Supporting Information

Rapid, mild, and selective ketone and aldehyde hydroboration/reduction mediated by a simple lanthanum catalyst

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Materials and Methods. All manipulations of air-sensitive materials were carried out with rigorous exclusion of oxygen and moisture in flame- or oven-dried Schlenk-type glassware on a dual-manifold Schlenk line, interfaced to a high-vacuum line (10^{-6} Torr), or in an argon-filled vacuum atmospheres glovebox with a high capacity recirculator (<1 ppm O_2). Benzene-d6 (Cambridge Isotope Laboratories; 99+ atom % D) was stored over Na/K alloy and vacuum transferred immediately prior to use. $La[N(SiMe_3)_2]_3$ (La^{NTMS})and hexamethylbenzene were purchased from Sigma-Aldrich Co. and sublimed under high-vacuum (10^{-6} Torr). Pinacolborane ("HBpin") was purchased from Sigma-Aldrich Co. and distilled under high-vacuum (10^{-6} Torr). Carbonyl-containing substrates were purchased from Sigma-Aldrich Co. and dried over 3Å molecular sieves and distilled off prior to use (for liquid substrates) or dried under vacuum (for solid substrates). Known boryl esters were characterized by ^{1}H, ^{13}C, and ^{11}B NMR and compared to literature values. Unknown boryl esters were also fully characterized by NMR, and then hydrolyzed by refluxing in 1*M* NaOH/H_2O and MeOH for 1 hour (for dicyclohexyl methanol and phenyl cyclohexyl methanol) or by refluxing with silica gel and H_2O for 3 hours (for perflouorodiphenyl methanol and 2-ethynyl benzyl alcohol). The product was extracted with DCM and the organic layer was dried over $MgSO_4$, and the solvent was removed by rotary evaporation. If necessary, the crude was purified by column chromatography, using 30% THF in hexanes. The resulting alcohol was characterized by ^{1}H and ^{13}C NMR and EI- or ESI-MS.

Physical and Analytical Measurements. NMR spectra were recorded on a Bruker Avance III (500 MHz, ^{1}H ; 125 MHz, ^{13}C), Varian Inova 500 (500 MHz, ^{1}H; 125 MHz, ^{13}C), Agilent DD MR-400

(400 MHz, ^{1}H; 100 MHz, ^{13}C; 128 MHz, ^{11}B), or Agilent DD2 500 (500 MHz, ^{1}H ; 125 MHz, ^{13}C). Chemical shifts (δ) for ^{1}H and ^{13}C are referenced to residual solvent resonances (7.16 and 128.06 ppm, resp., for benzene-d_6). ^{11}B shifts are referenced to an external $BF_3 \cdot OEt_2$ standard. NMR scale reactions were carried out either in Teflon-sealed J. Young tubes or PTFE septum-sealed tubes. Mass spectra were recorded on a Bruker AmaZon SL LC-MS (ESI, Quadrupole ion trap) or Agilent 5973 GC-MS (EI, Quadrupole ion trap).

Typical NMR-Scale Reaction of HBpin with Solid Ketones and Aldehydes and La^{NTMS} Catalyst. In a glovebox, the aldehyde/ketone (0.25 mmol) was massed in a vial. 500 μL of a stock solution containing HBpin (0.30 mmol, 1.2 equivalents vs. aldehyde/ketone) and the internal standard hexamethylbenzene (50 μmol) was added to the vial, and the vial was shaken until all solids were dissolved. This solution was added to a J. Young tap NMR tube, and 100 μL of a stock solution containing an appropriate loading of $La[N(SiMe_3)_2]_3$ was added. The tube was capped and shaken, and the reaction was monitored by ^{1}H NMR.

Typical NMR-Scale Reaction of HBpin with Liquid Ketones and Aldehydes and La^{NTMS} Catalyst. In a glovebox, 100 μL of a stock solution containing an appropriate loading of $La[N(SiMe_3)_2]_3$ was added to a septum-sealed NMR tube. 500 μL of a stock solution containing HBpin (0.30 mmol, 1.2 equivalents vs. aldehyde/ketone) and the internal standard hexamethylbenzene (50 μmol) was added to a septum-sealed vial, and both were brought out of the glovebox. The liquid aldehyde/ketone (0.25 mmol) was injected into the vial with HBpin and standard, the vial was shaken, and the contents were injected into the NMR tube with catalyst, all under N_2. The tube was shaken, and the reaction was monitored by ^{1}H NMR.

Scale-Up/Air and Moisture Tolerance Test Reaction. Benzophenone (1.0 g, 5.5 mmol) and HBpin (0.96 mL, 6.6 mmol) were dissolved in benzene (5 mL) in a vial outside of a glovebox. To this solution was added La^{NTMS} (34 mg, 0.055 mmol). After stirring for 5 minutes, volatiles were removed in vacuo, and the resulting white powder was taken up in 10 mL of 10% NaOH in MeOH. The mixture was sonicated and refluxed for 1 hour. The product (diphenylmethanol) was extracted in ethyl acetate and purified by column chromatography (1:5 THF:hexanes). Final yield of diphenylmethanol: 0.87g (86%).

Typical NMR-Scale Reaction for Kinetic Monitoring by ^{1}H-NMR Arrays. In a glovebox, 500 μL of a stock solution of aldehyde/ketone and 500 μL of a stock solution containing HBpin and the internal standard, hexamethylbenzene (50 μmol), were mixed in a vial. This solution was then added to a rubber septum-sealed NMR tube, wrapped with parafilm, and removed from the box. At the NMR, the magnet was locked, tuned, and shimmed to the sample, then 100 μL of a stock solution containing an appropriate loading of $La[N(SiMe_3)_2]_3$ was added. The tube was shaken and reinserted into the instrument and scanning was begun. Single (^{1}H NMR) scans were collected at regular intervals. Substrate and/or product concentrations were determined relative to the intensity of the internal standard resonance plotted versus time.

Kinetic Analysis. Kinetic analysis of the NMR-scale reactions described above was carried out by collecting multiple (>15) data points early in the reaction (<20% conversion). Under these conditions, the reaction can be approximated as pseudo-zero-order with respect to the substrate concentrations. The product concentration was measured from the area of the $R_2CHOBpin$ or RCH_2OBpin peak formed in the product standardized to the methyl peak area of the C_6Me_6 internal standard. Data were fit by least-squares analysis ($R^2 > 0.98$) according to eq S1, where t is time, [product] is the concentration of product at time t, and m is the rate of reaction.

$$[product] = mt \qquad \text{(Eq. S1)}$$

Orders for each reactant were determined from the average rates (≥3 trials) at varying concentrations. Ketone/ aldehyde and HBpin concentrations were varied from 25% to 125% (relative to the other reactant) and catalyst concentration was measured at 0.05%, 0.10%, 0.15%, and 0.20% (for dicyclohexylketone) or 0.025%, 0.05%, 0.075%, and 0.1% (for cyclohexylcarboxaldehyde). (Note: in general, ketones react more quickly than aldehydes, except in the case of dicyclohexylketone). These data

were then plotted as ln(rate) vs. ln[ketone].[1] The negative rate of disappearance of ketone is proportional to the concentration of ketone to the order (α) (see eq. S2). Therefore, the order is the slope of a plot of ln(rate) vs. ln[ketone] (eq. S3).

$$\frac{-d[ketone]}{dt} = k_{obs}[ketone]^{\alpha} \quad \text{(Eq. S2)}$$

$$\ln(rate) = lnk_{obs} + \propto \ln[ketone] \quad \text{(Eq. S3)}$$

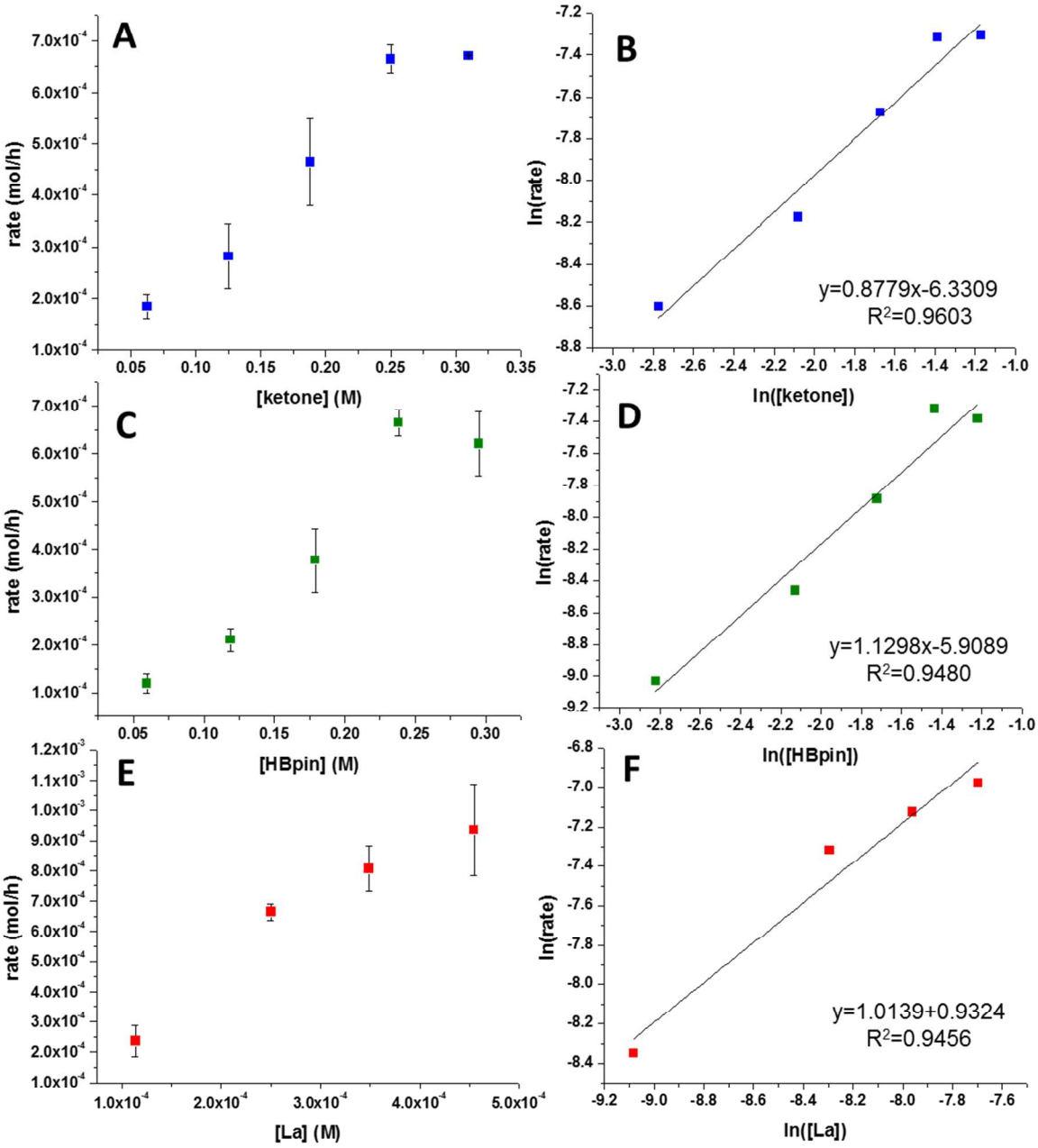


Figure S1. (A) Plot of concentration ketone vs. reaction rate (mol/h); (B) Plot for reaction rate law order in [ketone]; (C) Plot of concentration HBpin vs. rate (mol/h); (D) Plot for reaction rate law order in [HBpin]; (E) Plot of concentration **La**^{NTMS} vs. rate (mol/h); (F) Plot for reaction rate law order in **La**^{NTMS}.

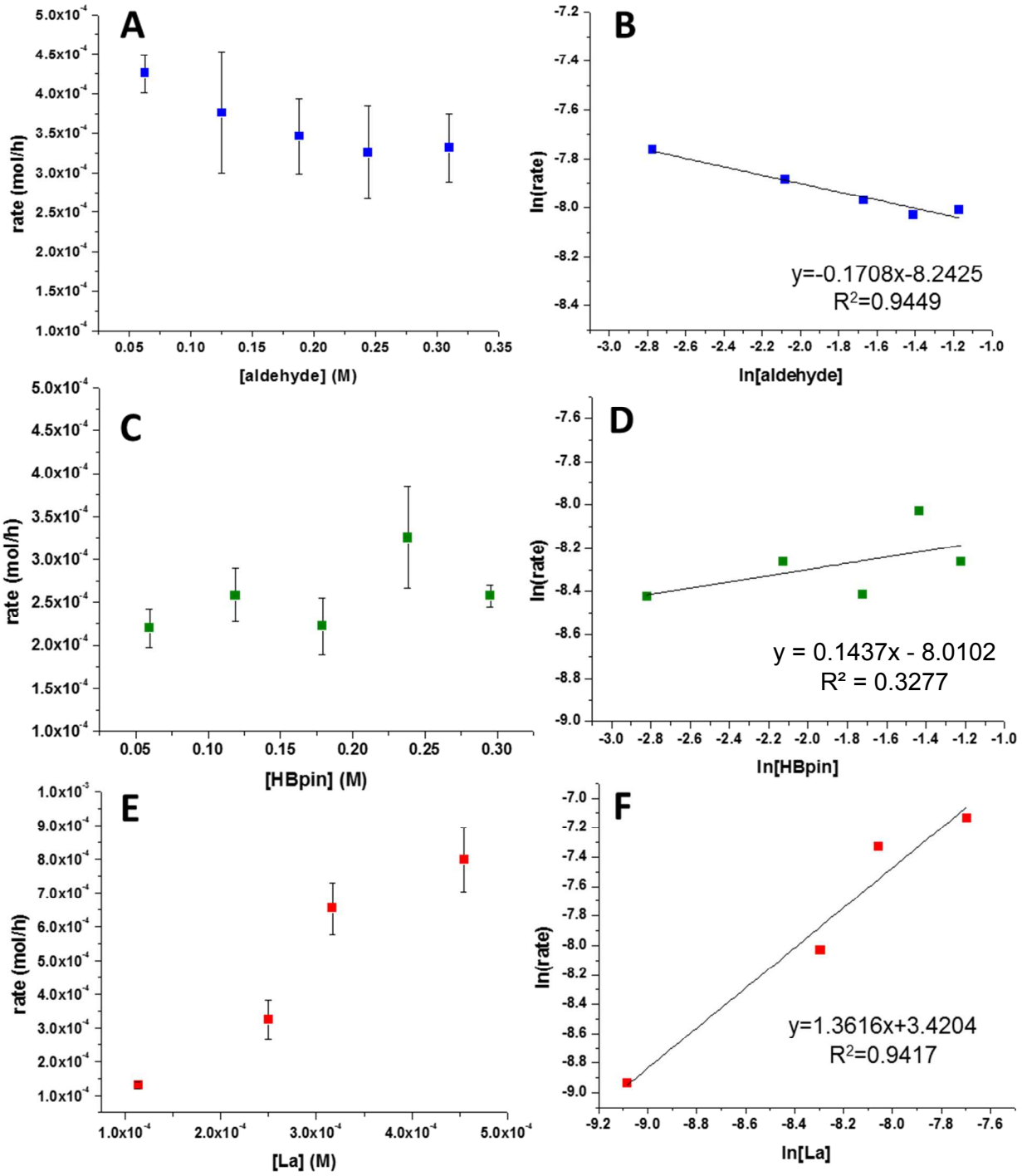


Figure S2. (A) Plot of concentration aldehyde vs. reaction rate (mol/h); (B) plot for reaction rate law order in [aldehyde]; (C) Plot of concentration HBpin vs. rate (mol/h); (D) plot for reaction rate law order

in [HBpin]; (E) Plot of concentration $\mathbf{La}^{\mathbf{NTMS}}$ vs. rate (mol/h); (F) plot for reaction rate law order in $\mathbf{La}^{\mathbf{NTMS}}$.

Temperature Analysis. Data on the rate dependence on temperature was obtained as shown above. A rate at each temperature were determined from the average rates (≥3 trials) at temperatures set on the NMR and measured using a methanol (<25°C) or ethylene glycol (>25°C) standard.

These data were then plotted as 1000/T vs. ln(k/T)[1] from which the enthalpy and entropy of the transition state could be obtained using the Eyring equation (see eq. S4). $\Delta H^{\neq}$ is the negative slope times R and $\Delta S^{\neq}$ is the intercept minus the natural log of k_b/h times R.

$$\ln\frac{k}{T} = \frac{\Delta H^{\neq}}{RT}\left[\frac{\Delta S^{\neq}}{R} - \ln\frac{k_b}{h}\right] \qquad \text{(Eq. S4)}$$

From a plot of 1000/T vs. ln(k), the activation energy can be obtained using the Arrhenius equation (eq. S5). E_a is the negative slope times R.

$$\ln k = -\frac{E_a}{RT} - \ln A \qquad \text{(Eq. S5)}$$

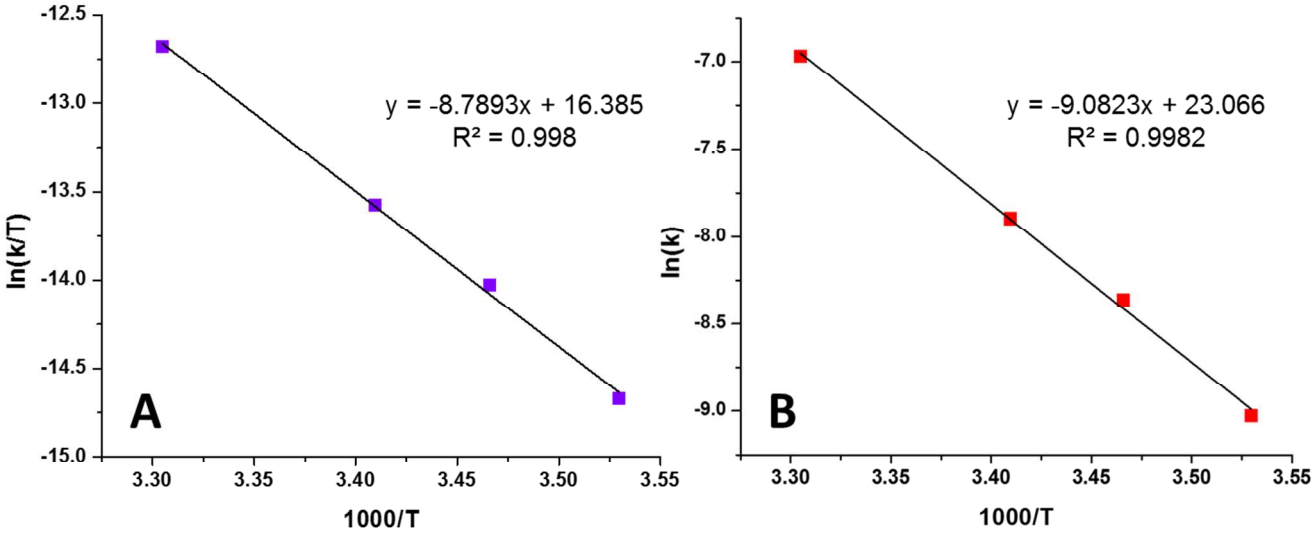


Figure S3. (A) Plot of 1000/temperature vs. ln(k/T) for the lanthanum-catalyzed hydroboration of dicyclohexylketone. (B) Plot of 1000/temperature vs. ln (k).

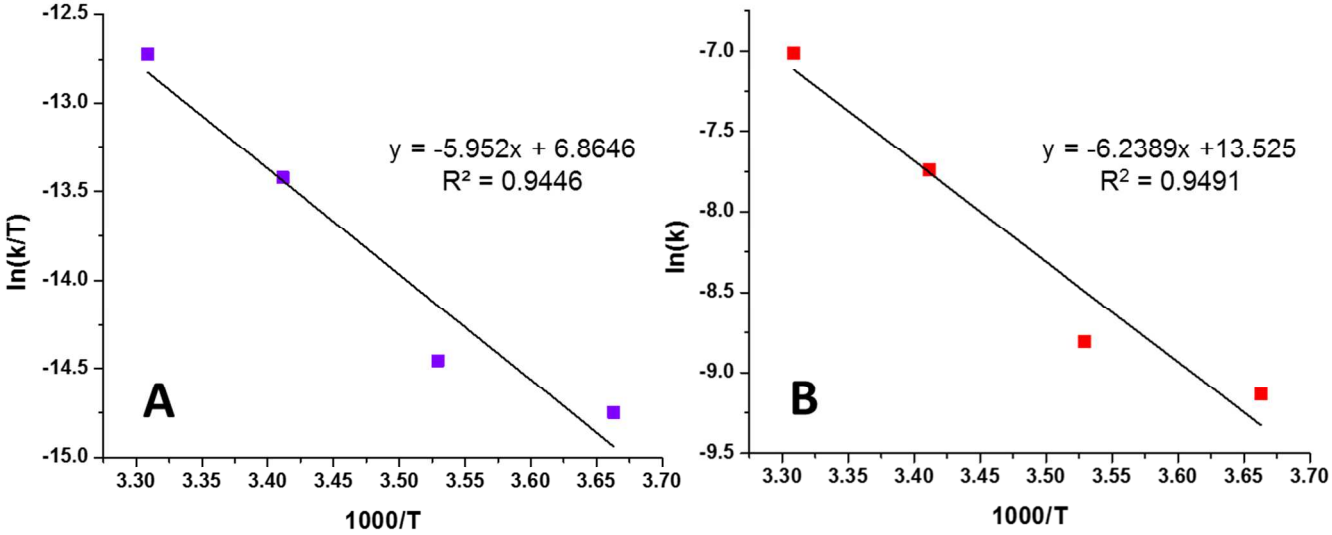
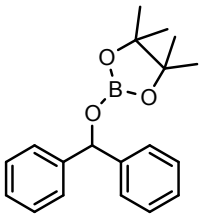


Figure S4. (A) Plot of 1000/temperature vs. ln(k/T) for the lanthanum-catalyzed hydroboration of cyclohexylcarboxaldehyde. (B) Plot of 1000/temperature vs. ln (k).

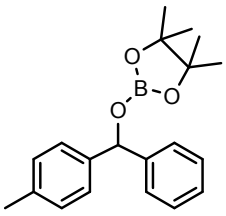
Characterization Data for Ketone/Aldehyde Hydroboration Products



2-(diphenylmethoxy)pinacolborane.

^{1}H, $^{11}B\{^{1}H\}$ and $^{13}C\{^{1}H\}$ spectra are identical to those reported in the literature.[2]

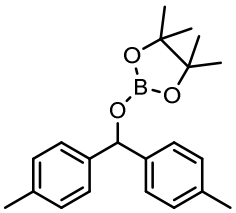
^{1}H NMR (C_6D_6, 500 MHz): 7.45-7.41 (m, 4H), 7.12-7.07 (m, 4H), 7.03-6.98 (tt, 2H, $^{3}J_{HH}$ = 7.4, $^{4}J_{HH}$ = 1.2), 6.41 (s, 1H), 0.98 (s, 12H). **$^{11}B\{^{1}H\}$ NMR (C_6D_6, 128 MHz):** 22.83. **$^{13}C\{^{1}H\}$ NMR (C_6D_6, 125 MHz):** 143.89, 128.57, 127.54, 126.97, 82.85, 78.53, 24.62.



2-(*para*-tolylphenylmethoxy)pinacolborane.

^{1}H, $^{11}B\{^{1}H\}$ and $^{13}C\{^{1}H\}$ spectra are identical to those reported in the literature.[3]

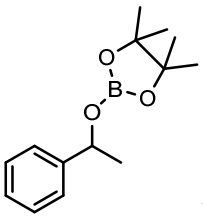
^{1}H NMR (C_6D_6, 500 MHz): 7.46 (d, 2H, $^{3}J_{HH}$= 7.7 Hz), 7.37 (d, 2H, $^{3}J_{HH}$= 7.7 Hz), 7.11 (t, 2H, $^{3}J_{HH}$= 7.5 Hz), 7.01 (t, 1H, 7.5 Hz), 6.93 (d, 2H, $^{3}J_{HH}$= 7.7 Hz), 6.43 (s, 1H), 2.05 (s, 3H), 0.99 (s, 12H). **$^{11}B\{^{1}H\}$ NMR (C_6D_6, 128 MHz):** 22.86. **$^{13}C\{^{1}H\}$ NMR (C_6D_6, 125 MHz):** 144.15, 141.10, 136.93, 129.28, 128.54, 127.46, 127.01, 126.94, 82.80, 78.43, 24.64, 21.06



2-(di-*para*-tolylmethoxy)pinacolborane.

^{1}H, $^{11}B\{^{1}H\}$ and $^{13}C\{^{1}H\}$ spectra are identical to those reported in the literature.[4]

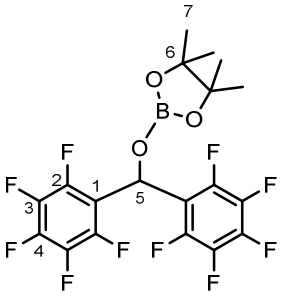
^{1}H NMR (C_6D_6, 500 MHz): 7.39 (d, 4H, $^{3}J_{HH}$= 7.7 Hz), 6.94 (d, 4H, $^{3}J_{HH}$= 7.7 Hz), 6.44 (s, 1H), 2.05 (s, 6H), 1.00 (s, 12H). **$^{11}B\{^{1}H\}$ NMR (C_6D_6, 128 MHz):** 22.84. **$^{13}C\{^{1}H\}$ NMR (C_6D_6, 125 MHz):** 141.35, 136.82, 129.24, 126.99, 82.76, 78.33, 24.66, 21.06



2-(1-phenylethoxy)pinacolborane.

^{1}H, $^{11}B\{^{1}H\}$ and $^{13}C\{^{1}H\}$ spectra are identical to those reported in the literature.[2]

^{1}H NMR (C_6D_6, 500 MHz): 7.37-7.33 (m, 2H), 7.17-7.11 (m, 2H), 7.08-7.02 (tt, ^{1}H, $^{3}J_{HH}$ = 7.4, $^{4}J_{HH}$ = 2.1 Hz), 5.39 (q, 1H, $^{3}J_{HH}$ = 6.4 Hz), 1.45 (d, 3H, $^{3}J_{HH}$ = 6.5 Hz), 1.00 (s, 12H). **$^{11}B\{^{1}H\}$ NMR (C_6D_6, 128 MHz):** 22.52. **$^{13}C\{^{1}H\}$ NMR (C_6D_6, 125 MHz):** 145.39, 128.54, 127.35, 125.70, 82.54, 72.94, 25.79, 24.70, 24.62.

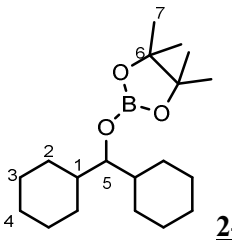


2-(di-perfluorophenylmethoxy)pinacolborane.

^{1}H NMR (C_6D_6, 500 MHz): 6.90 (s, 1H, H-*5*), 1.03 (s, 12H, H-*7*). **$^{11}B\{^{1}H\}$ NMR (C_6D_6, 128 MHz):** 22.62. **$^{13}C\{^{1}H\}$ NMR (C_6D_6, 125 MHz):** 145.13 (dm, C-*Ar* , J=253.6 Hz), 141.60 (dt, C-*Ar*, J= 255.4 Hz, J= 13.2 Hz), 137.92 (dt, C-*Ar*, J=250.7 Hz, J=14.1 Hz), 131.78 (s, C-*1*), 84.14 (s, C-*6*), 62.77 (s, C-*5*), 24.45 (s, C-*7*).

Perfluorodiphenylmethanol. 62% isolated yield.

^{1}H NMR (C_6D_6, 500 MHz): 5.94 (d, 1H, H-5, $^{3}J_{HH}$ = 5.8 Hz), 2.20 (d, 1H, O*H*, $^{3}J_{HH}$ = 5.8 Hz). **$^{19}F\{^{1}H\}$ NMR (C_6D_6, 376 MHz)**: -143.5 - -143.8 (m, 2F), -153.8 (t, 1F, J=22Hz), -161.6 - -162.0 (m, 2F). **$^{13}C\{^{1}H\}$ NMR (C_6D_6, 125 MHz)**: 144.4 (dm, C-*Ar* , J=253 Hz), 140.9 (dm, C-*Ar*, J= 255 Hz), 137.4 (dm, C-*Ar*, J=251 Hz), 125.5 (s, C-*Ar*), 113.7 (s, *C*-OH). **LC-MS:** $[2M-H]^-$: Calc: 726.9813. Found: 726.9818

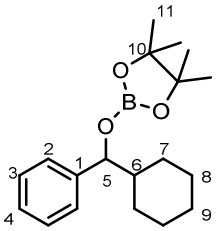


2-(dicyclohexylmethoxy)pinacolborane.

^{1}H NMR (C_6D_6, 500 MHz): 3.78 (t, 1H, H-*5*, $^{3}J_{HH}$ = 6.0 Hz), 1.89-1.82 (m, 2H, H-*1*), 1.75-1.66 (m, 4H, H-*Cy*), 1.64-1.49 (m, 6H, H-*Cy*), 1.29-1.07 (m, 10H, H-*Cy*), 1.10 (s, 12H, H-*7*). **^{11}B{^{1}H} NMR (C_6D_6, 128 MHz):** 22.46. **^{13}C{^{1}H} NMR (C_6D_6, 125 MHz):** 82.79 (C-*6*), 82.14 (C-*5*), 39.66 (C-*1*), 30.19 (C-*Cy*), 27.64 (C-*Cy*), 26.94 (C-*Cy*), 26.82 (C-*Cy*), 26.58 (C-*Cy*), 24.68 (C-*Cy*).

Dicyclohexylmethanol. 92% isolated yield.

^{1}H NMR (C_6D_6, 500 MHz): 2.88 (q, 1H, H-*5*, $^{3}J_{HH}$ = 5.7 Hz), 1.85-1.78 (m, 2H, H-*Cy*), 1.77-1.67 (m, 4H, H-*Cy*), 1.66-1.60 (m, 2H, H-*Cy*), 1.51-1.44 (m, 2H, H-*Cy*), 1.40-1.31 (m, 2H, H-*Cy*), 1.25-0.97 (m, 10H, H-*Cy*), 0.81-0.76 (m, 1H, H-O*H*). **^{13}C{^{1}H} NMR (C_6D_6, 125 MHz):** 80.13 (C-*5*), 40.30 (C-*1*), 30.33 (C-*Cy*), 27.69 (C-*Cy*), 27.02 (C-*Cy*), 26.96 (C-*Cy*), 26.65 (C-*Cy*). **GC-MS** $[M\text{-}H_2O]^{+}$**:** Calc: 178.17; Found: 178.25.

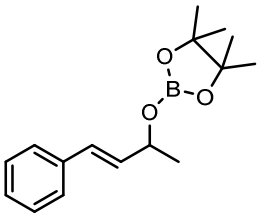


2-(cyclohexylphenylmethoxy)pinacolborane.

^{1}H NMR (C_6D_6, 500 MHz): 7.38-7.33 (m, 2H, H-*2*), 7.20-7.12 (m, 2H, H-*3*), 7.10-7.04 (m, ^{1}H, H-*4*), 5.03 (d, 1H, H-*5*, $^{3}J_{HH}$ = 6.4 Hz), 2.03-1.94 (m, ^{1}H, H-*6*), 1.75-1.45 (m, 6H, H-*Cy*), 1.25-1.05 (m, 4H, H-*Cy*), 1.03 (s, 6H, H-*11*), 0.99 (s, 6H, H-*11*). **^{11}B{^{1}H} NMR (C_6D_6, 128 MHz):** 22.60. **^{13}C{^{1}H} NMR (C_6D_6, 125 MHz):** 143.13 (C-*1*), 128.25 (C-*Ar*), 127.38 (C-*Ar*), 127.05 (C-*Ar*), 82.47 (C-*10*), 81.48 (C-*5*), 45.45 (C-*6*), 29.65 (C-*Cy*), 28.63 (C-*Cy*), 26.78 (C-*Cy*), 26.47 (C-*Cy*), 26.40 (C-*Cy*), 24.64 (C-*Cy*).

Cyclohexyl(phenyl)methanol. 83% isolated yield.

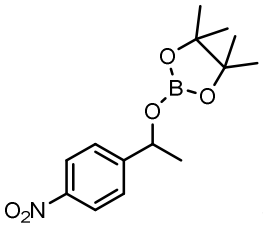
^{1}H NMR (C_6D_6, 500 MHz): 7.22-7.17 (m, 4H, H-*Ar*), 7.12-7.08 (m, 1H, H-*Ar*), 4.10 (dd, 1H, H-*5*, $^{3}J_{HH}$ = 6.8 Hz, $^{4}J_{HH}$ = 3.3 Hz), 2.04-1.98 (m, 1H, H-*6*), 1.72-1.65 (m, 1H, H-*Cy*), 1.61-1.48 (m, 3H, H-*Cy*), 143-1.36 (m, 1H, H-*Cy*), 1.19 (d, 1H, H-*Cy*, $^{3}J_{HH}$ = 3.4 Hz), 1.18-0.98 (m, 4H, H-*Cy*), 0.94-0.85 (m, 1H, H-*Cy*). **^{13}C{^{1}H} NMR (C_6D_6, 125 MHz):** 144.61 (C-*1*), 127.40 (C-*Ar*), 126.99 (C-*Ar*), 79.15 (C-*5*), 45.54 (C-*6*), 29.71 (C-*Cy*), 28.92 (C-*Cy*), 26.86 (C-*Cy*), 26.54 (C-*Cy*), 26.47 (C-*Cy*). **GC-MS** $[M]^{+}$**:** Calc: 190.14; Found: 190.20.



2-(1-cinnamylethoxy)pinacolborane.

^{1}H, ^{11}B{^{1}H} and ^{13}C{^{1}H} spectra are identical to those reported in the literature.[2]

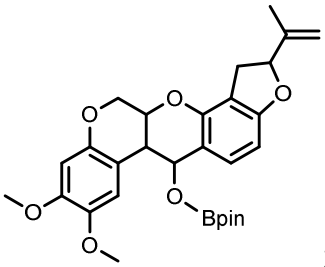
^{1}H NMR (C_6D_6, 500 MHz): 7.22-7.17 (m, 2H), 7.12-7.06 (m, 2H), 7.05-6.99 (m, 1H), 6.64 (dd, 1H, $^{3}J_{HH}$ = 16 Hz, $^{4}J_{HH}$ = 0.95 Hz), 6.19 (dd, 1H, $^{3}J_{HH}$ = 16 Hz, $^{3}J_{HH}$ = 5.9 Hz), 4.98 (ddq, 1H, $^{3}J_{HH}$ = 6.2 Hz, $^{3}J_{HH}$ = 6.4 Hz, $^{4}J_{HH}$ = 1.2 Hz), 1.33 (d, 3H, $^{3}J_{HH}$ = 6.4 Hz), 1.06 (d, 12H, $^{3}J_{HH}$ = 2.3 Hz) **^{11}B{^{1}H} NMR (C_6D_6, 128 MHz):** 22.50. **^{13}C{^{1}H} NMR (C_6D_6, 125 MHz):** 137.43, 132.72, 129.49, 128.76, 127.65, 126.88, 82.51, 71.47, 24.95, 24.80, 24.67, 23.43.



2-(1-(4-nitrophenyl)ethoxy)pinacolborane.

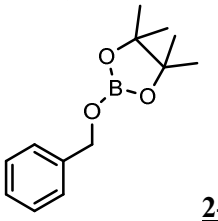
^{1}H, ^{11}B{^{1}H} and ^{13}C{^{1}H} spectra are identical to those reported in the literature.[2]

^{1}H NMR (C_6D_6, 500 MHz): 7.80-7.72 (m, 2H), 7.00-6.92 (m, 2H), 5.13 (q, ^{1}H, $^{3}J_{HH}$ = 6.5 Hz), 1.20 (d, 3H, $^{3}J_{HH}$ = 6.5 Hz), 0.94 (s, 12H). **^{11}B{^{1}H} NMR (C_6D_6, 128 MHz):** 22.43. **^{13}C{^{1}H} NMR (C_6D_6, 125 MHz):** 151.82, 147.47, 126.09, 123.64, 82.94, 71.96, 25.33, 24.62.



2-(Rotenoxy)pinacolborane.

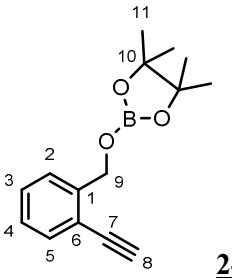
^{1}H NMR (C_6D_6, 500 MHz): 7.26 (d, 1H, J=8.2 Hz), 6.71 (s, 1H), 6.60 (d, 1H, J=8.2 Hz), 6.51 (s, 1H), 5.48 (d, 1H, J=4.0), 5.08-5.05 (m, 1H), 4.96 (t, 1H, J=8.8 Hz), 4.89 (t, 1H, J=10 Hz), 4.76-4.73 (m, 1H), 4.67-4.61 (m, 1H), 4.17 (ddd, 1H, J=1.2, 4.8, 9.8 Hz), 3.59 (s, 3H), 3.31 (s, 3H), 3.12-3.01 (m, 2H), 2.93-2.85 (m, 1H), 1.58 (s, 3H), 0.95 (s, 6H), 0.92 (s, 6H). **^{11}B{^{1}H} NMR (C_6D_6, 128 MHz):** 22.29. **^{13}C{^{1}H} NMR (C_6D_6, 125 MHz):** 162.60, 150.67, 150.19, 150.12, 144.54, 144.40, 130.38, 114.64, 113.96, 113.20, 111.15, 109.91, 102.88, 101.54, 86.70, 82.67, 70.17, 69.41, 65.45, 56.63, 55.36, 38.03, 32.57, 24.80, 24.31, 17.32. **LC-MS** $[M+Na]^+$ Calc.: 545.232, Found: 545.233



2-(benzyloxy)pinacolborane.

^{1}H, ^{11}B{^{1}H} and ^{13}C{^{1}H} spectra are identical to those reported in the literature.[2]

^{1}H NMR (C_6D_6, 500 MHz): 7.32-7.28 (m, 2H), 7.16-7.10 (m, 2H), 7.08-7.02 (m, 1H), 4.94 (s, 2H), 1.04 (s, 12H). **^{11}B{^{1}H} NMR (C_6D_6, 128 MHz):** 22.79. **^{13}C{^{1}H} NMR (C_6D_6, 125 MHz):** 140.1, 128.59, 127.57, 127.05, 82.75, 66.96, 24.70.



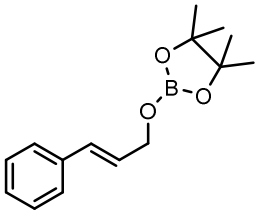
2-(2-ethynylbenzyloxy)pinacolborane.

^{1}H NMR (C_6D_6, 500 MHz): 7.61 (m, 1H), 7.35 (dd, 1H, $^{3}J_{HH}$= 7.7 Hz), 7.04 (dt, 1H, $^{3}J_{HH}$= 7.7 Hz, $^{4}J_{HH}$ = 0.96 Hz), 6.86 (m, 1H), 5.34 (s, 2H) 2.89 (s, 1H), 1.03 (s, 12H). **^{11}B{^{1}H} NMR (C_6D_6, 128 MHz):** 22.76.

$^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): 142.45, 132.67, 129.22, 127.10, 126.24, 119.94, 82.83, 81.11, 65.26, 24.68

2-ethynylbenzyl alcohol. 77% isolated yield.

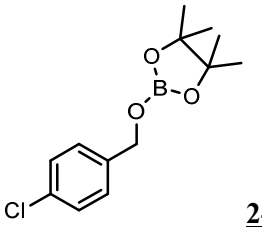
^1H NMR (C_6D_6, 500 MHz): 7.38 (dd, 1H, H-*2*, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 0.9 Hz), 7.32 (d, 1H, H-*5*, $^3J_{HH}$ = 7.7 Hz), 7.01 (dt, 1H, H-*3*, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.1 Hz), 6.85 (t, 1H, H-*4*, $^3J_{HH}$ = 7.7 Hz), 4.67 (s, 2H, H-*9*), 2.85 (s, 1H, H-*8*), 1.42 (br s, 1H, O*H*). **$^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz):** 144.34 (C-*1*), 132.82 (C-*Ar*), 129.23 (C-*Ar*), 127.15 (C-*Ar*), 127.00 (C-*Ar*), 120.22 (C-*6*), 82.37 (C-*9*), 81.53 (C-*7*), 63.43 (C-*8*). **GC-MS** $[M]^+$**:** Calc: 132.06; Found: 132.10.



2-(cinnamylmethoxy)pinacolborane.

^1H, $^{11}B\{^1H\}$ and $^{13}C\{^1H\}$ spectra are identical to those reported in the literature.[5]

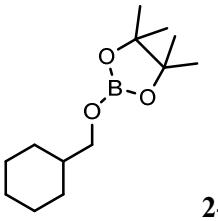
^1H NMR (C_6D_6, 500 MHz): 7.22-7.16 (m, 2H), 7.13-7.07 (m, 2H), 7.06-7.00 (m, 1H), 6.62 (dt, 1H, $^3J_{HH}$ = 15.9 Hz, $^4J_{HH}$ = 1.7 Hz), 6.19 (dt, 1H, $^3J_{HH}$ = 15.9 Hz, $^3J_{HH}$ = 5.3 Hz), 4.55 (dd, 2H, $^3J_{HH}$ = 5.3 Hz, $^4J_{HH}$ = 1.7 Hz), 1.08 (s, 12H). **$^{11}B\{^1H\}$ NMR (C_6D_6, 128 MHz):** 22.70. **$^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz):** 137.36, 130.91, 128.76, 127.69, 127.52, 126.85, 82.70, 65.54, 24.74.



2-(4-chlorobenzyloxy)pinacolborane.

^1H, $^{11}B\{^1H\}$ and $^{13}C\{^1H\}$ spectra are identical to those reported in the literature.[2]

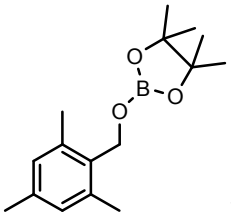
^1H NMR (C_6D_6, 500 MHz): 7.09-7.04 (m, 2H), 7.02-6.96 (m, 2H), 4.76 (s, 2H), 1.03 (s, 12H). **$^{11}B\{^1H\}$ NMR (C_6D_6, 128 MHz):** 22.64. **$^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz):** 138.46, 133.35, 128.71, 128.40, 82.87, 66.09, 24.69.



2-(cyclohexylmethoxy)pinacolborane.

^1H, $^{11}B\{^1H\}$ and $^{13}C\{^1H\}$ spectra are identical to those reported in the literature.[2]

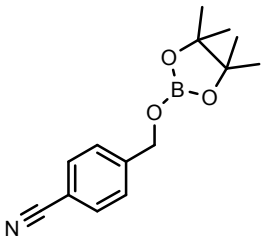
^1H NMR (C_6D_6, 500 MHz): 3.76 (d, 2H, $^3J_{HH}$ = 64 Hz), 1.75-1.67 (m, 2H), 1.65-1.57 (m, 2H), 1.56-1.45 (m, 2H), 1.18-1.04 (m, 3H), 1.07 (s, 12H), 0.97-0.84 (m, 2H). **$^{11}B\{^1H\}$ NMR (C_6D_6, 128 MHz):** 22.29. **$^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz):** 82.37, 70.60, 39.86, 29.74, 26.90, 26.18, 24.77.



2-(mesitylmethoxy)pinacolborane.

^{1}H, $^{11}B\{^{1}H\}$ and $^{13}C\{^{1}H\}$ spectra are identical to those reported in the literature.[6]

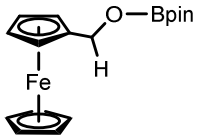
^{1}H NMR (C_6D_6, 500 MHz): 6.73 (s, 2H), 5.03 (s, 2H), 2.37 (s, 6H), 2.12 (s, 3H), 1.04 (s, 12H). **$^{11}B\{^{1}H\}$ NMR (C_6D_6, 128 MHz):** 22.58. **$^{13}C\{^{1}H\}$ NMR (C_6D_6, 125 MHz):** 137.78, 137.39, 132.98, 129.35, 82.53, 61.53, 24.70, 21.07, 14.64.



2-(4-cyanobenzyloxy)pinacolborane.

^{1}H, $^{11}B\{^{1}H\}$ and $^{13}C\{^{1}H\}$ spectra are identical to those reported in the literature.[4]

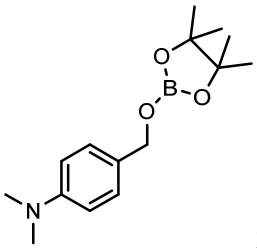
^{1}H NMR (C_6D_6, 500 MHz): 7.03-6.99 (m, 2H), 6.92-6.87 (m, 2H), 4.667 (s, 2H), 1.04 (s, 12H). **$^{11}B\{^{1}H\}$ NMR (C_6D_6, 128 MHz):** 22.66. **$^{13}C\{^{1}H\}$ NMR (C_6D_6, 125 MHz):** 144.57, 132.10, 126.78, 118.85, 111.61, 83.10, 65.84, 24.67.



2-(ferrocenylmethoxy)pinacolborane.

^{1}H, $^{11}B\{^{1}H\}$ and $^{13}C\{^{1}H\}$ spectra are identical to those reported in the literature.[2]

^{1}H NMR (C_6D_6, 500 MHz): 4.75 (s, 2H), 4.21 (dd, 2H, $^{3}J_{HH}$ = 1.9 Hz, $^{4}J_{HH}$ = 1.9 Hz), 3.98 (s, 5H), 3.95 (dd, 2H, $^{3}J_{HH}$ = 1.9 Hz, $^{4}J_{HH}$ = 1.9 Hz), 1.07 (s, 12H). **$^{11}B\{^{1}H\}$ NMR (C_6D_6, 128 MHz):** 22.67. **$^{13}C\{^{1}H\}$ NMR (C_6D_6, 125 MHz):** 86.08, 82.61, 69.02, 68.80, 68.52, 63.44, 24.82.



2-(4-N,N-dimethylaminobenzyloxy)pinacolborane

^{1}H, $^{11}B\{^{1}H\}$ and $^{13}C\{^{1}H\}$ spectra are identical to those reported in the literature.[4]

^{1}H NMR (C_6D_6, 500 MHz): 7.36-7.32 (m, 2H), 6.60-6.53 (m, 2H), 5.00 (s, 2H), 2.50 (s, 6H), 1.07 (s, 12H). **$^{11}B\{^{1}H\}$ NMR (C_6D_6, 128 MHz):** 22.80. **$^{13}C\{^{1}H\}$ NMR (C_6D_6, 125 MHz):** 150.16, 128.57, 112.42, 82.15, 66.85, 39.92, 24.39.

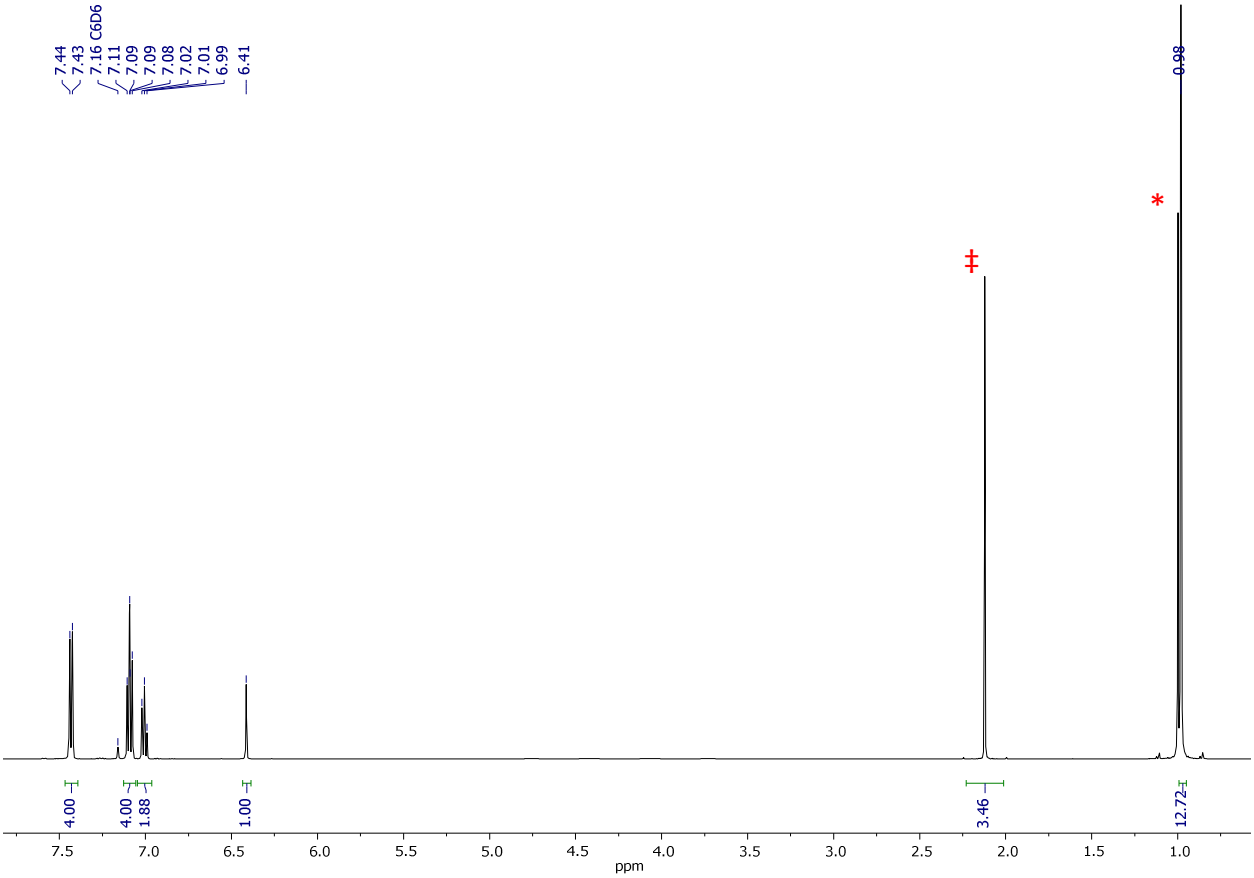
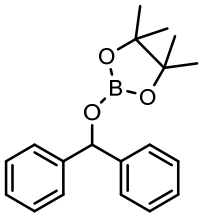


Figure S5. ^{1}H NMR spectrum of 2-(diphenylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



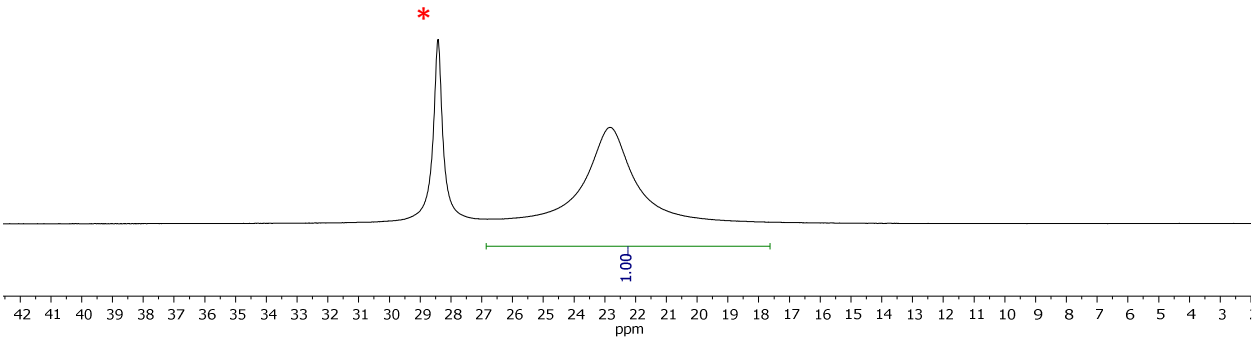
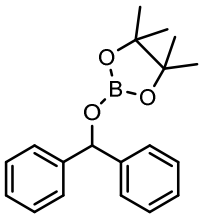


Figure S6. ^{11}B NMR spectrum of 2-(diphenylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



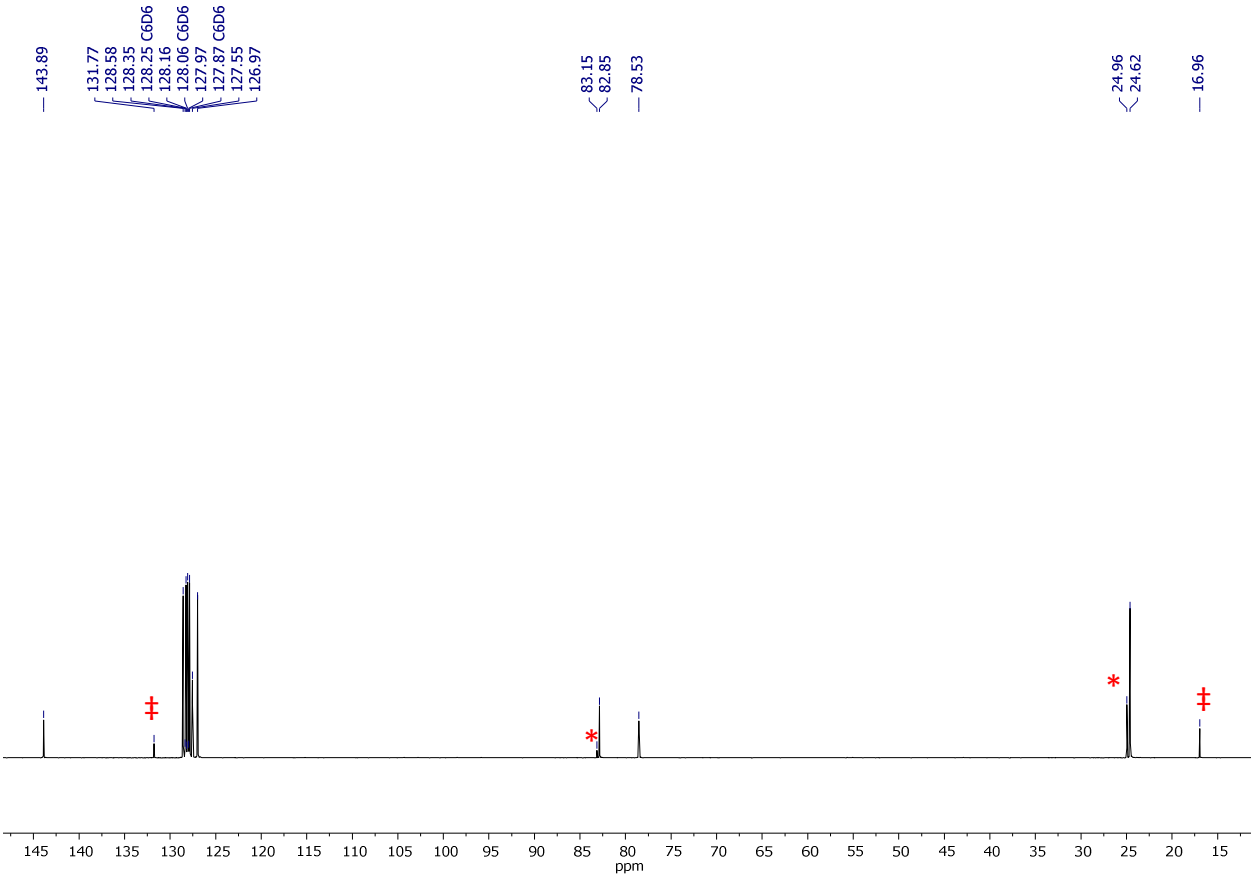
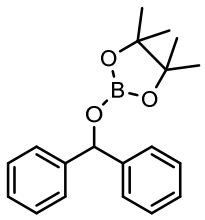


Figure S7. ^{13}C NMR spectrum of 2-(diphenylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



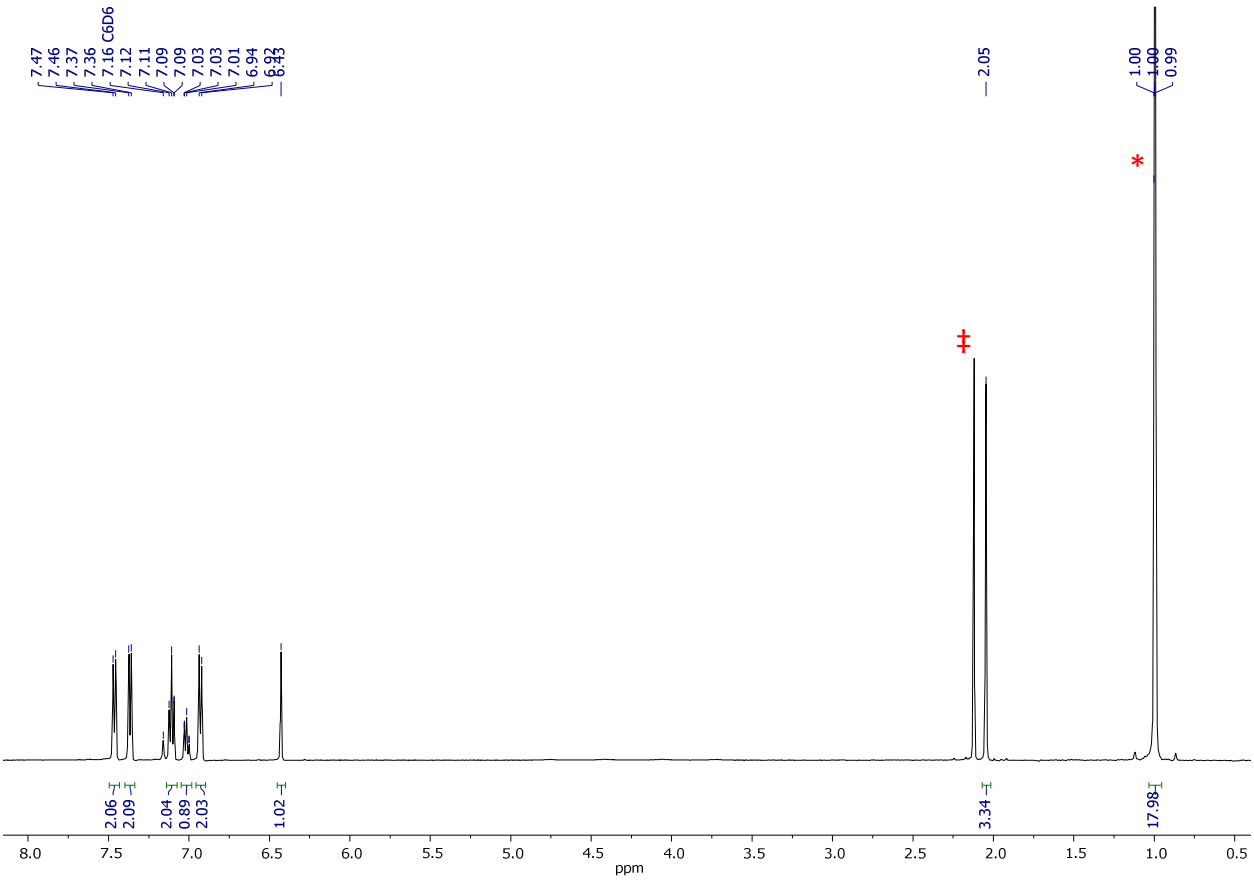
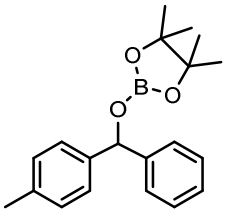


Figure S8. ^{1}H NMR spectrum of 2-(para-tolylphenylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



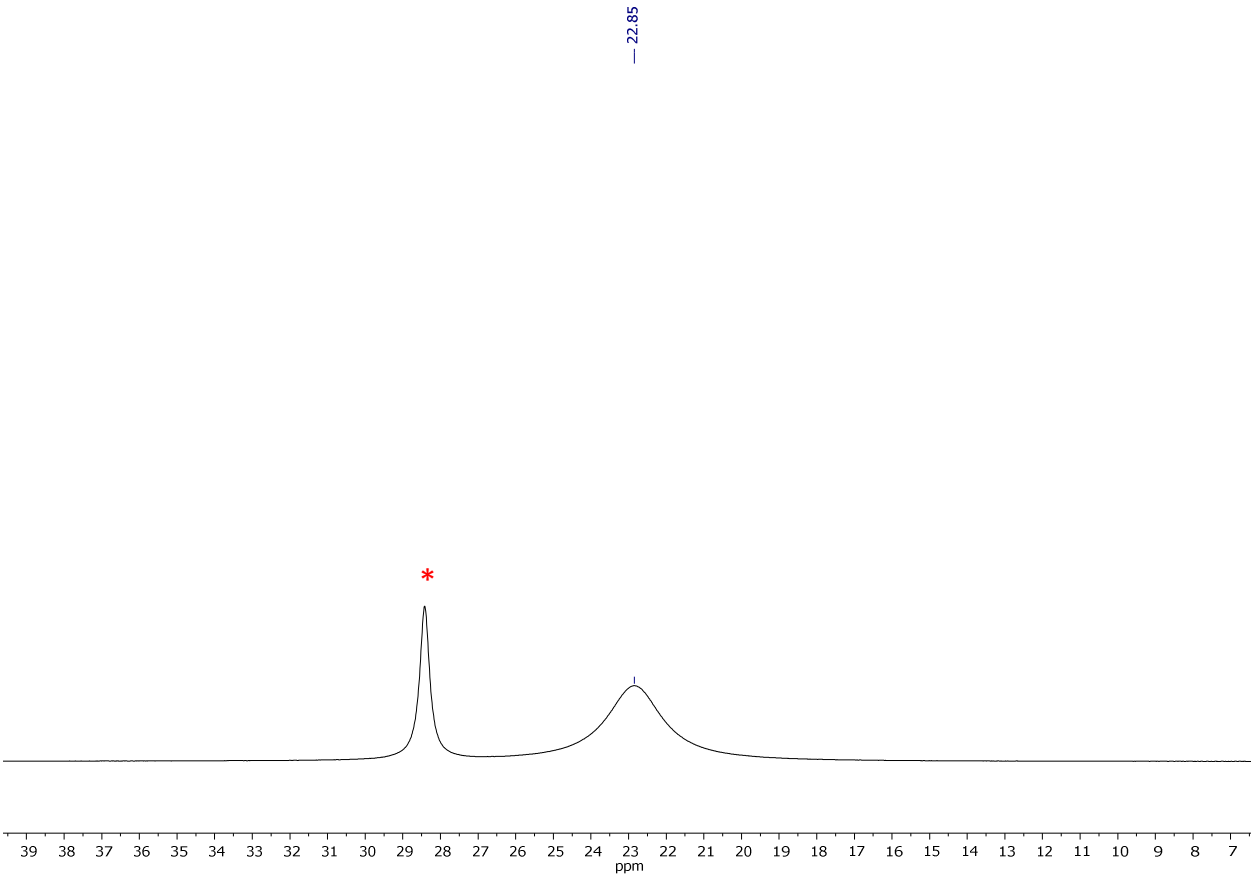
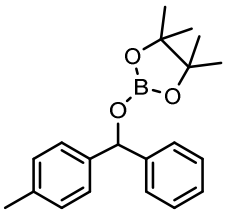


Figure S9. ^{11}B NMR spectrum of 2-(para-tolylphenylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



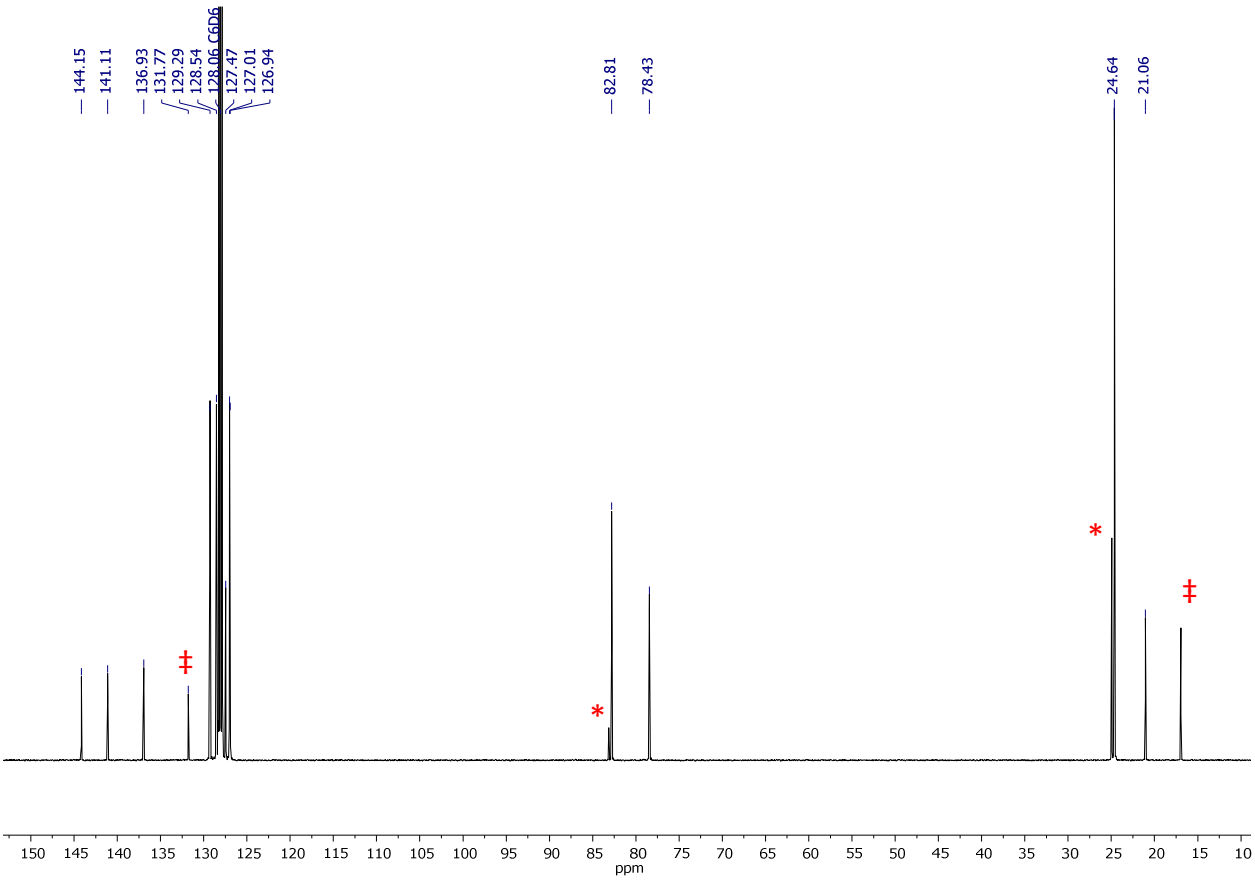
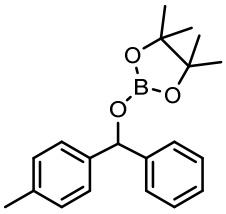


Figure S10. ^{13}C NMR spectrum of 2-(para-tolylphenylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



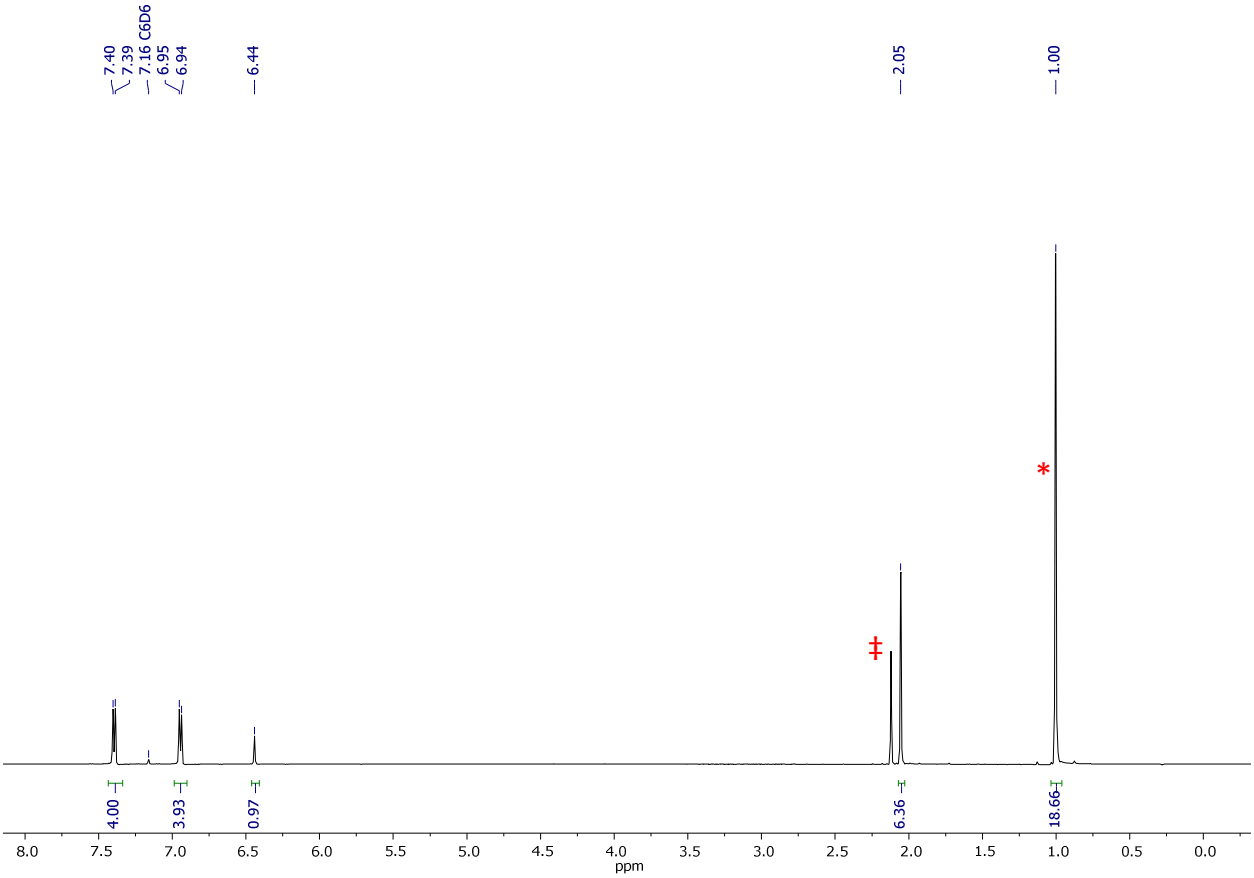
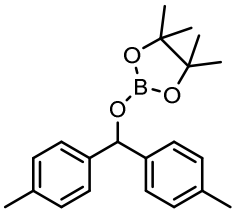


Figure S11. ^{1}H NMR spectrum of 2-(di-para-tolylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



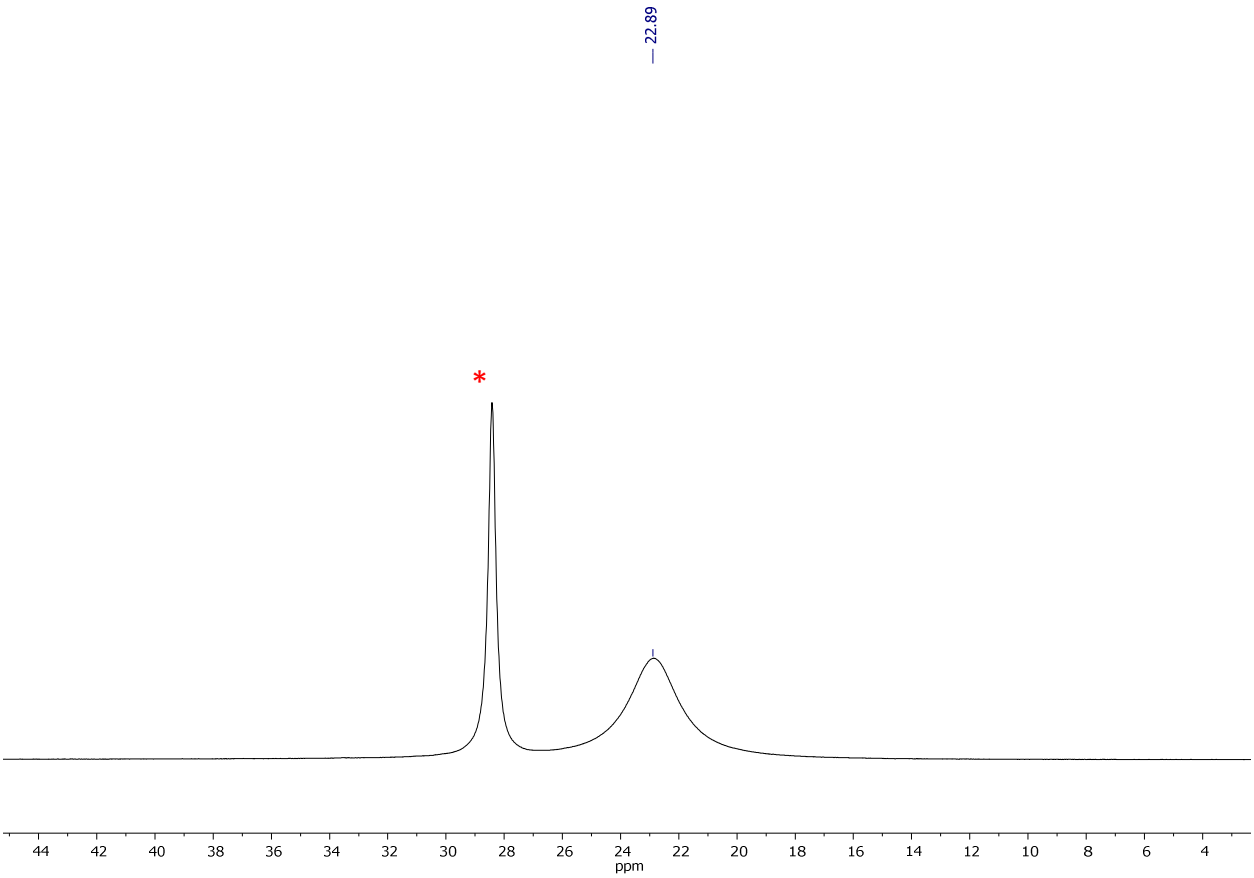
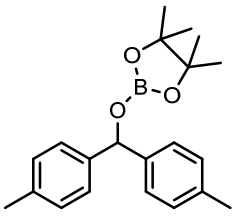


Figure S12. ^{11}B NMR spectrum of 2-(di-para-tolylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



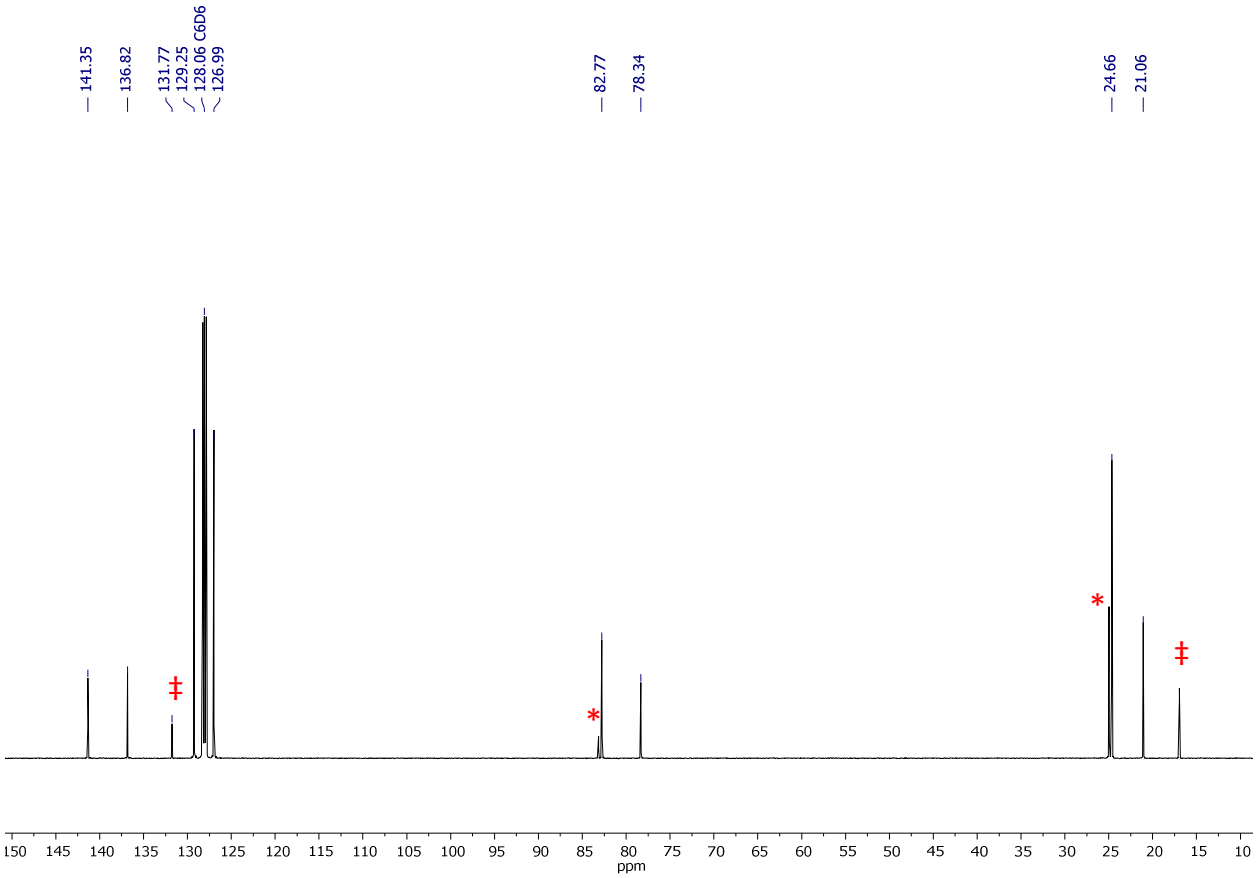
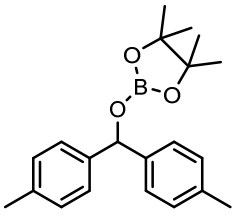


Figure S13. ^{13}C NMR spectrum of 2-(di-para-tolylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



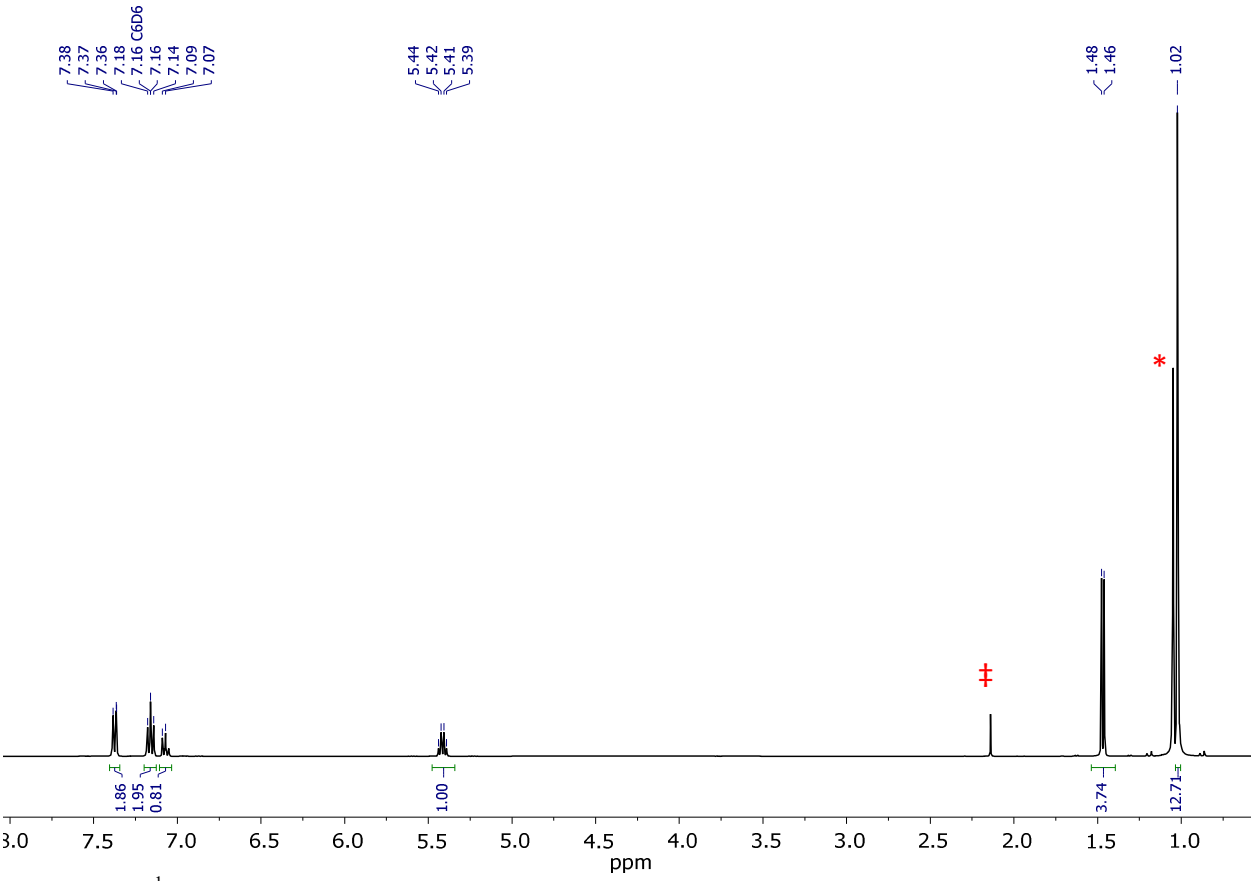
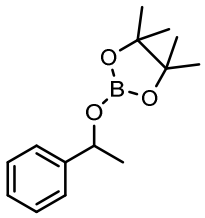


Figure S14. ^{1}H NMR spectrum of 2-(1-phenylethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



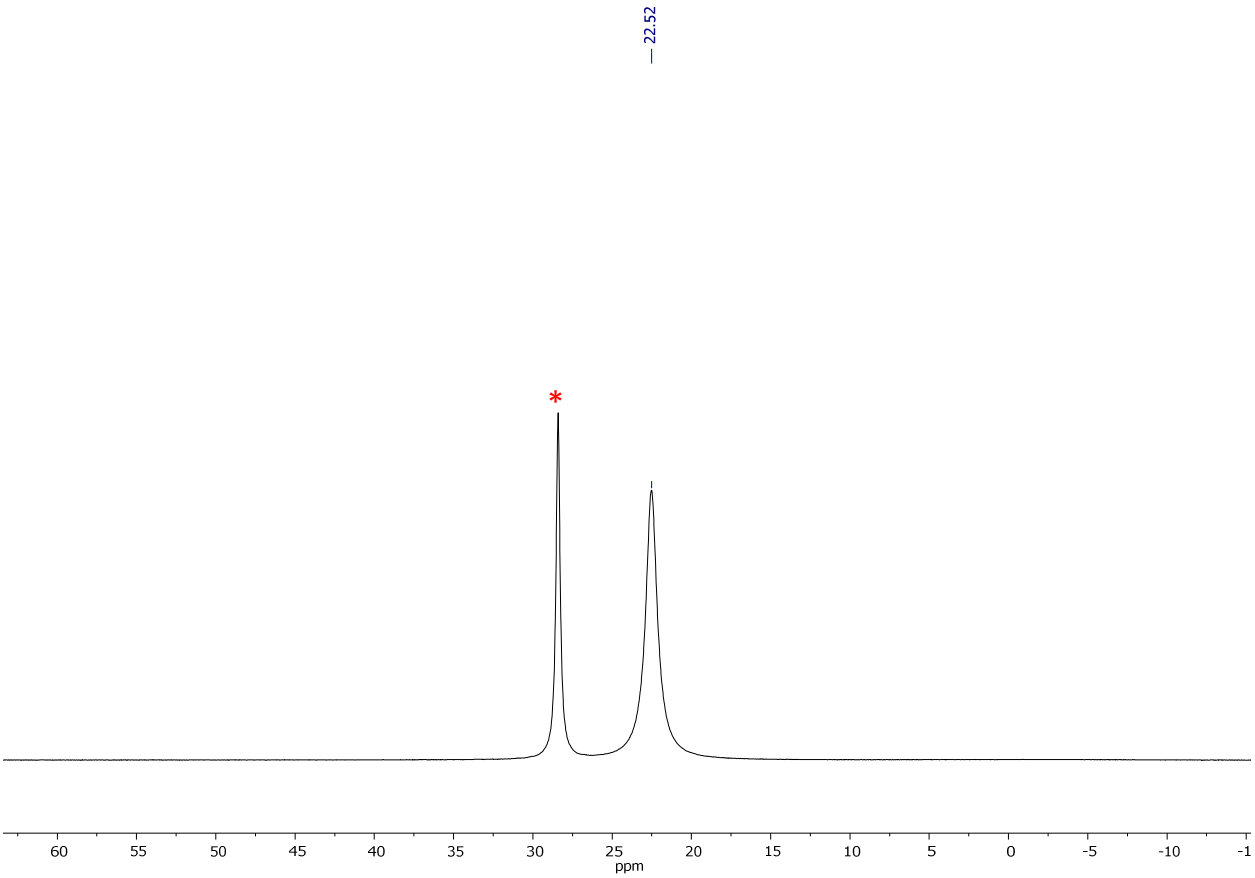
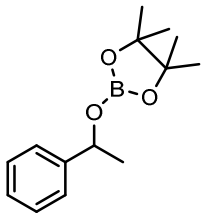


Figure S15. ^{11}B NMR spectrum of 2-(1-phenylethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



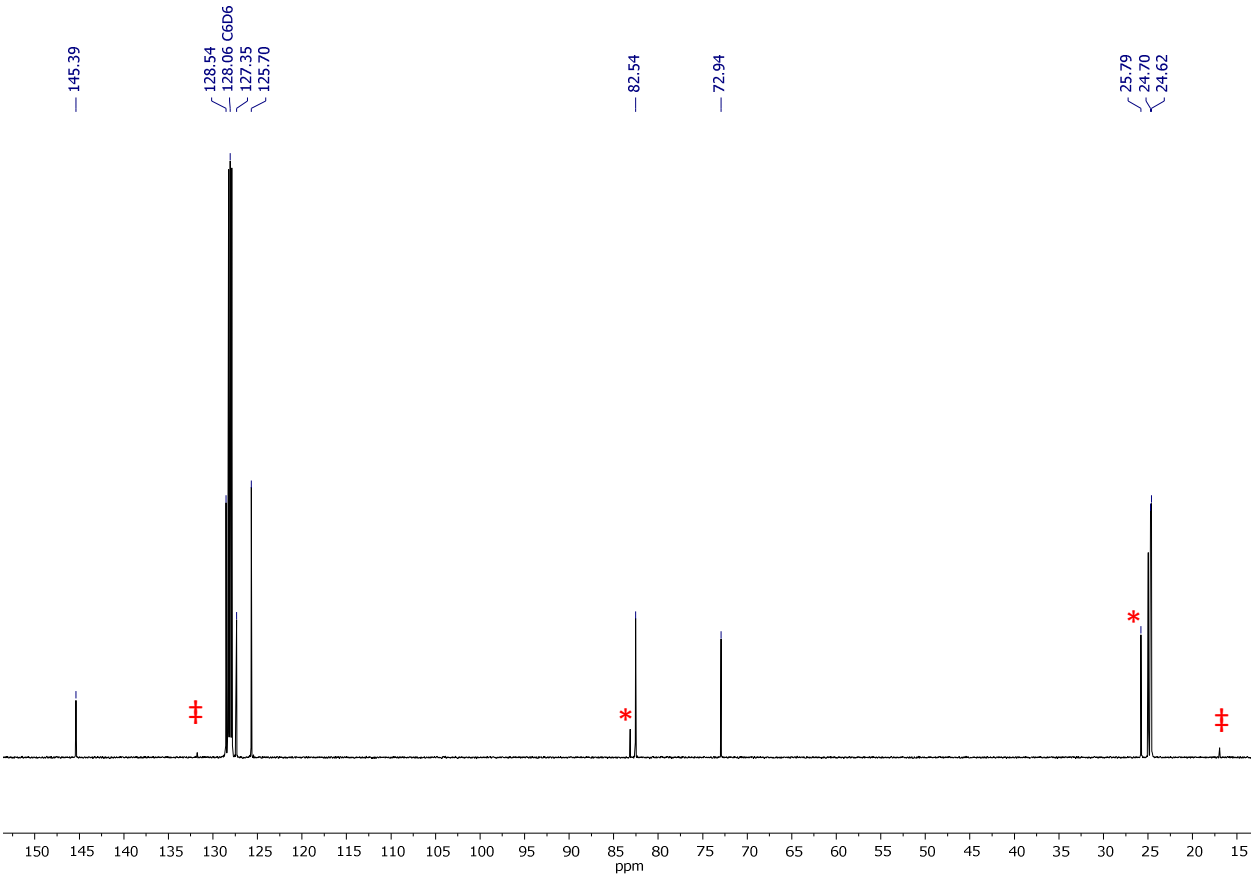
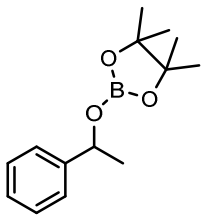


Figure S16. ^{13}C NMR spectrum of 2-(1-phenylethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



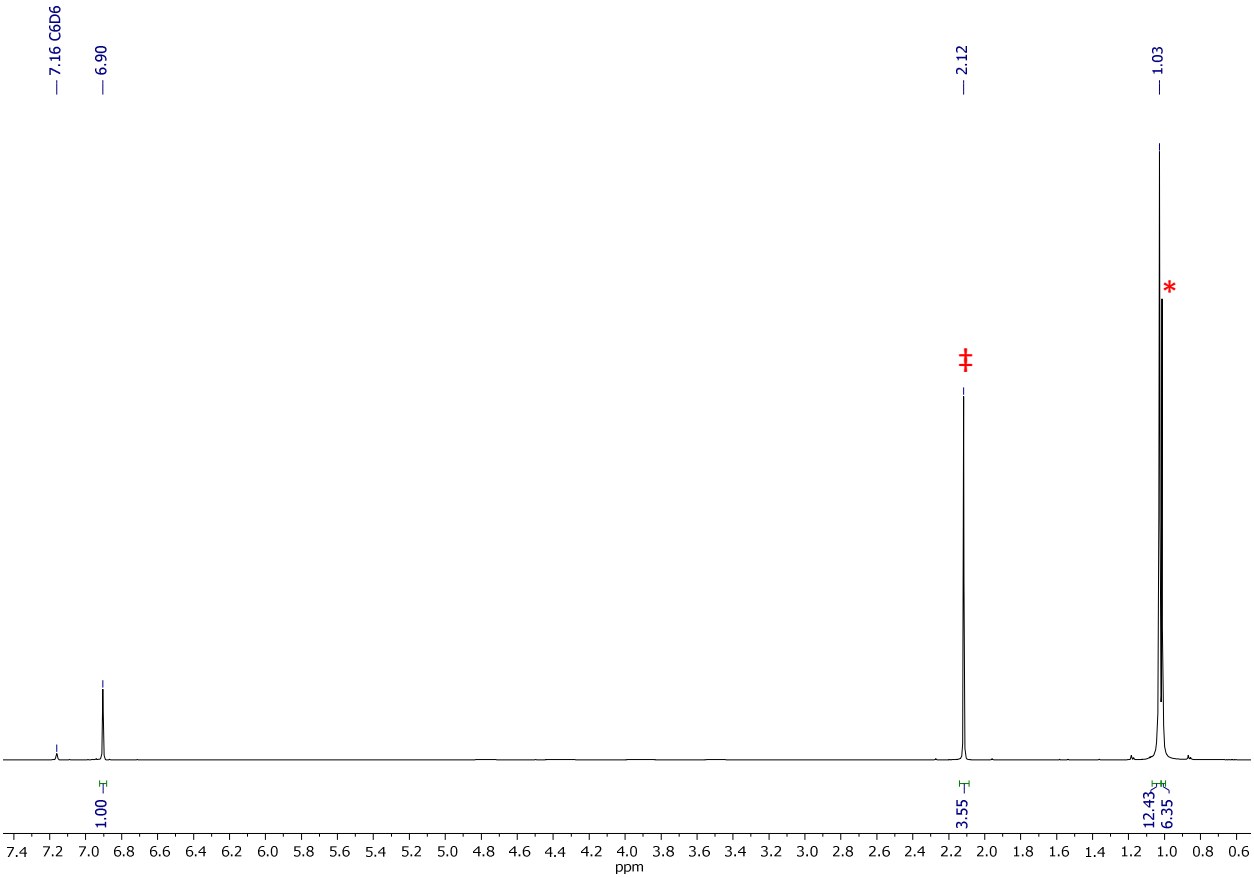
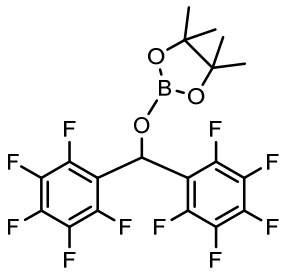


Figure S17. ^{1}H NMR spectrum of 2-(di-perfluorophenylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



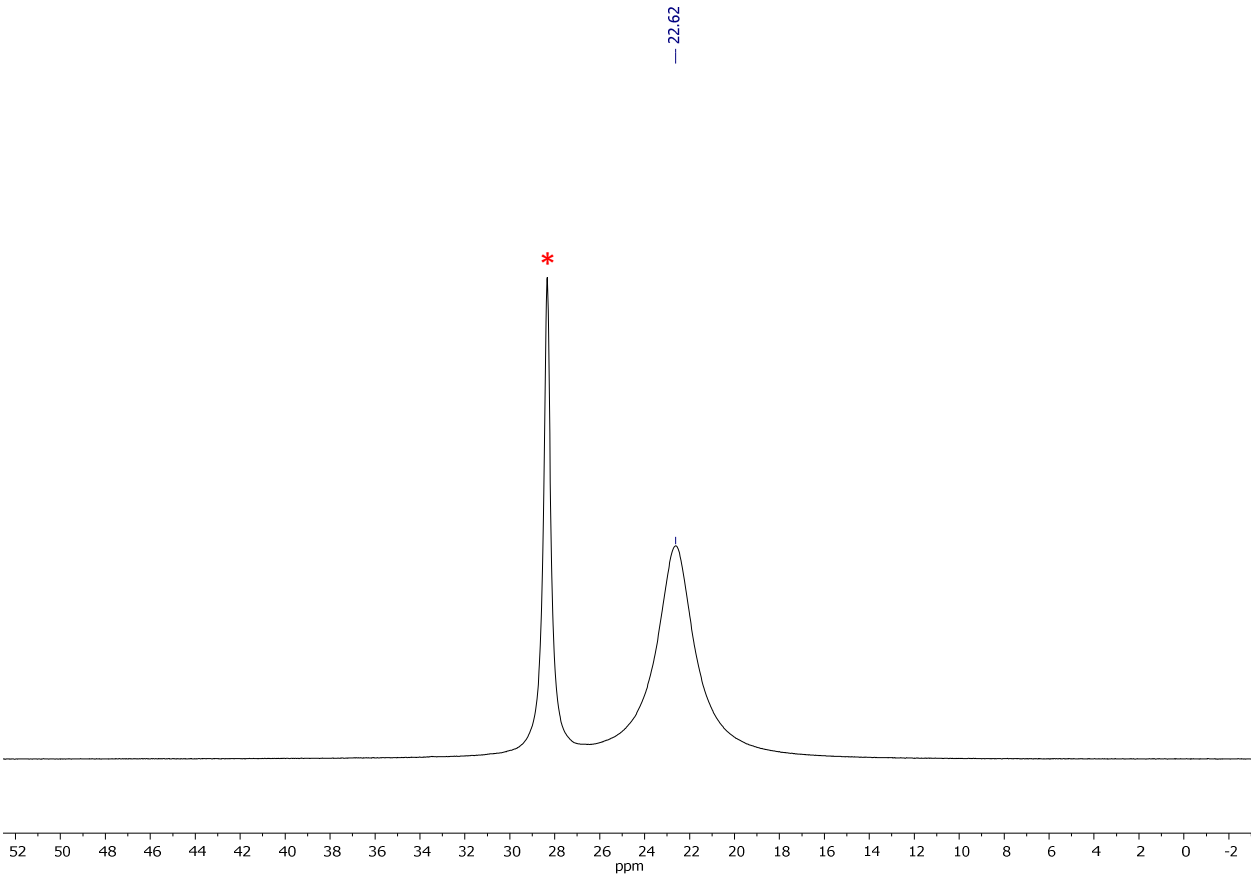
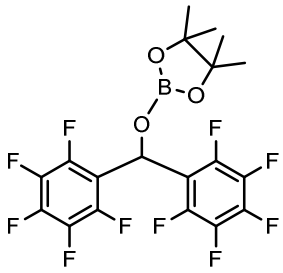


Figure S18. ^{11}B NMR spectrum of 2-(di-perfluorophenylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



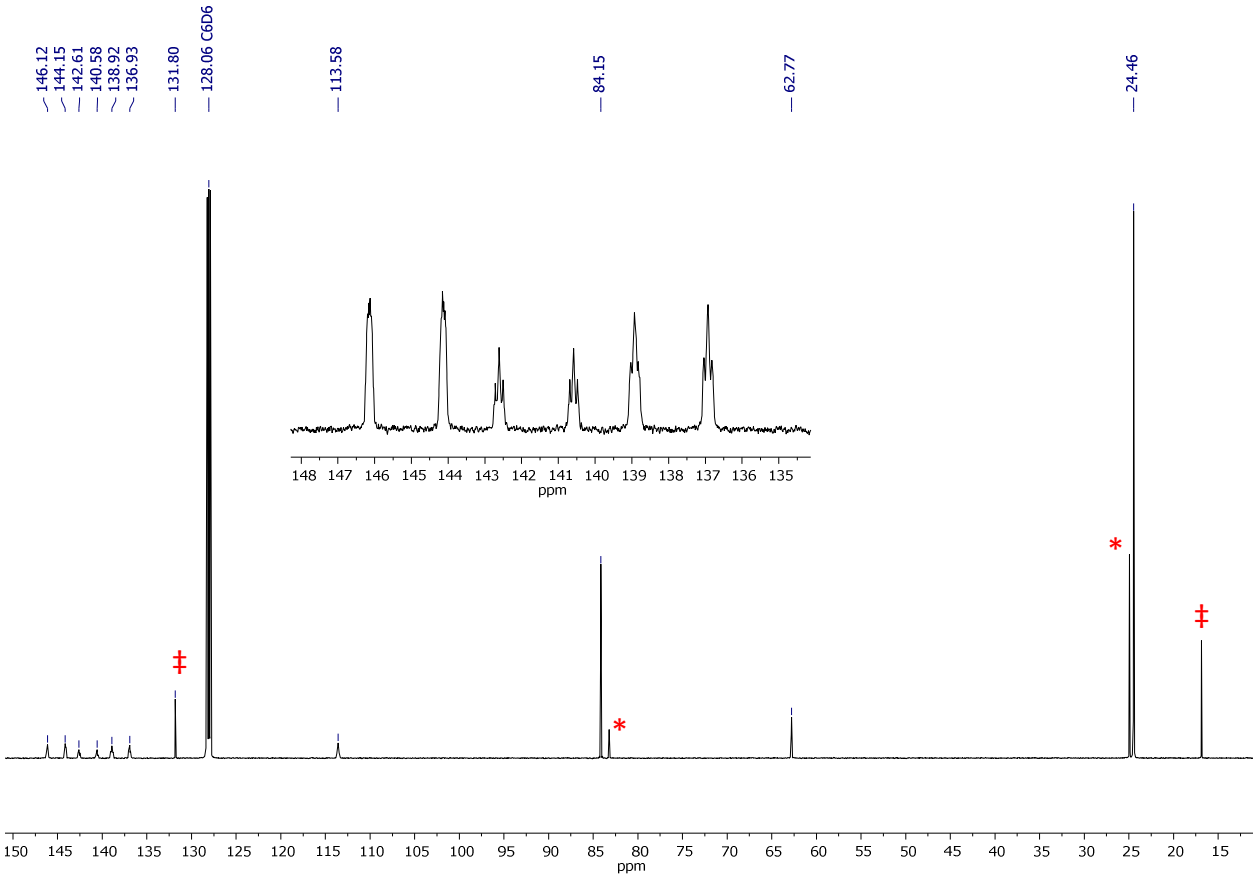
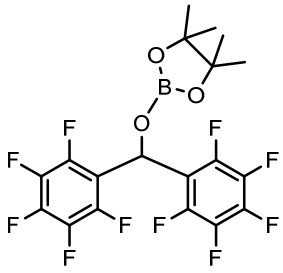


Figure S19. ^{13}C NMR spectrum of 2-(di-perfluorophenylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



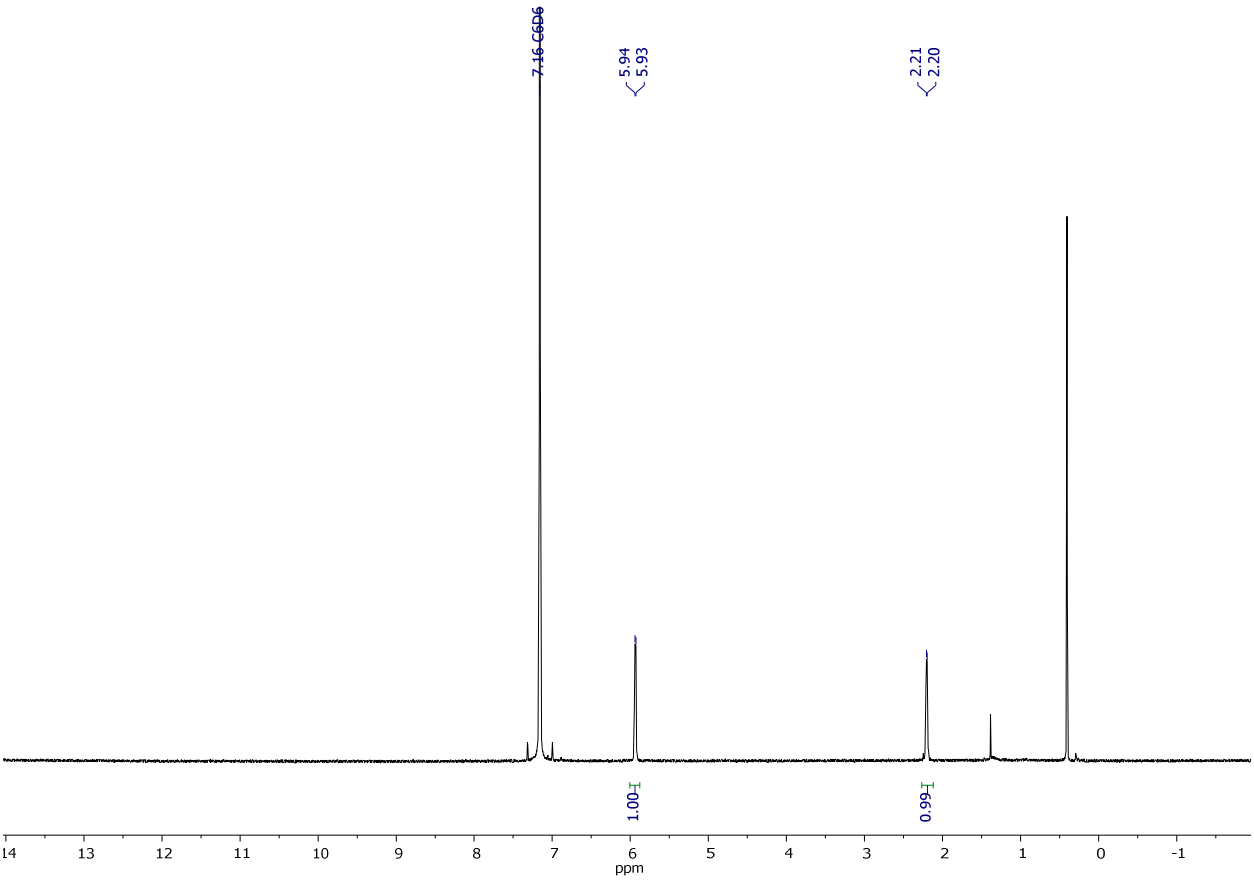
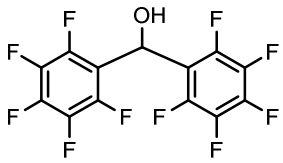


Figure S20. ^{1}H NMR spectrum of perfluorobenzhydrol acquired in benzene-d_6.



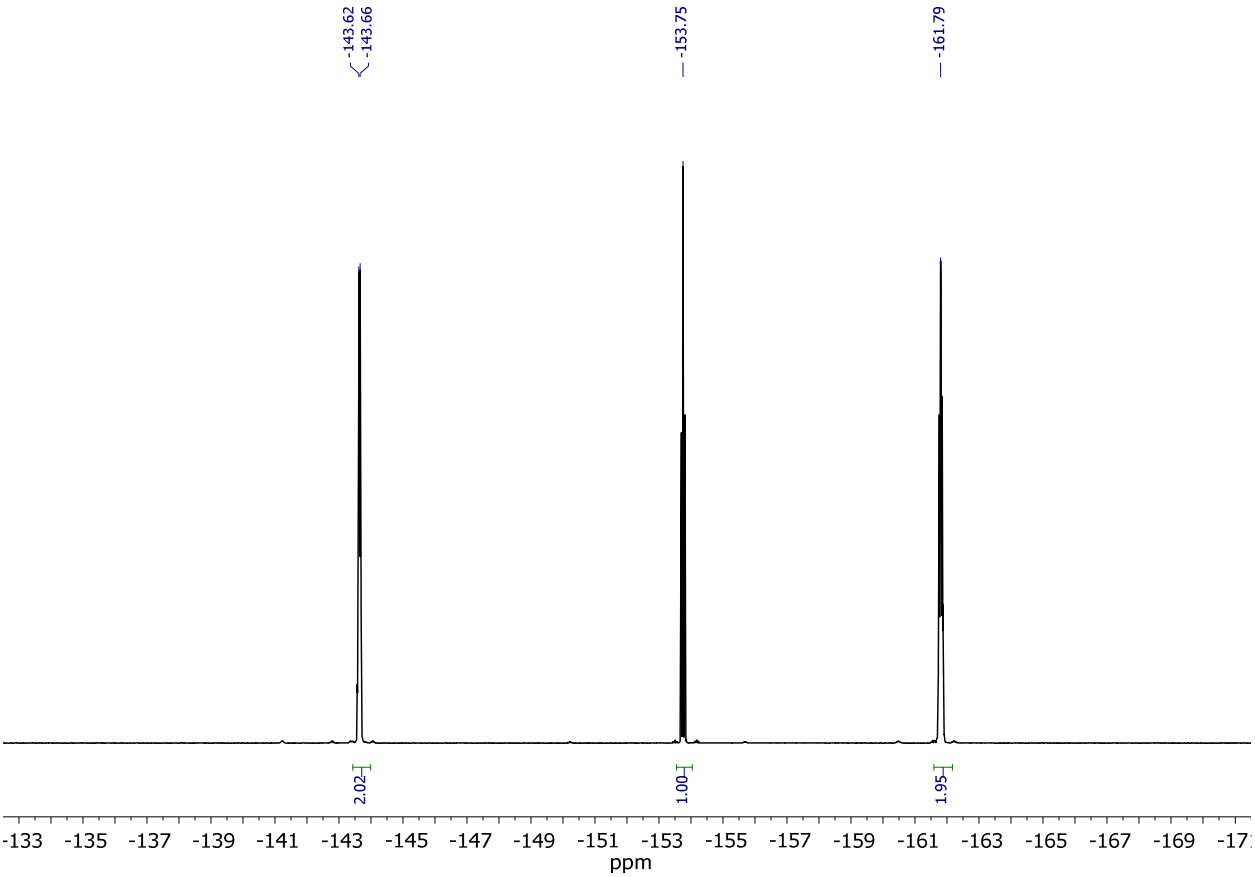
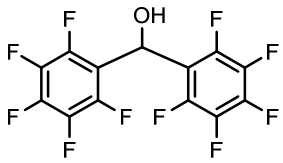


Figure S21. ^{19}F NMR spectrum of perfluorobenzhydrol acquired in benzene-d_6.



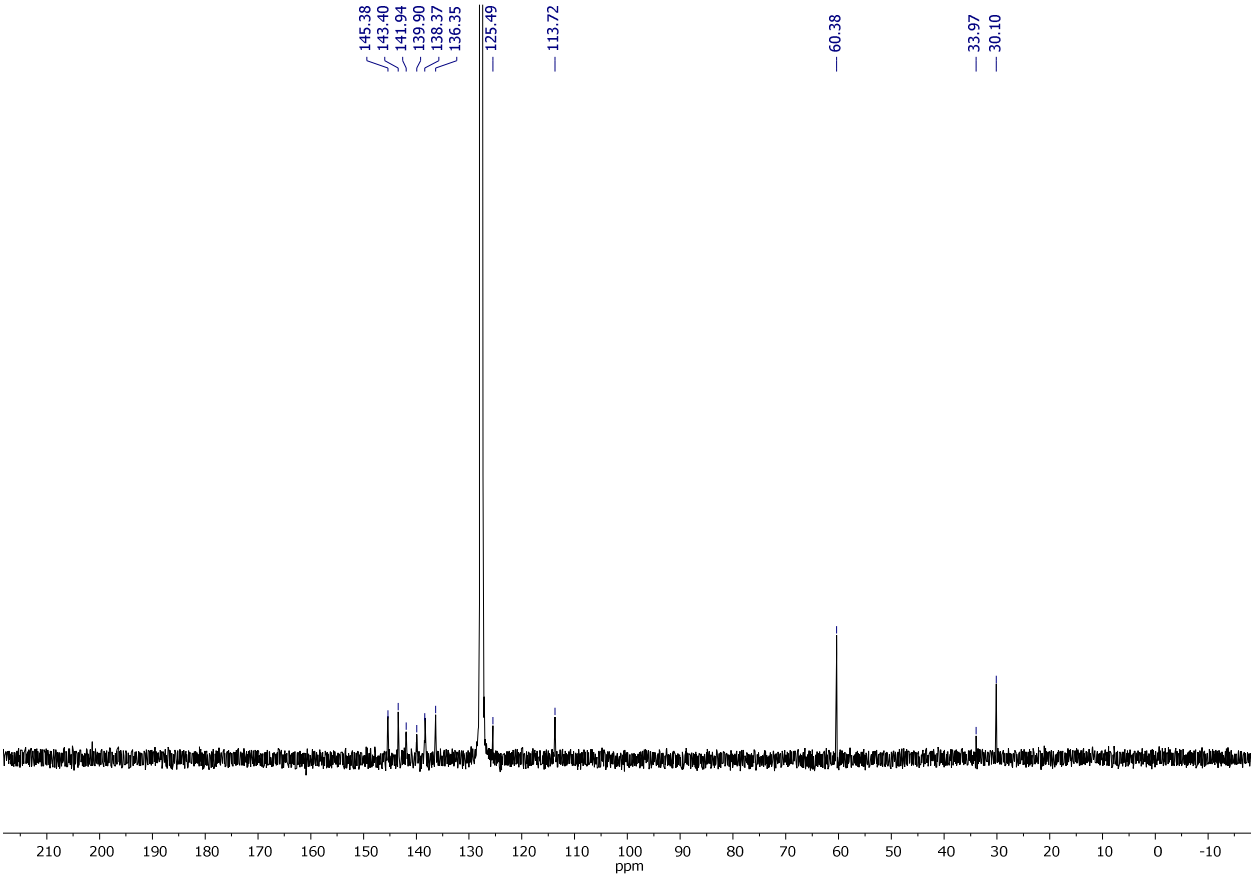
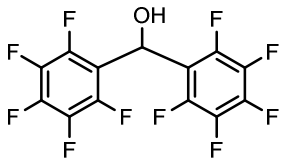


Figure S22. ^{13}C NMR spectrum of perfluorobenzhydrol acquired in benzene-d_6.



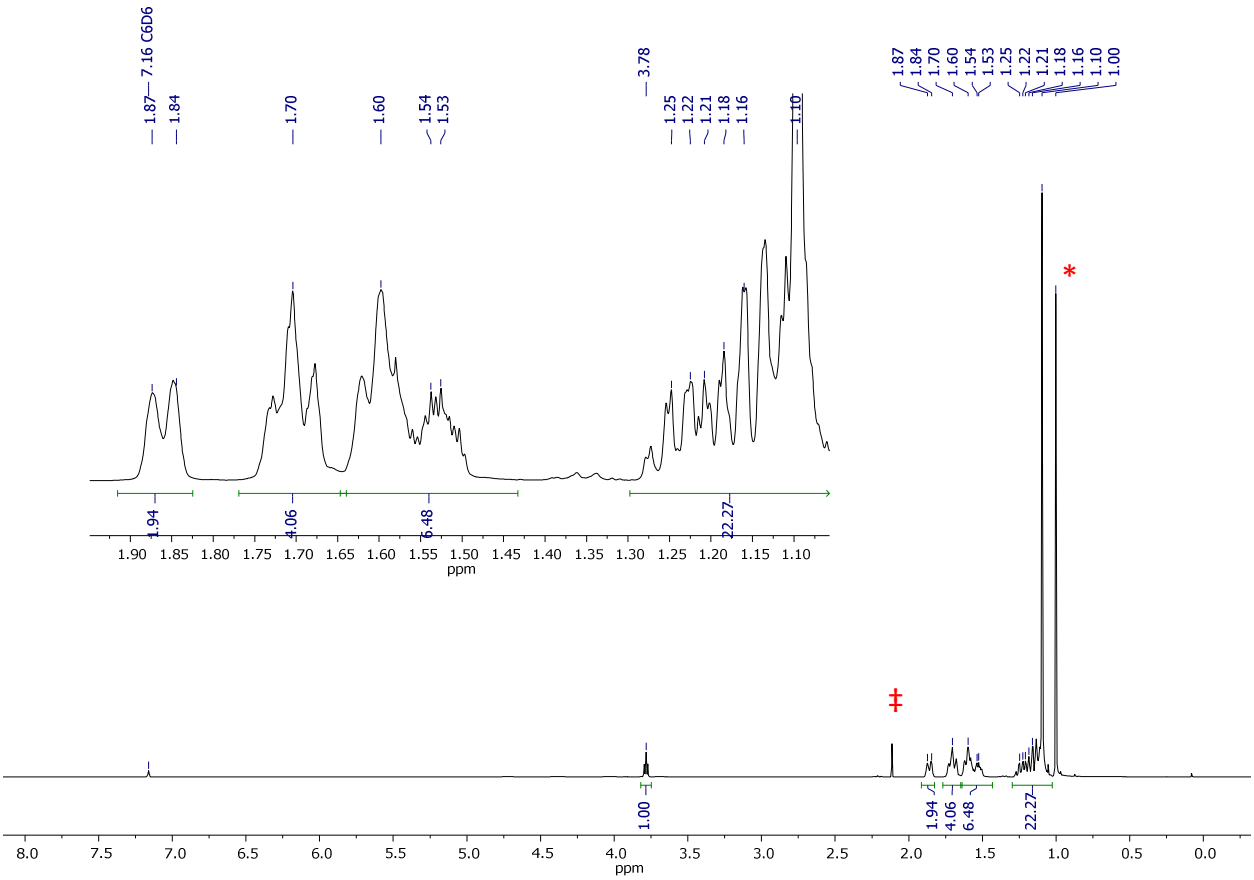
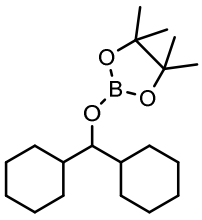


Figure S23. ^{1}H NMR spectrum of 2-(dicyclohexylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



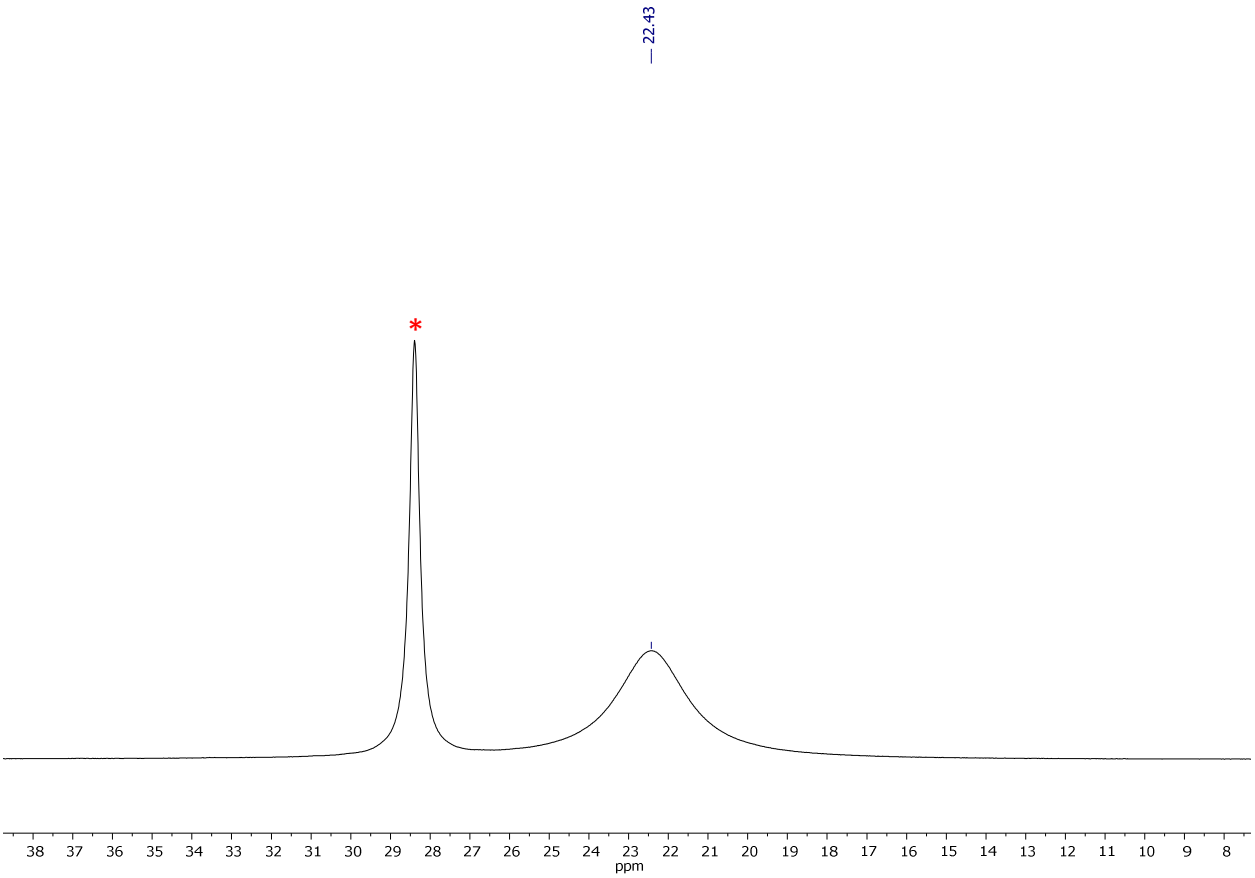
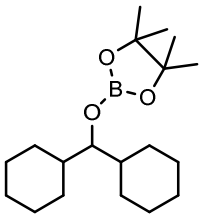


Figure S24. ^{11}B NMR spectrum of 2-(dicyclohexylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



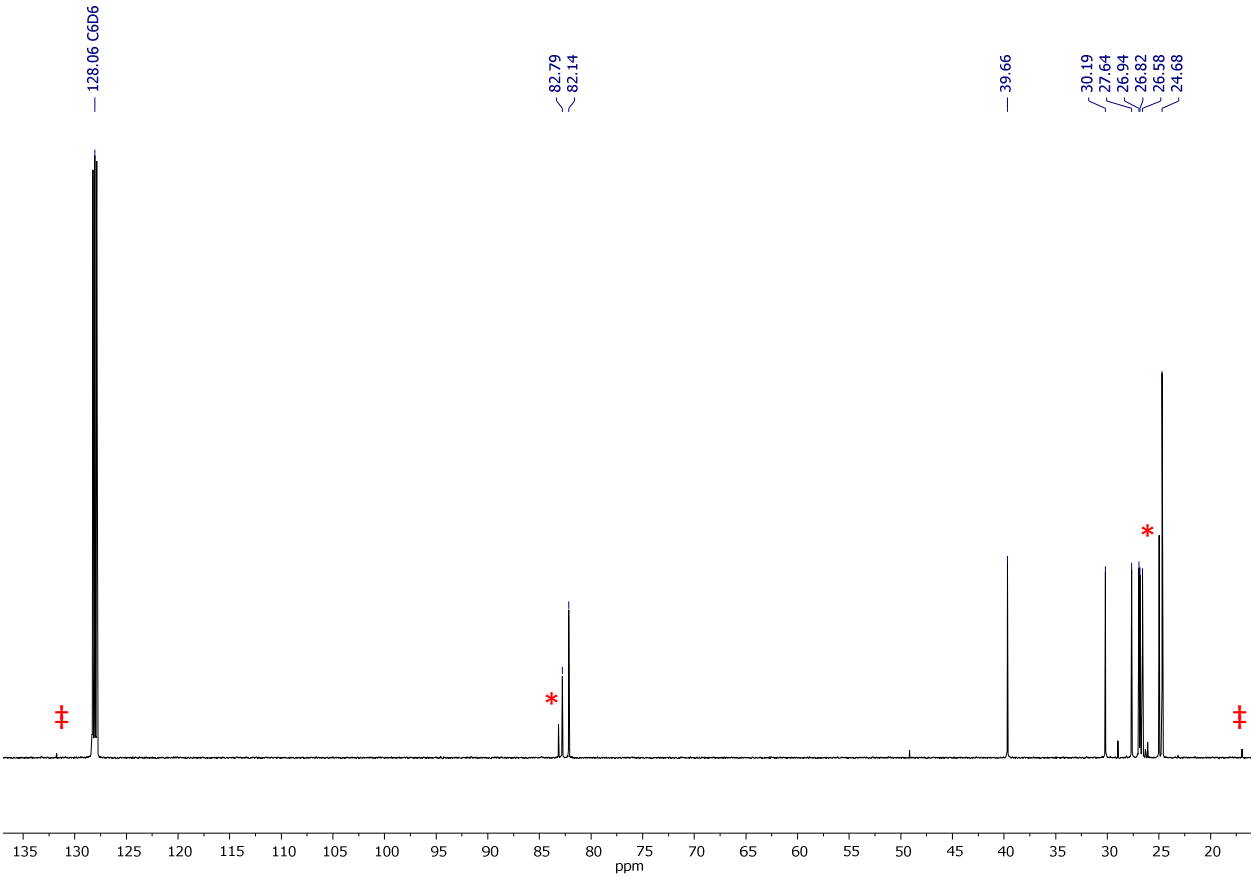
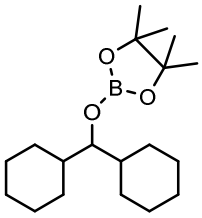


Figure S25. ^{13}C NMR spectrum of 2-(dicyclohexylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



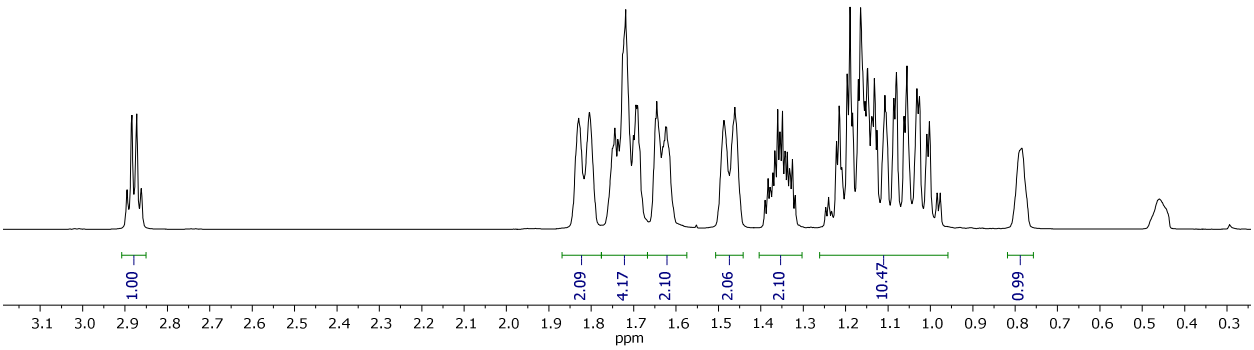
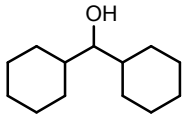


Figure S26. ^{1}H NMR spectrum of dicyclohexyl methanol acquired in benzene-d_6.



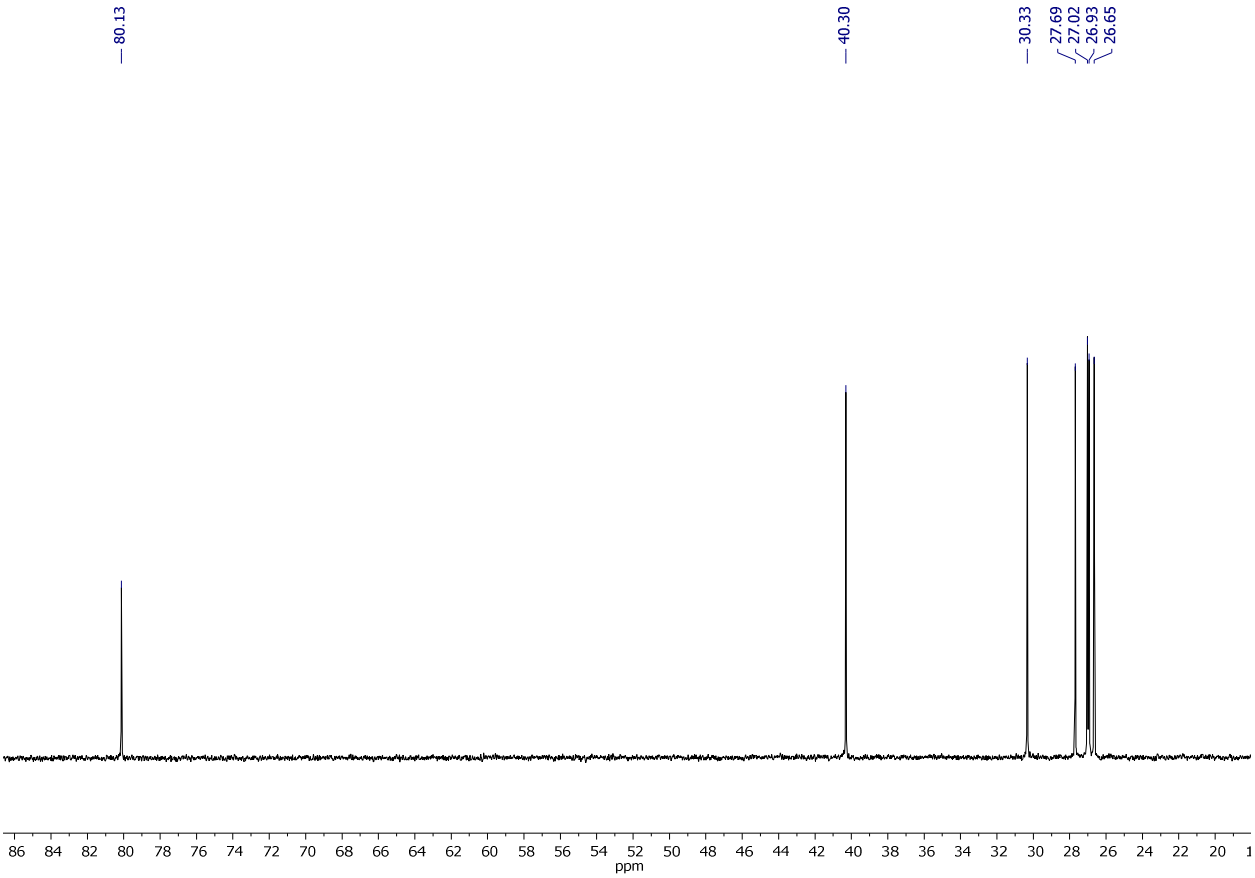
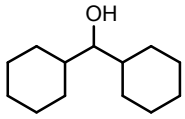


Figure S27. ^{13}C NMR spectrum of dicyclohexyl methanol acquired in benzene-d_6.



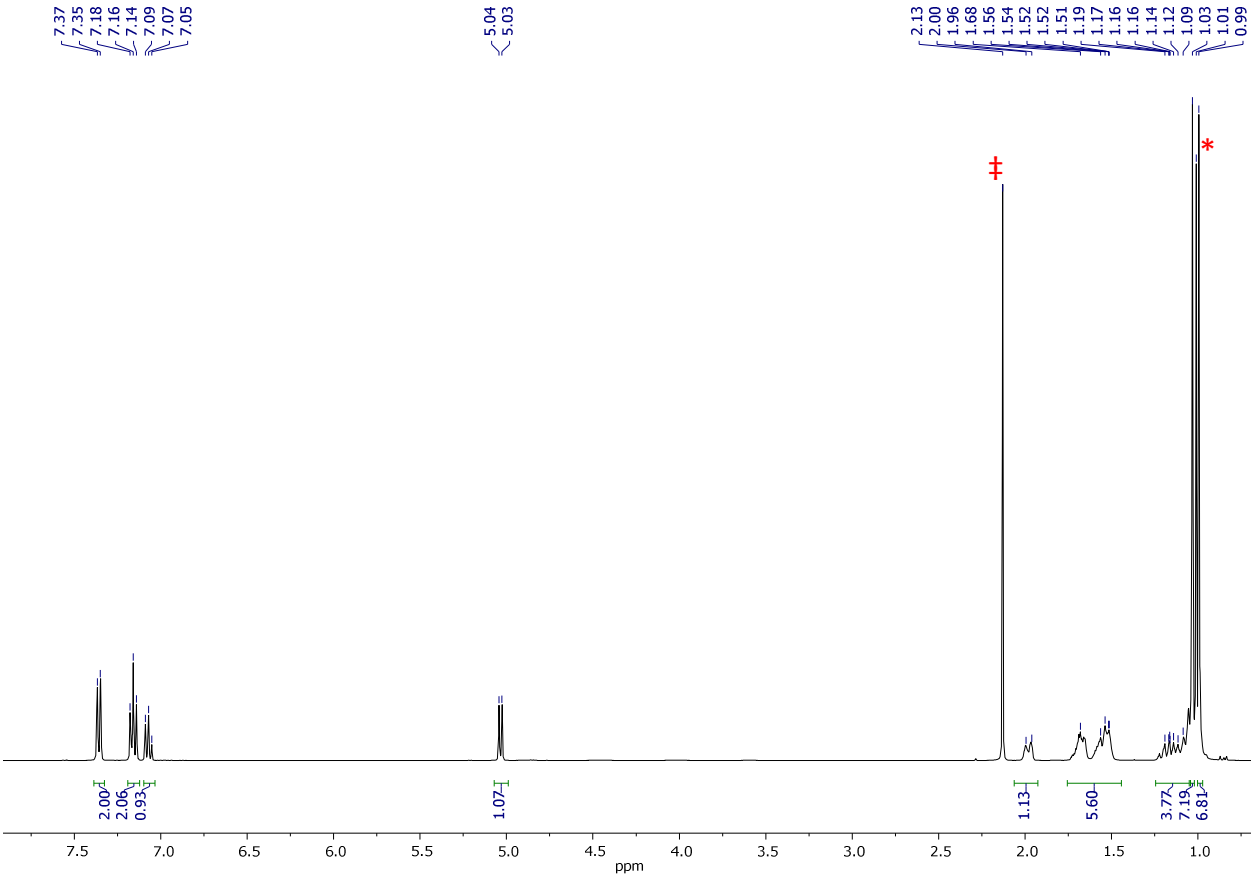
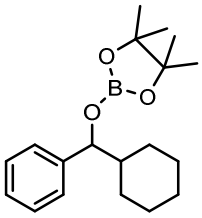


Figure S28. ^{1}H NMR spectrum of 2-(phenylcyclohexylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



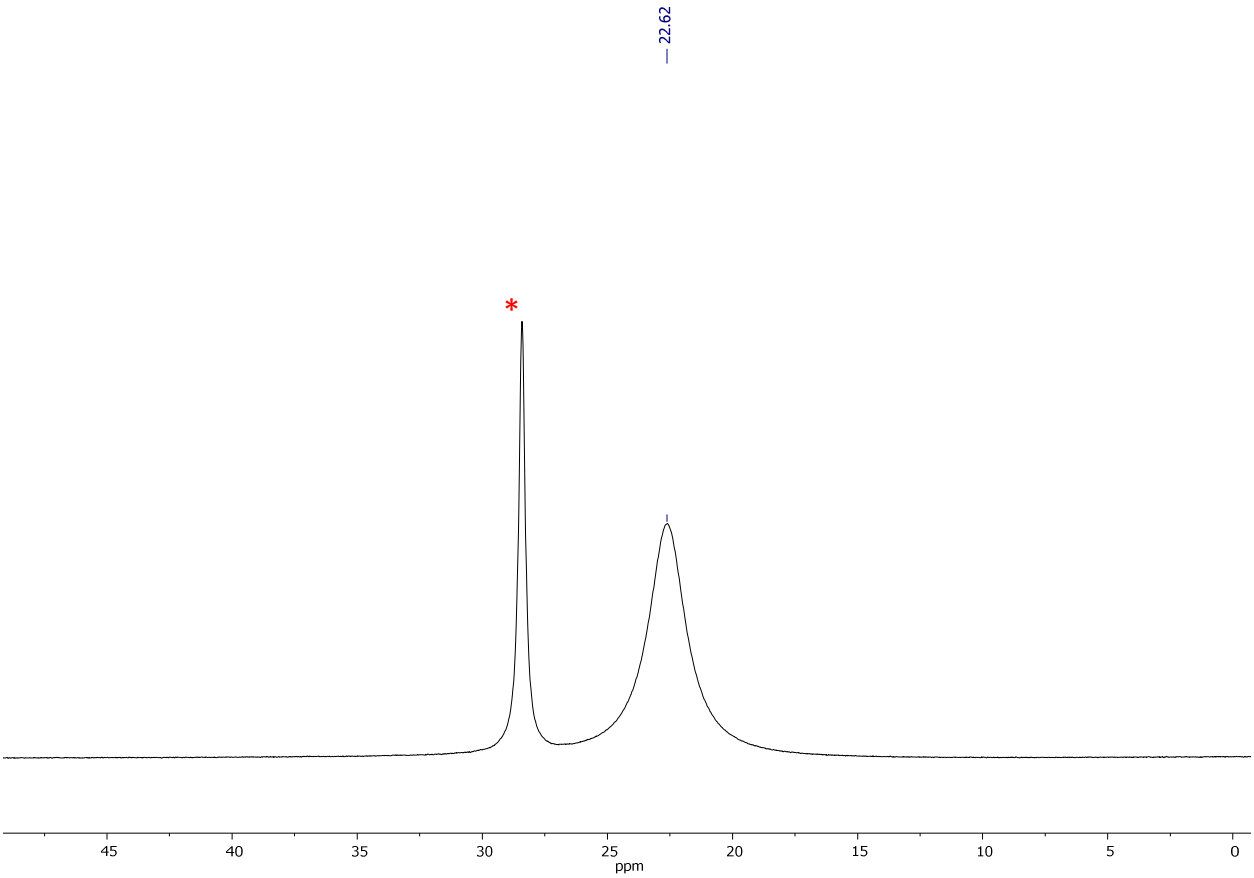
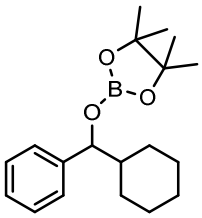


Figure S29. ^{11}B NMR spectrum of 2-(phenylcyclohexylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



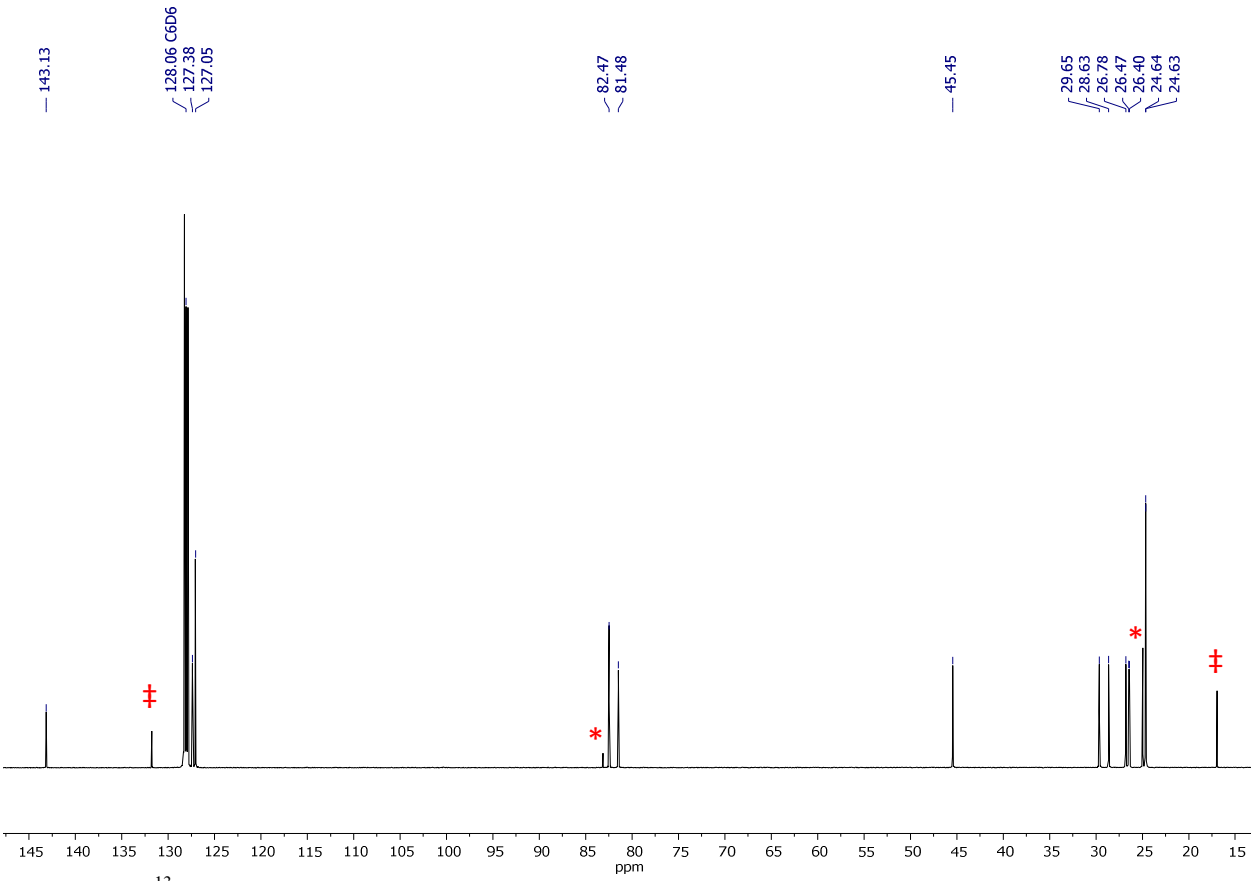
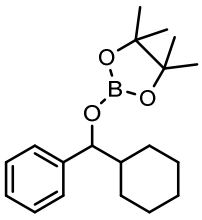


Figure S30. ^{13}C NMR spectrum of 2-(phenylcyclohexylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



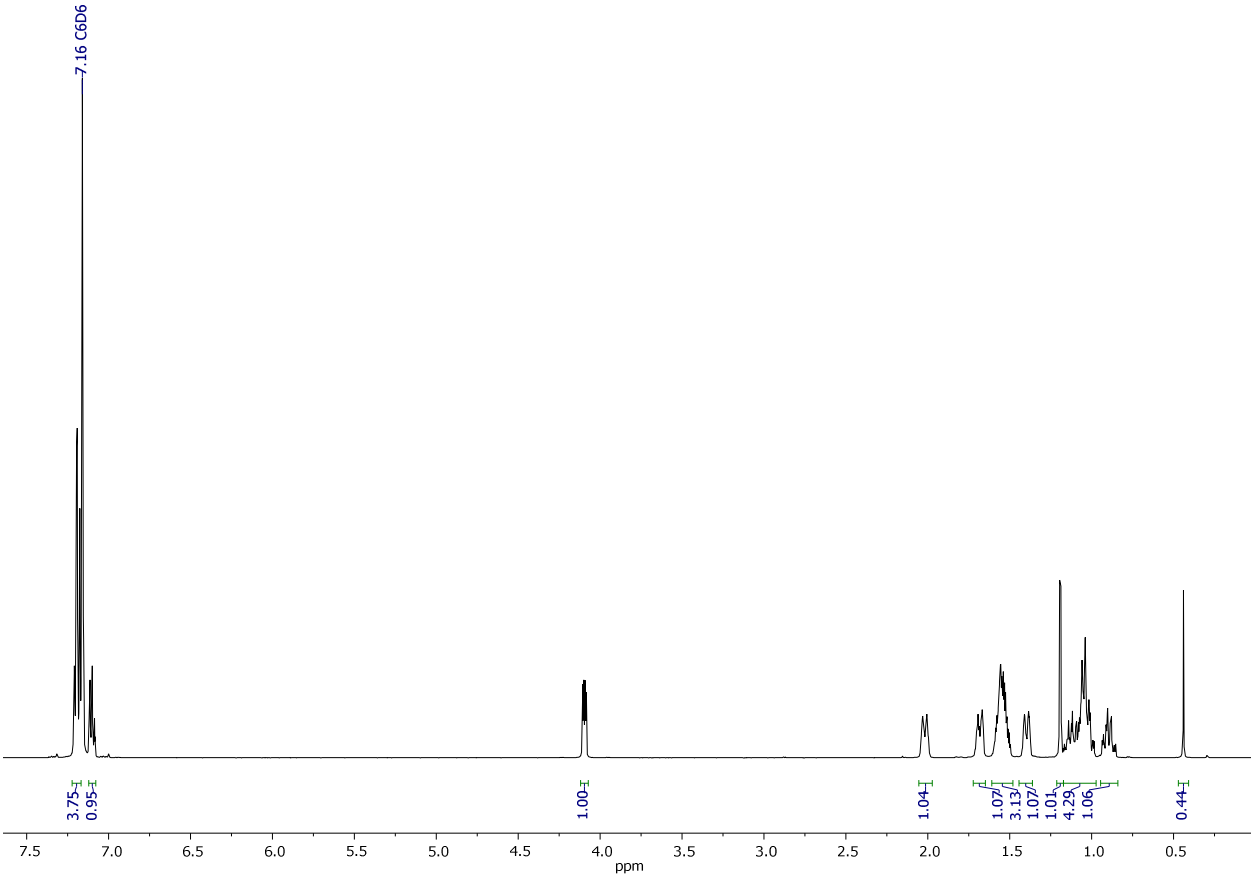
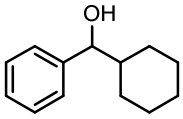


Figure S31. ^{1}H NMR spectrum of cyclohexyl(benzyl)alcohol acquired in benzene-d_6.



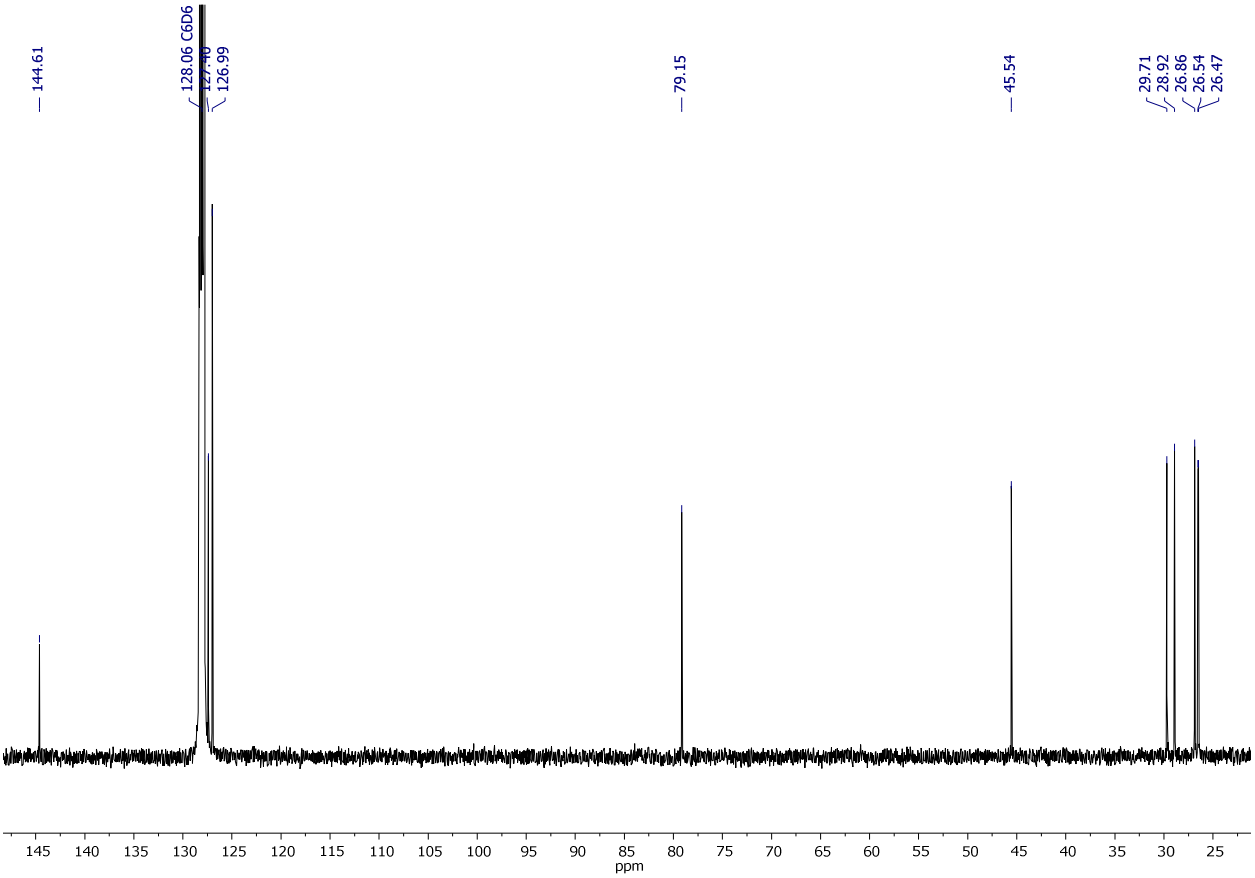
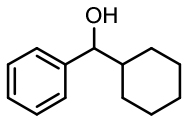


Figure S32. ^{13}C NMR spectrum of cyclohexyl(benzyl)alcohol acquired in benzene-d_6.



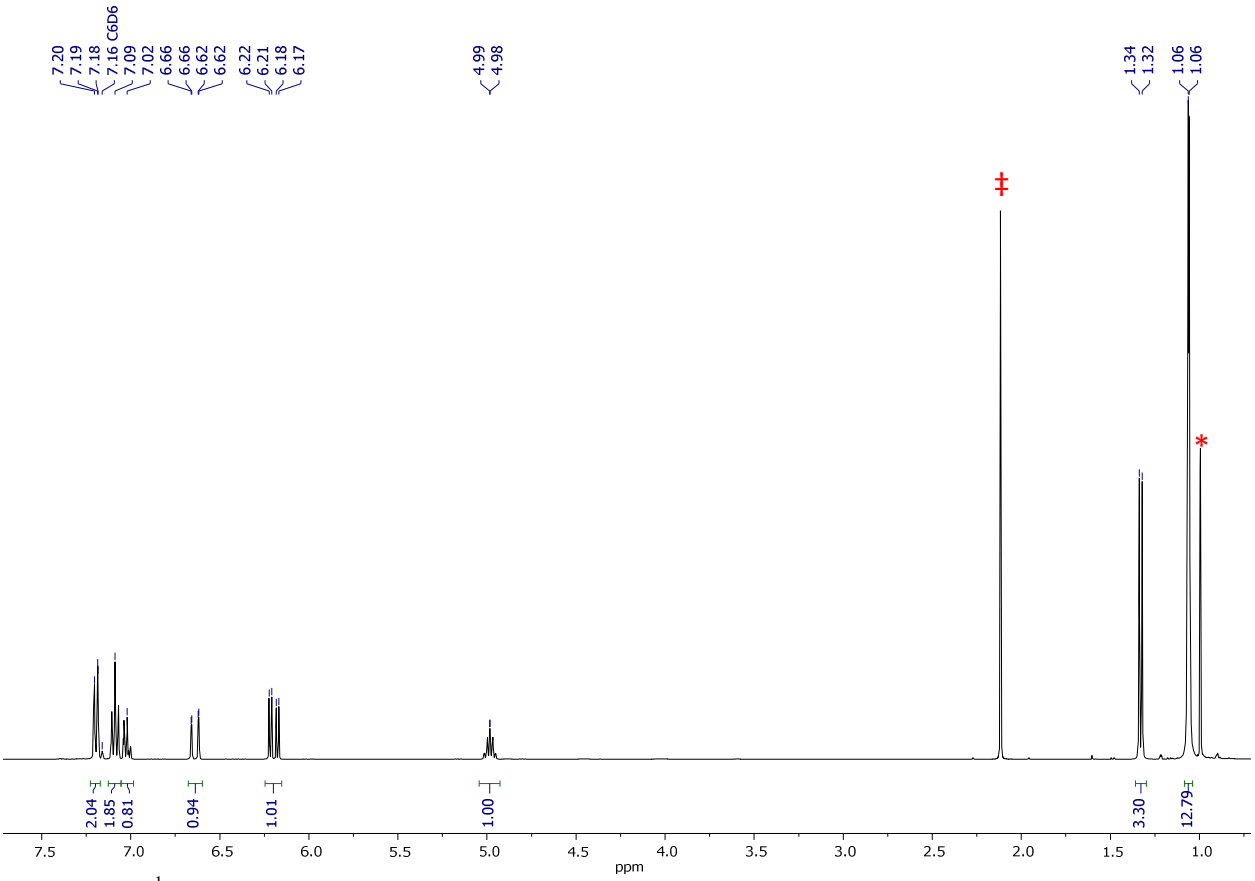
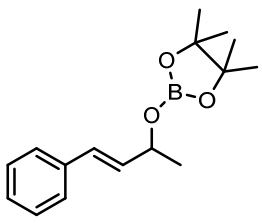


Figure S33. ^{1}H NMR spectrum of 2-(3-phenylprop-3-enylethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



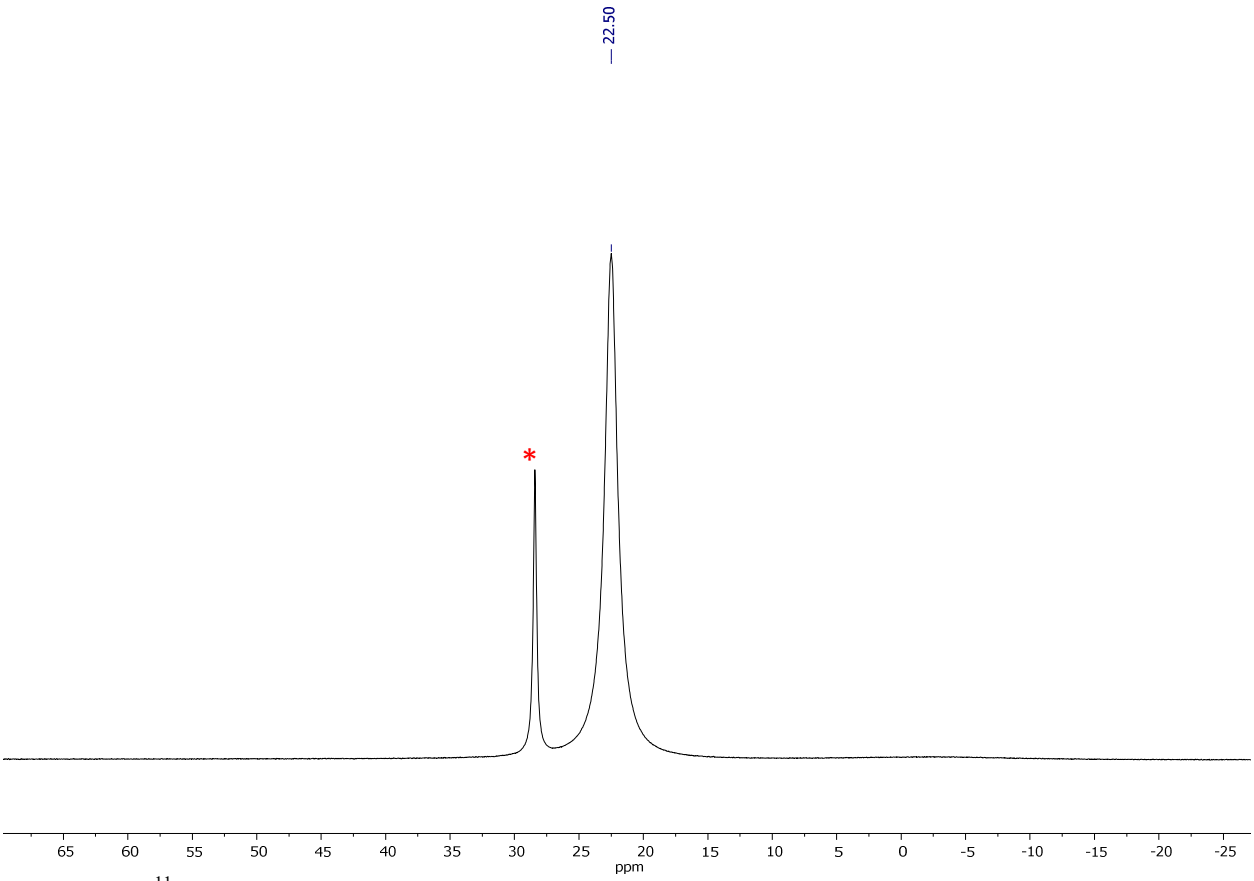
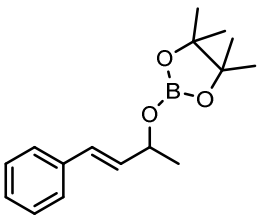


Figure S34. ^{11}B NMR spectrum of 2-(3-phenylprop-3-enylethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



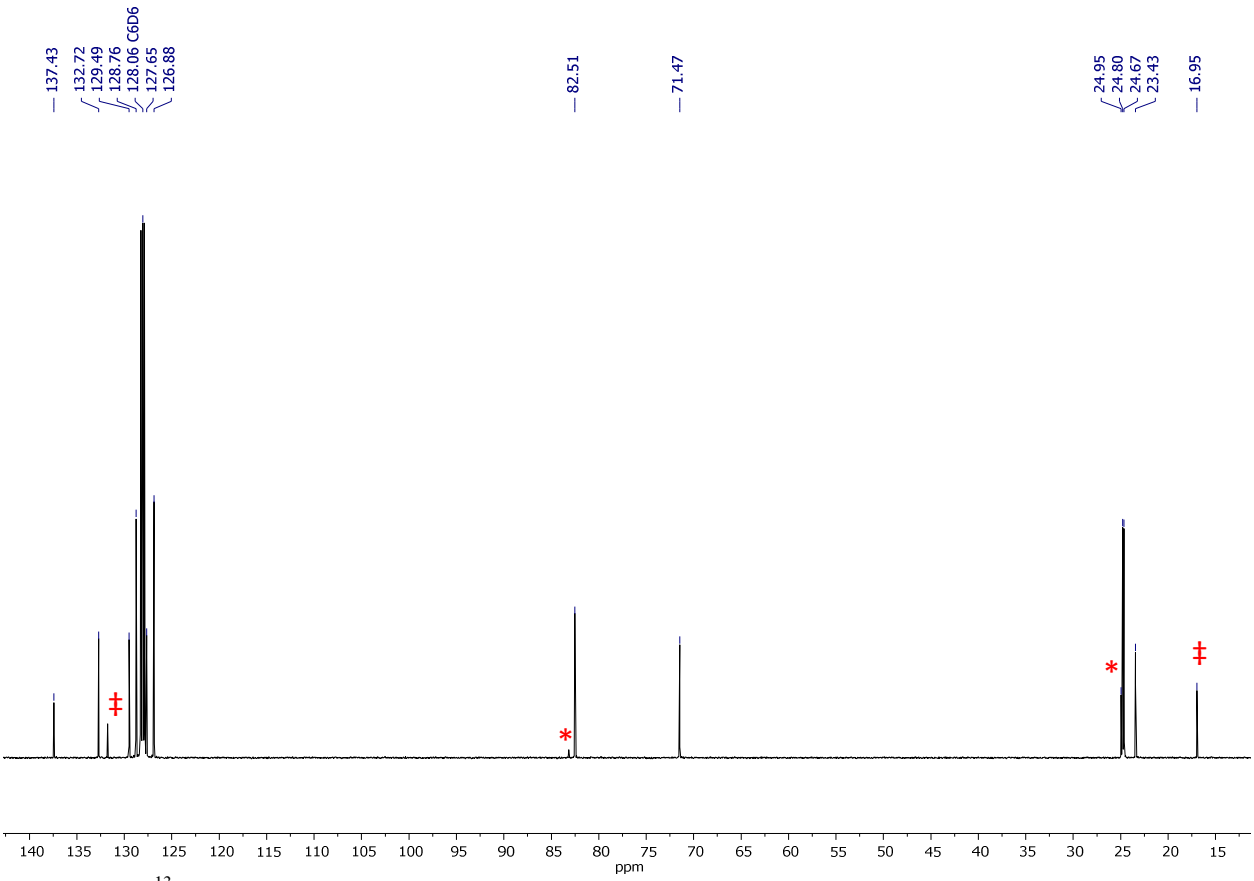
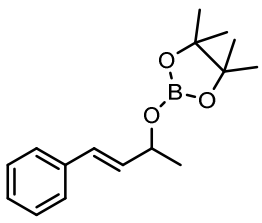


Figure S35. ^{13}C NMR spectrum of 2-(3-phenylprop-3-enylethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



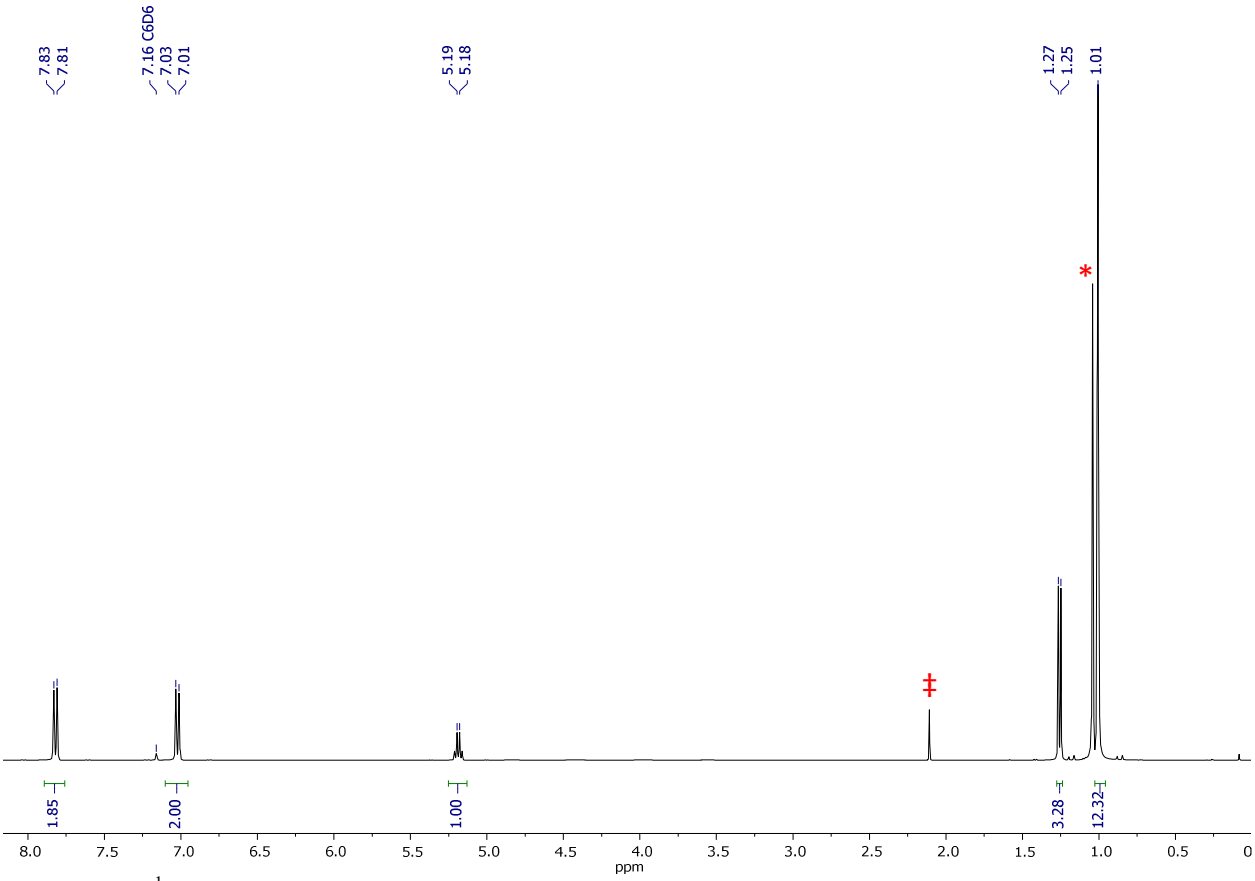
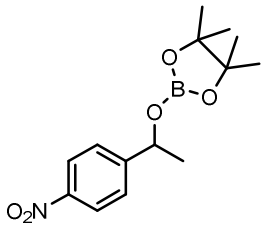


Figure S36. ^{1}H NMR spectrum of 2-(4-nitrophenylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



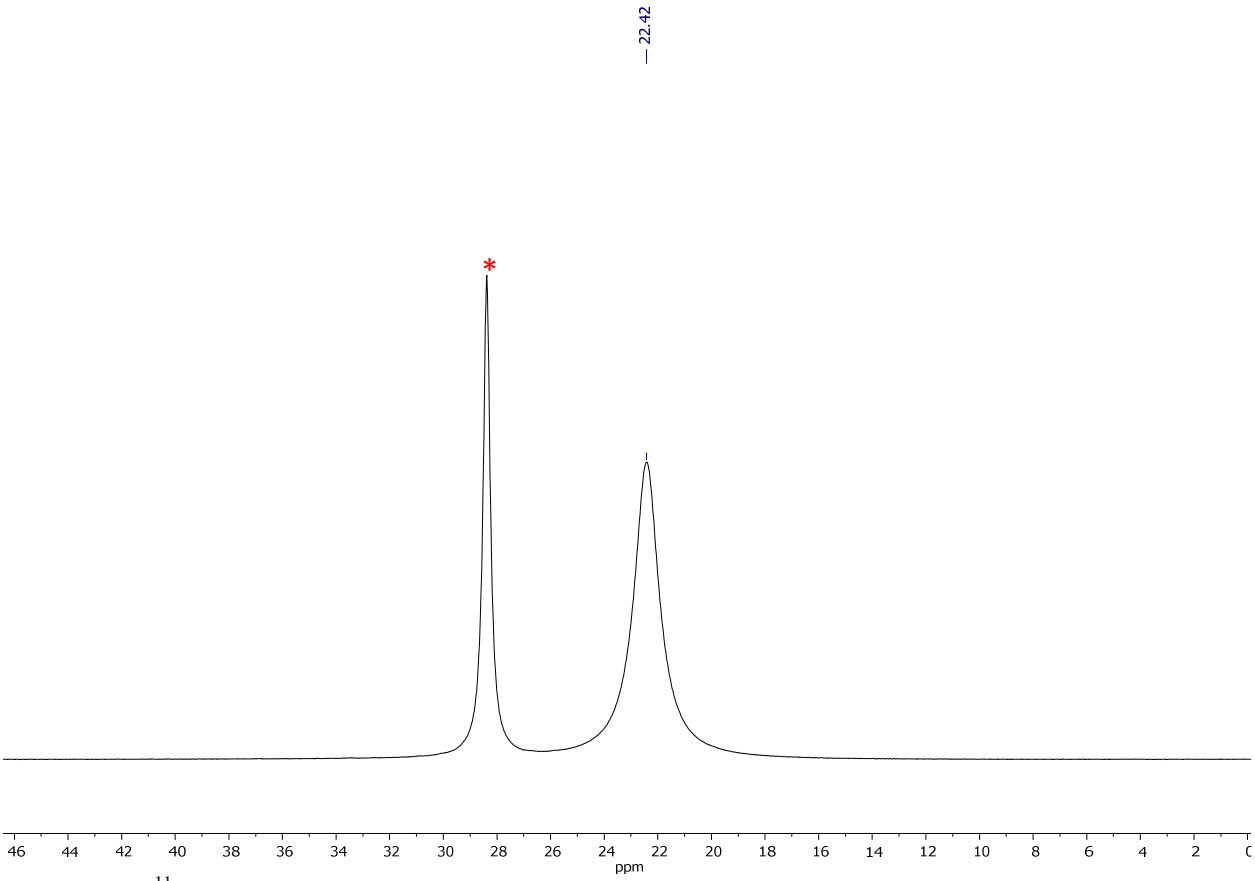
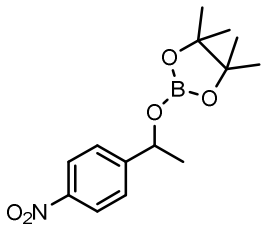


Figure S37. ^{11}B NMR spectrum of 2-(4-nitrophenylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



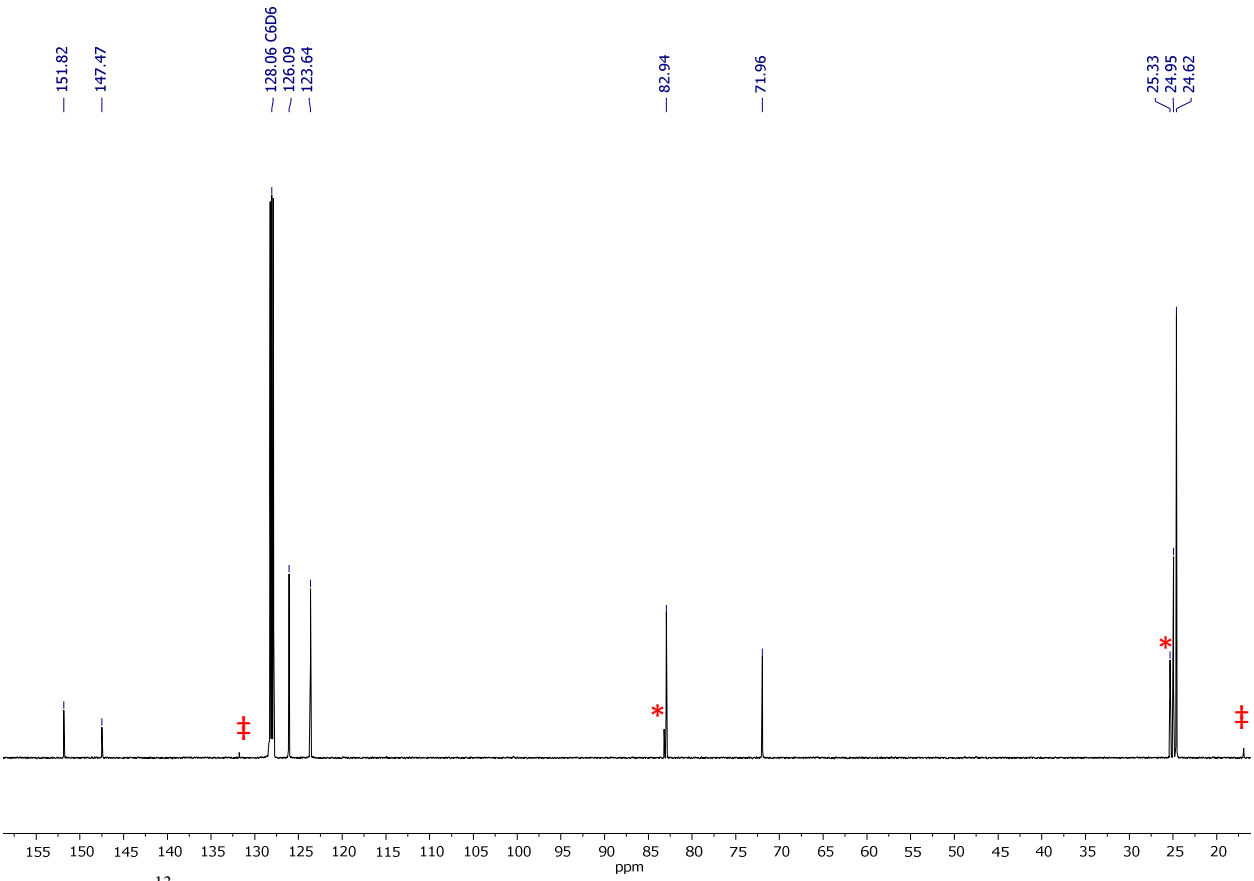
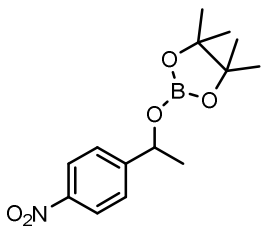


Figure S38. ^{13}C NMR spectrum of 2-(4-nitrophenylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



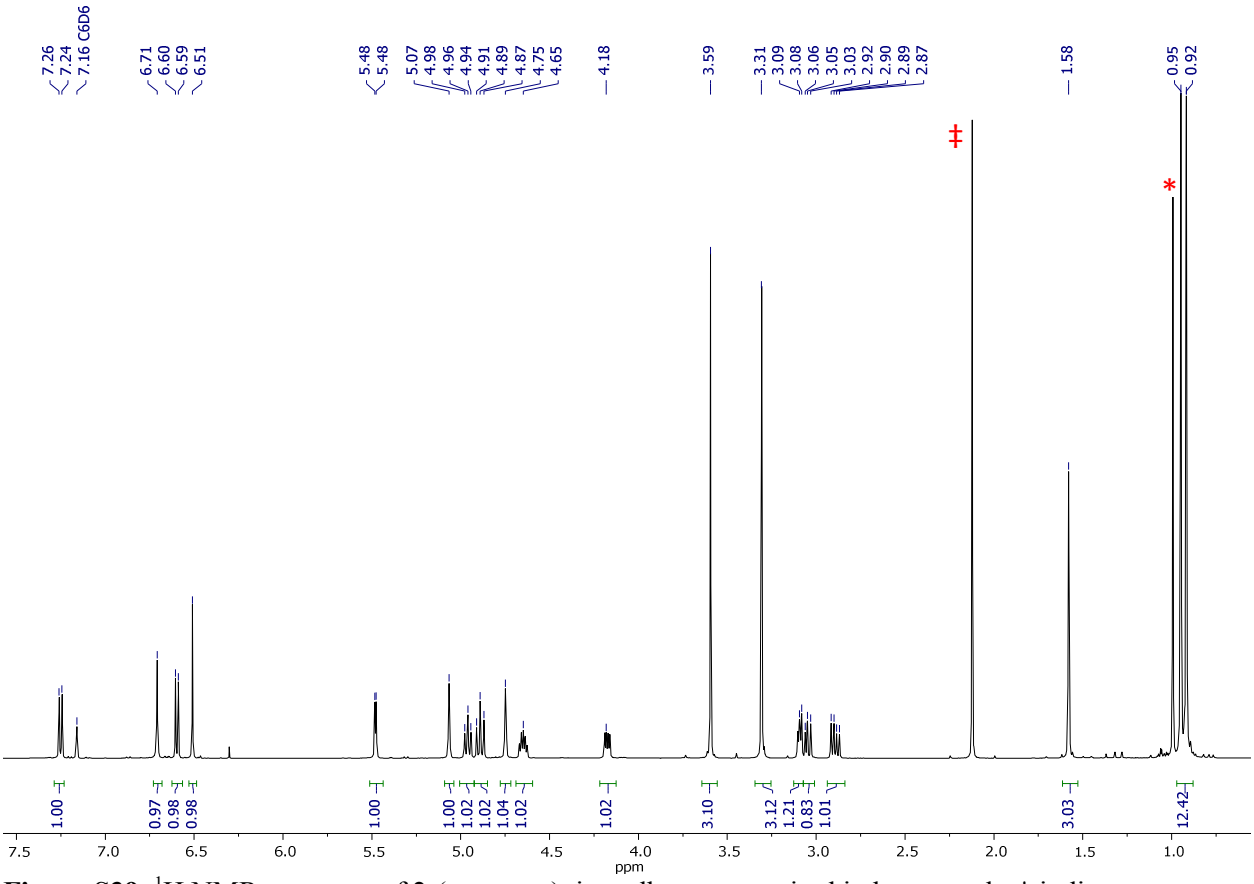
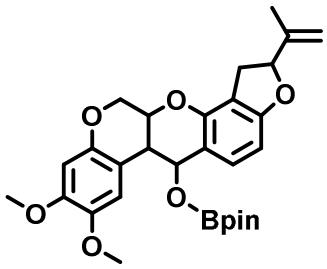


Figure S39. ^{1}H NMR spectrum of 2-(rotenoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



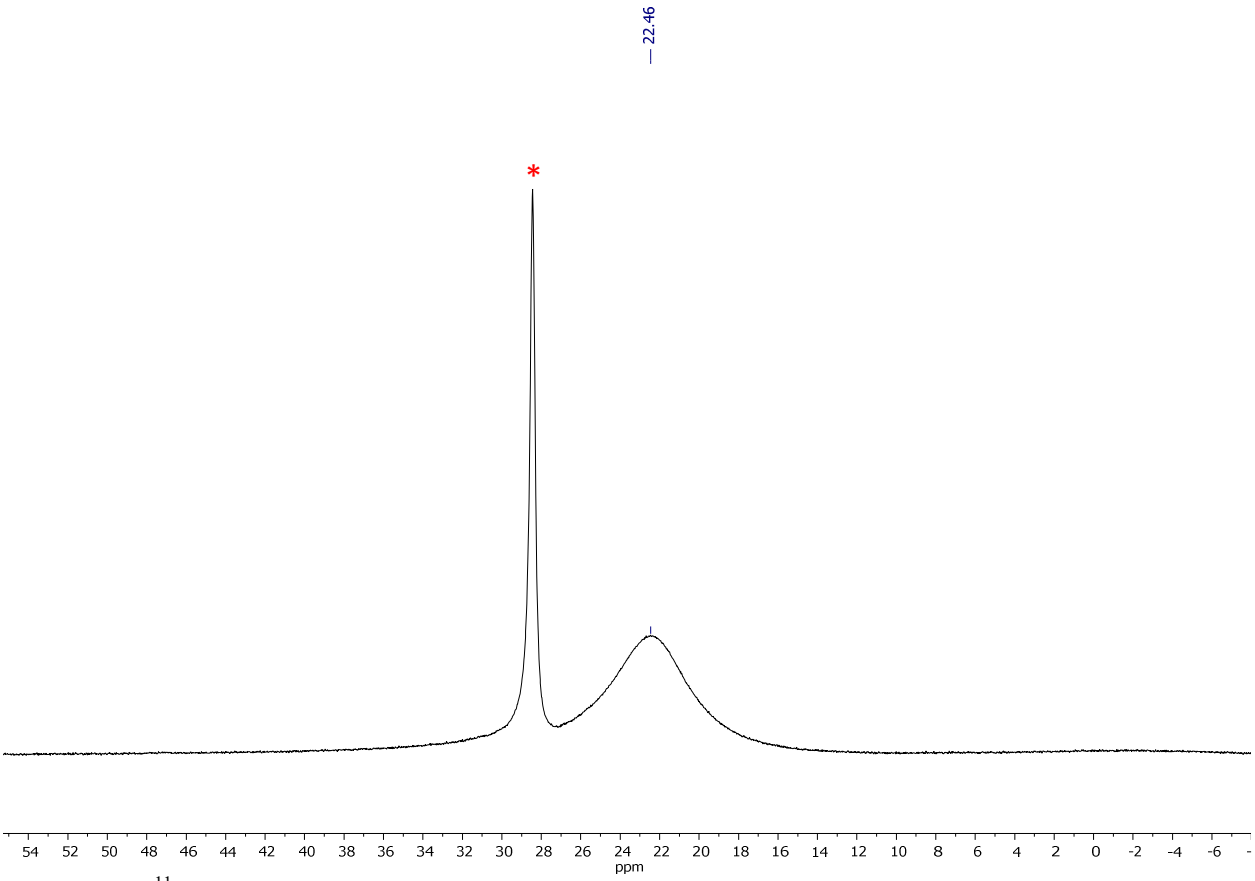
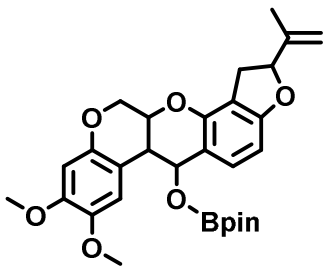


Figure S40. ^{11}B NMR spectrum of 2-(rotenoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



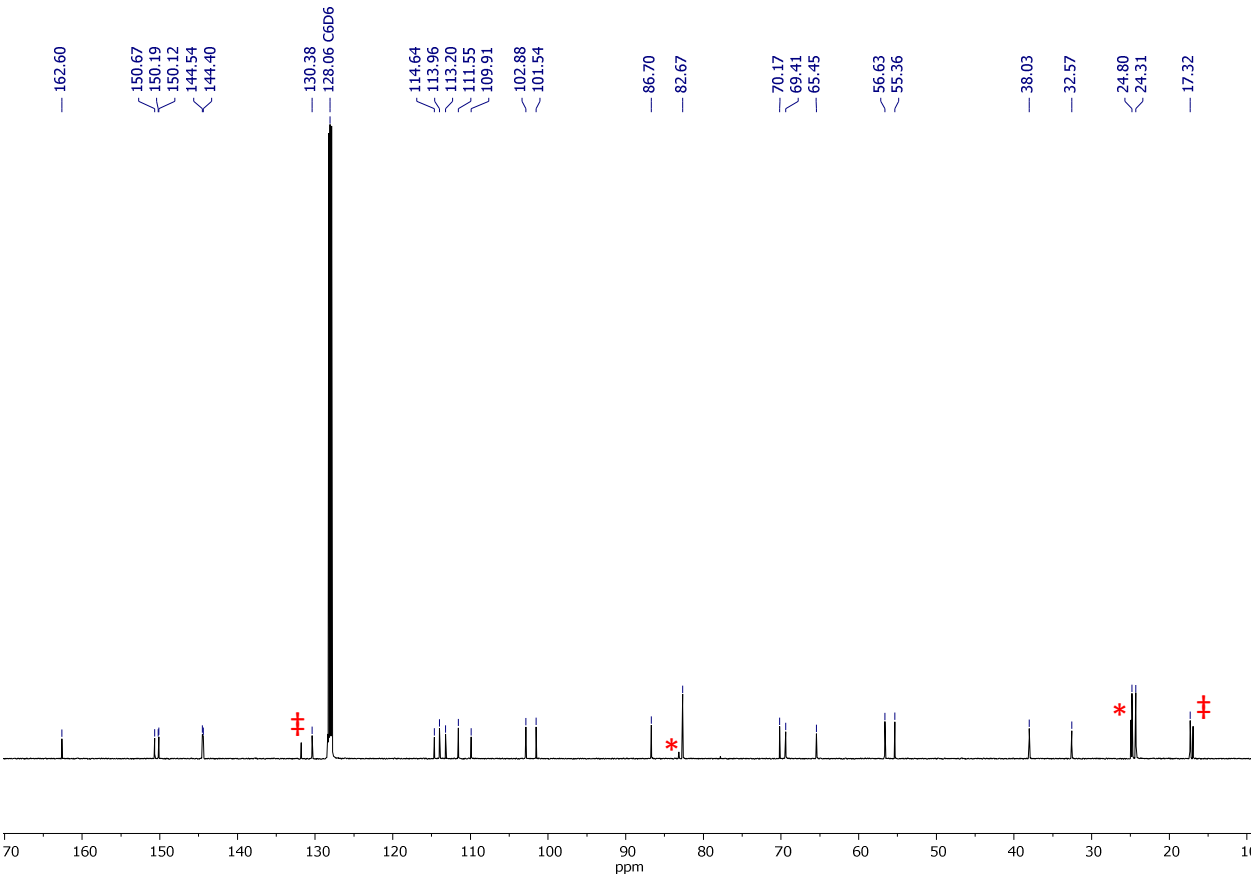
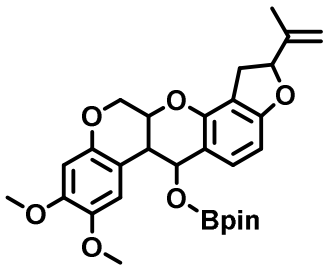


Figure S41. ^{13}C NMR spectrum of 2-(rotenoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



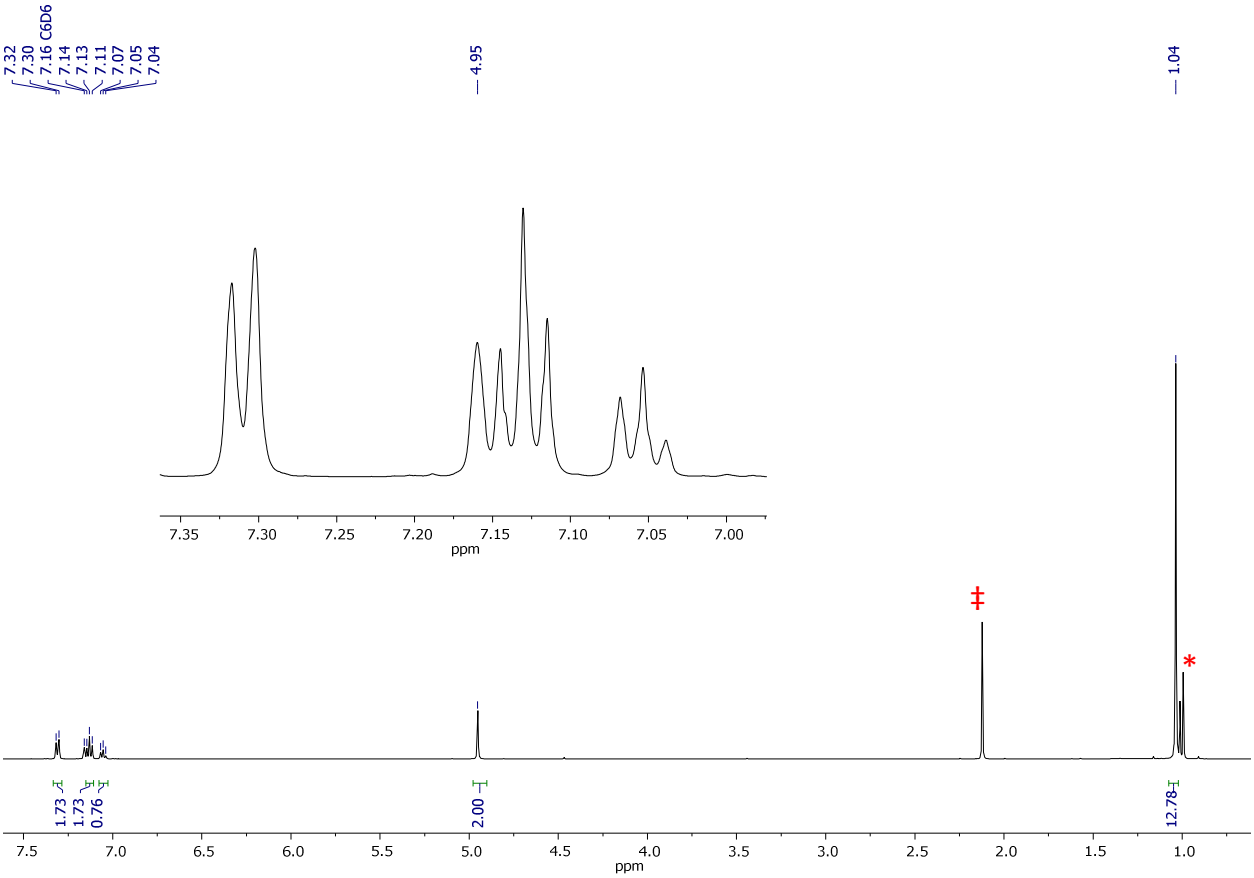
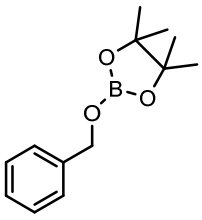


Figure S42. ^{1}H NMR spectrum of 2-(benzyloxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



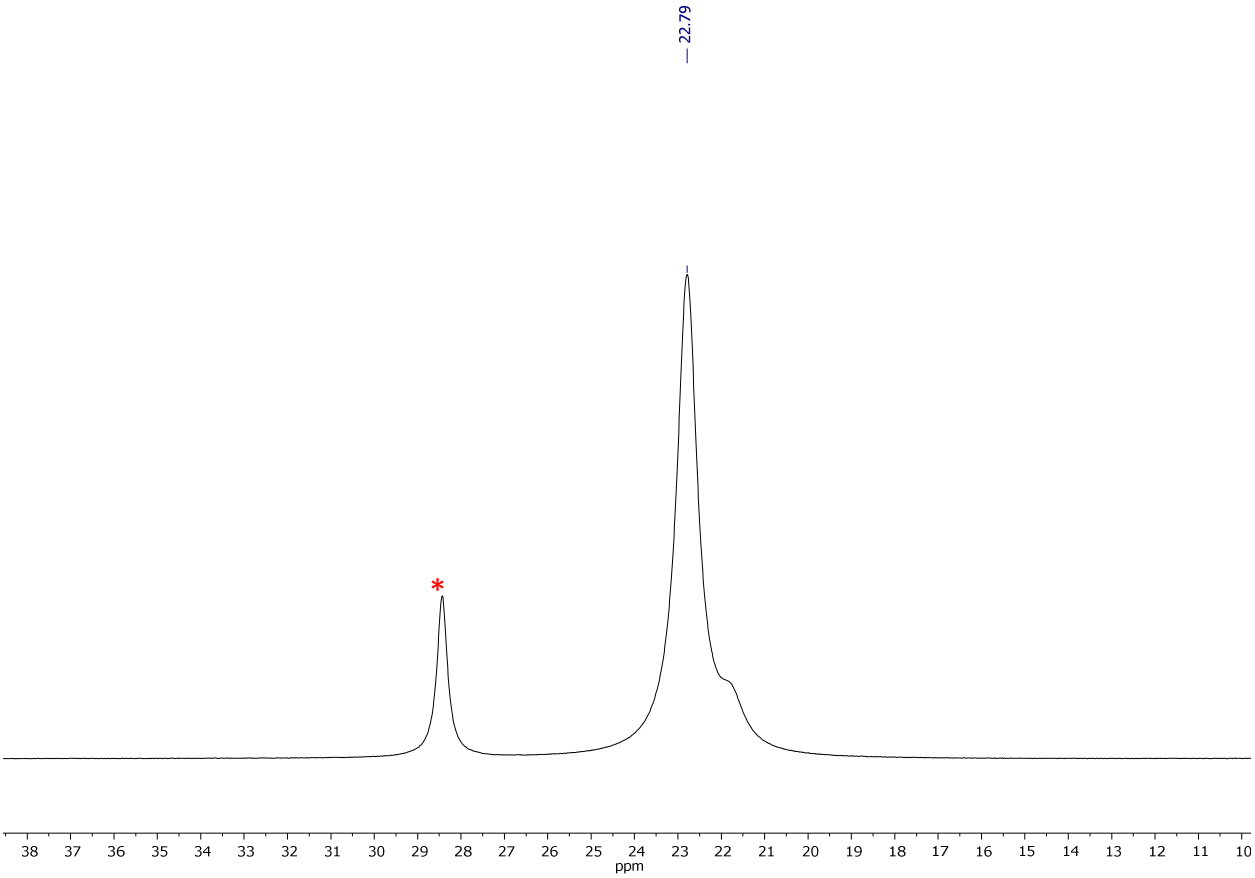
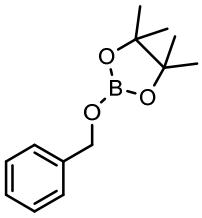


Figure S43. ^{11}B NMR spectrum of 2-(benzyloxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



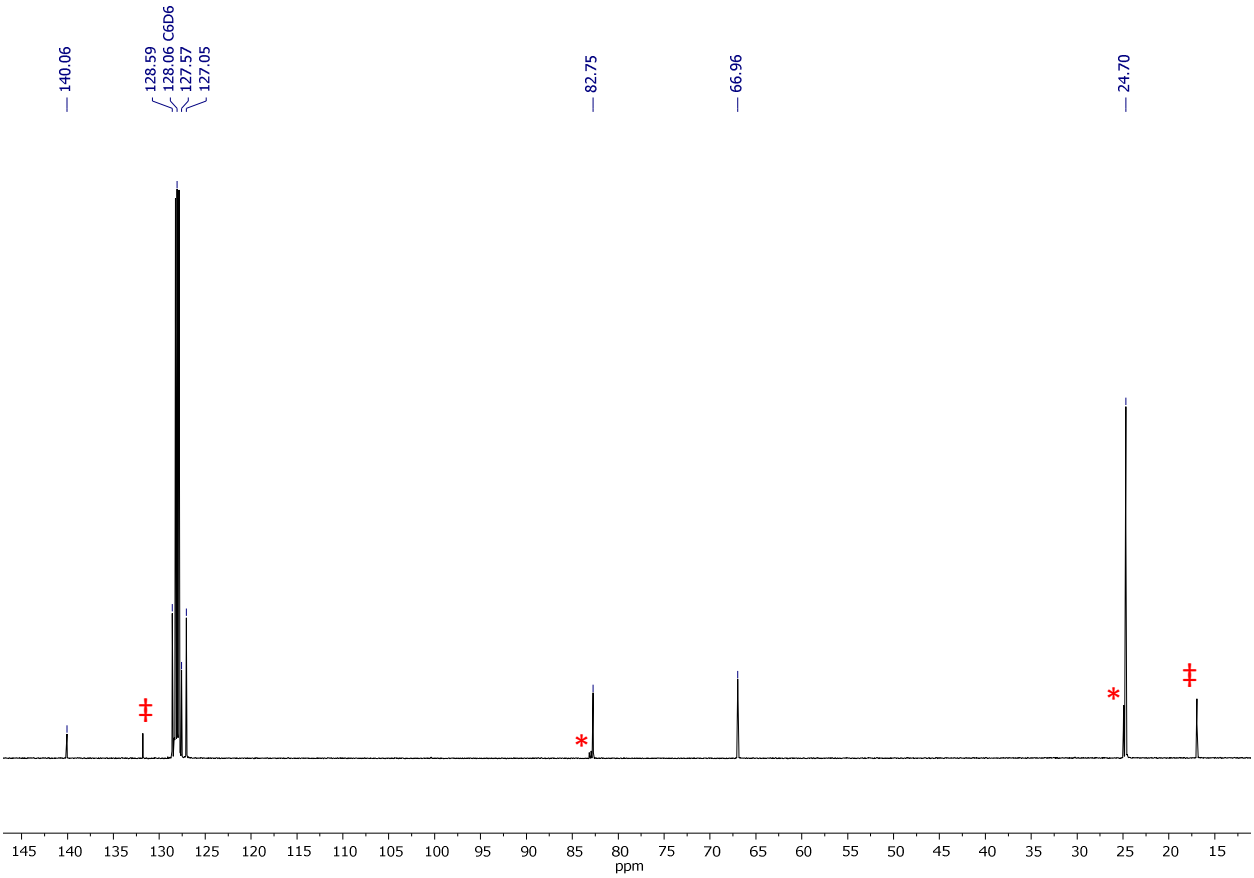
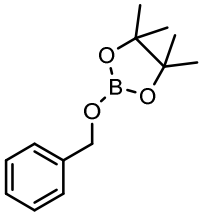


Figure S44. ^{13}C NMR spectrum of 2-(benzyloxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



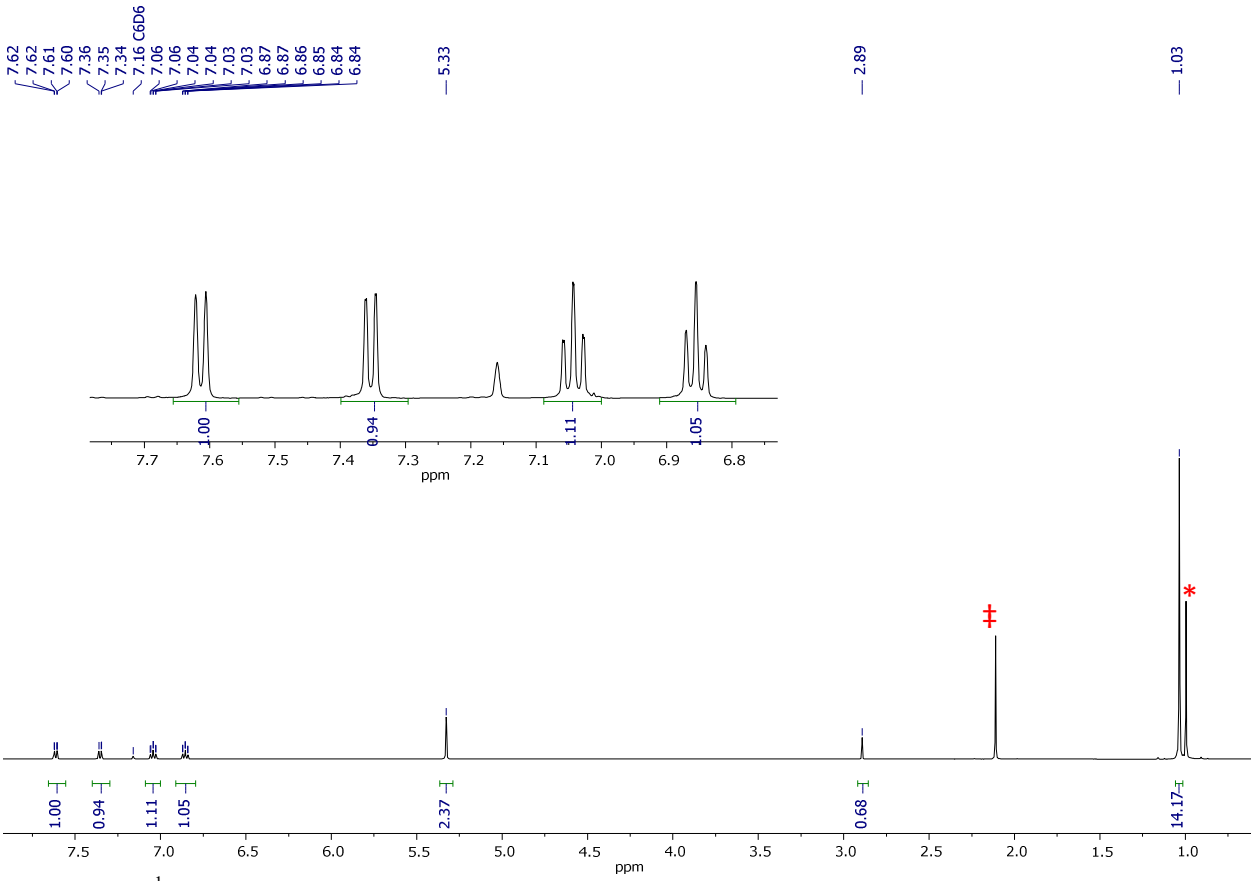
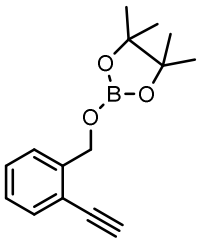


Figure S45. ^{1}H NMR spectrum of 2-(2-ethynylbenzyloxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



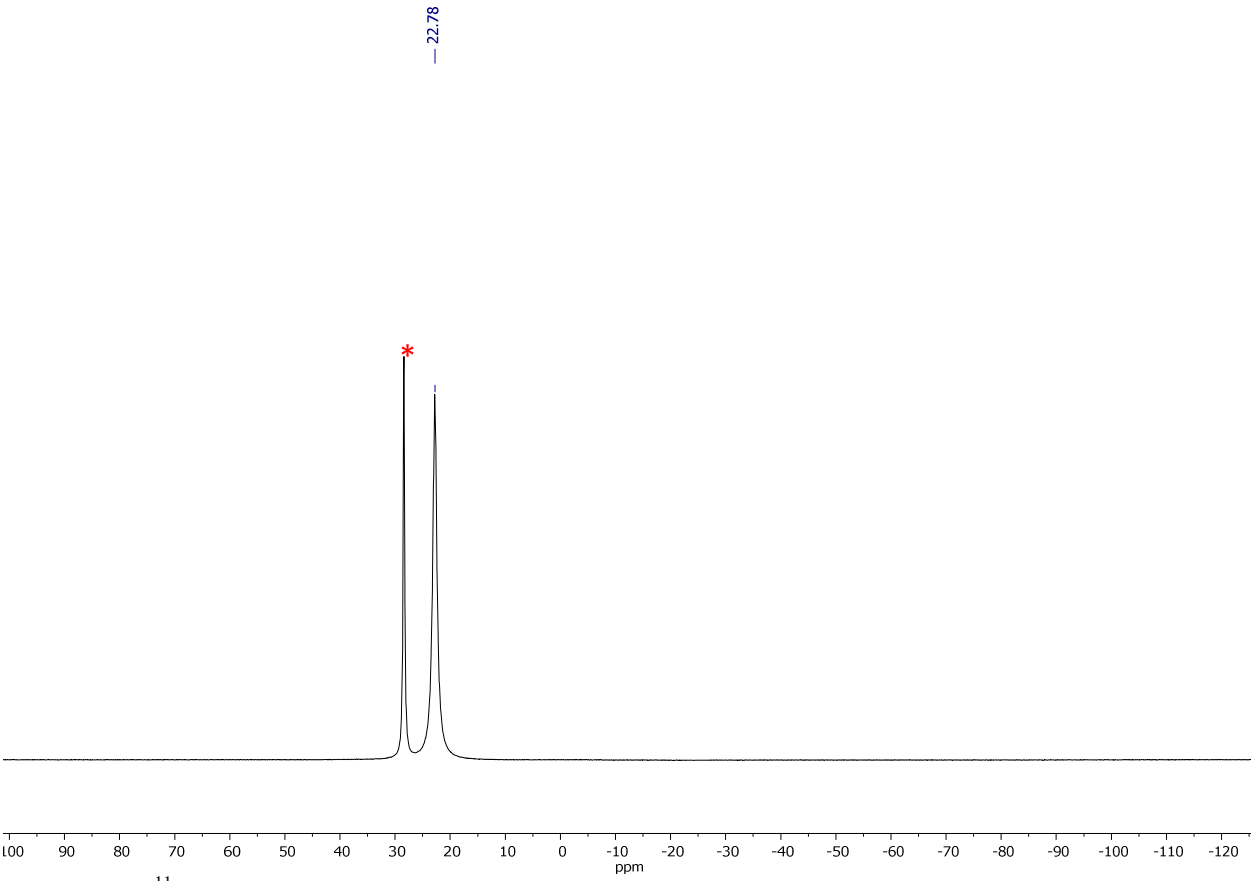
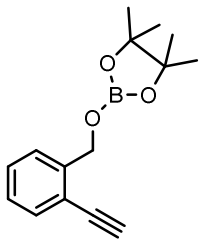


Figure S46. ^{11}B NMR spectrum of 2-(2-ethynylbenzyloxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



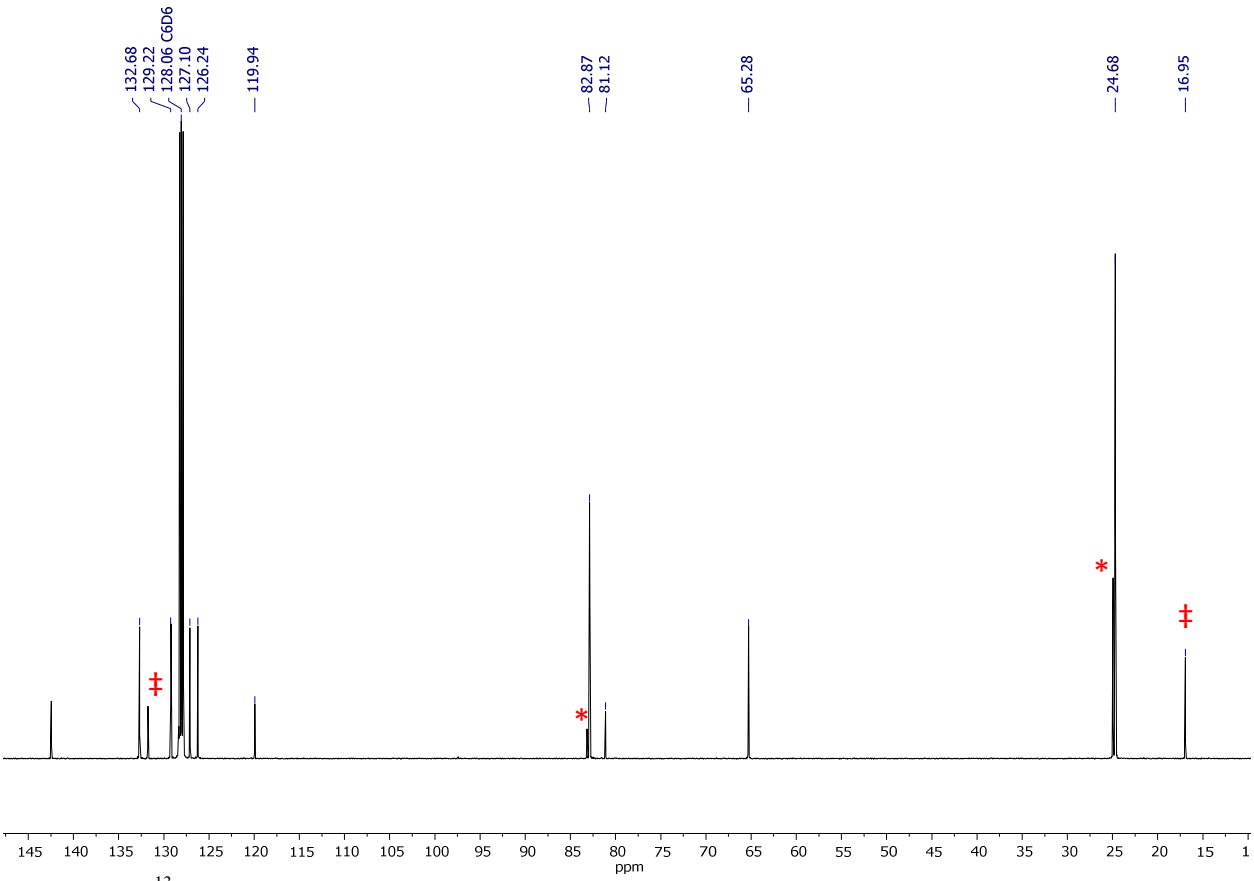
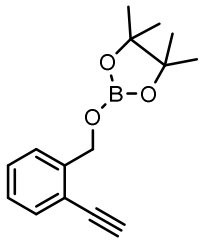


Figure S47. ^{13}C NMR spectrum of 2-(2-ethynylbenzyloxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



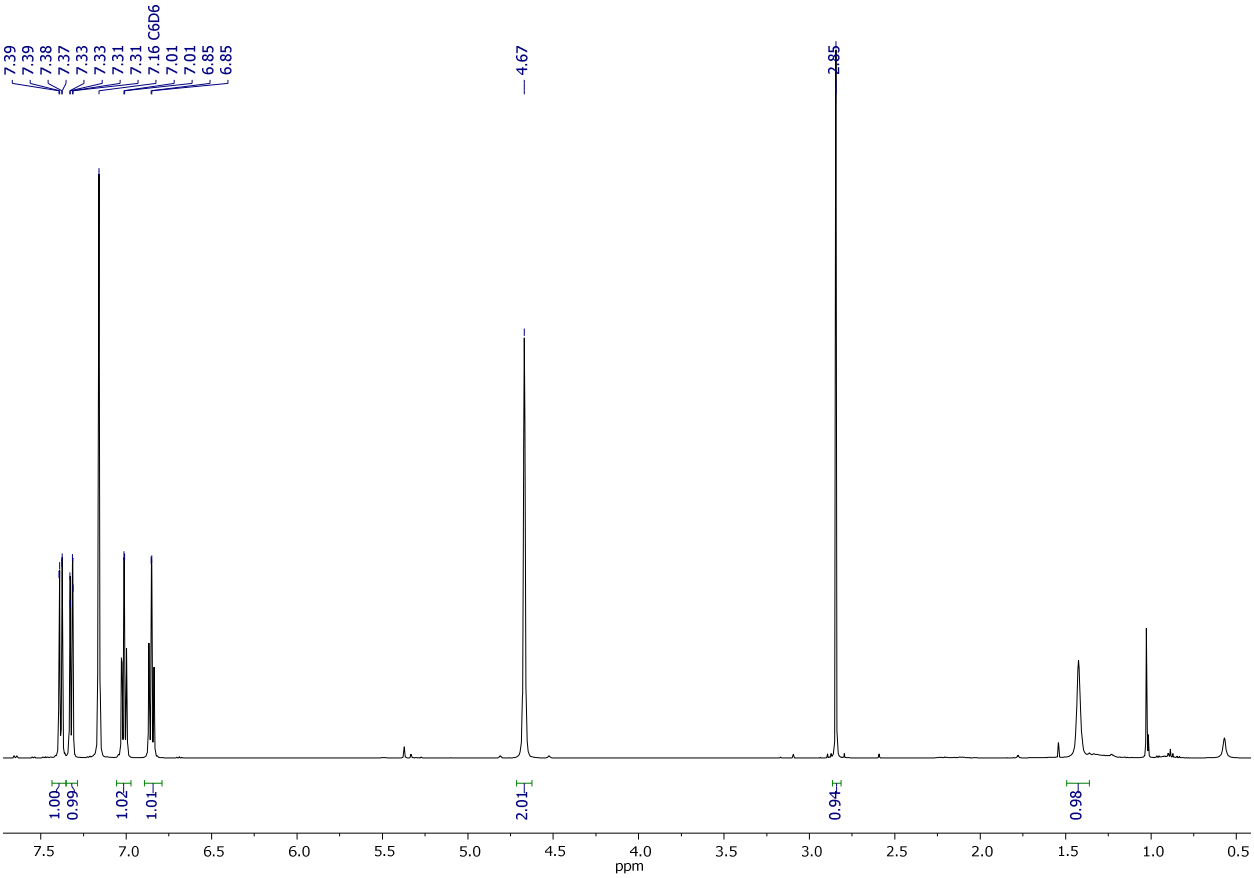
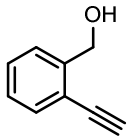


Figure S48. ^{1}H NMR spectrum of 2-ethynylbenzyl alcohol acquired in benzene-d_6.



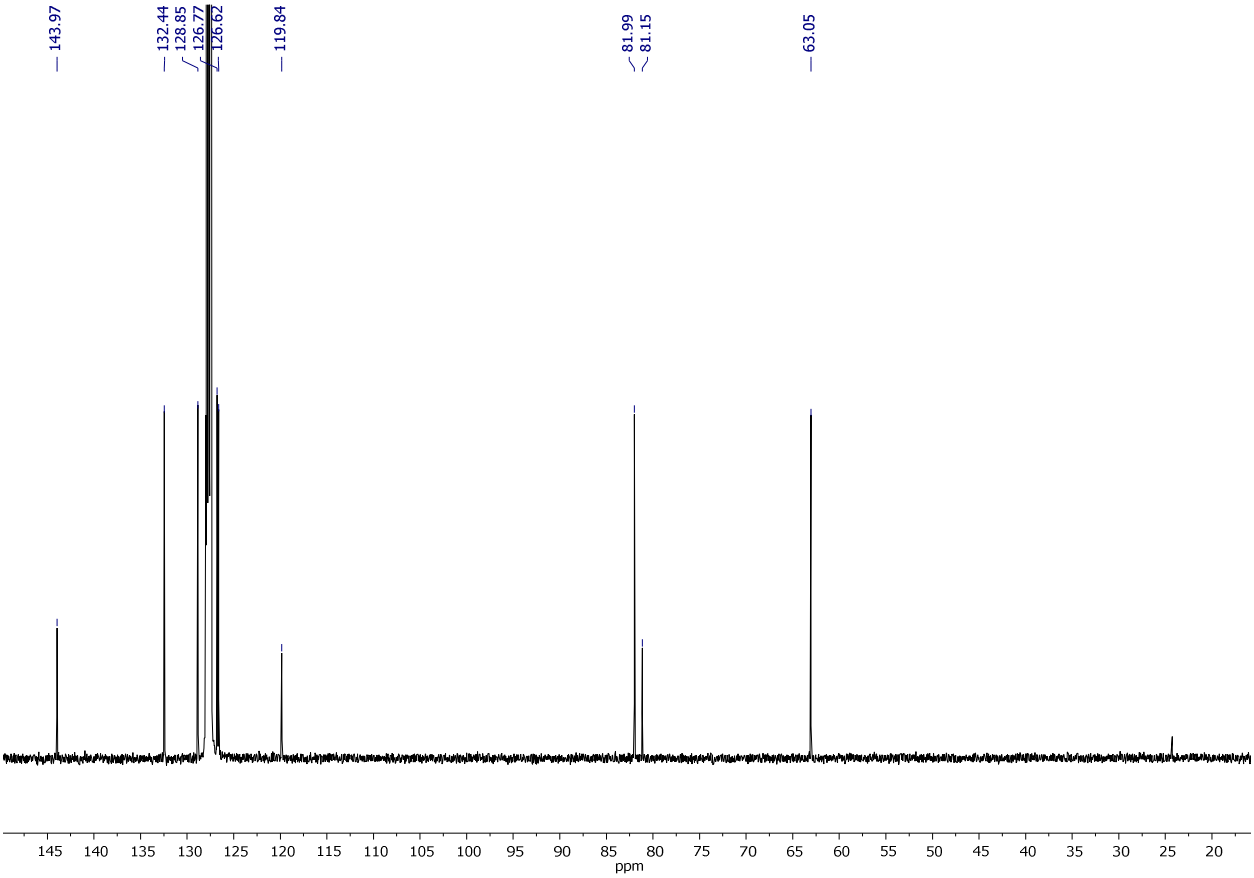
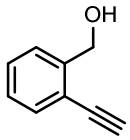


Figure S49. ^{13}C NMR spectrum of 2-ethynylbenzyl alcohol acquired in benzene-d_6.



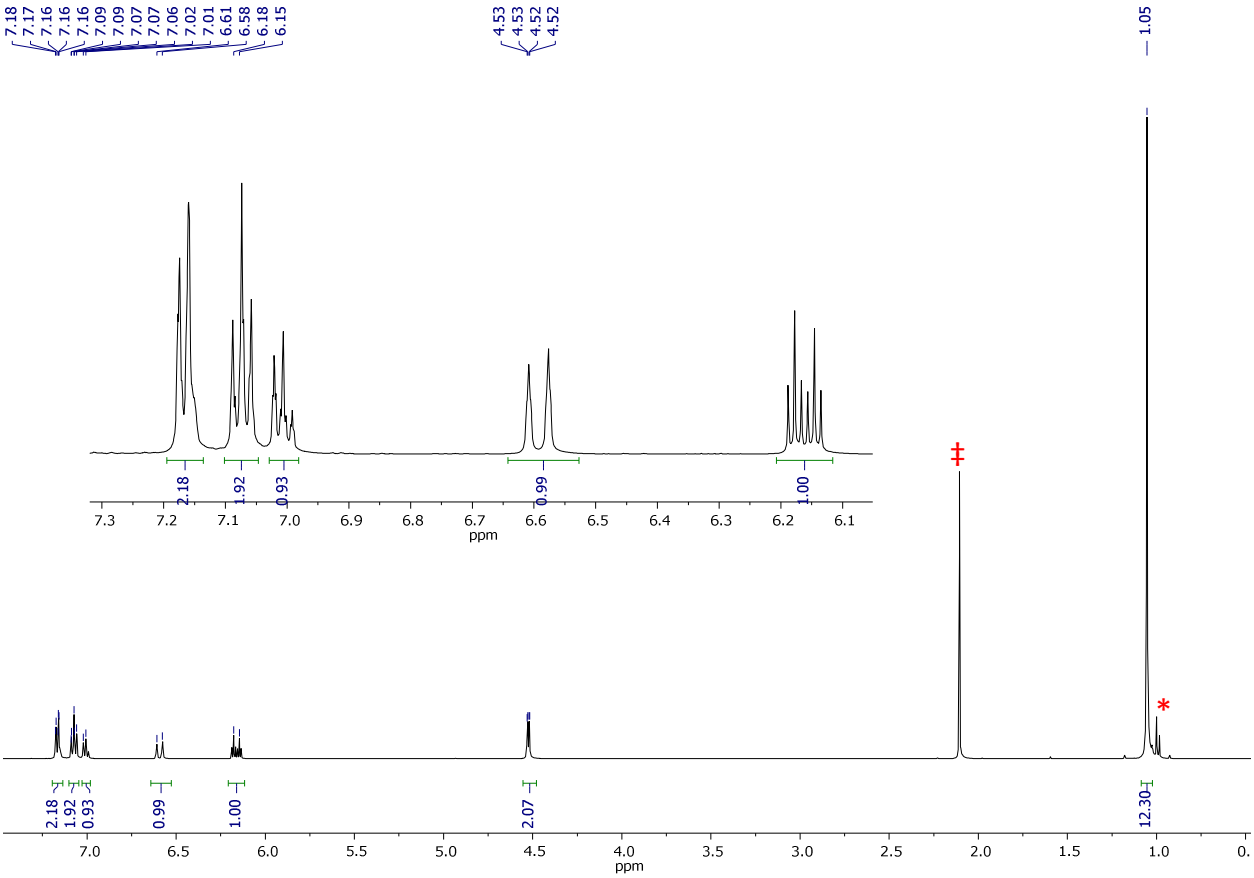
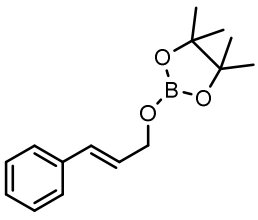


Figure S50. ^{1}H NMR spectrum of 2-(3-phenylprop-3-enylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



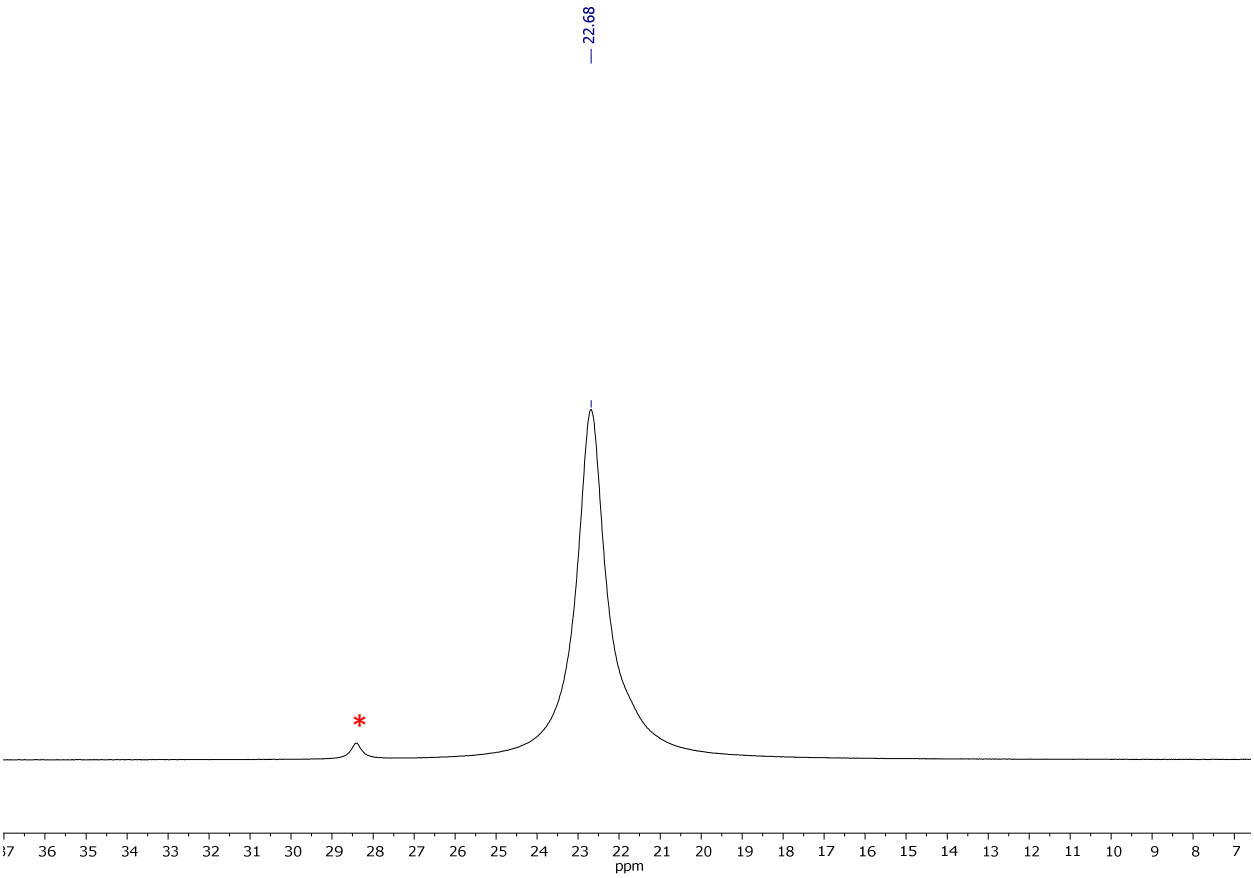
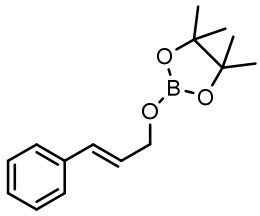


Figure S51. ^{11}B NMR spectrum of 2-(3-phenylprop-3-enylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



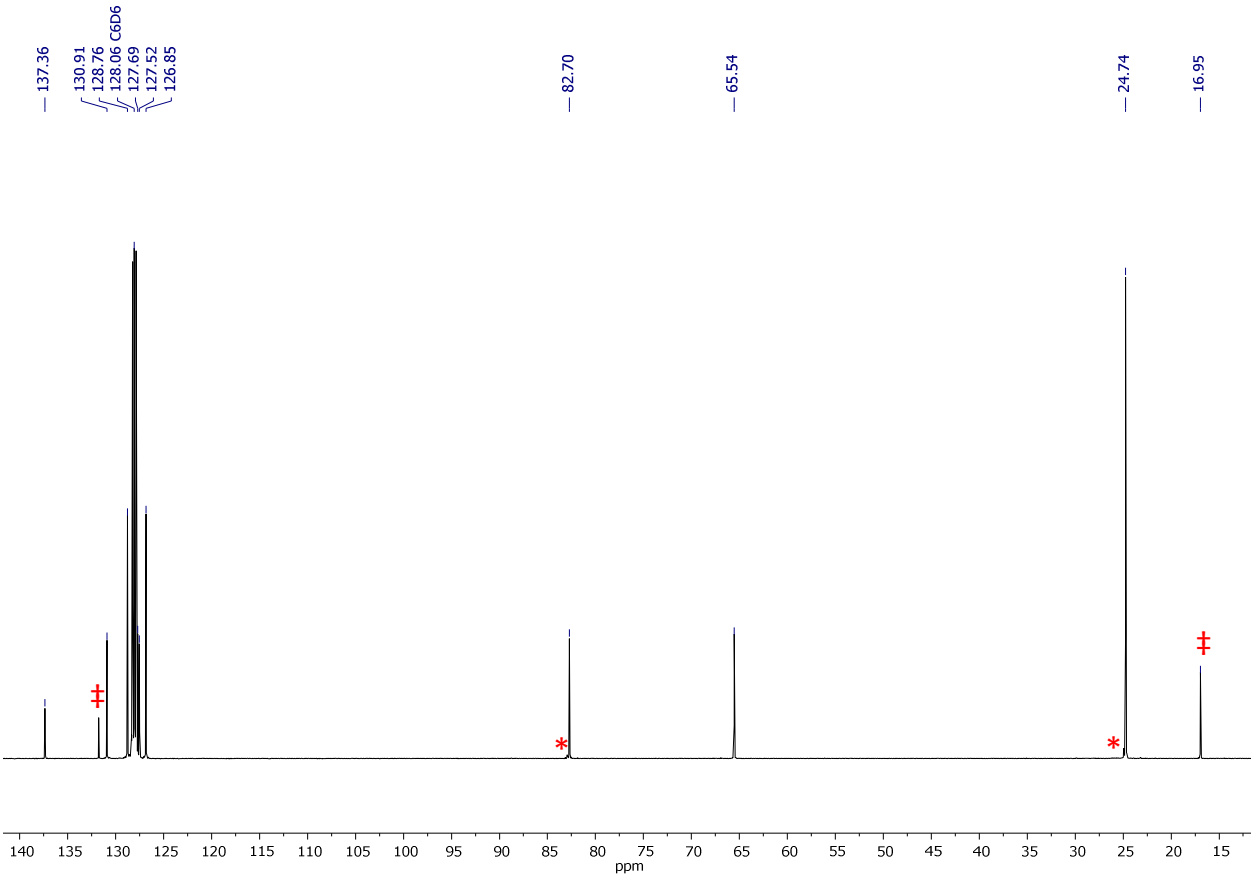
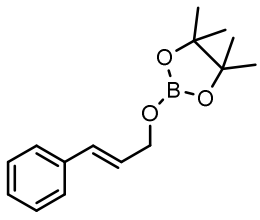


Figure S52. ^{13}C NMR spectrum of 2-(3-phenylprop-3-enylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



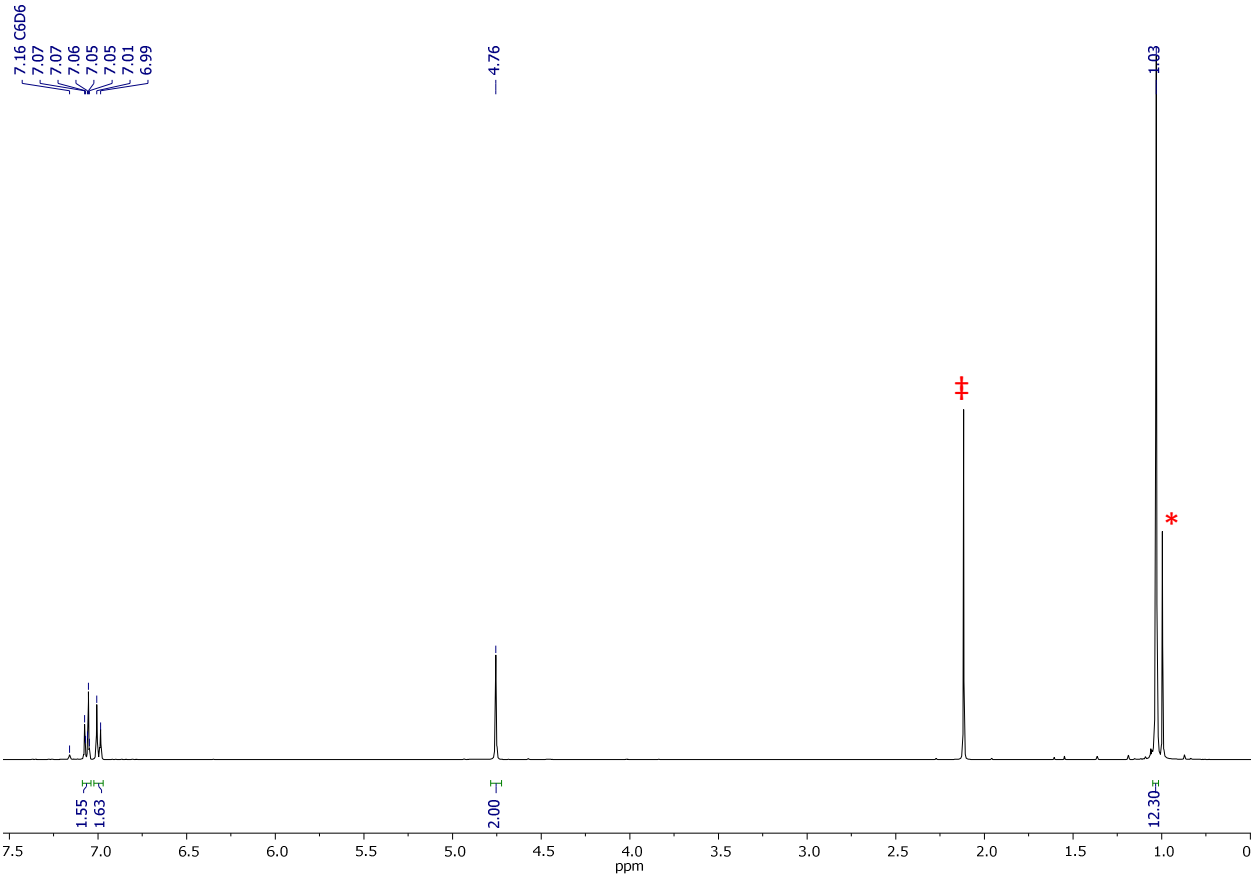
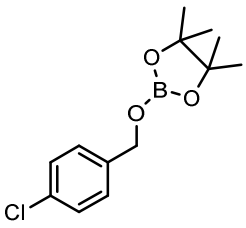


Figure S53. ^{1}H NMR spectrum of 2-(4-chlorobenzyloxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



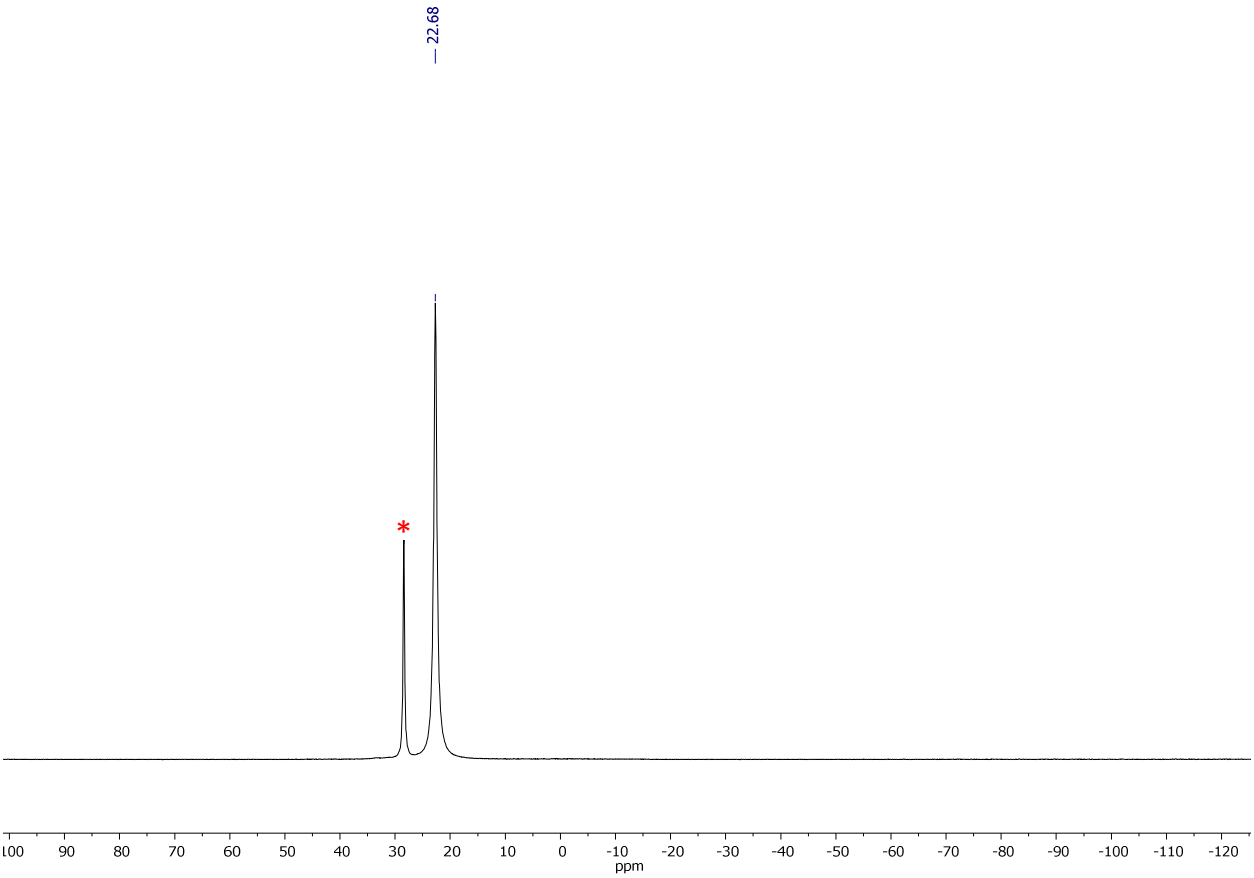
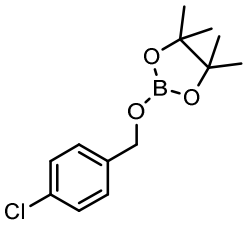


Figure S54. ^{11}B NMR spectrum of 2-(4-chlorobenzyloxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



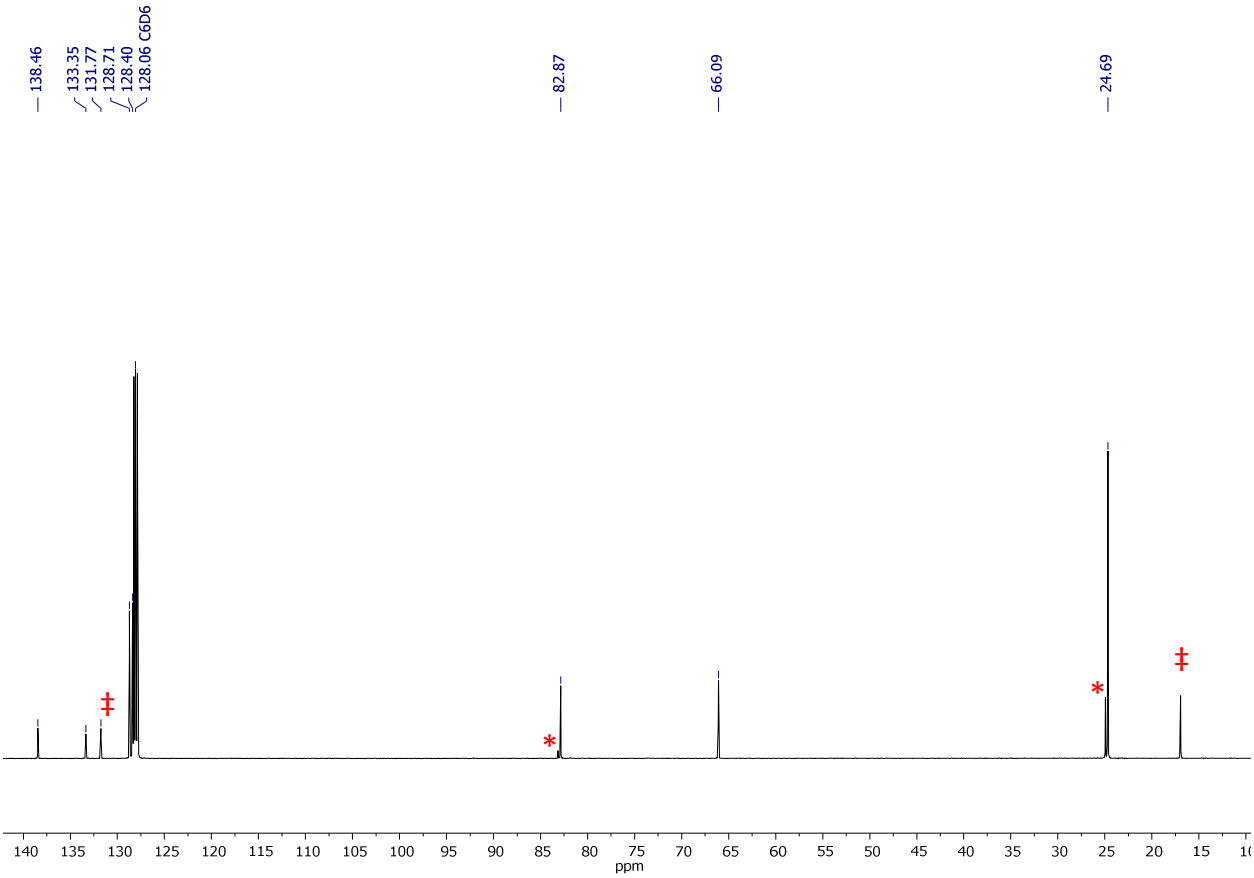
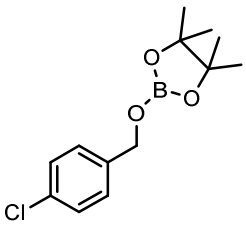


Figure S55. ^{13}C NMR spectrum of 2-(4-chlorobenzyloxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



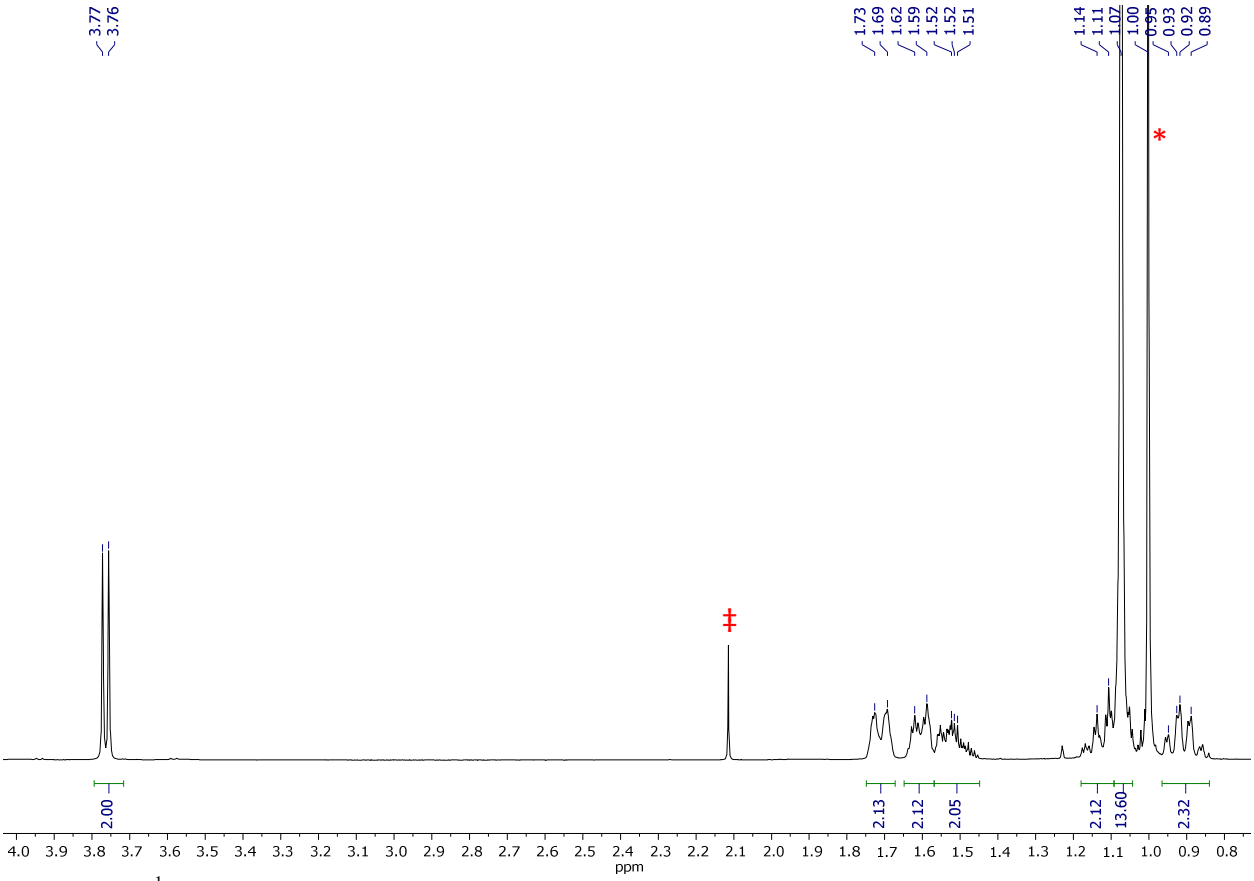
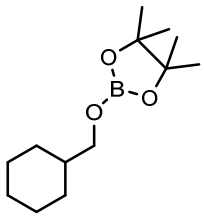


Figure S56. ^{1}H NMR spectrum of 2-(cyclohexylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



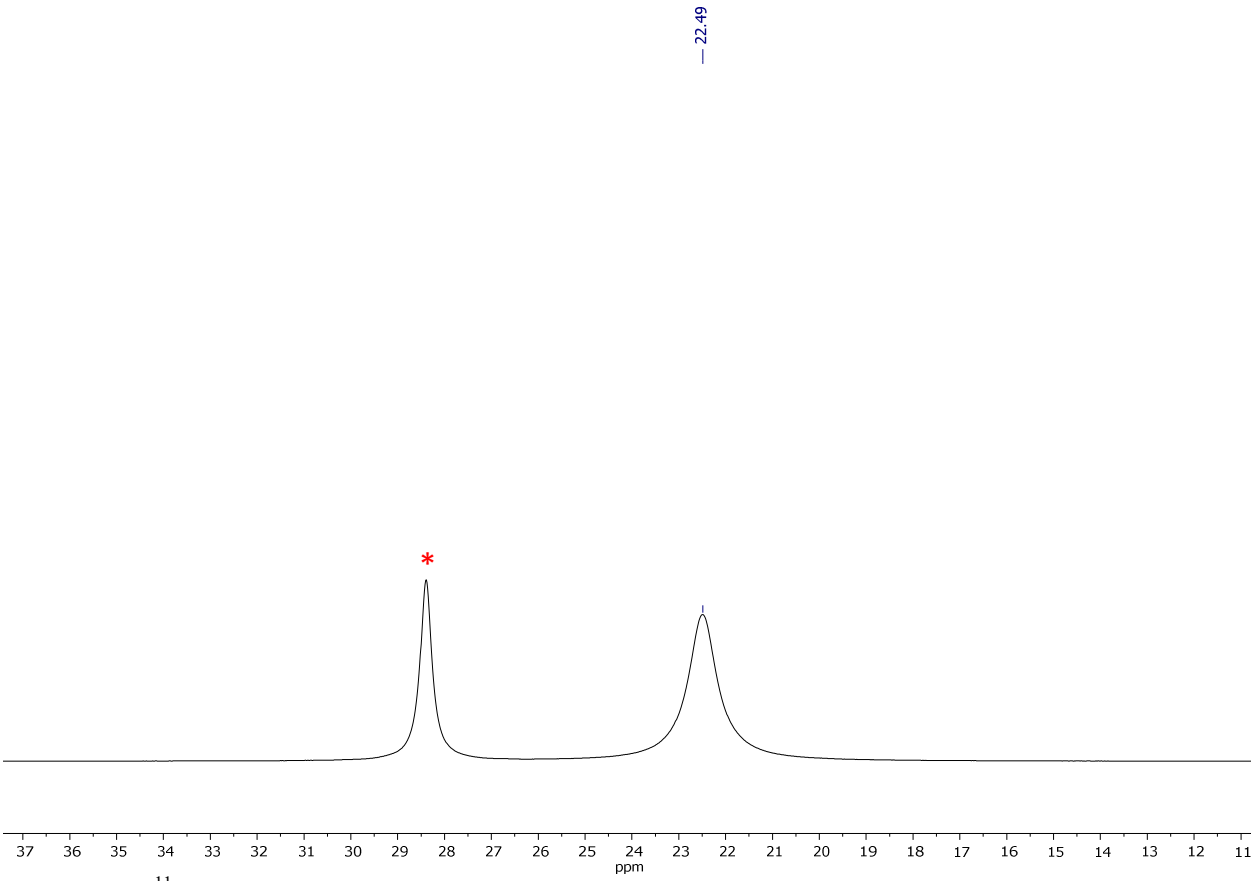
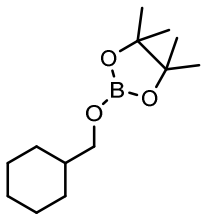


Figure S57. ^{11}B NMR spectrum of 2-(cyclohexylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



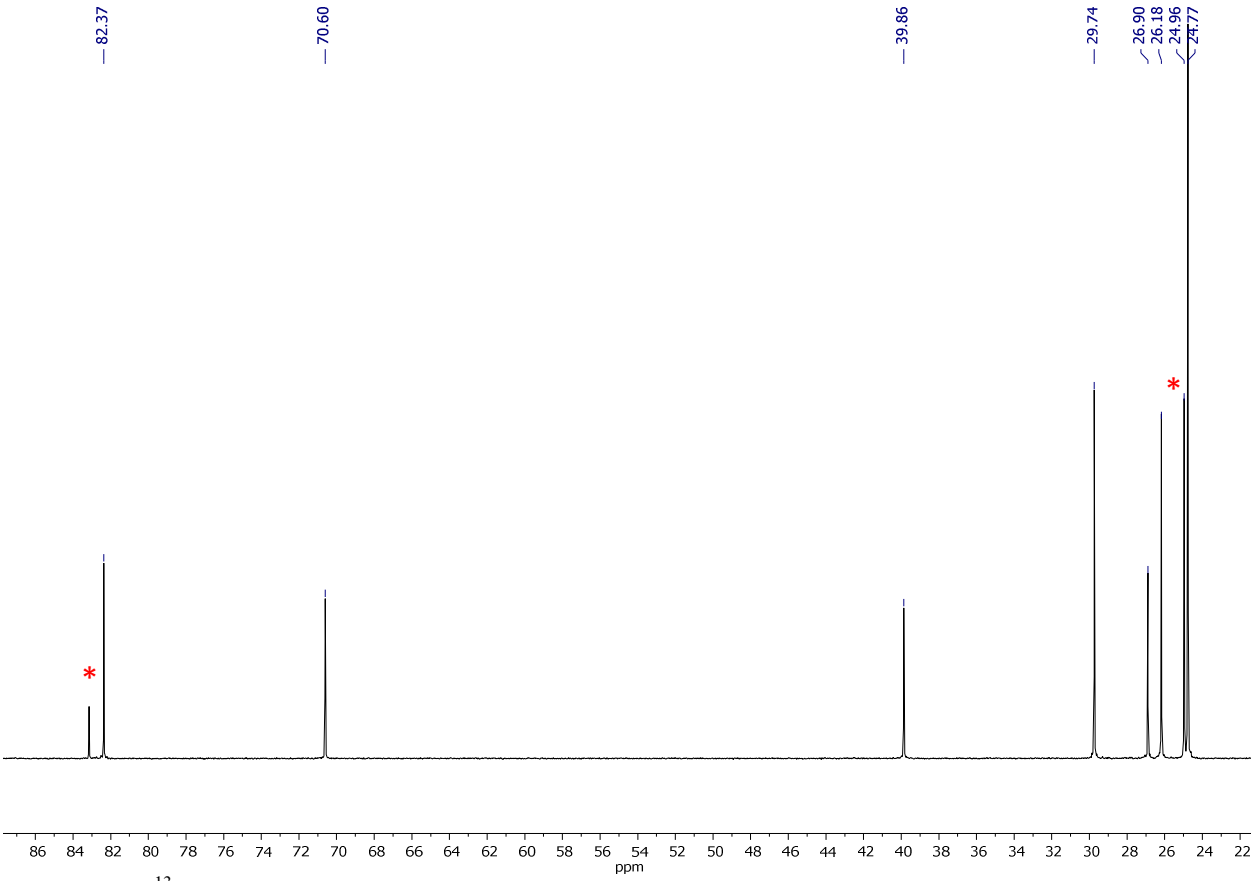
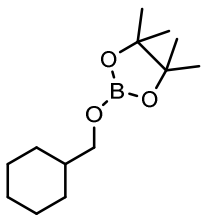


Figure S58. ^{13}C NMR spectrum of 2-(cyclohexylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



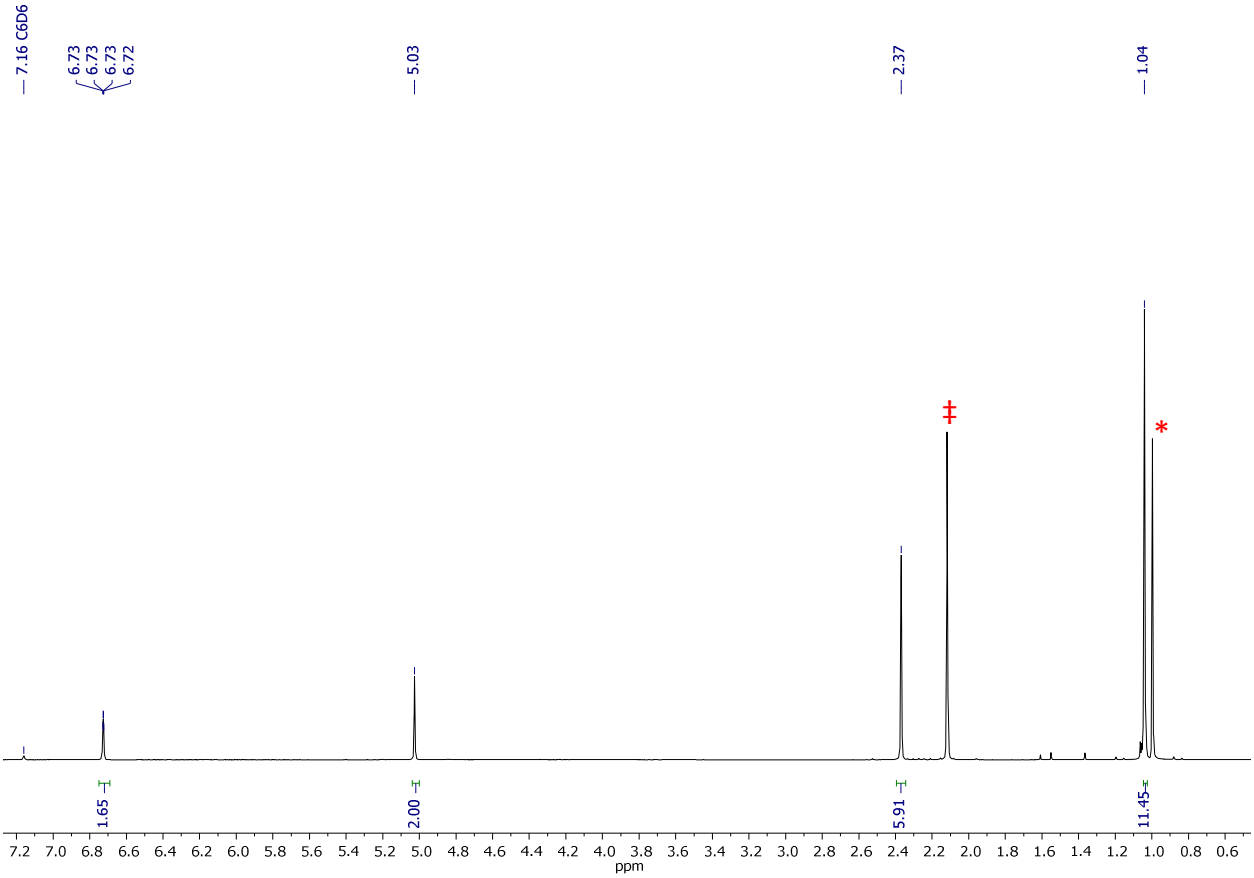
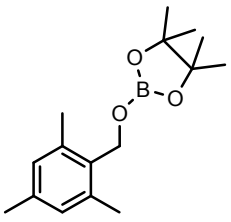


Figure S59. ^{1}H NMR spectrum of 2-(2,4,6-trimethylbenzyloxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



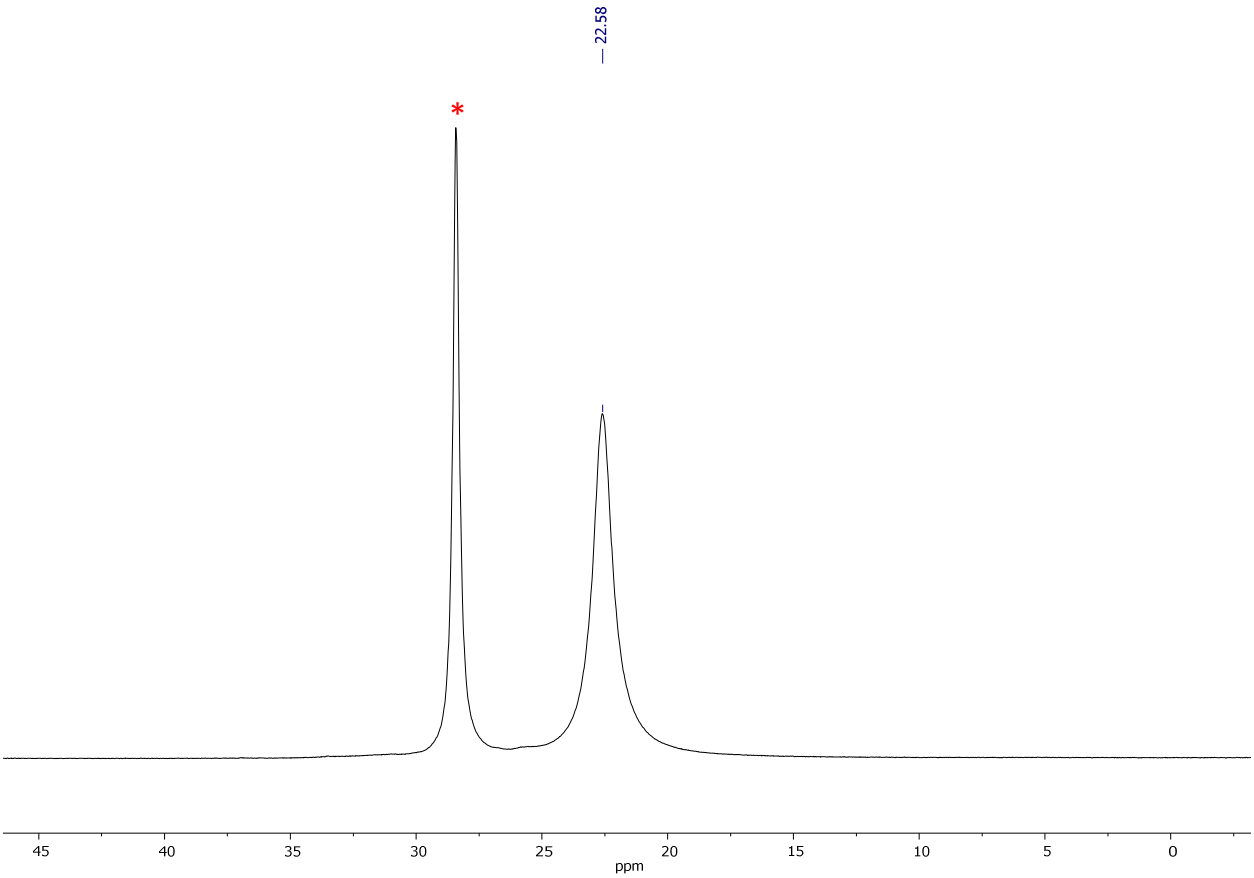
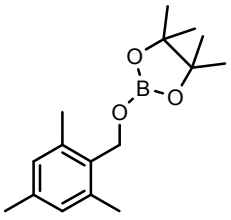


Figure S60. ^{11}B NMR spectrum of 2-(2,4,6-trimethylbenzyloxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



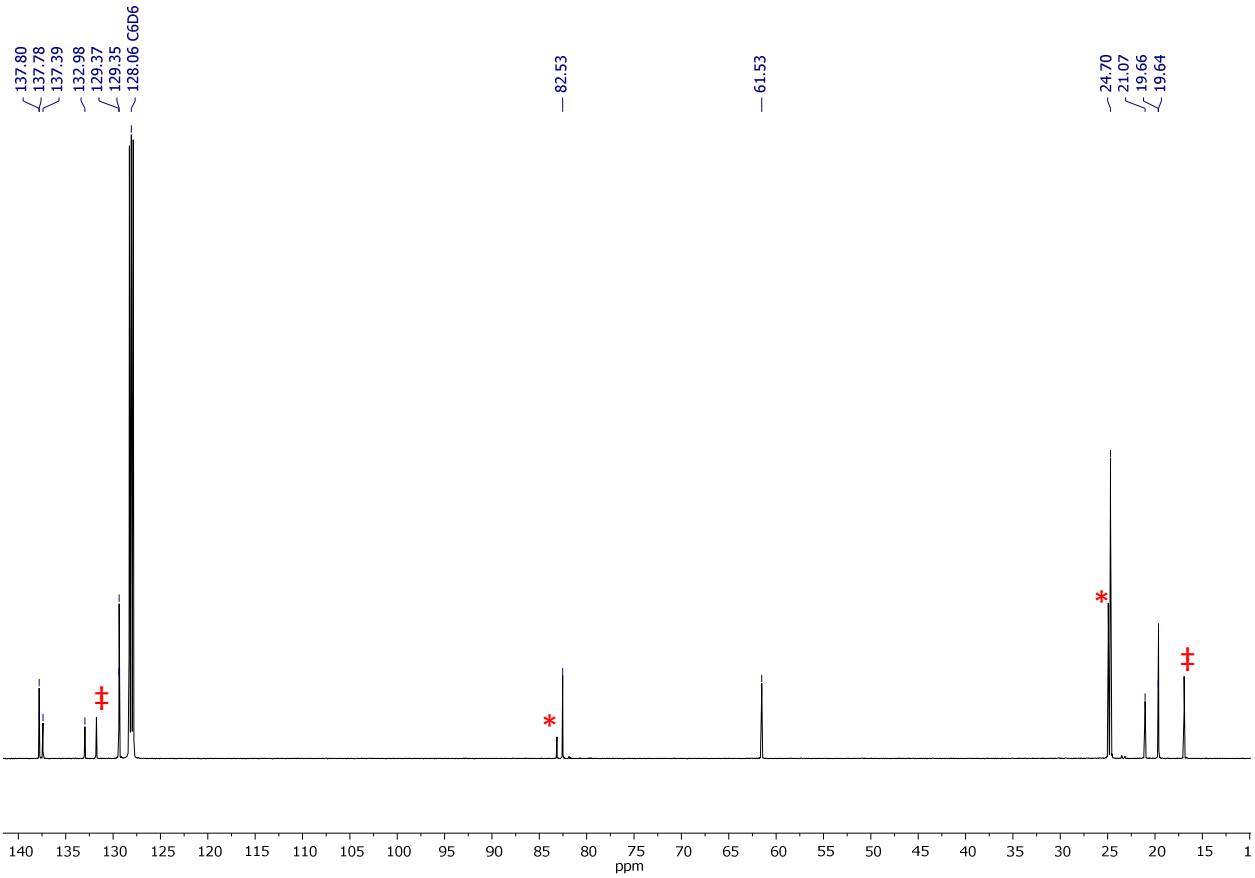
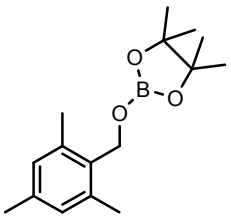


Figure S61. ^{13}C NMR spectrum of 2-(2,4,6-trimethylbenzyloxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



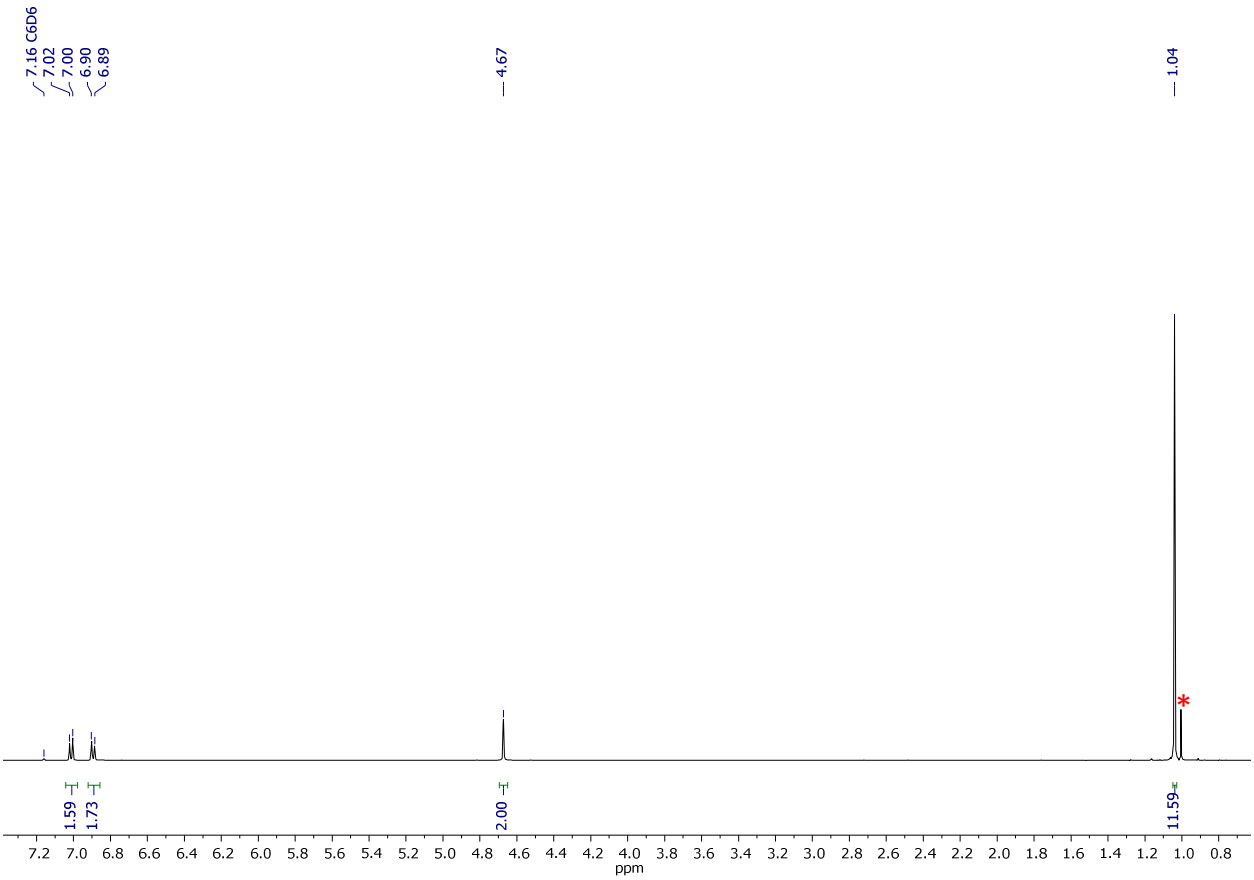
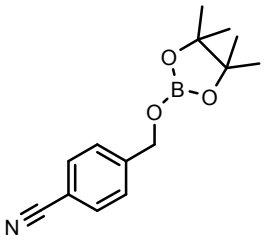


Figure S62. ^{1}H NMR spectrum of 2-(4-cyanobenzyloxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



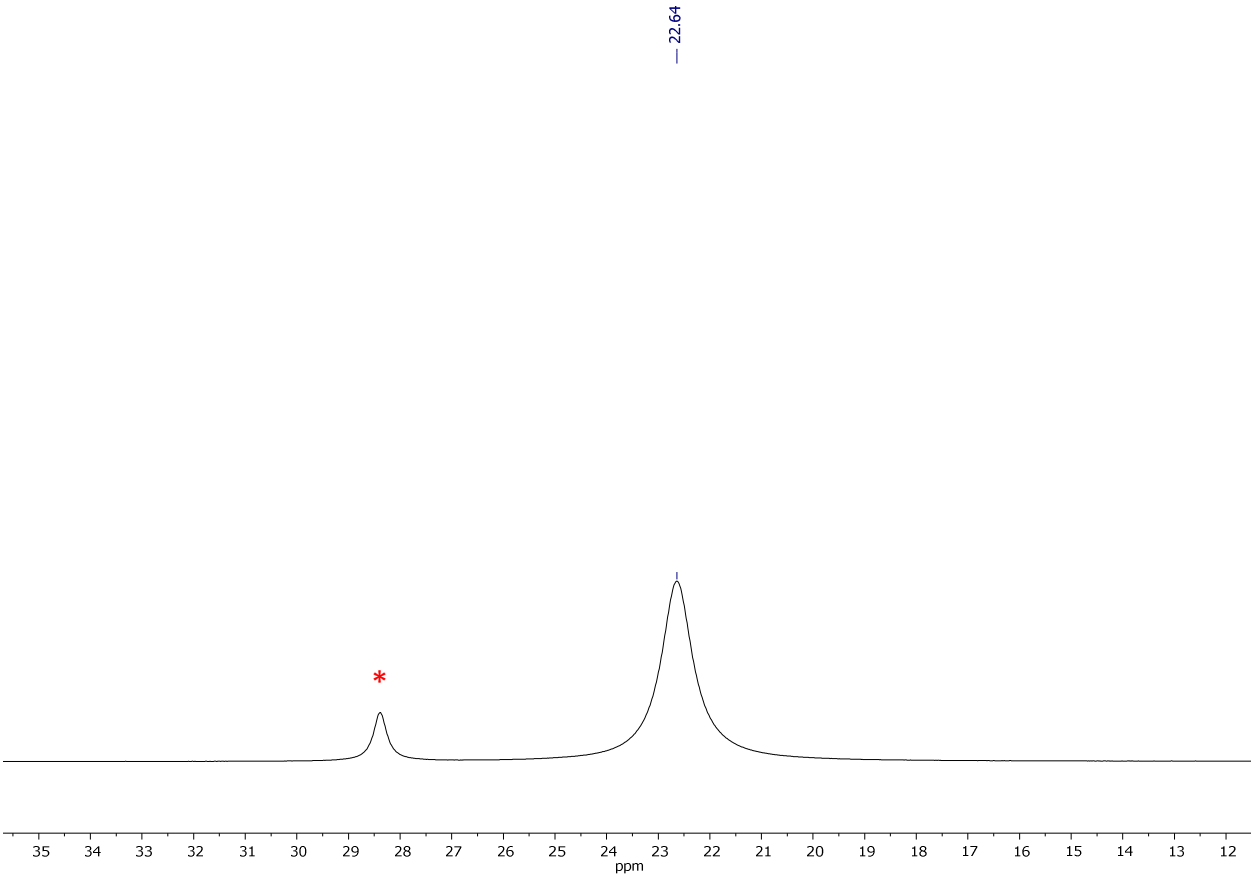
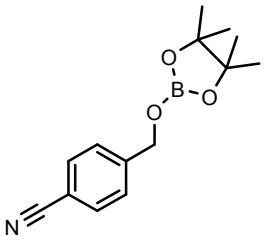


Figure S63. ^{11}B NMR spectrum of 2-(4-cyanobenzyloxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



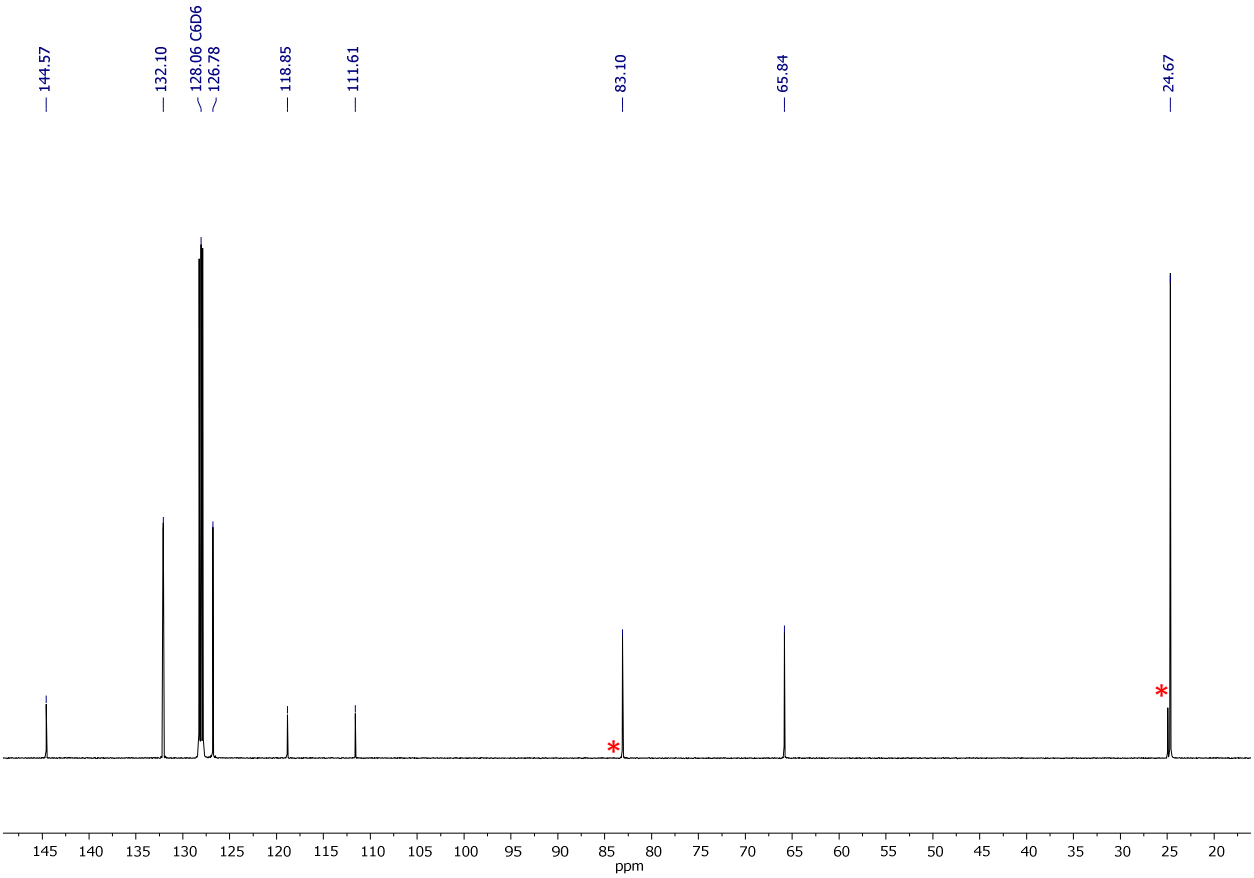
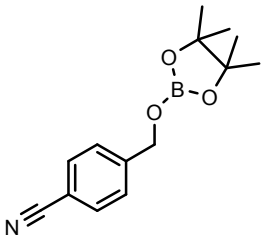


Figure S64. ^{13}C NMR spectrum of 2-(4-cyanobenzyloxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



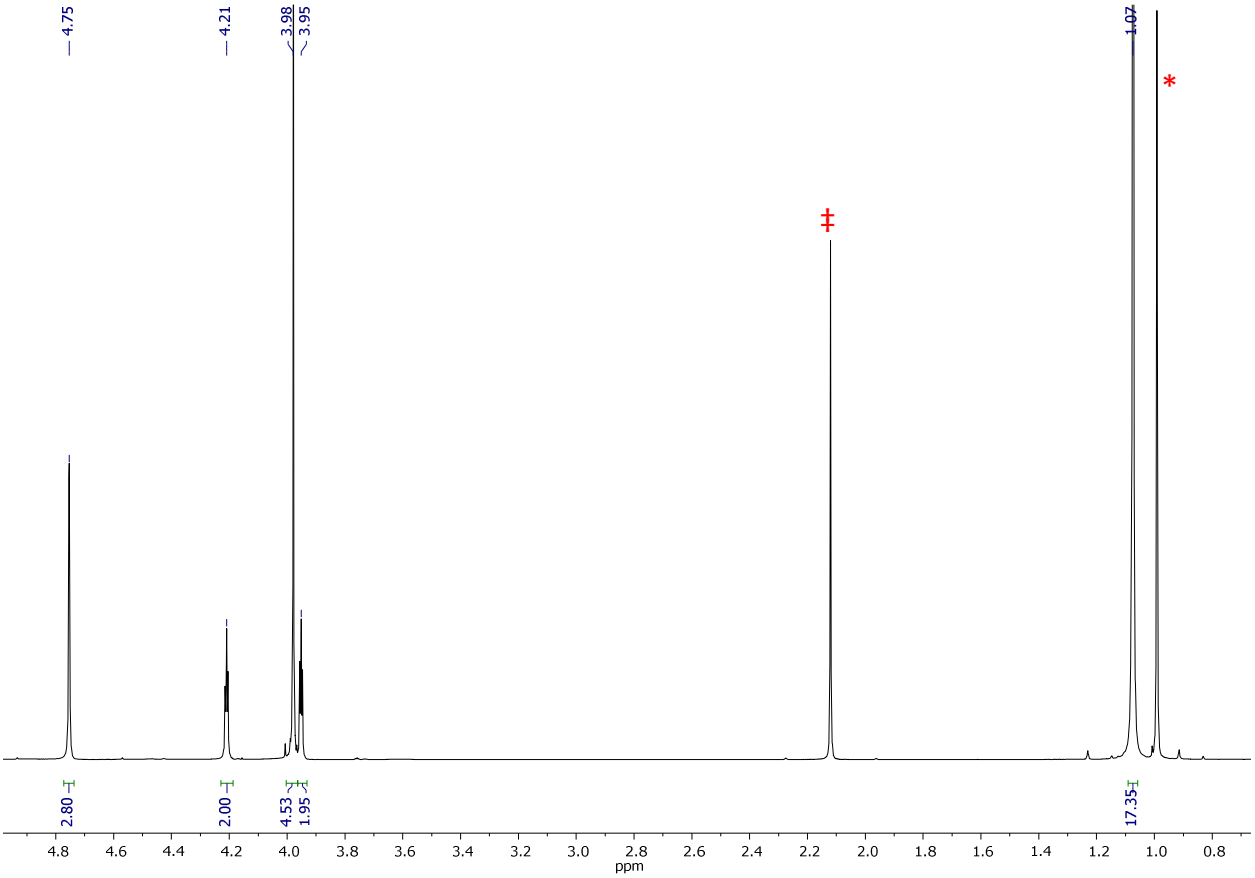
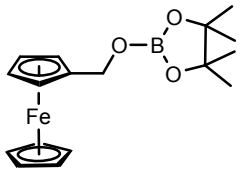


Figure S65. ^{1}H NMR spectrum of 2-(ferrocenylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin, ‡ indicates hexamethylbenzene (internal standard) resonance.



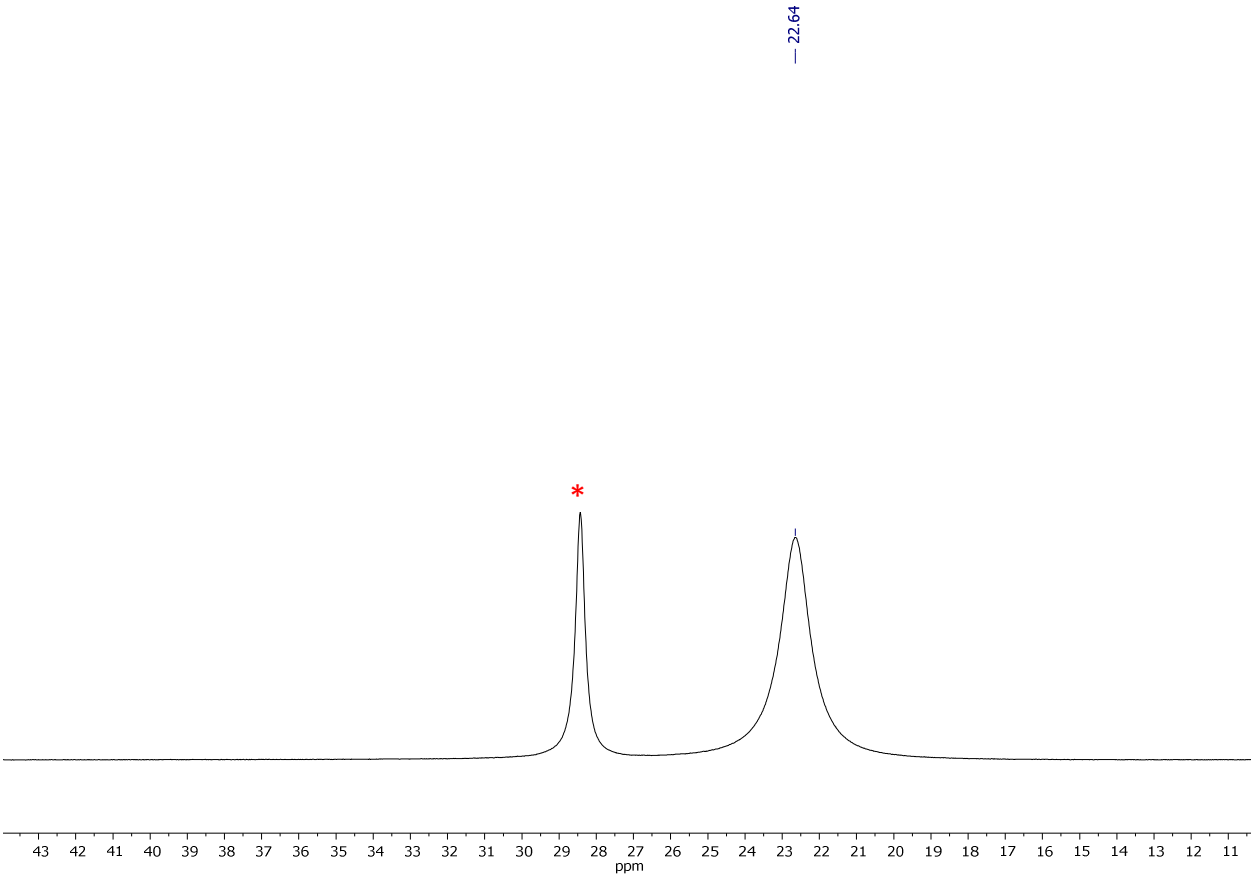
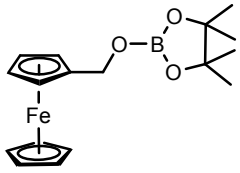


Figure S66. ^{11}B NMR spectrum of 2-(ferrocenylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



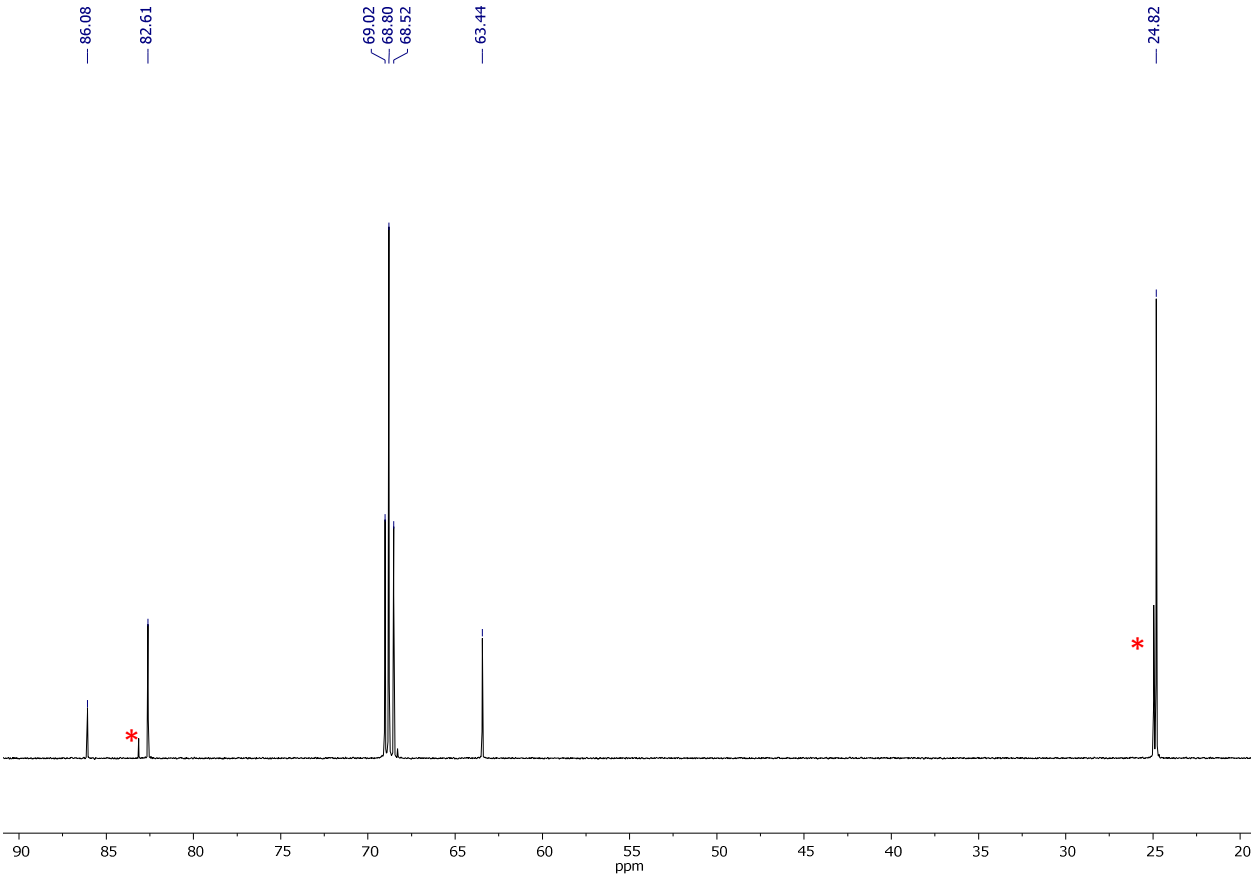
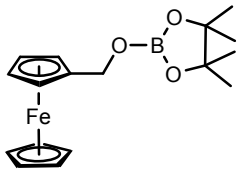


Figure S67. ^{13}C NMR spectrum of 2-(ferrocenylmethoxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



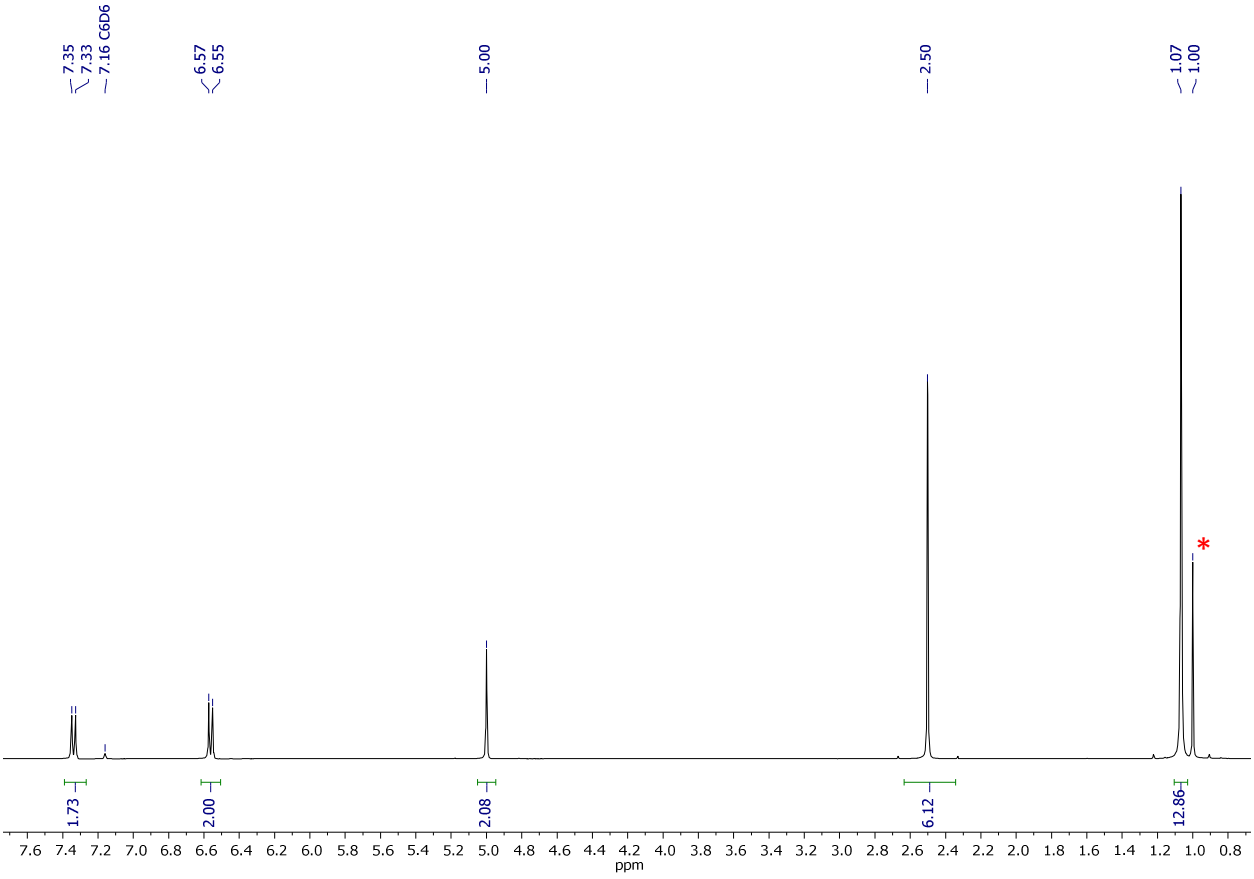
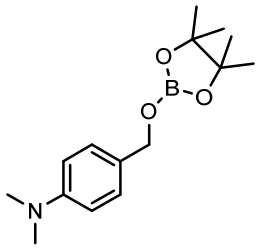


Figure S68. ^{1}H NMR spectrum of 2-(4-N,N-dimethylaminobenzyloxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



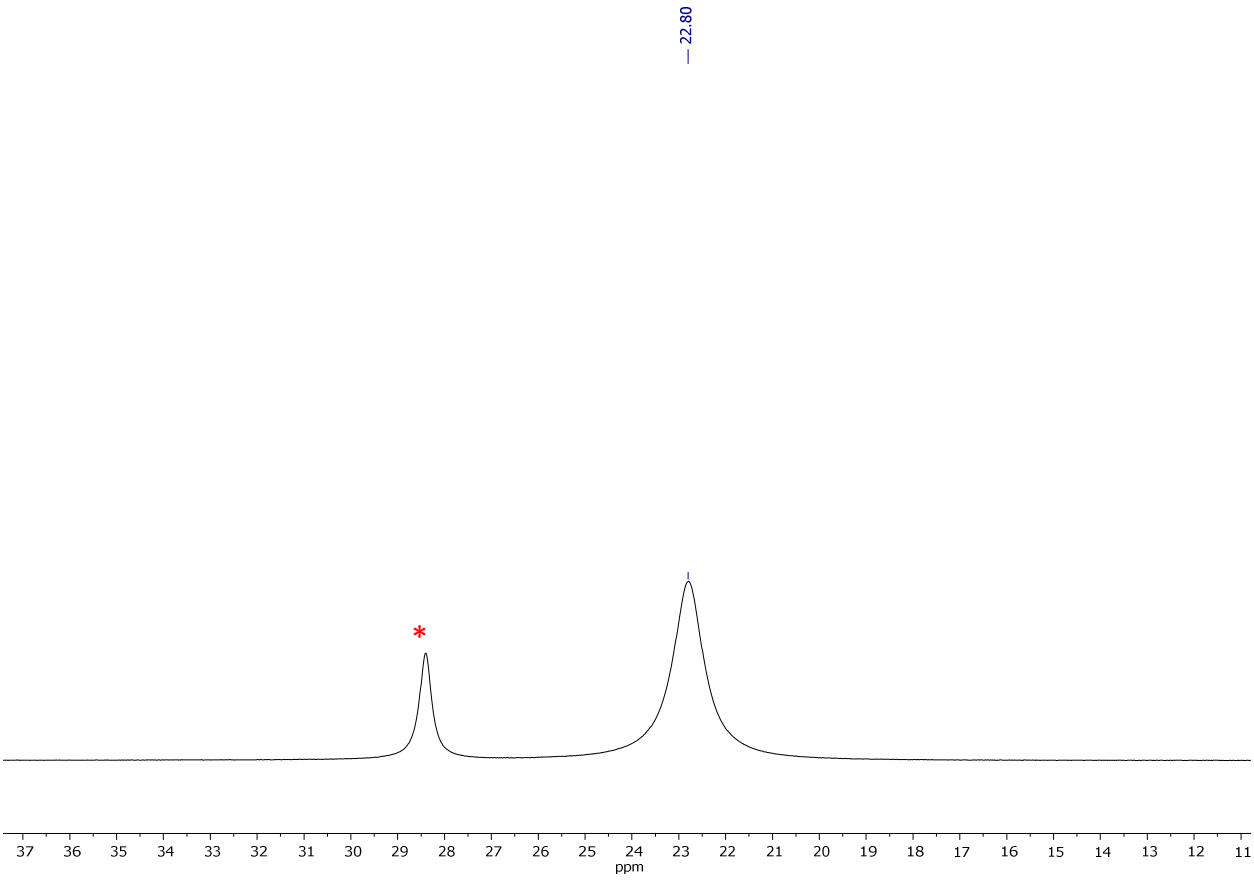
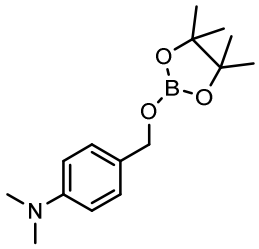


Figure S69. ^{11}B NMR spectrum of 2-(4-N,N-dimethylaminobenzyloxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



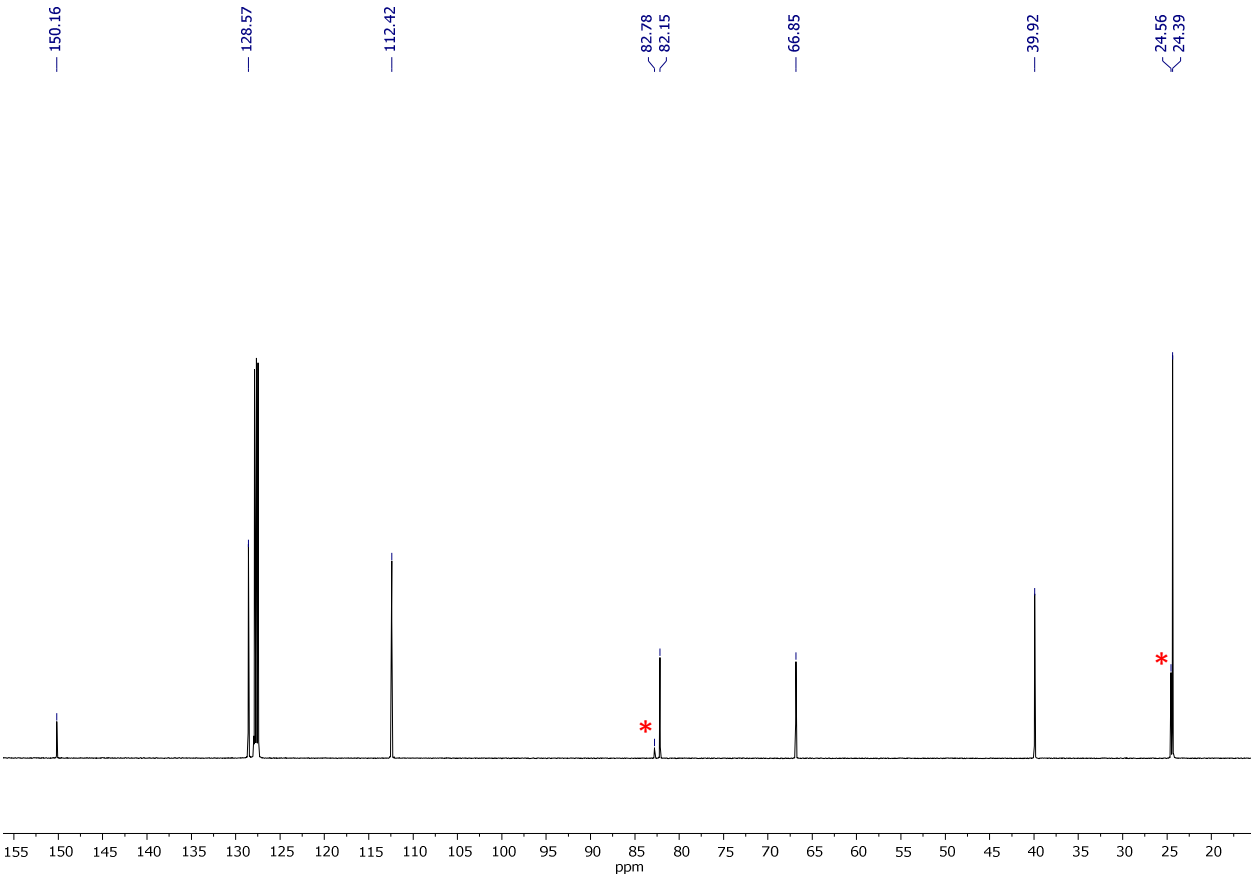
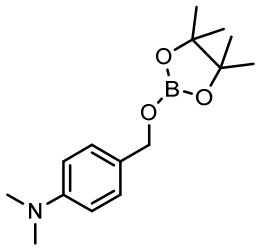


Figure S70. ^{13}C NMR spectrum of 2-(4-N,N-dimethylaminobenzyloxy)pinacolborane acquired in benzene-d_6. * indicates excess HBpin.



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