Synthesis of α-Substituted Cyclic Boronates via Titanium-Catalyzed Cyclization of Vinyl Boronates with Dichloroalkanes

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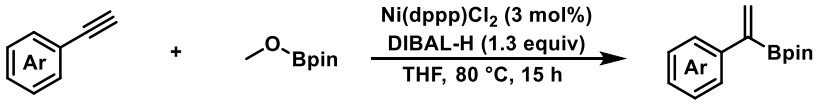
General Information

Manipulations were carried out under an atmosphere of dry and deoxygenated argon using Schlenk line or in a glovebox (H_2O and O_2 < 0.01 ppm). Glassware was pre-dried in an oven at 130 °C for several hours and cooled prior to use. Solvents were purchased as super dry solvent or purified via standard purification operations. Titanium complexes (such as Cp_2TiCl_2, Cp^*TiCl_3 and $InTiCl_3$) and manganese, lithium chloride, aluminum chloride were purchased from Sigma-Aldrich, Energy, Adamas, Macklin and AllyChem company. Dihaloalkanes were purchased from Sigma-Aldrich, Energy, Adamas, Bidepharm, Macklin company or synthesized via known procedures. Vinyl boronates were synthesized according to literature. ^{1}H NMR, ^{13}C NMR, ^{11}B NMR, ^{19}F spectra were recorded on Bruker Advance Neo 400 MHz NMR at room temperature using $CDCl_3$ as a solvent. Chemical shifts (δ) are given in parts per million (ppm). Coupling constants (*J*) are given in Hertz (Hz). Thin-layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C). High-resolution MS analyses were performed on Waters Micromass Q-TOF Premier mass spectrometer. Electron impact (EI) mass spectra were recorded on Shimadzu GCMS-QP2010 SE mass spectrometer.

Synthetic Procedures

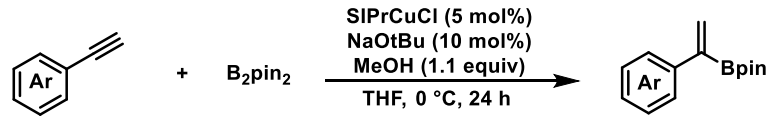
Synthesis of vinyl boronates-Procedure A



Following a reported procedure.[1] To a solution of $Ni(dppp)Cl_2$ in THF was added 1M solution of DIBAL in heptane at 25 °C and the mixture was cooled to 0 °C. Alkyne was added dropwise, the reaction mixture was allowed to warm to 25 °C and stirred for 2 hours. Then, methoxyboronic acid pinacol ester (2 equiv) was added dropwise at 0 °C and the reaction mixture was stirred at 80 °C for additional 15 hours. The reaction mixture was cooled to 0 °C, quenched with H_2O (50 mL) and stirred at 25 °C for additional 1 hour, then it was poured into a saturated solution of Rochelle salt (100 mL), and the mixture was extracted with Ethyl acetate (4 × 150 mL). The organic extracts were washed with brine (200 mL), dried over Na_2SO_4, filtered,

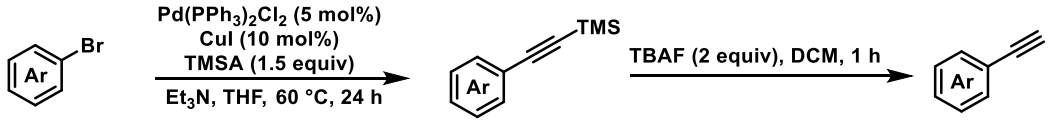
and the solvent was evaporated. The residue was purified by column chromatography (PE and EA as eluent) to afford the desired product.

Synthesis of vinyl boronates-Procedure B



Following a reported procedure.[2] An oven-dried 100 mL screw cap reaction tube with magnetic stir bar was charged with *NHC*-Cu, NaO^{t}Bu and THF under Ar atmosphere. The mixture was sealed with cap and allowed to stir for 10 min. Bis(pinacolato)diboron (1.1 equiv) was added to the solution, causing it to turn dark brown immediately. The mixture was allowed to stir at rt for 30 min under an atmosphere of Ar. After this time, the mixture was allowed to cool to 0 °C (ice bath). A solution of alkynes and MeOH (1.1 eq) were added (syringe). The tube was placed in ice bath After 24 h, the reaction was quenched by H_2O, extracted with ethyl acetate (100 mL) and washed with water (3 times).The filtrate was concentrated in vacuo, the residue was purified by silica gel chromatography (PE and EA as eluent) to afford the desired product.

Synthesis of alkynes



Step 1: Sonogashira coupling

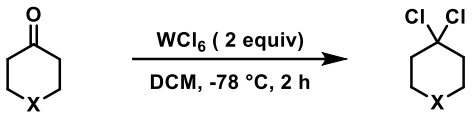
Following a reported procedure.[2a] A magnetic stir-bar, $Pd(PPh_3)_2Cl_2$ (5 mol%), CuI (10 mol%) and aryl bromide were charged into an oven-dried screw cap reaction tube under an atmosphere of argon gas. Then dry THF followed by triethylamine was added. After stirring for 15 min, TMSA was added to the reaction mixture slowly. Gradually, the reaction turned dark. The reaction was stirred continuously for 24 h at 60 ºC. After cooling to room temperature, the reaction mixture diluted with 25 mL EtOAc and filtered through the celite. The filtrate was evaporated under reduced pressure and the crude material was purified by column chromatography using petroleum ether/ethyl acetate as eluent to give pure silylated product.

Step 2: Desilylation

To an oven dried 100 mL round bottom flask, the crude silylated product was added using THF and then TBAF (2.0 eq) was added portion-wise into the flask under Ar atmosphere at 0 ºC. The reaction mixture was stirred at room temperature for 1 h. After completion (judged by GC-

MS), the reaction mixture was extracted with ethyl acetate (100 mL) and washed with water (100 mL). After drying over Na_2SO_4, the solvent was evaporated under reduced pressure and chromatographic separation with silica gel (PE and EA as eluent) to give pure alkyne product.

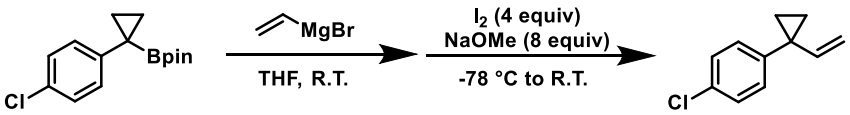
Synthesis of dihaloalkanes



Following a reported procedure.[3] Cyclohexanone, CH_2Cl_2, and a magnetic stir bar were added to a round bottom flask. The solution was cooled to -78 °C, and stirring was commenced. WCl_6 (2.00 equiv) was added in portions. The reaction was allowed to warm to room temperature, and stirring was continued for an additional 2 h. After the 2 h, Et_2O (200 mL) was added, and the reaction was quenched with 1 M NaOH, added dropwise until bubbling ceased. The organic phase was separated, and the aqueous phase was extracted with Et_2O (100 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography.

Synthetic Derivatization

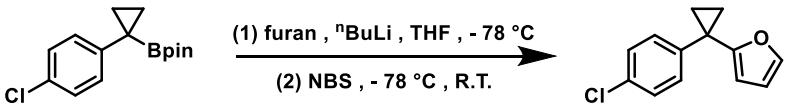
Procedure for the Synthesis of 13a from 3h



3h 13a, 41% yield

The literature procedure was followed with modification.[4] An oven-dried 10 mL vial with magnetic stir bar was charged with **3h** (139 mg, 0.5 mmol) and anhydrous THF (5.0 mL) under argon. Vinyl magnesium bromide (1.0 M in THF, 2 mL,2 mmol) was added to this solution and stirred for 0.5 h. Then the reaction mixture was cool to –78 °C and a solution of iodine (0.52 g, 2 mmol) in MeOH (6 mL) was added. The mixture was stirred at −78 °C for 0.5 h, then a solution of NaOMe (216 mg, 4 mmol) in MeOH (5.0 mL) was added. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. Upon completion, sat. $Na_2S_2O_3$ solution (4 mL) was added, and the crude mixture was diluted with pentane, washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. After evaporation under reduced pressure, the crude reaction mixture was purified by column chromatography on silica gel (PE) to afford a colorless oil (36.5 mg, 41% yield).

Procedure for the Synthesis of 13b from 3h

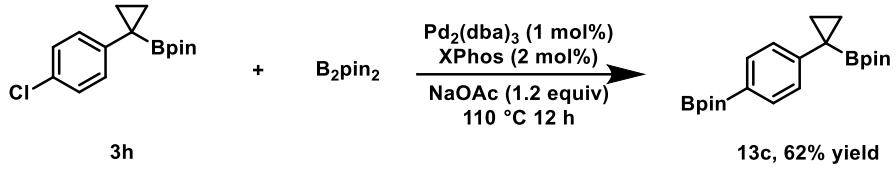


3h 13b, 68% yield

The literature procedure was followed with modification.[4] An oven-dried 10 mL vial with magnetic stir bar was charged with furan (48.0 μL,0.66 mmol) and anhydrous THF (2.0 mL) under argon, then cooled to -78 °C. 1.6 M *n*BuLi (0.42 mL, 0.66 mmol) was added to this solution dropwise. The reaction mixture was warmed to room temperature and stirred for 1 h, then cooled to -78 °C. A solution of **3h** (139 mg, 0.5 mmol) in THF (1 mL) was added and stirred for 1 h, then a solution of NBS (106.8 mg, 0.6 mmol) in THF (2.0 mL) was added to the mixture and stirred for 2 h at -78 °C. The reaction was quenched with sat. $Na_2S_2O_3$ solution (2 mL) and the reaction mixture was allowed to warm to room temperature. Upon completion, the crude mixture was diluted with Et_2O, washed with brine, dried over Na_2SO_4, filtered, and concentrated

in vacuo. After evaporation under reduced pressure, the crude reaction mixture was purified by column chromatography on silica gel (PE:EA = 100:1) to afford a colorless oil (74.1 mg, 68% yield).

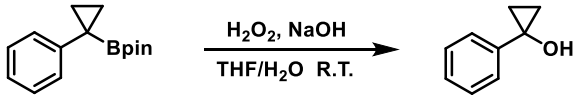
Procedure for the Synthesis of 13c from 3h



3h 13c, 62% yield

Following a reported procedure.[5] A magnetic stir-bar, $Pd_2(dba)_3$ (4.6 mg, 1 mol%), XPhos (2.4 mg, 2 mol%), NaOAc (49.2 mg, 1.2 equiv), Bis(pinacolato)diboron (133.4mg, 1.02 equiv) and **3h** (139 mg, 0.5 mmol) were charged into an oven-dried screw cap reaction tube under an atmosphere of argon gas, heated to 110 °C for 11 h. Upon completion, the crude mixture was diluted with EtOAc, washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. After evaporation under reduced pressure, the crude reaction mixture was purified by column chromatography on silica gel (PE:EA = 20:1) to afford a white solid (115.3 mg, 62% yield).

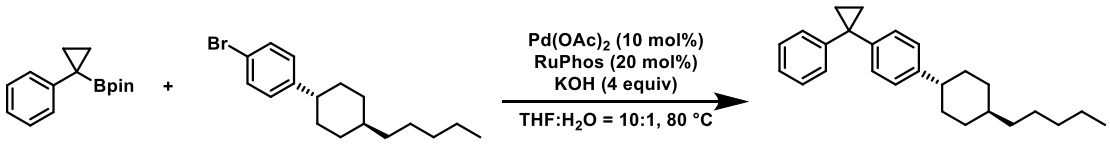
Procedure for the Synthesis of 13d from 3a



3a 13d, 73% yield

The literature procedure was followed with modification.[6] To a solution of **3a** (139 mg, 0.5 mmol) in THF (10 mL) was added with NaOH (2M aq., 1 mL). The mixture was then cooled to 0 °C and H_2O_2 (30% aq., 0.5 mL) was added dropwise with constant stirring in 5 minutes. The cooling bath was removed and the reaction mixture was allowed to warmed up to room temperature and further stirred for 30 minutes. Then the reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo to give product **13d** as colourless oil (48.9 mg, 73% yield).

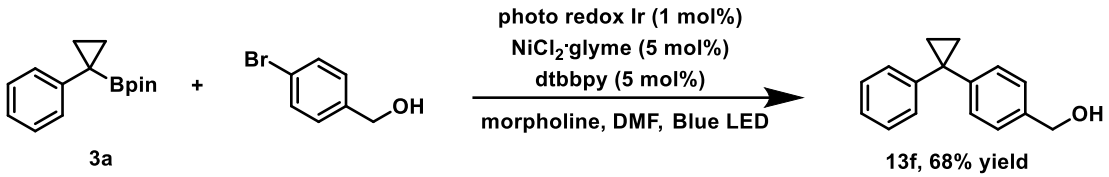
Procedure for the Synthesis of 13e from 3a



3a 13e, 41% yield

The literature procedure was followed with modification.[4] In glovebox, an oven-dried 10 mL vial with magnetic stir bar was charged with $Pd(OAc)_2$ (11.3 mg, 0.05 mmol), RuPhos (46.7 mg, 0.1 mmol) and anhydrous THF (4.0 mL). **3a** (139 mg, 0.5 mmol), 1-Bromo-4-(trans-4-propylcyclohexyl)benzene (281 mg, 1 mmol) and KOH (112 mg, 2 mmol) were added to the reaction mixture. The reaction vessel was moved out of the glovebox, 0.5 mL DI-water was added. Then the reaction was heat to 80 °C and stirred for 16 h. Upon completion, the crude mixture was diluted with Et_2O, washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. After evaporation under reduced pressure, the crude reaction mixture was purified by column chromatography on silica gel (PE) to afford a yellow solid (70.9 mg, 41% yield).

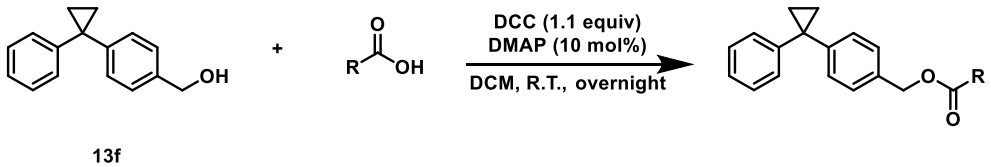
Procedure for the Synthesis of 13f from 3a



3a **13f, 68% yield**

Following a reported procedure.[7] In a 1 mL glass vial equipped with a magnetic stir bar $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (1 mol %), 4-Bromobenzyl alcohol (1.0 equiv, 0.5 mmol), **3a** (2.0 equiv, 1.0 mmol) and morpholine (1.5 equiv) were dissolved in DMF (0.2 M). In a second 1 mL glass vial $NiCl_2$·glyme (5 mol %) and dtbbpy (5 mol %) were dissolved in DMF (0.2 M). The Ni-complex stock solution was sonicated for 5 min and then heated to 100 °C (heat gun) to ensure complete complexation. Afterwards both solutions were combined, and the reaction mixture was irradiated by blue LEDs (445 nm; 100 mW) for 2 h. Upon completion, the crude mixture was diluted with EtOAc, washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. After evaporation under reduced pressure, the crude reaction mixture was purified by column chromatography on silica gel (PE:EA = 10:1) to afford a yellow oil (76.2 mg, 68% yield).

Procedure for the Synthesis of 13g and 13h from 13f



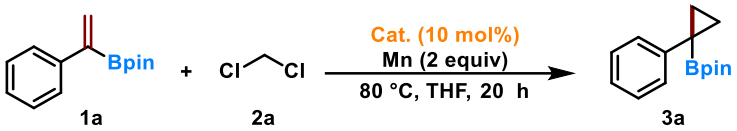
13f

Following a reported procedure.[8] To a stirred solution of carboxylic acid (0.5 mmol) and DMAP (0.05 mmol) in 2 mL anhydrous DCM, **13f** (0.75 mmol) was added. After 15 minutes of stirring, DCC (0.55 mmol) was added to the reaction mixture at 0˚C, and then allowed to stir overnight

at room temperature. Upon completion of reaction, precipitated urea is then filtered off. Filtrate is evaporated and the residue was dissolved in DCM and washed with saturated $NaHCO_3$ solution, and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (PE and EA as eluent) to afford the desired ester.

Condition Optimization Tables

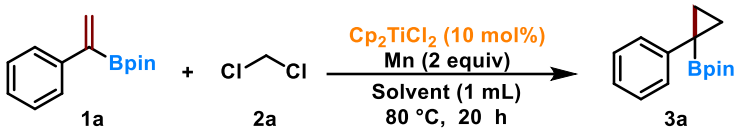
Table S1. Titanium-catalyzed cyclization of vinyl boronate **1a** with DCM: effect of catalysts[a]



entries	catalysts	**3a** yield (%)[b]
1	Rosenthal	27
2	Cp_2TiCl_2	35
3	$Cp^*_2TiCl_2$	8
4	$InTiCl_3$	14
5	$CpTiCl_3$	16
6	Cp^*TiCl_3	17
7	TiO_2	NR
8	TiH_2	NR

[a]Reaction conditions: 0.2 mmol **1a**, 1 mmol **2a**, Mn (2 equiv), various titanium catalysis (10 mol%) and I mL THF in 15 mL pressure tube and heated at 80 °C for 20 h; [b]yields were determined by GC with dodecane as internal standard.

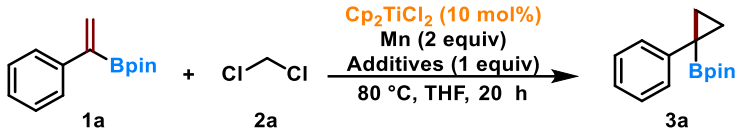
Table S2. Titanium-catalyzed cyclization of vinyl boronate **1a** with DCM: effect of solvents[a]



entries	solvents	**3a** yield (%)[b]
1	THF	35
2	Toluene	NR
3	MTBE	NR
4	MeOH	NR
5	DMA	2
6	DMF	12
7	DME	trace

[a]Reaction conditions: 0.2 mmol **1a**, 1 mmol **2a**, Cp_2TiCl_2 (10 mol%), and Mn (2 equiv), 1 mL different solvent in 15 mL pressure tube and heated at 80 °C for 20 h; [b]yields were determined by GC with dodecane as internal standard.

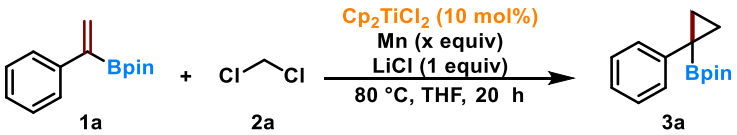
Table S3. Titanium-catalyzed cyclization of vinyl boronate **1a** with DCM: effect of additives[a]



entries	additives	**3a** yield (%)[b]
1	-	35
2	$ZnCl_2$	9
3	$MgCl_2$	40
4	LiCl	48
5	TMS-Cl	23

[a]Reaction conditions: 0.2 mmol **1a**, 1 mmol **2a**, Cp_2TiCl_2 (10 mol%), Mn (2 equiv), different additives and 1mL THF in 15 mL pressure tube heated at 80 °C for 20 h; [b]yields were determined by GC with dodecane as internal standard.

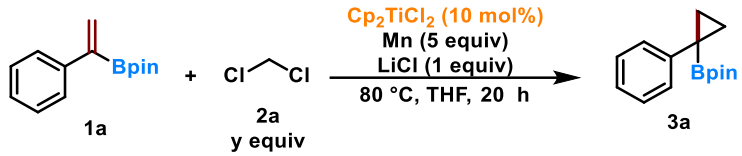
Table S4. Titanium-catalyzed cyclization of vinyl boronate **1a** with DCM: effect of manganese amount[a]



entries	x	**3a** yield (%)[b]
1	1	16
2	2	48
3	3	54
4	4	53
5	5	62
6	6	50

[a]Reaction conditions: 0.2 mmol **1a**, 1 mmol **2a**, Cp_2TiCl_2 (10 mol%), Mn (x equiv), LiCl (1 equiv), and 1mL THF in 15 mL pressure tube heated at 80 °C for 20 h; [b]yields were determined by GC with dodecane as internal standard.

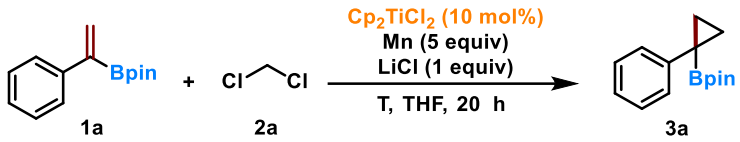
Table S5. Titanium-catalyzed cyclization of vinyl boronate **1a** with DCM: effect of dichloromethane amount[a]



entries	y	**3a** yield (%)[b]
1	2	40
2	4	67
3	5	62
4	6	63
5	8	72
6	10	80
7	12	68

[a]Reaction conditions: 0.2 mmol **1a**, **2a** (y equiv), Cp_2TiCl_2 (10 mol%), Mn (5 equiv), LiCl (1 equiv) and 1mL THF in 15 mL pressure tube heated at 80 °C for 20 h; [b]yields were determined by GC with dodecane as internal standard.

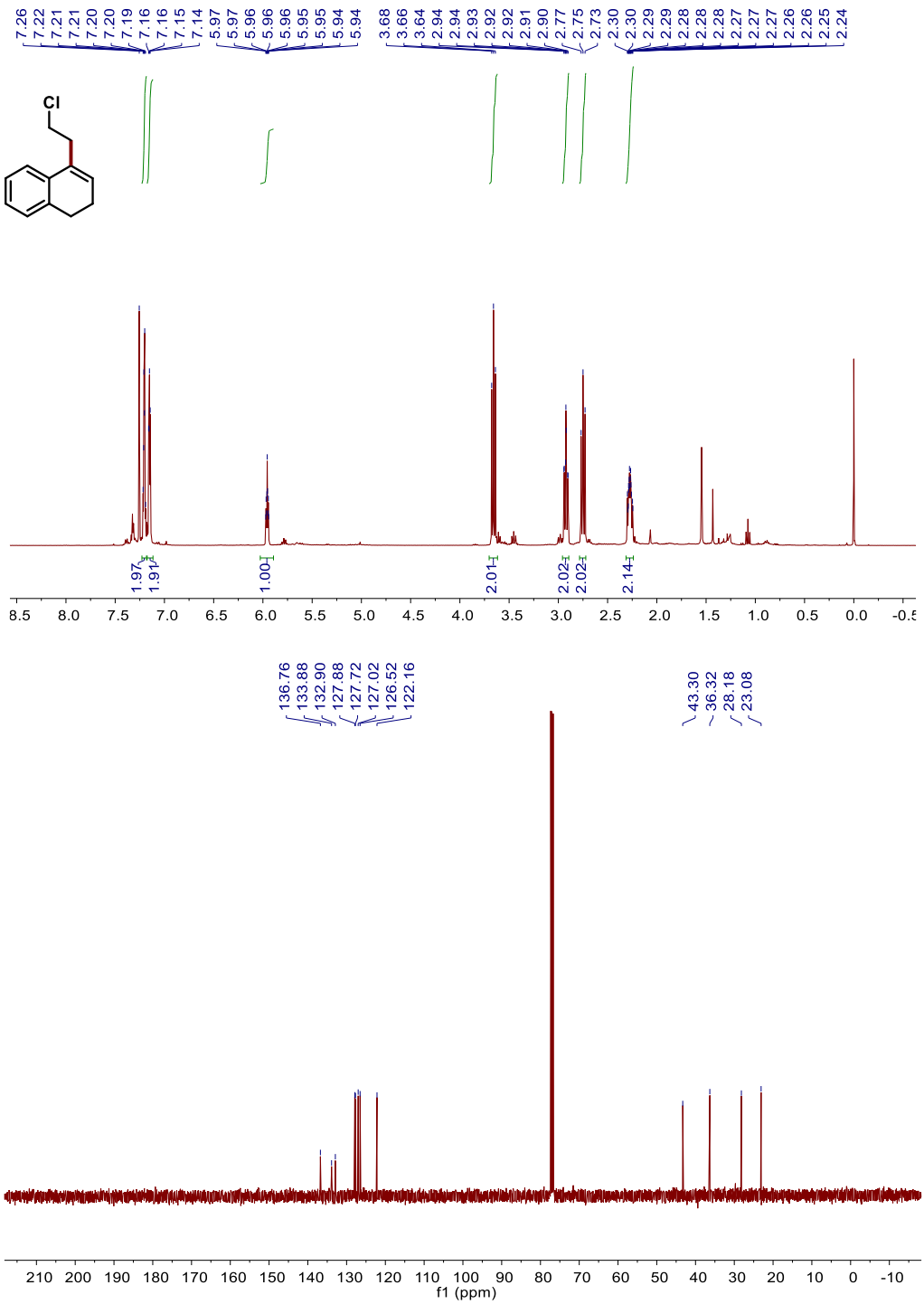
Table S6. Titanium-catalyzed cyclization of vinyl boronate **1a** with DCM: effect of temperature[a]



entries	T (°C)	**3a** yield (%)[b]
1	R.T.	0.5
2	40	35
3	60	68
4	80	78
5	100	69
6	120	87

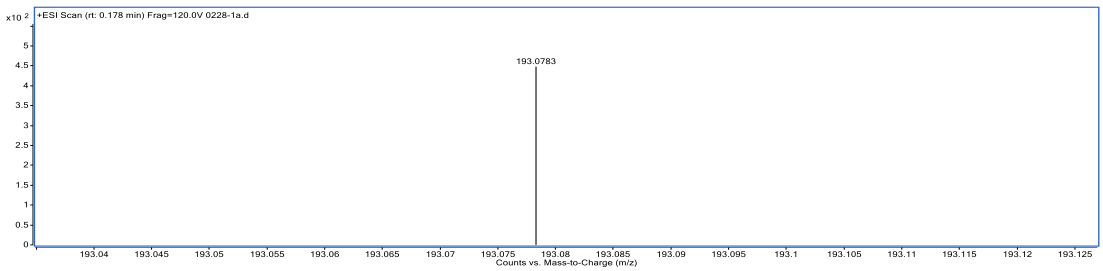
[a]Reaction conditions: 0.2 mmol **1a**, 2 mmol **2a**, Cp_2TiCl_2 (10 mol%), Mn (5 equiv), LiCl (1 equiv) and 1mL THF in 15 mL pressure tube heated at the temperature shown in the table for 20 h; [b]yields were determined by GC with dodecane as internal standard.

Supplementary Figures and Schemes



^{1}H NMR of 14b (400 MHz, Chloroform-*d*) δ 7.21 (dd, *J* = 4.4, 2.2 Hz, 2H), 7.15 (dd, *J* = 4.0, 2.4 Hz, 2H), 5.96 (tt, *J* = 4.6, 1.2 Hz, 1H), 3.70 – 3.62 (m, 2H), 2.92 (ddd, *J* = 8.6, 7.1, 1.2 Hz, 2H), 2.78 – 2.72 (m, 2H), 2.31 – 2.24 (m, 2H). **^{13}C NMR of 14b** (101 MHz, $CDCl_3$) δ 136.76, 133.88, 132.90, 127.88, 127.72, 127.02, 126.52, 122.16, 43.30, 36.32, 28.18, 23.08.

Figure S1. ^{1}H and ^{13}C NMR spectra and data of **14b**.



HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}Cl^+$: 193.0779; found: 193.0783.

Figure S2. HRMS spectrum of **14b**.

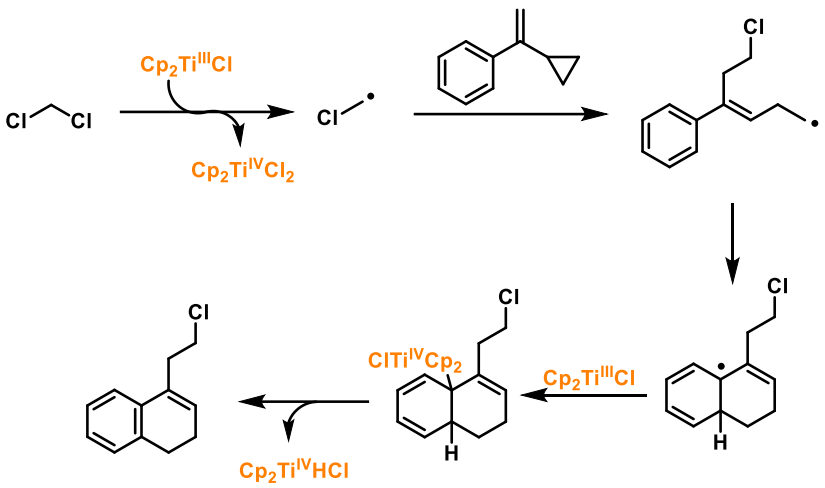
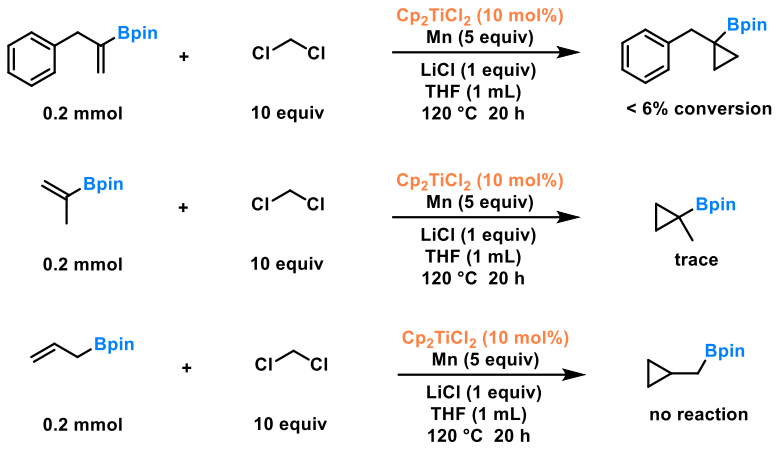
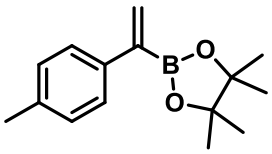


Figure S3. Tentatively proposed reaction pathway for the generation of **14b**. Cp_2TiHCl could (re)generate $Cp_2Ti(III)X$ (X = H or Cl) via (0.5) H_2 release or with the help of Mn.



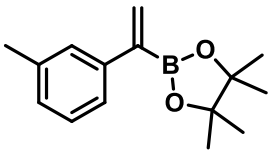
Scheme S1. reaction results with aliphatic alkenyl-B(pin).

Substrates and Products Characterization



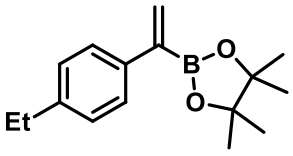
4,4,5,5-tetramethyl-2-(1-(*p*-tolyl)vinyl)-1,3,2-dioxaborolane 1b

The compound was prepared according to procedure A. Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, yellow oil, 1.76 g, 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.22 (m, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.01 – 5.89 (m, 2H), 2.25 (s, 3H), 1.24 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.58, 136.70, 130.04, 128.92, 127.09, 83.76, 24.82, 21.14. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.65. Spectroscopic data are in agreement with those previously reported.[1a]



4,4,5,5-tetramethyl-2-(1-(*m*-tolyl)vinyl)-1,3,2-dioxaborolane 1c

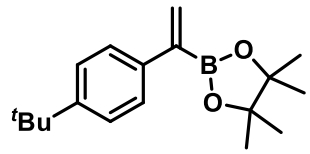
The compound was prepared according to procedure A. Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, yellow oil, 1.29 g, 53% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 7.7 Hz, 2H), 7.12 (td, *J* = 7.4, 1.0 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.03 – 5.90 (m, 2H), 2.26 (s, 3H), 1.23 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.46, 137.64, 130.70, 128.11, 127.85, 124.48, 83.80, 24.84, 21.59. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.63. Spectroscopic data are in agreement with those previously reported.[1a]



2-(1-(4-ethylphenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 1d

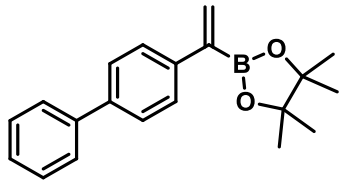
The compound was prepared according to procedure A. Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, yellow oil, 1.75 g, 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.2 Hz, 2H), 7.10 – 7.00 (m, 2H), 5.98 – 5.90 (m, 2H), 2.53 (q, *J* = 7.6 Hz, 2H), 1.25 – 1.19 (m, 12H), 1.13 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.08, 138.85, 130.13, 127.78, 127.20,

83.77, 77.48, 77.16, 76.84, 28.63, 24.88, 15.65. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.42. Spectroscopic data are in agreement with those previously reported.[1a]



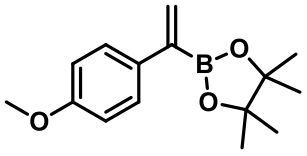
2-(1-(4-(*tert*-butyl)phenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 1e

The compound was prepared according to procedure A. Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, yellow solid, 2.31 g, 83% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 2H), 7.36 – 7.31 (m, 2H), 6.07 (d, *J* = 3.1 Hz, 1H), 6.02 (d, *J* = 3.0 Hz, 1H), 1.32 (m, 21H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.88, 138.41, 130.19, 126.81, 125.17, 83.75, 34.47, 31.37, 24.83. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.40. Spectroscopic data are in agreement with those previously reported.[1a]



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

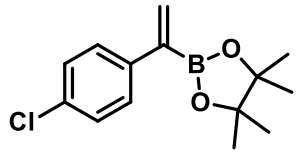
The compound was prepared according to procedure A. Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, white solid, 2.61 g, 85% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 6H), 7.44 – 7.40 (m, 2H), 7.35 – 7.31 (m, 1H), 6.11 (dd, *J* = 19.5, 3.0 Hz, 2H), 1.34 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.11, 140.46, 139.89, 130.92, 128.76, 127.64, 127.14, 127.06, 127.02, 83.90, 24.87. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.39. Spectroscopic data are in agreement with those previously reported.[1a]



2-(1-(4-methoxyphenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 1g

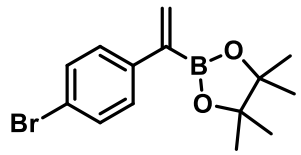
The compound was prepared according to procedure A. Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, yellow solid, 2.37 g, 91% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.36 (m, 2H), 6.93 – 6.80 (m, 2H), 5.99 (dd, *J* = 19.4, 3.0 Hz, 2H), 3.80 (s, 3H), 1.32 (s, 12H). **^{13}C NMR**

(101 MHz, $CDCl_3$) δ 158.90, 133.95, 129.02, 128.29, 113.64, 83.75, 55.26, 24.82. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.38. Spectroscopic data are in agreement with those previously reported.[1a]



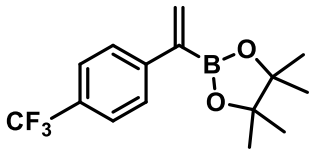
2-(1-(4-chlorophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 1h

The compound was prepared according to procedure A. Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, yellow solid, 1.87 g, 71% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 2H), 7.22 – 7.17 (m, 2H), 5.99 (q, *J* = 2.8 Hz, 2H), 1.24 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.85, 132.89, 131.37, 128.54, 128.30, 83.94, 24.81. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.54. Spectroscopic data are in agreement with those previously reported.[1a]



2-(1-(4-bromophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 1i

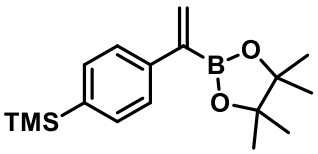
The compound was prepared according to procedure A. Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, yellow solid, 1.61 g, 52% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.21 – 7.14 (m, 2H), 6.02 – 5.92 (m, 2H), 1.22 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.88, 132.92, 131.40, 128.57, 128.33, 83.95, 24.84. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.20. Spectroscopic data are in agreement with those previously reported.[1a]



4,4,5,5-tetramethyl-2-(1-(4-(trifluoromethyl)phenyl)vinyl)-1,3,2-dioxaborolane 1j

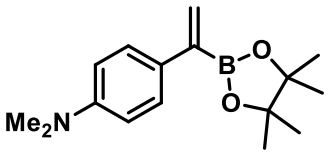
The compound was prepared according to procedure A. Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, yellow solid, 1.28 g, 43% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (s, 4H), 6.15 (dd, *J* = 20.3, 2.8 Hz, 2H), 1.32 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.10, 132.99, 129.11, 128.79, 127.50, 125.78, 125.17, 125.13, 125.09, 125.06, 84.07, 24.78. **^{11}B NMR** (128 MHz,

$CDCl_3$) δ 30.28. **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -62.41. Spectroscopic data are in agreement with those previously reported.[1a]



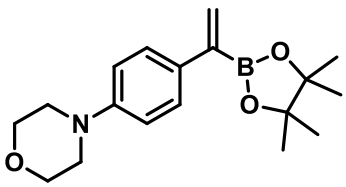
trimethyl(4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)silane 1k

The compound was prepared according to procedure A. Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, white solid, 1.78 g, 59% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 4H), 6.06 – 5.94 (m, 2H), 1.25 (s, 12H), 0.18 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.96, 139.90, 134.38, 132.17, 127.58, 84.88, 25.90，0.00. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.32. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{27}BNaO_2Si^+$: 325.1766; found: 325.1756.



***N*,*N*-dimethyl-4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)aniline 1l**

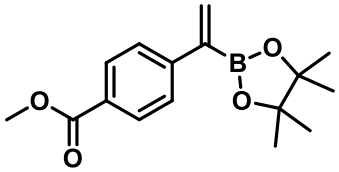
The compound was prepared according to procedure A. Eluent: petroleum ether/ethyl acetate (10:1), Rf = 0.5, white solid, 1.15 g, 42% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 6.74 – 6.70 (m, 2H), 6.00 (d, *J* = 3.0 Hz, 1H), 5.89 (d, *J* = 3.0 Hz, 1H), 2.95 (s, 6H), 1.33 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.93, 129.73, 127.92, 127.03, 112.48, 83.61, 40.70, 24.85. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.80. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{27}BNaO_2Si^+$: 325.1766; found: 325.1756. Spectroscopic data are in agreement with those previously reported.[1a]



4-(4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)morpholine 1m

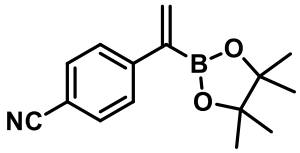
The compound was prepared according to procedure A. Eluent: petroleum ether/ethyl acetate (5:1), Rf = 0.5, yellow solid, 1.54 g, 49% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H), 6.89 – 6.85 (m, 2H), 6.01 (d, *J* = 3.0 Hz, 1H), 5.94 (d, *J* = 3.0 Hz, 1H), 3.87 – 3.84 (m, 4H),

3.16 – 3.14 (m, 4H), 1.32 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.39, 133.09, 128.51, 127.97, 115.41, 83.71, 66.94, 49.34, 24.82. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 31.09. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{27}BNO_3^+$: 316.2079; found: 316.2087.



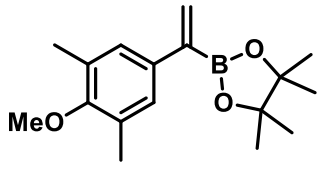
methyl 4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate 1n

The compound was prepared according to procedure B. Eluent: petroleum ether/ethyl acetate (10:1), Rf = 0.5, white solid, 1.32 g, 46% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 – 7.97 (m, 2H), 7.55 – 7.52 (m, 2H), 6.16 (t, *J* = 2.2 Hz, 2H), 3.90 (s, 3H), 1.33 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.16, 146.14, 132.79, 129.55, 128.55, 127.19, 84.01, 52.00, 24.80. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.59. Spectroscopic data are in agreement with those previously reported.[2a]



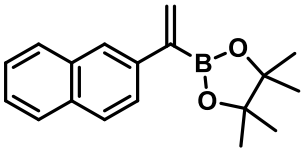
4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzonitrile 1o

The compound was prepared according to procedure A. Eluent: petroleum ether/ethyl acetate (10:1), Rf = 0.5, yellow solid, 1.63 g, 64% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 4H), 6.21 (d, *J* = 2.7 Hz, 1H), 6.15 (d, *J* = 2.7 Hz, 1H), 1.33 (d, *J* = 3.7 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.12, 133.84, 132.03, 129.78, 127.90, 119.22, 110.46, 84.19, 24.80. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.25. Spectroscopic data are in agreement with those previously reported.[1a]



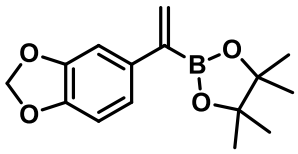
2-(1-(4-methoxy-3,5-dimethylphenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 1p

The compound was prepared according to procedure A. Eluent: petroleum ether/ethyl acetate (15:1), Rf = 0.5, yellow solid, 1.76 g, 61% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 (s, 2H), 5.99 (d, *J* = 3.1 Hz, 1H), 5.96 (d, *J* = 3.0 Hz, 1H), 3.71 (s, 3H), 2.28 (d, *J* = 0.6 Hz, 6H), 1.32 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.32, 136.94, 130.34, 129.79, 127.67, 83.76, 59.64, 24.79, 16.23. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.33. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{26}BO_3^+$: 289.1970; found: 289.1971.



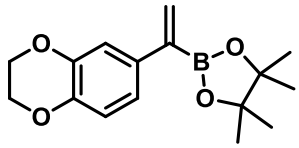
4,4,5,5-tetramethyl-2-(1-(naphthalen-2-yl)vinyl)-1,3,2-dioxaborolane 1q

The compound was prepared according to procedure A. Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, white solid, 2.18 g, 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 1.8 Hz, 1H), 7.86 – 7.71 (m, 3H), 7.62 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.47 – 7.31 (m, 2H), 6.18 (dd, *J* = 18.5, 3.0 Hz, 2H), 1.32 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.95, 133.64, 132.78, 131.32, 128.35, 127.72, 127.60, 126.26, 125.92, 125.65, 83.95, 77.49, 77.17, 76.85, 24.92. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.40. Spectroscopic data are in agreement with those previously reported.[1a]



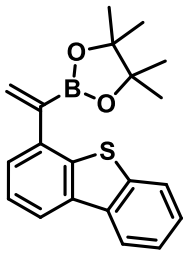
2-(1-(benzo[*d*][1,3]dioxol-5-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 1r

The compound was prepared according to procedure A. Eluent: petroleum ether/ethyl acetate (10:1), Rf = 0.5, white solid, 1.18 g, 43% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.94 – 6.91 (m, 2H), 6.69 (d, *J* = 8.0 Hz, 1H), 5.91 (d, *J* = 2.9 Hz, 1H), 5.89 (d, *J* = 2.8 Hz, 1H), 5.85 (s, 2H), 1.24 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.51, 146.77, 135.64, 129.56, 120.84, 108.08, 107.64, 100.85, 83.83, 24.80. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.41. Spectroscopic data are in agreement with those previously reported.[9]



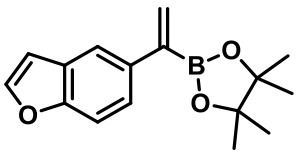
2-(1-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 1s

The compound was prepared according to procedure A. Eluent: petroleum ether/ethyl acetate (10:1), Rf = 0.5, white solid, 1.18 g, 41% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 2.1 Hz, 1H), 7.00 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.00 (d, *J* = 3.0 Hz, 1H), 5.96 (d, *J* = 2.9 Hz, 1H), 4.24 (s, 4H), 1.31 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.08, 142.93, 134.95, 129.50, 120.42, 116.95, 116.07, 83.78, 64.45, 64.39, 24.81. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 29.76. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{22}BO_4^+$: 289.1606; found: 289.1606.



2-(1-(dibenzo[*b*,*d*]thiophen-4-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 1t

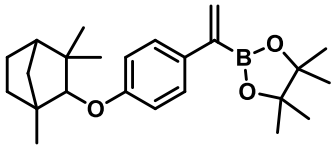
The compound was prepared according to procedure A. Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, yellow solid, 2.10 g, 61% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 – 8.13 (m, 1H), 8.07 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.88 – 7.83 (m, 1H), 7.49 – 7.43 (m, 3H), 7.40 (dd, *J* = 7.4, 1.2 Hz, 1H), 6.40 (dd, *J* = 22.8, 2.9 Hz, 2H), 1.35 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.60, 138.06, 137.33, 135.94, 135.88, 134.03, 126.59, 126.55, 124.72, 124.21, 122.61, 121.65, 120.09, 84.12, 24.85. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.04. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{20}H_{21}BNaO_2S^+$: 359.1248; found: 359.1254.



2-(1-(benzofuran-5-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 1u

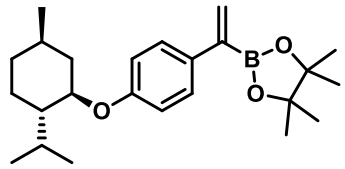
The compound was prepared according to procedure A. Eluent: petroleum ether/ethyl acetate (15:1), Rf = 0.5, white solid, 1.38 g, 51% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (t, *J* = 1.3 Hz, 1H), 7.49 (t, *J* = 2.2 Hz, 1H), 7.35 (s, 2H), 6.68 – 6.65 (m, 1H), 5.99 (q, *J* = 3.0 Hz, 2H), 1.25 (s,

12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.47, 145.09, 136.50, 130.45, 127.45, 123.92, 119.78, 110.92, 106.86, 106.77, 83.86, 24.84. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.45. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{19}BNaO_3^+$: 293.1319; found: 293.1325.



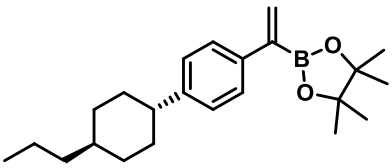
4,4,5,5-tetramethyl-2-(1-(4-((1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)phenyl)vinyl)-1,3,2-dioxaborolane 1v

The compound was prepared according to procedure A. Eluent: petroleum ether/ethyl acetate (15:1), Rf = 0.5, yellow solid, 1.49 g, 39% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 6.87 – 6.85 (m, 2H), 5.97 (dd, *J* = 25.5, 3.0 Hz, 2H), 3.84 (d, *J* = 1.7 Hz, 1H), 2.03 (dddd, *J* = 12.4, 9.0, 5.8, 2.2 Hz, 1H), 1.80 – 1.71 (m, 2H), 1.61 – 1.41 (m, 3H), 1.32 (s, 12H), 1.18 (s, 4H), 1.08 (s, 3H), 0.86 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.70, 133.30, 128.65, 128.12, 115.41, 90.04, 83.71, 49.60, 49.13, 41.44, 40.04, 30.50, 26.42, 25.90, 24.83, 20.44, 19.94. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.90. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{36}BO_3^+$: 383.2752; found: 383.2762.



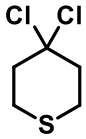
2-(1-(4-(((2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)phenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 1w

The compound was prepared according to procedure A. Eluent: petroleum ether/ethyl acetate (15:1), Rf = 0.5, white solid, 1.81 g, 47% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.34 (m, 2H), 6.78 – 6.76 (m, 2H), 5.90 (dd, *J* = 23.2, 3.0 Hz, 2H), 3.94 (td, *J* = 10.5, 4.1 Hz, 1H), 2.17 – 2.06 (m, 3H), 1.67 – 1.59 (m, 3H), 1.41 (dddt, *J* = 13.5, 10.5, 7.2, 3.1 Hz, 3H), 1.24 (s, 12H), 0.85 – 0.82 (m, 6H), 0.69 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.71, 133.57, 128.78, 128.30, 115.46, 83.71, 77.35, 48.06, 40.35, 34.58, 31.46, 26.10, 24.83, 23.79, 22.18, 20.80, 16.66. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.10. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{37}BNaO_3^+$: 407.2728; found: 407.2744.



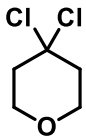
4,4,5,5-tetramethyl-2-(1-(4-((1*s*,4*r*)-4-propylcyclohexyl)phenyl)vinyl)-1,3,2-dioxaborolane 1x

The compound was prepared according to procedure A. Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, yellow solid, 2.55 g, 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.26 (m, 2H), 7.11 – 6.99 (m, 2H), 5.94 (dd, *J* = 15.4, 3.1 Hz, 2H), 2.35 (tt, *J* = 12.2, 3.2 Hz, 1H), 1.77 (ddd, *J* = 14.8, 12.5, 3.5 Hz, 4H), 1.41 – 1.25 (m, 4H), 1.21 (s, 12H), 1.15 – 1.08 (m, 3H), 1.00 – 0.89 (m, 2H), 0.81 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.58, 137.77, 129.03, 125.99, 125.63, 82.60, 43.29, 38.73, 36.00, 33.27, 32.56, 23.74, 19.01, 13.42. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.34. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{35}BNaO_2^+$: 377.2622; found: 377.2623.



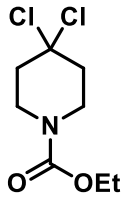
4,4-dichlorotetrahydro-2*H*-thiopyran 2h

Eluent: petroleum ether/ethyl acetate (50:1), Rf = 0.5, brown solid, 952 mg, 56% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.88 – 2.73 (m, 4H), 2.65 – 2.56 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 90.07, 46.67, 26.20. Spectroscopic data are in agreement with those previously reported.[3]



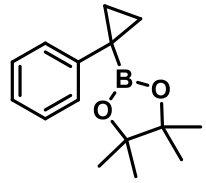
4,4-dichlorotetrahydro-2*H*-pyran 2i

Eluent: petroleum ether/ethyl acetate (50:1), Rf = 0.5, black liquid, 662 mg, 43% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.82 (dd, *J* = 5.8, 4.4 Hz, 4H), 2.46 – 2.39 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 87.22, 64.91, 46.24. Spectroscopic data are in agreement with those previously reported.[3]



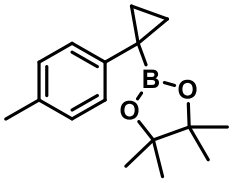
ethyl 4,4-dichloropiperidine-1-carboxylate 2j

Eluent: petroleum ether/ethyl acetate (5:1), Rf = 0.5, colorless oil, 1.53 mg, 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.14 (q, *J* = 7.1 Hz, 2H), 3.63 (t, *J* = 5.5 Hz, 4H), 2.35 (t, *J* = 5.5 Hz, 4H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.11, 88.22, 61.74, 41.37, 14.65, 14.59. Spectroscopic data are in agreement with those previously reported.[3]



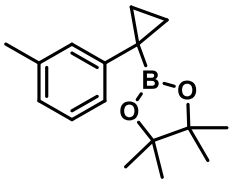
4,4,5,5-tetramethyl-2-(1-phenylcyclopropyl)-1,3,2-dioxaborolane 3a

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, yellow oil, 29.8 mg, 61% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 – 7.14 (m, 4H), 7.09 – 7.02 (m, 1H), 1.14 (s, 12H), 1.03 (q, *J* = 3.5 Hz, 2H), 0.84 (q, *J* = 3.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.82, 128.94, 128.00, 125.26, 83.34, 24.62, 13.39. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.33. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{21}BNaO_2^+$: 267.1527; found: 267.1521.



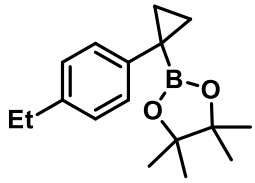
4,4,5,5-tetramethyl-2-(1-(*p*-tolyl)cyclopropyl)-1,3,2-dioxaborolane 3b

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, yellow oil, 40.8 mg, 79% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 – 7.14 (m, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 2.29 (s, 3H), 1.21 (s, 12H), 1.07 (q, *J* = 3.5 Hz, 2H), 0.89 – 0.86 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.78, 134.65, 128.89, 128.77, 83.31, 24.62, 21.07, 13.25. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.35. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{24}BO_2^+$: 259.1864; found: 259.1880.



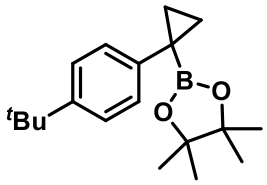
4,4,5,5-tetramethyl-2-(1-(*m*-tolyl)cyclopropyl)-1,3,2-dioxaborolane 3c

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, yellow oil, 30.4 mg, 59% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 – 7.04 (m, 3H), 6.96 – 6.92 (m, 1H), 2.31 (s, 3H), 1.21 (s, 12H), 1.08 (q, *J* = 3.5 Hz, 2H), 0.89 (q, *J* = 3.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.36, 129.66, 127.87, 126.25, 126.13, 83.31, 24.61, 21.56, 13.21. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.76. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{24}BO_2^+$: 259.1864; found: 259.1871.



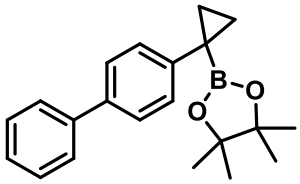
2-(1-(4-ethylphenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3d

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, colorless oil, 39.2 mg, 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 – 7.09 (m, 2H), 7.01 – 6.98 (m, 2H), 2.53 (q, *J* = 7.5 Hz, 2H), 1.16 – 1.12 (m, 15H), 1.01 (q, *J* = 3.5 Hz, 2H), 0.81 (h, *J* = 3.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.95, 140.88, 128.78, 127.50, 83.29, 28.39, 24.83, 24.61, 15.45, 13.35, 1.05. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.78. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{26}BO_2^+$: 273.2020; found: 273.2025.



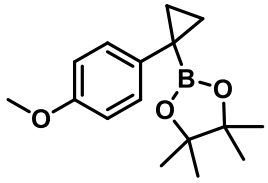
2-(1-(4-(*tert*-butyl)phenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3e

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, colorless oil, 25.2 mg, 42% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.9 Hz, 2H), 7.21 – 7.16 (m, 2H), 1.29 (s, 12H), 1.22 (s, 9H), 1.08 (p, *J* = 3.8 Hz, 2H), 0.89 (p, *J* = 3.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.63, 141.54, 128.18, 124.91, 83.26, 34.27, 31.43, 31.40, 24.60, 13.62. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.86. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{30}BO_2^+$: 301.2333; found: 301.2328.



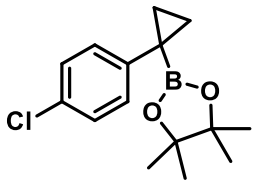
2-(1-([1,1'-biphenyl]-4-yl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3f

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, white solid, 42.9 mg, 67% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 – 7.58 (m, 2H), 7.51 – 7.48 (m, 2H), 7.47 – 7.40 (m, 3H), 7.38 – 7.35 (m, 2H), 1.26 (s, 12H), 1.17 (q, *J* = 3.5 Hz, 2H), 1.00 – 0.95 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.06, 141.31, 138.10, 129.28, 128.69, 127.03, 126.86, 126.83, 83.45, 24.87, 24.65, 13.66. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.33. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{25}BNaO_2^+$: 343.1840; found: 343.1855.



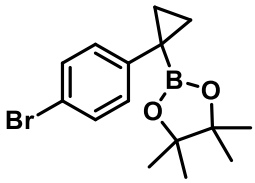
2-(1-(4-methoxyphenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3g

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, white solid, 24.1 mg, 44% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 – 7.16 (m, 2H), 6.80 – 6.77 (m, 2H), 3.77 (s, 3H), 1.21 (s, 12H), 1.06 (q, *J* = 3.5 Hz, 2H), 0.85 (q, *J* = 3.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.27, 136.94, 129.88, 113.44, 83.31, 55.20, 24.61, 13.29. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.72. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{23}BNaO_3^+$: 297.1632; found: 297.1636.



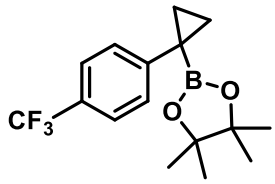
2-(1-(4-chlorophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3h

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, coloeless oil, 41.7 mg, 75% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (s, 4H), 1.21 (s, 12H), 1.11 (q, *J* = 3.5 Hz, 2H), 0.86 (q, *J* = 3.6 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.41, 130.88, 130.37, 128.10, 83.51, 24.61, 13.52. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.11. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{21}BClO_2^+$: 279.1318; found: 279.1319.



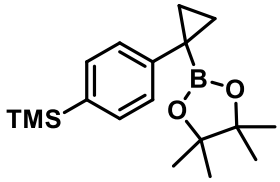
2-(1-(4-bromophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3i

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, yellow oil, 37.4 mg, 58% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 2H), 7.08 – 7.06 (m, 2H), 1.14 (d, *J* = 2.0 Hz, 12H), 1.04 (q, *J* = 3.6 Hz, 2H), 0.80 (dt, *J* = 6.2, 3.2 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.94, 131.02, 130.80, 118.97, 83.51, 24.61, 13.49, 1.06. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.65. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{20}BBrNaO_2^+$: 345.0632; found: 345.0646.



4,4,5,5-tetramethyl-2-(1-(4-(trifluoromethyl)phenyl)cyclopropyl)-1,3,2-dioxaborolane 3j

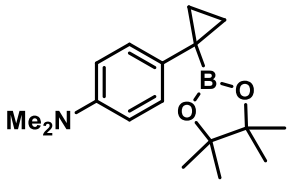
Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, yellow oil, 38.1 mg, 61% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 2H), 7.38 – 7.36 (m, 2H), 1.22 (s, 12H), 1.17 (q, *J* = 3.6 Hz, 2H), 0.93 (q, *J* = 3.6 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.10, 129.15, 127.50, 124.96, 124.92, 124.89, 83.61, 24.82, 24.61, 13.77. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.25. **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -62.19. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{20}BF_3NaO_2^+$: 335.1401; found: 335.1402.



trimethyl(4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)phenyl)silane 3k

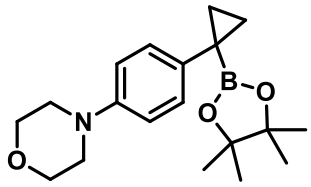
Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, yellow oil, 43.6 mg, 69% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.32 (m, 2H), 7.20 – 7.17 (m, 2H), 1.15 (s, 12H), 1.03 (q, *J* = 3.5 Hz, 2H), 0.85 (q, *J* = 3.6 Hz, 2H), 0.16 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.43, 137.43,

134.17, 129.22, 84.35, 25.60, 25.57, 14.51, 0.00. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.69. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{29}BNaO_2Si^+$: 339.1922; found: 339.1935.



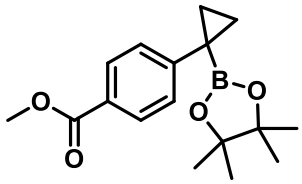
***N*,*N*-dimethyl-4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)aniline 3l**

Eluent: petroleum ether/ethyl acetate (10:1), Rf = 0.5, colorless oil, 43.6 mg, 76% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09 – 7.06 (m, 2H), 6.61 – 6.58 (m, 2H), 2.82 (s, 6H), 1.14 (s, 12H), 0.96 (q, *J* = 3.5 Hz, 2H), 0.77 (q, *J* = 3.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 129.54, 112.88, 83.19, 41.00, 24.61, 13.13. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.04. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{27}BNO_2^+$: 288.2129; found: 288.2115.



4-(4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)phenyl)morpholine 3m

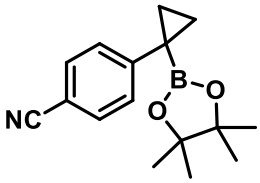
Eluent: petroleum ether/ethyl acetate (5:1), Rf = 0.5, yellow oil, 43.4 mg, 66% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.3 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 3.85 (q, *J* = 4.7 Hz, 4H), 3.12 (q, *J* = 4.4 Hz, 4H), 1.21 (s, 12H), 1.06 (q, *J* = 3.5 Hz, 2H), 0.85 (q, *J* = 3.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 129.56, 115.68, 83.27, 67.00, 49.75, 24.61, 13.28. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.12. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{29}BNO_3^+$: 330.2235; found: 330.2252.



methyl 4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)benzoate 3n

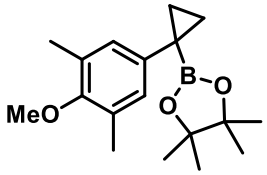
Eluent: petroleum ether/ethyl acetate (10:1), Rf = 0.5, yellow oil, 35.0 mg, 58% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.83 (m, 2H), 7.27 – 7.25 (m, 2H), 3.81 (s, 3H), 1.15 (s, 12H), 1.10 (q, *J* = 3.7 Hz, 2H), 0.87 (q, *J* = 3.6 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.29, 150.65,

129.39, 128.79, 127.09, 83.54, 51.90, 24.81, 24.60, 13.92. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.66. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{24}BO_4^+$: 303.1762; found: 303.1768.



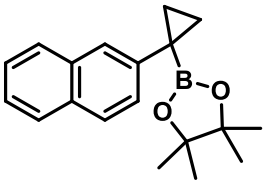
4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)benzonitrile 3o

Eluent: petroleum ether/ethyl acetate (10:1), Rf = 0.5, yellow oil, 36.6 mg, 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.51 (m, 2H), 7.37 – 7.34 (m, 2H), 1.22 (s, 14H), 0.93 (q, *J* = 3.7 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.84, 131.87, 129.54, 119.43, 108.81, 83.73, 24.60, 14.20. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.39. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{20}BNNaO_2^+$: 292.1479; found: 292.1489.



2-(1-(4-methoxy-3,5-dimethylphenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3p

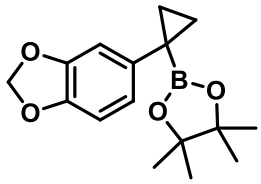
Eluent: petroleum ether/ethyl acetate (15:1), Rf = 0.5, yellow oil, 24.8 mg, 41% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.87 (s, 2H), 3.68 (s, 3H), 2.23 (s, 6H), 1.22 (s, 12H), 1.04 (q, *J* = 3.4 Hz, 2H), 0.84 (q, *J* = 3.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.57, 139.85, 129.93, 129.24, 83.28, 59.58, 24.58, 16.20, 13.26. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.89. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{28}BO_3^+$: 303.2126; found: 303.2132.



4,4,5,5-tetramethyl-2-(1-(naphthalen-2-yl)cyclopropyl)-1,3,2-dioxaborolane 3q

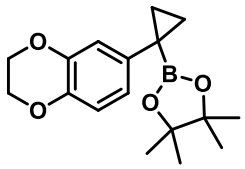
Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, yellow oil, 41.7 mg, 71% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 3H), 7.67 – 7.63 (m, 1H), 7.49 – 7.37 (m, 3H), 1.23 (s, 12H), 1.19 (q, *J* = 3.5 Hz, 2H), 1.02 (q, *J* = 3.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.57, 133.57, 131.84, 128.88, 127.51, 127.37, 126.35, 125.62, 124.91, 83.43, 24.64, 13.25, 1.07. **^{11}B**

NMR (128 MHz, $CDCl_3$) δ 33.61. **HRMS** (ESI) m/z: $[M+K]^+$ calcd for $C_{19}H_{23}BKO_2^+$: 333.1423; found: 333.1438.



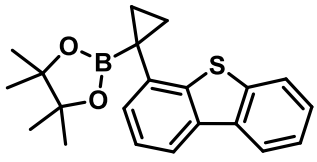
2-(1-(benzo[*d*][1,3]dioxol-5-yl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3r

Eluent: petroleum ether/ethyl acetate (10:1), Rf = 0.6, yellow oil, 39.2 mg, 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.78 (d, *J* = 1.7 Hz, 1H), 6.73 – 6.64 (m, 2H), 5.89 (s, 2H), 1.21 (s, 12H), 1.05 (q, *J* = 3.5 Hz, 2H), 0.83 (q, *J* = 3.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.11, 145.17, 138.84, 121.59, 110.02, 107.81, 100.66, 83.38, 24.80, 24.59, 13.42. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.75. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{21}BNaO_4^+$: 311.1425; found: 311.1443.



2-(1-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3s

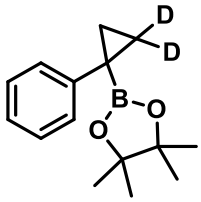
Eluent: petroleum ether/ethyl acetate (10:1), Rf = 0.6, yellow oil, 35.0 mg, 58% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.77 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.73 (t, *J* = 1.3 Hz, 2H), 4.23 – 4.19 (m, 4H), 1.21 (s, 12H), 1.04 (q, *J* = 3.5 Hz, 2H), 0.83 (q, *J* = 3.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 121.88, 117.60, 116.70, 83.32, 64.40, 64.31, 24.59, 13.45. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.86. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{24}BO_4^+$: 303.1762; found: 303.1757.



2-(1-(dibenzo[*b*,*d*]thiophen-4-yl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3t

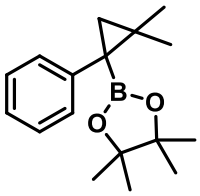
Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, yellow oil, 54.6 mg, 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 – 8.12 (m, 1H), 7.99 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.90 – 7.86 (m, 1H), 7.45 – 7.42 (m, 2H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.32 (dd, *J* = 7.4, 1.2 Hz, 1H), 1.30 (q, *J* = 3.5 Hz, 2H), 1.20 (s, 12H), 1.05 (q, *J* = 3.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.64, 139.85,

139.33, 136.36, 135.15, 126.90, 126.31, 124.61, 124.05, 122.70, 121.68, 119.10, 83.59, 24.86, 24.58, 12.88. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.84. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{23}BNaO_2^+$: 373.1404; found: 373.1395.



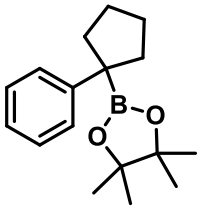
4,4,5,5-tetramethyl-2-(1-phenylcyclopropyl-2,2-d_2)-1,3,2-dioxaborolane 3u

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, colorless oil, 22.6 mg, 46% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 4H), 7.15 – 7.11 (m, 1H), 1.22 (s, 12H), 1.10 (d, *J* = 3.5 Hz, 1H), 0.90 (d, *J* = 3.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.81, 128.94, 127.99, 125.24, 83.33, 24.83, 24.61, 13.21. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.98. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{20}D_2BO_2^+$: 247.1833; found: 247.1827.



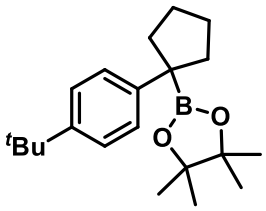
2-(2,2-dimethyl-1-phenylcyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3v

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, colorless oil, 37.5 mg, 69% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 – 7.11 (m, 4H), 7.06 – 7.01 (m, 1H), 1.23 (s, 3H), 1.12 (s, 6H), 1.07 (s, 6H), 1.06 (s, 1H), 0.89 (d, *J* = 3.9 Hz, 1H), 0.64 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.93, 130.31, 127.49, 124.88, 83.30, 24.92, 24.65, 24.52, 24.40, 23.51, 23.46. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.49. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{25}BNaO_2^+$: 295.1840; found: 295.1846.



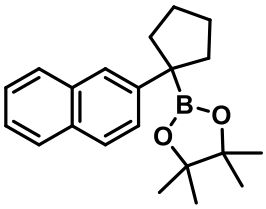
4,4,5,5-tetramethyl-2-(1-phenylcyclopentyl)-1,3,2-dioxaborolane 4a

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, colorless oil, 37.0 mg, 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 – 7.16 (m, 4H), 7.06 – 7.01 (m, 1H), 2.30 – 2.22 (m, 2H), 1.65 – 1.57 (m, 6H), 1.06 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.16, 127.93, 127.01, 124.76, 83.30, 35.18, 24.55, 24.39. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.96. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{26}BO_2^+$: 273.2020; found: 273.2019.



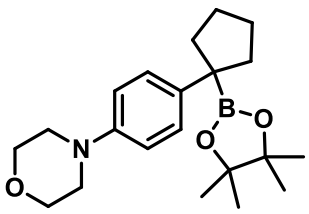
2-(1-(4-(*tert*-butyl)phenyl)cyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4b

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, colorless oil, 24.9 mg, 38% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 – 7.17 (m, 2H), 7.13 – 7.09 (m, 2H), 2.22 (pd, *J* = 7.8, 2.0 Hz, 2H), 1.62 – 1.56 (m, 6H), 1.22 (s, 9H), 1.07 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.27, 142.88, 125.49, 123.77, 82.20, 34.28, 33.18, 30.39, 23.61, 23.38. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.94. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{34}BO_2^+$: 329.2646; found: 329.2652.



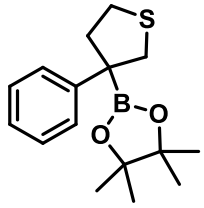
4,4,5,5-tetramethyl-2-(1-(naphthalen-2-yl)cyclopentyl)-1,3,2-dioxaborolane 4c

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, colorless oil, 29.6 mg, 46% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.60 (m, 4H), 7.40 – 7.28 (m, 3H), 2.36 – 2.32 (m, 2H), 1.76 – 1.61 (m, 6H), 1.05 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.76, 133.62, 131.51, 127.73, 127.40, 127.27, 126.88, 125.56, 124.78, 124.29, 83.41, 35.25, 24.60, 24.44. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.99. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{27}BNaO_2^+$: 345.1996; found: 345.2000.



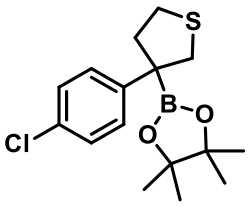
4-(4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl)phenyl)morpholine 4d

Eluent: petroleum ether/ethyl acetate (5:1), Rf = 0.5, colorless oil, 34.3 mg, 48% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 – 7.17 (m, 2H), 6.86 – 6.81 (m, 2H), 3.86 – 3.84 (m, 4H), 3.13 – 3.10 (m, 4H), 2.29 – 2.26 (m, 2H), 1.70 – 1.61 (m, 7H), 1.13 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.47, 138.83, 127.65, 115.59, 83.22, 67.05, 49.75, 35.28, 24.56, 24.42. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.70. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{33}BO_3^+$: 358.2548; found: 358.2554.



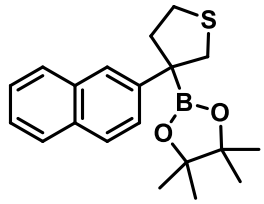
4,4,5,5-tetramethyl-2-(3-phenyltetrahydrothiophen-3-yl)-1,3,2-dioxaborolane 5a

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, colorless oil, 27.3 mg, 47% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 4H), 7.20 – 7.13 (m, 1H), 3.39 (d, *J* = 10.0 Hz, 1H), 3.03 – 2.91 (m, 2H), 2.85 (ddd, *J* = 10.3, 7.3, 4.1 Hz, 1H), 2.67 (ddd, *J* = 11.2, 6.7, 4.2 Hz, 1H), 2.04 (dt, *J* = 12.0, 8.0 Hz, 1H), 1.17 (d, *J* = 8.3 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.12, 128.30, 126.80, 125.78, 83.89, 38.48, 38.46, 30.19, 24.45, 24.34. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.69. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{24}BO_2^+$: 297.1585; found: 297.1577.



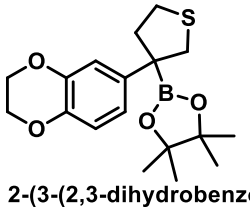
2-(3-(4-chlorophenyl)tetrahydrothiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5b

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, colorless oil, 50.5 mg, 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (s, 4H), 3.36 (d, *J* = 10.1 Hz, 1H), 2.98 – 2.91 (m, 2H), 2.82 (ddd, *J* = 10.2, 7.3, 4.5 Hz, 1H), 2.65 – 2.58 (m, 1H), 2.07 – 1.98 (m, 1H), 1.17 (d, *J* = 7.7 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.65, 131.57, 128.40, 128.20, 84.05, 38.48, 38.42, 30.11, 24.47, 24.35. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.02. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{22}BClNaO_2S^+$: 347.1014; found: 347.1015.



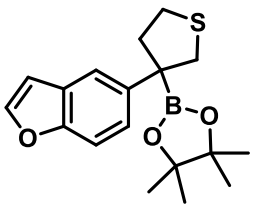
4,4,5,5-tetramethyl-2-(3-(naphthalen-2-yl)tetrahydrothiophen-3-yl)-1,3,2-dioxaborolane 5c

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, colorless oil, 35.4 mg, 52% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 4H), 7.51 – 7.42 (m, 3H), 3.50 (d, *J* = 10.0 Hz, 1H), 3.12 (d, *J* = 10.1 Hz, 1H), 3.02 (ddd, *J* = 10.1, 8.3, 6.6 Hz, 1H), 2.88 (ddd, *J* = 10.2, 7.3, 4.3 Hz, 1H), 2.77 (ddd, *J* = 11.4, 6.6, 4.3 Hz, 1H), 2.17 (dt, *J* = 12.0, 7.8 Hz, 1H), 1.18 (d, *J* = 9.3 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.64, 133.56, 131.86, 127.86, 127.74, 127.43, 125.99, 125.89, 125.35, 124.67, 84.00, 38.55, 38.48, 30.25, 24.49, 24.38. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.77. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{26}BO_2S^+$: 347.1741; found: 347.1744.



2-(3-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)tetrahydrothiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5d

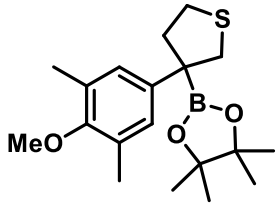
Eluent: petroleum ether/ethyl acetate (15:1), Rf = 0.5, colorless oil, 36.2 mg, 52% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.83 (d, *J* = 1.9 Hz, 1H), 6.81 – 6.76 (m, 2H), 4.23 (s, 4H), 3.31 (s, 1H), 2.88 (d, *J* = 32.9 Hz, 3H), 2.57 (ddd, *J* = 11.4, 6.6, 4.2 Hz, 1H), 2.03 – 1.95 (m, 1H), 1.18 (d, *J* = 6.5 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.17, 141.60, 136.43, 119.96, 116.92, 115.58, 83.86, 64.40, 64.34, 38.71, 38.64, 30.19, 24.48, 24.37. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.98. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{25}BNaO_4S^+$: 371.1459; found: 371.1463.



2-(3-(benzofuran-5-yl)tetrahydrothiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5e

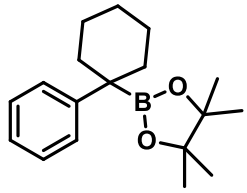
Eluent: petroleum ether/ethyl acetate (15:1), Rf = 0.5, colorless oil, 31.7 mg, 48% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 2.2 Hz, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.41 (dt, *J* = 8.6, 0.8 Hz, 1H), 7.28 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.72 (dd, *J* = 2.2, 0.9 Hz, 1H), 3.48 – 3.40 (m, 1H), 3.06 –

2.92 (m, 2H), 2.86 (ddd, *J* = 10.1, 7.3, 4.2 Hz, 1H), 2.76 – 2.66 (m, 1H), 2.09 (ddd, *J* = 11.9, 8.5, 7.3 Hz, 1H), 1.17 (d, *J* = 9.0 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.42, 145.04, 137.65, 127.45, 123.66, 118.79, 110.96, 106.69, 83.89, 38.99, 38.91, 30.24, 24.46, 24.35. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.55. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{23}BNaO_3S^+$: 353.1353; found: 353.1369.



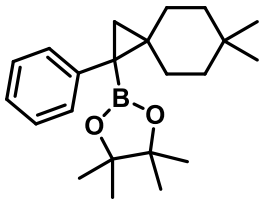
2-(3-(4-methoxy-3,5-dimethylphenyl)tetrahydrothiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5f

Eluent: petroleum ether/ethyl acetate (15:1), Rf = 0.5, colorless oil, 34.1 mg, 49% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.94 (s, 2H), 3.69 (s, 3H), 3.38 – 3.22 (m, 1H), 2.99 – 2.89 (m, 2H), 2.85 (ddd, *J* = 10.1, 7.4, 4.0 Hz, 1H), 2.66 – 2.54 (m, 1H), 2.25 (s, 6H), 1.99 (ddd, *J* = 12.0, 8.8, 7.4 Hz, 1H), 1.18 (d, *J* = 8.1 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.00, 138.16, 130.35, 127.14, 83.84, 59.65, 38.65, 30.25, 24.45, 24.33, 16.24. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.08. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{30}BO_3S^+$: 349.2003; found: 349.2007.



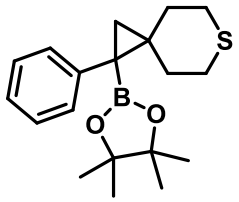
4,4,5,5-tetramethyl-2-(1-phenylcyclohexyl)-1,3,2-dioxaborolane 6a

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, colorless oil, 24.6 mg, 43% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.6 Hz, 2H), 7.20 – 7.15 (m, 3H), 2.24 (d, *J* = 12.1 Hz, 2H), 1.74 – 1.67 (m, 2H), 1.34 – 1.29 (m, 3H), 1.24 – 1.20 (m, 3H), 1.07 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 128.06, 126.22, 124.94, 83.24, 34.84, 26.25, 25.76, 24.51. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.11. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{27}BNaO_2^+$: 309.1996; found: 309.1987.



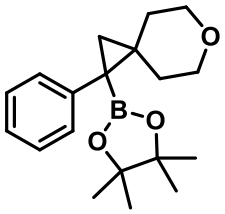
2-(6,6-dimethyl-1-phenylspiro[2.5]octan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7a

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, colorless oil, 35.4 mg, 52% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.4 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.16 – 7.10 (m, 1H), 1.80 (ddd, *J* = 13.9, 9.5, 4.9 Hz, 2H), 1.40 (ddt, *J* = 20.4, 12.8, 6.0 Hz, 4H), 1.18 (d, *J* = 19.9 Hz, 14H), 1.07 (d, *J* = 3.9 Hz, 1H), 0.97 (d, *J* = 3.9 Hz, 1H), 0.91 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.29, 130.38, 127.35, 124.83, 83.26, 38.71, 30.67, 30.30, 29.92, 29.05, 24.89, 24.64, 22.24. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.15. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{33}BNaO_2^+$: 363.2466; found: 363.2463.



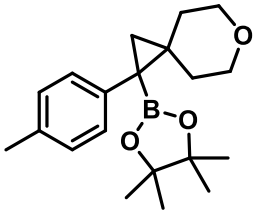
4,4,5,5-tetramethyl-2-(1-phenyl-6-thiaspiro[2.5]octan-1-yl)-1,3,2-dioxaborolane 8a

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, colorless oil, 51.5 mg, 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 4H), 7.21 – 7.16 (m, 1H), 2.78 – 2.75 (m, 2H), 2.56 – 2.50 (m, 2H), 2.09 (ddd, *J* = 12.9, 7.6, 5.3 Hz, 1H), 1.96 – 1.92 (m, 1H), 1.50 – 1.48 (m, 1H), 1.22 (d, *J* = 17.2 Hz, 12H), 1.16 – 1.06 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.92, 130.45, 127.59, 125.25, 83.50, 36.00, 34.31, 29.53, 28.15, 27.50, 24.85, 24.67, 21.84. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.18. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{27}BNaO_2S^+$: 353.1717; found: 353.1731.



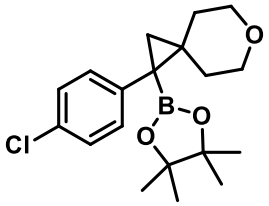
4,4,5,5-tetramethyl-2-(1-phenyl-6-oxaspiro[2.5]octan-1-yl)-1,3,2-dioxaborolane 9a

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, yellow oil, 46.5 mg, 74% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 4H), 7.15 – 7.13 (m, 1H), 3.90 (dt, *J* = 11.1, 4.1 Hz, 1H), 3.74 (dt, *J* = 11.2, 4.2 Hz, 1H), 3.62 (ddd, *J* = 11.2, 9.9, 2.8 Hz, 1H), 3.45 (ddd, *J* = 11.1, 9.9, 2.9 Hz, 1H), 2.01 – 1.92 (m, 1H), 1.64 – 1.56 (m, 1H), 1.48 – 1.38 (m, 1H), 1.18 (d, *J* = 17.4 Hz, 13H), 1.09 (dd, *J* = 4.1, 1.0 Hz, 1H), 0.57 (ddt, *J* = 13.6, 4.5, 2.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.36, 130.31, 127.60, 125.21, 83.48, 67.58, 67.45, 34.59, 33.54, 28.57, 24.86, 24.72, 21.94. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.44. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{27}BNaO_3^+$: 337.1945; found: 337.1957.



4,4,5,5-tetramethyl-2-(1-(*p*-tolyl)-6-oxaspiro[2.5]octan-1-yl)-1,3,2-dioxaborolane 9b

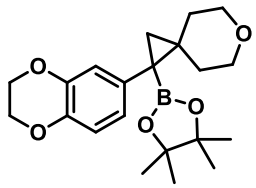
Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, colorless oil, 33.5 mg, 51% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 – 7.12 (m, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 3.89 (dt, *J* = 11.2, 4.1 Hz, 1H), 3.73 (dt, *J* = 11.1, 4.2 Hz, 1H), 3.62 (ddd, *J* = 11.1, 9.9, 2.8 Hz, 1H), 3.45 (ddd, *J* = 11.0, 9.8, 2.9 Hz, 1H), 2.30 (s, 3H), 1.95 (ddd, *J* = 13.6, 9.6, 4.0 Hz, 1H), 1.59 (ddt, *J* = 13.3, 4.3, 2.3 Hz, 1H), 1.46 – 1.37 (m, 1H), 1.17 (d, *J* = 15.6 Hz, 13H), 1.06 (dd, *J* = 4.1, 1.0 Hz, 1H), 0.58 (ddt, *J* = 13.8, 4.4, 2.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.16, 134.52, 130.12, 128.38, 83.43, 67.61, 67.49, 34.58, 33.48, 28.46, 24.84, 24.75, 21.92, 21.06. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.25. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{30}BO_3^+$: 329.2283; found: 329.2287.



2-(1-(4-chlorophenyl)-6-oxaspiro[2.5]octan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 9c

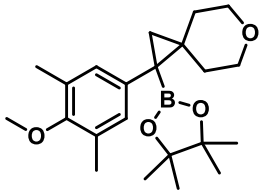
Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, colorless oil, 35.5 mg, 51% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 – 7.15 (m, 4H), 3.88 (dt, *J* = 11.1, 4.1 Hz, 1H), 3.73 (dt, *J* = 11.1, 4.2 Hz, 1H), 3.60 (ddd, *J* = 11.1, 9.9, 2.8 Hz, 1H), 3.45 (ddd, *J* = 11.1, 10.0, 2.9 Hz, 1H), 1.94 (ddd, *J* = 13.8, 9.9, 4.0 Hz, 1H), 1.59 (ddt, *J* = 13.4, 4.5, 2.4 Hz, 1H), 1.40 (ddd, *J* = 14.1, 10.1, 3.9

Hz, 1H), 1.17 (d, *J* = 17.9 Hz, 13H), 1.06 – 1.02 (m, 1H), 0.58 – 0.52 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.99, 131.60, 130.93, 127.78, 83.65, 67.54, 67.37, 34.38, 33.53, 28.83, 24.87, 24.67, 22.17. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.14. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{26}BClNaO_3^+$: 371.1556; found: 371.1565.



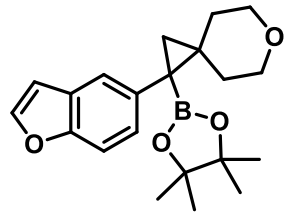
2-(1-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-6-oxaspiro[2.5]octan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 9d

Eluent: petroleum ether/ethyl acetate (10:1), Rf = 0.5, colorless oil, 43.2 mg, 58% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.72 (d, *J* = 2.6 Hz, 3H), 4.22 (s, 4H), 3.87 (dt, *J* = 11.1, 4.1 Hz, 1H), 3.74 (dt, *J* = 11.1, 4.2 Hz, 1H), 3.59 (ddd, *J* = 11.1, 9.8, 2.8 Hz, 1H), 3.45 (ddd, *J* = 11.0, 9.8, 2.9 Hz, 1H), 1.90 (ddd, *J* = 13.6, 9.7, 4.0 Hz, 1H), 1.57 (dp, *J* = 13.5, 2.3 Hz, 1H), 1.46 – 1.38 (m, 1H), 1.17 (d, *J* = 13.1 Hz, 12H), 1.12 (dd, *J* = 4.2, 1.1 Hz, 1H), 1.02 – 0.97 (m, 1H), 0.65 – 0.61 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.61, 141.21, 134.58, 123.38, 118.77, 116.25, 83.44, 67.58, 67.51, 64.37, 64.29, 34.50, 33.34, 28.63, 24.81, 24.77, 22.03. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.40. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{29}BNaO_5^+$: 395.2000; found: 395.2010.



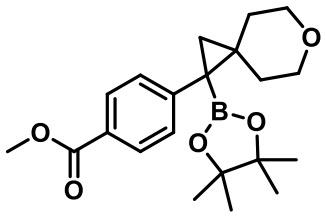
2-(1-(4-methoxy-3,5-dimethylphenyl)-6-oxaspiro[2.5]octan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 9e

Eluent: petroleum ether/ethyl acetate (10:1), Rf = 0.5, colorless oil, 46.9 mg, 63% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.84 (s, 2H), 3.89 (dt, *J* = 11.2, 4.1 Hz, 1H), 3.74 (dt, *J* = 11.0, 4.2 Hz, 1H), 3.68 (s, 3H), 3.60 (ddd, *J* = 11.1, 9.9, 2.8 Hz, 1H), 3.45 (ddd, *J* = 11.0, 9.9, 2.9 Hz, 1H), 2.23 (s, 6H), 1.93 (ddd, *J* = 13.7, 9.8, 4.0 Hz, 1H), 1.53 (ddt, *J* = 13.4, 4.5, 2.3 Hz, 1H), 1.46 – 1.37 (m, 2H), 1.17 (d, *J* = 13.4 Hz, 12H), 1.10 (dd, *J* = 4.1, 1.1 Hz, 1H), 1.03 – 0.99 (m, 1H), 0.66 – 0.51 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.61, 136.16, 130.52, 129.44, 83.38, 67.60, 67.53, 59.63, 34.73, 33.40, 28.27, 24.80, 24.76, 21.89, 16.17. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.66. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{33}BNaO_4^+$: 395.2364; found: 395.2378.



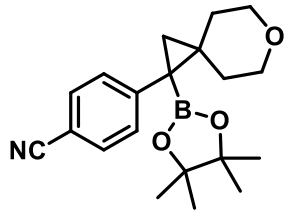
2-(1-(benzofuran-5-yl)-6-oxaspiro[2.5]octan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 9f

Eluent: petroleum ether/ethyl acetate (15:1), Rf = 0.5, colorless oil, 43.9 mg, 62% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 2.2 Hz, 1H), 7.42 (d, *J* = 1.8 Hz, 1H), 7.39 – 7.33 (m, 1H), 7.23 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.69 (dd, *J* = 2.2, 0.9 Hz, 1H), 3.92 (dt, *J* = 11.2, 4.0 Hz, 1H), 3.74 (dt, *J* = 11.1, 4.1 Hz, 1H), 3.63 (ddd, *J* = 11.1, 10.0, 2.8 Hz, 1H), 3.45 (ddd, *J* = 11.1, 10.0, 2.9 Hz, 1H), 2.04 – 1.93 (m, 1H), 1.61 (ddt, *J* = 13.4, 4.4, 2.4 Hz, 1H), 1.51 – 1.40 (m, 1H), 1.25 – 1.23 (m, 1H), 1.17 (d, *J* = 18.7 Hz, 12H), 1.12 (dd, *J* = 4.2, 1.0 Hz, 1H), 0.54 (ddt, *J* = 13.7, 4.5, 2.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.33, 144.72, 135.80, 127.18, 126.96, 122.11, 110.31, 106.53, 83.49, 67.62, 67.51, 34.61, 33.57, 28.51, 24.84, 24.72, 22.42. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.16. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{28}BO_4^+$: 355.2075; found: 355.2067.



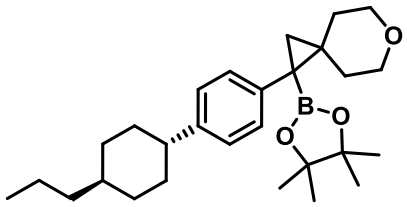
methyl 4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-oxaspiro[2.5]octan-1-yl)benzoate 9g

Eluent: petroleum ether/ethyl acetate (10:1), Rf = 0.5, colorless oil, 52.8 mg, 71% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 – 7.84 (m, 2H), 7.36 – 7.27 (m, 2H), 3.92 – 3.88 (m, 1H), 3.87 (s, 3H), 3.72 (dt, *J* = 11.2, 4.2 Hz, 1H), 3.61 (ddd, *J* = 11.1, 10.0, 2.8 Hz, 1H), 3.43 (ddd, *J* = 11.1, 9.9, 2.9 Hz, 1H), 1.96 (ddd, *J* = 13.8, 9.9, 4.1 Hz, 1H), 1.61 (ddt, *J* = 13.4, 4.3, 2.3 Hz, 1H), 1.40 (ddd, *J* = 14.1, 9.1, 4.2 Hz, 1H), 1.26 (dd, *J* = 4.3, 1.2 Hz, 1H), 1.16 (d, *J* = 20.2 Hz, 13H), 0.51 (dd, *J* = 13.7, 4.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.32, 147.41, 130.32, 129.00, 127.19, 83.71, 67.51, 67.31, 51.90, 34.38, 33.58, 29.27, 24.87, 24.64, 22.25. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.41. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{30}BO_5^+$: 373.2181; found: 373.2182.



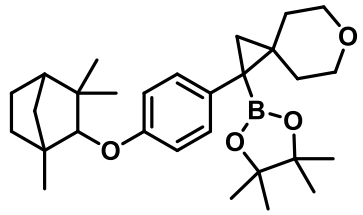
4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-oxaspiro[2.5]octan-1-yl)benzonitrile 9h

Eluent: petroleum ether/ethyl acetate (10:1), Rf = 0.5, colorless oil, 29.2 mg, 43% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.46 (m, 2H), 7.39 – 7.30 (m, 2H), 3.90 (dt, *J* = 11.2, 4.0 Hz, 1H), 3.73 (dt, *J* = 11.2, 4.1 Hz, 1H), 3.61 (ddd, *J* = 11.2, 10.2, 2.8 Hz, 1H), 3.45 (ddd, *J* = 11.2, 10.1, 2.8 Hz, 1H), 2.03 – 1.90 (m, 1H), 1.64 (dt, *J* = 4.2, 2.3 Hz, 1H), 1.47 – 1.35 (m, 1H), 1.31 (dd, *J* = 4.4, 1.3 Hz, 1H), 1.18 (d, *J* = 20.1 Hz, 12H), 1.12 (dd, *J* = 4.3, 1.0 Hz, 1H), 0.48 (dd, *J* = 10.9, 6.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.71, 131.52, 131.05, 108.98, 83.93, 67.48, 67.24, 34.21, 33.69, 29.66, 24.88, 24.65, 22.36. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.72. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{20}H_{26}BNNaO_3^+$: 362.1898; found: 362.1909.



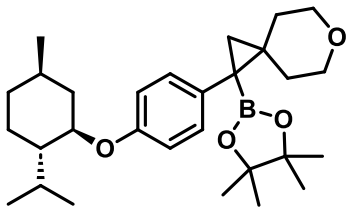
4,4,5,5-tetramethyl-2-(1-(4-((1*s*,4*r*)-4-propylcyclohexyl)phenyl)-6-oxaspiro[2.5]octan-1-yl)-1,3,2-dioxaborolane 9j

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, colorless oil, 44.7 mg, 51% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 – 7.09 (m, 2H), 7.10 – 7.00 (m, 2H), 3.89 (dt, *J* = 11.1, 4.1 Hz, 1H), 3.73 (dt, *J* = 11.0, 4.2 Hz, 1H), 3.61 (ddd, *J* = 11.1, 9.9, 2.8 Hz, 1H), 3.44 (ddd, *J* = 11.0, 9.8, 2.9 Hz, 1H), 2.41 (tt, *J* = 12.2, 3.3 Hz, 1H), 1.99 – 1.79 (m, 5H), 1.62 – 1.53 (m, 1H), 1.45 – 1.25 (m, 7H), 1.18 (d, *J* = 15.1 Hz, 14H), 1.10 – 0.99 (m, 3H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.58 (ddt, *J* = 13.5, 4.3, 2.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.46, 138.38, 130.01, 125.97, 83.37, 67.58, 67.49, 44.09, 39.79, 37.11, 34.71, 34.38, 34.35, 33.69, 33.41, 28.47, 24.80, 24.79, 21.82, 20.03, 14.40. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.00. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{43}BNaO_3^+$: 461.3197; found: 461.3219.



4,4,5,5-tetramethyl-2-(1-(4-((1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)phenyl)-6-oxaspiro[2.5]octan-1-yl)-1,3,2-dioxaborolane 9k

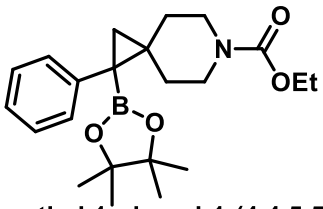
Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, colorless oil, 45.7 mg, 49% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12 – 7.05 (m, 2H), 6.80 – 6.74 (m, 2H), 3.88 (dt, *J* = 11.1, 4.1 Hz, 1H), 3.81 (t, *J* = 1.3 Hz, 1H), 3.74 (dt, *J* = 11.1, 4.2 Hz, 1H), 3.61 (ddd, *J* = 11.1, 9.7, 2.8 Hz, 1H), 3.46 (dddd, *J* = 11.0, 9.7, 3.0, 1.2 Hz, 1H), 2.02 (dtd, *J* = 12.7, 6.0, 2.9 Hz, 1H), 1.92 (ddd, *J* = 13.6, 9.7, 3.9 Hz, 1H), 1.79 – 1.69 (m, 2H), 1.57 (dt, *J* = 7.7, 2.1 Hz, 2H), 1.50 – 1.40 (m, 2H), 1.17 (d, *J* = 15.5 Hz, 18H), 1.09 (s, 3H), 1.03 – 1.00 (m, 1H), 0.85 (s, 3H), 0.63 (dt, *J* = 13.9, 3.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.06, 132.72, 130.85, 115.24, 115.22, 90.30, 83.35, 67.57, 67.51, 67.50, 49.60, 49.11, 41.45, 34.73, 33.31, 33.29, 30.54, 28.37, 28.33, 26.40, 25.93, 24.82, 24.74, 21.90, 21.87, 20.53, 20.00. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.05. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{29}H_{43}BNaO_4^+$: 489.3147; found: 489.3172.



2-(1-(4-(((2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)phenyl)-6-oxaspiro[2.5]octan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 9l

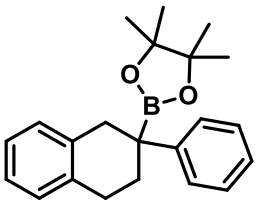
Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, colorless oil, 40.2 mg, 43% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 – 7.04 (m, 2H), 6.81 – 6.69 (m, 2H), 3.96 (tdd, *J* = 10.6, 4.2, 1.8 Hz, 1H), 3.88 (dt, *J* = 11.1, 4.1 Hz, 1H), 3.74 (dtd, *J* = 10.7, 4.3, 1.6 Hz, 1H), 3.61 (ddd, *J* = 11.1, 9.8, 2.9 Hz, 1H), 3.46 (dddd, *J* = 10.9, 9.7, 2.9, 1.0 Hz, 1H), 2.23 (qt, *J* = 7.0, 3.5 Hz, 1H), 2.15 (dtt, *J* = 12.4, 5.1, 2.5 Hz, 1H), 1.92 (ddd, *J* = 13.7, 9.8, 4.0 Hz, 1H), 1.74 – 1.67 (m, 2H), 1.56 (dddt, *J* = 13.5, 4.5, 3.0, 1.7 Hz, 1H), 1.44 (ddt, *J* = 12.4, 9.2, 4.2 Hz, 3H), 1.34 – 1.28 (m, 1H), 1.21 – 1.13 (m, 12H), 1.04 – 0.98 (m, 2H), 0.91 (dd, *J* = 6.8, 4.5 Hz, 8H), 0.76 (d, *J* = 6.9 Hz, 3H), 0.63 (dp, *J* = 14.4, 2.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.09, 133.04, 131.05, 115.27, 115.22, 83.37, 67.58, 67.52, 48.20, 40.55, 34.69, 34.60, 33.34, 31.45, 25.94, 24.81,

24.77, 24.75, 23.67, 22.15, 21.92, 20.84, 16.50. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.62. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{29}H_{45}BNaO_4^+$: 491.3303; found: 491.3334.



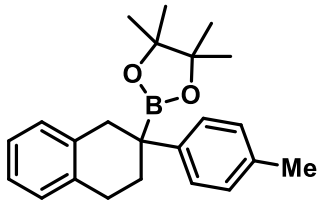
ethyl 1-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-azaspiro[2.5]octane-6-carboxylate 10a

Eluent: petroleum ether/ethyl acetate (5:1), Rf = 0.5, colorless oil, 48.5 mg, 63% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.17 (m, 4H), 7.12 (ddd, *J* = 8.6, 5.5, 2.5 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.94 – 3.77 (m, 1H), 3.66 (t, *J* = 8.9 Hz, 1H), 3.22 (ddd, *J* = 13.1, 9.8, 3.3 Hz, 1H), 3.00 (ddd, *J* = 13.1, 9.7, 3.4 Hz, 1H), 1.83 (ddd, *J* = 13.6, 9.4, 3.6 Hz, 1H), 1.61 (dt, *J* = 13.7, 4.4 Hz, 1H), 1.30 – 1.11 (m, 17H), 1.09 (d, *J* = 4.2 Hz, 1H), 0.65 (dt, *J* = 14.3, 4.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.67, 141.24, 130.26, 127.62, 125.28, 83.53, 61.11, 43.83, 43.39, 29.09, 24.85, 24.69, 21.47, 14.72. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.11. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{32}BNNaO_4^+$: 408.2317; found: 408.2333.



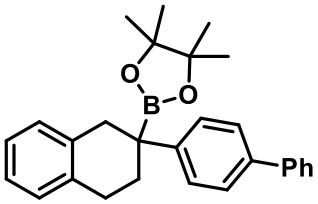
4,4,5,5-tetramethyl-2-(2-phenyl-1,2,3,4-tetrahydronaphthalen-2-yl)-1,3,2-dioxaborolane 11a

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, colorless oil, 44.1 mg, 66% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 1.4 Hz, 2H), 7.20 – 7.13 (m, 2H), 7.09 – 7.01 (m, 2H), 6.99 – 6.88 (m, 3H), 3.21 (d, *J* = 16.0 Hz, 1H), 2.94 – 2.82 (m, 2H), 2.64 (dt, *J* = 17.3, 5.7 Hz, 1H), 2.30 (dtd, *J* = 11.3, 5.9, 1.7 Hz, 1H), 1.91 (ddd, *J* = 13.0, 8.9, 6.0 Hz, 1H), 0.93 (d, *J* = 25.1 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.77, 136.75, 136.36, 129.30, 128.73, 128.29, 126.65, 125.55, 125.38, 125.31, 83.40, 37.47, 31.42, 27.21, 24.39, 24.23. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.26. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{27}BNaO_2^+$: 357.1996; found: 357.1998.



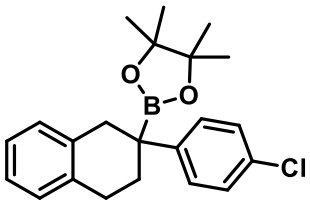
4,4,5,5-tetramethyl-2-(2-(*p*-tolyl)-1,2,3,4-tetrahydronaphthalen-2-yl)-1,3,2-dioxaborolane 11b

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, colorless oil, 32.7 mg, 47% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.22 – 7.17 (m, 1H), 7.14 – 7.01 (m, 5H), 3.32 (dd, *J* = 16.0, 1.7 Hz, 1H), 3.05 – 2.93 (m, 2H), 2.77 (dt, *J* = 17.3, 5.7 Hz, 1H), 2.42 (dddd, *J* = 13.3, 6.6, 5.3, 1.9 Hz, 1H), 2.32 (s, 3H), 2.01 (ddd, *J* = 13.1, 9.0, 6.1 Hz, 1H), 1.06 (d, *J* = 26.3 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.72, 136.87, 136.38, 134.63, 129.29, 129.02, 128.71, 126.49, 125.50, 125.33, 83.34, 37.63, 31.50, 27.25, 24.40, 24.24, 20.94. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 35.67. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{29}BNaO_2^+$: 371.2153.1996; found: 371.2153.



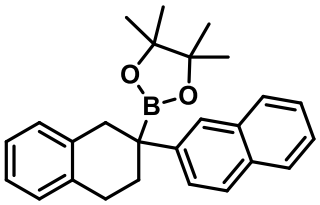
2-(2-([1,1'-biphenyl]-4-yl)-1,2,3,4-tetrahydronaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 11c

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, colorless oil, 50.0 mg, 61% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 2H), 7.56 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.50 – 7.39 (m, 4H), 7.37 – 7.29 (m, 1H), 7.25 – 7.20 (m, 1H), 7.15 – 7.04 (m, 3H), 3.38 (d, *J* = 15.9 Hz, 1H), 3.13 – 2.96 (m, 2H), 2.81 (dt, *J* = 17.3, 5.8 Hz, 1H), 2.53 – 2.42 (m, 1H), 2.08 (ddd, *J* = 13.5, 8.8, 6.2 Hz, 1H), 1.09 (d, *J* = 25.1 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.98, 141.06, 138.03, 136.70, 136.36, 129.33, 128.76, 128.70, 127.07, 126.97, 126.94, 125.60, 125.42, 83.48, 37.50, 31.45, 27.22, 24.42, 24.26. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.43. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{31}BNaO_2^+$: 433.2309; found: 433.2333.



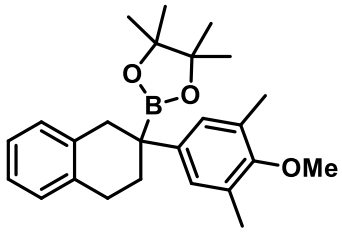
2-(2-(4-chlorophenyl)-1,2,3,4-tetrahydronaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 11d

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, colorless oil, 42.7 mg, 58% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 2H), 7.20 – 7.15 (m, 2H), 7.11 (dd, *J* = 6.3, 2.7 Hz, 1H), 7.06 – 6.99 (m, 2H), 6.98 – 6.93 (m, 1H), 3.29 – 3.16 (m, 1H), 2.97 – 2.83 (m, 2H), 2.65 (dt, *J* = 17.3, 6.0 Hz, 1H), 2.30 (dtd, *J* = 13.4, 6.0, 1.6 Hz, 1H), 1.94 (ddd, *J* = 13.0, 8.5, 6.1 Hz, 1H), 0.99 (d, *J* = 23.7 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.19, 136.25, 136.13, 131.03, 129.26, 128.75, 128.35, 128.13, 125.68, 125.48, 83.55, 37.20, 31.29, 26.92, 24.38, 24.23. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.05. **HRMS** (ESI) m/z: [M] calcd for $C_{22}H_{26}BClO_2$: 368.1714; found: 368.1710.



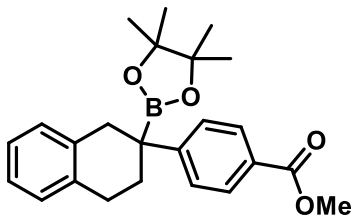
2-(3,4-dihydro-[2,2'-binaphthalen]-2(1*H*)-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 11e

Eluent: petroleum ether/ethyl acetate (20:1), Rf = 0.5, colorless oil, 27.6 mg, 36% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.71 (m, 4H), 7.63 – 7.56 (m, 1H), 7.46 – 7.37 (m, 2H), 7.23 (dd, *J* = 7.3, 1.7 Hz, 1H), 7.15 – 7.00 (m, 3H), 3.44 (d, *J* = 15.9 Hz, 1H), 3.13 (d, *J* = 15.9 Hz, 1H), 3.02 (ddd, *J* = 15.9, 8.9, 6.3 Hz, 1H), 2.78 (dt, *J* = 17.3, 5.7 Hz, 1H), 2.53 (dtd, *J* = 13.1, 6.0, 1.7 Hz, 1H), 2.12 (ddd, *J* = 13.0, 8.9, 6.1 Hz, 1H), 1.05 (d, *J* = 24.2 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.30, 136.66, 136.33, 133.73, 131.69, 129.31, 128.73, 127.88, 127.58, 127.37, 125.92, 125.64, 125.58, 125.41, 125.08, 124.60, 83.49, 37.48, 31.37, 27.24, 24.39, 24.23. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.56. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{29}BNaO_2^+$: 407.2153; found: 407.2157.



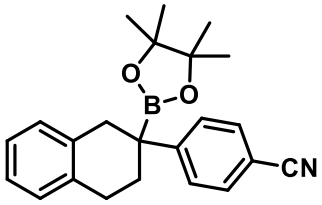
2-(2-(4-methoxy-3,5-dimethylphenyl)-1,2,3,4-tetrahydronaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 11f

Eluent: petroleum ether/ethyl acetate (15:1), Rf = 0.5, colorless oil, 44.7.6 mg, 57% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 – 7.14 (m, 1H), 7.13 – 6.97 (m, 5H), 3.70 (s, 3H), 3.28 (dd, *J* = 15.8, 2.0 Hz, 1H), 3.03 (ddd, *J* = 16.8, 10.1, 6.4 Hz, 1H), 2.92 (d, *J* = 15.8 Hz, 1H), 2.87 – 2.78 (m, 1H), 2.41 (dddd, *J* = 12.6, 6.2, 4.1, 2.0 Hz, 1H), 2.27 (s, 6H), 1.92 (ddd, *J* = 12.9, 10.0, 6.2 Hz, 1H), 1.03 (d, *J* = 32.5 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.69, 141.16, 137.08, 136.32, 130.22, 129.29, 128.65, 126.88, 125.50, 125.27, 83.33, 59.65, 38.22, 31.70, 27.62, 24.31, 24.15, 16.30. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 35.04. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{34}BO_3^+$: 393.2596; found: 393.2579.



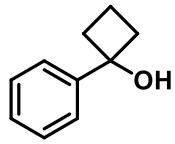
methyl 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydronaphthalen-2-yl)benzoate 11g

Eluent: petroleum ether/ethyl acetate (10:1), Rf = 0.5, colorless oil, 56.4 mg, 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 – 7.92 (m, 2H), 7.51 – 7.41 (m, 2H), 7.22 – 7.16 (m, 1H), 7.13 – 7.05 (m, 2H), 7.05 – 6.99 (m, 1H), 3.89 (s, 3H), 3.34 (d, *J* = 16.0 Hz, 1H), 3.08 – 2.92 (m, 2H), 2.72 (dt, *J* = 17.3, 5.9 Hz, 1H), 2.49 – 2.36 (m, 1H), 2.07 (ddd, *J* = 13.0, 8.4, 6.1 Hz, 1H), 1.05 (d, *J* = 22.5 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.27, 151.45, 136.17, 136.10, 129.58, 129.27, 128.75, 127.20, 126.75, 125.72, 125.51, 83.62, 51.93, 37.01, 31.19, 26.94, 24.35, 24.21. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.04. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{29}BNaO_4^+$: 405.2051; found: 405.2074.



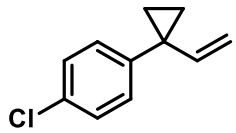
4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydronaphthalen-2-yl)benzonitrile 11h

Eluent: petroleum ether/ethyl acetate (10:1), Rf = 0.5, colorless oil, 44.5 mg, 62% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.54 (m, 2H), 7.49 – 7.36 (m, 2H), 7.19 – 7.13 (m, 1H), 7.13 – 7.05 (m, 2H), 7.05 – 6.97 (m, 1H), 3.31 (d, *J* = 16.0 Hz, 1H), 3.03 (d, *J* = 16.0 Hz, 1H), 2.97 – 2.90 (m, 1H), 2.67 (dt, *J* = 17.3, 6.2 Hz, 1H), 2.38 (dtd, *J* = 12.7, 6.2, 1.5 Hz, 1H), 2.06 (ddd, *J* = 13.5, 8.1, 6.1 Hz, 1H), 1.06 (d, *J* = 21.5 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.62, 135.87, 135.65, 132.04, 129.22, 127.59, 125.87, 125.65, 119.24, 109.06, 83.81, 36.67, 31.05, 26.68, 24.35, 24.21. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.04. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{26}BNNaO_2^+$: 382.1949; found: 382.1970.



1-phenylcyclobutan-1-ol 12a

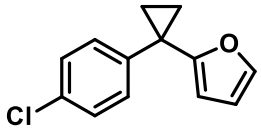
Eluent: petroleum ether/ethyl acetate (5:1), Rf = 0.5, colorless oil, 10.0 mg, 34% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 2H), 7.32 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.26 – 7.19 (m, 1H), 2.52 (dtd, *J* = 13.8, 5.2, 2.6 Hz, 2H), 2.36 – 2.27 (m, 2H), 2.03 – 1.91 (m, 2H), 1.64 (dtd, *J* = 11.1, 8.7, 4.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.24, 128.48, 127.29, 124.98, 36.84, 13.03. Spectroscopic data are in agreement with those previously reported.[6]



1-chloro-4-(1-vinylcyclopropyl)benzene 13a

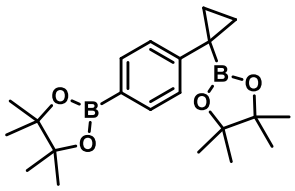
Eluent: petroleum ether/ethyl acetate (PE), Rf = 0.8, colorless oil, 36.5 mg, 41% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.18 (m, 4H), 5.66 (dd, *J* = 17.0, 10.4 Hz, 1H), 4.91 (dd, *J* = 10.4, 1.3 Hz, 1H), 4.57 (dd, *J* = 17.1, 1.3 Hz, 1H), 1.07 – 1.02 (m, 2H), 1.01 – 0.96 (m, 2H). **^{13}C NMR**

(101 MHz, $CDCl_3$) δ 144.89, 141.49, 132.11, 131.30, 128.36, 112.48, 28.24, 14.80. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_{12}Cl^+$: 179.0622; found: 179.0624.



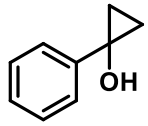
2-(1-(4-chlorophenyl)cyclopropyl)furan 13b

Eluent: petroleum ether/ethyl acetate (50:1), Rf = 0.5, colorless oil, 74.1 mg, 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 5H), 6.24 (dd, *J* = 3.2, 1.9 Hz, 1H), 5.83 (dd, *J* = 3.2, 0.8 Hz, 1H), 1.42 – 1.38 (m, 2H), 1.21 – 1.18 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.25, 141.32, 141.02, 132.36, 130.31, 128.46, 110.25, 105.70, 23.99, 15.11. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{12}ClO^+$: 219.0571; found: 219.0573.



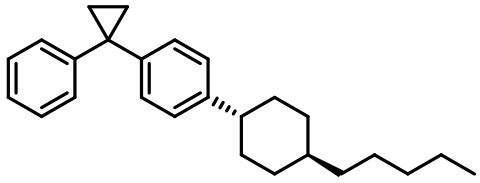
4,4,5,5-tetramethyl-2-(4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)phenyl)-1,3,2-dioxaborolane 13c

Eluent: petroleum ether/ethyl acetate (10:1), Rf = 0.5, colorless oil, 115.3 mg, 62% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.65 (m, 2H), 7.29 – 7.25 (m, 2H), 1.32 (s, 12H), 1.20 (s, 12H), 1.11 (q, *J* = 3.5 Hz, 2H), 0.91 (q, *J* = 3.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.41, 134.55, 128.46, 83.49, 83.33, 24.84, 24.58, 13.22. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.23, 30.94. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{32}B_2NaO_4^+$: 365.2066; found: 365.2085.



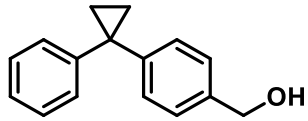
1-phenylcyclopropan-1-ol 13d

Eluent: petroleum ether/ethyl acetate (5:1), Rf = 0.5, colorless oil, 48.9 mg, 73% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 4H), 7.21 – 7.15 (m, 1H), 2.69 (s, 1H), 1.23 – 1.17 (m, 2H), 1.02 – 0.95 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.32, 128.37, 124.45, 56.57. Spectroscopic data are in agreement with those previously reported.[6]



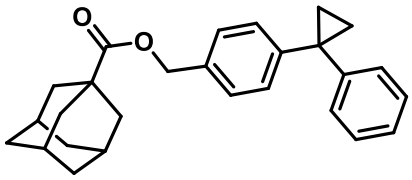
1-((1*s*,4*r*)-4-pentylcyclohexyl)-4-(1-phenylcyclopropyl)benzene 13e

Eluent: petroleum ether/ethyl acetate (PE), Rf = 0.7, colorless oil, 70.9 mg, 41% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.23 (m, 4H), 7.22 – 7.04 (m, 5H), 2.41 (tt, *J* = 12.2, 3.3 Hz, 1H), 1.89 – 1.82 (m, 4H), 1.33 – 1.18 (m, 15H), 1.02 (tdd, *J* = 14.0, 11.2, 3.6 Hz, 2H), 0.91 – 0.87 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.60, 145.48, 143.12, 128.54, 128.20, 128.13, 126.65, 44.17, 37.41, 37.36, 34.38, 33.67, 32.23, 29.56, 26.65, 22.70, 16.33, 14.08. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{35}^+$: 347.2733; found: 347.2738.



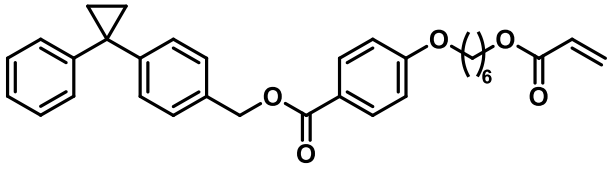
(4-(1-phenylcyclopropyl)phenyl)methanol 13f

Eluent: petroleum ether/ethyl acetate (10:1), Rf = 0.5, colorless oil, 76.2 mg, 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.16 (m, 9H), 4.64 (s, 2H), 1.31 (dt, *J* = 5.1, 1.9 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.63, 145.37, 138.55, 128.66, 128.41, 128.31, 127.11, 126.01, 65.16, 29.70, 16.44. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{17}O^+$: 225.1274; found: 225.1279.



4-(1-phenylcyclopropyl)benzyl (3*r*,5*r*,7*r*)-adamantane-1-carboxylate 13g

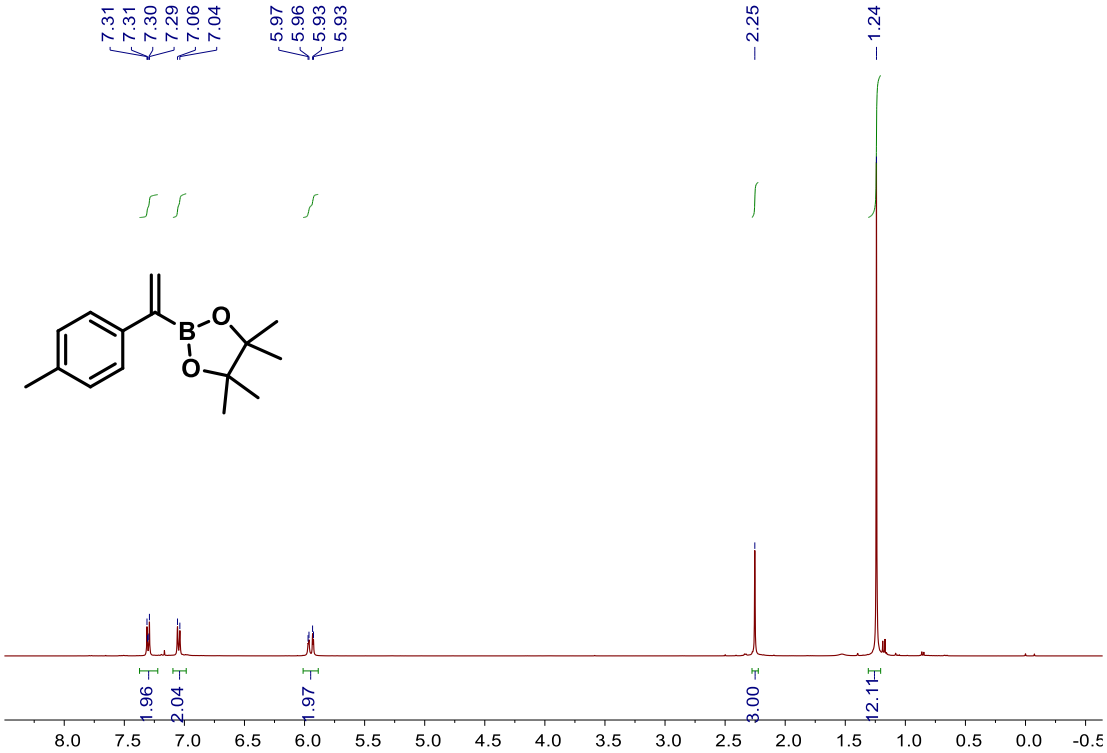
Eluent: petroleum ether/ethyl acetate (10:1), Rf = 0.5, colorless oil, 76.2 mg, 59% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.05 (m, 9H), 4.98 (s, 2H), 1.93 (p, *J* = 3.1 Hz, 3H), 1.83 (s, 6H), 1.67 – 1.59 (m, 6H), 1.23 – 1.18 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.53, 145.61, 134.15, 128.59, 128.38, 128.32, 127.63, 126.08, 65.55, 40.80, 38.87, 36.53, 29.72, 27.98, 16.45.



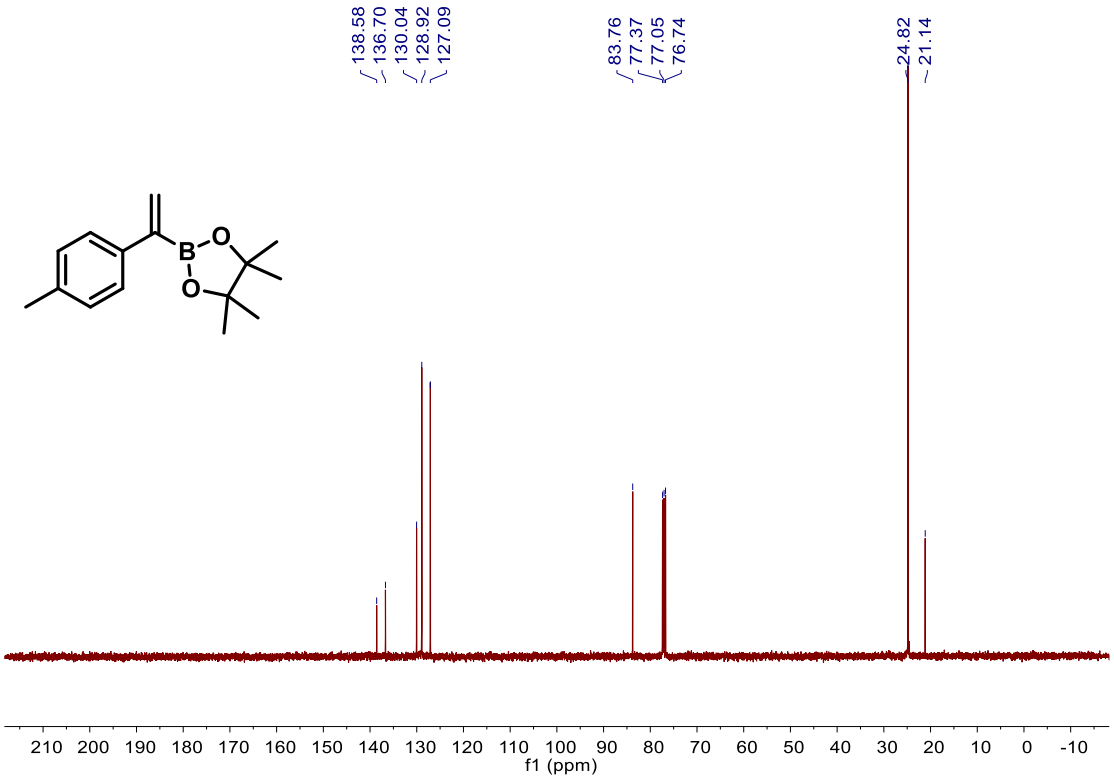
4-(1-phenylcyclopropyl)benzyl 4-((6-(acryloyloxy)hexyl)oxy)benzoate 13h

Eluent: petroleum ether/ethyl acetate (10:1), Rf = 0.5, colorless oil, 67.7 mg, 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 – 8.00 (m, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.23 (m, 6H), 7.23 – 7.15 (m, 1H), 6.93 – 6.88 (m, 2H), 6.41 (dd, *J* = 17.3, 1.4 Hz, 1H), 6.14 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.82 (dd, *J* = 10.4, 1.5 Hz, 1H), 5.30 (s, 2H), 4.19 (t, *J* = 6.6 Hz, 2H), 4.01 (t, *J* = 6.4 Hz, 2H), 1.88 – 1.68 (m, 4H), 1.55 – 1.44 (m, 4H), 1.34 – 1.27 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.32, 166.25, 162.97, 145.88, 133.93, 131.75, 130.55, 128.60, 128.53, 128.51, 128.32, 128.21, 126.07, 114.08, 67.99, 66.19, 64.48, 29.75, 29.01, 28.57, 25.74, 25.71, 16.46. **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{32}H_{34}NaO_5^+$: 521.2298; found: 521.2314.

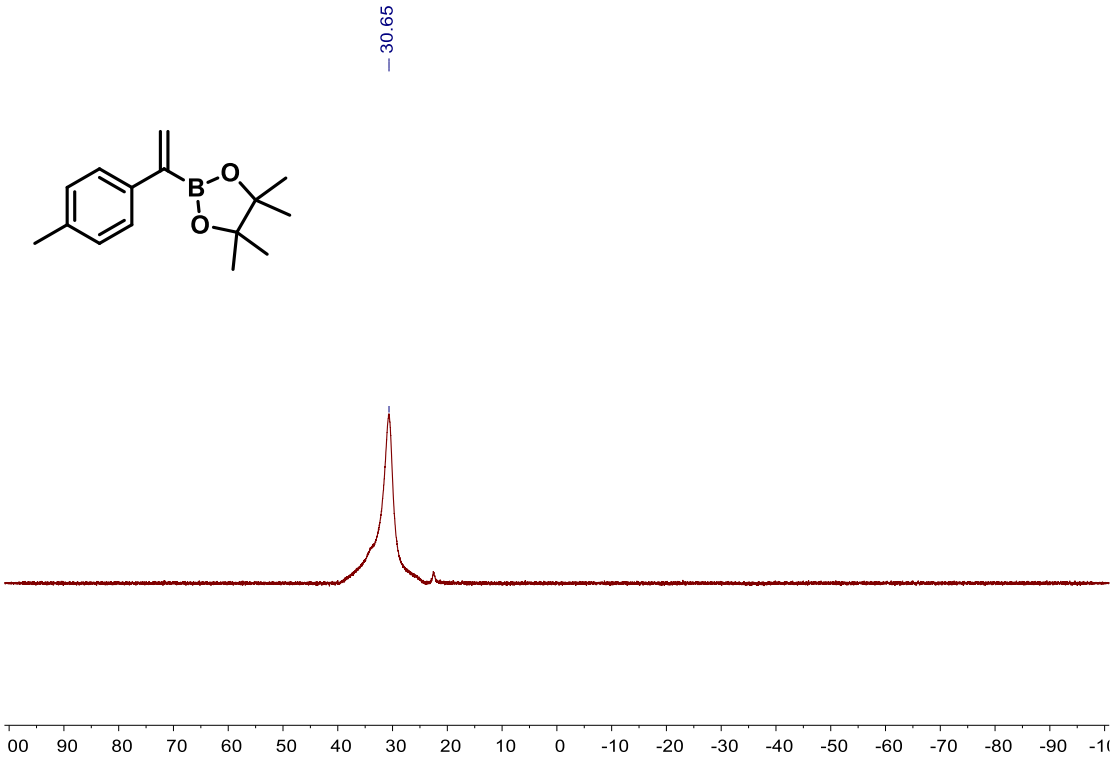
NMR Spectra



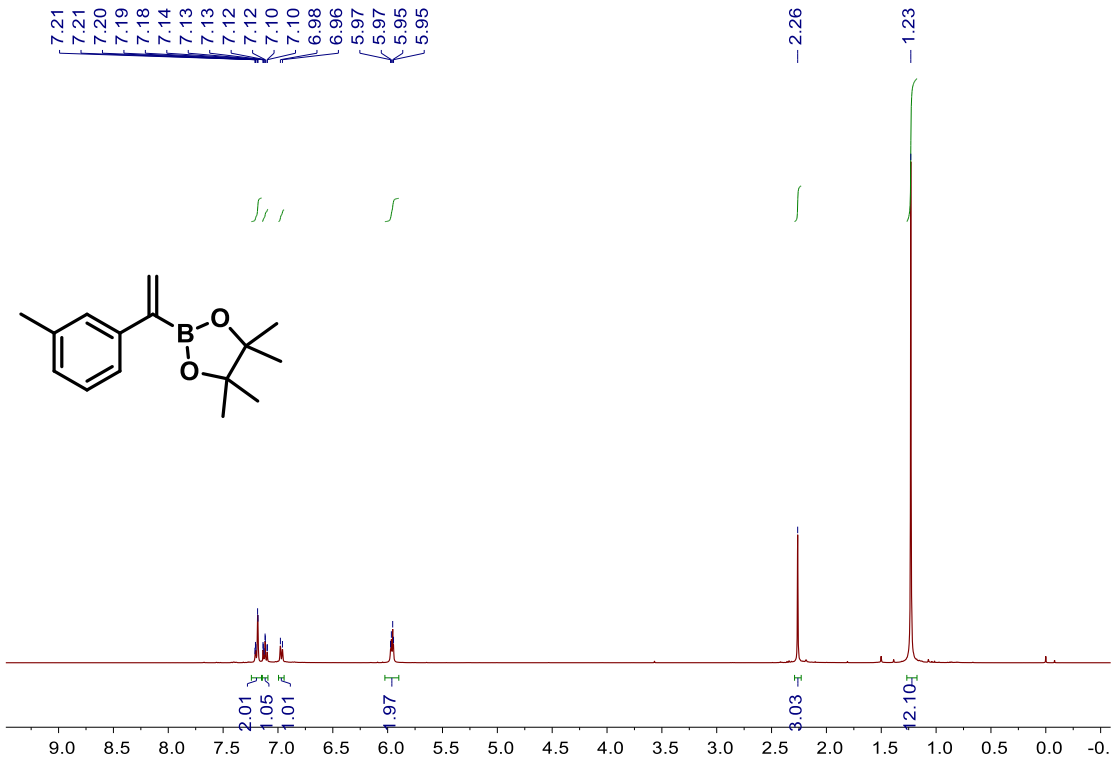
^{1}H NMR spectrum of **1b** (400 MHz, Chloroform-*d*)



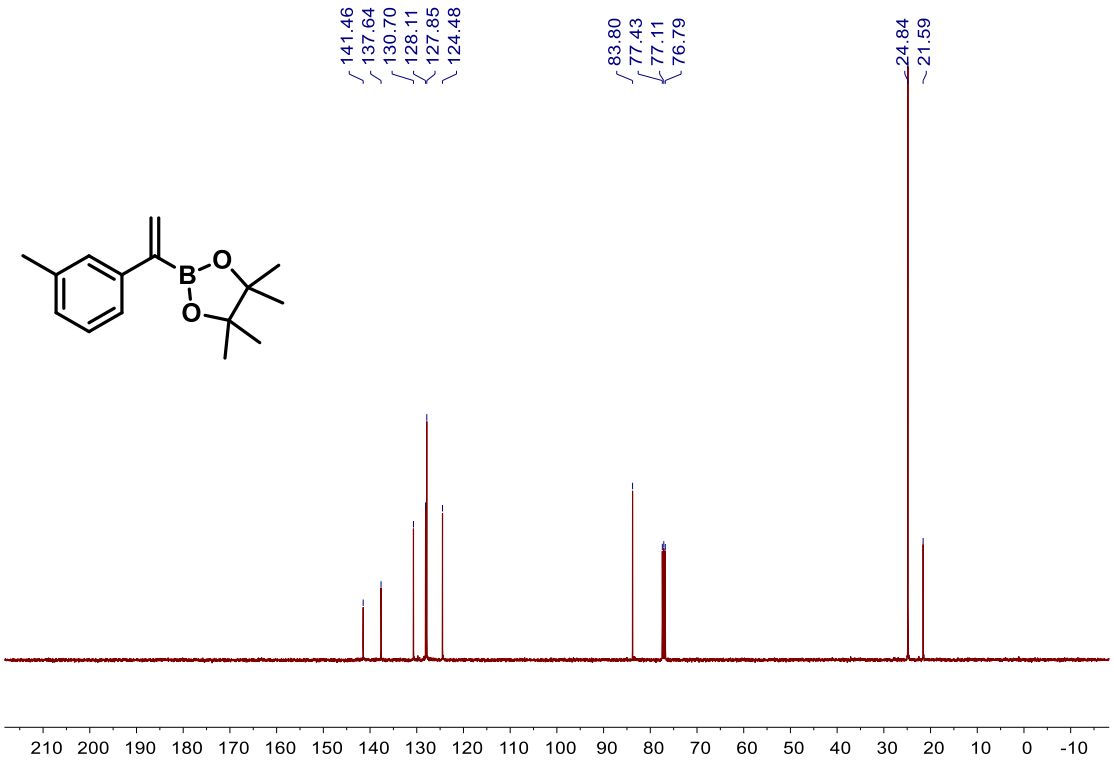
^{13}C NMR spectrum of **1b** (101 MHz, Chloroform-*d*)



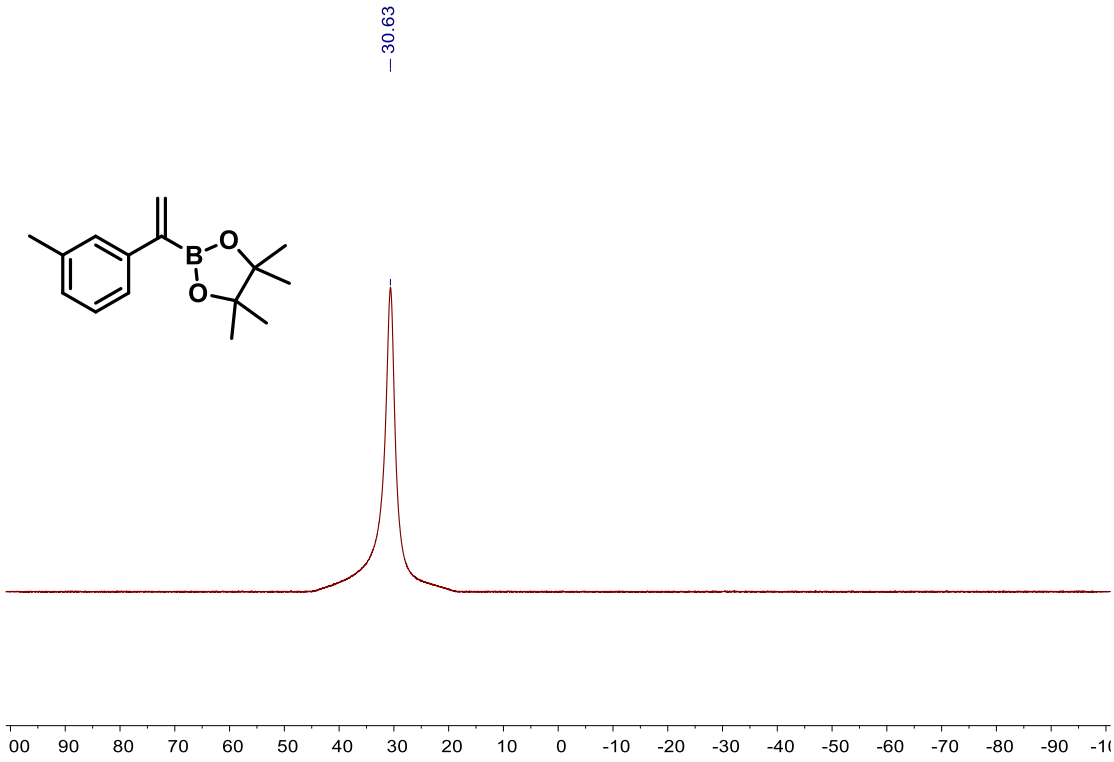
^{11}B NMR spectrum of **1b** (128 MHz Chloroform-*d*)



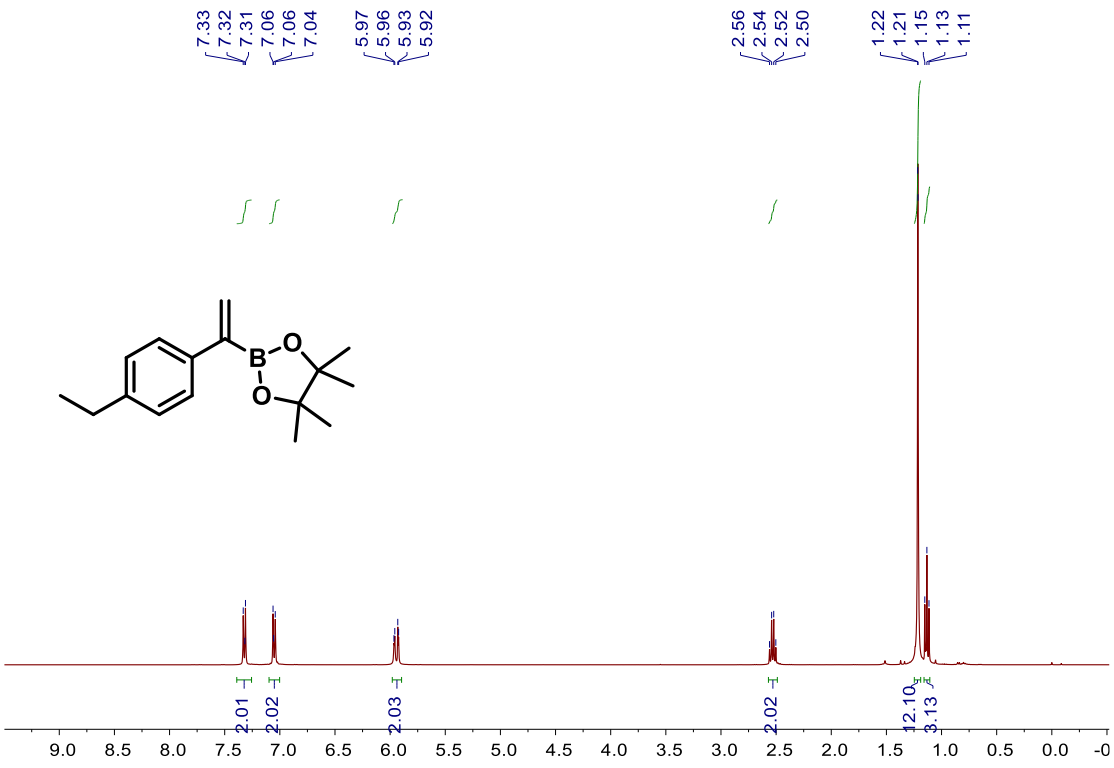
^{1}H NMR spectrum of **1c** (400 MHz, Chloroform-*d*)



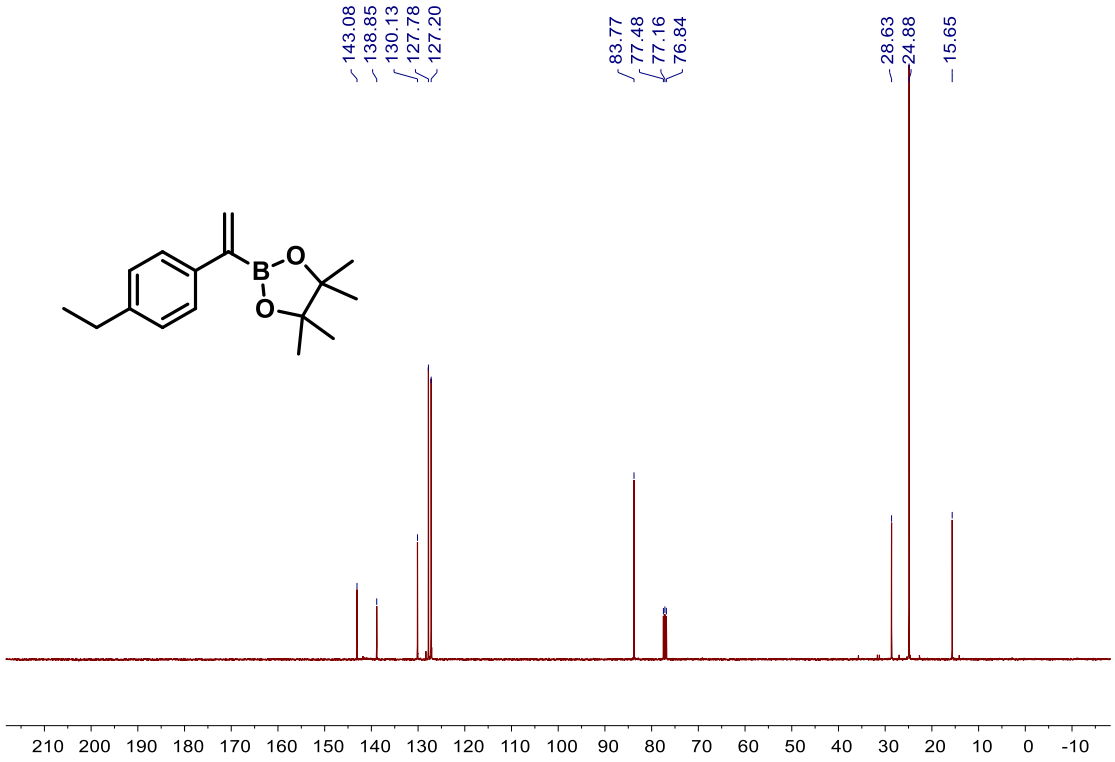
^{13}C NMR spectrum of **1c** (101 MHz, Chloroform-*d*)



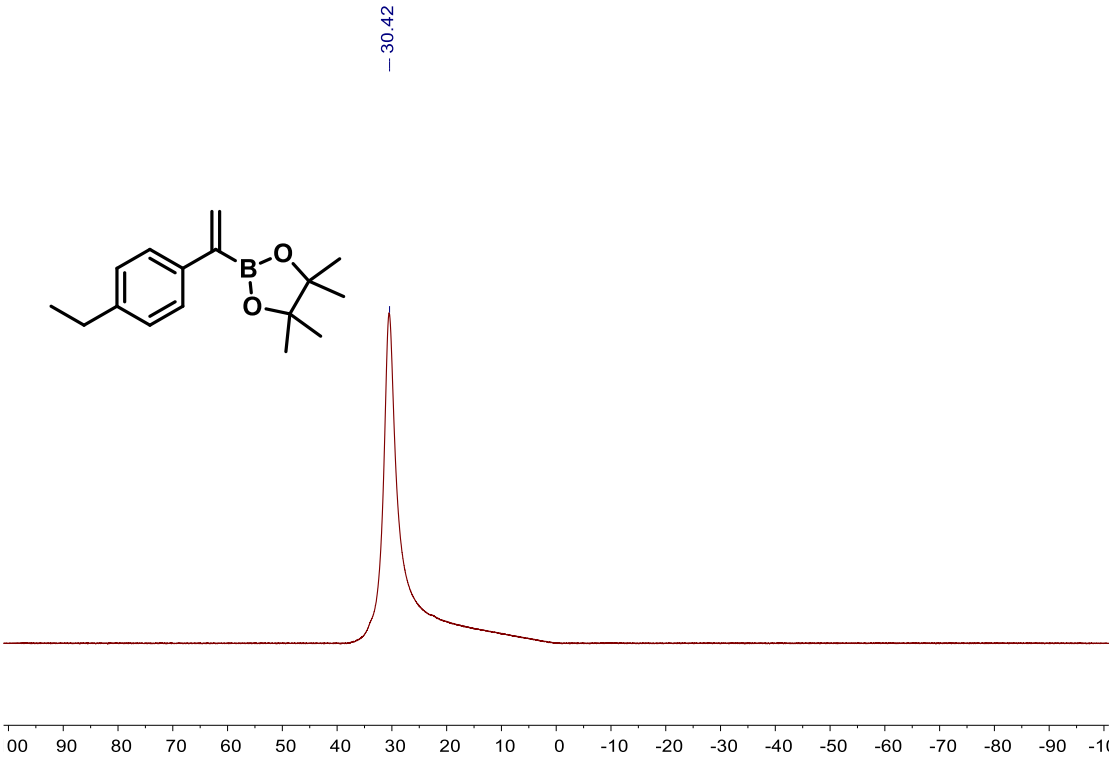
^{11}B NMR spectrum of **1c** (128 MHz Chloroform-*d*)



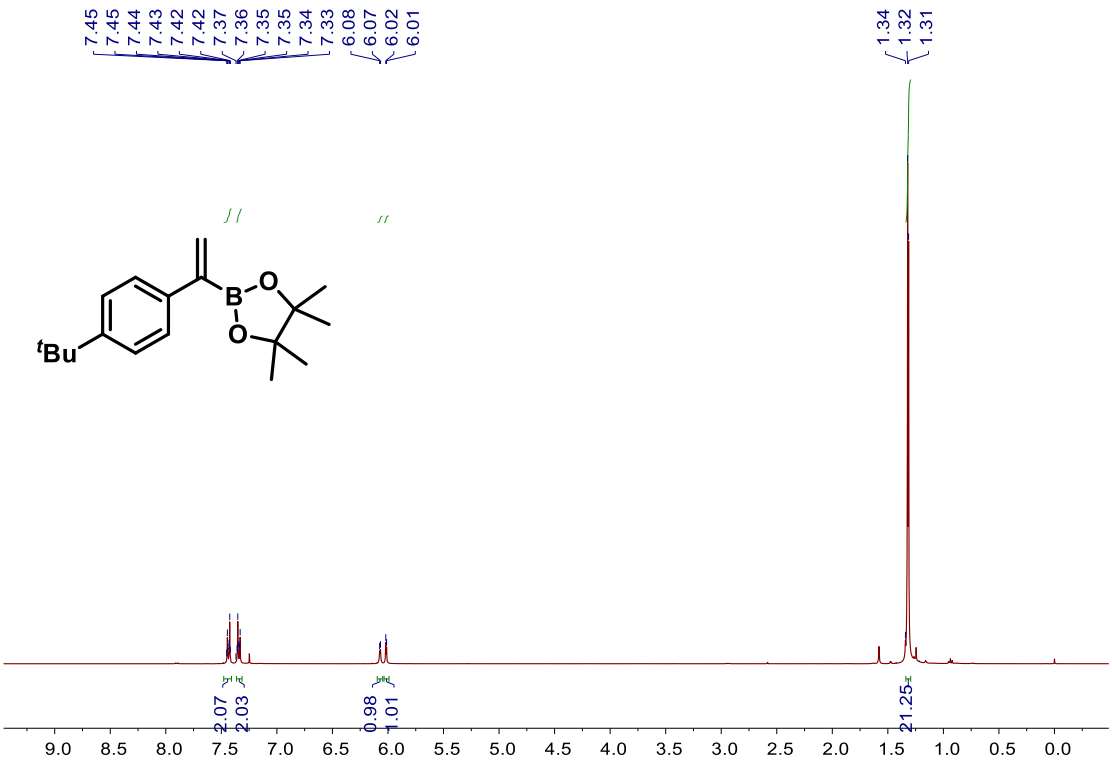
^{1}H NMR spectrum of **1d** (400 MHz, Chloroform-*d*)



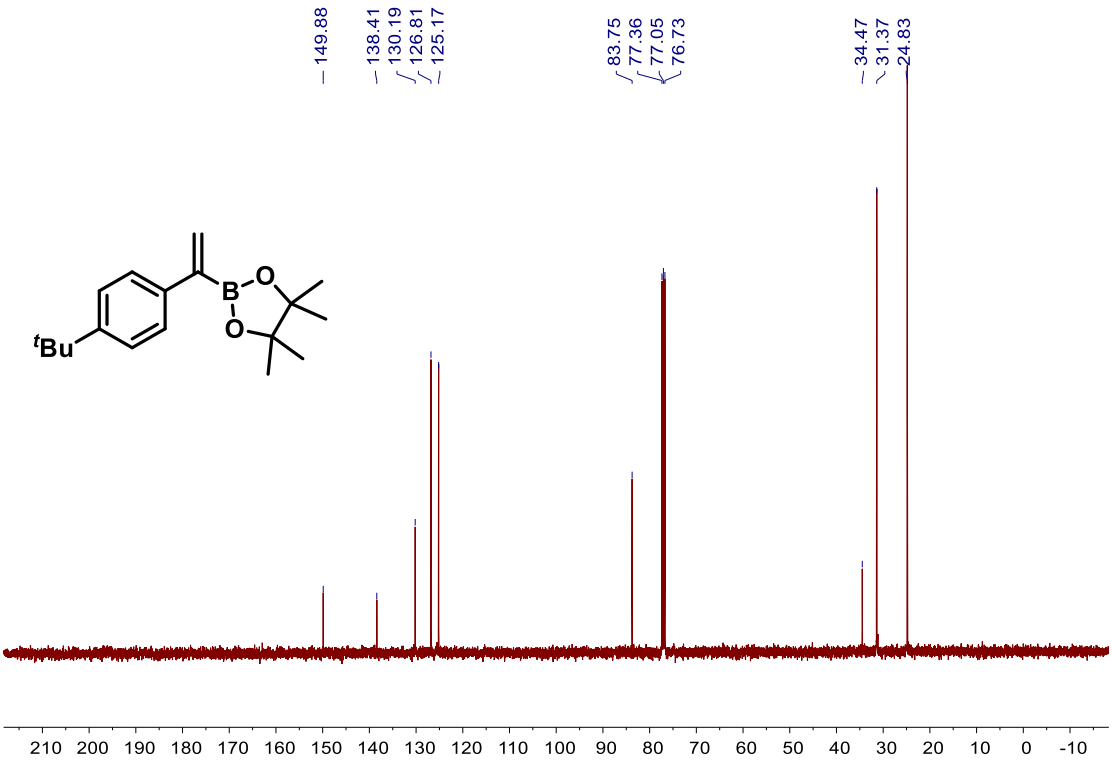
^{13}C NMR spectrum of **1d** (101 MHz, Chloroform-*d*)



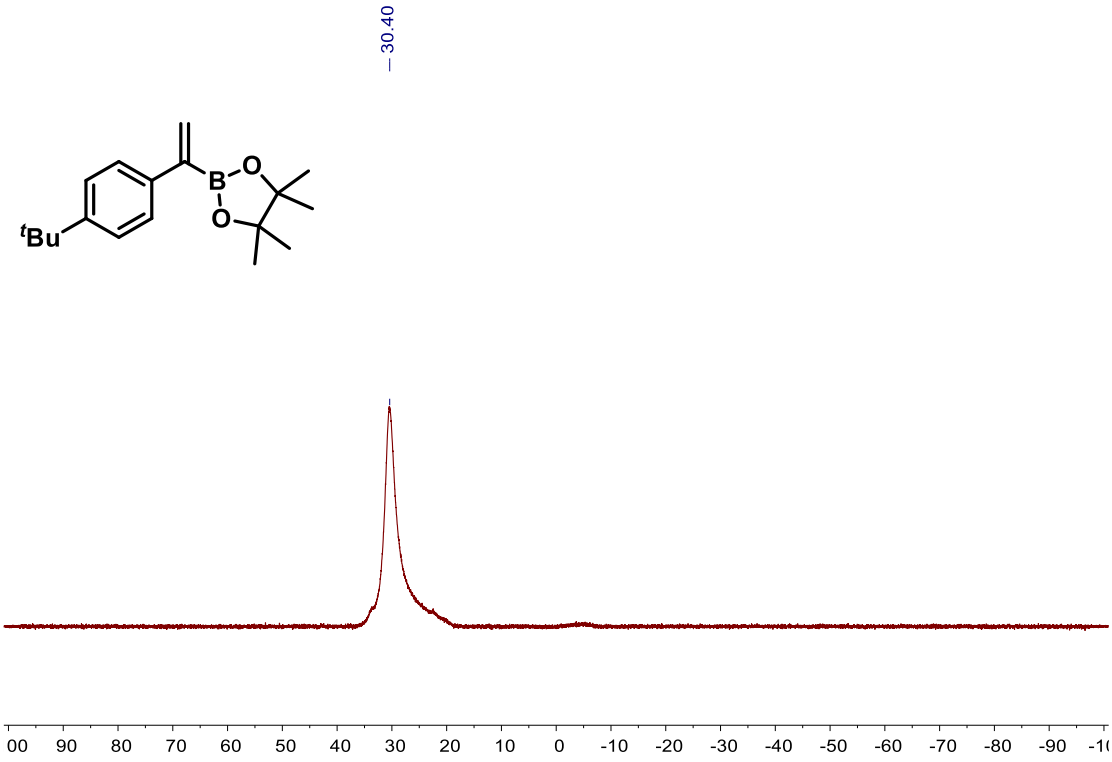
^{11}B NMR spectrum of **1d** (128 MHz Chloroform-*d*)



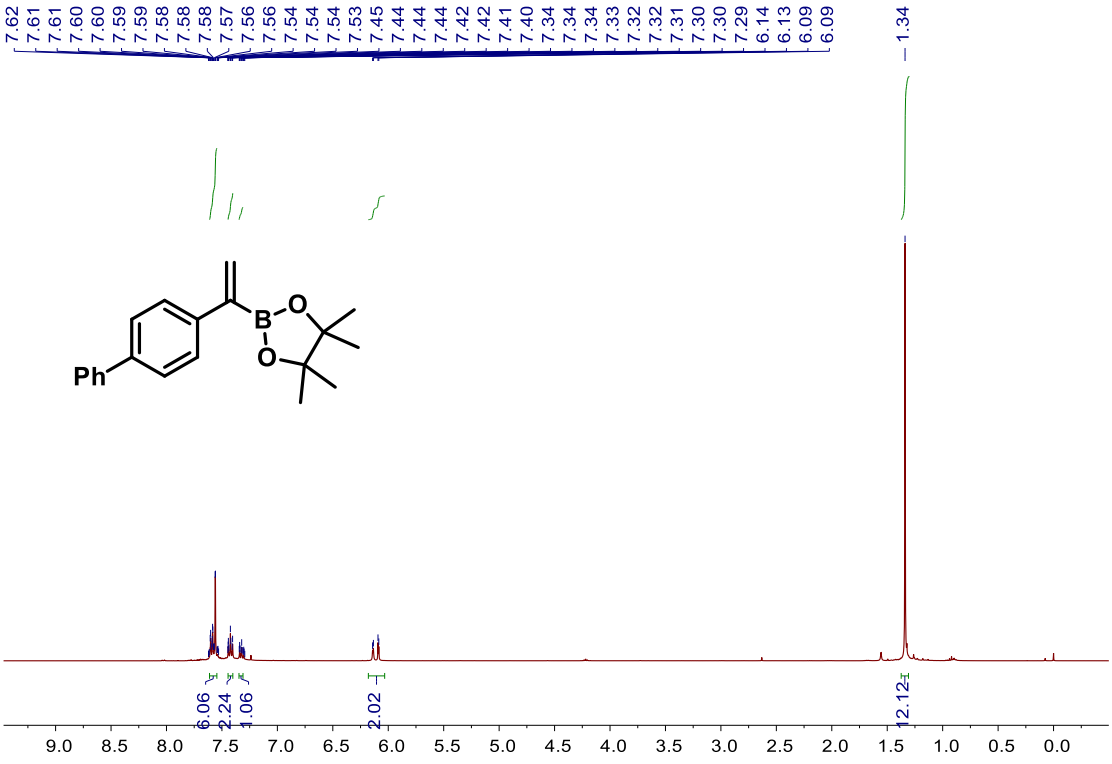
^{1}H NMR spectrum of **1e** (400 MHz, Chloroform-*d*)



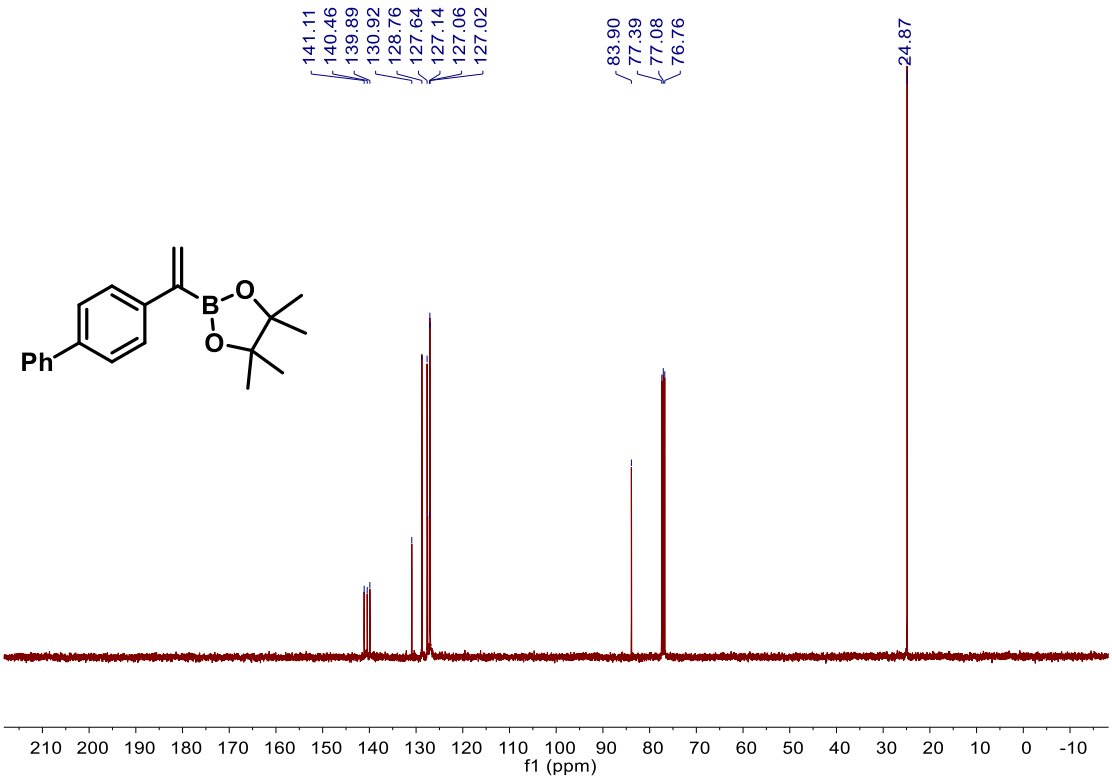
^{13}C NMR spectrum of **1e** (101 MHz, Chloroform-*d*)



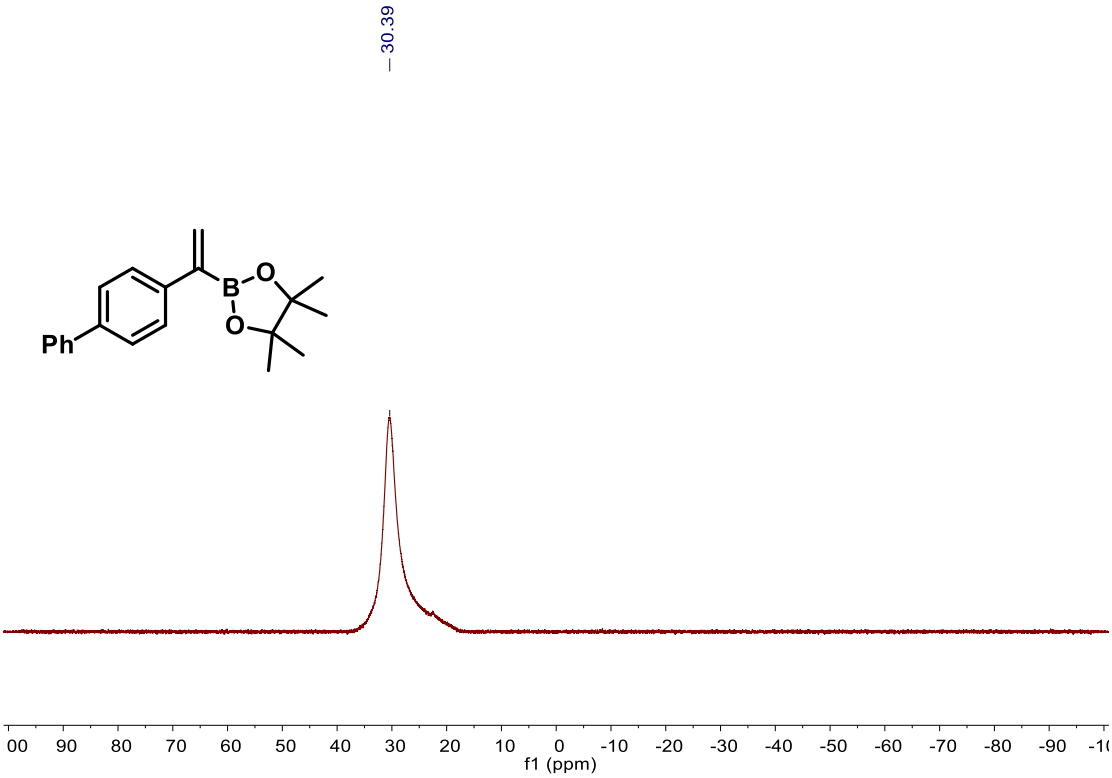
^{11}B NMR spectrum of **1e** (128 MHz Chloroform-*d*)



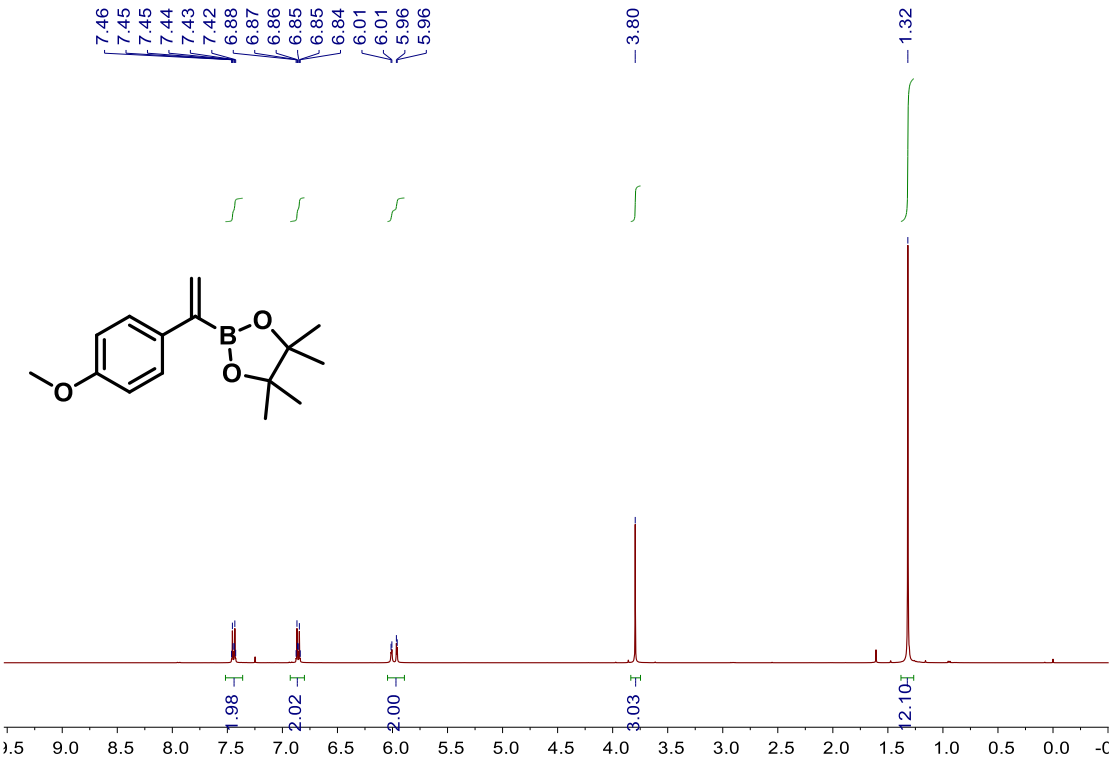
^{1}H NMR spectrum of **1f** (400 MHz, Chloroform-*d*)



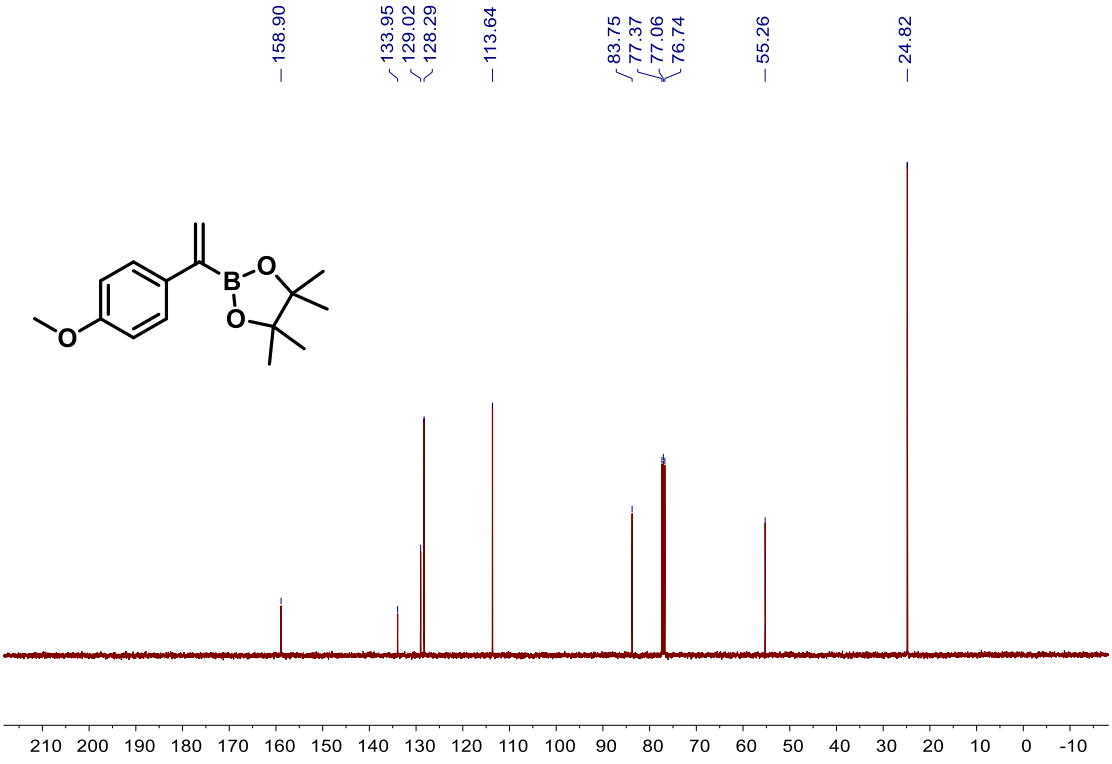
^{13}C NMR spectrum of **1f** (101 MHz, Chloroform-*d*)



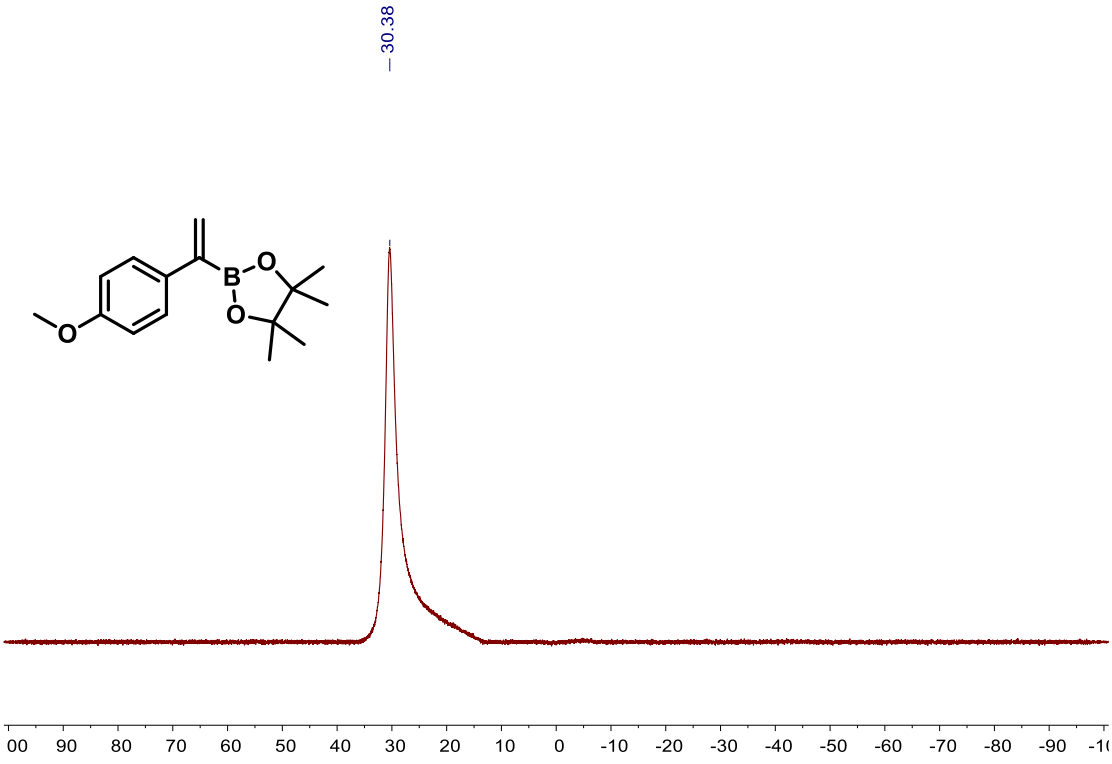
^{11}B NMR spectrum of **1f** (128 MHz Chloroform-*d*)



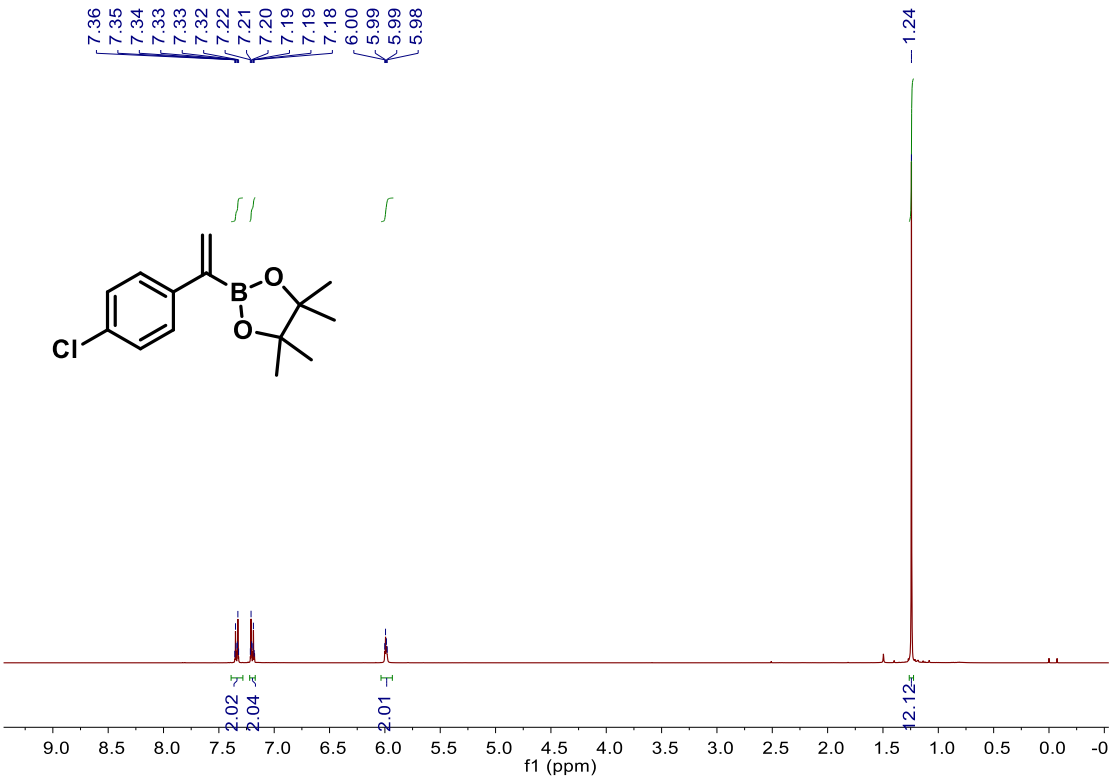
^{1}H NMR spectrum of **1g** (400 MHz, Chloroform-*d*)



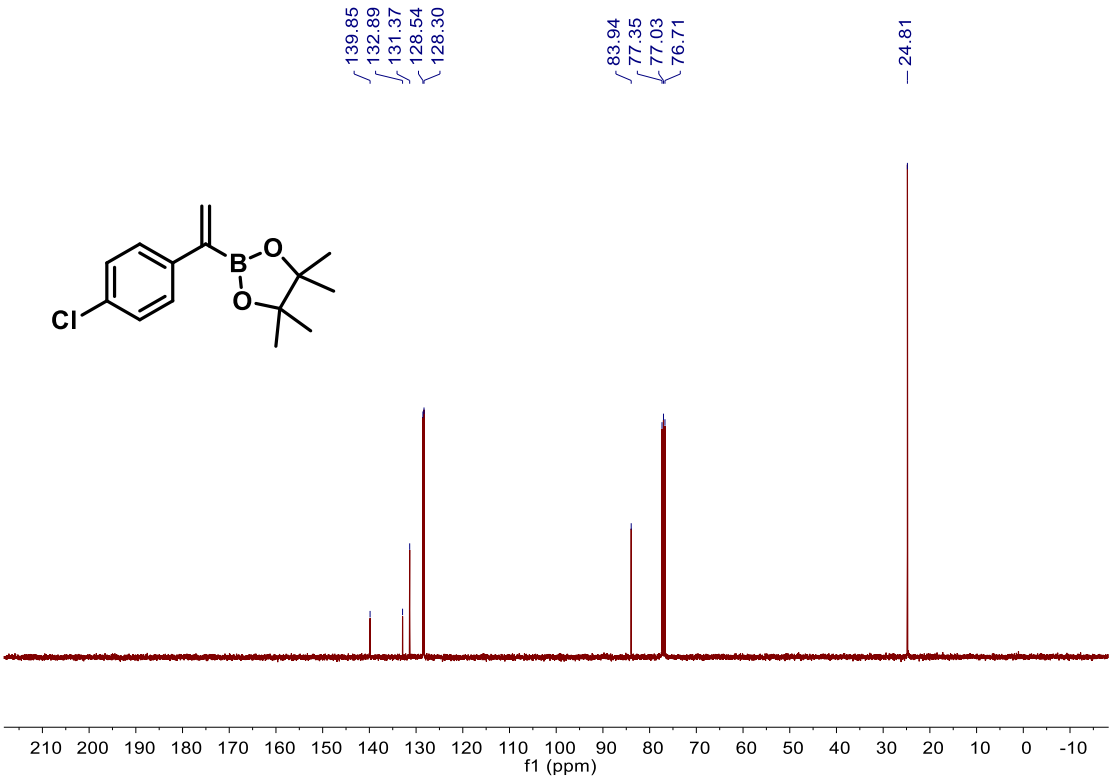
^{13}C NMR spectrum of **1g** (101 MHz, Chloroform-*d*)



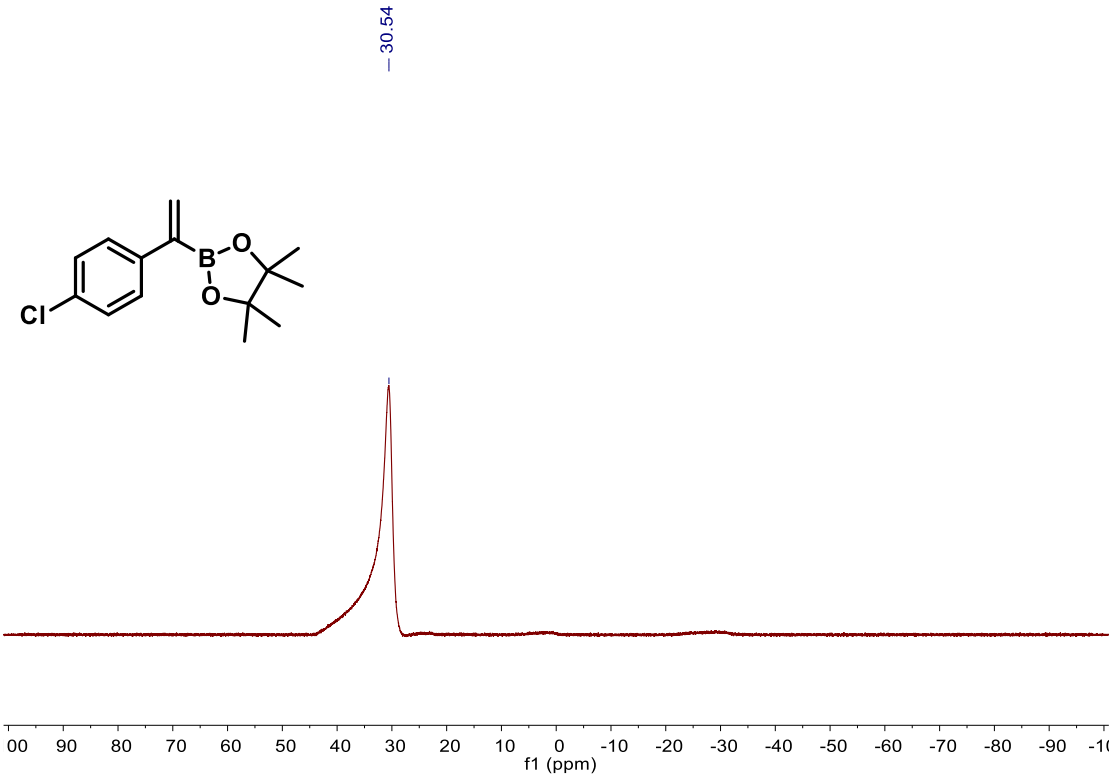
^{11}B NMR spectrum of **1g** (128 MHz Chloroform-*d*)



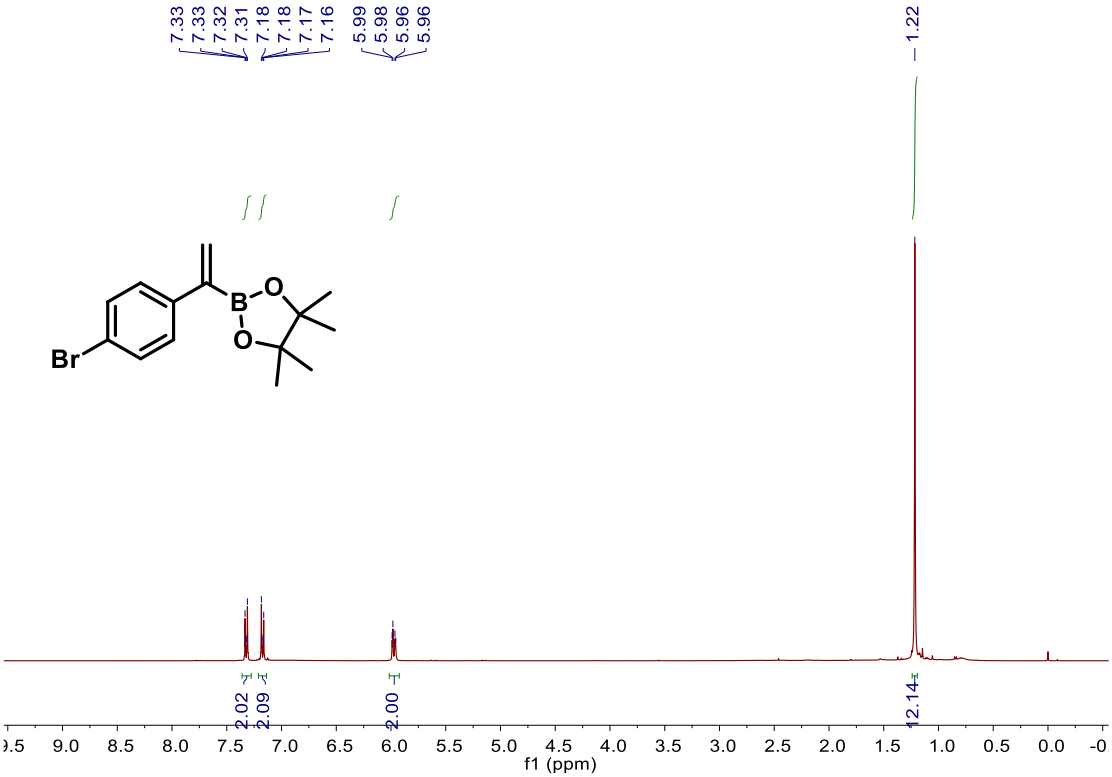
^{1}H NMR spectrum of **1h** (400 MHz, Chloroform-*d*)



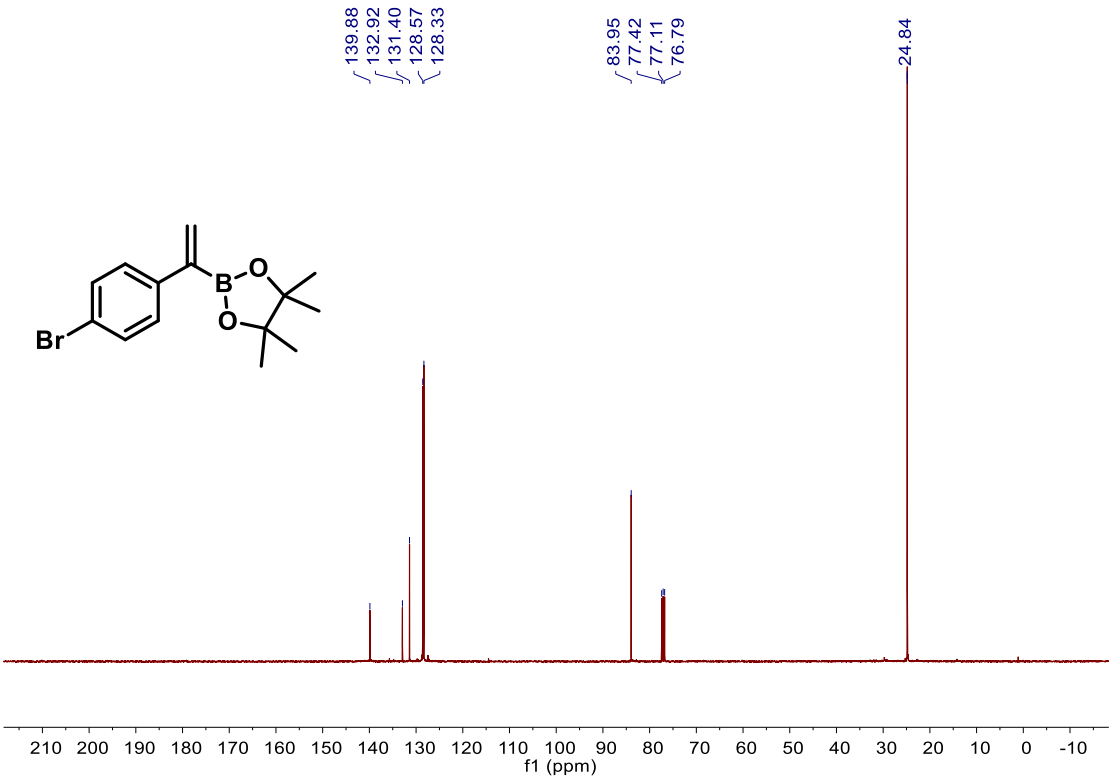
^{13}C NMR spectrum of **1h** (101 MHz, Chloroform-*d*)



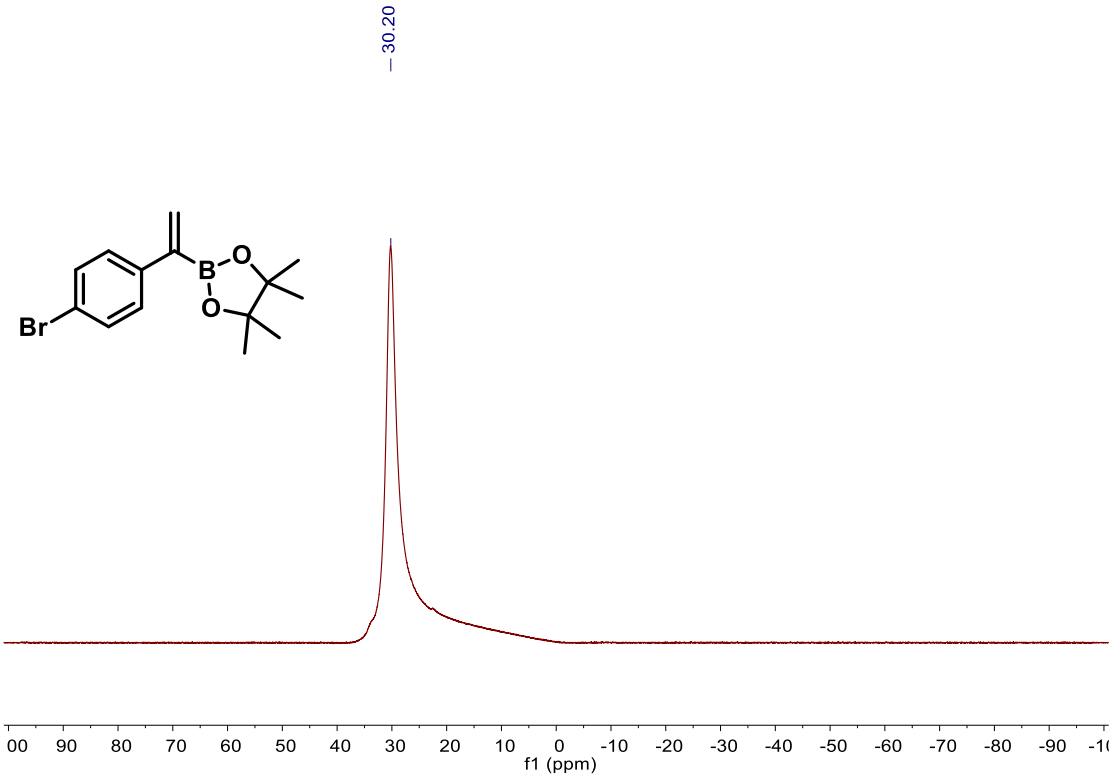
^{11}B NMR spectrum of **1h** (128 MHz Chloroform-*d*)



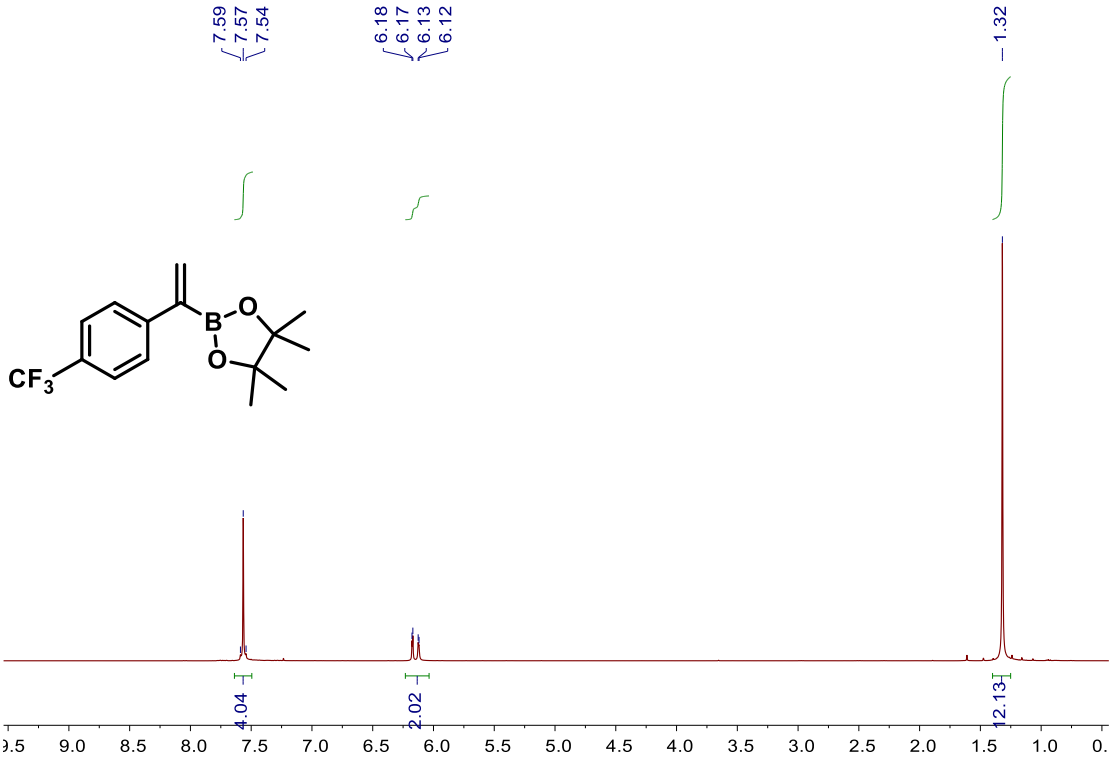
^{1}H NMR spectrum of **1i** (400 MHz, Chloroform-*d*)



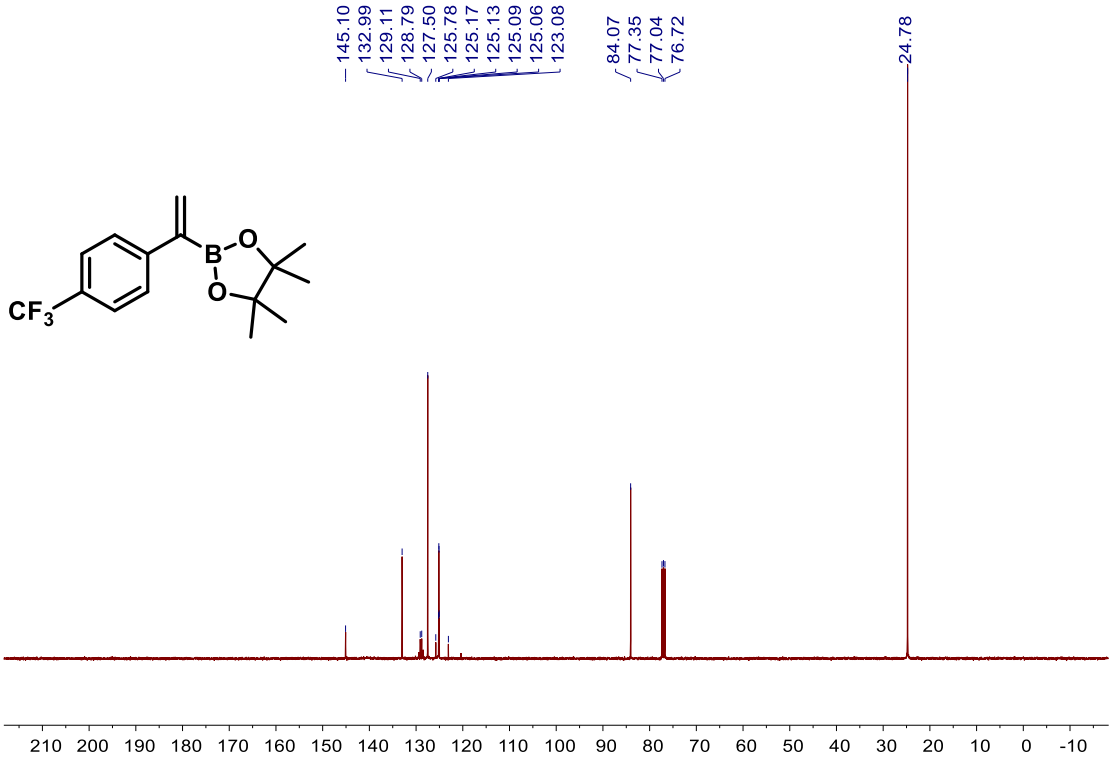
^{13}C NMR spectrum of **1i** (101 MHz, Chloroform-*d*)



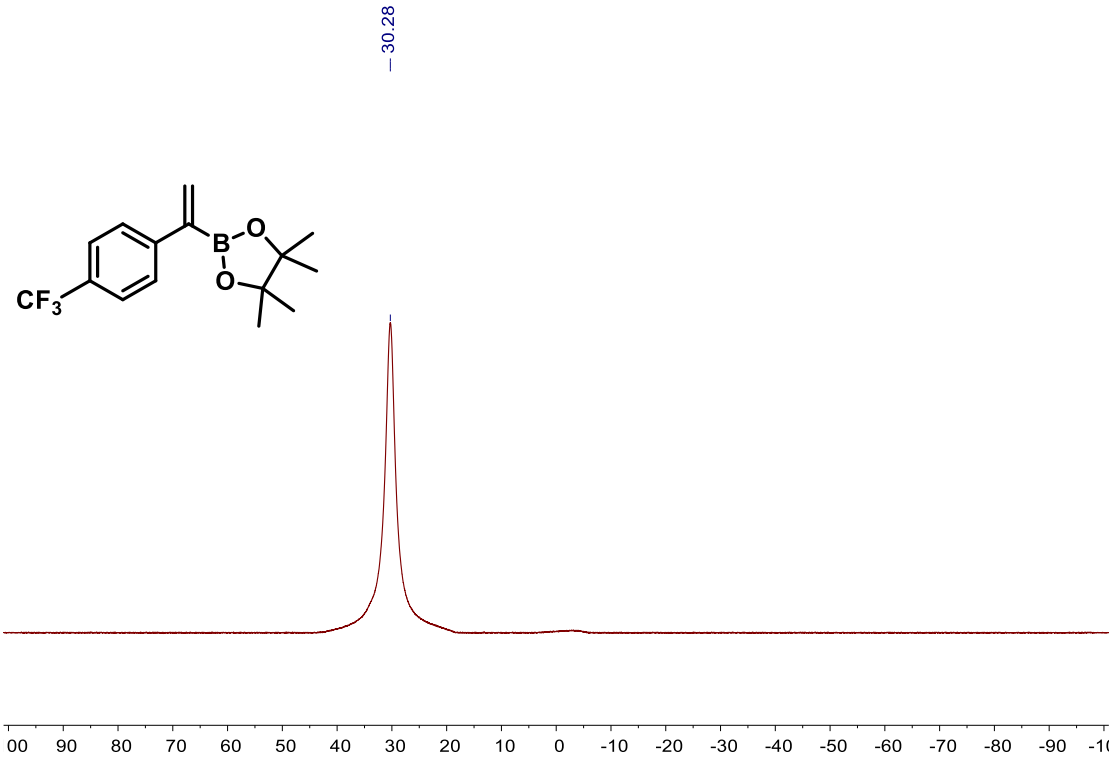
^{11}B NMR spectrum of **1i** (128 MHz Chloroform-*d*)



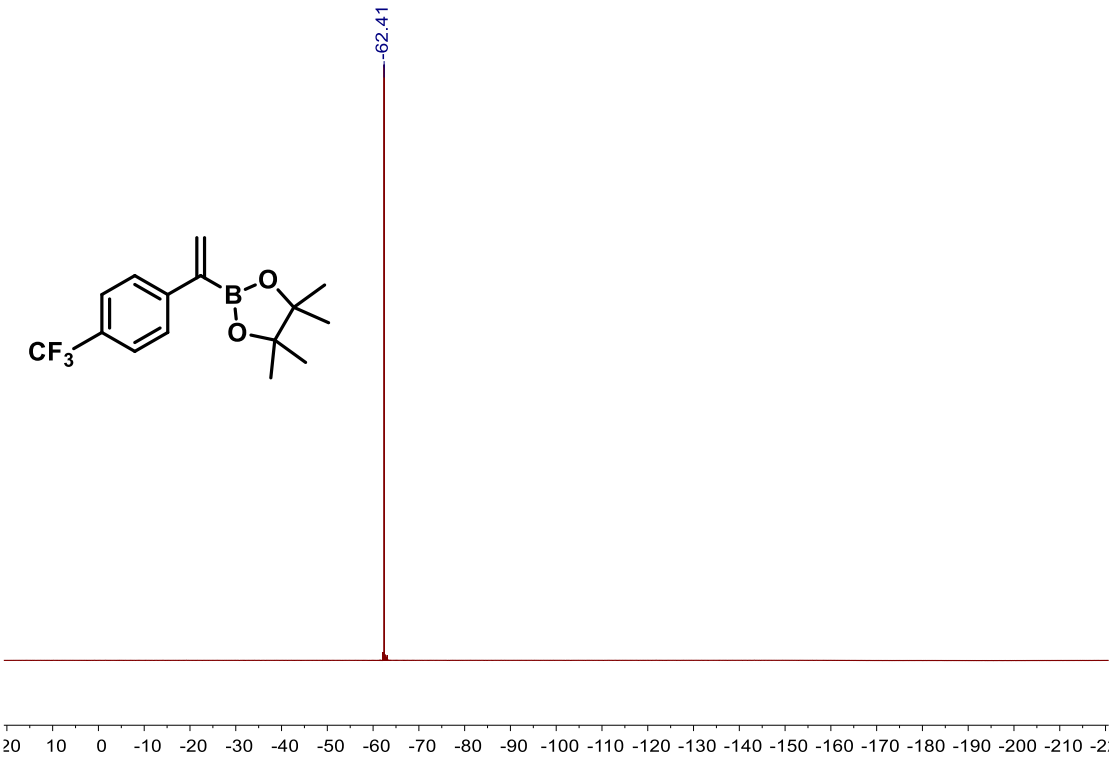
^{1}H NMR spectrum of **1j** (400 MHz, Chloroform-*d*)



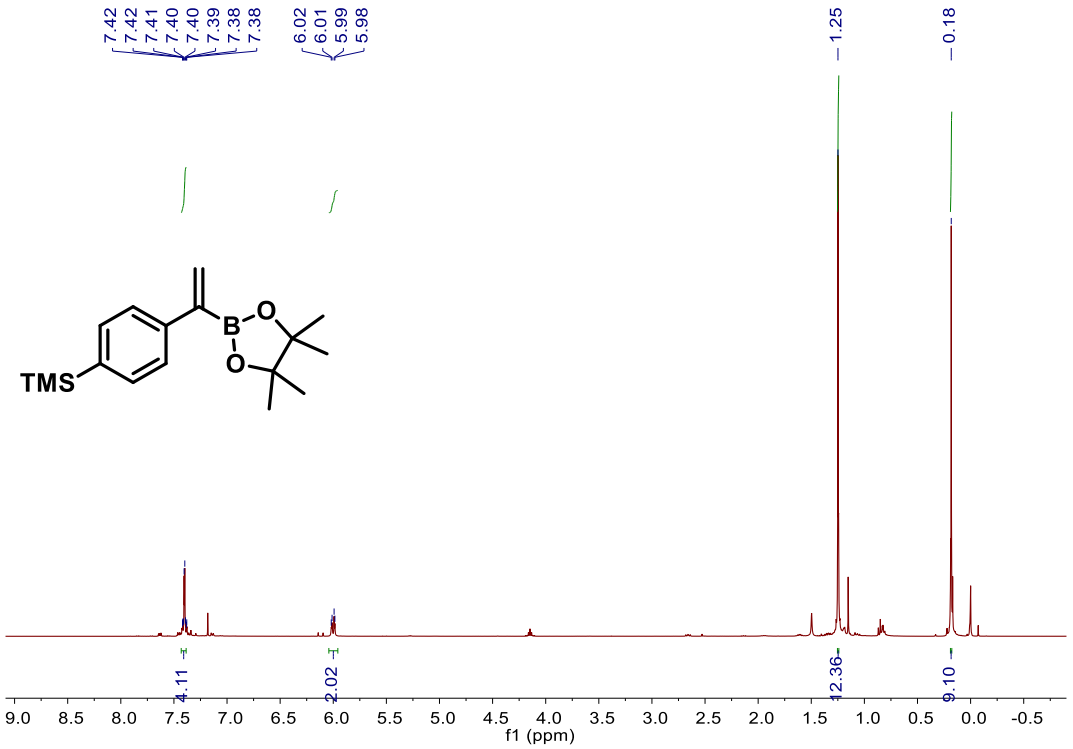
^{13}C NMR spectrum of **1j** (101 MHz, Chloroform-*d*)



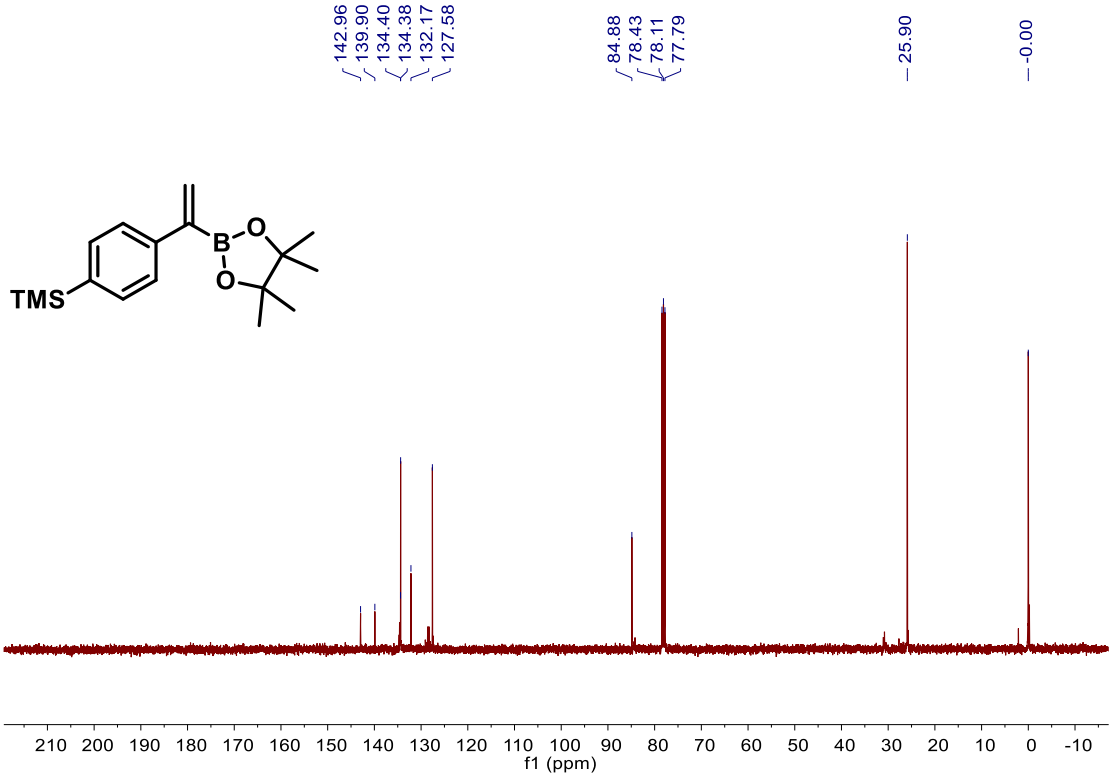
^{11}B NMR spectrum of **1j** (128 MHz Chloroform-*d*)



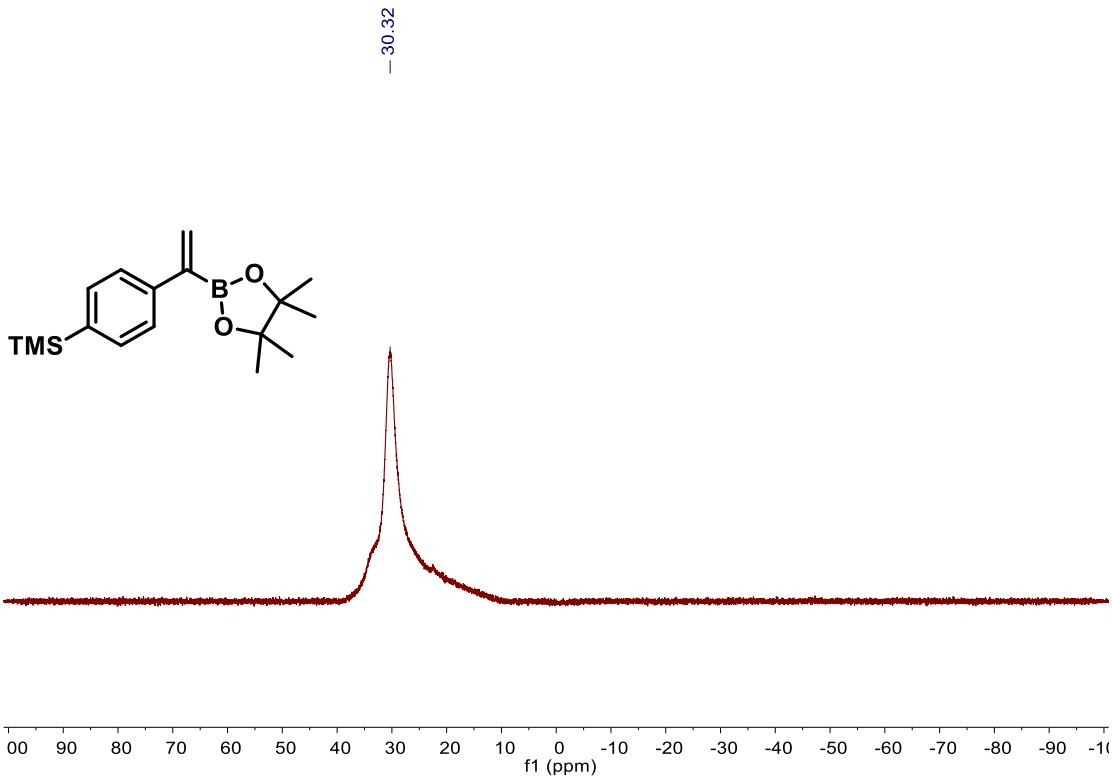
^{19}F NMR spectrum of **1j** (377 MHz, Chloroform-*d*)



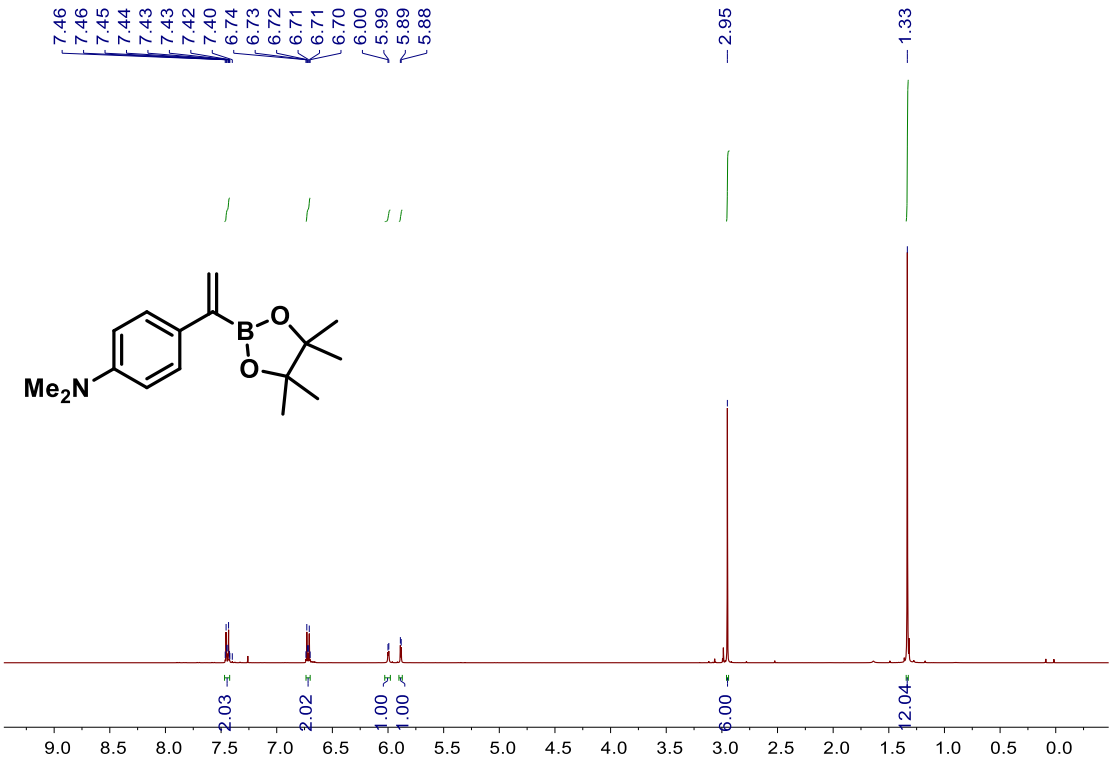
^{1}H NMR spectrum of **1k** (400 MHz, Chloroform-*d*)



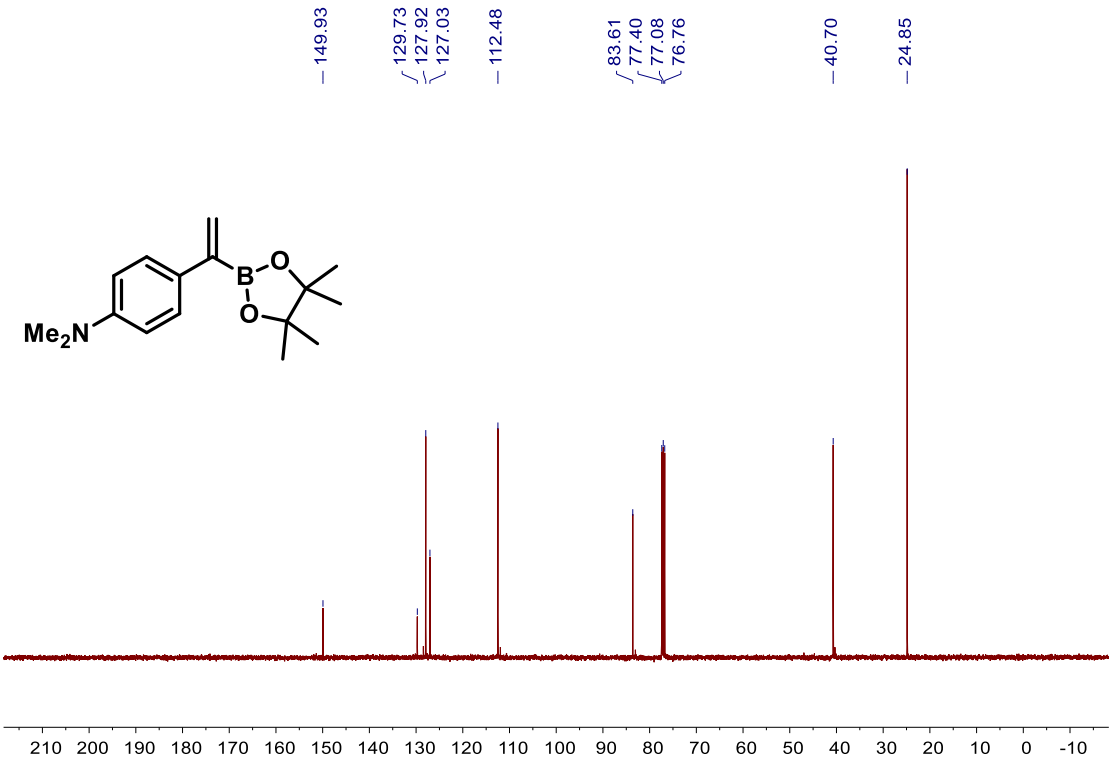
^{13}C NMR spectrum of **1k** (101 MHz, Chloroform-*d*)



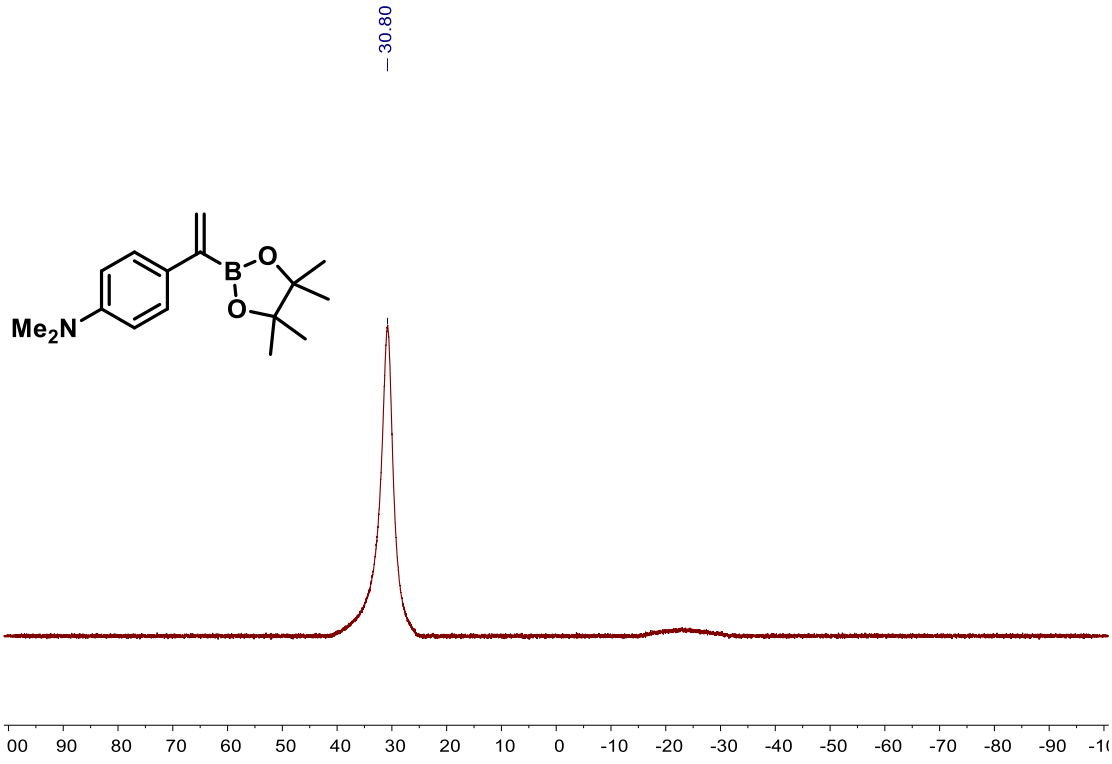
^{11}B NMR spectrum of **1k** (128 MHz Chloroform-*d*)



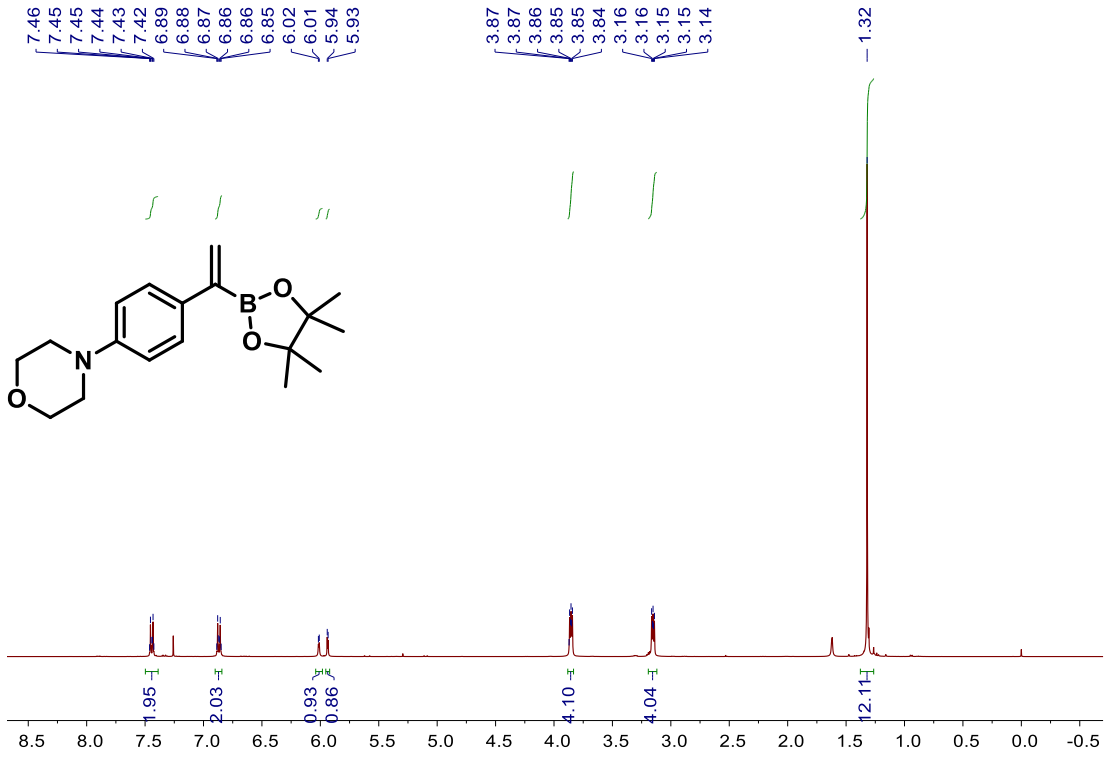
^{1}H NMR spectrum of **1l** (400 MHz, Chloroform-*d*)



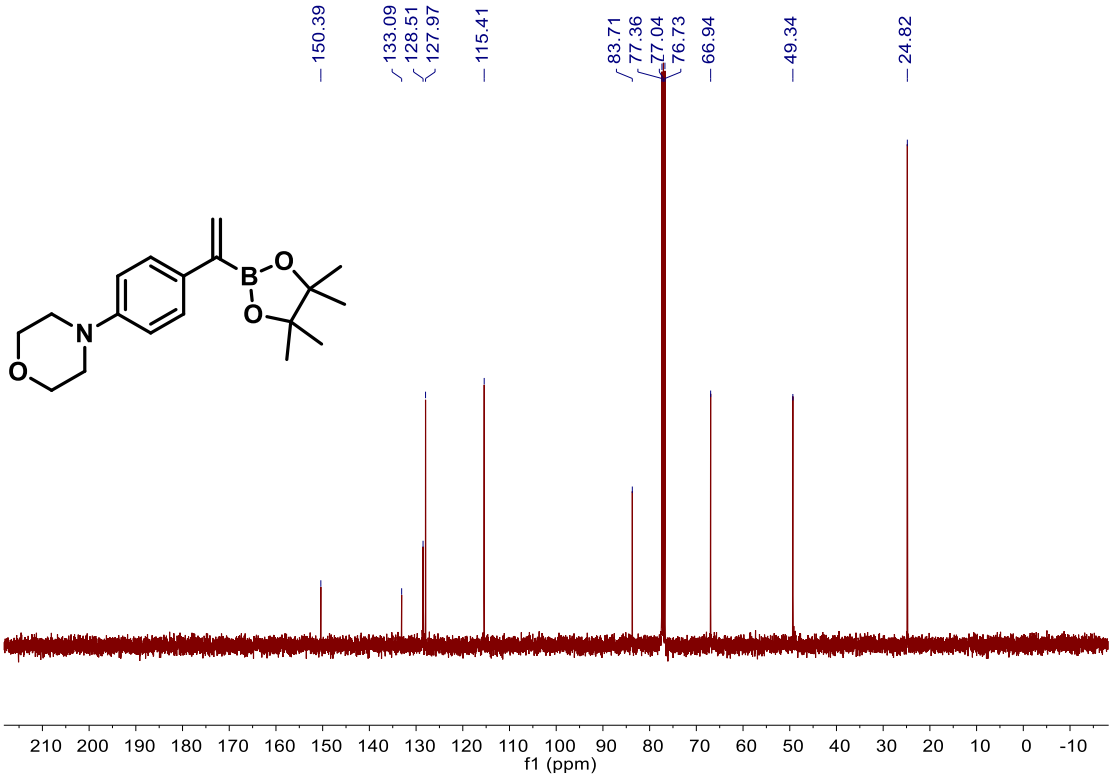
^{13}C NMR spectrum of **1l** (101 MHz, Chloroform-*d*)



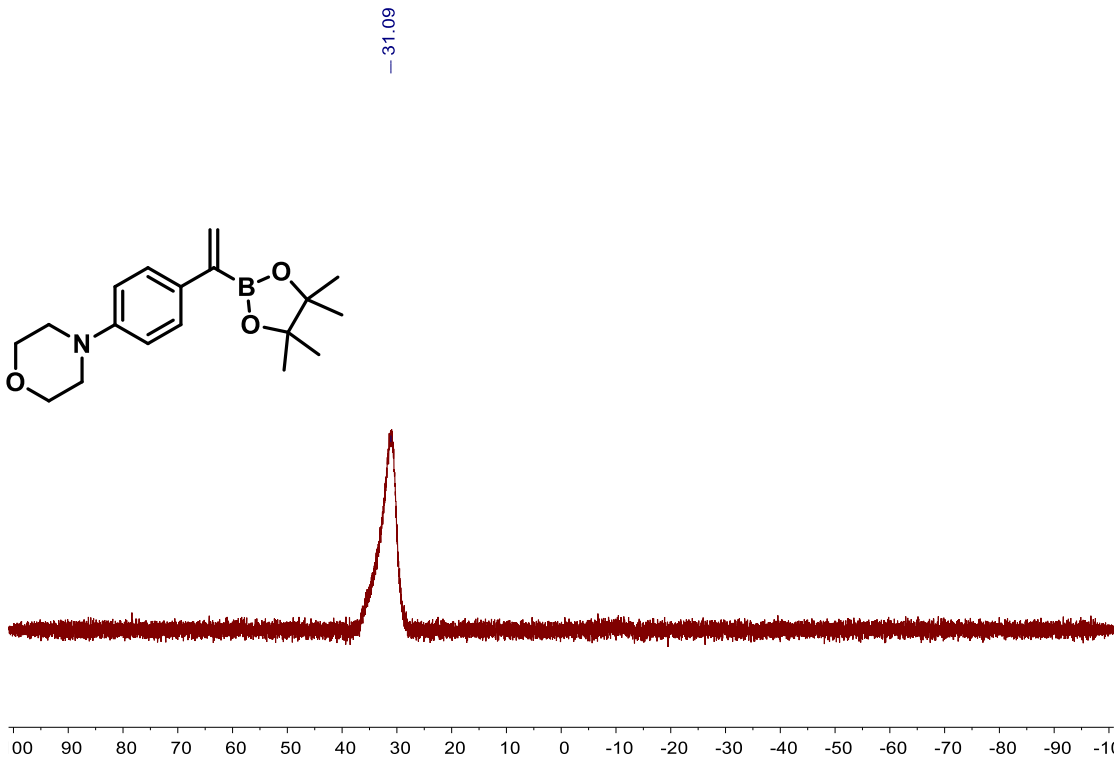
^{11}B NMR spectrum of **1l** (128 MHz Chloroform-*d*)



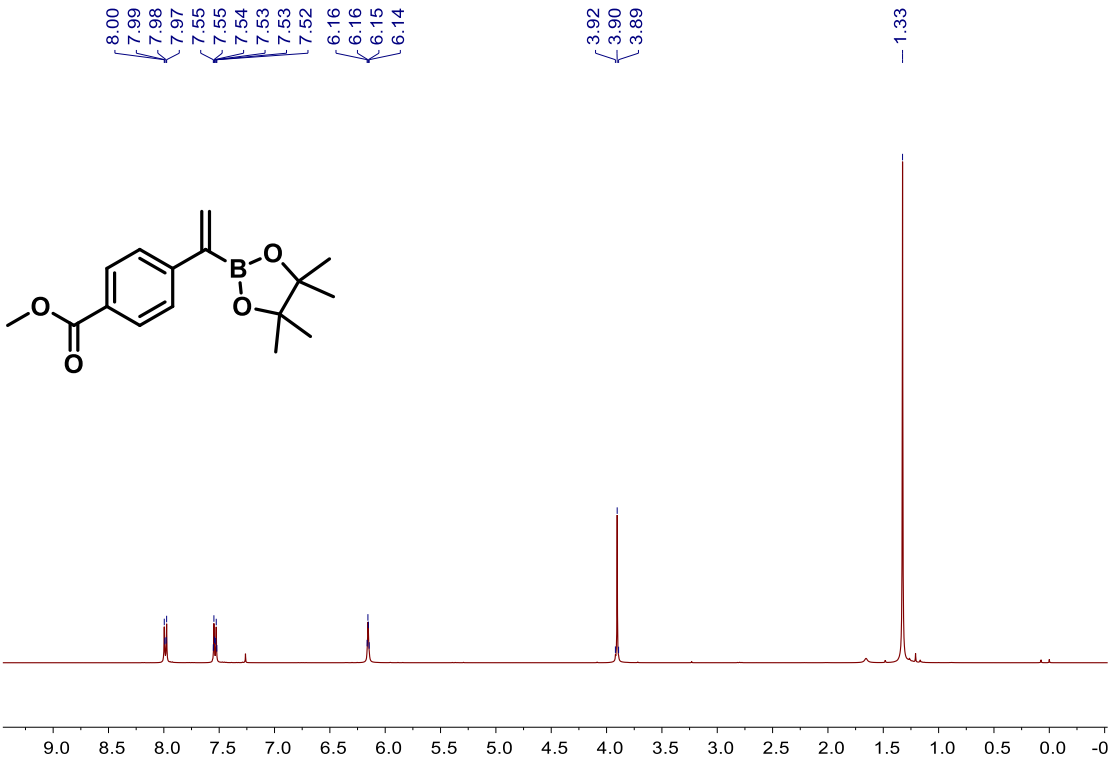
^{1}H NMR spectrum of **1m** (400 MHz, Chloroform-*d*)



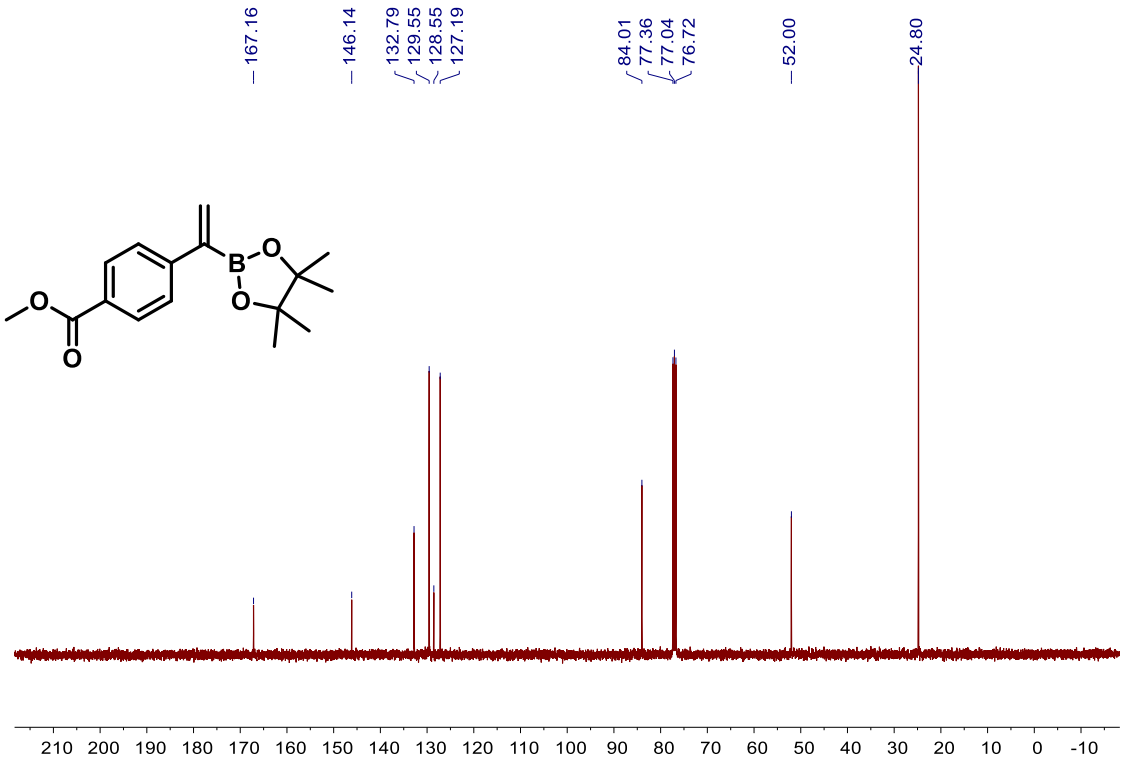
^{13}C NMR spectrum of **1m** (101 MHz, Chloroform-*d*)



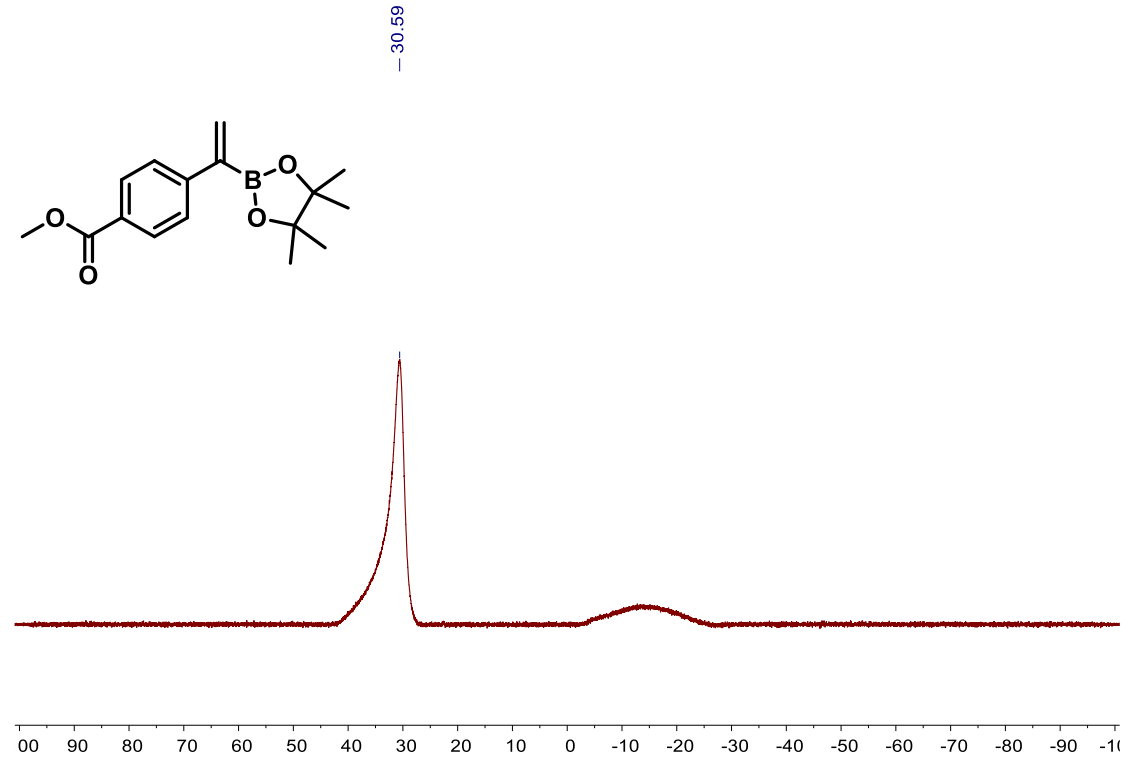
^{11}B NMR spectrum of **1m** (128 MHz Chloroform-*d*)



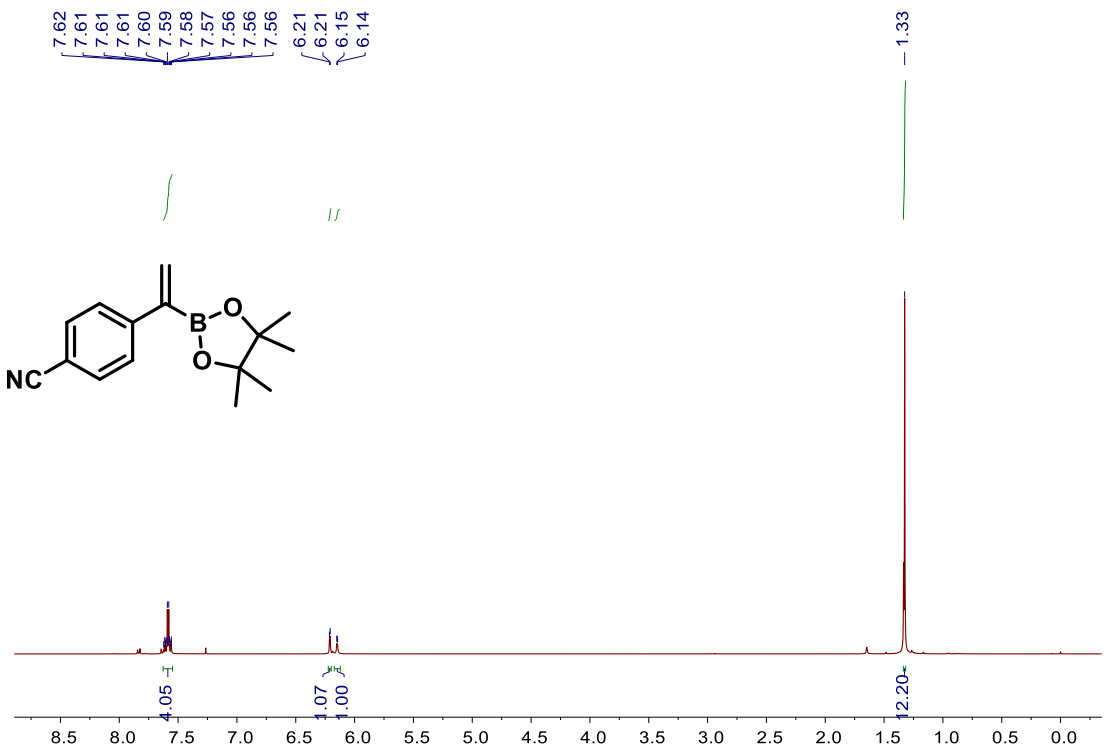
^{1}H NMR spectrum of **1n** (400 MHz, Chloroform-*d*)



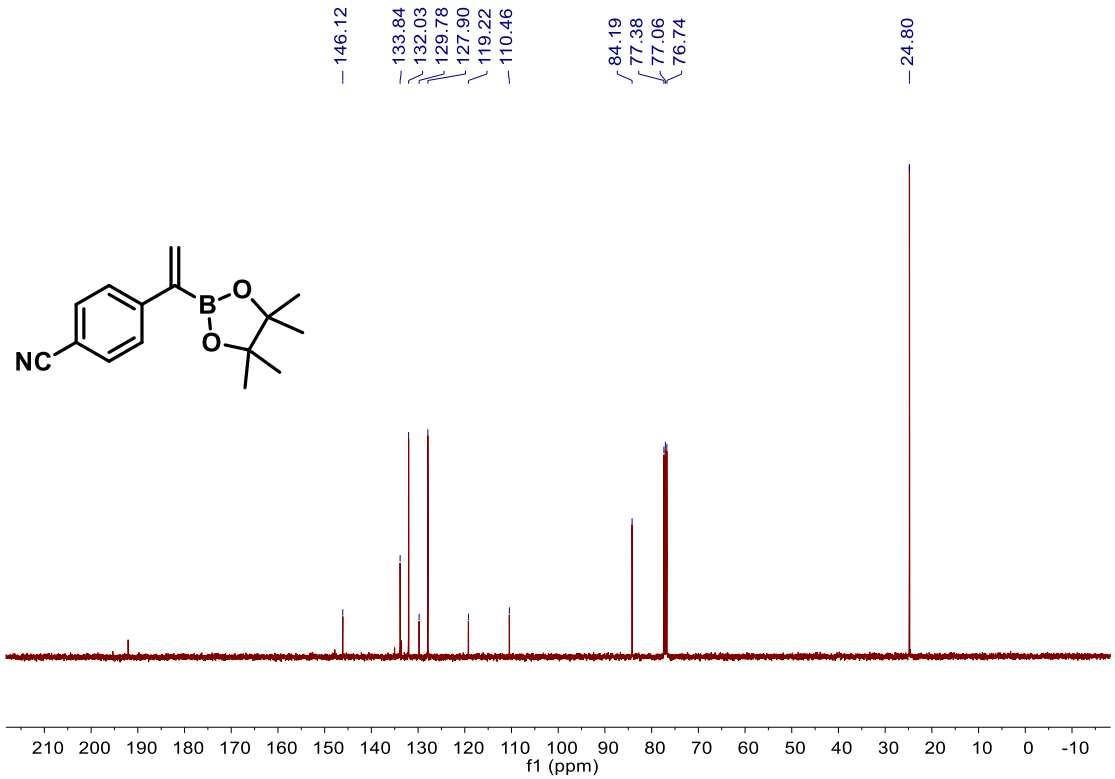
^{13}C NMR spectrum of **1n** (101 MHz, Chloroform-*d*)



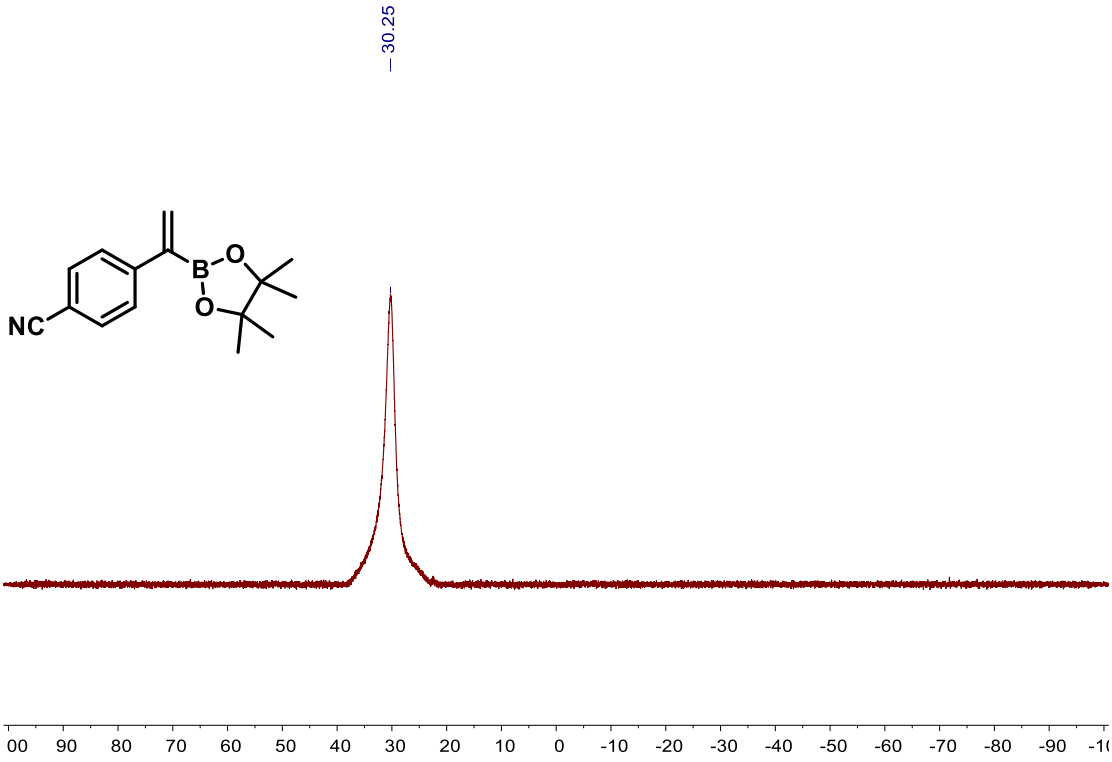
^{11}B NMR spectrum of **1n** (128 MHz Chloroform-*d*)



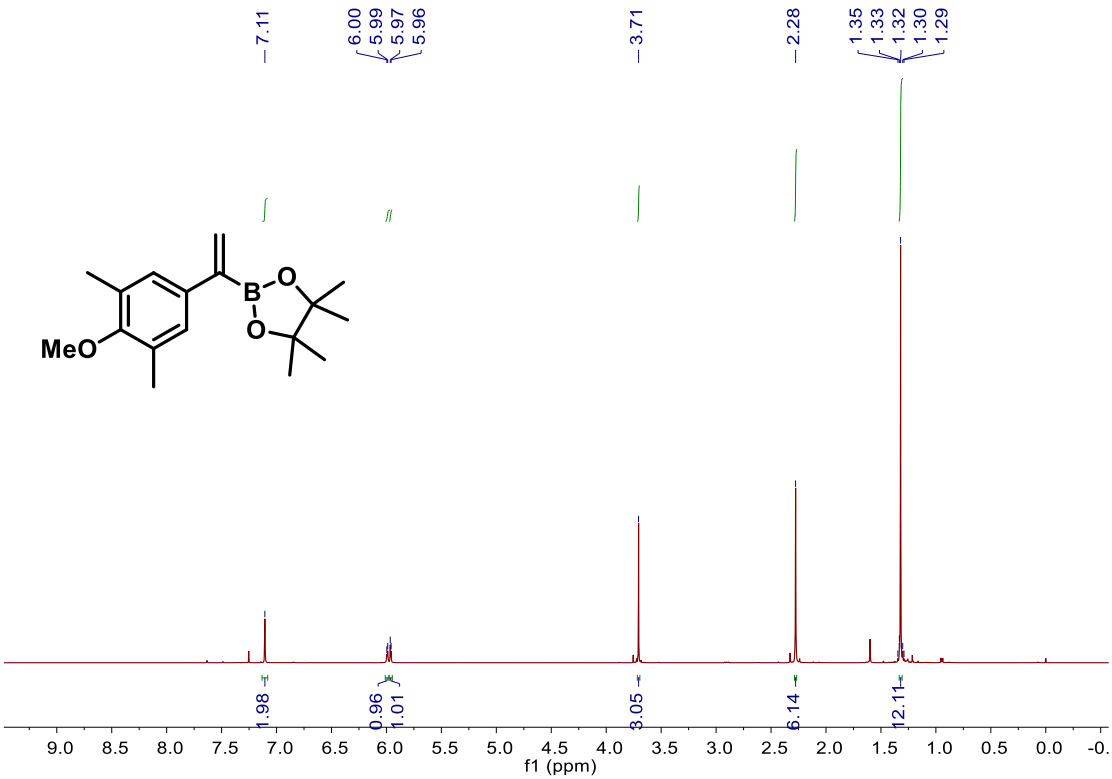
^{1}H NMR spectrum of **1o** (400 MHz, Chloroform-*d*)



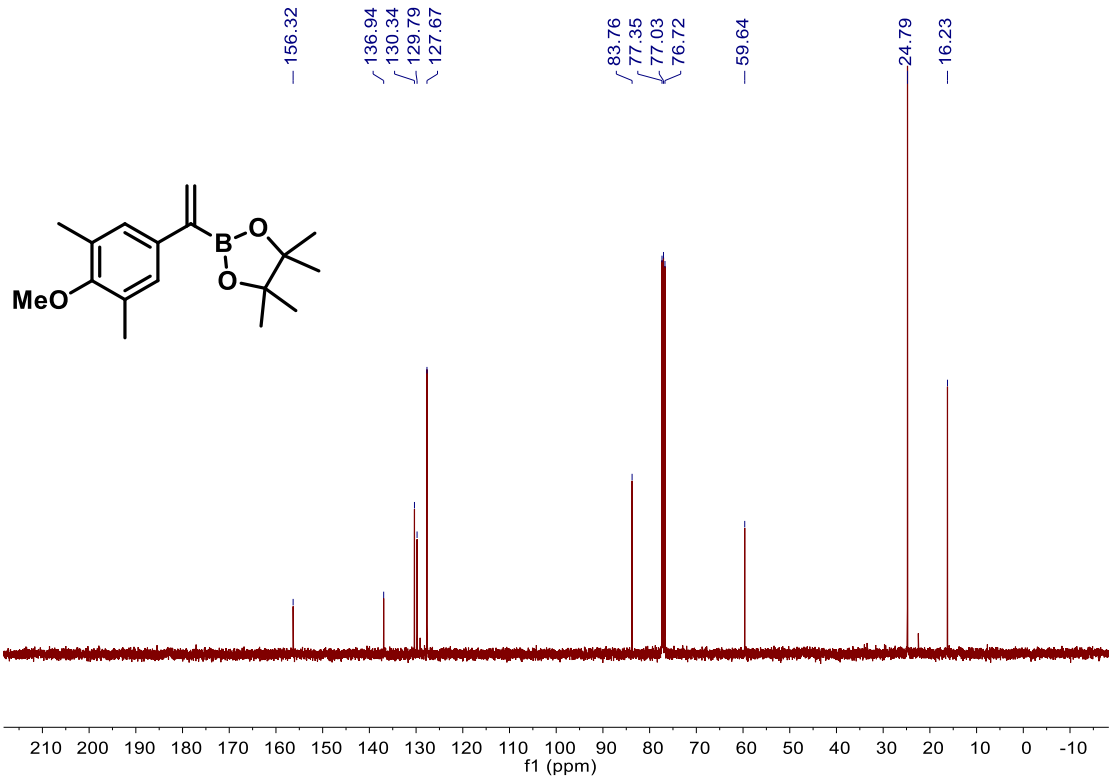
^{13}C NMR spectrum of **1o** (101 MHz, Chloroform-*d*)



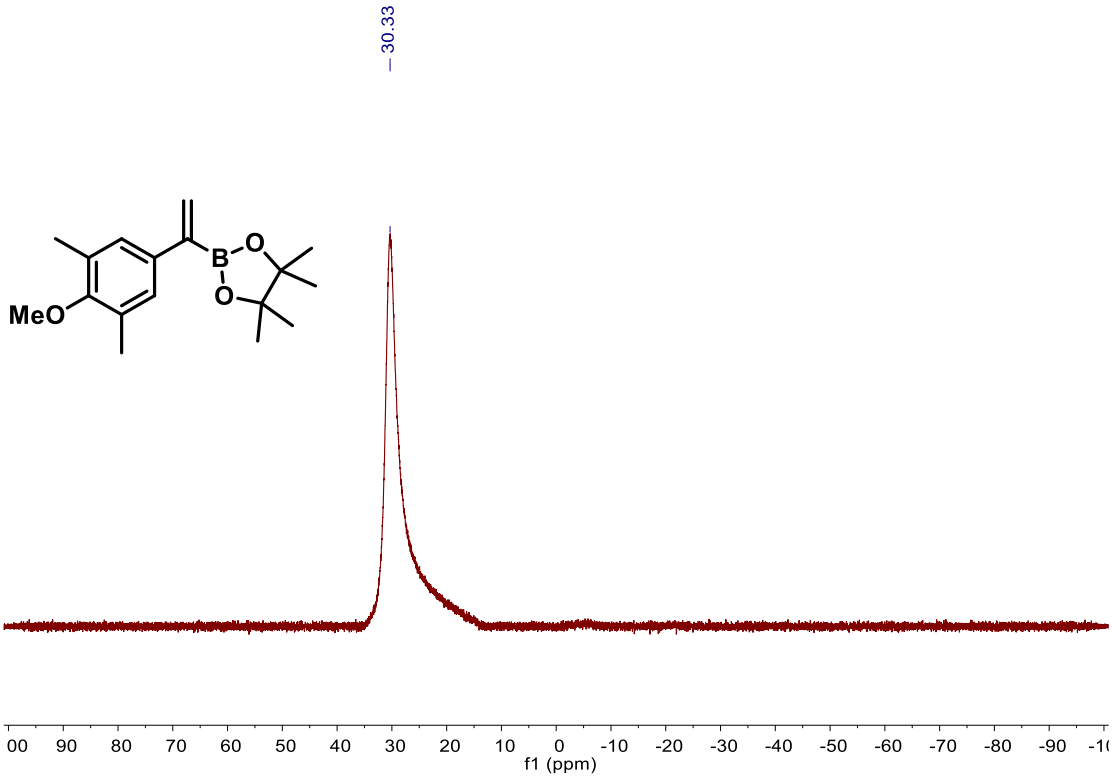
^{11}B NMR spectrum of **1o** (128 MHz Chloroform-*d*)



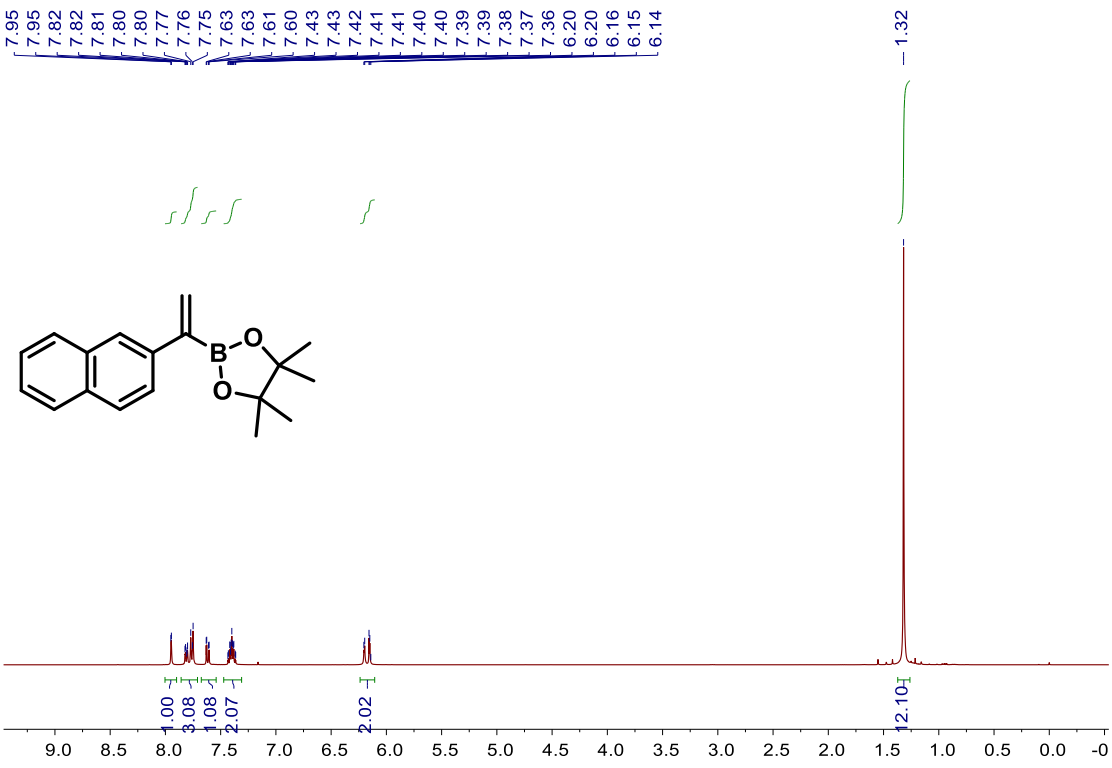
^{1}H NMR spectrum of **1p** (400 MHz, Chloroform-*d*)



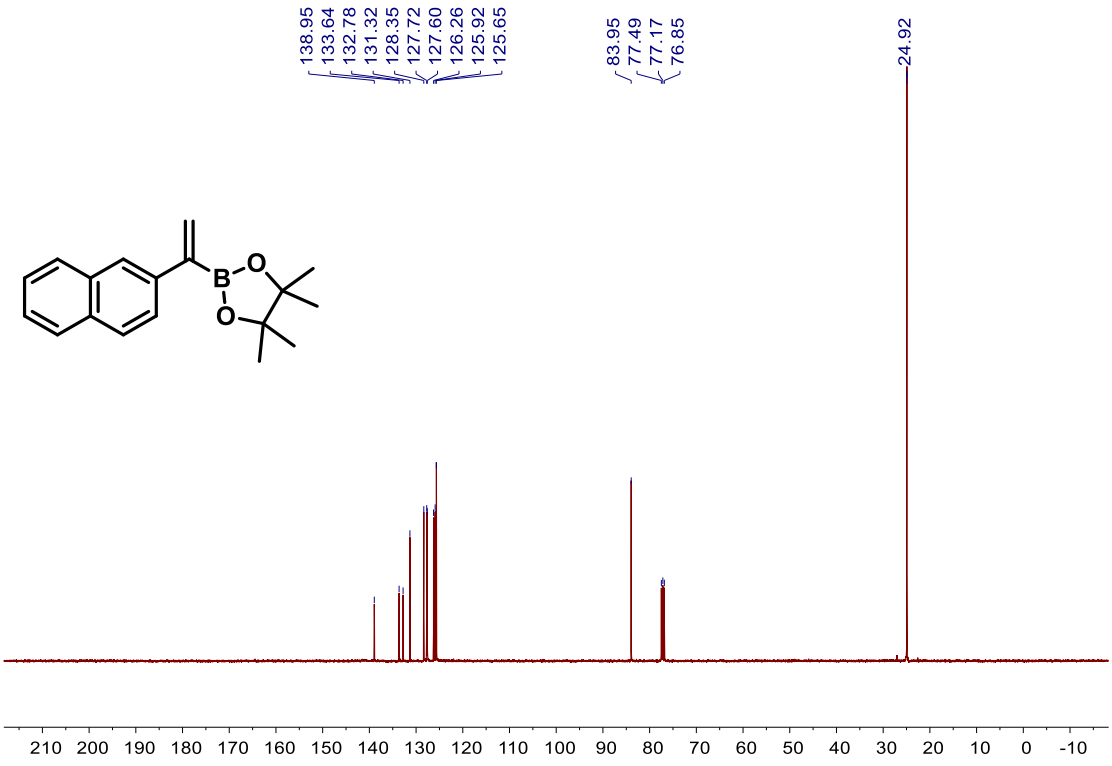
^{13}C NMR spectrum of **1p** (101 MHz, Chloroform-*d*)



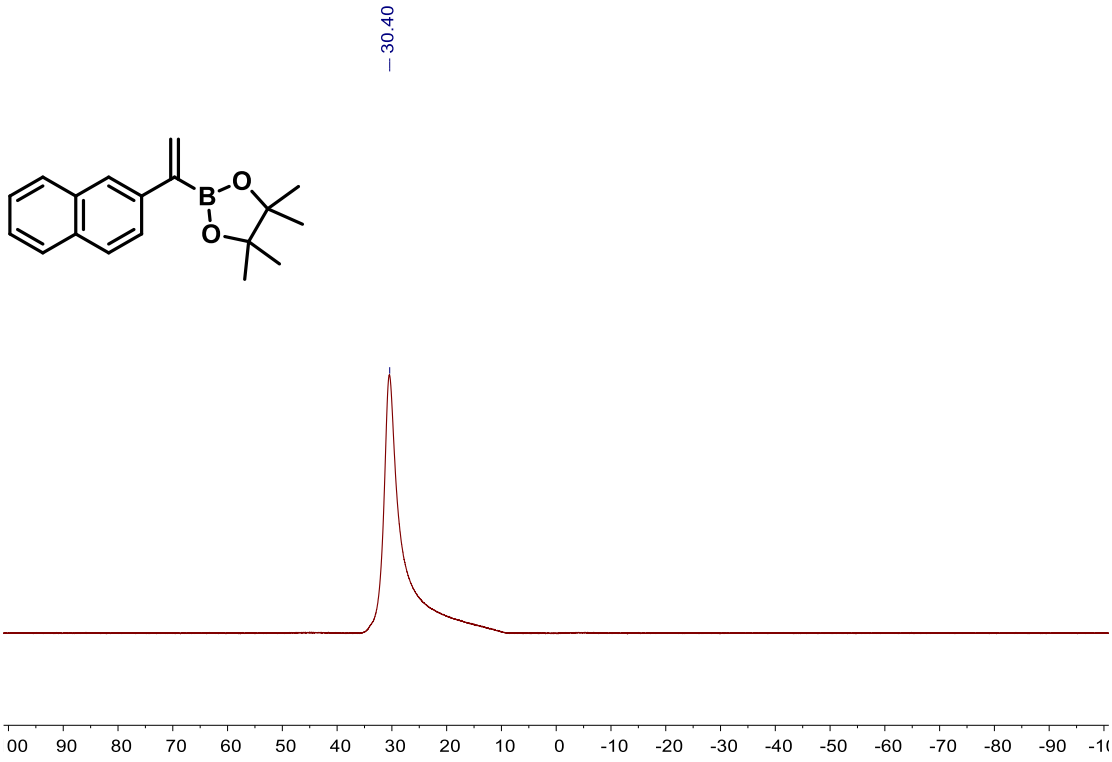
^{11}B NMR spectrum of **1p** (128 MHz Chloroform-*d*)



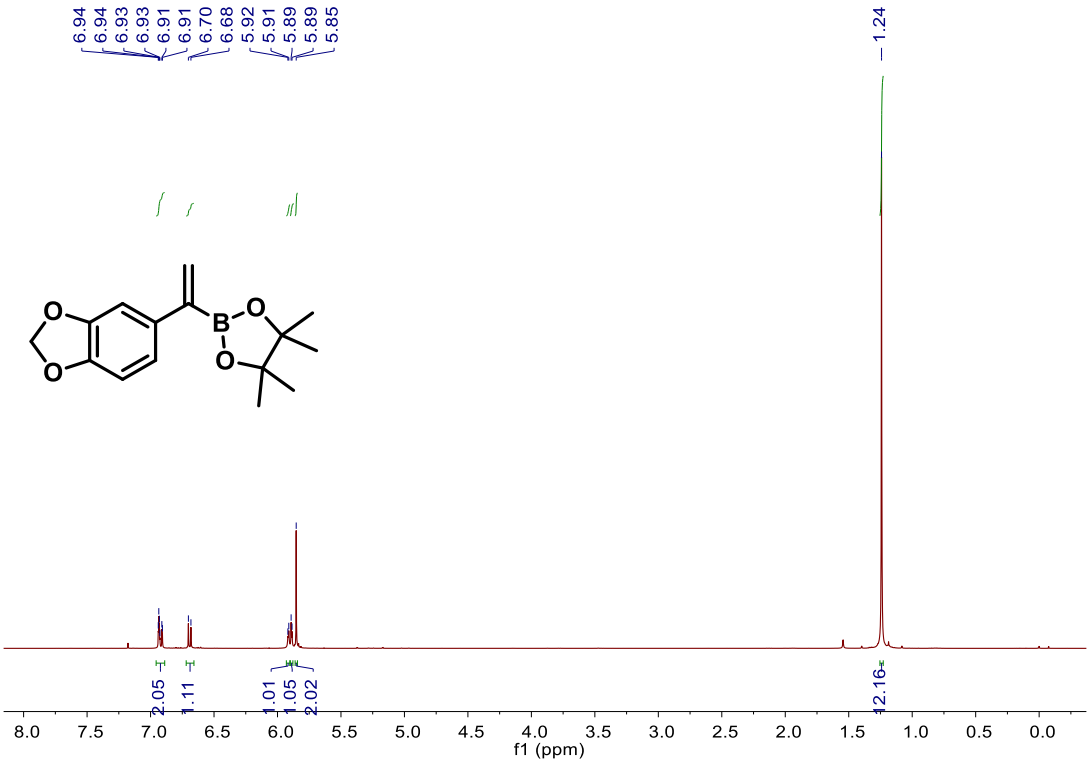
^{1}H NMR spectrum of **1q** (400 MHz, Chloroform-*d*)



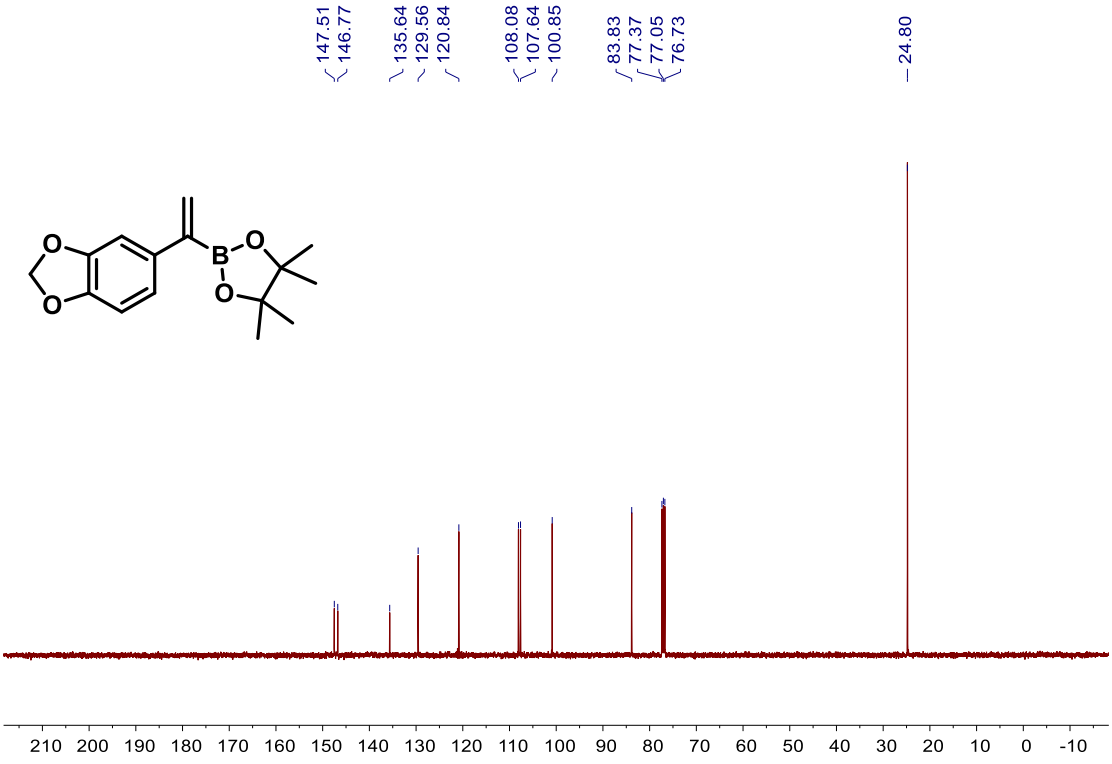
^{13}C NMR spectrum of **1q** (101 MHz, Chloroform-*d*)



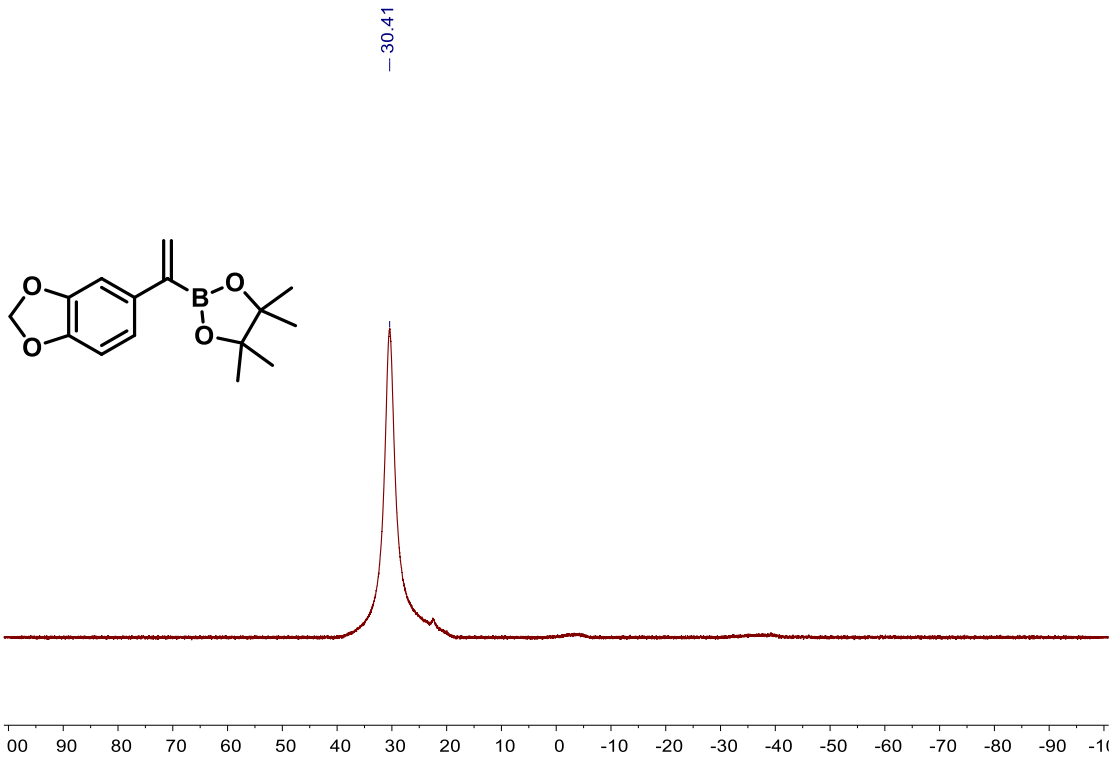
^{11}B NMR spectrum of **1q** (128 MHz Chloroform-*d*)



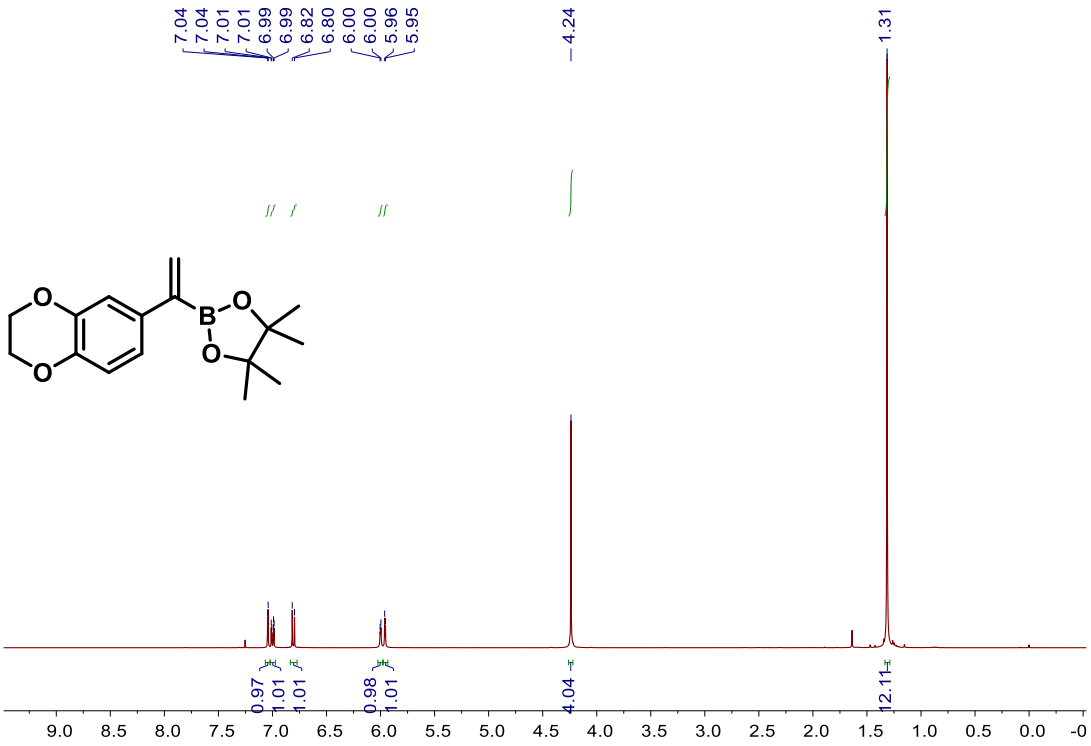
^{1}H NMR spectrum of **1r** (400 MHz, Chloroform-*d*)



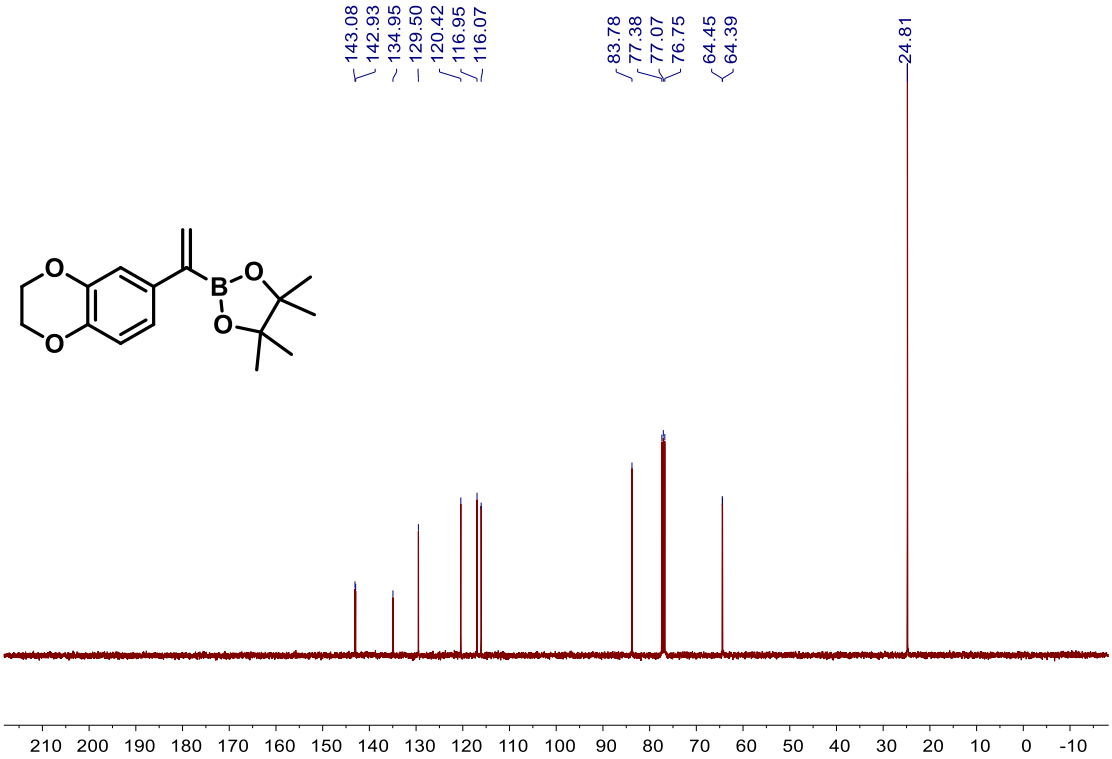
^{13}C NMR spectrum of **1r** (101 MHz, Chloroform-*d*)



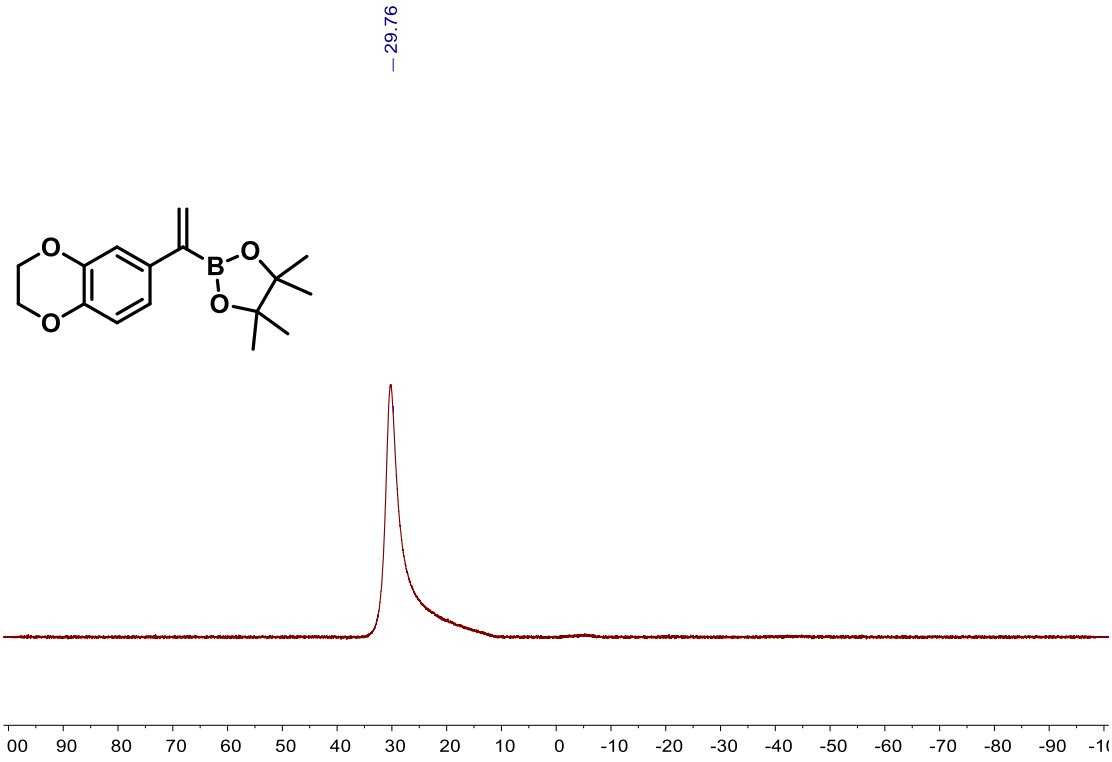
^{11}B NMR spectrum of **1r** (128 MHz Chloroform-*d*)



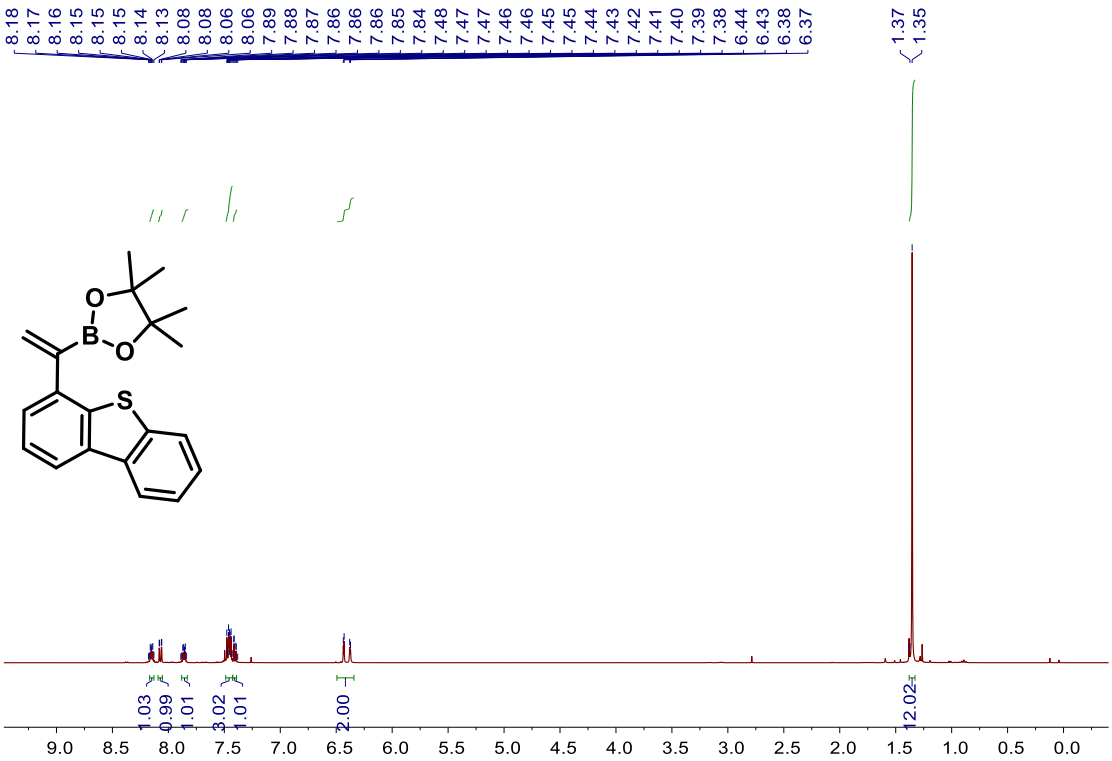
^{1}H NMR spectrum of **1s** (400 MHz, Chloroform-*d*)



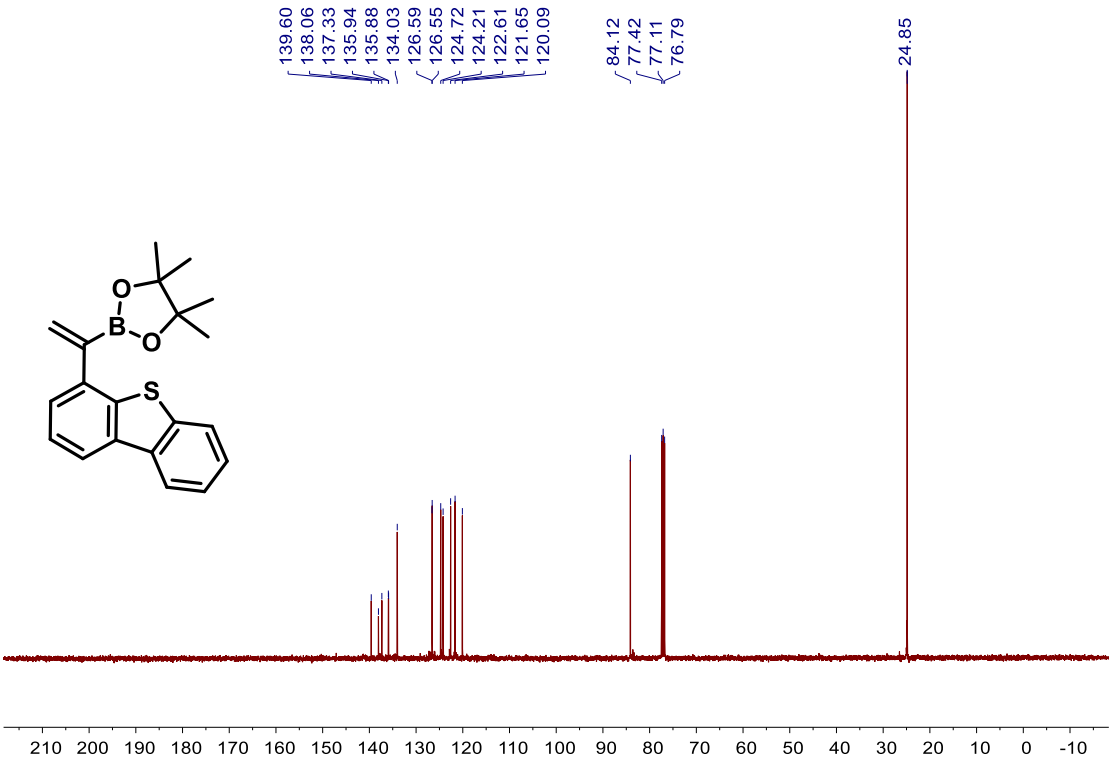
^{13}C NMR spectrum of **1s** (101 MHz, Chloroform-*d*)



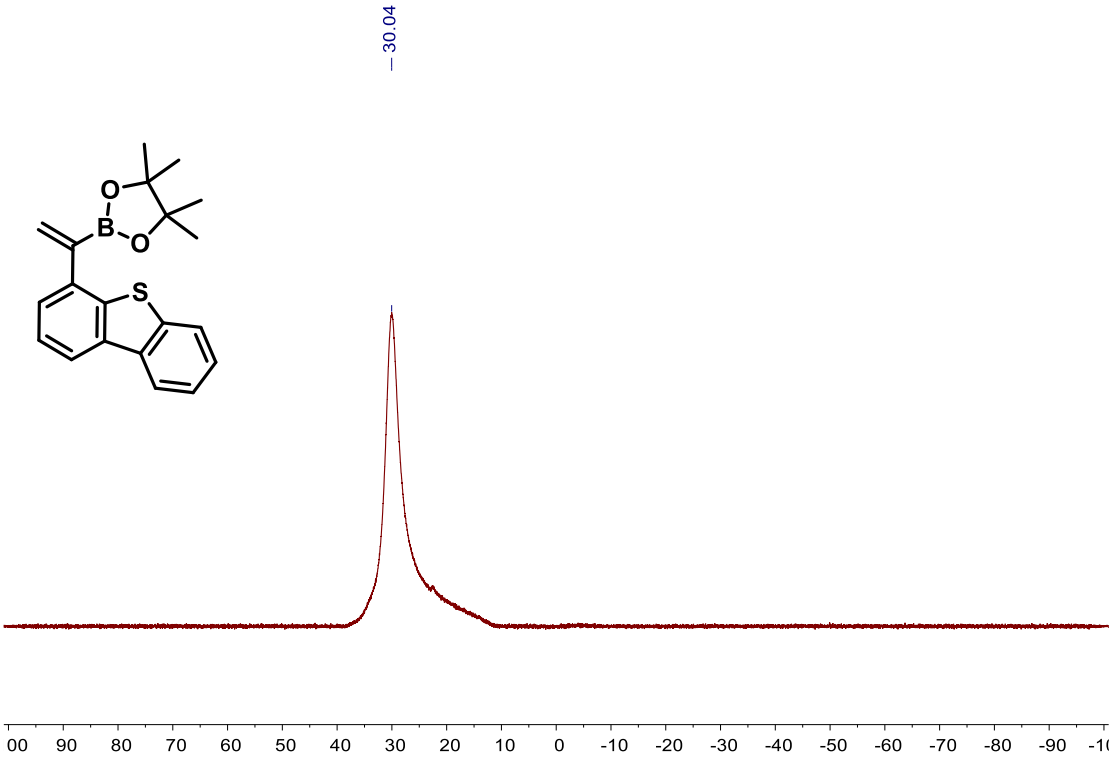
^{11}B NMR spectrum of **1s** (128 MHz Chloroform-*d*)



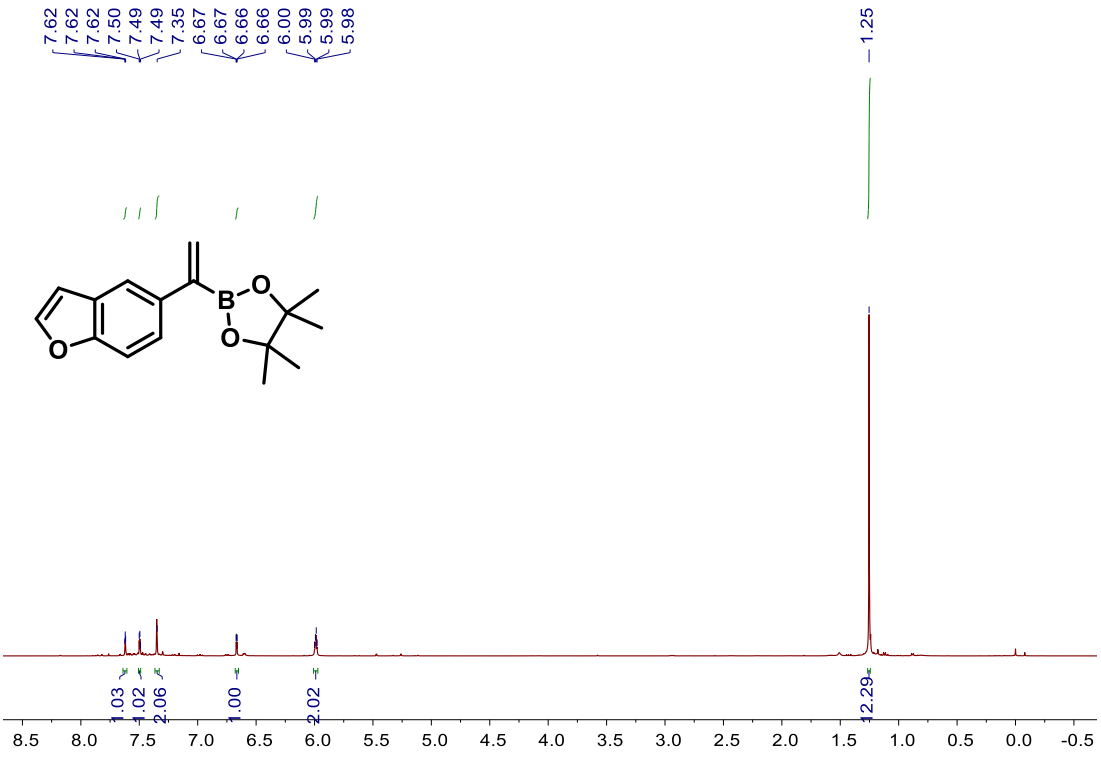
^{1}H NMR spectrum of **1t** (400 MHz, Chloroform-*d*)



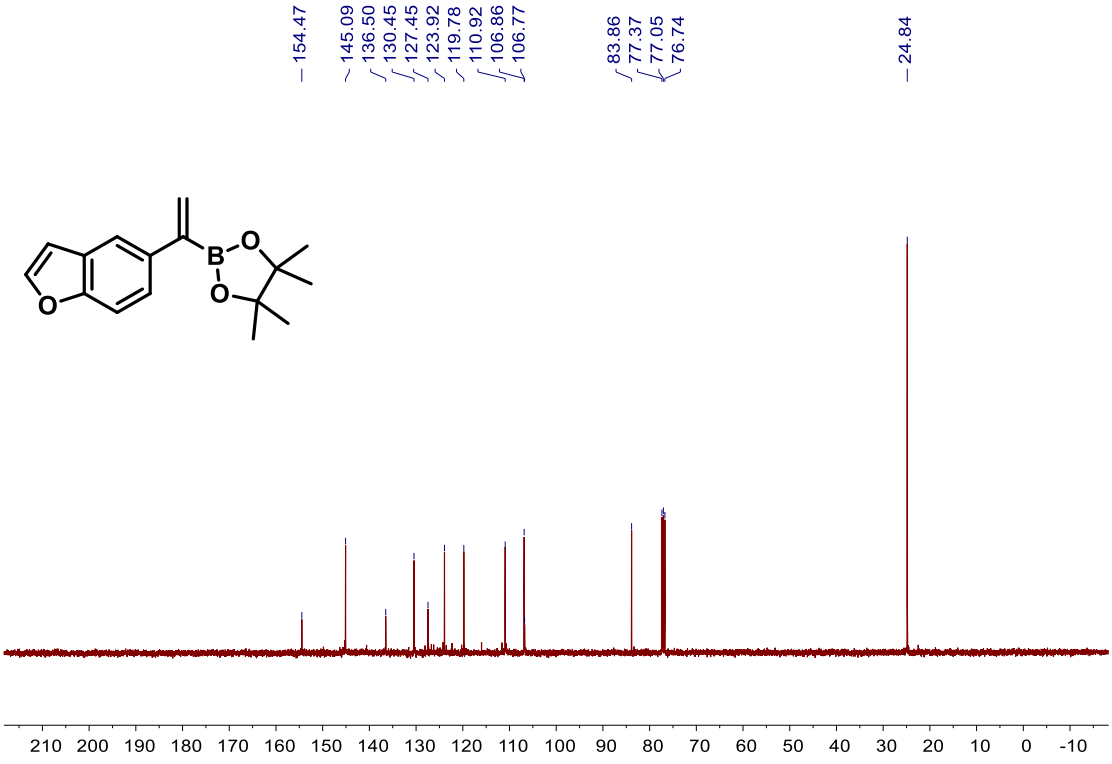
^{13}C NMR spectrum of **1t** (101 MHz, Chloroform-*d*)



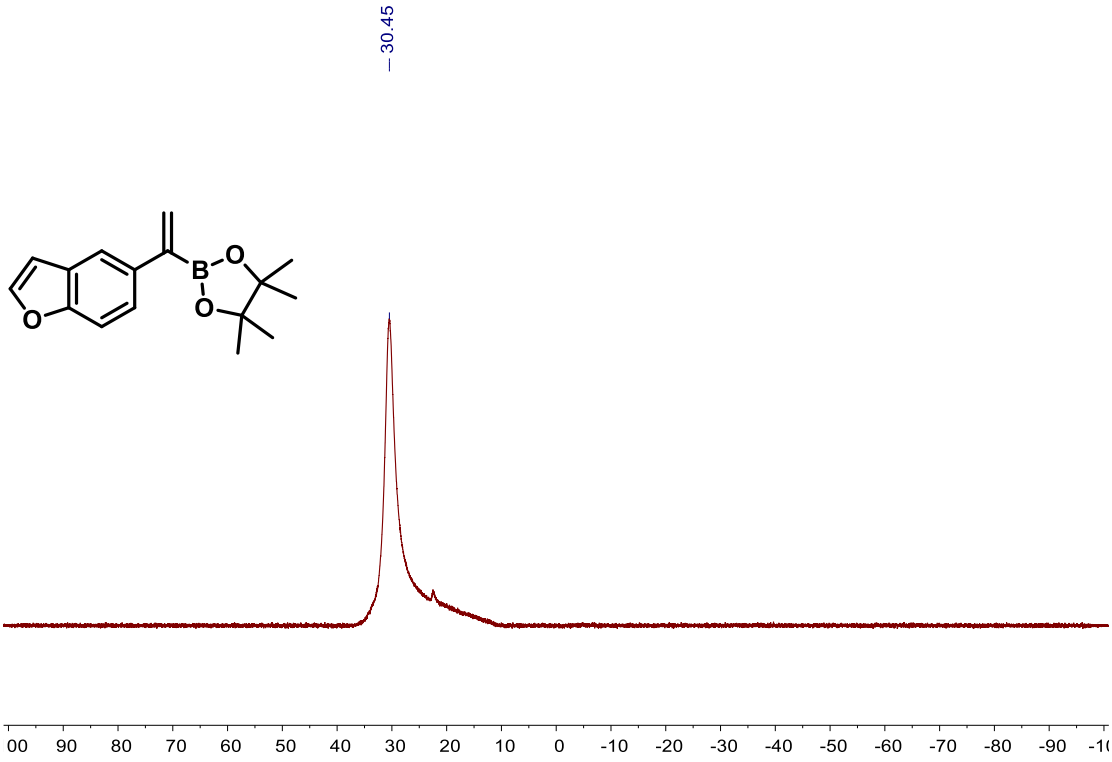
^{11}B NMR spectrum of **1t** (128 MHz Chloroform-*d*)



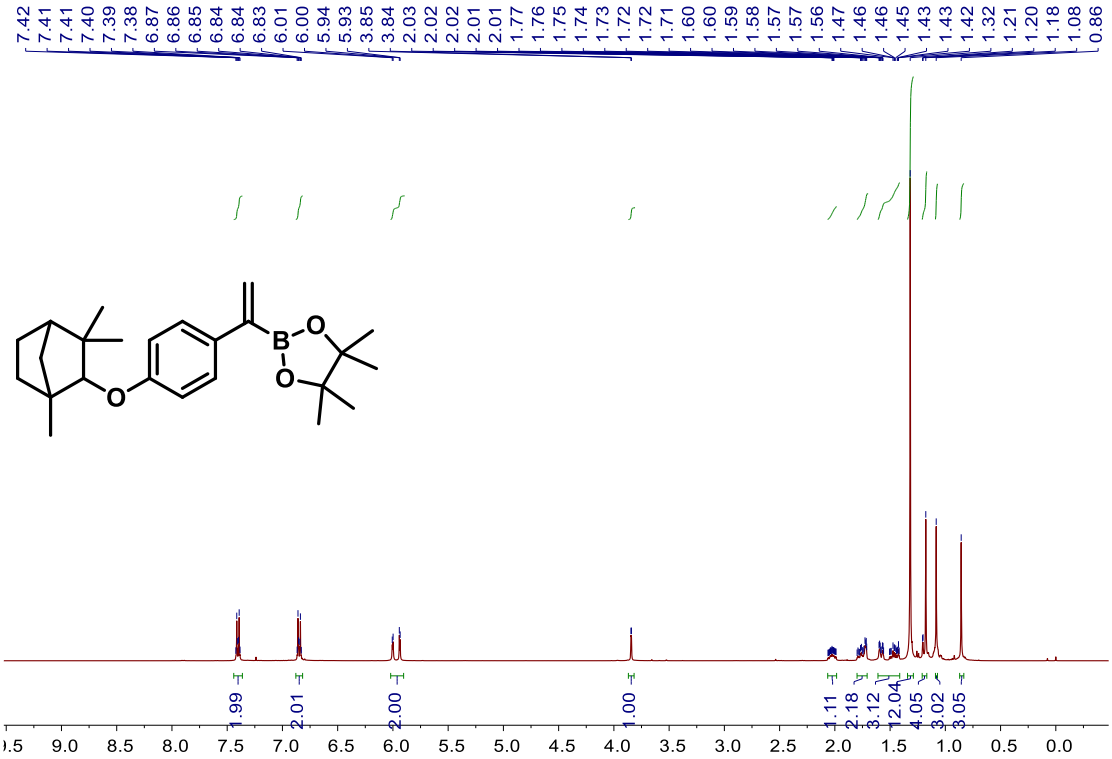
^{1}H NMR spectrum of **1u** (400 MHz, Chloroform-*d*)



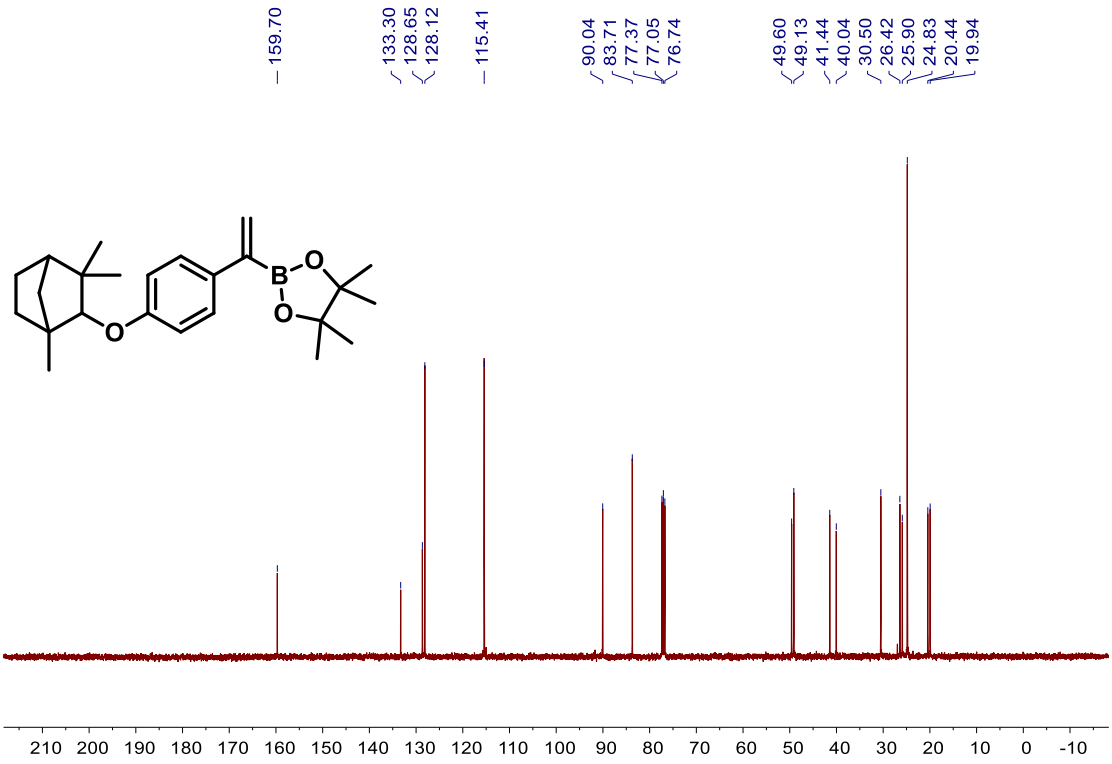
^{13}C NMR spectrum of **1u** (101 MHz, Chloroform-*d*)



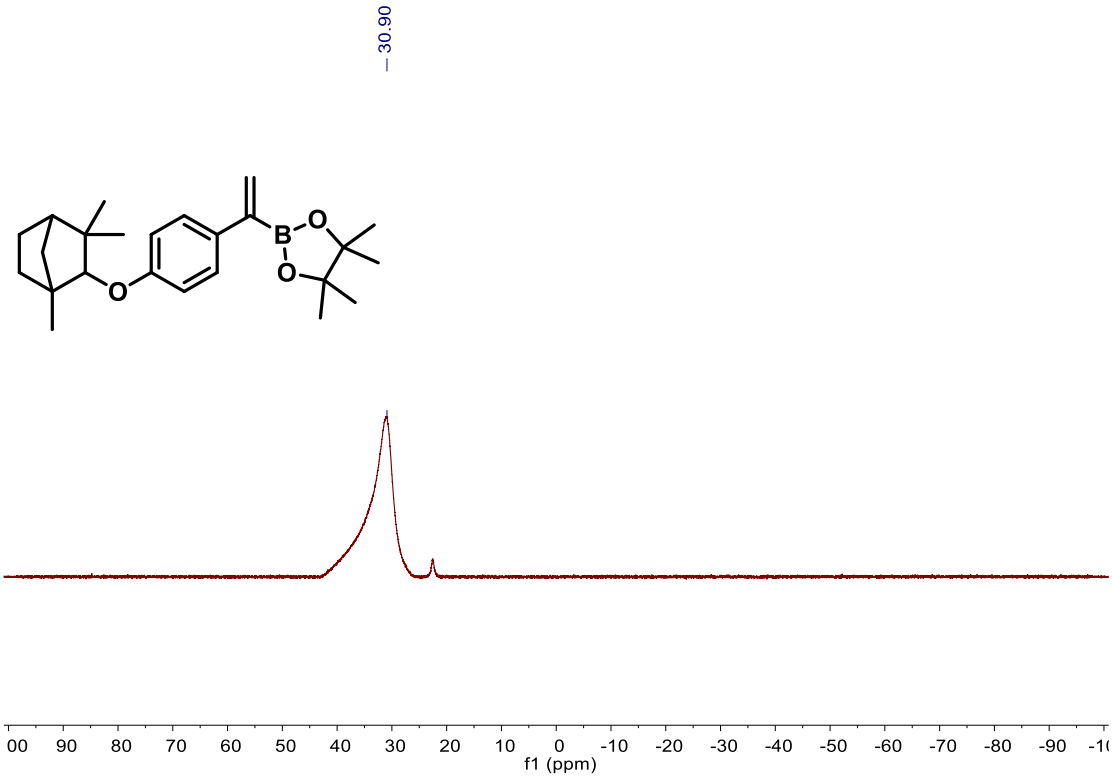
^{11}B NMR spectrum of **1u** (128 MHz Chloroform-*d*)



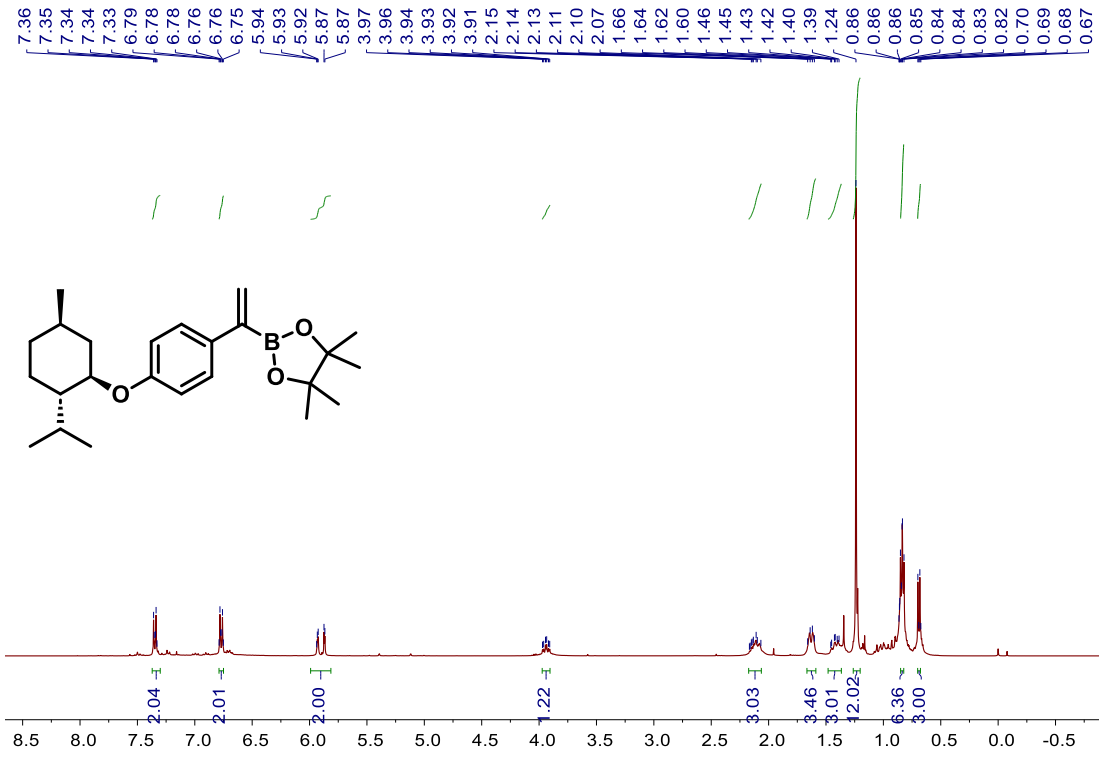
^{1}H NMR spectrum of **1v** (400 MHz, Chloroform-*d*)



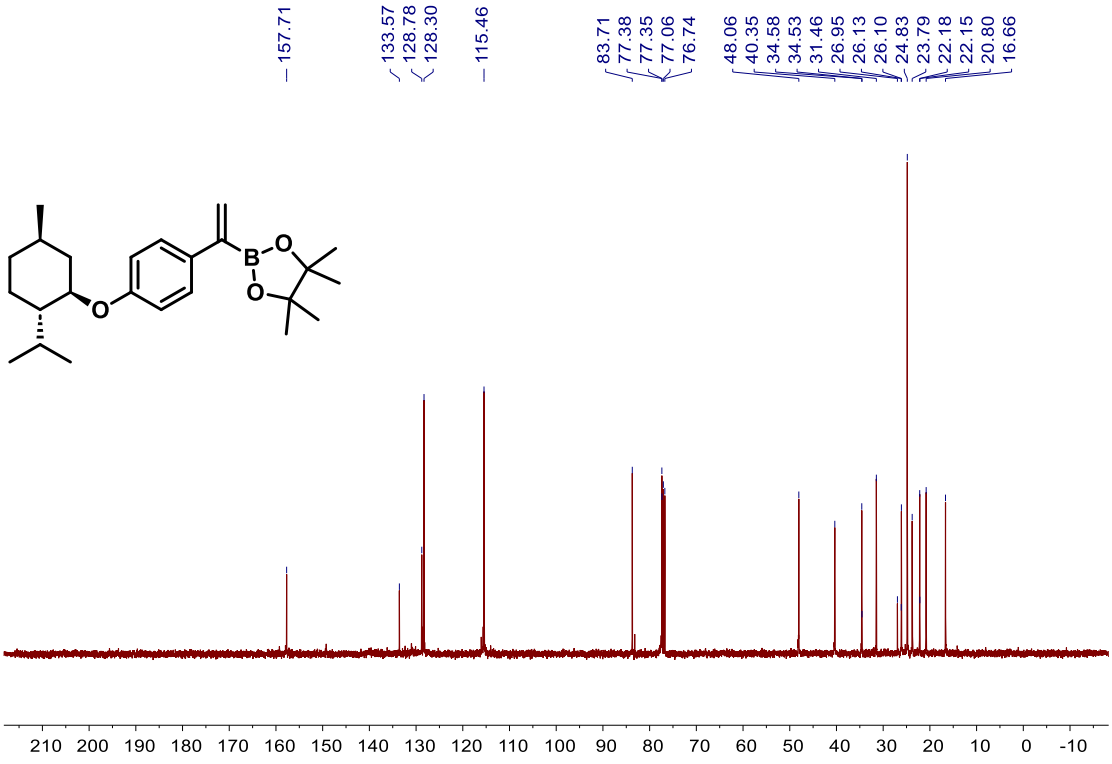
^{13}C NMR spectrum of **1v** (101 MHz, Chloroform-*d*)



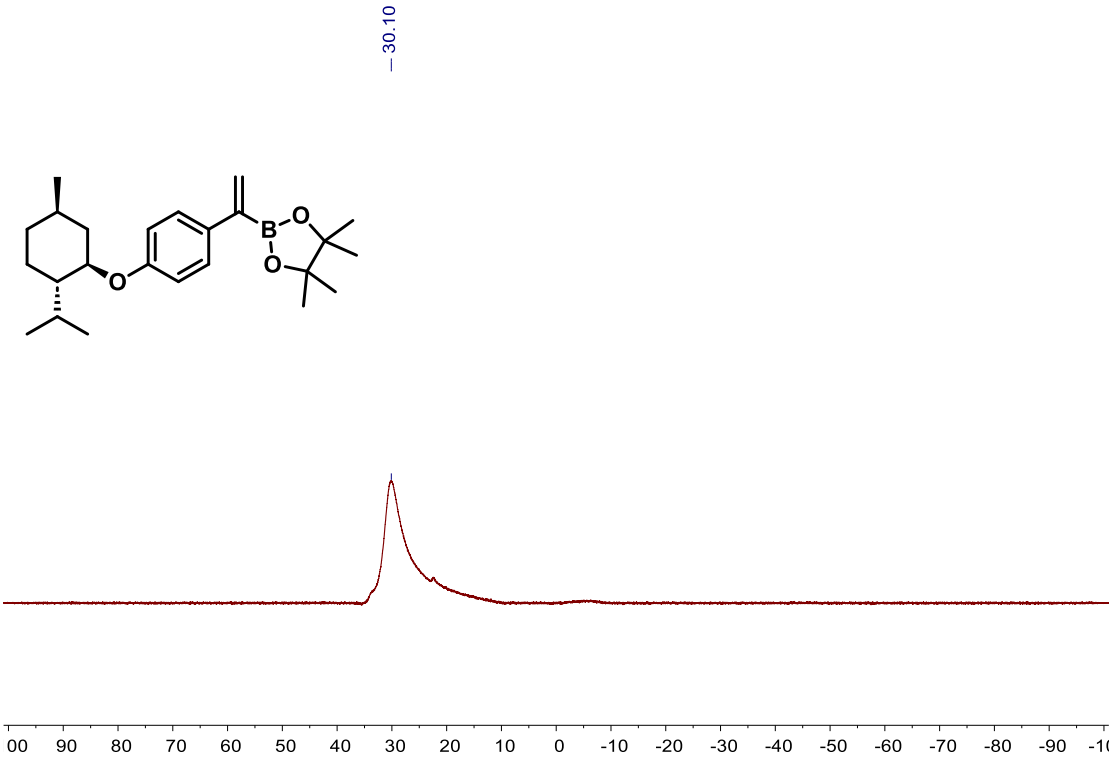
^{11}B NMR spectrum of **1v** (128 MHz Chloroform-*d*)



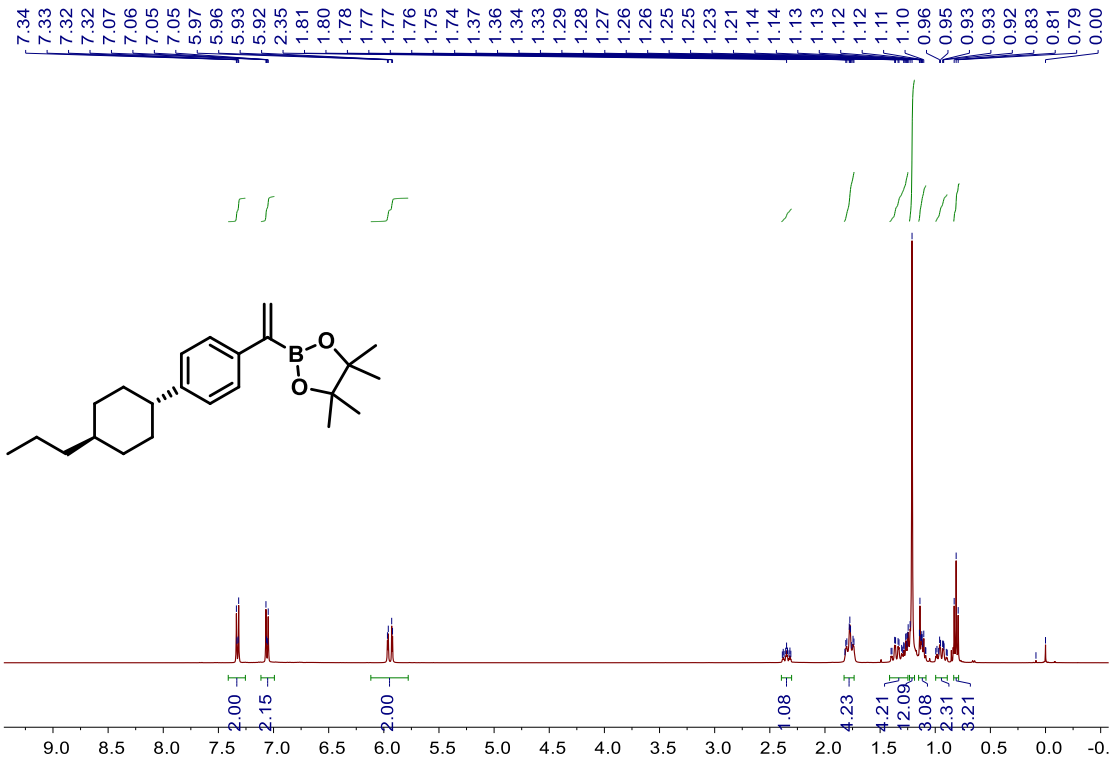
^{1}H NMR spectrum of **1w** (400 MHz, Chloroform-*d*)



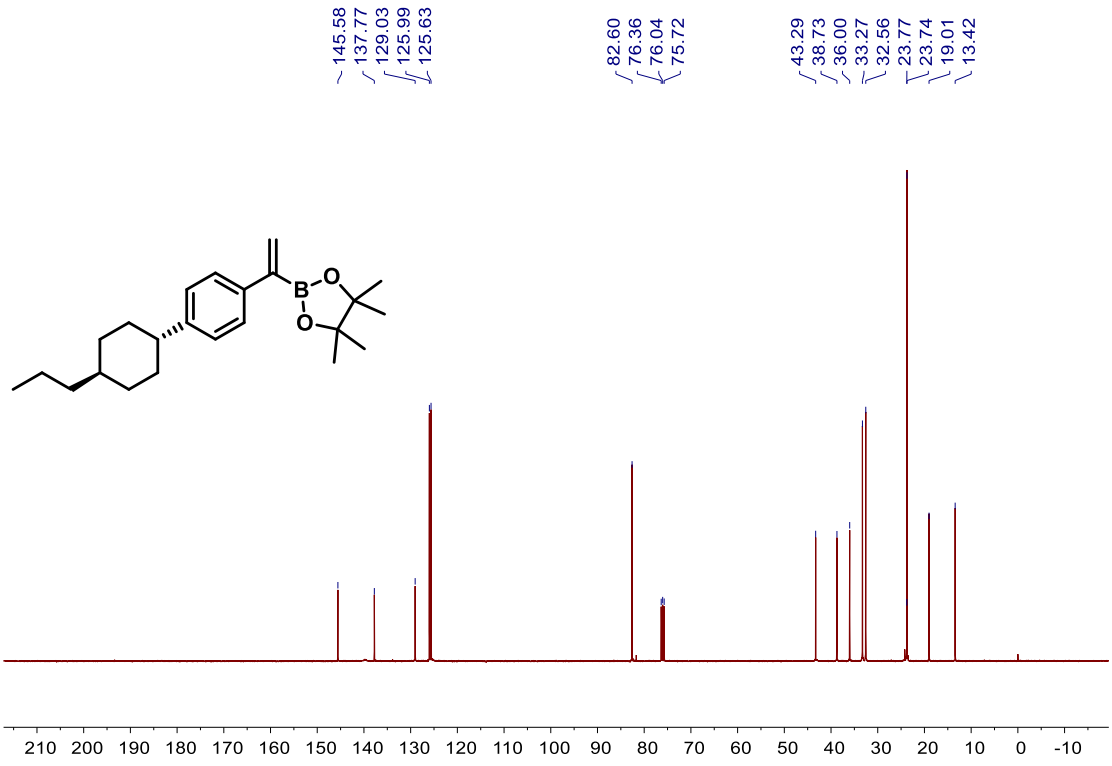
^{13}C NMR spectrum of **1w** (101 MHz, Chloroform-*d*)



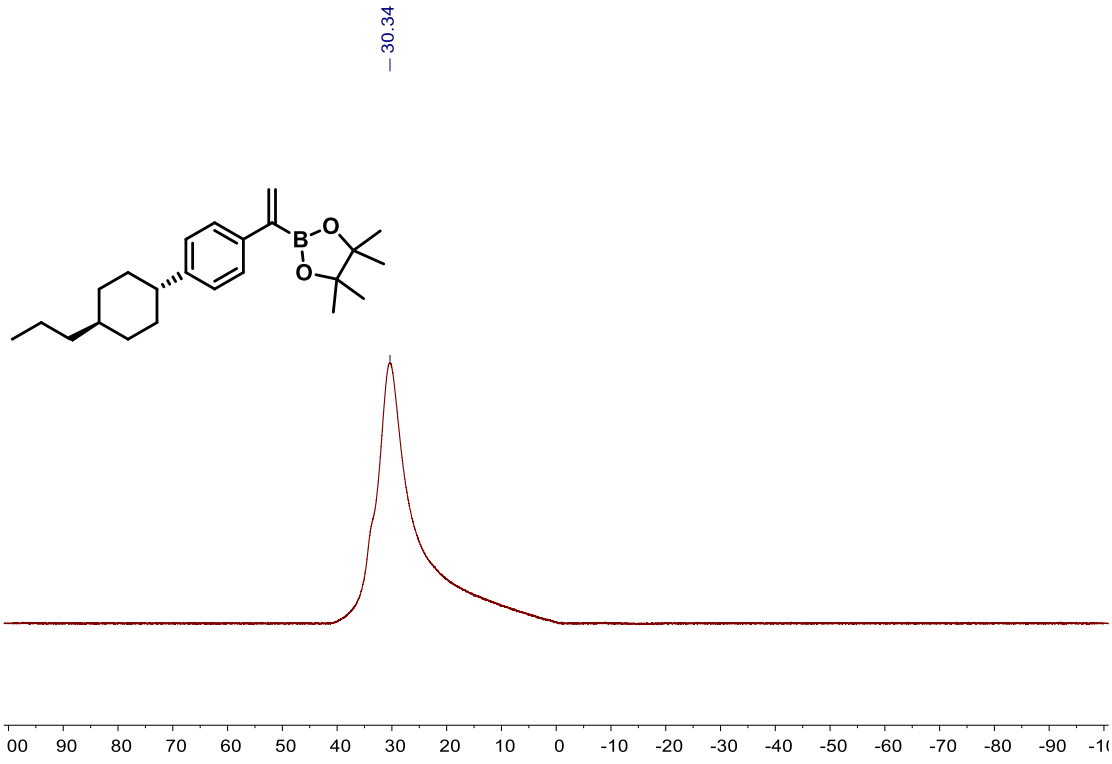
^{11}B NMR spectrum of **1w** (128 MHz Chloroform-*d*)



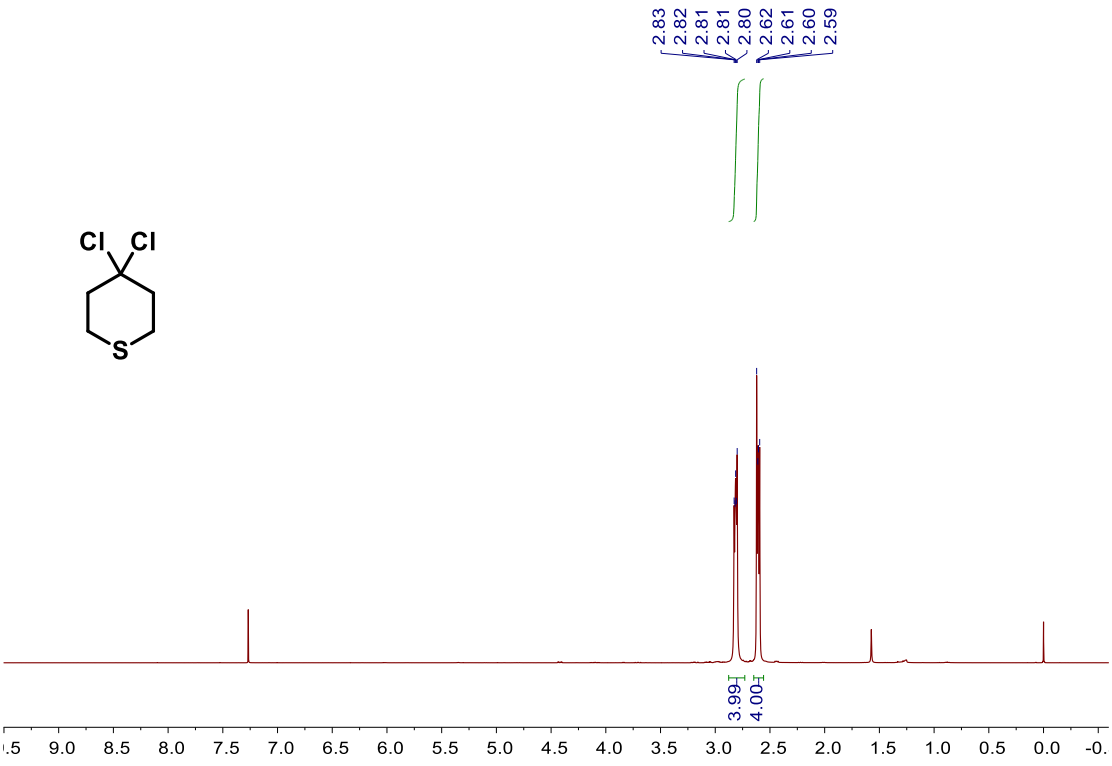
^{1}H NMR spectrum of **1x** (400 MHz, Chloroform-*d*)



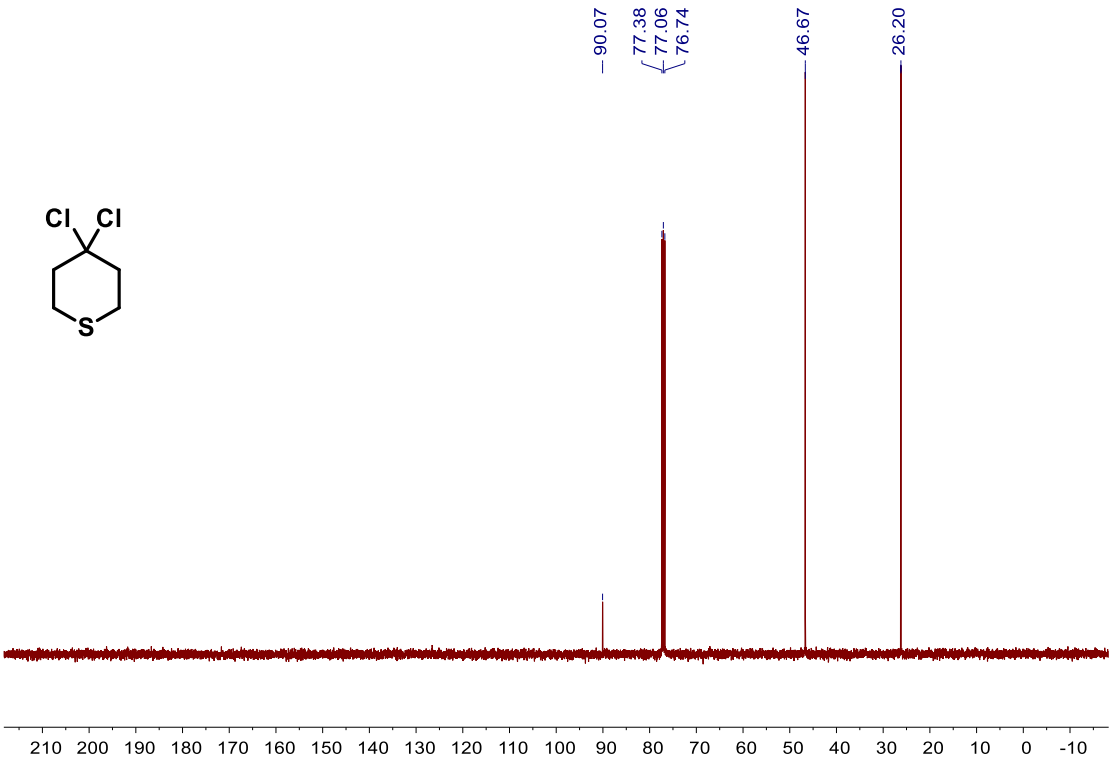
^{13}C NMR spectrum of **1x** (101 MHz, Chloroform-*d*)



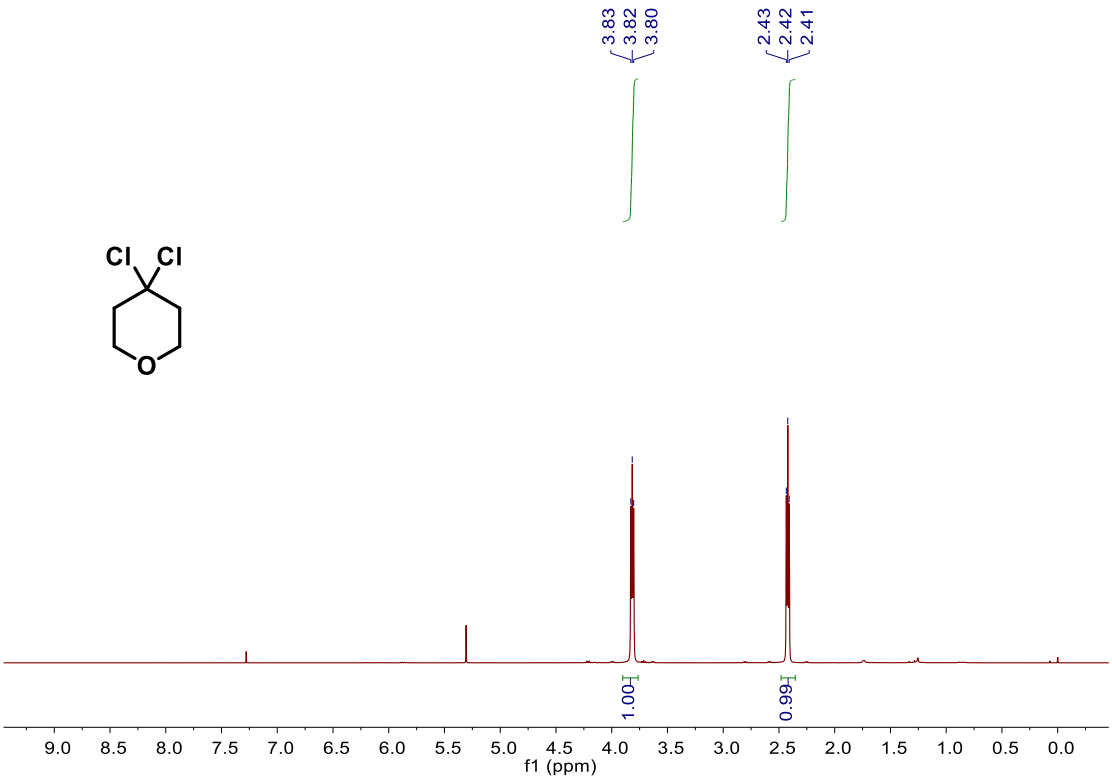
^{11}B NMR spectrum of **1x** (128 MHz Chloroform-*d*)



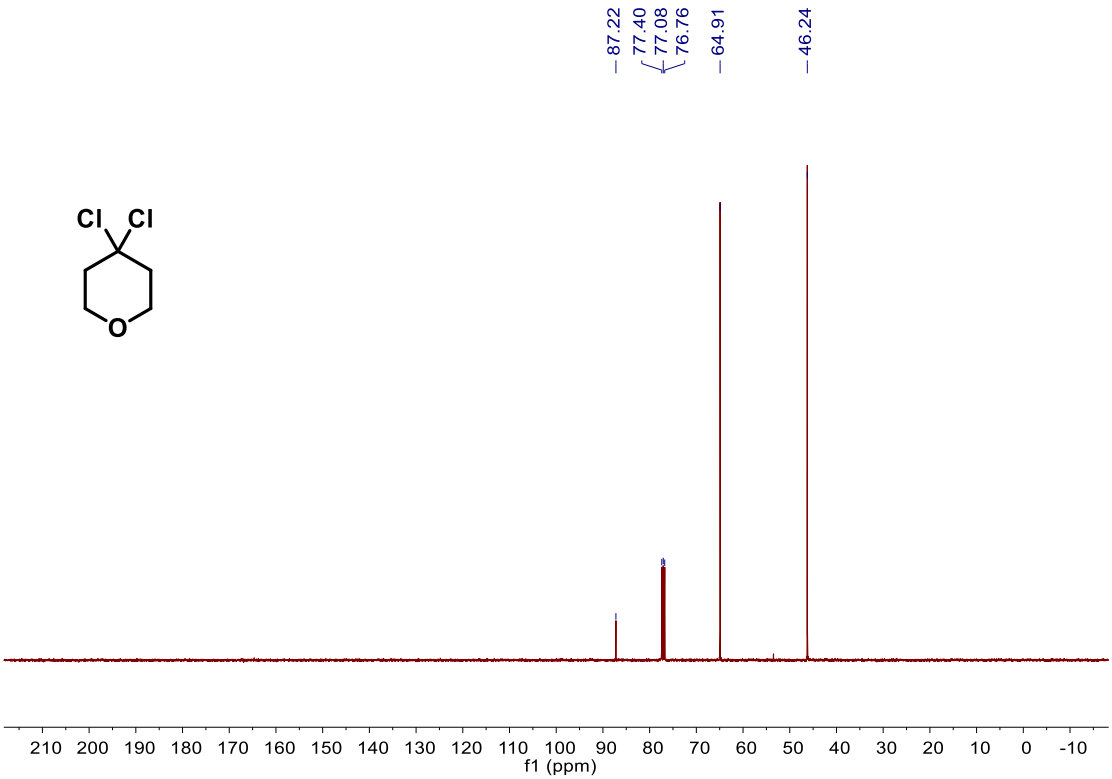
^{1}H NMR spectrum of **2h** (400 MHz, Chloroform-*d*)



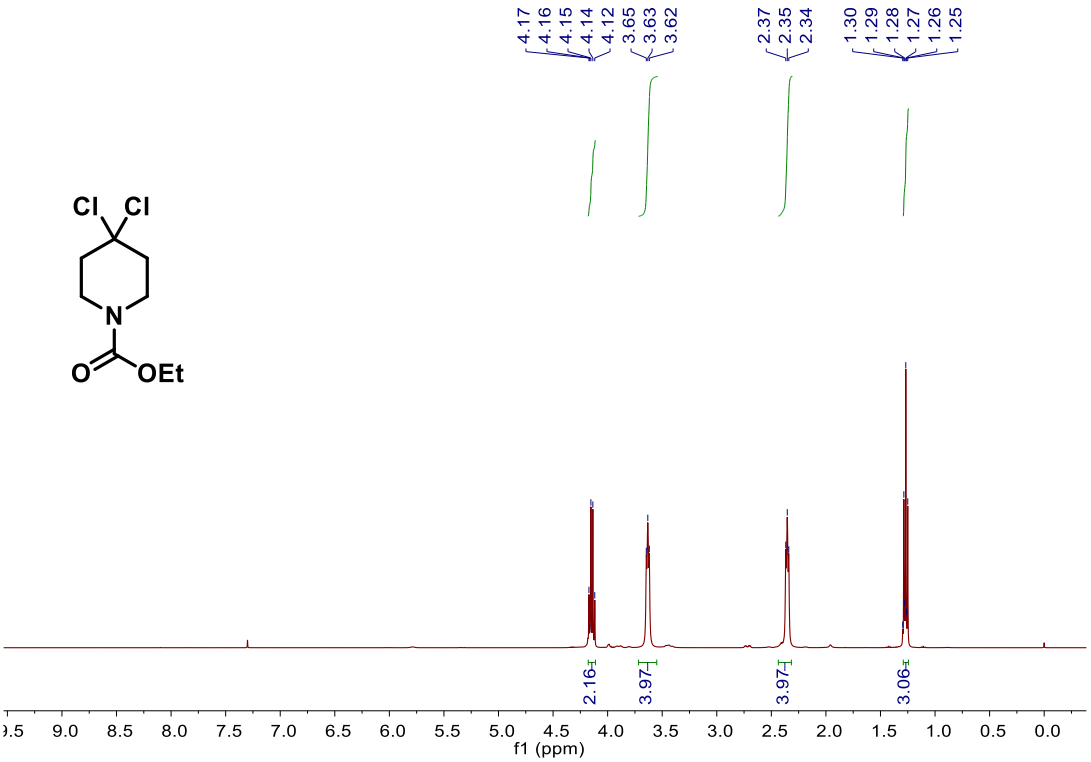
^{13}C NMR spectrum of **2h** (101 MHz, Chloroform-*d*)



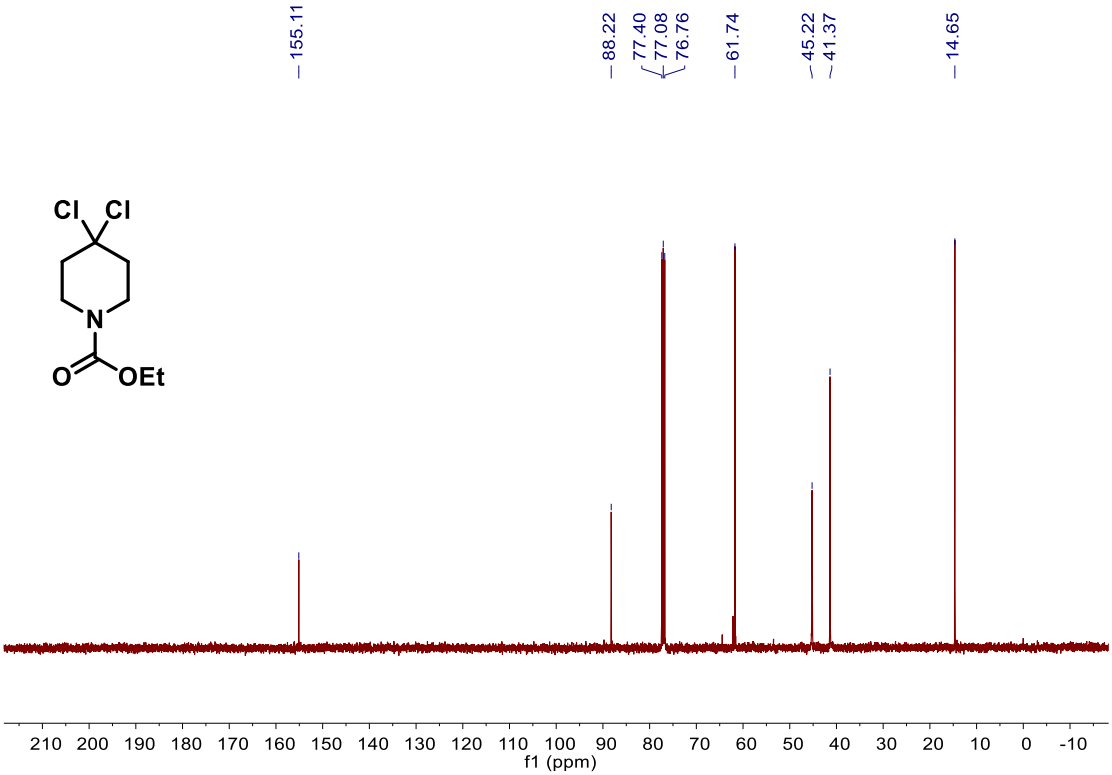
^{1}H NMR spectrum of **2i** (400 MHz, Chloroform-*d*)



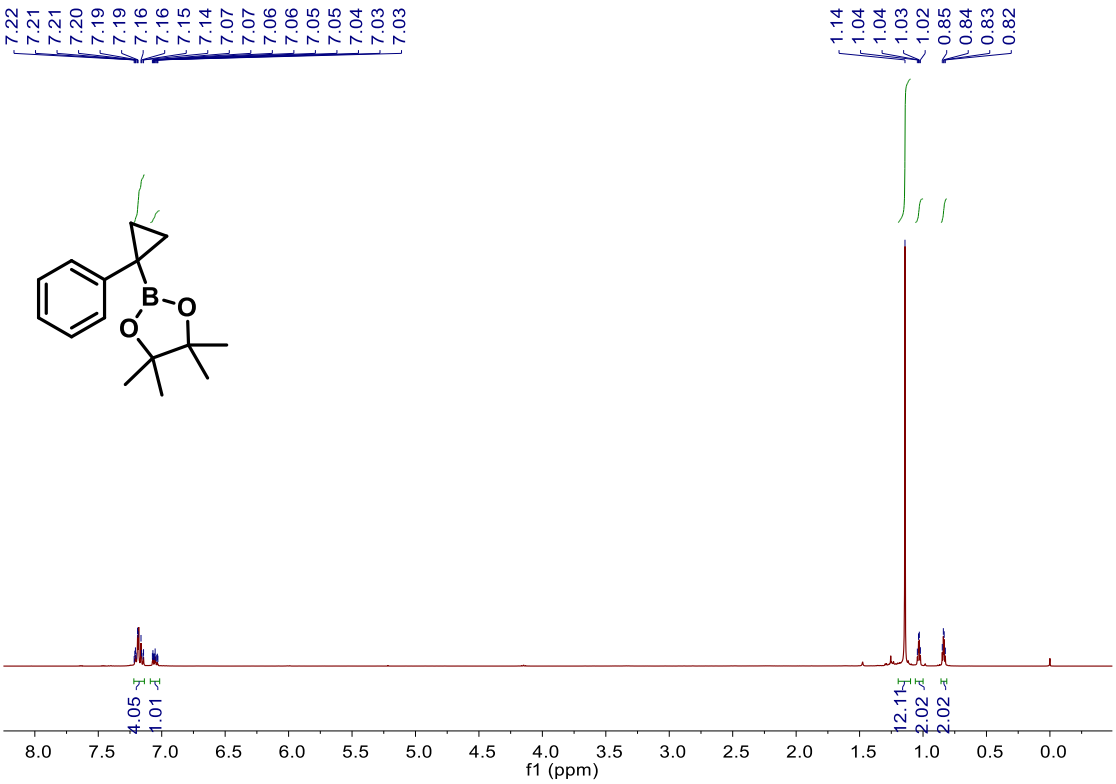
^{13}C NMR spectrum of **2i** (101 MHz, Chloroform-*d*)



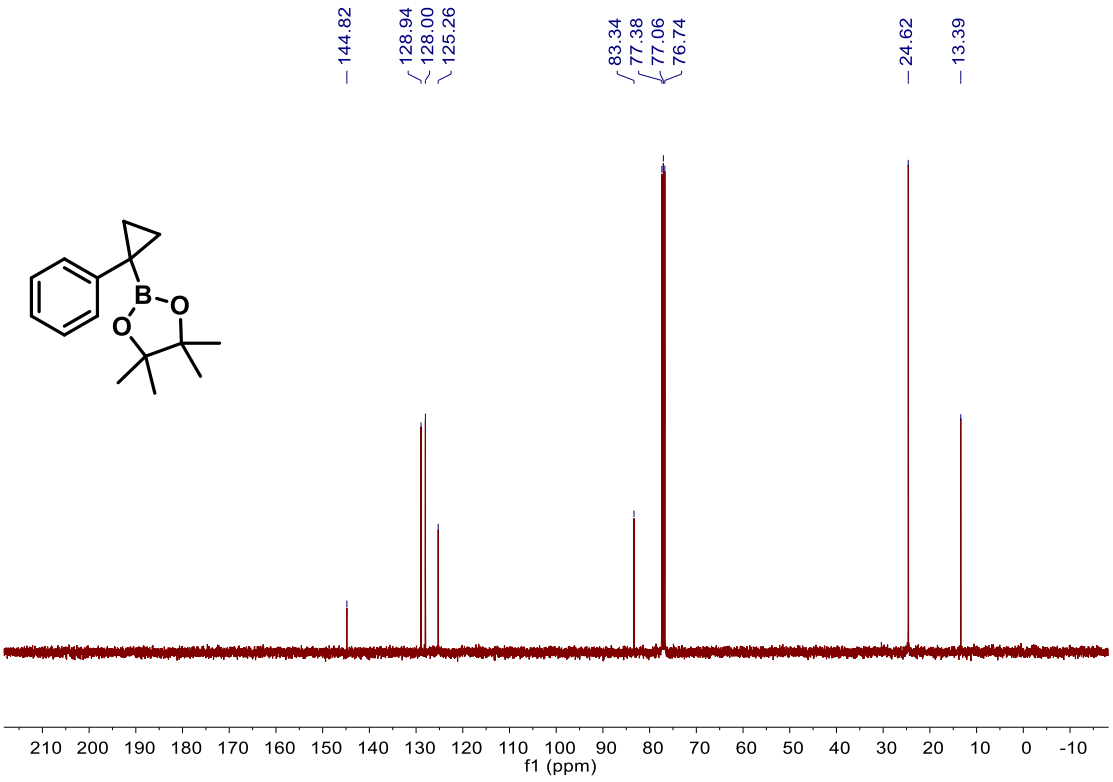
^{1}H NMR spectrum of **2j** (400 MHz, Chloroform-*d*)



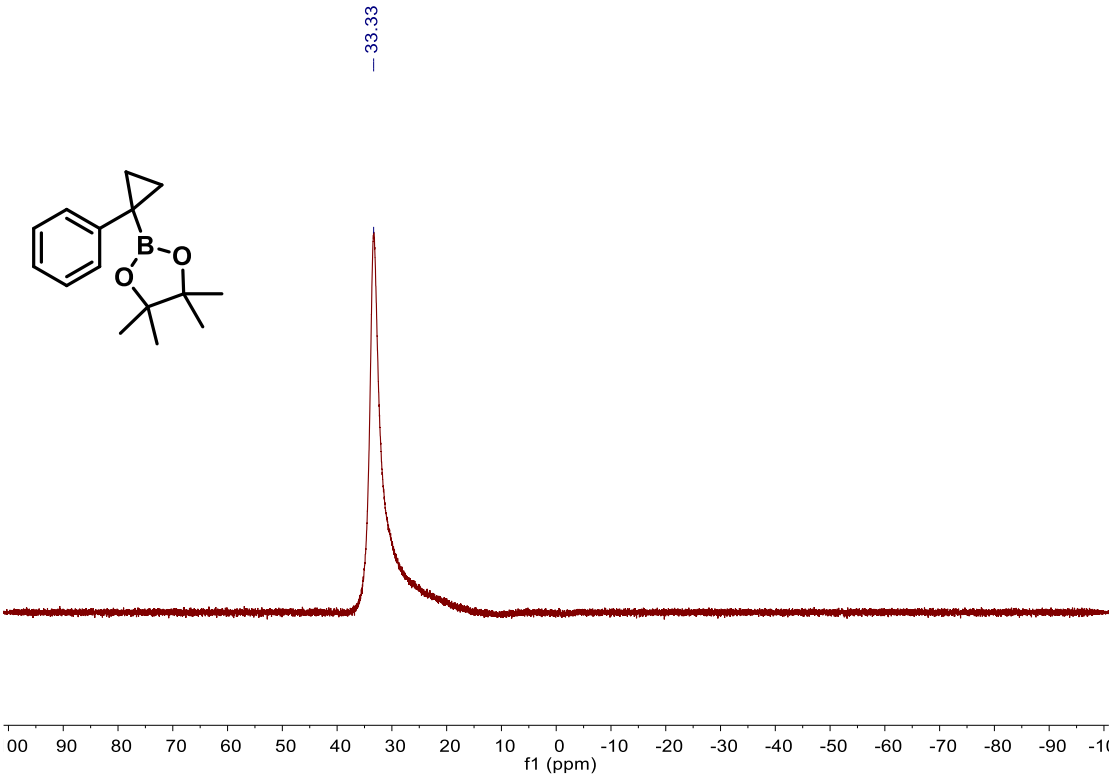
^{13}C NMR spectrum of **2j** (101 MHz, Chloroform-*d*)



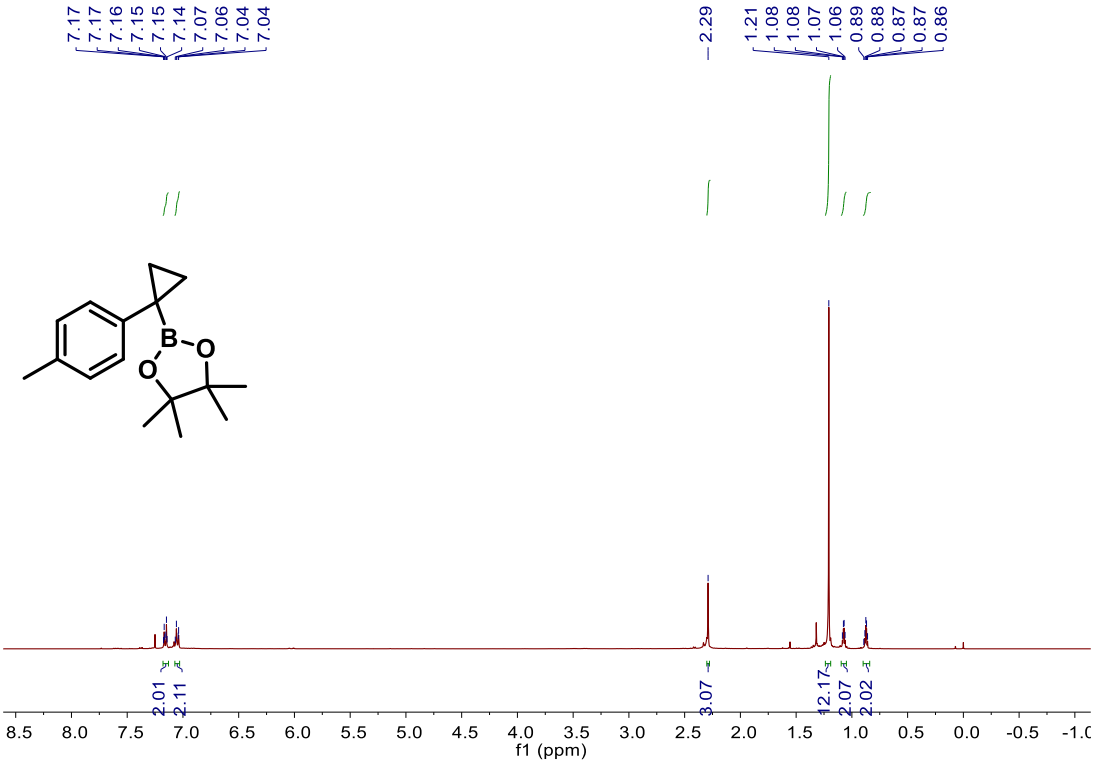
^{1}H NMR spectrum of **3a** (400 MHz, Chloroform-*d*)



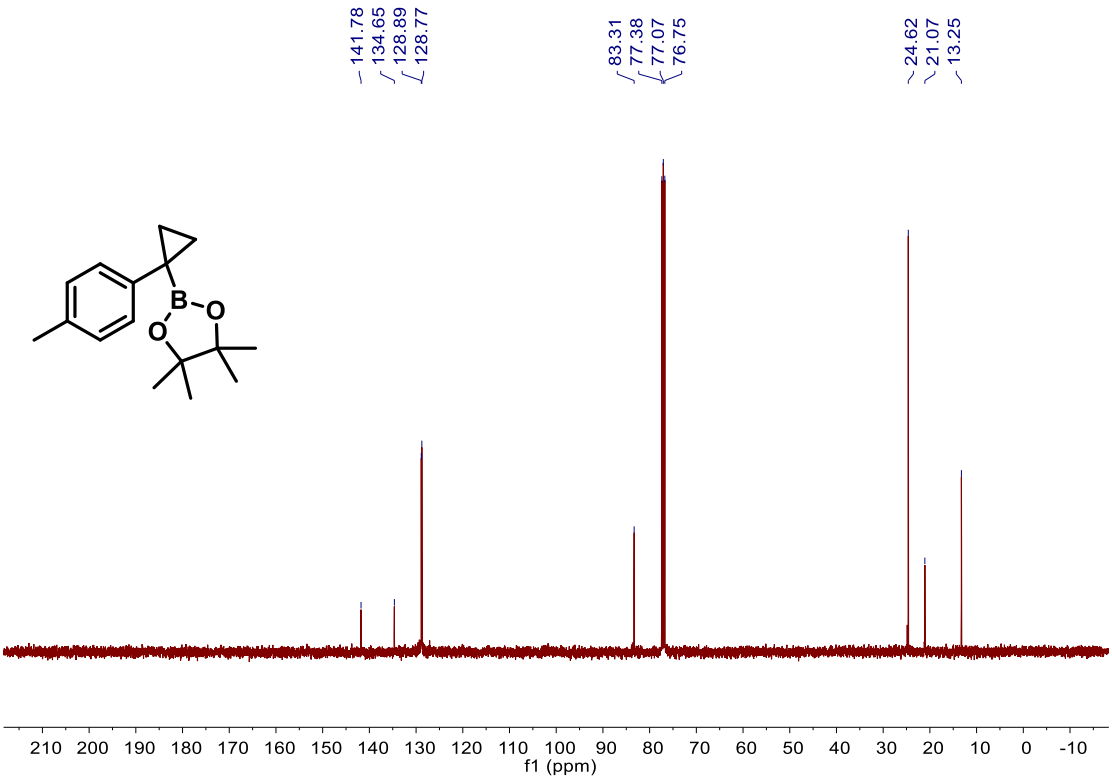
^{13}C NMR spectrum of **3a** (101 MHz, Chloroform-*d*)



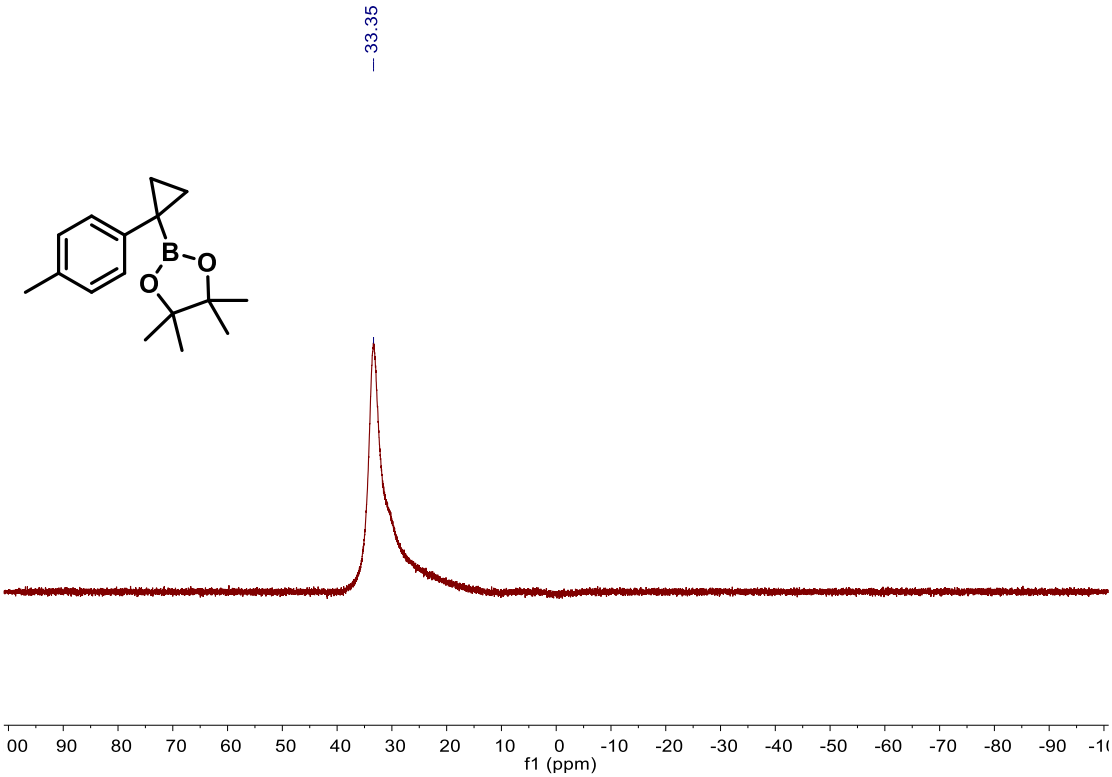
^{11}B NMR spectrum of **3a** (128 MHz Chloroform-*d*)



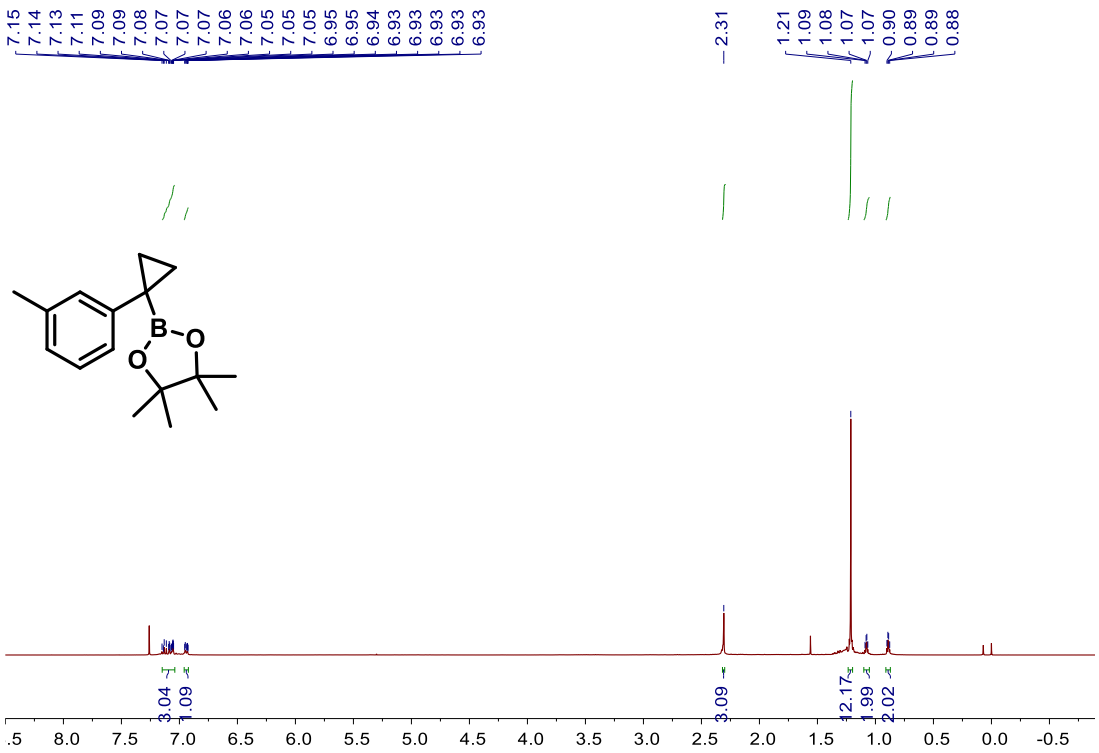
^{1}H NMR spectrum of **3b** (400 MHz, Chloroform-*d*)



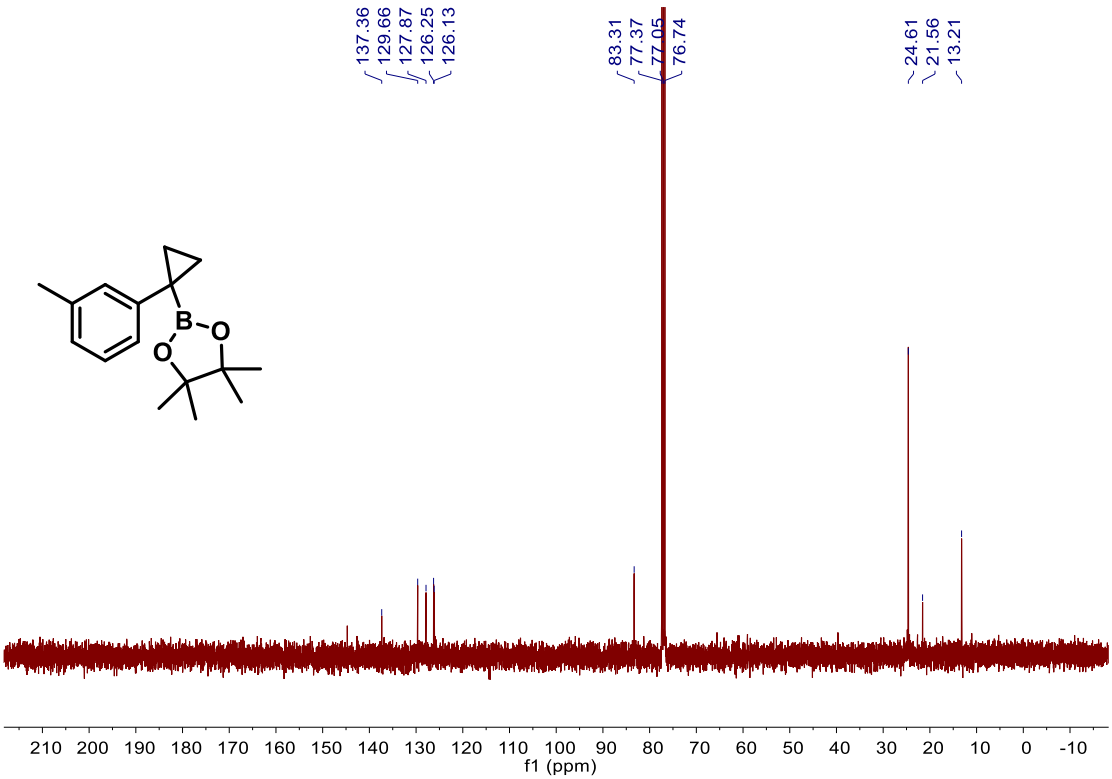
^{13}C NMR spectrum of **3b** (101 MHz, Chloroform-*d*)



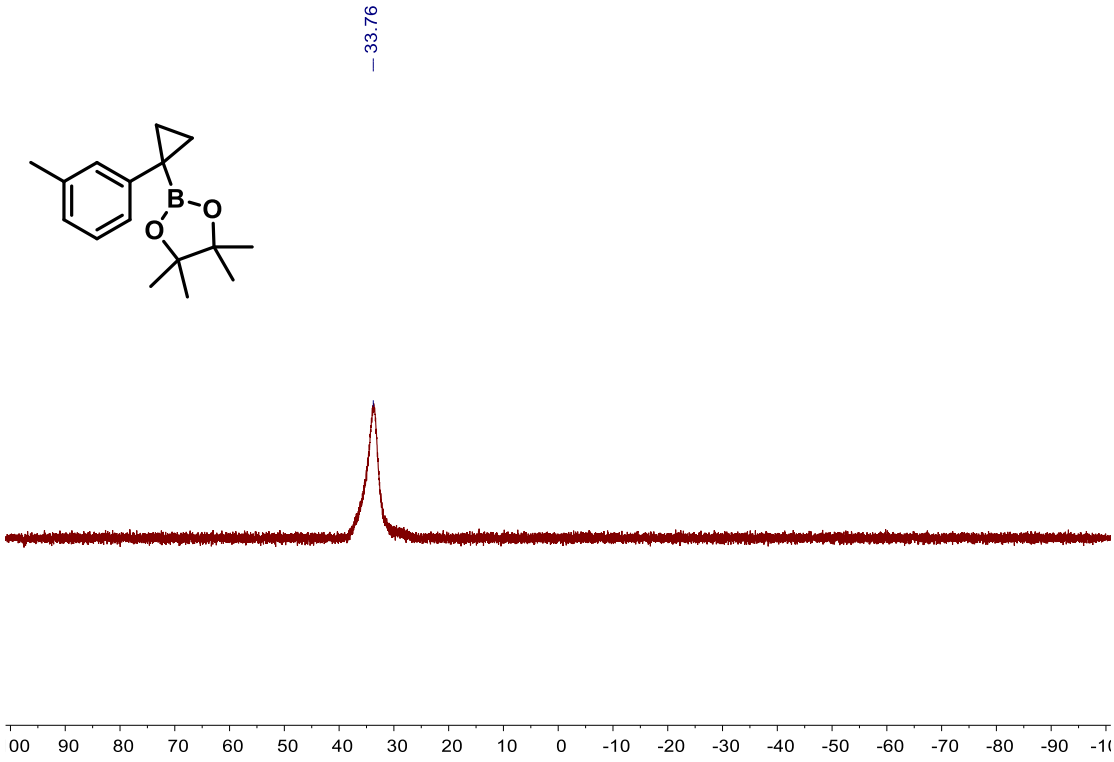
^{11}B NMR spectrum of **3b** (128 MHz Chloroform-*d*)



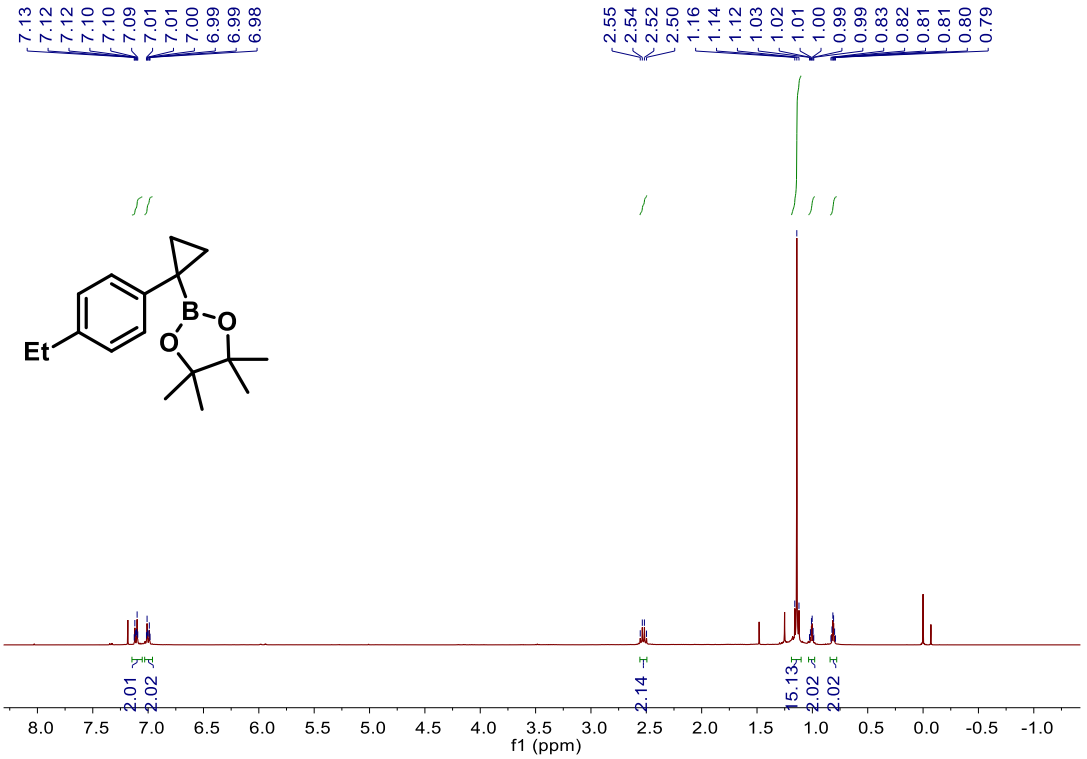
^{1}H NMR spectrum of **3c** (400 MHz, Chloroform-*d*)



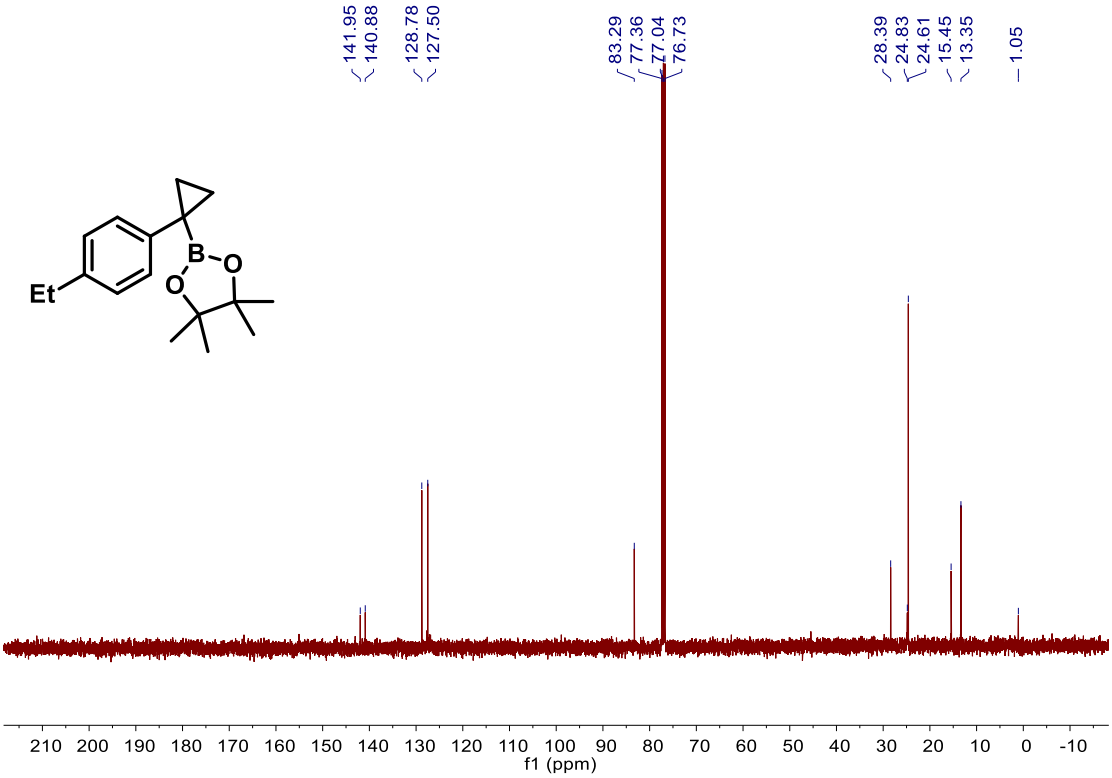
^{13}C NMR spectrum of **3c** (101 MHz, Chloroform-*d*)



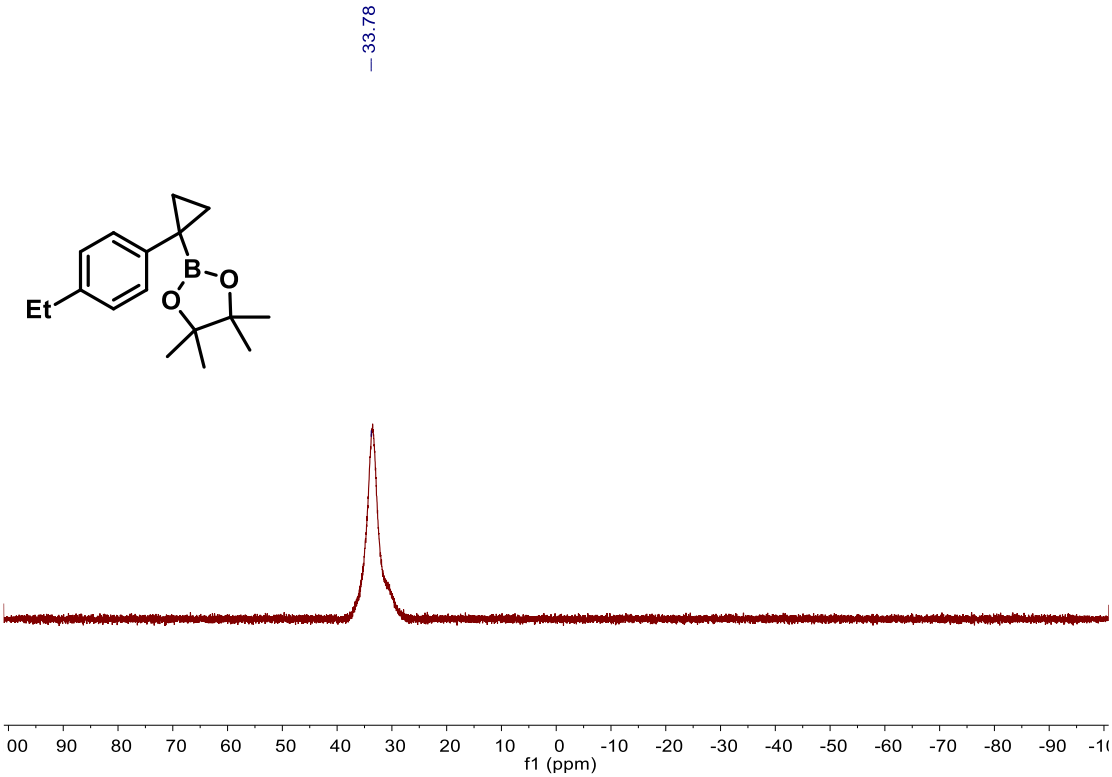
^{11}B NMR spectrum of **3c** (128 MHz Chloroform-*d*)



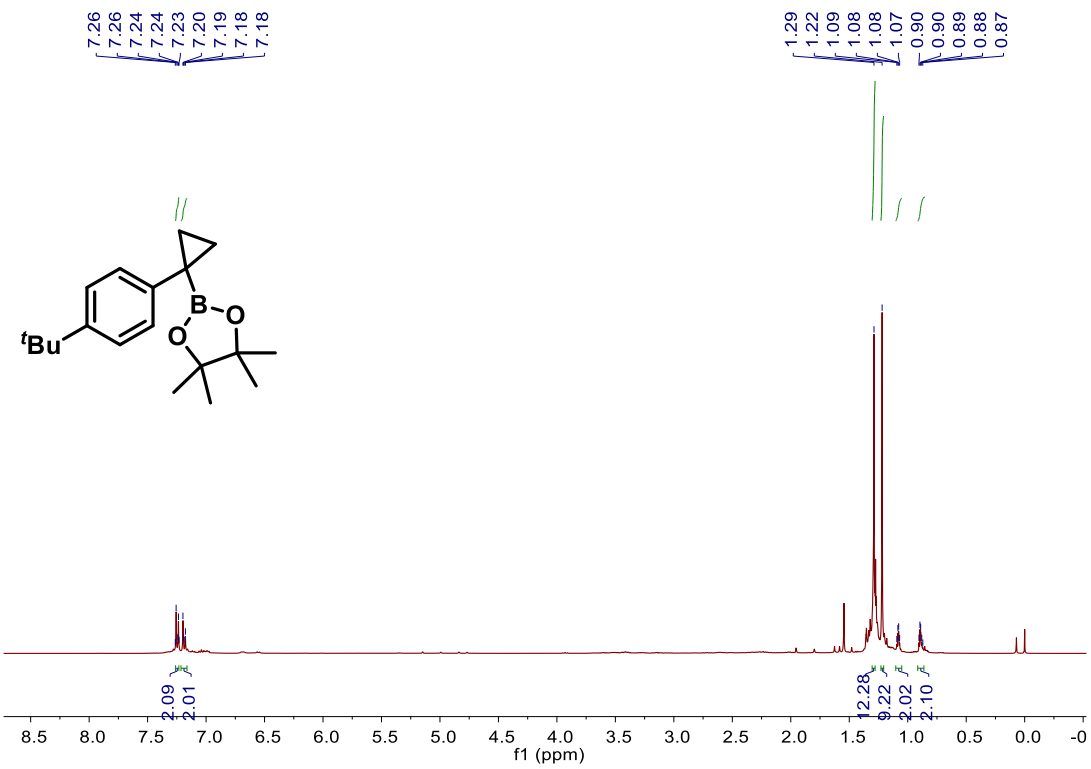
^{1}H NMR spectrum of **3d** (400 MHz, Chloroform-*d*)



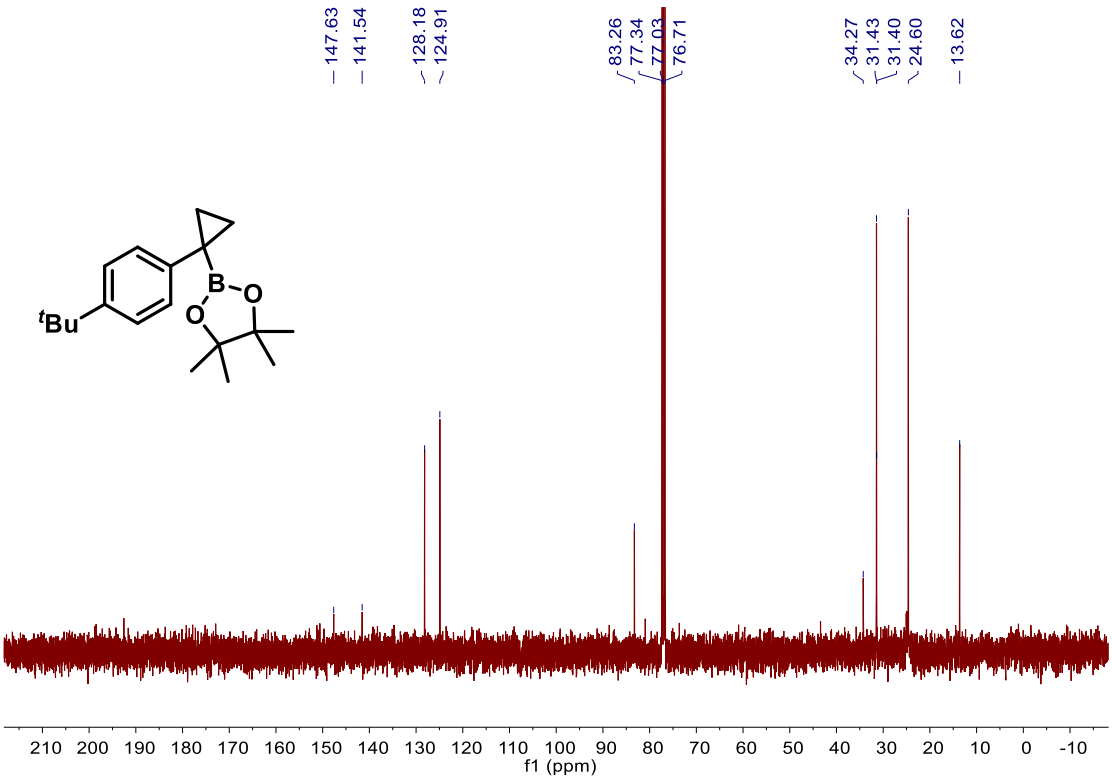
^{13}C NMR spectrum of **3d** (101 MHz, Chloroform-*d*)



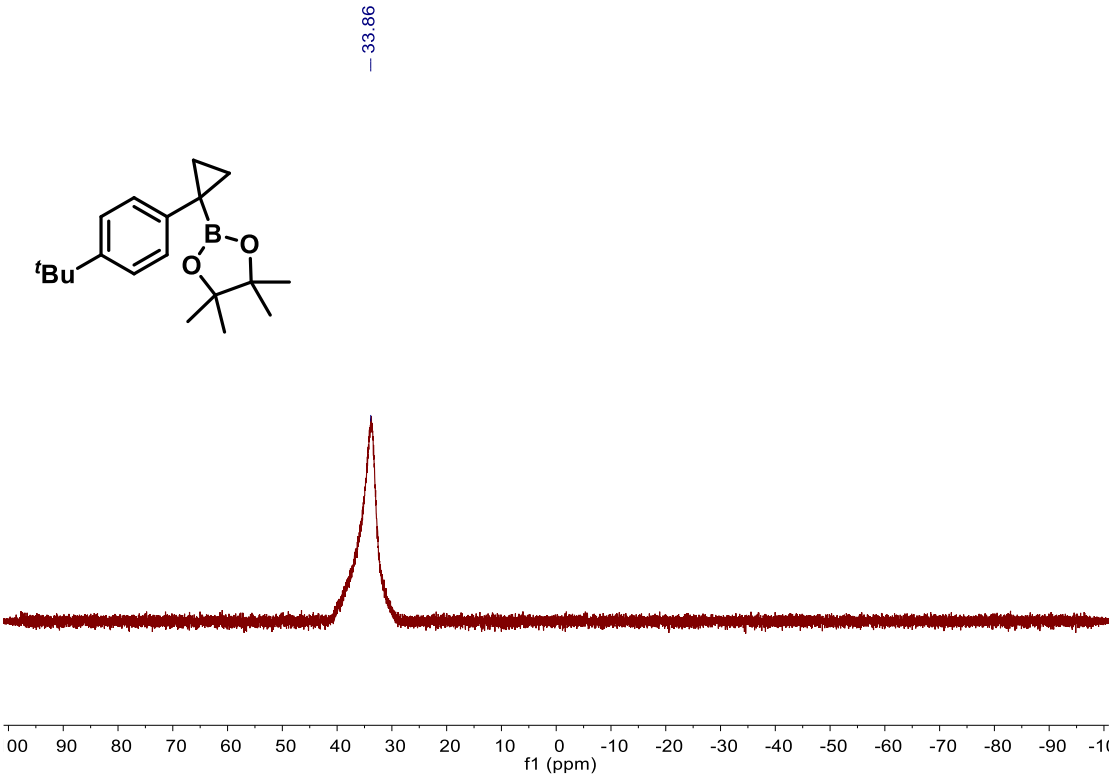
^{11}B NMR spectrum of **3d** (128 MHz Chloroform-*d*)



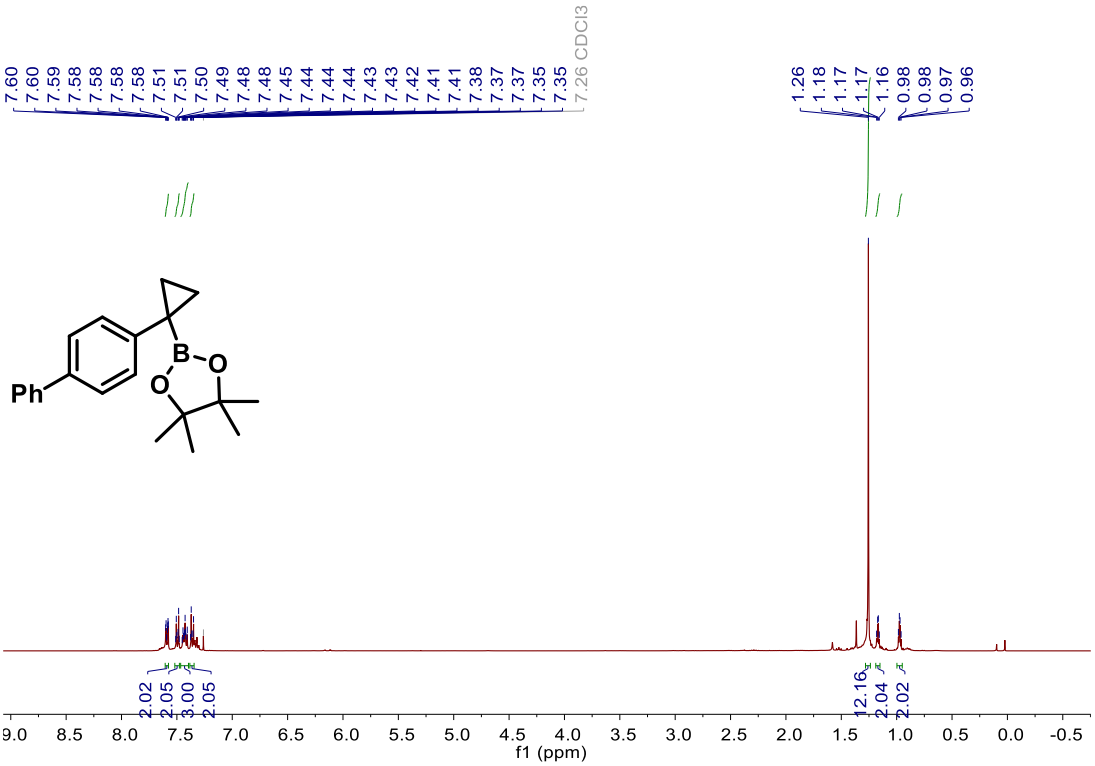
^{1}H NMR spectrum of **3e** (400 MHz, Chloroform-*d*)



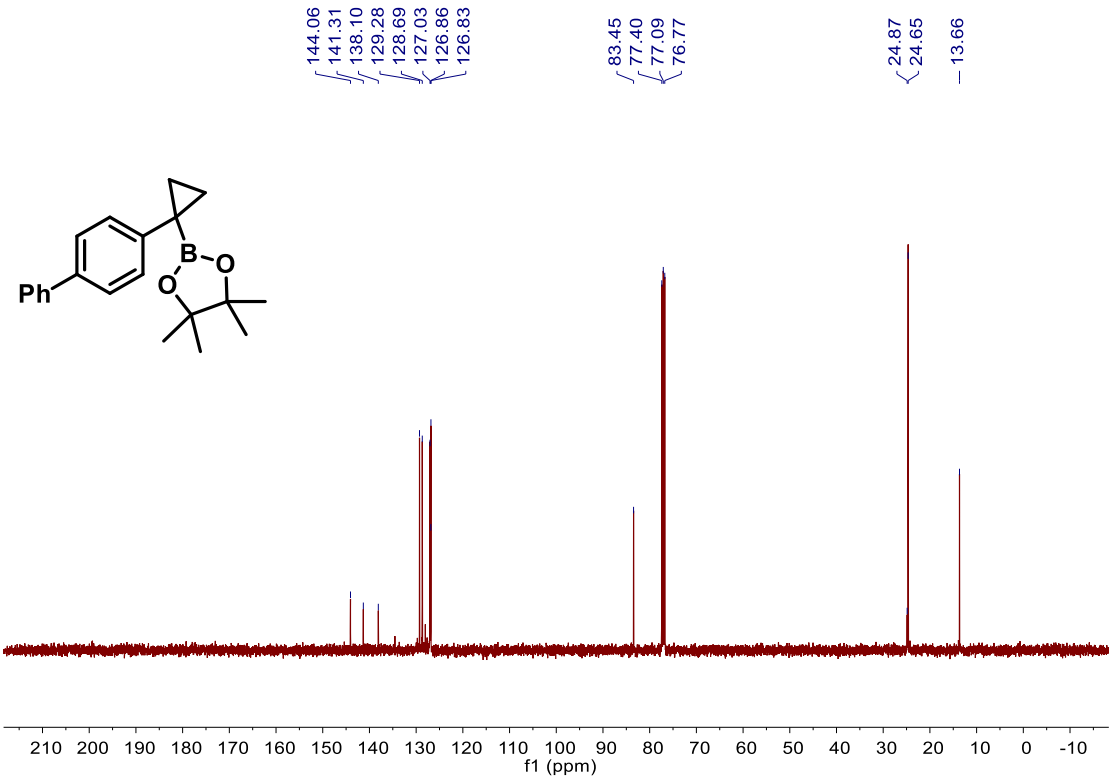
^{13}C NMR spectrum of **3e** (101 MHz, Chloroform-*d*)



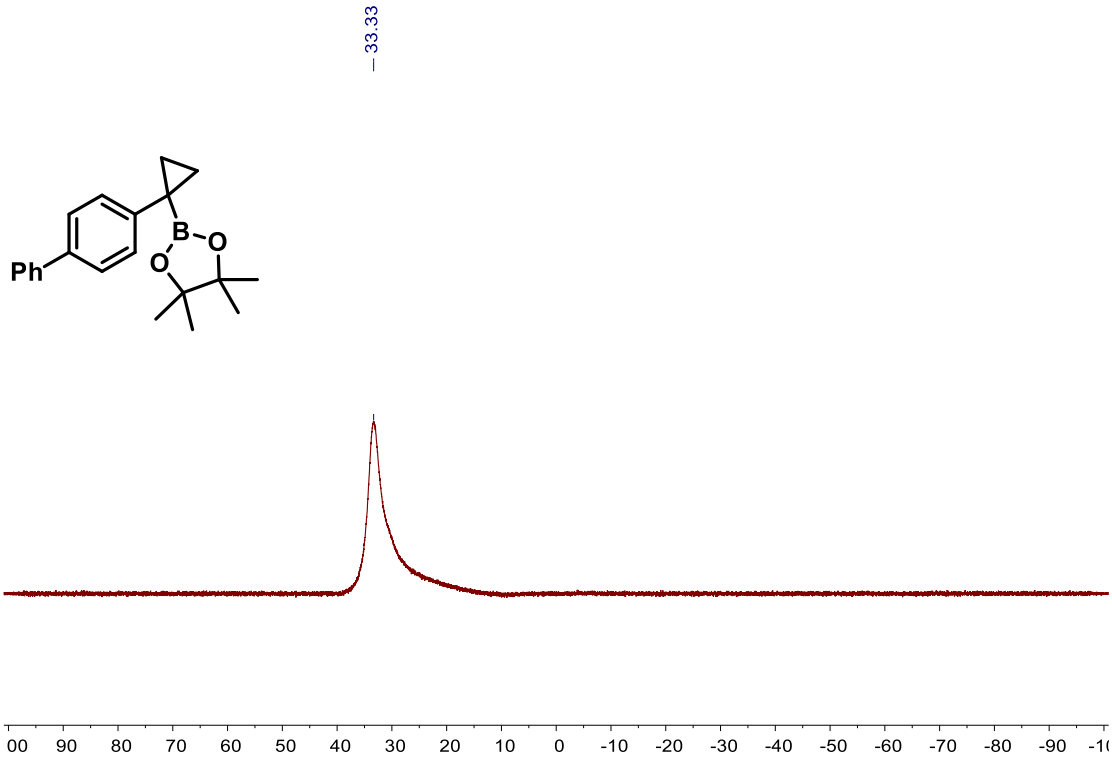
^{11}B NMR spectrum of **3e** (128 MHz Chloroform-*d*)



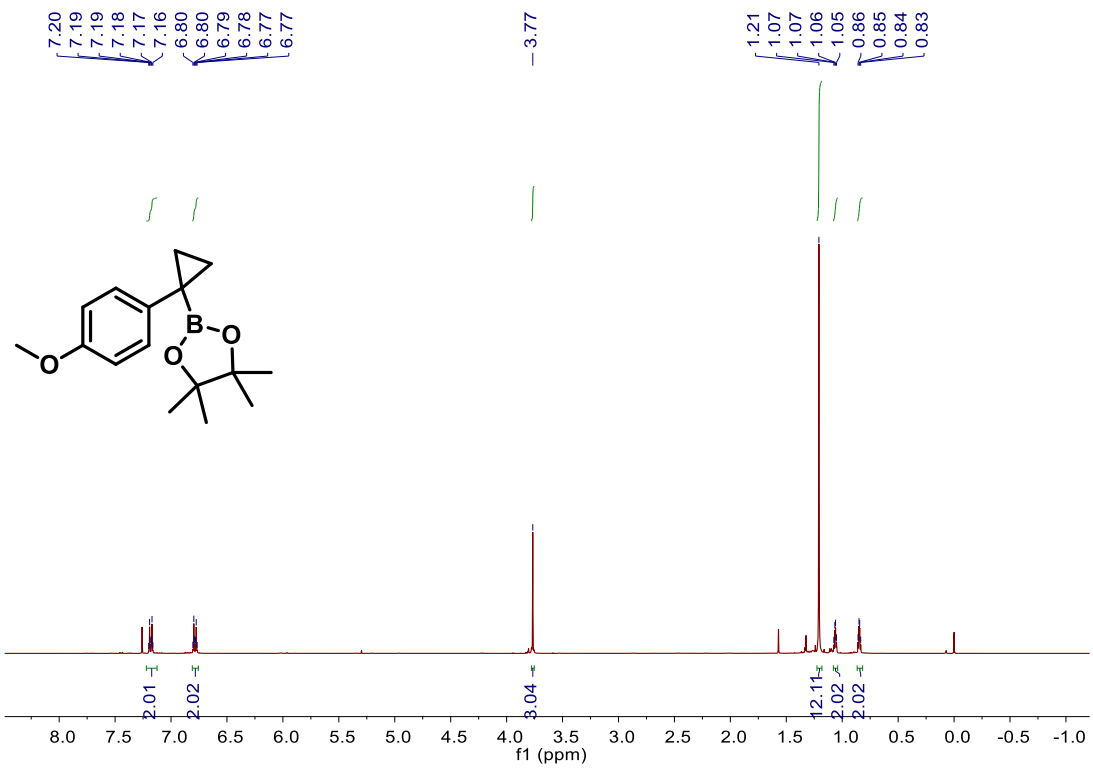
^{1}H NMR spectrum of **3f** (400 MHz, Chloroform-*d*)



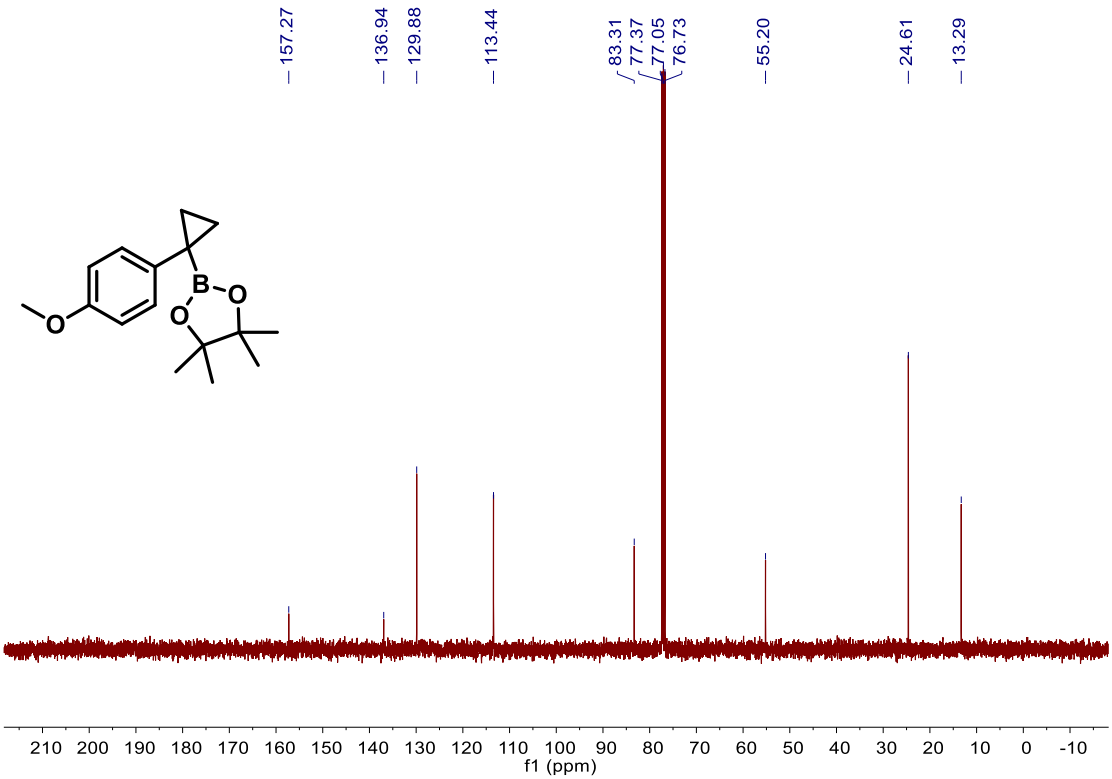
^{13}C NMR spectrum of **3f** (101 MHz, Chloroform-*d*)



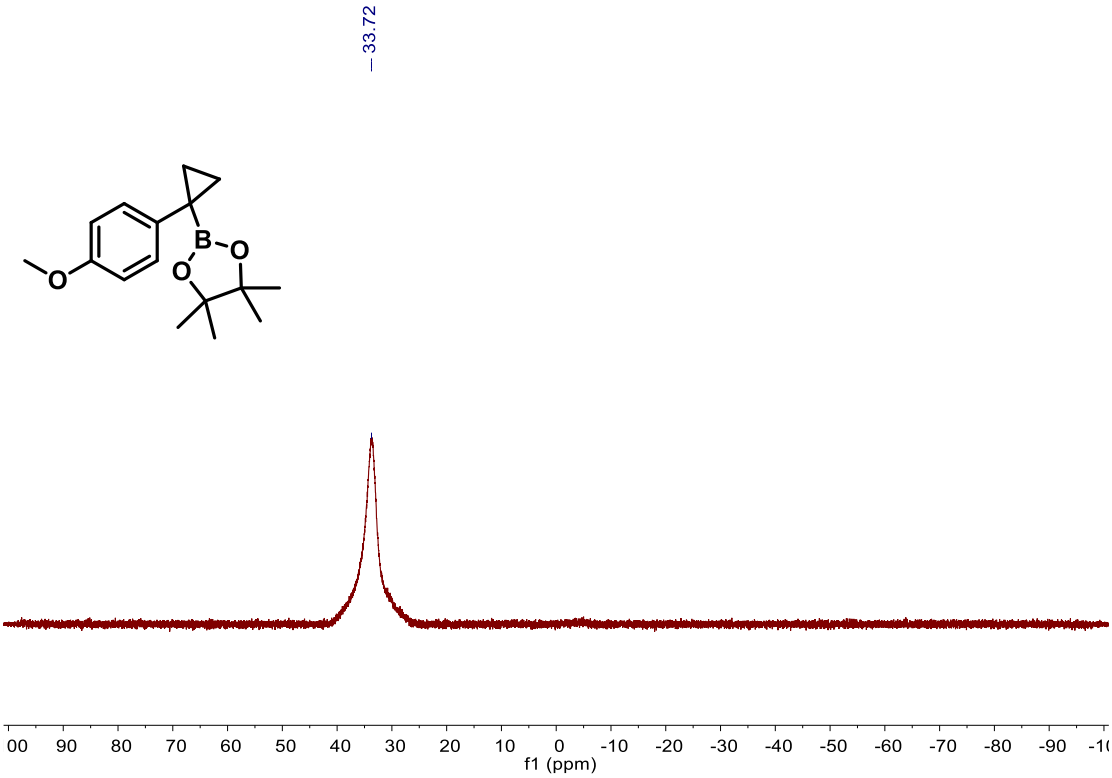
^{11}B NMR spectrum of **3f** (128 MHz Chloroform-*d*)



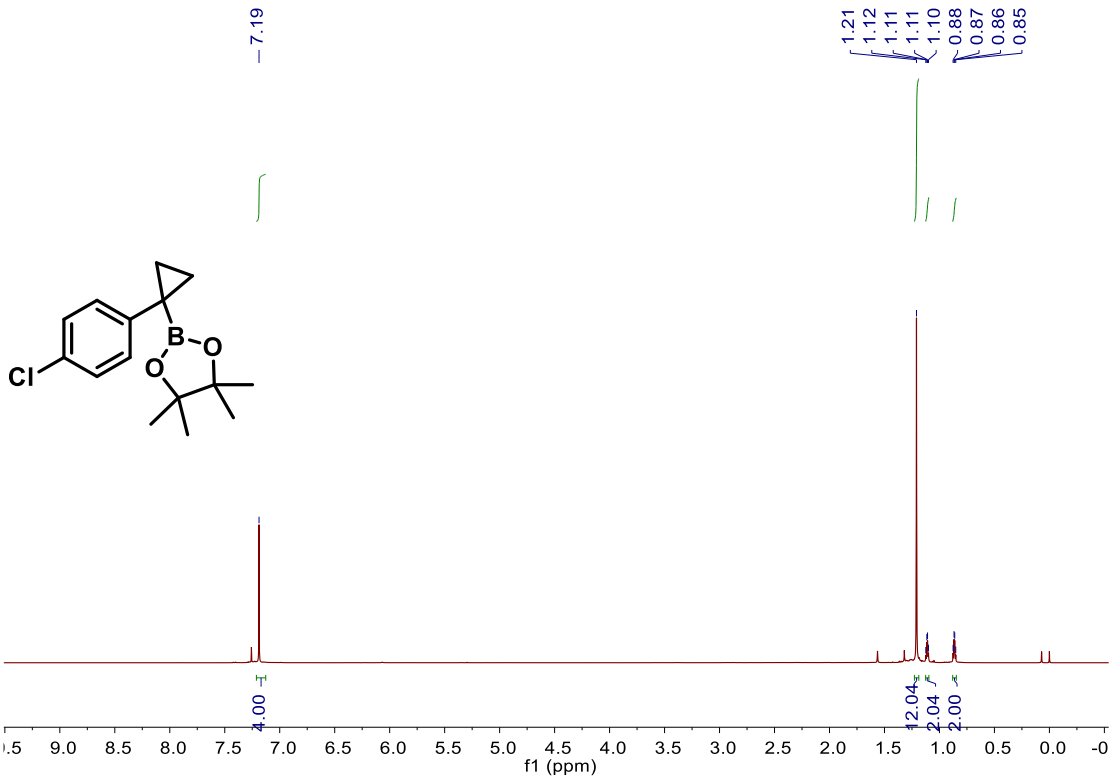
^{1}H NMR spectrum of **3g** (400 MHz, Chloroform-*d*)



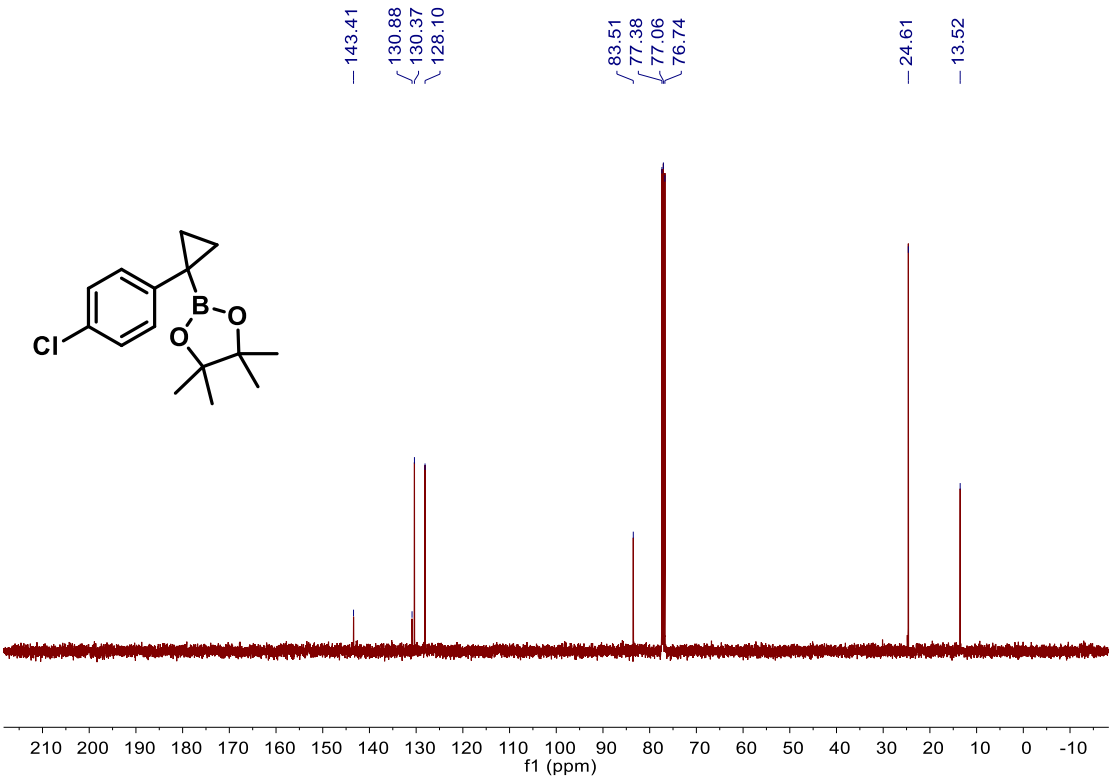
^{13}C NMR spectrum of **3g** (101 MHz, Chloroform-*d*)



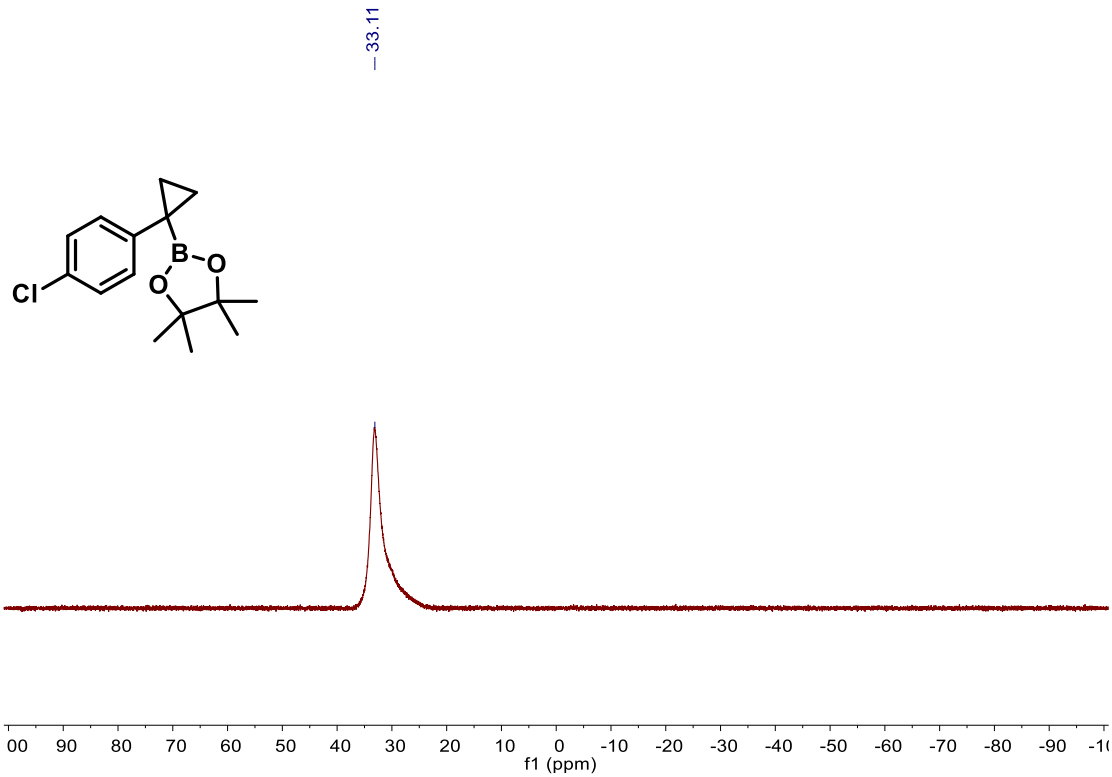
^{11}B NMR spectrum of **3g** (128 MHz Chloroform-*d*)



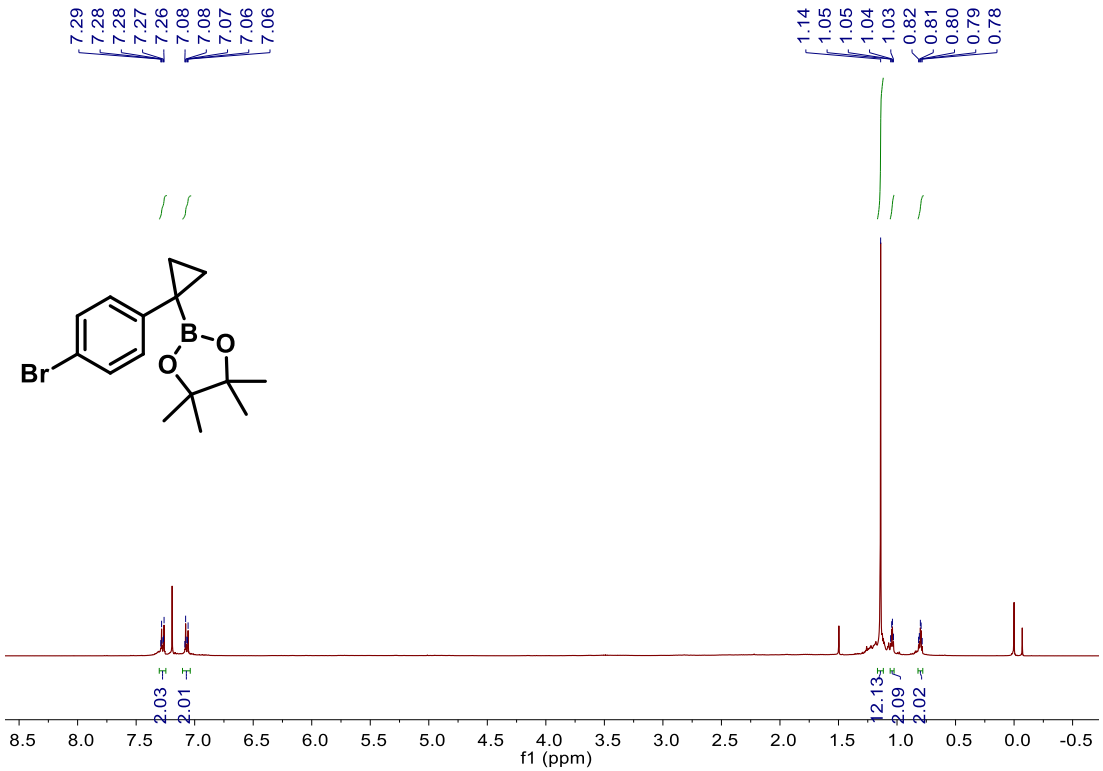
^{1}H NMR spectrum of **3h** (400 MHz, Chloroform-*d*)



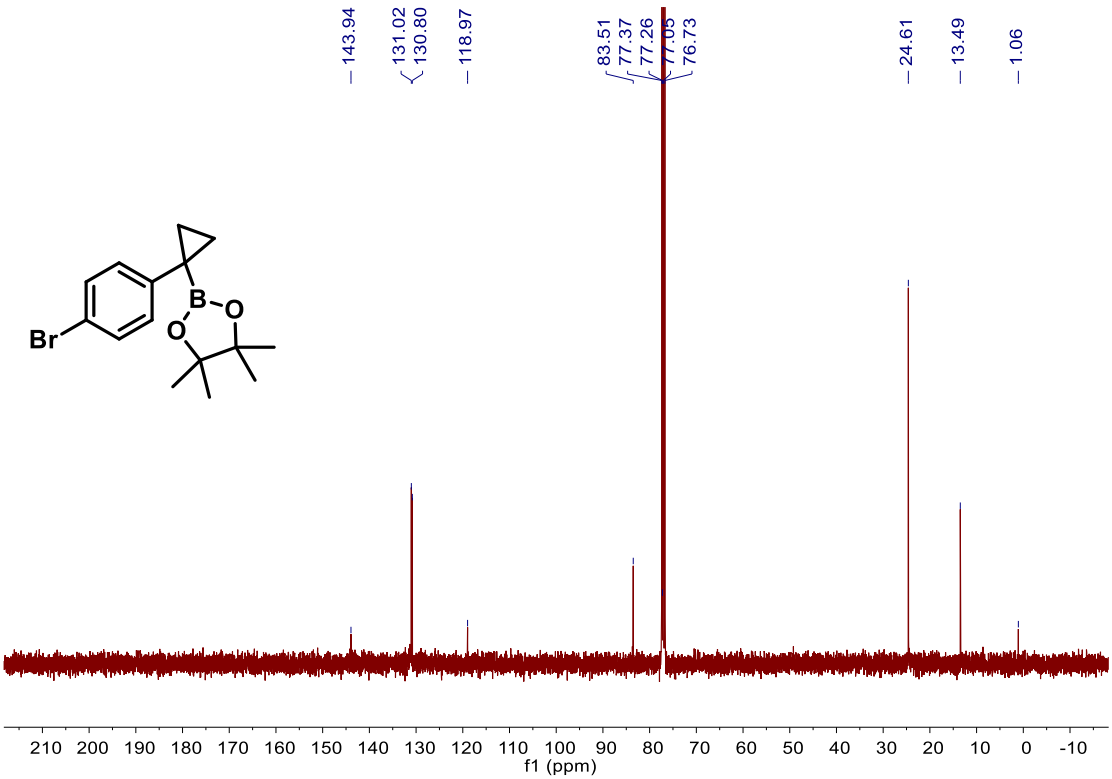
^{13}C NMR spectrum of **3h** (101 MHz, Chloroform-*d*)



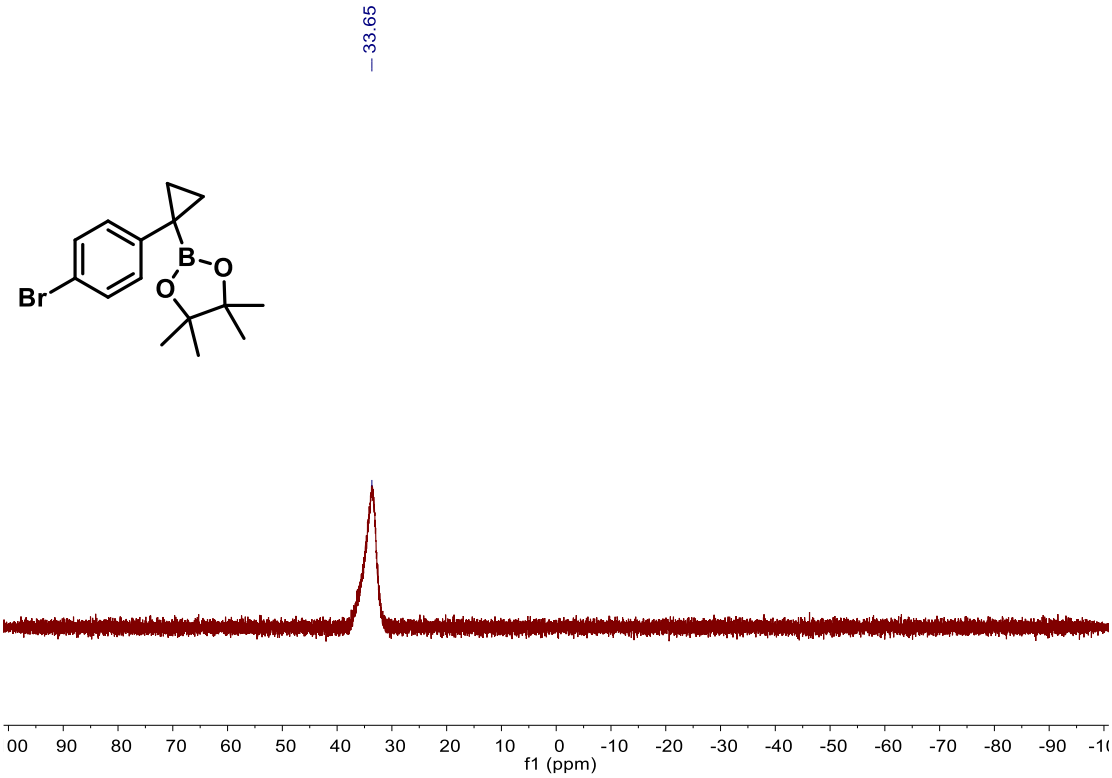
^{11}B NMR spectrum of **3h** (128 MHz Chloroform-*d*)



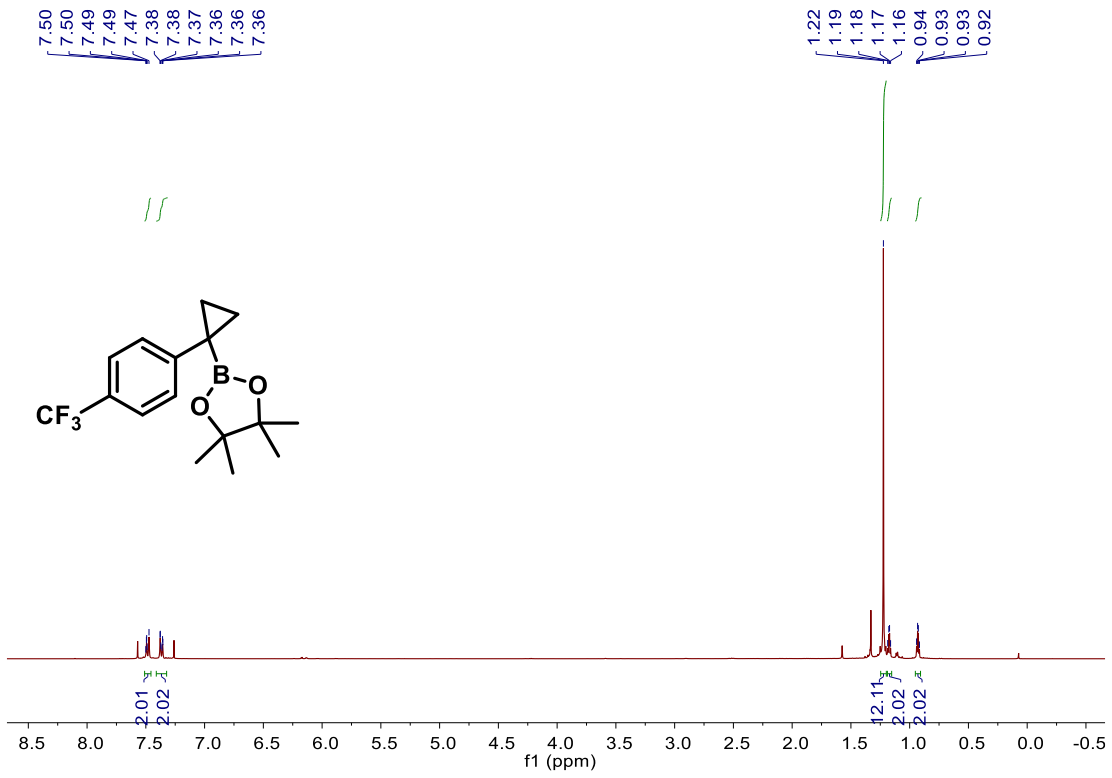
^{1}H NMR spectrum of **3i** (400 MHz, Chloroform-*d*)



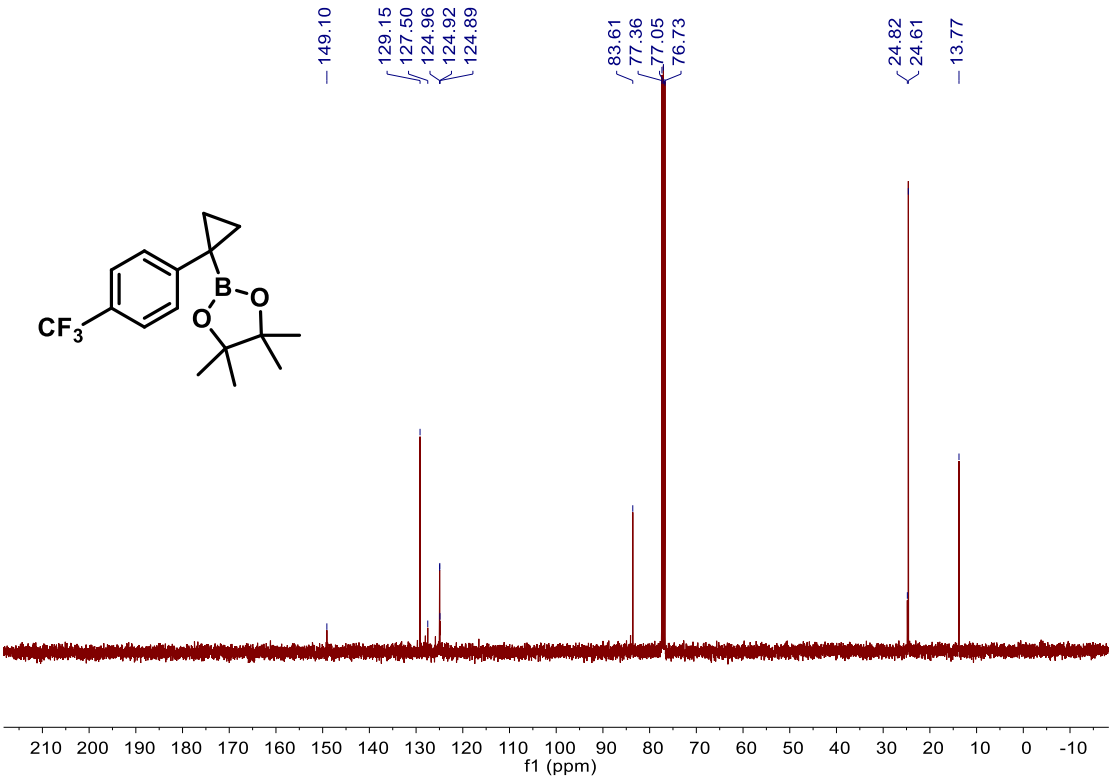
^{13}C NMR spectrum of **3i** (101 MHz, Chloroform-*d*)



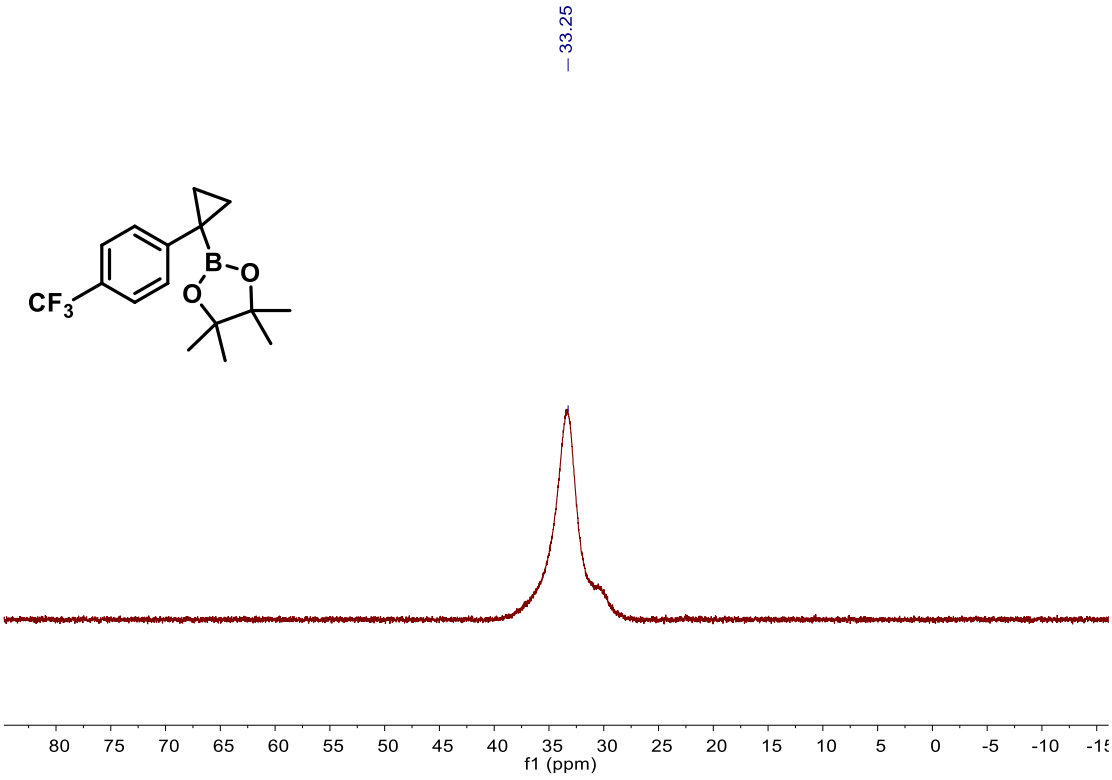
^{11}B NMR spectrum of **3i** (128 MHz Chloroform-*d*)



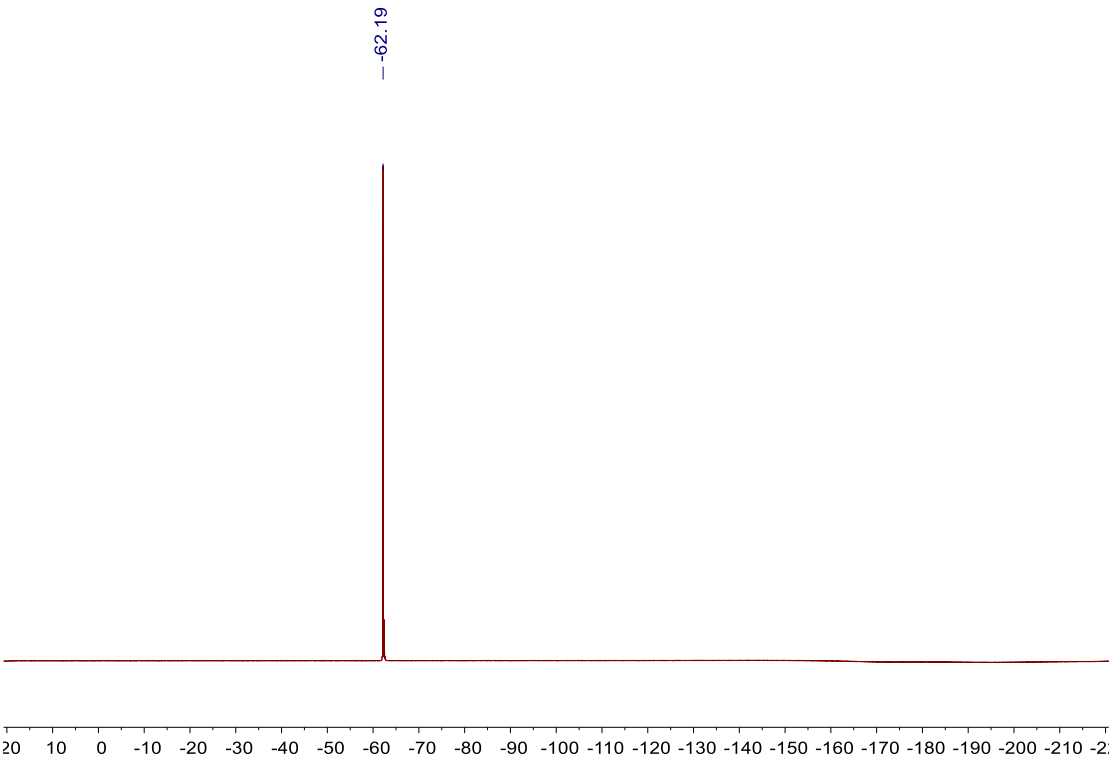
^{1}H NMR spectrum of **3j** (400 MHz, Chloroform-*d*)



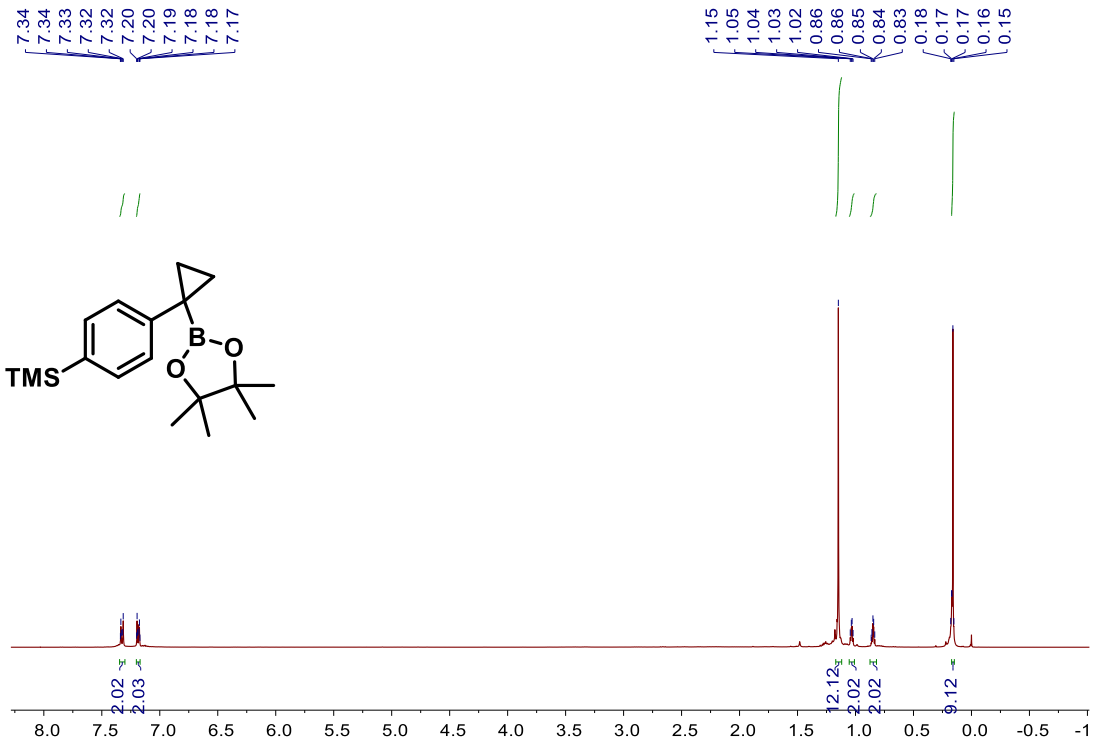
^{13}C NMR spectrum of **3j** (101 MHz, Chloroform-*d*)



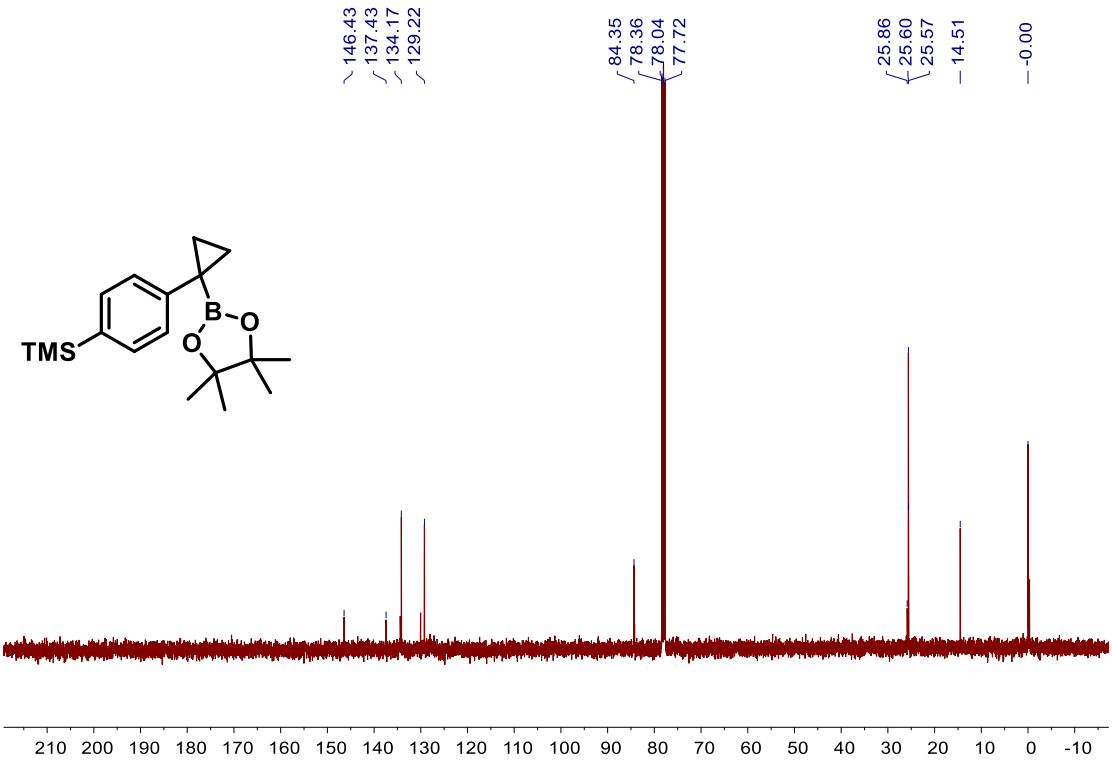
^{11}B NMR spectrum of **3j** (128 MHz Chloroform-*d*)



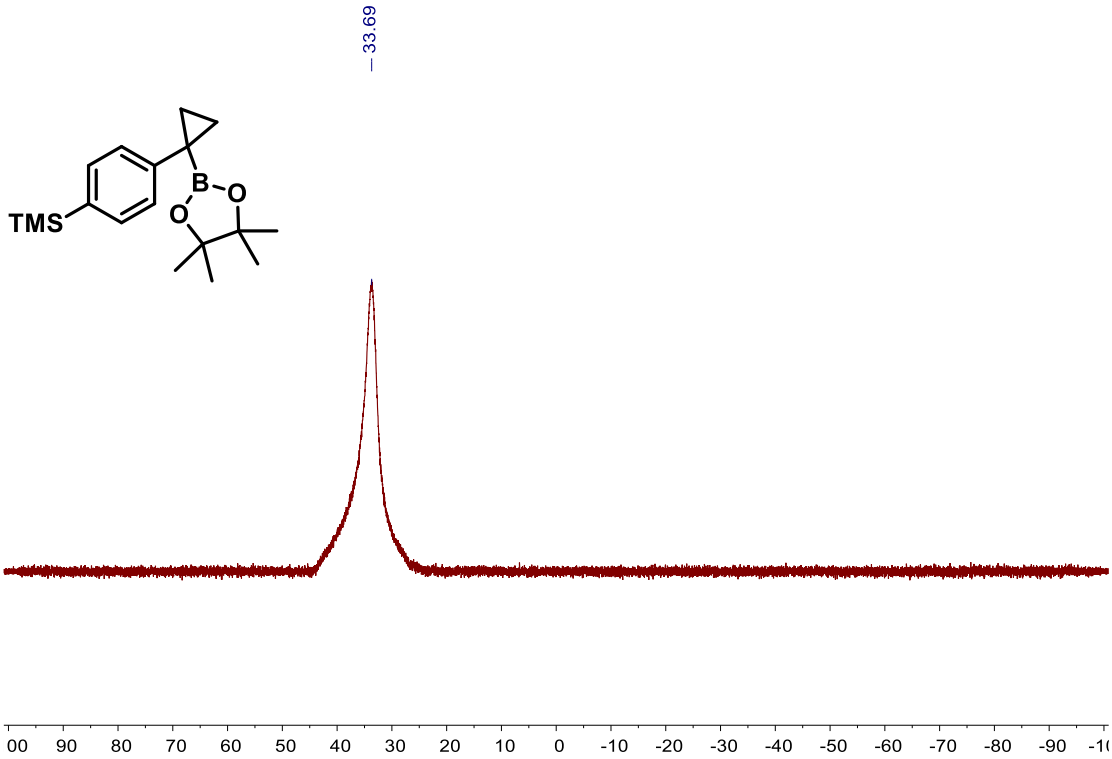
^{19}F NMR spectrum of **3j** (377 MHz, Chloroform-*d*)



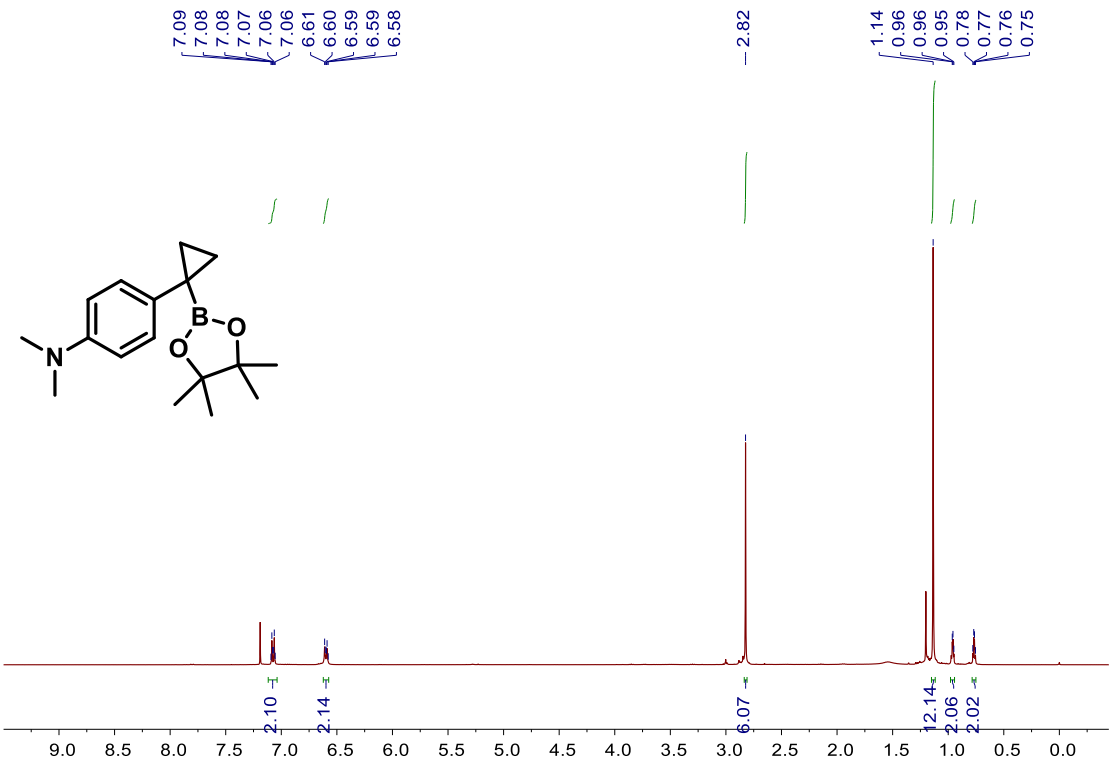
^{1}H NMR spectrum of **3k** (400 MHz, Chloroform-*d*)



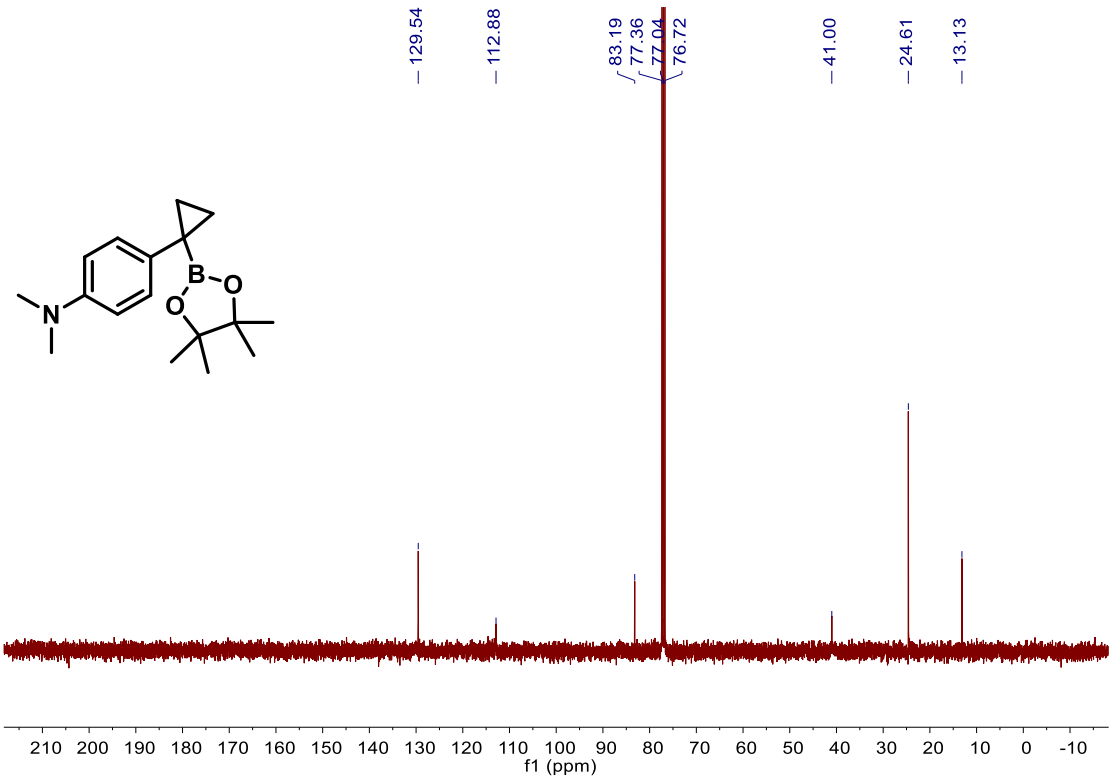
^{13}C NMR spectrum of **3k** (101 MHz, Chloroform-*d*)



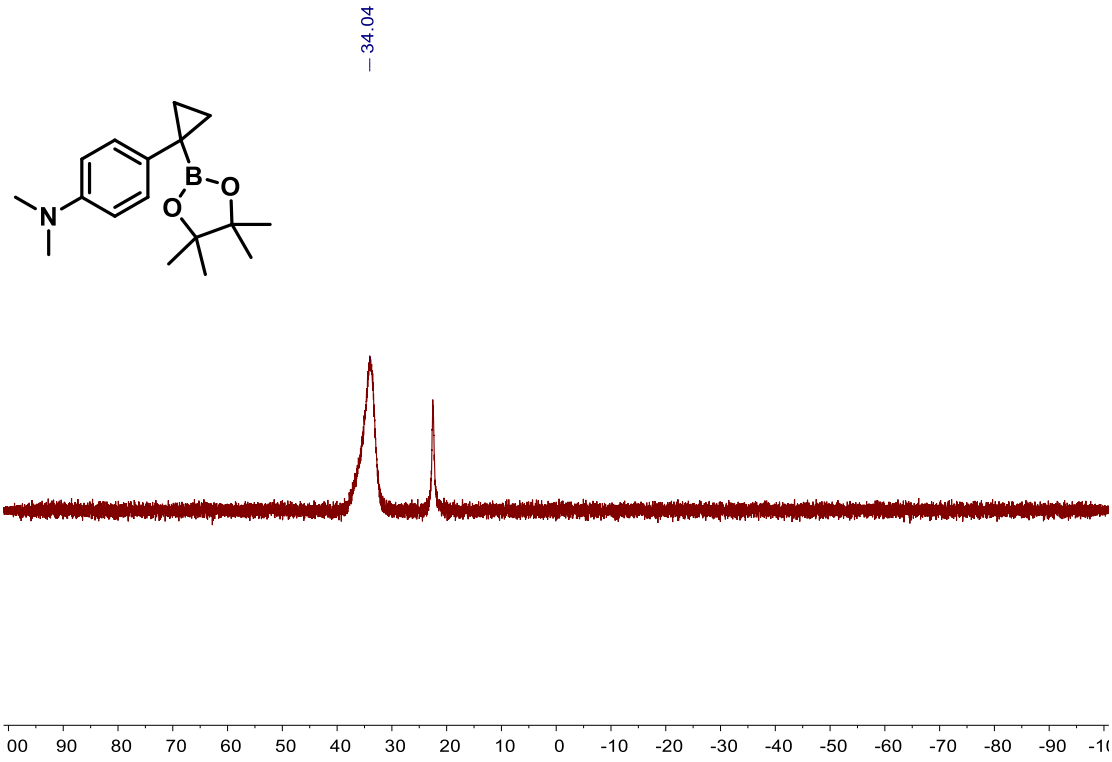
^{11}B NMR spectrum of **3k** (128 MHz Chloroform-*d*)



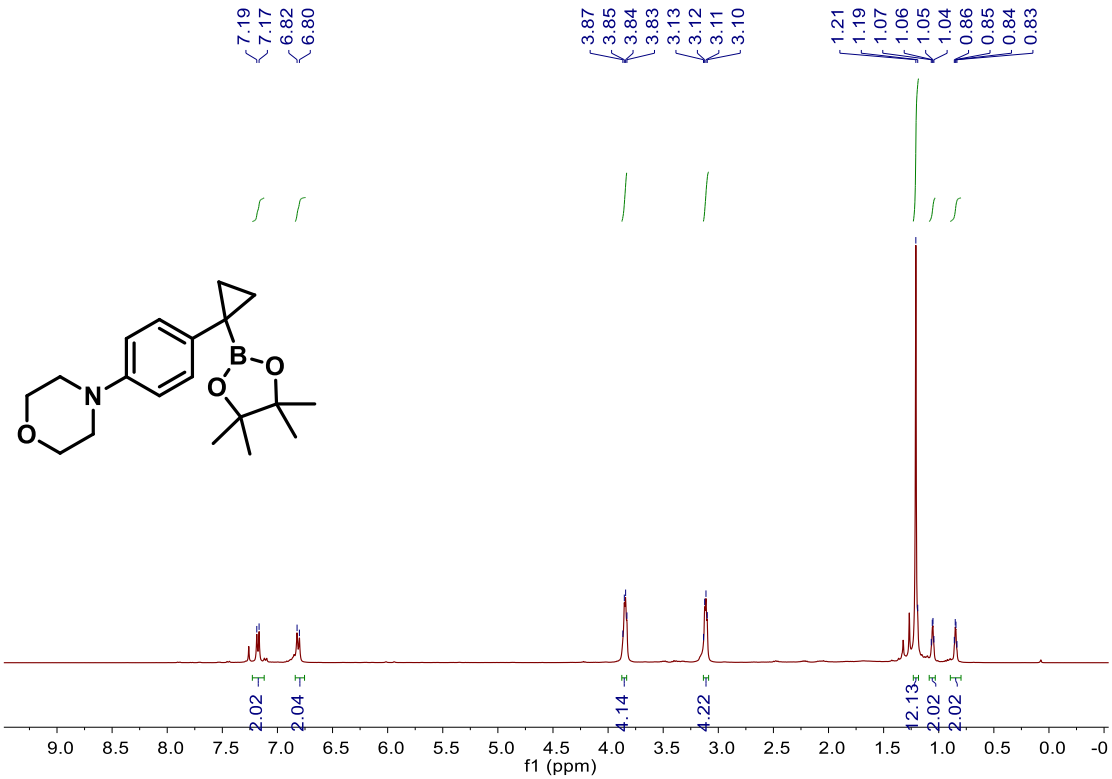
^{1}H NMR spectrum of **3l** (400 MHz, Chloroform-*d*)



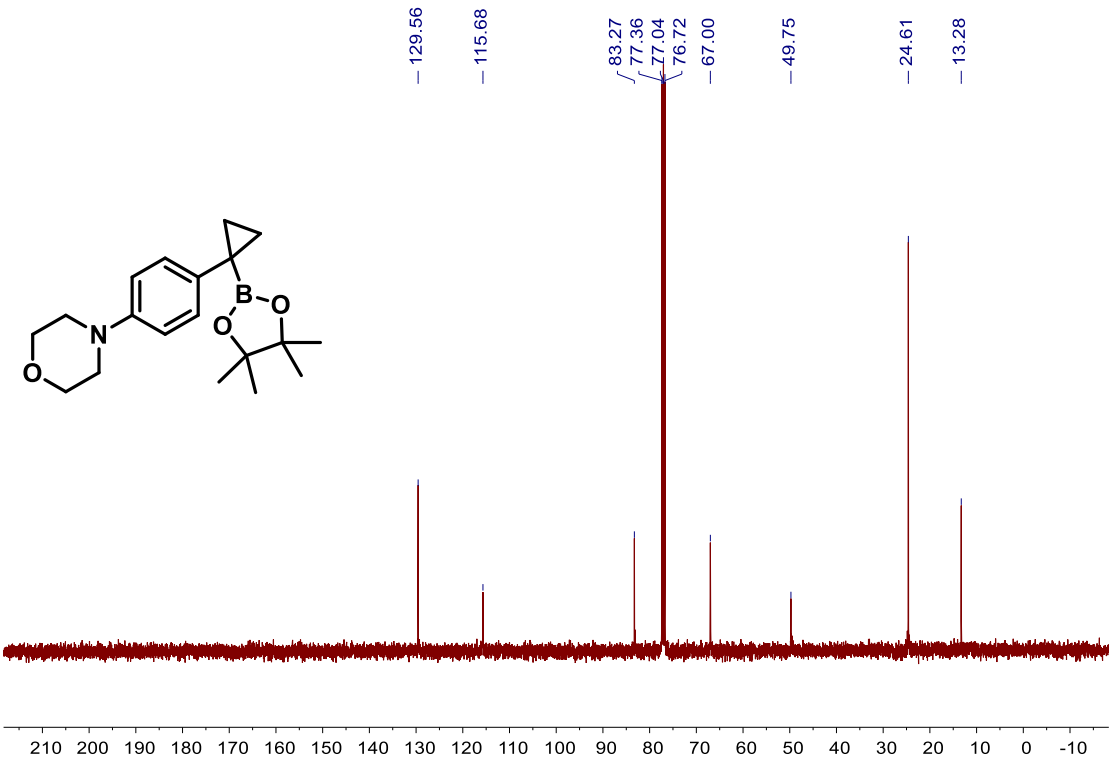
^{13}C NMR spectrum of **3l** (101 MHz, Chloroform-*d*)



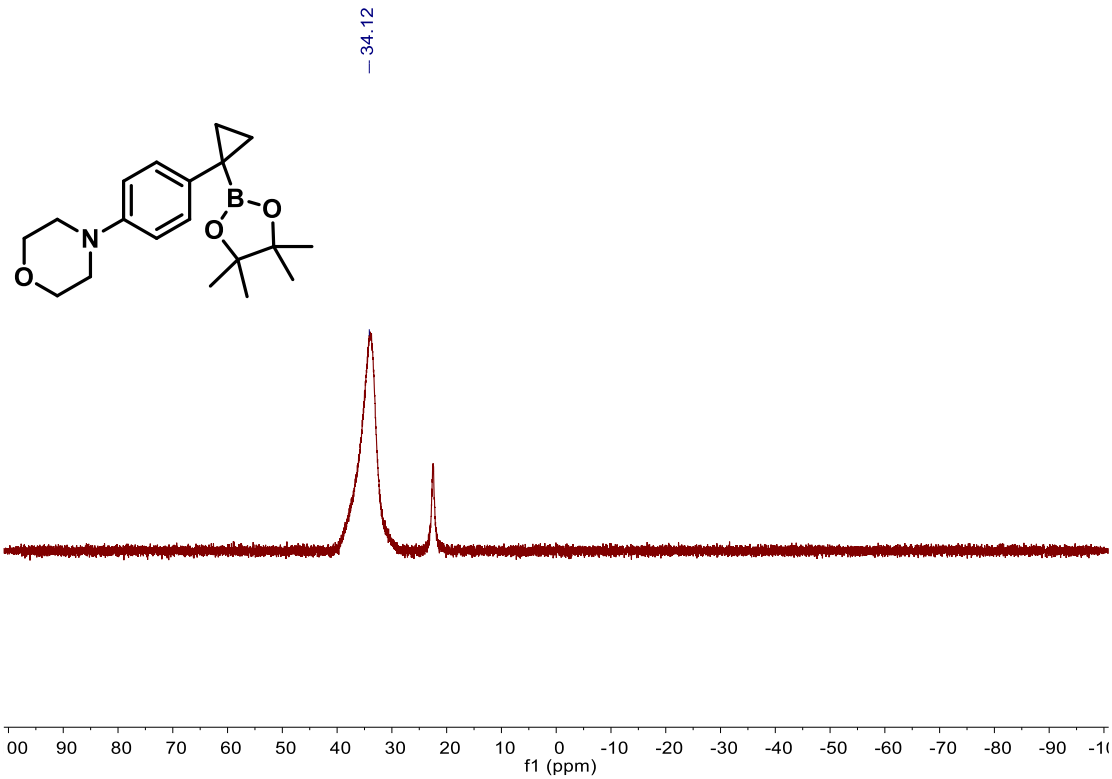
^{11}B NMR spectrum of **3l** (128 MHz Chloroform-*d*)



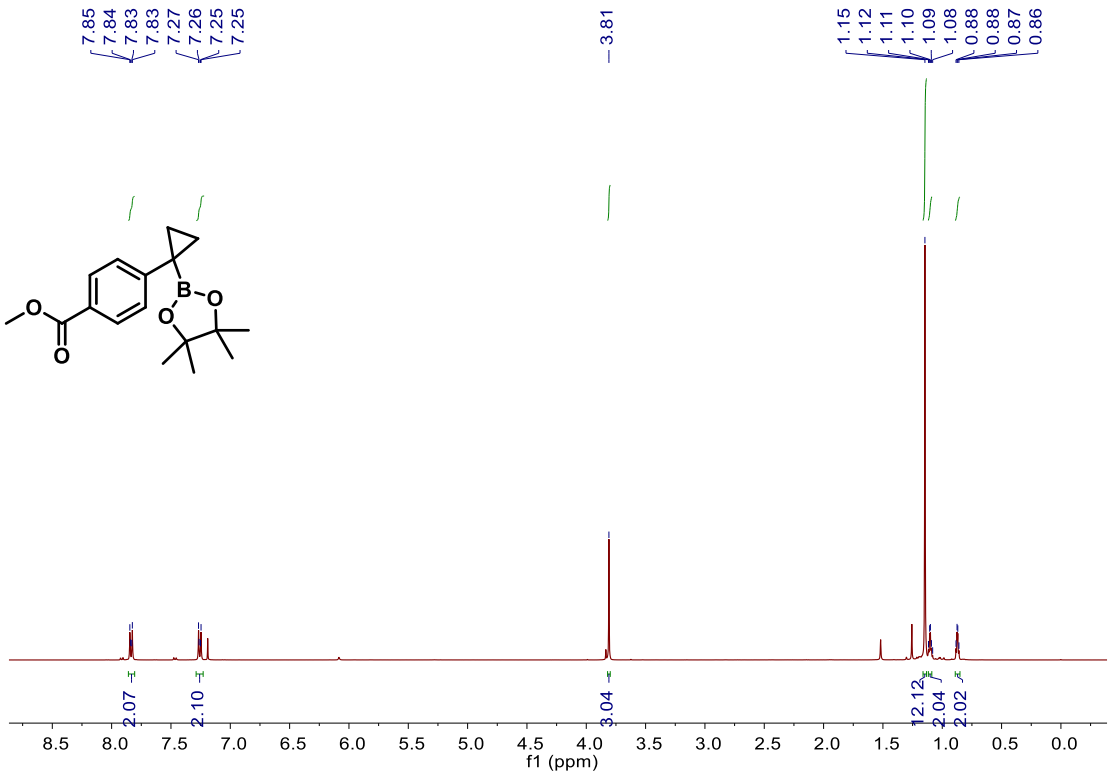
^{1}H NMR spectrum of **3m** (400 MHz, Chloroform-*d*)



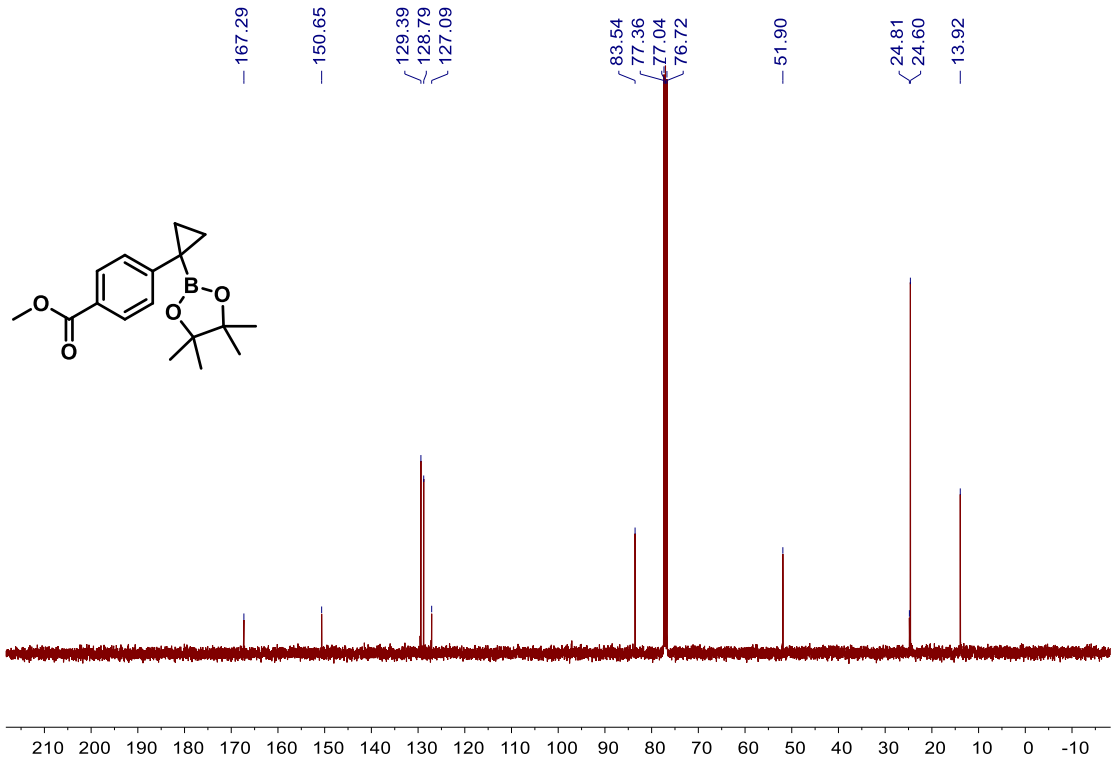
^{13}C NMR spectrum of **3m** (101 MHz, Chloroform-*d*)



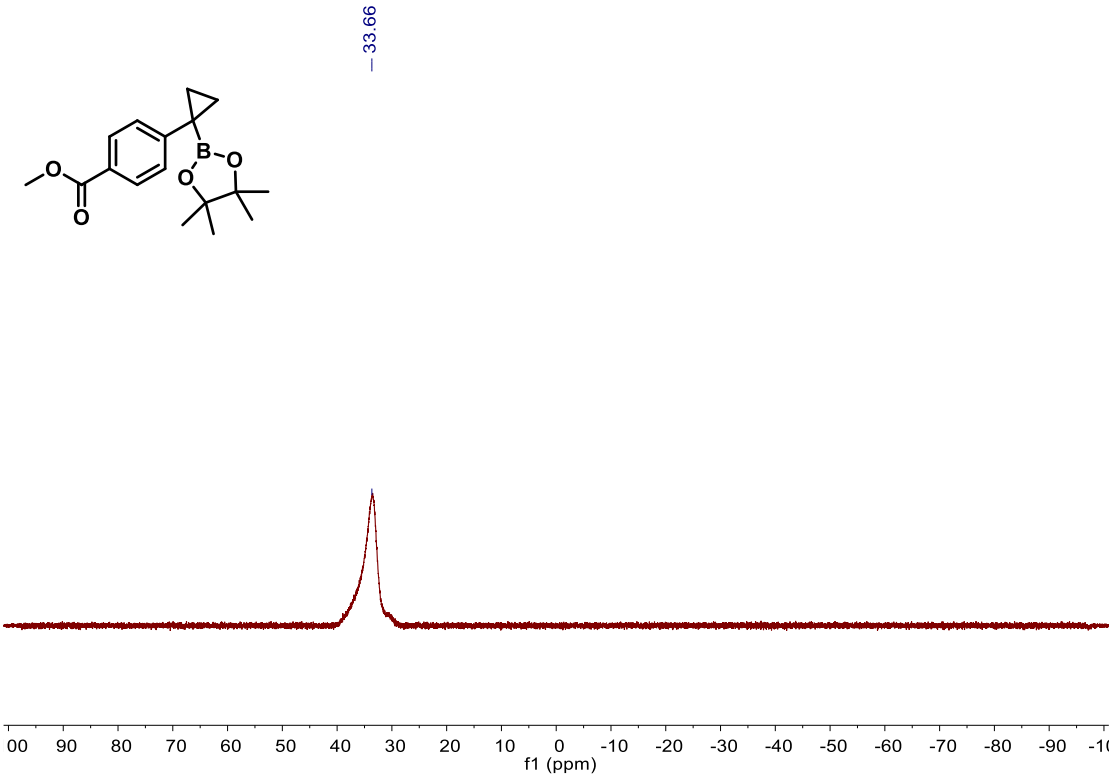
^{11}B NMR spectrum of **3m** (128 MHz Chloroform-*d*)



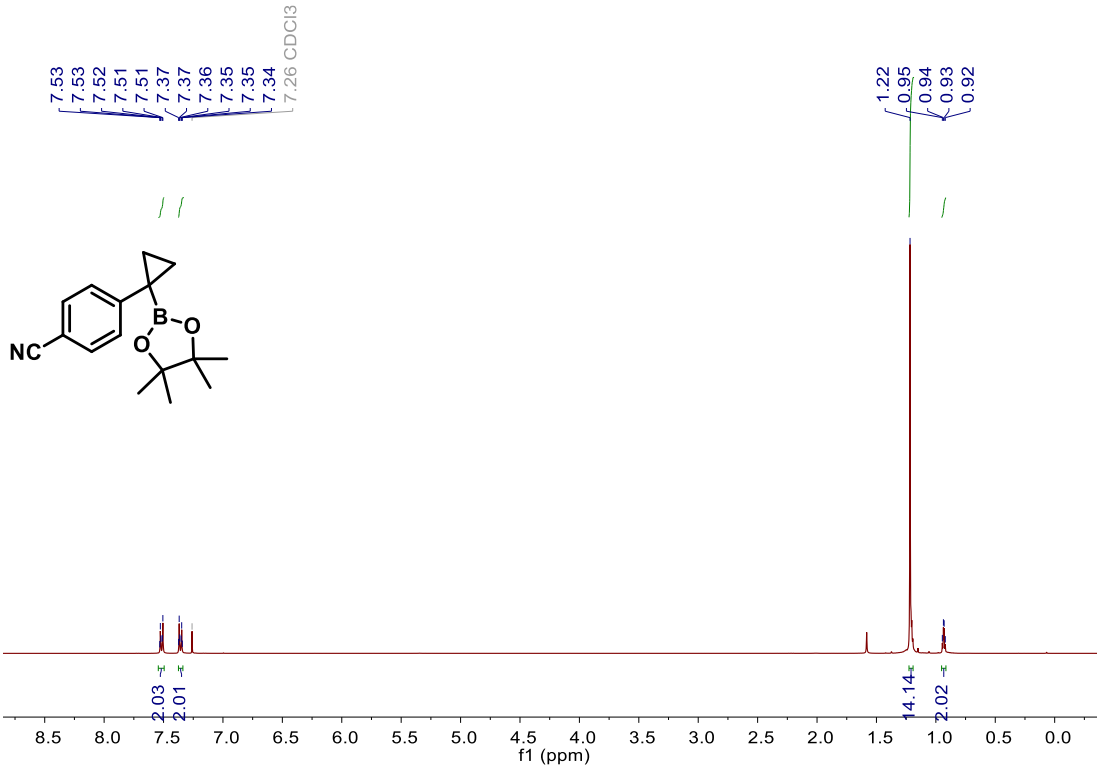
^{1}H NMR spectrum of **3n** (400 MHz, Chloroform-*d*)



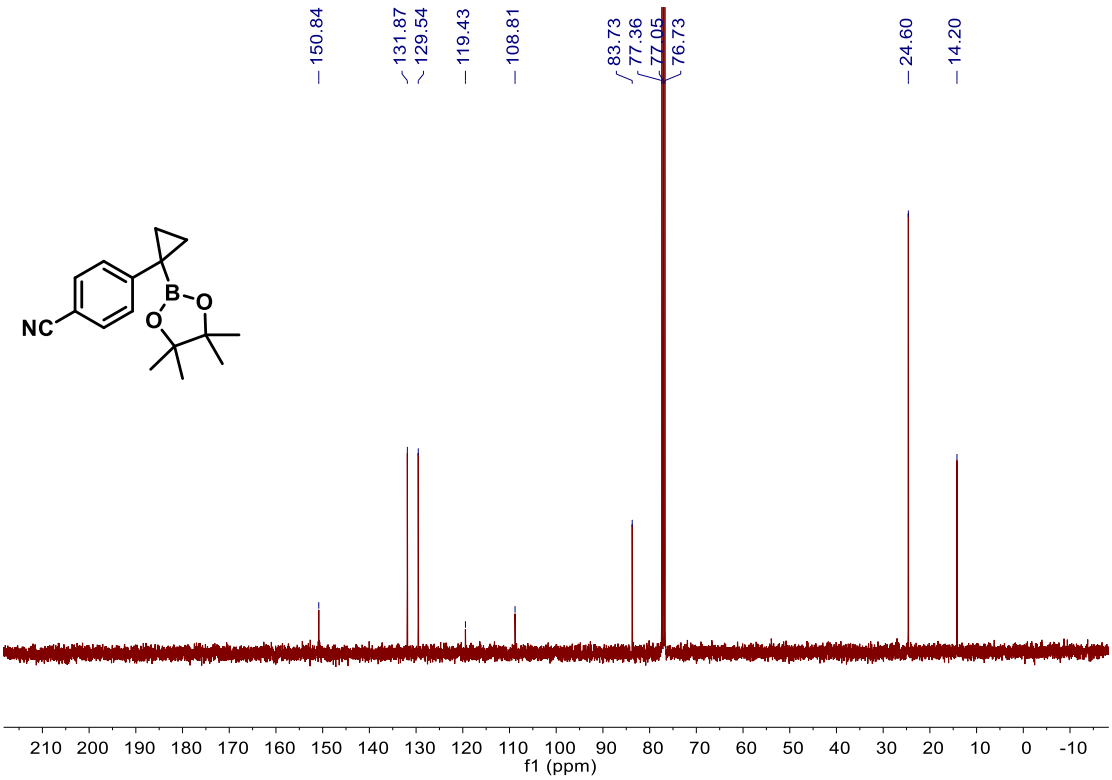
^{13}C NMR spectrum of **3n** (101 MHz, Chloroform-*d*)



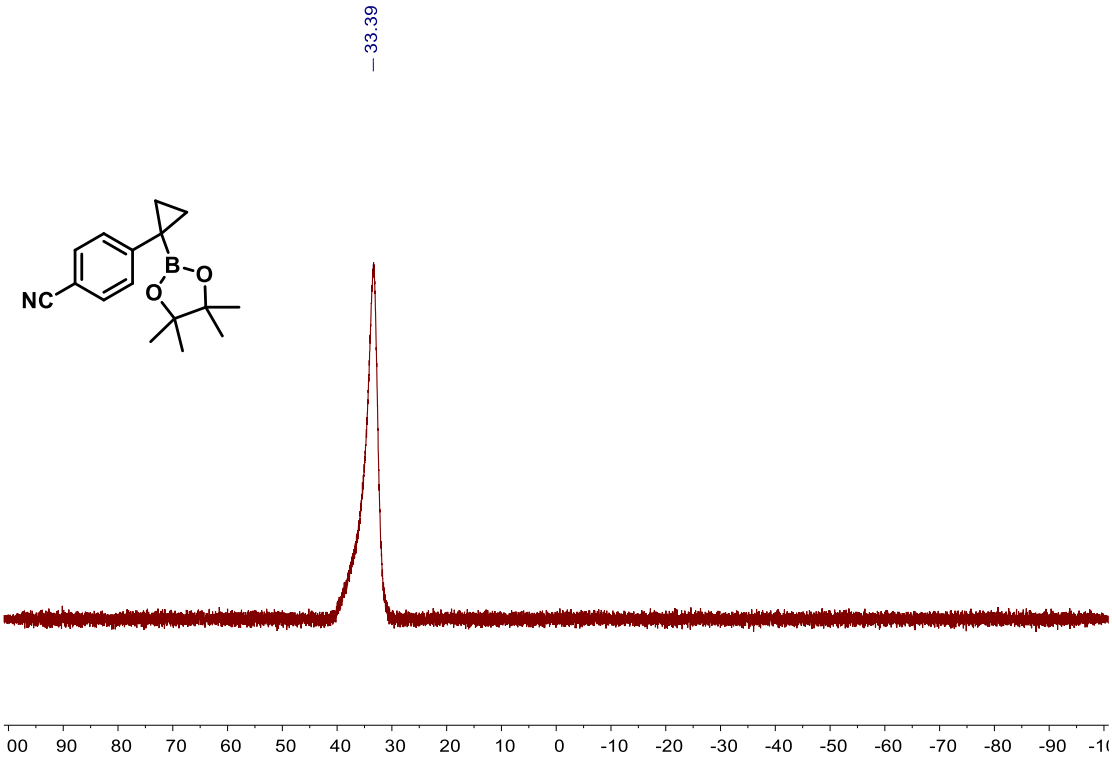
^{11}B NMR spectrum of **3n** (128 MHz Chloroform-*d*)



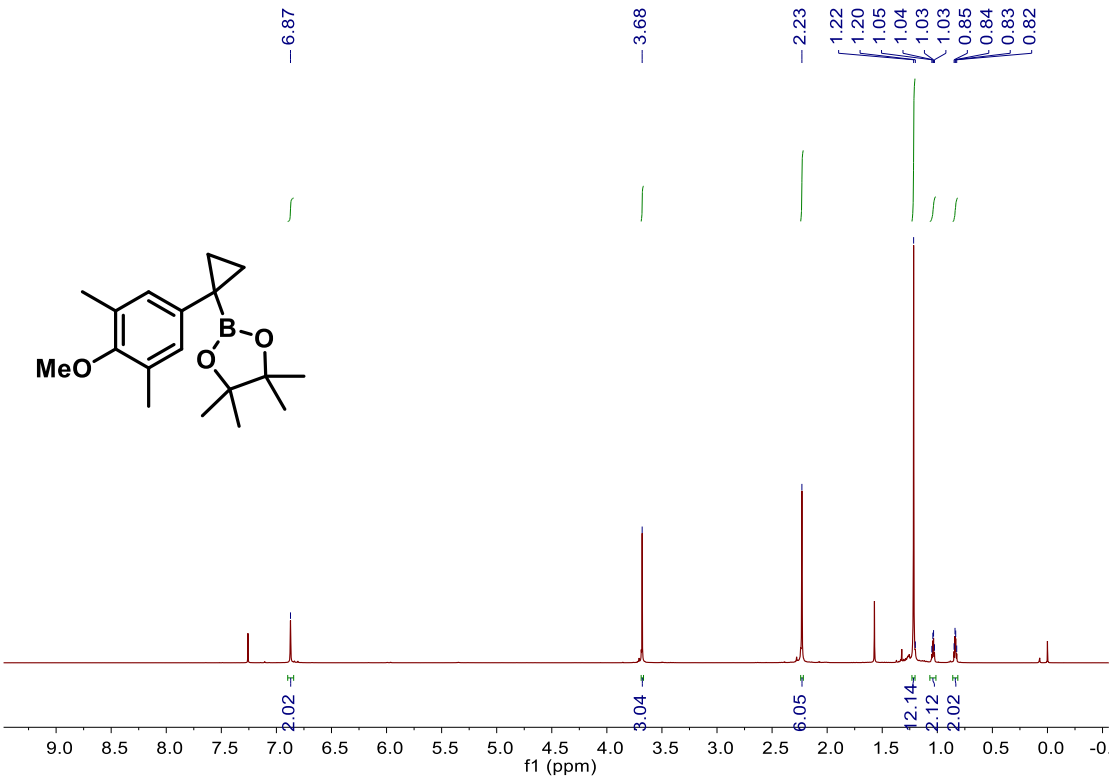
^{1}H NMR spectrum of **3o** (400 MHz, Chloroform-*d*)



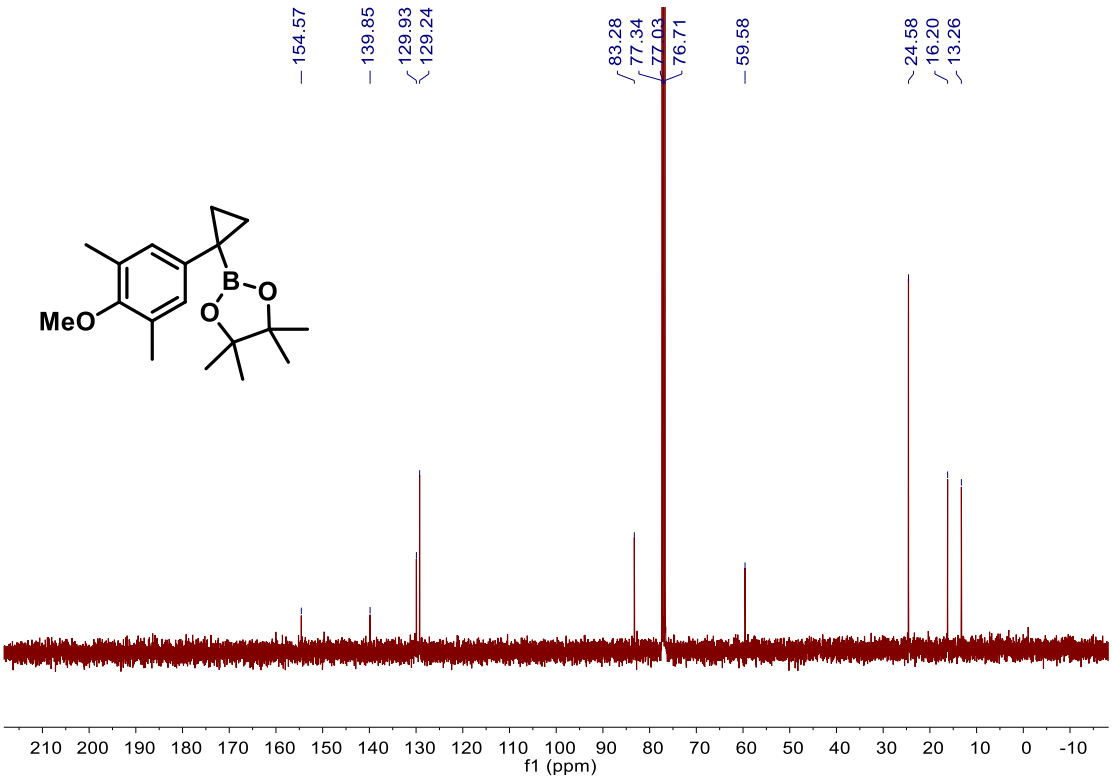
^{13}C NMR spectrum of **3o** (101 MHz, Chloroform-*d*)



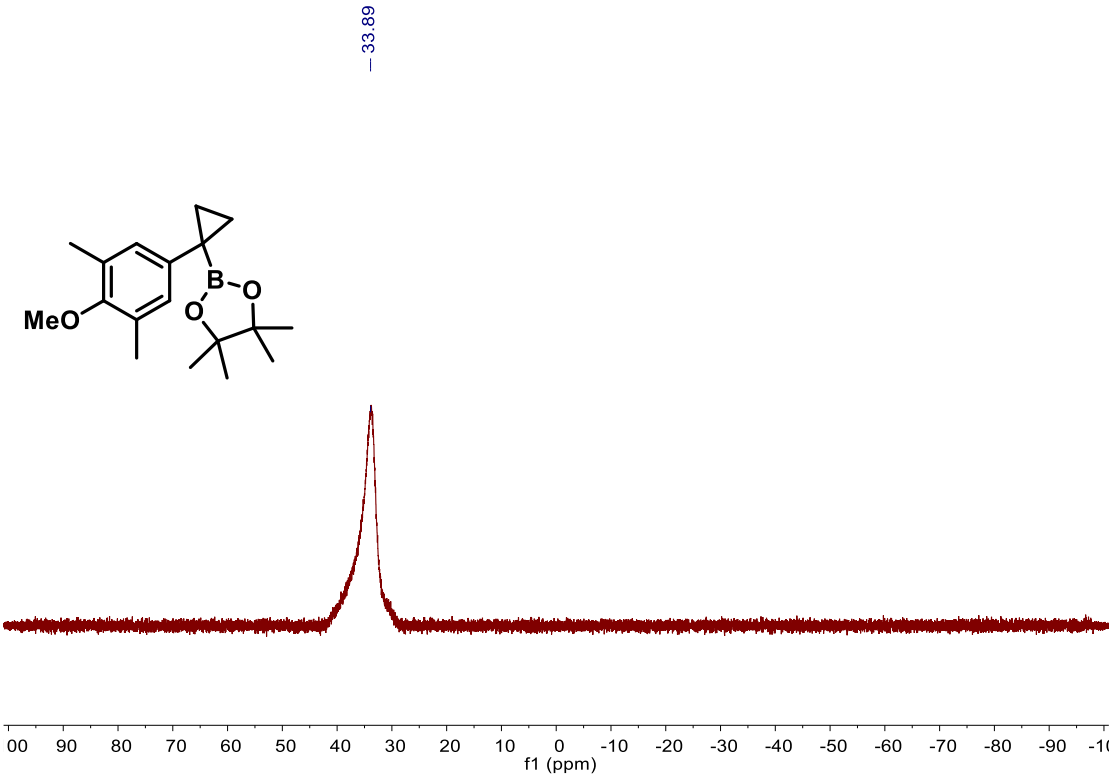
^{11}B NMR spectrum of **3o** (128 MHz Chloroform-*d*)



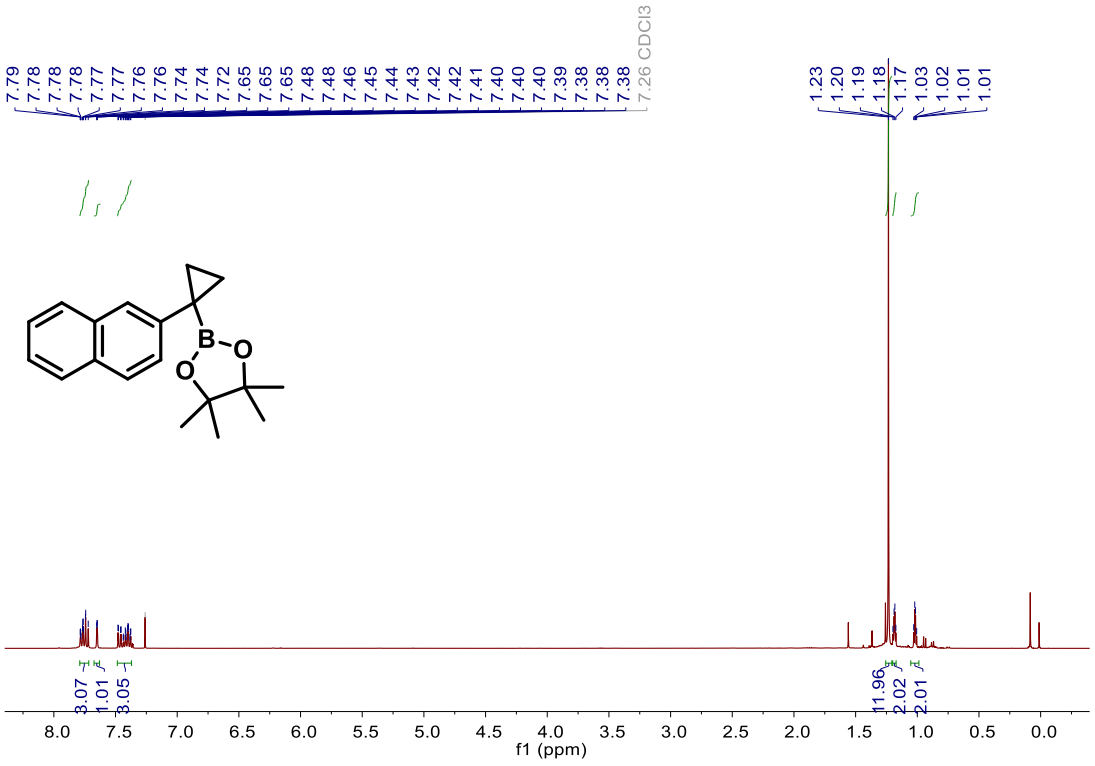
^{1}H NMR spectrum of **3p** (400 MHz, Chloroform-*d*)



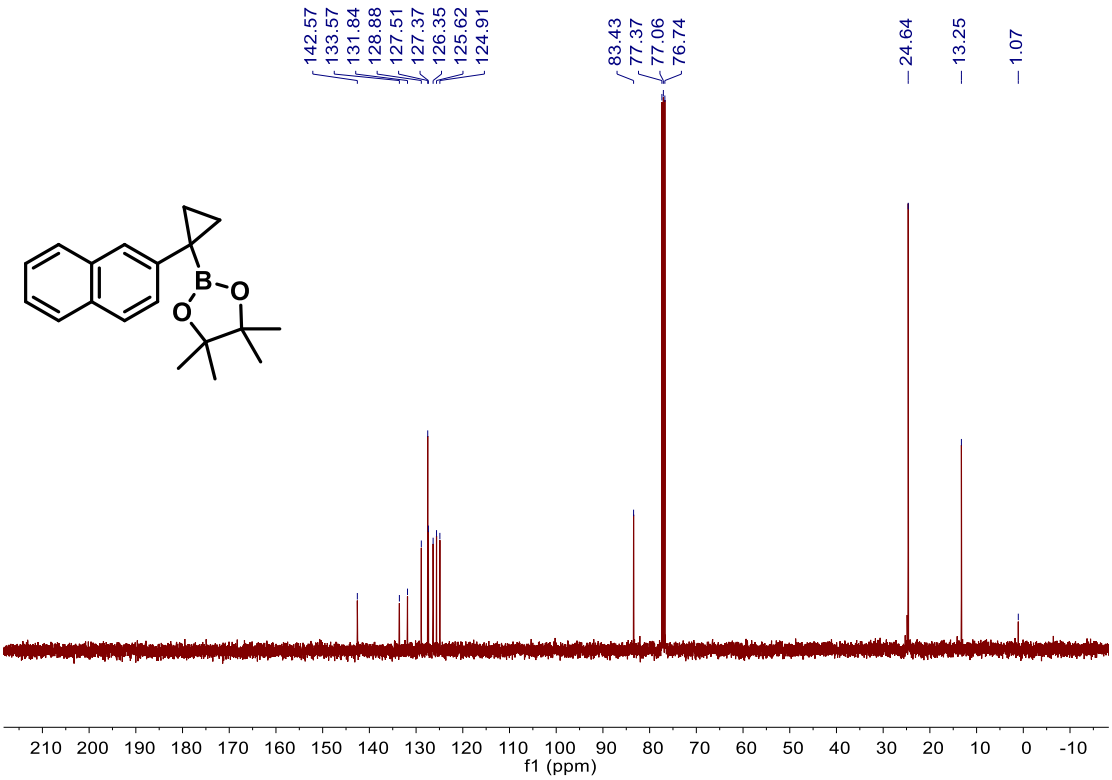
^{13}C NMR spectrum of **3p** (101 MHz, Chloroform-*d*)



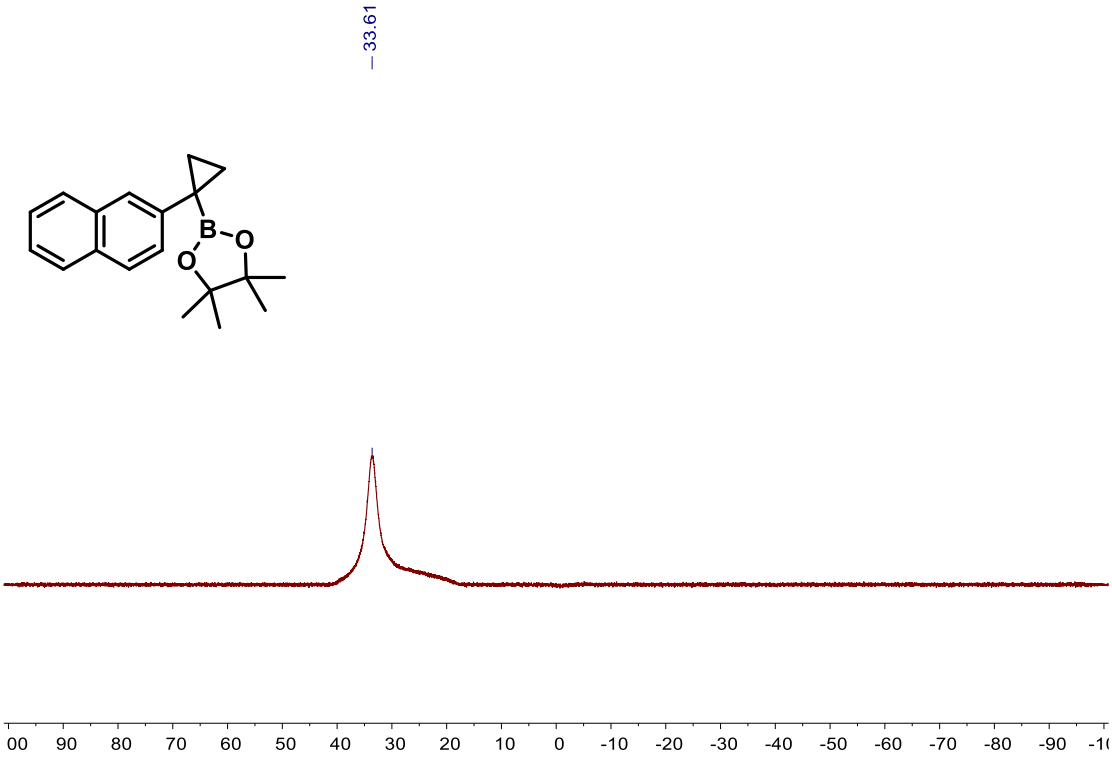
^{11}B NMR spectrum of **3p** (128 MHz Chloroform-*d*)



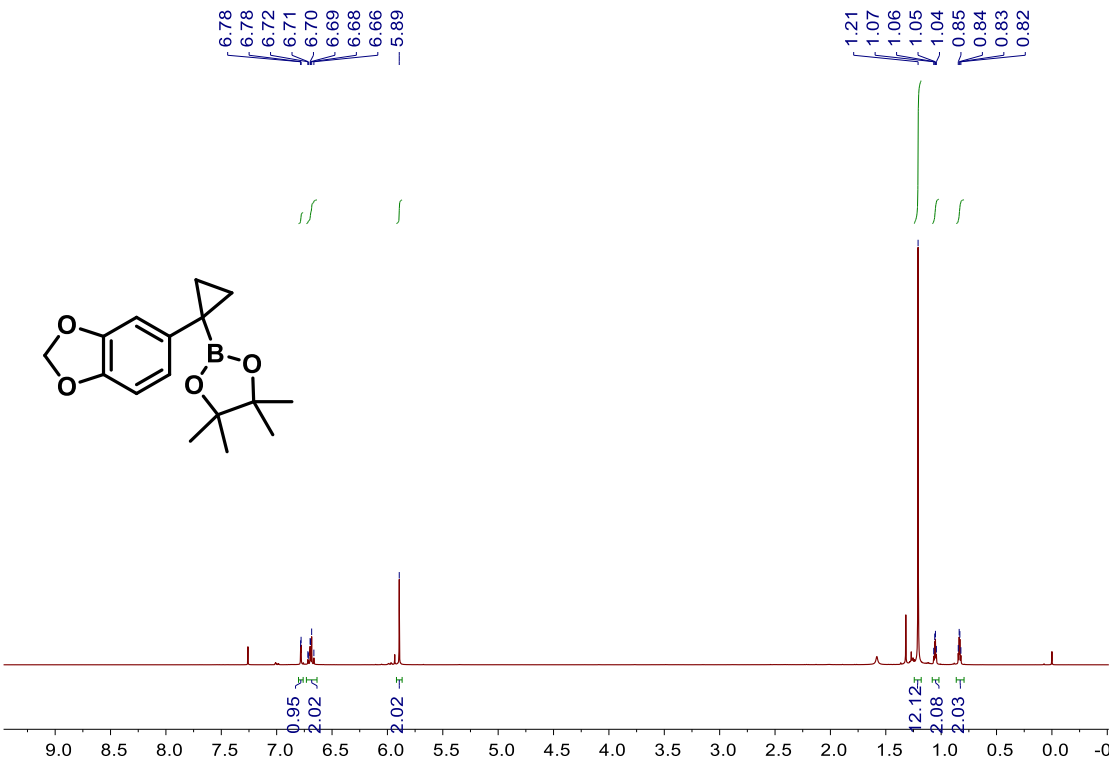
^{1}H NMR spectrum of **3q** (400 MHz, Chloroform-*d*)



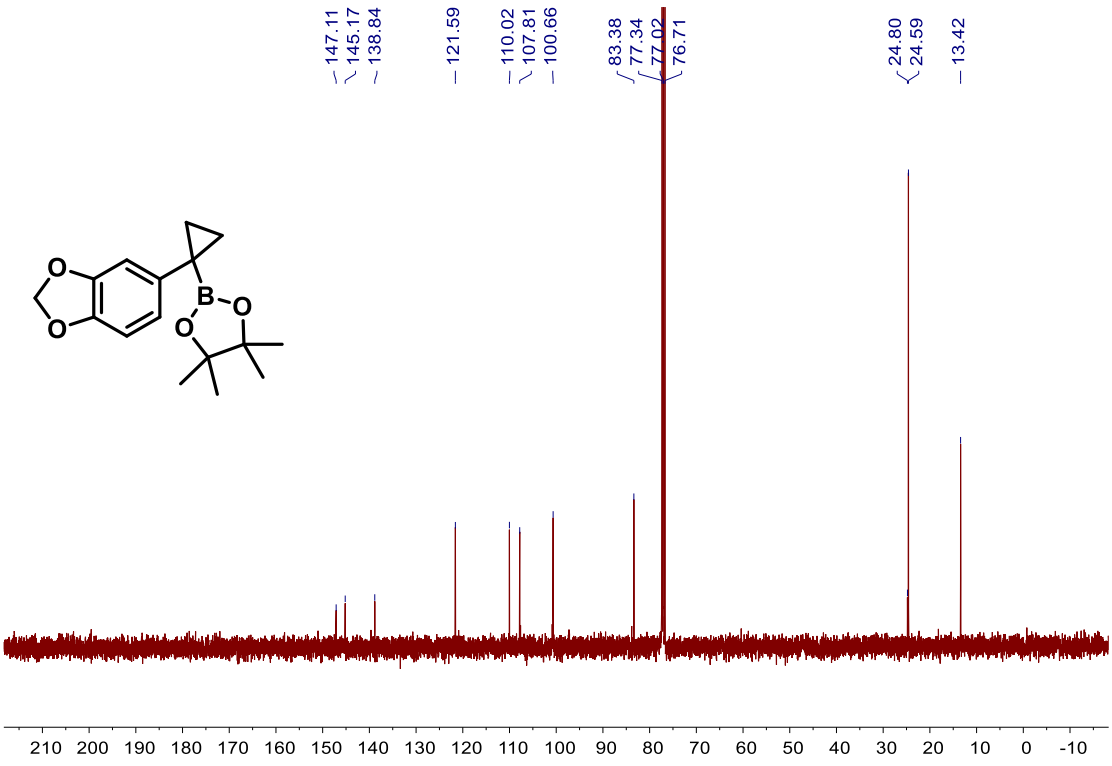
^{13}C NMR spectrum of **3q** (101 MHz, Chloroform-*d*)



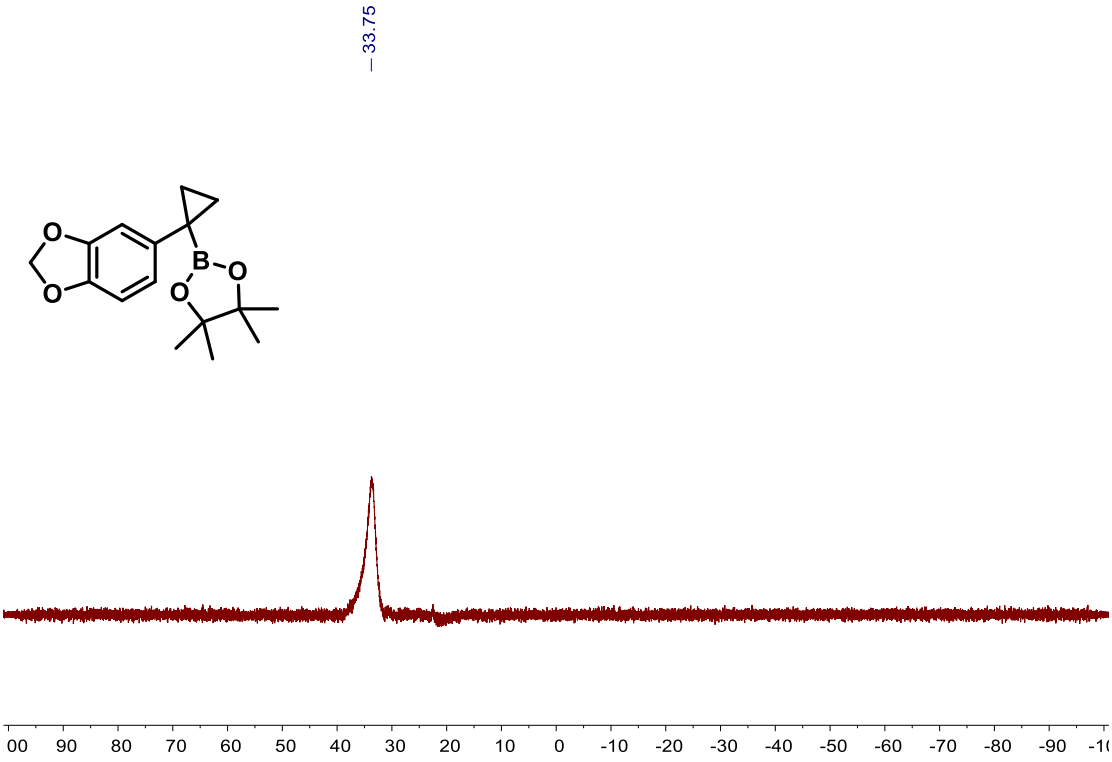
^{11}B NMR spectrum of **3q** (128 MHz Chloroform-*d*)



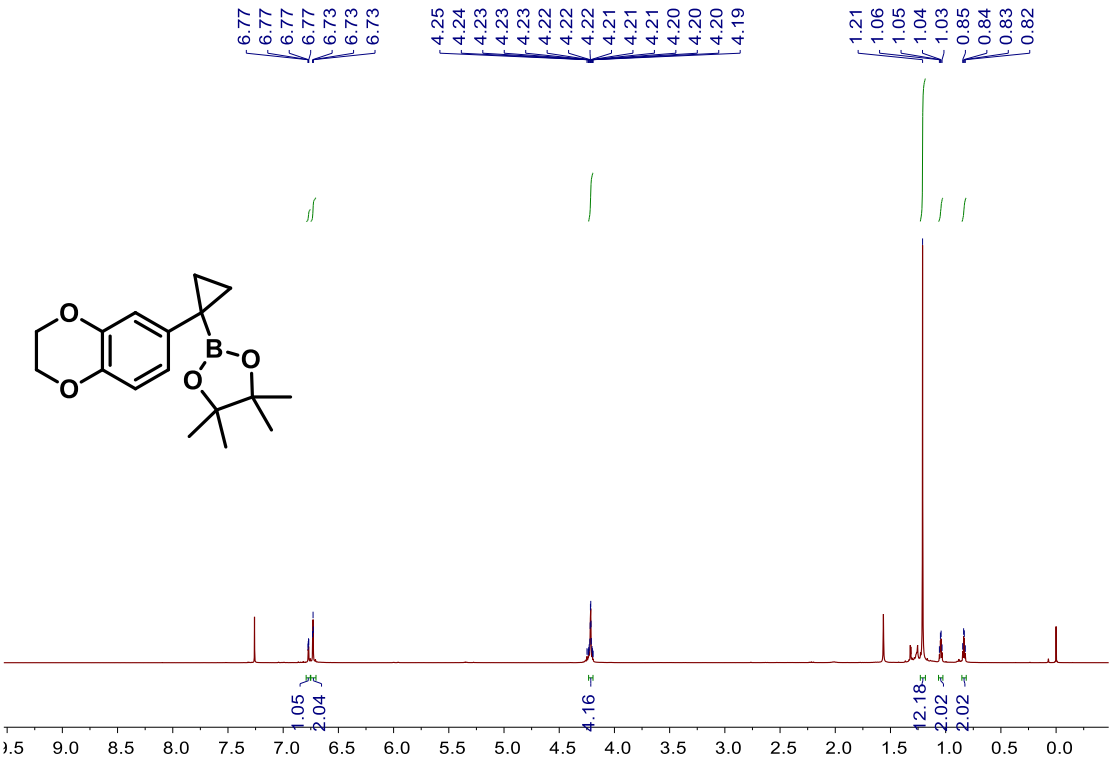
^{1}H NMR spectrum of **3r** (400 MHz, Chloroform-*d*)



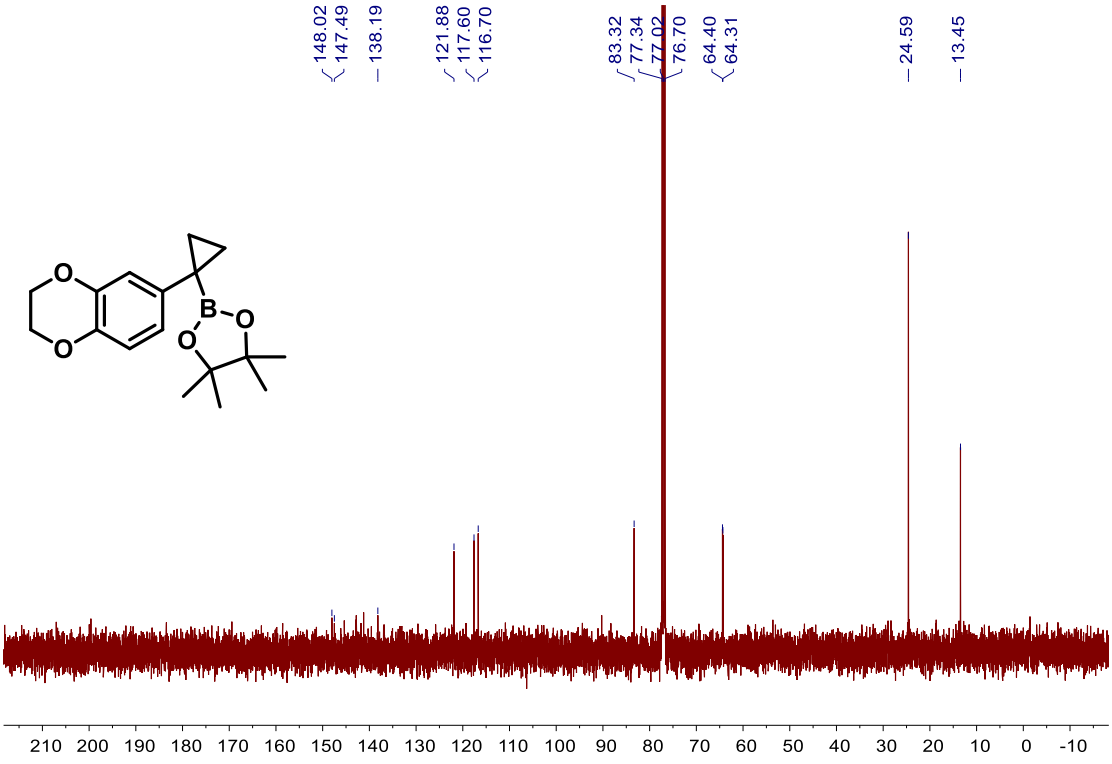
^{13}C NMR spectrum of **3r** (101 MHz, Chloroform-*d*)



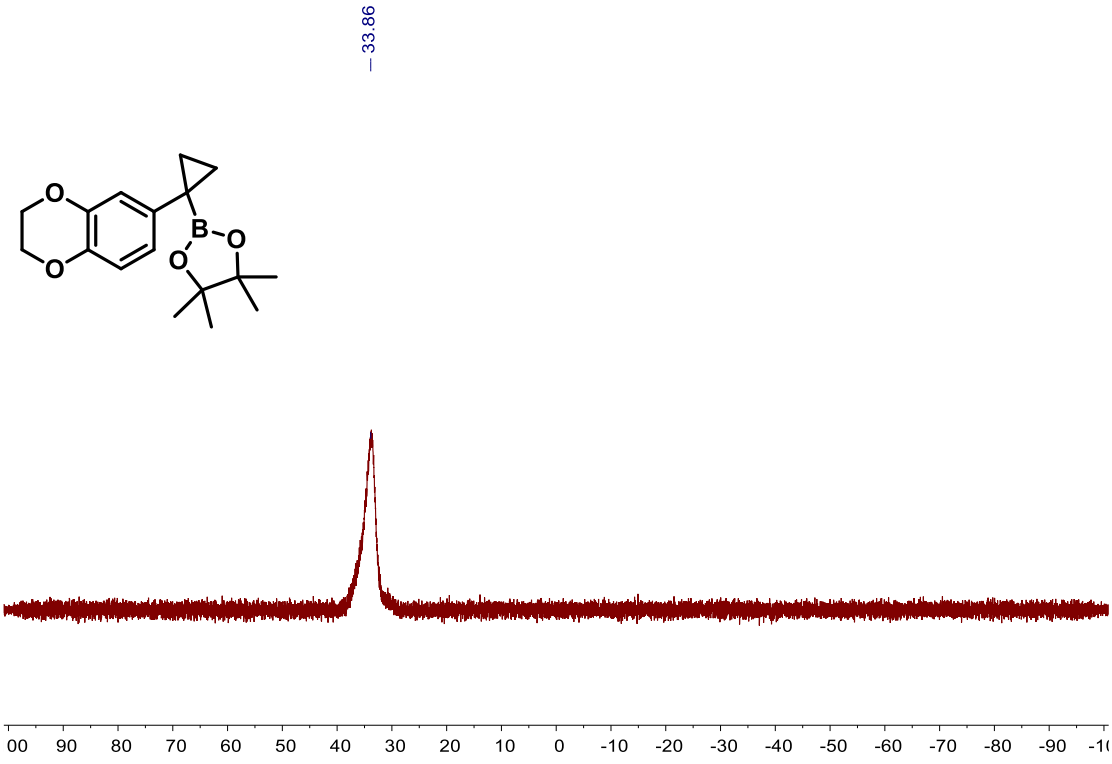
^{11}B NMR spectrum of **3r** (128 MHz Chloroform-*d*)



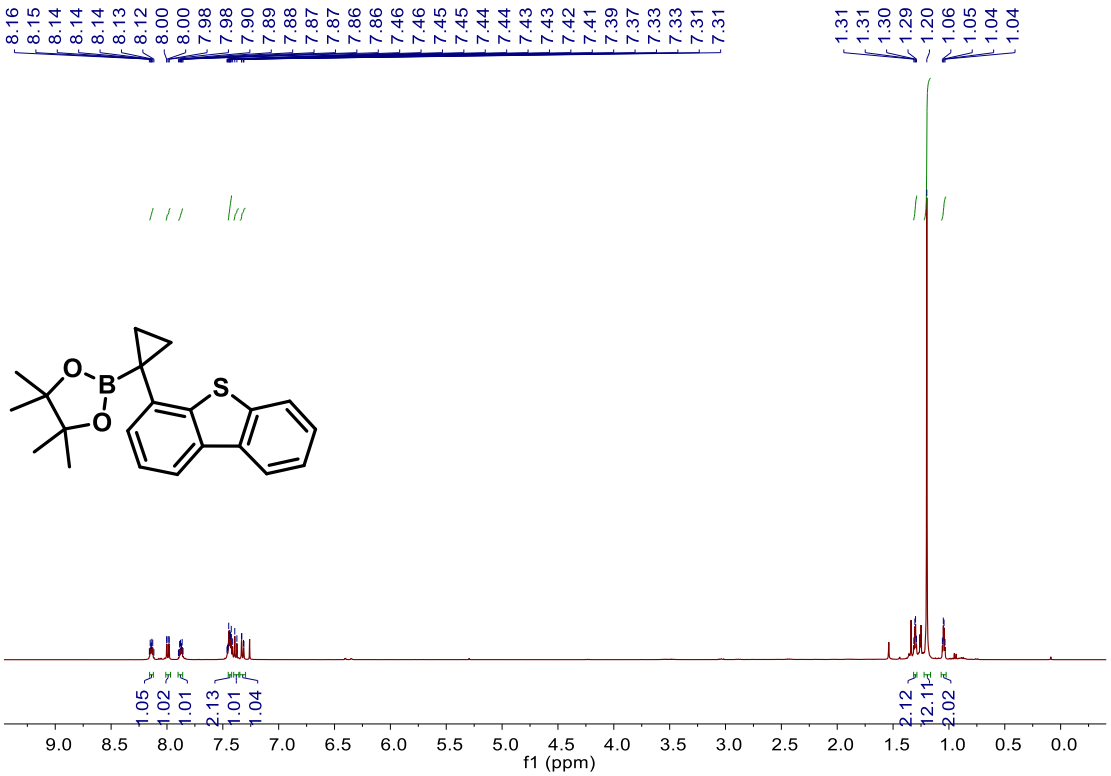
^{1}H NMR spectrum of **3s** (400 MHz, Chloroform-*d*)



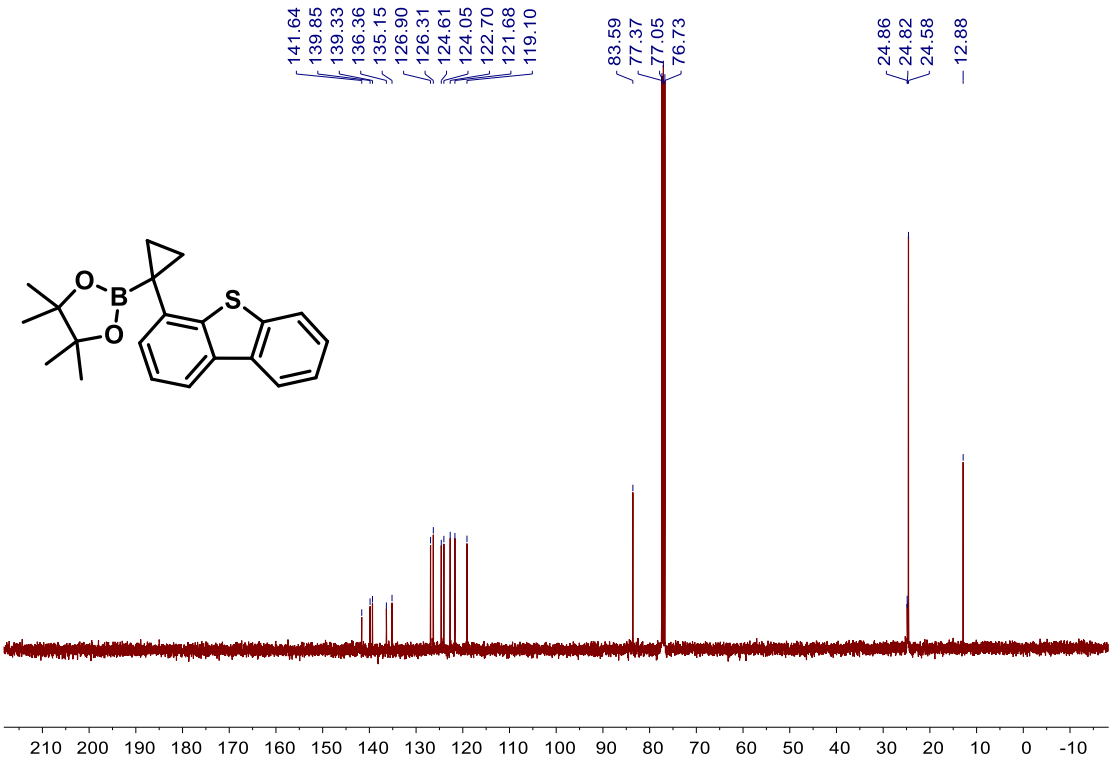
^{13}C NMR spectrum of **3s** (101 MHz, Chloroform-*d*)



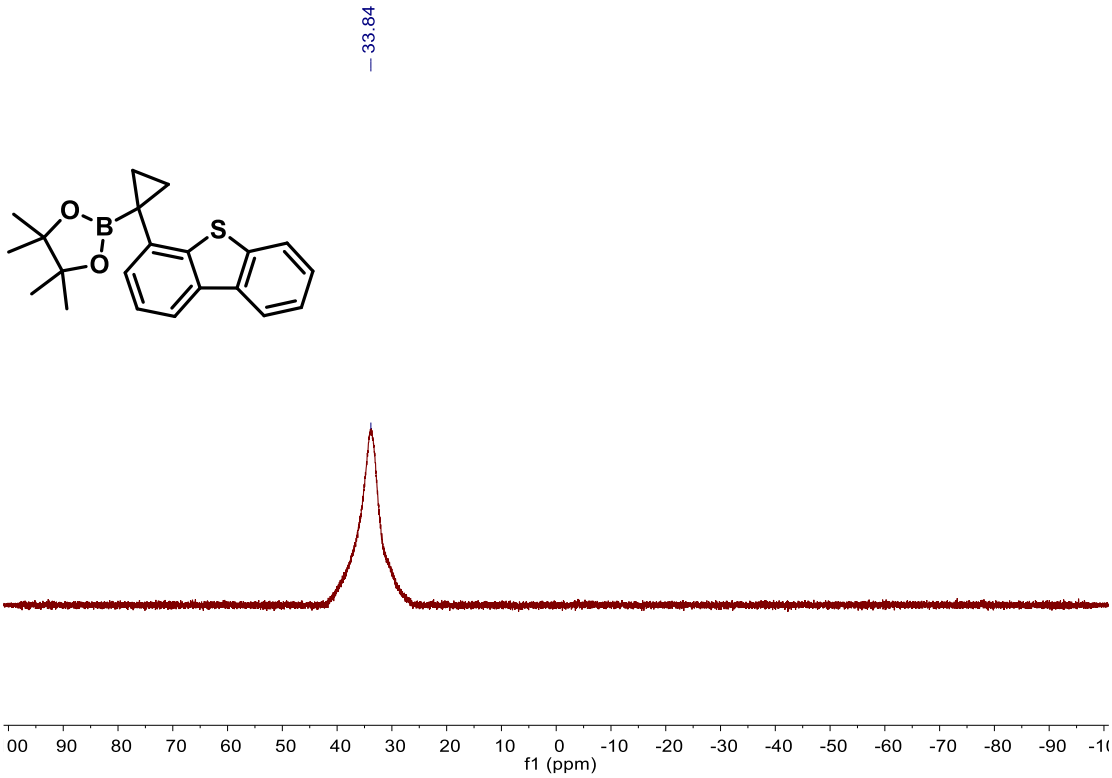
^{11}B NMR spectrum of **3s** (128 MHz Chloroform-*d*)



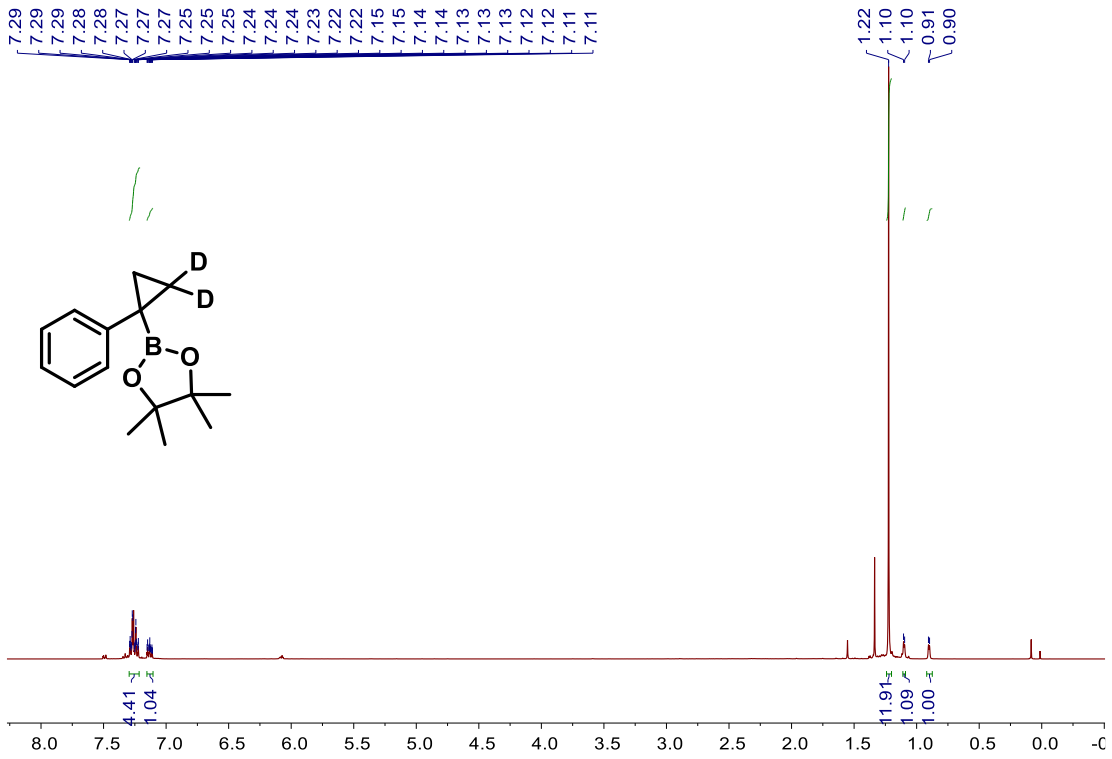
^{1}H NMR spectrum of **3t** (400 MHz, Chloroform-*d*)



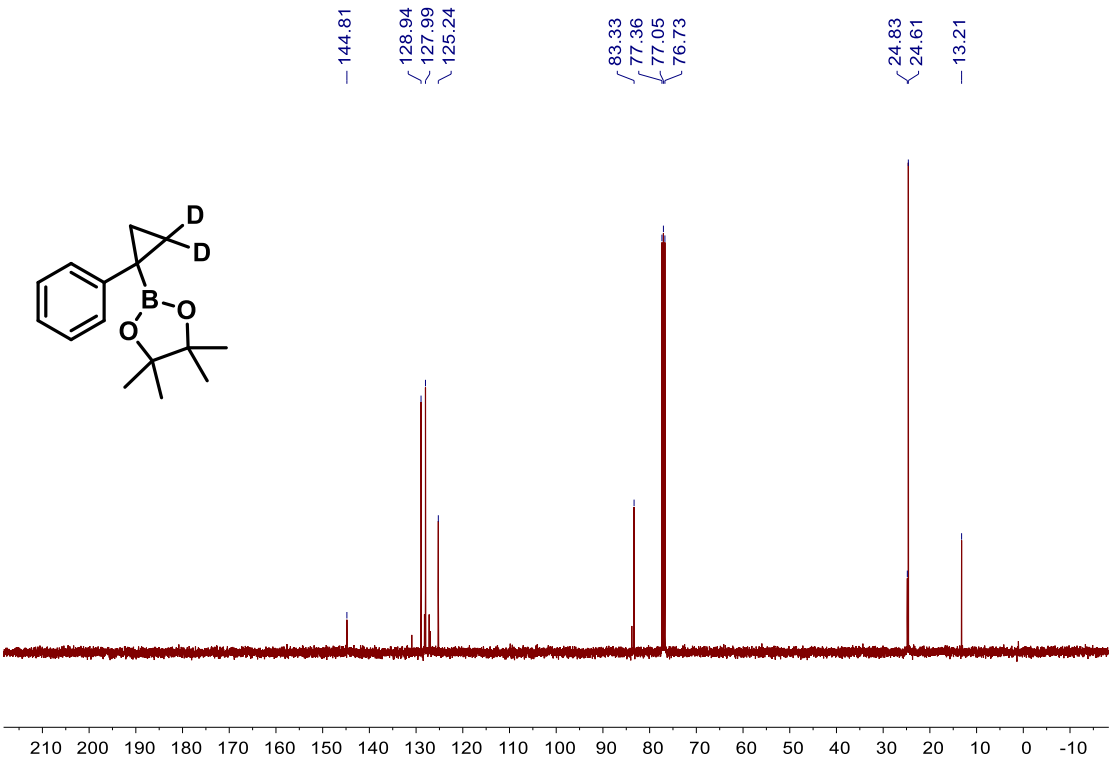
^{13}C NMR spectrum of **3t** (101 MHz, Chloroform-*d*)



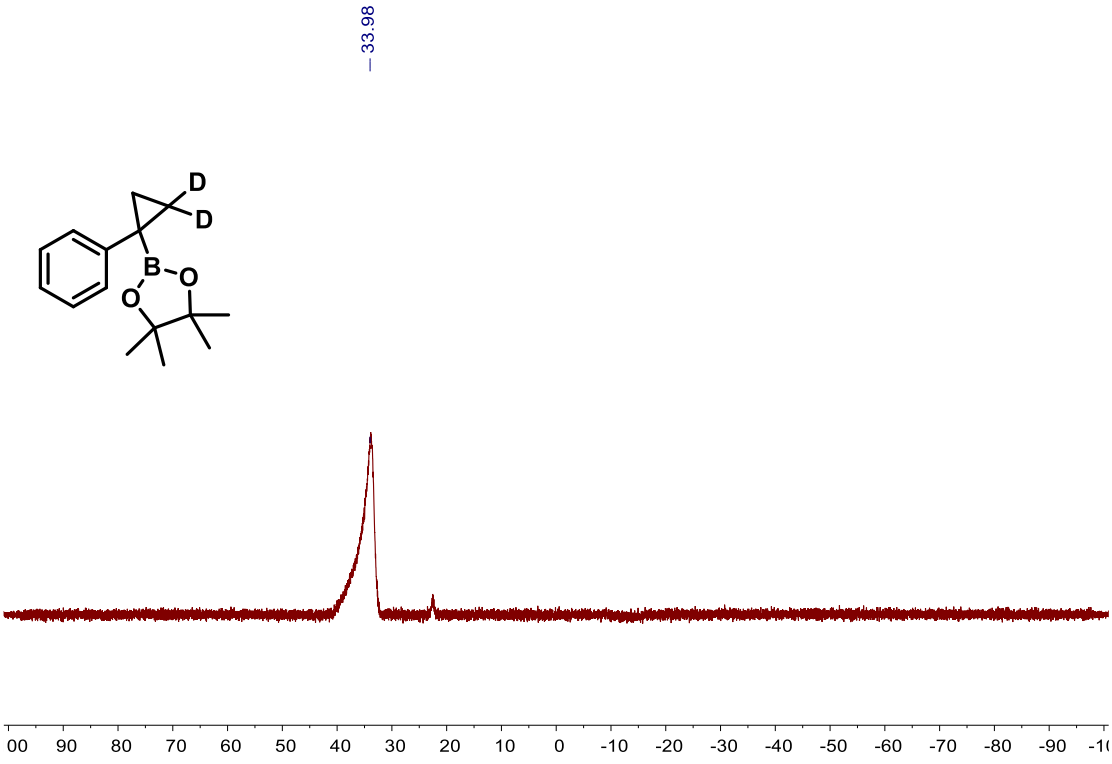
^{11}B NMR spectrum of **3t** (128 MHz Chloroform-*d*)



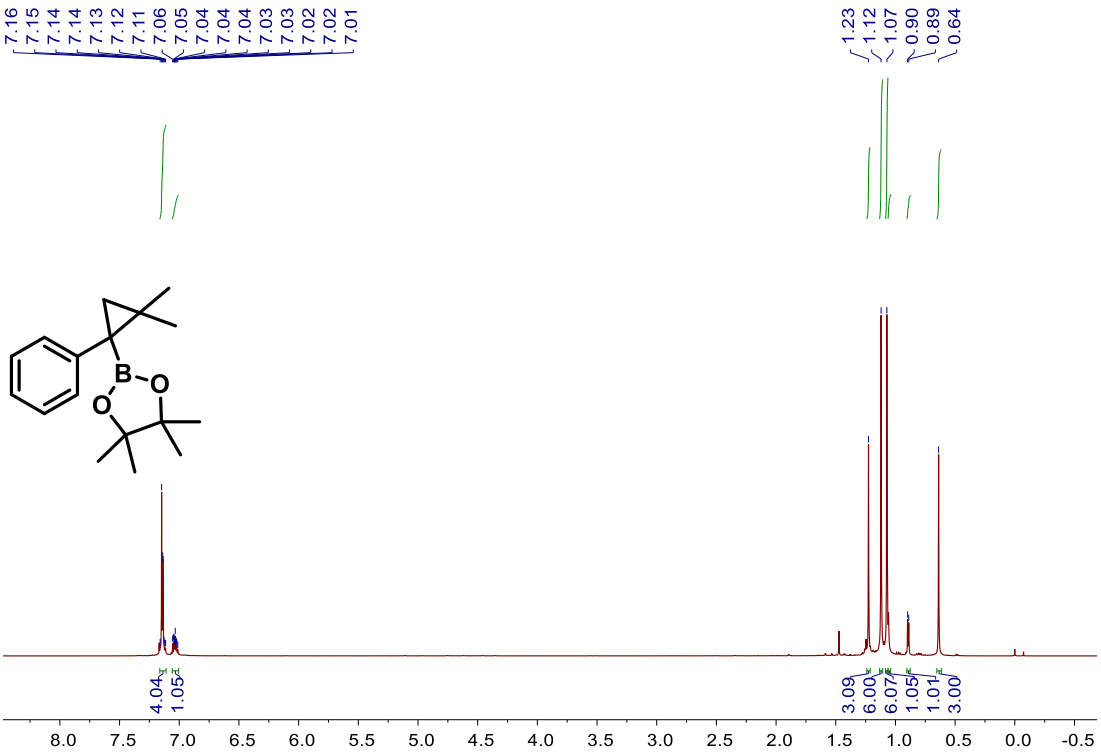
^{1}H NMR spectrum of **3u** (400 MHz, Chloroform-*d*)



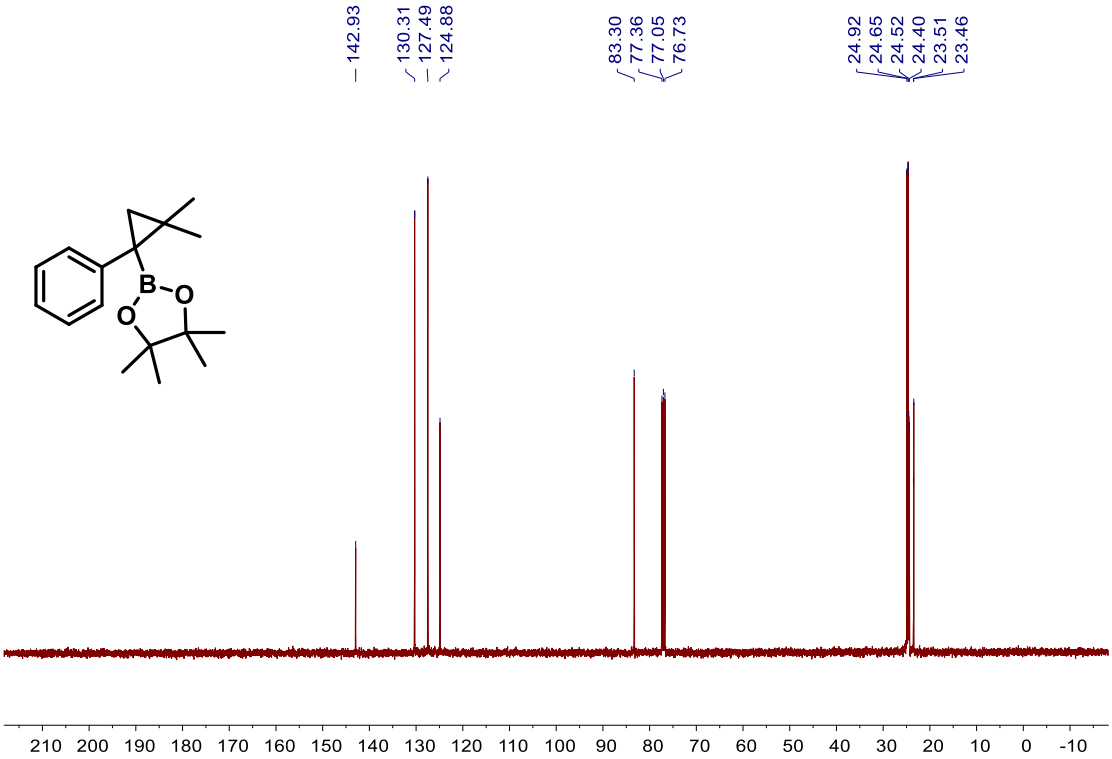
^{13}C NMR spectrum of **3u** (101 MHz, Chloroform-*d*)



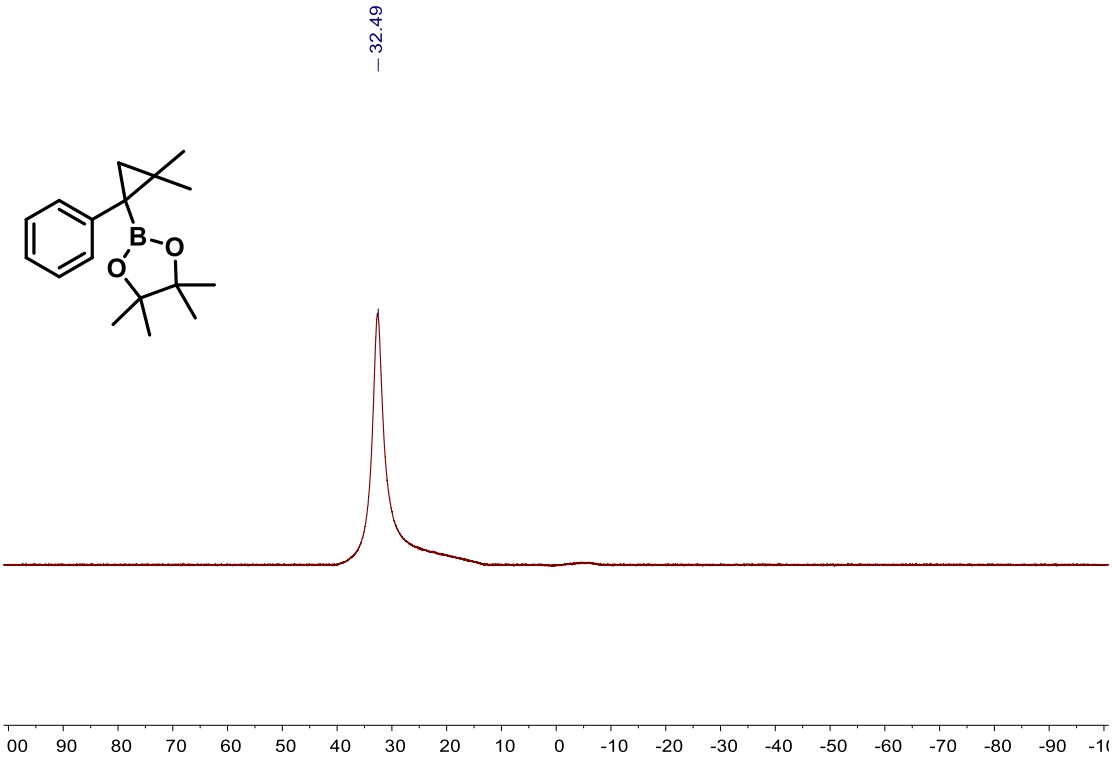
^{11}B NMR spectrum of **3u** (128 MHz Chloroform-*d*)



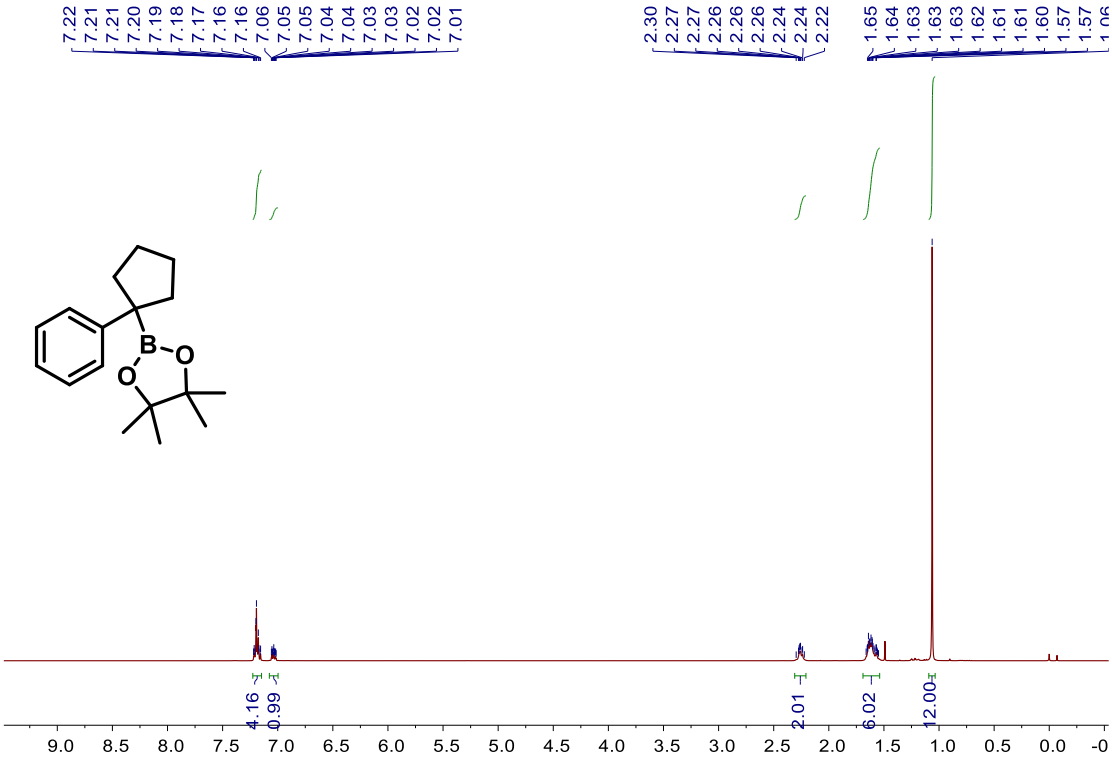
^{1}H NMR spectrum of **3v** (400 MHz, Chloroform-*d*)



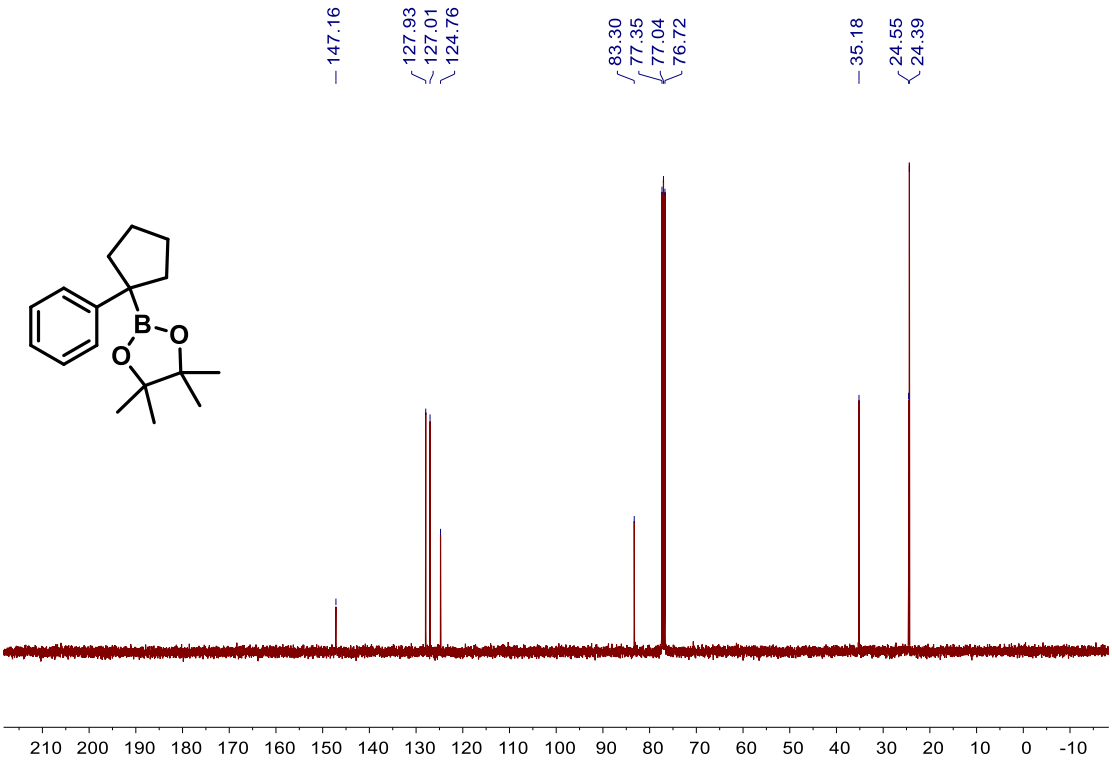
^{13}C NMR spectrum of **3v** (101 MHz, Chloroform-*d*)



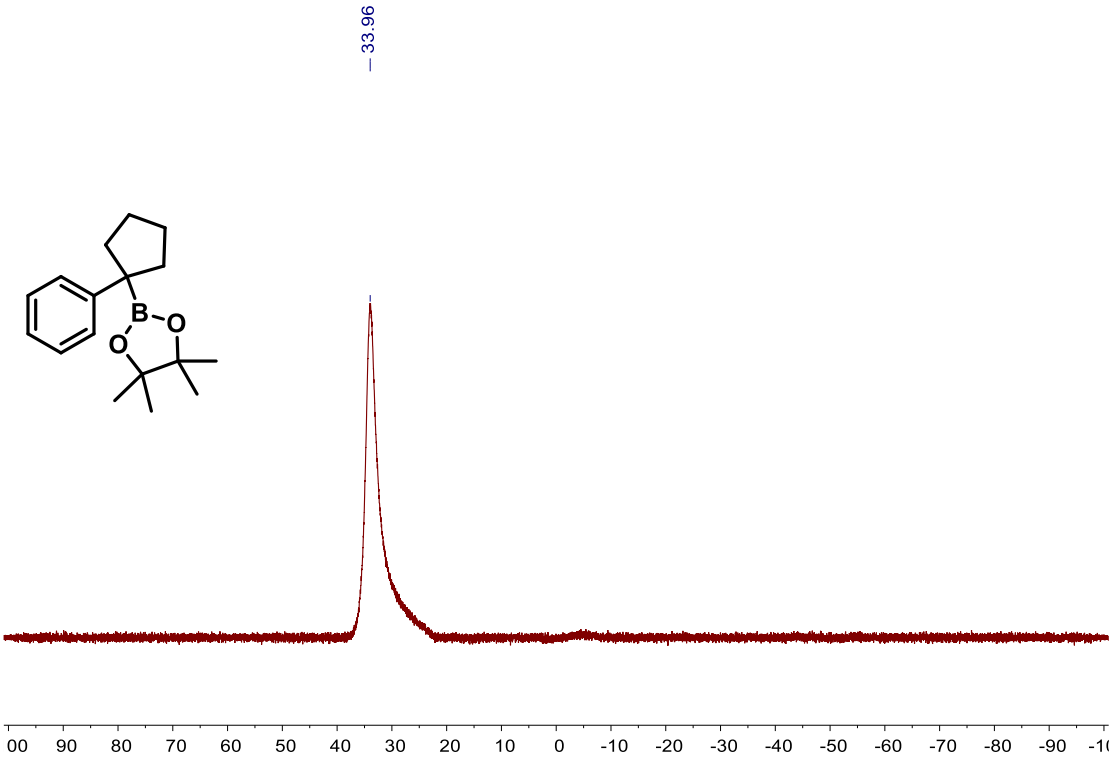
^{11}B NMR spectrum of **3v** (128 MHz Chloroform-*d*)



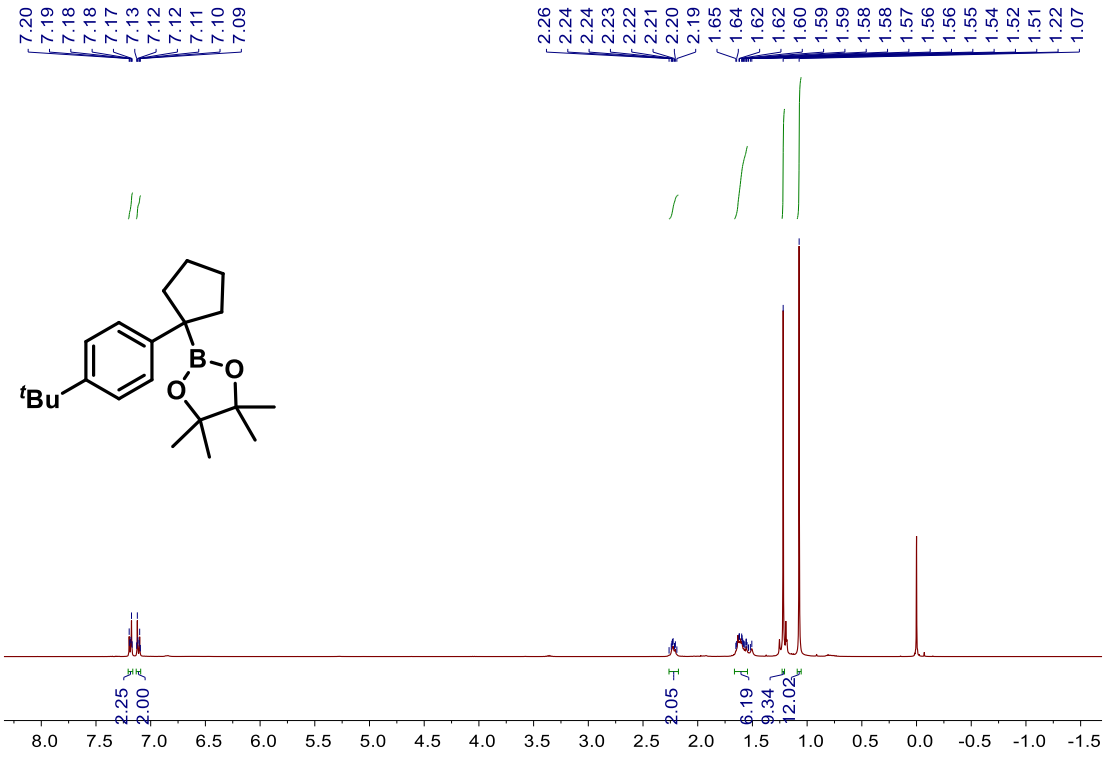
^{1}H NMR spectrum of **4a** (400 MHz, Chloroform-*d*)



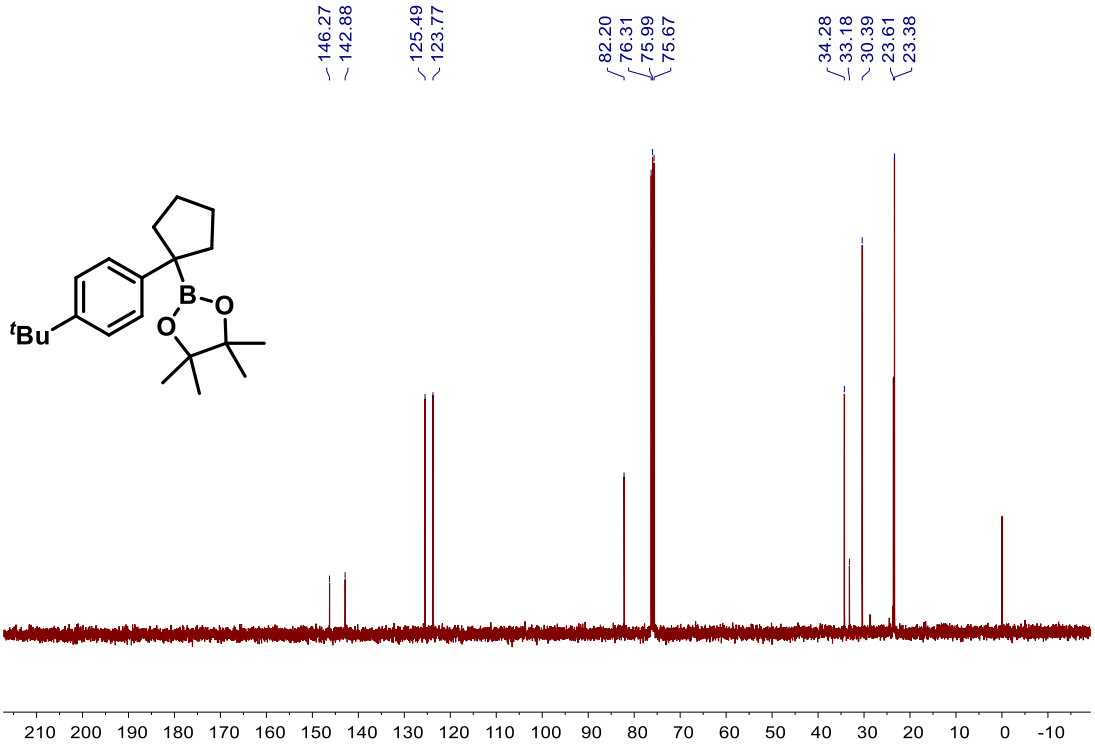
^{13}C NMR spectrum of **4a** (101 MHz, Chloroform-*d*)



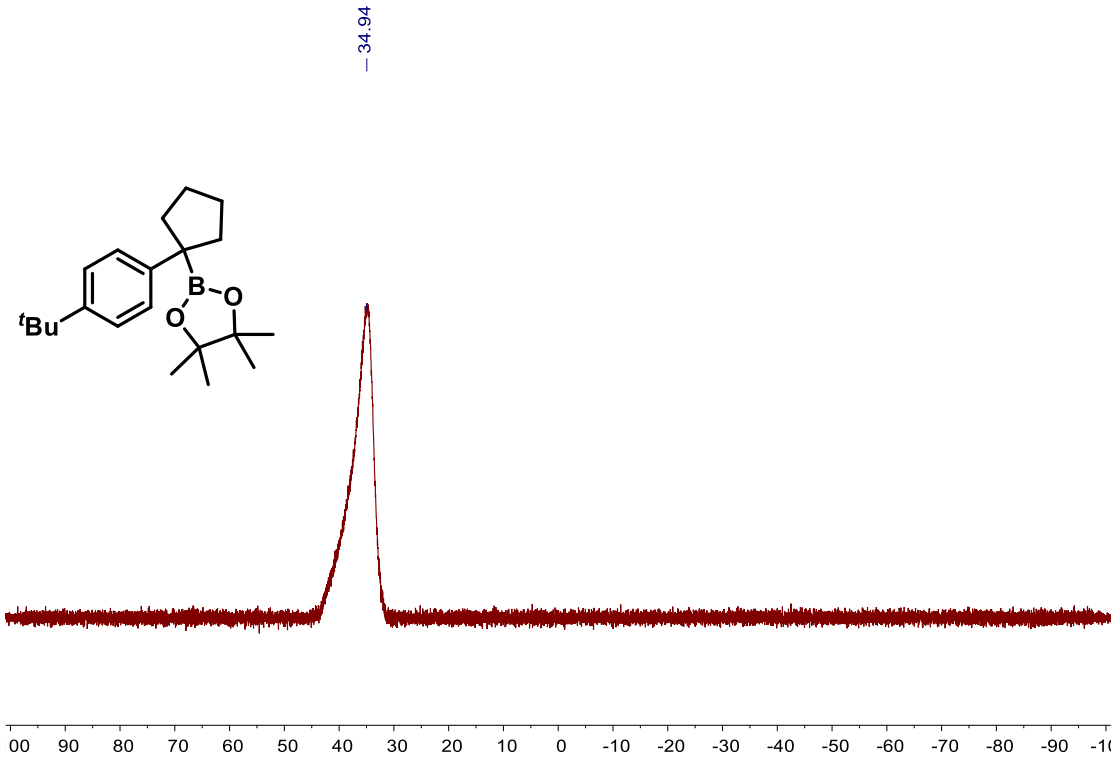
^{11}B NMR spectrum of **4a** (128 MHz Chloroform-*d*)



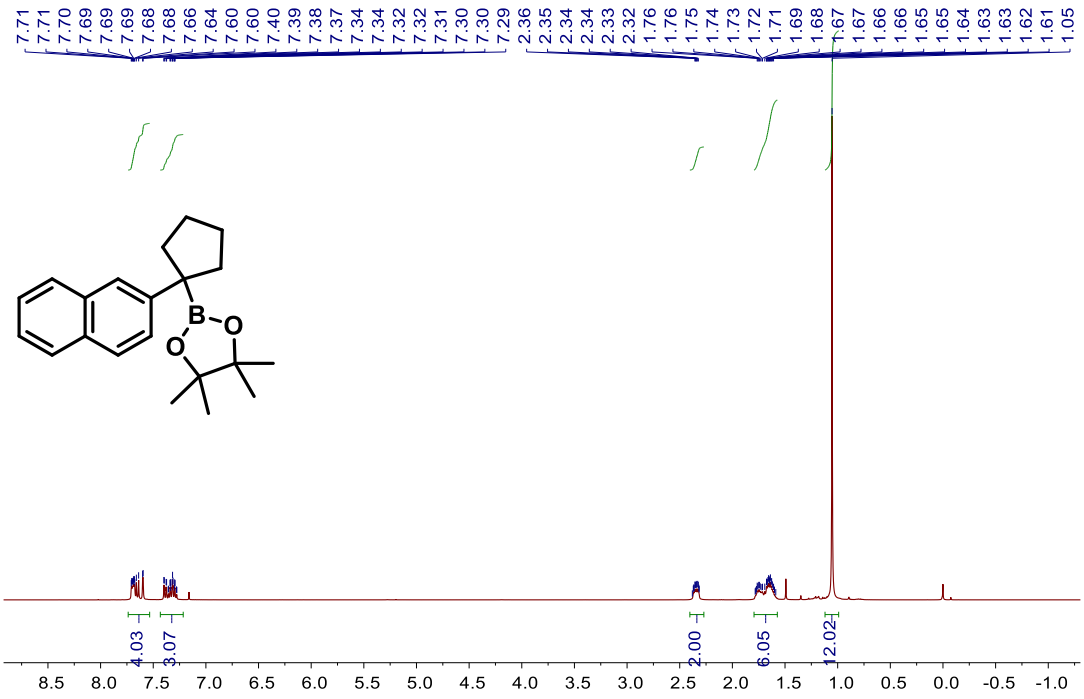
^{1}H NMR spectrum of **4b** (400 MHz, Chloroform-*d*)



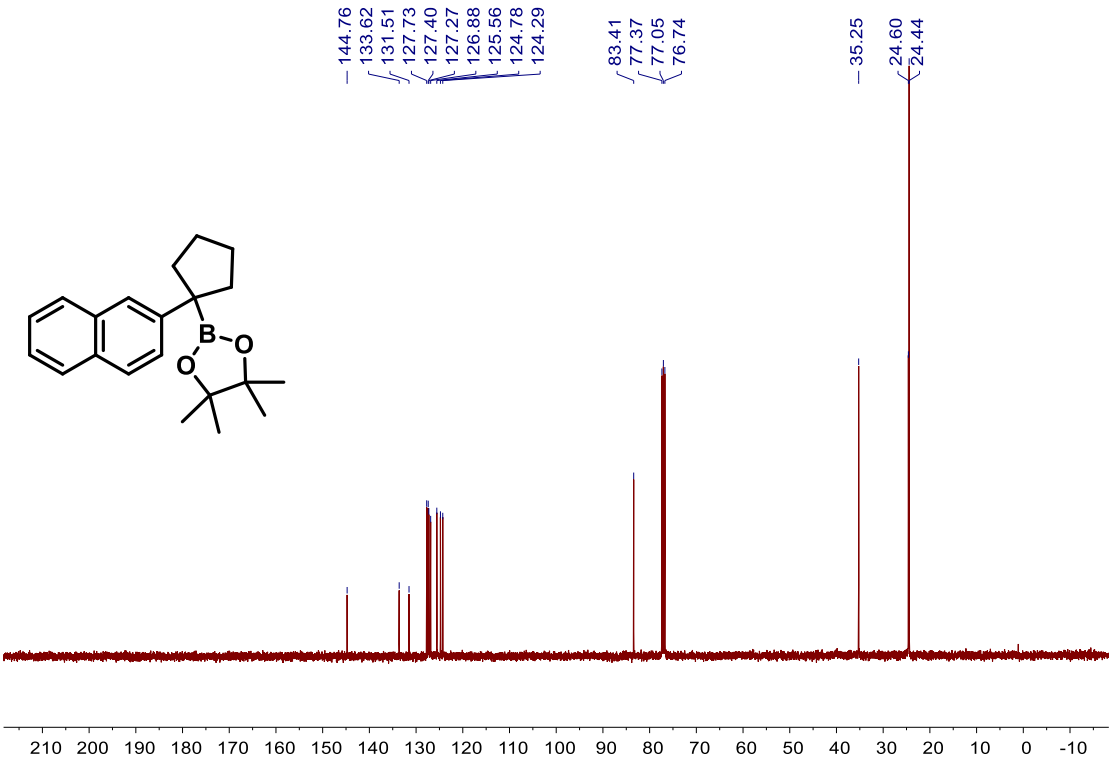
^{13}C NMR spectrum of **4b** (101 MHz, Chloroform-*d*)



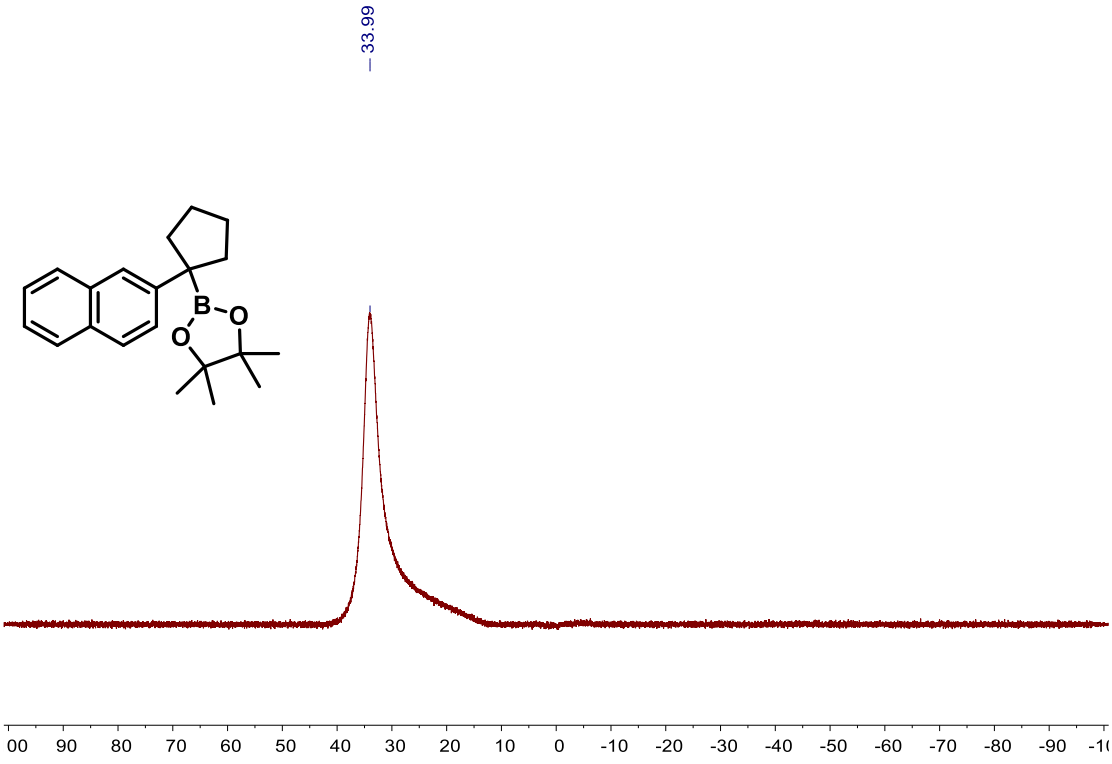
^{11}B NMR spectrum of **4b** (128 MHz Chloroform-*d*)



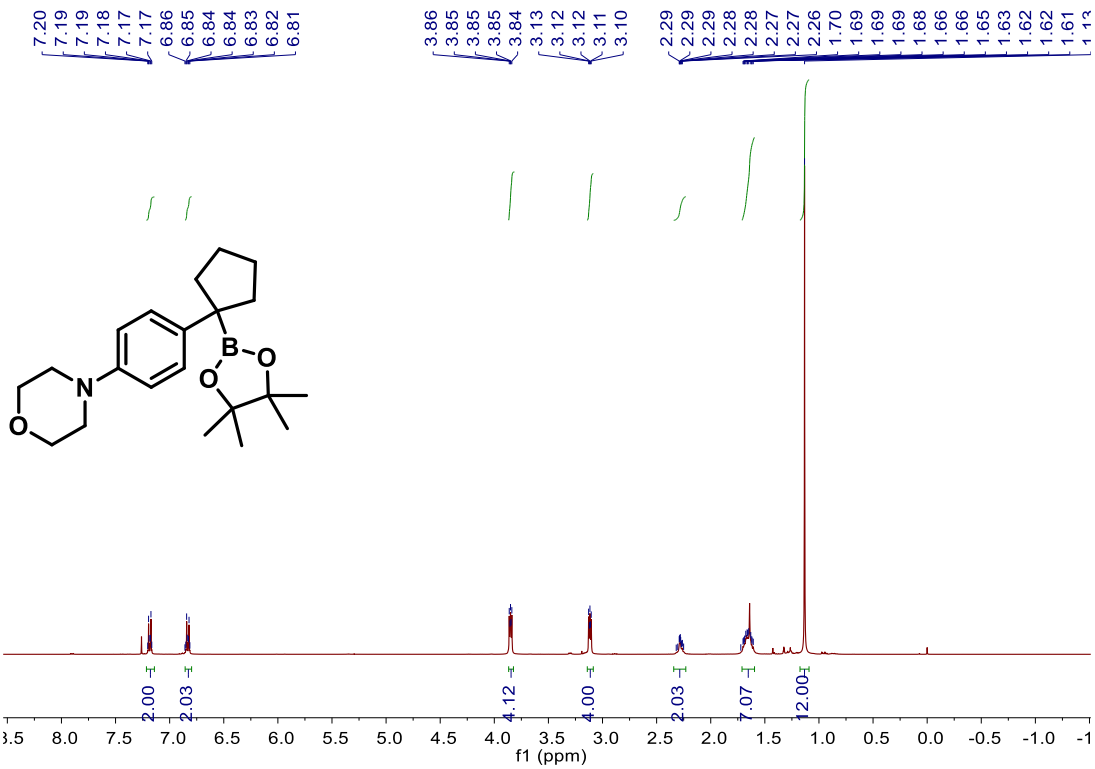
^{1}H NMR spectrum of **4c** (400 MHz, Chloroform-*d*)



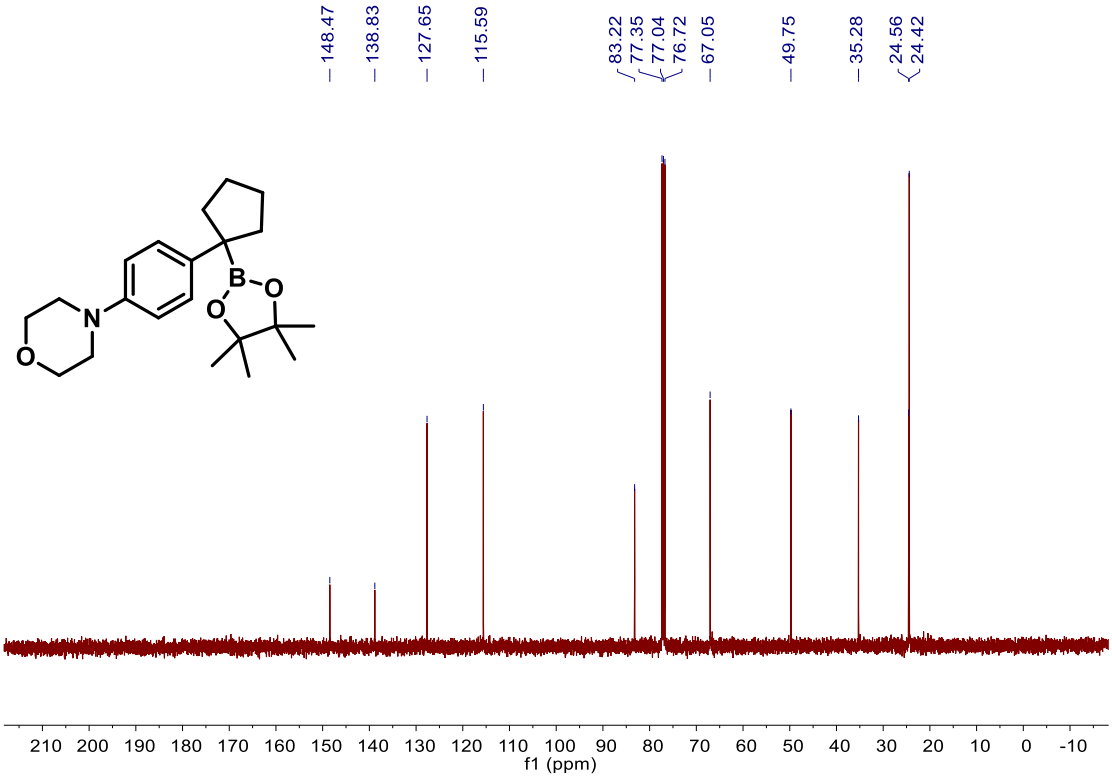
^{13}C NMR spectrum of **4c** (101 MHz, Chloroform-*d*)



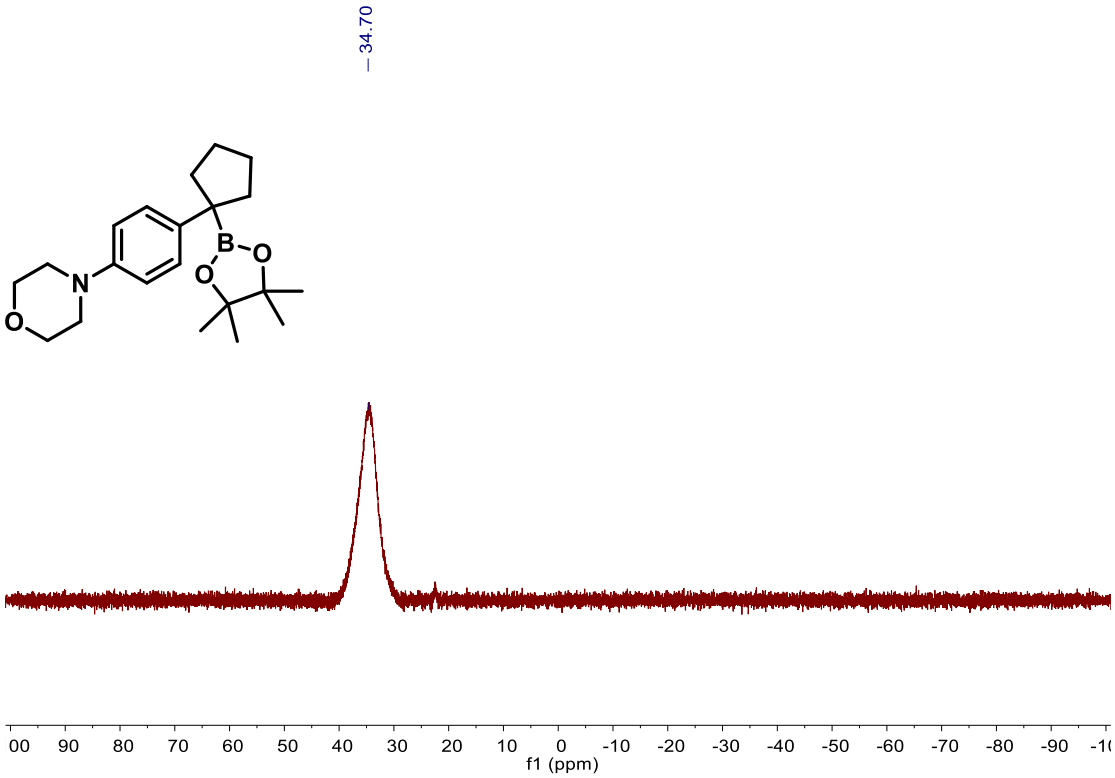
^{11}B NMR spectrum of **4c** (128 MHz Chloroform-*d*)



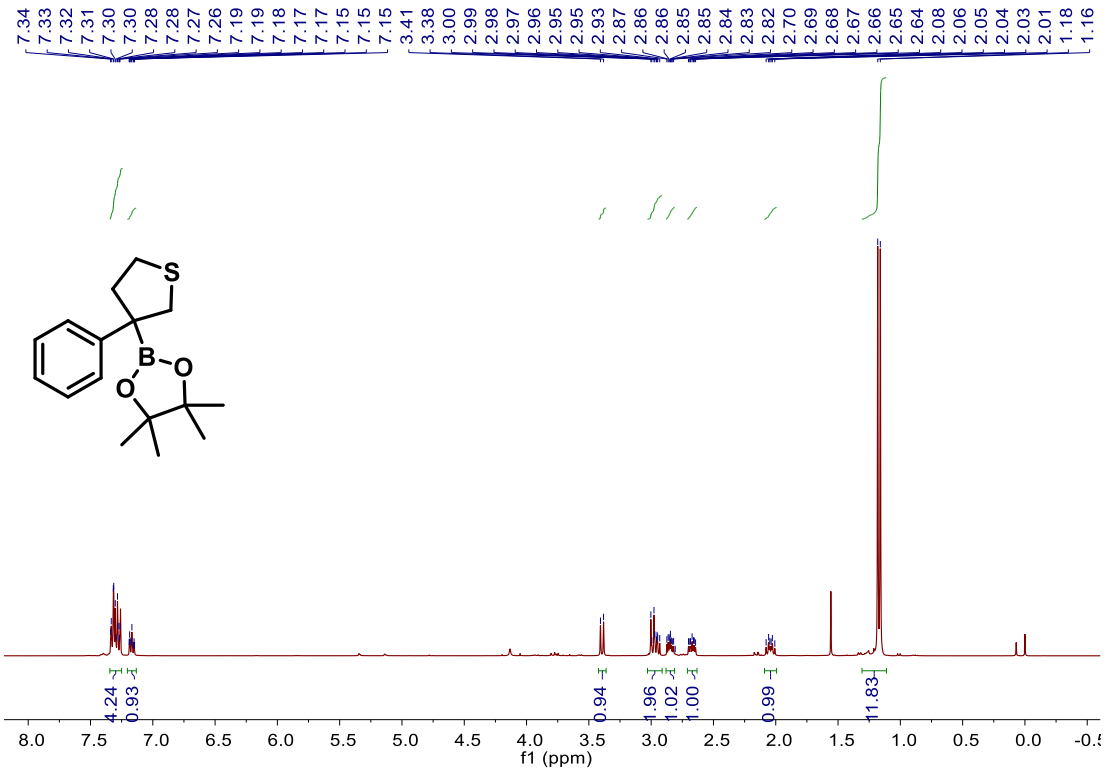
^{1}H NMR spectrum of **4d** (400 MHz, Chloroform-*d*)



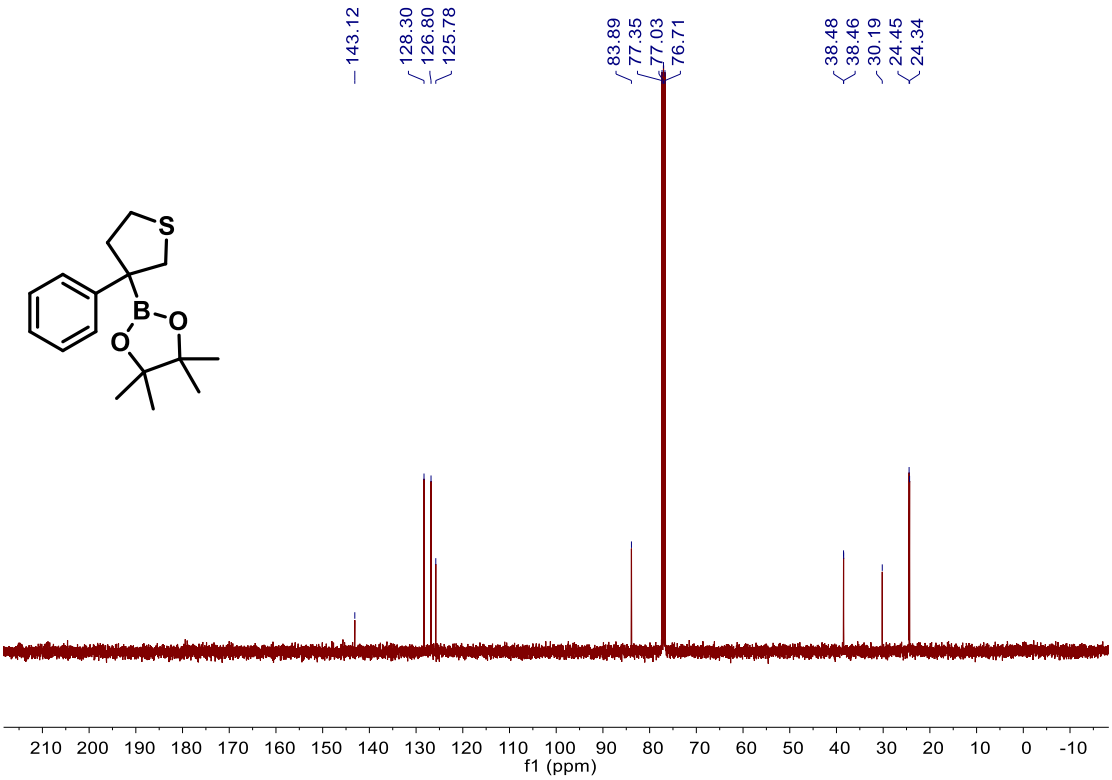
^{13}C NMR spectrum of **4d** (101 MHz, Chloroform-*d*)



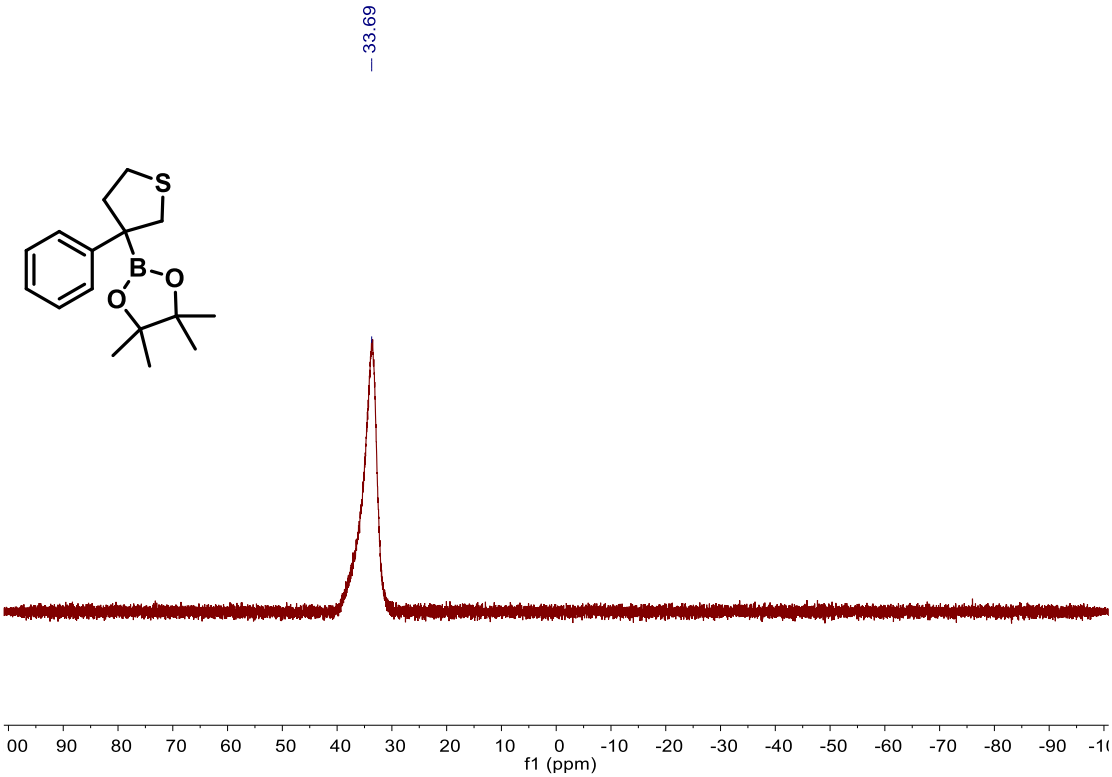
^{11}B NMR spectrum of **4d** (128 MHz Chloroform-*d*)



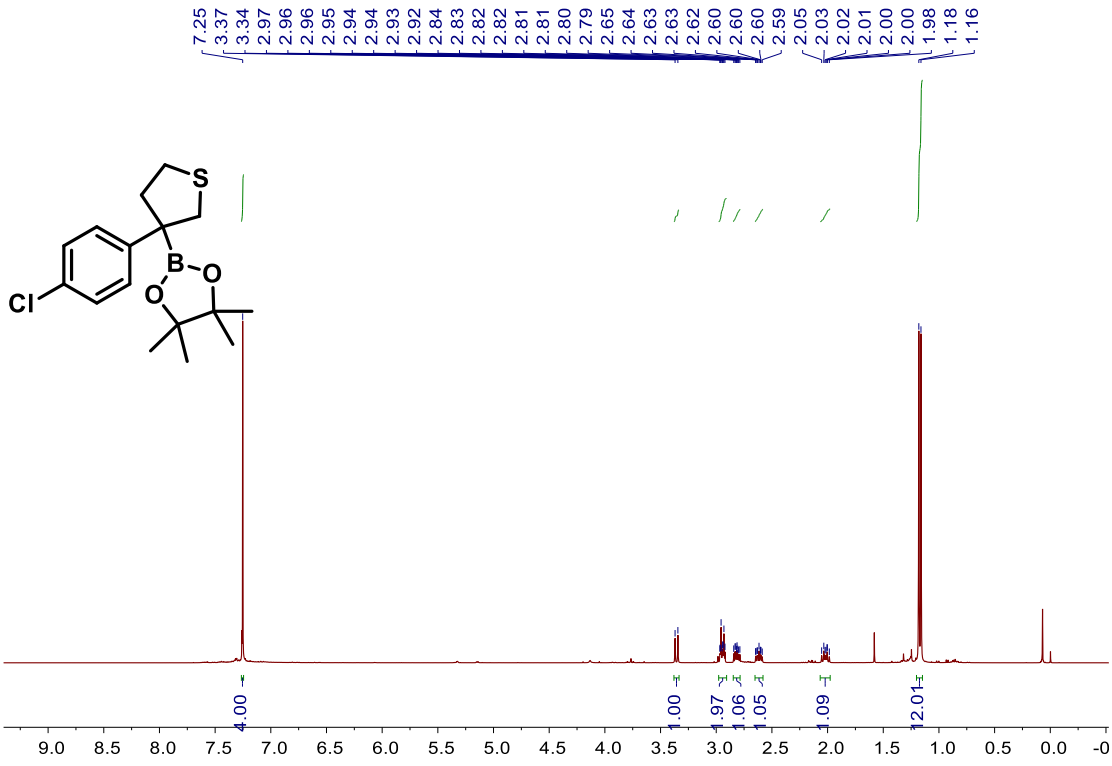
^{1}H NMR spectrum of **5a** (400 MHz, Chloroform-*d*)



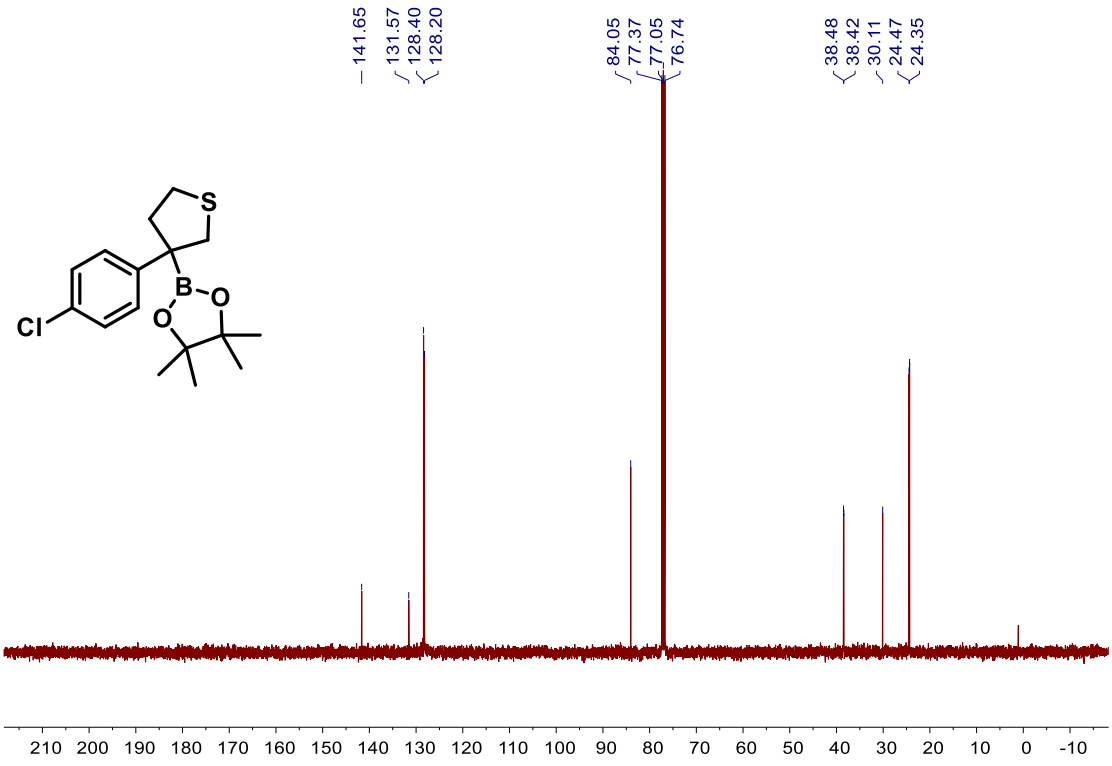
^{13}C NMR spectrum of **5a** (101 MHz, Chloroform-*d*)



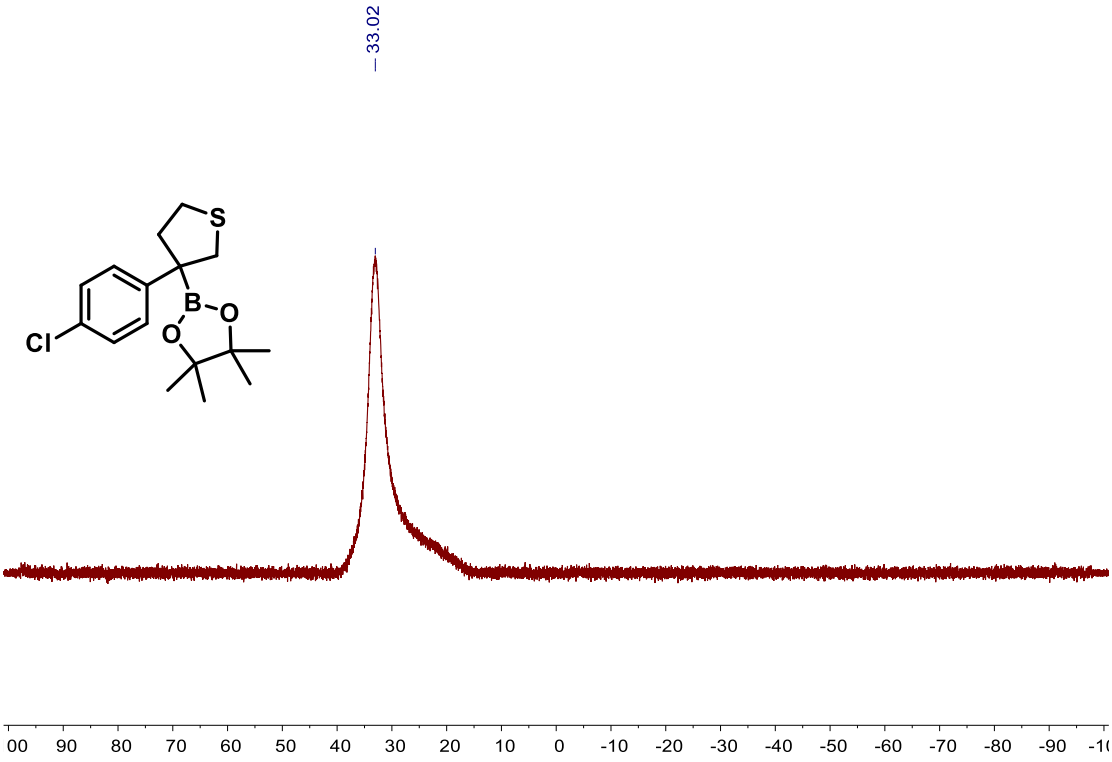
^{11}B NMR spectrum of **5a** (128 MHz Chloroform-*d*)



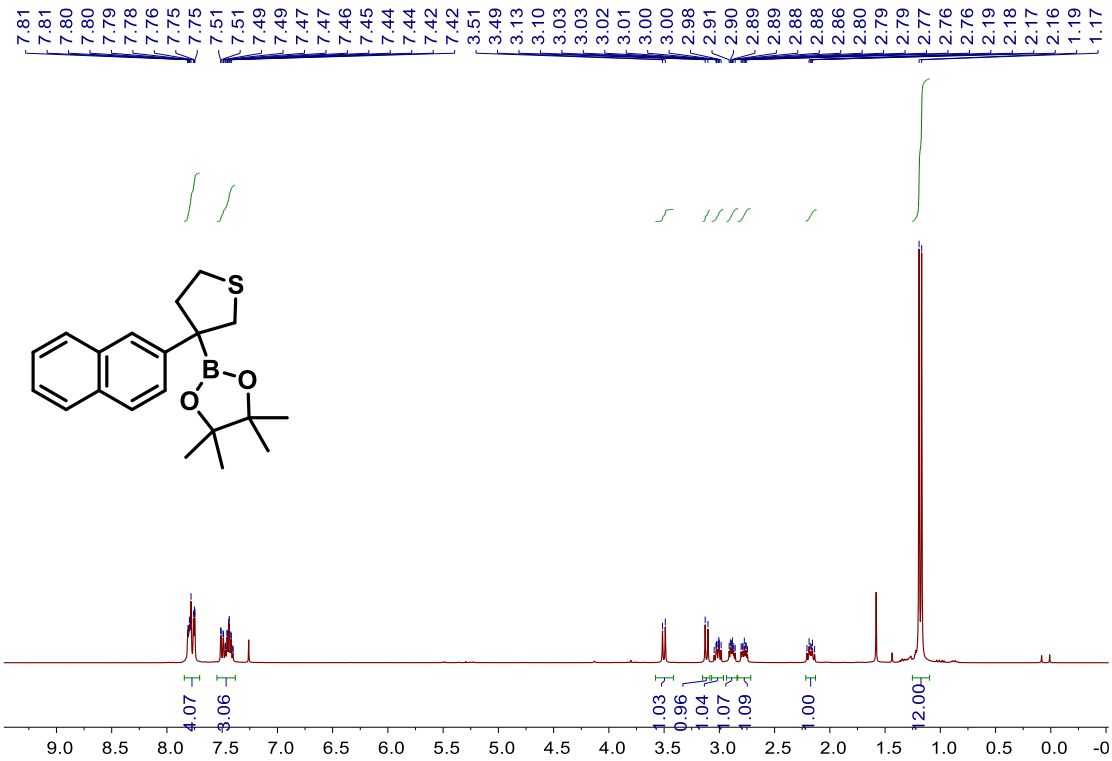
^{1}H NMR spectrum of **5b** (400 MHz, Chloroform-*d*)



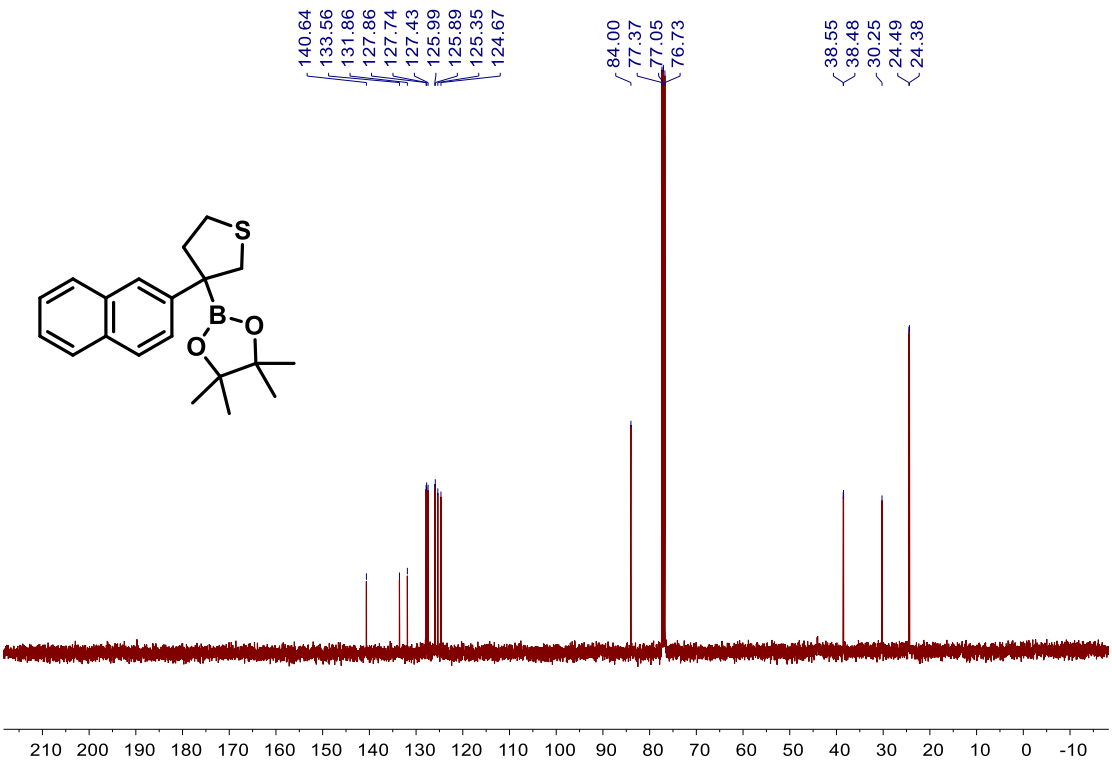
^{13}C NMR spectrum of **5b** (101 MHz, Chloroform-*d*)



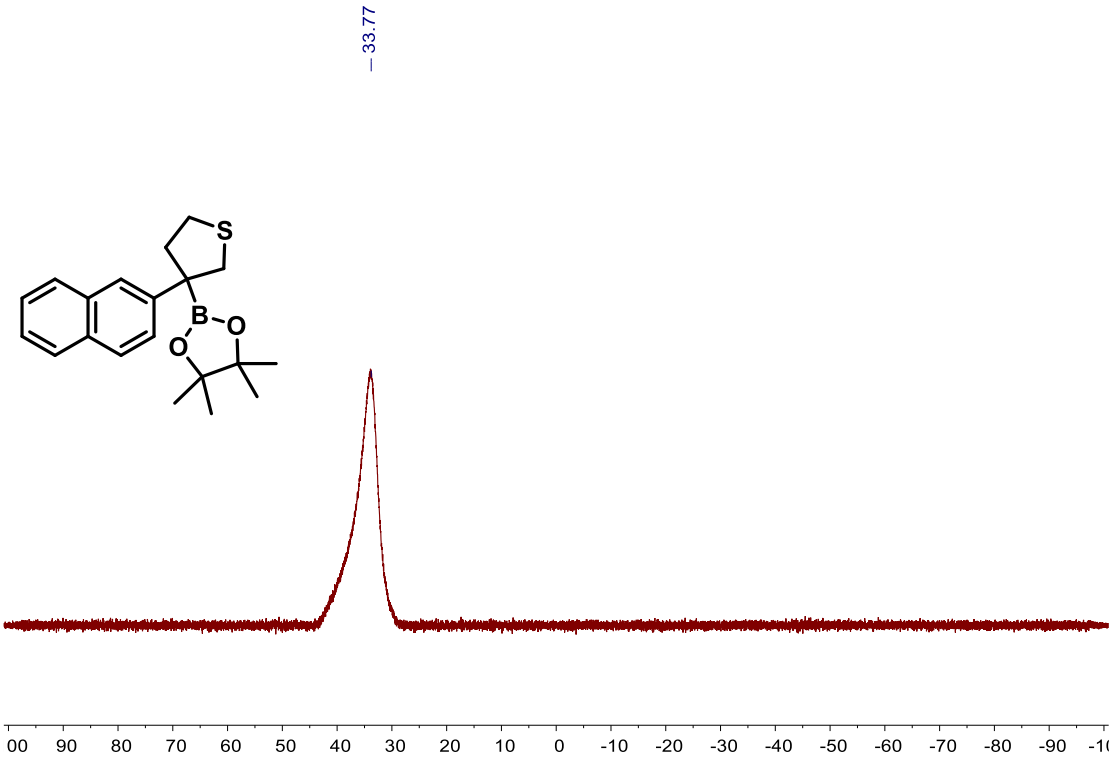
^{11}B NMR spectrum of **5b** (128 MHz Chloroform-*d*)



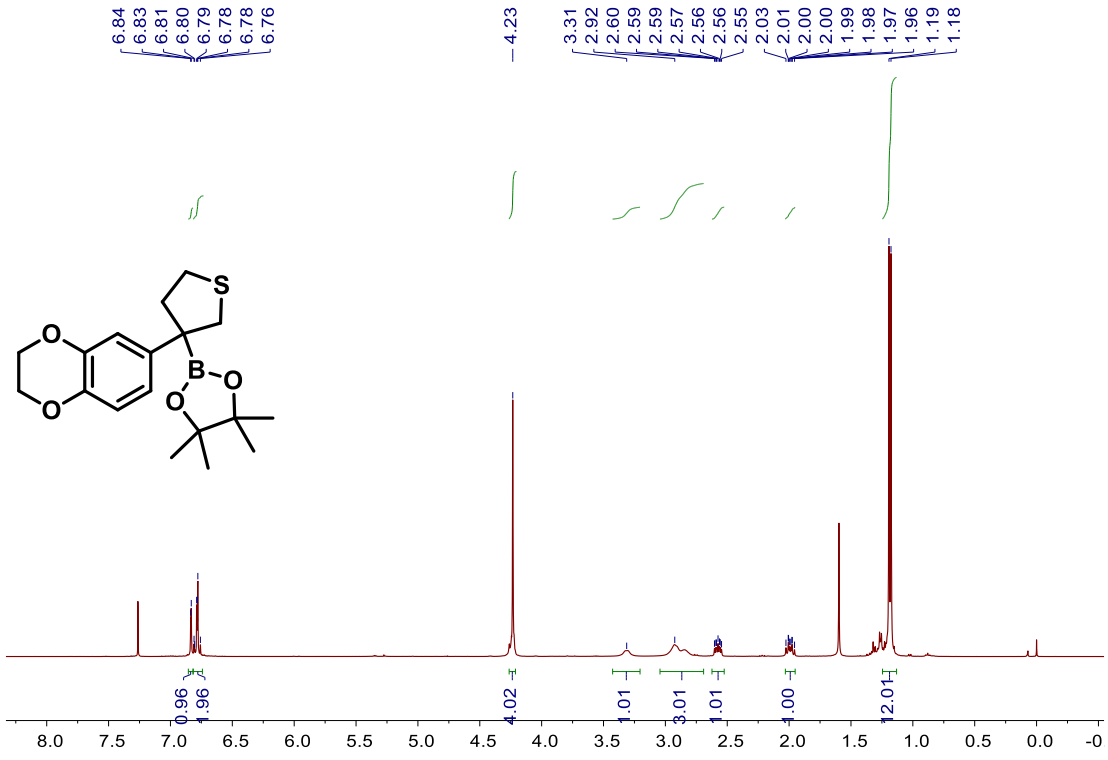
^{1}H NMR spectrum of **5c** (400 MHz, Chloroform-*d*)



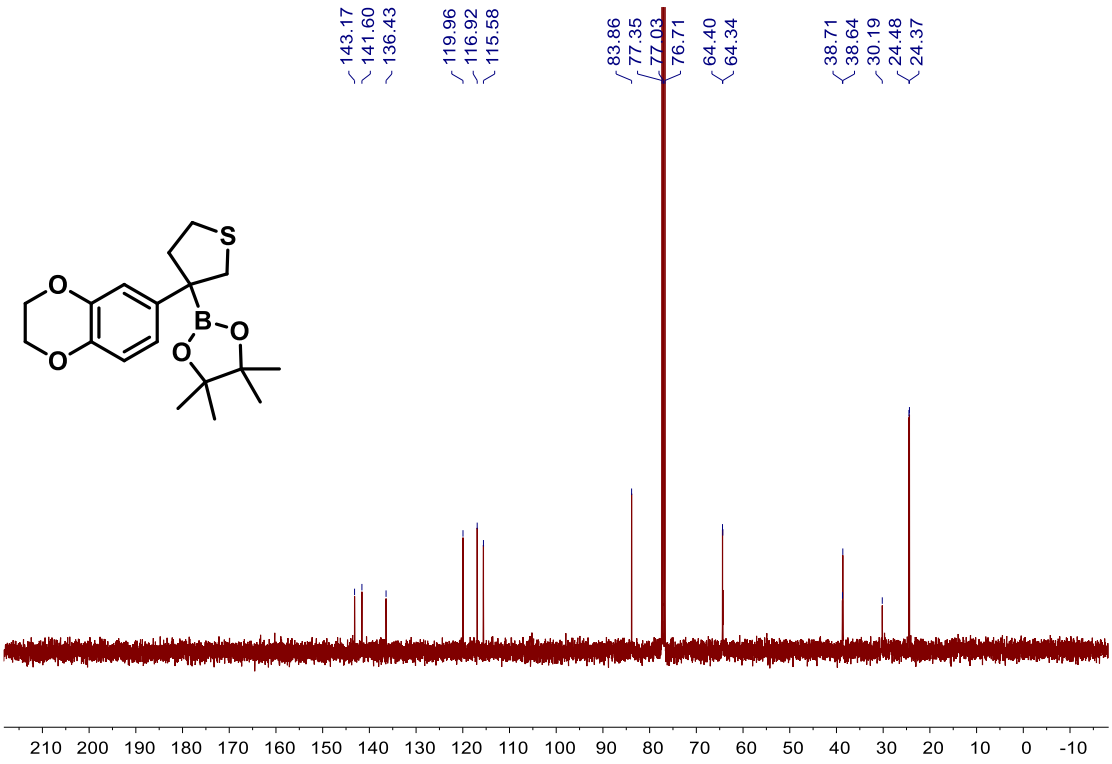
^{13}C NMR spectrum of **5c** (101 MHz, Chloroform-*d*)



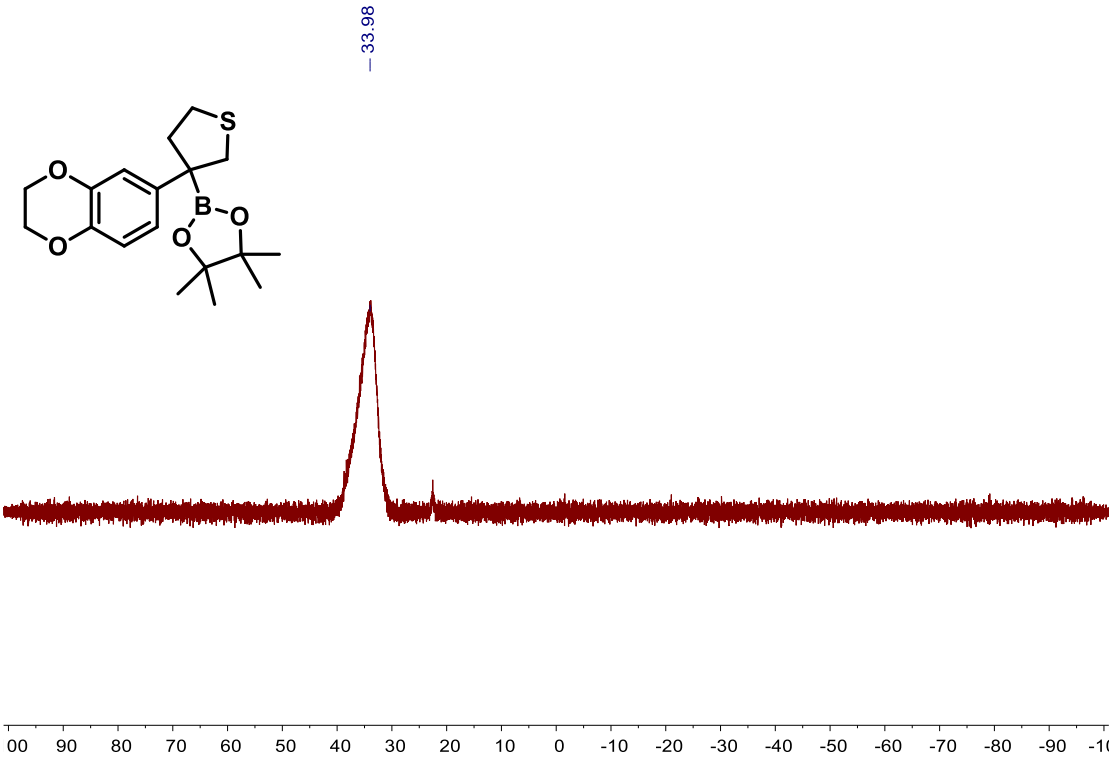
^{11}B NMR spectrum of **5c** (128 MHz Chloroform-*d*)



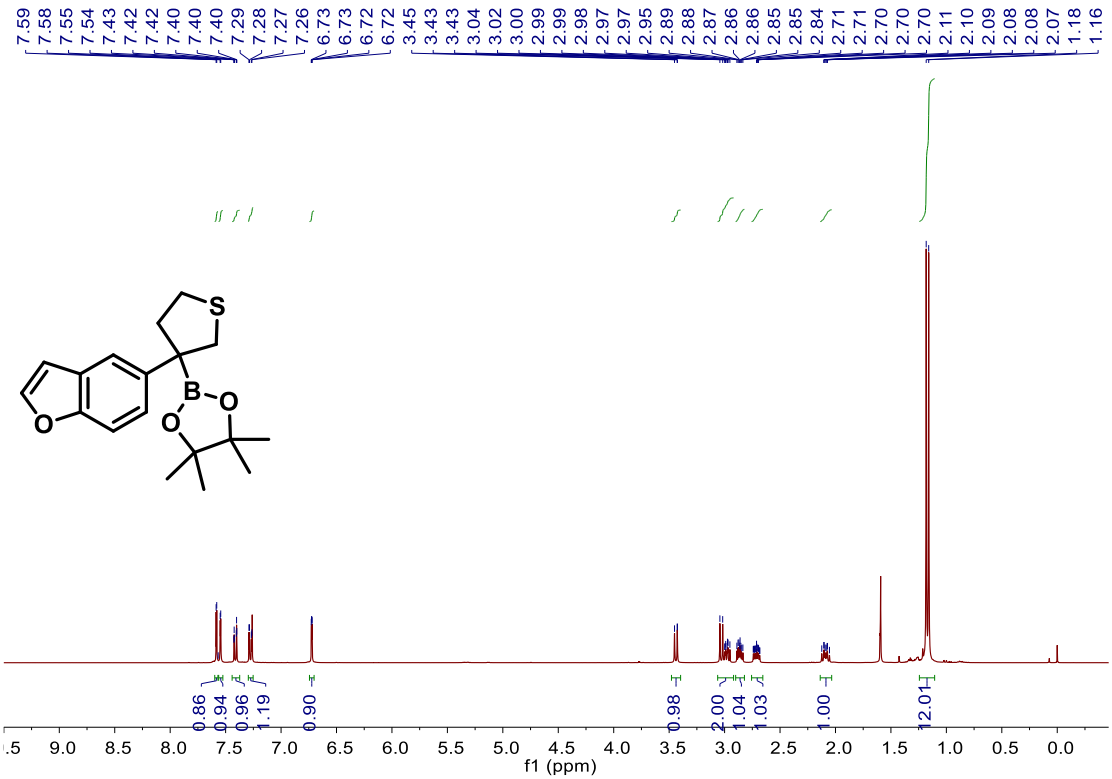
^{1}H NMR spectrum of **5d** (400 MHz, Chloroform-*d*)



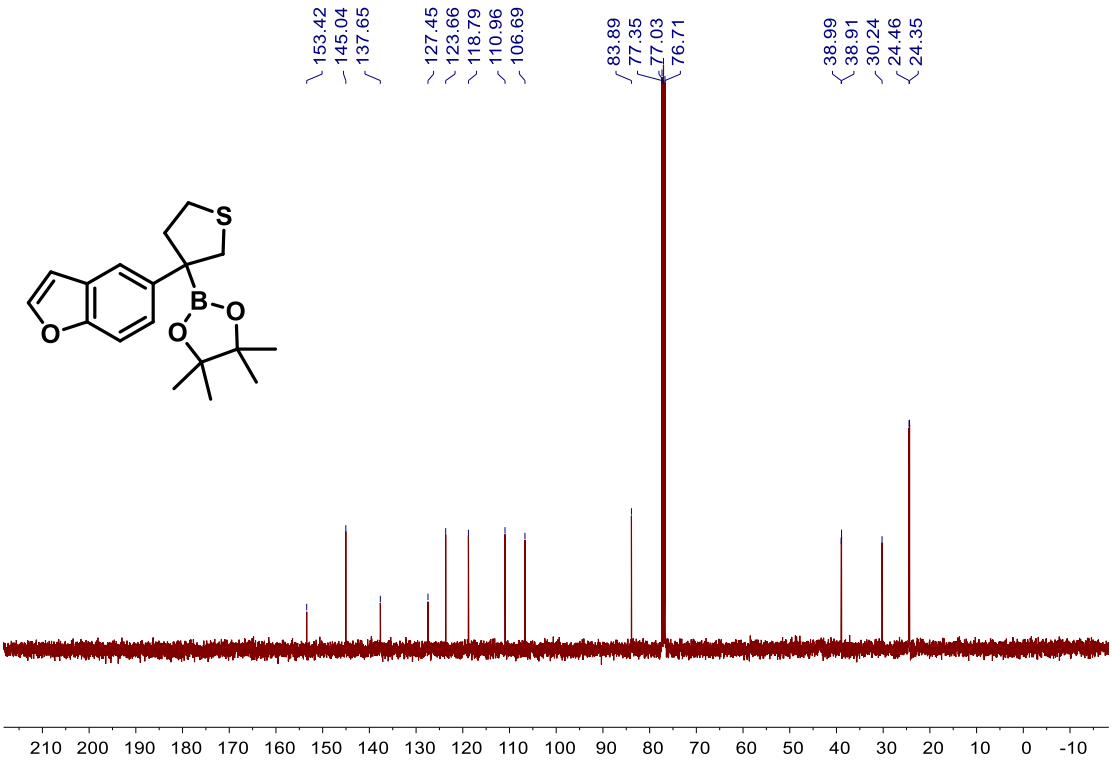
^{13}C NMR spectrum of **5d** (101 MHz, Chloroform-*d*)



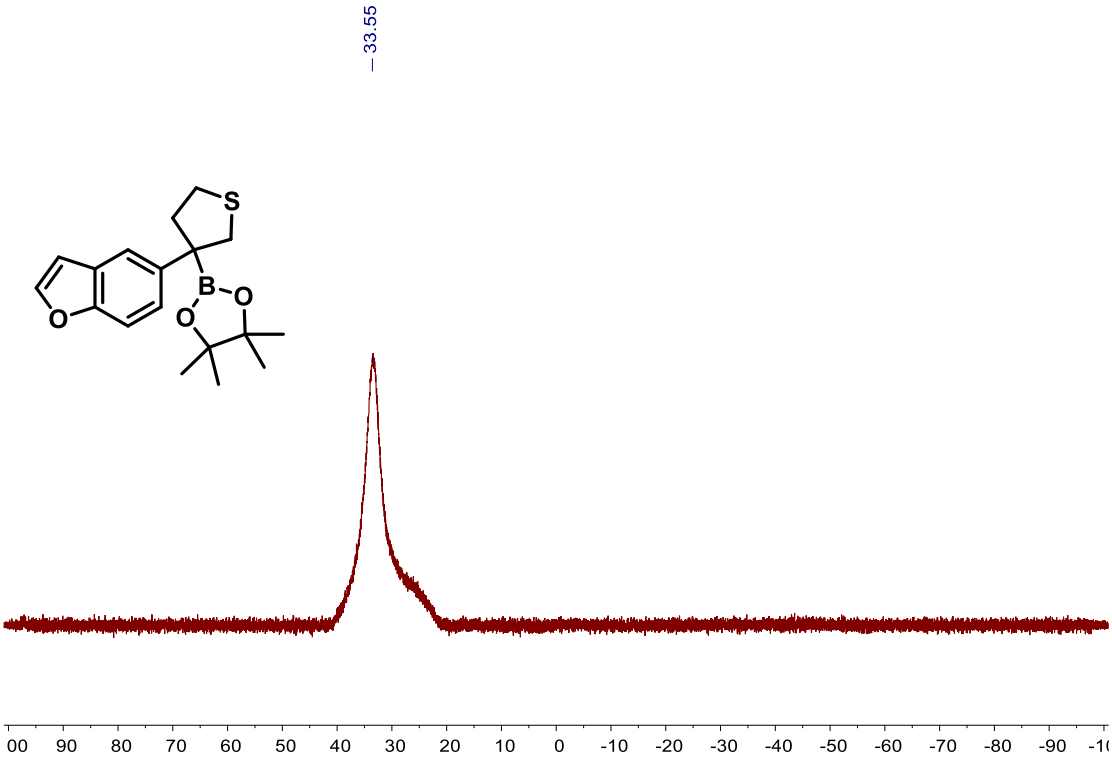
^{11}B NMR spectrum of **5d** (128 MHz Chloroform-*d*)



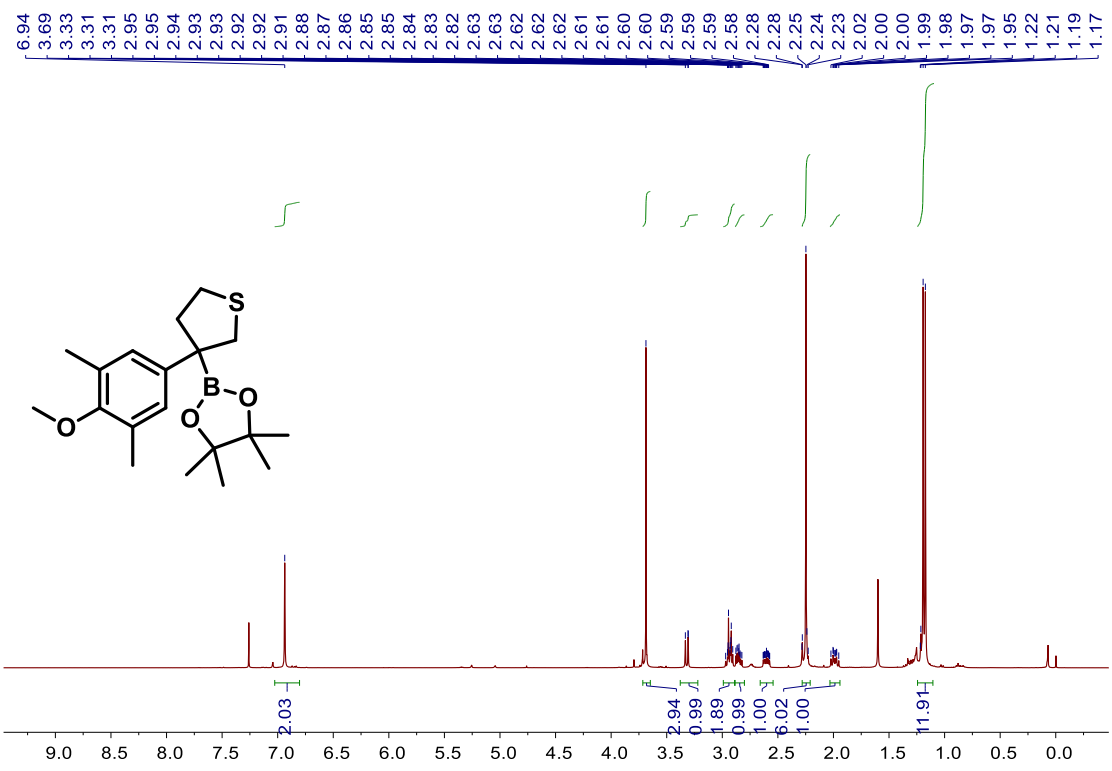
^{1}H NMR spectrum of **5e** (400 MHz, Chloroform-*d*)



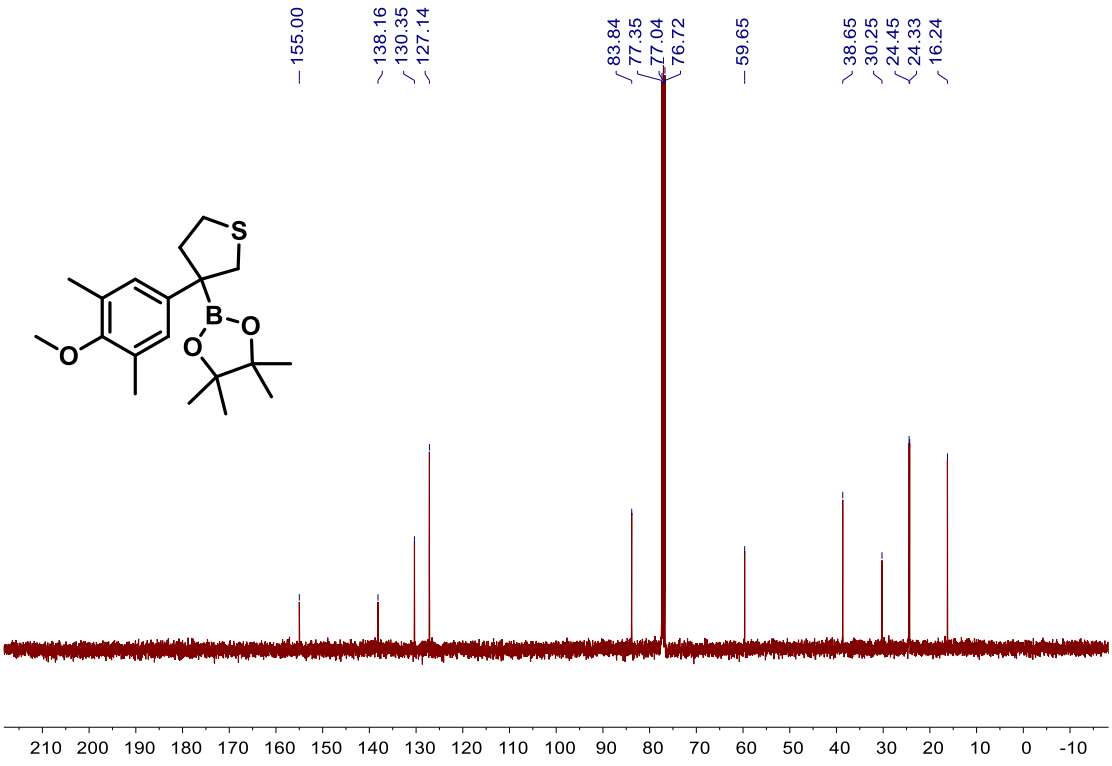
^{13}C NMR spectrum of **5e** (101 MHz, Chloroform-*d*)



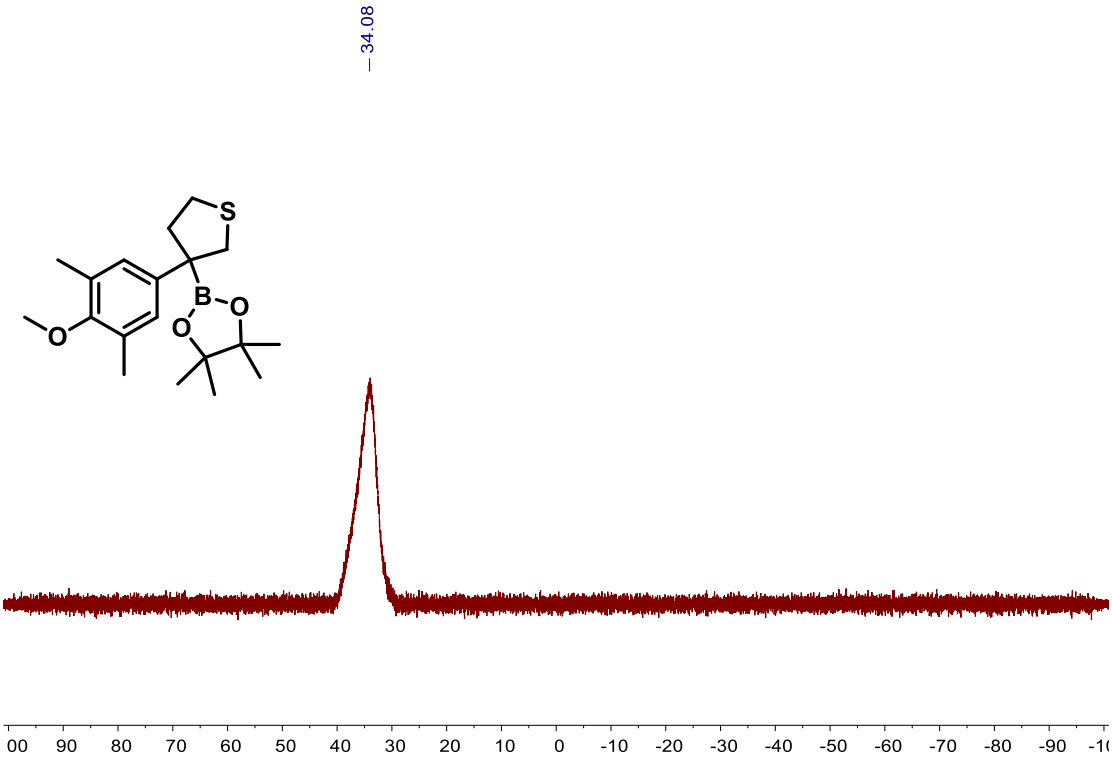
^{11}B NMR spectrum of **5e** (128 MHz Chloroform-*d*)



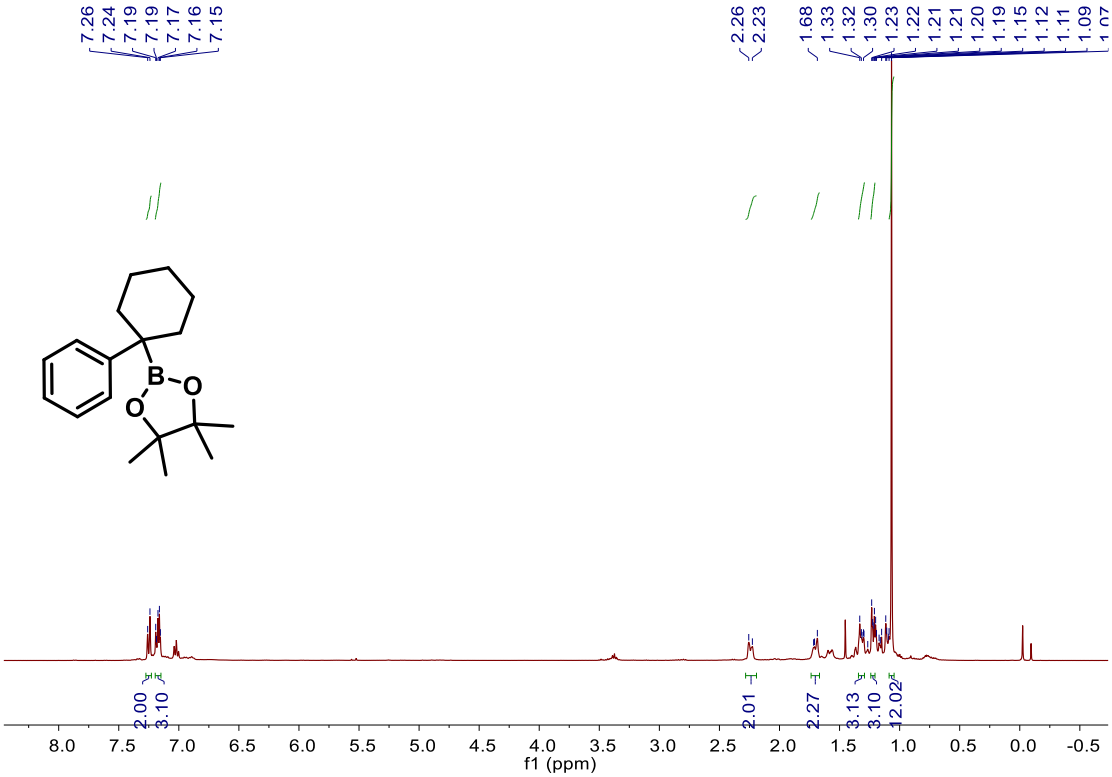
^{1}H NMR spectrum of **5f** (400 MHz, Chloroform-*d*)



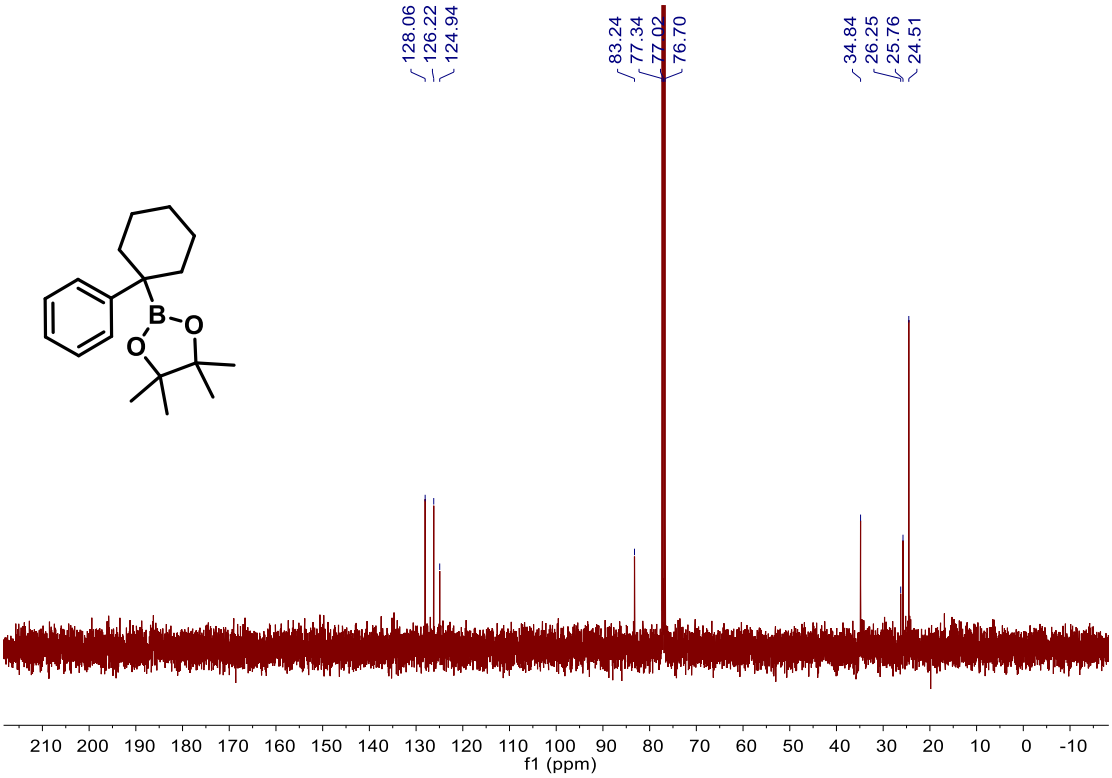
^{13}C NMR spectrum of **5f** (101 MHz, Chloroform-*d*)



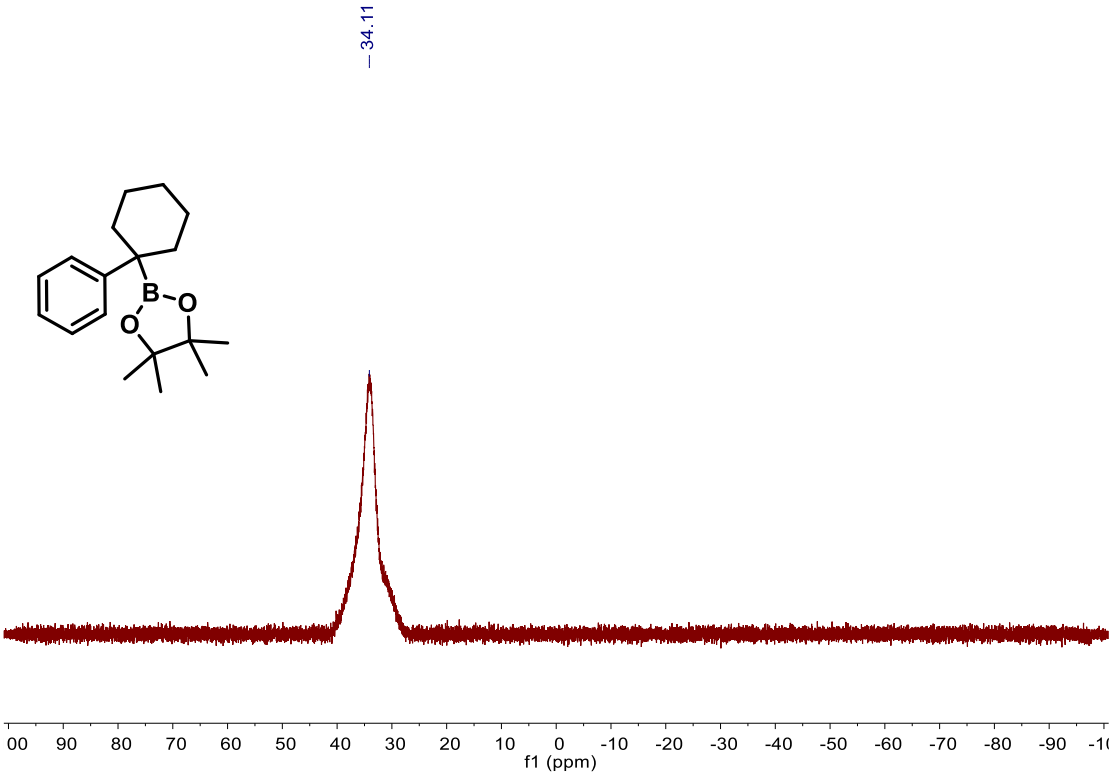
^{11}B NMR spectrum of **5f** (128 MHz Chloroform-*d*)



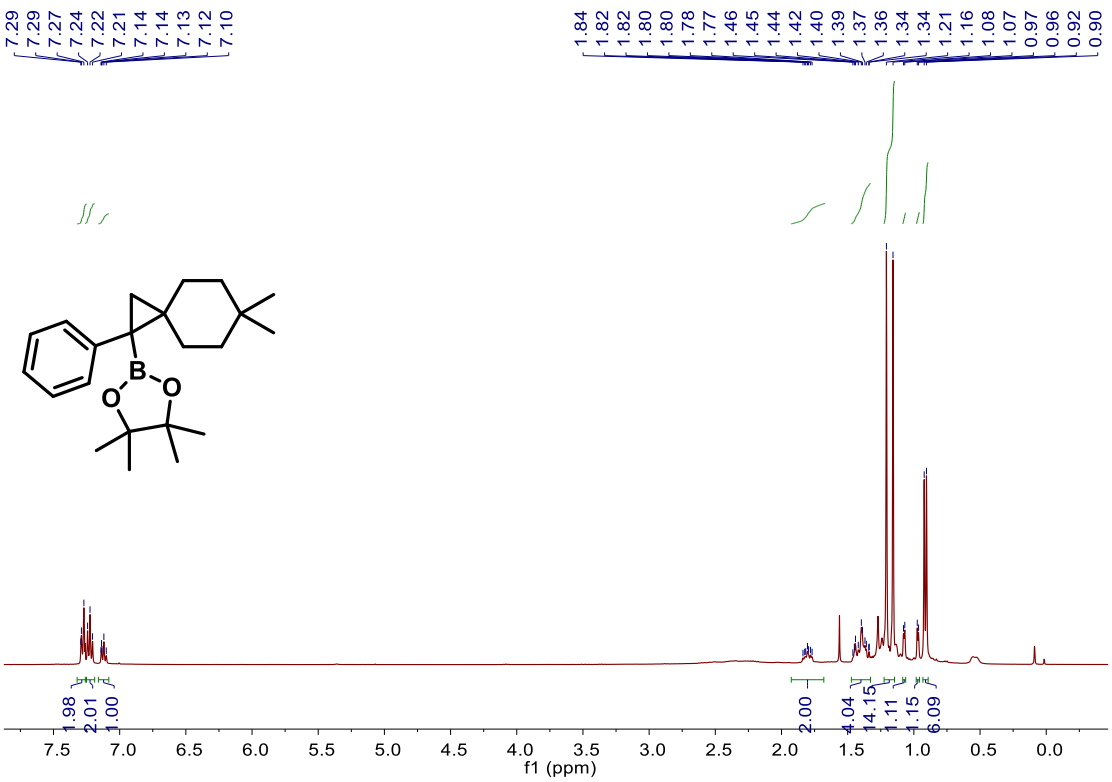
^{1}H NMR spectrum of **6a** (400 MHz, Chloroform-*d*)



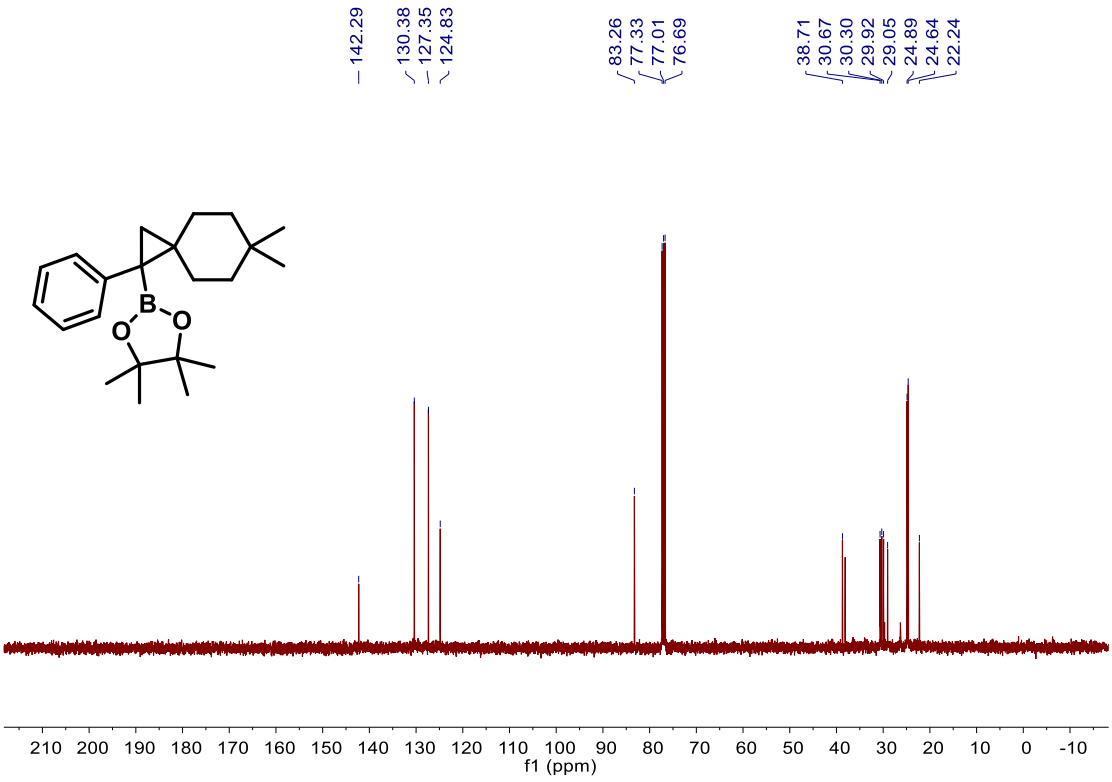
^{13}C NMR spectrum of **6a** (101 MHz, Chloroform-*d*)



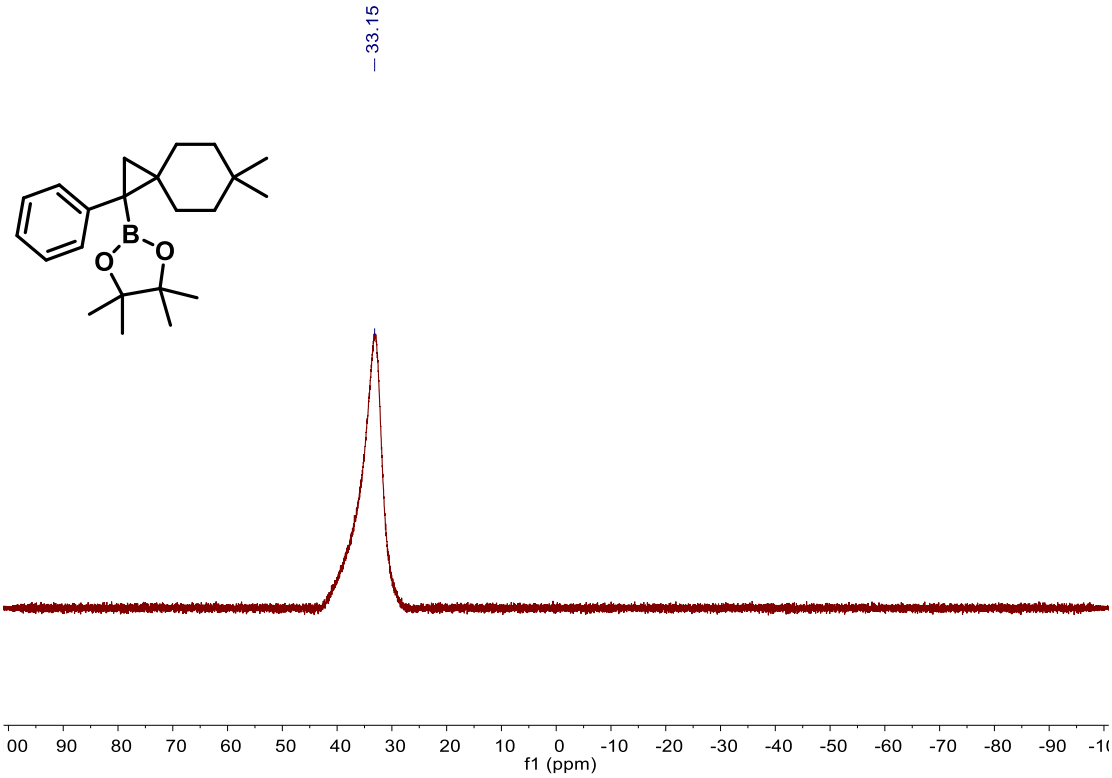
^{11}B NMR spectrum of **6a** (128 MHz Chloroform-*d*)



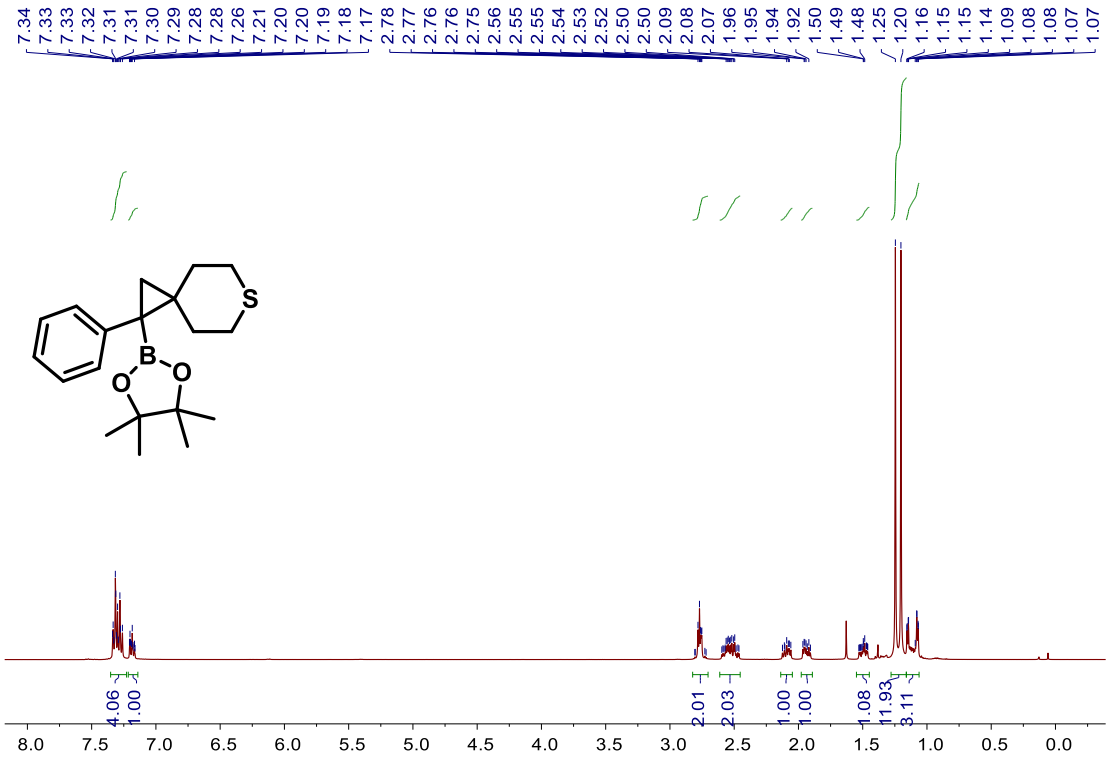
^{1}H NMR spectrum of **7a** (400 MHz, Chloroform-*d*)



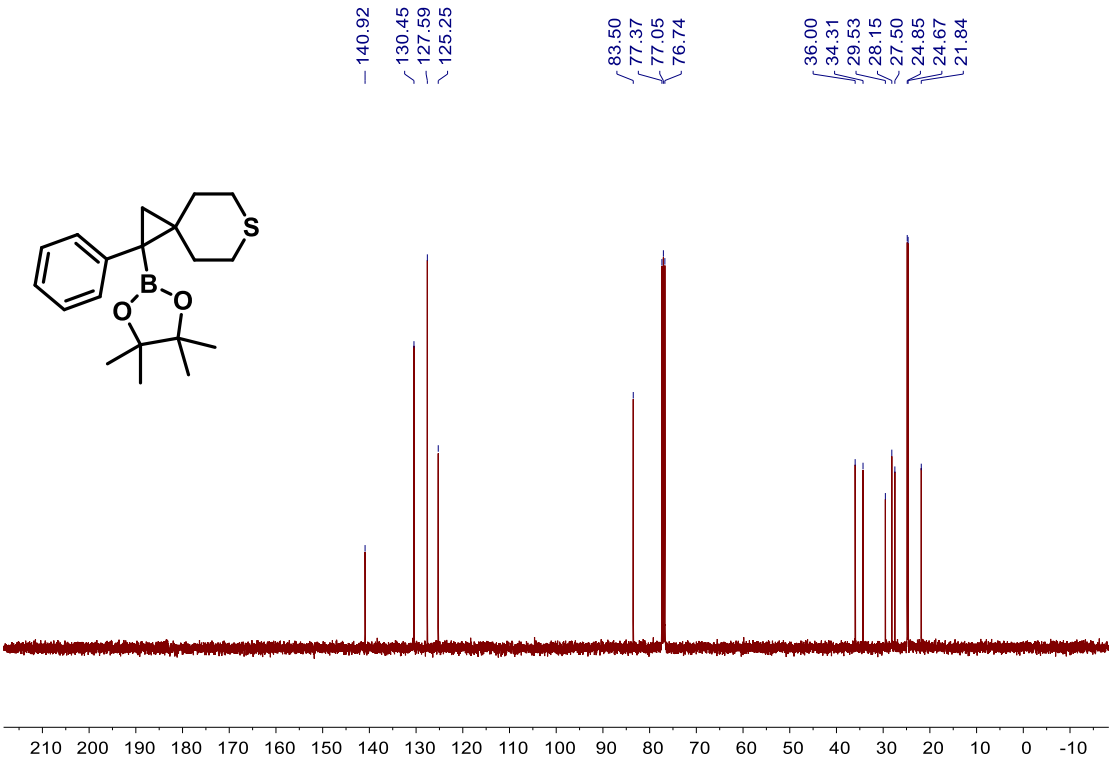
^{13}C NMR spectrum of **7a** (101 MHz, Chloroform-*d*)



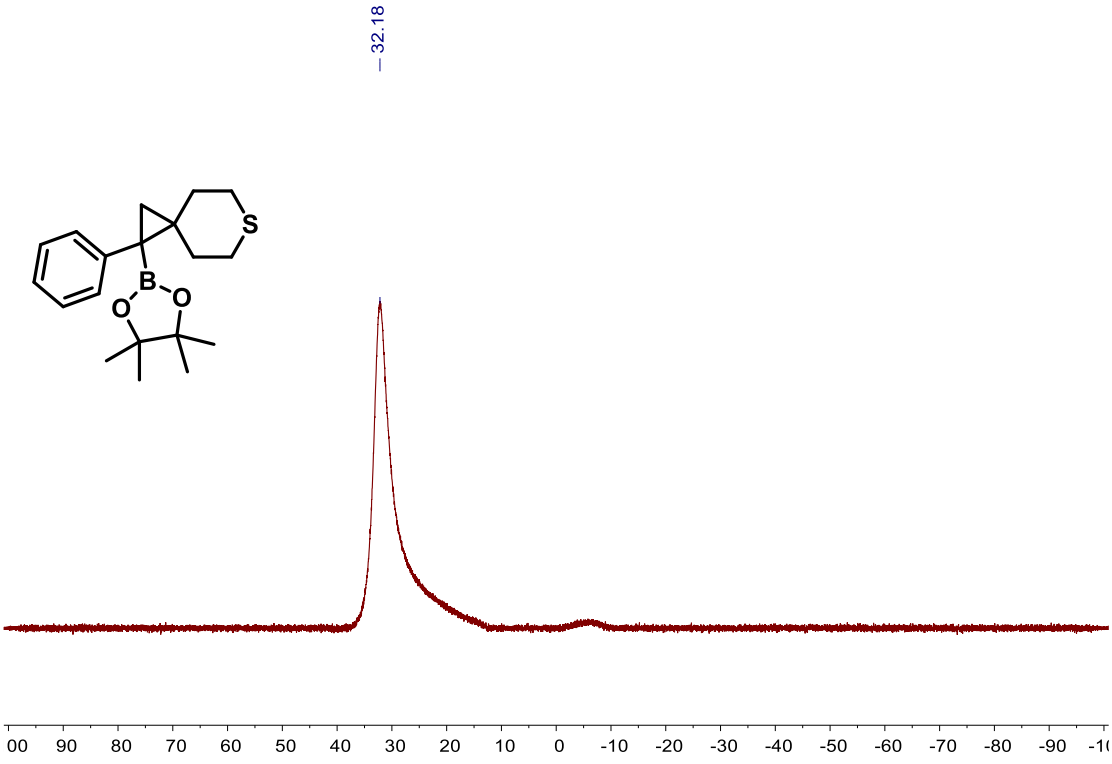
^{11}B NMR spectrum of **7a** (128 MHz Chloroform-*d*)



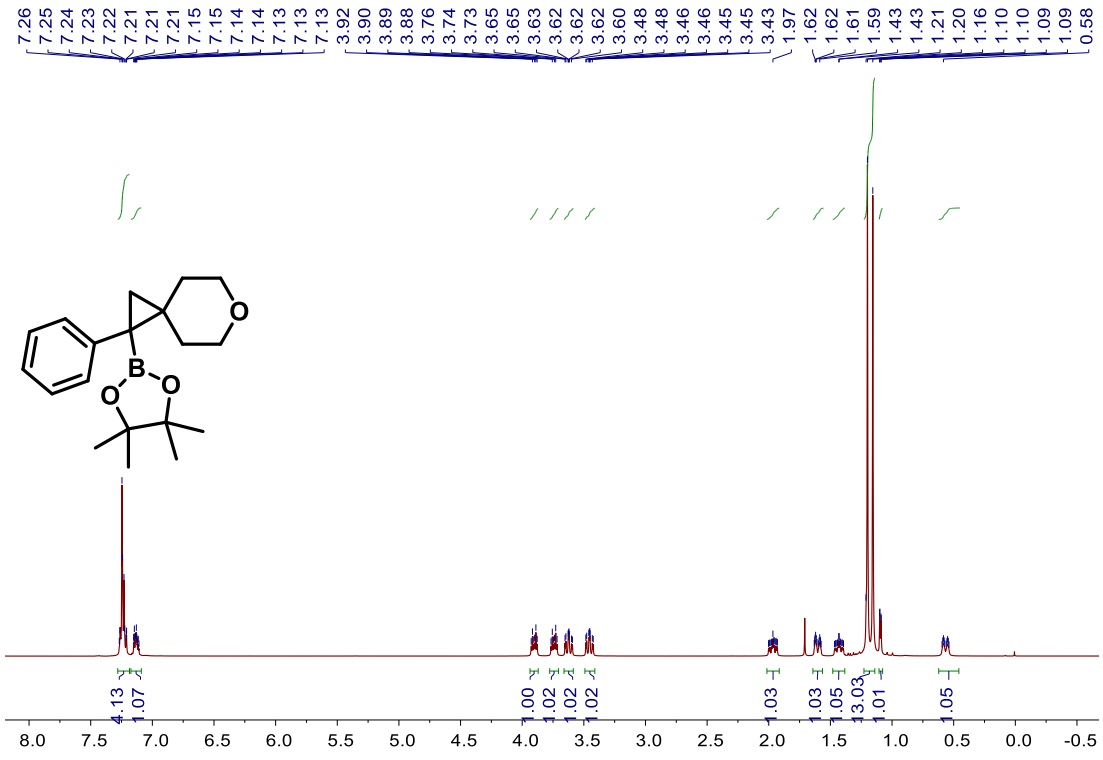
^{1}H NMR spectrum of **8a** (400 MHz, Chloroform-*d*)



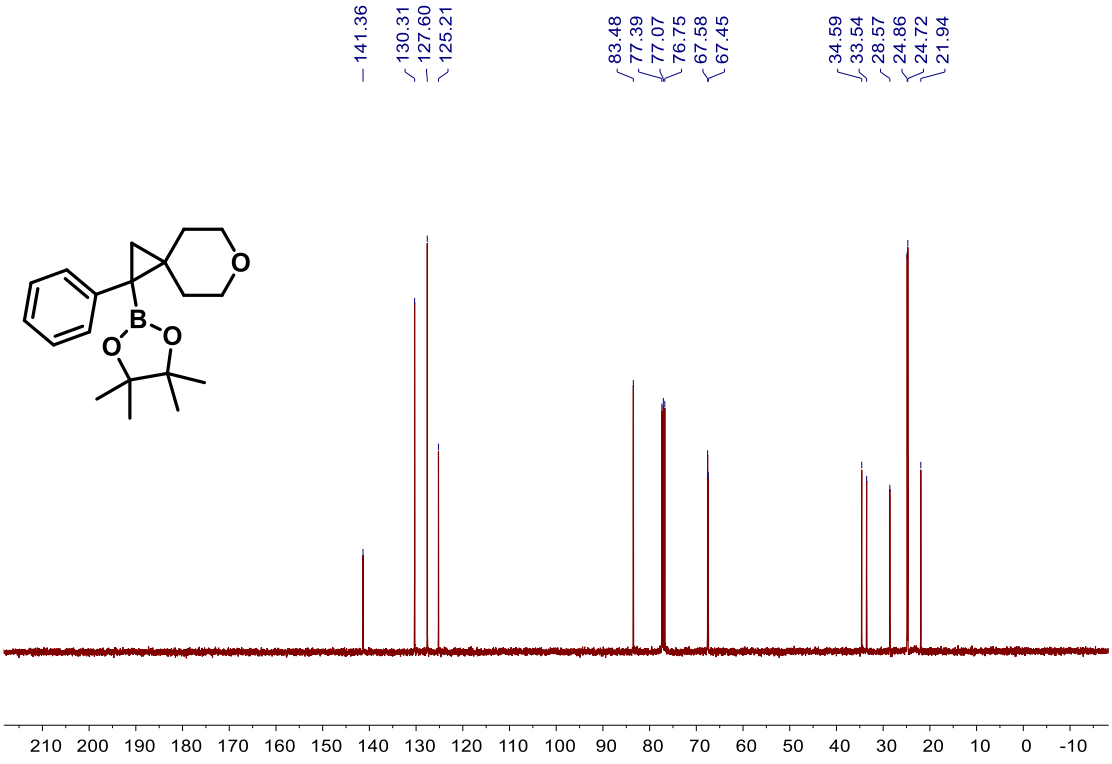
^{13}C NMR spectrum of **8a** (101 MHz, Chloroform-*d*)



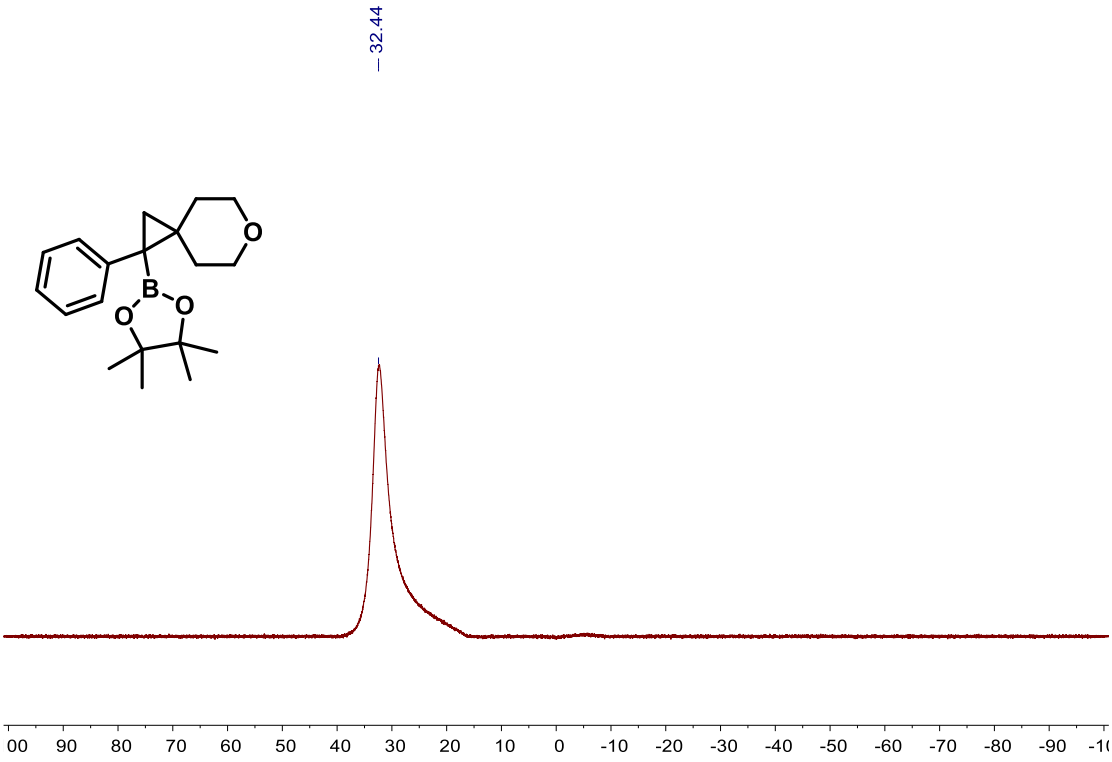
^{11}B NMR spectrum of **8a** (128 MHz Chloroform-*d*)



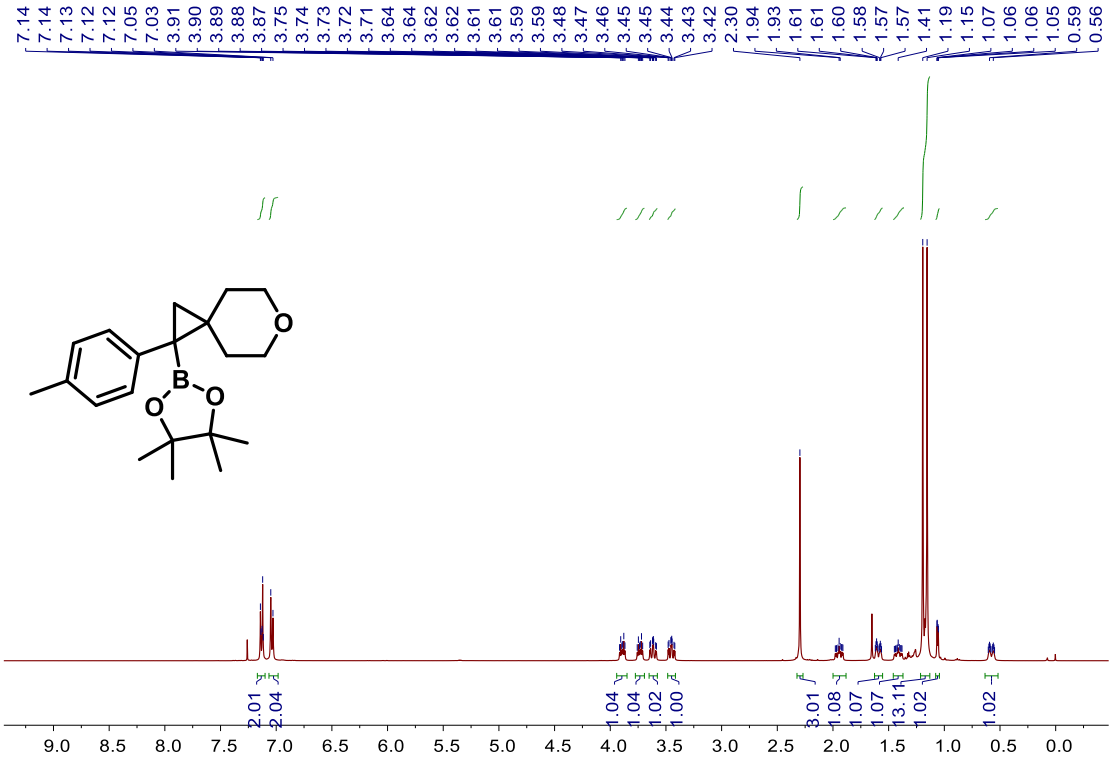
^{1}H NMR spectrum of **9a** (400 MHz, Chloroform-*d*)



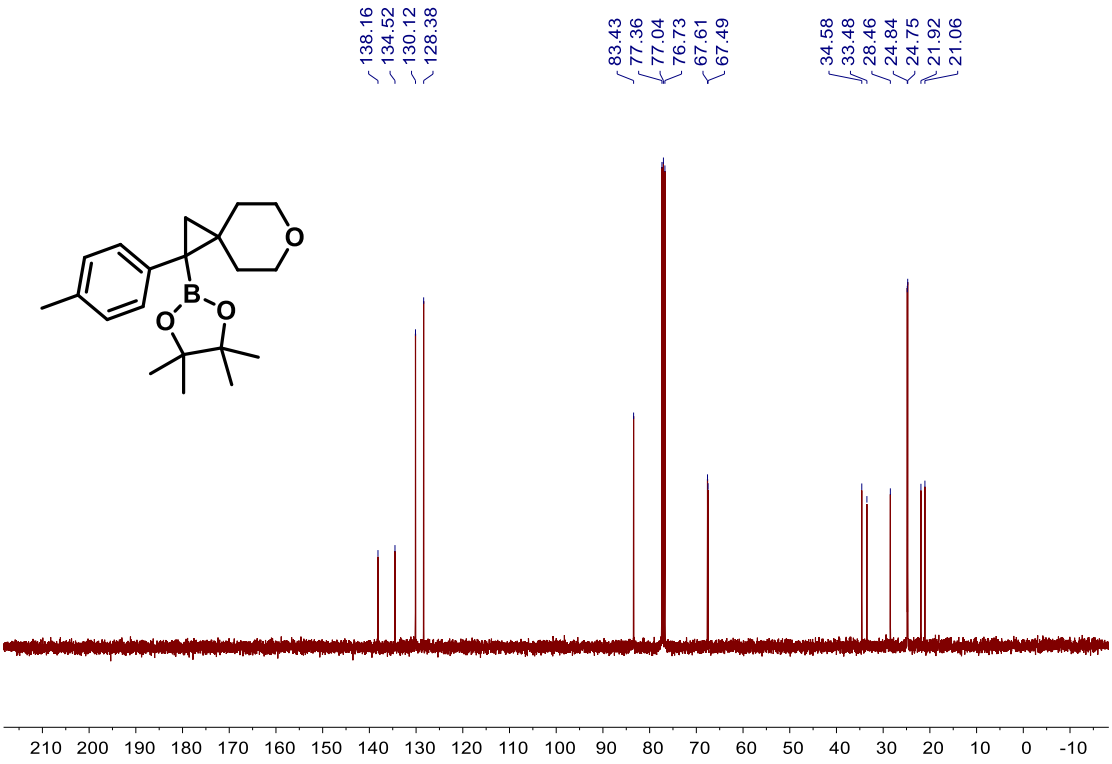
^{13}C NMR spectrum of **9a** (101 MHz, Chloroform-*d*)



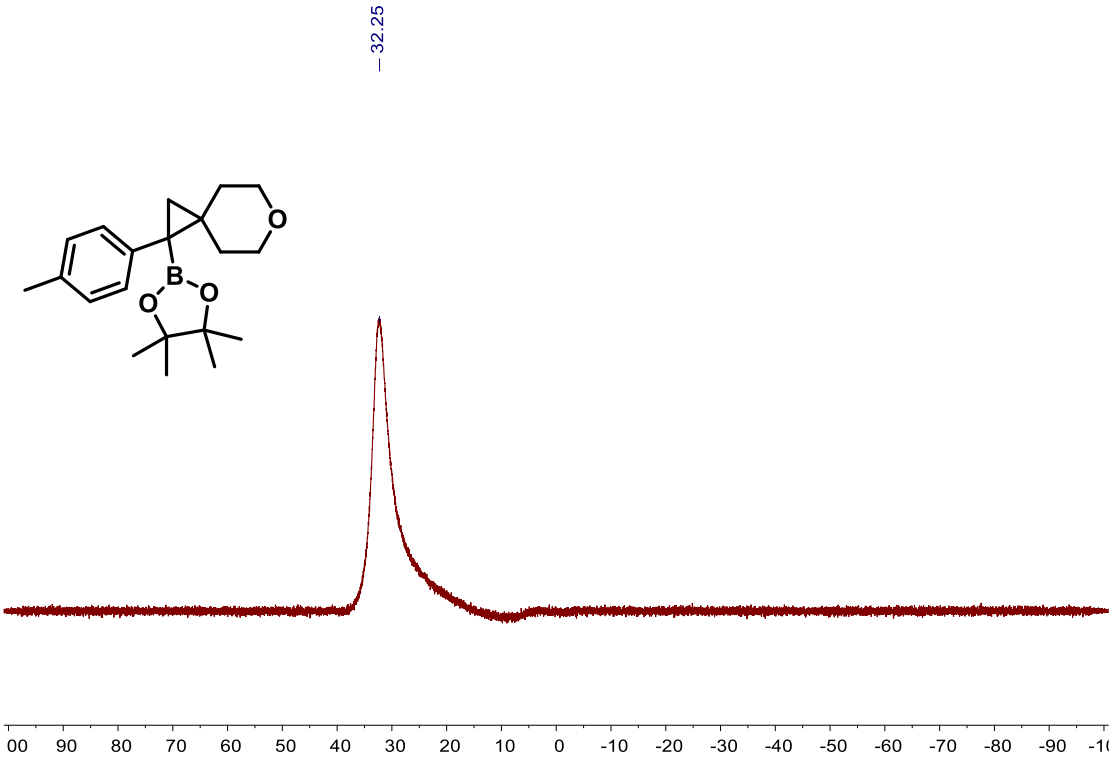
^{11}B NMR spectrum of **9a** (128 MHz Chloroform-*d*)



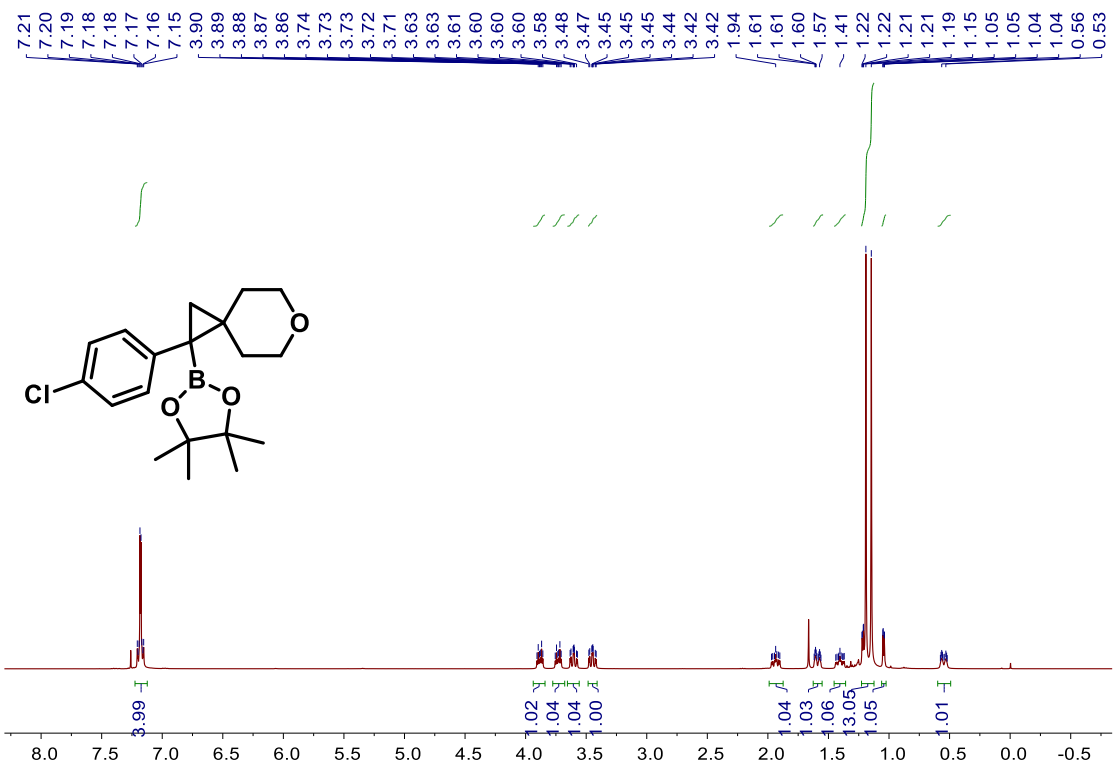
^{1}H NMR spectrum of **9b** (400 MHz, Chloroform-*d*)



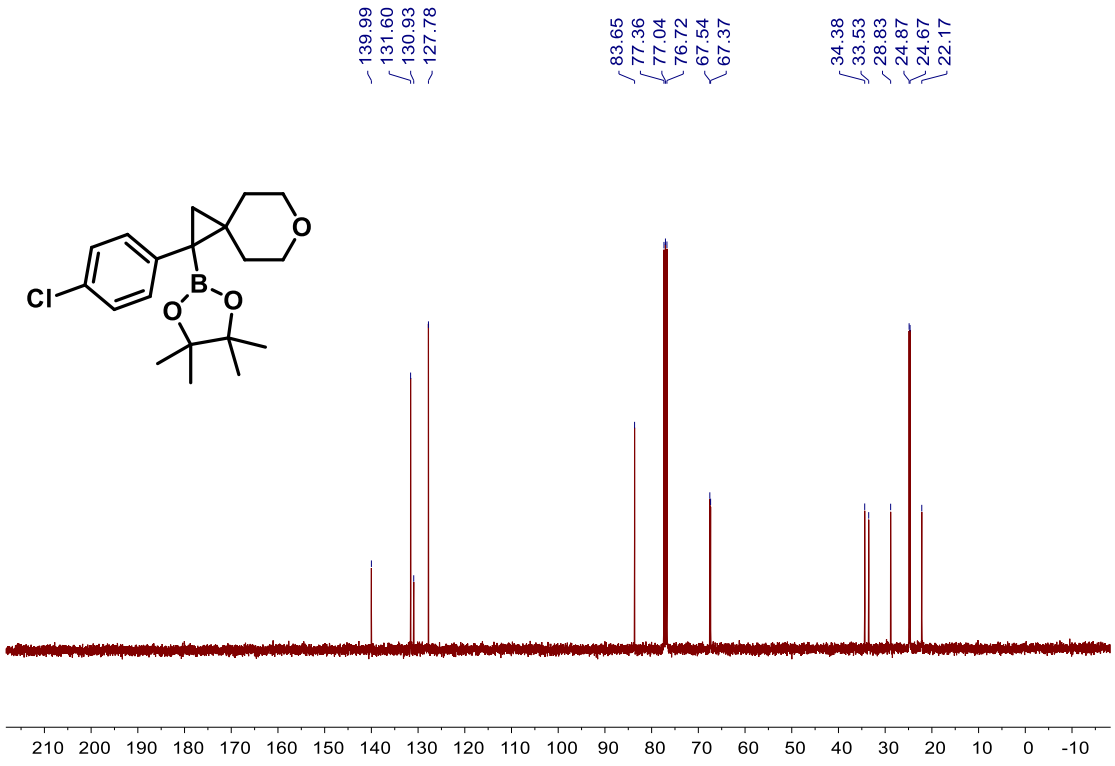
^{13}C NMR spectrum of **9b** (101 MHz, Chloroform-*d*)



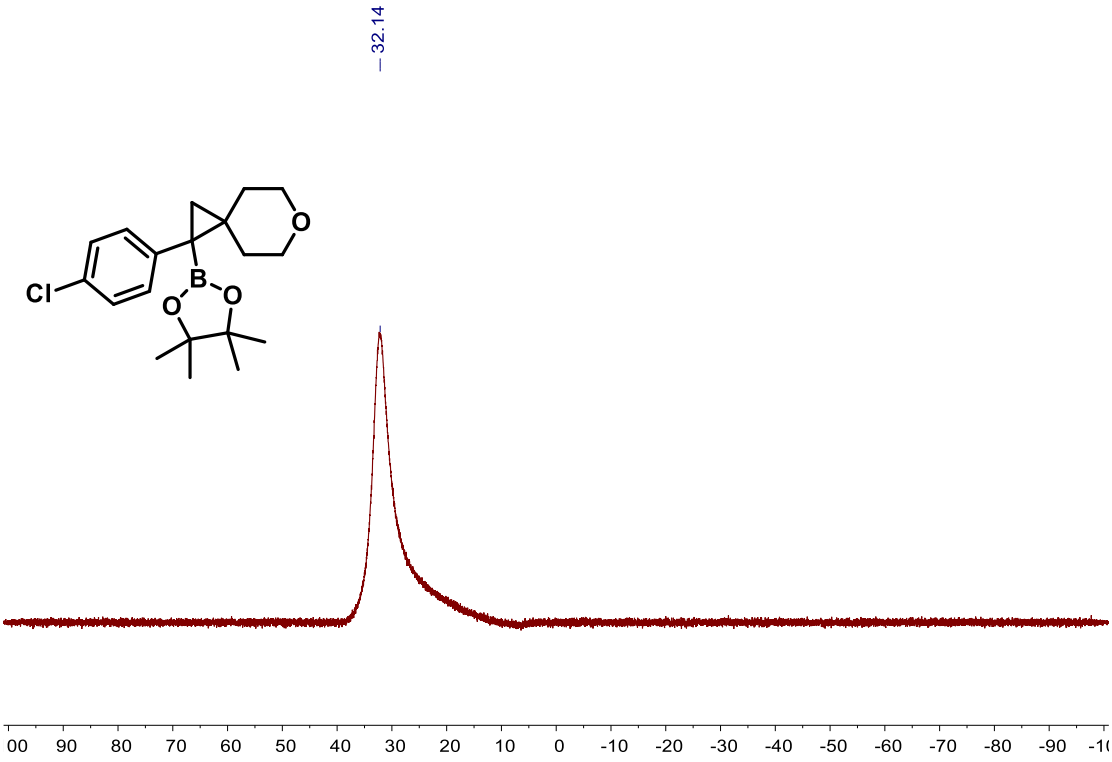
^{11}B NMR spectrum of **9b** (128 MHz Chloroform-*d*)



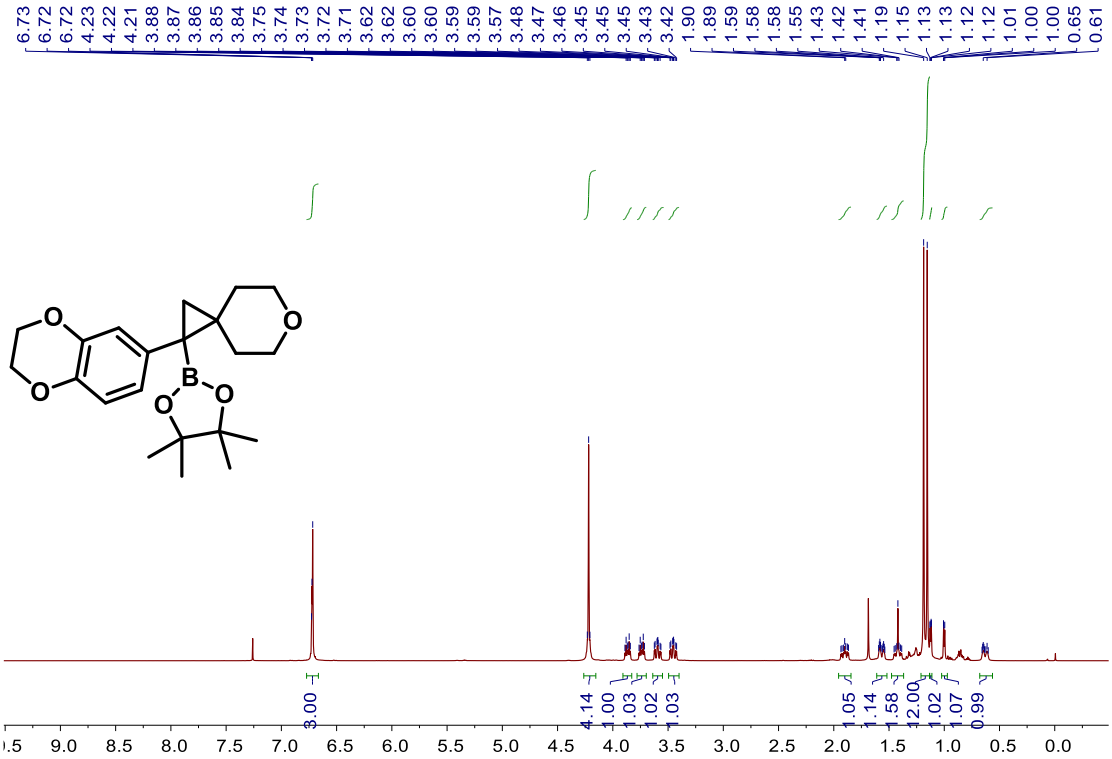
^{1}H NMR spectrum of **9c** (400 MHz, Chloroform-*d*)



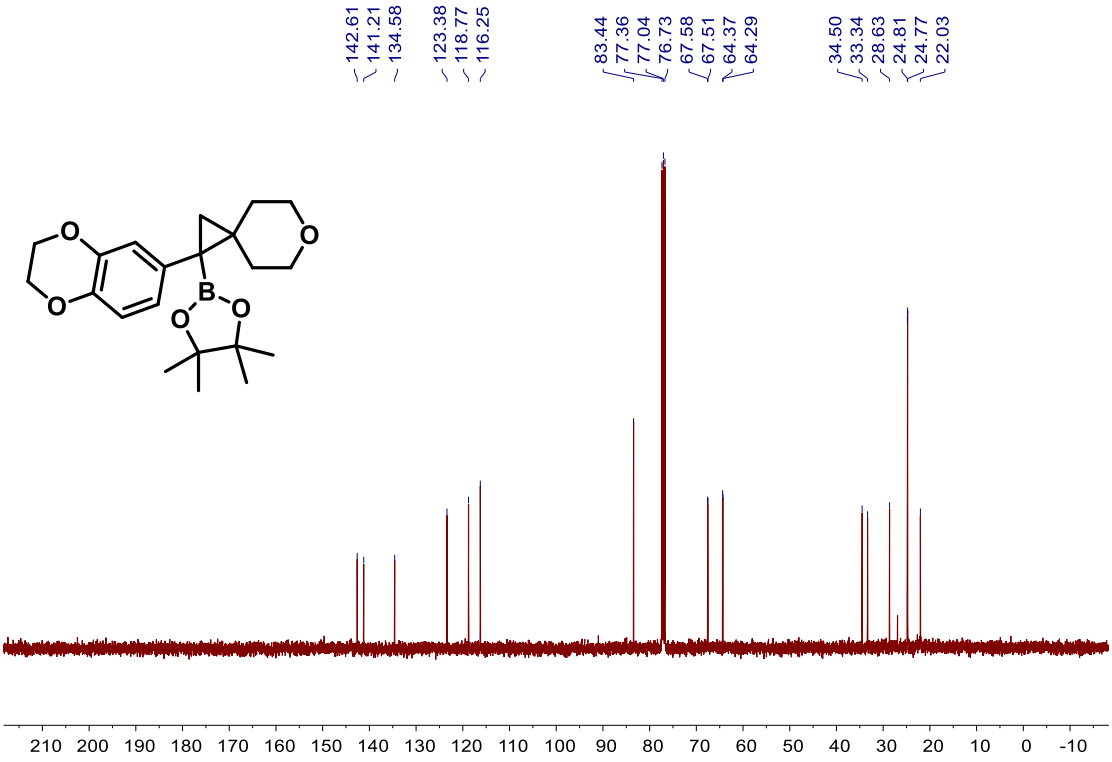
^{13}C NMR spectrum of **9c** (101 MHz, Chloroform-*d*)



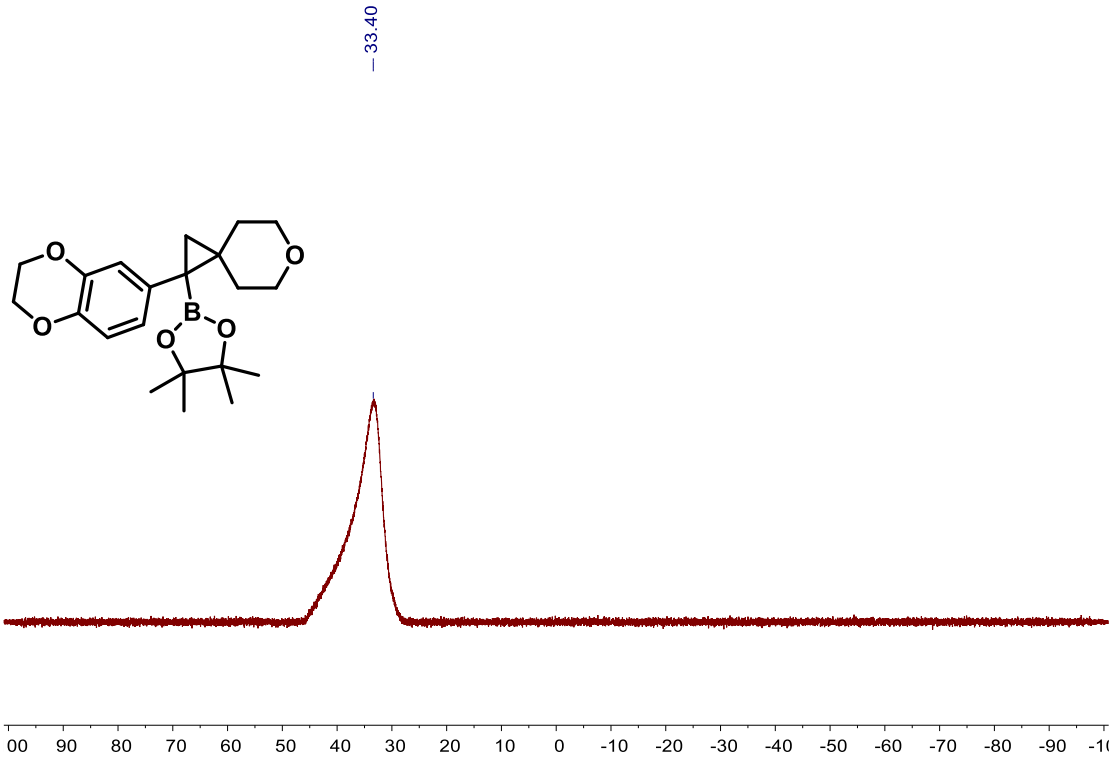
^{11}B NMR spectrum of **9c** (128 MHz Chloroform-*d*)



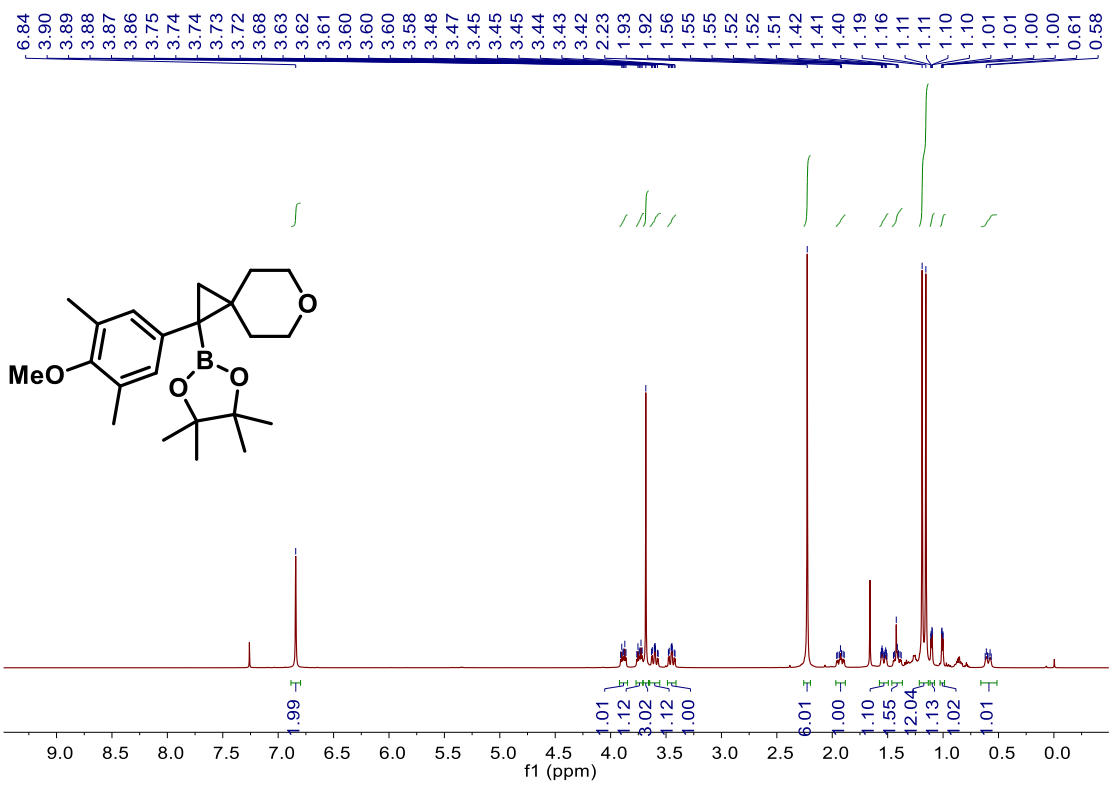
^{1}H NMR spectrum of **9d** (400 MHz, Chloroform-*d*)



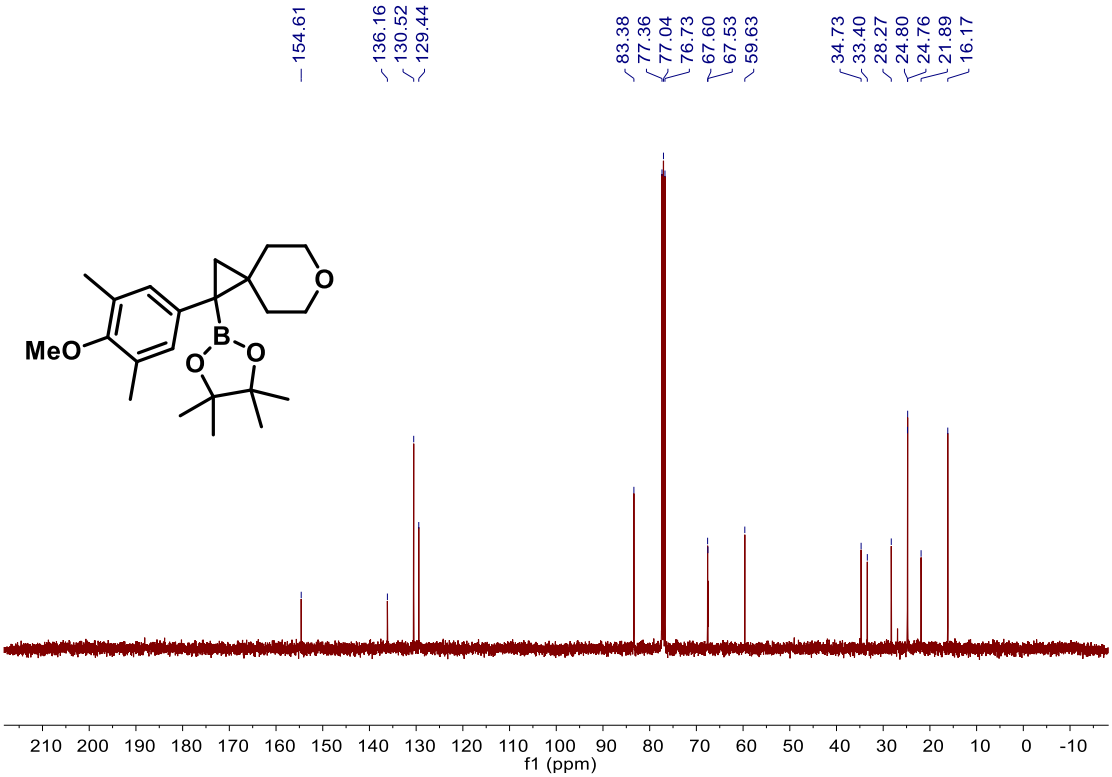
^{13}C NMR spectrum of **9d** (101 MHz, Chloroform-*d*)



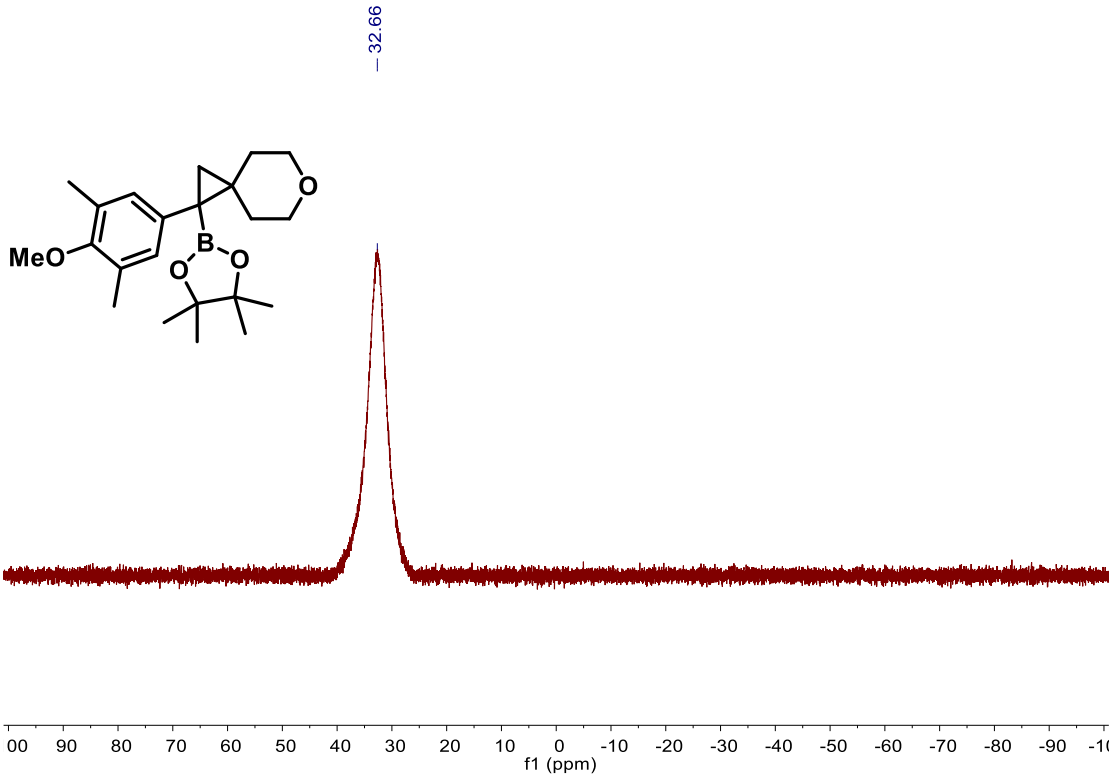
^{11}B NMR spectrum of **9d** (128 MHz Chloroform-*d*)



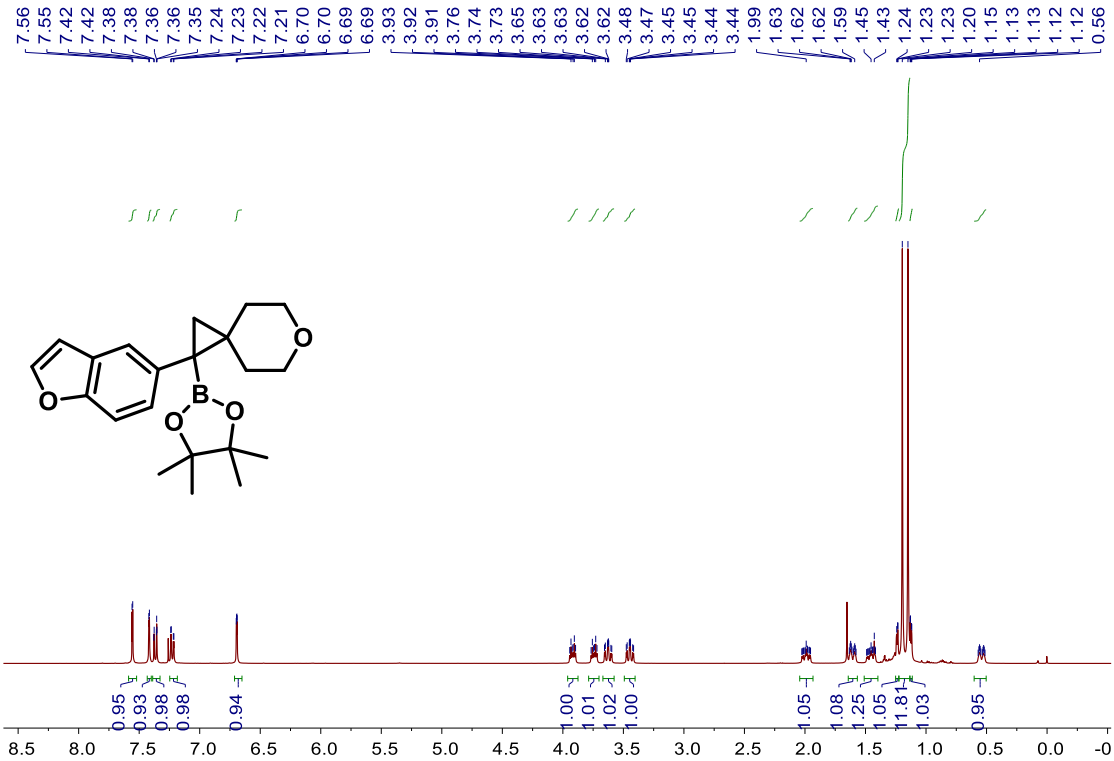
^{1}H NMR spectrum of **9e** (400 MHz, Chloroform-*d*)



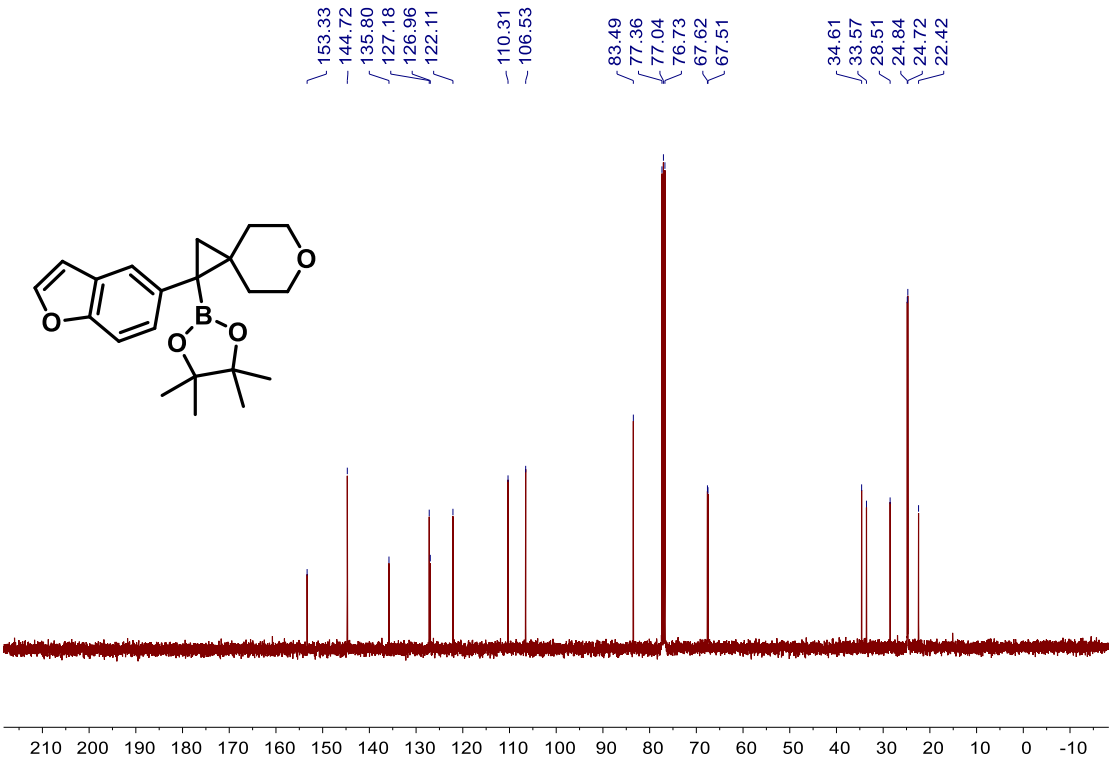
^{13}C NMR spectrum of **9e** (101 MHz, Chloroform-*d*)



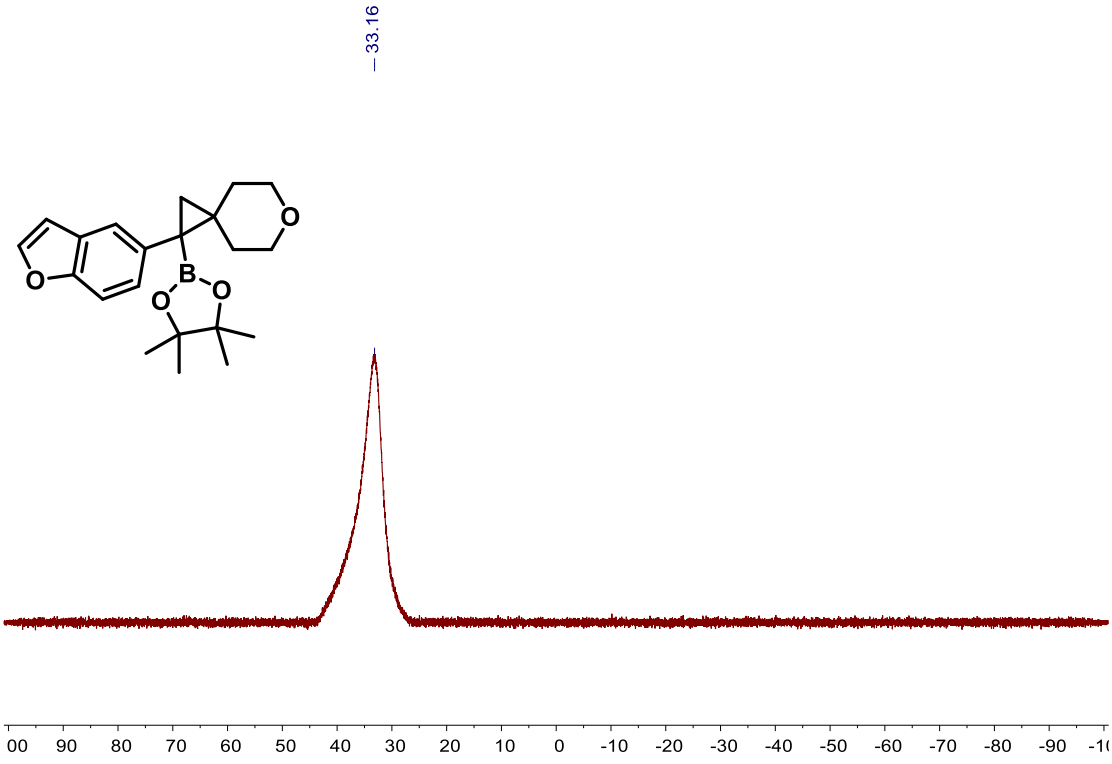
^{11}B NMR spectrum of **9e** (128 MHz Chloroform-*d*)



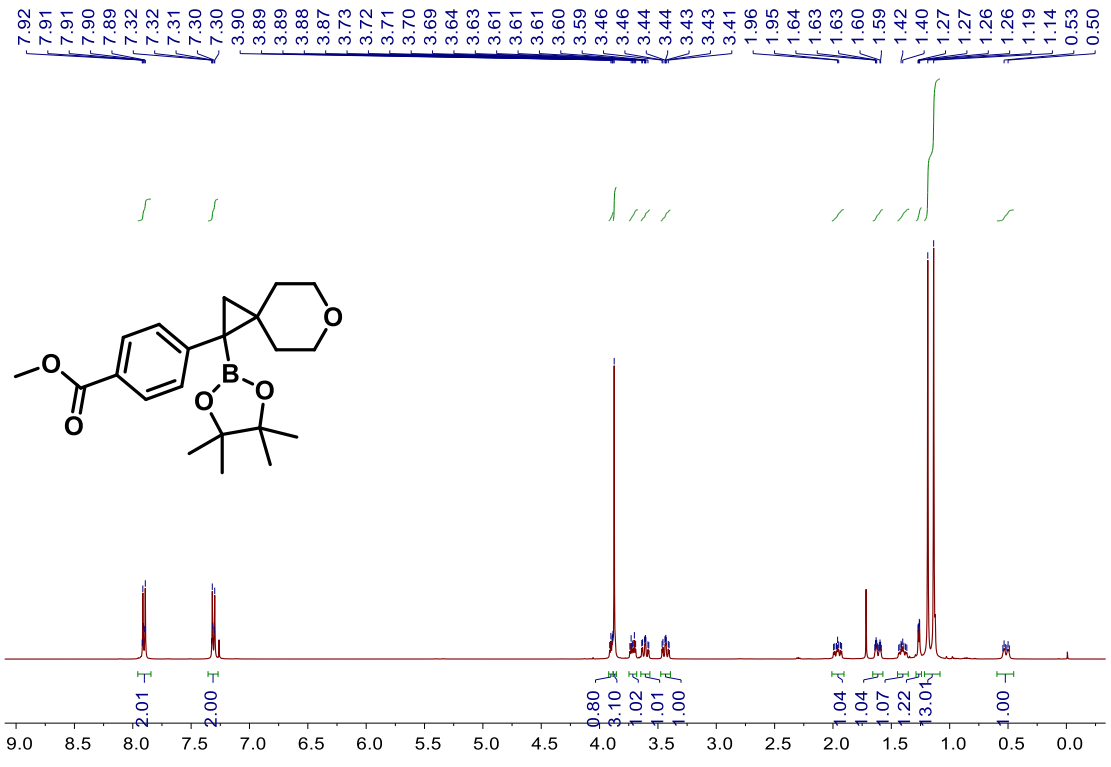
^{1}H NMR spectrum of **9f** (400 MHz, Chloroform-*d*)



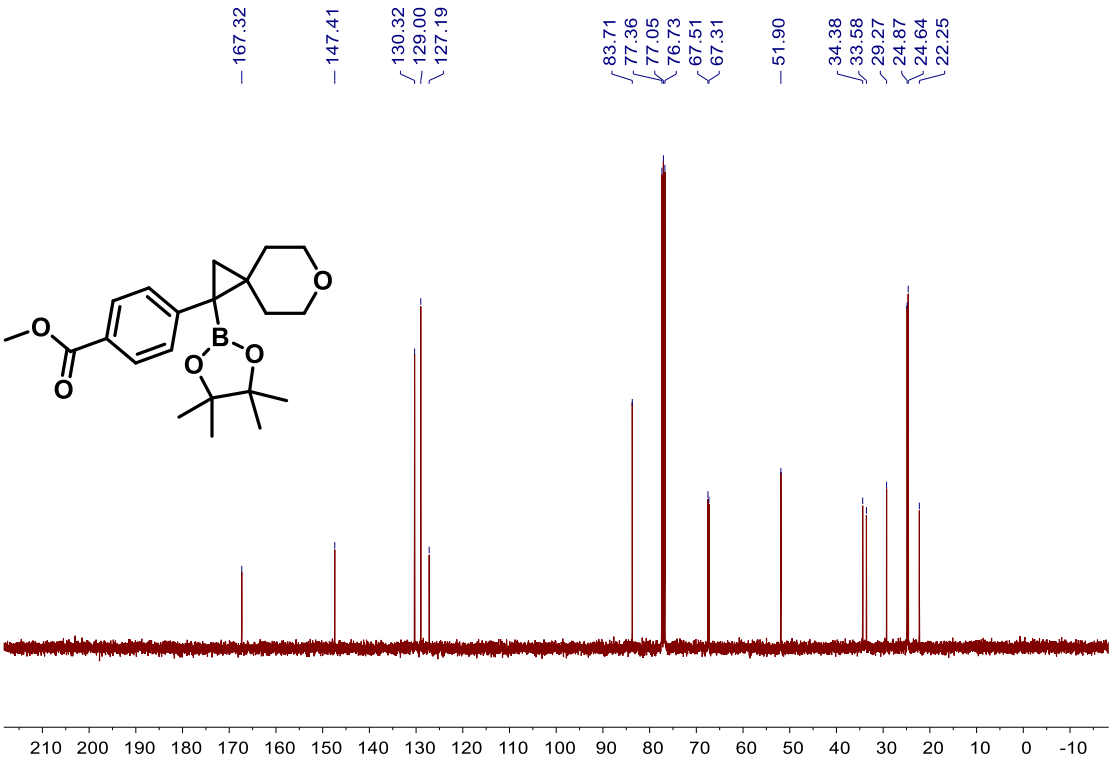
^{13}C NMR spectrum of **9f** (101 MHz, Chloroform-*d*)



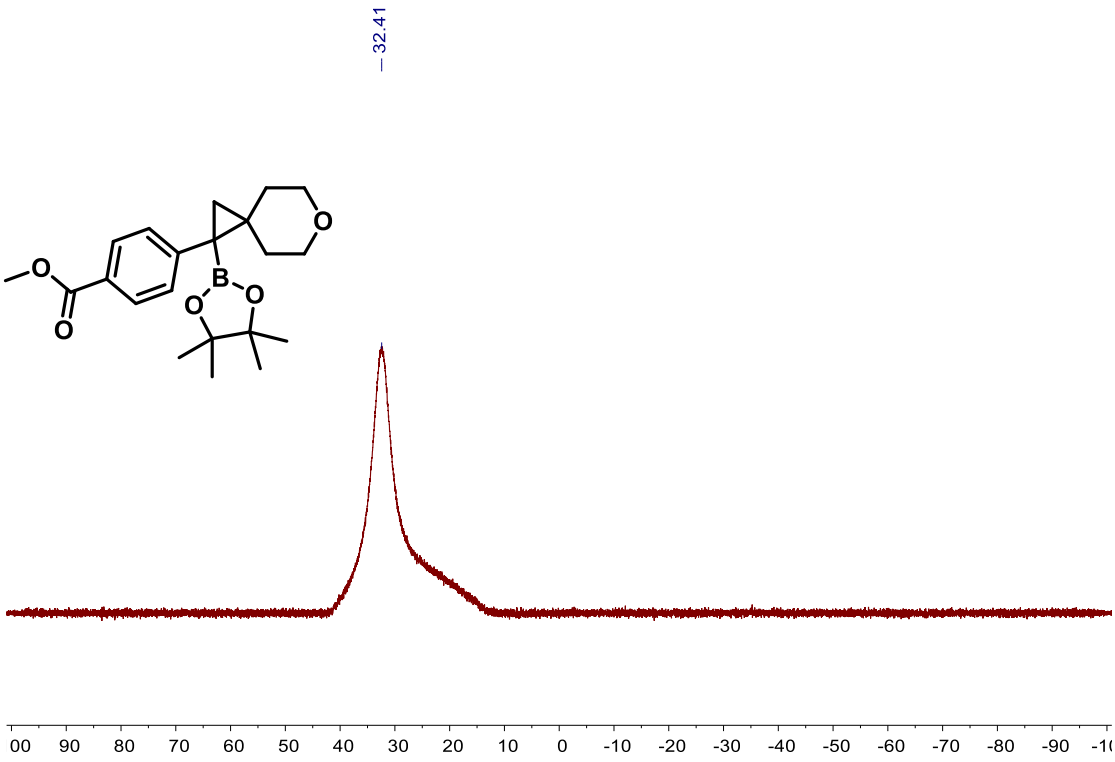
^{11}B NMR spectrum of **9f** (128 MHz Chloroform-*d*)



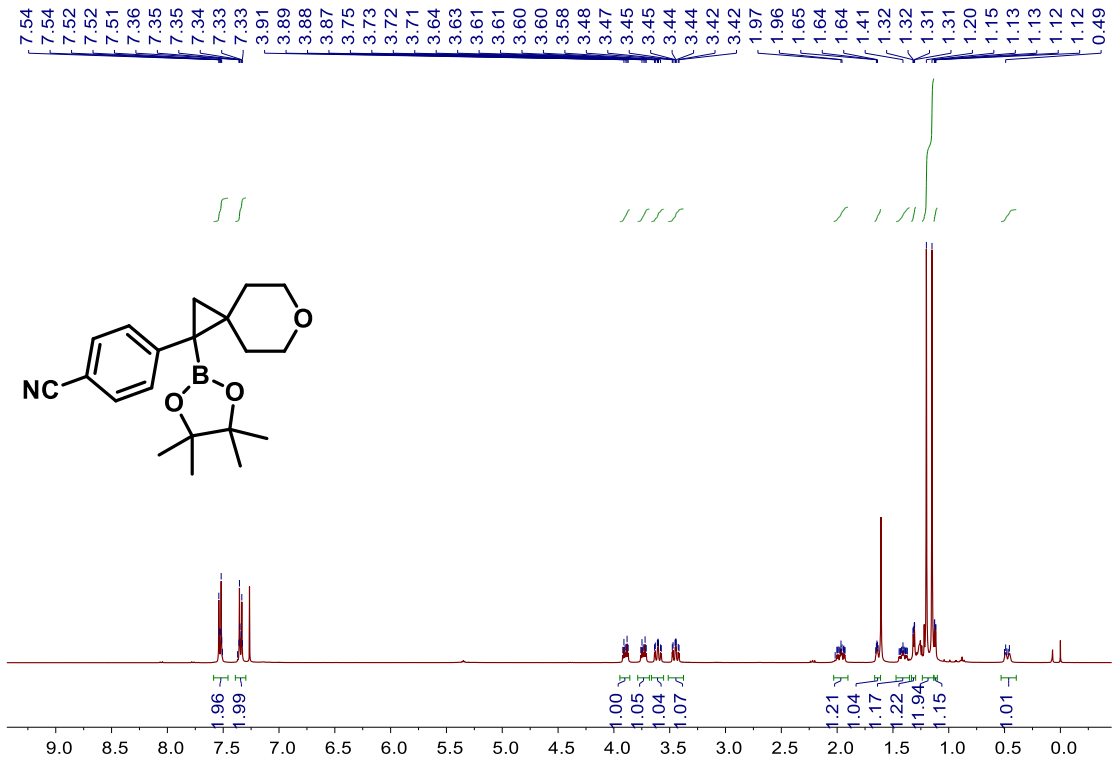
^{1}H NMR spectrum of **9g** (400 MHz, Chloroform-*d*)



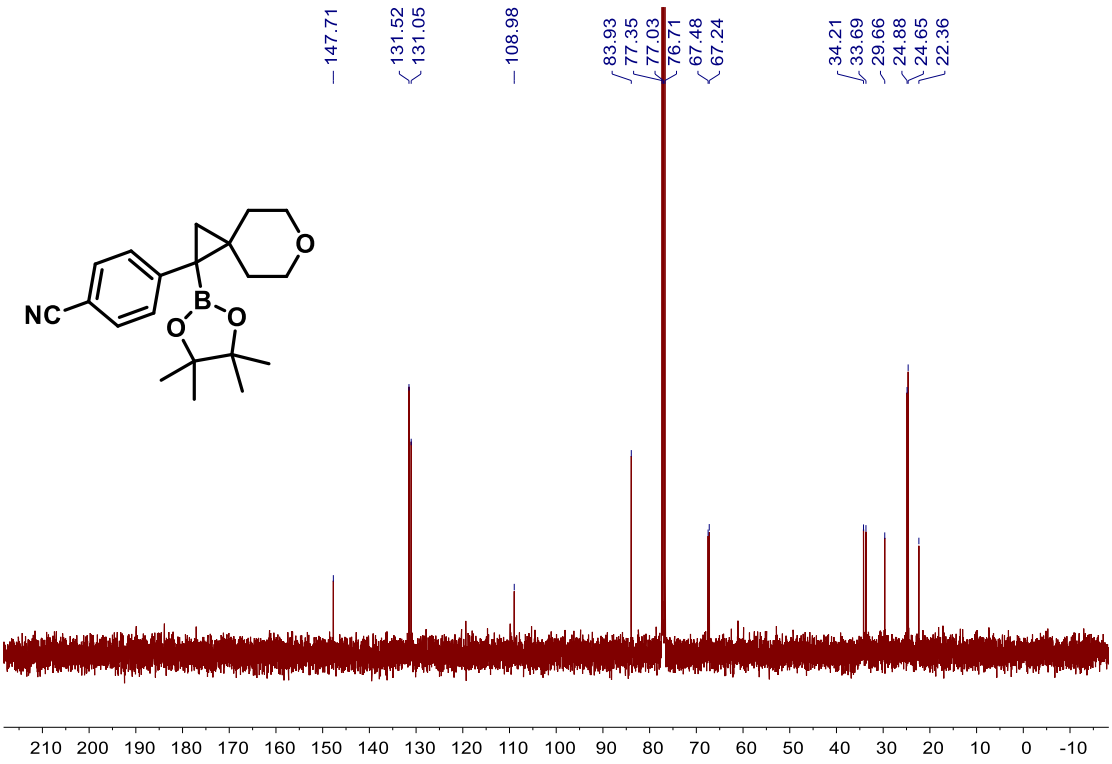
^{13}C NMR spectrum of **9g** (101 MHz, Chloroform-*d*)



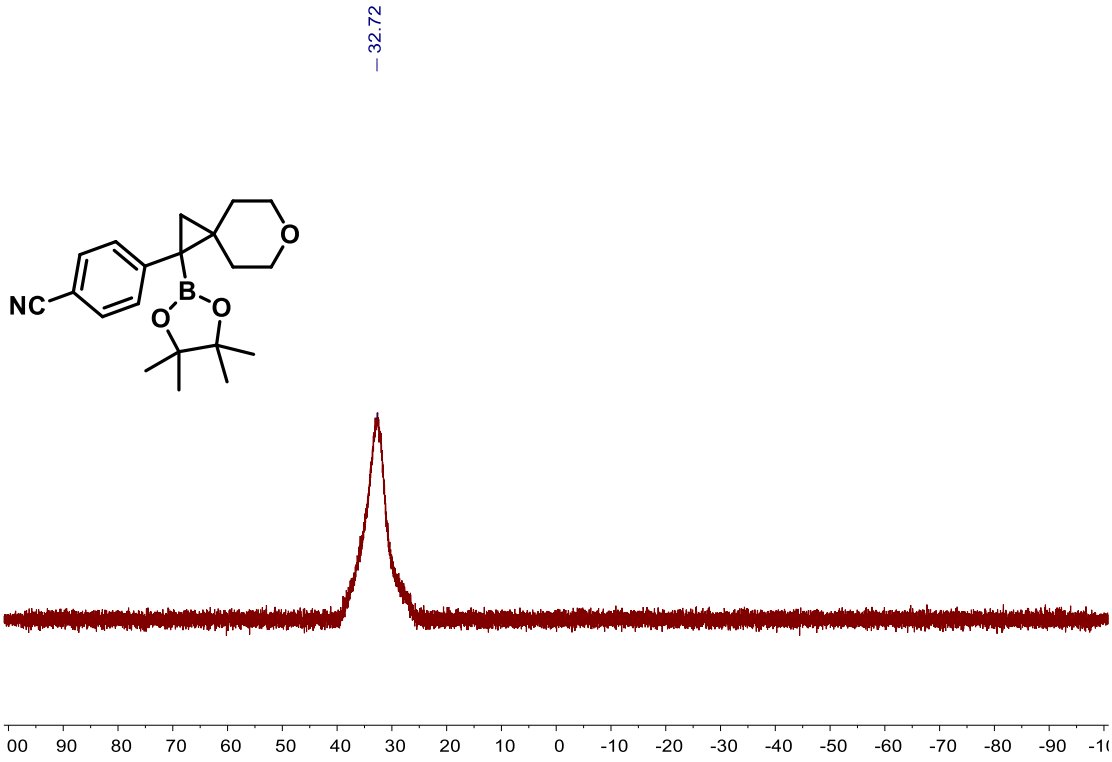
^{11}B NMR spectrum of **9g** (128 MHz Chloroform-*d*)



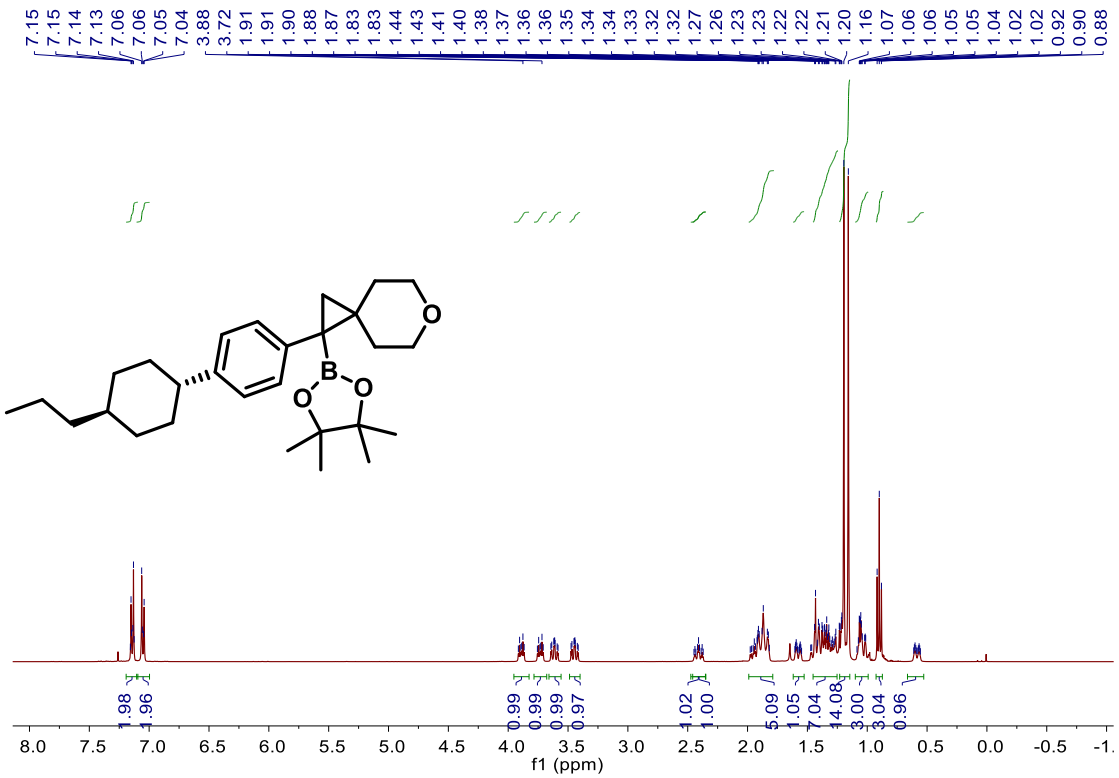
^{1}H NMR spectrum of **9h** (400 MHz, Chloroform-*d*)



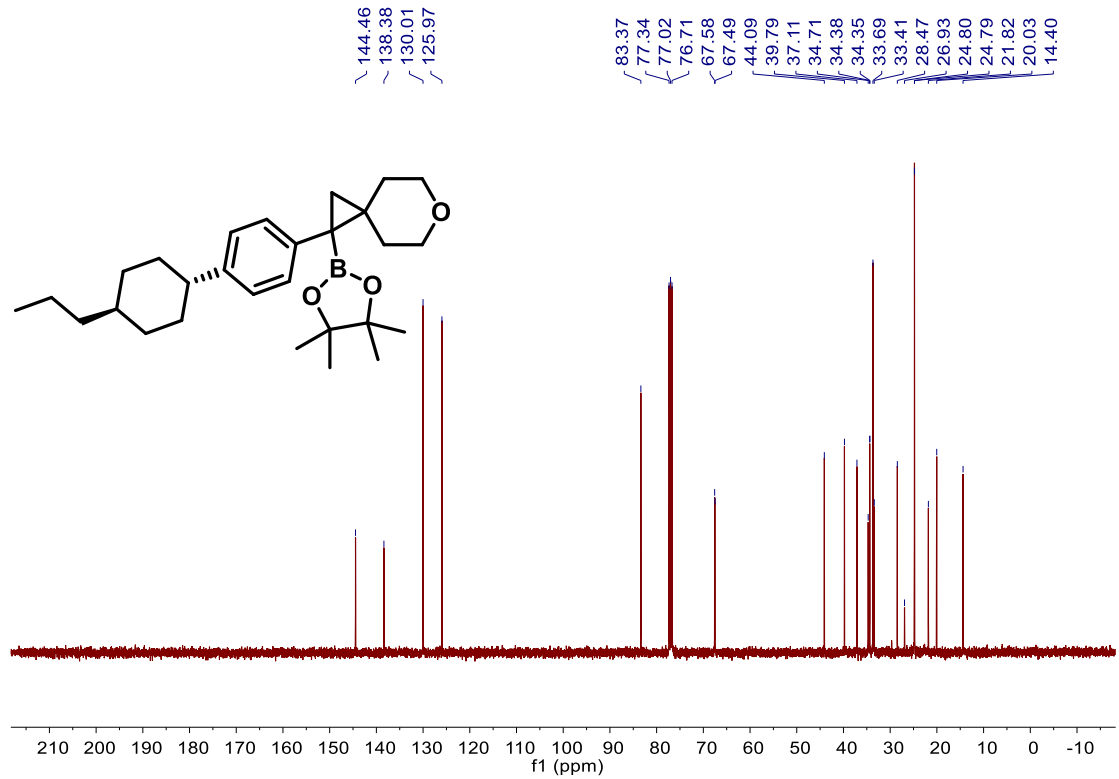
^{13}C NMR spectrum of **9h** (101 MHz, Chloroform-*d*)



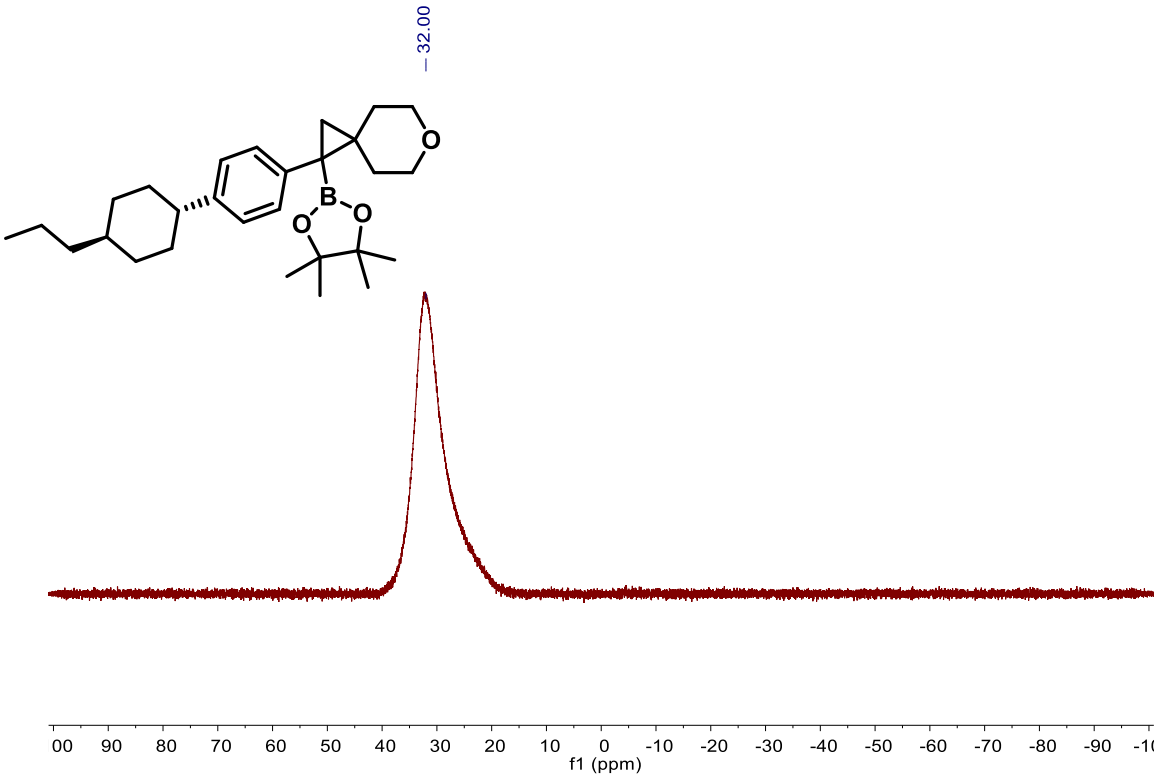
^{11}B NMR spectrum of **9h** (128 MHz Chloroform-*d*)



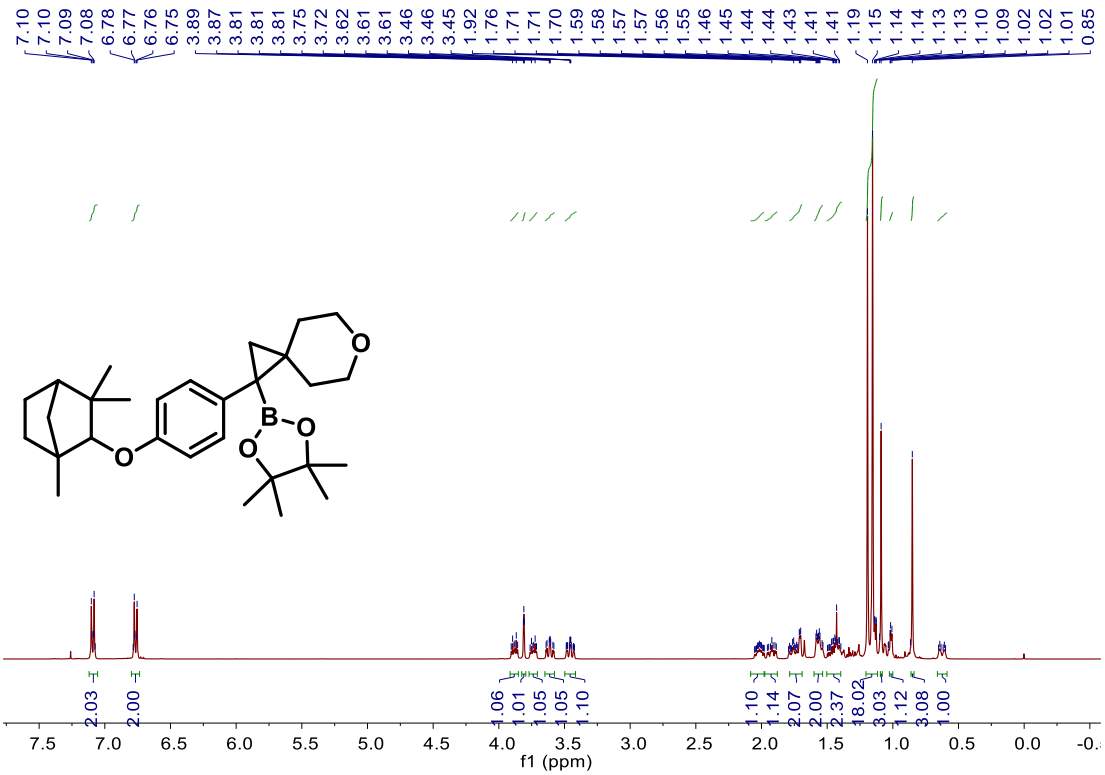
^{1}H NMR spectrum of **9j** (400 MHz, Chloroform-*d*)



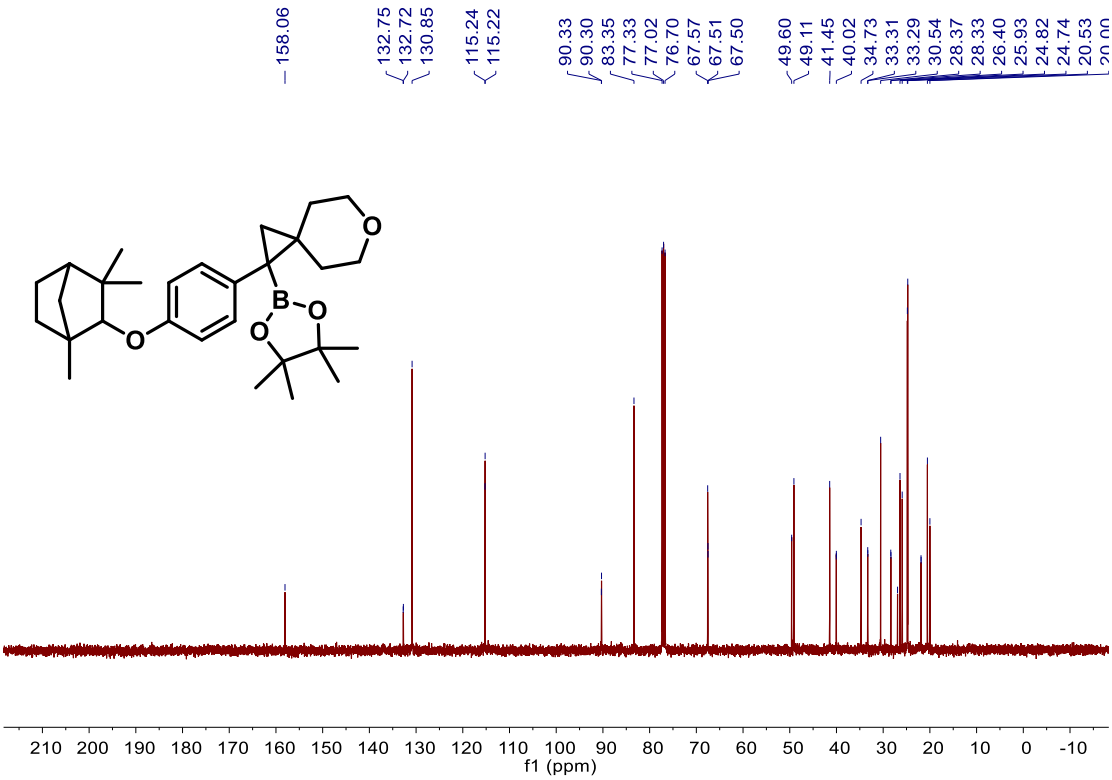
^{13}C NMR spectrum of **9j** (101 MHz, Chloroform-*d*)



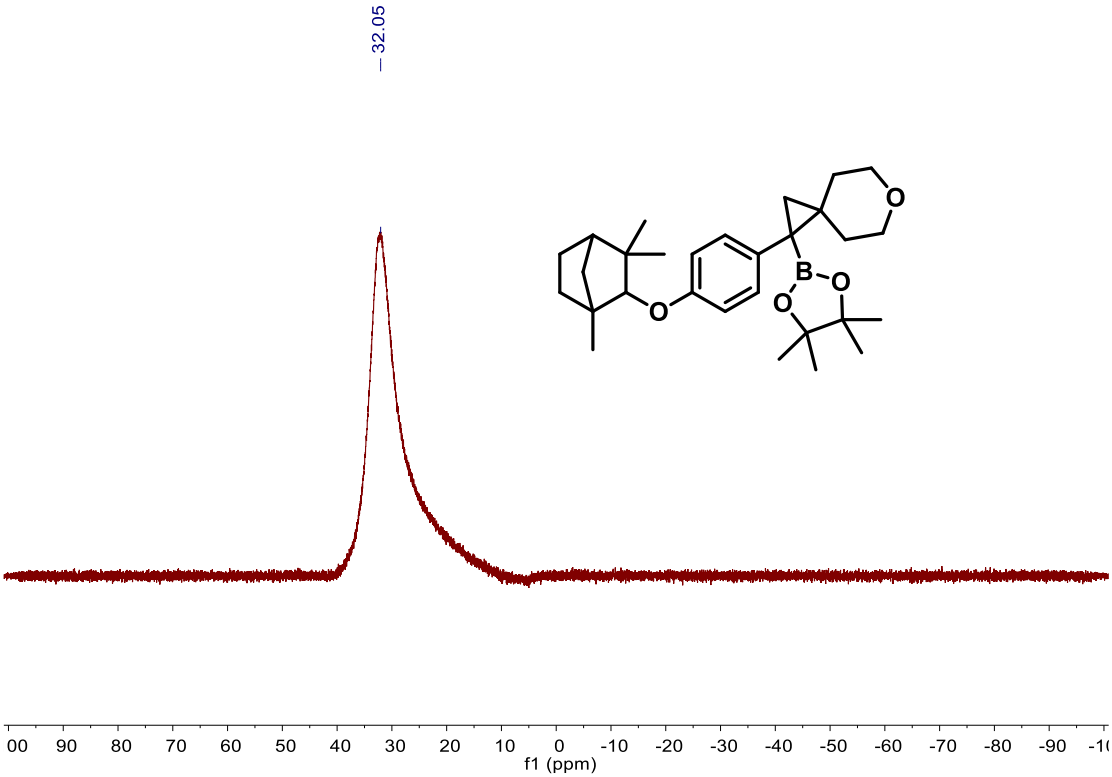
^{11}B NMR spectrum of **9j** (128 MHz Chloroform-*d*)



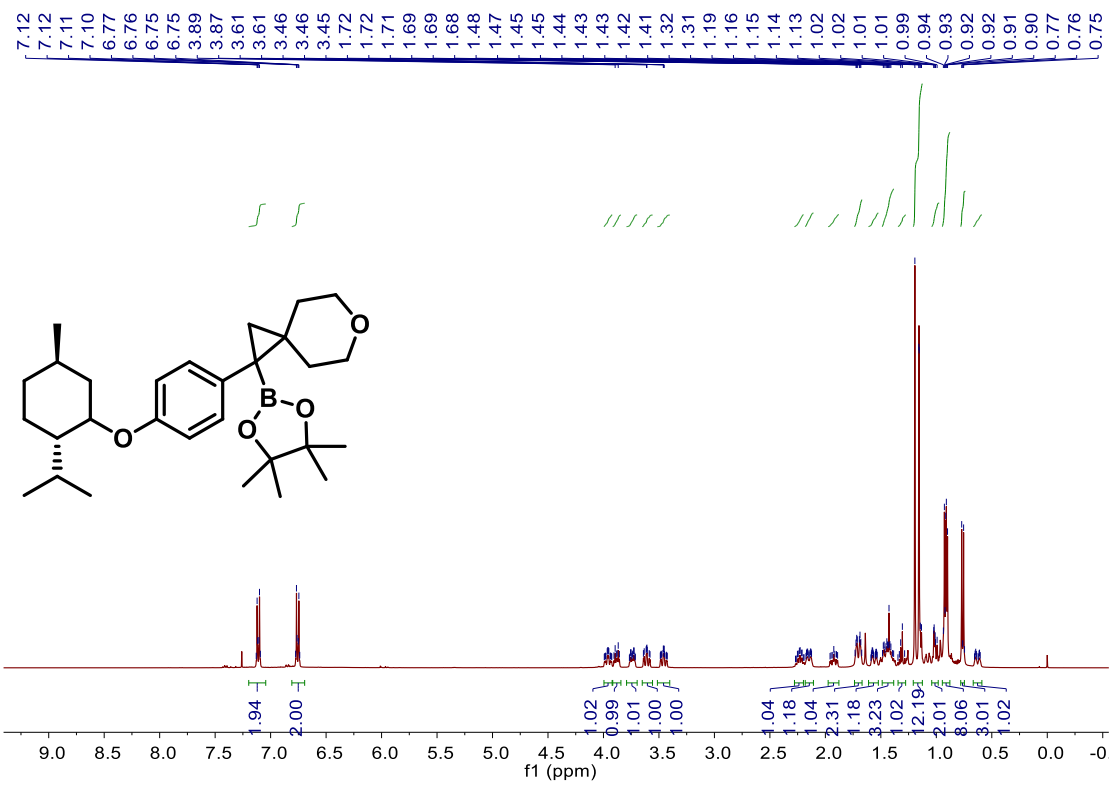
^{1}H NMR spectrum of **9k** (400 MHz, Chloroform-*d*)



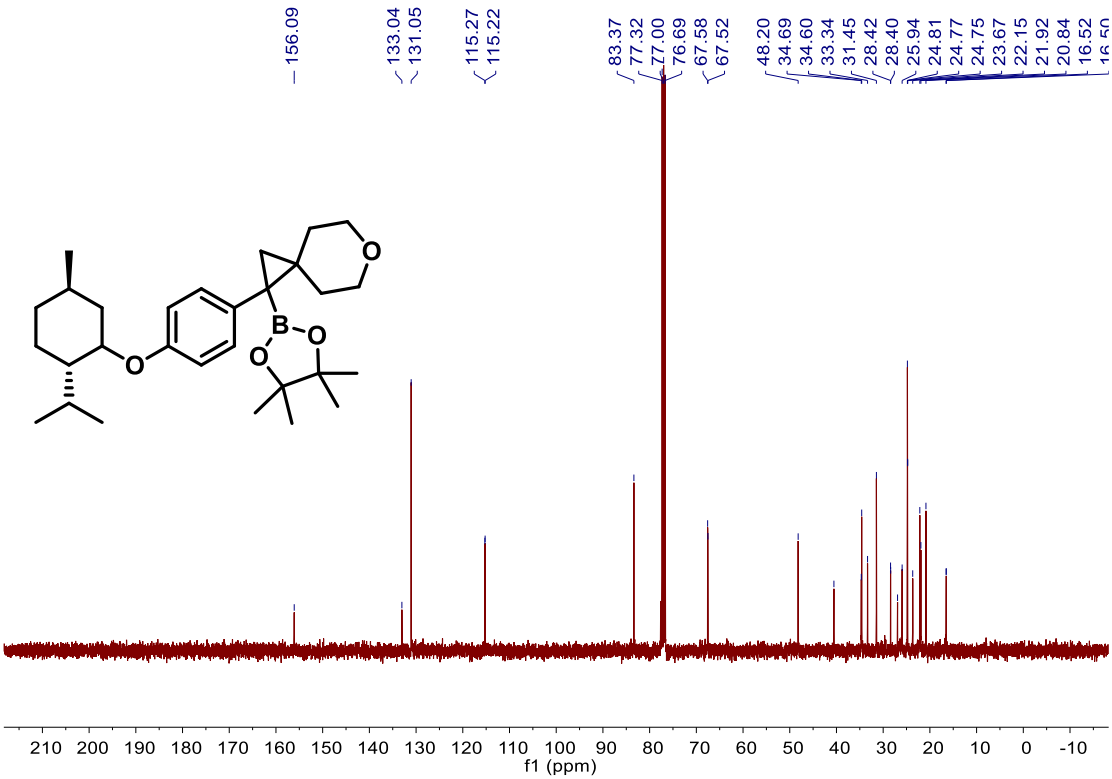
^{13}C NMR spectrum of **9k** (101 MHz, Chloroform-*d*)



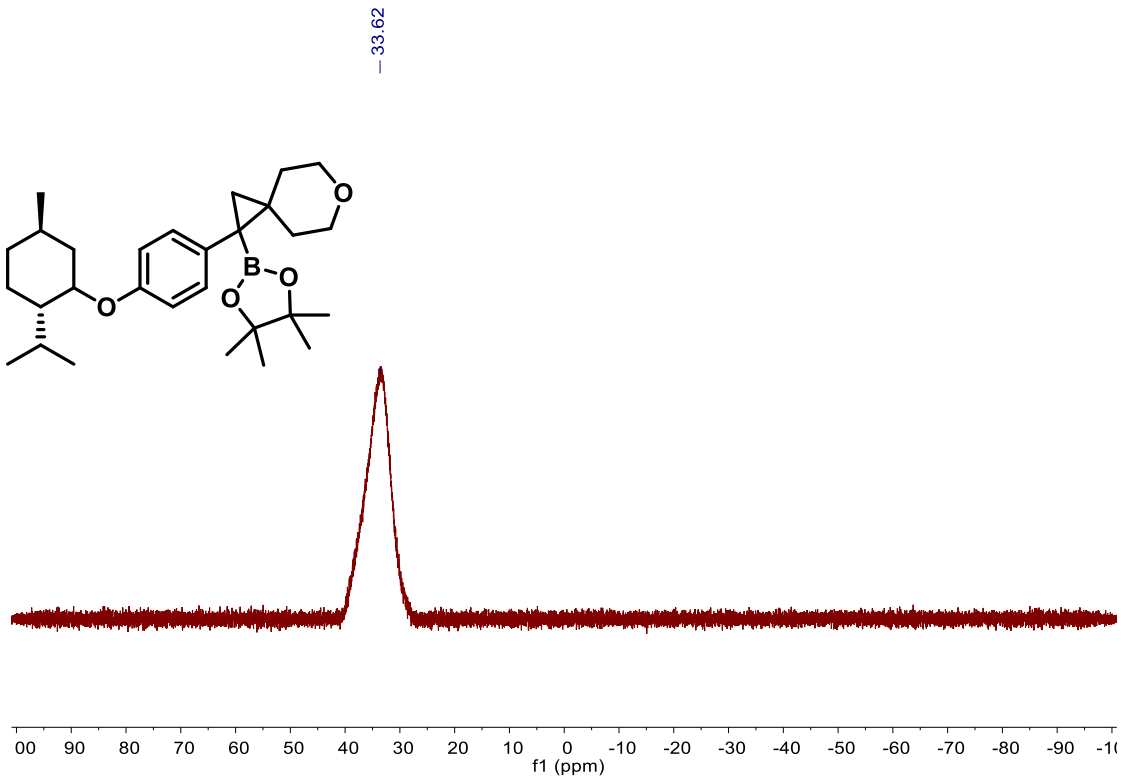
^{11}B NMR spectrum of **9k** (128 MHz Chloroform-*d*)



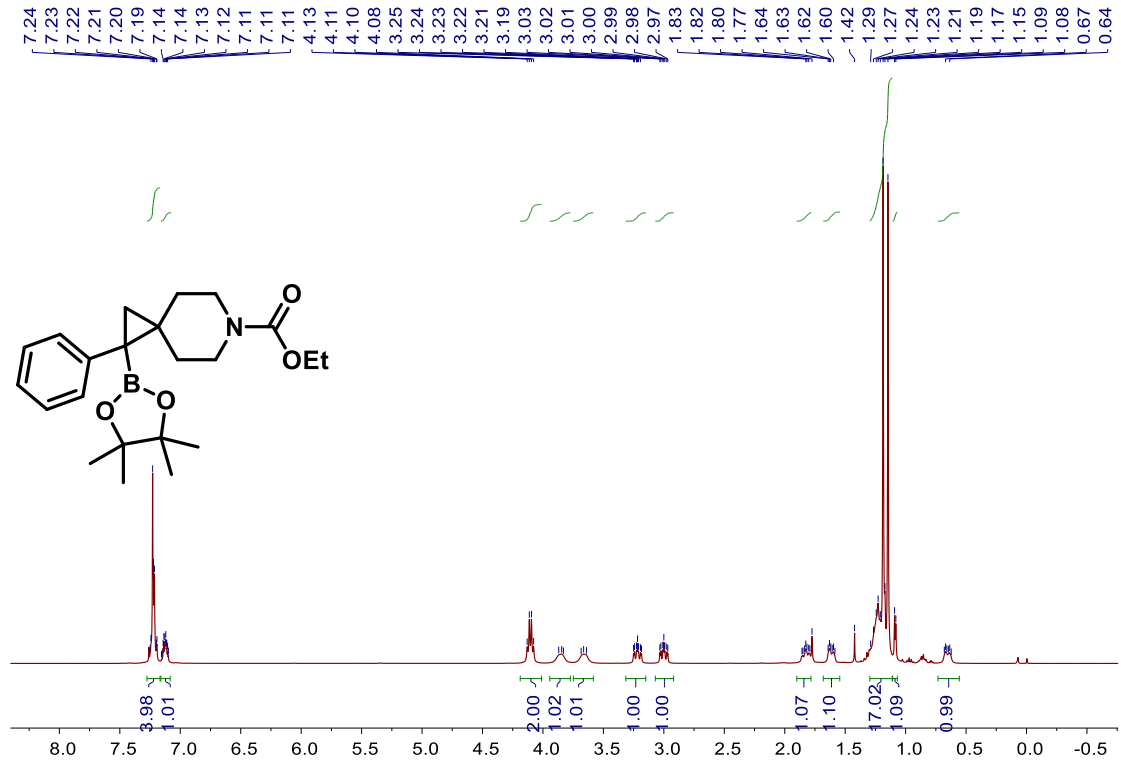
^{1}H NMR spectrum of **9l** (400 MHz, Chloroform-*d*)



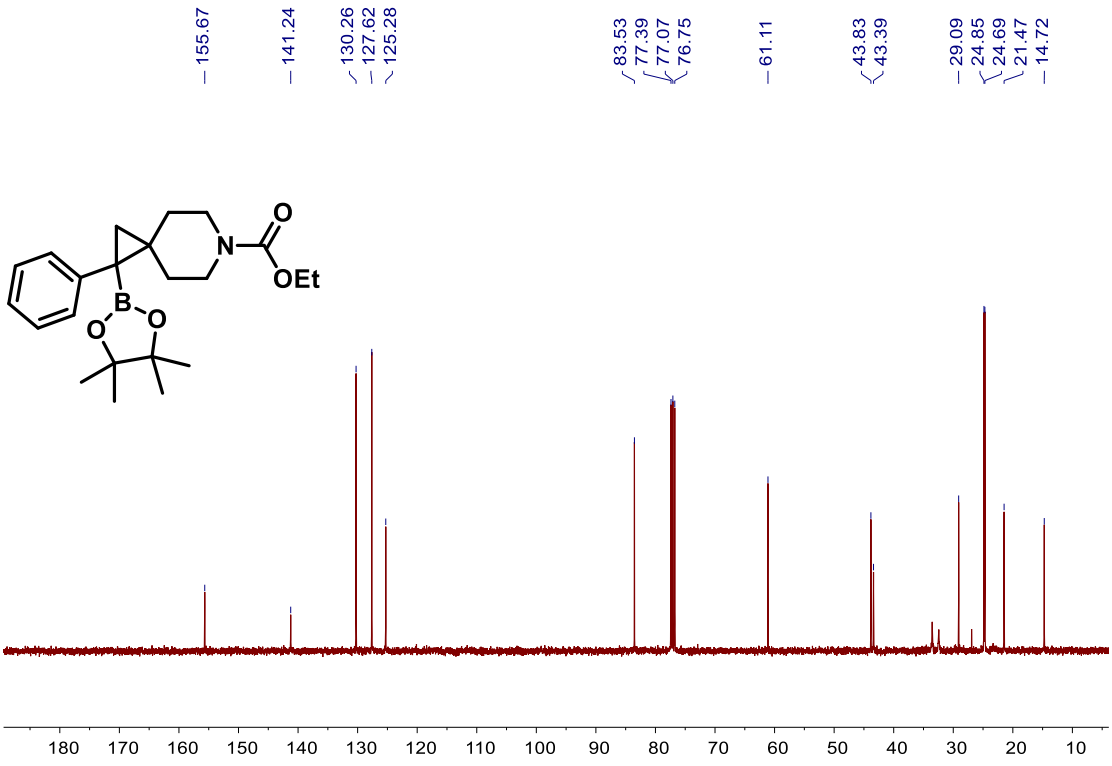
^{13}C NMR spectrum of **9l** (101 MHz, Chloroform-*d*)



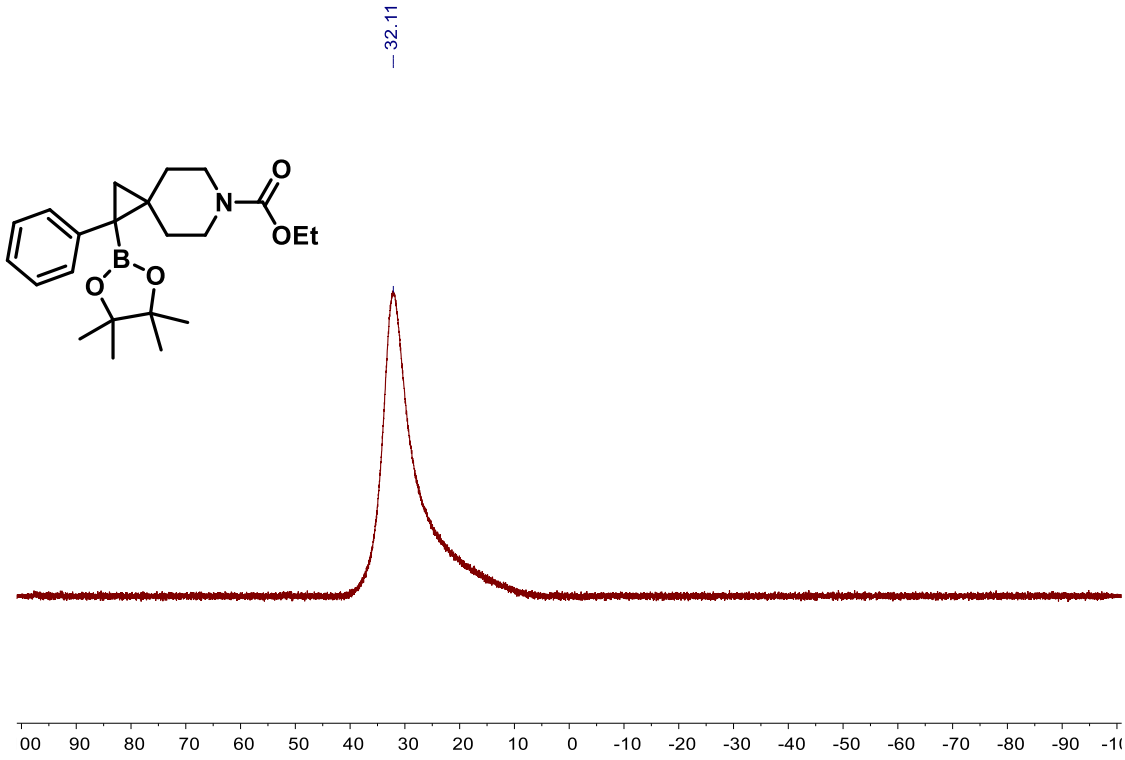
^{11}B NMR spectrum of **9l** (128 MHz Chloroform-*d*)



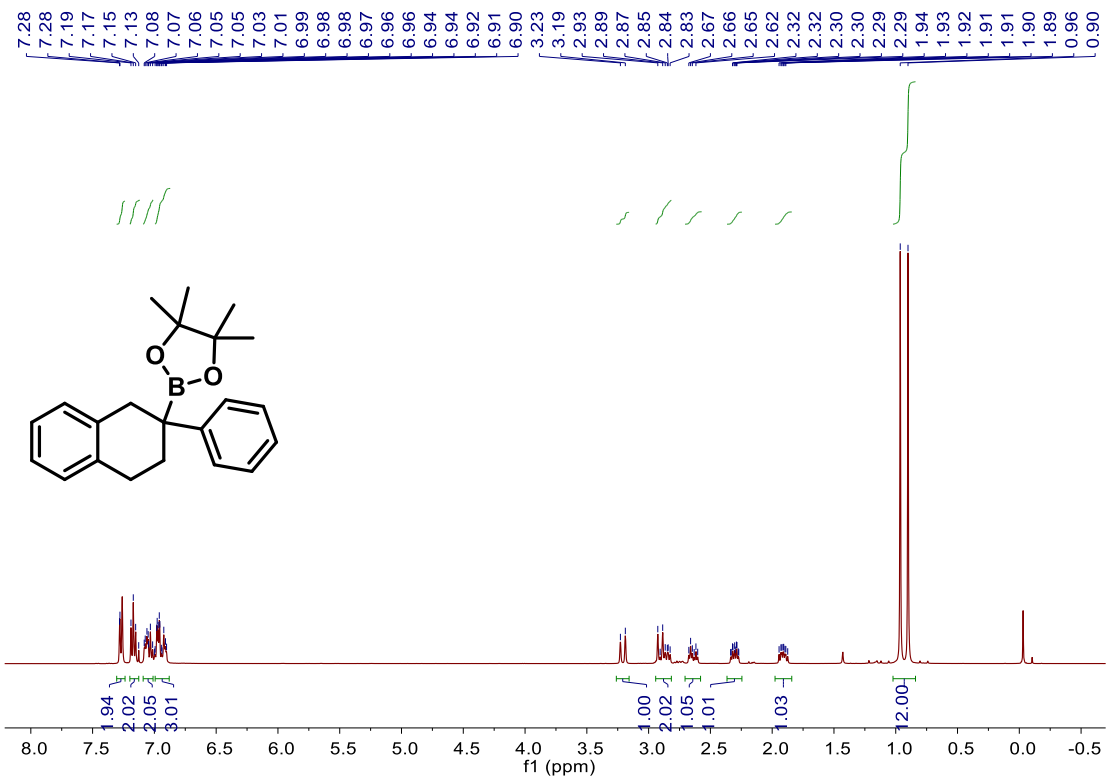
^{1}H NMR spectrum of **10a** (400 MHz, Chloroform-*d*)



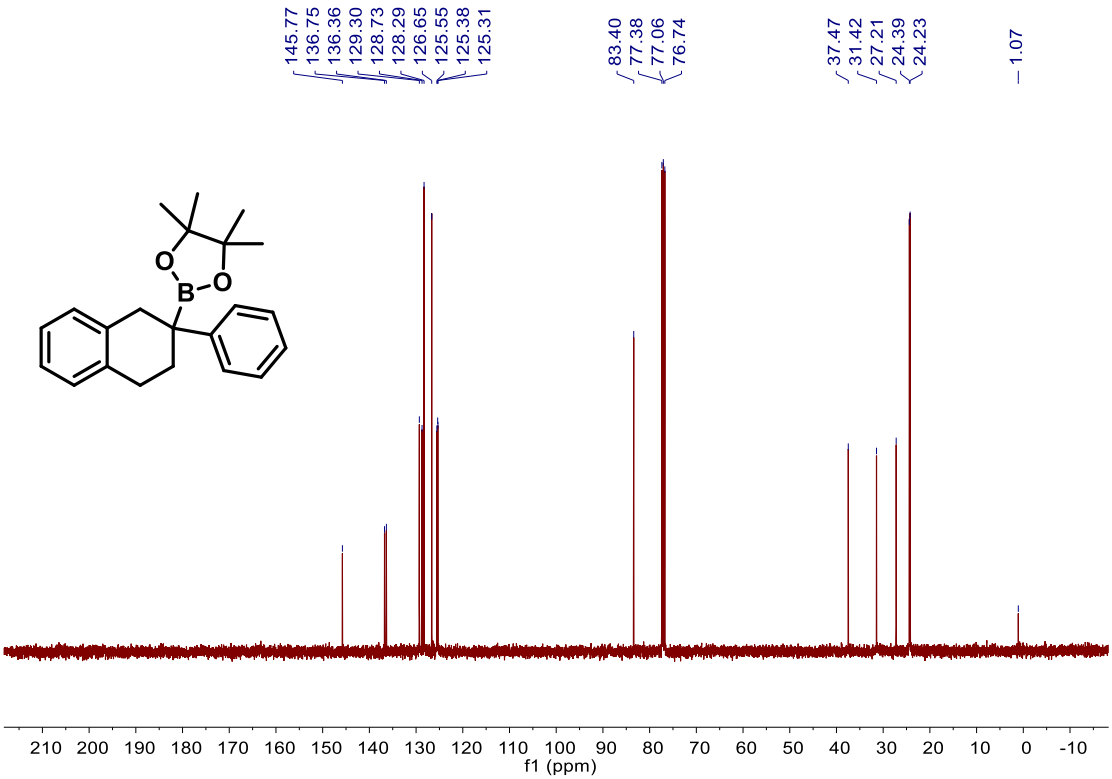
^{13}C NMR spectrum of **10a** (101 MHz, Chloroform-*d*)



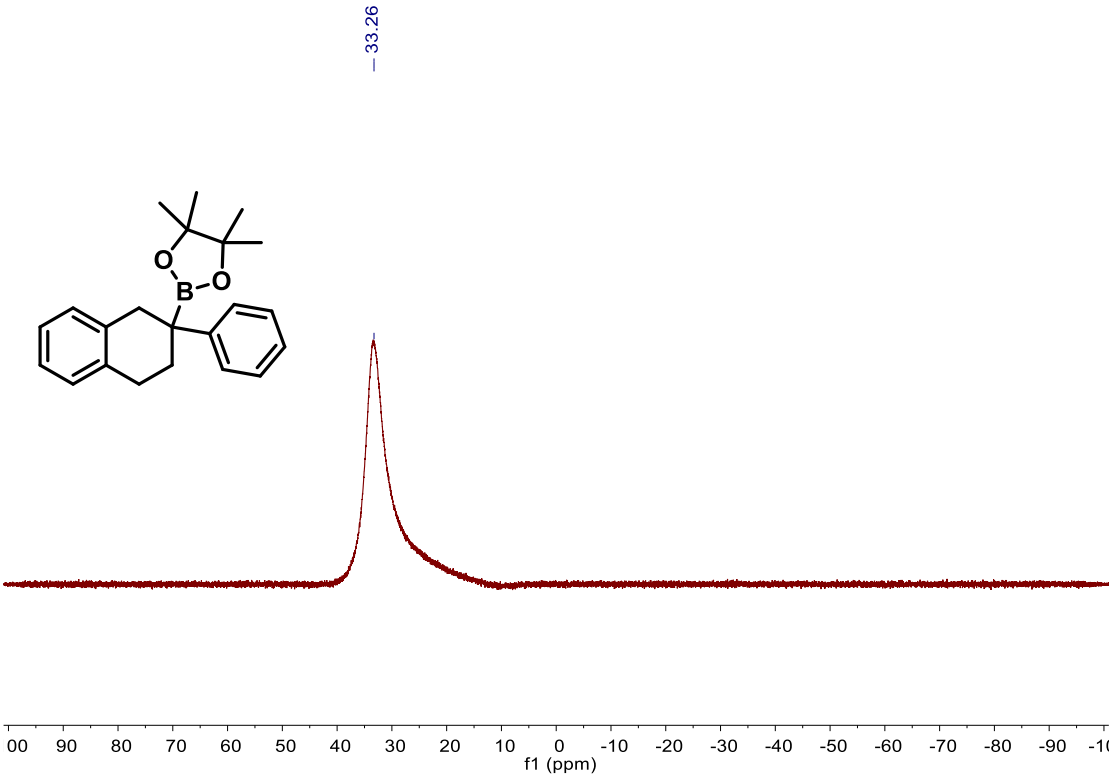
^{11}B NMR spectrum of **10a** (128 MHz Chloroform-*d*)



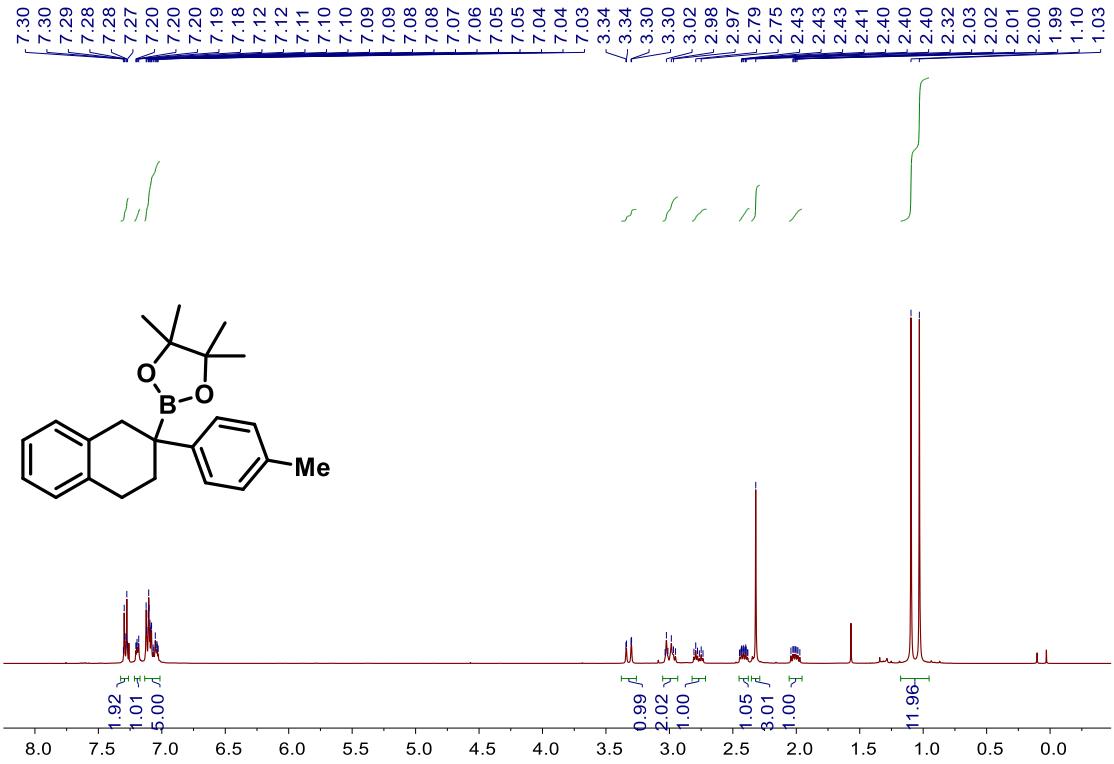
^{1}H NMR spectrum of **11a** (400 MHz, Chloroform-*d*)



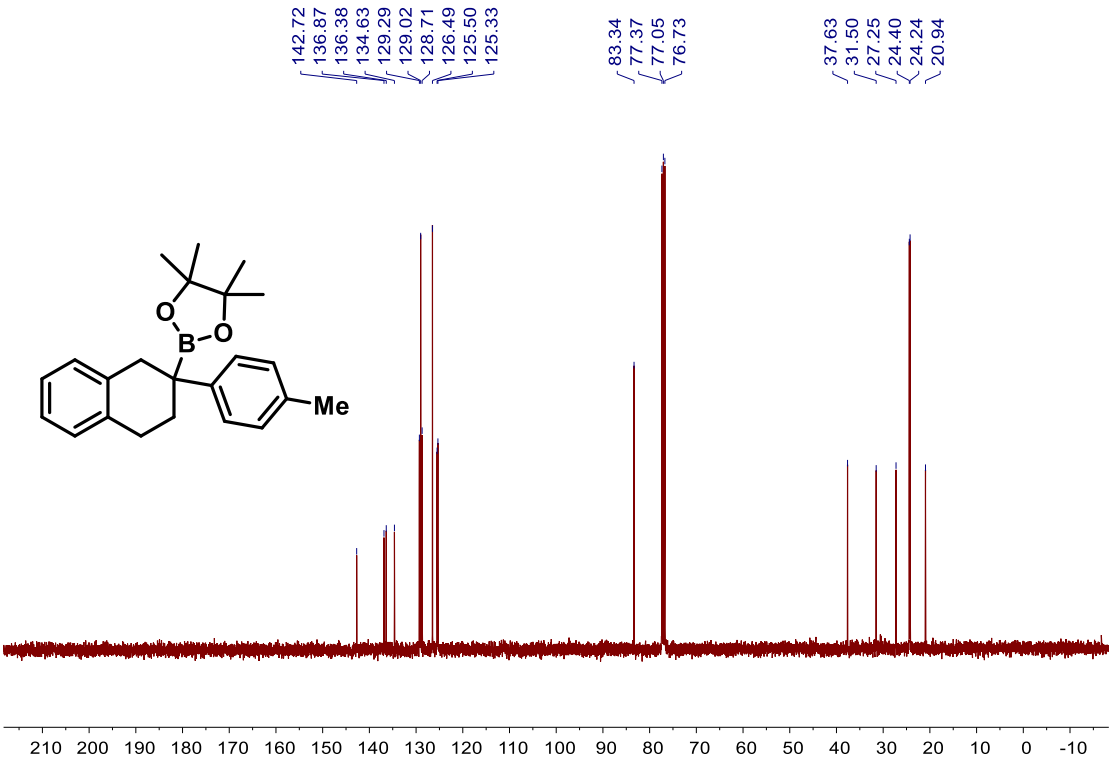
^{13}C NMR spectrum of **11a** (101 MHz, Chloroform-*d*)



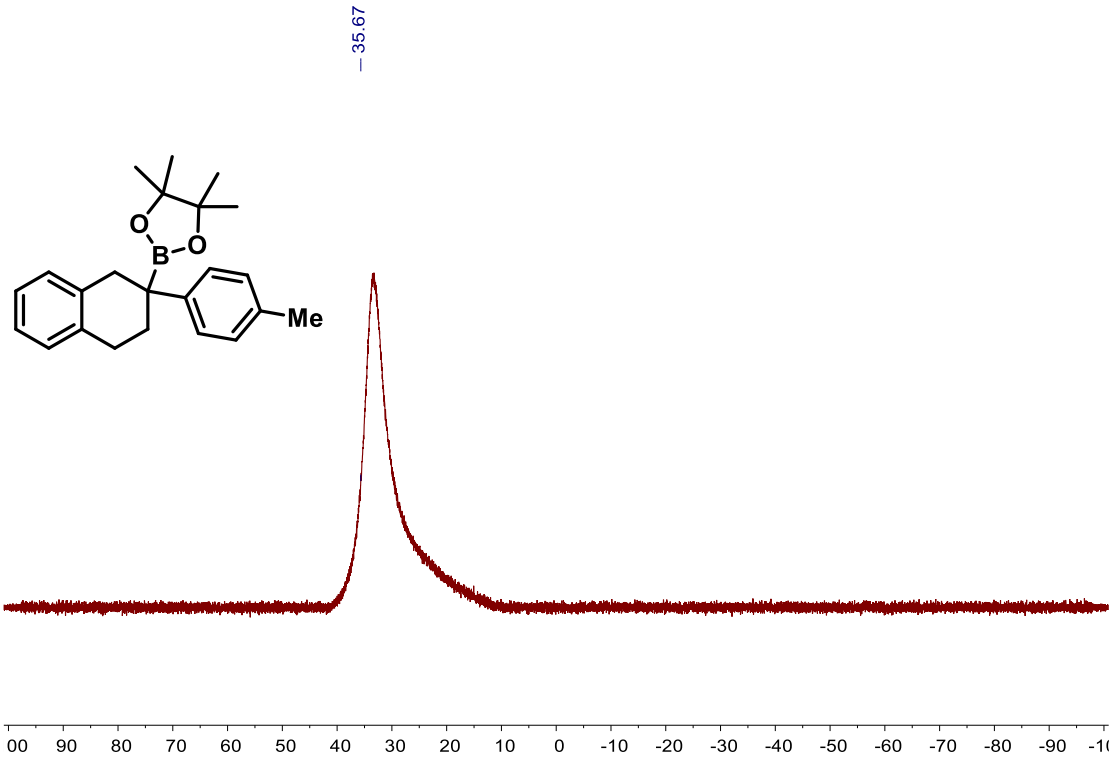
^{11}B NMR spectrum of **11a** (128 MHz Chloroform-*d*)



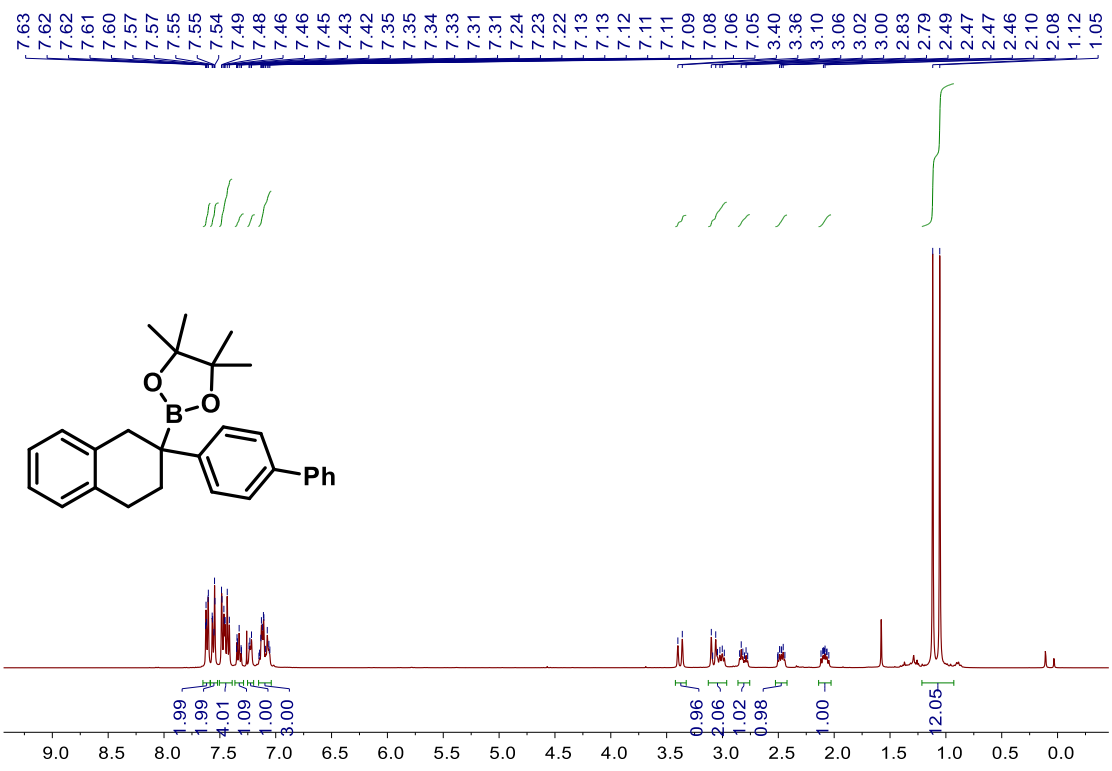
^{1}H NMR spectrum of **11b** (400 MHz, Chloroform-*d*)



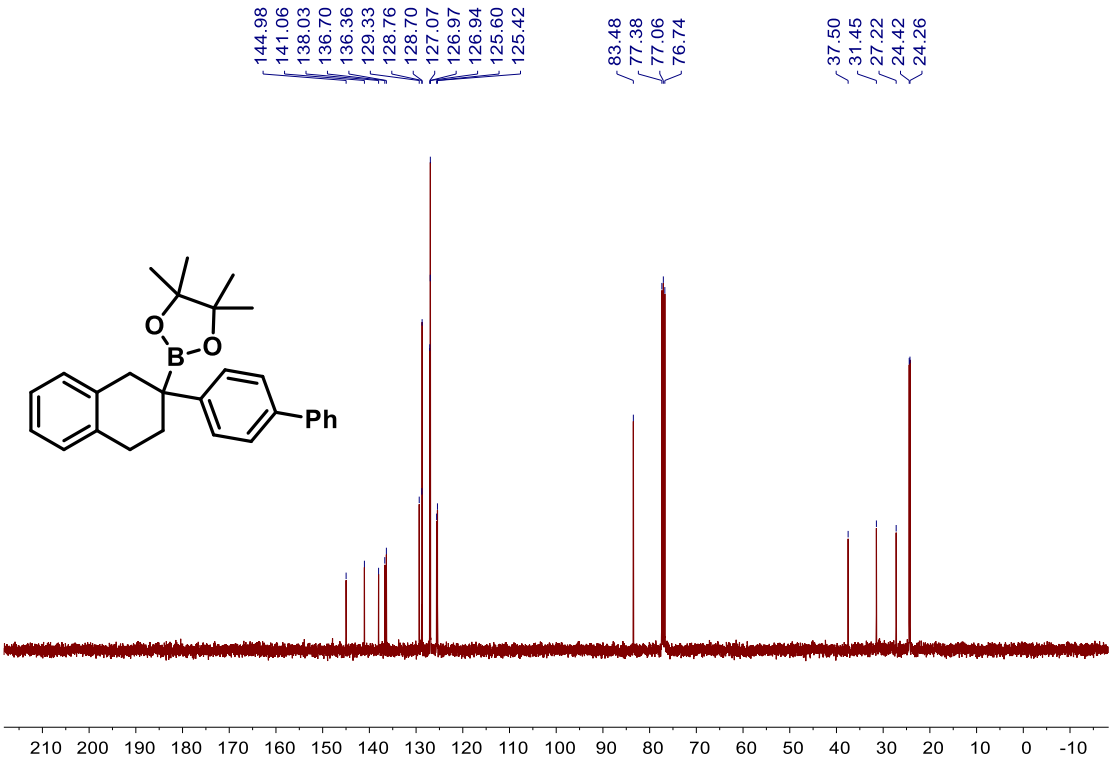
^{13}C NMR spectrum of **11b** (101 MHz, Chloroform-*d*)



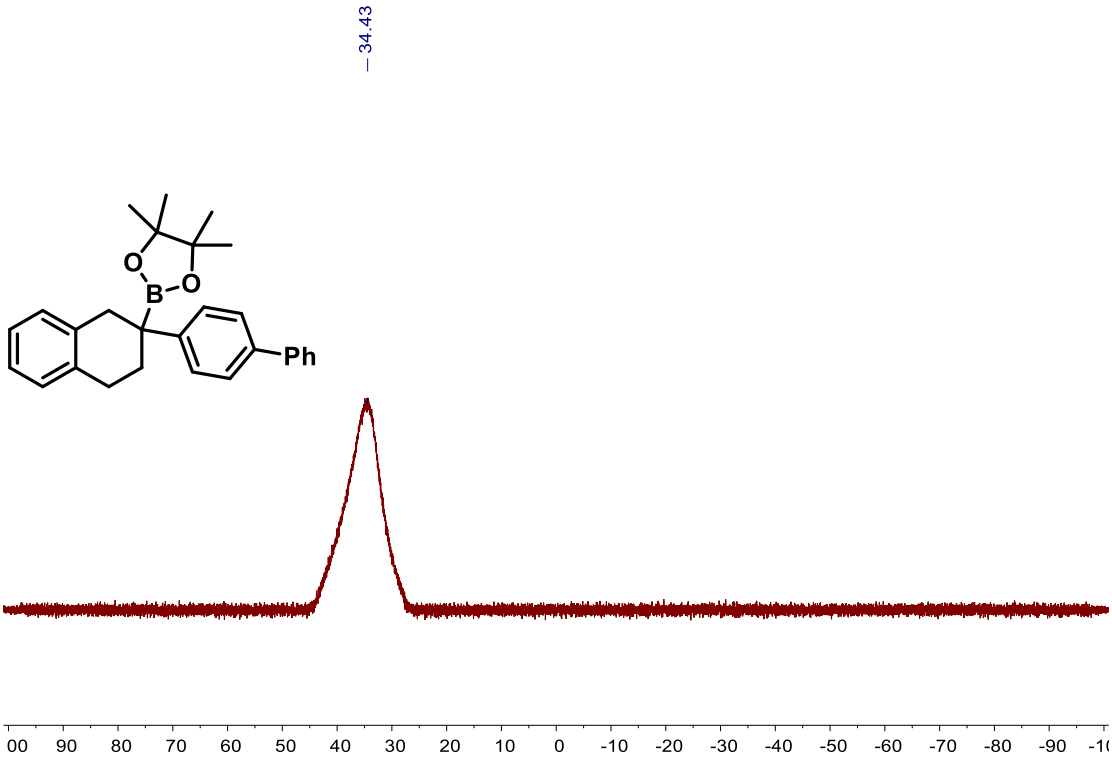
^{11}B NMR spectrum of **11b** (128 MHz Chloroform-*d*)



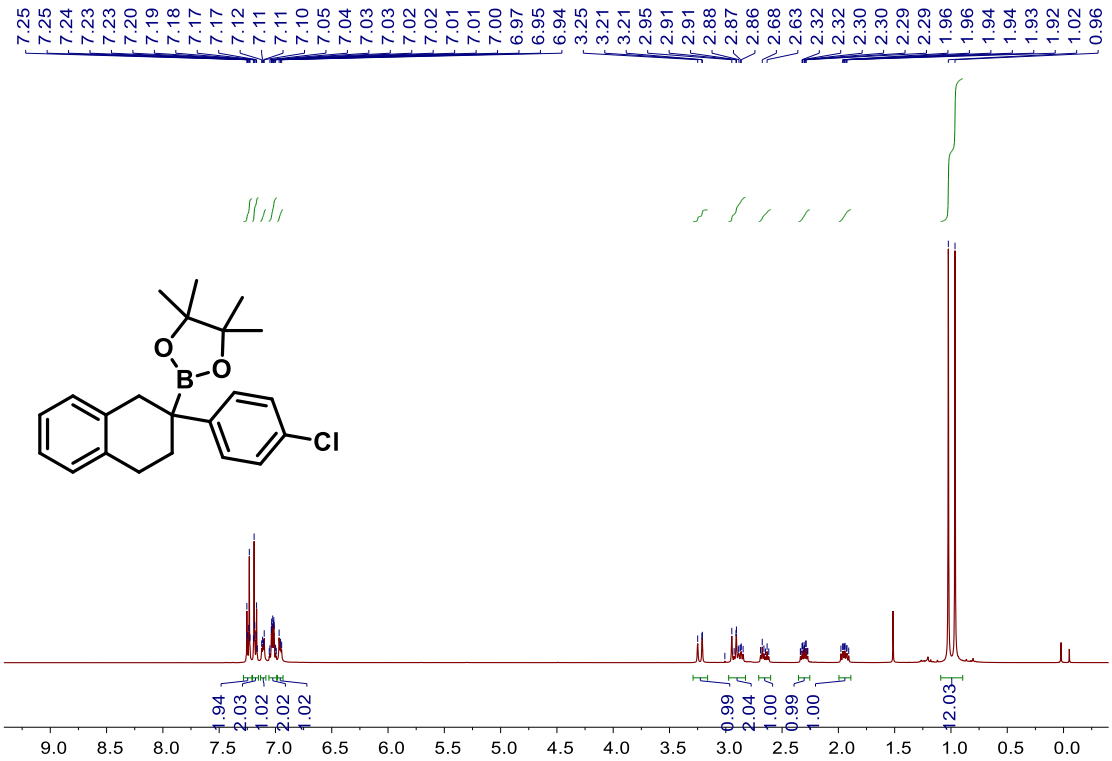
^{1}H NMR spectrum of **11c** (400 MHz, Chloroform-*d*)



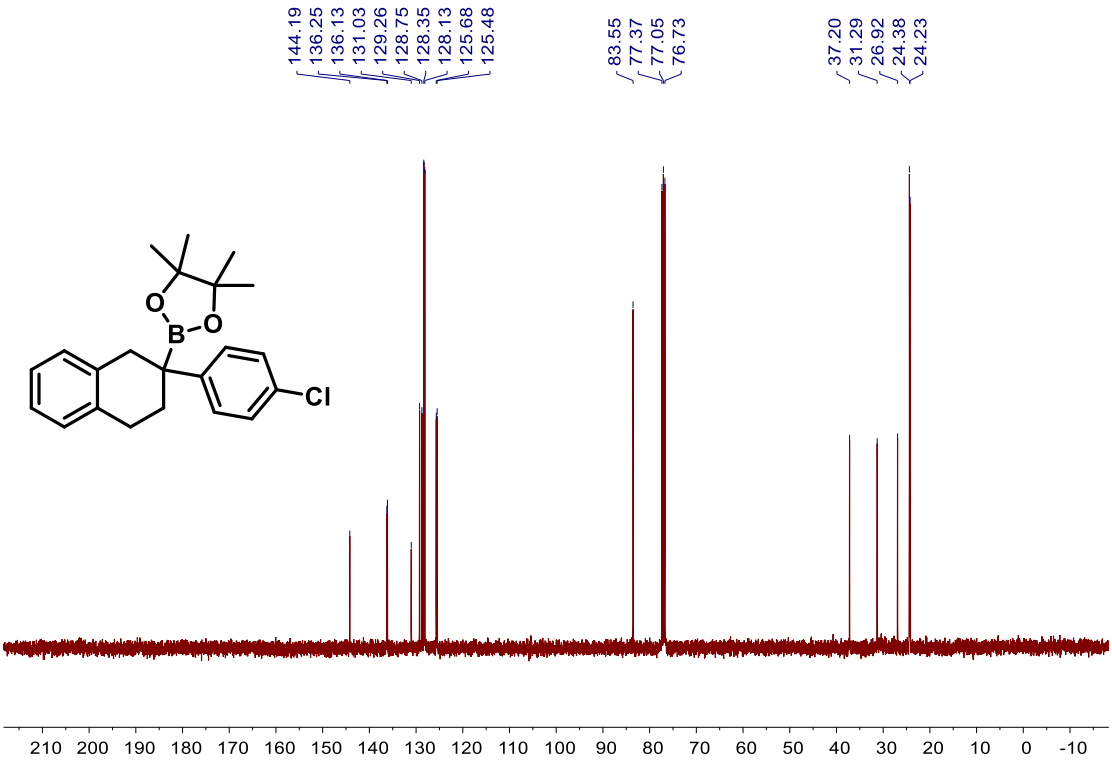
^{13}C NMR spectrum of **11c** (101 MHz, Chloroform-*d*)



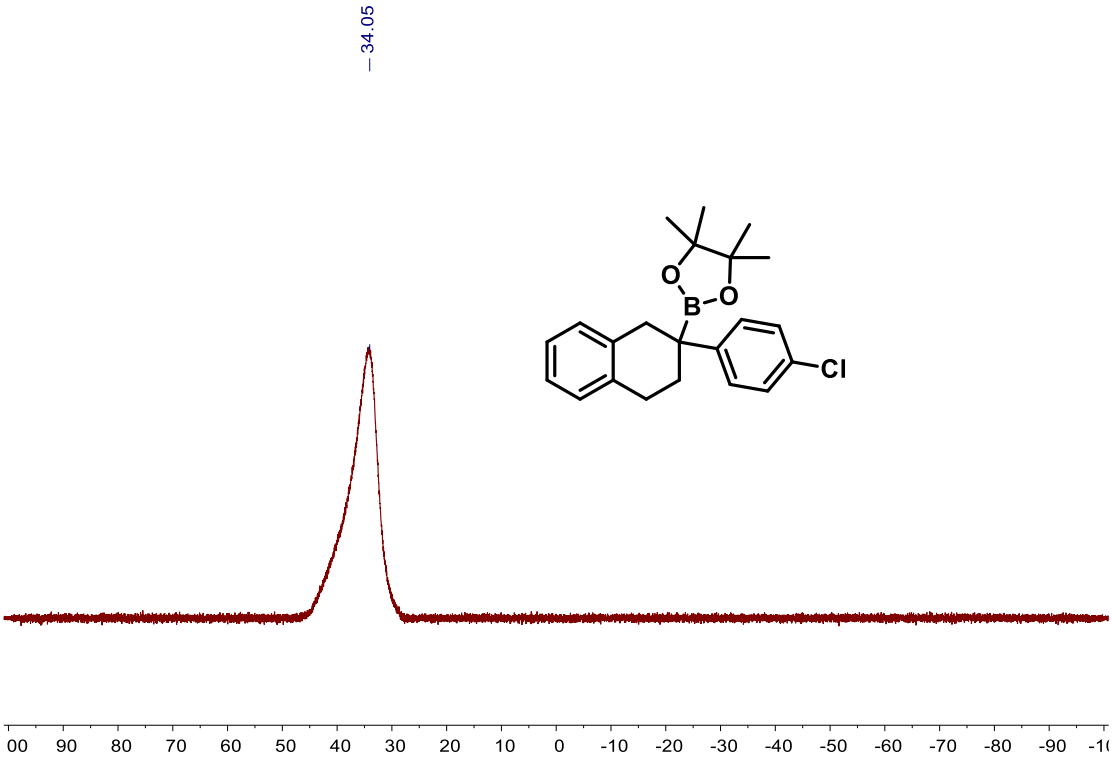
^{11}B NMR spectrum of **11c** (128 MHz Chloroform-*d*)



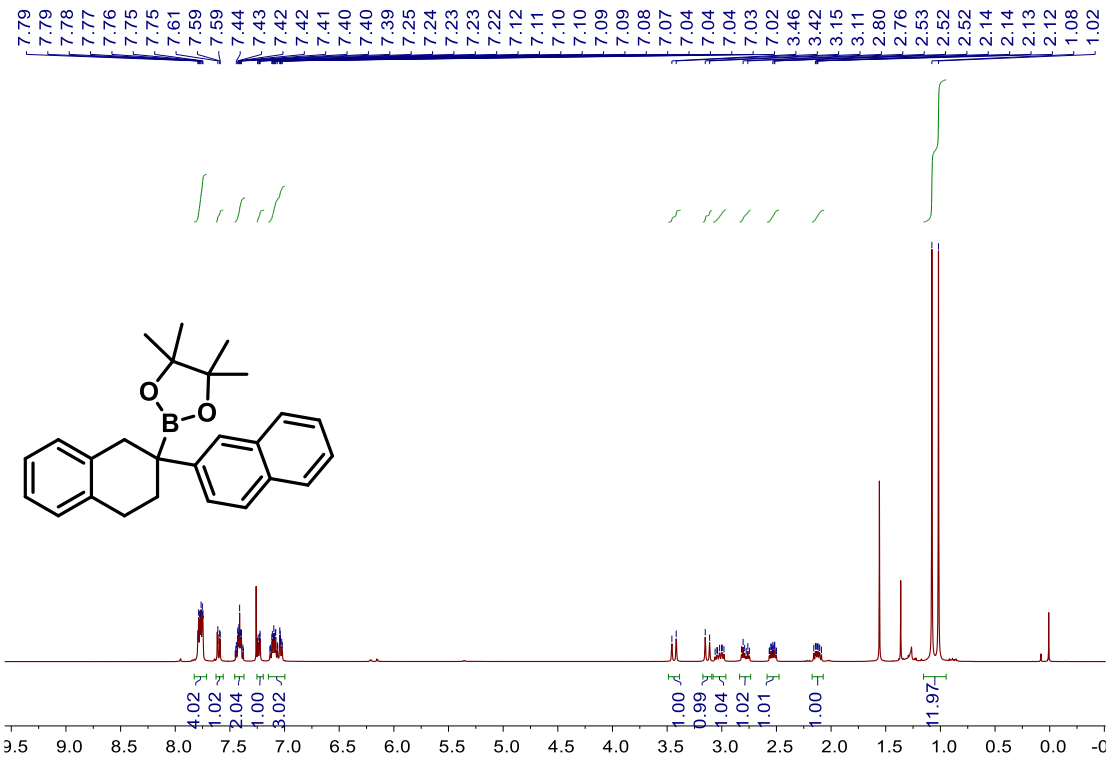
^{1}H NMR spectrum of **11d** (400 MHz, Chloroform-*d*)



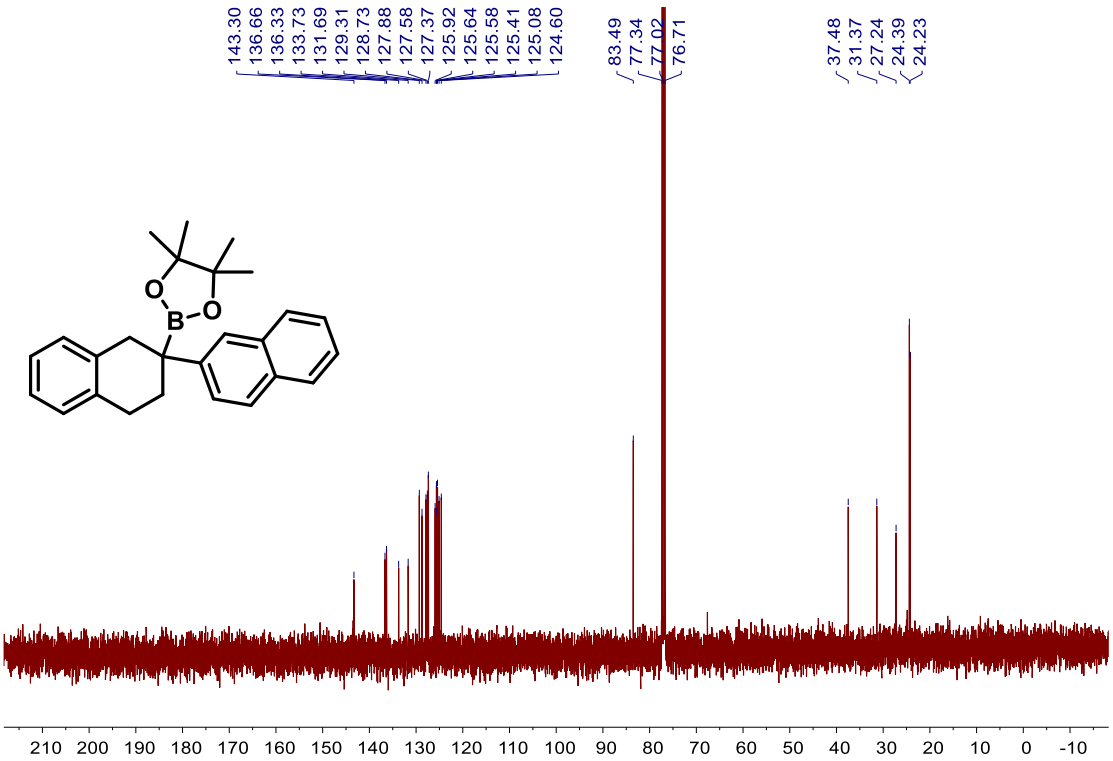
^{13}C NMR spectrum of **11d** (101 MHz, Chloroform-*d*)



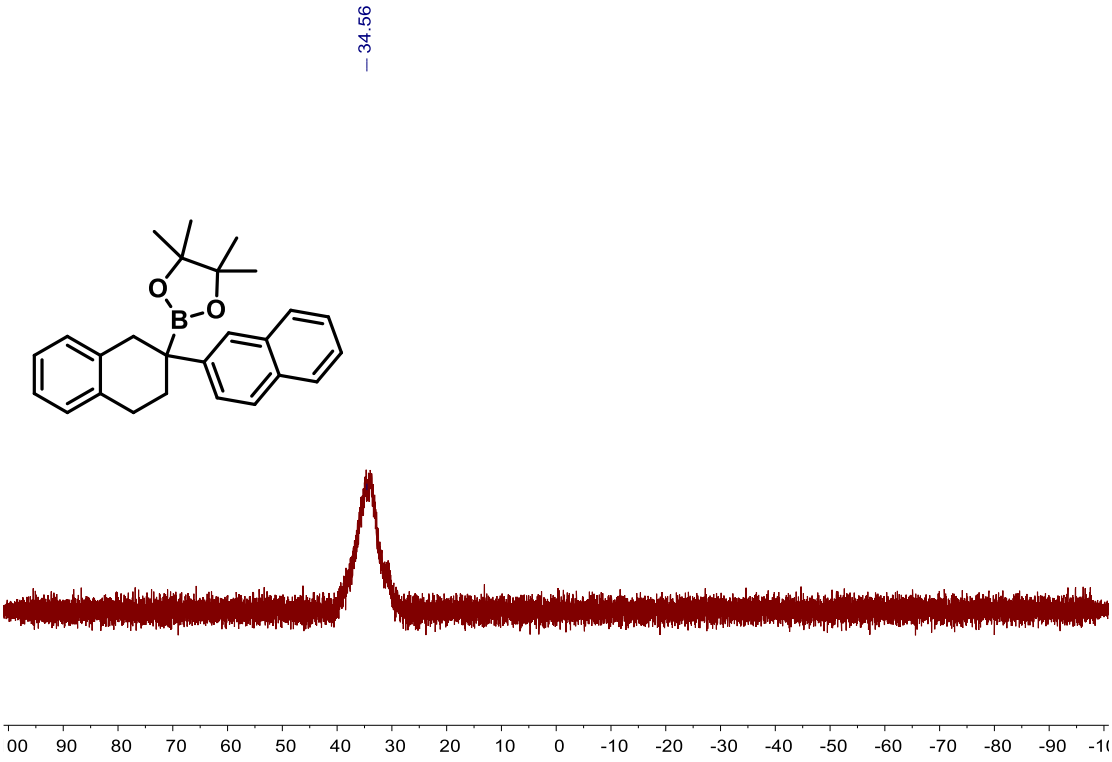
^{11}B NMR spectrum of **11d** (128 MHz Chloroform-*d*)



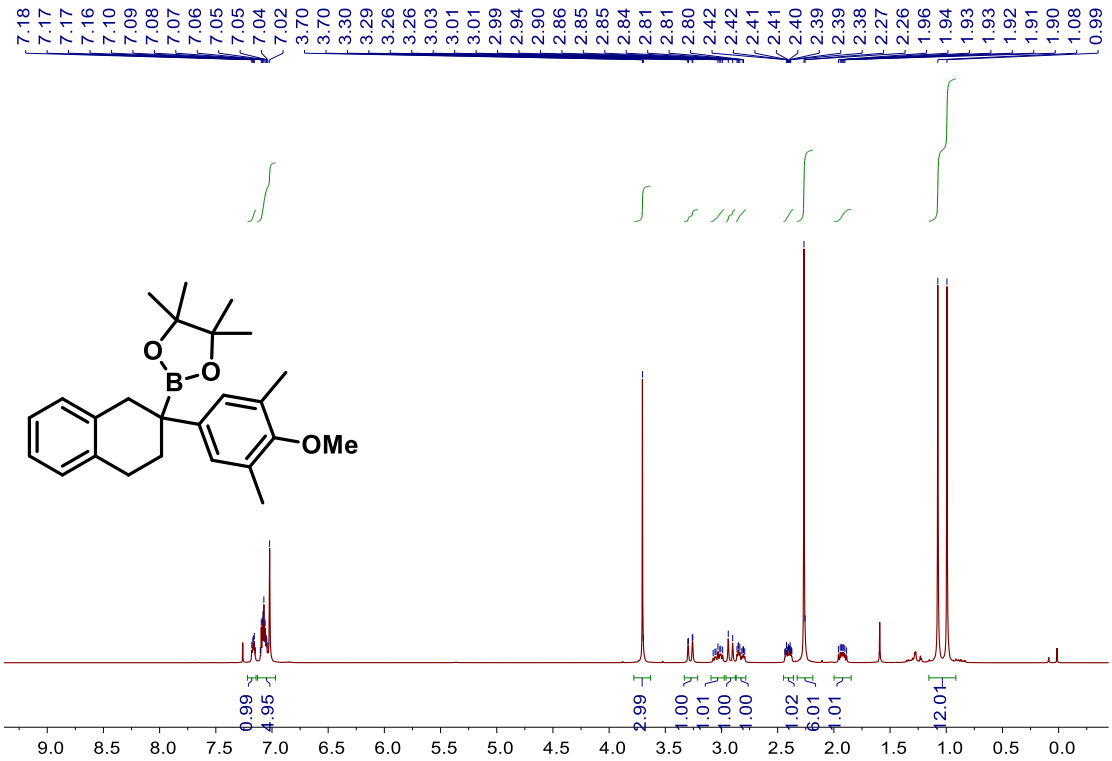
^{1}H NMR spectrum of **11e** (400 MHz, Chloroform-*d*)



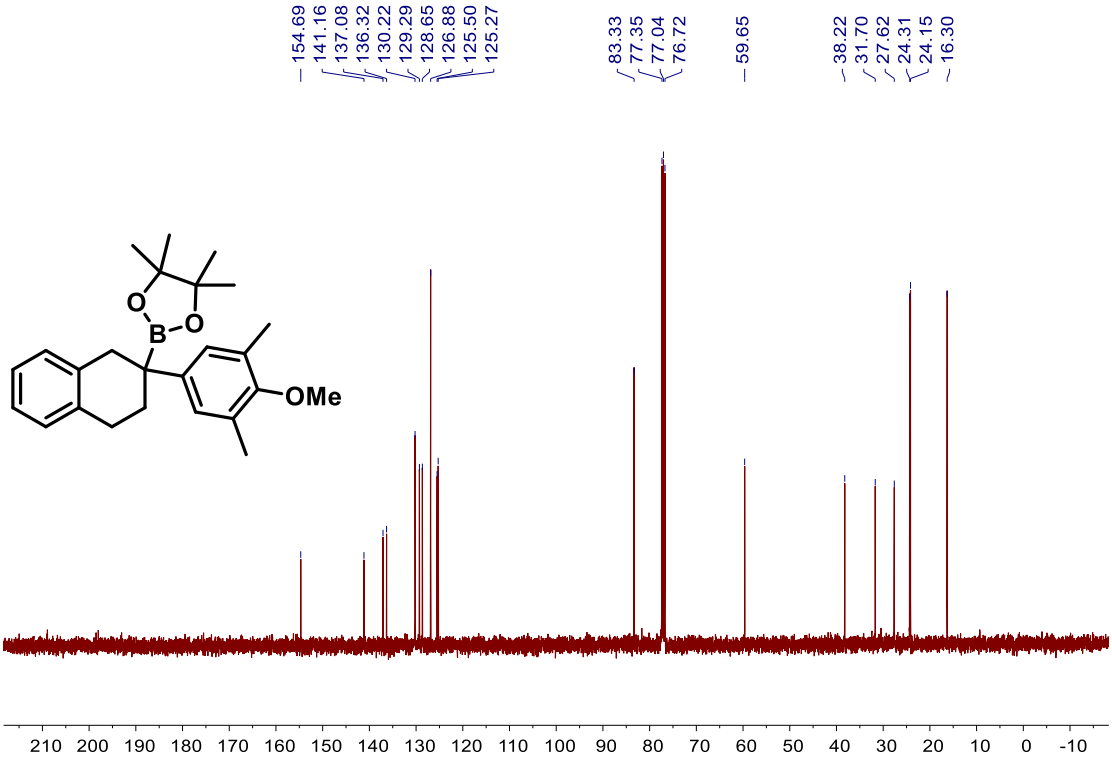
^{13}C NMR spectrum of **11e** (101 MHz, Chloroform-*d*)



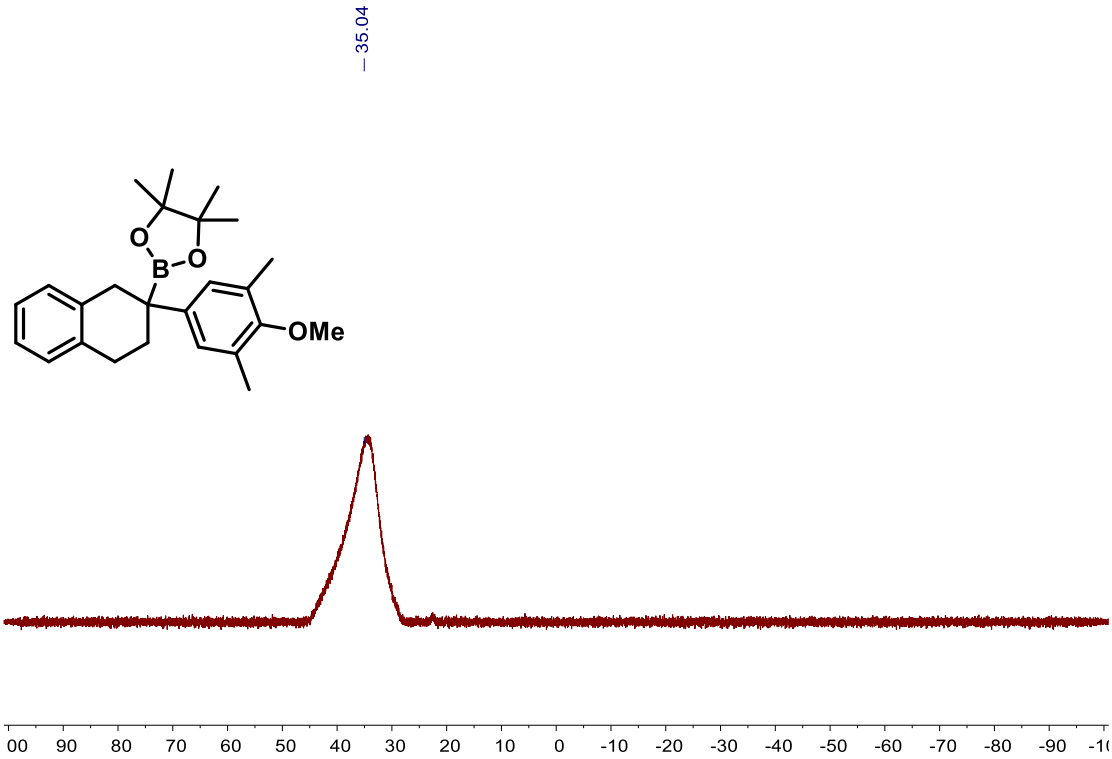
^{11}B NMR spectrum of **11e** (128 MHz Chloroform-*d*)



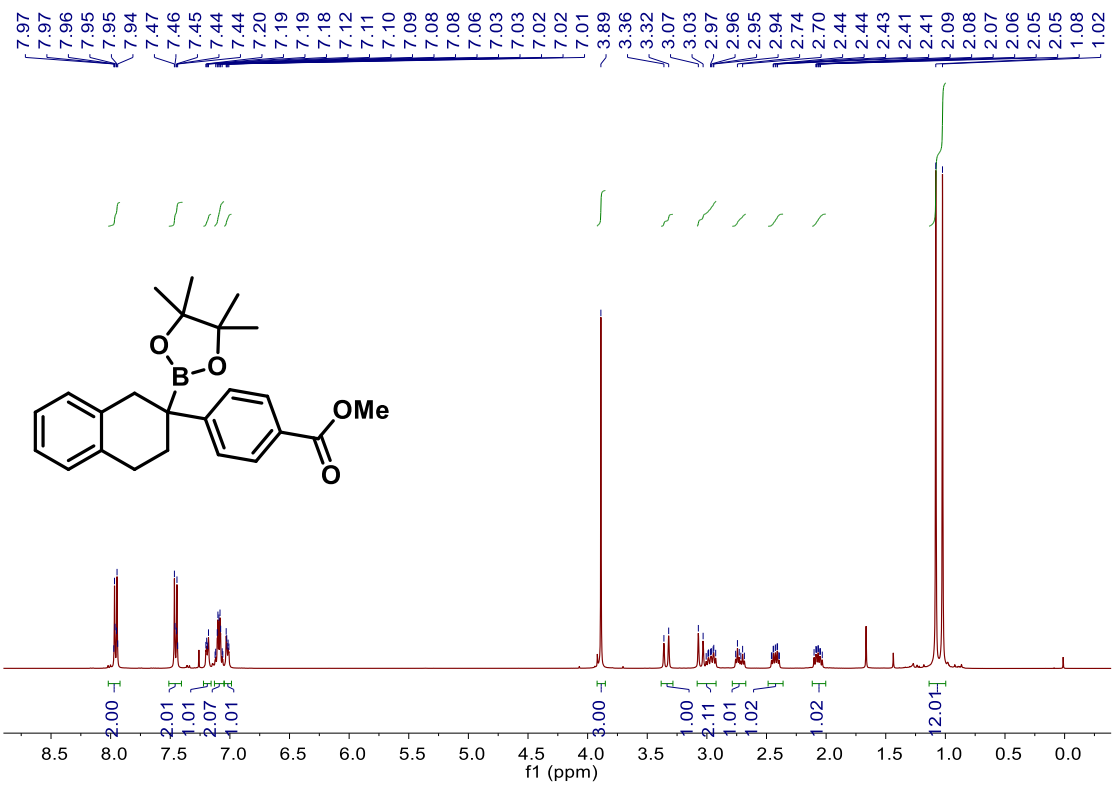
^{1}H NMR spectrum of **11f** (400 MHz, Chloroform-*d*)



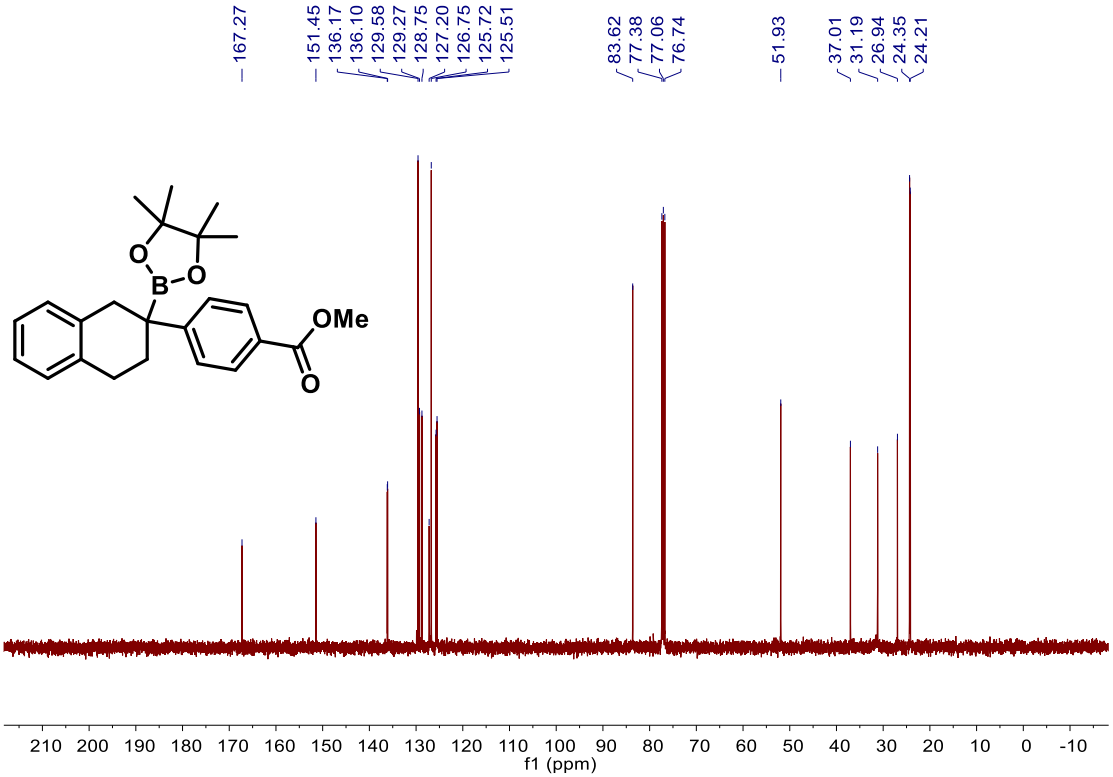
^{13}C NMR spectrum of **11f** (101 MHz, Chloroform-*d*)



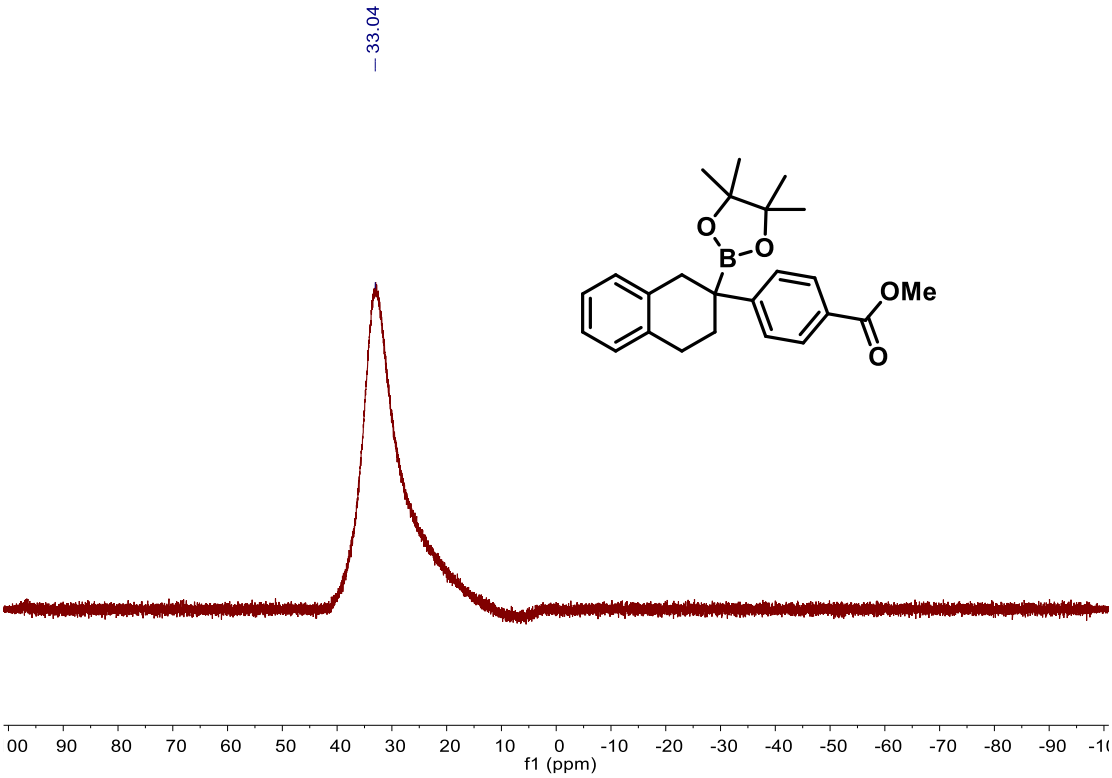
^{11}B NMR spectrum of **11f** (128 MHz Chloroform-*d*)



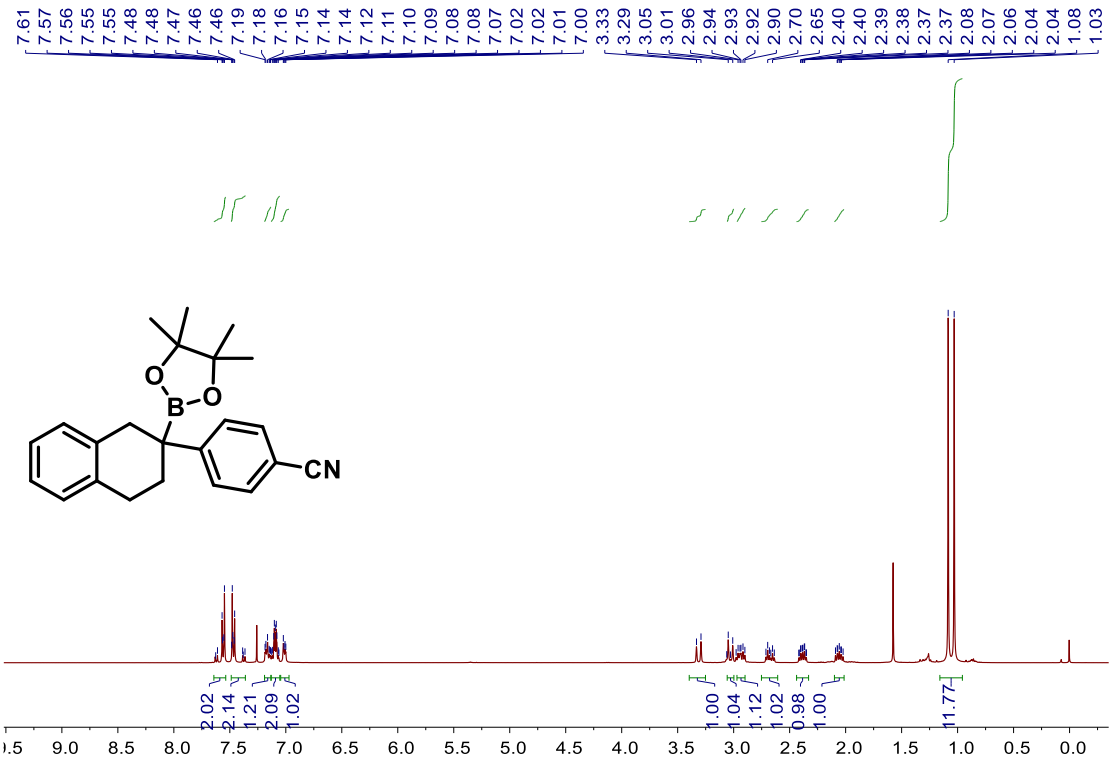
^{1}H NMR spectrum of **11g** (400 MHz, Chloroform-*d*)



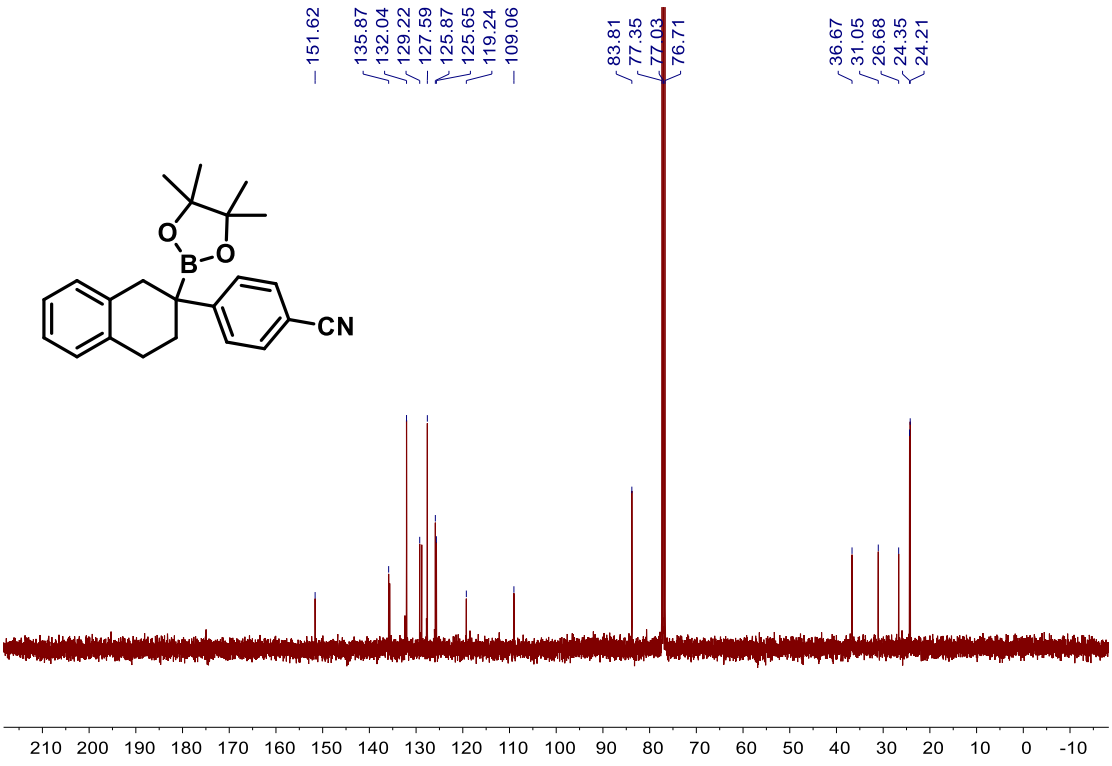
^{13}C NMR spectrum of **11g** (101 MHz, Chloroform-*d*)



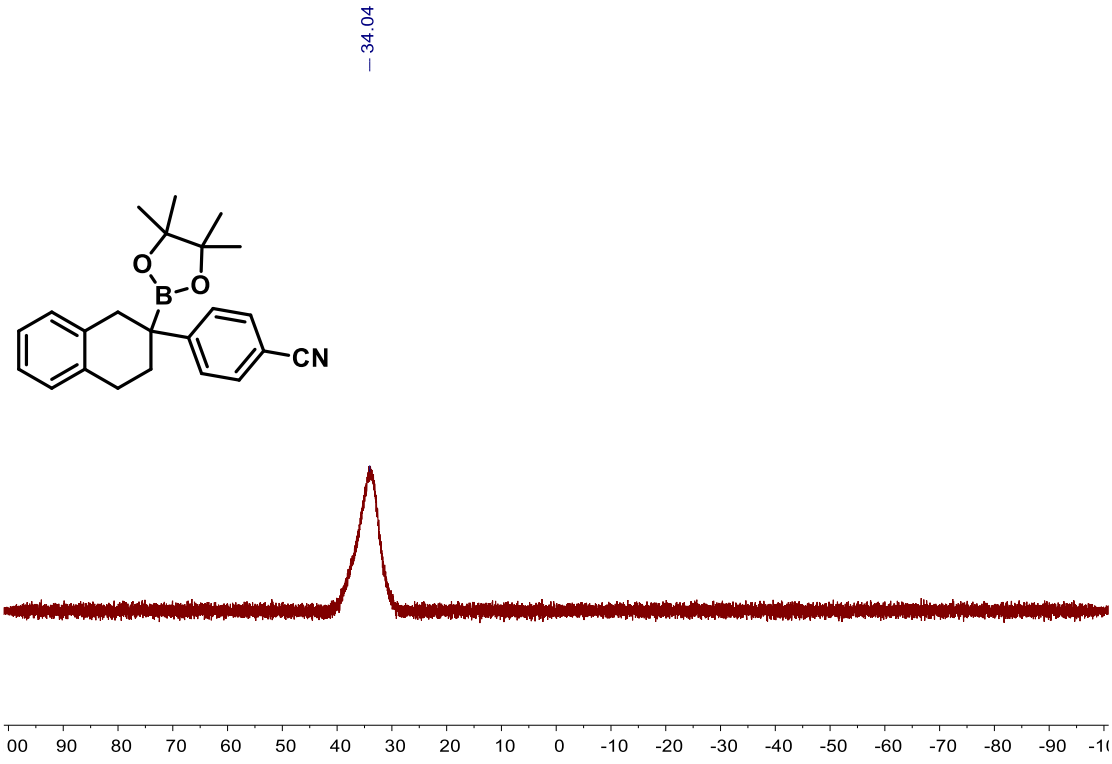
^{11}B NMR spectrum of **11g** (128 MHz Chloroform-*d*)



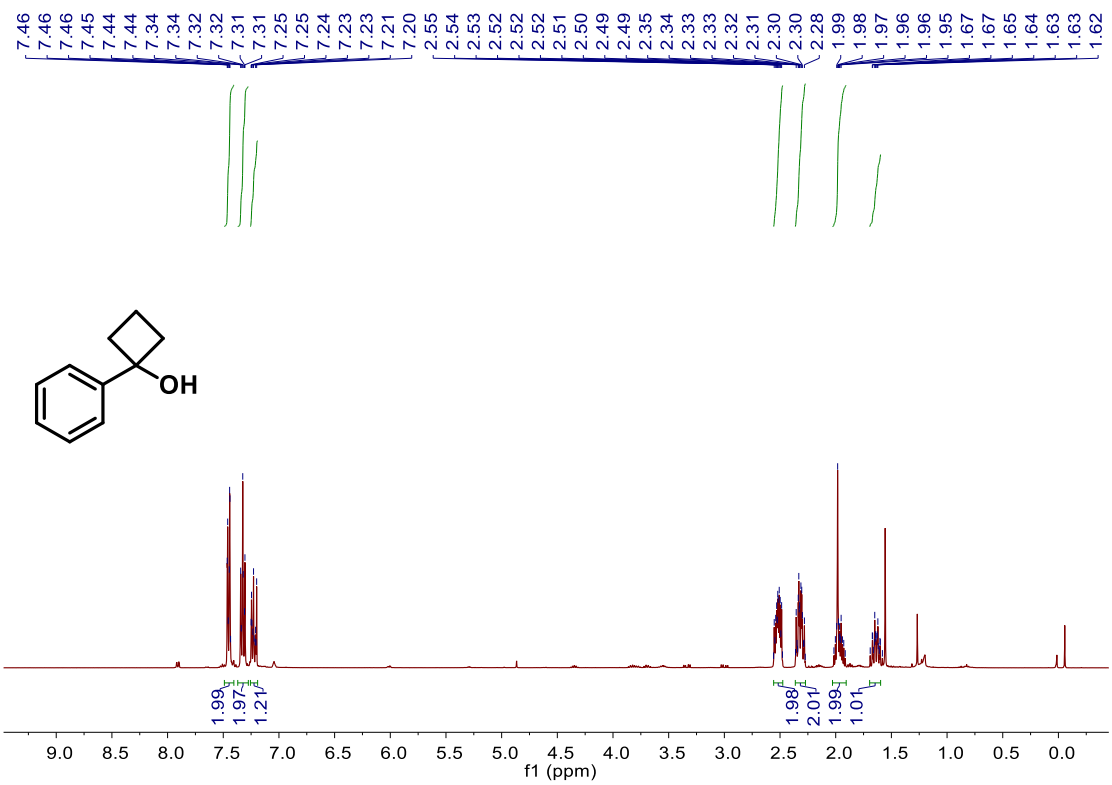
^{1}H NMR spectrum of **11h** (400 MHz, Chloroform-*d*)



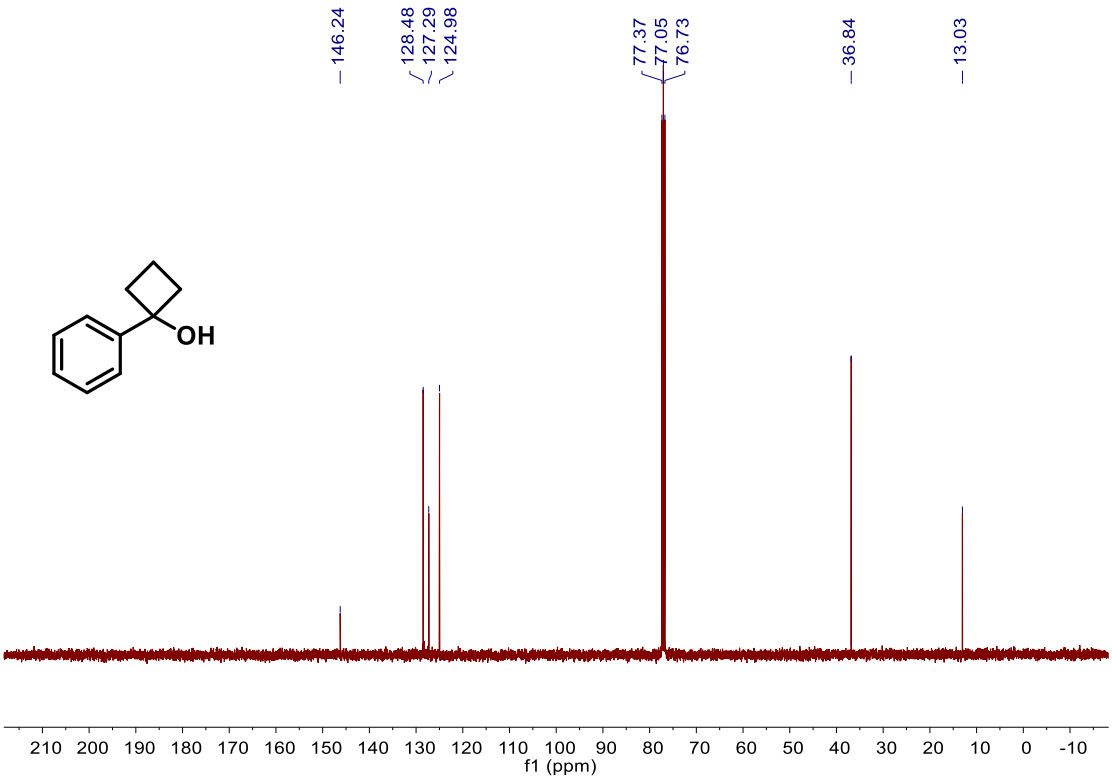
^{13}C NMR spectrum of **11h** (101 MHz, Chloroform-*d*)



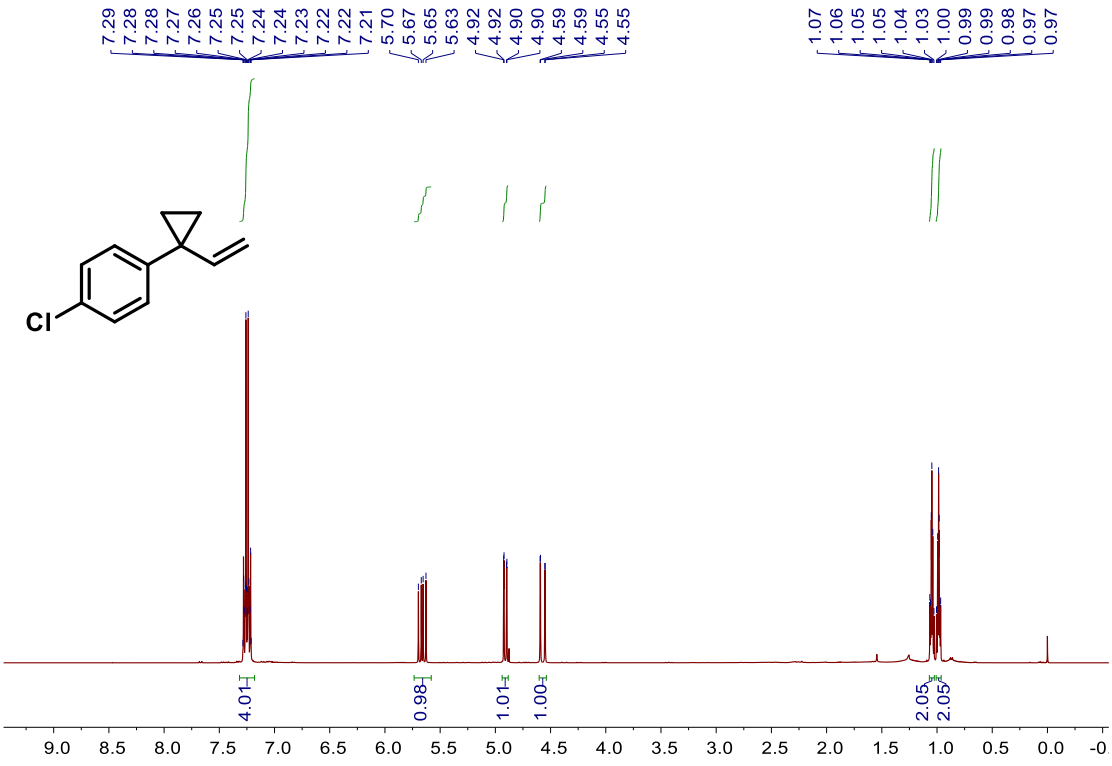
^{11}B NMR spectrum of **11h** (128 MHz Chloroform-*d*)



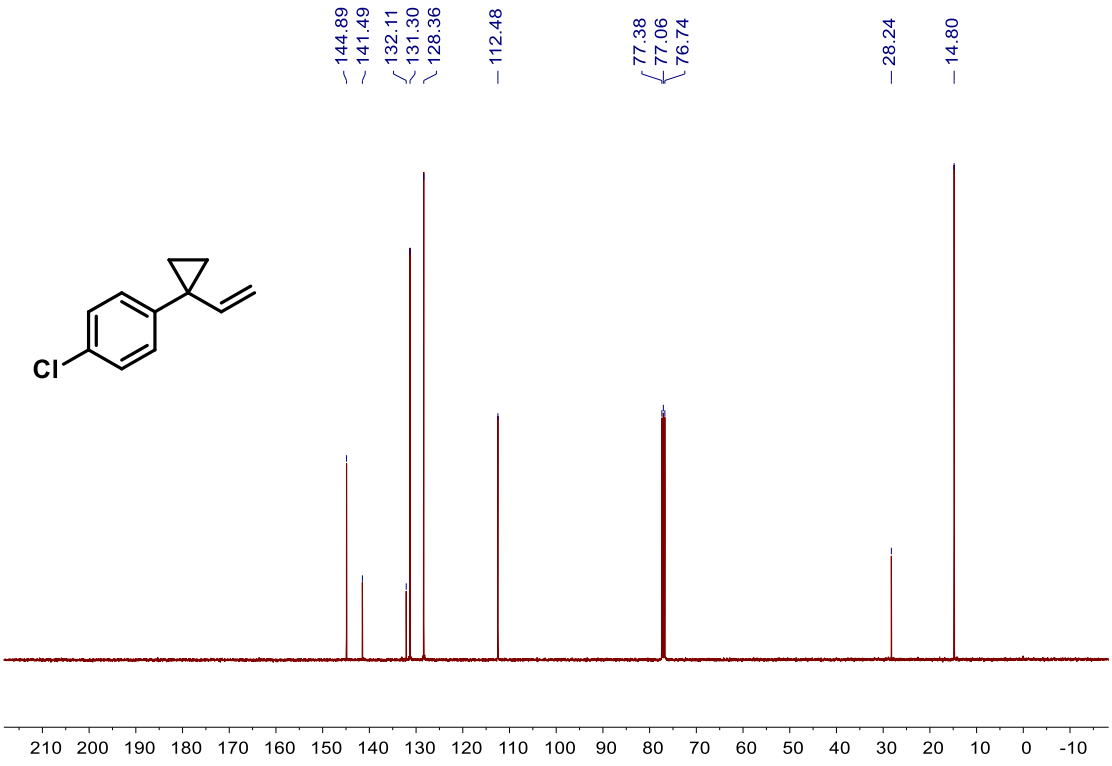
^{1}H NMR spectrum of **12a** (400 MHz, Chloroform-*d*)



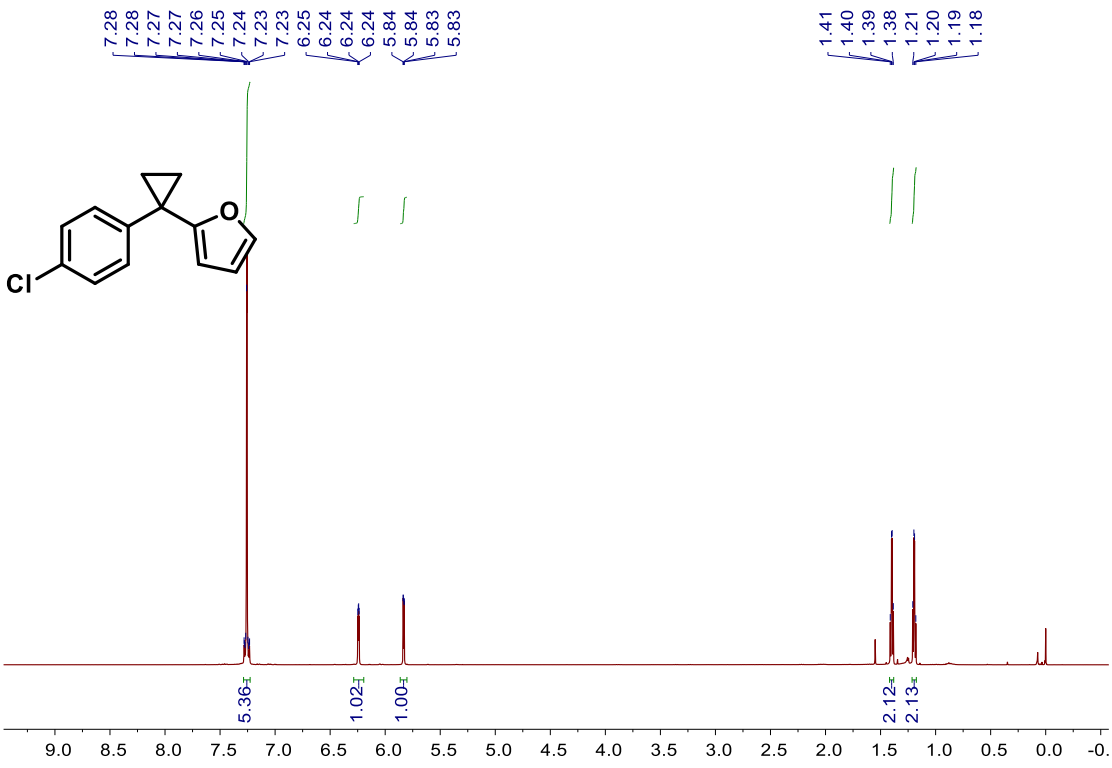
^{13}C NMR spectrum of **12a** (101 MHz, Chloroform-*d*)



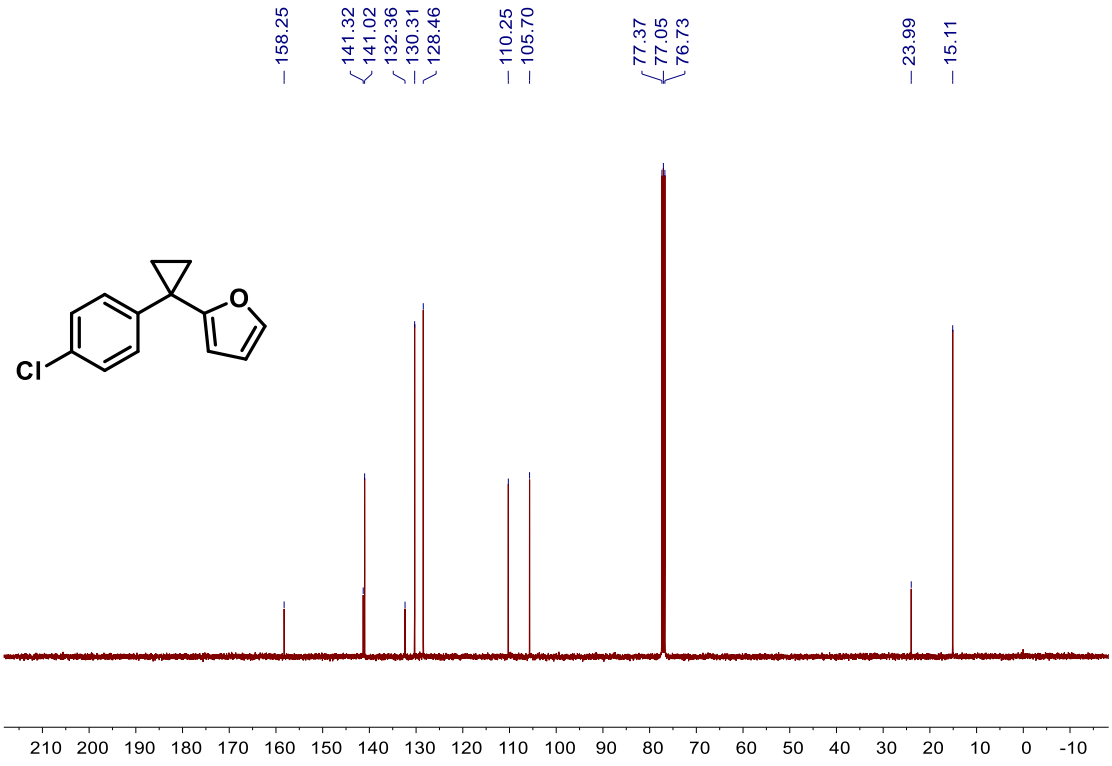
^{1}H NMR spectrum of **13a** (400 MHz, Chloroform-*d*)



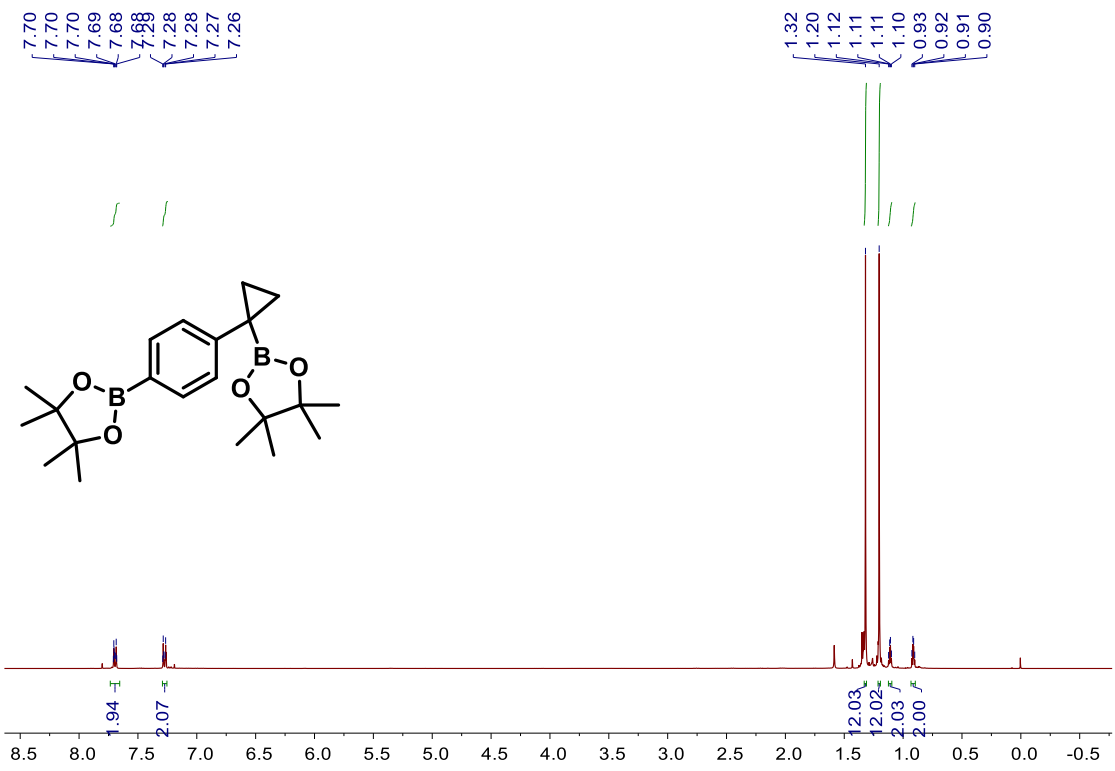
^{13}C NMR spectrum of **13a** (101 MHz, Chloroform-*d*)



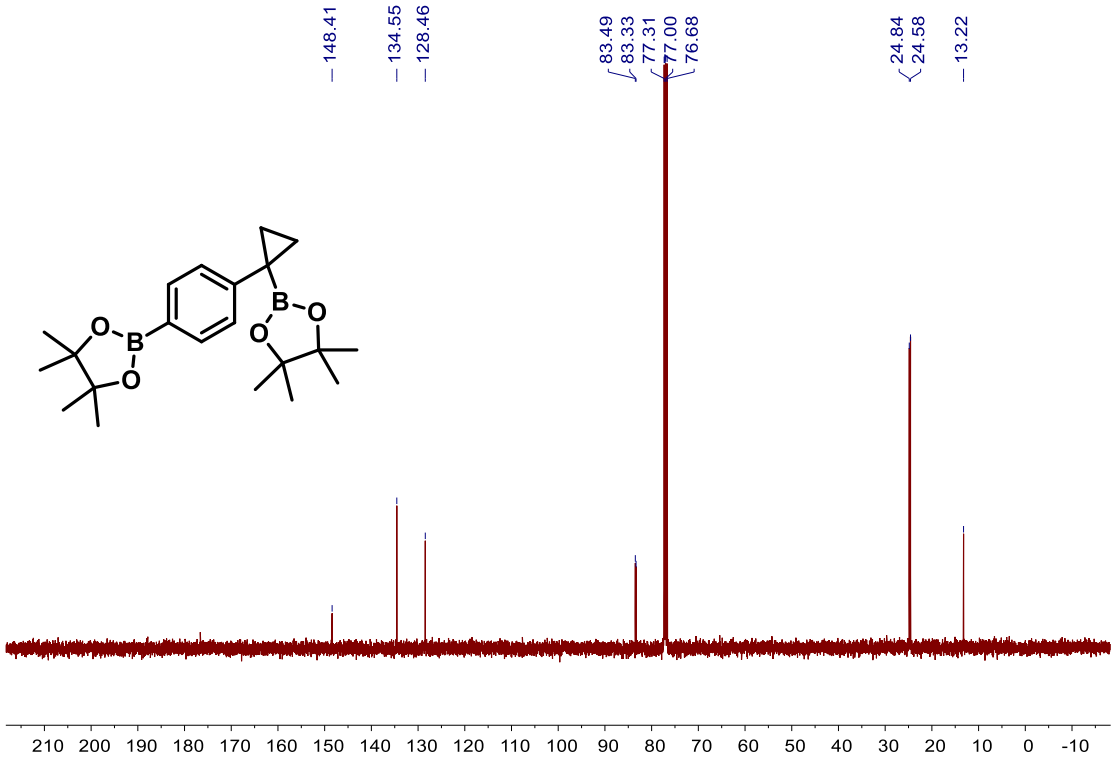
^{1}H NMR spectrum of **13b** (400 MHz, Chloroform-*d*)



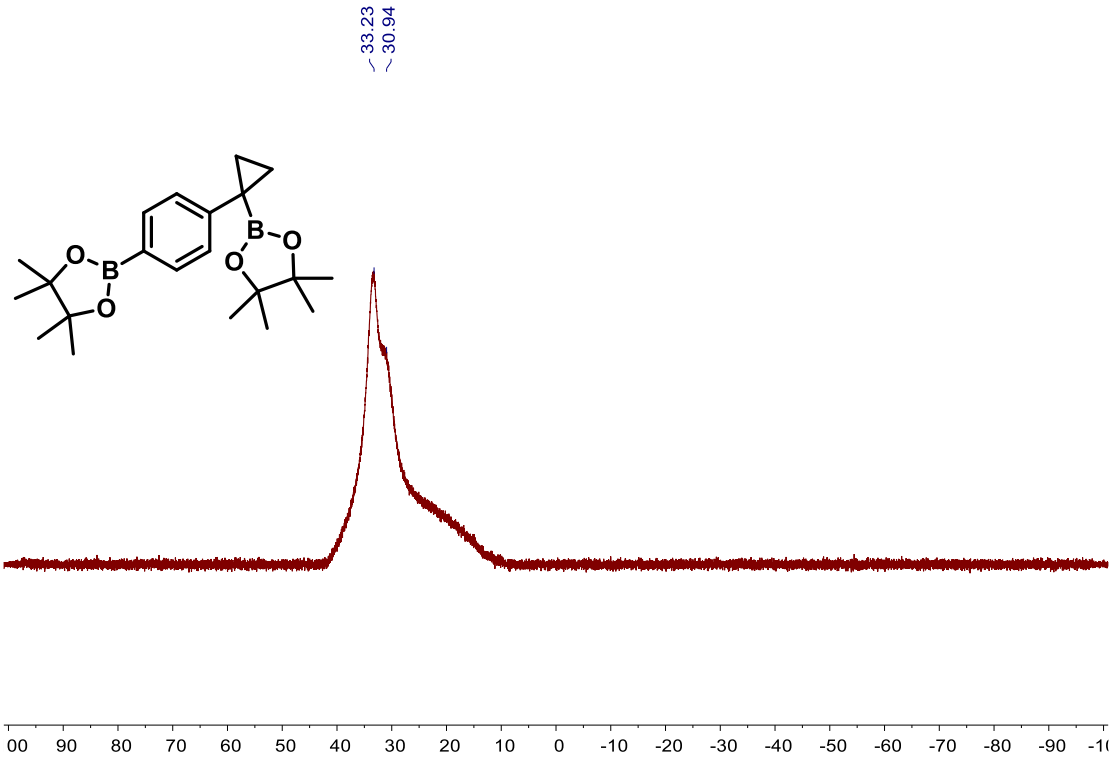
^{13}C NMR spectrum of **13b** (101 MHz, Chloroform-*d*)



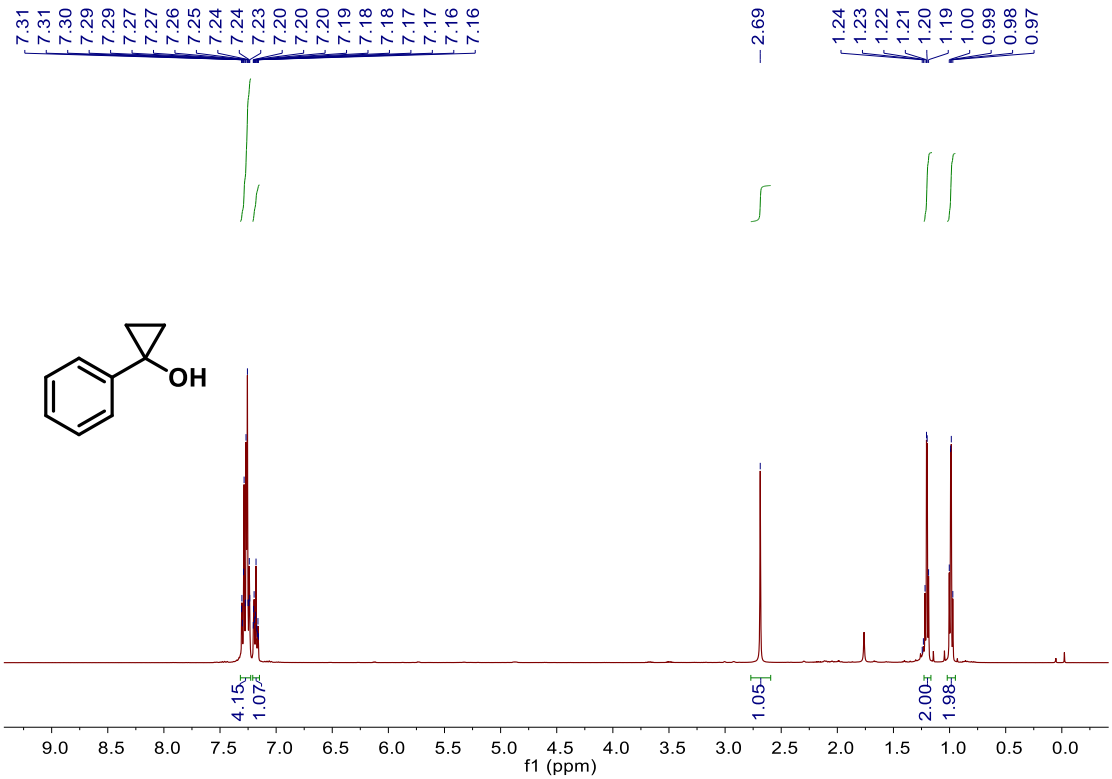
^{1}H NMR spectrum of **13c** (400 MHz, Chloroform-*d*)



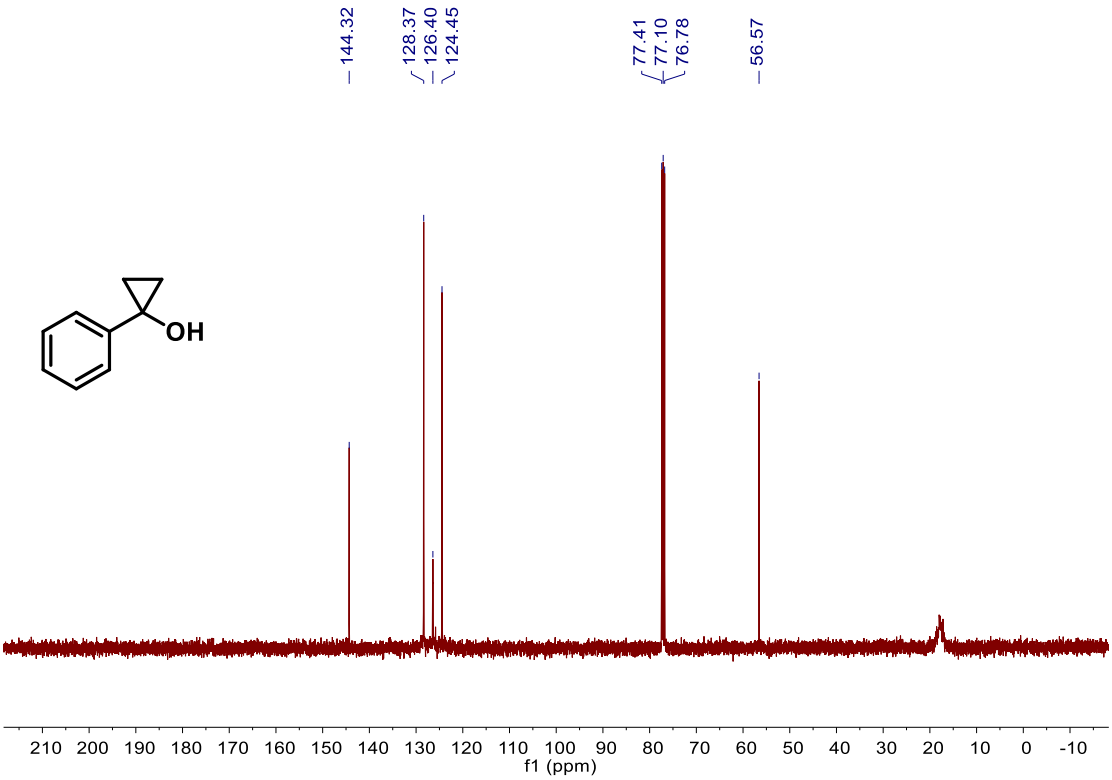
^{13}C NMR spectrum of **13c** (101 MHz, Chloroform-*d*)



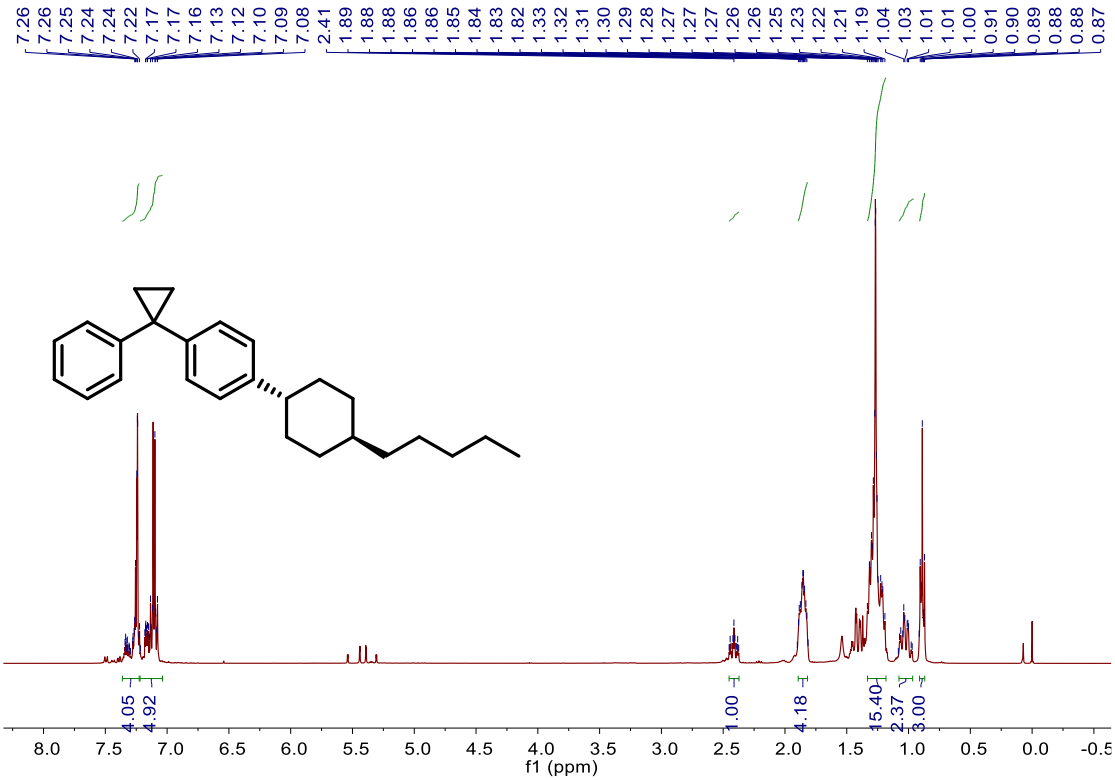
^{11}B NMR spectrum of **13c** (128 MHz Chloroform-*d*)



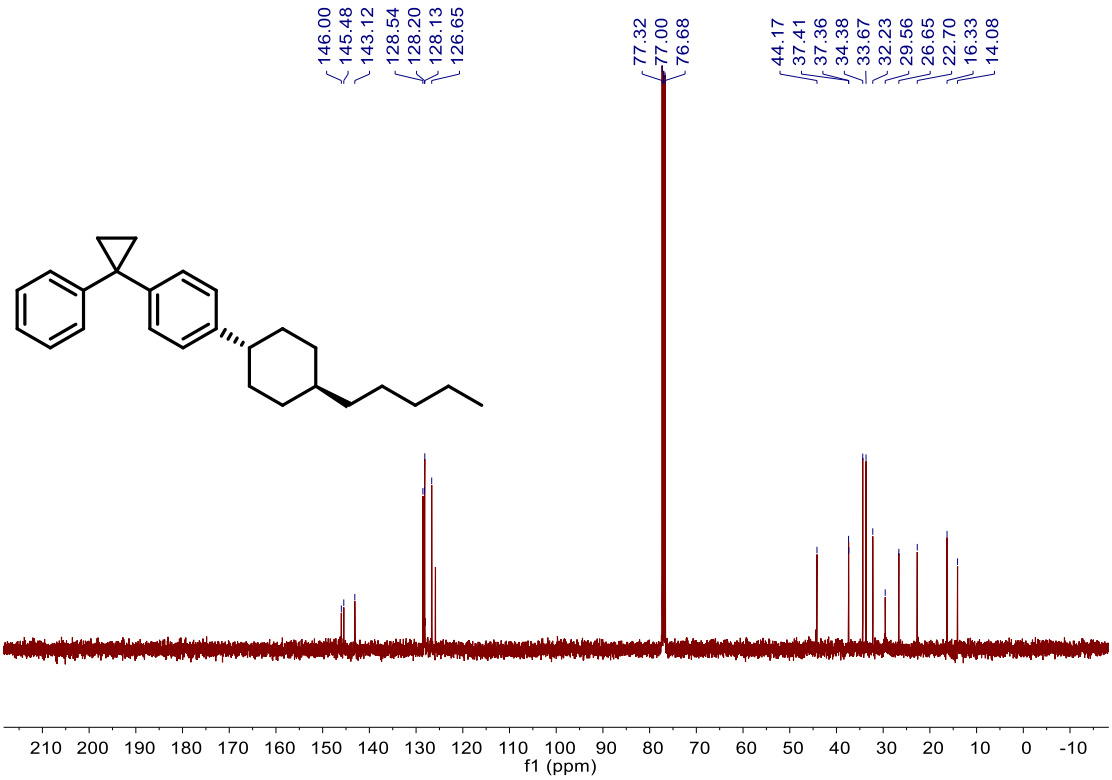
^{1}H NMR spectrum of **13d** (400 MHz, Chloroform-*d*)



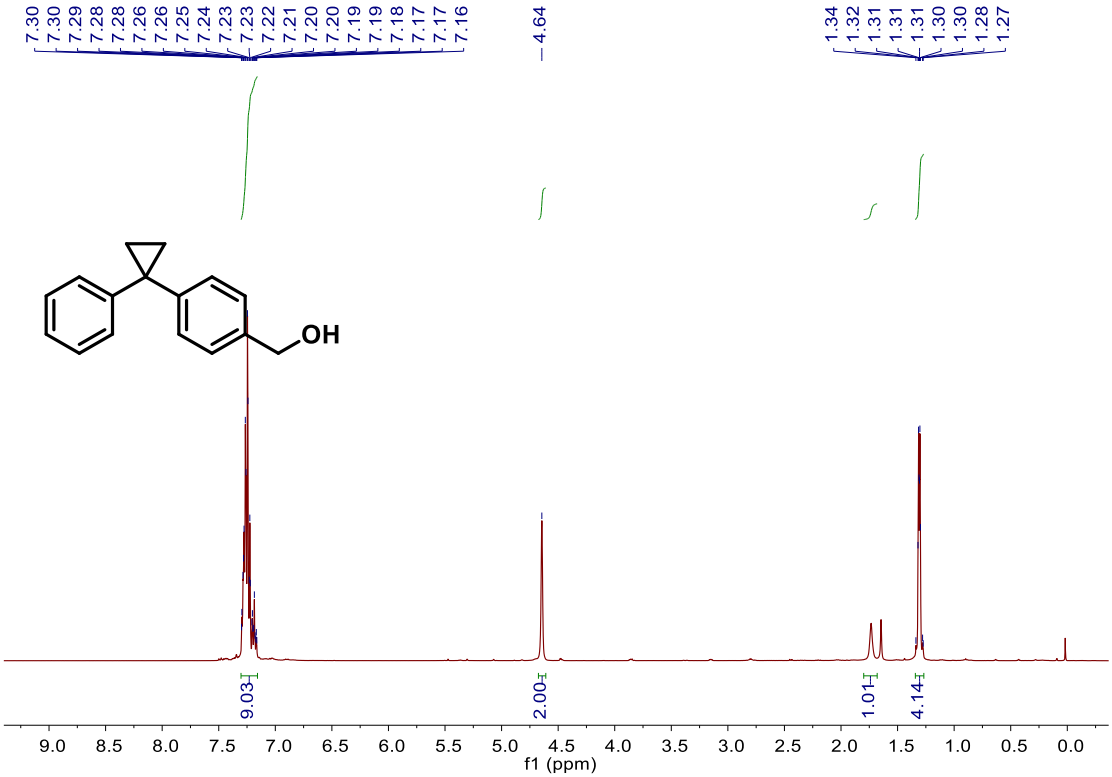
^{13}C NMR spectrum of **13d** (101 MHz, Chloroform-*d*)



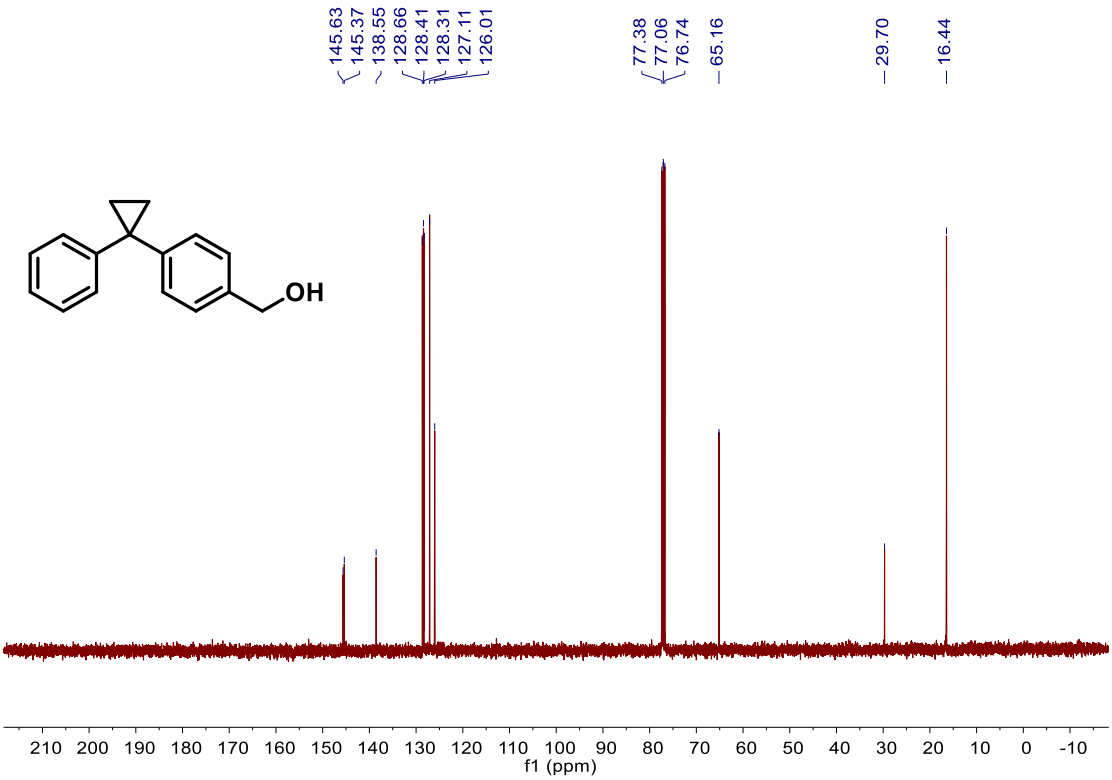
^{1}H NMR spectrum of **13e** (400 MHz, Chloroform-*d*)



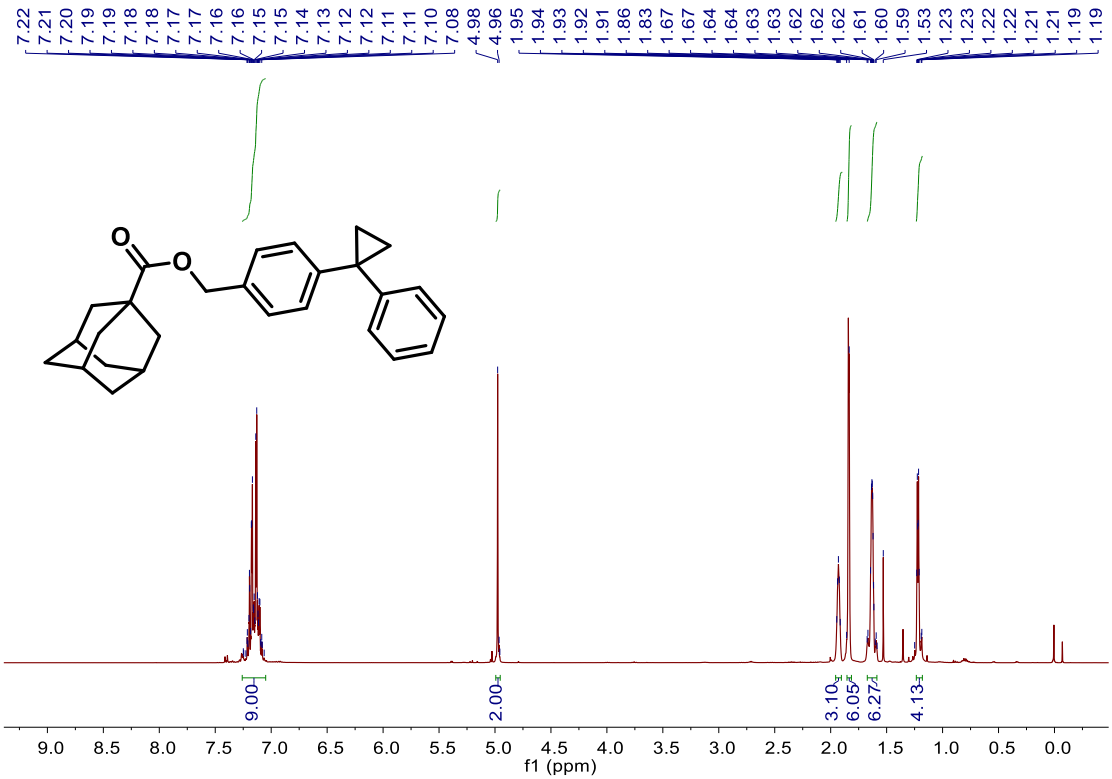
^{13}C NMR spectrum of **13e** (101 MHz, Chloroform-*d*)



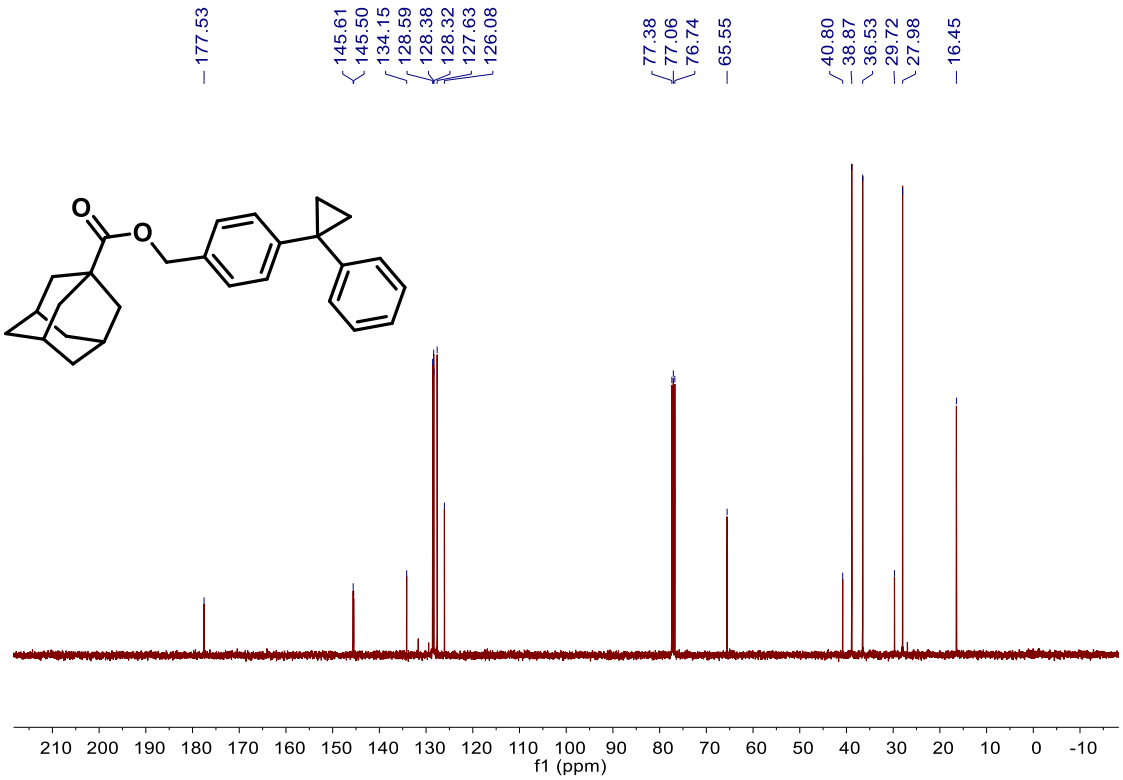
^{1}H NMR spectrum of **13f** (400 MHz, Chloroform-*d*)



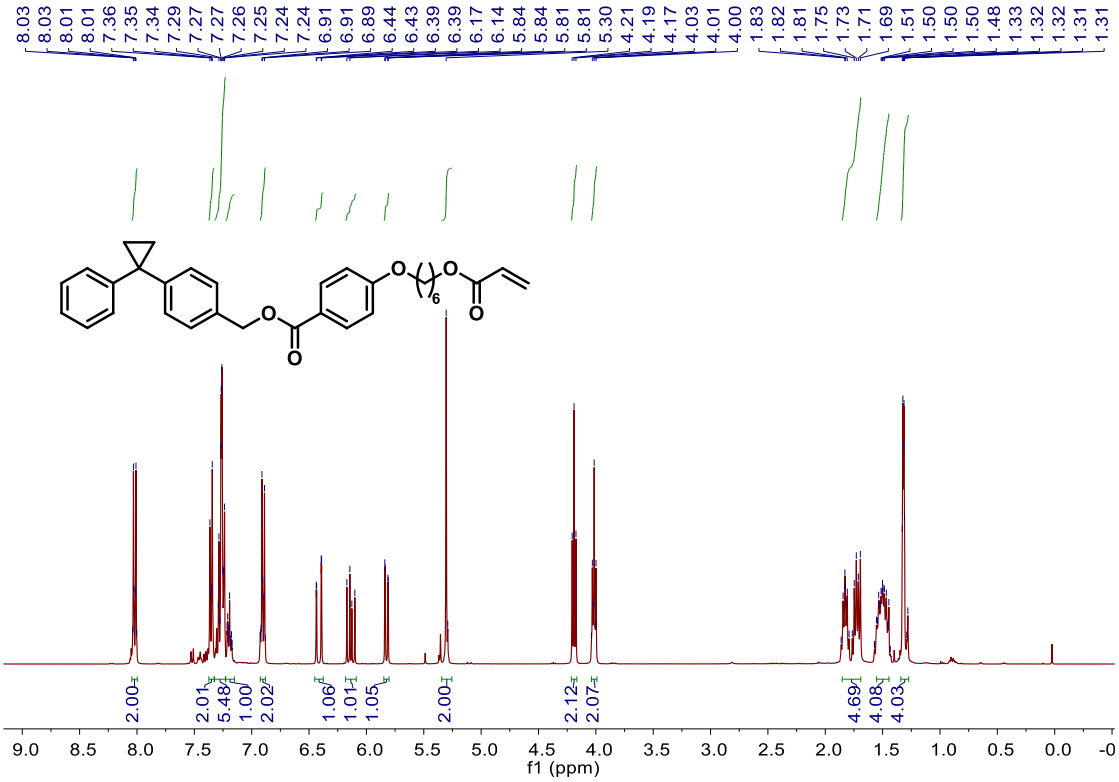
^{13}C NMR spectrum of **13f** (101 MHz, Chloroform-*d*)



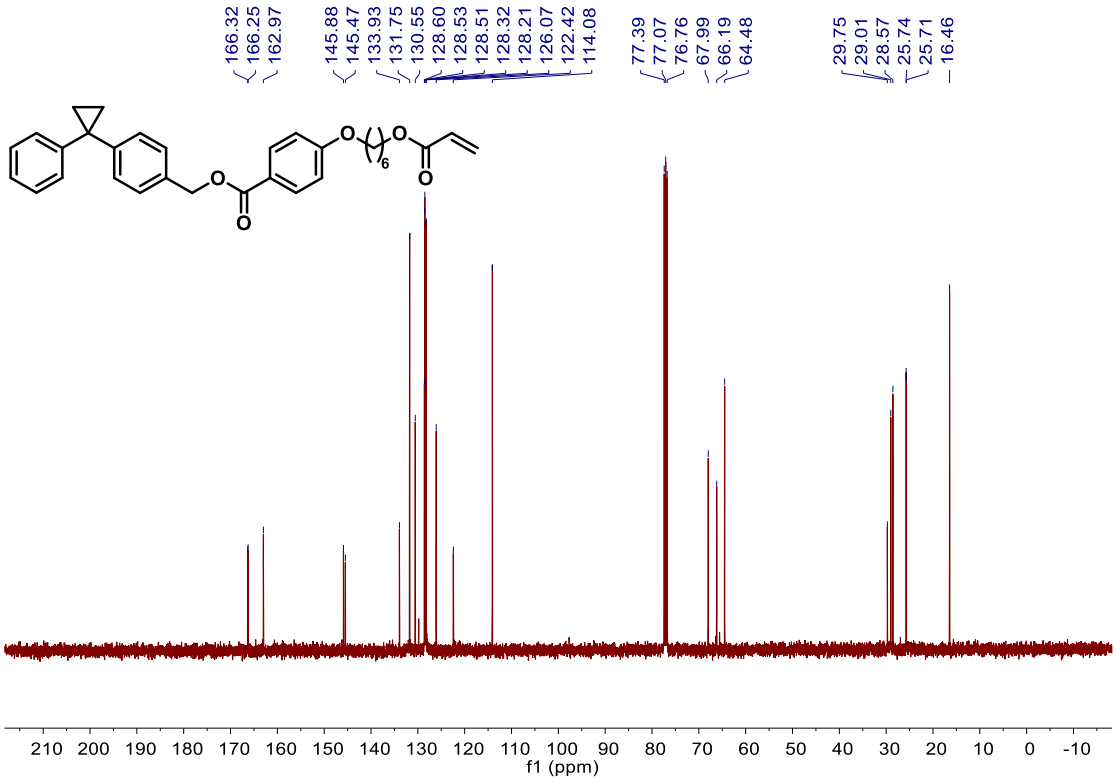
^{1}H NMR spectrum of **13g** (400 MHz, Chloroform-*d*)



^{13}C NMR spectrum of **13g** (101 MHz, Chloroform-*d*)



^{1}H NMR spectrum of **13h** (400 MHz, Chloroform-*d*)



^{13}C NMR spectrum of **13h** (101 MHz, Chloroform-*d*)

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