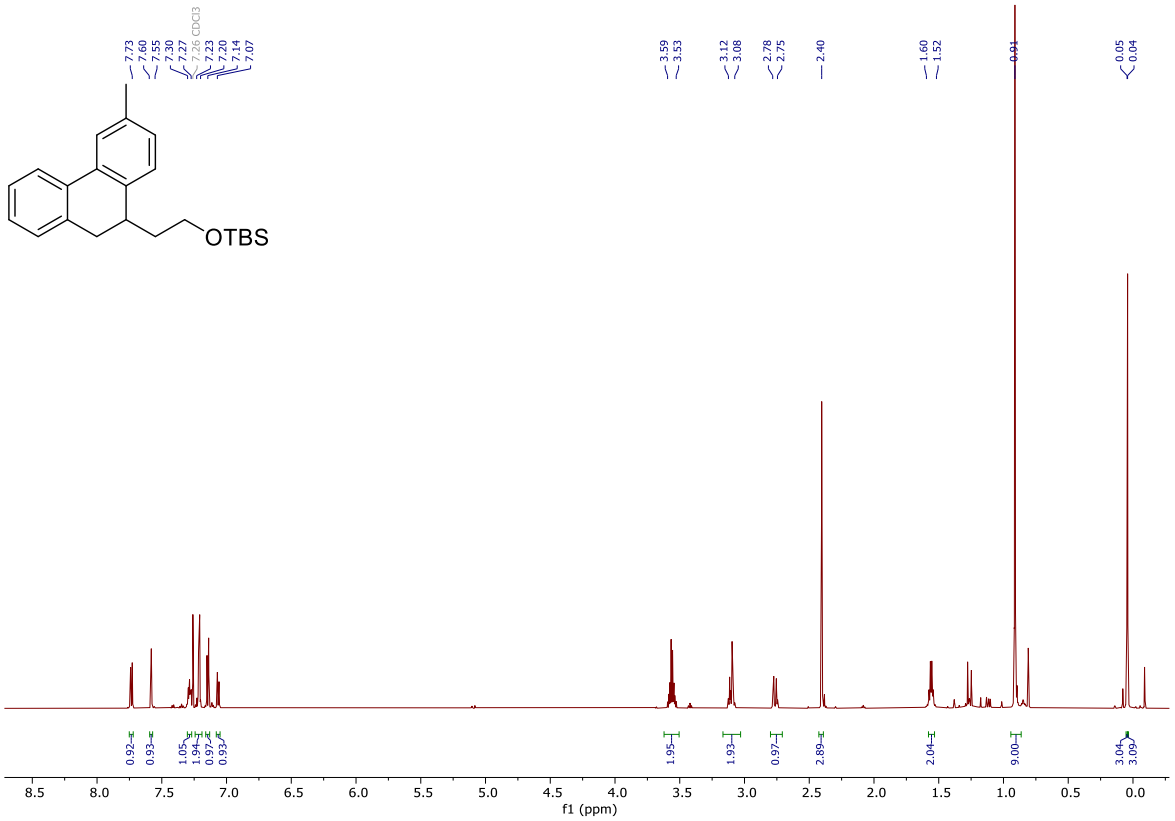
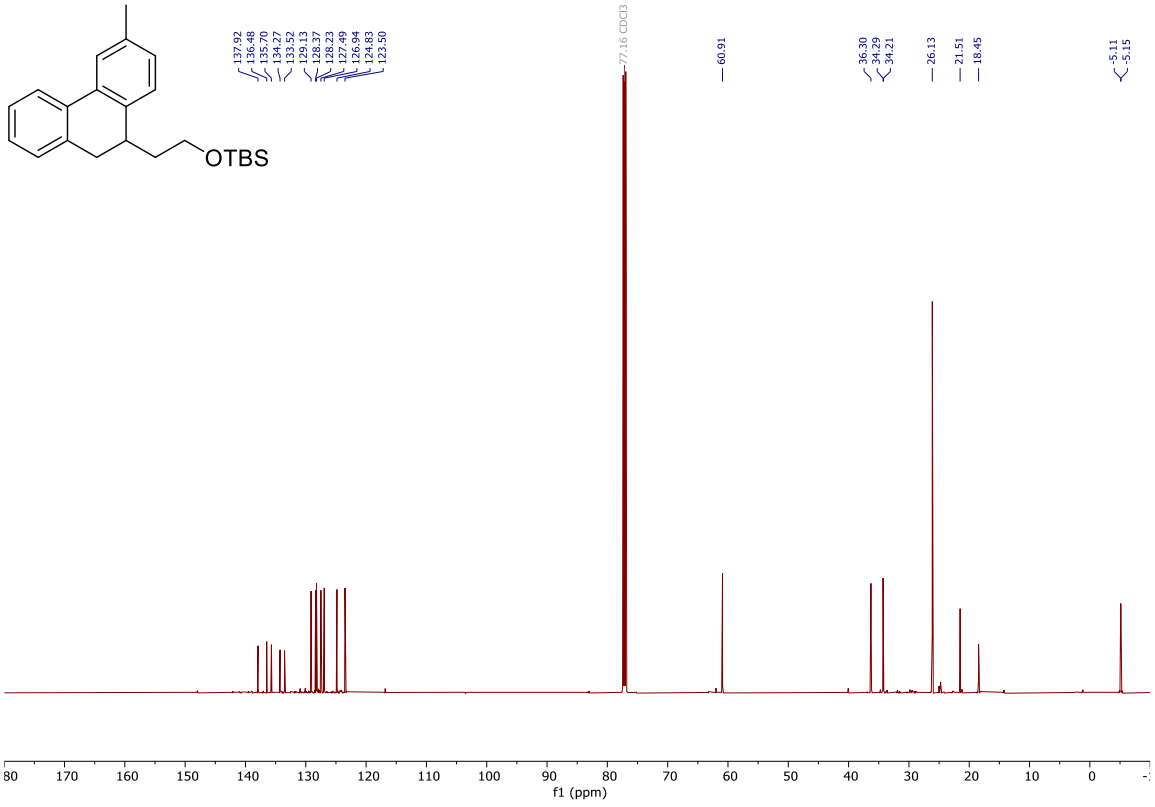


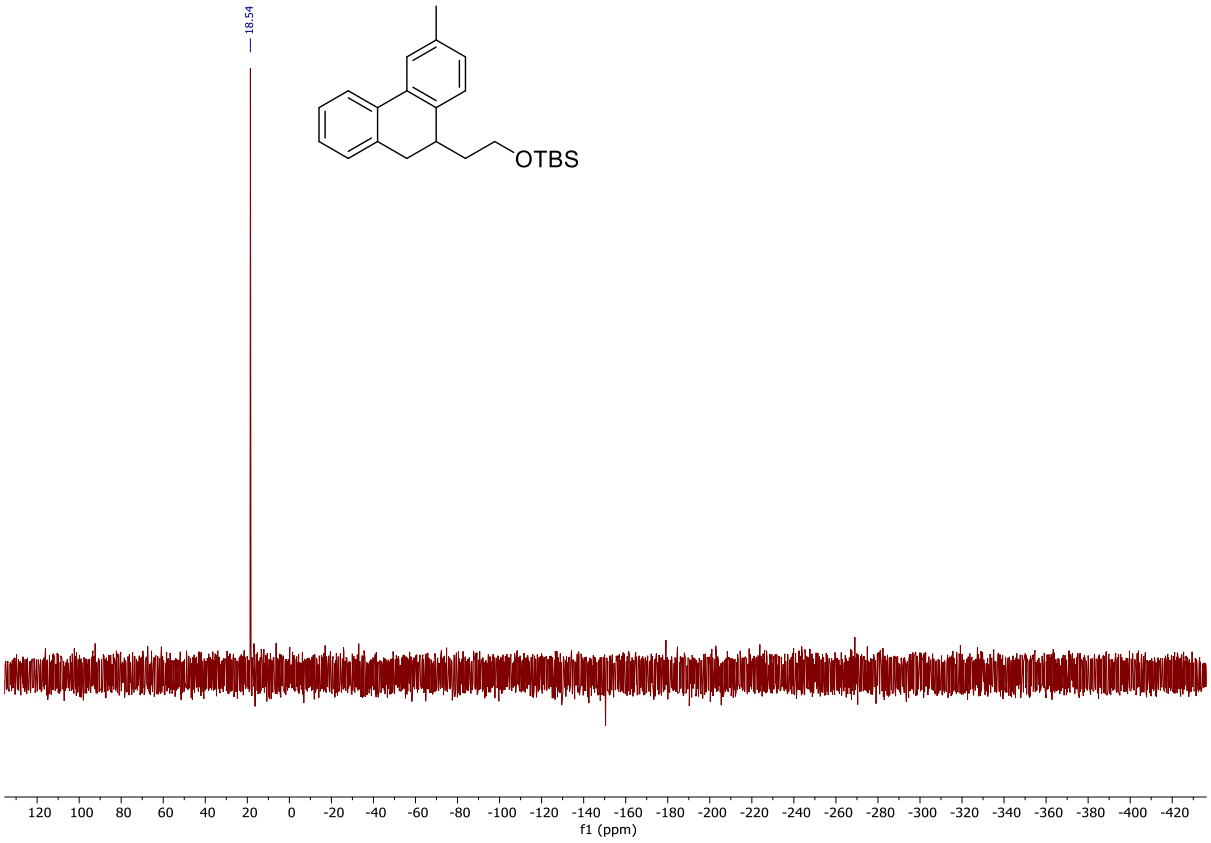
^{1}H NMR, $CDCl_3$, 600 MHz, *tert*-butyldimethyl(2-(6-methyl-9,10-dihydrophenanthren-9-yl) ethoxy)silane (**3d**)



^{13}C NMR, $CDCl_3$, 151 MHz, *tert*-butyldimethyl(2-(6-methyl-9,10-dihydrophenanthren-9-yl) ethoxy)silane (**3d**)



^{29}Si NMR, $CDCl_3$, 99 MHz, *tert*-butyldimethyl(2-(6-methyl-9,10-dihydrophenanthren-9-yl) ethoxy)silane (**3d**)



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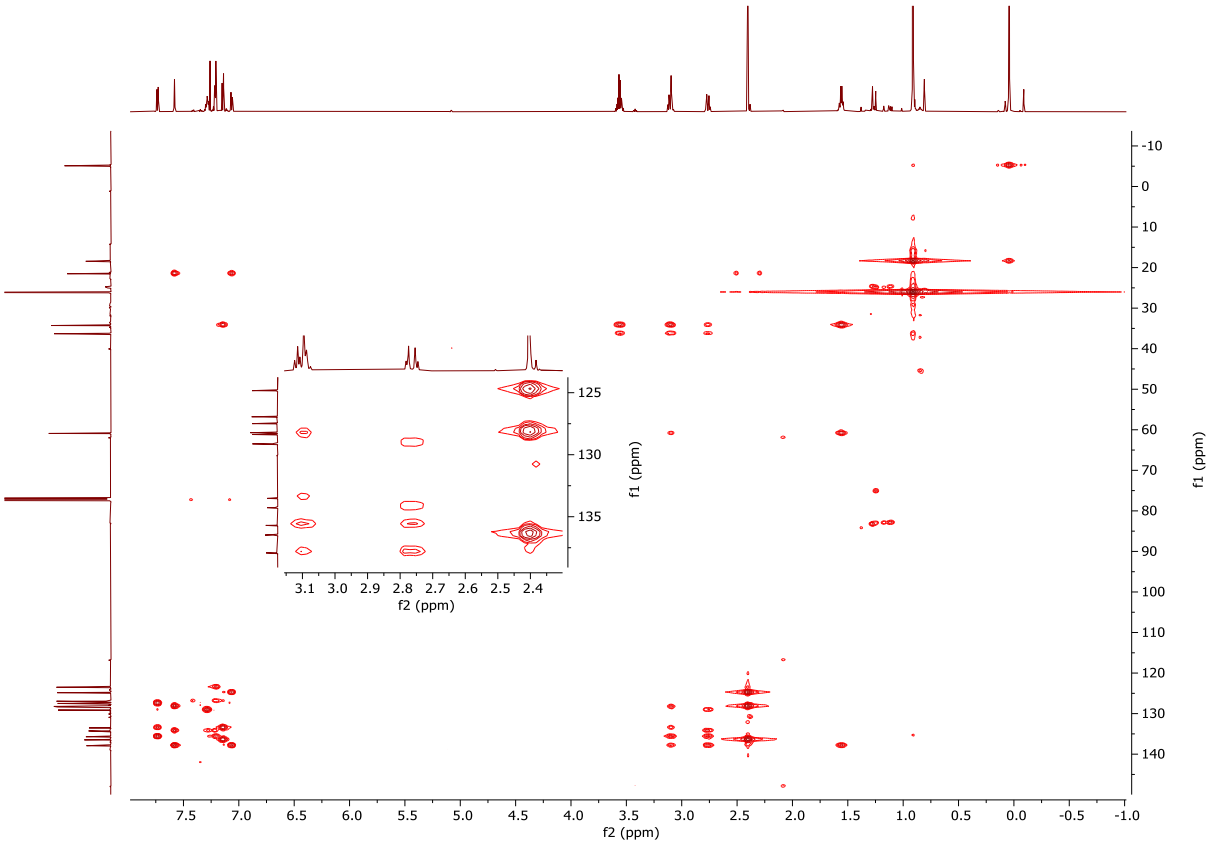

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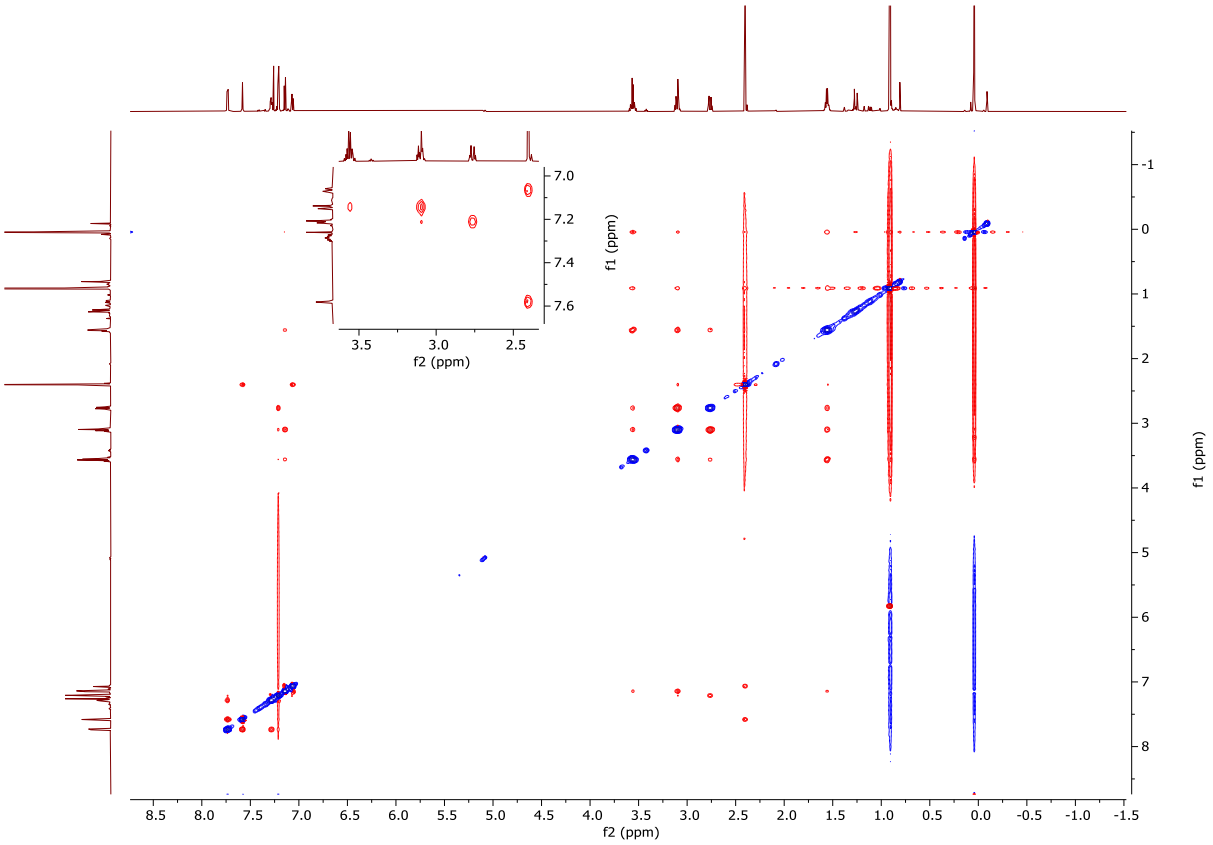
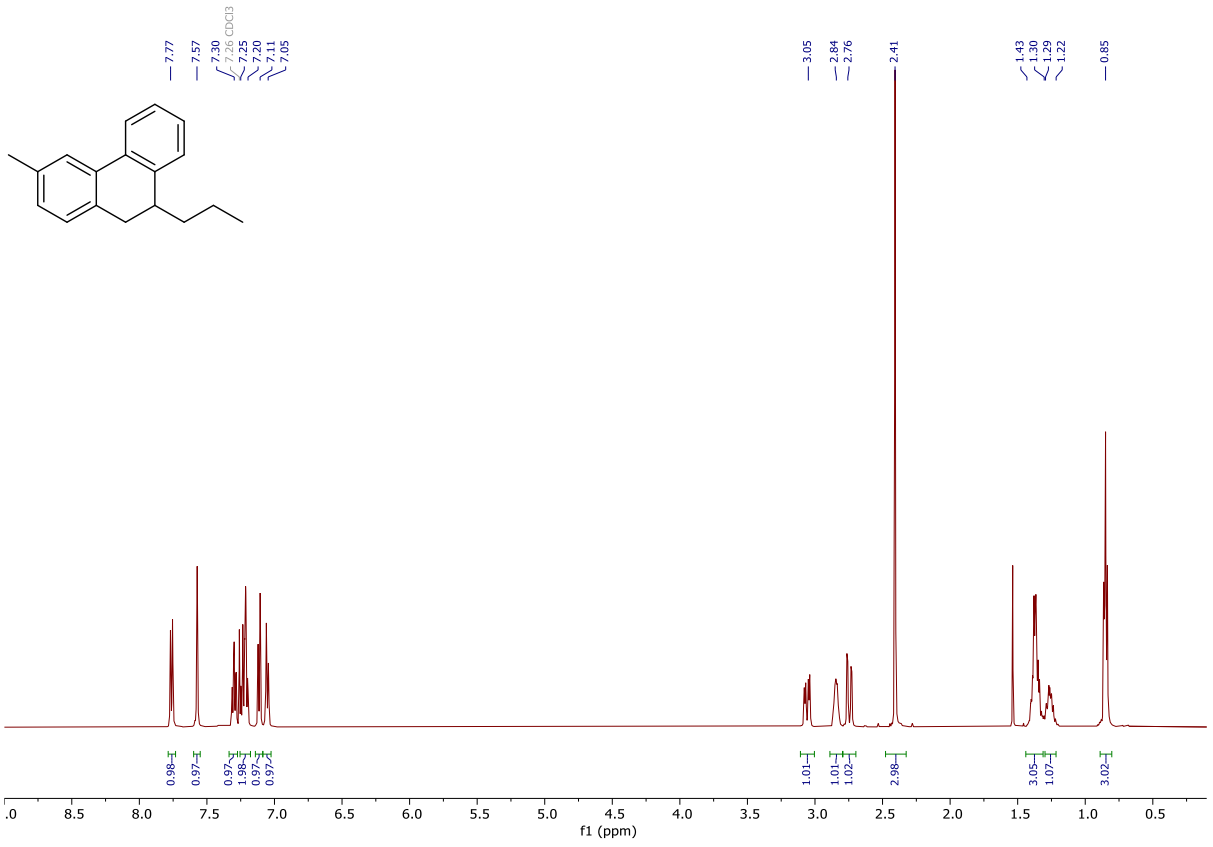
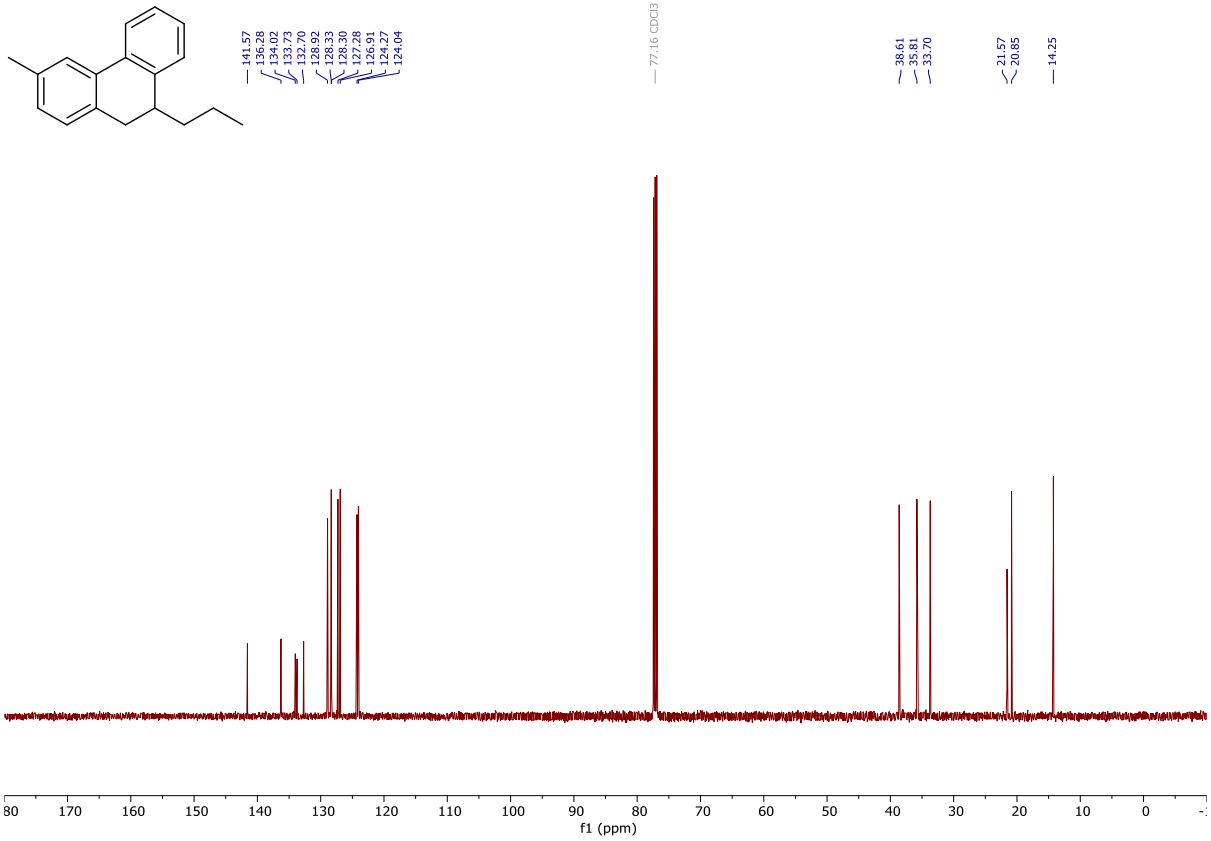


^{1}H NMR, $CDCl_3$, 501 MHz, 3-methyl-9-propyl-9,10-dihydrophenanthrene (**3e**)



^{13}C NMR, $CDCl_3$, 126 MHz, 3-methyl-9-propyl-9,10-dihydrophenanthrene (**3e**)



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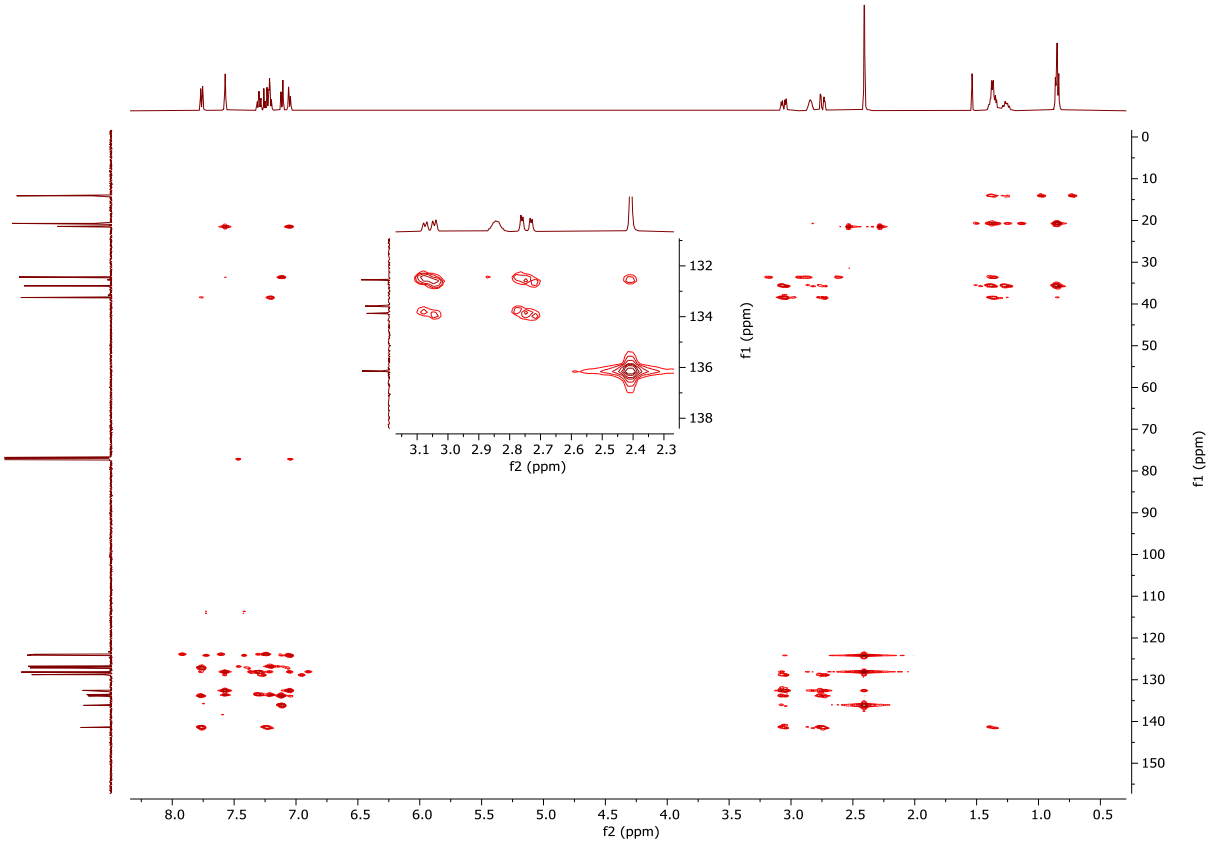

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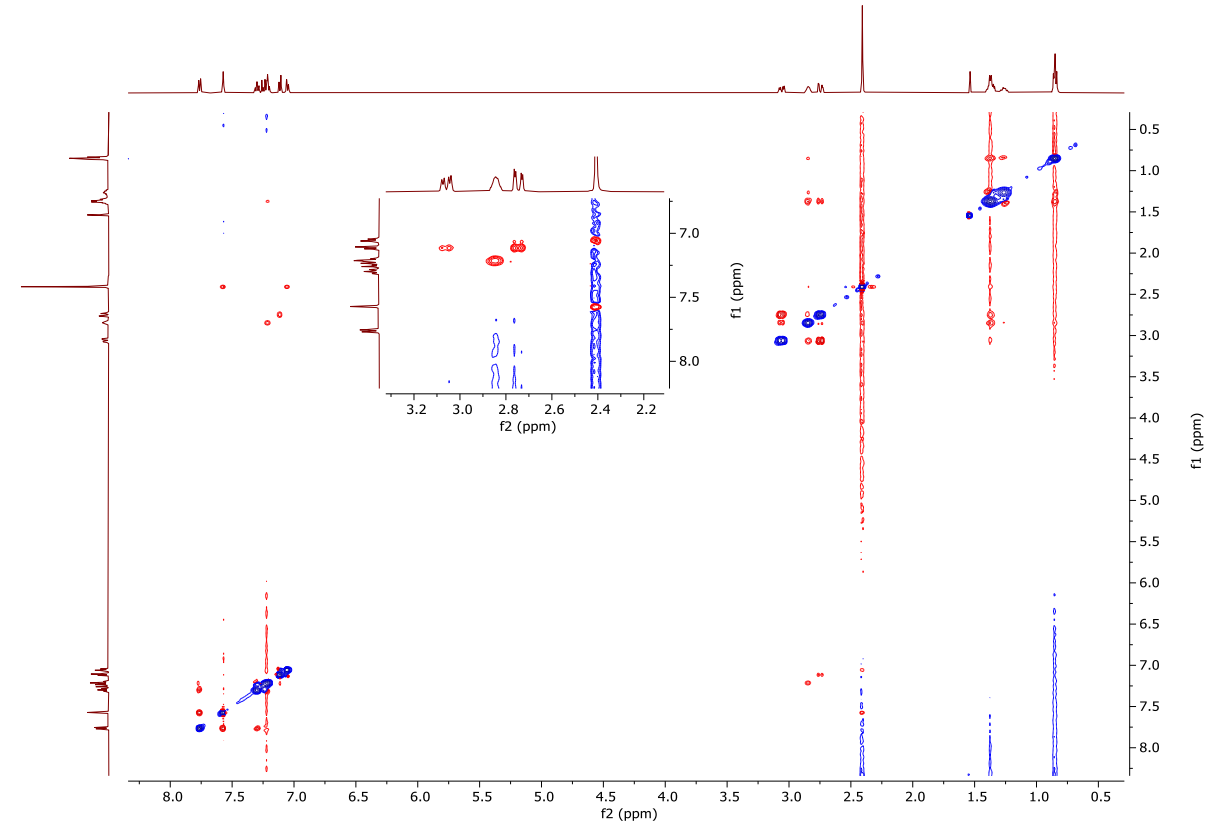
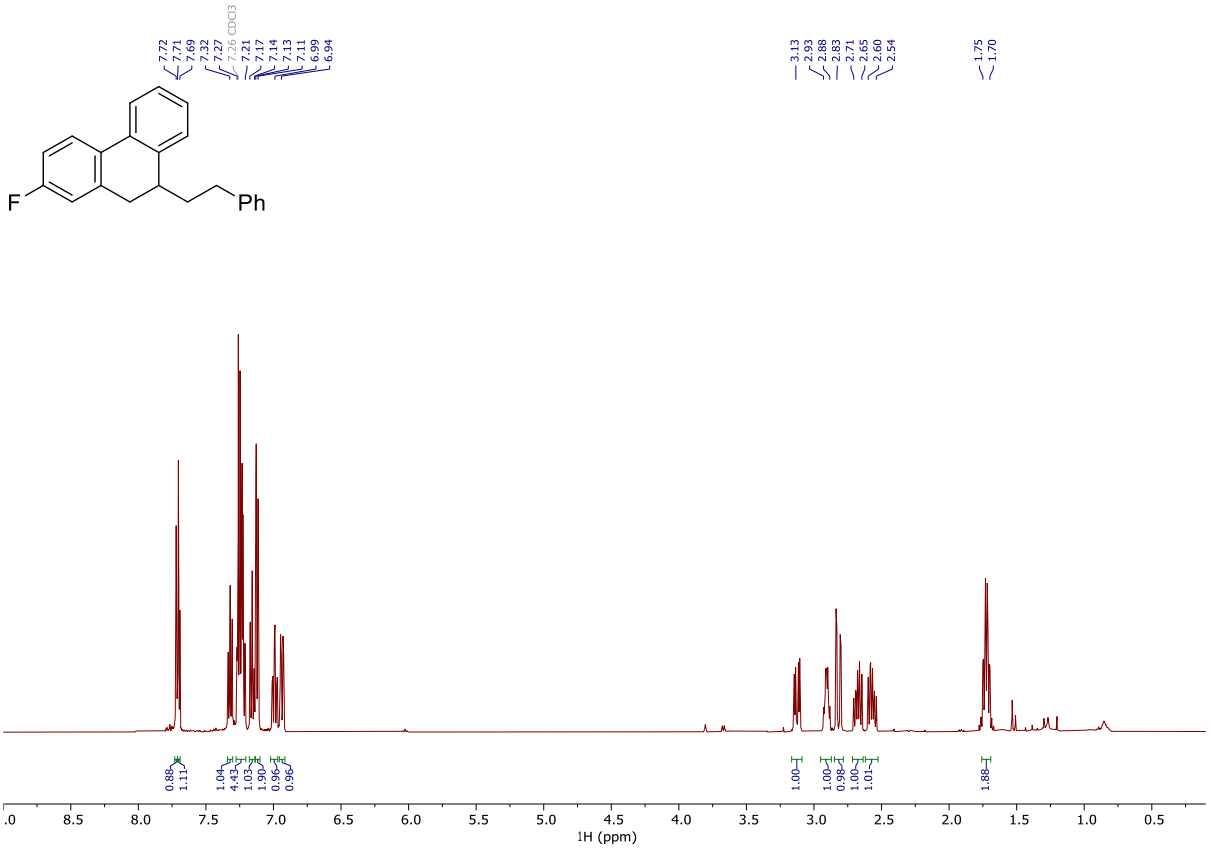
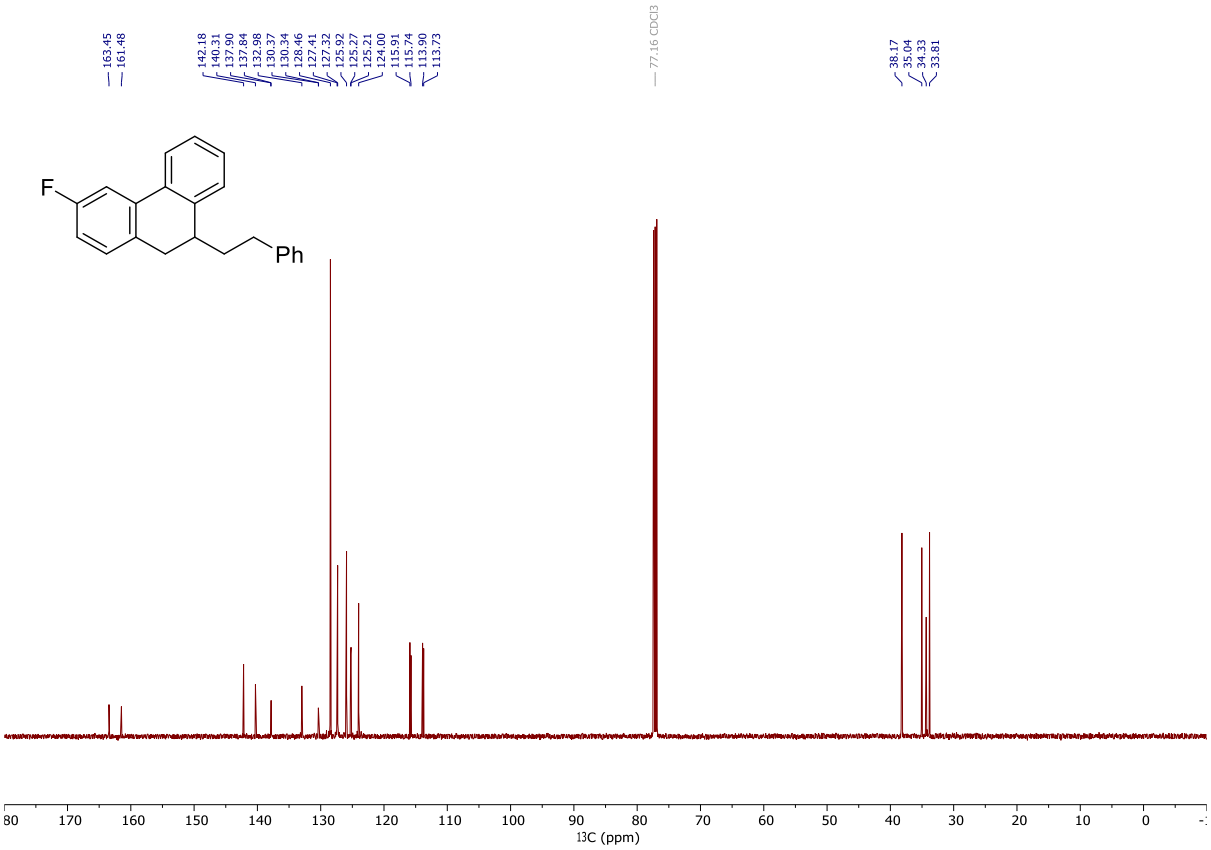


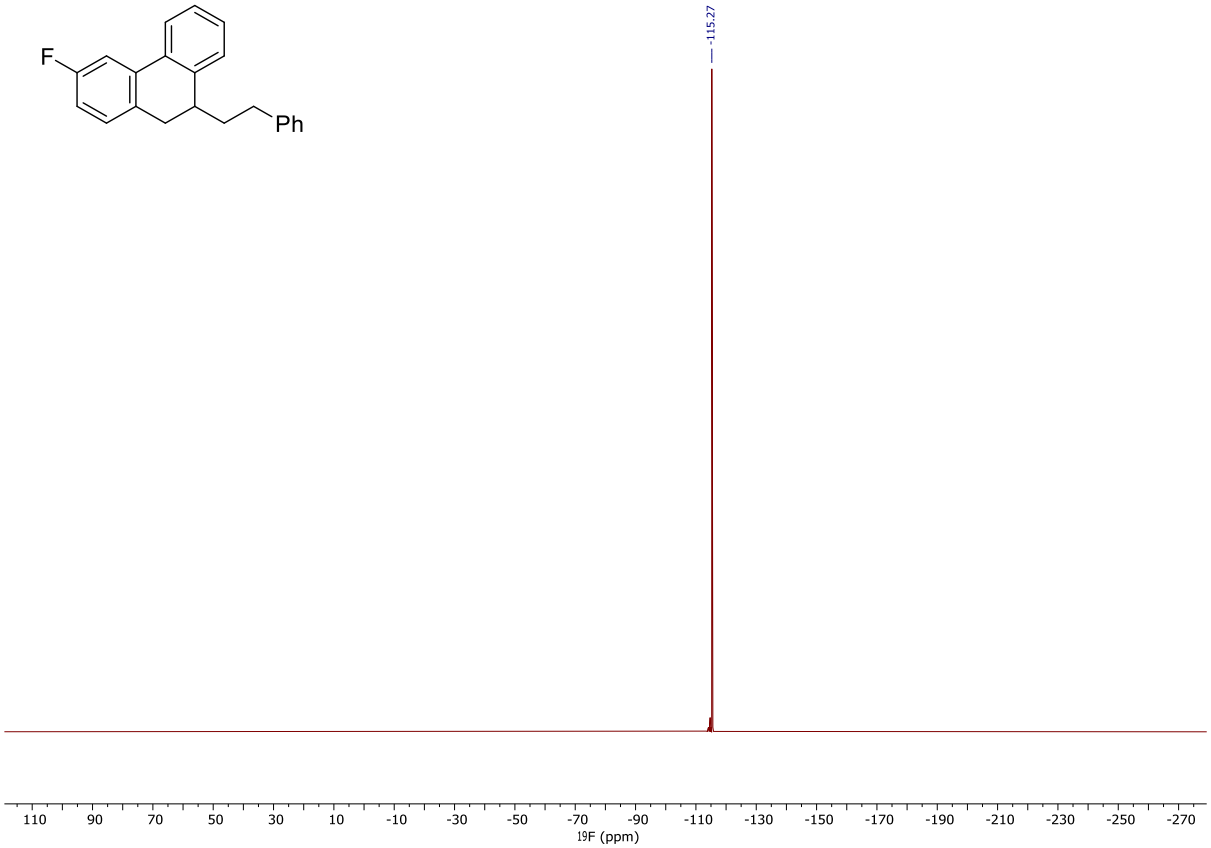
^{1}H NMR, $CDCl_3$, 501 MHz, 2-fluoro-9-phenethyl-9,10-dihydrophenanthrene **(3f)**



^{13}C NMR, $CDCl_3$, 126 MHz, 3-fluoro-9-phenethyl-9,10-dihydrophenanthrene **(3f)**



^{19}F NMR, $CDCl_3$, 470 MHz, 3-fluoro-9-phenethyl-9,10-dihydrophenanthrene **(3f)**



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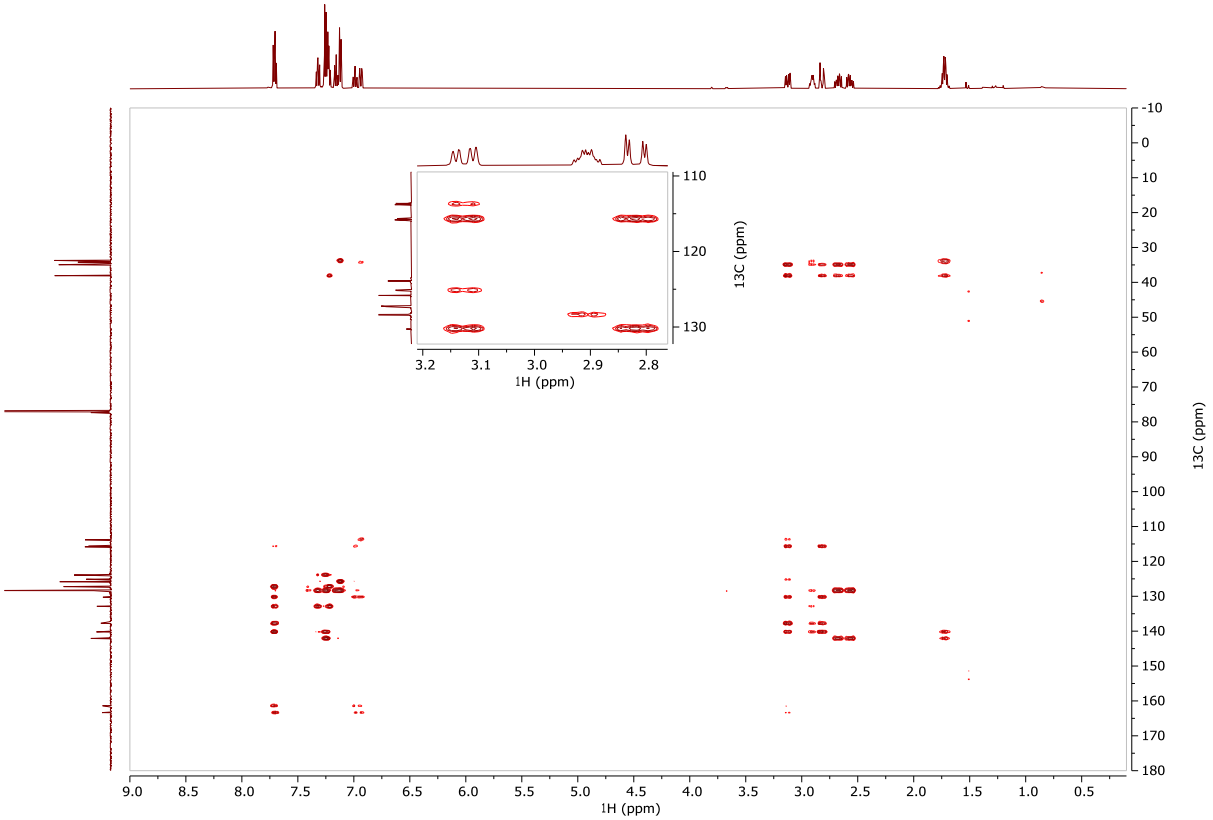

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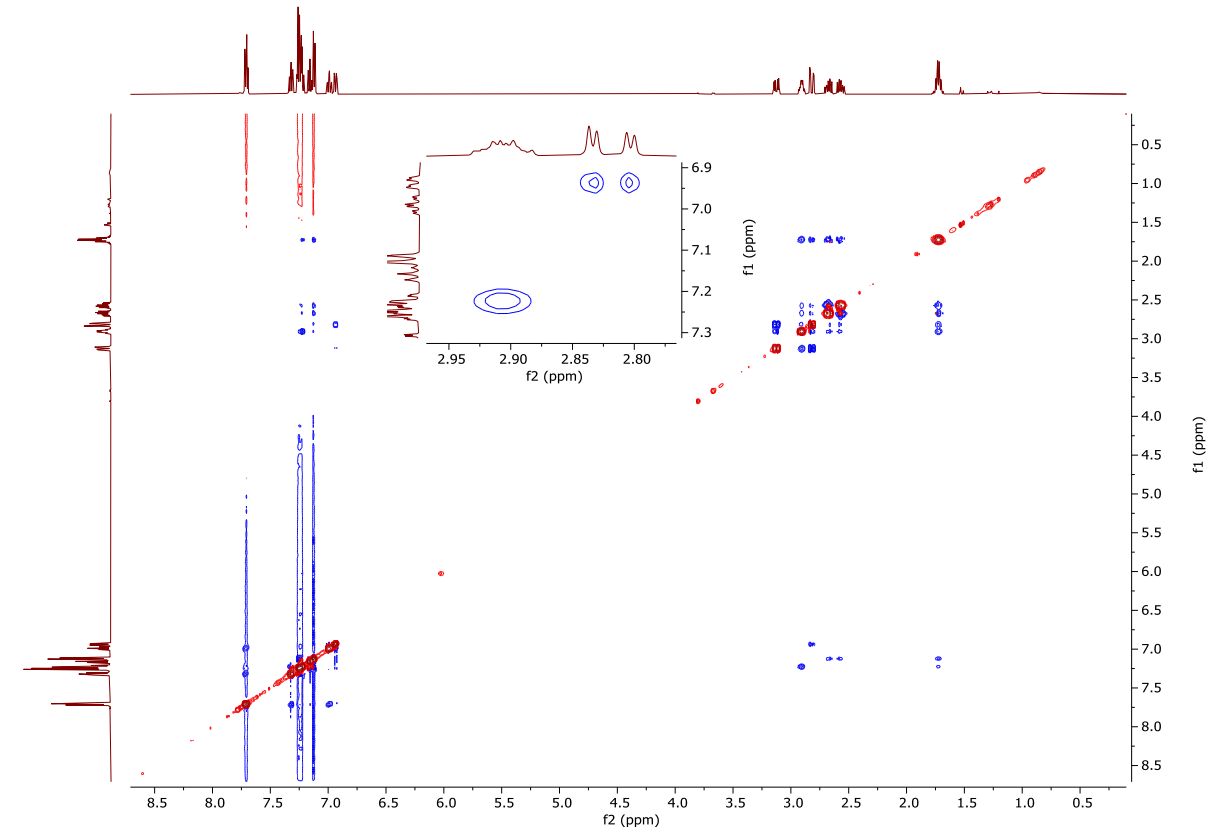
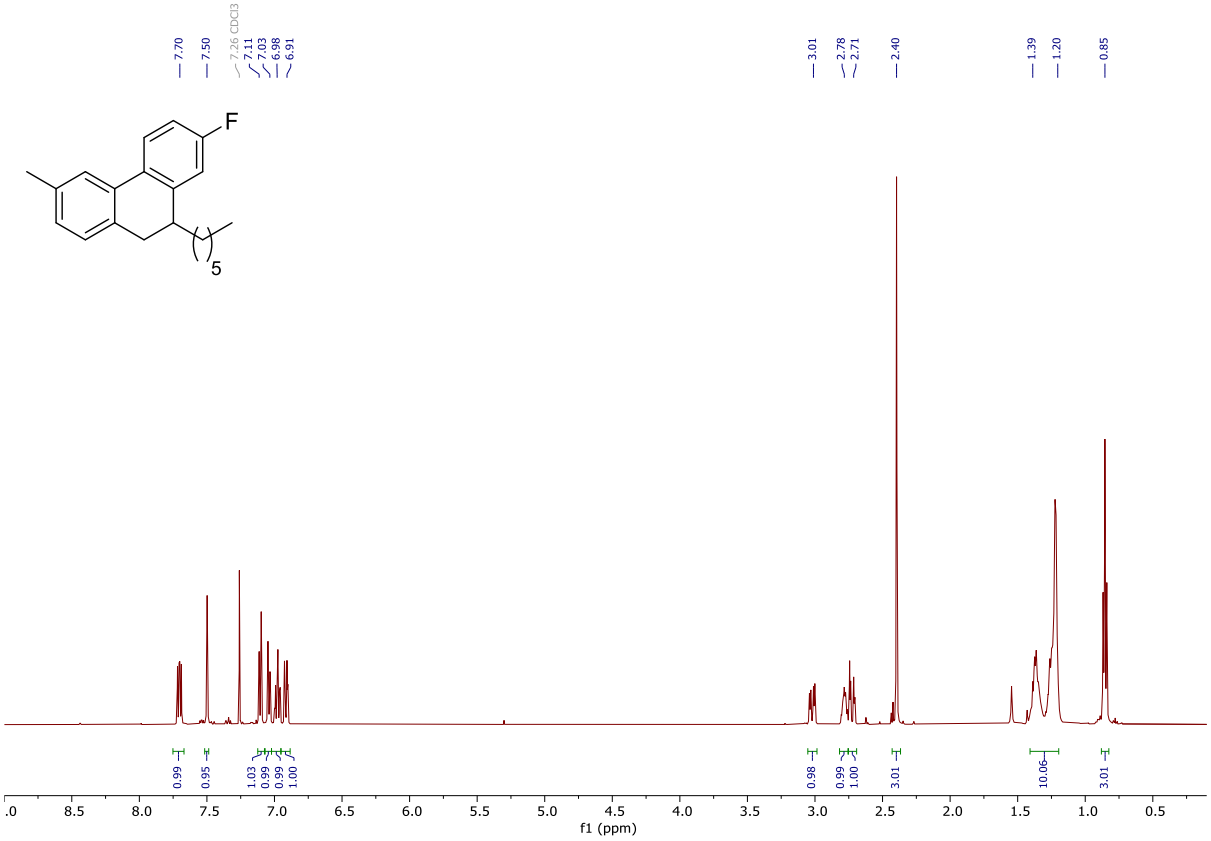
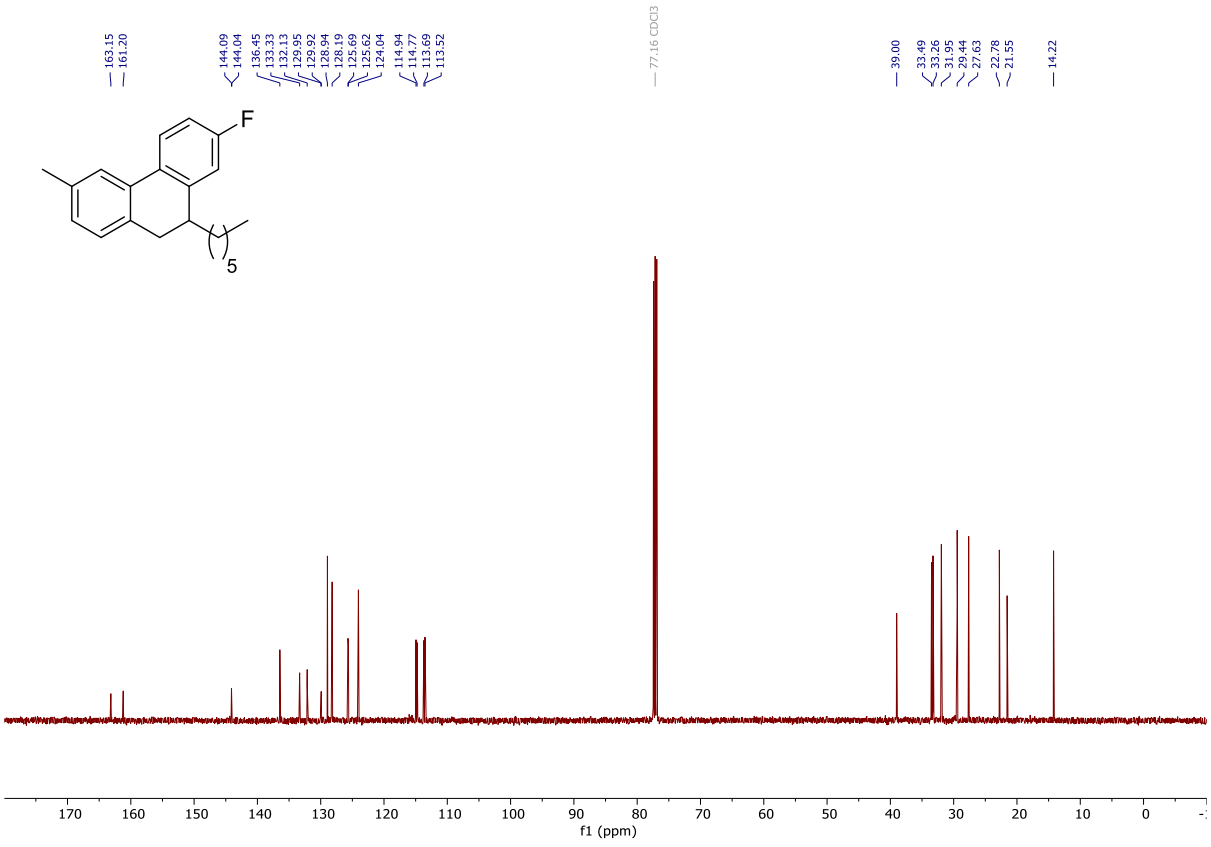


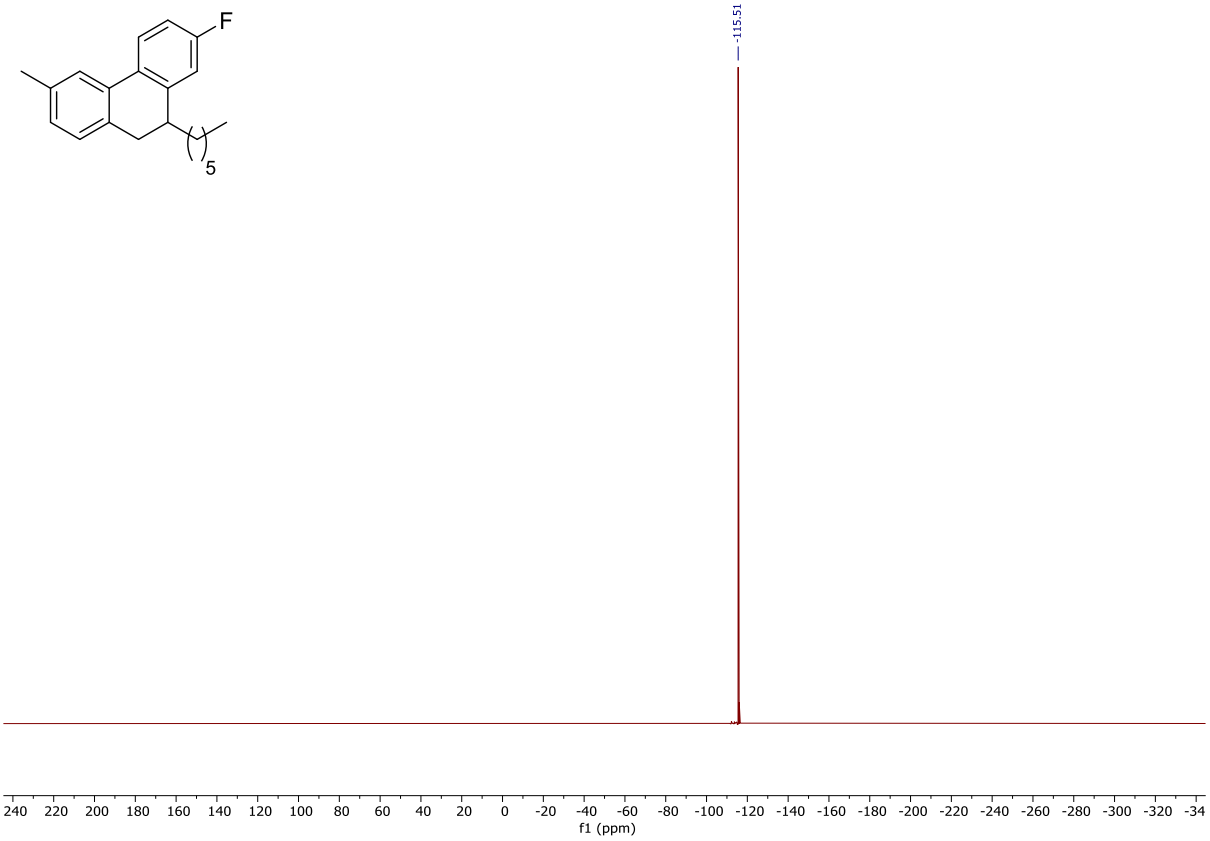
^{1}H NMR, $CDCl_3$, 501 MHz, 2-fluoro-10-hexyl-6-methyl-9,10-dihydrophenanthrene (**3g**)



^{13}C NMR, $CDCl_3$, 126 MHz, 2-fluoro-10-hexyl-6-methyl-9,10-dihydrophenanthrene (**3g**)



^{19}F NMR, $CDCl_3$, 471 MHz, 2-fluoro-10-hexyl-6-methyl-9,10-dihydrophenanthrene (**3g**)



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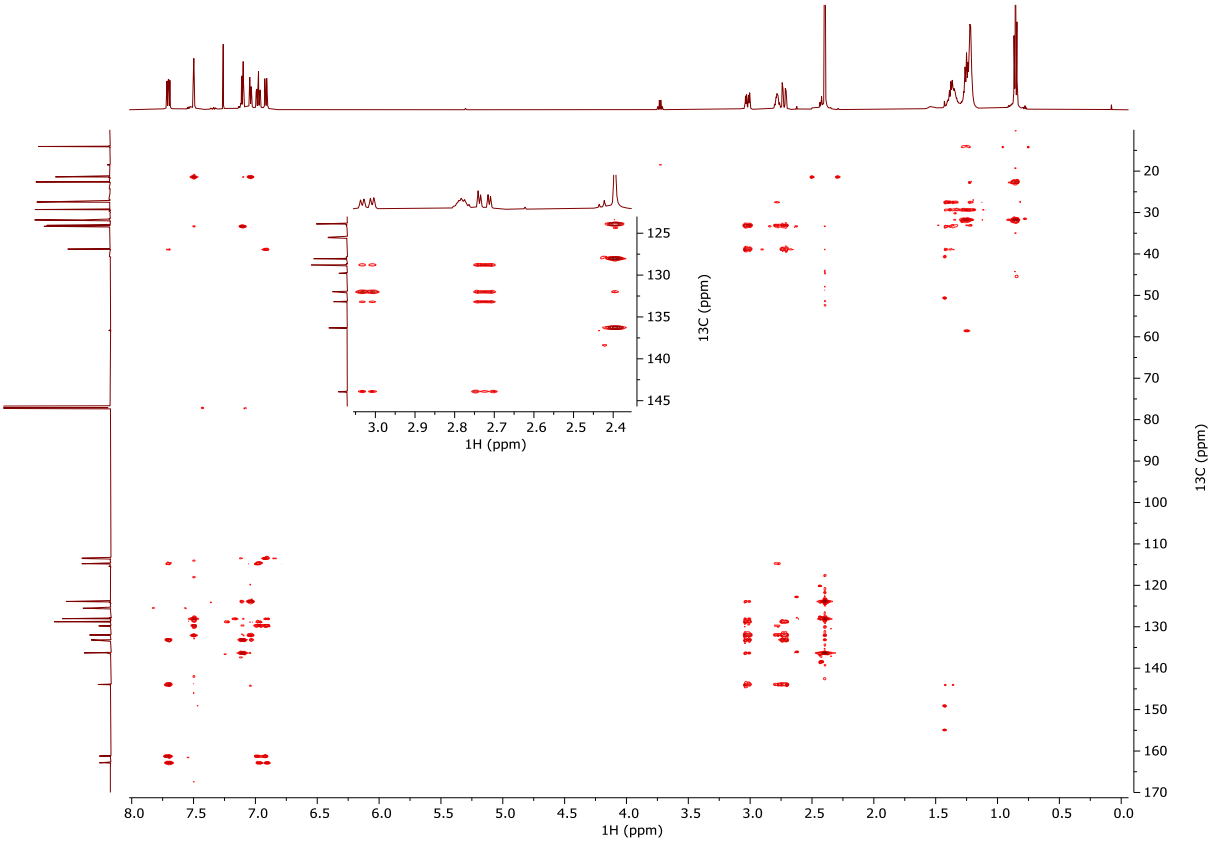

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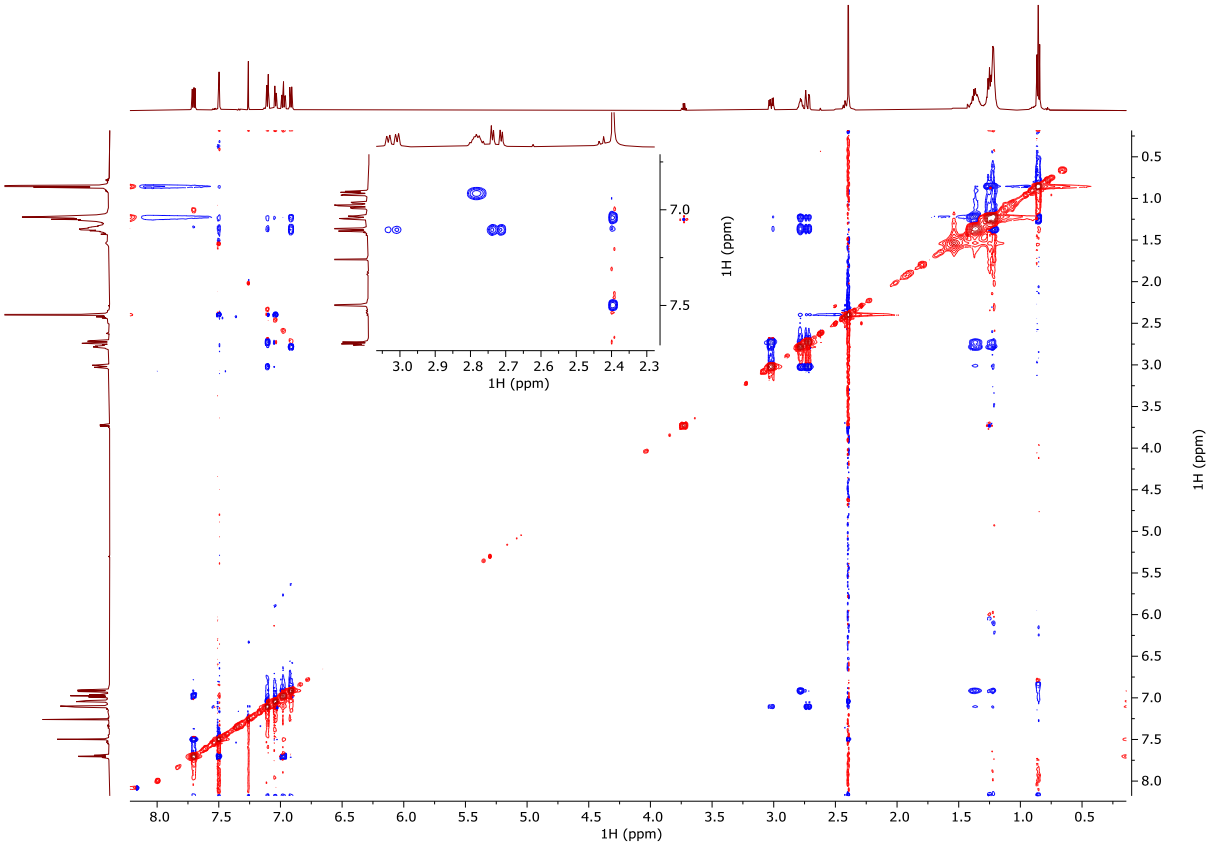
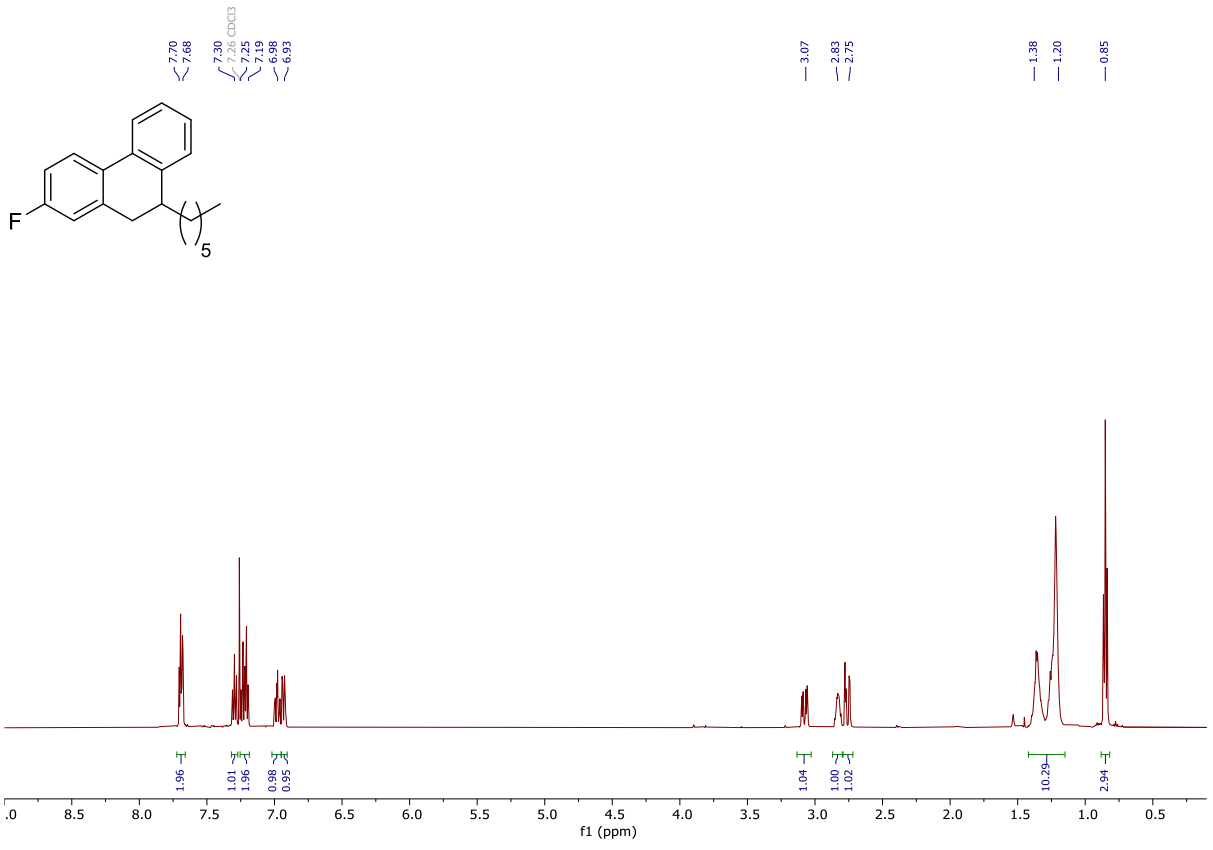
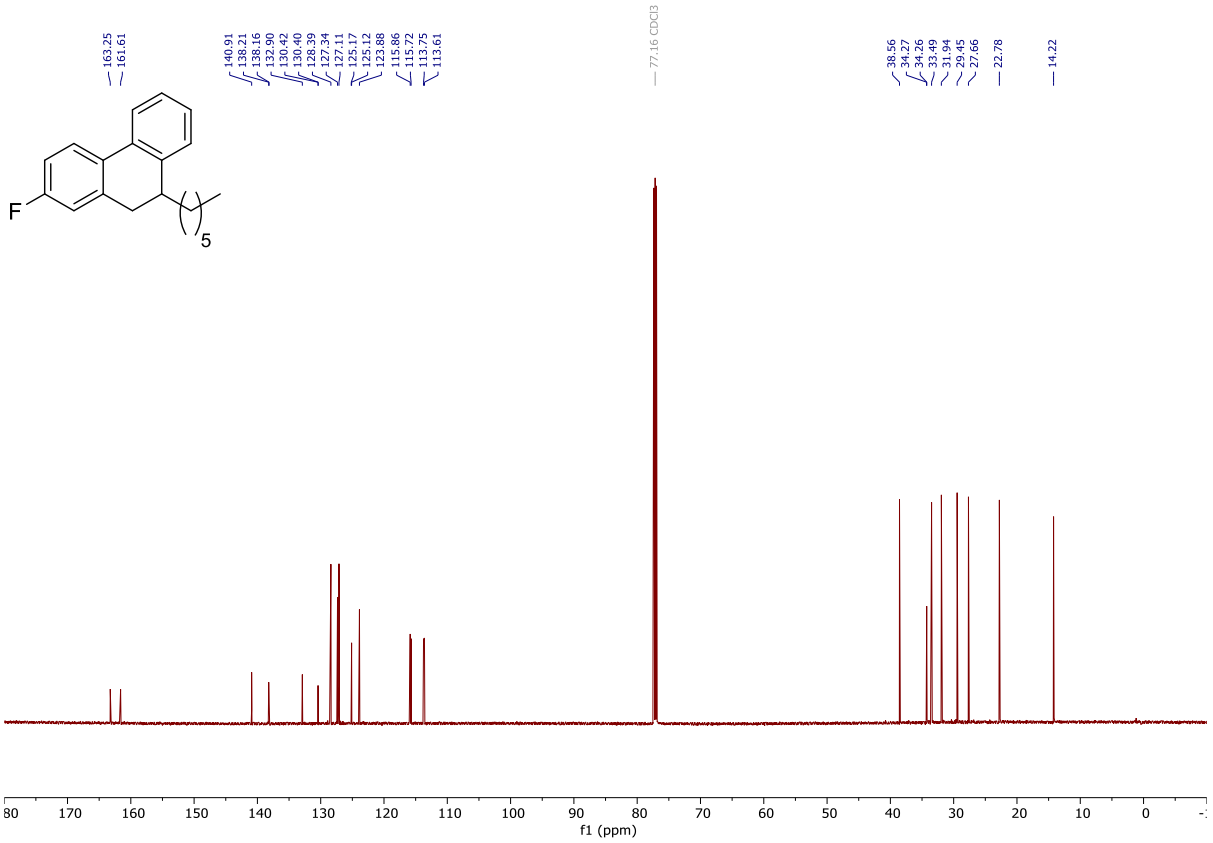


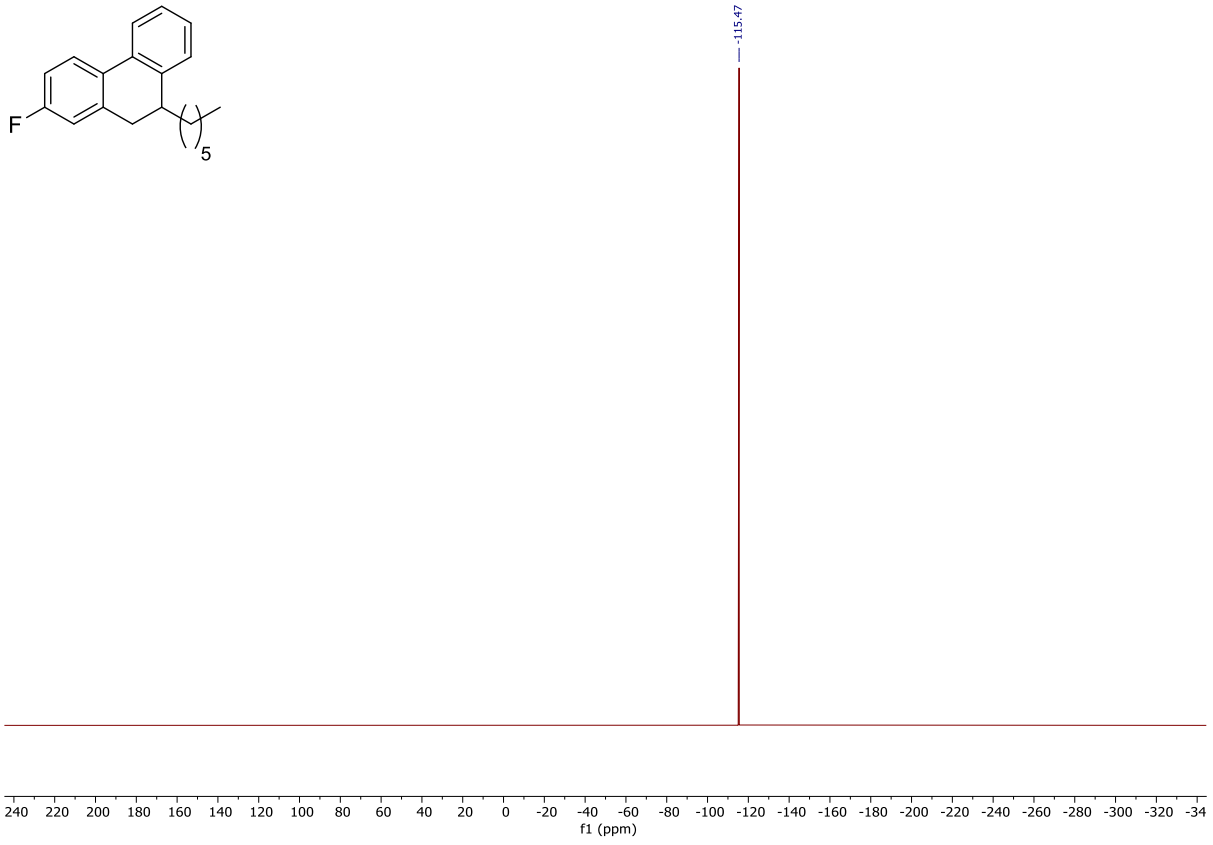
^{1}H NMR, $CDCl_3$, 501 MHz, 2-fluoro-9-hexyl-9,10-dihydrophenanthrene (**3h**)



^{13}C NMR, $CDCl_3$, 126 MHz, 2-fluoro-9-hexyl-9,10-dihydrophenanthrene (**3h**)



^{19}F NMR, $CDCl_3$, 471 MHz, 2-fluoro-9-hexyl-9,10-dihydrophenanthrene (**3h**)



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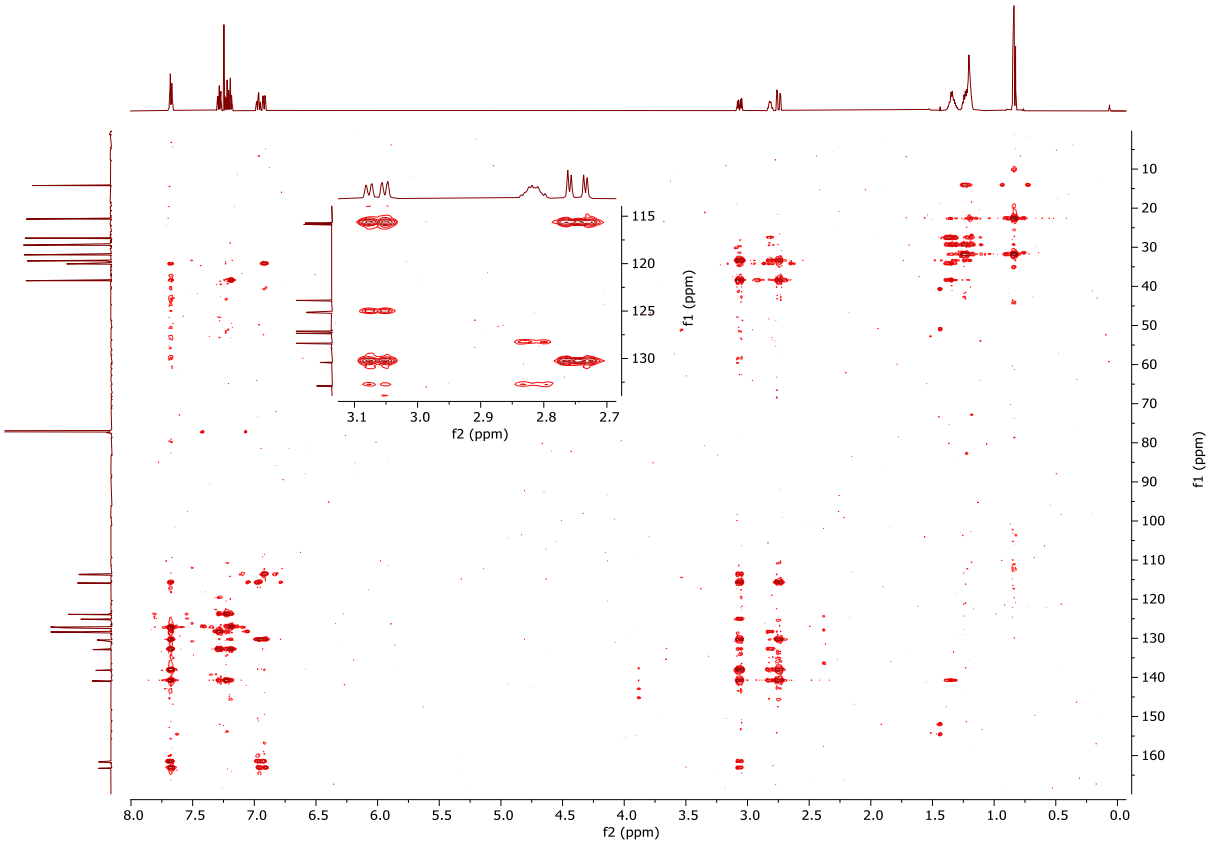
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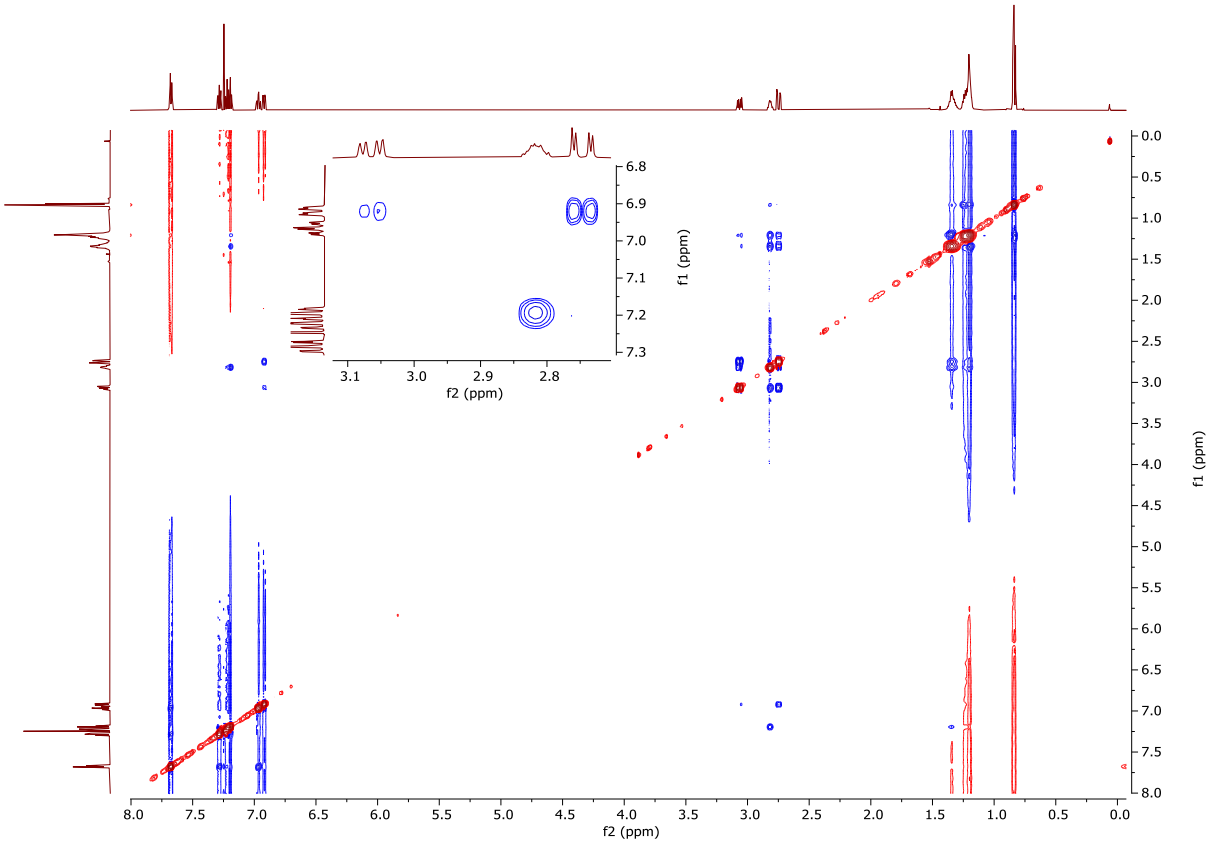
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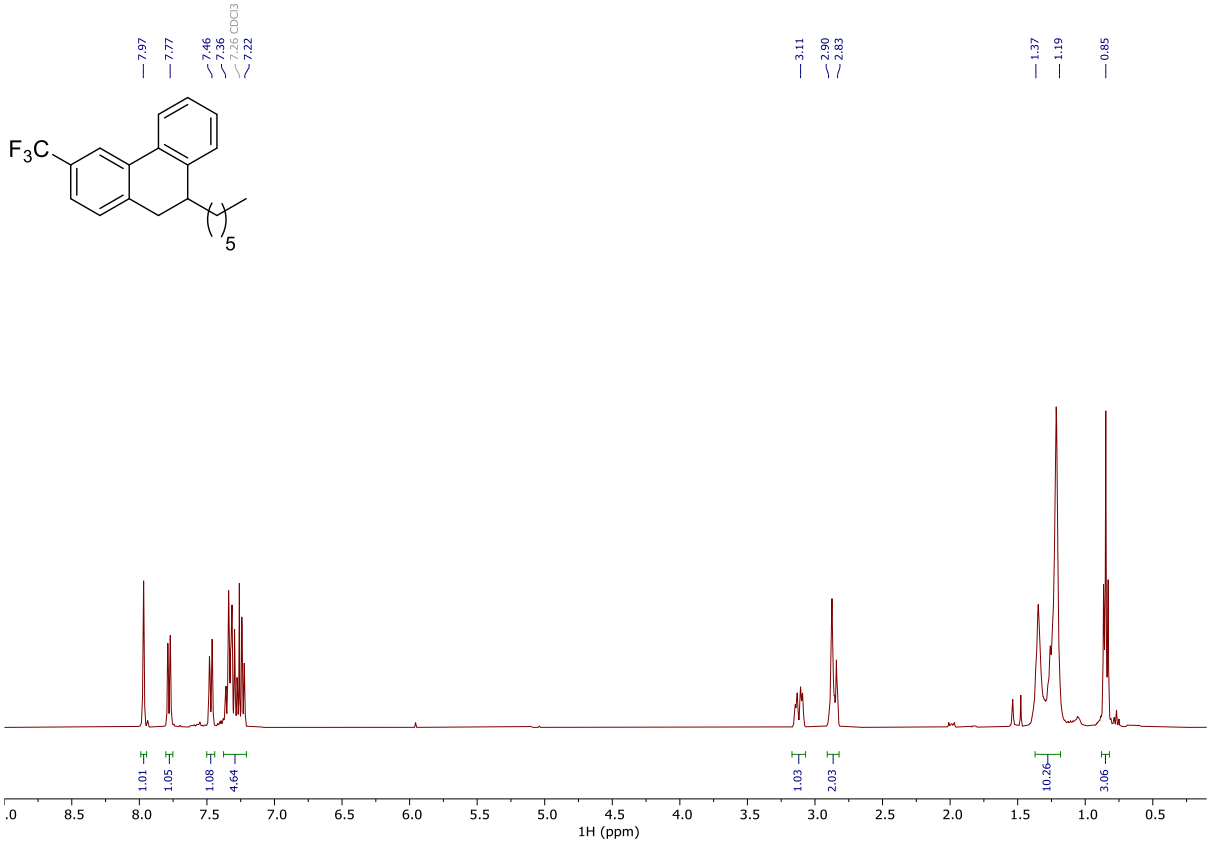
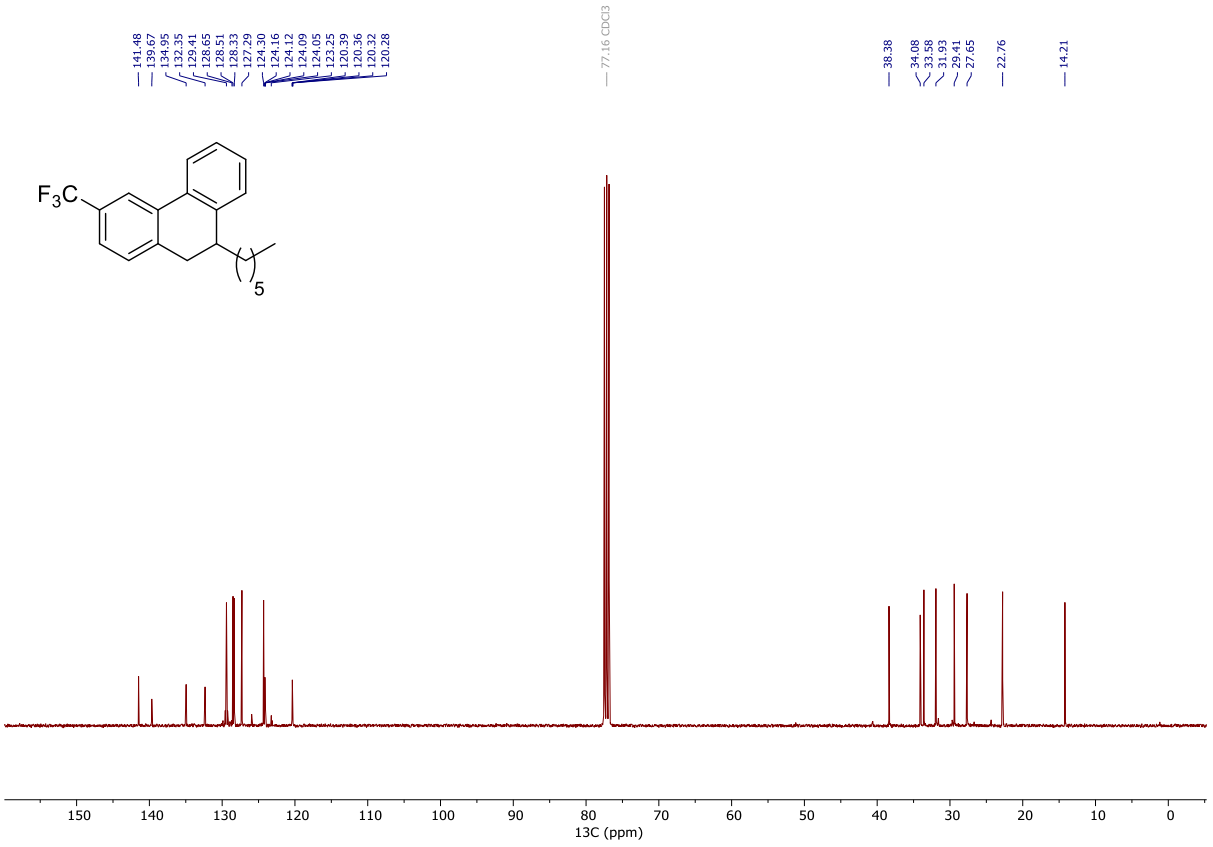
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0
3.1 3.0 2.9 2.8
6.8 6.9 7.0 7.1 7.2 7.3

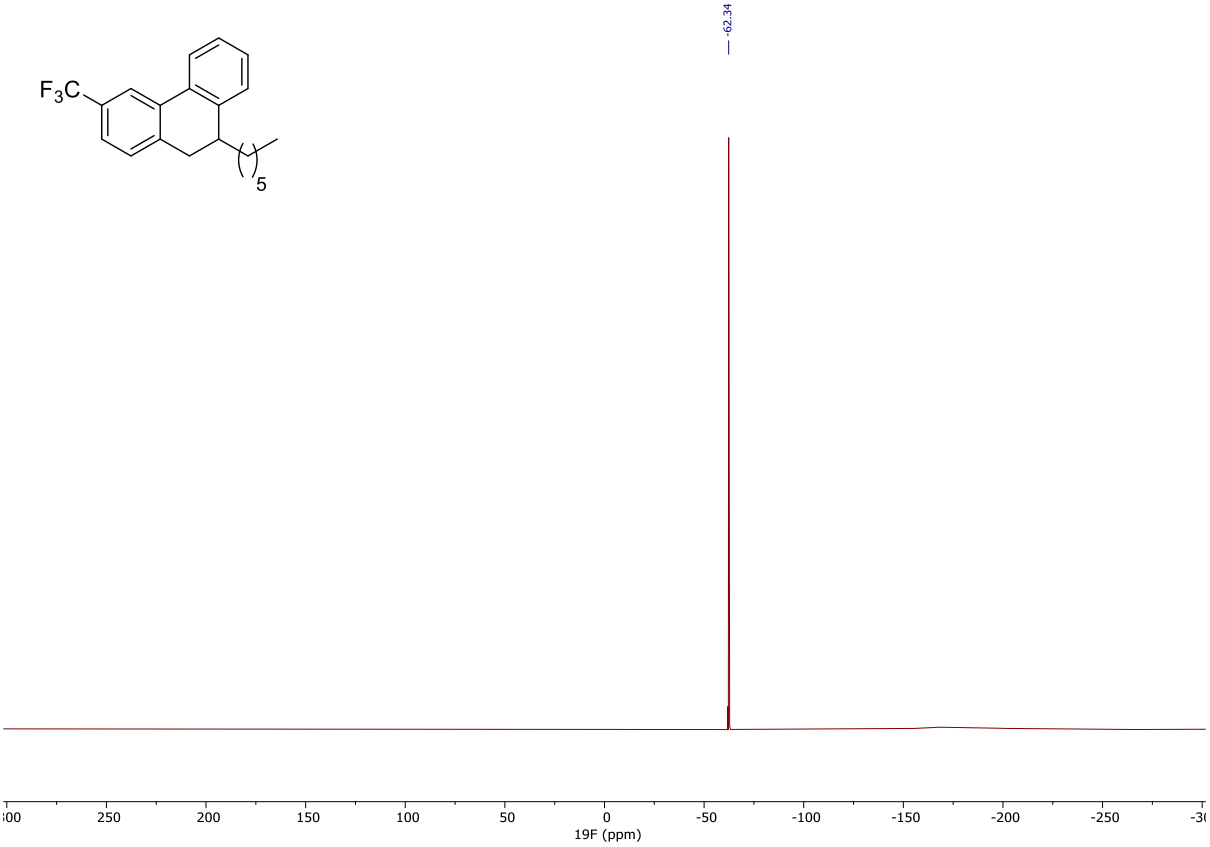
^{1}H NMR, $CDCl_3$, 400 MHz, 9-hexyl-3-(trifluoromethyl)-9,10-dihydrophenanthrene (**3i**)



^{13}C NMR, $CDCl_3$, 101 MHz, 9-hexyl-3-(trifluoromethyl)-9,10-dihydrophenanthrene (**3i**)



^{19}F NMR, $CDCl_3$, 376 MHz, 9-hexyl-3-(trifluoromethyl)-9,10-dihydrophenanthrene (**3i**)



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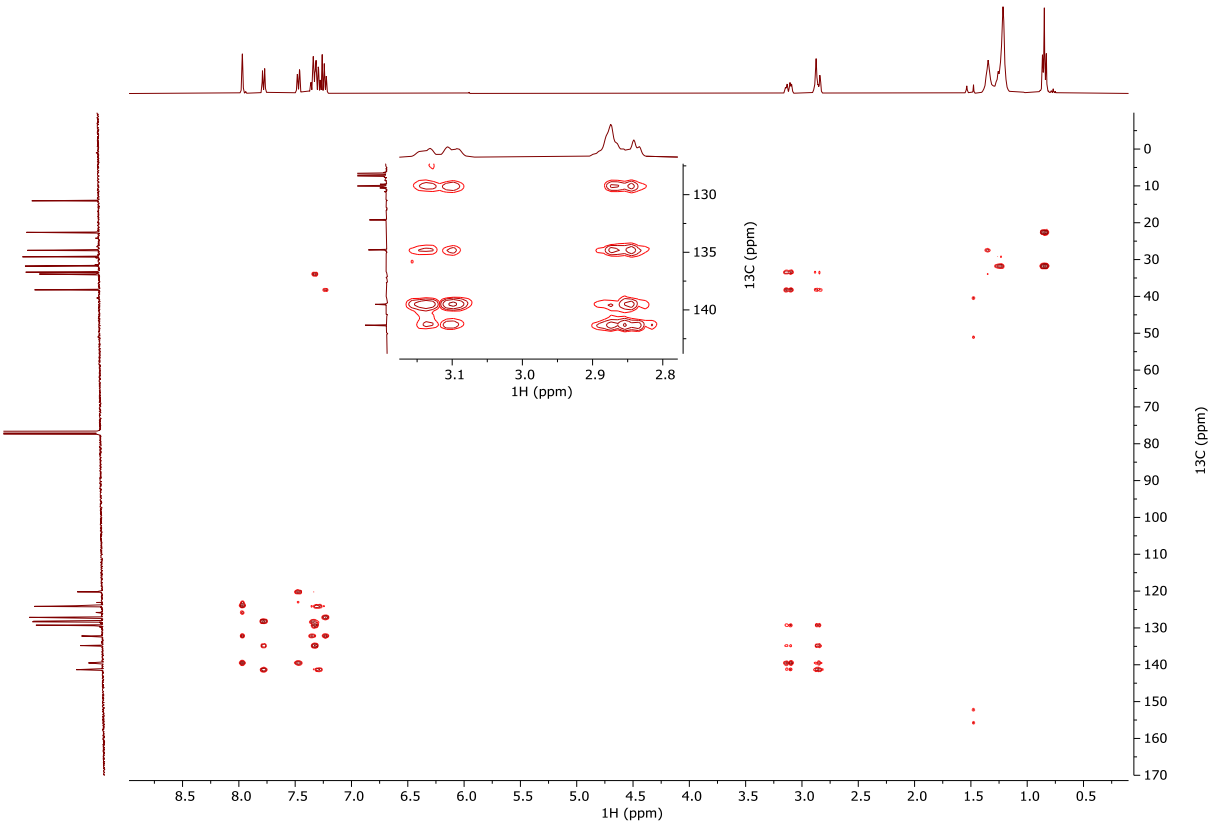
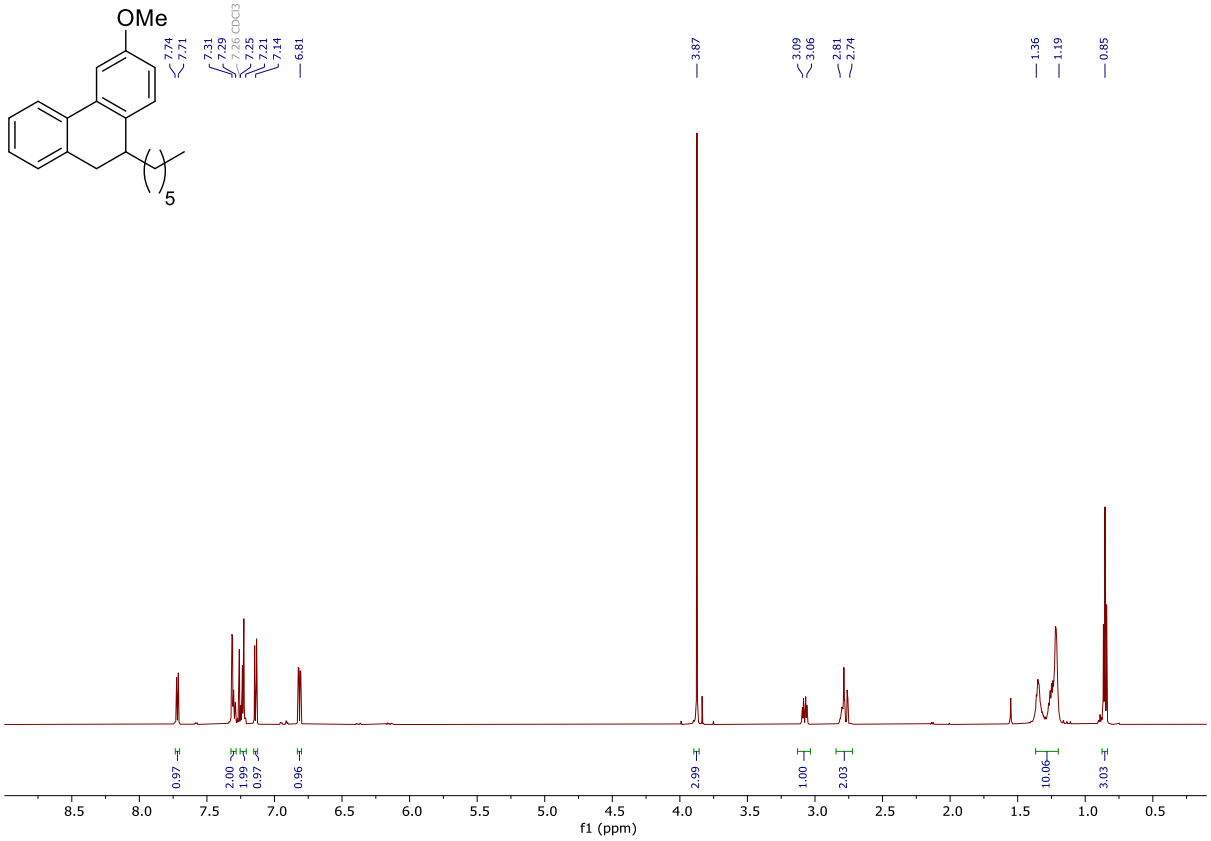
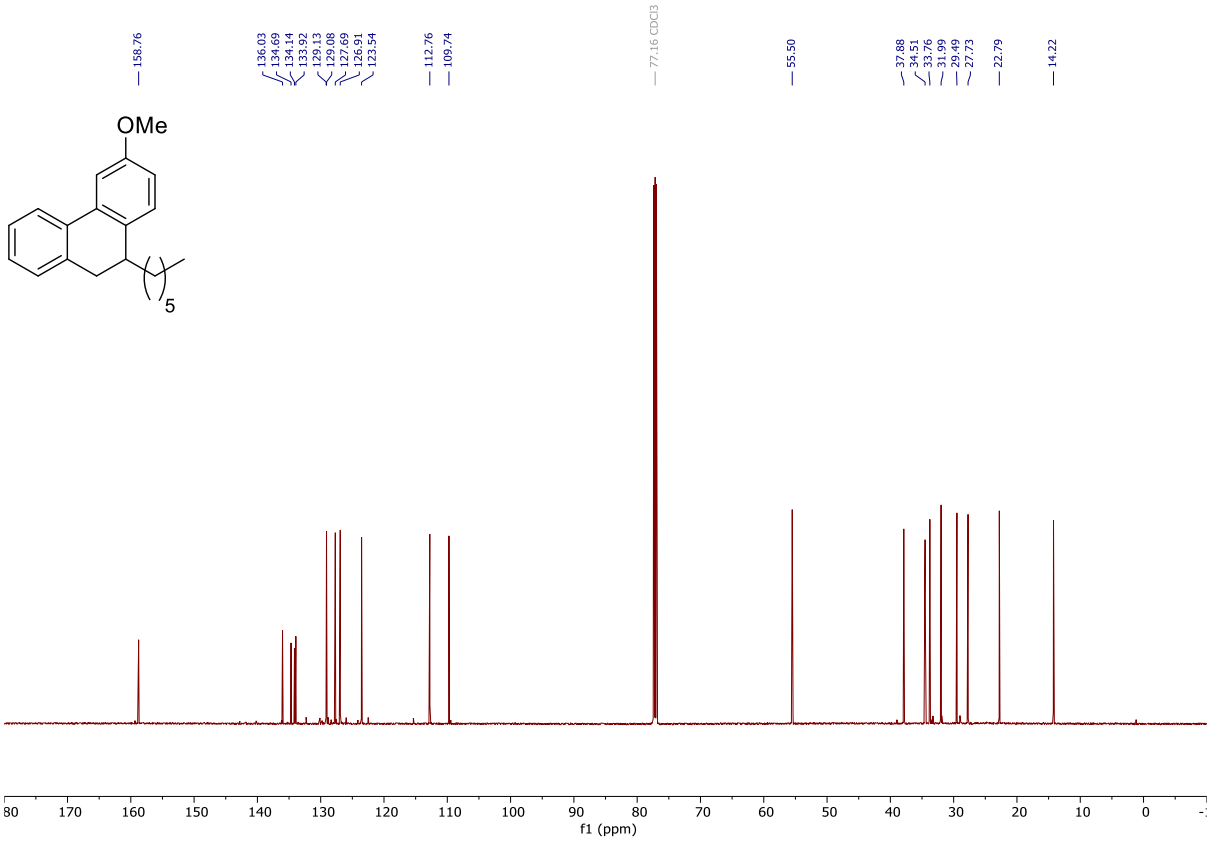


^{1}H NMR, $CDCl_3$, 600 MHz, 10-hexyl-3-methoxy-9,10-dihydrophenanthrene (**3j**)



^{13}C NMR, $CDCl_3$, 151 MHz, 10-hexyl-3-methoxy-9,10-dihydrophenanthrene (**3j**)



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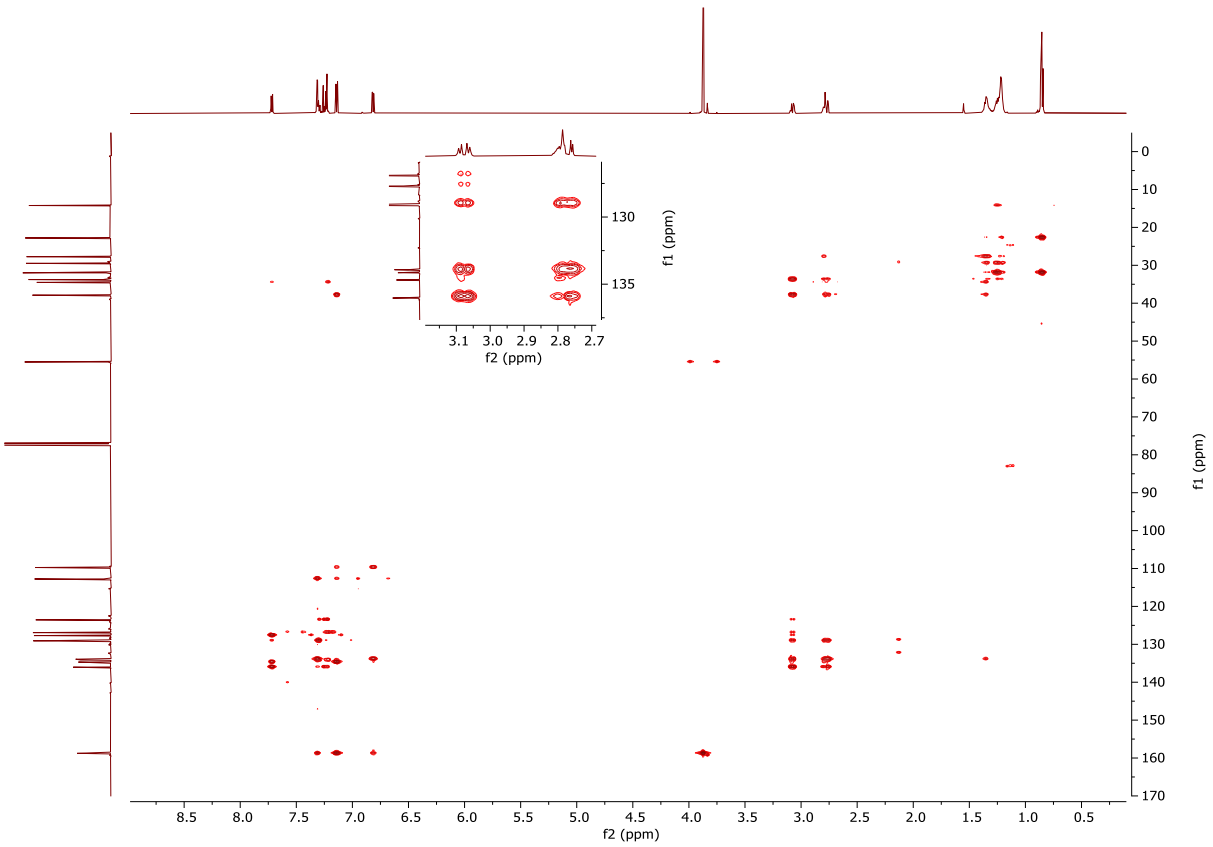

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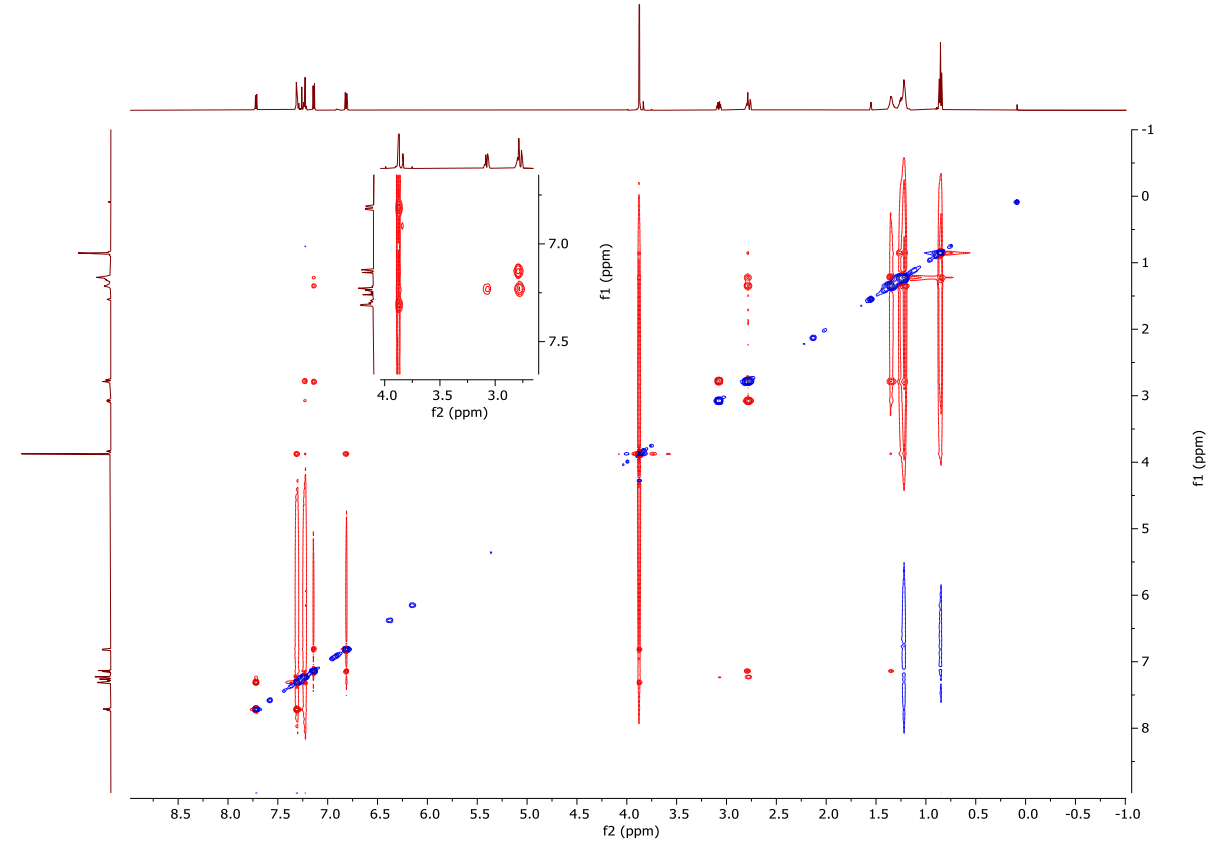
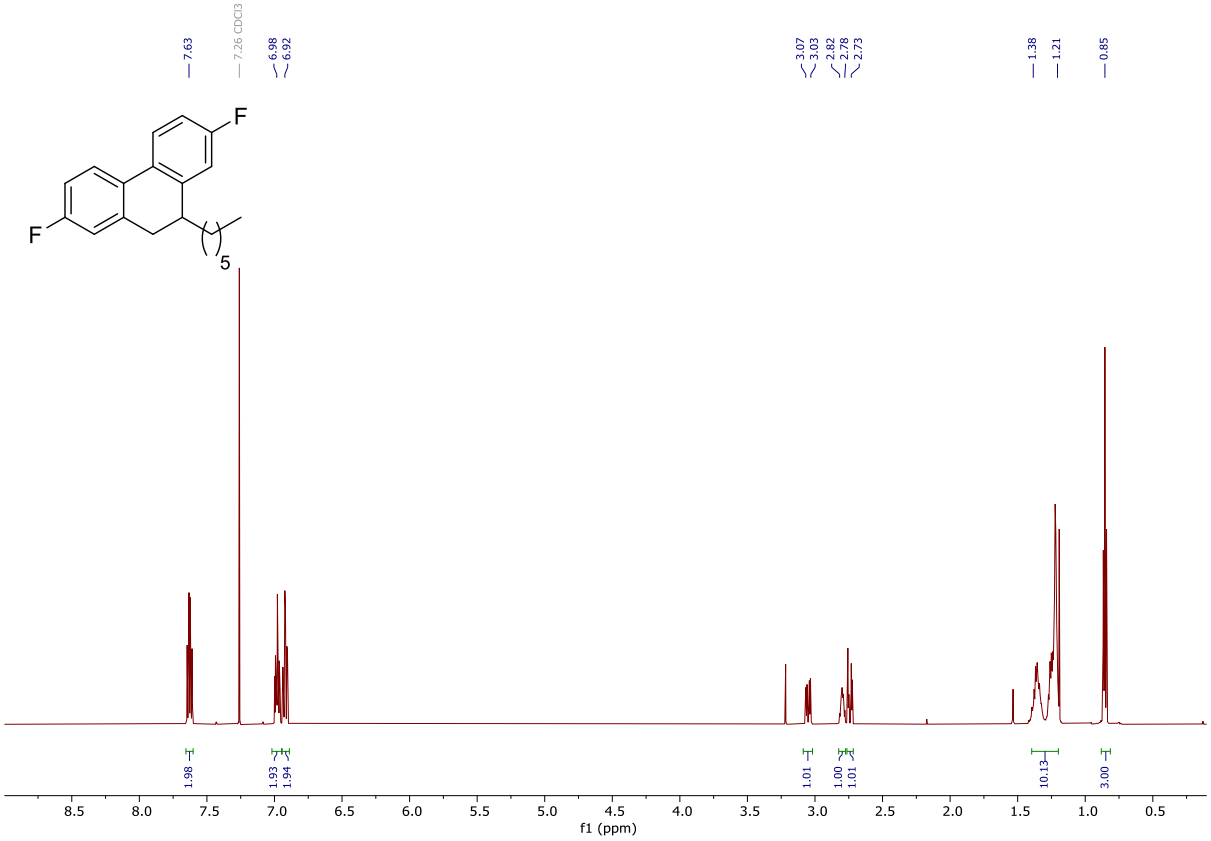
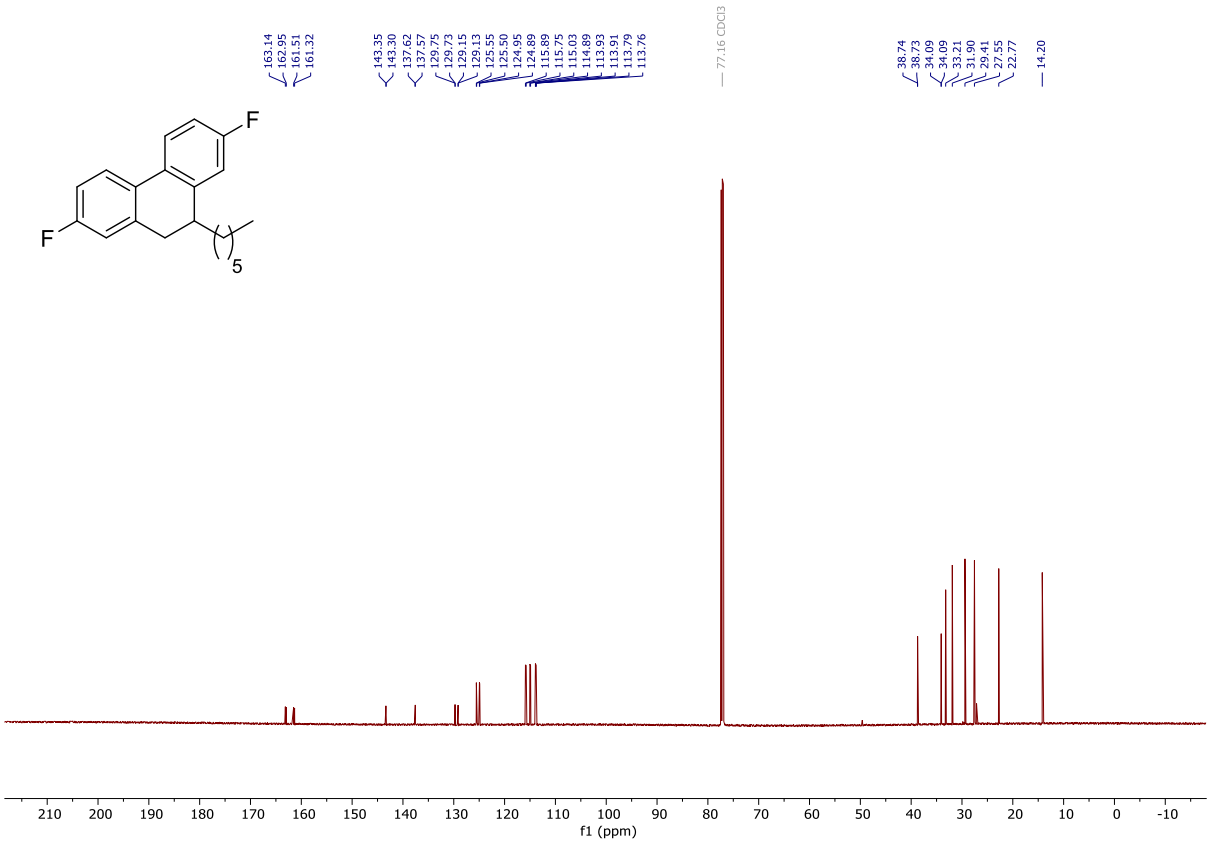


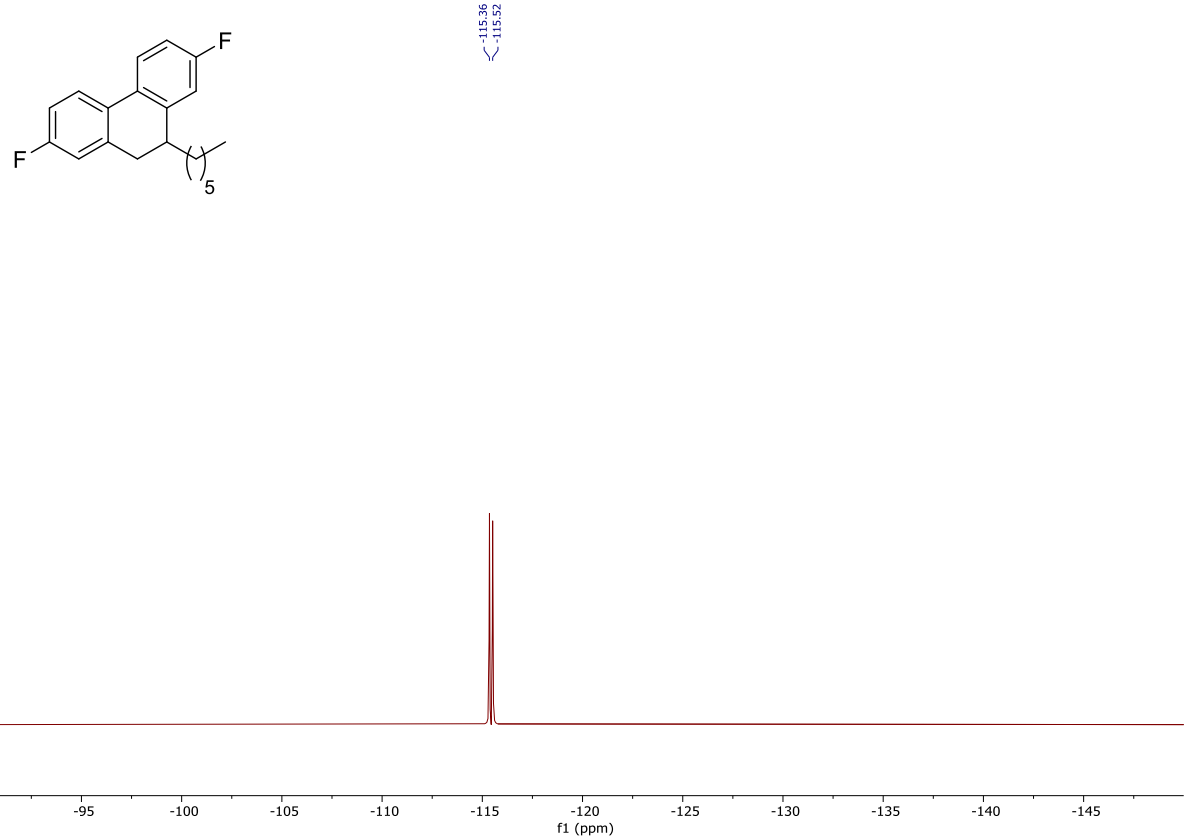
^{1}H NMR, $CDCl_3$, 600 MHz, 2,7-difluoro-9-hexyl-9,10-dihydrophenanthrene (**3k**)



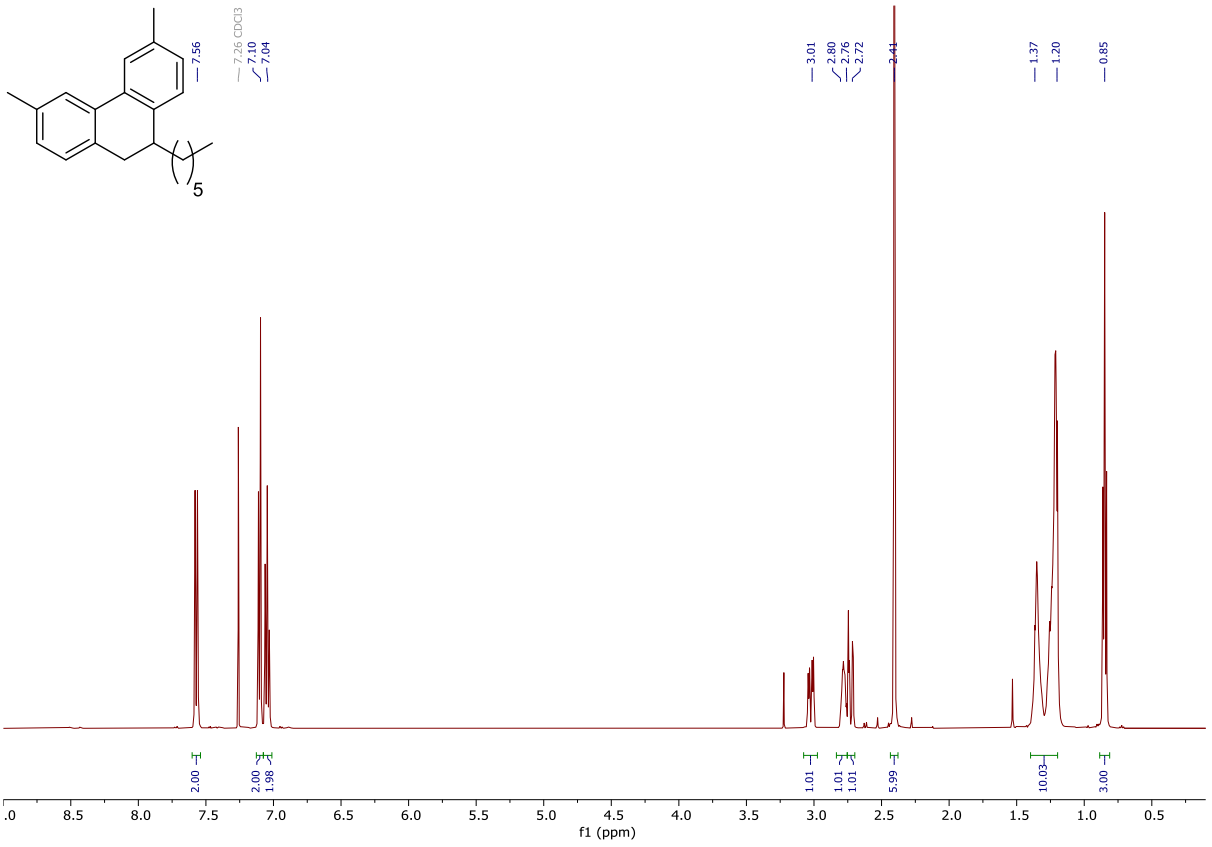
^{13}C NMR, $CDCl_3$, 151 MHz, 2,7-difluoro-9-hexyl-9,10-dihydrophenanthrene (**3k**)



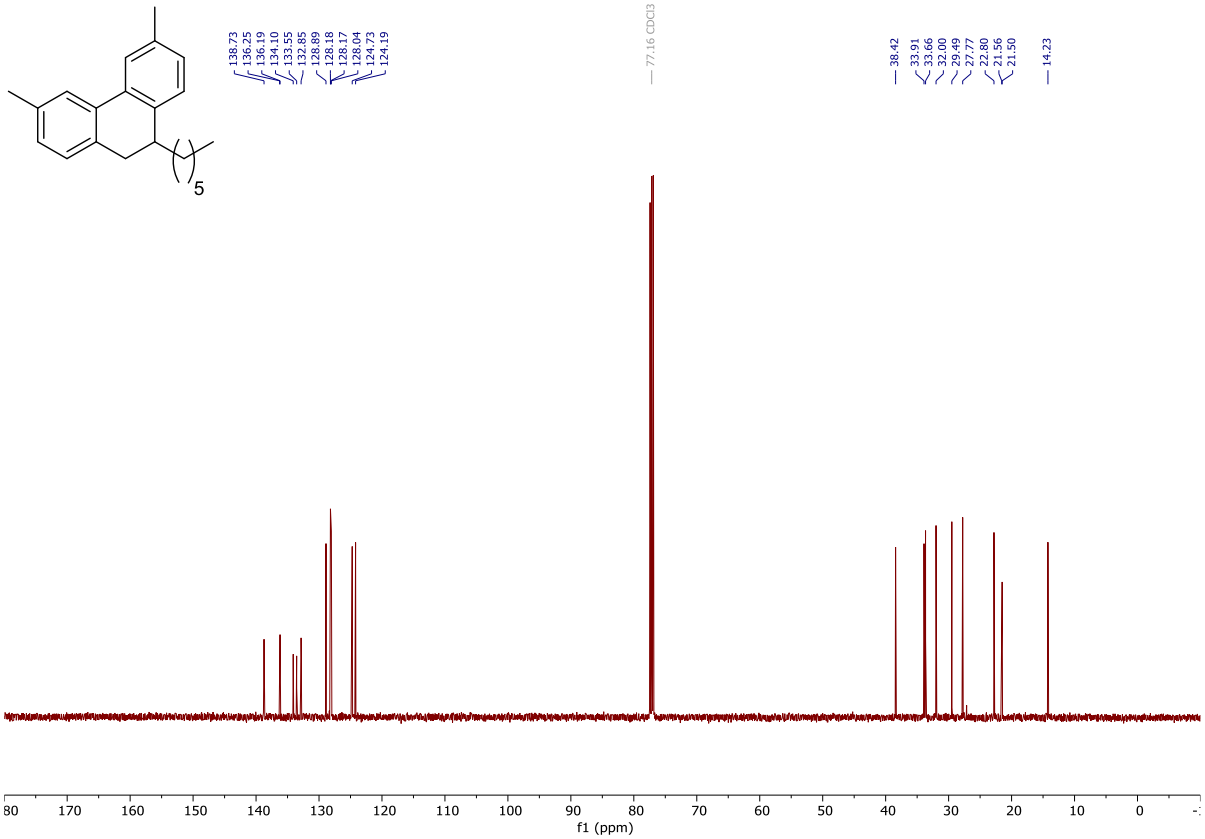
^{19}F NMR, $CDCl_3$, 565 MHz, 2,7-difluoro-9-hexyl-9,10-dihydrophenanthrene (**3k**)



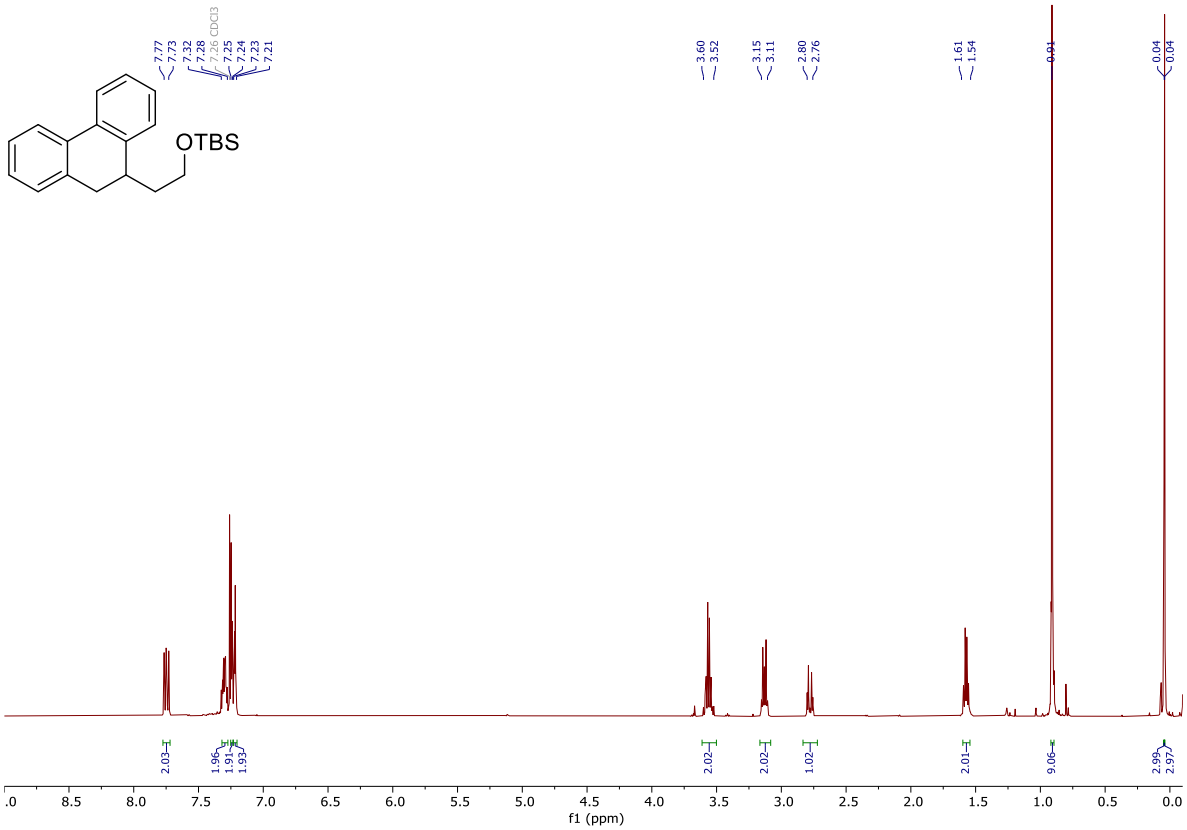
^{1}H NMR, $CDCl_3$, 600 MHz, 9-hexyl-3,6-dimethyl-9,10-dihydrophenanthrene (**3l**)



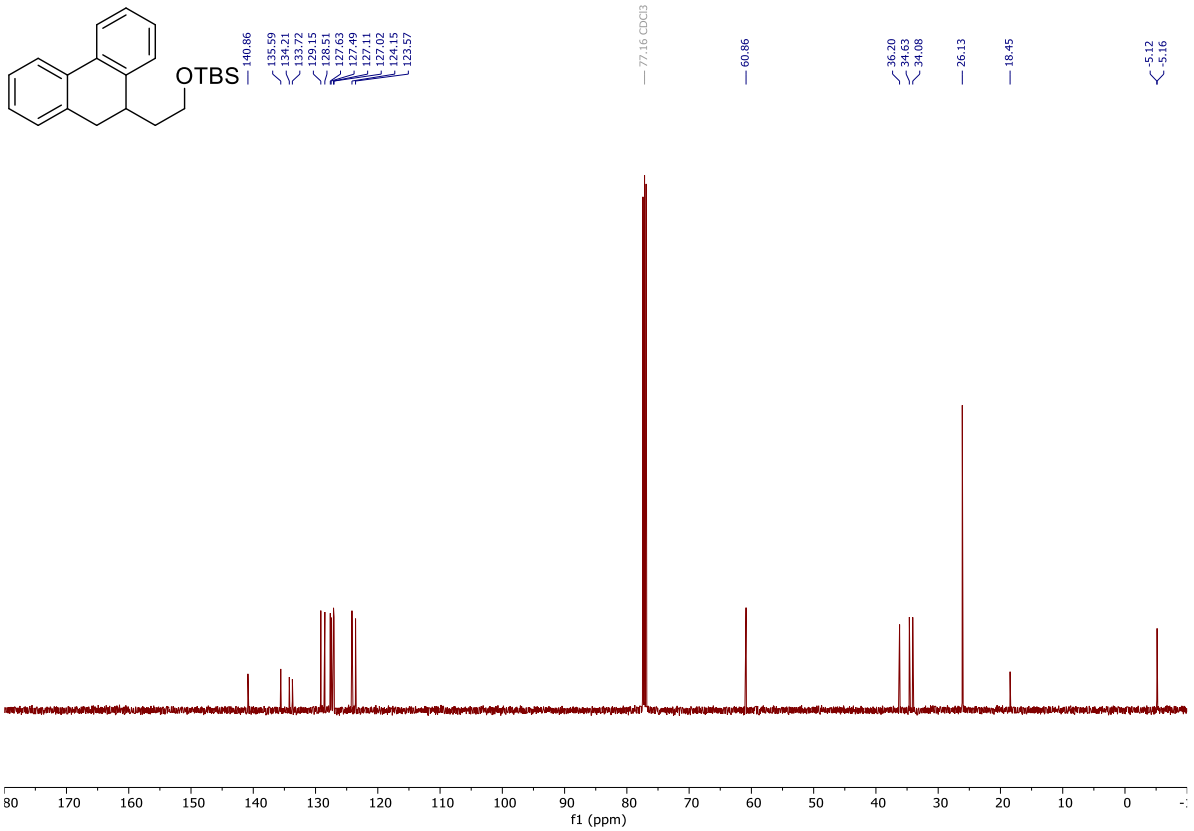
^{13}C NMR, $CDCl_3$, 151 MHz, 9-hexyl-3,6-dimethyl-9,10-dihydrophenanthrene (**3l**)



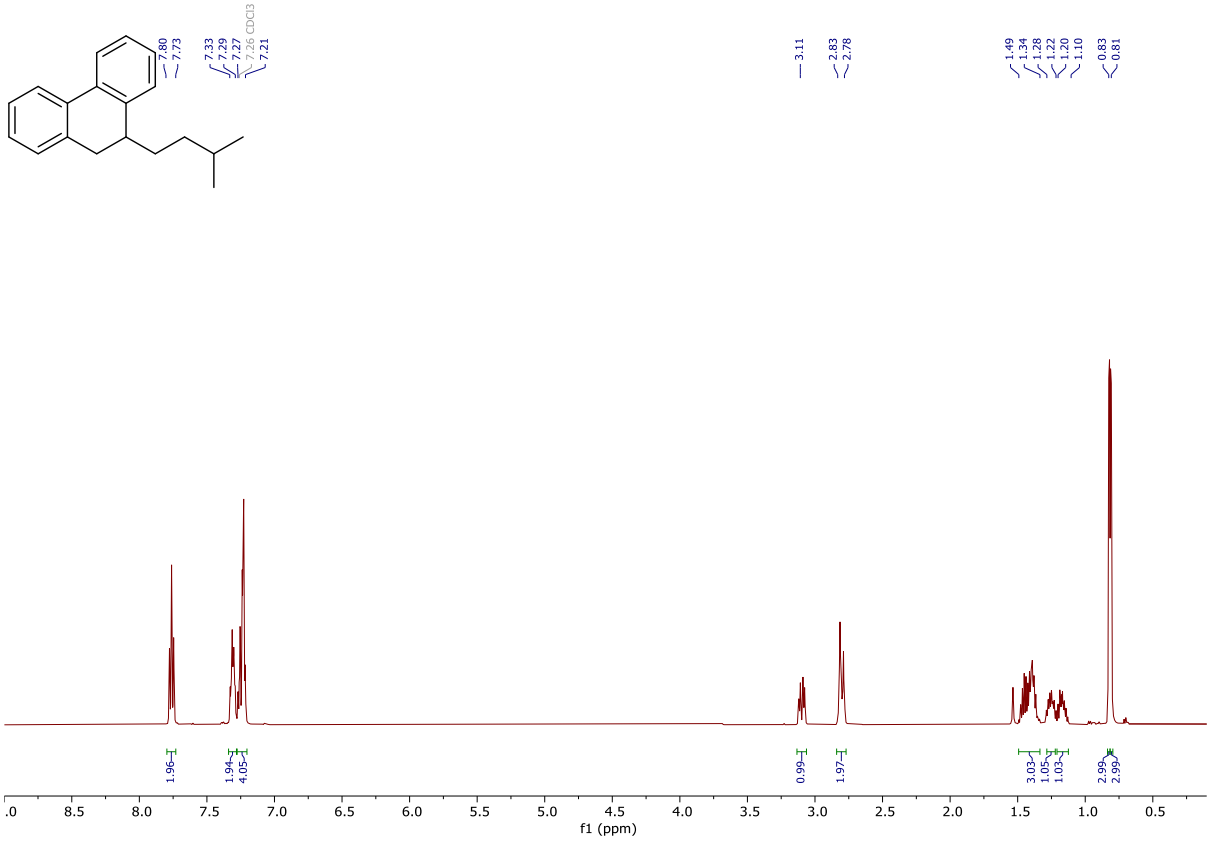
^{1}H NMR, $CDCl_3$, 600 MHz, *tert*-butyl (2-(9,10-dihydrophenanthren-9-yl)ethoxy) dimethyl-silane (**3m**)



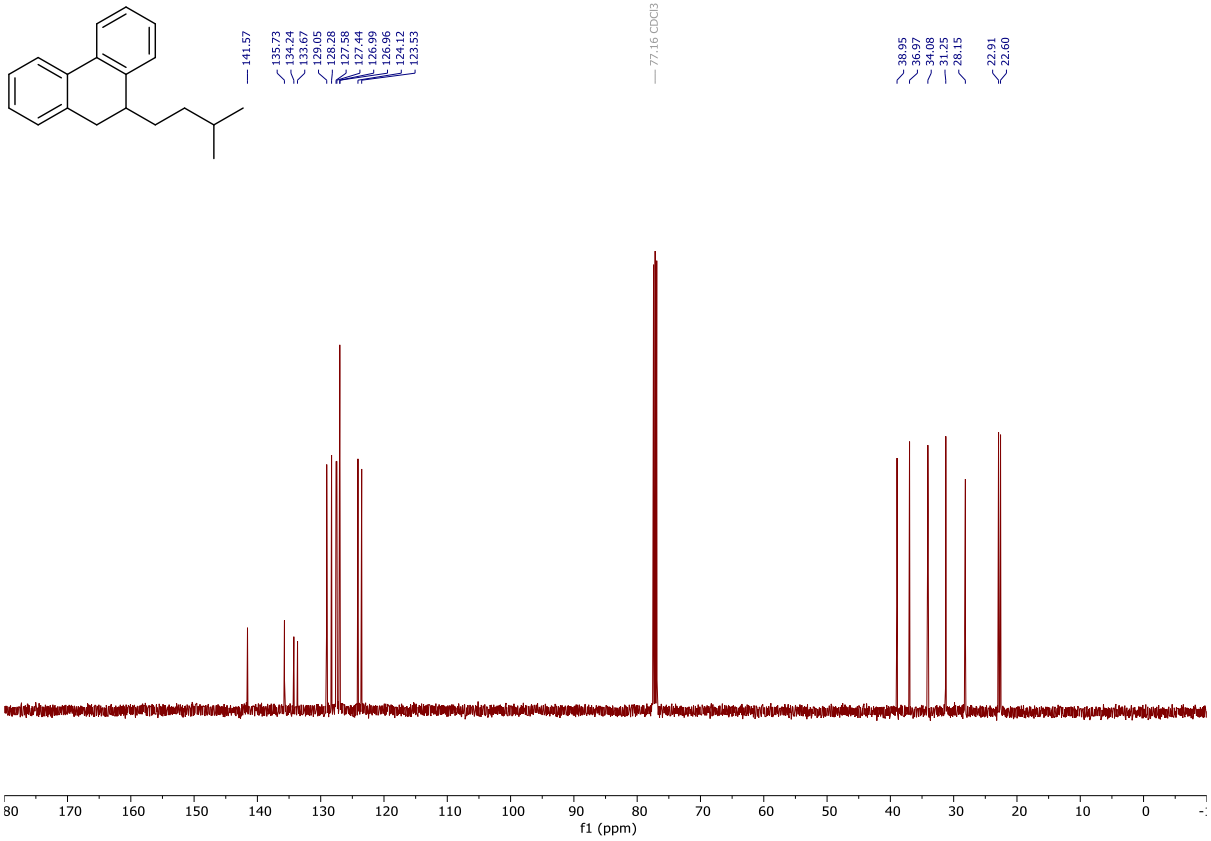
^{13}C NMR, $CDCl_3$, 151 MHz, *tert*-butyl (2-(9,10-dihydrophenanthren-9-yl)ethoxy) dimethyl-silane (**3m**)



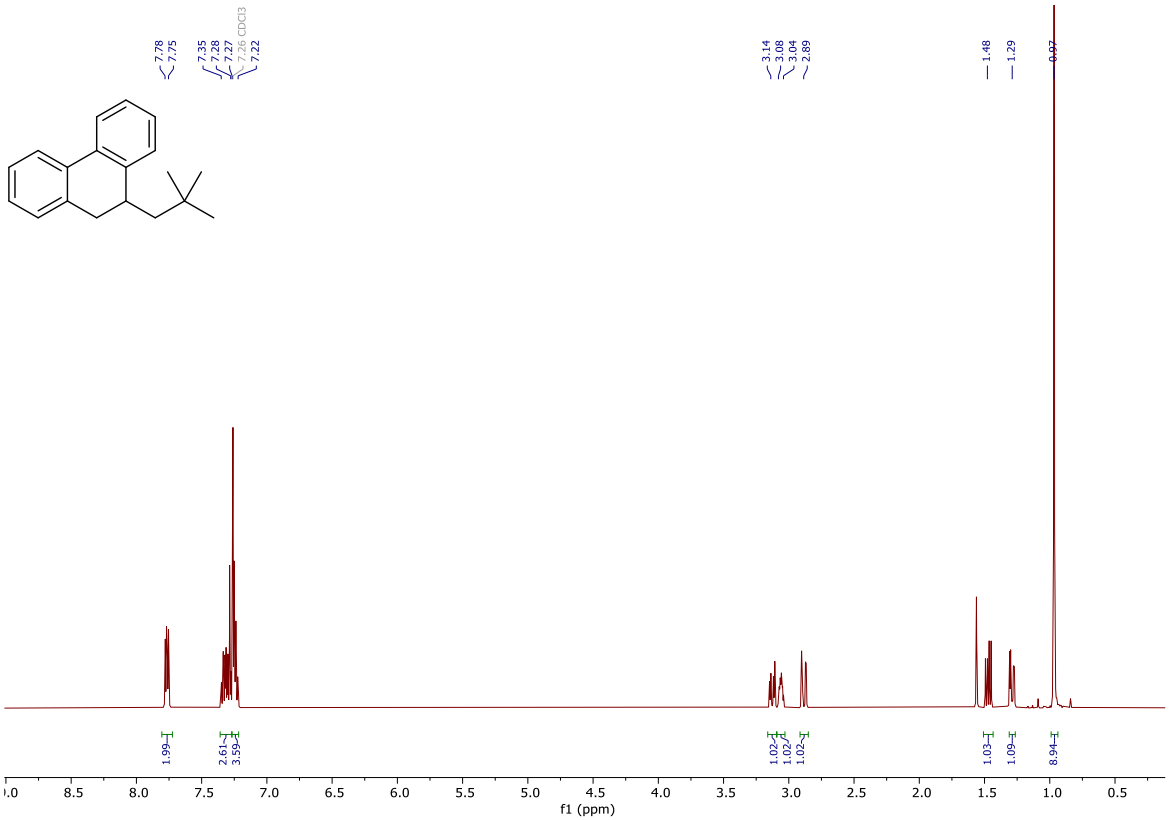
^{1}H NMR, $CDCl_3$, 501 MHz, 9-isopentyl-9,10-dihydrophenanthrene (**3n**)



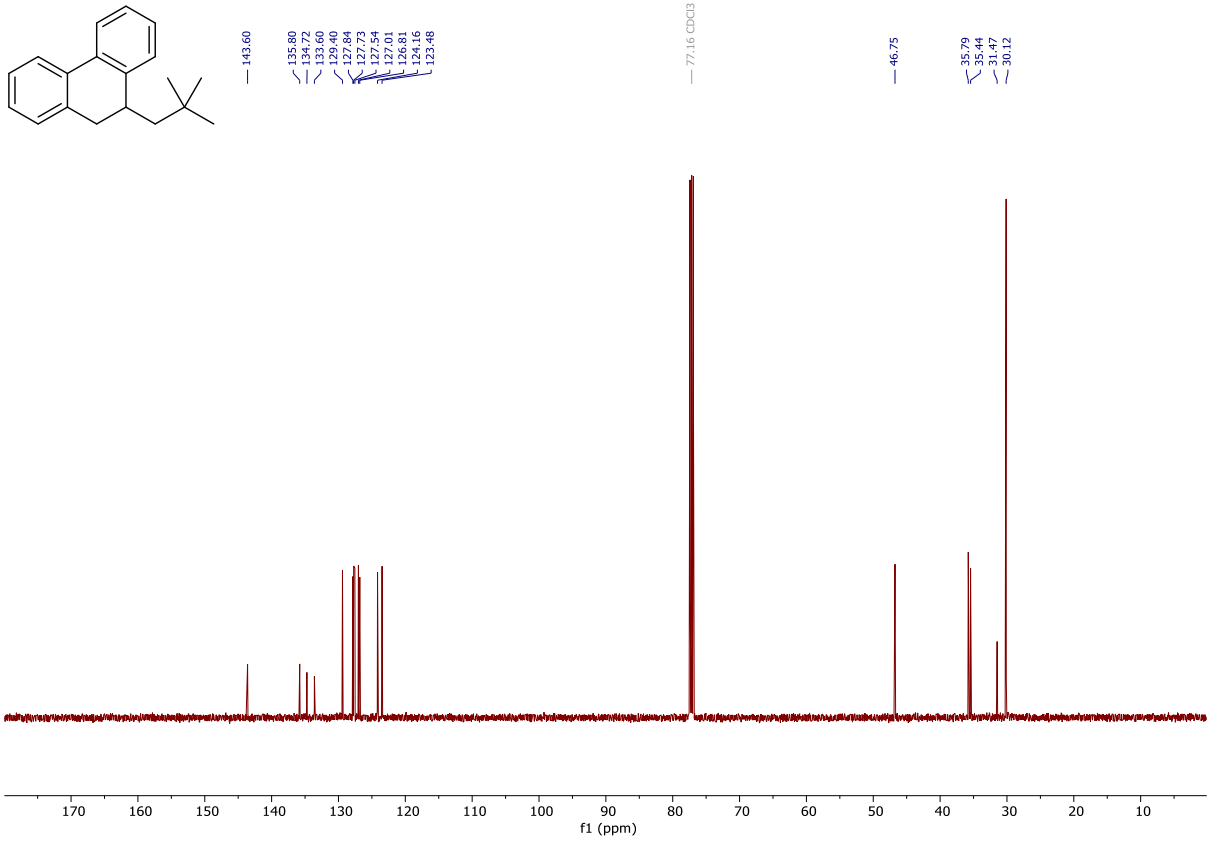
^{13}C NMR, $CDCl_3$, 126 MHz, 9-isopentyl-9,10-dihydrophenanthrene (**3n**)



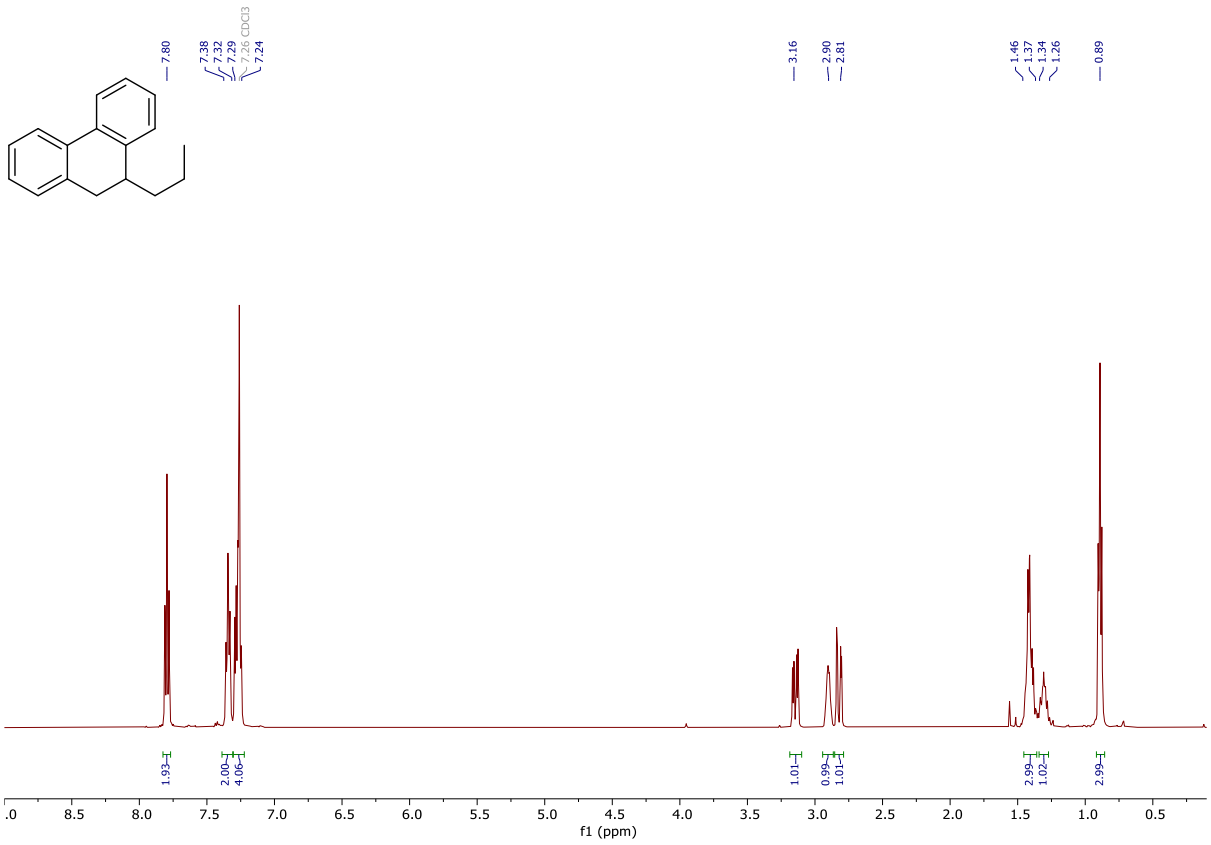
^{1}H NMR, $CDCl_3$, 501 MHz, 9-neopentyl-9,10-dihydrophenanthrene (**3o**)



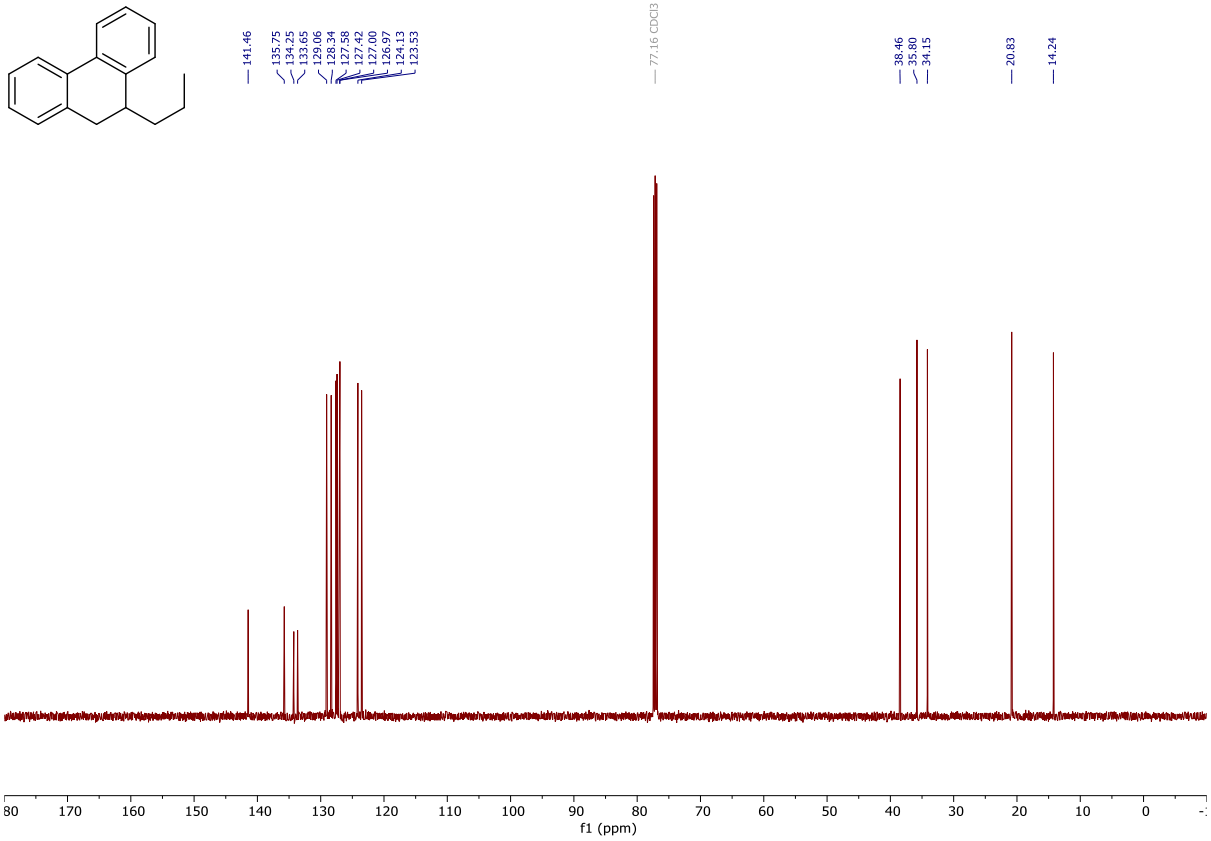
^{13}C NMR, $CDCl_3$, 126 MHz, 9-neopentyl-9,10-dihydrophenanthrene (**3o**)



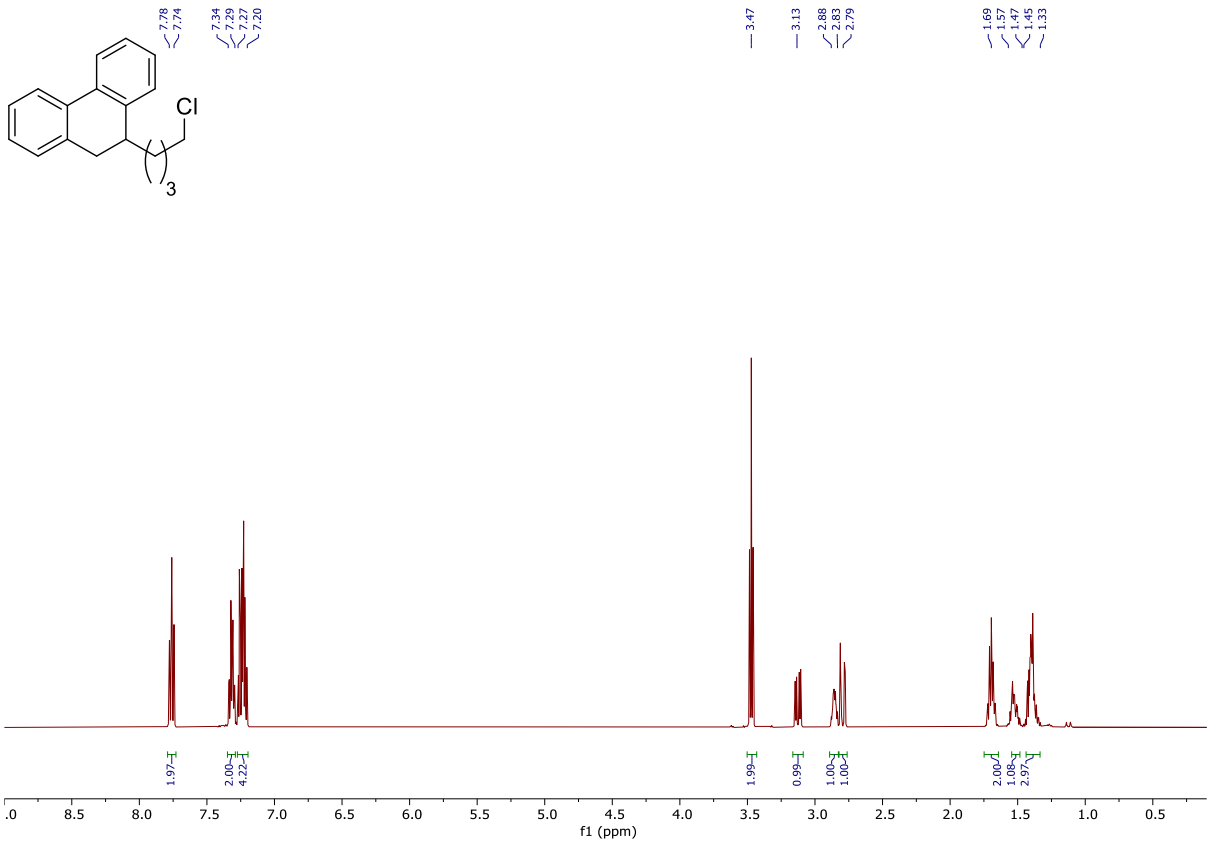
^{1}H NMR, $CDCl_3$, 501 MHz, 9-propyl-9,10-dihydrophenanthrene (**3p**)



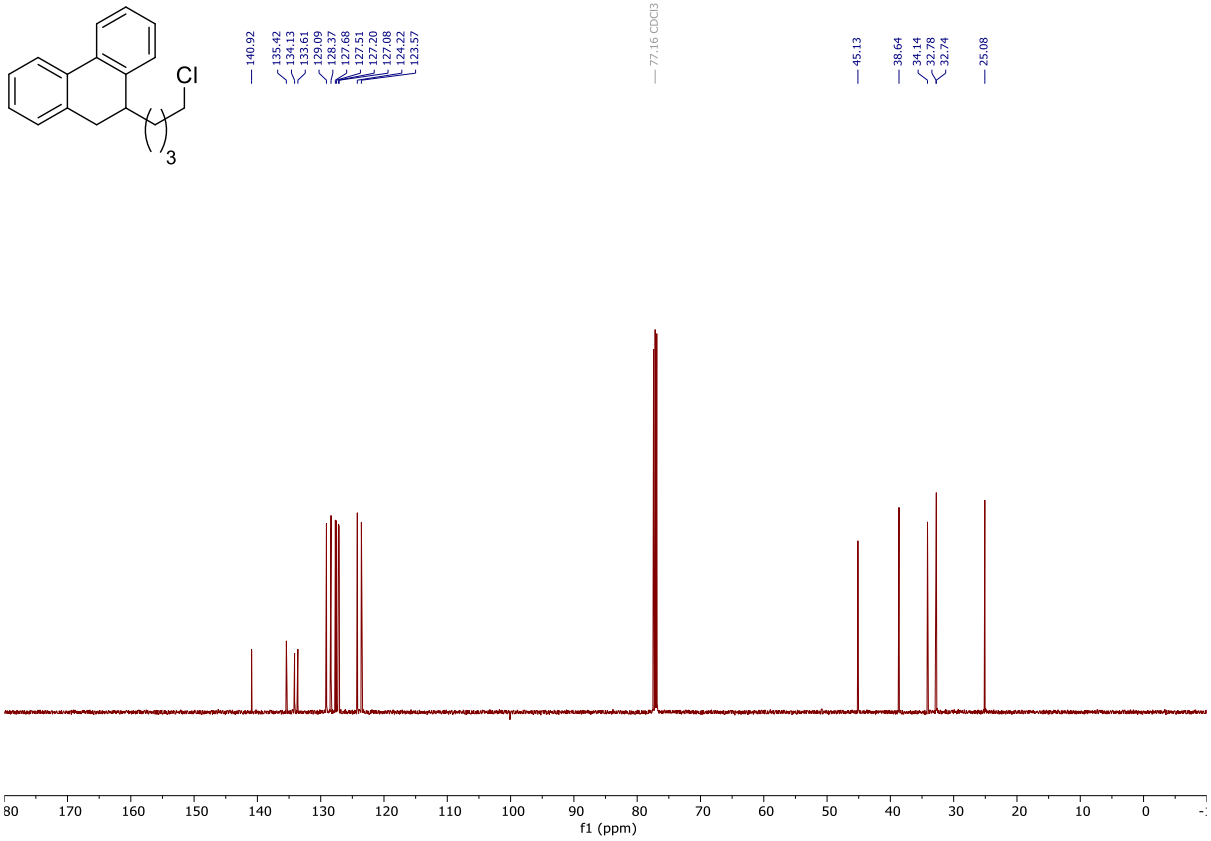
^{13}C NMR, $CDCl_3$, 126 MHz, 9-propyl-9,10-dihydrophenanthrene (**3p**)



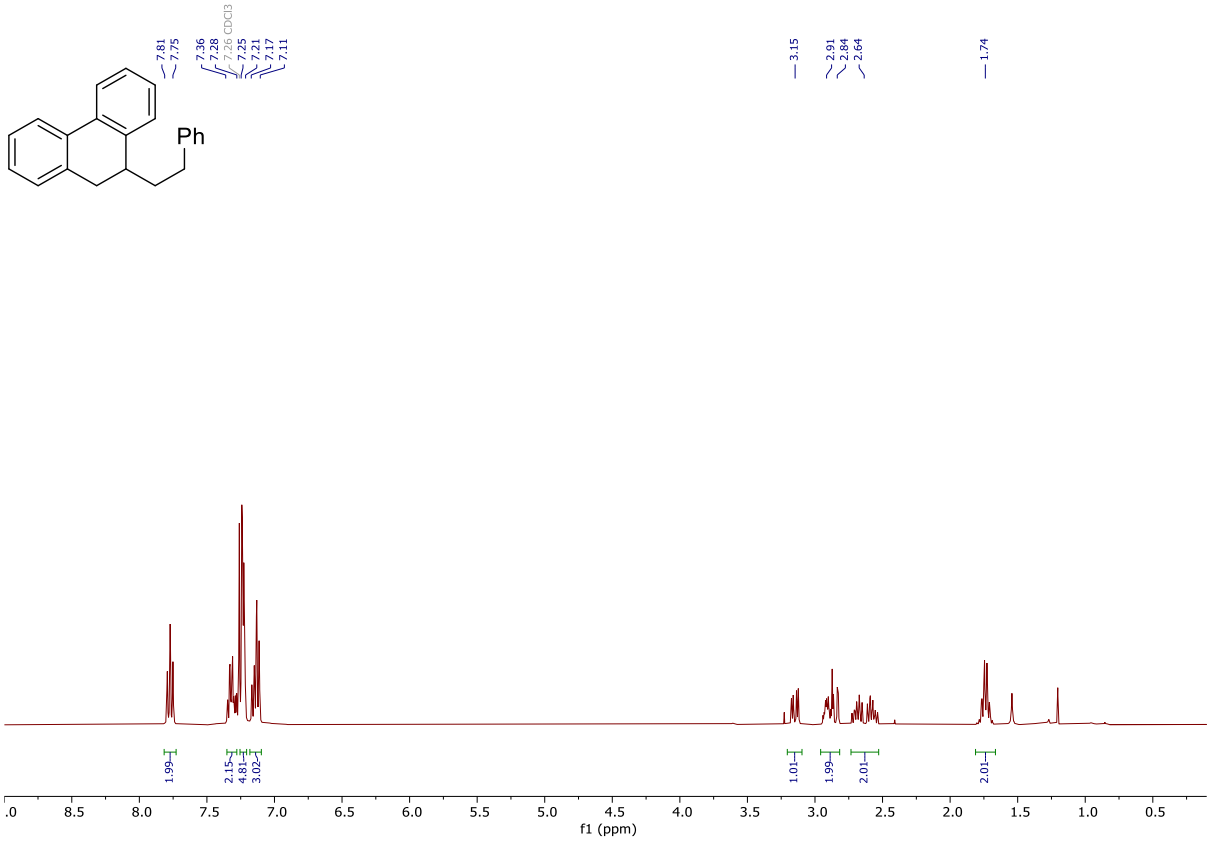
^{1}H NMR, $CDCl_3$, 501 MHz, 9-propyl-9,10-dihydrophenanthrene (**3q**)



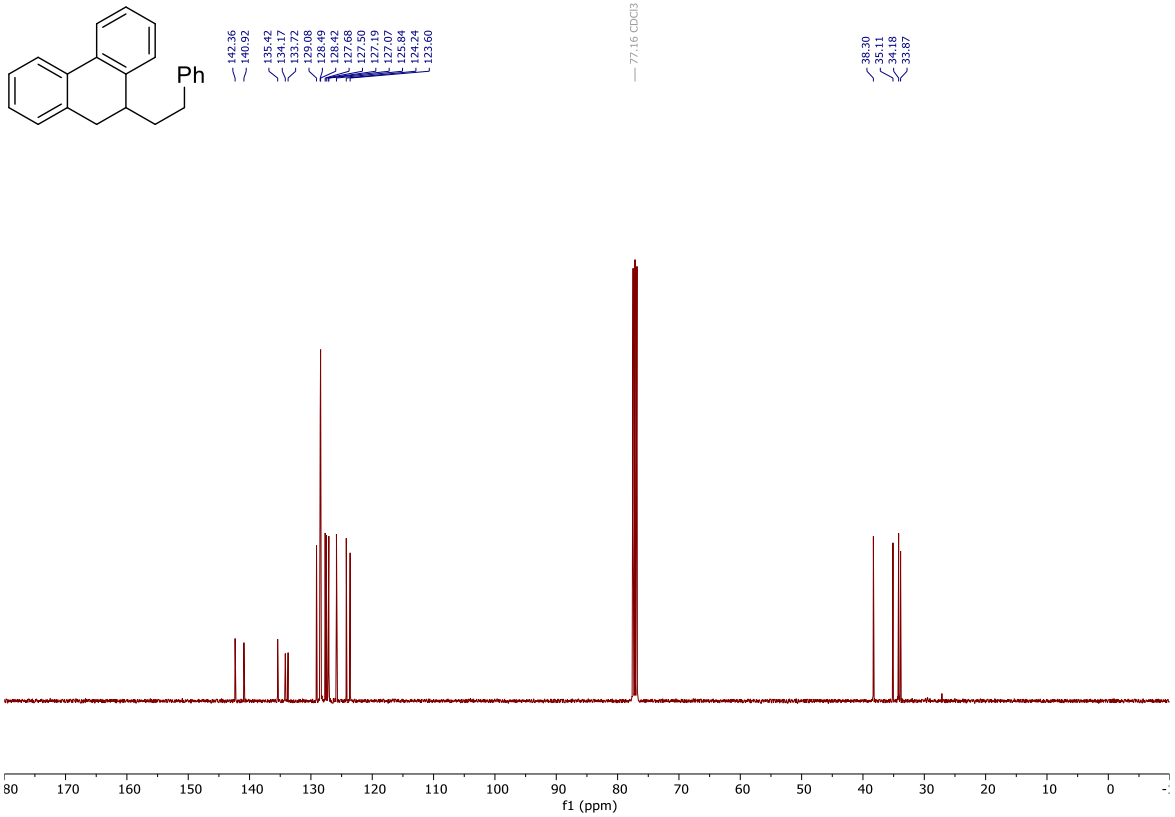
^{13}C NMR, $CDCl_3$, 126 MHz, 9-propyl-9,10-dihydrophenanthrene (**3q**)



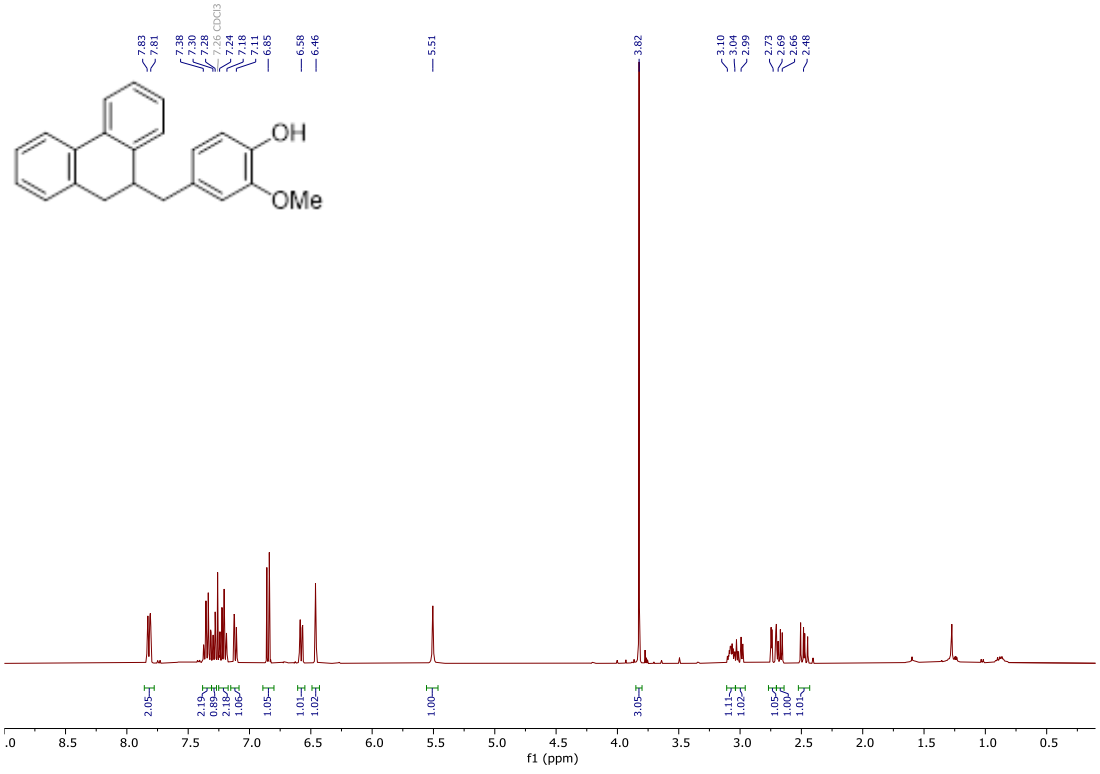
^{1}H NMR, $CDCl_3$, 400 MHz, 9-phenethyl-9,10-dihydrophenanthrene (**3r**)



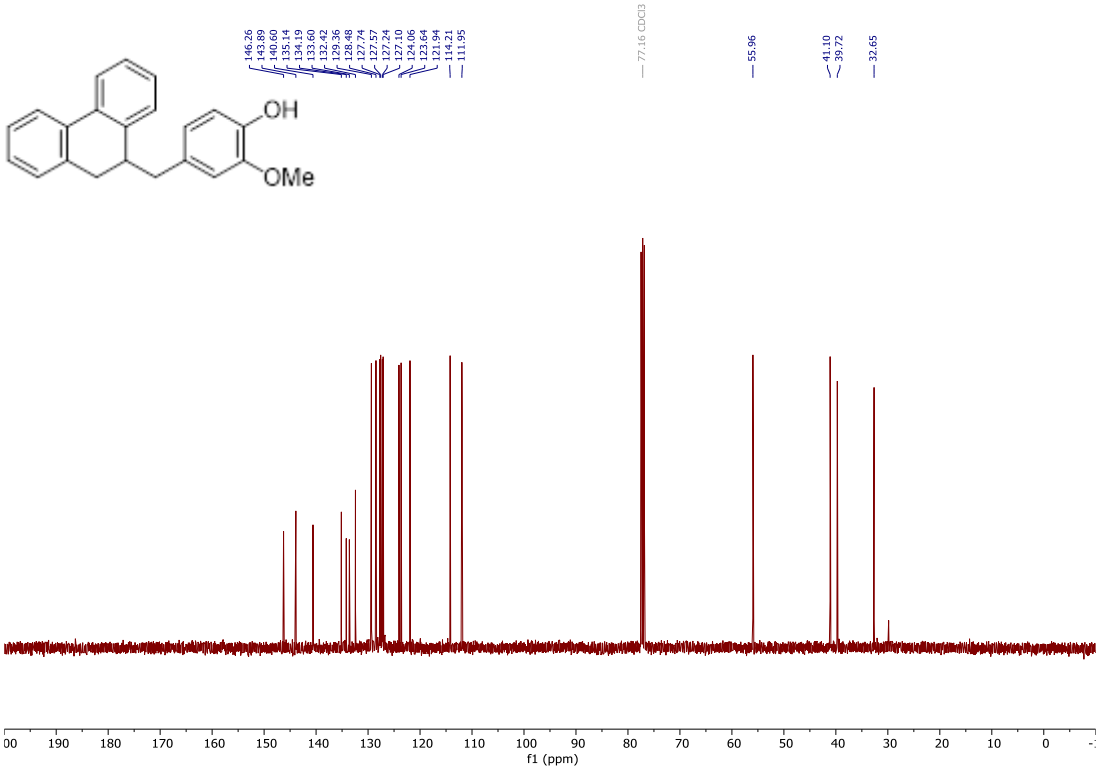
^{13}C NMR, $CDCl_3$, 101 MHz, 9-phenethyl-9,10-dihydrophenanthrene (**3r**)



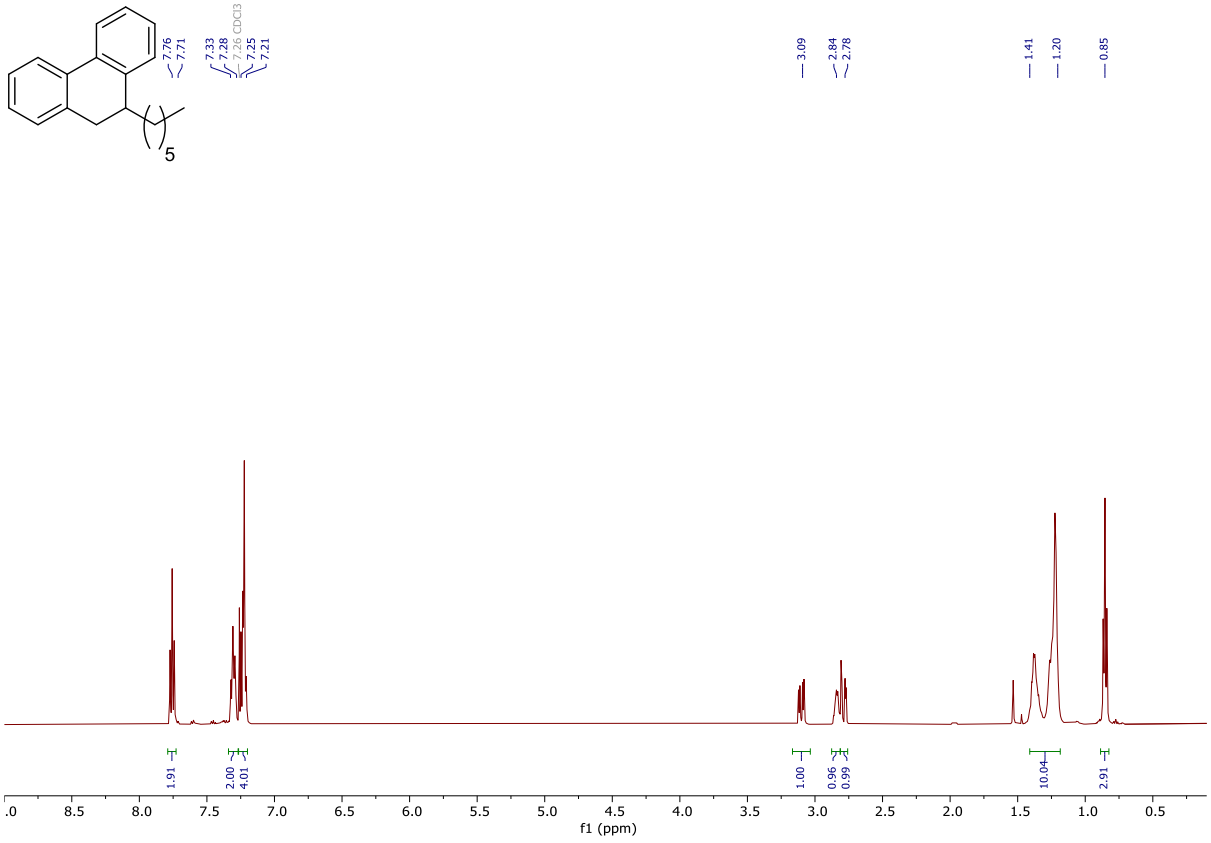
^{1}H NMR, $CDCl_3$, 400 MHz, 4-((9,10-dihydrophenanthren-9-yl)methyl)-2-methoxyphenol **(3s)**



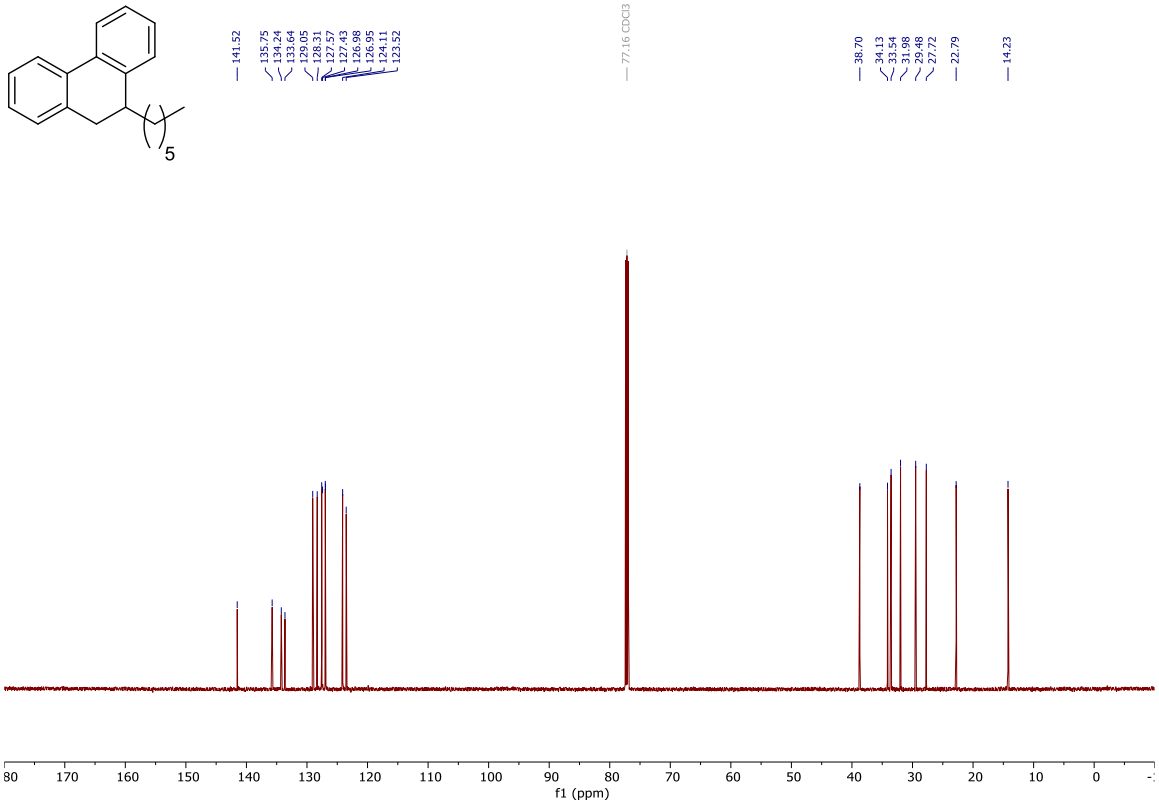
^{13}C NMR, $CDCl_3$, 101 MHz, 4-((9,10-dihydrophenanthren-9-yl)methyl)-2-methoxyphenol **(3s)**



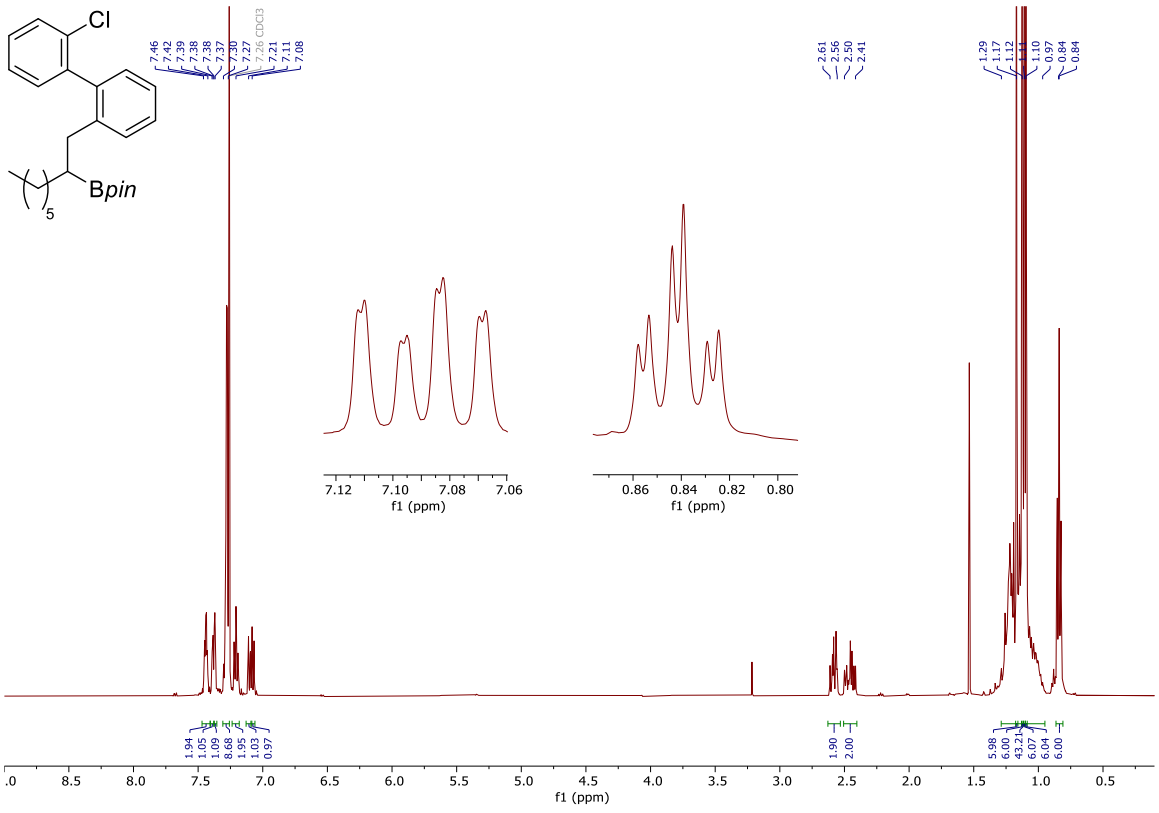
^{1}H NMR, $CDCl_3$, 501 MHz, 9-hexyl-9,10-dihydrophenanthrene (**3**)



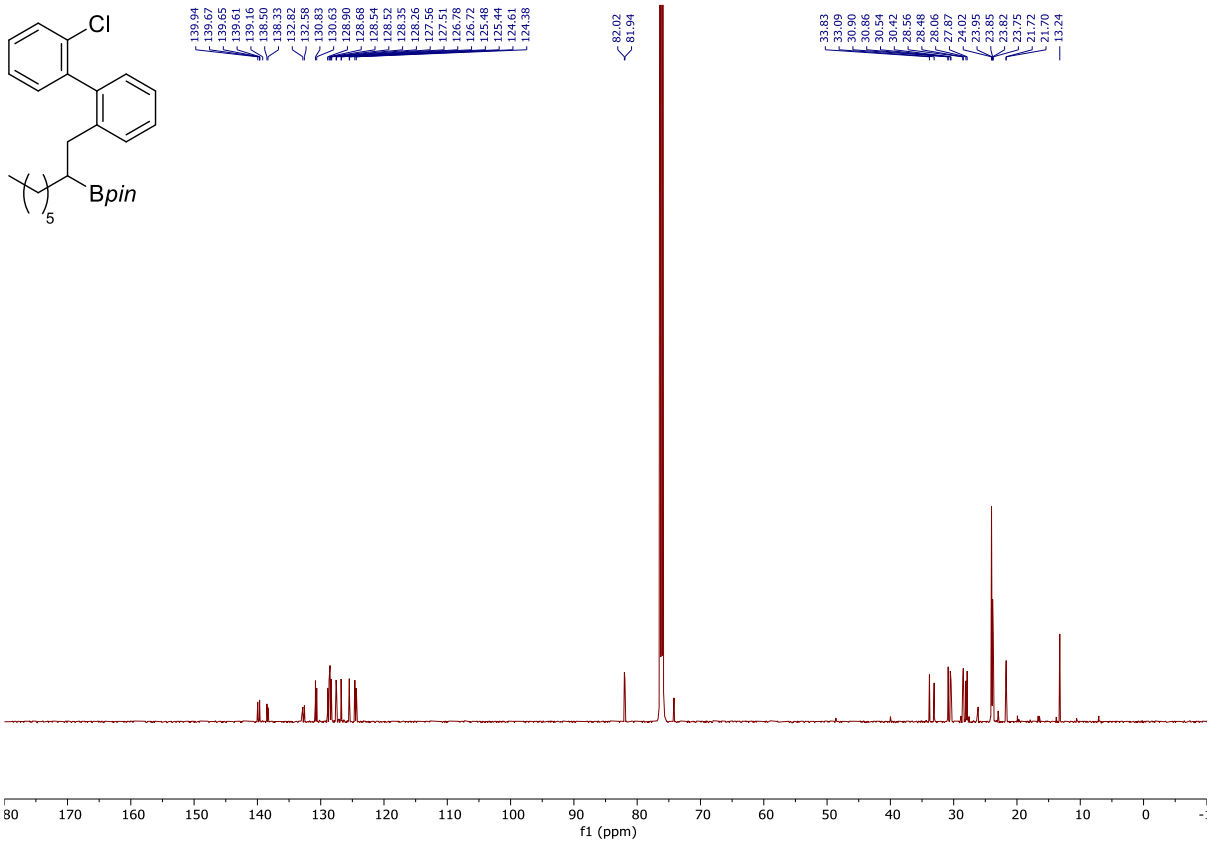
^{13}C NMR, $CDCl_3$, 151 MHz, 9-hexyl-9,10-dihydrophenanthrene (**3**)



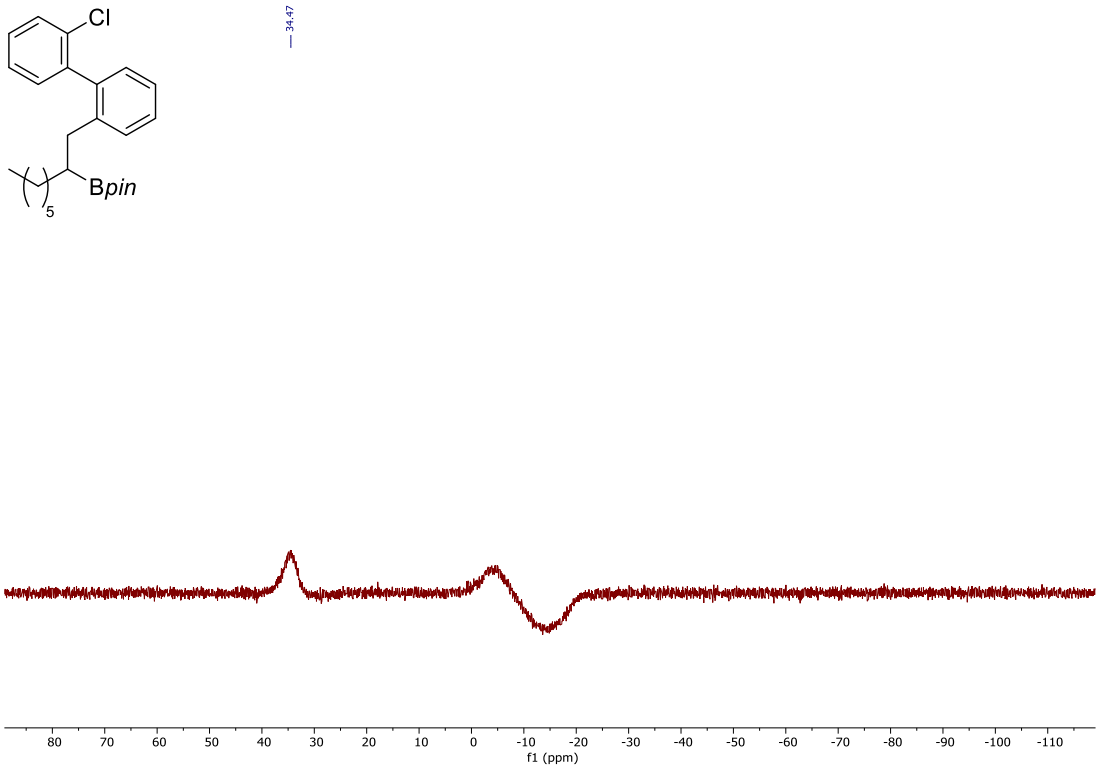
^{1}H NMR, $CDCl_3$, 400 MHz, 2-(1-(2'-chloro-[1,1'-biphenyl]-2-yl)octan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(4)**



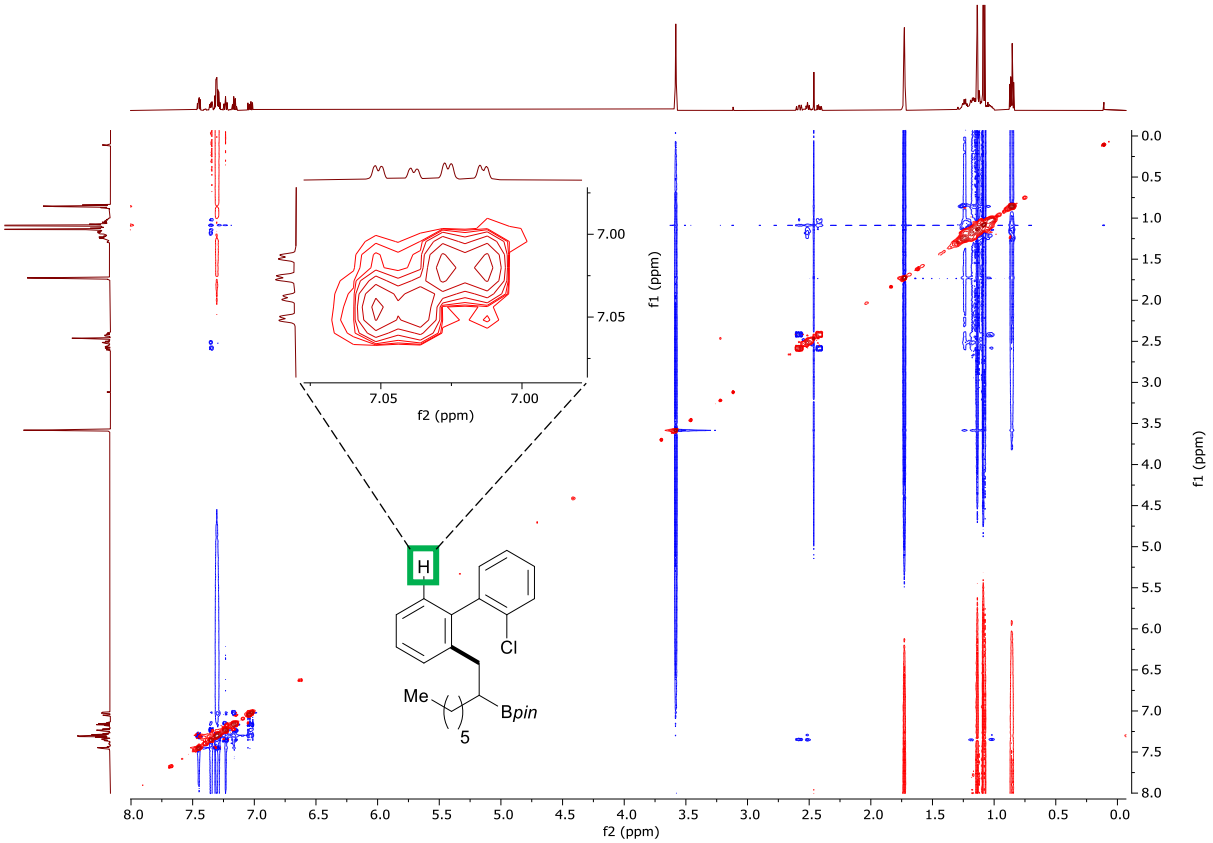
^{13}C NMR, $CDCl_3$, 151 MHz, 2-(1-(2'-chloro-[1,1'-biphenyl]-2-yl)octan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(4)**



^{11}B NMR, $CDCl_3$, 161 MHz, 2-(1-(2'-chloro-[1,1'-biphenyl]-2-yl)octan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(4)**

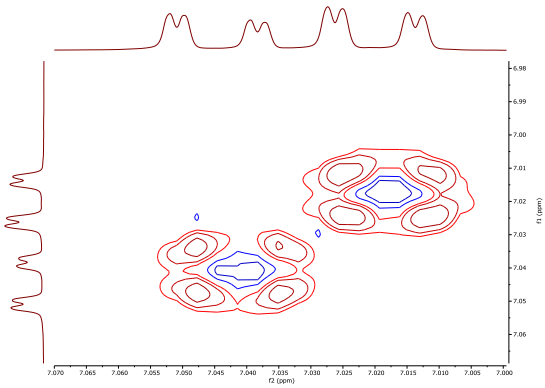


Full NOESY in THF-d6/D_2O 10:1 at 298 K 2-(1-(2'-chloro-[1,1'-biphenyl]-2-yl)octan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(4)**

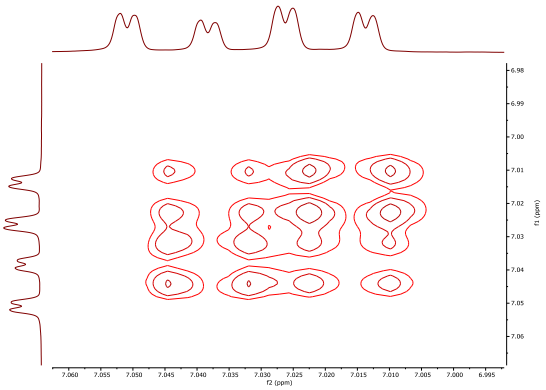


Partial NOESY in THF-d6/D_2O 10:12-(1-(2'-chloro-[1,1'-biphenyl]-2-yl)octan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(4)**

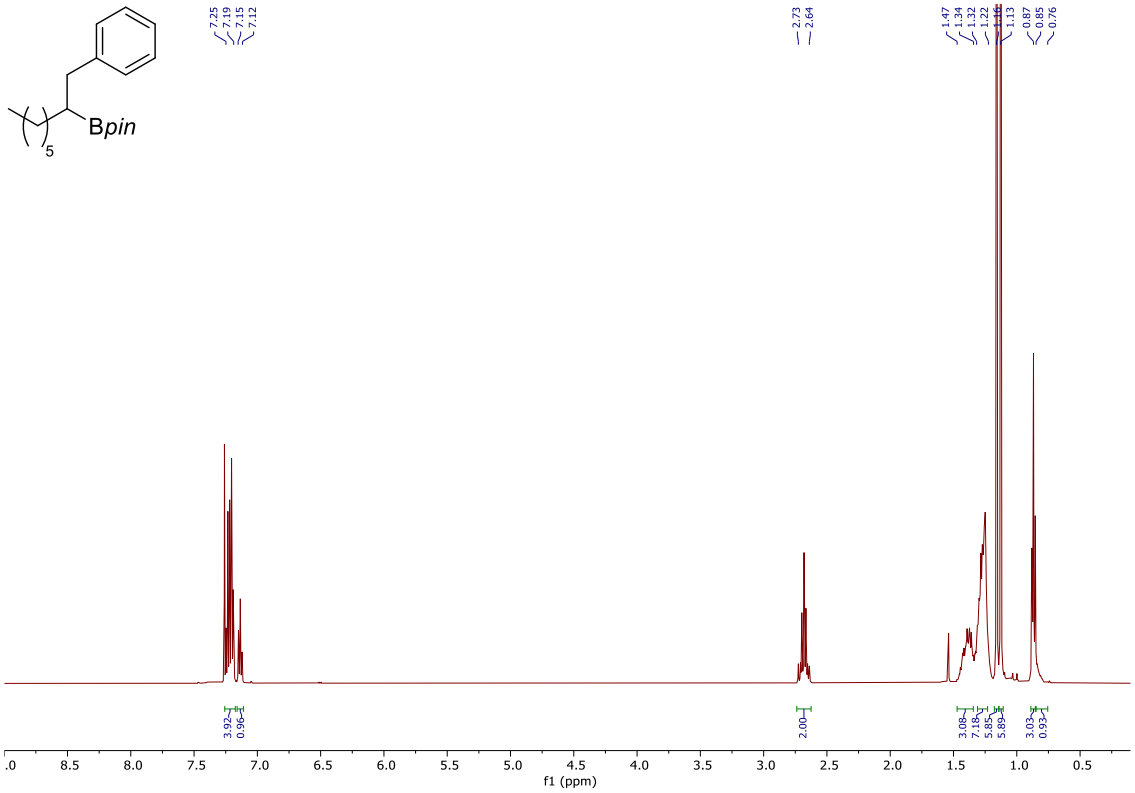
at 323 K



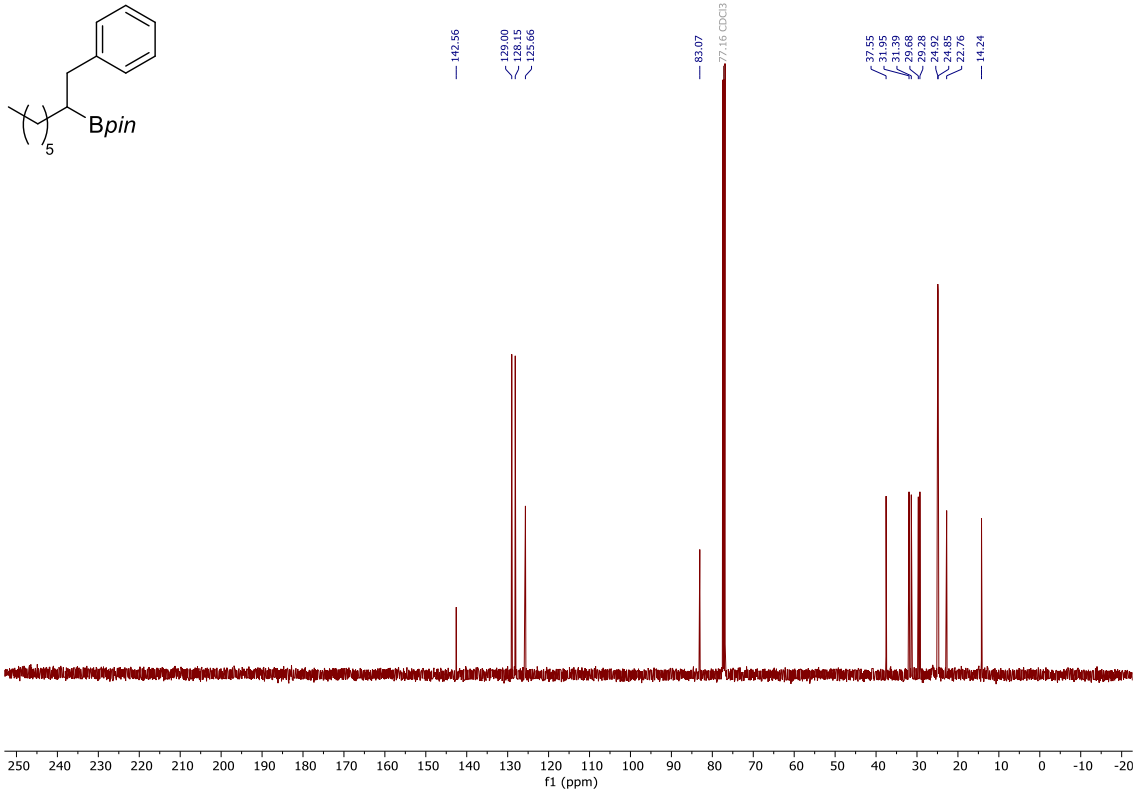
at 348 K



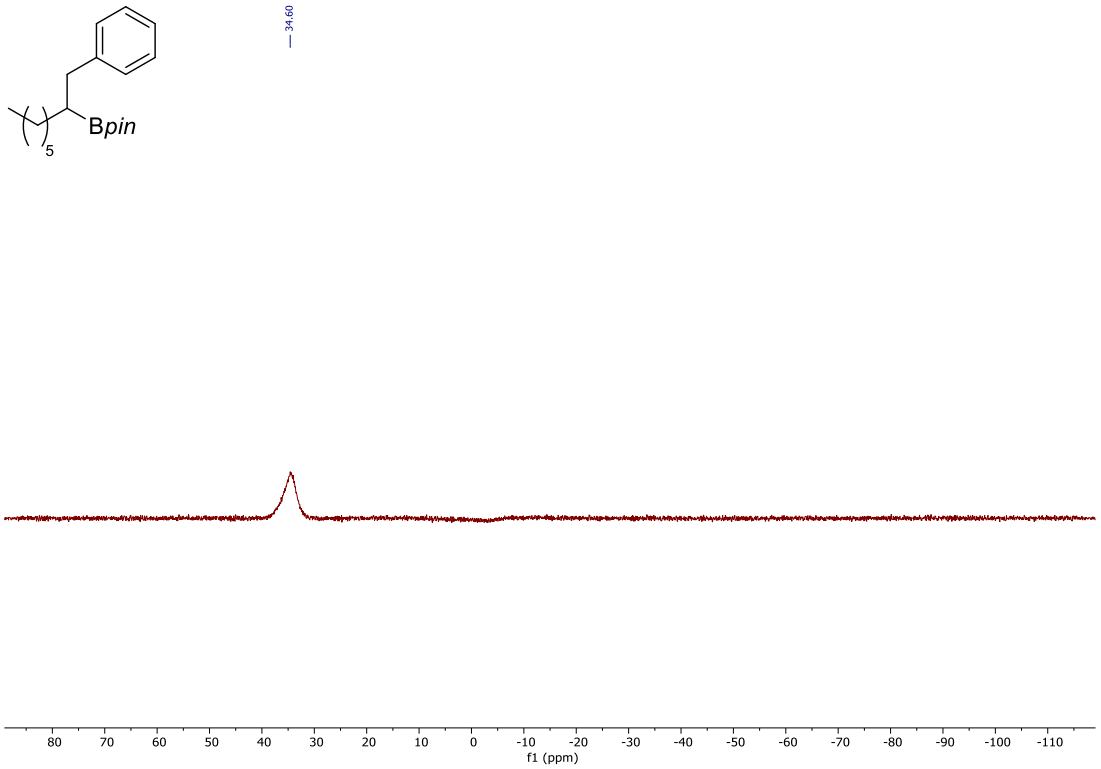
^{1}H NMR, $CDCl_3$, 400 MHz, 4,4,5,5-tetramethyl-2-(1-phenyloctan-2-yl)-1,3,2-dioxaborolane **(S3)**



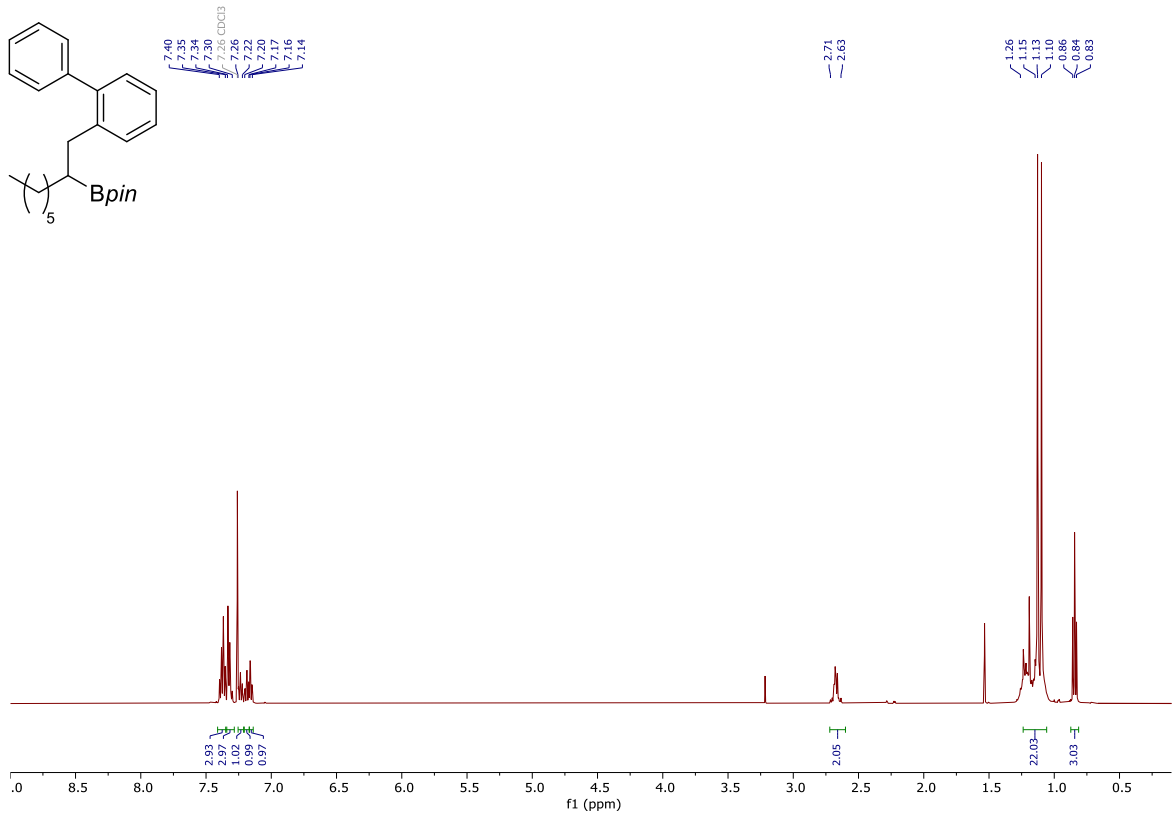
^{13}C NMR, $CDCl_3$, 151 MHz, 4,4,5,5-tetramethyl-2-(1-phenyloctan-2-yl)-1,3,2-dioxaborolane **(S3)**



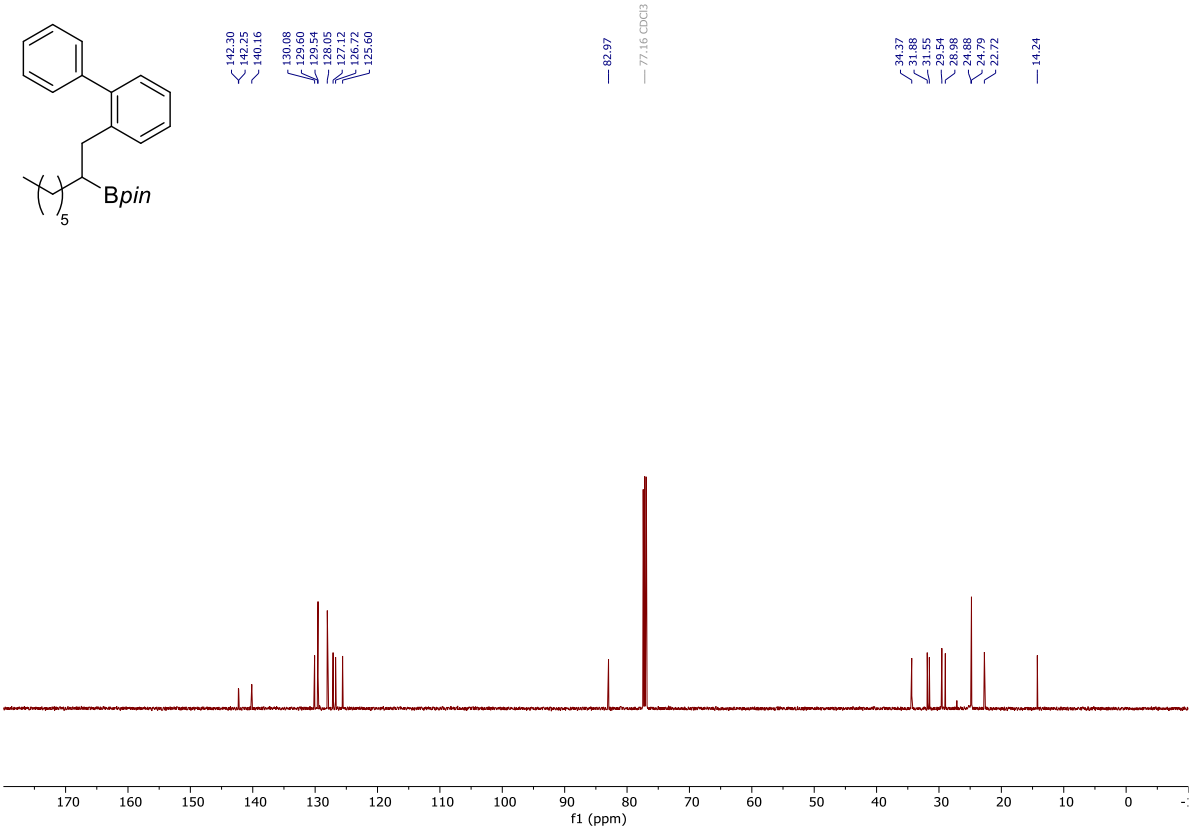
^{11}B NMR, $CDCl_3$, 161 MHz, 4,4,5,5-tetramethyl-2-(1-phenyloctan-2-yl)-1,3,2-dioxaborolane **(S3)**



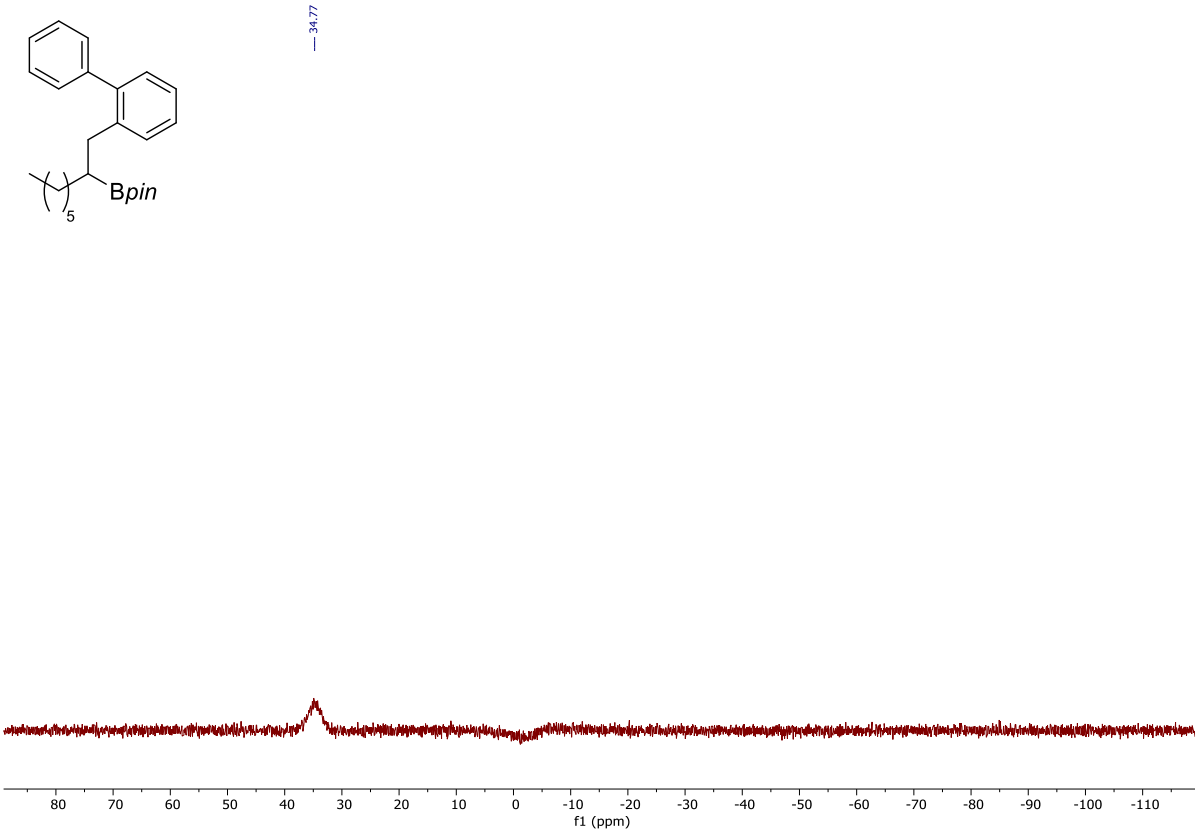
^{1}H NMR, $CDCl_3$, 501 MHz, 2-(1-([1,1'-biphenyl]-2-yl)octan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(SP)**



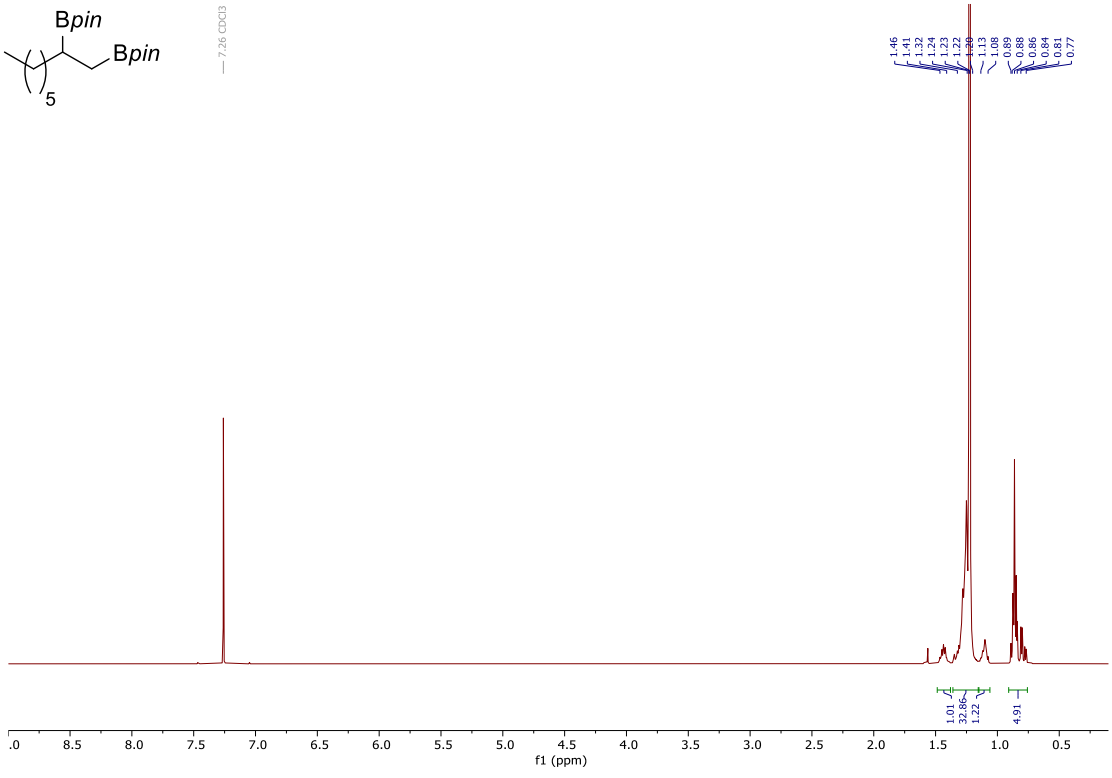
^{13}C NMR, $CDCl_3$, 126 MHz, 2-(1-([1,1'-biphenyl]-2-yl)octan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(SP)**



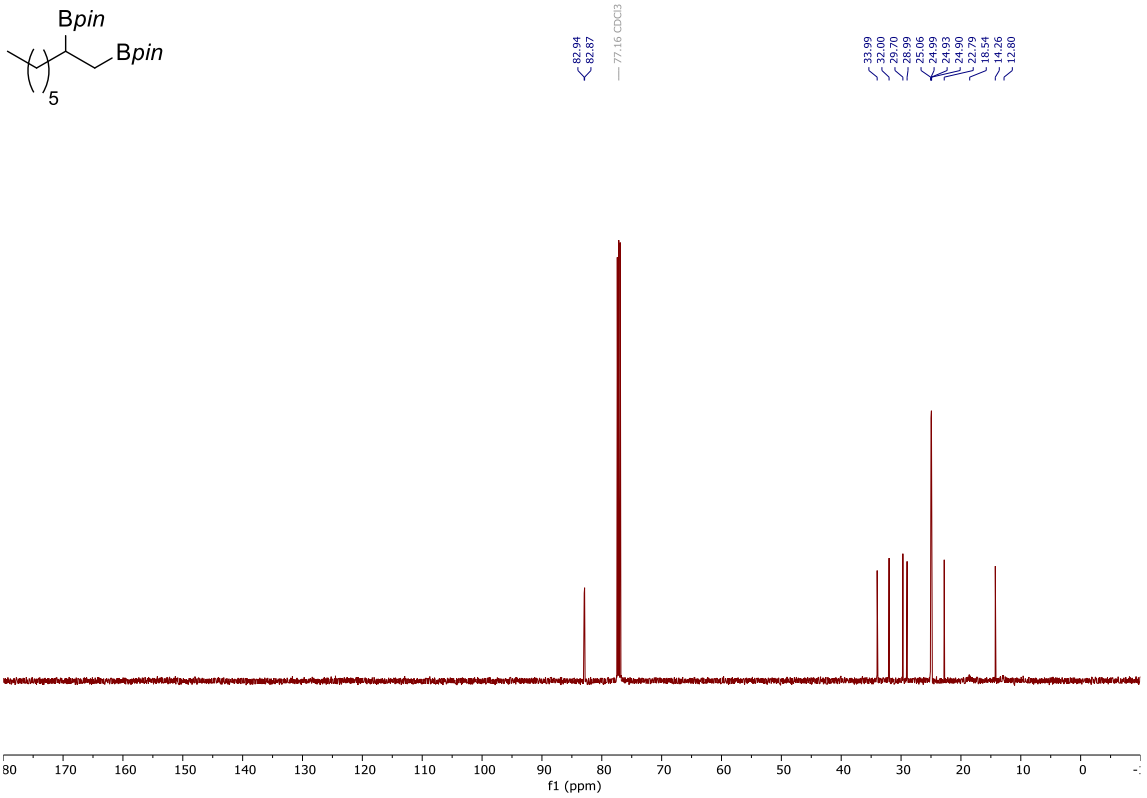
^{11}B NMR, $CDCl_3$, 161 MHz, 2-(1-([1,1'-biphenyl]-2-yl)octan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(SP)**



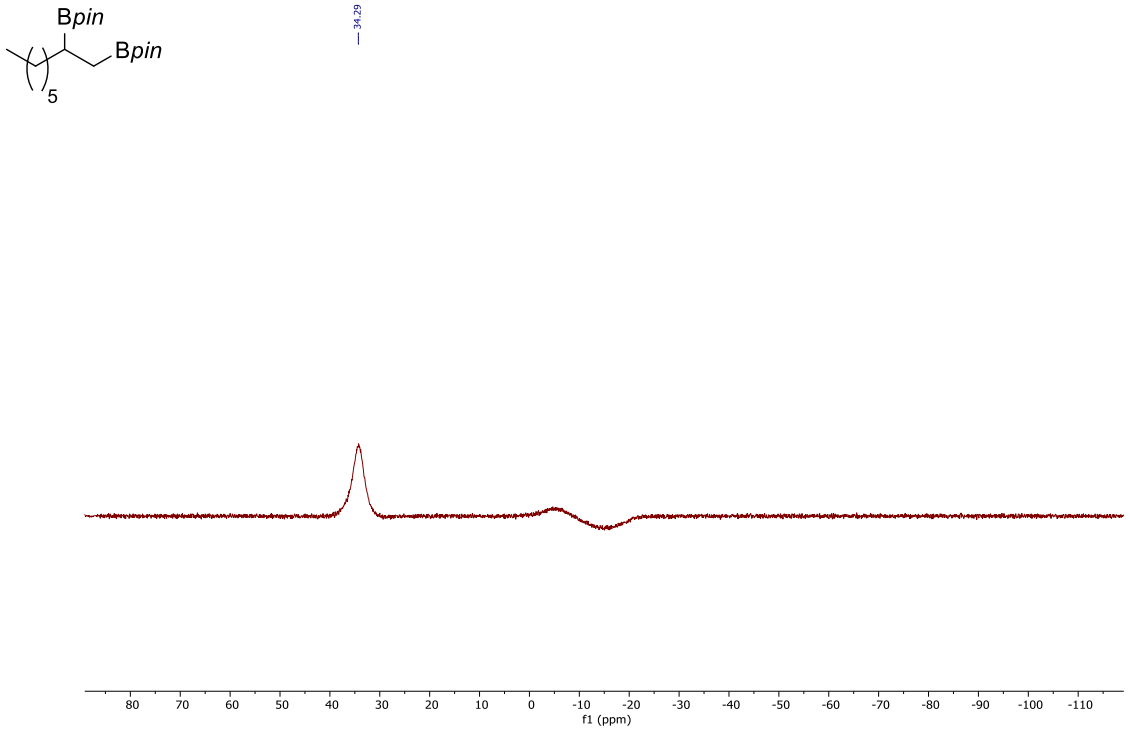
^{1}H NMR, $CDCl_3$, 501 MHz, 2,2'-(octane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(1)**



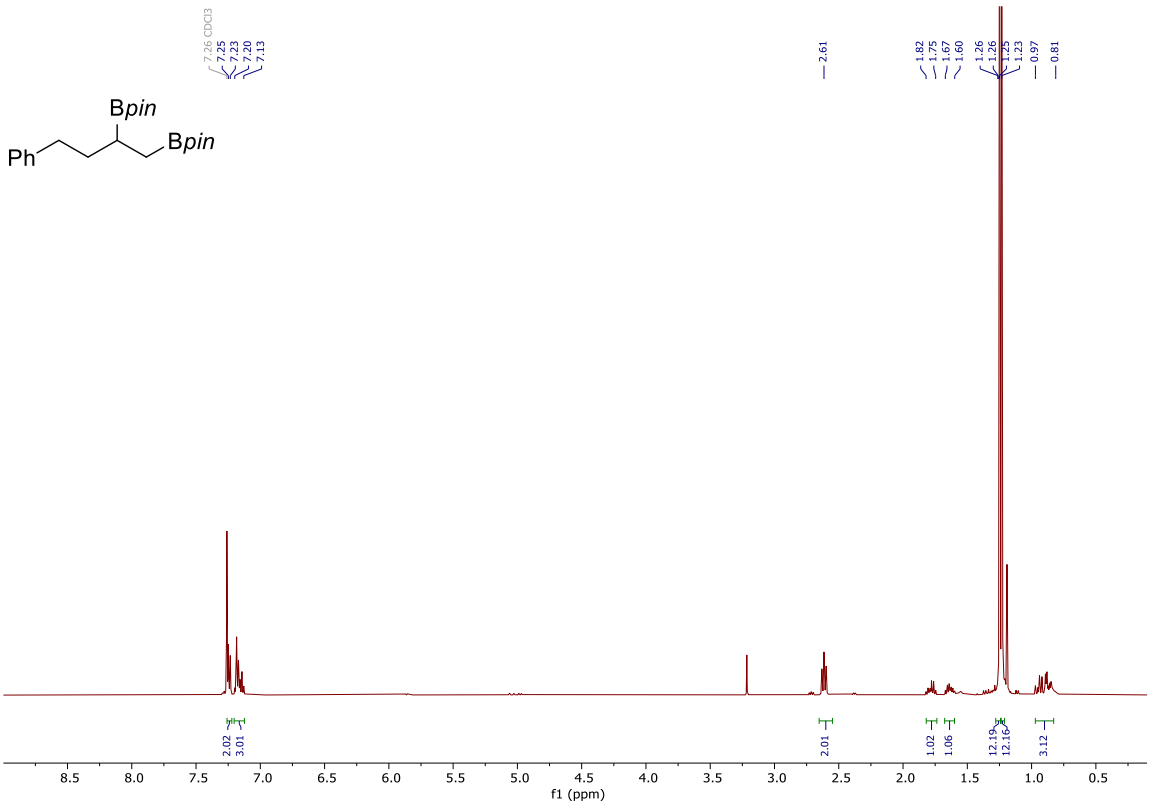
^{13}C NMR, $CDCl_3$, 126 MHz, 2,2'-(octane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(1)**



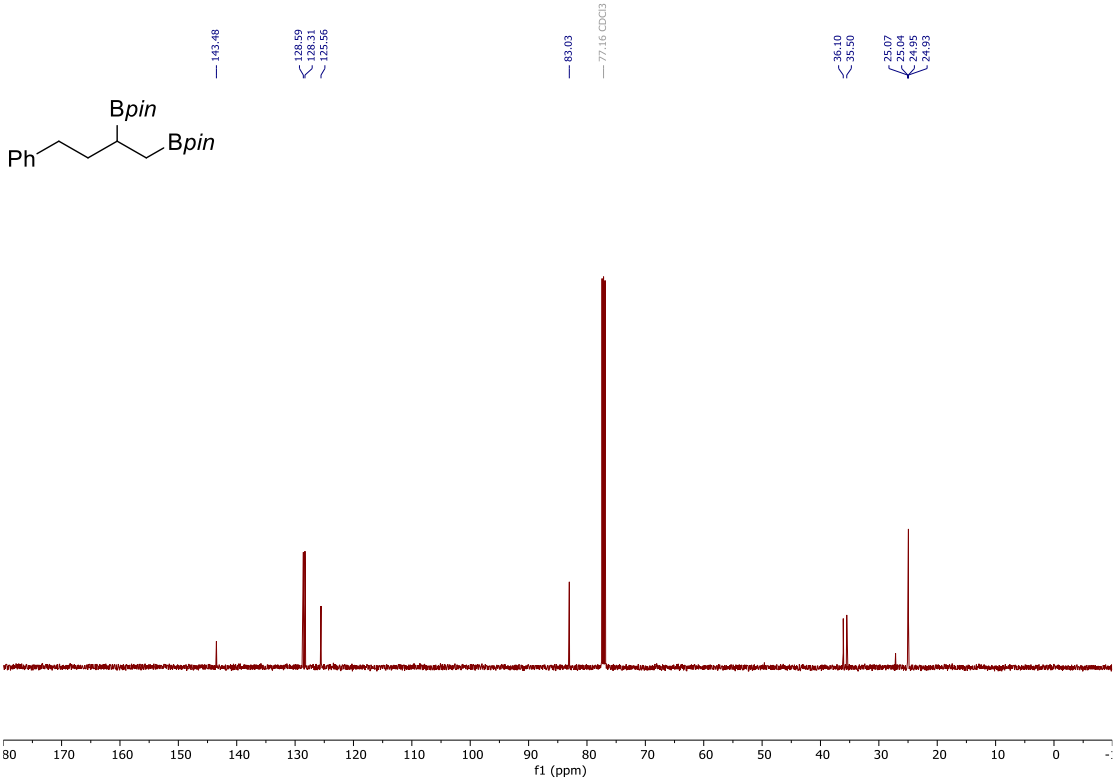
^{11}B NMR, $CDCl_3$, 161 MHz, 2,2'-(octane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(1)**



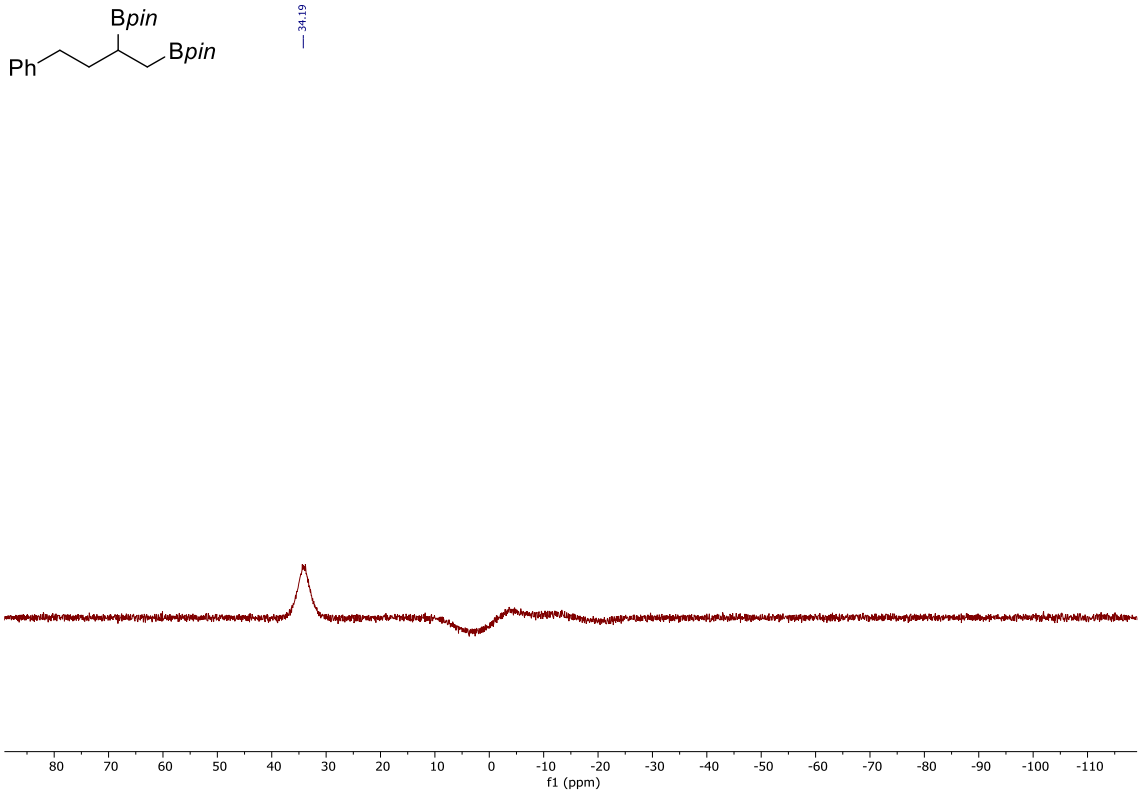
^{1}H NMR, $CDCl_3$, 501 MHz, 2,2'-(4-phenylbutane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(S1a)**



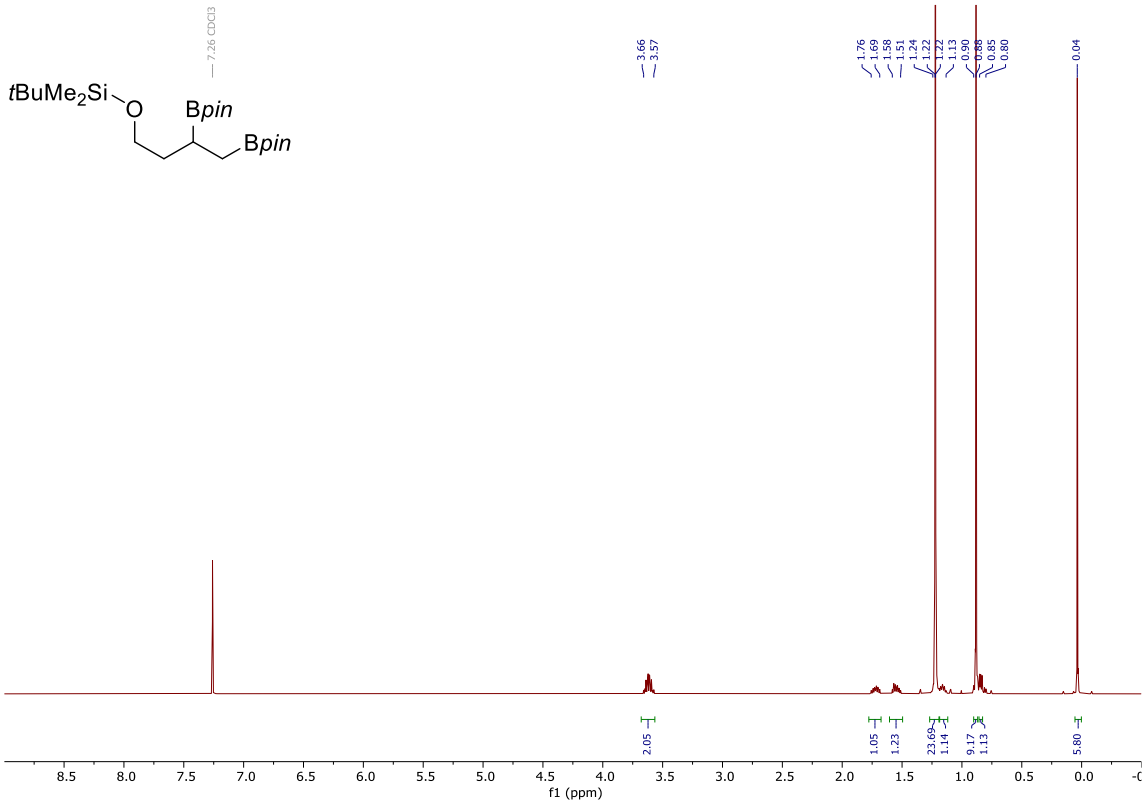
^{13}C NMR, $CDCl_3$, 126 MHz, 2,2'-(4-phenylbutane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(S1a)**



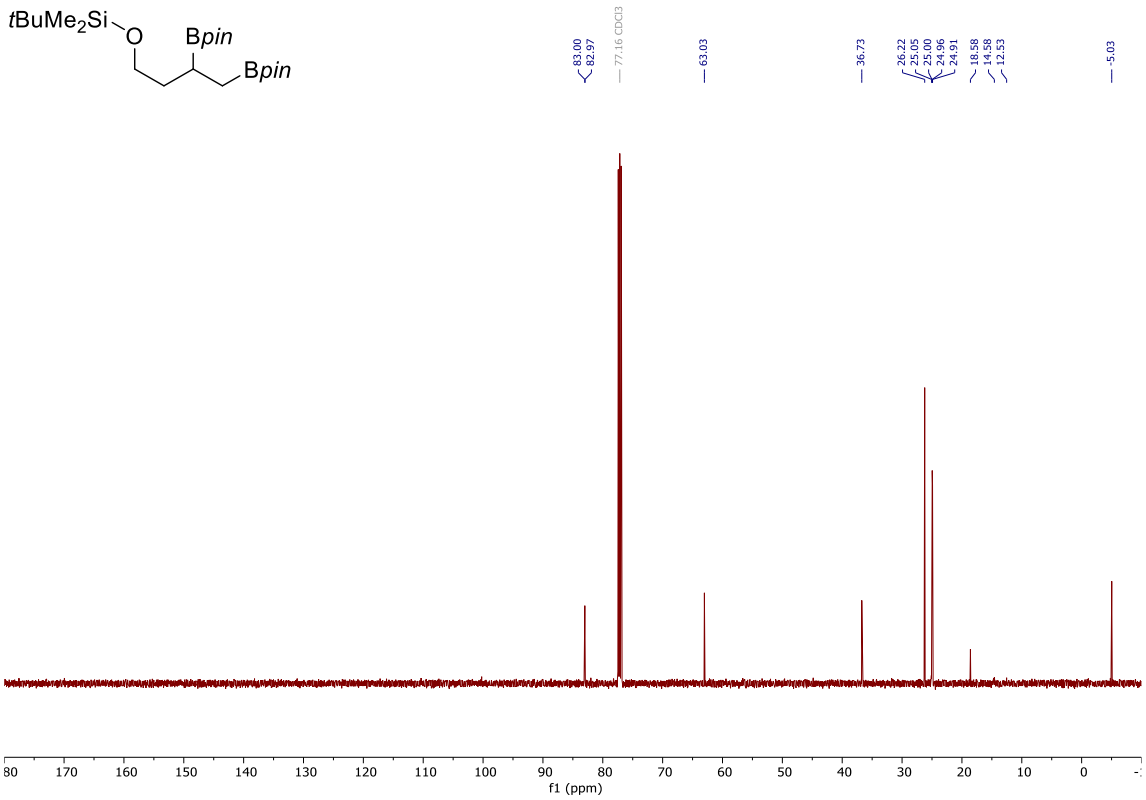
^{11}B NMR, $CDCl_3$, 161 MHz, 2,2'-(4-phenylbutane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(S1a)**



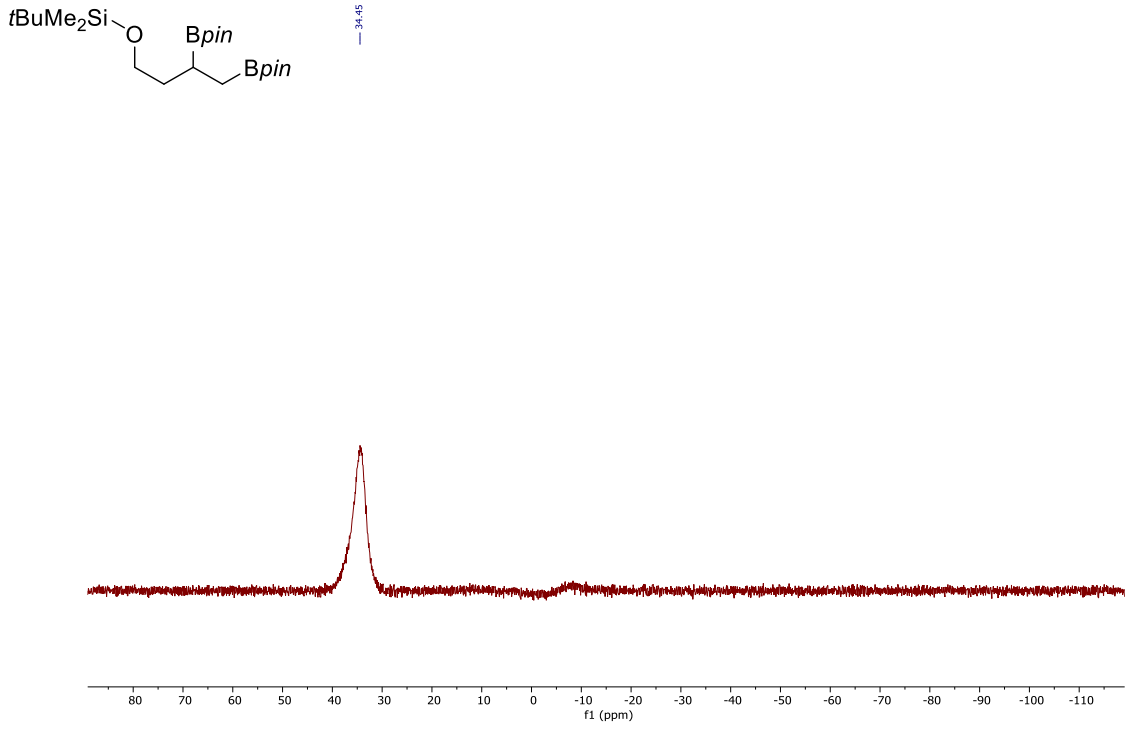
^{1}H NMR, $CDCl_3$, 501 MHz, (3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butoxy)(tert-butyl)dimethylsilane **(S1b)**



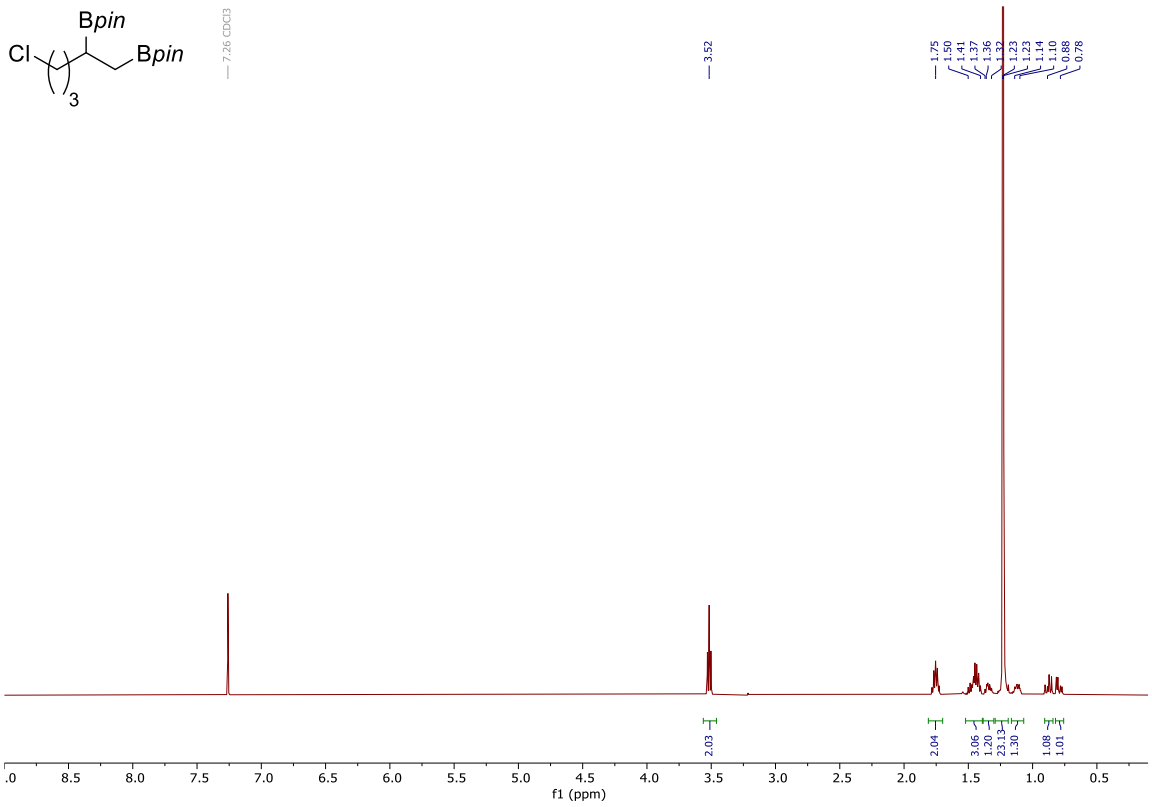
^{13}C NMR, $CDCl_3$, 126 MHz, 2(3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butoxy) (tert-butyl)dimethylsilane **(S1b)**



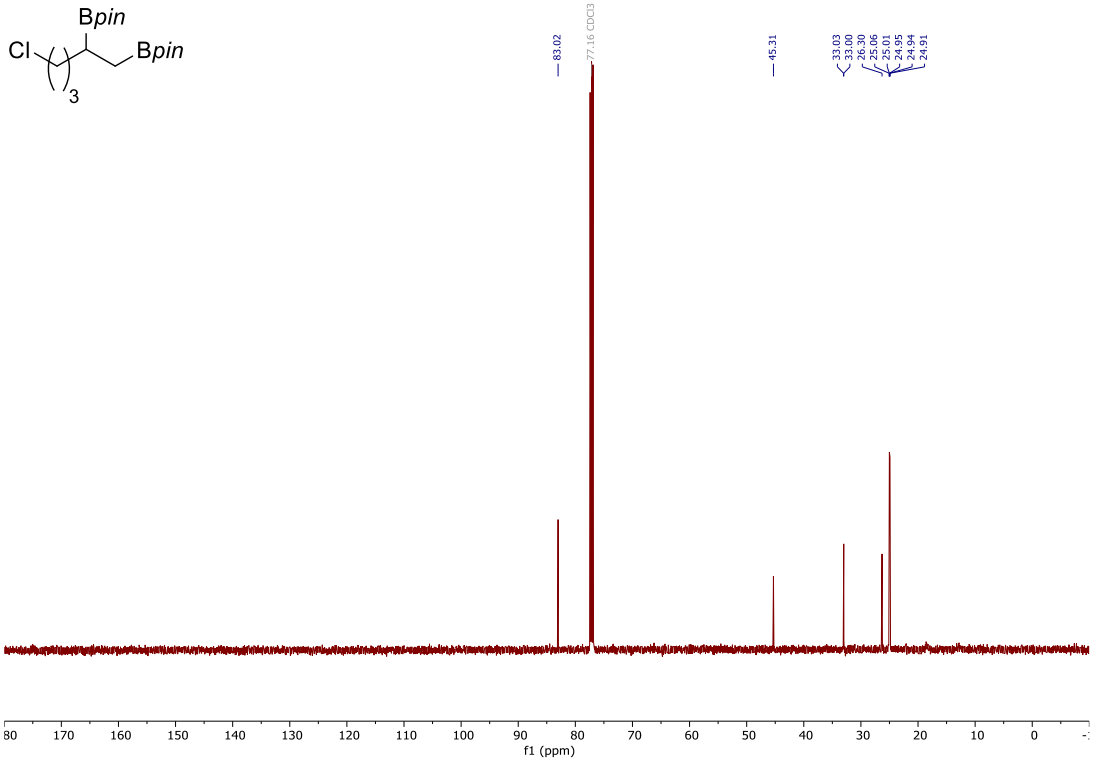
^{11}B NMR, $CDCl_3$, 161 MHz, (3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butoxy) (tert-butyl)dimethylsilane **(S1b)**



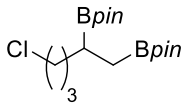
^{1}H NMR, $CDCl_3$, 501 MHz, 2,2'-(6-chlorohexane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(S1c)**



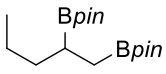
^{13}C NMR, $CDCl_3$, 126 MHz, 2,2'-(6-chlorohexane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(S1c)**



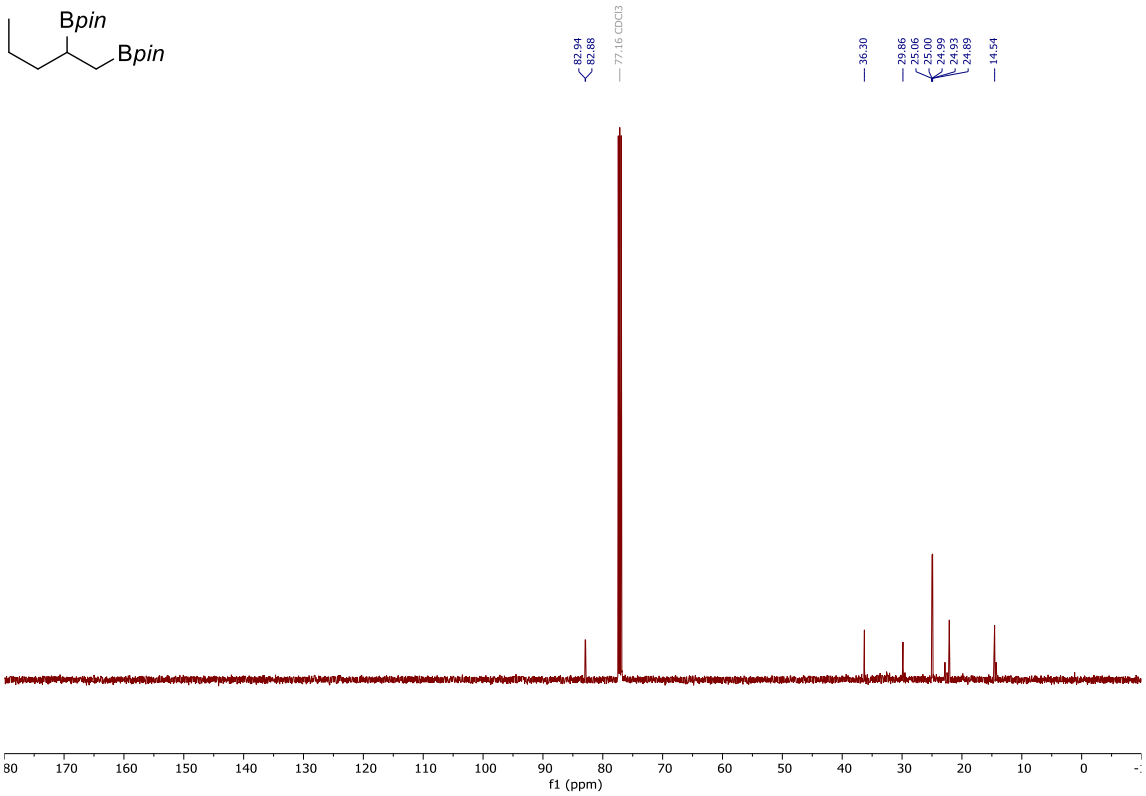
^{11}B NMR, $CDCl_3$, 161 MHz, 2,2'-(6-chlorohexane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(S1c)**



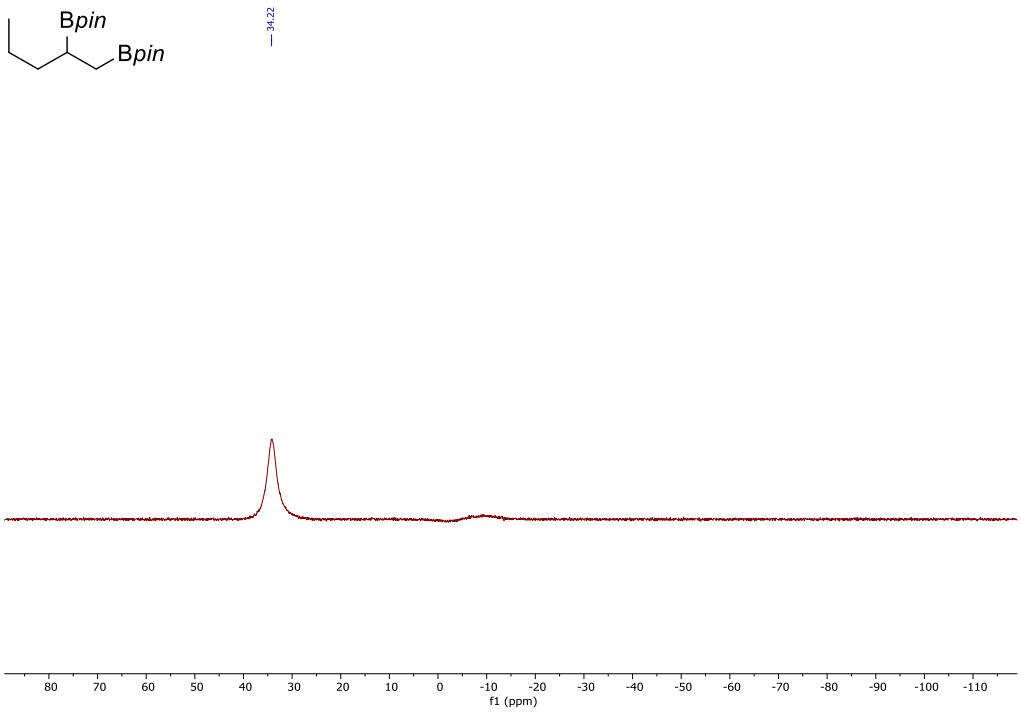
^{1}H NMR, $CDCl_3$, 501 MHz, 2,2'-(pentane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(S1d)**



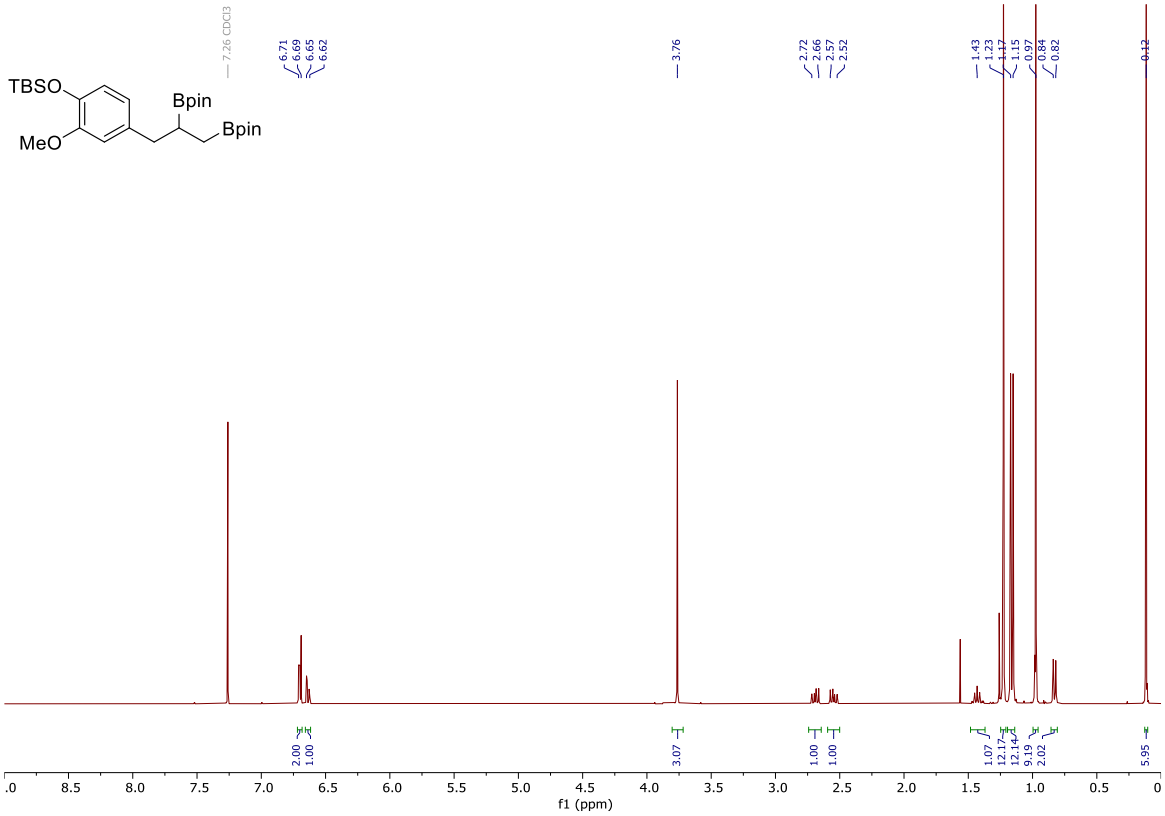
^{13}C NMR, $CDCl_3$, 126 MHz, 2,2'-(pentane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(S1d)**



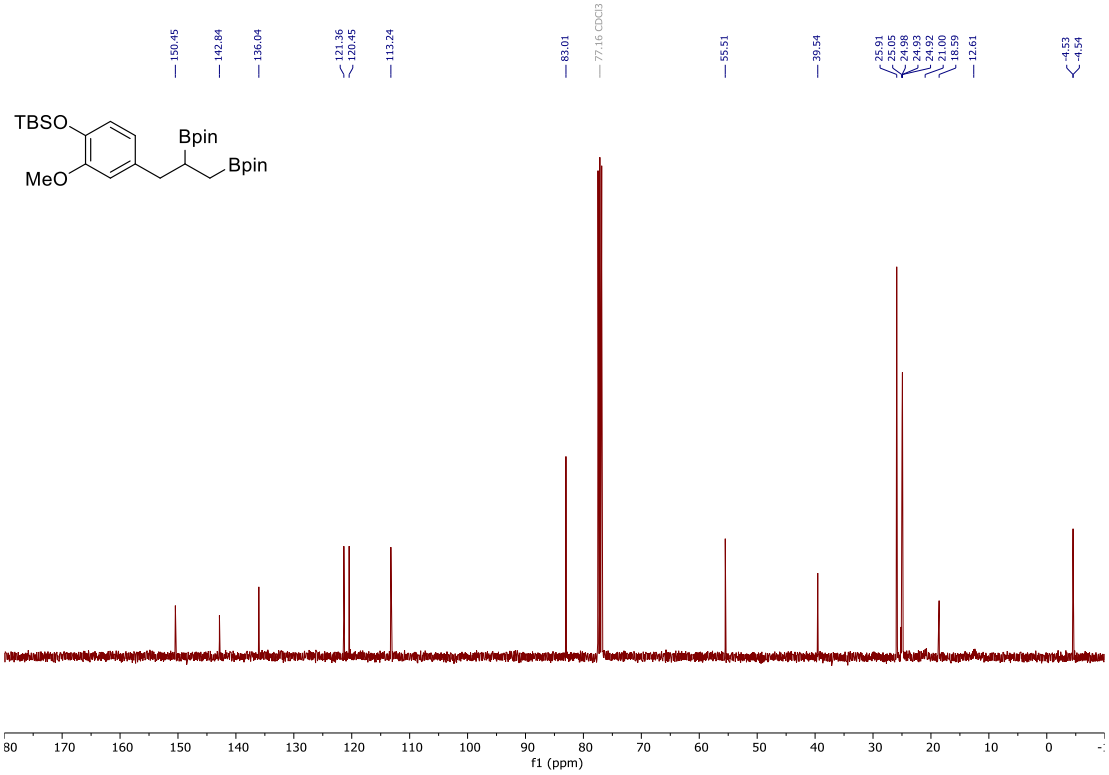
^{11}B NMR, $CDCl_3$, 161 MHz, 2,2'-(pentane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(S1d)**



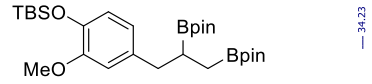
^{1}H NMR, $CDCl_3$, 400 MHz, (4-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-2-methoxyphenyl)(tert-butyl)dimethylsilane (**S1e)**

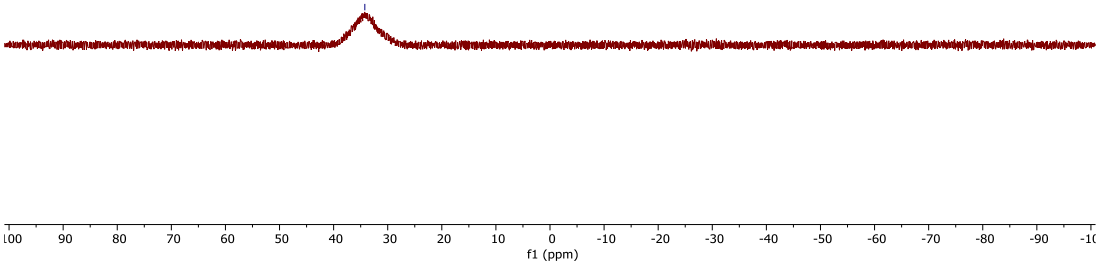


^{13}C NMR, $CDCl_3$, 101 MHz, (4-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-2-methoxyphenyl)(tert-butyl)dimethylsilane (**S1e)**

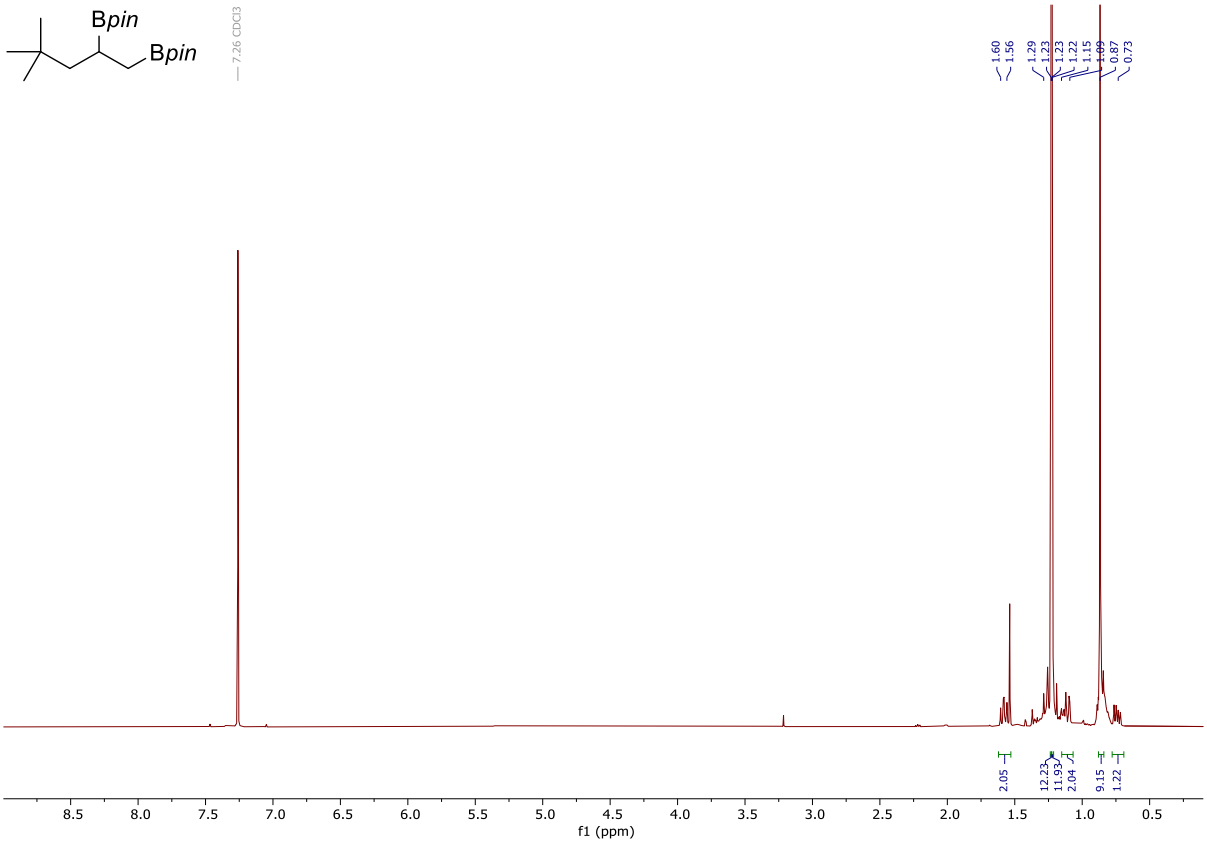


^{11}B NMR, $CDCl_3$, 161 MHz, (4-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-2-methoxyphenyl)(tert-butyl)dimethylsilane **(S1e)**

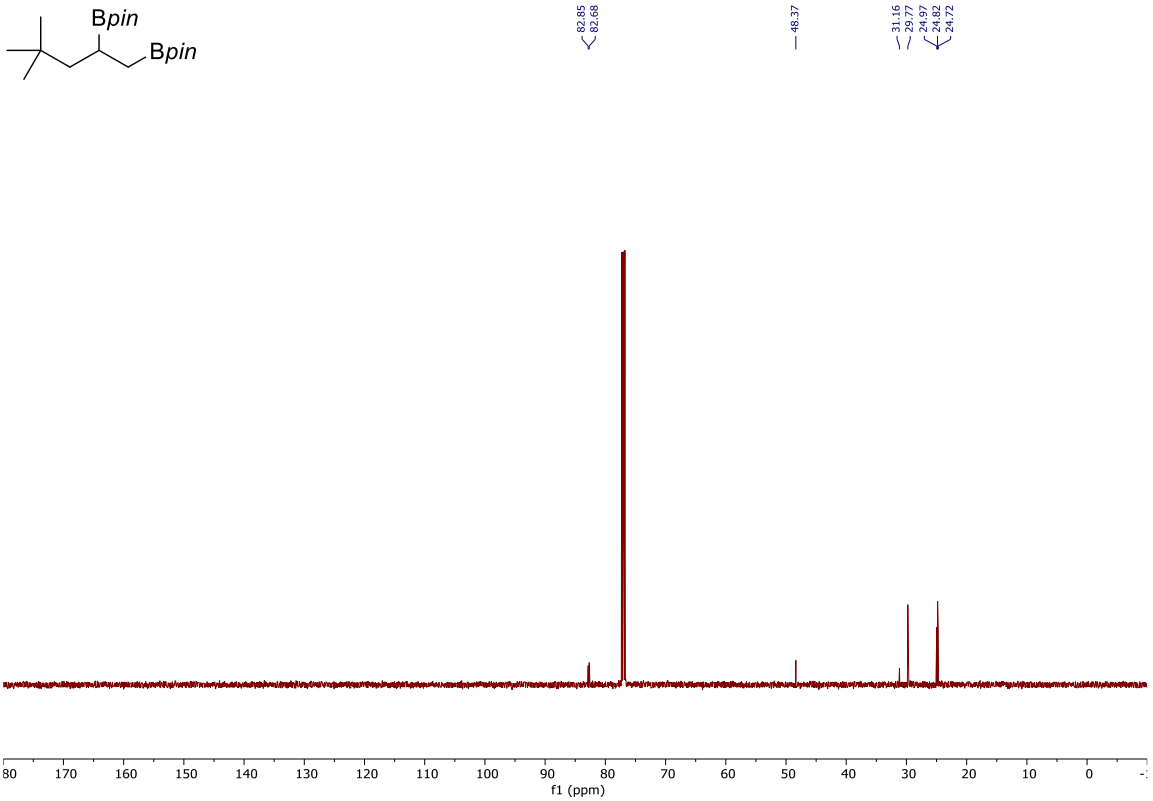




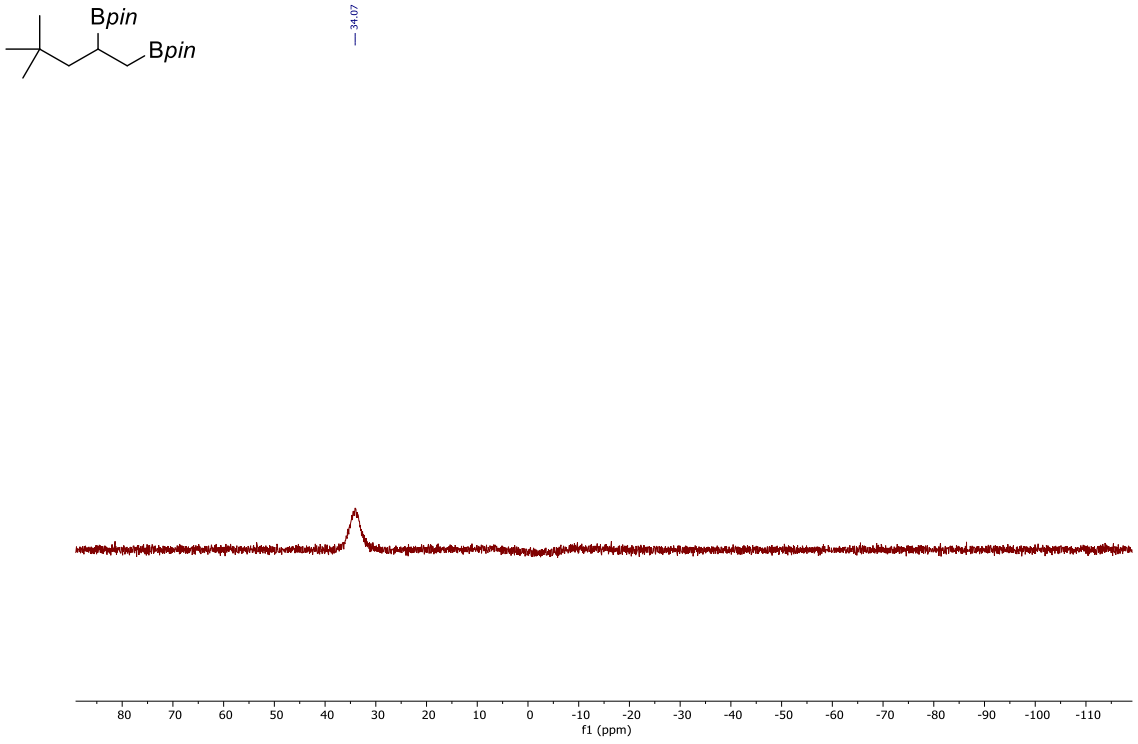
^{1}H NMR, $CDCl_3$, 501 MHz, 2,2'-(4,4-dimethylpentane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(S1f)**



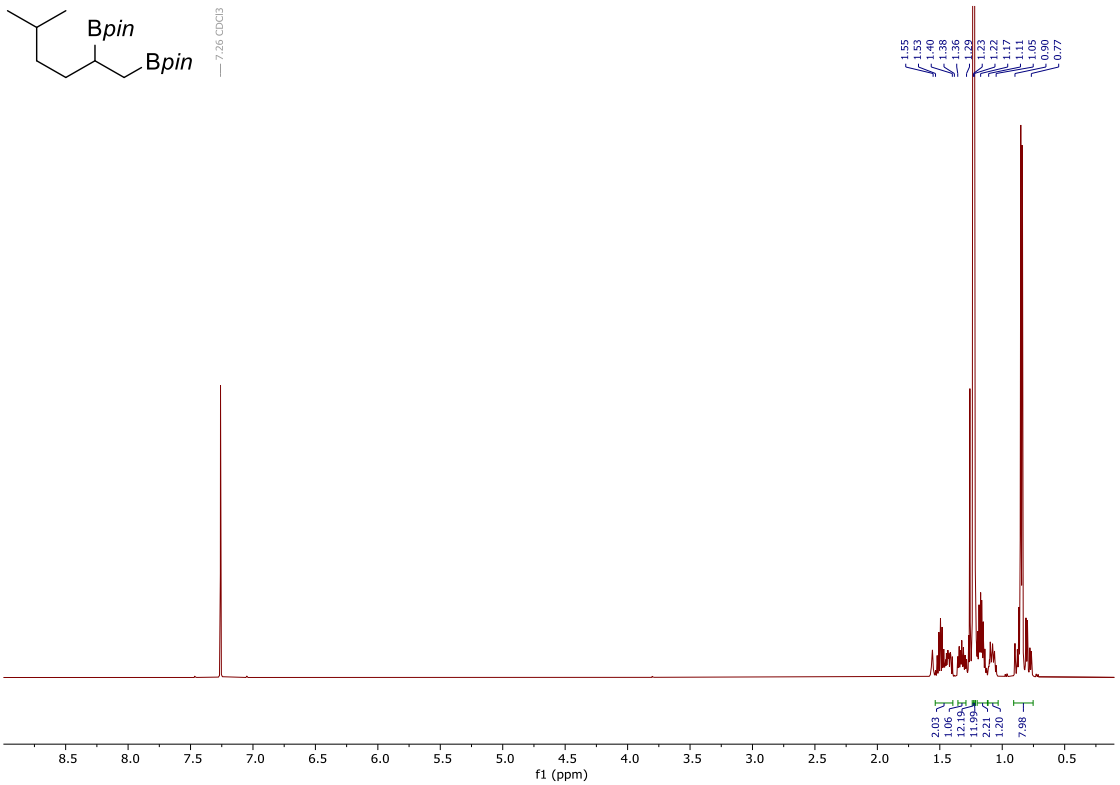
^{13}C NMR, $CDCl_3$, 126 MHz, 2,2'-(4,4-dimethylpentane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(S1f)**



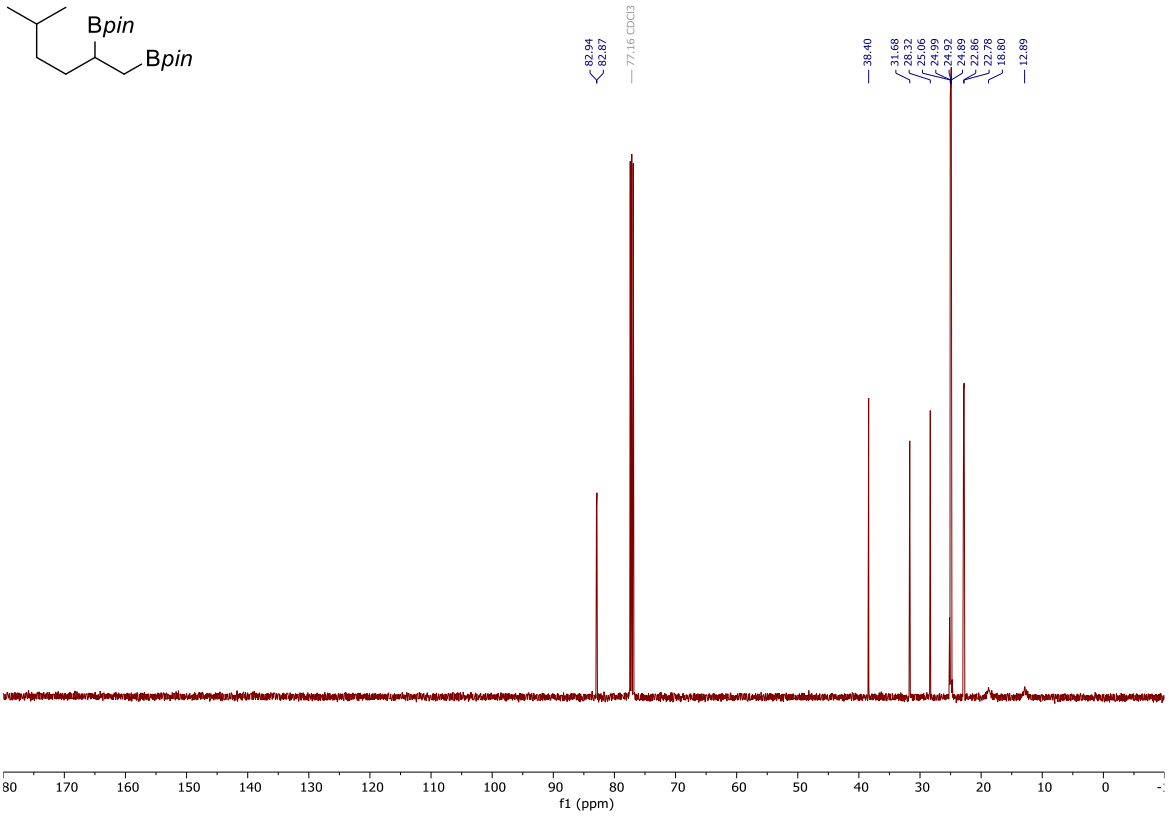
^{11}B NMR, $CDCl_3$, 161 MHz, 2,2'-(4,4-dimethylpentane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(S1f)**



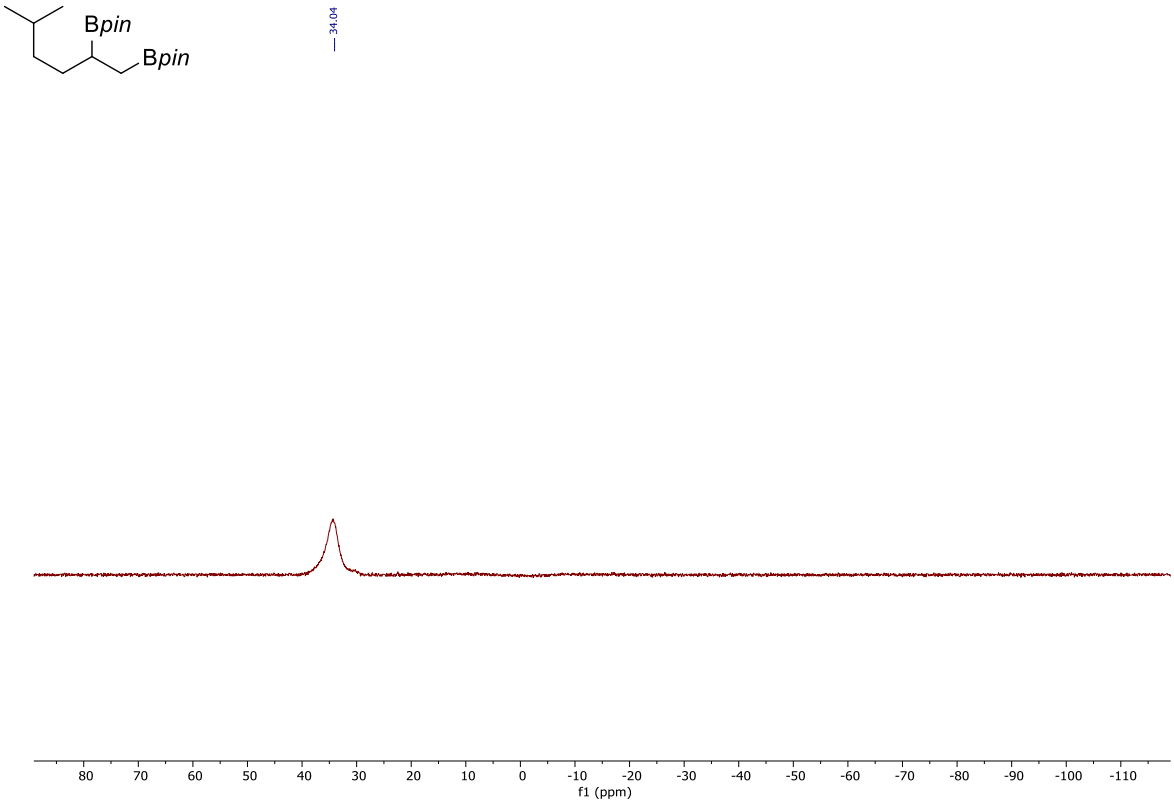
^{1}H NMR, $CDCl_3$, 501 MHz, 2,2'-(5-methylhexane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(S1g)**



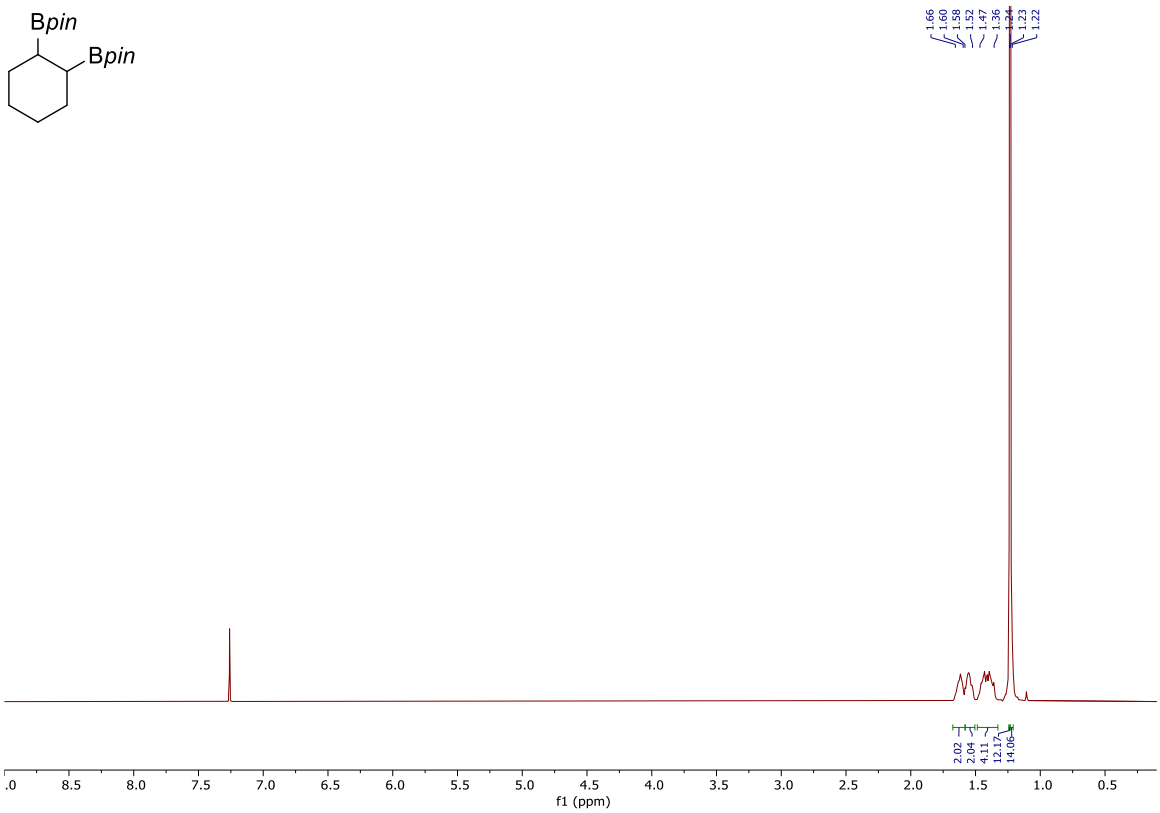
^{13}C NMR, $CDCl_3$, 126 MHz, 2,2'-(5-methylhexane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(S1g)**



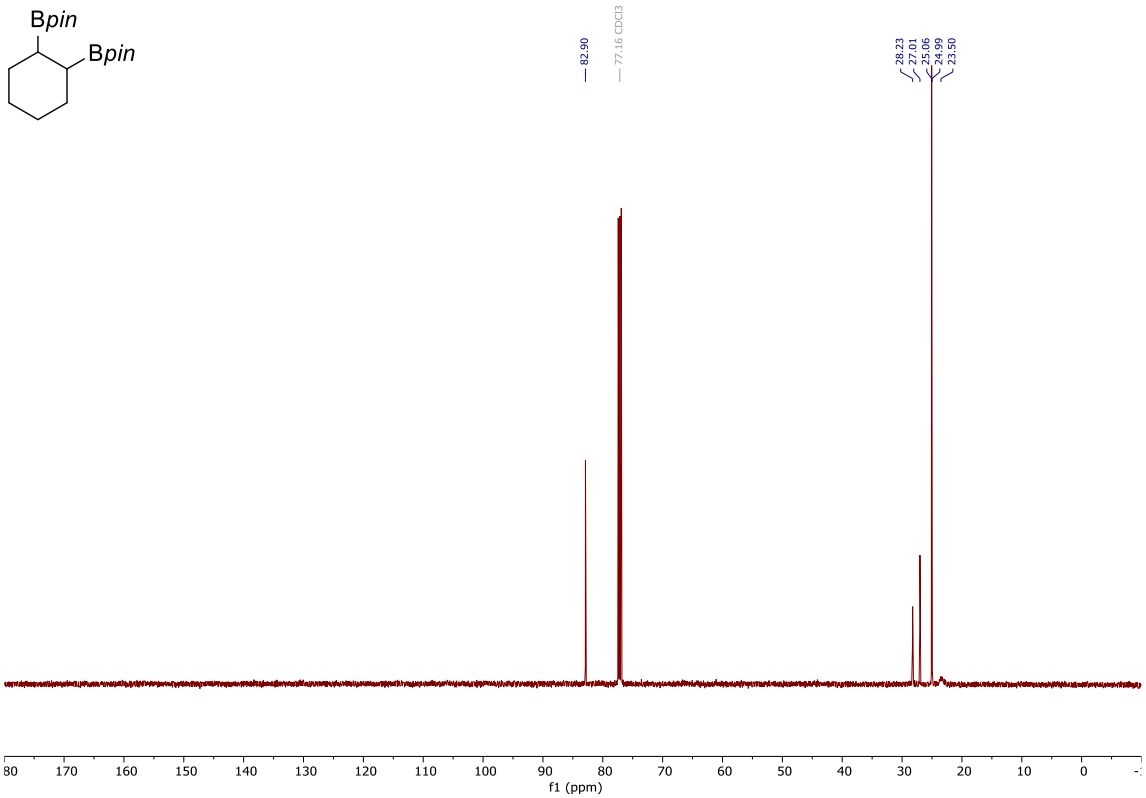
^{11}B NMR, $CDCl_3$, 161 MHz, 2,2'-(5-methylhexane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(S1g)**



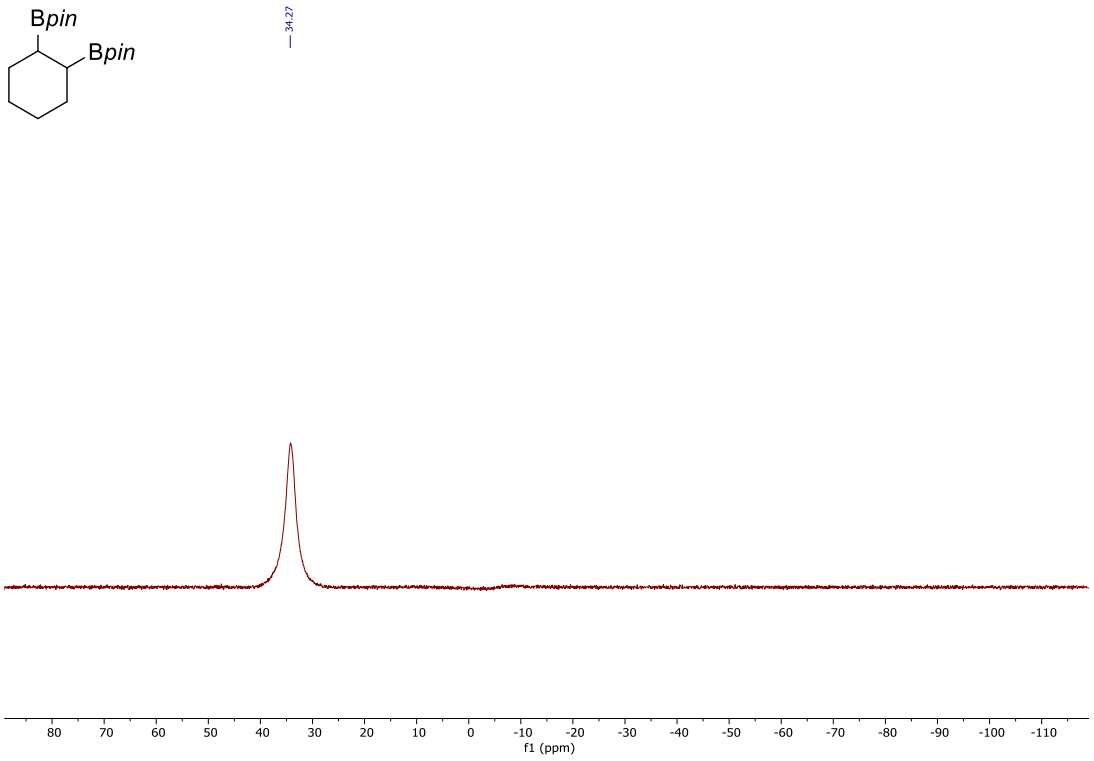
^{1}H NMR, $CDCl_3$, 501 MHz, 1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane **(S1h)**



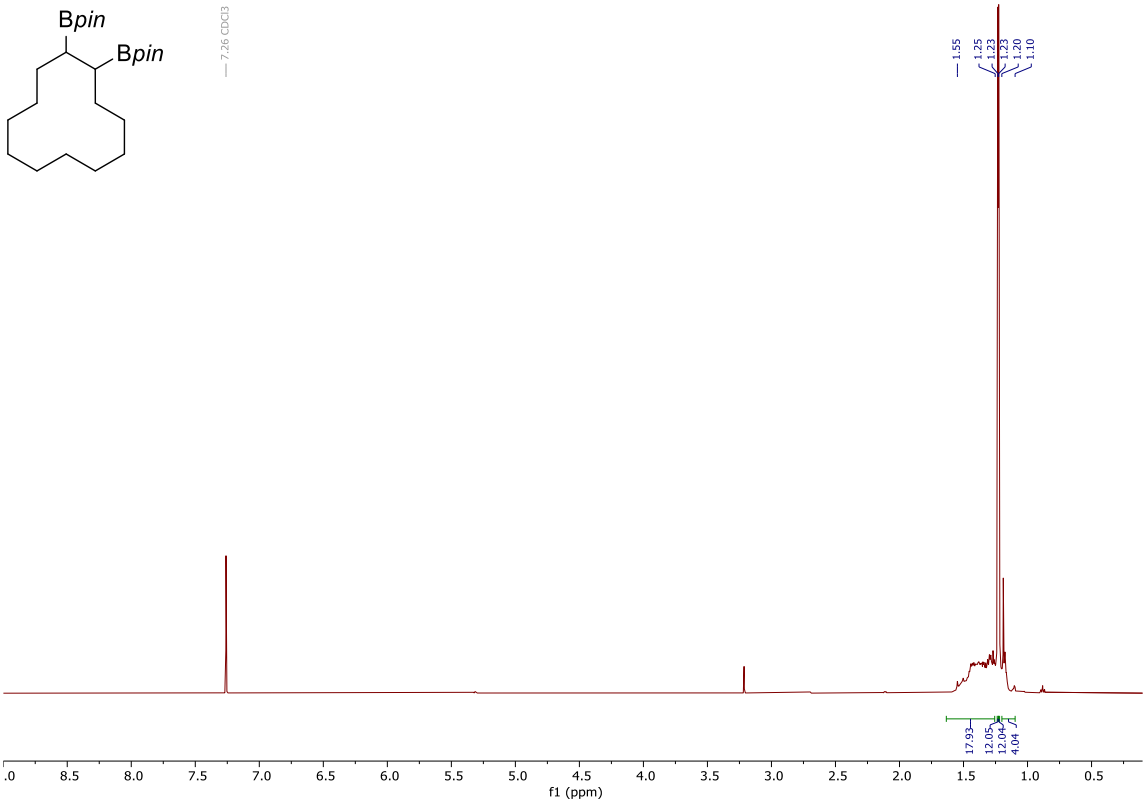
^{13}C NMR, $CDCl_3$, 126 MHz, 1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane **(S1h)**



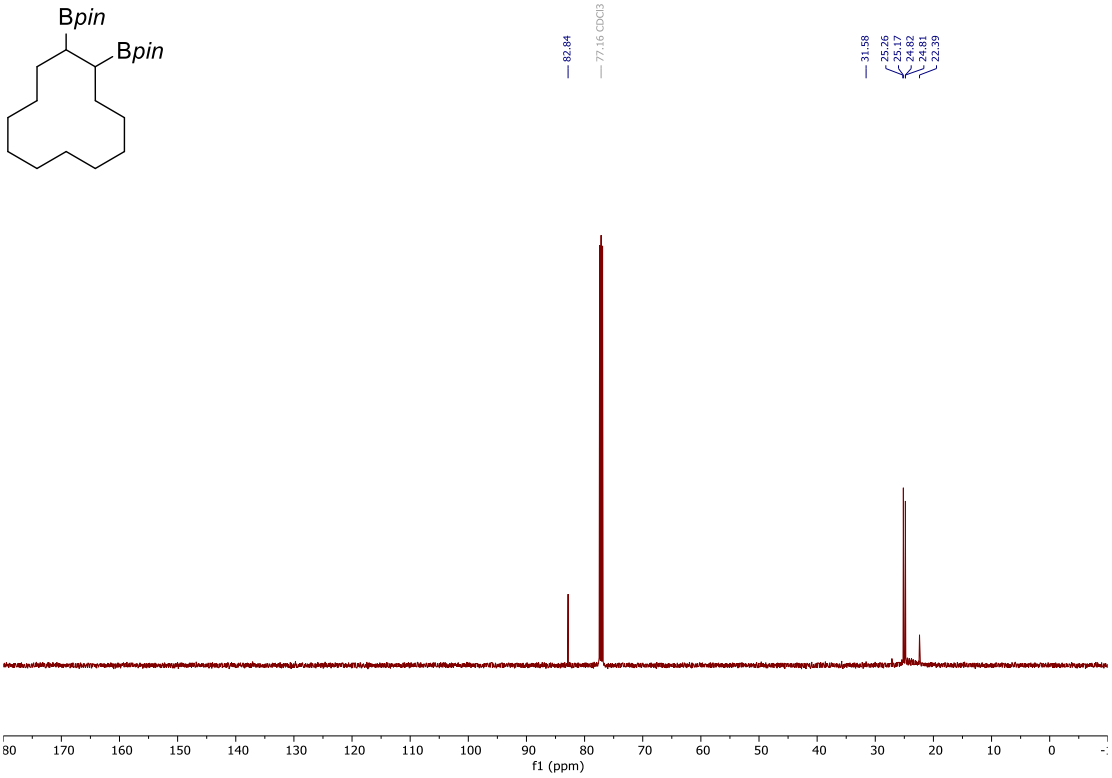
^{11}B NMR, $CDCl_3$, 161 MHz, 1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexane **(S1h)**



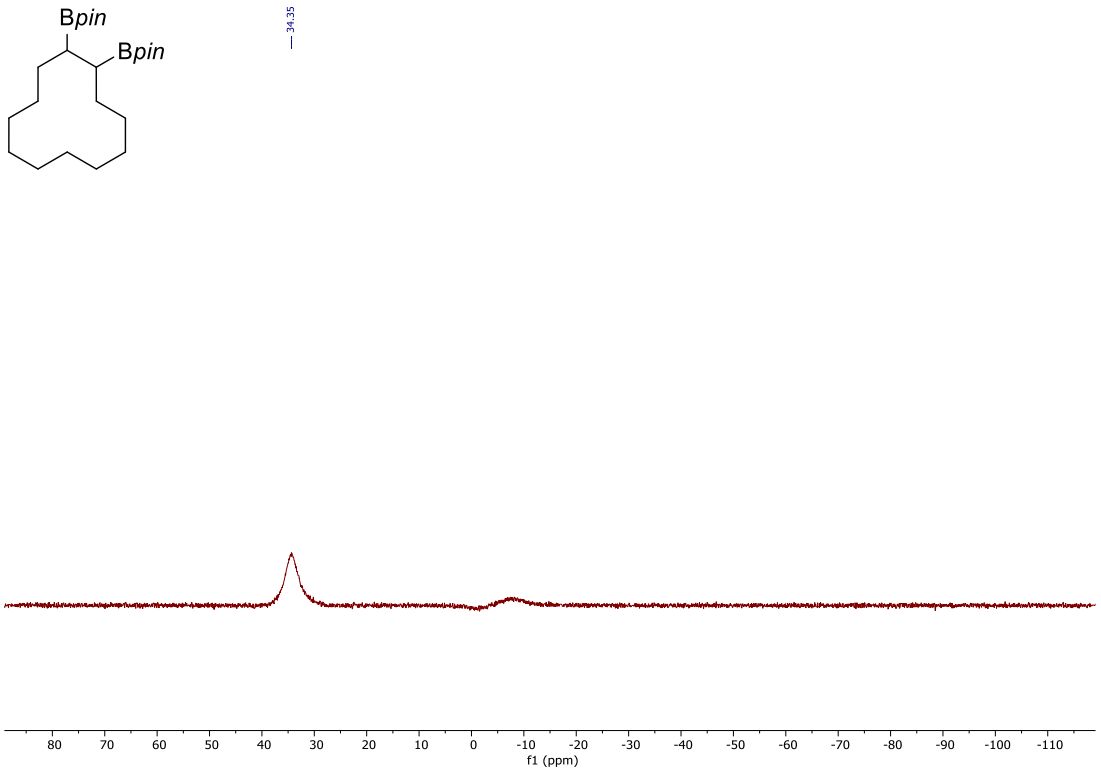
^{1}H NMR, $CDCl_3$, 501 MHz, 1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclo-dodecane **(S1i)**



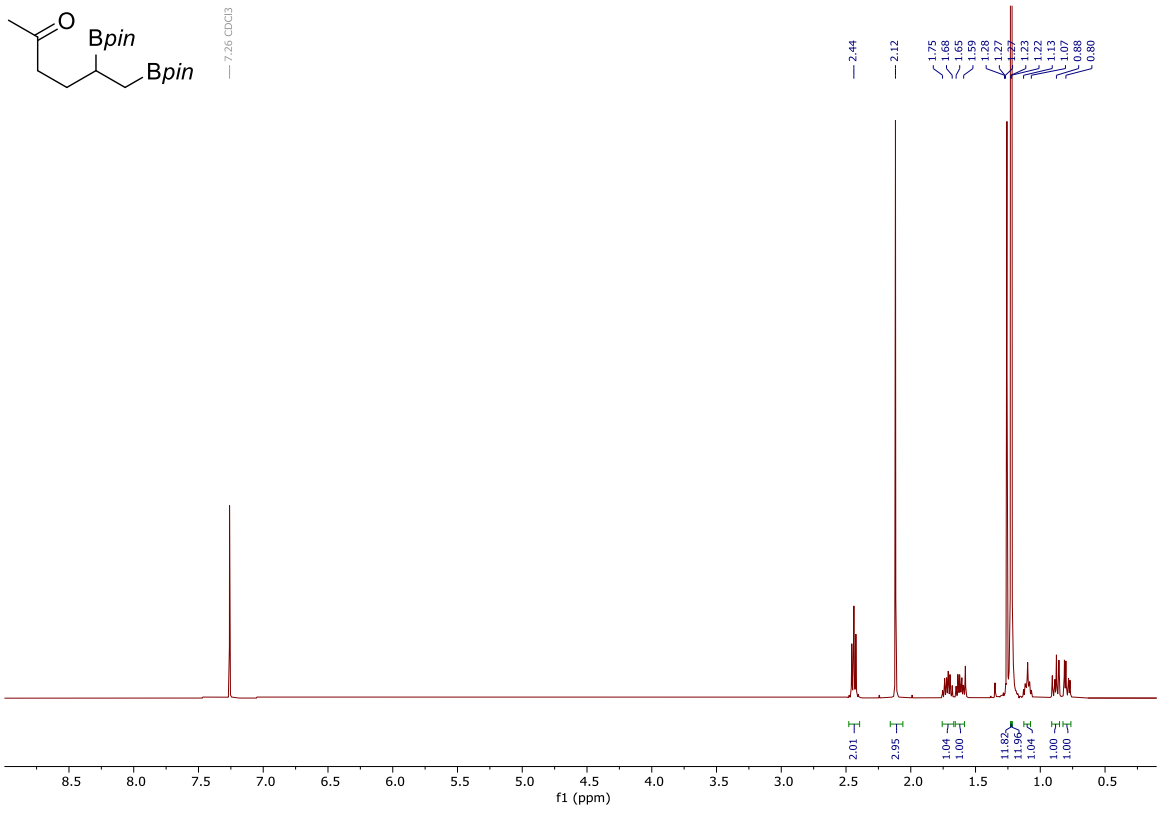
^{13}C NMR, $CDCl_3$, 126 MHz, 1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclo-dodecane **(S1i)**



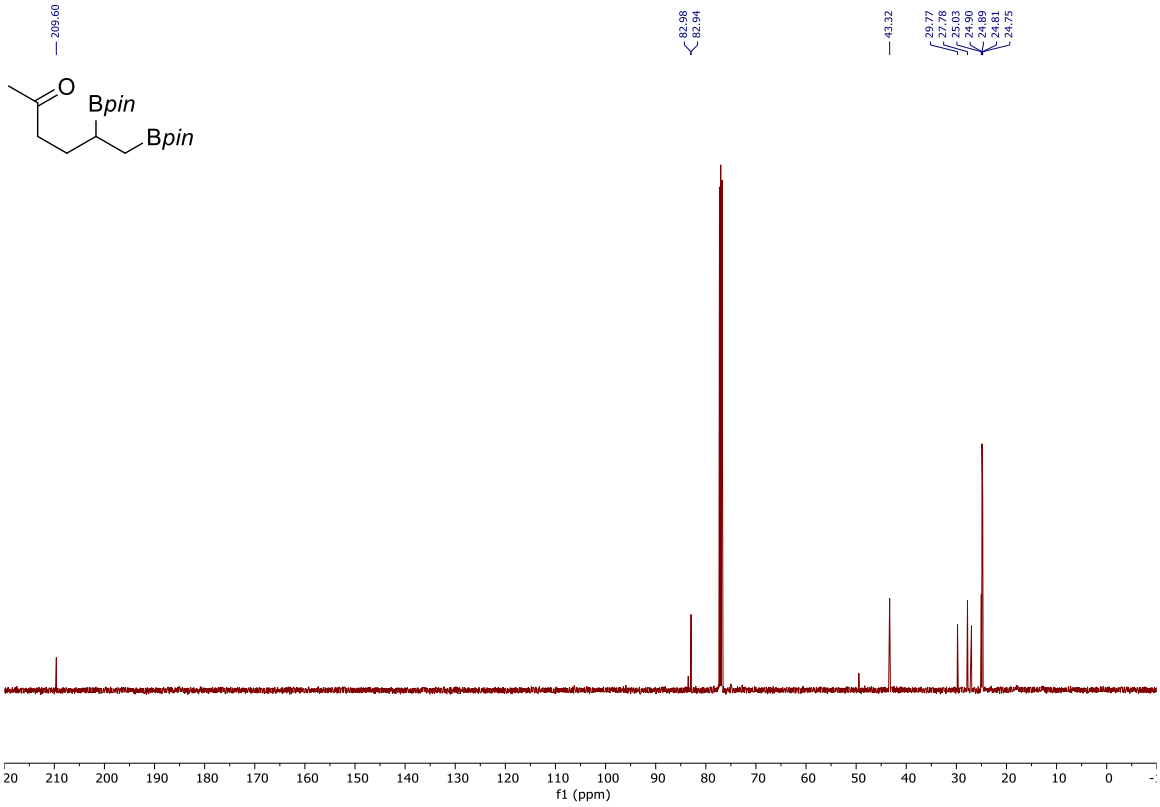
^{11}B NMR, $CDCl_3$, 161 MHz, 1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclo-dodecane **(S1i)**



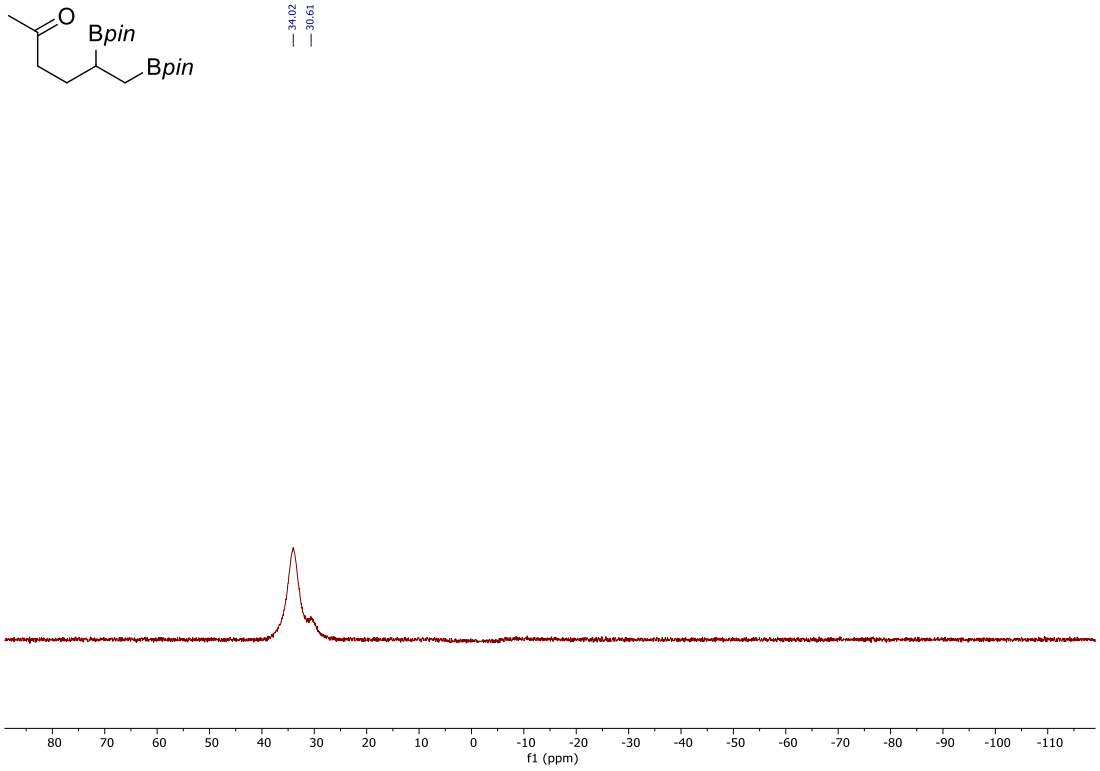
^{1}H NMR, $CDCl_3$, 501 MHz, 1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclo-dodecane **(S1j)**



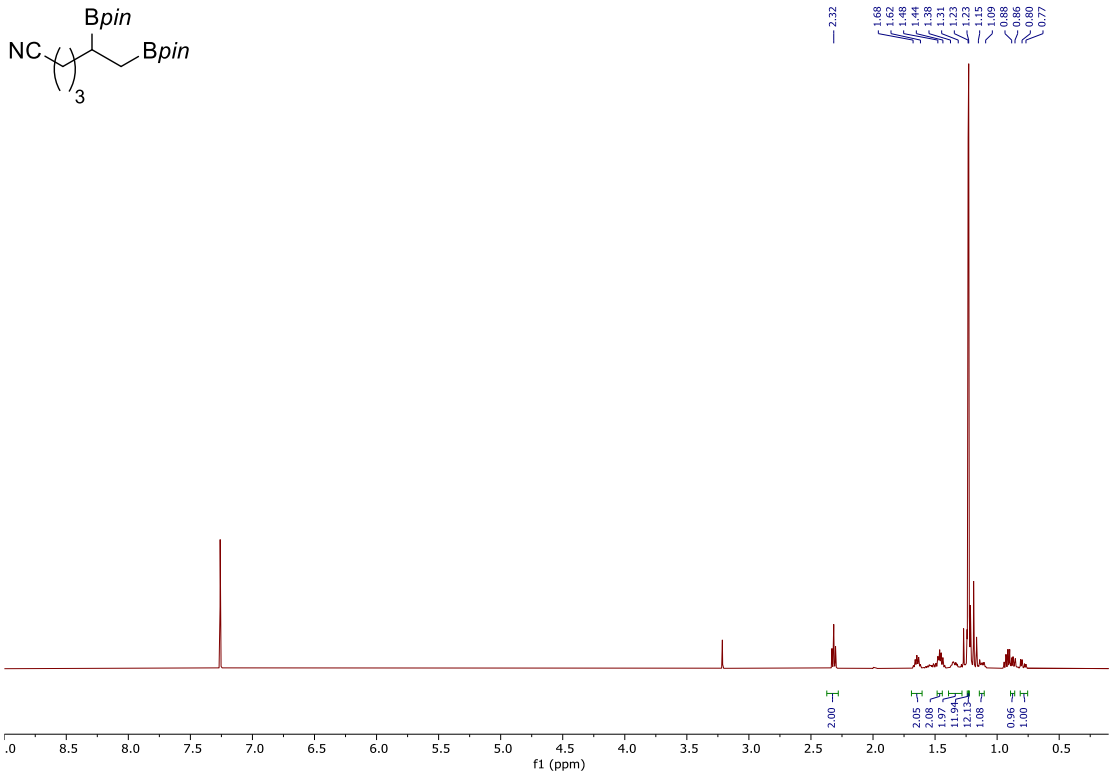
^{13}C NMR, $CDCl_3$, 126 MHz, 1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclo-dodecane **(S1j)**



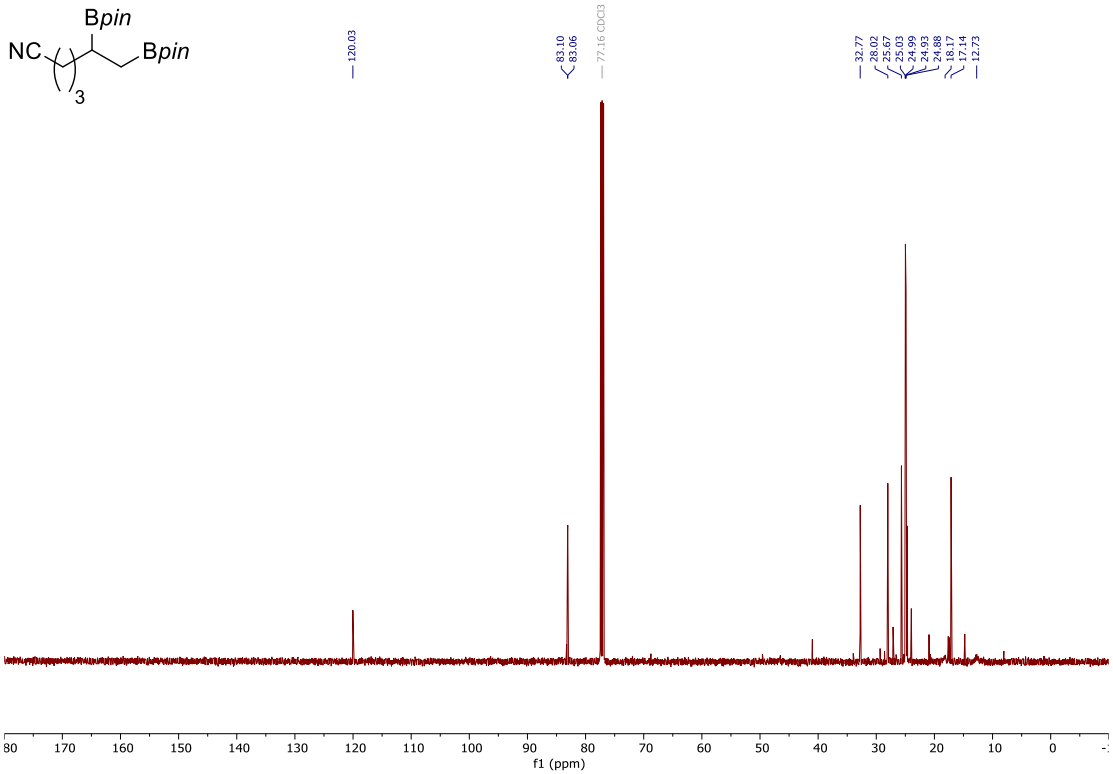
^{11}B NMR, $CDCl_3$, 161 MHz, 1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclo-dodecane **(S1j)**



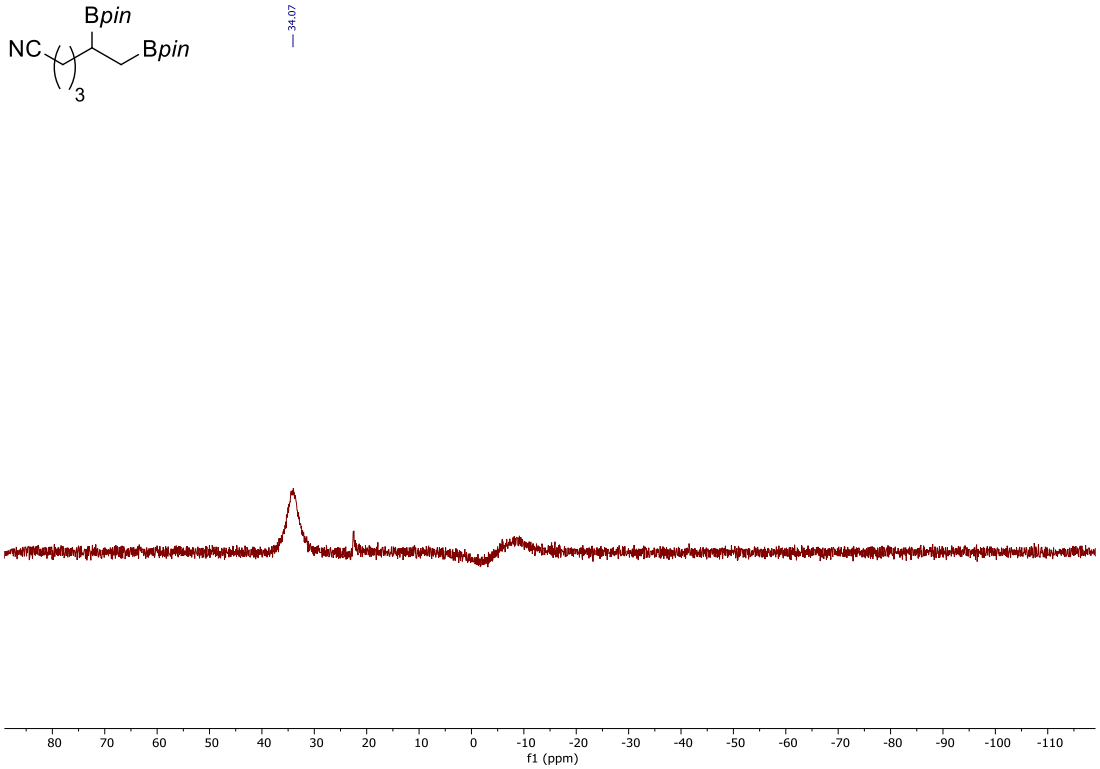
^{1}H NMR, $CDCl_3$, 501 MHz, 6,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptanenitrile **(S1k)**



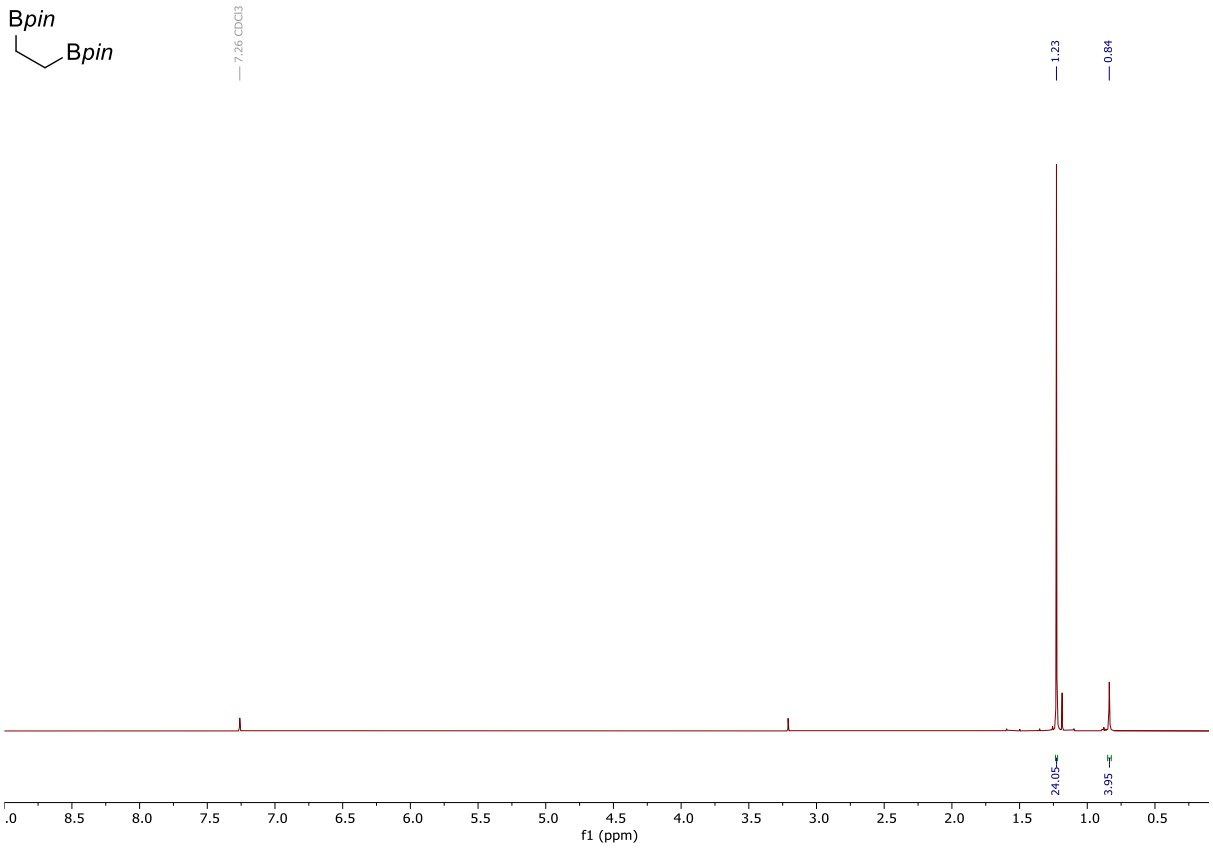
^{13}C NMR, $CDCl_3$, 126 MHz, 6,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptanenitrile **(S1k)**



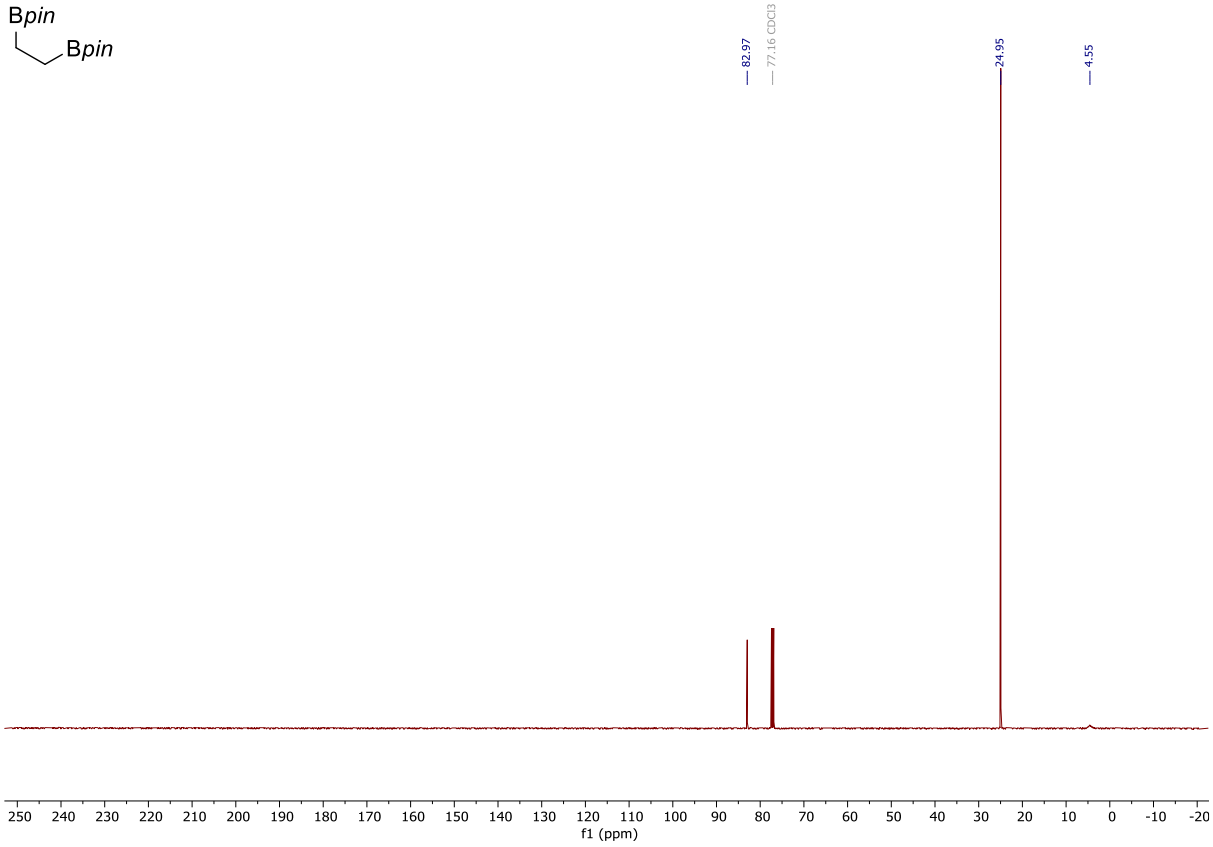
^{11}B NMR, $CDCl_3$, 161 MHz, 6,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptanenitrile **(S1k)**



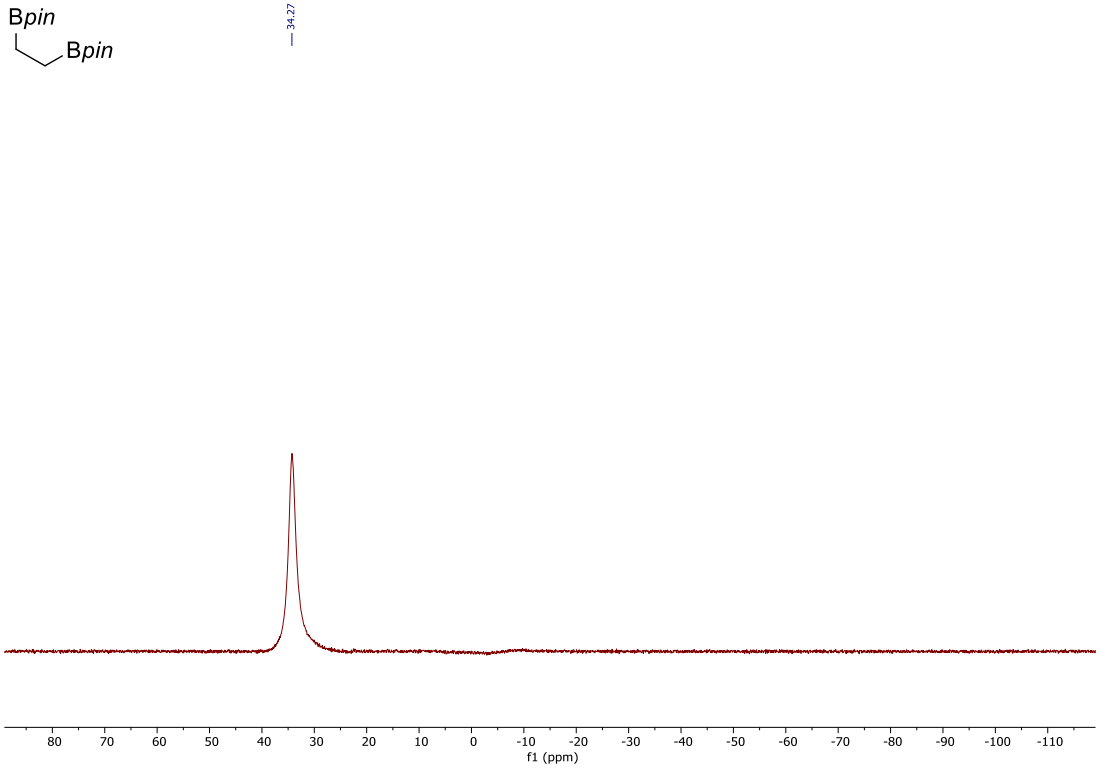
^{1}H NMR, $CDCl_3$, 501 MHz, 1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane **(S1l)**



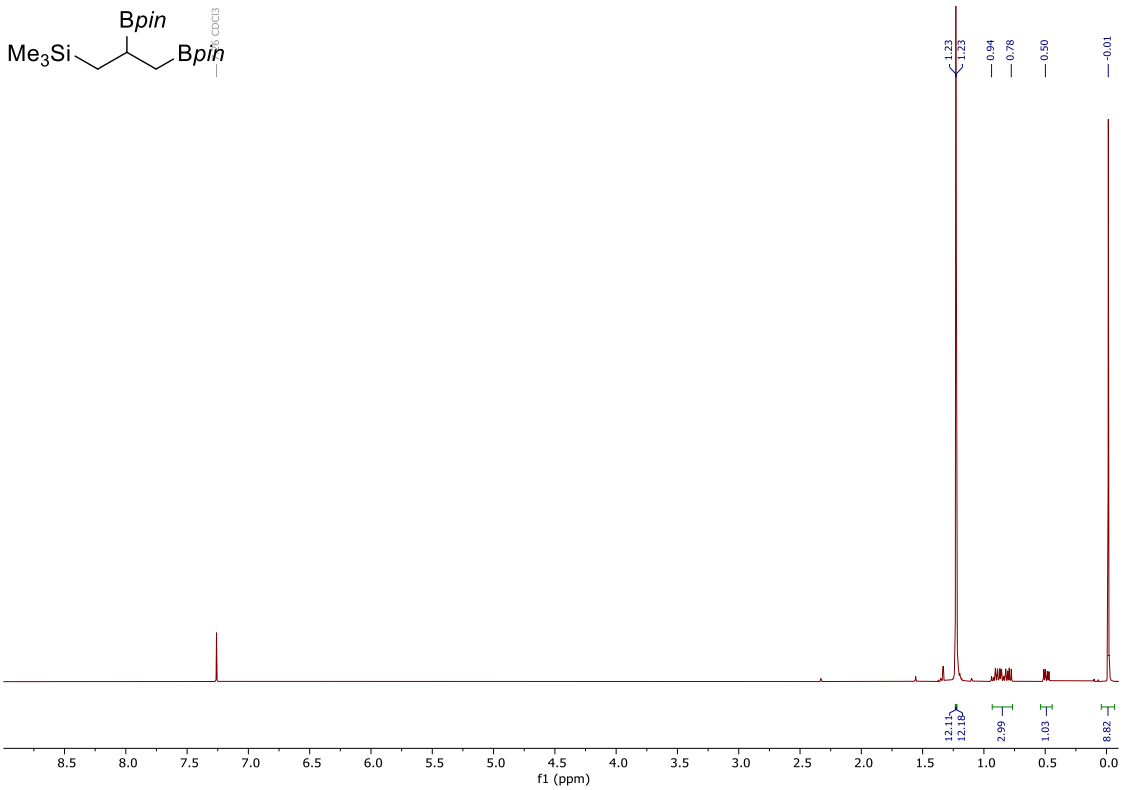
^{13}C NMR, $CDCl_3$, 126 MHz, 1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane (**S1l**)



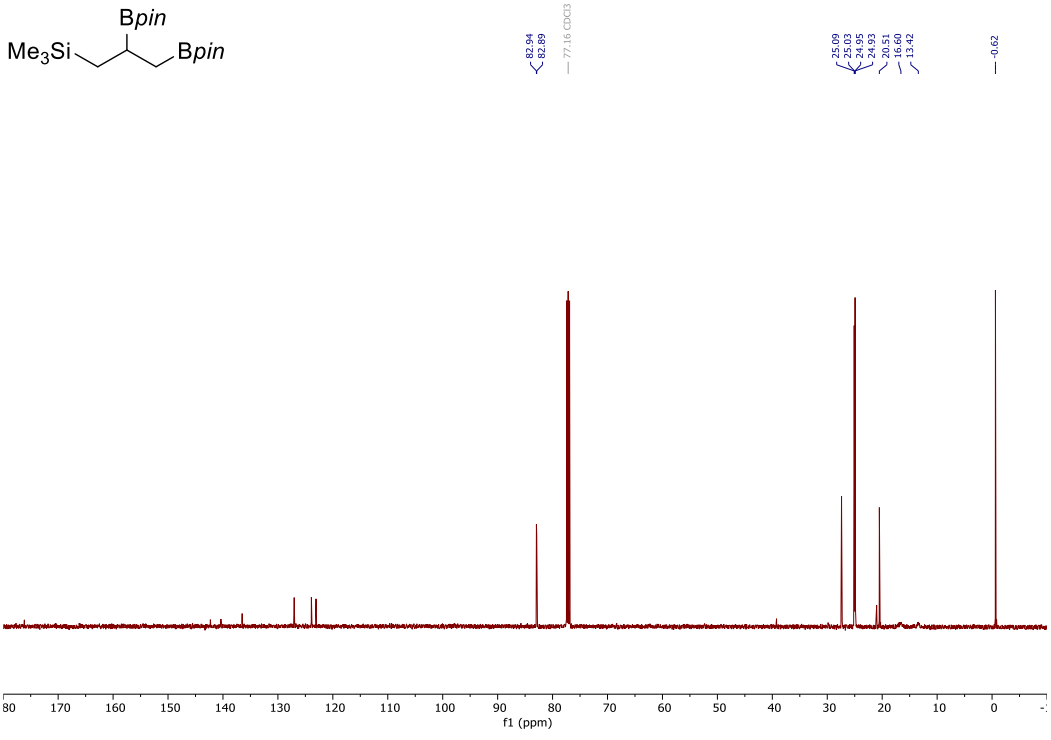
^{11}B NMR, $CDCl_3$, 161 MHz, 1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane (**S1l**)



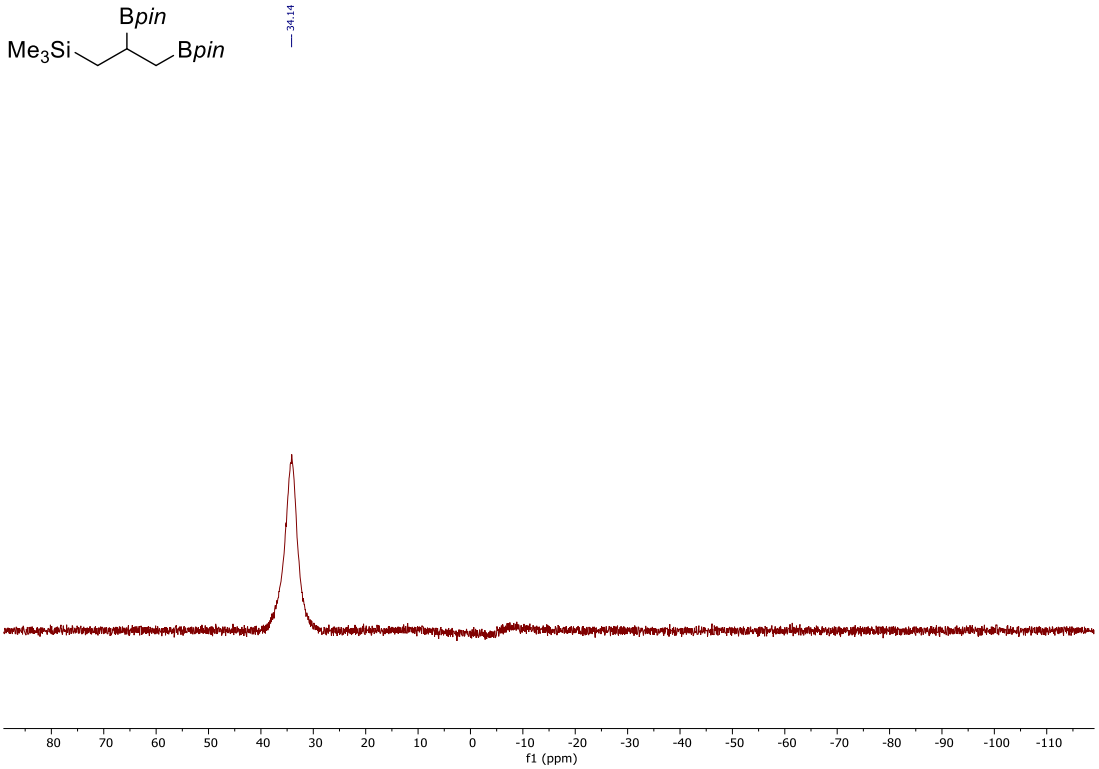
^{1}H NMR, $CDCl_3$, 501 MHz, (2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl) trimethylsilane **(S1m)**



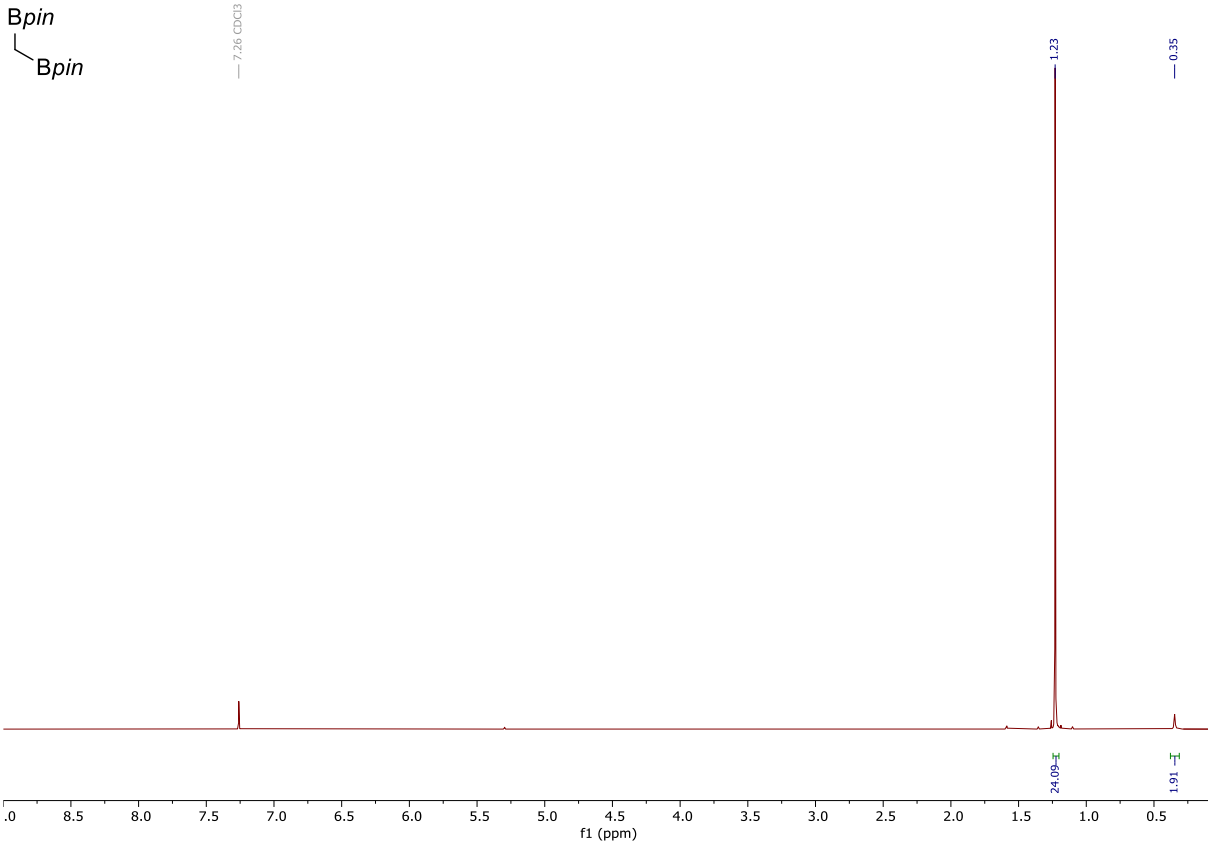
^{13}C NMR, $CDCl_3$, 126 MHz, (2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl) trimethylsilane **(S1m)**



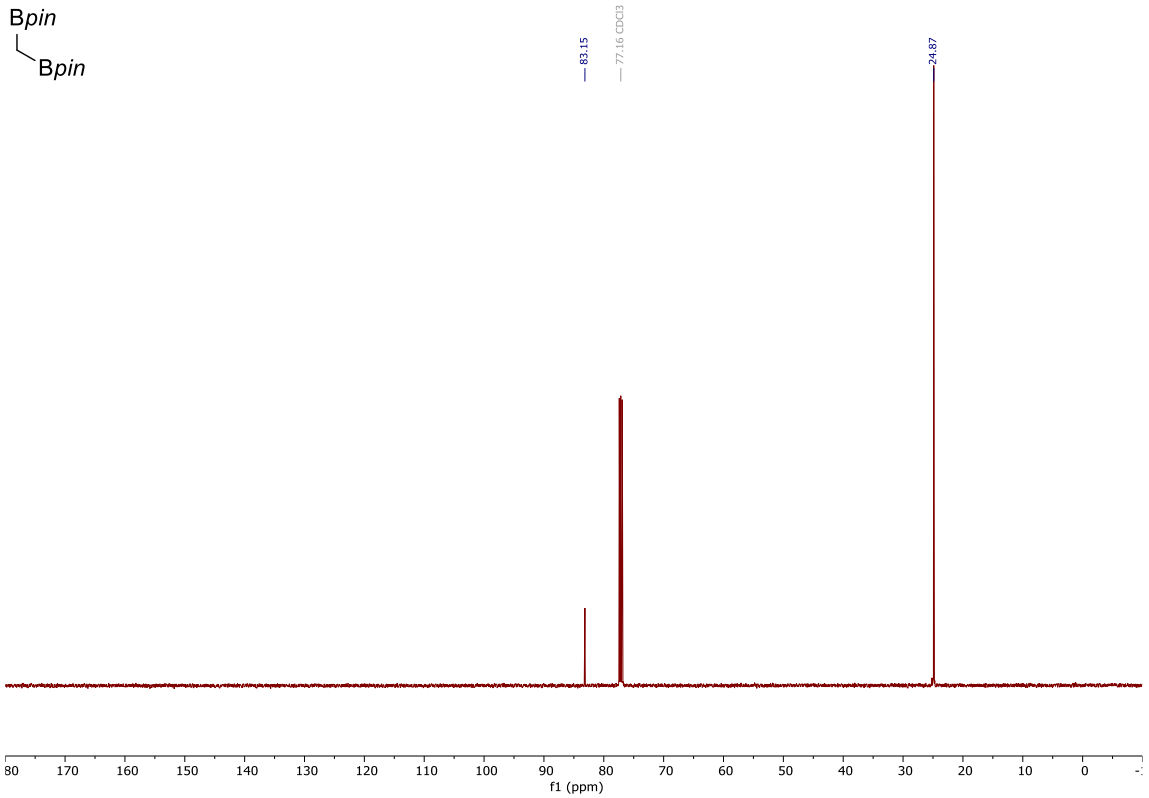
^{11}B NMR, $CDCl_3$, 161 MHz, (2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl) trimethylsilane **(S1m)**



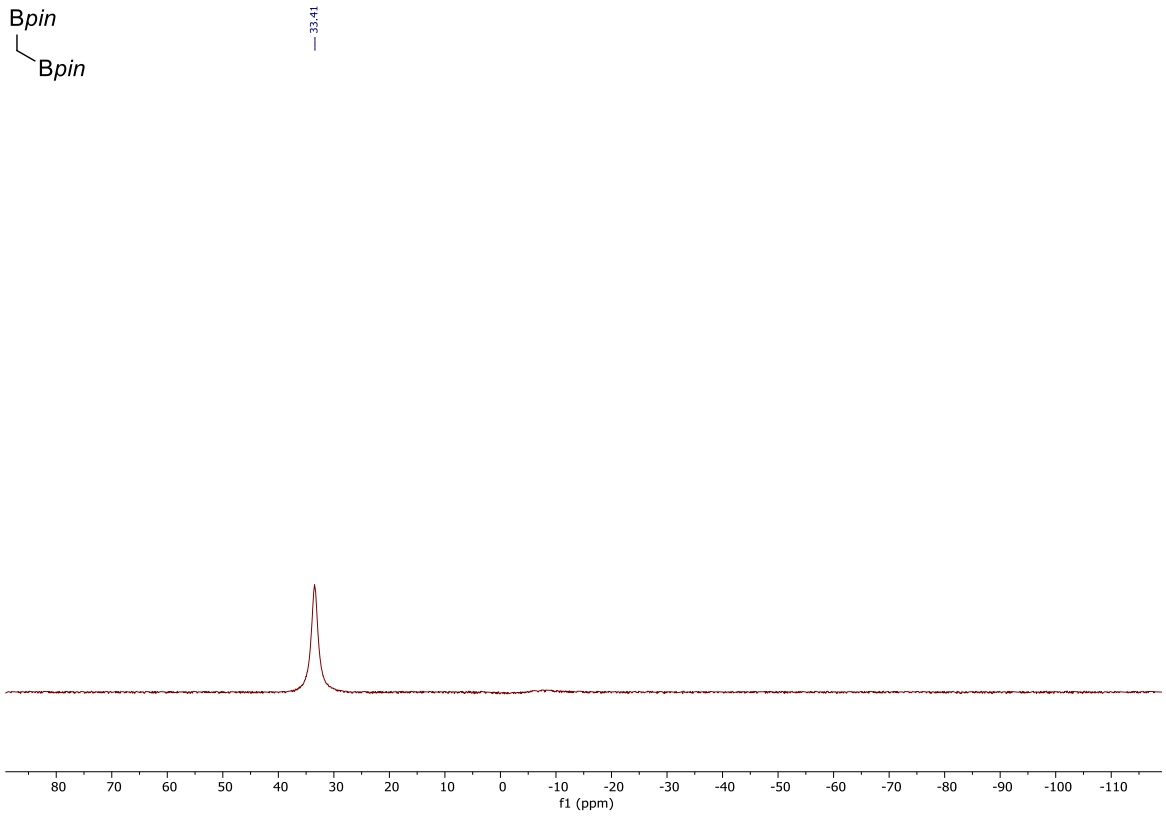
^{1}H NMR, $CDCl_3$, 501 MHz, Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methan**e (S1n)**



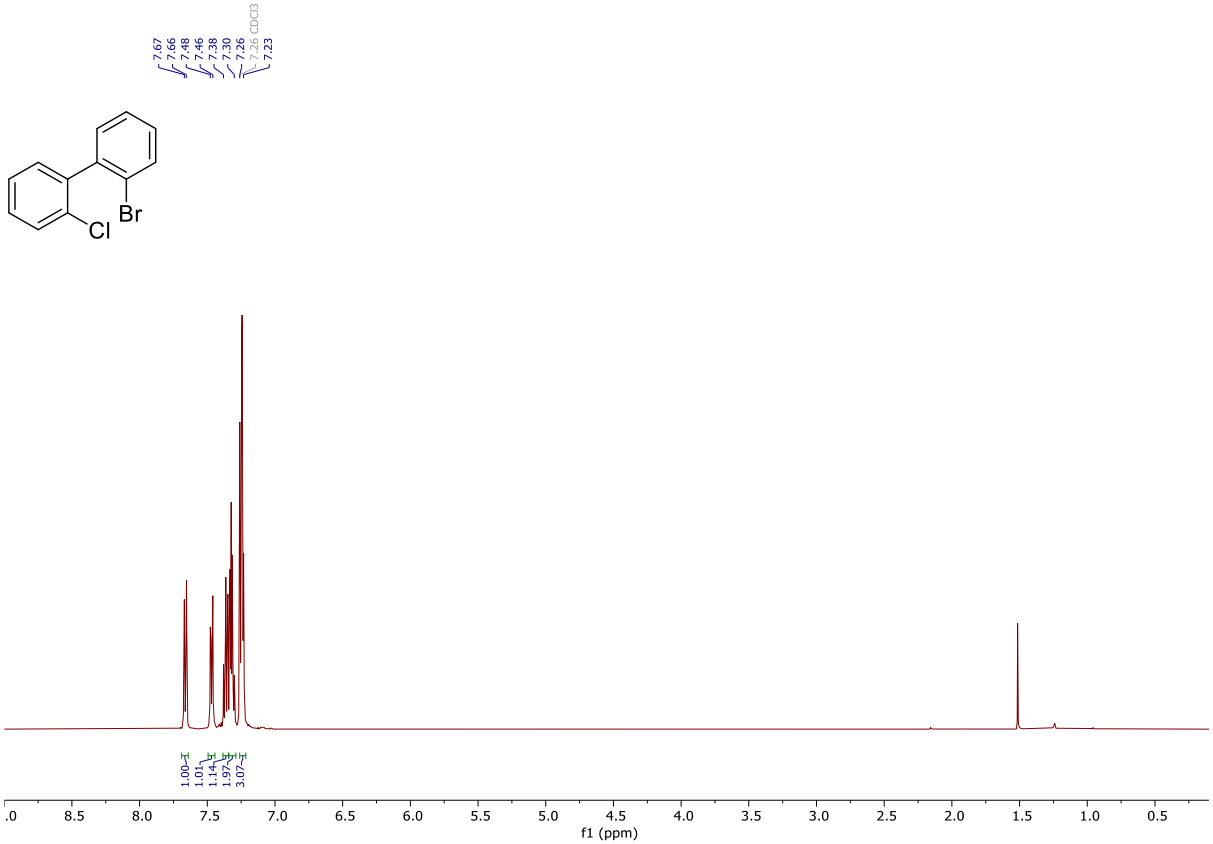
^{13}C NMR, $CDCl_3$, 126 MHz, Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methan**e (S1n)**



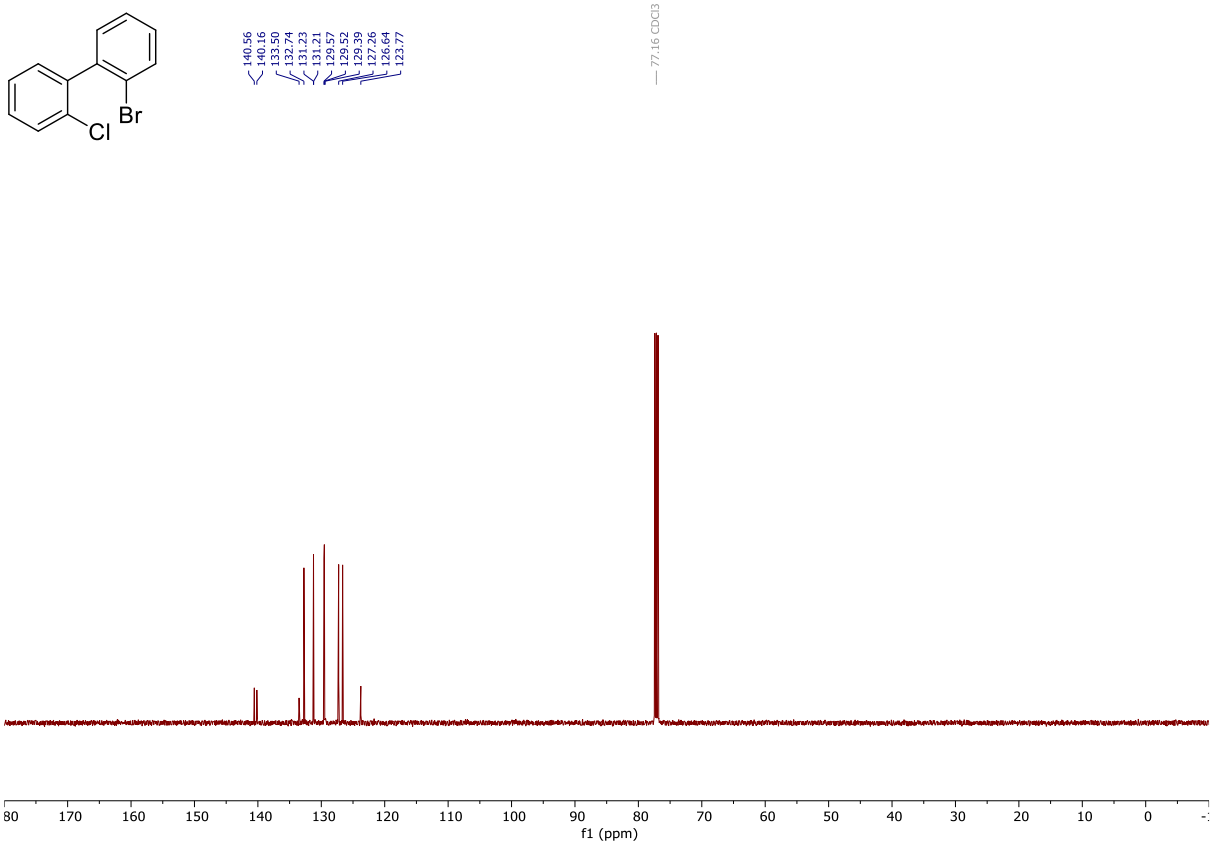
^{11}B NMR, $CDCl_3$, 161 MHz, Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methan**e (S1n)**



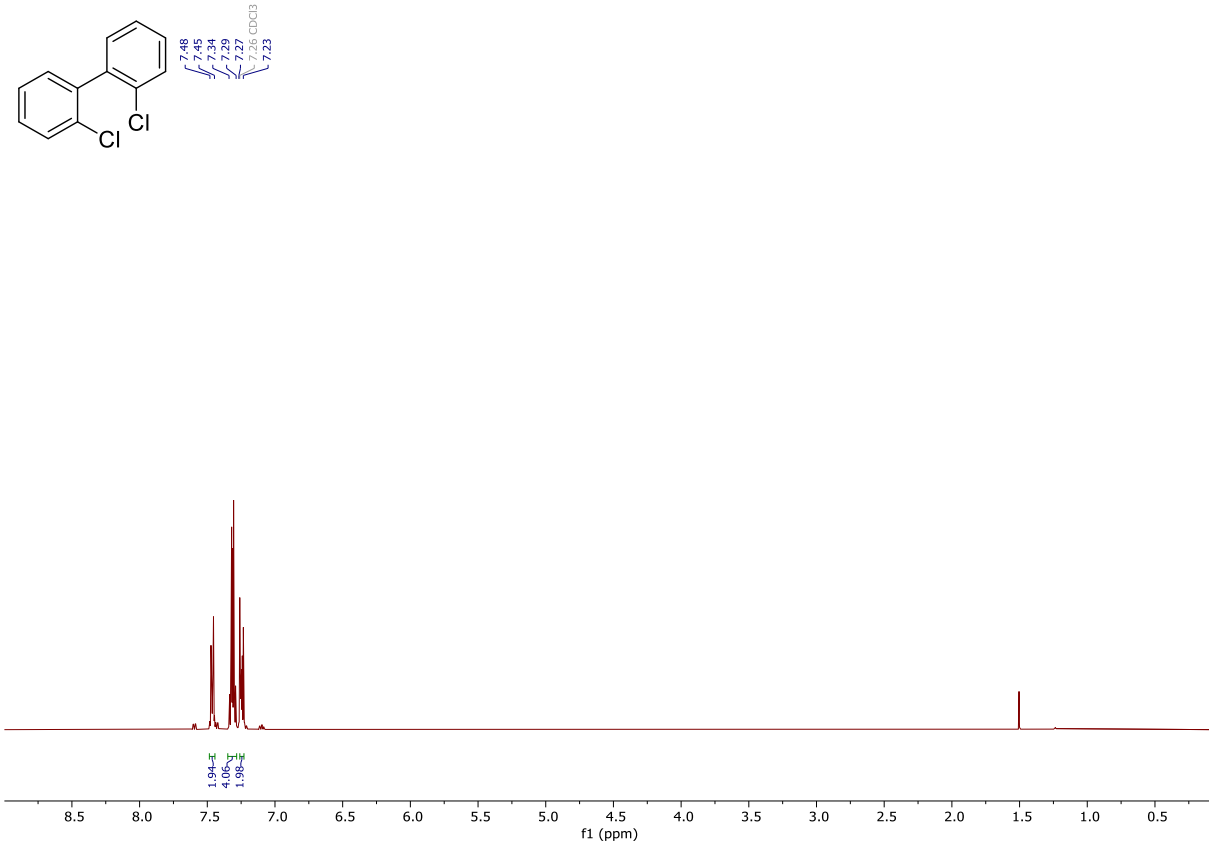
^{1}H NMR, $CDCl_3$, 501 MHz, 2-bromo-2'-chloro-1,1'-biphenyl (**2**)



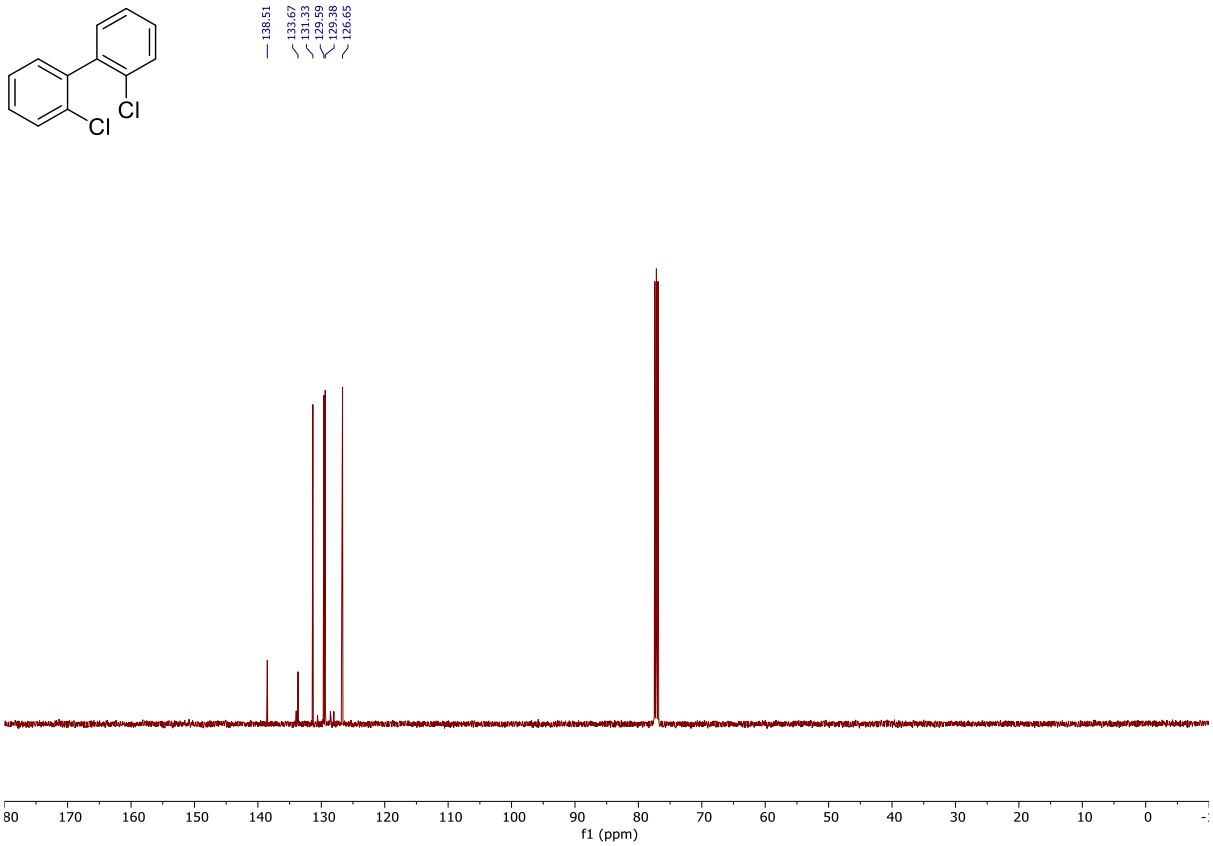
^{13}C NMR, $CDCl_3$, 126 MHz, 2-bromo-2'-chloro-1,1'-biphenyl (**2**)



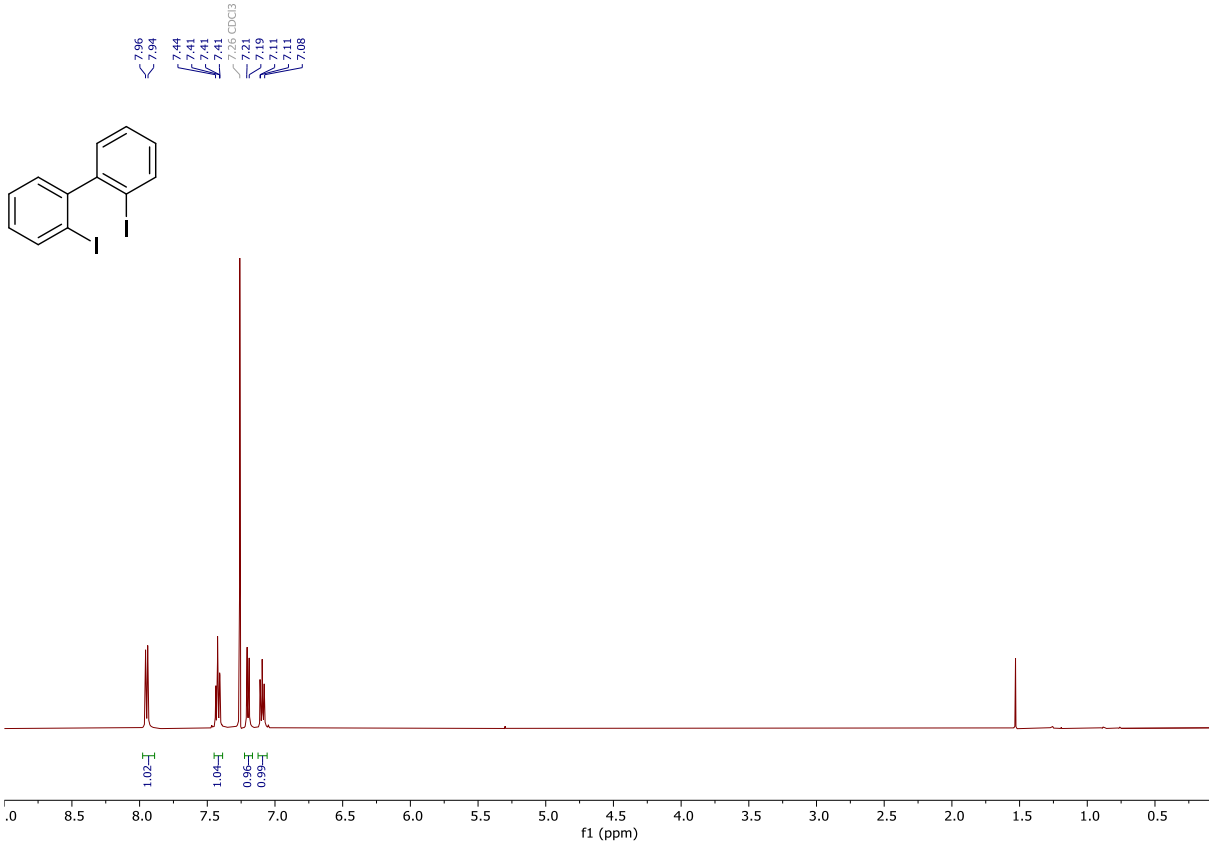
^{1}H NMR, $CDCl_3$, 501 MHz, 2,2'-dichloro-1,1'-biphenyl (**2b**)



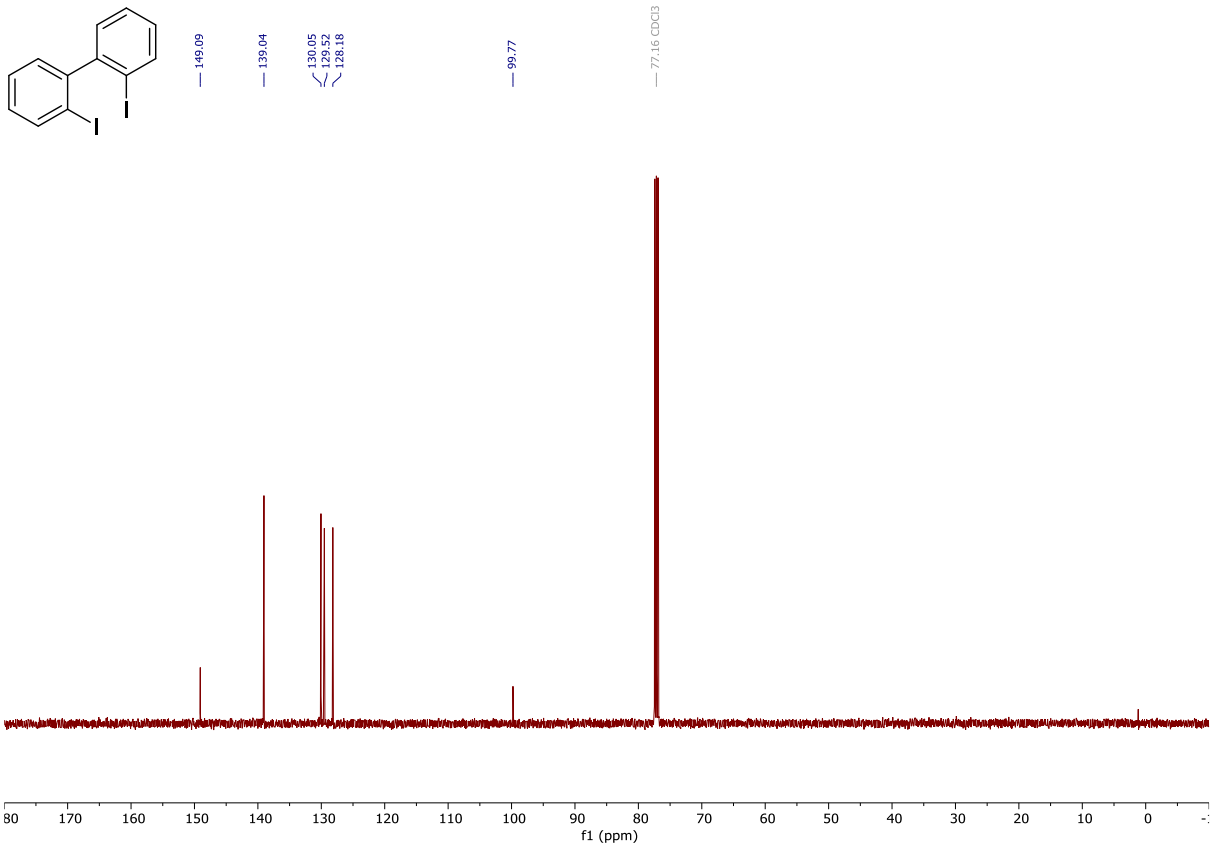
^{13}C NMR, $CDCl_3$, 126 MHz, 2,2'-dichloro-1,1'-biphenyl (**2b**)



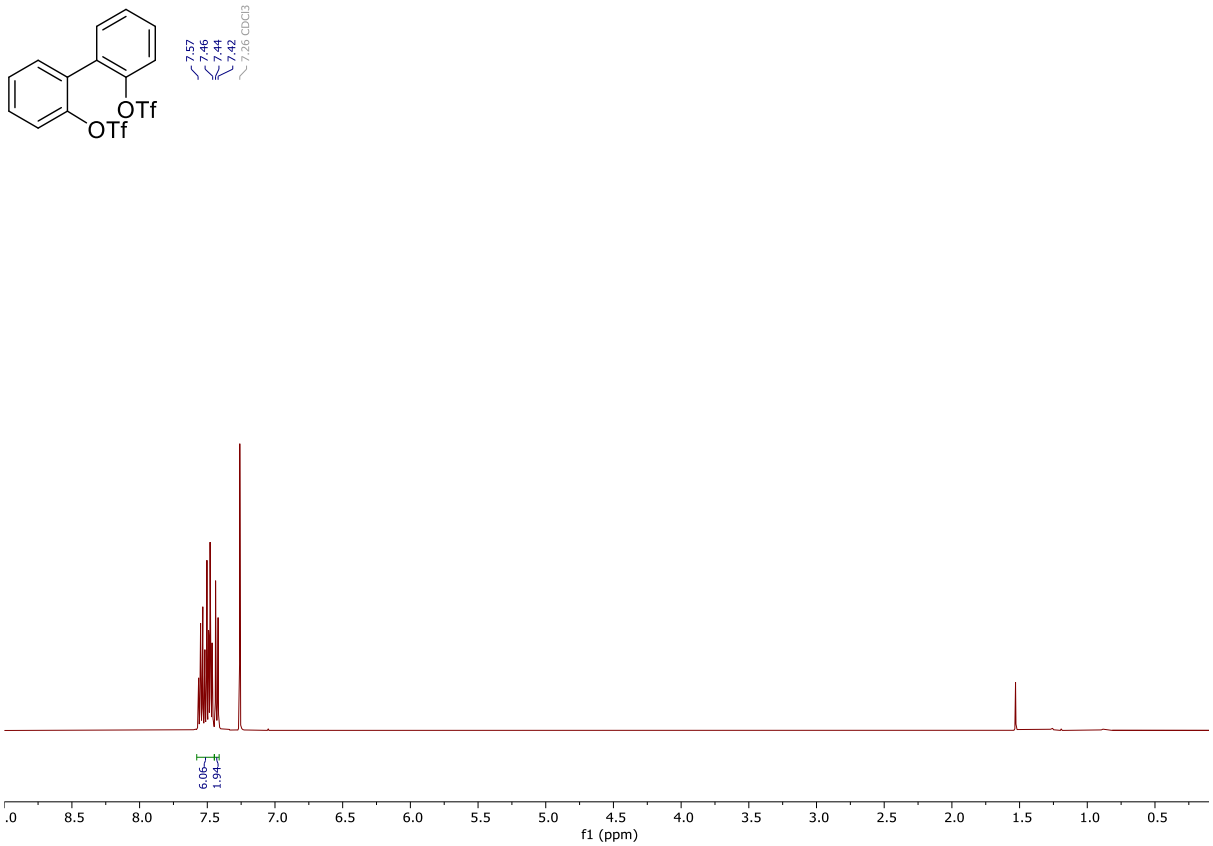
^{1}H NMR, $CDCl_3$, 501 MHz, 2,2'-diiodo-1,1'-biphenyl (**2c**)



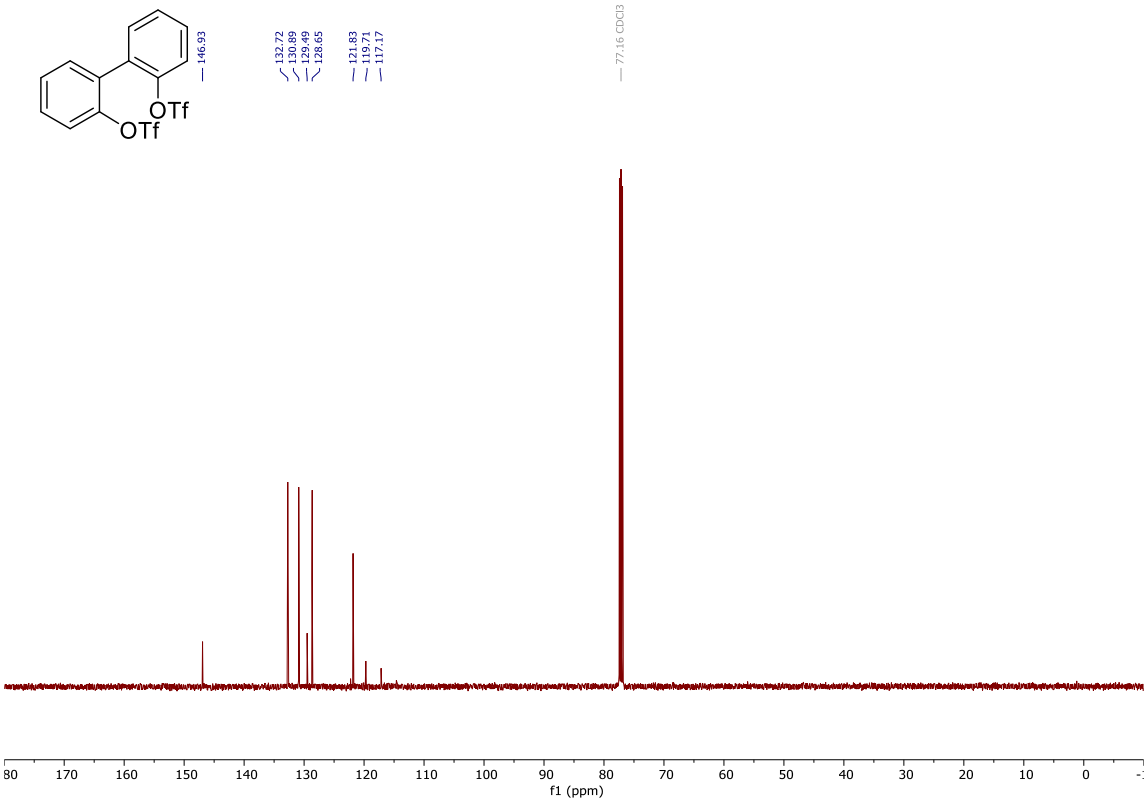
^{13}C NMR, $CDCl_3$, 126 MHz, 2,2'-diiodo-1,1'-biphenyl (**2c**)



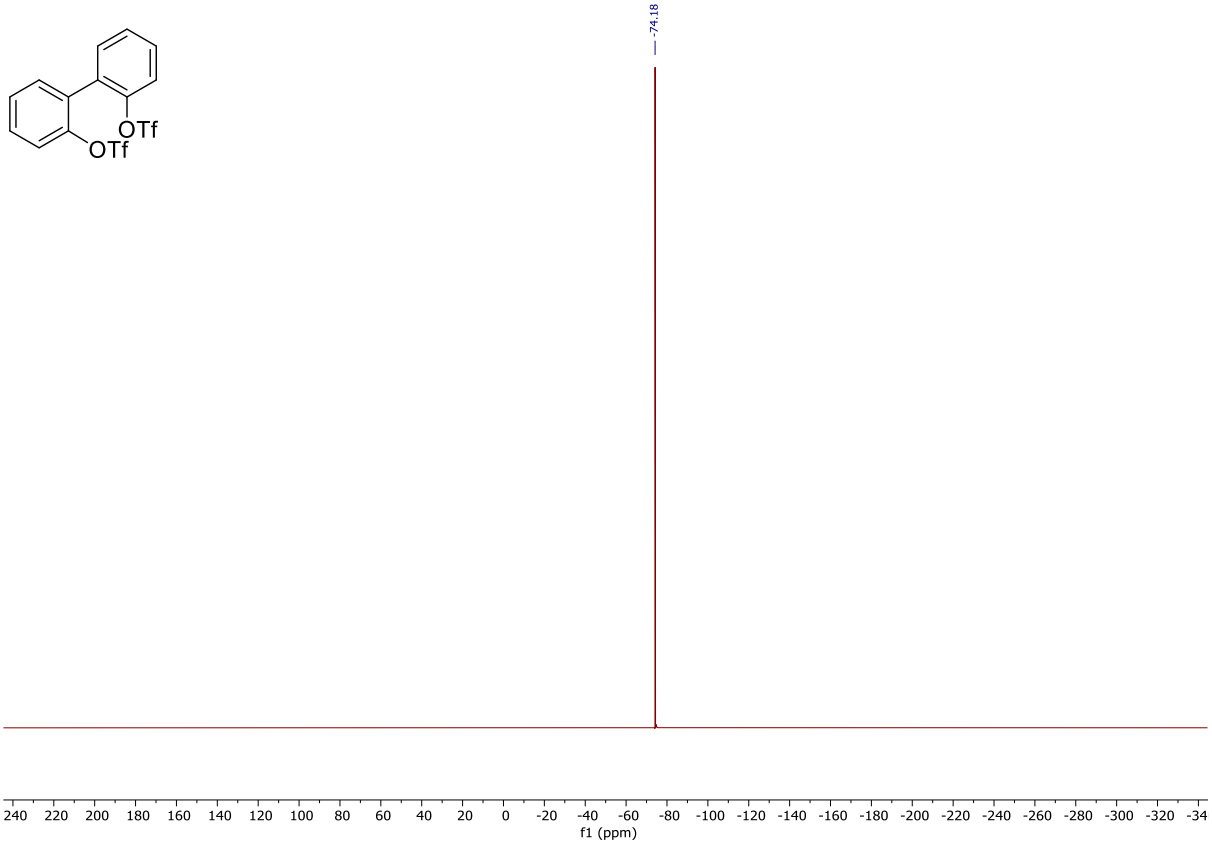
^{1}H NMR, $CDCl_3$, 501 MHz, [1,1'-biphenyl]-2,2'-diyl bis(trifluoromethanesulfonate) (**2d**)



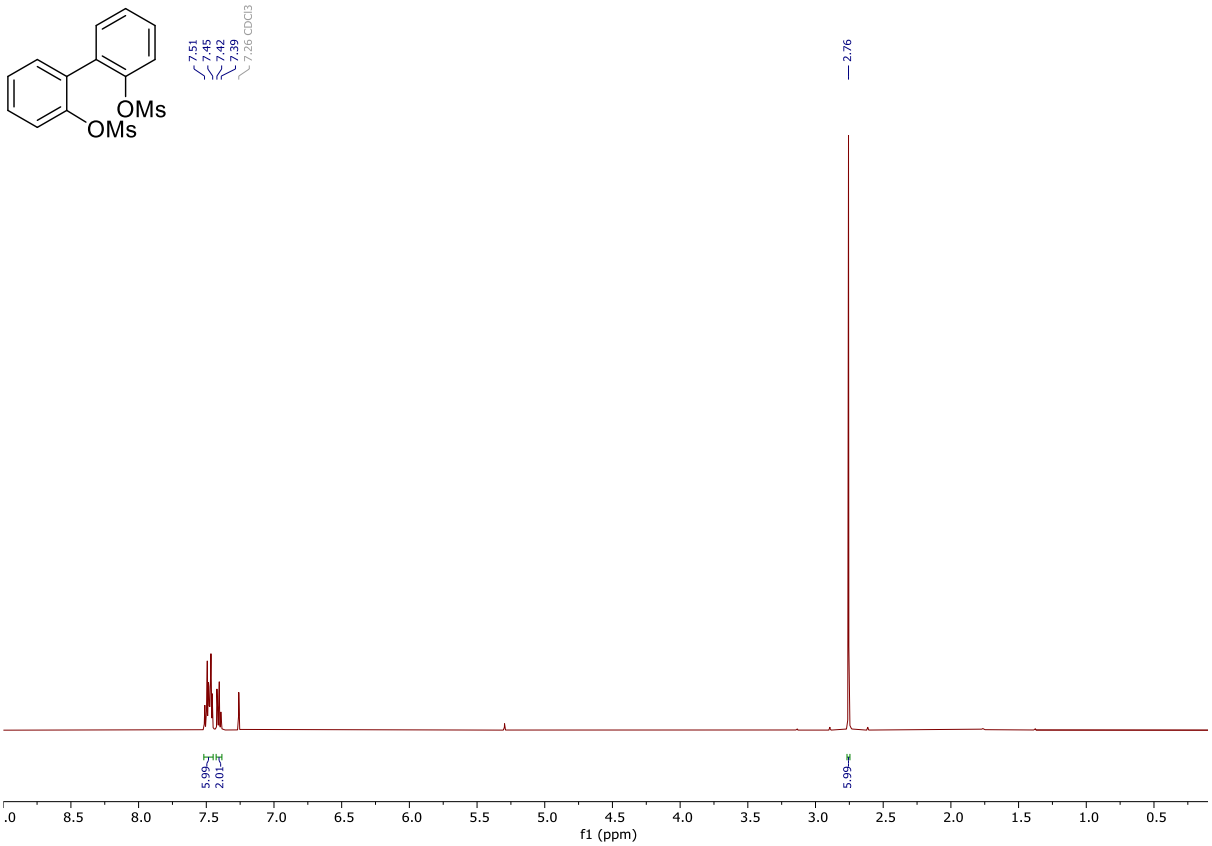
^{13}C NMR, $CDCl_3$, 126 MHz, [1,1'-biphenyl]-2,2'-diyl bis(trifluoromethanesulfonate) (**2d**)



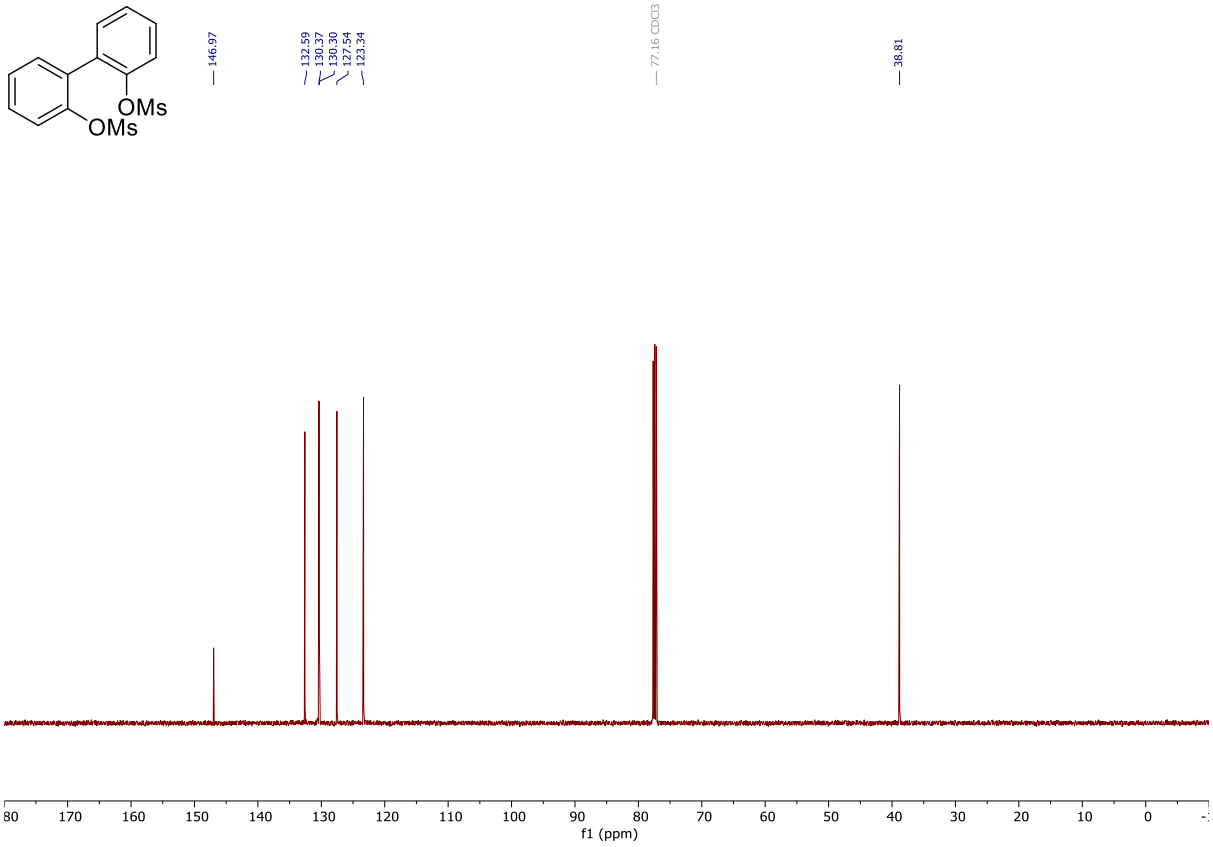
^{19}F NMR, $CDCl_3$, 471 MHz, [1,1'-biphenyl]-2,2'-diyl bis(trifluoromethanesulfonate) (**2d**)



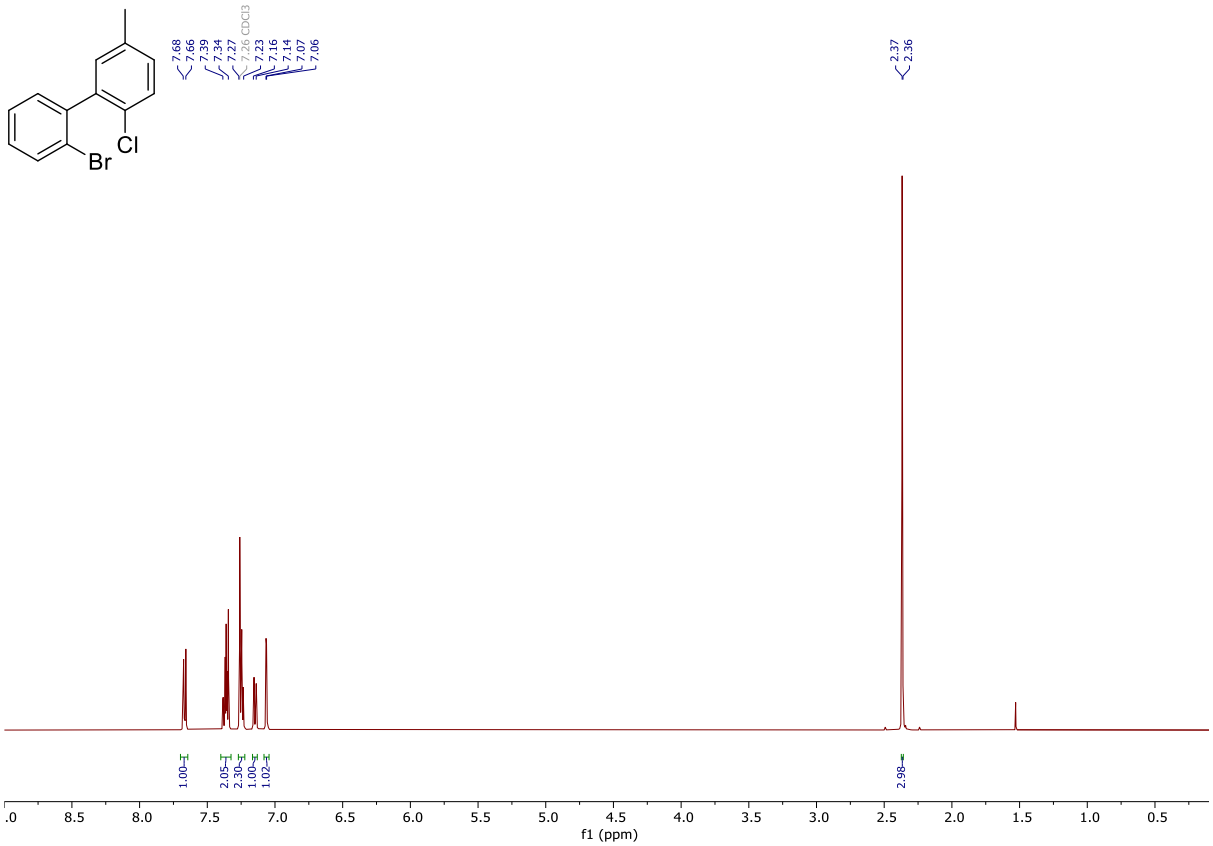
^{1}H NMR, $CDCl_3$, 501 MHz, [1,1'-biphenyl]-2,2'-diyl bis(trifluoromethanesulfonate) (**2e**)



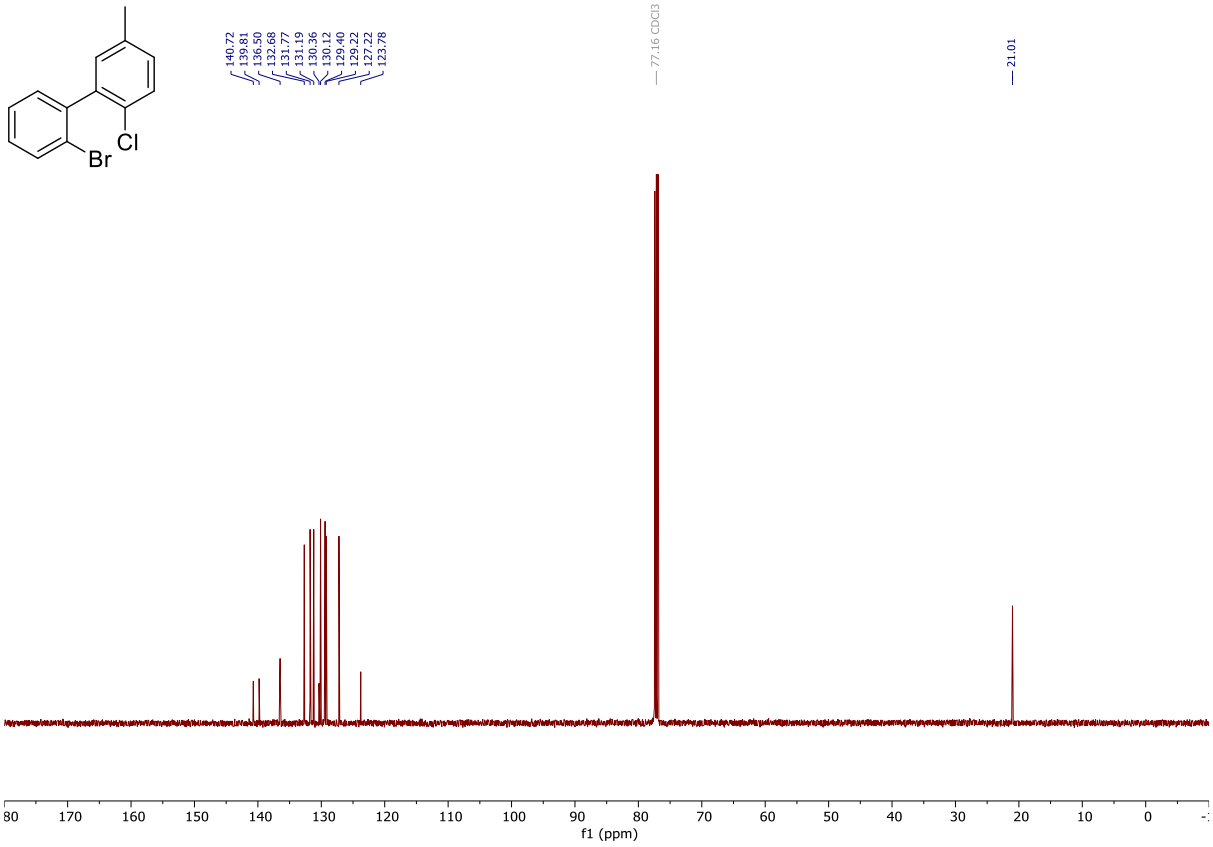
^{13}C NMR, $CDCl_3$, 126 MHz, [1,1'-biphenyl]-2,2'-diyl bis(trifluoromethanesulfonate) (**2e**)



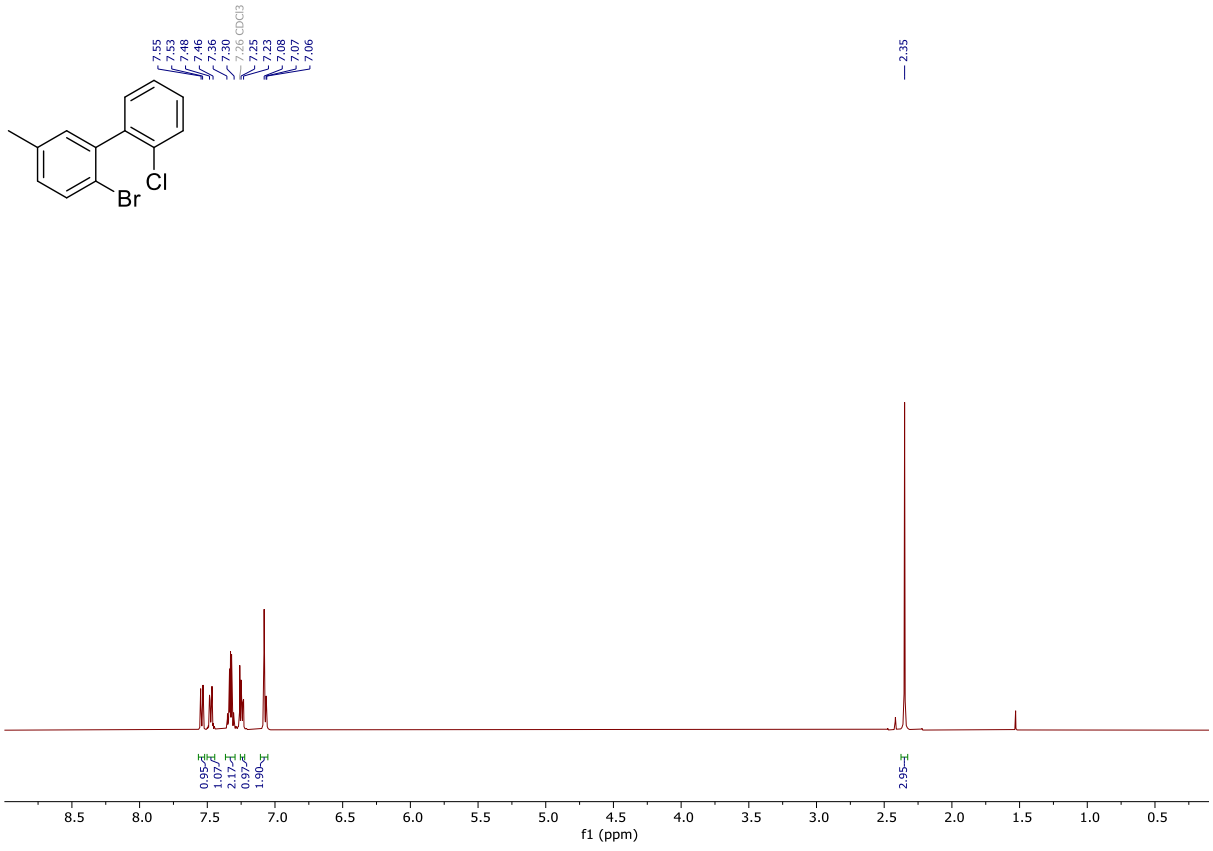
^{1}H NMR, $CDCl_3$, 501 MHz, 2'-bromo-2-chloro-5-methyl-1,1'-biphenyl (**S2a**)



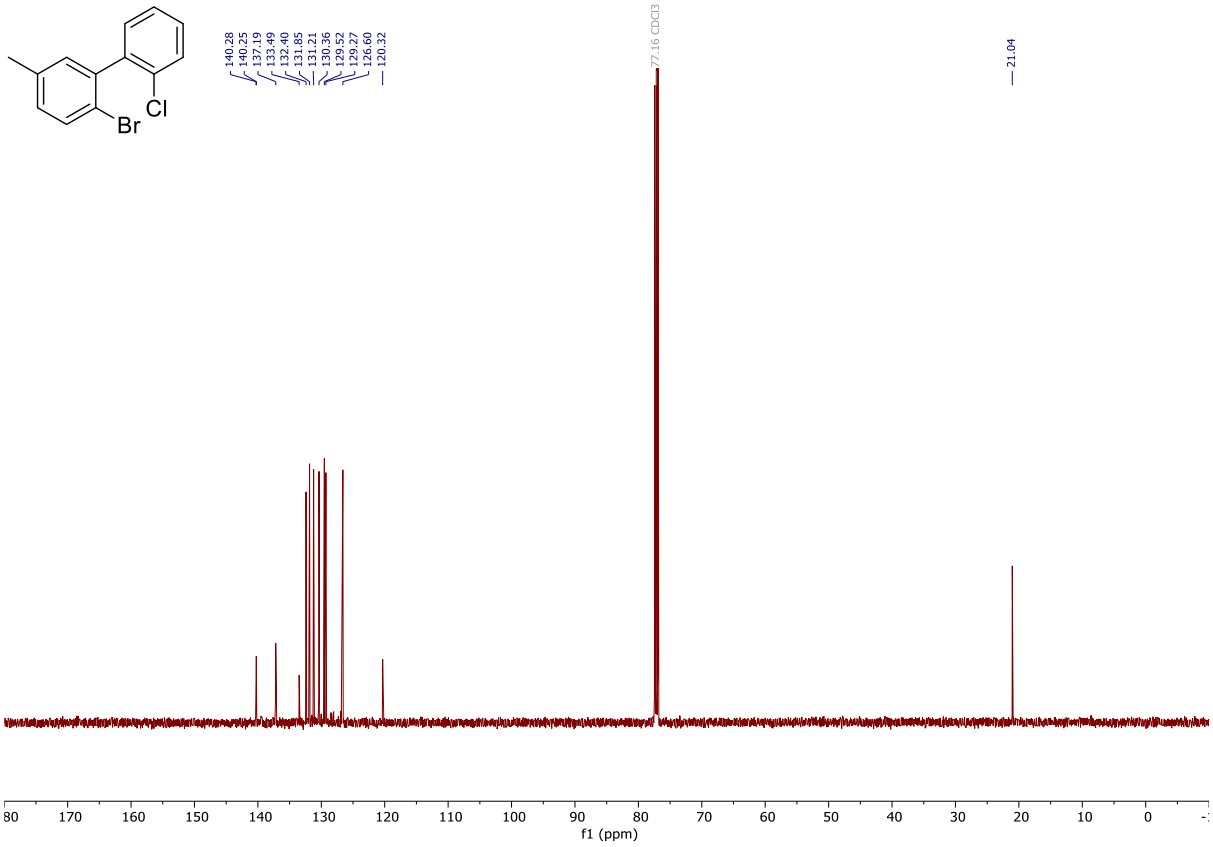
^{13}C NMR, $CDCl_3$, 126 MHz, 2'-bromo-2-chloro-5-methyl-1,1'-biphenyl (**S2a**)



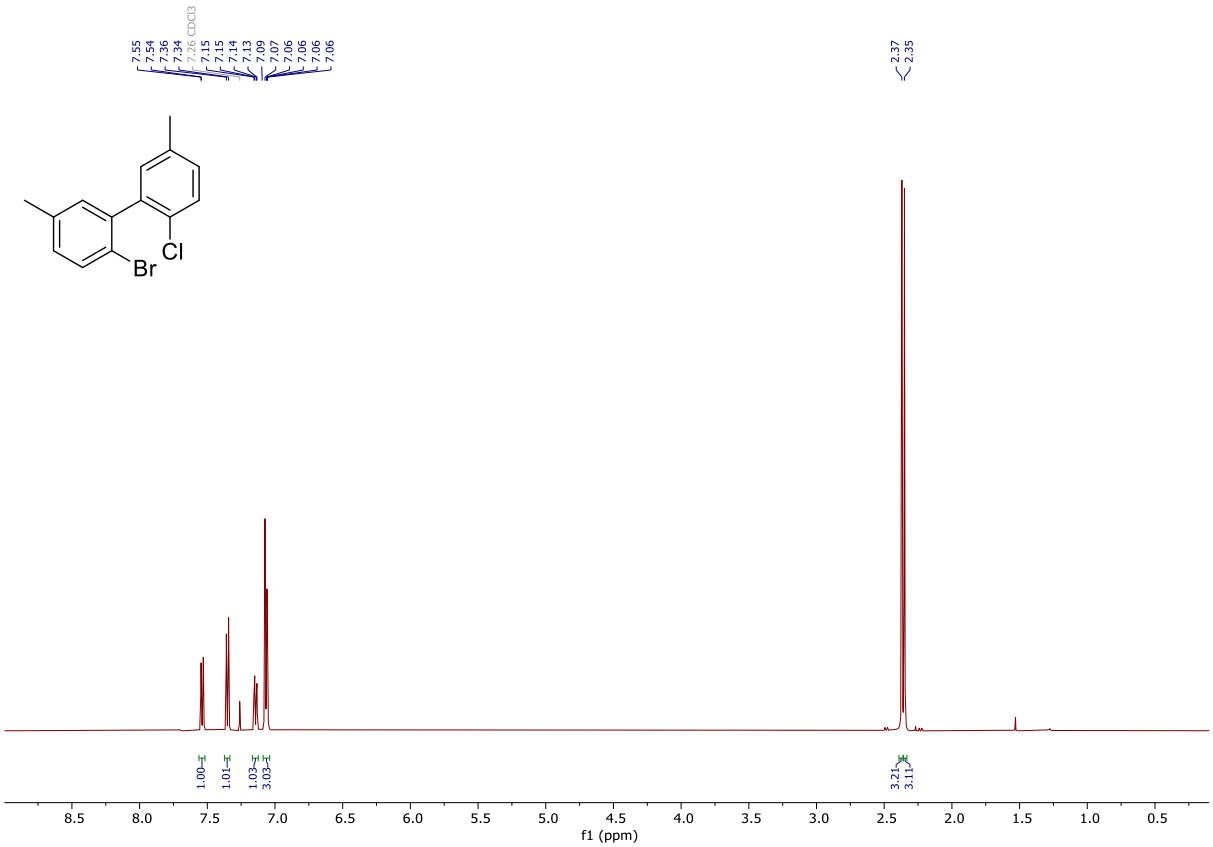
^{1}H NMR, $CDCl_3$, 501 MHz, 2-bromo-2'-chloro-5-methyl-1,1'-biphenyl (**S2b**)



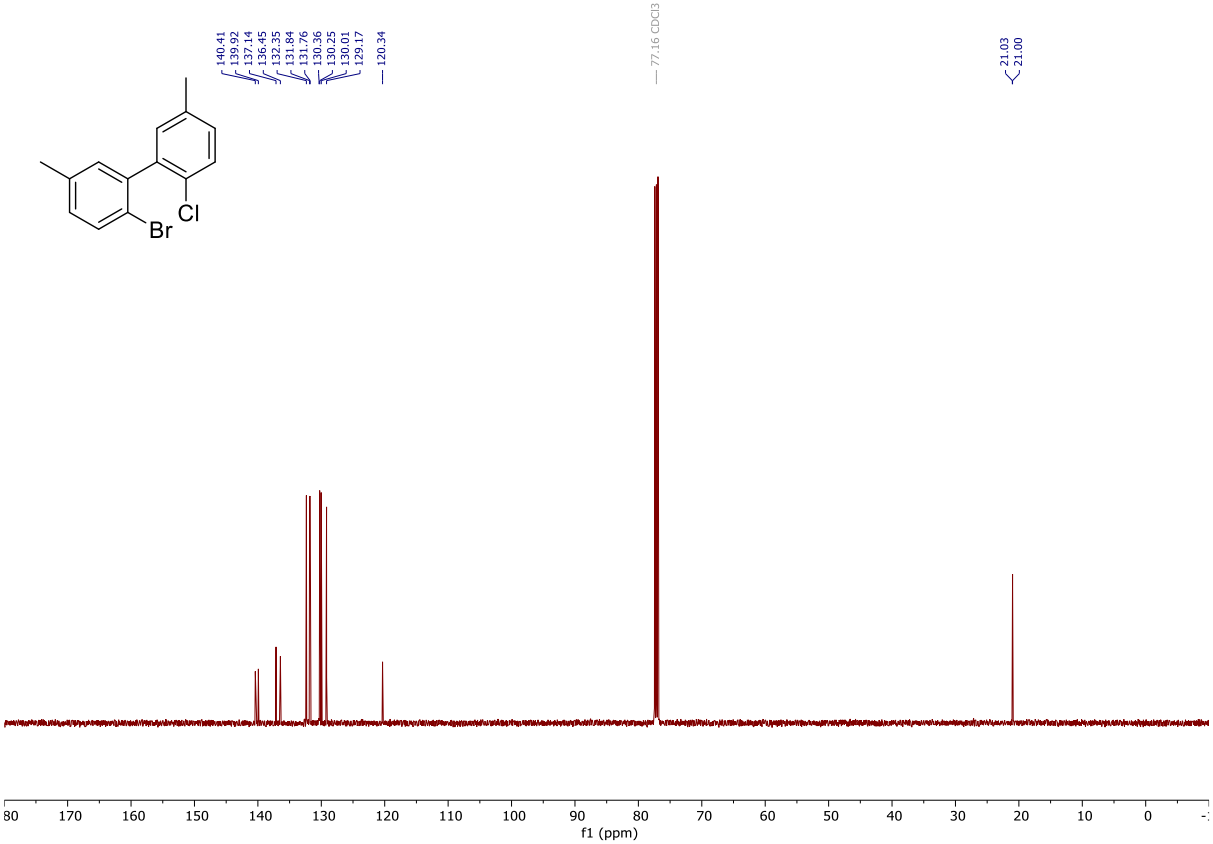
^{13}C NMR, $CDCl_3$, 126 MHz, 2'-bromo-2-chloro-5-methyl-1,1'-biphenyl (**S2b**)



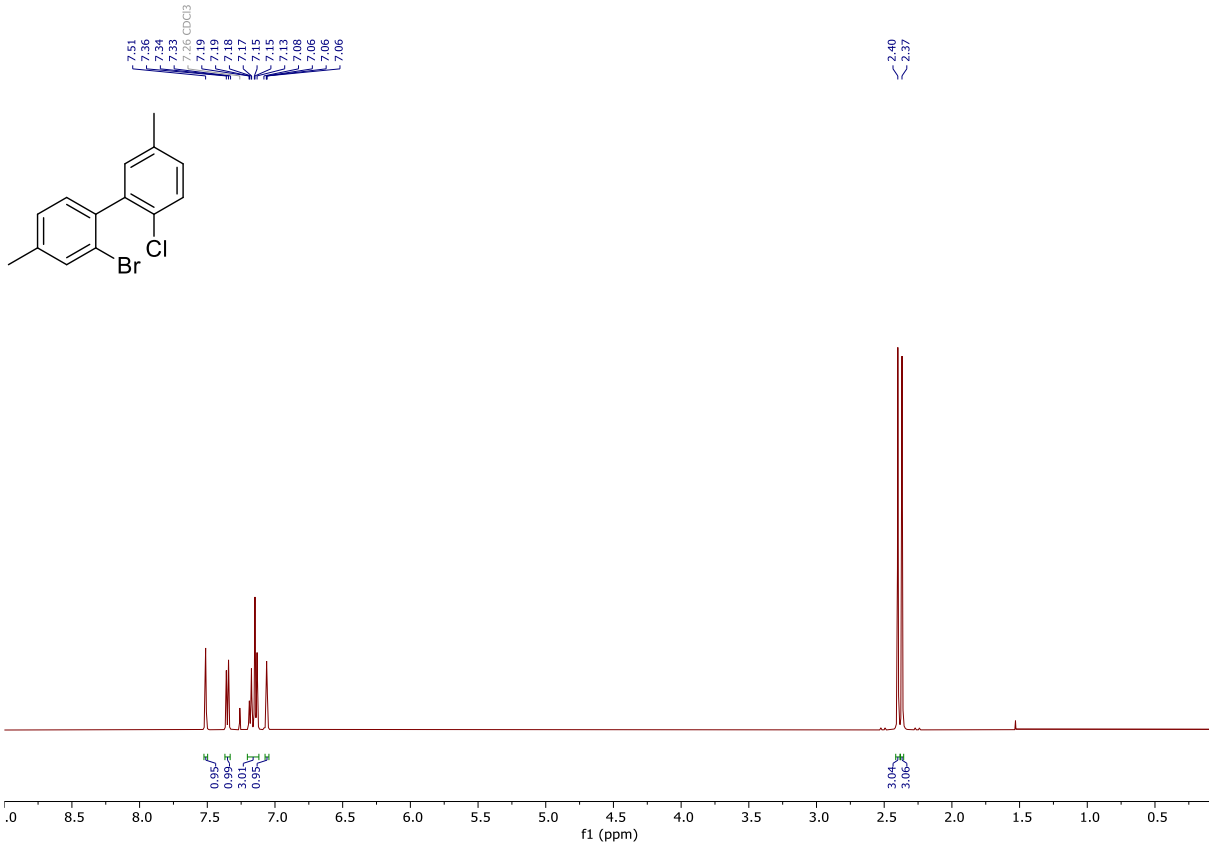
^{1}H NMR, $CDCl_3$, 501 MHz, 2-bromo-2'-chloro-5,5'-dimethyl-1,1'-biphenyl (**S2c**)



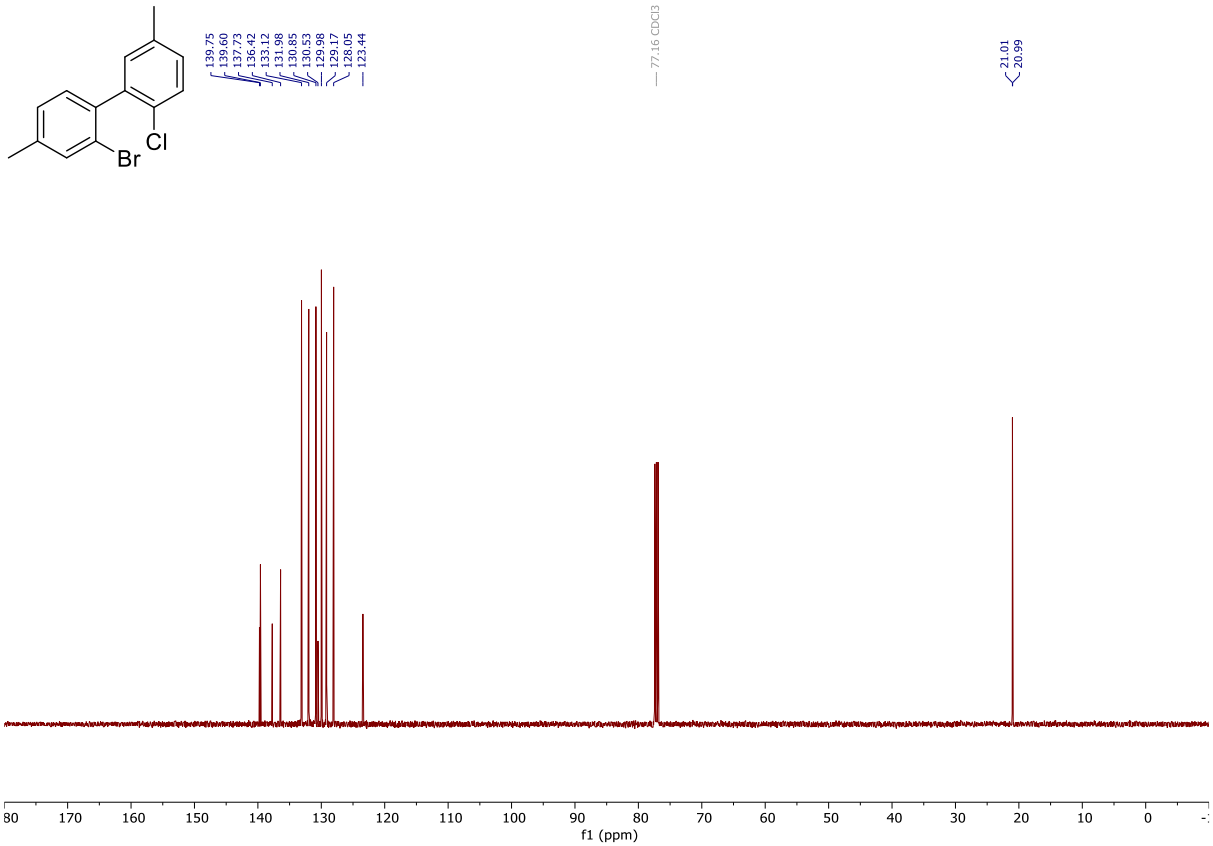
^{13}C NMR, $CDCl_3$, 126 MHz, 2-bromo-2'-chloro-5,5'-dimethyl-1,1'-biphenyl (**S2c**)



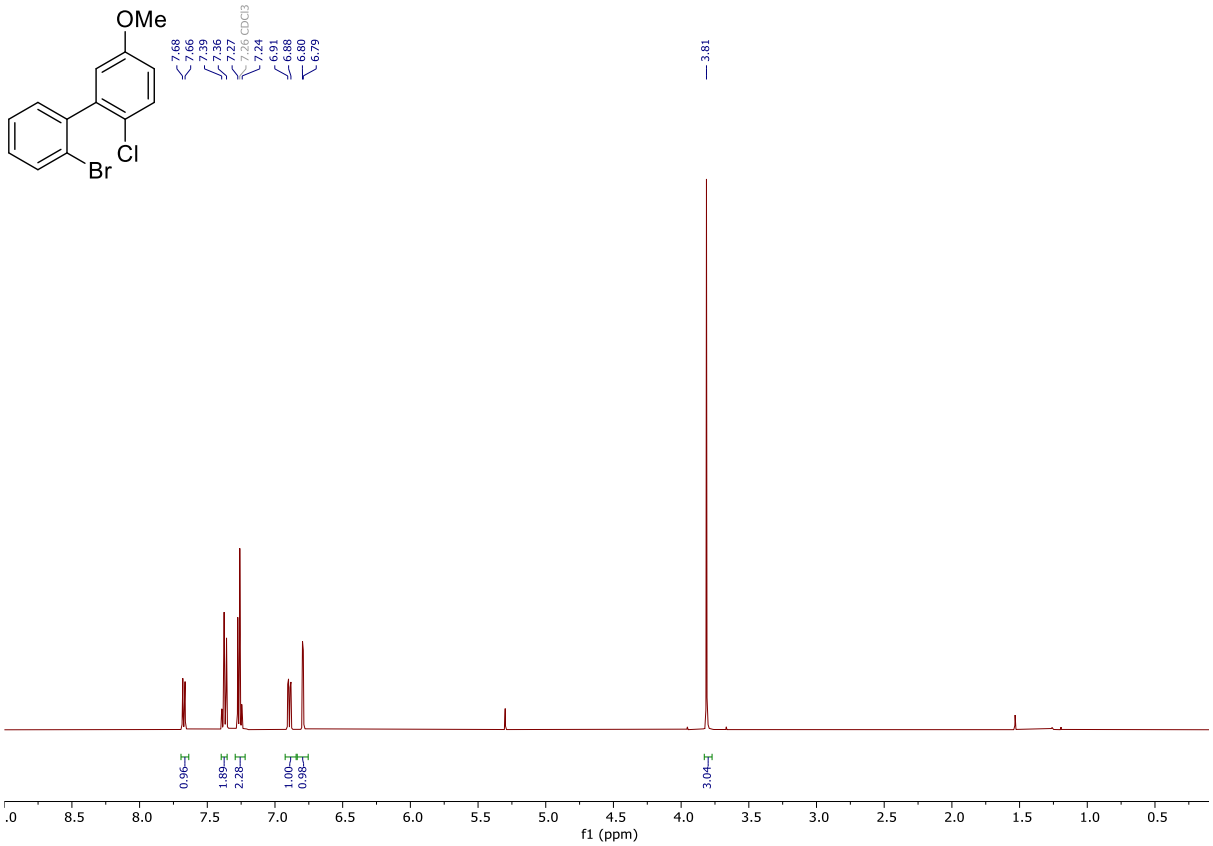
^{1}H NMR, $CDCl_3$, 501 MHz, 2-bromo-2'-chloro-4,5'-dimethyl-1,1'-biphenyl (**S2d**)



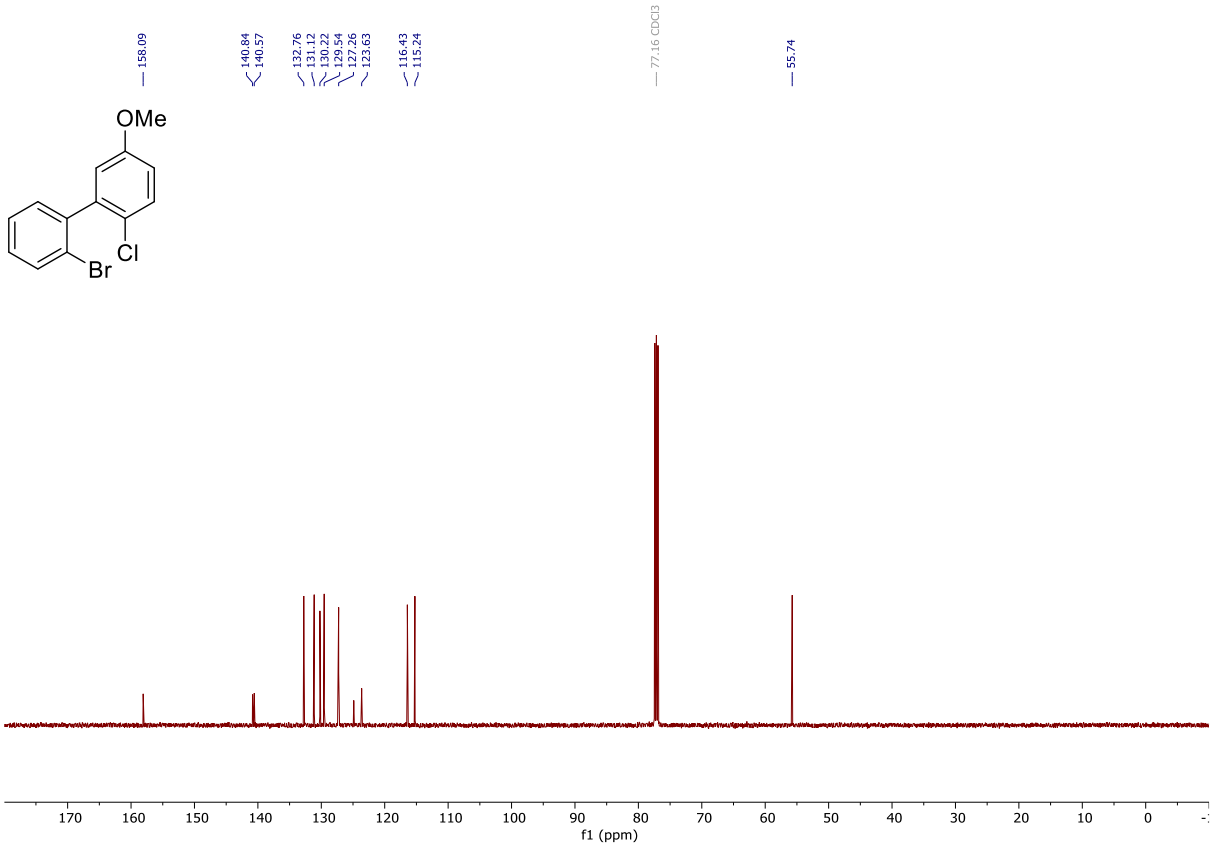
^{13}C NMR, $CDCl_3$, 126 MHz, 2-bromo-2'-chloro-4,5'-dimethyl-1,1'-biphenyl (**S2d**)



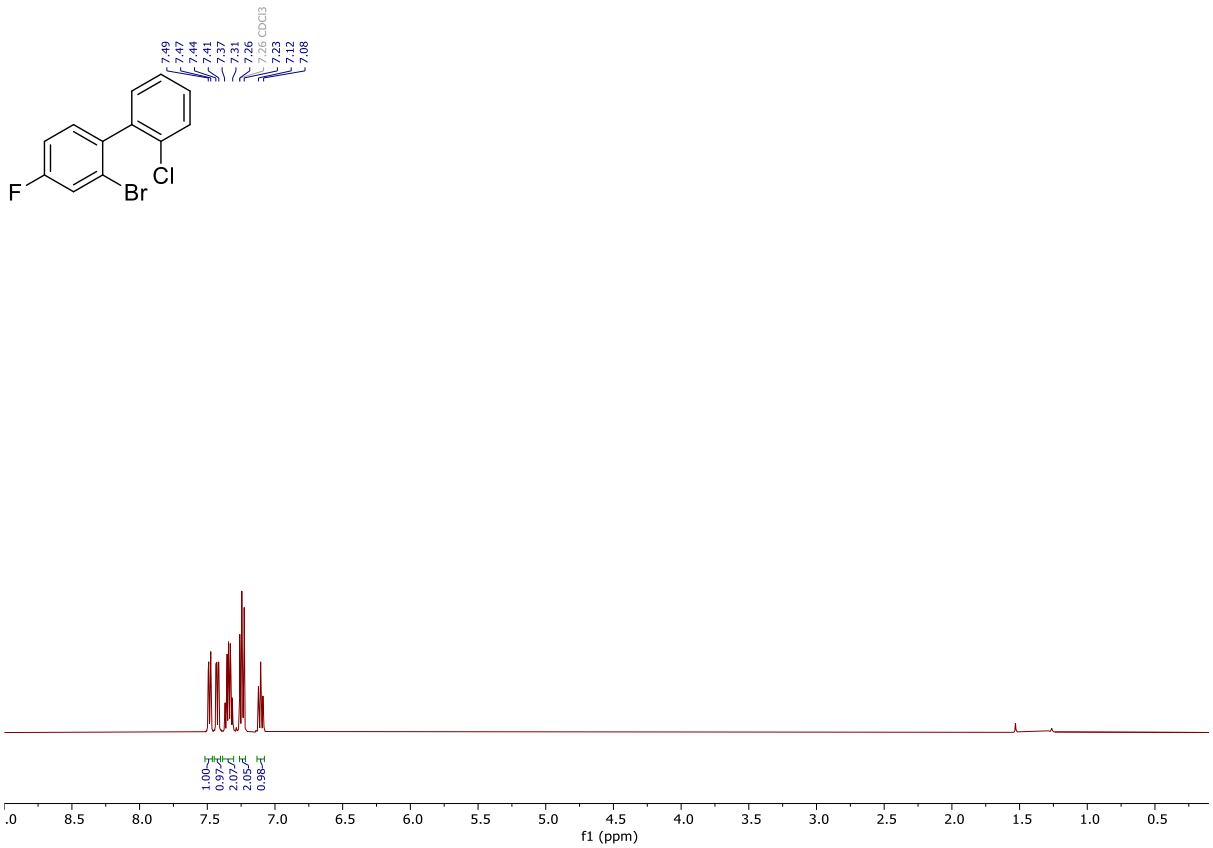
^{1}H NMR, $CDCl_3$, 501 MHz, 2'-bromo-2-chloro-5-methoxy-1,1'-biphenyl (**S2e**)



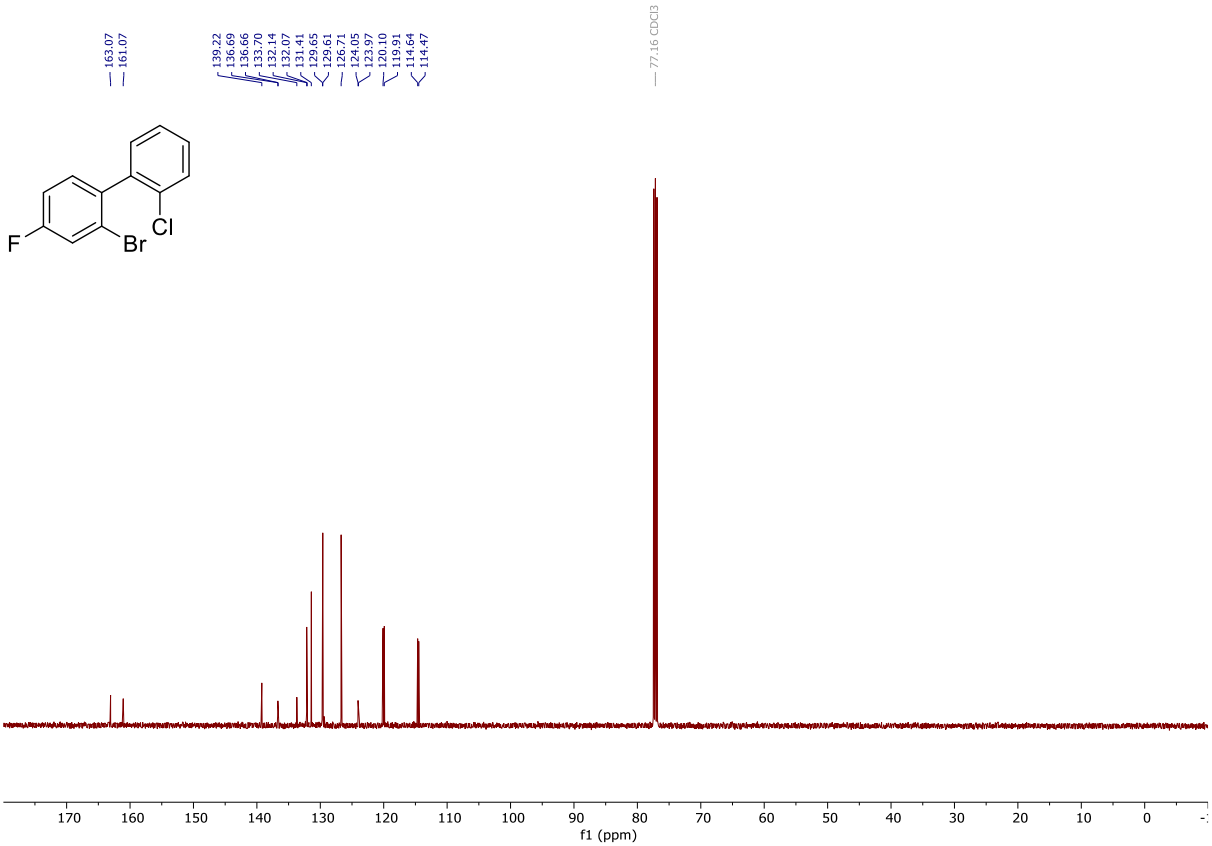
^{13}C NMR, $CDCl_3$, 126 MHz, 2'-bromo-2-chloro-5-methoxy-1,1'-biphenyl (**S2e**)



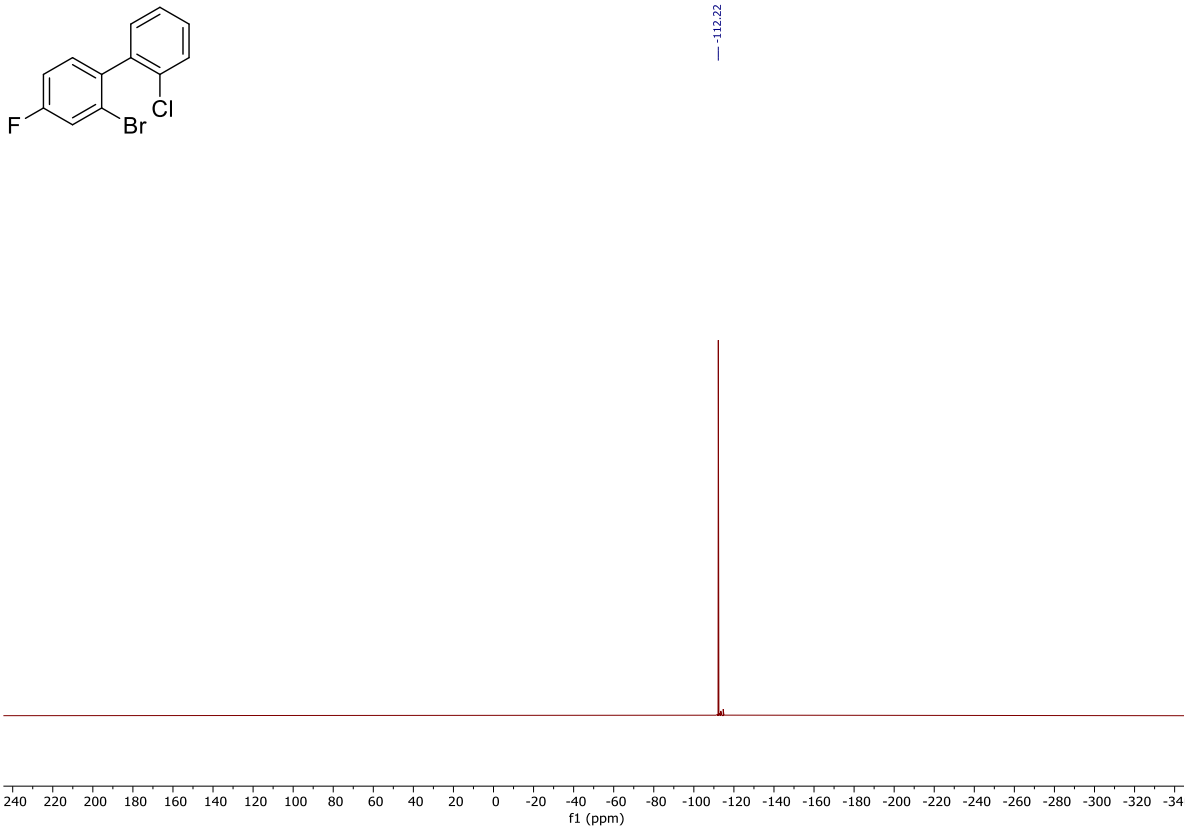
^{1}H NMR, $CDCl_3$, 501 MHz, 2'-bromo-2-chloro-5-methoxy-1,1'-biphenyl (**S2f**)



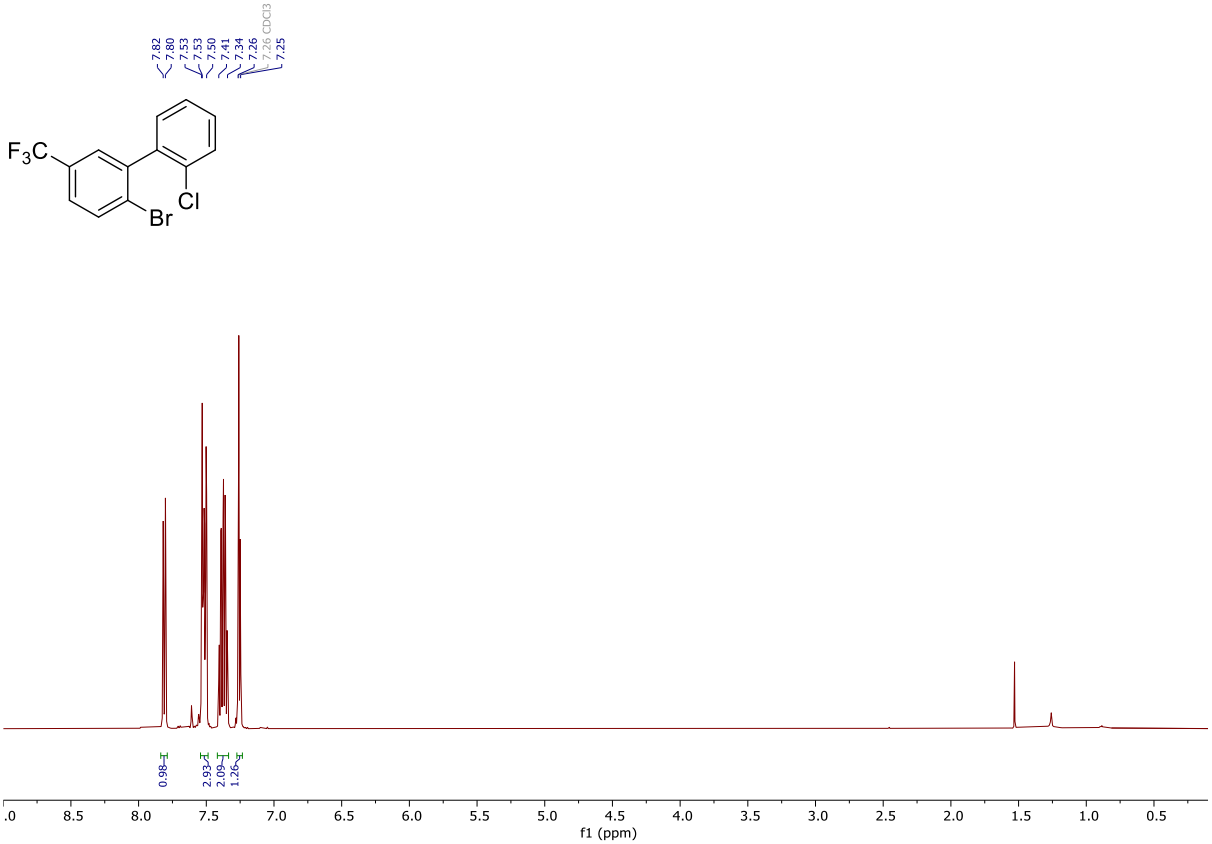
^{13}C NMR, $CDCl_3$, 126 MHz, 2'-bromo-2-chloro-5-methoxy-1,1'-biphenyl (**S2f**)



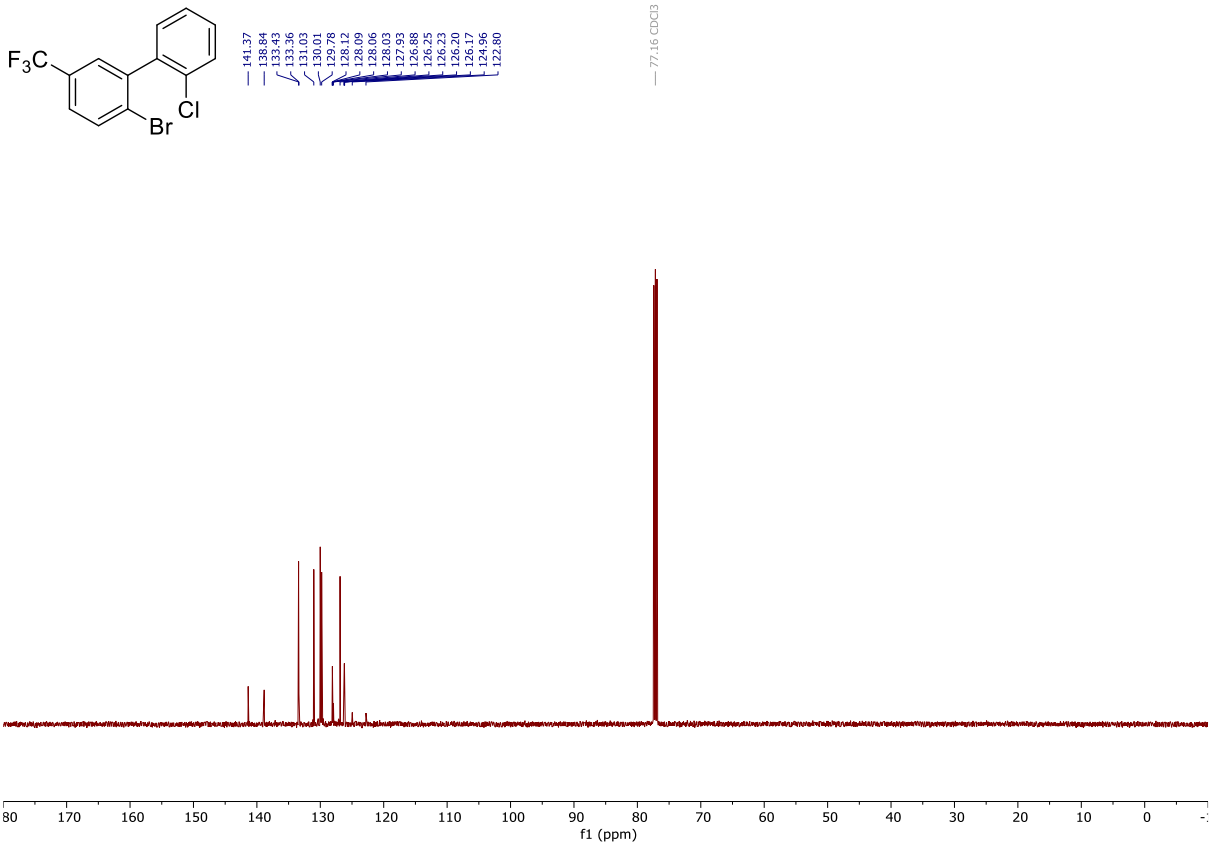
^{19}F NMR, $CDCl_3$, 471 MHz, 2'-bromo-2-chloro-5-methoxy-1,1'-biphenyl (**S2f**)



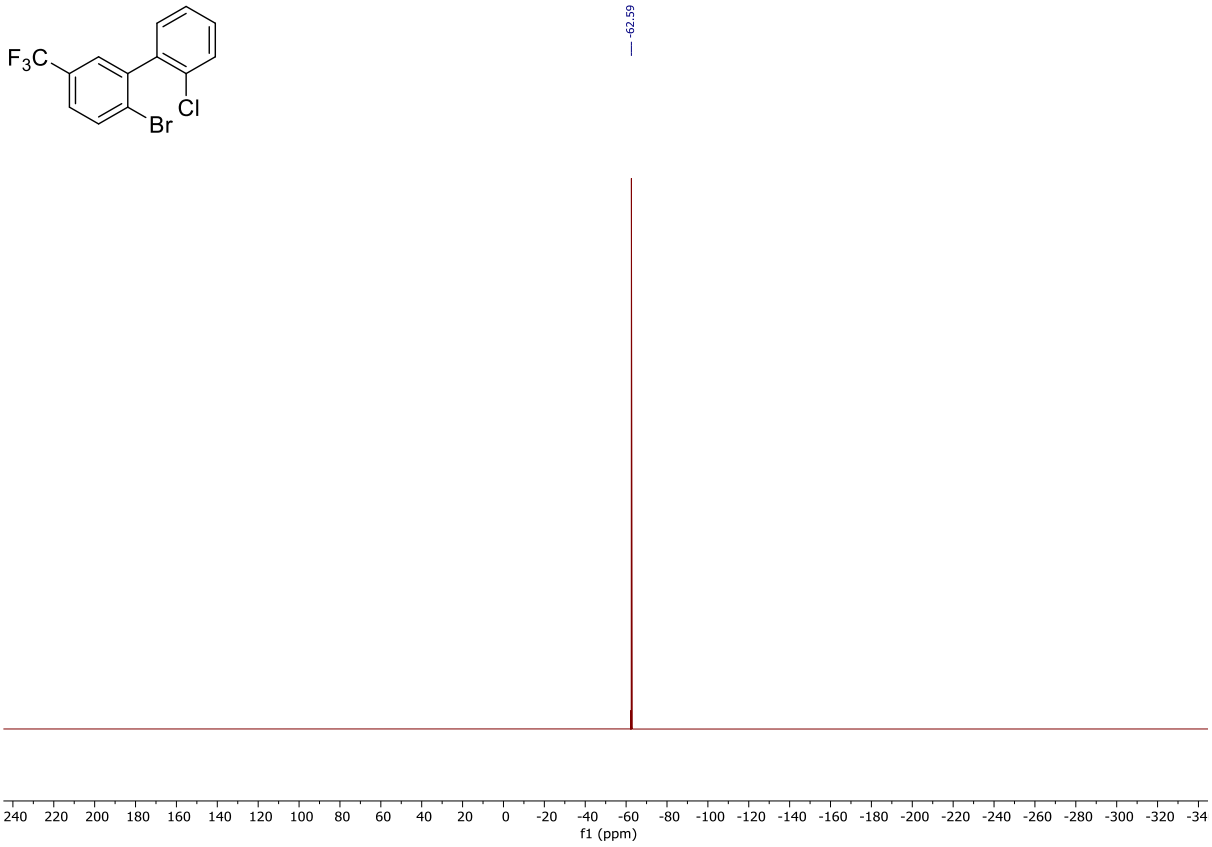
^{1}H NMR, $CDCl_3$, 501 MHz, 2-bromo-2'-chloro-5-(trifluoromethyl)-1,1'-biphenyl (**S2g**)



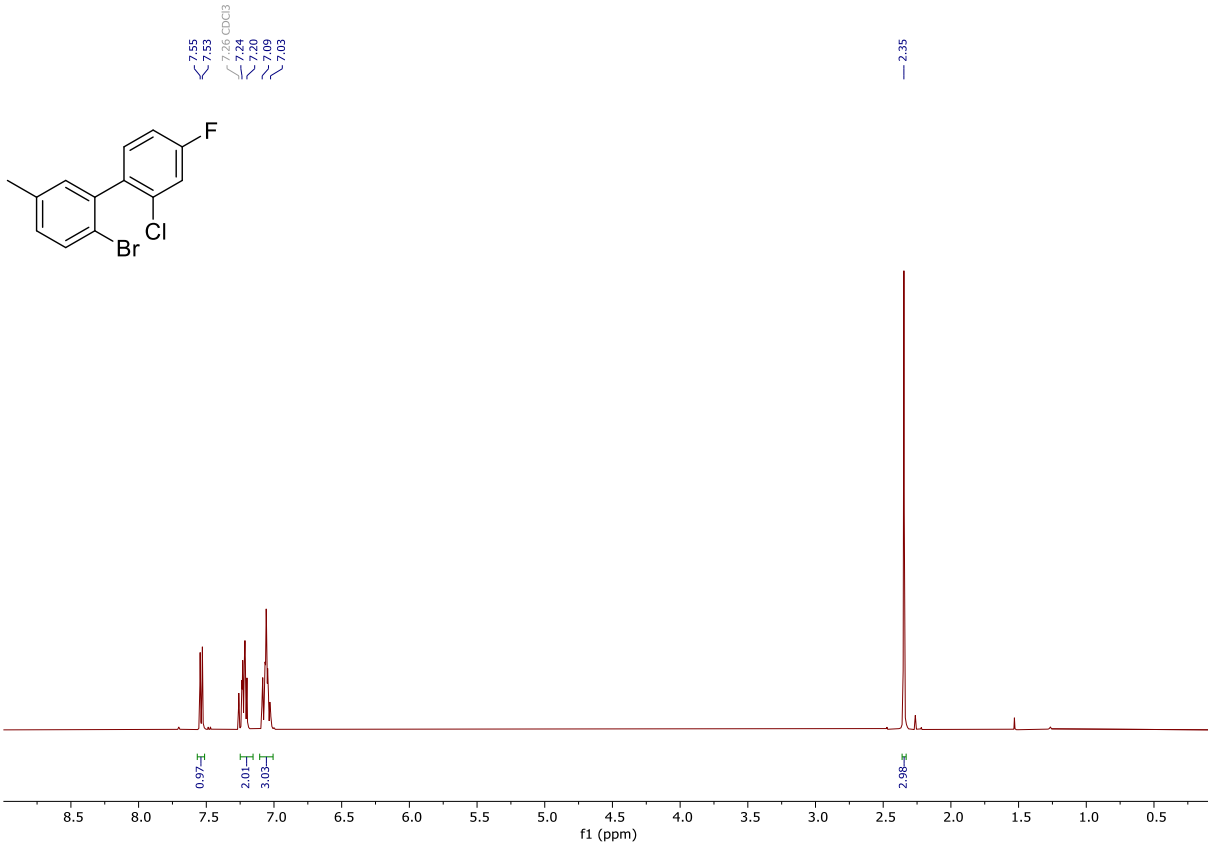
^{13}C NMR, $CDCl_3$, 126 MHz, 2-bromo-2'-chloro-5-(trifluoromethyl)-1,1'-biphenyl (**S2g**)



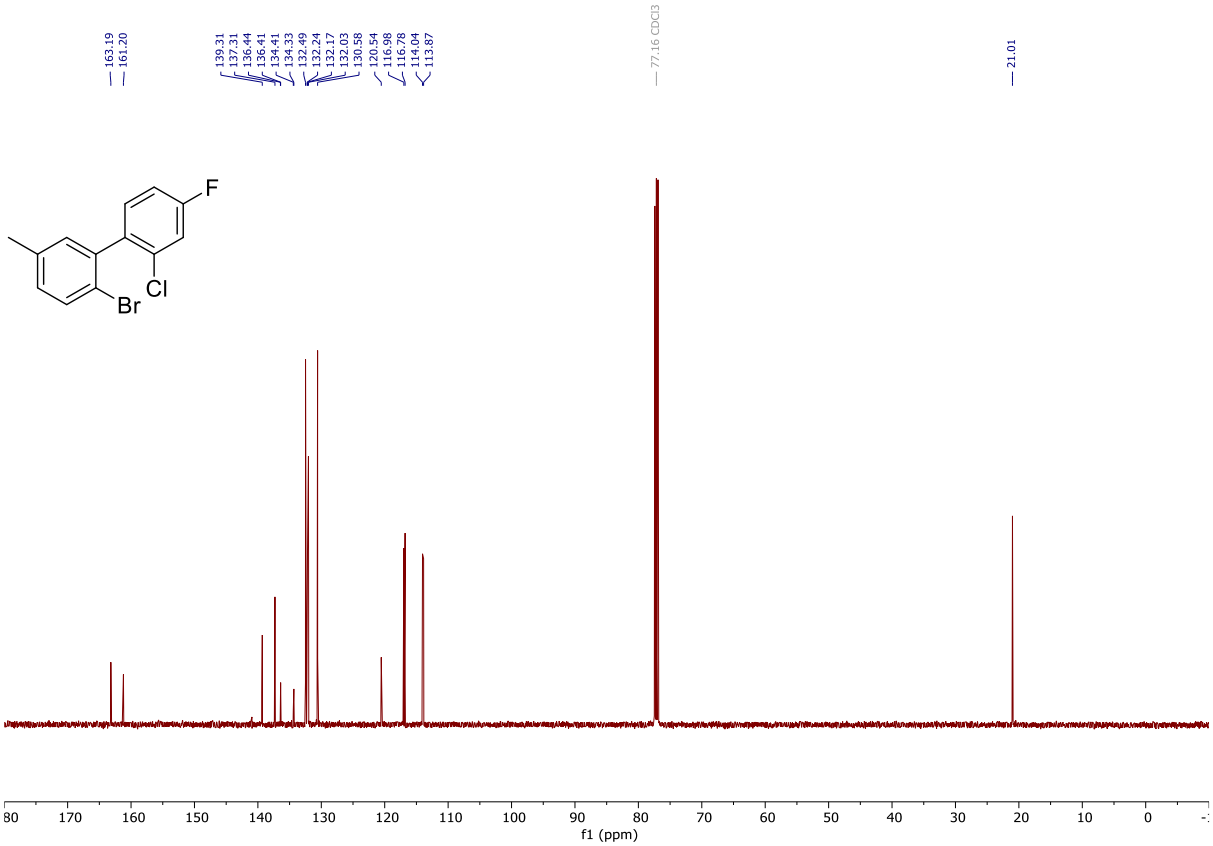
^{19}F NMR, $CDCl_3$, 471 MHz, 2-bromo-2'-chloro-5-(trifluoromethyl)-1,1'-biphenyl (**S2g**)



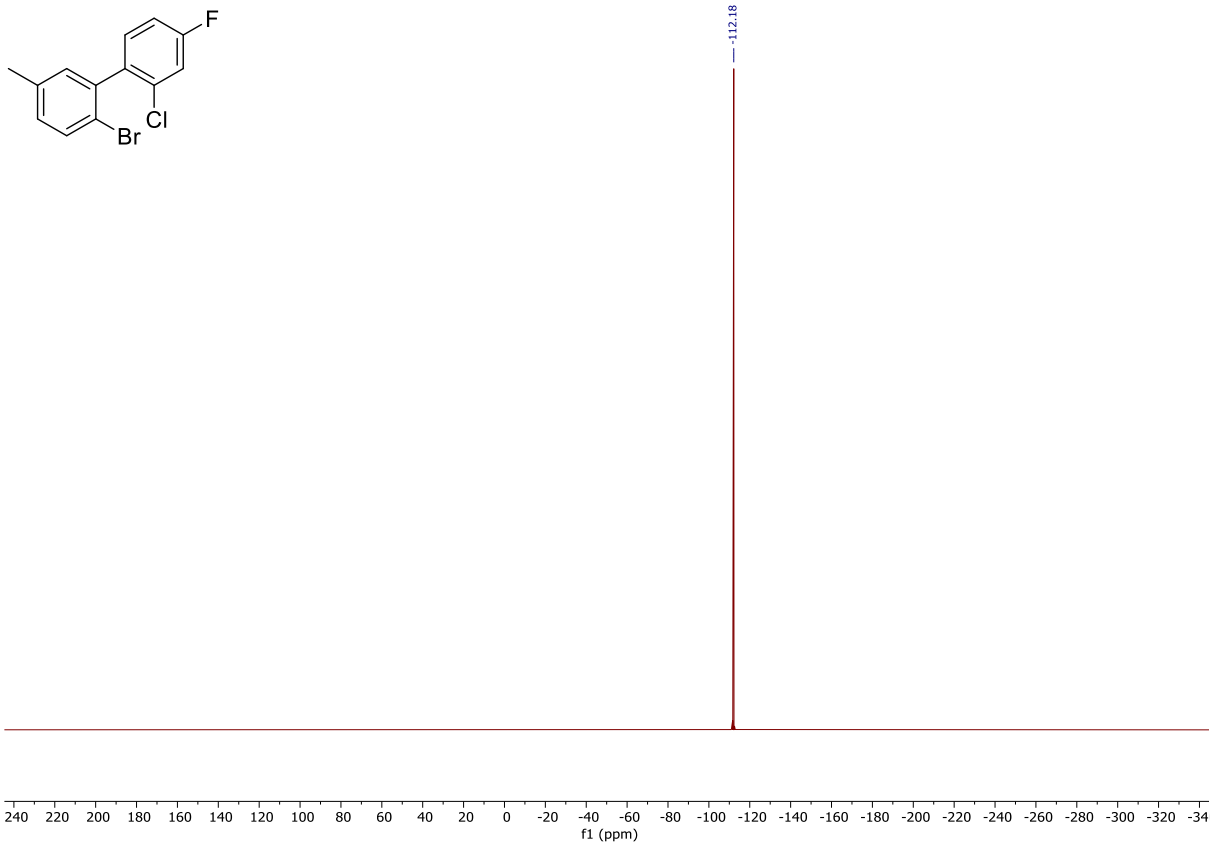
^{1}H NMR, $CDCl_3$, 501 MHz, 2'-bromo-2-chloro-4-fluoro-5'-methyl-1,1'-biphenyl (**S2h**)



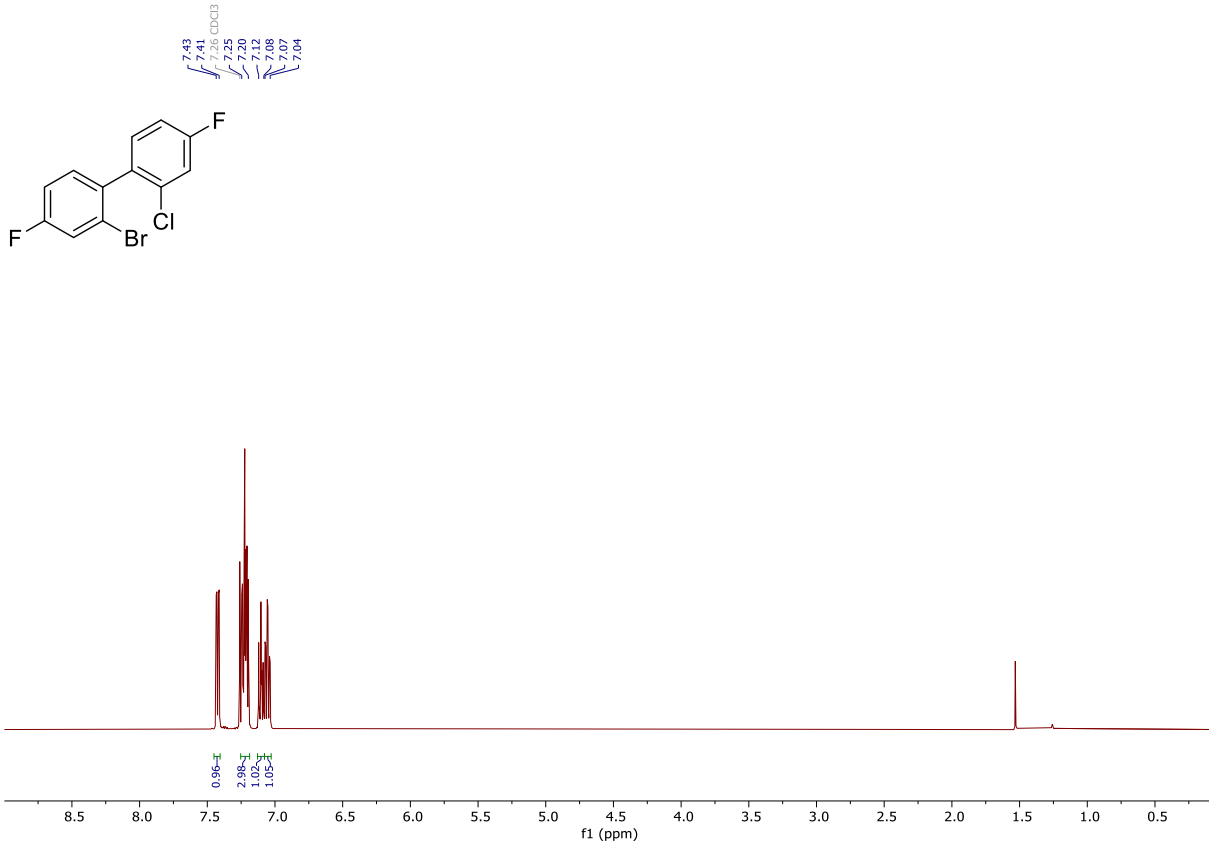
^{13}C NMR, $CDCl_3$, 126 MHz, 2'-bromo-2-chloro-4-fluoro-5'-methyl-1,1'-biphenyl (**S2h**)



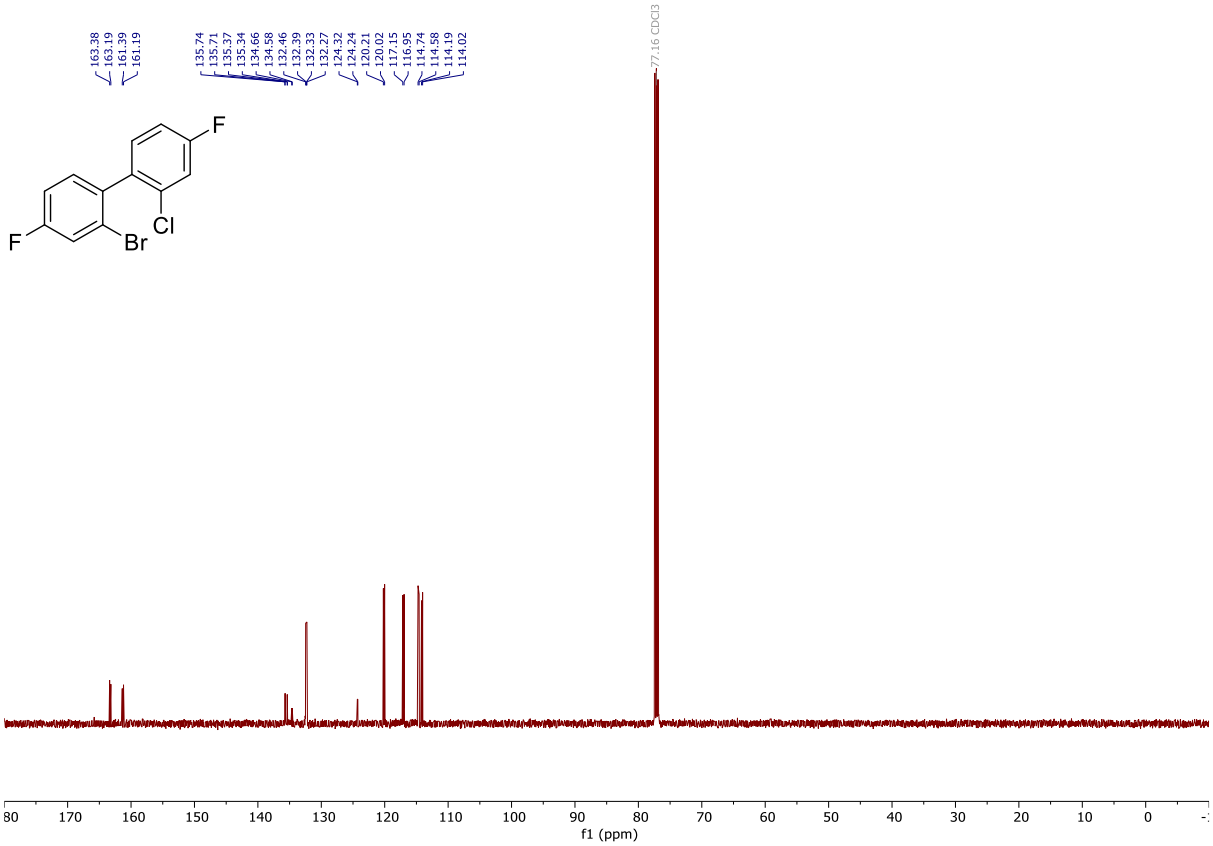
^{19}F NMR, $CDCl_3$, 471 MHz, 2'-bromo-2-chloro-4-fluoro-5'-methyl-1,1'-biphenyl (**S2h**)



^{1}H NMR, $CDCl_3$, 501 MHz, 2-bromo-2'-chloro-4,4'-difluoro-1,1'-biphenyl (**S2i**)



^{13}C NMR, $CDCl_3$, 126 MHz, 2-bromo-2'-chloro-4,4'-difluoro-1,1'-biphenyl (**S2i**)



^{19}F NMR, $CDCl_3$, 471 MHz, 2-bromo-2'-chloro-4,4'-difluoro-1,1'-biphenyl (**S2i**)