Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Catalytic Regeneration of a Th-H bond from a Th-O bond Through a Mild and Chemoselective Carbonyl Hydroboration

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General procedures and materials:

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware or J-Young Teflon valve-sealed NMR tubes on a dual manifold Schlenk line interfaced to a high vacuum (10^{-5} Torr) line, or in a nitrogen-filled Innovative Technologies glovebox with a medium-capacity recirculator (1 – 2 ppm of O_2). Argon and nitrogen were purified by passage through MnO oxygen-removal column and a Davison 4Å molecular sieve column. Hydrocarbon solvents benzene-d_6 (Cambridge Isotopes), toluene (Bio-Lab), and diethyl ether (Bio-Lab) were distilled under vacuum from Na/K alloy. Pinacolborane (HBpin), $NaBD_4$ was purchased from Sigma-Aldrich and distilled under high-vacuum (10^{-6} Torr). Carbonyl-containing substrates were purchased from Sigma-Aldrich and dried over 4Å molecular sieves and distilled off prior to use (for liquid substrates) or dried under vacuum (for solid substrates). The actinide complexes $[(Me_3Si)_2N]_2An[\kappa^2\text{-}(N,C)CH_2Si(CH_3)_2N(SiMe_3)]$ (An = Th (**1**) U (**2**))[1], 5,7-diisopropyl-5,7-dihydro-*6H*-dibenzo[*d*,*f*][1,3]diazepin-6-imine (LH)[2] were prepared according to published procedures. All the aforementioned reagents were stored in an inert atmosphere glovebox prior to use.

NMR spectra were recorded on Bruker Avance 300, Bruker Avance III 400 spectrometers on crude reaction mixtures. Chemical shifts for ^1H and ^{13}C NMR are referenced to internal protic solvent and reported relative to tetramethylsilane. J-values are reported for ^1H NMR coupling constants in the unit of Hertz (Hz). Infrared spectra were recorded on a Bruker Vertex 70 FTIR spectrophotometer in the ranges from 400 to 4000 cm^{-1}.

Kappa CCD difractometer under a cold stream of nitrogen. Data collection was performed using monochromated Mo Kα radiation using φ and ω scans to cover the Ewald sphere.[3] Accurate cell parameters were obtained with the amount of indicated reflections.[4] The structure was solved by SHELXS-97 direct methods[5] and refined by the SHELXL- 97 program package.[6] The atoms were refined anisotropically. Hydrogen atoms were included using the riding model. Figures were drawn (50% probability thermal ellipsoids) using Diamond V3.1.[7]

General Procedure for the Synthesis of complexes 3 and 4:

A toluene (10 mL) solution of actinide metallacycle **1** or **2** (200 mg) was reacted with LH (1 eq in 10 mL) at room temperature and reaction was stirred for additional 12 hrs at room temperate. The solvent was removed under reduced pressure to afford the crude solid **3**–**4**. X-ray quality crystals were grown from concentrated toluene solution at –35°C.

[(L)Th(IV){N(SiMe$_3$)$_2$}$_3$] (3):

Yield 94 % (260 mg, 0.265 mmol); ^{1}H NMR (300.0 MHz, C_6D_6): δ = 7.36 (dd, *J* = 6.0 Hz, *J* = 3.0 Hz, 2H, ArC*H*), 7.18 (dd, *J* = 6.0 Hz, *J* = 3.0 Hz, 2H, ArC*H*), 7.09 (dd, *J* = 6.0 Hz, *J* = 3.0 Hz, 2H, ArC*H*), 7.06–6.99 (m, 2H, ArC*H*), 4.44 (sep, *J* = 6.0 Hz, 2H, C*H*Me$_2$), 1.14 (d, *J* = 6.0 Hz, 2H, CH*Me*$_2$), 0.75 (d, *J* = 6.0 Hz, 2H, CH*Me*$_2$), 0.43 (s, 54H, Si(C*H*$_3$)$_3$); ^{13}C NMR (75.5 MHz, C_6D_6): δ = 152.88 (*C*$_{ipso=N}$), 142.54 (Ar*C*), 141.72 (Ar*C*), 137.58 (Ar*C*), 136.81 (Ar*C*), 127.12 (Ar*C*), 126.89 (Ar*C*), 126.56 (Ar*C*), 125.32 (Ar*C*), 48.37 (*C*HMe$_2$), 23.57 (*C*H$_3$), 4.58 (Si(*C*H$_3$)$_3$) ppm. Calcd for $C_{37}H_{76}N_6Si_6Th$: C, 44.19; H, 7.61; N, 8.35. Found: C, 43.94; H, 7.47; N, 8.12.

[(L)U(IV){N(SiMe$_3$)$_2$}$_3$] (4):

Yield 94 % (260 mg, 0.265 mmol); ^{1}H NMR (300.0 MHz, C_6D_6): δ = 18.74 (brs, 6H, CH*Me*$_2$), 11.61 (d, *J* = 9.0 Hz, 2H, C*H*Me$_2$), 8.92 (t, *J* = 7.5 Hz, 2H, ArC*H*), 7.76 (t, *J* = 6.0 Hz, 2H, ArC*H*), 7.16 (s, 2H, ArC*H*), 4.14 (s, 6H, CH*Me*$_2$), 0.12 (s, 2H, ArC*H*), -10.71 (s, 54H, Si(C*H*$_3$)$_3$); ^{13}C NMR (75.5 MHz, C_6D_6): δ = 155.52 (*C*$_{ipso=N}$), 144.28 (Ar*C*), 131.71 (Ar*C*), 128.86 (Ar*C*), 126.14 (Ar*C*), 122.91 (Ar*C*), 38.29 (*C*HMe$_2$), 31.58 (*C*HMe$_2$), 24.86 (CH$_3$), 22.56 (*C*H$_3$), 13.86 (*C*H$_3$), 6.19 (Si(*C*H$_3$)$_3$) ppm. Calcd for $C_{37}H_{76}N_6Si_6U$: C, 43.93; H, 7.57; N, 8.30. Found: C, 43.70; H, 7.21; N, 8.02.

General Procedure for the Catalytic Hydroboration reaction of HBpin with Ketones and Aldehyde and Actinide catalysts:

A sealable J. Young NMR tube was loaded with the appropriate amount of complexes **2** and **3** from a stock solution in C_6D_6 inside the glovebox. The respective ketone/aldehyde (0.373 mmol) and HBpin (0.448 mmol, 1.2 equivalents vs carbonyl substrates) were added, and the reaction was immediately diluted to 550 µL with C_6D_6. Solid substrates were dissolved in 300 µL of C_6D6 before being added to the solution of the precatalyst. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. The products were identified by ^{1}H NMR and ^{13}C spectroscopy and the chemical shifts were compared with previously reported literature data[8].

Kinetic Studies of Hydroboration Reaction of HBpin with Ketones and Aldehyde and Actinide catalysts

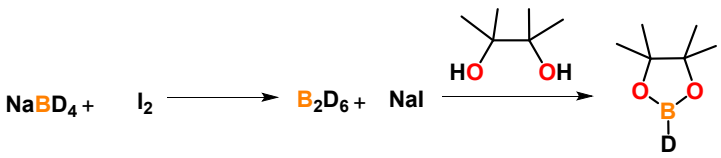
In a typical experiment, an NMR sample was prepared as described above in presence of C_6Me_6 as internal standard (δ = 2.12 ppm). Experiments for reagent order determination were performed at variable concentrations of precatalyst, HBpin, and carbonyl substrates, spanning

one order of magnitude concentration differences while keeping the other reagent concentration constant. The sample tube was inserted into the probe of the Bruker Avance 300 spectrometer which had been previously set to the desired temperature (T = 25 ± 0.1 °C; checked with ethylene glycol temperature standard). Data were acquired every 10 seconds up to 240 seconds, and product concentrations were measured. Reaction rates were determined by a least-squares fit of product concentration versus time, and the collective rate data plotted to determine reagent orders. Representative plots are shown in Figures S70.

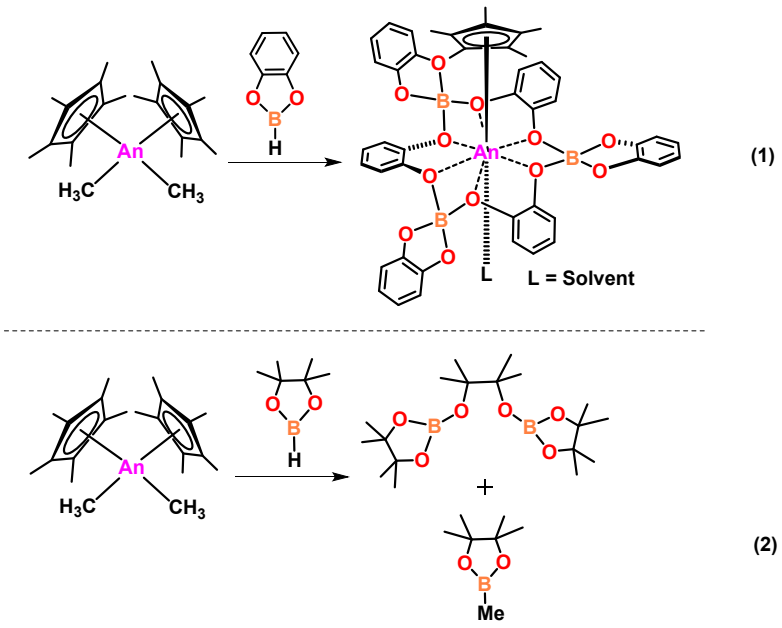
Kinetic Isotope Effect Study of Hydroboration Reaction of DBpin:

Kinetic effect study was performed following an identical way as described above. The sealable J. Young NMR tube was loaded with the appropriate amount of **3**, DBpin, ketone in toluene in presence of C_6D_6 as an internal standard.

Preparation of deuterated pinacol borane:



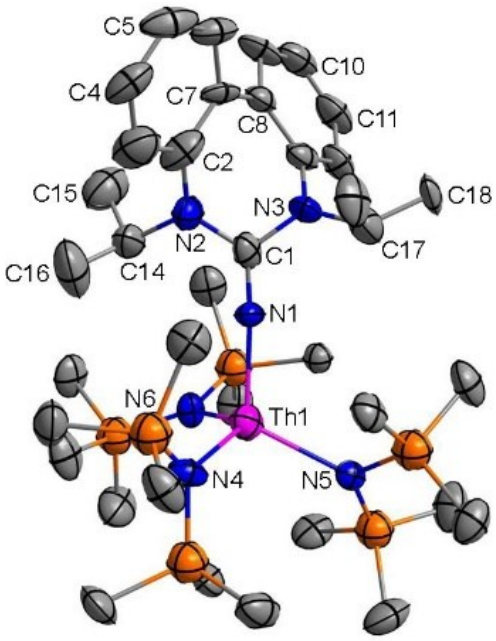
In a round-bottomed flask, connected with a dropping funnel and an N_2 inlet was charged with $NaBD_4$ (0.65 g, 15.5 mmol) in 15 mL of diglyme. The flask containing $NaBD_4$ was connected through a Teflon cannula to a second flask containing a solution of pinacol (0.61 g, 5.2 mmol) in 10 mL of anhydrous THF maintaining 0 °C temperature. The flask containing pinacol was vented through a Teflon cannula bubbling into THF. The diglyme solution (10 mL) of I_2 (1.90 g, 7.5 mmol) was loaded in a dropping funnel and was allowed to add dropwise over an hour. The steam of N_2 was continued for an additional 2 h after addition of I_2, this step allowed complete elimination of any excess trace of polydeuterated diborane in the solution of DBPin. The removal of excess THF by a continuous flow of N_2 steam resulted in pure DBpin.



(1)

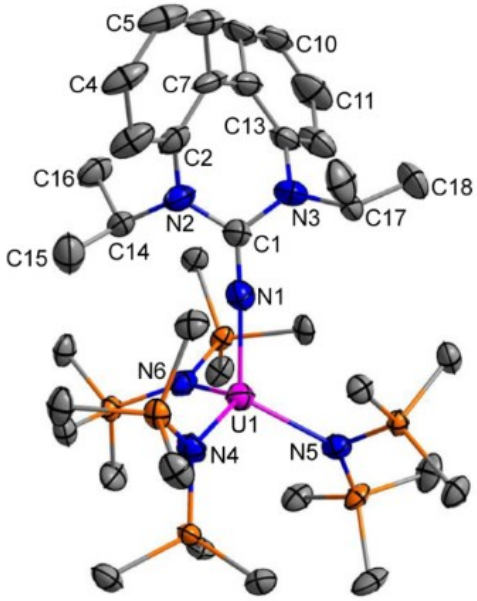
(2)

Scheme S1: (1) Schematic presentation of Stoichiometric reaction between $Cp^*_2AnMe_2$ and catecholborane, (2) $Cp^*_2AnMe_2$ and pinacolborane



(a)

Figure S1 (a): Molecular structure of complex **3** (a) with thermal ellipsoid set at the 50% probability levels. All Hydrogen atoms are omitted for the clarity. All Hydrogen atoms are omitted for the clarity. Selected bond distances (Å) and angles (°):Th1–N1 2.184(10), Th1–N5 2.351(9), Th1–N6 2.354(9), Th1–N4 2.392(10), N1–C1 1.273(16); C1–N1–Th1 171.8(9).



(b)

Figure S1 (b): Molecular structure of complex **4** (b) with thermal ellipsoid set at the 50% probability levels. All Hydrogen atoms are omitted for the clarity. All Hydrogen atoms are omitted for the clarity. Selected bond distances (Å) and angles (°):U1–N1 2.141(4), U1–N5 2.290(5), U1–N6 2.306(4), U1–N4 2.312(5), N1–C1 1.273(16); C1–N1–U1 171.0(4).

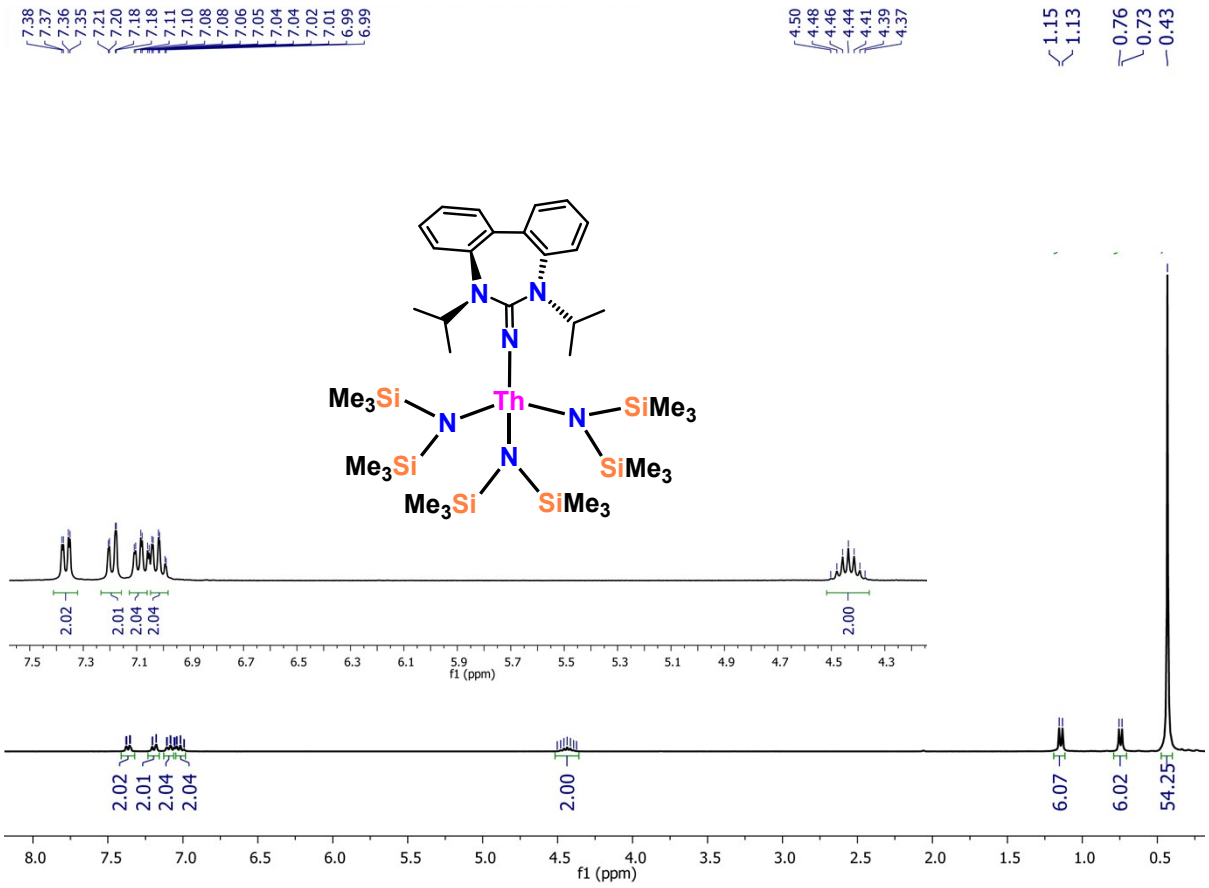


Figure S2: ^{1}H NMR spectrum of Compound **3**.

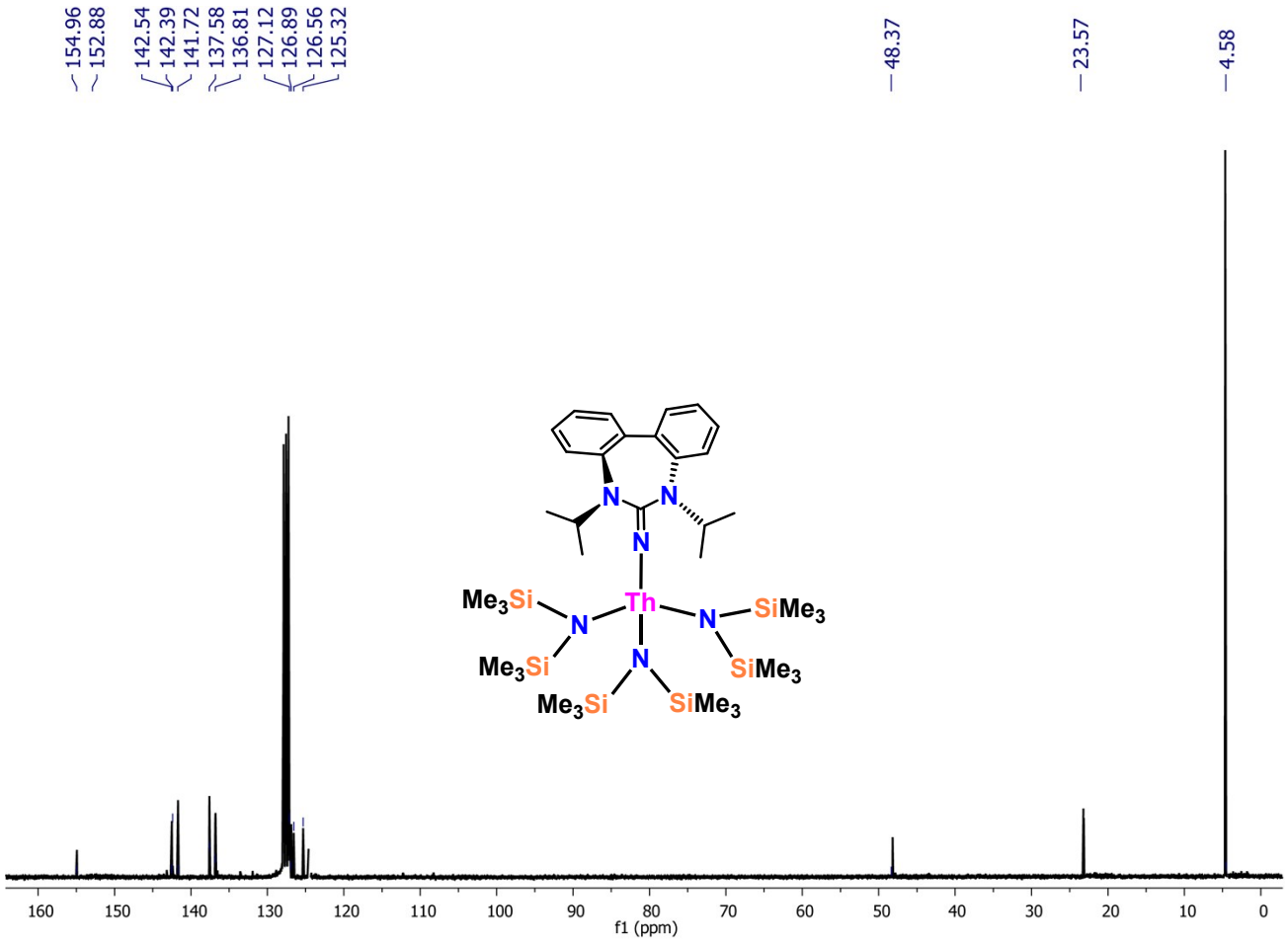


Figure S3: ^{13}C NMR spectrum of Compound **3**.

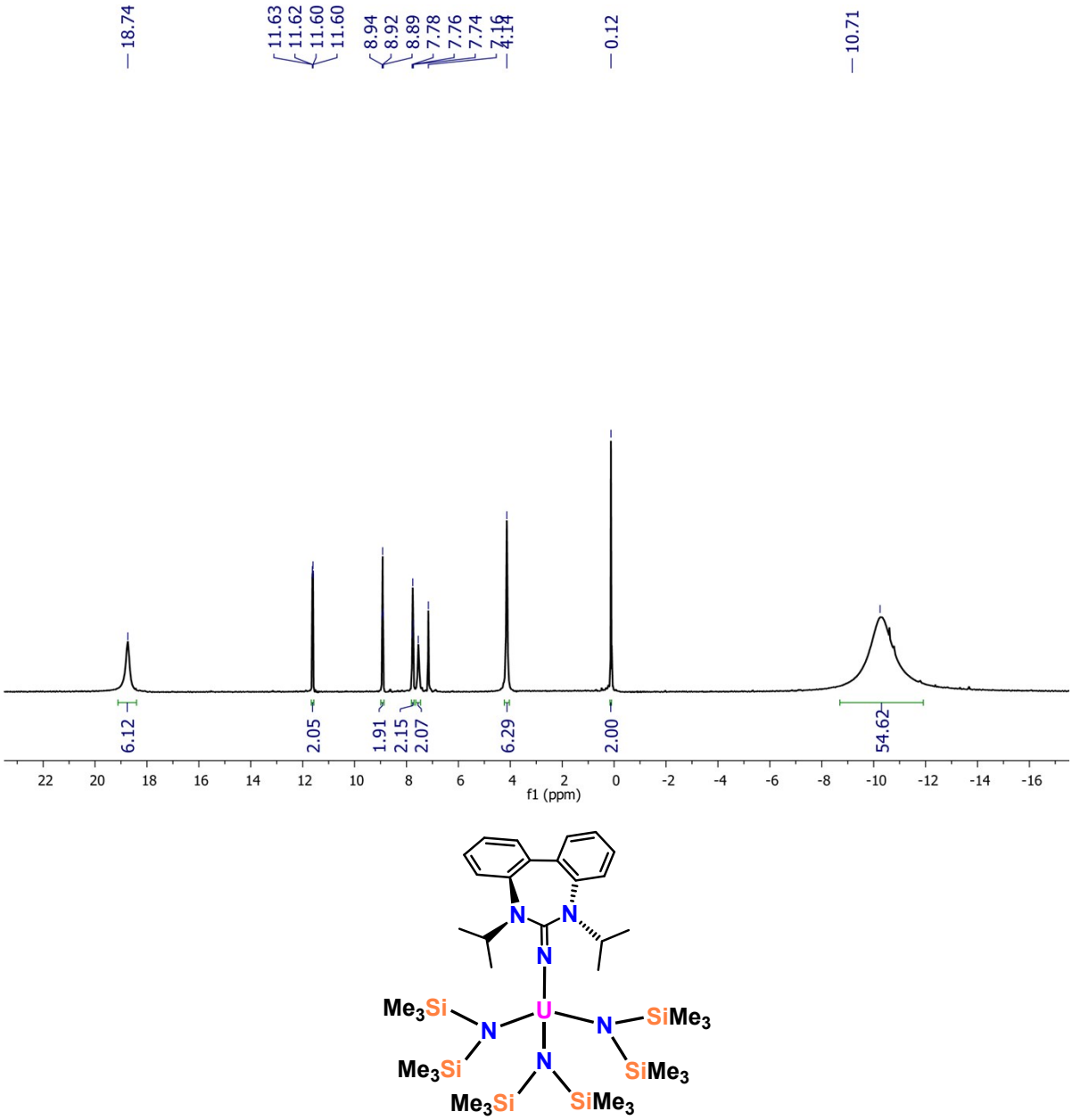
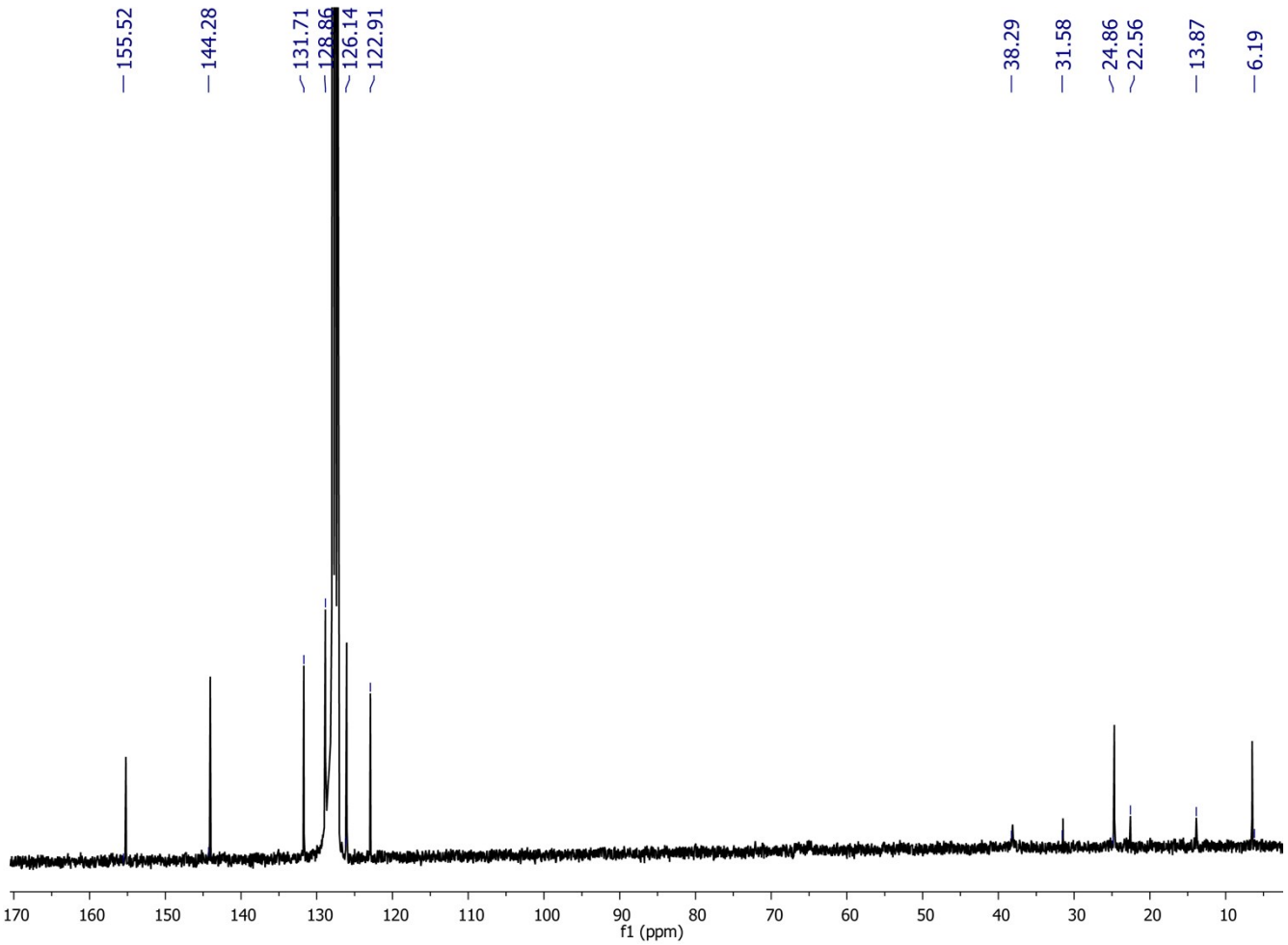


Figure S4: ^{1}H NMR spectrum of Compound **4**.



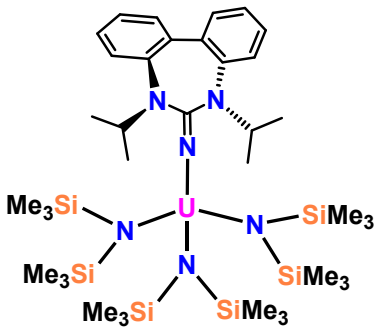


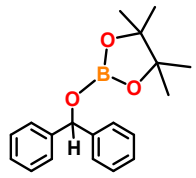
Figure S5: ^{13}C NMR spectrum of Compound **4**.

Table S1. Crystallographic data and pertinent refinement parameters for complexes **3 – 4**.

	3	**4**
Empirical formula	C_{37} $H_{76}N_6Si_6Th$	C37 H76 N6 Si6 U
Formula Weight	1005.62	1011.61
Crystal System	monoclinic	monoclinic
Space Group	P21/c	*P21/c*
a (Å)	18.619(6)	18.570(3)
b (Å)	11.246(2)	11.240(7)
c (Å)	28.548(9)	28.4300(17)
α (deg)	90.00	90.00
β (deg)	123.219(17)	122.980(3)
γ (deg)	90.00	90.00
V (Å^3)	5001(2)	4978(3)
Z	4	4
ρcalcd (g cm^{-3})	1.336	1.350
μ (mm^{-1})	3.156	3.435
F(000)	2056	2064
Reflections Collected	7439	7377
Independent	7439	7377
Observed [I >2σ (I)]	6121	6410
No. of variables	468	473
GooF	1.217	1.071
Rint	0.0850	0.0690
Final R indices	R1 = 0.0779	R1 = 0.0363
[I > 2σ(I)][a]	wR2 = 0.1478	wR2 = 0.0852
R indices (all data)[a]	R1 = 0.1543	R1 = 0.0887
	wR2 = 0.0984	wR2 = 0.0454

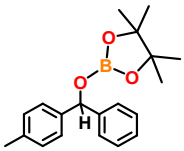
Characterization Data for Hydroboration Products:

2-(diphenylmethoxy)pinacolborane (1a):



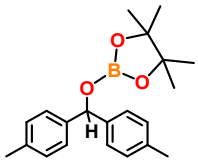
^{1}H NMR (300 MHz, C_6D_6) δ 7.55 ─ 7.52 (m, 4H), 7.21 ─ 7.16 (m, 4H), 7.12 ─ 7.07 (m, 2H), 6.52 (s, 1H), 1.07 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 143.39, 137.86, 131.78, 129.71, 128.07, 127.88, 127.04, 126.47, 82.34, 78.02, 24.10. IR data (cm^{-1}): 2985 (m), 1492 (s), 1423 (s), 1377 (m), 1269 (s), 1138, 967 (m), 847 (m), 756 (m), 698 (s), 653 (s).

2-(*para*-tolylmethoxy)pinacolborane (1b):



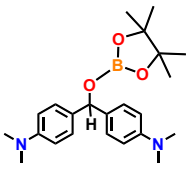
^{1}H NMR (300 MHz, C_6D_6) δ 7.42 (d, J = 6.0 Hz, 2H), 7.32 (d, J = 9.0 Hz, 2H), 7.08 (t, 2H, J = 7.5), 6.87 (d, J = 9.0 Hz, 2H), 6.39 (s, 1H), 1.99 (s, 3H), 0.94 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 143.65, 142.35, 140.60, 136.47, 131.51, 129.99, 128.66, 128.04, 127.86, 126.96, 126.51, .82.51, 77.98, 24.87, 20.87. IR data (cm^{-1}): 2959 (m), 1486 (m), 1450 (m), 1275 (vs), 1170, 967 (m), 990 (m), 818 (m), 693 (m), 653 (s), 618 (m), 596 (m).

2-(di-*para*-tolylmethoxy)pinacolborane (1c):



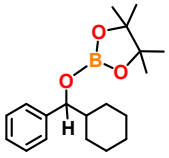
^{1}H NMR (300 MHz, C_6D_6) δ 7.44 (d, J = 9.0 Hz, 4H), 6.97 (d, J = 9.0 Hz, 4H), 6.50 (s, 1H), 2.08 (s, 6H), 1.03 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 146.88, 136.31, 130.12, 128.95, 128.60, 126.53, 82.37, 77.80, 24.31, 20.96. IR data (cm^{-1}): 2965 (m), 1456 (vs), 1367 (vs), 1341 (vs), 1148 (s), 943 (m), 848 (m), 763 (m), 660 (m).

2-(di-*para*-N,N-dimethylmethoxy)pinacolborane (1d):



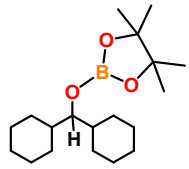
^{1}H NMR (300 MHz, C_6D_6) δ 7.45 (d, J = 6.0 Hz, 2H), 7.10 (d, J = 6.0 Hz, 2H), 6.39 (d, J = 9.0 Hz, 4H), 3.85 (s, 2H), 2.38 (s, 12H), 0.96 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 152.32, 149.82, 132.01, 129.46, 112.92, 112.31, 110.58, 82.70, 40.13, 39.11, 24.15. IR data (cm^{-1}): 2985 (m), 1446 (vs), 1366 (vs), 1321 (s), 1058 (m), 938 (m), 813 (m), 761 (m), 676 (m), 562 (m), 504 (m).

2-(cyclohexylphenylmethoxy)pinacolborane (1e):



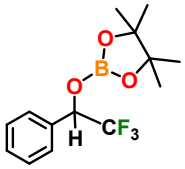
^{1}H NMR (300 MHz, C_6D_6): δ 7.46 ─ 7.33 (m, 2H), 7.16 ─ 7.11 (m, 2H), 7.07 ─ 7.02 (m, 1H), 5.02 (d, J = 6.0 Hz, 1H), 1.98 ─ 1.94 (m, 1H), 1.66 ─ 1.64 (m, 6H), 1.24 ─ 1.09 (m, 4H), 1.01 (s, 6H), 0.97 (s, 6H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 142.69, 127.73, 126.54, 82.02, 80.97, 44.90, 29.12, 28.10, 26.25, 25.94, 25.86, 24.22. IR data (cm^{-1}):

2933 (m), 1442 (s), 1373 (m), 1325 (s), 1147 (m), 1065 (m), 852 (m), 765 (m), 688 (m), 578 (m).



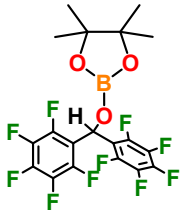
2-(dicyclohexylmethoxy)pinacolborane (1f):

^{1}H NMR (300 MHz, C_6D_6): δ 3.74 (t, J = 6.0 Hz, 1H), 1.84 ─ 1.79 (m, 2H), 1.63 ─ 1.53 (m, 12H), 1.23 ─ 1.08 (m, 8H), 1.03 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 82.52, 81.85, 39.36, 29.85, 27.31, 26.64, 26.51, 26.33, 24.37. IR data (cm^{-1}): 2984 (m), 2920 (s), 2843 (m), 1446 (vs), 1366 (s), 1317 (m), 1149 (s), 964 (m), 853 (m), 670 (m), 496 (m).



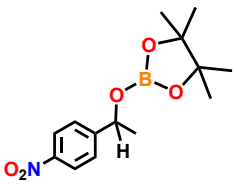
2-(2,2,2-trifluoro-1-phenylethyoxy)pinacolborane (1g):

^{1}H NMR (300 MHz, C_6D_6): δ 7.49 ─ 7.47 (m, 2H), 7.13 ─ 7.09 (m, 3H), 15.68 (q, J = 9.0 Hz, 1H), 1.07 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 139.68, 128.08, 127.06, 126.53, 82.16, 77.77, 66.58, 24.58. IR data (cm^{-1}): 1464 (s), 1438 (s), 1378 (s), 1340 (m), 1260 (s), 1162 (vs), 1131 (vs), 1057 (m), 970 (m), 848 (m), 699 (m), 496 (m).



2-(di-perfluorophenylmethoxy)pinacolborane (1h):

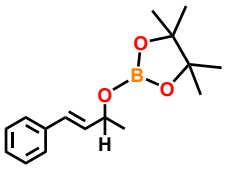
^{1}H NMR (300 MHz, C_6D_6): δ 6.92 (s, 1H), 1.01 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 144.76, 140.36, 137.31, 130.24, 83.85, 62.26, 24.32. IR data (cm^{-1}): 1508 (vs), 1431 (vs), 1315 (s), 1135 (vs), 992 (vs), 847 (s), 660 (m).



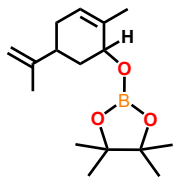
2-(1-(4-nitrophenyl)ethoxy)pinacolborane (1i):

^{1}H NMR (300 MHz, C_6D_6) δ 7.93 ─ 7.47 (m, 2H), 7.12 ─ 7.08 (m, 2H), 5.28 (q, J = 7.0 Hz, 1H), 1.35 (q, J = 12.0 Hz, 3H), 1.10 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 151.63, 125.61, 123.28, 82.92, 71.63, 25.23, 24.32. IR data (cm^{-1}): 2972 (m), 1439 (s), 1374 (s), 1347 (vs), 1146 (vs), 848 (s), 701 (s).

2-(1-cinnamylethoxy)pinacolborane (1j):



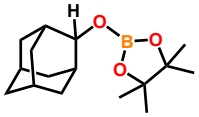
^{1}H NMR (300 MHz, C_6D_6) δ 7.18 ─ 7.14 (m, 2H), 7.10 ─ 7.06 (m, 2H), 7.02 ─ 6.98 (m, 1H), 6.66 ─ 6.58 (m, 2H), 6.22 ─ 6.11 (m, 2H), 4.99 (q, J = 9.0 Hz, 1H), 1.30 (d, J = 12.0 Hz, 3H), 1.02 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 137.14, 132.44, 129.21, 128.50, 126.62, 82.29, 71.13, 24.52, 24.38, 23.21. IR data (cm^{-1}): 2978 (m), 1434 (vs), 1366 (s), 1325 (s), 1140 (vs), 1065 (m), 969 (m), 852 (s), 750 (vs), 681 (s).



2-(2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-yl)pinacolborane (1k):

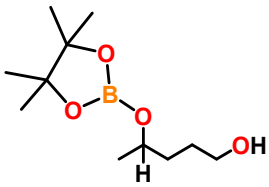
^{1}H NMR (300 MHz, C_6D_6) δ 5.30 (br, s, 1H), 4.86 ─ 4.84 (m, 1H), 4.65 (s, 1H), 2.23 ─ 2.19 (m, 1H), 2.17 ─ 2.08 (m, 1H), 1.80 ─ 1.67 (m, 6H) 1.47 (s, 3H), 1.03 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 148.06, 136.00, 122.38, 108.30, 81.49, 40.15, 37.65, 30.37, 23.59, 19.68, 18.65. IR data (cm^{-1}): 2998 (w), 2920 (w), 2844 (s), 1440 (vs), 1371 (m), 1314 (s), 1151 (vs), 976 (m), 850 (m), 674 (m), 499 (m).

2-(1-adamentylethoxy)pinacolborane (1l):



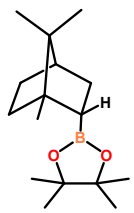
^{1}H NMR (300 MHz, C_6D_6): δ 4.43 (t, *J* =3.0 Hz, 1H), 2.36 ─ 2.32 (m, 2H), 2.04 (br, s, 2H), 1.67 ─ 1.55 (m, 10H), 1.05 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 82.12, 76.83, 46.75, 38.70, 36.31, 34.25, 31.21, 27.58, 27.34, 27.10, 24.31. IR data (cm^{-1}): 2890 (vs), 2844 (s), 1440 (vs), 1369 (s), 1323 (s), 1143 (vs), 1091 (m), 1057 (m), 967 (m), 845 (m), 675 (m).

4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)pentan-1-ol (1m):



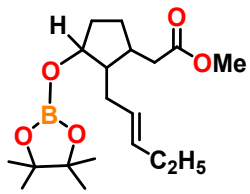
^{1}H NMR (300 MHz, C_6D_6): δ 4.04 (br, s, 1H), 3.76 ─ 3.70 (m, 2H), 3.60 ─ 3.56 (m, 1H), 1.45 ─ 1.38 (m, 4H), 1.30 (d, *J* = 12.0 Hz, 3H), 1.04 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 84.62, 64.73, 62.55, 37.71, 29.44, 25.56, 24.76. IR data (cm^{-1}): 3549 (m), 2976 (s), 2920 (s), 1434 (s), 1357 (m), 1082 (s), 1040 (m), 945 (m).

2-{1-(1,7,7-trimethyl-bicyclo[2.2.1]heptyl)ethoxy}pinacolborane (1n):



^{1}H NMR (300 MHz, C_6D_6): δ 4.21 ─ 4.17 (m, 1H), 1.91 ─ 1.86 (m, 1H), 1.69 ─ 1.61 (m, 1H), 1.52 ─ 1.39 (m, 1H), 1.35 ─ 1.30 (m, 2H), 1.12 (s, 3H), 1.02 (s, 12H), 0.97 (s, 3H), 0.91 ─ 0.84 (m, 2H), 0.80 (s, 3H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 81.71, 78.74, 48.50, 45.98, 44.80, 40.09, 33.21, 26.73, 23.93, 19.74, 11.03. IR data (cm^{-1}): 2960 (m), 1431 (vs), 1375 (m), 1320 (m), 1144 (vs), 1072 (m), 1012 (w), 969 (m), 853 (s), 815 (m), 674 (m), 498 (m).

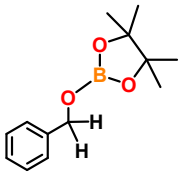
methyl (E)-2-(2-(pent-2-en-1-yl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)cyclopentyl)acetate (1o):



^{1}H NMR (300 MHz, C_6D_6): δ 5.49 ─ 5.34 (m, 2H), 4.62 (br, 1H), 3.29 (s, 3H), 2.35 ─ 2.23 (m, 3H), 2.12 ─ 1.99 (m, 4H), 1.94─ 1.86 (m, 1H), 1.68 ─ 1.63 (m, 2H), 1.22 ─ 1.11 (m, 2H), 1.02 (s, 12H), 0.91 ─

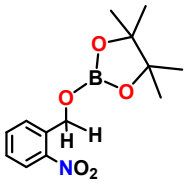
0.87 (m, 3H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 170.52, 130.14, 79.90, 75.24, 48.67, 48.47, 36.93, 36.71, 23.93, 31.26, 27.23, 23.48, 22.28, 18.70, 12.15. IR data (cm^{-1}): 2972 (m), 1739 (m), 1444 (vs), 1368 (s), 1327 (m), 1147 (vs), 978 (m), 849 (m), 815 (m), 670 (m).

2-(benzyloxy)pinacolborane (2a):



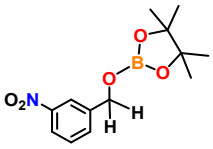
^{1}H NMR (300 MHz, C_6D_6): δ 7.33 ─ 7.29 (m, 2H), 7.17 ─ 7.09 (m, 3H), 4.95 (s, 2H), 1.03 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 143.53, 131.63, 129.71, 127.89, 127.05, 126.47, 82.56, 78.03, 24.30. IR data (cm^{-1}): 2980 (s), 1444 (vs), 1371 (vs), 1333 (vs), 1144 (vs), 969 (m), 845 (m), 738 (m), 682 (m).

2-(2-nitrobenzyloxy)pinacolborane (2b):



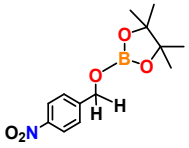
^{1}H NMR (300 MHz, C_6D_6): δ 7.63 ─ 7.59 (m, 2H), 6.94 ─ 6.89 (m, 1H), 6.65 ─ 6.60 (m, 1H), 5.32 (s, 2H), 0.99 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 133.10, 132.89, 132.44, 128.79, 127.17, 123.87, 82.81, 77.83, 25.30, 24.25. IR data (cm^{-1}): 2985 (m), 1522 (m), 1440 (vs), 1337 (vs), 1142 (vs), 972 (m), 849 (m), 793 (w), 726 (m), 670 (m).

2-(3-nitrobenzyloxy)pinacolborane (2c):



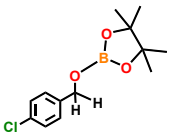
^{1}H NMR (300 MHz, C_6D_6): δ 7.96 (s, 1H), 7.68 (d, J = 9.0 Hz, 1H), 7.10 (d, J = 6.0 Hz, 1H), 6.72 ─ 6.67 (m, 1H), 4.62 (s, 2H), 1.00 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 147.65, 141.72, 131.15, 128.21, 126.02, 121.23, 120.63, 82.43, 73.95, 23.94, 23.70. IR data (cm^{-1}): 2985 (m), 1527 (s), 1445 (s), 1342 (vs), 1034 (m), 803 (m), 726 (m), 680 (m).

2-(4-nitrobenzyloxy)pinacolborane (2d):



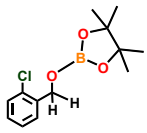
^{1}H NMR (300 MHz, C_6D_6): δ 7.80 ─ 7.76 (m, 2H), 6.92 ─ 6.87 (m, 1H), 4.67 (s, 2H), 1.03 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 152.88, 150.84, 146.85, 125.27, 122.84, 122.78, 82.18, 71.18, 23.77. IR data (cm^{-1}): 1520 (vs), 1448 (s), 1337 (vs), 1035 (m), 801 (m), 729 (m), 682 (m).

2-(4-chlorobenzyloxy)pinacolborane (2e):



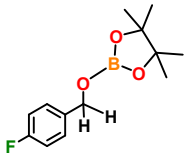
^{1}H NMR (300 MHz, C_6D_6): δ 7.21 ─ 7.08 (m, 1H), 7.08 ─ 6.98 (m, 3H), 4.76 (s, 2H), 1.03 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 137.94, 132.53, 130.29, 128.79, 128.21, 127.89, 82.09, 65.48, 24.22. IR data (cm^{-1}): 2972 (w), 1440 (vs), 1368 (s), 1332 (m), 1142 (s), 1086 (m), 1008 (w), 972 (w), 839 (s), 808 (s), 670 (m).

2-(2-chlorobenzyloxy)pinacolborane (2f):



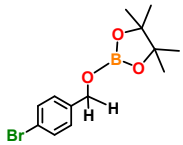
^{1}H NMR (300 MHz, C_6D_6): δ 7.72 ─ 7.68 (m, 1H), 6.90 ─ 6.86 (m, 1H), 6.79 ─ 6.66 (m, 2H), 5.13 (s, 2H), 1.03 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 136.98, 133.88, 132.10, 129.63, 128.62, 128.44, 126.21, 82.62, 64.88, 23.80. IR data (cm^{-1}): 2979 (w), 1449 (s), 1361 (s), 1340 (s), 1152 (m), 1078 (m), 1021 (w), 962 (w), 832 (s), 799 (s), 677 (s).

2-(4-fluorobenzyloxy)pinacolborane (2g):



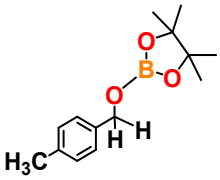
^{1}H NMR (300 MHz, C_6D_6): δ 7.20 ─ 7.13 (m, 2H), 6.90 ─ 6.82 (m, 2H), 4.90 (s, 2H), 1.13 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 160.94, 135.43, 129.21, 115.71, 84.19, 61.45, 24.28. IR data (cm^{-1}): 2967 (m), 2879 (m), 1446 (s), 1372 (s), 1326 (s), 1144 (vs), 972 (m), 847 (s), 738 (m), 682 (s).

2-(4-bromobenzyloxy)pinacolborane (2h):



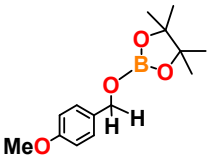
^{1}H NMR (300 MHz, C_6D_6): δ 7.27 ─ 7.25 (d, *J* = 6.0 Hz, 2H), 6.99 ─ 6.97 (d, *J* = 6.0 Hz, 2H), 4.78 (s, 2H), 1.08 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 138.65, 132.02, 131.28, 130.49, 128.19, 121.12, 82.51, 65.55, 24.12. IR data (cm^{-1}): 2984 (m), 1453 (s), 1392 (s), 1252 (m), 956 (s).

2-(*p*-methylbenzyloxy)pinacolborane (2i):

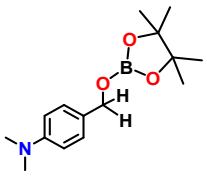


^{1}H NMR (300 MHz, C_6D_6): δ 7.27 ─ 7.23 (d, *J* = 12.0 Hz, 2H), 6.97 ─ 6.93 (d, *J* = 12.0 Hz, 2H), 4.96 (s, 2H), 2.07 (s, 3H), 1.03 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 143.82, 133.96, 128.83, 130.49, 126.21, 81.85, 66.05, 23.82, 20.17. IR data (cm^{-1}): 2972 (m), 1444 (s), 1367 (s), 1330 (s), 1143 (vs), 974 (m), 846 (m), 800 (m), 673 (m).

2-(*p*-N, N'-dimethylbenzyloxy)pinacolborane (2j):

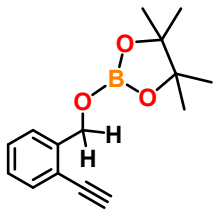


^{1}H NMR (300 MHz, C_6D_6): δ 7.39 ─ 7.36 (d, *J* = 9.0 Hz, 2H), 6.87 ─ 6.84 (d, *J* = 9.0 Hz, 2H), 5.04 (s, 2H), 3.38 (s, 3H), 1.15 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 131.82, 131.40, 128.53, 113.89, 82.30, 66.37, 54.39, 39.82, 24.36. IR data (cm^{-1}): 2972 (m), 1514 (m), 1446 (vs), 1361 (s), 1326 (s), 1241 (vs), 1144 (vs), 1024 (m), 978 (m), 824 (s), 670 (m).



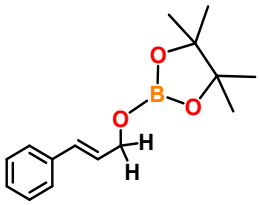
2-(*p*-N, N'-dimethylbenzyloxy)pinacolborane (2k):

^{1}H NMR (300 MHz, C_6D_6): δ 7.36 ─ 7.30 (m, 2H), 6.57 ─ 6.51 (m, 2H), 5.00 (s, 2H), 2.47 (s, 6H), 1.03 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 128.21, 112.40, 128.83, 82.16, 66.74, 39.82, 24.20. IR data (cm^{-1}): 2959 (m), 1573 (m), 1486 (s), 1413 (vs), 1302 (vs), 1117 (vs), 1030 (m), 952 (w), 817 (m), 773 (m), 642 (m).



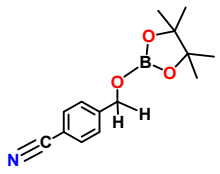
2-(2-ethynylbenzyloxy)pinacolborane (2l):

^{1}H NMR (300 MHz, C_6D_6): δ 7.63 (d, J = 6.0 Hz, 1H), 7.35 (d, J = 6.0 Hz, 1H), 7.06 ─ 7.01 (m, 1H), 6.87 ─ 6.82 (m, 1H), 5.35 (s, 2H), 2.86 (s, 1H), 1.03 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 141.85, 132.20, 128.73, 126.62, 125.69, 82.34, 80.77, 64.86, 24.54. IR data (cm^{-1}): 3408 (s), 2965 (m), 1444 (s), 1375 (m), 1316 (vs), 1149 (vs), 849 (vs), 759 (s), 678 (m).



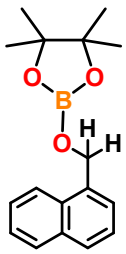
2-(cinnamylmethoxy)pinacolborane (2m):

^{1}H NMR (300 MHz, C_6D_6): δ 7.14 ─ 7.11 (m, 2H), 7.06 ─ 7.01 (m, 2H), 6.99 ─ 6.96 (m, 1H), 6.55 (m, 1H), 6.12 (d, J = 18.0 Hz, J = 6.0 Hz, 1H), 4.48 (m, 2H), 1.01 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 144.05, 132.09, 131.59, 129.67, 118.68, 111.11, 82.69, 65.47, 54.39, 24.14. IR data (cm^{-1}): 2972 (m), 1440 (vs), 1376 (s), 1324 (s), 1260 (w), 1144 (vs), 1076 (m), 981 (s), 866 (m), 738 (m), 678 (s).



2-(*p*-cyanobenzyloxy)pinacolborane (2n):

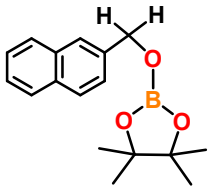
^{1}H NMR (300 MHz, C_6D_6): δ 6.97 ─ 6.95 (d, J = 6.0 Hz, 2H), 6.85 ─ 6.82 (d, J = 9.0 Hz, 2H), 4.62 (s, 2H), 0.99 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 144.05, 132.09, 131.59, 129.67, 118.68, 111.11, 82.69, 65.47, 54.39, 24.14. IR data (cm^{-1}): 2947 (m), 2242 (s), 1477 (s), 1409 (vs), 1312 (vs), 1130 (vs), 1037 (m), 952 (m).



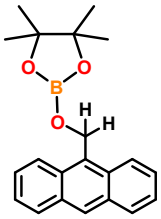
2-(naphthalen-1-ylmethyl)pinacolborane (2o):

^{1}H NMR (300 MHz, C_6D_6): δ 7.95 ─ 7.91 (m, 1H), 7.65 ─ 7.54 (m, 3H), 7.25 ─ 7.18 (m, 3H), 5.42 (s, 2H), 1.03 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 135.03, 133.68, 131.16, 128.72, 128.39, 128.03, 127.95, 125.81, 125.39, 125.16, 124.57, 123.37, 82.41, 65.05, 24.41. IR data (cm^{-1}): 2978 (m), 1444 (s), 1373 (vs), 1322 (s), 1143 (s), 1065 (m), 974 (w), 846 (m), 770 (s), 668 (m).

2-(naphthalen-1-ylmethyl)pinacolborane (2p):

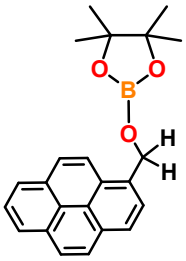


^{1}H NMR (300 MHz, C_6D_6): δ 7.72 (s, 1H), 7.56 ─ 7.52 (m, 3H), 7.36 ─ 7.32 (m, 1H), 7.22 ─ 7.16 (m, 2H), 5.05 (s, 2H), 1.00 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 136.94, 133.68, 132.73, 125.74, 125.43, 125.21, 124.79, 82.46, 66.84, 24.07. IR data (cm^{-1}): 2989 (m), 1449 (s), 1356 (vs), 1157 (s), 1165 (m), 964 (m), 852 (m), 770 (s), 663 (w).



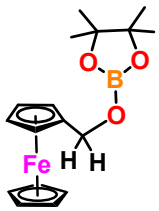
2-(anthracene-9-ylmethoxy)pinacolborane (2q):

^{1}H NMR (300 MHz, C_6D_6): δ 8.55 (d, J = 9.0 Hz, 2H), 8.09 (s, 1H), 7.71 (d, J = 9.0 Hz, 2H), 7.29 (t, J = 7.5 Hz, 2H), 7.18 (t, J = 7.5 Hz, 2H), 5.86 (s, 2H), 0.97 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 130.53, 130.01, 128.74, 128.33, 125.72, 124.70, 124.63, 123.63, 82.34, 59.19, 24.84. IR data (cm^{-1}): 2978 (m), 1584 (s), 1454 (s), 1322 (s), 1283 (s), 1157 (s), 1052 (m), 937 (m), 852 (m), 770 (s), 663 (s).



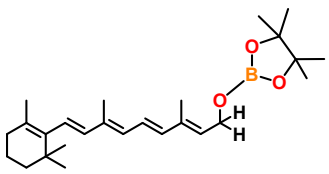
2-(pyren-1-ylmethoxy) pinacolborane (2r):

^{1}H NMR (300 MHz, C_6D_6): δ 4.74 (s, 2H), 4.20 (d, J = 9.0 Hz, 2H), 7.75 ─ 7.58 (m, 5H), 5.60 (s, 2H), 1.01 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 135.03, 131.39, 131.17, 130.93, 130.50, 130.19, 127.13, 126.52, 126.15, 125.72, 125.58, 125.06, 124.98, 124.58, 124.25, 123.21, 82.39, 63.23, 24.28. IR data (cm^{-1}): 2869 (w), 1598 (m), 1433 (s), 1380 (m), 1328 (m), 1226 (m), 1174 (m), 1145 (m), 1061 (m), 1014 (s), 995 (s), 840 (vs), 746 (m), 703 (s), 666 (m).



2-(ferrocenylmethoxy)pinacolborane (2s):

^{1}H NMR (300 MHz, C_6D_6): δ 4.74 (s, 2H), 4.20 (m, 2H), 3.98 (s, 5H), 1.07 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 85.66, 82.22, 68.49, 68.30, 68.00, 63.15, 24.51. IR data (cm^{-1}): 2972 (m), 1442 (vs), 1365 (m), 1326 (s), 1147 (s), 1174 (m), 977 (w), 851 (m), 746 (m), 671 (m).



2-(((2E,4E,6E,8E)-3,7-dimethyl-9-(2,6,6-trimethylcyclohex-1-en-1-yl)nona-2,4,6,8-tetraen-1-yl)oxy)pinacolborane (2t):

^{1}H NMR (300 MHz, C_6D_6): δ 6.63 (dd, $^3J_{HH}$ = 12 Hz, $^3J_{HH}$ = 3.0 Hz, 1H), 6.29 (t, J = 7.5 Hz, 3H), 6.17 (d, J = 12.0 Hz, 1H), 5.83 (t, J = 7.5 Hz, 1H), 4.65 (d, J = 6.0 Hz, 1H), 1.99 ─ 1.95 (m, 2H), 1.86 (s, 3H), 1.79 (s, 3H), 1.68 (s, 3H), 1.62 ─ 1.57 (m, 2H), 1.52 ─ 1.47 (m, 2H), 1.13 (s, 6H), 1.07 (s, 12H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 138.40, 138.07, 137.07, 136.35, 135.46, 131.51, 131.06, 129.82, 126.96, 126.39, 124.87, 82.86, 82.46, 61.89, 39.64, 34.26, 33.17, 28.93, 24.47, 24.38, 21.72, 19.48,

12.48. IR data (cm^{-1}): 2985 (s), 2920 (s), 1445 (vs), 1368 (vs), 1137 (vs), 1147 (s), 1060 (vs), 967 (s), 851 (m).

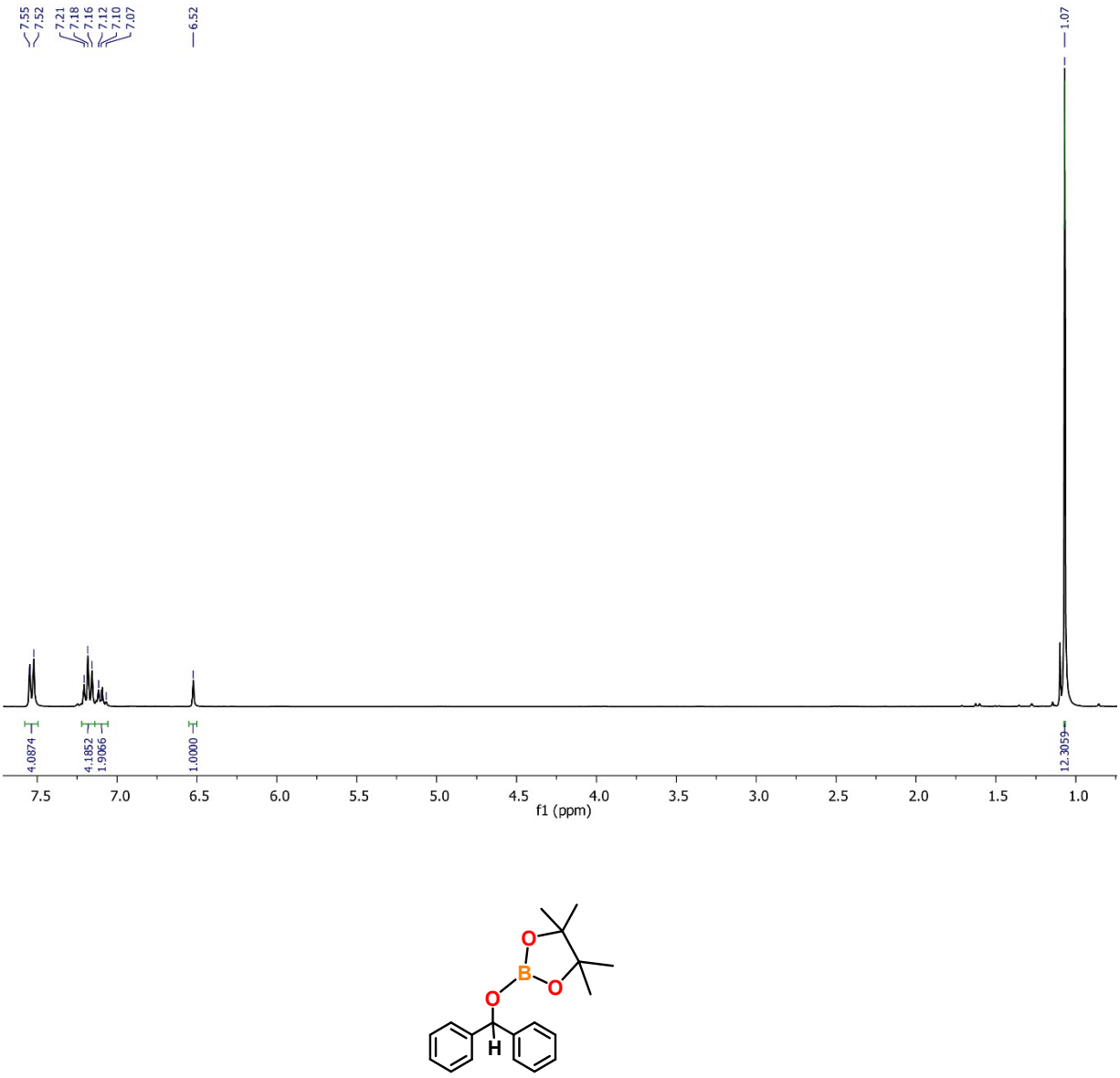


Figure S6: ^{1}H NMR spectrum of 2-(diphenylmethoxy)pinacolborane (1a)

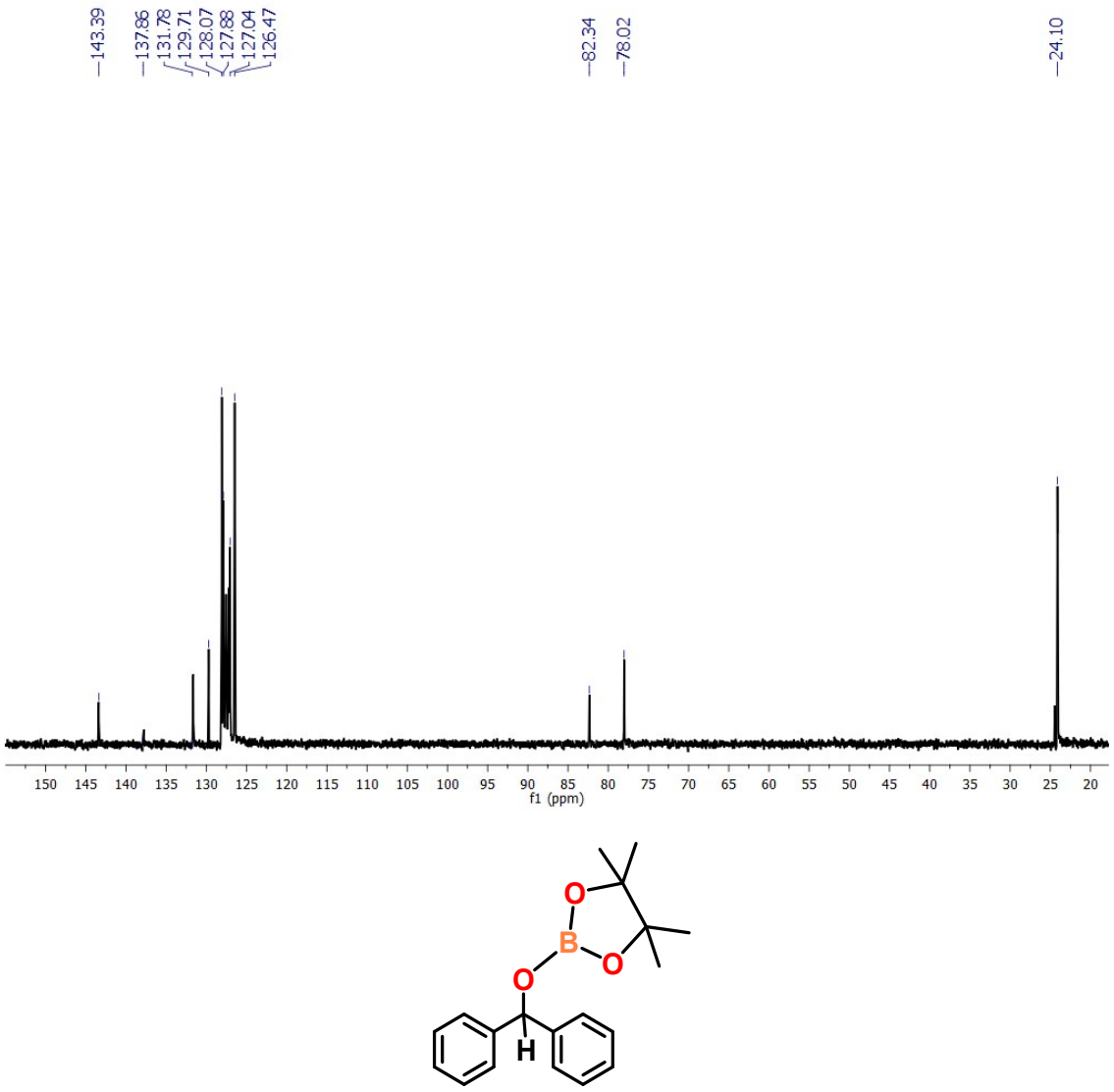


Figure S7: ^{13}C NMR spectrum of 2-(diphenylmethoxy)pinacolborane (1a)

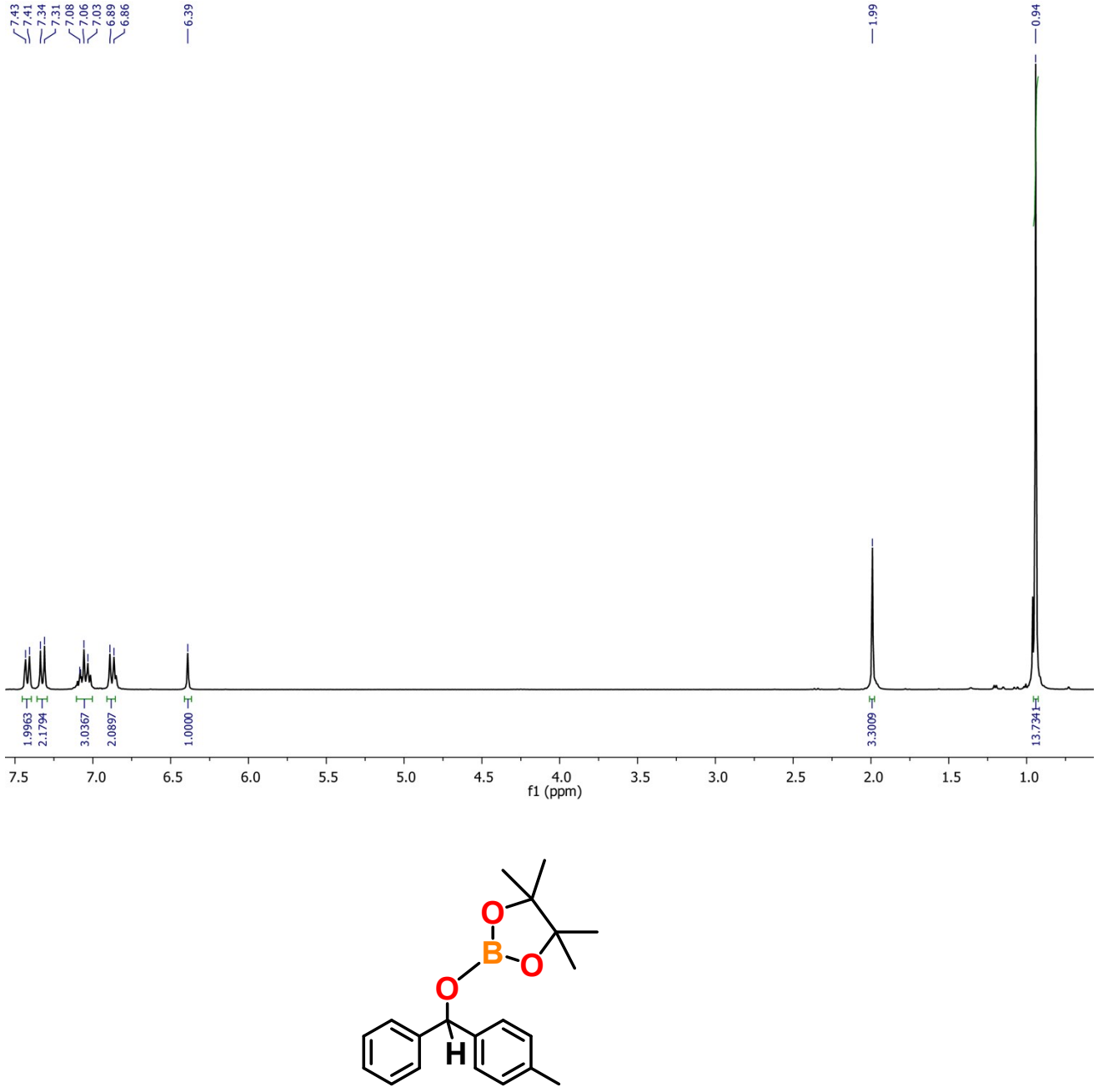


Figure S8: ^{1}H NMR spectrum of 2-(*p*-tolylmethoxy)pinacolborane (1b)

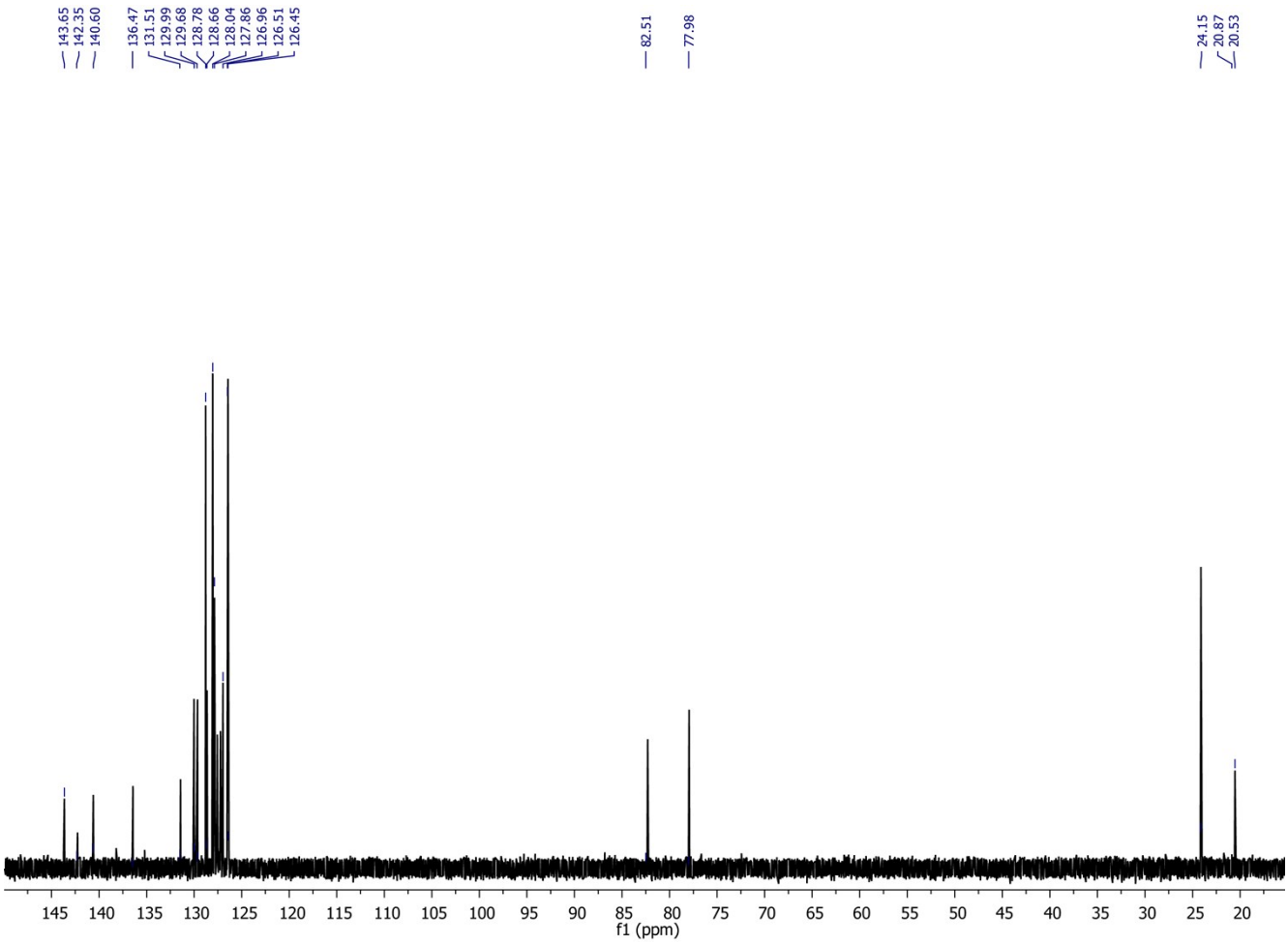


Figure S9: ^{13}C NMR spectrum of 2-(*p*-tolylmethoxy)pinacolborane (1b)

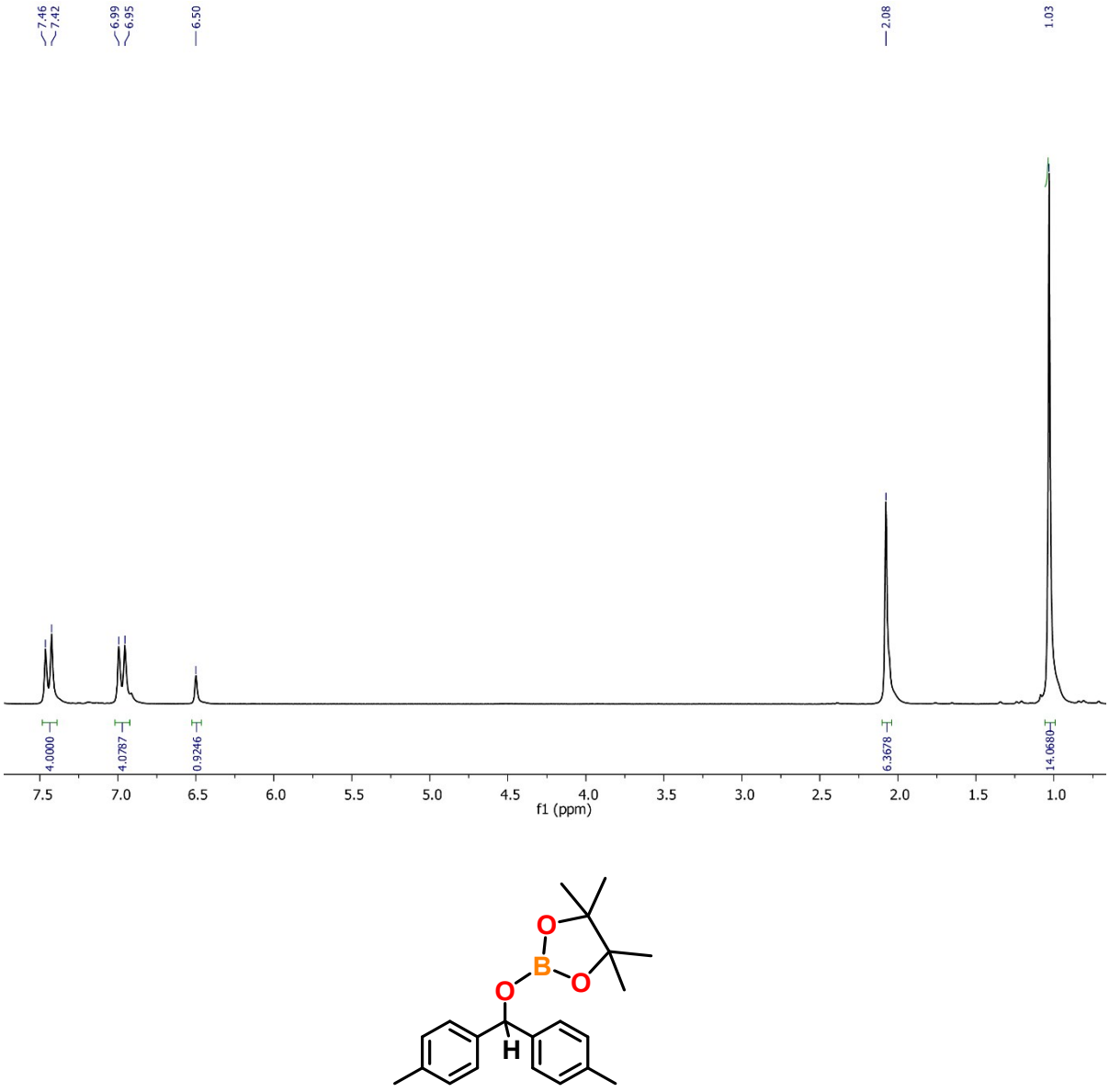


Figure S10: ^{1}H NMR spectrum of 2-(di-*para*-tolylmethoxy)pinacolborane (1c)

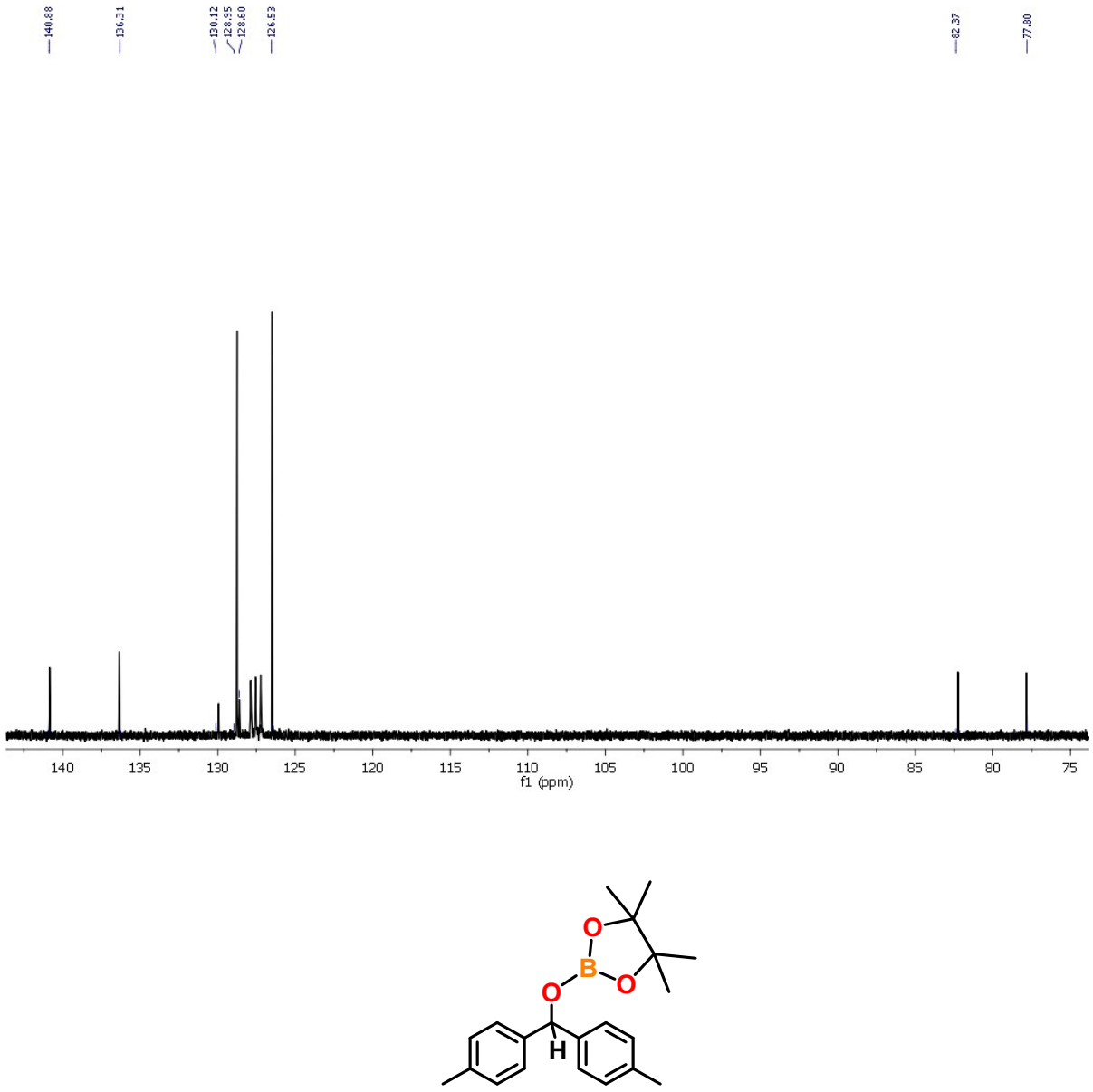


Figure S11: ^{13}C NMR spectrum of 2-(di-*para*-tolylmethoxy)pinacolborane (1c)

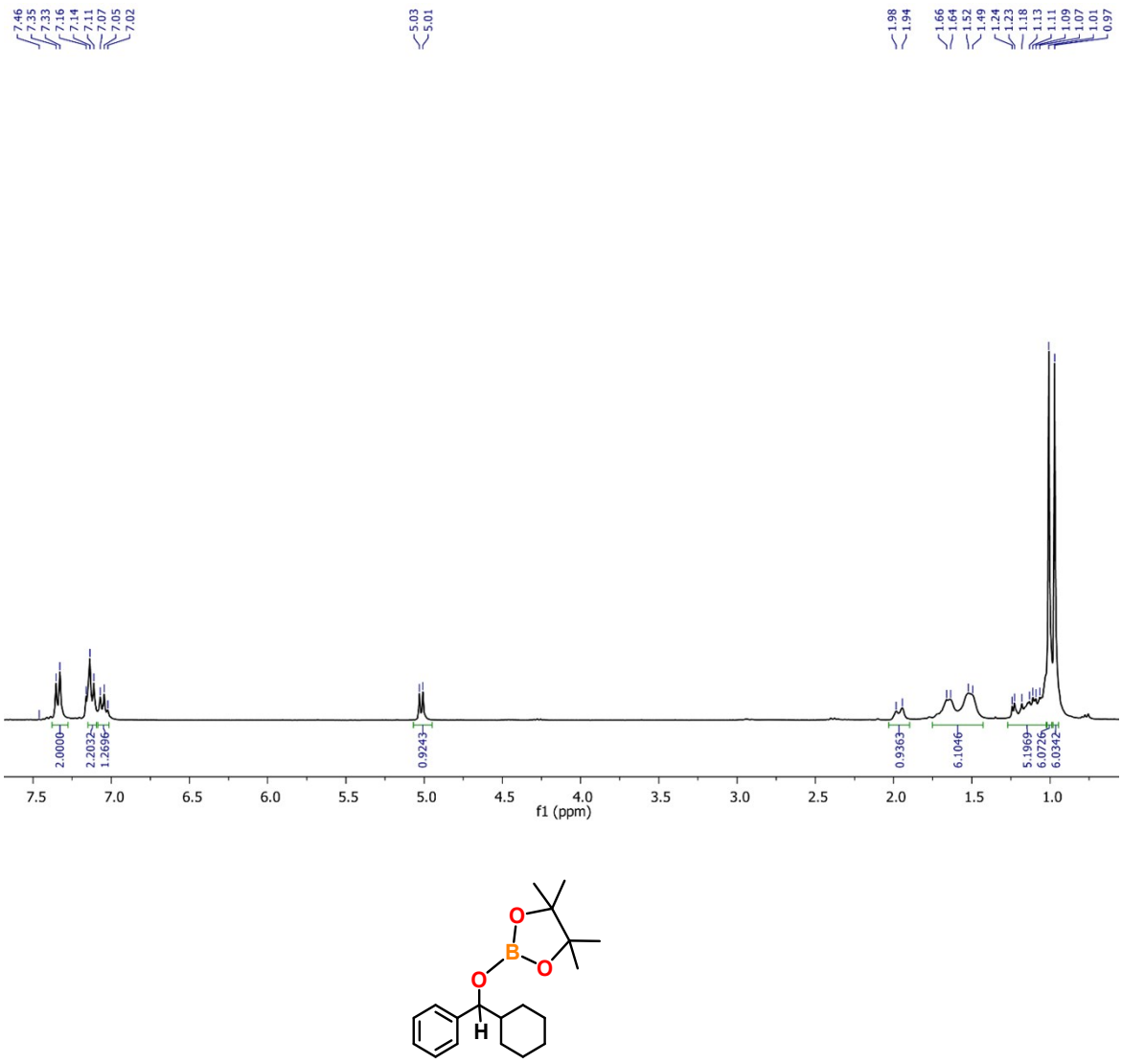


Figure S12: ^{1}H NMR spectrum of 2-(cyclohexylphenylmethoxy)pinacolborane (1e)

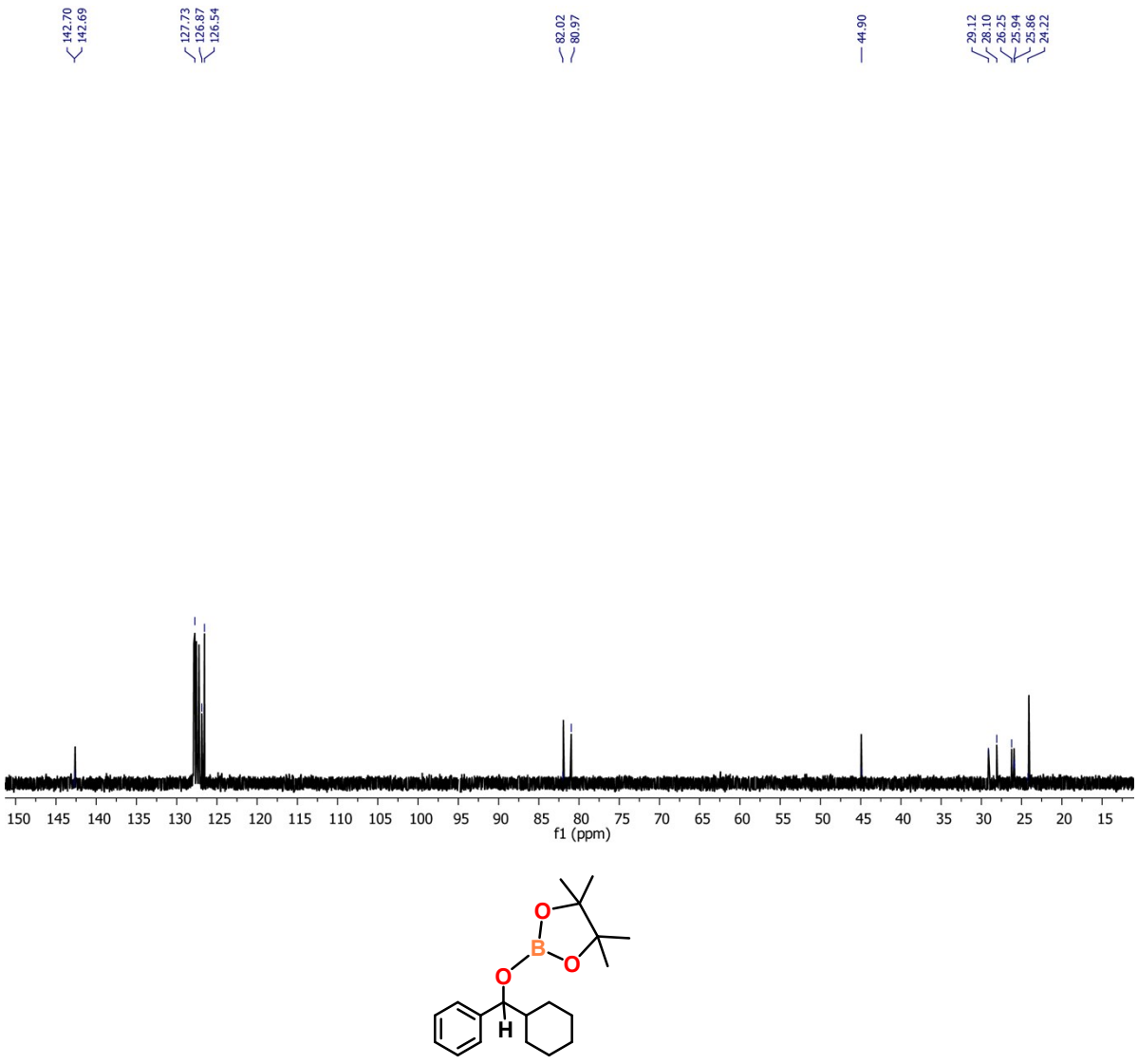


Figure S13: ^{13}C NMR spectrum of 2-(cyclohexylphenylmethoxy)pinacolborane (1e)

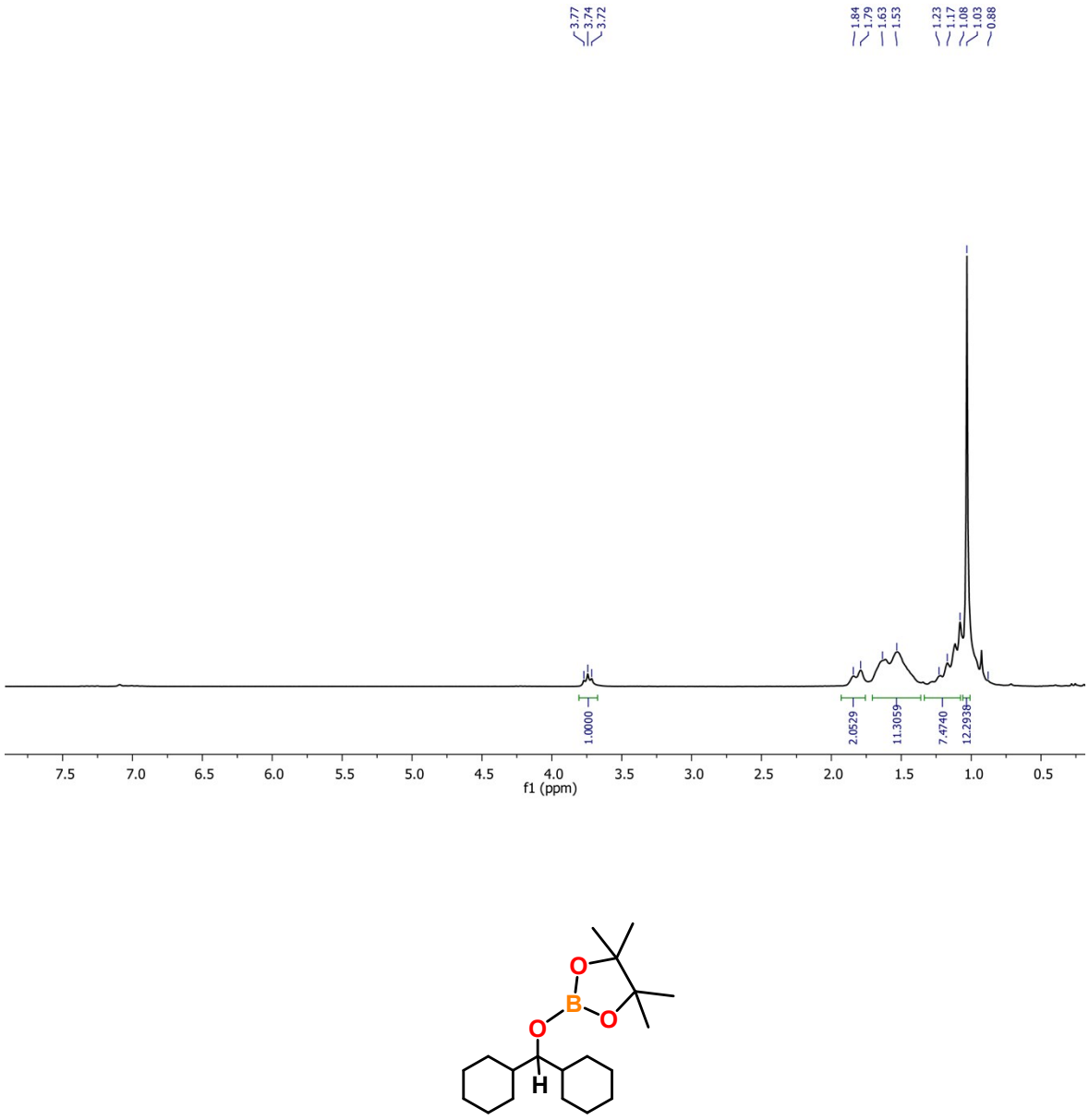


Figure S14: ^{1}H NMR spectrum of 2-(dicyclohexylmethoxy)pinacolborane (1f)

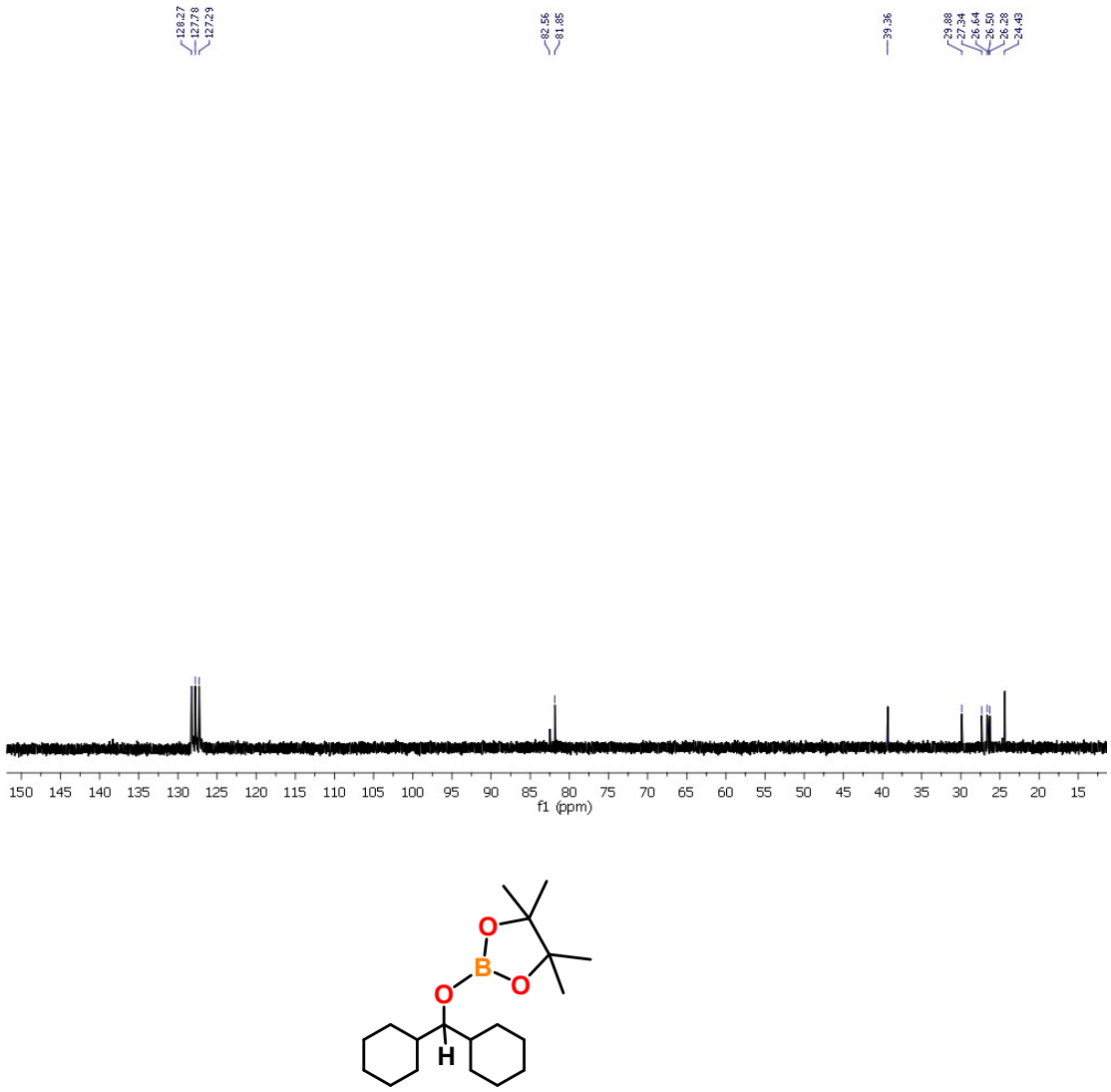


Figure S15: ^{13}C NMR spectrum of 2-(dicyclohexylmethoxy)pinacolborane (1f)

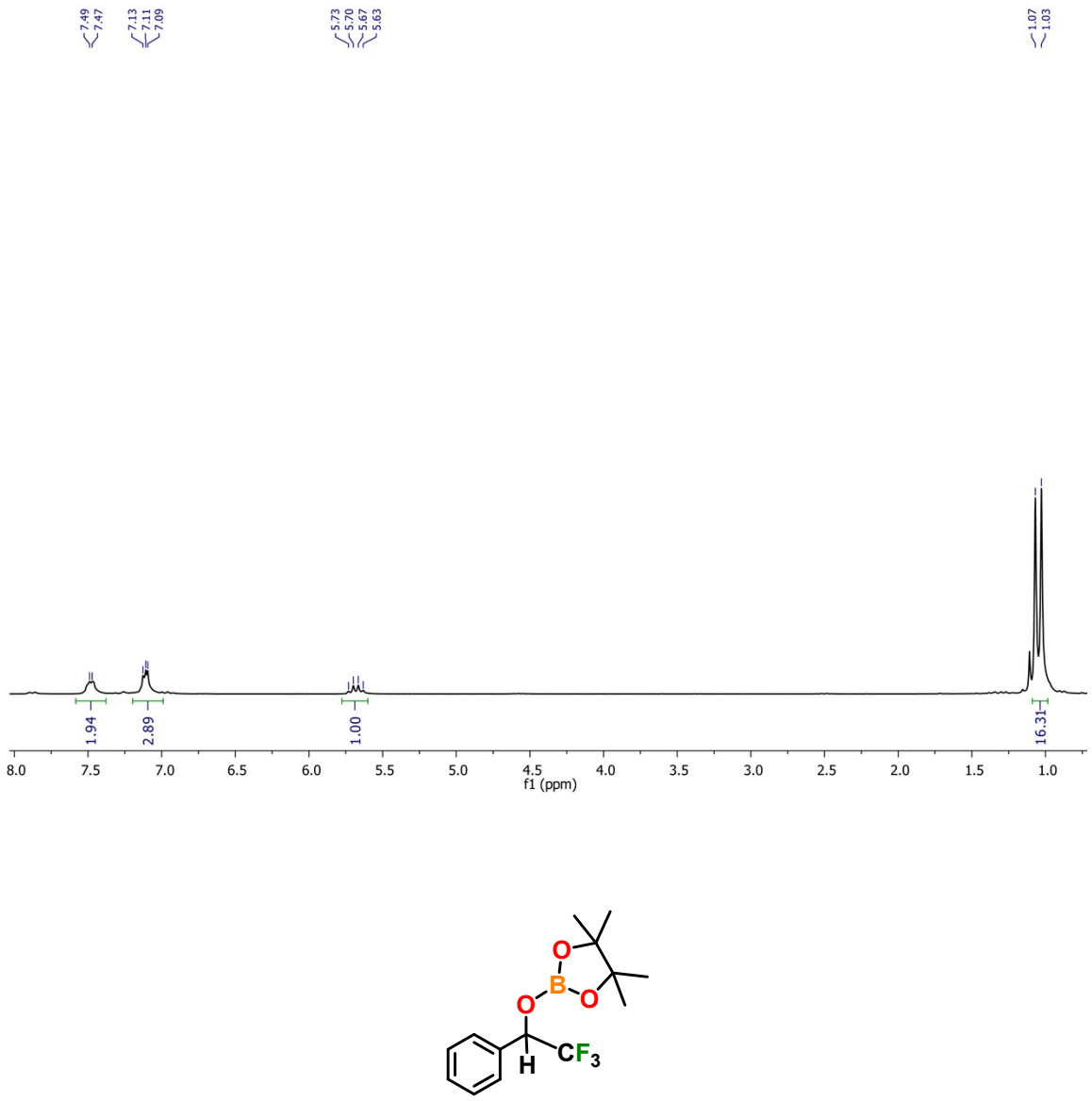


Figure S16: ^{1}H NMR spectrum of 2-(2,2,2-trifluoro-1-phenylethyoxy)pinacolborane (1g)

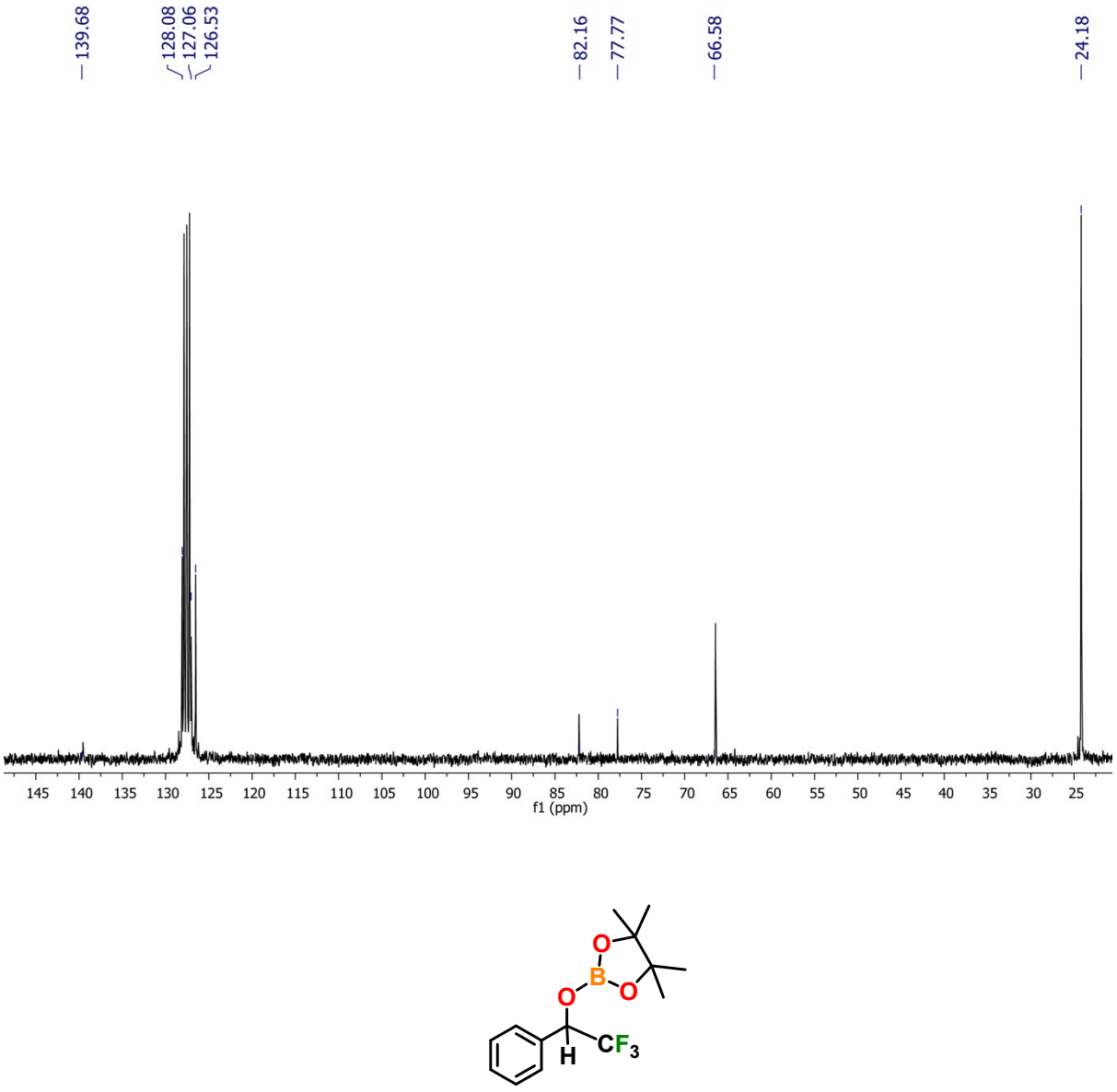


Figure S17: ^{13}C NMR spectrum of 2-(2,2,2-trifluoro-1-phenylethyoxy)pinacolborane (1g)

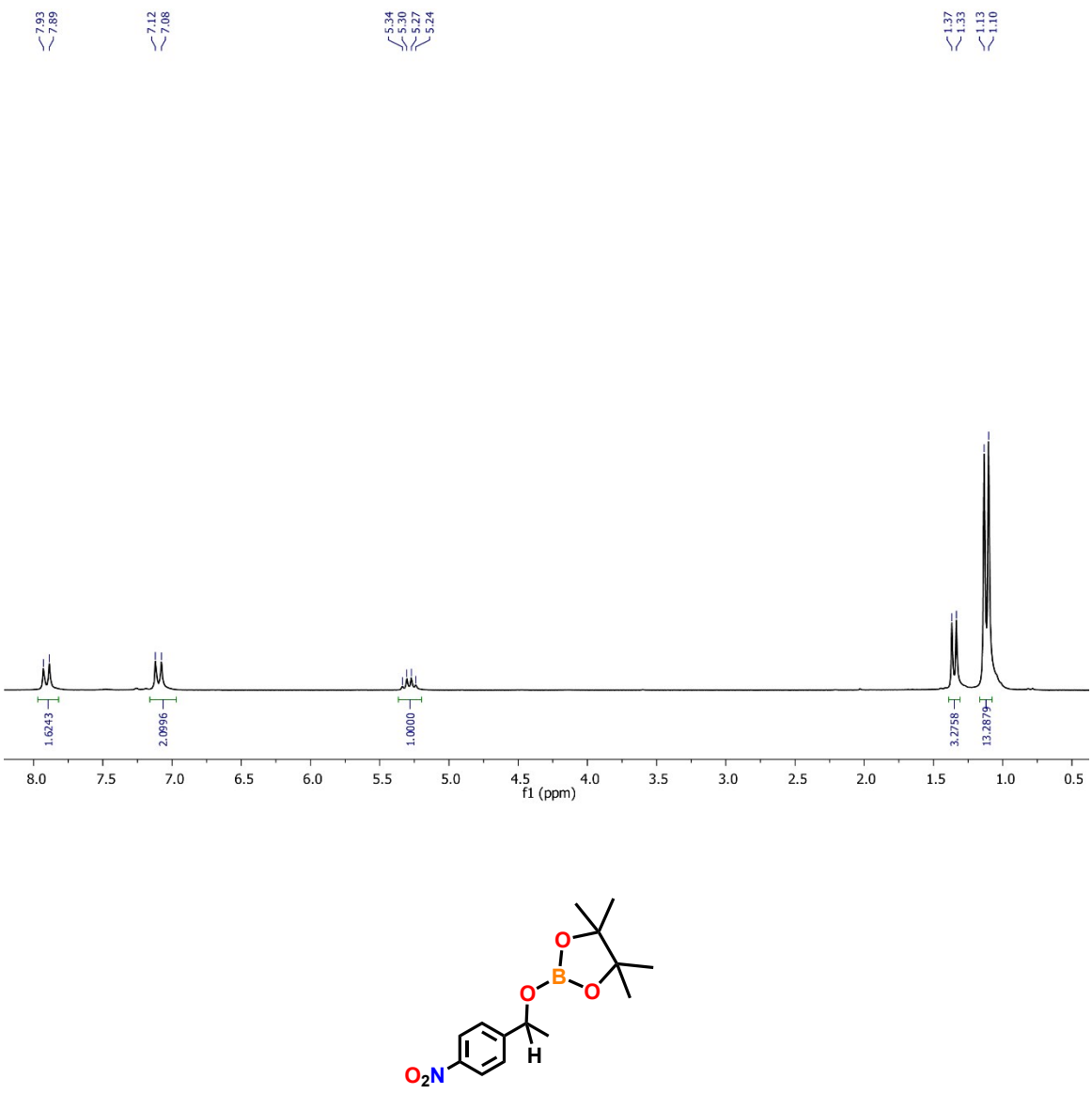


Figure S18: ^{1}H NMR spectrum of 2-(4-nitrophenyl)ethoxy)pinacolborane (1i)

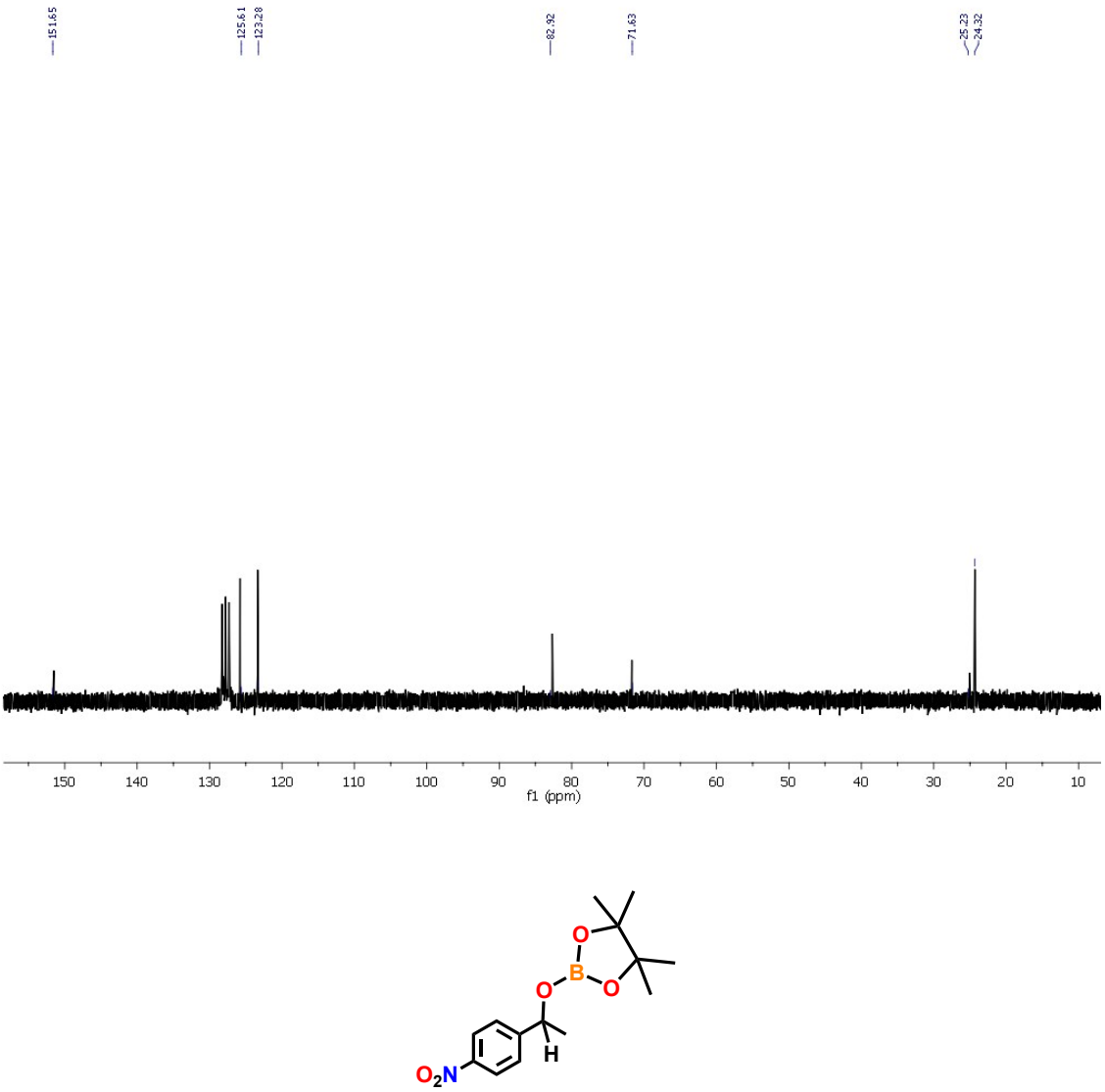
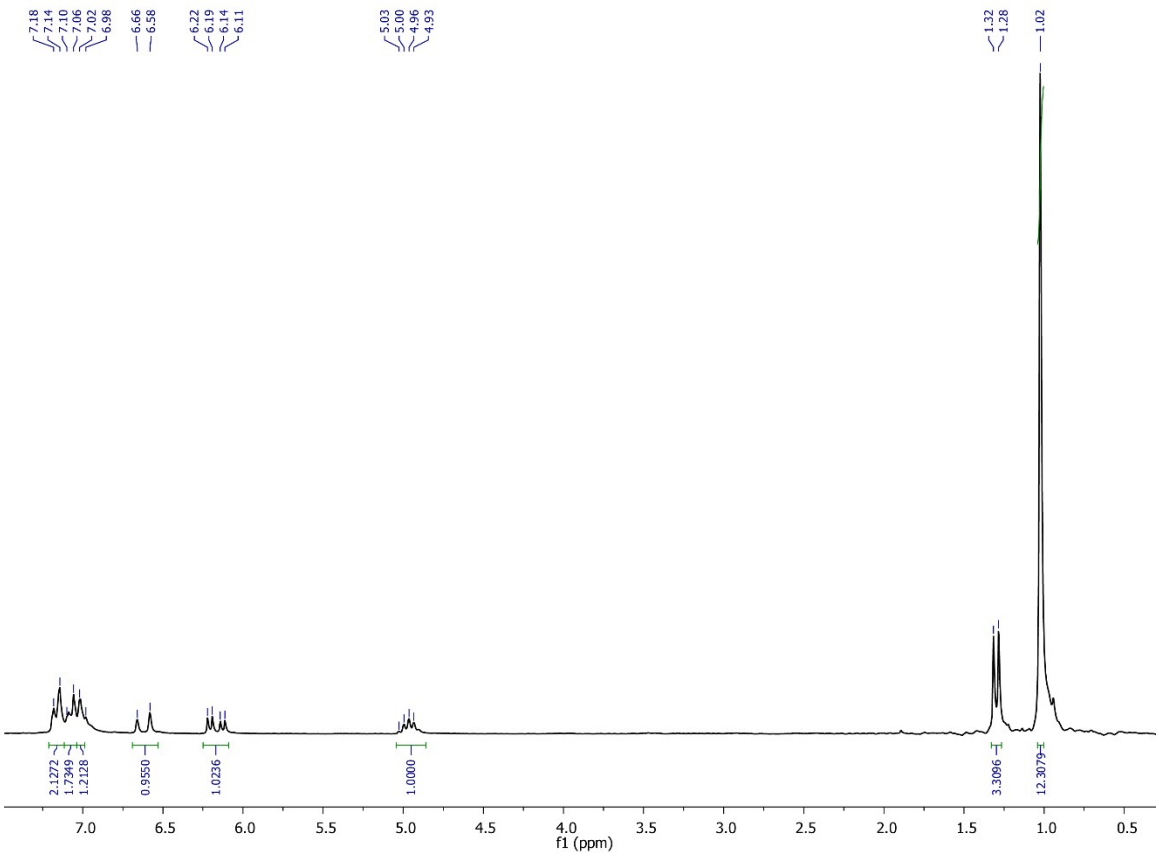


Figure S19: ^{13}C NMR spectrum of 2-(4-nitrophenyl)ethoxy)pinacolborane (1i)



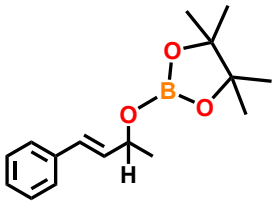


Figure S20: ^{1}H NMR spectrum of 2-(1-cinnamylethoxy)pinacolborane (1j)

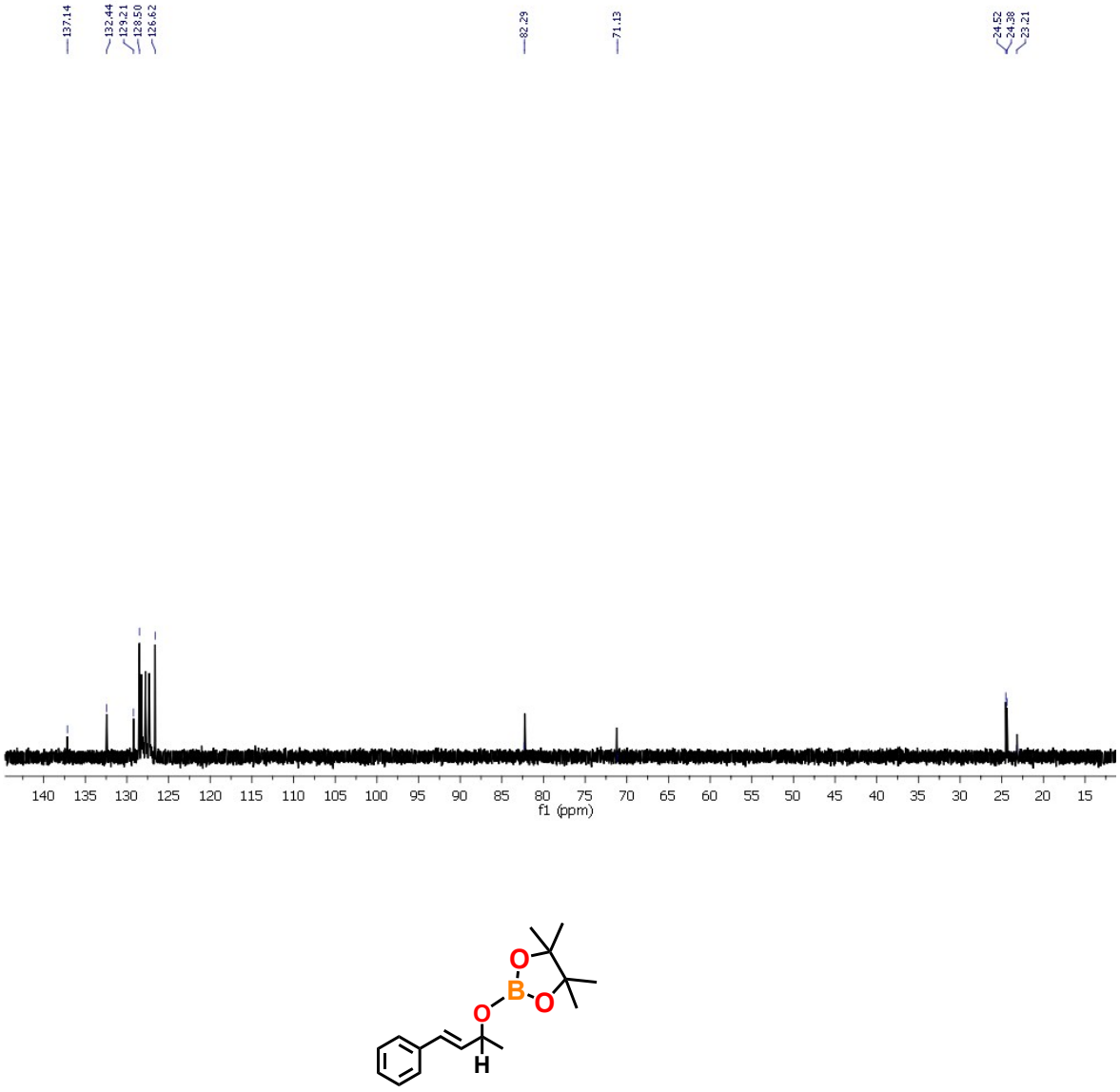


Figure S21: ^{13}C NMR spectrum of 2-(1-cinnamylethoxy)pinacolborane (1j)

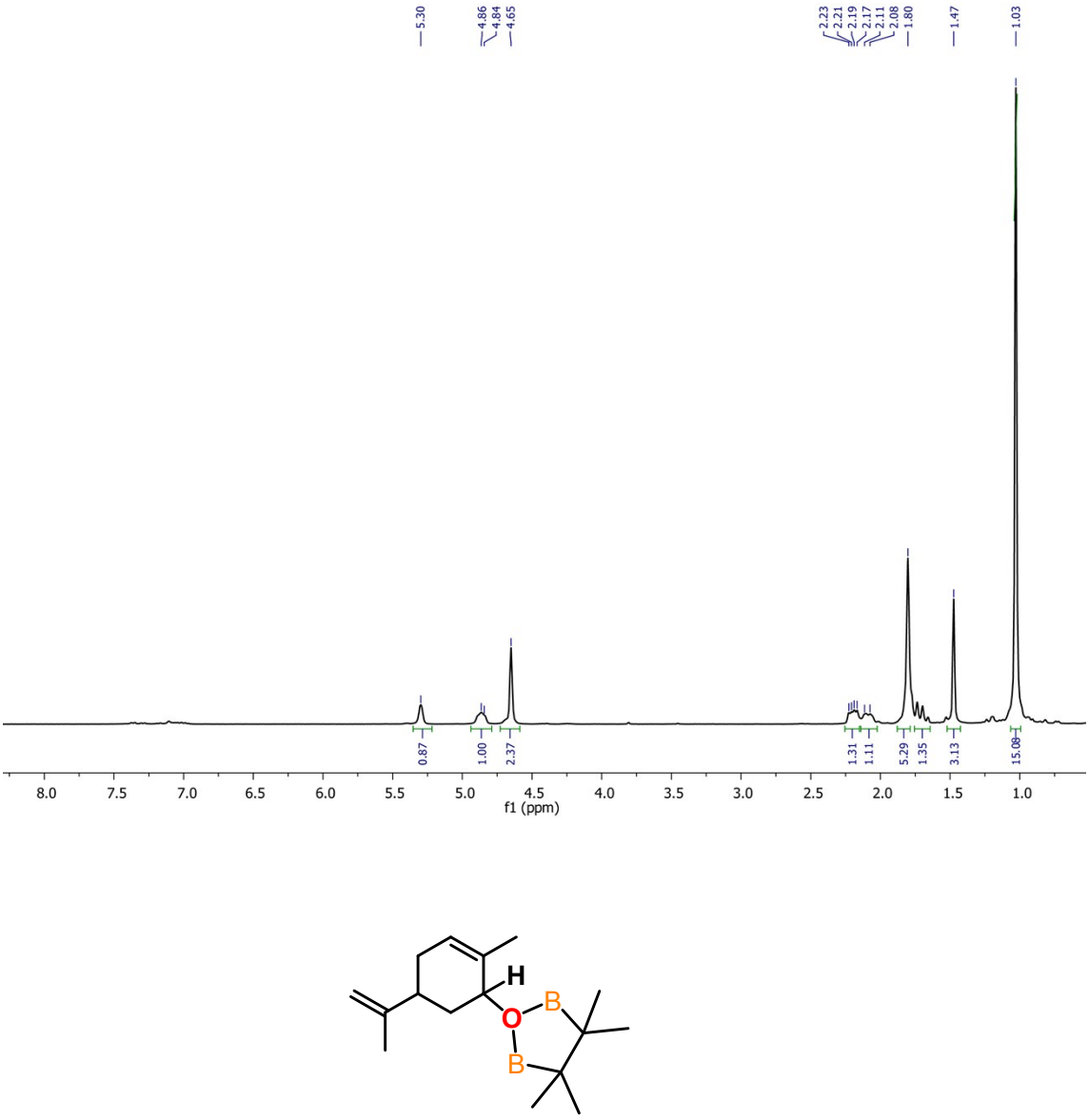


Figure S22: ^{1}H NMR spectrum of 2-(2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-yl)pinacolborane (1k)

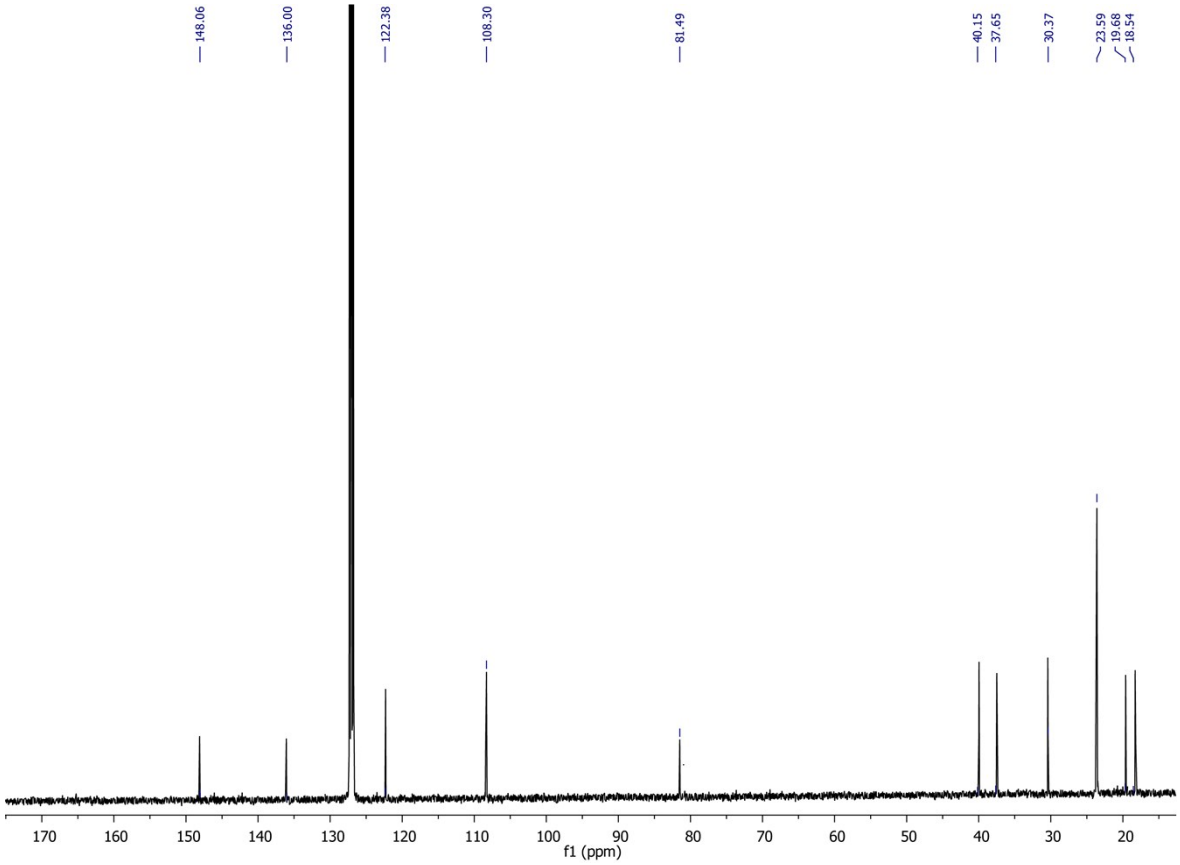
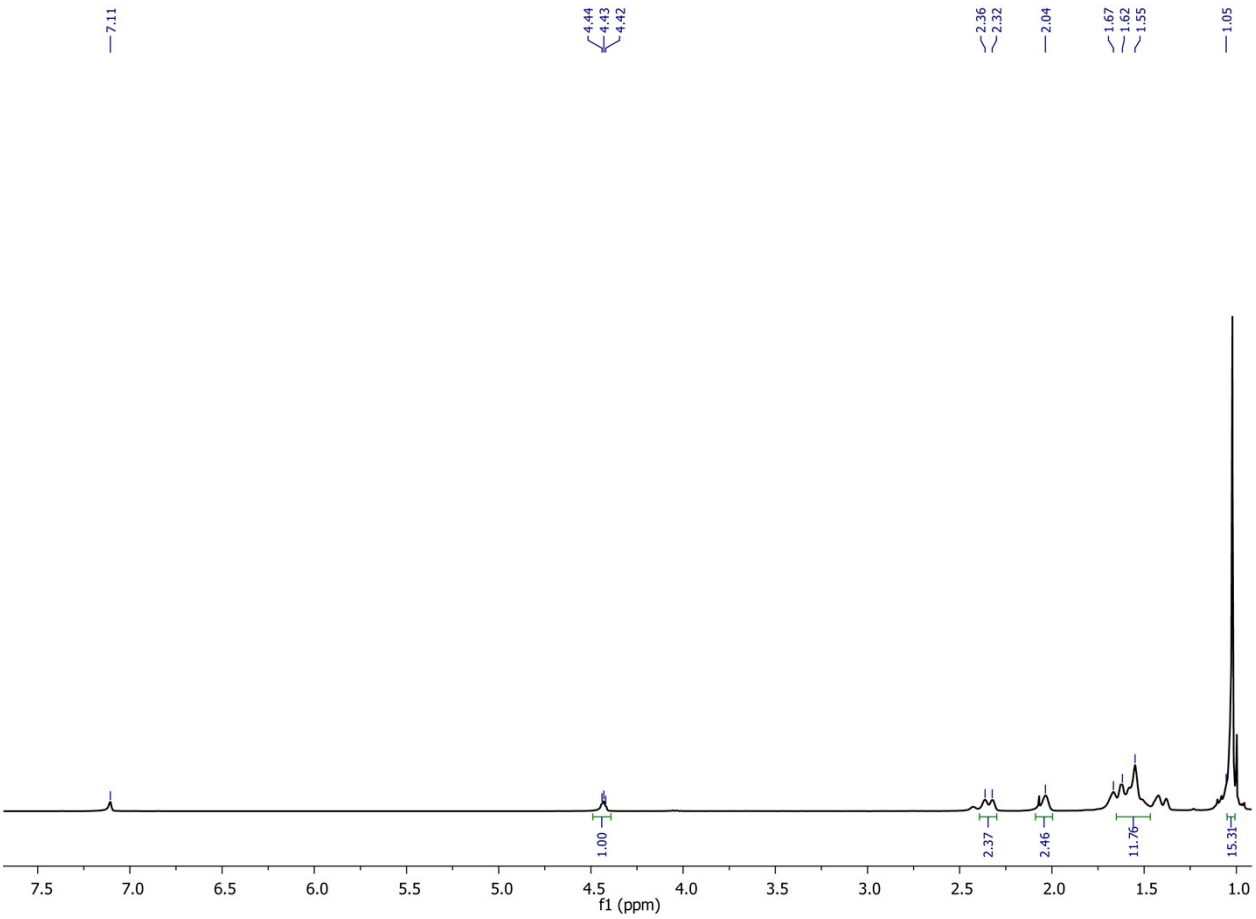


Figure S23: ^{13}C NMR spectrum of 2-(2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-yl)pinacolborane (1k)



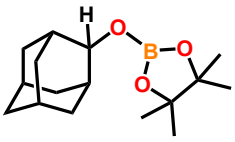


Figure S24: ^{1}H NMR spectrum of 2-(1-adamentylethoxy)pinacolborane (1l)

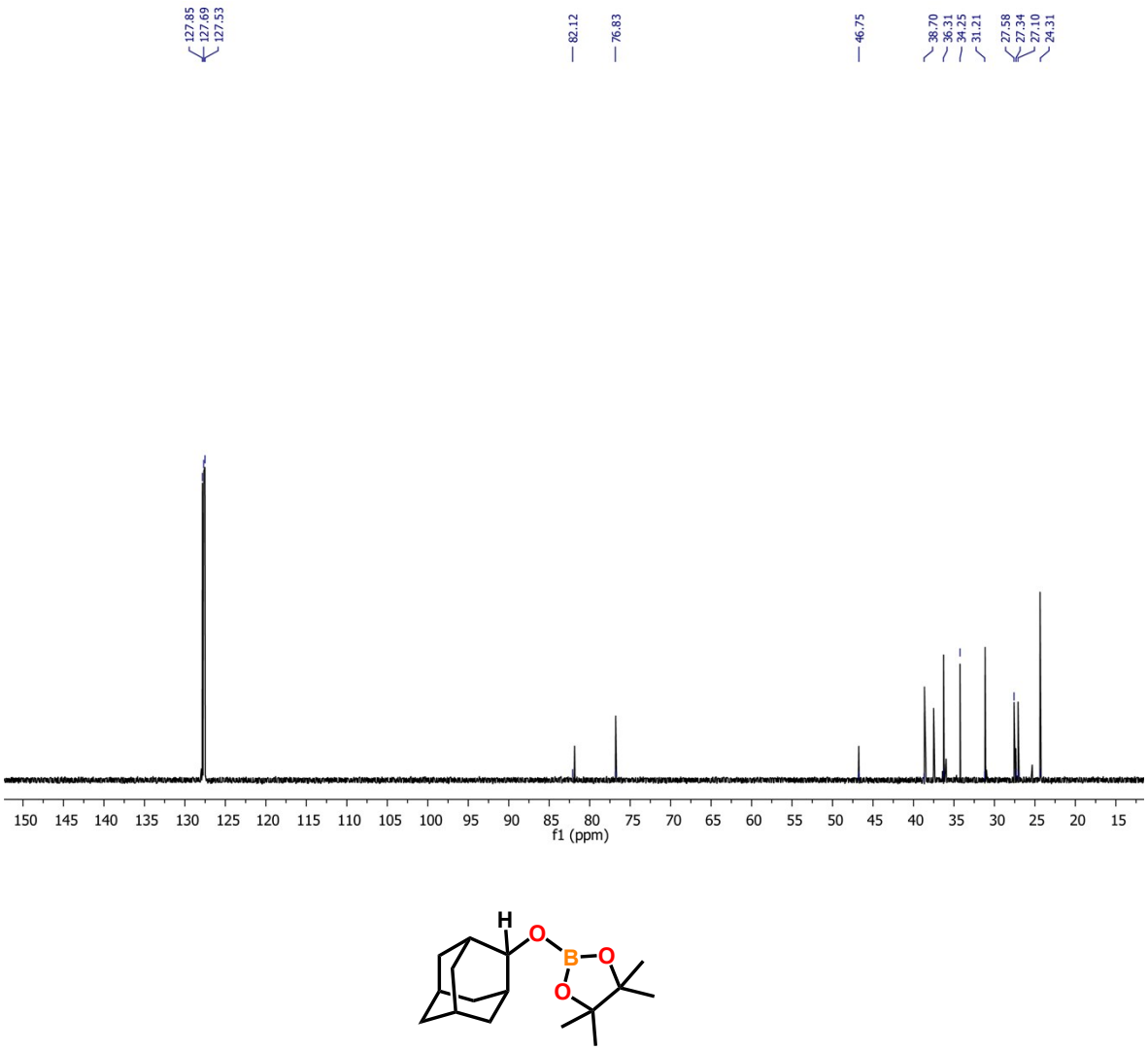
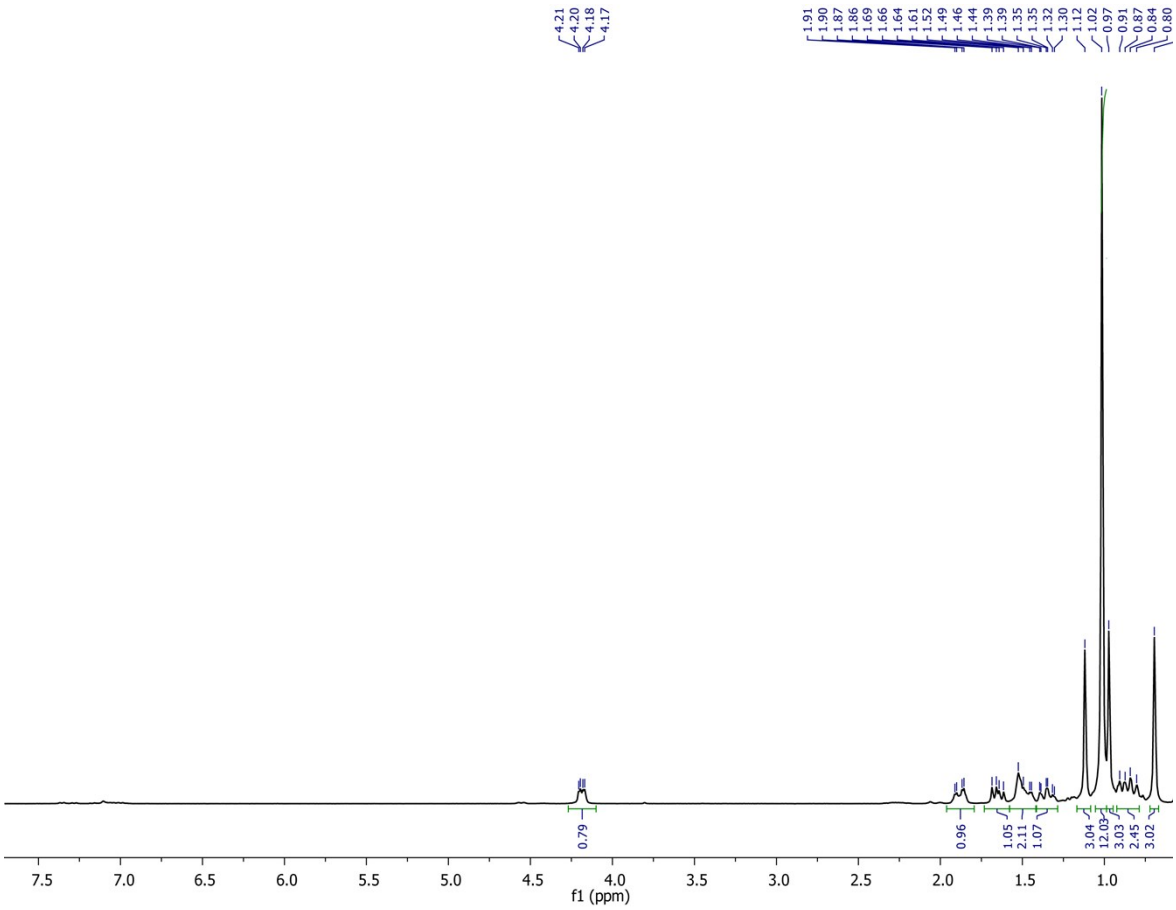


Figure S25: ^{13}C NMR spectrum of 2-(1-adamentylethoxy)pinacolborane (1l)



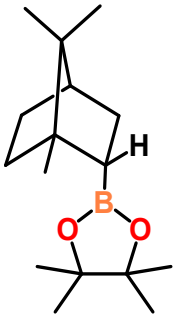
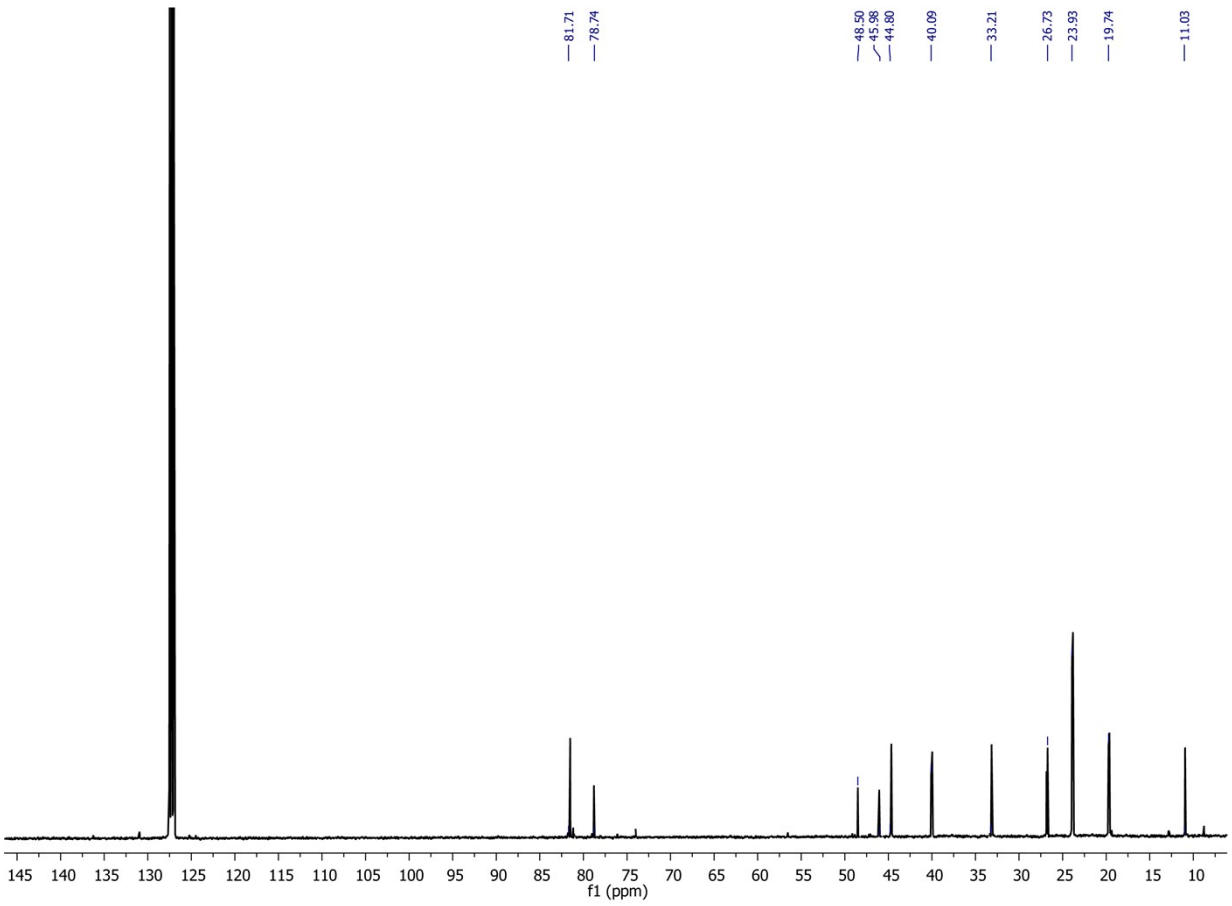


Figure S26: ^{1}H NMR spectrum of 2-{1-(1,7,7-trimethyl bicyclo[2.2.1]heptyl)ethoxy}pinacolborane (1n)



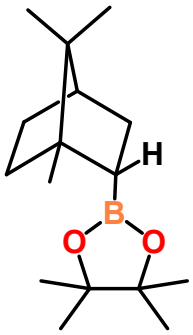


Figure S27: ^{13}C NMR spectrum of 2-{1-(1,7,7-trimethyl bicyclo[2.2.1]heptyl)ethoxy}pinacolborane (1n)

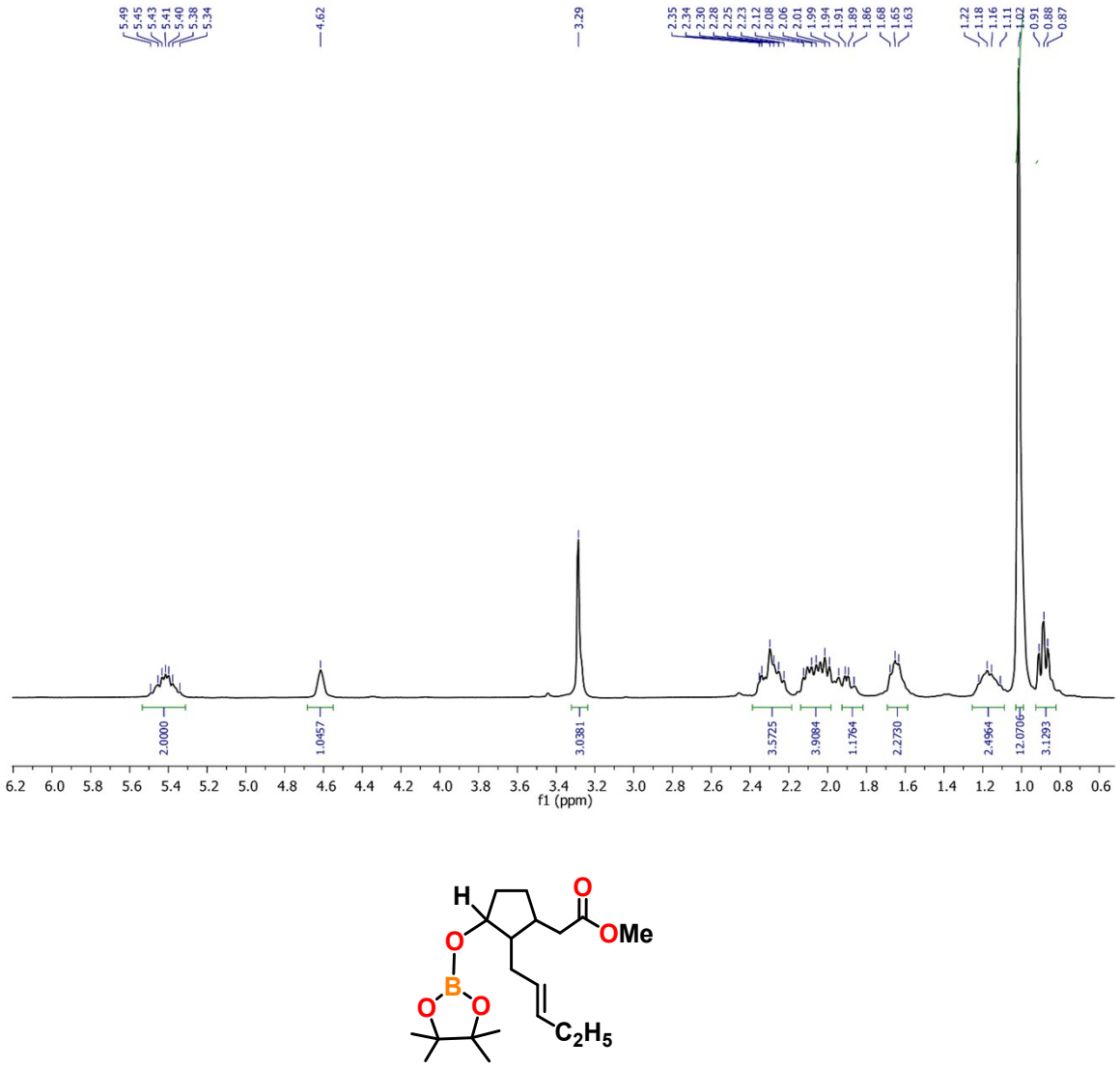


Figure S28: ^{1}H NMR spectrum of methyl (E)-2-(2-(pent-2-en-1-yl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)cyclopentyl)acetate (1o)

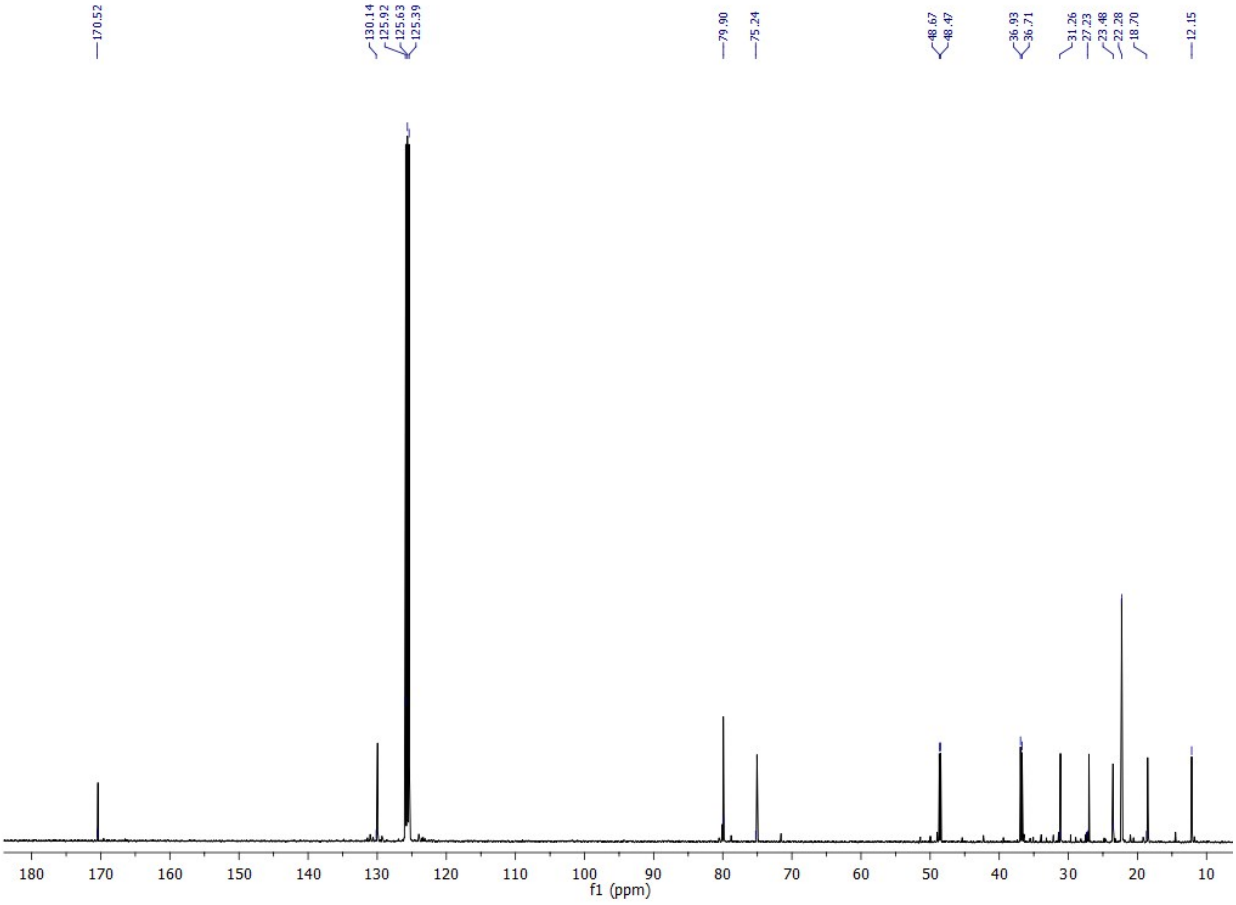


Figure S29: ^{13}C NMR spectrum of methyl (E)-2-(2-(pent-2-en-1-yl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)cyclopentyl)acetate (1o)

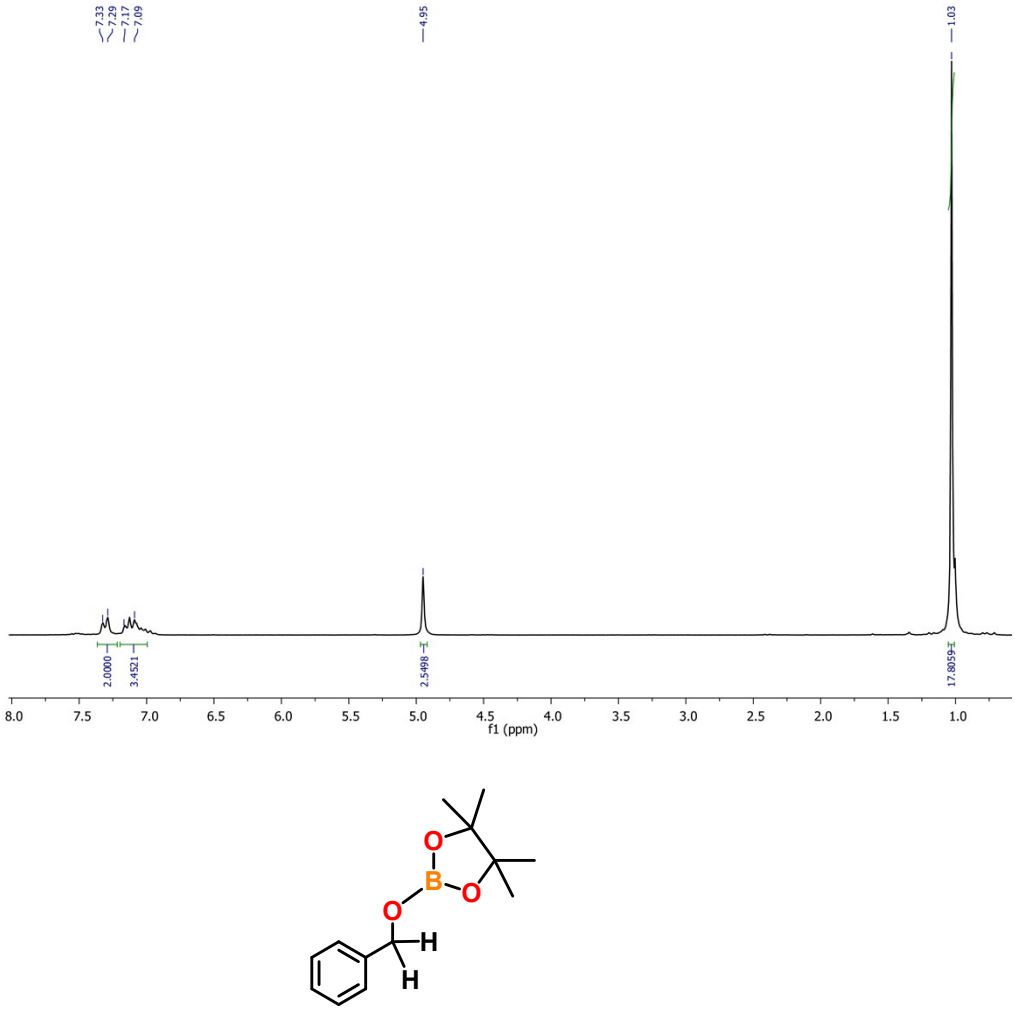


Figure S30: ^{1}H NMR spectrum of 2-(benzyloxy)pinacolborane (2a)

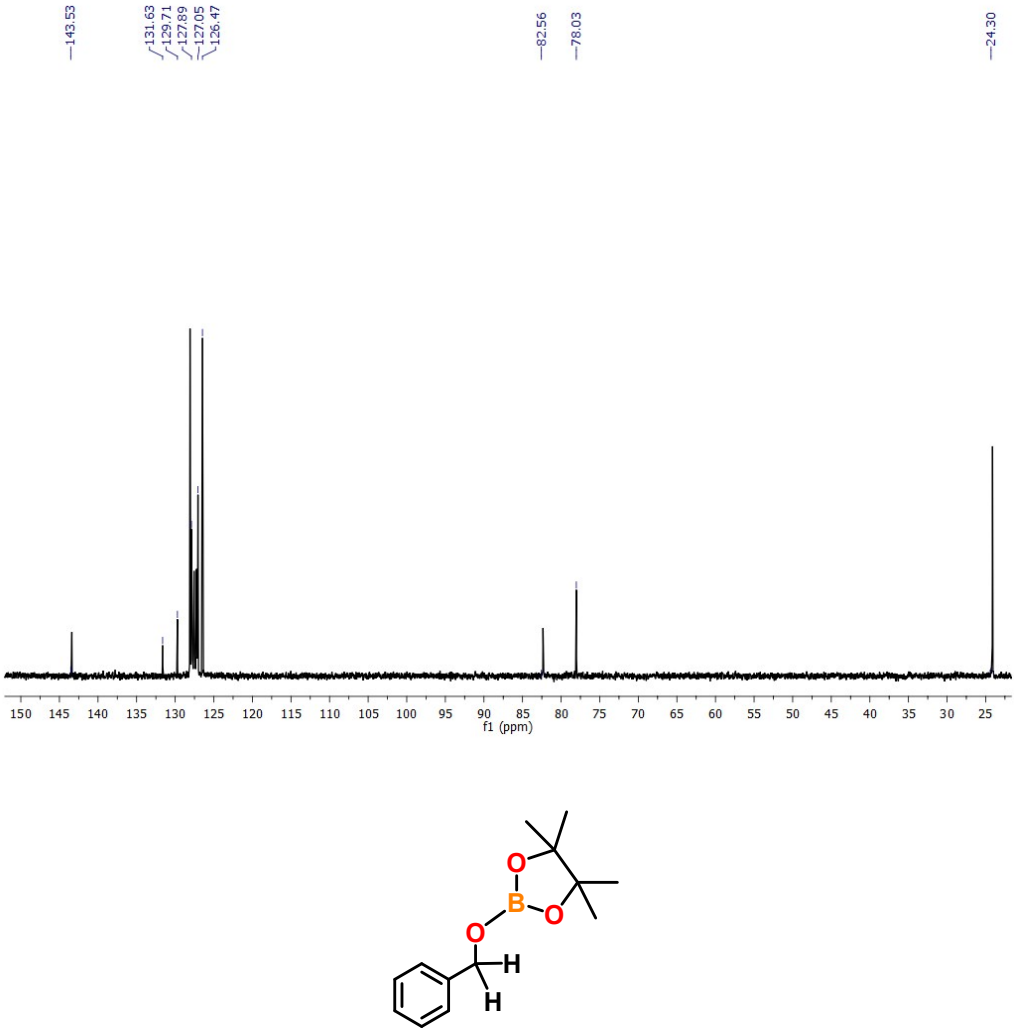


Figure S31: ^{13}C NMR spectrum of 2-(benzyloxy)pinacolborane (2a)

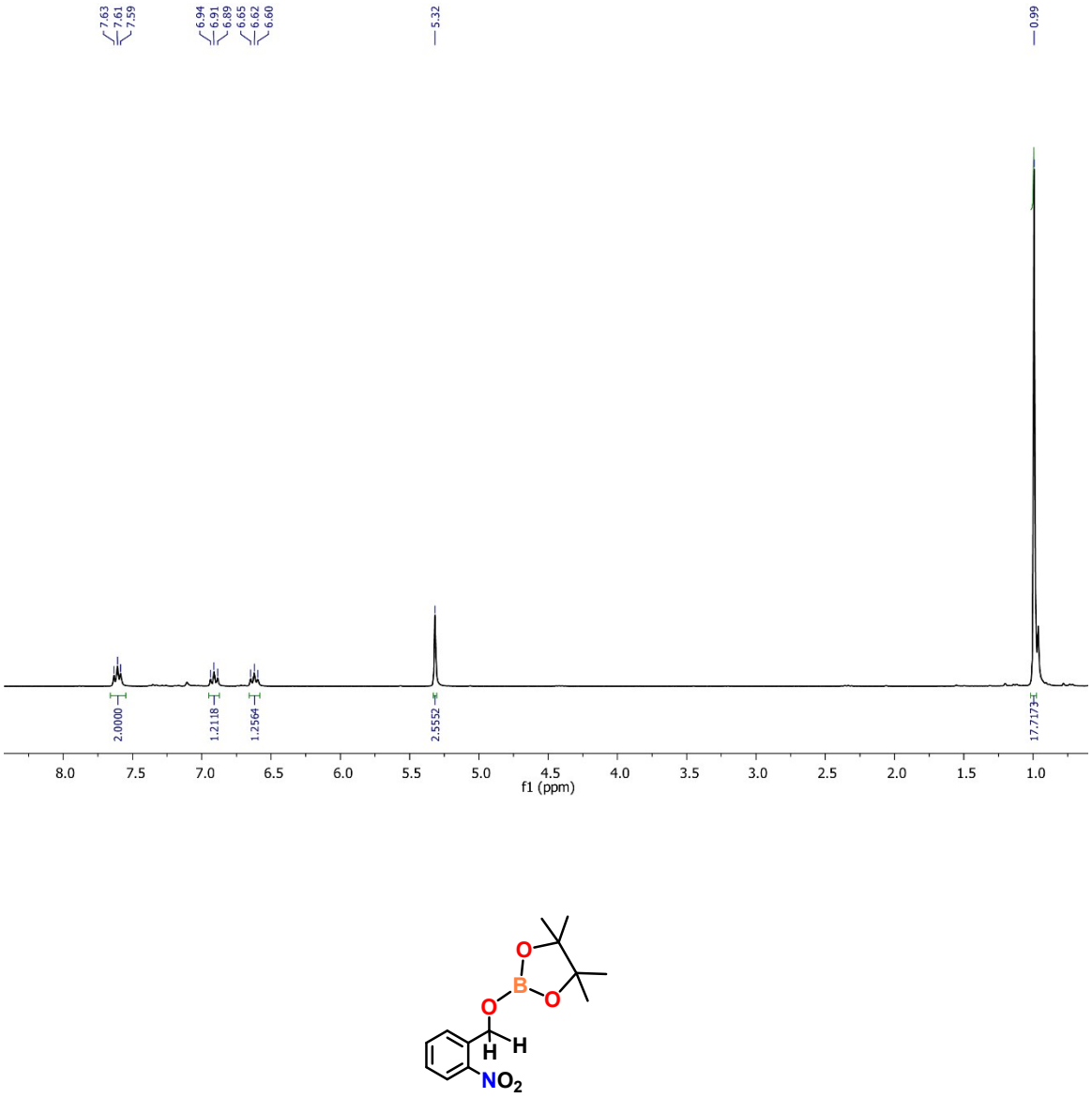


Figure S32: ^{1}H NMR spectrum of 2-(2-nitrobenzyloxy)pinacolborane (2b)

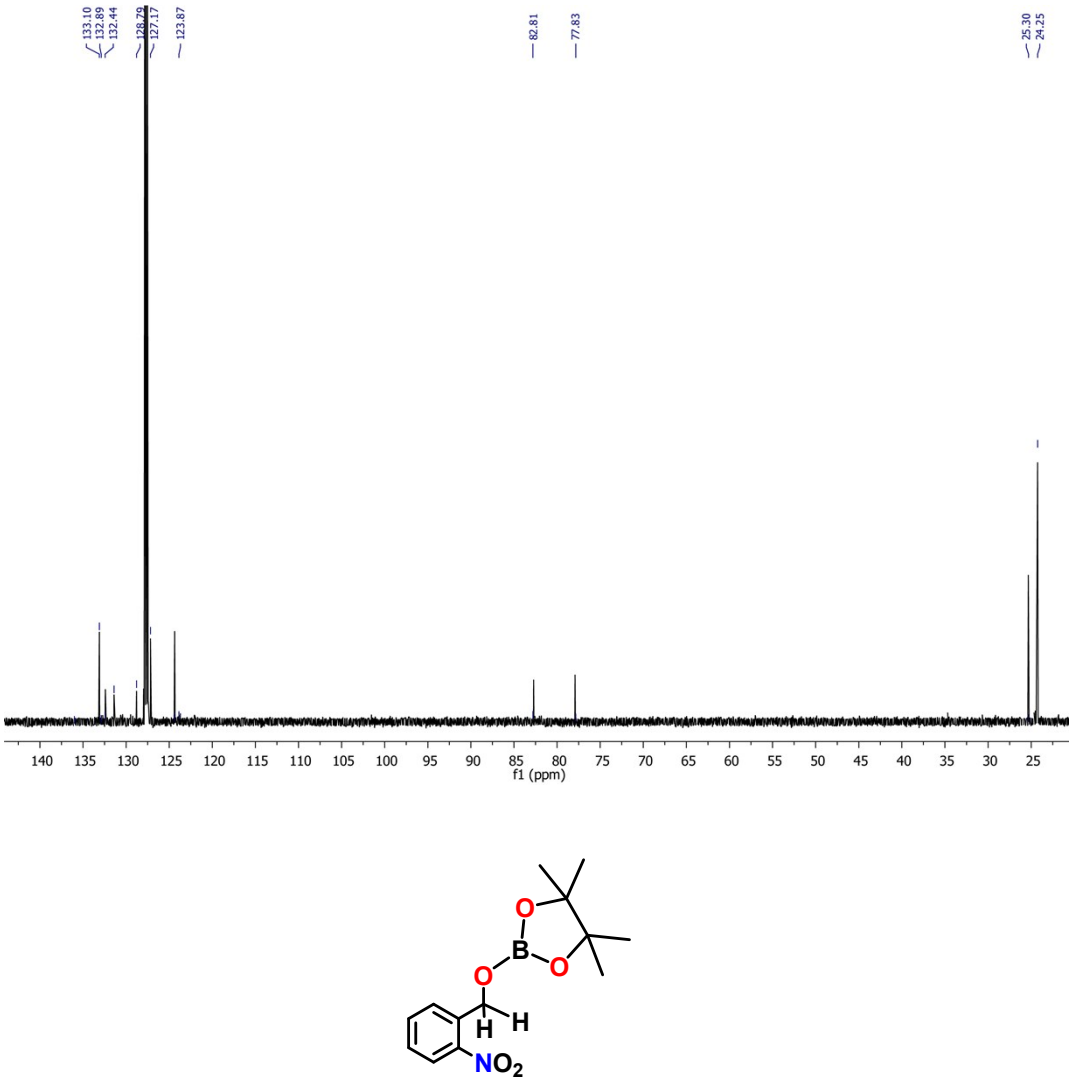


Figure S33: ^{13}C NMR spectrum of 2-(2-nitrobenzyloxy)pinacolborane (2b)

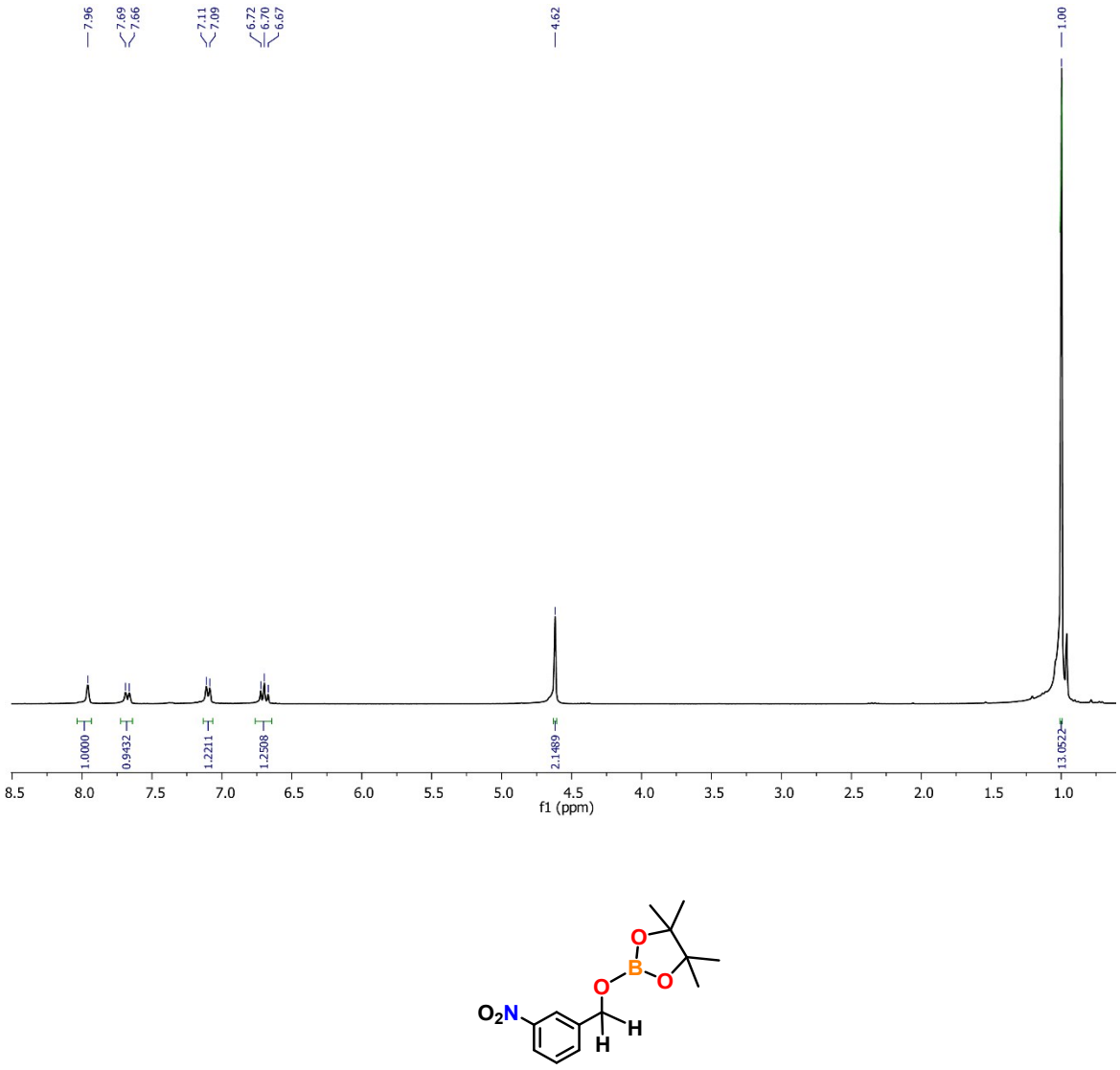


Figure S34: ^{1}H NMR spectrum of 2-(3-nitrobenzyloxy)pinacolborane (2c)

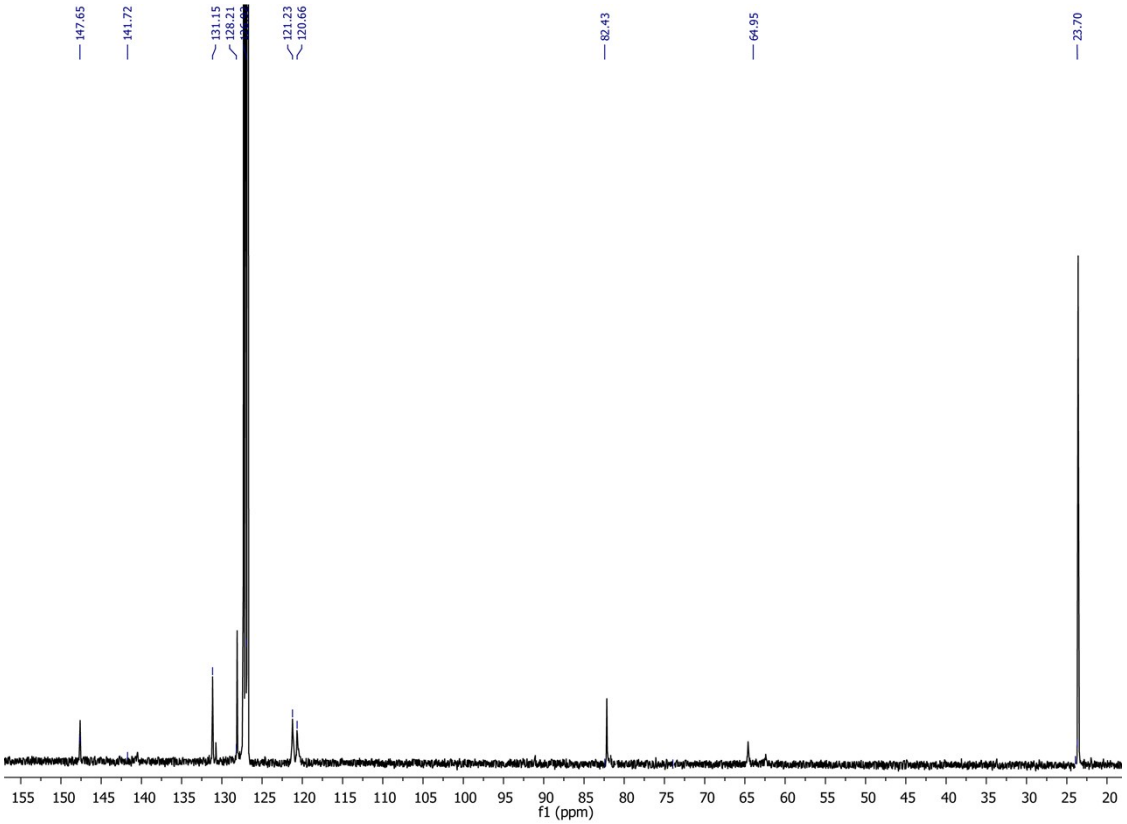
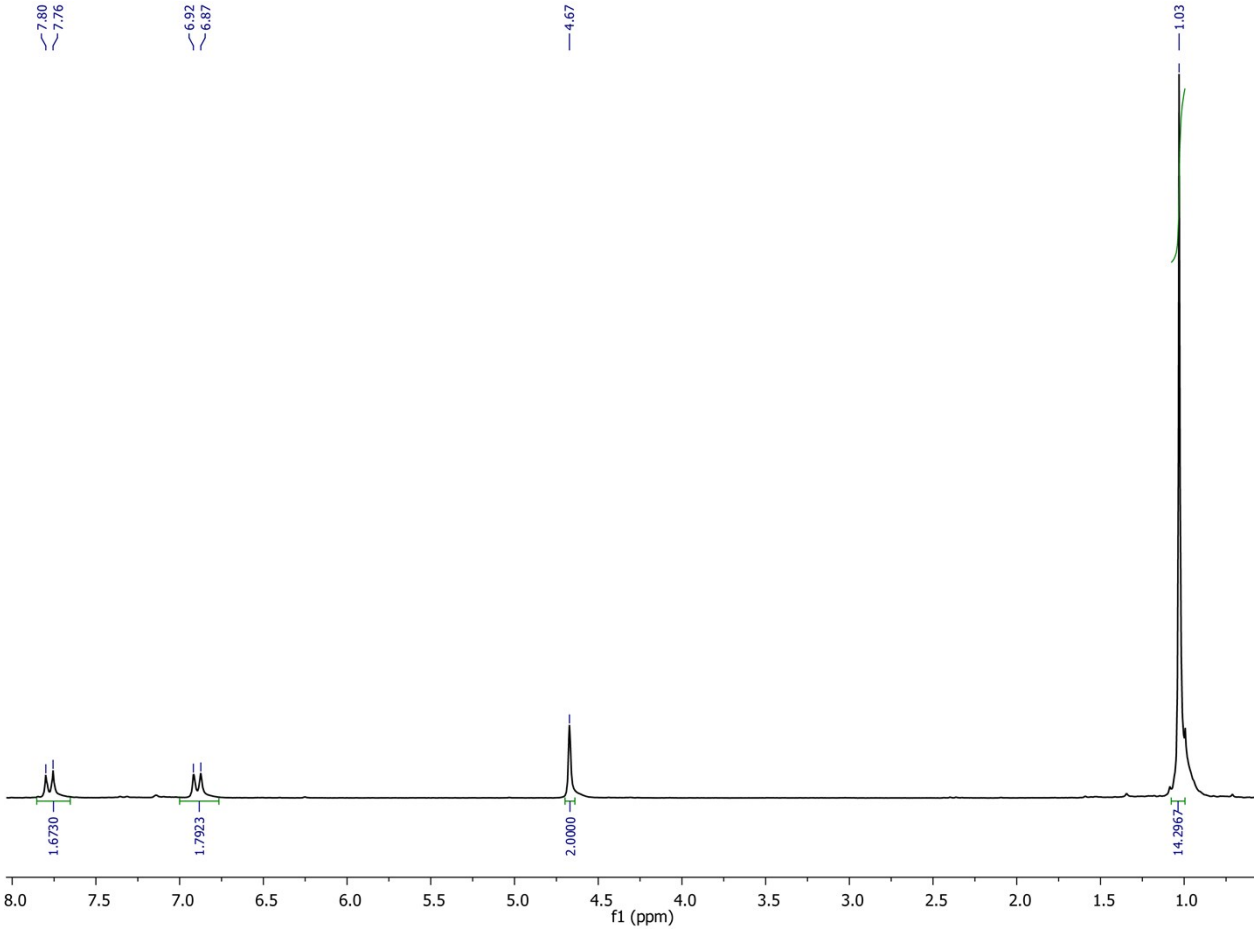


Figure S35: ^{13}C NMR spectrum of 2-(3-nitrobenzyloxy)pinacolborane (2c)



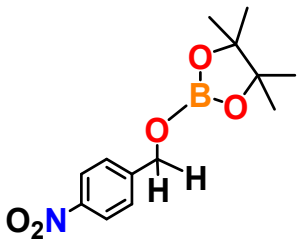


Figure S36: ^{1}H NMR spectrum of 2-(4-nitrobenzyloxy)pinacolborane (2d)

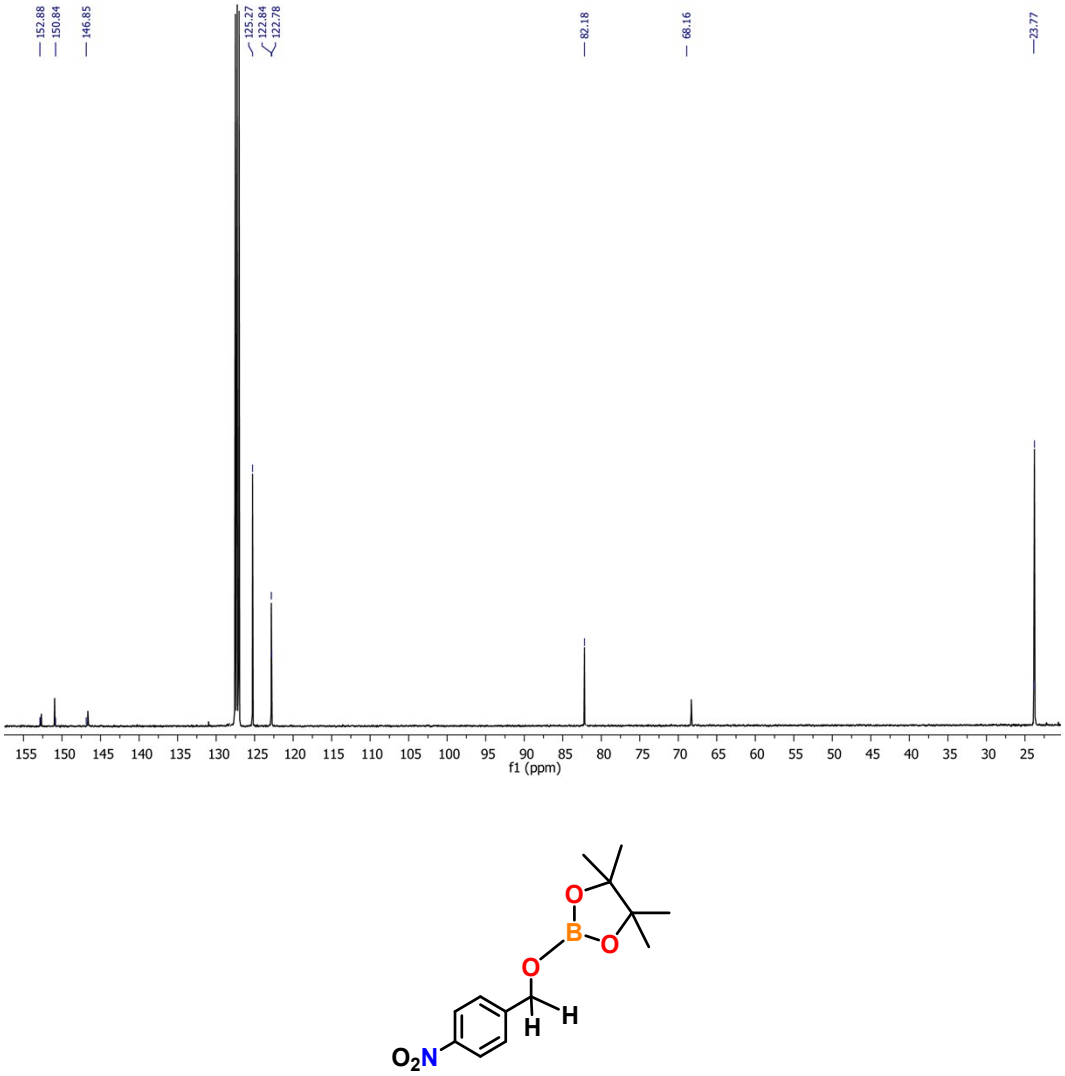


Figure S37: ^{13}C NMR spectrum of 2-(4-nitrobenzyloxy)pinacolborane (2d)

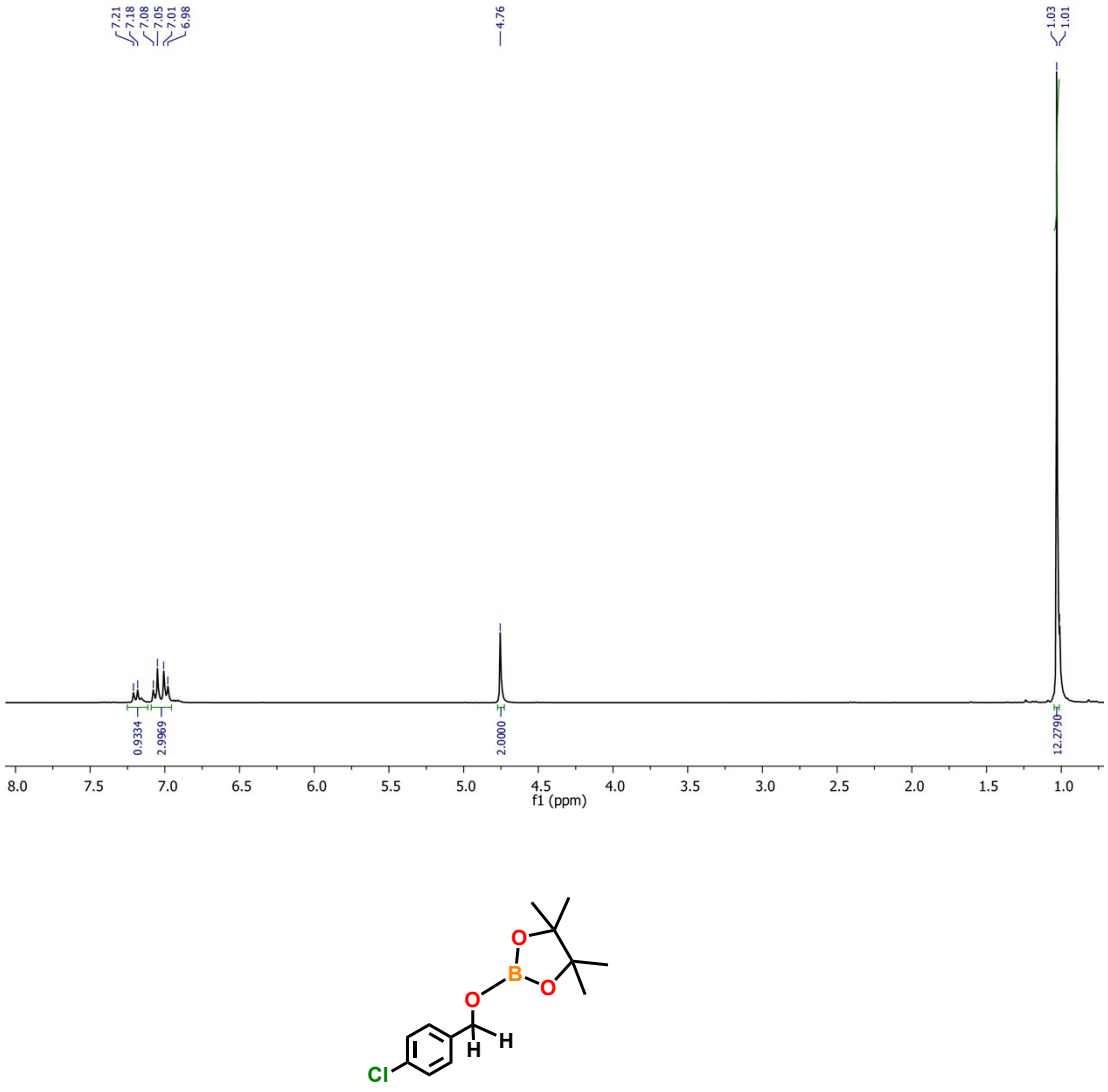


Figure S38: ^{1}H NMR spectrum of 2-(4-chlorobenzyloxy)pinacolborane (2e)

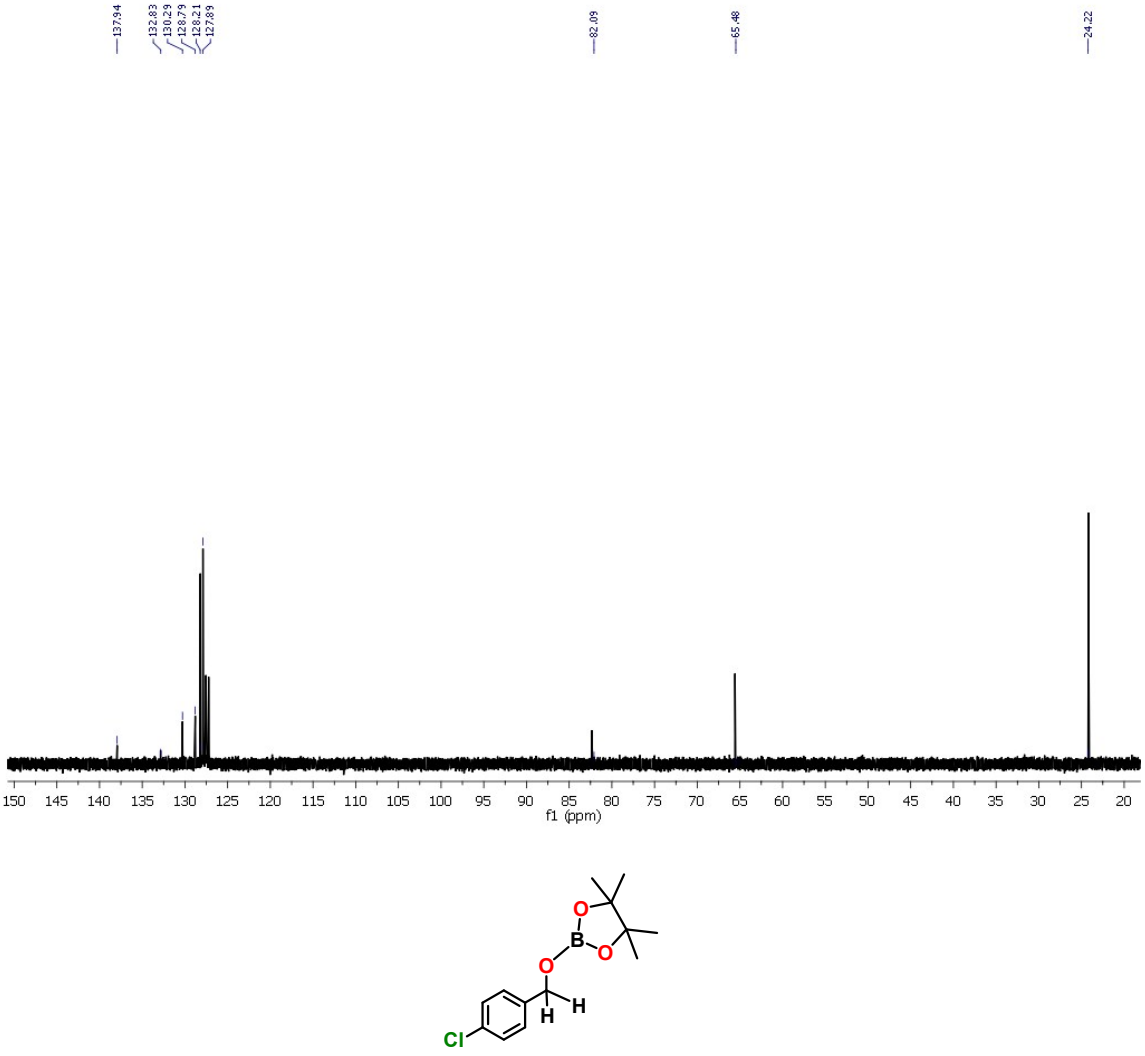
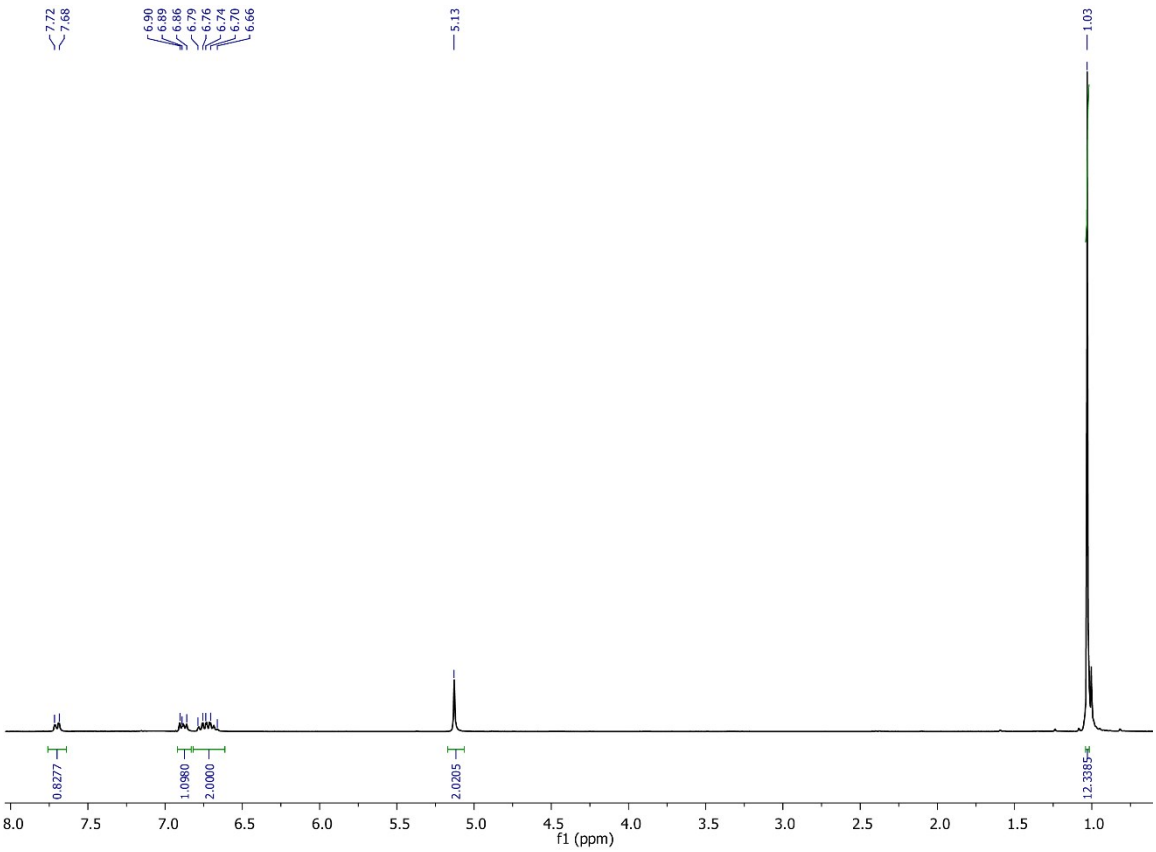


Figure S39: ^{1}H NMR spectrum of 2-(4-chlorobenzyloxy)pinacolborane (2e)



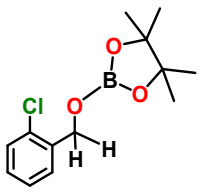


Figure S40: ^{1}H NMR spectrum of 2-(2-chlorobenzyloxy)pinacolborane (2f)

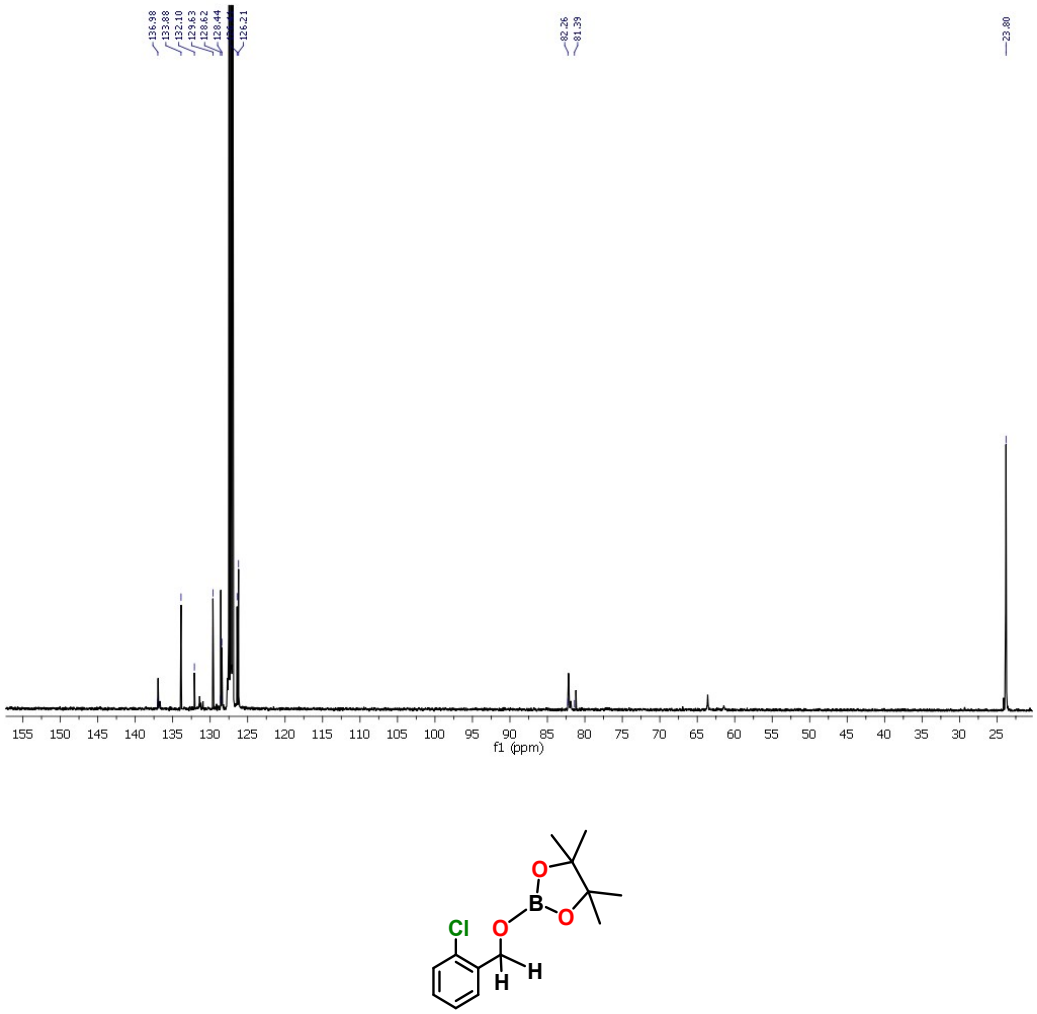


Figure S41: ^{13}C NMR spectrum of 2-(2-chlorobenzyloxy)pinacolborane (2f)

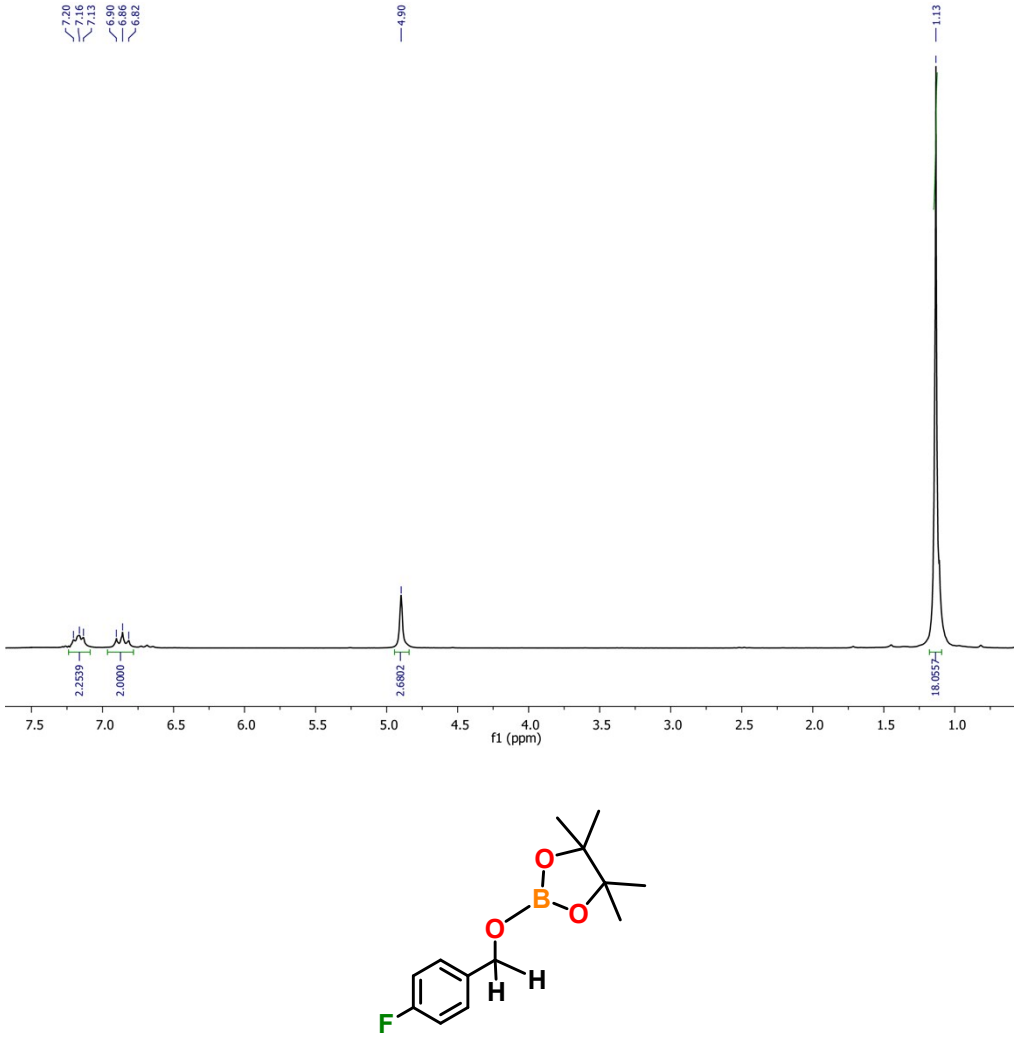


Figure S42: ^{1}H NMR spectrum of 2-(2-fluorobenzyloxy)pinacolborane (2g)

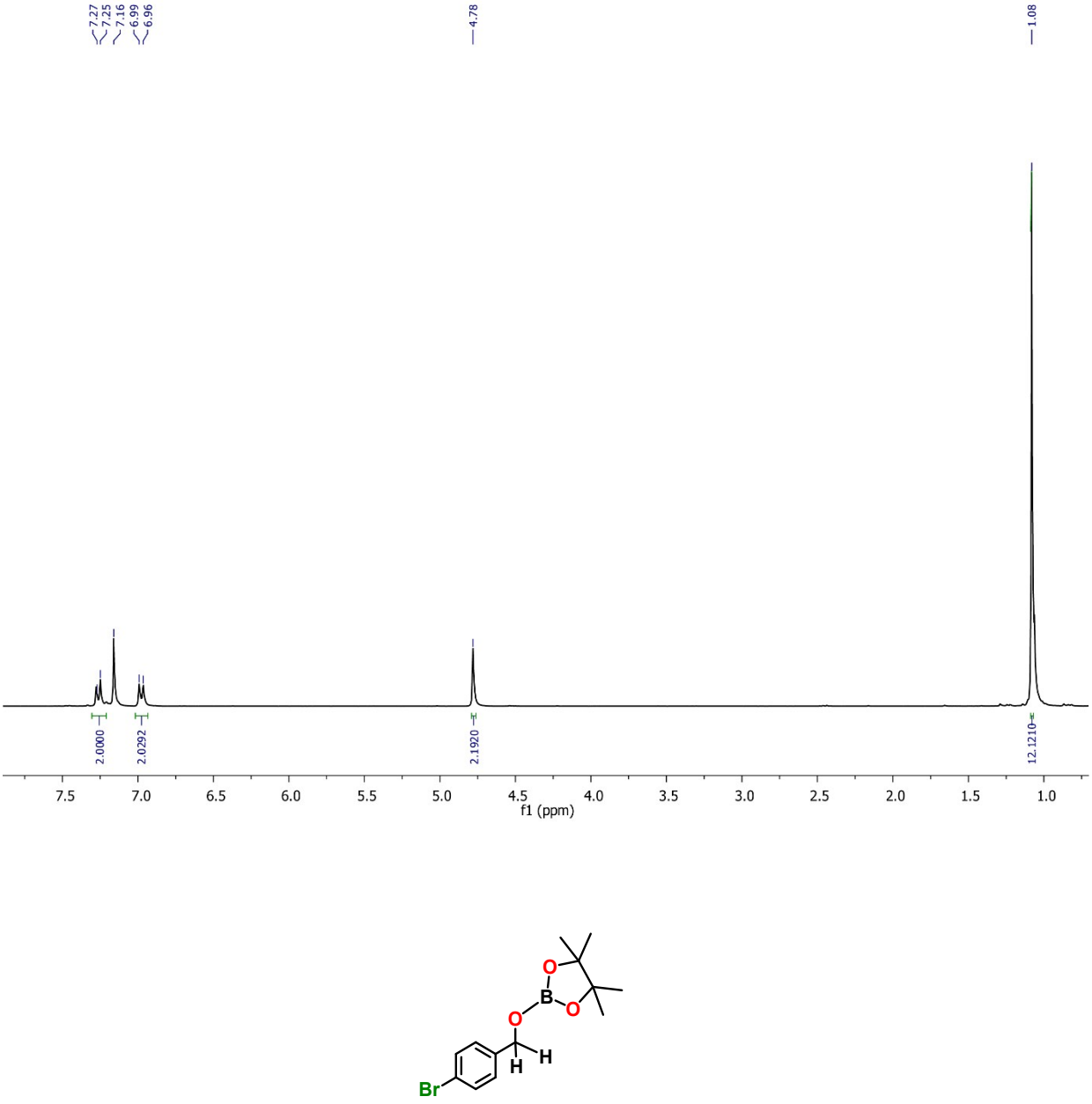


Figure S43: ^{1}H NMR spectrum of 2-(2-bromobenzyloxy)pinacolborane (2h)

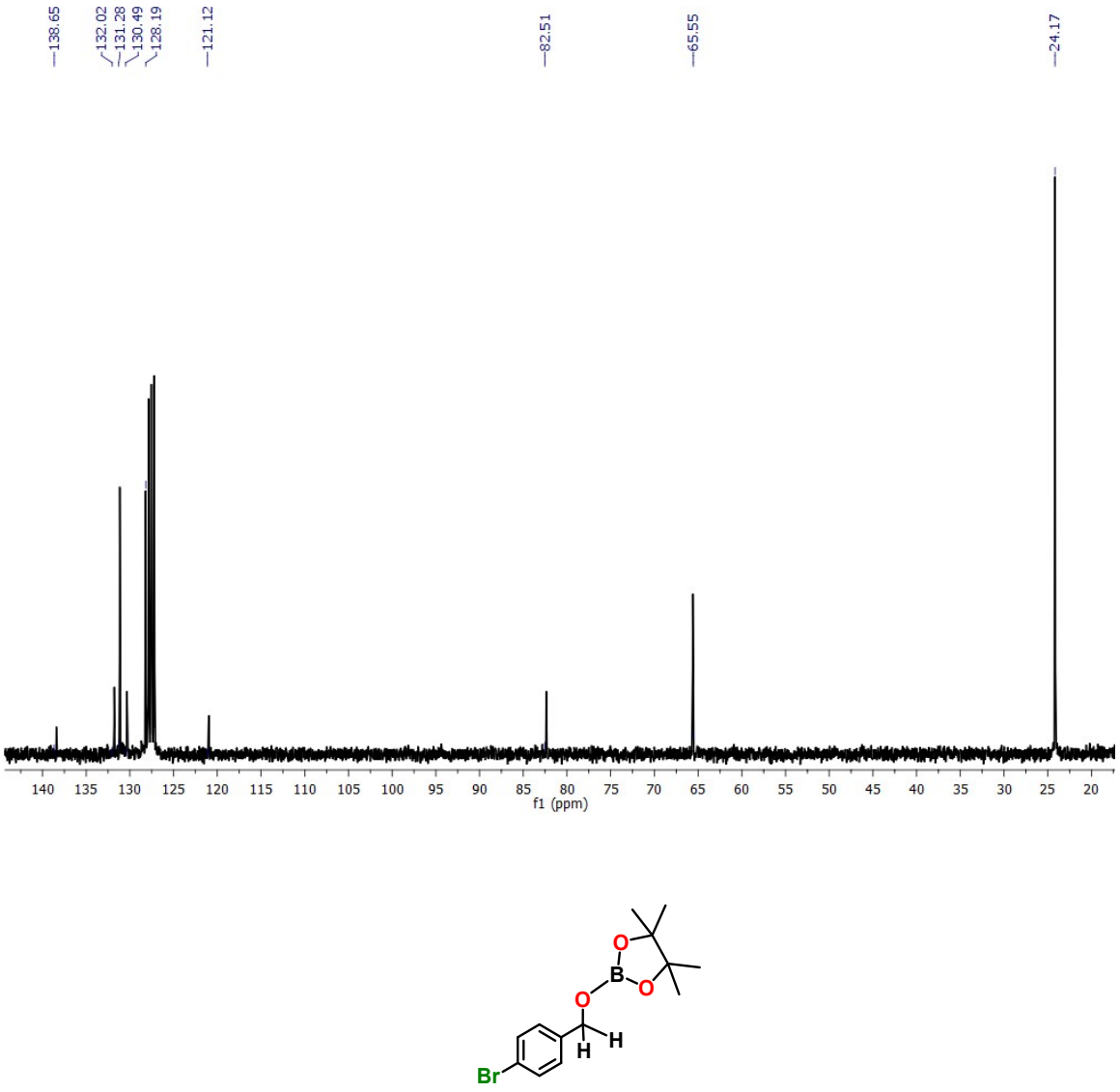


Figure S44: ^{13}C NMR spectrum of 2-(2-bromobenzyloxy)pinacolborane (2h)

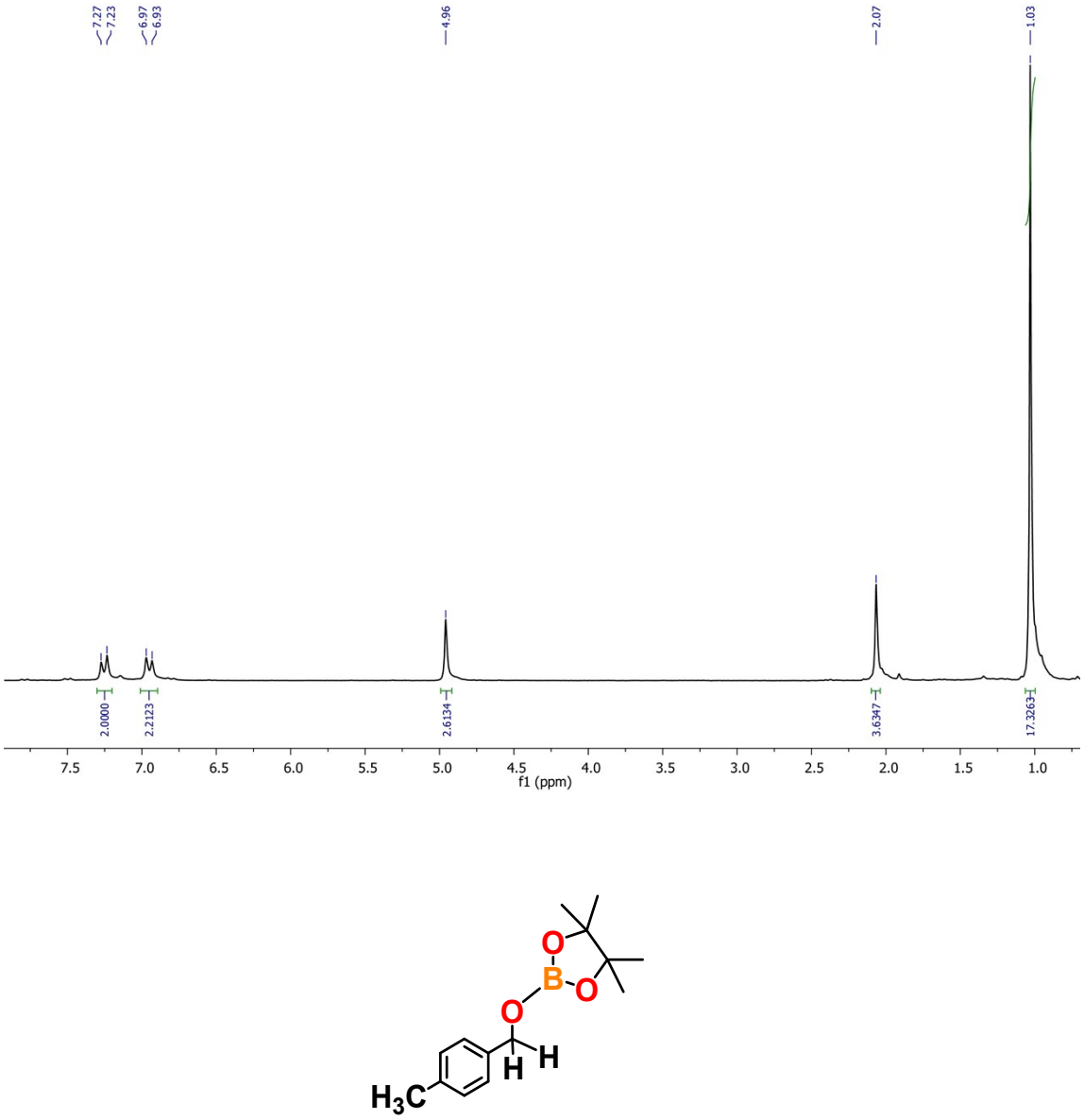


Figure S45: ^{1}H NMR spectrum of 2-(4-methyl benzyloxy)pinacolborane (2i)

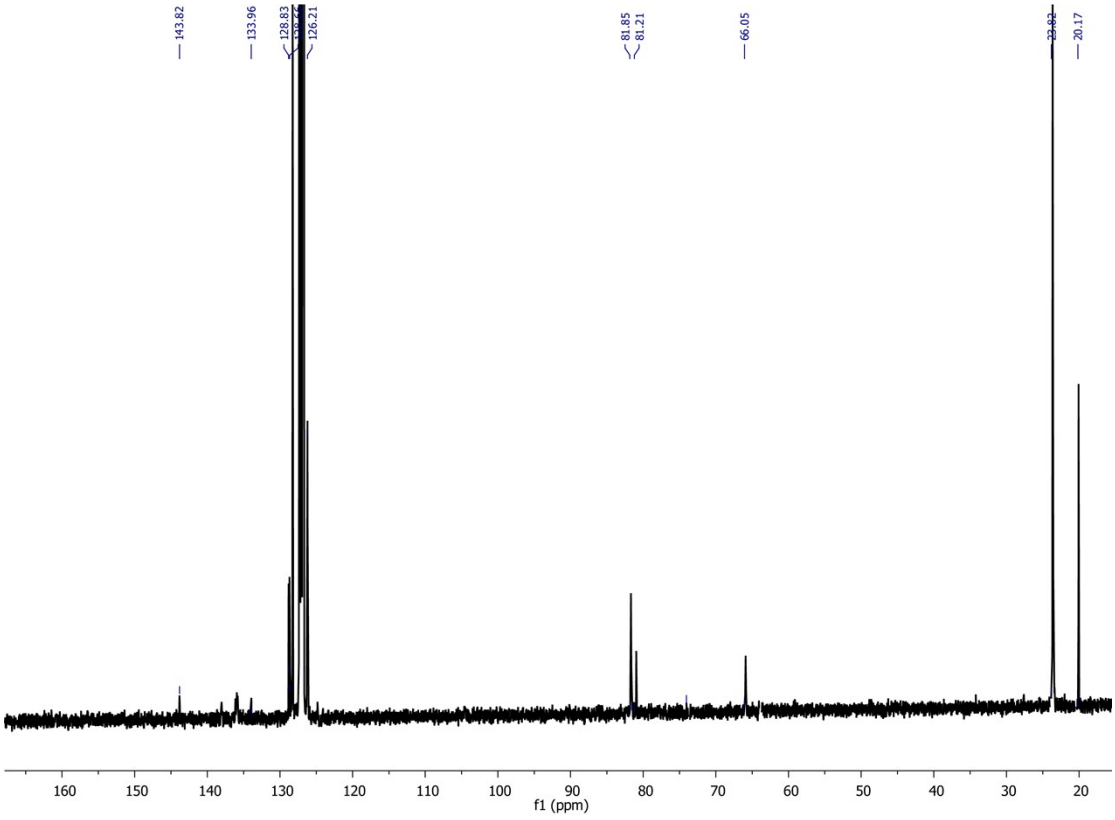


Figure S46: ^{13}C NMR spectrum of 2-(4-methyl benzyloxy)pinacolborane (2i)

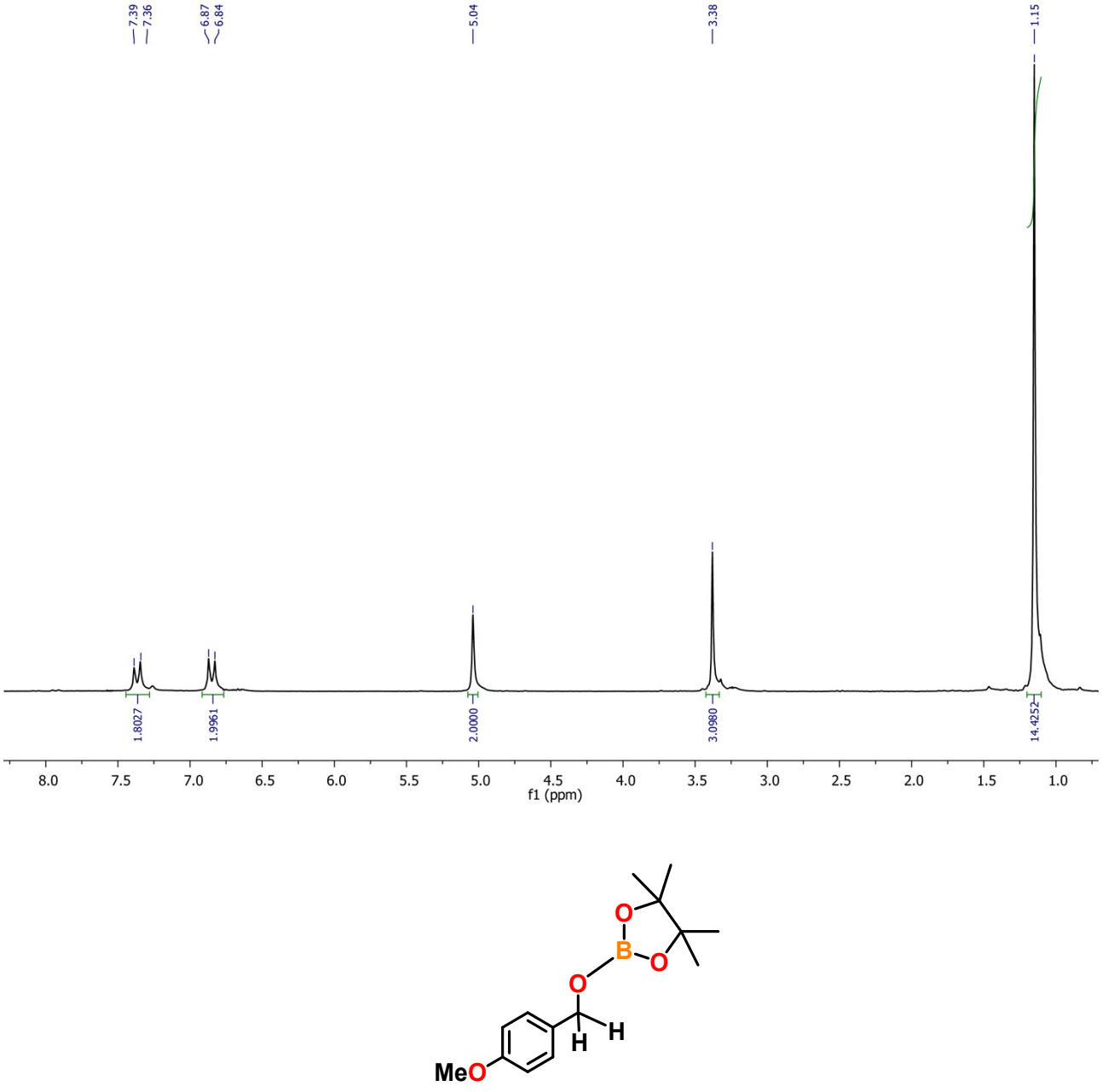


Figure S47: ^{1}H NMR spectrum of 2-(4-methoxybenzyloxy)pinacolborane (2j)

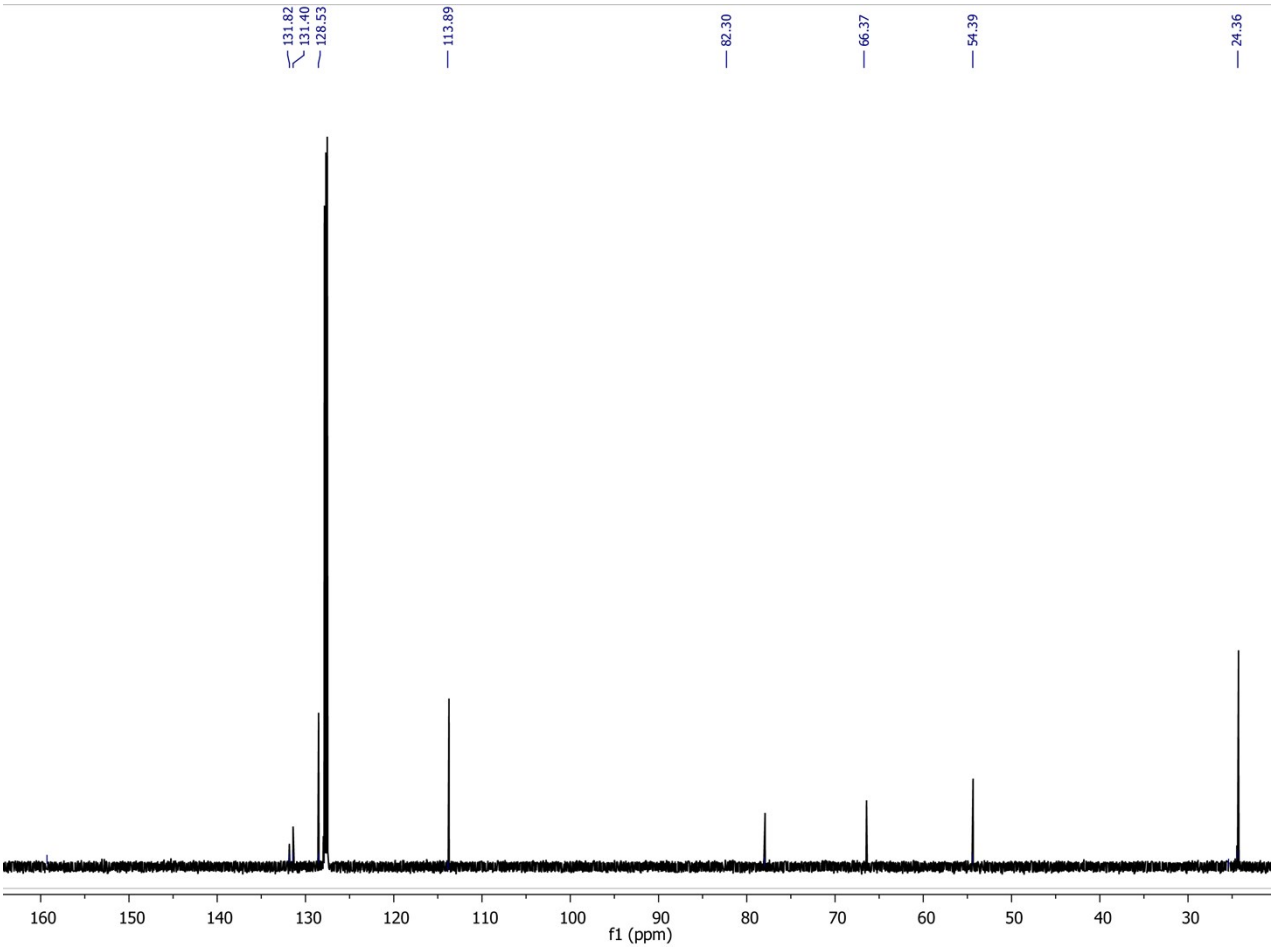


Figure S48: ^{13}C NMR spectrum of 2-(4-methoxybenzyloxy)pinacolborane (2j)

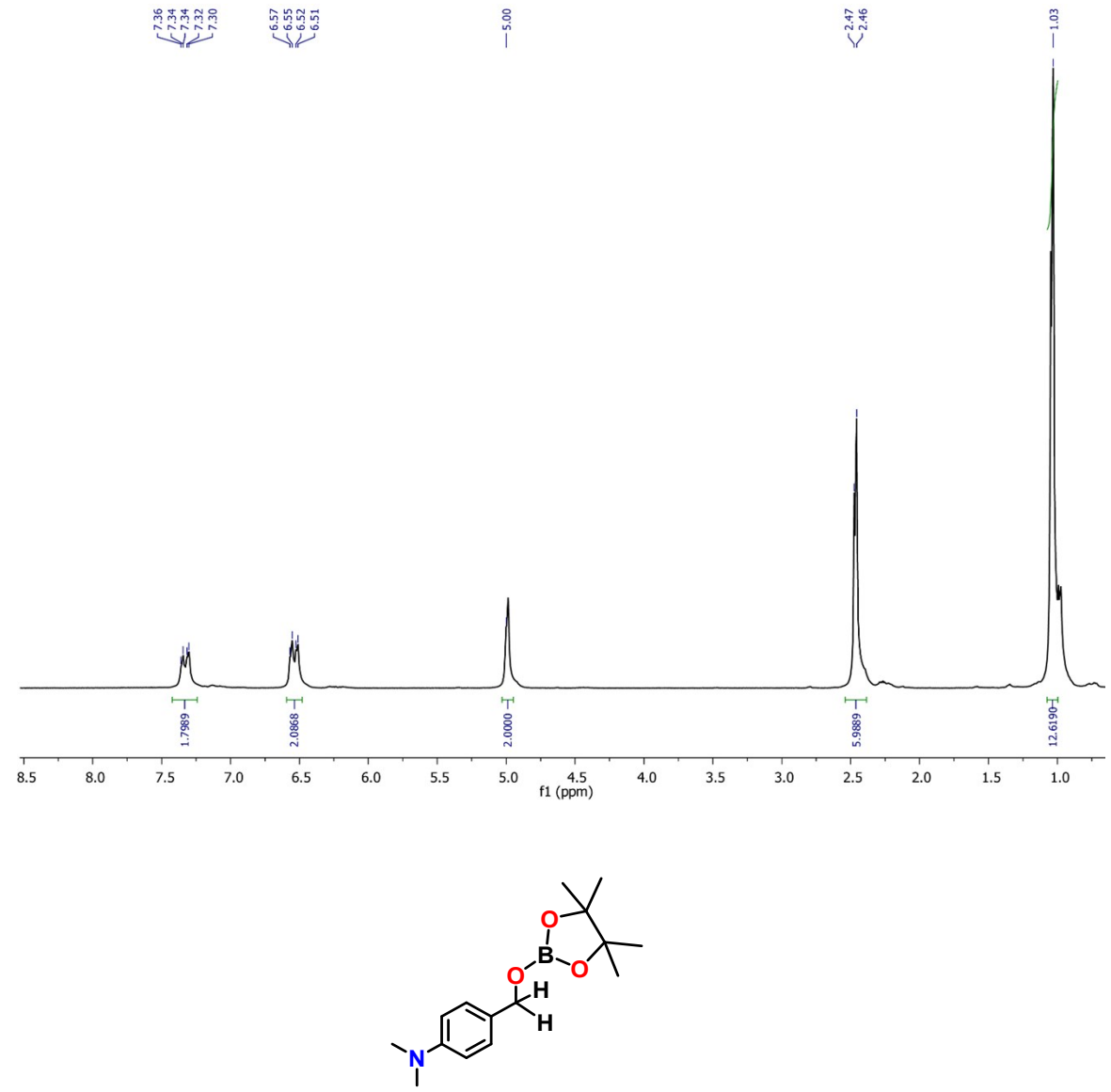


Figure S49: ^{1}H NMR spectrum of 2-(*p*-N, N'-dimethylbenzyloxy)pinacolborane (2k)

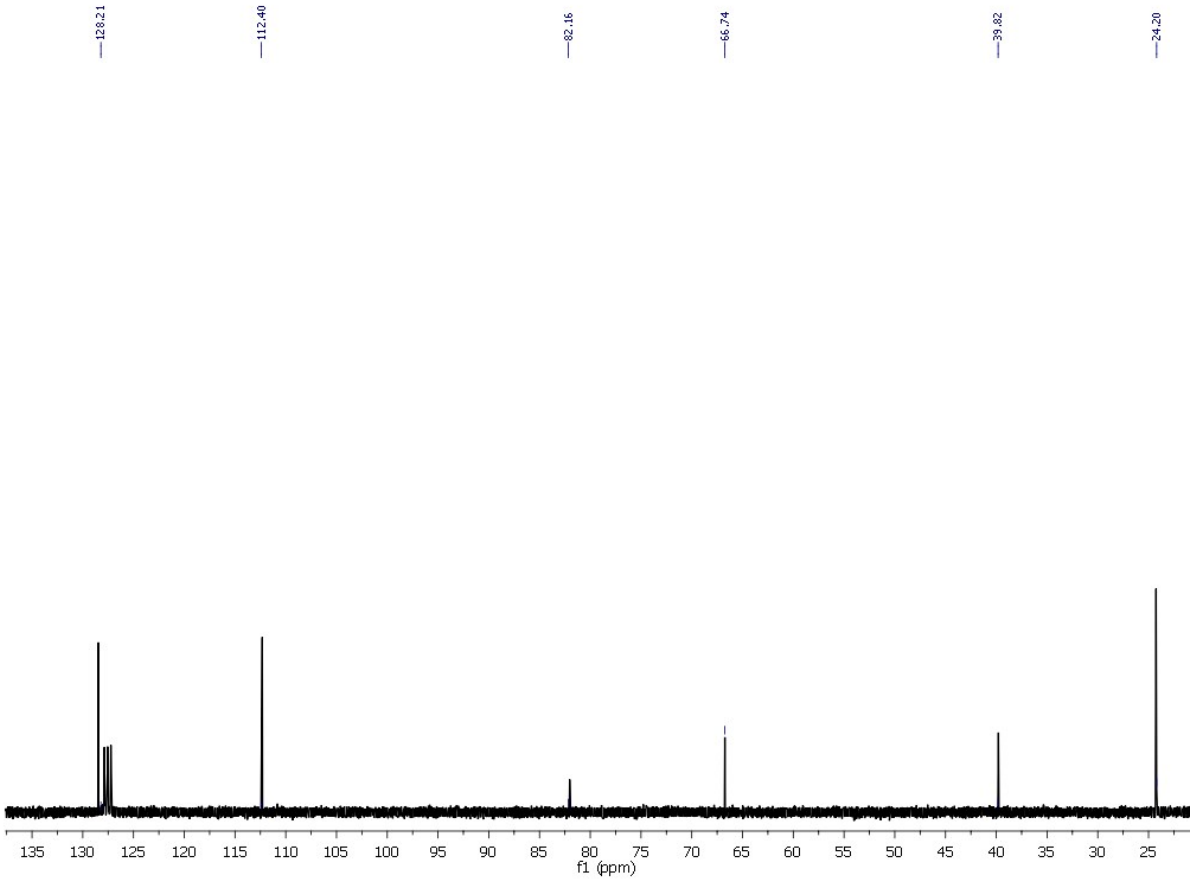


Figure S50: ^{13}C NMR spectrum of 2-(*p*-N, N'-dimethylbenzyloxy)pinacolborane (2k)

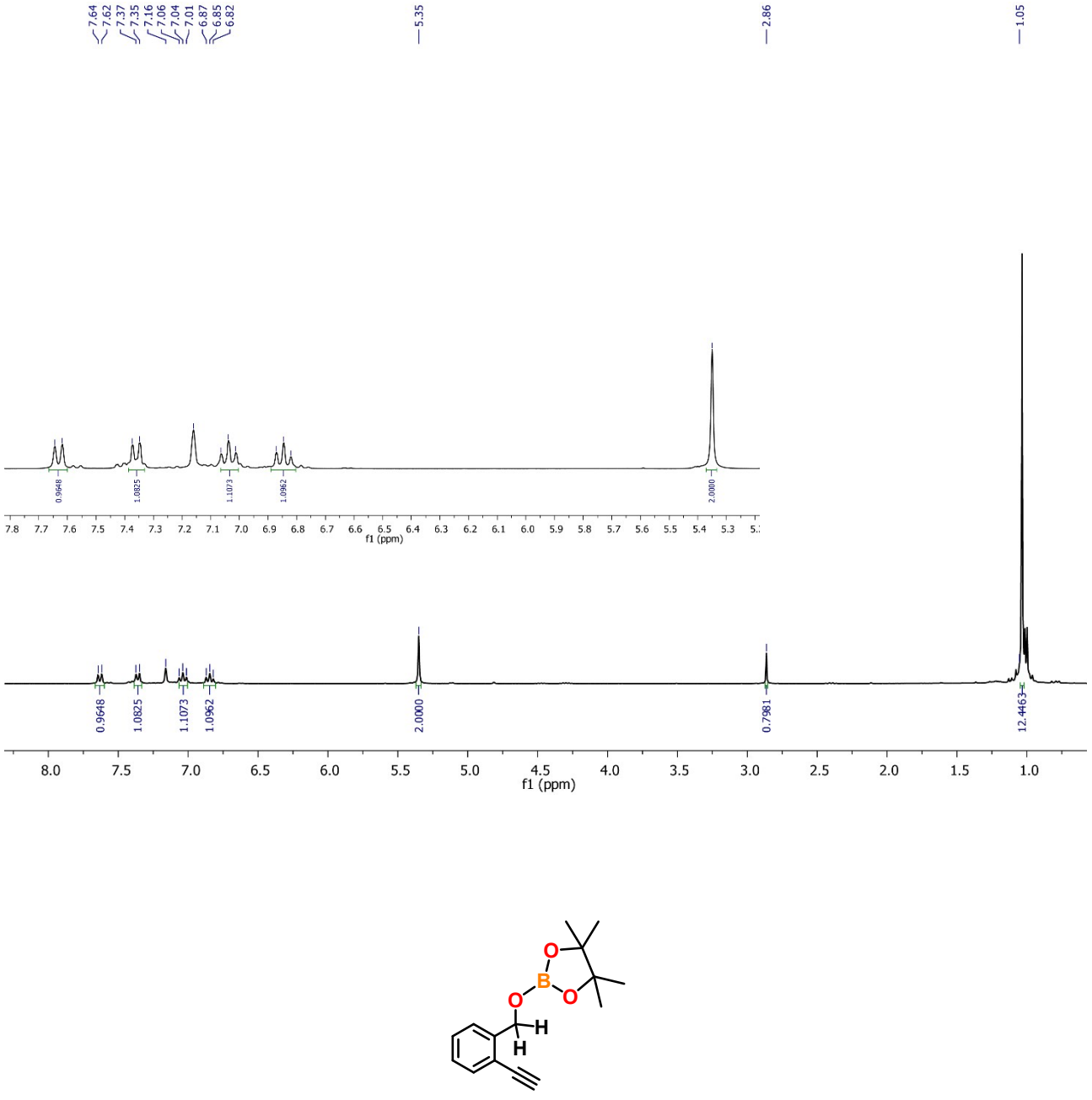


Figure S51: ^{1}H NMR spectrum of 2-(2-ethynyl benzyloxy)pinacolborane (2l)

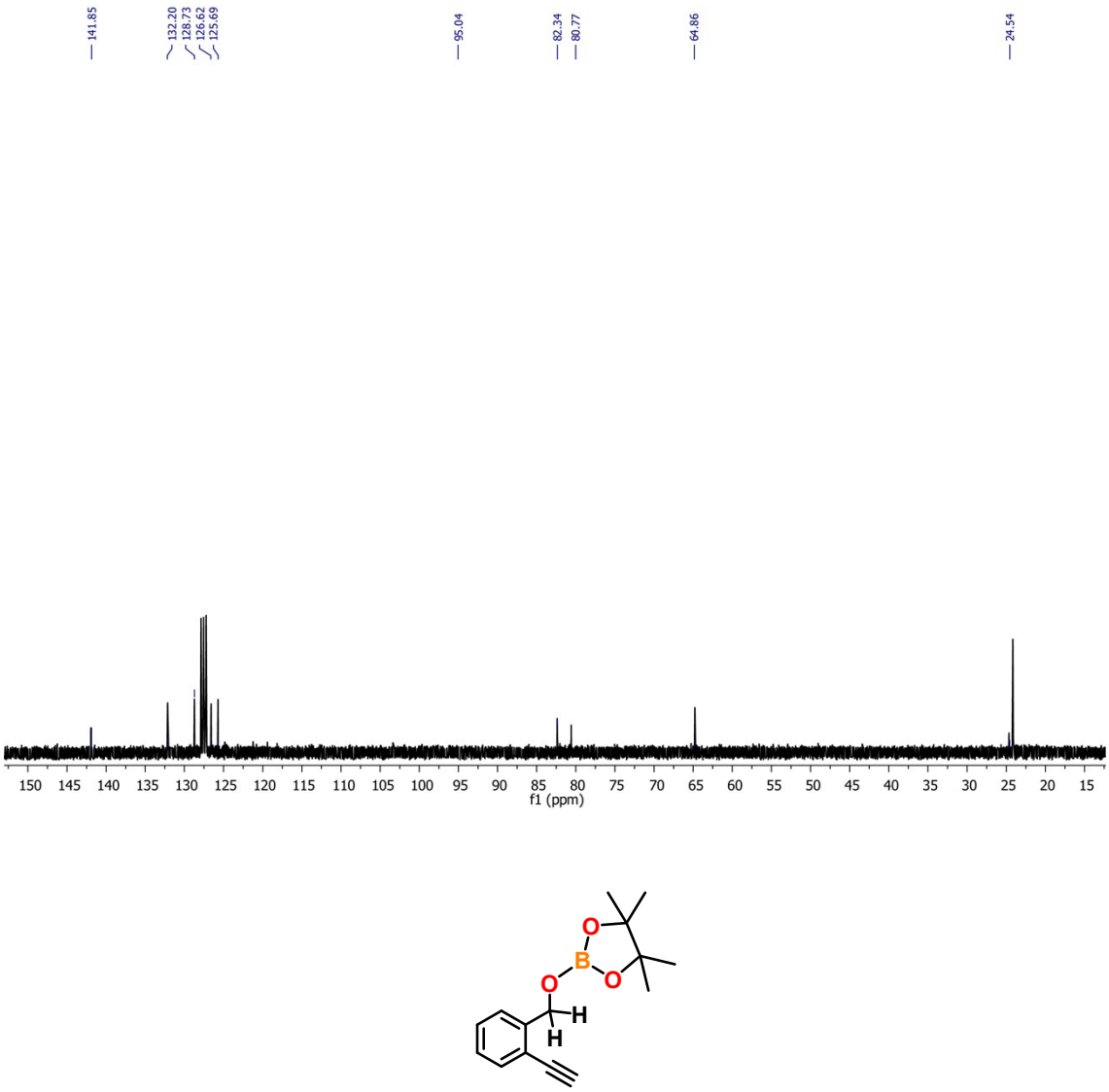


Figure S52: ^{13}C NMR spectrum of 2-(2-ethynyl benzyloxy)pinacolborane (2l)

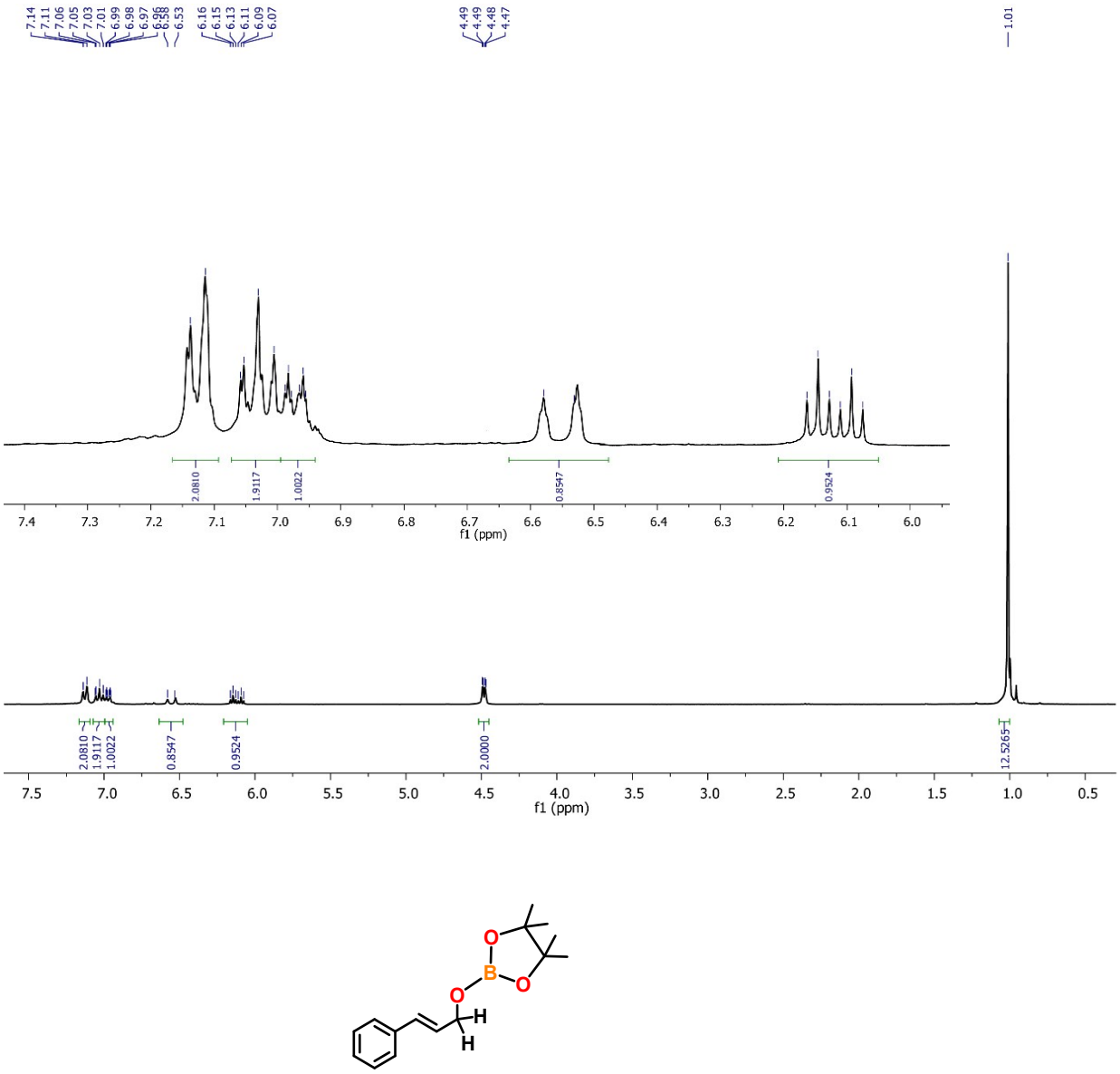


Figure S53: ^{1}H NMR spectrum of 2-(cinnamylmethoxy)pinacolborane (2m)

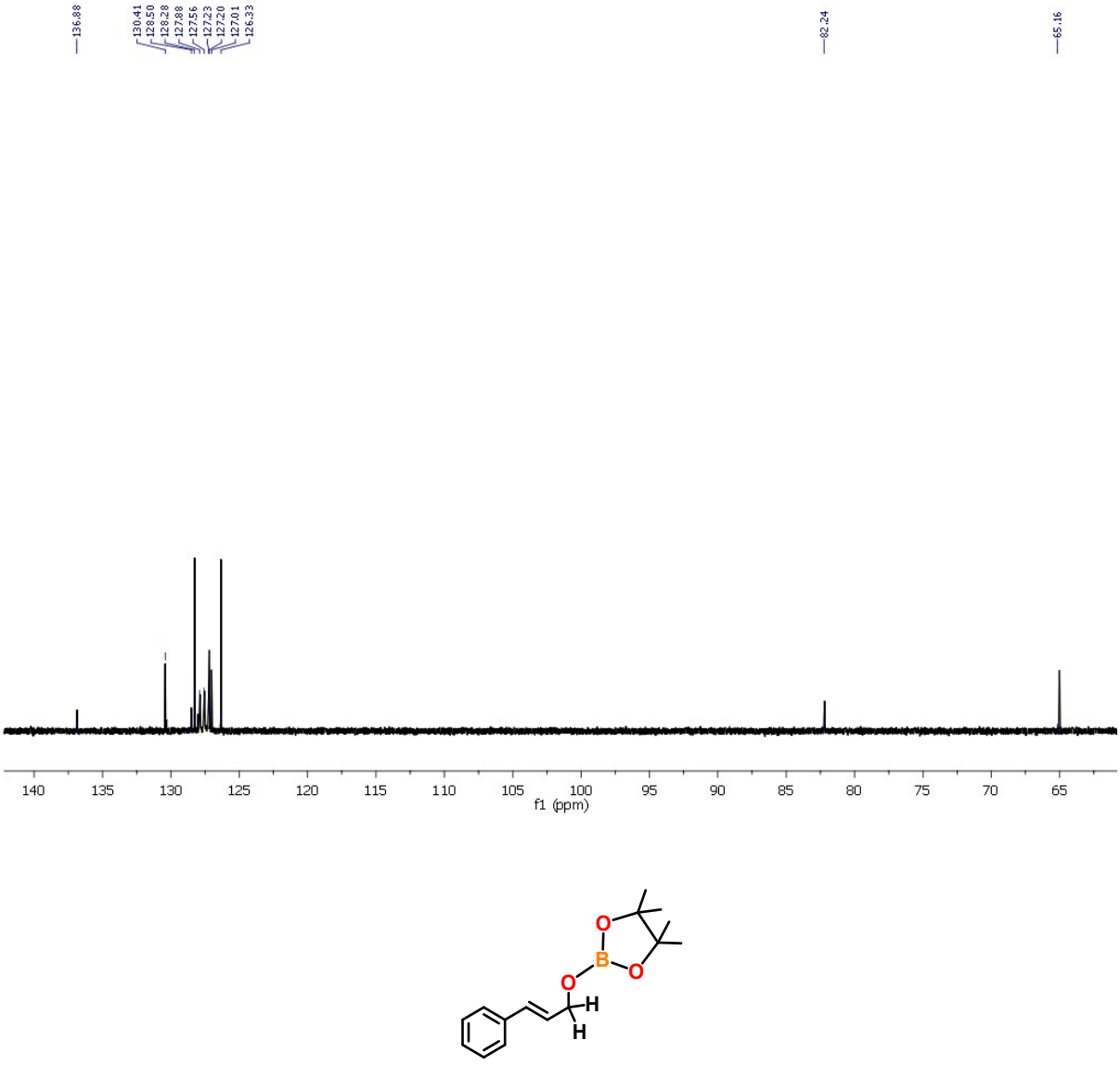


Figure S54: ^{13}C NMR spectrum of 2-(cinnamylmethoxy)pinacolborane (2m)

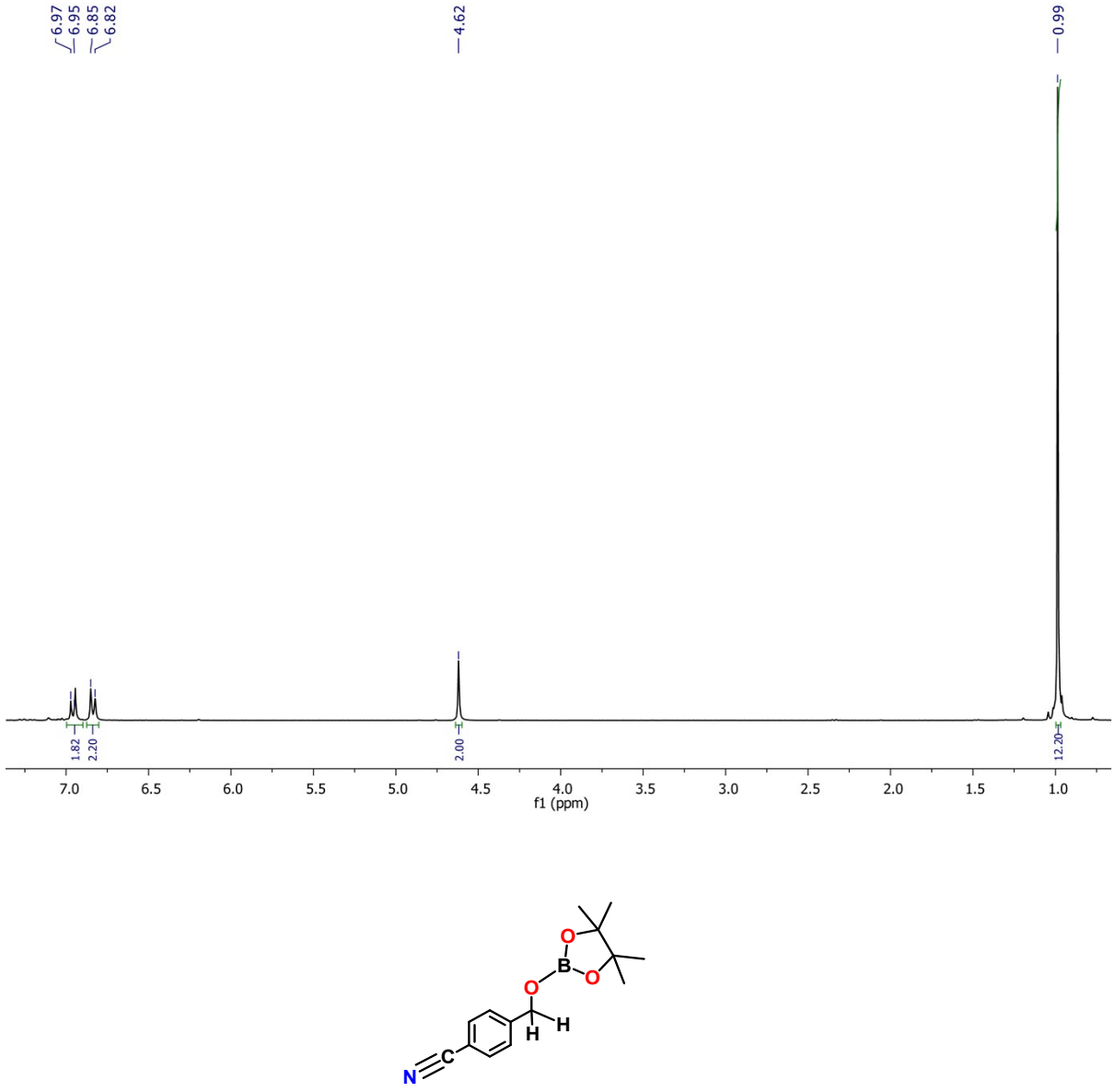


Figure S55: ^{1}H NMR spectrum of 2-(*p*-cyanobenzyloxy)pinacolborane (2n)

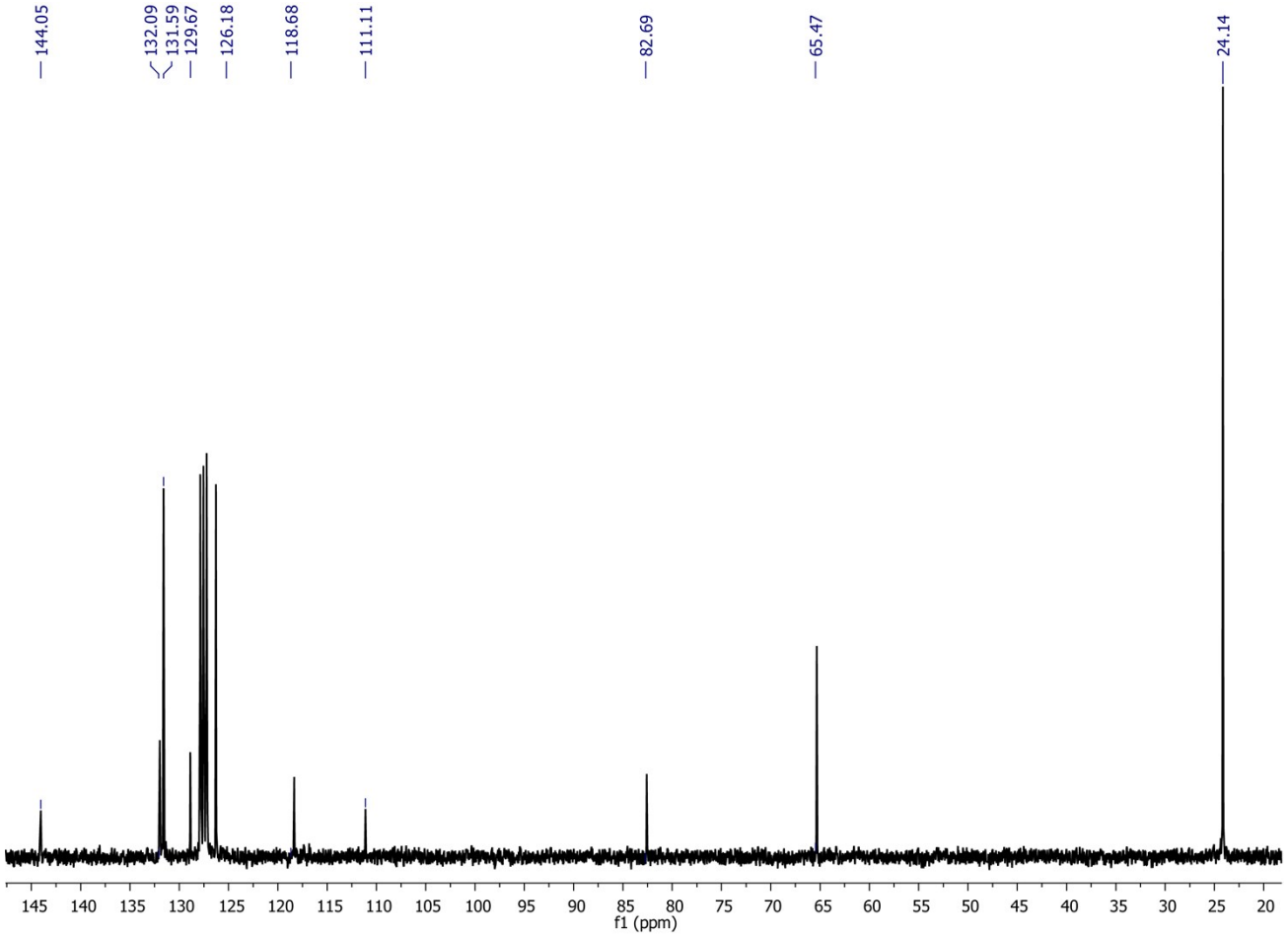


Figure S56: ^{13}C NMR spectrum of 2-(*p*-cyanobenzyloxy)pinacolborane (2n)

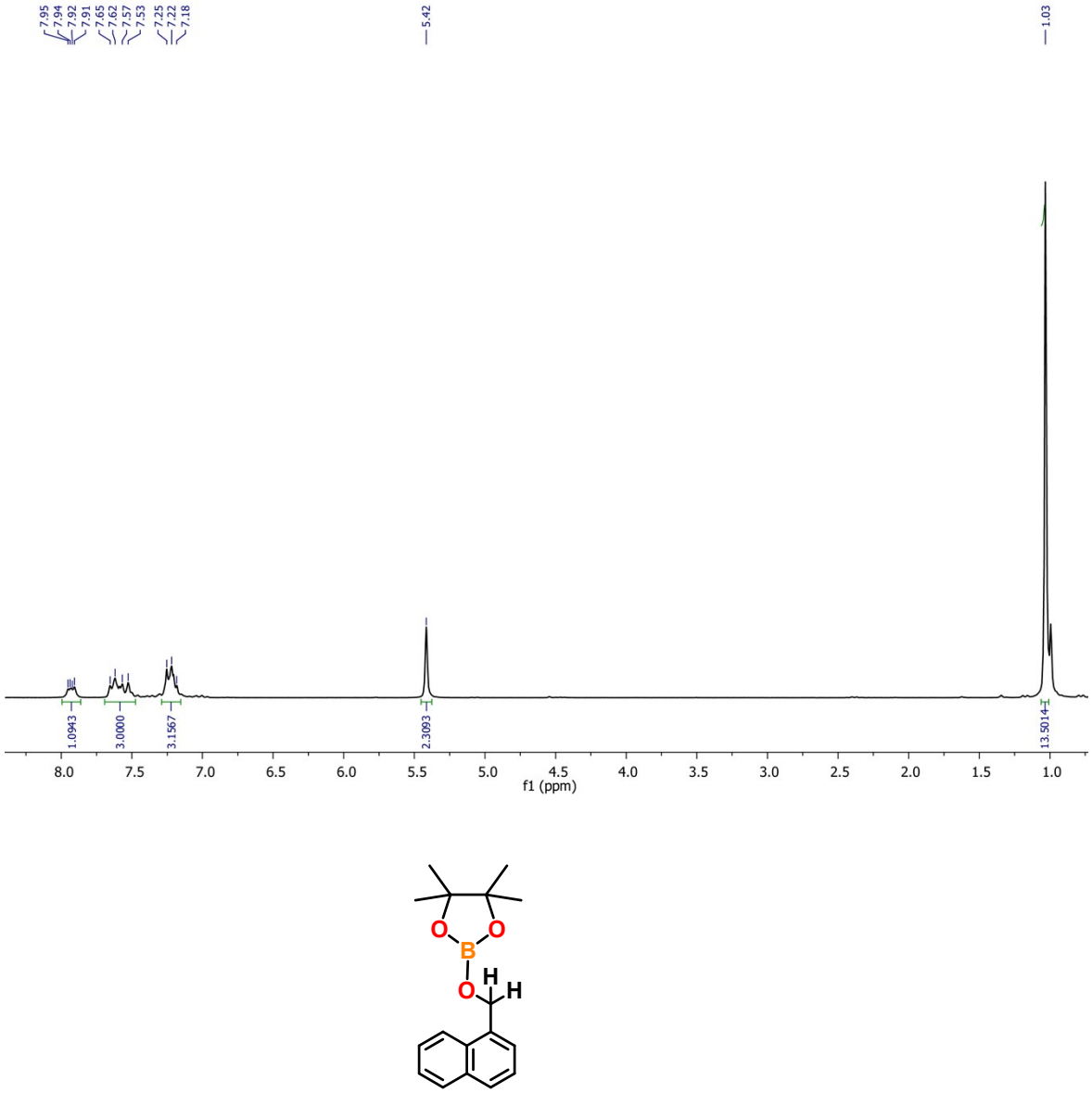
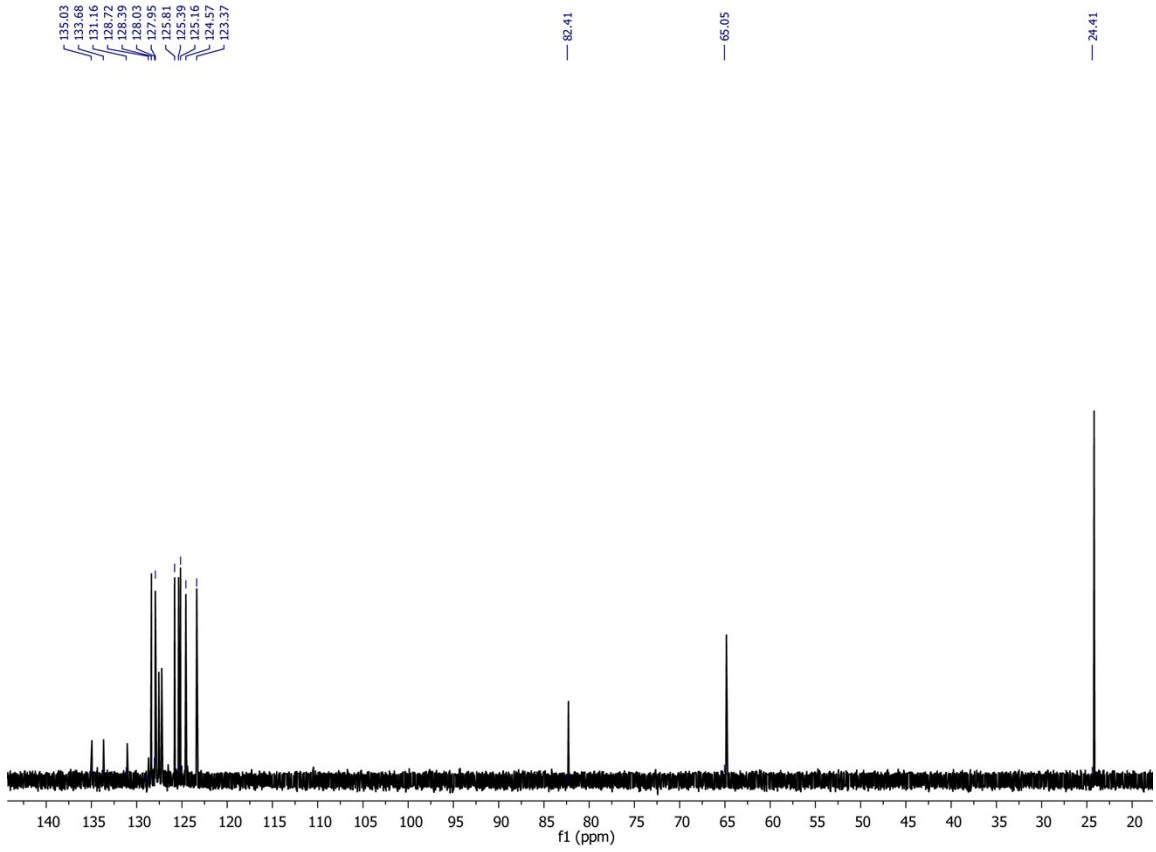


Figure S57: ^{1}H NMR spectrum of 2-(naphthalene-1-ylmethyl)pinacolborane (2o)



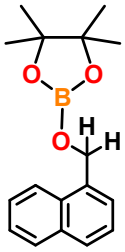


Figure S58: ^{13}C NMR spectrum of 2-(naphthalene-1-ylmethyl)pinacolborane (2o)

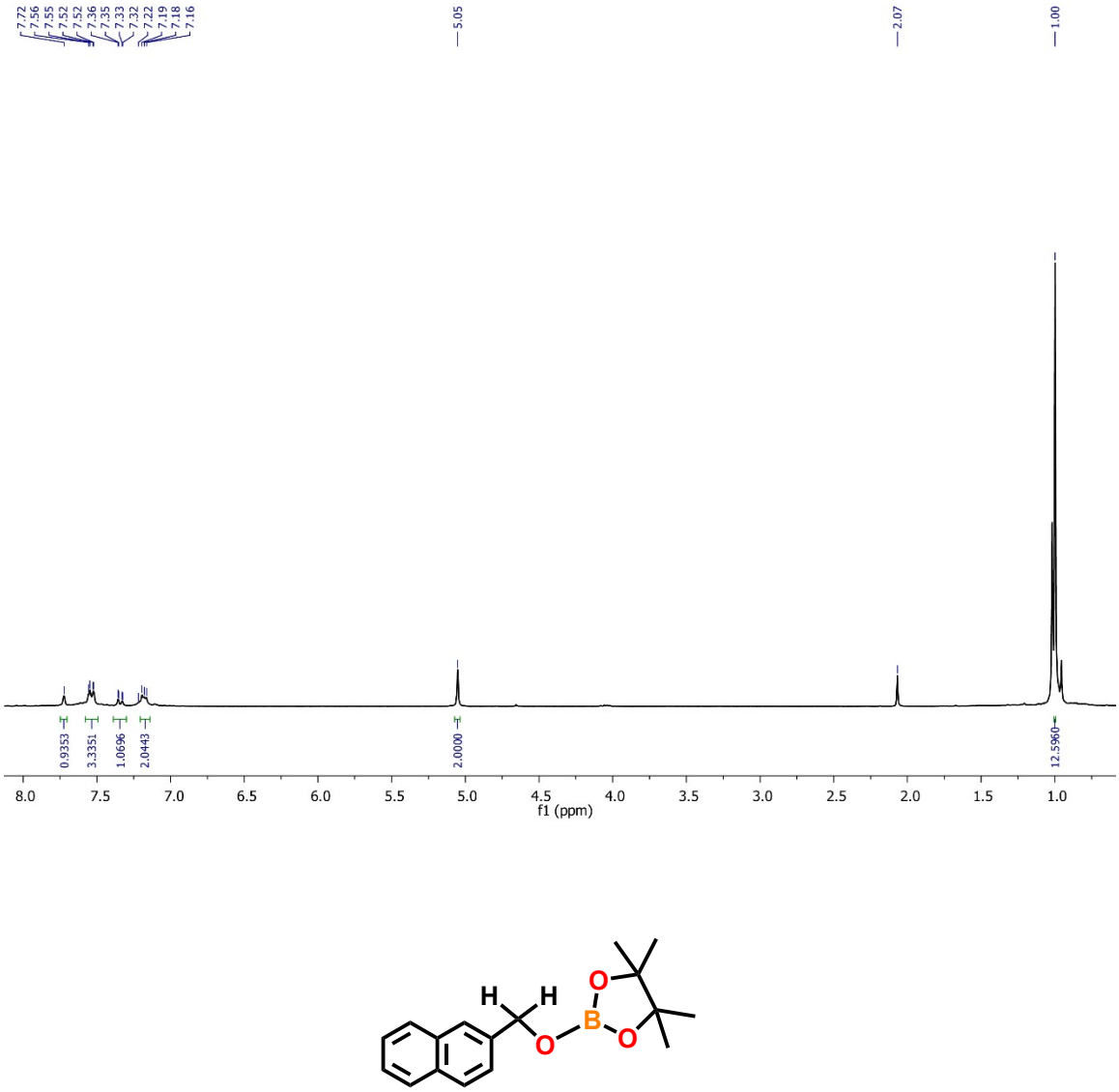


Figure S59: ^{1}H NMR spectrum of 2-(naphthalene-2-ylmethyl)pinacolborane (2p)

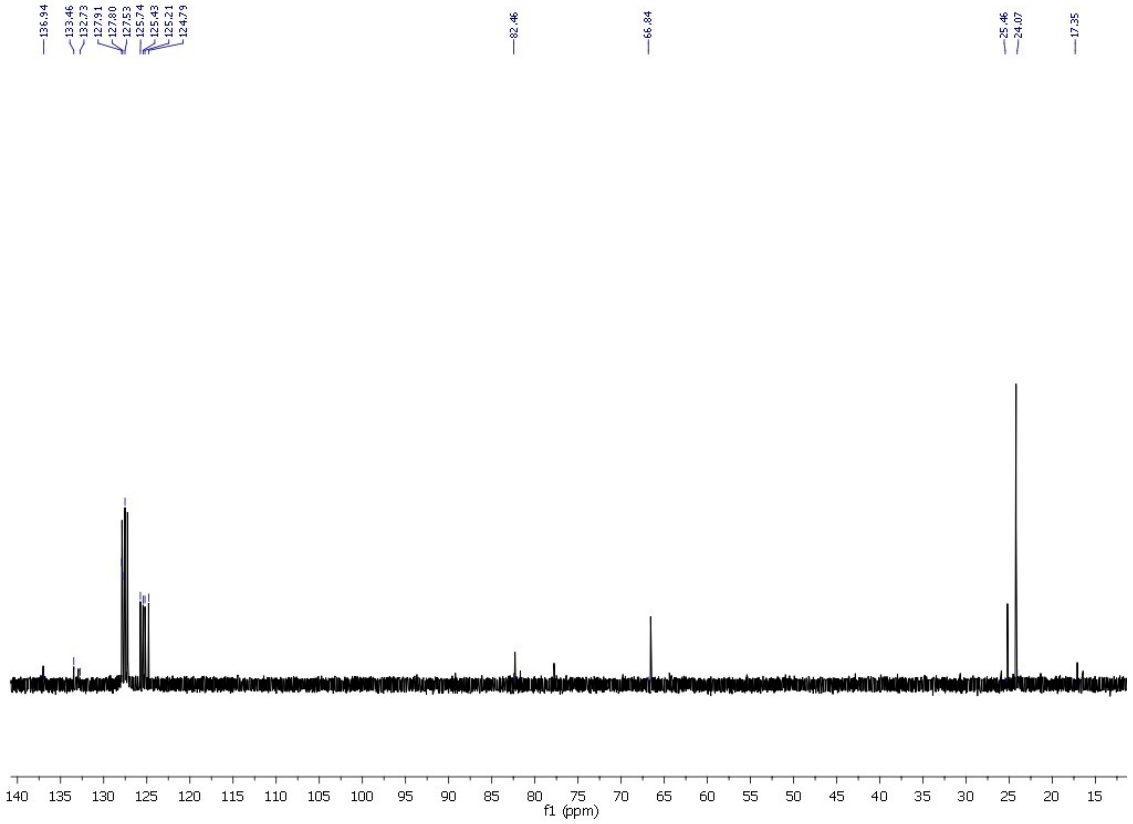


Figure S60: ^{13}C NMR spectrum of 2-(naphthalene-2-ylmethyl)pinacolborane (2p)

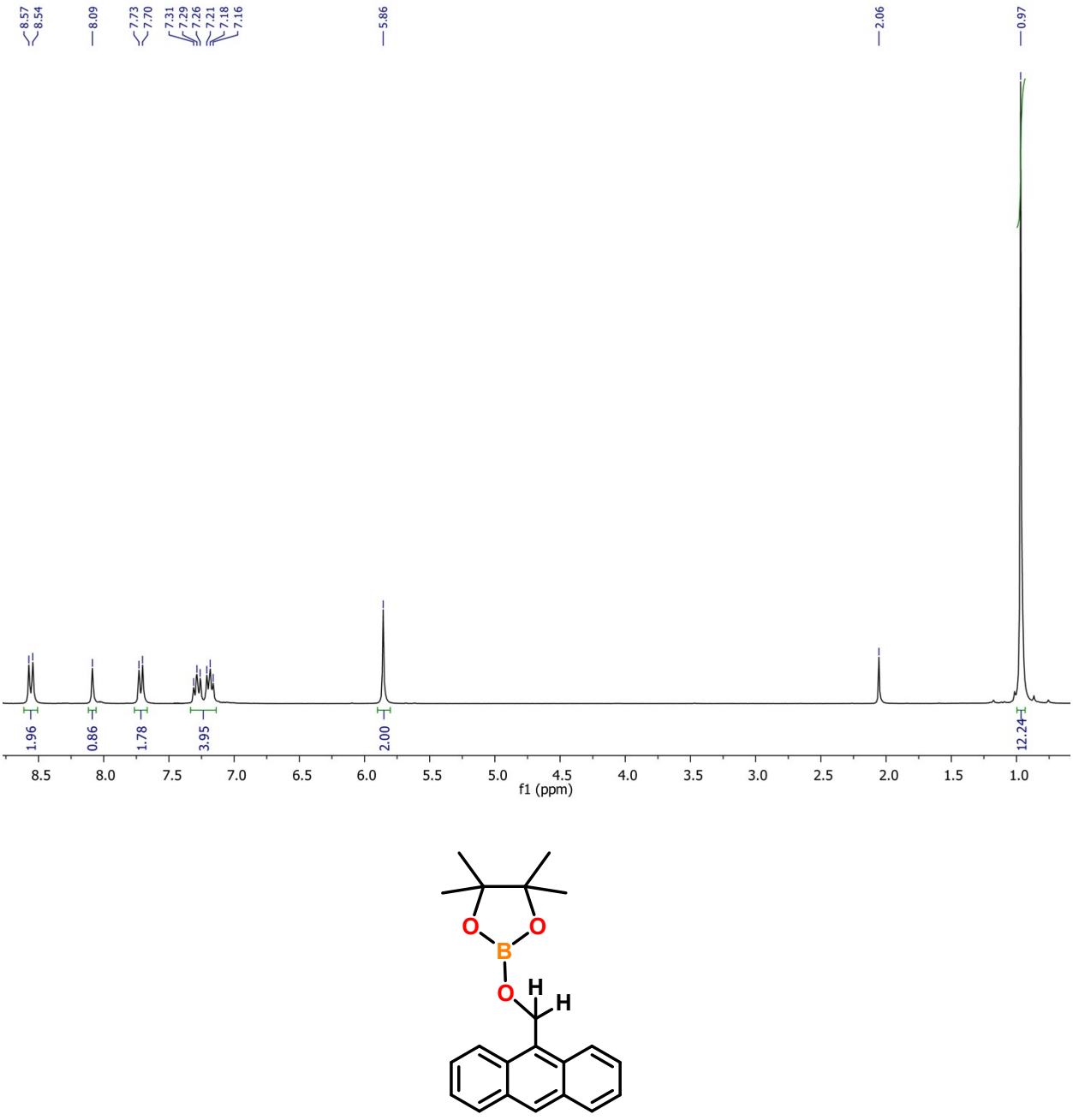


Figure S61: ^{1}H NMR spectrum of 2-(anthracene-9-ylmethoxy)pinacolborane (2q)

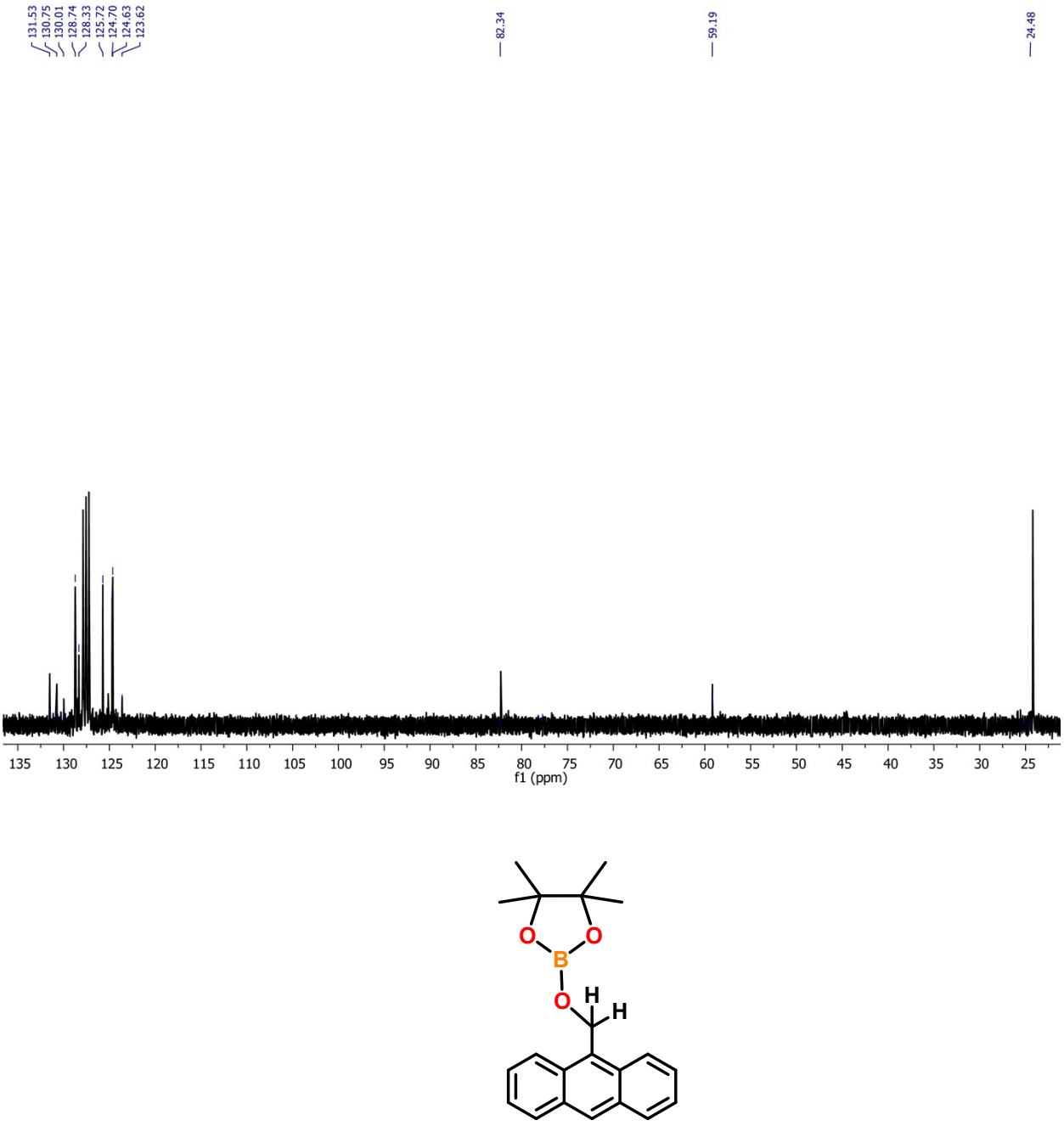


Figure S62: ^{13}C NMR spectrum of 2-(anthracene-9-ylmethoxy)pinacolborane (2q)

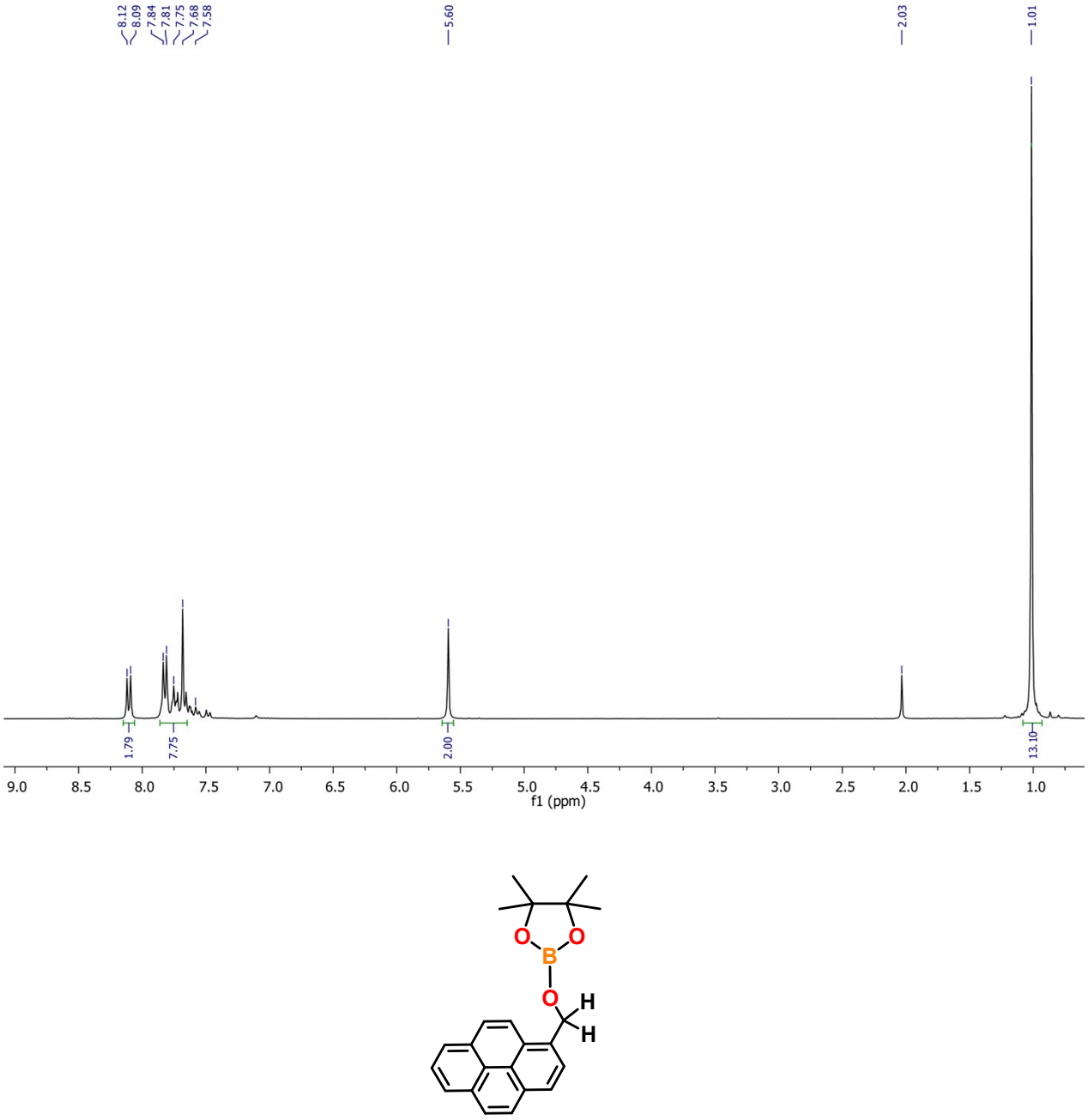


Figure S63: ^{1}H NMR spectrum of 2-(pyrene-1-ylmethoxy) pinacolborane (2r)

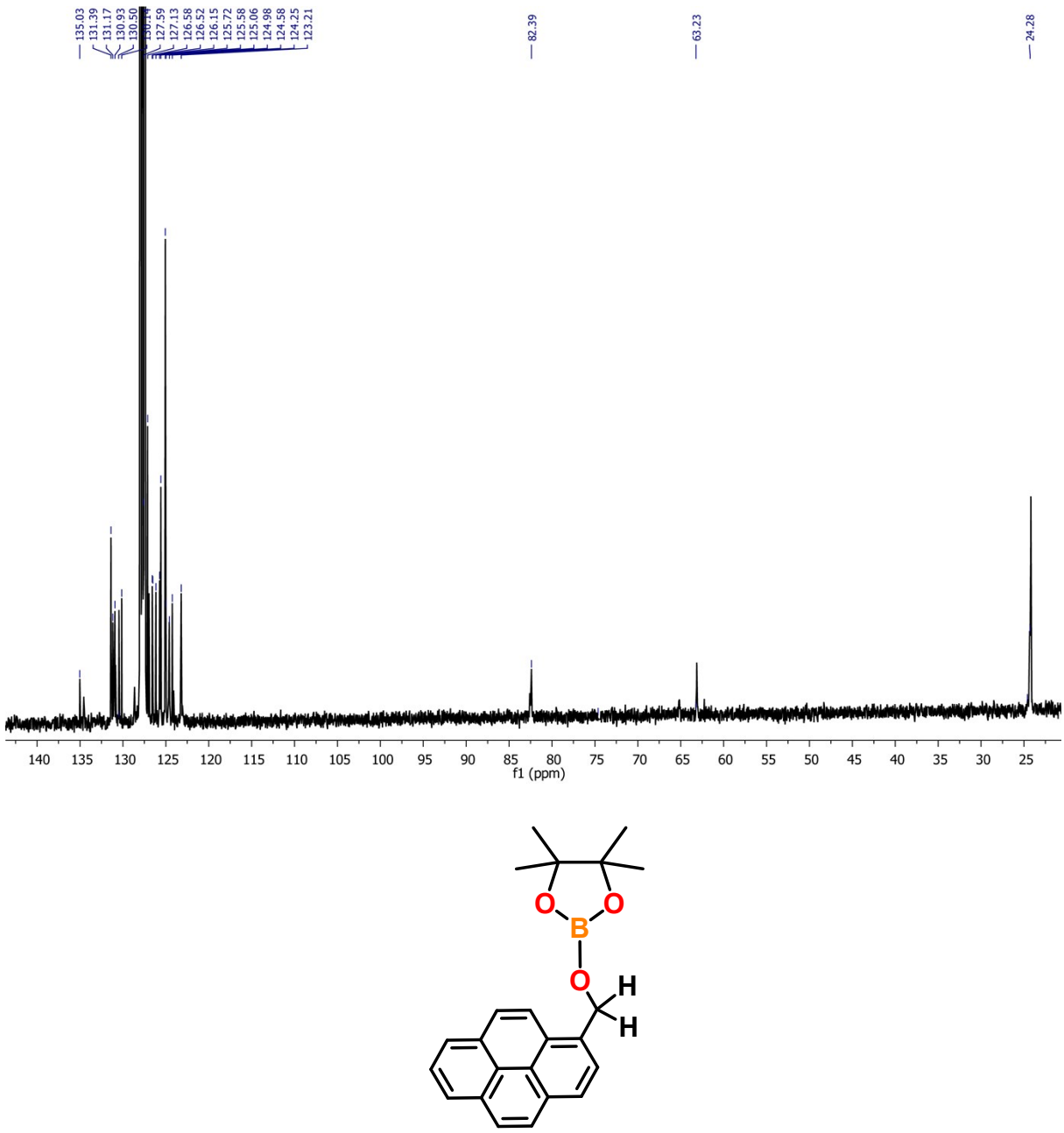


Figure S64: ^{13}C NMR spectrum of 2-(pyrene-1-ylmethoxy) pinacolborane (2r)

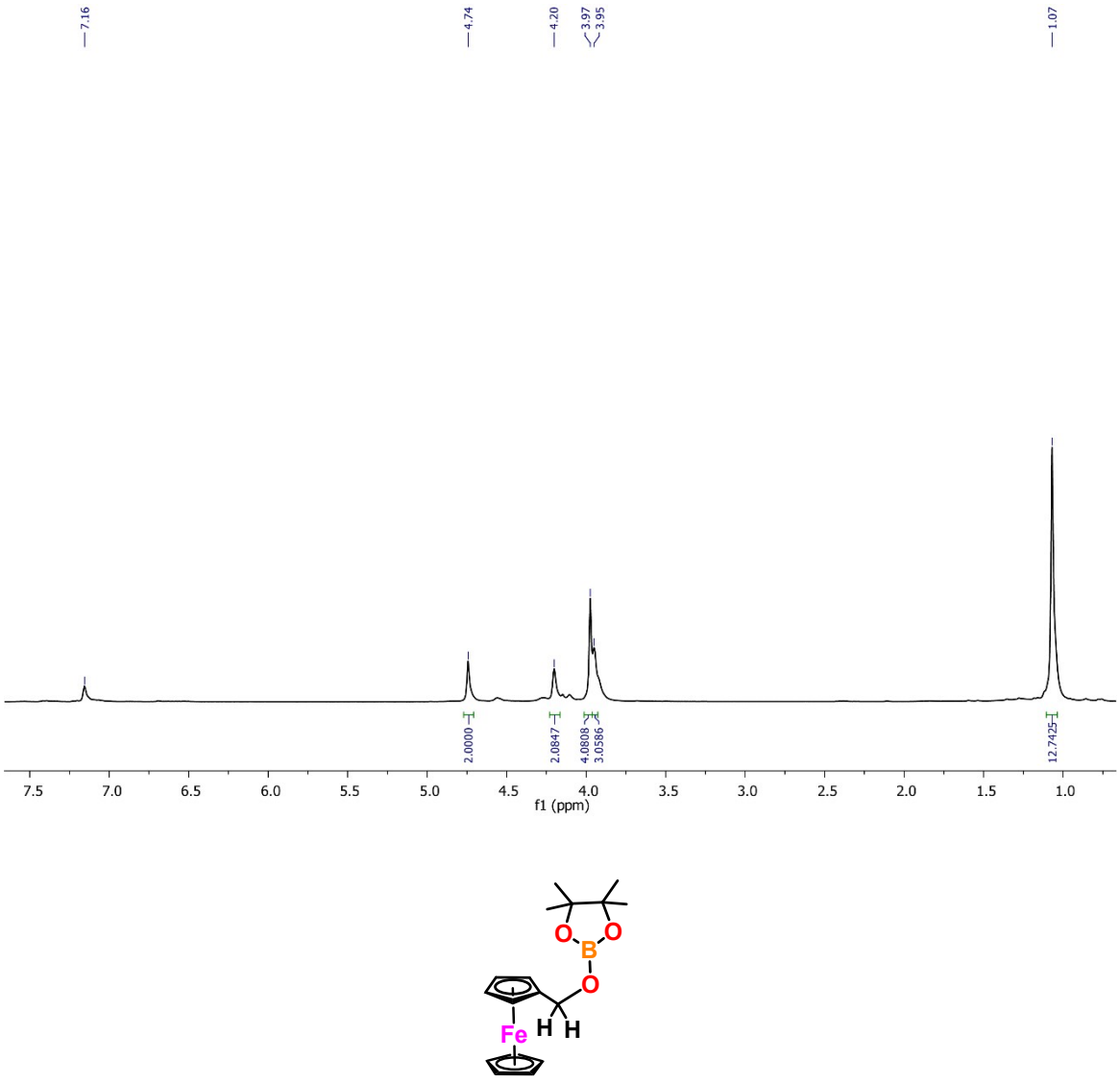


Figure S65: ^{1}H NMR spectrum of 2-(ferrocenylmethoxy)pinacolborane (2s)

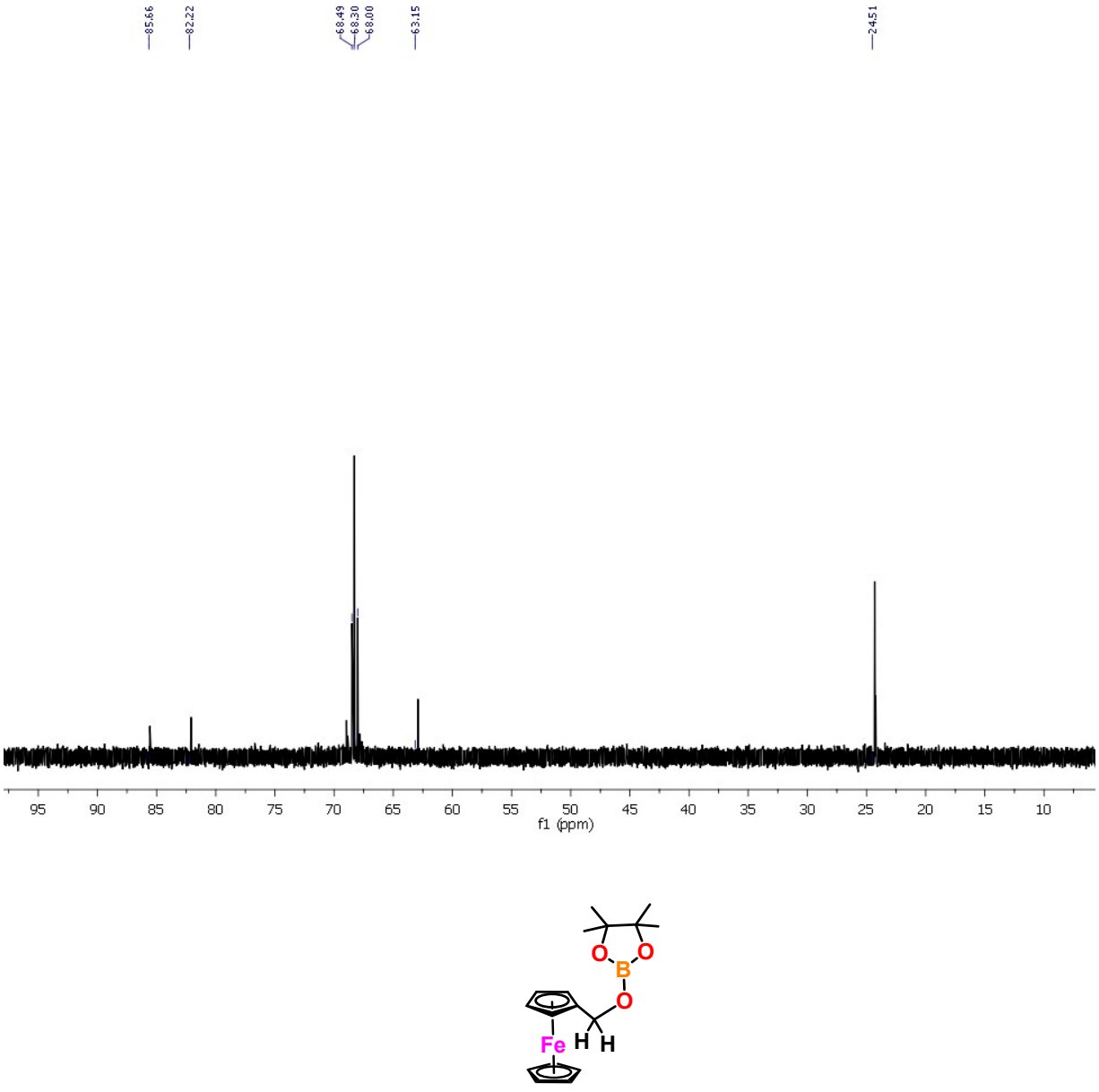


Figure S66: ^{13}C NMR spectrum of 2-(ferrocenylmethoxy)pinacolborane (2s)

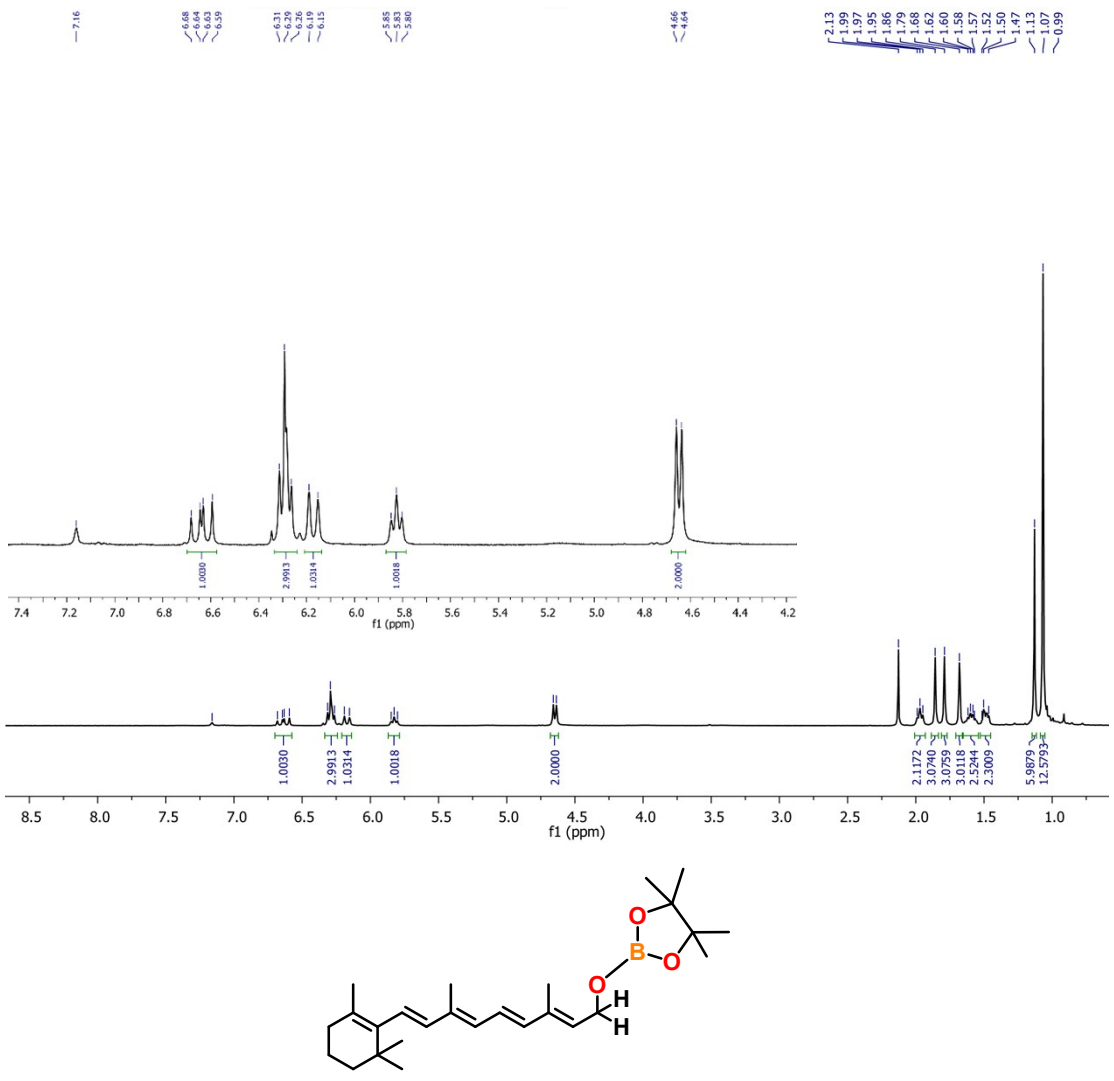


Figure S67: ^{1}H NMR spectrum of 2-(((2E,4E,6E,8E)-3,7-dimethyl-9-(2,6,6-trimethylcyclohex-1-en-1-yl)nona-2,4,6,8-tetraen-1-yl)oxy)pinacolborane (2t)

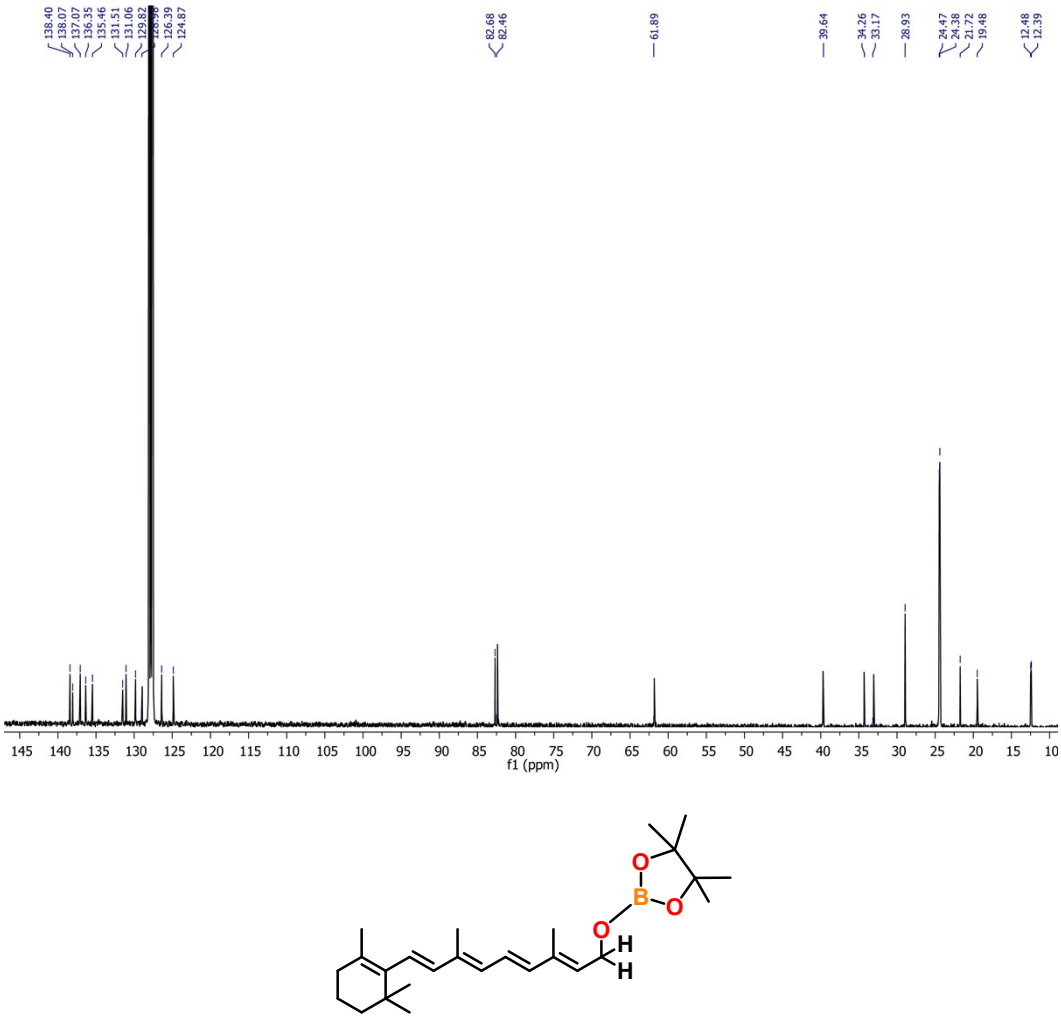


Figure S68: ^{13}C NMR spectrum of 2-(((2E,4E,6E,8E)-3,7-dimethyl-9-(2,6,6-trimethylcyclohex-1-en-1-yl)nona-2,4,6,8-tetraen-1-yl)oxy)pinacolborane (2t)

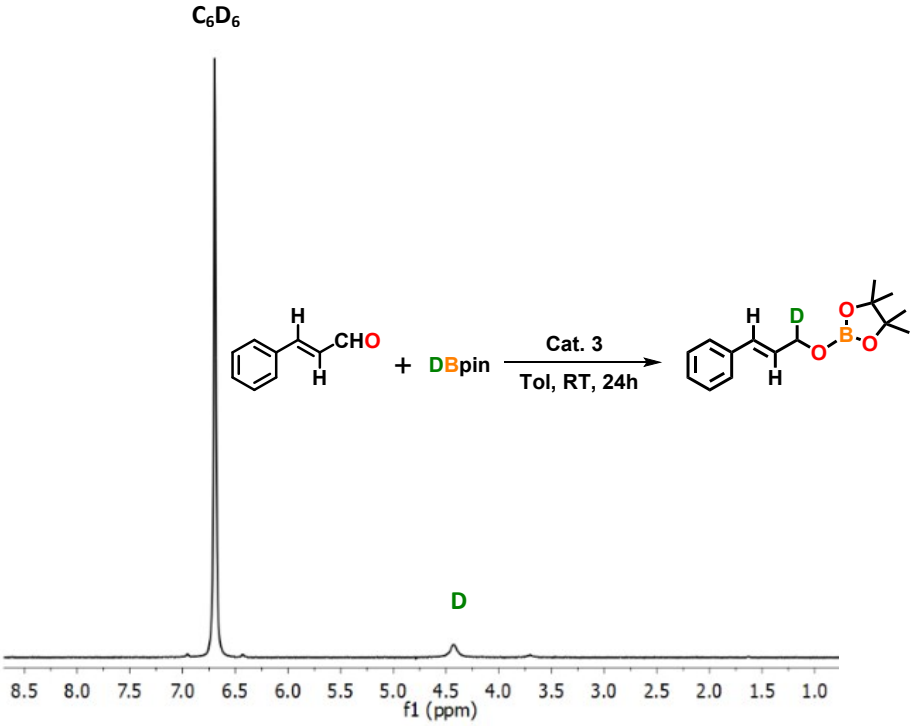
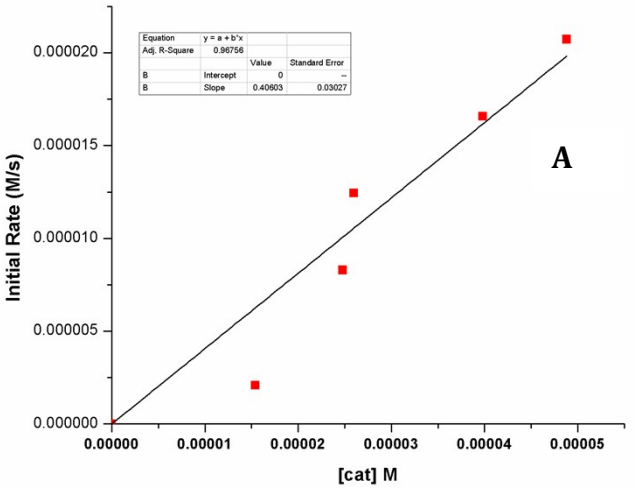
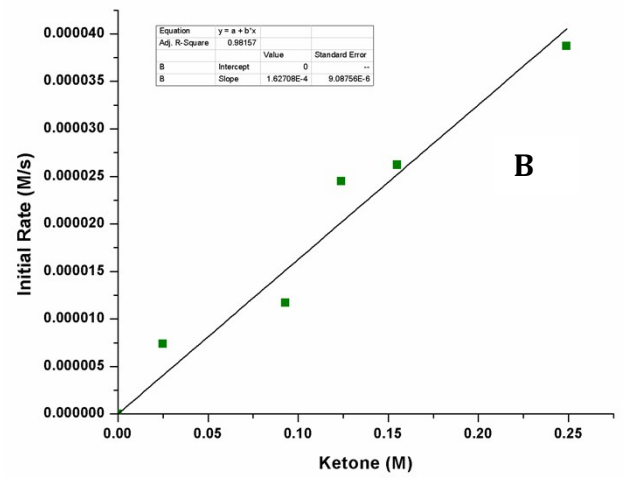


Figure S69: ^{2}H NMR spectrum of the hydroboration of *trans*-cinnamaldehyde





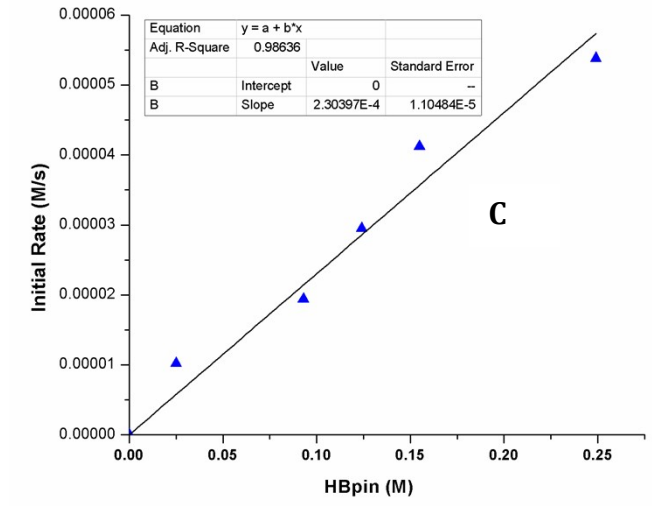
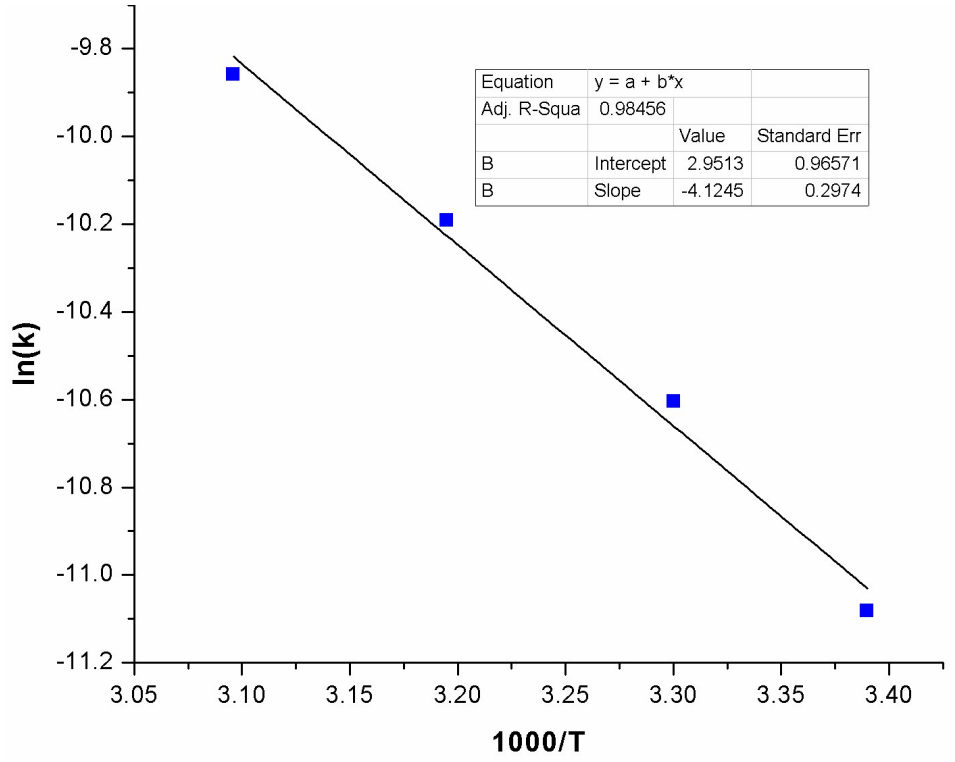


Figure S70: Variation of initial reaction rate with a concentration of Catalyst (A), Ketone (B), HBpin (C) for actinide catalyzed hydroboration reaction.



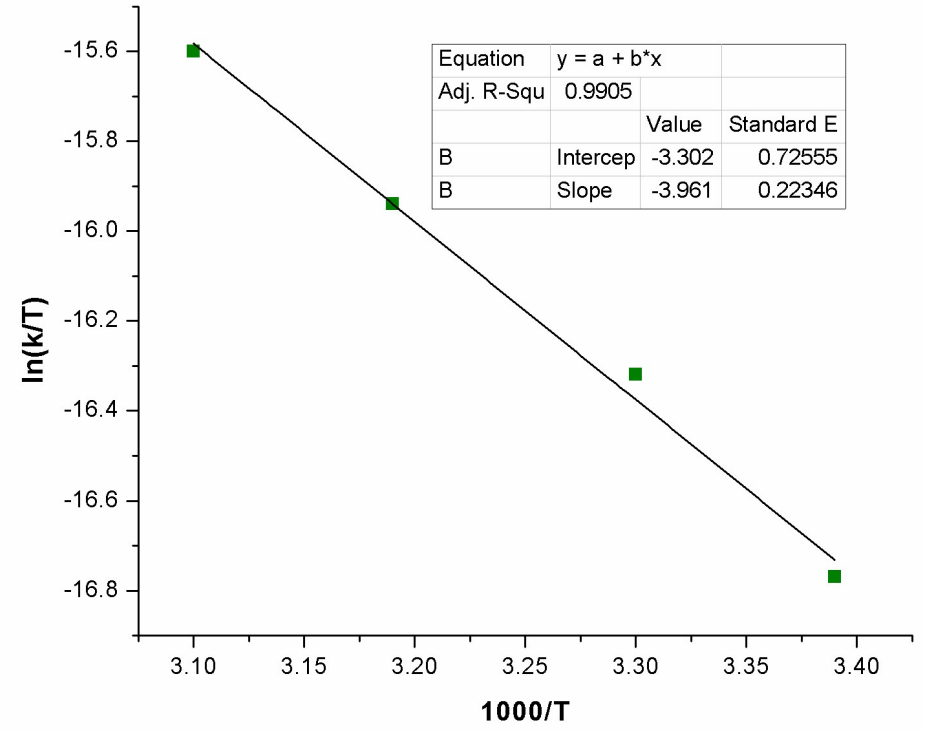


Figure S71: Plot of 1000/temperature vs ln(k) (top), 1000/temperature vs ln(k/T) (bottom) for actinide catalyzed hydroboration reaction.

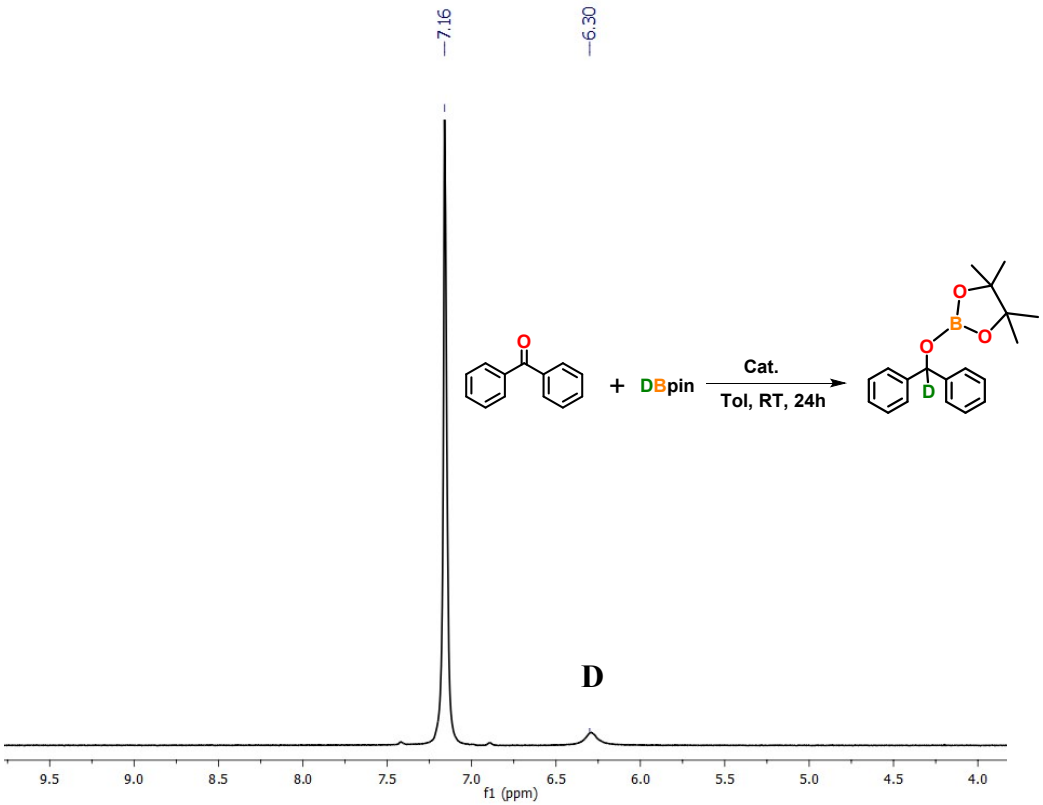


Figure S72: ^{2}H NMR spectrum of the hydroboration of benzophenone

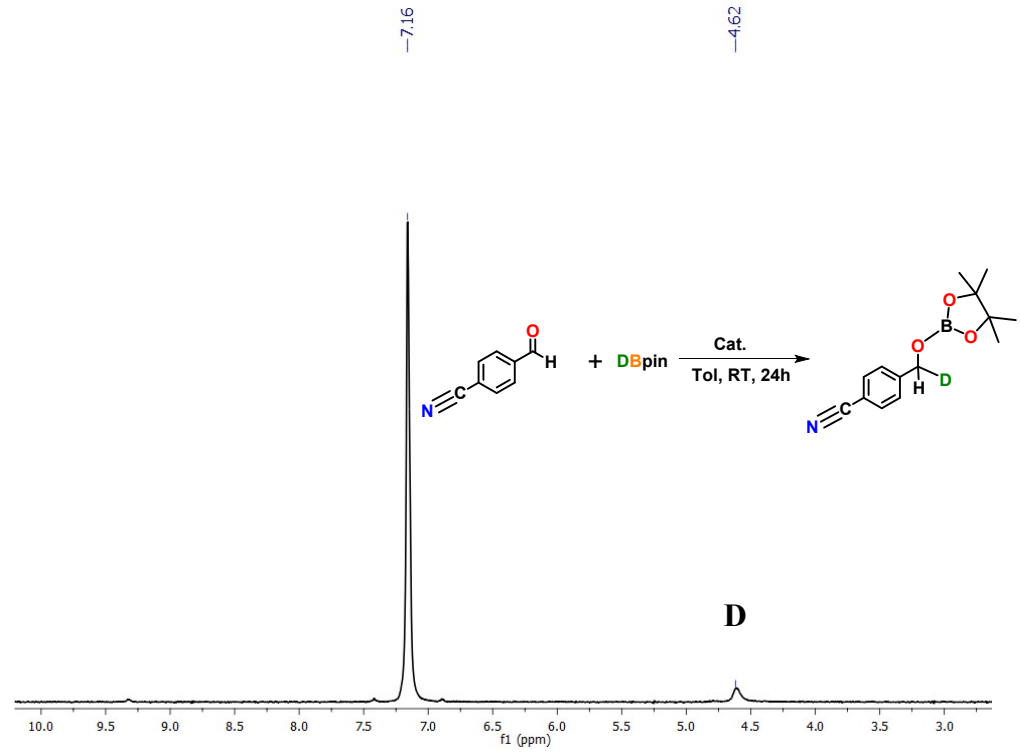


Figure S73: ^{2}H NMR spectrum of the hydroboration of *p*-cyanobenzaldehyde

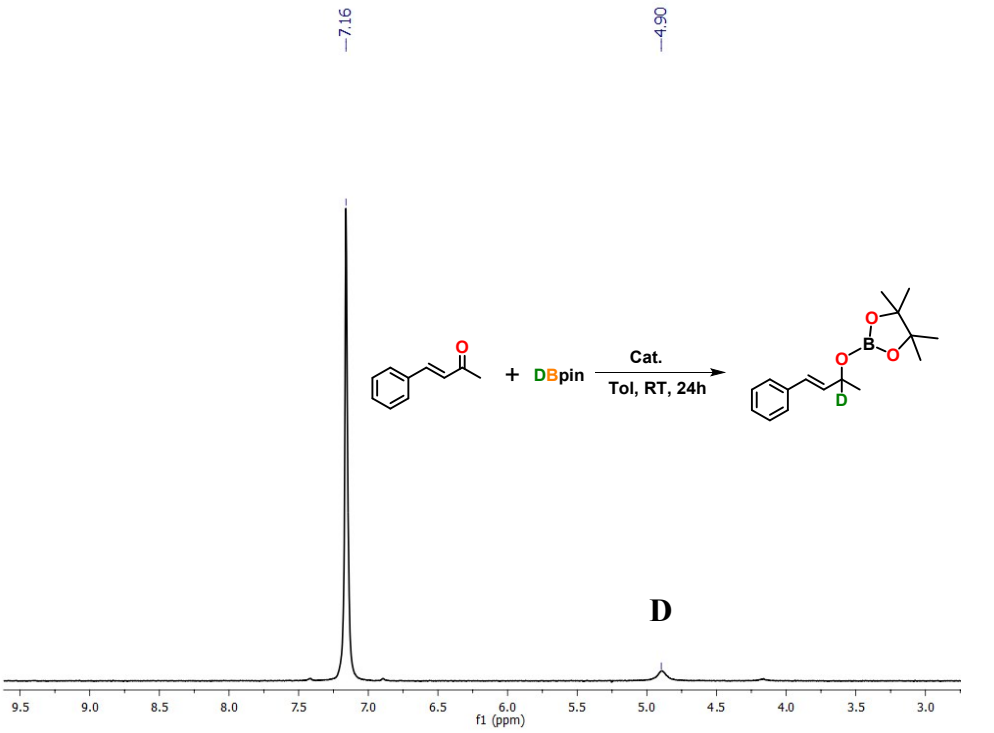


Figure S74: ^{2}H NMR spectrum of the hydroboration of benzylideneacetone

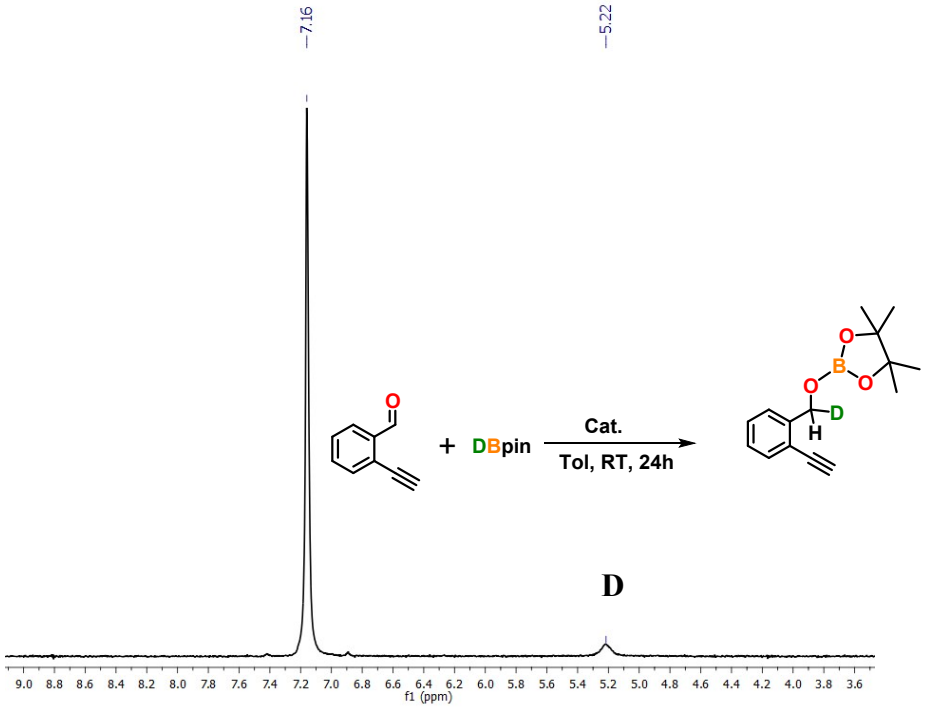


Figure S75: ^{2}H NMR spectrum of the hydroboration of 2-Ethynylbenzaldehyde

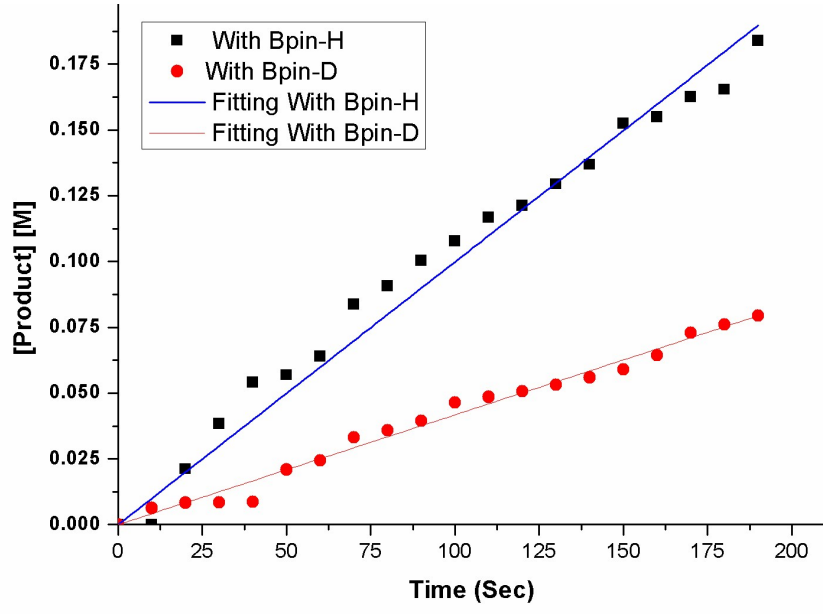


Figure S76: Kinetic isotopic effect on the hydroboration reaction of a ketone with [HBpin] and [DBpin] promoted by complex **3**.

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