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Supporting Information

for

Pyridylpyrrolido ligand in Ge(II) and Sn(II) chemistry: synthesis, reactivity and catalytic application

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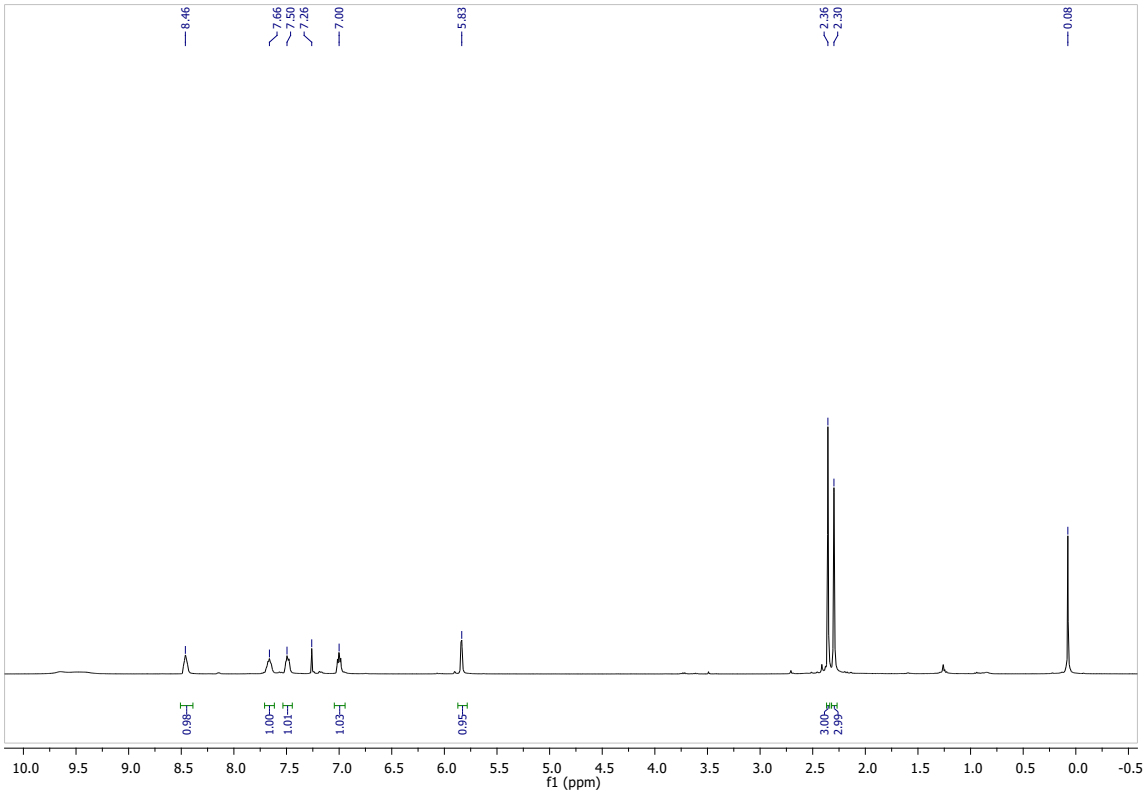
1. General Experimental Information. All experiments including NMR sample preparation were carried out under an inert atmosphere of argon applying standard Schlenk techniques or in a Glove box. The solvents used were purified by an MBRAUN solvent purification system as MB SPS-800. All chemicals purchased from Sigma Aldrich were used without further purification. Ligand **L**[S1] was prepared according to the previously reported literature procedure. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded in C_6D_6 or $CDCl_3$ using a Bruker Avance DPX 200 or a Bruker Avance DRX 500 spectrometer and were referenced to external $SiMe_4$. HRMS and LC-mass spectra were obtained using an Agilent Technologies 6120. Melting points were measured in a sealed glass tube on a Stuart SMP-30 melting point apparatus and were uncorrected.

2. High yield synthesis of compound B. A solution of *n*-BuLi (7.25 mL, 14.51 mmol, 2M) in *n*–hexane was added drop by drop to a stirred solution of 2-(3,5-dimethyl-1H-pyrrol-2-yl)pyridine (2.0 g, 11.61 mmol, in THF 20 mL) at –78 °C over a period of 20 min. The suspension was allowed to warm up to room temperature and stirred for 6 h. Next, the THF (20 mL) solution of $GeCl_2$·dioxane (2.82 g, 12.19 mmol) was added drop by drop to the above suspension at –30 °C via cannula. The reaction mixture was further warmed to room temperature and stirred for another 15 h. Subsequently, all volatiles were removed in vacuo and the residue was extracted with toluene (30 mL). The resultant toluene solvent was concentrated to 10–12 mL and stored at –30 °C in a freezer, which afforded yellow crystals of **B** within one day. Yield: 3.04 g (93.8%). All the spectroscopic data have already been reported.[S2]

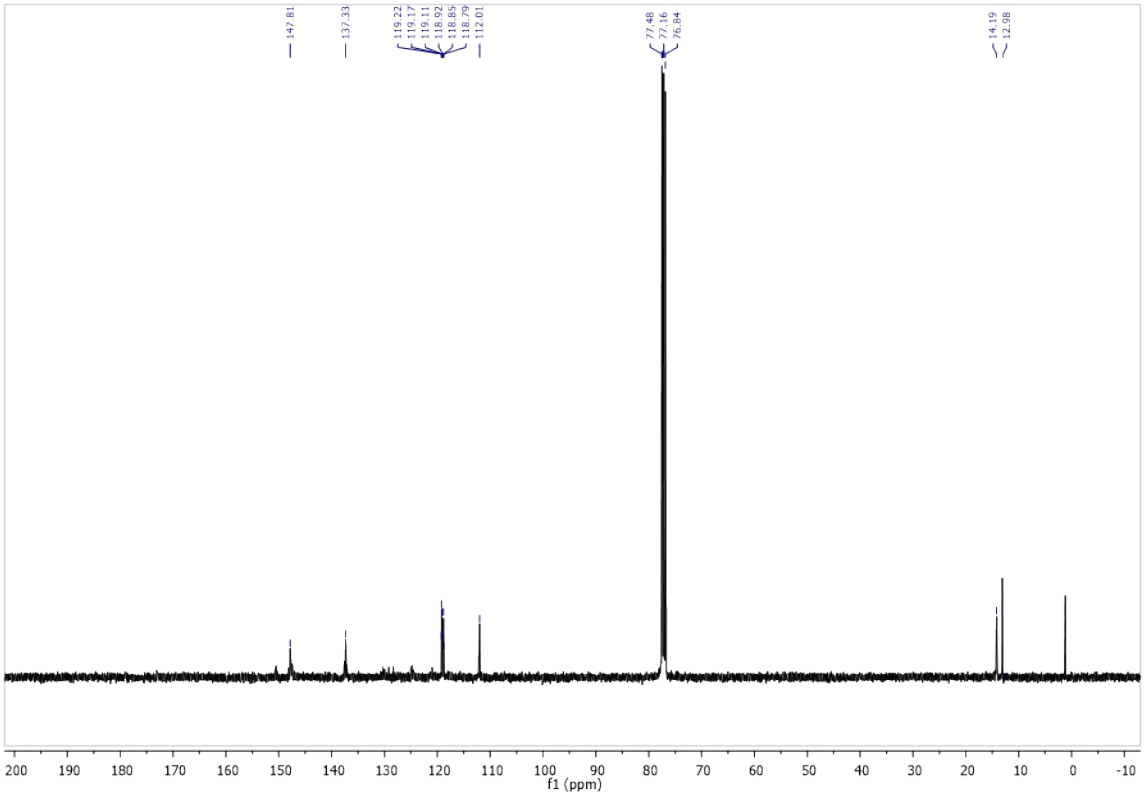
3. Synthesis of compound 1. A solution of $SnCl_2$ (0.70 g, 3.65 mmol) in THF (20 mL) was added drop by drop to a stirred solution of **B** (1.0 g, 3.58 mmol, in THF 20 mL) at –78 °C, over a period of 20 min. The suspension was allowed to warm up to room temperature and stirred for 15 h. Subsequently, all volatiles were removed in vacuo and the residue was

extracted with THF (30 mL). The resultant THF solvent was concentrated to 8-10 mL and stored at –30 °C in a freezer, which afforded yellow crystals of **1**. Yield: 0.998 g (86%). M.p.: 213.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.46 (s, 1H), 7.66 (s, 1H), 7.50 (s, 1H), 7.00 (s, 1H), 5.83 (s, 1H), 2.36 (s, 3H), 2.30 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ 147.81 (s), 137.33 (s), 119.42 (s), 119.17 (s), 119.11 (s), 118.92 (s), 118.85 (s), 118.79 (s), 112.01 (s), 14.19 (s), 12.98 (s) ppm. ^{119}Sn NMR (149 MHz, C_6D_6, 298 K): δ -151.86 ppm. HRMS: Calcd: 325.96, found: 325.9627.

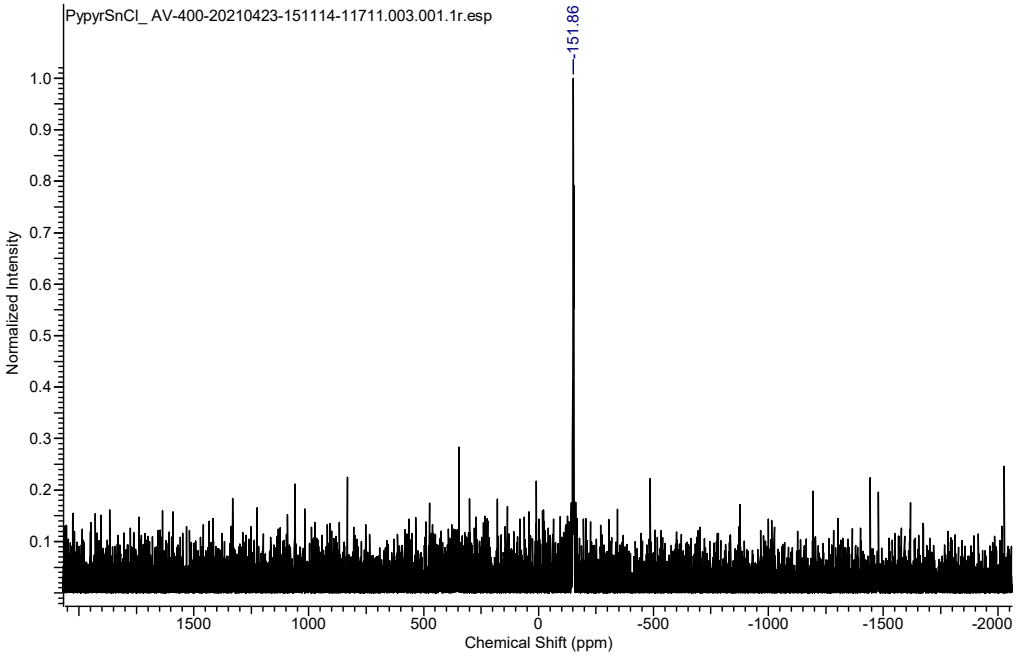
a) ^{1}H NMR of compound 1:



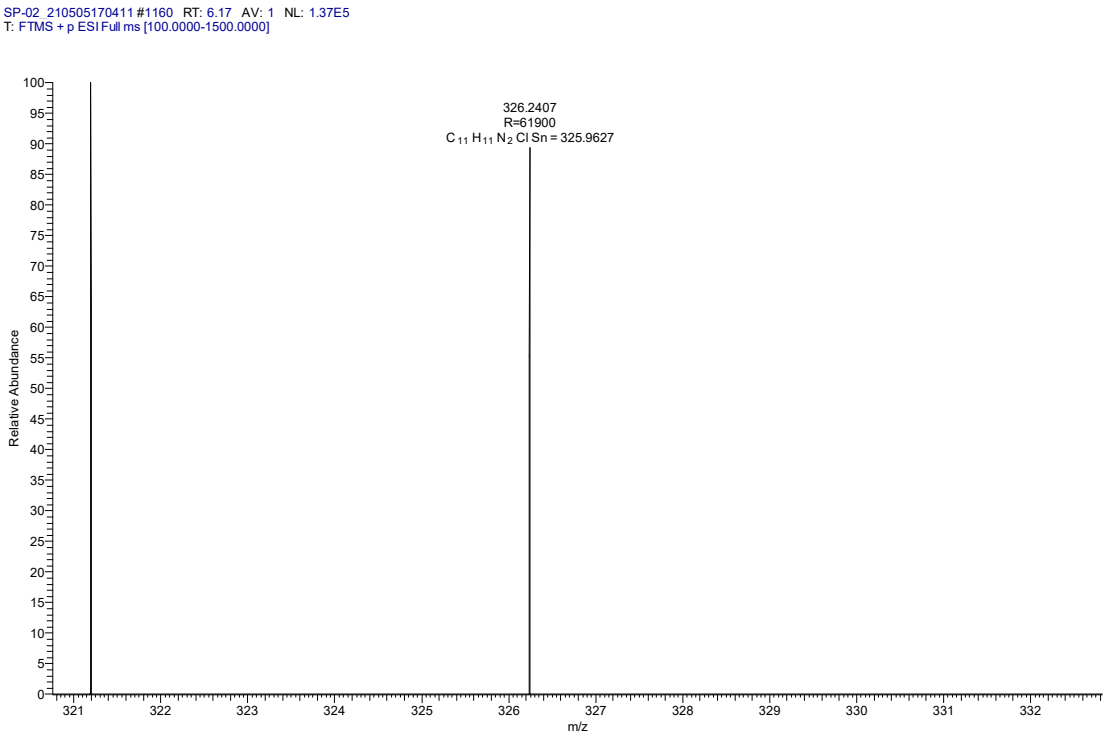
b) **^{13}C NMR of compound 1:**



c) **^{119}Sn NMR of compound 1:**

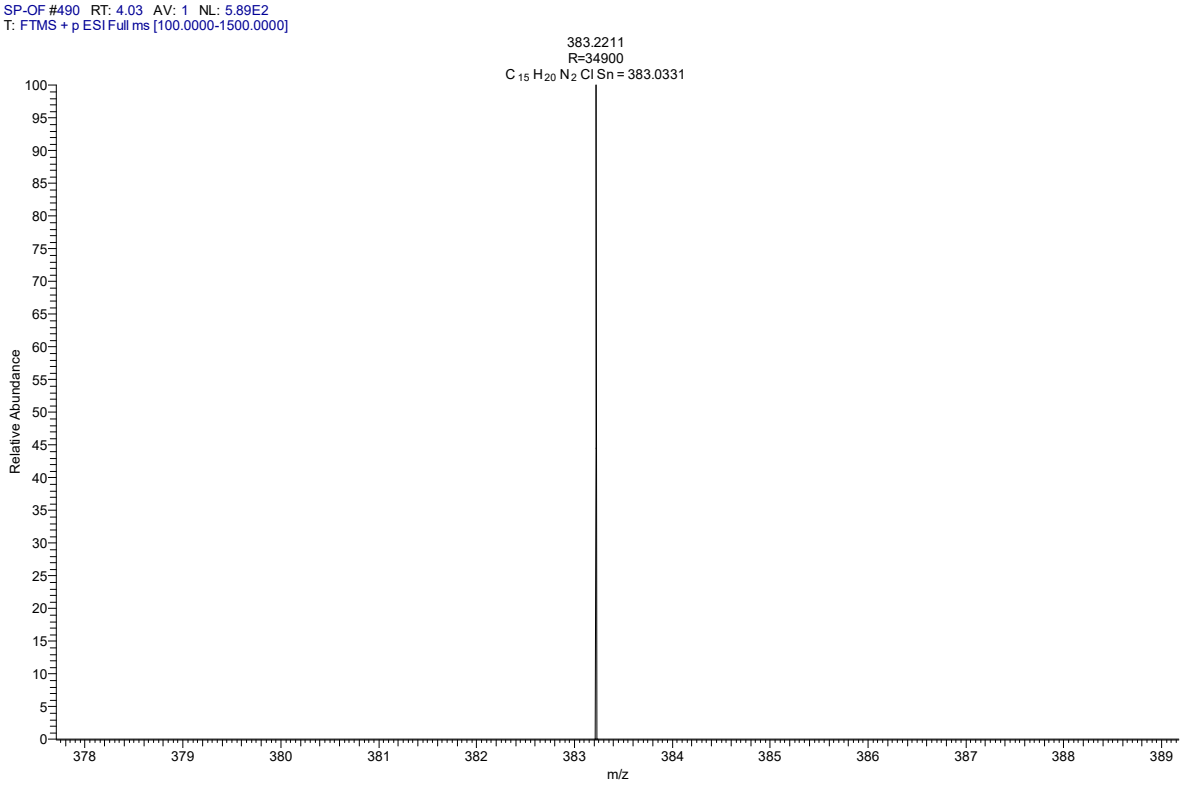


d) HRMS data of compound 1:



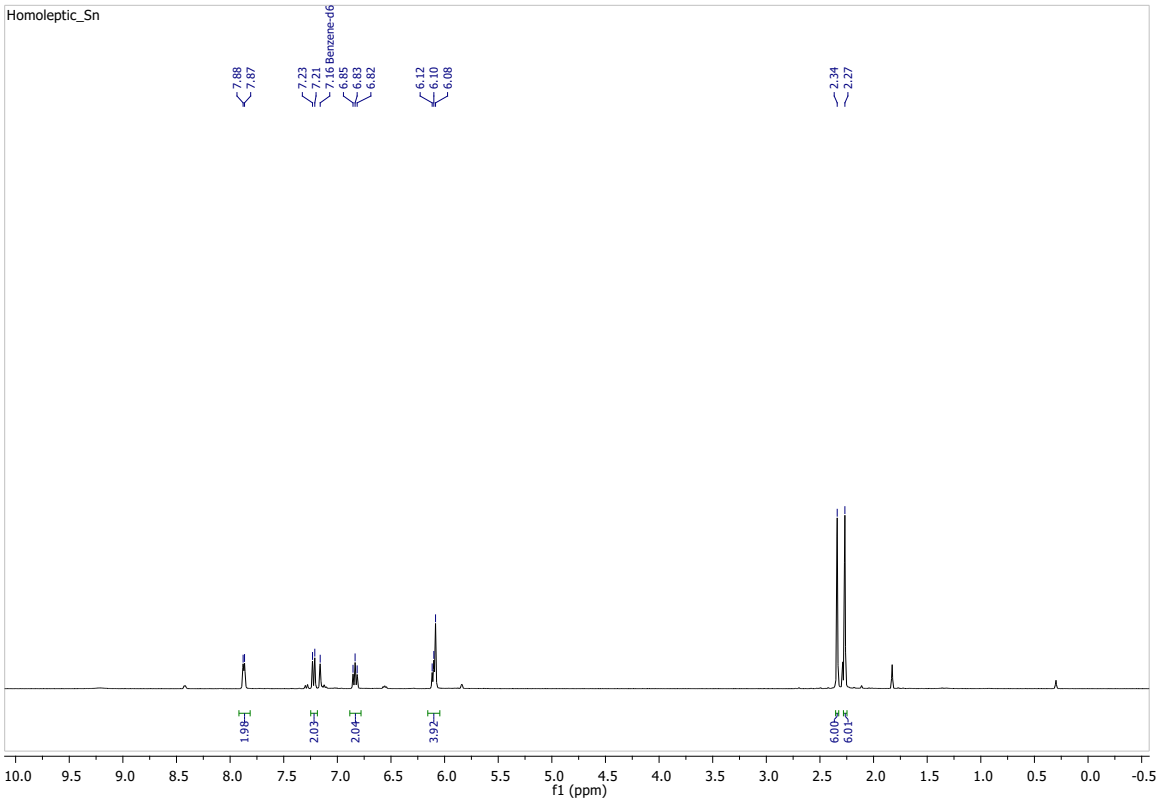
4. Synthesis of compound 2. A solution of *n*-BuLi in *n*–hexane (6.38 mL, 12.77 mmol, 2M, 1.1 equiv.) was added drop wise to a stirred solution of 2-(3,5-dimethyl-1H-pyrrol-2-yl)pyridine (2.0 g, 11.61 mmol, in THF 20 mL) at –78 °C, over a period of 20 min. The suspension was allowed to warm up to room temperature and stirred for 6 h. Next, the solution of $SnCl_2$ (2.31 g, 12.19 mmol) in THF was added drop by drop to the above suspension at –30 °C via cannula. The reaction mixture was further warmed to room temperature and stirred for another 15 h. Subsequently, all volatiles were removed in vacuo and the residue was extracted into toluene (30 mL). The resultant toluene solvent was concentrated to 10–12 mL and stored at –30 °C in a freezer, which afforded yellow crystals of **1** and **2** within one day in the same flask. HRMS: Calcd: 382.03, found: 383.0331.

a) HRMS data of compound 2:

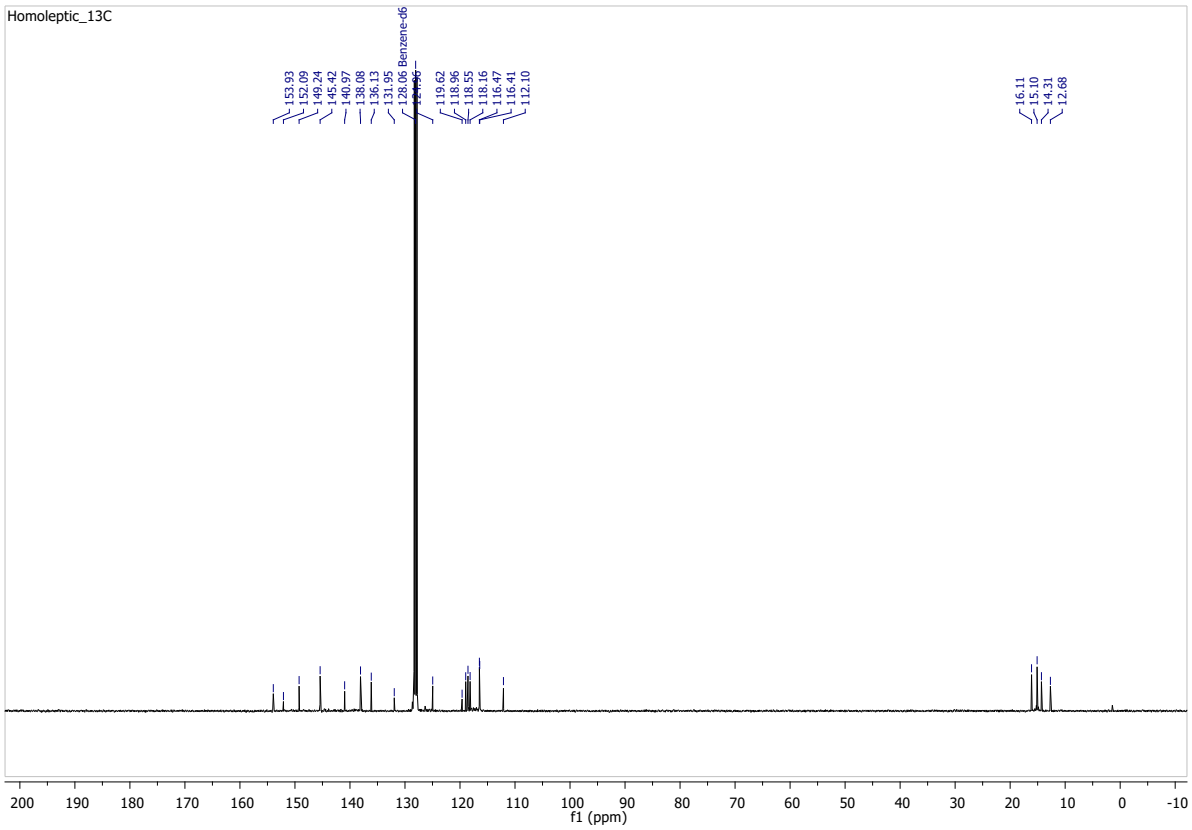


5. Synthesis of compound 3. A solution of potassium tert-butoxide (72.42 mg, 0.645mmol in 10 mL toluene) was added to a solution of compound **2** (200 mg, 0.614 mmol in 15 mL toluene) at -78 °C over a period of 10 min and the reaction mixture was allowed to warm up to room temperature and further stirred for 15 h. Subsequently, all volatiles were removed in vacuo and the residue was extracted into toluene (15 mL). The resultant toluene was concentrated to 5-8 mL and stored at –30 °C in a freezer, which afforded colorless crystals of **3** within one day. Yield: 0.257 g (90.8%). M.p.: 164.6 °C. ^{1}H NMR (400 MHz, C_6D_6, 298 K): 7.87 (d, 2H), 7.22 (d, 2H), 6.83 (t, 2H), 6.12 – 6.08 (m, 4H), 2.34 (s, 6H), 2.27 (s, 6H) ppm. ^{13}C NMR (100.56 MHz, C_6D_6, 298 K); δ 153.93 (s), 152.09 (s), 149.24 (s), 145.42 (s), 140.97 (s), 138.08 (s), 136.13 (s), 131.95 (s), 124.96 (s), 119.62 (s), 118.96 (s), 118.55 (s), 118.16 (s), 116.47 (s), 116.41 (s), 112.10 (s), 16.11 (s), 15.10 (s), 14.31 (s), 12.68 (s) ppm. HRMS: Calcd: 462.09, found: 463.2427.

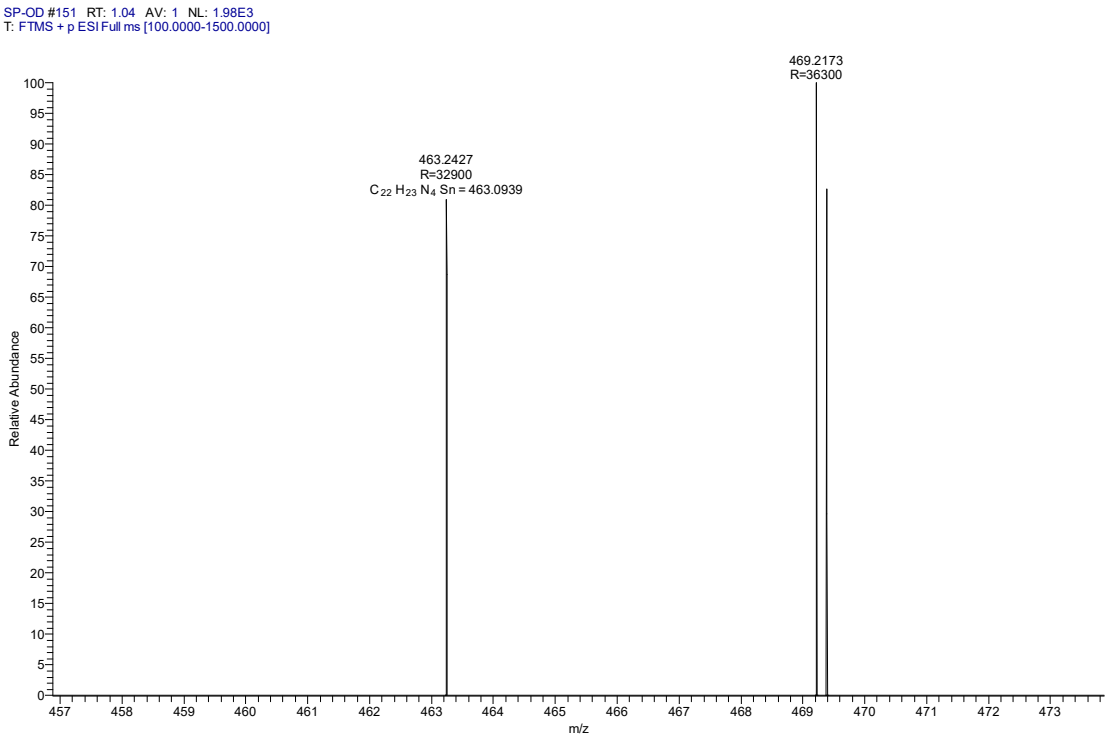
a) ^{1}H NMR of compound 3:



b) ^{13}C NMR of compound 3:

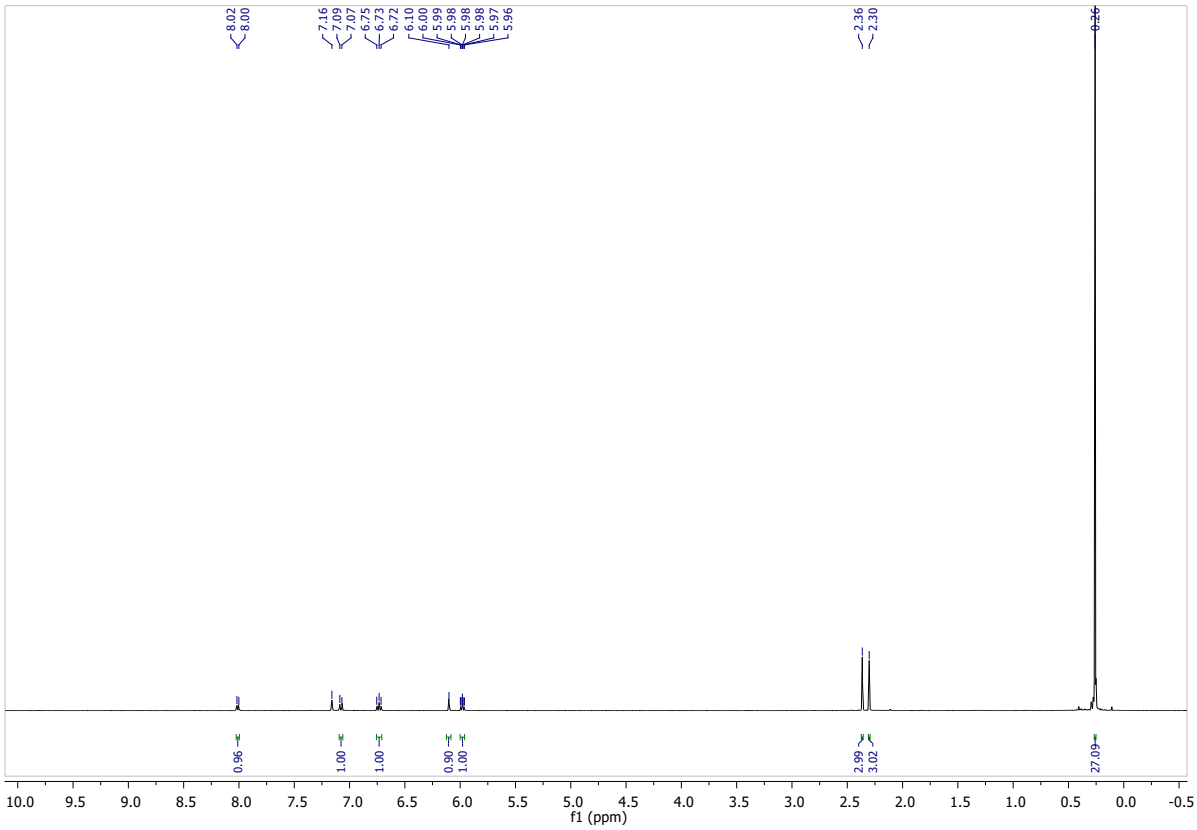


c) HRMS data of compound 3:

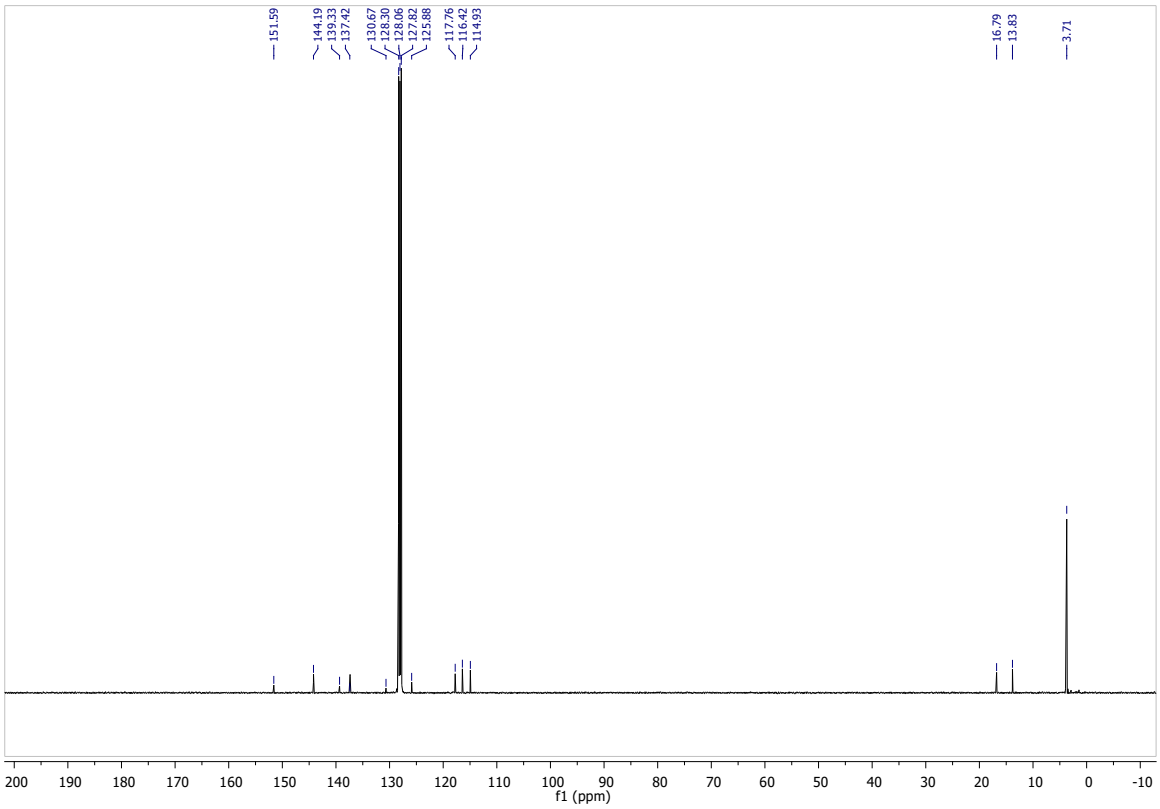


6. Synthesis of compound 4. A solution of potassium tris(trimethylsilyl)silane (324.38 mg, 0.753 mmol in 10 mL toluene) was added to a solution of compound **B** (200 mg, 0.717 mmol in 15 mL toluene) at -78 °C over a period of 15 min and the color changes slowly from pale yellow to deep red. Then the reaction mixture was allowed to warm up to room temperature and further stirred for 12 h. Subsequently, all volatiles were removed in vacuo and the residue was extracted into toluene (15 mL). The resultant toluene was concentrated to 5-8 mL and stored at –30 °C in a freezer, which afforded colorless crystals of **4** within two-three days. Yield: 330 mg (93.5 %). M.p.: 128.3 °C. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 8.01 (d, 1H), 7.08 (d, 1H), 6.73 (t, 1H), 6.10 (s, 1H), 5.98 (dt, 1H), 2.36 (s, 3H), 2.30 (s, 3H), 0.26 (s, 27H) ppm. ^{13}C NMR (100.56 MHz, C_6D_6, 298 K): δ 151.59 (s), 144.19 (s), 139.33 (s), 137.42 (s), 130.67 (s), 125.88 (s), 117.76 (s), 116.42 (s), 114.93 (s), 16.79 (s), 13.83 (s), 3.71 (s) ppm. ^{29}Si CP/MAS NMR (298 K): δ -105.84 (*Si*(SiMe$_3$)), -8.27 (Si(*Si*Me$_3$)) ppm. HRMS: Calcd: 492.13, found: 493.3547.

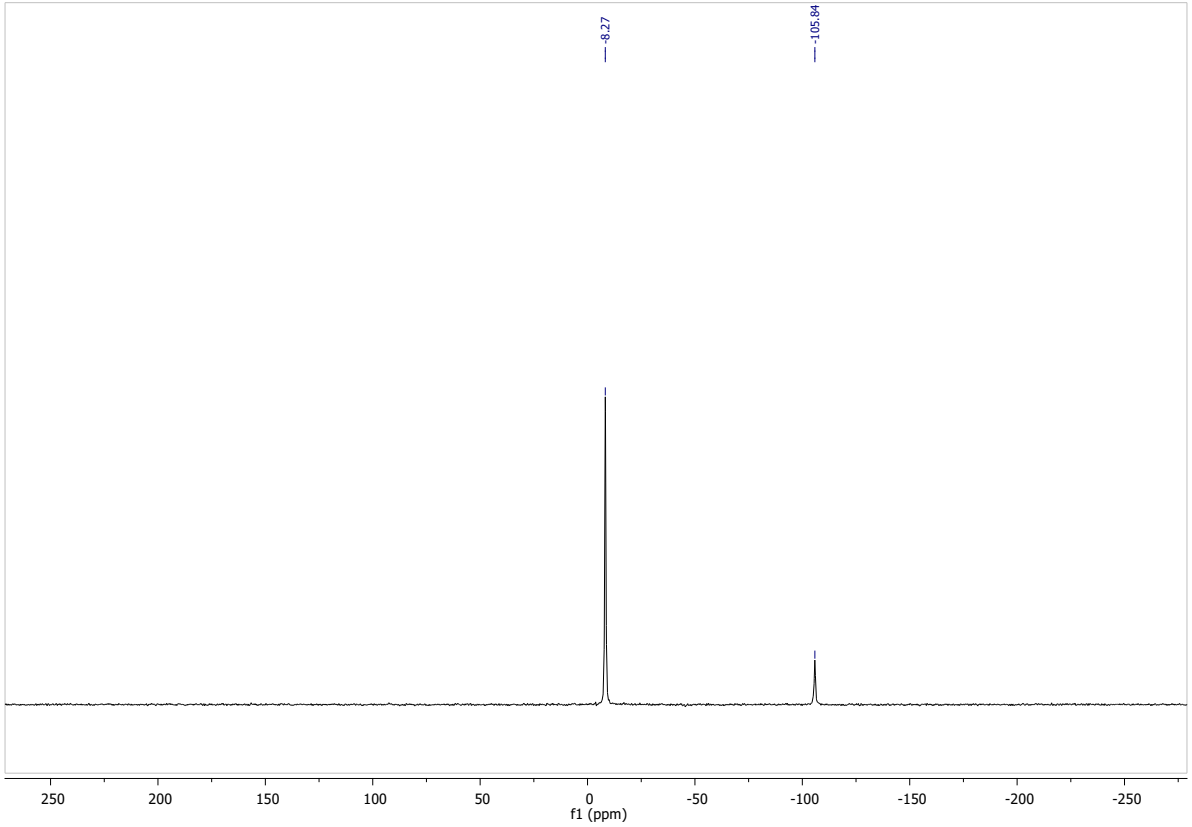
a) **^{1}H NMR of compound 4:**



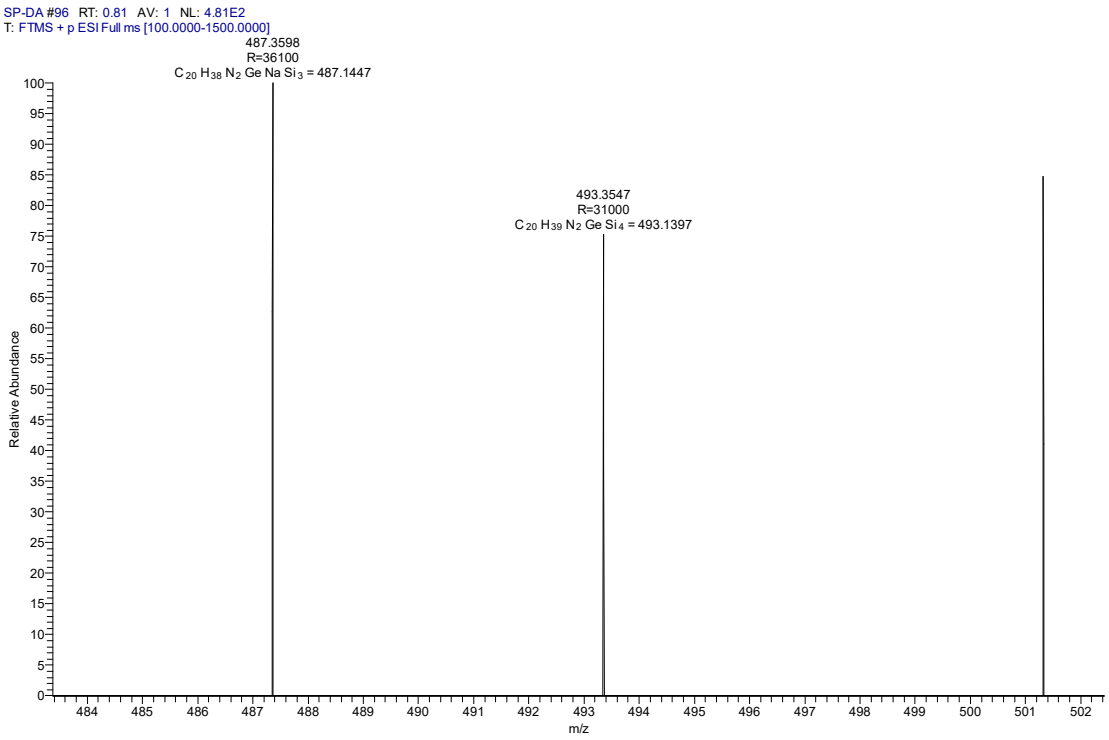
b) **^{13}C NMR of compound 4:**



c) Solid state ^{29}Si NMR (CP/MAS) of compound 4:

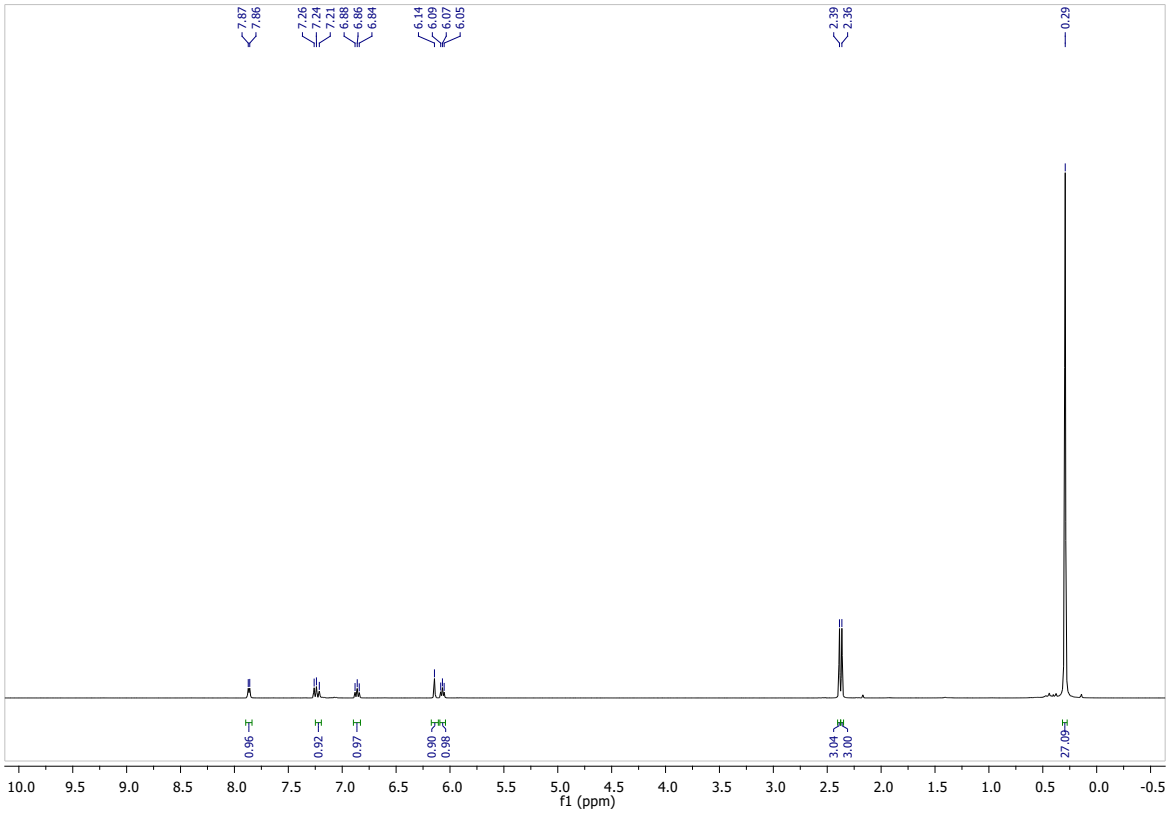


d) HRMS data of compound 4:

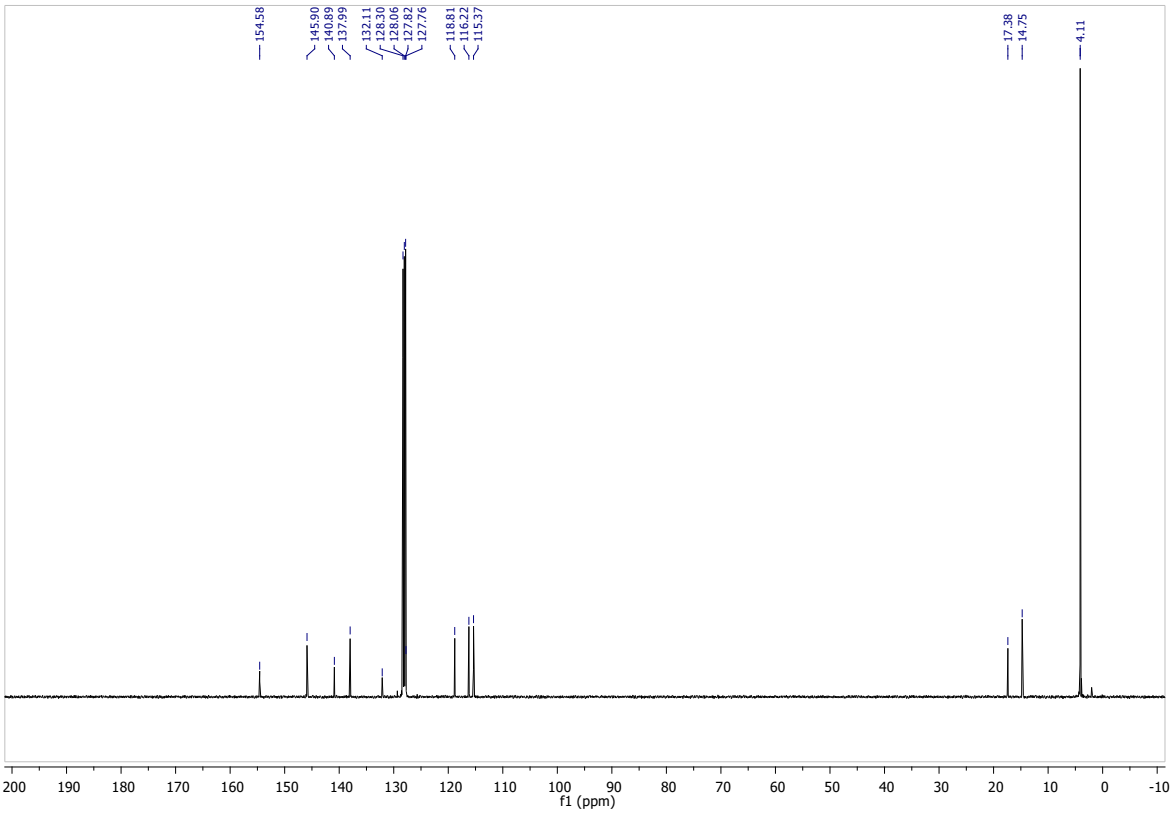


7. Synthesis of compound 5. A solution of potassium tris(trimethylsilyl)silane (277.97 mg, 0.645mmol in 10 mL toluene) was added to a solution of compound **2** (200 mg, 0.614 mmol in 15 mL toluene) at -78 °C over a period of 15-20 min and the reaction mixture was allowed to warm up to room temperature. The color of the reaction mixture changes slowly from yellow to deep red. Further, the reaction was stirred for additional 12 h. Subsequently, all volatiles were removed in vacuo and the residue was extracted into toluene (15 mL). The resultant toluene solvent was concentrated to 5-8 mL and stored at –30 °C in a freezer, which afforded colorless crystals of **5** within two days. Yield: 312 mg (94.5%). M.p.: 138.9 °C. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 7.86 (d, 1H), 7.23 (d, 1H), 6.86 (t, 1H), 6.14 (s, 1H), 6.07 (t, 1H), 2.39 (s, 3H), 2.36 (s, 3H), 0.29 (s, 27H) ppm. ^{13}C NMR (100.56 MHz, C_6D_6, 298 K): δ 154.58 (s), 145.90 (s), 140.89 (s), 137.99 (s), 132.11 (s), 128.30 (s), 127.76 (s), 118.81 (s), 116.22 (s), 115.37 (s), 17.38 (s), 14.75 (s), 4.11 (s) ppm. ^{29}Si CP/MAS NMR (298 K): δ -99.86(*Si*($SiMe_3$)), -6.28 (Si(*Si*Me_3)) ppm. HRMS: Calcd: 538.11, found: 539.032.

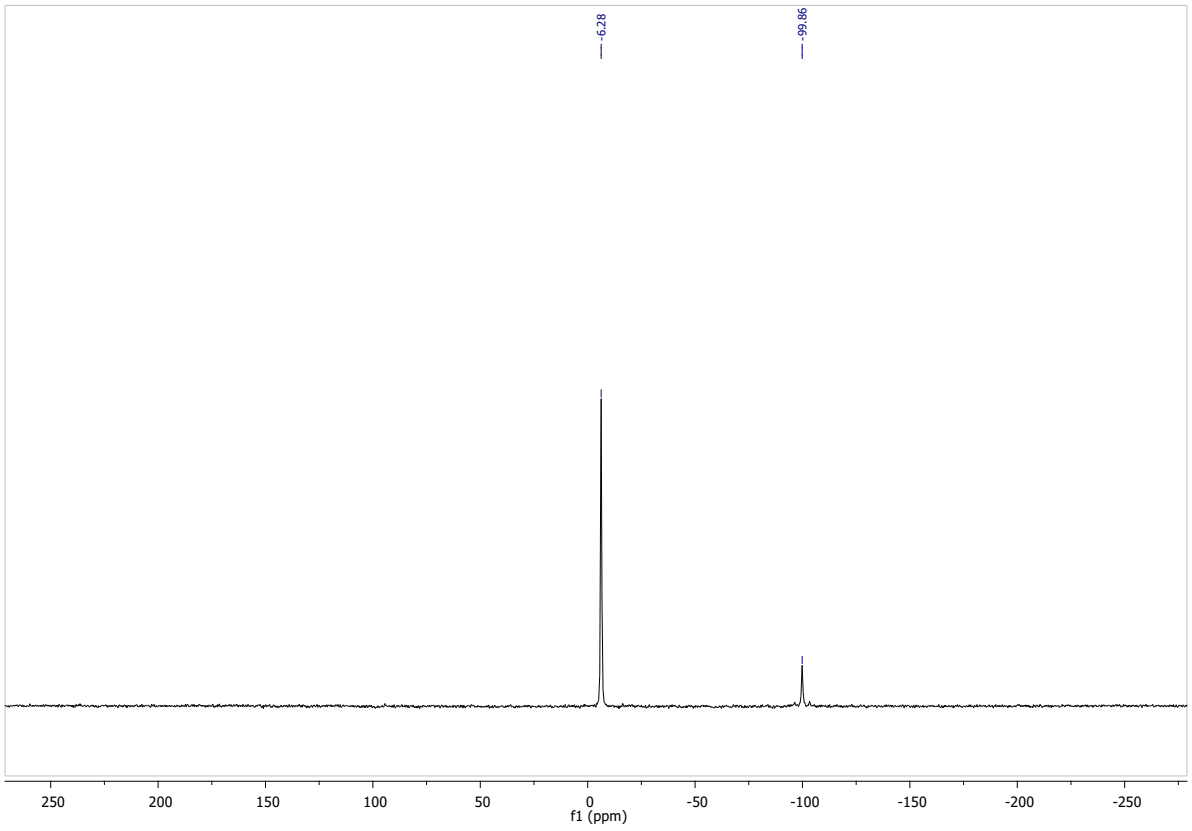
a) ^{1}H NMR of compound 5:



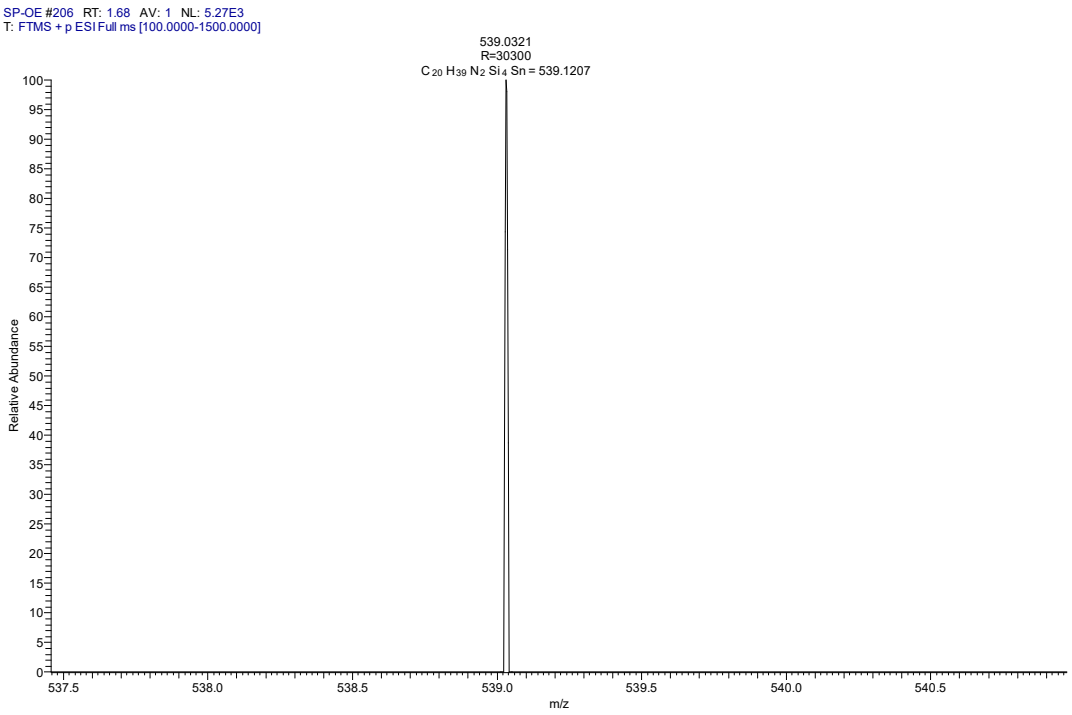
b) ^{13}C NMR of compound 5:



c) Solid state ^{29}Si NMR (CP/MAS) of compound 5:

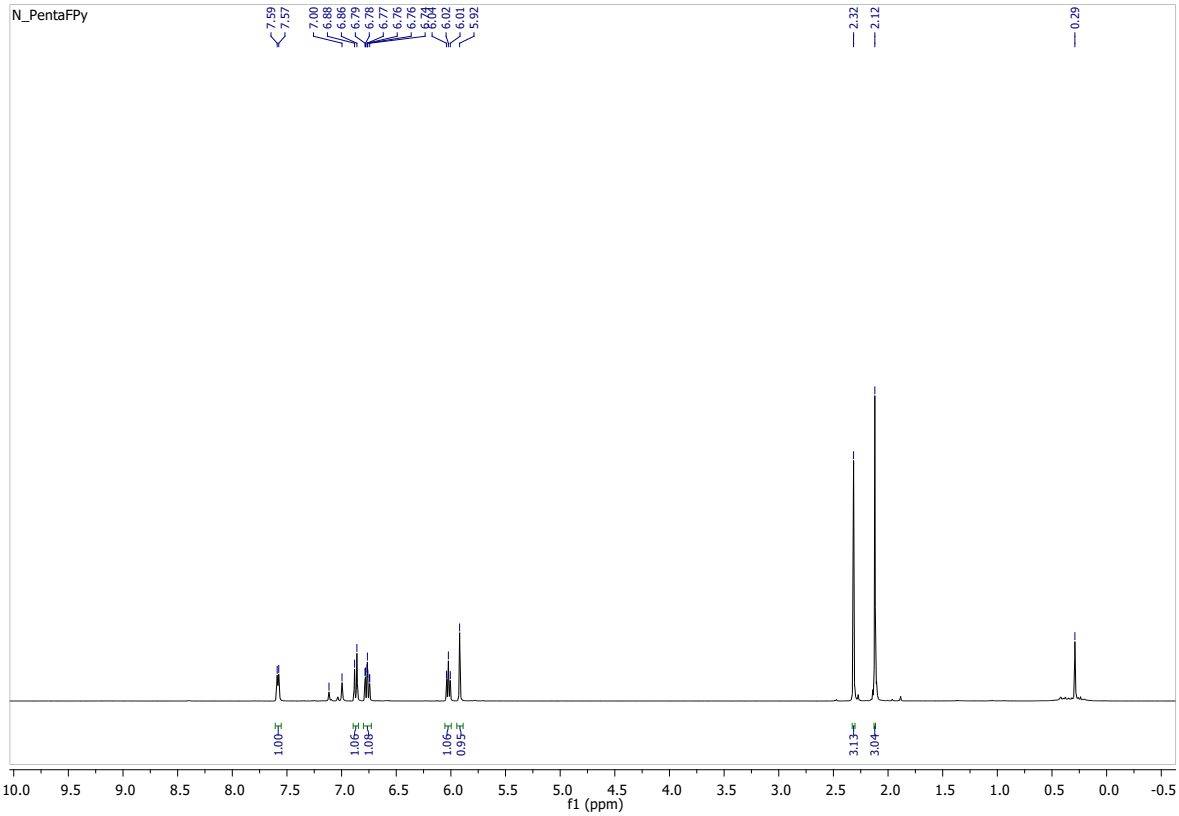


d) HRMS data of compound 5:

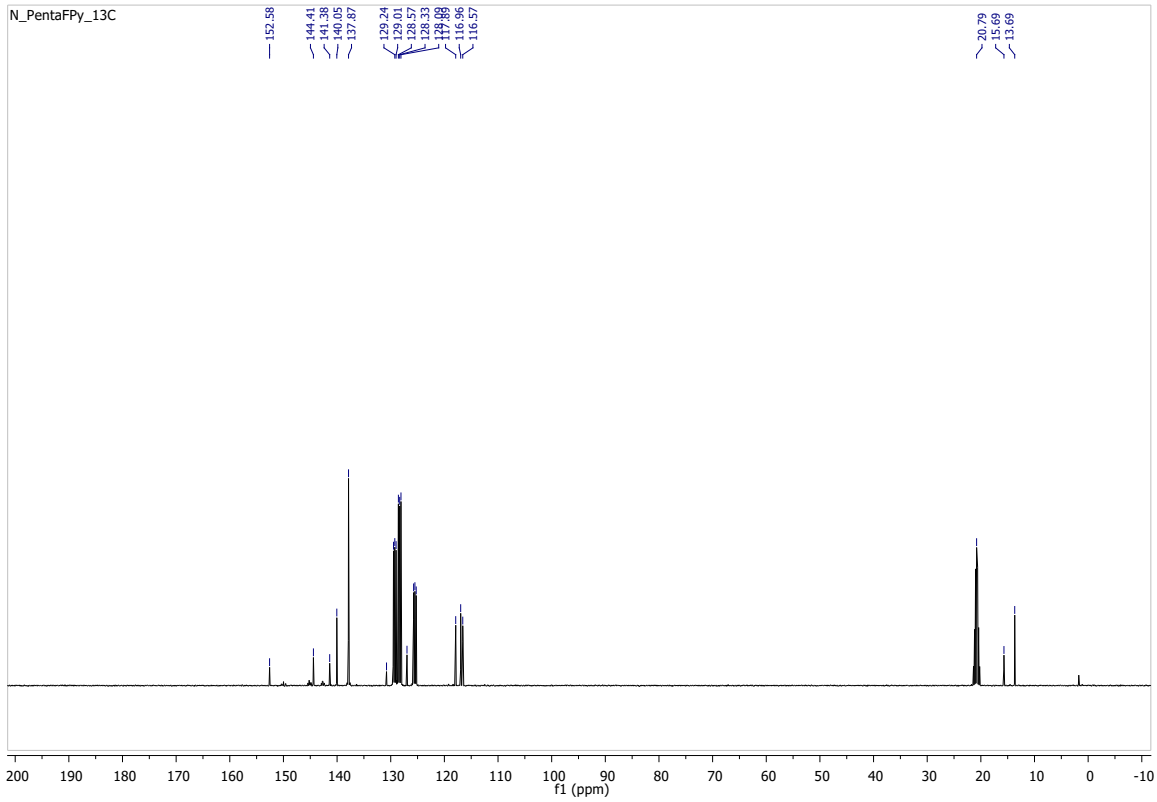


8. Synthesis of compound 6. A 10 mL toluene solution of pentafluoropyridie (70.07 mg, 0.415 mmol) was added to a solution of compound **4** (200 mg, 0.406 mmol in toluene 10 mL) at -30 °C over a period of 10 min and the reaction mixture was allowed to warm up to room temperature and further stirred for 15 h. Subsequently, all volatiles were removed in vacuo and the residue was extracted into toluene (15 mL). The resultant toluene solvent was concentrated to 5-8 mL and stored at –30 °C in a freezer, which afforded colorless crystals of **6** within a week. Yield: 148 mg (91.9%). M.p.: 155.6 °C. ^{1}H NMR (400 MHz, toluene-d_8, 298 K): δ 7.58 (1 H, d), 6.87 (d, 1H), 6.76 (dt, 1H), 6.02 (t, 1H), 5.92 (s, 1H), 2.32 (s, 3H), 2.12 (s, 3H) ppm. ^{13}C NMR (100.56 MHz, toluene-d_8, 298 K); δ 152.58 (s), 144.41 (s), 141.38 (s), 140.05 (s), 137.87 (s), 130.78 (s), 126.97 (s), 125.73 (s), 125.49 (s), 125.25 (s), 117.89 (s), 116.96 (s), 116.57 (s), 20.79 (s), 15.69 (s), 13.69 (s) ppm. ^{19}F NMR (376 MHz, toluene-d_8, 298 K) -94.48 (*o*-F), -134.17 (*m*-F) ppm. HRMS: Calcd: 395.01, found: 396.0174.

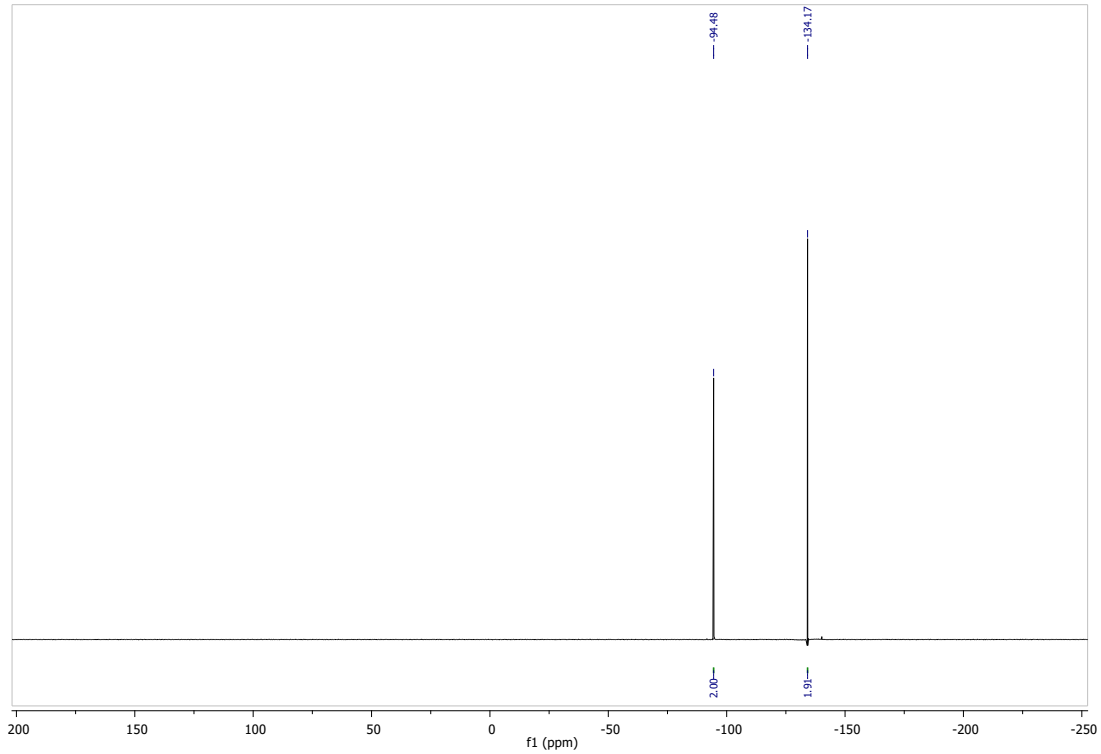
a) **^{1}H NMR of compound 6:**



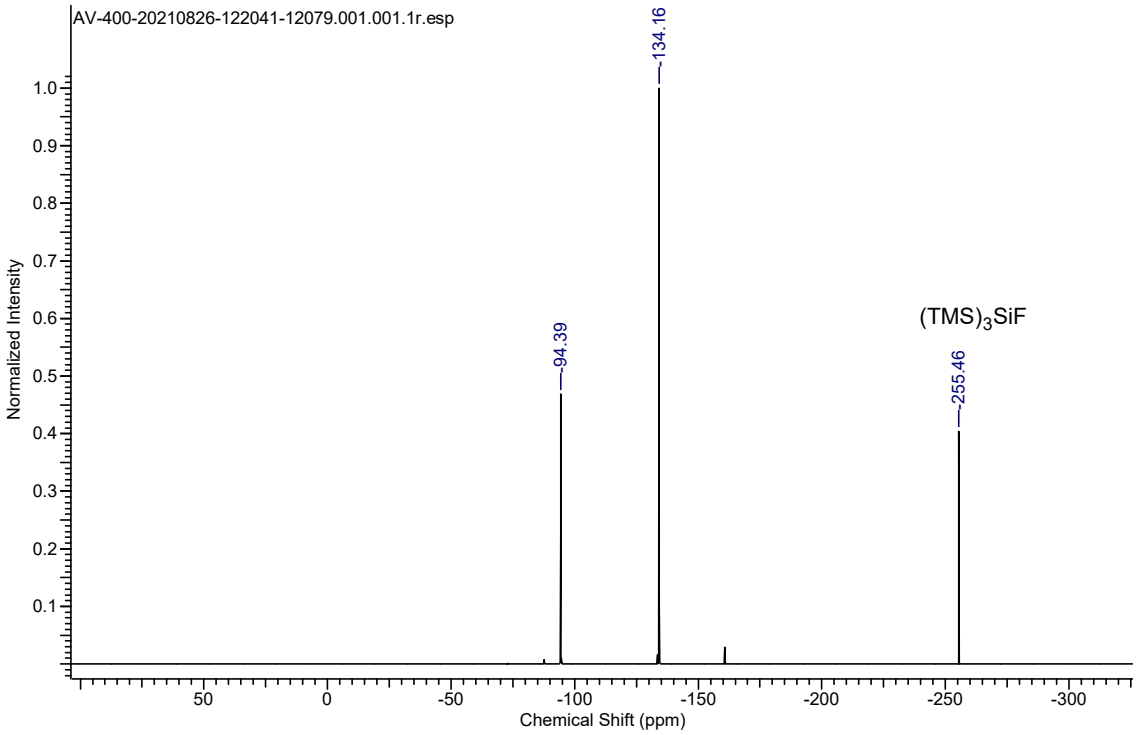
b) **^{13}C NMR of compound 6:**



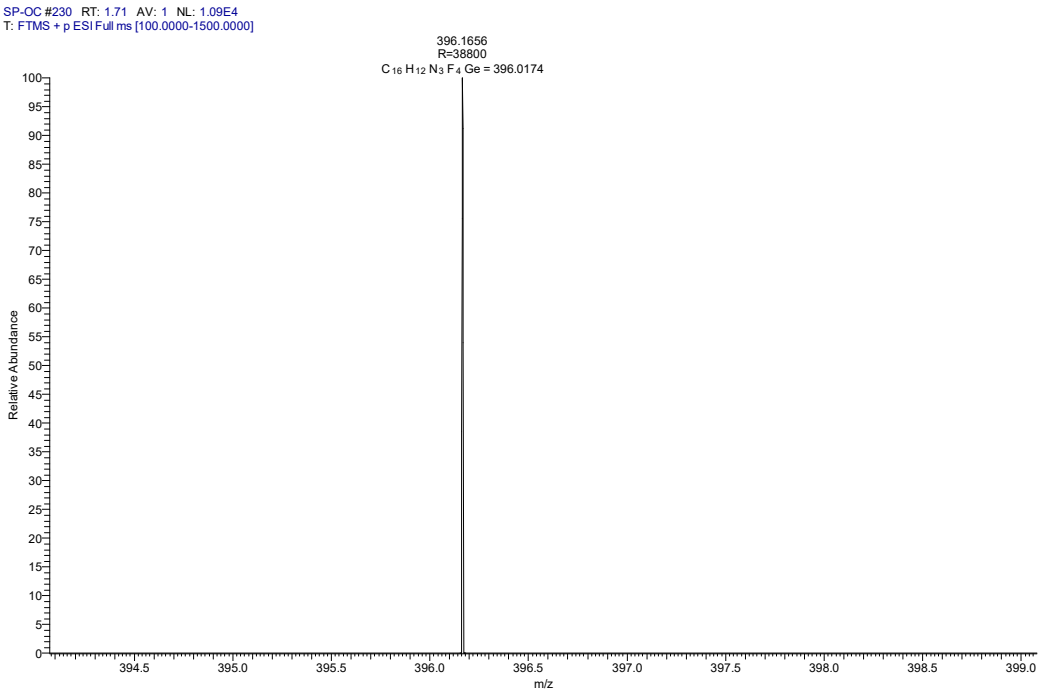
c) **^{19}F NMR of compound 6:**



d) **^{19}F NMR of reaction mixture:**



e) HRMS data of compound 6:



9. Crystallographic data for the structural analysis of compounds 1–6.

Good quality single crystals were hand-picked under polarized optical microscopy and then mounted in the diffractometer. The data collection was done at 100-150 K. X-ray intensity data measurements of **1-6** were carried out on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (MoK_{α}= 0.71073 Å) radiation. The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from three sets of 36 frames. Data were collected with ω scan width of 0.5° at different settings of φ and 2θ keeping the sample-to-detector distance fixed at 5.00 cm. The X-ray data collection was monitored by APEX2 program (Bruker, 2006).[S3] All the data were corrected for Lorentzian, polarization, and absorption effects using SAINT and SADABS programs (Bruker, 2006). SHELX-97 was used for structure solution and full matrix least-squares refinement on F^2.[S4] All the hydrogen atoms were placed in geometrically idealized positionand constrained to ride on their parent atoms. An *ORTEPIII*[S5] view of **1-6** were drawn with 50% probability displacement ellipsoids and H atoms omitted for clarity.

a) **Crystal data of compound 1:** $C_{11}H_{11}ClSn$**,** M = 321.36, CCDC: 2109664, Colorless, block, 0.15 x 0.12 x 0.08 mm^3, triclinic, space group '*P-1'*, *a = 8.05(5)Å, b = 9.04(6)Å, c = 9.04(7)Å*, α = 112.1(3)°, β = 105.4(2)°, γ = 97.0(3)°, Volume = 570(7)Å^3, Z = 2, *T* = 100(2), D_{calc} (g cm^{-3}) = 1.872, *F*(*000*) = 312, μ (mm^{-1}) = 2.437, 26604 reflections collected, 2339 unique reflections (R_{int}= 0.0699), 2163 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.5829, T_{max} = 0.7454, 138 refined parameters, *S* = 1.113, *R*1 = 0.0282, *wR*2 = 0.0760 (all data *R* = 0.0320, *wR*2 = 0.0779), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 1.01, $\Delta\rho_{min}$= -0.71(eÅ^{-3}).

b) **Crystal data of compound 2:** $C_{15}H_{19}N_2SnCl$**,** M = 381.46, CCDC: 2109665, Colorless, block, 0.12 x 0.10 x 0.08 mm^3, monoclinic, space group '*P2$_1$/*n', *a = 8.713(4)Å, b = 14.390(6)Å, c = 12.347(5)Å*, α = 90°, β = 101.929(16)°, γ = 90°, Volume = 1514.7(11)Å^3, Z = 4, *T* = 100(2), D_{calc} (g cm^{-3}) = 1.637, *F*(*000*) = 760, μ (mm^{-1}) = 1.852, 69227 reflections collected, 2655 unique reflections (R_{int}= 0.0582), 2497 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.5704, T_{max} = 0.7464, 175 refined parameters, *S* = 1.360, *R*1 = 0.0281, *wR*2 = 0.0873 (all data *R* = 0.0321, *wR*2 = 0.1000), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.96, $\Delta\rho_{min}$= -1.22 (eÅ^{-3}).

c) **Crystal data of compound 3:** $C_{22}H_{22}N_4Sn$**,** M = 461.15, CCDC: 2109666, Yellow, Plate, 0.31 x 0.28 x 0.27 mm^3, triclinic, space group '*P-1'*, *a = 11.9136(7)Å, b = 12.1859(7)Å, c = 13.5673(8)Å*, α = 91.477(2)°, β = 103.126(2)°, γ = 90.790(2)°, Volume = 1917.18(19)Å^3, Z = 4, *T* = 100(2), D_{calc} (g cm^{-3}) = 1.598, *F*(*000*) = 928, μ (mm^{-1}) = 1.347, 41117 reflections collected, 8809 unique reflections (R_{int}= 0.0585), 7299 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.665, T_{max} = 0.695, 504 refined parameters, *S* = 1.268, *R*1 = 0.0491, *wR*2 = 0.1004 (all data *R* = 0.0633, *wR*2 = 0.1004), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.96, $\Delta\rho_{min}$= -0.90 (eÅ^{-3}).

d) **Crystal data of compound 4:** $C_{20}H_{38}GeN_2Si_4$, M = 491.49, CCDC: 2109667, Orange, Block, 0.36 x 0.32 x 0.29 mm^3, triclinic, space group '*P-1'*, *a = 8.7746(3)Å, b = 9.7135(4)Å, c = 17.1214(7)Å*, α = 77.682(1)°, β = 83.909(1)°, γ = 69.398(1)°, Volume = 1333.75(9)Å^3, Z = 2, *T* = 100.0, D_{calc} (g cm^{-3}) = 1.224, *F*(*000*) = 520, μ (mm^{-1}) = 1.337, 26560 reflections collected, 8173 unique reflections (R_{int}= 0.0281), 7294 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.624, T_{max} = 0.679, 256 refined parameters, *S* = 1.024, *R*1 = 0.0281, *wR*2 = 0.0718 (all data *R* = 0.0324, *wR*2 = 0.0743), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.69, $\Delta\rho_{min}$= -0.52 (eÅ^{-3}).

e) **Crystal data of compound 5:** $C_{20}H_{38}N_2Si_4Sn$**,** M = 537.57, CCDC: 2109668, Red, Block, 0.12 x 0.09 x 0.08 mm^3, triclinic, space group '*P-1'*, *a = 8.930(3)Å, b = 9.723(3)Å, c = 17.277(5)Å*, α = 78.349(14)°, β = 84.063(9)°, γ = 68.696(11)°, Volume = 1368.0(7)Å^3, Z = 2, *T* = 293.15, D_{calc} (g cm^{-3}) = 1.305, *F*(*000*) = 556, μ (mm^{-1}) = 1.117, 75997 reflections collected, 6779 unique reflections (R_{int}= 0.0566), 6418 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.6602, T_{max} = 0.7457, 255 refined parameters, *S* = 1.231, *R*1 = 0.0196, *wR*2 = 0.0548 (all data *R* = 0.0226, *wR*2 = 0.0636), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.90, $\Delta\rho_{min}$= -0.82 (eÅ^{-3}).

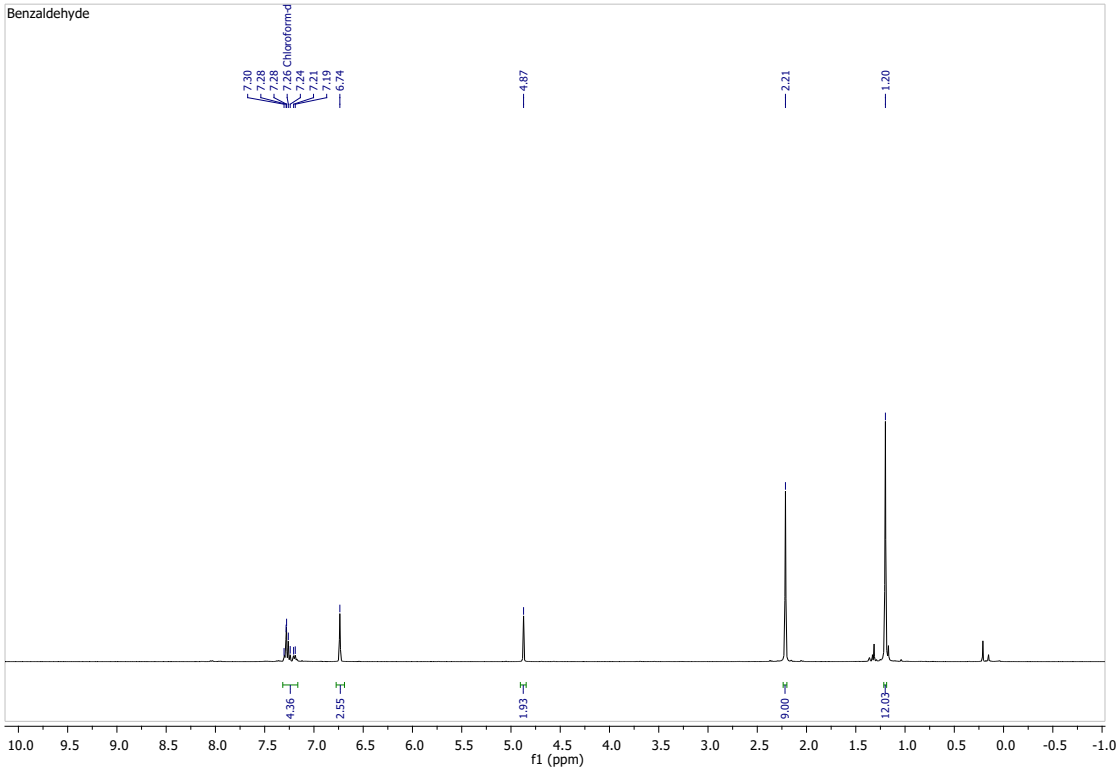
f) **Crystal data of compound 6:** $C_{16}H_{11}F_4GeN_3$, M = 393.89, CCDC: 2109460, Yellow, Plate, 0.34 x 0.32 x 0.29 mm^3, triclinic, space group '*P-1'*, *a = 7.8354(7)Å, b = 11.7342(10)Å, c = 16.9181(16)Å*, α = 83.968(3)°, β = 84.442(3)°, γ = 75.253(2)°, Volume = 1491.9(2)Å^3, Z = 4, *T* = 100(2), D_{calc} (g cm^{-3}) = 1.754, *F*(*000*) = 784, μ (mm^{-1}) = 2.101, 85931 reflections collected, 9196 unique reflections (R_{int}= 0.0339), 7369 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.494, T_{max} = 0.544, 437 refined parameters, *S* = 1.045, *R*1 = 0.0339, *wR*2 = 0.0722 (all data *R* = 0.0503, *wR*2 = 0.0800), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.81, $\Delta\rho_{min}$= -0.74 (eÅ^{-3}).

10. General procedure for catalytic hydroboration

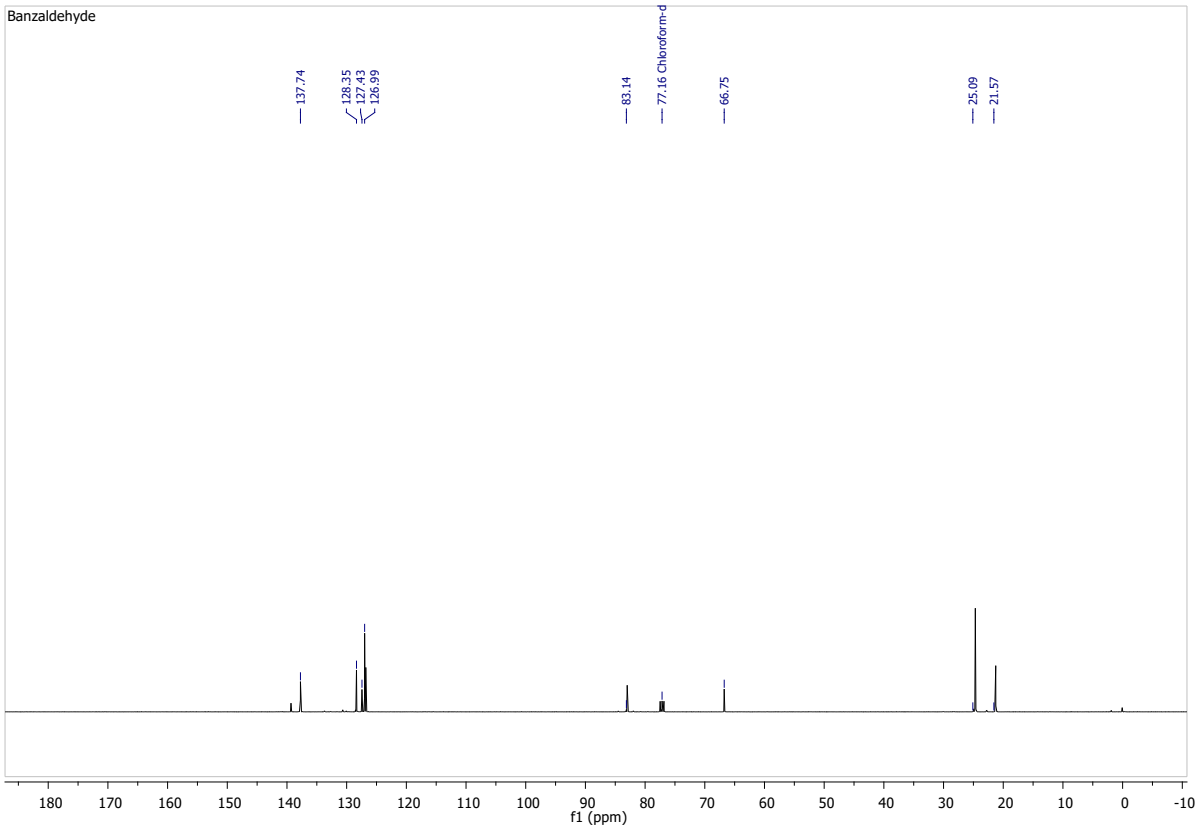
Substrate (0.25 mmol), pinacolborane (0.25 mmol), catalyst (5 mol%) were charged in Schlenk tube inside glove box. The reaction mixture was allowed to run at room temperature in neat condition. The progress of the reaction was monitored by ^{1}H NMR, which indicated the completion of the reaction by the appearance of a new CH_2 (aldehyde and alkene)/CH (ketone and alkyne) peak. Upon completion of reaction mesitylene (0.25 mmol) as internal standard, was added while making the NMR in $CDCl_3$.

11. Spectroscopic data for hydroborated products

2-(benzyloxy)-pinacolborane (1a) : ^{1}H NMR(400 MHz, $CDCl_3$, 298 K): δ 7.32 – 7.16 (5 H, m), 6.74 (3 H, s), 4.87 (2 H, s), 2.21 (9 H, s), 1.20 (12 H, s) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ 137.74 (s), 128.35 (s), 127.43 (s), 126.99 (s), 83.14 (s), 66.75 (s), 25.09 (s) ppm.

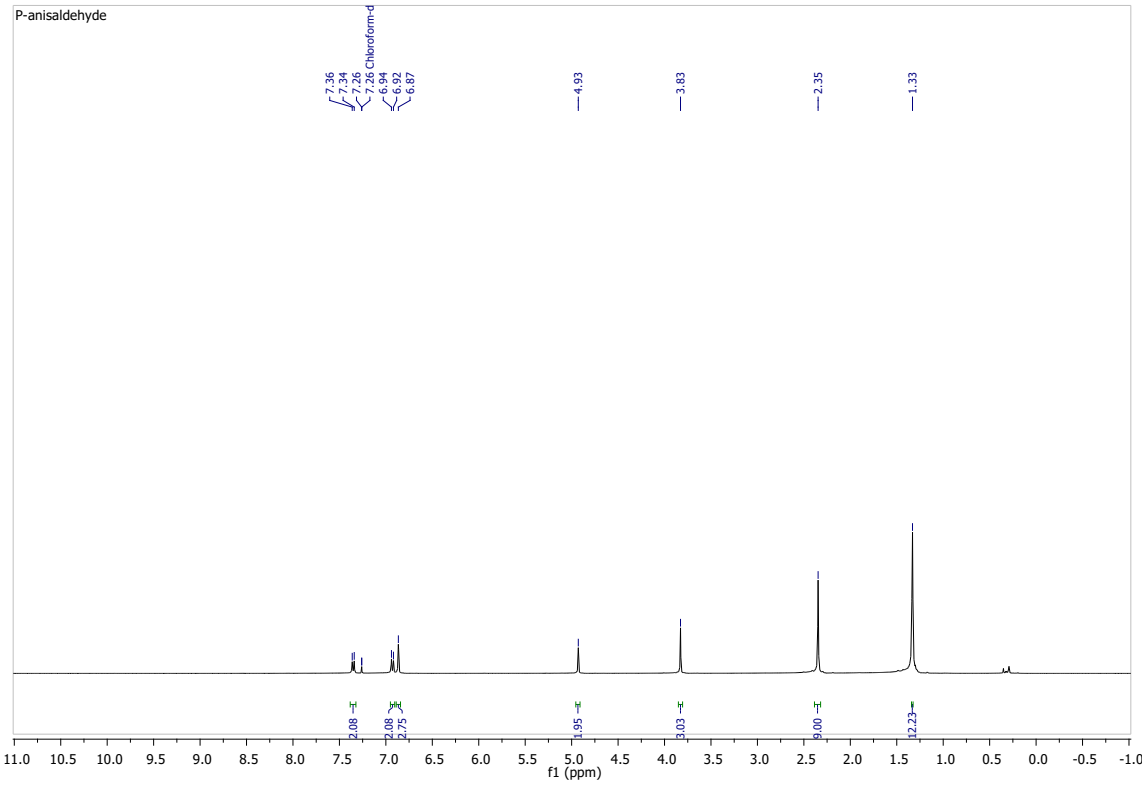


^{1}H NMR of 2-(benzyloxy)-pinacolborane (1a)

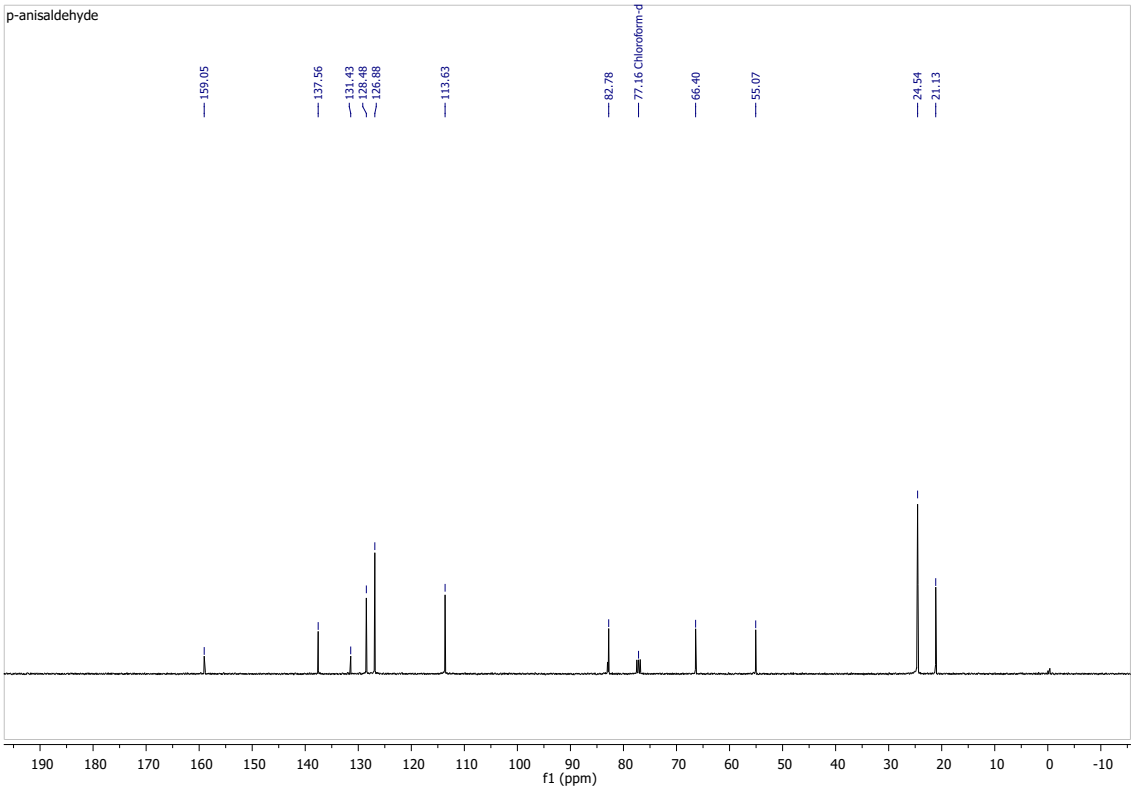


^{13}C NMR of 2-(benzyloxy)-pinacolborane (1a)

2-((4-methylbenzyl)oxy)-pinacolborane (1b) : ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.35 (2 H, d), 6.93 (2 H, d), 6.87 (3 H, s), 4.93 (2 H, s), 3.83 (3 H, s), 2.35 (9 H, s), 1.33 (12 H, s) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ 137.56 (s), 131.43 (s), 128.48 (s), 126.88 (s), 82.78 (s), 66.40 (s), 55.07 (s), 24.54 (s), 21.13 (s) ppm.

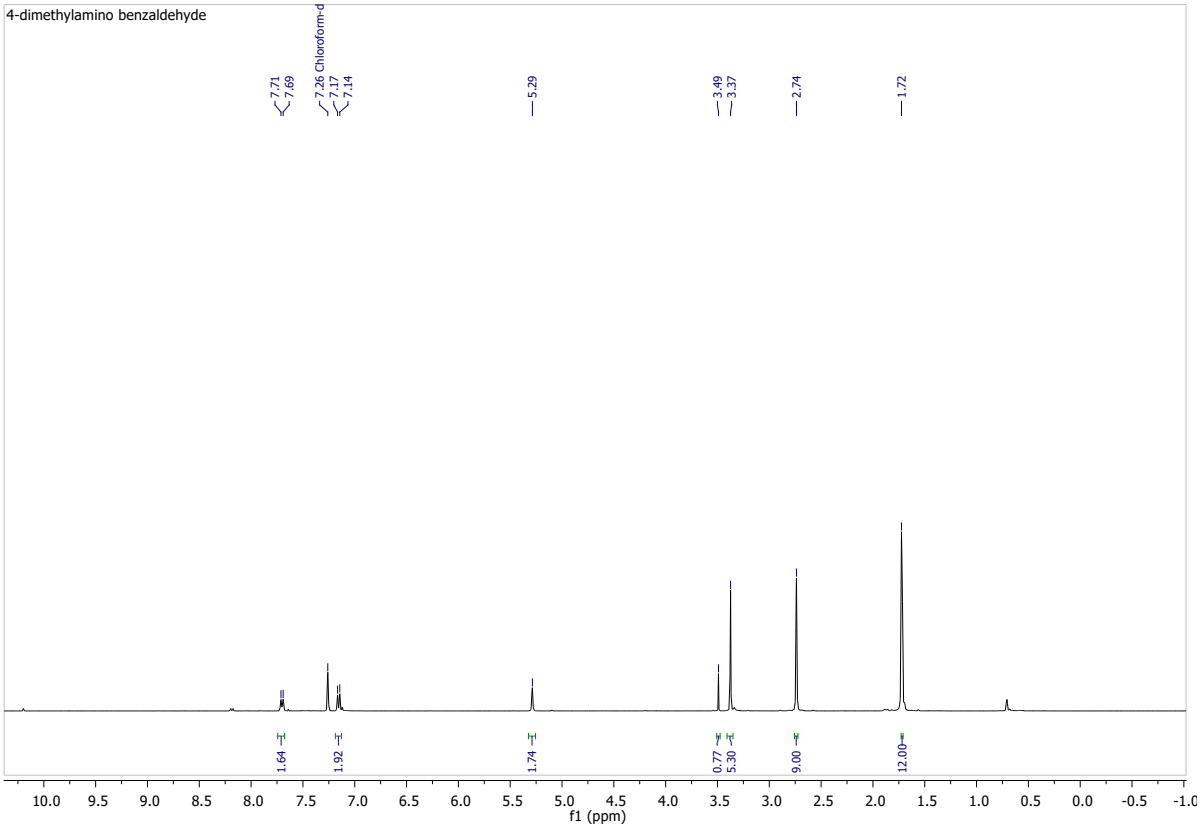


^{1}H NMR of 2-((4-methylbenzyl)oxy)-pinacolborane (1b)

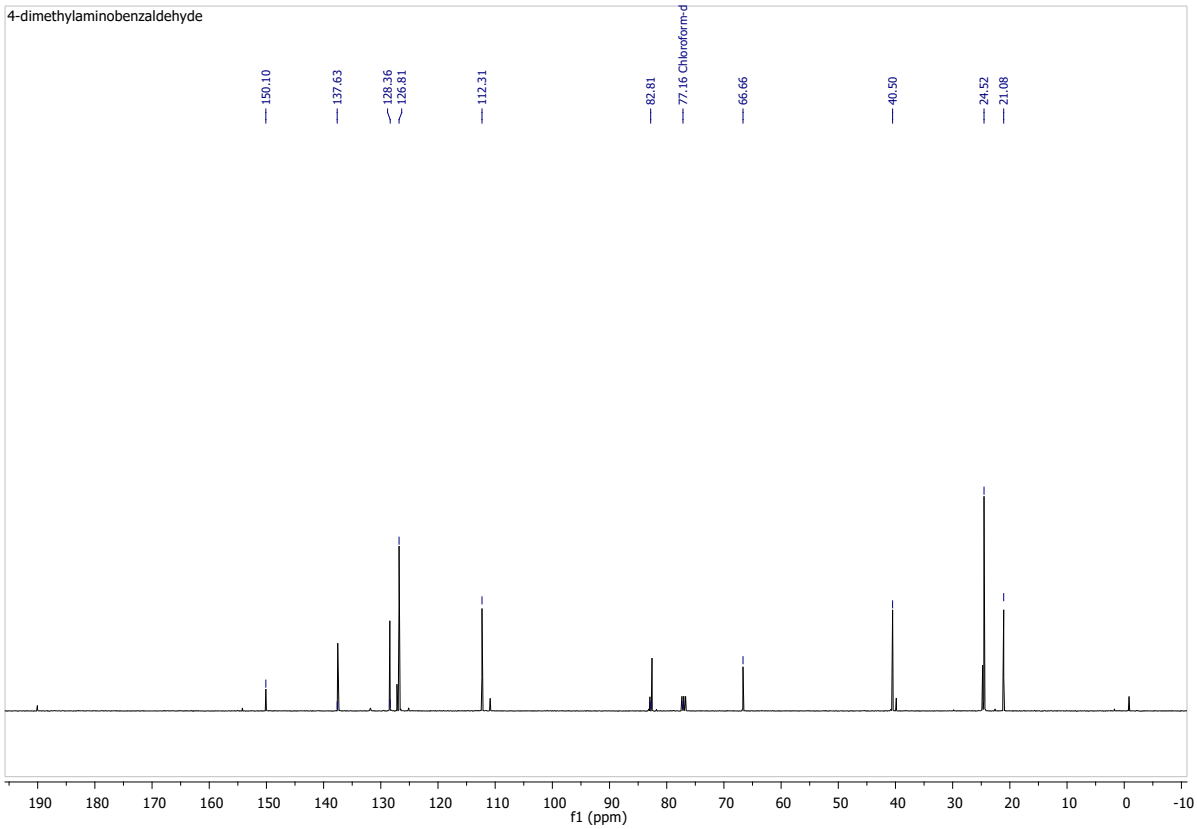


^{13}C NMR of 2-((4-methylbenzyl)oxy)-pinacolborane (1b)

2-(4-dimethylaminobenzyloxy)-pinacolborane (1c) : ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.70 (2 H, d), 7.15 (2 H, d), 5.29 (2 H, s), 3.49 (1 H, s), 3.37 (6 H, s), 2.74 (9H, s), 1.72 (12 H, s) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ 137.63 (s), 128.36 (s), 126.81 (s), 82.81 (s), 66.66 (s), 40.50 (s), 24.52 (s), 21.08 (s) ppm.

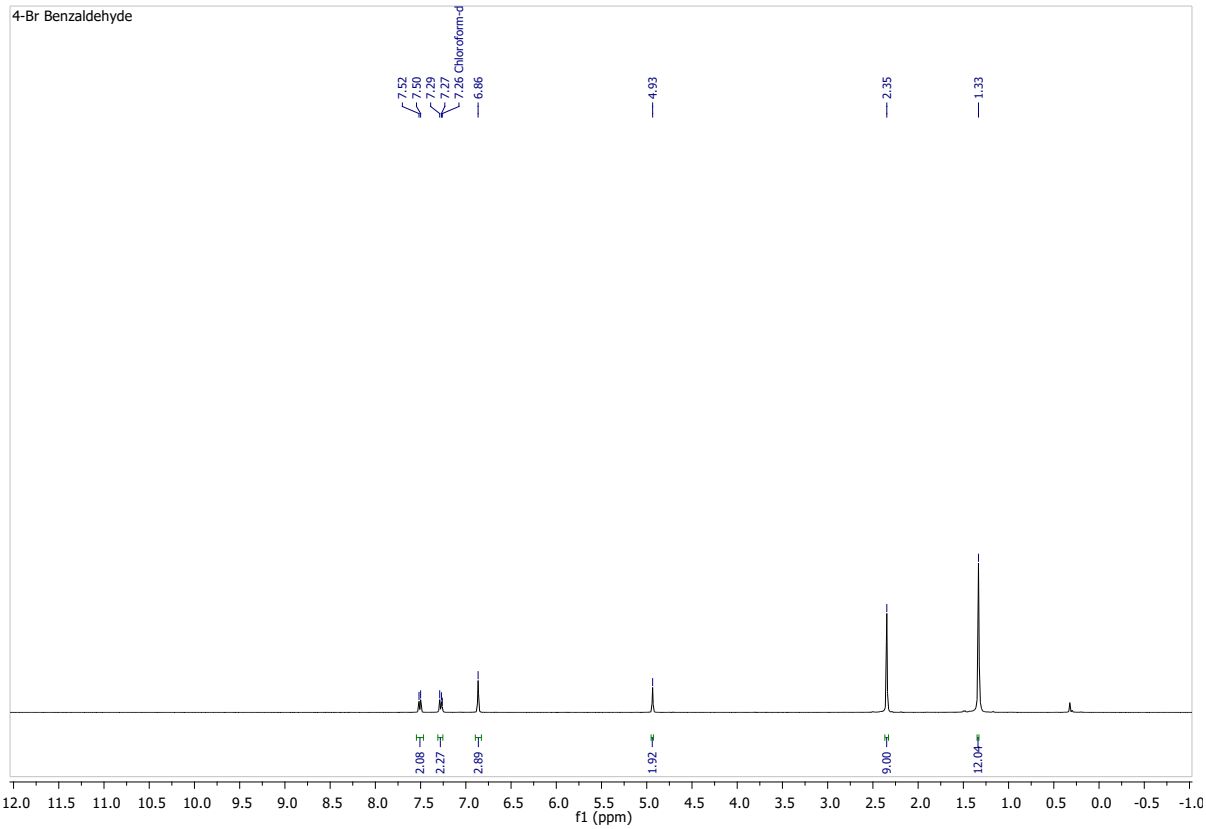


^{1}H NMR of 2-(4-dimethylaminobenzyloxy)-pinacalborane (1c)

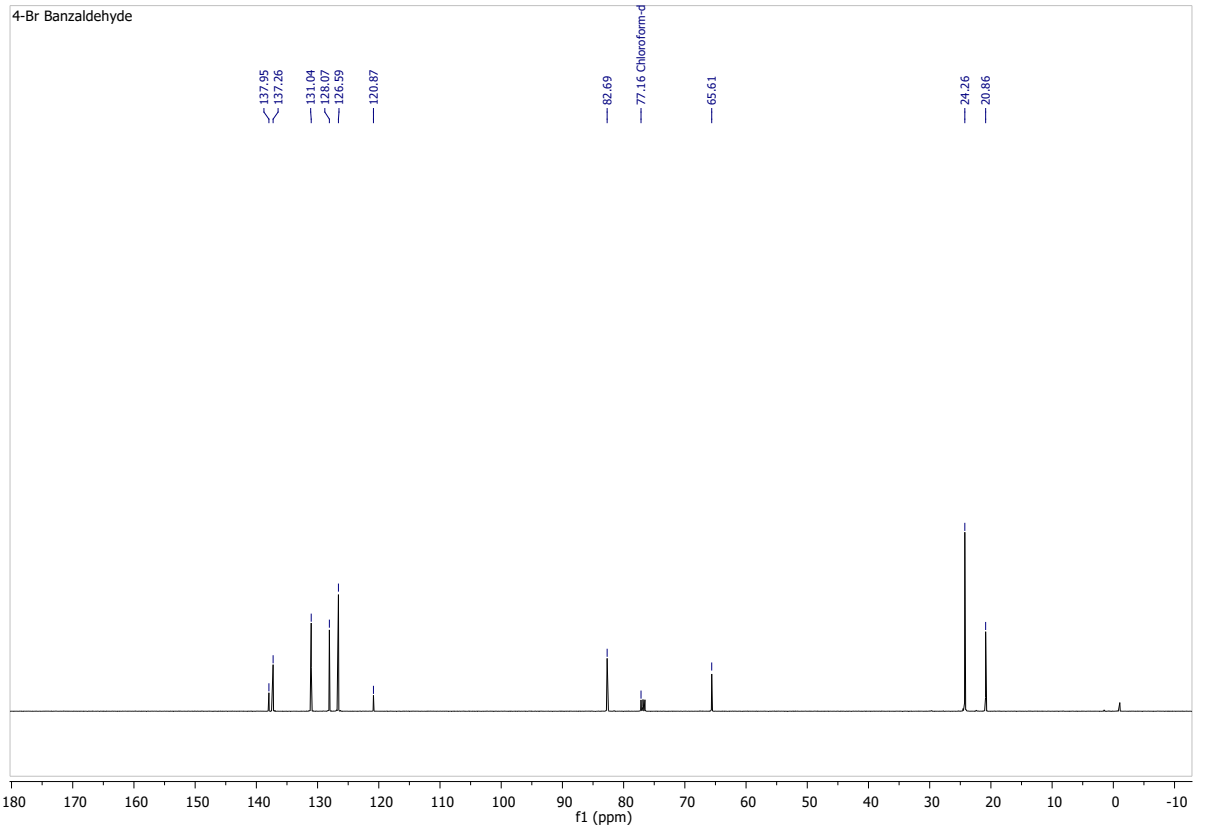


^{13}C NMR of 2-(4-dimethylaminobenzyloxy)-pinacalborane (1c)

2-(4-bromobenzyloxy)-pinacolborane (1d): ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.51 (2 H, d), 7.31 – 7.25 (2 H, m), 6.86 (3 H, s), 4.93 (2 H, s), 2.35 (9 H, s), 1.33 (12 H, s) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ 137.95 (s), 137.26 (s), 131.04 (s), 128.07 (s), 126.59 (s), 120.87 (s), 82.69 (s), 65.61 (s), 24.26 (s) ppm.

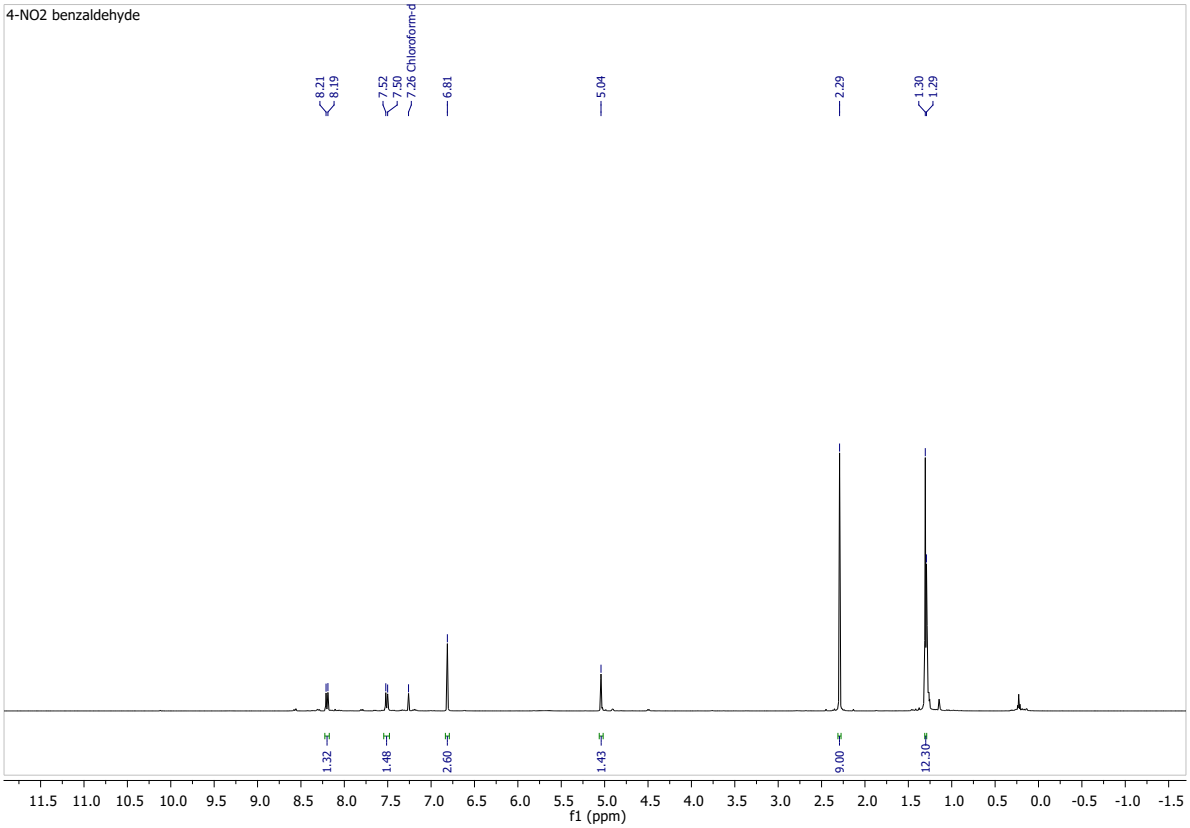


^{1}H NMR of 2-(4-bromobenzyloxy)-pinacolborane (1d)

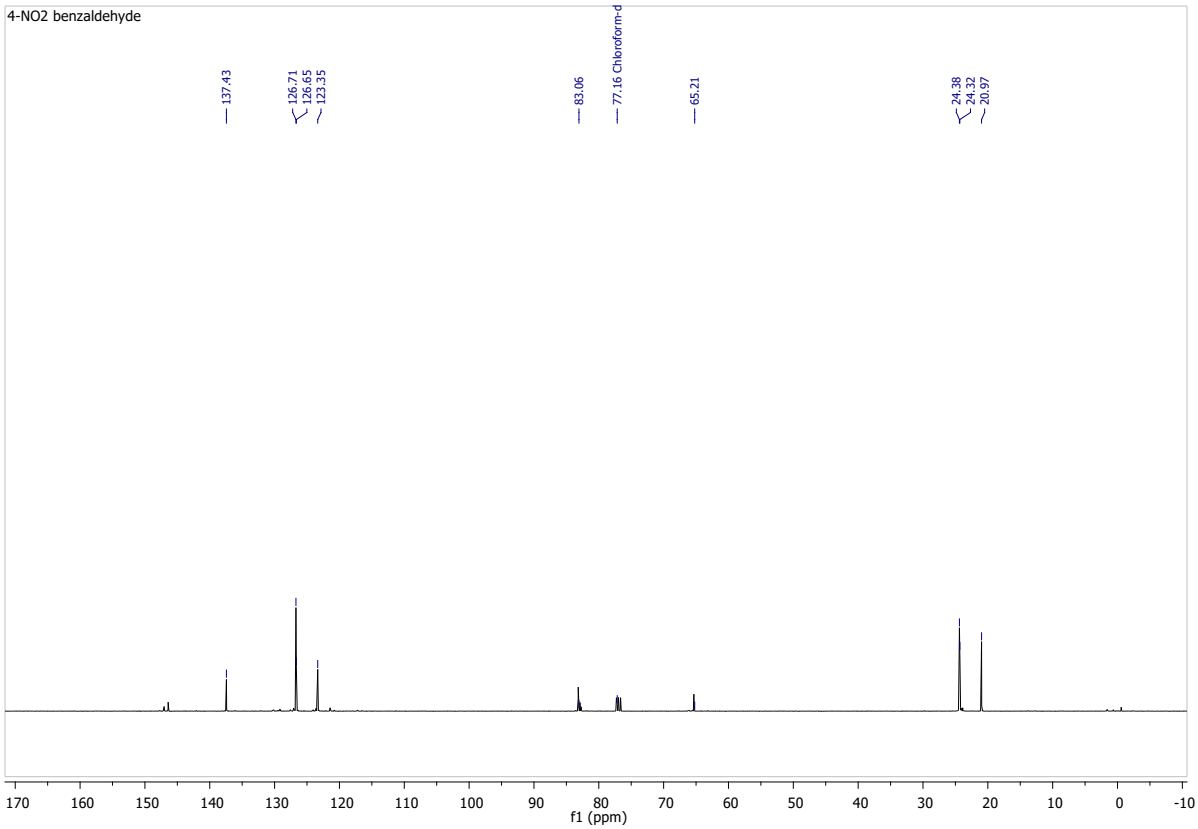


^{13}C NMR of 2-(4-bromobenzyloxy)-pinacolborane (1d)

2-(4-nitrobenzyloxy)-pinacolborane (1e): ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.20 (2 H, d), 7.51 (2 H, d), 6.81 (3 H, s), 5.04 (2 H, s), 2.29 (9 H, s), 1.30 (12 H, d) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ 137.43 (s), 126.68 (s), 126.66(s), 123.35 (s), 83.06 (s), 24.35 (s), 20.97 (s) ppm.

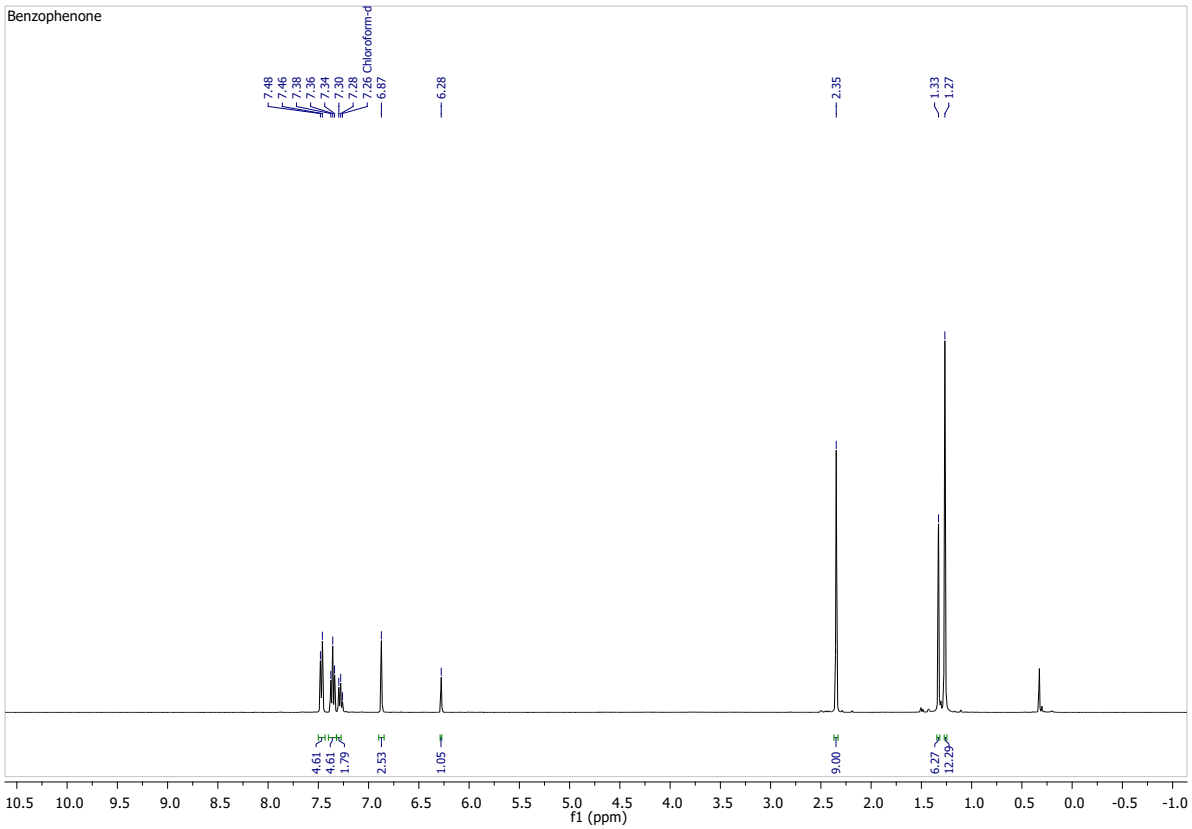


^{1}H NMR of 2-(4-nitrobenzyloxy)-pinacolborane (1e)

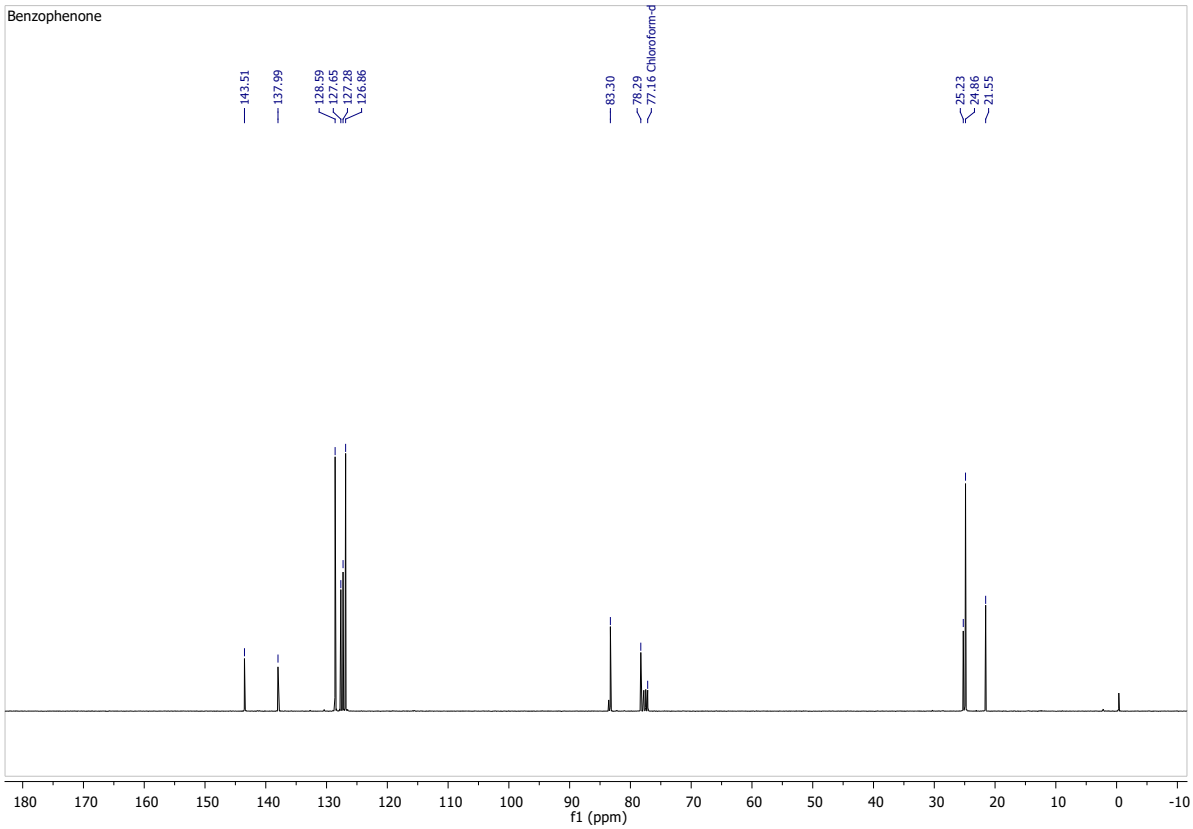


^{13}C NMR of 2-(4-nitrobenzyloxy)-pinacalborane (1e)

2-(benzhydryloxy)-pinacolborane (1f): ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.47 (5 H, d), 7.36 (4 H, t,), 7.29 (2 H, d), 6.87 (3 H, s), 6.28 (1 H, s), 2.35 (9 H, s), 1.33 (6 H, s), 1.27 (12 H, s) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ 143.51 (s), 137.99 (s), 128.59 (s), 127.65 (s), 127.28 (s), 126.86 (s), 83.30 (s), 78.29 (s), 25.23 (s), 24.86 (s), 21.55 (s) ppm.

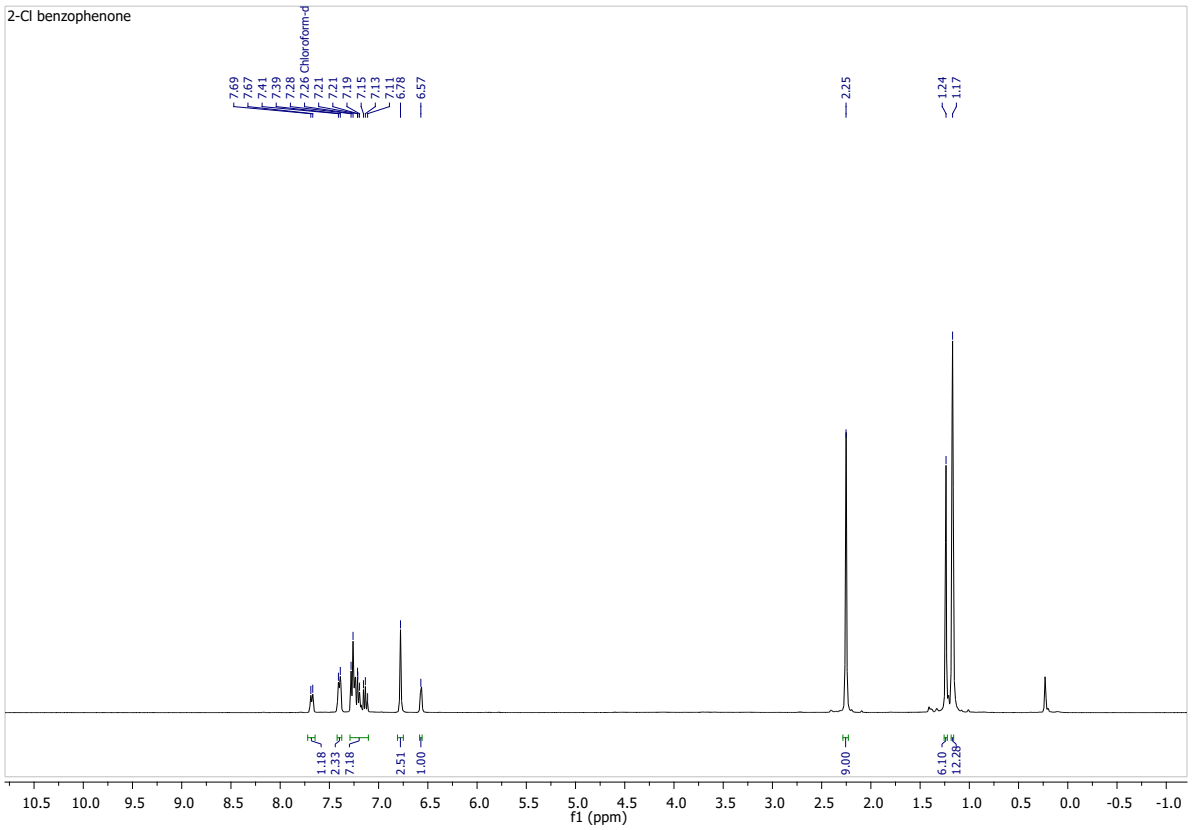


^{1}H NMR of 2-(benzhydryloxy)-pinacolborane (1f)

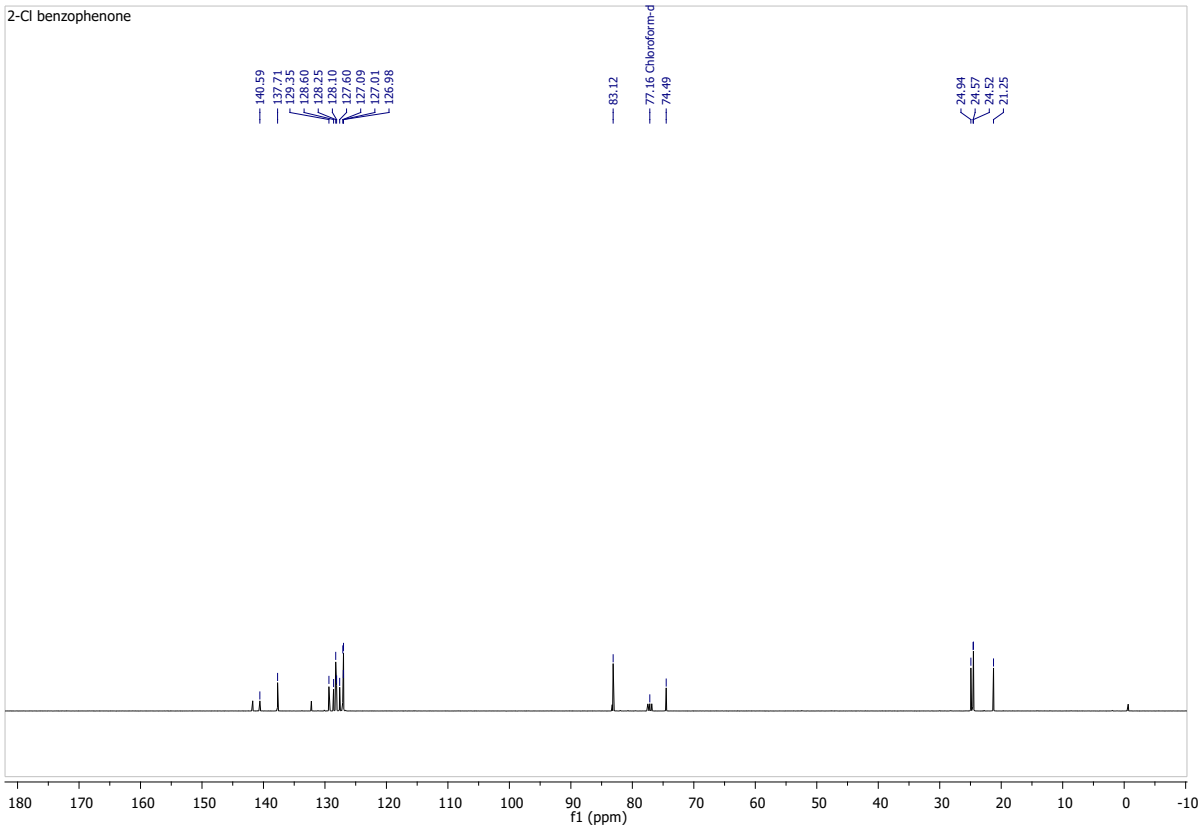


^{13}C NMR of 2-(benzhydryloxy)-pinacolborane (1f)

2-(2-chlorobenzhydryloxy)-pinacolborane (1g): ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.68 (1 H, d), 7.40 (2 H, d), 7.20 (6 H, ddd), 6.78 (3 H, s), 6.57 (1 H, s), 2.25 (9 H, s), 1.24 (6 H, s), 1.17 (12 H, s) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ 140.59 (s), 137.71 (s), 129.35 (s), 128.60 (s), 128.18 (d), 127.60 (s), 127.20 – 126.88 (m), 83.12 (s), 74.49 (s), 24.94 (s), 24.54 (d), 21.25 (s) ppm.

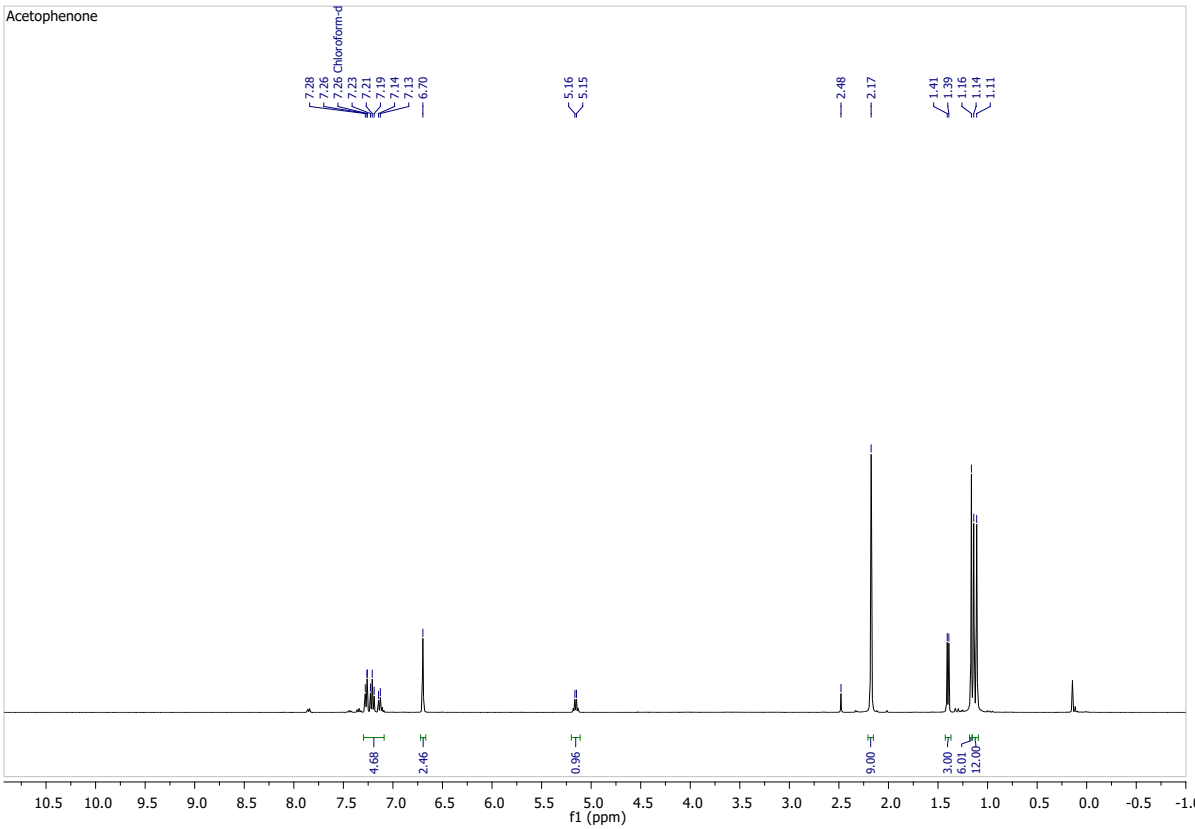


^{1}H NMR of 2-(2-chlorobenzhydryloxy)-pinacolborane (1g)

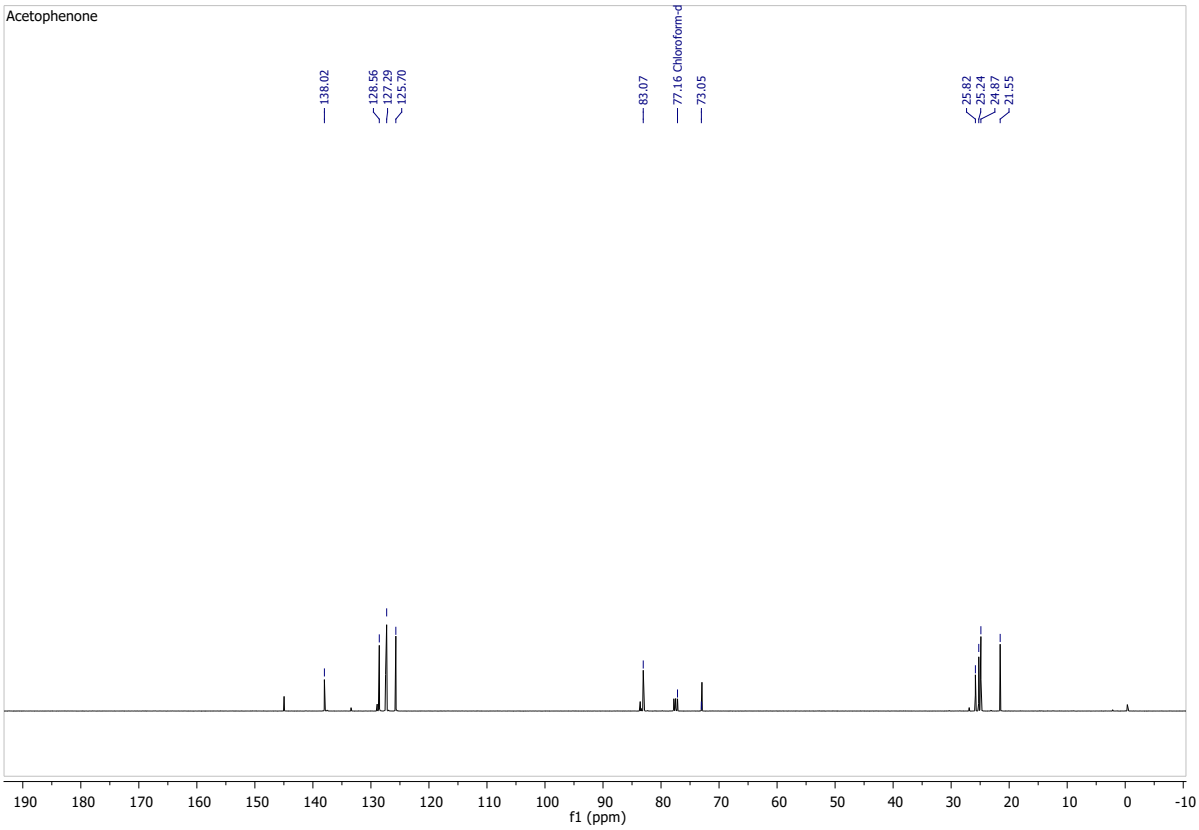


^{13}C NMR of 2-(2-chlorobenzhydryloxy)-pinacolborane (1g)

2-(1-phenylethoxy)-pinacolborane (1h): ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.51 (2 H, d), 7.31 – 7.25 (2 H, m), 6.86 (3 H, s), 4.93 (2 H, s), 2.35 (9 H, s), 1.33 (12 H, s) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ 138.02 (s), 128.56 (s), 127.29 (s), 125.70 (s), 83.07 (s), 73.05 (s), 25.82 (s), 24.87 (s), 21.55 (s) ppm.

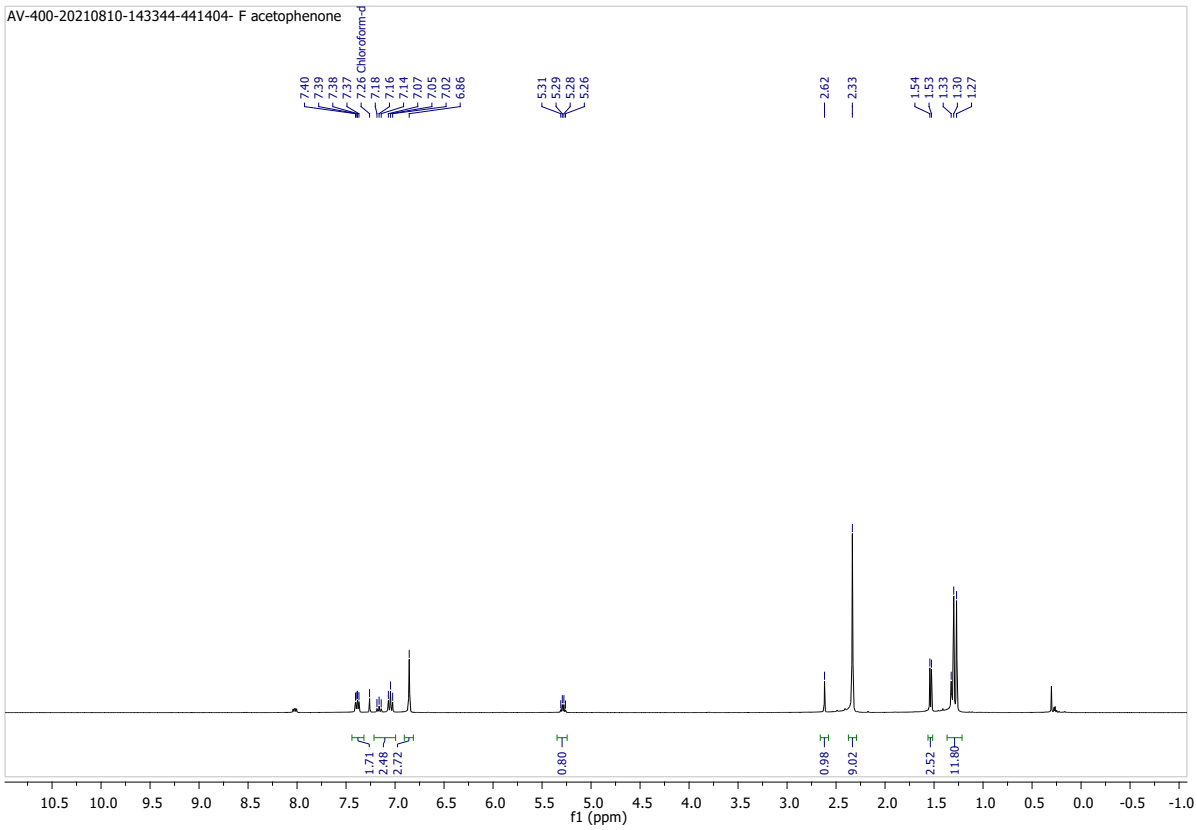


^{1}H NMR of 2-(1-phenylethoxy)-pinacolborane (1h)

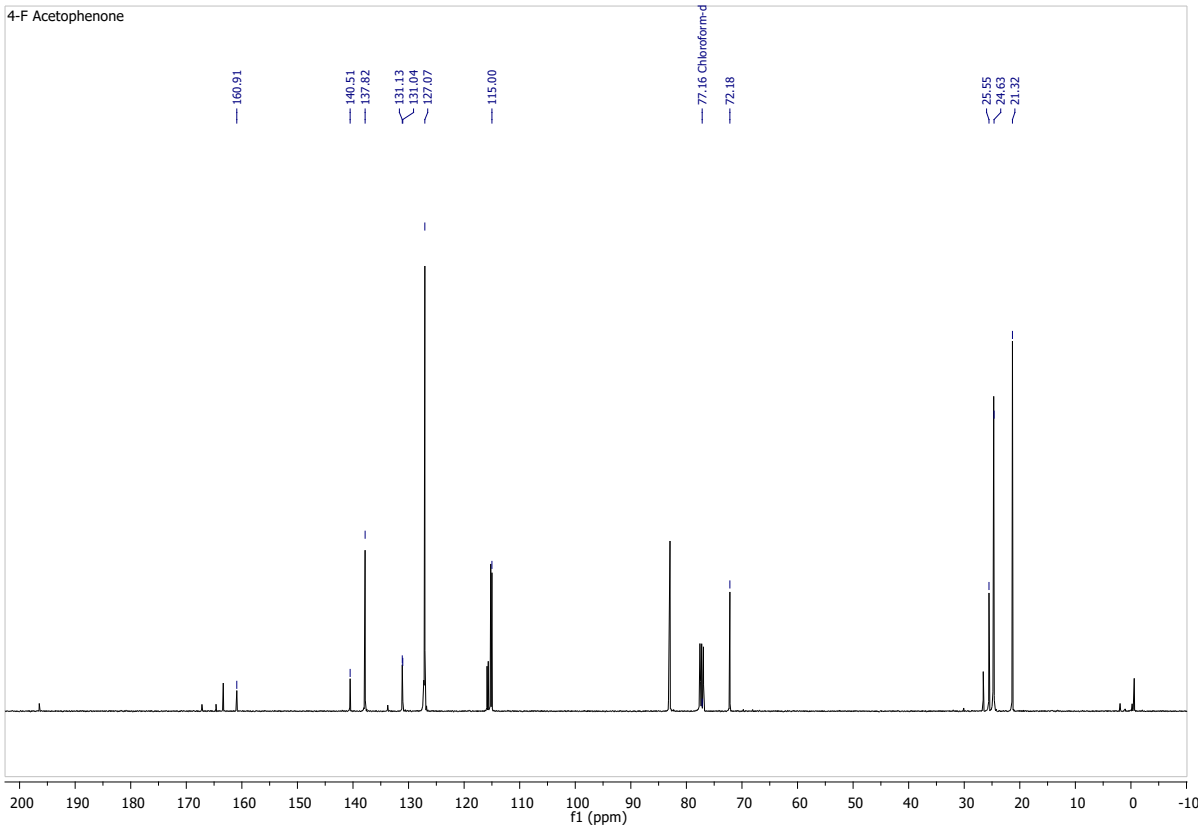


^{13}C NMR of 2-(1-phenylethoxy)-pinacolborane (1h)

2-(1-(4-fluorophenyl)ethoxy)-pinacolborane (1i) : ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.39 (2 H, dd), 7.10 (2 H, d), 6.86 (3 H, s), 5.29 (1 H, q), 2.62 (1 H, s), 2.33 (9 H, s), 1.53 (3 H, d), 1.30 (12 H, s) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ δ C (101 MHz, $CDCl_3$, 298 K) δ 160.91 (s), 140.51 (s), 137.82 (s), 131.09 (d), 127.07 (s), 115.00 (s), 72.18 (s), 25.55 (s), 24.63 (s), 21.32 (s) ppm.

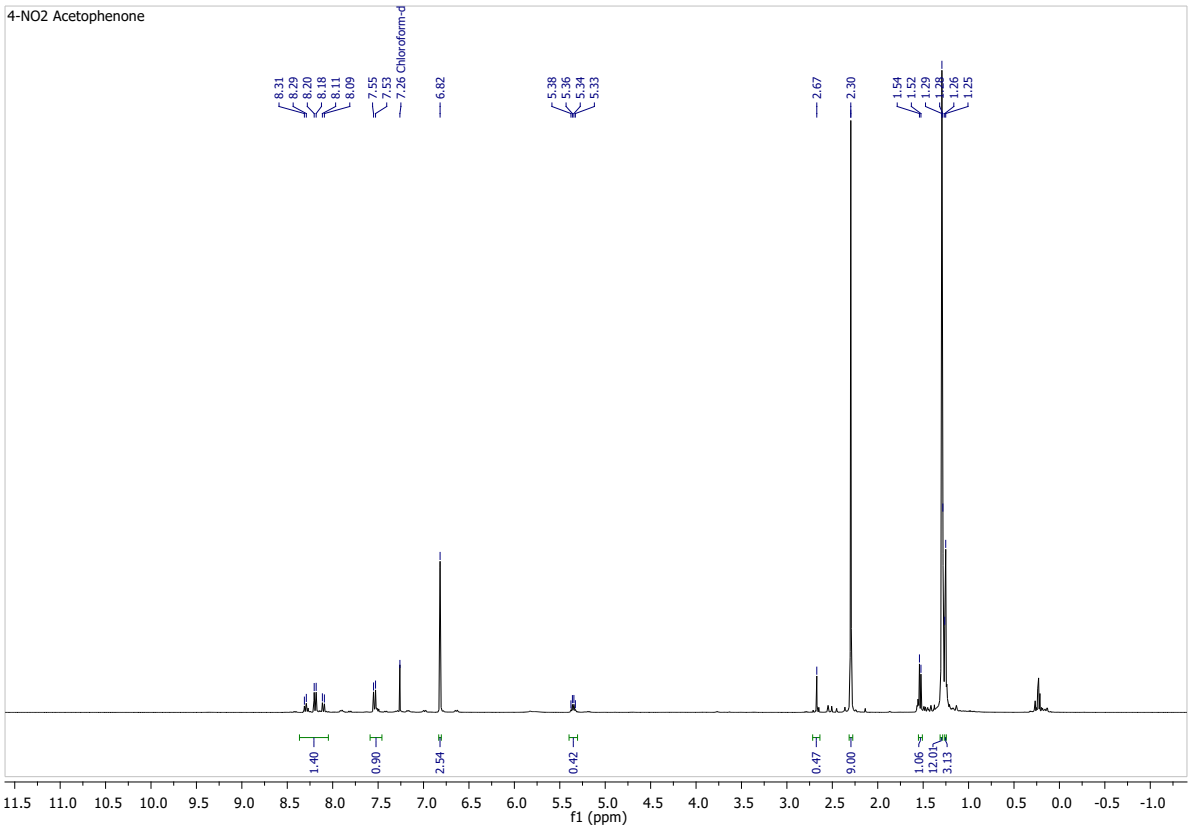


^{1}H NMR of 2-(1-(4-fluorophenyl)ethoxy)-pinacolborane (1i)

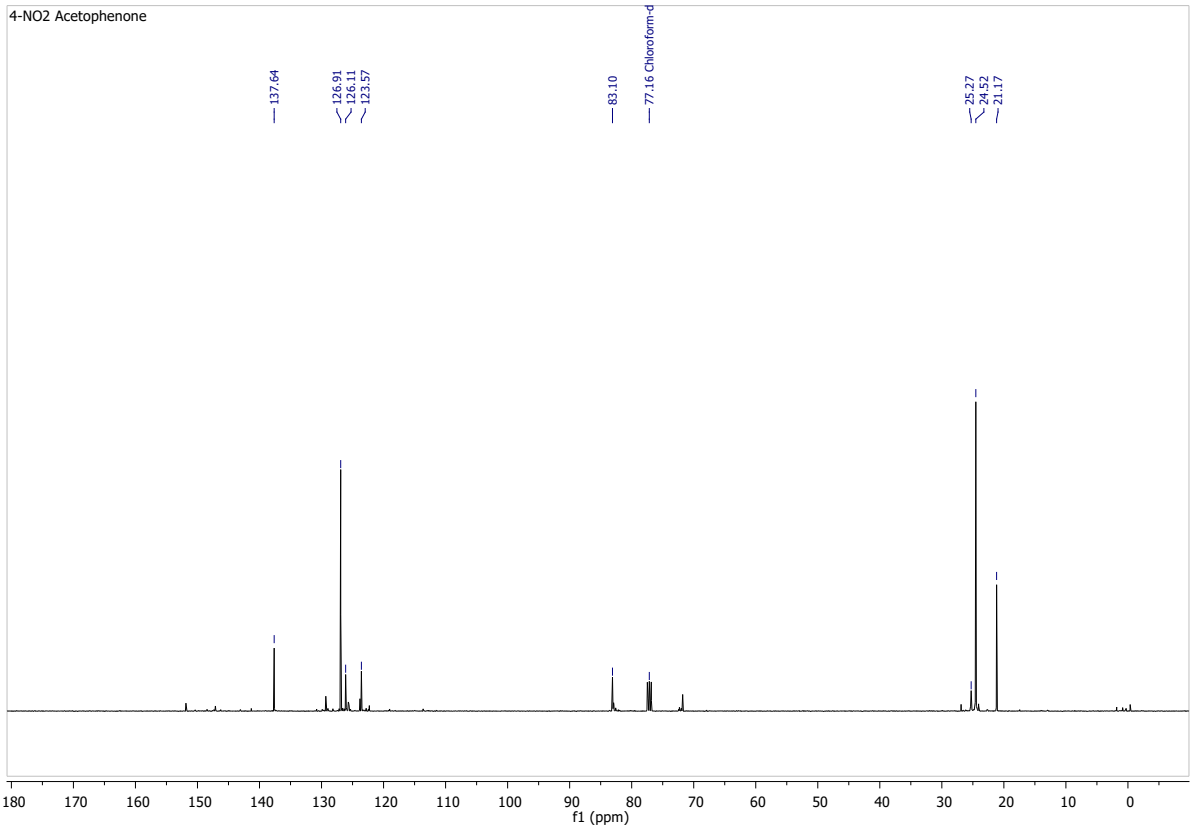


^{13}C NMR of 2-(1-(4-fluorophenyl)ethoxy)-pinacolborane (1i)

2-(1-(4-nitrophenyl)ethoxy)-pinacolborane (1j): ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.37 – 8.05 (2 H, m), 7.54 (2 H,d), 6.82 (3 H, s), 5.35 (1 H, q), 2.67 (1 H, s), 2.30 (9 H, s), 1.53 (2 H, d), 1.29 (12 H, s), 1.26 (6 H, d) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ 137.64 (s), 126.91 (s), 126.11 (s), 123.57 (s), 83.10 (s), 25.27 (s), 24.52 (s), 21.17 (s) ppm.

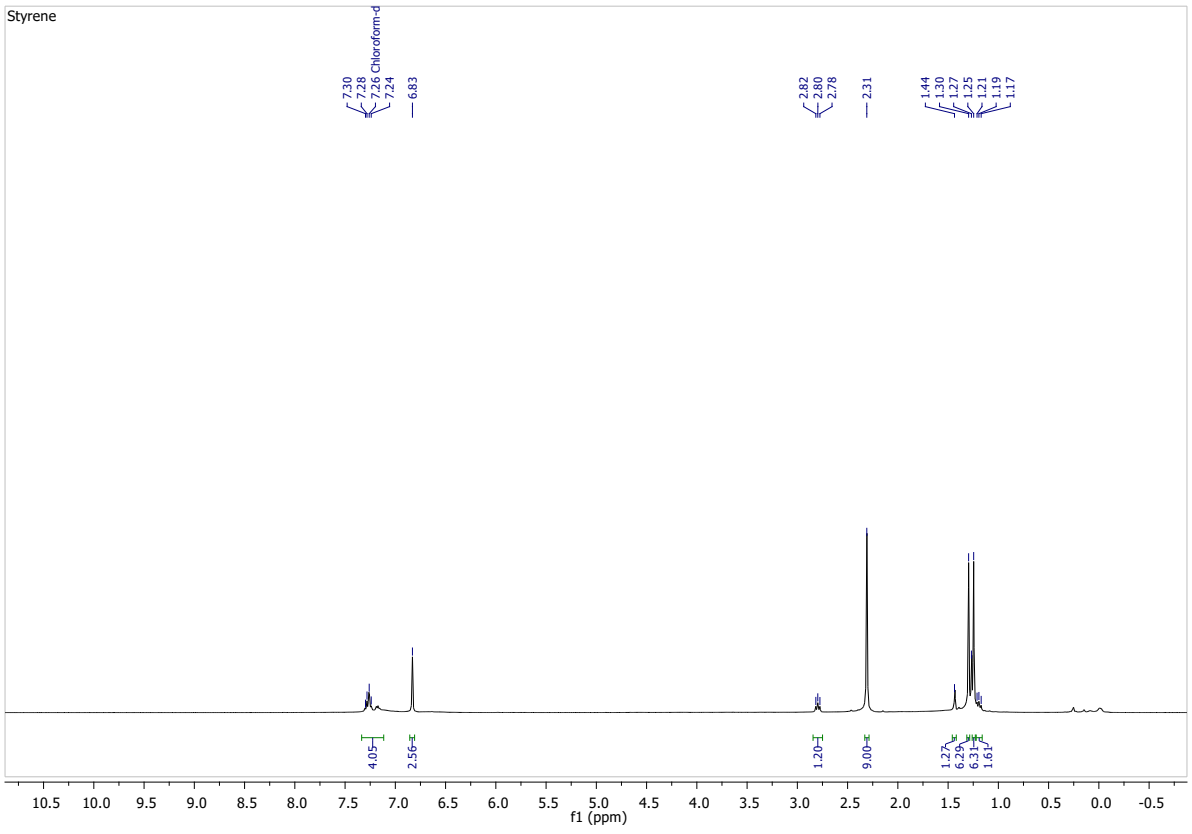


^{1}H NMR of 2-(1-(4-nitrophenyl)ethoxy)-pinacolborane (1j)

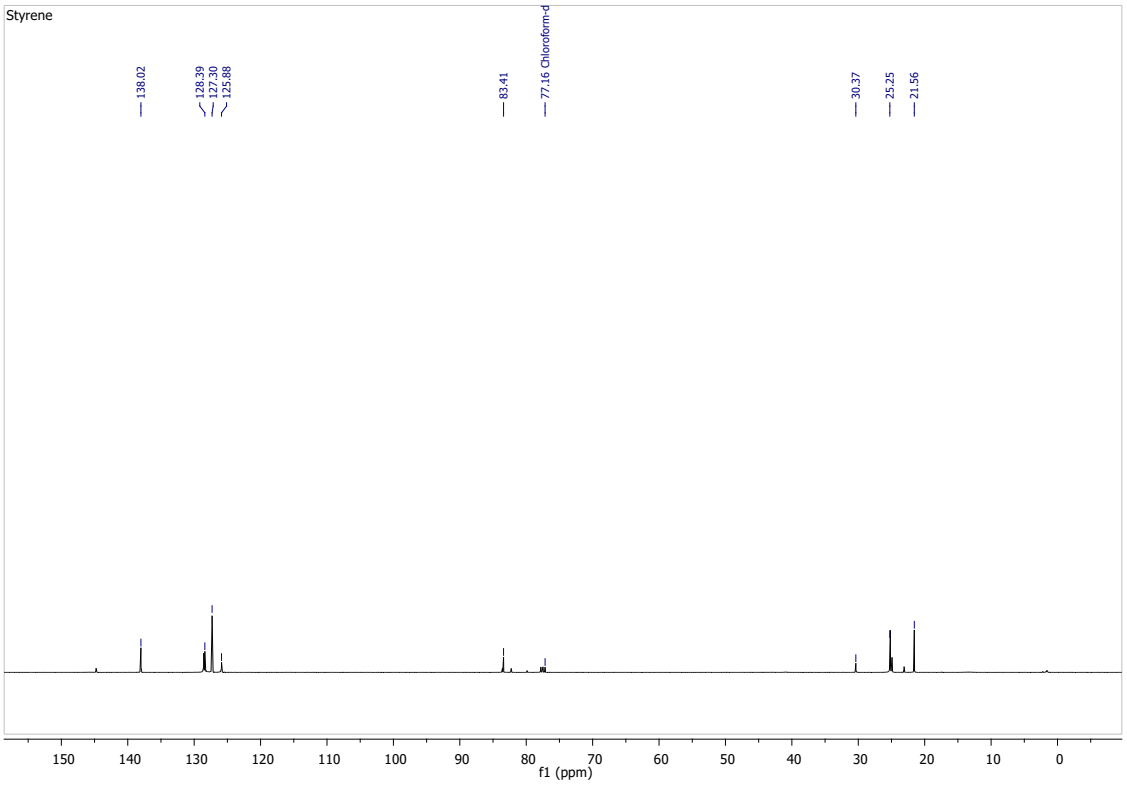


^{13}C NMR of 2-(1-(4-nitrophenyl)ethoxy)-pinacolborane (1j)

4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane (2a): ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.34 – 7.12 (5 H, m), 6.83 (3 H, s), 2.80 (2 H, t), 2.31 (9 H, s), 1.30 (6 H, s), 1.25 (6 H, s), 1.19 (2 H, t) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ 138.02 (s), 128.39 (s), 127.30 (s), 125.88 (s), 83.41 (s), 30.37 (s), 25.25 (s), 21.56 (s) ppm.

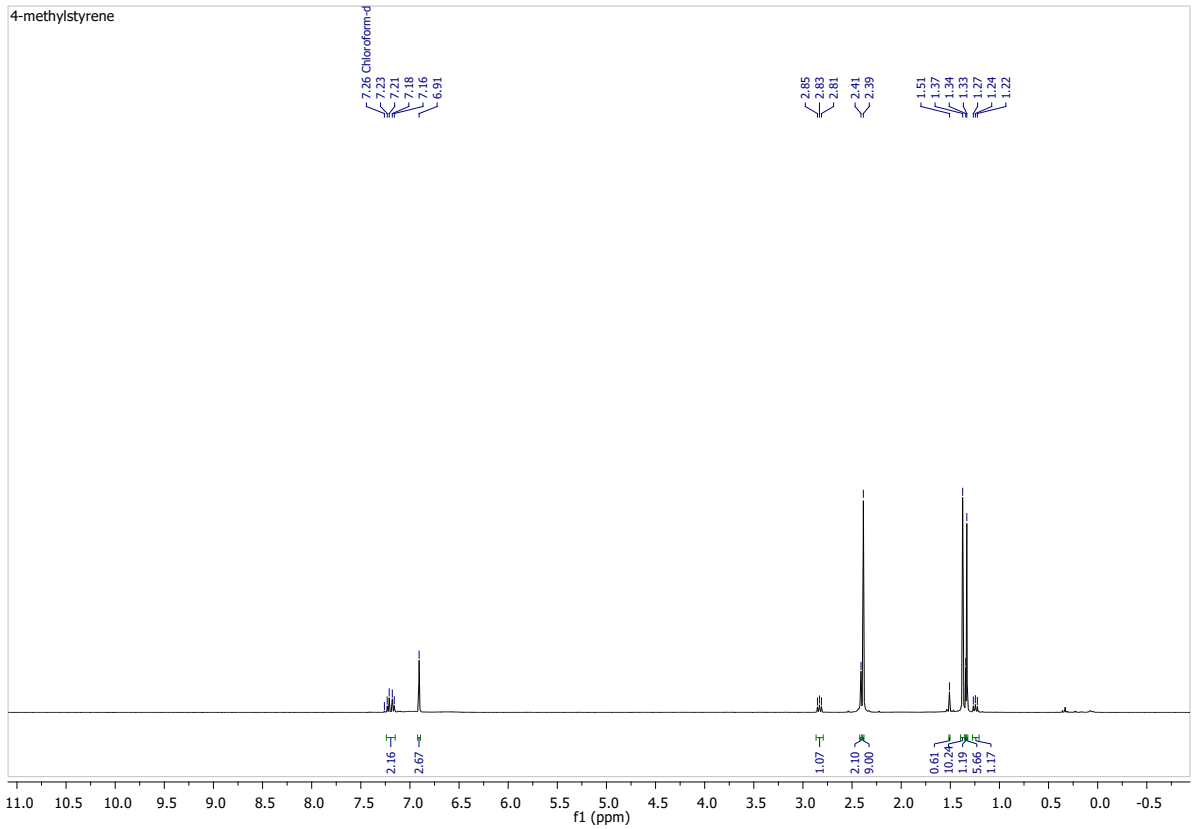


^{1}H NMR of 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane (2a)

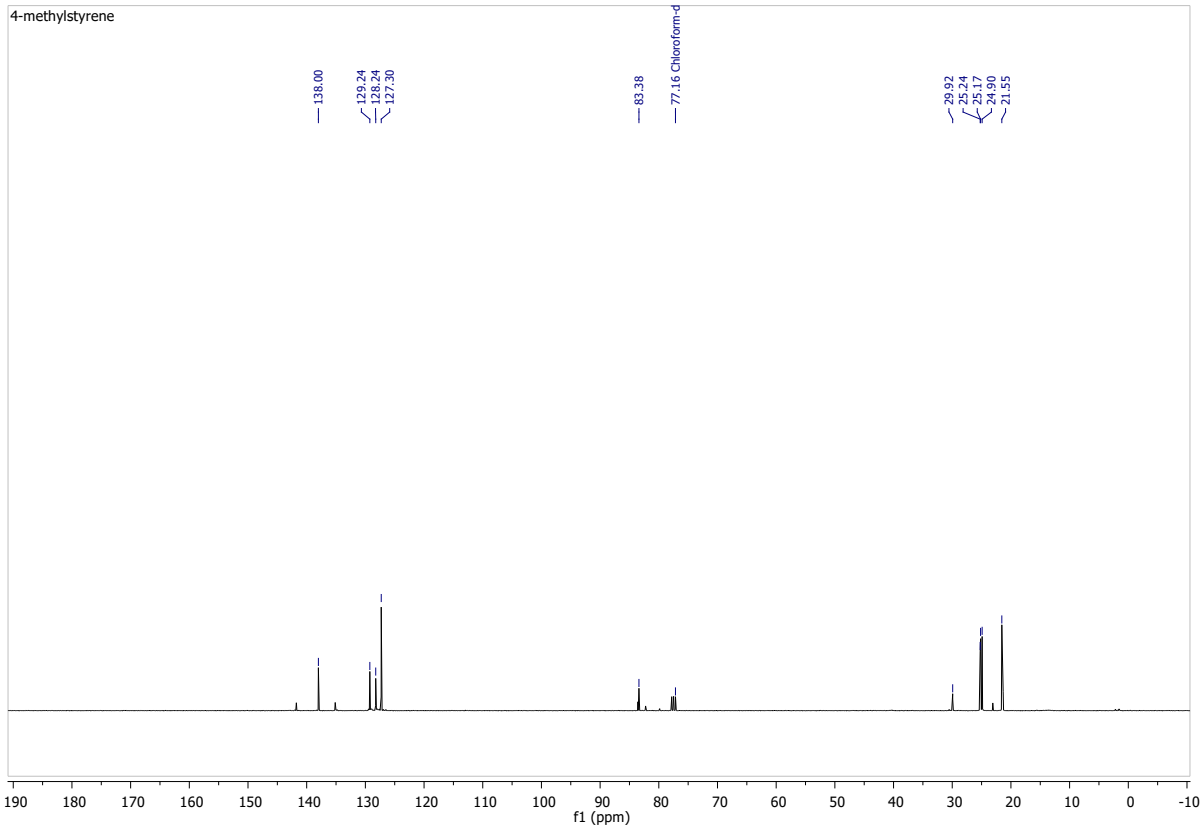


^{13}C NMR of 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane (2a)

4,4,5,5-tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane (2b): ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.20 (4 H, dd), 6.91 (3 H, s), 2.87 – 2.79 (2 H, t), 2.41 (3 H, s), 2.39 (9 H, s), 1.37 (6 H, s), 1.33 (6 H, s), 1.27 – 1.21 (2 H, t) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ 138.00 (s), 129.24 (s), 128.24 (s), 127.30 (s), 83.38 (s), 29.92 (s), 25.20 (d), 24.90 (s), 21.55 (s) ppm.

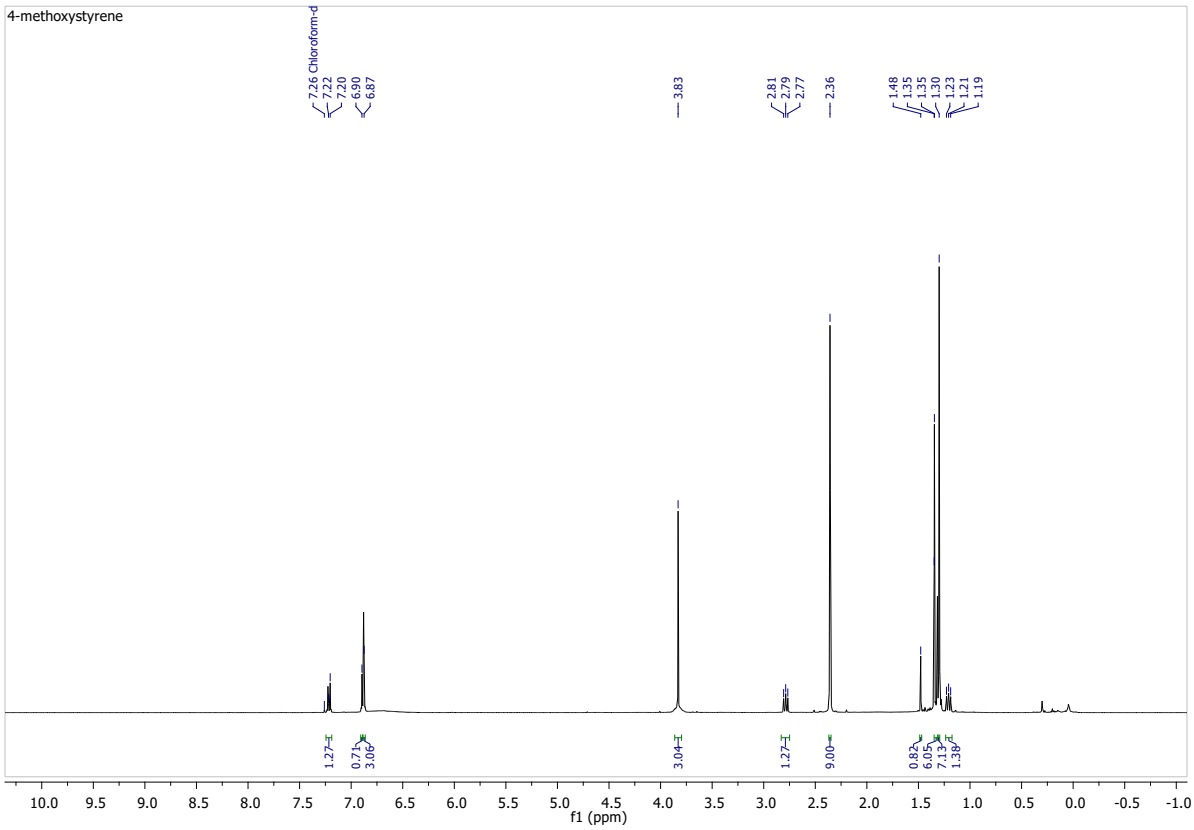


^{1}H NMR of 4,4,5,5-tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane (2b)

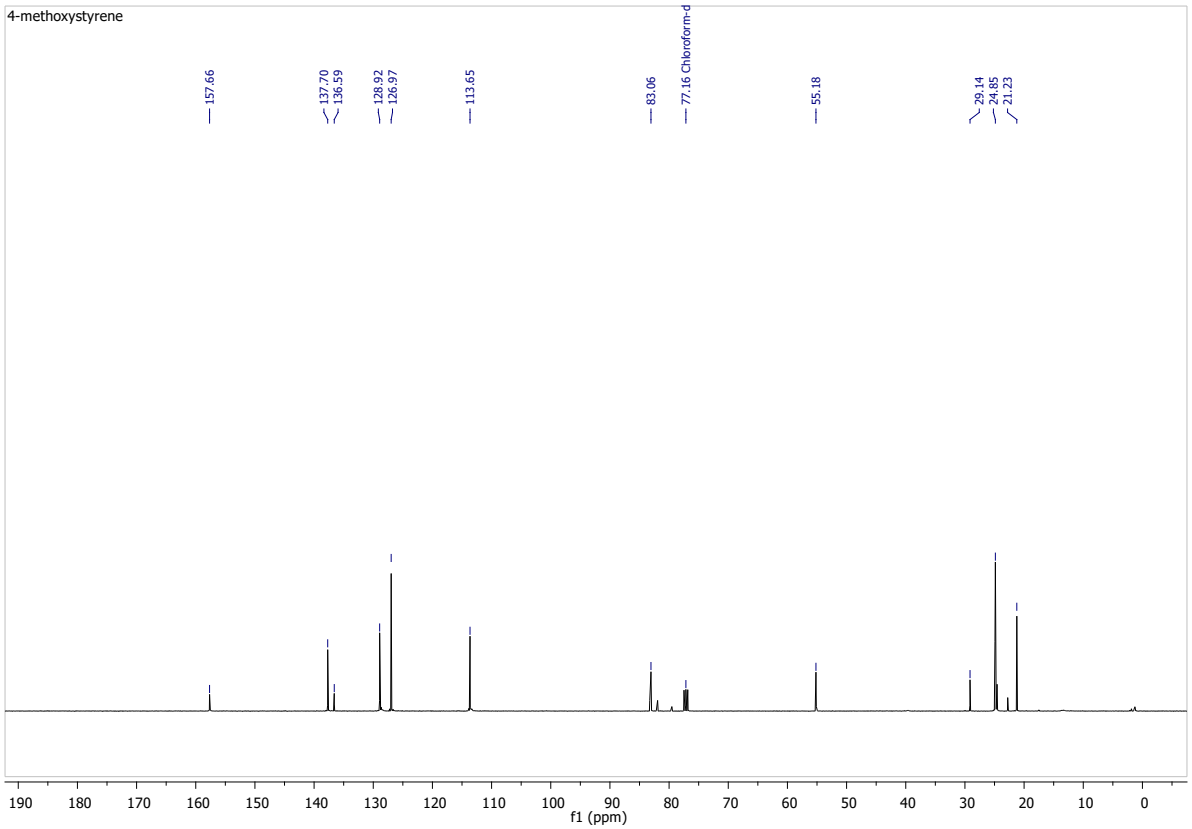


^{13}C NMR of 4,4,5,5-tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane (2b)

2-(4-methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c): ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.21 (2 H, d), 6.90 (2 H, s), 6.87 (3 H, s), 3.83 (3 H, s), 2.83 – 2.75 (2 H, t), 2.36 (9 H, s), 1.35 (6 H, s), 1.30 (6 H, s), 1.24 – 1.17 (2 H, t) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ 157.66 (s), 137.70 (s), 136.59 (s), 128.92 (s), 126.97 (s), 83.06 (s), 55.18 (s), 29.14 (s), 24.85 (s), 21.23 (s) ppm.

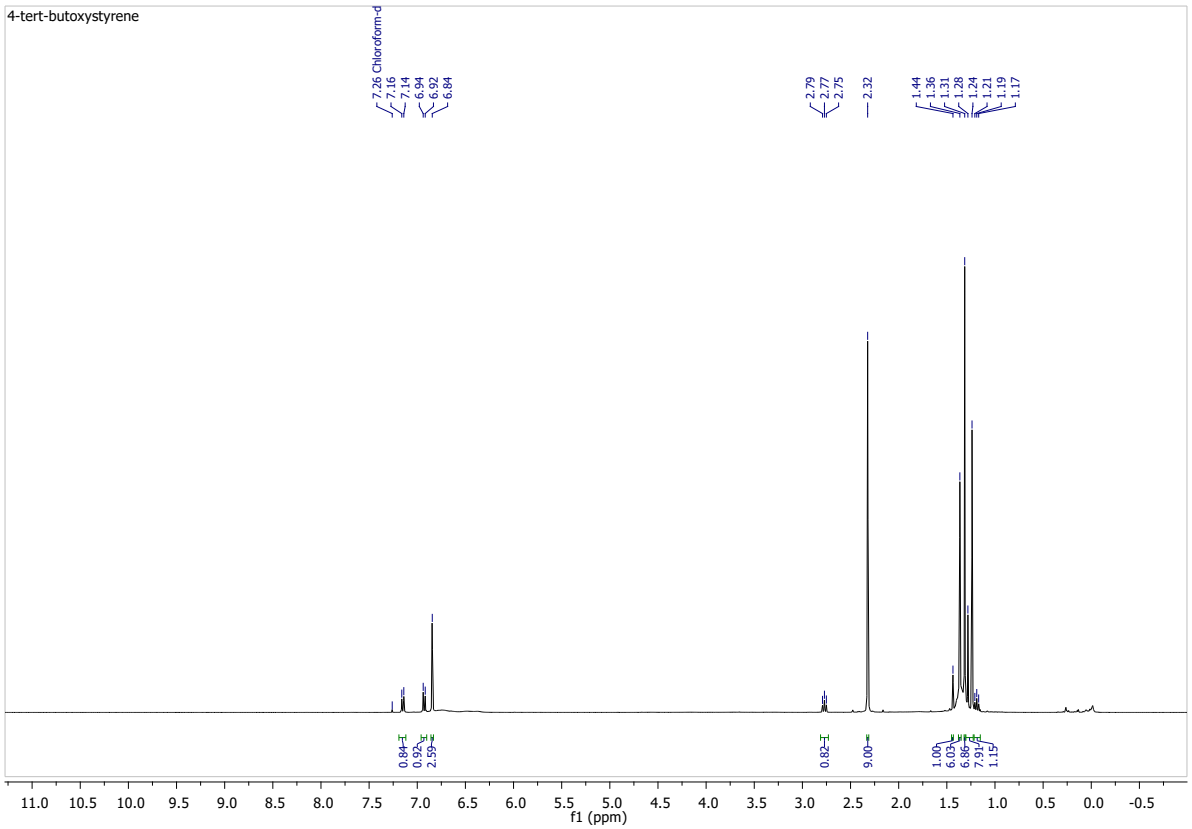


^{1}H NMR of 2-(4-methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c)

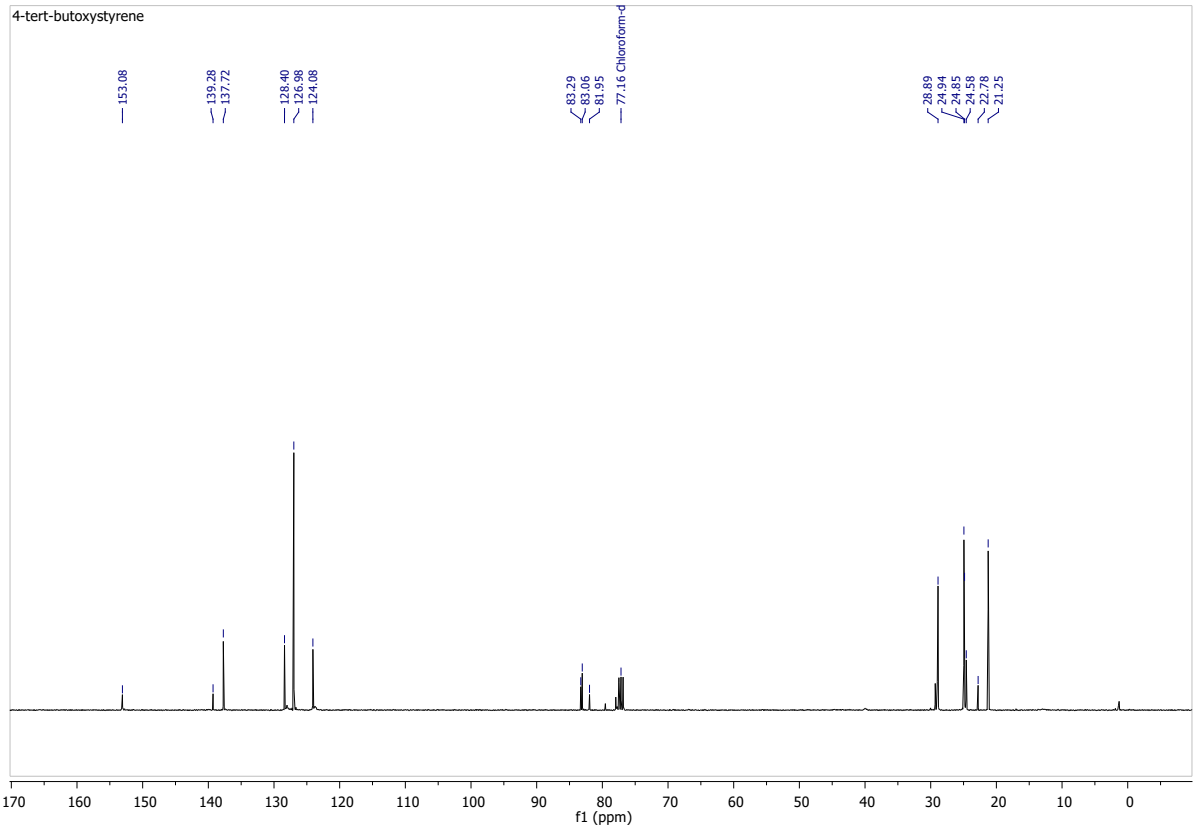


^{13}C NMR of 2-(4-methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c)

2-(4-(tert-butoxy)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d): ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.15 (2 H, d), 6.93 (2 H, d), 6.84 (3 H, s), 2.77 (2 H, t), 2.32 (9 H, s), 1.36 (6 H, s), 1.31 (6 H, s), 1.26 (9 H, d), 1.22 – 1.15 (2 H, t) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ 153.08 (s), 139.28 (s), 137.72 (s), 128.40 (s), 126.98 (s), 124.08 (s), 83.29 (s), 83.06 (s), 81.95 (s), 28.89 (s), 24.89 (d), 24.58 (s), 22.78 (s), 21.25 (s) ppm.

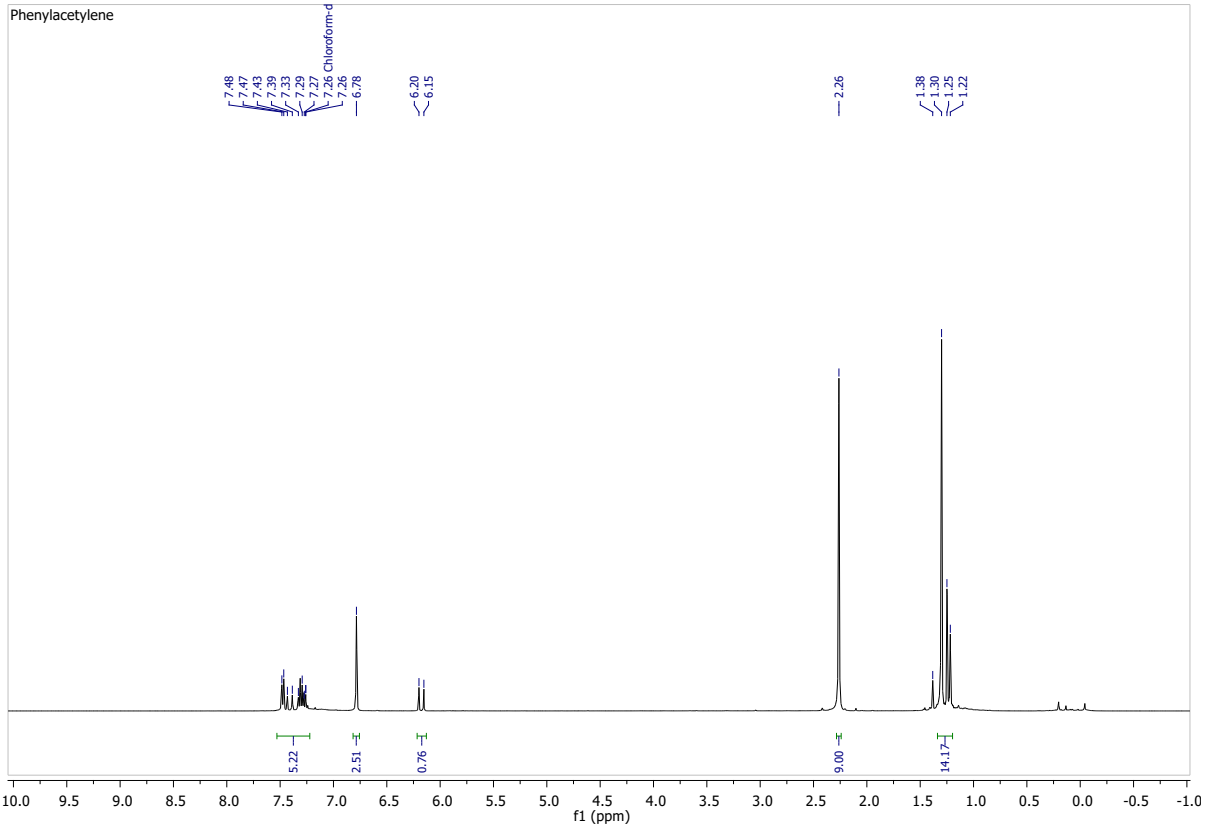


^{1}H NMR of 2-(4-(tert-butoxy)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d)

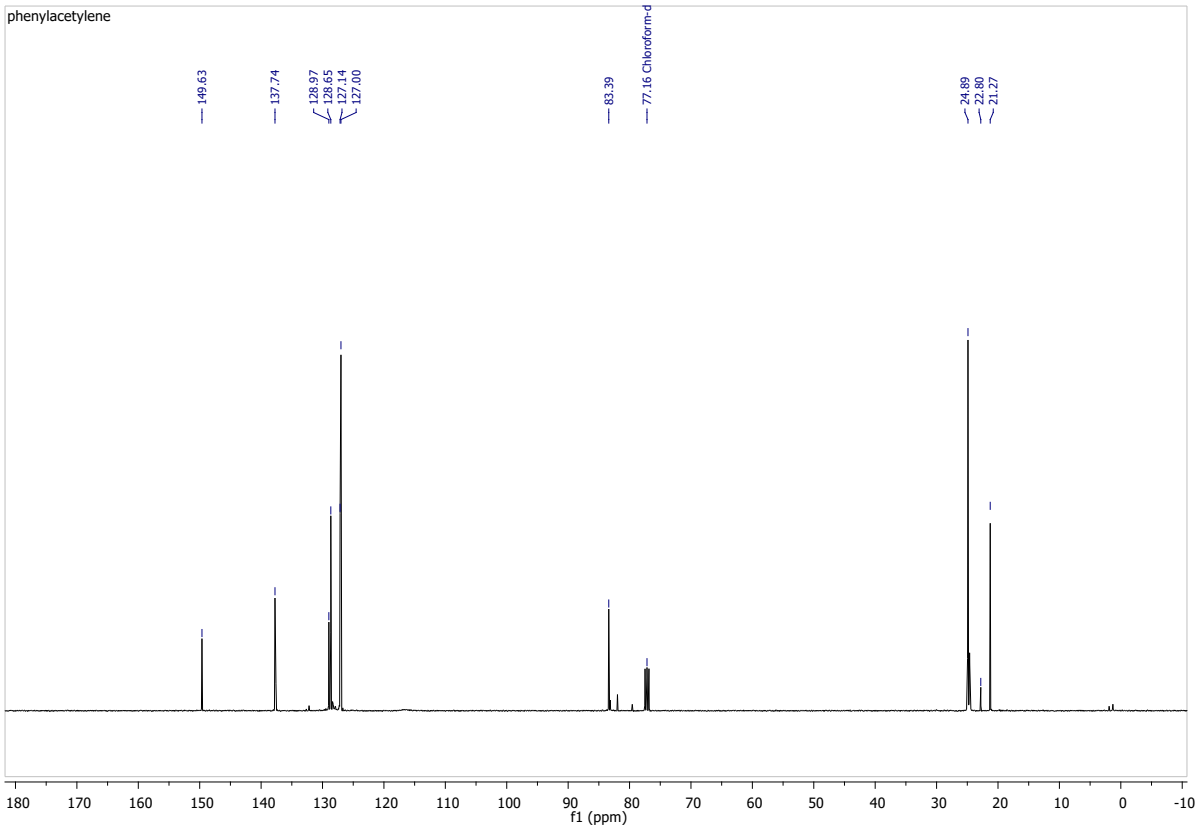


^{13}C NMR of 2-(4-(tert-butoxy)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d)

4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (3a): ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.53 – 7.22 (5 H, m), 6.78 (3 H, s), 6.18 (1 H, d), 2.26 (9 H, s), 1.34 – 1.20 (14 H, m) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ 149.63 (s), 137.74 (s), 128.97 (s), 128.65 (s), 127.07 (d), 83.39 (s), 24.89 (s), 22.80 (s), 21.27 (s) ppm.

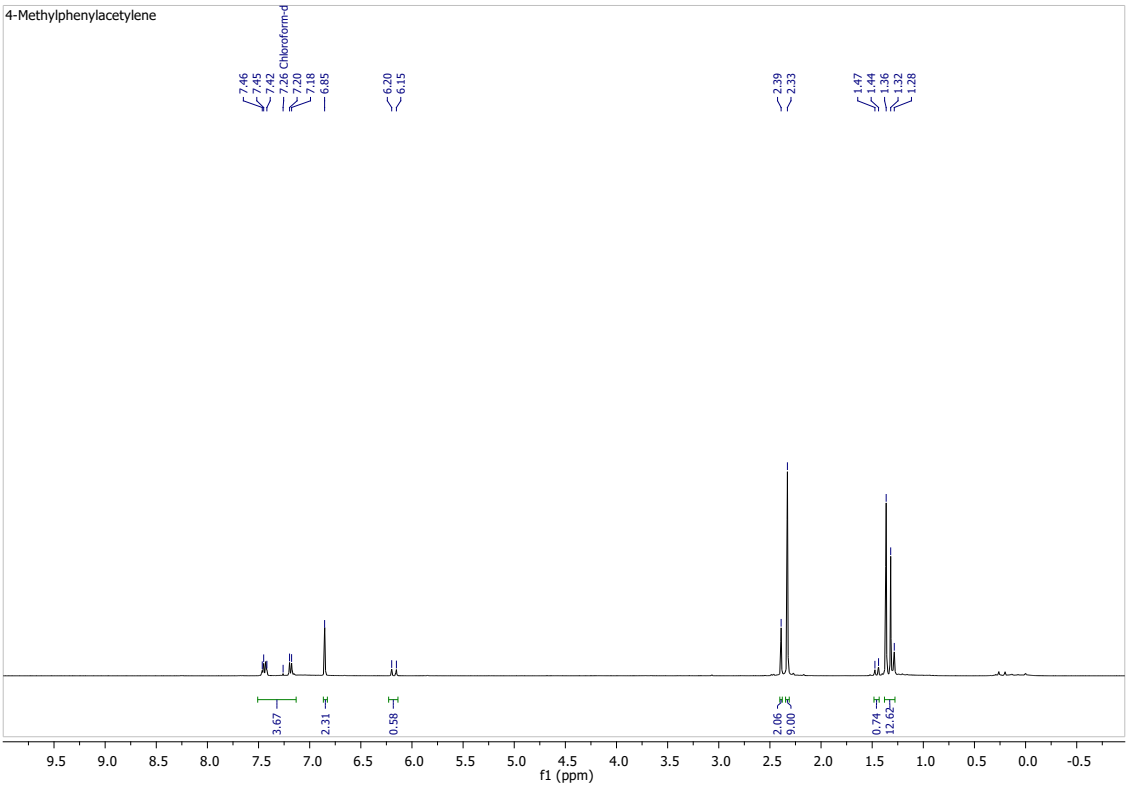


^{1}H NMR of 4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (3a)

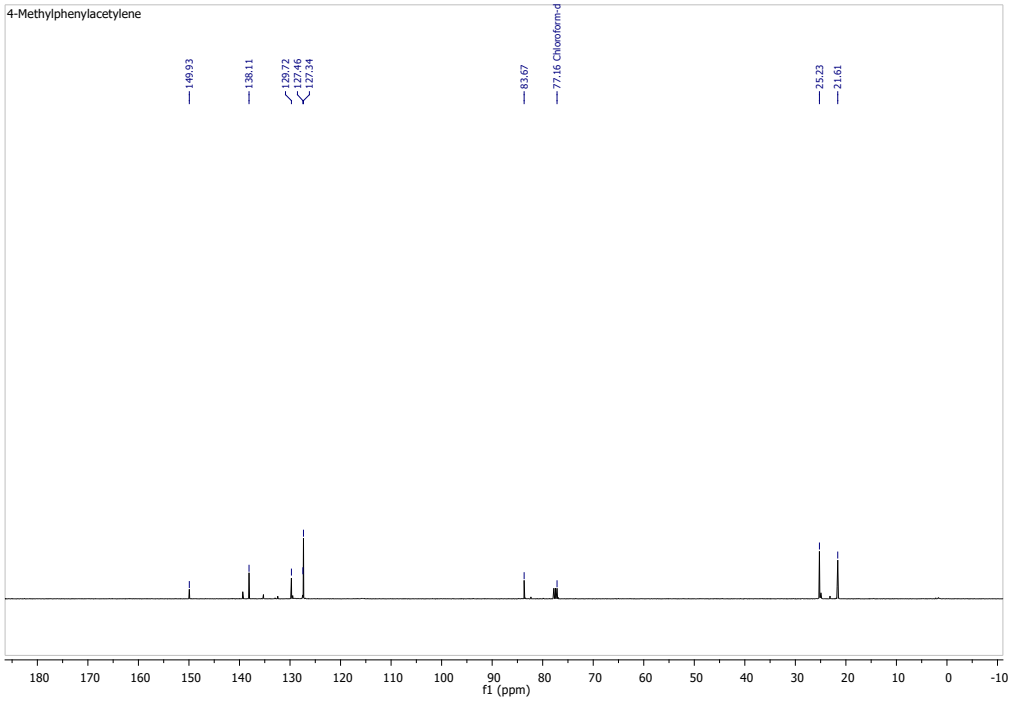


^{13}C NMR of 4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (3a)

4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (3b): ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.51 – 7.13 (4 H, m), 6.85 (3 H, s), 6.18 (1 H, d), 2.39 (3 H, s), 2.33 (9 H, s), 1.46 (1 H, d), 1.38 – 1.28 (12 H, d) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ 149.93 (s), 138.11 (s), 129.72 (s), 127.40 (d), 83.67 (s), 25.23 (s), 21.61 (s) ppm.

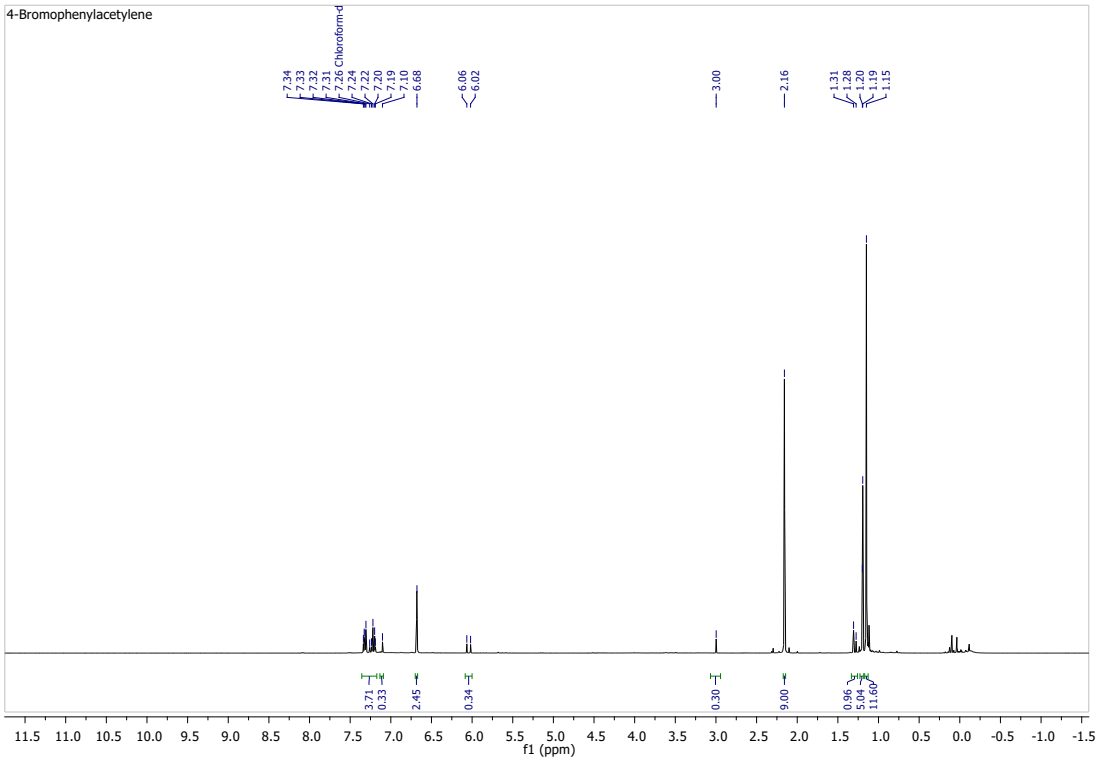


^{1}H NMR of 4,4,5,5-tetramethyl-2-(4-methylstyryl) -1,3,2-dioxaborolane (3b)

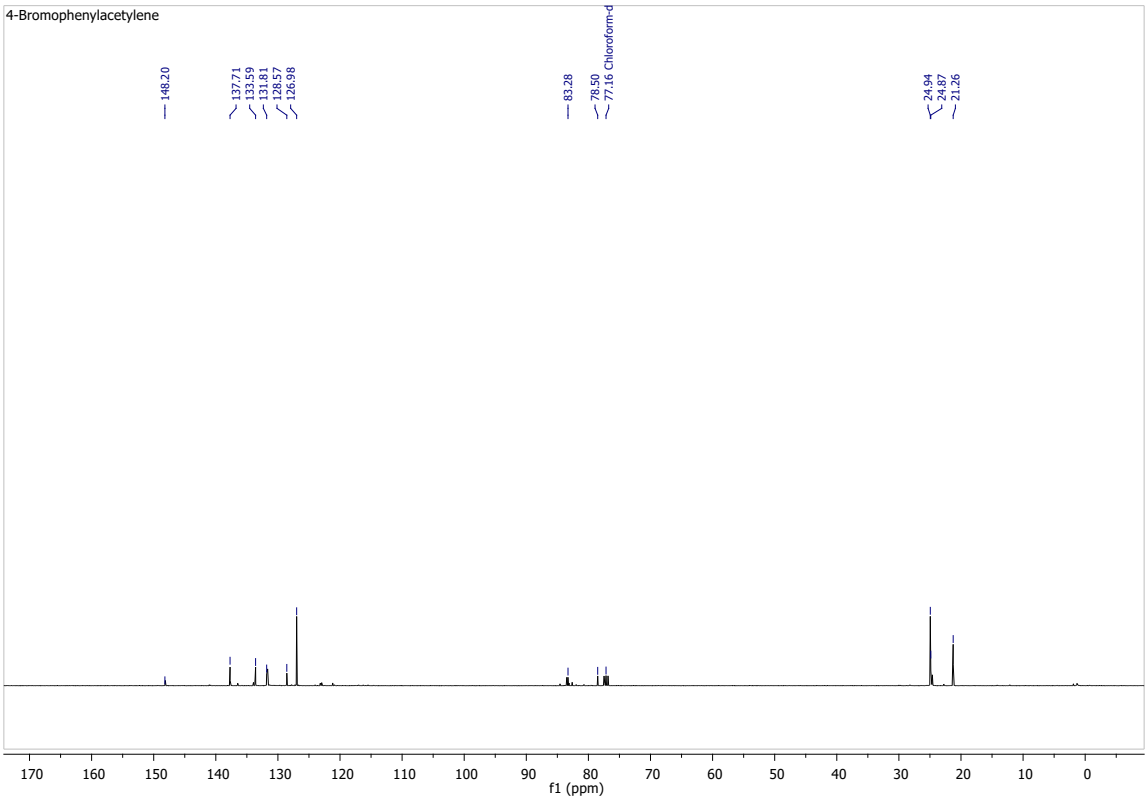


^{13}C NMR of 4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (3b)

2-(4-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c): ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.36 – 7.17 (3 H, m), 7.10 (1 H, s), 6.68 (3 H, s), 6.04 (1 H, d), 3.00 (1 H, s), 2.16 (9 H, s), 1.29 -1.20 (6 H, d) 1.15 (12 H, s) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ 148.20 (s), 137.71 (s), 133.59 (s), 131.81 (s), 128.57 (s), 126.98 (s), 83.28 (s), 78.50 (s), 24.90 (d), 21.26 (s) ppm.

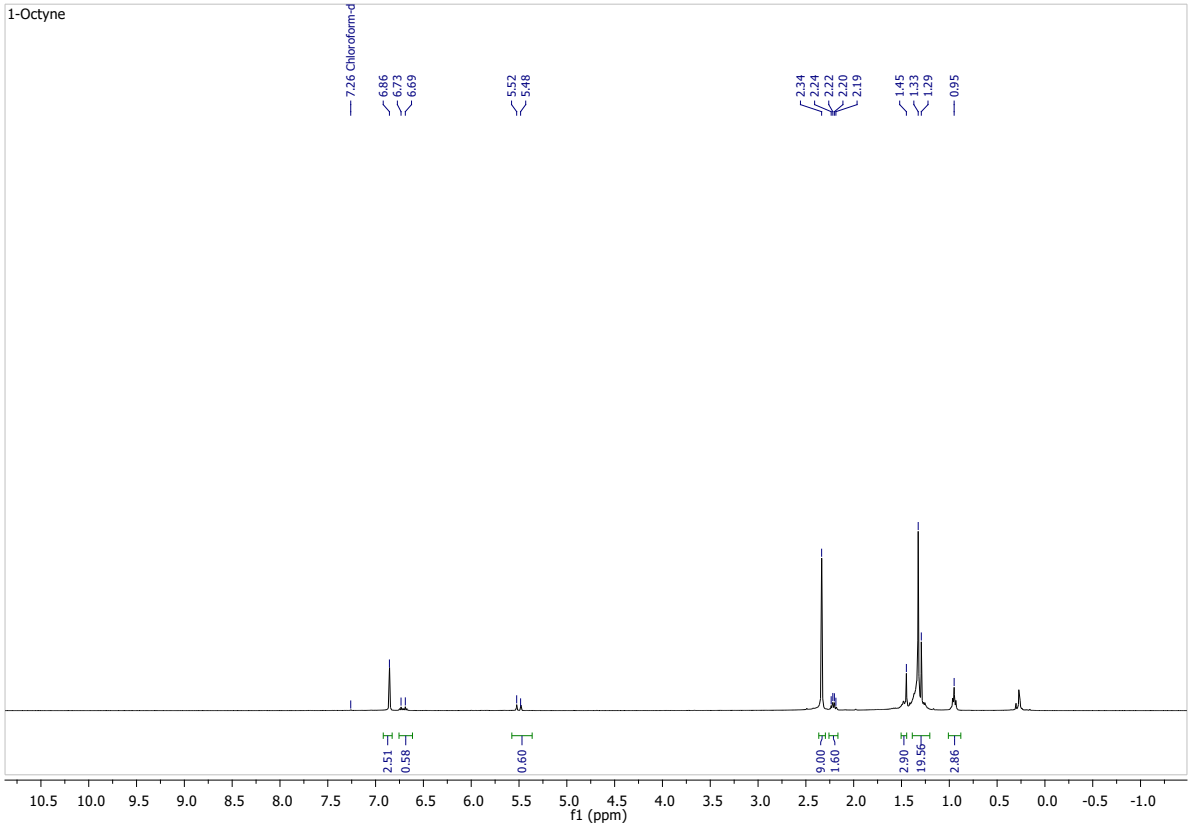


^{1}H NMR of 2-(4-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)

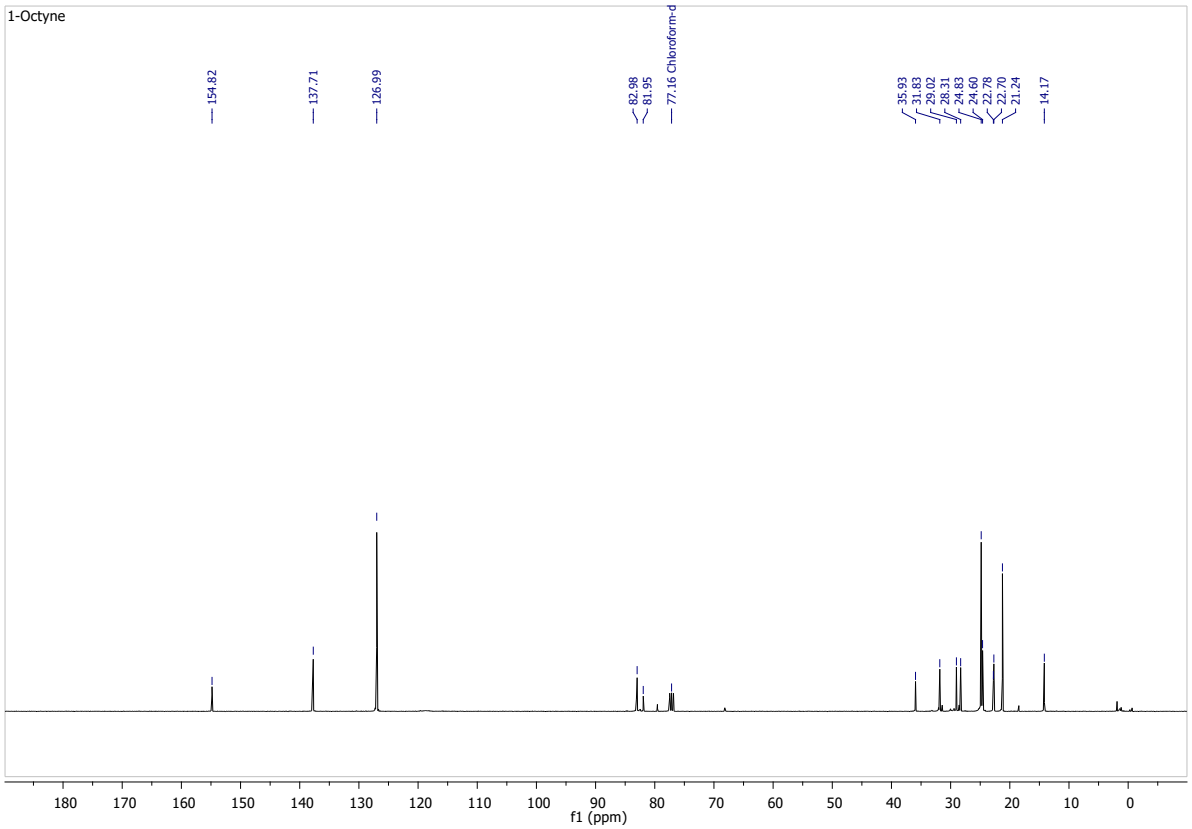


^{13}C NMR of 2-(4-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)

4,4,5,5-tetramethyl-2-(oct-1-en-1-yl)-1,3,2-dioxaborolane (3d): ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 6.86 (3 H, s), 6.71 (2 H, d), 5.50 (1 H, d), 2.34 (9H, s), 2.24-2.19 (2 H, quat), 1.45 (3 H, s), 1.33-1.29 (20 H, m), 0.95 (3 H, s) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ 154.82 (s), 137.71 (s), 126.99 (s), 82.98 (s), 81.95 (s), 35.93 (s), 31.83 (s), 29.02 (s), 24.87 (s), 24.72 (d), 22.74 (d), 21.24 (s), 14.17 (s) ppm.



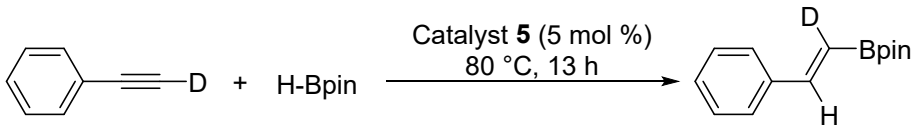
^{1}H NMR of 4,4,5,5-tetramethyl-2-(oct-1-en-1-yl)-1,3,2-dioxaborolane (3d)

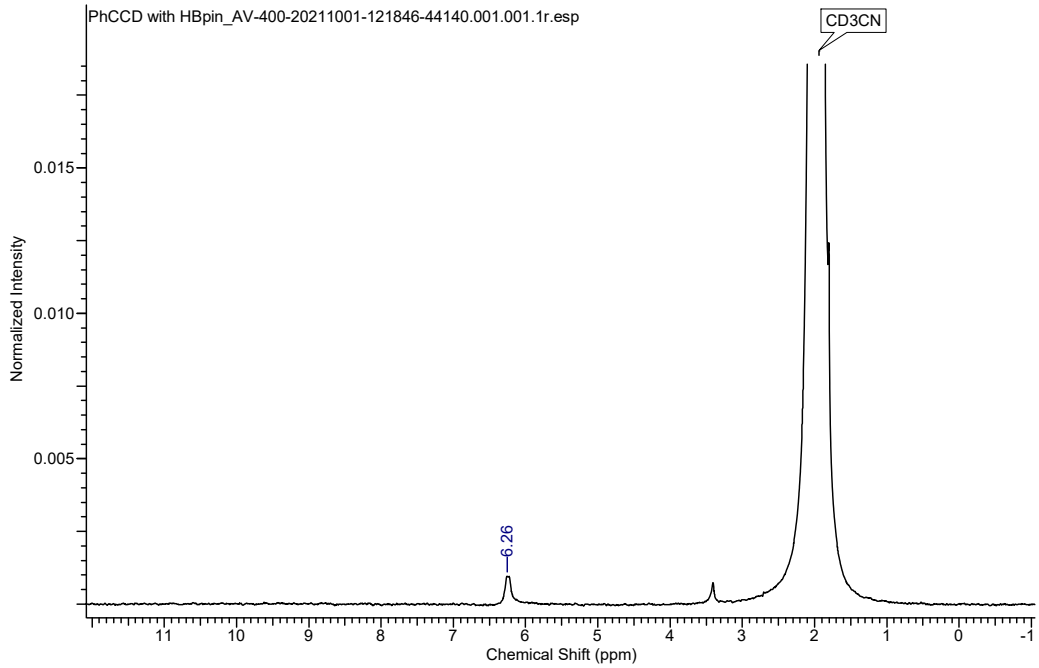


^{13}C NMR of 4,4,5,5-tetramethyl-2-(oct-1-en-1-yl)-1,3,2-dioxaborolane (3d)

12. Regioselectivity studies

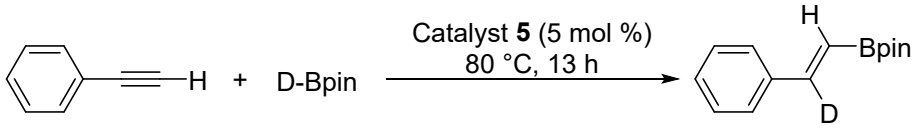
Phenylacetylene-d1 (25.7 mg, 0.25 mmol), pinacolborane (35.5 mg, 0.27 mmol) and catalyst **5** (5.0 mol%) were charged in a screw cap NMR tube inside the glove box. The reaction mixture was heated at 80 °C for 13 h. The progress of the reaction was monitored by the ^{2}H NMR. After dissolving in CD_3CN, the spectrum shows a peak at δ = 6.26 ppm, which indicates a *cis* orientation of deuterium and phenyl group.

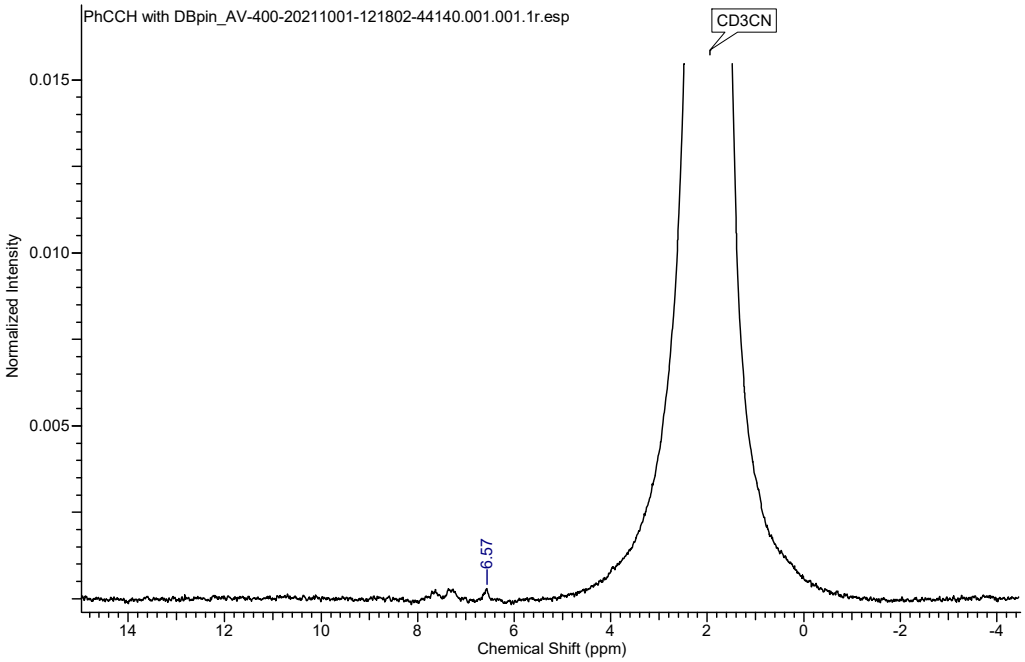




^{2}H NMR spectrum of the reaction of PhC≡CD with HBpin in presence of catalyst **5** (CD_3CN, 76.77 MHz, 298 K)

Phenylacetylene (25.5 mg, 0.25 mmol), pinacolborane-d1 (50 mg, 0.27 mmol) and catalyst **5** (5.0 mol%) were charged in a screw cap NMR tube inside the glove box. The reaction mixture was heated at 80 °C for 13 h. The progress of the reaction was monitored by ^{2}H NMR after dissolving in CD_3CN, which indicated the peak at δ = 6.57 ppm, due to the *cis* orientation of deuterium and Bpin unit.

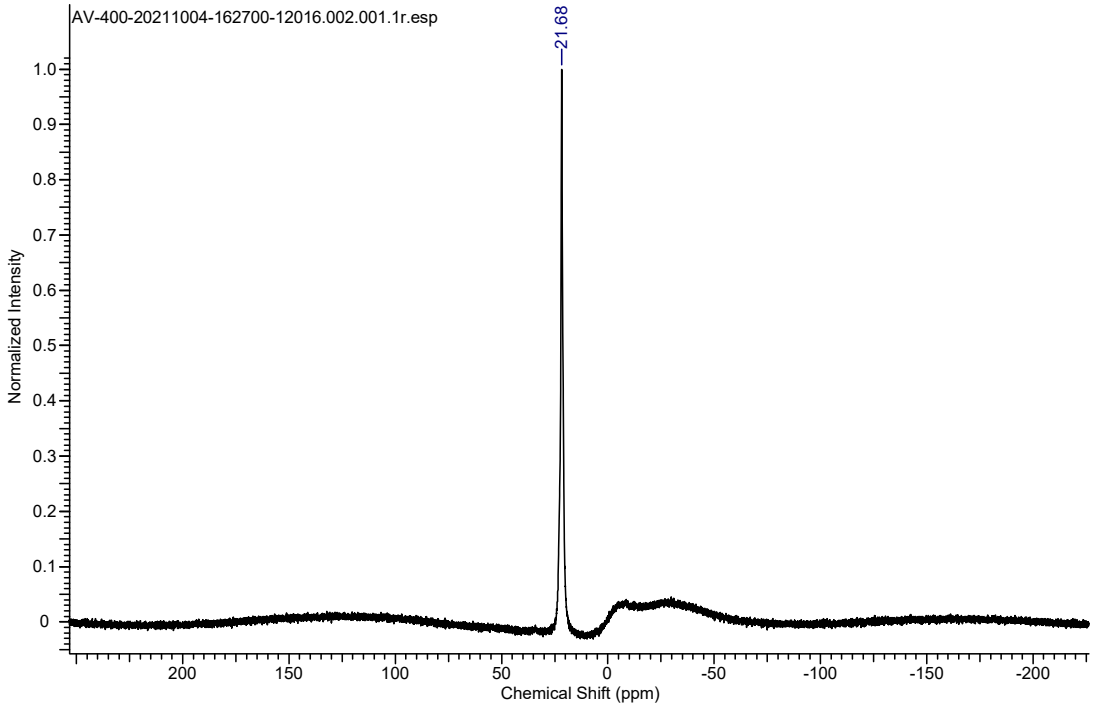




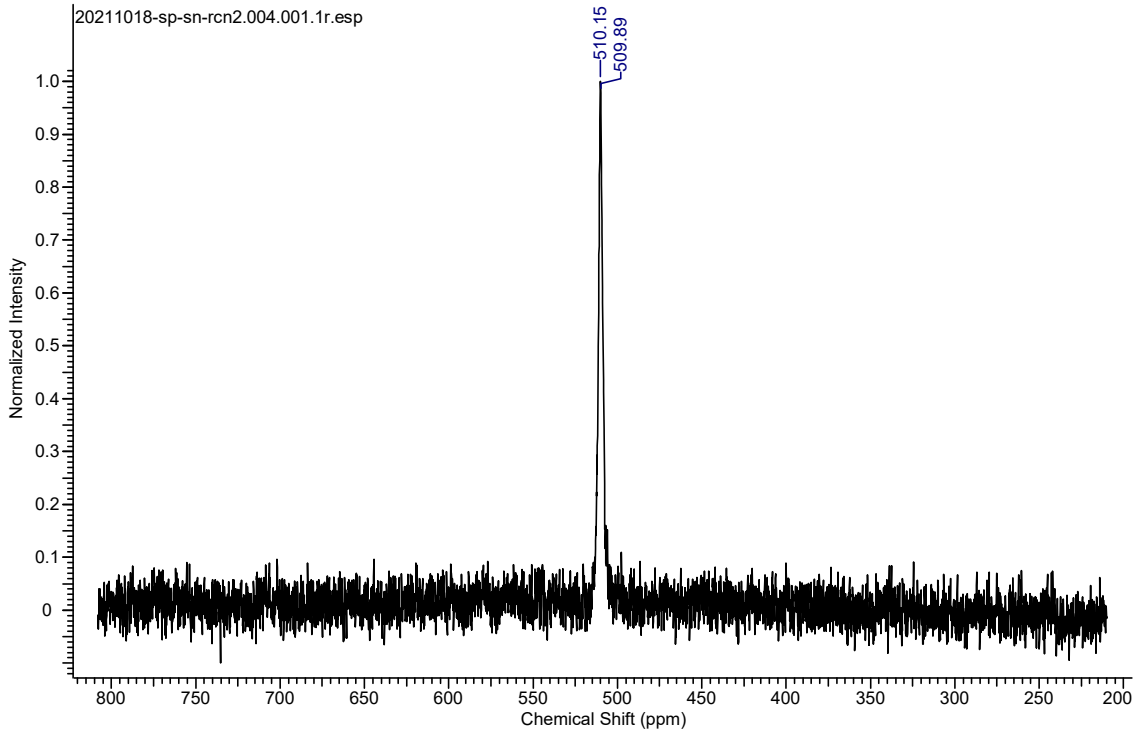
^{2}H NMR spectrum of the reaction of PhC≡CH with DBpin in presence of catalyst **5**

(CD_3CN, 76.77 MHz, 298 K)

13. Mechanistic studies

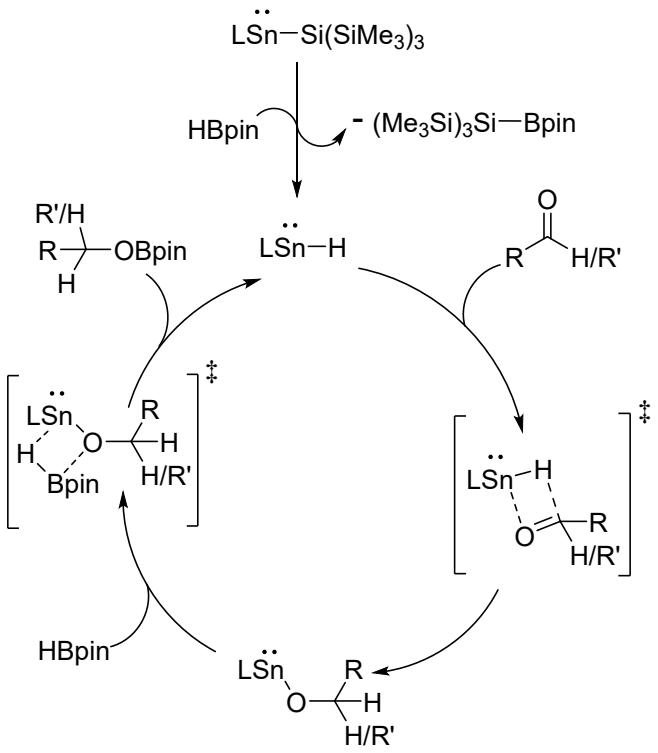


^{11}B NMR for reaction of 5 with HBpin



^{119}Sn NMR for the reaction of 5 with HBpin

Based on the NMR experiments, we describe the following catalytic cycle as a possible mechanistic pathway



Scheme S1. The plausible mechanism of the catalytic hydroboration

14. References

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