Metal-free alkene hydroboration with pinacolborane employing the $C_6F_5BH_2{\cdot}SMe_2$ catalyst

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Supplementary Information

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General Infromation

Unless otherwise noted, all reactions and manipulations were performed under an argon atmosphere in a glovebox (Mbraun Unilab) or using standard Schlenk techniques with dried and degassed solvents. All Schlenk flasks and materials were dried prior to their use. All solvents were purified by common distillation techniques: Ethyl acetate (EtOAc) and dichloroethane (DCE) were distilled over CaH_2. n-Hexane (C_6H_{14}), toluene (C_7H_8), benzene (C_6H_6), dioxane ($C_4H_8O_2$), tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled under argon over sodium/benzophenone. d6-Benzene (C_6D_6) and $CDCl_3$ were dried over molecular sieves (4Å). Deuterated solvents were purchased from Eurisotop. Pinacolborane (HBpin) was purchased from Manchester Organics and were used as received. Ceric ammonium molybdate solution (containing H_2SO_4) was purchased from TCI. All alkene substrates were purchased from commercial suppliers and were used as received. Trimethyl(pent-4-en-1-yloxy)silane was synthesized according to reported procedure.[1] Pregnenolone derivative **4** was synthesized following reported procedures from pregnenolone.[2]

All new compounds have been characterized by ^{1}H, ^{13}C, ^{19}F, ^{11}B NMR spectroscopy and ESI-HRMS.

NMR spectra were recorded at Bruker Avance NEO 400 MHz or 500 MHz spectrometers. If not otherwise stated: NMR spectra were recorded at 25 °C; ^{13}C spectra were ^{1}H decoupled; ^{11}B spectra were not ^{1}H decoupled. Chemical shifts for the ^{1}H and ^{13}C spectra were referenced to the residual $^{1}H/^{13}C$ resonances of the deuterated solvent: C_6D_6: δ = 7.16; δ = 128.06; CD_2Cl_2: δ = 5.32; δ = 53.84; $CDCl_3$: δ = 7.26; δ = 77.16; and are reported as ppm relative to Me_4Si. Chemical shifts for the ^{11}B and ^{19}F spectra were referenced to external standard ($BF_3{\cdot}Et_2O$, $CFCl_3$, respectively). Quaternary carbon atom connected to boron is not visible in ^{13}C NMR spectra due to quadrupole relaxation. For mechanistic studies, Wilmad quartz NMR tube were used to suppress borosilicate background signal in the ^{11}B NMR spectra for mechanistic studies.

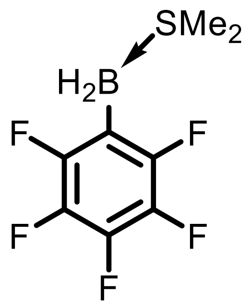
Gas chromatographic analyses were carried out an Agilent 6890N GC equipped with 5973 MSD using a HP-5MS UI (30m, 0.25 mm, 0.25 μm) column.

High-resolution mass spectra (ESI-HRMS) were recorded on Agilent 6230 LC/TOF Dual Spray Esi Source Mass Spectrometer. All HRMS experiments were recorded with positive ion detector and the recorded masses were under 5 ppm error. All samples were prepared with 1 ppm concetration in LC-MS grade methanol together with 2.5 mM formic acid as ionization agent.

Specific rotations $[\alpha]_D^{20}$ were measured on JASCO DIP-1000 with sodium lamp (589 nm filter).

Preparation

2,3,4,5,6-Pentafluorophenylborane - dimethyl sulfide adduct (1)



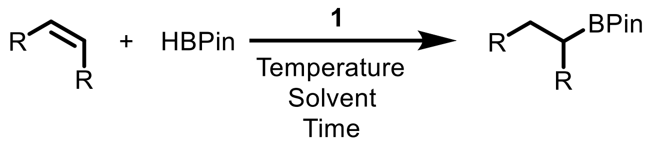
To a solution of bromopentalfluorobenzene (4 g, 16.2 mmol) in diethyl ether (60 mL) in a 200 mL Schlenk tube, n-BuLi (6.5 mL, 16.2 mmol, 2.5M hexane solution) was added dropwise *via* syringe over a period 30 minutes at -78°C. After 1h of stirring at -78°C, borane-dimethyl sulfide (8.1 mL, 16.2 mmol, 2.5M toluene solution) was added dropwise via syringe over a period of 5 minutes and the reaction mixture was stirred at -78°C for another 2h.* Afterwards, the reaction was allowed to slowly warm up to room temperature while stirring overnight immersed in the cooling bath. Next, bromotrimethylsilane (2.31 mL, 17 mmol) was added in one portion *via* syringe at room temperature. The resulting suspension was stirred 4h at room temperature and subsequently the volatiles was evaporated *in vacuo*. Then, the obtained solid was transferred in the glass filter funnel and washed out with hot hexane (20mL x 4) in the adjusted 200 mL Schlenk tube. The filtrate was evaporated to incipient crystallization and was placed at -30°C overnight. This afforded needle-shaped colourless crystals of $C_6F_5BH_2{\cdot}SMe_2$ (**1,** 2.83 g, 11.69 mmol, 72%), which were isolated by removing solvent with cannula filtration and drying *in vacuo* for 4h at room temperature. The NMR spectroscopic data are in accordance with those reported.[3]

* - It is extremely important to hold the mixture at -78°C for 2 h. Upon warming to temperatures higher than -60°C, undesired Li-F elimination (potentially explosive) could happen, forming undesired byproducts (through formation of benzyne) and posing a significant safety hazard.

^{1}H NMR (400 MHz, C_6D_6) δ 3.54 – 2.22 (m, 2H), 1.16 (s, 6H).
^{19}F {^{1}H} NMR (376 MHz, C_6D_6) δ -130.49 (d, J = 24.3 Hz, 2F), -157.53 (t, J = 20.8 Hz, 1F), -163.71 – -163.96 (m, 2F).
^{11}B NMR (128 MHz, C_6D_6) δ -17.25 (t, J = 114.8 Hz).
^{13}C {^{1}H} NMR (101 MHz, C_6D_6) δ 150.12 (ddt, *J* = 14.5, 8.4, 4.0 Hz), 147.74 (ddt, *J* = 14.9, 8.4, 4.0 Hz), 141.53 (tt, *J* = 13.8, 6.0 Hz), 139.38 – 138.16 (m), 136.25 (ddd, *J* = 20.7, 12.5, 5.3 Hz), 22.56.

Optimization study

Table S1: Optimization of the hydroboration of 1-octene and cyclohexene with $C_6F_5BH_2{\cdot}SMe_2$ as a catalyst.[a]



#	Substrate	HBpin, (eq)	1, (mol %)	Solvent	Temp, (°C)	Time, (h)	Yield[b], (%)
1	1-octene	1.2	10%	neat	40°C	24h	47%
2	1-octene	1.2	10%	neat	**80°C**	24h	69%
3[c]	1-octene	1.2	10%	neat	**60°C**	24h	87%
4[c]	1-octene	1.2	10%	**dioxane**	60°C	24h	21%
5[c]	1-octene	1.2	10%	**DCE**	60°C	24h	34%
6[c]	1-octene	1.2	10%	**PhMe**	60°C	24h	72%
7[c]	1-octene	1.2	10%	**hexane**	60°C	24h	50%
8[c]	1-octene	1.2	10%	**benzene**	60°C	24h	37%
9[c]	1-octene	1.2	10%	**THF**	60°C	24h	8%
10[c]	1-octene	1.2	10%	**dioxane/ 1% $CDCl_3$**	60°C	24h	18%
11	1-octene	1.2	10%	neat	60°C	**1h**	11%
12	1-octene	1.2	10%	neat	60°C	**2h**	30%
13	1-octene	1.2	10%	neat	60°C	**4h**	63%
14	1-octene	1.2	10%	neat	60°C	**18h**	81%
15	1-octene	1.2	10%	neat	60°C	**72h**	85%
16	1-octene	**1**	10%	neat	60°C	18h	71%
17	1-octene	**1.5**	10%	neat	60°C	18h	93%
18	1-octene	**3**	10%	neat	60°C	18h	99%
19[d]	1-octene	1.5	**5%**	neat	60°C	18h	92%
20	1-octene	1.5	**2.5%**	neat	60°C	18h	52%
21	1-octene	1.5	**1%**	neat	60°C	18h	31%
22	1-octene	1.5	**2.5%**	neat	**80°C**	**4h**	55%
23	1-octene	1.5	**2.5%**	neat	**80°C**	**18h**	85%
24	1-octene	1.5	**2.5%**	neat	**60°C**	**24h**	57%
25	1-octene	1.5	**-**	neat	60°C	24h	traces
26	**cyclohexene**	1.5	5%	neat	60°C	18h	19%
27	cyclohexene	**3**	**10%**	neat	60°C	18h	45%
28	cyclohexene	1.5	5%	neat	**80°C**	18h	50%
29	cyclohexene	1.5	5%	neat	60°C	**48h**	28%
30	cyclohexene	1.5	5%	neat	**100°C**	18h	30%
31	cyclohexene	1.5	**10%**	neat	**100°C**	18h	43%
32[d]	cyclohexene	2	**10%**	neat	**80°C**	**65h**	96%
33	cyclohexene	2	**-**	neat	80°C	65h	traces

[a]Alkene (100mg). Work-up for all reactions described in GP1 and GP2 (see below). Deviations from previous reactions are in bold; [b]Isolated yields; [c]Solvent (2mL); [d]Optimized reactions for 1-octene and cyclohexene are shaded.

General Procedures

General Procedure for the Hydroboration of Terminal Alkenes (GP1)

$$\mathbf{A} \quad \underset{1.5\ \text{eq}}{\text{HBPin}} \quad \underset{5\ \text{mol\%}}{C_6F_5BH_2{\cdot}SMe_2} \xrightarrow[\substack{60°C \\ 18h}]{\text{neat}} \mathbf{2a\text{-}l}$$

25 mL Shlenk flask with a stirring bar was charged with $C_6F_5BH_2{\cdot}SMe_2$ (5 mol %) and HBpin (1.5 eq.) in a glovebox. An appropriate amount of alkene (1 eq.) was introduced with a syringe. The schlenk flask was immersed in oil bath and heated at 60°C for 18h. After cooling to RT, all volatiles were removed *in vacuo*. Obtained material was purified with flash column chromatography on silica gel using hexane/EtOAc (30:1) as eluent. TLC plates for indicating boronic ester product were visualized with ceric ammonium molybdate solution (deep blue spot). Afforded pinacol boronic esters were characterized with ^{1}H, ^{11}B, ^{13}C NMR and GC-MS.

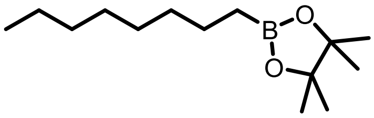
General Procedure for the Hydroboration of Internal Alkenes (GP2)

$$\mathbf{A} \quad \underset{2\ \text{eq}}{\text{HBPin}} \quad \underset{10\ \text{mol\%}}{C_6F_5BH_2{\cdot}SMe_2} \xrightarrow[\substack{80°C \\ 65h}]{\text{neat}} \mathbf{3a\text{-}j}$$

25 mL Shlenk flask with a stirring bar was charged with $C_6F_5BH_2{\cdot}SMe_2$ (10 mol %) and HBpin (2 eq.) in a glovebox. An appropriate amount of alkene (1 eq.) was introduced with a syringe. The schlenk flask was immersed in oil bath and heated at 80°C for 65h. After cooling to RT, all volatiles were removed *in vacuo*. Obtained material was purified with flash column chromatography on silica gel using hexane/EtOAc (30:1). TLC plates for indicating boronic ester product were visualized with ceric ammonium molybdate solution (deep blue spot). Afforded pinacol boronic esters were characterized with ^{1}H, ^{11}B, ^{13}C NMR and GC-MS.

Characterization Data

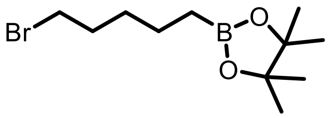
4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane (2a)



Compound **2a** was synthesized according to **GP1** using 1-octene (100 mg, 0.891 mmol), HBpin (171 mg, 1.34 mmol) and **1** (11 mg, 0.045 mmol). The title compound **2a** (196 mg, 92%) was obtained as a colourless liquid. Spectral data are in accordance with those reported.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (q, J = 6.7 Hz, 2H), 1.23 – 1.26 (m, 22H), 0.87 (t, J = 6.8 Hz, 3H), 0.76 (t, J = 7.8 Hz, 2H).
^{11}B NMR (128 MHz, $CDCl_3$) δ 34.31.
^{13}C NMR (101 MHz, $CDCl_3$) δ 14.27, 22.83, 24.16, 24.96, 29.41, 32.05, 32.60, 82.97.
GC-MS 240 m/z $[M]^+$ at 8.43

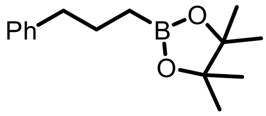
2-(5-bromopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b)



Compound **2b** was synthesized according to **GP1** using 5-bromopentene-1 (100 mg, 0.671 mmol), HBpin (129 mg, 1.01 mmol) and **1** (8 mg, 0.033 mmol). The title compound **2b** (116 mg, 62%) was obtained as a colourless liquid. Spectral data are in accordance with those reported.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 (t, J = 6.9 Hz, 2H), 1.85 (p, J = 7.0 Hz, 2H), 1.47 – 1.40 (m, 4H), 1.24 (s, 12H), 0.83 – 0.74 (m, 2H).
^{11}B NMR (128 MHz, $CDCl_3$) δ 34.19.
^{13}C NMR (101 MHz, $CDCl_3$) δ 23.33, 24.97, 30.96, 32.79, 34.16, 83.11.
GC-MS 261 m/z $[M]^+$ at 8.79

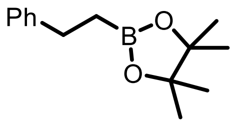
4,4,5,5-tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (2c)



Compound **2c** was synthesized according to **GP1** using allylbenzene (100 mg, 0.846 mmol), HBpin (162 mg, 1.27 mmol) and **1** (10 mg, 0.043 mmol). The title compound **2c** (183 mg, 88%) was obtained as a colourless liquid. Spectral data are in accordance with those reported.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 2H), 7.17 (dd, J = 7.4, 2.7 Hz, 3H), 2.65 – 2.55 (m, 2H), 1.73 (p, J = 7.8 Hz, 2H), 1.24 (s, 12H), 0.83 (t, J = 7.9 Hz, 2H).
^{11}B NMR (128 MHz, $CDCl_3$) δ 34.17.
^{13}C NMR (101 MHz, $CDCl_3$) δ 24.98, 26.25, 38.74, 83.09, 125.70, 128.31, 128.70, 142.85.
GC-MS 246 m/z $[M]^+$ at 9.62

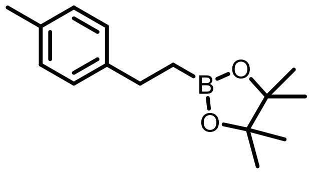
4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane (2d)



Compound **2d** was synthesized according to **GP1** using styrene (100 mg, 0.960 mmol), HBpin (184 mg, 1.44 mmol) and **1** (12 mg, 0.048 mmol). The title compound **2d** (194 mg, 87%) was obtained as a colourless liquid. Spectral data are in accordance with those reported.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.20 (m, 2H), 7.19 – 7.11 (m, 1H), 2.75 (t, J = 8.2 Hz, 2H), 1.22 (s, 12H), 1.15 (t, J = 8.0 Hz, 2H).
^{11}B NMR (128 MHz, $CDCl_3$) δ 34.06.
^{13}C NMR (101 MHz, $CDCl_3$) δ 24.95, 30.09, 83.24, 125.63, 128.14, 128.32, 144.56.
GC-MS 232 m/z $[M]^+$ at 8.92

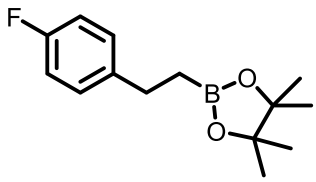
4,4,5,5-tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane (2e)



Compound **2e** was synthesized according to **GP1** using 4-methylstyrene (100 mg, 0.846 mmol), HBpin (162 mg, 1.27 mmol) and **1** (10 mg, 0.042 mmol). The title compound **2e** (160 mg, 77%) was obtained as a colourless liquid. Spectral data are in accordance with those reported.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (q, J = 8.1 Hz, 4H), 2.71 (t, J = 8.4 Hz, 2H), 2.31 (s, 3H), 1.23 (s, 12H), 1.12 (t, J = 8.1 Hz, 2H).
^{11}B NMR (128 MHz, $CDCl_3$) δ 33.91.
^{13}C NMR (101 MHz, $CDCl_3$) δ 21.12, 24.96, 29.66, 83.22, 127.99, 129.01, 135.00, 141.54.
GC-MS 246 m/z $[M]^+$ at 9.51

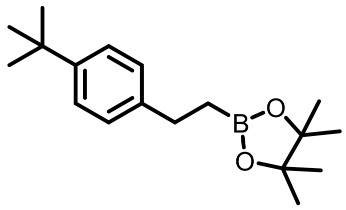
4,4,5,5-tetramethyl-2-(4-fluorophenethyl)-1,3,2-dioxaborolane (2f)



Compound **2f** was synthesized according to **GP1** using 4-fluorostyrene (100 mg, 0.819 mmol), HBpin (157 mg, 1.23 mmol) and **1** (10 mg, 0.041 mmol). The title compound **2f** (162 mg, 79%) was obtained as a colourless liquid. Spectral data are in accordance with those reported.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (dd, J = 8.8, 5.5 Hz, 1H), 6.93 (t, J = 8.8 Hz, 1H), 2.71 (t, J = 8.1 Hz, 1H), 1.21 (s, 7H), 1.11 (t, J = 8.1 Hz, 1H).
^{11}B NMR (128 MHz, $CDCl_3$) δ 33.72.
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.25 (d, *J* = 242.3 Hz), 140.08, 129.46 (d, *J* = 7.6 Hz), 114.96 (d, *J* = 21.1 Hz), 83.29, 29.30, 24.95.
GC-MS 250 m/z $[M]^+$ at 8.91

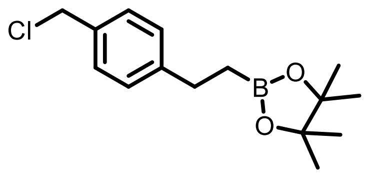
2-(4-(tert-butyl)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2g)



Compound **2g** was synthesized according to **GP1** using 4-tertbutylstyrene (300 mg, 1.87 mmol), HBpin (359 mg, 2.81 mmol) and **1** (23 mg, 0.094 mmol). The title compound **2g** (403 mg, 75%) was obtained as a white solid. Spectral data are in accordance with those reported.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, J = 7.9 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 2.62 (t, J = 8.4 Hz, 2H), 1.21 (s, 9H), 1.13 (s, 12H), 1.04 (t, J = 8.2 Hz, 2H).
^{11}B NMR (128 MHz, $CDCl_3$) δ 33.93.
^{13}C NMR (101 MHz, $CDCl_3$) δ 24.95, 29.51, 31.57, 34.45, 83.20, 125.20, 127.77, 141.49, 148.38.
GC-MS 288 m/z $[M]^+$ at 10.68

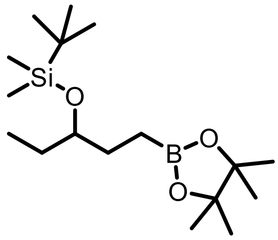
2-(4-(chloromethyl)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2h)



Compound **2h** was synthesized according to **GP1** using 1-(chloromethyl)-4-vinylbenzene (300 mg, 1.97 mmol), HBpin (377 mg, 2.95 mmol) and **1** (24 mg, 0.098 mmol). The title compound **2h** (359 mg, 65%) was obtained as a white solid. Spectral data are in accordance with those reported.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 4.56 (s, 2H), 2.74 (t, J = 8.3 Hz, 2H), 1.22 (s, 12H), 1.13 (t, J = 8.1 Hz, 2H).
^{11}B NMR (128 MHz, $CDCl_3$) δ 33.79.
^{13}C NMR (101 MHz, $CDCl_3$) δ 24.95, 29.82, 46.49, 83.30, 128.53, 128.68, 134.82, 145.01.
GC-MS 280 m/z $[M]^+$ at 10.97

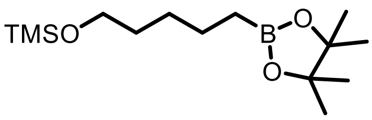
tert-butyldimethyl((1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-3-yl)oxy)silane (2i)



Compound **2i** was synthesized according to **GP1** using *tert*-butyldimethyl(pent-1-en-3-yloxy)silane (100 mg, 0.499 mmol), HBpin (96 mg, 0.749 mmol) and **1** (6 mg, 0.025 mmol). The title compound **2i** (89 mg, 54%) was obtained as a colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.51 (p, J = 5.7 Hz, 1H), 1.54 – 1.39 (m, 4H), 1.24 (s, 12H), 0.91 – 0.83 (m, 14H, overlapped tBu and Et), 0.04 (s, 3H), 0.03 (s, 3H).
^{11}B NMR (128 MHz, $CDCl_3$) δ 34.24.
^{13}C NMR (101 MHz, $CDCl_3$) δ -4.32, -4.22, 9.65, 18.33, 24.97, 26.13, 29.38, 30.62, 75.04, 83.03.
GC-MS 327 m/z $[M-H]^+$ at 9.69
ESI-HRMS m/z: exp. for 329.2671 $[M+H]^+$ (calcd. for $C_{17}H_{37}BO_3Si$ 329.2683)

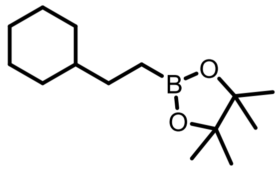
trimethyl((5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)oxy)silane (2j)



Compound **2j** was synthesized according to **GP1** using trimethyl(pent-4-en-1-yloxy)silane (300 mg, 1.89 mmol), HBpin (364 mg, 2.84 mmol) and **1** (23 mg, 0.095 mmol). The title compound **2j** (281 mg, 52%) was obtained as a colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.55 (t, J = 6.7 Hz, 2H), 1.52 (p, J = 7.0 Hz, 2H), 1.46 – 1.36 (m, 2H), 1.35 – 1.28 (m, 2H), 1.23 (s, 12H), 0.77 (t, J = 7.7 Hz, 2H), 0.09 (s, 9H).
^{11}B NMR (128 MHz, $CDCl_3$) δ 34.18.
^{13}C NMR (101 MHz, $CDCl_3$) δ -0.31, 1.48, 23.98, 24.95, 28.74, 32.70, 62.88, 83.00.
GC-MS 286 m/z $[M]^+$ at 8.89
ESI-HRMS m/z: exp. for 287.2224 $[M+H]^+$ (calcd. for $C_{14}H_{31}BO_3Si$ 287.2214)

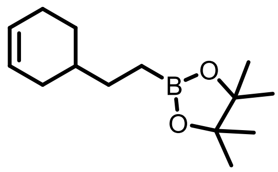
2-(2-cyclohexylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)



Compound **2k** was synthesized according to **GP1** using vinylcyclohexane (100 mg, 0.907 mmol), HBpin (174 mg, 1.36 mmol) and **1** (11 mg, 0.045 mmol). The title compound **2k** (189 mg, 88%) was obtained as a colourless liquid. Spectral data are in accordance with those reported.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75 – 1.63 (m, 5H), 1.34 – 1.24 (m, 2H), 1.24 (s, 12H), 1.22 – 1.05 (m, 4H), 0.88 – 0.80 (m, 2H), 0.80 – 0.71 (m, 2H).
^{11}B NMR (128 MHz, $CDCl_3$) δ 34.31.
^{13}C NMR (101 MHz, $CDCl_3$) δ 24.95, 26.59, 26.92, 31.52, 33.13, 40.11, 82.98.
GC-MS 238 m/z $[M]^+$ at 8.80

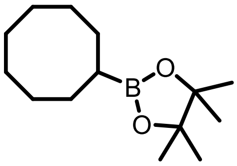
2-(2-(cyclohex-3-en-1-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2l)



Compound **2l** was synthesized according to **GP1** using 4-vinylcyclohexene-1 (300 mg, 2.77 mmol), HBpin (532 mg, 4.16 mmol) and **1** (34 mg, 0.139 mmol). The title compound **2l** (423 mg, 66%) was obtained as a colourless liquid. Spectral data are in accordance with those reported.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.64 (d, J = 2.4 Hz, 2H), 2.14 – 2.06 (m, 1H), 2.06 – 1.97 (m, 2H), 1.75 (dd, J = 13.3, 3.5 Hz, 1H), 1.68 – 1.55 (m, 1H), 1.50 – 1.31 (m, 3H), 1.24 (s, 12H), 1.21 – 1.04 (m, 1H), 0.79 (t, J = 7.5 Hz, 2H).
^{11}B NMR (128 MHz, $CDCl_3$) δ 34.31.
^{13}C NMR (101 MHz, $CDCl_3$) δ 8.26, 24.95, 25.51, 28.68, 30.81, 31.74, 35.95, 83.04, 126.89, 127.16.
GC-MS 236 m/z $[M]^+$ at 8.93

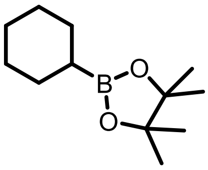
2-cyclooctyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a)



Compound **3a** was synthesized according to **GP2** using *cis*-cyclooctene (300 mg, 2.72 mmol), HBpin (697 mg, 5.44 mmol) and **1** (66 mg, 0.272 mmol). The title compound **3a** (302 mg, 47%) was obtained as a colourless liquid. Spectral data are in accordance with those reported.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.76 – 1.59 (m, 4H), 1.59 – 1.42 (m, 10H), 1.23 (s, 12H), 1.11 (p, J = 5.0 Hz, 1H).
^{11}B NMR (128 MHz, $CDCl_3$) δ 34.57.
^{13}C NMR (101 MHz, $CDCl_3$) δ 24.88, 26.80, 27.00, 27.15, 27.71, 82.89.
GC-MS 238 m/z $[M]^+$ at 9.09

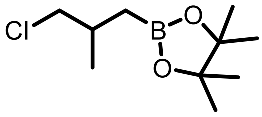
2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)



Compound **3b** was synthesized according to **GP2** using cyclohexene (300 mg, 3.65 mmol), HBpin (935 mg, 7.30 mmol) and **1** (88 mg, 0.365 mmol). The title compound **3b** (739 mg, 96%) was obtained as a colourless liquid. Spectral data are in accordance with those reported.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.70 – 1.54 (m, 4H), 1.40 – 1.25 (m, 6H), 1.23 (s, 12H), 1.02 – 0.92 (m, 1H).
^{11}B NMR (128 MHz, $CDCl_3$) δ 33.96.
^{13}C NMR (101 MHz, $CDCl_3$) δ 24.90, 26.91, 27.28, 28.11, 82.87.
GC-MS 210 m/z $[M]^+$ at 7.37

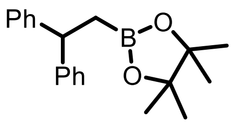
2-(3-chloro-2-methylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)



Compound **3c** was synthesized according to **GP2** using 3-chloro-2-methylprop-1-ene (300 mg, 3.31 mmol), HBpin (848 mg, 6.63 mmol) and **1** (80 mg, 0.331 mmol). The title compound **3c** (695 mg, 96%) was obtained as a colourless liquid. Spectral data are in accordance with those reported.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.51 – 3.36 (m, 2H), 2.15 – 2.01 (m, 1H), 1.24 (s, 12H), 1.03 (d, J = 6.6 Hz, 3H), 0.97 (dd, J = 15.8, 5.8 Hz, 1H), 0.77 (dd, J = 15.8, 8.3 Hz, 1H).
^{11}B NMR (128 MHz, $CDCl_3$) δ 33.54.
^{13}C NMR (101 MHz, $CDCl_3$) δ 17.12, 20.22, 24.90, 24.99, 32.42, 53.10, 83.27.
GC-MS 203 m/z $[M-CH_3]^+$ at 7.16

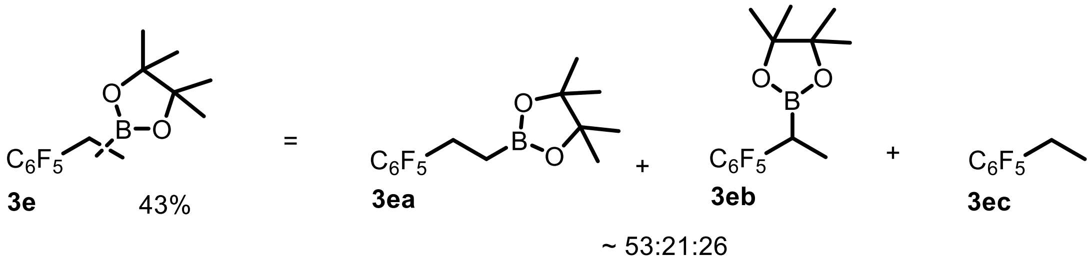
2-(2,2-diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d)



Compound **3d** was synthesized according to **GP2** using 1,1-diphenylethylene (300 mg, 1.66 mmol), HBpin (426 mg, 3.33 mmol) and **1** (40 mg, 0.166 mmol). The title compound **3d** (454 mg, 89%) was obtained as a white solid. Spectral data are in accordance with those reported.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.18 (m, 8H), 7.13 (tt, J = 6.1, 1.9 Hz, 2H), 4.28 (t, J = 8.5 Hz, 1H), 1.60 (d, J = 8.5 Hz, 2H), 1.05 (s, 12H).
^{11}B NMR (128 MHz, $CDCl_3$) δ 33.16.
^{13}C NMR (101 MHz, $CDCl_3$) δ 24.72, 46.67, 83.26, 126.04, 127.82, 128.36, 146.73.
GC-MS 308 m/z $[M]^+$ at 11.98

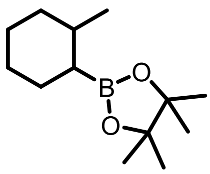
4,4,5,5-tetramethyl-2-(2-(perfluorophenyl)ethyl)-1,3,2-dioxaborolane (3e)



Compound **3e** was synthesized according to **GP2** using 2,3,4,5,6-pentafluorostyrene (300 mg, 1.55 mmol), HBpin (396 mg, 3.09 mmol) and **1** (37 mg, 0.155 mmol). The title compound **3e** (214 mg, 43%) was obtained as a colourless liquid. Spectral data are in accordance with those reported.[8]

3ea - ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.79 (t, J = 8.2 Hz, 2H), 1.23 (s, 12H), 1.10 (t, J = 8.2 Hz, 2H).
3eb - ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.68 (q, J = 7.6 Hz, 1H), 1.29 (d, J = 7.6 Hz, 3H), 1.24 (s, 12H).
3ec - ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 – 0.79 (overlapped d and t, 5H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -143.34 – -143.84 (m), -144.45 (dd, *J* = 22.2, 8.3 Hz), -159.01 (t, *J* = 20.8 Hz), -159.51 (t, *J* = 20.8 Hz), -163.37 – -163.75 (m).
^{11}B NMR (128 MHz, $CDCl_3$) δ 33.6 (mixture of **2pa** and **2pb**).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.81 – 145.49 (m), 145.18 – 142.66 (m), 141.57 – 139.96 (m), 139.28 – 137.89 (m), 136.27 (dddd, *J* = 17.8, 12.7, 5.1, 2.2 Hz), 118.90 (td, *J* = 19.1, 3.9 Hz), 117.34 (td, *J* = 18.7, 3.7 Hz), 84.27, 83.54, 82.95, 37.89, 35.26, 34.38, 28.95, 24.90, 24.85, 24.65, 21.46, 19.87, 18.76, 18.66, 18.52, 17.12, 15.55. (mixture of all)
3ea - GC-MS 322 m/z $[M]^+$ at 8.31
3eb - GC-MS 322 m/z $[M]^+$ at 7.92

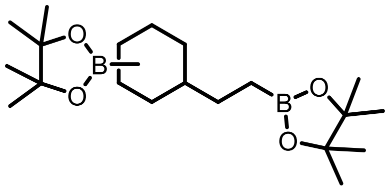
4,4,5,5-tetramethyl-2-(2-methylcyclohexyl)-1,3,2-dioxaborolane (3f)



Compound **3f** was synthesized according to **GP2** using 1-methylcycloxene (300 mg, 3.12 mmol), HBpin (798 mg, 6.24 mmol) and **1** (75 mg, 0.312 mmol). The title compound **3f** (446 mg, 64%) was obtained as a white powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81 – 1.53 (m, 5H), 1.47 – 1.24 (m, 3H), 1.23 (m, 12H), 1.15 – 1.03 (m, 1H), 0.97 – 0.86 (m, 2H), 0.86 – 0.82 (m, 3H).
^{11}B NMR (128 MHz, $CDCl_3$) δ 34.03.
^{13}C NMR (101 MHz, $CDCl_3$*)* δ 22.45, 23.22, 23.25, 24.73, 24.88, 24.93, 24.98, 26.70, 27.01, 27.59, 28.00, 28.98, 30.97, 32.79, 33.65, 34.45, 35.15, 35.50, 36.07, 36.27, 36.61, 82.87, 82.94, 82.97.
GC-MS 224 m/z $[M]^+$ at 7.60; 7.70; 7.75. 209 m/z $[M-CH_3]^+$ at 7.65.
ESI-HRMS m/z: exp. for 247.1849 $[M+Na]^+$ (calcd. for $C_{13}H_{25}BO_2Na$ 247.1846)

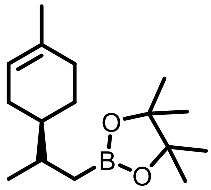
4,4,5,5-tetramethyl-2-(2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)ethyl)-1,3,2-dioxaborolane (3g)



Compound **3g** was synthesized according to **GP2** using 4-vinylcyclohexene-1 (300 mg, 2.77 mmol), HBpin (1.42 g, 11.1 mmol) and **1** (67 mg, 0.277 mmol). The title compound **3g** (982 mg, 97%) was obtained as a colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.83 – 1.66 (m, 4H), 1.29 (dd, *J* = 9.3, 6.9 Hz, 3H), 1.22 (d, *J* = 6.4 Hz, 24H), 1.16 – 1.04 (m, 2H), 0.93 – 0.70 (m, 5H).
^{11}B NMR (128 MHz, $CDCl_3$) δ 34.13.
^{13}C NMR (101 MHz, $CDCl_3$*)* δ 24.88, 24.96, 27.59, 27.98, 28.04, 31.75, 31.80, 33.10, 33.87, 34.20, 39.90, 40.77, 82.83, 82.93.
GC-MS 349 m/z $[M-CH_3]^+$ at 11.94; 12.02; 12.07 and 12.27.
ESI-HRMS m/z: exp. for 387.2867 $[M+Na]^+$ (calcd. for $C_{20}H_{38}B_2O_4Na$ 387.2848)

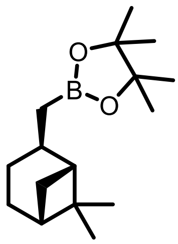
4,4,5,5-tetramethyl-2-((S)-2-((R)-4-methylcyclohex-3-en-1-yl)propyl)-1,3,2-dioxaborolane (3h)



Compound **3g** was synthesized according to **GP2** using R-(+)-limonene (300 mg, 2.20 mmol), HBpin (564 mg, 4.40 mmol) and **1** (53 mg, 0.220 mmol). The title compound **3g** (487 mg, 84%) was obtained as a colourless liquid. Spectral data are in accordance with those reported.[9]

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 (s, 1H), 2.02 – 1.85 (m, 3H), 1.77 – 1.67 (m, 3H), 1.63 (s, 3H), 1.35 – 1.28 (m, 2H), 1.25 (s, 6H), 1.24 (s, 6H), 0.90 (dd, J = 6.8, 3.9 Hz, 4H), 0.63 (dd, J = 15.4, 9.8 Hz, 1H).
^{11}B NMR (128 MHz, $CDCl_3$) δ 34.22.
^{13}C NMR (101 MHz, $CDCl_3$) δ 19.17, 19.50, 23.62, 24.88, 25.06, 26.06, 26.96, 28.56, 29.30, 31.13, 33.87, 34.04, 40.71, 83.00, 121.23, 134.05.
GC-MS 264 m/z [M]+ at 9.79

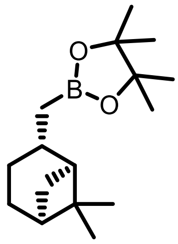
2-(((1R,2R,5R)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i)



Compound **3h** was synthesized according to **GP2** using *α*-(+)-pinene (300 mg, 2.20 mmol), HBpin (564 mg, 4.40 mmol) and **1** (53 mg, 0.220 mmol). The title compound **3h** (190 mg, 33%) was obtained as a colourless liquid. Spectral data are in accordance with those reported.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.20 (p, J = 8.3 Hz, 1H), 2.00 (dtd, J = 11.2, 5.8, 1.2 Hz, 1H), 1.83 (q, J = 4.6 Hz, 1H), 1.77 – 1.66 (m, 3H), 1.61 (td, J = 5.6, 1.5 Hz, 1H), 1.33 (d, J = 10.0 Hz, 1H), 1.24 (s, 13H), 1.17 (s, 3H), 0.82 (s, 3H), 0.78 (dd, J = 14.8, 8.7 Hz, 1H), 0.67 (dd, J = 14.9, 6.5 Hz, 1H).
^{11}B NMR (128 MHz, $CDCl_3$) δ 34.02.
^{13}C NMR (101 MHz, $CDCl_3$) δ 20.34, 23.26, 24.47, 24.85, 24.96, 27.07, 31.36, 39.74, 40.86, 48.76, 82.97.
GC-MS 264 m/z [M]+ at 9.50
$[\alpha]_D^{20}$ 12 (*c* 0.703, $CDCl_3$)

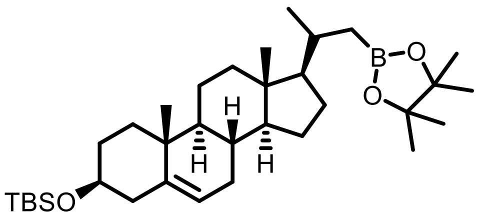
2-(((1S,2S,5S)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j)



Compound **3i** was synthesized according to **GP2** using *β*-(-)-pinene (300 mg, 2.20 mmol), HBpin (564 mg, 4.40 mmol) and **1** (53 mg, 0.220 mmol). The title compound **3i** (524 mg, 90%) was obtained as a colourless liquid. Spectral data are in accordance with those reported.[10]

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.20 (pd, J = 7.7, 1.3 Hz, 1H), 1.99 (dtt, J = 10.0, 5.8, 1.2 Hz, 1H), 1.82 (qd, J = 5.3, 1.5 Hz, 1H), 1.75 – 1.64 (m, 3H), 1.61 (td, J = 5.5, 1.5 Hz, 1H), 1.33 (d, J = 10.0 Hz, 1H), 1.23 (s, 13H), 1.16 (s, 3H), 0.82 (s, 3H), 0.78 (dd, J = 14.9, 8.8 Hz, 1H), 0.67 (dd, J = 14.9, 6.5 Hz, 1H).
^{11}B NMR (128 MHz, $CDCl_3$) δ 34.03.
^{13}C NMR (101 MHz, $CDCl_3$) δ 20.34, 23.25, 24.46, 24.85, 25.05, 27.07, 31.36, 39.73, 40.85, 48.75, 82.96.
^{1}H-^{1}H COSY ((400, 400) MHz, $CDCl_3$) δ (0.68 2.18), (0.68 0.79), (0.77 0.66), (0.77 2.19), (0.82 1.16), (1.16 0.82), (1.21 1.72), (1.34 1.98), (1.34 1.61), (1.34 1.81), (1.60 1.98), (1.61 2.20), (1.61 1.32), (1.62 1.82), (1.67 1.74), (1.70 1.82), (1.72 1.22), (1.72 2.18), (1.75 1.66), (1.82 1.61), (1.82 1.35), (1.83 1.71), (1.83 1.99), (1.99 1.32), (2.00 1.83), (2.00 1.63), (2.01 2.19), (2.19 1.72), (2.20 1.61), (2.20 0.75), (2.20 0.68), (2.21 1.97).
^{1}H-^{13}C HSQC ((400, 101) MHz, $CDCl_3$) δ (0.82 20.32), (1.17 27.09), (1.23 25.00), (1.35 23.22), (1.61 48.69), (1.72 24.84), (1.82 40.79), (2.00 23.22), (2.20 31.44).
GC-MS 264 m/z [M]+ at 9.50
$[\alpha]_D^{20}$ -3 (*c* 0.683, $CDCl_3$)

tert-butyl(((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)dimethylsilane (5)

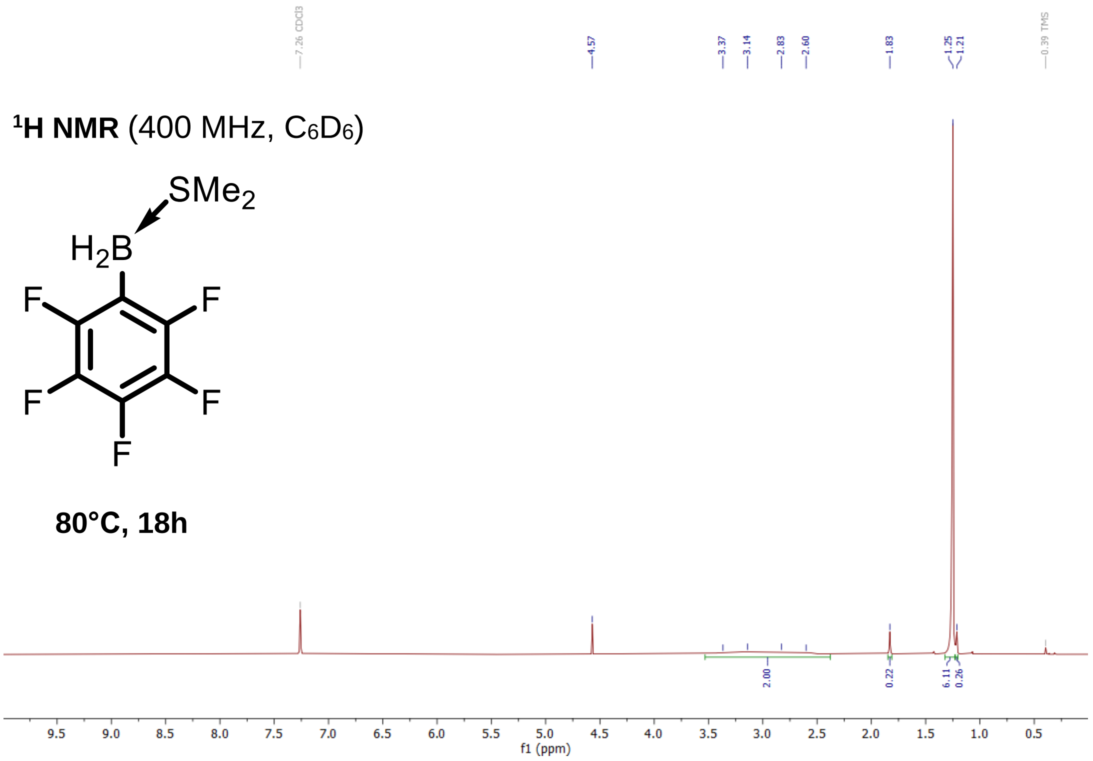


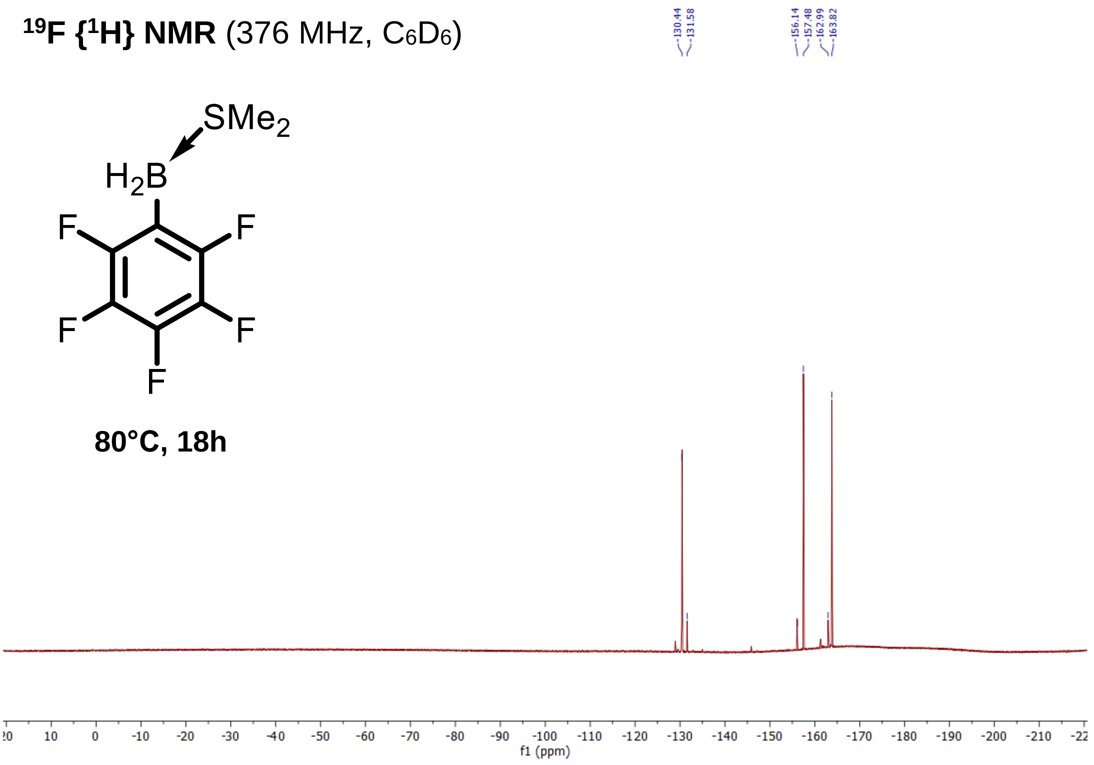
Compound **5** was synthesized according to **GP2** (with 3 eq. HBpin) using **4** (300 mg, 0.70 mmol), HBpin (269 mg, 2.10 mmol) and **1** (17 mg, 0.07 mmol). The title compound **5** (276 mg, 71%) was obtained as a white solid.

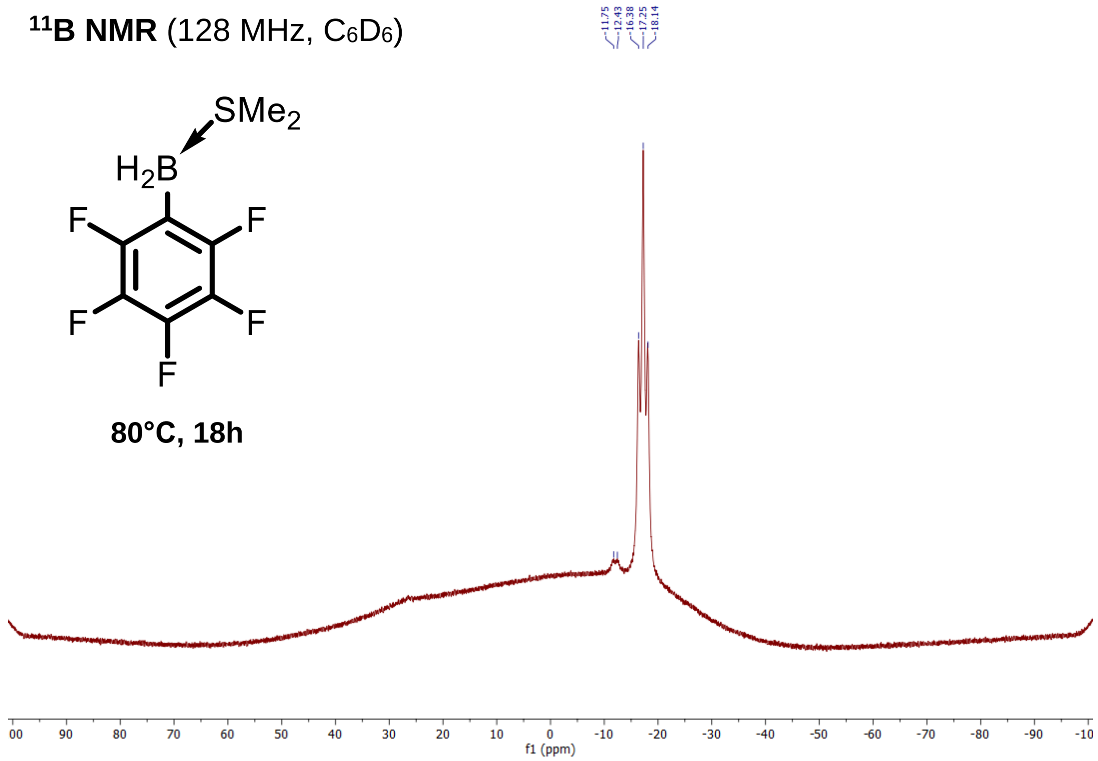
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.31 (d, J = 5.2 Hz, 1H), 3.47 (td, J = 11.0, 5.5 Hz, 1H), 2.26 (ddd, J = 13.2, 10.5, 2.3 Hz, 1H), 2.16 (ddd, J = 13.5, 5.1, 2.3 Hz, 1H), 1.98 (ddt, J = 16.6, 12.3, 3.8, 2H), 1.88 – 1.75 (m, 2H), 1.76 – 1.61 (m, 2H), 1.59 – 1.38 (m, 6H), 1.34 – 1.28 (m, 1H), 1.24 (s, 12H), 1.16 – 1.02 (m, 4H), 0.99 (s, 3H), 0.97 (d, J = 6.6 Hz, 3H), 0.90 – 0.87 (m, 11H), 0.75 – 0.62 (m, 4H), 0.55 (dd, J = 15.2, 9.8 Hz, 1H), 0.05 (s, 6H).
^{11}B NMR (128 MHz, $CDCl_3$) δ 34.30.
^{13}C NMR (101 MHz, $CDCl_3$) δ -4.43, 12.12, 18.42, 19.58, 21.22, 22.23, 24.37, 25.12, 26.10, 28.80, 32.06, 32.12, 32.25, 32.82, 36.74, 37.54, 39.93, 42.49, 42.98, 50.34, 57.07, 58.98, 72.81, 82.94, 121.33, 141.72.
^{13}C-DEPT 135 NMR (101 MHz, $CDCl_3$) δ 12.12, 19.58, 21.22, 22.24, 24.38, 25.12, 26.10, 28.80, 32.06, 32.08, 32.26, 32.82, 37.54, 39.93, 42.99, 50.33, 57.07, 58.98, 72.81, 121.33.
^{1}H-^{1}H COSY ((400, 400) MHz, $CDCl_3$) δ (0.56 0.94), (0.58 1.66), (0.65 1.14), (0.91 0.55), (0.91 1.48), (0.96 1.66), (1.06 1.81), (1.06 1.68), (1.06 1.29), (1.14 0.65), (1.15 1.98), (1.15 1.48), (1.28 1.06), (1.29 1.84), (1.39 1.50), (1.45 1.11), (1.45 1.96), (1.46 0.94), (1.49 5.31), (1.51 1.38), (1.51 1.71), (1.52 3.45), (1.52 2.26), (1.54 1.80), (1.57 1.27), (1.65 0.56), (1.66 0.97), (1.66 0.89), (1.66 1.12), (1.70 2.17), (1.71 1.53), (1.71 3.47), (1.72 1.78), (1.81 1.69), (1.81 1.52), (1.82 1.30), (1.83 1.03), (1.94 2.27), (1.95 5.31), (1.97 1.45), (2.00 1.13), (2.15 2.29), (2.17 3.47), (2.18 1.73), (2.26 1.95), (2.26 1.49), (2.27 3.45), (2.27 2.16), (2.27 5.31), (3.45 1.53), (3.46 1.69), (3.47 2.17), (3.50 2.24), (5.31 1.49), (5.31 1.95), (5.31 2.27).
^{1}H-^{13}C HSQC ((400, 101) MHz, $CDCl_3$) δ (0.05 -4.08), (0.68 12.35), (0.88 22.51), (0.89 26.38), (0.90 50.71), (0.97 57.32), (0.99 19.77), (1.03 37.82), (1.04 24.44), (1.07 59.25), (1.15 40.23), (1.25 25.25), (1.27 28.95), (1.42 21.38), (1.43 32.34), (1.48 21.54), (1.52 32.34), (1.54 32.50), (1.56 24.60), (1.66 32.82), (1.72 32.50), (1.83 28.95), (1.83 37.82), (1.98 32.34), (2.01 40.23), (2.17 43.14), (2.26 43.30), (3.47 73.11), (5.31 121.62).
^{1}H-^{13}C HMBC ((400, 101) MHz, $CDCl_3$) δ (0.05 18.51), (0.52 12.06), (0.55 22.37), (0.55 32.69), (0.68 39.56), (0.68 42.57), (0.68 57.61), (0.97 32.69), (0.97 58.90), (1.00 36.12), (1.00 38.27), (1.00 50.30), (1.00 141.83), (1.04 57.18), (1.07 12.06), (1.07 43.00), (1.24 82.96), (1.44 50.30), (1.47 32.26), (1.47 142.15), (1.50 121.20), (1.53 43.00), (1.53 73.08), (1.78 142.26), (1.83 72.65), (2.14 73.08), (2.14 121.63), (2.14 141.83), (2.16 32.69), (2.16 36.55), (2.27 72.65), (2.27 121.20), (2.27 141.83), (5.30 43.00), (5.32 32.26), (5.32 36.55).
ESI-HRMS m/z: exp. for 557.4577 $[M+H]^+$ (calcd. for $C_{34}H_{62}BO_3Si$ 557.4561)

Mechanistic studies

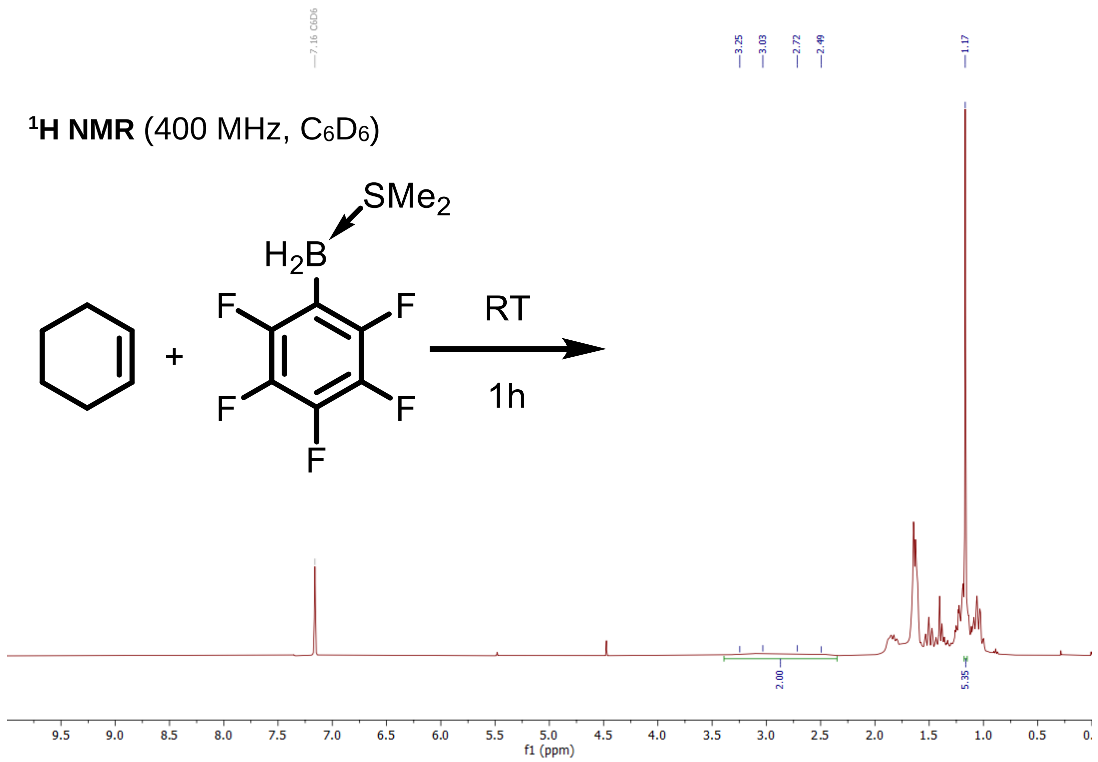
$C_6F_5BH_2 \cdot SMe_2$ (20 mg) was heated at 80°C 18h in neat conditions. Then, the sample was dissolved in C_6D_6 and NMR spectra were recorded. Only little decomposition was observed.



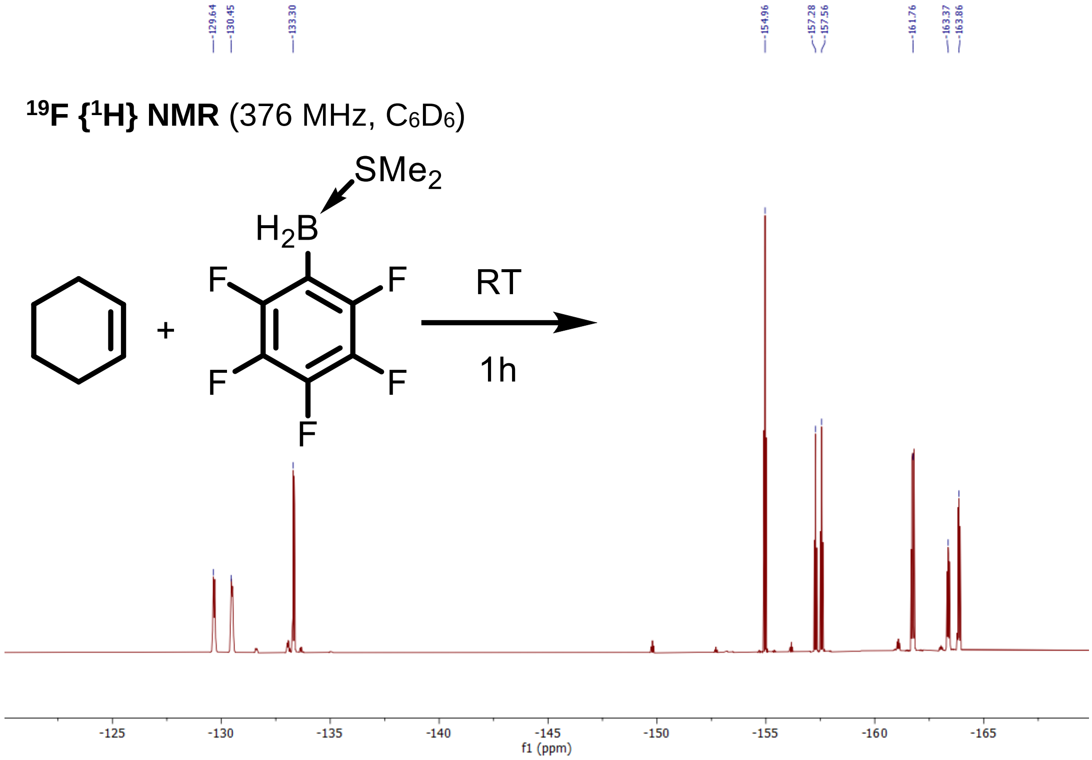




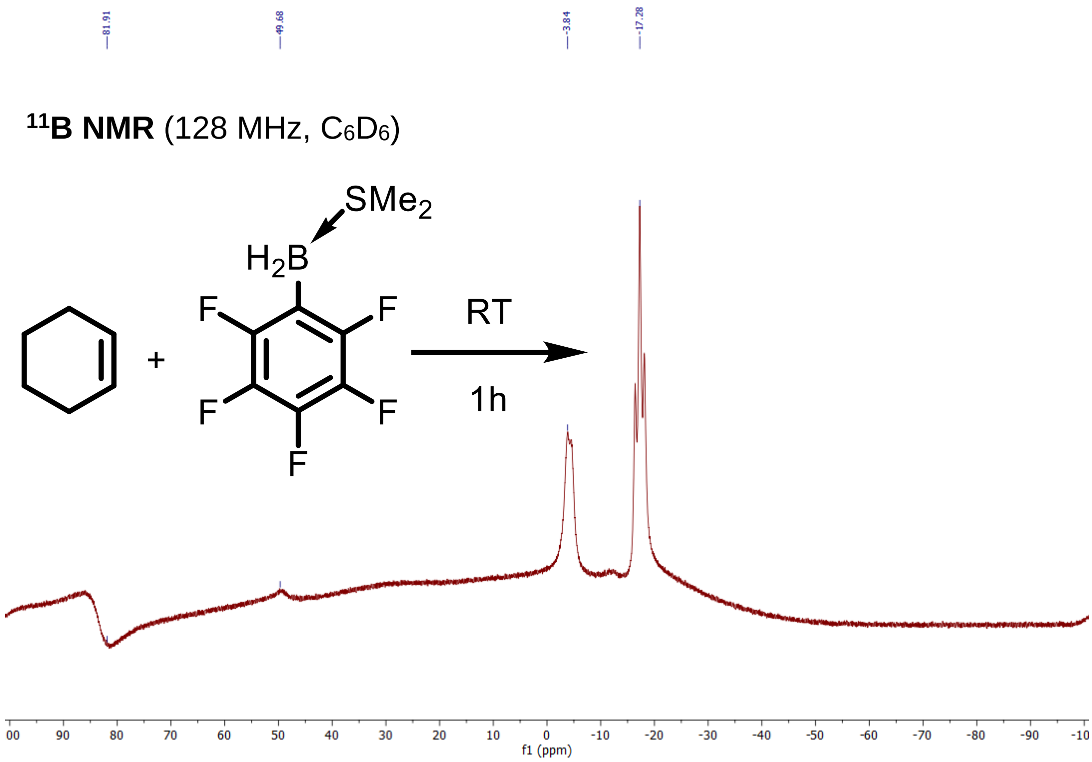
Cyclohexene (10 mg, 0.122 mmol) and **1** (29 mg, 0.122 mmol) were mixed at RT 1h in neat conditions. Then, the sample was dissolved in C_6D_6 and NMR spectra were recorded. Three sets of signals were observed in ^{19}F NMR indicating on 3 different compounds with C_6F_5 motif. Unreacted **1**, secondary borane and tertiary borane were observed in the ^{11}B NMR, indicating the formation of C_6F_5BHCy and $C_6F_5BCy_2$.



^{19}F {^{1}H} NMR (376 MHz, C_6D_6)

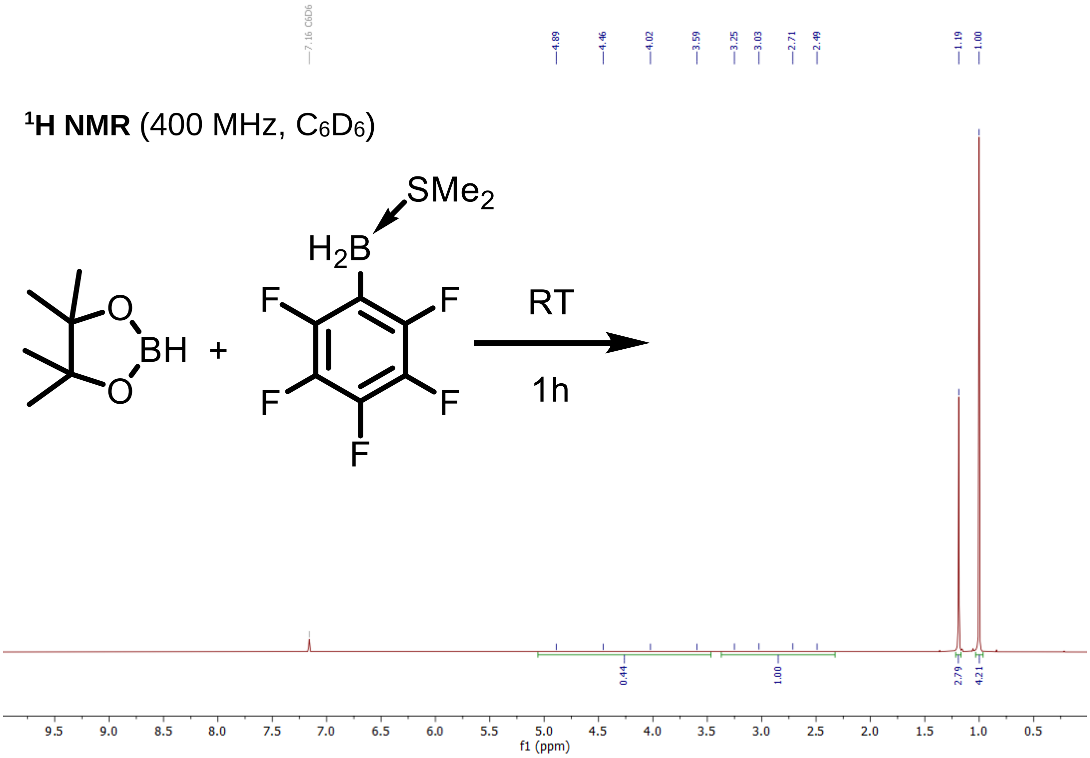


^{11}B NMR (128 MHz, C_6D_6)

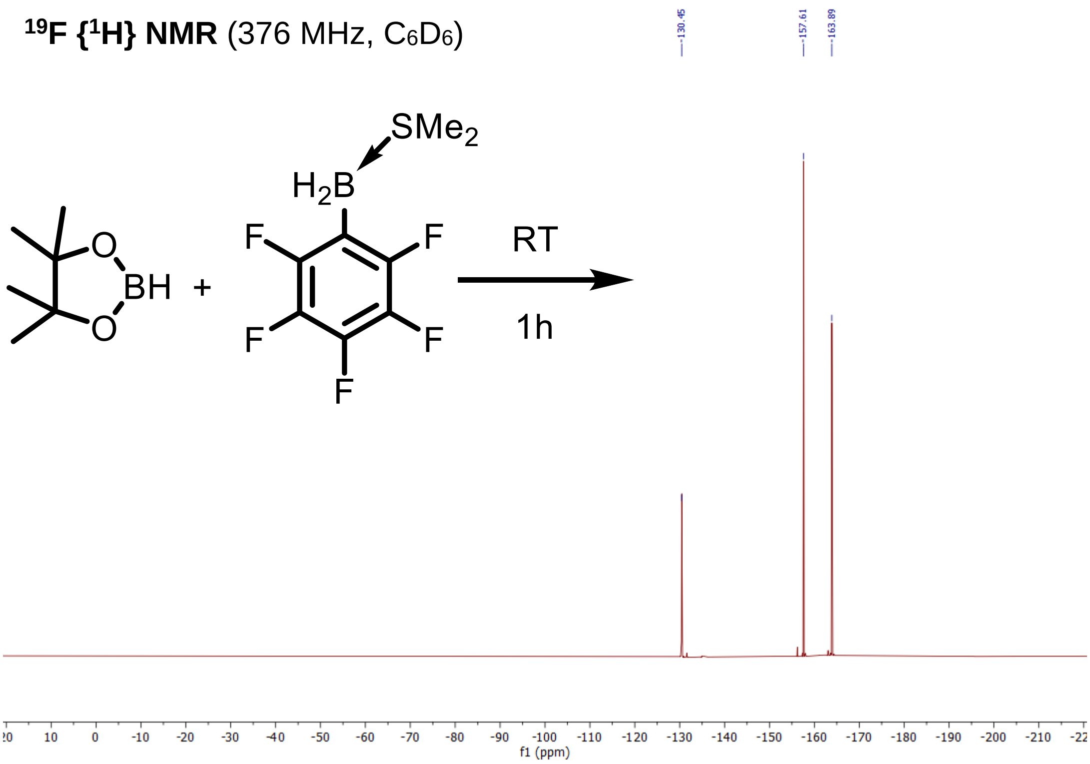


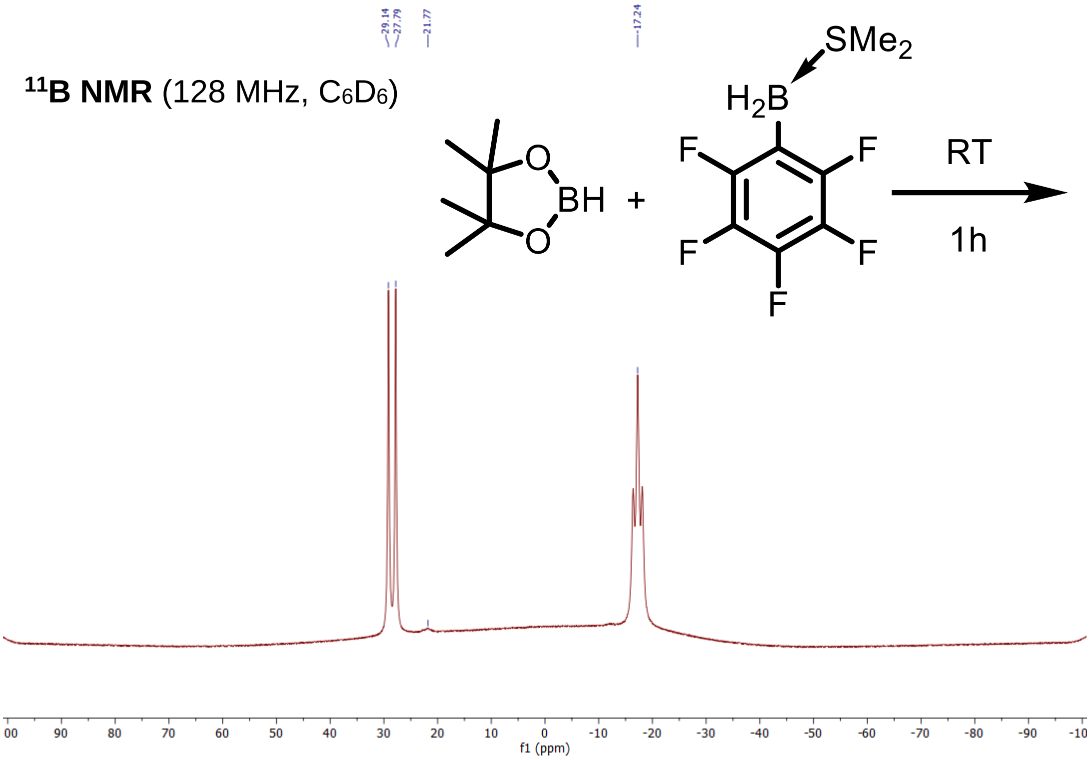
HBpin (10 mg, 0.078 mmol) and **1** (28 mg, 0.117 mmol) were mixed at RT 1h in neat conditions. Then, the sample was dissolved in C_6D_6 and NMR spectra were recorded. No reaction and BH_3 formation were observed.

^{1}H NMR (400 MHz, C_6D_6)

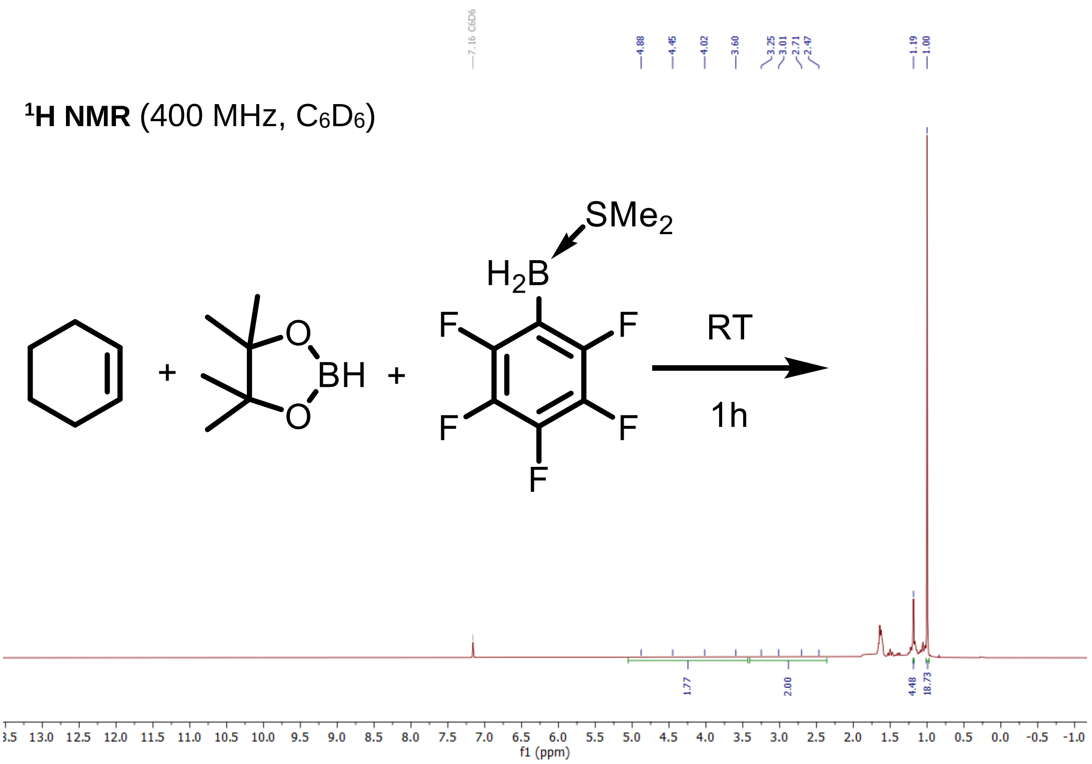


^{19}F {^{1}H} NMR (376 MHz, C_6D_6)

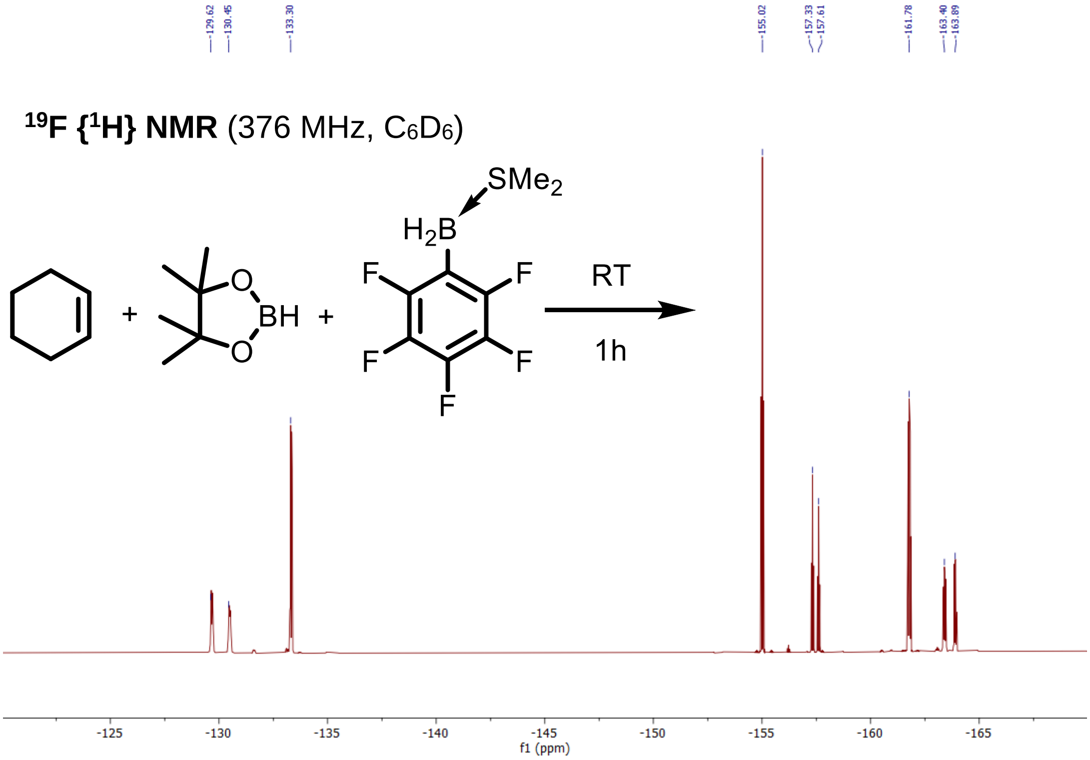




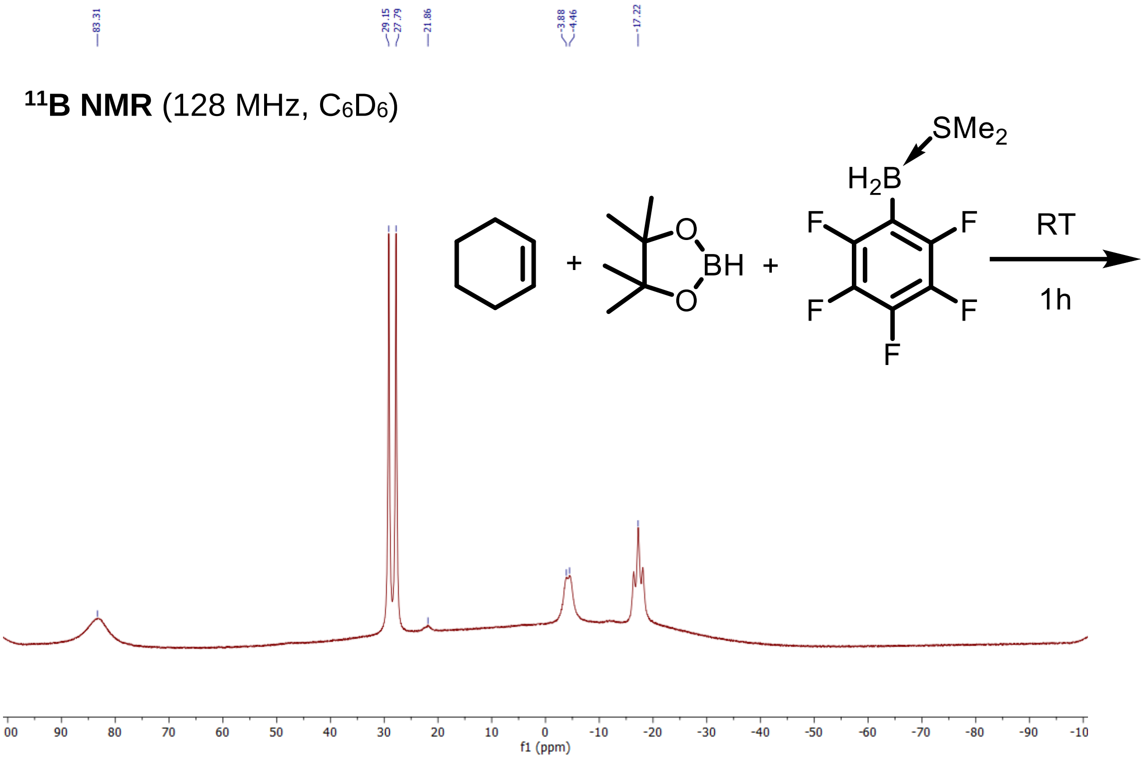
HBpin (10 mg, 0.078 mmol), cyclohexene (10 mg, 0.122 mmol) and **1** (28 mg, 0.117 mmol) were mixed at RT 1h in neat conditions. Then, the sample was dissolved in C_6D_6 and NMR spectra were recorded. The reaction profile is the same as in case of mixing cyclohexene and **1**.



19F {1H} NMR (376 MHz, C_6D_6)

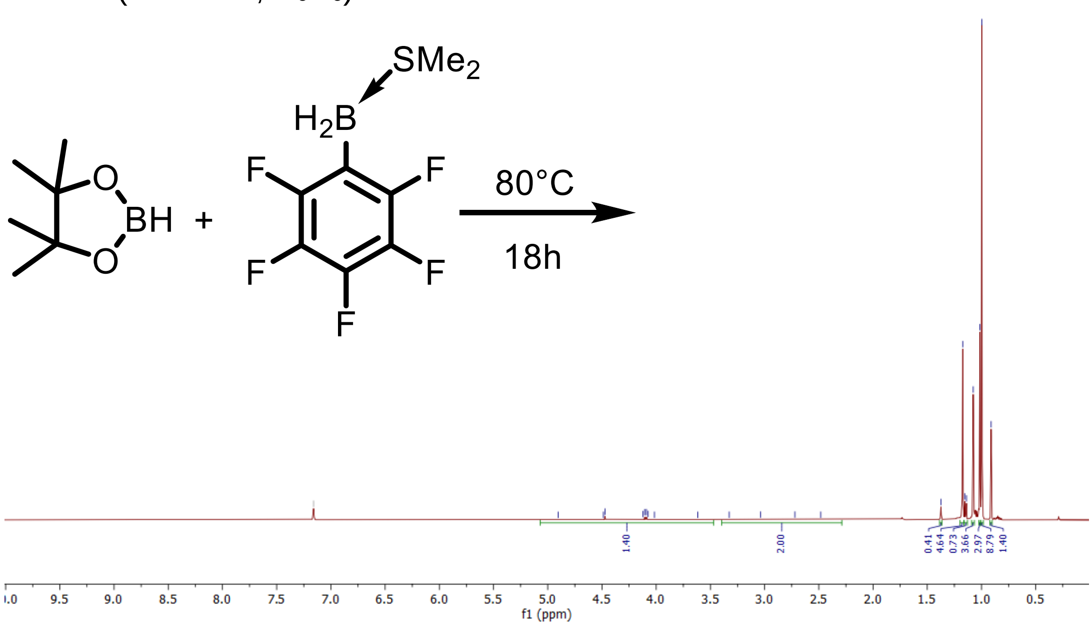


11B NMR (128 MHz, C_6D_6)

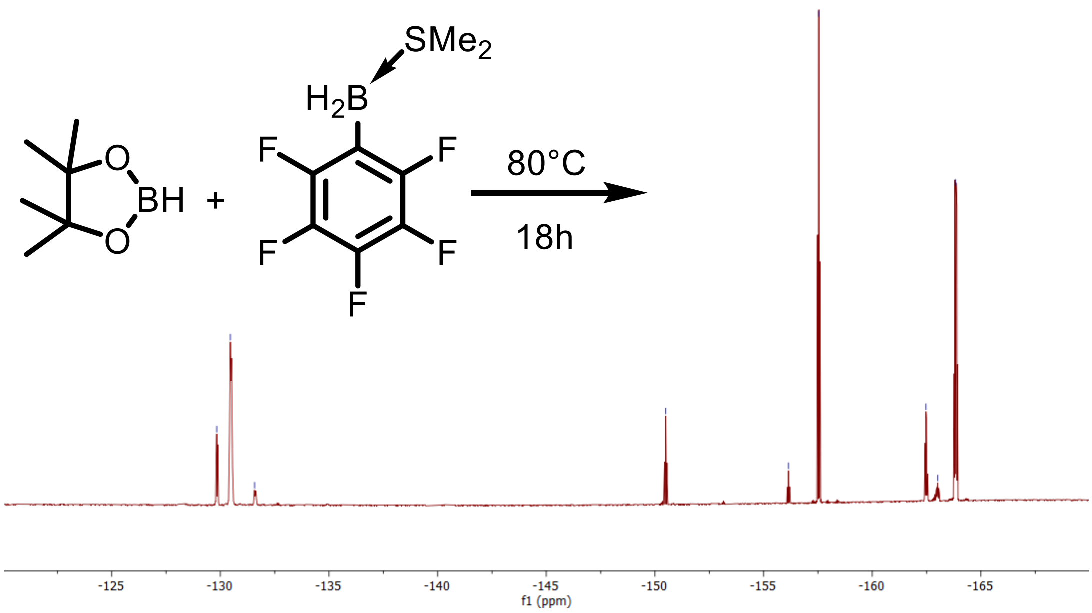


HBpin (10 mg, 0.078 mmol) and **1** (28 mg, 0.117 mmol) were mixed and heated at 80°C 18h in neat conditions. Then, the sample was dissolved in C_6D_6 and NMR spectra were recorded. Decomposition of **1**, HBpin and BH_3 formation were observed.

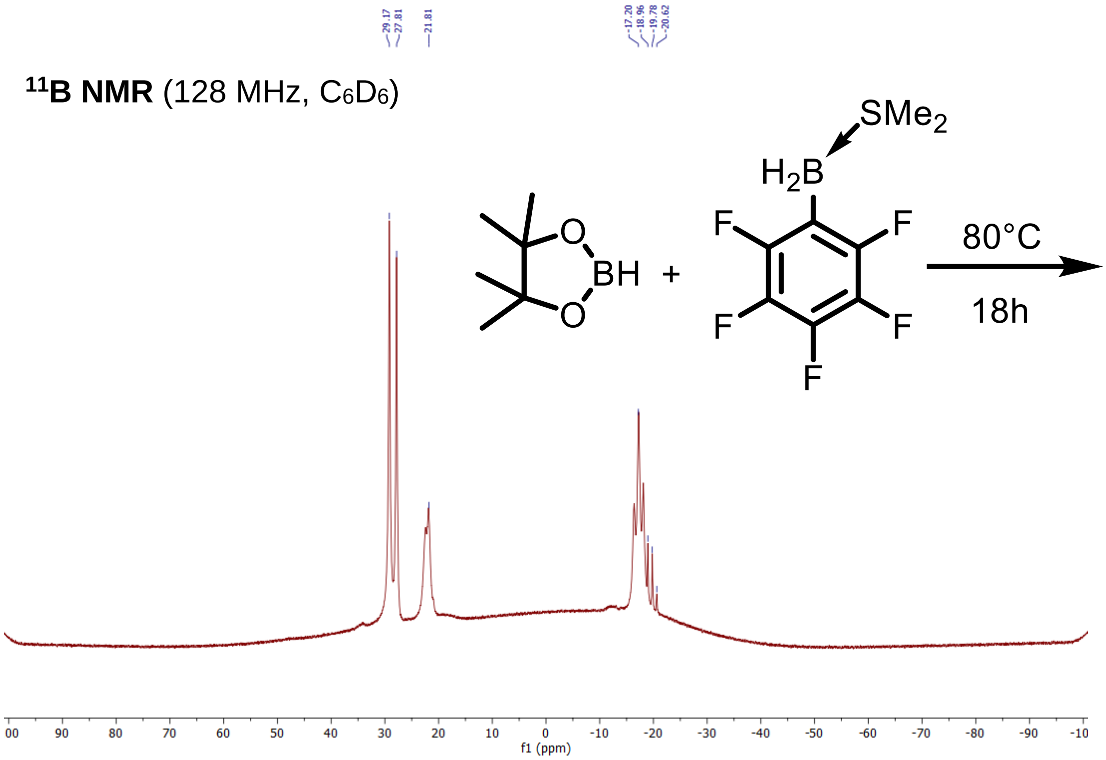
^{1}H NMR (400 MHz, C_6D_6)



^{19}F {^{1}H} NMR (376 MHz, C_6D_6)



^{11}B NMR (128 MHz, C_6D_6)



Computational Details

All computational work reported here was carried out at the density functional theory (DFT) level, using Gaussian16 (Revision C.02).[11] The exchange correlation functional PBE1PBE[12-14] was employed in conjunction with the Def2-TZVP[15,16] basis set, Grimme's empirical dispersion correction (GD3BJ)[17] and an ultrafine integration grid for the optimization and frequency calculations. The nature of the stationary points (minima and transition states) was confirmed by frequency calculations at the Def2-TZVP level, and are characterized by zero or one imaginary frequency, respectively.

Pinene products analysis

Intriguingly, α-(+)-pinene yielded a product that has the same NMR and GC-MS profile as that of β-(-)-pinene. Since the two different enantiomerically pure pinenes gave products with identical NMR and GC-MS profiles, the corresponding diastereomers are either the same compounds or enantiomers of each other. We measured specific rotation for both products and observed that they are different enantiomers (see S16, S17). To identify which diastereomers were obtained, we used DFT at the PBE0-GD3BJ/Def2-TZVP level to optimize the two β-(-)-pinene structures and calculated the dihedral angles between the atoms. In the ^{1}H and ^{1}H-^{13}C HSQMBC NMR spectra, well-resolved signals were chosen from those atoms whose J-coupling constant will be different depending on the formed chiral center, and J-couplings of those signals were identified. Advanced Pachler equation[18] and Karplus-like equation[20] can be used to calculate J-couplings of both isomers based on their dihedral angles. Both J-couplings and the calculated free energy values were found to be in better agreement with the S-isomer. As a result, we suggest that S-isomer is formed for **3j** and R-isomer for **3i** (see S16, S17). However, how pinenes transform to produce the observed diastereomers remains unclear at this point.

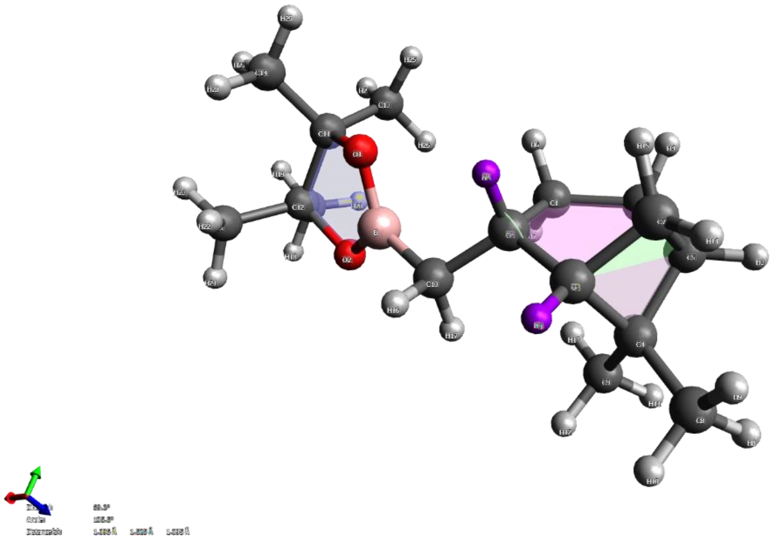


Figure S1. Optimized structure of R-isomer of **3i**. Dihedral angle between H_a and H_e (coloured as purple): 69.3°. Free energy (kcal/mol): -502986.350

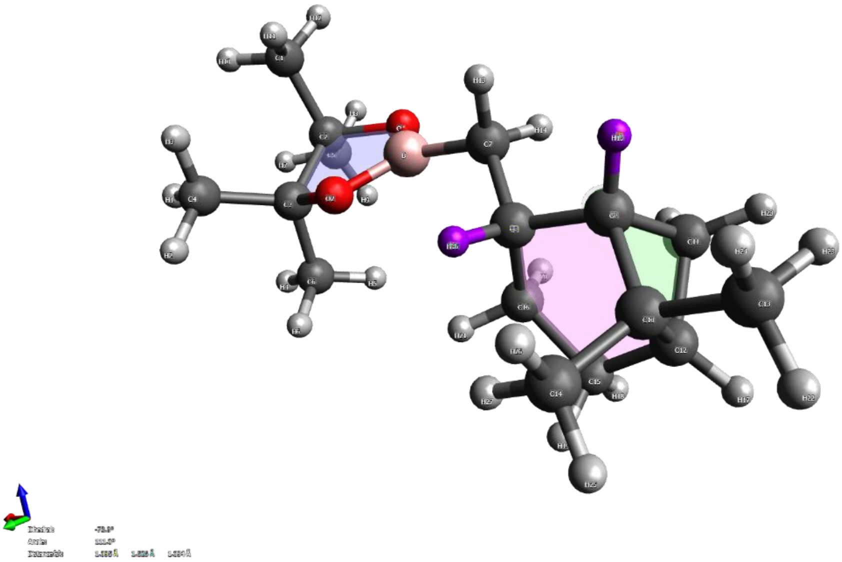


Figure S2. Optimized structure of S-isomer of **3i**. Dihedral angle between H_a and H_e (coloured as purple): 73.9°. Free energy (kcal/mol): -502988.843

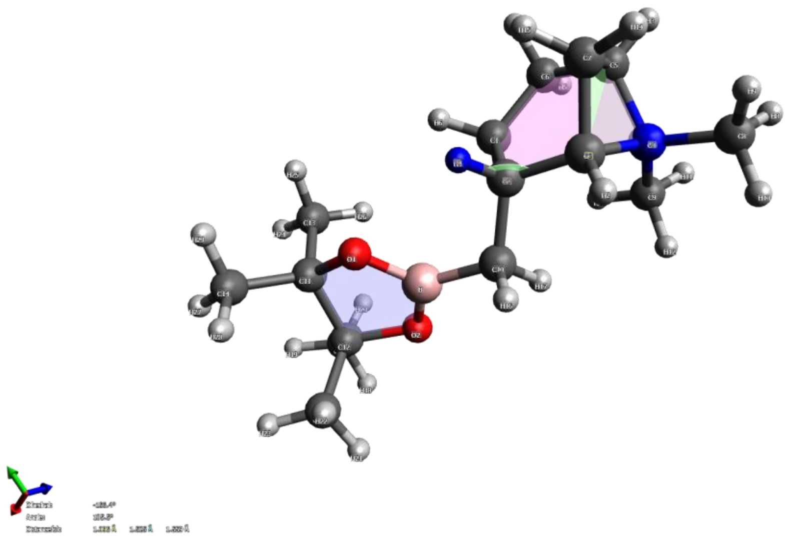


Figure S3. Optimized structure of R-isomer of **3i**. Dihedral angle between H_a and C_d (coloured as blue): -156.4°. Free energy (kcal/mol): -502986.350

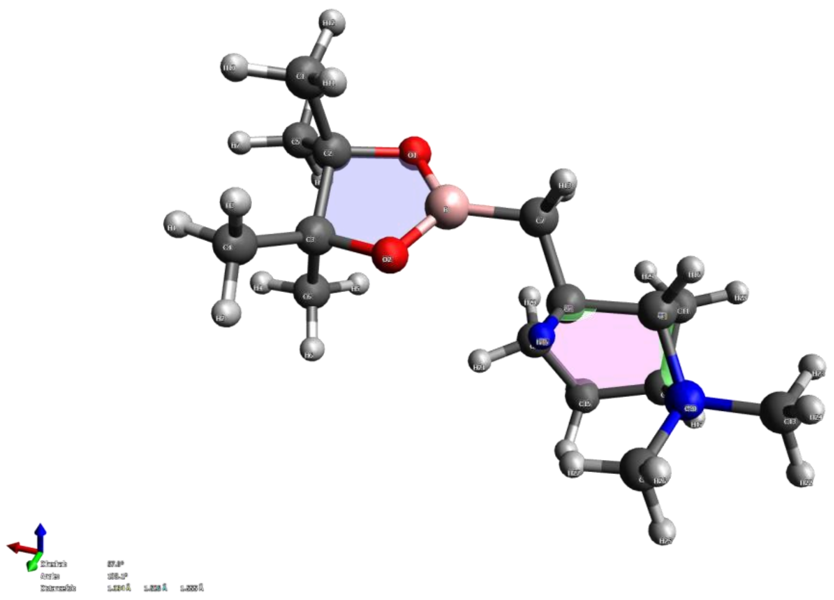


Figure S4. Optimized structure of S-isomer of **3i**. Dihedral angle between H_a and C_d (coloured as blue): 57.9°. Free energy (kcal/mol): -502988.843

Caclulation of the $^3J(H_aH_e)$ coupling constant

$$^3J_{HH} = P_1cos^2\varphi + P_2cos\varphi + P_3 + \sum_i^4 \Delta\chi_i[P_4 + P_5cos^2(\xi\varphi + P_6|\Delta\chi_i|)]$$

Equation S1. Advanced Pachler equation for $^3J_{HH}$ coupling constant.[18]

$$\begin{aligned} ^3J_{HH} = 13.24cos^2\varphi - 0.91cos\varphi \\ + 2\{0.4[0.53 - 2.41cos^2(\varphi + 15.5° * 0.4)]\} \\ + 2\{0.4[0.53 - 2.41cos^2(-\varphi + 15.5° * 0.4)]\} \end{aligned}$$

Equation S2. Transformed Eq. S1 (Equation E with 4 substituents; rms-deviation = 0.359)[18] with Huggins electronegativity[19] ($\Delta\chi_i = \chi_C - \chi_H = 0.4$) .

$$^3J_{HH}(R_{isomer}(\varphi = 69.3°)) = 1.67\ Hz$$

$$^3J_{HH}(S_{isomer}(\varphi = 73.9°)) = 1.28\ Hz$$

Equation S3. Calculated $^3J(H_aH_e)$ coupling contstants of R- and S-isomers of **3i** based on dihedral angle φ between H_a and H_e.

Calculation of the $^3J(C_dH_a)$ coupling constant

$$^3J_{CH} = (10.2 \pm 0.9)cos^2\varphi - (1.3 \pm 1.2)cos\varphi + (0.2 \pm 0.2)$$

Equation S4. Karplus-like equation for $^3J_{CH}$ coupling constant.[20]

$$^3J_{CH}\left(R_{isomer}(\varphi = -156.4°)\right) = (9.84 \pm 1.94)\ Hz$$

$$^3J_{CH}(S_{isomer}(\varphi = 57.9°)) = (2.39 \pm 1.09)\ Hz$$

Equation S5. Calculated $^3J(C_dH_a)$ coupling contstants of R- and S-isomers of **3i** based on dihedral angle φ between C_d and H_a.

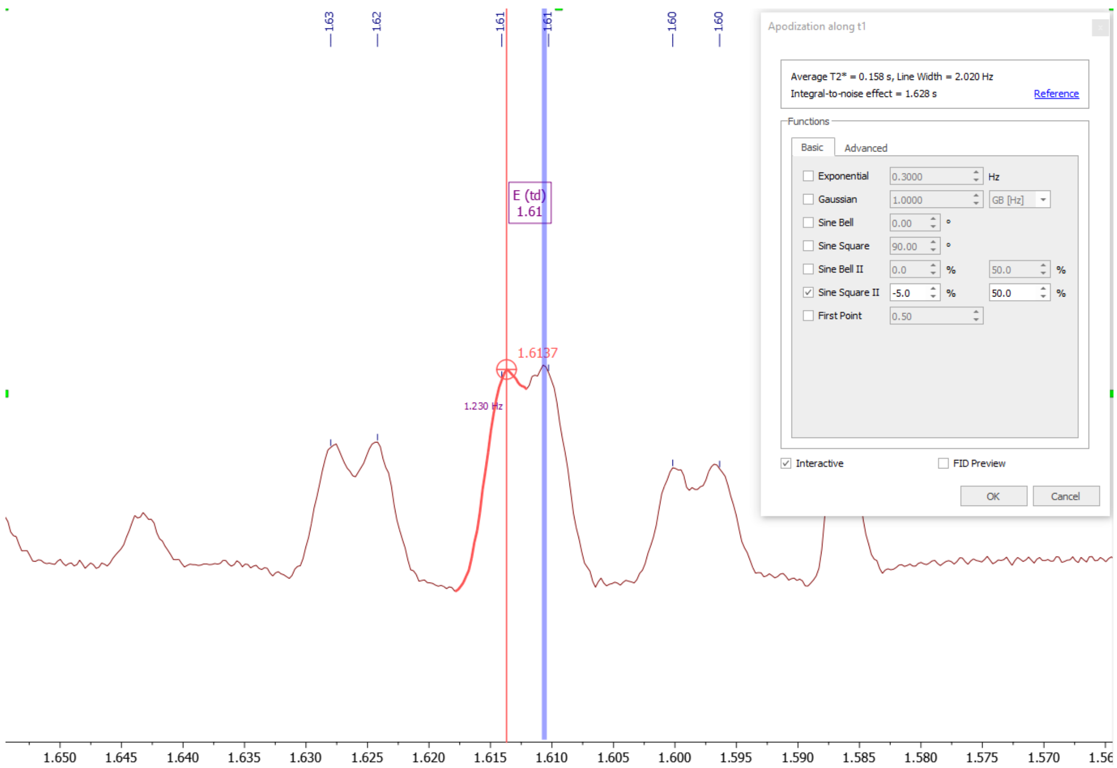


Figure S5. Selected region of ^{1}H NMR of **3i** with applied Sine Square II function (-5.0%; 50%) for better resolution. Experimental $^{3}J(H_{a}H_{e})$ = 1.23 Hz. In a positive-phased NMR spectrum, overlapped peaks in a one signal create a less value of coupling constant than the actual one.

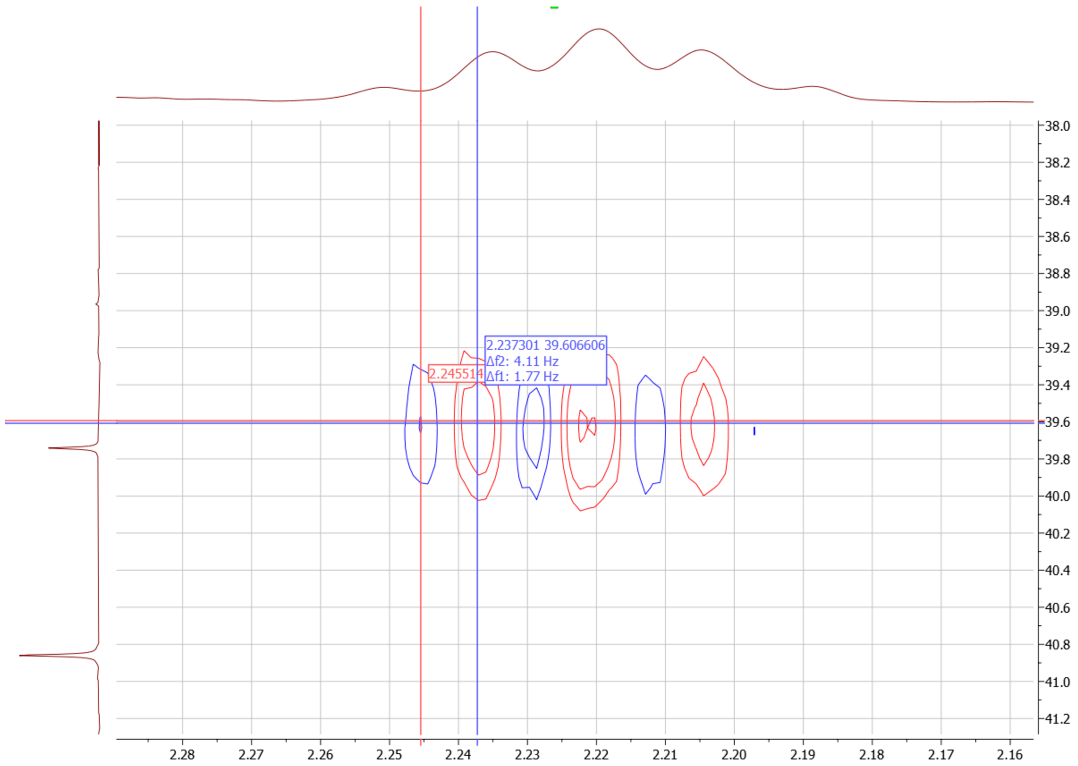


Figure S6. Selected region of ^{1}H-^{13}C LR-HSQMBC NMR[21] of **3i** with the signal between H_{a} and C_{d}. Experimental $^{3}J(H_{a}C_{d})$ = 4.11 Hz. In an anti-phased NMR spectrum, overlapped peaks in a one signal create a higher value of coupling constant than the actual one.

Optimized xyz-coordinates

R-isomer of **3i**

48

scf done: -801.944808

C	0.630099	-0.855563	0.533355
C	0.220946	-2.090888	-0.307690
C	-1.024105	-2.760740	0.264994
C	-1.065294	-2.831362	1.822318
C	-1.563245	-1.362334	1.742806
C	-0.409999	-0.384931	1.575611
C	-2.127951	-1.688443	0.349282
H	-0.069706	-1.734645	-1.302854
C	-2.166998	-3.773770	2.290488
C	0.179671	-3.138120	2.633927
H	-1.244785	-3.688187	-0.273205
H	-2.257092	-1.028126	2.520065
H	-0.828359	0.582903	1.282081
H	0.084259	-0.223425	2.538403
H	0.879461	-0.033603	-0.140641
H	1.563447	-1.090384	1.052236
H	-2.356489	-3.637631	3.359541
H	-3.110076	-3.622497	1.764263
H	-1.865566	-4.814450	2.137814
H	-0.038294	-3.023594	3.700674
H	0.496656	-4.173509	2.479037
H	1.024996	-2.494070	2.400966
H	-3.137064	-2.096340	0.372723
H	-2.086767	-0.890039	-0.396340
C	1.396637	-3.046709	-0.512920
H	1.065276	-3.893608	-1.130154
B	2.619314	-2.388989	-1.230454
H	1.722678	-3.481213	0.435665
O	2.498900	-1.493410	-2.261804
C	3.804544	-0.937647	-2.505625
C	4.746708	-2.041170	-1.930630
O	3.926892	-2.641506	-0.909663
C	3.879727	0.368017	-1.729928
C	3.961339	-0.675184	-3.986995
C	6.020387	-1.524457	-1.299018
C	5.065845	-3.131991	-2.940448
H	6.605177	-2.363110	-0.917144
H	6.628555	-0.994349	-2.036021
H	5.810565	-0.851085	-0.469030
H	5.548651	-3.961153	-2.420863
H	4.156854	-3.509717	-3.412691
H	5.740192	-2.772865	-3.720049
H	4.822271	0.888478	-1.909166
H	3.061663	1.014755	-2.051458
H	3.774032	0.195547	-0.657119
H	4.970967	-0.322471	-4.211191
H	3.764789	-1.570575	-4.575160
H	3.255802	0.097464	-4.297555

S-isomer of **3i**

48

scf done: -801.948794

C	0.439542	-0.315809	1.957288
C	0.394850	-0.730338	0.495205
O	-0.806038	-1.505237	0.315271
B	-1.777946	-0.656670	-0.144750
O	-1.276580	0.571982	-0.490477
C	0.159845	0.473183	-0.470190
C	0.738928	1.789219	-0.000633
C	1.591840	-1.591923	0.159167
C	0.602204	0.183390	-1.895850
C	-3.291940	-1.030156	-0.249251
H	1.825099	1.719760	0.096384
H	0.513187	2.568609	-0.730580
H	0.320514	2.091042	0.958605
H	1.689986	0.154981	-1.981518
H	0.199160	-0.768292	-2.247688
H	0.225538	0.973508	-2.547627
H	2.514145	-1.008392	0.212790
H	1.666210	-2.409914	0.877863
H	1.507513	-2.022615	-0.837692
H	1.357281	0.225975	2.193338
H	-0.413538	0.315307	2.214016
H	0.398067	-1.212284	2.577910
H	-3.783084	-0.676182	0.668023
C	-4.002459	-0.433689	-1.463105
H	-3.401283	-2.120608	-0.241252
C	-5.488113	-0.783364	-1.481453
H	-3.910461	0.654406	-1.390247
C	-6.219292	-0.084114	-2.661761
C	-5.701154	-2.120877	-2.221380
H	-5.931297	-0.664270	-0.487468
C	-5.713106	-1.280754	-3.515916
C	-7.730483	-0.114339	-2.485928
C	-5.810357	1.322385	-3.053340
C	-4.280104	-1.046486	-3.971431
H	-6.354076	-1.603220	-4.341700
C	-3.331261	-0.914291	-2.767267
H	-3.951613	-1.884281	-4.594243
H	-4.238995	-0.159813	-4.610217
H	-2.900688	-1.900554	-2.567063
H	-2.484825	-0.267133	-3.009718
H	-8.229590	0.174880	-3.415770
H	-8.103890	-1.099159	-2.202266
H	-8.038769	0.593294	-1.710387
H	-6.312082	1.618434	-3.979926
H	-6.109373	2.034947	-2.278455
H	-4.737898	1.438499	-3.207742
H	-6.663858	-2.578757	-2.001953
H	-4.925568	-2.883175	-2.122849

Cy
16
scf done: -234.451244

C	-0.067146	-0.170485	0.160390
C	0.239783	0.421810	1.309902
H	0.655106	-0.836551	-0.303846
C	-0.697661	1.325763	2.048166
H	1.216037	0.246964	1.753918
C	-2.122668	1.219505	1.522028
H	-0.668794	1.088912	3.117165
H	-0.341558	2.361946	1.968945
C	-2.137416	1.226323	0.001002
H	-2.568399	0.283860	1.878954
H	-2.735273	2.033081	1.919735
C	-1.368248	0.033788	-0.551241
H	-3.163241	1.223908	-0.377194
H	-1.670393	2.151427	-0.356167
H	-1.974767	-0.878427	-0.468970
H	-1.182839	0.164528	-1.622780

$C_6F_5BH_2$
14
scf done: -753.395253

B	-0.000000	0.000000	0.007750
C	-0.000000	0.000000	1.544507
C	1.188201	-0.000000	2.283315
C	1.205280	-0.000000	3.664775
C	0.000000	0.000000	4.352465
C	-1.205280	0.000000	3.664775
C	-1.188201	0.000000	2.283315
F	2.358499	-0.000000	1.665904
F	2.343912	-0.000000	4.339741
F	0.000000	0.000000	5.668930
F	-2.343912	0.000000	4.339741
F	-2.358499	0.000000	1.665904
H	1.034353	-0.000000	-0.581061
H	-1.034353	0.000000	-0.581061

HBpin
22
scf done: -411.554937

C	0.436779	-1.378914	1.223218
C	0.169938	-0.705818	-0.113095
C	0.159491	0.853380	-0.020846
C	0.421339	1.530408	-1.356340
C	1.082721	-1.274497	-1.176482
O	-1.199986	-1.004764	-0.462942
B	-1.952768	0.059791	-0.069751
O	-1.215115	1.134421	0.325137
C	1.061598	1.433885	1.045321
H	-3.142479	0.052297	-0.072012
H	2.104973	1.176265	0.848137
H	0.974855	2.521728	1.043374
H	0.793726	1.073463	2.037556
H	1.462558	1.418894	-1.664173
H	-0.219779	1.121010	-2.139288
H	0.201535	2.594720	-1.259794
H	2.121957	-1.002616	-0.976540
H	1.010863	-2.363428	-1.174405
H	0.812853	-0.918166	-2.169625
H	1.475594	-1.253600	1.533915
H	-0.211821	-0.977624	2.004191
H	0.231361	-2.446088	1.126568

TS1
30
scf done: -987.867414

B	3.032040	-3.436295	1.257532
C	2.763958	-2.431035	0.053227
C	2.585226	-2.814761	-1.267199
F	2.574755	-4.112016	-1.596700
C	2.411892	-1.913116	-2.303813
F	2.235816	-2.333042	-3.550659
C	2.427488	-0.556014	-2.031120
F	2.262589	0.322361	-3.008152
C	2.623383	-0.123979	-0.730263
F	2.650219	1.175756	-0.464467
C	2.790192	-1.060614	0.275445
F	2.992722	-0.592743	1.509276
C	1.727982	-3.444339	2.425432
H	2.195358	-3.287292	3.389084
C	0.512216	-2.588772	2.159987
H	0.800352	-1.545797	2.017400
H	-0.086685	-2.610527	3.078821
C	-0.349187	-3.076137	1.003498
H	0.111376	-2.803273	0.049501
H	-1.317581	-2.570950	1.038318
C	-0.527907	-4.582785	1.063462
H	-1.206212	-4.926983	0.279141
H	-0.985488	-4.858064	2.020665
C	0.815179	-5.286449	0.914258
H	0.719207	-6.354895	1.122671
H	1.158917	-5.208397	-0.117670
C	1.851314	-4.721977	1.858321
H	2.464185	-5.444299	2.385108
H	3.207797	-4.561491	0.790493
H	4.011934	-3.266640	1.924295

C_6F_5BHCy
30
scf done: -987.899717

B	-0.196900	0.298378	0.158728
C	-0.096634	0.086220	1.698245
C	1.139545	0.222053	2.339345
C	1.307437	0.038104	3.699963
C	0.208367	-0.288836	4.477475
C	-1.040359	-0.429264	3.892057
C	-1.170748	-0.243846	2.528621
F	2.226772	0.533340	1.648368
F	2.496558	0.170315	4.267851

F	0.349005	-0.465024	5.776195
F	-2.086598	-0.736215	4.644295
F	-2.393987	-0.382695	2.031111
H	0.800639	0.684478	-0.377854
C	-1.478779	0.134422	-0.709537
C	-1.187252	-0.210127	-2.171243
H	-2.169215	-0.611751	-0.301836
C	-2.447716	-0.198207	-3.023474
H	-0.469693	0.516855	-2.571848
H	-0.699773	-1.188046	-2.235703
C	-3.161298	1.142522	-2.932681
H	-2.202065	-0.428330	-4.064552
H	-3.123792	-0.991045	-2.679496
C	-3.462187	1.509707	-1.487475
H	-2.524939	1.918902	-3.375912
H	-4.085216	1.125311	-3.518149
C	-2.203096	1.500655	-0.629080
H	-3.937227	2.494254	-1.434940
H	-4.178087	0.790917	-1.071188
H	-1.526622	2.292242	-0.977169
H	-2.459021	1.737416	0.407529

CyBpin

38

scf done: -646.060263

C	2.694142	-1.683506	0.649213
C	2.373205	-0.197451	0.666609
C	3.649428	0.613460	0.623892
O	1.602018	0.078531	-0.517716
B	0.278017	0.031165	-0.166560
O	0.100868	-0.034386	1.190714
C	1.382136	0.196378	1.806136
C	1.486753	-0.643627	3.059766
C	1.441896	1.674378	2.157782
C	-0.895751	0.029119	-1.202137
H	2.478618	-0.545671	3.507702
H	0.750182	-0.303376	3.789740
H	1.298646	-1.696364	2.853157
H	2.362141	1.924281	2.688984
H	1.376874	2.294860	1.261798
H	0.594394	1.916631	2.800931
H	4.220140	0.483334	1.546603
H	4.269201	0.275454	-0.208462
H	3.444773	1.674265	0.485642
H	3.333531	-1.966157	1.487517
H	1.782911	-2.283629	0.688175
H	3.216945	-1.919090	-0.279115
C	-0.532217	0.735428	-2.510570
H	-1.068356	-1.033565	-1.446831
C	-1.667853	0.667807	-3.521388
H	-0.305004	1.788137	-2.297030
H	0.382148	0.305936	-2.928012
C	-2.963065	1.219706	-2.942058
H	-1.397723	1.210596	-4.432605
H	-1.822848	-0.378402	-3.815037
C	-3.335234	0.513234	-1.645880
H	-2.837717	2.291693	-2.742337
H	-3.774633	1.131961	-3.670834
C	-2.203592	0.579531	-0.630398
H	-4.248344	0.946447	-1.225823
H	-3.559781	-0.539174	-1.862391
H	-2.050024	1.624719	-0.331428
H	-2.471904	0.040015	0.281684

$C_6F_5BCy_2$

46

scf done: -1222.397166

C	-2.019662	1.516898	-1.069072
C	-1.365852	0.184171	-0.643508
C	-1.263992	-0.729833	-1.872260
C	-2.635747	-0.978727	-2.484334
C	-3.324239	0.325884	-2.858128
C	-3.396914	1.275342	-1.671250
B	-0.008906	0.413786	0.135157
C	-0.028563	0.262811	1.718737
C	1.043776	-0.263127	2.440437
C	1.040988	-0.414282	3.816013
C	-0.063704	-0.005941	4.542487
C	-1.151096	0.534691	3.879063
C	-1.119594	0.645720	2.500017
F	2.139097	-0.691647	1.815761
F	2.082103	-0.943398	4.442640
F	-0.080056	-0.131038	5.856659
F	-2.208590	0.938563	4.568359
F	-2.200157	1.186991	1.940567
C	1.366211	0.783137	-0.552508
H	-2.078725	-0.297296	0.038220
H	-0.616403	-0.267427	-2.625293
H	-0.798641	-1.683912	-1.606042
H	-2.543671	-1.624554	-3.362995
H	-3.256266	-1.521657	-1.760607
H	-2.761263	0.808260	-3.667315
H	-4.326092	0.128973	-3.251029
H	-3.843129	2.227604	-1.974482
H	-4.053900	0.851287	-0.902295
H	-1.387237	2.009327	-1.813469
H	-2.100313	2.202761	-0.223008
C	1.292692	1.912727	-1.588908
H	2.060899	1.125660	0.225204
C	2.678622	2.269334	-2.108833
H	0.665056	1.602293	-2.431489
H	0.818642	2.800549	-1.159082
C	3.379224	1.056996	-2.704782
H	2.606875	3.069481	-2.851956
H	3.279729	2.664567	-1.280548
C	3.424654	-0.099497	-1.716904
H	2.837649	0.737275	-3.604161
H	4.390060	1.322098	-3.028484
C	2.033444	-0.447009	-1.205460
H	3.880452	-0.978506	-2.183220

H	4.061387	0.170276	-0.865711
H	1.420854	-0.788655	-2.044842
H	2.094658	-1.280344	-0.502221

TS2a

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scf done: -1399.450294

C	4.649402	-1.387978	-1.336233
C	3.751572	-0.676873	-0.347745
O	2.800268	0.120659	-1.070929
B	1.612185	0.088552	-0.353220
O	1.679017	-0.787471	0.715434
C	2.834435	-1.615963	0.496950
C	2.395794	-2.853198	-0.269562
C	4.570437	0.271694	0.514846
C	3.399513	-2.014392	1.842390
H	0.698553	-0.736635	-1.435144
H	3.228238	-3.544889	-0.409971
H	1.613787	-3.361260	0.295068
H	1.992617	-2.598892	-1.251400
H	4.333376	-2.568180	1.719672
H	3.587629	-1.144315	2.470184
H	2.688031	-2.660394	2.359698
H	5.371386	-0.250967	1.041022
H	5.018347	1.031915	-0.127350
H	3.941514	0.774165	1.252747
H	5.335245	-2.063244	-0.818846
H	4.070508	-1.961787	-2.058571
H	5.244337	-0.654166	-1.882995
B	-0.113442	0.171783	-1.437441
H	-0.100764	0.751900	-2.482455
C	-1.505230	-0.275136	-0.831100
C	-2.581856	0.600769	-0.785852
C	-3.818277	0.262062	-0.270104
C	-4.011060	-1.020706	0.217963
C	-2.970890	-1.933412	0.182504
C	-1.744586	-1.549986	-0.337049
F	-2.428891	1.848347	-1.241567
F	-4.812144	1.138901	-0.237765
F	-5.186246	-1.371824	0.711755
F	-3.159620	-3.162875	0.641377
F	-0.788254	-2.472865	-0.360187
C	0.718261	1.452688	-0.179452
C	1.591446	2.636440	-0.621165
H	-0.208265	1.667344	-0.758880
C	0.902620	3.960206	-0.326446
H	2.545053	2.582888	-0.087078
H	1.831412	2.539488	-1.681585
C	0.493427	4.066336	1.136034
H	1.563663	4.788121	-0.598480
H	0.010446	4.052170	-0.958932
C	-0.403306	2.906901	1.547231
H	1.394580	4.064139	1.762229
H	-0.011704	5.018693	1.319476
C	0.259347	1.564048	1.277392
H	-0.662371	2.983186	2.607121
H	-1.346481	2.966017	0.990435
H	1.134473	1.441391	1.922825
H	-0.411508	0.737970	1.522341

TS2b

46

scf done: -1222.359447

C	3.108844	-3.497329	1.216401
C	2.834836	-2.564577	0.226746
C	2.588248	-3.095185	-1.032067
C	2.602810	-4.451503	-1.306787
C	2.876386	-5.344133	-0.284251
C	3.132559	-4.863554	0.988098
B	2.913525	-0.978021	0.455171
C	3.921946	-0.124919	-0.500719
C	4.967722	0.629029	0.327083
C	6.029100	1.304965	-0.529526
C	5.404826	2.226630	-1.565492
C	4.381731	1.481258	-2.408285
C	3.319555	0.820422	-1.539231
F	2.316427	-2.276363	-2.053296
F	2.354731	-4.904142	-2.529543
F	2.892511	-6.646770	-0.521834
F	3.396866	-5.714341	1.972354
F	3.362539	-3.101784	2.468728
C	1.691813	0.005244	1.520932
C	1.184739	-0.534663	2.835022
C	-0.193770	-1.167605	2.691208
C	-0.219442	-2.133226	1.518900
C	0.057565	-1.402462	0.213398
C	1.177087	-0.400060	0.301086
H	2.230413	0.946307	1.554652
H	1.258981	0.281644	-0.534510
H	-0.836152	-0.834294	-0.074741
H	0.232800	-2.108663	-0.600476
H	-1.186974	-2.636930	1.454411
H	0.528920	-2.914937	1.676970
H	-0.944331	-0.384526	2.533847
H	-0.459687	-1.676685	3.620520
H	1.158498	0.292732	3.549075
H	1.887926	-1.264689	3.239487
H	3.325499	-0.848094	1.597860
H	4.473044	-0.888082	-1.070113
H	4.463992	1.394145	0.936264
H	5.440856	-0.057631	1.036066
H	6.731921	1.858502	0.101291
H	6.613578	0.531824	-1.044055
H	4.909011	3.061765	-1.053623
H	6.177751	2.667331	-2.202375
H	3.912486	2.159785	-3.127697
H	4.891764	0.707143	-2.994928
H	2.754242	1.615850	-1.030045
H	2.608567	0.284431	-2.174884

TS3

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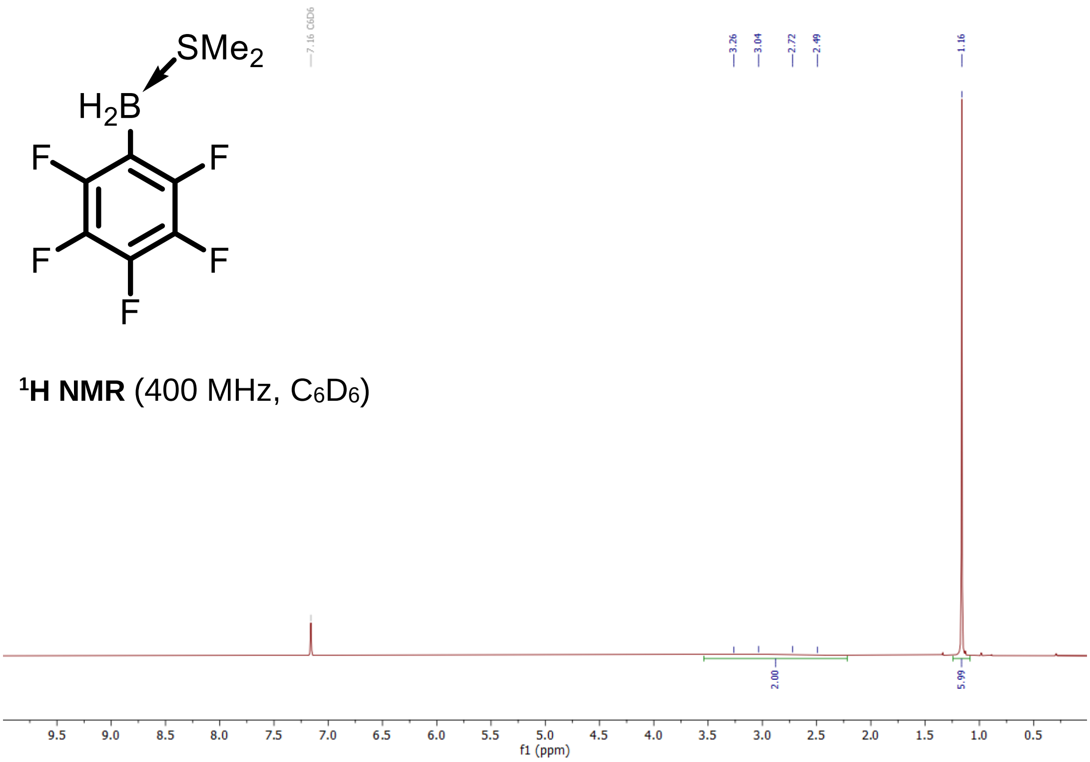
scf done: -1633.950440

C	1.768300	-0.902714	-1.250544
C	1.469756	0.038043	-0.273946
C	2.512085	0.368194	0.580447
C	3.764111	-0.213974	0.513958
C	4.012471	-1.162493	-0.464885
C	3.010879	-1.506425	-1.356135
B	0.050499	0.746156	-0.198994
O	-1.178373	-1.853701	-0.115391
B	-1.420224	-0.506552	0.149684
O	-2.743346	-0.167634	-0.145586
C	-3.223831	-1.188912	-1.030540
C	-4.722555	-1.306319	-0.862924
F	2.316949	1.277362	1.542033
F	4.722106	0.123891	1.366303
F	5.204794	-1.727840	-0.553540
F	3.254236	-2.398657	-2.306119
F	0.859733	-1.245356	-2.160619
C	0.002296	2.317961	-0.454804
C	0.361935	2.518579	-1.936887
C	0.391995	3.986531	-2.335173
C	-0.929228	4.668413	-2.017625
C	-1.281722	4.500533	-0.548478
C	-1.308397	3.034974	-0.134765
C	-2.410976	-2.435469	-0.560679
C	-3.044031	-3.127004	0.637249
C	-2.112590	-3.444770	-1.648483
C	-2.890131	-0.777623	-2.457974
H	-0.719292	0.188562	-0.984572
H	-3.952373	-3.665586	0.360251
H	-2.329634	-3.843973	1.045574
H	-3.291462	-2.406905	1.419803
H	-3.037789	-3.845748	-2.069841

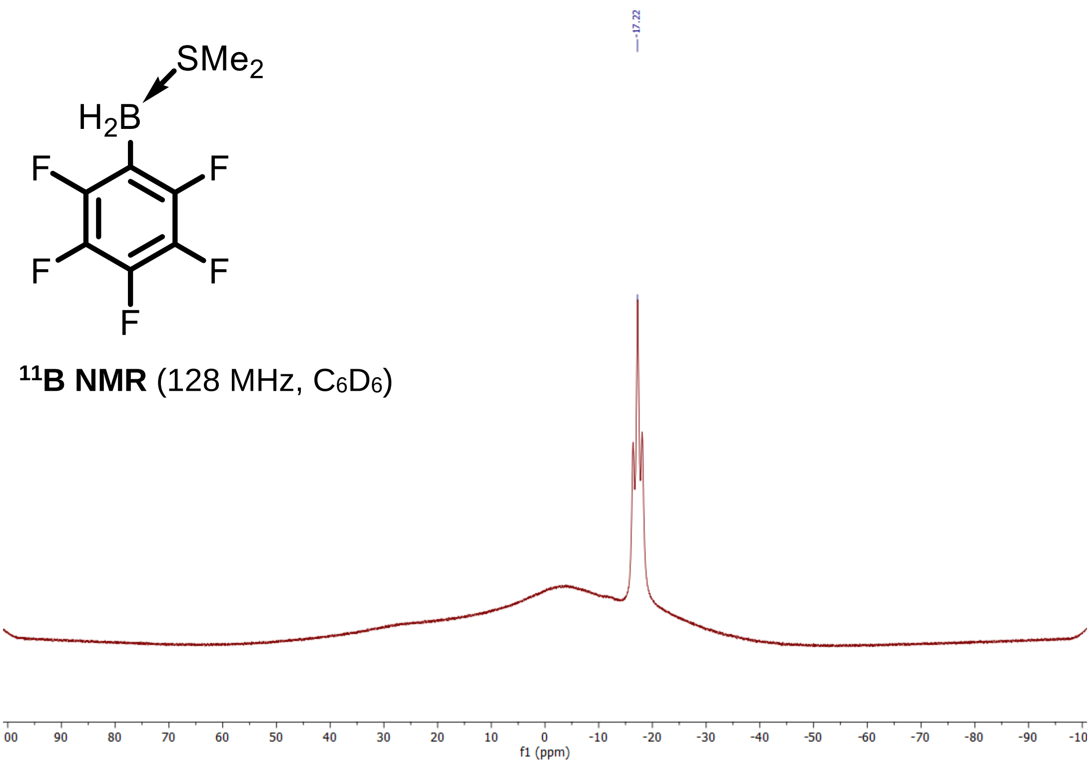
H	-1.521727	-3.002825	-2.449431
H	-1.543686	-4.276422	-1.228688
H	-3.311640	-1.476418	-3.182628
H	-3.313333	0.210823	-2.646325
H	-1.812368	-0.728175	-2.624958
H	-5.112994	-2.141616	-1.449188
H	-4.994775	-1.452847	0.181579
H	-5.202991	-0.391465	-1.214861
C	-0.741123	0.130739	1.536043
H	0.796666	2.796825	0.135804
H	-2.137842	2.522308	-0.636662
H	-1.513299	2.977277	0.936624
H	-2.247960	4.966065	-0.331243
H	-0.536895	5.029628	0.059642
H	-1.721270	4.223187	-2.633104
H	-0.886640	5.729157	-2.282039
H	0.626285	4.079946	-3.400019
H	1.199680	4.490977	-1.790381
H	-0.381719	1.997883	-2.555299
H	1.326526	2.051172	-2.157764
C	-0.044329	-0.986614	2.318826
H	-0.034841	0.985969	1.551579
C	0.396432	-0.507572	3.695364
H	-0.750976	-1.814926	2.423318
H	0.799885	-1.387494	1.756728
C	-0.767469	0.067537	4.489580
H	0.854273	-1.336702	4.242774
H	1.173054	0.257286	3.582687
C	-1.483718	1.162617	3.712586
H	-1.482371	-0.734702	4.711305
H	-0.418287	0.449481	5.453084
C	-1.936906	0.669120	2.347860
H	-2.347837	1.525603	4.277075
H	-0.811491	2.020795	3.583264
H	-2.650978	-0.151317	2.472647
H	-2.467394	1.442105	1.796687

NMR and MS data

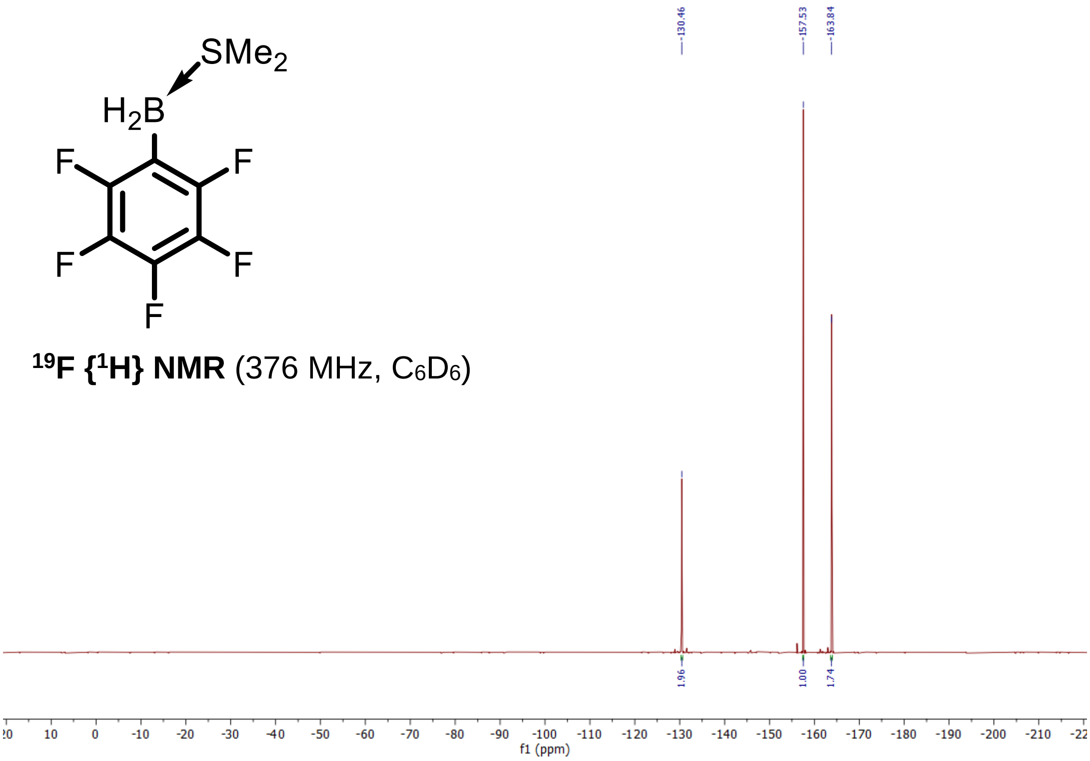
2,3,4,5,6-Pentafluorophenylborane - dimethyl sulfide adduct (1)



^{1}H NMR (400 MHz, C_6D_6)



^{11}B NMR (128 MHz, C_6D_6)


SMe2
H2B
F
F
F
F
F
19F {1H} NMR (376 MHz, C6D6)
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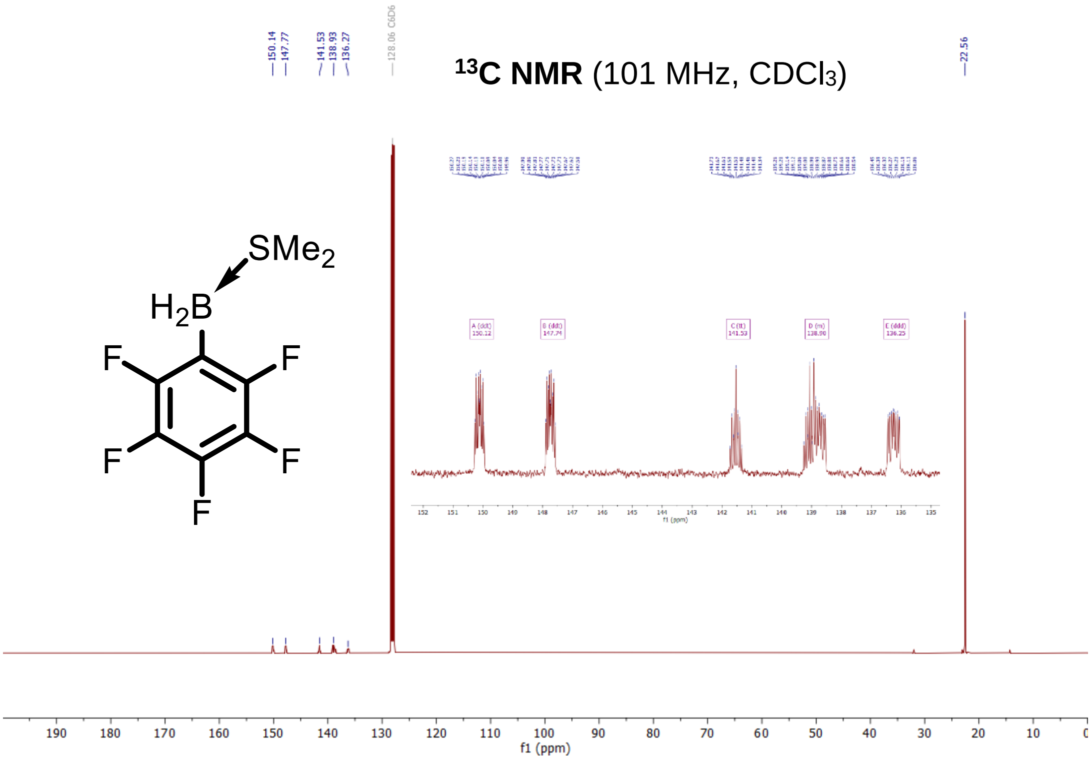
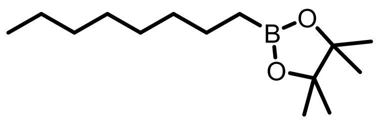
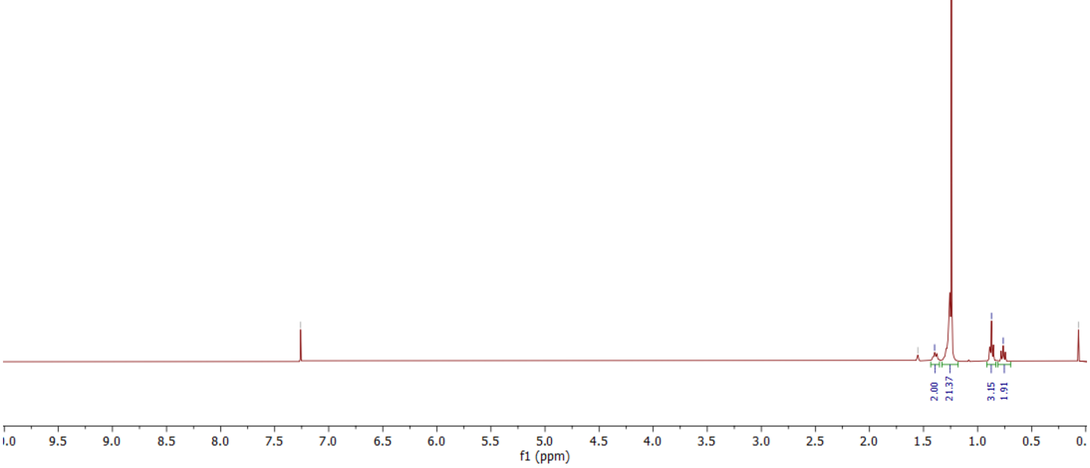
-157.53
-163.84
1.96
1.00
1.74
f1 (ppm)

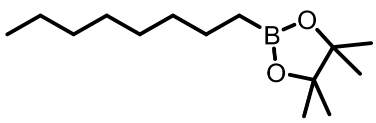

150.14
147.77
141.53
138.93
136.27
128.06 C6D6
13C NMR (101 MHz, CDCl3)
22.56
SMe2
H2B
F
F
F
F
F
f1 (ppm)

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

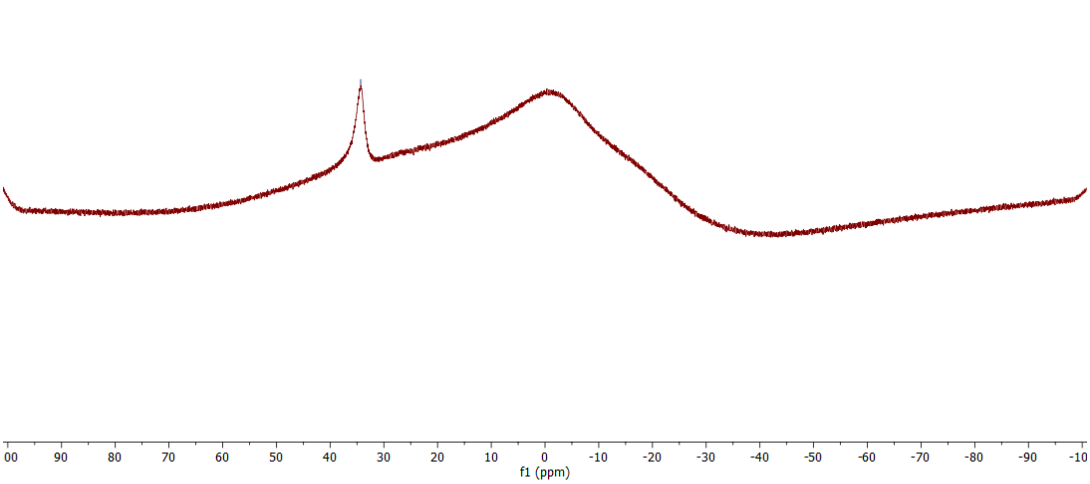


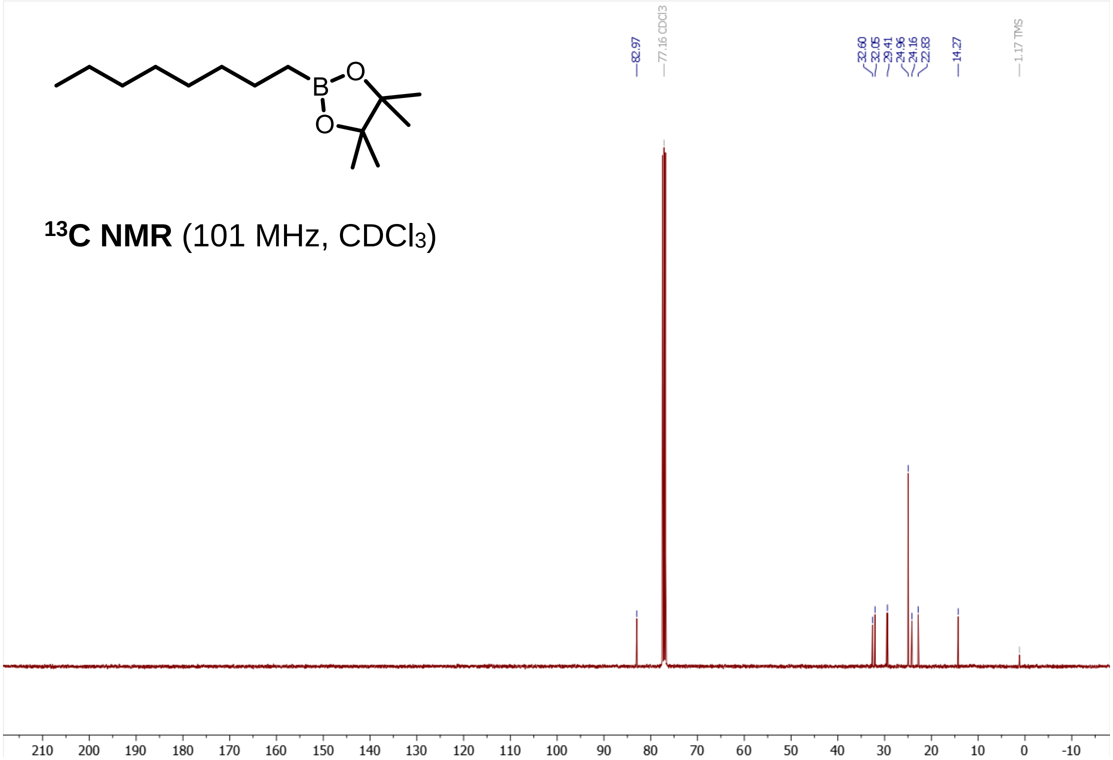
^{1}H NMR (400 MHz, $CDCl_3$)



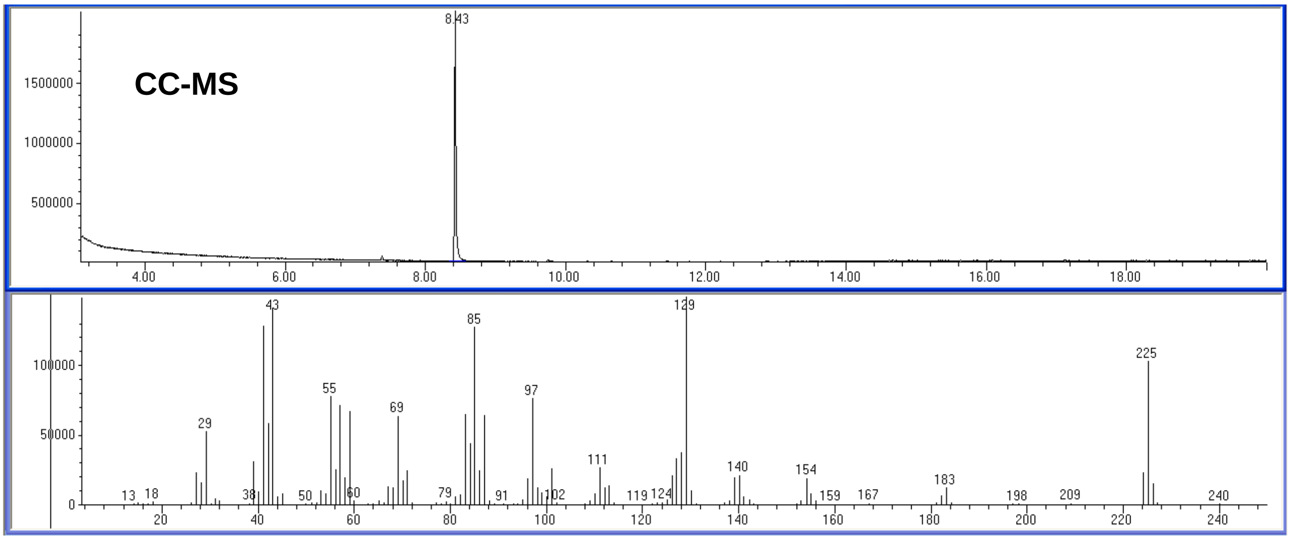


^{11}B NMR (128 MHz, $CDCl_3$)



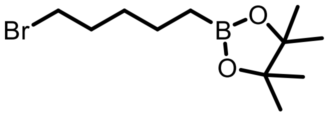


82.97
77.16 CDCl3
32.60
32.05
29.41
24.96
24.16
22.83
14.27
1.17 TMS
13C NMR (101 MHz, CDCl3)

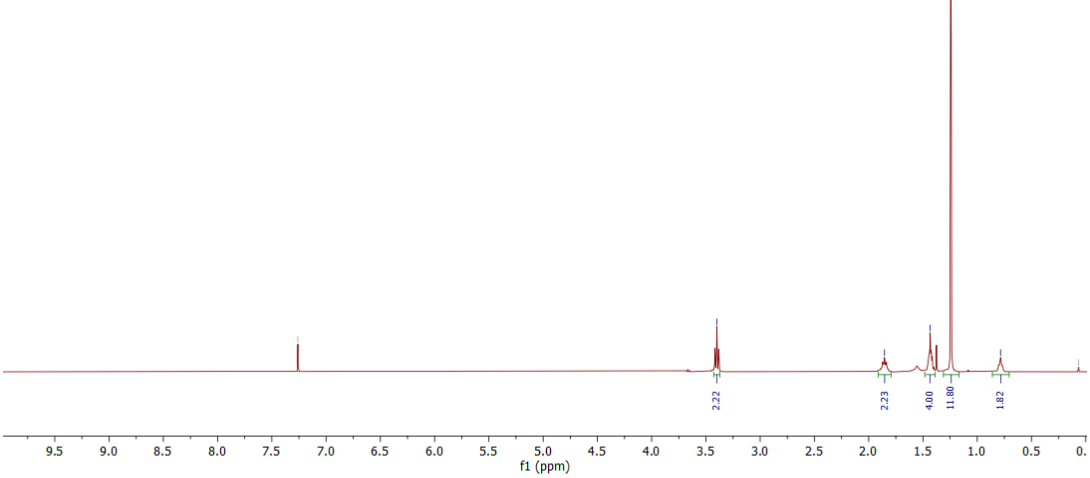


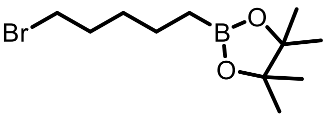
CC-MS
8.43
1500000
1000000
500000
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
43
129
85
225
55
97
69
29
111
140
154
183
13
18
38
50
60
79
91
102
119
124
159
167
198
209
240

2-(5-bromopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b)

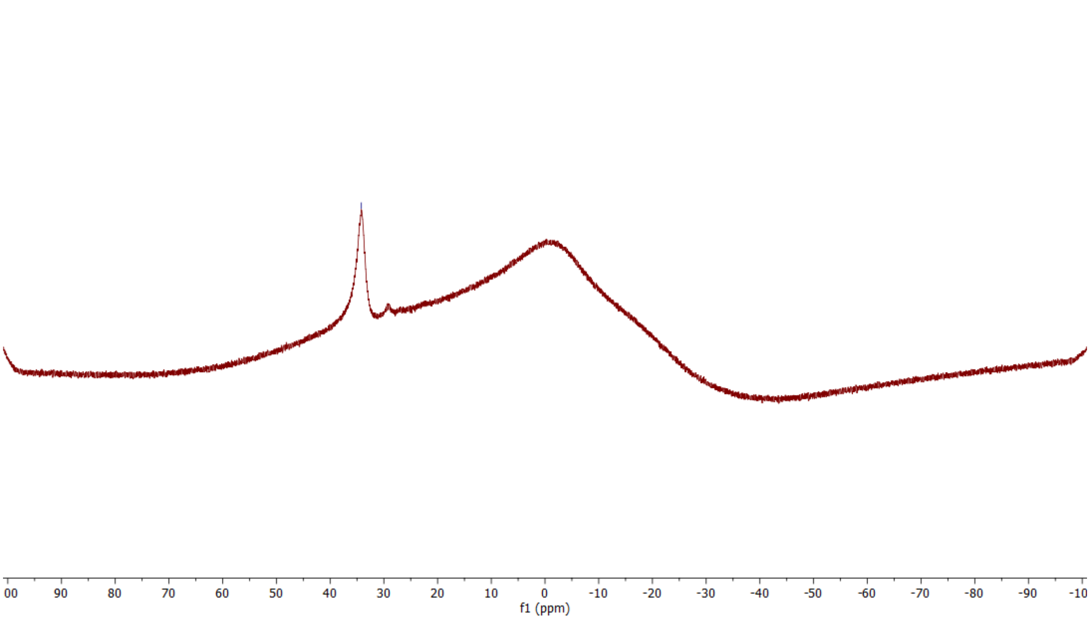


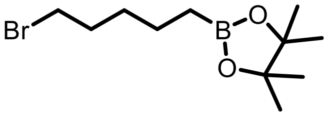
^{1}**H NMR** (400 MHz, $CDCl_3$)



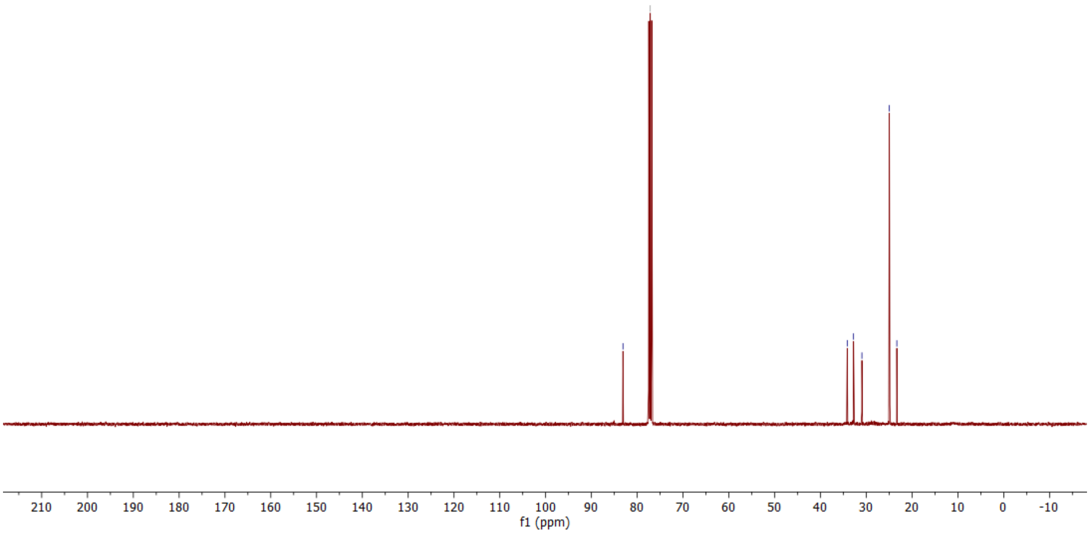


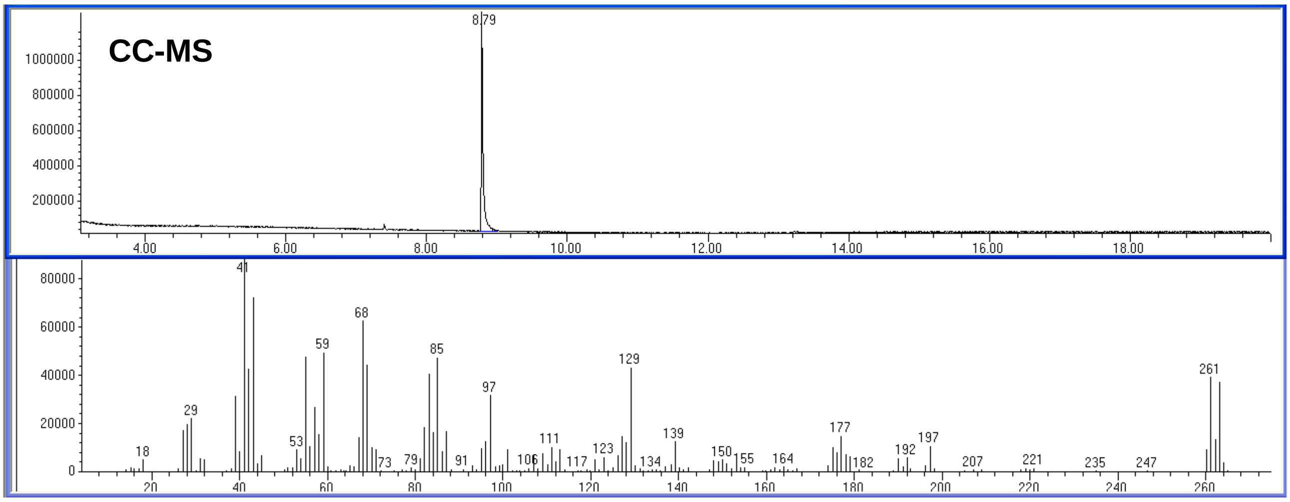
^{11}**B NMR** (128 MHz, $CDCl_3$)



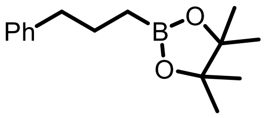


[13]C NMR (101 MHz, CDCl3)

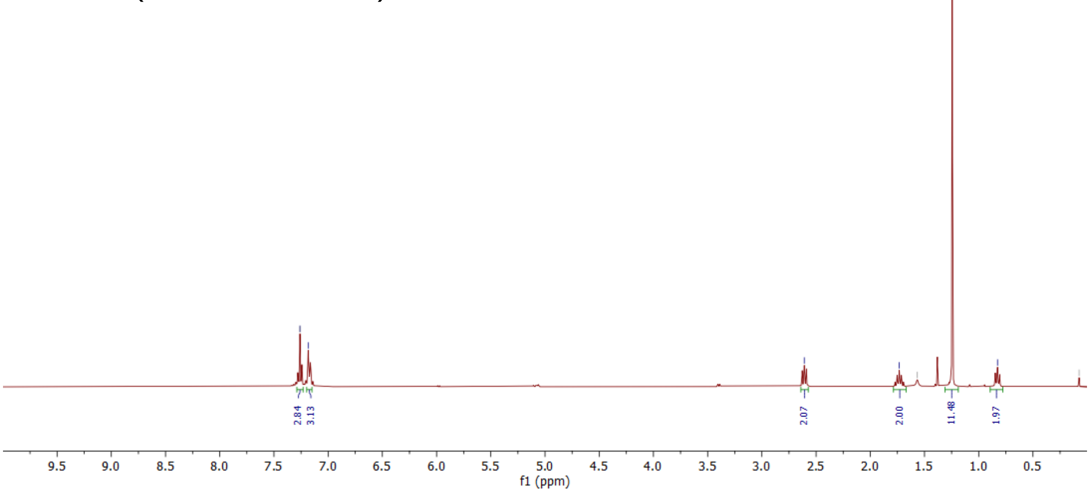


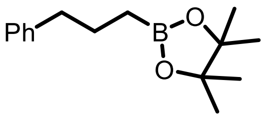


4,4,5,5-tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (2c)

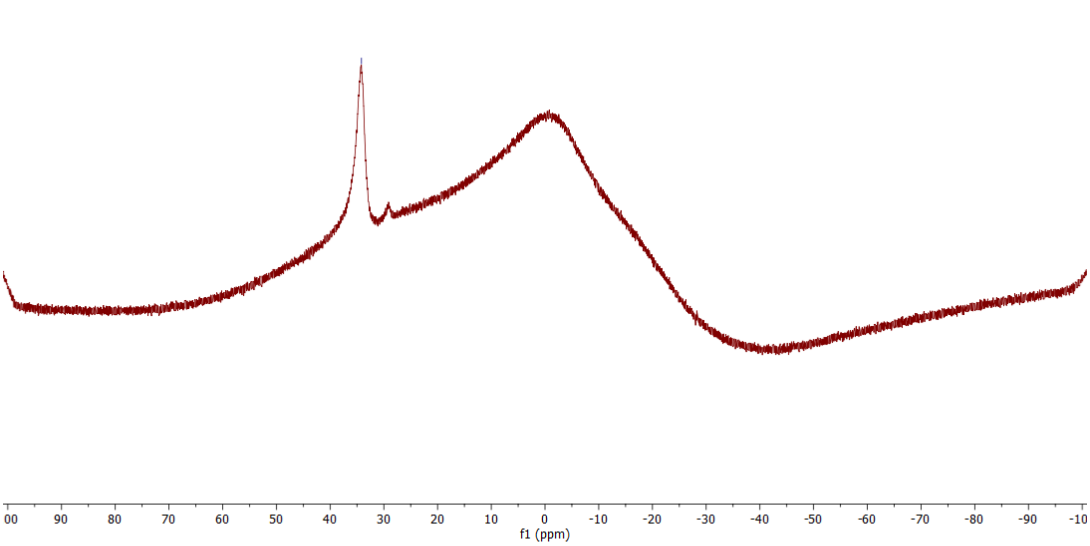


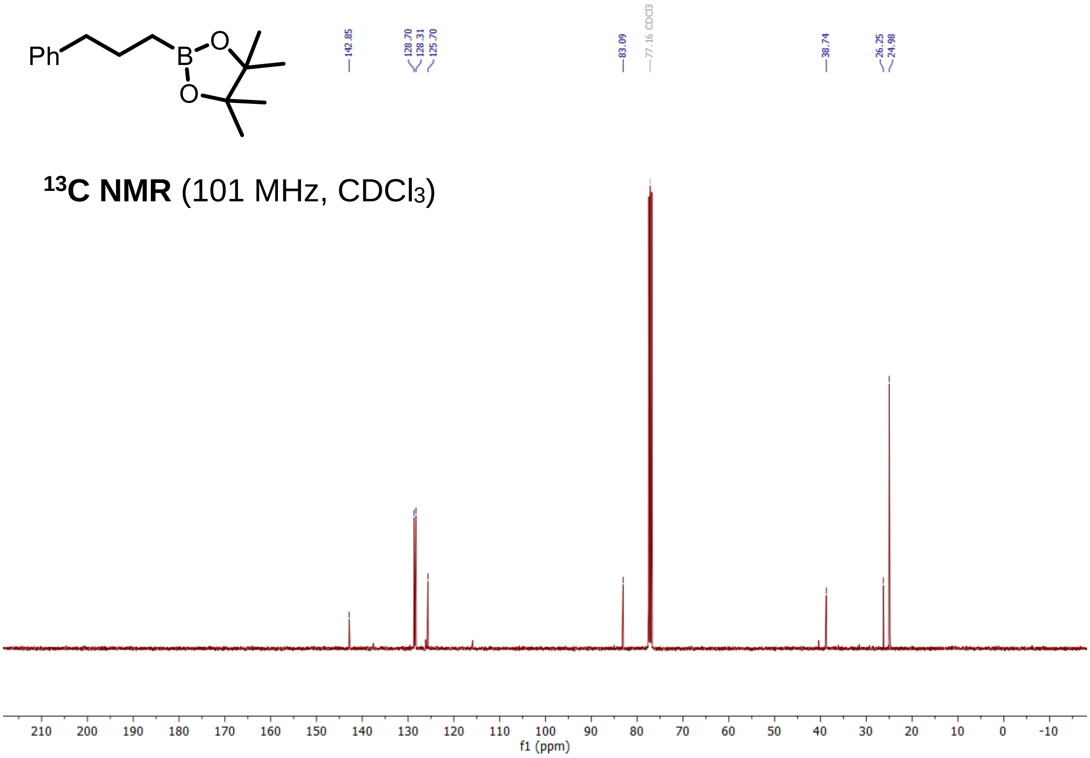
^{1}H NMR (400 MHz, $CDCl_3$)

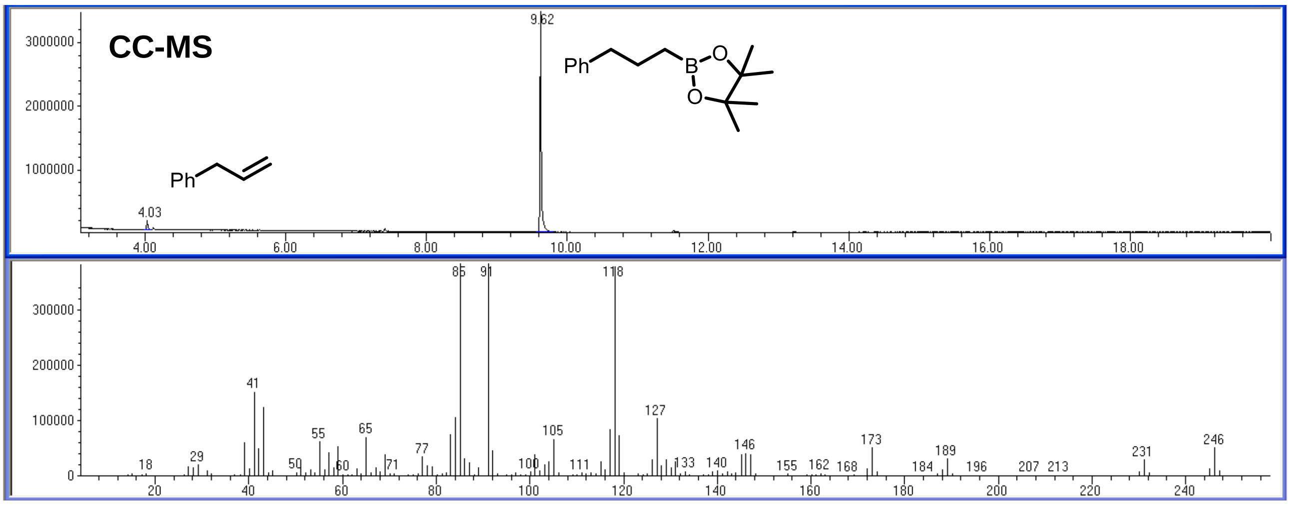




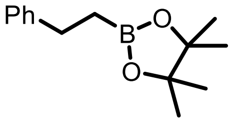
^{11}B NMR (128 MHz, $CDCl_3$)



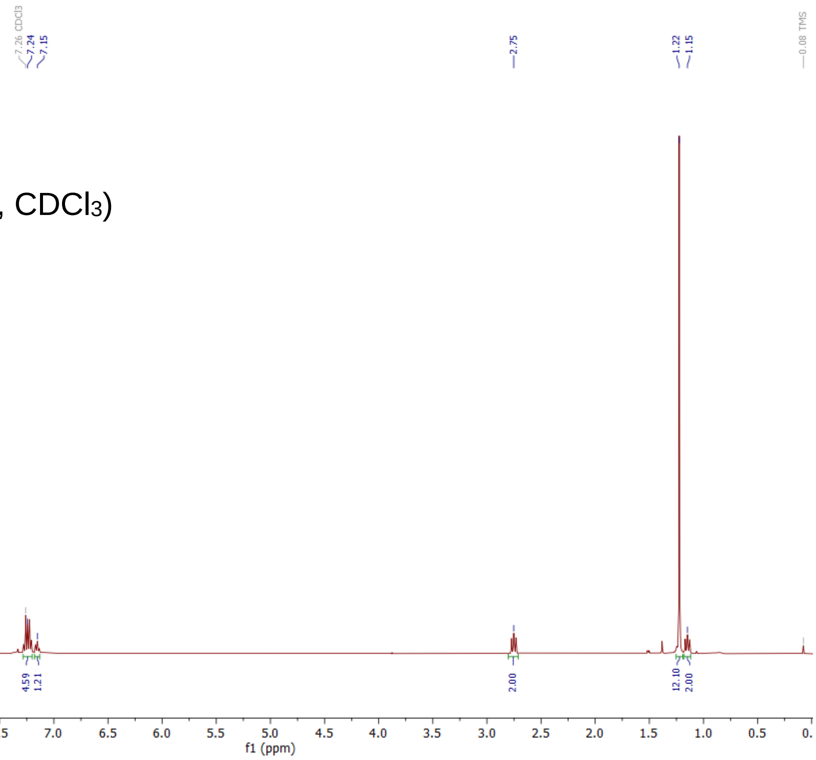

Ph
B
O
O
13C NMR (101 MHz, CDCl3)
142.85
128.70
128.31
125.70
83.09
77.16 CDCl3
38.74
26.25
24.98
f1 (ppm)

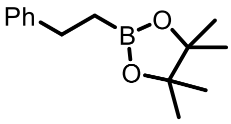

CC-MS
9.62
4.03
Ph
B
O
O
85
91
118
41
127
105
55
65
77
173
246
231
189
146

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

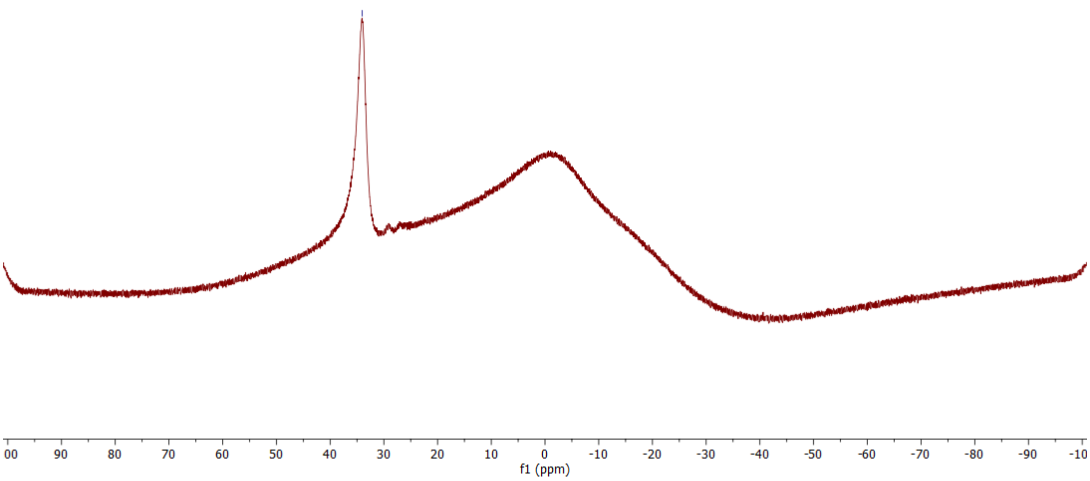


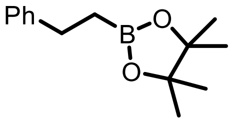
^{1}H NMR (400 MHz, $CDCl_3$)

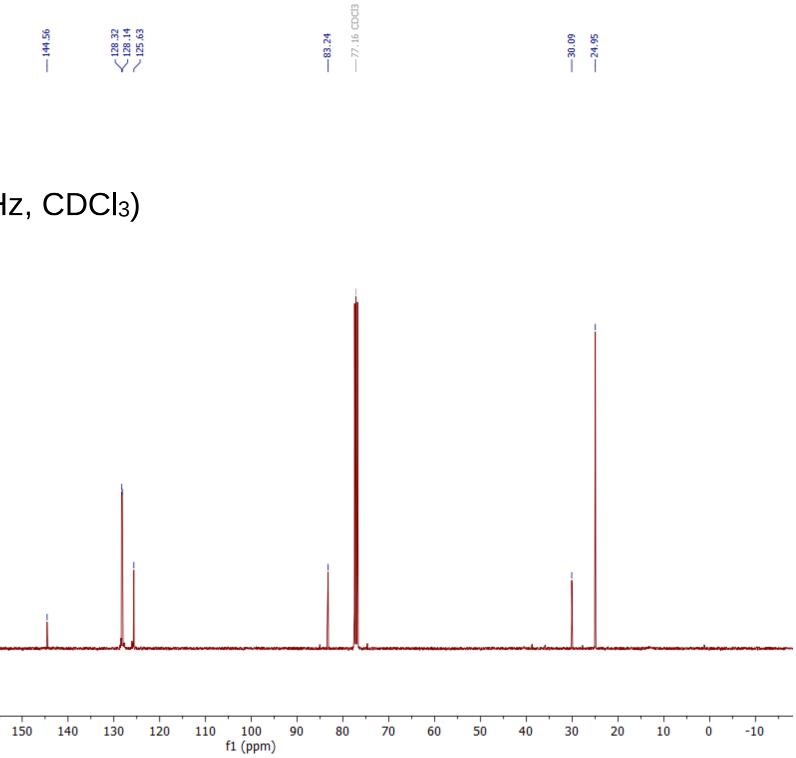




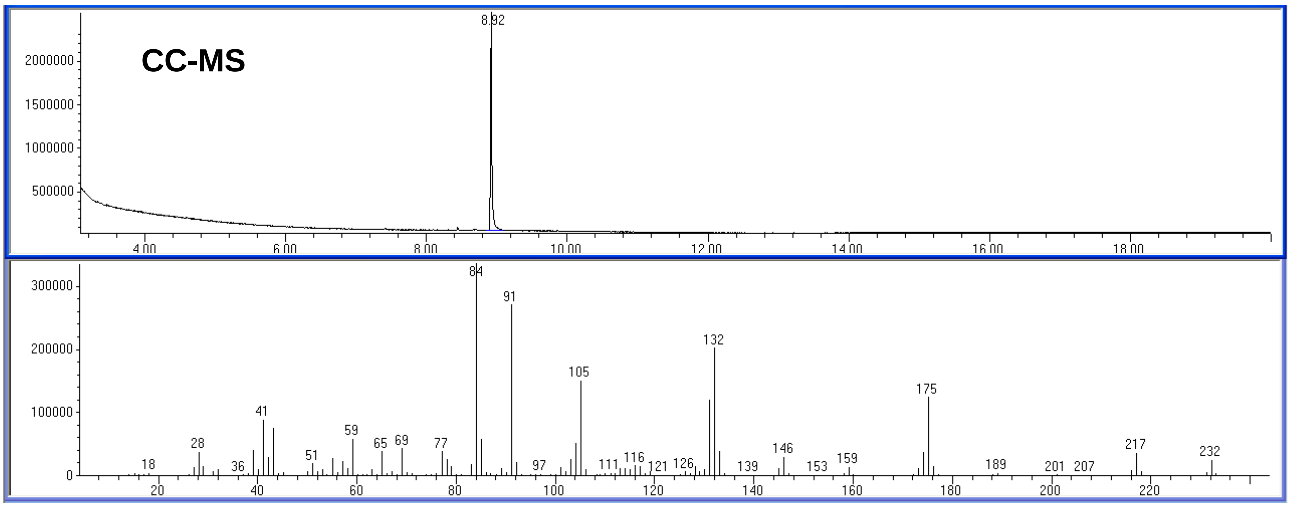
^{11}B NMR (128 MHz, $CDCl_3$)



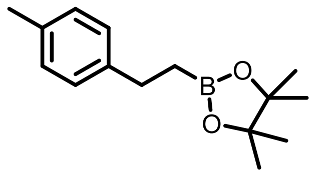




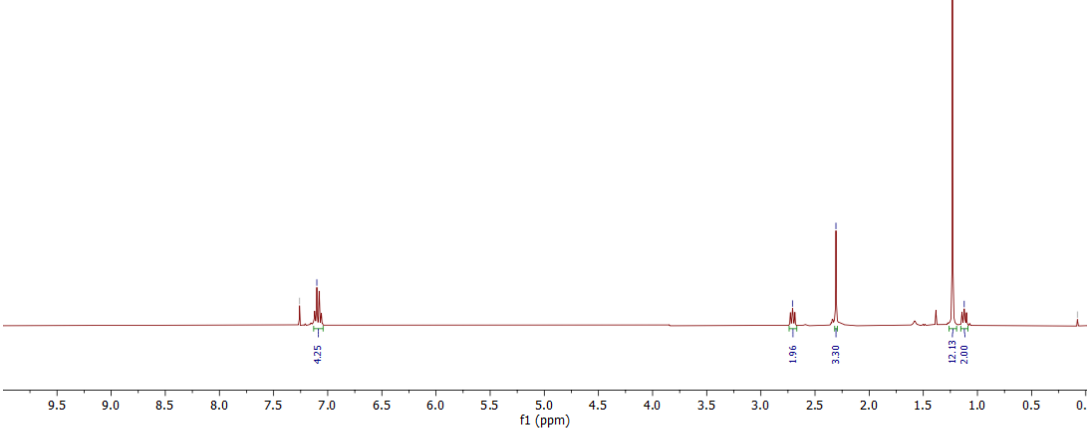
^{13}C NMR (101 MHz, $CDCl_3$)

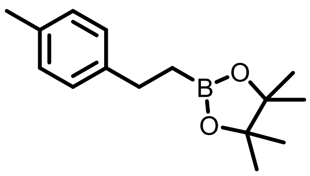


4,4,5,5-tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane (2e)

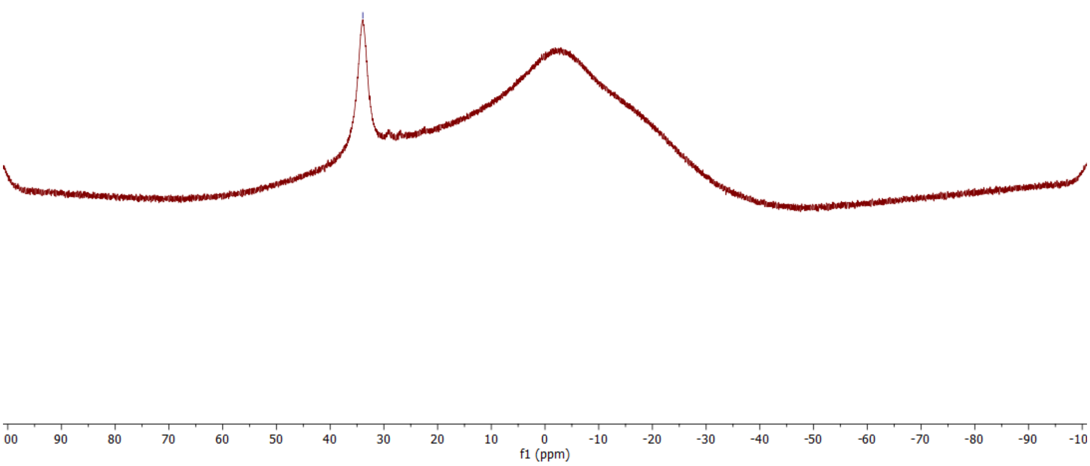


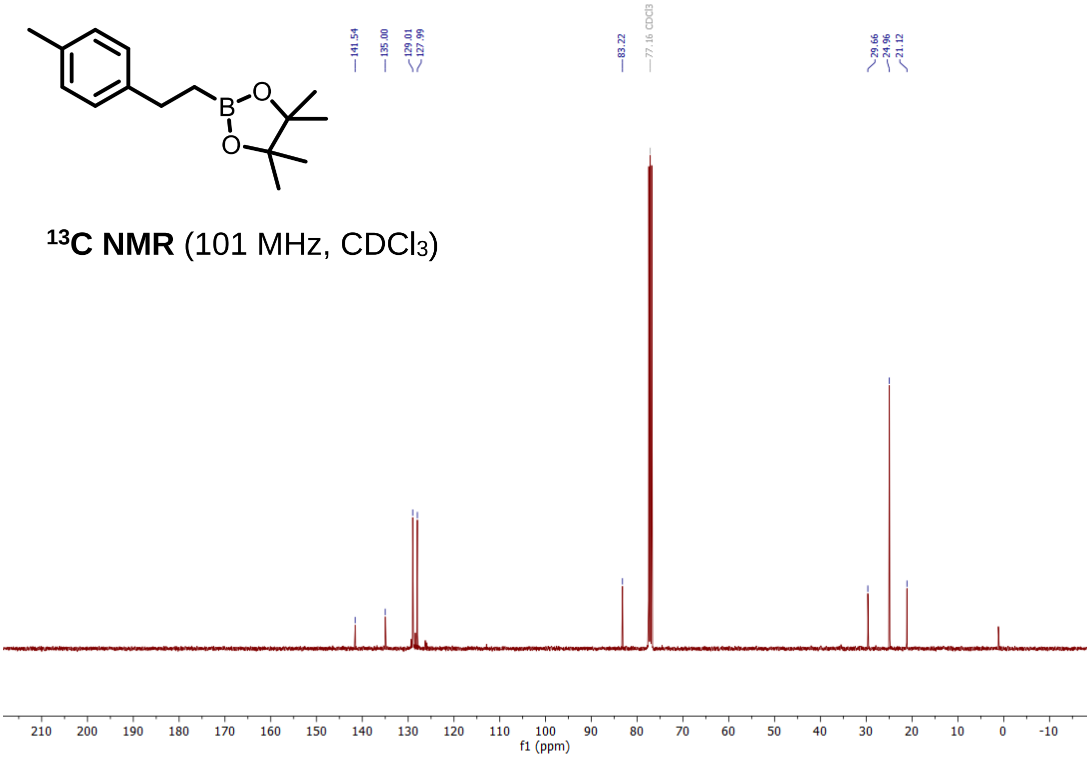
^{1}H NMR (400 MHz, $CDCl_3$)



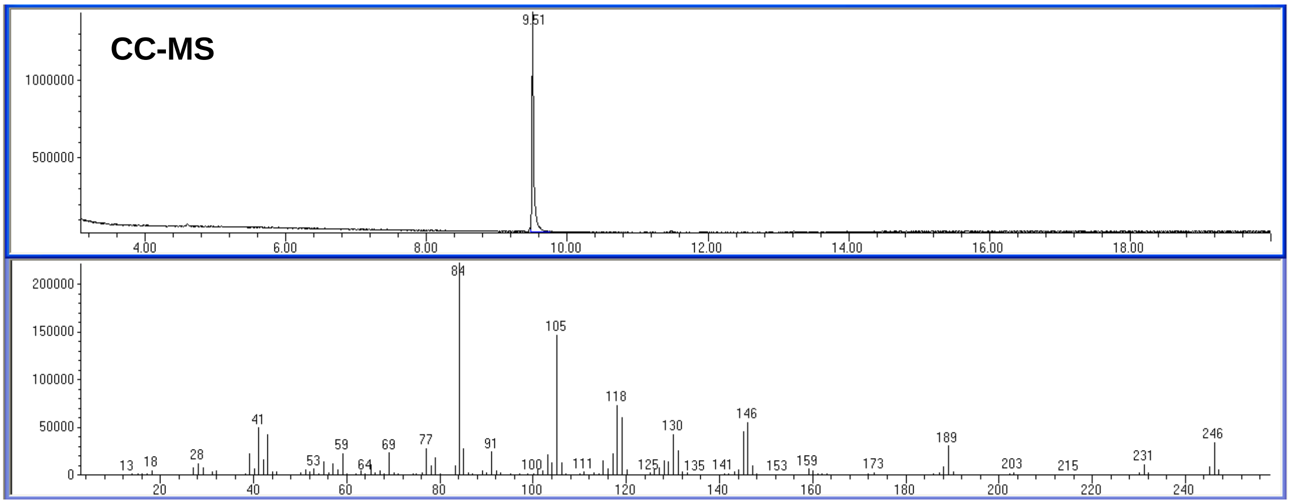


^{11}B NMR (128 MHz, $CDCl_3$)

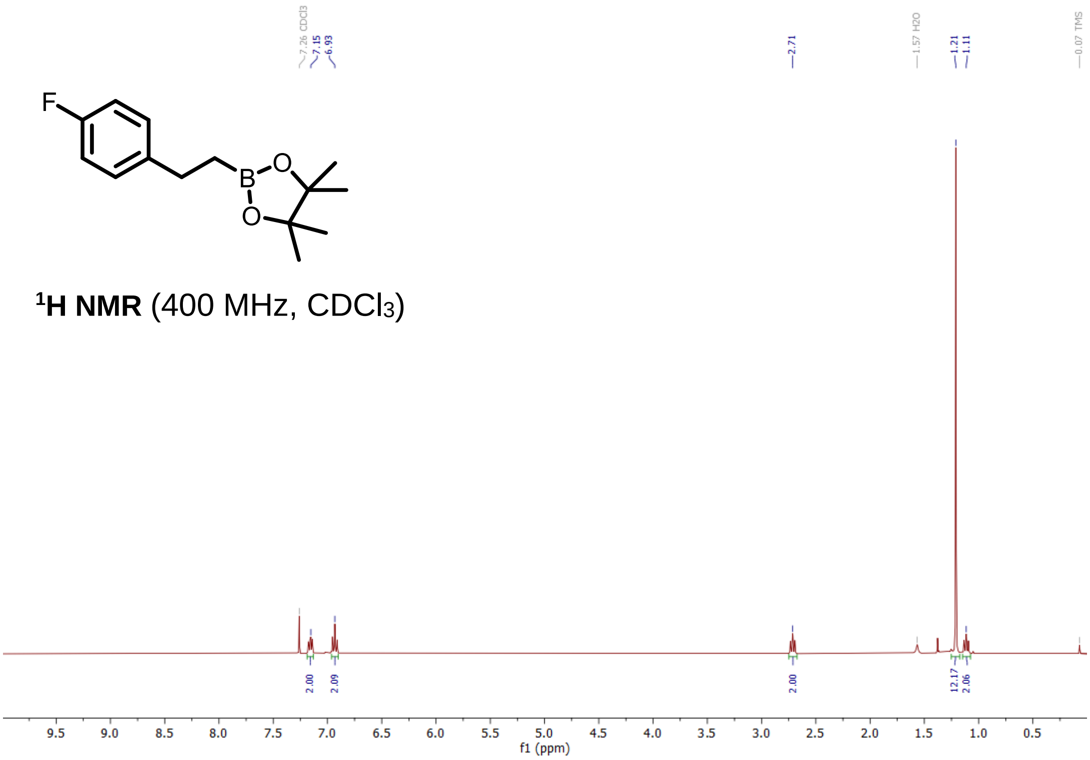




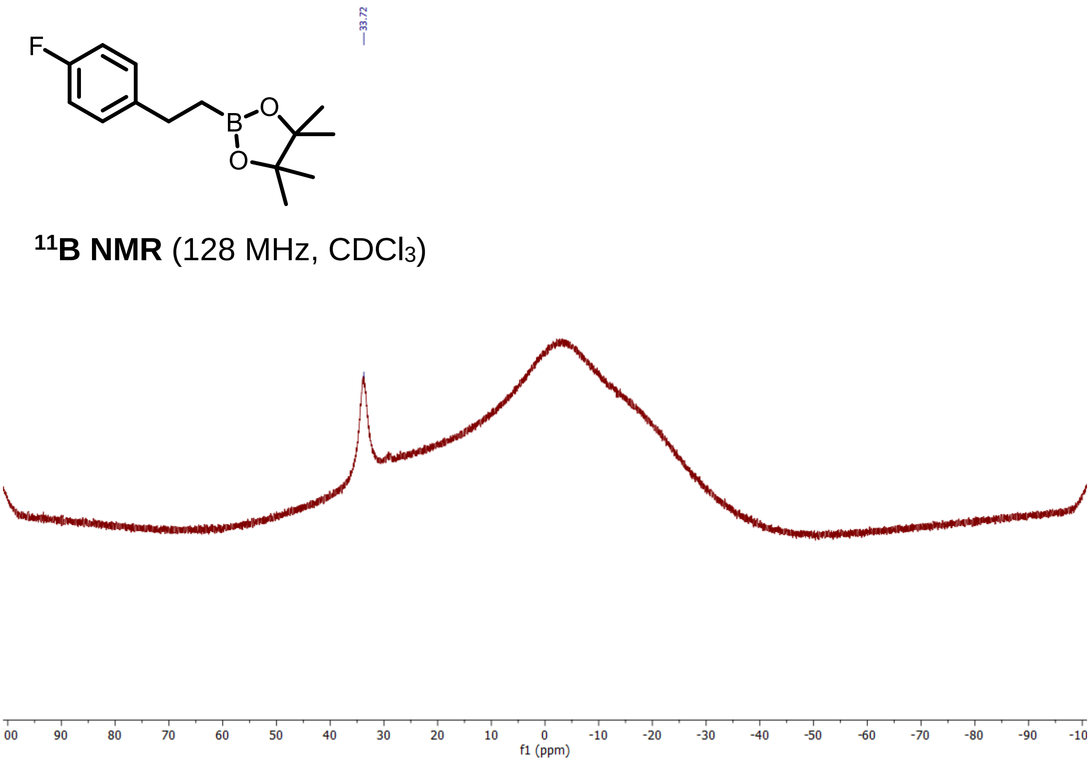
^{13}C NMR (101 MHz, $CDCl_3$)



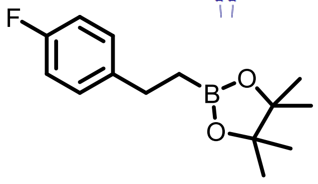
4,4,5,5-tetramethyl-2-(4-fluorophenethyl)-1,3,2-dioxaborolane (2f)



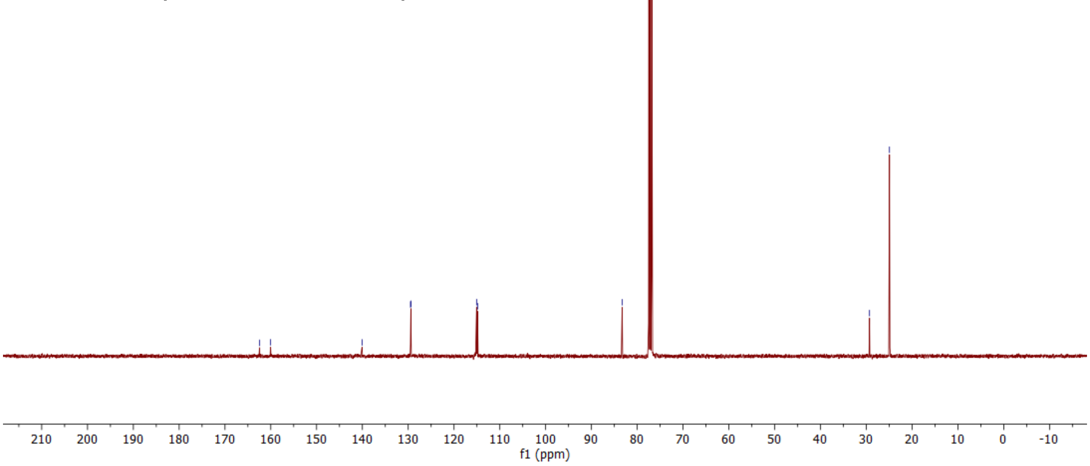
^{1}H NMR (400 MHz, $CDCl_3$)

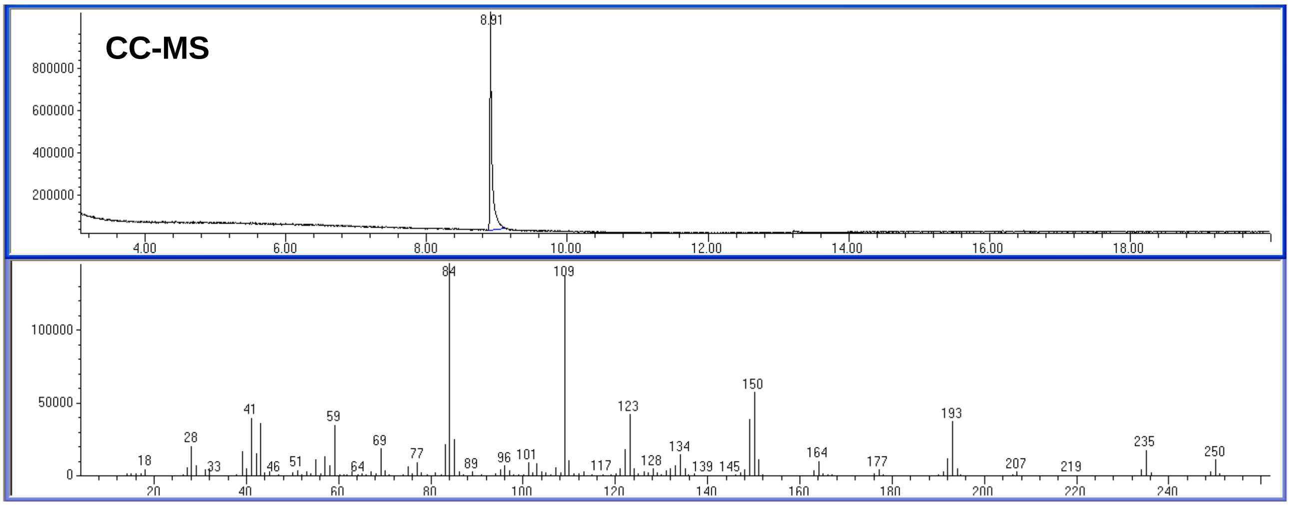


^{11}B NMR (128 MHz, $CDCl_3$)

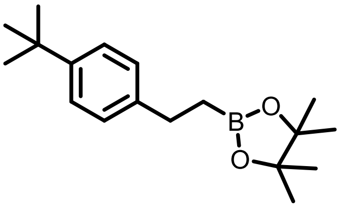


^{13}**C NMR** (101 MHz, $CDCl_3$)

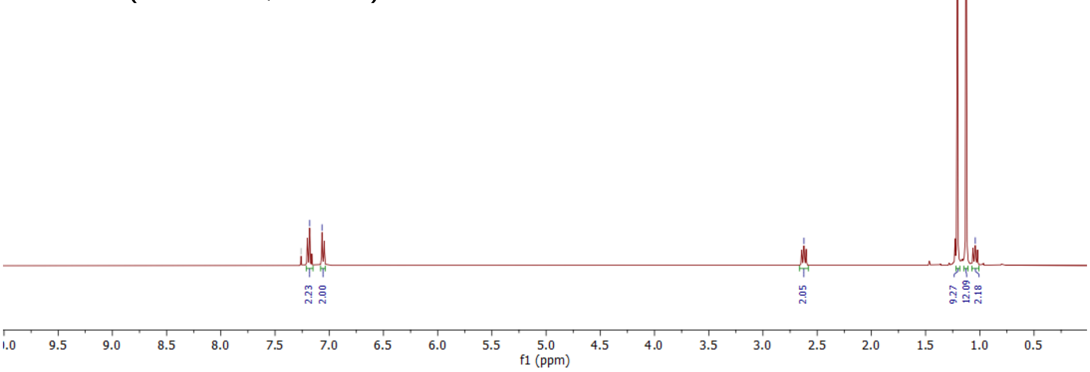


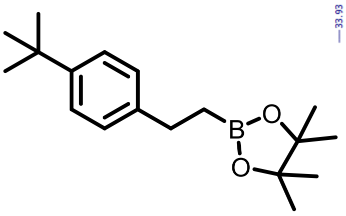


2-(4-(tert-butyl)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2g)

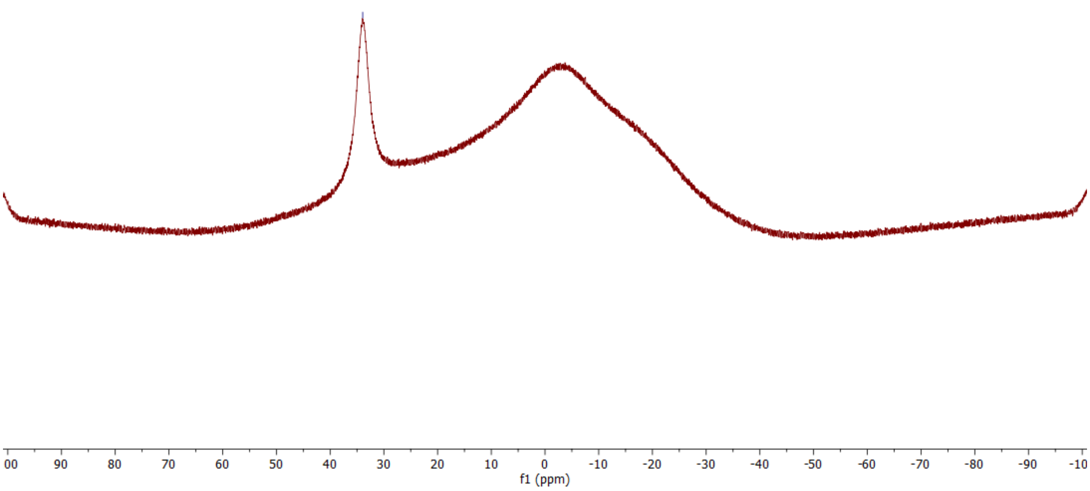


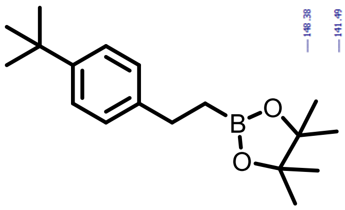
^{1}H NMR (400 MHz, $CDCl_3$)



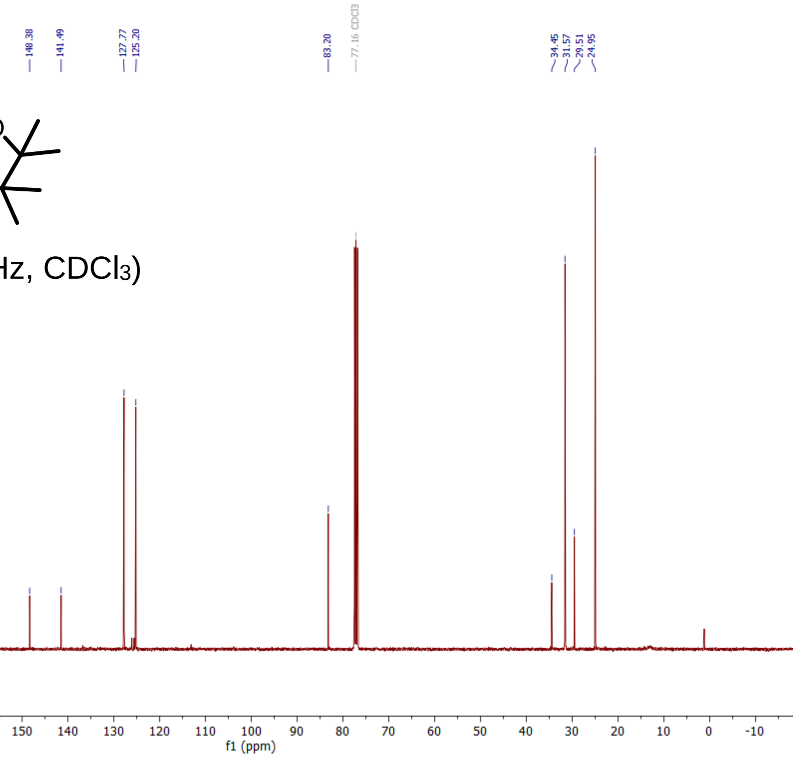


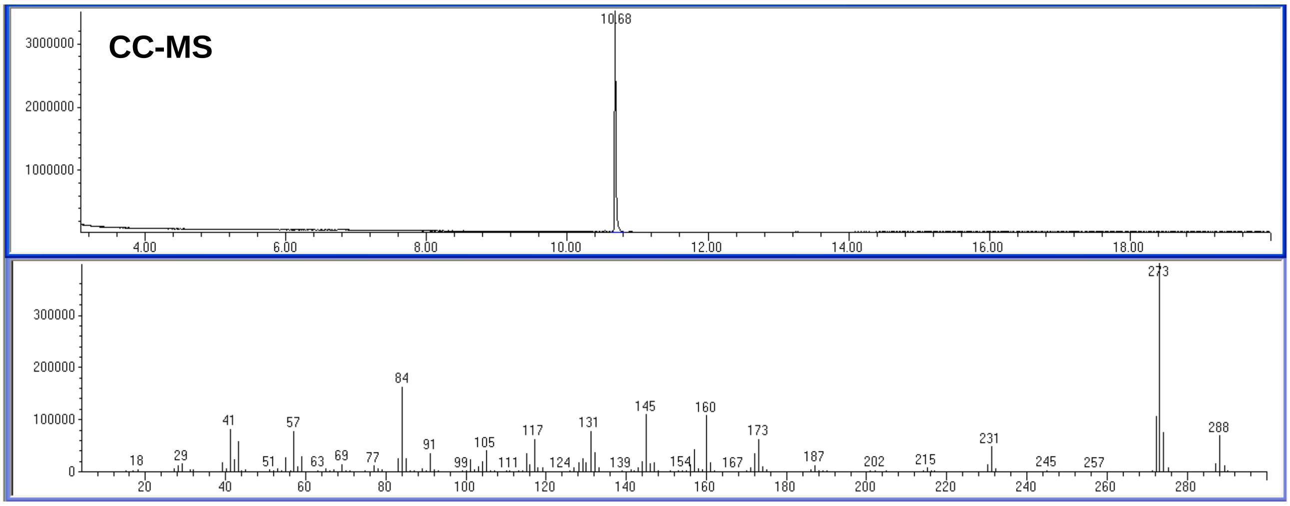
^{11}B NMR (128 MHz,



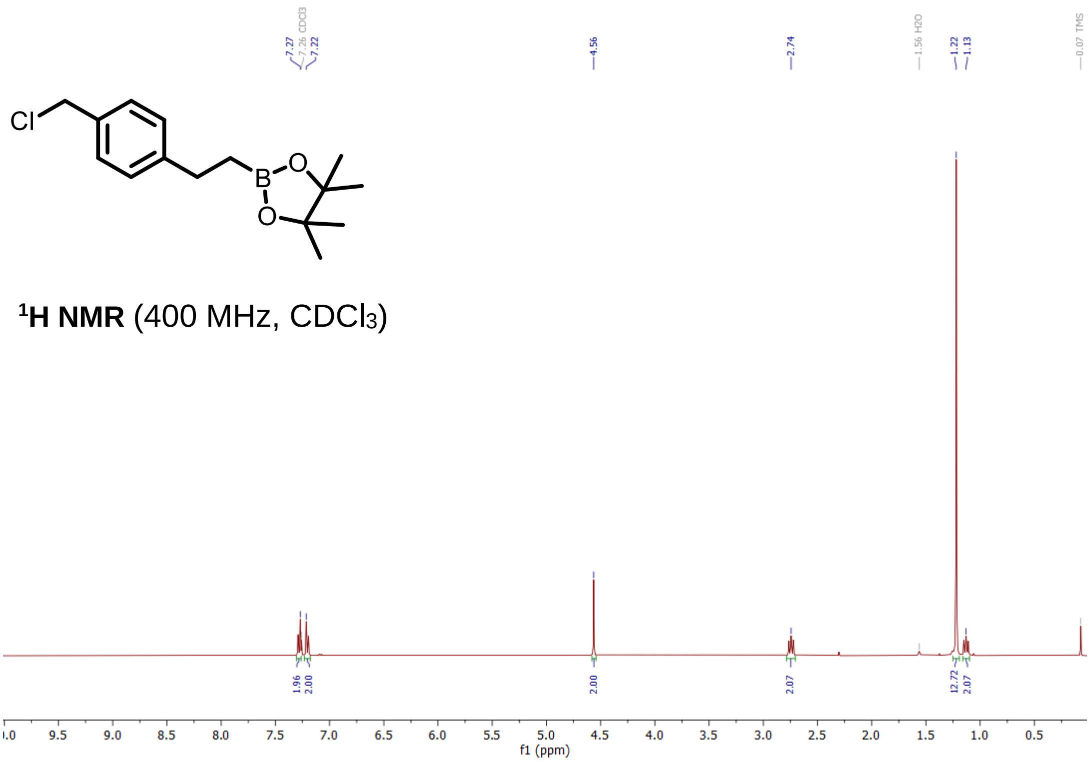


^{13}C NMR (101 MHz, $CDCl_3$)

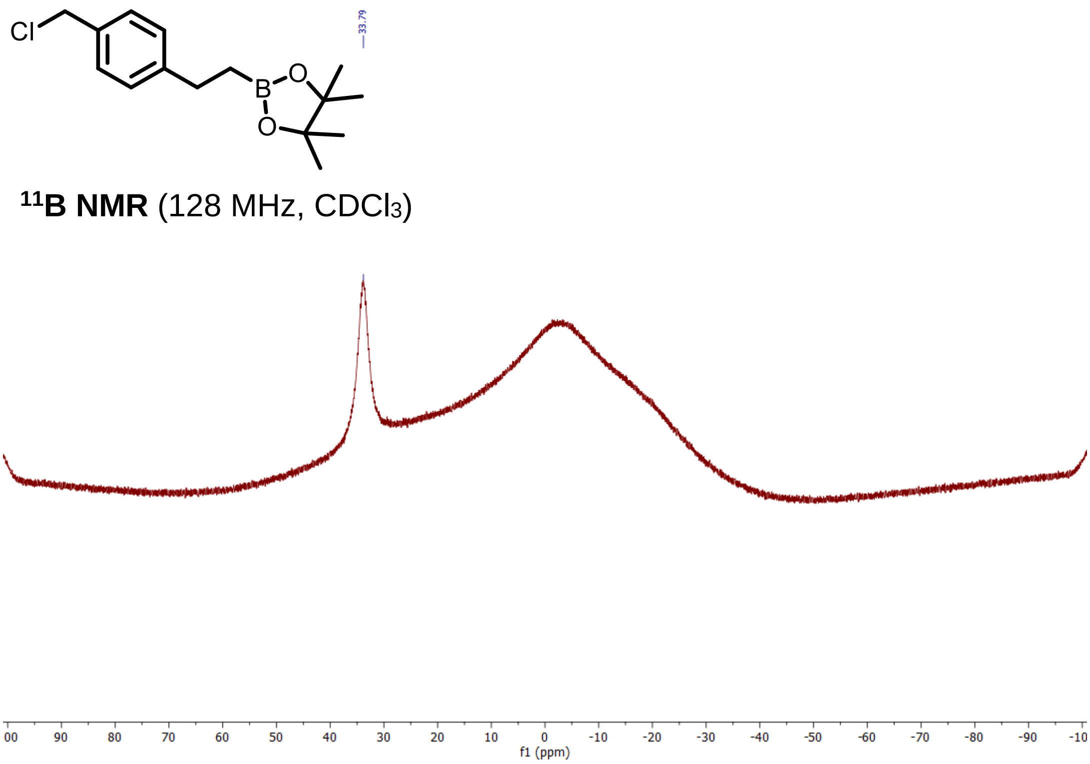




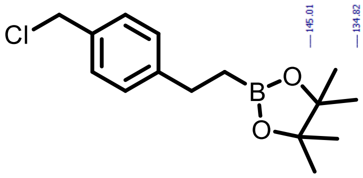
2-(4-(chloromethyl)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2h)



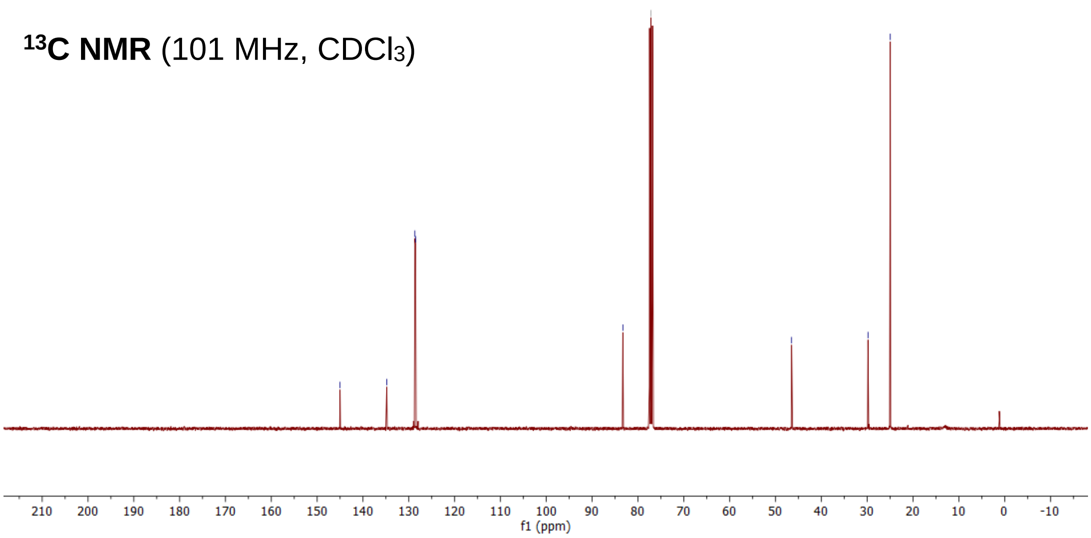
^{1}H NMR (400 MHz, $CDCl_3$)

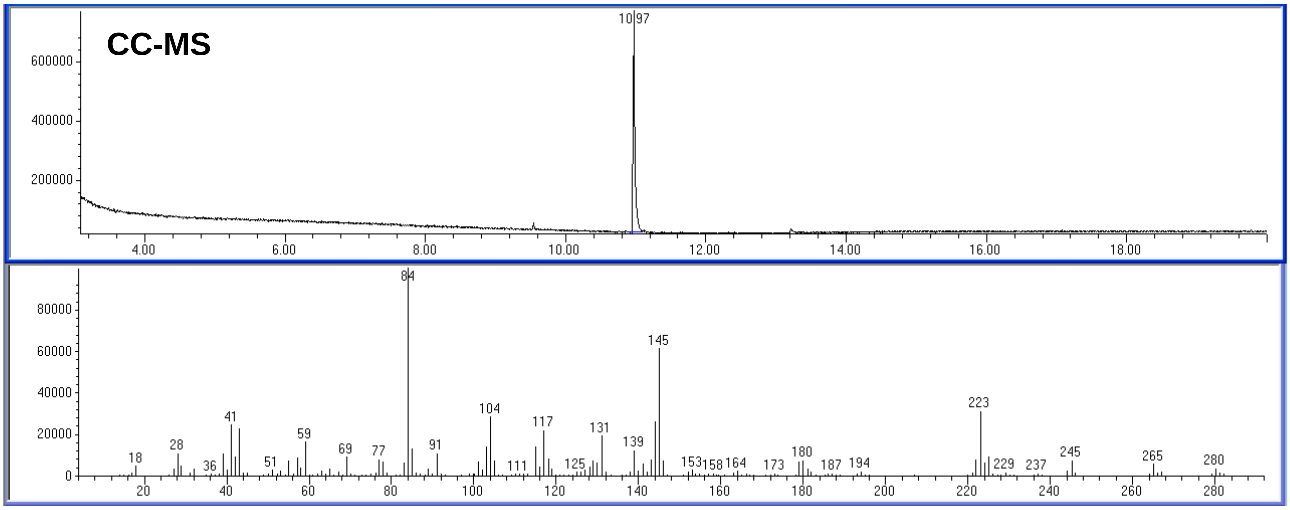


^{11}B NMR (128 MHz, $CDCl_3$)

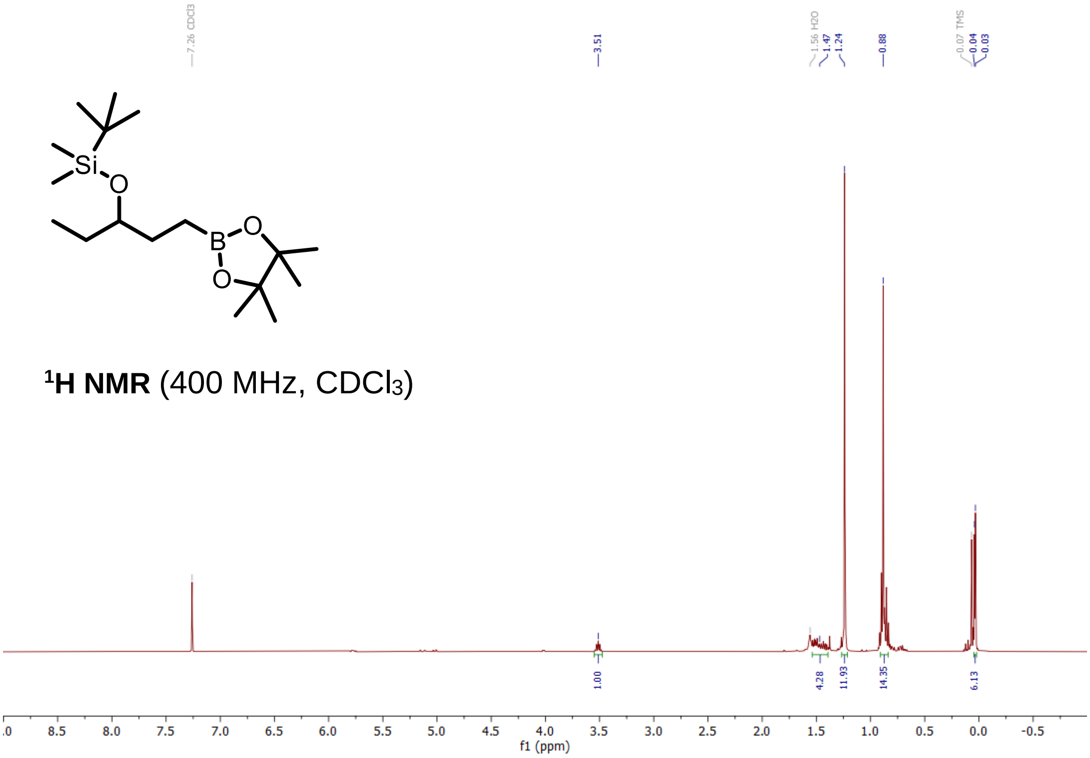


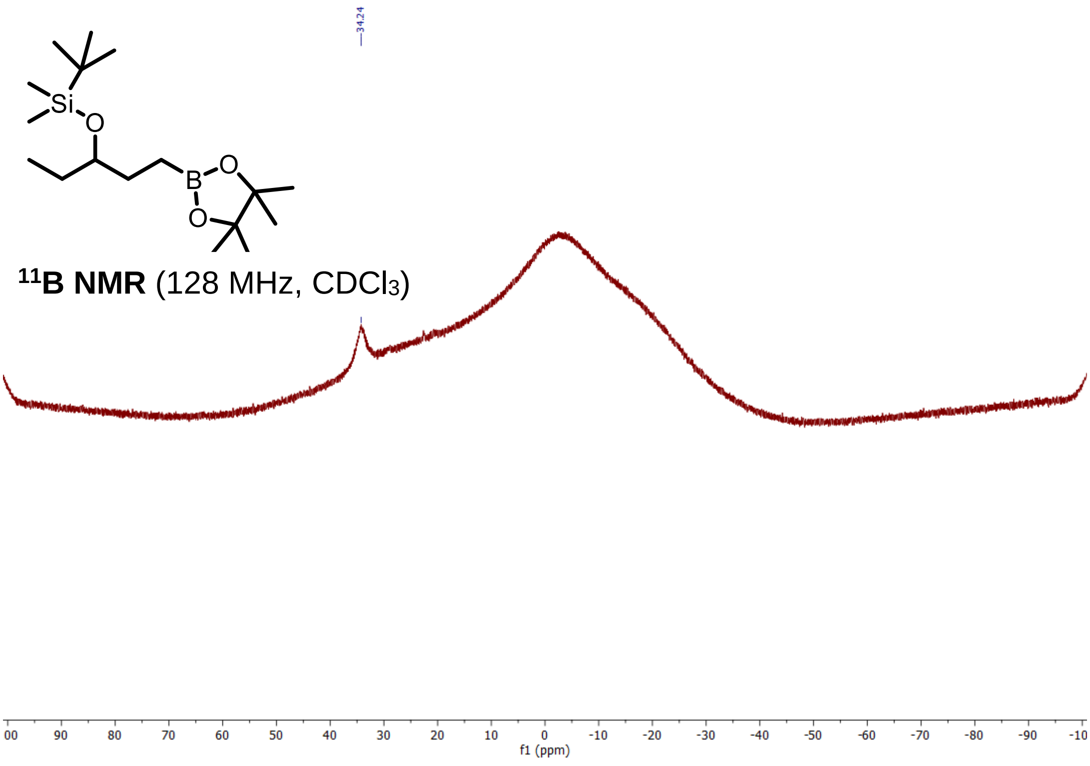
13C NMR (101 MHz, $CDCl_3$)

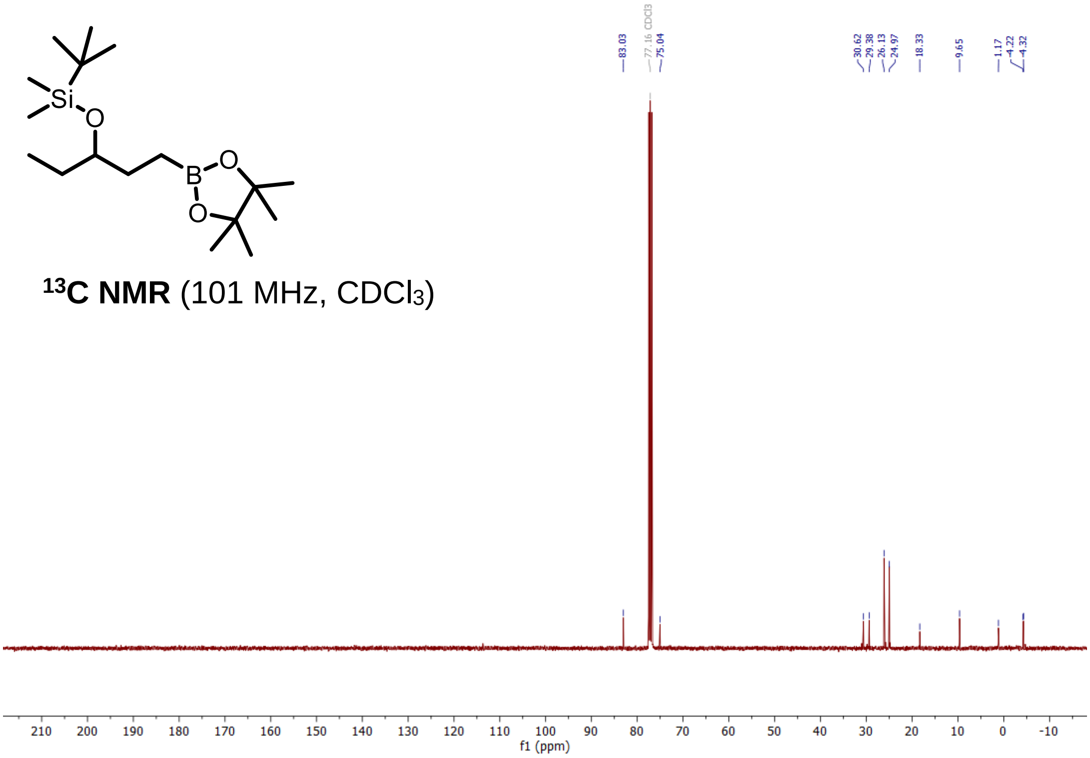




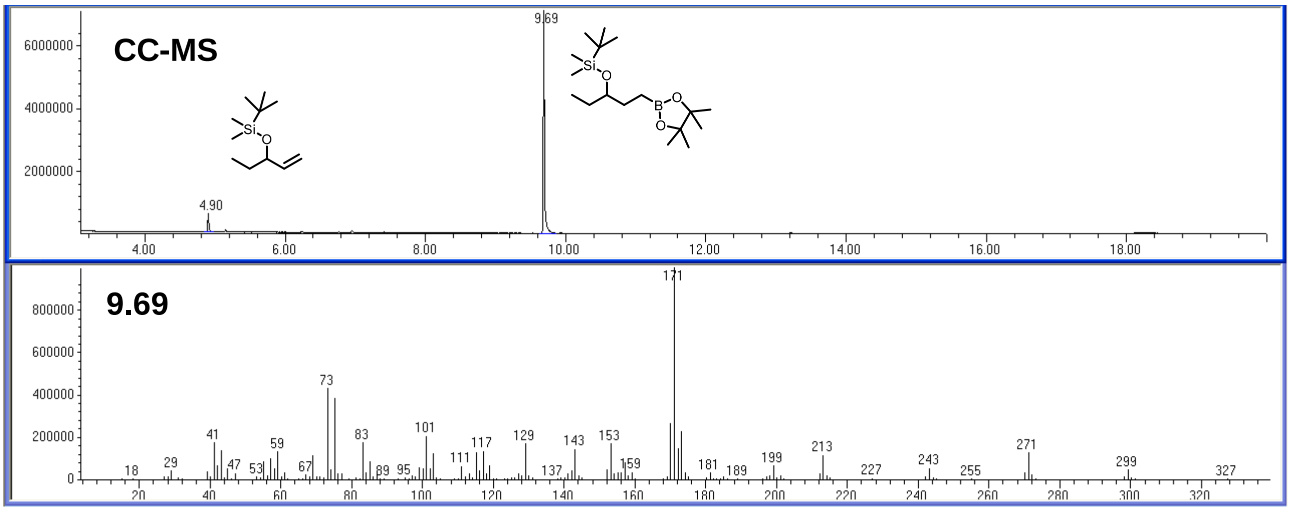
tert-butyldimethyl((1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-3-yl)oxy)silane (2i)



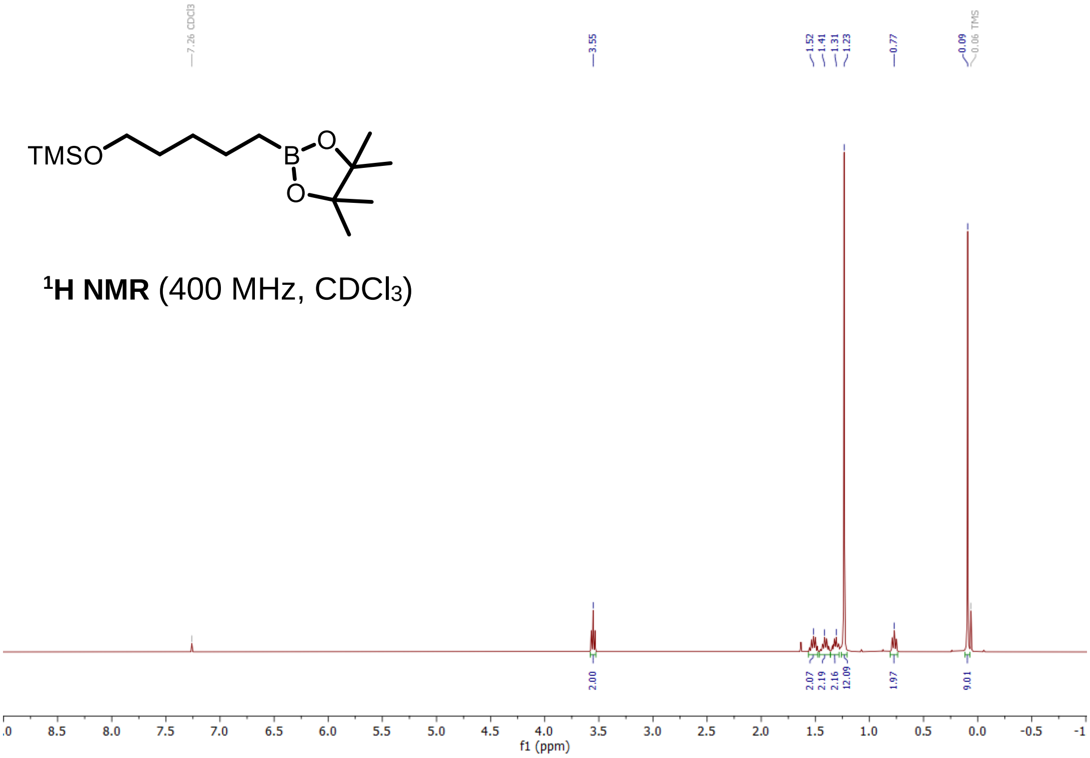


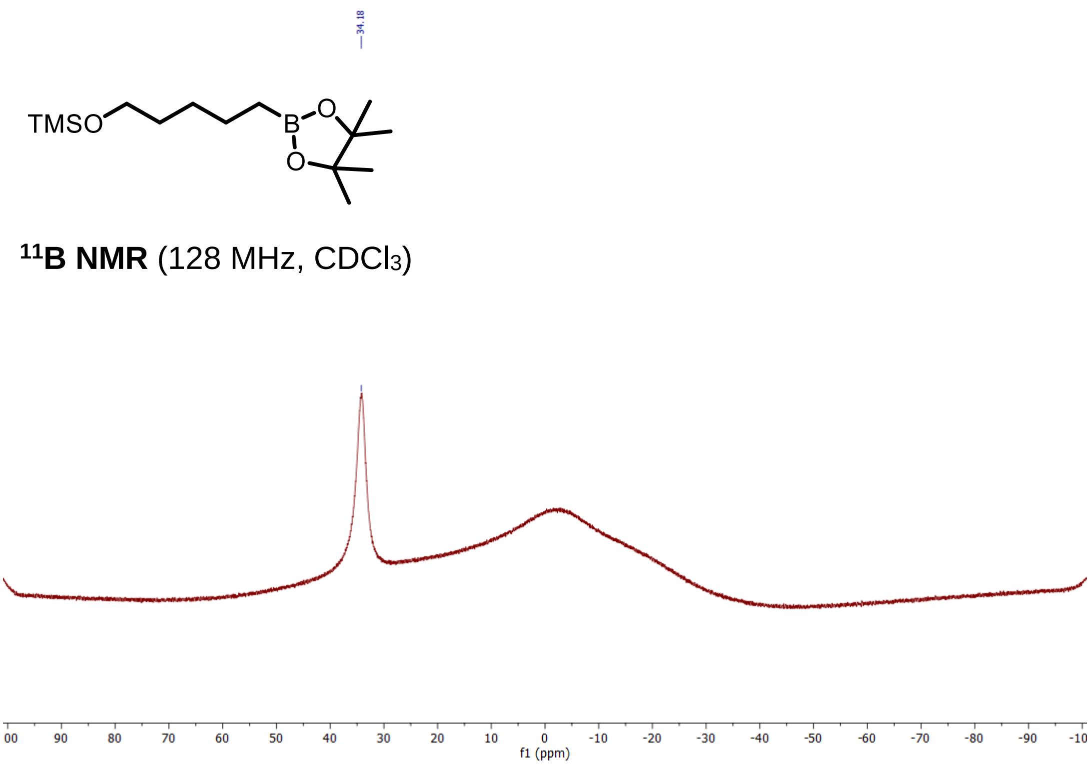


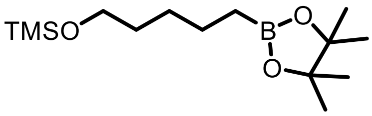
^{13}C NMR (101 MHz, $CDCl_3$)



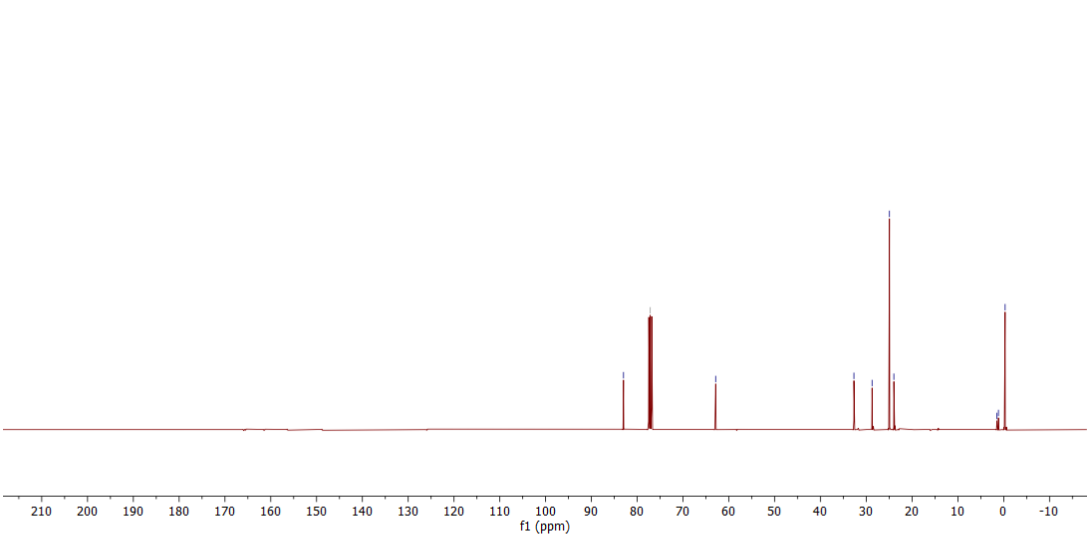
trimethyl((5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)oxy)silane (2j)

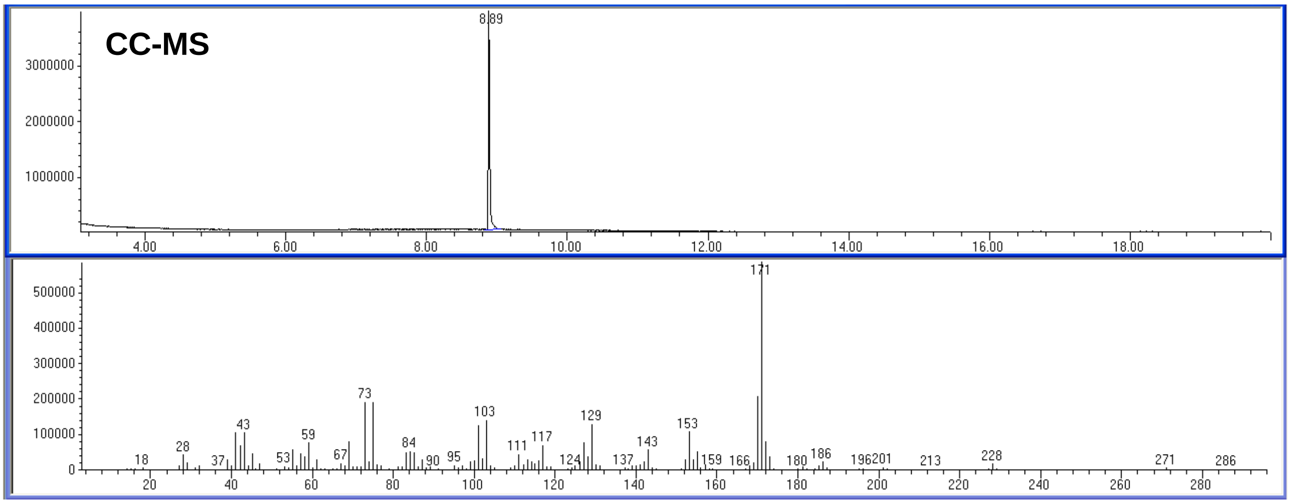




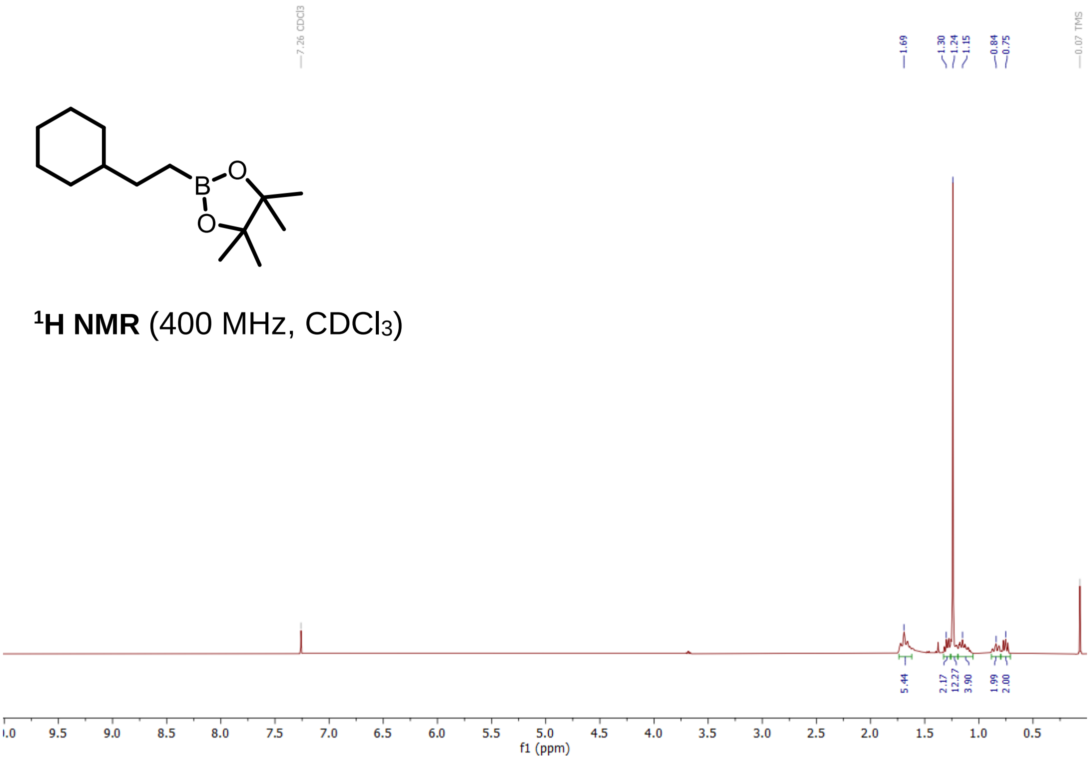


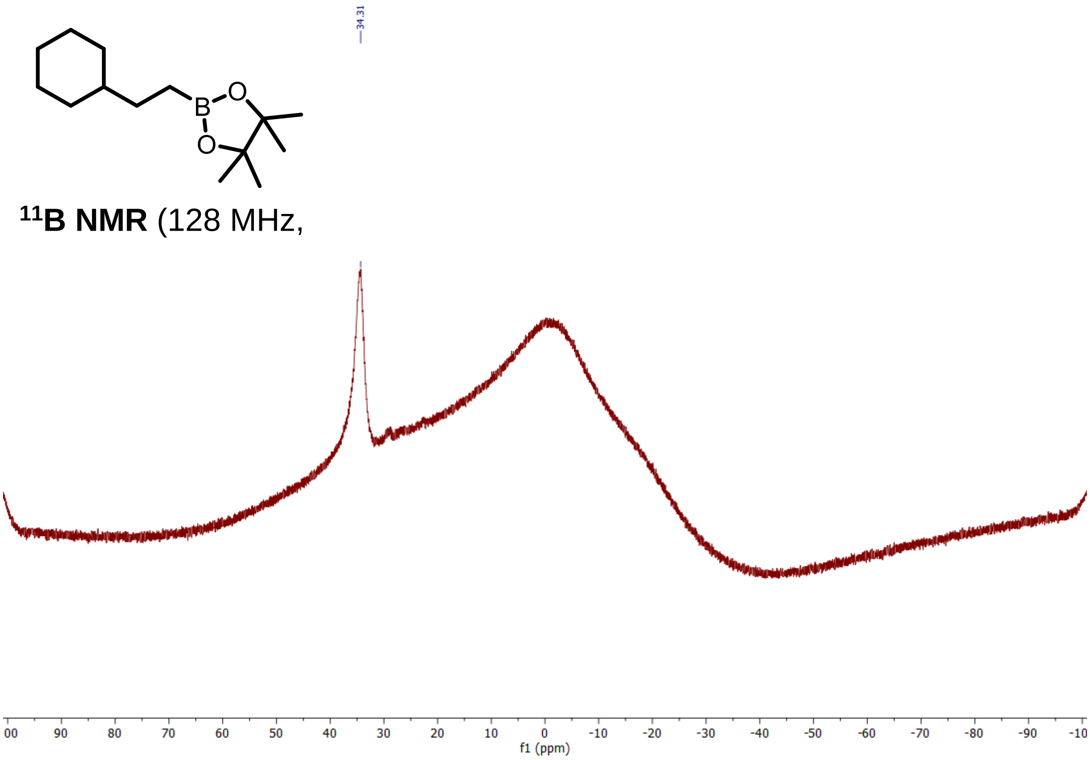
^{13}C NMR (101 MHz,

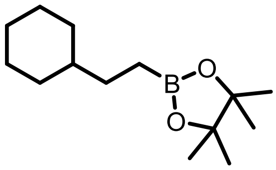




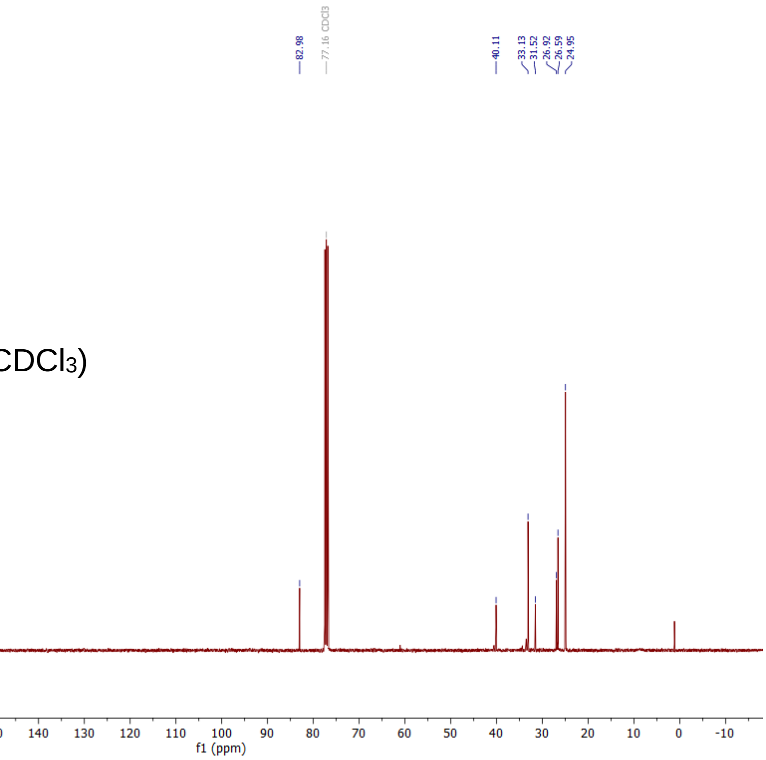
2-(2-cyclohexylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)

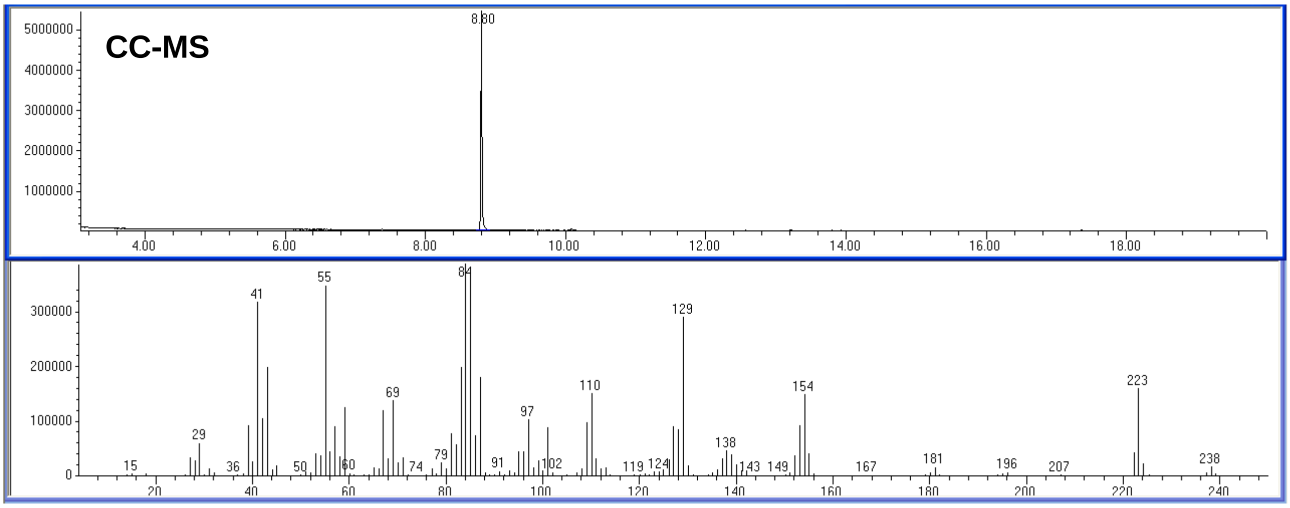




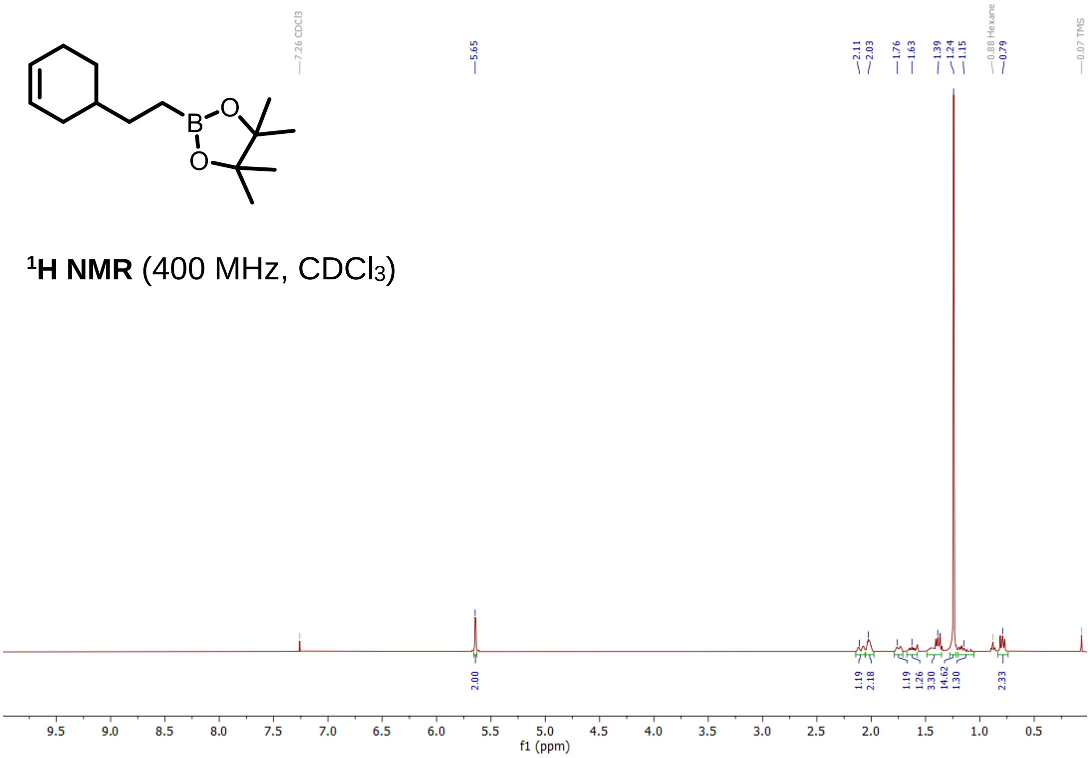


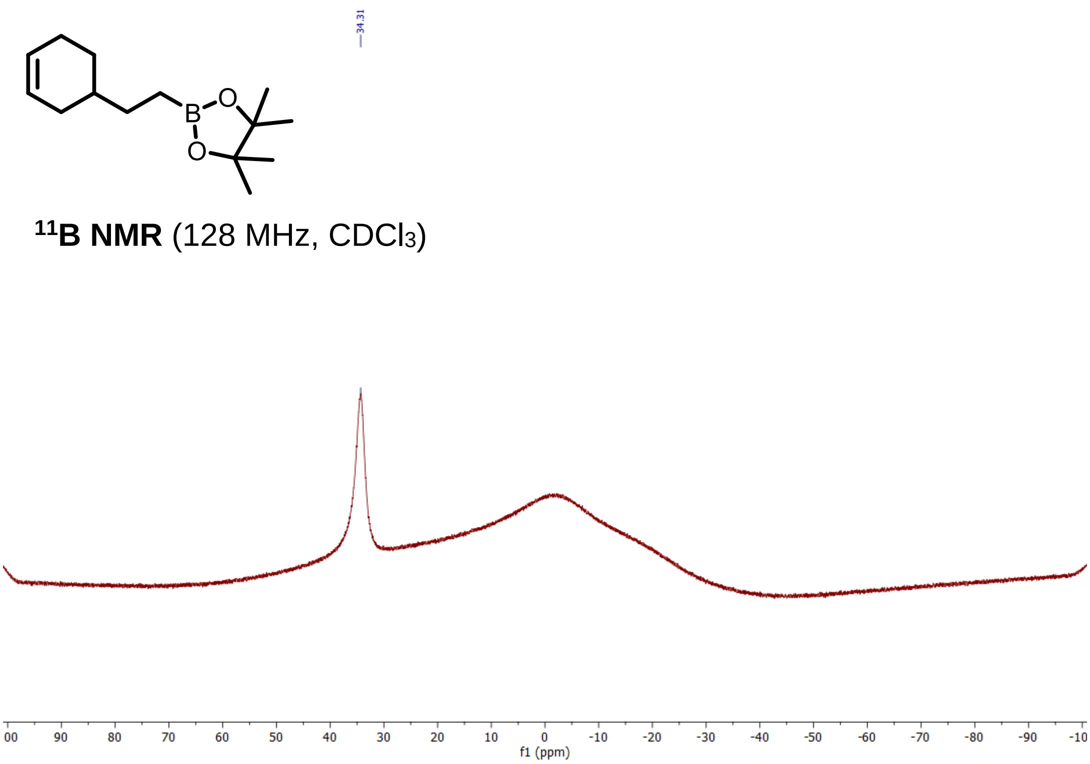
^{13}C NMR (101 MHz, $CDCl_3$)

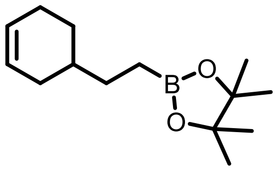




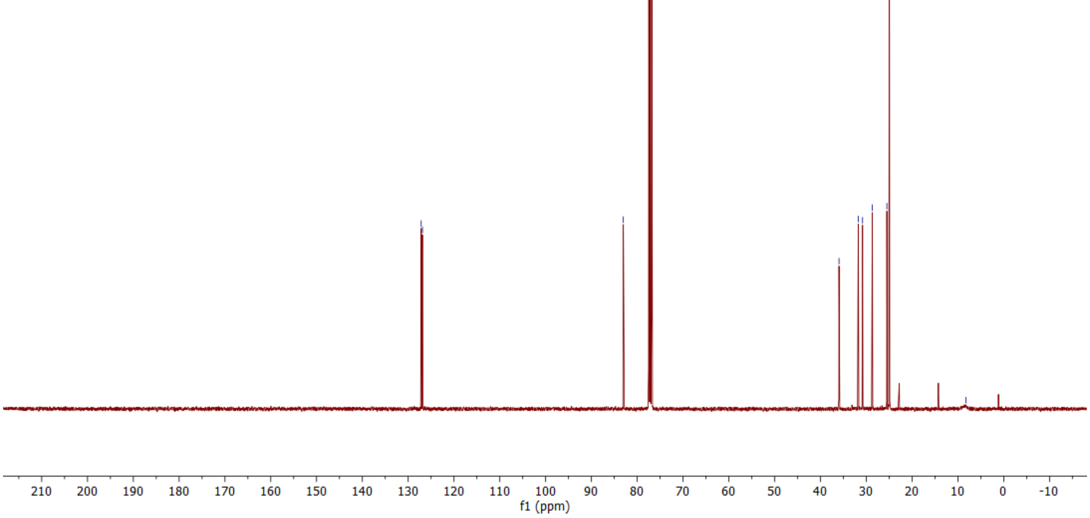
2-(2-(cyclohex-3-en-1-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2l)

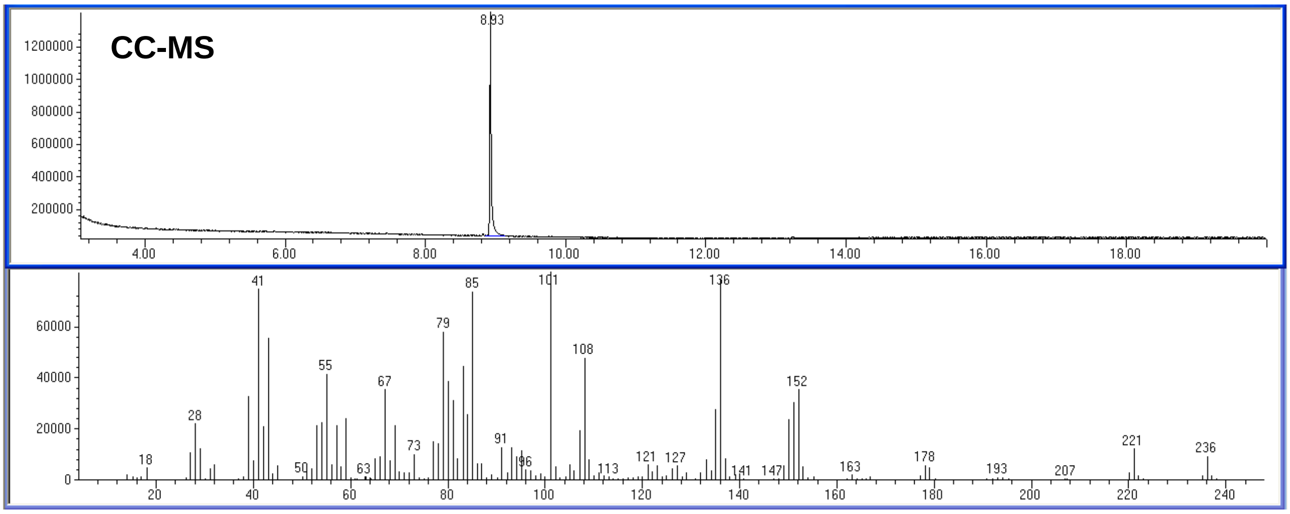




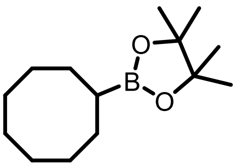


^{13}C NMR (101 MHz, $CDCl_3$)

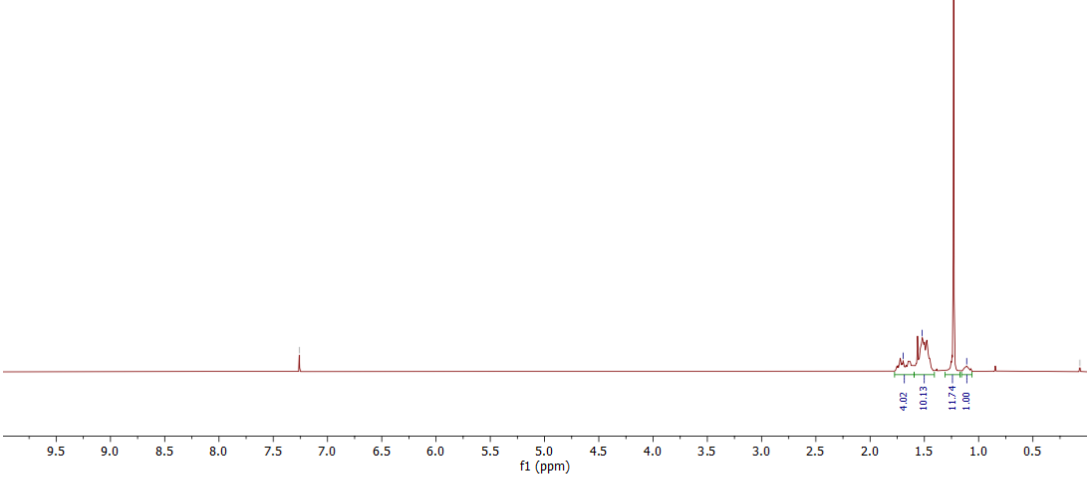


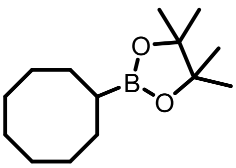


2-cyclooctyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a)

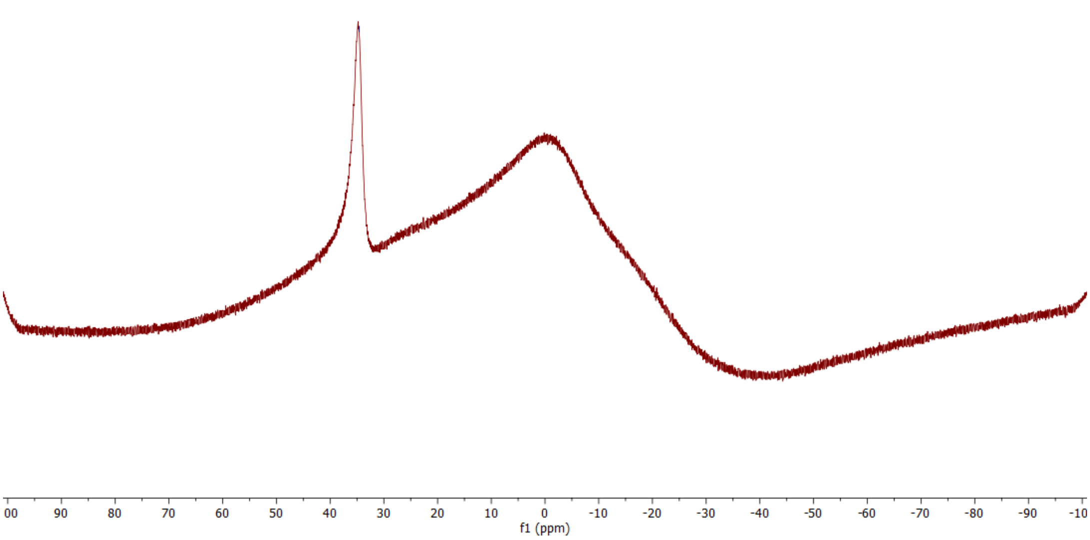


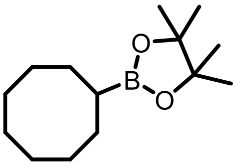
^{1}H NMR (400 MHz, $CDCl_3$)



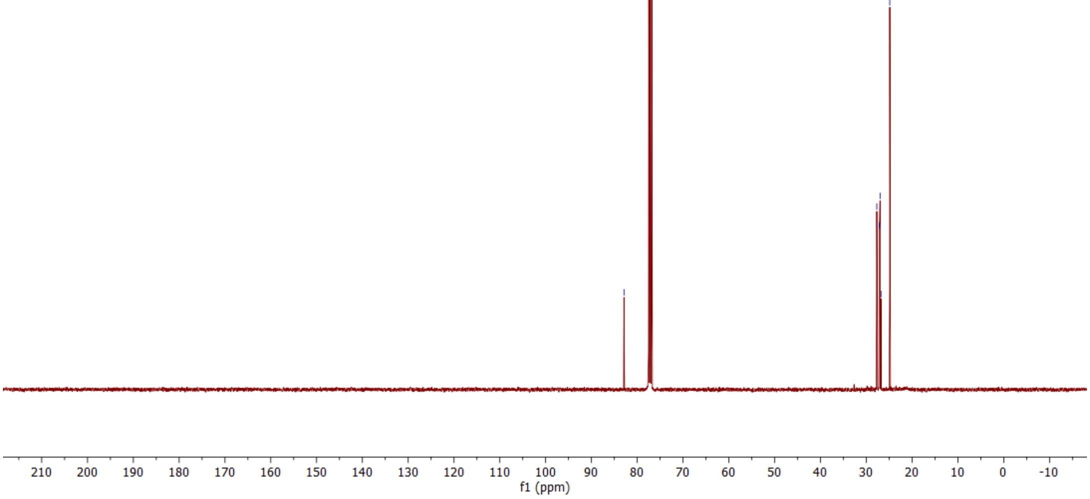


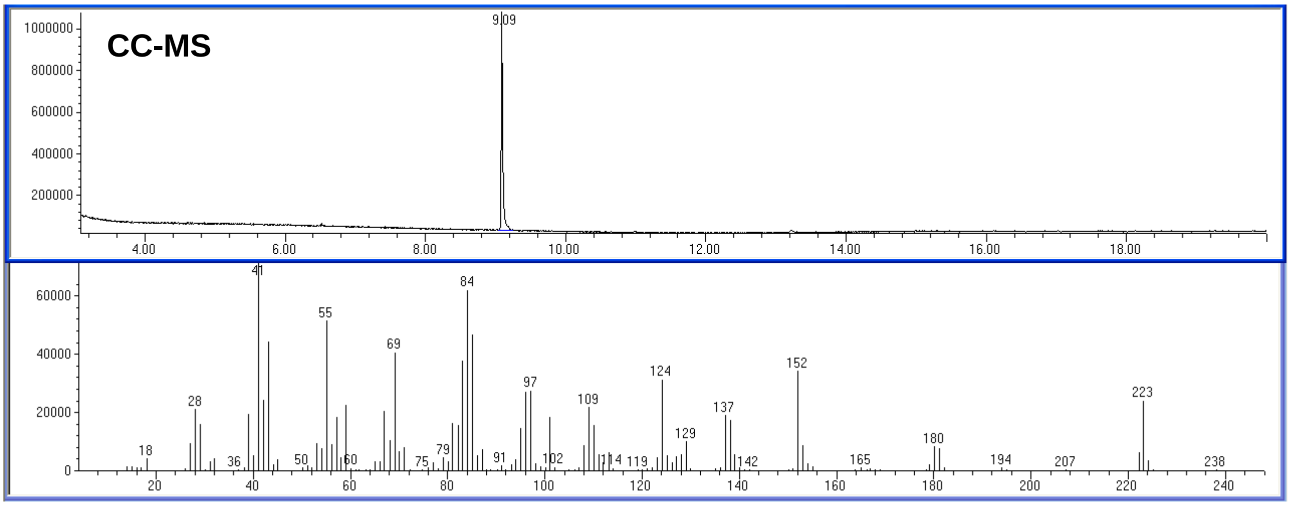
^{11}B NMR (128 MHz, $CDCl_3$)



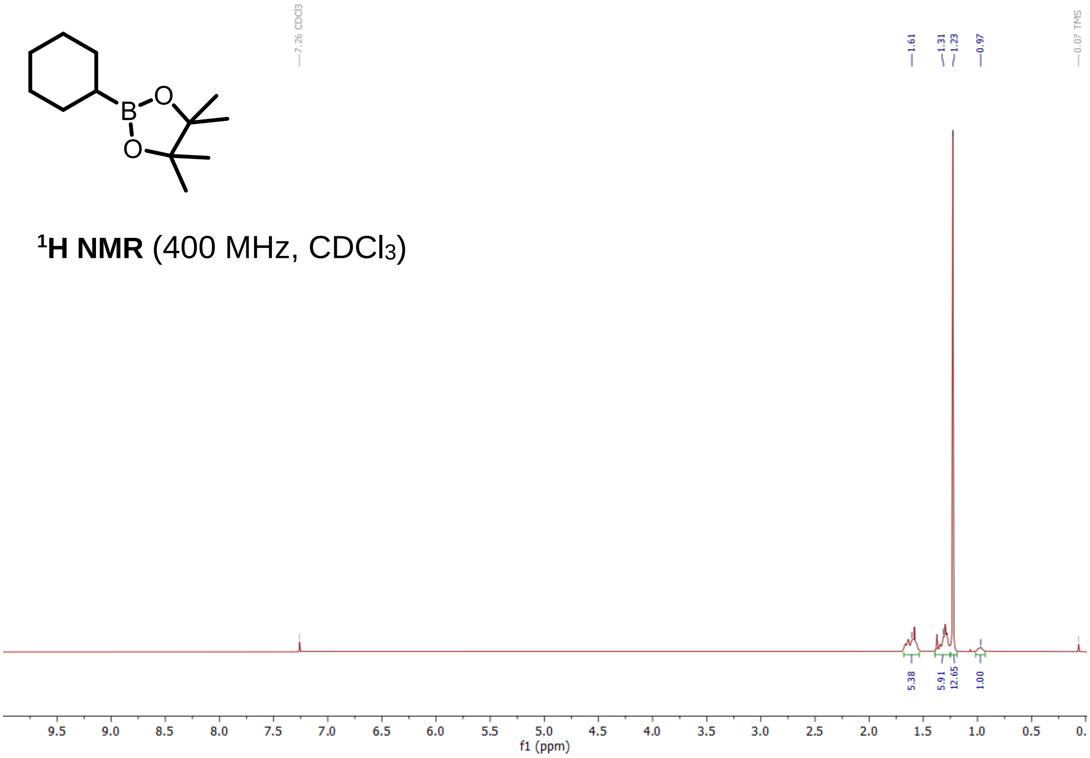


^{13}C NMR (101 MHz, $CDCl_3$)

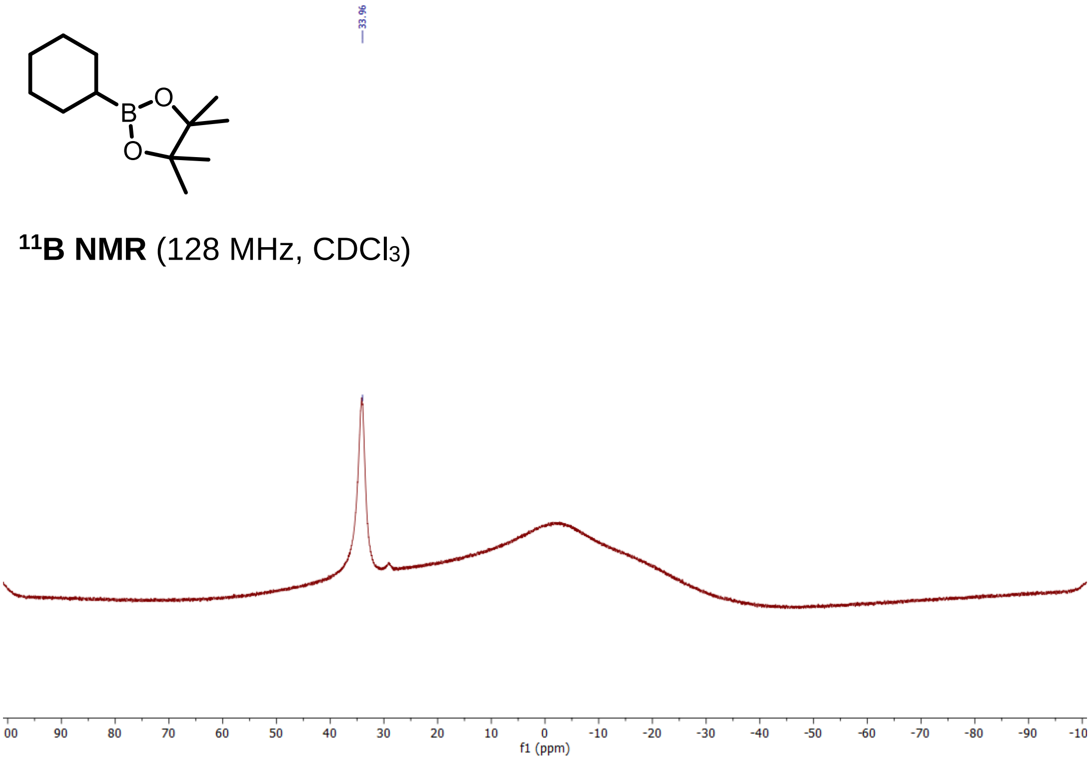




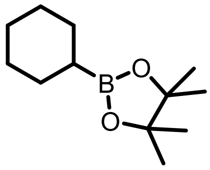
2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)



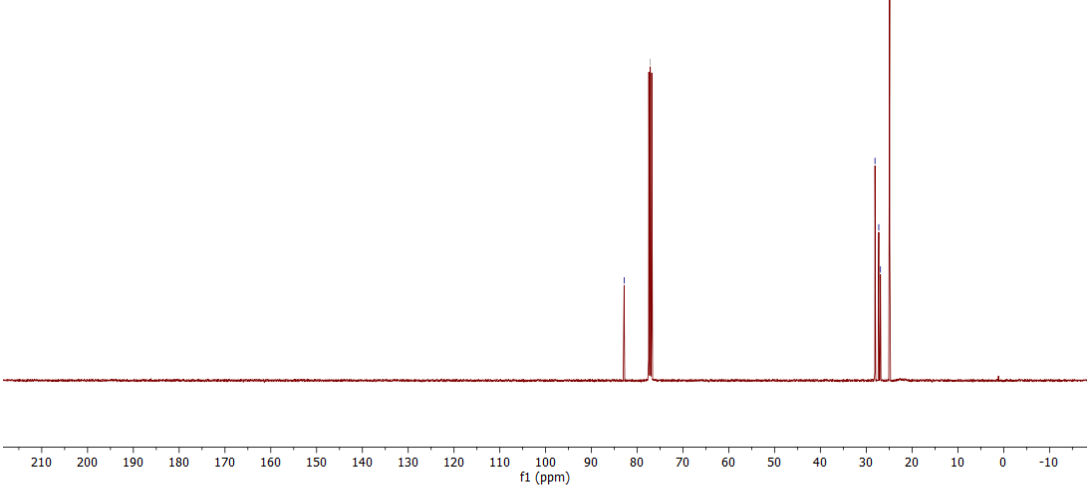
^{1}H NMR (400 MHz, $CDCl_3$)

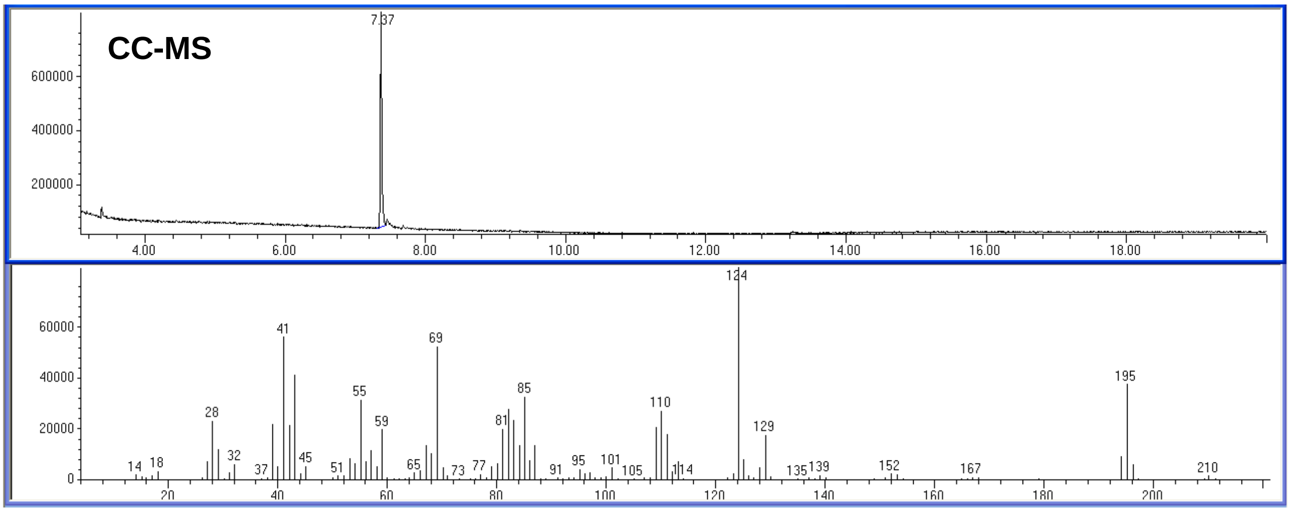


^{11}B NMR (128 MHz, $CDCl_3$)



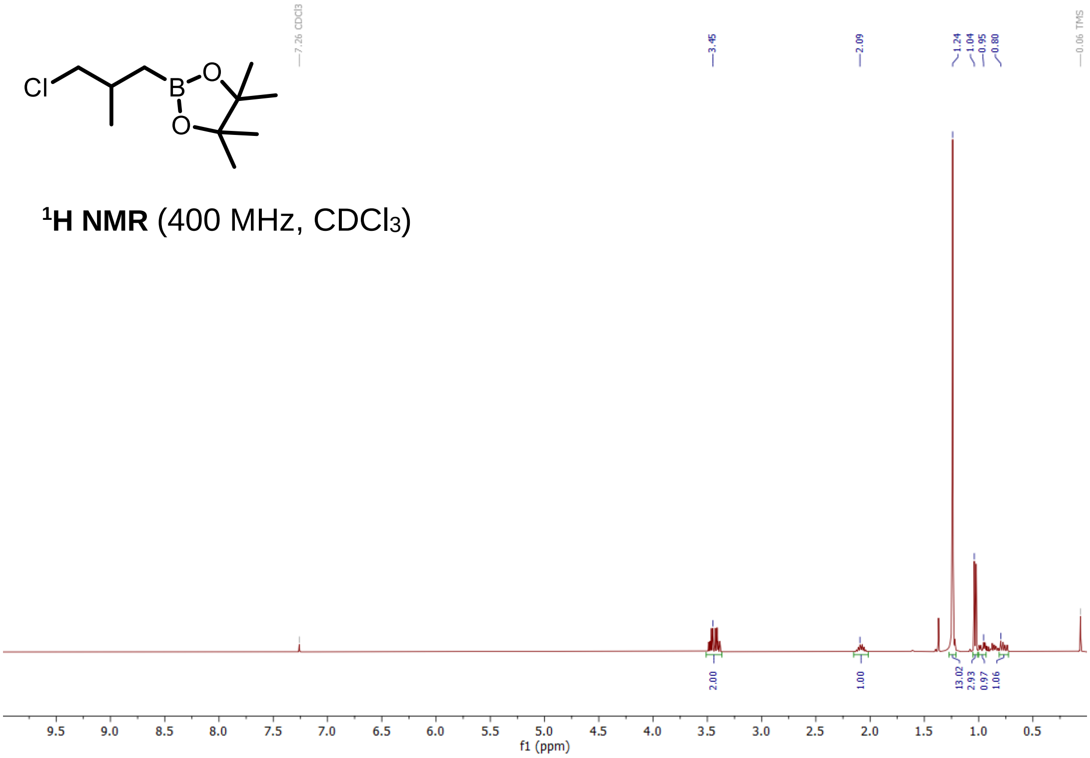
^{13}C NMR (101 MHz, $CDCl_3$)



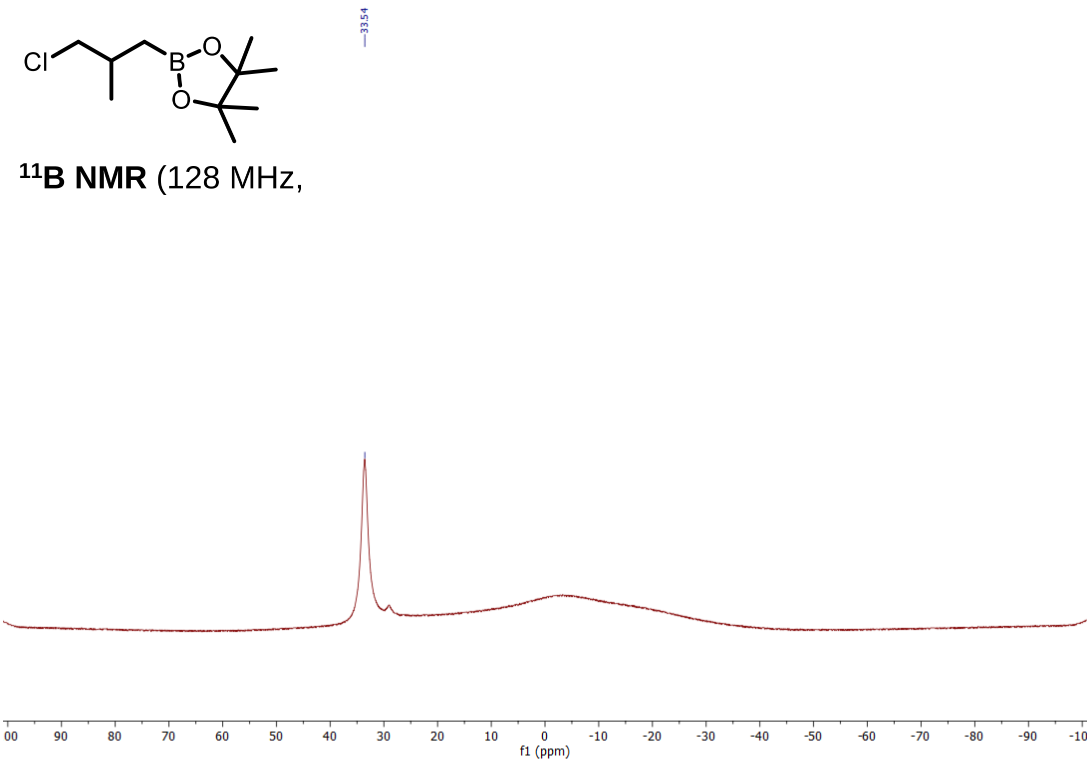


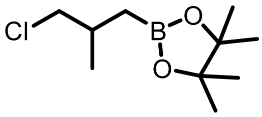
2-(3-chloro-2-methylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)

[1]H NMR (400 MHz, $CDCl_3$)

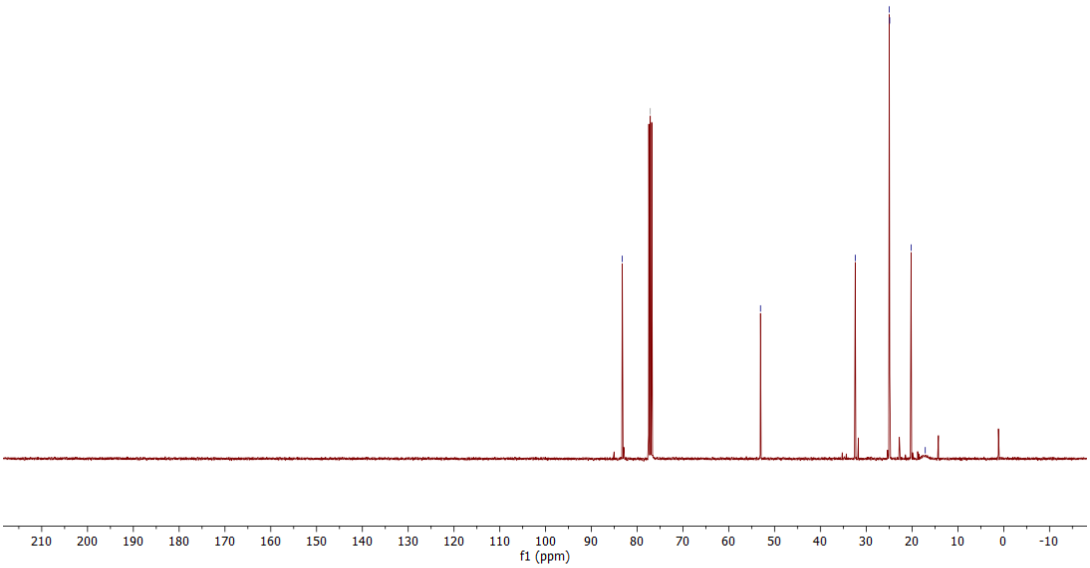


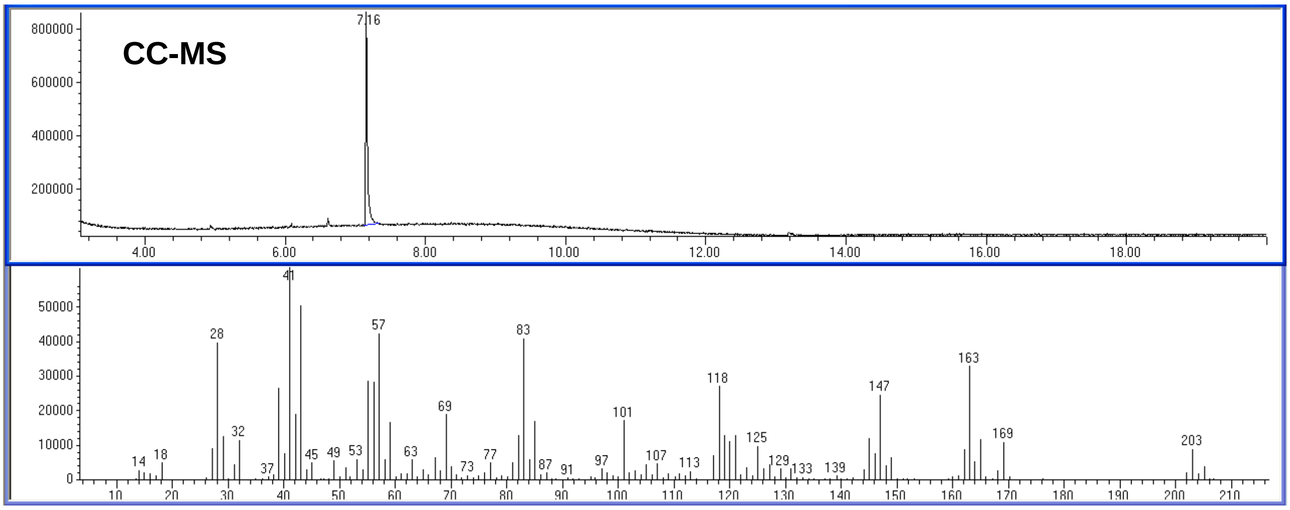
[11]B NMR (128 MHz,



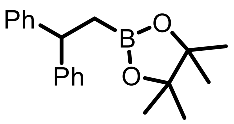


^{13}C NMR (101 MHz, $CDCl_3$)

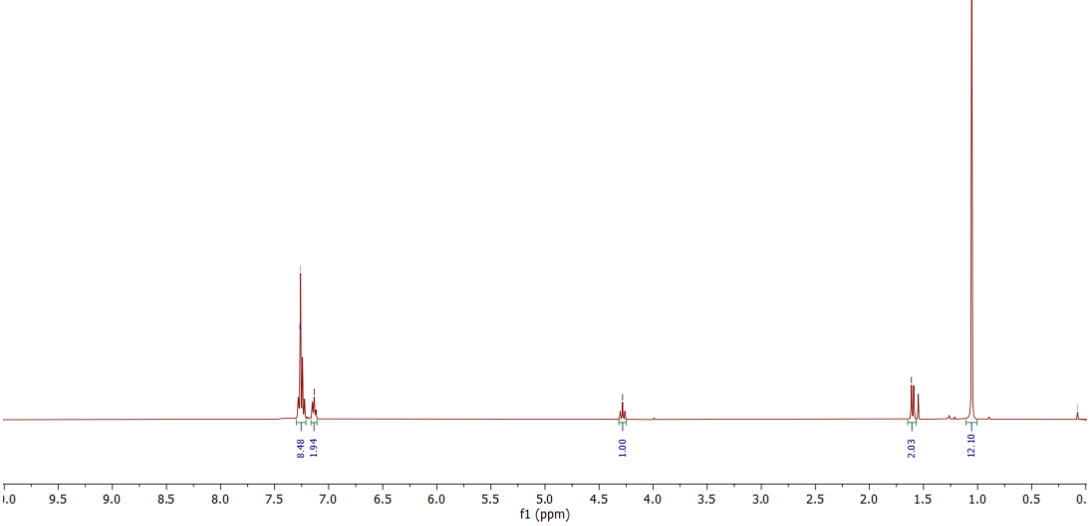


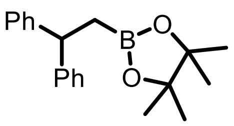


2-(2,2-diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d)

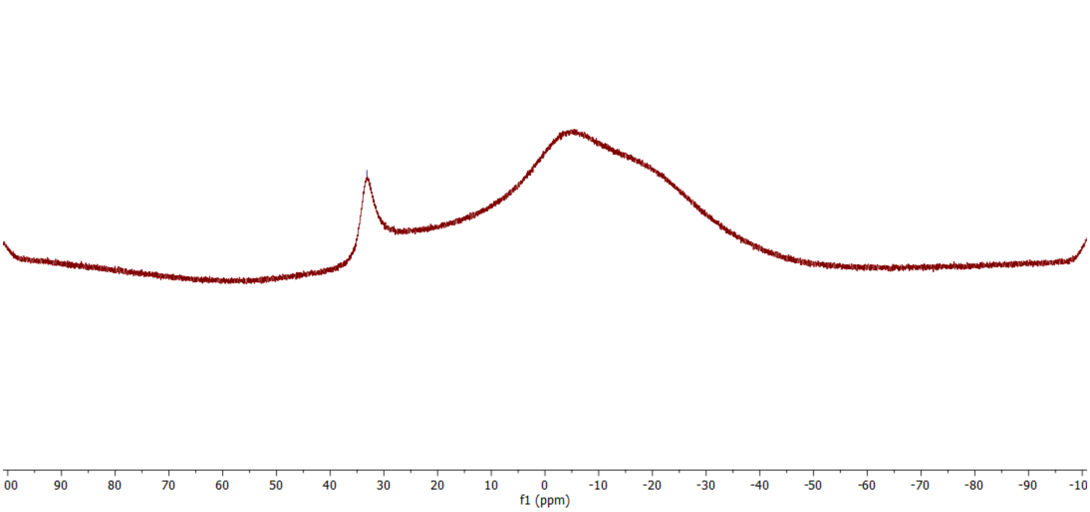


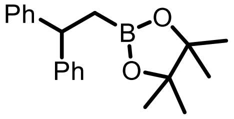
[1]H NMR (400 MHz, CDCl3)



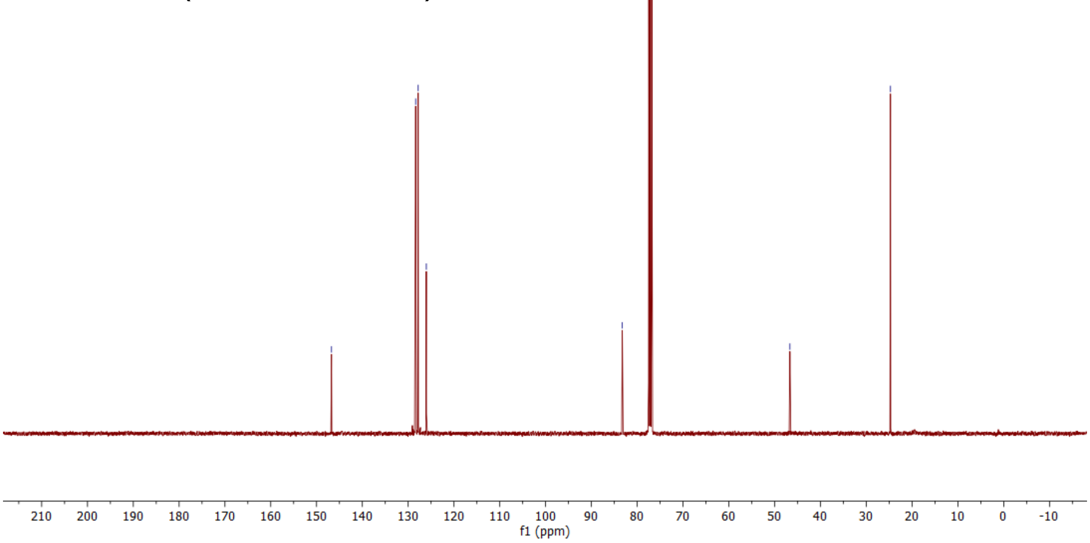


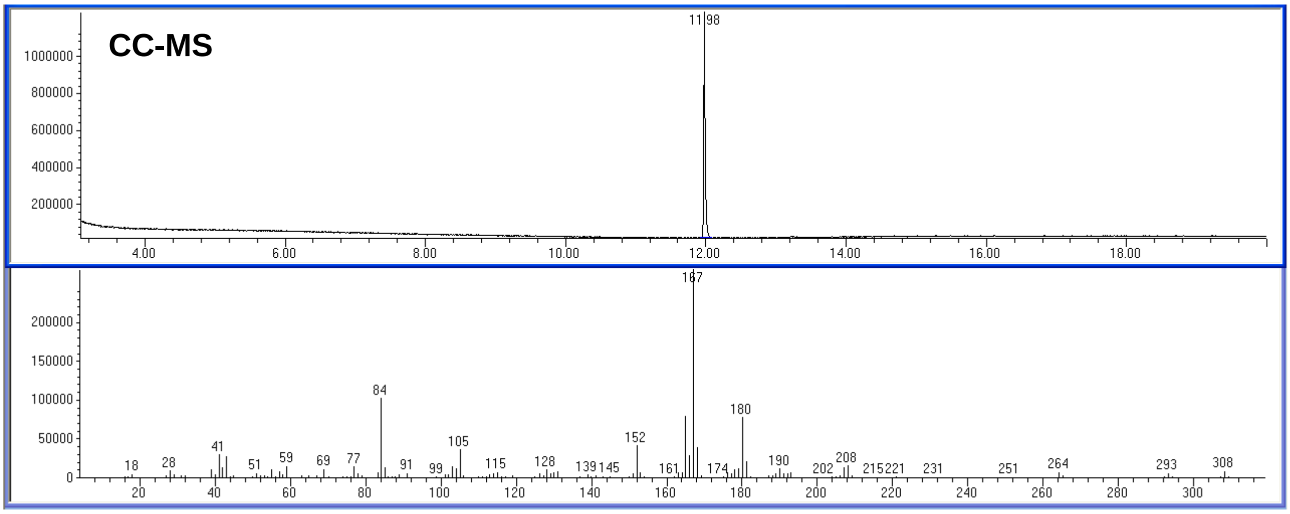
[11]B NMR (128 MHz, CDCl3)



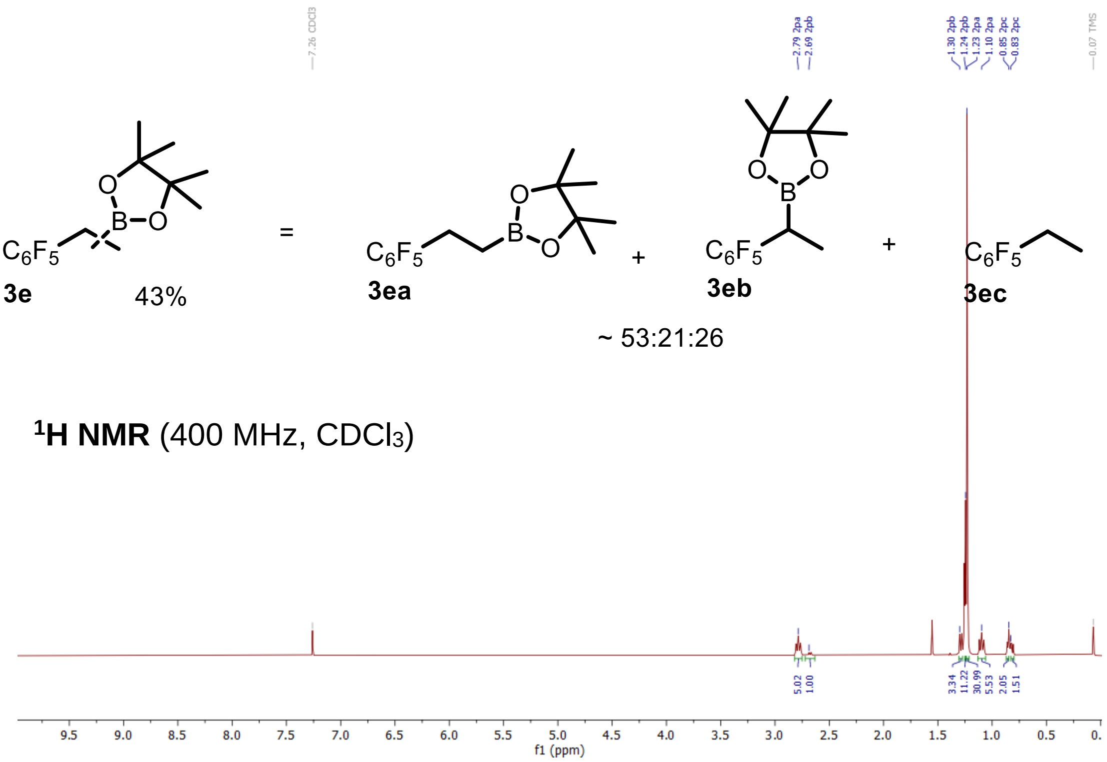


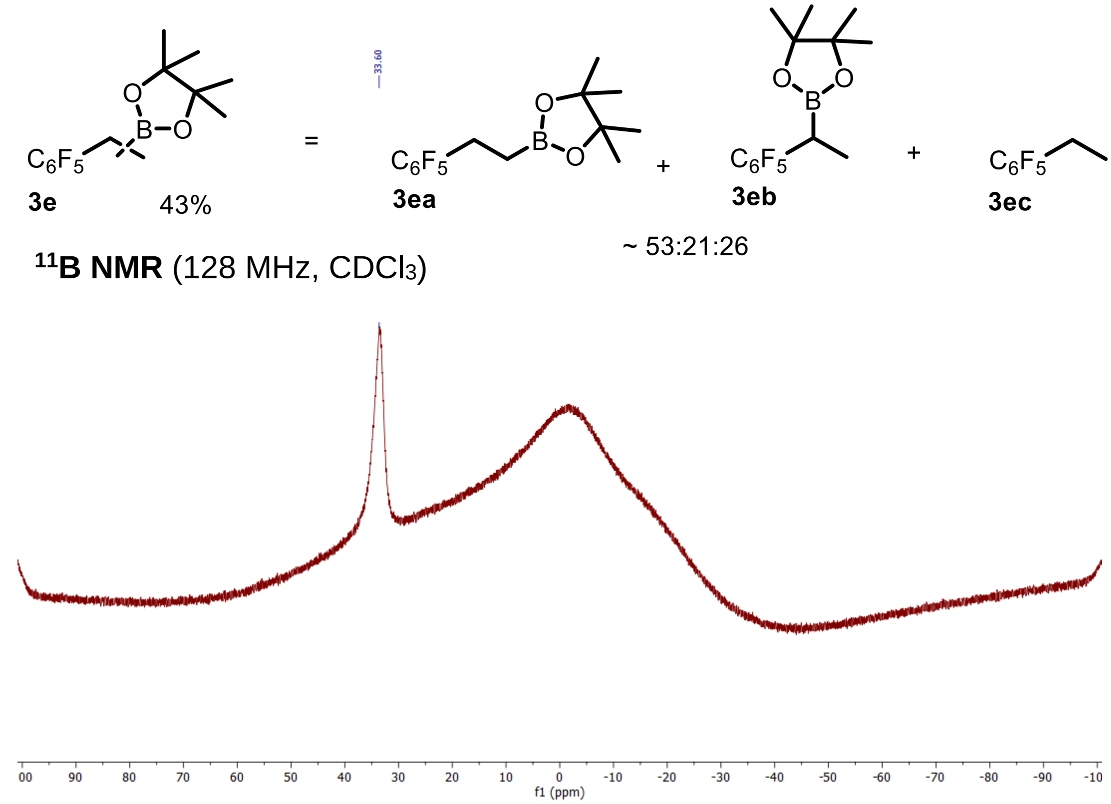
^{13}C NMR (101 MHz, $CDCl_3$)



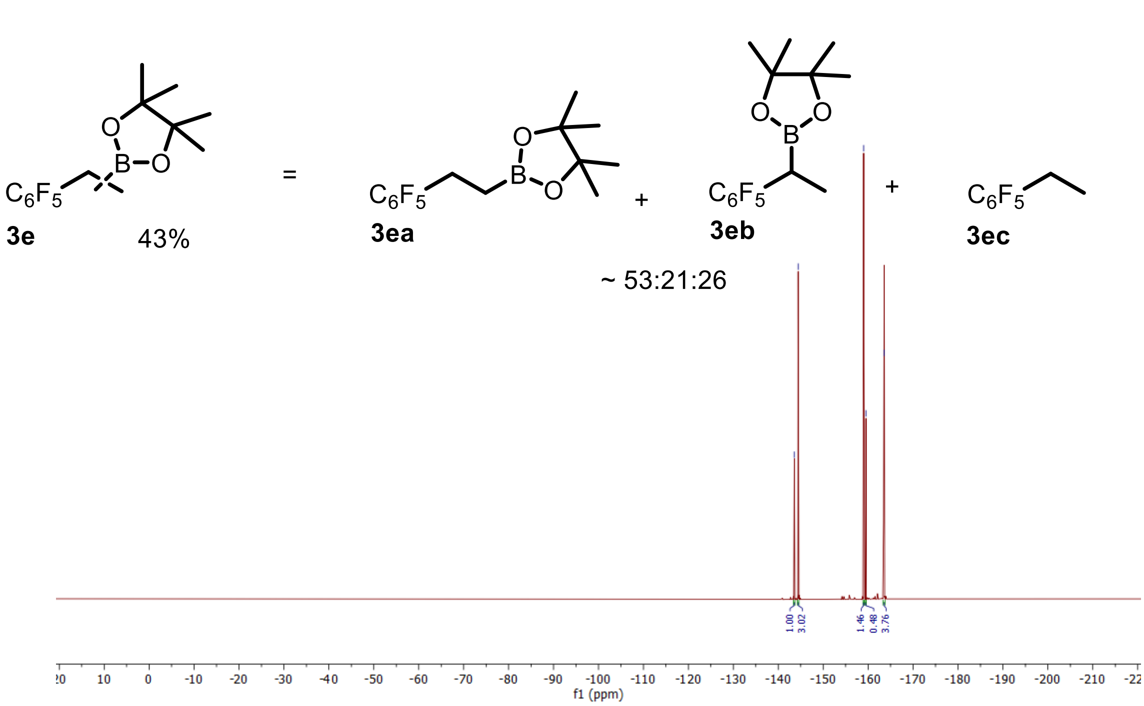


4,4,5,5-tetramethyl-2-(2-(perfluorophenyl)ethyl)-1,3,2-dioxaborolane (3e)

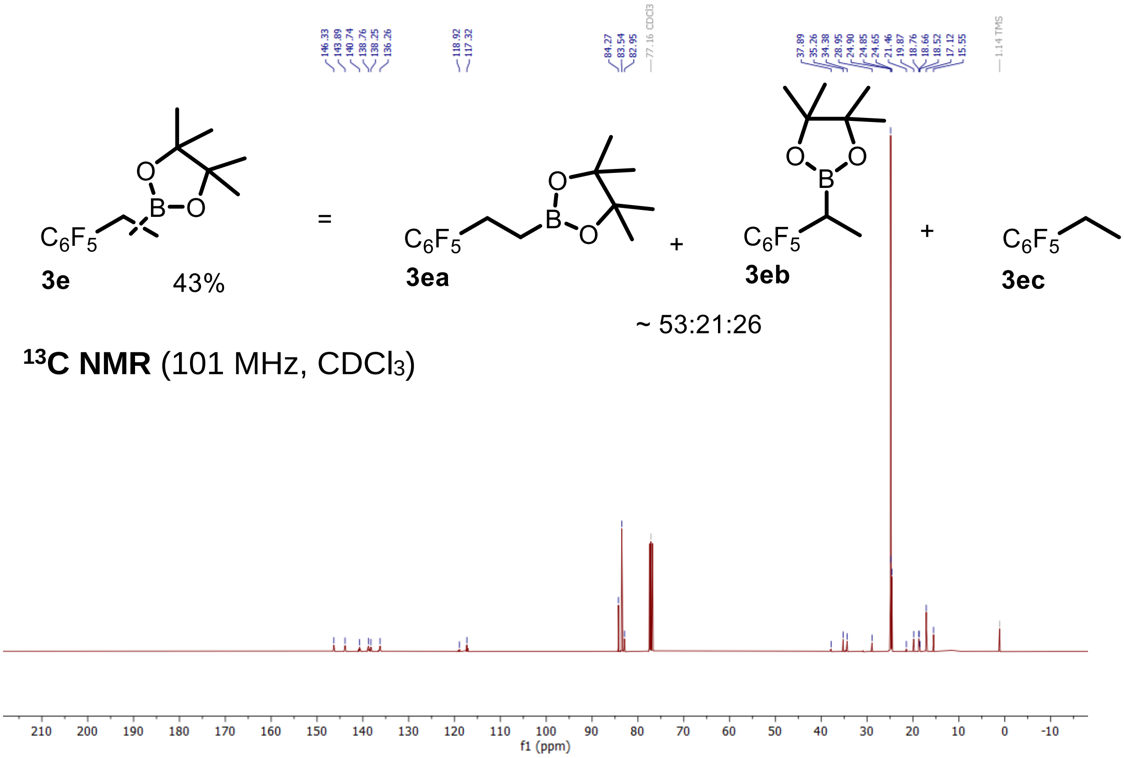


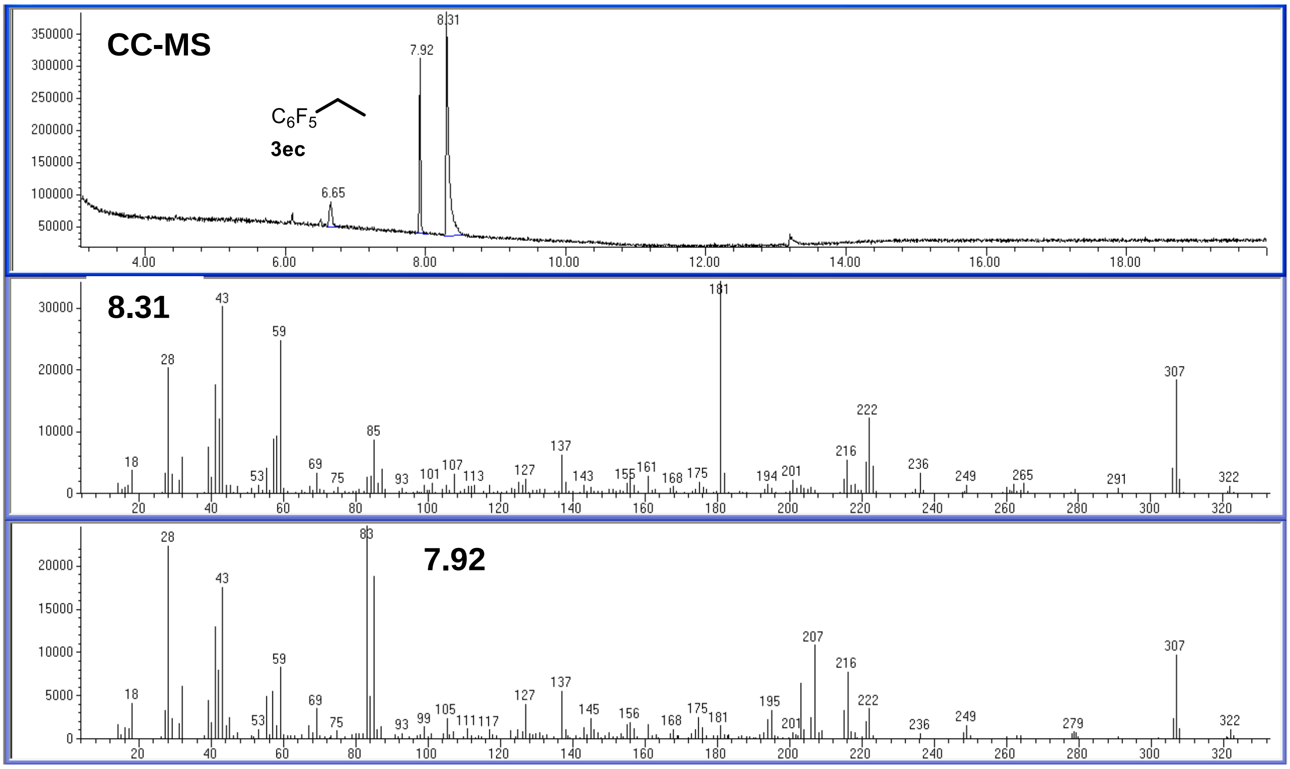


[19]F {[1]H} NMR (376 MHz, C_6D_6)

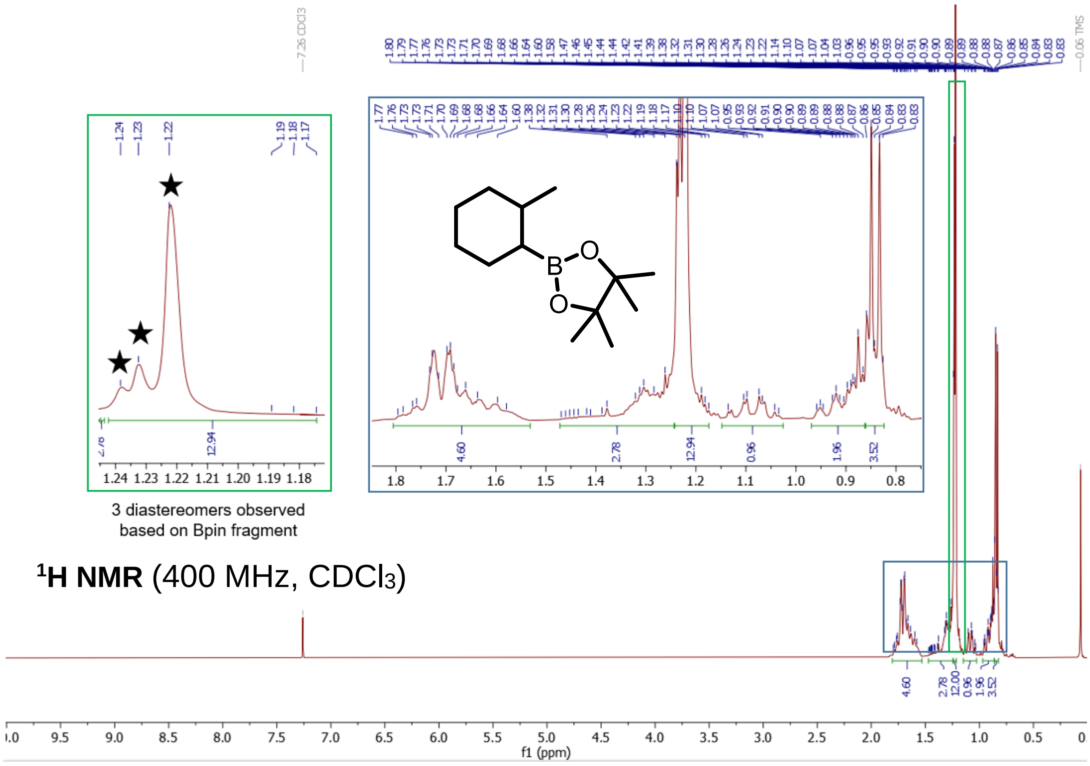


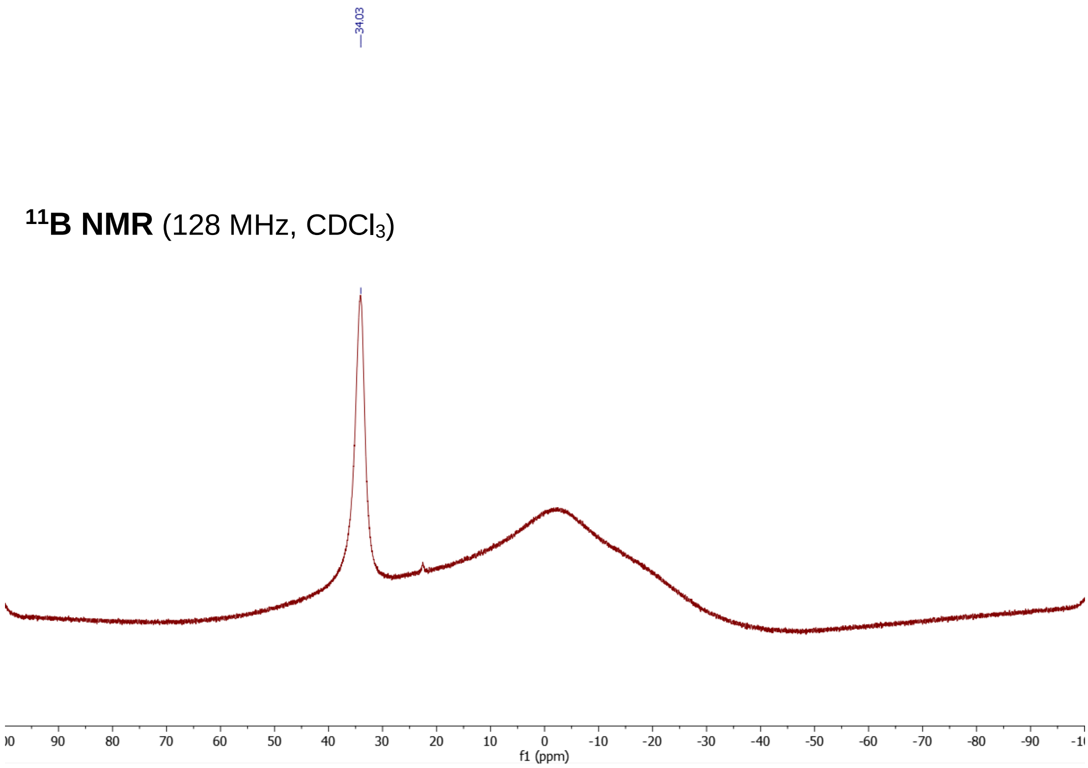
[13]C NMR (101 MHz, $CDCl_3$)

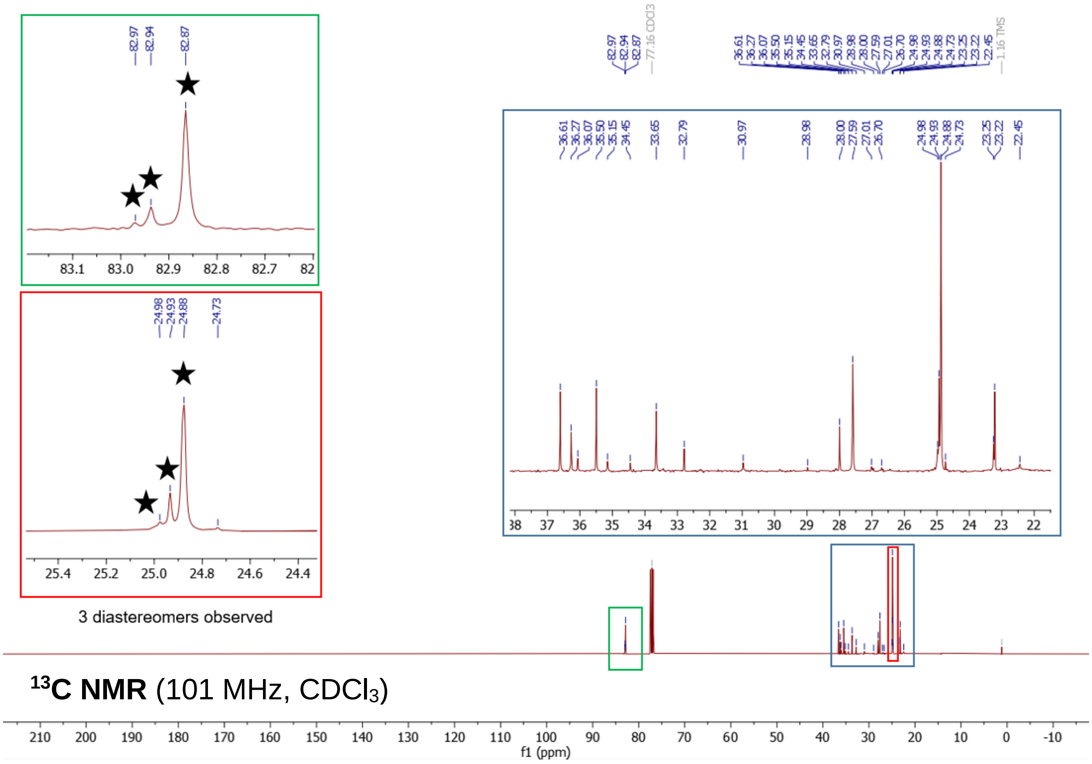



CC-MS
C_6F_5
3ec
8.31
7.92

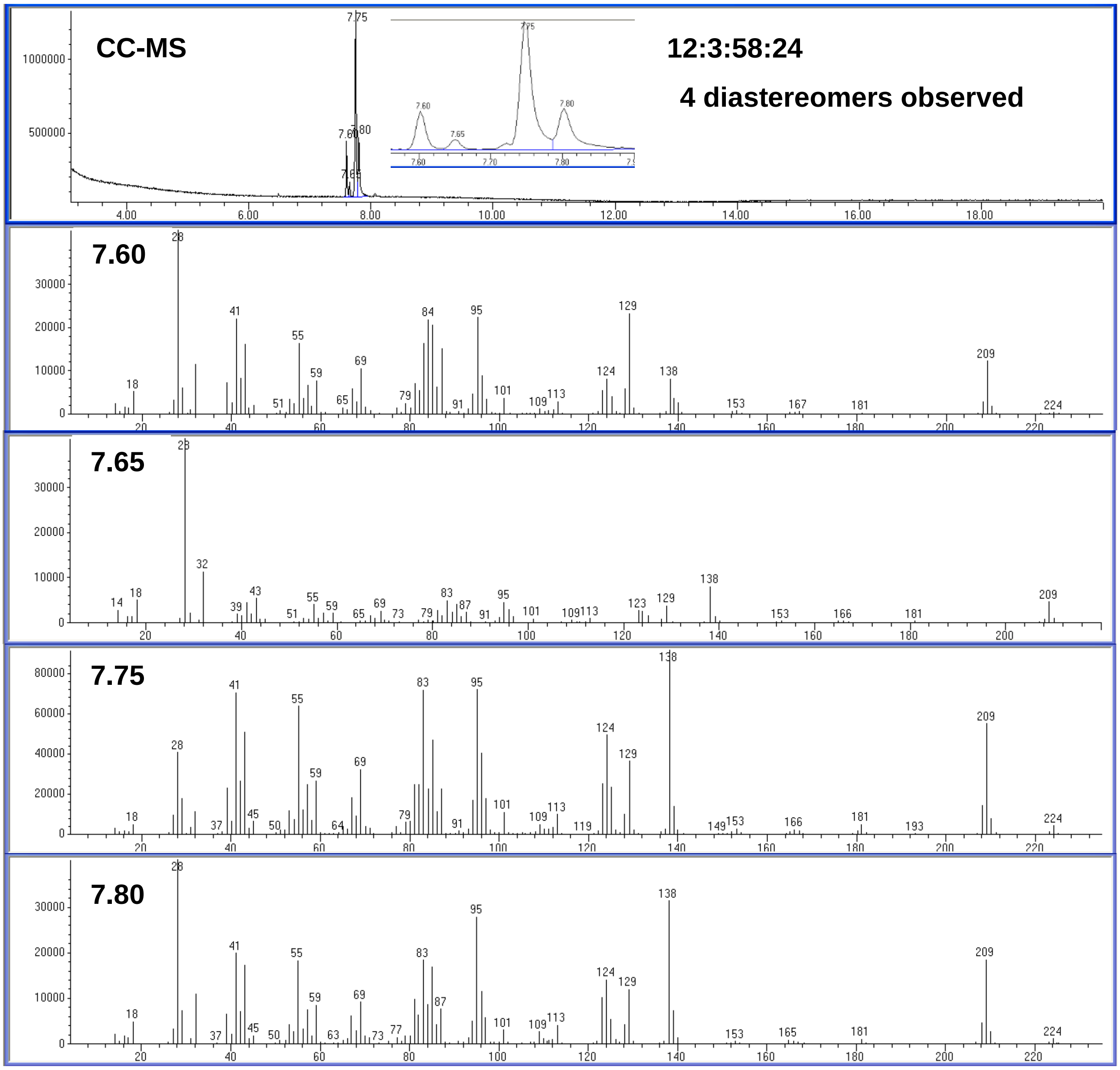
4,4,5,5-tetramethyl-2-(2-methylcyclohexyl)-1,3,2-dioxaborolane (3f)







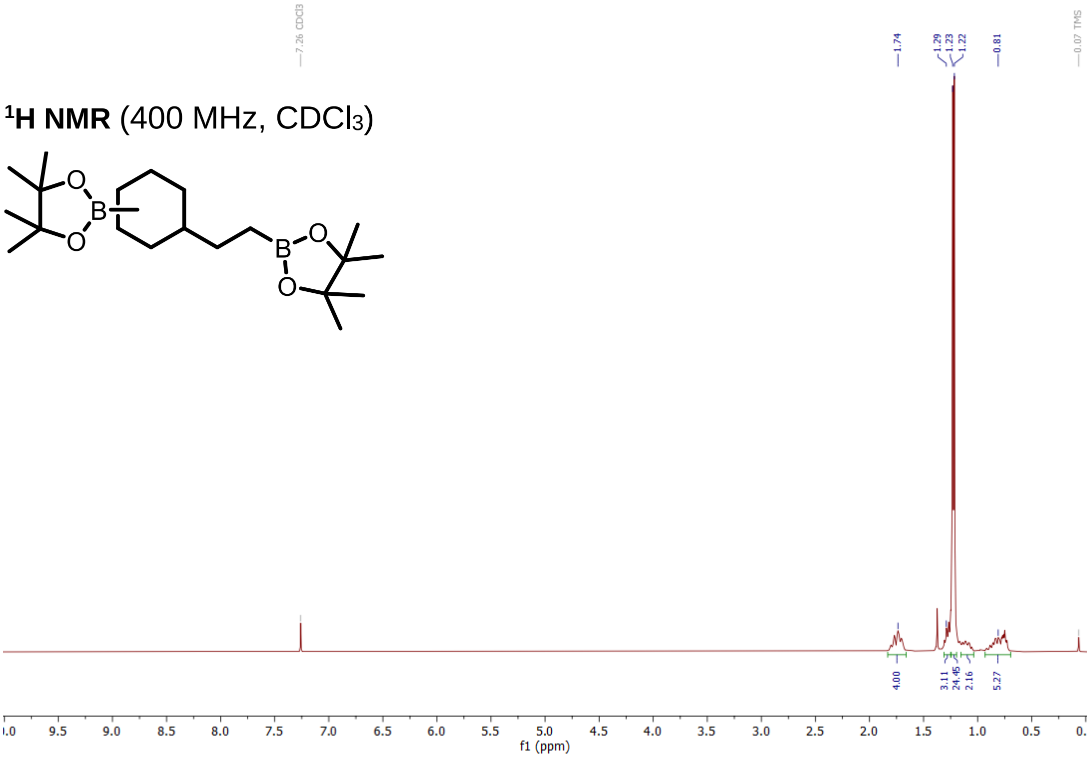
^{13}C NMR (101 MHz, $CDCl_3$)



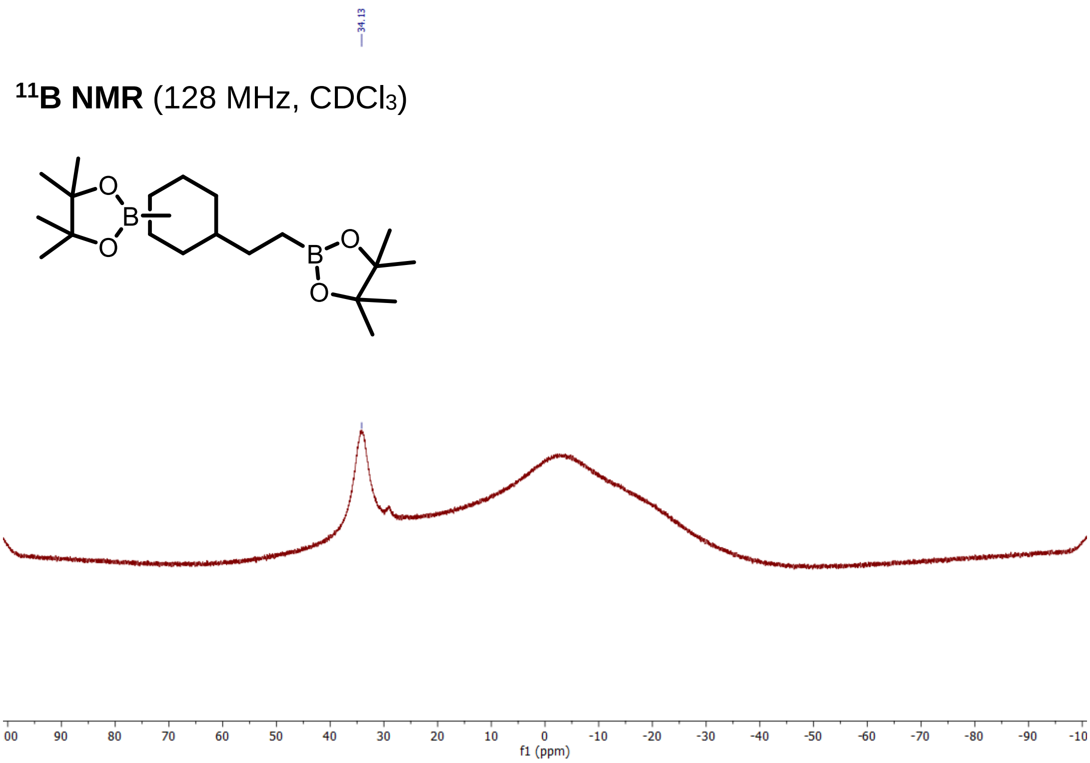
CC-MS
12:3:58:24
4 diastereomers observed
7.60
7.65
7.75
7.80

4,4,5,5-tetramethyl-2-(2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)ethyl)-1,3,2-dioxaborolane (3g)

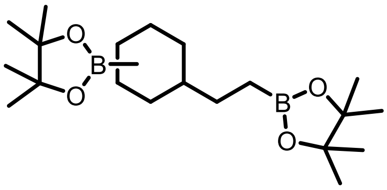
¹H NMR (400 MHz, $CDCl_3$)

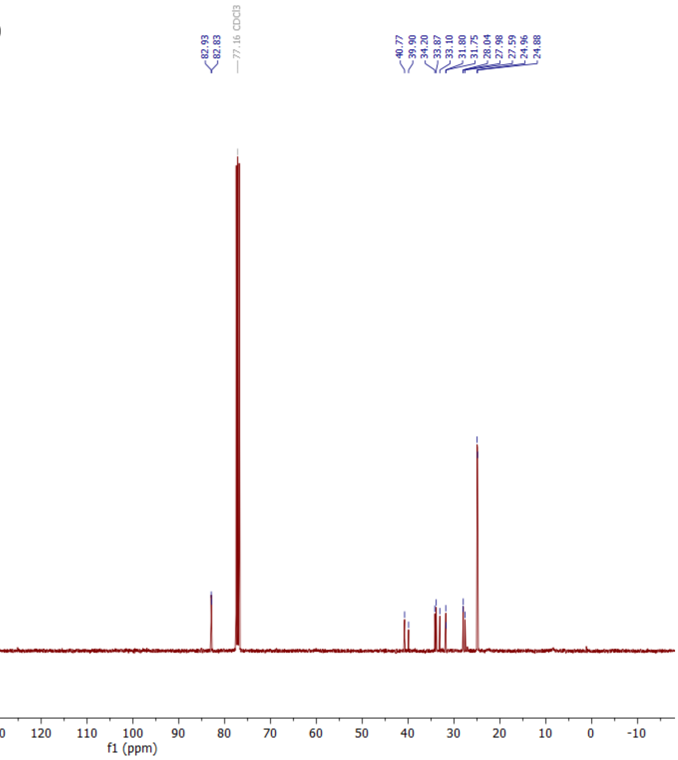


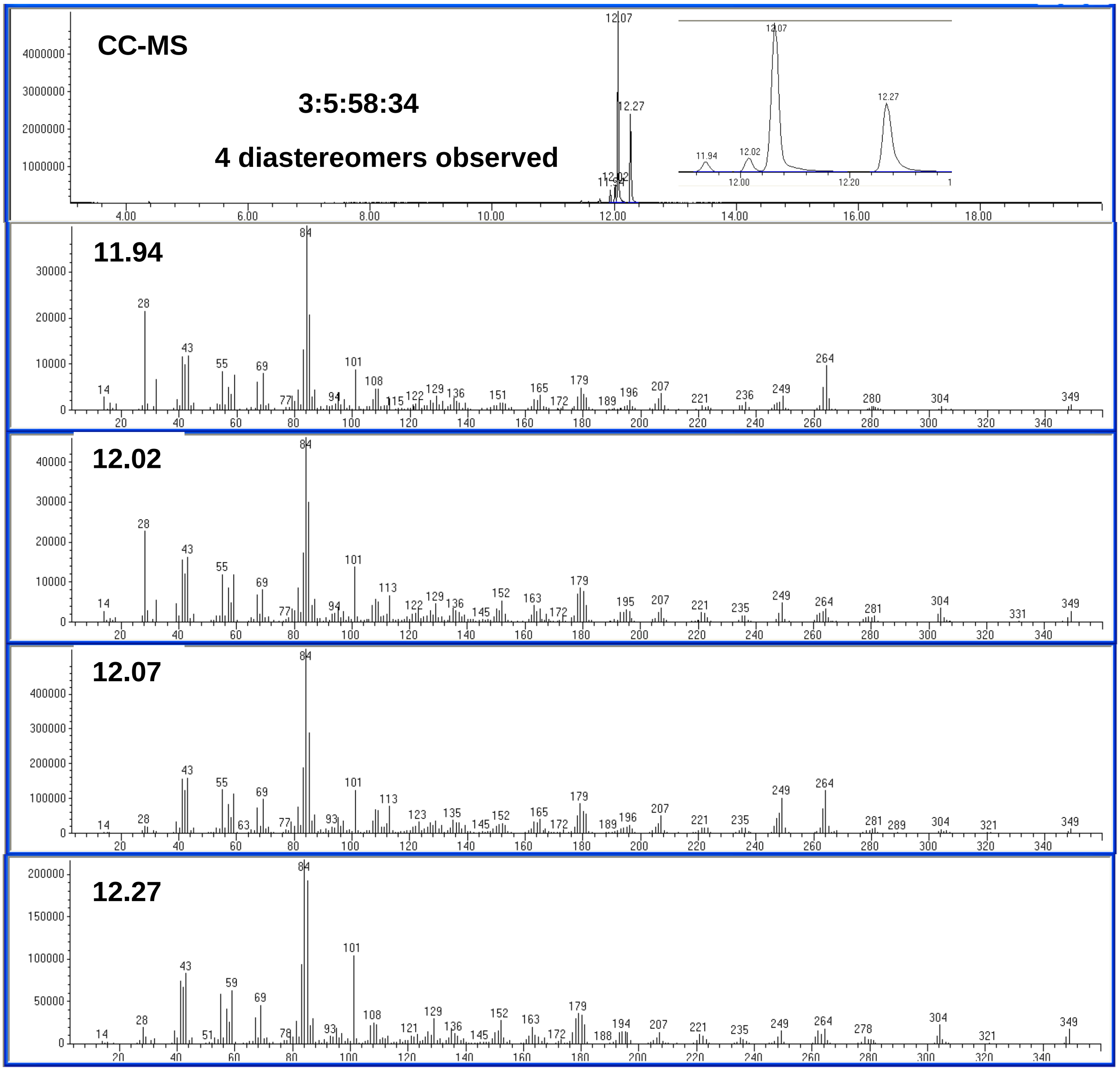
¹¹B NMR (128 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

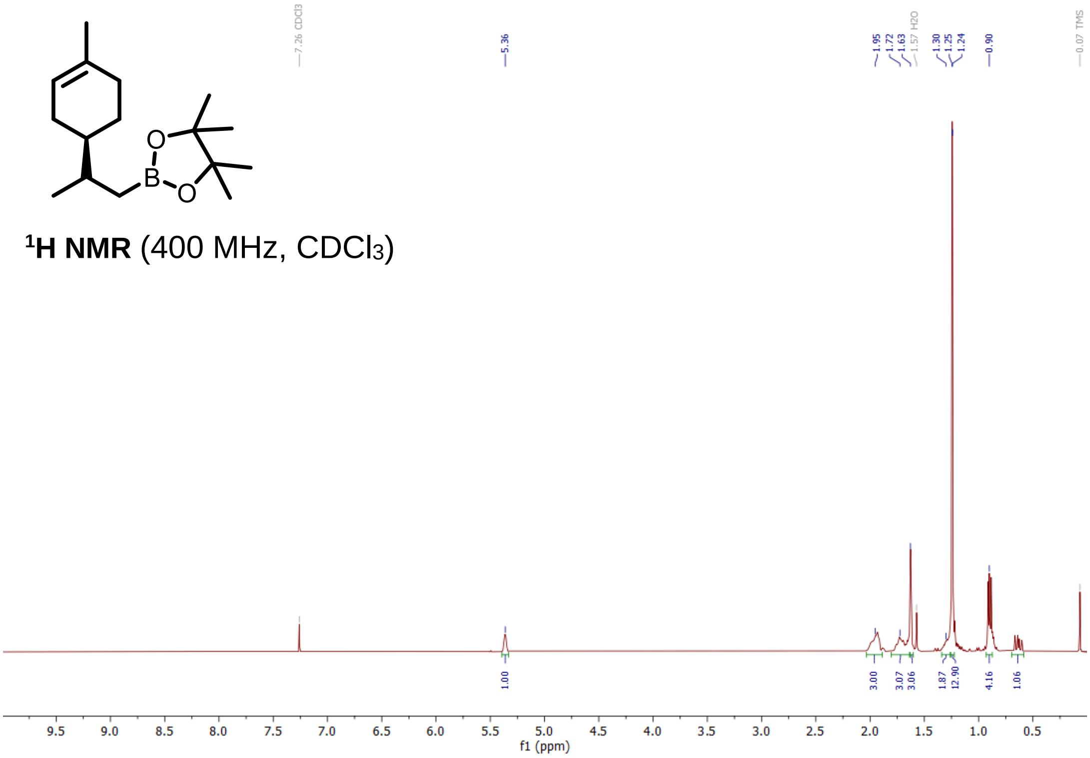




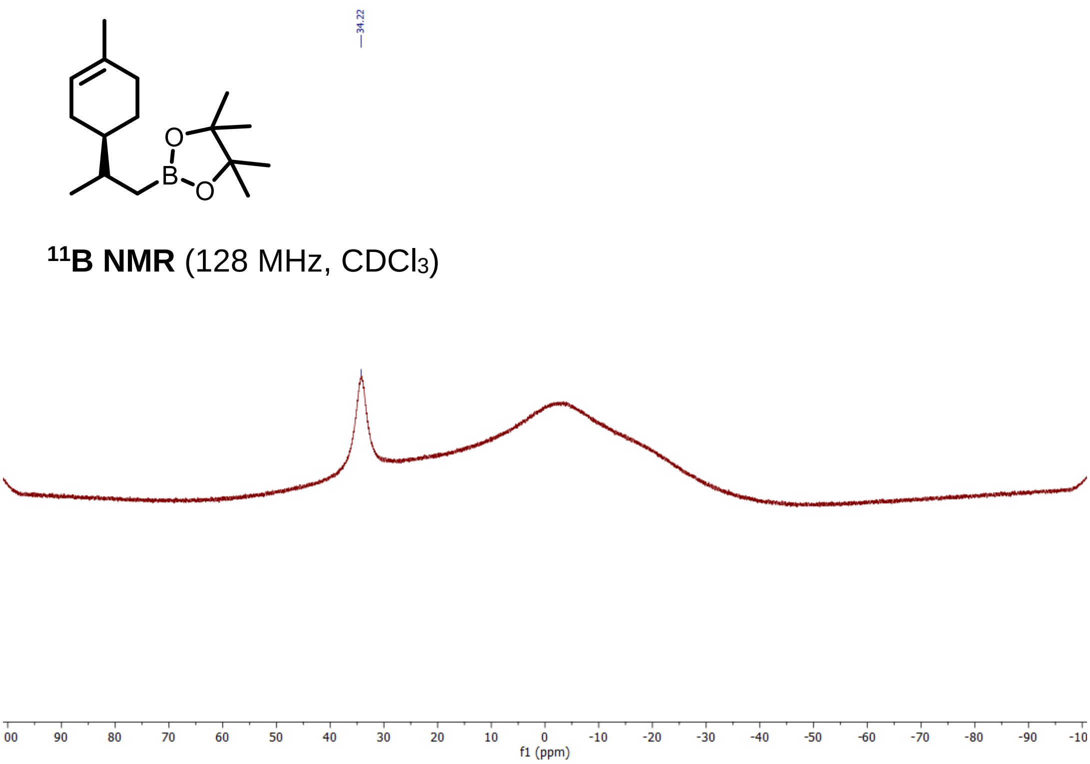


CC-MS
3:5:58:34
4 diastereomers observed
11.94
12.02
12.07
12.27

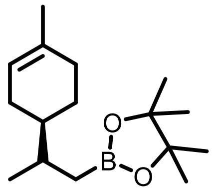
4,4,5,5-tetramethyl-2-((S)-2-((R)-4-methylcyclohex-3-en-1-yl)propyl)-1,3,2-dioxaborolane (3h)



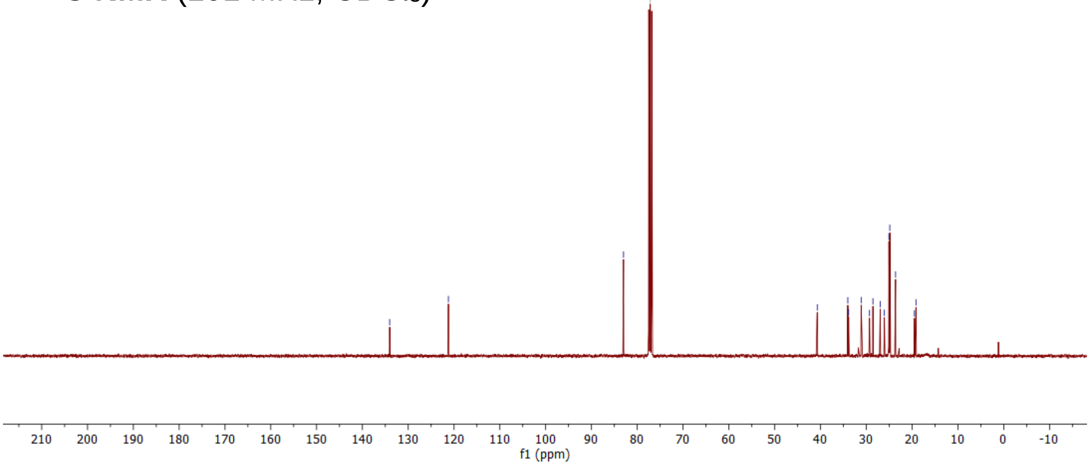
^{1}H NMR (400 MHz, $CDCl_3$)

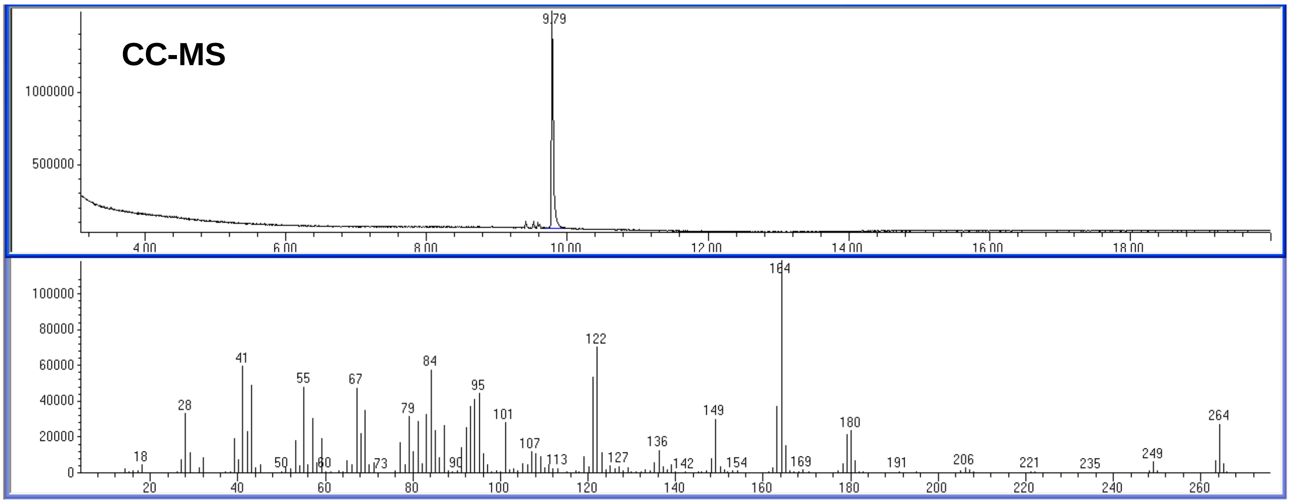


^{11}B NMR (128 MHz, $CDCl_3$)

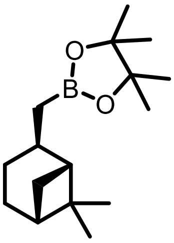


^{13}C NMR (101 MHz, $CDCl_3$)

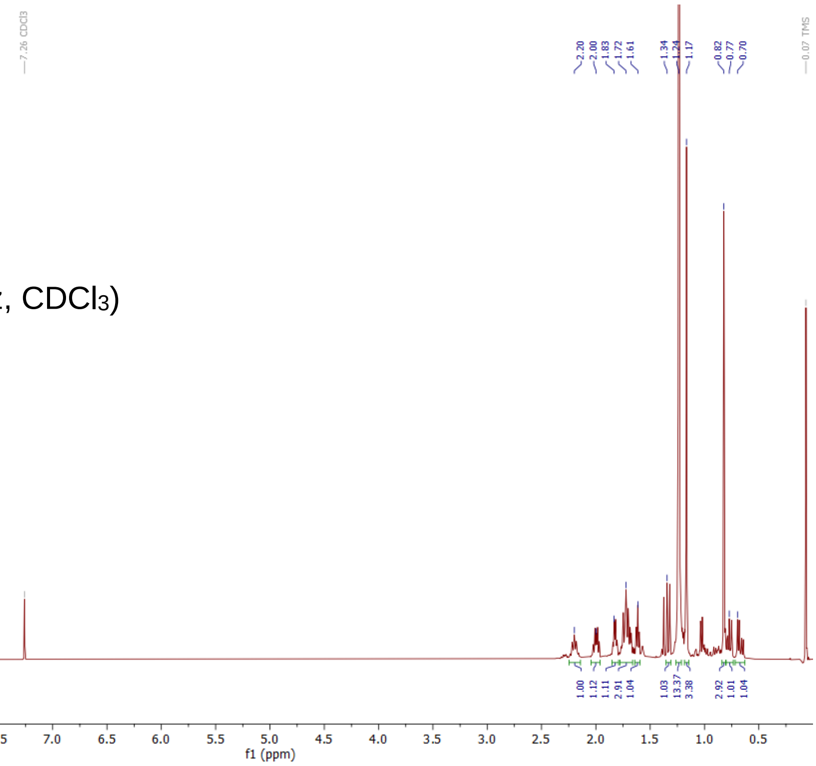


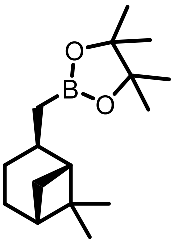


2-(((1R,2R,5R)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i)

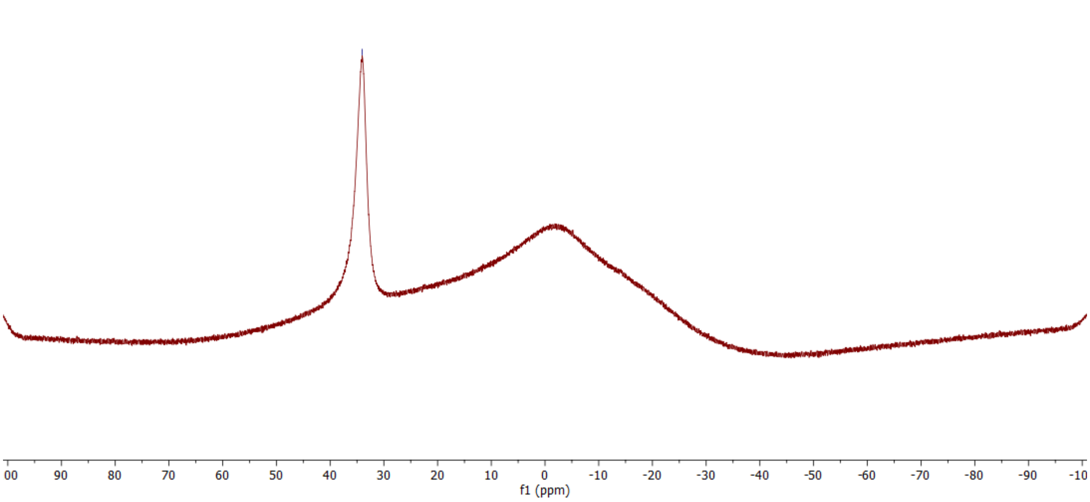


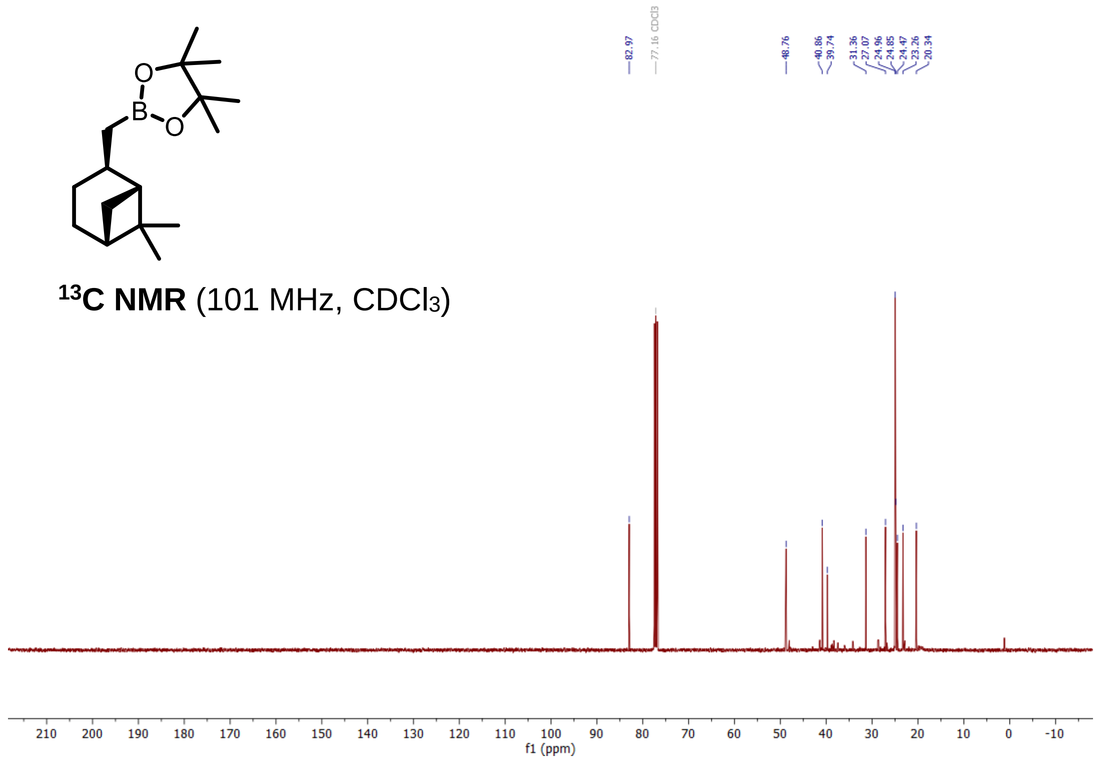
^{1}H NMR (400 MHz, $CDCl_3$)



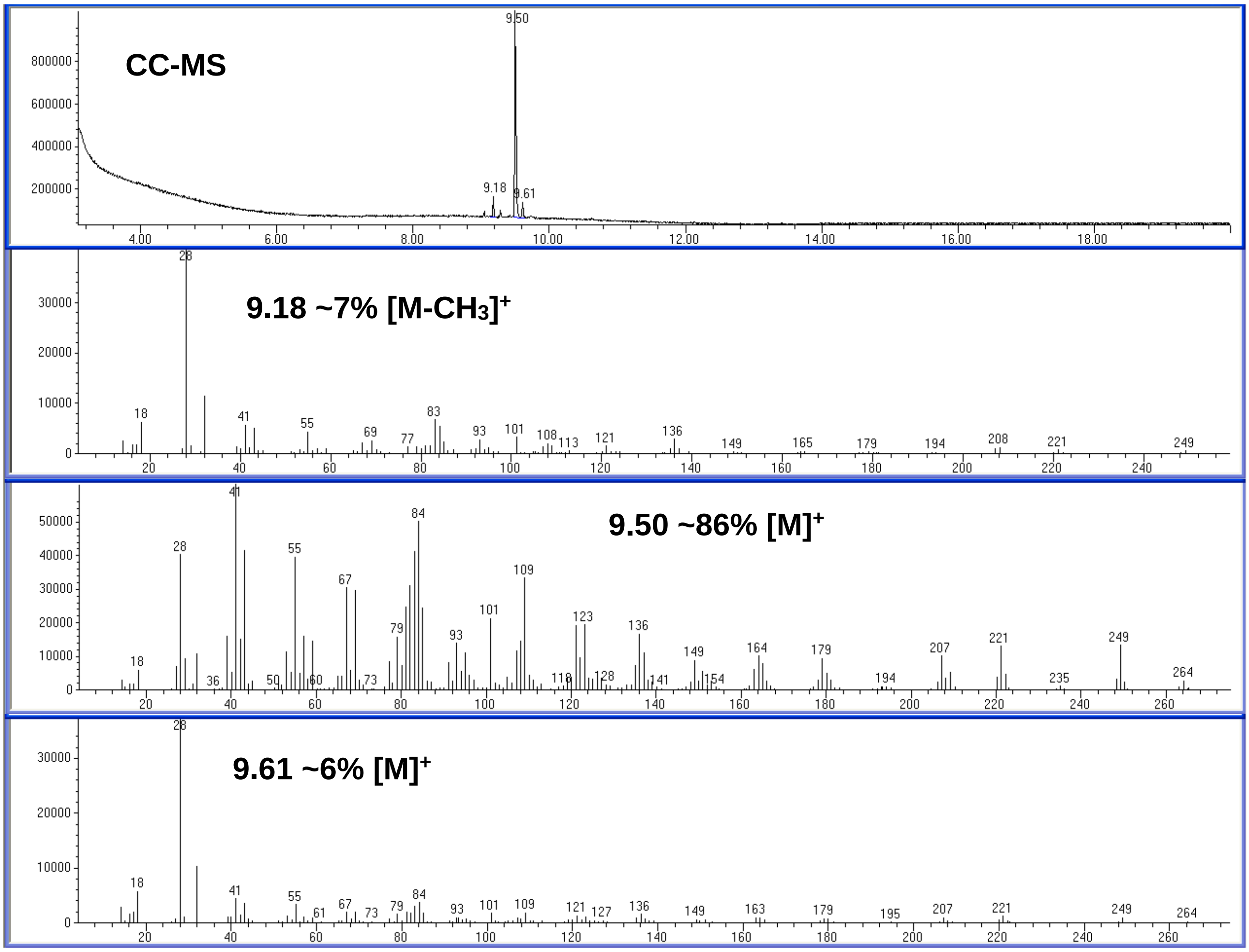


^{11}B NMR (128 MHz, $CDCl_3$)

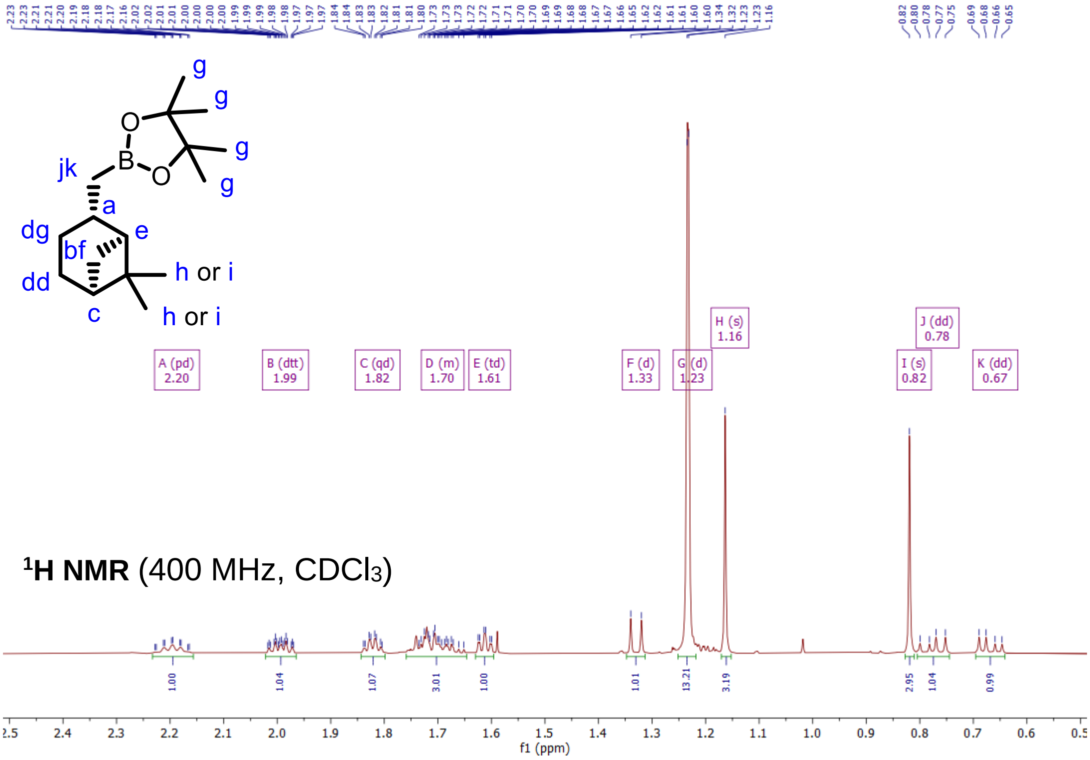




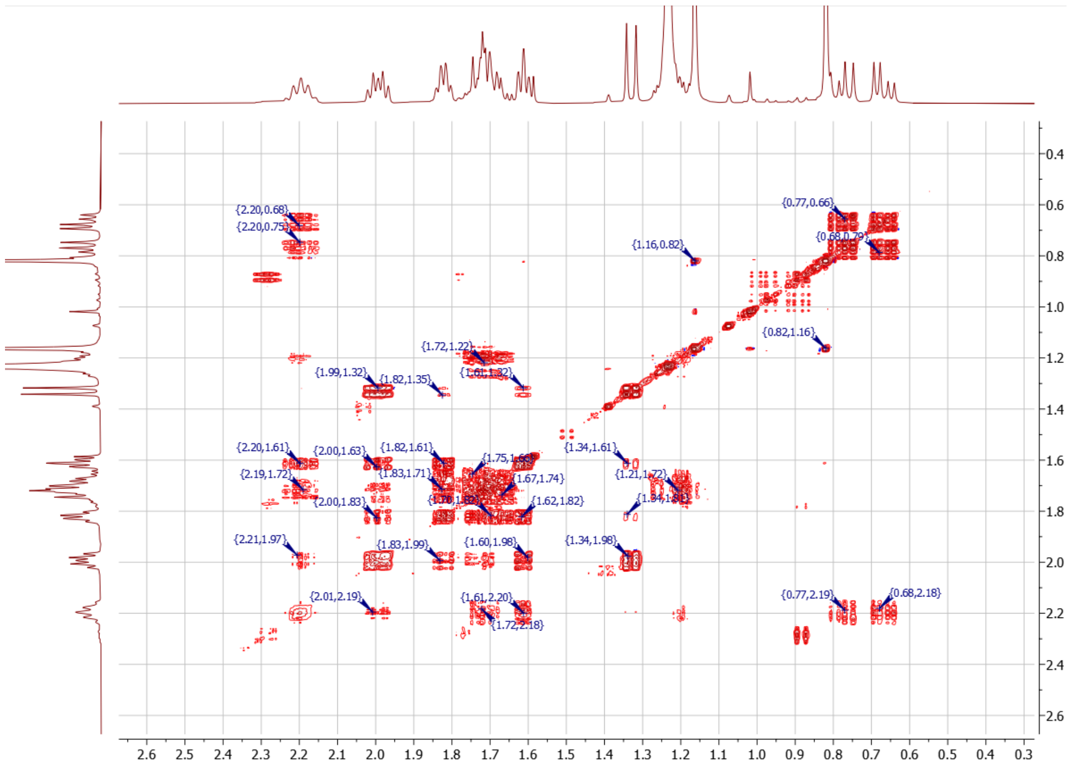
^{13}C NMR (101 MHz, $CDCl_3$)



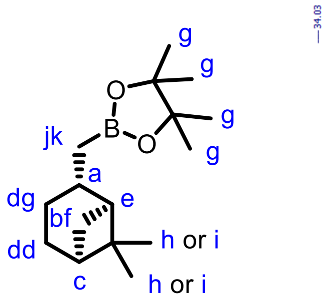
2-(((1S,2S,5S)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j)



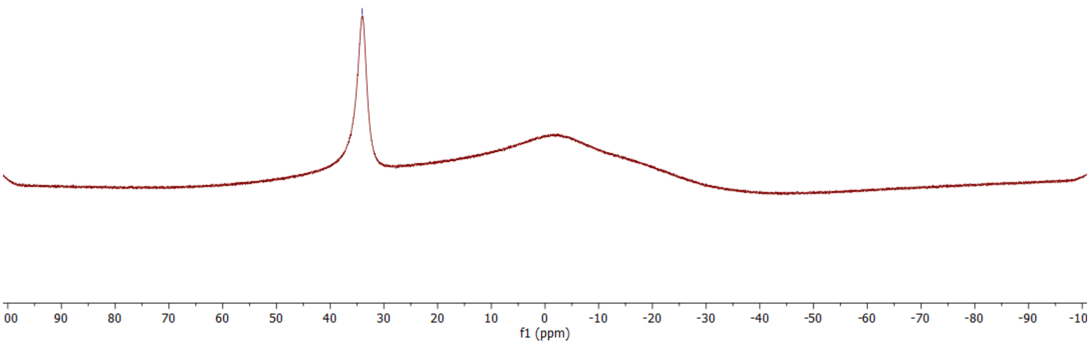
^{1}**H NMR** (400 MHz, $CDCl_3$)

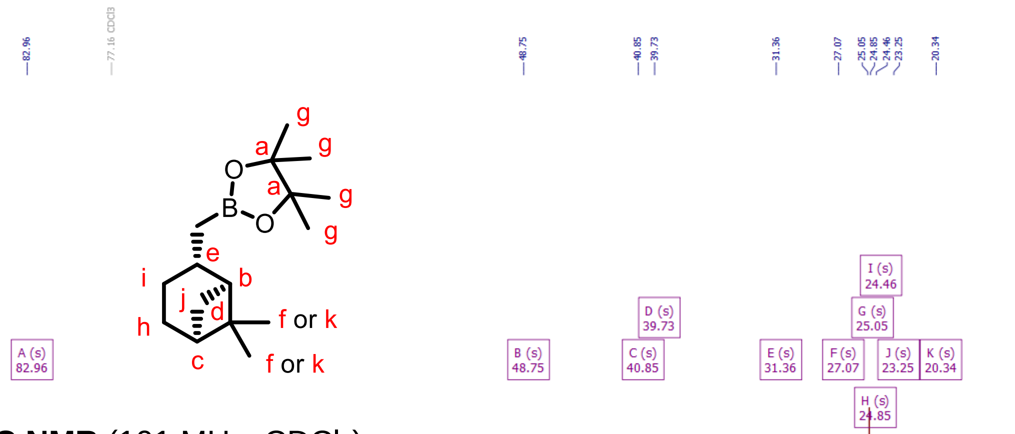


^{1}**H-**^{1}**H COSY** ((400, 400) MHz, $CDCl_3$)

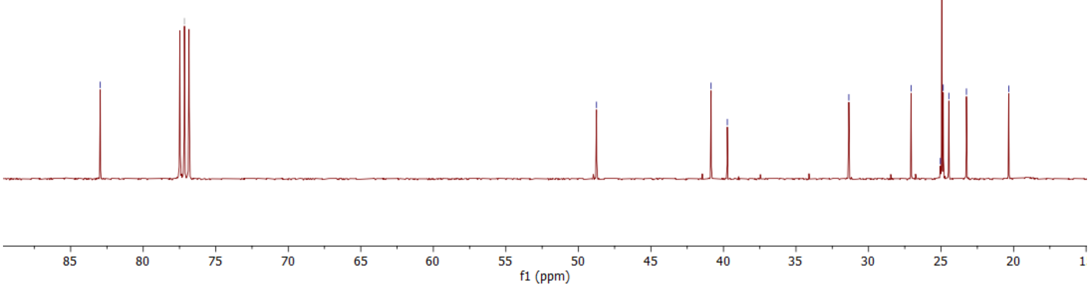


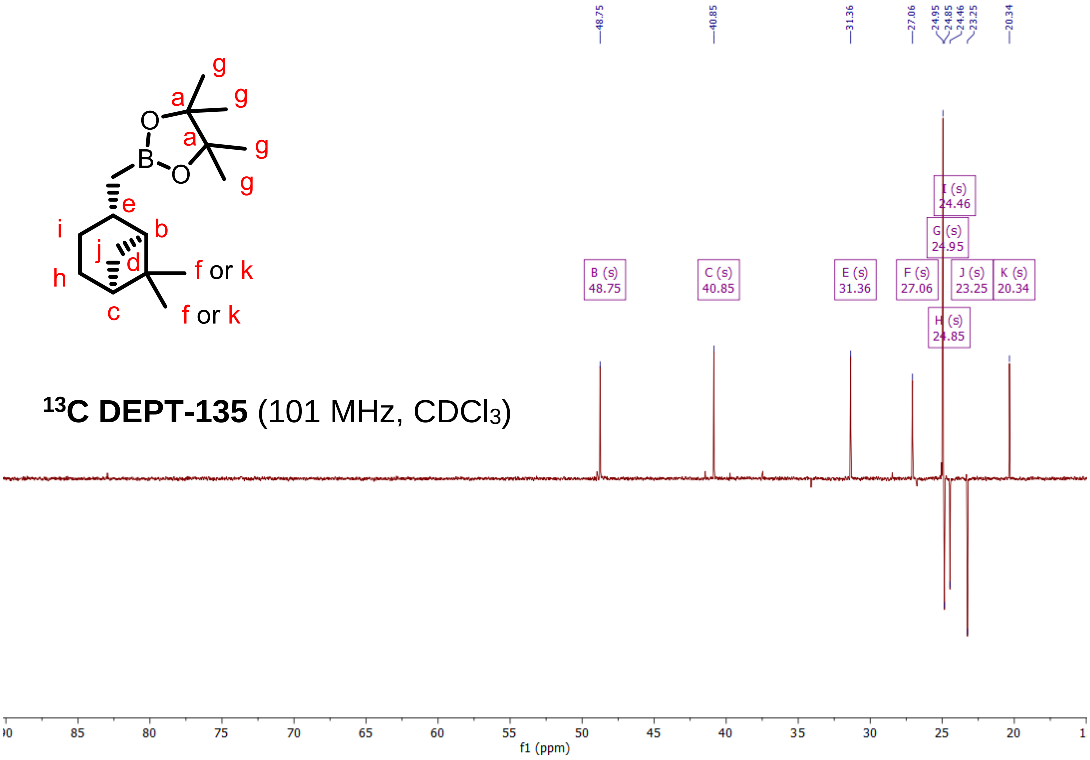
[11]B NMR (128 MHz, $CDCl_3$)



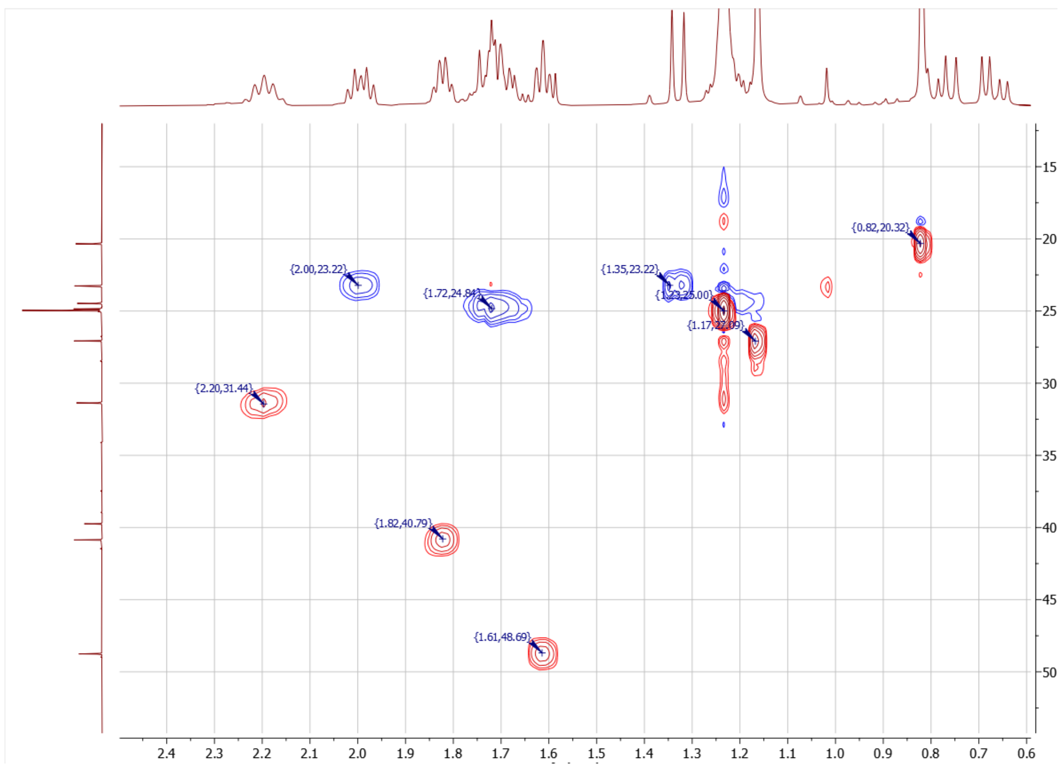


[13]C NMR (101 MHz, $CDCl_3$)

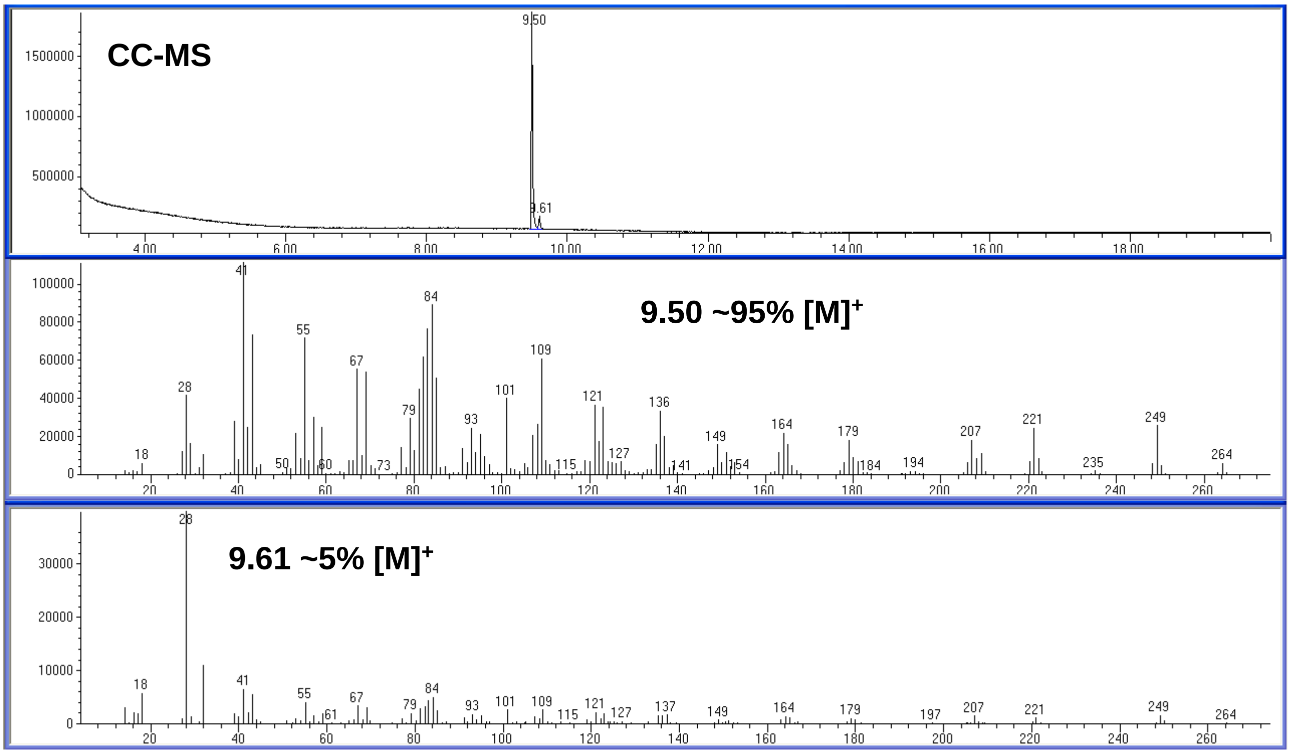




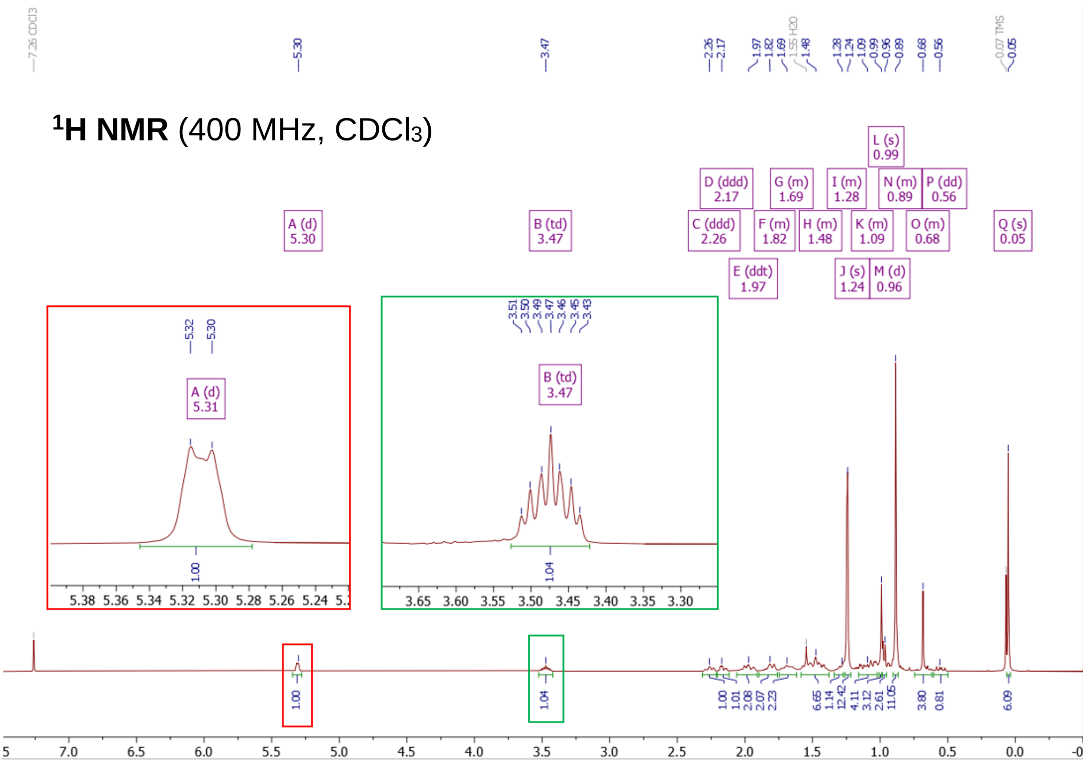
^{13}C DEPT-135 (101 MHz, $CDCl_3$)

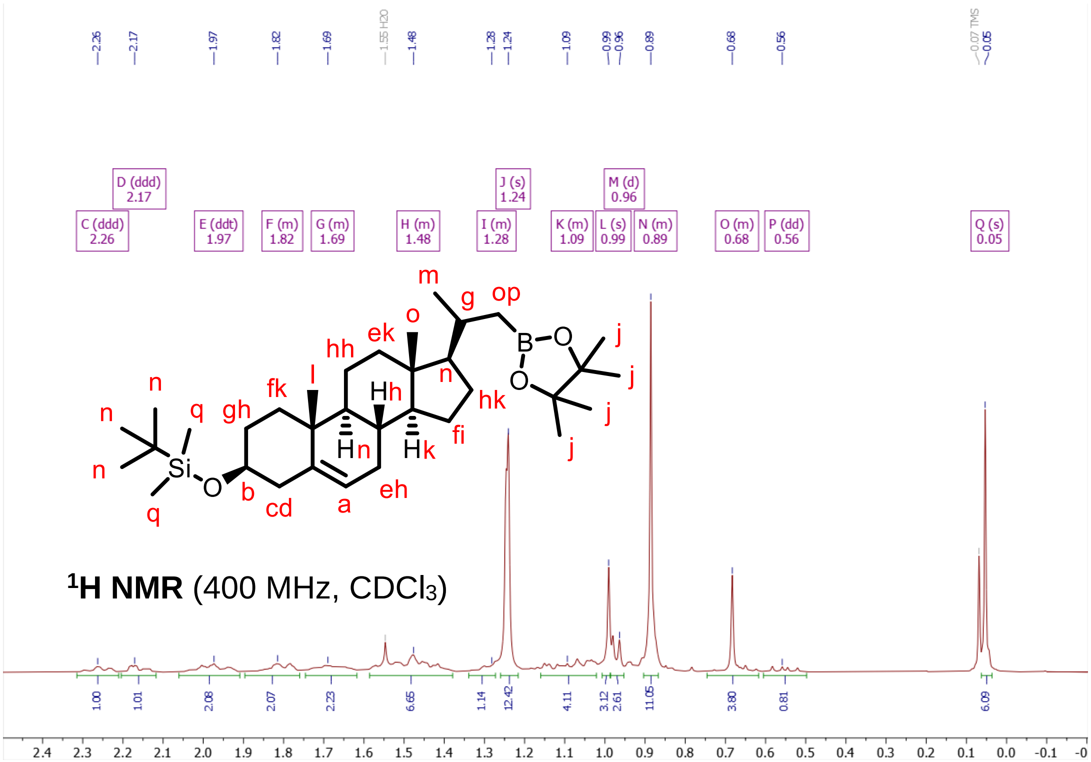


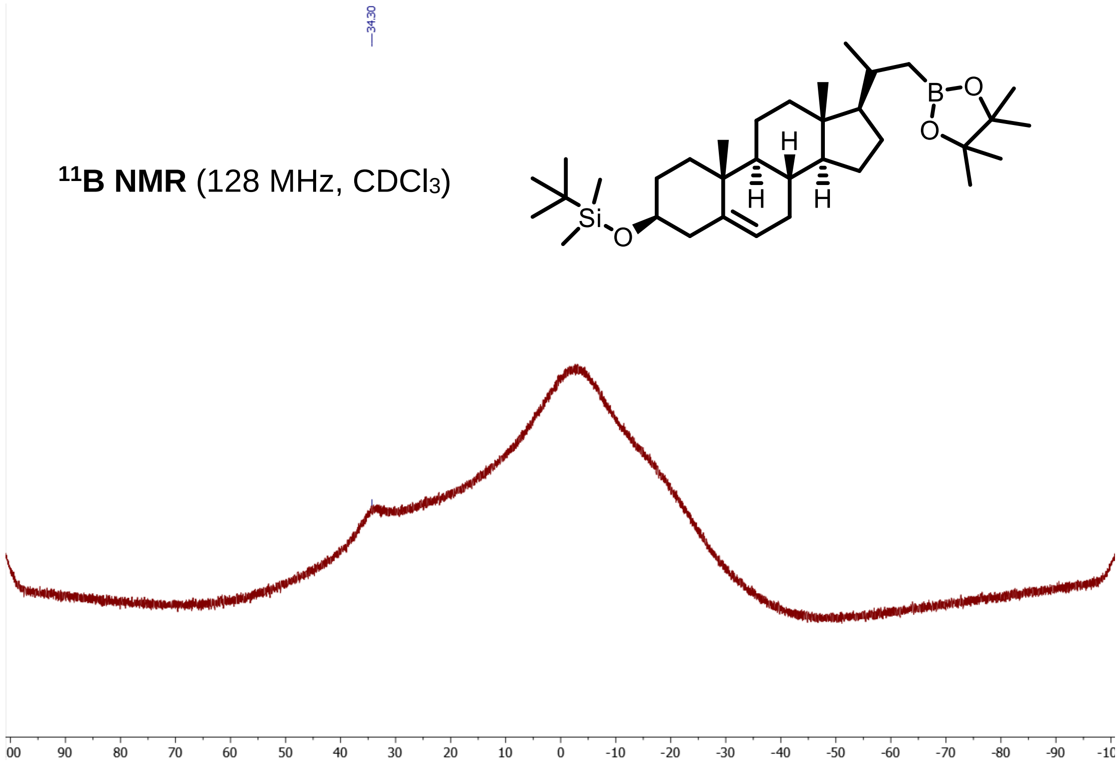
^{1}H-^{13}C HSQC ((400, 101) MHz, $CDCl_3$)


CC-MS
9.50
9.61
9.50 ~95% [M]+
9.61 ~5% [M]+

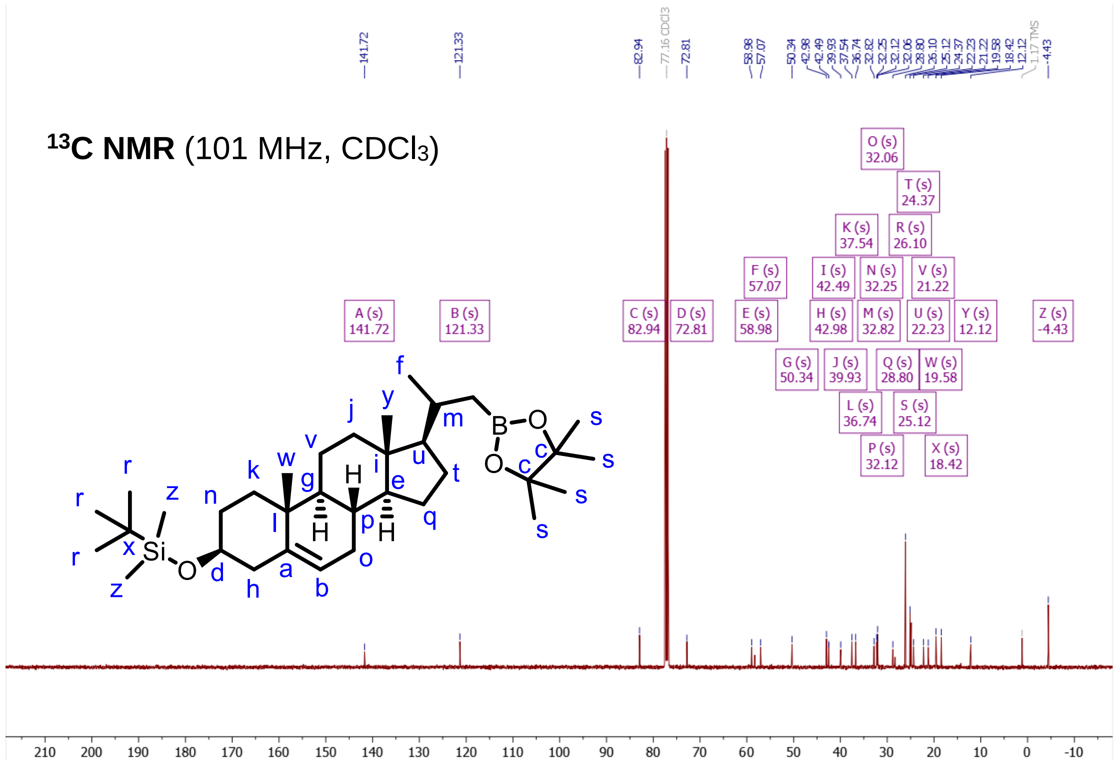
tert-butyl(((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)dimethylsilane (5)





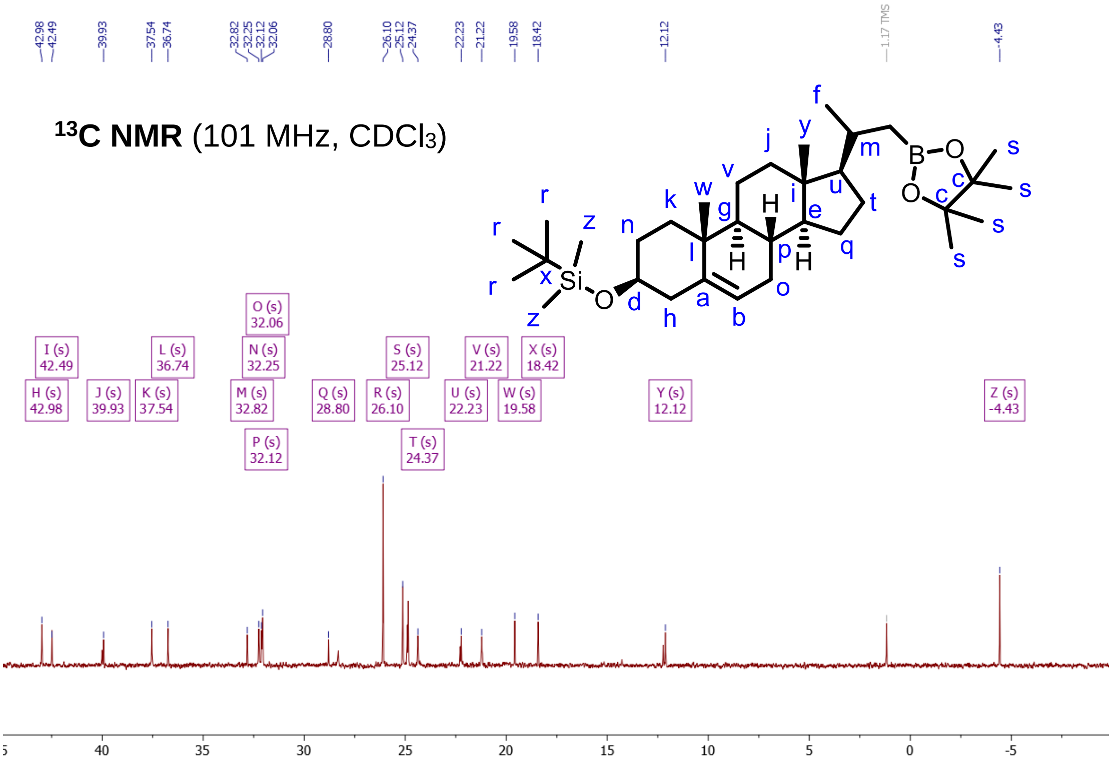


11B NMR (128 MHz, CDCl3)
34.30

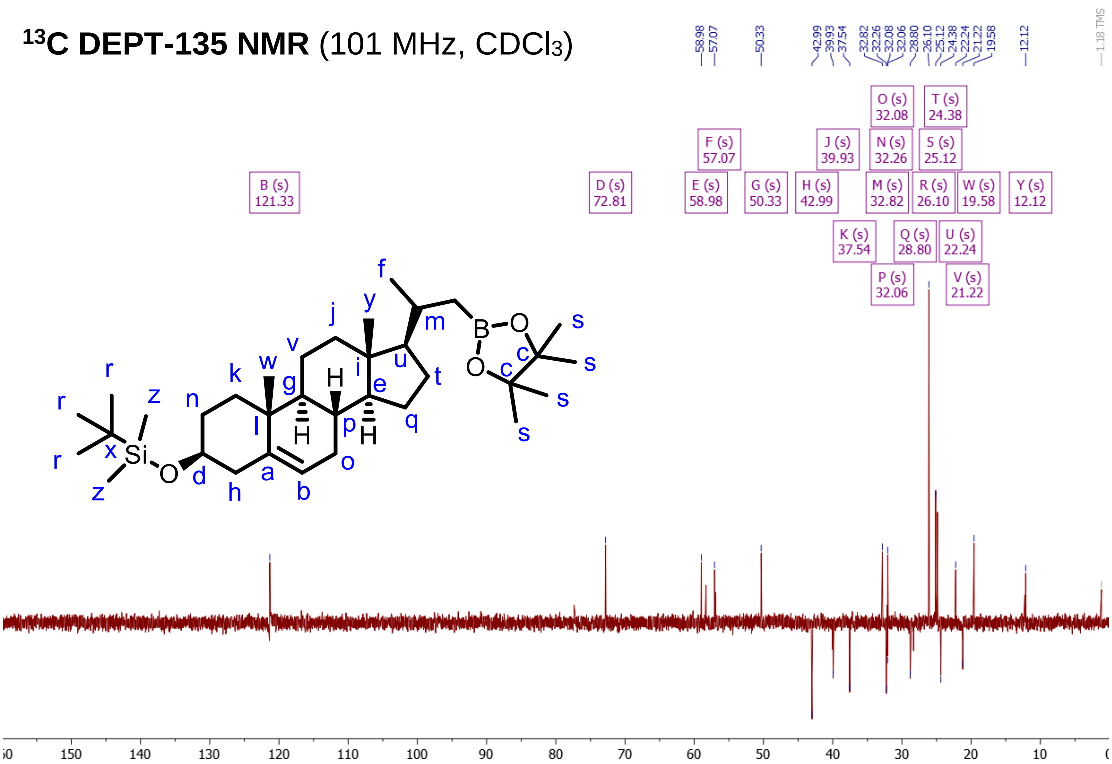


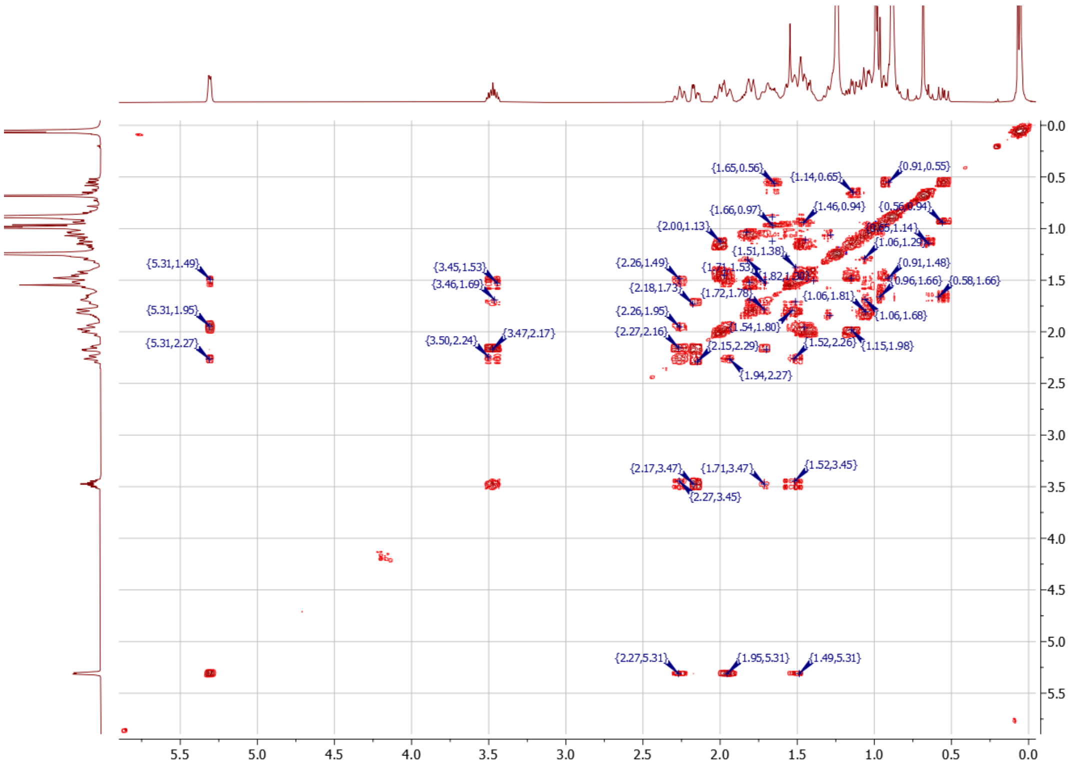
13C NMR (101 MHz, CDCl3)
141.72
121.33
82.94
77.16 CDCl3
72.81
58.98
57.07
50.34
42.98
42.49
39.93
37.54
36.74
32.82
32.25
32.12
32.06
28.80
26.10
25.12
24.37
22.23
21.22
19.58
18.42
12.12
1.17 TMS
-4.43

13C NMR (101 MHz, CDCl3)

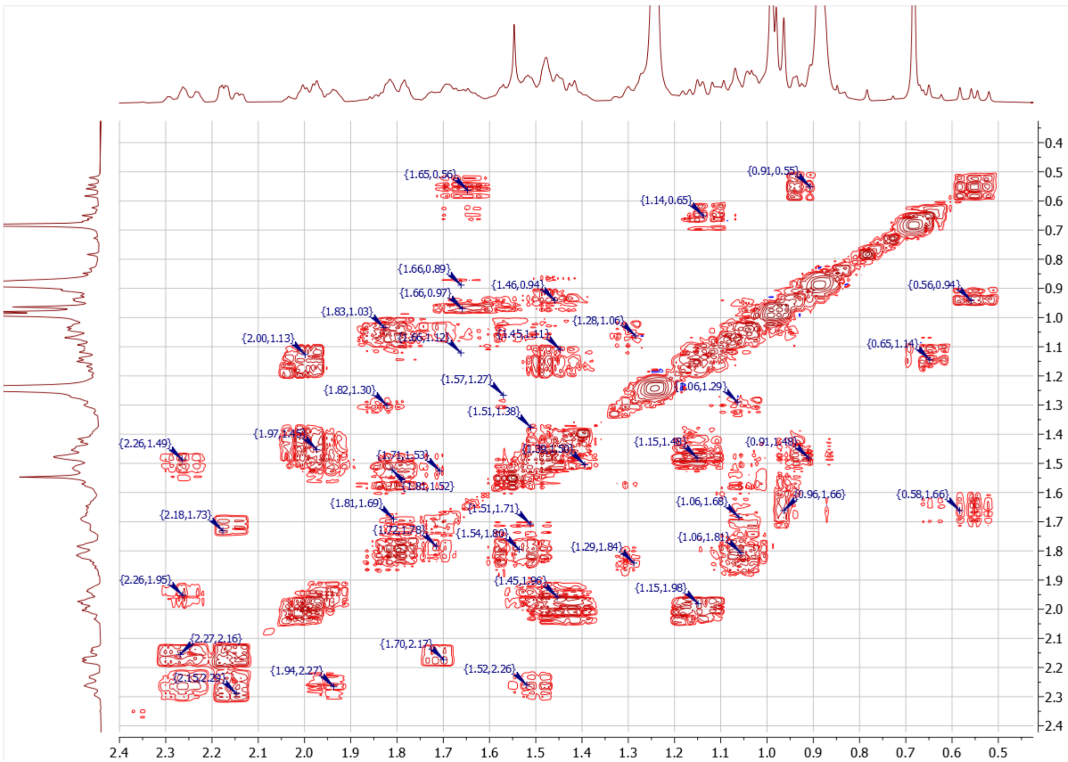


13C DEPT-135 NMR (101 MHz, CDCl3)

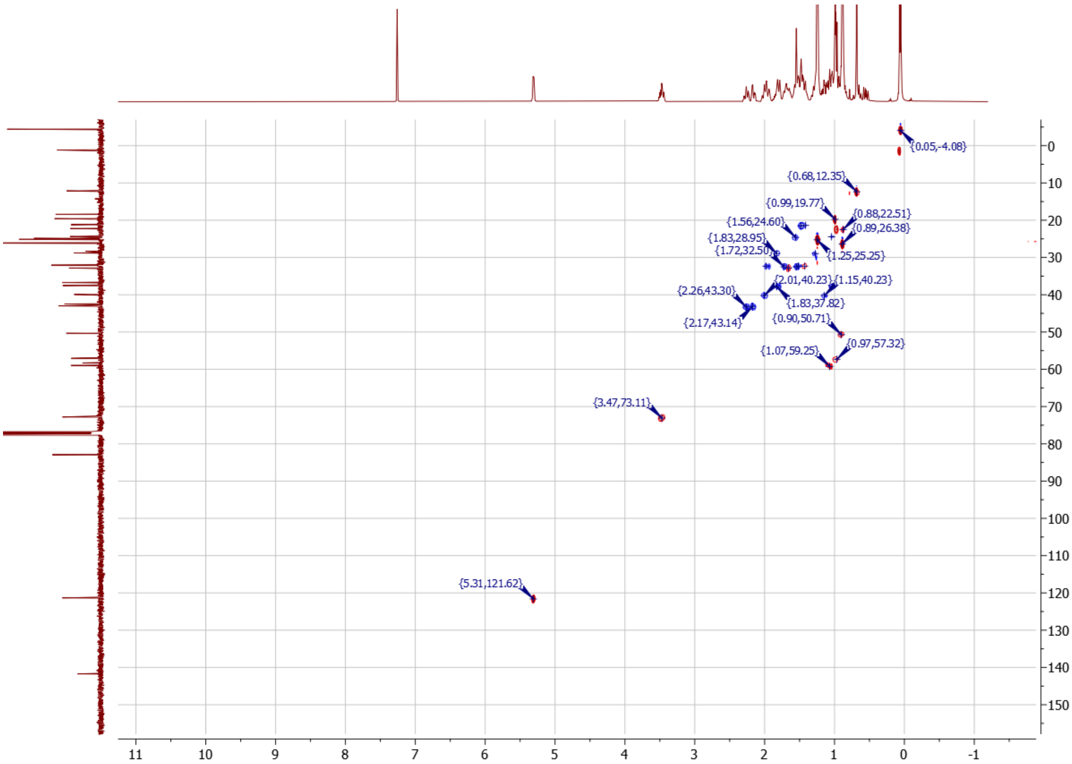




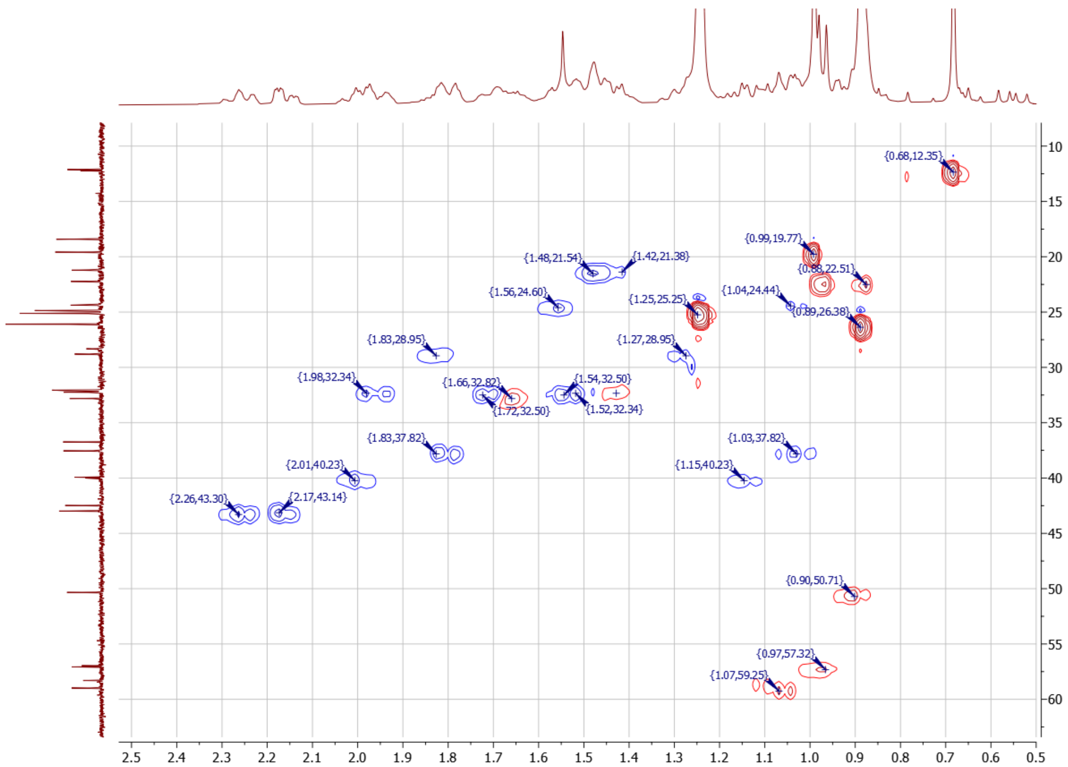
^{1}H-^{1}H COSY ((400, 400) MHz, $CDCl_3$)



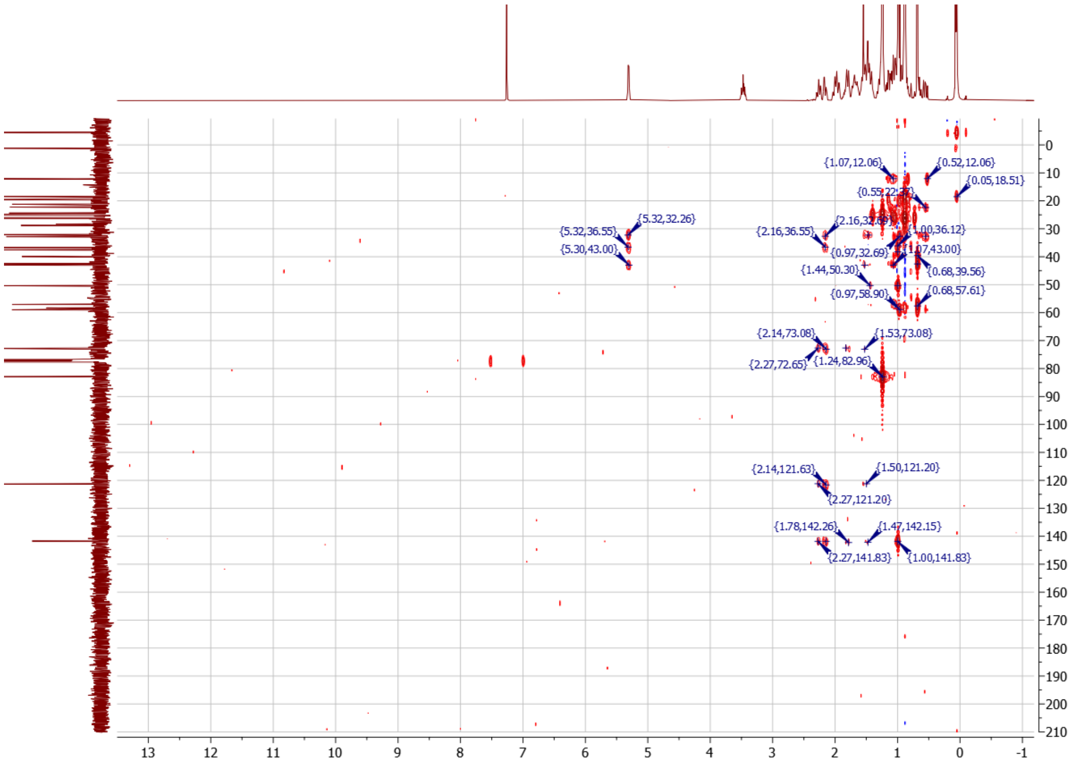
^{1}H-^{1}H COSY ((400, 400) MHz, $CDCl_3$)



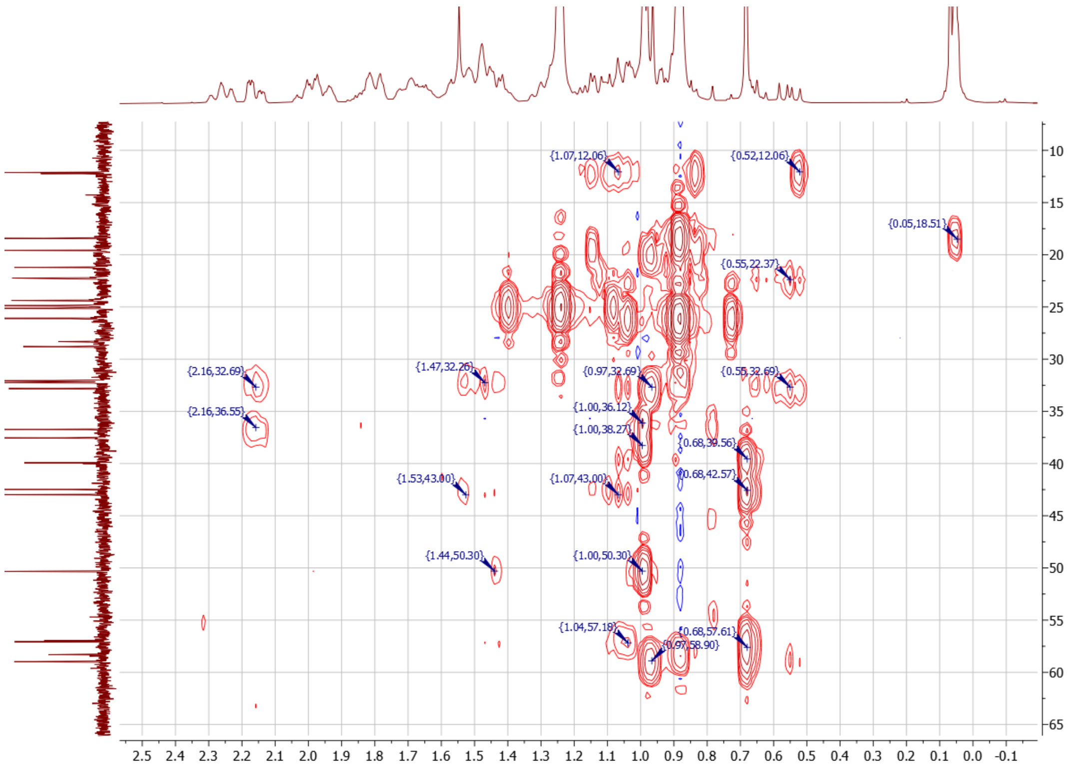
[1]H-[13]C HSQC ((400, 101) MHz, $CDCl_3$)



[1]H-[13]C HSQC ((400, 101) MHz, $CDCl_3$)



^{1}H-^{13}C HMBC ((400, 101) MHz, $CDCl_3$)



^{1}H-^{13}C HMBC ((400, 101) MHz, $CDCl_3$)

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