SUPPORTING INFORMATION

Efficient Hydroboration of Carbonyls by Iron(II) Amide Catalyst

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I. General Information

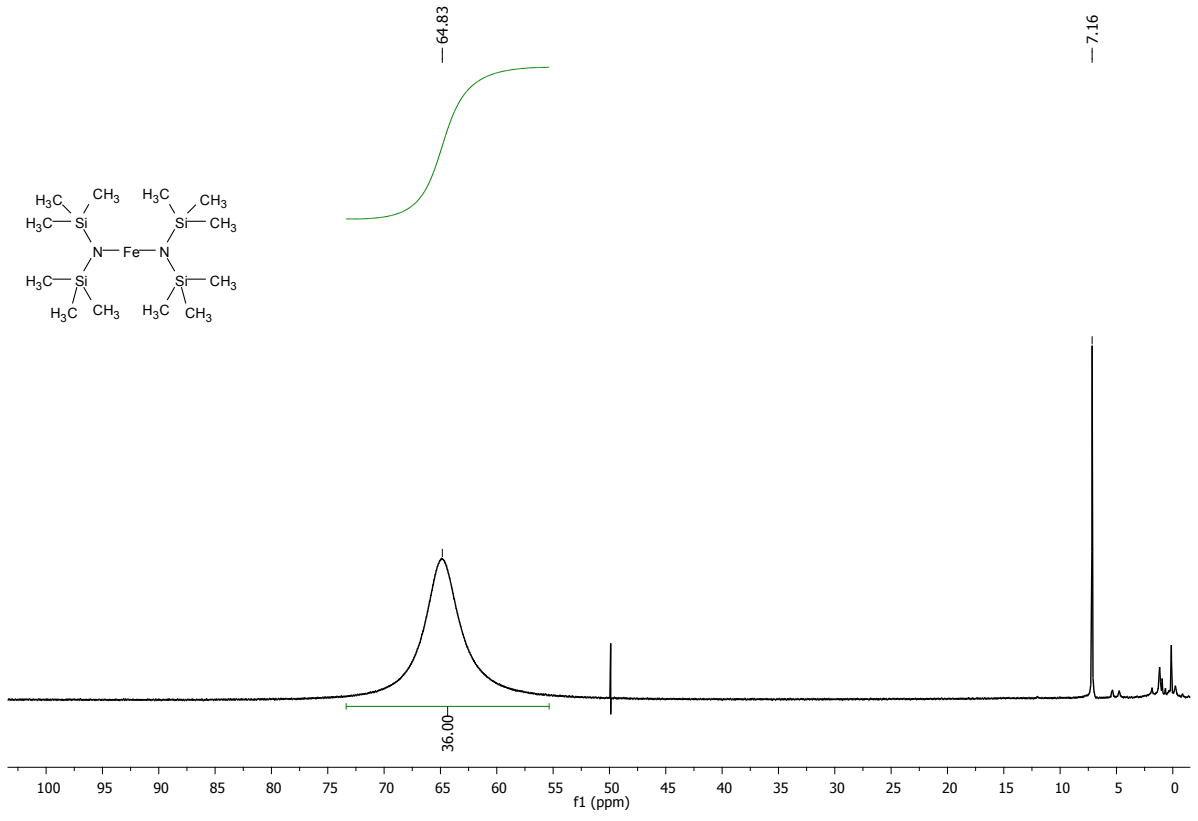
Unless otherwise noted, all manipulations were performed using standard Schlenk or glovebox (MBraun) techniques under nitrogen. Solvents were purchased from a chemical supplier and were dried, distilled and degassed using three freeze-pump-thaw cycles; and stored in an inert atmosphere glovebox. C_6D_6 and $CDCl_3$ were purchased from Cambridge Isotope Laboratories and were dried using molecular sieves and deoxygenated using the freeze-pump-thaw method.

Reagents were purchased from Avra, Alfa-Aesar or Aldrich and were checked for purity by GC-MS and/or ^{1}H NMR spectroscopy and used as received. Iron precursors have been purchased from Sigma-Aldrich in the form of $FeBr_2$, anhydrous powder (98%) and $FeCl_3$, anhydrous powder. $Fe[N(SiMe_3)_2]_2$ (**1**) was prepared according to the literature procedure.[1] IMes (1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene),[2] SIMes (1,3-bis-(2,4,6-trimethylphenyl)imidaz- olin-2-ylidene),[3] and IPr (1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene)[2] were prepared according to literature procedures. Commercially available, pre-coated TLC-sheets ALUGRAM® Xtra Sil G/UV_{254} was purchased from MACHEREY-NAGEL GmbH & Co. KG. The removal of solvent was performed on a rotary evaporator *in vacuo* at a maximum temperature of 40 °C.

All NMR spectra were recorded at ambient temperature using a Bruker Advance 400 NMR spectrometer (^{1}H, 400 MHz; ^{13}C, 100 MHz; ^{11}B, 128 MHz). ^{1}H NMR chemical shifts are reported relative to TMS and were referenced *via* residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm, C_6D_6: 7.16 ppm, CD_3OD: 3.31 ppm) whereas ^{13}C NMR spectra are reported relative to TMS using the carbon signals of the deuterated solvent ($CDCl_3$: 77.16 ppm, C_6D_6: 128.06 ppm, CD_3OD: 49.00 ppm). ^{11}B{^{1}H} NMR chemical shifts are quoted relative to $BF_3{\cdot}Et_2O$ as external standard. All ^{11}B and ^{13}C NMR spectra were broad-band ^{1}H decoupled. The IR spectra were obtained with a BRUKER ALPHA spectrometer in the range of 400 to 4000 cm^{-1} using KBr windows. GC−MS data were acquired using GCMS-QP2010 SE SHIMADZU system.

II. Experimental Details

Synthesis of catalyst, $Fe[N(TMS)_2]_2$, (1). In a nitrogen-filled glovebox, a Schlenk tube was charged with anhydrous $FeBr_2$ (0.50 g, 2.31 mmol) equipped with a magnetic stirring bar. To the stirred suspension of $FeBr_2$ in Et_2O (20 mL) at 0 °C, a solution of $Li[N(TMS)_2]$ (4.63, mmol) in Et_2O (20 mL) was added dropwise. The reaction mixture was stirred at 0 °C for 12 hrs. Volatile materials were removed under reduced pressure, and the dark-brown residue was extracted with Pentane (40 mL). The dark solution was evaporated to dryness and distilled under reduced pressure (10^{-2} mm) to afford a green oil at 80-90 °C. The product was further re-crystallized from a saturated pentane solution at -30 °C to afford light green crystals (0.652 g, 75 %). ^{1}H NMR (400 MHz, C_6D_6 ppm): δ 64.9 (b, 36H). IR (ν cm^{-1}): 2953 m, 2895 w, 1249 s, 1181 m, 989 w, 933 s, 837 s, 753 w, 680 w. ESI-MS: 305.21 [M^+–($SiMe_3$); $(C_9H_{28}FeN_2Si_3+H)^+$].



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

Optimization of reaction conditions for the Iron bis(amide) Catalyzed Hydroboration of Aldehydes.

Experimental Procedures for Table 1. In a nitrogen-filled glovebox, pinacol borane (0.3 mmol), solvent (1 mL), benzaldehyde **2a** (0.25 mmol) and indicated amount of Fe-catalyst were added to a Schlenk tube equipped with a magnetic stirring bar. The reaction mixture was stirred at room temperature for the indicated amount of time. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. Then reaction mixture was diluted with Et_2O (2 mL) and filtered through a plug of celite (Ø 3 mm × 8 mm). The solvents were removed using high vacuum in Schlenk line and the product yield was determined by ^{1}H NMR using nitromethane as an internal standard.

We have carried out the hydroboration reaction of benzaldehyde using methanol as a solvent under standard conditions. No hydroborated product was observed, which might be due to the decomposition of HBpin. Further, the hydroboration of **2a** was performed in the presence of 1 equiv of CH_3OH under standard reaction conditions, which gave 88% of the desired borate ester. When similar reaction was performed in the presence of 1 equiv of phenol, 98% of corresponding borate ester product was obtained.

We have also performed the hydroboration reaction using HBcat as the boron source with benzaldehyde as the substrate under standard reaction conditions. The reaction proceeded with a low yield of the desired product along with the formation of some unknown impurities. We have also performed the hydroboration reactions in the presence of hydride sources ($NaBH_4$ and $NaBHEt_3$) in a 1:1 ratio with the precatalyst, while using equimolar quantities of substrate and HBpin. The hydride source $NaBH_4$ gave 55% of hydroborated product and $NaBHEt_3$ yielded 48% of borate ester.

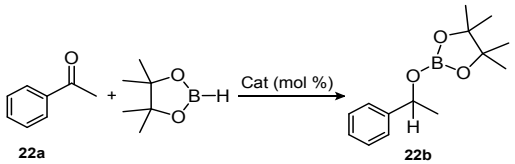
The hydroboration reactions using HMDS as a catalyst under standard reaction conditions has been performed using cinnamaldehyde and *p*-methoxybenzaldehyde as substrates. In both cases, reactions were observed to be sluggish with the lower yield of hydroborated products (17% for cinnamaldehyde and 18% for *p*-methoxybenzaldehyde).

Experimental Procedures for Optimization of the Reaction Conditions for the Iron bis(amide) Catalyzed Hydroboration of Acetophenone.

In a nitrogen-filled glovebox, pinacol borane (0.3 mmol), solvent (1 mL), acetophenone (0.25 mmol) and indicated amount of Fe-catalyst were added to a Schlenk tube equipped with a magnetic stirring bar. The reaction mixture was stirred at room temperature for the indicated amount of time, then diluted with Et_2O (2 mL) and filtered through a plug of celite

(Ø 3 mm × 8 mm). The progress of the reaction was monitored by ^{1}H NMR spectroscopy. The solvents were removed using high vacuum in Schlenk line and the product yield was determined by ^{1}H NMR using nitromethane as an internal standard.

Table S1. Optimization of the Reaction Conditions for Iron bis(amide) Catalyzed Hydroboration of Acetophenone.[a]



entry	catalyst	(mol %)	time (h)	temp. (°C)	solvent	yield (%)
1	$Fe[N\{SiMe_3\}_2]_2$	1	12	25	Et_2O	73
2	$Fe[N\{SiMe_3\}_2]_2$	3	12	25	Et_2O	87
3	$Fe[N\{SiMe_3\}_2]_2$	3	12	25	THF	99
4	$Fe[N\{SiMe_3\}_2]_2$	3	10	25	THF	98
5	$Fe[N\{SiMe_3\}_2]_2$	3	8	25	THF	74
6	$Fe[N\{SiMe_3\}_2]_2$	3	1	60	THF	62

[a] Reaction conditions: $C_6H_5COCH_3$ **22a** (0.25 mmol, 1 equiv), HBpin (0.3 mmol, 1.2 equiv) and solvent (1 mL) at room temperature.[b] The yields were determined by ^{1}H NMR analysis using nitromethane as an internal standard (0.093 mmol), and are averages of two experiments.

We have also performed the hydroboration of 4-bromoacetophenone (**27a**) at 60 °C for 1 hour under standard reaction condition. The reaction was sluggish, with lower yield of the hydroborated product (74% for **27b**), and formation of unassigned compound peak was observed in the ^{1}H NMR spectrum.

Experimental Procedures for Examples Described in Tables 2 and 3.

General procedure (A) for catalytic hydroboration of aldehydes with HBpin

In a nitrogen-filled glovebox, pinacol borane (0.3 mmol), THF (1 mL) and the aldehyde (0.25 mmol) were added to a Schlenk tube equipped with a magnetic stirring bar. 1 mol% of $Fe[N(SiMe_3)_2]_2$ was then added, and the reaction mixture was stirred for 1 hour at room temperature. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. The reaction mixture was diluted with diethyl ether (2 mL) and filtered through a plug of celite (Ø 3 mm × 8 mm). The solvents were removed using high vacuum in Schlenk line and the product yield was determined by ^{1}H NMR using nitromethane as an internal standard.

General procedure (B) for catalytic conversion of aldehydes to 1° alcohols

In a nitrogen-filled glovebox, pinacol borane (1.2 mmol), THF (2 mL) and the aldehyde (1.0 mmol) were added to a Schlenk tube equipped with a magnetic stirring bar. 1 mol% of $Fe[N(SiMe_3)_2]_2$ was then added, and the reaction mixture was stirred for 1 hour at room

temperature. Then methanol (5 mL) and 1N HCl (1 mL) were added and the reaction mixture was refluxed at 50º C for 1 hour. The organic layer was extracted with dichloromethane (3 x 10 mL). Then the volatiles were removed under vacuum and the residue was purified by silica gel column chromatography using a mixture of hexane and ethyl acetate as eluent.

Alternative work up method: The resulted boronate ester residue was hydrolysed with silica gel at 50 °C for 2-4 h. Then the organic layer was extracted with dichloromethane (3 x 10 mL) and the volatiles were removed under vacuum and the residue was purified by silica gel column chromatography using a mixture of hexane and ethyl acetate as eluent.

General procedure (C) for catalytic hydroboration of Ketones with HBpin

In a nitrogen-filled glovebox, pinacol borane (0.3 mmol), THF (1 mL) and the ketone (0.25 mmol) were added to a Schlenk tube equipped with a magnetic stirring bar. 3 mol% of $Fe[N(SiMe_3)_2]_2$ was then added, and the reaction mixture was stirred at room temperature for 10 h, then diluted with Et_2O (2 mL) and filtered through a plug of celite (Ø 3 mm × 8 mm). The progress of the reaction was monitored by ^1H NMR spectroscopy. The solvents were removed using high vacuum in Schlenk line and the product yield was determined by ^1H NMR using nitromethane as an internal standard.

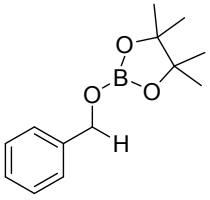
General procedure (D) for catalytic conversion of ketones to 2º alcohols

In a nitrogen-filled glovebox, pinacol borane (1.2 mmol), THF (2 mL) and the ketones (1.0 mmol) were added to a Schlenk tube equipped with a magnetic stirring bar. 3 mol% of $Fe[N(SiMe_3)_2]_2$ was then added, and the reaction mixture was stirred at room temperature for 10 h. Then methanol (5 mL) and 1N HCl (1 mL) were added and the reaction mixture was refluxed at 50º C for 3 hours. The organic layer was extracted with dichloromethane (3 x 10 mL). Then the volatiles were removed under vacuum and the residue was purified by silica gel column chromatography using a mixture of hexane and ethyl acetate as eluent.

Alternative work up method: The resulted boronate ester residue was hydrolysed with silica gel at 50 °C for 4-6 h. The organic layer was extracted with dichloromethane (3 x 10 mL). Then the volatiles were removed under vacuum and the residue was purified by silica gel column chromatography using a mixture of hexane and ethyl acetate as eluent.

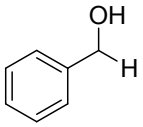
III. Spectroscopic Data of Hydroboration Products and Relevant Alcohols

2-(Benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 2b).[4]



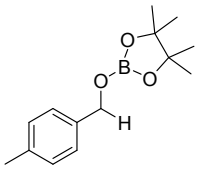
Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.42-7.29 (m, 5H, Ar*H*), 4.98 (s, 2H, OCH_2), 1.31 (s, 12H, CH_3). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.45.

Phenylmethanol (Table 2, 2c).[5]



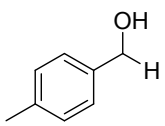
Following general procedure B, colorless oil. Yield - 104 mg (96 %). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.39 - 7.29 (m, 5H, Ar*H*), 4.62 (s, 2H, OCH_2), 2.73 (br s, 1H, O*H*). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 140.95, 128.63, 127.71, 127.09, 65.32.

4,4,5,5-Tetramethyl-2-((4-methylbenzyl)oxy)-1,3,2-dioxaborolane (Table 2, 3b).[4]



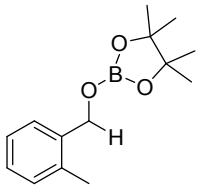
Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.22 (d, *J* = 8 Hz, 2H, Ar*H*), 7.12 (d, *J* = 8 Hz, 2H, Ar*H*), 4.87 (s, 2H, OCH_2), 2.31 (s, 3H, ArCH_3), 1.24 (s, 12H, C(CH_3)$_2$)). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.39.

***p*-Tolylmethanol (Table 2, 3c).[5]**



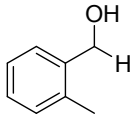
Following general procedure B, colorless oil. Yield - 112 mg (92 %). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.18 (d, *J* = 8 Hz, 2H, Ar*H*), 7.12 (d, *J* = 8 Hz, 2H, Ar*H*), 4.52 (s, 2H, OCH_2), 2.77 (br s, 1H, O*H*), 2.32 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 137.96, 137.2, 129.17, 127.14, 64.9, 21.15.

4,4,5,5-Tetramethyl-2-((2-methylbenzyl)oxy)-1,3,2-dioxaborolane (Table 2, 4b).[6]



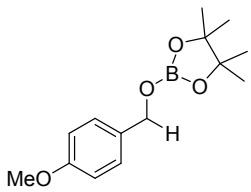
Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.43 (m, 1H, Ar*H*), 7.23 – 7.19 (m, 3H, Ar*H*), 4.96 (s, 2H, OCH_2), 2.35 (s, 3H, ArCH_3), 1.30 (s, 12H, C(CH_3)$_2$)). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.42.

***o*-Tolylmethanol (Table 2, 4c).[7]**



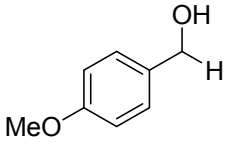
Following general procedure B, colorless oil. Yield - 109 mg (89 %). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.26 – 7.24 (m, 1H, Ar*H*), 7.14 – 7.08 (m, 3H, Ar*H*), 4.51 (s, 2H, CH_2), 2.99 (br s, 1H, O*H*), 2.24 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 138.71, 135.99, 130.22, 127.63, 127.47, 125.99, 63.08,18.59.

2-((4-Methoxybenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 5b).[4]



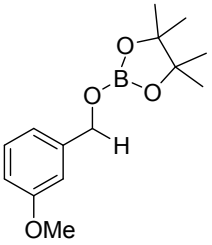
Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.28 (br, 2H, Ar*H*), 6.87 (br, 2H, Ar*H*), 4.85 (s, 2H, OCH_2), 3.79 (s, 3H, OCH_3), 1.24 (s, 12H, C(CH_3)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.36.

(4-Methoxyphenyl)methanol (Table 2, 5c).[8]



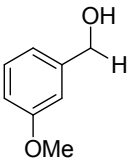
Following general procedure B, colorless oil. Yield - 109 mg (79 %). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.22 (d, *J* = 8 Hz, 2H, Ar*H*), 6.85 (d, *J* = 8 Hz, 2H, Ar*H*), 4.49 (s, 2H, CH_2), 3.76 (s, 3H, OCH_3), 3.45 (br s, 1H, O*H*). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 158.88, 133.16, 128.52, 113.74, 64.37, 55.13.

2-((3-Methoxybenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 6b).[9]



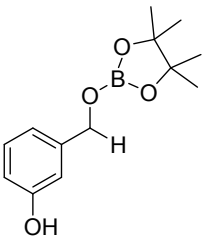
Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.27 (br, 1H, Ar*H*), 6.96 – 6.85 (m, 3H, Ar*H*), 4.95 (s, 2H, OCH_2), 3.83 (s, 3H, ArOCH_3), 1.31 (s, 12H, C(CH_3)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 21.71.

(3-Methoxyphenyl)methanol (Table 2, 6c).[10]



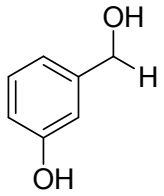
Following general procedure B, colorless oil. Yield - 115 mg, 84 %. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.29 – 7.25 (m, 1H, Ar*H*), 6.93 – 6.91 (m, 2H, Ar*H*), 6.85 – 6.82 (m, 1H, Ar*H*), 4.59 (s, 2H, CH_2), 3.79 (s, 3H, OCH_3), 3.37 (s, 1H, O*H*). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 159.62, 142.62, 129.42, 119.08, 112.98, 112.18, 64.66, 55.08.

3-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)phenol (Table 2, 7b).[9]



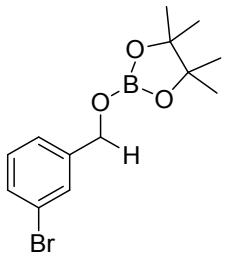
Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.22-7.14 (m, 2H, Ar*H*), 7.04-6.98 (m, 1H, Ar*H*), 6.76 (br, 1H, Ar*H*), 4.87 (s, 2H, OCH_2), 1.26 (s, 12H, C(CH_3)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 21.82.

3-(hydroxymethyl)phenol (Table 2, 7c).[7]



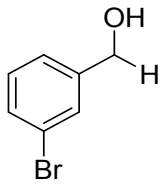
Following general procedure B, a white solid. Yield - 53 mg (43%). ^{1}H NMR (400 MHz, CD_3OD, ppm): δ 7.16-7.14 (m, 1H, Ar*H*), 6.81-6.79 (m, 2H, Ar*H*), 6.69-6.67 (m, 1H, Ar*H*), 4.53 (s, 2H, OCH_2). ^{13}C NMR (100 MHz, CD_3OD, ppm): δ 158.49, 144.20, 130.35, 119.07, 115.11, 114.73, 65.12.

2-((3-Bromobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 8b).[9]



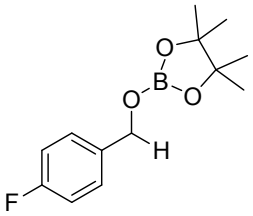
Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.50 (m, 1H, Ar*H*), 7.37 (m, 1H, Ar*H*), 7.25 - 7.16 (m, 2H, Ar*H*), 4.91 (s, 2H, OCH_2), 1.25 (s, 12H, C(CH_3)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.27.

(3-Bromophenyl)methanol (Table 2, 8c).[10]



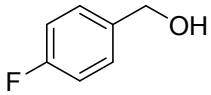
Following general procedure B, colorless oil. Yield - 159 mg (85 %). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.43 (m, 1H, Ar*H*), 7.39 - 7.36 (m, 1H, Ar*H*), 7.19 - 7.15 (m, 2H, Ar*H*), 4.52 (s, 2H, CH_2), 3.50 (br s, 1H, O*H*). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 143.05, 130.51, 130.08, 129.80, 125.34, 122.54, 64.02.

2-((4-Fluorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 9b).[10]



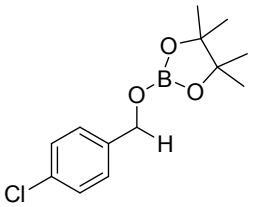
Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.31 - 7.26 (m, 2H, Ar*H*), 7.01 - 6.97 (m, 2H, Ar*H*), 4.85 (s, 2H, OCH_2), 1.24 (s, 12H, C(CH_3)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.37.

(4–Fluorophenyl)methanol (Table 2, 9c).[8]



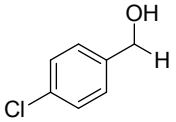
Following general procedure B, colorless oil. Yield - 115 mg, 86 %. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.26-7.22 (m, 2H, Ar*H*), 7.01- 6.96 (m, 2H, Ar*H*), 4.53 (s, 2H, CH_2), 2.84 (br, 1H, O*H*). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 162.3 (d, *J*C–F = 244 Hz), 136.6 (d, *J*C–F = 3 Hz), 128.8 (d, *J*C–F = 8 Hz), 115.3 (d, *J*C–F = 20 Hz), 64.32.

2-((4-Chlorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 10b).[4]



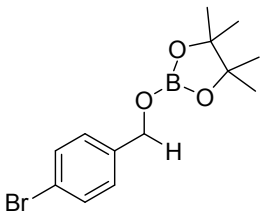
Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.27 (br, 4H, Ar*H*), 4.87 (s, 2H, OCH_2), 1.25 (s, 12H, C(CH_3)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.05.

(4–Chlorophenyl)methanol (Table 2, 10c)[10]



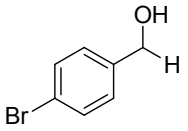
Following general procedure B, a white solid. Yield - 117 mg, 83 %. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.31 - 7.28 (m, 2H, Ar*H*), 7.26 - 7.23 (m, 2H, Ar*H*), 4.60 (s, 2H, CH_2), 2.31 (br s, 1H, O*H*). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 139.33, 133.41, 128.74, 128.36, 64.52.

2-((4-Bromobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 11b).[9]



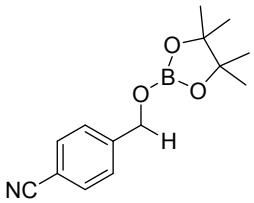
Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.44 (d, *J* = 8 Hz, 2H, Ar*H*), 7.21 (d, *J* = 8 Hz, 2H, Ar*H*), 4.85 (s, 2H, OCH_2), 1.25 (s, 12H, C(CH_3)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 21.34.

(4–Bromophenyl)methanol (Table 2, 11c)[8]



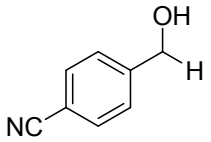
Following general procedure B, a white solid. Yield - 162 mg, 87 %. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.41 (m, 2H, Ar*H*), 7.11 (m, 2H, Ar*H*), 4.47 (s, 2H, CH_2), 3.65 (br s, 1H, O*H*). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 139.65, 131.47, 128.53, 121.26, 64.02.

4-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzonitrile (Table 2, 12b).[9]



Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.54 (br, 2H, Ar*H*), 7.37 (br, 2H, Ar*H*), 4.89 (s, 2H, OCH_2), 1.17 (s, 12H, C(CH_3)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.32.

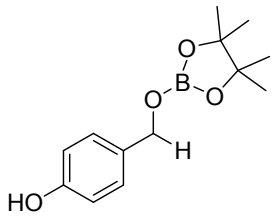
4-(Hydroxymethyl)benzonitrile (Table 2, 12c).[10]



Following general procedure B, a white crystalline solid. Yield - 118 mg (89 %). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.57 (d, *J* = 8 Hz, 2H, Ar*H*), 7.42 (d, *J* = 8 Hz, 2H, Ar*H*), 4.70 (s,

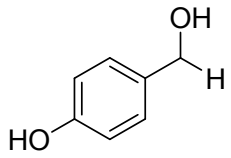
2H, CH_2), 3.11 (br s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 146.64, 132.23, 127.01, 118.92, 110.69, 63.88.

4-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)phenol (Table 2, 13b).[9]



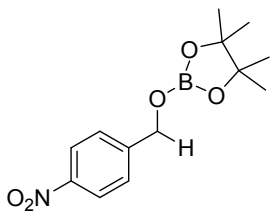
Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.15 (d, J = 8 Hz, 2H, ArH), 6.74 (d, J = 8 Hz, 2H, ArH), 4.78 (s, 2H, OCH_2), 1.22 (s, 12H, C(CH_3)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.32.

4-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)phenol (Table 2, 13c).[7]



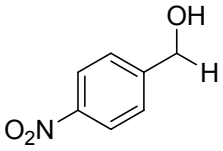
Following general procedure B, a white solid. Yield - 76 mg (61 %). ^{1}H NMR (400 MHz, CD_3OD, ppm): δ 7.17 (d, J = 8 Hz, 2H, ArH), 6.75 (d, J = 8 Hz, 2H, ArH), 4.48 (s, 2H, OCH_2). ^{13}C NMR (100 MHz, CD_3OD, ppm): δ 157.89, 133.48, 129.81, 116.05, 65.09. GC−MS (m/z): 124.05.

4,4,5,5-Tetramethyl-2-((4-nitrobenzyl)oxy)-1,3,2-dioxaborolane (Table 2, 14b).[4]



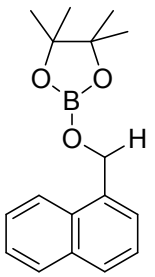
Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.16 (d, *J* = 8 Hz, 2H, Ar*H*), 7.48 (m, *J* = 8 Hz, 2H, Ar*H*), 5.00 (s, 2H, OCH_2), 1.24 (s, 12H, C(CH_3)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.33.

(4-Nitrophenyl)methanol (Table 2, 14c)[11]



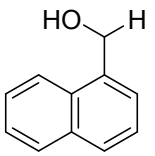
Following general procedure B, brown crystalline solid. Yield - 109 mg (71 %). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.18 (d, *J* = 8 Hz, 2H, Ar*H*), 7.51 (d, *J* = 8 Hz, 2H, Ar*H*), 4.82 (s, 2H, CH_2), 2.36 (br s, 1H, O*H*). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.38, 147.34, 127.11, 123.82, 64.06.

4,4,5,5-Tetramethyl-2-(naphthalen-1-ylmethoxy)-1,3,2-dioxaborolane (Table 2, 15b).[4]



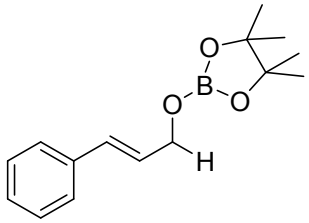
Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.06 (br, 1H, Ar*H*), 7.86 - 7.79 (m, 2H, Ar*H*), 7.60 - 7.50 (m, 4H, Ar*H*), 5.43 (s, 2H, OCH_2), 1.29 (s, 12H, C(CH_3)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.51.

Naphthalen-2-ylmethanol (Table 2, 15c):[12]



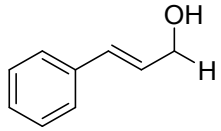
Following general procedure B, colorless oil. Yield - 106 mg (69 %). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.11–8.09 (m, 1H, Ar*H*), 7.90 - 7.88 (m, 1H, Ar*H*), 7.83 - 7.81 (m, 1H, Ar*H*), 7.56 - 7.42 (m, 4H, Ar*H*), 5.10 (s, 2H, CH_2), 2.18 (br s, 1H, O*H*). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 136.34, 133.86, 131.29, 128.74, 128.62, 126.42, 125.95, 125.49, 125.39, 123.73, 63.64.

2-(Cinnamyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 16b).[9]



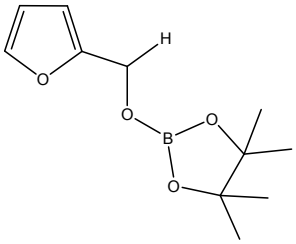
Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.41 – 7.34 (m, 2H, Ar*H*), 7.34 – 7.27 (m, 2H, Ar*H*), 7.26 – 7.23 (m, 1H, Ar*H*), 6.67 – 6.63 (m, 1H), 6.34 - 6.28 (m, 1H), 4.57 (dd, *J* = 8, 4 Hz, 2H, OCH_2), 1.29 (s, 12H, BPin-CH_3). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.20.

3-Phenyl-2-propene-1-ol (Table 2, 16c)[12]



Following general procedure B, colorless oil. Yield - 89 mg (66 %). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.45-7.43 (m, 2H, Ar*H*), 7.39-7.35 (m, 2H, Ar*H*), 7.32 – 7.30 (m, 1H, Ar*H*), 6.69 – 6.65 (m, 1H), 6.45 – 6.40 (m, 1H), 4.37 (dd, *J* = 8, 4 Hz, 2H, CH_2), 1.89 (br s, 1H, O*H*). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 136.78, 131.25, 128.71, 128.61, 127.81, 126.58, 63.82.

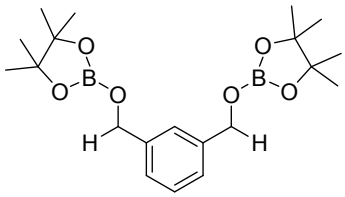
2-(Furan-2-ylmethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 17b).[9]



Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.33 (br, 1H, OC*H*), 6.26 (br, 2H, C*H*), 4.77 (s, 2H, pinBOCH_2), 1.22 (s, 12H, Bpin-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 152.45, 142.44, 110.25, 108.30, 83.05, 59.19, 24.59. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.31.

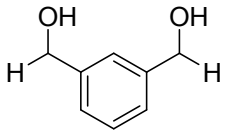
Note: The desired primary alcohol was not isolated upon hydrolysis due to the volatile nature of the product.

1,3-bis(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzene (Table 2, 18b).[4]



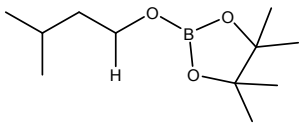
Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.33 - 7.29 (m, 4H, Ar*H*), 4.92 (s, 4H, CH_2), 1.26 (s, 24H, CH_3). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.14.

1,3-Phenylenedimethanol (Table 2, 18c).[13]



Following general procedure B, colorless oil. Yield - 107 mg (78 %). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.35 – 7.33 (m, 2H, Ar*H*), 7.28 – 7.25 (m, 2H, Ar*H*), 4.65 (s, 4H, CH_2), 2.51 (br s, 2H, O*H*). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 141.27, 128.71, 126.29, 125.65, 64.95.

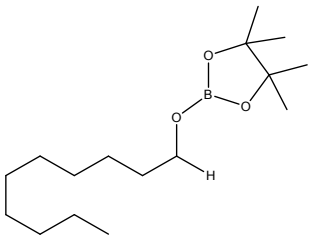
2-(Isopentyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 19b).[6]



Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.85 (m, 2H, pinBOCH_2), 1.68 (m, 1H), 1.44 (m, 2H), 1.23 (s, 12H, Bpin-CH_3), 0.88 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 82.70, 65.94, 40.40, 24.67, 22.60, 15.33. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.01.

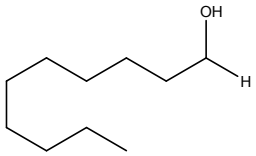
Note: The desired primary alcohol was not isolated upon hydrolysis probably due to the volatile nature of the product.

2-(decyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 20b).[5]



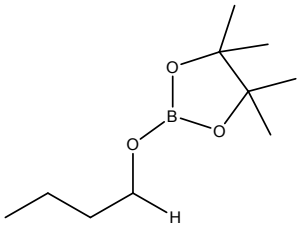
Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.80 (t, *J* = 6.5 Hz, 2H, PinBOCH_2), 1.54-1.51 (m, 2H), 1.22 (br, 26H, CH_2, CH_3), 0.85 (t, *J* = 6.6 Hz, 2H, CH_3). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.39.

Decan-1-ol (Table 2, 20c) [5]



Following general procedure B. Yield - 128 mg (81 %). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.55 (t, *J* = 6.7 Hz, 2H, CH_2OH), 2.73 (br, 1H, O*H*), 1.52-1.47 (m, 2H, CH_2,), 1.26-1.23 (m, 14H, CH_2), 0.85 (t, *J* = 6.7 Hz, 2H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 62.80, 32.81, 31.99, 29.74, 29.67, 29.57, 29.42, 25.88, 22.75, 14.13.

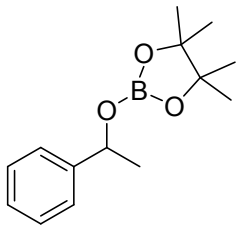
2-butoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 21b).[5]



Following general procedure A. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.82 (t, *J* = 6.4 Hz, 2H, PinBOCH_2), 1.55-1.52 (m, 2H, CH_2), 1.38-1.32 (m, 2H, CH_2), 1.24 (br, 12H, CH_3), 0.85 (t, *J* = 7.2 Hz, 2H, CH_3). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.06.

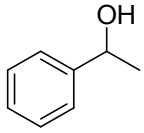
Note: The desired primary alcohol was not isolated upon hydrolysis due to the volatile nature of the product.

4,4,5,5-Tetramethyl-2-(1-phenylethoxy)-1,3,2-dioxaborolane (Table 3, 22b)[4]



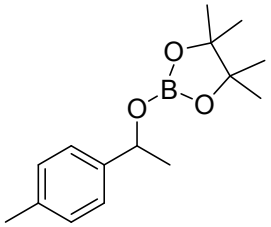
Following general procedure C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 - 7.30 (m, 4H, Ar*H*), 7.26 - 7.24 (m, 1H, Ar*H*), 5.25 (q, *J* = 6.4 Hz, 1H, OC*H*), 1.50 (d, *J* = 8 Hz, 3H, CH_3), 1.25 (s, 6H, CH_3), 1.22 (s, 6H, CH_3). ^{11}B NMR (128 MHz, $CDCl_3$) δ 22.09.

1-Phenylethanol (Table 3, 22c).[5]



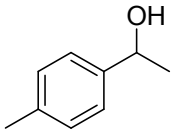
Following general procedure D, colorless oil. Yield - 117 mg (96 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 - 7.37 (m, 4H, Ar*H*), 7.34 - 7.30 (m, 1H, Ar*H*), 4.92 (q, *J* = 6.5 Hz, 1H, OC*H*), 2.15 (br s, 1H, O*H*), 1.54 (d, *J* = 4 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.93, 128.59, 127.55, 125.5, 70.48, 25.24.

4,4,5,5-Tetramethyl-2-(1-(p-tolyl)ethoxy)-1,3,2-dioxaborolane (Table 3, 23b).[4]



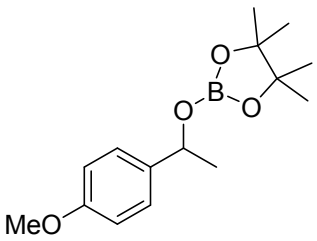
Following general procedure C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 4 Hz, 2H, Ar*H*), 7.13 (d, *J* = 4 Hz, 2H, Ar*H*), 5.22 (q, *J* = 5.6 Hz, 1H, OC*H*), 2.33 (s, 3H, ArCH_3), 1.47 (d, *J* = 8 Hz, 3H, CH_3), 1.25 (s, 6H, CH_3), 1.22 (s, 6H, CH_3). ^{11}B NMR (128 MHz, $CDCl_3$) δ 22.20.

1-(p-Tolyl)ethanol (Table 3, 23c)[5]



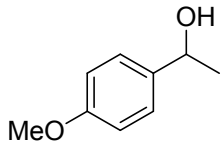
Following general procedure D, colorless oil. Yield - 94 mg (69 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8 Hz, 2H, Ar*H*), 7.15 (d, *J* = 8 Hz, 2H, Ar*H*), 4.85 (q, *J* = 6.4 Hz, 1H, OC*H*), 2.34 (s, 3H, CH_3), 1.90 (s, 1H, O*H*), 1.47 (d, *J* = 8 Hz, 3H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 137.26, 129.28, 125.47, 70.36, 25.19, 21.21.

2-(1-(4-Methoxyphenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 24b)[4]



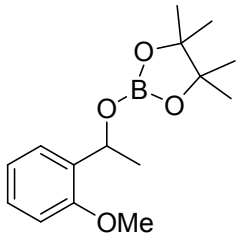
Following general procedure C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8 Hz, 2H, Ar*H*), 6.85 (d, *J* = 8 Hz, 2H, Ar*H*), 5.21 (q, *J* = 5.5 Hz, 1H, OC*H*), 3.78 (s, 3H, ArCH_3), 1.48 (d, *J* = 4 Hz, 3H, CH_3), 1.24 (s, 6H, CH_3), 1.22 (s, 6H, CH_3). ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.29.

1-(4-Methoxyphenyl)ethanol (Table 3, 24c).[14]



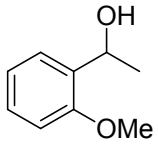
Following general procedure D, colorless oil. Yield - 123 mg (81 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8 Hz, 2H, Ar*H*), 6.89 (d, *J* = 8 Hz, 2H, Ar*H*), 4.83 (q, *J* = 6.4 Hz, 1H, OC*H*), 3.81 (s, 3H, OCH_3), 2.53 (s, 1H, O*H*), 1.47 (d, *J* = 4 Hz, 2H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 138.12, 126.72, 113.82, 69.86, 55.28, 25.05.

2-(1-(2-Methoxyphenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 25b)



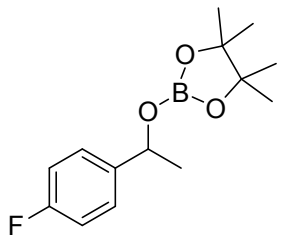
Following general procedure C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8 Hz, 1H, Ar*H*), 7.23 (m, 1H, Ar*H*), 6.97 (m, 1H, Ar*H*), 6.85 (m, 1H, Ar*H*), 5.60 (q, *J* = 6.2 Hz, 1H, OC*H*), 3.83 (s, 3H, OCH_3), 1.46 (d, *J* = 4 Hz, 3H, CH_3), 1.27 (s, 12H, CH_3), 1.24 (s, 12H, CH_3). ^{11}B NMR (128 MHz, $CDCl_3$) δ 22.14.

1-(2-Methoxyphenyl)ethanol (Table 3, 25c)[15]



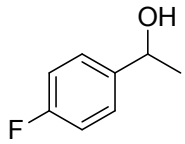
Following general procedure D, colorless oil. Yield - 89 mg, 59 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (m, 1H, Ar*H*), 7.30 – 7.25 (m, 1H, Ar*H*), 7.01 – 6.97 (m, 1H, Ar*H*), 6.91 – 6.89 (m, 1H, Ar*H*), 5.13 (q, *J* = 6.3 Hz, 1H, OC*H*), 3.86 (s, 3H, OCH_3), 3.06 (s, 1H, O*H*), 1.52 (d, *J* = 8 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.40, 133.59, 128.19, 126.02, 120.76, 110.37, 66.14, 55.21, 22.97.

2-(1-(4-Fluorophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 26b)[12]



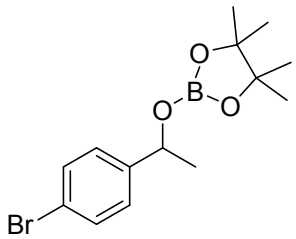
Following general procedure C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 2H, Ar*H*), 6.98 (m, 2H, Ar*H*), 5.21 (q, *J* = 6.1 Hz, 1H, OC*H*), 1.46 (d, *J* = 8 Hz, 3H, CH_3), 1.23 (s, 6H, CH_3), 1.20 (s, 6H, CH_3). ^{11}B NMR (128 MHz, $CDCl_3$) δ 22.02.

1-(4-Fluorophenyl)ethanol (Table 3, 26c).[12]



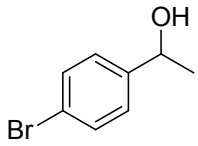
Following general procedure D, colorless oil. Yield - 110 mg (78 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.29 (m, 2H, Ar*H*), 7.03 – 6.99 (m, 2H, Ar*H*), 4.84 (q, *J* = 6.4 Hz, 1H, OC*H*), 2.32 (s, 1H, O*H*), 1.45 (d, *J* = 8 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 162.18 (d, *J*C–F = 243 Hz), 141.63 (br), 127.15 (d, *J*C–F = 8 Hz), 115.32 (d, *J*C–F = 21 Hz), 69.81, 25.34.

2-(1-(4-Bromophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 27b)[4]



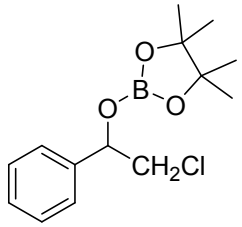
Following general procedure C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8 Hz, 2H, Ar*H*), 7.22 (d, *J* = 8 Hz, 2H, Ar*H*), 5.17 (q, *J* = 6.4 Hz, 1H, OC*H*), 1.44 (d, *J* = 8 Hz, 3H, CH_3), 1.22 (s, 6H, CH_3), 1.19 (s, 6H, CH_3). ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.09.

1-(4-bromophenyl)ethanol (Table 3, 27c)[6]



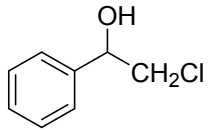
Following general procedure D, colorless oil. Yield - 154 mg (77 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8 Hz, 2H, Ar*H*), 7.21 (d, *J* = 8 Hz, 2H, Ar*H*), 4.81 (q, *J* = 6.4 Hz, 1H, OC*H*), 2.74 (s, 1H, O*H*), 1.44 (d, *J* = 8 Hz, 3H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ 144.83, 131.56, 127.23, 121.14, 69.71, 25.24.

2-(2-chloro-1-phenylethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 28b).[16]



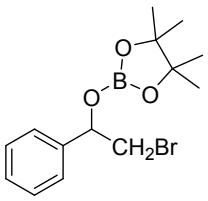
Following general procedure C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.34 (m, 5H, Ar*H*), 5.26 (m, 1H, OC*H*), 3.63 (m, 2H, CH_2Cl), 1.25 (s, 6H, CH_3), 1.25 (s, 6H, CH_3), 1.22 (s, 6H, CH_3). ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.12.

2-Chloro-1-phenylethan-1-ol (Table 3, 28c). [17]



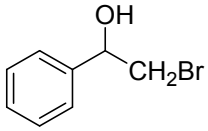
Following general procedure D, colorless oil. Yield - 105 mg (67 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.34 (m, 5H, Ar*H*), 4.89 (dt, *J* = 8.7, 3.3 Hz, 1H, OC*H*), 3.63 (ddd, *J* = 20.0, 11.2, 6.1 Hz, 2H, CH_2), 2.82 (d, *J* = 3.1 Hz, 1H, O*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.06, 128.72, 128.50, 126.15, 74.12, 50.82.

2-(1-(2-Bromophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 29b):



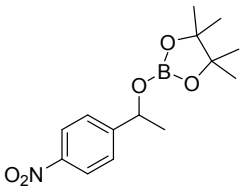
Following general procedure C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.29 (m, 4H, Ar*H*), 5.30 (m, 1H, OC*H*), 3.53 (m, 2H, CH_2Cl), 1.25 (s, 6H, CH_3), 1.22 (s, 6H, CH_3). ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.15.

2-Bromo-1-phenylethan-1-ol (Table 3, 29c). [18]



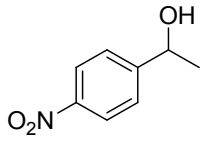
Following general procedure D, colorless oil. Yield - 73 mg (36 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.34 (m, 5H, Ar*H*), 4.92 (dt, *J* = 8.9, 3.2 Hz, 1H, OC*H*), 3.59 (ddd, *J* = 19.4, 10.5, 6.2 Hz, 2H, CH_3), 2.78 (d, *J* = 3.2 Hz, 1H, O*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.42, 128.68, 128.45, 126.04, 73.79, 39.99.

4,4,5,5-Tetramethyl-2-(1-(4-nitrophenyl)ethoxy)-1,3,2-dioxaborolane (Table 3, 30b).



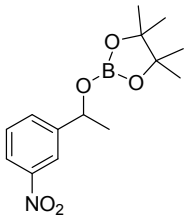
Following general procedure C. ^{1}H NMR (400 MHz, C_6D_6) δ 7.82 (d, *J* = 8.3 Hz, 2H, Ar*H*), 7.04 (d, *J* = 8.3 Hz, 2H, Ar*H*), 5.19 (q, *J* = 6.3 Hz, 1H, OC*H*), 1.26 (d, *J* = 6.4 Hz, 3H, CH_3), 1.05 (br, 12H, CH_3). ^{11}B NMR (128 MHz, C_6D_6): δ 21.84.

1-(4-Nitrophenyl)ethanol (Table 3, 30c).[19]



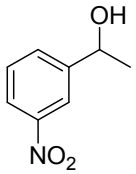
Following general procedure D, brown liquid. Yield - 62 mg, (37%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.7 Hz, 2H, Ar*H*), 7.54 (d, *J* = 8.6 Hz, 2H, Ar*H*), 5.02 (q, *J* = 6.4 Hz, 1H, OC*H*), 2.04 (s, 1H, O*H*), 1.52 (d, *J* = 6.5 Hz, 3H, CH_3), ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.20, 147.33, 126.26, 123.90, 69.64, 25.64.

4,4,5,5-Tetramethyl-2-(1-(3-nitrophenyl)ethoxy)-1,3,2-dioxaborolane (Table 3, 31b).



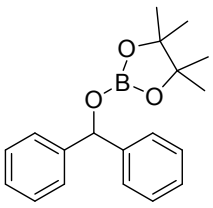
Following general procedure C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H, Ar*H*), 8.06 (m, 1H, Ar*H*), 7.67 (m, 1H, Ar*H*), 7.46 (m, 1H, Ar*H*), 5.29 (q, *J* = 6.3 Hz, 1H, OC*H*), 1.49 (d, *J* = 4 Hz, 3H, CH_3), 1.21 (s, 6H, CH_3), 1.18 (s, 6H, CH_3). ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.33.

1-(3-Nitrophenyl)ethanol (Table 3, 31c).[19]



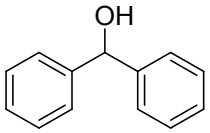
Following general procedure D, brown solid. Yield - 63 mg, (38%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H, Ar*H*), 8.09 (d, *J* = 8 Hz, 1H, Ar*H*), 7.70 (d, *J* = 8 Hz, 1H, Ar*H*), 7.51 (t, *J* = 8 Hz, 1H, Ar*H*), 5.0 (q, *J* = 6.5 Hz, 1H, OC*H*), 2.80 (s, 1H, O*H*), 1.51 (d, *J* = 8 Hz, 2H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.34, 148.0, 131.74, 129.49, 122.35, 120.44, 69.36, 25.46.

2-(Benzhydryloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 32b).[9]



Following general procedure C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.38 (m, 4H, Ar*H*), 7.38-7.35 (m, 4H, Ar*H*), 7.31-7.27 (m, 2H, Ar*H*), 6.26 (s, 1H, OC*H*), 1.28 (s, 6H, CH_3), 1.27 (s, 6H, CH_3). ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.26.

Diphenylmethanol (Table 3, 32c).[5]

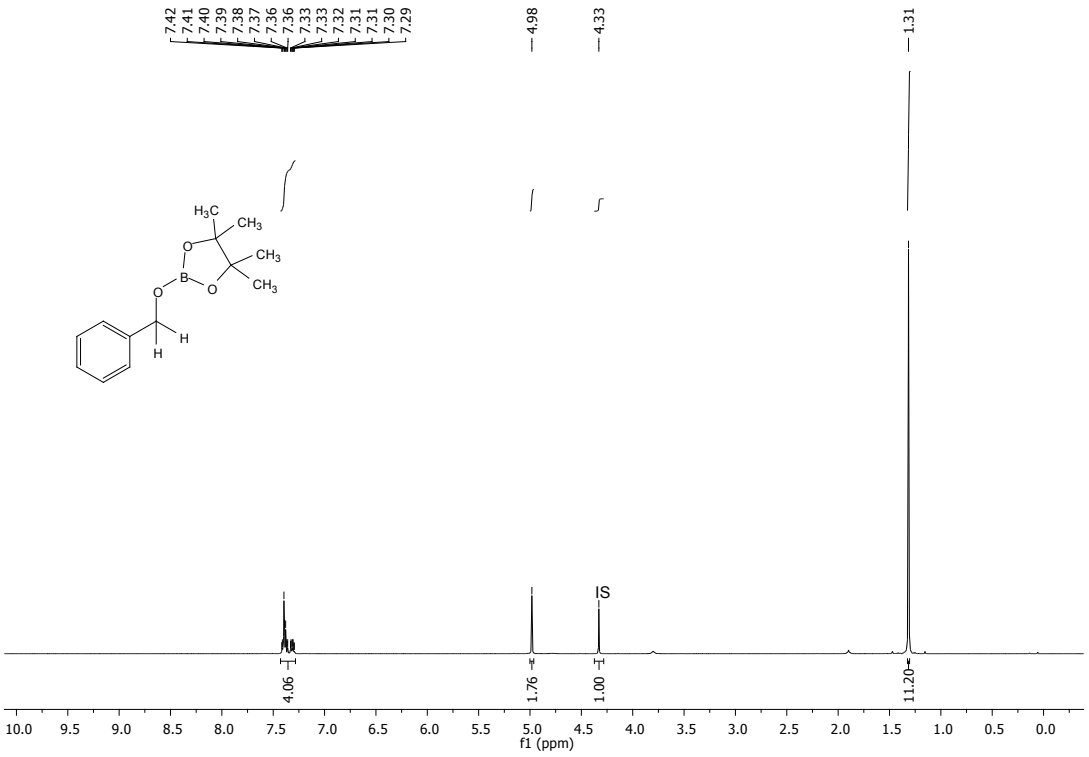


Following general procedure D, white solid. Yield-154 mg (77 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17-7.07 (m, 10H, Ar*H*), 5.48 (s, 1H, OC*H*), 3.20 (s, 1H, O*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.79, 128.31, 127.32, 126.56, 75.85.

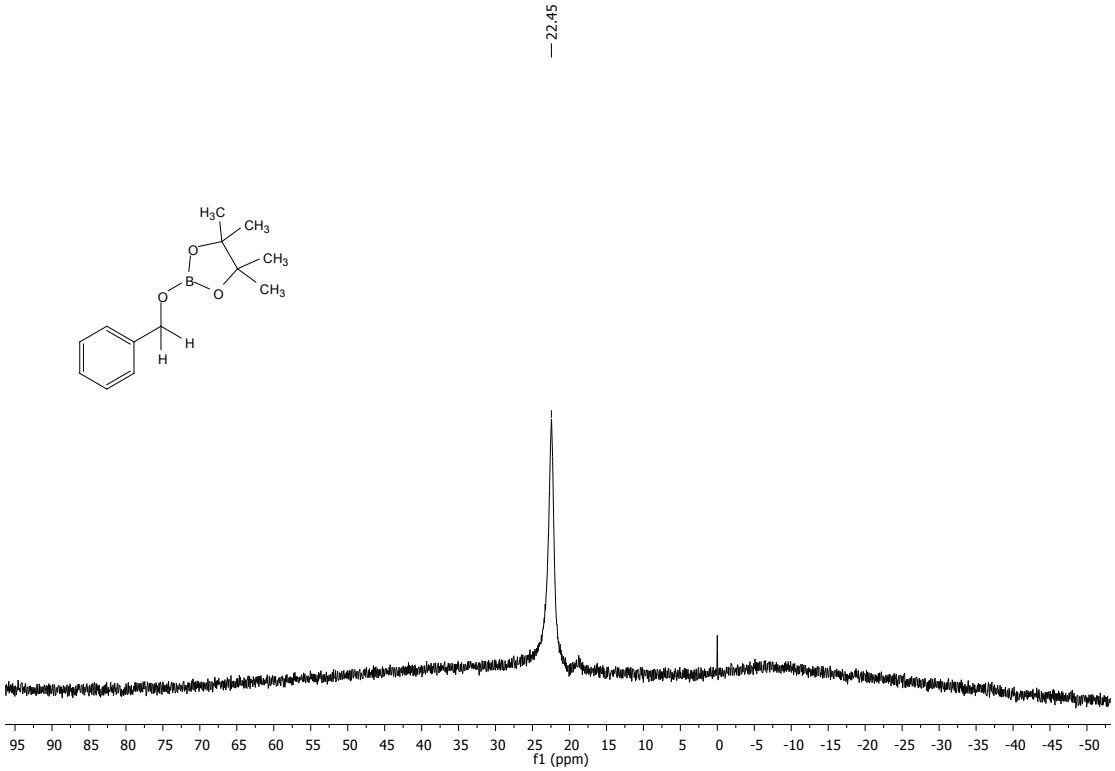
IV. NMR Spectra of Hydroboration Products and Relevant Alcohols

***Note*:** The hydroborated product spectra are shown along with internal standard (IS) nitromethane. Resonances are denoted as follows: unreacted aldehydic or ketonic product (*), and solvent/grease (#).

2-(Benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**Table 2, 2b**). [4]

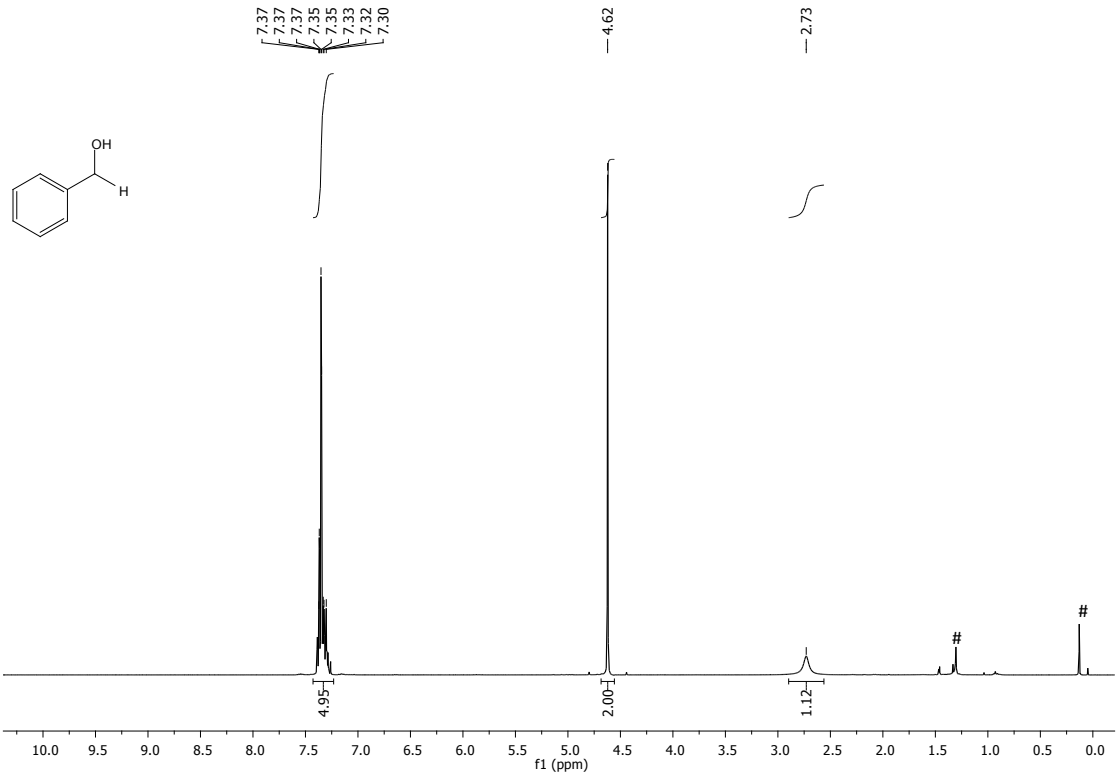


^{1}H NMR of **2b** (400 MHz, $CDCl_3$)

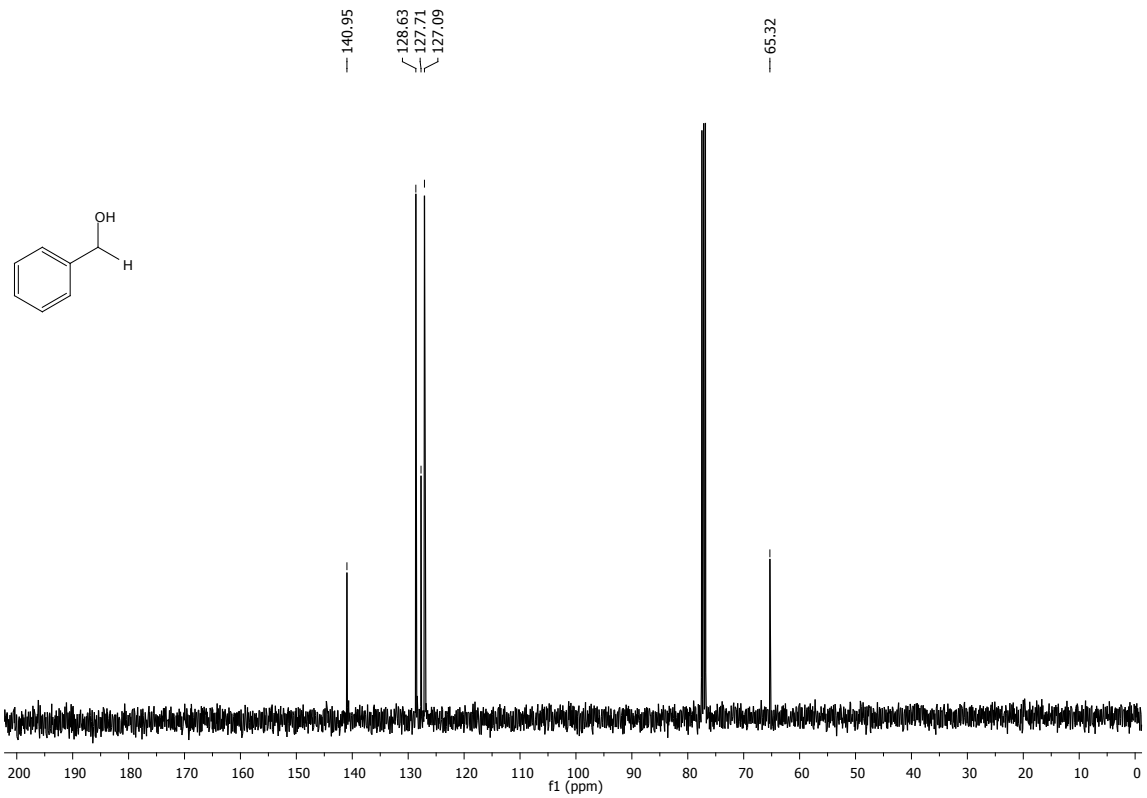


^{11}B NMR of **2b** (128 MHz, $CDCl_3$)

Phenylmethanol (**Table 2, 2c**).[5]

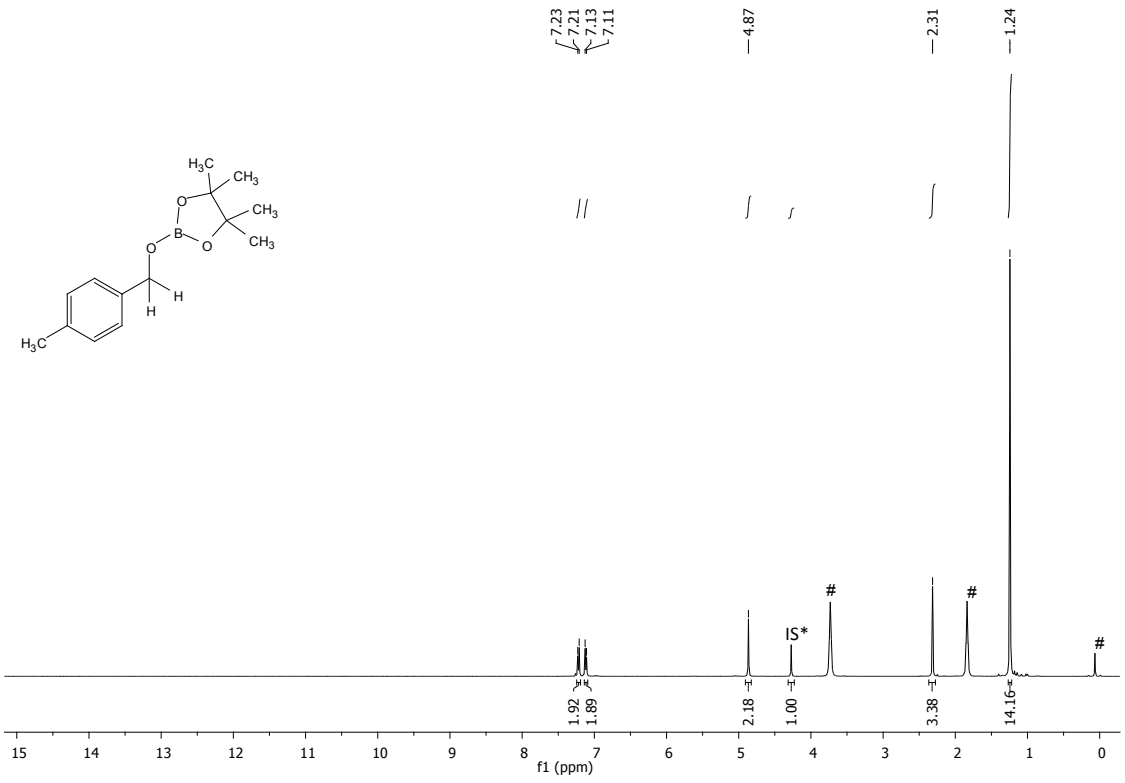


^{1}H NMR of **2c** (400 MHz, $CDCl_3$)

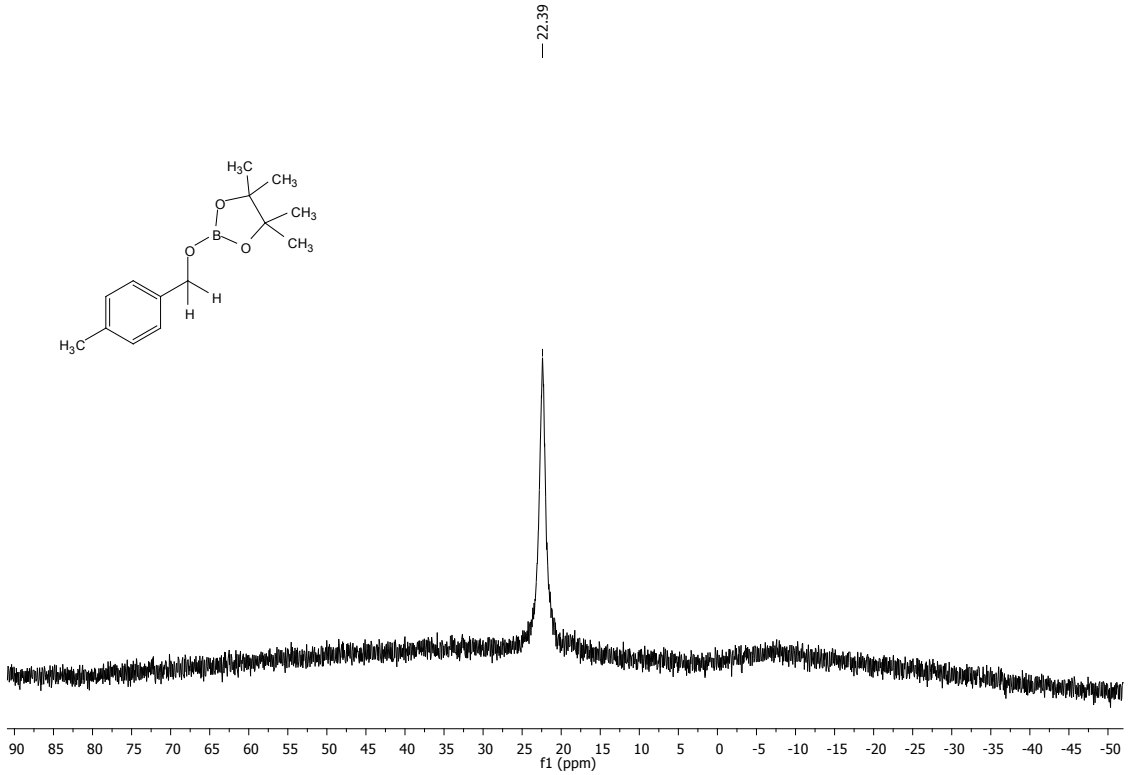


^{13}C NMR of **2c** (100 MHz, $CDCl_3$)

4,4,5,5-Tetramethyl-2-((4-methylbenzyl)oxy)-1,3,2-dioxaborolane (Table 2, 3b).[4]

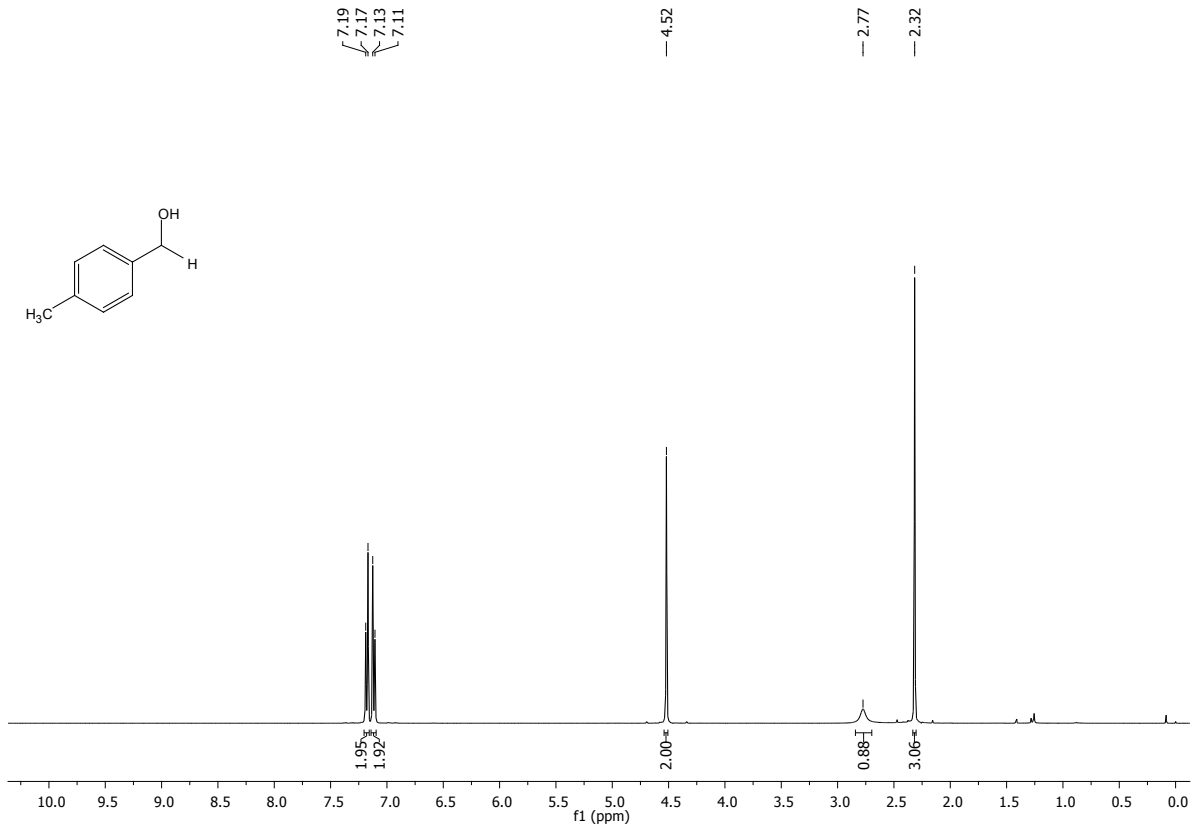


^{1}H NMR of **3b** (400 MHz, $CDCl_3$) (IS* nitromethane (0.0747 mmol))

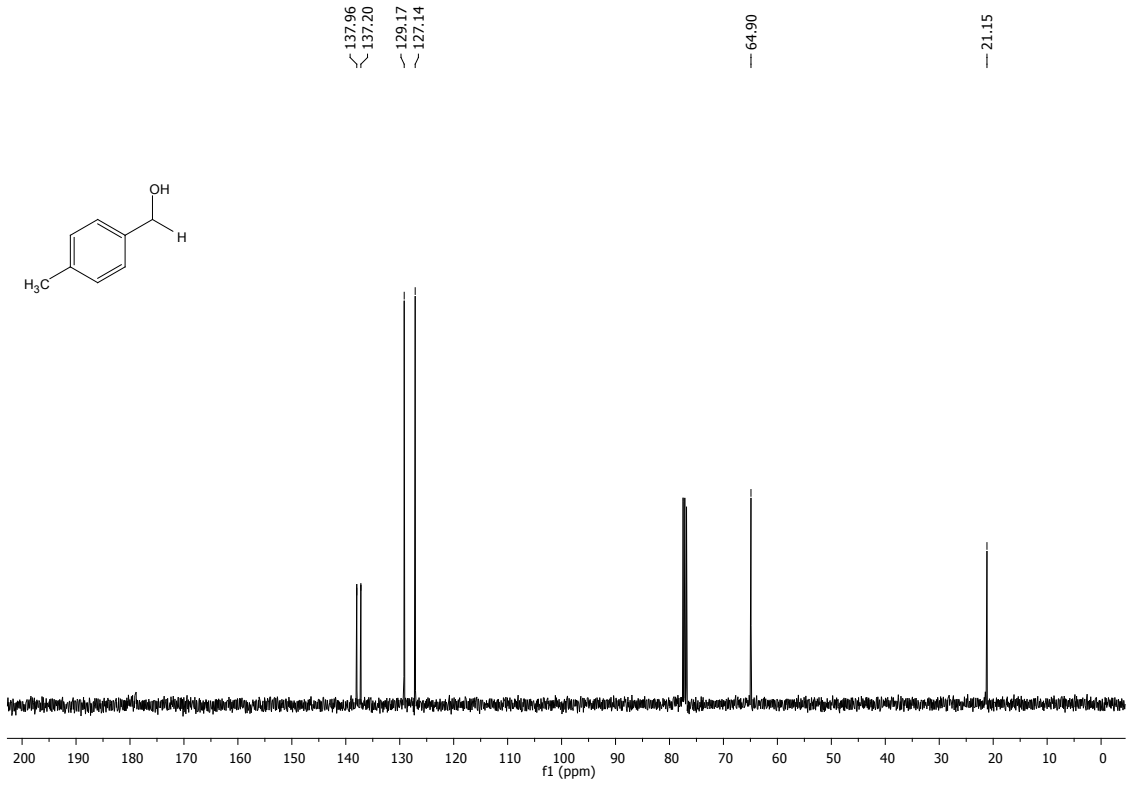


^{11}B NMR of **3b** (128 MHz, $CDCl_3$)

p-Tolylmethanol (Table 2, 3c).[5]

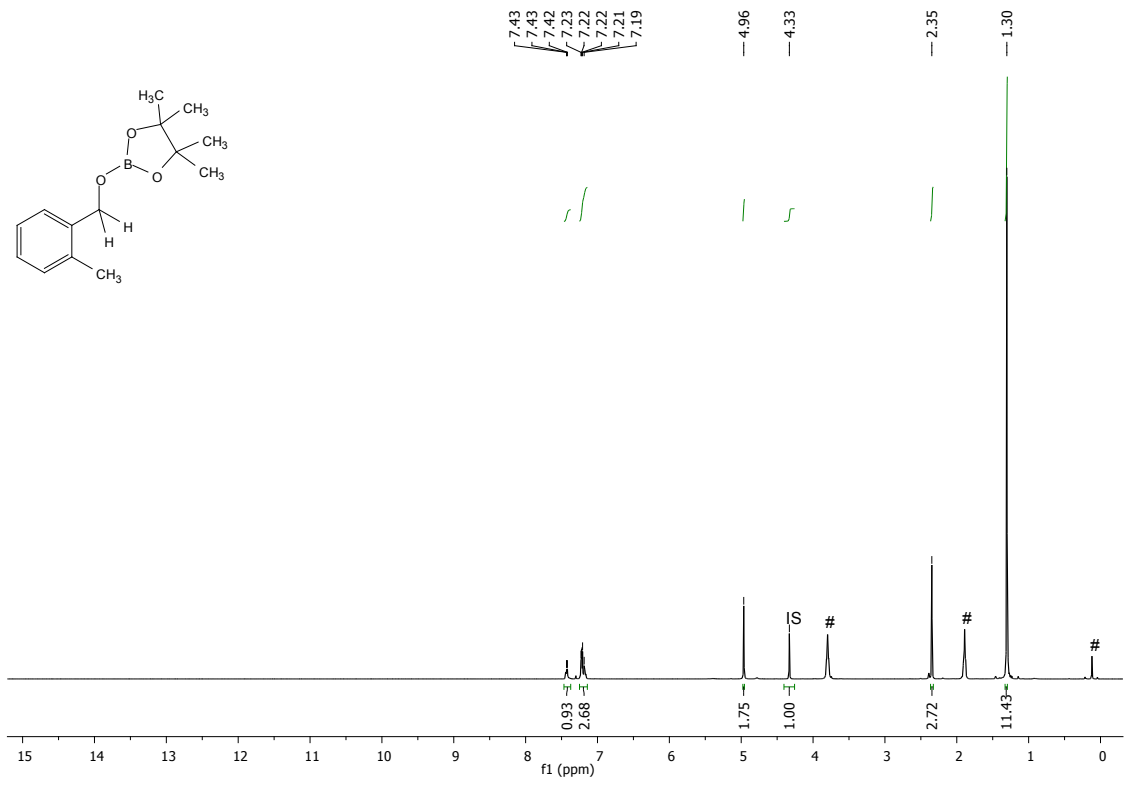


^{1}H NMR of **3c** (400 MHz, $CDCl_3$)

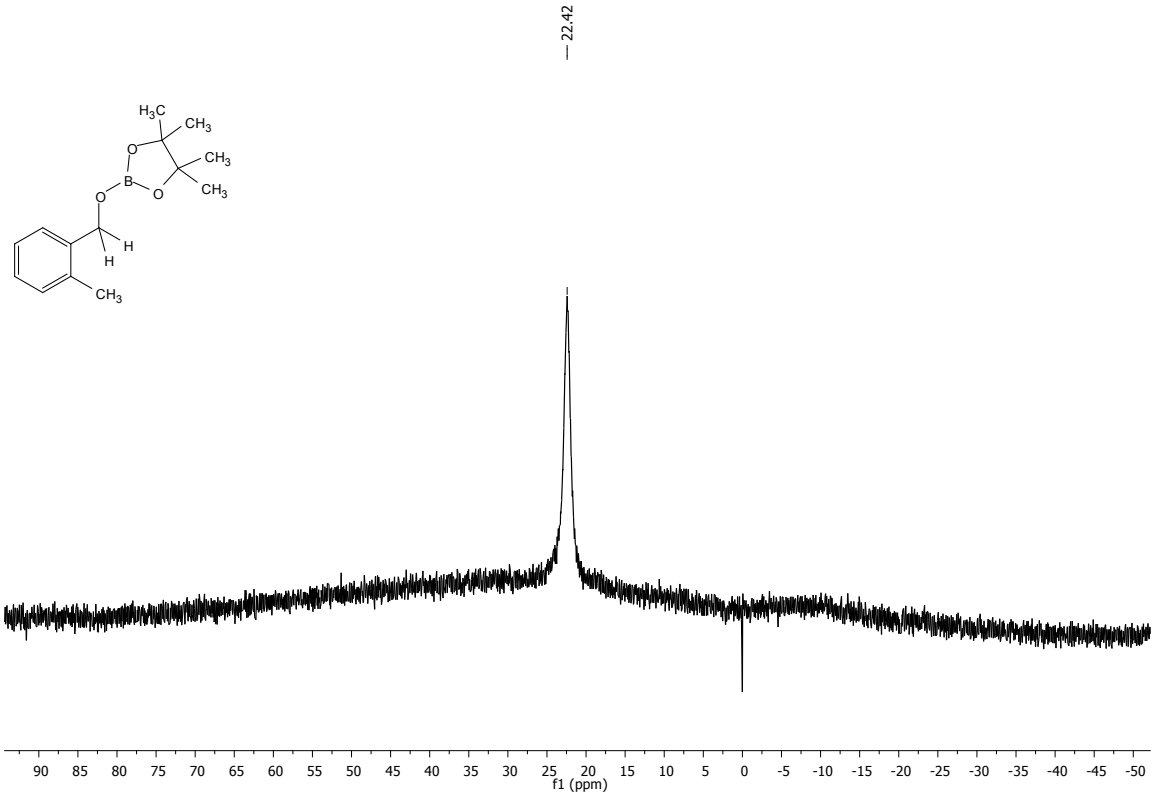


^{13}C NMR of **3c** (100 MHz, $CDCl_3$)

4,4,5,5-Tetramethyl-2-((2-methylbenzyl)oxy)-1,3,2-dioxaborolane (Table 2, 4b).[6]

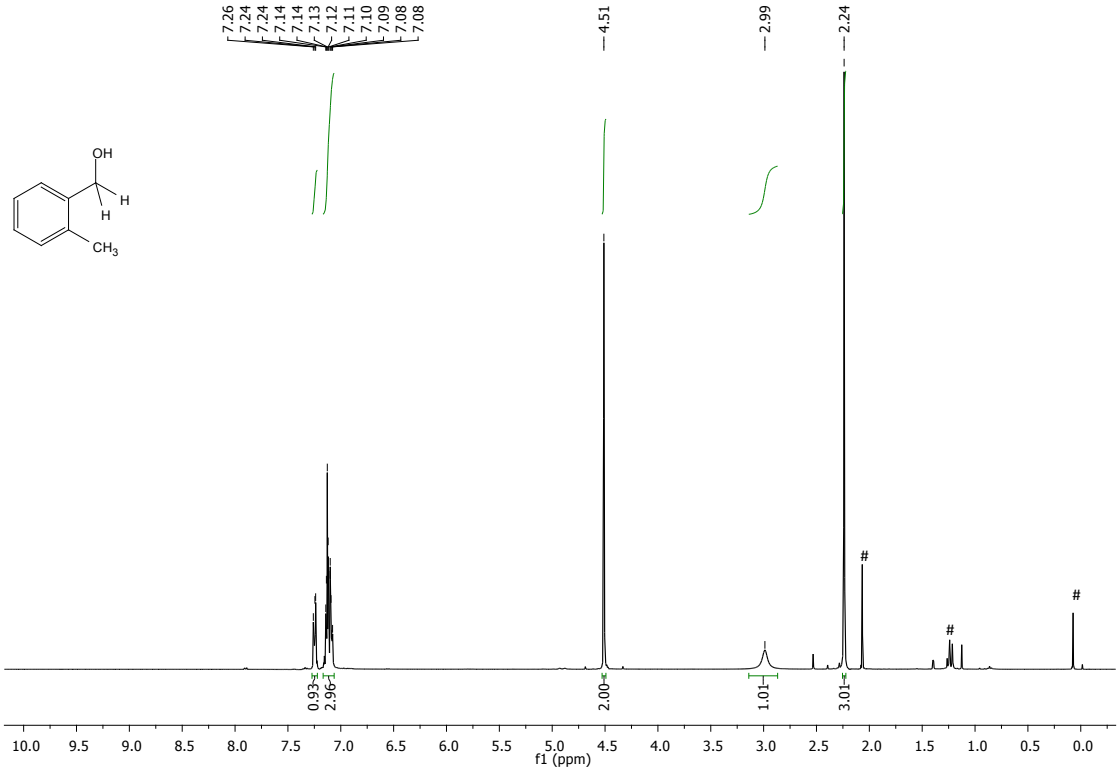


^{1}H NMR of **4b** (400 MHz, $CDCl_3$)

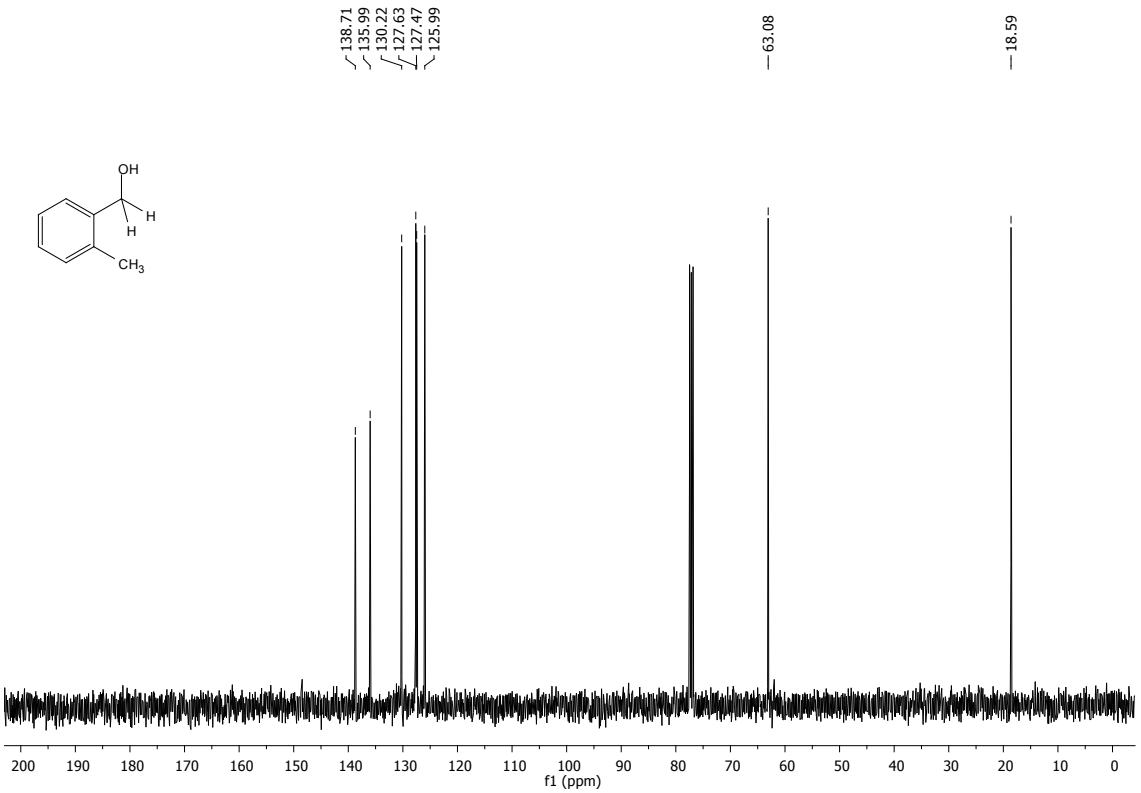


^{11}B NMR of **4b** (128 MHz, $CDCl_3$)

***o*-Tolylmethanol (Table 2, 4c)**.[7]

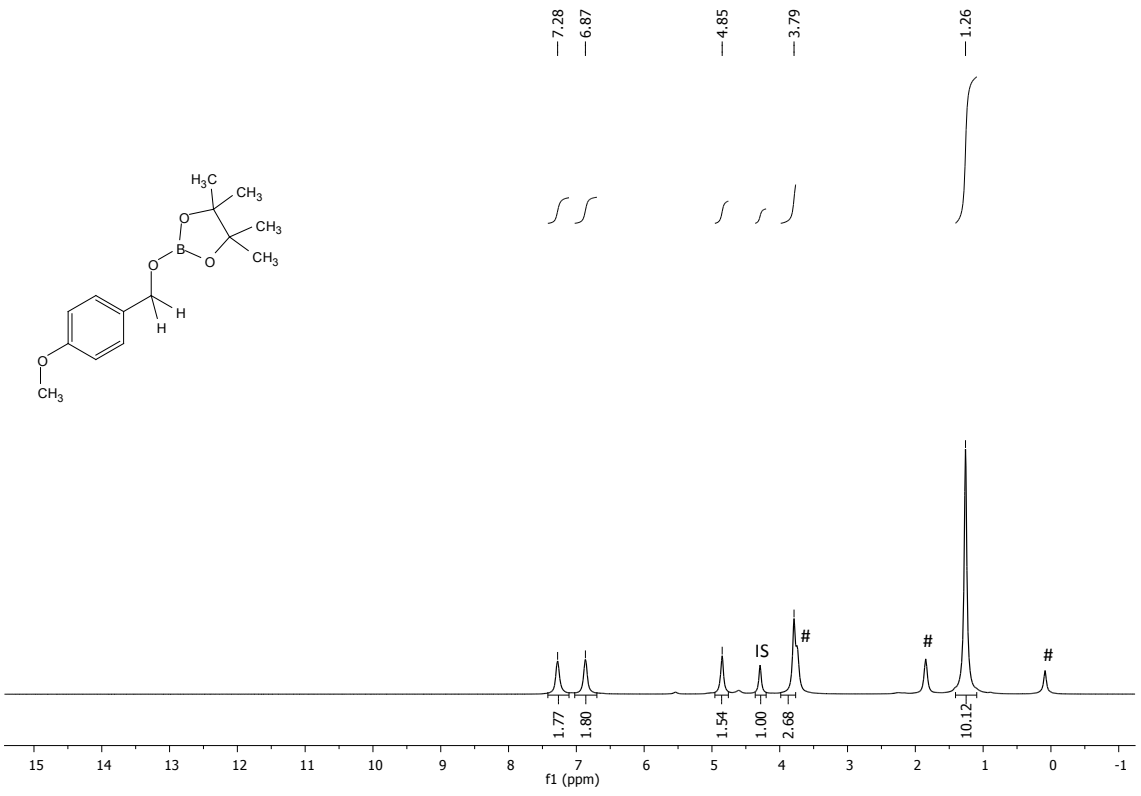


^{1}H NMR of **4c** (400 MHz, $CDCl_3$)

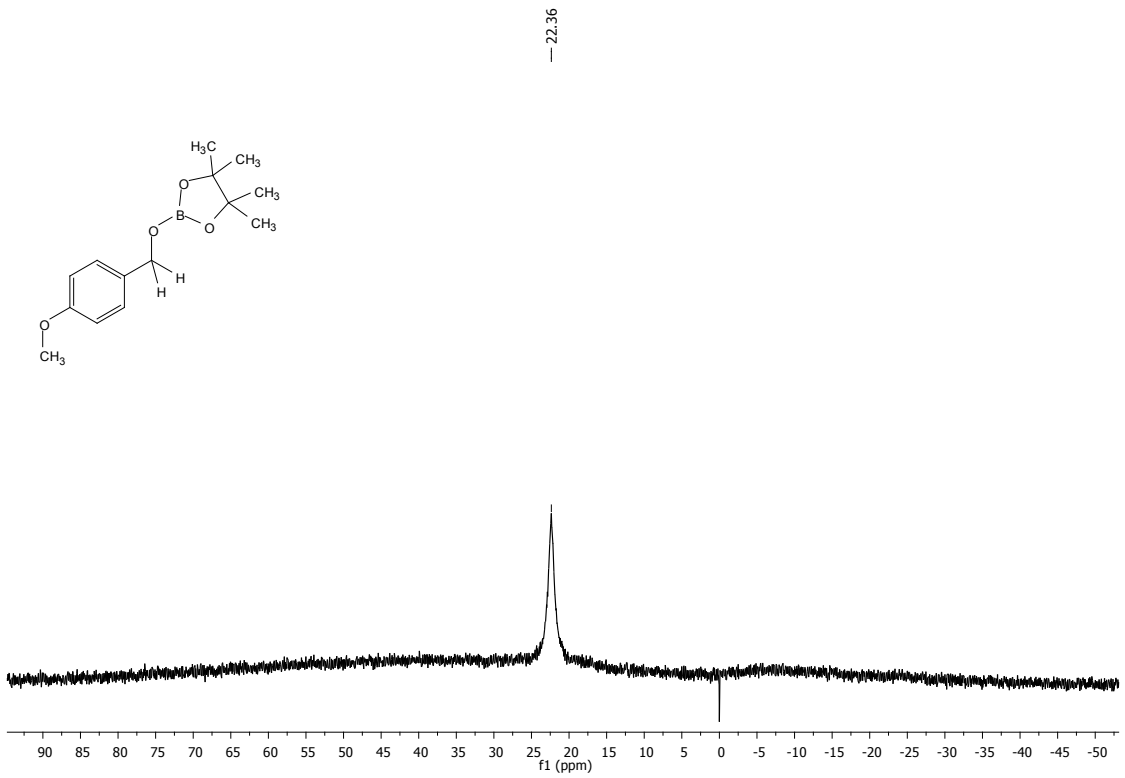


^{13}C NMR of **4c** (100 MHz, $CDCl_3$)

2-((4-Methoxybenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 5b).[4]

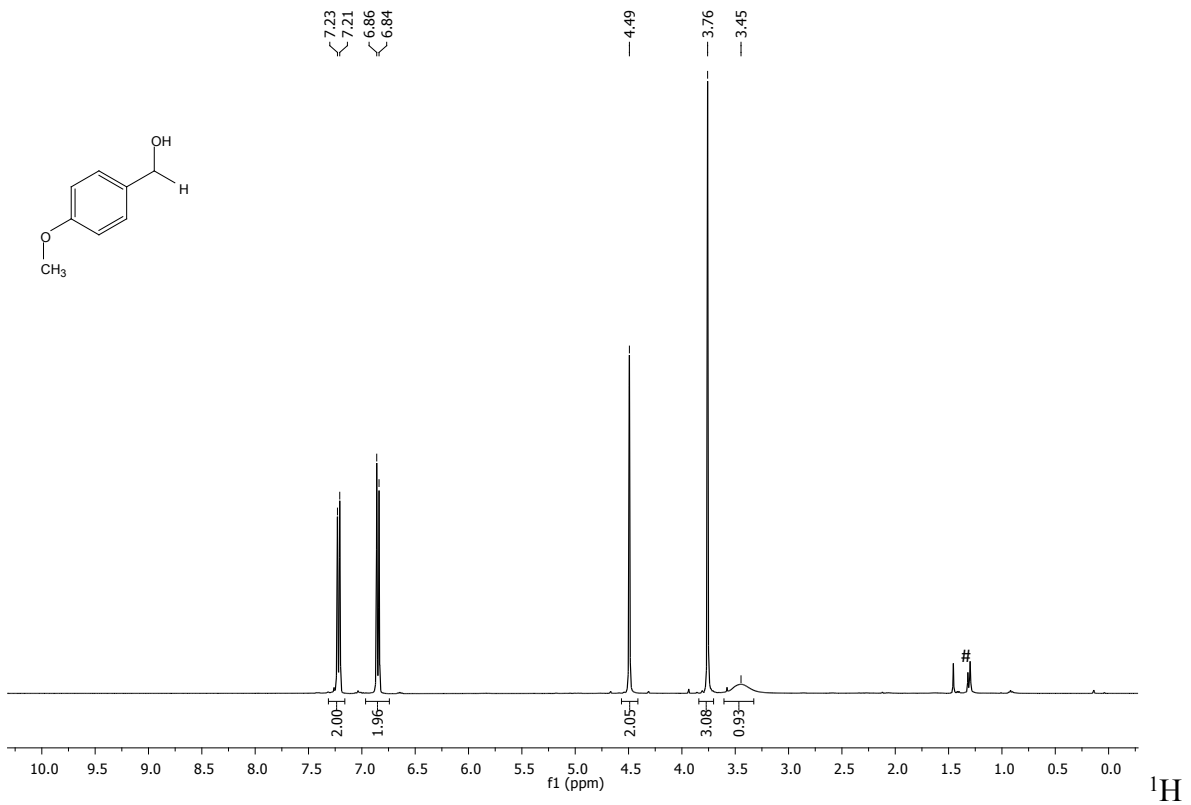


^{1}H NMR of **5b** (400 MHz, $CDCl_3$)

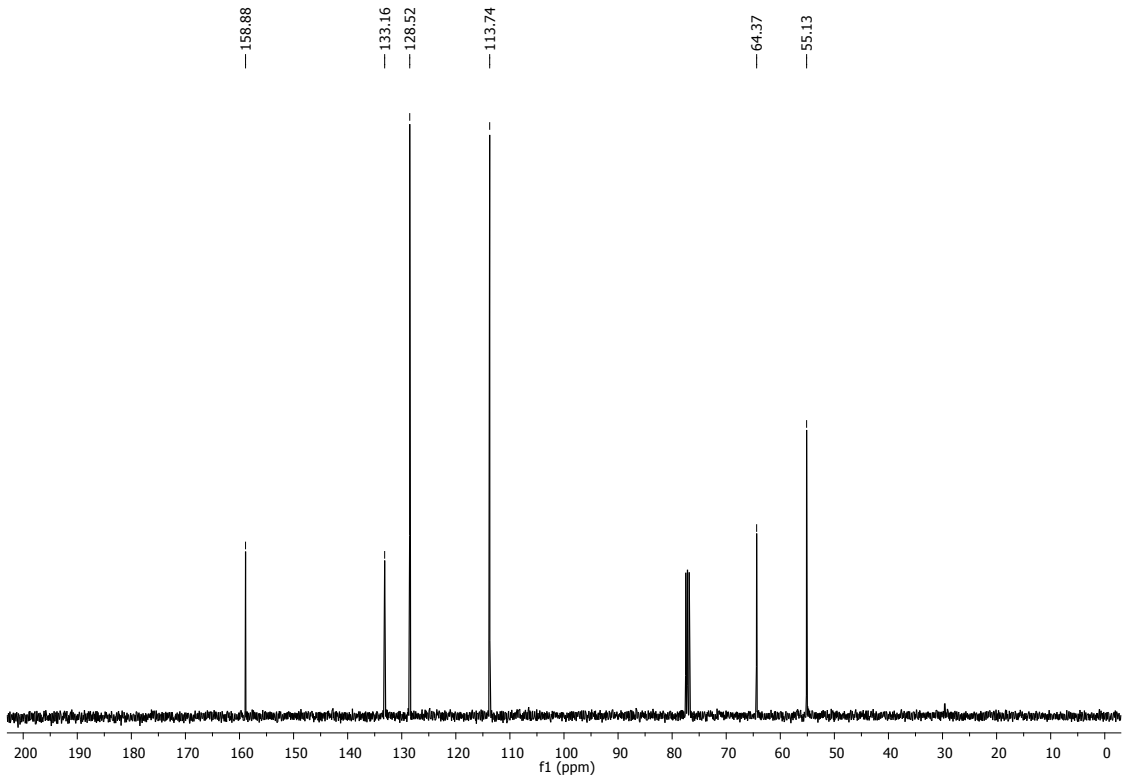


^{11}B NMR of **5b** (128 MHz, $CDCl_3$)

(4-Methoxyphenyl)methanol (Table 2, 5c).[8]

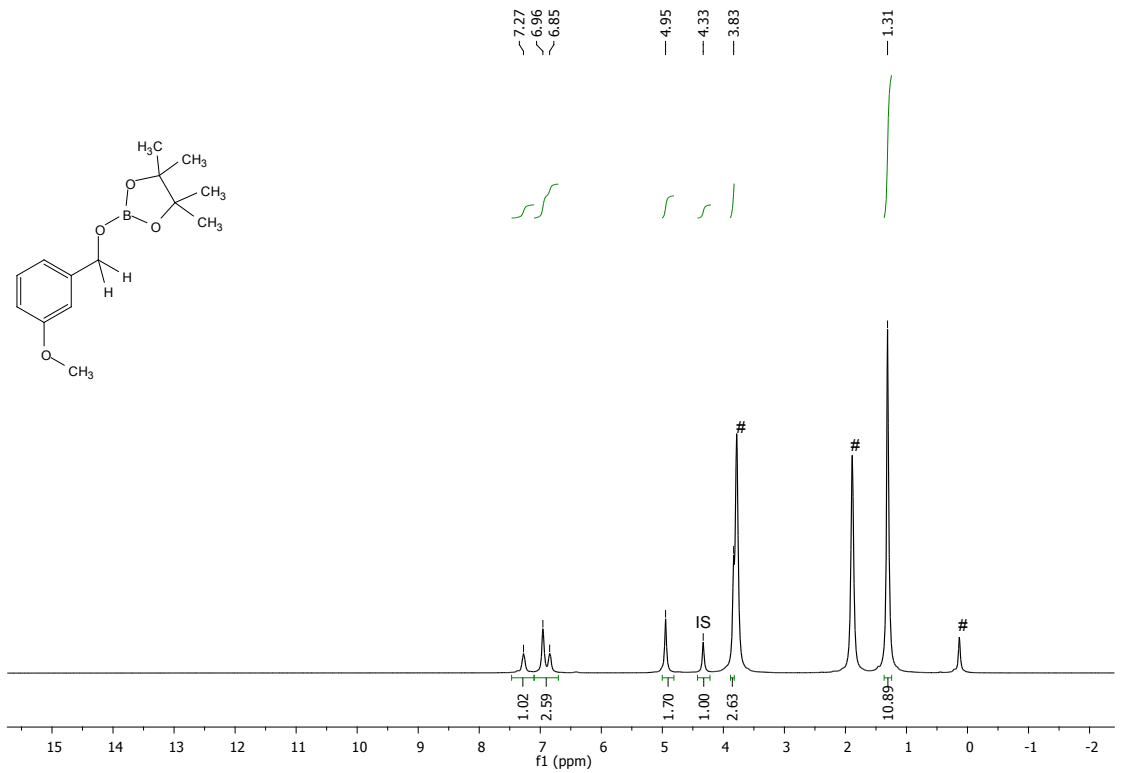


^{1}H NMR of **5c** (400 MHz, $CDCl_3$)

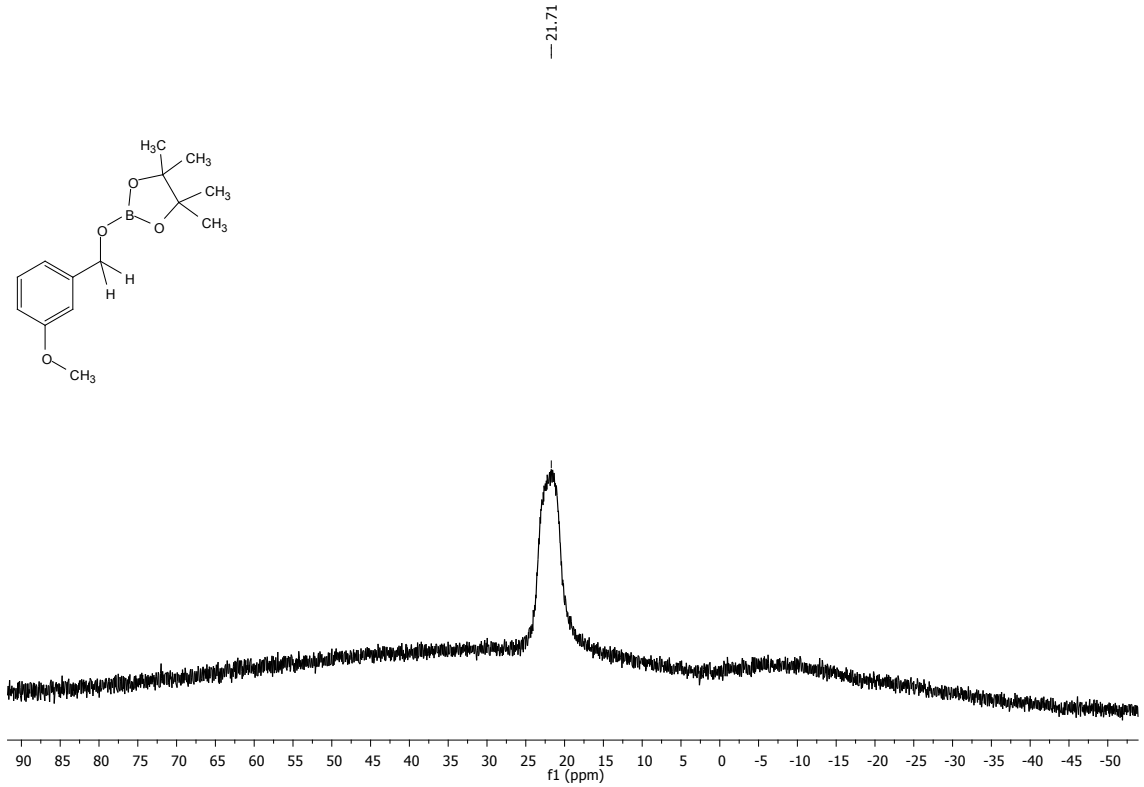


^{13}C NMR of **5c** (100 MHz, $CDCl_3$)

2-((3-Methoxybenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 6b).[9]

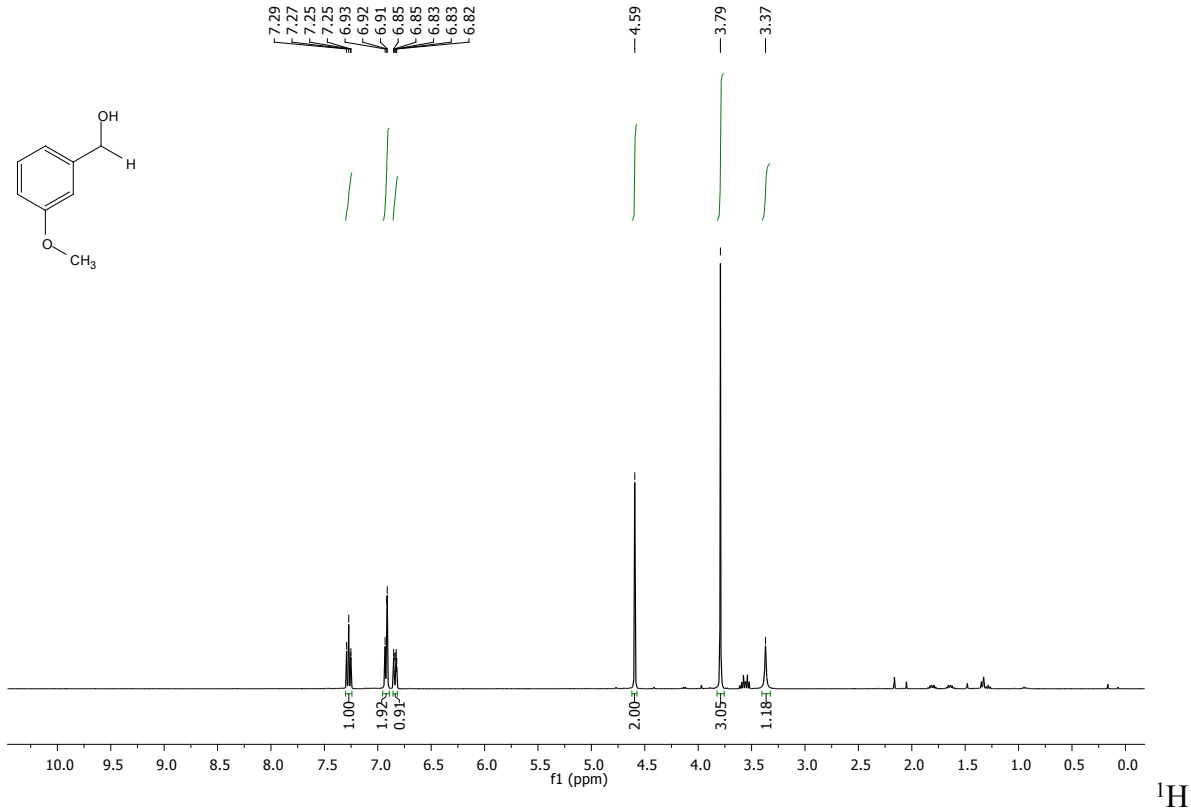


^{1}H NMR of **6b** (400 MHz, $CDCl_3$)

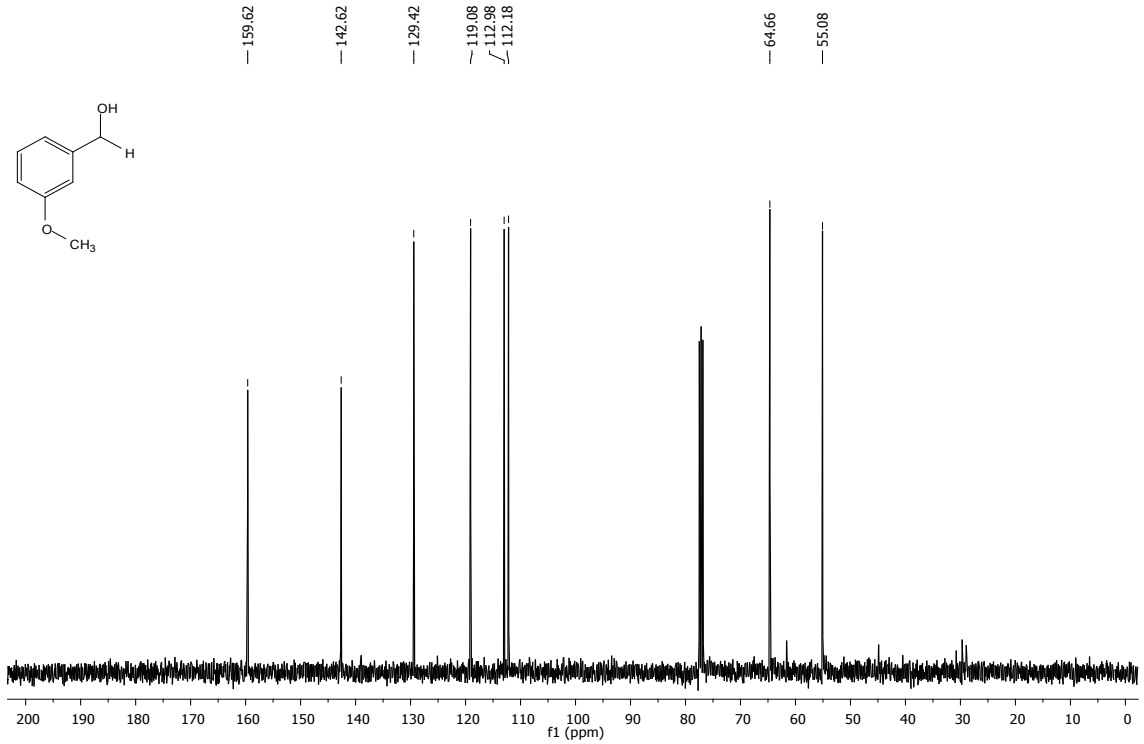


^{11}B NMR of **6b** (128 MHz, $CDCl_3$)

(3-Methoxyphenyl)methanol (Table 2, 6c).[10]

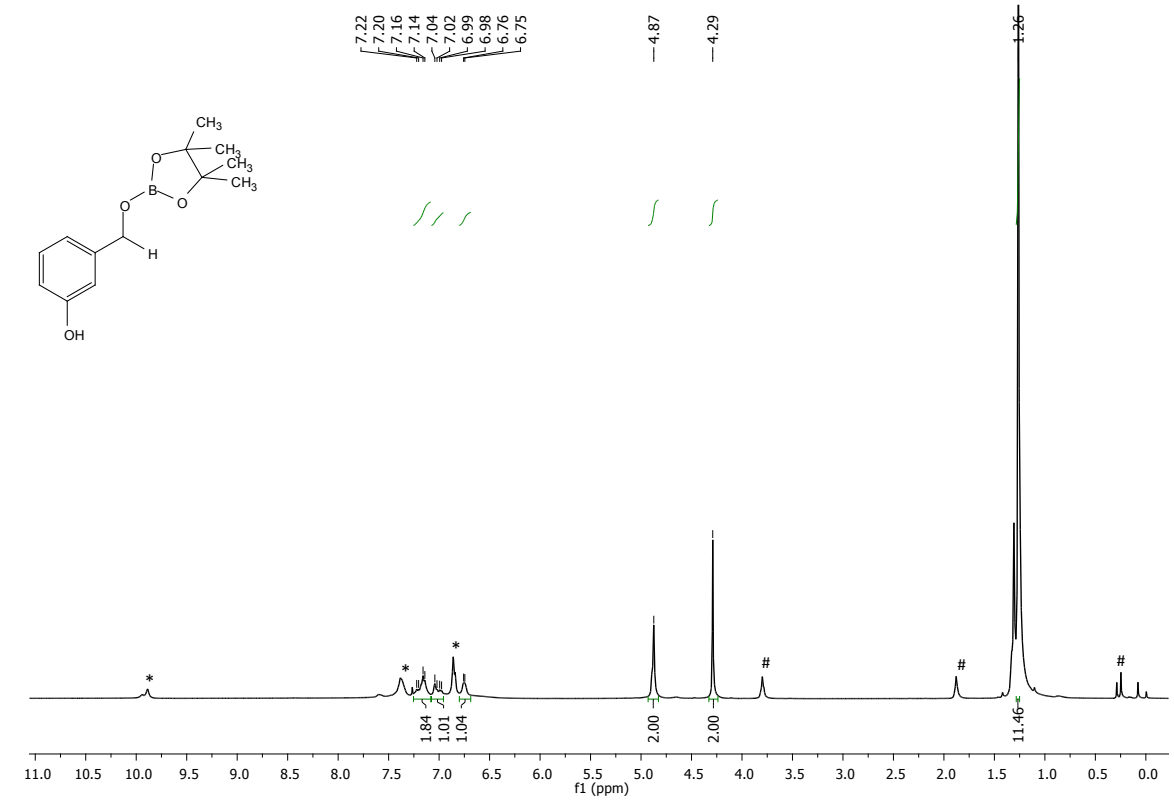


^{1}H NMR of **6c** (400 MHz, $CDCl_3$)

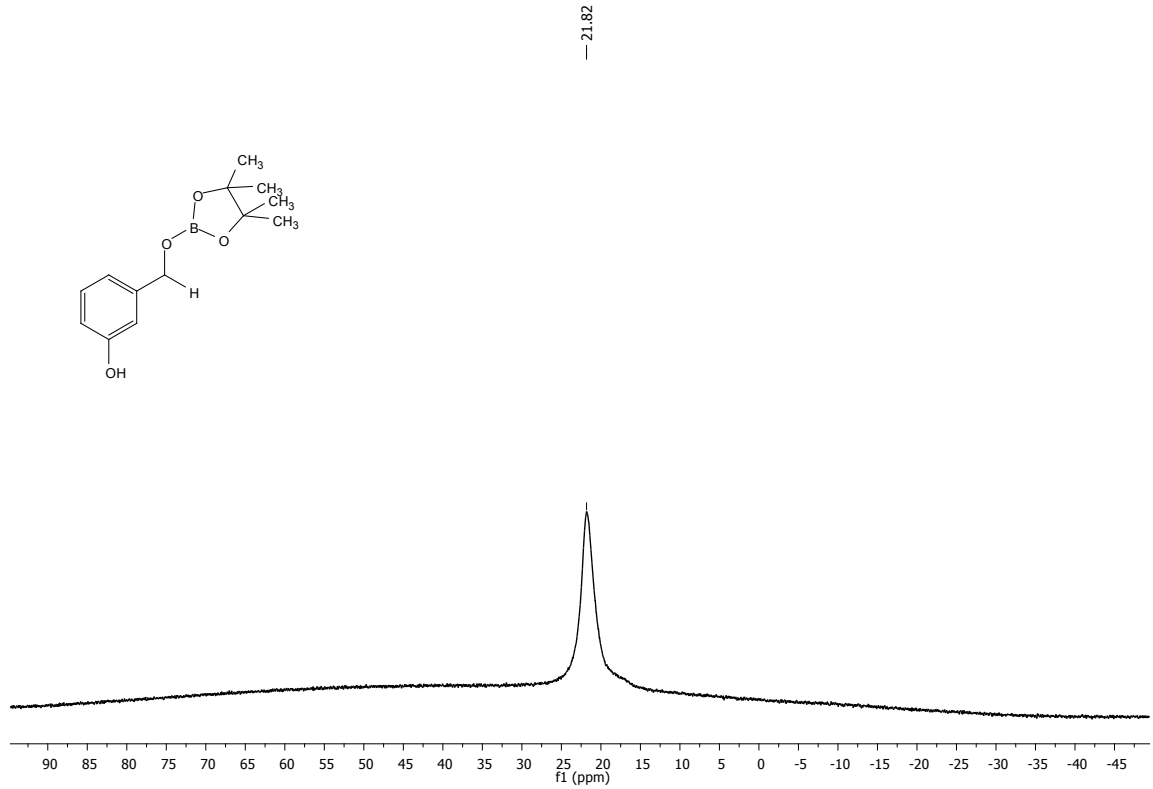


^{13}C NMR of **6c** (100 MHz, $CDCl_3$)

3-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)phenol (Table 2, 7b).

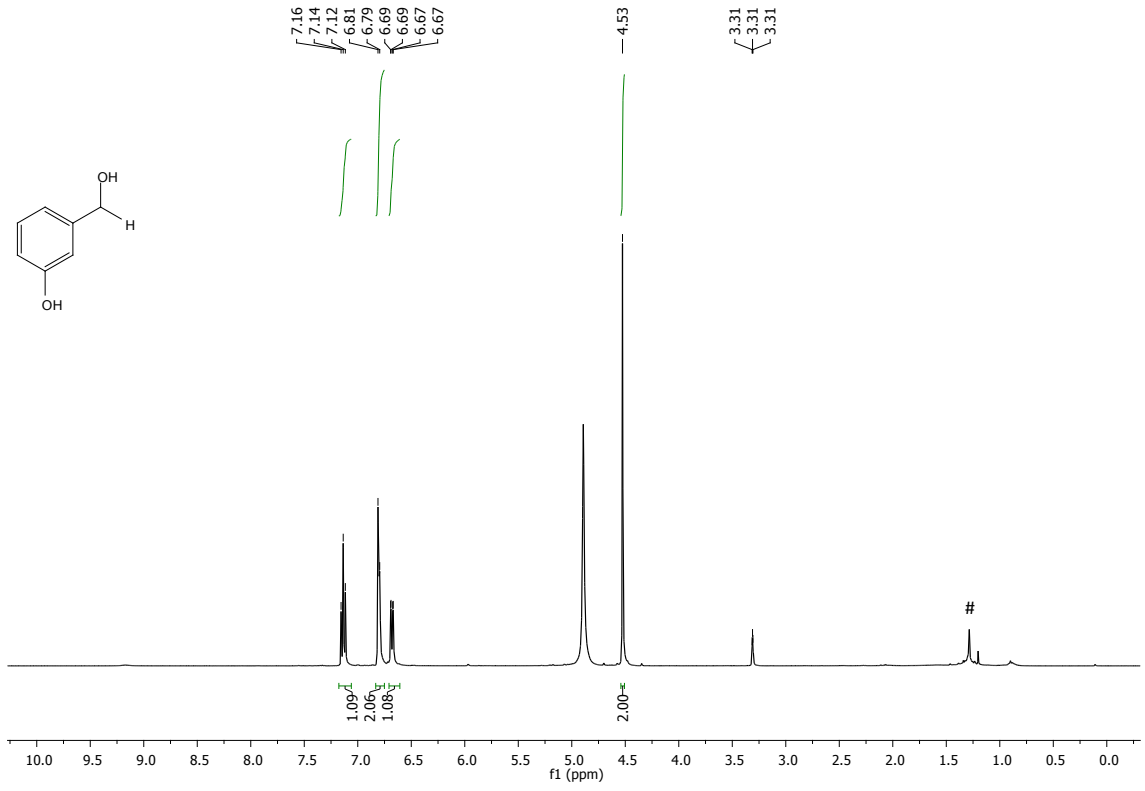


^{1}H NMR of **7b** (400 MHz, $CDCl_3$)

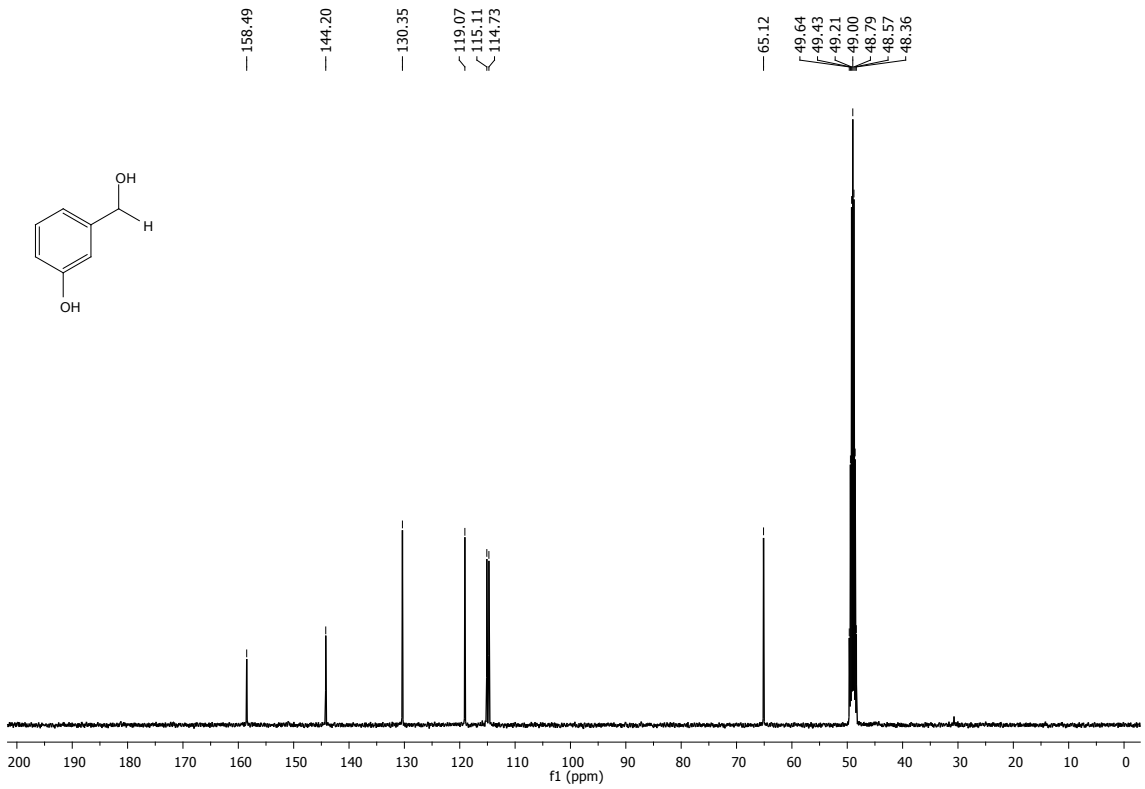


^{11}B NMR of **7b** (400 MHz, $CDCl_3$)

(3-(hydroxymethyl)phenol (Table 2, 7c).

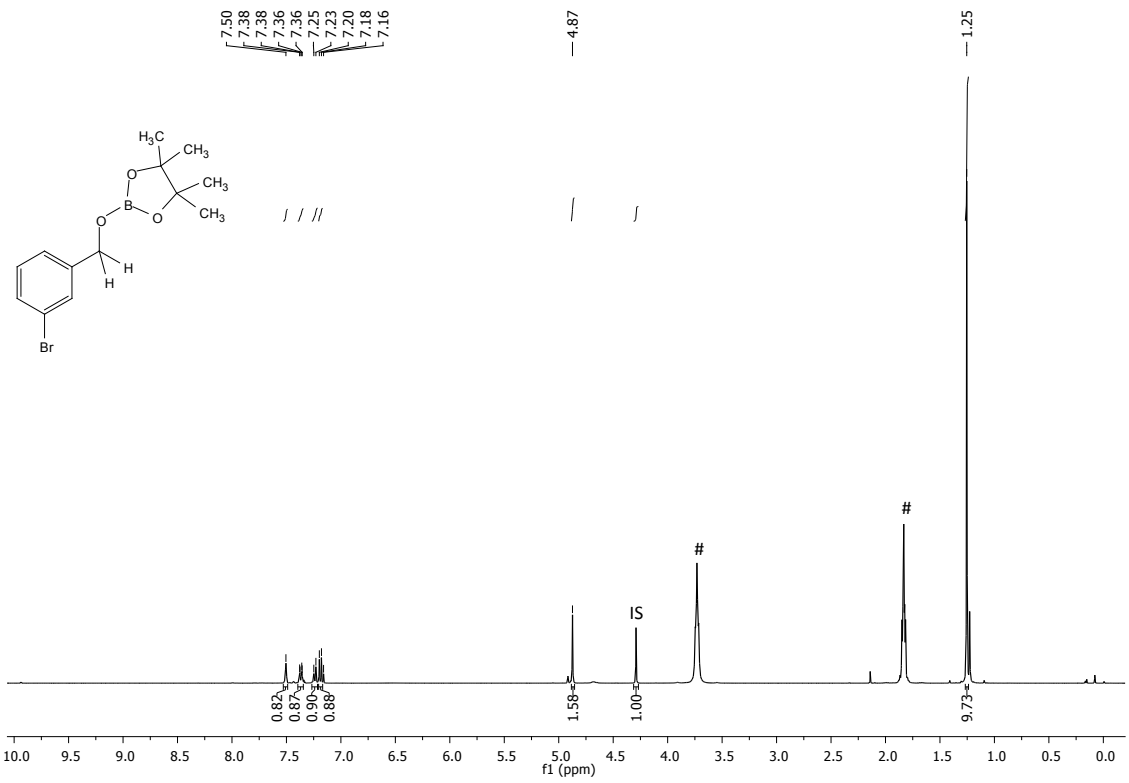


^{1}H NMR of **7c** (400 MHz, CD_3OD)

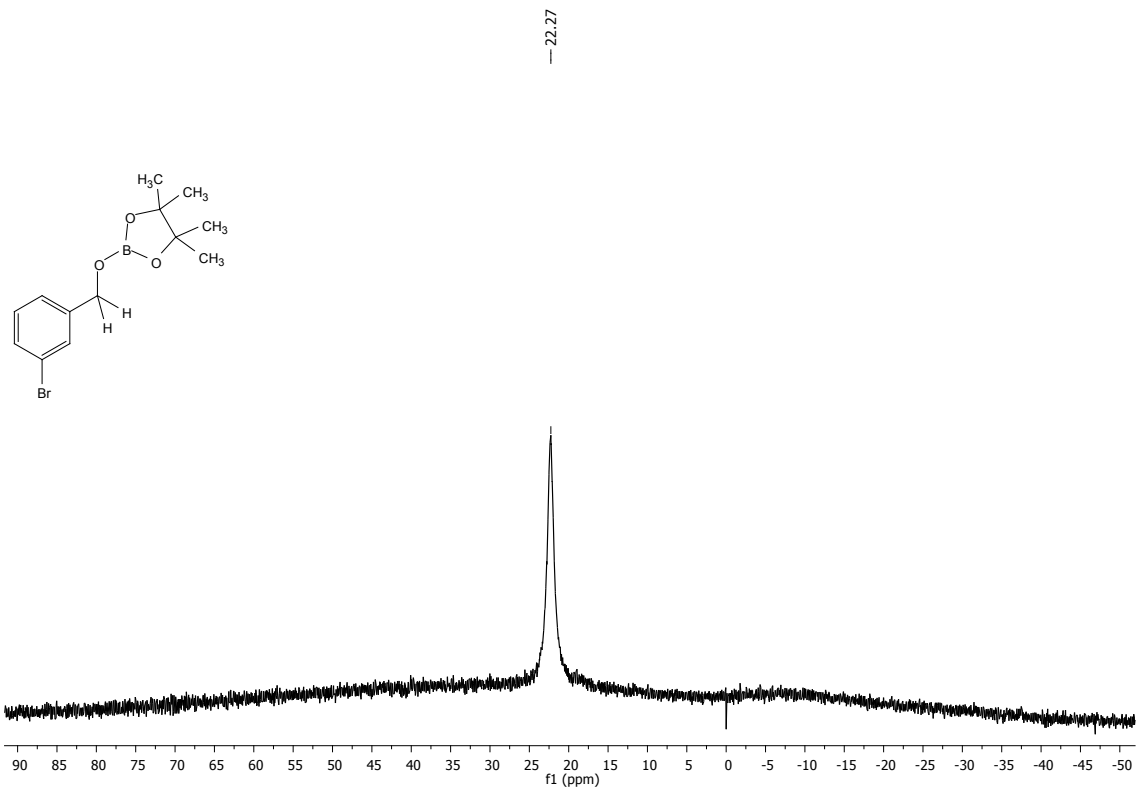


^{13}C NMR of **7c** (400 MHz, CD_3OD)

2-((3-Bromobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 8b).[9]

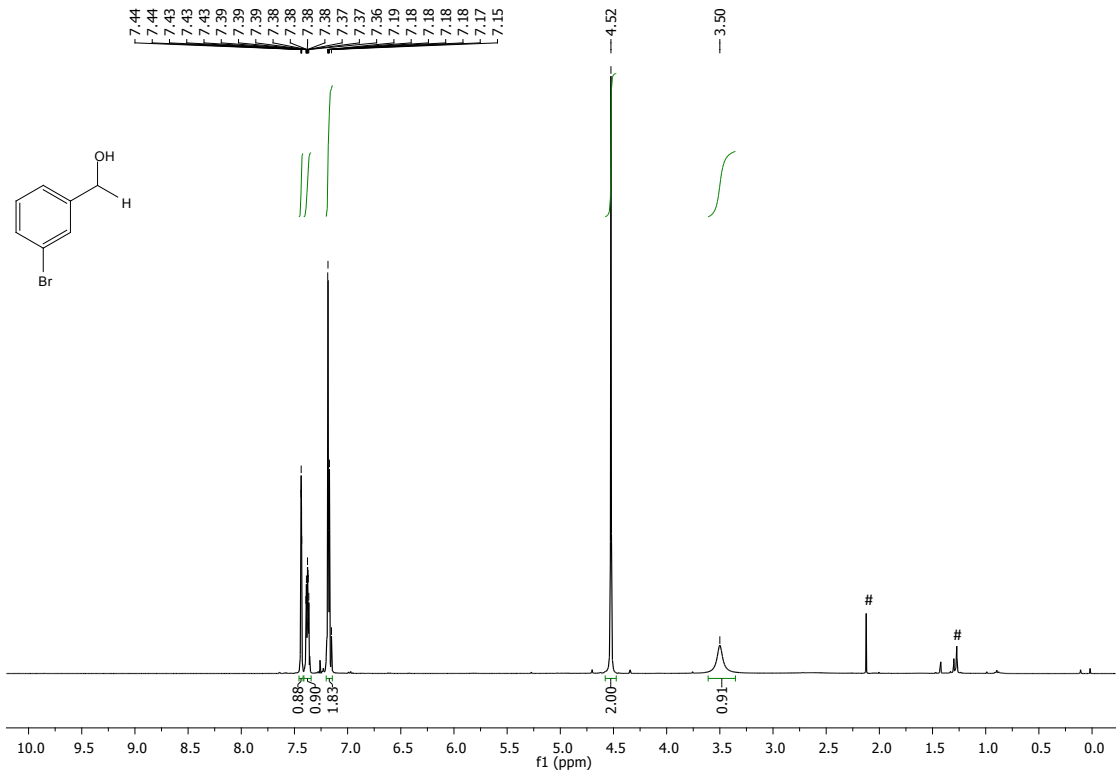


^{1}H NMR of **8b** (400 MHz, $CDCl_3$)

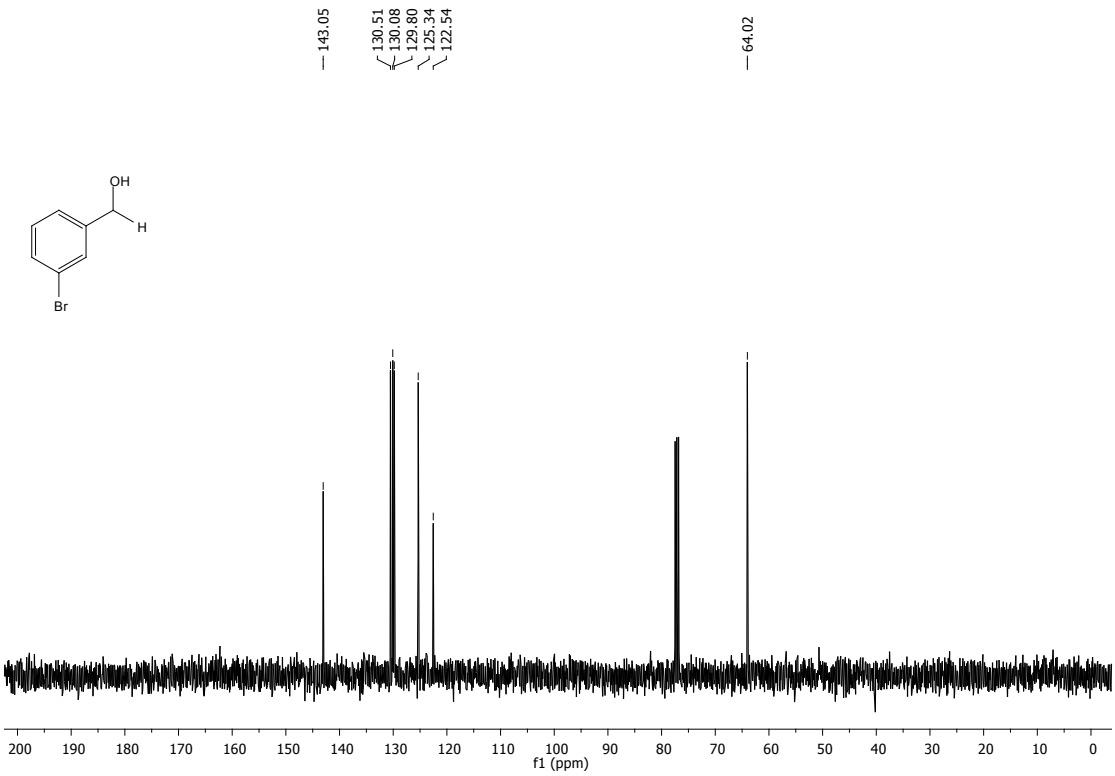


^{11}B NMR of **8b** (128 MHz, $CDCl_3$)

(3-Bromophenyl)methanol (Table 2, 8c).[10]

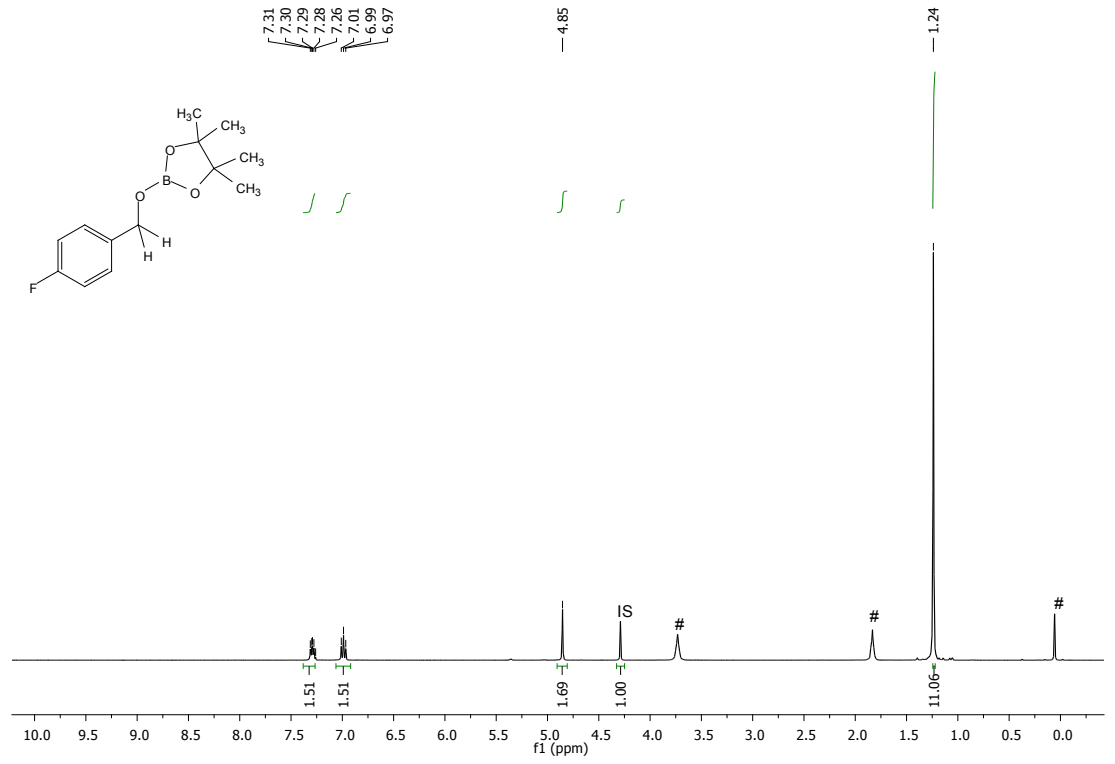


^{1}H NMR of **8c** (400 MHz, $CDCl_3$)

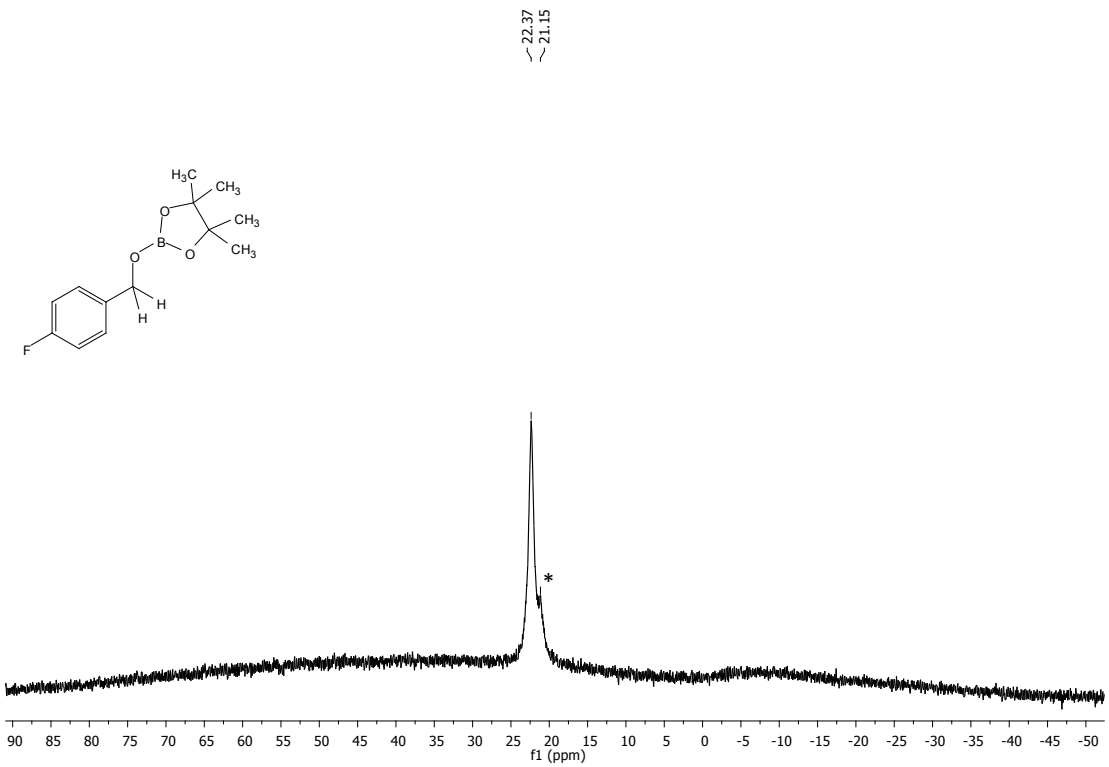


^{13}C NMR of **8c** (100 MHz, $CDCl_3$)

2-((4-Fluorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 9b).[10]

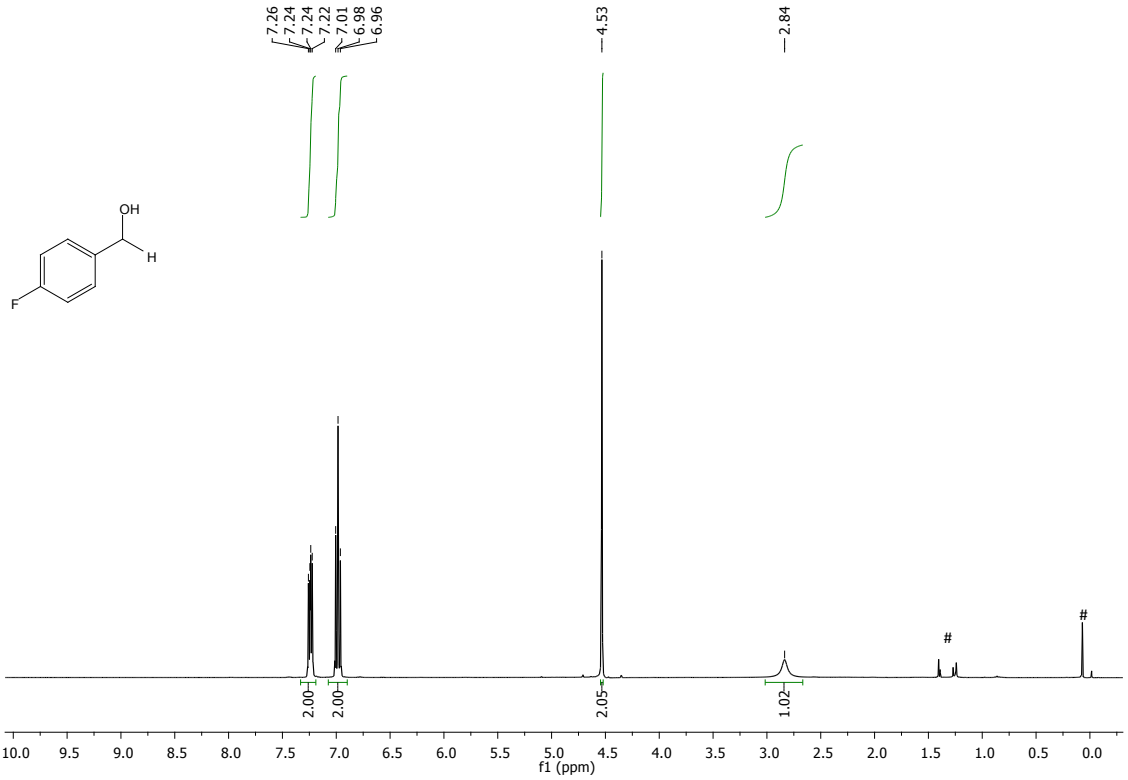


^{1}H NMR of **9b** (400 MHz, $CDCl_3$)

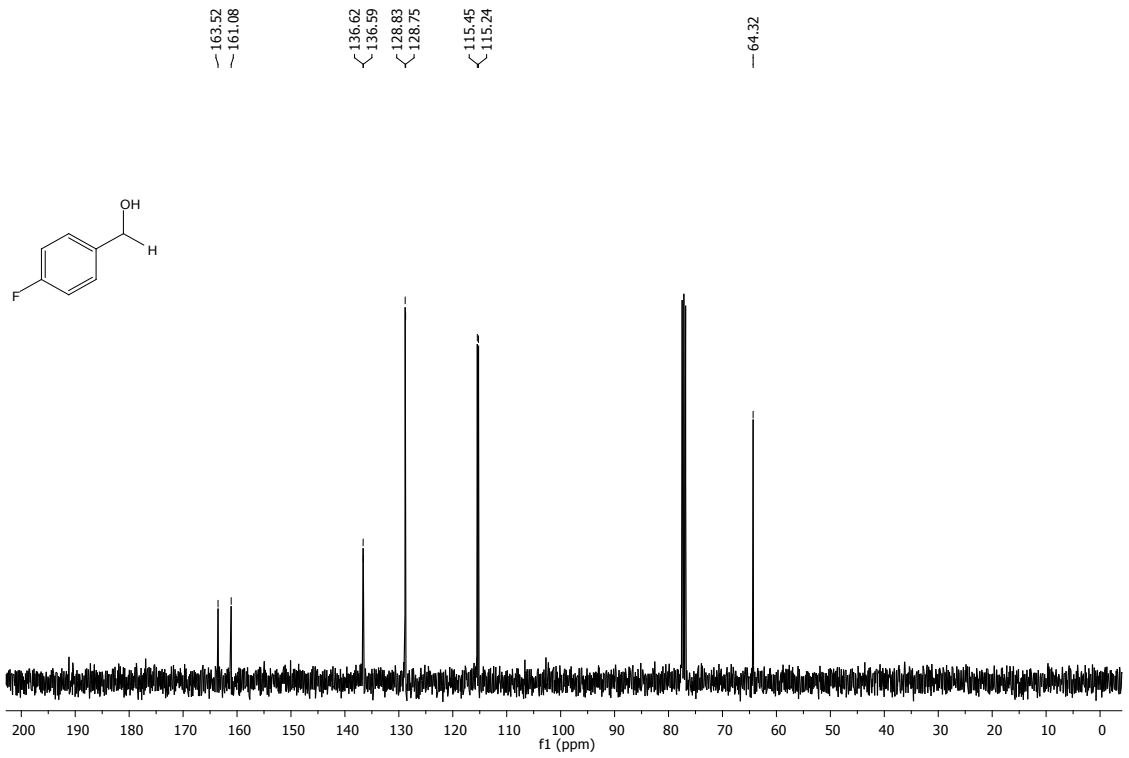


^{11}B NMR of **9b** (128 MHz, $CDCl_3$) (* impurity from B_2pin_3/RO-Bpin/BpinOBpin)

(4–Fluorophenyl)methanol (Table 2, 9c).[8]

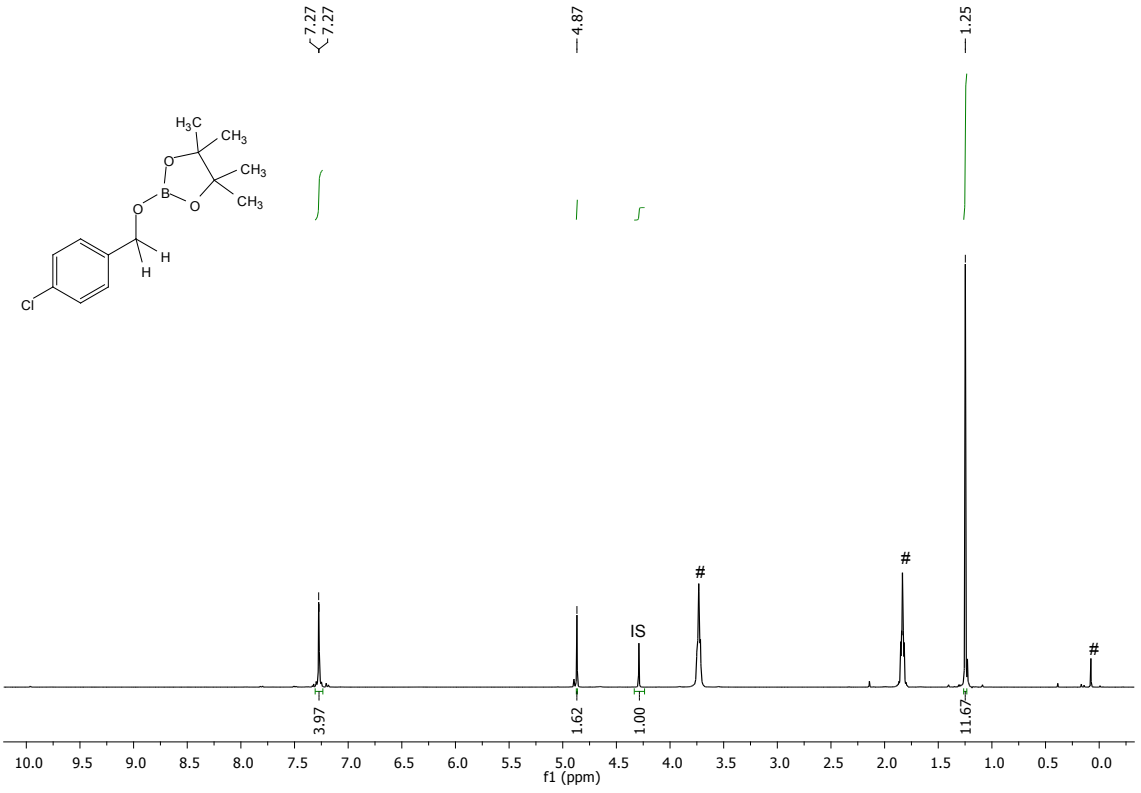


^{1}H NMR of **9c** (400 MHz, $CDCl_3$)

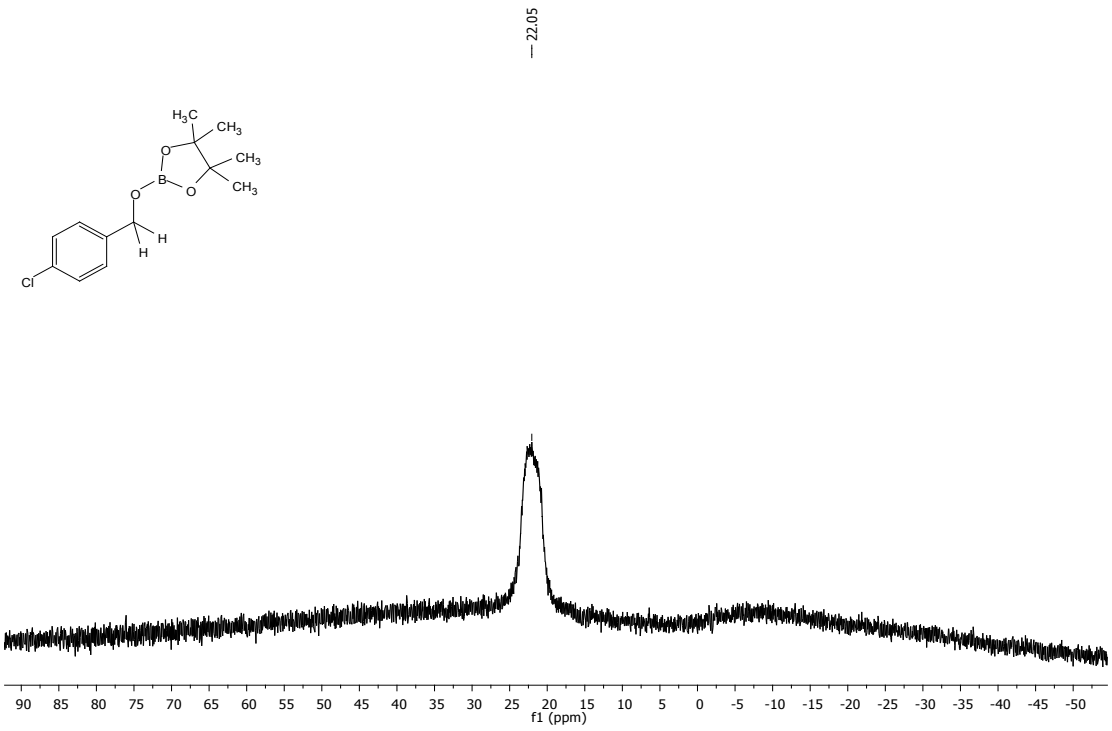


^{13}C NMR of **9c** (100 MHz, $CDCl_3$)

2-((4-Chlorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 10b).[4]

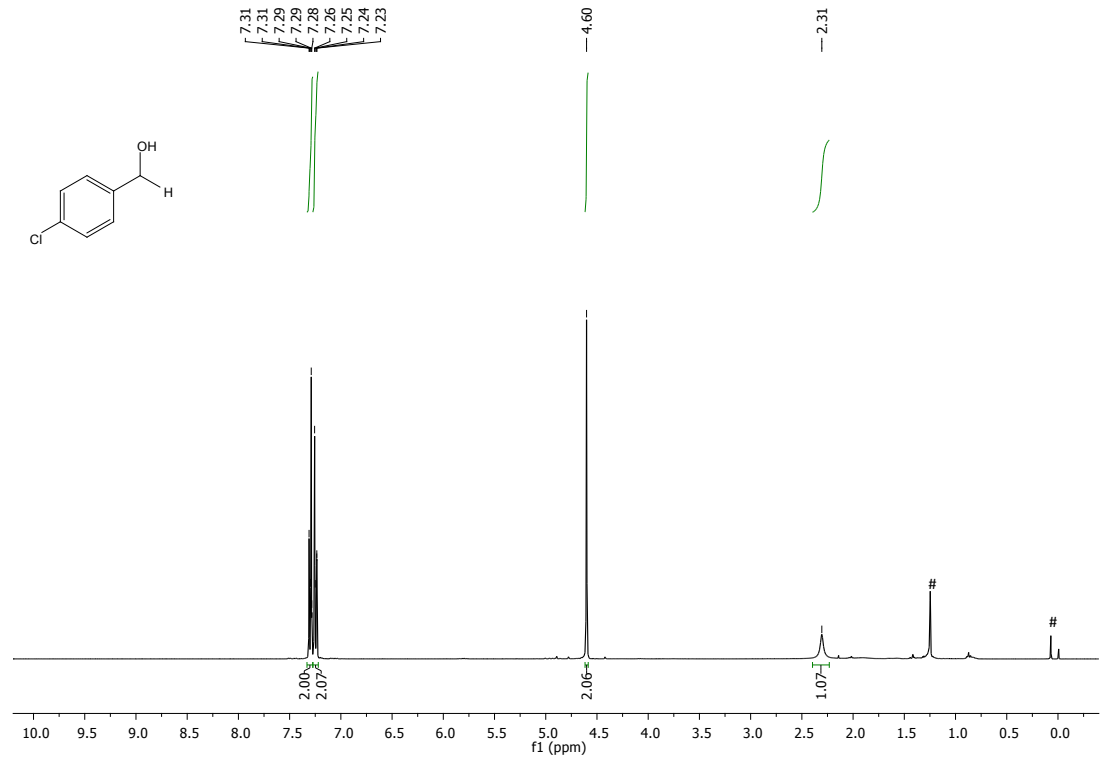


^{1}H NMR of **10b** (400 MHz, $CDCl_3$)

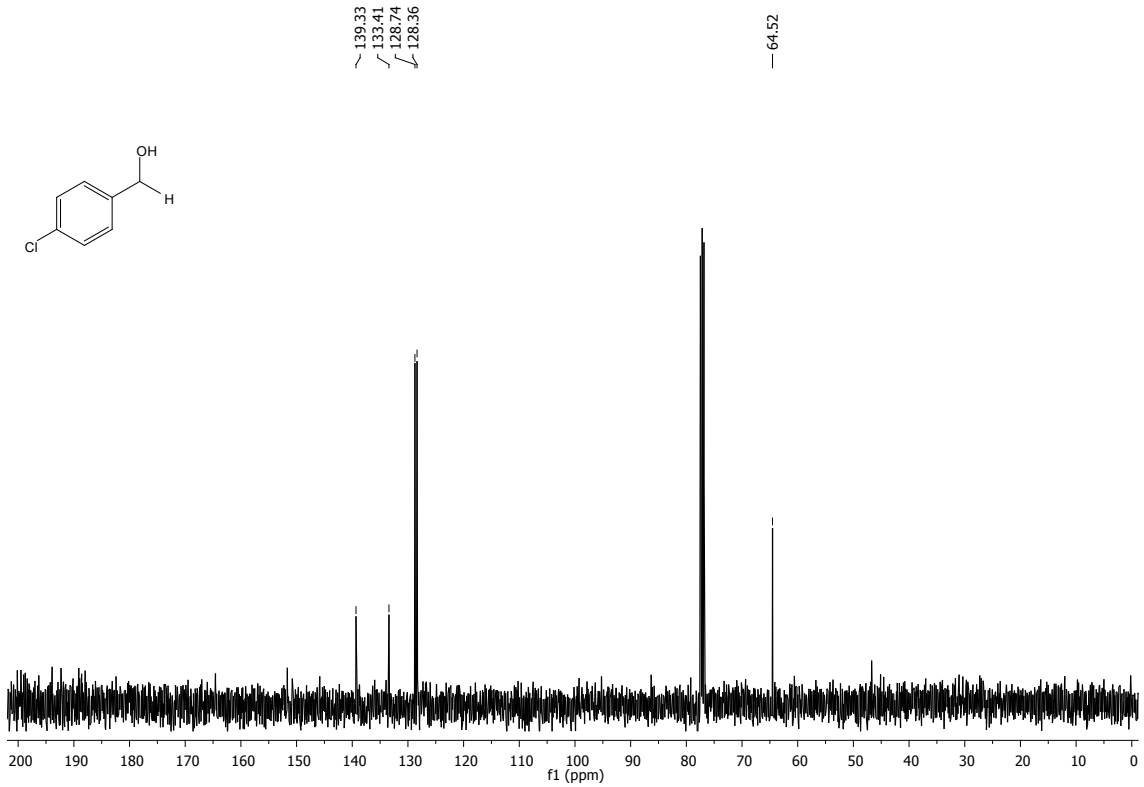


^{11}B NMR of **10b** (128 MHz, $CDCl_3$)

(4–Chlorophenyl)methanol (Table 2, 10c)[10]

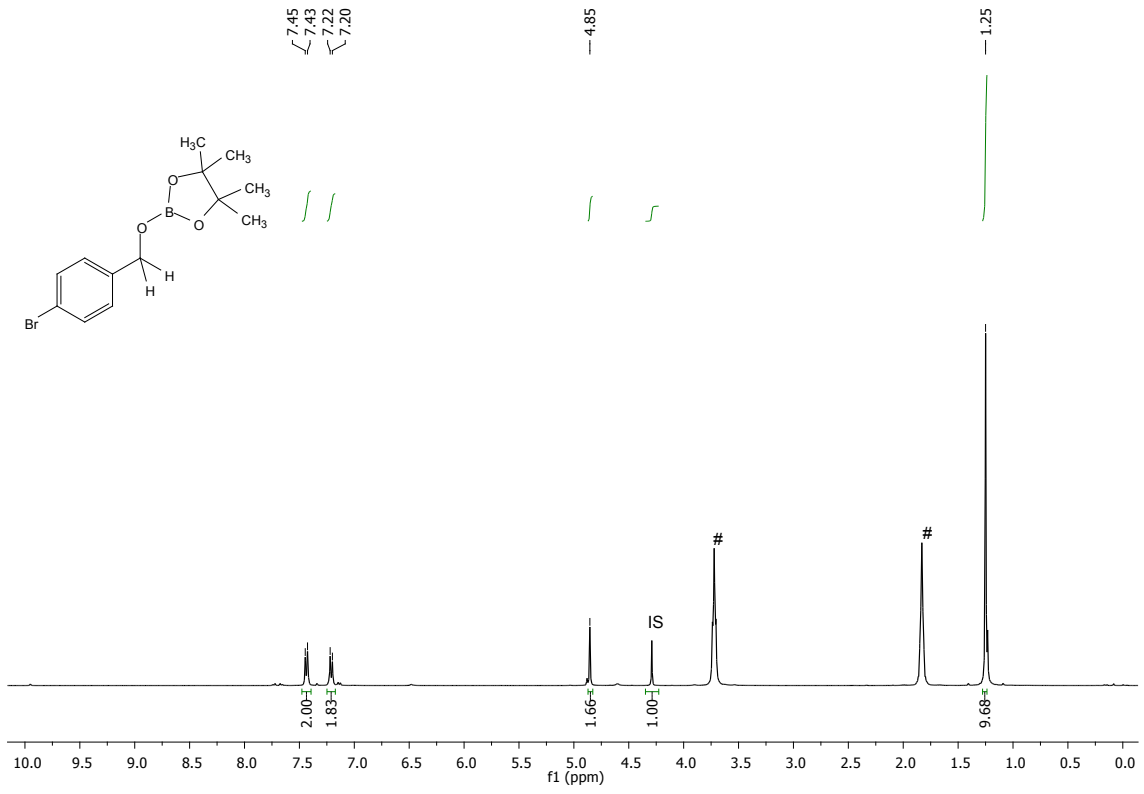


^{1}H NMR of **10c** (400 MHz, $CDCl_3$)

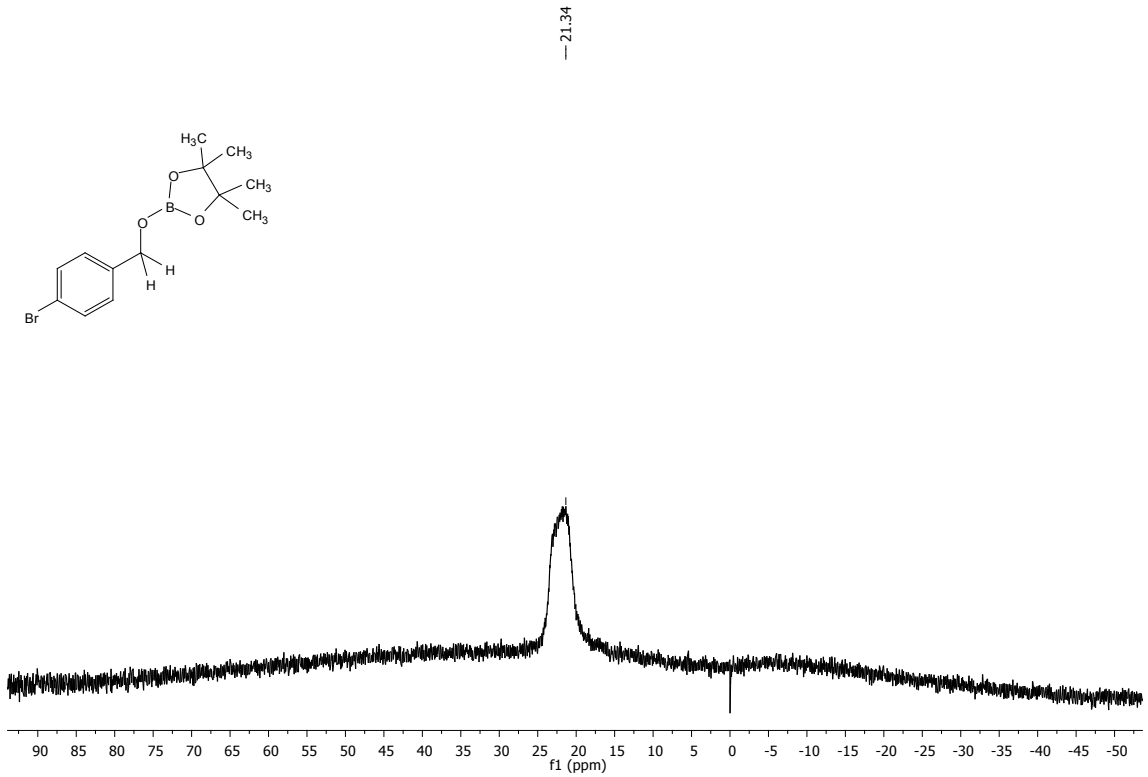


^{13}C NMR of **10c** (100 MHz, $CDCl_3$)

2-((4-Bromobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 11b).[9]

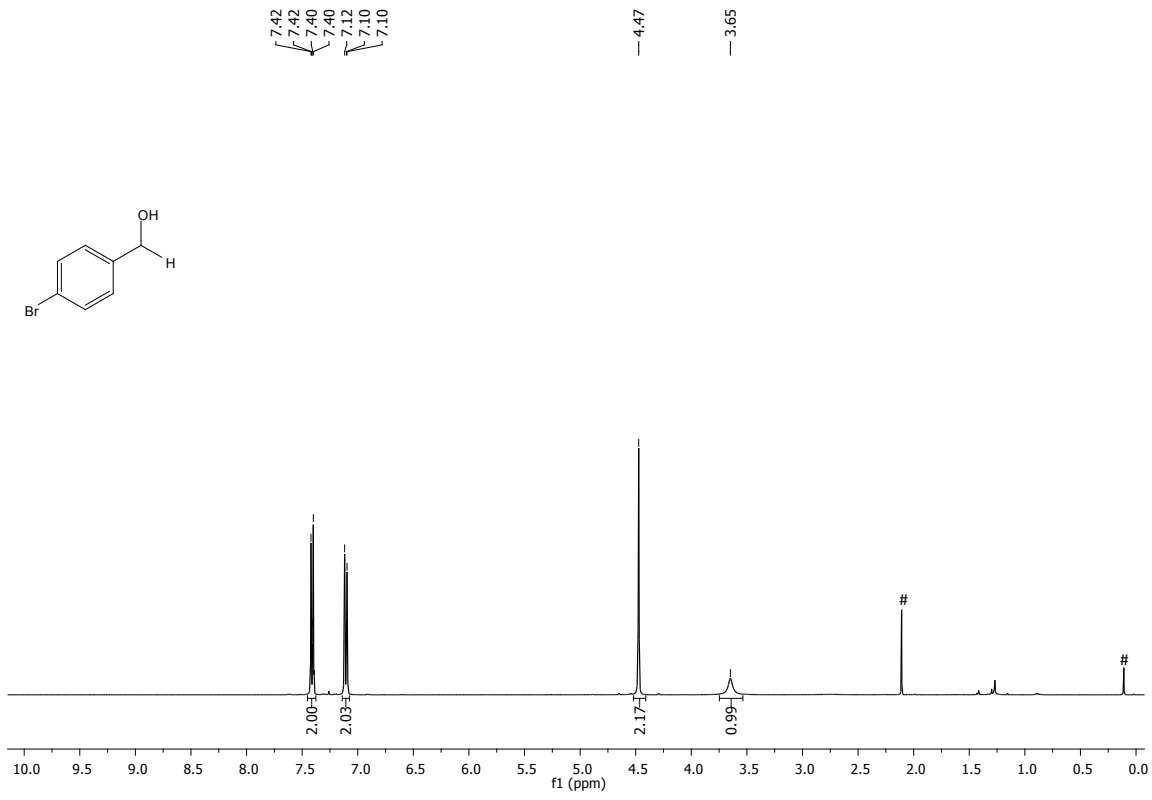


^{1}H NMR of **11b** (400 MHz, $CDCl_3$)

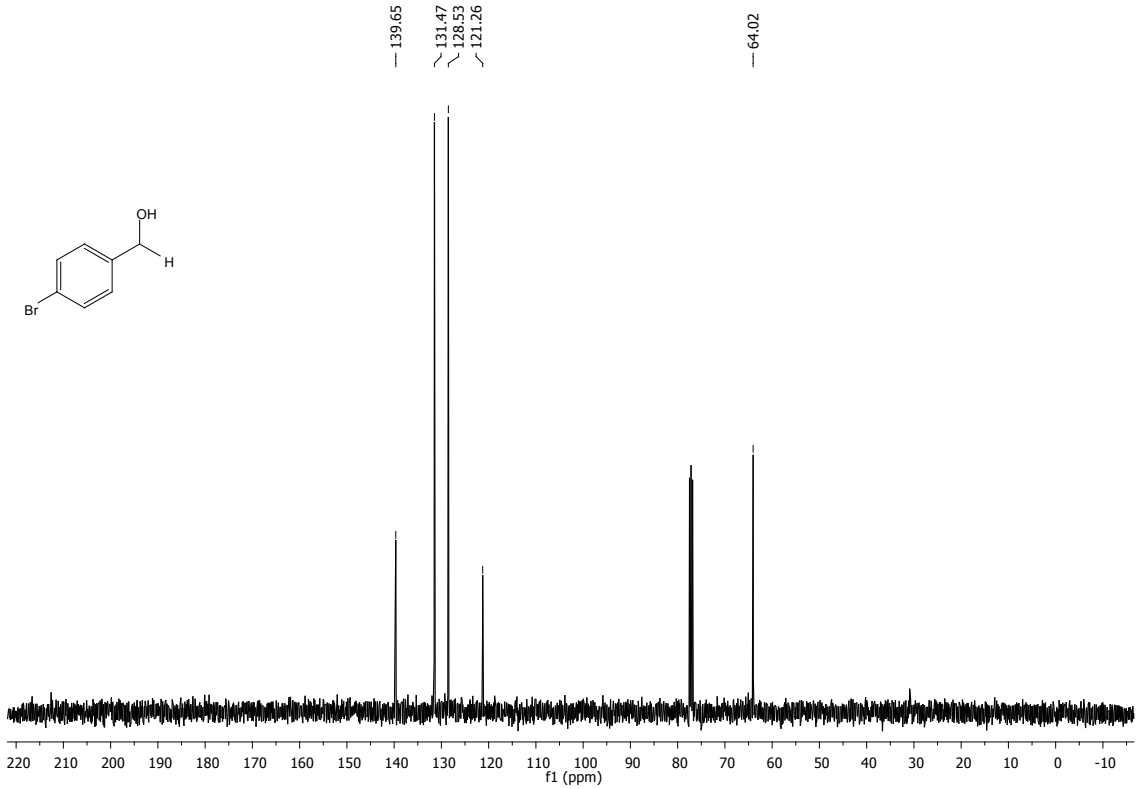


^{11}B NMR of **11b** (128 MHz, $CDCl_3$)

(4–Bromophenyl)methanol (Table 2, 11c)[8]

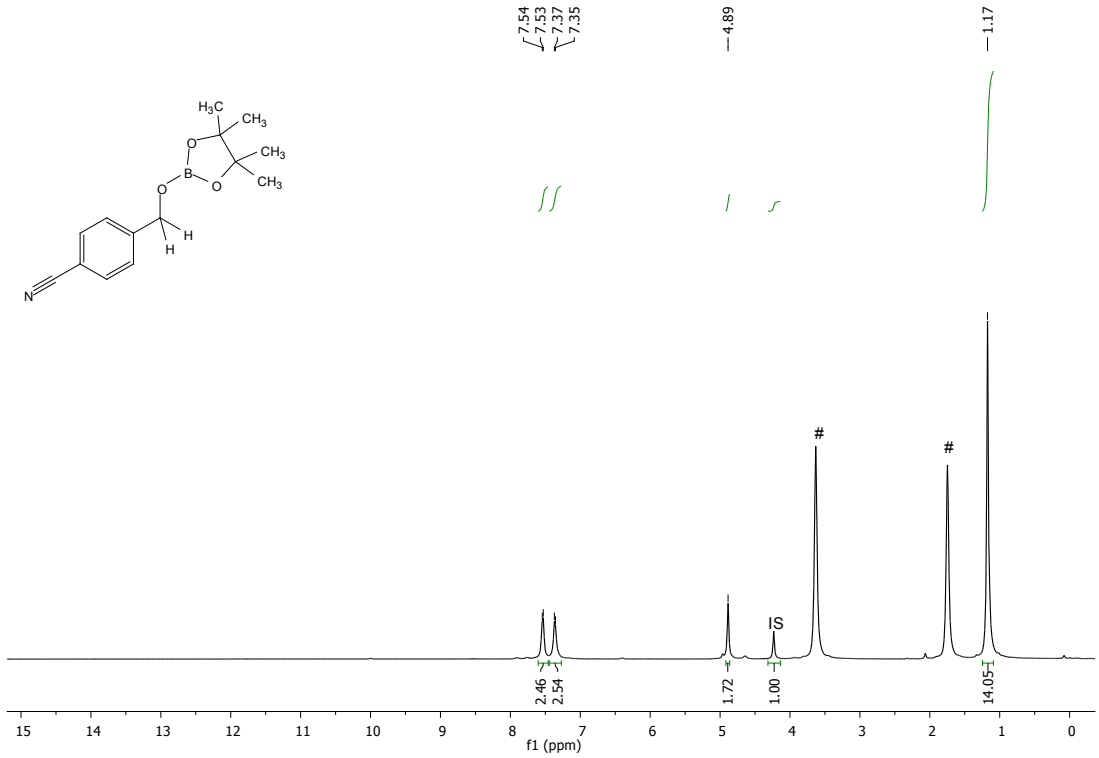


^{1}H NMR of **11c** (400 MHz, $CDCl_3$)

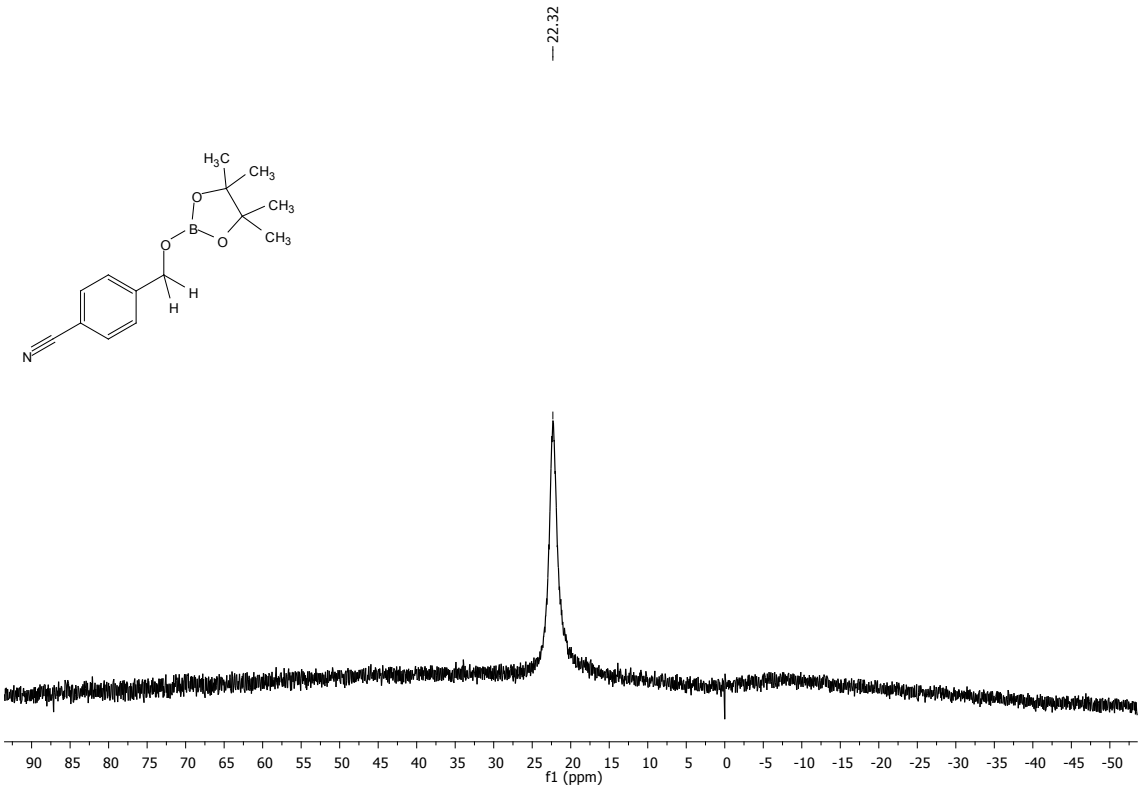


^{13}C NMR of **11c** (100 MHz, $CDCl_3$)

4-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzonitrile (Table 2, 12b).[9]

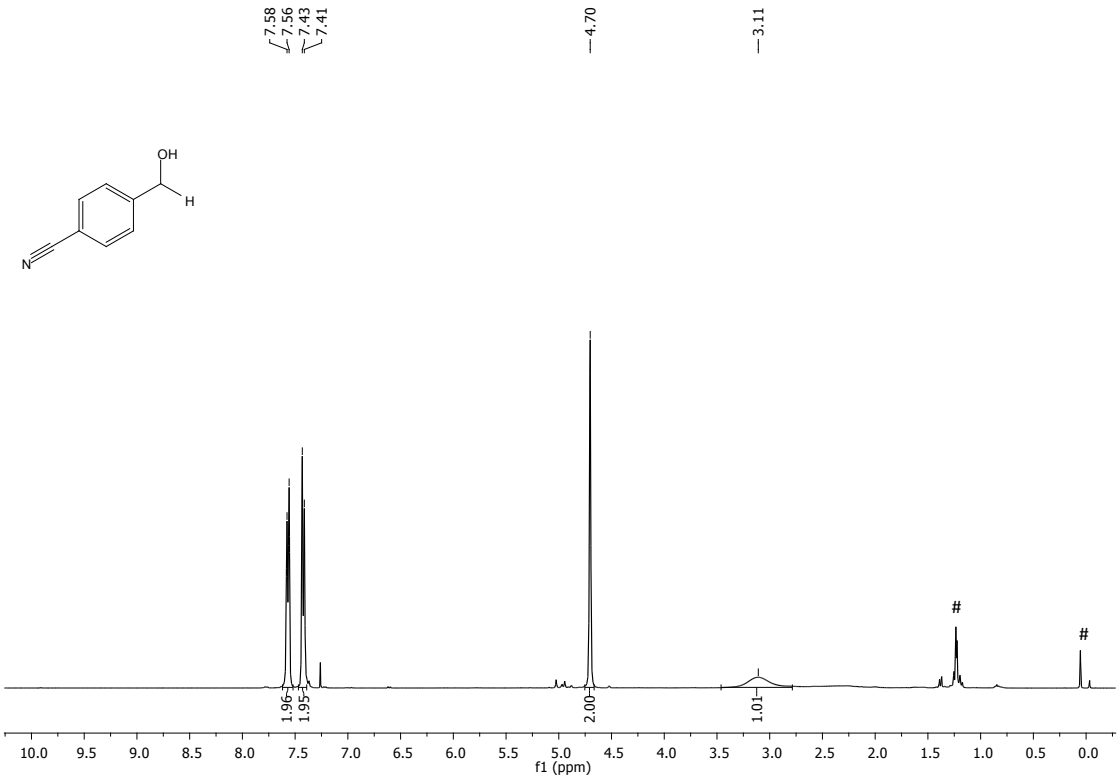


^{1}H NMR of **12b** (400 MHz, $CDCl_3$)

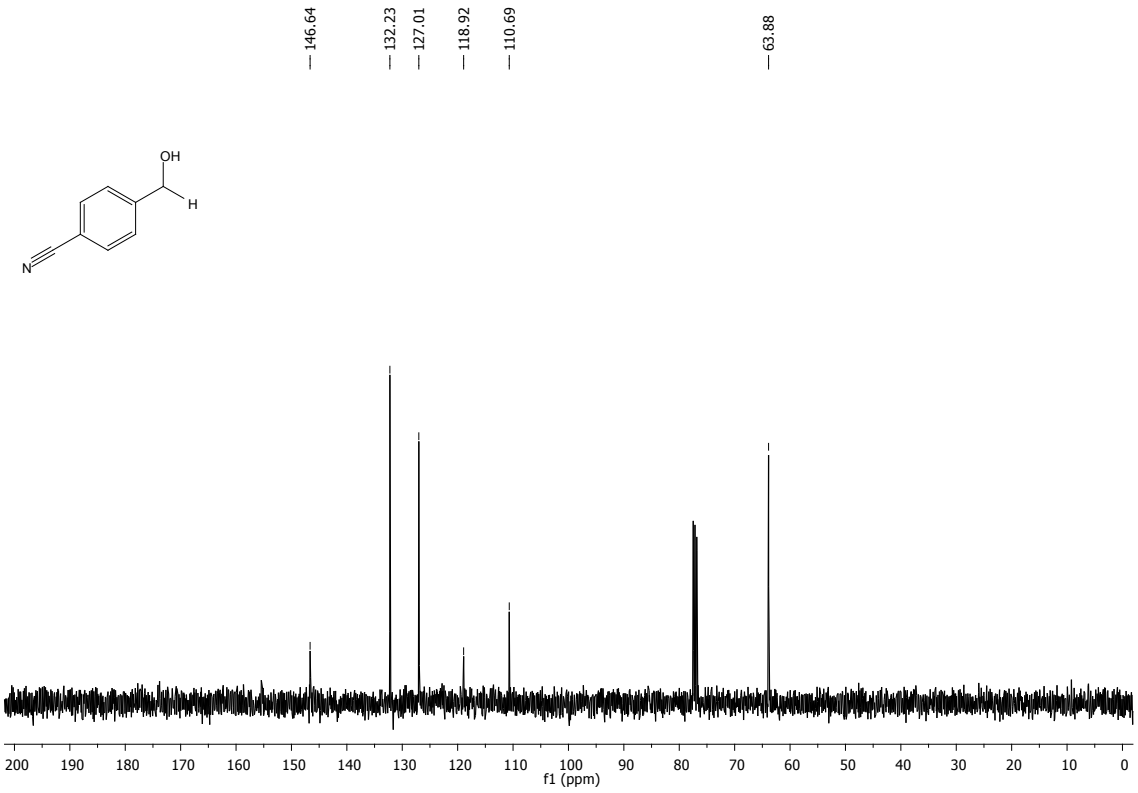


^{11}B NMR of **12b** (128 MHz, $CDCl_3$)

4-(Hydroxymethyl)benzonitrile (Table 2, 12c).[10]

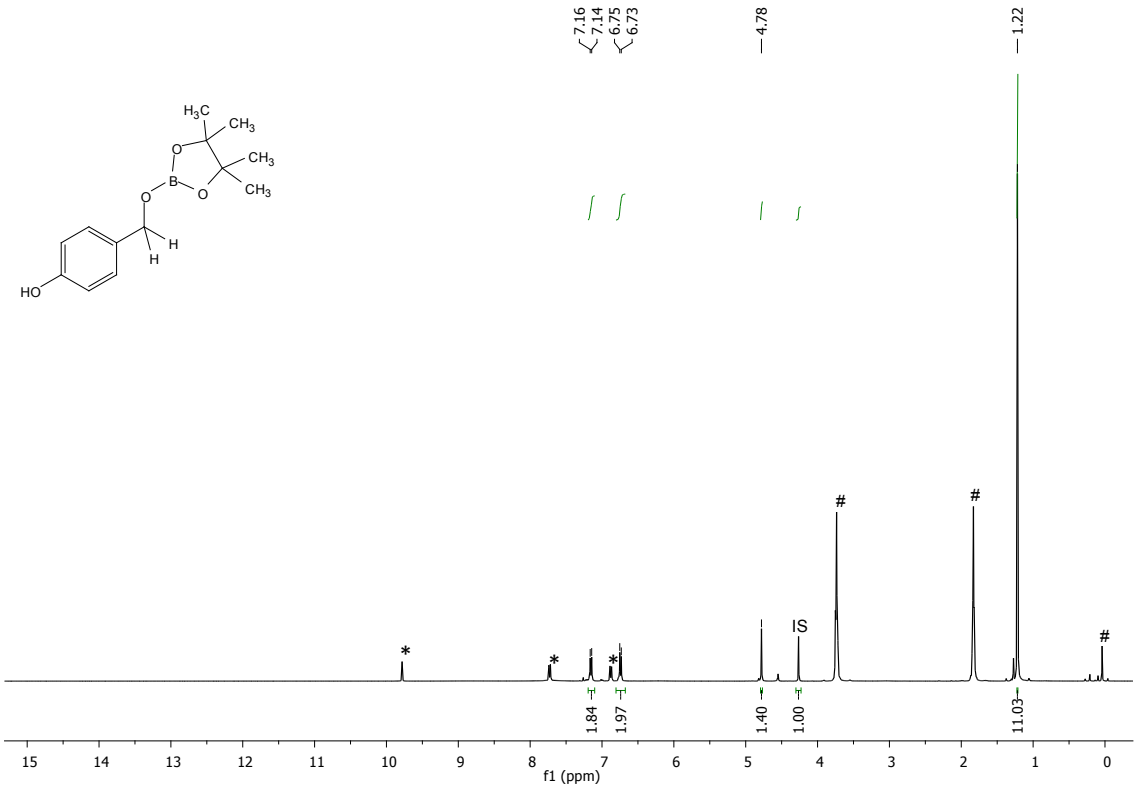


^{1}H NMR of **12c** (400 MHz, $CDCl_3$)

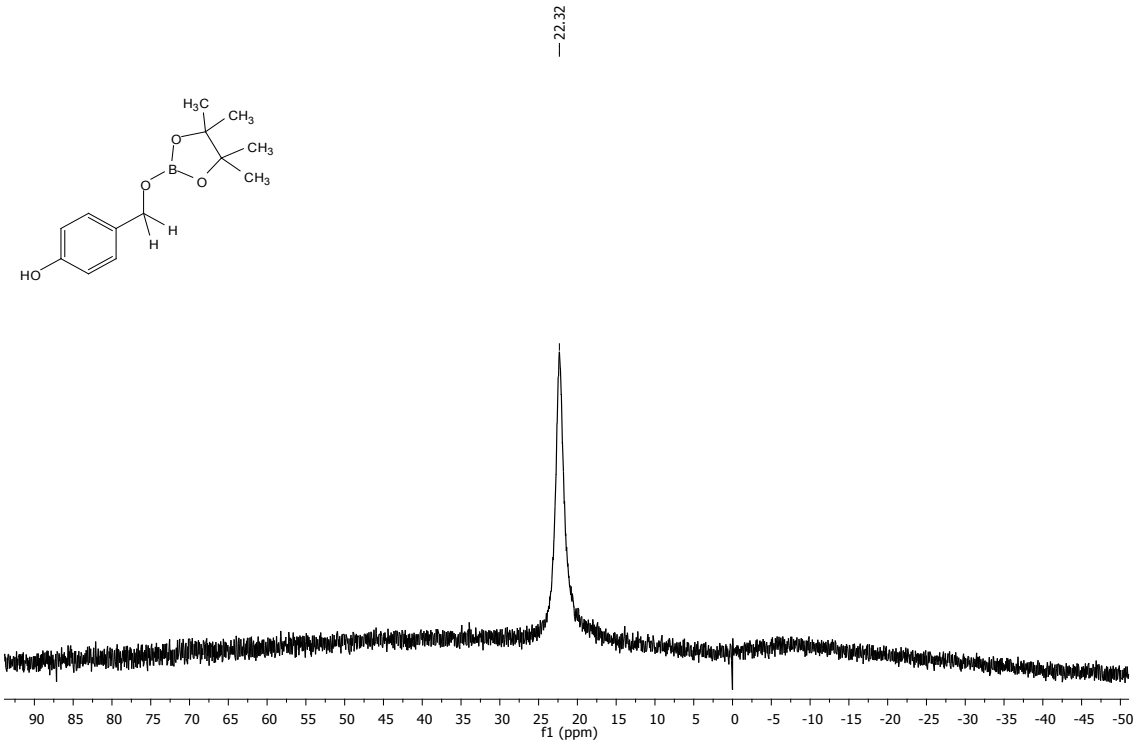


^{13}C NMR of **12c** (100 MHz, $CDCl_3$)

4-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)phenol (Table 2, 13b).[9]

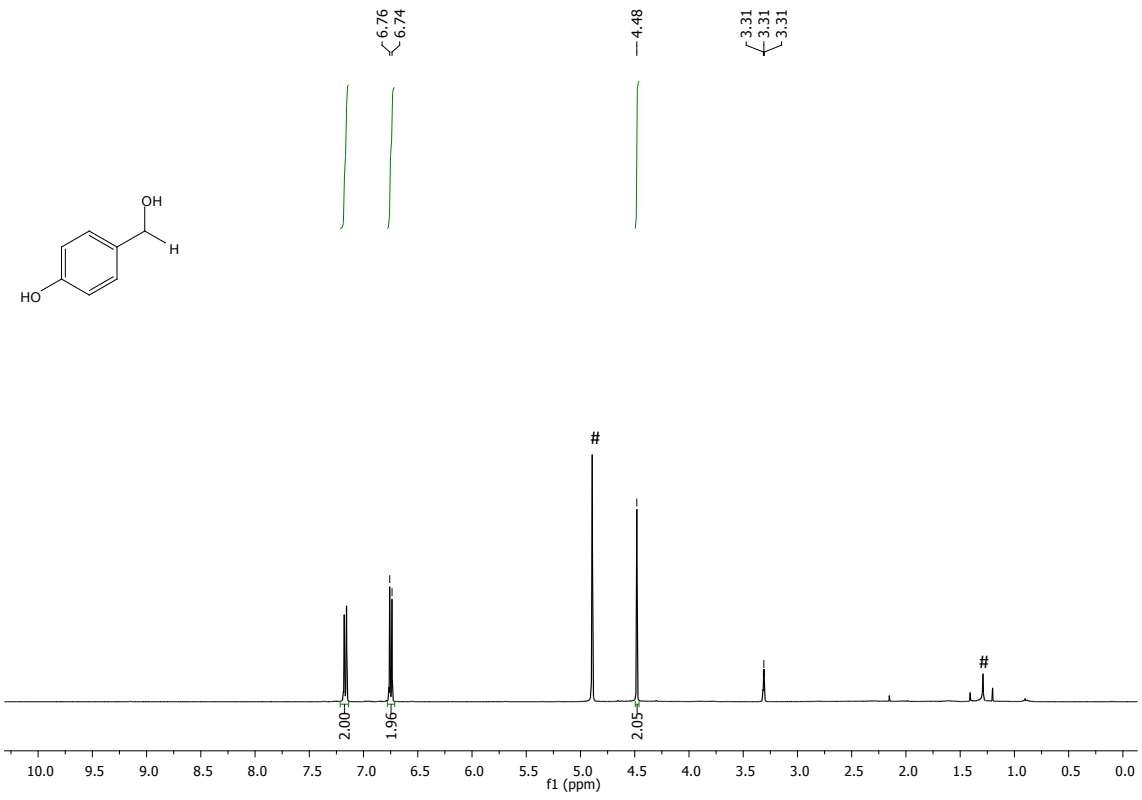


^{1}H NMR of **13b** (400 MHz, $CDCl_3$)

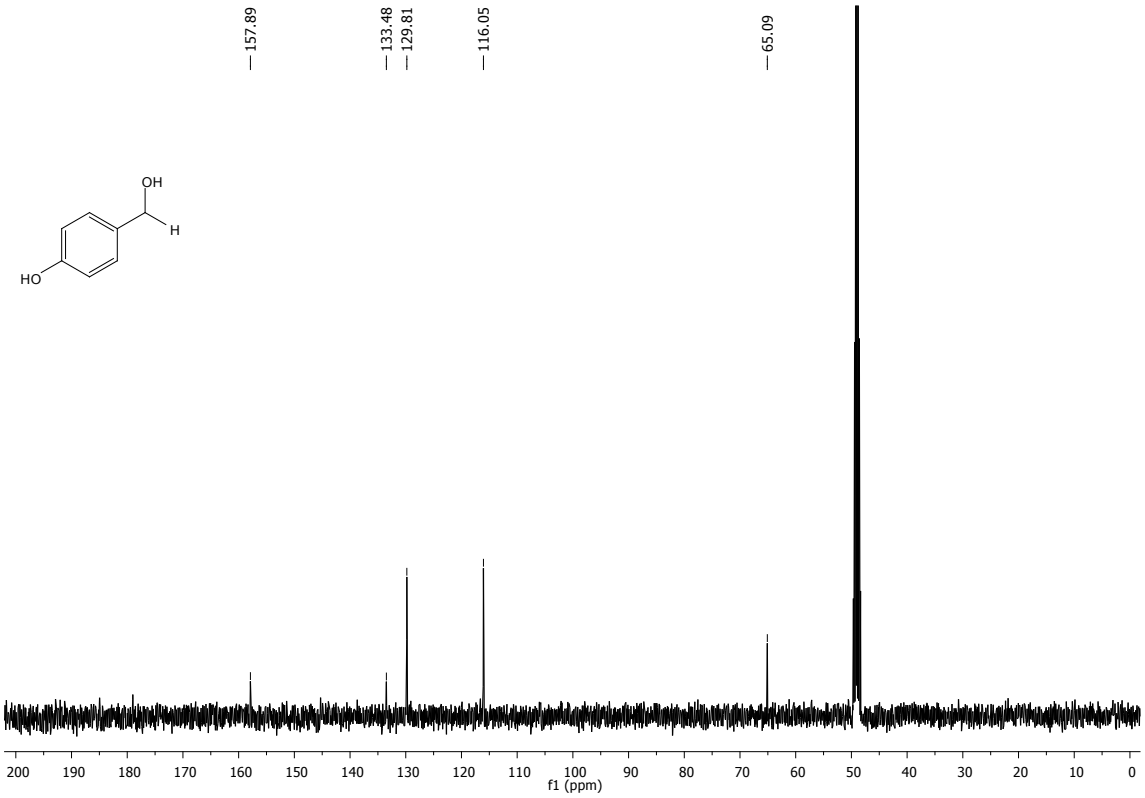


^{11}B NMR of **13b** (128 MHz, $CDCl_3$)

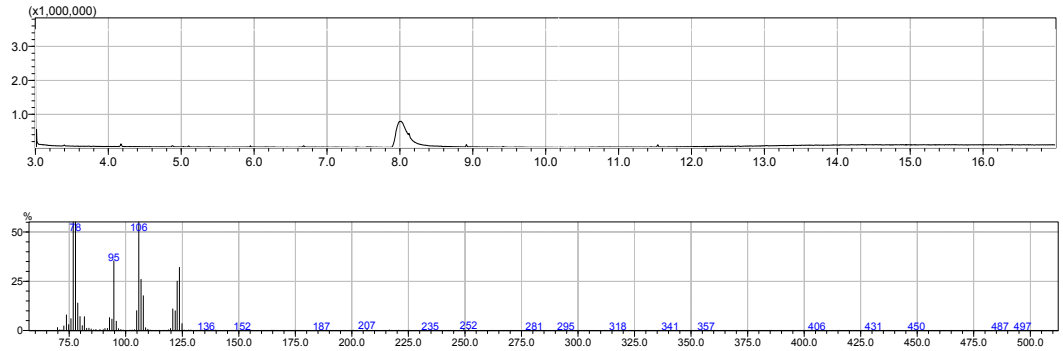
4-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)phenol (Table 2, 13c).[7]



^{1}H NMR of **13c** (400 MHz, CD_3OD)

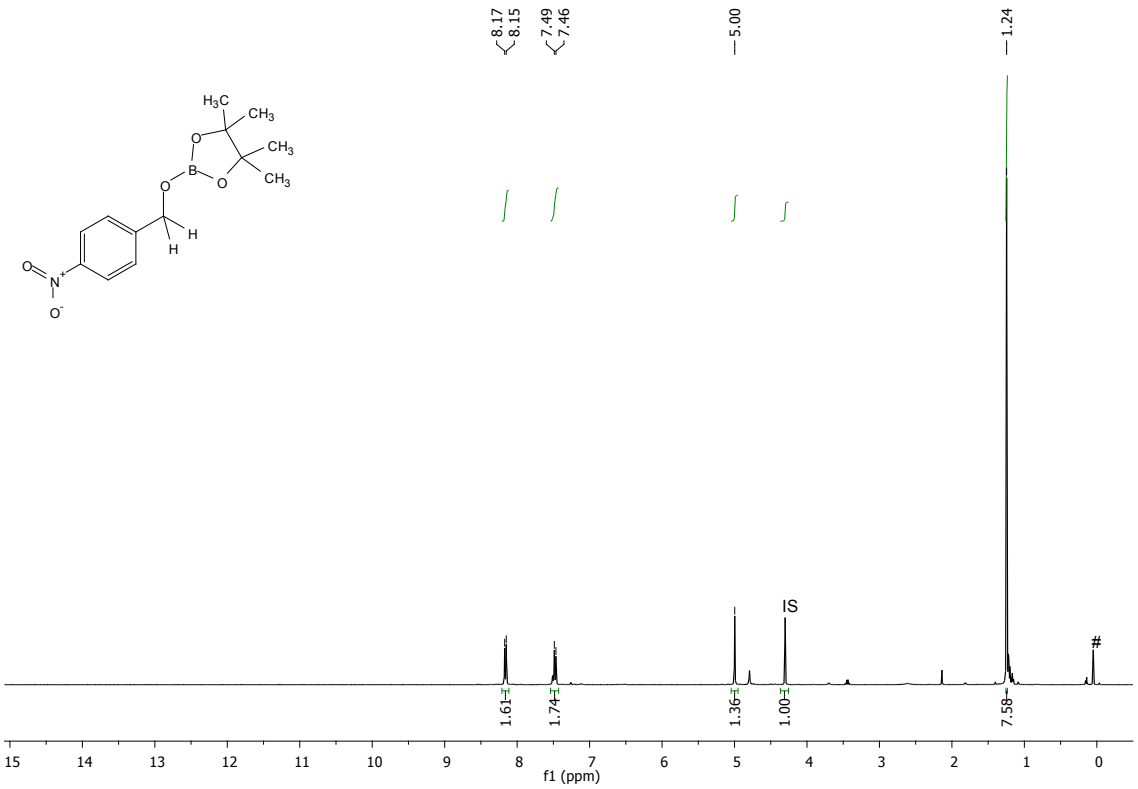


^{13}C NMR of **13c** (100 MHz, CD_3OD)

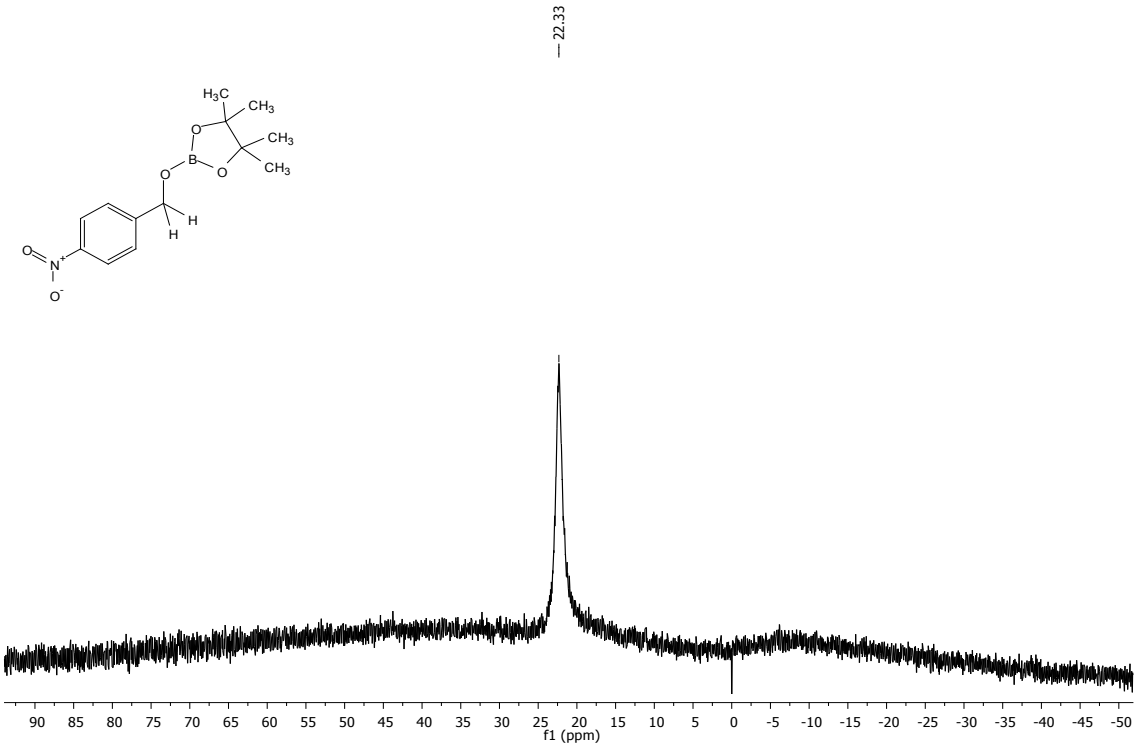


GC-MS of **13c**. Mass at 124.05 corresponds to 4-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)phenol.

4,4,5,5-Tetramethyl-2-((4-nitrobenzyl)oxy)-1,3,2-dioxaborolane (Table 2, 14b).[4]

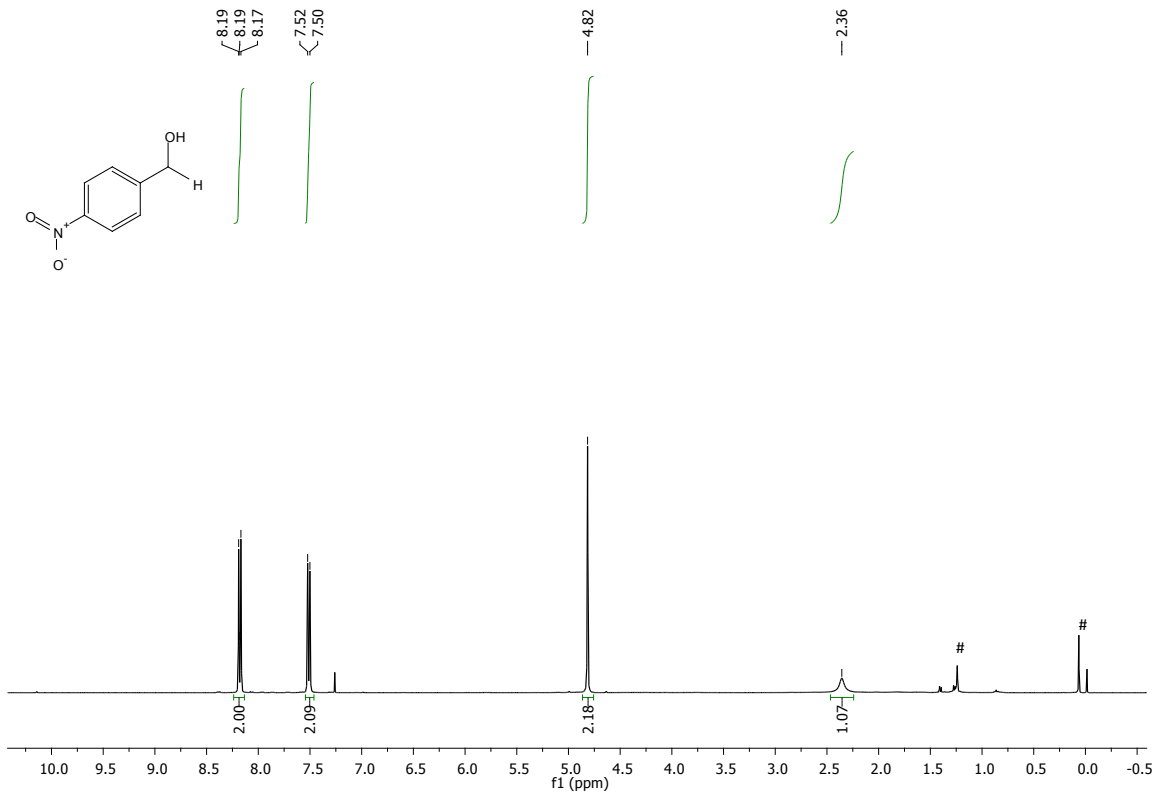


^{1}H NMR of **14b** (400 MHz, $CDCl_3$)

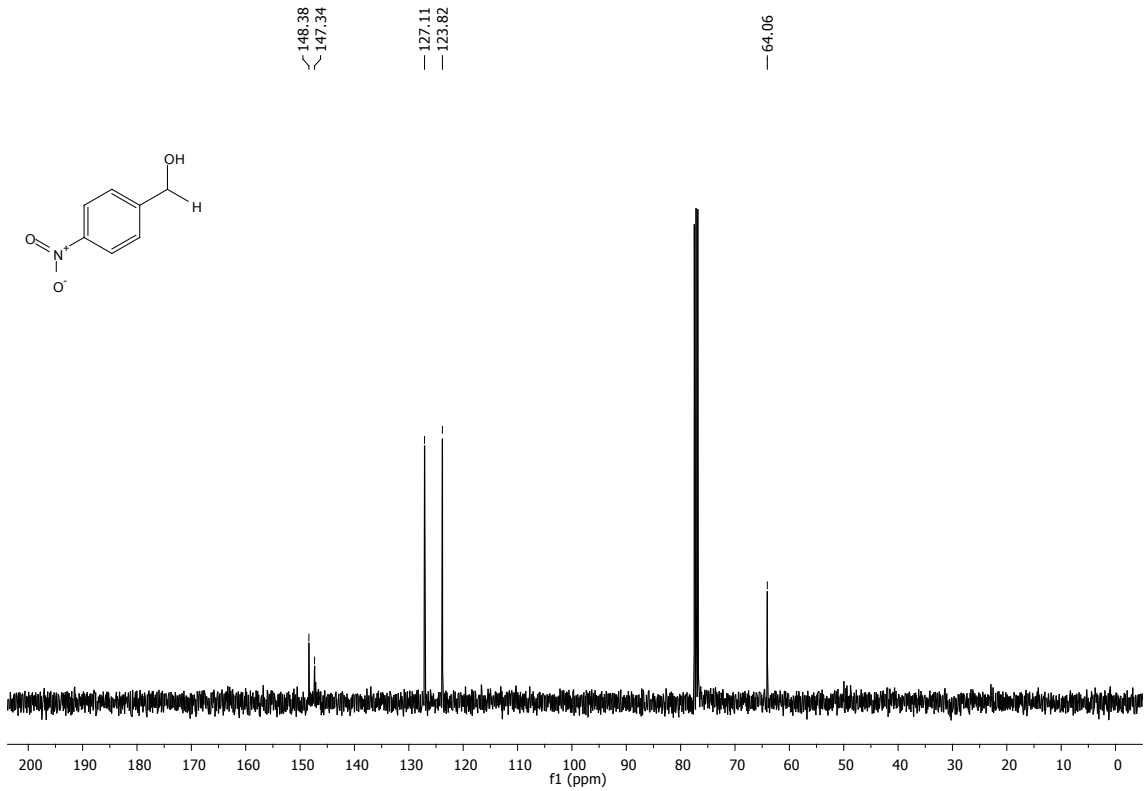


^{11}B NMR of **14b** (128 MHz, $CDCl_3$)

(4-Nitrophenyl)methanol (Table 2, 14c)[11]

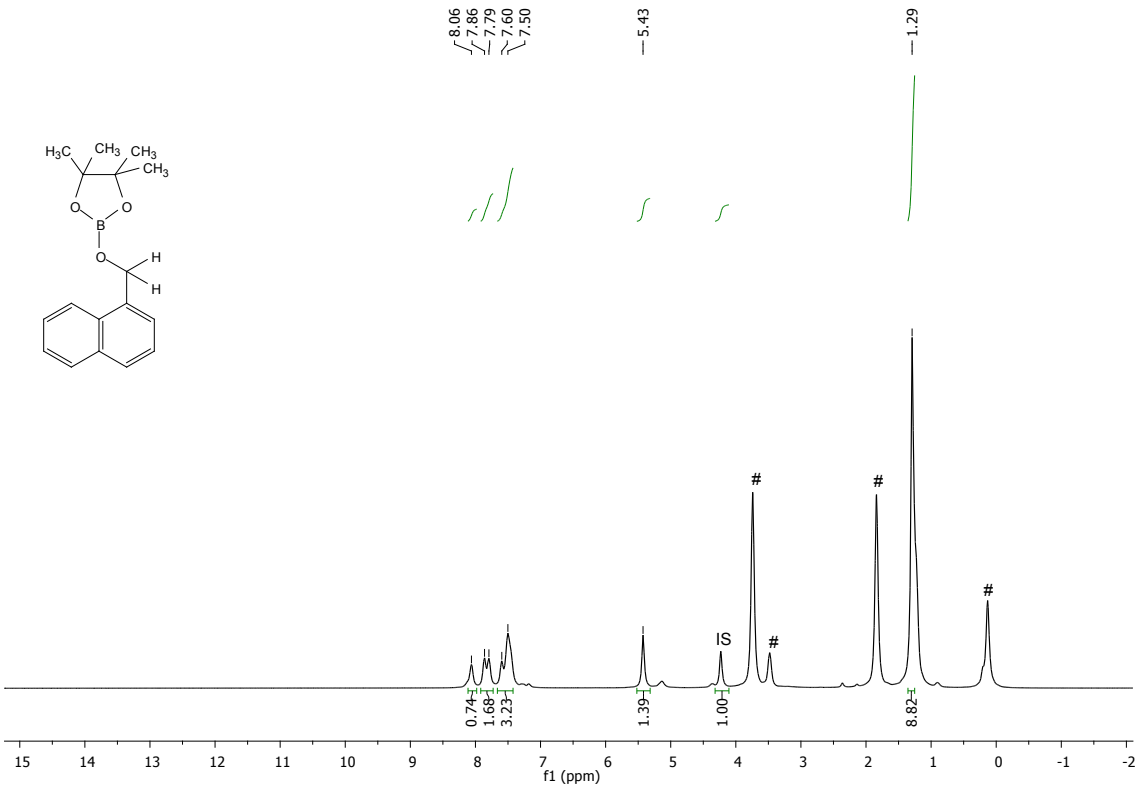


^{1}H NMR of **14c** (400 MHz, $CDCl_3$)

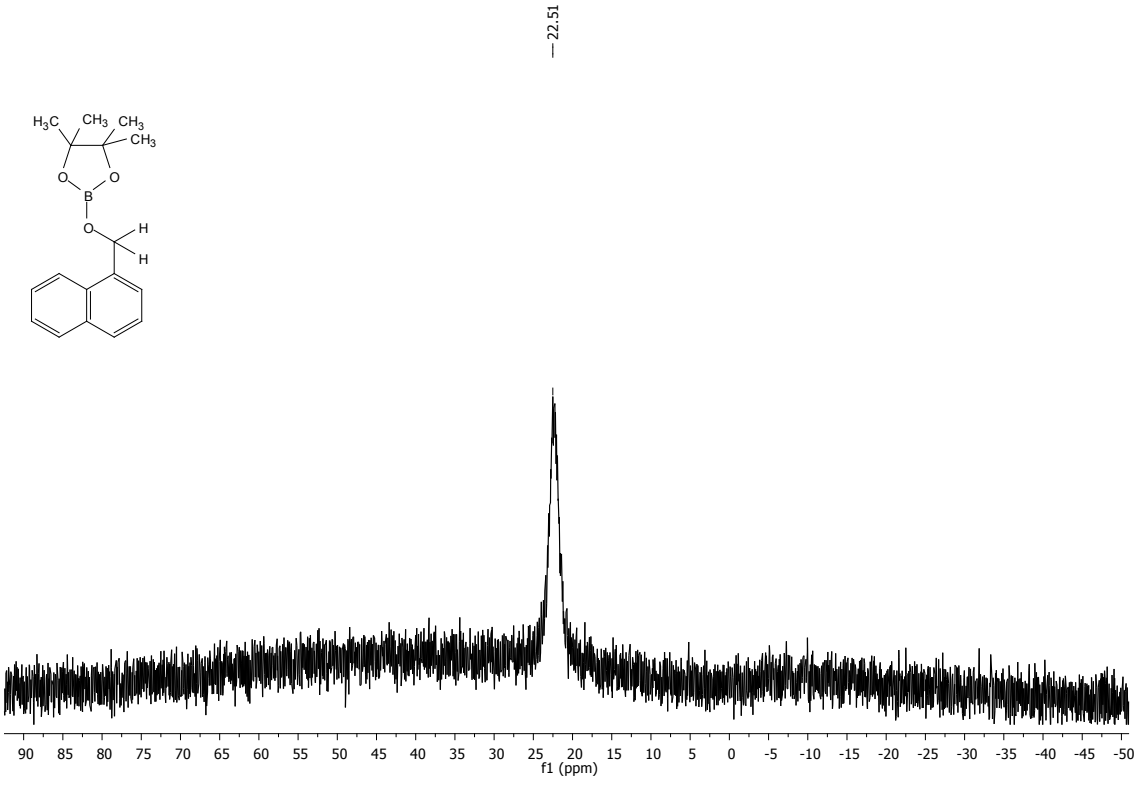


^{13}C NMR of **14c** (100 MHz, $CDCl_3$)

4,4,5,5-Tetramethyl-2-(naphthalen-1-ylmethoxy)-1,3,2-dioxaborolane (Table 2, 15b).[4]

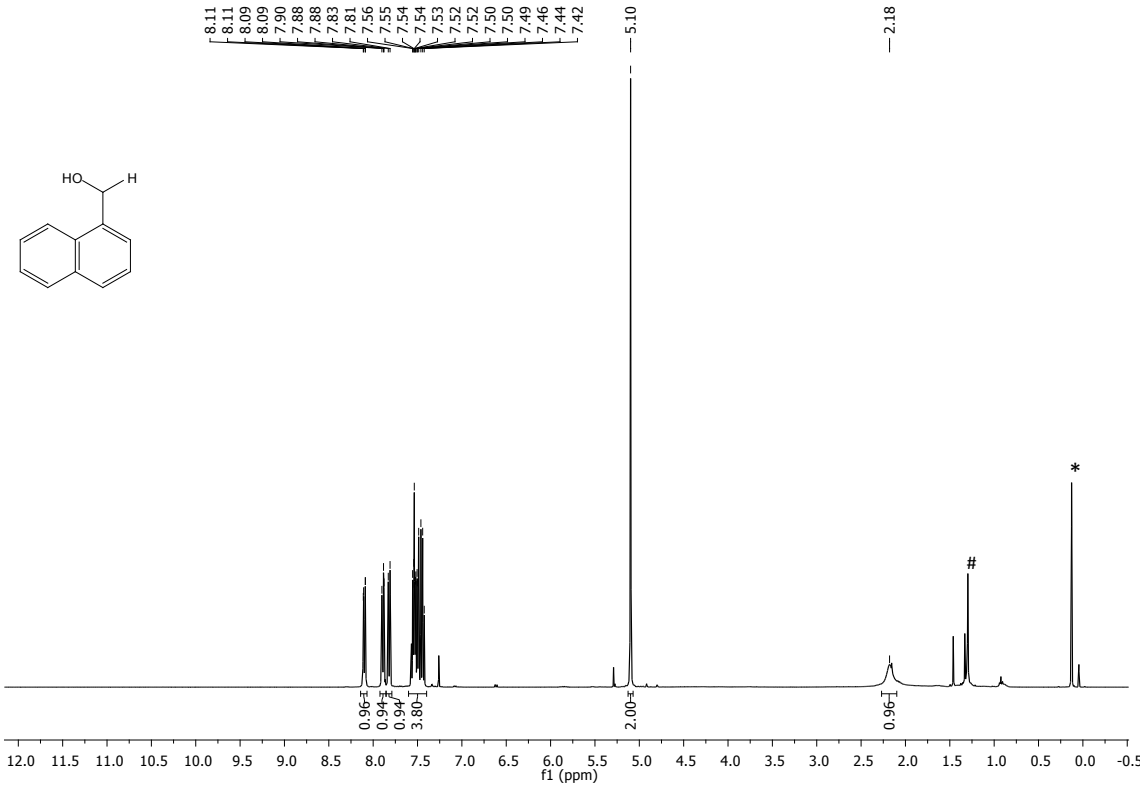


^{1}H NMR of **15b** (400 MHz, $CDCl_3$)

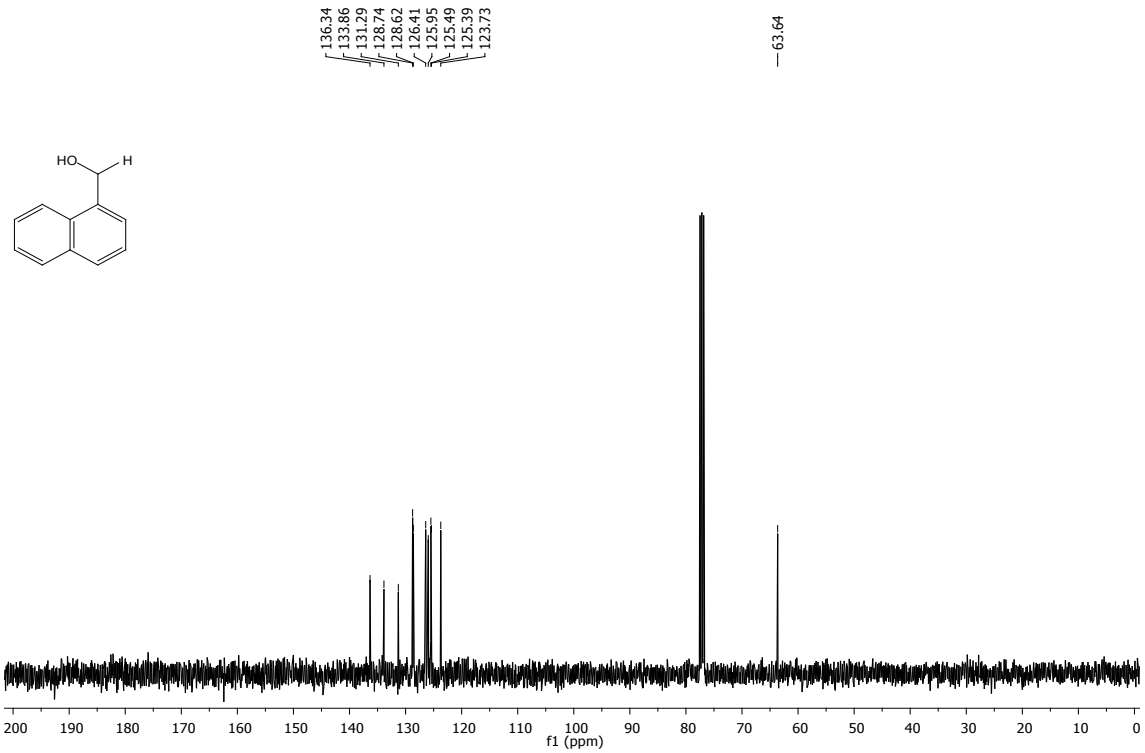


^{11}B NMR of **15b** (128 MHz, $CDCl_3$)

Naphthalen-2-ylmethanol (Table 2, 15c):[12]

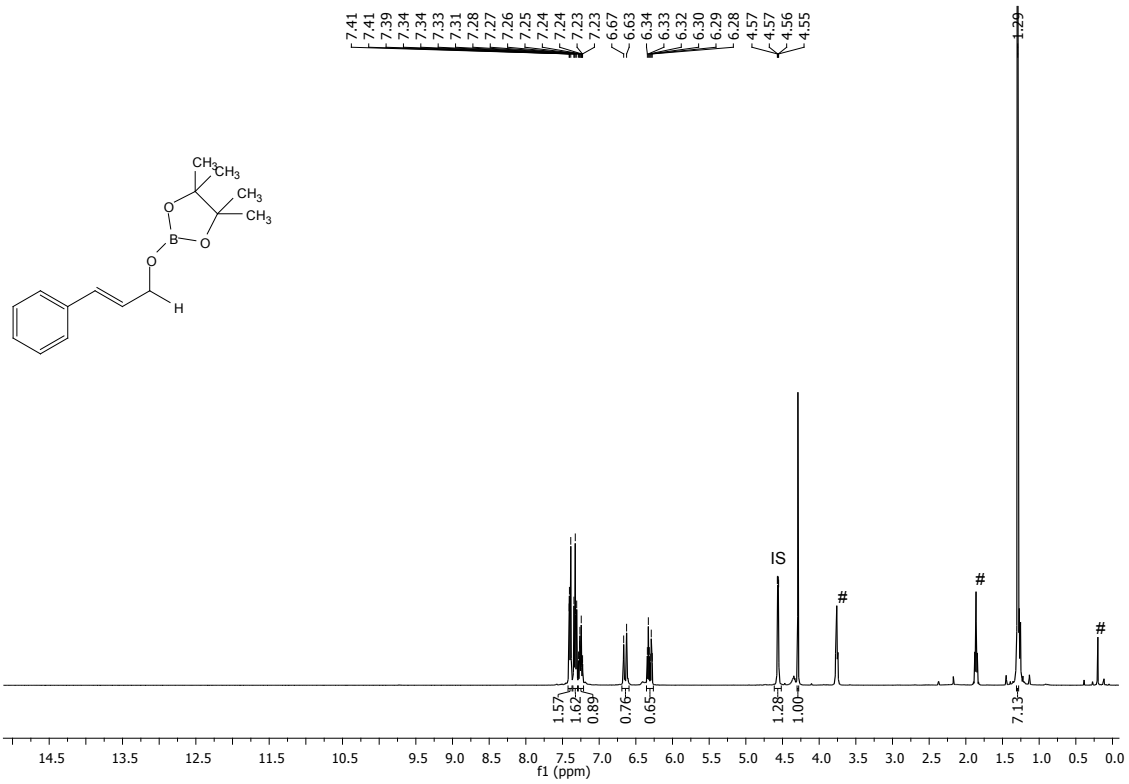


^{1}H NMR of **15c** (400 MHz, $CDCl_3$)

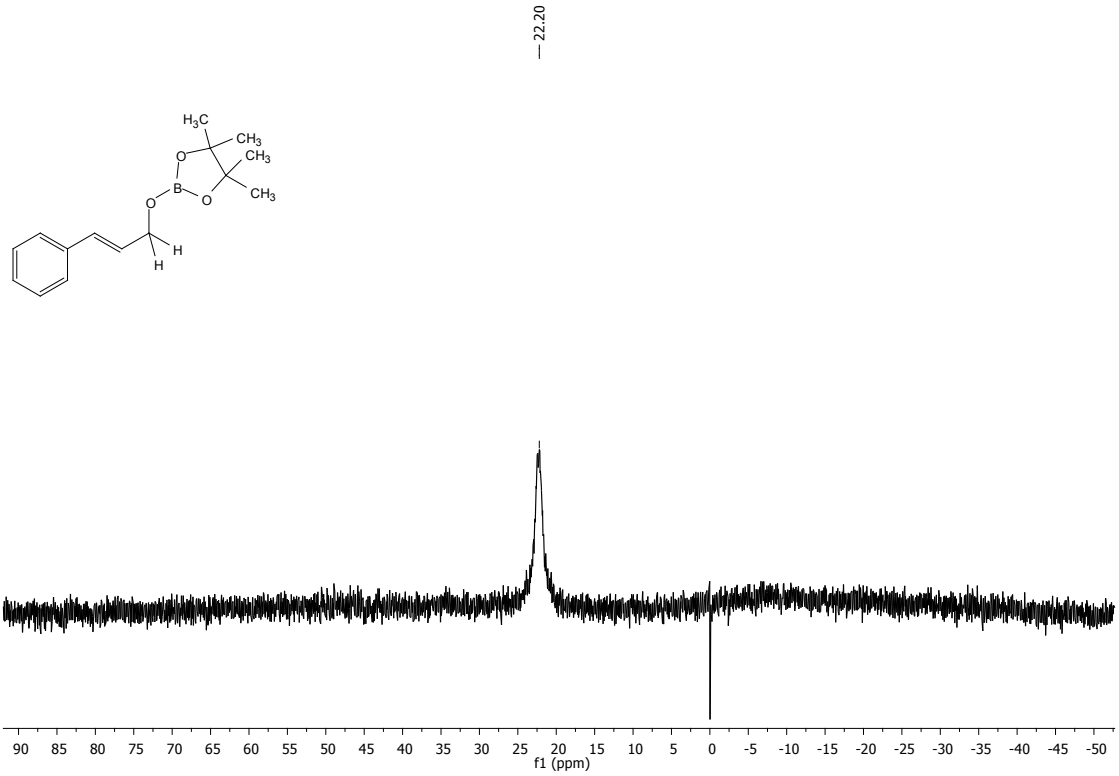


^{13}CNMR of **15c** (100 MHz, $CDCl_3$)

2-(Cinnamyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 16b).[9]

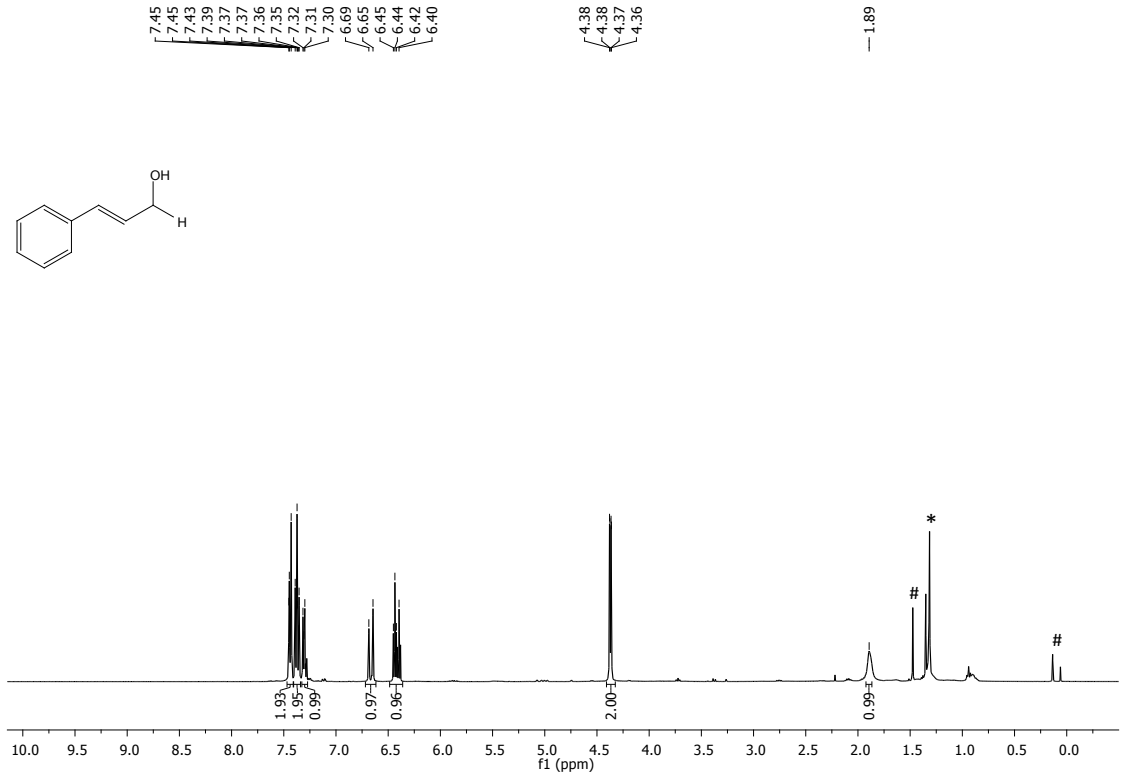


^{1}H NMR of **16b** (400 MHz, $CDCl_3$)

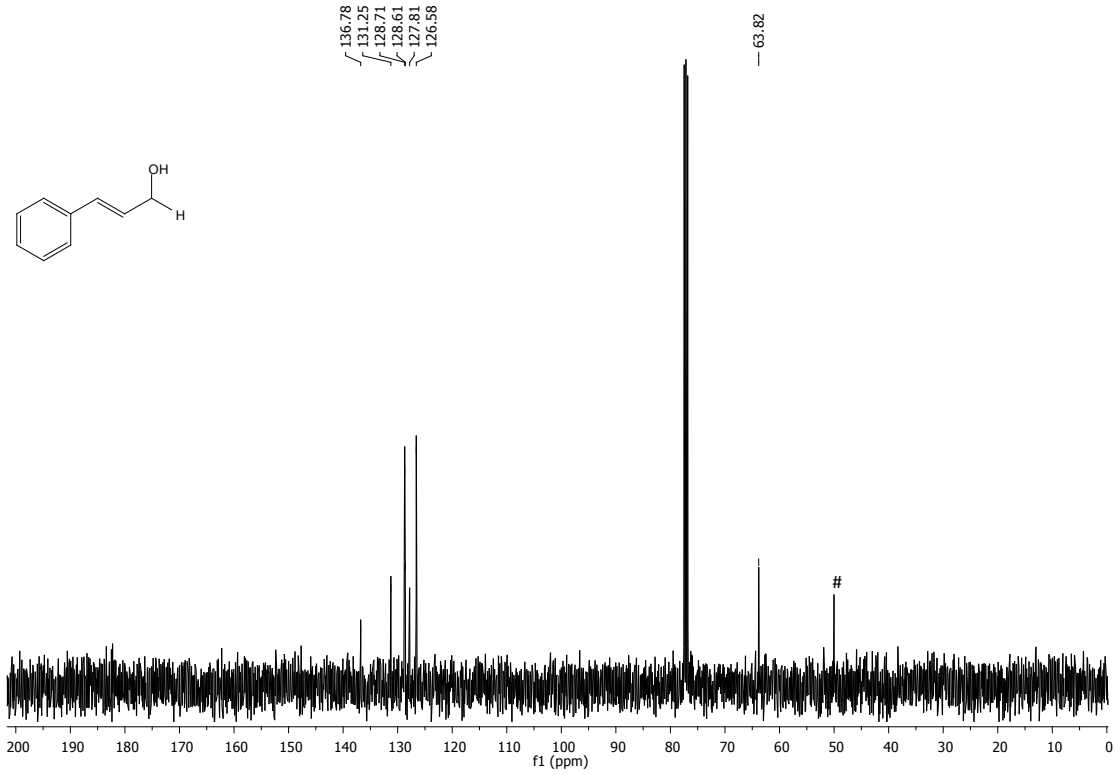


^{11}B NMR of **16b** (128 MHz, $CDCl_3$)

3-Phenyl-2-propene-1-ol (Table 2, 16c)[12]

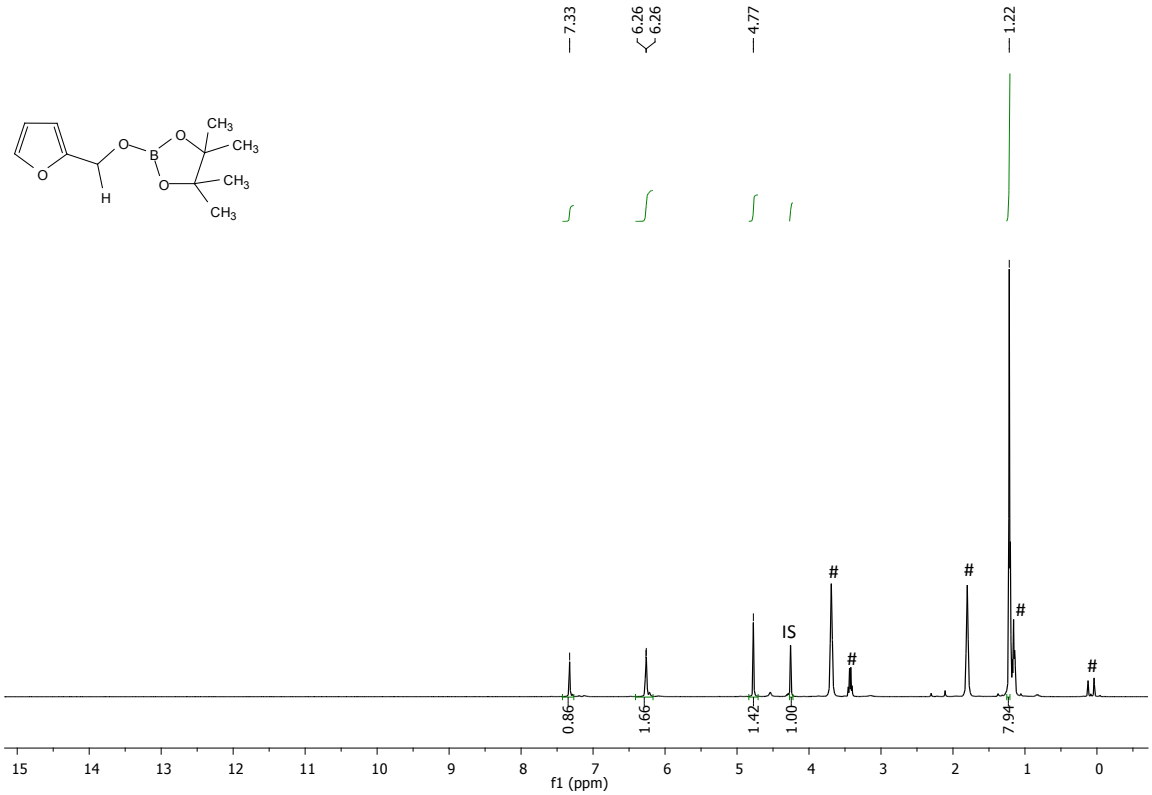


^{1}H NMR of **16c** (400 MHz, $CDCl_3$)

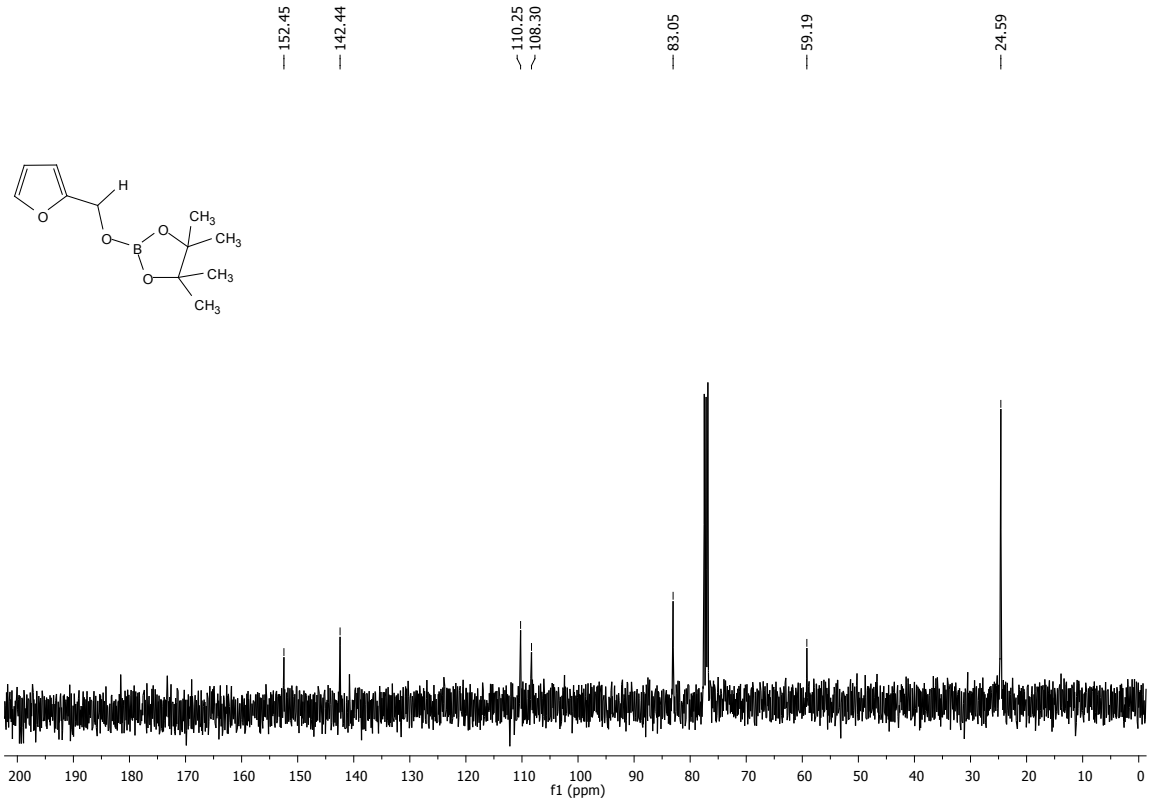


^{13}CNMR of **16c** (100 MHz, $CDCl_3$)

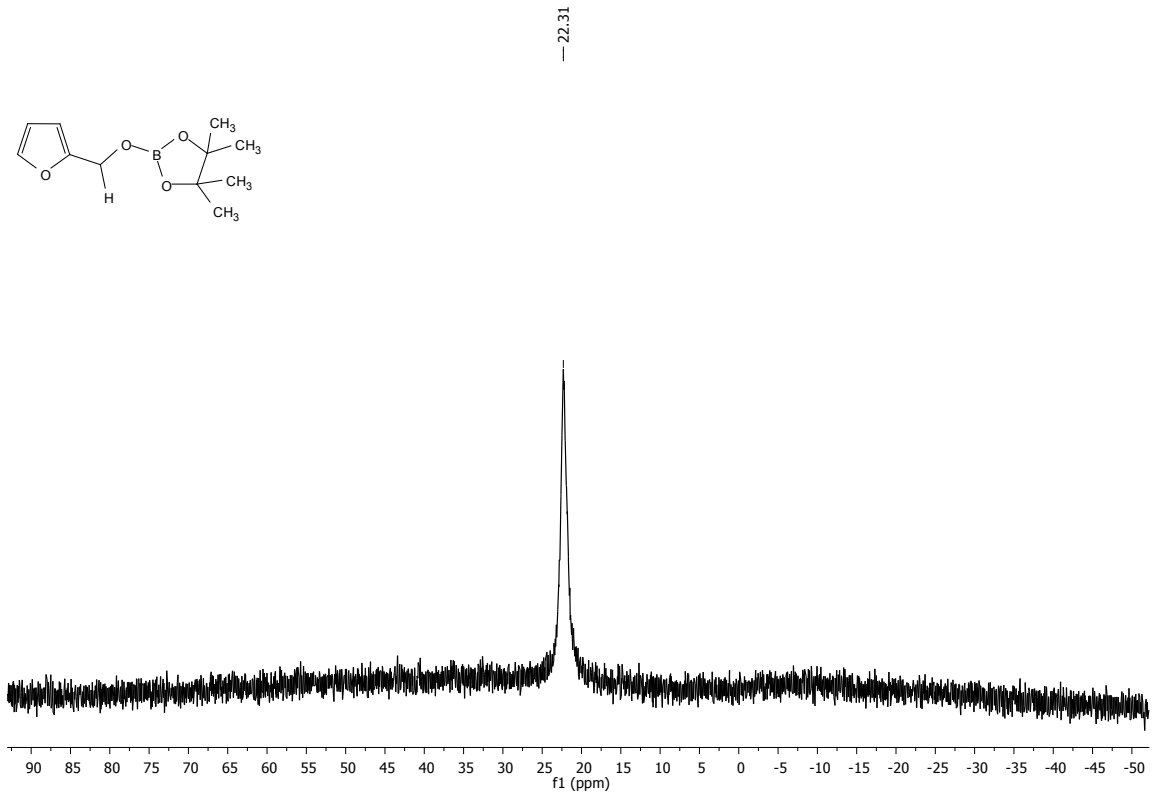
2-(Furan-2-ylmethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 17b).[9]



^{1}H NMR of **17b** (400 MHz, $CDCl_3$)

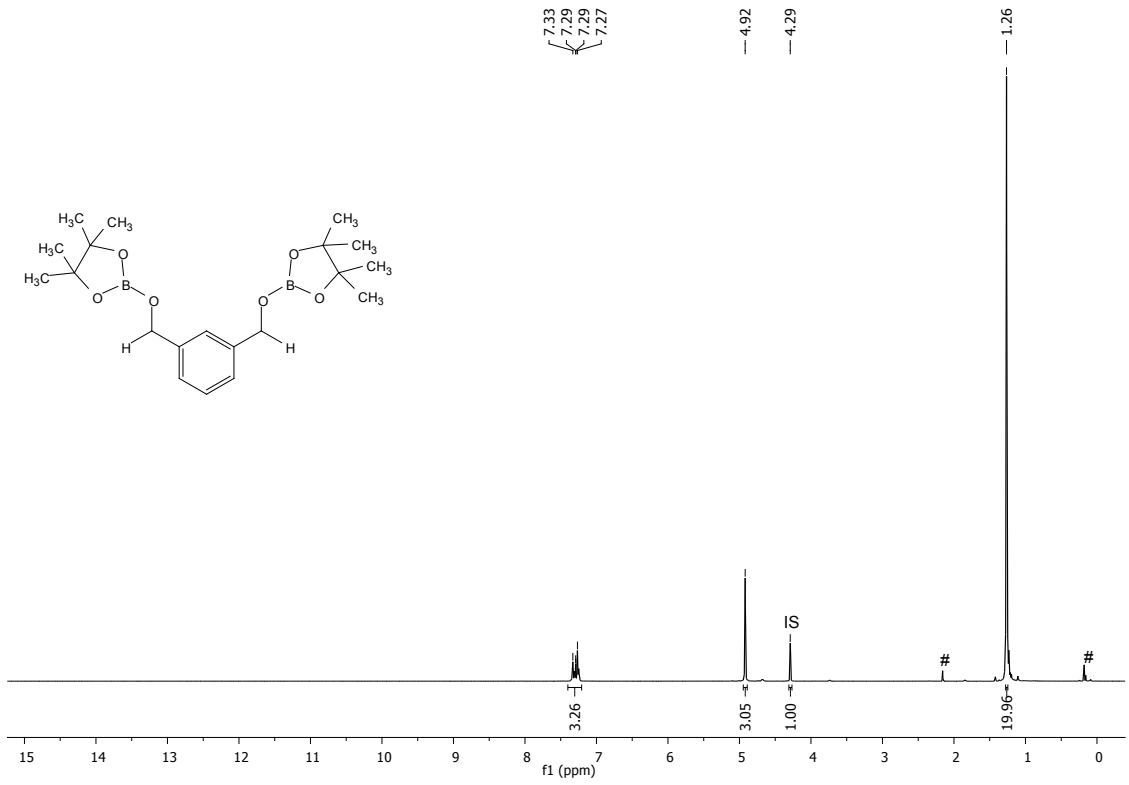


^{13}C NMR of **17b** (100 MHz, $CDCl_3$)

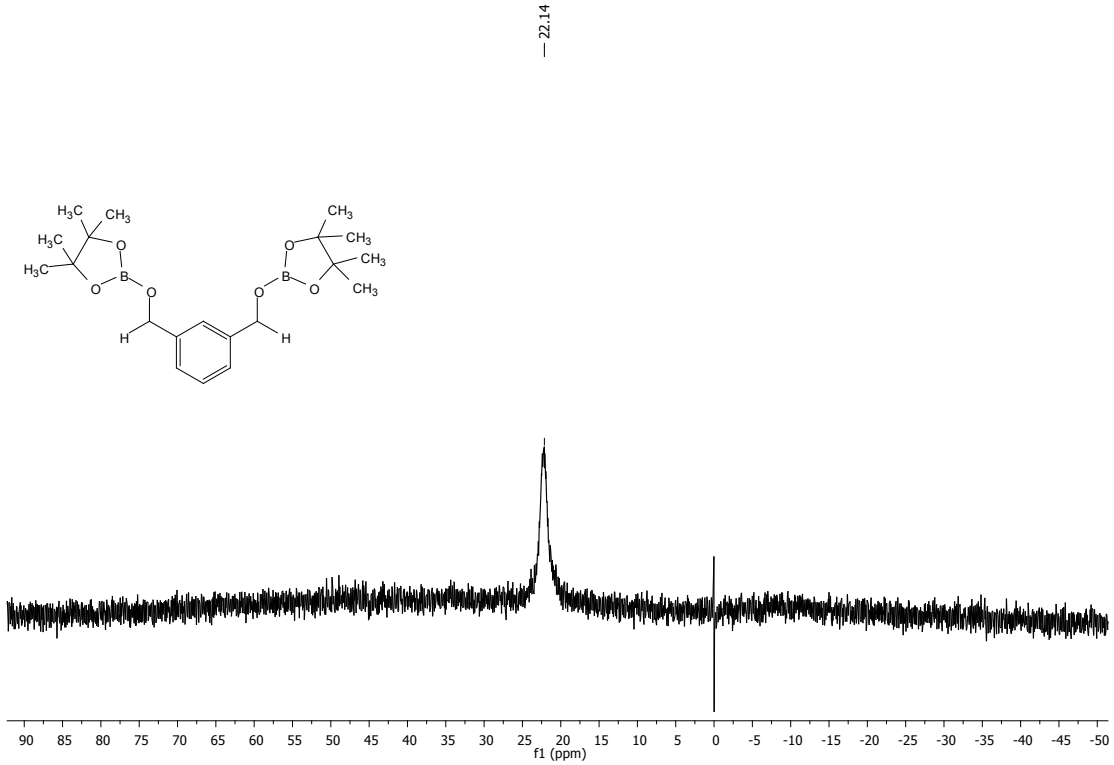


^{11}B NMR of **17b** (128 MHz, $CDCl_3$)

1,3-bis(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzene (Table 2, 18b).[4]

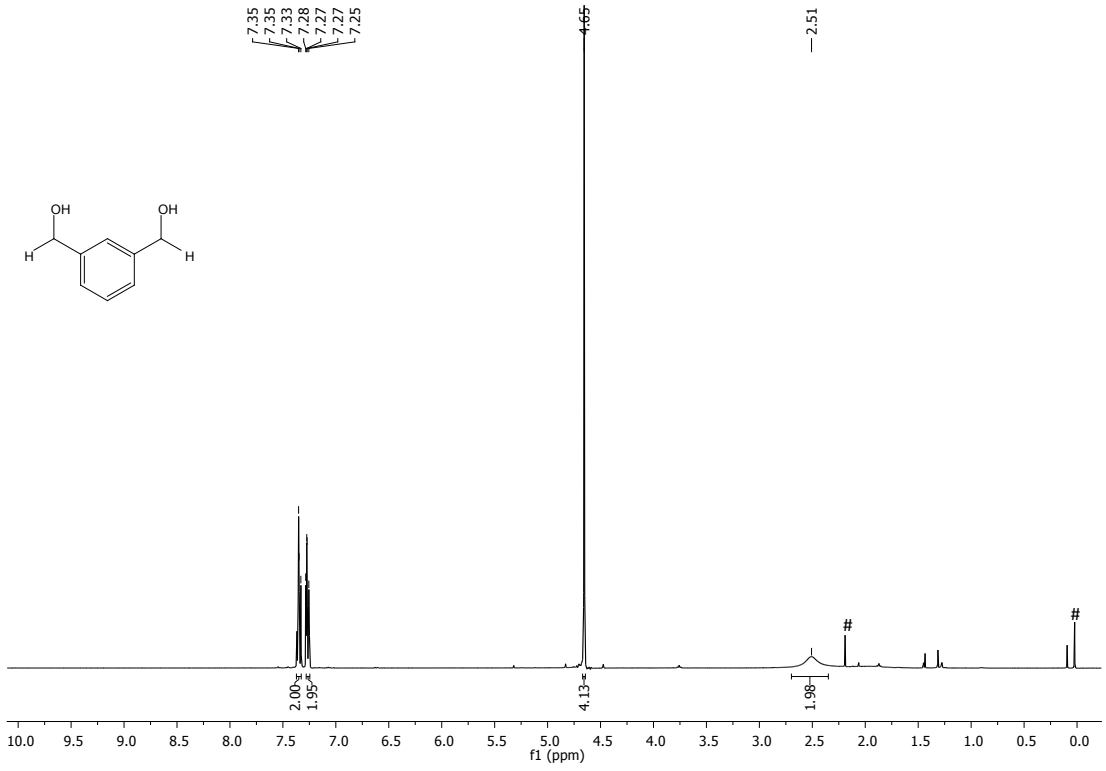


^{1}H NMR of **18b** (400 MHz, $CDCl_3$)

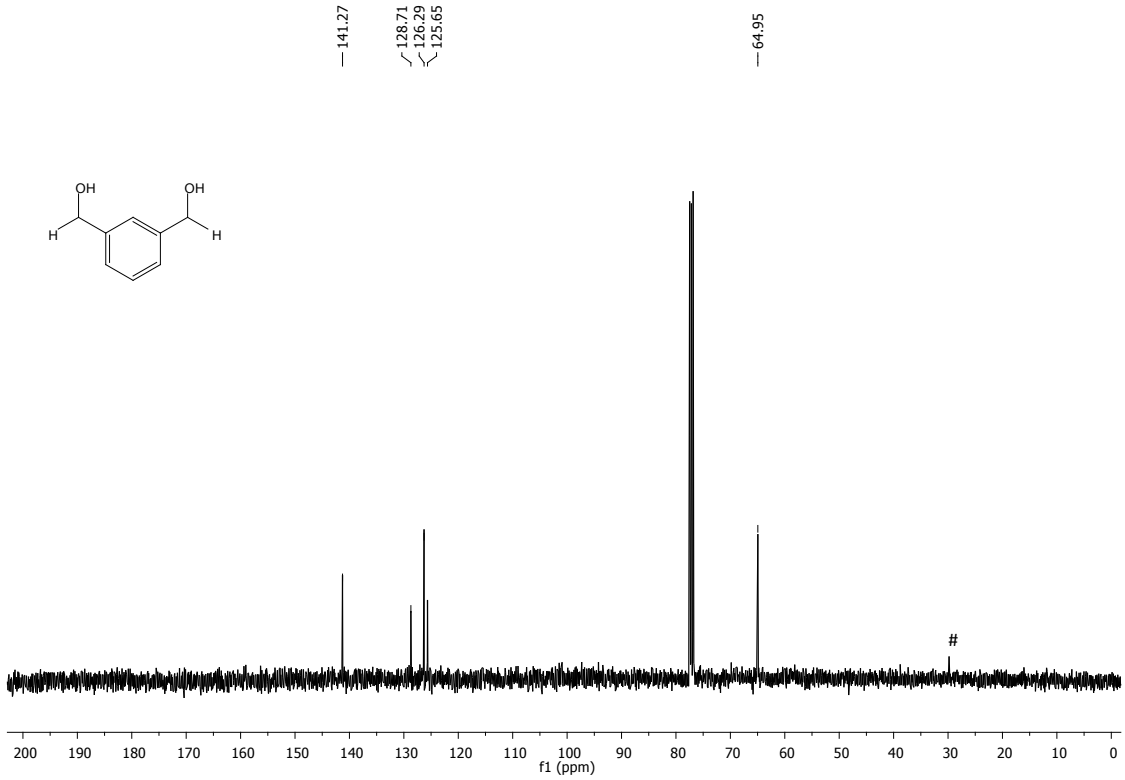


^{11}B NMR of **18b** (128 MHz, $CDCl_3$)

1,3-Phenylenedimethanol (Table 2, 18c).[13]

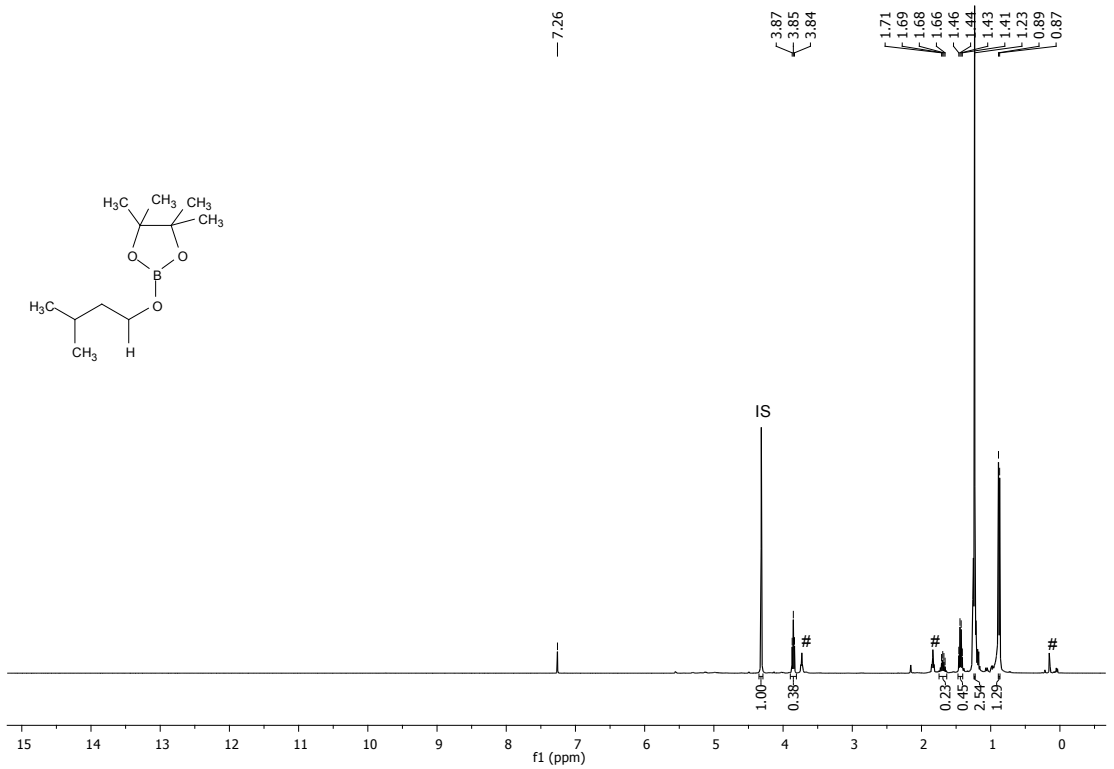


^{1}H NMR of **18c** (400 MHz, $CDCl_3$)

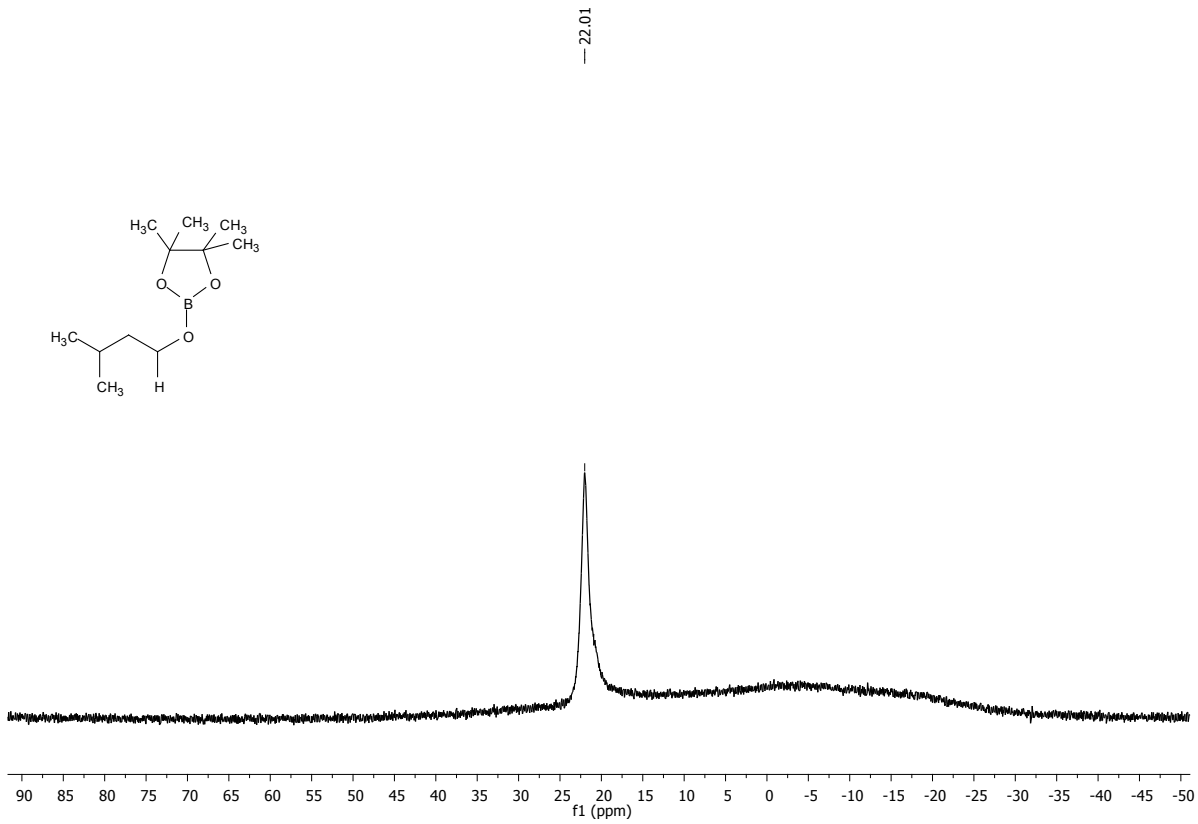


^{13}C NMR of **18c** (100 MHz, $CDCl_3$)

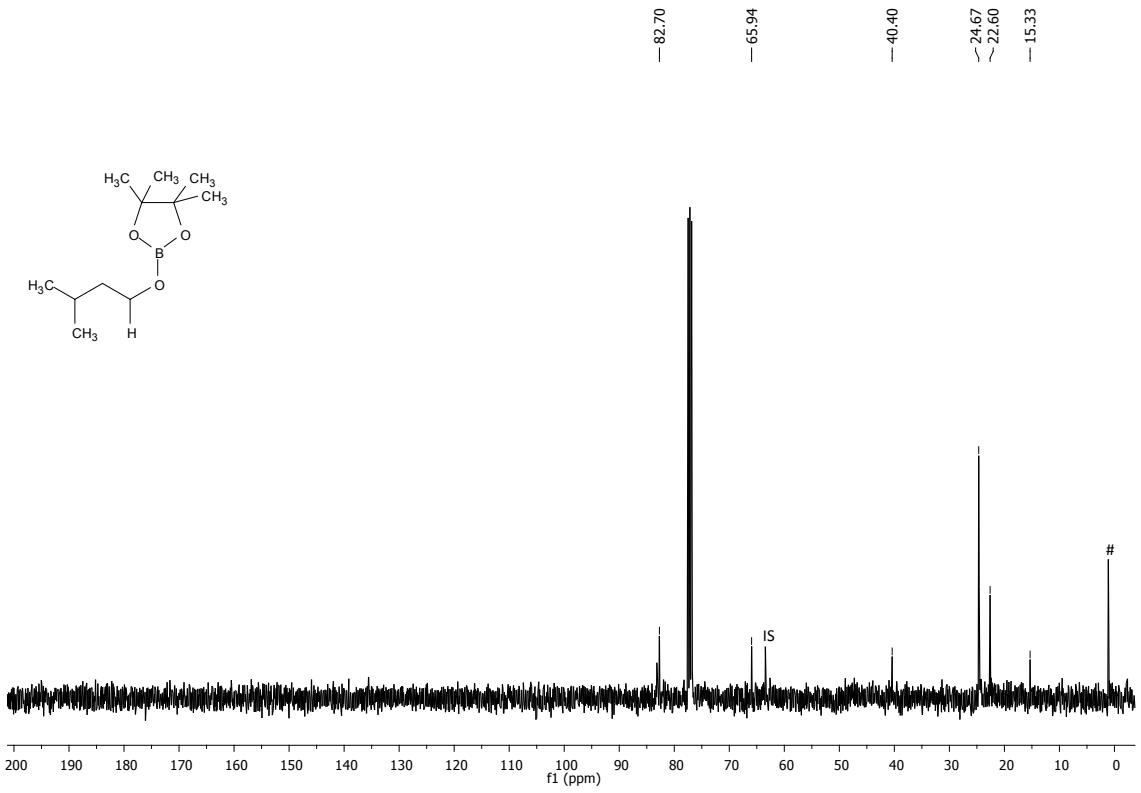
2-(Isopentyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 19b).[6]



^{1}H NMR of **19b** (400 MHz, $CDCl_3$)

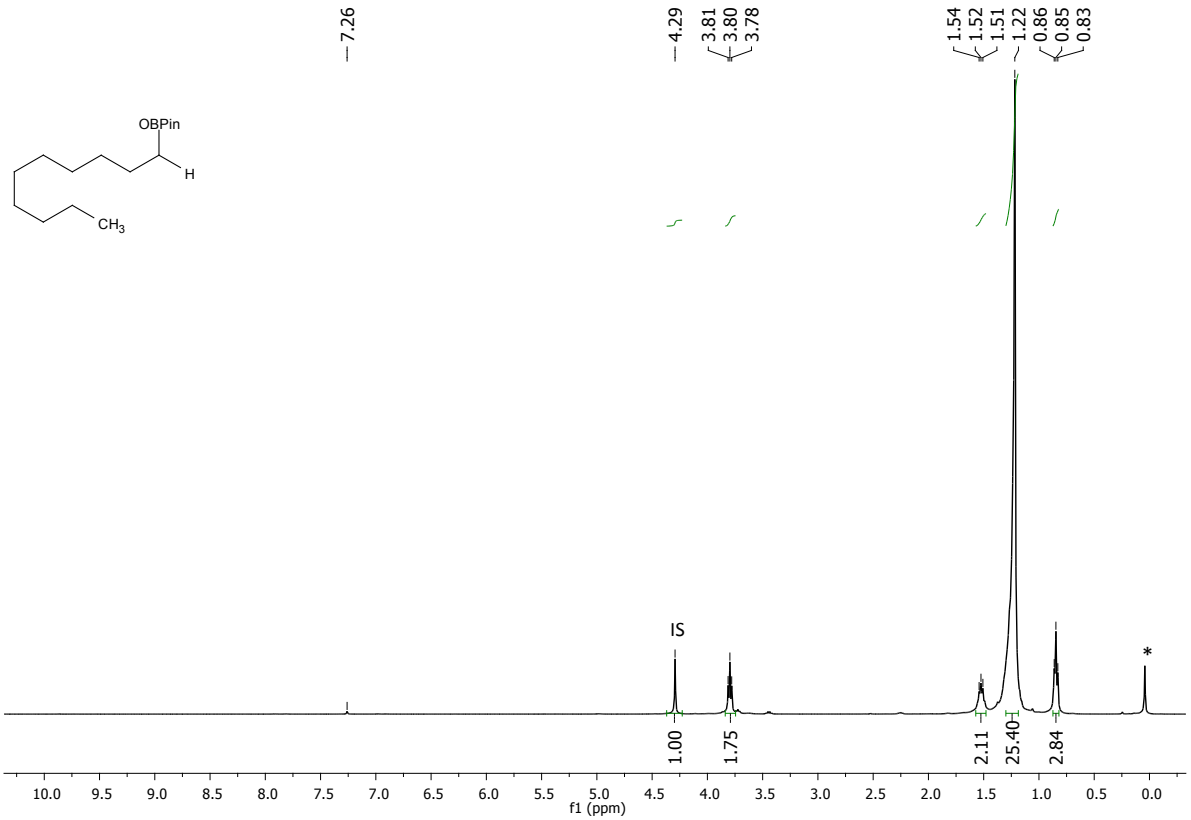


^{11}B NMR of **19b** (128 MHz, $CDCl_3$)

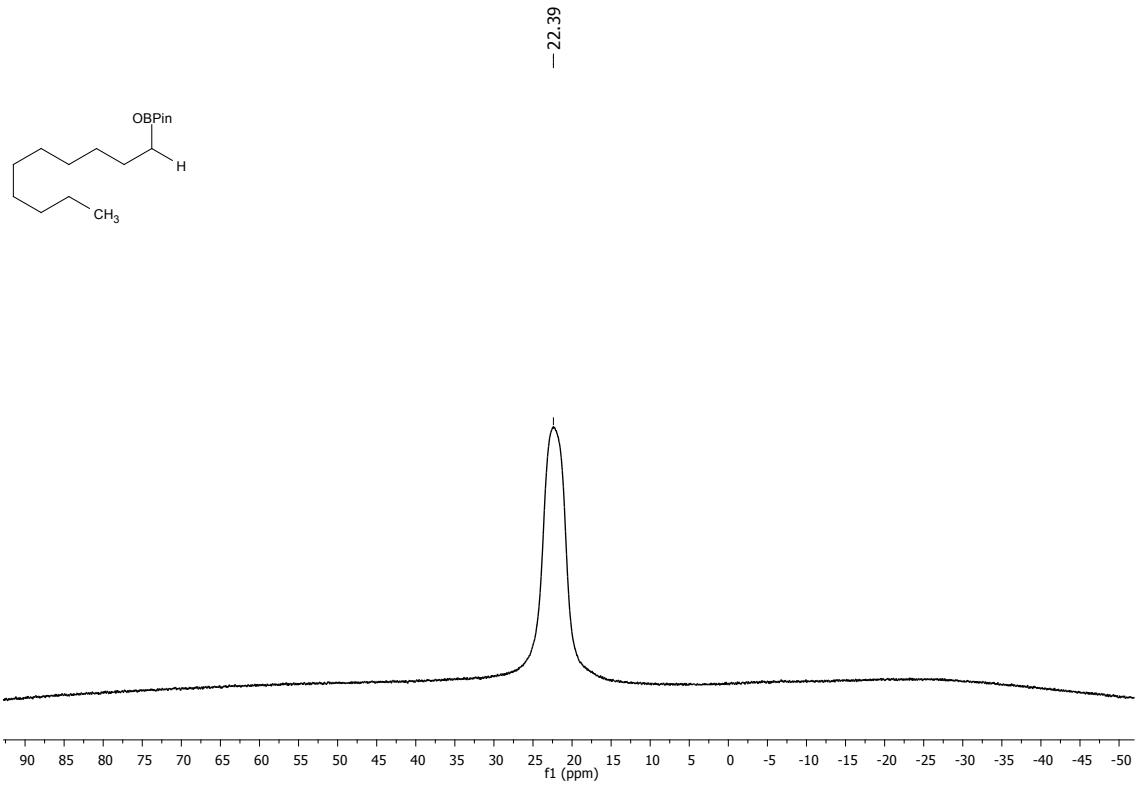


^{13}C NMR of **19b** (100 MHz, $CDCl_3$)

2-(decyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 20b).[5]

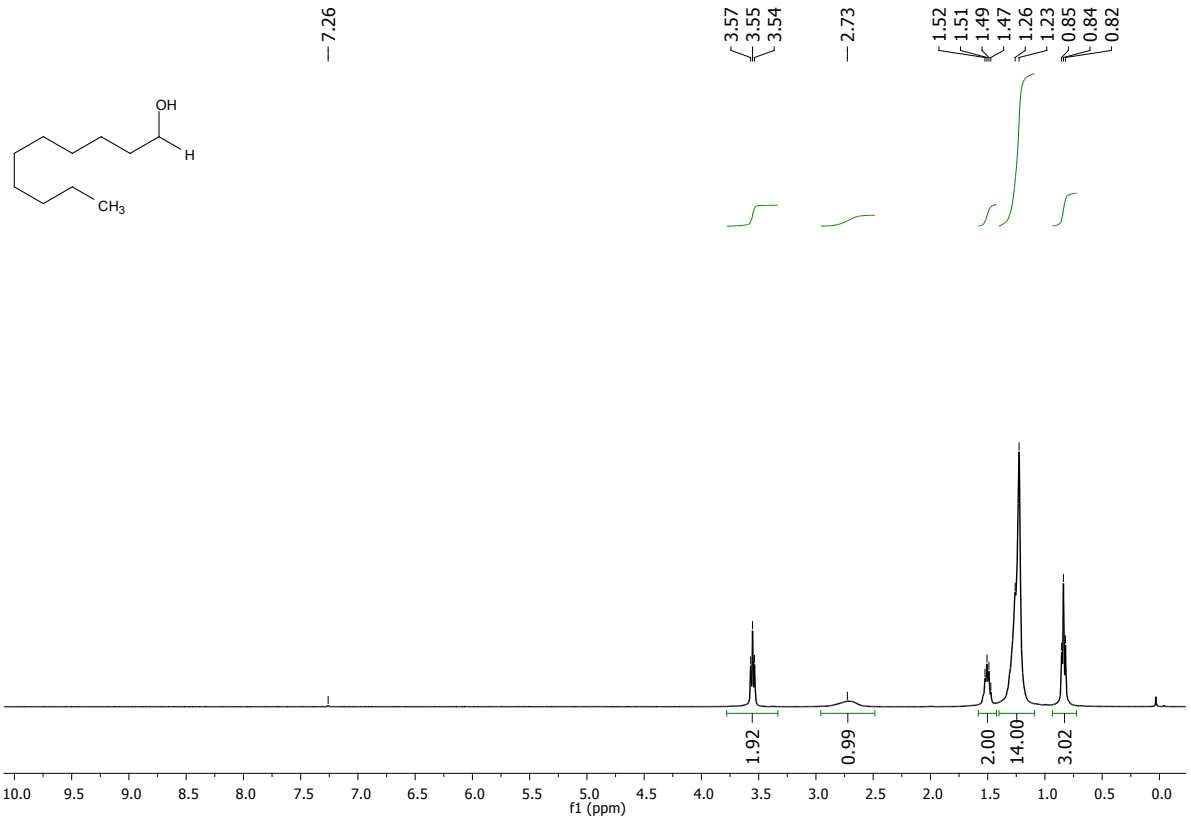


^{1}H NMR of **20b** (400 MHz, $CDCl_3$)

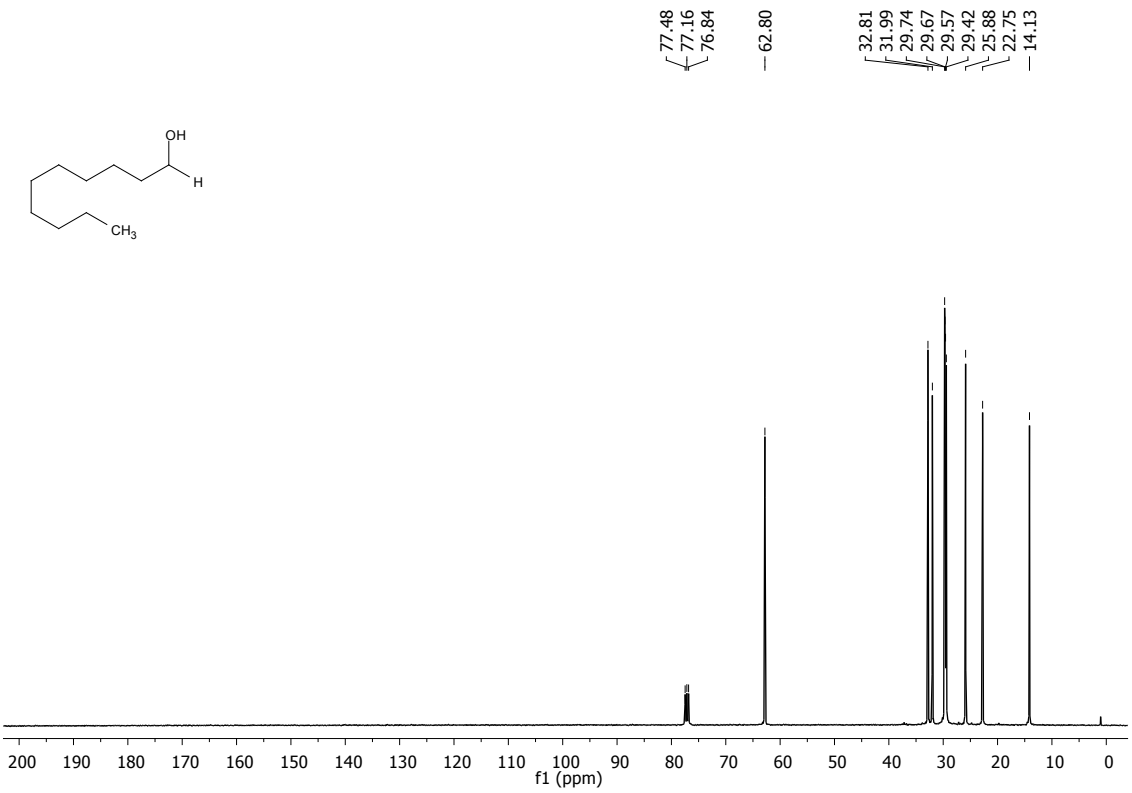


^{11}B NMR of **20b** (128 MHz, $CDCl_3$)

Decan-1-ol (Table 2, 20c) [5]

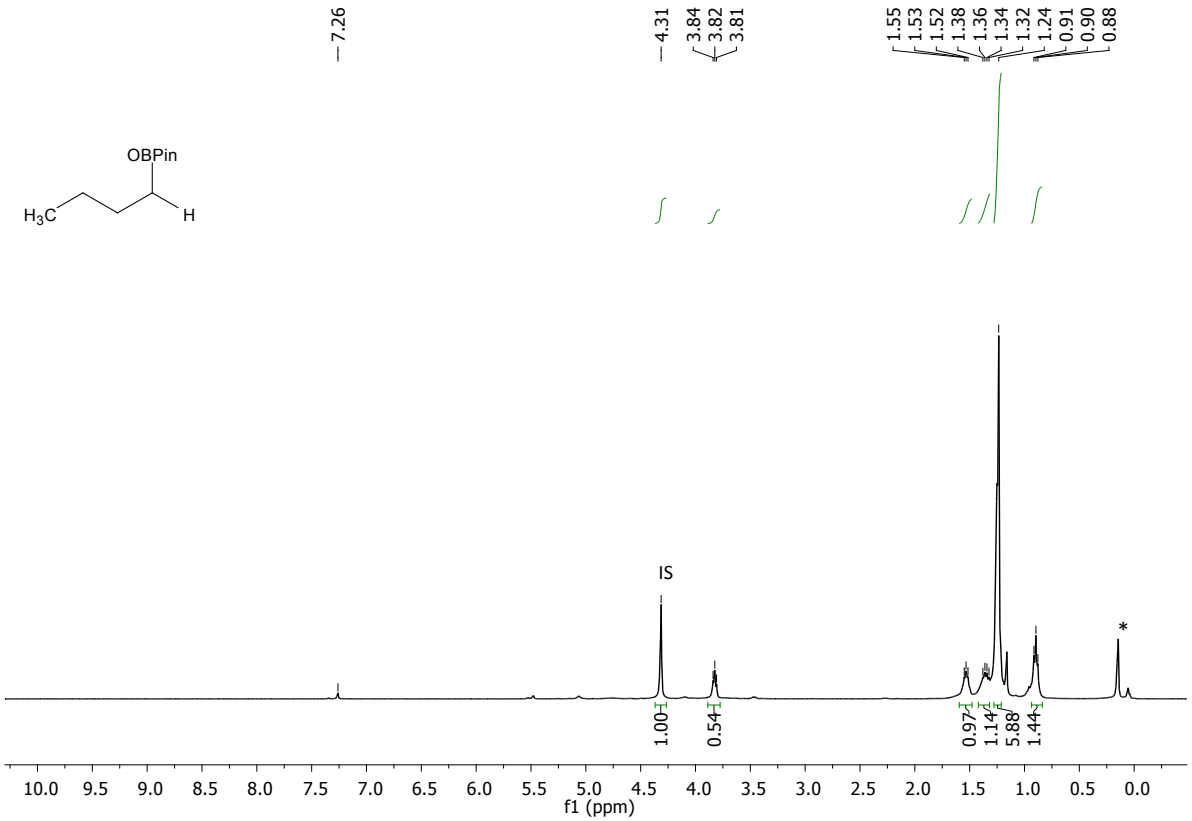


^{1}H NMR of **20c** (400 MHz, $CDCl_3$)

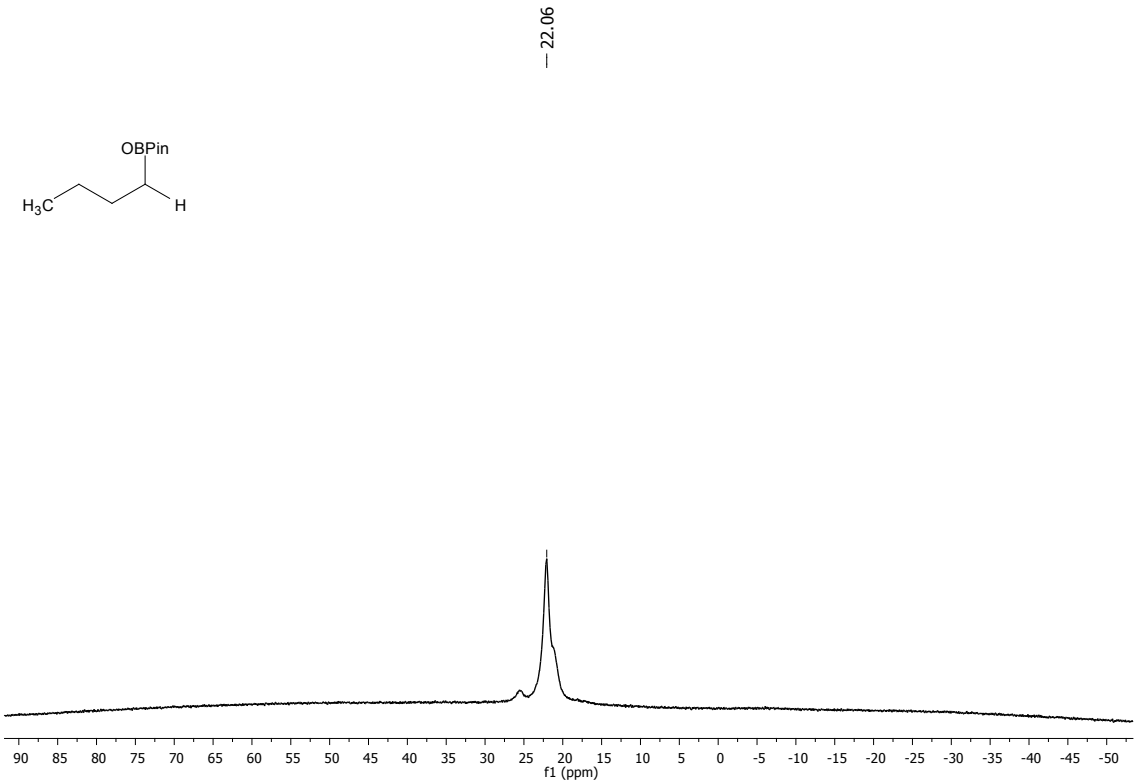


^{13}C NMR of **20c** (100 MHz, $CDCl_3$)

2-butoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 21b).[5]

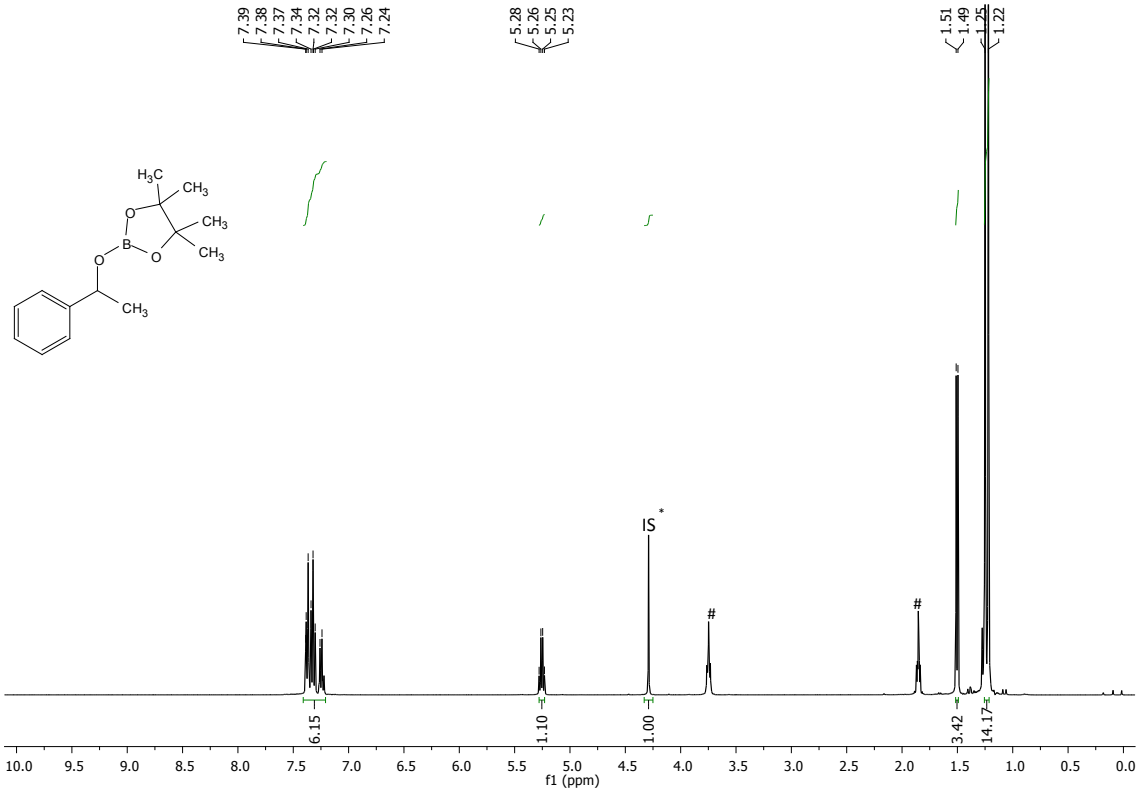


^{1}H NMR of **21b** (400 MHz, $CDCl_3$)

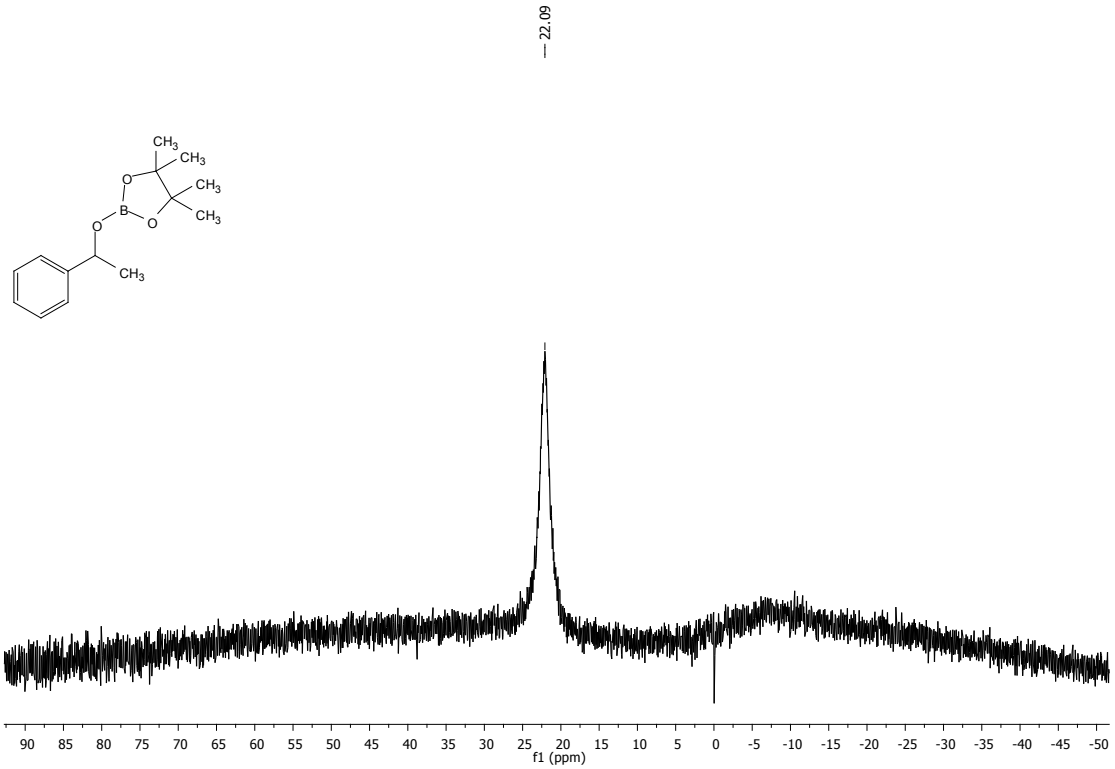


^{11}B NMR of **21b** (128 MHz, $CDCl_3$)

4,4,5,5-Tetramethyl-2-(1-phenylethoxy)-1,3,2-dioxaborolane (Table 3, 22b)[4]

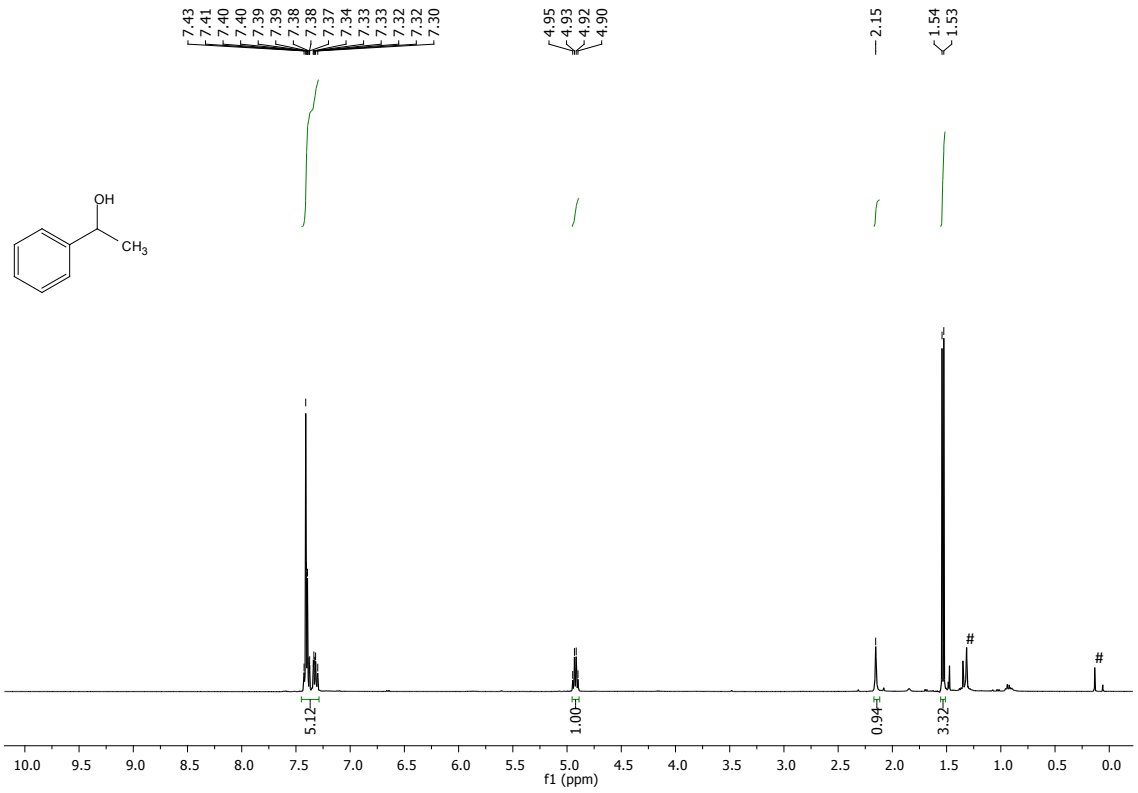


^{1}H NMR of **22b** (400 MHz, $CDCl_3$)

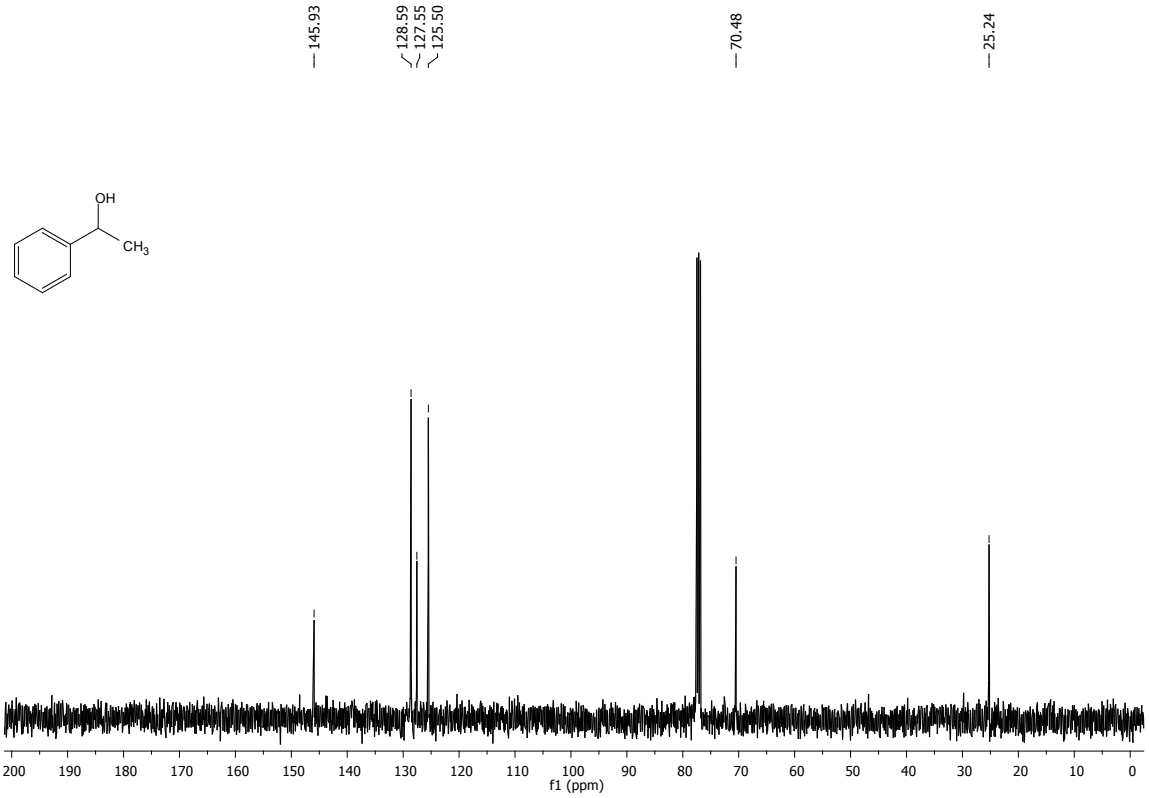


^{11}B NMR of **22b** (128 MHz, $CDCl_3$)

1-Phenylethanol (Table 3, 22c).[5]

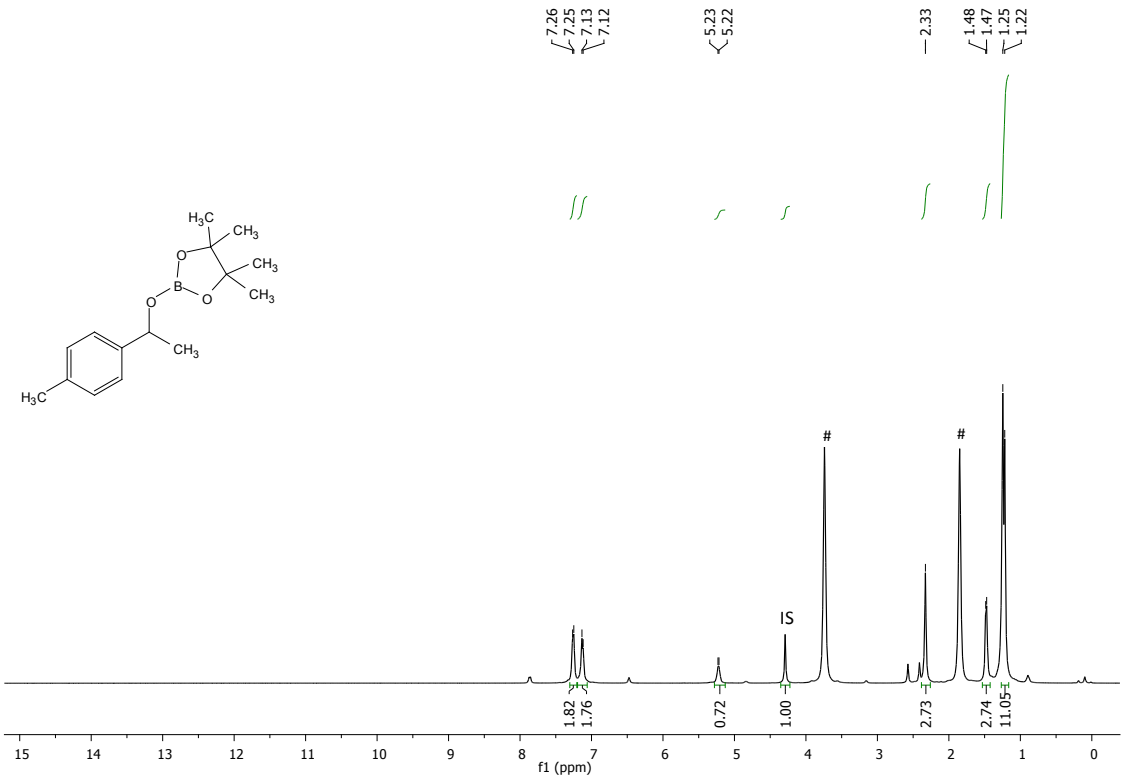


^{1}H NMR of **22c** (400 MHz, $CDCl_3$)

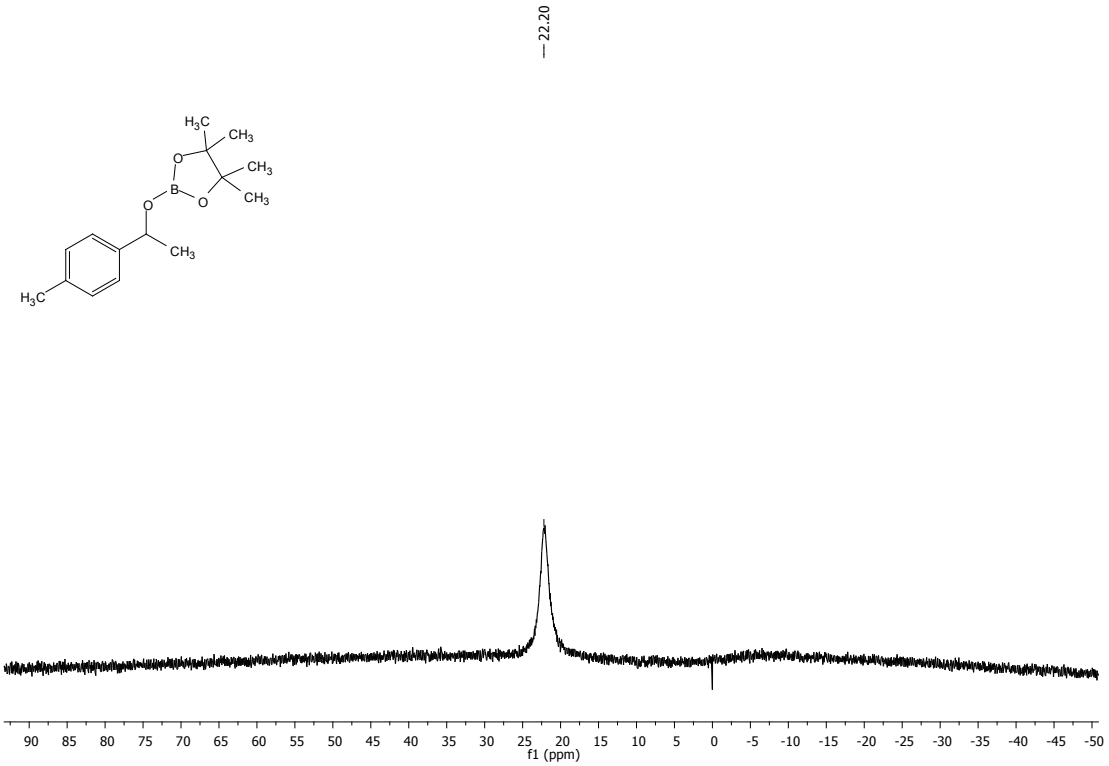


^{13}C NMR of **22c** (100 MHz, $CDCl_3$)

4,4,5,5-Tetramethyl-2-(1-(p-tolyl)ethoxy)-1,3,2-dioxaborolane (Table 3, 23b).[4]

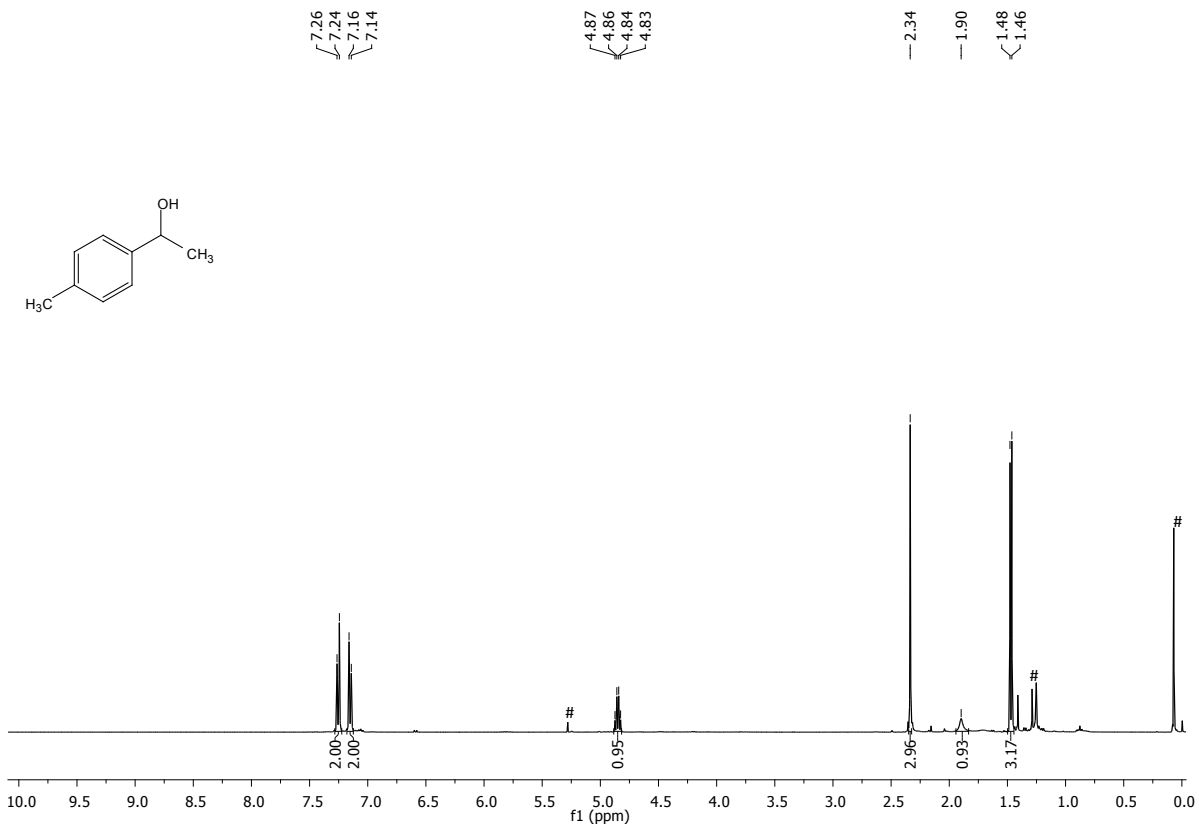


^{1}H NMR of **23b** (400 MHz, $CDCl_3$)

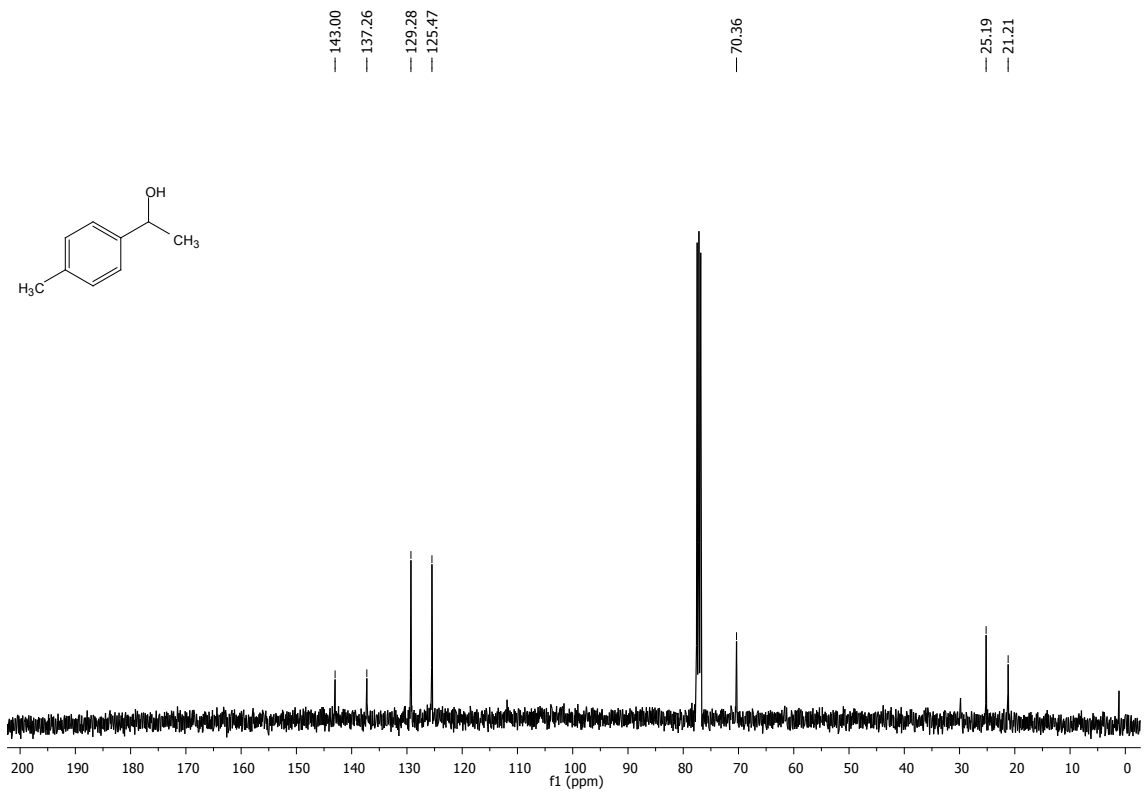


^{11}B NMR of **23b** (128 MHz, $CDCl_3$)

1-(p-Tolyl)ethanol (Table 3, 23c)[5]

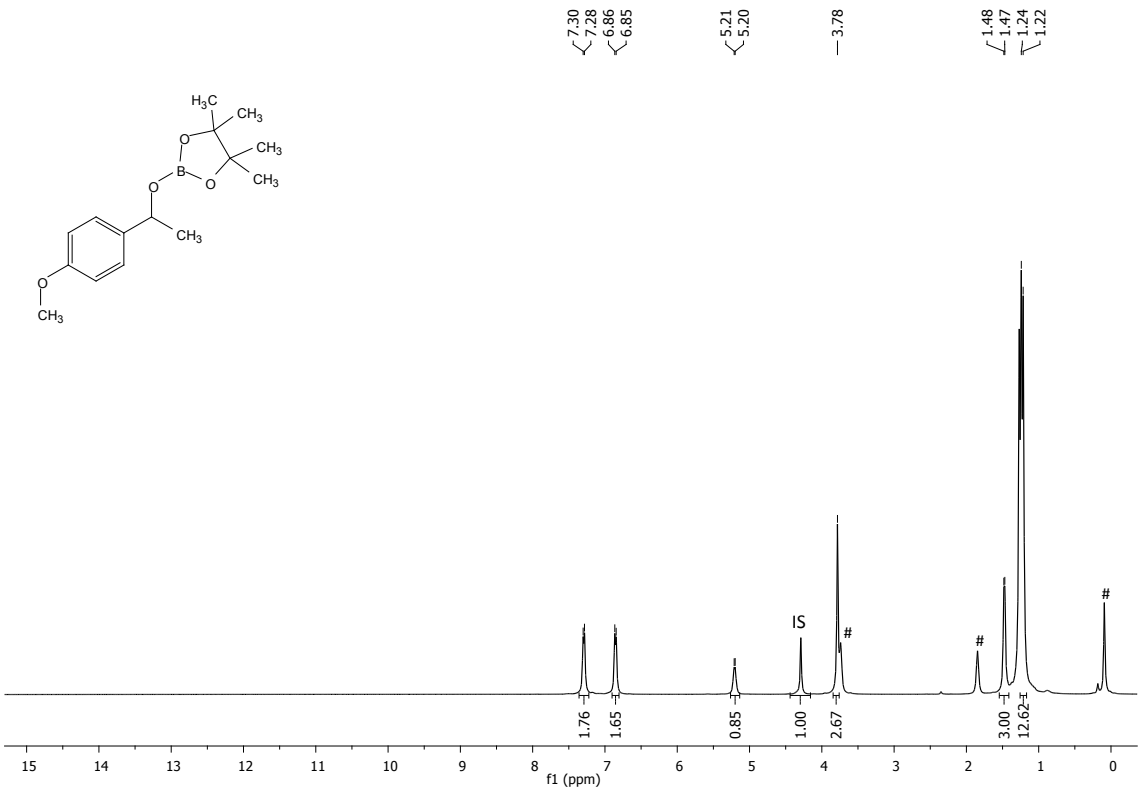


^{1}H NMR of **23c** (400 MHz, $CDCl_3$)

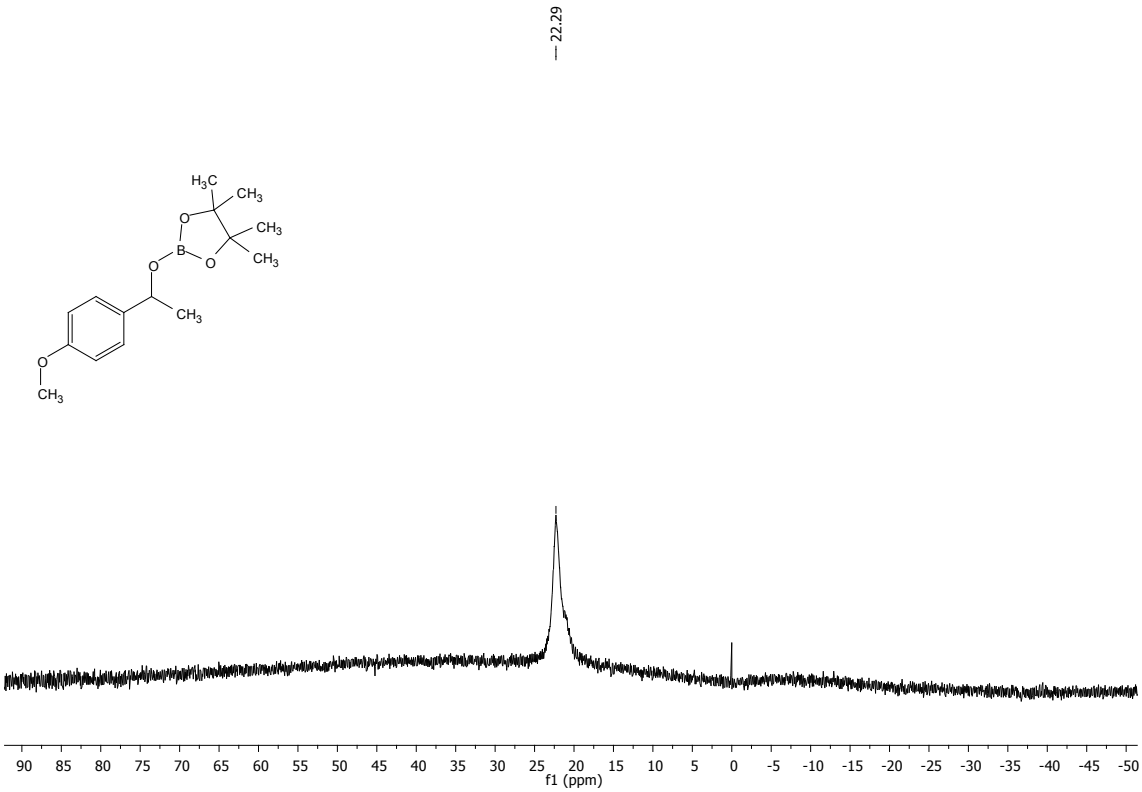


^{13}C NMR of **23c** (100 MHz, $CDCl_3$)

2-(1-(4-Methoxyphenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 24b)[4]

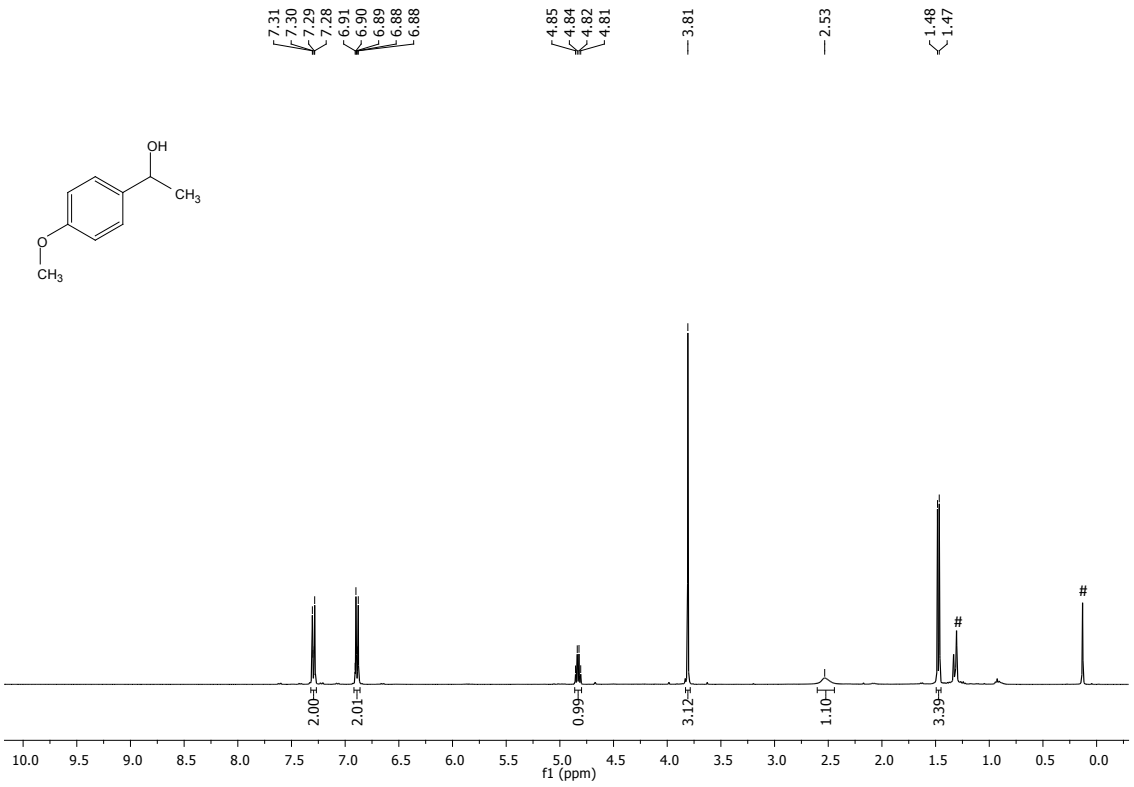


^{1}H NMR of **24b** (400 MHz, $CDCl_3$)

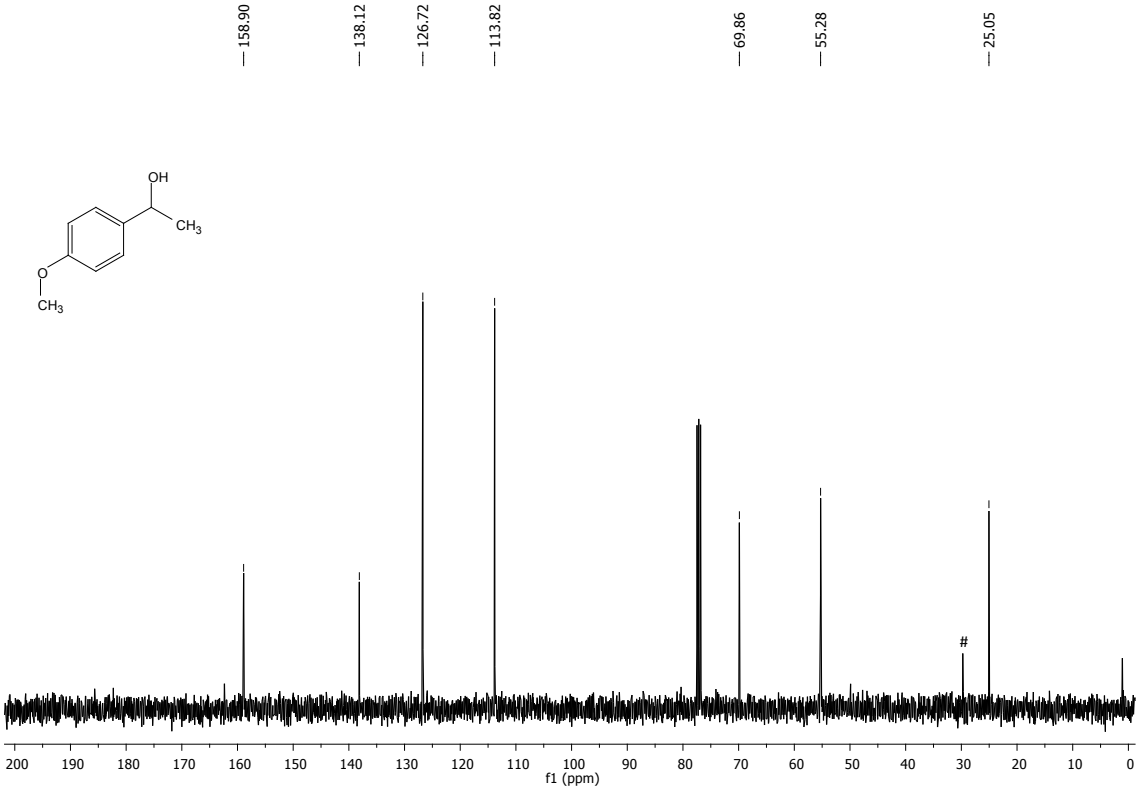


^{11}B NMR of **24b** (128 MHz, $CDCl_3$)

1-(4-Methoxyphenyl)ethanol (Table 3, 24c).[14]

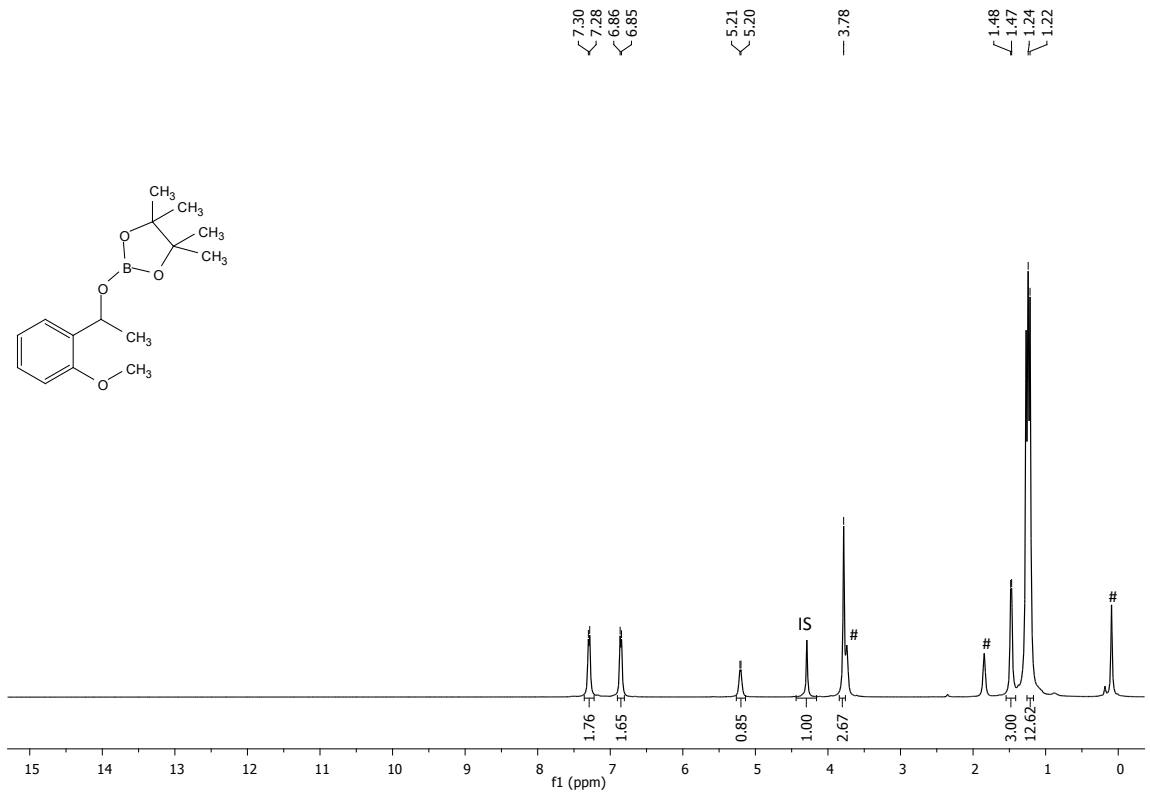


^{1}H NMR of **24c** (400 MHz, $CDCl_3$)

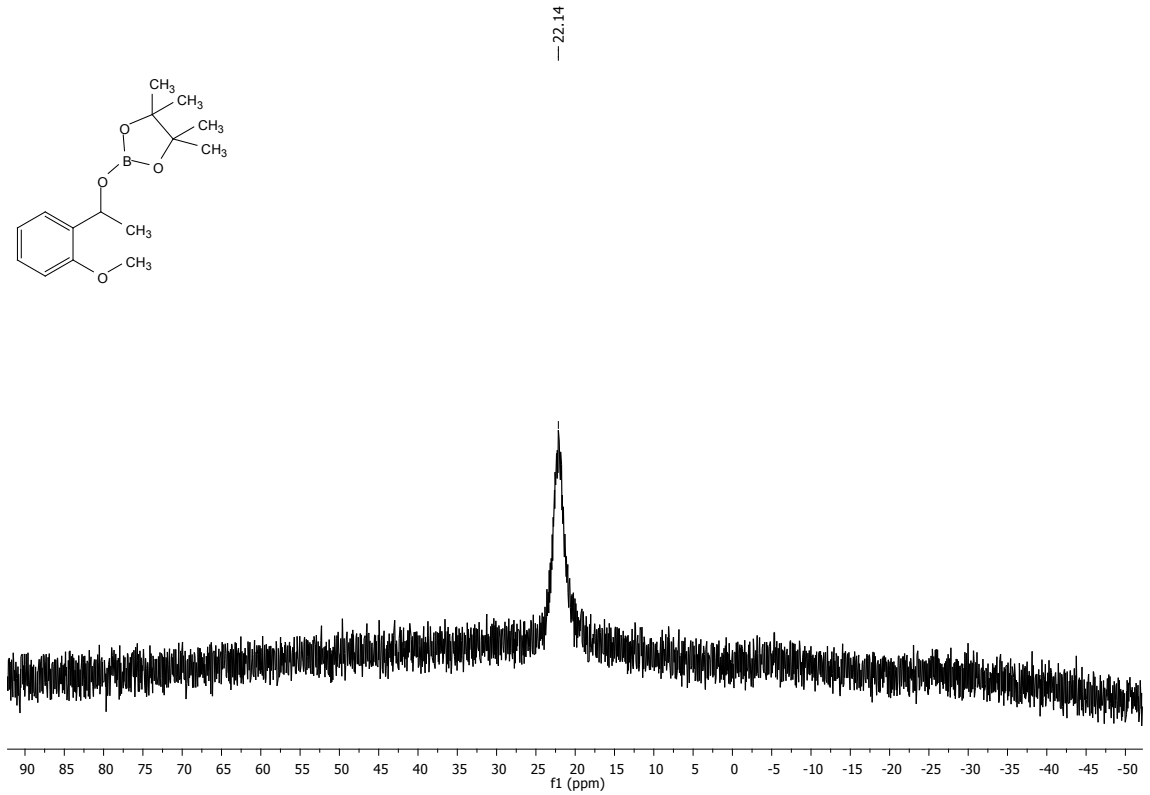


^{13}C NMR of **24c** (100 MHz, $CDCl_3$)

2-(1-(2-Methoxyphenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 25b)

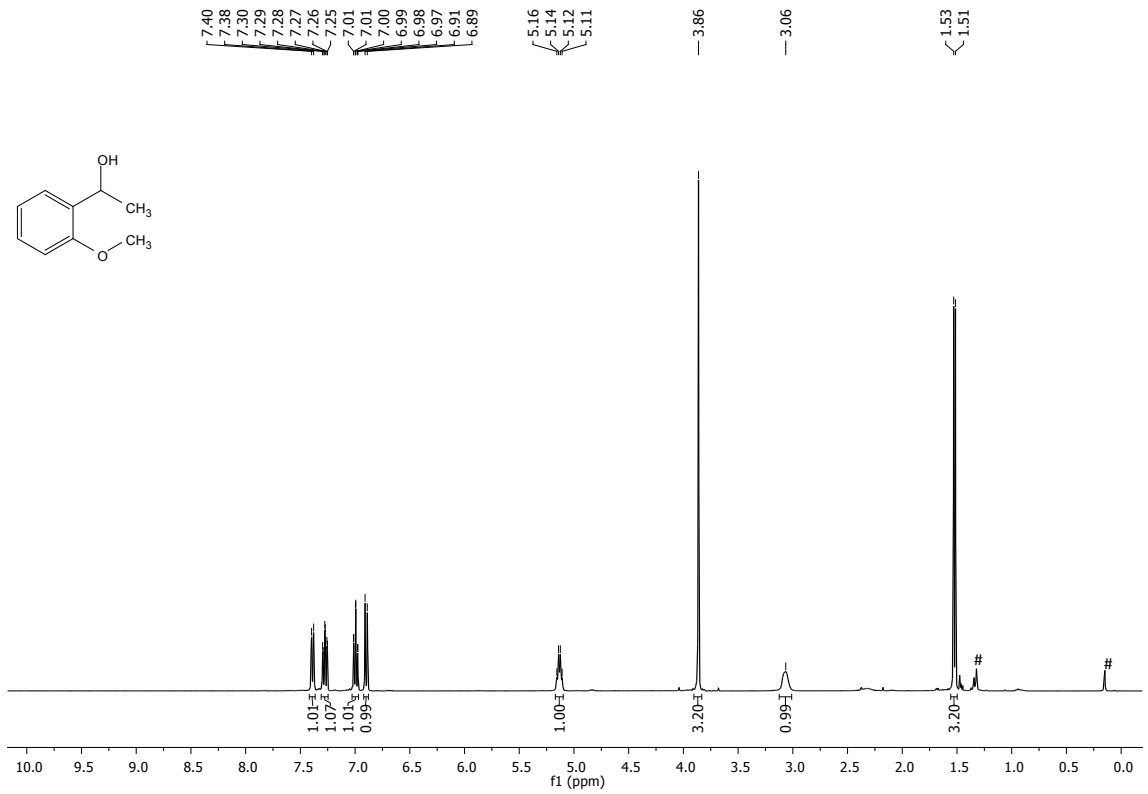


^{1}H NMR of **25b** (400 MHz, $CDCl_3$)

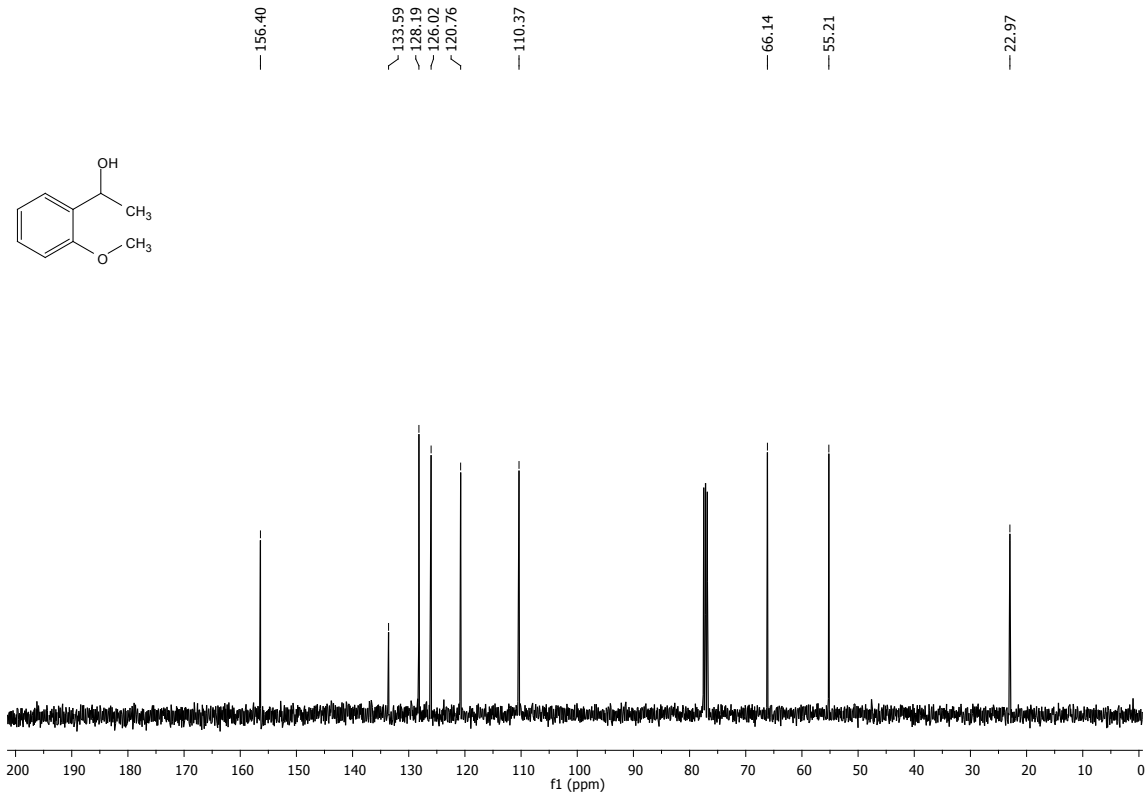


^{11}B NMR of **25b** (128 MHz, $CDCl_3$)

1-(2-Methoxyphenyl)ethanol (Table 3, 25c)[15]

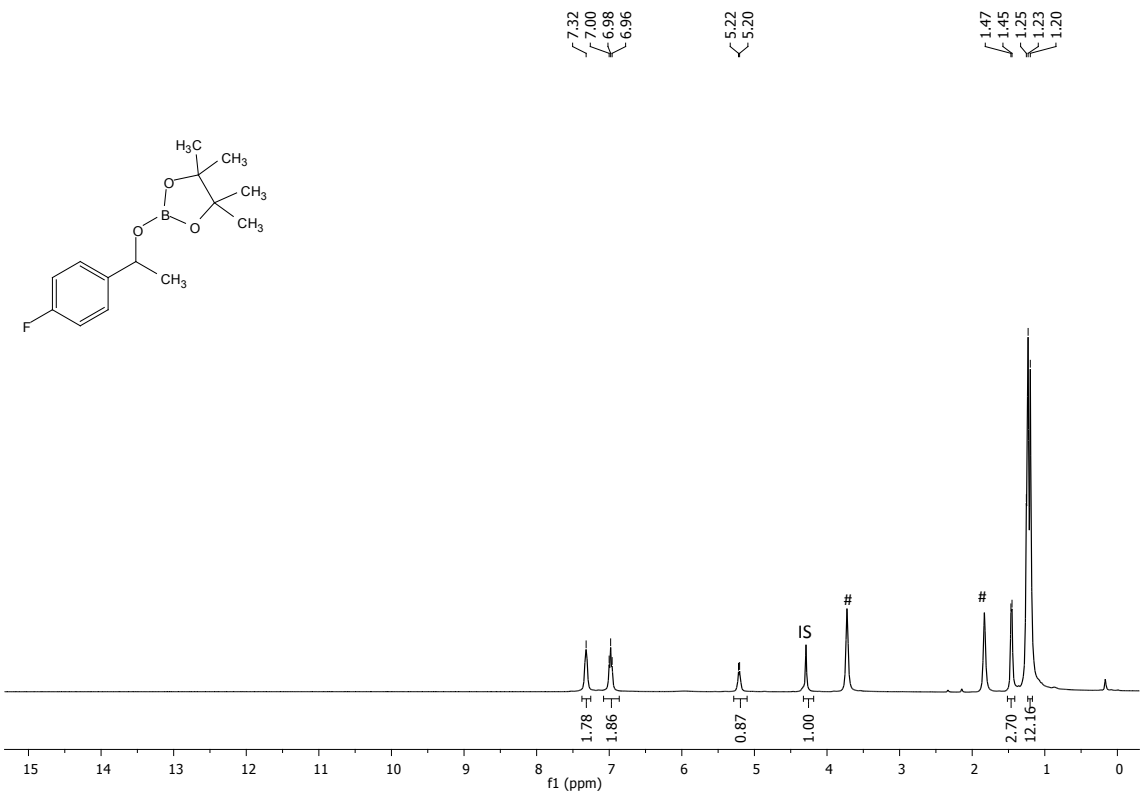


^{1}H NMR of **25c** (400 MHz, $CDCl_3$)

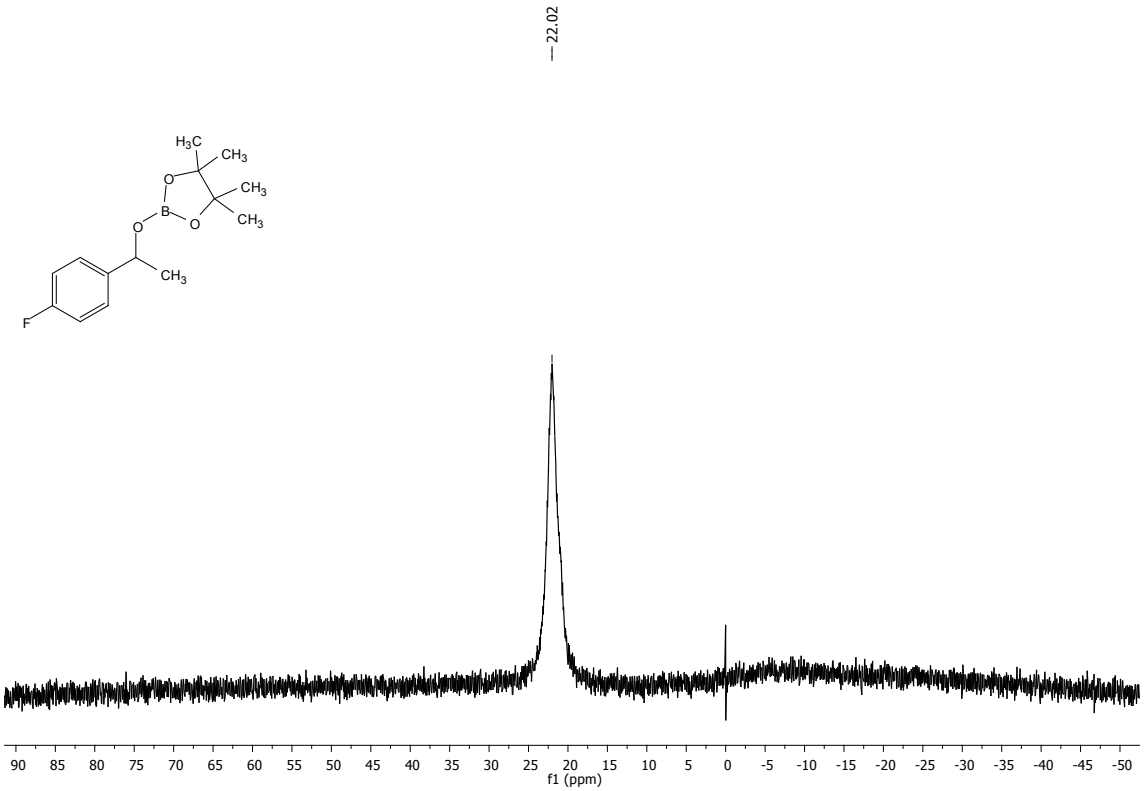


^{13}C NMR of **25c** (100 MHz, $CDCl_3$)

2-(1-(4-Fluorophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 26b)[12]

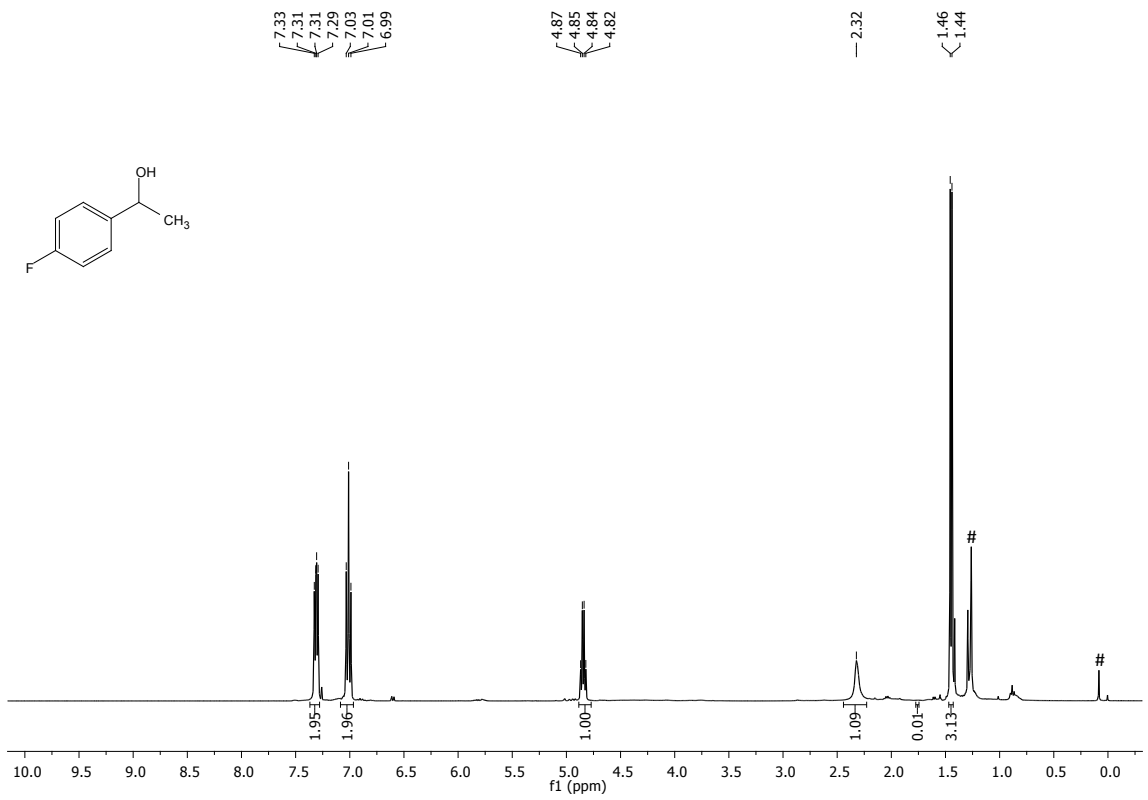


^{1}H NMR of **26b** (400 MHz, $CDCl_3$)

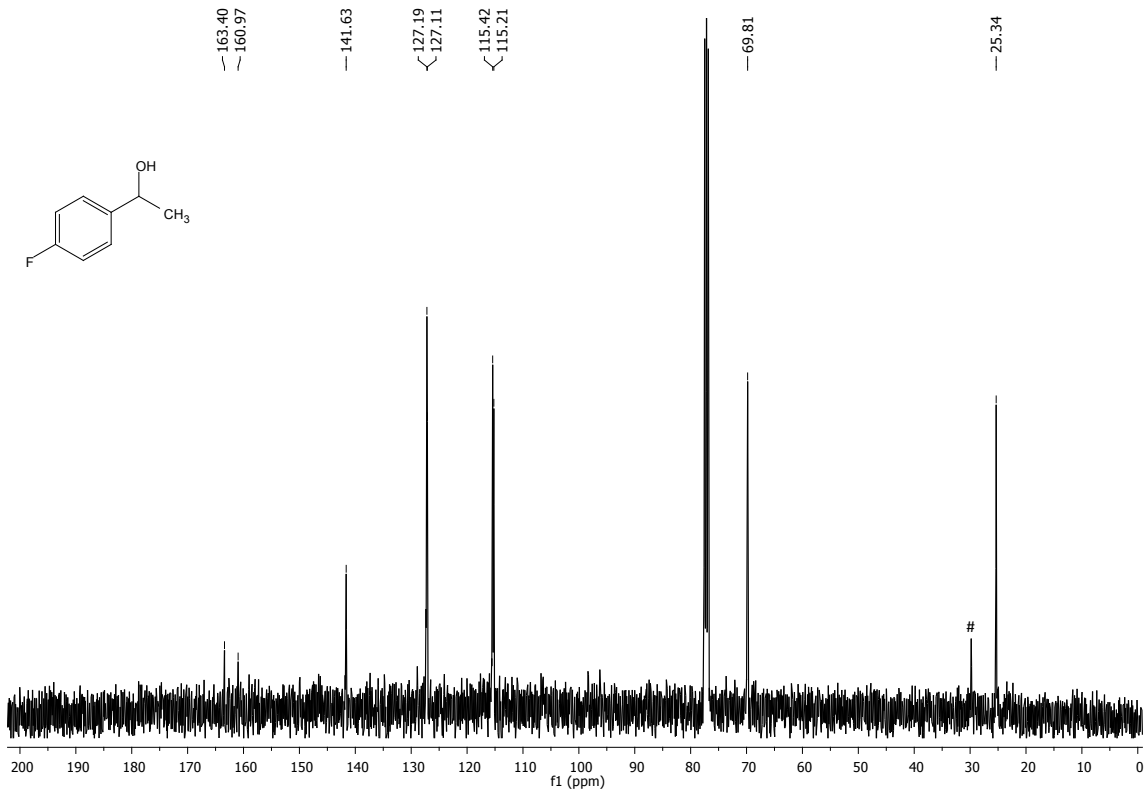


^{11}B NMR of **26b** (128 MHz, $CDCl_3$)

1-(4-Fluorophenyl)ethanol (Table 3, 26c).[12]

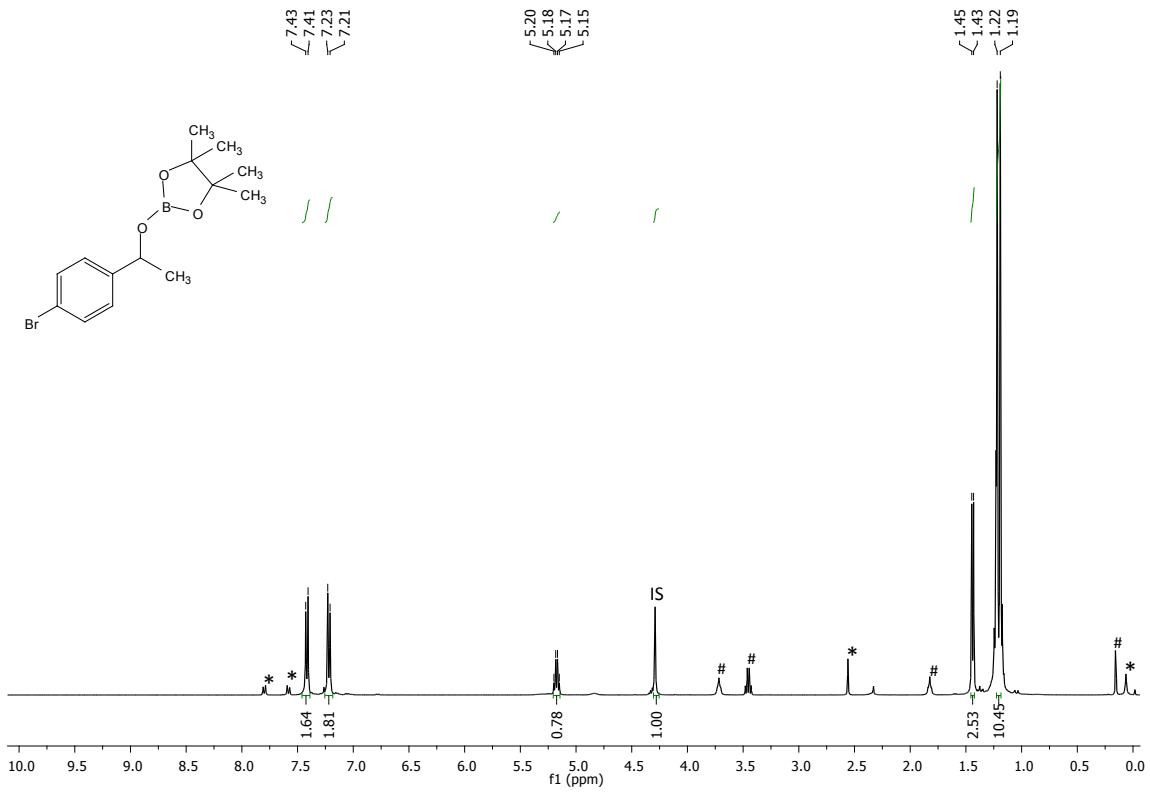


^{1}H NMR of **26c** (400 MHz, $CDCl_3$)

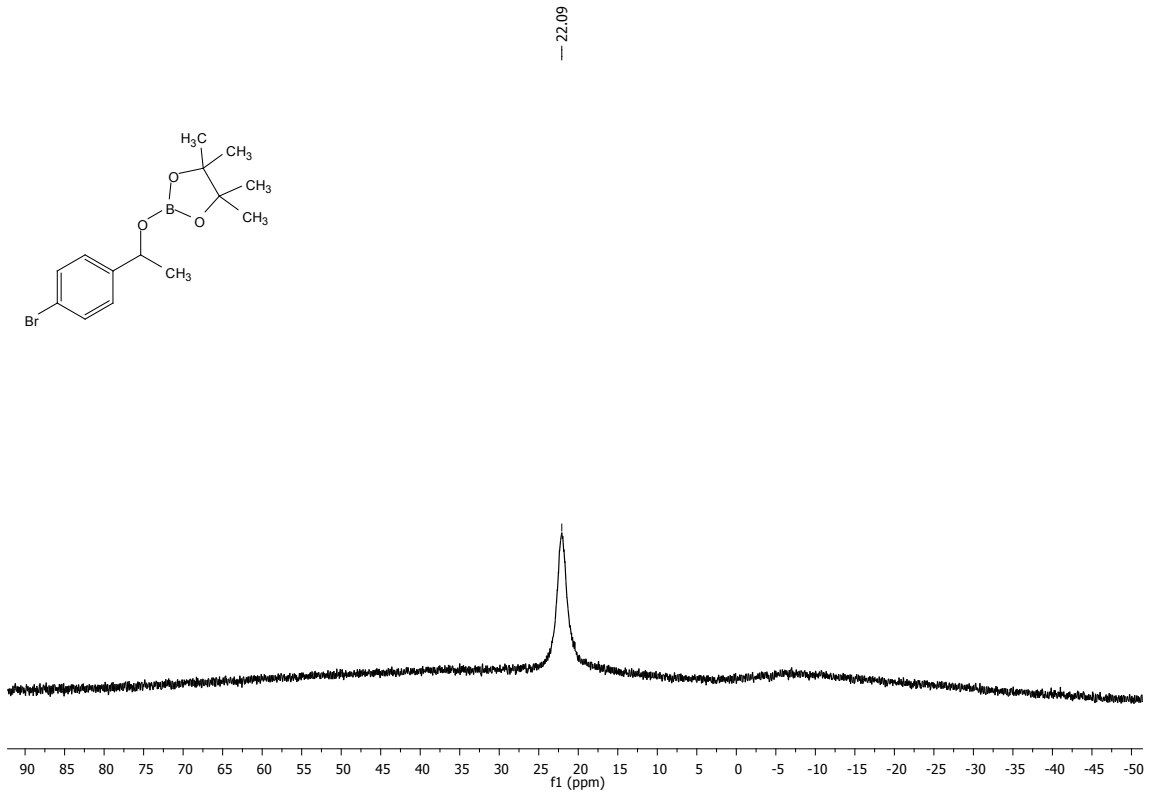


^{13}C NMR of **26c** (100 MHz, $CDCl_3$)

2-(1-(4-Bromophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 27b)[4]

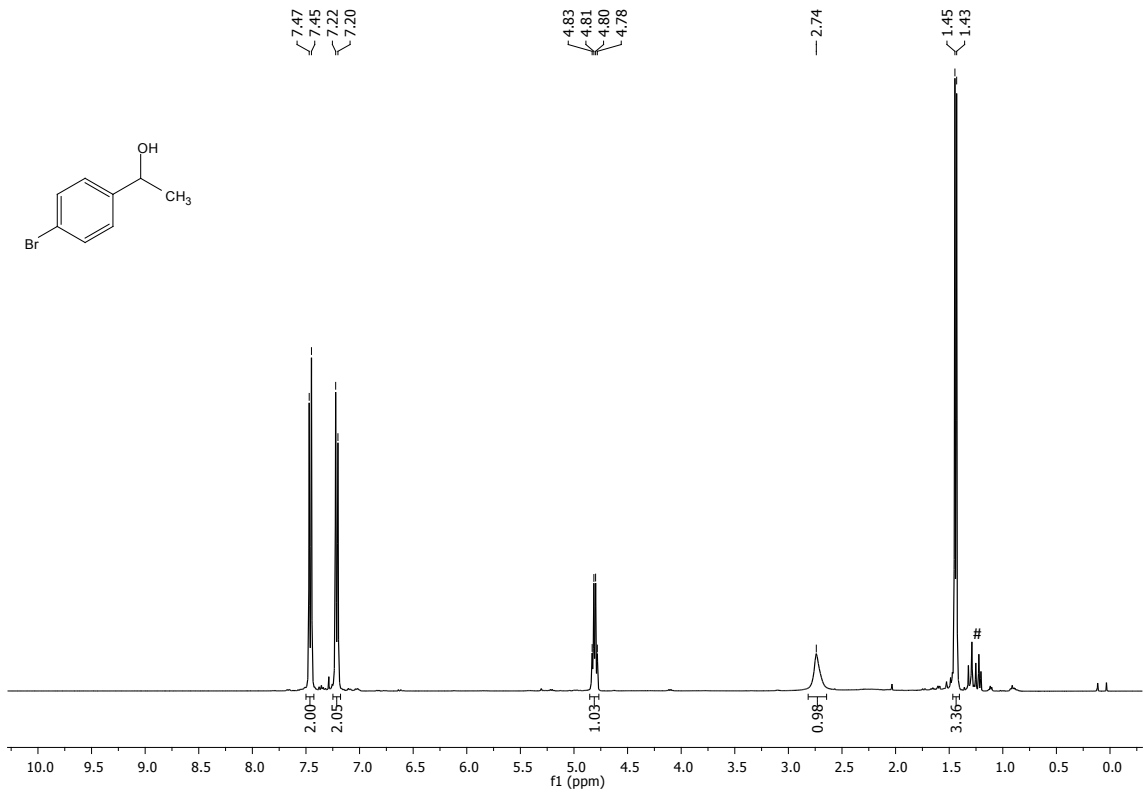


^{1}H NMR of **27b** (400 MHz, $CDCl_3$)

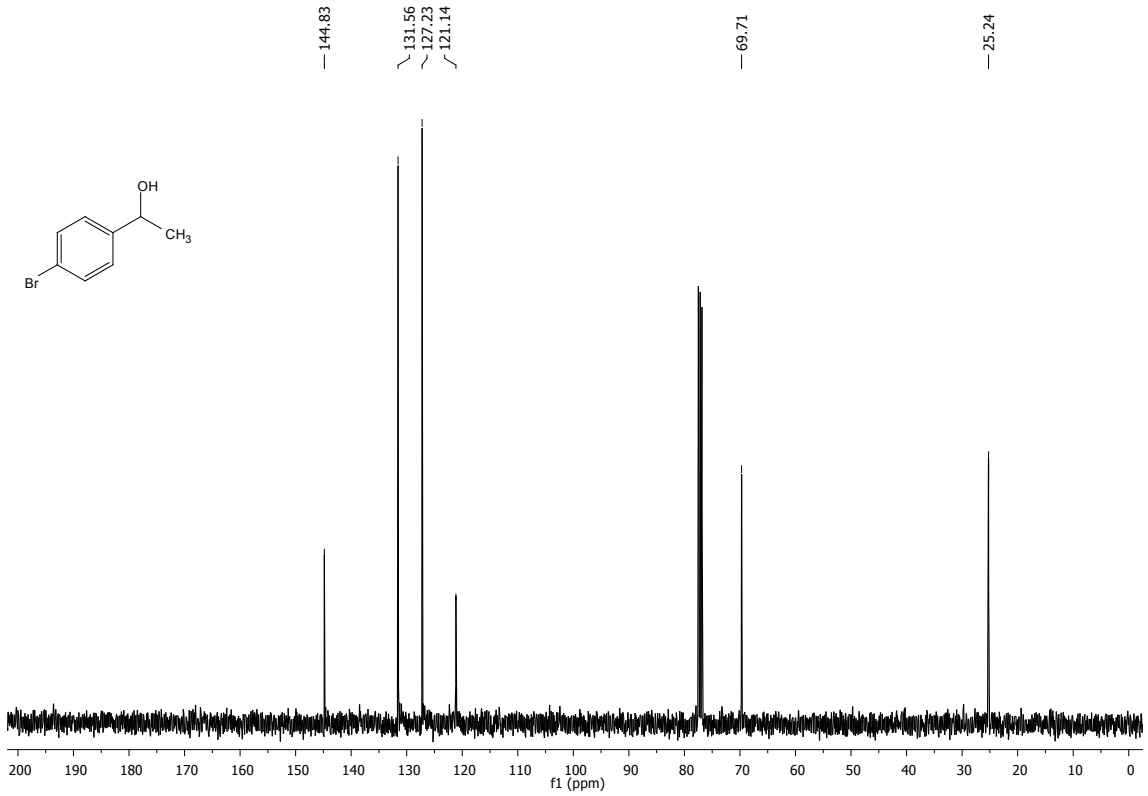


^{11}B NMR of **27b** (128 MHz, $CDCl_3$)

1-(4-bromophenyl)ethanol (Table 3, 27c)[6]

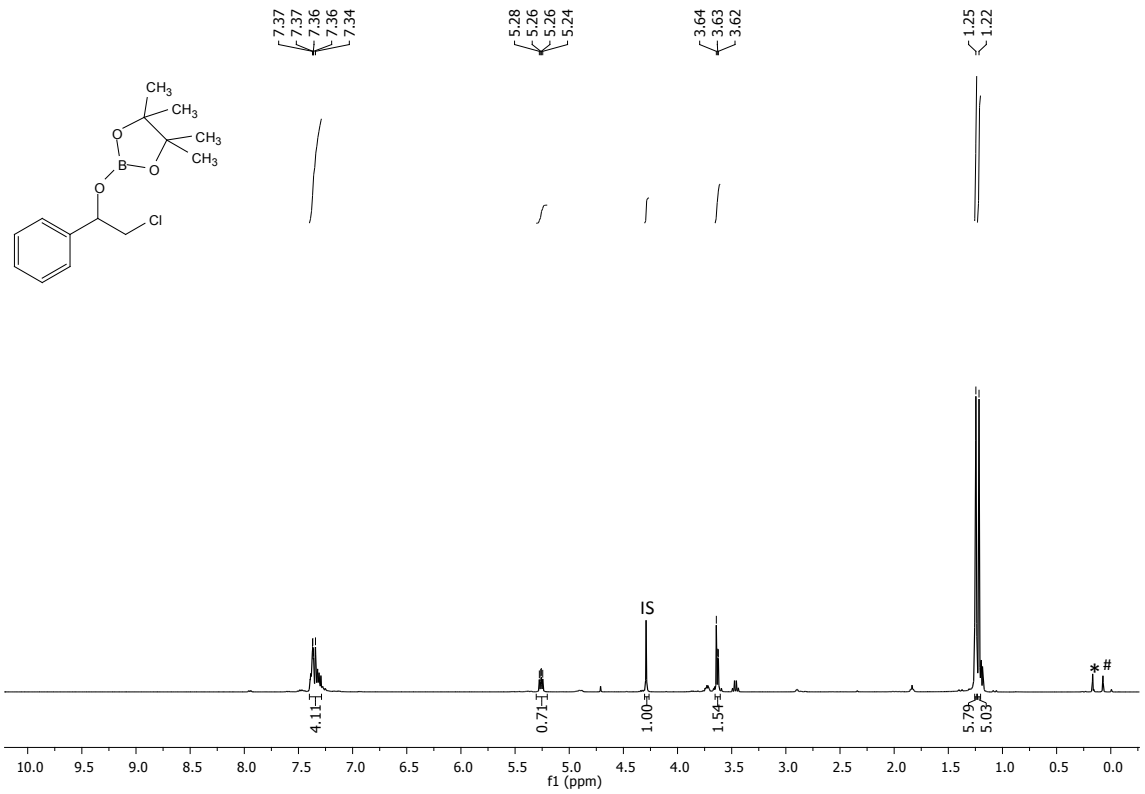


^{1}H NMR of **27c** (400 MHz, $CDCl_3$)

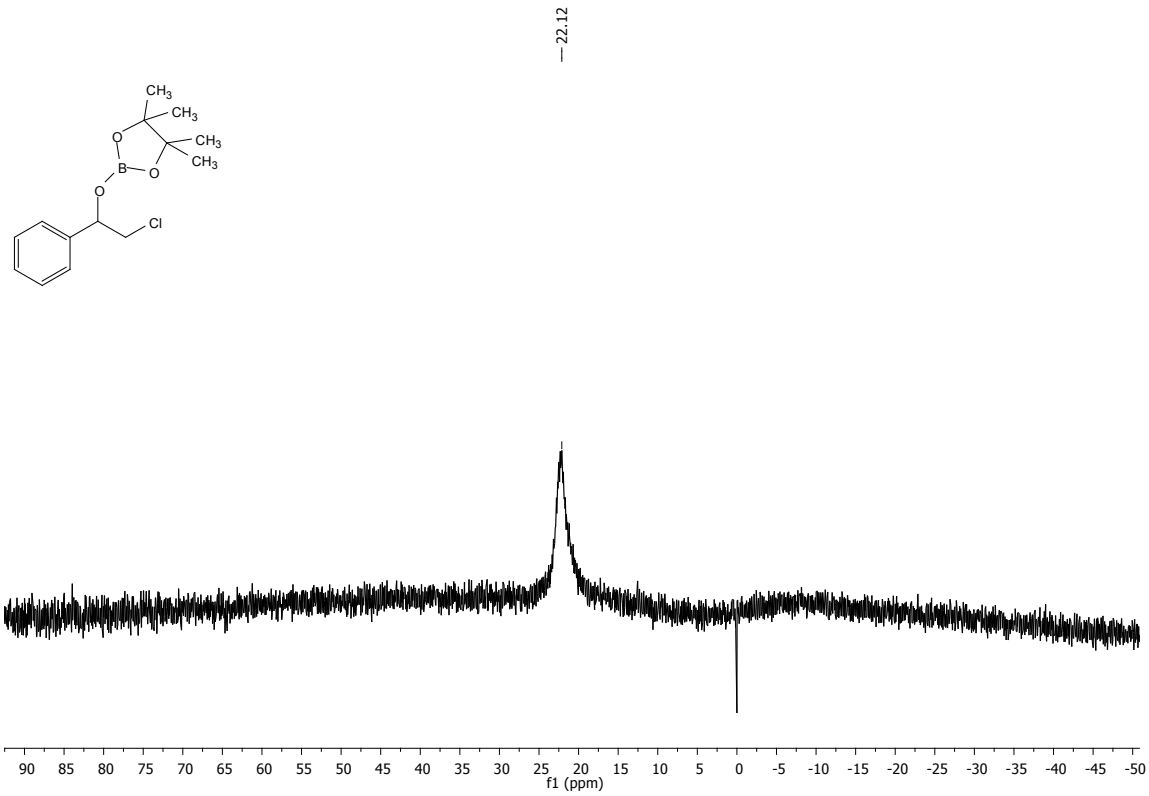


^{13}C NMR of **27c** (100 MHz, $CDCl_3$)

2-(1-(2-Chlorophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 28b).[16]

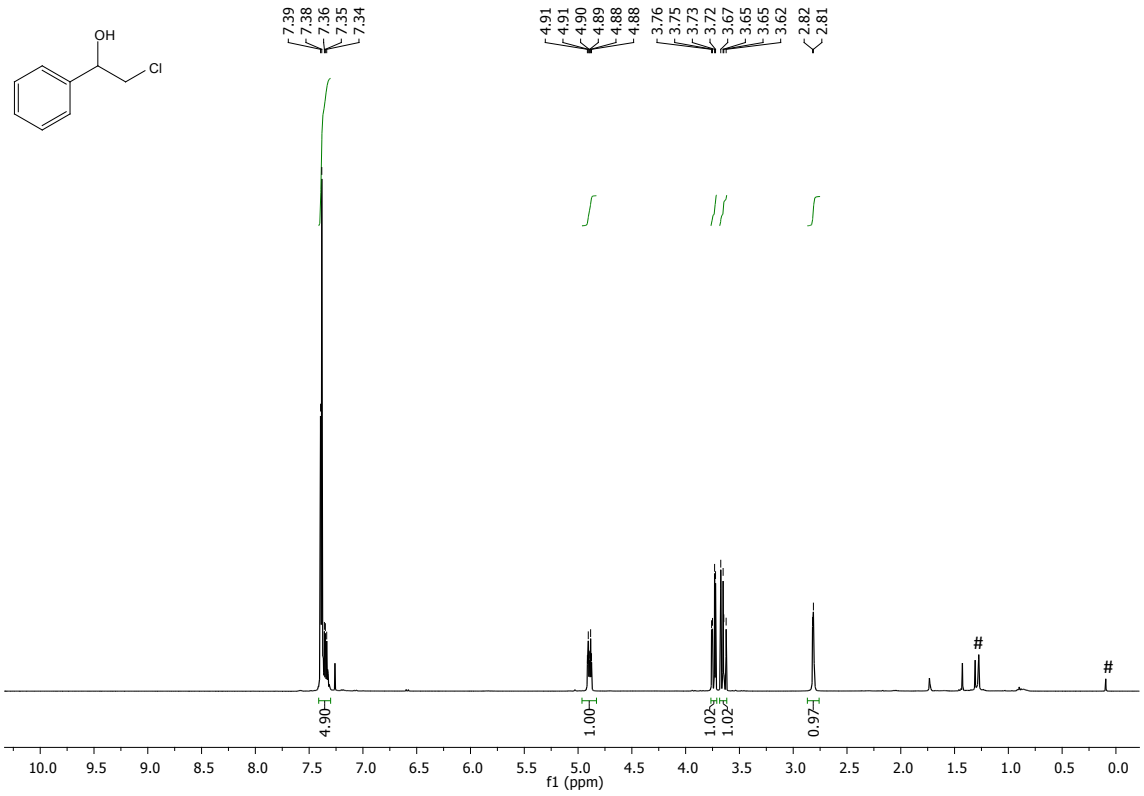


^{1}H NMR of **28b** (400 MHz, $CDCl_3$)

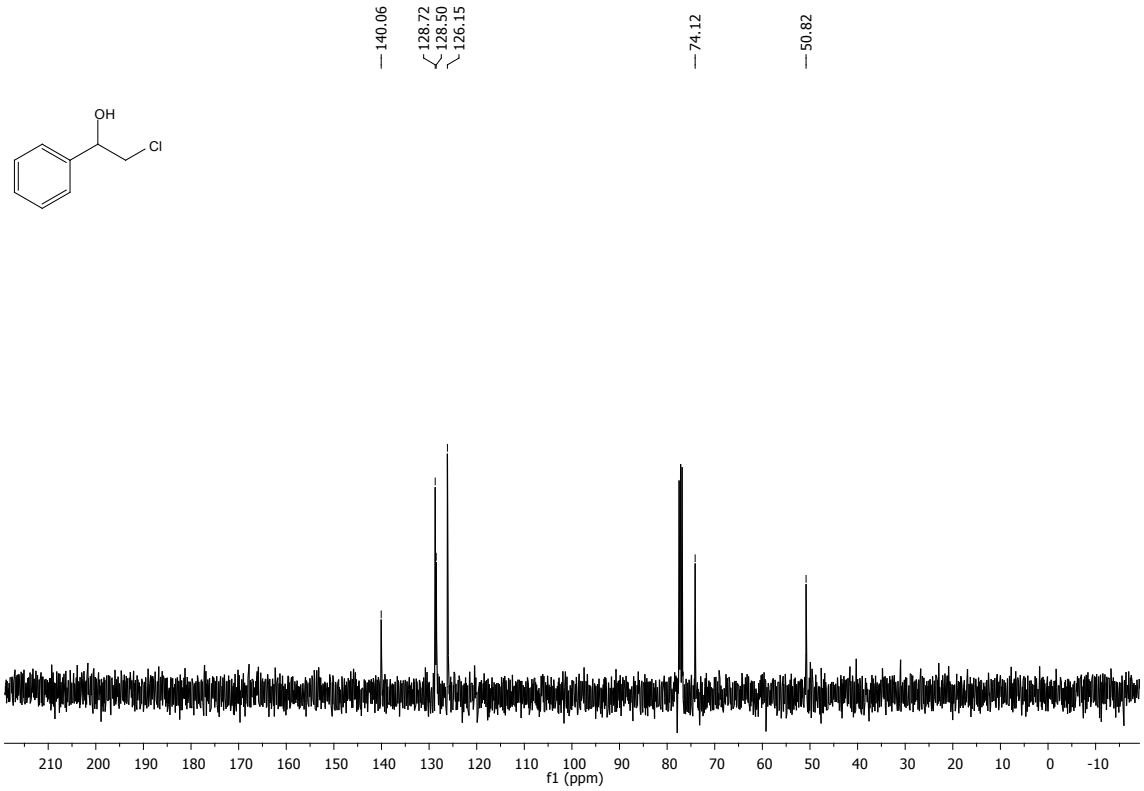


^{11}B NMR of **28b** (128 MHz, $CDCl_3$)

2-chloro-1-phenylethan-1-ol (Table 3, 28c):[17]

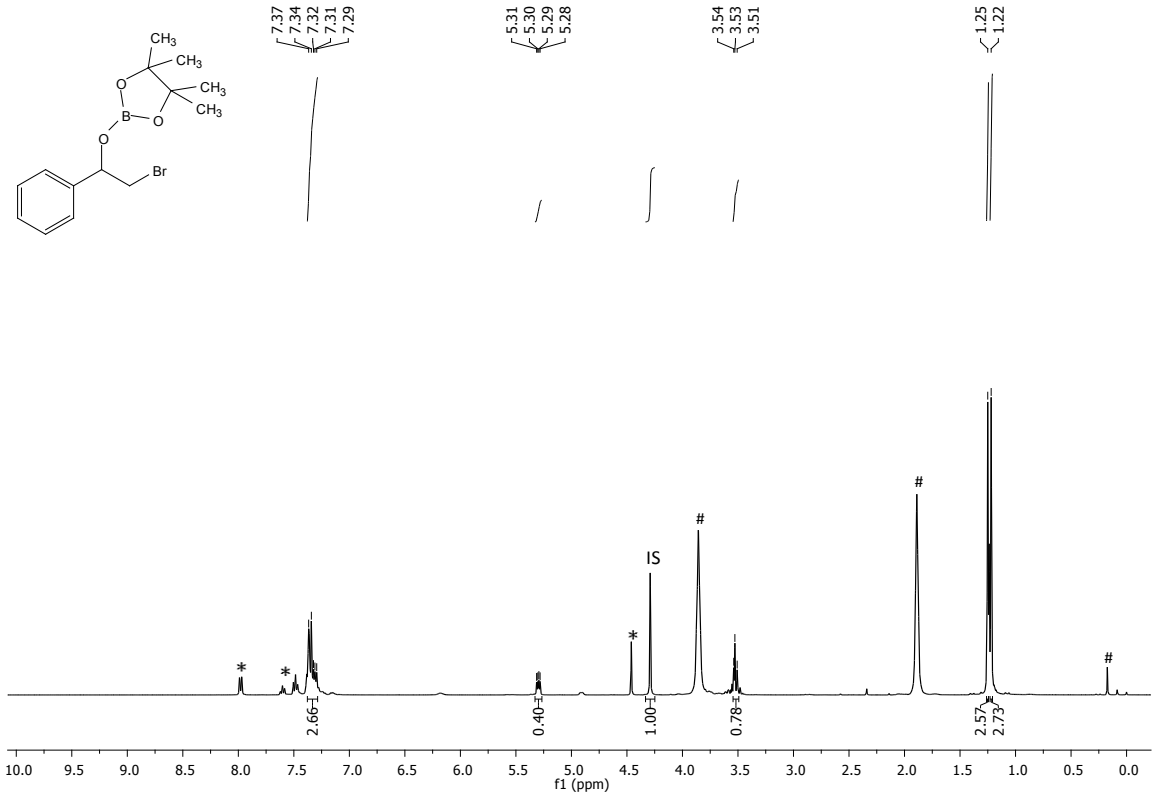


^{1}H NMR of **28c** (400 MHz, $CDCl_3$)

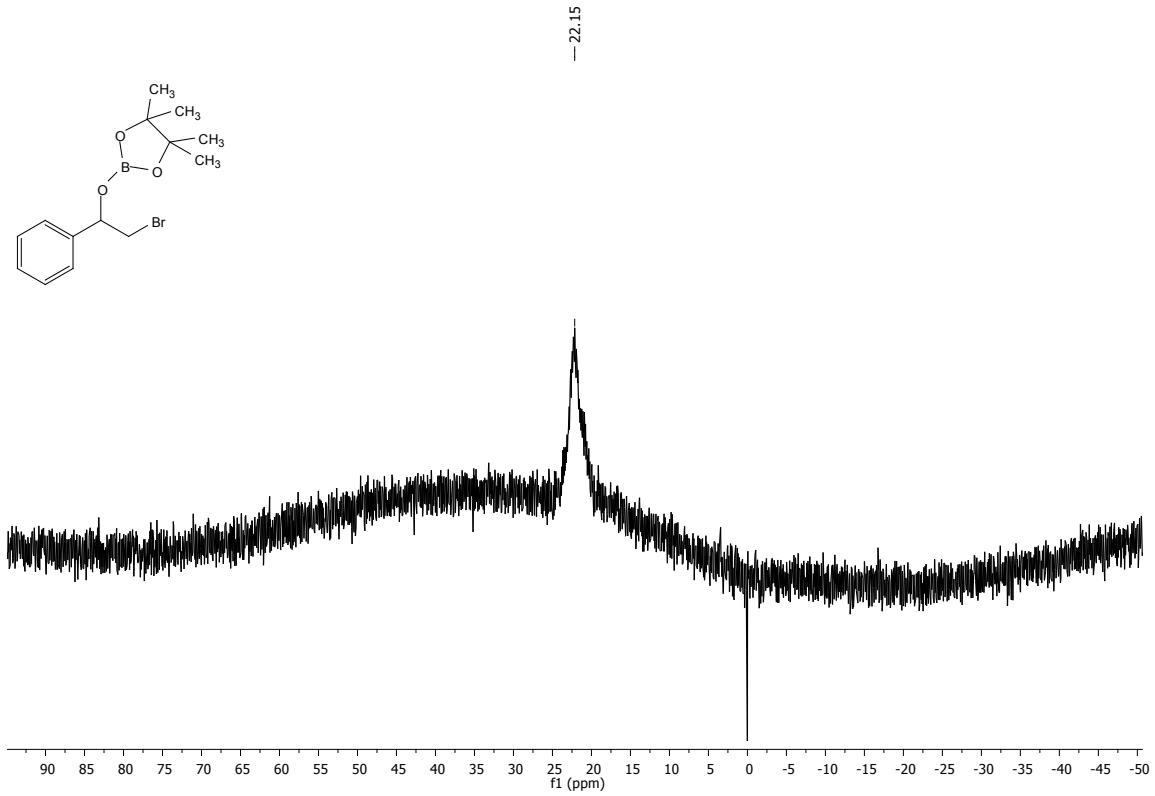


^{13}C NMR of **28c** (100 MHz, $CDCl_3$)

2-(1-(2-Bromophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 29b).

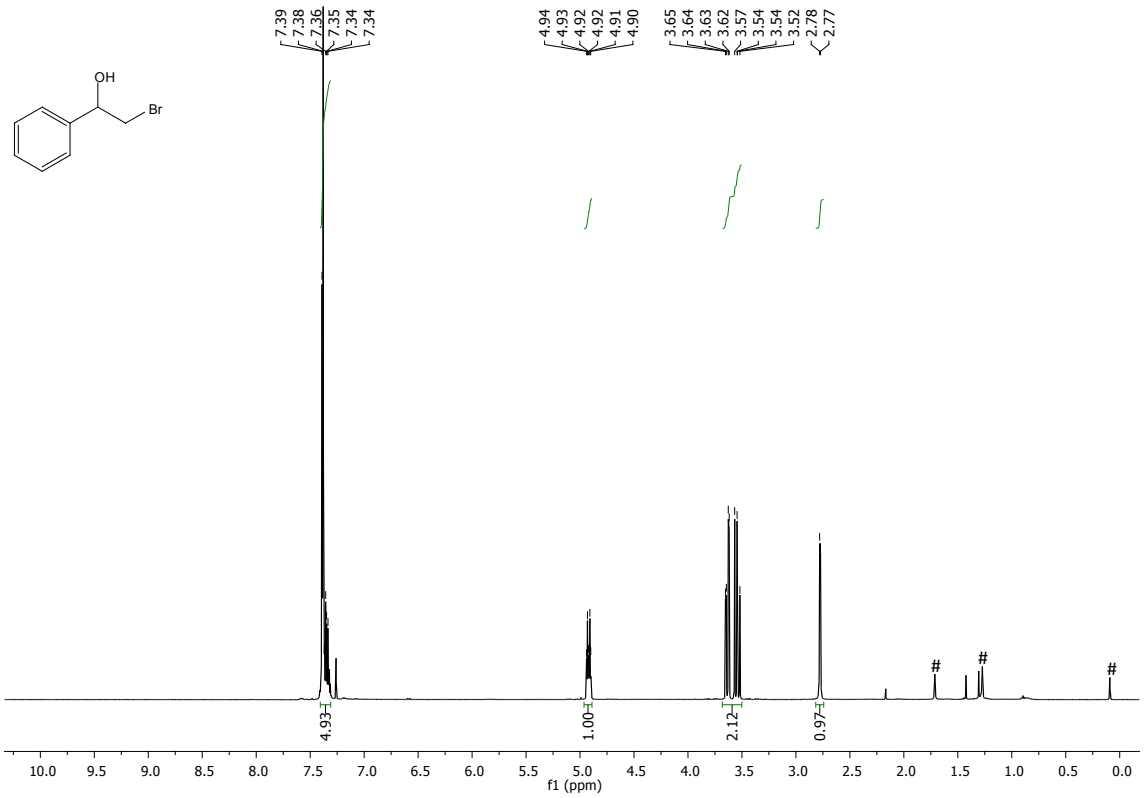


^{1}H NMR of **29b** (400 MHz, $CDCl_3$)

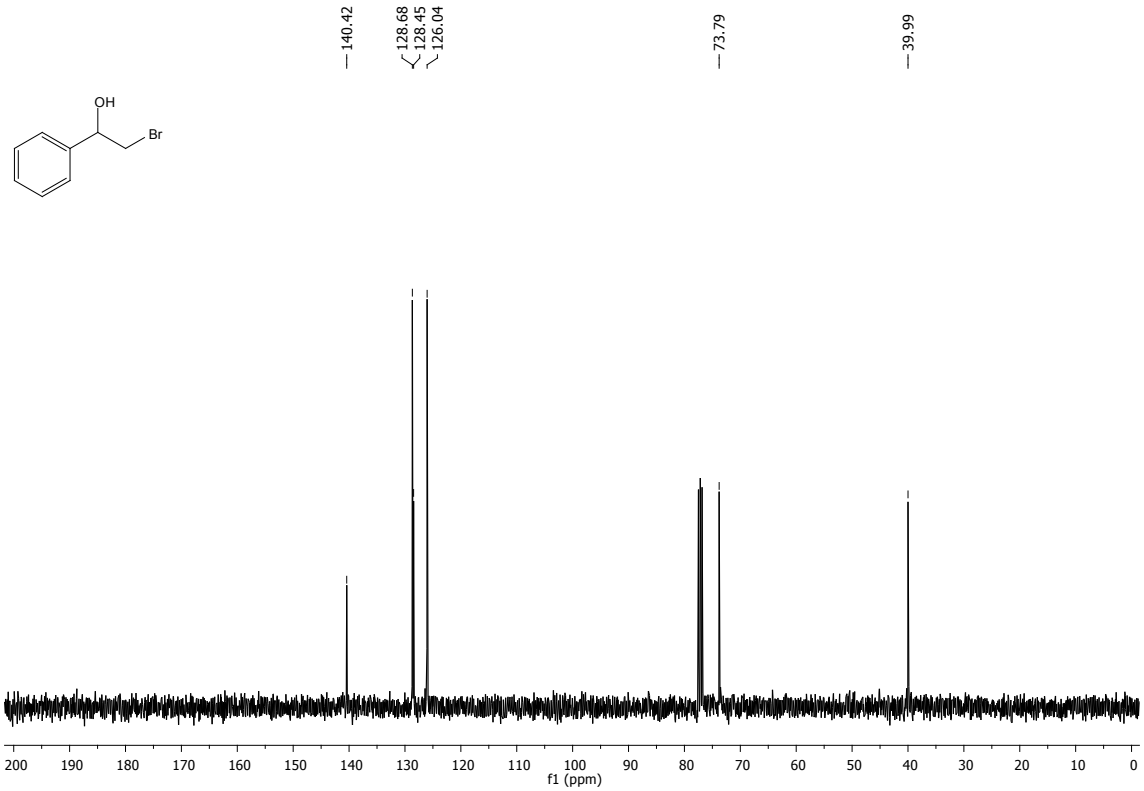


^{11}B NMR of **29b** (128 MHz, $CDCl_3$)

2-Bromo-1-phenylethan-1-ol (Table 3, 29c):[18]

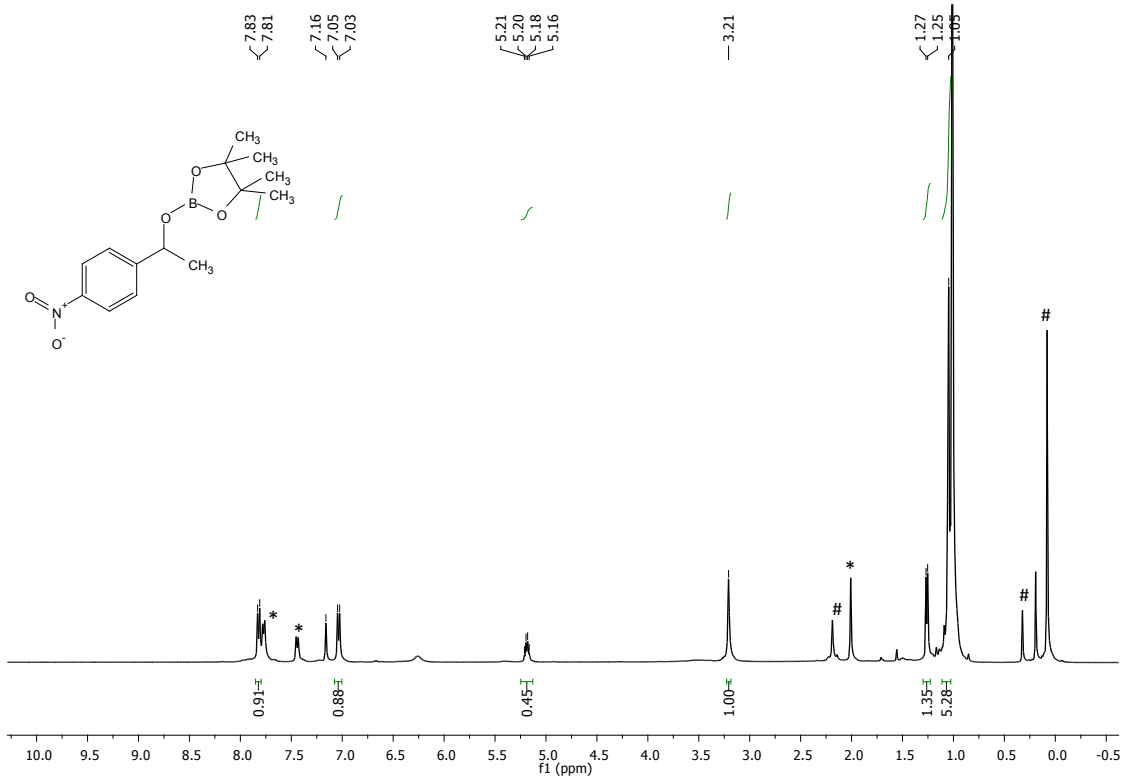


^{1}H NMR of **29c** (400 MHz, $CDCl_3$)

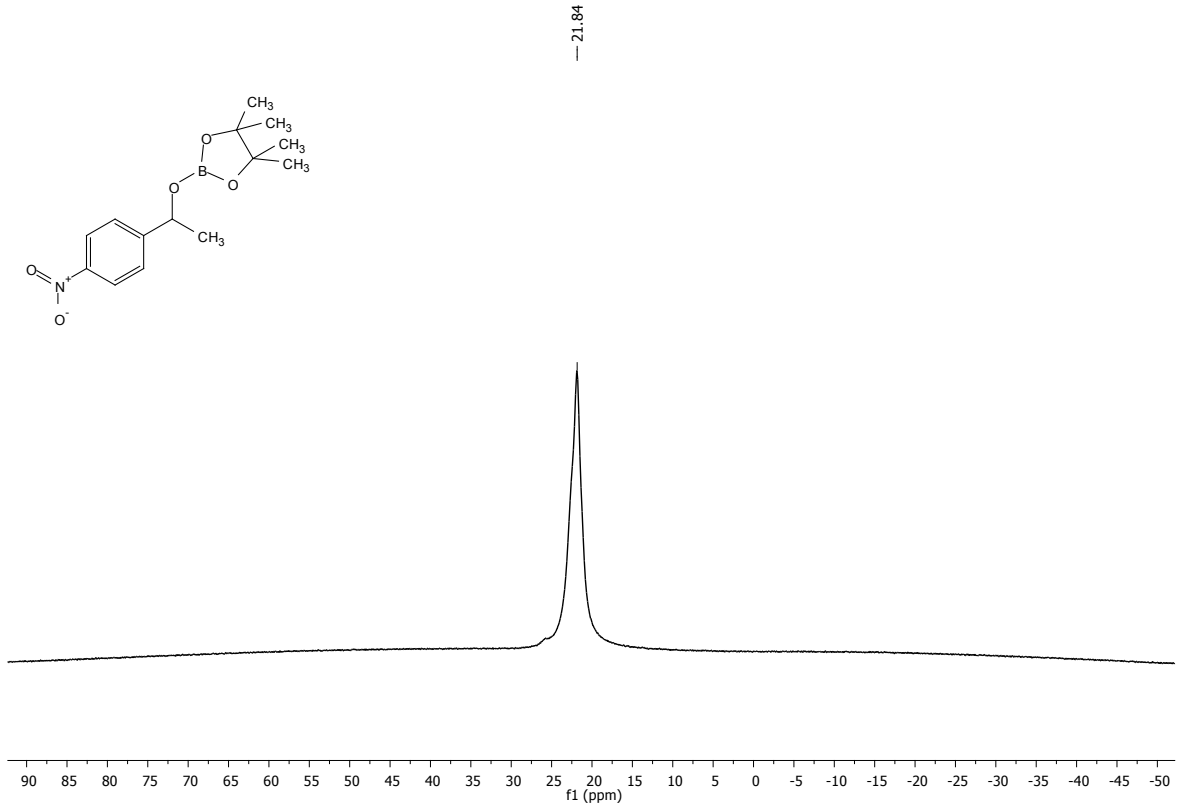


^{13}C NMR of **29c** (100 MHz, $CDCl_3$)

4,4,5,5-Tetramethyl-2-(1-(4-nitrophenyl)ethoxy)-1,3,2-dioxaborolane (Table 3, 30b).

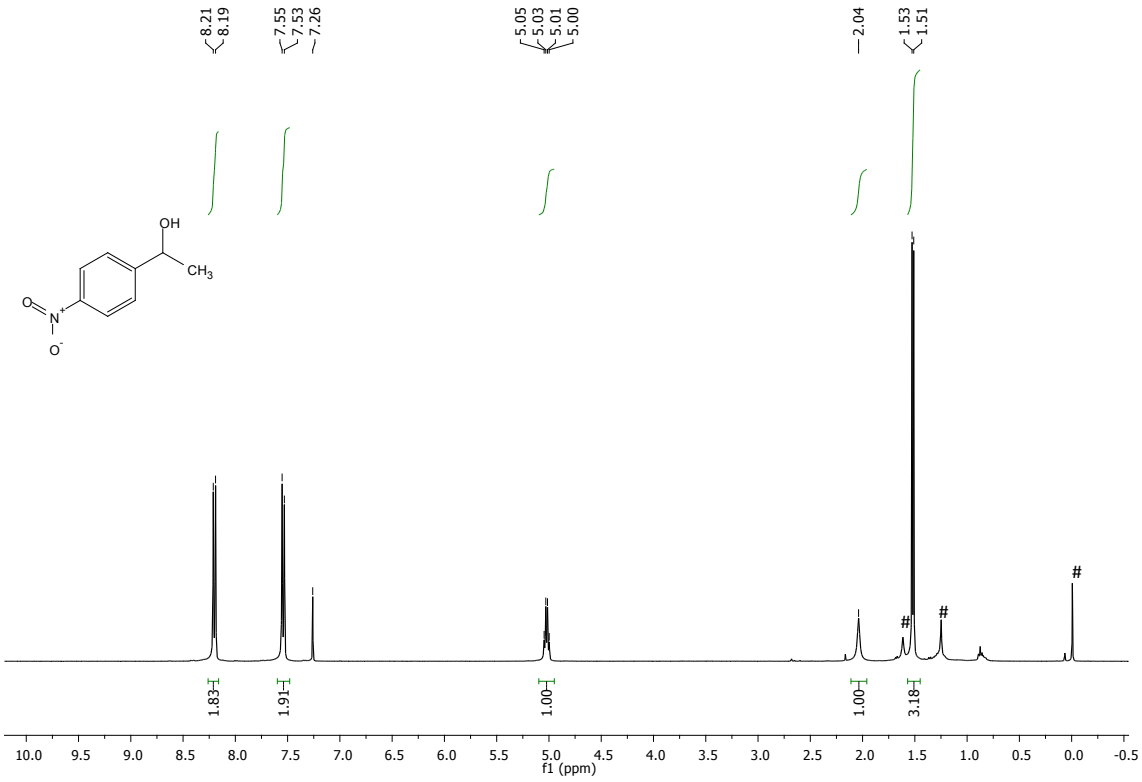


^{1}H NMR of **30b** (400 MHz, C_6D_6)

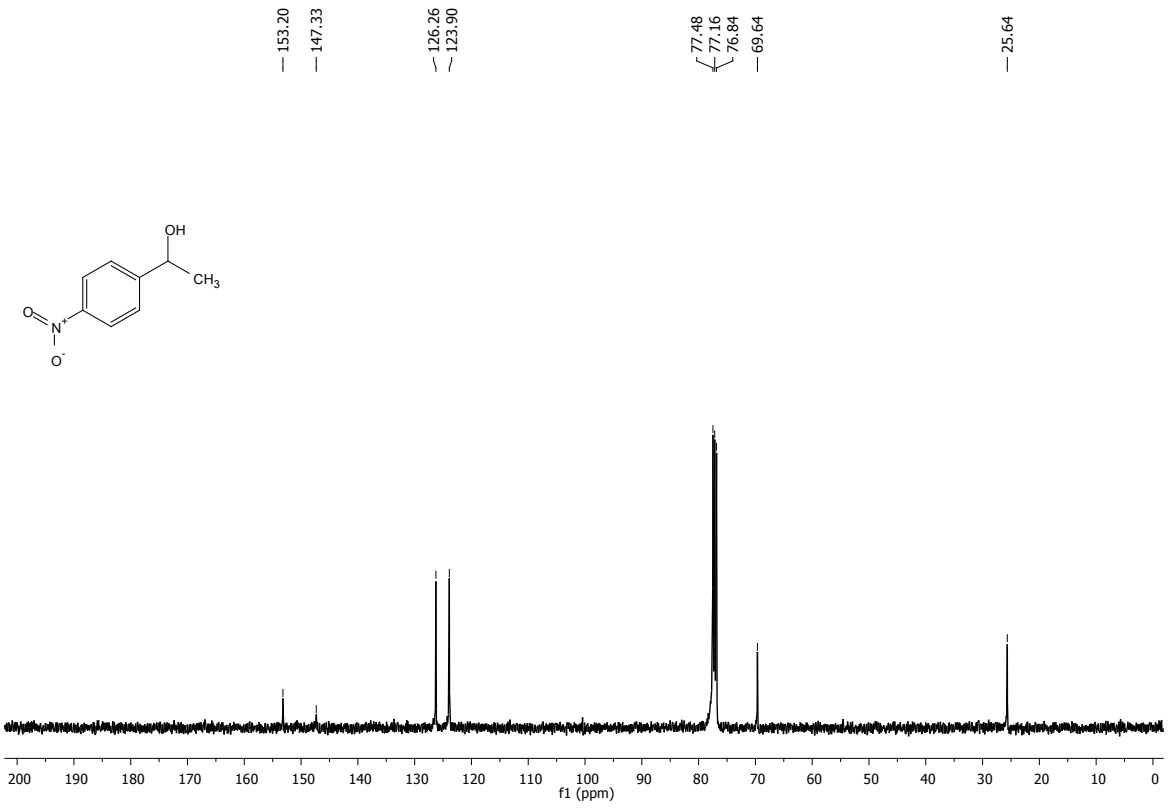


^{11}B NMR of **30b** (128 MHz, C_6D_6)

1-(4-Nitrophenyl)ethanol (Table 3, 30c).[19]

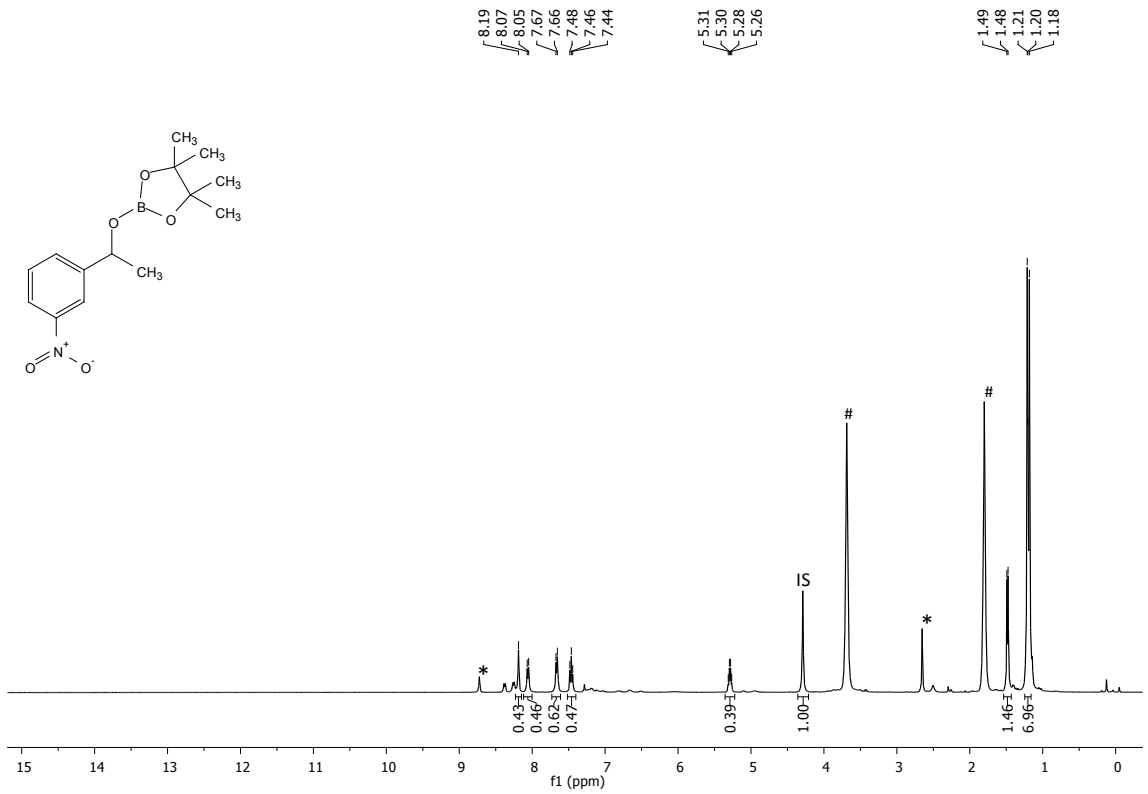


^{1}H NMR of **30c** (400 MHz, $CDCl_3$)

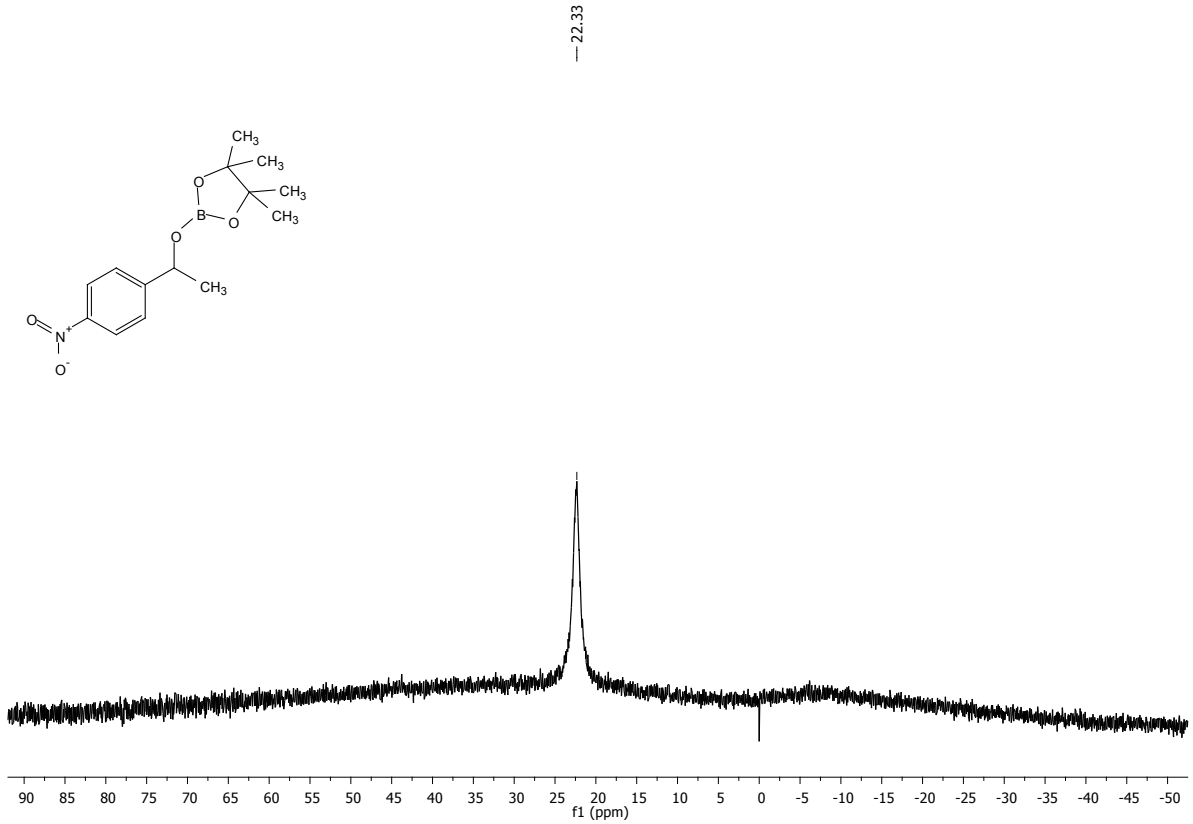


^{13}C NMR of **30c** (100 MHz, $CDCl_3$)

4,4,5,5-Tetramethyl-2-(1-(4-nitrophenyl)ethoxy)-1,3,2-dioxaborolane (Table 3, 31b).

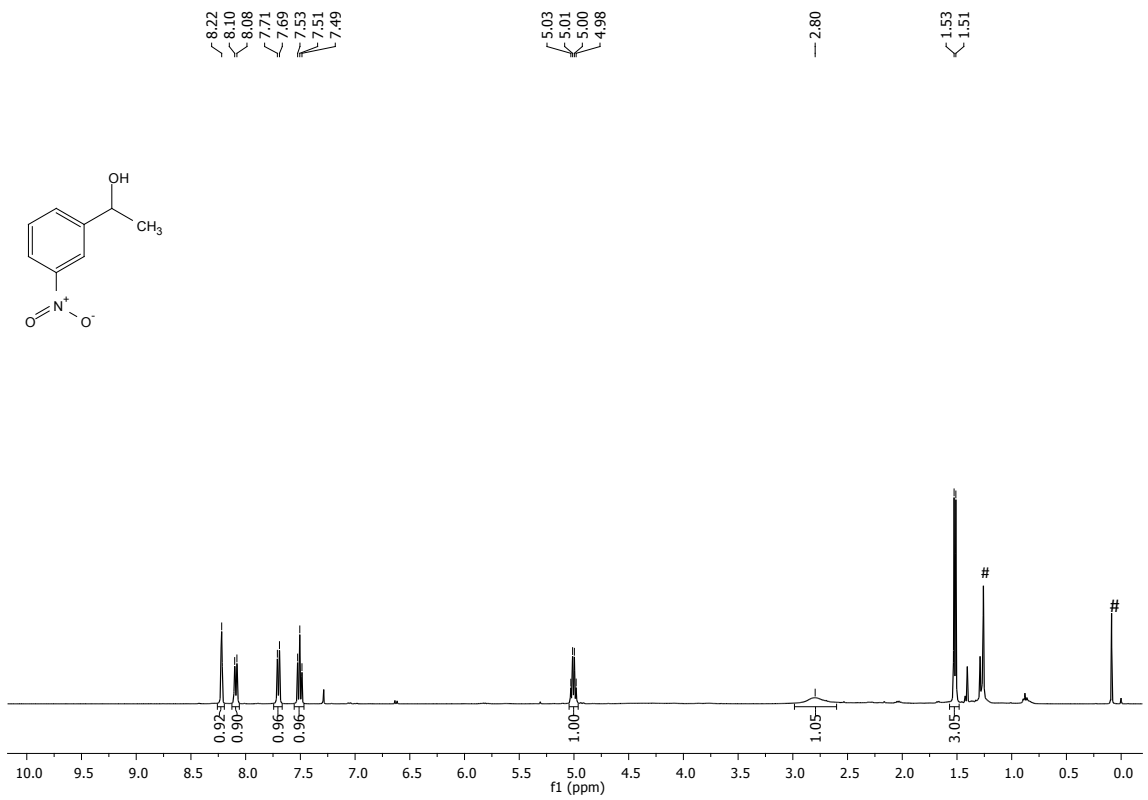


^{1}H NMR of **31b** (400 MHz, $CDCl_3$)

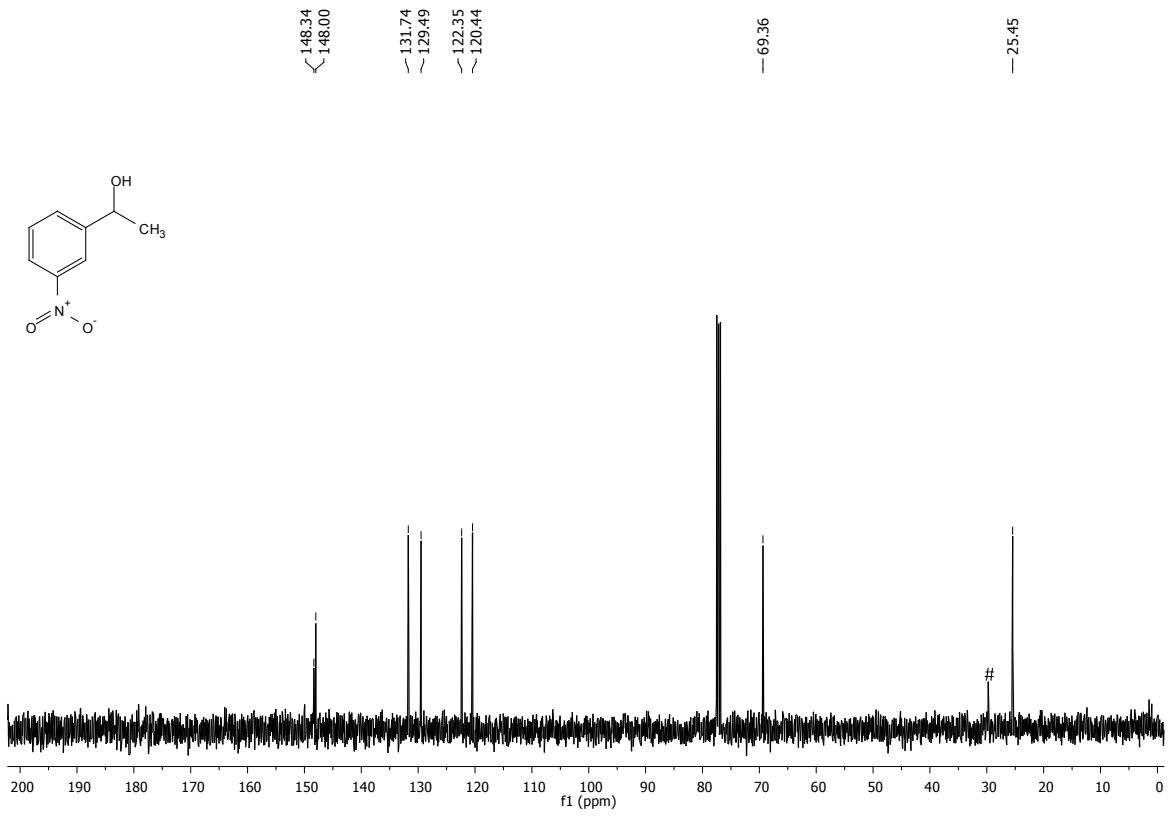


^{11}B NMR of **31b** (128 MHz, $CDCl_3$)

1-(4-Nitrophenyl)ethanol (Table 3, 31c).[19]

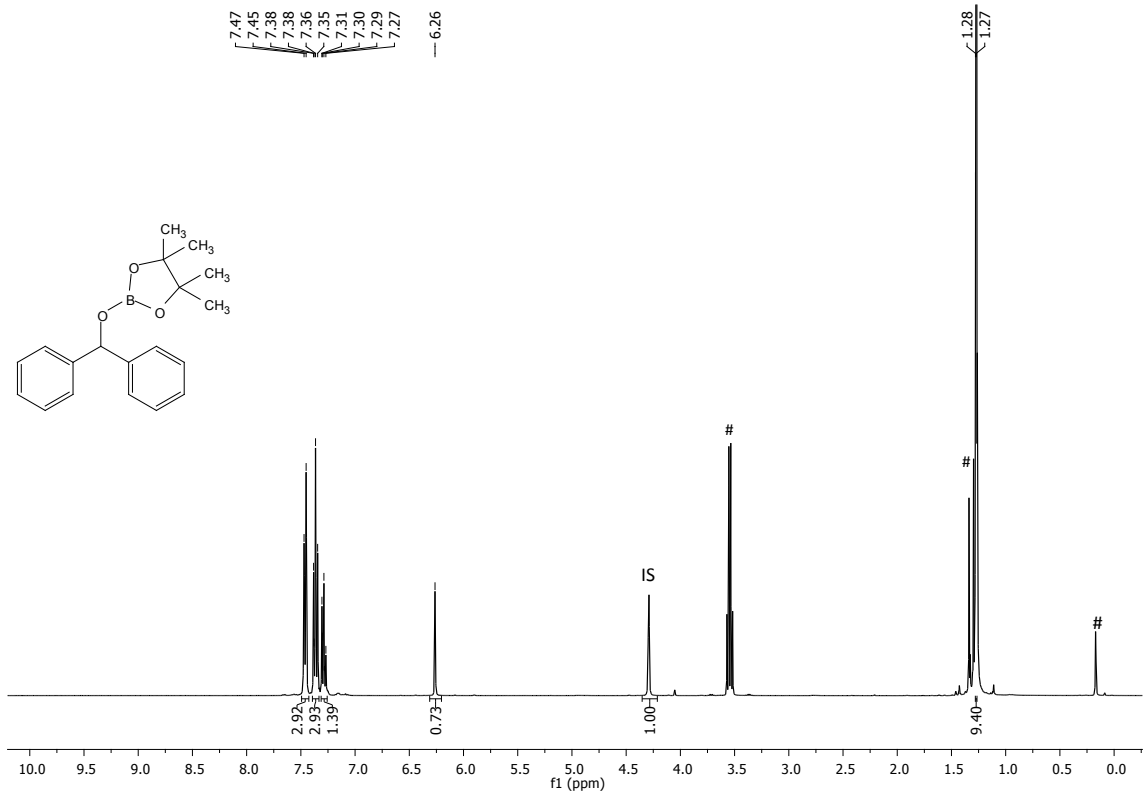


^{1}H NMR of **31c** (400 MHz, $CDCl_3$)

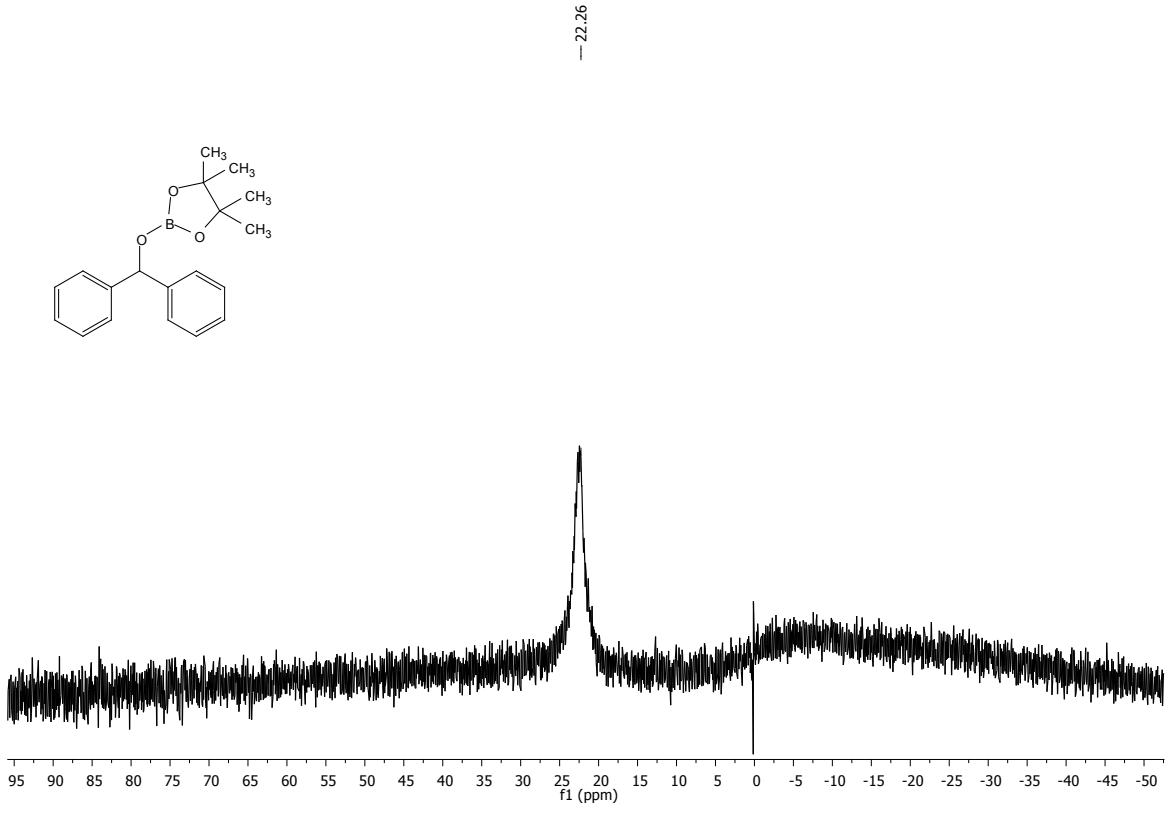


^{13}C NMR of **31c** (100 MHz, $CDCl_3$)

2-(Benzhydryloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 32b).[9]

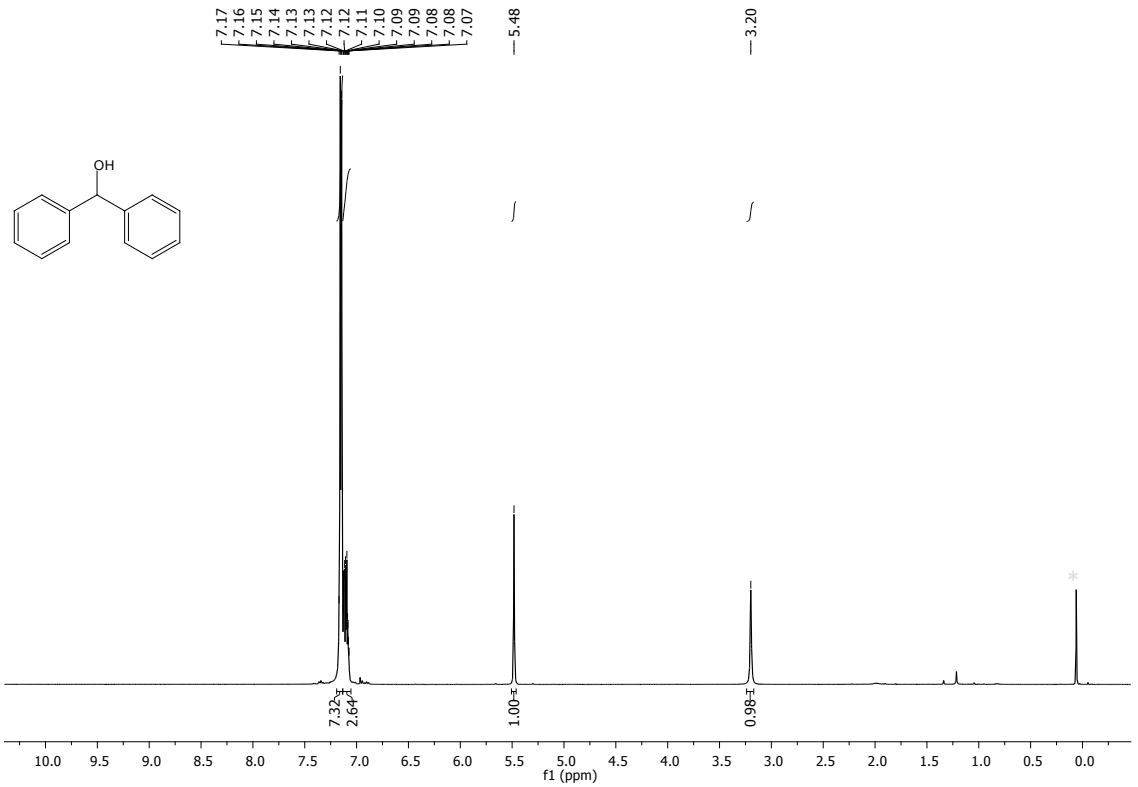


^{1}H NMR of **32b** (400 MHz, $CDCl_3$)

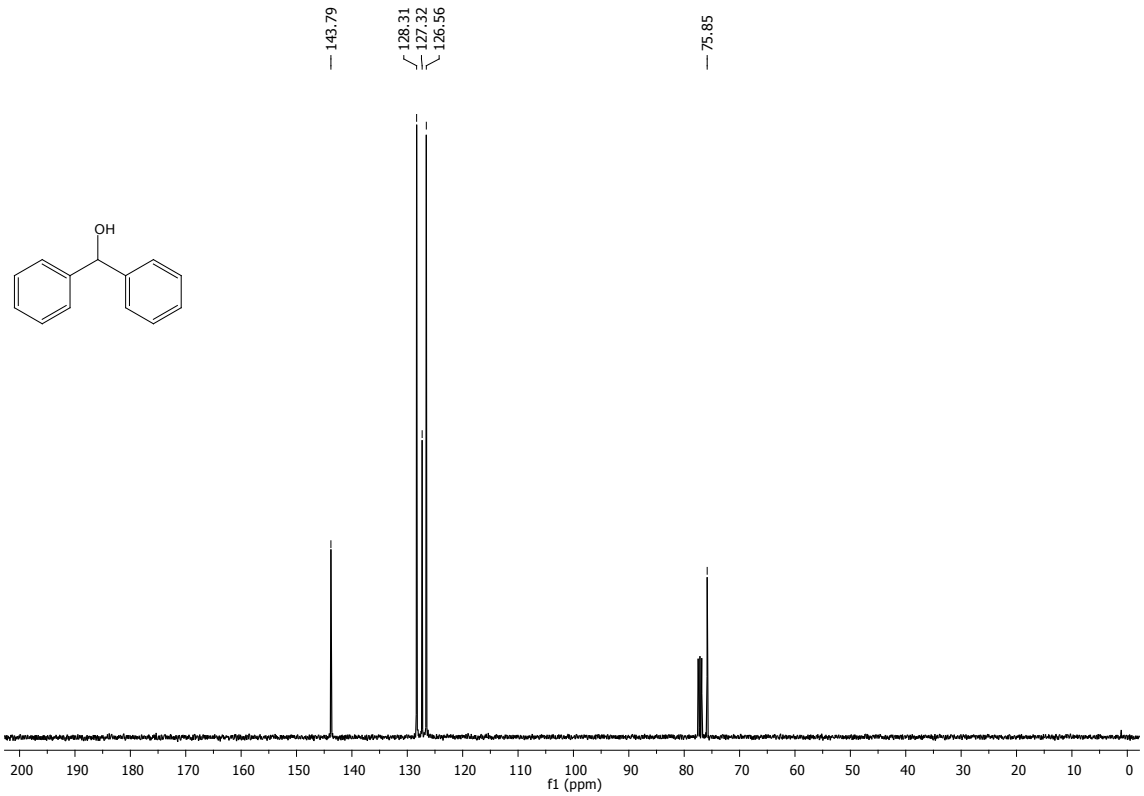


^{11}B NMR of **32b** (128 MHz, $CDCl_3$)

Diphenylmethanol (Table 3, 32c).[5]



^{1}H NMR of **32c** (400 MHz, $CDCl_3$)

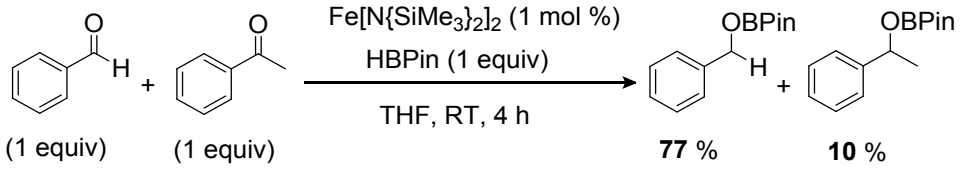


^{13}C NMR of **32c** (100 MHz, $CDCl_3$)

V. Competitive Chemoselective Hydroboration Reactions (Described in Scheme 1)

General Procedure for Intermolecular Chemoselective Catalytic Hydroboration. In a nitrogen-filled glovebox, HBPin (0.25 mmol), THF (1 mL), aldehyde (0.25 mmol) and ketone (0.25 mmol) were added to a Schlenk tube equipped with a magnetic stirring bar. Then 1 mol% of **1** was added and the reaction mixture was stirred at room temperature for 4 h. The reaction mixture was diluted with diethyl ether (2 mL) and filtered through a plug of celite (Ø 3 mm × 8 mm). The solvents were removed under vacuum using Schlenk line. The products yields were determined by ^{1}H NMR using nitromethane as an internal standard.

(a1)



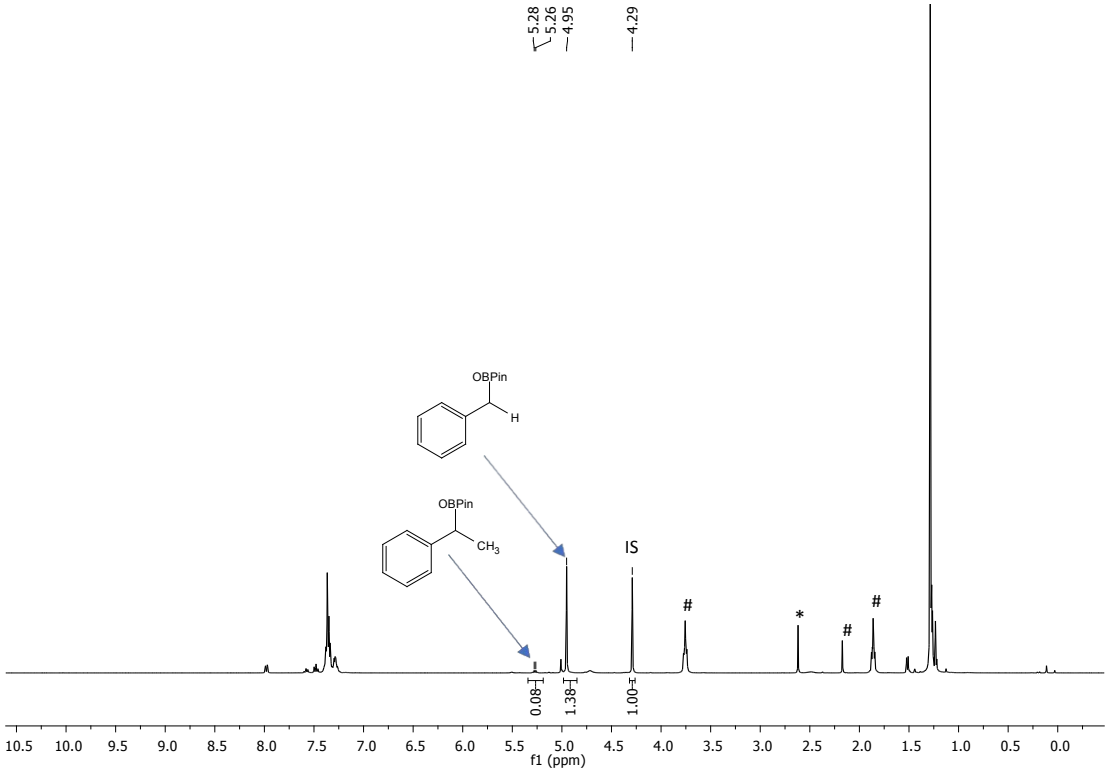


Figure S1. ^{1}H NMR spectra of competitive hydroboration reaction between benzaldehyde and acetophenone.

(a2)

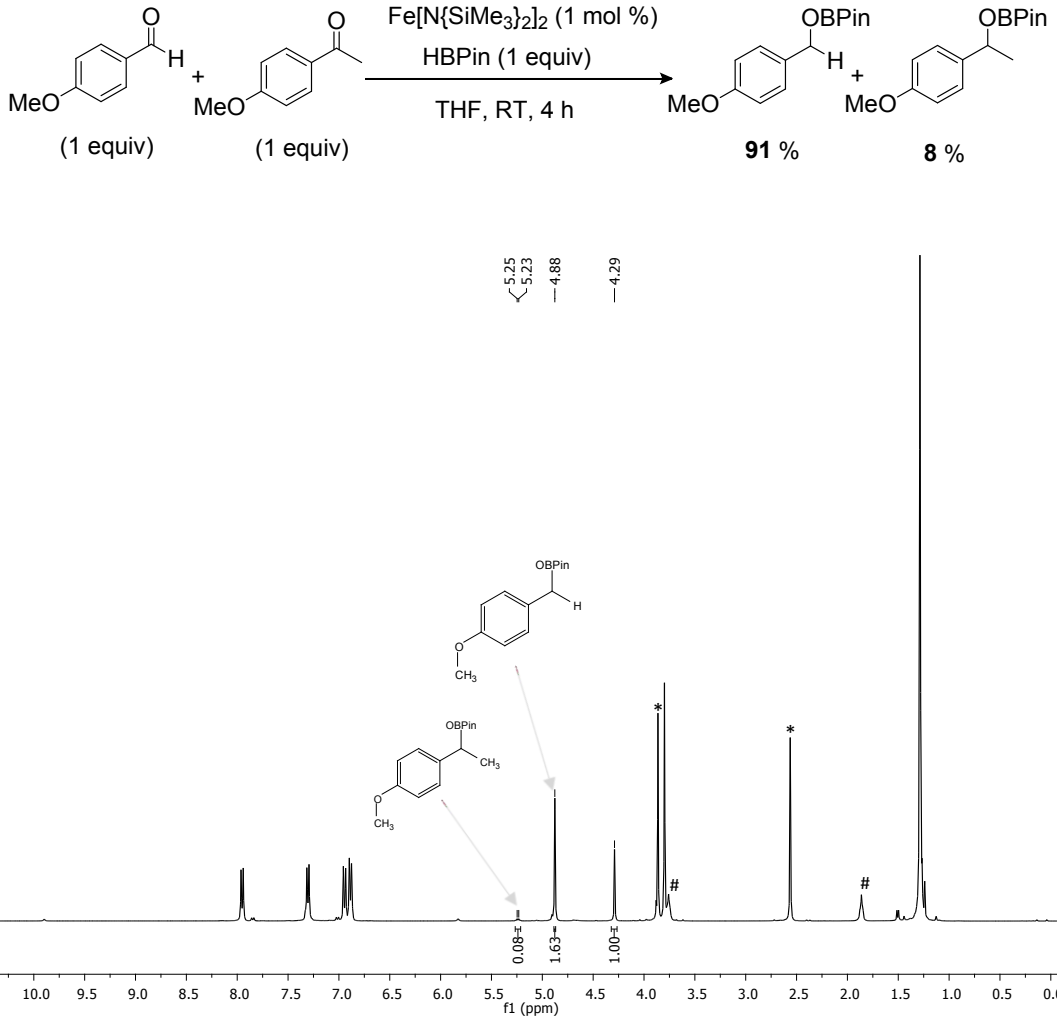
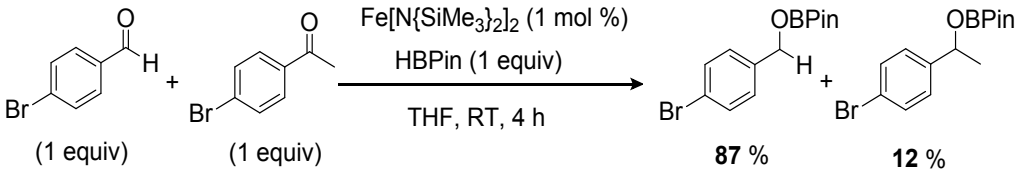


Figure S2. ^{1}H NMR spectra of competitive hydroboration reaction between *p*-methoxy benzaldehyde and *p*-methoxy acetophenone.

(a3)



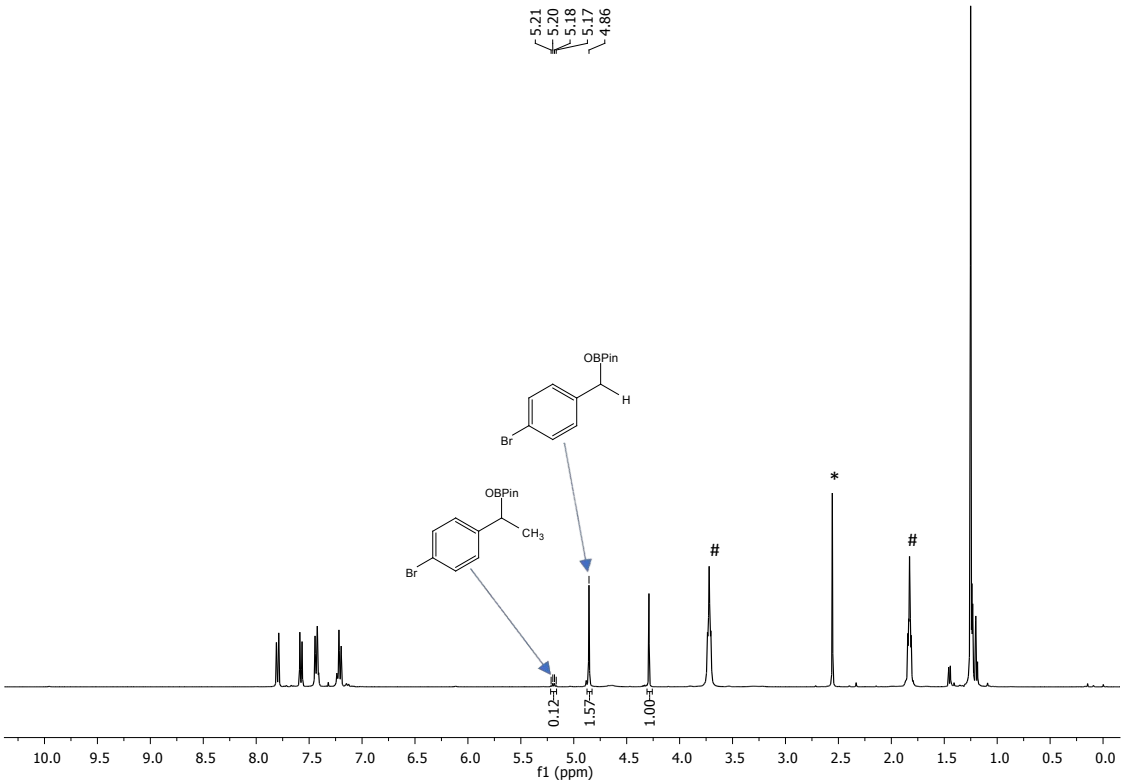
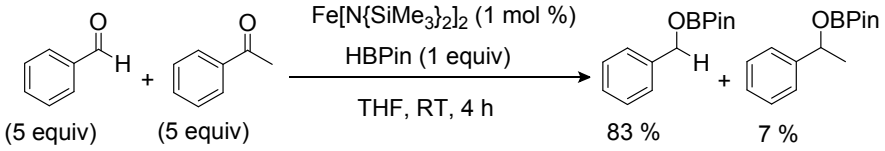


Figure S3. ^{1}H NMR spectra of competitive hydroboration reaction between *p*-bromo benzaldehyde and *p*-bromo acetophenone.

(a4)



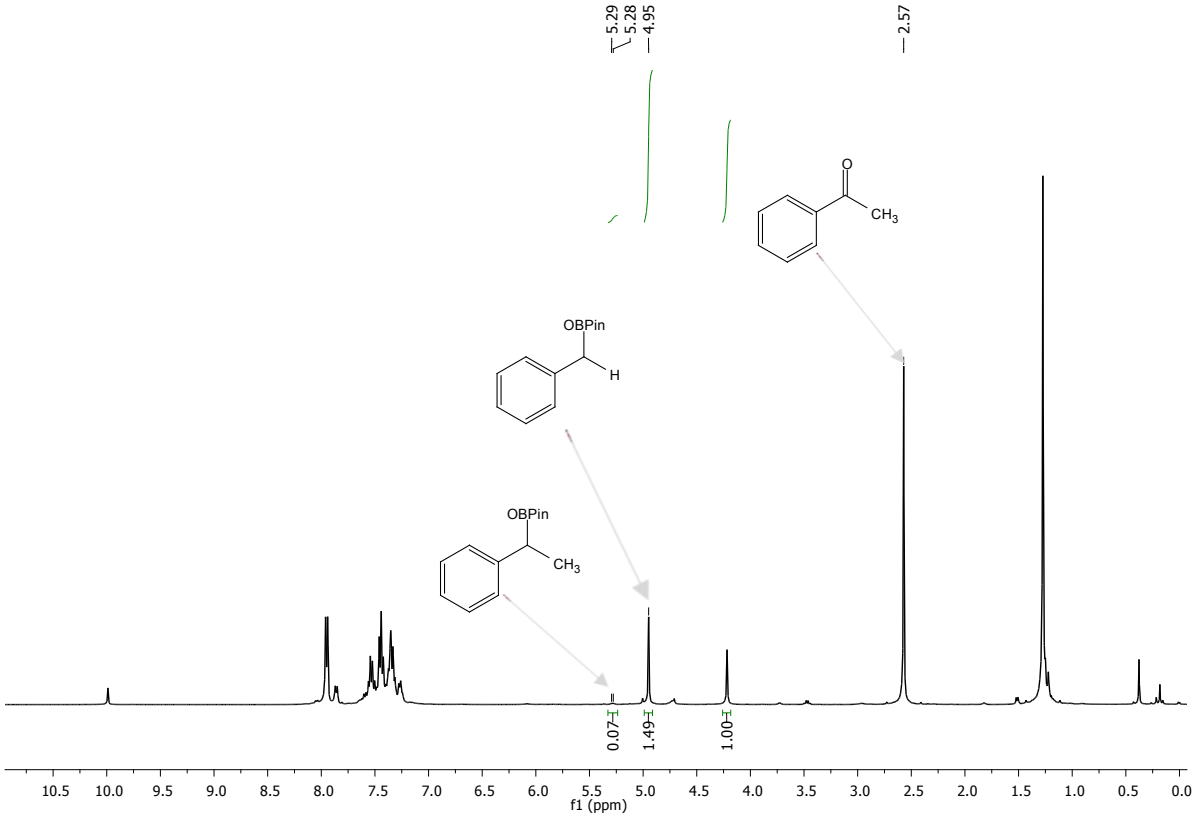


Figure S4. ^{1}H NMR spectra of competitive hydroboration reaction between benzaldehyde (5 equiv.) and acetophenone (5 equiv.).

General Procedure for Intramolecular Chemoselective Catalytic Hydroboration. In a nitrogen-filled glovebox, HBPin (0.25 mmol), THF (1 mL) and substrate (0.25 mmol) were added to a Schlenk tube equipped with a magnetic stirring bar. Then 1 mol% of **1** was added and the reaction mixture was stirred at room temperature for 4 h. The reaction mixture was diluted with diethyl ether (2 mL) and filtered through a plug of celite (Ø 3 mm × 8 mm). The solvents were removed under vacuum using Schlenk line. The products yields were determined by ^{1}H NMR using nitromethane as an internal standard.

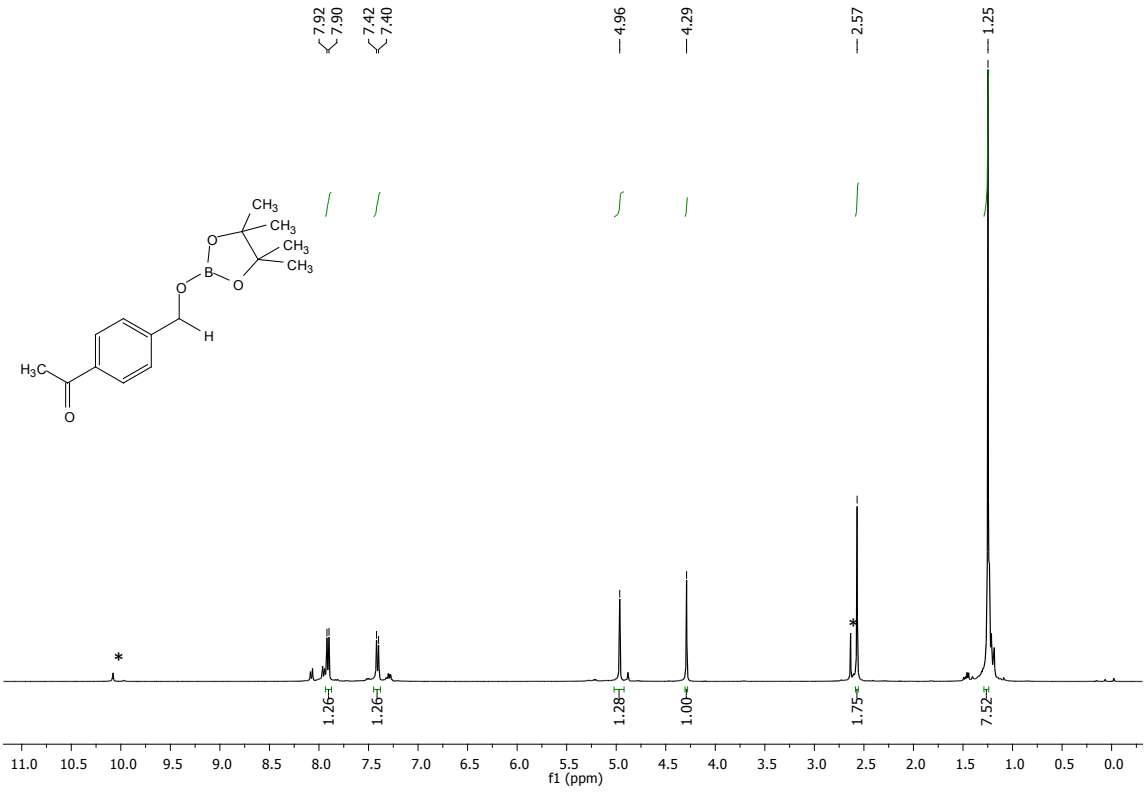


Figure S5. ^{1}H NMR spectra of competitive hydroboration reaction of 4-acetylbenzaldehyde.

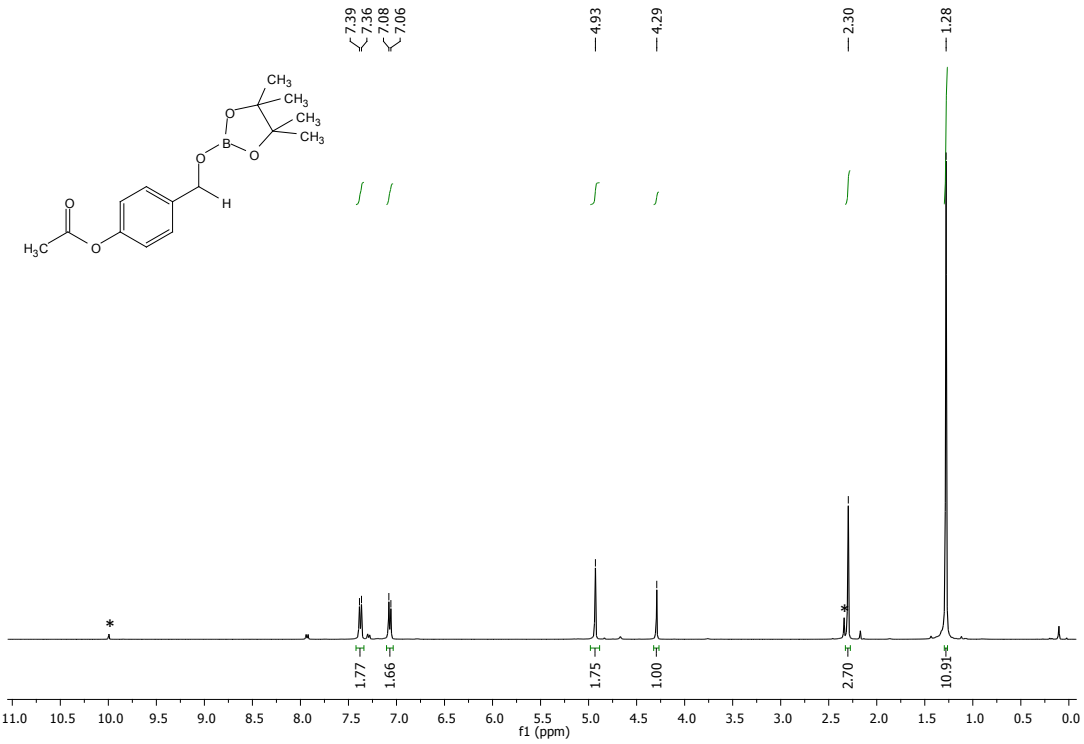


Figure S6. ^{1}H NMR spectra of competitive hydroboration reaction of 4-acetoxylbenzaldehyde.

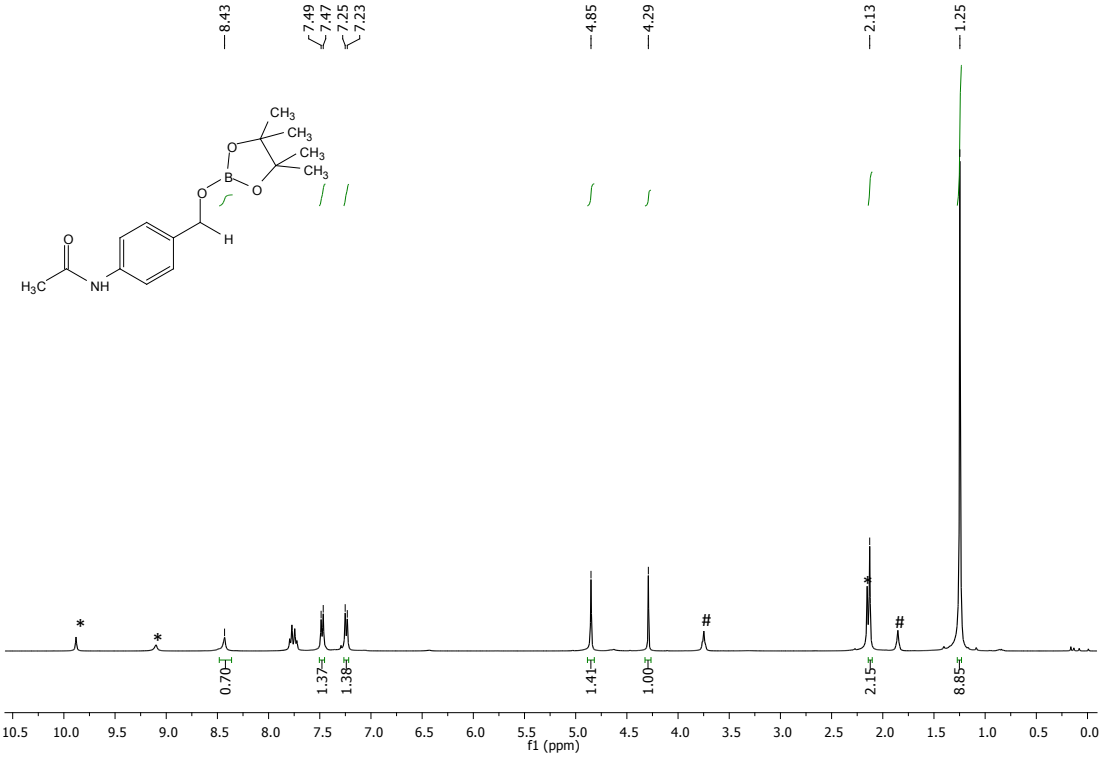


Figure S7. ^{1}H NMR spectra of competitive hydroboration reaction of 4-acetamidolbenzaldehyde.

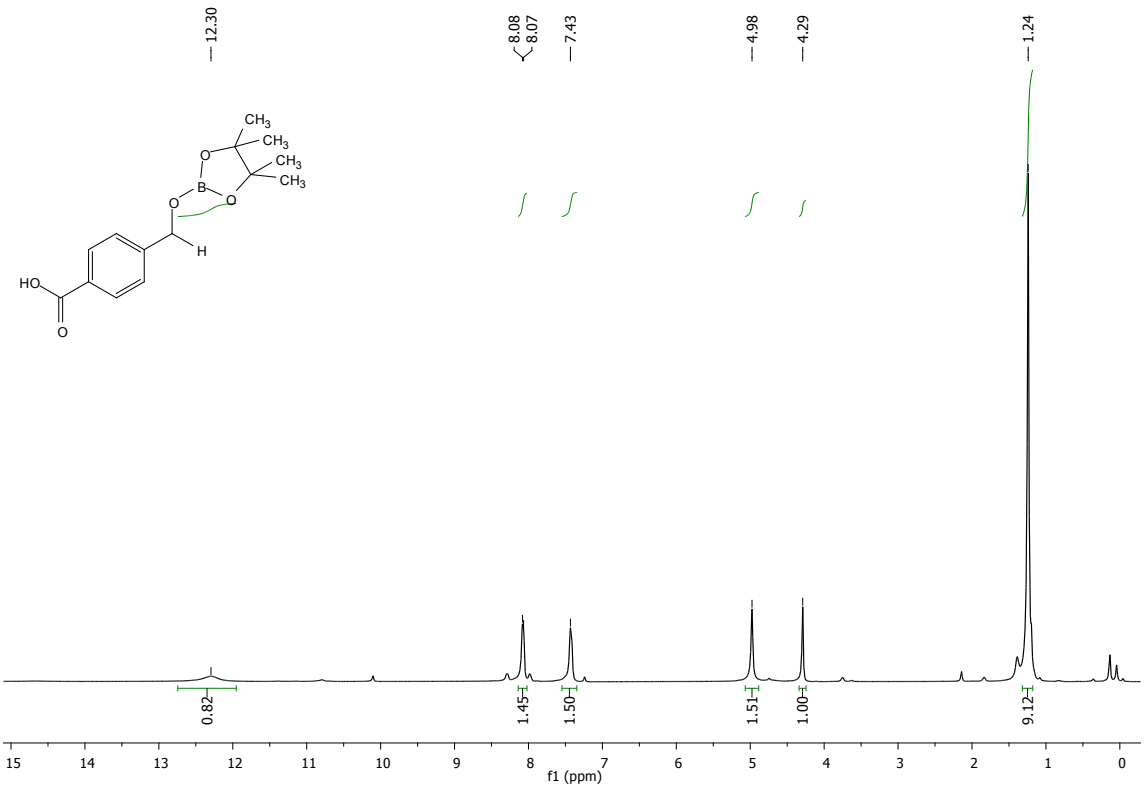


Figure S8. ^{1}H NMR spectra of competitive hydroboration reaction of Terephthaldehydic acid.

General Procedure for Intermolecular Chemoselective Catalytic Hydroboration of Aldehydes. In a nitrogen-filled glovebox, HBpin (0.25 mmol), THF (1 mL) and aldehydes (0.25 mmol) were added to a Schlenk tube equipped with a magnetic stirring bar. Then 1 mol% of **1** was added and the reaction mixture was stirred at room temperature for 4 h. The reaction mixture was diluted with diethyl ether (2 mL) and filtered through a plug of celite (Ø 3 mm × 8 mm). The solvents were removed under vacuum using Schlenk line. The products yields were determined by ^{1}H NMR using nitromethane as an internal standard.

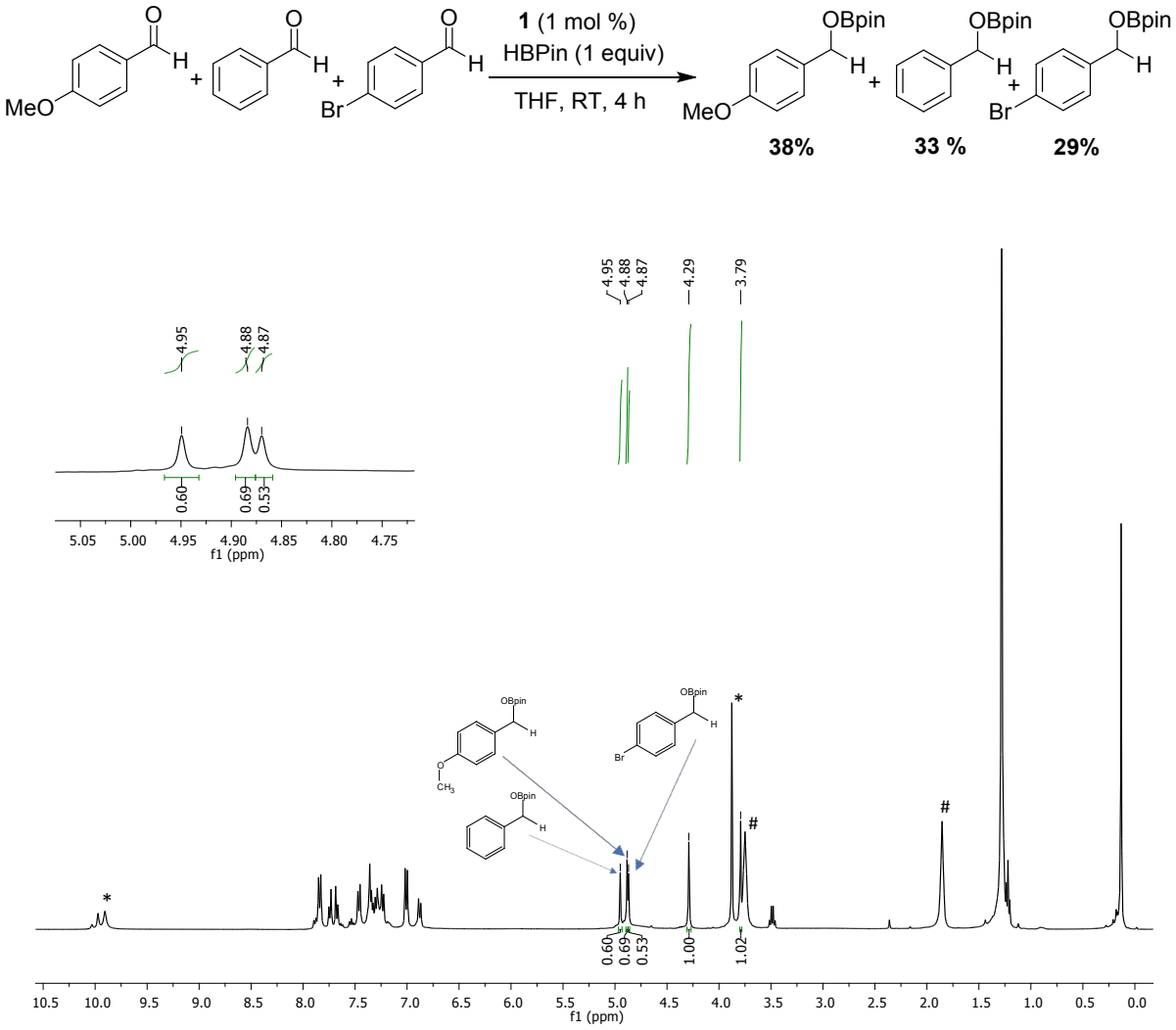


Figure S9. ^{1}H NMR spectra of competitive hydroboration reaction of *p*-methoxy benzaldehyde, benzaldehyde and *p*-bromo benzaldehyde.

VI. Mechanistic Investigations

General Procedure for Stoichiometric Reaction of Catalyst 1 with HBpin. In a nitrogen-filled glove box, **1** (20 mg, 0.0531 mmol) and HBPin (7 mg, 0.0532 mmol) were mixed in benzene-d_6 and the color of the reaction mixture changes from green to dark brown. The sample was analyzed by ^{11}B NMR at T= 10 min (Figure S10) and GC-MS analysis (Figure S11). Subsequent addition of benzaldehyde (6 mg, 0.0565 mmol) resulted a paramagnetic solution and data obtained was not informative.

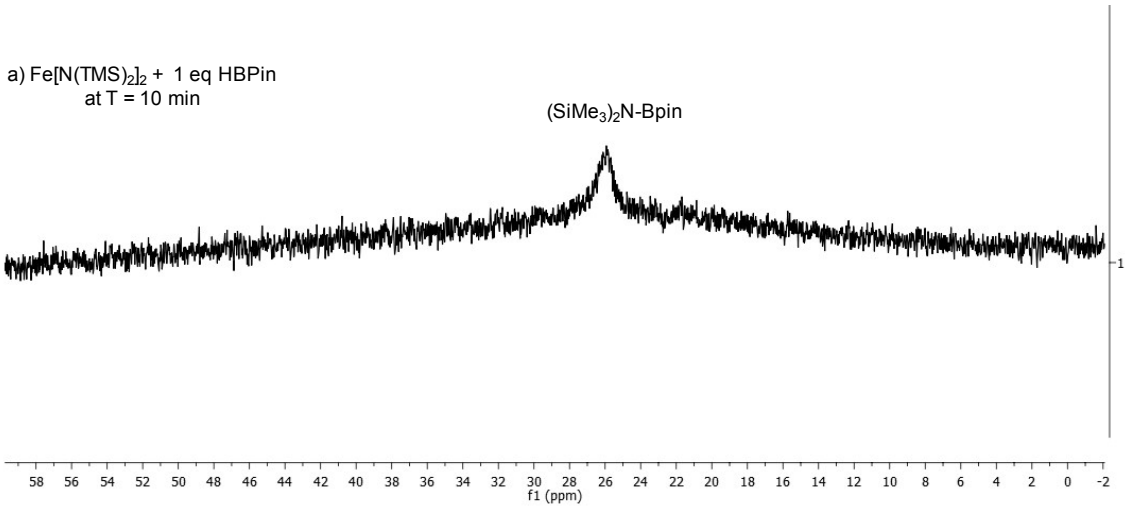


Figure S10. ^{11}B NMR spectrum of: a) $Fe[N(SiMe_3)_2]_2$ + HBpin;

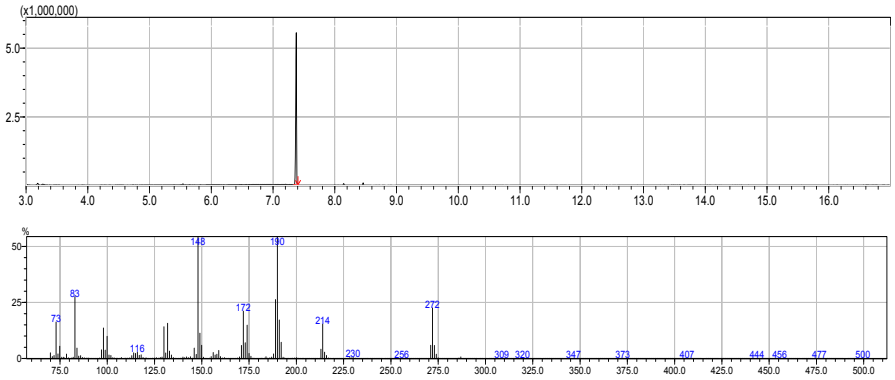


Figure S11. GC-MS of the reaction mixture ($Fe[N(SiMe_3)_2]_2$ + HBpin). Mass at 272 corresponds to pinB-$N(SiMe_3)_2$.

General Procedure for Stoichiometric Reaction of Catalyst 1 with benzaldehyde. In a nitrogen-filled glove box, **1** (20 mg, 0.0531 mmol) and C_6H_5CHO (6 mg, 0.0565 mmol) were mixed in benzene-d_6 and the color of the reaction mixture changes from green to brown. The sample was analyzed by ^{1}H and ^{11}B NMR at T= 10 min. Subsequently, 1 equiv. of HBpin (7 mg, 0.0532 mmol) was added to the reaction mixture and analyzed by ^{1}H, ^{11}B and IR spectroscopy at T= 30 min (Figure S12-14).

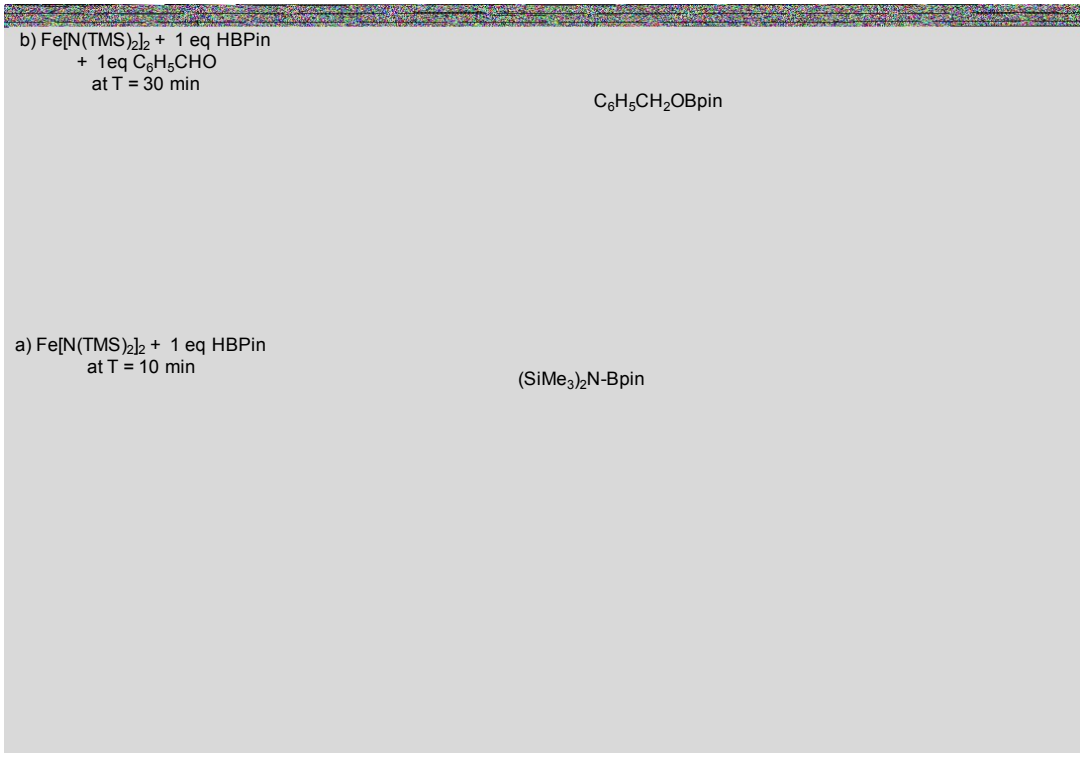


Figure S12. ^{11}B NMR of: a) $Fe[N(SiMe_3)_2]_2$ + HBpin; b) $Fe[N(SiMe_3)_2]_2$ + HBpin + C_6H_5CHO.

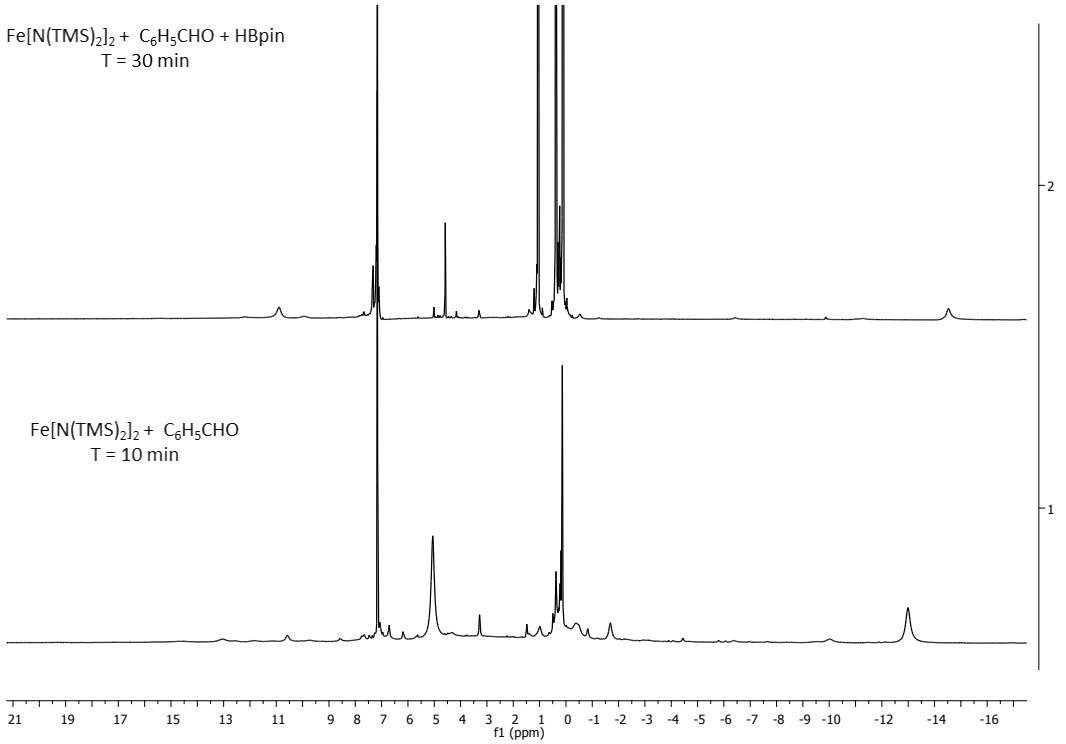


Figure S13. ^{1}H NMR of: a) $Fe[N(SiMe_3)_2]_2$ + C_6H_5CHO and b) $Fe[N(SiMe_3)_2]_2$ + C_6H_5CHO + HBpin.

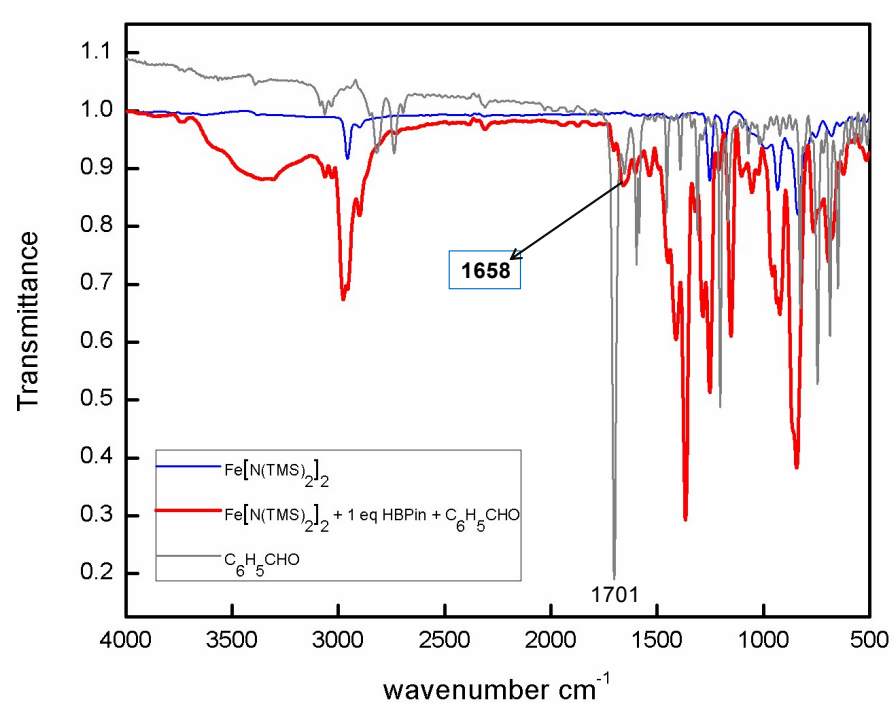


Figure S14. IR spectra of: a) $Fe[N(SiMe_3)_2]_2$; b) $Fe[N(SiMe_3)_2]_2$ + HBpin + C_6H_5CHO; c) C_6H_5CHO. The band at 1658 cm^{-1} represents the $\nu_{Fe\text{-}H}$ band.

Determination of Fe-D using IR spectroscopy.

General Procedure for stoichiometric reactions with DBpin. In a nitrogen-filled glove box catalyst **1** was added to the reaction mixture of Dbpin[20] in Toluene-d_8. The reaction mixture was analyzed by NMR and IR spectroscopy. To collect necessary information from NMR and IR studies was unsuccesful. However, subsequent addition of benzaldehyde to the reaction mixture was analysed from ^{2}H NMR and IR. The IR studies gives a broad hump at 1204 cm $^{-1}$ corespondind to Fe-D stretching resonance.[21] Whereas the ^{2}H NMR indictaes the formation of $PhCD_2OBpin$, as analysed from the peak at 4.89 ppm in toluene-d_8.

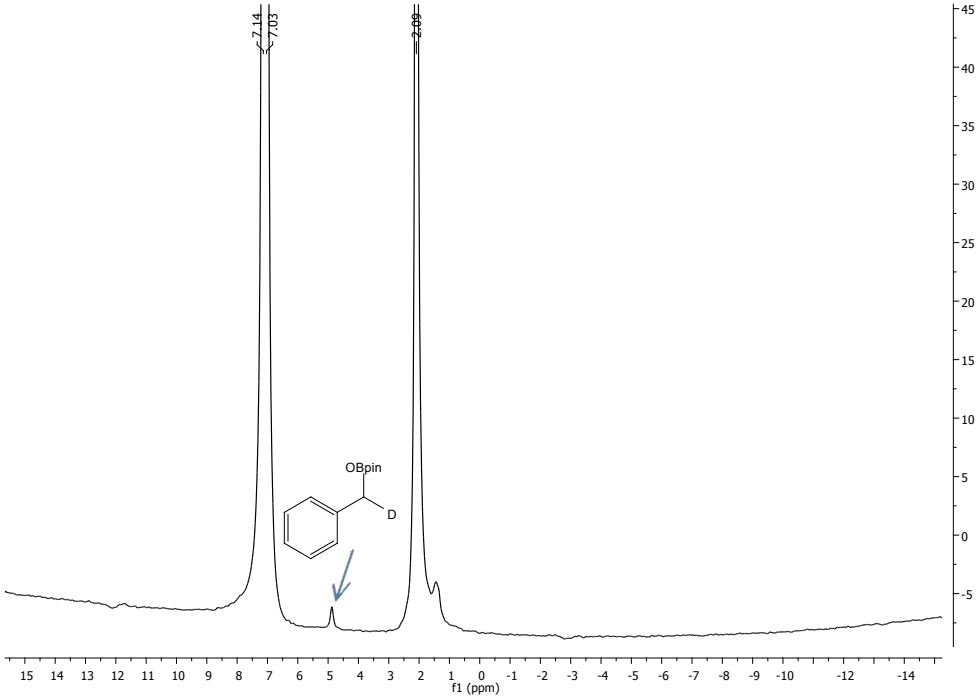


Figure S15. ^{2}H NMR of $Fe[N(SiMe_3)_2]_2$ + DBpin + C_6H_5CHO, peak at 4.89 corresponds to $PhCD_2OBpin$.

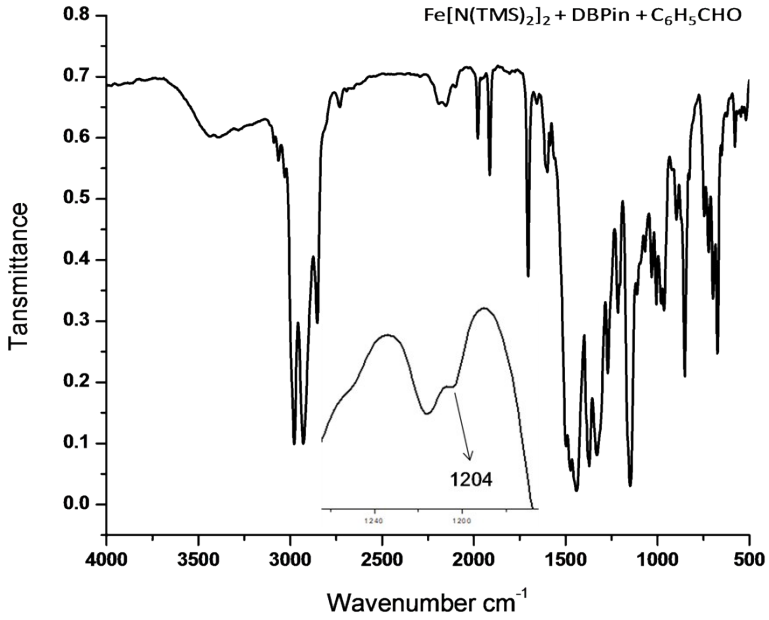


Figure S16. IR spectra of: $Fe[N(SiMe_3)_2]_2$ + DBpin + C_6H_5CHO. The band at 1204 cm^{-1} represents the $\nu_{Fe\text{-}D}$ band.

General Procedure for Mercury Poisoning Experiments. In a nitrogen-filled glovebox, HBpin (0.3 mmol), solvent (1 mL), benzaldehyde (0.25 mmol) and 1 mol% of **1** were added to a Schlenk tube equipped with a magnetic stirring bar. The poisoning reagent (Hg, 5 equiv vs substrate) was added to the reaction mixture and stirred at room temperature for 1 h. The reaction mixture was filtered through a plug of celite and solvents were removed from the light brown filtrate under vacuum using Schlenk line. The product yield was determined by ^1H NMR using nitromethane as an internal standard (Figure S17).

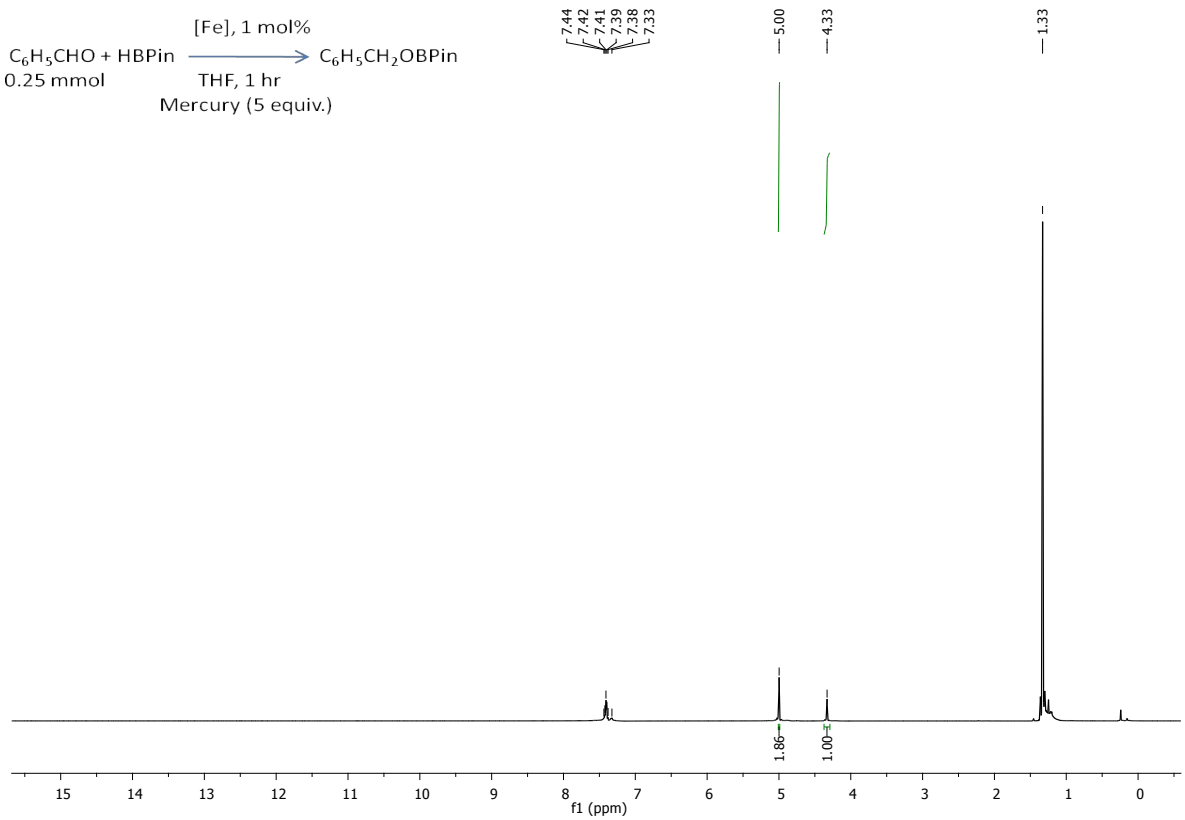


Figure S17. ^{1}H NMR spectra of hydroboration reaction of benzaldehyde and pinacolborane catalysed by $Fe[N(SiMe_3)_2]_2$ (1 mol%) in presence of mercury. (Yield - 91%) was determined by ^{1}H NMR analysis using nitromethane as an internal standard (0.081 mmol).

General Procedure for Catalyst Homogeneity: Filtrate Experiment. In a nitrogen-filled glovebox, HBPin (0.3 mmol), solvent (1 mL), benzaldehyde (0.25 mmol) and 1 mol % of **1** were added to a Schlenk tube equipped with a magnetic stirring bar. The reaction mixture was stirred at room temperature for 1 h and filtered through a plug of celite. The progress of the reaction mixture was monitored by ^{1}H NMR spectroscopy (Figure S18). For the second run, a fresh batch of substrate i.e. benzaldehyde (0.25 mmol) and HBPin (0.3 mmol) were added without adding any further catalyst into the reaction mixture. Further, reaction mixture was stirred at room temperature for 1 h and solvents were removed under high vacuum using Schlenk line. The product yield was determined by ^{1}H NMR using nitromethane as an internal standard (Figure S19).

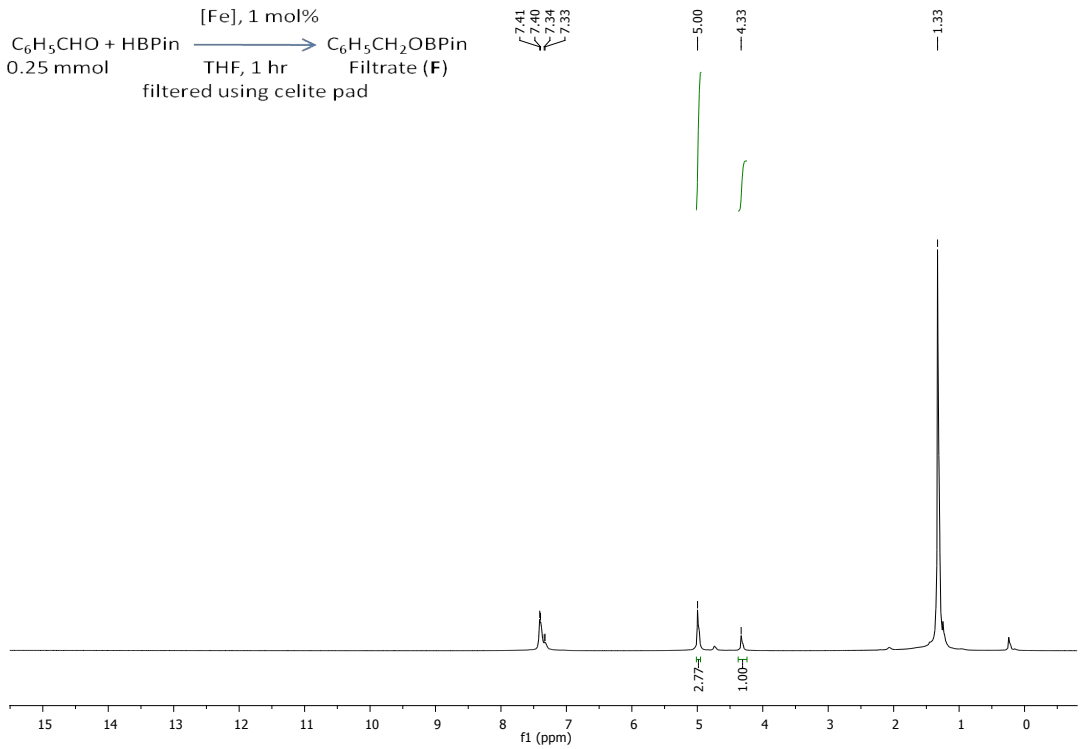


Figure S18. ^{1}H NMR spectra of hydroboration reaction of benzaldehyde and pinacolborane catalysed by $Fe[N(SiMe_3)_2]_2$ (1 mol%). (Yield - 98%) was determined by ^{1}H NMR analysis using nitromethane as an internal standard (0.058 mmol).

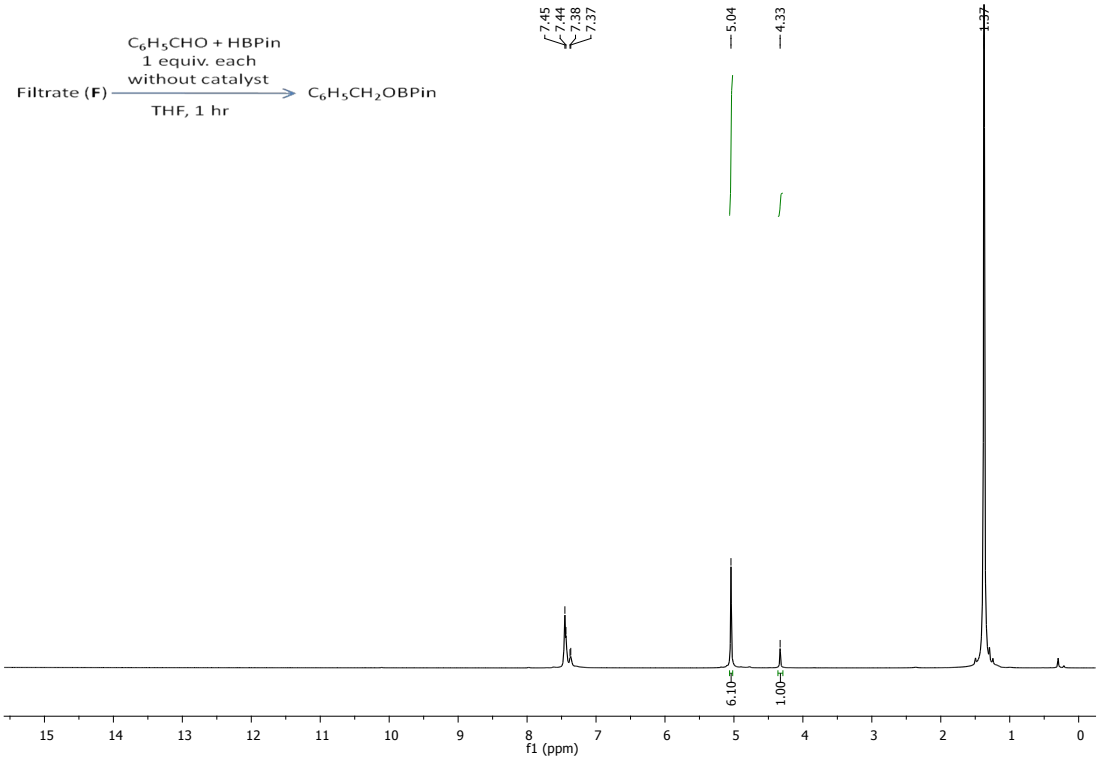


Figure S19. ^{1}H NMR spectra of filtrate, fresh batch of benzaldehyde (0.25 mmol) and pinacol borane (0.3 mmol). (Yield - 90%) was determined by ^{1}H NMR analysis using nitromethane as an internal standard (0.049 mmol).

Kinetic Experiments. Kinetic analysis of the NMR scale reaction was carried out by collecting multiple data points early in the reaction. The reaction was monitored by ^{1}H NMR (400 MHz, C_6D_6) analysis at uniform intervals over 1 hr at 298 K. The product concentration was measured from the area of the R*CH*$_2$OBpin peak relative to nitromethane (internal standard).

General Procedure for Kinetic measurements by ^{1}H NMR Experiments. In a nitrogen-filled glovebox, HBpin, Benzene-d_6 (0.5 mL), 4-methylbenzaldehyde and pre-catalyst **1** were mixed in a J. Young NMR tube. The NMR tube of the resulting solution was put in a pre-cooled bath at -30 ^{o}C. The tube was sealed immediately and removed quickly from the glovebox. It was then placed in an ethylacetate/liquid nitrogen bath and placed in the NMR probe at 298 K. The product concentration was monitored at nearly 1 min interval.

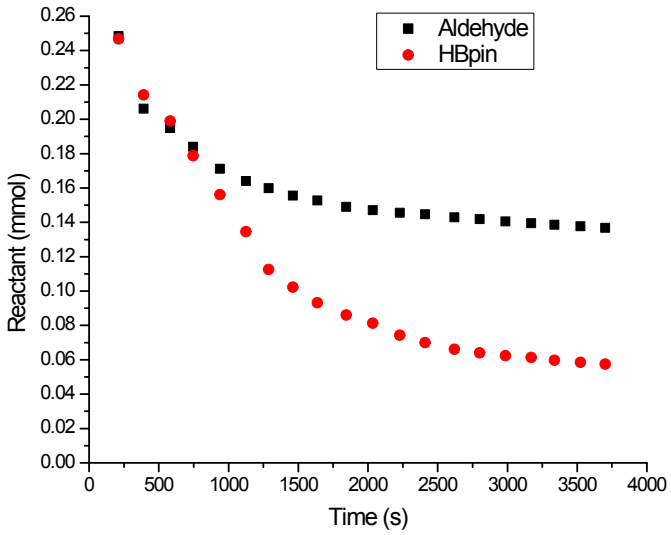


Figure S20. Rates of consumption of reactants from an equimolar reaction of HBpin (0.25 mmol) and 4-methylbenzaldehyde (0.25 mmol) by pre-catalyst **1** (0.01 mol%) in benzene-d_6. The product concentration was monitored at nearly 3 min interval.

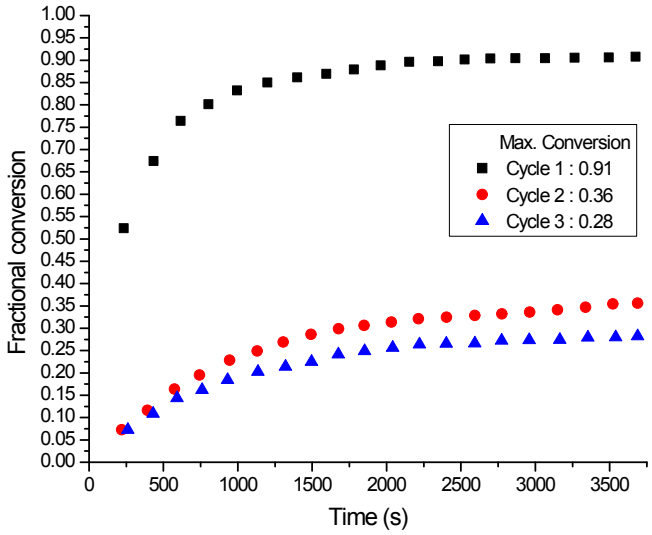


Figure S21. Comparing the catalyst proficiency for the first addition of substrates and subsequent additions. The experiment was initiated by addition of HBpin (0.25 mmol), 4-methylbenzaldehyde (0.25 mmol) and catalyst **1** (0.1 mol%) in benzene-d_6 under frozen conditions. The product concentration was monitored at nearly 3 min interval.

Determination of the Kinetic Isotope Effects. (KIE)

In a nitrogen-filled glovebox, precatalyst **1** (0.01 mol %), H(D)Bpin (0.3 mmol), 4-methylbenzaldehyde (0.25 mmol) and benzene-d_6 (0.5 mL) were loaded in a J. Young NMR tube. The NMR tube of the resulting solution was sealed and put in a pre-cooled bath at -30 ^{o}C. The reaction was monitored at every 60 s intervals over 1 hr at 298 k, data points before 26% conversion were subjected to the linear regression analysis. The KIE value was determined from the rates for each reactions.

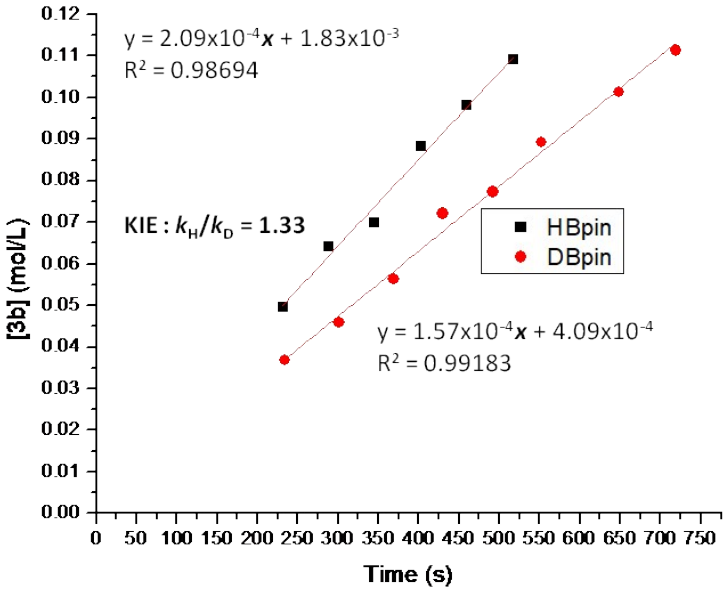
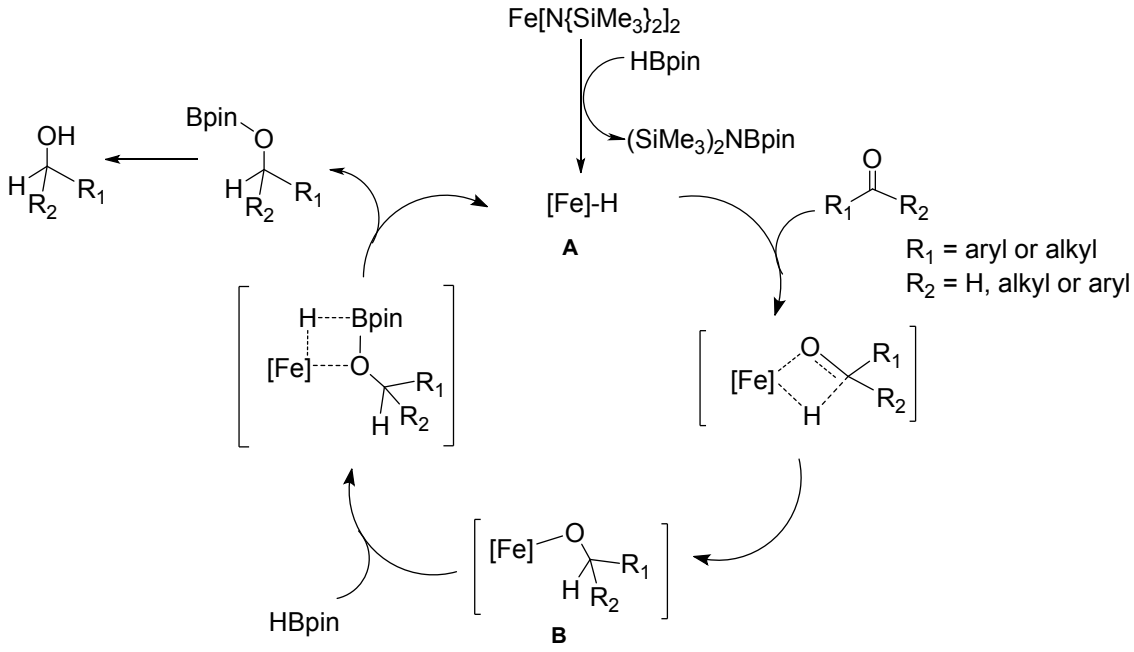


Figure S22. KIE for hydroboration of 4-methylbenzaldehyde.

Based on these experimental evidences we are proposing a Fe-H species as a key intermediate for the hydroboration of carbonyl compound and is consistent with Findlater's proposed mechanism.[12]



Scheme S1. Plausible Mechanism for Hydroboration of Carbonyl Compound.

VII. References

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