Electronic supplementary information(ESI)

Magnesium amide catalyzed selective hydroboration of esters

Milan Kr. Barman, Ashim Baishya and Sharanappa Nembenna*

School of Chemical Sciences, National Institute of Science Education and Research (NISER),

HBNI, Bhubaneswar, 752 050, India

Contents: **Page No.**

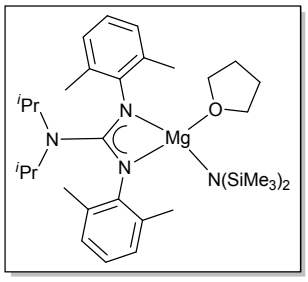
General Experimental:

All stoichiometric and catalytic reactions were carried out under atmosphere of high purity nitrogen gas using standard Schlenk–line and cannula techniques or nitrogen filled MBraun glove box. Chemicals were purchased from Sigma–Aldrich, Alfa-Aesar, Across chemicals and used without further purification. Required solvents were collected from MBraun Solvent Purification System and degassed prior to use. Catalyst **1**, $Mg\{N(SiMe_3)_2\}_2$ was prepared according to literature procedure[1]. Benzene– d_6 was dried and distilled from Na alloy prior to use. ^1H, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$ and ^{11}B NMR spectra were recorded on Bruker AV–400 (^1H: 400 MHz, $^{13}C\{^1H\}$: 100 MHz and $^{29}Si\{^1H\}$ NMR 80 MHz) were referenced to the resonances of the solvent used. Melting points were measured in sealed glass capillaries under nitrogen atmosphere on an electro thermal apparatus and are uncorrected. C, H and N analysis were done on Vario Micro Cube Elementar CHNS/O analyzer.

Preparation of complexes 2 & 3

Synthesis of ^{xyl}LMgN(SiMe$_3$)$_2$·THF (2) [^{xyl}L = ArNC(N^{i}Pr$_2$)NAr; (Ar = 2,6– Me$_2$–C$_6$H$_3$)]

Method A.



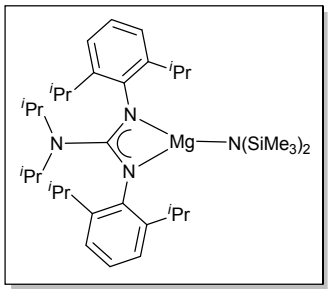
In a Schlenk tube ^{xyl}LH (1.00 g, 2.84 mmol, 1.0 equiv) was dissolved in THF (15 mL) and the solution was added drop by drop at −78 ^{o}C to an another Schlenk tube charged with $Mg\{N(SiMe_3)_2\}_2$ (0.979 g, 2.84 mmol, 1.0 equiv) in THF (5 mL). Once the addition is completed, the solution was allowed to warm to room temperature and stirred for 14 h. After removal of all the volatiles *in vacuo*, the residue was extracted with *n*–hexane (20 mL) and filtered through Celite and concentrated to about 5 mL and finally stored at –30 ^{o}C. Colorless crystals of compound **2** suitable for X–ray diffraction analysis are formed after one day. Yield: 1.38 g (80 %).

Method B.

^{xyl}LH (0.500 g, 1.42 mmol, 1.0 equiv.) and $KN(SiMe_3)_2$ (0.582 g, 2.91 mmol, 2.05 equiv.) were placed in a Schlenk tube and THF (10 mL) was added at room temperature and continued the stirring for 4 hours. The resulting solution was added drop by drop to a stirred suspension of $MgCl_2$ (0.135 g, 1.42 mmol, 1.0 equiv.) in THF (5 mL) at −78 °C. After coming to room temperature stirring was continued for another 24 h. Removal of all volatiles and recrystallized from *n*–hexane (20 mL) at −30 °C gave **2.** Yield: 0.675 g (78 %), Mp = 150 – 155 °C;

^{1}H NMR (400 MHz, C_6D_6) δ 7.08–6.99 (m, 4H, Ar–*H*), 6.95 – 6.86 (m, 2H, Ar–*H*), 3.86 (sept, *J* = 6 Hz, 2H, C*H*$(CH_3)_2$), 3.59 (t, 4H, THF), 2.46 (s, 3H, Ar–C*H*$_3$), 2.21 (s, 9H, Ar–C*H*$_3$), 1.25 (m, 4H, THF), 0.73 (d, *J* = 7.0 Hz, 12H, CH(C*H*$_3)_2$), 0.33 (s, 18H, NSi(C*H*$_3)_3$). ^{13}C NMR (100 MHz, C_6D_6) δ 170.6(N*C*N), 148.4(Ar–*C*), 132.9(Ar–*C*), 128.4(Ar–*C*), 122.2(Ar–*C*), 69.1(THF), 50.7(N–^{i}Pr–*C*H), 25.1(THF), 24.5 (^{i}Pr–*C*H$_3$), 19.3(Ar–*C*H$_3$), 6.1(Si–*C*) ppm. ^{29}Si NMR (80 MHz, C_6D_6) δ –8.11 ppm. Anal. Calcd. for $C_{33}H_{58}MgN_4OSi_2$: C, 65.26; H, 9.63; N, 9.23. Found: C, 65.06; H, 9.23; N, 8.93.

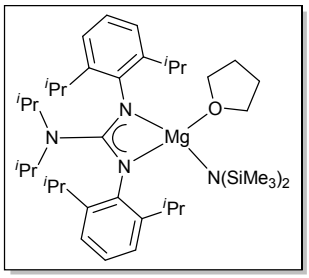
Synthesis of ^{dipp}LMgN(SiMe$_3)_2$ (3a) [^{dipp}L = ArNC(N^{i}Pr$_2$)NAr; (Ar = 2,6– ^{i}Pr$_2$–C$_6$H$_3$)]



In a Schlenk tube ^{dipp}LH (1.00 g, 2.15 mmol, 1.0 equiv.) and $Mg\{N(SiMe_3)_2\}_2$ (0.74 g, 2.15 mmol, 1.0 equiv.) were mixed inside the glovebox. To the above mixture benzene (15 mL) was added and heated at 80 °C for 12 h. After removal of all the volatiles, the residue was extracted with *n*–hexane (20 mL). Solvent was removed and dried in vacuum off−white solid compound isolated. Yield: 1.09 g (78 %).

^{1}H NMR (400 MHz, C_6D_6) δ 7.10 – 7.08 (m, 6H, Ar–*H*), 4.01(sept, 2H, C*H*$(CH_3)_2$), 3.61 (sept, *J* = 6.8 Hz, 4H, C*H*$(CH_3)_2$), 1.29 (dd, *J* = 11.1, 6.8 Hz, 24H, CH(C*H*$_3)_2$), 0.69 (d, *J* = 7.0 Hz, 12H, CH(C*H*$_3)_2$), 0.22 (s, 18H, NSi(C*H*$_3)_3$) ppm.

Synthesis of ^{dipp}LMgN(SiMe$_3$)$_2$·THF (3) [^{dipp}L = ArNC(N^{i}Pr$_2$)NAr; (Ar = 2,6– ^{i}Pr$_2$–C$_6$H$_3$)]



A solution of ^{dipp}LH (0.50 g, 1.07 mmol, 1.0 equiv.) in THF (10 mL) was added drop by drop to the Mg{N(SiMe$_3$)$_2$}$_2$ (0.371 g, 1.07 mmol, 1.0 equiv.) solution in THF (5 mL) at -78 ^{o}C. Once the addition is completed, the solution was allowed to warm to room temperature and stirred for 14 h. After removal of all the volatiles, the residue was extracted with *n*–hexane (20 mL) and concentrated to about 5 mL, few drops of THF was added and finally stored in –30 ^{o}C. Crystal came after 2 days. Yield: 0.61 g (76 %), Mp = 162 – 165 ^{o}C; ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 7.18 (d, *J* = 2.4 Hz, 4H, Ar–*H*), 7.14–7.10 (m, 2H, Ar–*H*), 4.08 (sept, 2H, C*H*(CH$_3$)$_2$), 3.93 (s, 4H, THF), 3.60 (sept, 4H, C*H*(CH$_3$)$_2$), 1.36 (d, *J* = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 1.25 (t, 4H, THF), 0.80 (d, *J* = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 0.11 (s, 18H, NSi(C*H*$_3$)$_3$). ^{13}C NMR (100 MHz, C$_6$D$_6$) δ 170.7(N*C*N), 145.3(Ar–*C*), 143.2(Ar–*C*), 124.0(Ar–*C*), 123.9(Ar–*C*), 70.0(THF), 50.3(N–*i*Pr–*C*H), 28.0(*i*Pr–*C*H$_3$), 26.6(*i*Pr–*C*H$_3$), 25.0(THF), 24.2(*i*Pr–*C*H$_3$), 23.9(*i*Pr–*C*H$_3$), 5.9(Si–*C*). ^{29}Si NMR (80 MHz, C$_6$D$_6$) δ – 8.36 ppm. Anal. Calcd. for C$_{41}$H$_{74}$MgN$_4$OSi$_2$: C, 68.44; H, 10.37; N, 7.79; Found: C, 68.16; H, 10.13; N, 7.56.

General procedure for the catalytic hydroboration of ester

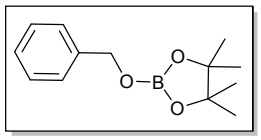
Ester (0.25 mmol), pinacolborane (0.525 mmol), [Mg] catalyst (0.1 mol%) [C_6D_6 (0.5 mL) for solid substrate and cat 0.5 mol%] (magnesium amide catalyst taken from a stock solution of appropriate concentration stock solution into vial and solvent was removed under pressure) were charged in a screw cap glass vial with a magnetic bead inside the glove box and stirred at room temperature until complete the reaction. Reaction progress was monitored by ^{1}H NMR spectroscopy which specifies disappearances of ester CH_2 proton and presences of new CH_2 proton of boronate ester.

Scale up reaction of hydroboration of benzyl benzoate

Ester (1 mmol), pinacolborane (2.1 mmol) were added to vial equipped with catalyst (0.1 mol%) inside the glove box. Reaction mixture was stirred under neat condition at room temperature. The reaction conversion was monitored by ^{1}H NMR, which indicated the completion of the reaction by the consumption of ester proton. Upon completion of the reaction, the resulted boronate ester residue was hydrolysed with silica gel at 60 ^{o}C for 4–6 h. The completion of hydrolysis was checked by TLC. After completion, the reaction mixture was washed 3−4 times with HCl with vigorous shaking and extracted with dichloromethane. The combined organic layers were dried, evaporated and the compound was purified by column chromatography over silica gel with hexane/ethyl acetate, which provided the pure primary alcohol.

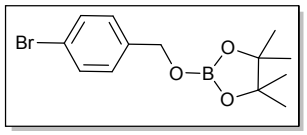
Spectral Data of Boronate Esters:

2−(benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[2]



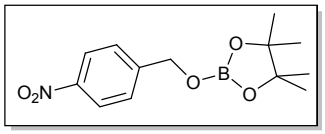
^{1}H NMR (400 MHz, C_6D_6) δ 7.30 (d, *J* = 7.4 Hz, 2H), 7.16 – 7.10 (m, 2H), 7.09 – 7.02 (m, 1H), 4.94 (s, 2H), 1.04 (s, 12H). ^{11}B NMR (128 MHz, C_6D_6) δ 22.69 (s).

2-((4-bromobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[2]



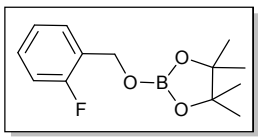
^{1}H NMR (400 MHz, C_6D_6) δ 7.21 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.3 Hz, 2H), 4.73 (s, 2H), 1.03 (s, 12H). ^{11}B NMR (128 MHz, C_6D_6) δ 22.62 (s).

4,4,5,5-tetramethyl-2-((4-nitrobenzyl)oxy)-1,3,2-dioxaborolane[3]



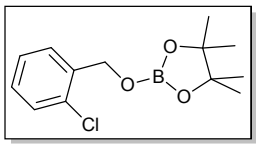
^{1}H NMR (400 MHz, C_6D_6) δ 7.95 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 4.79 (s, 3H), 1.08 (s, 12H). ^{11}B NMR (128 MHz, C_6D_6) δ 22.62 (s).

2-((2-fluorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[4]



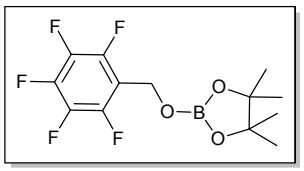
^{1}H NMR (400 MHz, C_6D_6) δ 7.45 – 7.41 (m, 1H), 6.85 – 6.80 (m, 2H), 6.77 – 6.72 (m, 1H), 5.10 (s, 1H), 1.04 (s, 12H). ^{11}B NMR (128 MHz, C_6D_6) δ 22.69 (s).

2-((2-chlorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[3]



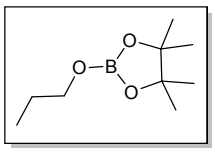
^{1}H NMR (400 MHz, C_6D_6) δ 7.42 (d, *J* = 7.7 Hz, 1H), 7.23 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.19-7.15 (m, 1H), 7.13-7.08 (m, 1H), 4.93 (s, 2H), 1.18 (s, 12H). ^{11}B NMR (128 MHz, C_6D_6) δ 22.54.

4,4,5,5-tetramethyl-2-((perfluorophenyl)methoxy)-1,3,2-dioxaborolane[5]



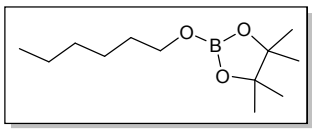
^{1}H NMR (400 MHz, C_6D_6) δ 4.77 (s, 2H), 1.05 (s, 12H). ^{11}B NMR (128 MHz, C_6D_6) δ 22.52.

4,4,5,5-tetramethyl-2-propoxy-1,3,2-dioxaborolane[6]



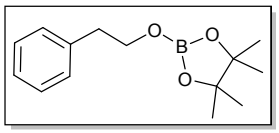
^{1}H NMR (400 MHz, C_6D_6) δ 3.83 (t, *J* = 6.6 Hz, 2H), 1.54 – 1.45 (m, 2H), 1.06 (s, 12H), 0.81 (t, *J* = 7.4 Hz, 3H). ^{11}B NMR (128 MHz, C_6D_6) δ 22.54.

2-(hexyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



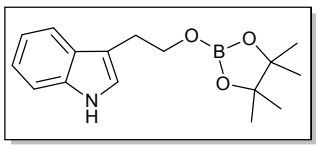
^{1}H NMR (400 MHz, C_6D_6) δ 3.87 (t, *J* = 6.5 Hz, 2H), 1.54 – 1.46 (m, 2H), 1.29 – 1.21 (m, 2H), 1.20 – 1.13 (m, 4H), 1.07 (s, 12H), 0.81 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, C_6D_6) 82.35(BO*C*Me$_2$), 65.05($CH_3(CH_2)_4$*C*H_2OBpin), 32.0(CH_3(*C*H_2)$_4$$CH_2$OBpin), 31.9($CH_3$(*C*$H_2$)$_4$$CH_2$OBpin), 25.7($CH_3$(*C*$H_2$)$_4$$CH_2$OBpin), 24.7(BOC*Me*$_2$), 23.0($CH_3$(*C*$H_2$)$_4$$CH_2$OBpin), 14.2(*C*$H_3$$(CH_2)_4$$CH_2$OBpin). ^{11}B NMR (128 MHz, C_6D_6) δ 22.68.

4,4,5,5-tetramethyl-2-phenethoxy-1,3,2-dioxaborolane[5]



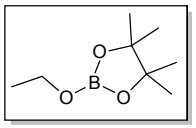
^{1}H NMR (400 MHz, C_6D_6) δ 7.13 – 7.00 (m, 5H), 4.07 (t, *J* = 6.9 Hz, 2H), 3.92 – 3.87 (m, 2H), 1.05 (s, 12H), ^{13}C NMR (100 MHz, C_6D_6) 138.9(Ar–*C*), 129.5(Ar–*C*), 128.5(Ar–*C*), 126.4(Ar–*C*), 82.4(BO*C*Me$_2$), 65.9(CH_2*C*H_2OBpin), 38.5(*C*$H_2$$CH_2$OBpin), 24.7(BOC*Me*$_2$); ^{11}B NMR (128 MHz, C_6D_6) δ 22.40.

3-(2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)ethyl)-1H-indole (See for the corresponding alcohol, *i.e,* 2(1H-Indol-3-yl)ethanol [7])



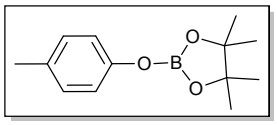
^{1}H NMR (400 MHz, C_6D_6) δ 7.67 (d, *J* = 7.7 Hz, 1H), 7.22 – 7.03 (m, 2H), 7.09 (d, *J* = 7.8 Hz, 1H), 7.03 (s, 1H), 6.60 (d, *J* = 2.1 Hz, 1H), 4.25 (t, *J* = 6.9 Hz, 2H), 3.06 (t, *J* = 6.9 Hz, 2H), 1.05 (s, 12H); ^{13}C NMR (100 MHz, C_6D_6) δ 136.7(Ar–*C*), 127.94(Ar–*C*), 122.5(Ar–*C*), 122.0(Ar–*C*), 119.5(Ar–*C*), 119.4(Ar–*C*), 112.5(Ar–*C*), 111.2(Ar–*C*), 82.3(BO*C*Me$_2$), 65.5(CH_2*C*H_2OBpin), 28.3(*C*$H_2$$CH_2$OBpin), 24.7(BOC*Me*$_2$); ^{11}B NMR (128 MHz, C_6D_6) δ 22.47.

2-ethoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[8]



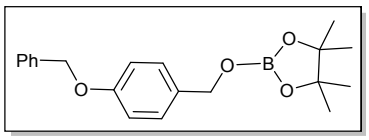
^{1}H NMR (400 MHz, C_6D_6) 5.66 (q, J = 6.4 Hz, 2H), 1.81 (s, 3H), 1.01 (s, 12H); ^{13}C NMR (100 MHz, C_6D_6) 82.2 (BO*C*Me$_2$), 67.7(CH$_3$*C*H$_2$OBpin), 24.1(BOC*Me*$_2$), 20.0(*C*H$_3$CH$_2$OBpin). ^{11}B NMR (128 MHz, C_6D_6) δ 22.68.

4,4,5,5-tetramethyl-2-(p-tolyloxy)-1,3,2-dioxaborolane[9]



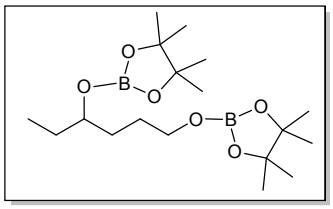
^{1}H NMR (400 MHz, C_6D_6) δ 7.15 – 7.13 (m, 2H), 6.87 (d, J = 8.4 Hz, 2H), 2.02 (s, 3H), 1.01 (s, 12H). ^{11}B NMR (128 MHz, C_6D_6) δ 22.42.

2-((4-(benzyloxy)benzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (See for the corresponding alcohol, *i.e,* [4-(benzyloxy)phenyl)methanol[10])



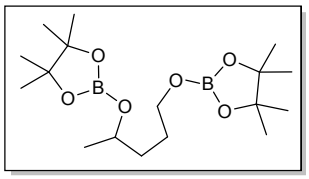
^{1}H NMR (400 MHz, C_6D_6) δ 7.28 (t, J = 8.9 Hz, 4H), 7.19 (d, J = 7.1 Hz, 2H), 7.13 – 7.10 (m, 1H), 6.87 (d, J = 8.6 Hz, 2H), 4.97 (s, 2H), 4.71 (s, 2H), 1.09 (s, 12H). ^{13}C NMR (100 MHz, C_6D_6) δ 158.8(Ar–*C*), 137.7(Ar–*C*), 132.5(Ar–*C*), 128.8(Ar–*C*), 128.6(Ar–*C*), 127.9(Ar–*C*), 127.6(Ar–*C*), 115.0(Ar–*C*), 82.6(BO*C*Me$_2$), 69.9(Ph*C*H$_2$OBpin), 66.7(Ar*C*H$_2$OBpin), 24.9(BOC*Me*$_2$); ^{11}B NMR (128 MHz, C_6D_6) δ 22.44.

4,4,5,5-tetramethyl-2-((4-((3,3,4,4-tetramethylborolan-1-yl)oxy)hexyl)oxy)-1,3,2-dioxaborolane



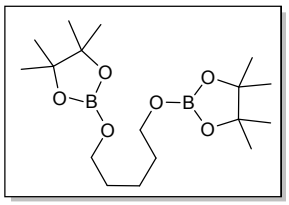
^{1}H NMR (400 MHz, C_6D_6) δ 4.11 – 4.05 (m, 1H), 3.97 – 3.87 (m, 2H), 1.80 – 1.61 (m, 2H), 1.54 – 1.49 (m, 2H), 1.47 – 1.33 (m, 2H), 1.06 (s, 24H), 0.86 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, C_6D_6) δ 82.3(BO*C*Me$_2$), 82.2(BO*C*Me$_2$), 75.6 (*C*HOBpin), 64.9(*C*H$_2$OBpin), 32.5(*C*H$_2$), 29.8(*C*H$_2$), 28.1(*C*H$_2$), 24.6(BOC*Me*$_2$), 24.6(BOC*Me*$_2$), 10.0(*C*H$_3$CH$_2$); ^{11}B NMR (128 MHz, C_6D_6) δ 22.68.

4,4,5,5-tetramethyl-2-((4-((4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)oxy)pentyl)oxy)-1,3,2-dioxaborolane



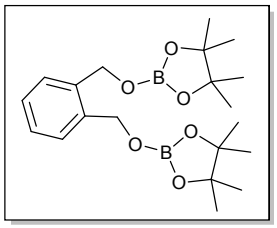
^{1}H NMR (400 MHz, C_6D_6) δ 4.32 – 4.24 (m, 1H), 3.94 – 3.84 (m, 2H), 1.75 – 1.58 (m, 2H), 1.57 – 1.44 (m, 2H), 1.11 (d, *J* = 6.2 Hz, 3H), 1.06 (s, 24H). ^{13}C NMR (100 MHz, C_6D_6) δ 82.3(BO*C*Me$_2$), 82.2(BO*C*Me$_2$), 70.6(CH$_3$*C*HOBpin), 64.9(CH$_2$*C*H$_2$OBpin), 34.7(*C*H$_2$), 28.1(*C*H$_2$), 24.6(BOC*Me*$_2$), 24.7(BOC*Me*$_2$), 22.8(*C*H$_3$CH); ^{11}B NMR (128 MHz, C_6D_6) δ 22.15.

1,5-bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)pentane



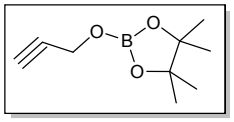
^{1}H NMR (400 MHz, C_6D_6) δ 3.83 (t, *J* = 6.5 Hz, 4H), 1.47 (dt, *J* = 14.3, 6.9 Hz, 4H), 1.36 – 1.28 (m, 2H), 1.06 (s, 24H). ^{13}C NMR (100 MHz, C_6D_6) δ 82.3(BO*C*Me$_2$), 64.9(*C*H$_2$OBpin), 31.6(*C*H$_2$CH$_2$OBpin), 24.7(BOC*Me*$_2$), 22.1(*C*H$_2$CH$_2$ CH$_2$OBpin); ^{11}B NMR (128 MHz, C_6D_6) δ 22.38.

1,2-bis(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzene[11]



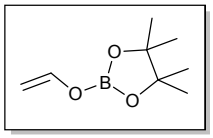
^{1}H NMR (400 MHz, C_6D_6) δ 7.50 (dd, *J* = 5.5, 3.4 Hz, 2H), 7.09 (dd, *J* = 5.7, 3.4 Hz, 2H), 5.06 (s, 4H), 1.03 (s, 24H). ^{11}B NMR (128 MHz, C_6D_6) δ 22.8.

4,4,5,5-tetramethyl-2-(prop-2-yn-1-yloxy)-1,3,2-dioxaborolane[12]



^{1}H NMR (400 MHz, C_6D_6) 4.94 (q, *J* = 6.4 Hz, 2H), 2.06 (t, *J* = 4Hz, 1H), 1.04 (s, 12H); ^{11}B NMR (128 MHz, C_6D_6) δ 22.38.

4,4,5,5-tetramethyl-2-(vinyloxy)-1,3,2-dioxaborolane[13]



^{1}H NMR (400 MHz, C_6D_6) 5.54 (q, J = 4.5 Hz, 1H), 4.18-4.07 (m, 1H), 4.0-3.87 (m, 1H), 1.04 (s, 12H); ^{11}B NMR (128 MHz, C_6D_6) δ 22.15.

Crystallographic data

X-ray crystal structure determination

Crystallographic data and structure determinations details are compiled in Table S1. After removing the crystal from Schlenk RB immediately coated with silicon oil on a glass slide. On a glass fiber suitable crystals were mounted at temperature 100K and it was controlled using an Oxford Cryostream 700 instrument. Crystal data were collected with a Bruker AXS SMART Apex CCD detector and with an INCOATEC micro source (Mo-Kα radiation, λ = 0.71073 Å, multilayer optics). The software SADABS was used for absorption correction SHELXTL[14] and OLEX2[15] for space group, structure determination and refinements. The least-squares refinement techniques on F^2 were done until the model converged. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were fixed at calculated positions and their positions were refined by a riding model. CCDC 1506291 & 1506292 (for compounds **2** & **3**) contains the supplementary crystallographic data for this paper (Table S1).

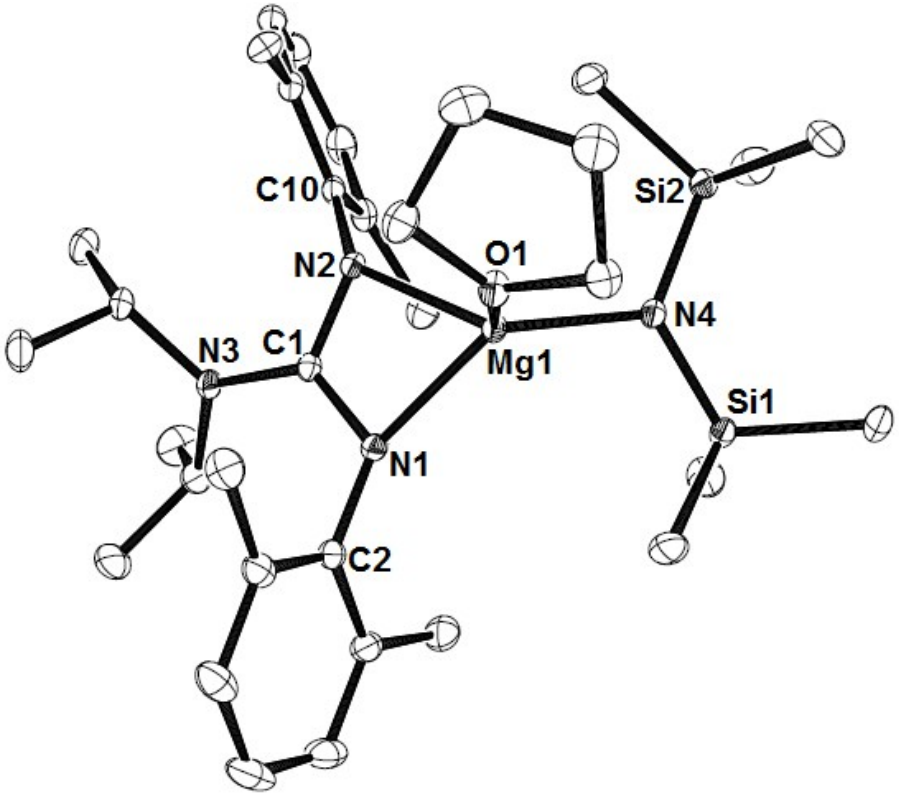


Figure S1. Molecular structure of $C_{33}H_{58}N_4MgOSi_2$ **(2)** (ORTEP view, 30% probability level) Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Mg1–N1 2.0987(18), Mg1–N2 2.0747(18), Mg1–O1 2.0359(17), Mg1–N4 1.9904(18), N1–C1 1.347(3), N2–C1 1.355(3), N3–C1 1.392(2), Si1–N4 1.6907(18), Si2–N4 1.7008(18); N2–Mg1–N1 65.37(7), N4–Mg1–N1 131.29(8), O1–Mg1–N1 112.12(7), O1–Mg1–N2 109.27(7), N4–Mg1–O1 104.02(7), N1–C1–N2 113.03(17), N1–C1–N3 124.57(18), Si1–N4–Si2 125.87(10), Si1–N4–Mg1 116.48(9), Si2–N4–Mg1 117.64(9), C1–N2–Mg1 91.21(12), C1–N1–Mg1 90.39(12).

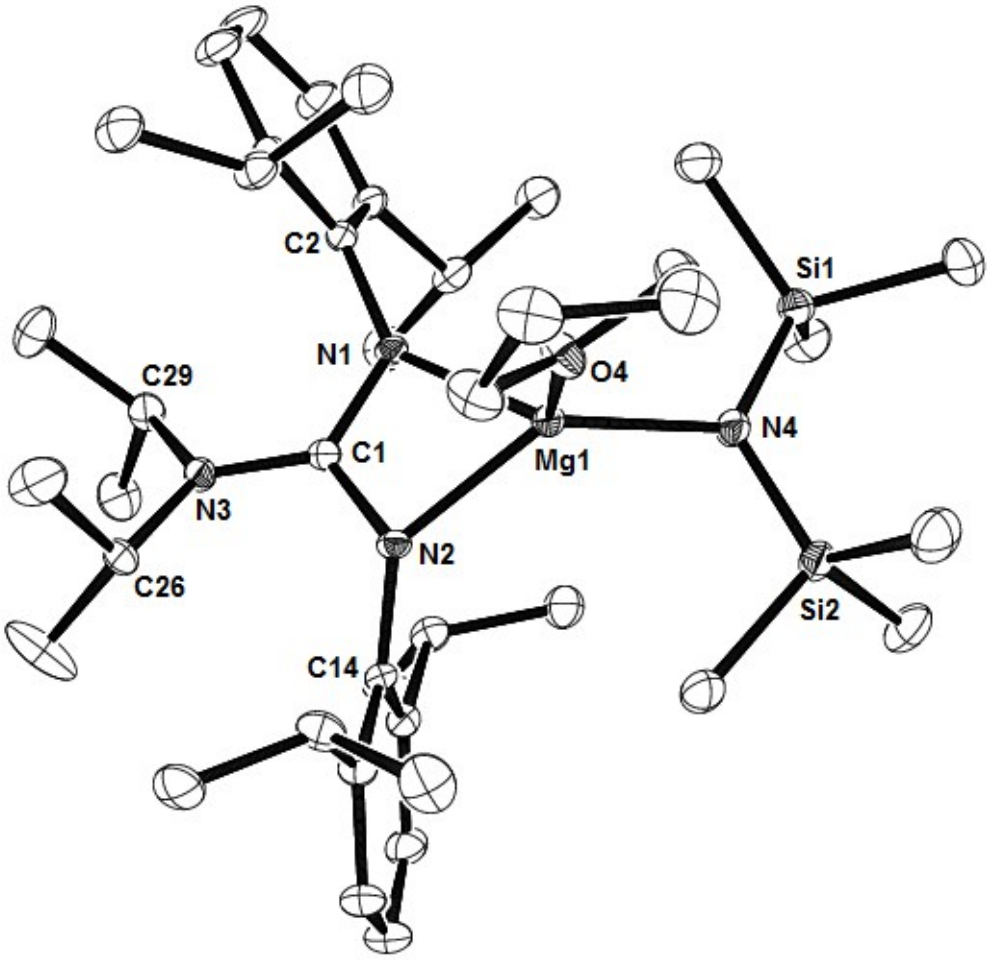


Figure S2. Molecular structure of $C_{51}H_{58}N_4MgOSi_2$ **(3)** (ORTEP view, 30% probability level) Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Mg1–N1 2.0996(16), Mg1–N2 2.0724(15), Mg1–N4 1.9995(16), Mg1–O4 2.0649(14), Si1–N4 1.7015(17), Si2–N4 1.7036(17), N1–C1 1.350(2), N2–C1 1.365(2), N3–C1 1.386(2); N2–Mg1–N1 65.11(6), N4–Mg1–O4 99.67(7), N1–C1–N2 111.59(15), O4–Mg1–N1 113.60(6), O4–Mg1–N2 107.57(6), N1–C1–N3 126.73(15), C1–N1–Mg1 91.14(10), Si1–N4–Si2 124.06(9), Si1–N4–Mg1 119.83(9), Si2–N4–Mg1 116.08(8).

Table S1. Details of the crystal structure determination of **2** & **3**

Empirical formula	$C_{33}H_{58}MgN_4OSi_2$(**2**)		$C_{41}H_{74}MgN_4OSi_2$(**3**)	
CCDC No.	1506291		1506292	
Formula weight	607.32		719.53	
Temperature	100(2) K		100(2) K	
Wavelength	0.71069 Å		0.71069 Å	
Crystal system	Monoclinic		Monoclinic	
Space group	*C* 2/*c*		*P* 21/*n*	
Unit cell dimensions	a = 30.059(5) Å b = 19.808(5)Å c = 15.024(5) Å	α = 90° β = 117.992(5)° γ = 90°	a =10.752(5) Å b = 36.875(5)Å c = 11.551(5) Å	α= 90 β= 107.486(5)° γ = 90
Volume	7899(4) $Å^3$		4368(3) $Å^3$	
Z	8		4	
Density (calculated)	1.021 Mg/m^3		1.094 Mg/m^3	
Absorption coefficient	0.133 mm^{-1}		0.129 mm^{-1}	
F(000)	2656		1584	
Crystal size	0.2 x 0.23 x 0.26 mm^3		0.18 x 0.21 x 0.25 mm^3	
Theta range for data collection	1.283 to 30.585°.		2.061 to 29.626°	
Index ranges	–42<=h<=42, –28<=k<=28, –21<=l<=21		–14<=h<=14, –51<=k<=51, –15<=l<=15	
Reflections collected	77623		64589	
Independent reflections	12074 [R(int) = 0.0573]		11918 [R(int) = 0.0593]	
Completeness to theta = 25.240°	99.9 %		99.5 %	
Refinement method	Full–matrix least–squares on F^2		Full–matrix least–squares on F^2	
Data / restraints / parameters	12074 / 0 / 384		11918 / 0 / 460	
Goodness–of–fit on F^2	1.063		1.097	
Final R indices [I>2sigma(I)]	R1 = 0.0645, wR2 = 0.2126		R1 = 0.0602, wR2 = 0.1286	
R indices (all data)	R1 = 0.0877, wR2 = 0.2249		R1 = 0.0773, wR2 = 0.1355	
Largest diff. peak and hole	2.400 and –0.369 e.$Å^{-3}$		0.445 and –0.277 e.$Å^{-3}$	

Kinetic study for the Hydroboration of ester

Kinetic studies were carried out for benzyl benzoate to the corresponding product 2-(benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane using catalyst **1** and **2** in C_6D_6 at room temperature.

To determine the order of the reaction of ester hydroboration reaction was done with 0.5 mol % of **1** and **2** and 0.25 mmol of benzyl benzoate. From the plot of $\ln(C/C_0)$ vs time results a straight line with negative slope (Figure S3 and S4) revealing a pseudo first order reaction.

To determine the order of the reaction with respect to the catalyst (**1**) concentration, reactions were done with substrate benzyl benzoate and different concentration of **1** (0.1 mol % to 1 mol %) while the substrate benzyl benzoate concentration is fixed *i.e.,* 0.25 mmol. A straight-line reveals from the plot of k_{obs} vs different concentration of catalyst that the reaction is first order with respect to the catalyst concentration (Figure S3). Using Vant hoff plot the first order rate of the reaction with respect to the catalyst concentration was further confirmed (see figure S3). Reaction progress of benzylbenzoate to boronate ester was monitored by different time interval with 0.5 mol % of catalysts (**1**-**3**) and yield vs time plot have shown (Figure S5).

Kinetic Studies

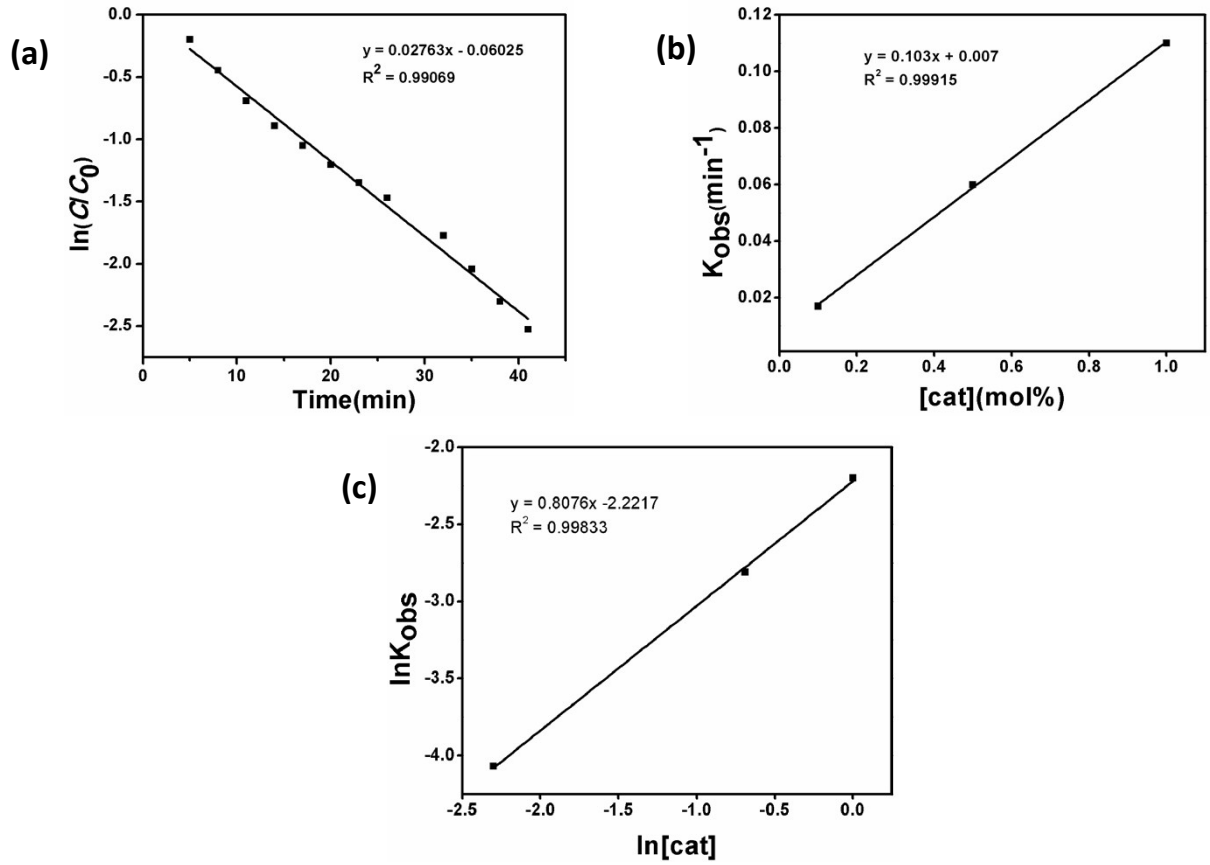


Figure S3. Kinetic studies of ester (benzyl benzoate) hydroboration process monitored by ^{1}H NMR spectroscopy in C_6D_6; (a) Plot of ln(C/C_0) vs time for the hydroboration of benzyl benzoate; (b) plot of K_{obs} vs [cat] for the hydroboration of benzyl benzoate; (c) plot of lnK_{obs} vs ln[cat] for the hydroboration of benzyl benzoate using catalyst **1.**

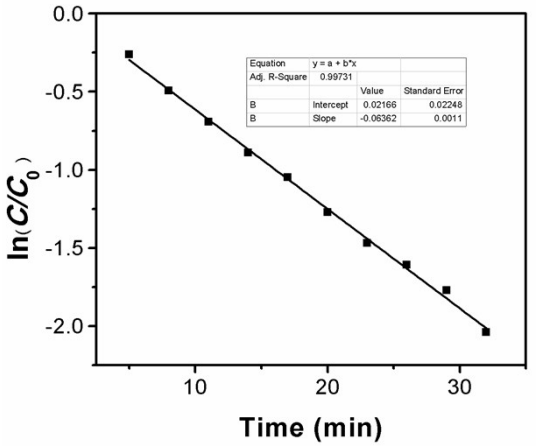
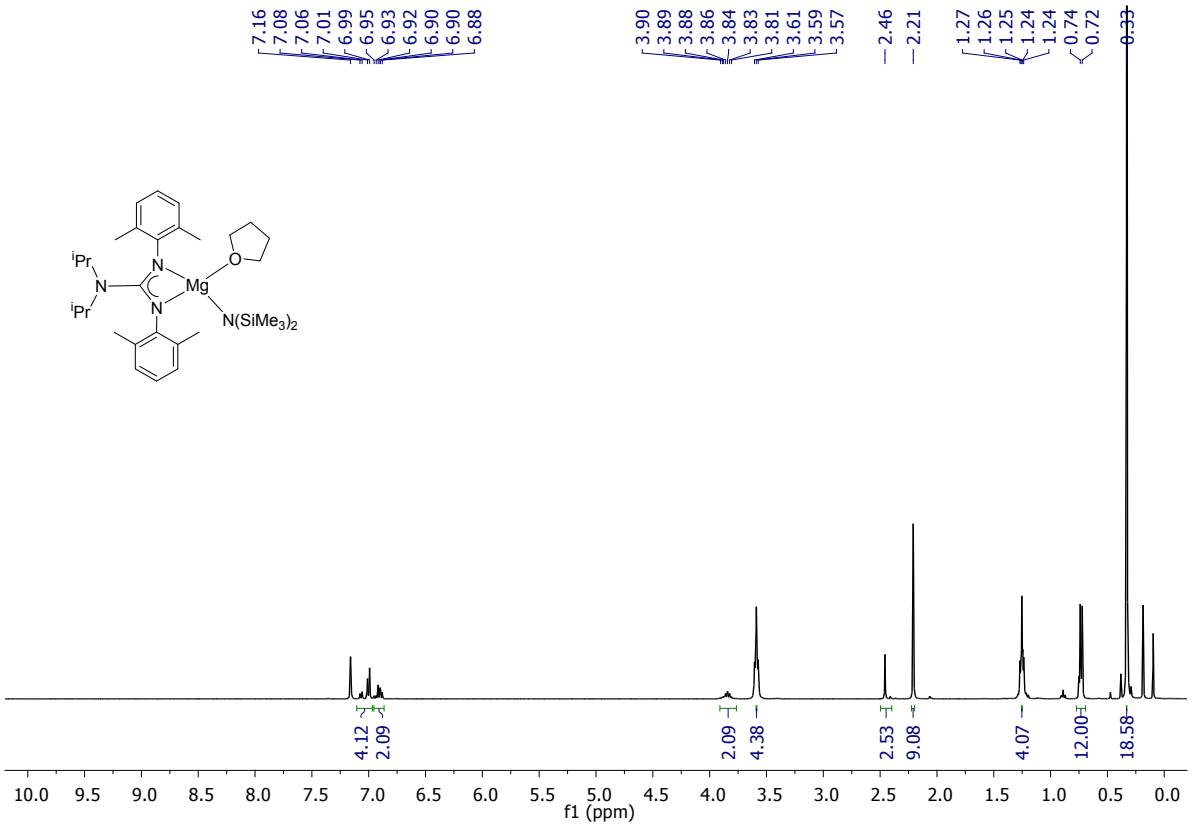
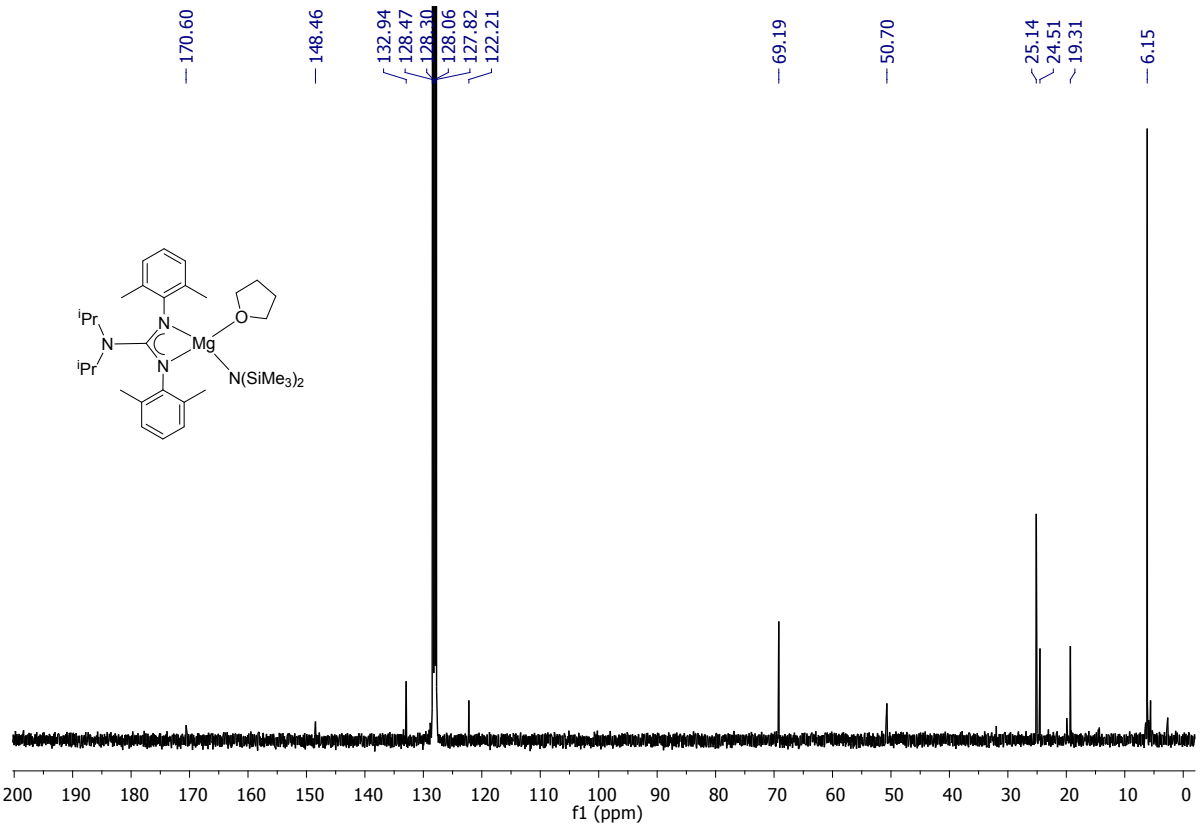


Figure S4. Kinetic studies of hydroboration process for benzyl benzoate monitored by ^{1}H NMR spectroscopy in C_6D_6; (a) Plot of ln(C/C_0) vs time for the hydroboration of benzyl benzoate using catalyst **2**.

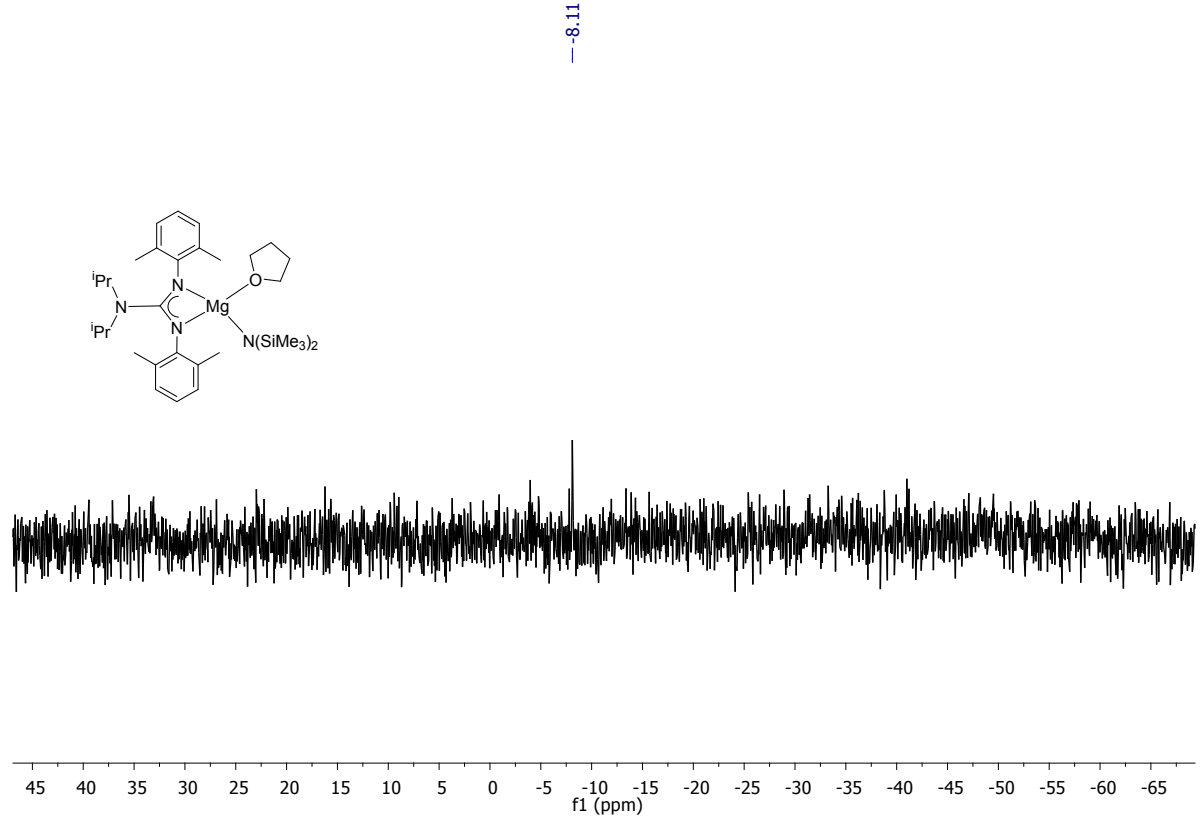
^{1}H NMR Spectrum of ^{xyl}LMgN(SiMe$_3$)$_2$·THF (**2**)



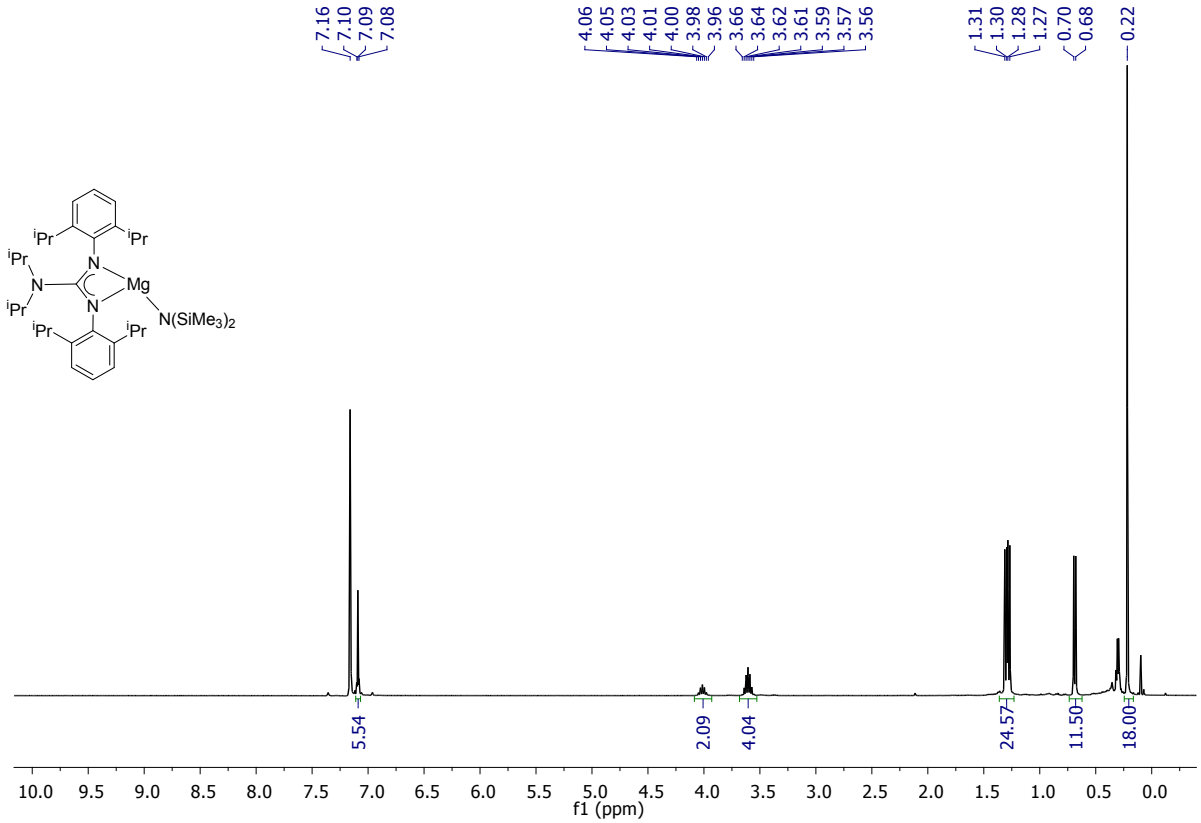
^{13}C NMR Spectrum of ^{xyl}LMgN(SiMe$_3$)$_2$·THF (**2**)



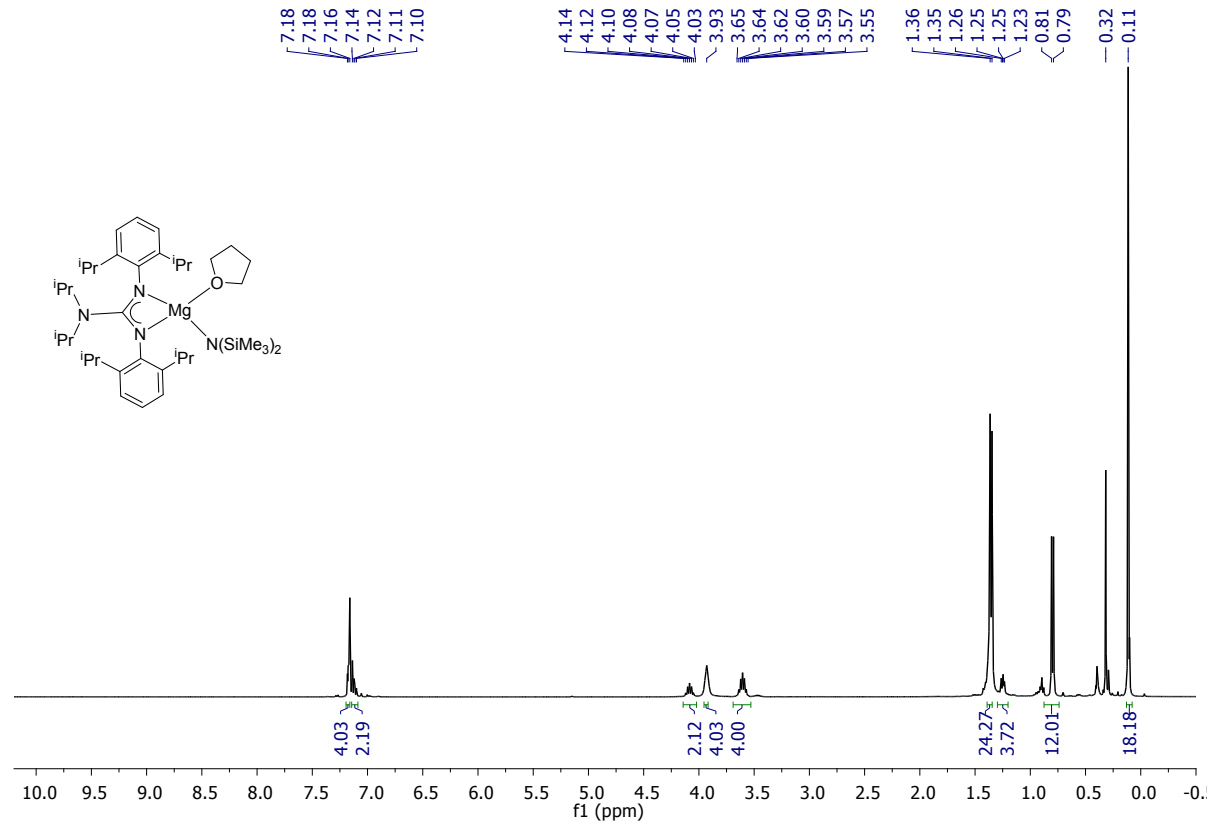
^{29}Si NMR Spectrum of ^{xyl}LMgN(SiMe$_3$)$_2$·THF (**2**)



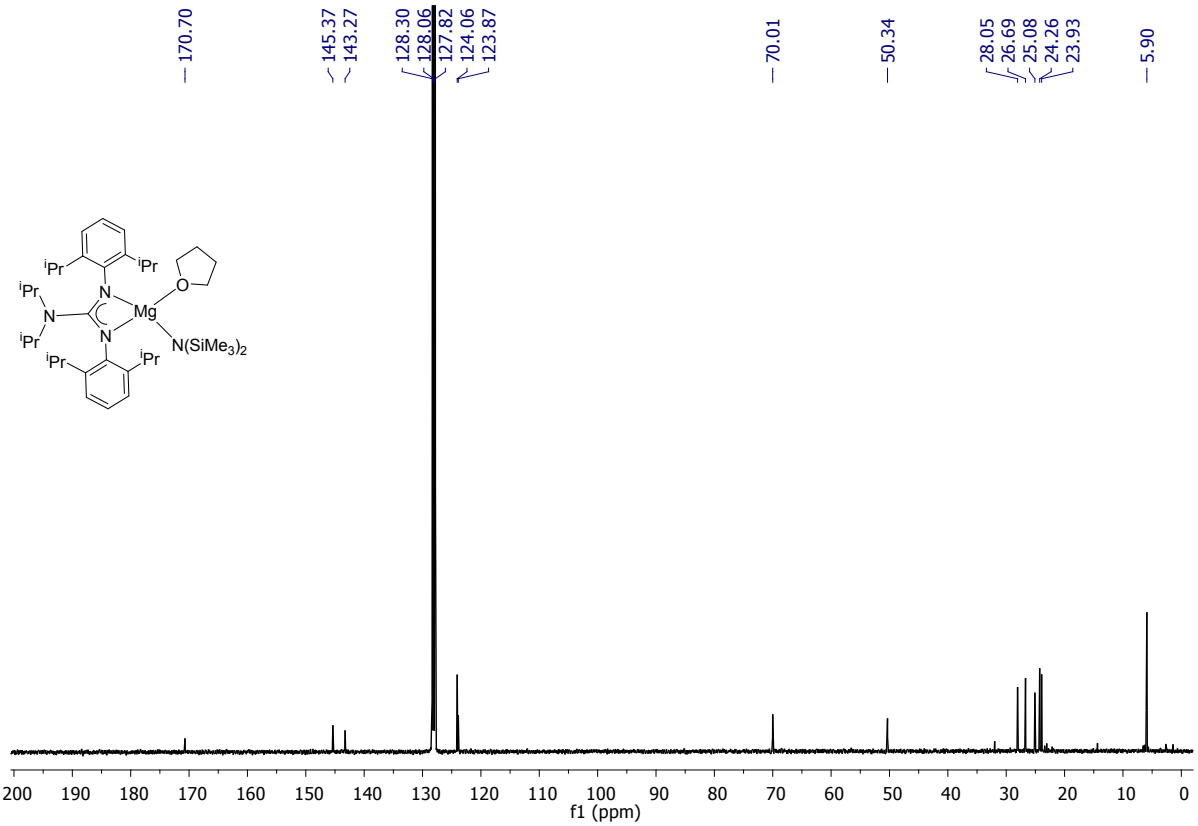
^{1}H NMR Spectrum of ^{dipp}LMgN(SiMe$_3$)$_2$ (**3a**)



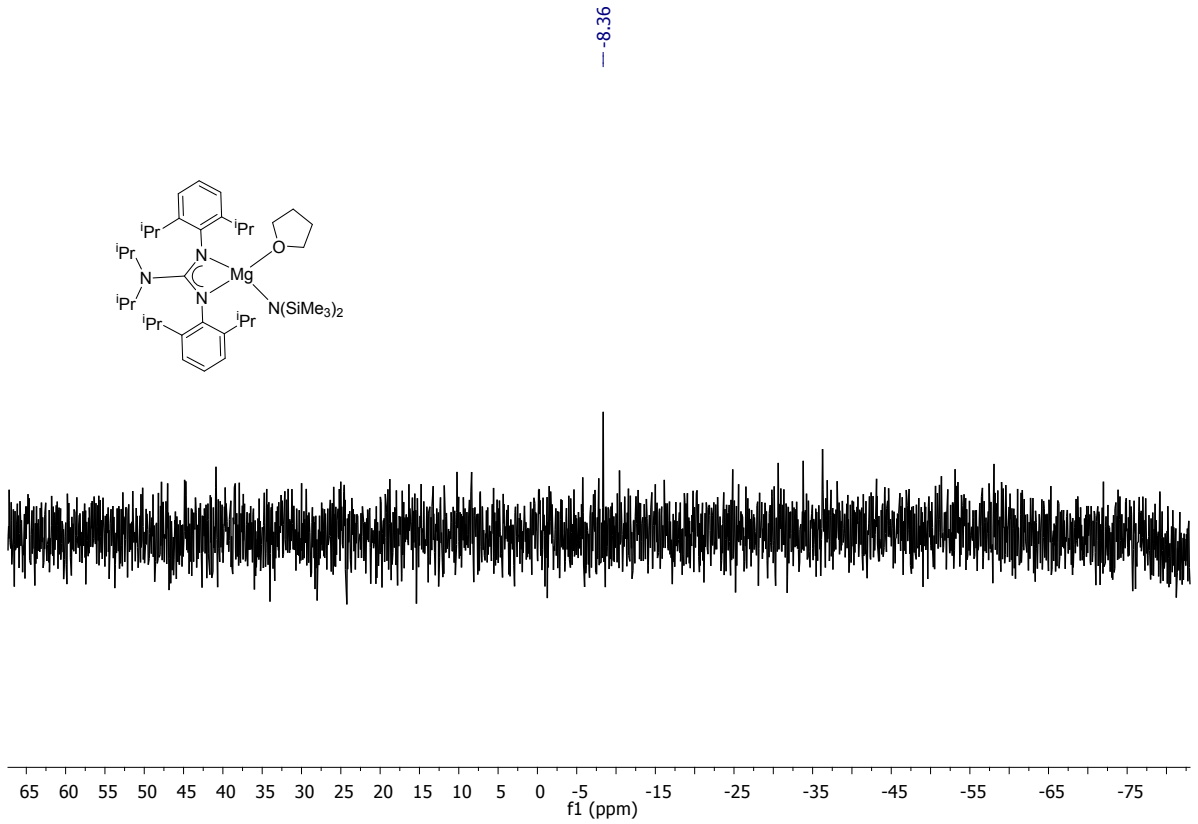
^{1}H NMR Spectrum of ^{dipp}LMgN(SiMe$_3$)$_2$·THF (**3**)



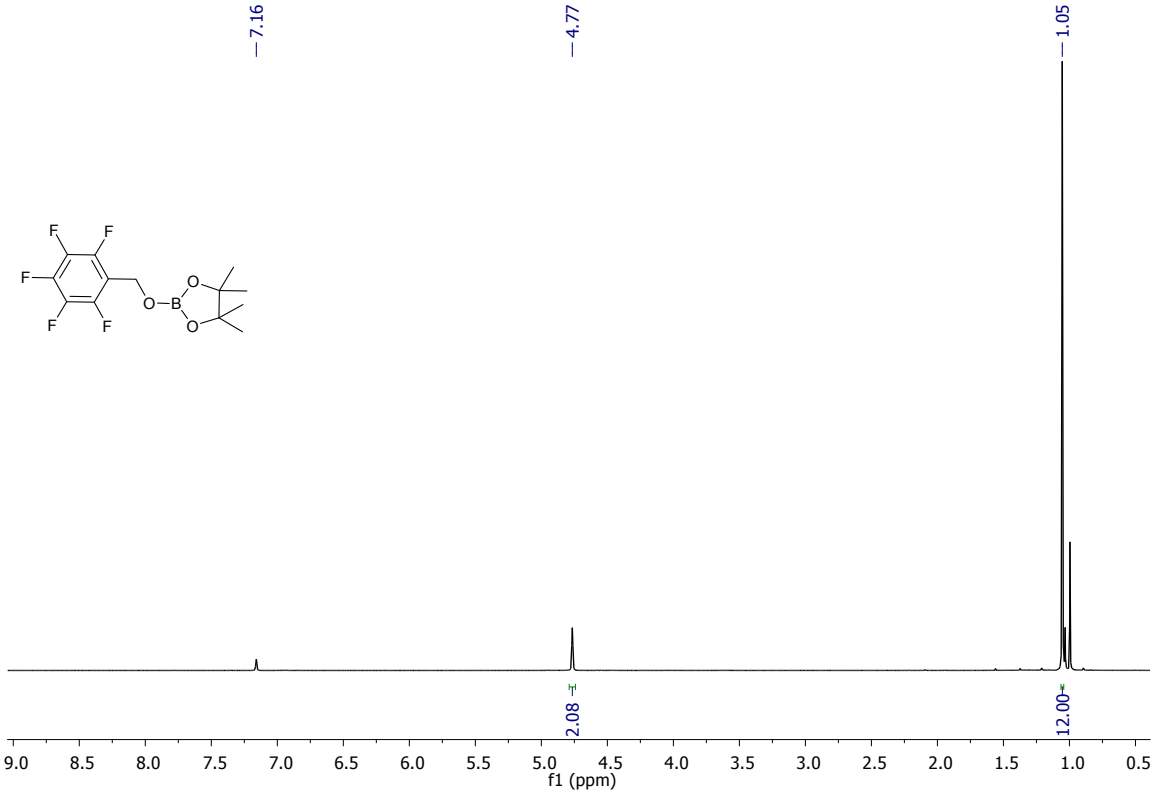
^{13}C NMR Spectrum of ^{dipp}LMgN(SiMe$_3$)$_2$·THF (**3**)



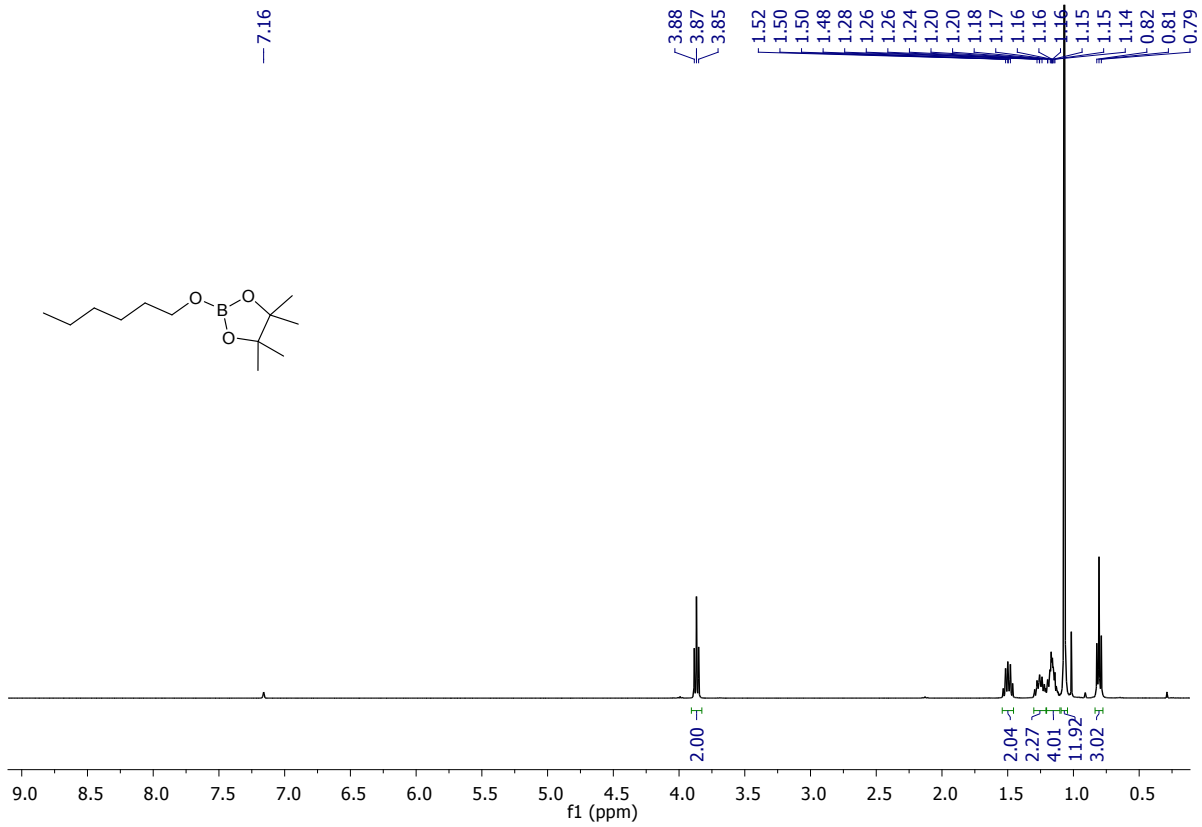
^{29}Si NMR Spectrum of ^{dipp}LMgN(SiMe$_3$)$_2$·THF (**3**)



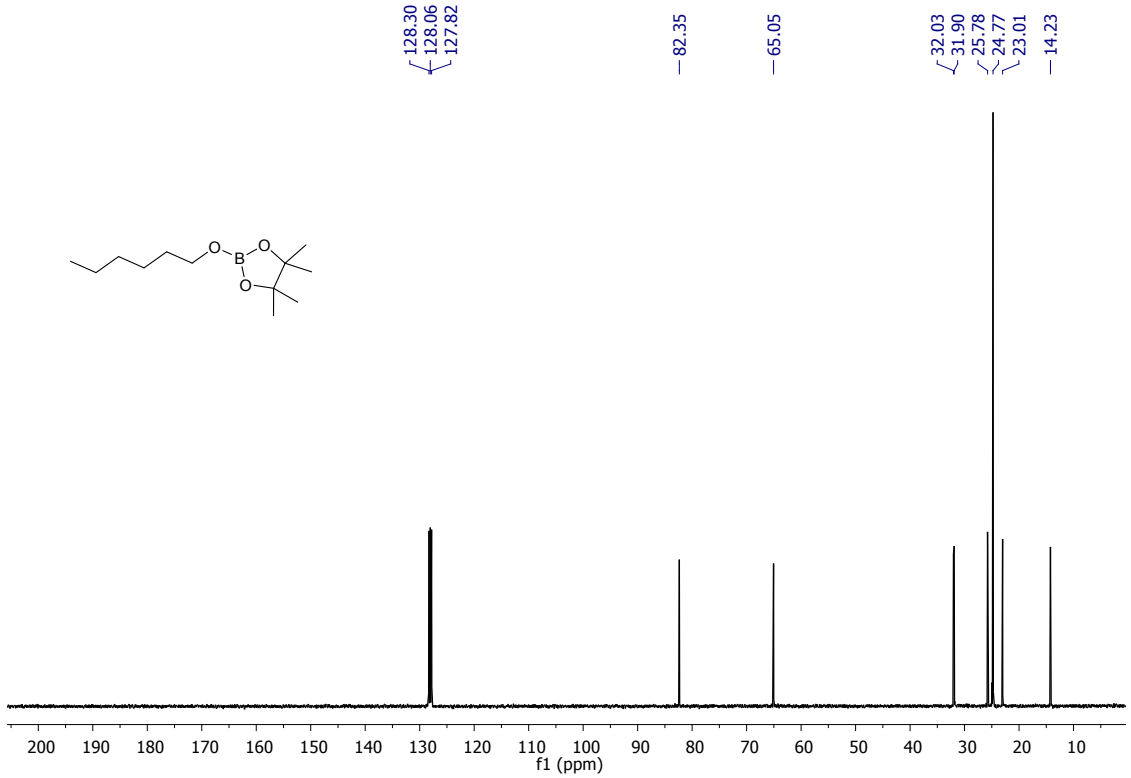
^{1}H NMR spectrum of 4,4,5,5-tetramethyl-2-((perfluorophenyl)methoxy)-1,3,2-dioxaborolane (400 MHz, C_6D_6):



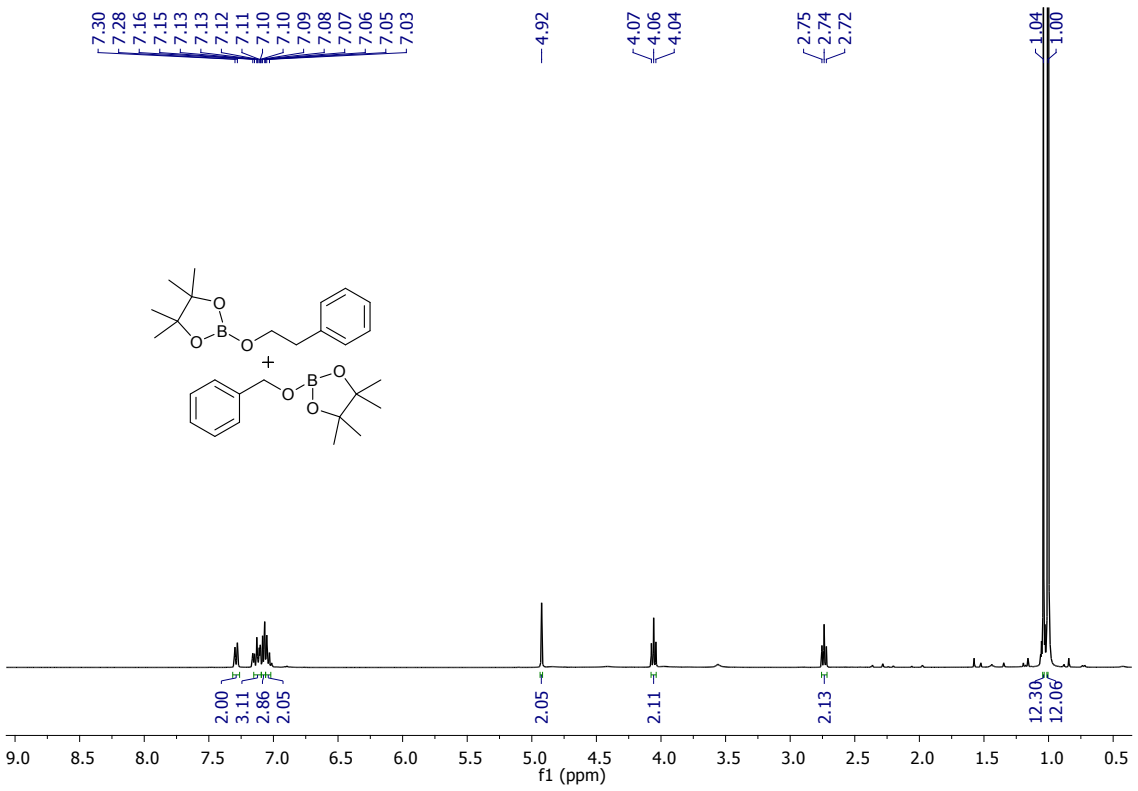
^{1}H NMR spectrum of 2-(hexyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (400 MHz, C_6D_6):



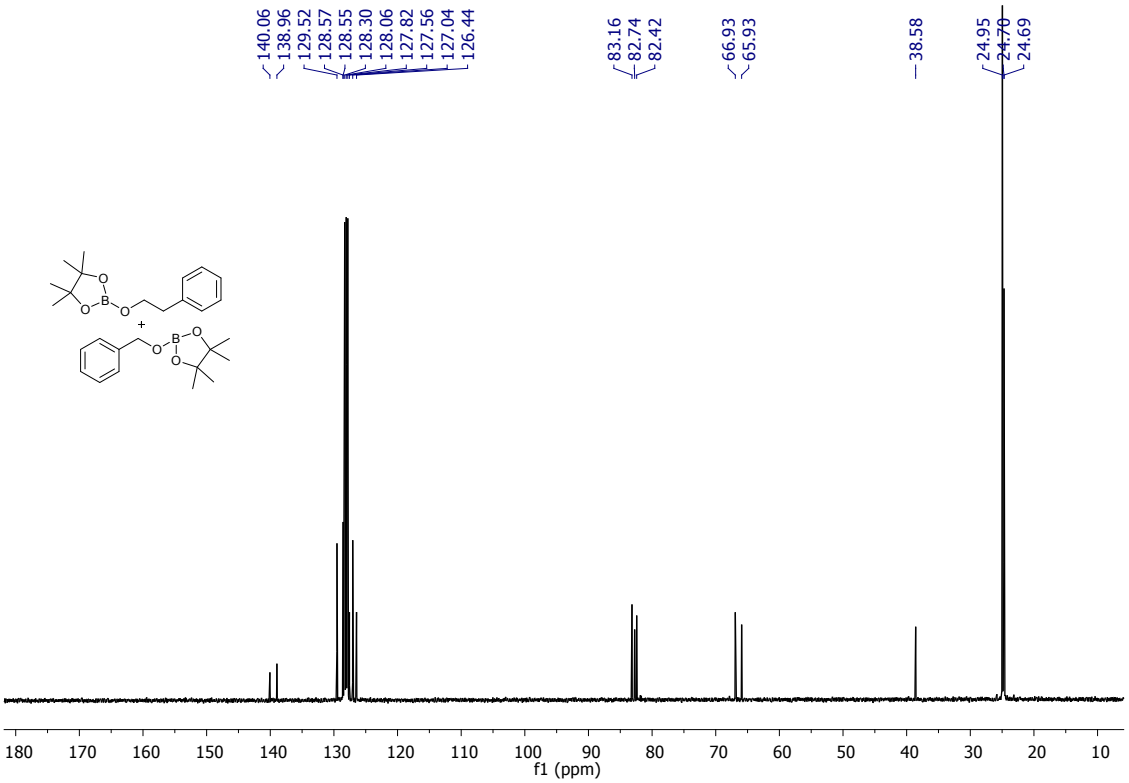
^{13}C NMR spectrum of 2-(hexyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (100.6 MHz, C_6D_6):



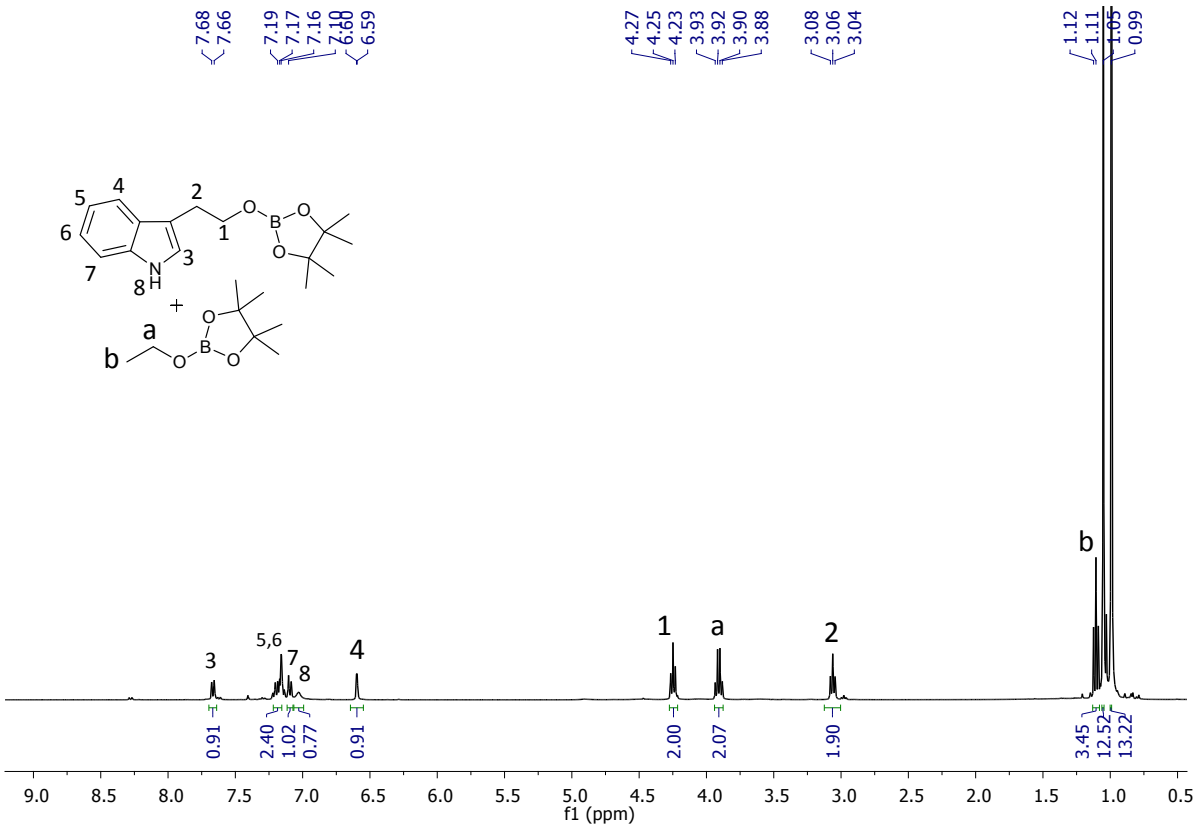
^{1}H NMR spectrum of 4,4,5,5-tetramethyl-2-phenethoxy-1,3,2-dioxaborolane (400 MHz, C_6D_6):



^{13}C NMR spectrum of 4,4,5,5-tetramethyl-2-phenethoxy-1,3,2-dioxaborolane (100.6 MHz, C_6D_6):

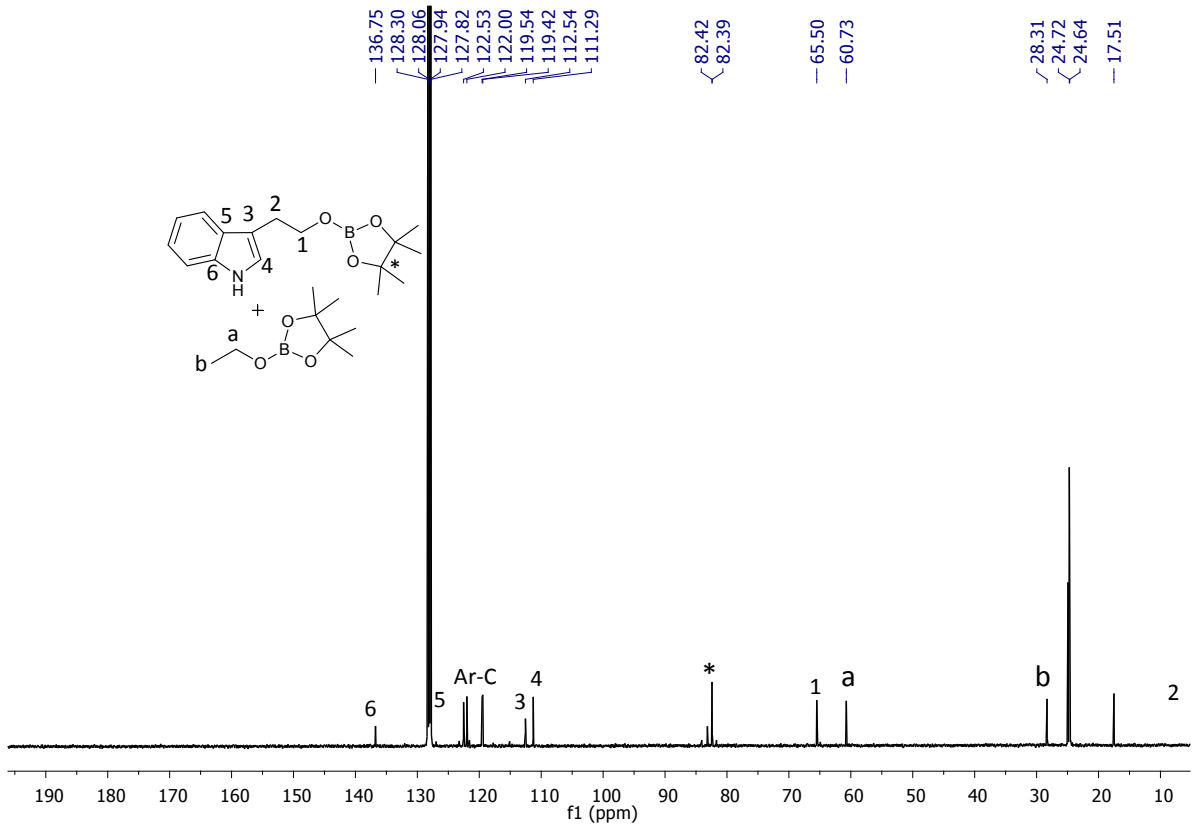


^{1}H NMR spectrum of 3-(2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)ethyl)-1H-indole (400 MHz, C_6D_6):

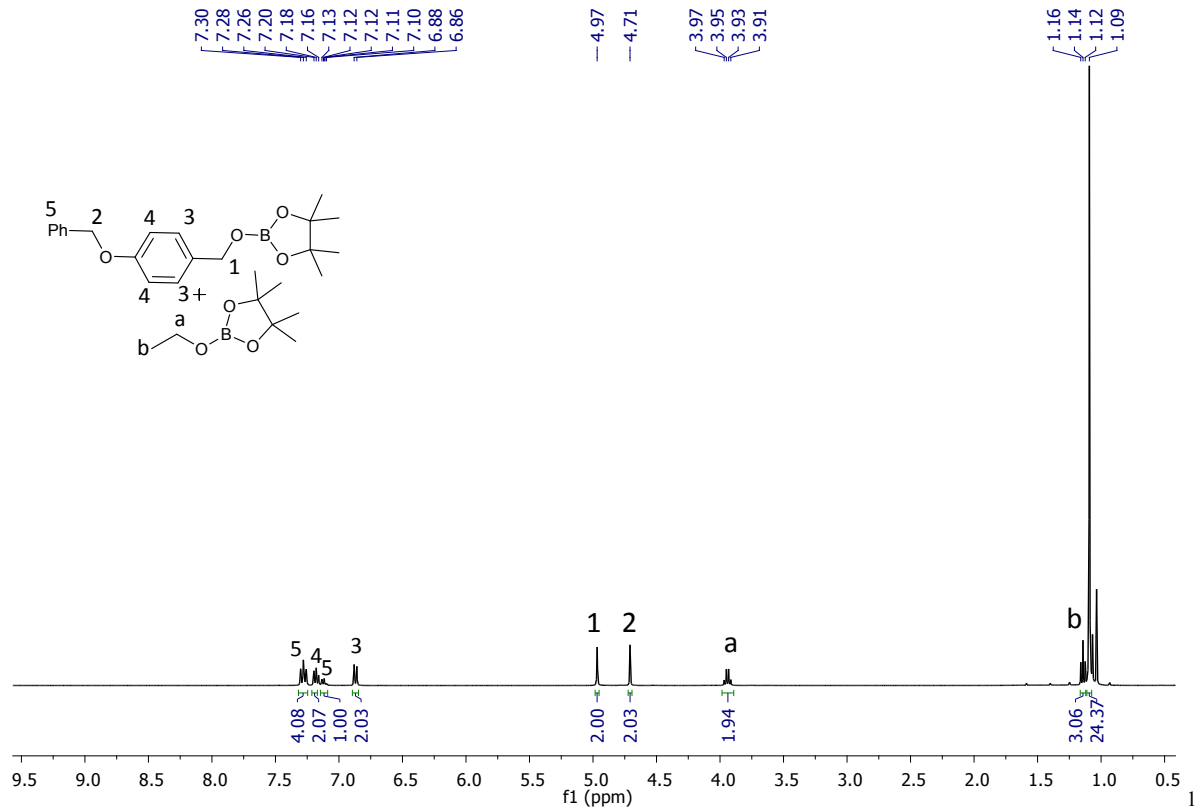


^{13}C NMR spectrum of 3-(2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)ethyl)-1H-

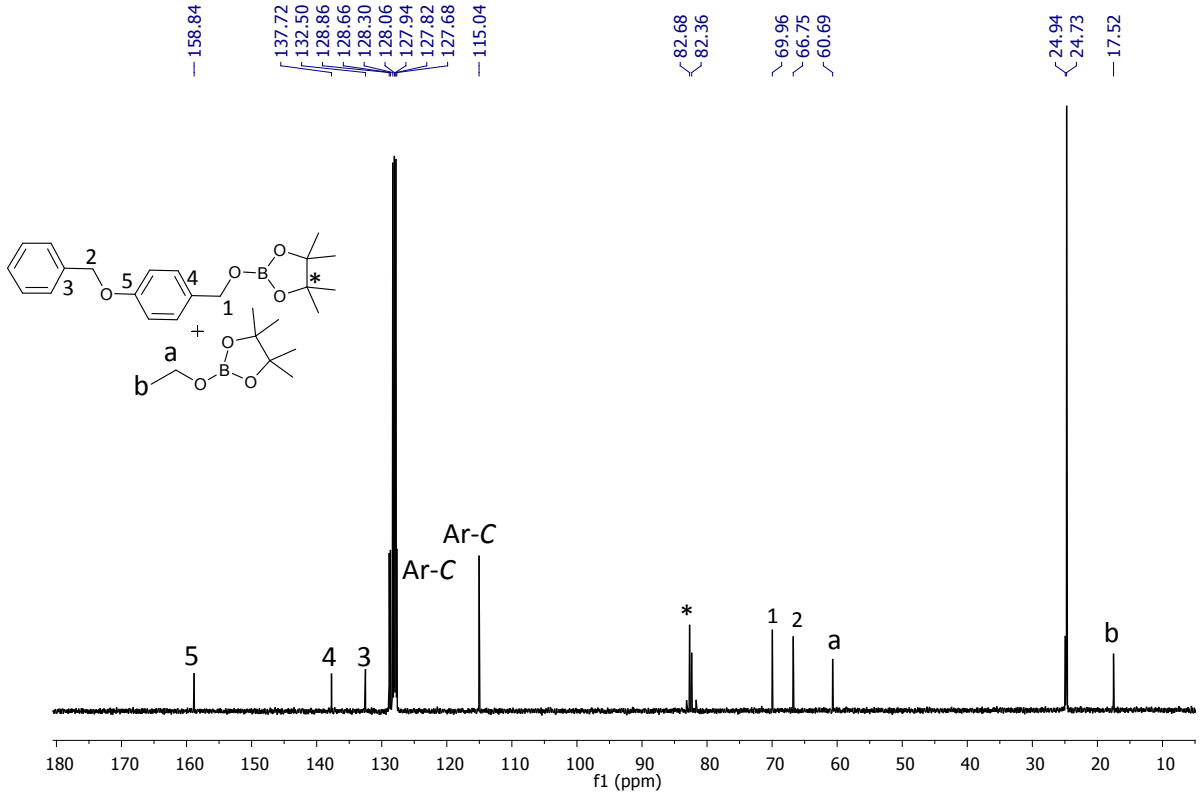
indole (100.6 MHz, C_6D_6)



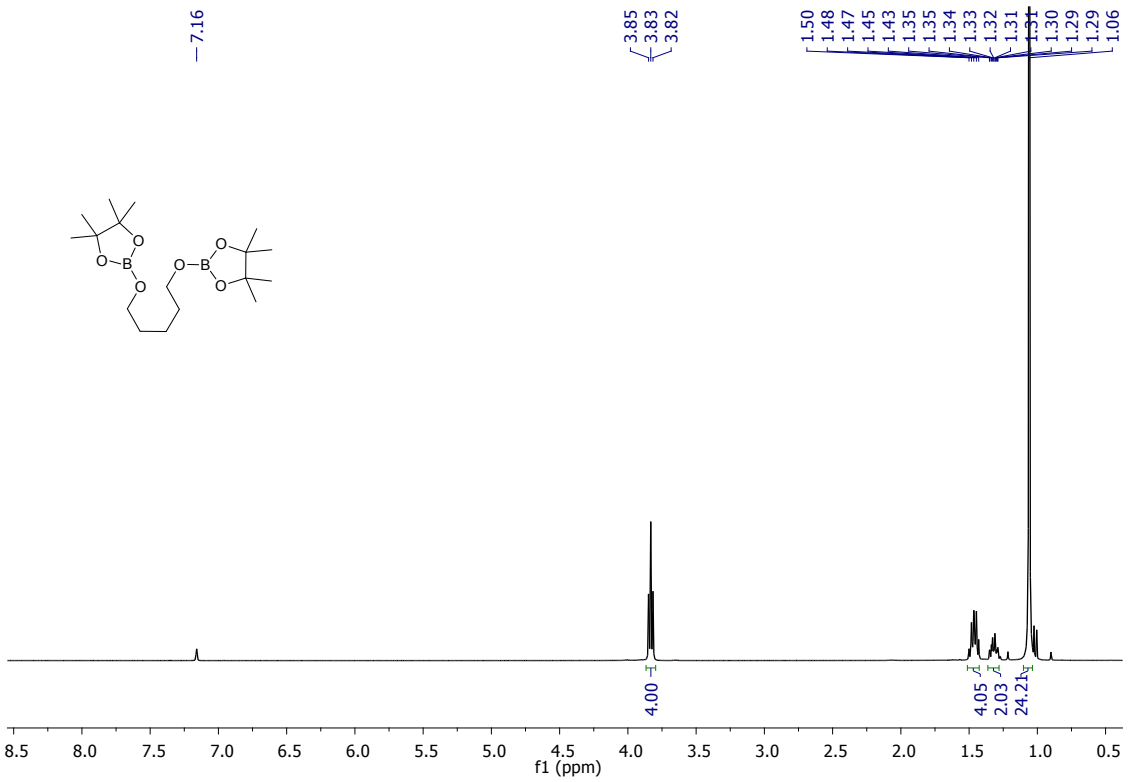
^{1}H NMR spectrum of 2-((4-(benzyloxy)benzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (400 MHz, C_6D_6):



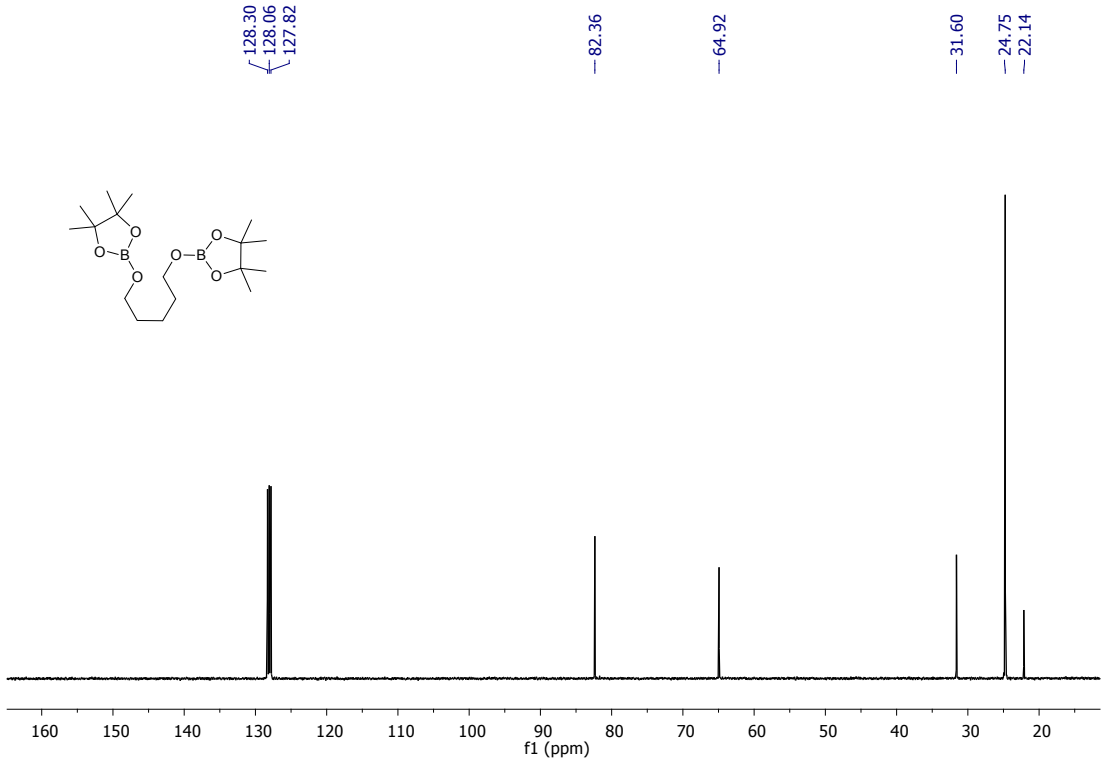
^{3}C NMR spectrum of 2-((4-(benzyloxy)benzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (100.6 MHz, C_6D_6):



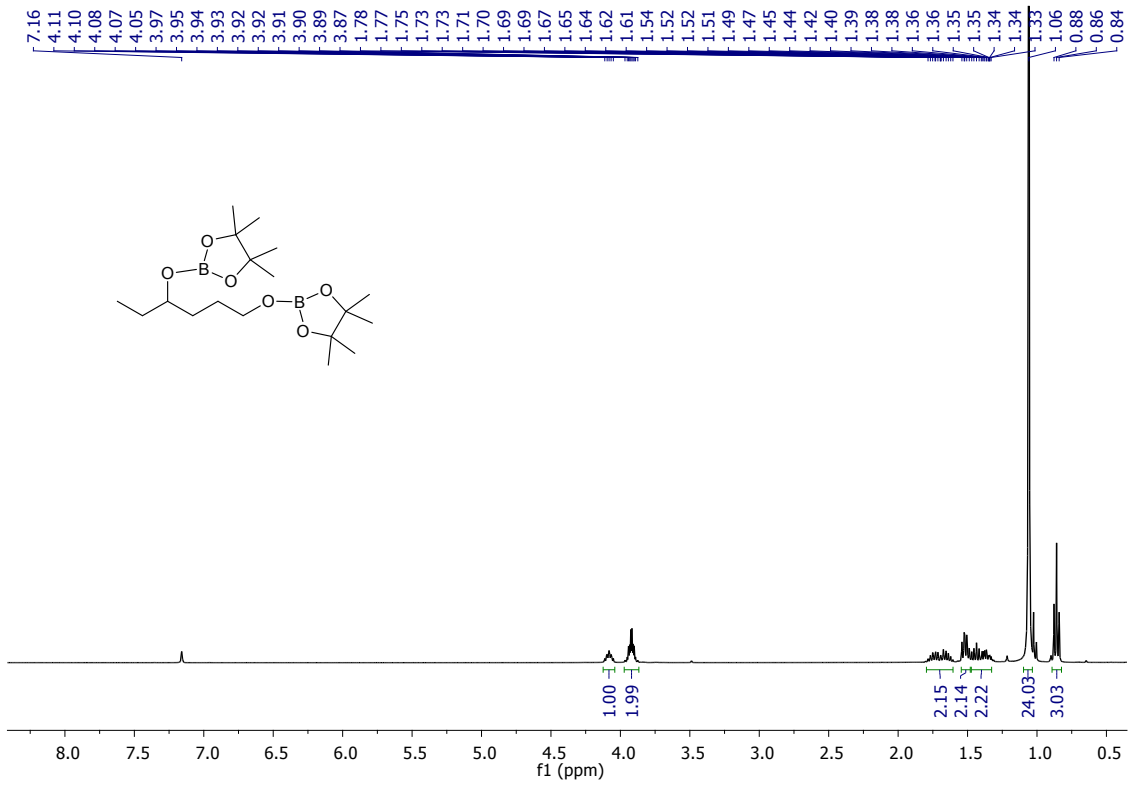
^{1}H NMR spectrum of 1,5-bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)pentane (400 MHz, C_6D_6):



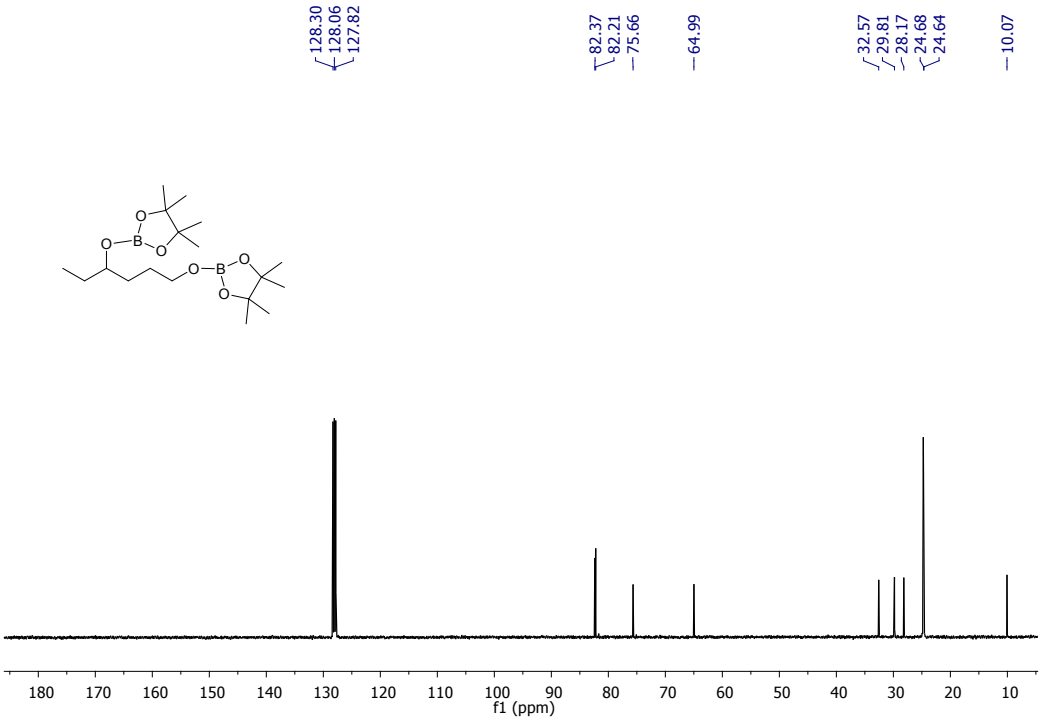
^{13}C NMR spectrum of 1,5-bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)pentane (100.6 MHz, C_6D_6):



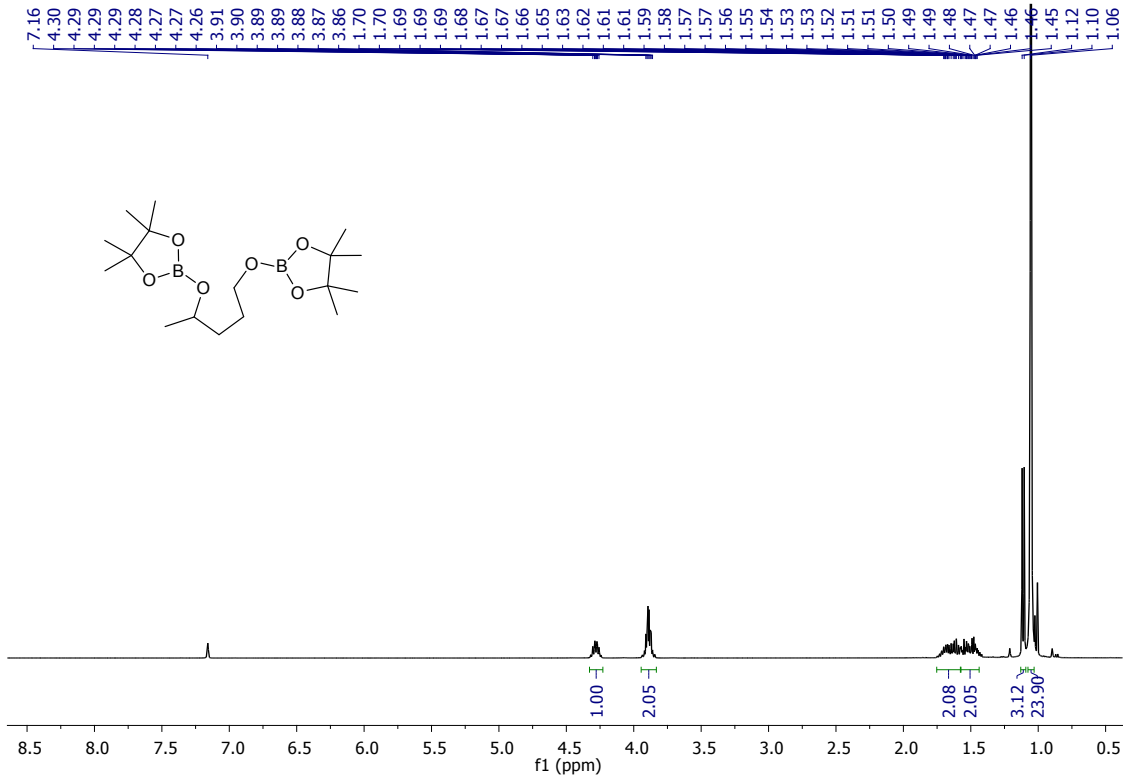
^{1}H NMR spectrum of 4,4,5,5-tetramethyl-2-((4-((3,3,4,4-tetramethylborolan-1-yl)oxy)hexyl)oxy)-1,3,2-dioxaborolane (400 MHz, C_6D_6):



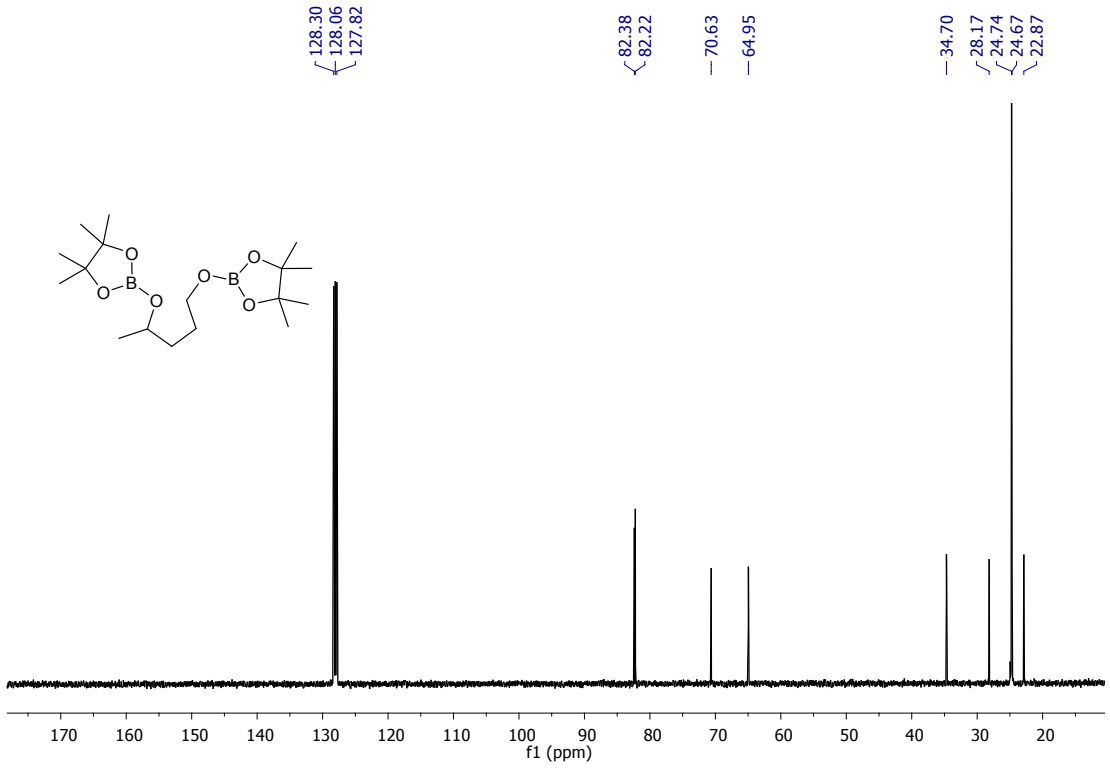
^{13}C NMR spectrum of 4,4,5,5-tetramethyl-2-((4-((3,3,4,4-tetramethylborolan-1-yl)oxy)hexyl)oxy)-1,3,2-dioxaborolane (100.6 MHz, C_6D_6):



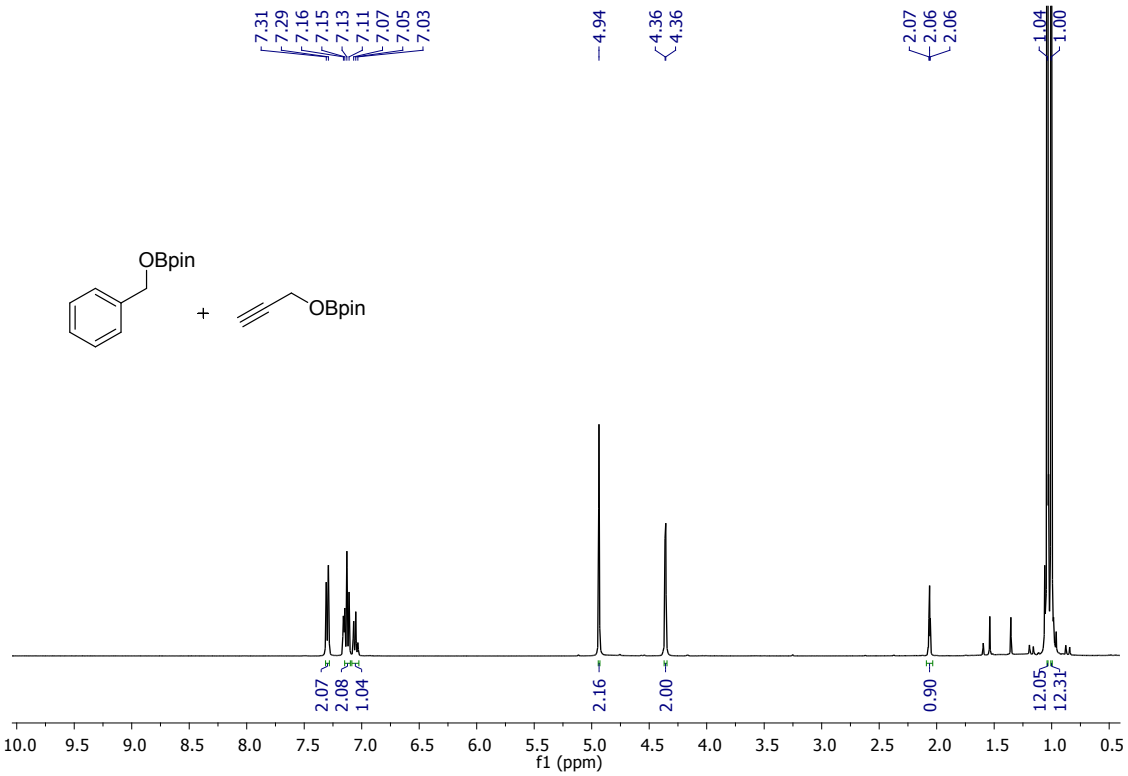
^{1}H NMR spectrum of 4,4,5,5-tetramethyl-2-((4-((4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)oxy)pentyl)oxy)-1,3,2-dioxaborolane (400 MHz, C_6D_6):



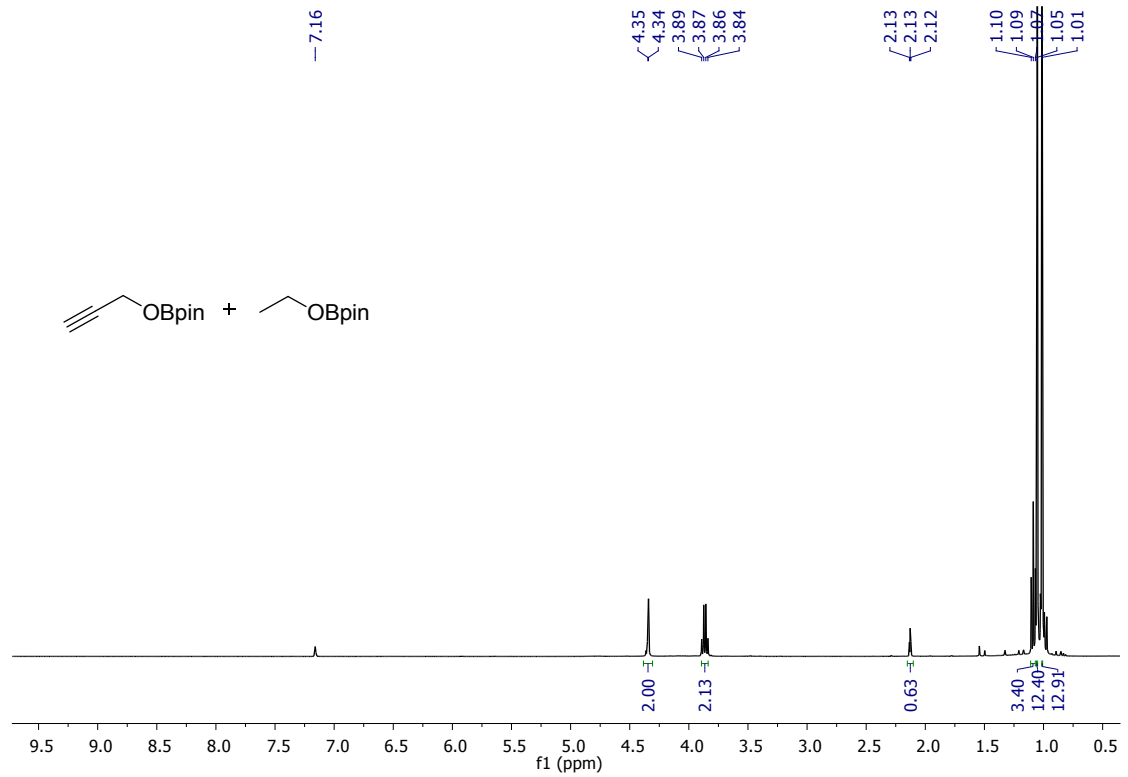
^{13}C NMR spectrum of 4,4,5,5-tetramethyl-2-((4-((4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)oxy)pentyl)oxy)-1,3,2-dioxaborolane (100.6 MHz, C_6D_6):



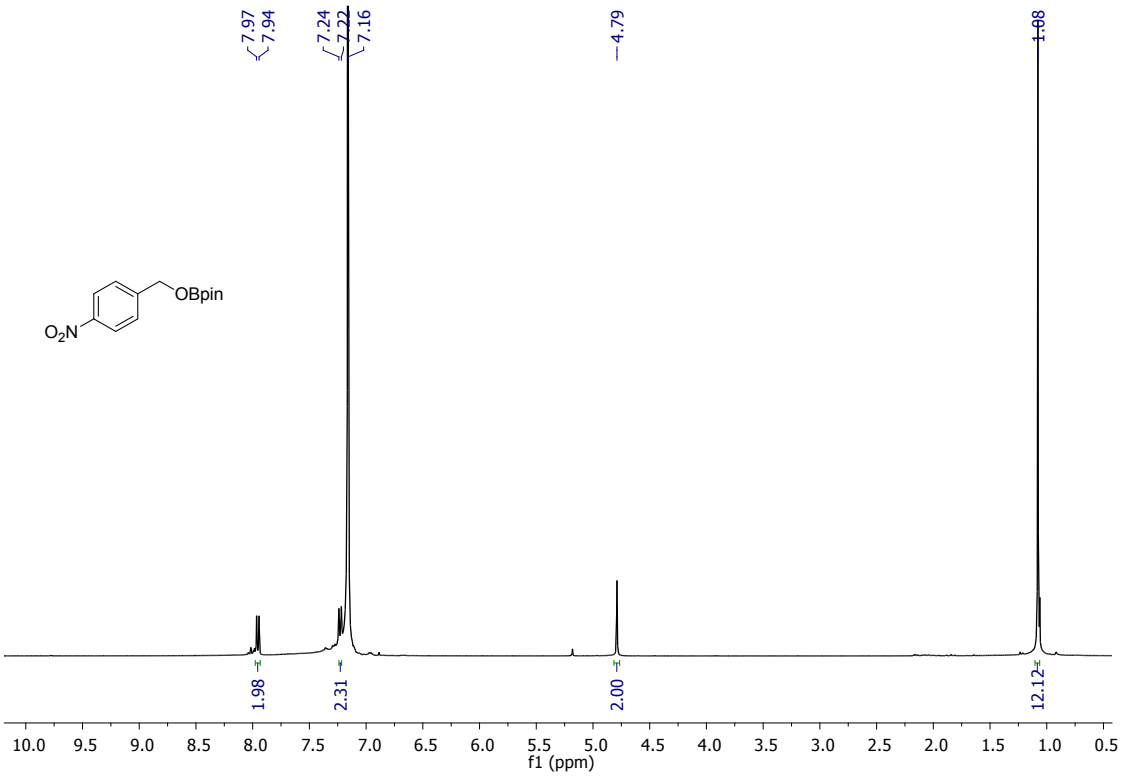
^{1}H NMR spectrum of 4,4,5,5-tetramethyl-2-(prop-2-yn-1-yloxy)-1,3,2-dioxaborolane (400 MHz, C_6D_6):



^{1}H NMR spectrum of 4,4,5,5-tetramethyl-2-(prop-2-yn-1-yloxy)-1,3,2-dioxaborolane (400 MHz, C_6D_6):



^{1}H NMR spectrum of 4,4,5,5-tetramethyl-2-((4-nitrobenzyl)oxy)-1,3,2-dioxaborolane (400 MHz, C_6D_6):



References

1. (a) U. Wannagat, H. Autzen, H. Kuckertz and H.-J. Wismar, *Z. Anorg. Allg. Chem.*, 1972, **394**, 254-262.; (b) L. Engelhardt, B. Jolly, P. Junk, C. Raston, B. Skelton and A. White, *Aus. J. Chem.*, 1986, **39**, 1337-1345.; (c) M. Westerhausen, *Inorg. Chem*. 1991, **30**, 96-101.; (d) W. Vargas, U. Englich and K. Ruhlandt-Senge, *Inorg. Chem.*, 2002, **41**, 5602-5608.
2. V. K. Jakhar, M. K. Barman and S. Nembenna, *Org. Lett.*, 2016, **18**, 4710-4713.
3. G. Zhang, H. Zeng, J. Wu, Z. Yin, S. Zheng and J. C. Fettinger, *Angew. Chem. Int. Ed.*, 2016, **55**, 14369-14372.
4. Z. Yang, M. Zhong, X. Ma, S. De, C. Anusha, P. Parameswaran and H. W. Roesky, *Angew. Chem., Int. Ed.*, 2015, **54**, 10225-10229.
5. K. Manna, P. Ji, F. X. Greene and W. Lin, *J. Am. Chem. Soc.*, 2016, **138**, 7488-7491.
6. G. Zhang, Y. Xie, Z. Wang, Y. Liu and H. Huang, *Chem. Commun.*, 2015, **51**, 1850-1853.
7. T. Zhao, K. Kurpiewska, J. Kalinowska-Tłuścik, E. Herdtweck and A. Dömling, *Chem. Eur. J*., 2016, **22**, 3009-3018.
8. T. Bolano, M. A. Esteruelas, M. P. Gay, E. Onate, I. M. Pastor and M. Yus, *Organometallics*, 2015, **34**, 3902-3908.
9. Z. Yang, M. Zhong, X. Ma, K. Nijesh, S. De, P. Parameswaran and H. W. Roesky, *J. Am. Chem. Soc.*, 2016, **138**, 2548-2551.
10. V. Skrypai, J. J. M. Hurley and M. J. Adler, *Eur. J. Org. Chem.,* 2016, 2207-2211.
11. D. Mukherjee, A. Ellern and A. D. Sadow, *Chem. Sci.*, 2014, **5**, 959-964.
12. C. A. Osborne, T. B. D. Endean and E. R. Jarvo, *Org. Lett.*, 2015, **17**, 5340-5343.
13. K. C. Nicolaou, A. Li, D. J. Edmonds, G. S. Tria and S. P. Ellery, *J. Am. Chem. Soc.*, 2009, **131**, 16905-16918.

14. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr*. 2008, **64**, 112-122.

15. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* 2009, **42**, 339-341.