Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Reusable Fe_2O_3-nanoparticles catalysed efficient and selective hydroboration of carbonyl compounds

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Index

I. General Information……..……..……..…S3

II. Experiment Details…….....……..…....……..…..…S4-S13

III. Spectroscopic Data of Hydroboration Products and Relevant Alcohols.…….....S14-S24

IV. NMR Spectra of Hydroboration Products and Relevant Alcohols ……....…S25-S79

V. Competitive Chemoselective Hydroboration Reactions…….....…S80-S86

VI. Mechanistic Investigations……..……...….S87-S92

VII. References ……...…….…….…….....…S93

I. General Information

All reagents were purchased from Avra, Alfa-Aesar or Aldrich and were used as received. The iron precursor $Fe(NO_3)_3 \cdot 9H_2O$ and Fe_2O_3 (nanopowder, <50 nm particle size) were purchased from Aldrich. 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. HBpin for bulk reactions was prepared from B_2pin_2 according to literature procedures.[1a] Fe_2O_3 nanoparticles were prepared according to the literature procedure.[1b] 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 Avance 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) 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). ^{11}B NMR signals were quoted relative to $BF_3 \cdot Et_2O$ and ^{19}F NMR signals were quoted using $FCCl_3$ as an internal 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 SHIMADZU GCMS QP 2010SE system.

The microstructure of the Fe_2O_3 NPs was studied by Rigaku Ultima IV powder X-ray diffractometer using Cu Kα radiation (scan rate of 3° min^{-1}). Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopic (EDX) spectra were performed on a JSM 7100F JEOL FESEM with EDS, and TEM was carried out using JEOL transmission electron microscope operating at 200 kV after casting a drop of nanoparticle dispersion in isopropyl alcohol over Cu grid.

II. Experimental Details

Synthesis of Fe_2O_3 nanoparticles.[1] To a solution of $Fe(NO_3)_3 \cdot 9H_2O$ (500 mL, 0.1M), aqueous ammonia was added dropwise using dropping funnel with constant stirring until the pH of the solution reached 10. The obtained precipitate was filtered off and washed several times with distilled water. The product was dried in oven at 70 °C for 24 h followed by calcined at 500 °C in a muffle furnace for 5 h. The Fe_2O_3 nanoparticles were characterised by using field emission scanning electron microscope (FE-SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX) and powder XRD (X-ray diffraction).

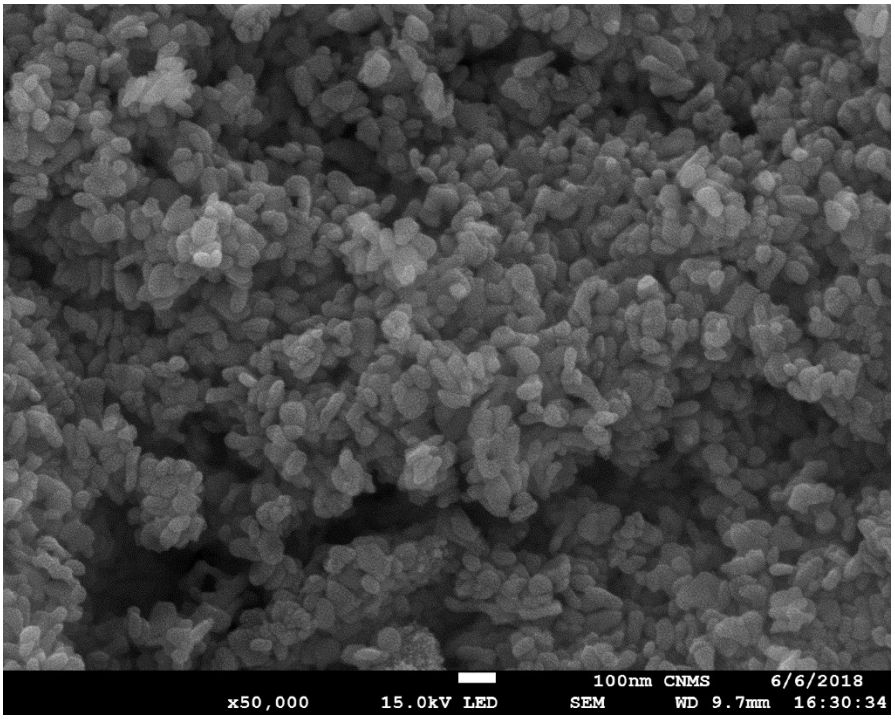


Figure S1. FESEM image of Fe_2O_3 nanoparticles.

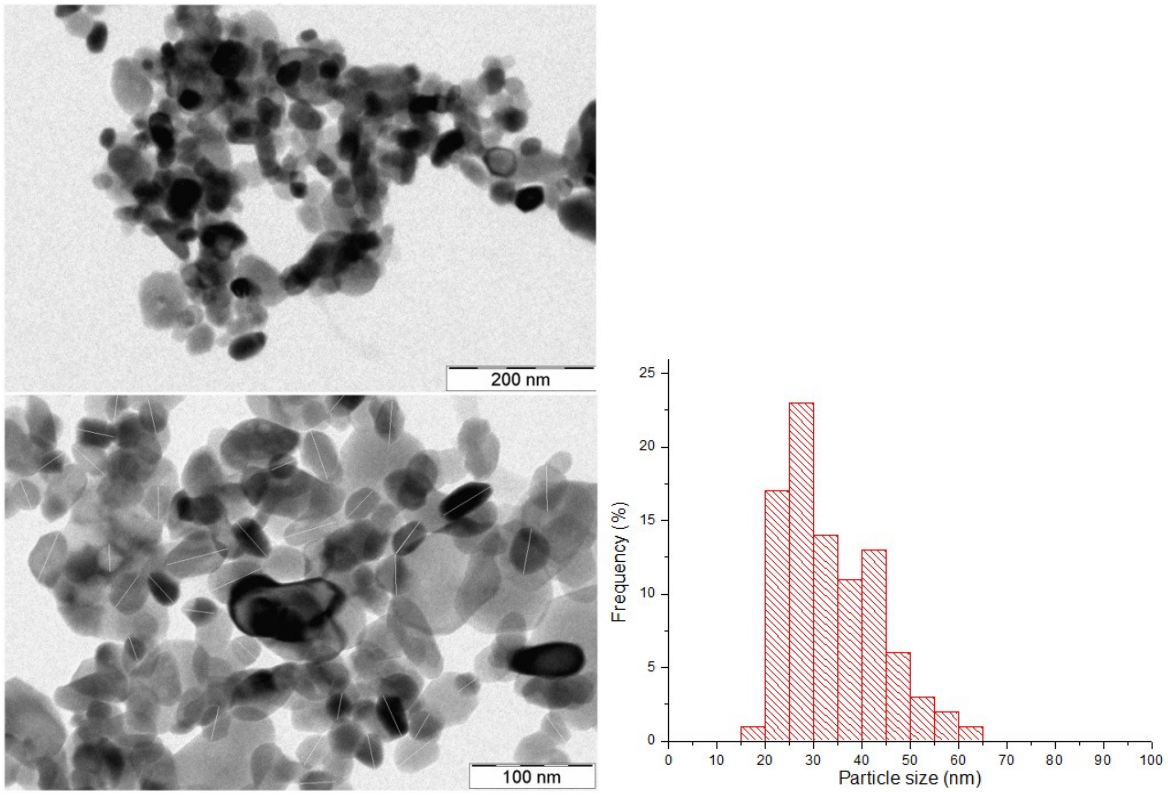
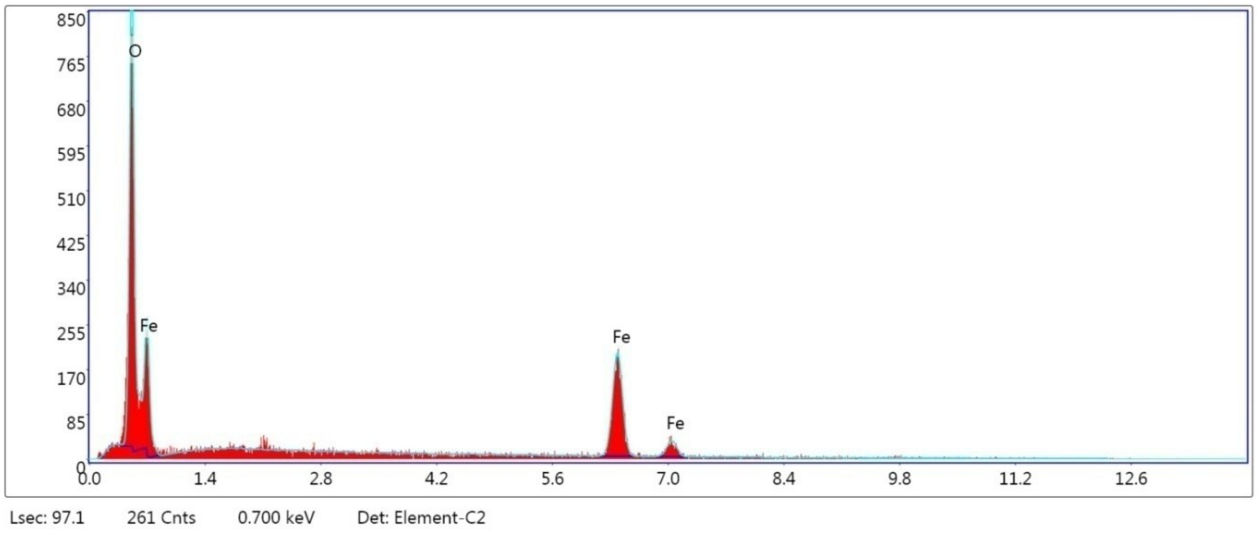


Figure S2. TEM images and particle size distribution chart of Fe_2O_3 nanoparticles.

The nanoparticle formed is characterized by transmission electron microscopy (TEM). The TEM images demonstrated that the nanoparticles were having particle size in the range of 19-62 nm and an average particle size of ~33.4 nm.



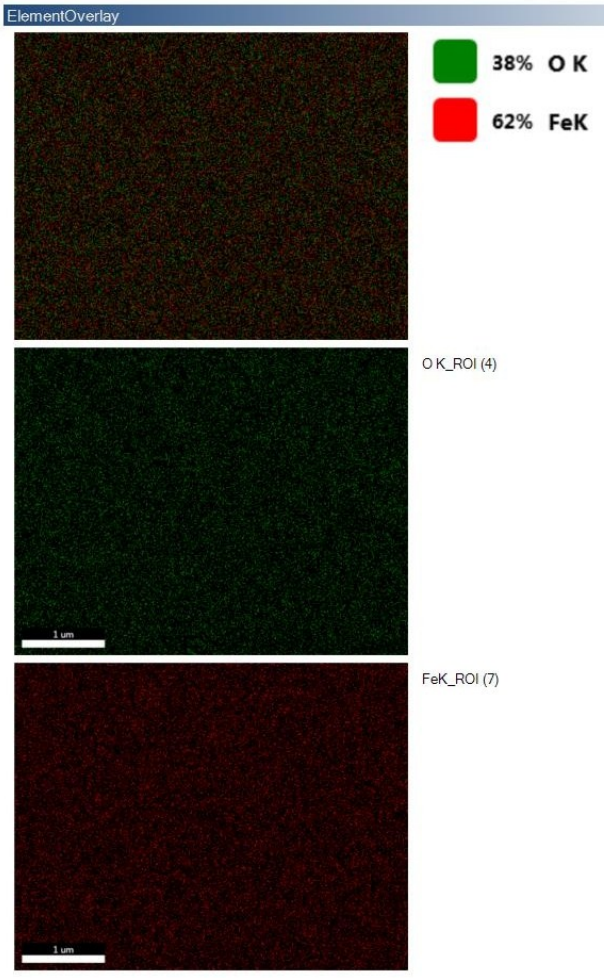


Figure S3. EDX spectrum and overlay map of Fe_2O_3 nanoparticles.

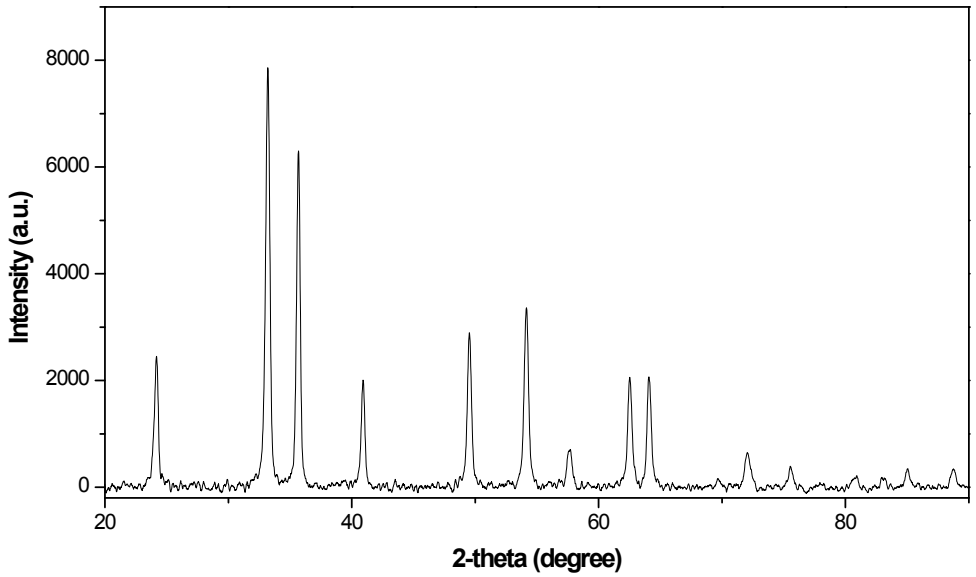
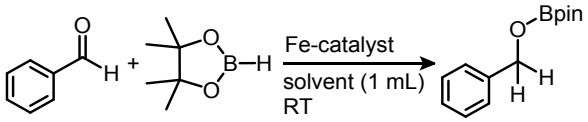


Figure S4. Powder XRD pattern of Fe_2O_3 nanoparticles.

Table S1. Optimizations of the reaction conditions for the Fe_2O_3 nanoparticle catalysed hydroboration of benzaldehyde (**1a**).[a]



Entry	Catalyst (mol%)	Temperature (°C)	Time (h)	HBpin (equiv)	Solvent (1 mL)	Product Yield (%)[b]
1	Fe_2O_3 NPs (5)	RT	1	1.2	Toluene	54
2	Fe_2O_3 NPs (5)	RT	2	1.2	Toluene	61
3	Fe_2O_3 NPs (5)	RT	4	1.2	Toluene	70
4	Fe_2O_3 NPs (5)	RT	8	1.2	Toluene	>99
5	$FeCl_3 \cdot 6H_2O$ (5)	RT	8	1.2	Toluene	22
6	$Fe(NO_3)_3 \cdot 9H_2O$ (5)	RT	8	1.2	Toluene	10
7	$FeBr_2$ (5)	RT	8	1.2	Toluene	19
8	$FeCl_3$ (5)	RT	8	1.2	Toluene	trace
9[c]	Fe_2O_3 (5)	RT	8	1.2	Toluene	45
10[d]	Fe_2O_3 (5)	RT	8	1.2	Toluene	92
10	-	RT	8	1.2	Toluene	5
11	Fe_2O_3 NPs (5)	RT	8	1.0	Toluene	88
12	Fe_2O_3 NPs (1)	RT	8	1.2	Toluene	44
13	Fe_2O_3 NPs (3)	RT	8	1.2	Toluene	66
14	Fe_2O_3 NPs (5)	RT	8	1.2	Benzene	98
15	Fe_2O_3 NPs (5)	RT	8	1.2	MTBE	88
16	Fe_2O_3 NPs (5)	RT	8	1.2	Et_2O	98
17[e]	Fe_2O_3 NPs (5)	RT	8	1.2	Toluene	90

[a] Reactions were carried out using 0.25 mmol of **1a** (1 equiv), 1.2 equiv of HBpin (0.30 mmol) in 1 mL of solvent at room temperature unless otherwise stated. [b] Yields were determined by ^{1}H NMR analysis, using nitromethane as an internal standard and are average of two experiments. [c] Reaction was performed using commercially available bulk Fe_2O_3. [d] Reaction was performed using commercially available Fe_2O_3 NPs (nanopowder, <50 nm particle size). [e] Reaction performed in air.

Experimental procedures for examples described in Table 1.

In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, Fe-catalyst (0.0125 mmol), HBpin (0.3 mmol), benzaldehyde (0.25 mmol) and solvent (1 mL) were added. 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 solvents were removed *in vacuo*, and nitromethane was added as an internal standard.

The product yield was determined by ^{1}H NMR spectroscopy using nitromethane as an internal standard.

General procedure of hydroborations of aldehydes (examples described in Tables 2). In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, Fe_2O_3 NPs (5 mol %, 2 mg, 0.0125 mmol), HBpin (1.2 equiv, 44 µL, 0.3 mmol), toluene (1 mL) and aldehyde (0.25 mmol) were added and the reaction was stirred vigorously at room temperature for 8 h. The reaction mixture was then diluted with Et_2O (2 mL) and filtered through a plug of celite (Ø 3 mm × 8 mm) with copious washing (Et_2O). The solvents were removed *in vacuo*, and the borate ester yield was determined by ^{1}H NMR spectroscopy using nitromethane as an internal standard.

General procedure of hydroborations of ketones (examples described in Tables 3). In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, Fe_2O_3 NPs (5 mol %, 2 mg, 0.0125 mmol), HBpin (1.2 equiv, 44 µL, 0.3 mmol), toluene (1 mL) and ketone (0.25 mmol) were added and the reaction mixture was stirred vigorously at room temperature for 18 h. The reaction mixture was then diluted with Et_2O (2 mL) and filtered through a plug of celite (Ø 3 mm × 8 mm) with copious washing (Et_2O). The solvents were removed *in vacuo*, and the borate ester yield was determined by ^{1}H NMR spectroscopy using nitromethane as an internal standard.

Experimental procedures for catalytic conversion of aldehydes/ketones to 1º/2º alcohols: In a 50 mL round bottom flask equipped with a magnetic stirring bar, 5 mol % of Fe_2O_3 (5 mol %, 0.05 mmol, 8 mg), HBpin (1.2 mmol, 174 µL), toluene (4 mL) and aldehyde (1.0 mmol) were added. The resulting reaction mixture was stirred vigorously at room temperature for 8 h (for ketone 18 h) and the progress of the reaction was monitored by TLC. After completion of the reaction, it was diluted with diethyl ether (10 mL) and filtered through a plug of celite (Ø 3 mm × 8 mm). The solvents were removed *in vacuo*, and then methanol (5 mL) and 1N HCl (1 mL) were added to the reaction mixture and was refluxed at 50 ºC for 1 h (for ketone 3 h). The organic layer was extracted with dichloromethane (3 x 10 mL) and was removed by vacuum to get the crude compound. The crude residue was purified by silica gel column chromatography using a mixture of hexane and ethyl acetate as eluent and characterized by ^{1}H and ^{13}C NMR spectroscopy.

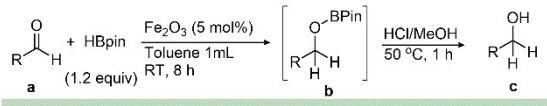
Alternative hydrolysis method: The resulted borate ester residue was hydrolysed with silica gel at 50 °C for 2-4 h. Then the organic layer was extracted with dichloromethane (3 x 10 mL) and the volatiles were removed under vacuum and the residue was purified by silica gel column chromatography using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

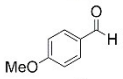
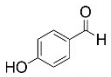
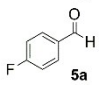
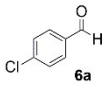
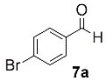
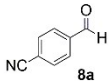
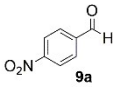
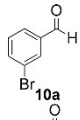
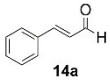
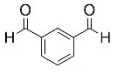
General procedure for preparative scale reactions.

In a 100 mL round bottom flask equipped with a magnetic stirring bar, 10 mol % of Fe_2O_3 (0.5 mmol, 80 mg), HBpin (1.2 equiv, 6.0 mmol, 0.87 mL), toluene (10 mL) and aldehyde (5.0 mmol) were added. The resulting reaction mixture was stirred vigorously at room temperature for 8 h and the progress of the reaction was monitored by TLC. After completion of the reaction, it was diluted with diethyl ether (50 mL) and filtered through a plug of celite. The solvents were removed *in vacuo*, and then methanol (10 mL) and 1N HCl (2 mL) were added to the reaction mixture and was refluxed at 50 ºC for 1 h. The organic layer was extracted with dichloromethane (3 x 20 mL) and was removed by vacuum to get the crude compound. The crude residue was purified by silica gel column chromatography using a mixture of hexane and ethyl acetate as eluent and characterized by ^{1}H and ^{13}C NMR spectroscopy.

The hydroboration of 4-bromobenzaldehyde (**7a**, 0.925 gm, 5 mmol), 2-methylbenzaldehyde (**11a**, 0.6 gm, 5 mmol) and 1-naphthaldehyde (**12a**, 0.781 gm, 5 mmol) gave the desired alcohols in good yields (**7c**: 0.804 gm, 87%; **11c**: 0.439 gm, 73% and **12c**: 0.484 gm, 62%).

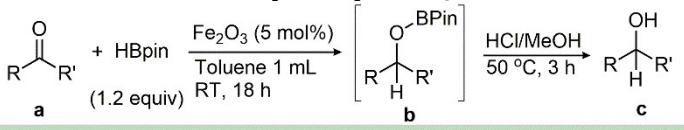
Table S2. Hydroboration of aldehydes catalysed by Fe_2O_3 NPs.[a]

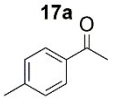
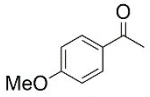
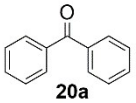
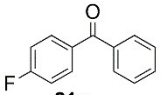
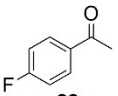
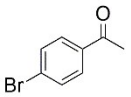
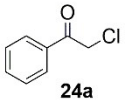
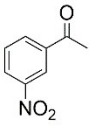
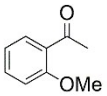
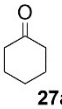
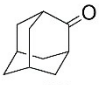


Entry	Aldehyde	Borate ester yield (%)[b]	1° alcohol yield (%)[c]
1	 **1a**	**1b:** >99	**1c:** 80
2	 **2a**	**2b:** >99	**2c:** 69
3	 **3a**	**3b:** >99	**3c:** 70
4	 **4a**	**4b:** 69	
5	 **5a**	**5b:** >99	**5c:** 86
6	 **6a**	**6b:** >99	**6c:** 63
7	 **7a**	**7b:** >99	**7c:** 79
8	 **8a**	**8b:** >99	**8c:** 78
9	 **9a**	**9b:** 83	**9c:** 70
10	 **10a**	**10b:** >99	**10c:** 76
11	 **11a**	**11b:** >99	**11c:** 84
12	 **12a**	**12b:** >99	**12c:** 87
13	 **13a**	**13b:** >99	
14	 **14a**	**14b:** 74	**14c:** 69
15	 **15a**	**15b:**[d] >99	
16	 **16a**	**16b:** 82	**16c:** 54

[a] Reaction conditions: Aldehyde (1.0 mmol), Fe_2O_3 NPs (5 mol %, 0.05 mmol, 8 mg), HBpin (1.2 mmol, 174 μL) and toluene (2 mL), at room temperature for 18 h unless otherwise stated. [b] The yields were determined by ^{1}H NMR analysis using nitromethane as an internal standard. [c] Isolated yield after chromatographic workup. [d] Reaction was performed using 2.2. equiv of HBpin.

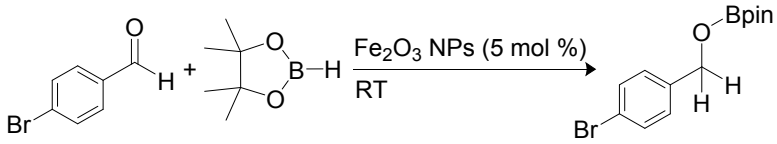
Table S3. Hydroboration of ketones catalysed by Fe_2O_3 NPs.[a]



Entry	Ketone	Borate ester yield (%)[b]	2° alcohol yield (%)[c]
1	 **17a**	**17b:** 82	**17c:** 70
2	 **18a**	**18b:** 70	**18c:** 58
3	 **19a**	**19b:** 77	**19c:** 61%
4	 **20a**	**20b:** >99	**20c:** 71%
5	 **21a**	**21b:** >99	**21c:** 72
6	 **22a**	**22b:** 84	**22c:** 62
7	 **23a**	**23b:** >99	**23c:** 82
8	 **24a**	**24b:** 58	**24c:** 35
9	 **25a**	**25b:** 63	**25c:** 48
10	 **26a**	**26b:** 70	**26c:** 52
11	 **27a**	**27b:** 49	
12	 **28a**	**28b:** 85	**28c:** 64

[a] Reaction conditions: ketone (1.0 mmol), Fe_2O_3 NPs (5 mol %, 0.05 mmol, 8 mg), HBpin (1.2 mmol, 174 µL) and toluene (2 mL), at room temperature for 18 h unless otherwise stated. [b] The yields were determined by ^{1}H NMR analysis using nitromethane as an internal standard. [c] Isolated yield after chromatographic workup.

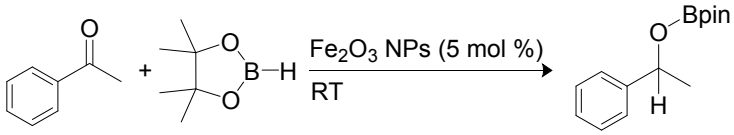
Table S4. Solvent effect on the Fe_2O_3 nanoparticle catalysed hydroboration of 4-bromobenzaldehyde (**7a**).[a]



Entry	Catalyst (mol%)	Temperature (°C)	Time (h)	HBpin (equiv)	Solvent (1 mL)	Product Yield (%)[b]
1	Fe_2O_3 NPs (5)	RT	8	1.2	Toluene	>99
2	Fe_2O_3 NPs (5)	RT	8	1.2	-	84
3	-	RT	8	1.2	-	18

[a] Reactions were carried out using 0.25 mmol of **7a** (1 equiv), 1.2 equiv of HBpin (0.30 mmol) in 1 mL of solvent at room temperature unless otherwise stated. [b] Yields were determined by ^{1}H NMR analysis, using nitromethane as an internal standard.

Table S5. Solvent effect on the Fe_2O_3 nanoparticle catalysed hydroboration of acetophenone (**17a**).[a]

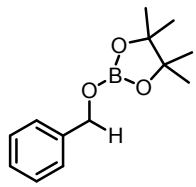


Entry	Catalyst (mol%)	Temperature (°C)	Time (h)	HBpin (equiv)	Solvent (1 mL)	Product Yield (%)[b]
1	Fe_2O_3 NPs (5)	RT	18	1.2	Toluene	82
2	Fe_2O_3 NPs (5)	RT	18	1.2	-	73

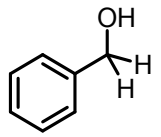
[a] Reactions were carried out using 0.25 mmol of **17a** (1 equiv), 1.2 equiv of HBpin (0.30 mmol) in 1 mL of solvent at room temperature unless otherwise stated. [b] Yields were determined by ^{1}H NMR analysis, using nitromethane as an internal standard.

III. Spectroscopic Data of Hydroboration Products and Relevant Alcohols

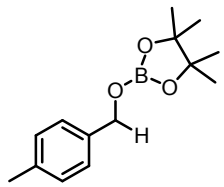
2-(Benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**Table 2, 1b**).[2,3] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38-7.29 (m, 5H), 4.96 (s, 2H), 1.30 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.4.



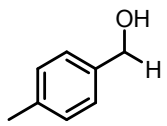
Phenylmethanol (**1c**).[2,4] **C**olourless oil. Yield: 80% (86 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.39-7.32 (m, 5H), 4.65 (s, 2H), 2.78 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 141.0, 128.7, 127.7, 127.1, 65.4.



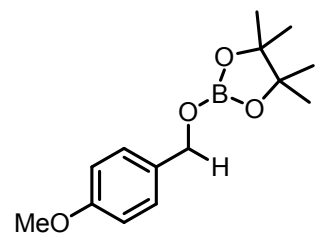
4,4,5,5-Tetramethyl-2-((4-methylbenzyl)oxy)-1,3,2-dioxaborolane (Table 2, 2b).[2,3] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.30 (d, *J* = 8 Hz, 2H), 7.20 (d, *J* = 8 Hz, 2H), 4.94 (s, 2H), 2.39 (s, 3H), 1.32 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.3.



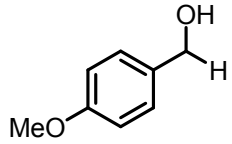
***p*-Tolylmethanol (2c)**.[2,4] Colourless oil. Yield: 69% (84 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.21 (d, *J* = 8 Hz, 2H), 7.14 (d, *J* = 8 Hz, 2H), 4.58 (s, 2H), 2.33 (s, 3H), 2.09 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 138.0, 137.4, 129.3, 127.2, 65.2, 21.2.



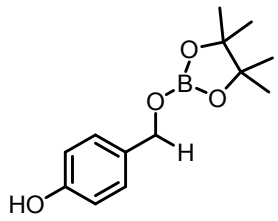
2-((4-Methoxybenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 3b).[2,3] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.33 (d, *J* = 8 Hz, 2H), 6.92 (d, *J* = 8 Hz, 2H), 4.90 (s, 2H), 3.84 (s, 3H), 1.31 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.4.



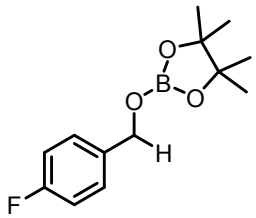
(4-Methoxyphenyl)methanol (3c).[2,5] Colourless oil. Yield: 70% (97 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.26 (d, J = 8 Hz, 2H), 6.89 (d, J = 8 Hz, 2H), 4.56 (s, 2H), 3.80 (s, 3H), 2.79 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 159.1, 133.2, 128.7, 113.9, 64.7, 55.3.



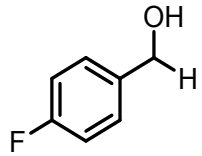
4-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)phenol (Table 2, 4b).[2,6] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.17 (d, J = 8 Hz, 2H), 6.80 (d, J = 8 Hz, 2H), 4.82 (s, 2H), 1.26 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.2.



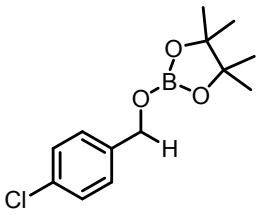
2-((4-Fluorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 5b).[2,8] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.35-7.31 (m, 2H), 7.04-7.00 (m, 2H), 4.89 (s, 2H), 1.27 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.4.



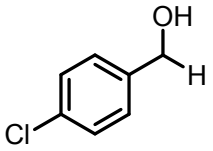
(4–Fluorophenyl)methanol (5c).[2,5] Colourless oil. Yield: 86% (108 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.32-7.29 (m, 2H), 7.06-7.02 (m, 2H), 4.60 (s, 2H), 2.70 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 162.4 (d, $J_{C–F}$ = 244 Hz), 136.7 (d, $J_{C–F}$ = 3 Hz), 128.8 (d, $J_{C–F}$ = 8 Hz), 115.4 (d, $J_{C–F}$ = 20 Hz), 64.6. ^{19}F NMR (376 MHz, $CDCl_3$, ppm): -114.91.



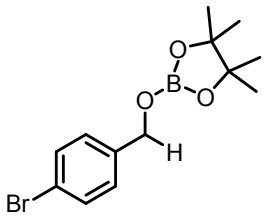
2-((4-Chlorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 6b).[2,3] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.37-7.33 (m, 2H), 7.07-7.02 (m, 2H), 4.91 (s, 2H), 1.29 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.1.



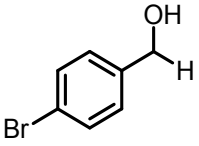
(4–Chlorophenyl)methanol (6c).[2,8] White solid. Yield: 63% (90 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.32-7.30 (m, 2H), 7.24-7.22 (m, 2H), 4.57 (s, 2H), 3.07 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 139.3, 133.3, 128.7, 128.3, 64.3.



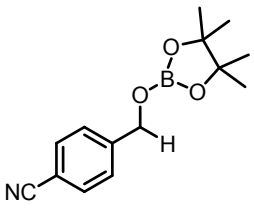
2-((4-Bromobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 7b).[2,6] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.49 (d, J = 8 Hz, 2H), 7.26 (d, J = 8 Hz, 2H), 4.90 (s, 2H), 1.30 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.4.



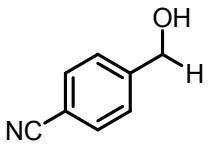
(4–Bromophenyl)methanol (7c).[2,5] White solid. Yield: 79% (148 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.45 (d, J = 8 Hz, 2H), 7.15 (d, J = 8 Hz, 2H), 4.52 (s, 2H), 3.32 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 140.2, 132.0, 129.1, 121.8, 64.7.



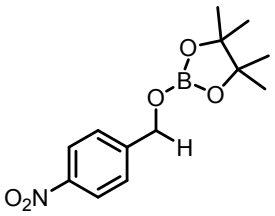
4-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzonitrile (Table 2, 8b).[2,6] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.63 (d, J = 8 Hz, 2H), 7.46 (d, J = 8 Hz, 2H), 4.99 (s, 2H), 1.27 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.3.



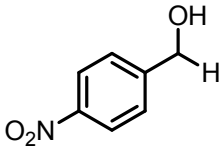
4-(Hydroxymethyl)benzonitrile (8c).[2,8] White crystalline solid. Yield: 78% (102 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.57 (d, J = 8 Hz, 2H), 7.42 (d, J = 8 Hz, 2H), 4.70 (s, 2H), 3.11 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 146.4, 132.4, 127.1, 119.0, 111.1, 64.3.



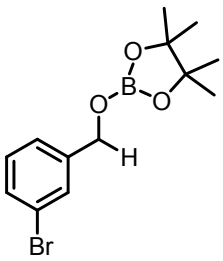
4,4,5,5-Tetramethyl-2-((4-nitrobenzyl)oxy)-1,3,2-dioxaborolane (Table 2, 9b).[2,3] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.18 (d, *J* = 8 Hz, 2H), 7.49 (d, *J* = 8 Hz, 2H), 5.01 (s, 2H), 1.26 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.4.



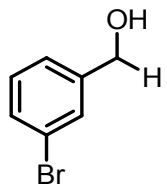
(4-Nitrophenyl)methanol (9c).[2,9] Brown crystalline solid. Yield: 70% (107 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.19 (d, *J* = 8 Hz, 2H), 7.52 (d, *J* = 8 Hz, 2H), 4.82 (s, 2H), 2.25 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.3, 147.4, 127.1, 123.9, 64.1.



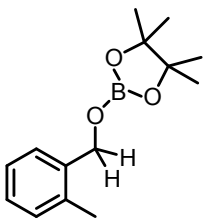
2-((3-Bromobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 10b).[2,6] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.54 (br, 1H), 7.41 (d, *J* = 8 Hz, 1H), 7.27 (d, *J* = 8 Hz, 1H), 7.23-7.19 (m, 1H), 4.91 (s, 2H), 1.29 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.3.



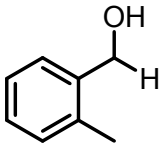
(3-Bromophenyl)methanol (10c).[2,8] Colourless oil. Yield: 76% (142 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.46 (br, 1H), 7.41-7.39 (m, 1H), 7.21-7.20 (m, 2H), 4.54 (s, 2H), 3.65 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 143.2, 130.7, 130.2, 130.0, 125.4, 122.7, 64.4.



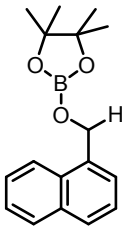
4,4,5,5-Tetramethyl-2-((2-methylbenzyl)oxy)-1,3,2-dioxaborolane (Table 2, 11b).[2,10] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.46 (br, 1H), 7.24-7.21 (m, 3H), 4.99 (s, 2H), 2.37 (s, 3H), 1.33 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.4.



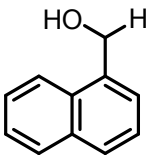
***o*-Tolylmethanol (11c)**.[2,7] Colourless oil. Yield: 84% (103 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.39-7.37 (m, 1H), 7.26-7.22 (m, 3H), 4.68 (s, 2H), 2.38 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 138.8, 136.2, 130.4, 127.9, 127.6, 126.2, 63.5, 18.7.



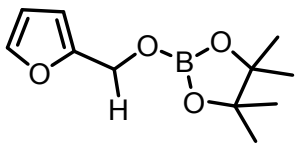
4,4,5,5-Tetramethyl-2-(naphthalen-1-ylmethoxy)-1,3,2-dioxaborolane (Table 2, 12b).[2,3] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.19-8.16 (m, 1H), 7.99-7.90 (m, 1H), 7.73-7.71 (m, 1H), 7.64-7.55 (m, 3H), 5.54 (s, 2H), 1.40 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.5.



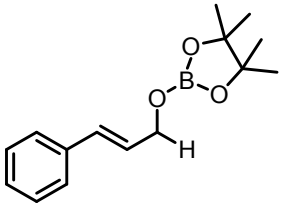
Naphthalen-2-ylmethanol (12c).[2,11] Colourless oil. Yield: 87% (138 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.12-8.10 (m, 1H), 7.93-7.91 (m, 1H), 7.85-7.83 (m, 1H), 7.58-7.45 (m, 4H), 5.10 (s, 2H), 2.40 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 136.3, 133.8, 131.3, 128.7, 128.6, 126.4, 125.9, 125.5, 125.4, 123.7, 63.6.



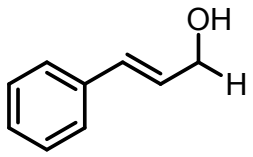
2-(Furan-2-ylmethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 13b).[2,6] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38 (br, 1H), 6.32 (br, 2H), 4.83 (s, 2H), 1.27 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 152.5, 142.4, 110.3, 108.3, 83.1, 59.2, 24.6. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.4.



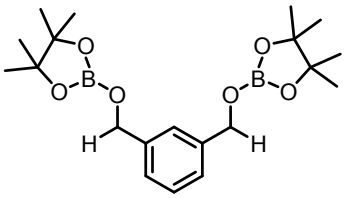
2-(Cinnamyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 14b).[2,6] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.47-7.38 (m, 2H), 7.34-7.30 (m, 2H), 7.26-7.24 (m, 1H), 6.64 (d, J = 16 Hz, 1H), 6.31 (dt, J = 16, 6 Hz, 1H), 4.56 (d, J = 6 Hz, 2H), 1.29 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.2.



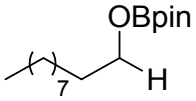
3-Phenyl-2-propene-1-ol (14c).[2,12] Colourless oil. Yield: 69% (93 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.43-7.41 (m, 2H), 7.37-7.33 (m, 2H), 7.30-7.28 (m, 1H), 6.64 (d, *J* = 16 Hz, 1H), 6.39 (dt, *J* = 16, 6 Hz, 1H), 4.35 (d, *J* = 6 Hz, 2H), 1.88 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 136.8, 131.3, 128.7, 128.6, 127.8, 126.6, 63.9.



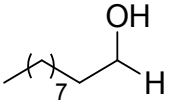
1,3-bis(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzene (Table 2, 15b).[2,3] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.34-7.25 (m, 4H), 4.92 (s, 4H), 1.26 (s, 24H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.3.



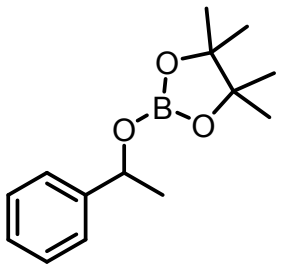
2-(Decyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 16b).[2,4] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.84 (t, *J* = 7 Hz, 2H), 1.59-1.55 (m, 2H), 1.26 (br, 26H), 0.89 (t, *J* = 7 Hz, 3H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.1.



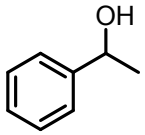
Decan-1-ol (16c).[2,4] Colorless oil. Yield: 54% (84 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.59 (t, *J* = 6 Hz, 2H), 2.16 (br, 1H), 1.55-1.50 (m, 2H), 1.26-1.24 (m, 14H), 0.85 (t, *J* = 6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 63.0, 32.9, 32.0, 29.7, 29.7, 29.6, 29.4, 25.9, 22.8, 14.2.



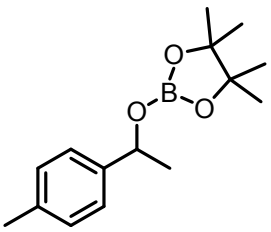
4,4,5,5-Tetramethyl-2-(1-phenylethoxy)-1,3,2-dioxaborolane (Table 3, 17b).[2,3] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.44-7.35 (m, 4H), 7.23-7.19 (m, 1H), 5.18 (q, *J* = 6 Hz, 1H), 1.42 (d, *J* = 8 Hz, 3H), 1.14 (s, 6H), 1.13 (s, 6H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.1.



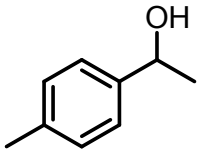
1-Phenylethanol (17c).[2,4] Colourless oil. Yield: 70% (85 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.30-7.25 (m, 4H), 7.23-7.15 (m, 1H), 4.85 (q, *J* = 7 Hz, 1H), 2.08 (br s, 1H), 1.46 (d, *J* = 7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 128.6, 127.6, 125.5, 70.5, 25.3.



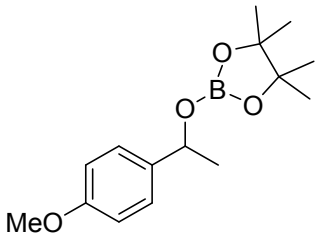
4,4,5,5-Tetramethyl-2-(1-(p-tolyl)ethoxy)-1,3,2-dioxaborolane (Table 3, 18b).[2,3] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.28 (d, *J* = 8 Hz, 2H), 7.15 (d, *J* = 8 Hz, 2H), 5.25 (q, *J* = 6 Hz, 1H), 2.35 (s, 3H), 1.50 (d, *J* = 8 Hz, 3H), 1.29 (s, 6H), 1.27 (s, 6H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.2.



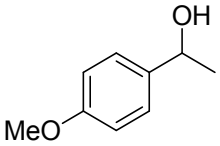
1-(p-Tolyl)ethanol (18c).[2,4] Colourless oil. Yield: 58% (79 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.29 (d, *J* = 6.4 Hz, 2H), 7.18 (d, *J* = 6.5 Hz, 2H), 4.87 (q, *J* = 6 Hz, 1H), 2.37 (s, 3H), 1.90 (s, 1H), 1.50 (d, *J* = 8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 143.0, 137.3, 129.3, 125.5, 70.4, 25.2, 21.2.



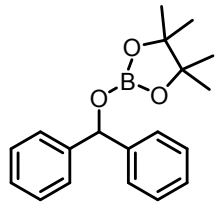
2-(1-(4-Methoxyphenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 19b).[2,3] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.31 (d, *J* = 8 Hz, 2H), 6.87 (d, *J* = 8 Hz, 2H), 5.23 (q, *J* = 6 Hz, 1H), 3.80 (s, 3H), 1.50 (d, *J* = 4 Hz, 3H), 1.26 (s, 6H), 1.23 (s, 6H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.2.



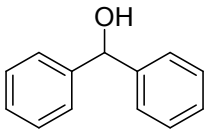
1-(4-Methoxyphenyl)ethanol (Table 3, 19c).[2] Colorless oil. Yield: 61% (92 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.21 (d, *J* = 8 Hz, 2H, Ar*H*), 6.80 (d, *J* = 8 Hz, 2H, Ar*H*), 4.73 (q, *J* = 6.4 Hz, 1H, OC*H*), 3.72 (s, 3H, OCH_3), 2.80 (s, 1H, O*H*), 1.38 (d, *J* = 4 Hz, 2H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 158.7, 138.1, 126.6, 113.7, 69.7, 55.2, 25.0.



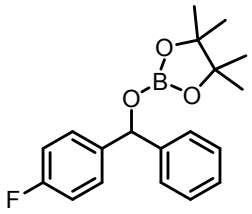
2-(Benzhydryloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 20b).[2,6] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.54-7.52 (m, 4H), 7.45-7.41 (m, 4H), 7.37-7.35 (m, 2H), 6.33 (s, 1H), 1.34 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.3.



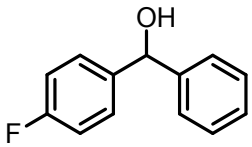
Diphenylmethanol (Table 3, 20c).[2] White solid. Yield-: 71% (129 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38-7.23 (m, 10H), 5.82 (s, 1H), 2.33 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 143.9, 128.6, 127.7, 126.7, 76.4.



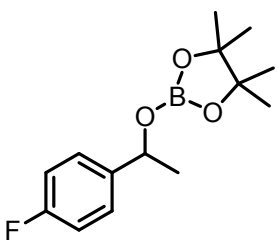
2-((4-Fluorophenyl)(phenyl)methoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 21b). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.45-7.40 (m, 5H), 7.38-7.31 (m, 2H), 7.08-7.03 (m, 2H), 6.25 (s, 1H), 1.28 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.4.



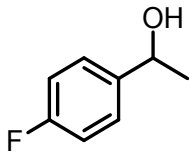
(4-Fluorophenyl)(phenyl)methanol (21c). White solid. Yield: 72% (144 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.36-7.29 (m, 7H), 7.04-7.0 (m, 2H), 5.79 (s, 1H), 2.58 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 162.3 (d, J = 245.9 Hz), 143.7, 139.6, 128.6, 128.3 (d, J = 8 Hz), 127.8, 126.5, 115.4 (d, J = 21 Hz), 75.6.



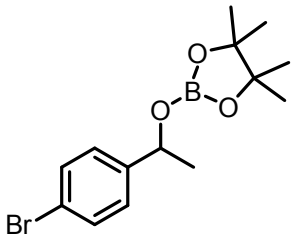
2-(1-(4-Fluorophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 22b).[2,12] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.37 (d, J = 8 Hz, 2H), 7.30 (d, J = 8 Hz, 2H), 5.37 (q, J = 6 Hz, 1H), 1.61 (d, J = 8 Hz, 3H), 1.37 (s, 6H), 1.34 (s, 6H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.1.



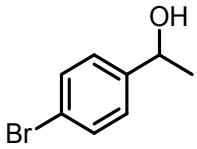
1-(4-Fluorophenyl)ethanol (22c).[2,12] Colorless oil. Yield: 62% (87 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.36-7.34 (m, 2H), 7.07-7.02 (m, 2H), 4.90 (q, *J* = 6 Hz, 1H), 2.07 (s, 1H), 1.49 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 162.2 (d, *J* = 245 Hz), 141.6, 127.2 (d, *J* = 8 Hz), 115.4 (d, *J* = 21 Hz), 69.9, 25.4. ^{19}F NMR (376 MHz, $CDCl_3$, ppm): -115.33.



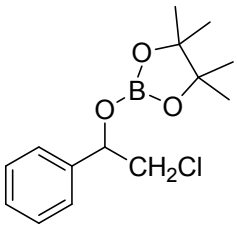
2-(1-(4-Bromophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 23b).[2,3] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.42 (d, *J* = 8 Hz, 2H), 7.40 (d, *J* = 8 Hz, 2H), 5.39 (q, *J* = 6.4 Hz, 1H), 1.64 (d, *J* = 8 Hz, 3H), 1.42 (s, 6H), 1.39 (s, 6H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.4.



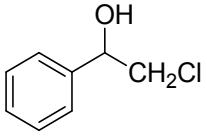
1-(4-Bromophenyl)ethanol (23c).[2,10] Colourless oil. Yield: 82% (164 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.47 (d, *J* = 8 Hz, 2H), 7.24 (d, *J* = 8 Hz, 2H), 4.85 (q, *J* = 6.4 Hz, 1H), 2.33 (s, 1H), 1.47 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 144.9, 131.7, 127.3, 121.3, 69.9, 25.4.



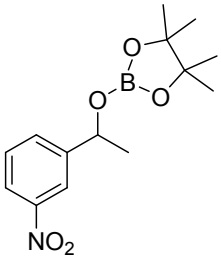
2-(2-Chloro-1-phenylethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 24b).[2,14] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.42-7.34 (m, 5H), 5.29 (m, 1H), 3.67 (m, 2H), 1.28 (s, 6H), 1.25 (s, 6H, C*H*$_3$). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.3.



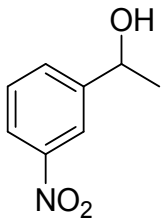
2-Chloro-1-phenylethan-1-ol (24c).[2,15] Colorless oil. Yield: 35% (54 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.39-7.34 (m, 5H), 4.88 (dt, *J* = 9, 3.3 Hz, 1H), 3.73 (dd, *J* = 11.3, 3.6 Hz, 1H), 3.64 (dd, *J* = 11.3, 8.6 Hz, 1H), 2.95 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 140.5, 129.2, 128.9, 126.6, 74.5, 51.3.



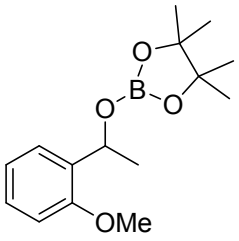
4,4,5,5-Tetramethyl-2-(1-(3-nitrophenyl)ethoxy)-1,3,2-dioxaborolane (Table 3, 25b).[2] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.20 (s, 1H), 8.09-8.07 (m, 1H), 7.69-7.67 (m, 1H), 7.50-7.46 (m, 1H), 5.30 (q, *J* = 6.4 Hz, 1H), 1.50 (d, *J* = 6.5 Hz, 3H), 1.24 (s, 6H), 1.20 (s, 6H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.3.



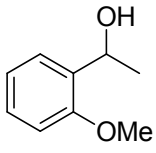
1-(3-Nitrophenyl)ethanol (25c).[2] Brown solid. Yield: 48% (79 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.23 (s, 1H), 8.10 (d, *J* = 8 Hz, 1H), 7.70 (d, *J* = 8 Hz, 1H), 7.50 (t, *J* = 8 Hz, 1H), 5.0 (q, *J* = 6.4 Hz, 1H), 2.37 (s, 1H), 1.52 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.4, 148.0, 131.7, 129.5, 122.4, 120.5, 69.4, 25.5.



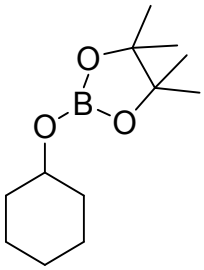
2-(1-(2-Methoxyphenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 26b).[2] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.55 (d, *J* = 8 Hz, 1H), 7.25-7.21 (m, 1H), 6.99-6.95 (m, 1H), 6.84 (d, *J* = 8 Hz, 1H), 5.59 (q, *J* = 6.3 Hz, 1H), 3.83 (s, 3H), 1.46 (d, *J* = 6 Hz, 3H), 1.27 (s, 6H), 1.24 (s, 6H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.3.



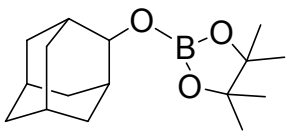
1-(2-Methoxyphenyl)ethanol (26c).[2,16] Colorless oil. Yield: 52% (78 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.37 (m, 1H), 7.28 (m, 1H), 6.99 (m, 1H), 6.91 (m, 1H), 5.13 (q, *J* = 6 Hz, 1H), 3.88 (s, 3H), 2.87 (s, 1H), 1.53 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 156.5, 133.5, 128.3, 126.1, 120.8, 110.5, 66.4, 55.3, 23.0.



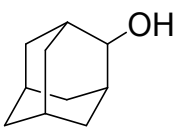
2-(Cyclohexyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 27b).[17] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.96 (m, 1H), 1.27-1.82 (m, 10H), 1.22 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.0. ^{13}C NMR (100 MHz, $CDCl_3$): δ 82.5, 72.7, 34.3, 25.5, 24.6, 23.8.



2-(Adamantan-2-yloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 28b).[17] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.17 (m, 1H), 2.13-1.41 (m, 14H), 1.23 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.0.



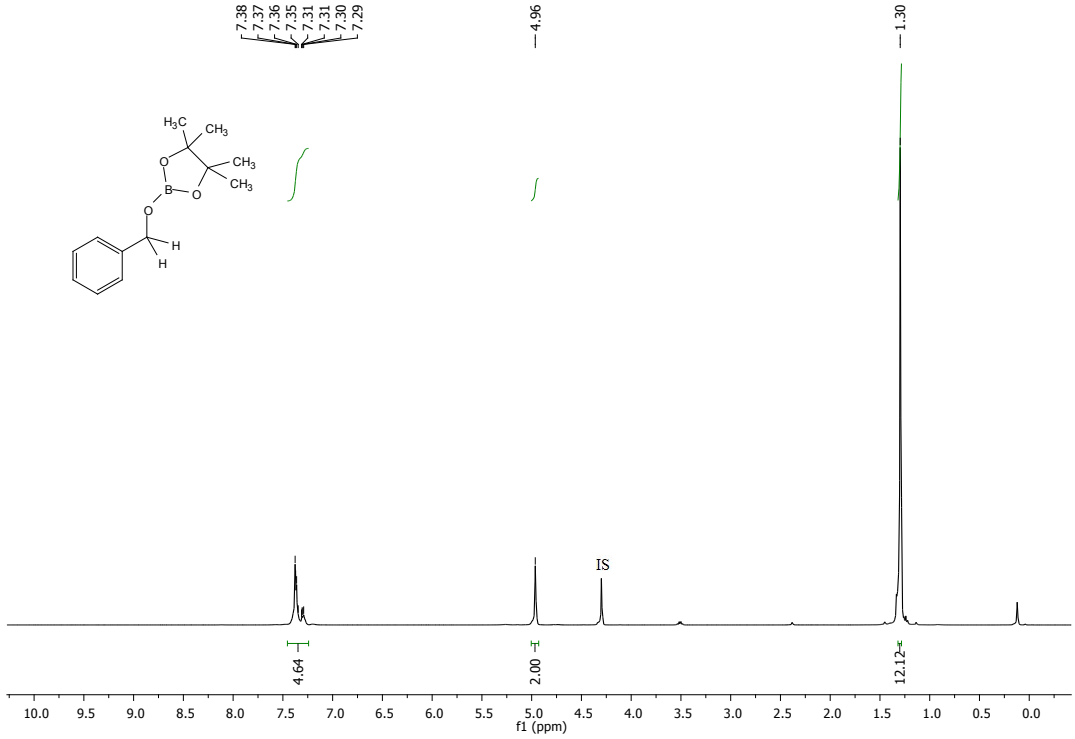
2-Adamantanol (28c). White solid. Yield: 64% (96 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.86 (br, 1H), 2.07-2.04 (m, 2H), 1.87-1.78 (m, 7H), 1.70-1.67 (m, 4H), 1.52-1.49 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 74.7, 37.7, 36.6, 34.7, 31.1, 27.6, 27.2.



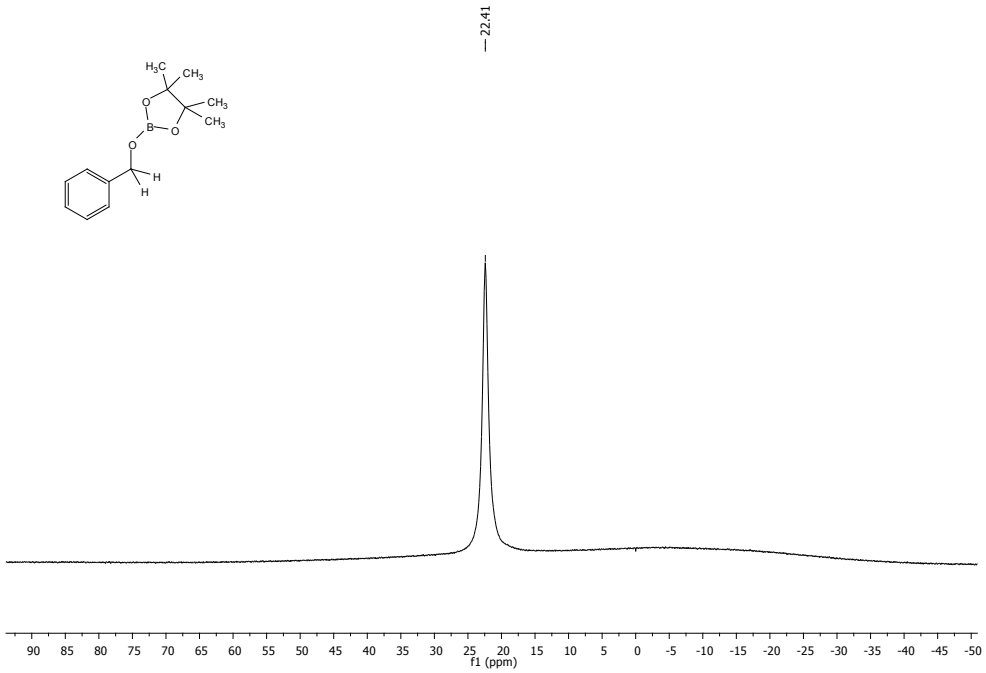
IV. NMR Spectra of Hydroboration Products and Relevant Alcohols

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

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

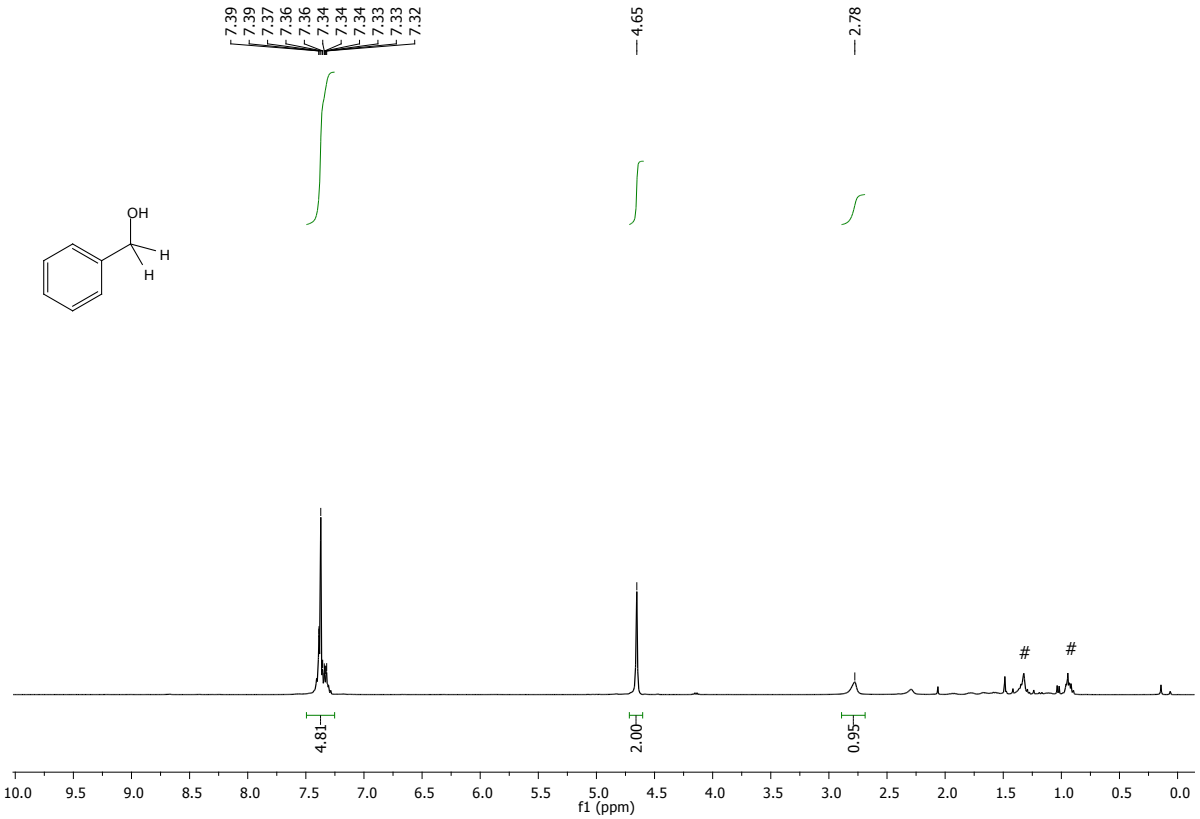


^{1}H NMR of **1b** (400 MHz, $CDCl_3$)

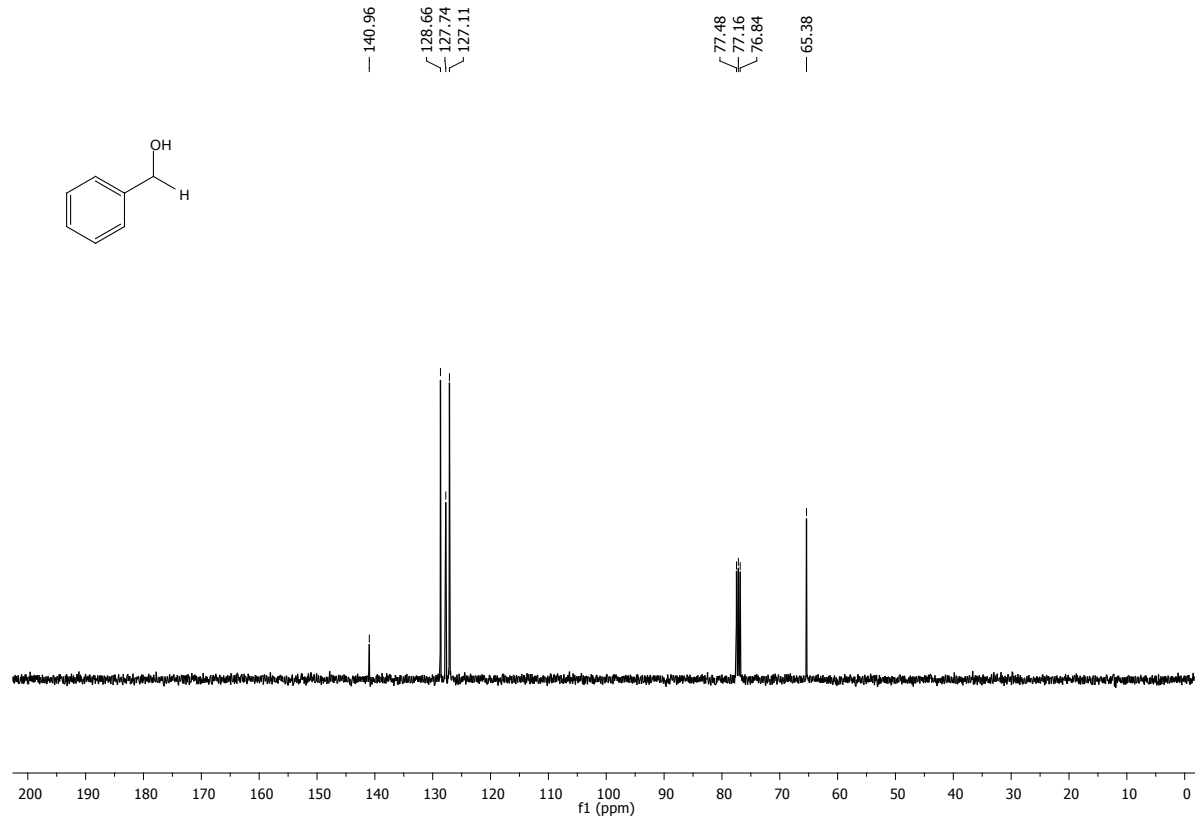


^{11}B NMR of **1b** (128 MHz, $CDCl_3$)

Phenylmethanol (1c).[2,4]

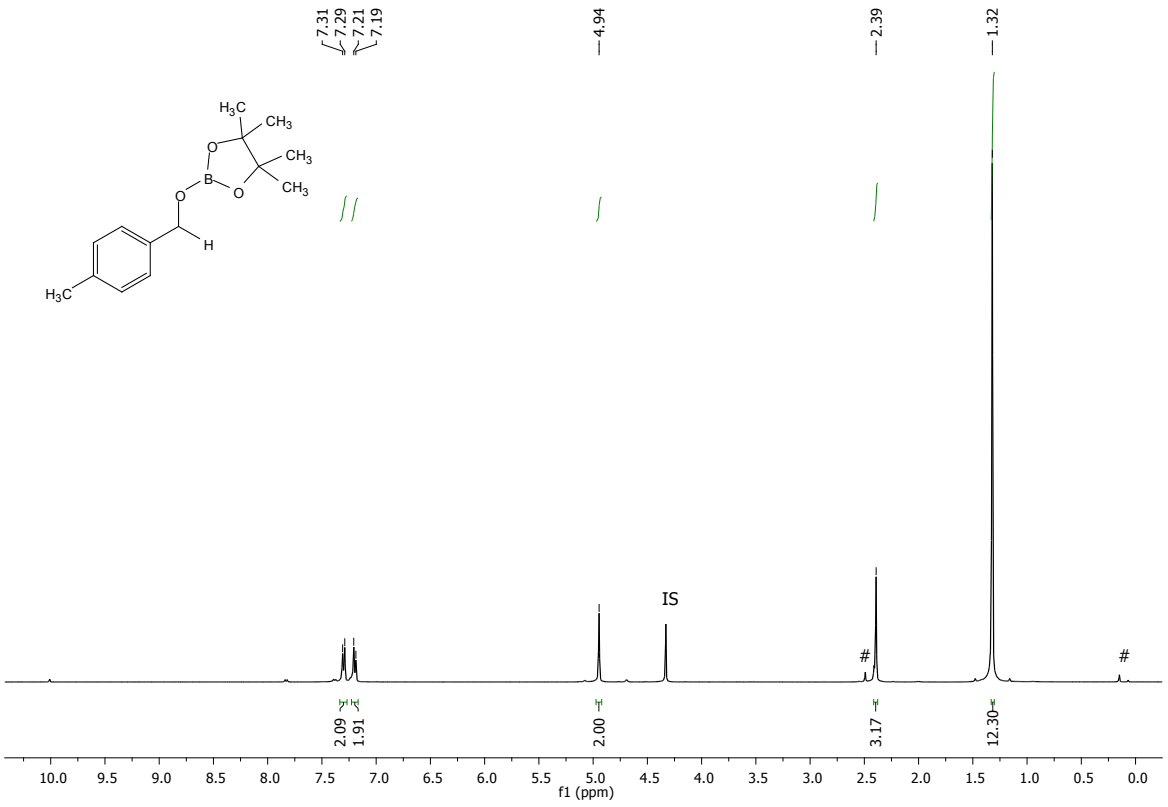


^{1}H NMR of **1c** (400 MHz, $CDCl_3$)

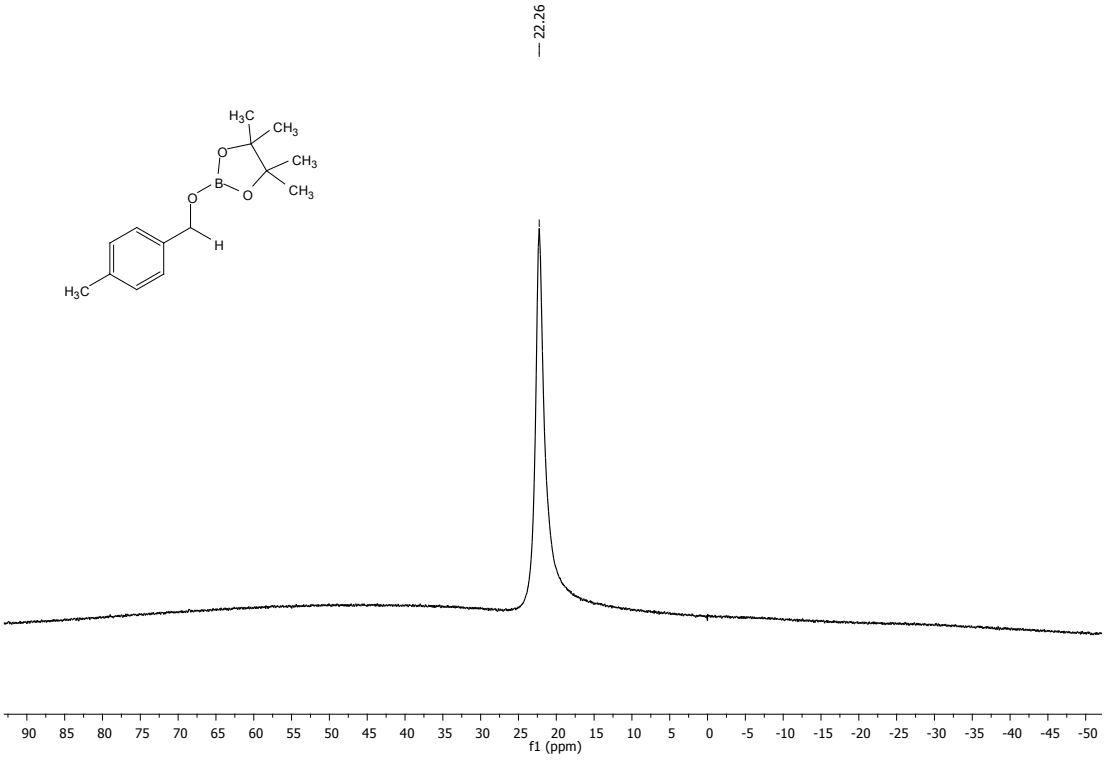


^{13}C NMR of **1c** (100 MHz, $CDCl_3$)

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

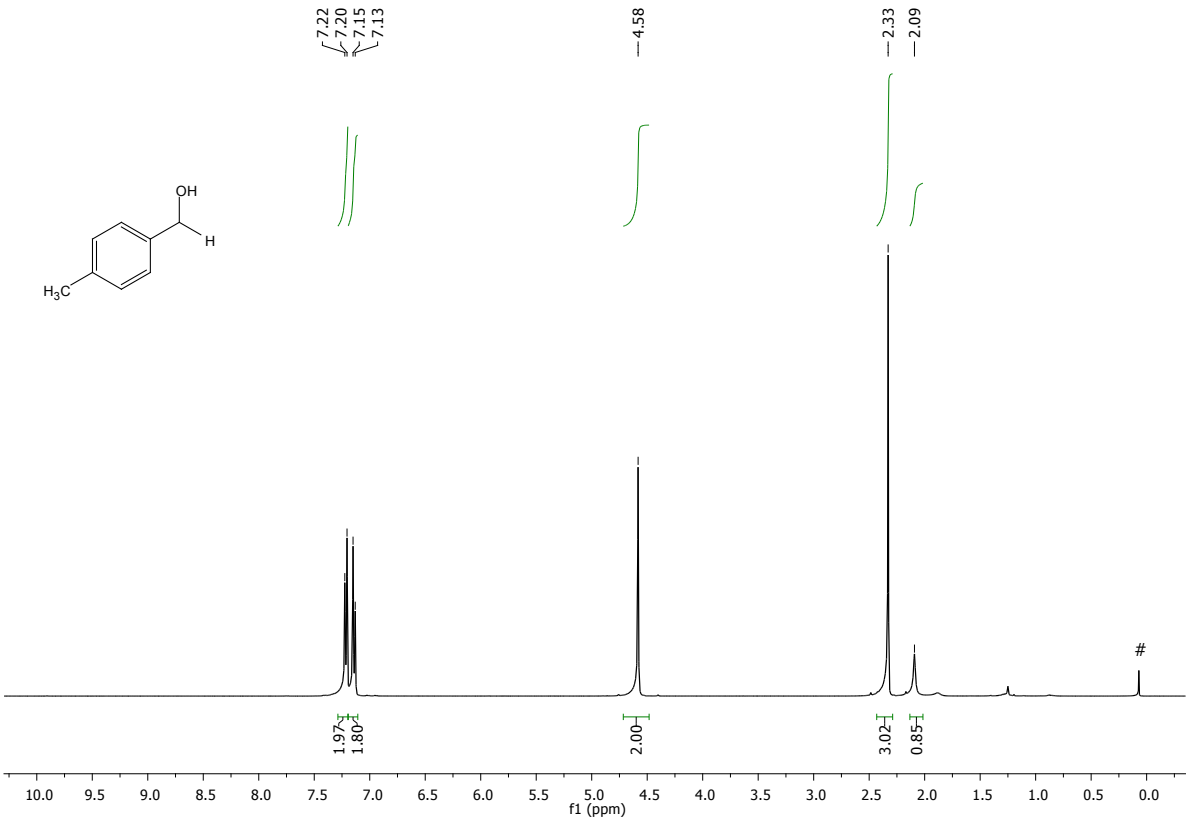


^{1}H NMR of **2b** (400 MHz, $CDCl_3$)

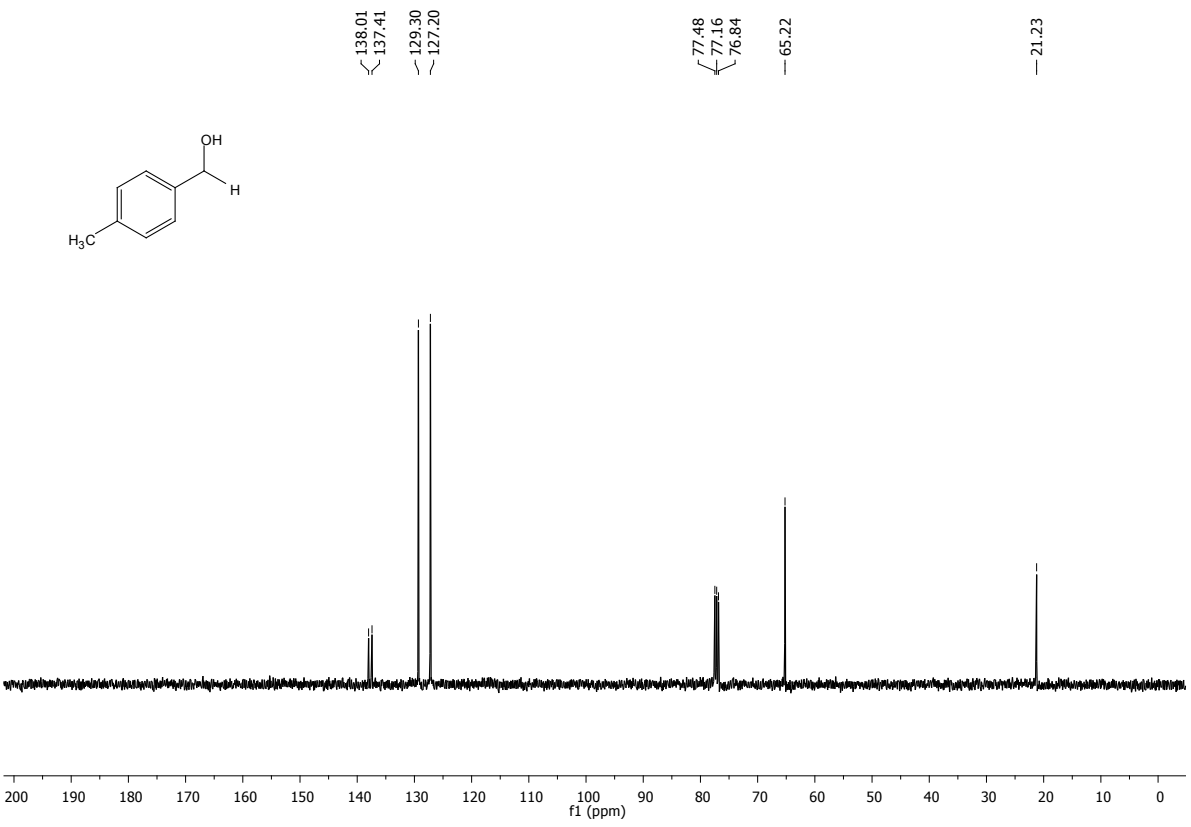


^{11}B NMR of **2b** (128 MHz, $CDCl_3$)

***p*-Tolylmethanol (2c)**.[2,4]

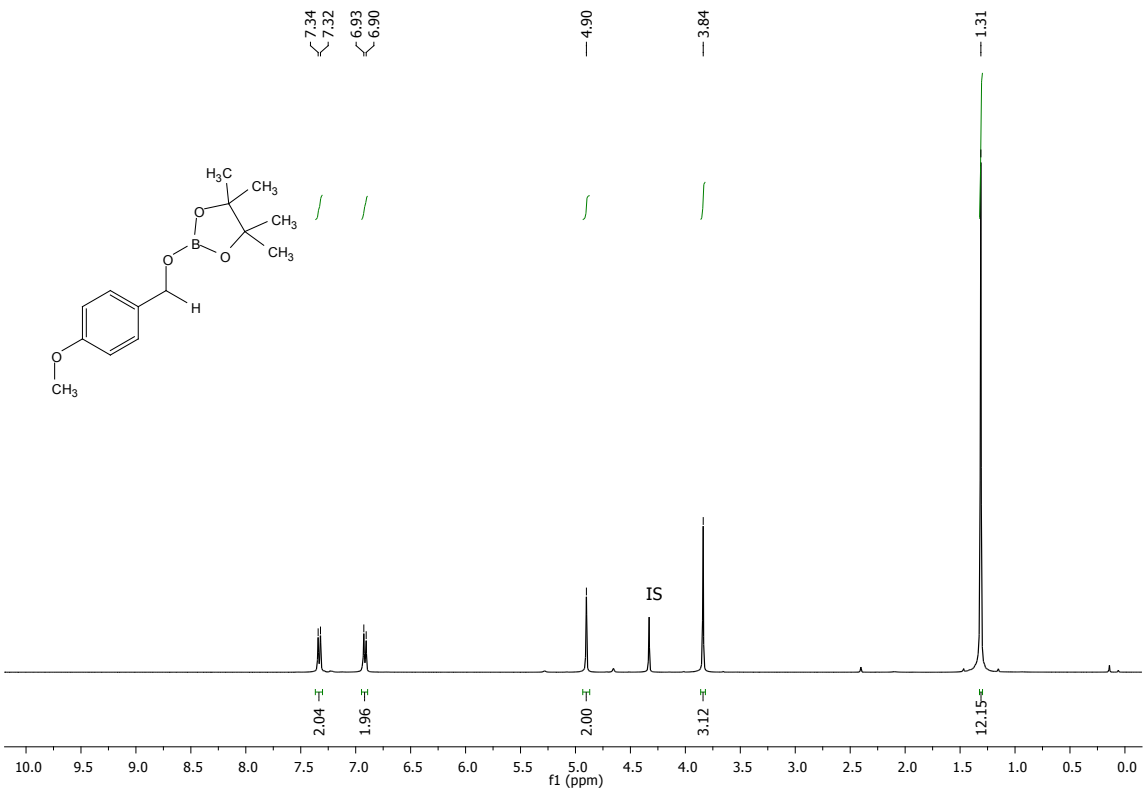


^{1}H NMR of **2c** (400 MHz, $CDCl_3$)

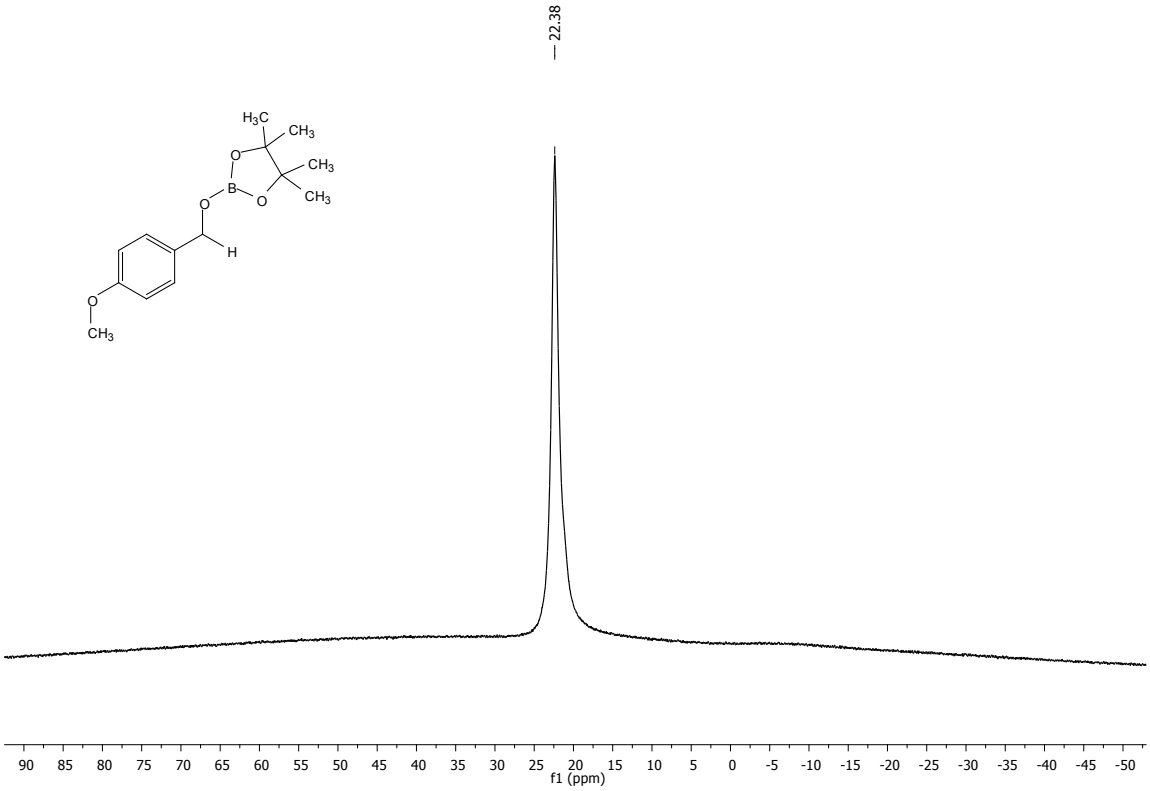


^{13}C NMR of **2c** (100 MHz, $CDCl_3$)

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

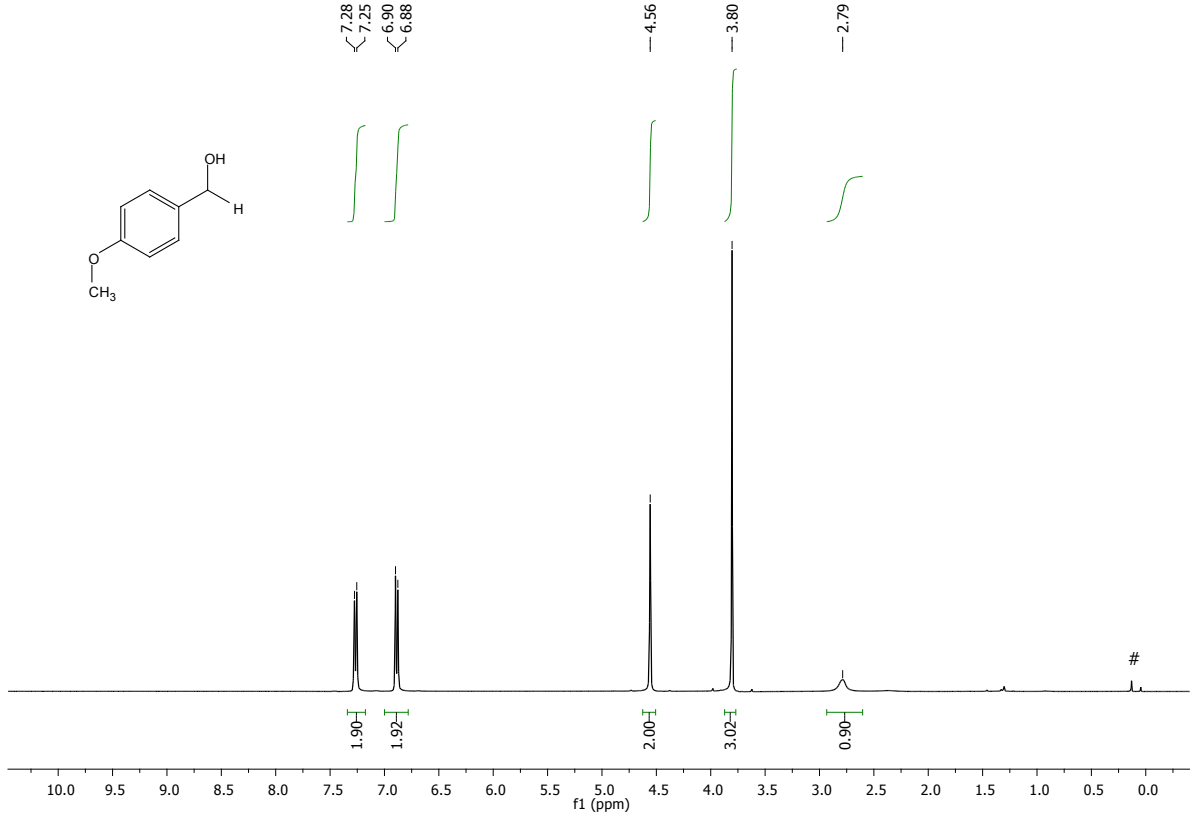


^{1}H NMR of **3b** (400 MHz, $CDCl_3$)

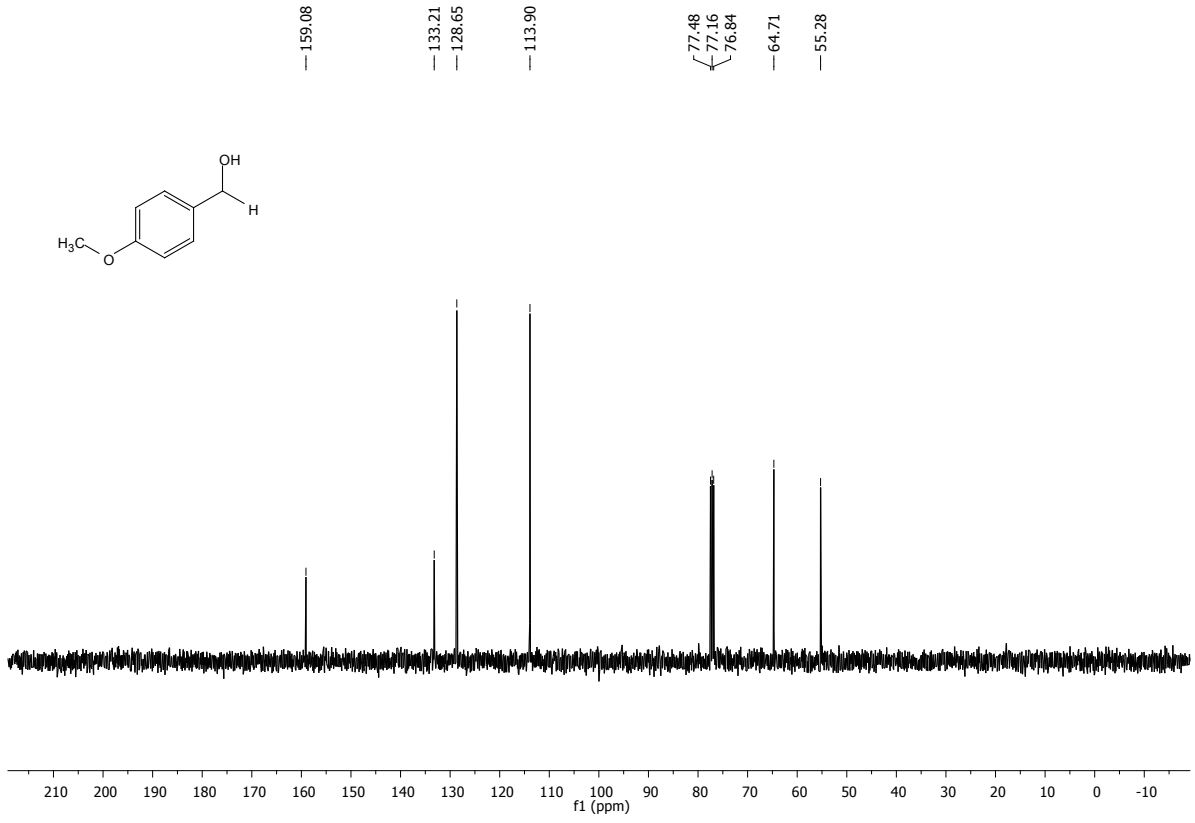


^{11}B NMR of **3b** (128 MHz, $CDCl_3$)

(4-Methoxyphenyl)methanol (3c).[2,5]

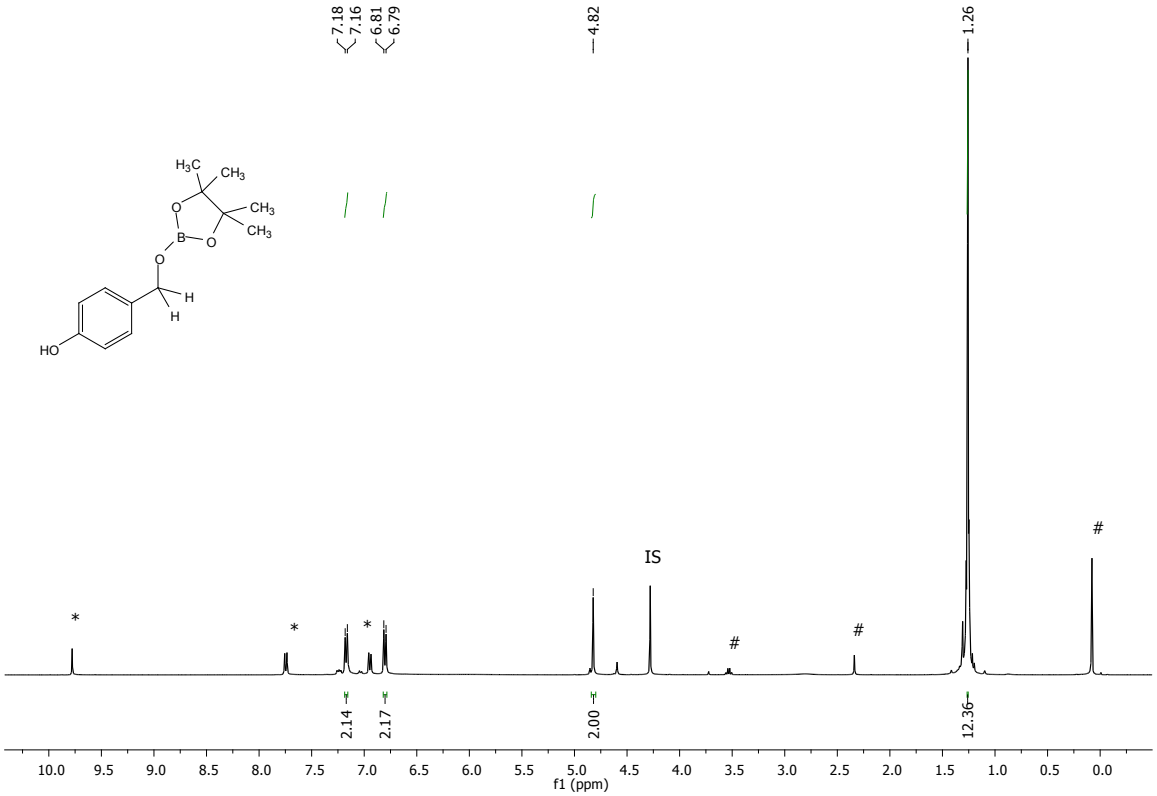


^{1}H NMR of **3c** (400 MHz, $CDCl_3$)

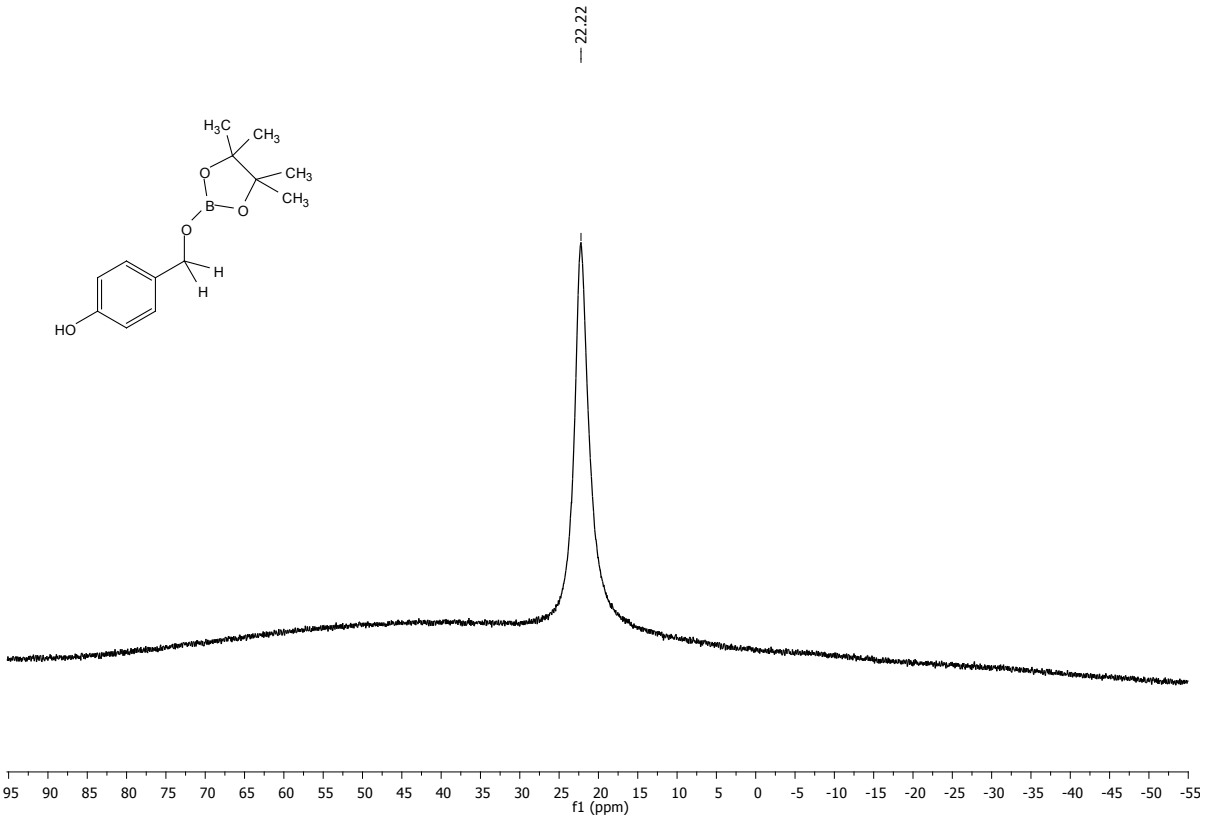


^{13}C NMR of **3c** (100 MHz, $CDCl_3$)

4-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)phenol (Table 2, 4b).[2,6]

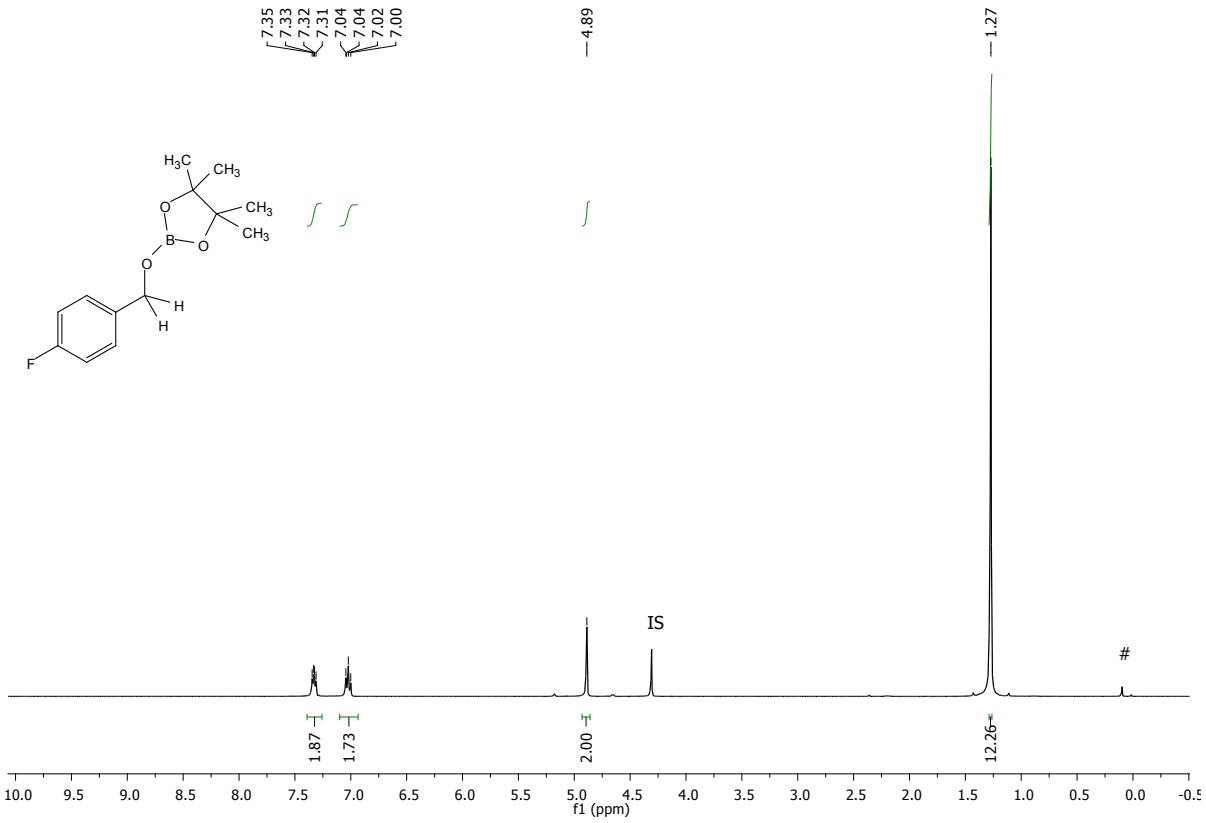


^{1}H NMR of **4b** (400 MHz, $CDCl_3$)

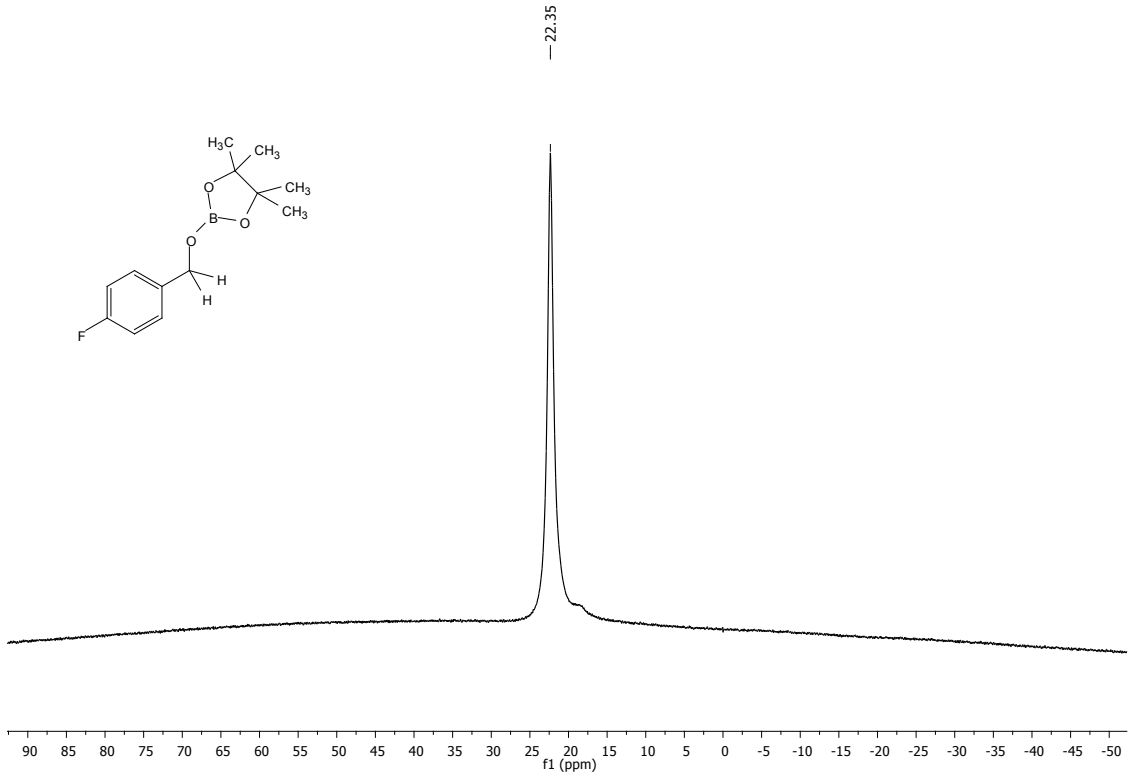


^{11}B NMR of **4b** (128 MHz, $CDCl_3$)

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

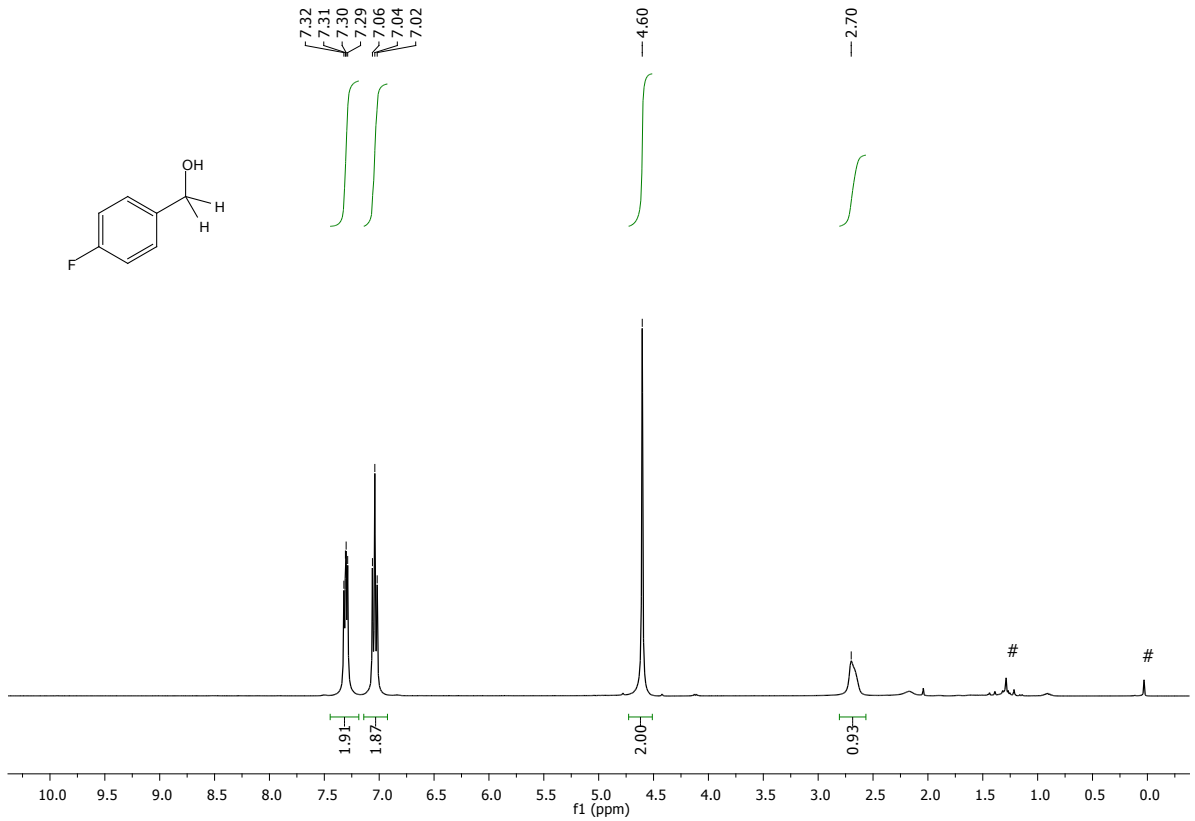


^{1}H NMR of **5b** (400 MHz, $CDCl_3$)

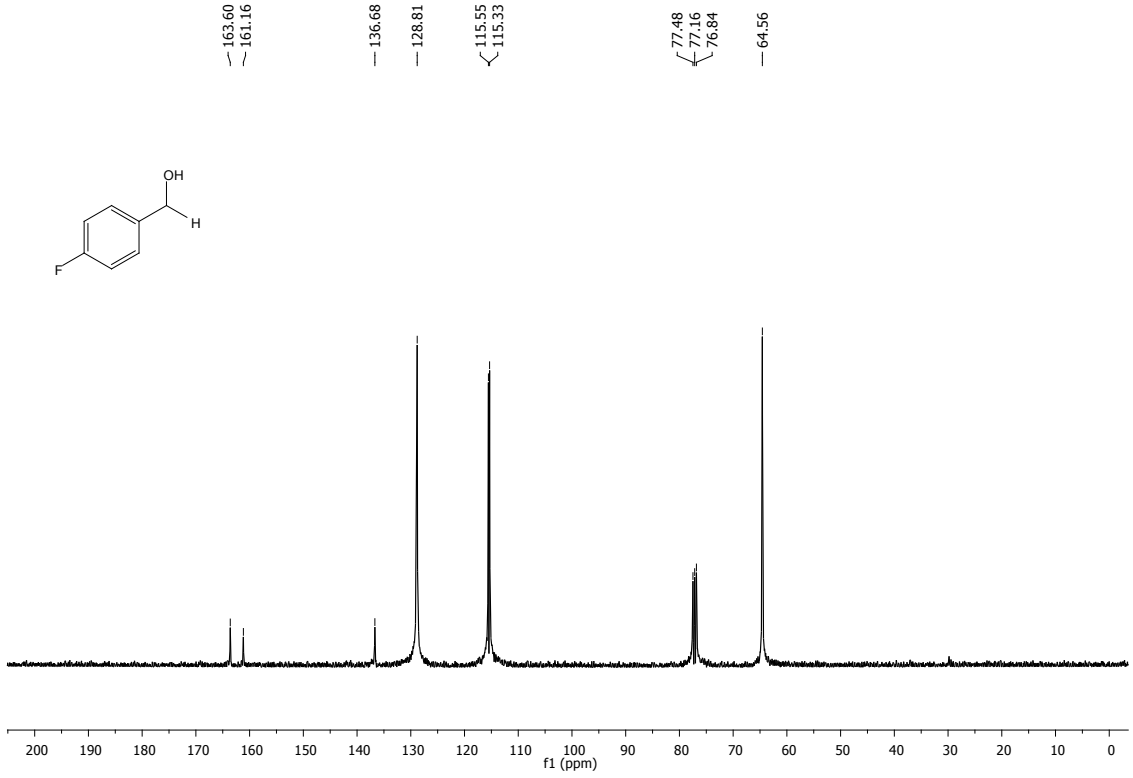


^{11}B NMR of **5b** (128 MHz, $CDCl_3$)

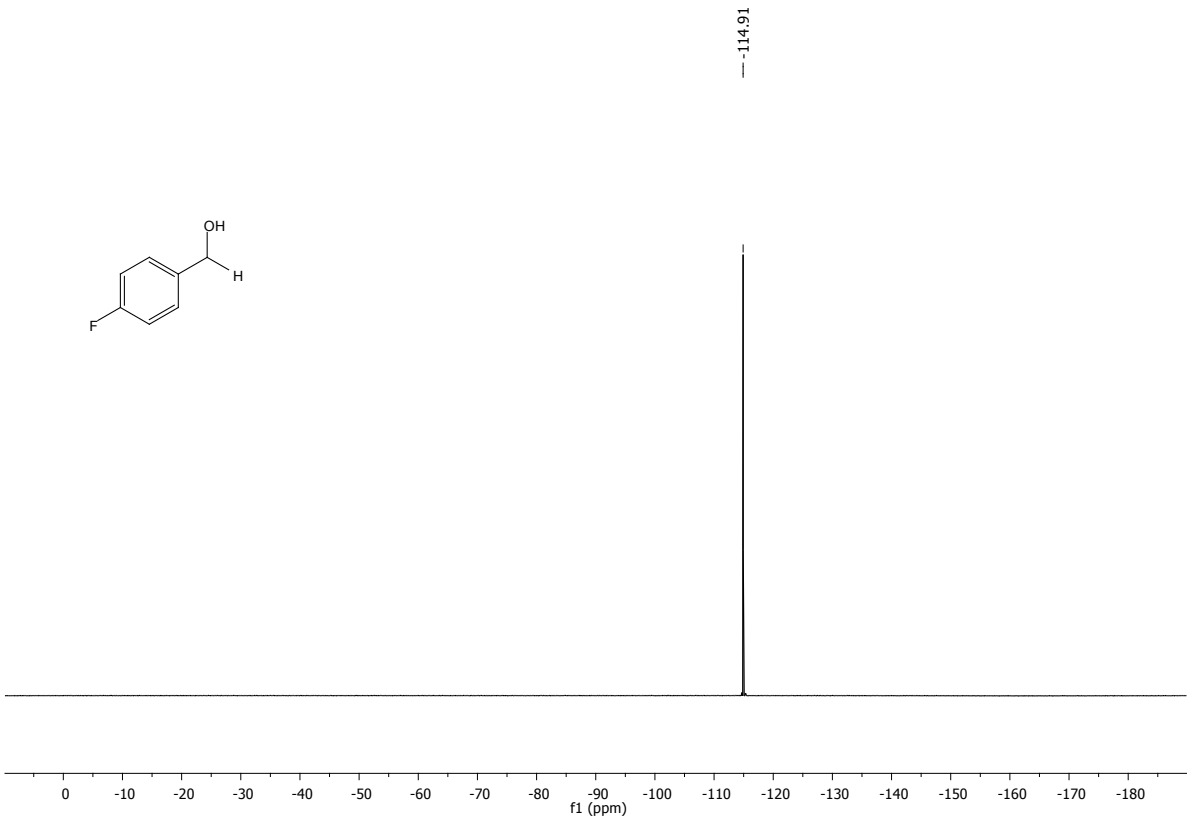
(4–Fluorophenyl)methanol (5c).[2,5]



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

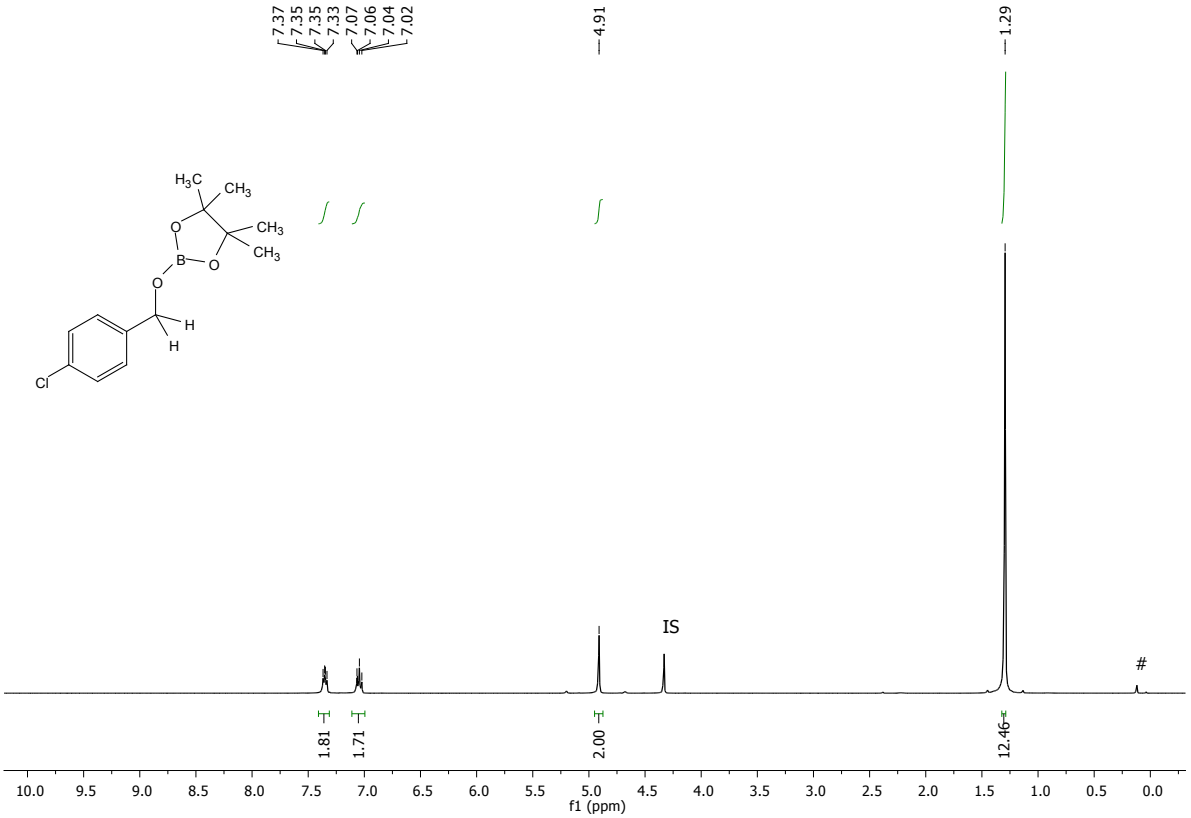


^{13}C NMR of **5c** (100 MHz, $CDCl_3$)

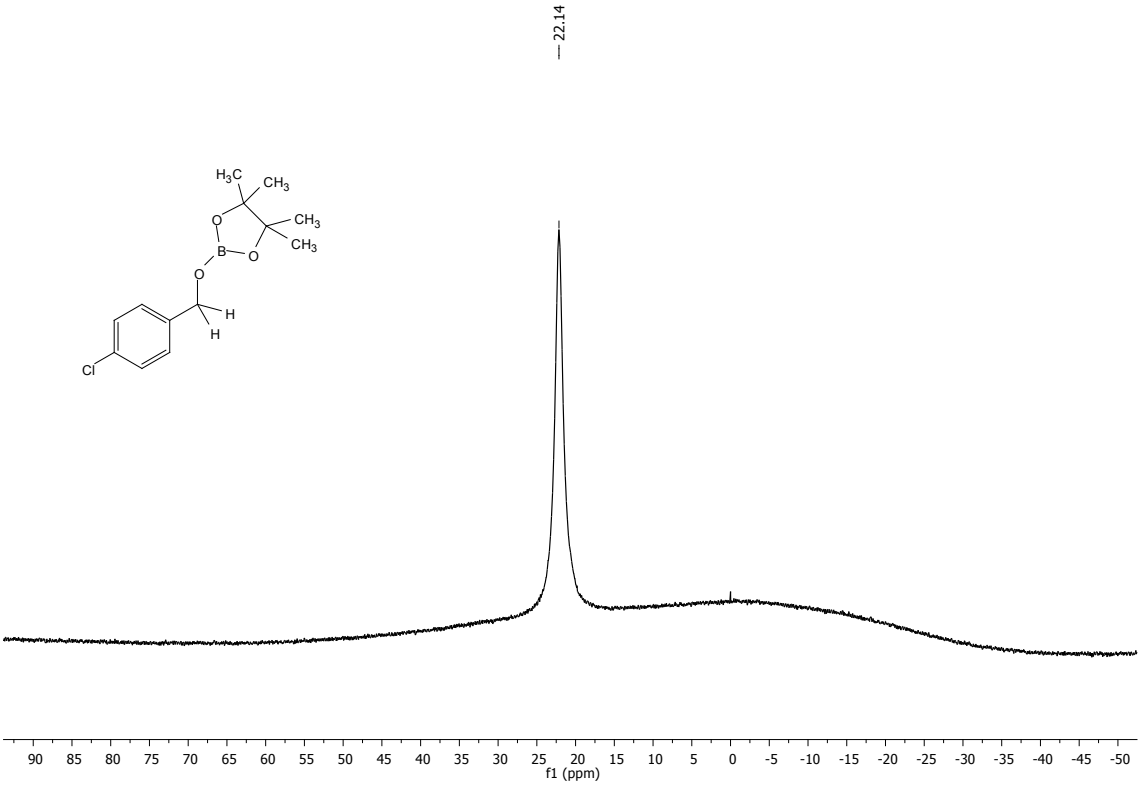


^{19}F NMR of **5c** (376 MHz, $CDCl_3$)

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

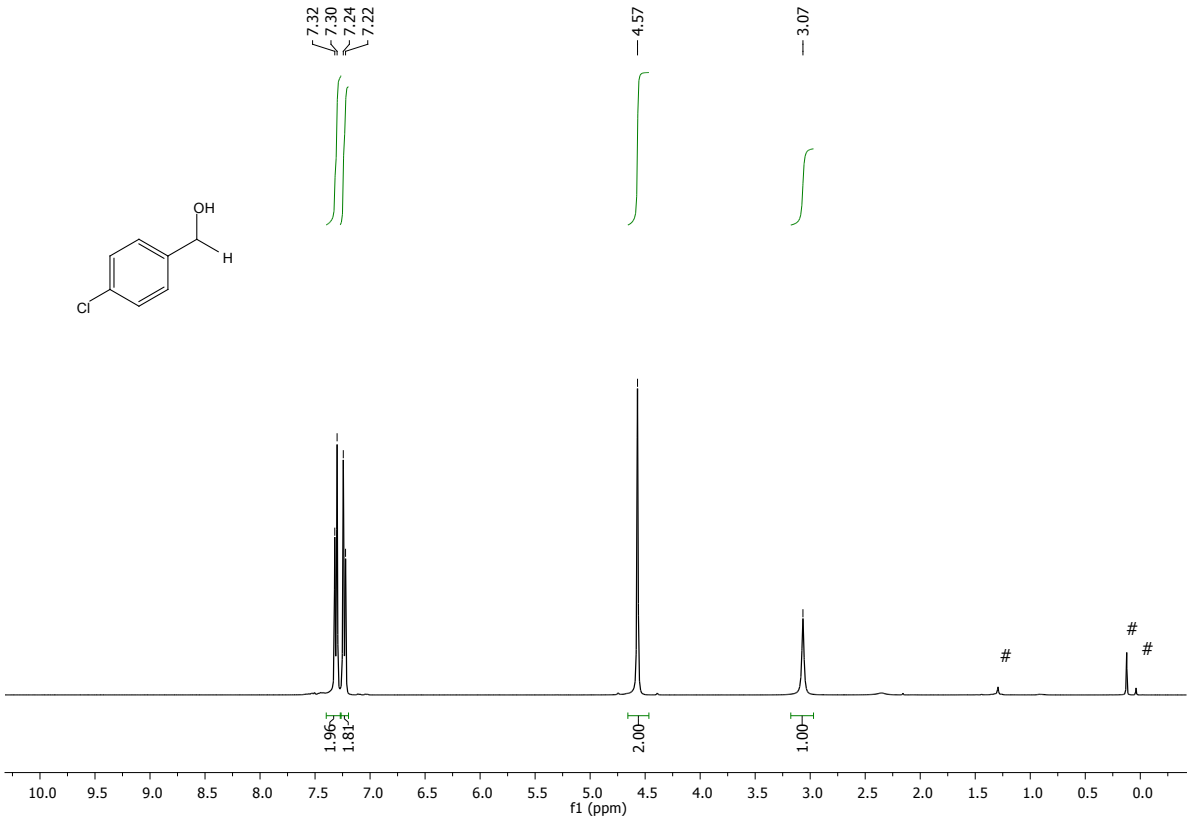


^{1}H NMR of **6b** (400 MHz, $CDCl_3$)

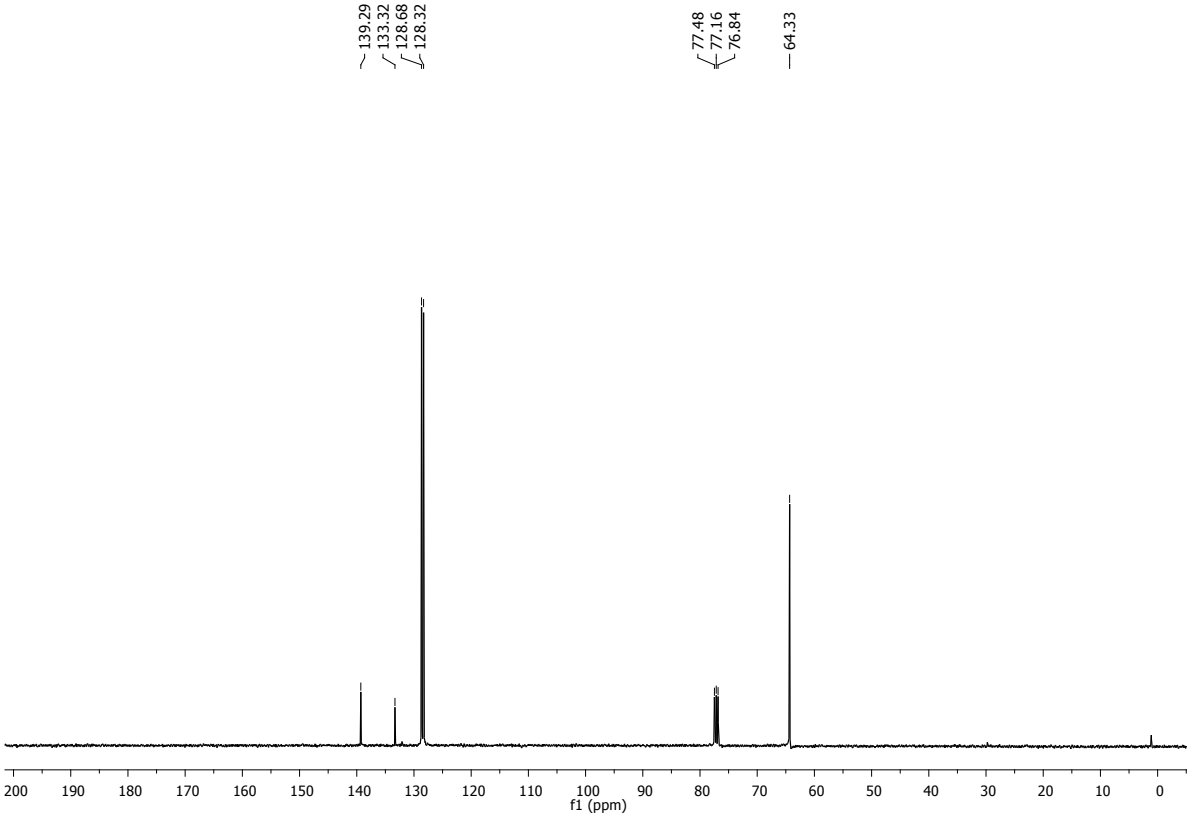


^{11}B NMR of **6b** (128 MHz, $CDCl_3$)

(4–Chlorophenyl)methanol (6c).[2,8]

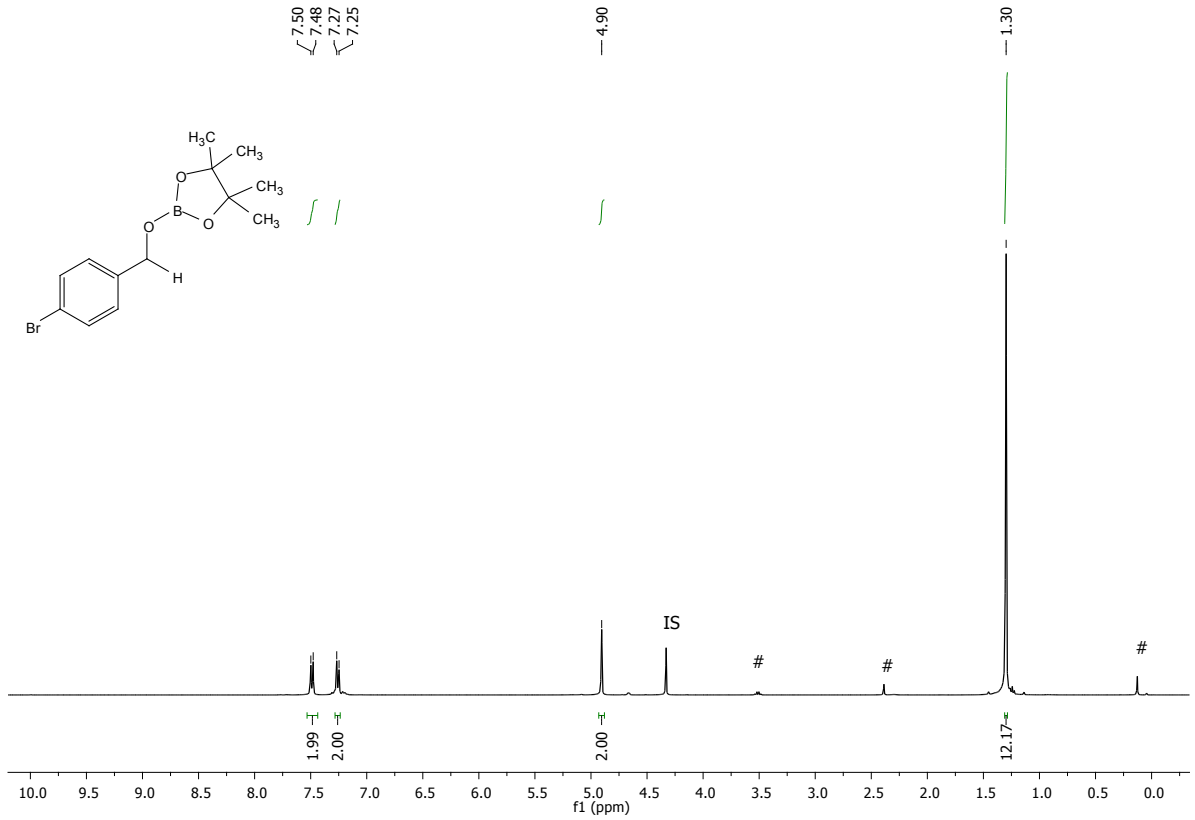


^{1}H NMR of **6c** (400 MHz, $CDCl_3$)

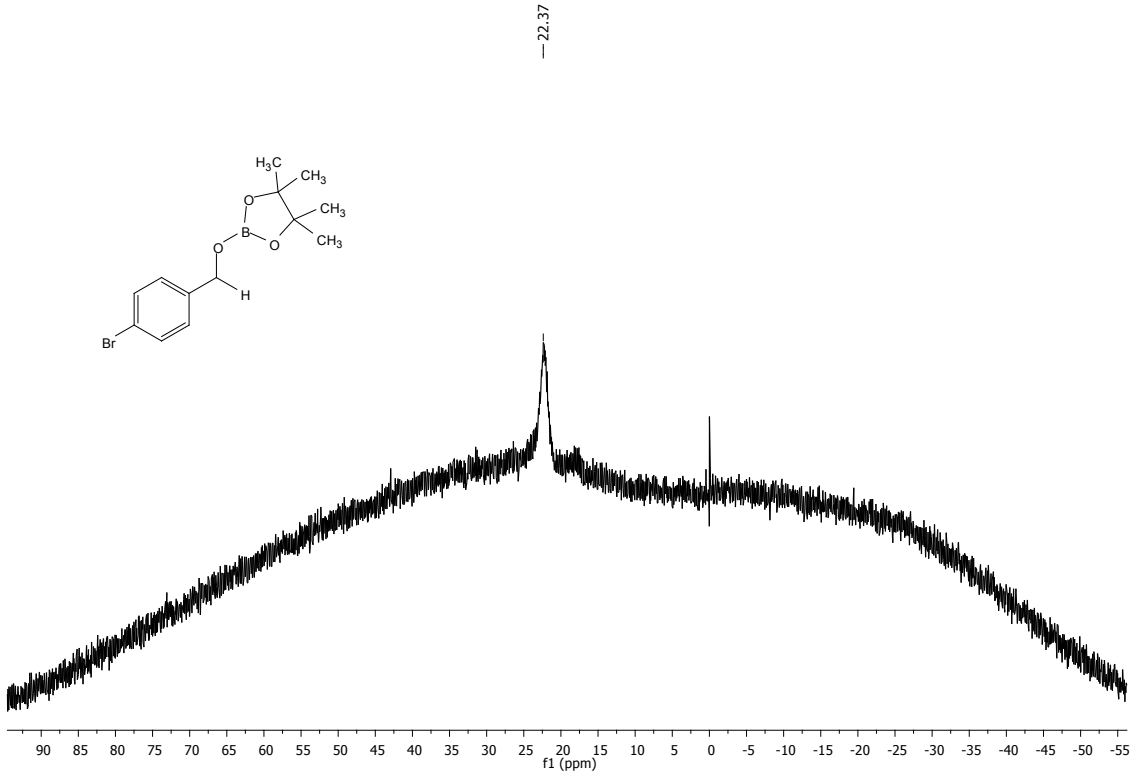


^{13}C NMR of **6c** (100 MHz, $CDCl_3$)

2-((4-Bromobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 7b).[2,6]

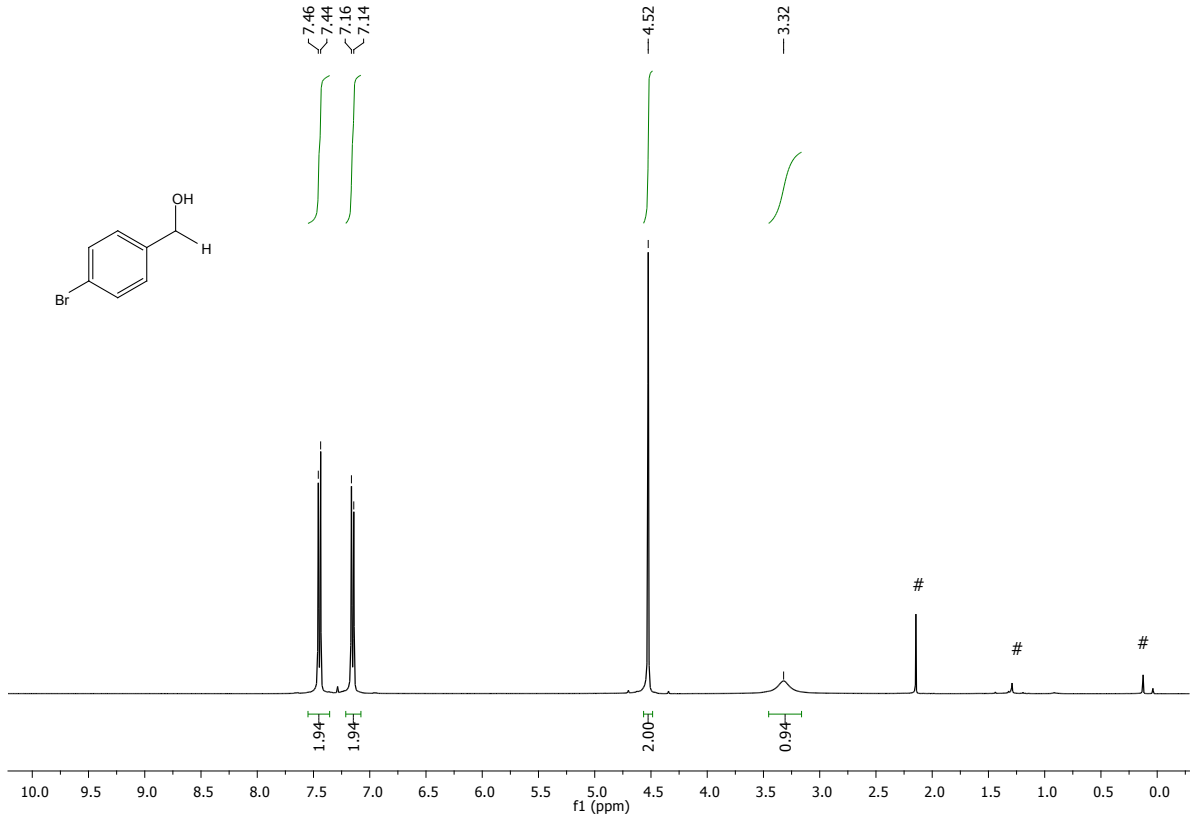


^{1}H NMR of **7b** (400 MHz, $CDCl_3$)

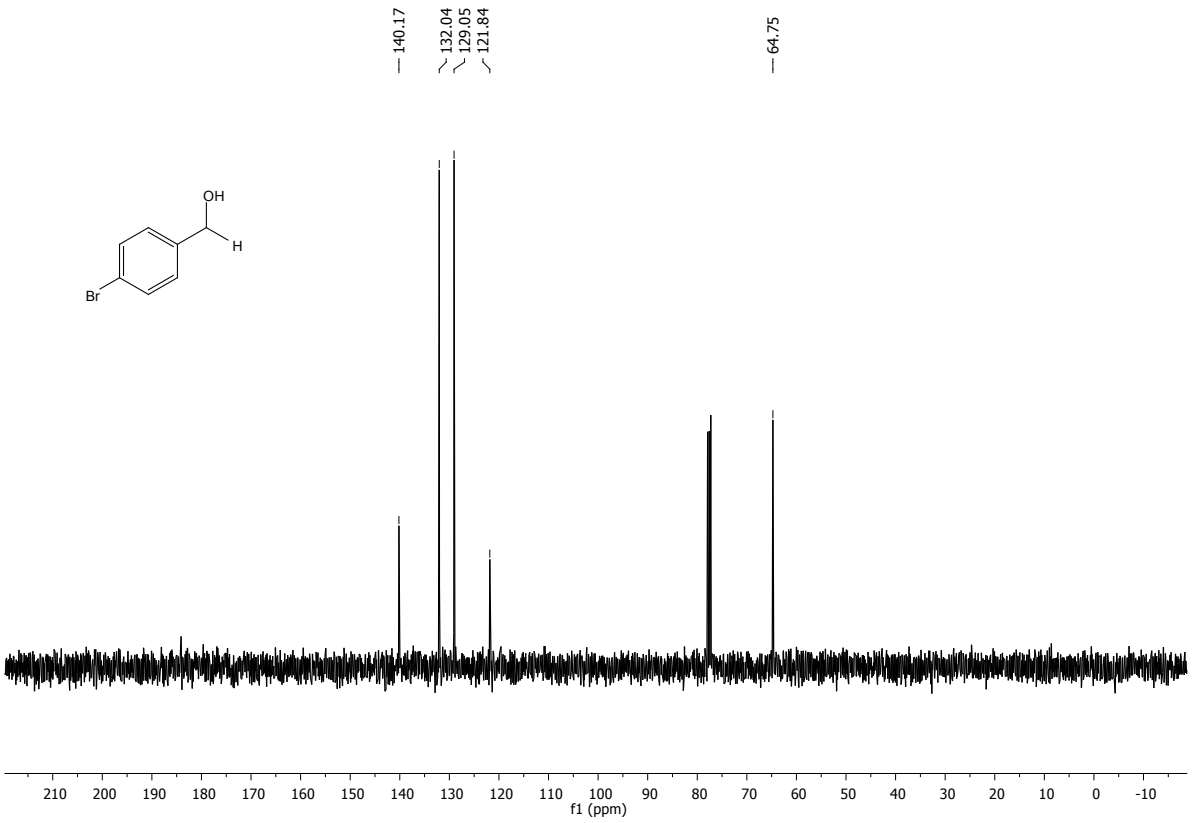


^{11}B NMR of **7b** (128 MHz, $CDCl_3$)

(4–Bromophenyl)methanol (7c).[2,5]

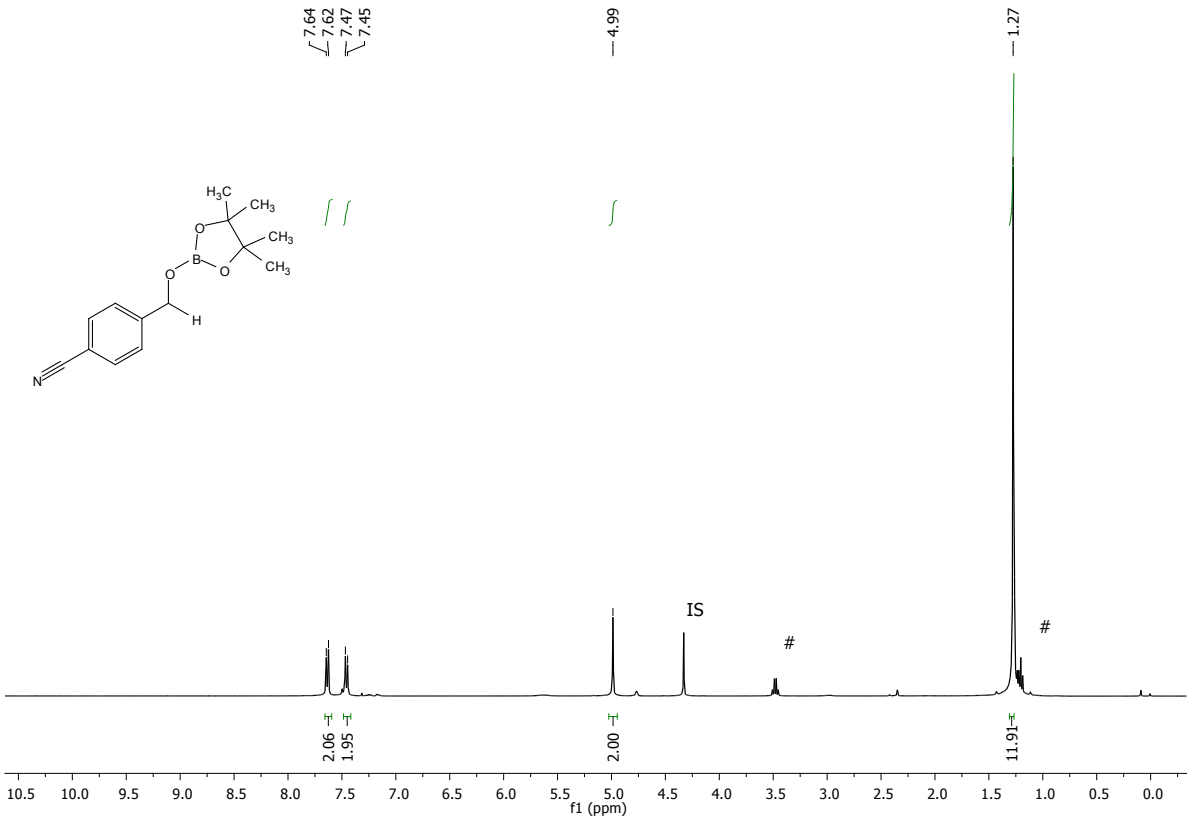


^{1}H NMR of **7c** (400 MHz, $CDCl_3$)

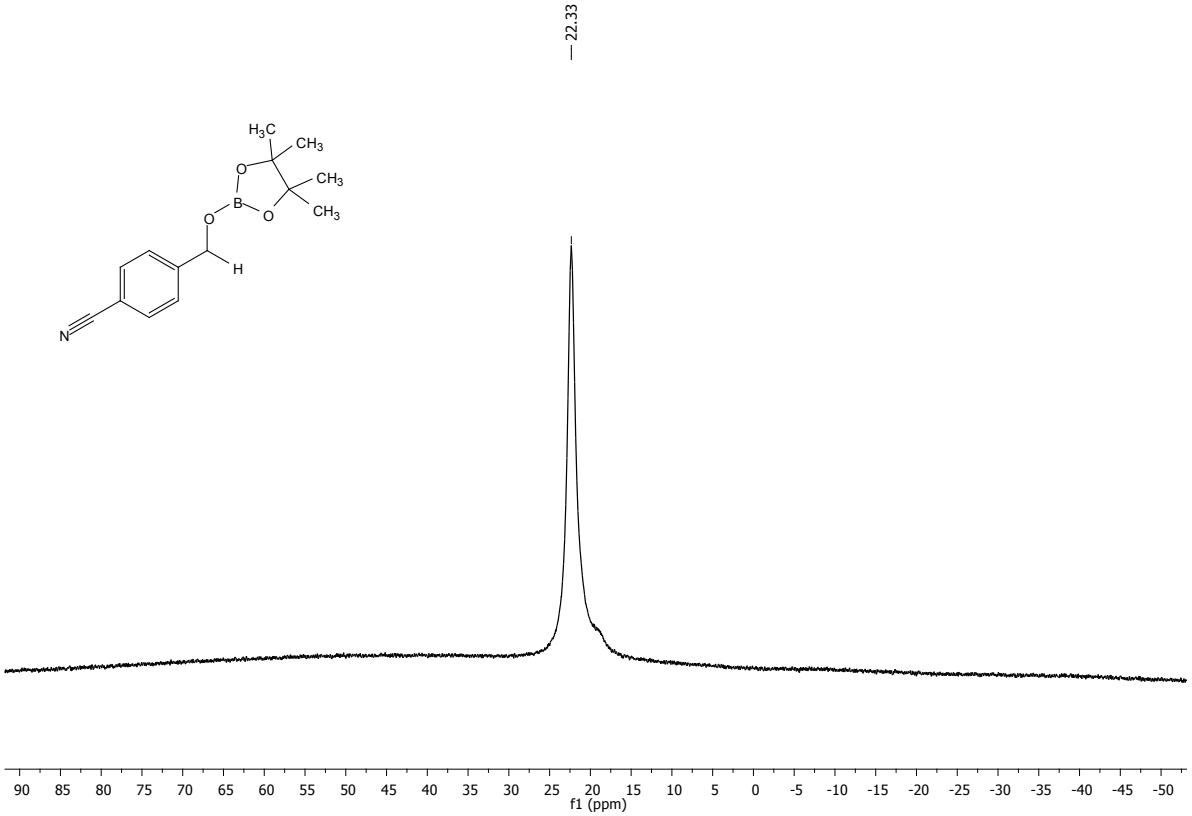


^{13}C NMR of **7c** (100 MHz, $CDCl_3$)

4-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzonitrile (Table 2, 8b).[2,6]

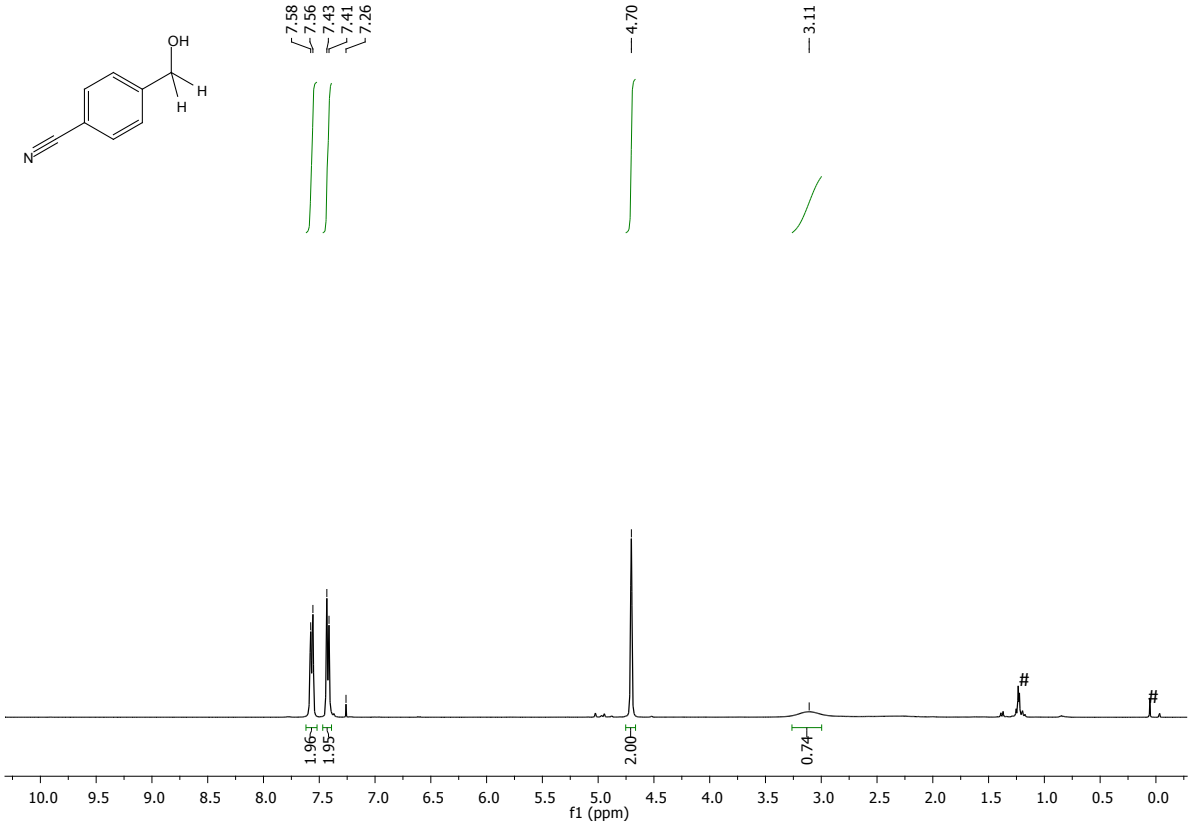


^{1}H NMR of **8b** (400 MHz, $CDCl_3$)

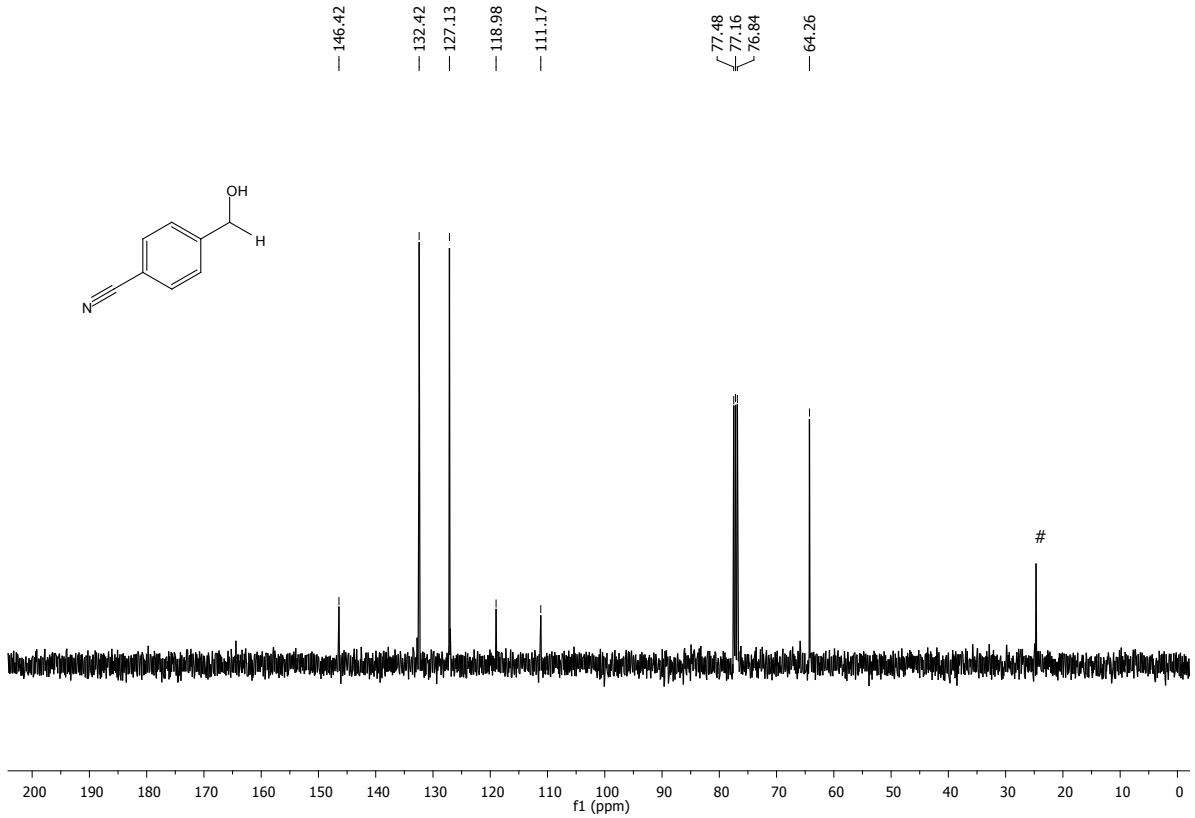


^{11}B NMR of **8b** (128 MHz, $CDCl_3$)

4-(Hydroxymethyl)benzonitrile (8c).[2,8]

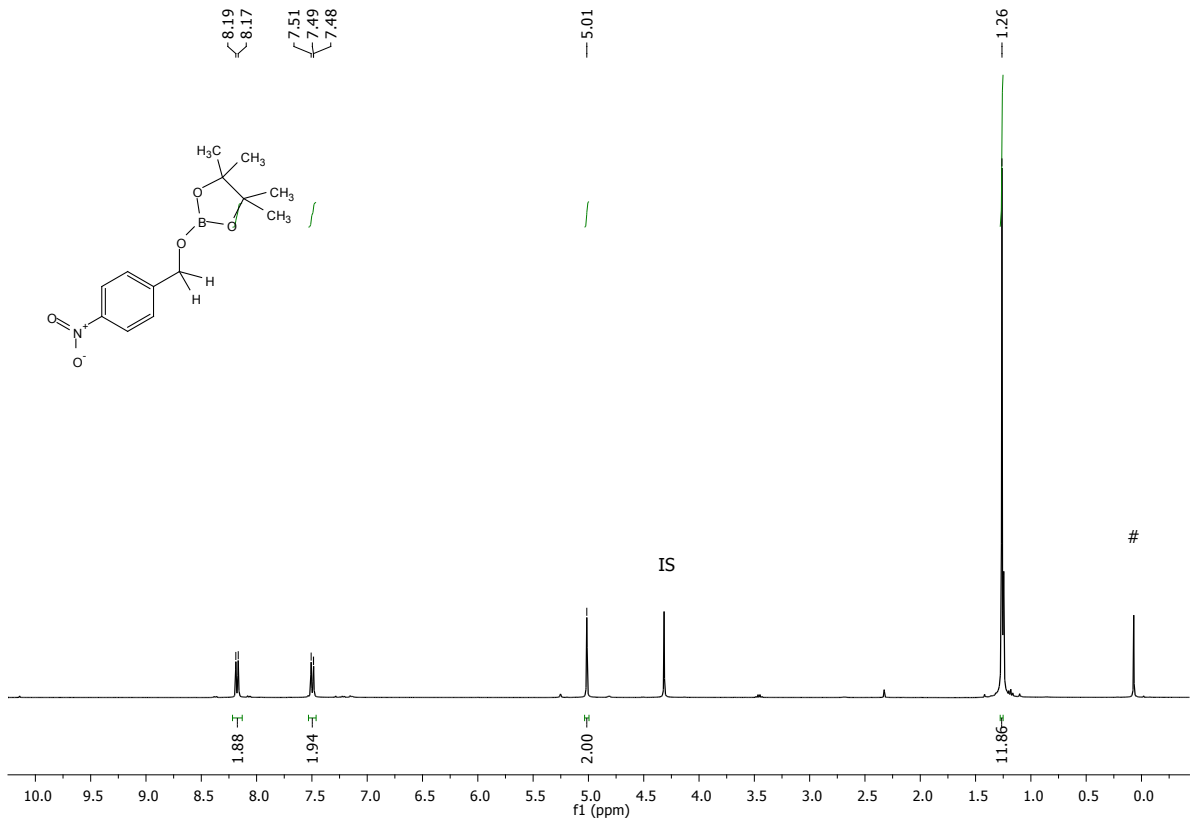


^{1}H NMR of **8c** (400 MHz, $CDCl_3$)

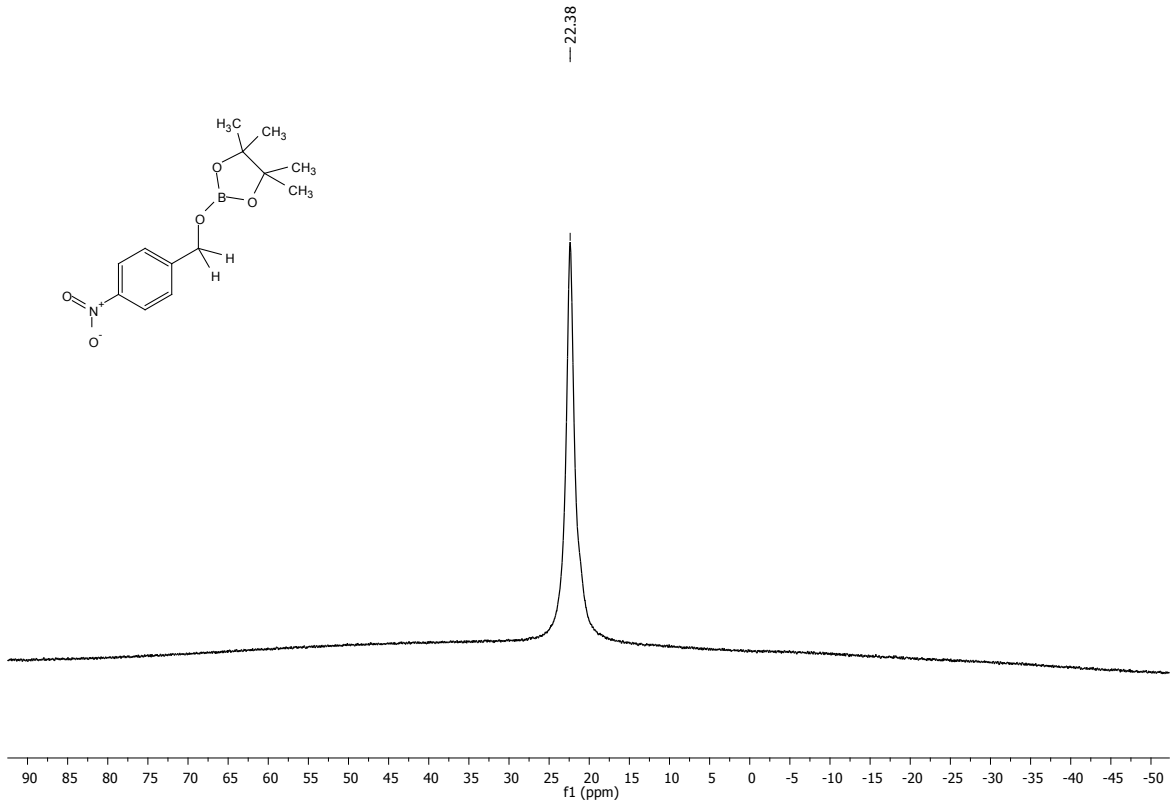


^{13}C NMR of **8c** (100 MHz, $CDCl_3$)

4,4,5,5-Tetramethyl-2-((4-nitrobenzyl)oxy)-1,3,2-dioxaborolane (Table 2, 9b).[2,3]

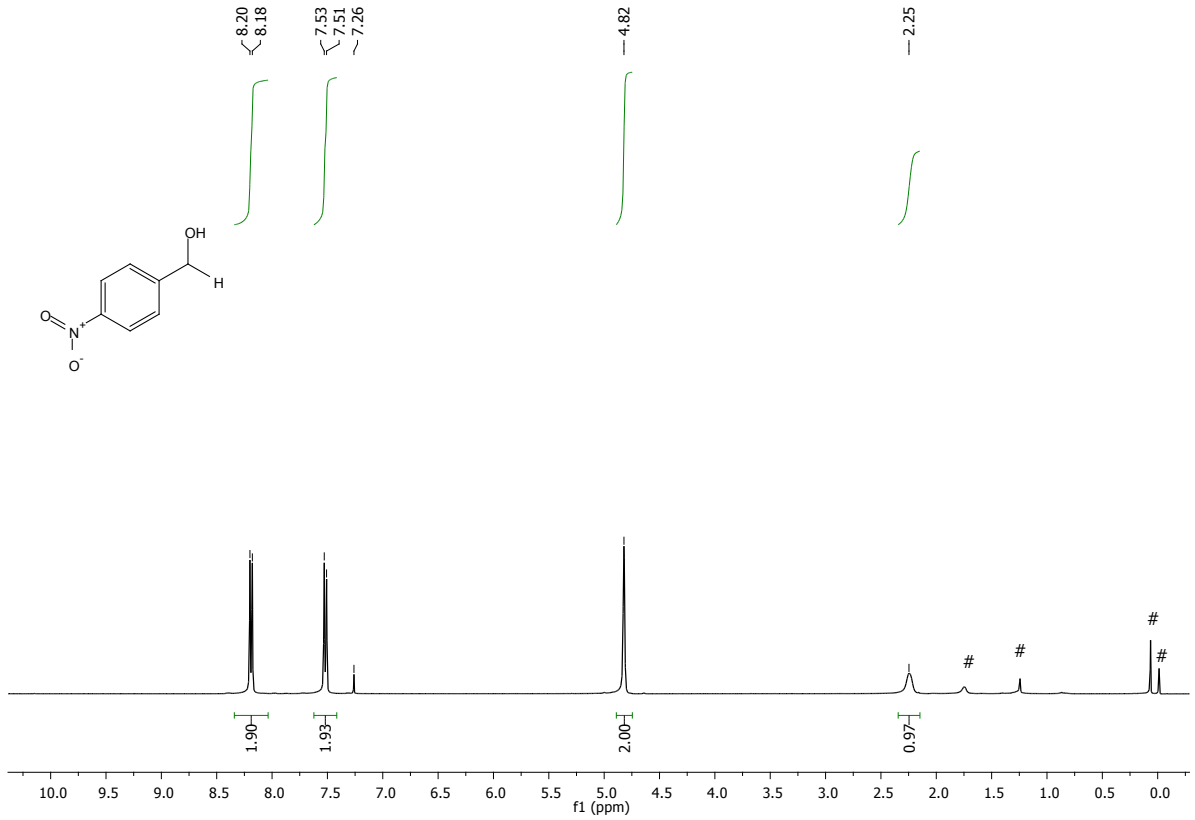


^{1}H NMR of **9b** (400 MHz, $CDCl_3$)

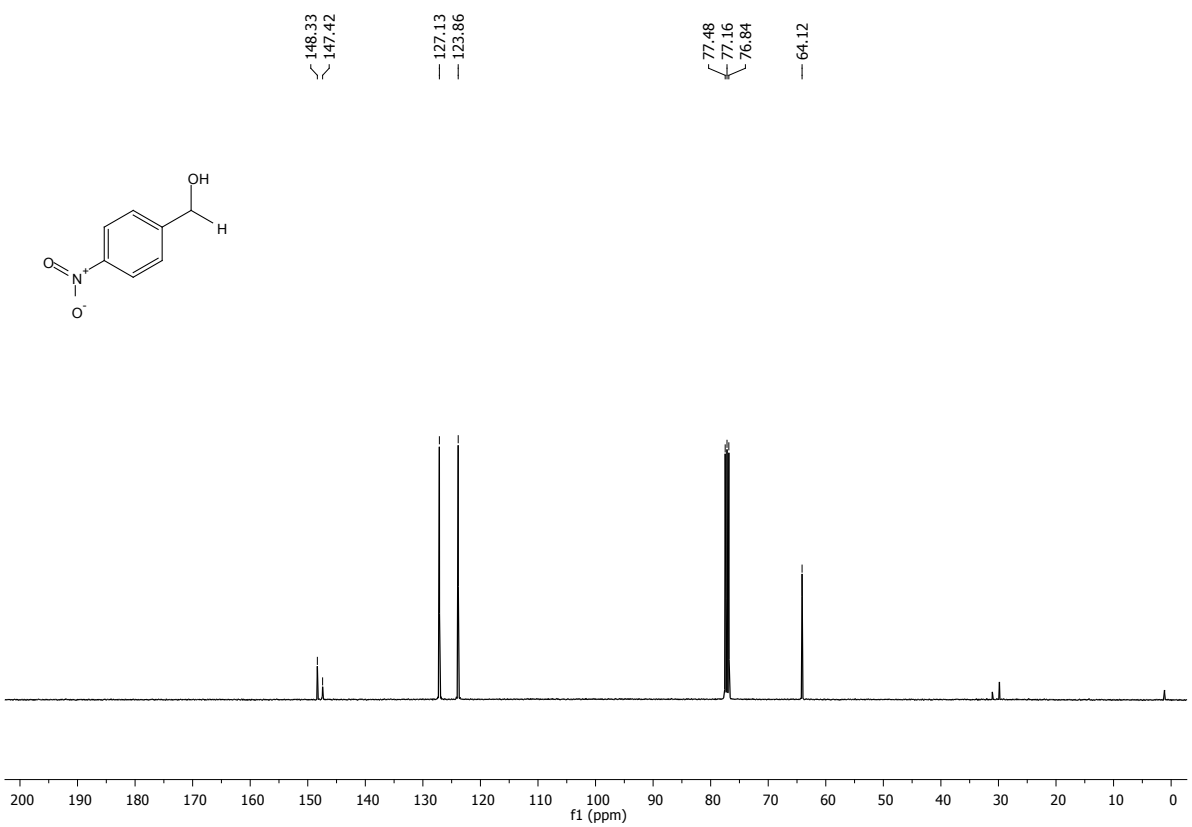


^{11}B NMR of **9b** (128 MHz, $CDCl_3$)

(4-Nitrophenyl)methanol (9c).[2,9]

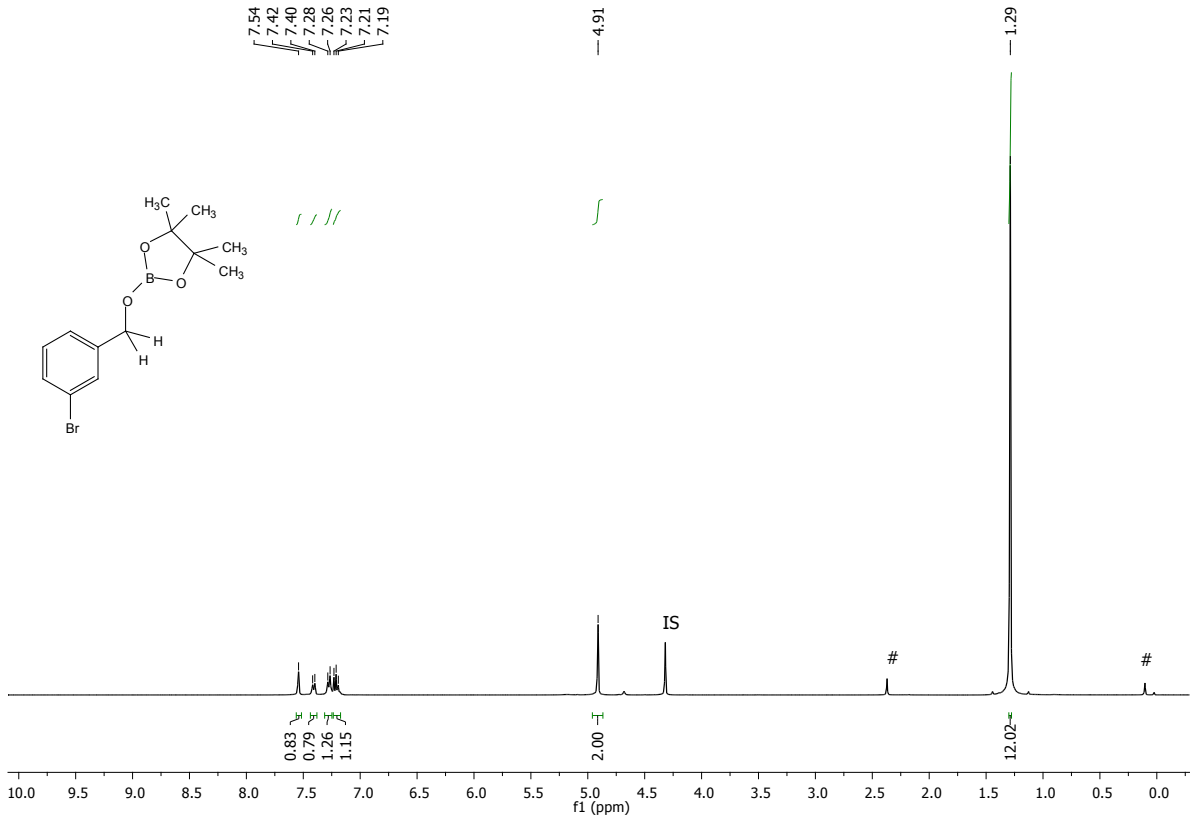


^{1}H NMR of **9c** (400 MHz, $CDCl_3$)

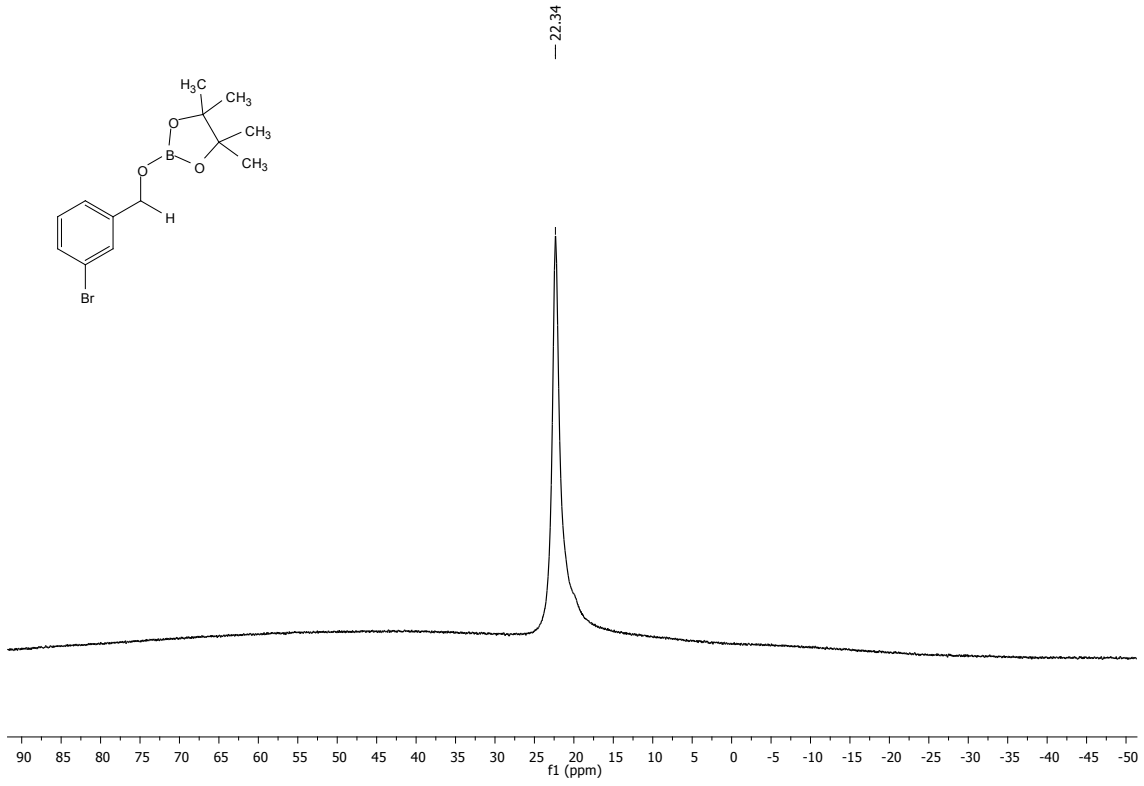


^{13}C NMR of **9c** (100 MHz, $CDCl_3$)

2-((3-Bromobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 10b).[2,6]

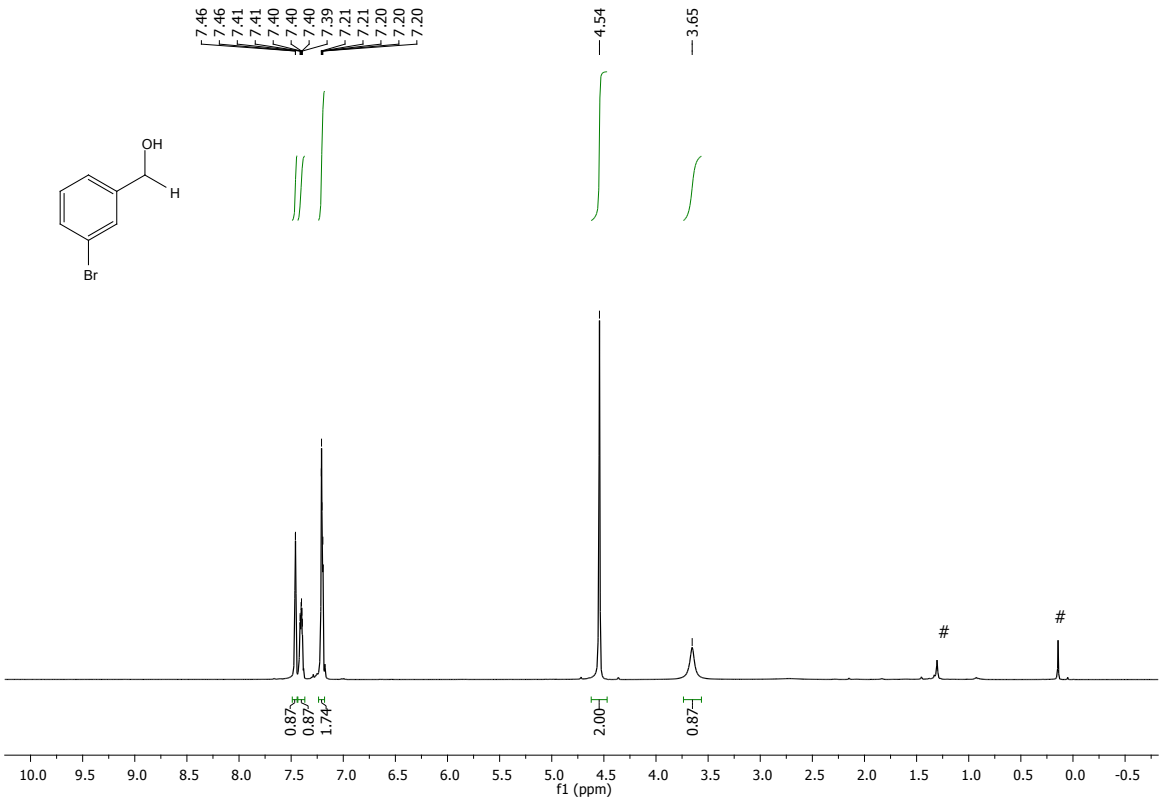


^{1}H NMR of **10b** (400 MHz, $CDCl_3$)

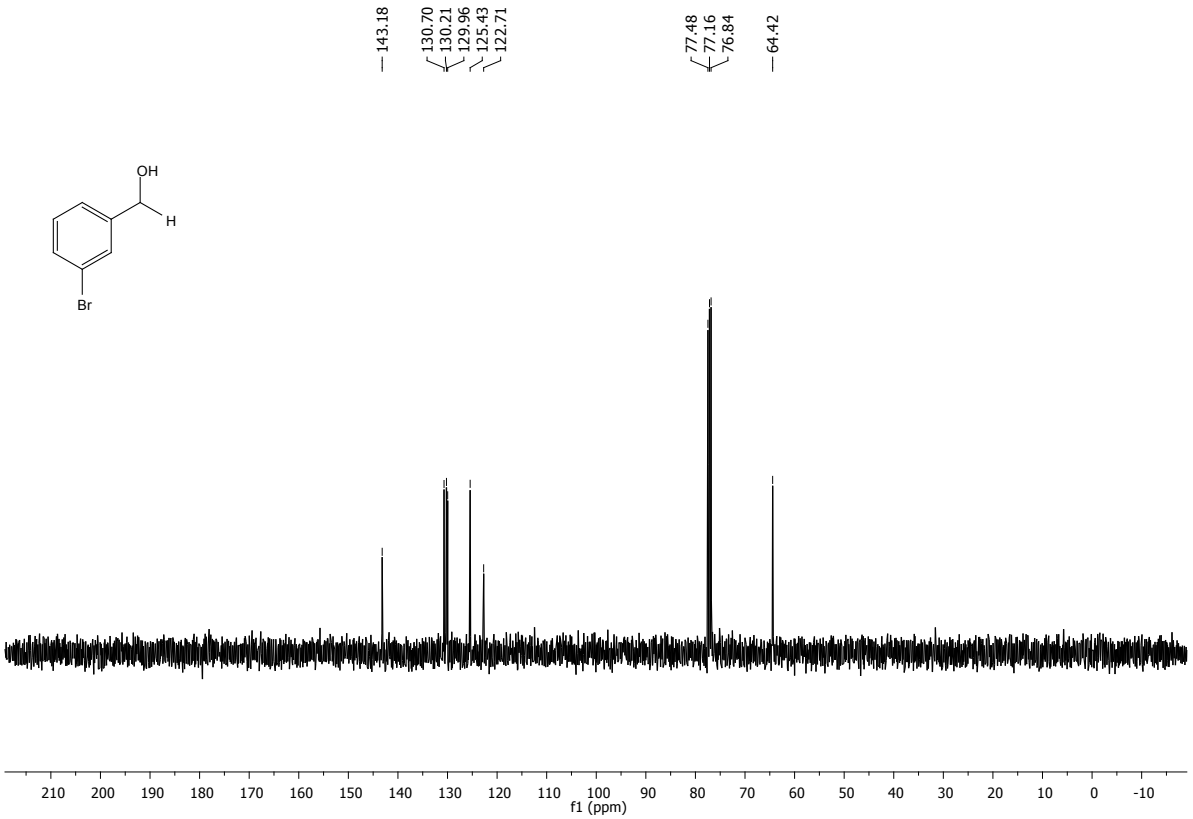


^{11}B NMR of **10b** (128 MHz, $CDCl_3$)

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

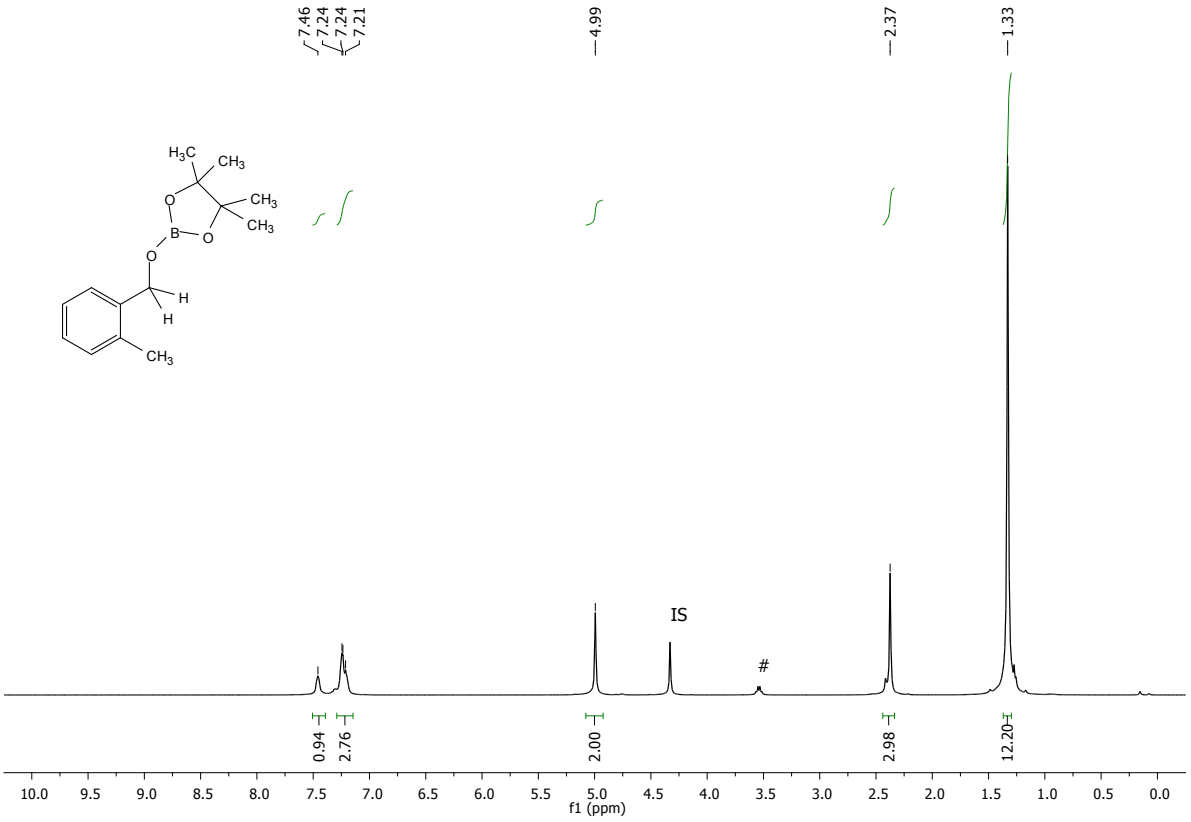


^{1}H NMR of **10c** (400 MHz, $CDCl_3$)

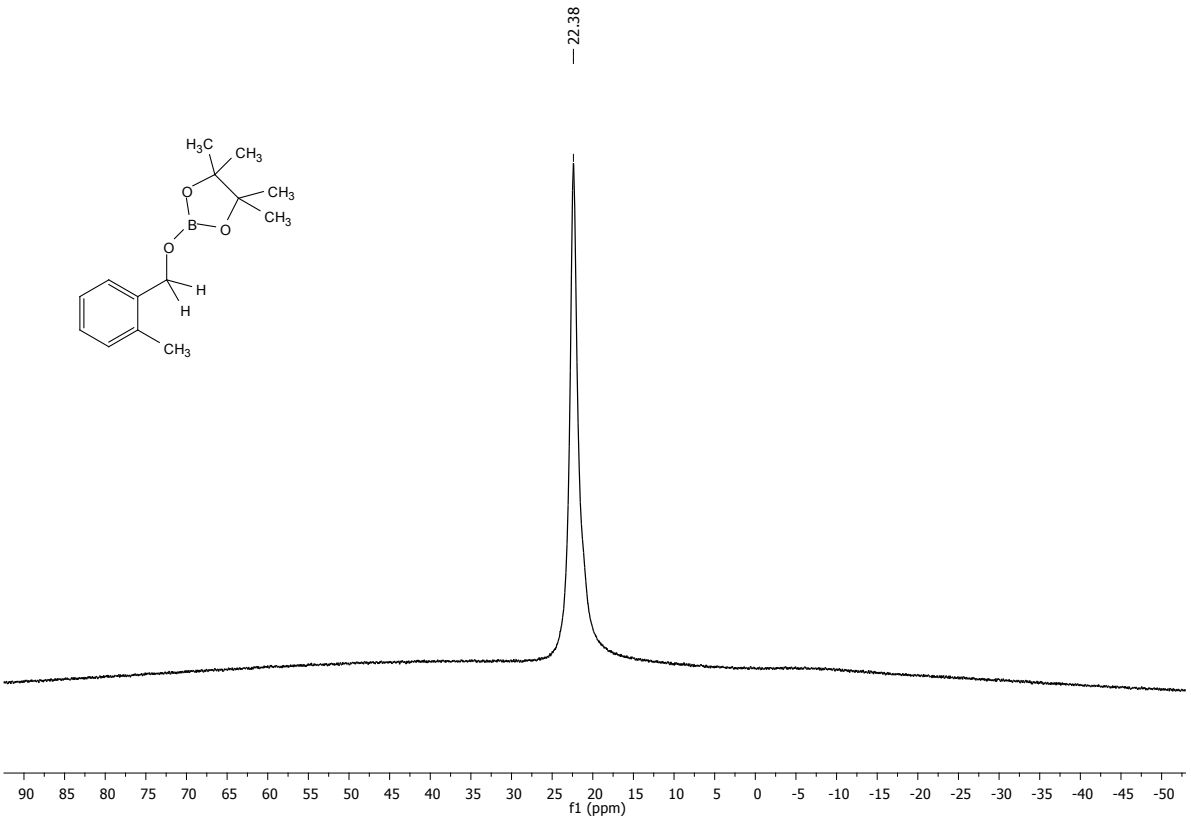


^{13}C NMR of **10c** (100 MHz, $CDCl_3$)

4,4,5,5-Tetramethyl-2-((2-methylbenzyl)oxy)-1,3,2-dioxaborolane (Table 2, 11b).[2,10]

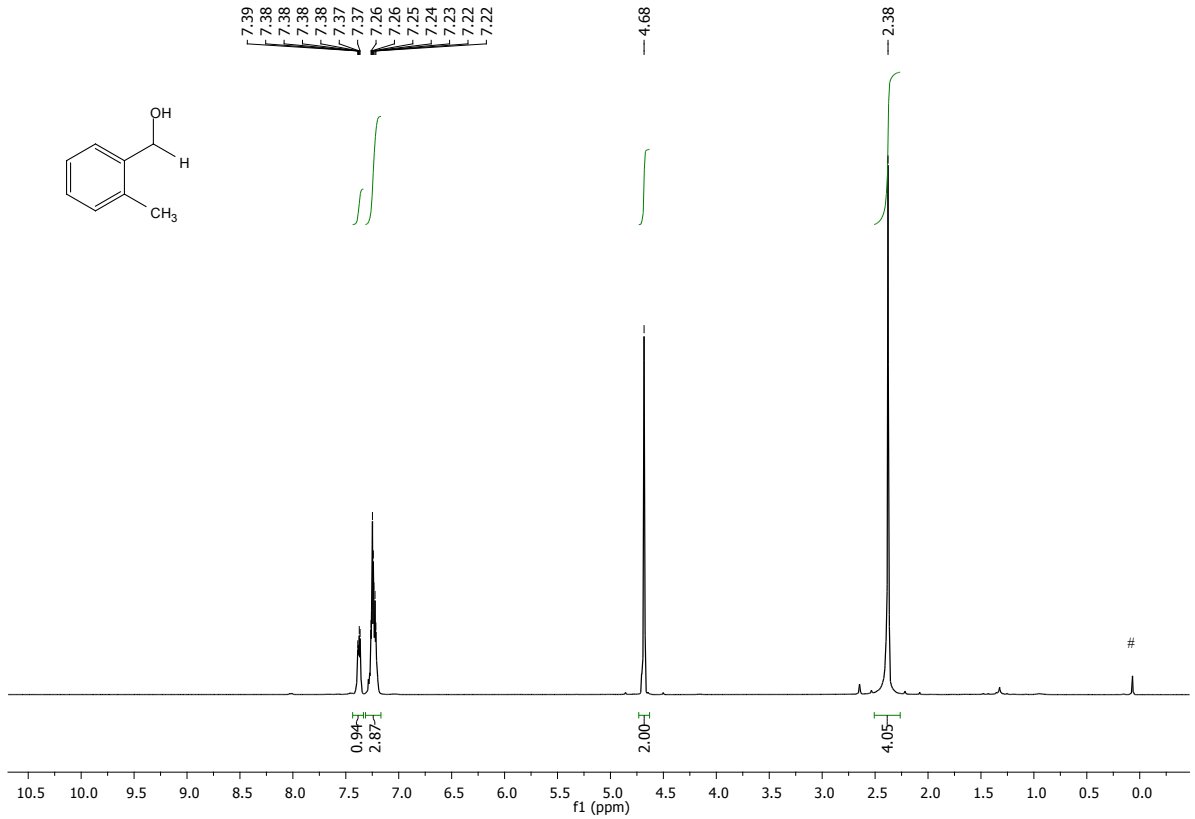


^{1}H NMR of **11b** (400 MHz, $CDCl_3$)

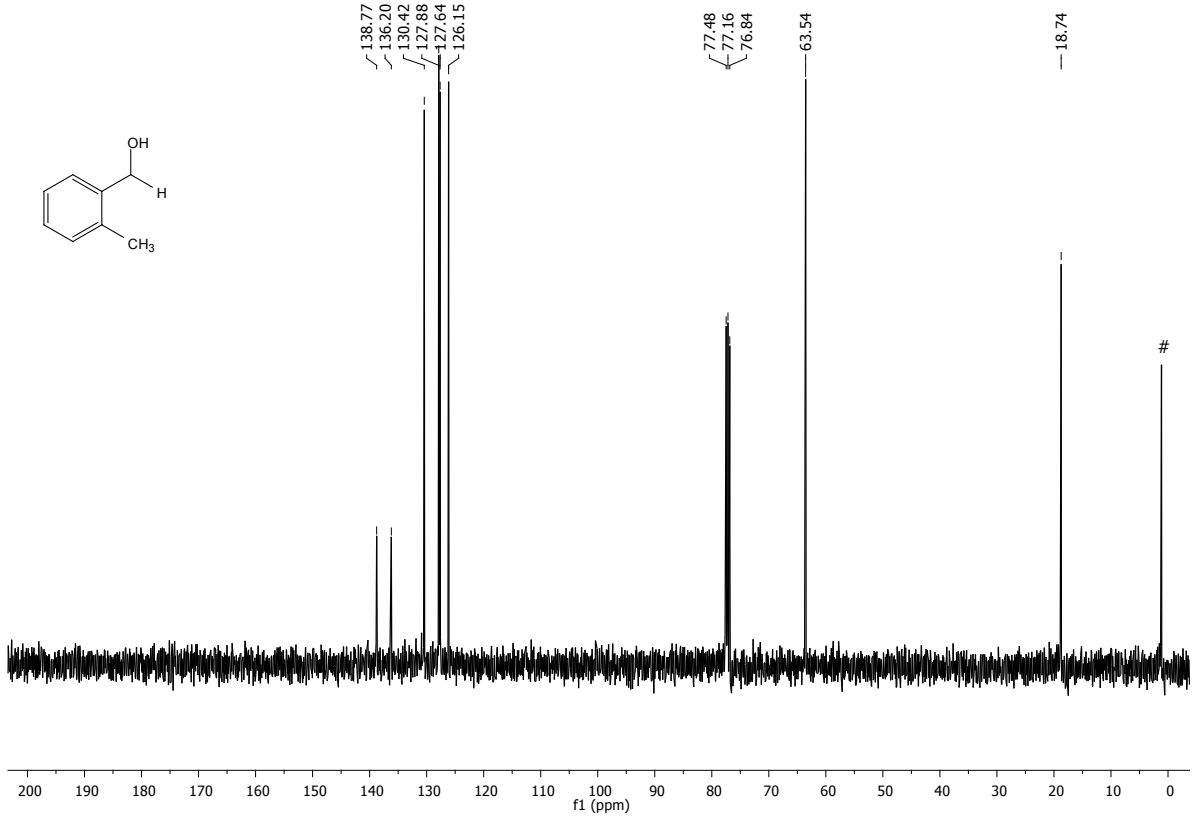


^{11}B NMR of **11b** (128 MHz, $CDCl_3$)

***o*-Tolylmethanol (11c)**.[2,7]

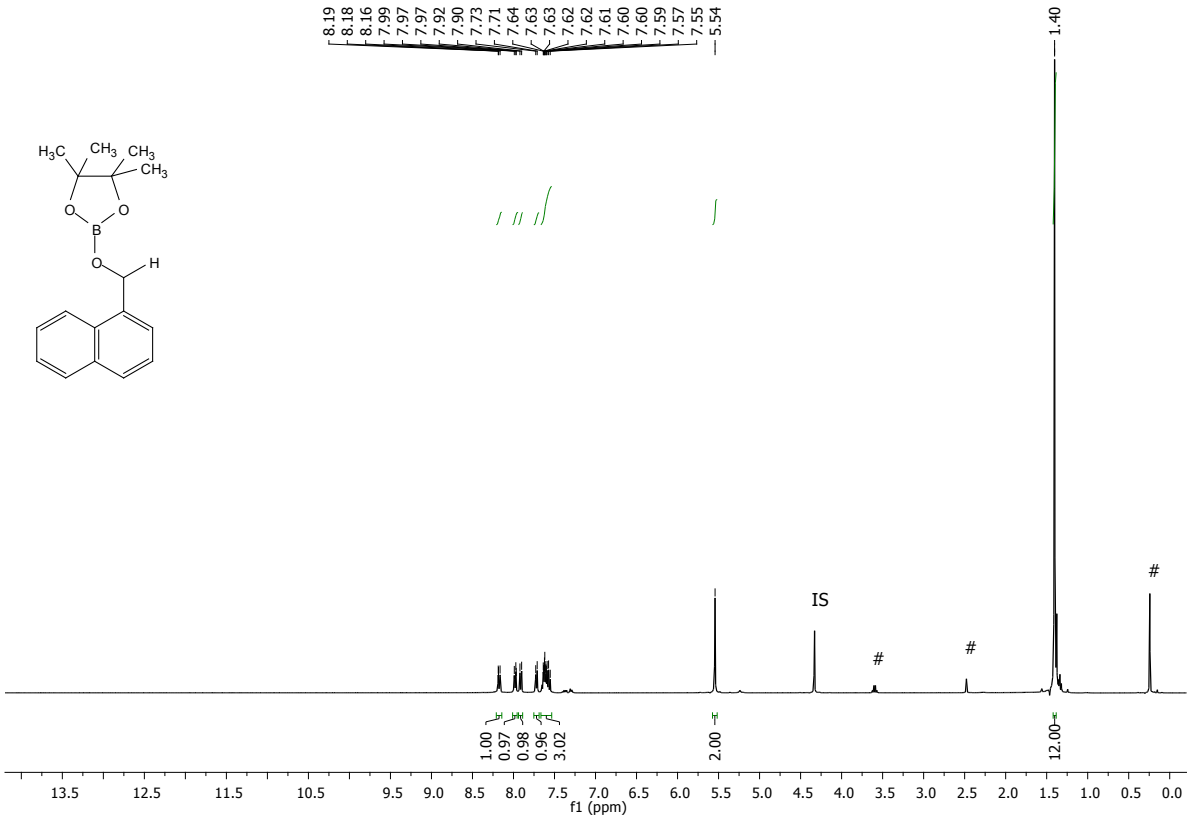


^{1}H NMR of **11c** (400 MHz, $CDCl_3$)

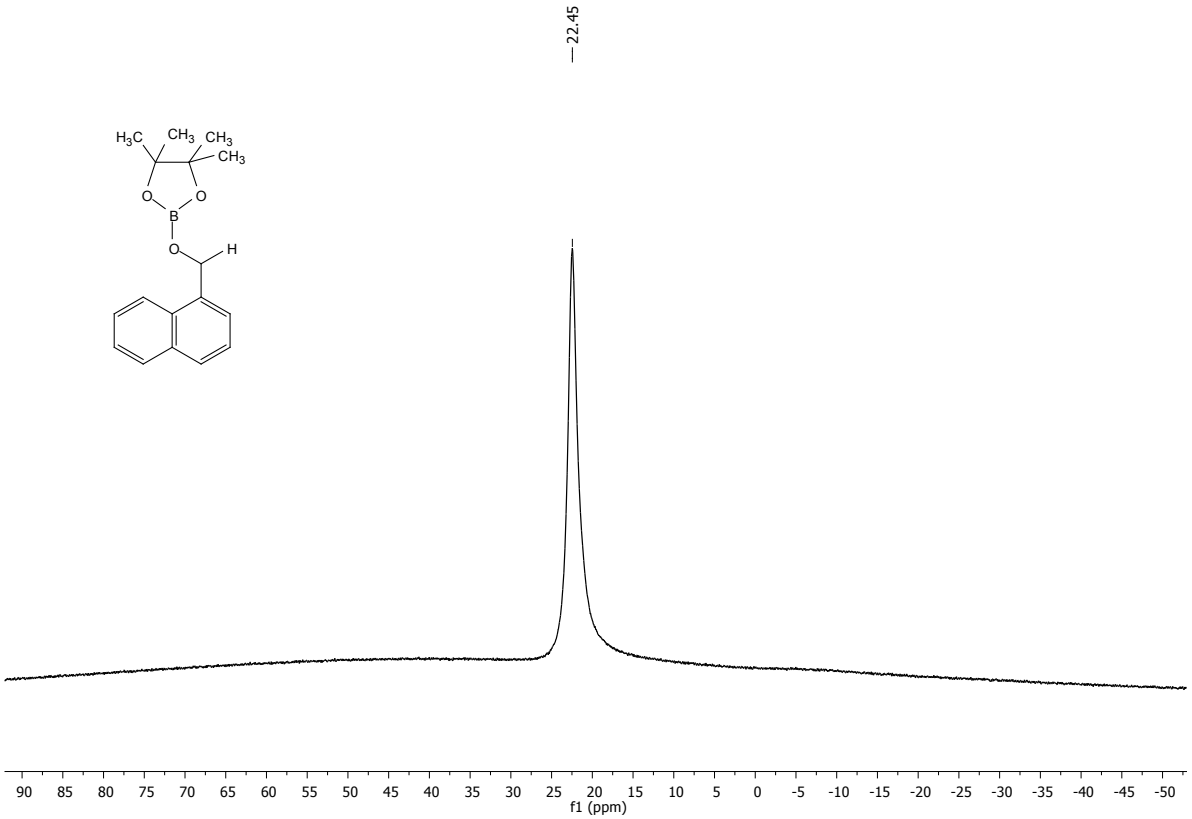


^{13}C NMR of **11c** (100 MHz, $CDCl_3$) # = grease.

4,4,5,5-Tetramethyl-2-(naphthalen-1-ylmethoxy)-1,3,2-dioxaborolane (Table 2, 12b).[2,3]

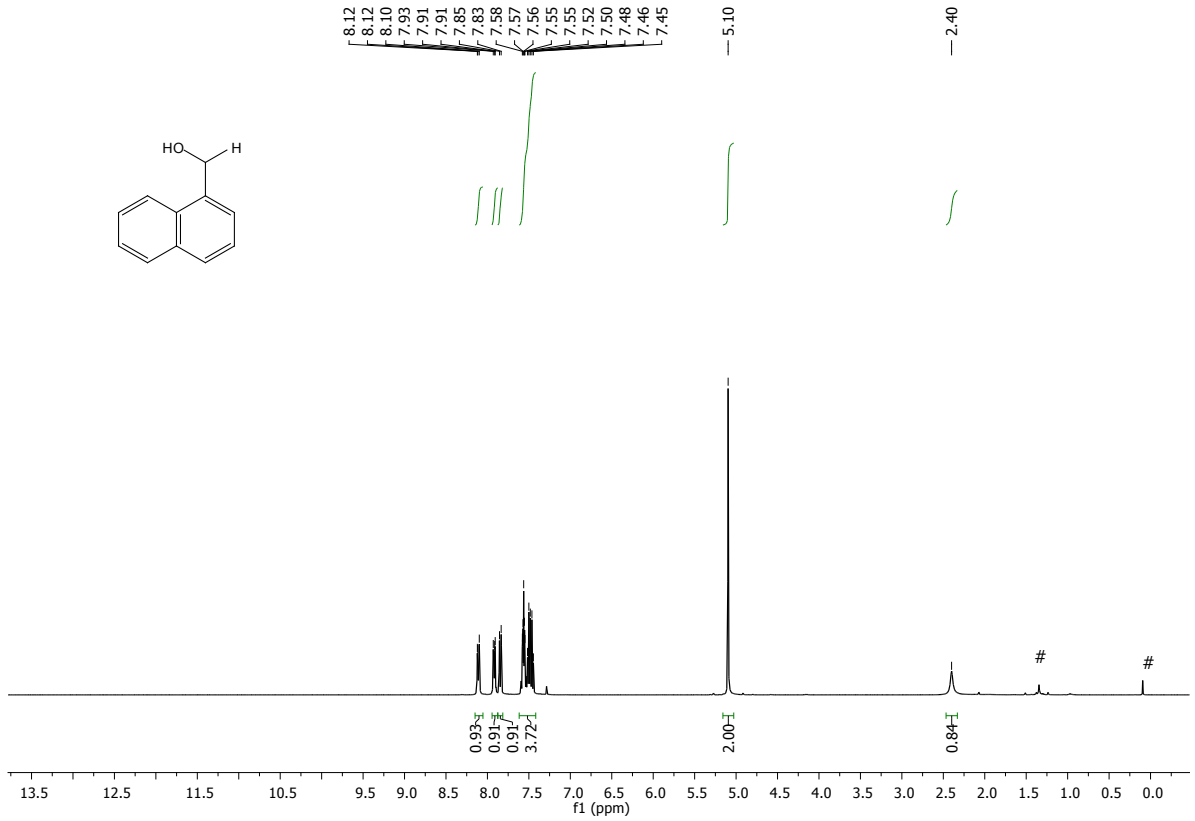


^{1}H NMR of **12b** (400 MHz, $CDCl_3$)

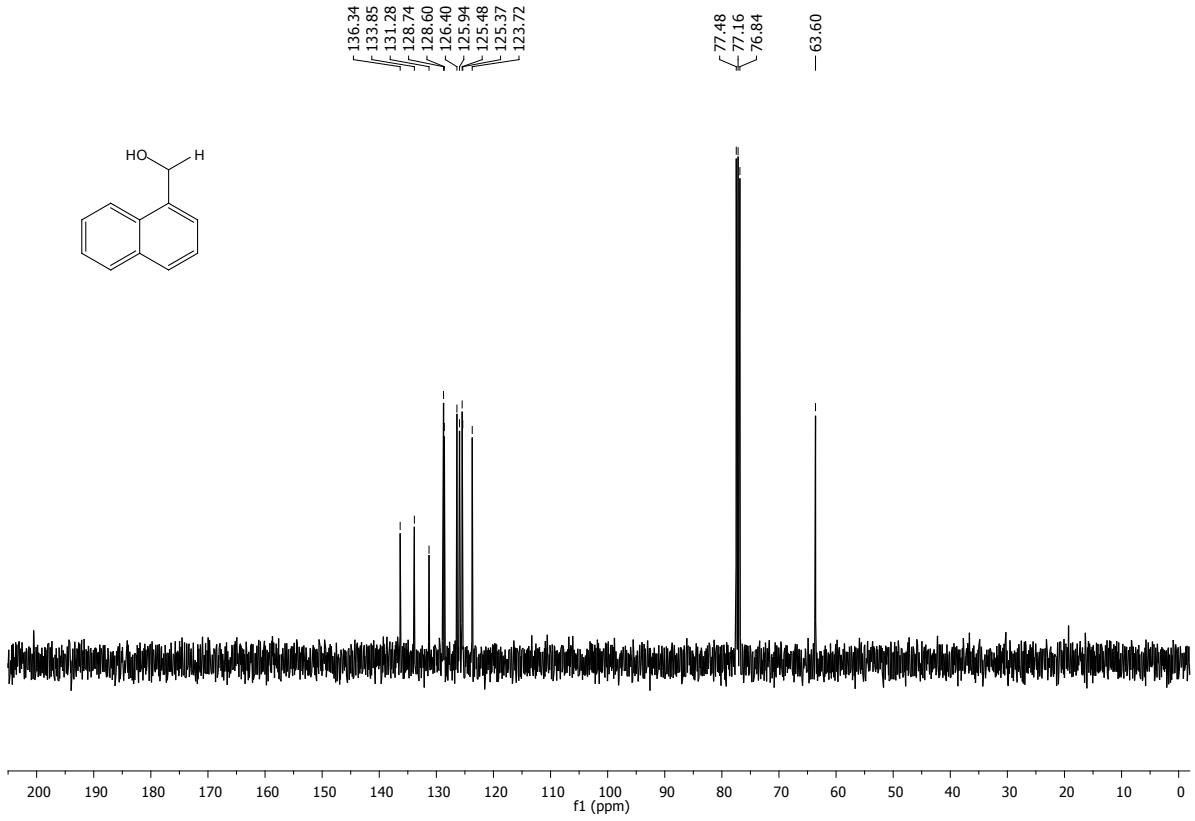


^{11}B NMR of **12b** (128 MHz, $CDCl_3$)

Naphthalen-2-ylmethanol (12c).[2,11]

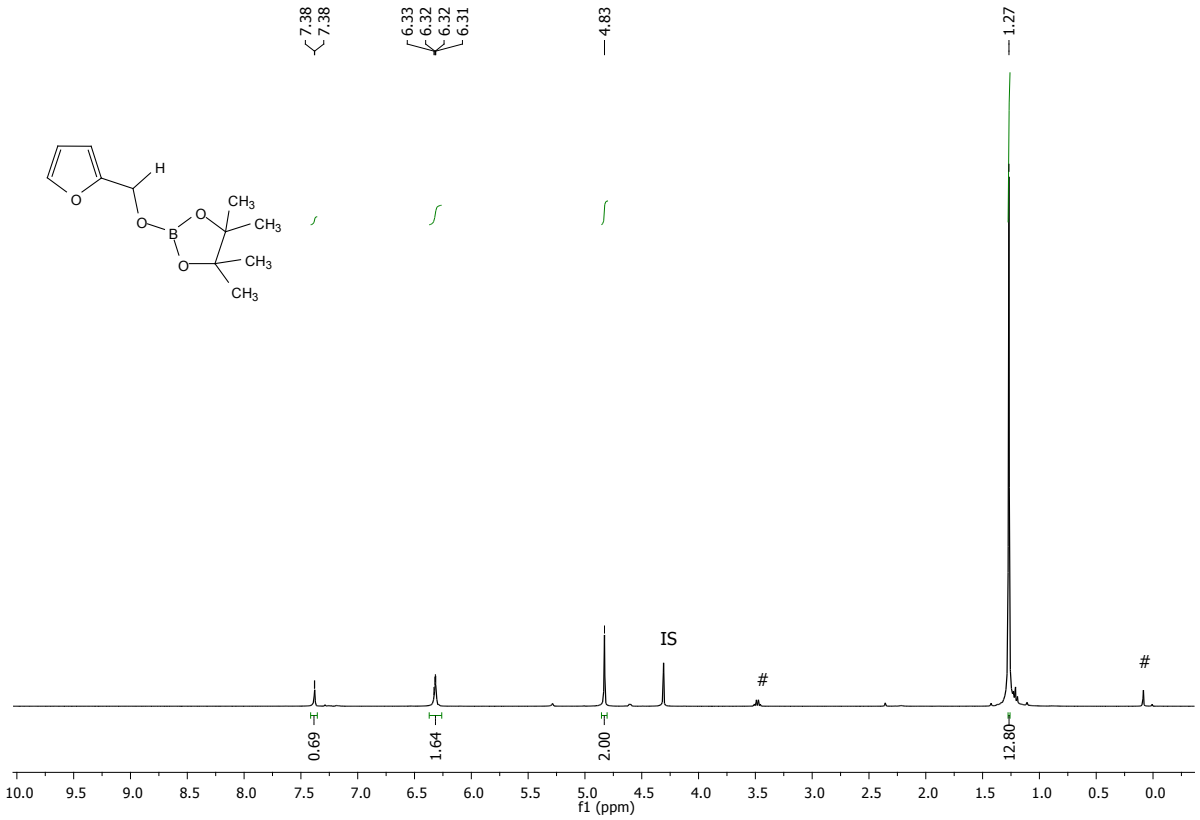


^{1}H NMR of **12c** (400 MHz, $CDCl_3$)

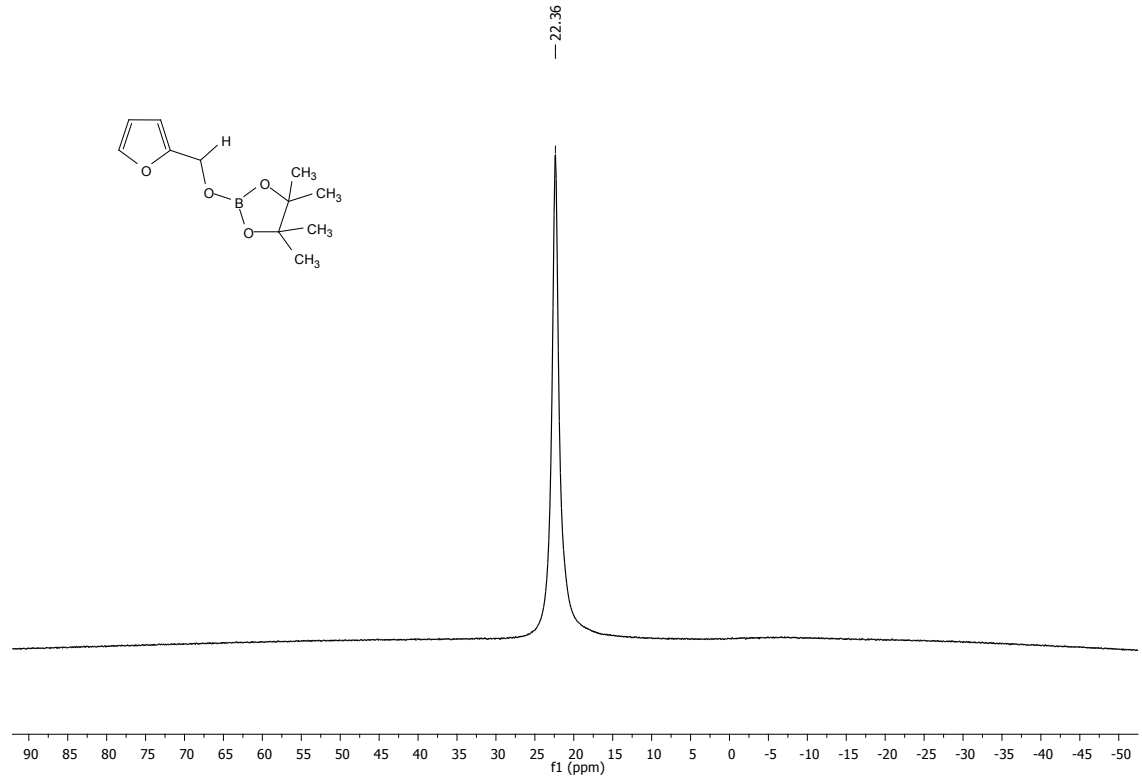


^{13}C NMR of **12c** (100 MHz, $CDCl_3$)

2-(Furan-2-ylmethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 13b).[2,6]

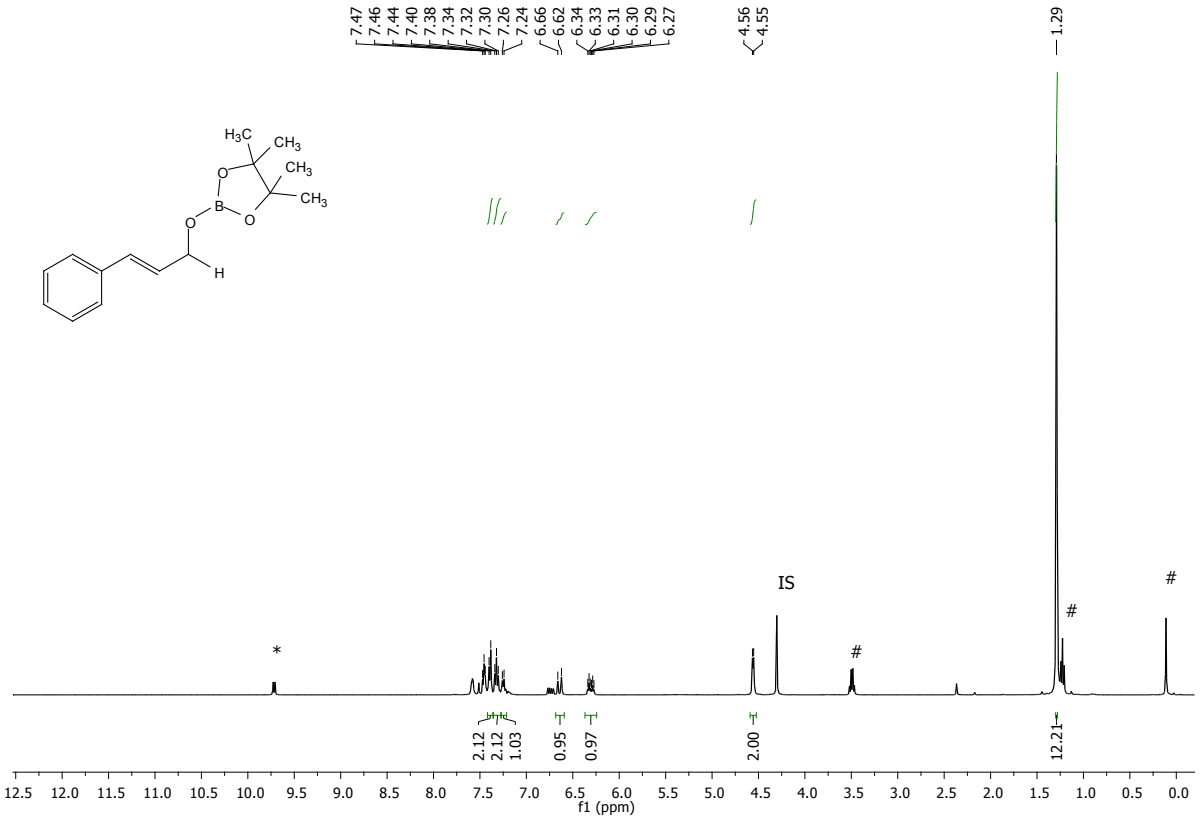


^{1}H NMR of **13b** (400 MHz, $CDCl_3$)

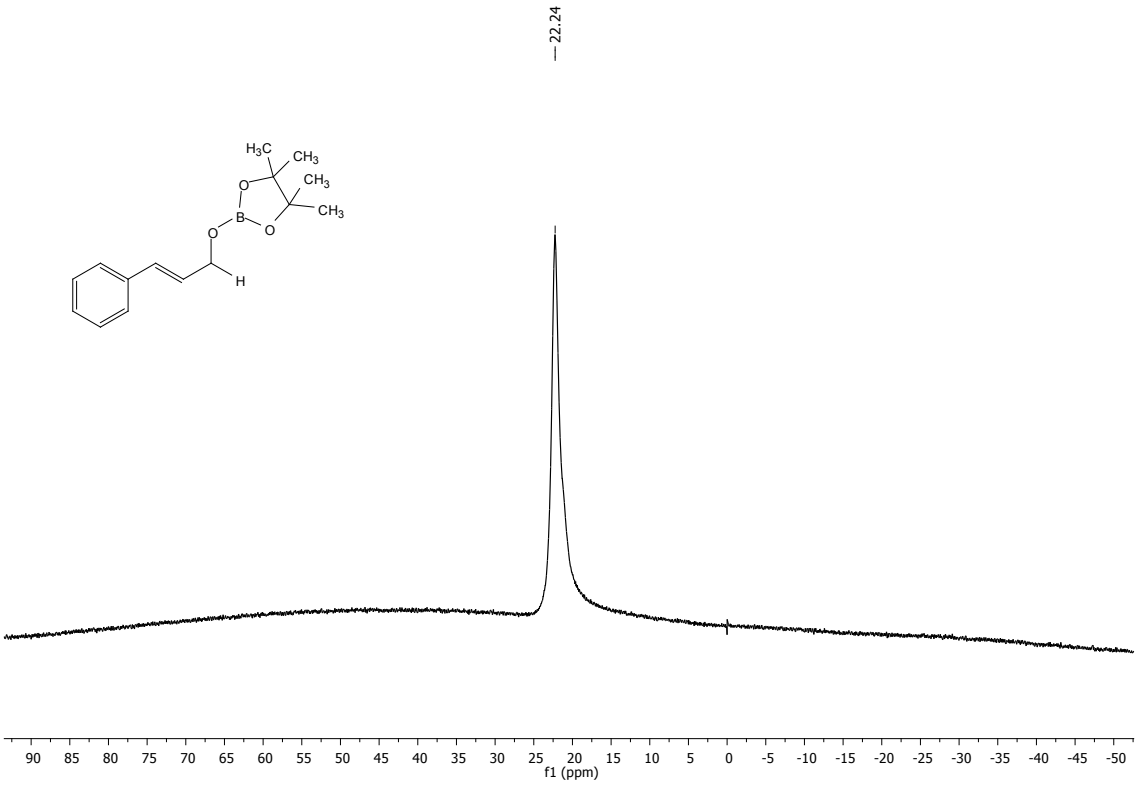


^{11}B NMR of **13b** (128 MHz, $CDCl_3$)

2-(Cinnamyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 14b).[2,6]

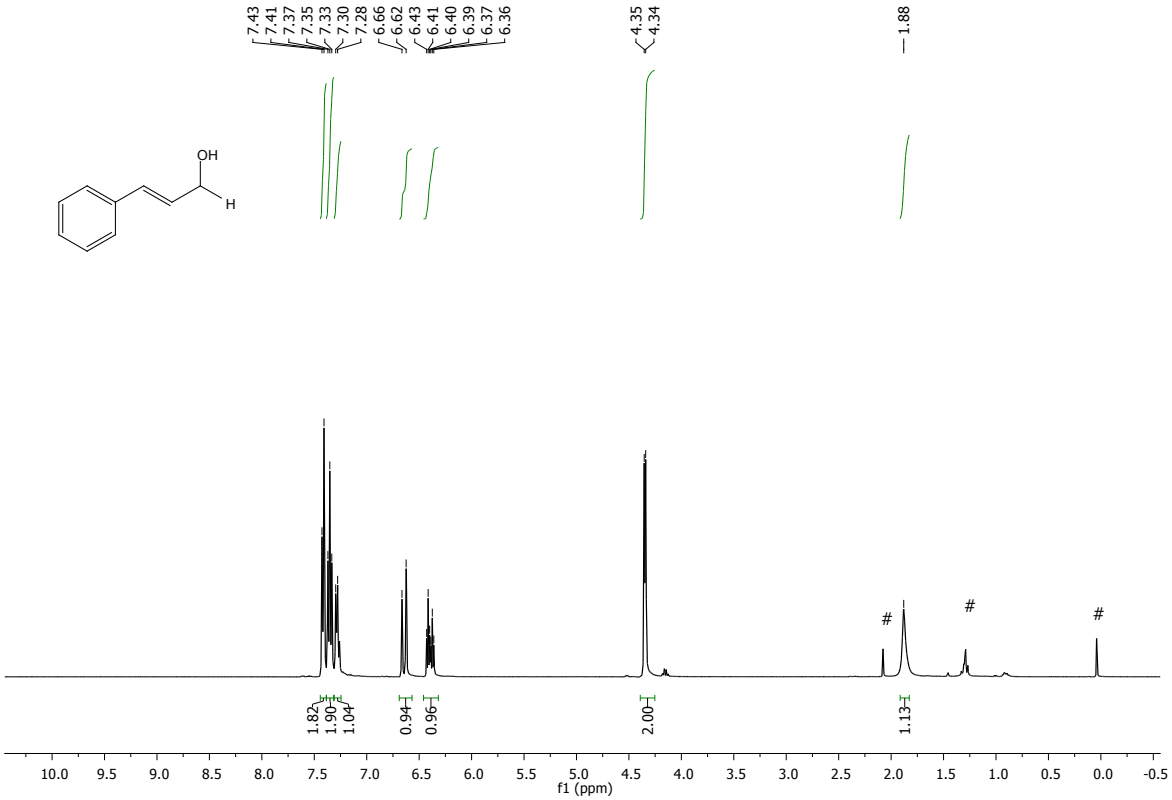


^{1}H NMR of **14b** (400 MHz, $CDCl_3$)

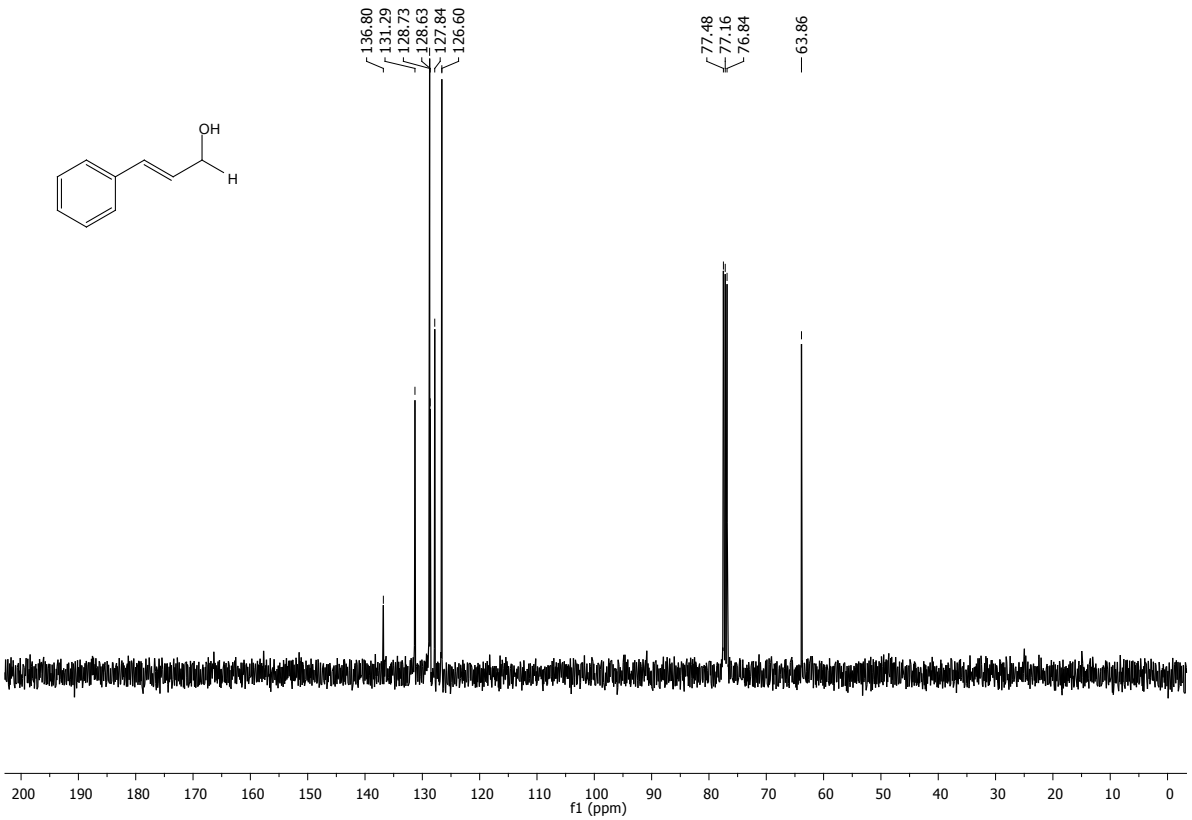


^{11}B NMR of **14b** (128 MHz, $CDCl_3$)

3-Phenyl-2-propene-1-ol (14c).[2,12]

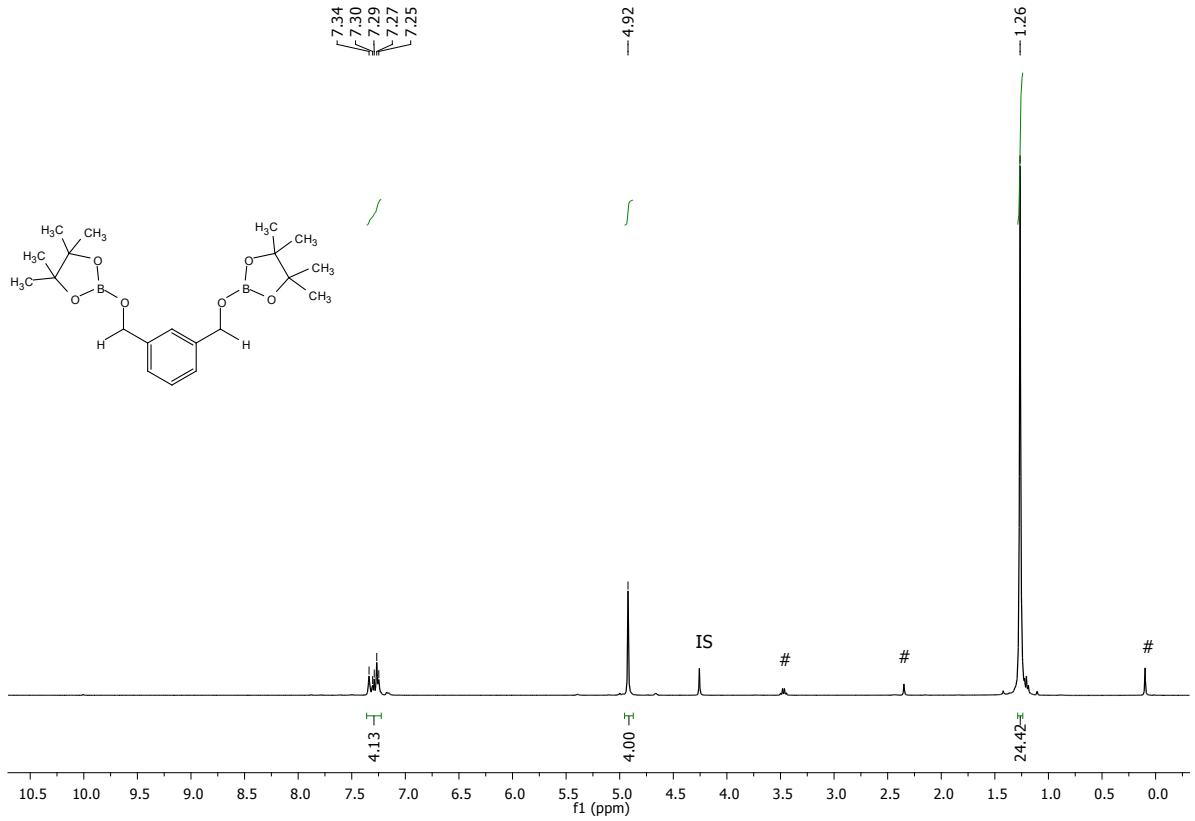


^{1}H NMR of **14c** (400 MHz, $CDCl_3$)

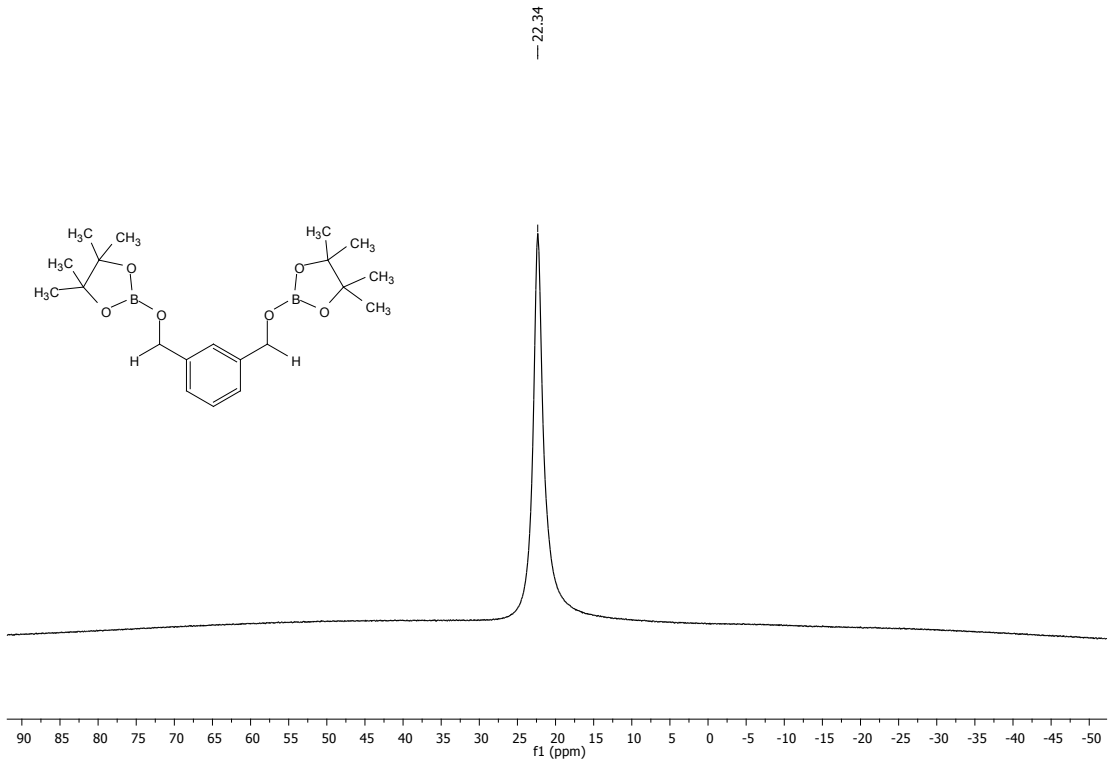


^{13}C NMR of **14c** (100 MHz, $CDCl_3$)

1,3-bis(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzene (Table 2, 15b).[2,3]

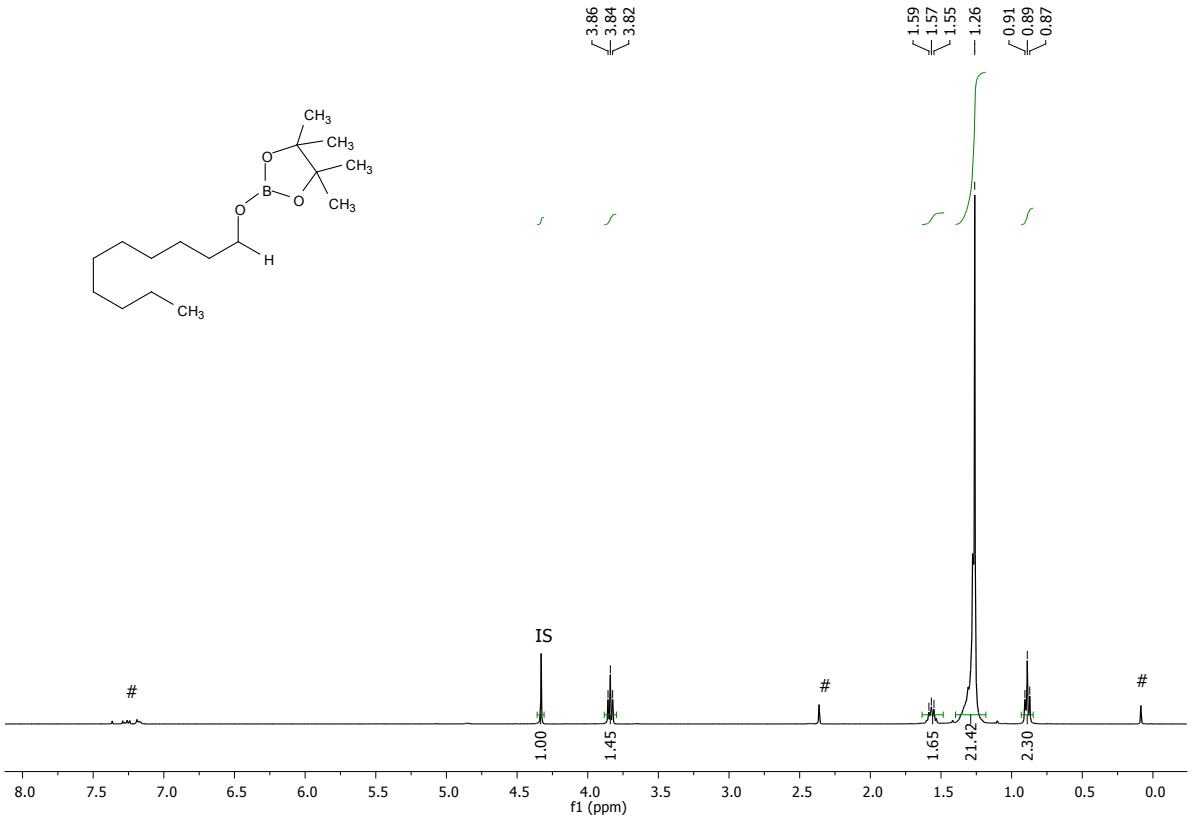


^{1}H NMR of **15b** (400 MHz, $CDCl_3$)

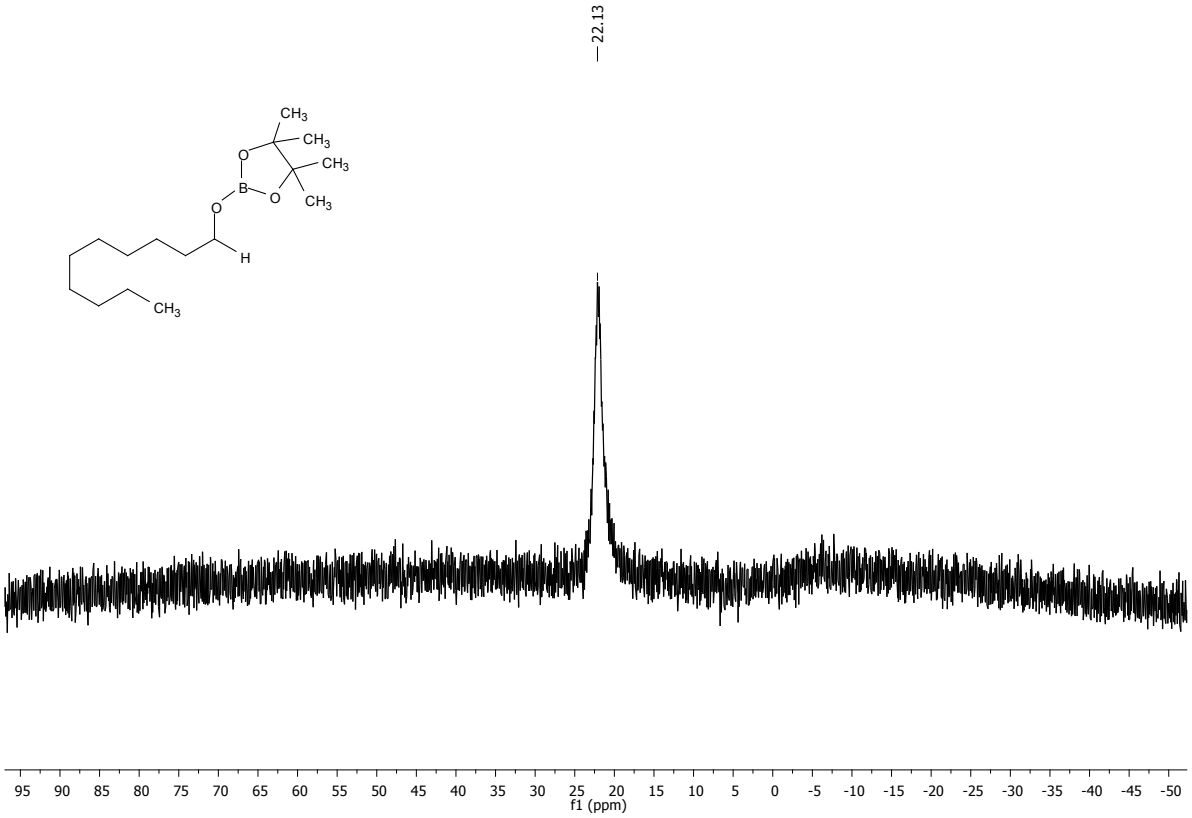


^{11}B NMR of **15b** (128 MHz, $CDCl_3$)

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

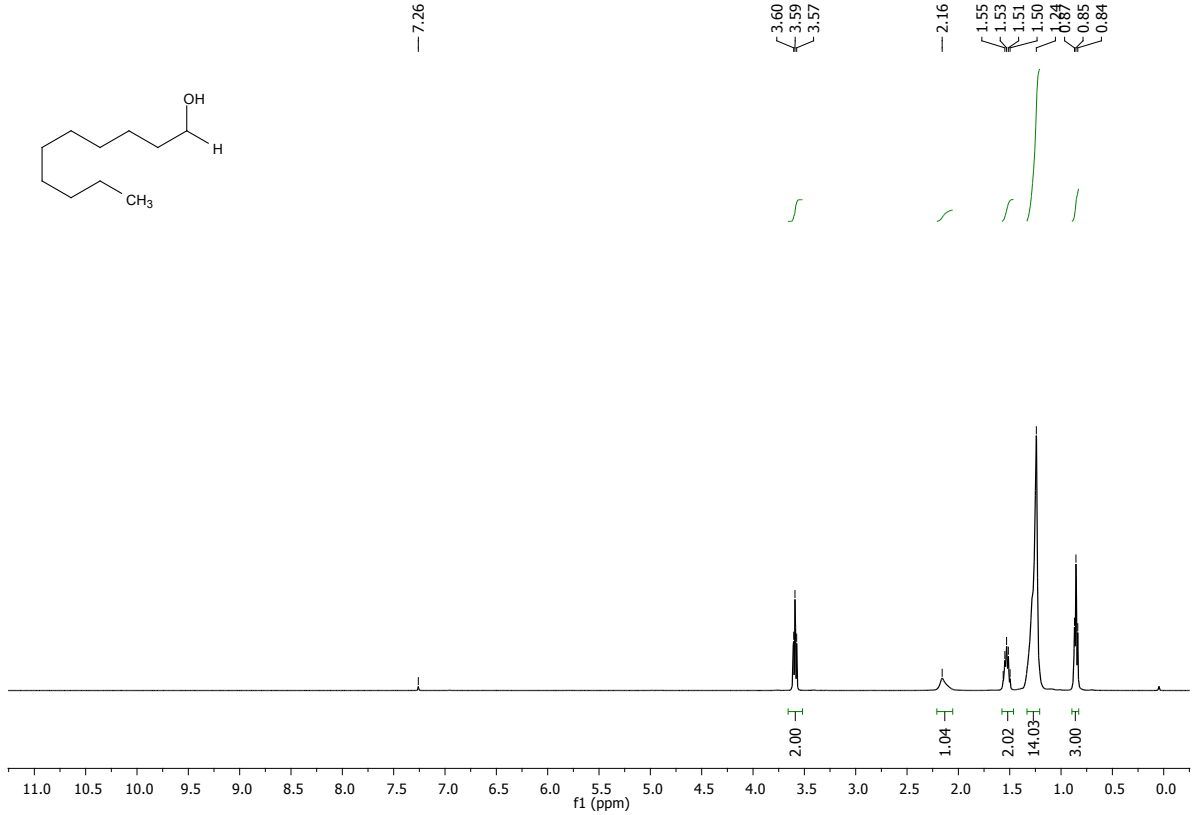


^{1}H NMR of **16b** (400 MHz, $CDCl_3$)

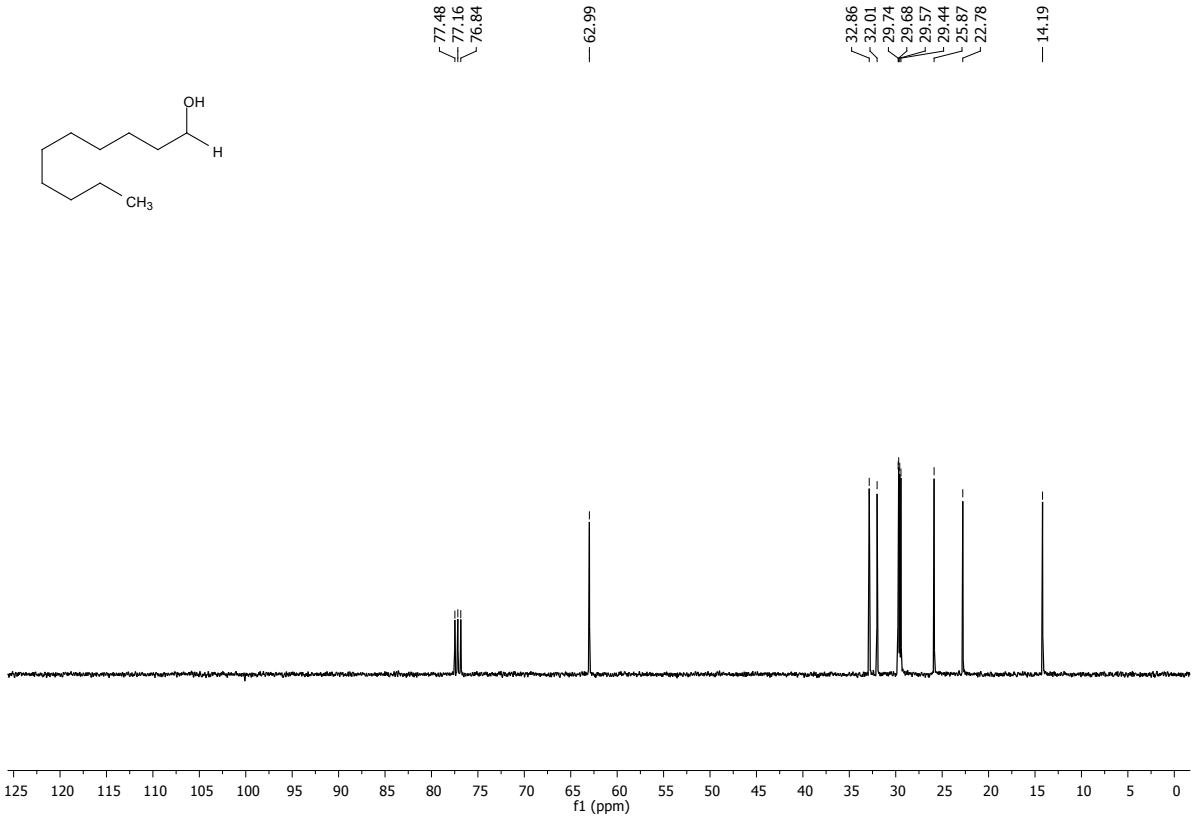


^{11}B NMR of **16b** (128 MHz, $CDCl_3$)

Decan-1-ol (16c).[2,4]

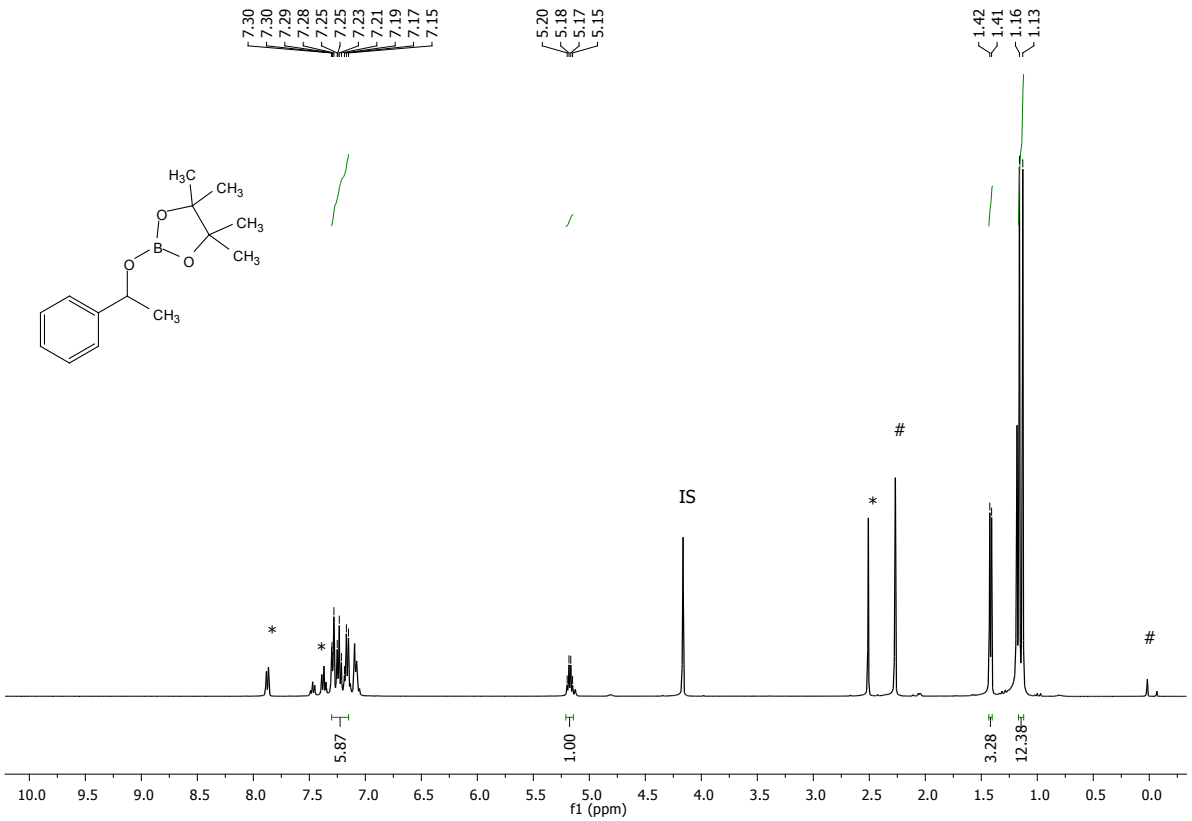


^{1}H NMR of **16c** (400 MHz, $CDCl_3$)

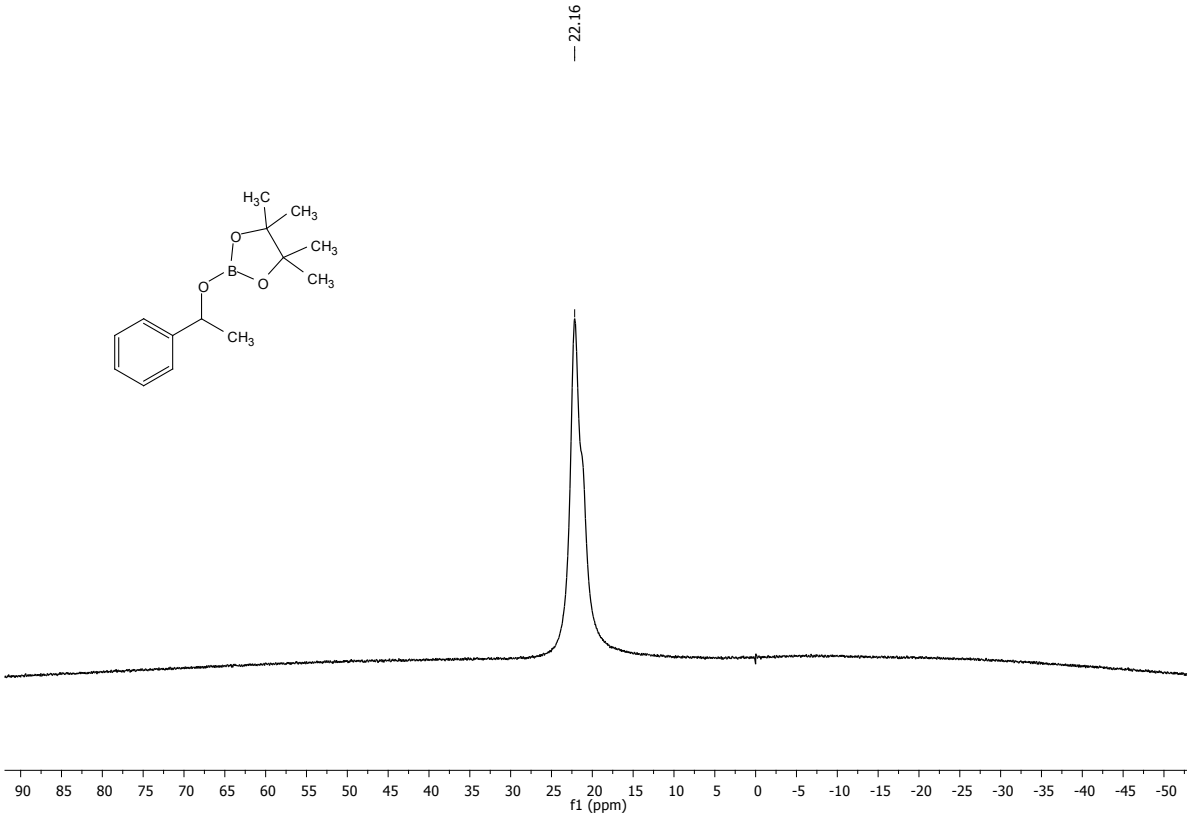


^{13}C NMR of **16c** (100 MHz, $CDCl_3$)

4,4,5,5-Tetramethyl-2-(1-phenylethoxy)-1,3,2-dioxaborolane (Table 3, 17b).[2,3]

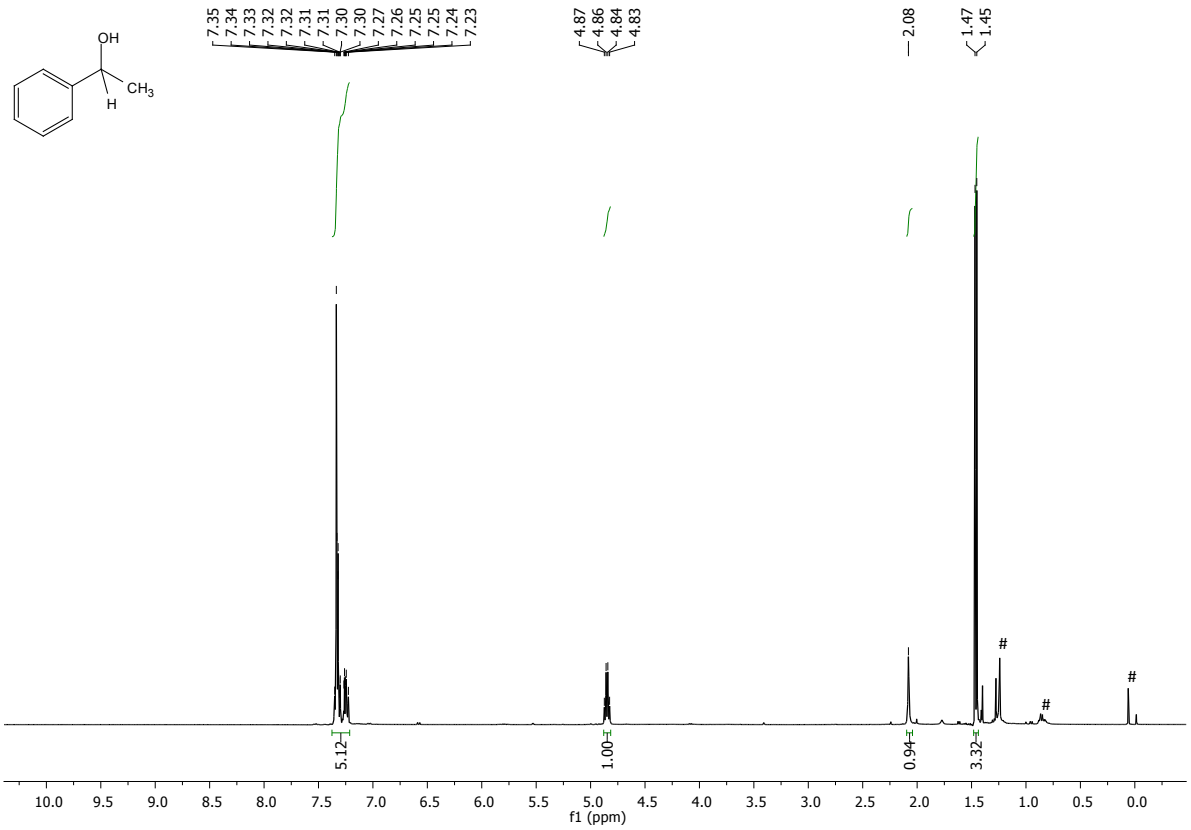


^{1}H NMR of **17b** (400 MHz, $CDCl_3$)

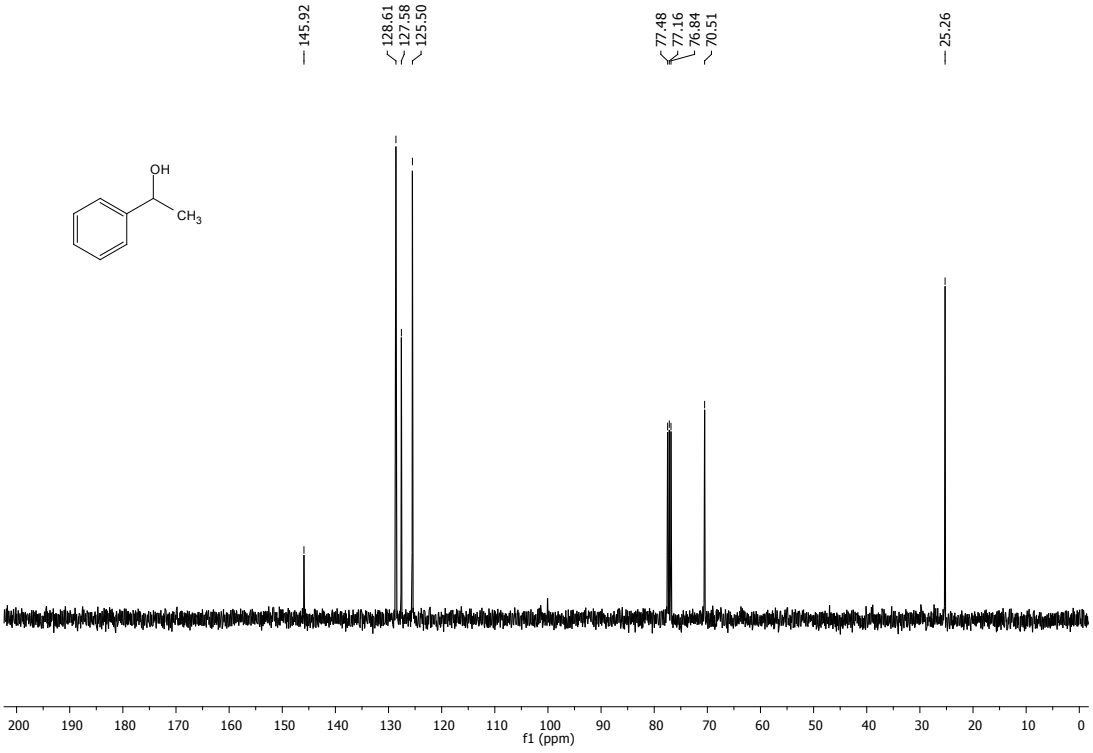


^{11}B NMR of **17b** (128 MHz, $CDCl_3$)

1-Phenylethanol (17c).[2,4]

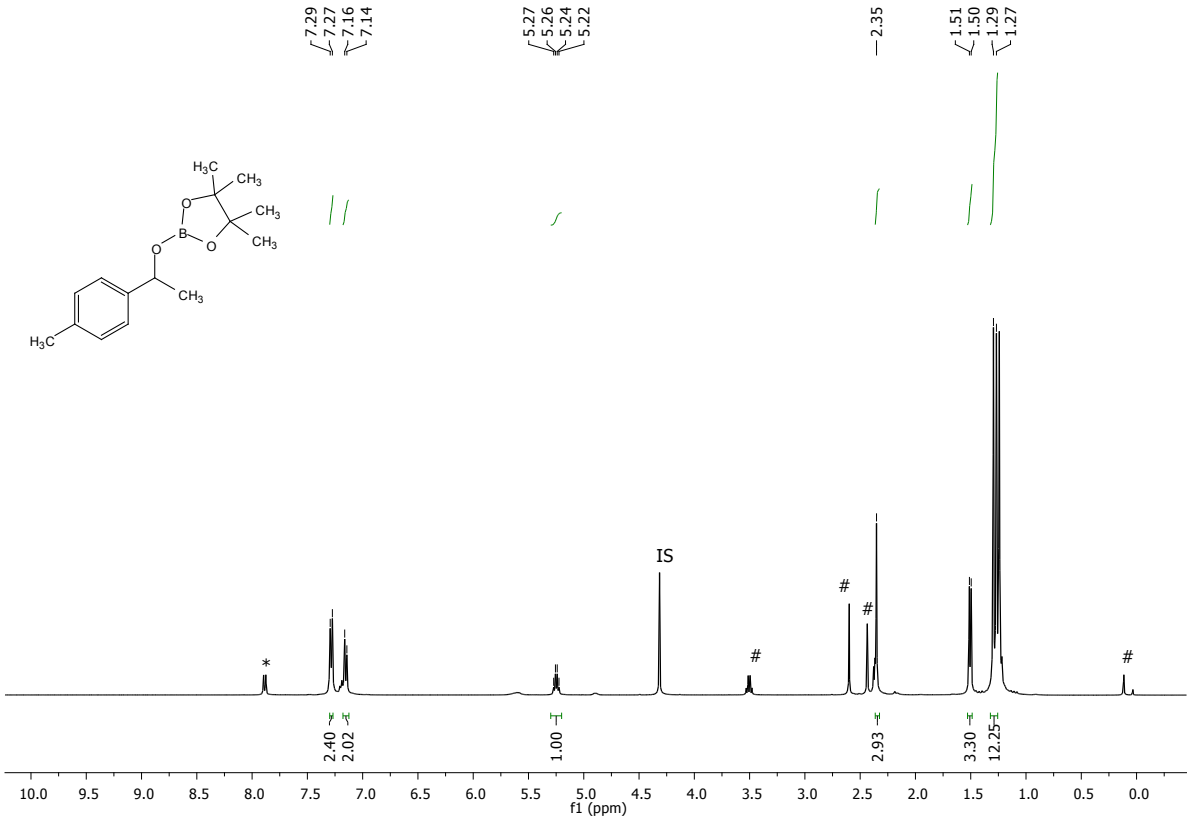


^{1}H NMR of **17c** (400 MHz, $CDCl_3$)

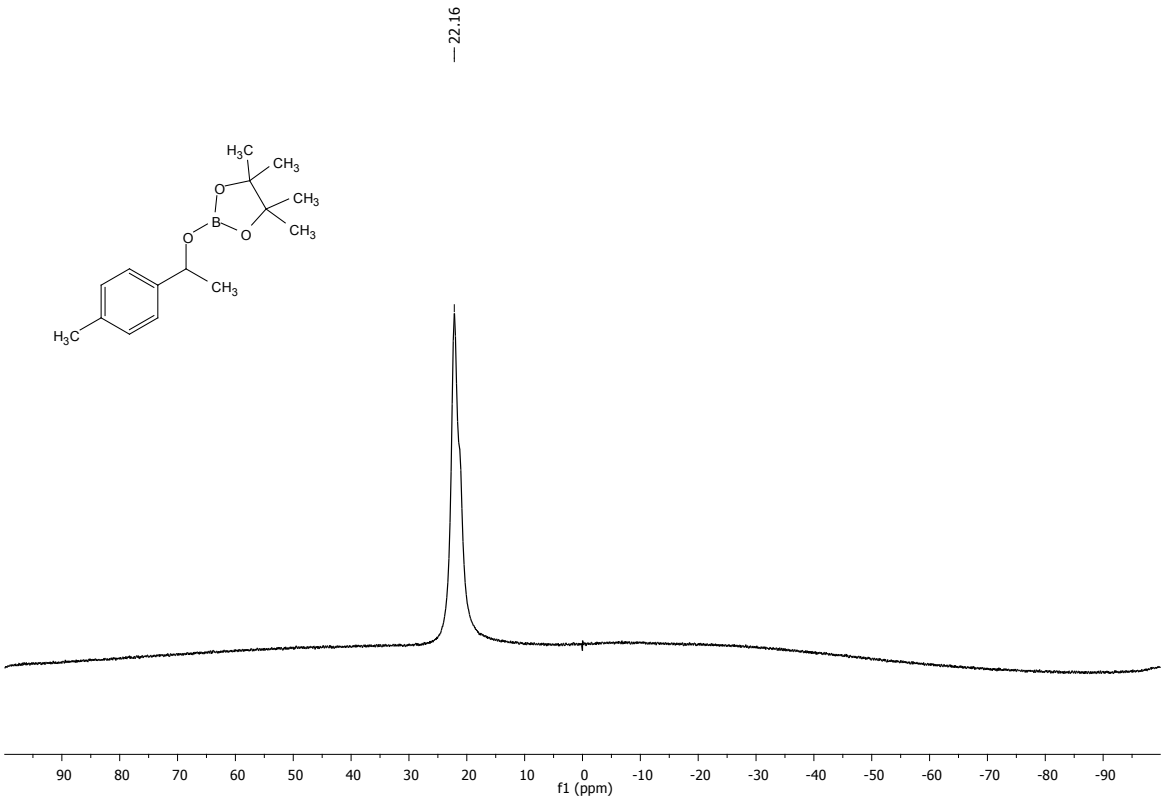


^{13}C NMR of **17c** (100 MHz, $CDCl_3$)

4,4,5,5-Tetramethyl-2-(1-(p-tolyl)ethoxy)-1,3,2-dioxaborolane (Table 3, 18b).[2,3]

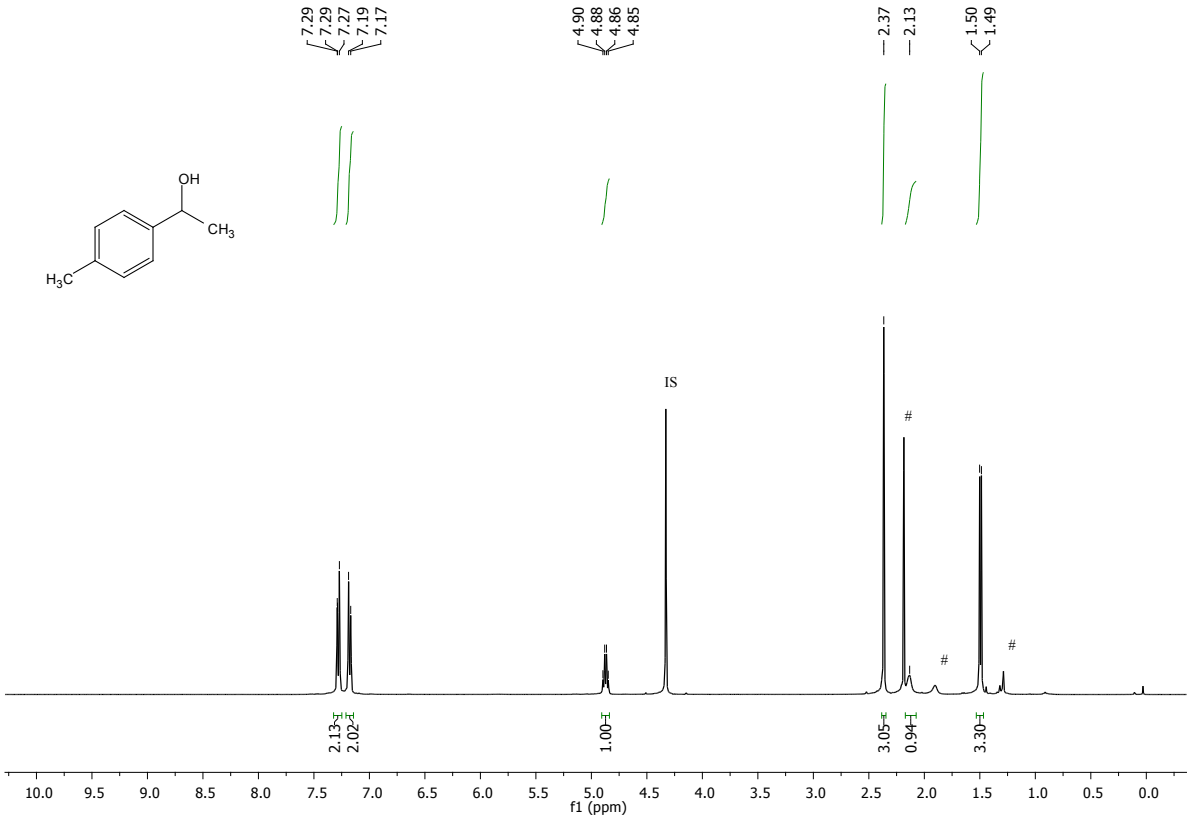


^{1}H NMR of **18b** (400 MHz, $CDCl_3$)

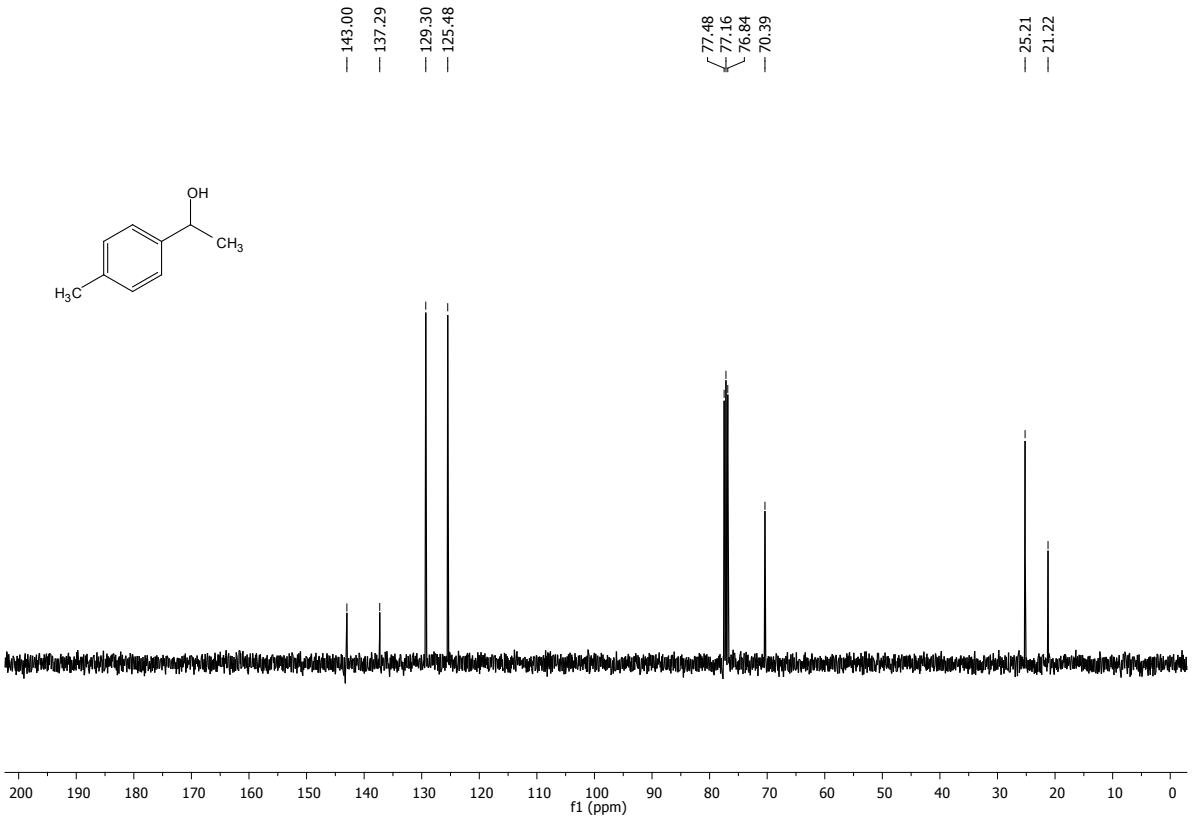


^{11}B NMR of **18b** (128 MHz, $CDCl_3$)

1-(p-Tolyl)ethanol (18c).[2,4]

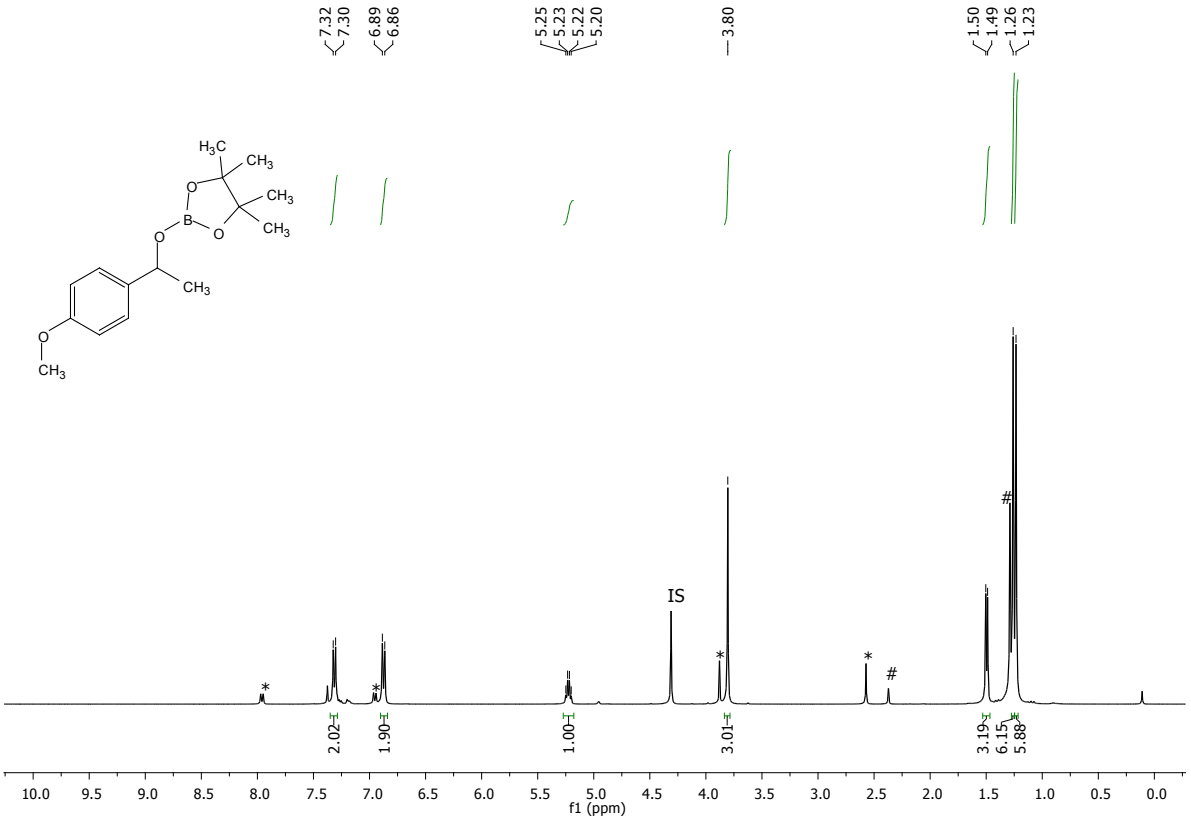


^{1}H NMR of **18c** (400 MHz, $CDCl_3$)

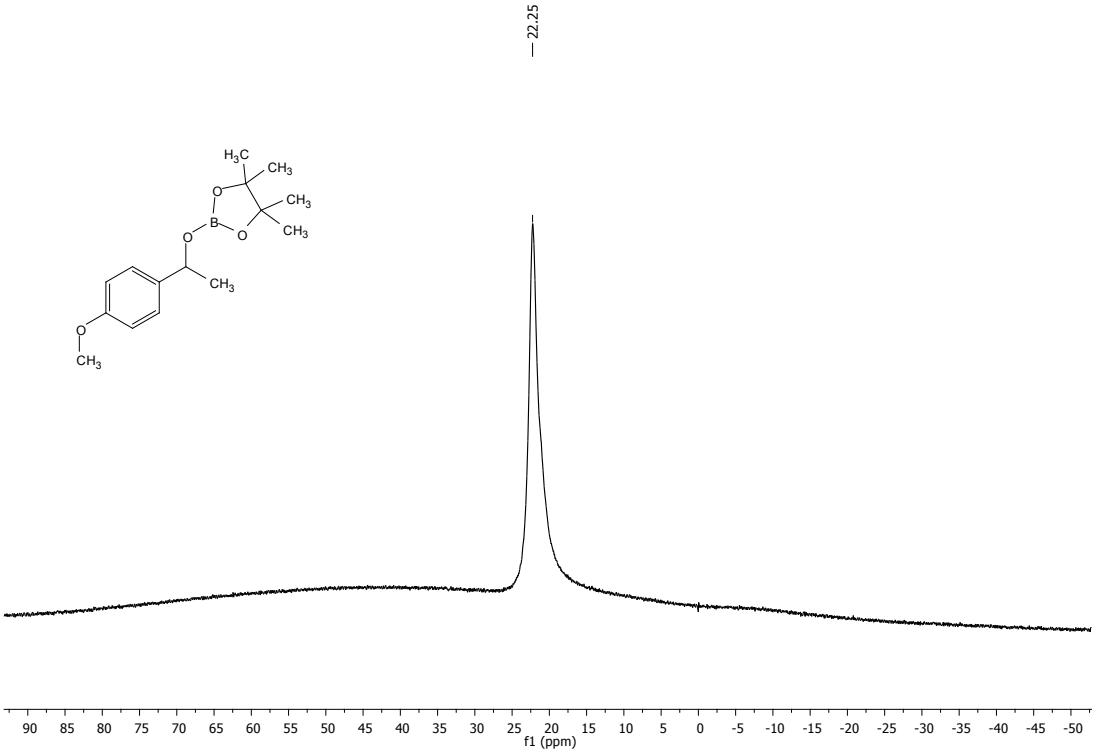


^{13}C NMR of **18c** (100 MHz, $CDCl_3$)

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

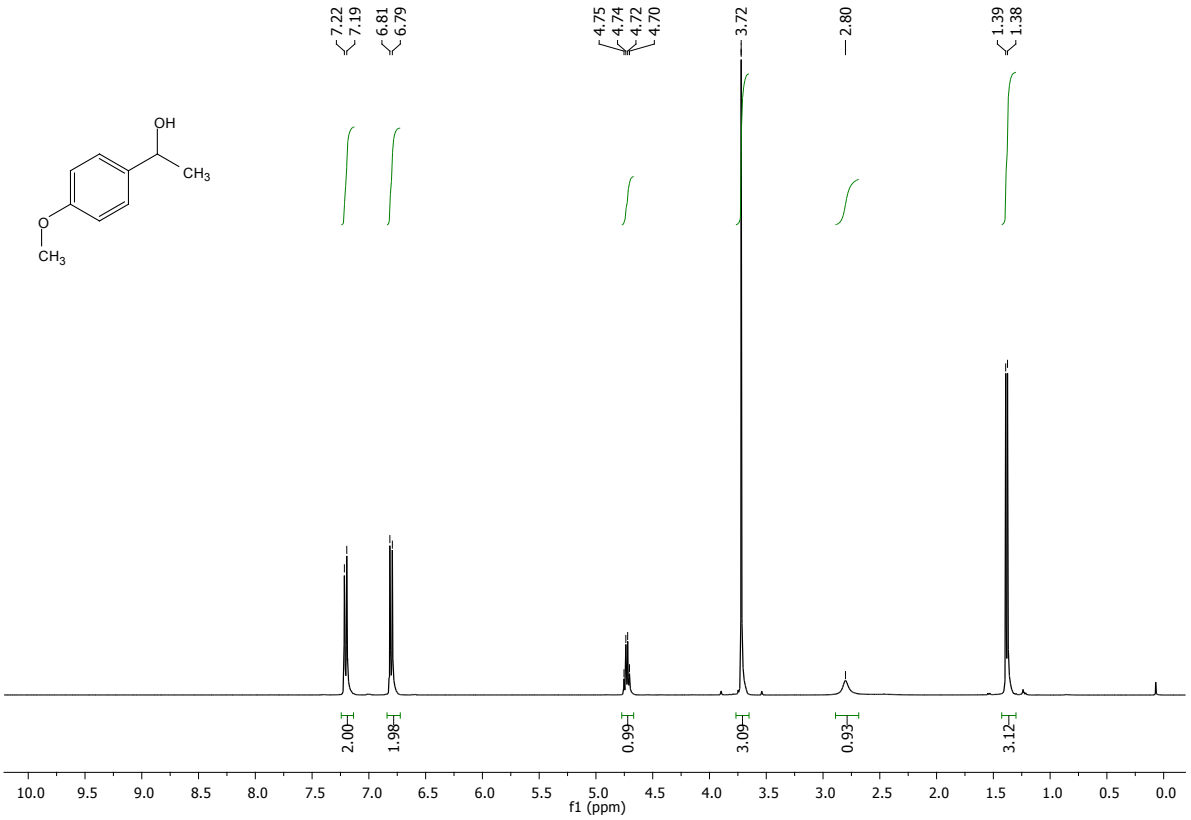


^{1}H NMR of **19b** (400 MHz, $CDCl_3$)

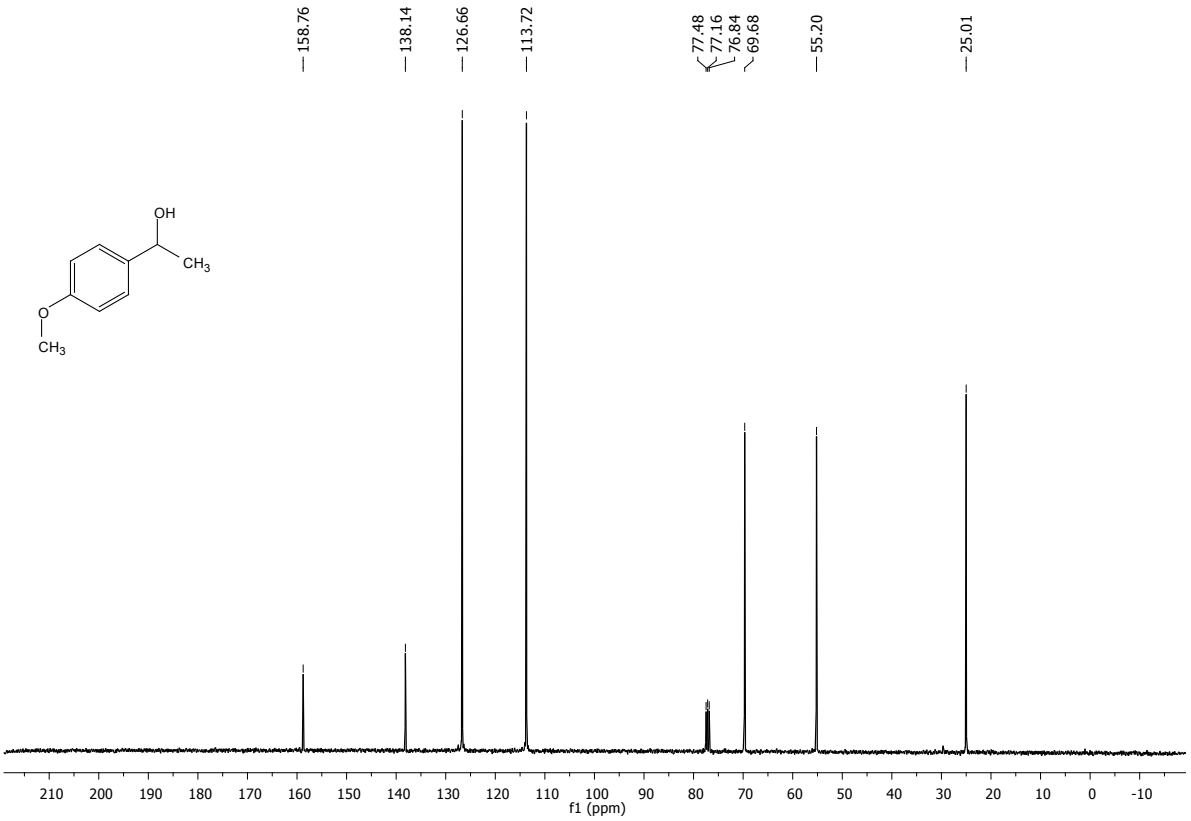


^{11}B NMR of **19b** (128 MHz, $CDCl_3$)

1-(4-Methoxyphenyl)ethanol (Table 3, 19c).[2]

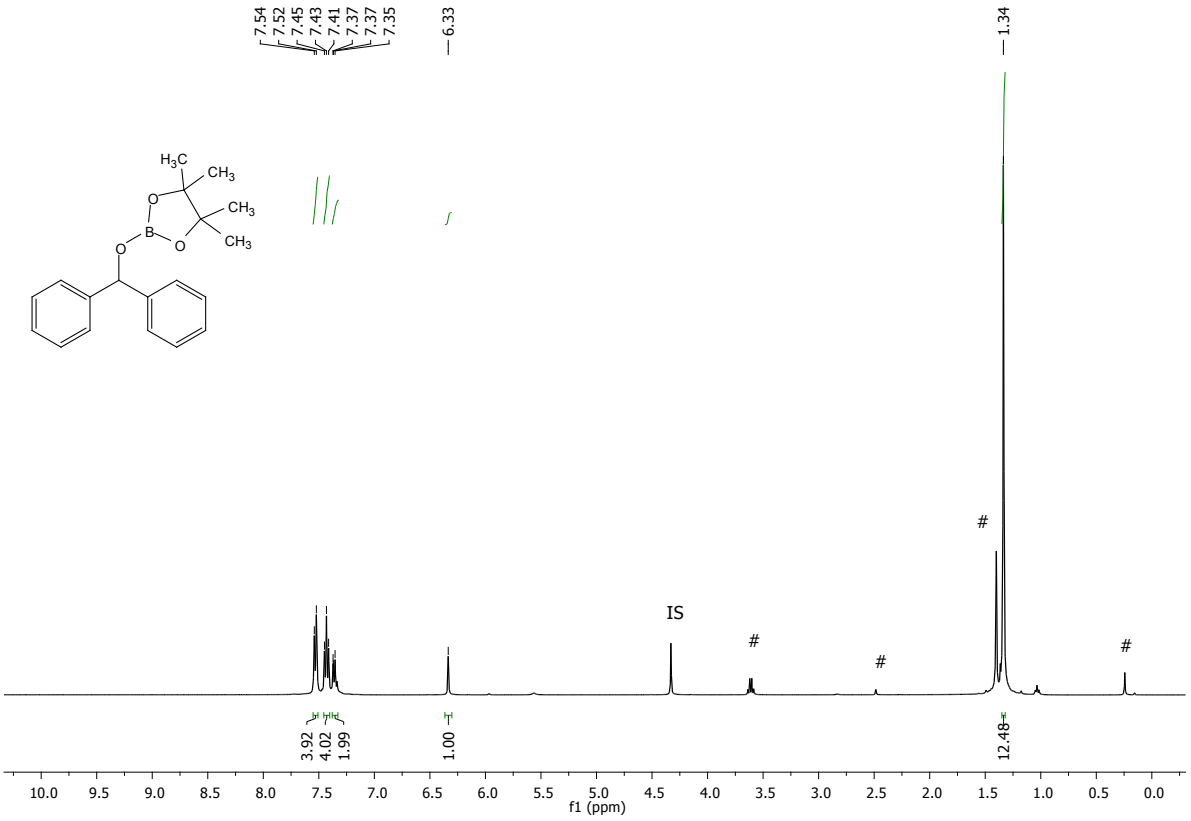


^{1}H NMR of **19c** (400 MHz, $CDCl_3$)

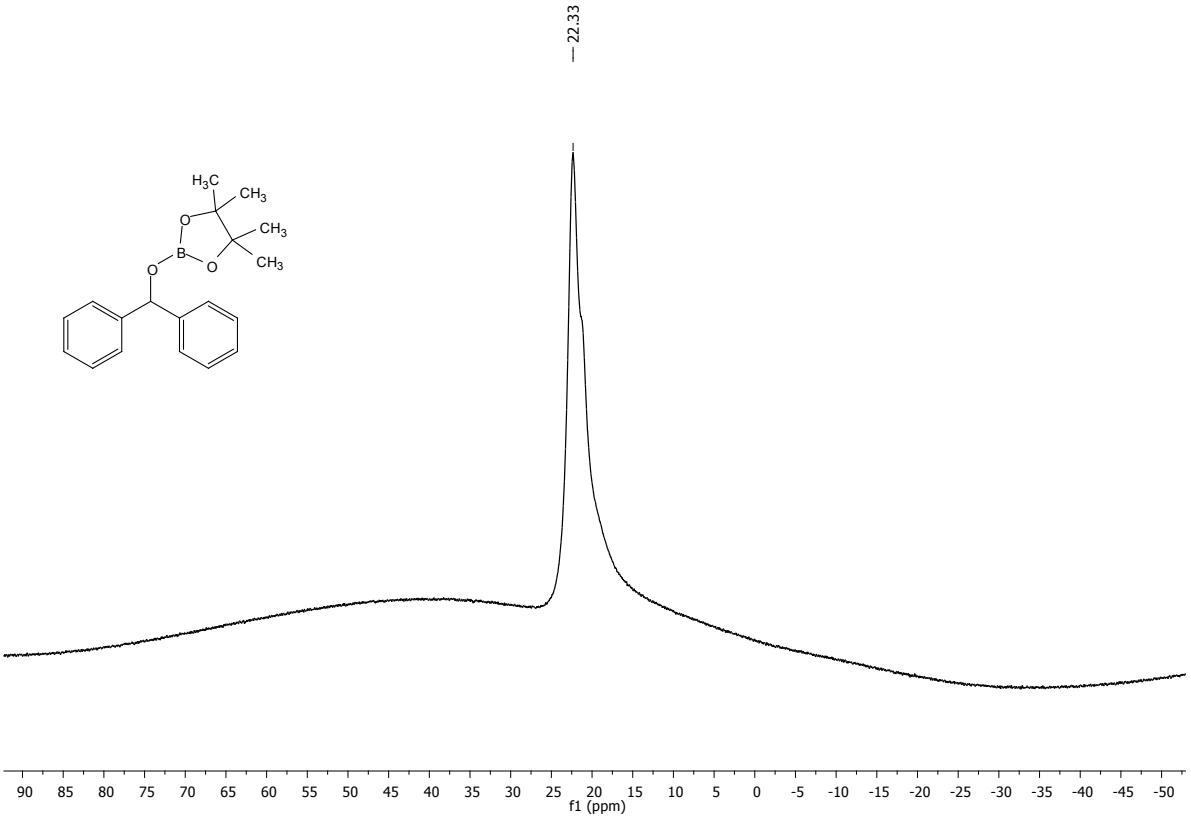


^{13}C NMR of **19c** (100 MHz, $CDCl_3$)

2-(Benzhydryloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 20b).[2,6]

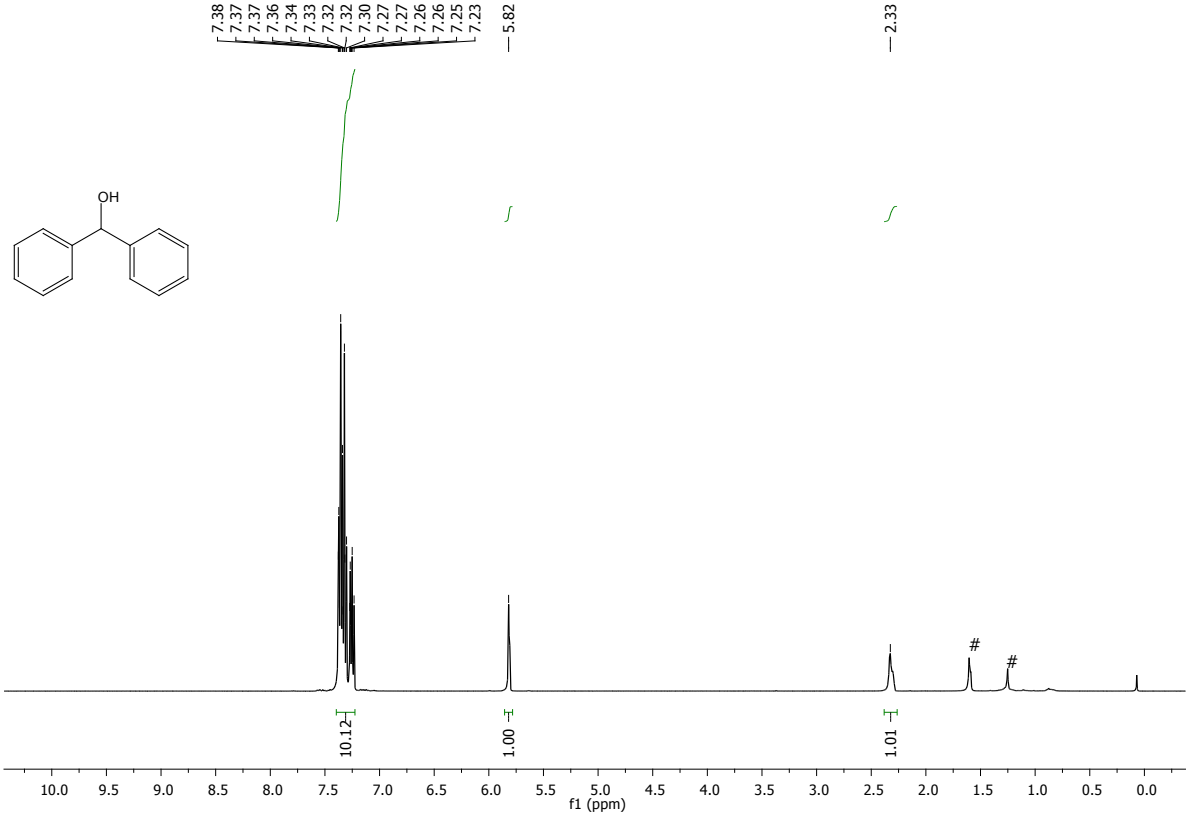


^{1}H NMR of **20b** (400 MHz, $CDCl_3$)

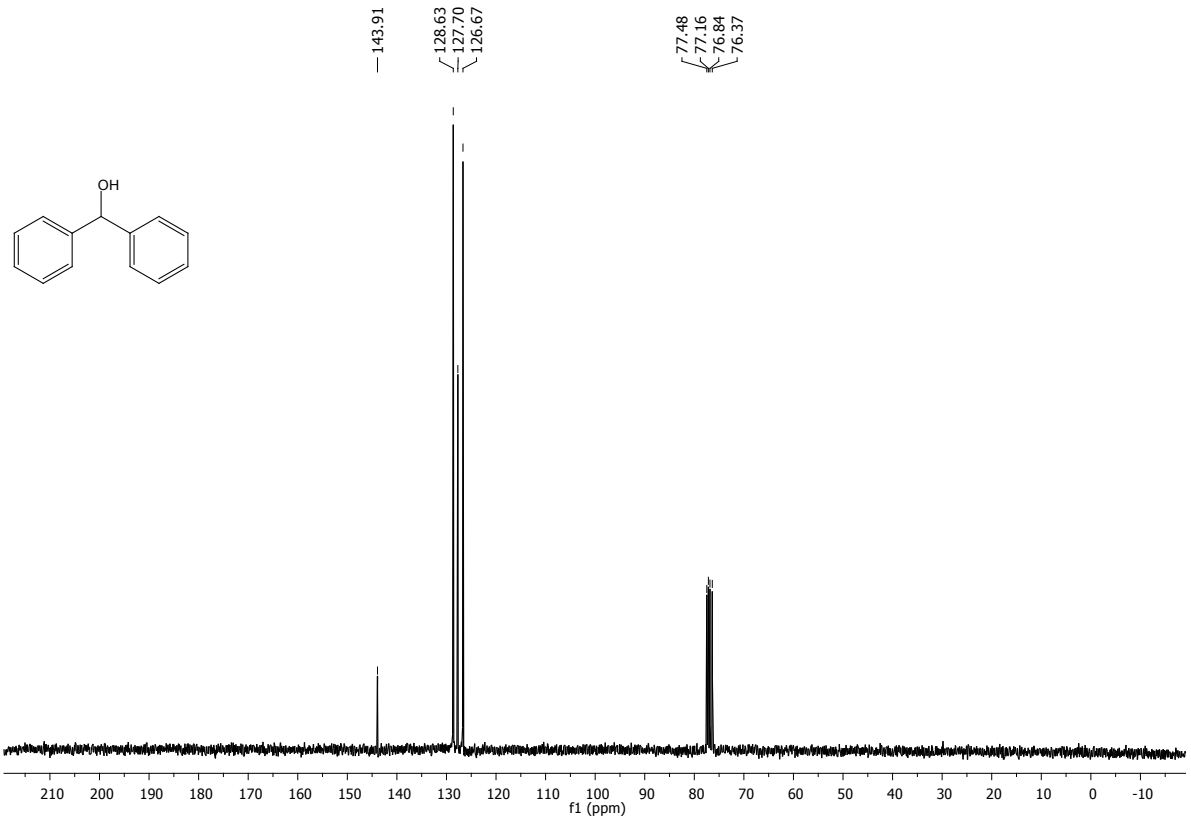


^{11}B NMR of **20b** (128 MHz, $CDCl_3$)

Diphenylmethanol (Table 3, 20c).[2]

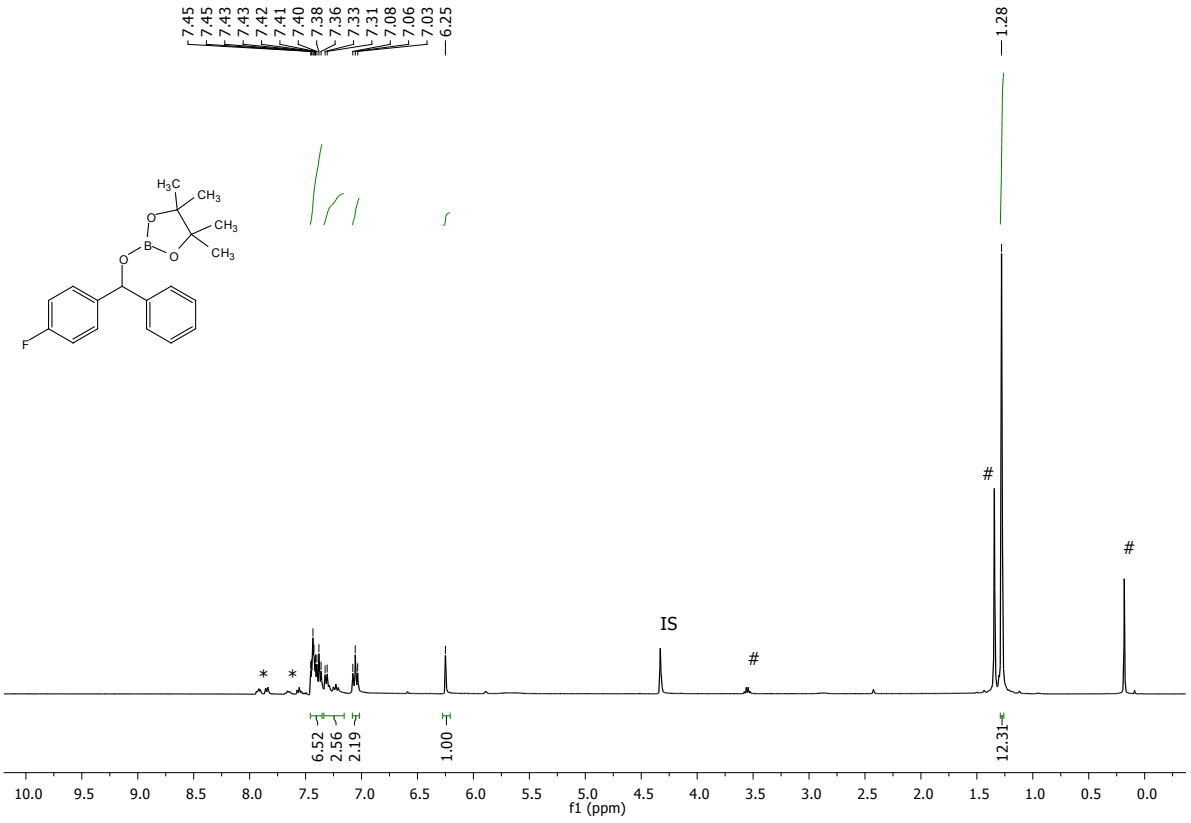


^{1}H NMR of **20c** (400 MHz, $CDCl_3$)

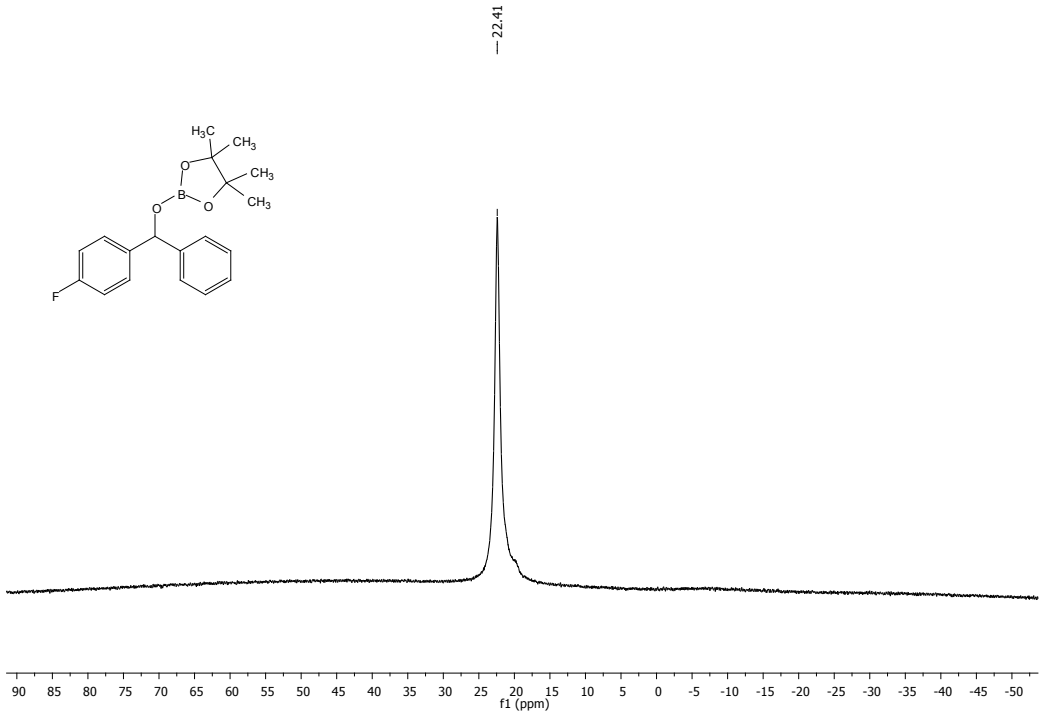


^{13}C NMR of **20c** (100 MHz, $CDCl_3$)

2-((4-Fluorophenyl)(phenyl)methoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 21b).

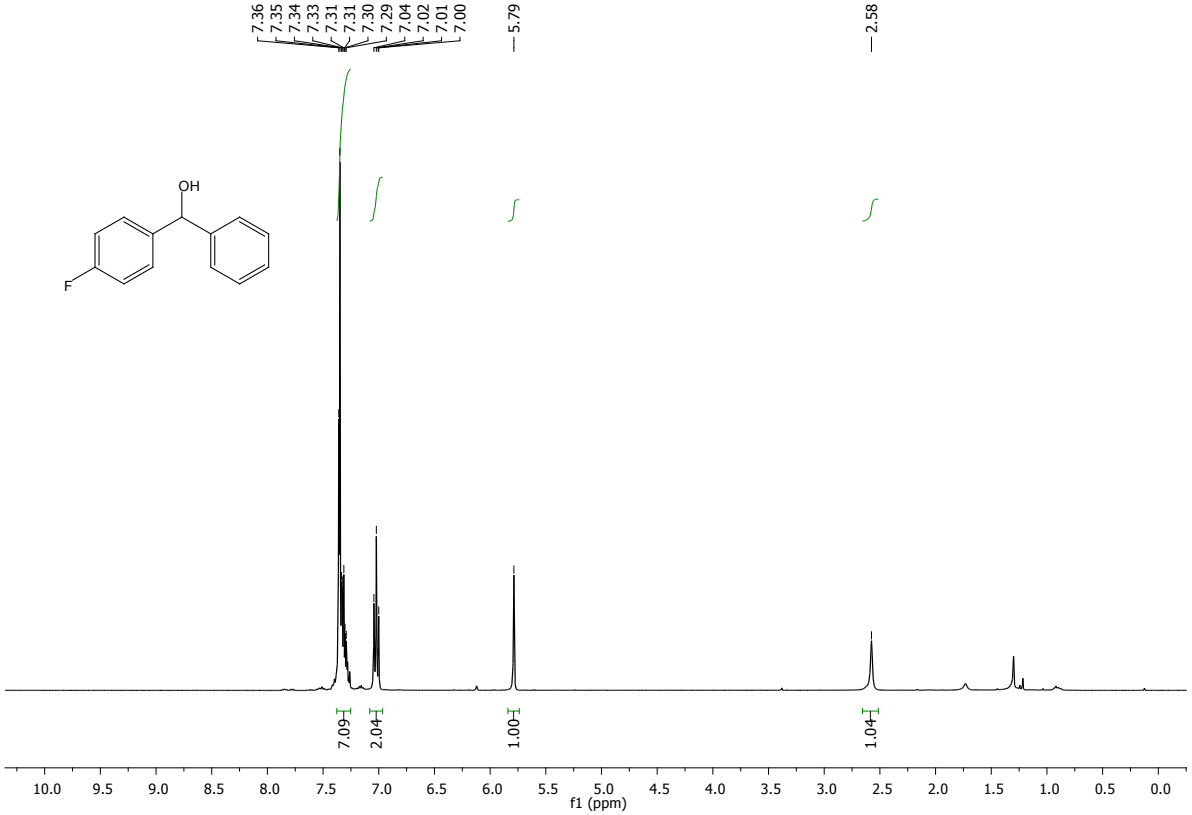


^{1}H NMR of **21b** (400 MHz, $CDCl_3$)

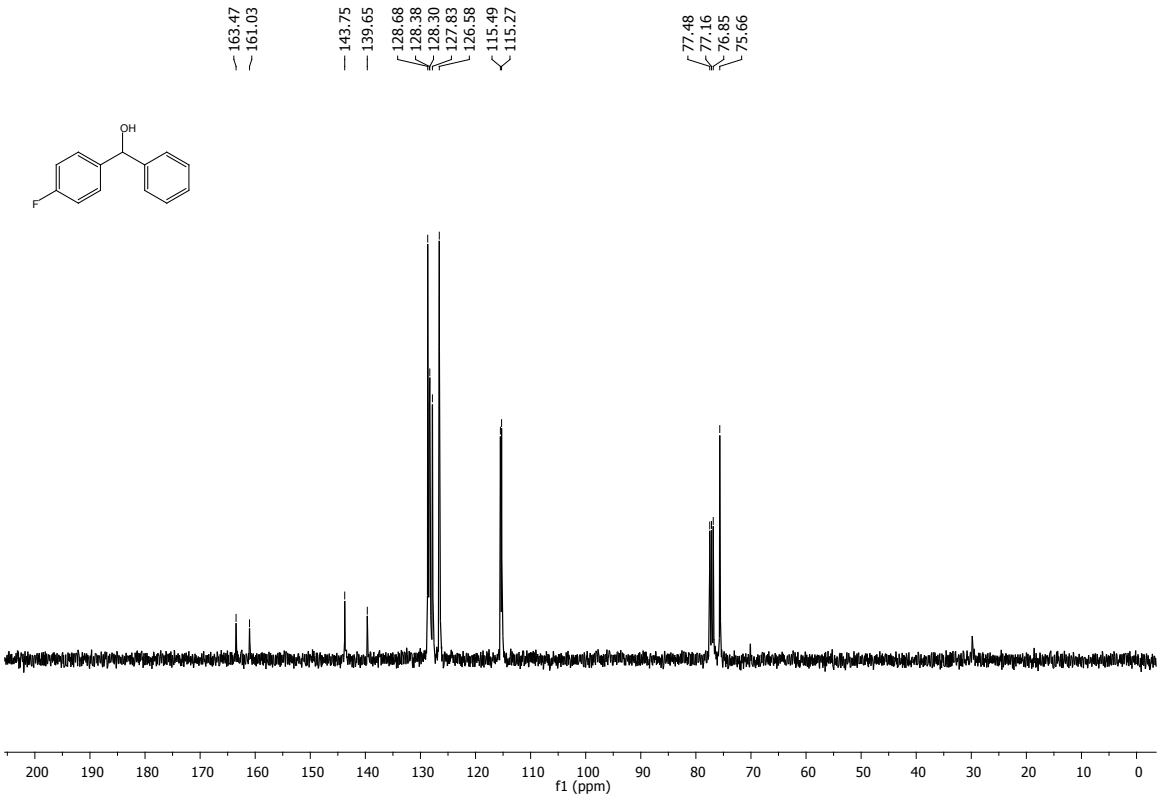


^{11}B NMR of **21b** (128 MHz, $CDCl_3$)

(4-Fluorophenyl)(phenyl)methanol (21c).[18]

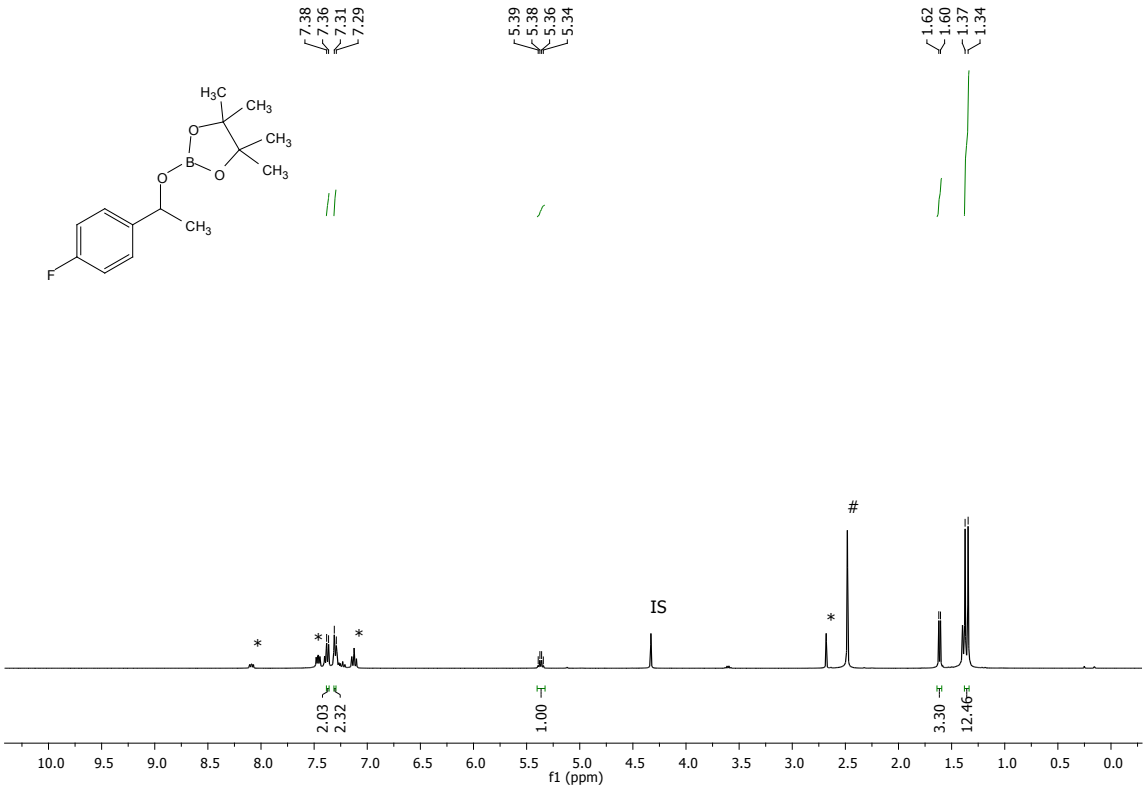


^{1}H NMR of **21c** (400 MHz, $CDCl_3$)

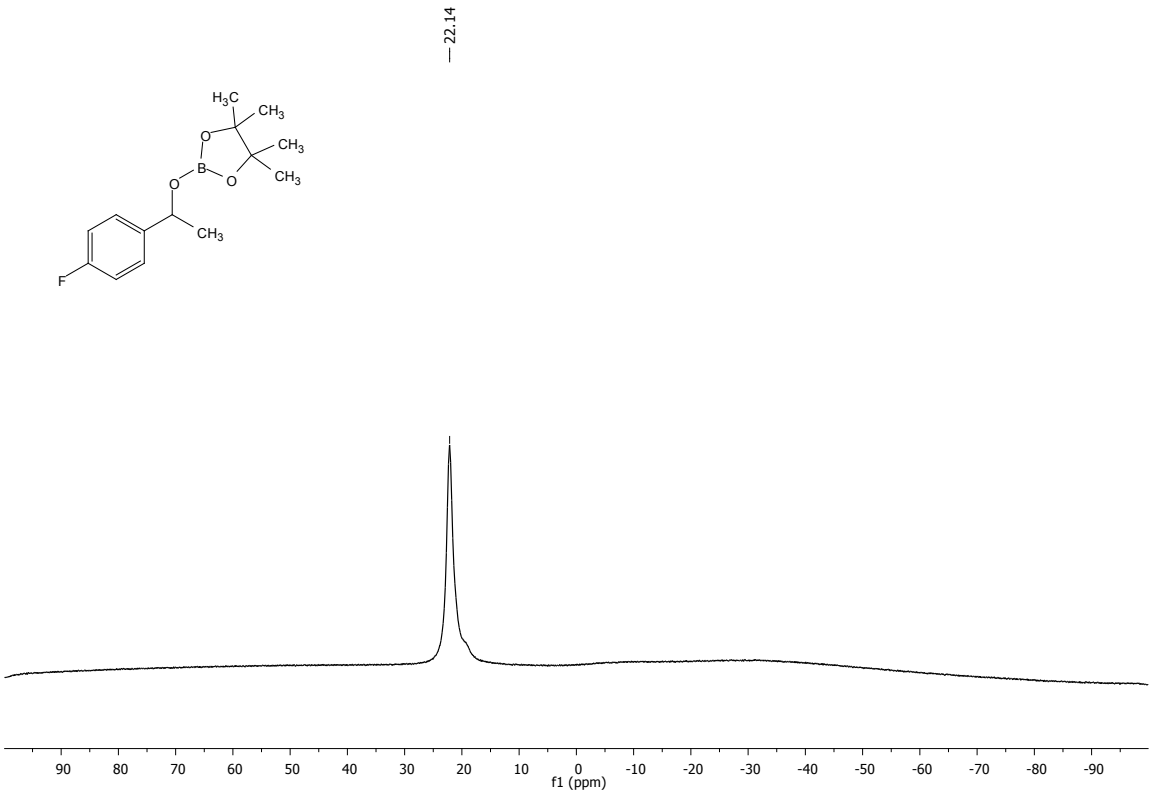


^{13}C NMR of **21c** (100 MHz, $CDCl_3$)

2-(1-(4-Fluorophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 22b).[2,12]

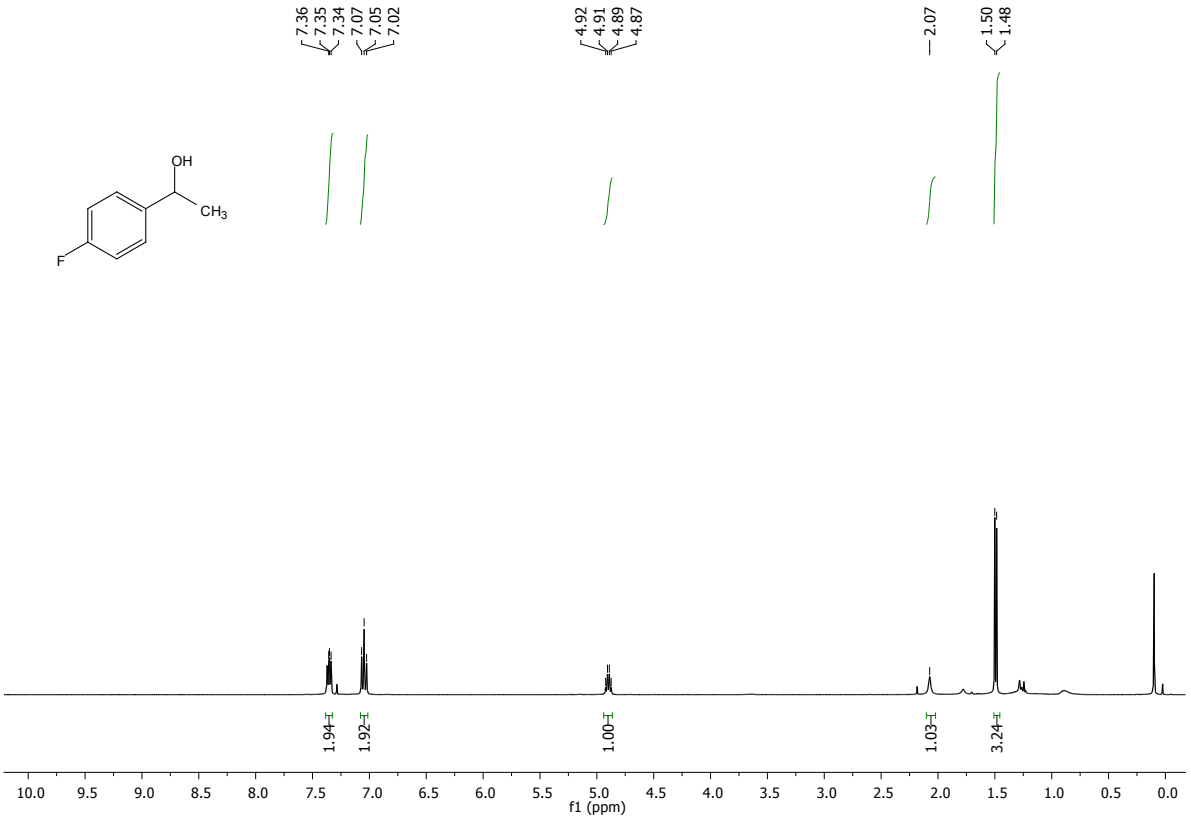


^{1}H NMR of **22b** (400 MHz, $CDCl_3$)

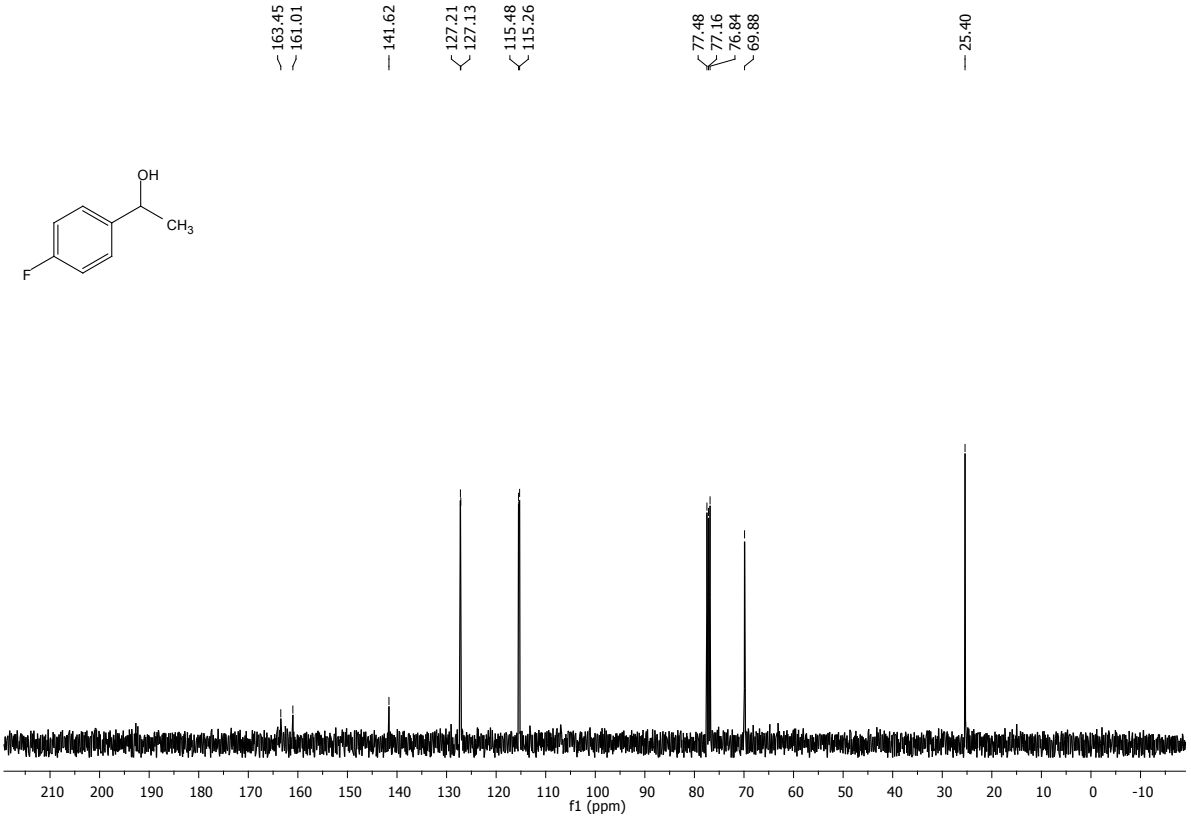


^{11}B NMR of **22b** (128 MHz, $CDCl_3$)

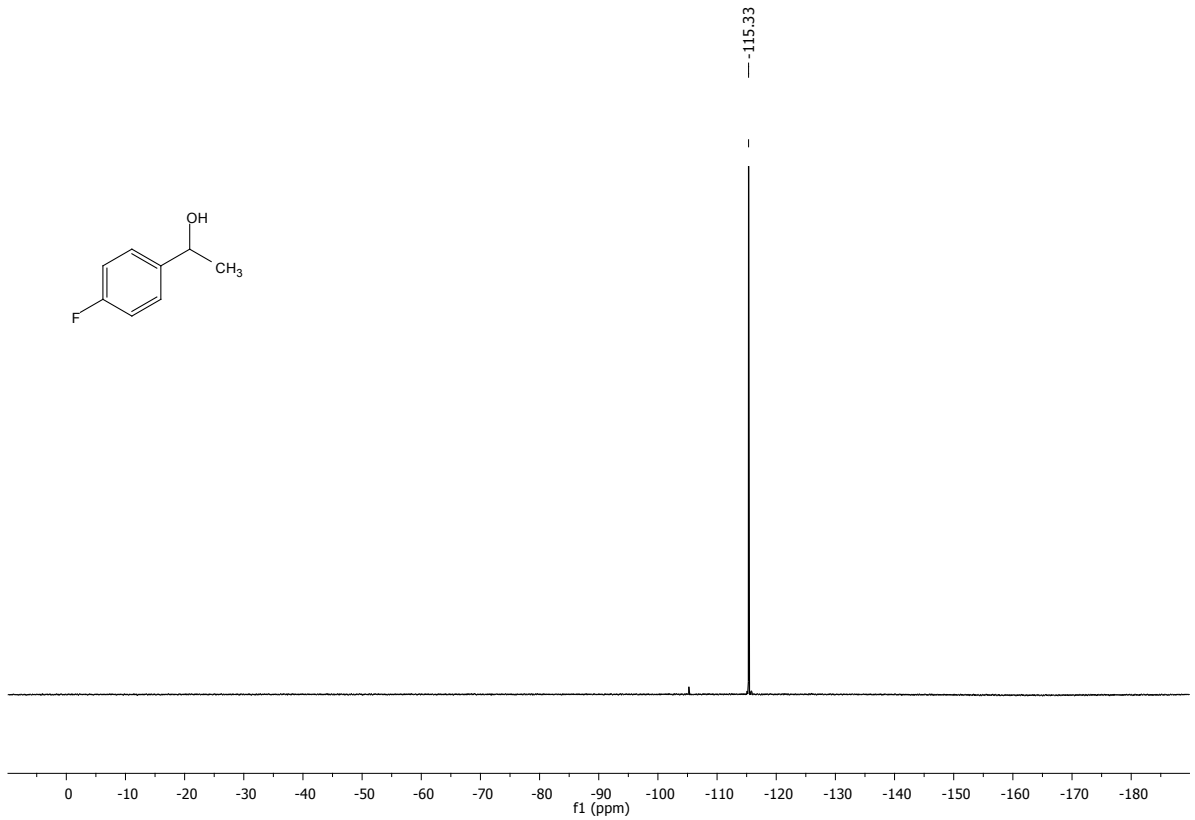
1-(4-Fluorophenyl)ethanol (22c).[2,12]



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

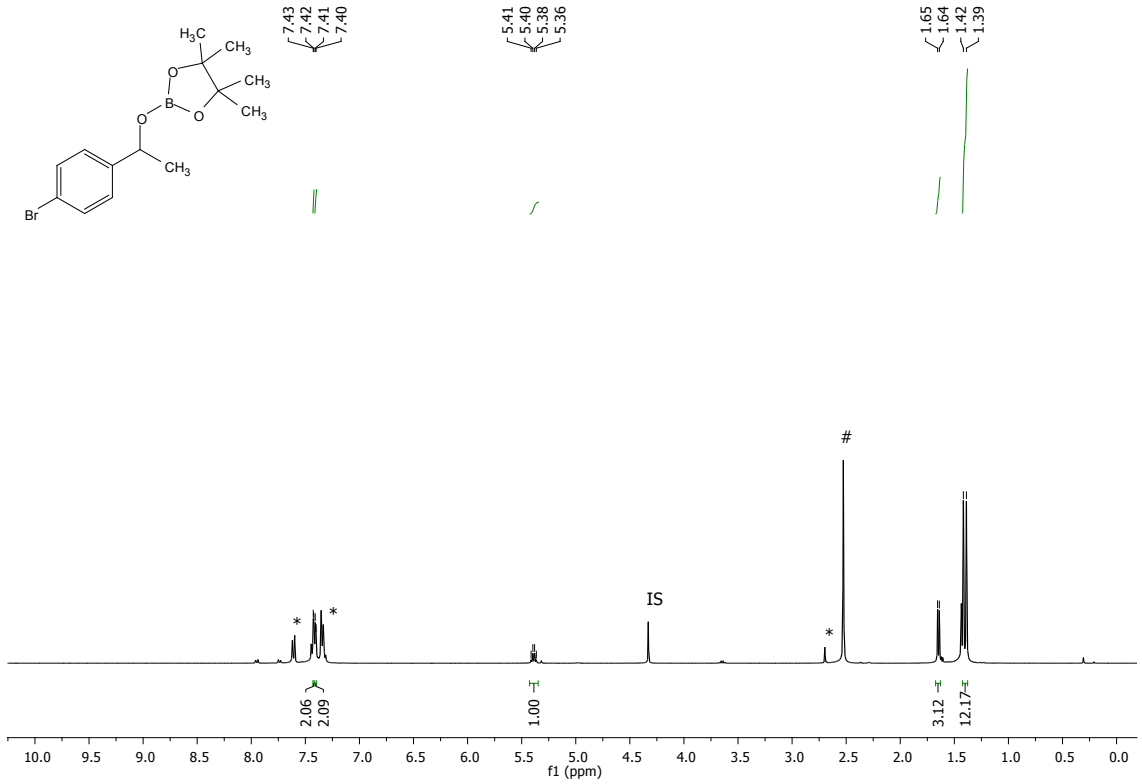


^{13}C NMR of **22c** (100 MHz, $CDCl_3$)

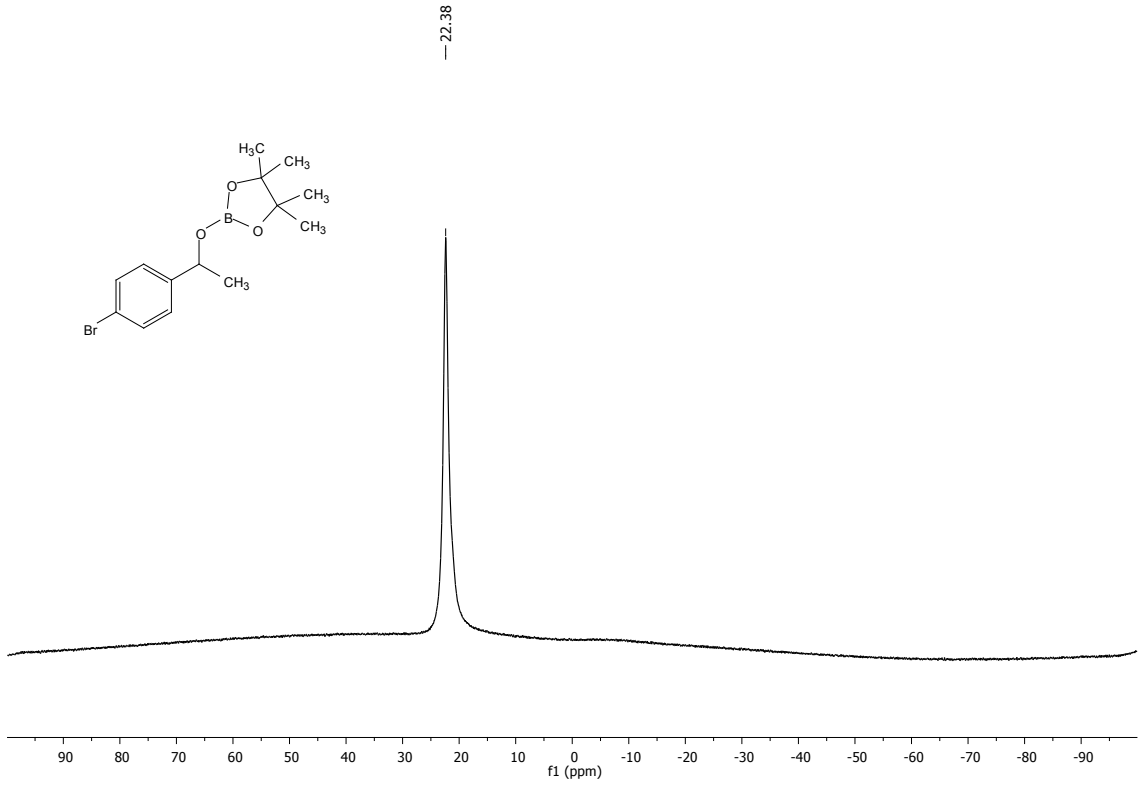


^{19}F NMR of **22c** (376 MHz, $CDCl_3$)

2-(1-(4-Bromophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 23b).[2,3]

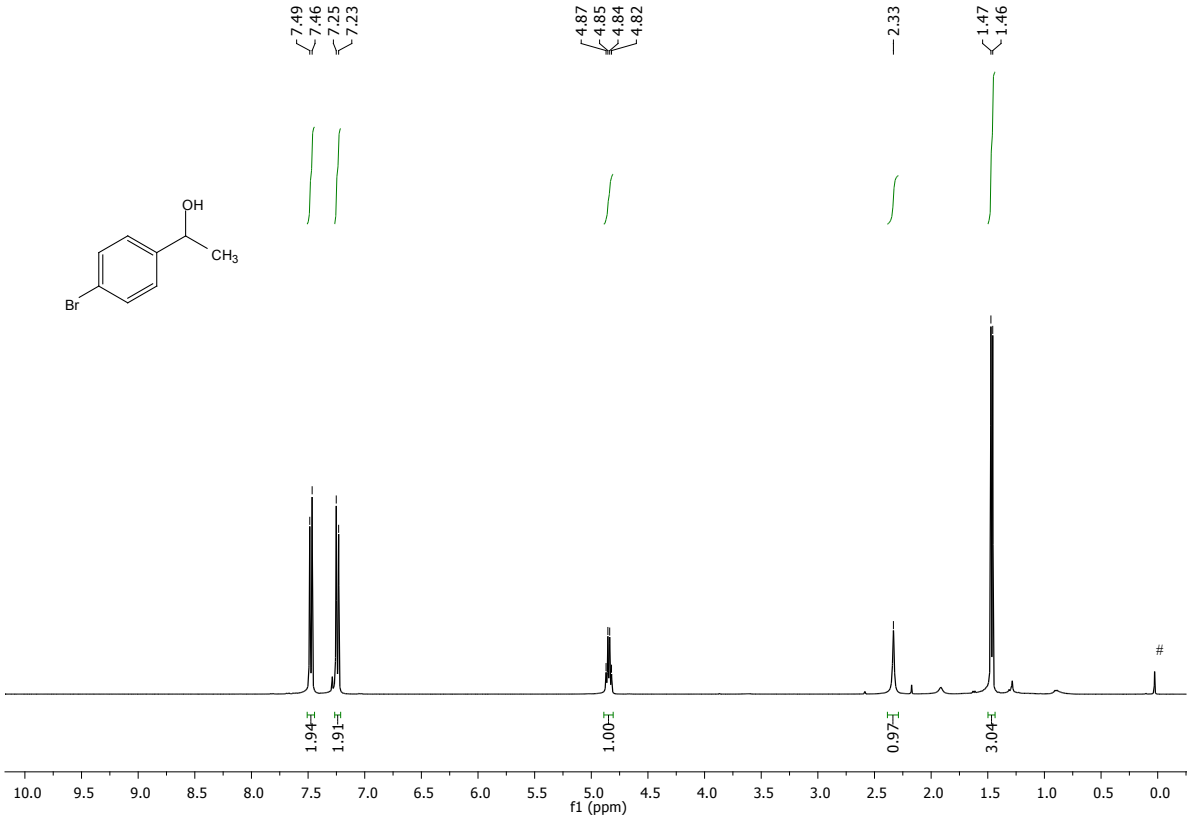


^{1}H NMR of **23b** (400 MHz, $CDCl_3$)

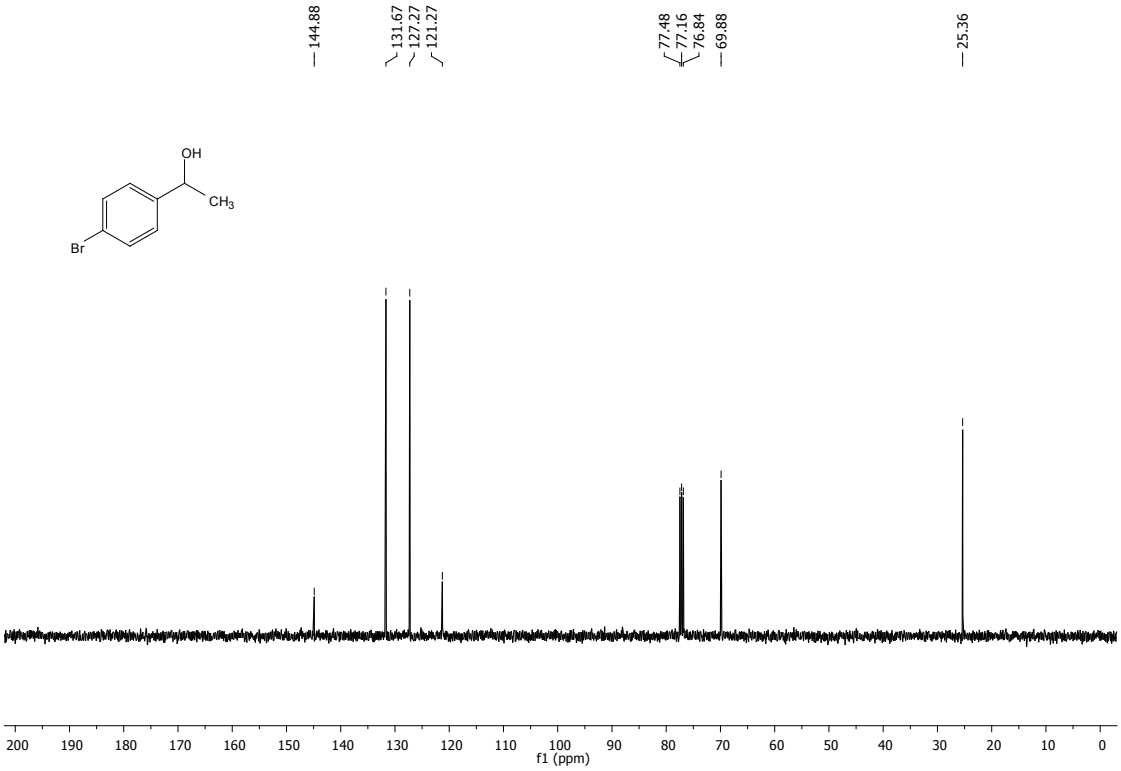


^{11}B NMR of **23b** (128 MHz, $CDCl_3$)

1-(4-Bromophenyl)ethanol (23c).[2,10]

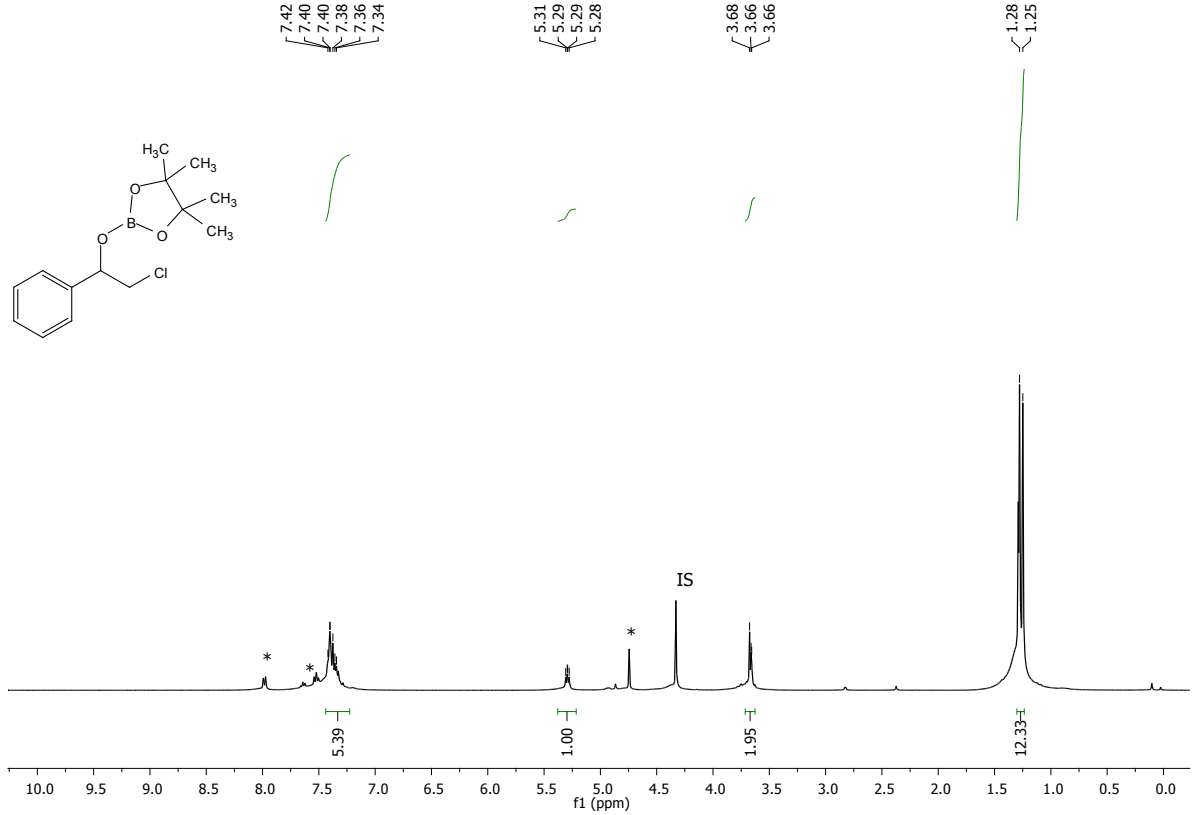


^{1}H NMR of **23c** (400 MHz, $CDCl_3$)

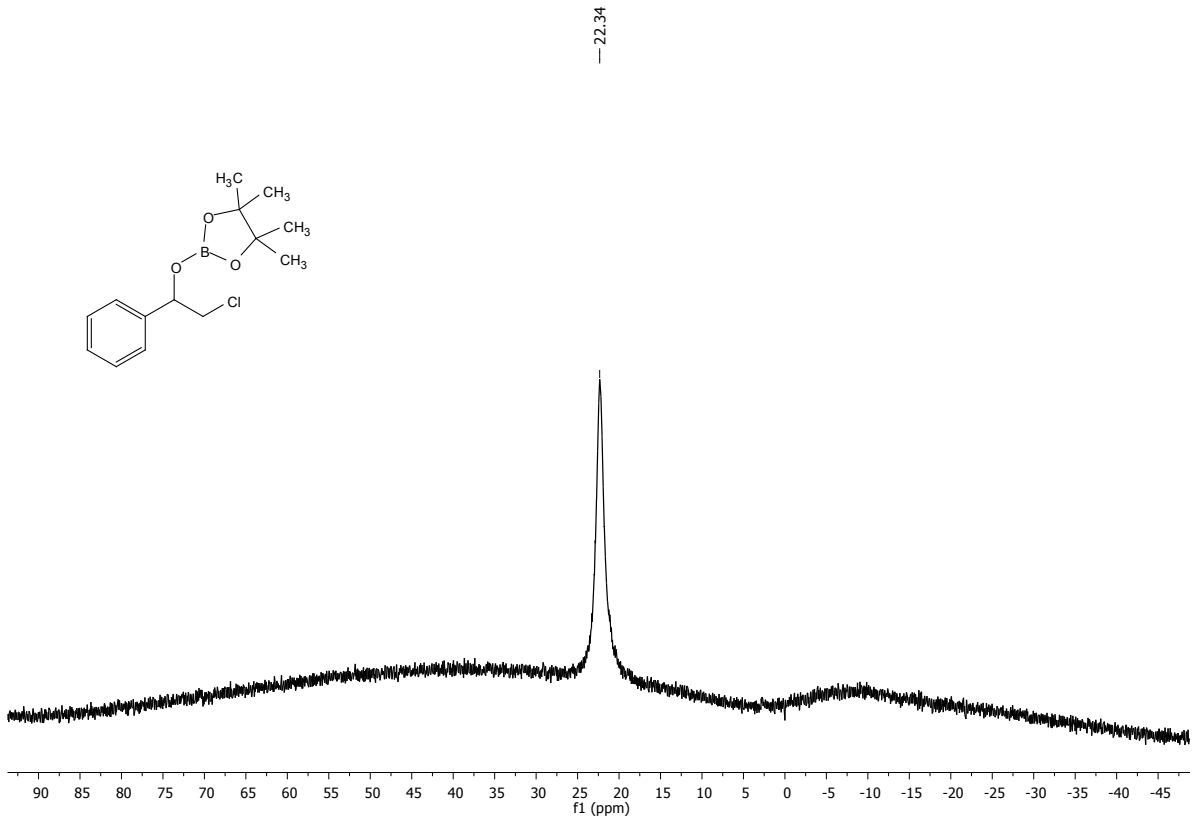


^{13}C NMR of **23c** (100 MHz, $CDCl_3$)

2-(2-Chloro-1-phenylethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 24b).[2,14]

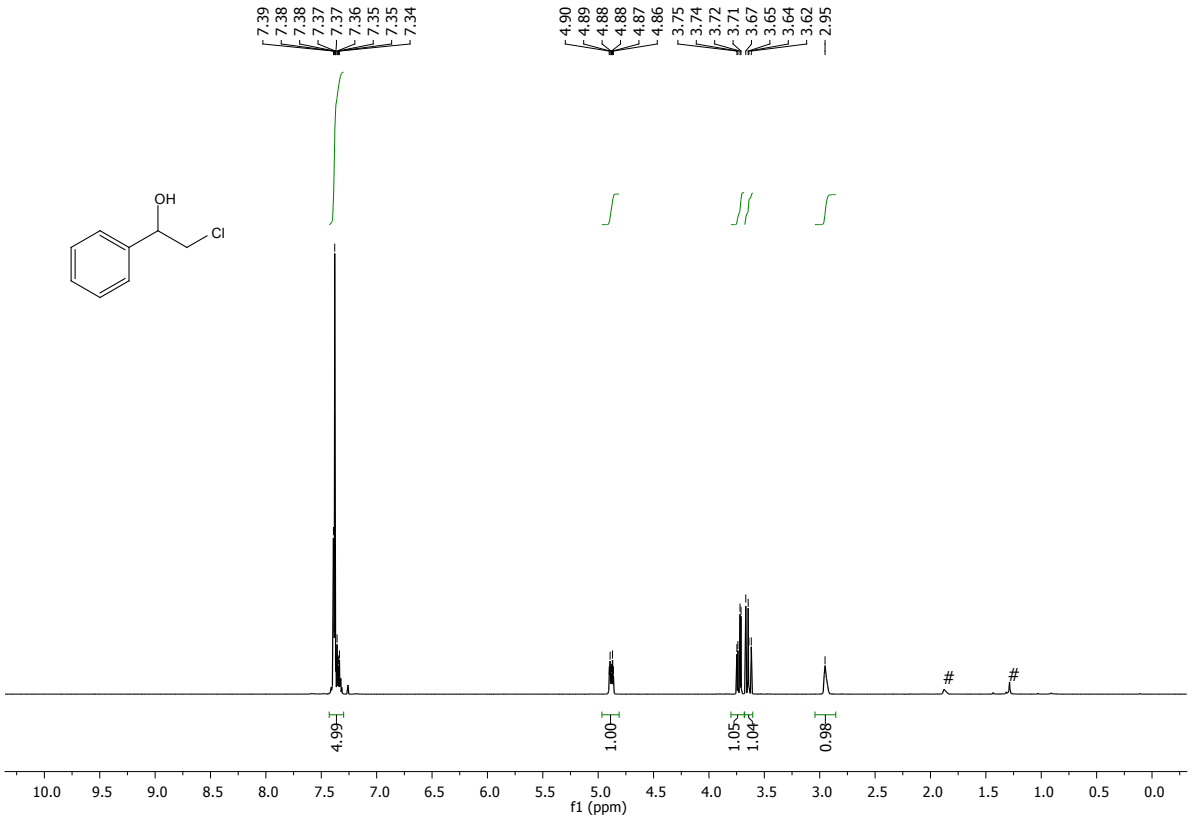


^{1}H NMR of **24b** (400 MHz, $CDCl_3$)

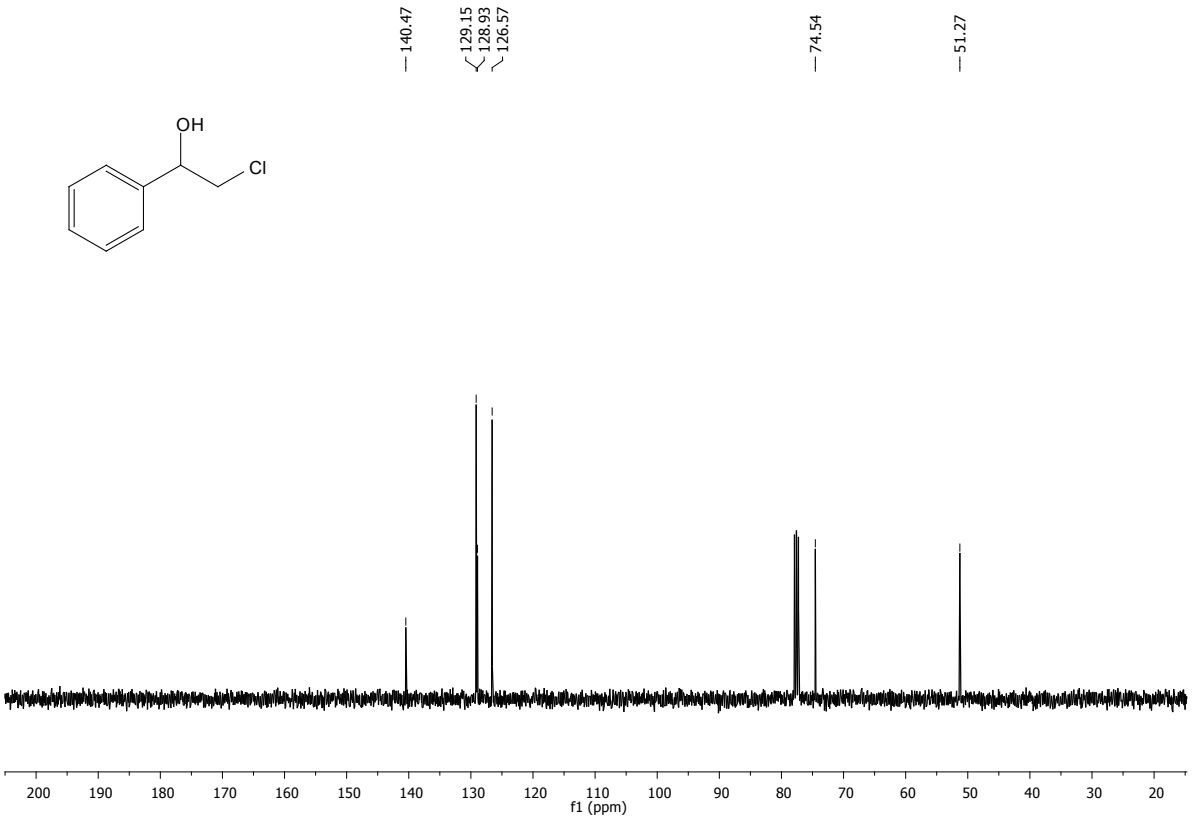


^{11}B NMR of **24b** (128 MHz, $CDCl_3$)

2-Chloro-1-phenylethan-1-ol (24c).[2,15]

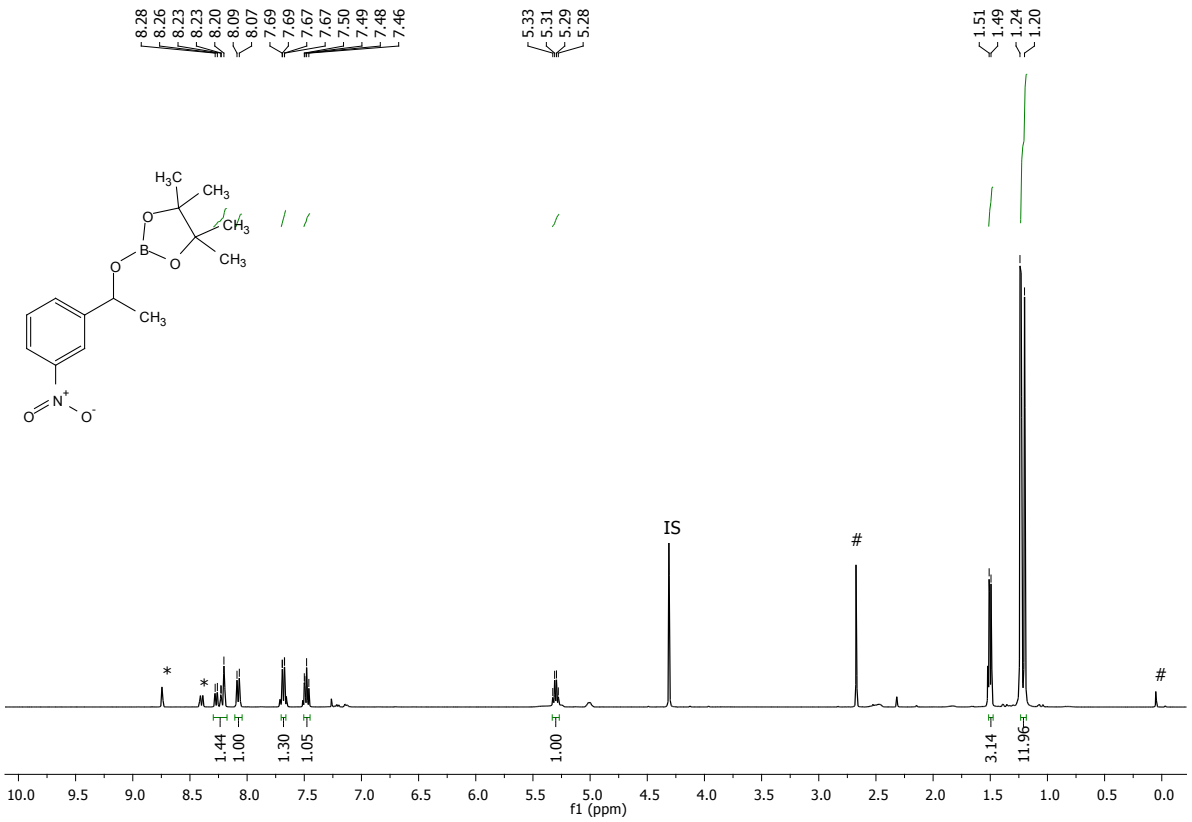


^{1}H NMR of **24c** (400 MHz, $CDCl_3$)

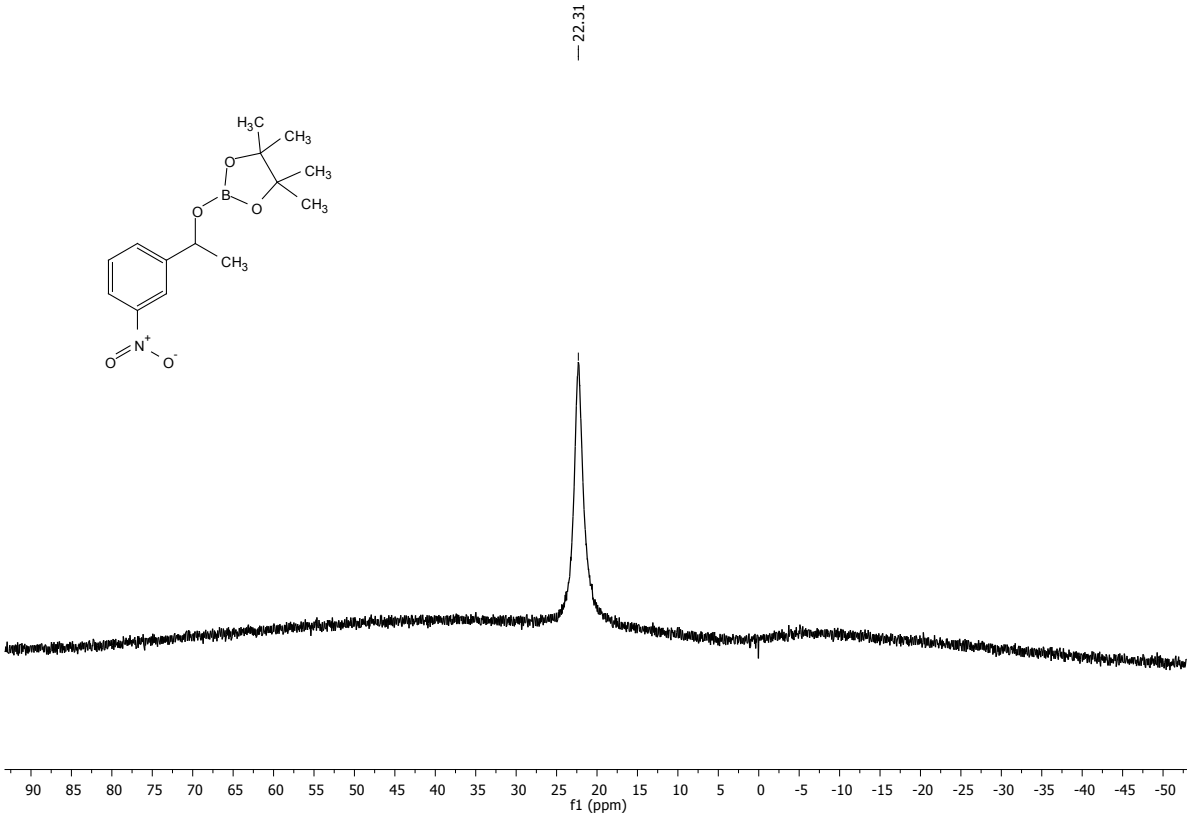


^{13}C NMR of **24c** (100 MHz, $CDCl_3$)

4,4,5,5-Tetramethyl-2-(1-(3-nitrophenyl)ethoxy)-1,3,2-dioxaborolane (Table 3, 25b).[2]

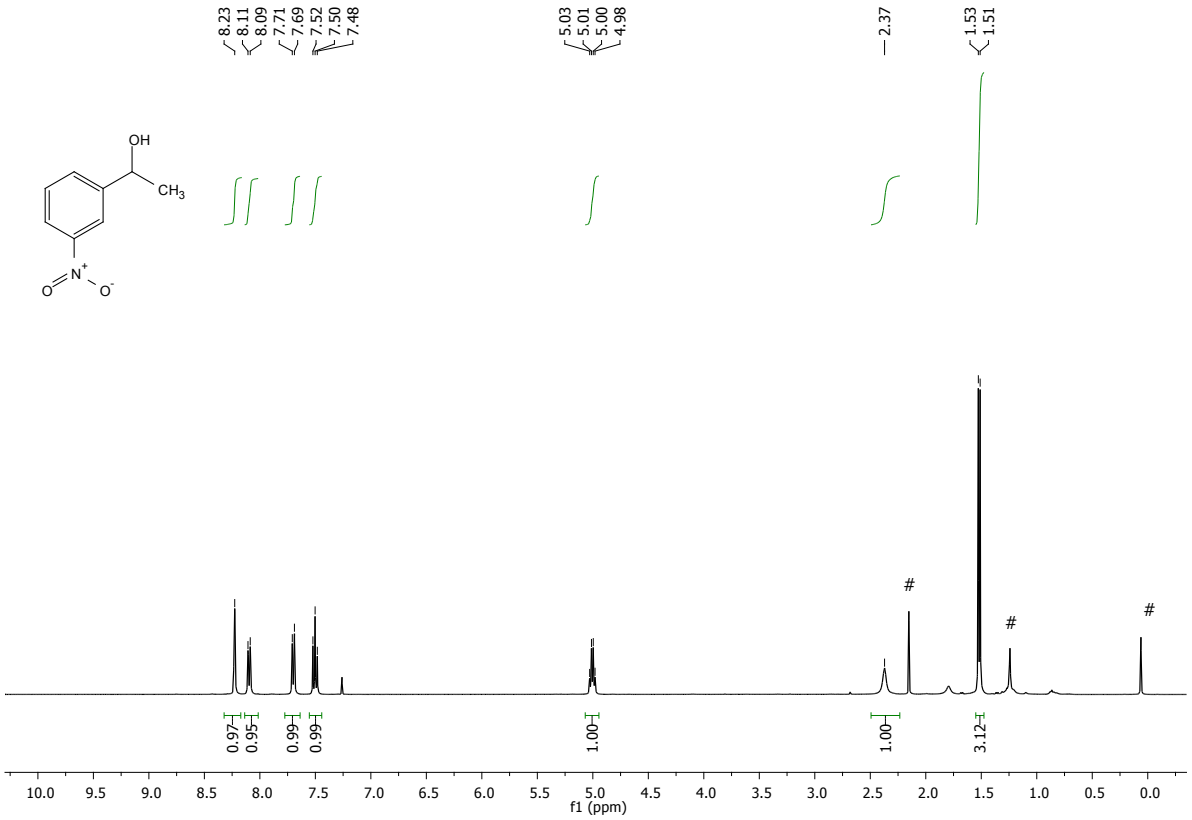


^{1}H NMR of **25b** (400 MHz, $CDCl_3$)

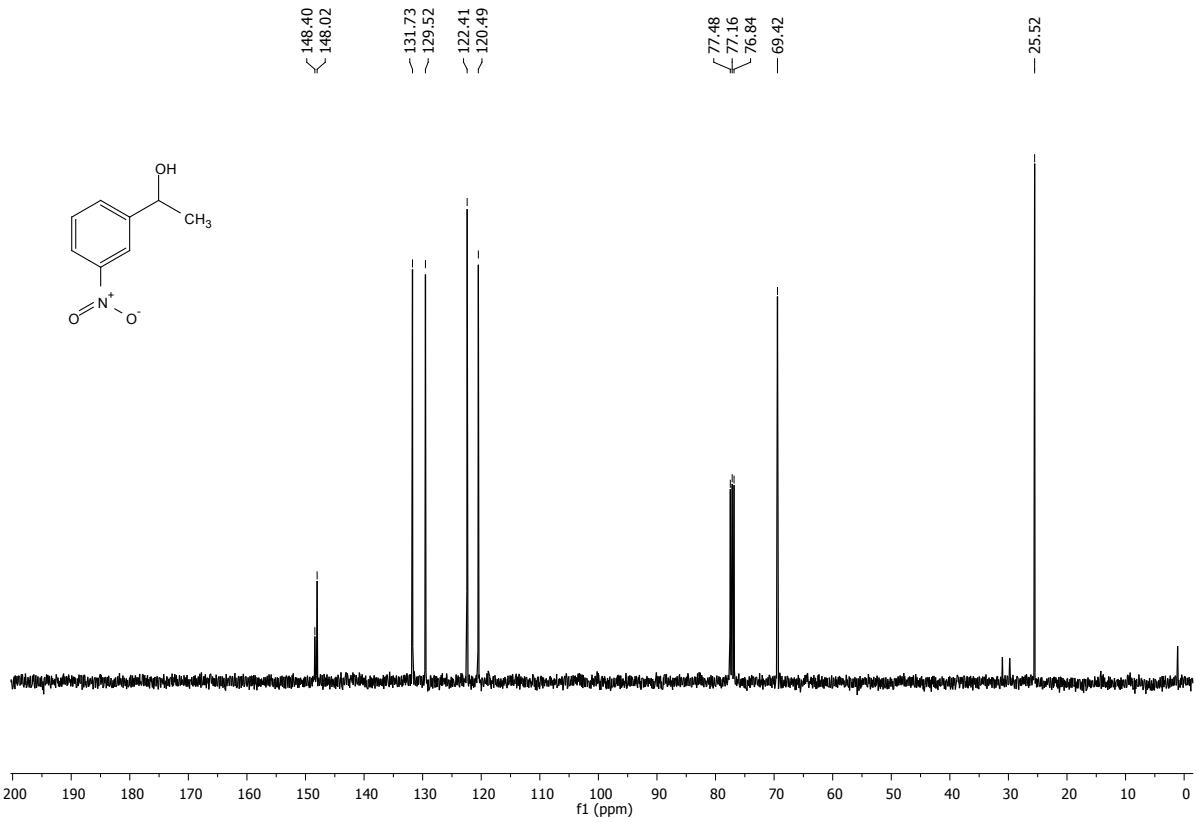


^{11}B NMR of **25b** (128 MHz, $CDCl_3$)

1-(3-Nitrophenyl)ethanol (25c).[2]

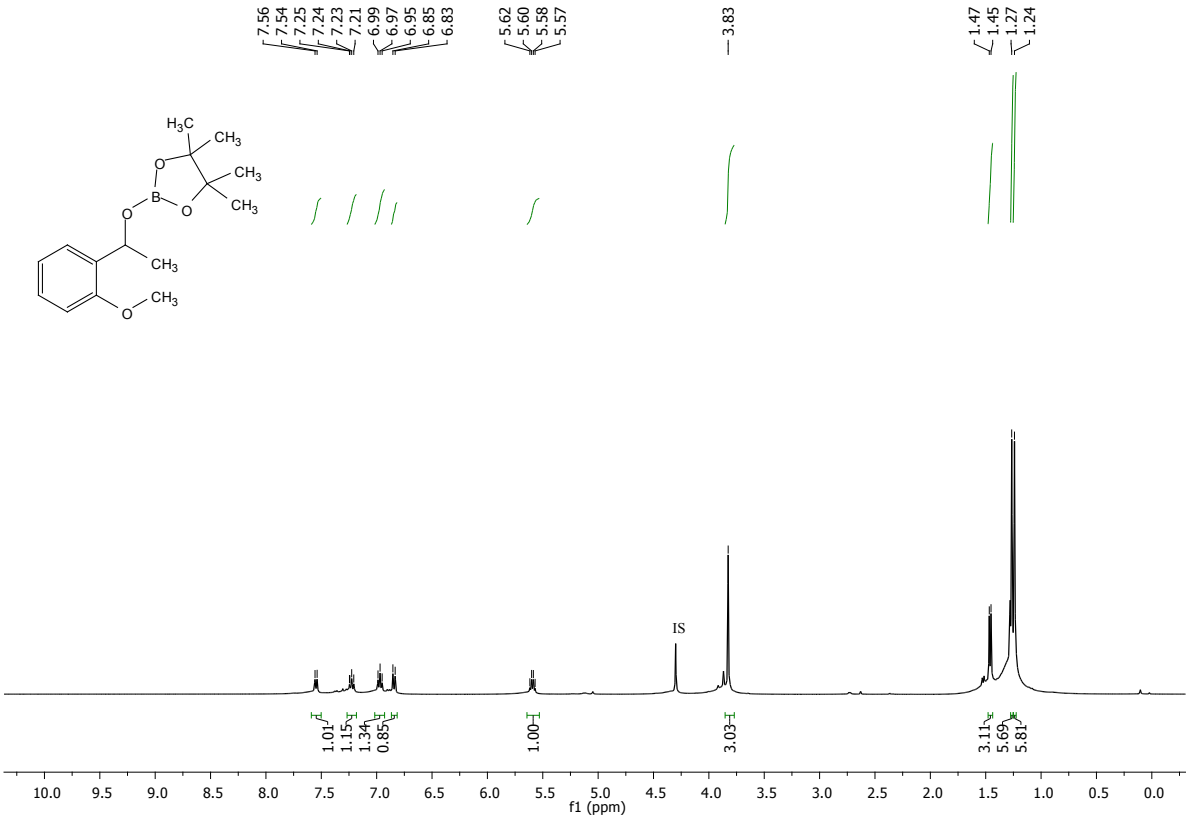


^{1}H NMR of **25c** (400 MHz, $CDCl_3$)

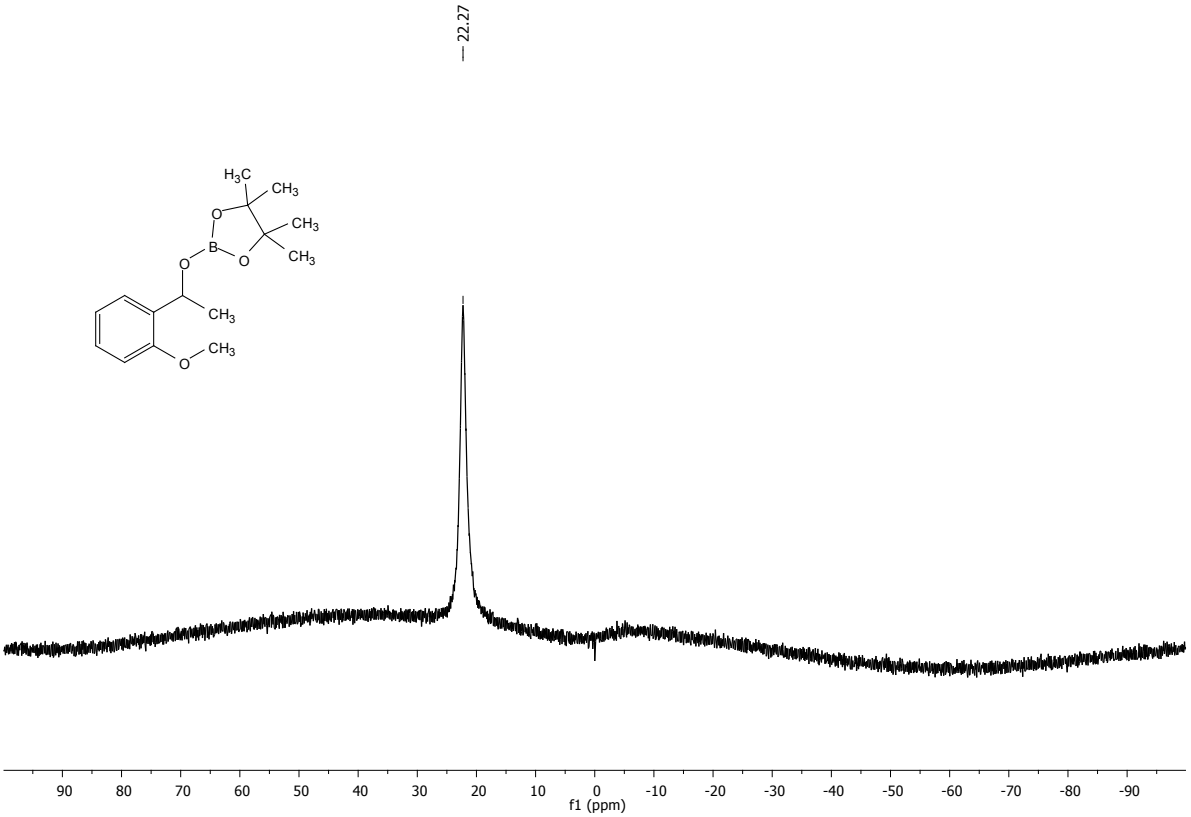


^{13}C NMR of **25C** (100 MHz, $CDCl_3$)

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

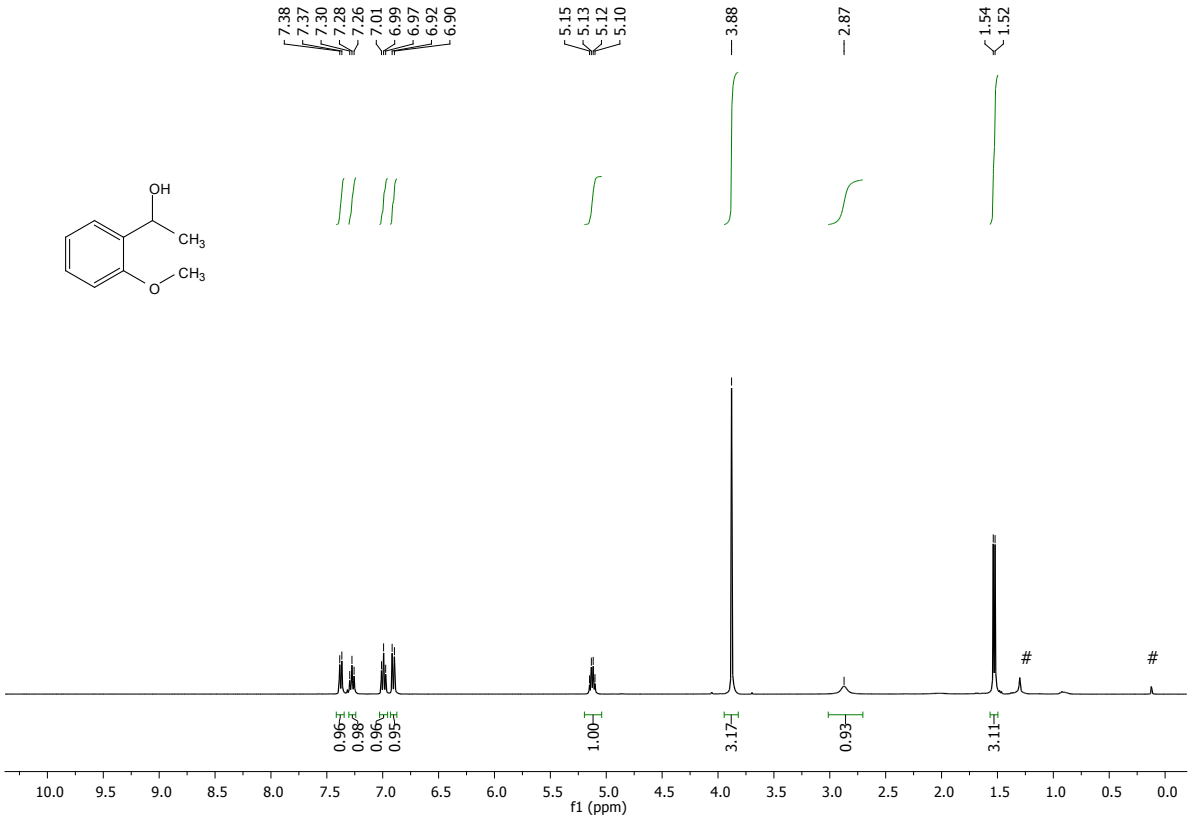


^{1}H NMR of **26b** (400 MHz, $CDCl_3$)

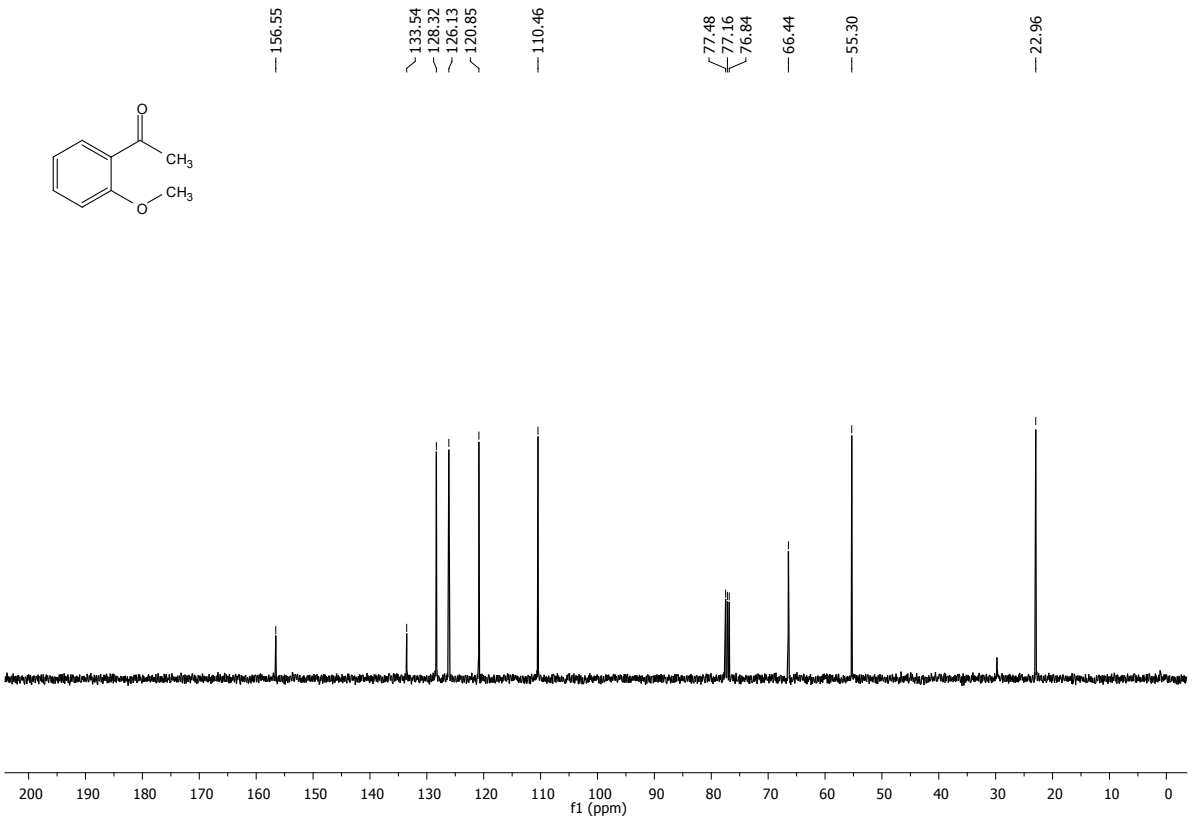


^{11}B NMR of **26b** (128 MHz, $CDCl_3$)

1-(2-Methoxyphenyl)ethanol (26c).[2,16]

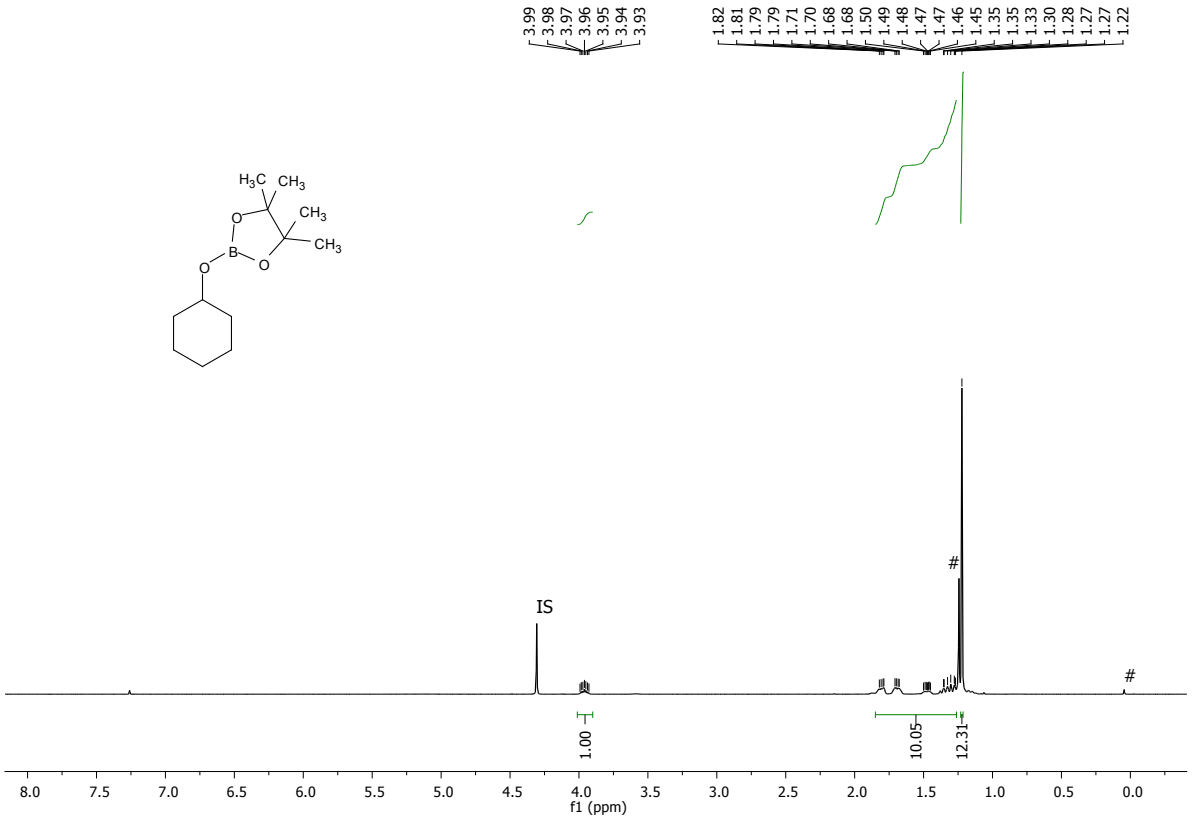


^{1}H NMR of **26c** (400 MHz, $CDCl_3$)

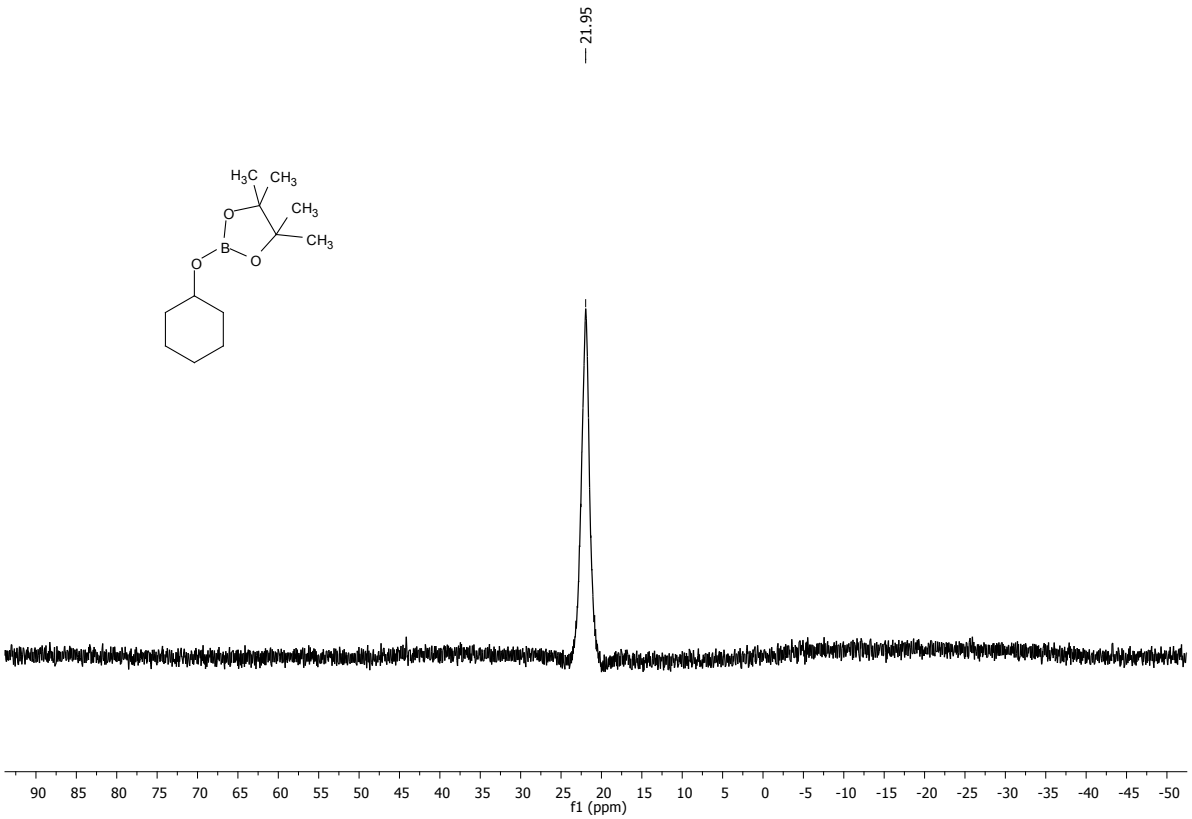


^{13}C NMR of **26c** (100 MHz, $CDCl_3$)

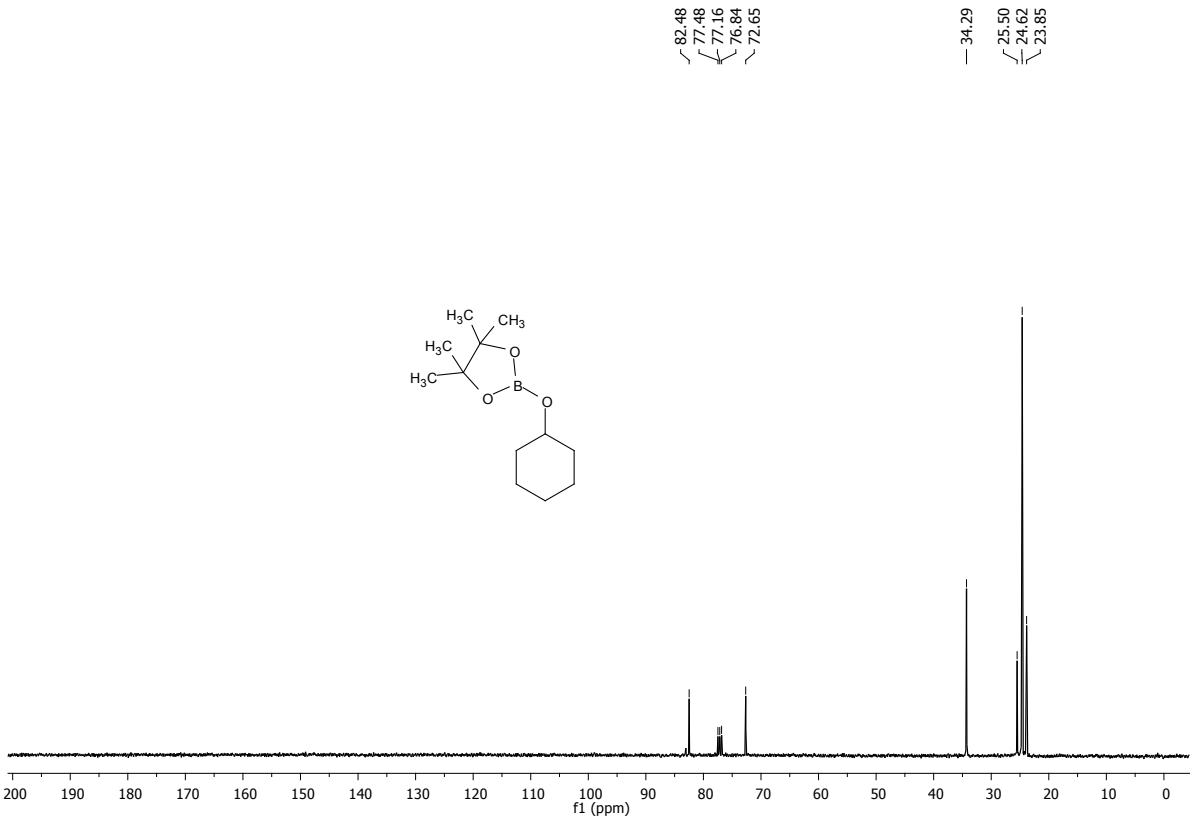
2-(Cyclohexyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 27b).[17]



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

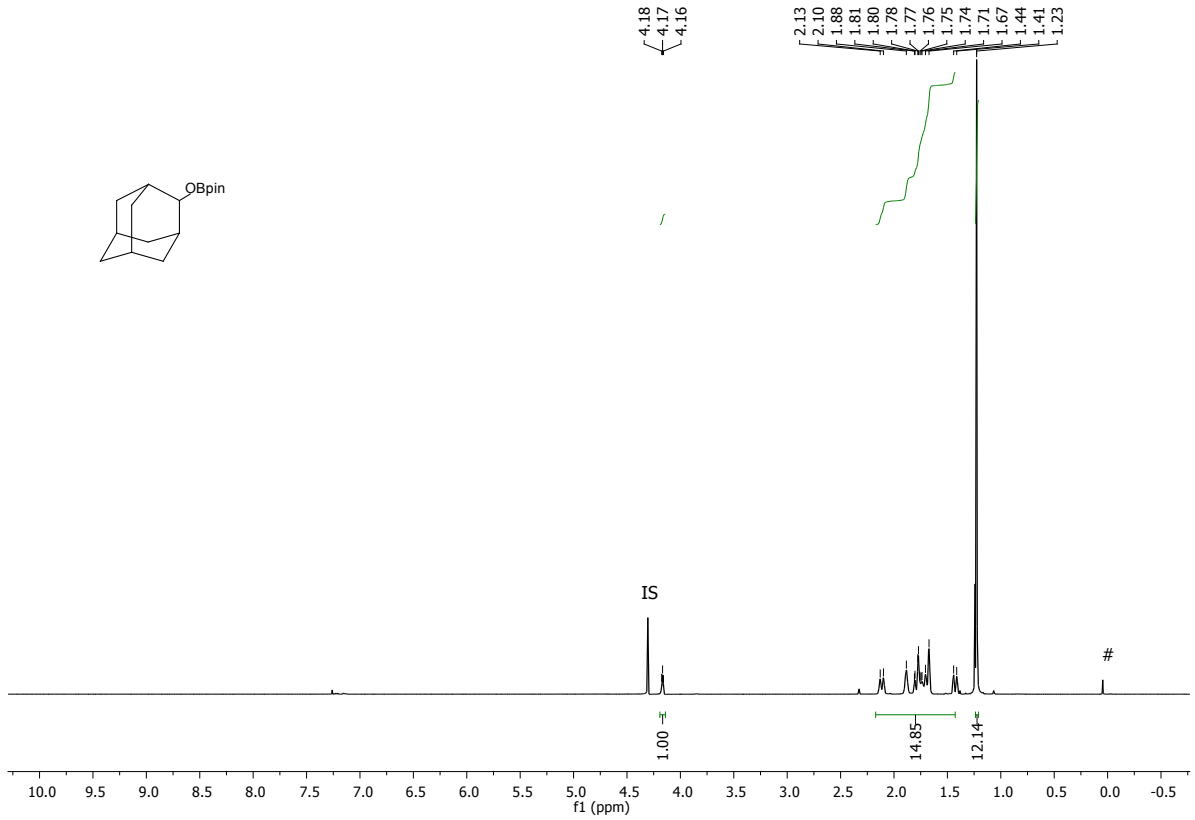


^{11}B NMR of **27b** (128 MHz, $CDCl_3$)

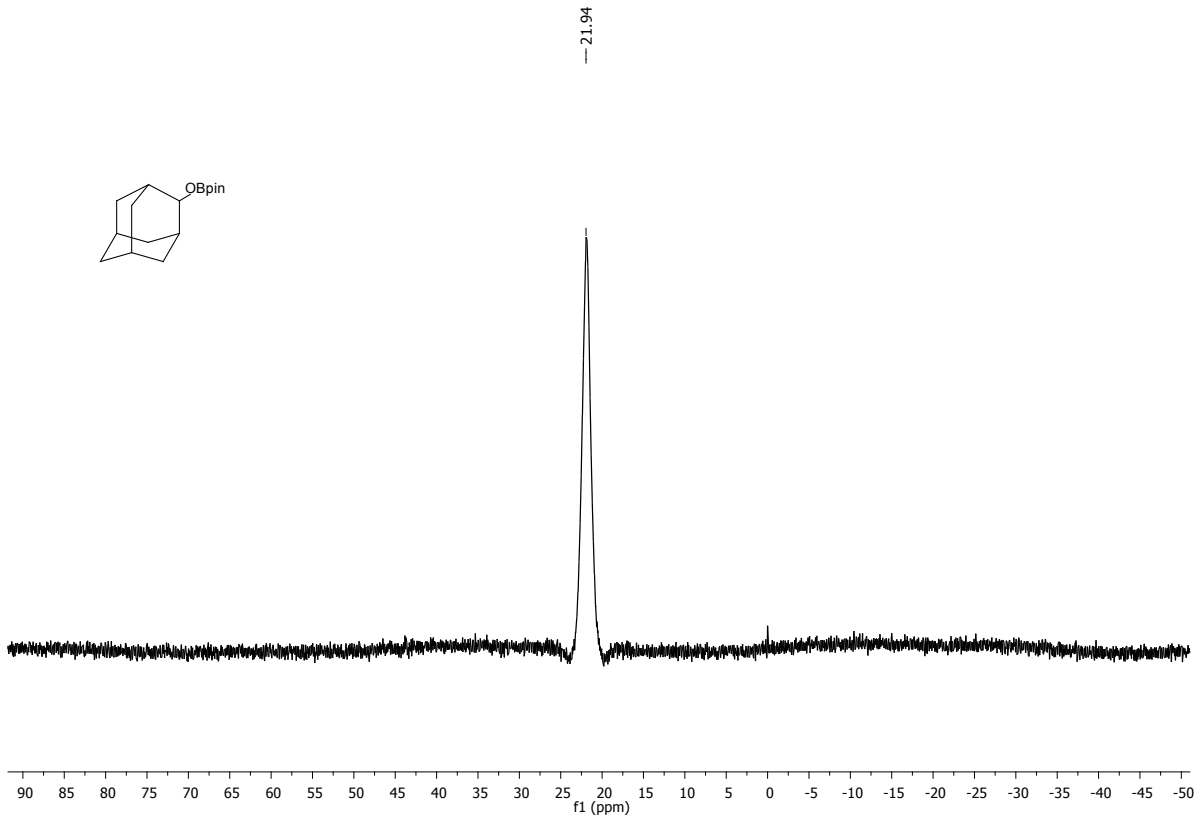


^{13}C NMR of **27b** (100 MHz, $CDCl_3$)

2-(Adamantan-2-yloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 28b).[17]

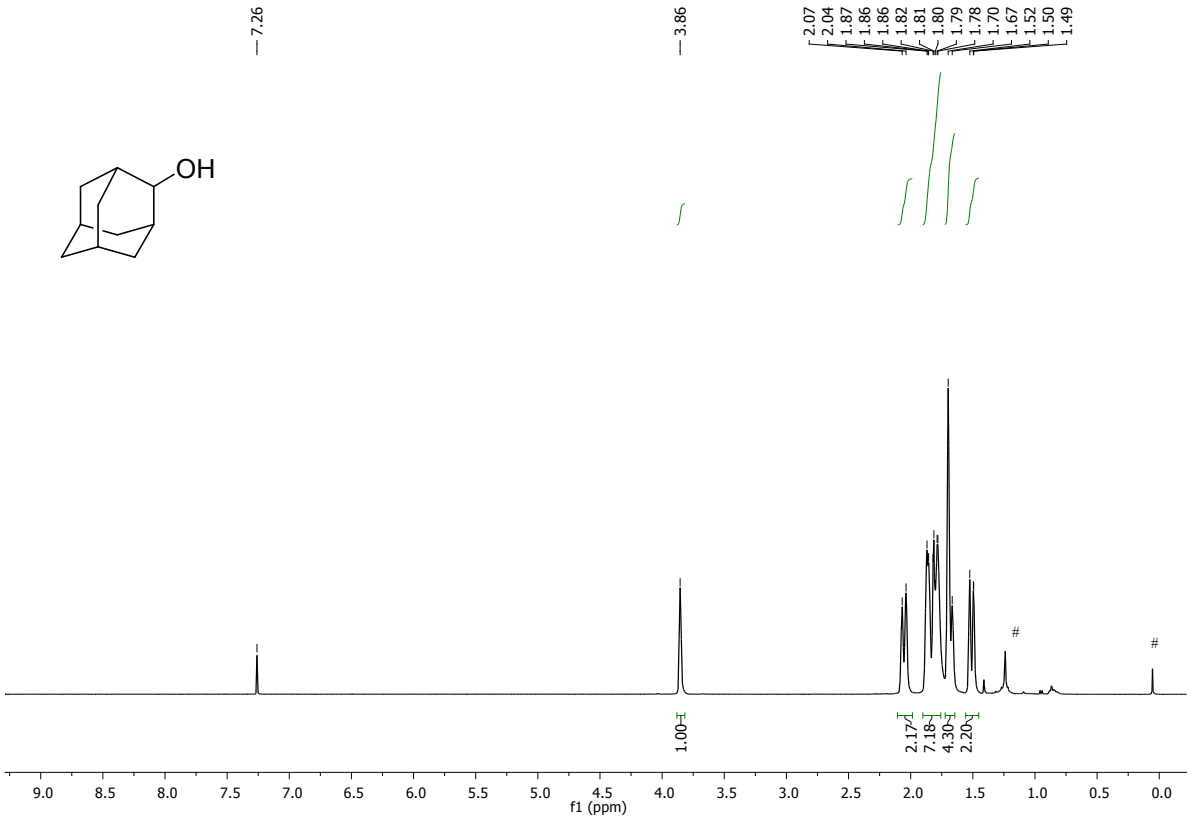


^{1}H NMR of **28b** (400 MHz, $CDCl_3$)

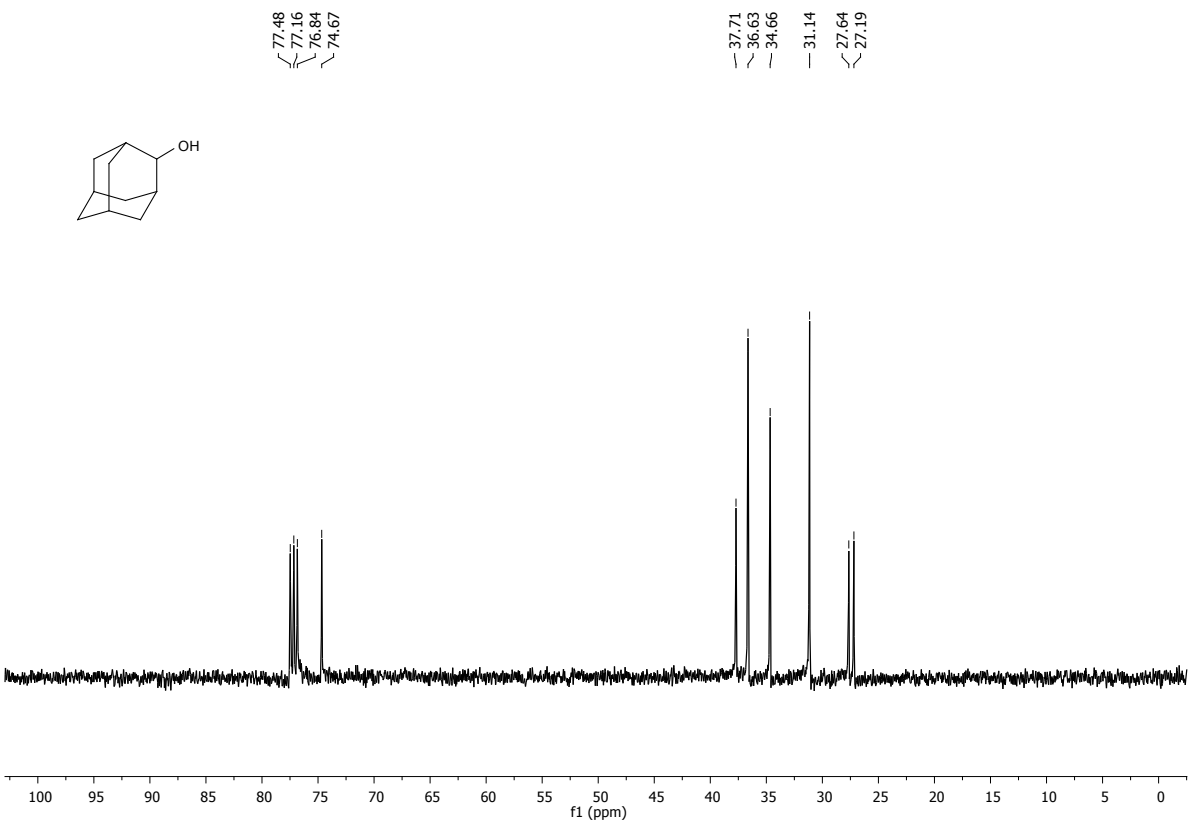


^{11}B NMR of **28b** (128 MHz, $CDCl_3$)

2-Adamantanol (28c).[19]



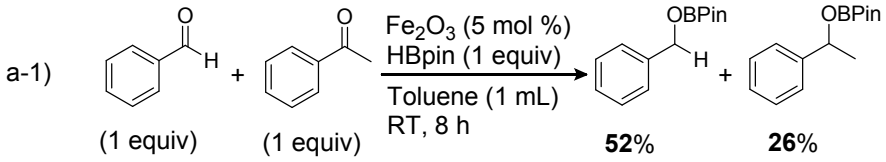
^{1}H NMR of **28c** (400 MHz, $CDCl_3$)



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

V. Competitive Chemoselective Hydroboration Reactions

Experimental Procedure for the Examples Described in Scheme 2a: In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, Fe_2O_3 NPs (5 mol %, 2 mg, 0.0125 mmol), HBpin (1.0 equiv, 36 µL, 0.25 mmol), toluene (1 mL), aldehyde (0.25 mmol) and ketone (0.25 mmol) were added and the reaction was stirred vigorously at room temperature for 8 h. The reaction mixture was then diluted with Et_2O (2 mL) and filtered through a plug of celite (Ø 3 mm × 8 mm) with copious washing (Et_2O). The solvents were removed *in vacuo*, and the borate esters yields were determined by ^1H NMR spectroscopy using nitromethane as an internal standard.



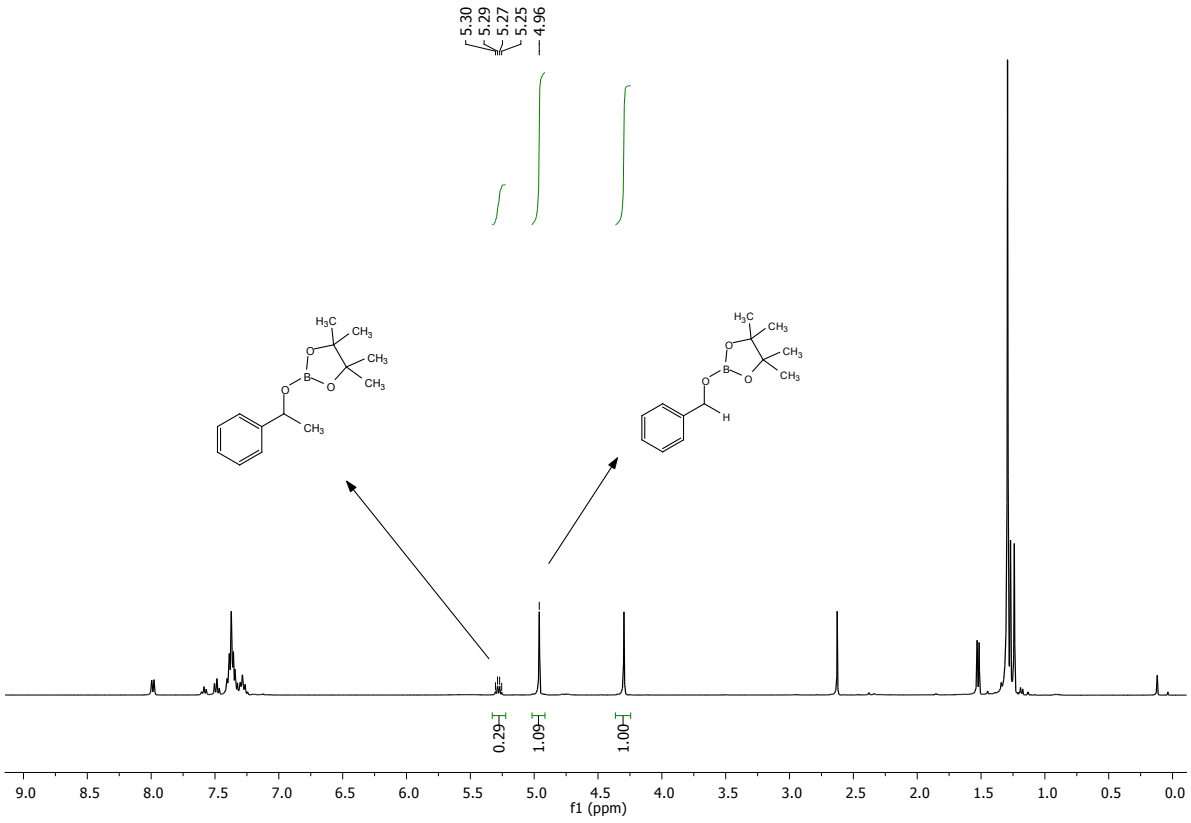


Figure S5. ^1H NMR spectra of competitive hydroboration reaction between benzaldehyde (**1a**) and acetophenone (**17a**).

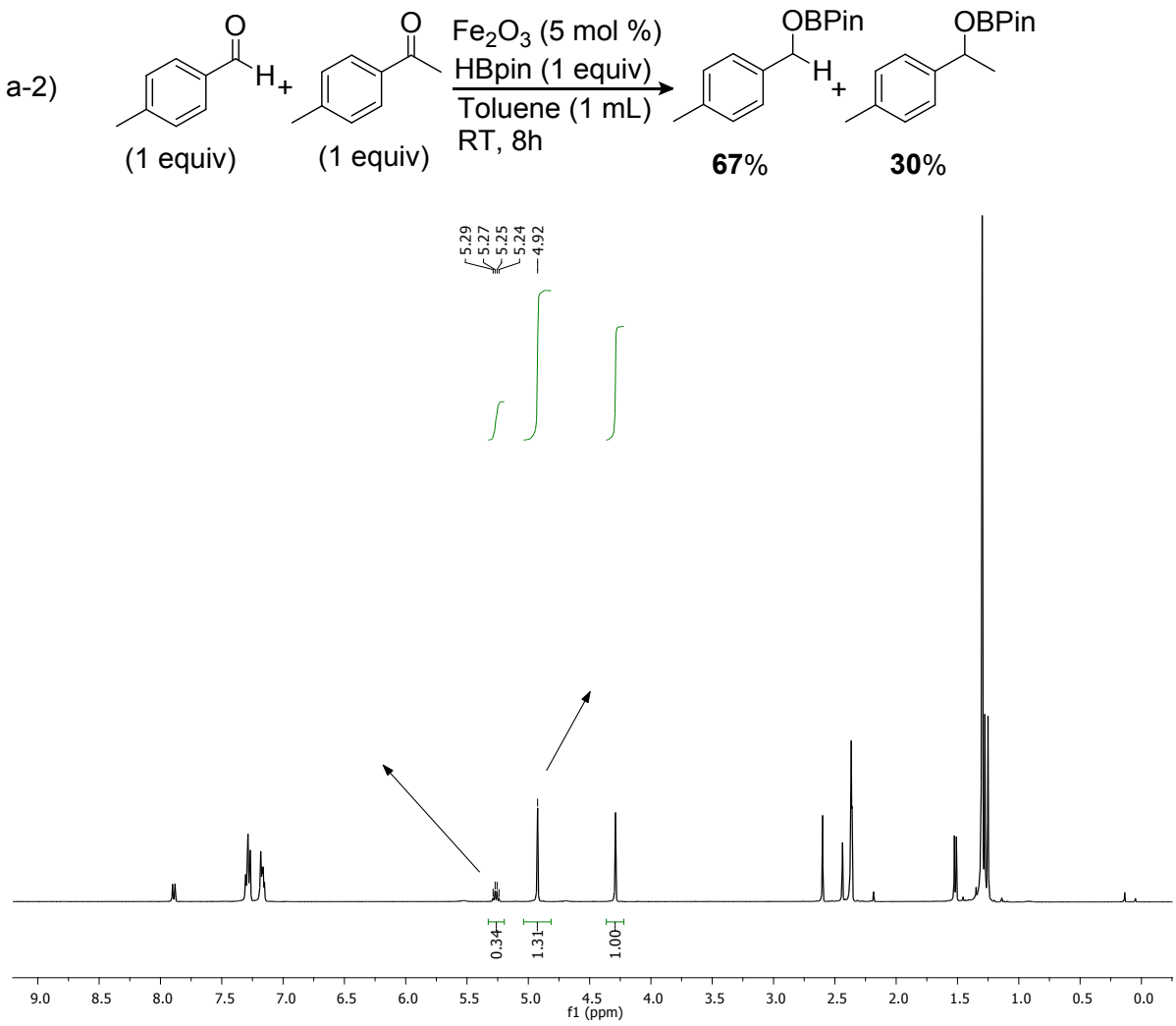


Figure S6. ^{1}H NMR spectra of competitive hydroboration reaction between 4-methylbenzaldehyde (**2a**) and 1-(*p*-tolyl)ethanone (**18a**).

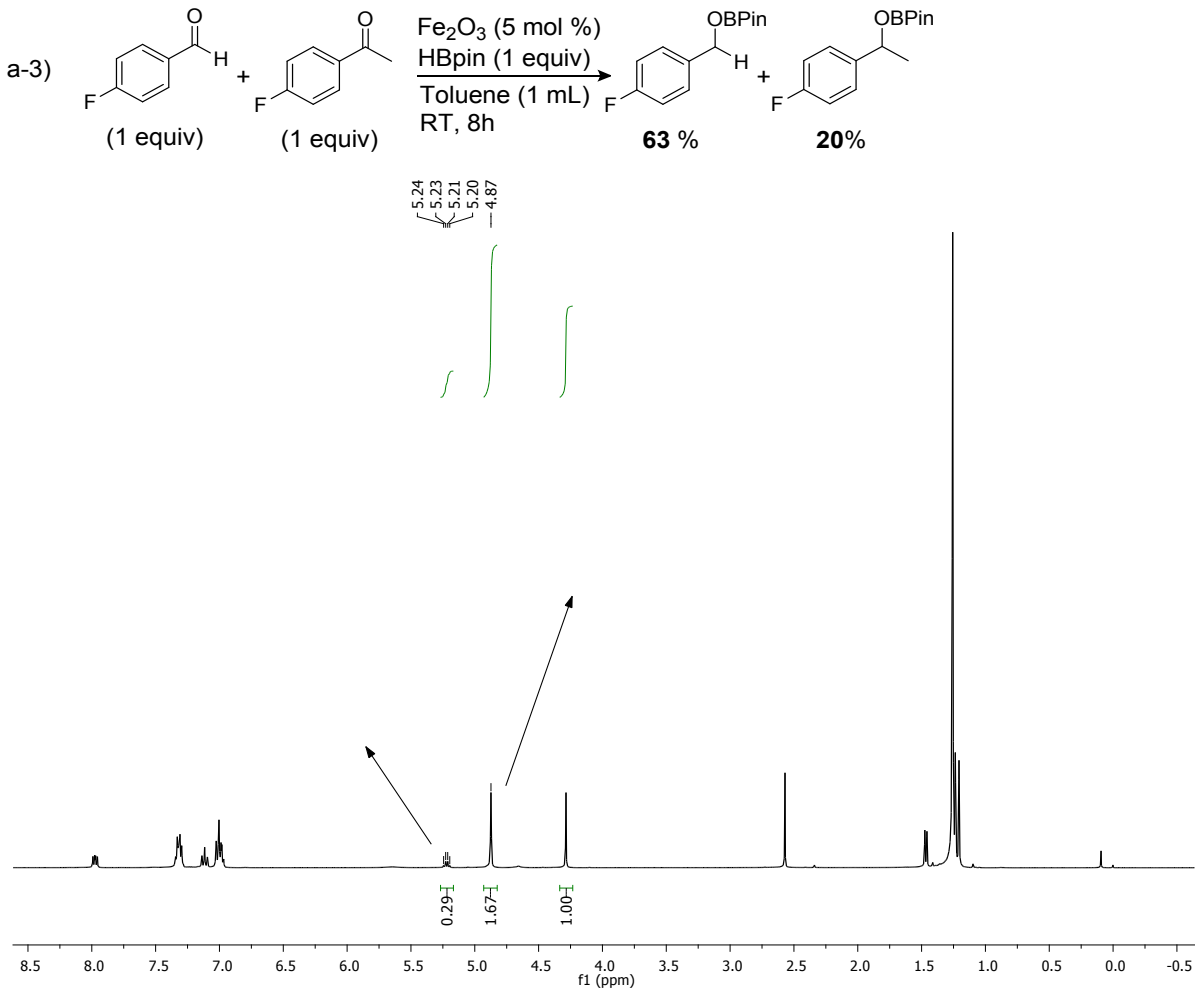


Figure S7. ^{1}H NMR spectra of competitive hydroboration reaction between 4-fluorobenzaldehyde (**5a**) and 1-(4-fluorophenyl)ethanone (**22a**).

Experimental Procedure for the Examples Described in Scheme 2b: In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, Fe_2O_3 NPs (5 mol %, 2 mg, 0.0125 mmol), HBpin (1.0 equiv, 36 µL, 0.25 mmol), toluene (1 mL) and substrate (0.25 mmol) were added and the reaction was stirred vigorously at room temperature for 10 h. The reaction mixture was then diluted with Et_2O (2 mL) and filtered through a plug of celite (Ø 3 mm × 8 mm) with copious washing (Et_2O). The solvents were removed *in vacuo*, and the borate ester yield was determined by ^1H NMR spectroscopy using nitromethane as an internal standard.

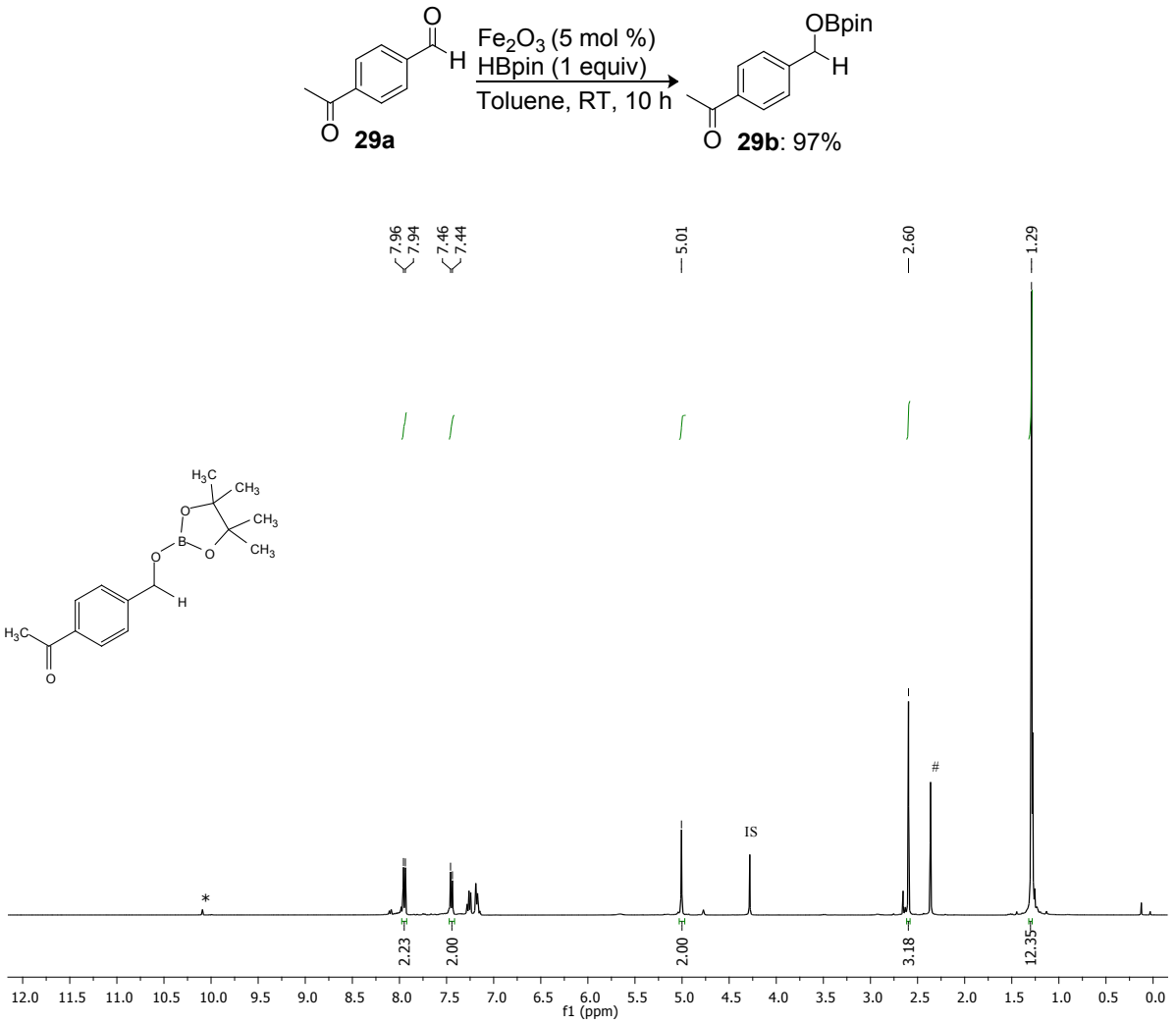


Figure S8. ^1H NMR spectra of intramolecular competitive hydroboration reaction of 4-acetylbenzaldehyde (**29a**).

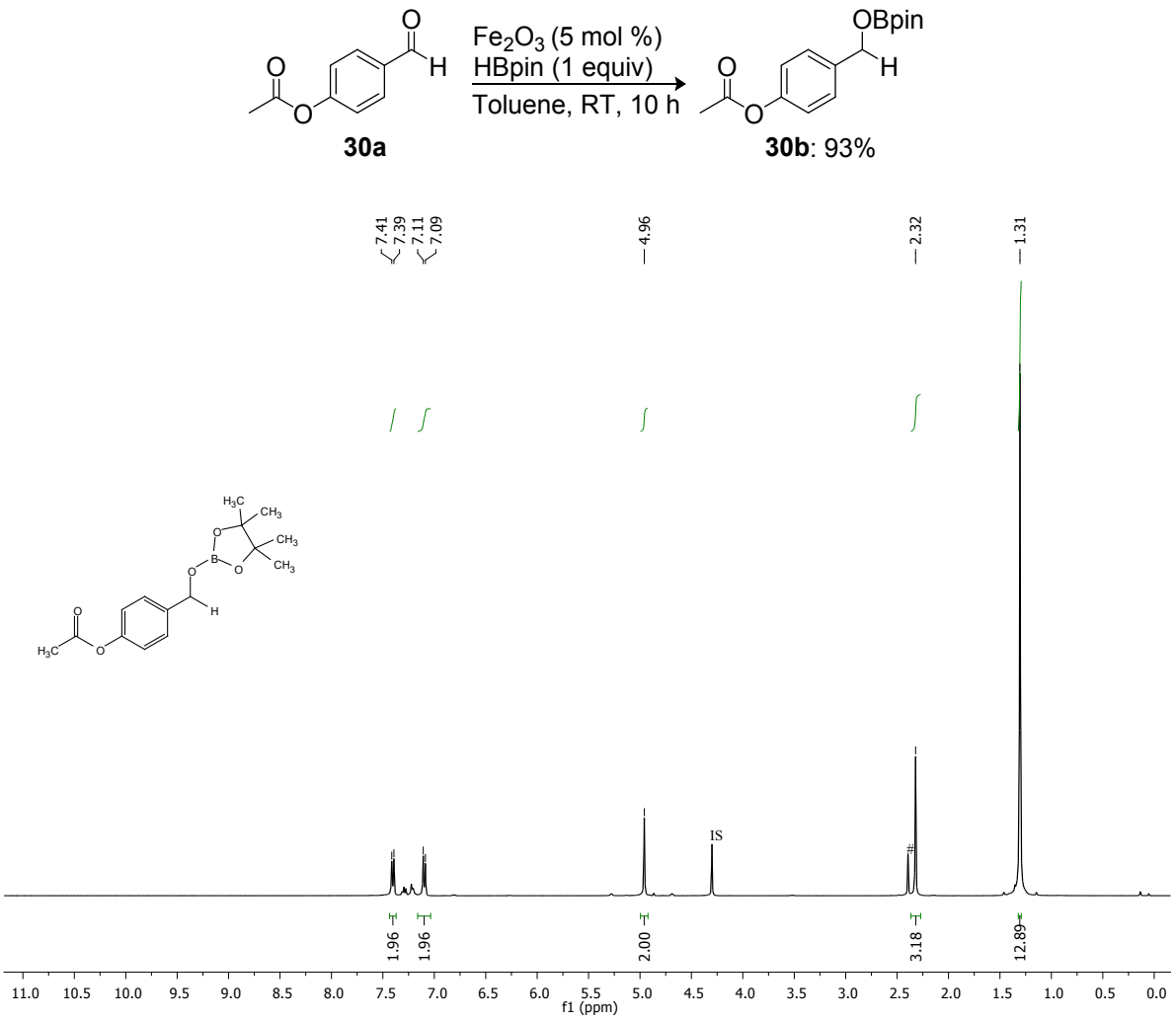


Figure S9. ^{1}H NMR spectra of intramolecular competitive hydroboration reaction of 4-formylphenyl acetate (**30a**).

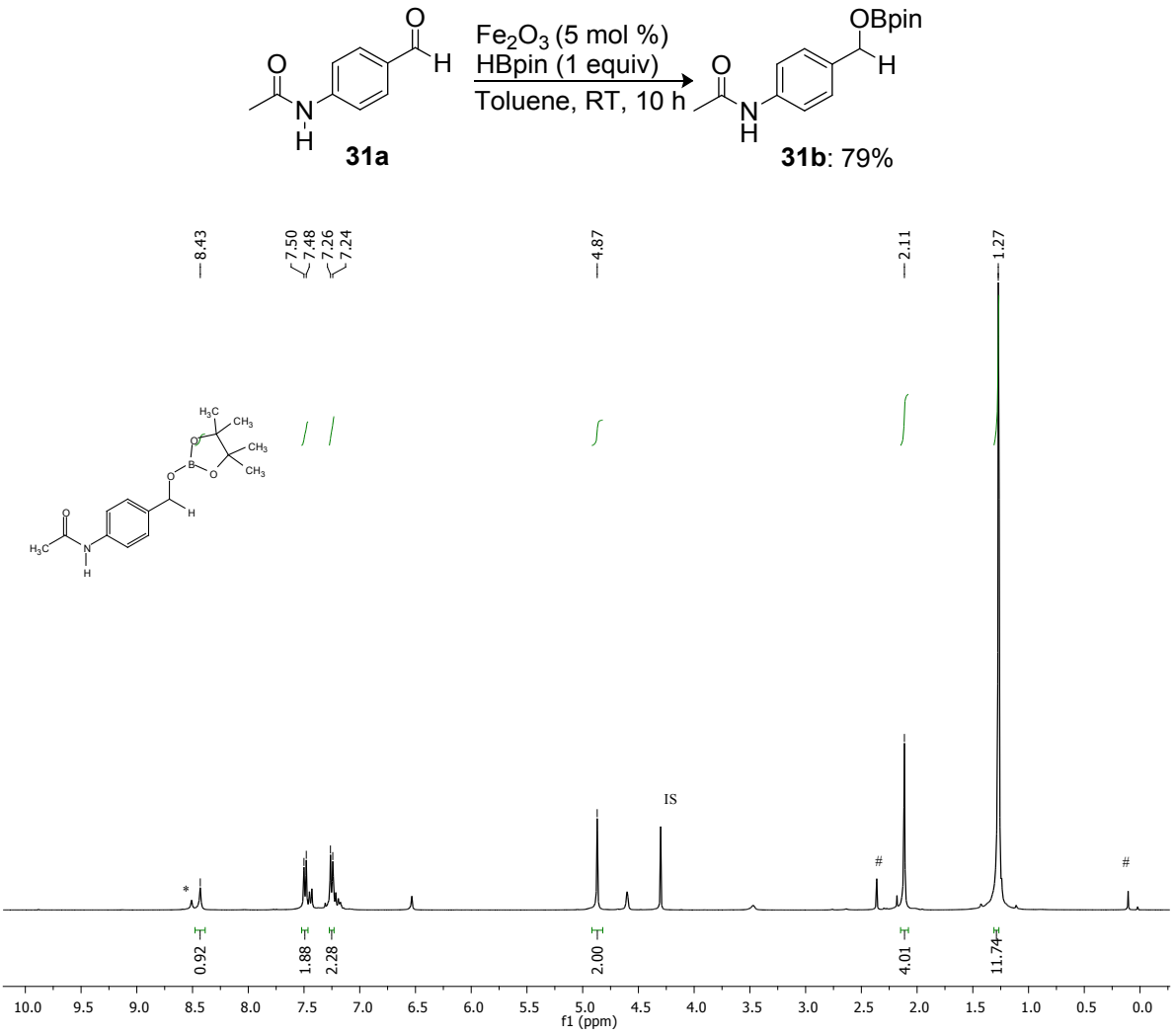


Figure S10. [1]H NMR spectra of intramolecular competitive hydroboration reaction of N-(4-formylphenyl)acetamide (**31a**).

Experimental Procedure for the Example Described in Scheme 2c: In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, Fe_2O_3 NPs (5 mol %, 2 mg, 0.0125 mmol), HBpin (1.2 equiv, 44 µL, 0.3 mmol), toluene (1 mL), benzaldehyde (0.25 mmol), 4-methoxybenzaldehyde (0.25 mmol) and fluorobenzaldehyde (0.25 mmol) were added and the reaction was stirred vigorously at room temperature for 8 h. The reaction mixture was then diluted with Et_2O (2 mL) and filtered through a plug of celite (Ø 3 mm × 8 mm) with copious washing (Et_2O). The solvents were removed *in vacuo*, and the borate esters yields were determined by ^1H NMR spectroscopy using nitromethane as an internal standard.

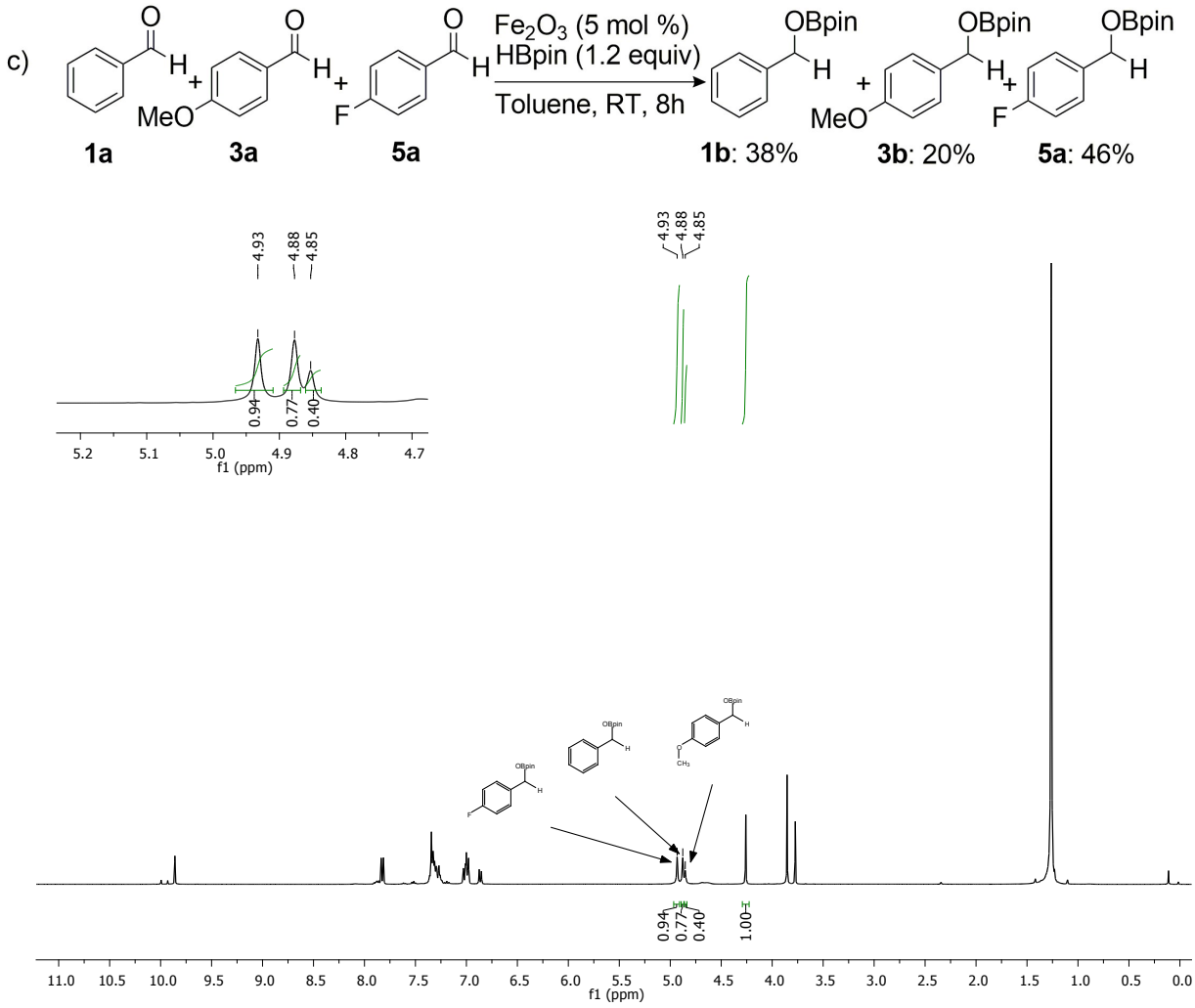
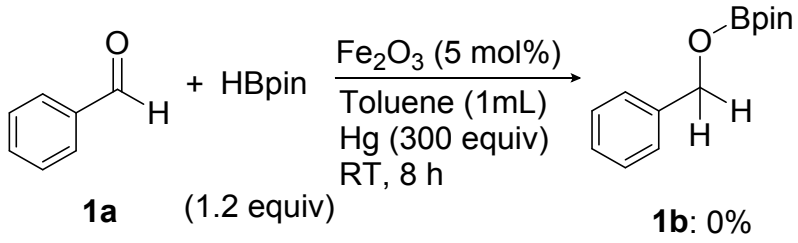


Figure S11. ^1H NMR spectra of competitive hydroboration reaction between benzaldehyde (**1a**), 4-methoxybenzaldehyde (**3a**) and 4-fluorobenzaldehyde (**5a**).

VI. Mechanistic Investigations

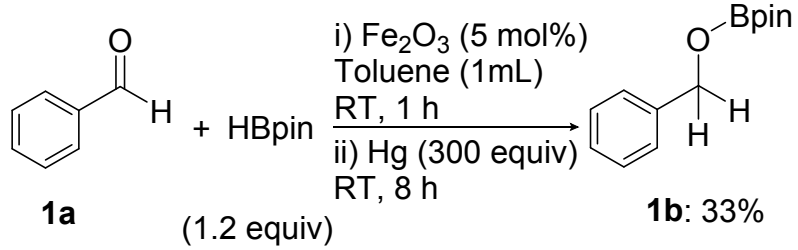
Mercury Poisoning Experiments.

a) In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, Fe_2O_3 NPs (5 mol %, 2 mg, 0.0125 mmol), HBpin (1.2 equiv, 44 μL, 0.3 mmol), toluene (1 mL), benzaldehyde (0.25 mmol, 20 μL) and Hg (300 equiv) were added and the reaction was stirred vigorously at room temperature for 8 h. The reaction mixture was then diluted with Et_2O (2 mL) and filtered through a plug of celite (Ø 3 mm × 8 mm) with copious washing (Et_2O). The solvents were removed *in vacuo*, and the borate ester yield was determined by ^1H NMR spectroscopy using nitromethane as an internal standard, no isolable product was obtained in this experiment.



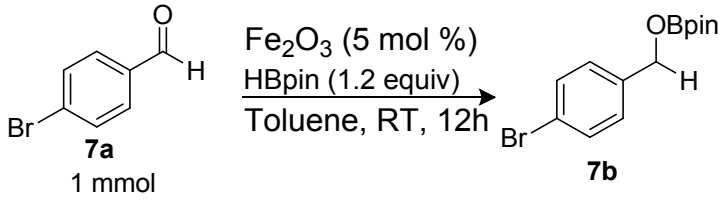
1a **1b**: 0%

b) In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, Fe_2O_3 NPs (5 mol %, 2 mg, 0.0125 mmol), HBpin (1.2 equiv, 44 μL, 0.3 mmol), toluene (1 mL) and benzaldehyde (0.25 mmol, 20 μL) were added, and the reaction was stirred vigorously at room temperature for 1 h. After 1 h reaction process, the reaction was interrupted and 300 equiv of Hg was added. After stirring for about 8 h at room temperature the reaction mixture was then diluted with Et_2O (2 mL) and filtered through a plug of celite (Ø 3 mm × 8 mm) with copious washing (Et_2O). The solvents were removed *in vacuo*, and the borate ester yield was determined by ^1H NMR spectroscopy using nitromethane as an internal standard.



1a **1b**: 33%

Recyclability Experiment for Hydroboration of 4-bromobenzaldehyde (7a).



In a 50 mL round bottom flask equipped with a magnetic stirring bar, 5 mol% of Fe_2O_3 (5 mol %, 0.05 mmol, 8 mg), HBpin (1.2 mmol, 174 μL), toluene (4 mL) and 4-bromobenzaldehyde (**7a**, 1.0 mmol, 185 mg) were added. The resulting reaction mixture was stirred vigorously at room temperature for 12 h. After completion of the reaction, the solid was centrifuged out of suspension and extracted with diethyl ether (three times). The solvents were removed *in vacuo*, and the combined organic extracts were analyzed by ^{1}H NMR spectroscopy using nitromethane as an internal standard.

The recovered Fe_2O_3 NPs was charged into 50 mL round bottom flask equipped with a magnetic stirring bar, to which additional HBpin (1.2 mmol, 174 μL), toluene (4 mL) and 4-bromobenzaldehyde (1.0 mmol, 185 mg) were added. The resulting reaction mixture was stirred vigorously at room temperature for 12 h. Then, NPs were centrifuged out of suspension and extracted with Et_2O. The combined organic product was extracted five times with Et_2O after each run and the reaction was continued with a fresh batch of substrate (4-bromobenzaldehyde, 1 mmol scale), HBpin(1.2 mmol, 174 μL) and toluene (4 mL) added to the separated Fe_2O_3 NPs. The combined organic extracts were analyzed by ^{1}H NMR spectroscopy using nitromethane as an internal standard. The results of 5 recycling experiments are summarized in Figure S12.

Yields: 1st cycle = 99%, 2nd cycle = 99%, 3rd cycle = 94%, 4th cycle = 89 %, 5th cycle = 52%.

Gratifyingly, when the recovered catalyst, after the fifth cycle of the reaction, was calcined at 500 °C for 3 h, and has been used as a catalyst for the hydroboration of 4-

bromobenzaldehyde (**7a**) under standard reaction conditions gave the desire borate ester **7b** in 99% yield confirmed by ^{1}H NMR spectroscopy.

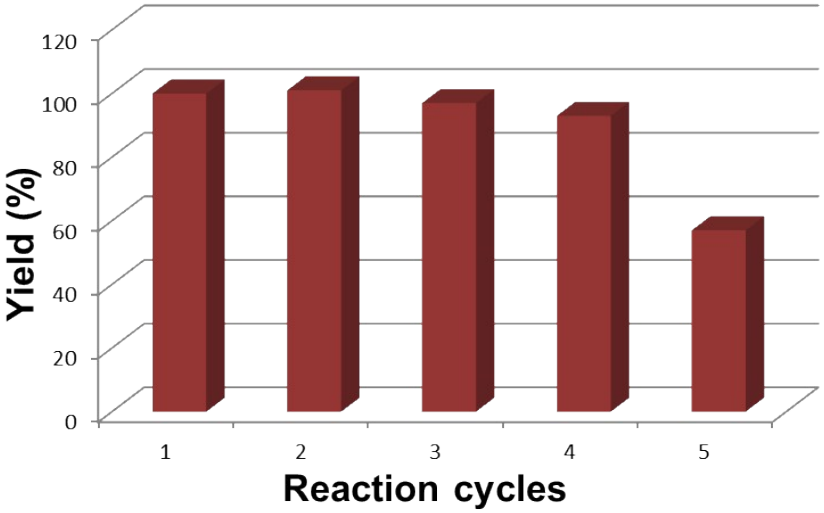


Figure S12.^{1}H NMR yields (%) of borate ester at different cycles in the recyclability experiment for Fe_2O_3 NPs catalysed hydroboration of 4-bromobenzaldehyde.

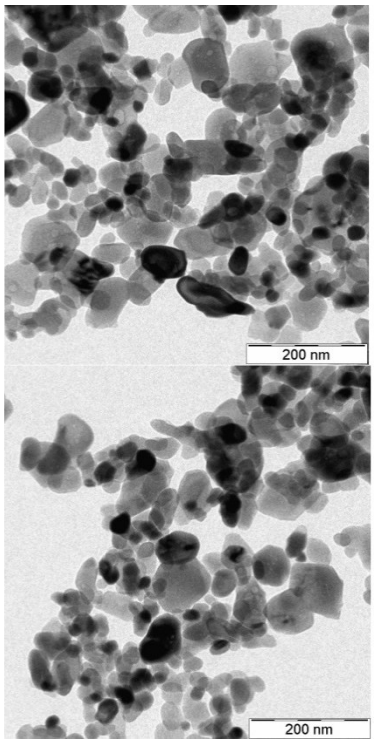


Figure S13. TEM images of Fe_2O_3 nanoparticles after 5 reuses.

The nanoparticles recovered after 5 reuses were characterized by transmission electron microscopy (TEM). The TEM images demonstrated that the nanoparticles were having particle size in the range of 20-65 nm and an average particle size of ~37.8 nm.

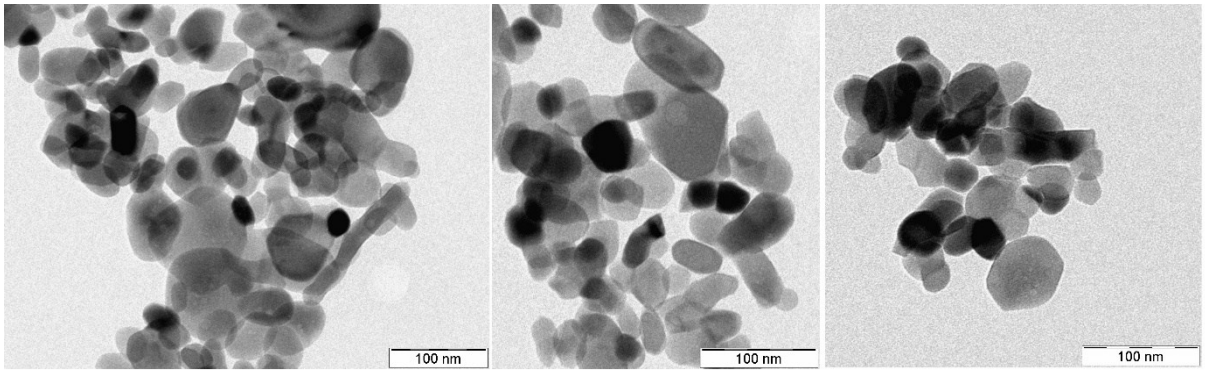


Figure S14. TEM images of calcined Fe_2O_3 nanoparticles, recovered after 5 catalytic cycles.

The calcined Fe_2O_3 nanoparticles recovered after 5 catalytic cycles were characterized by transmission electron microscopy (TEM). The TEM images demonstrated that the nanoparticles were having particle size in the range of 20-63 nm and an average particle size of ~35.7 nm.

Stoichiometric reaction of Fe_2O_3 NPs with substrate and HBpin.

In an argon-filled glovebox, the Fe_2O_3 NPs (20 mg, 0.125 mmol) and benzaldehyde (13 mg, 0.125 mmol) were mixed and the reaction mixture was analyzed by fourier transform infra-red (FT-IR) spectroscopy (Figure S15). The strong absorption peaks at 534 and 462 cm^{-1} can be attributed to the Fe–O band vibrations (Figure S15-a). The strong absorption peak at 1701 cm^{-1} is due to the CO stretching frequency (Figure S15-b). The FT-IR spectrum of the reaction mixture shows shift in the absorption band correspond to the Fe–O vibration as well as in the CO stretching frequency towards lower wavenumber indicating interaction between Fe_2O_3 and benzaldehyde (Figure S15-c)

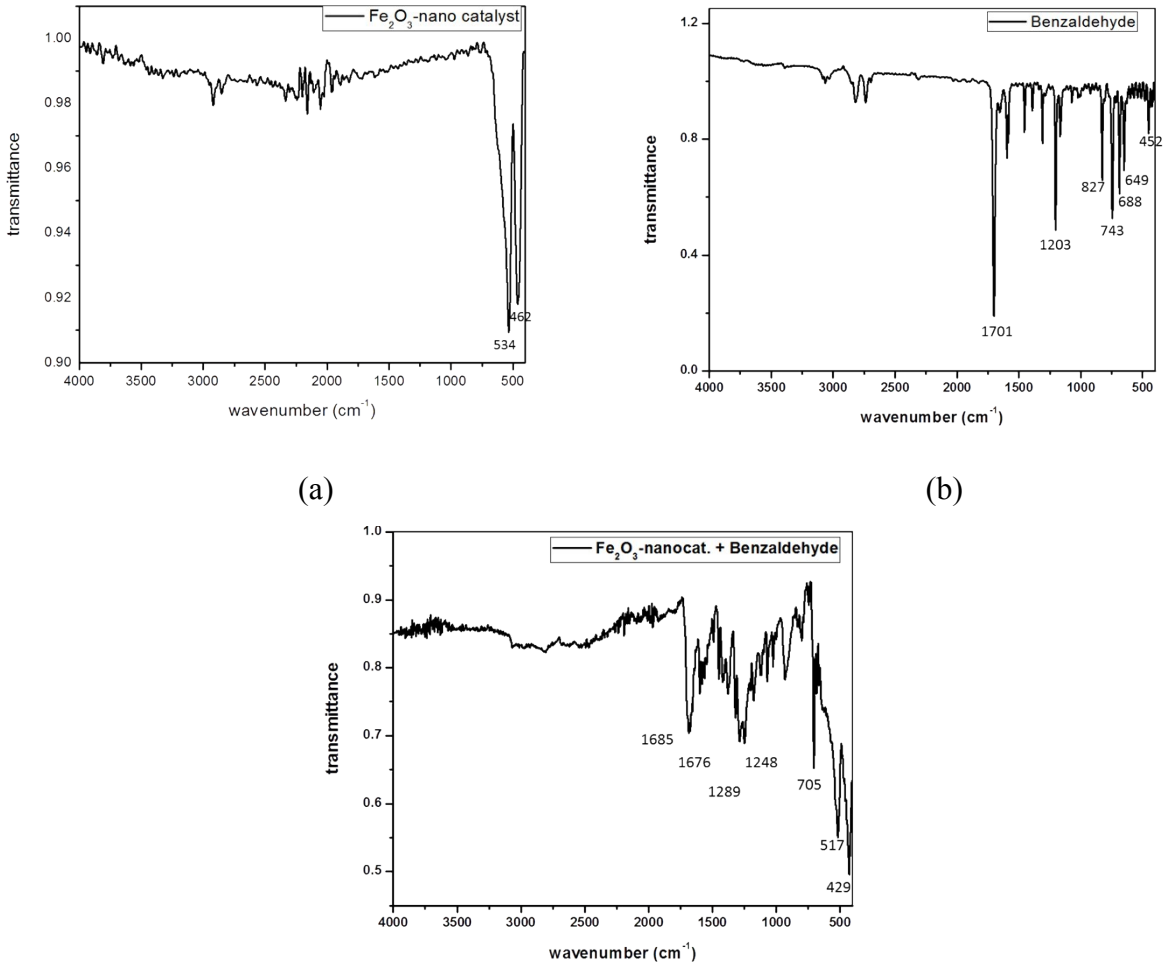
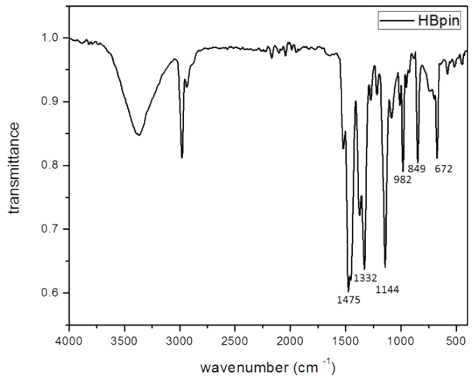


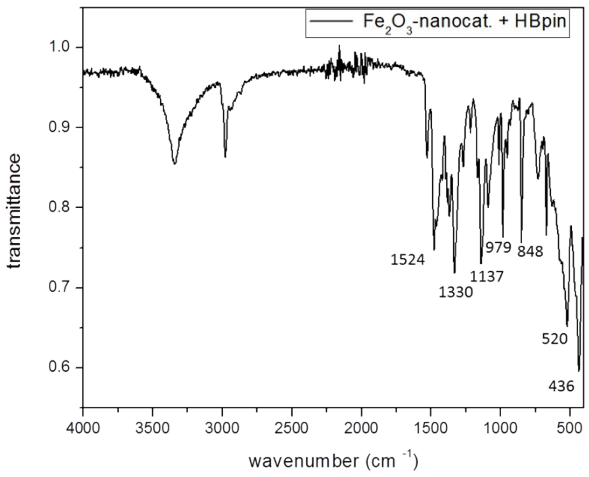
Figure S15. IR spectra of: (a) Fe_2O_3; (b) C_6H_5CHO and (c) Fe_2O_3 + C_6H_5CHO.

In an argon-filled glovebox, the Fe_2O_3 NPs (20 mg, 0.125 mmol) and excess HBpin (160 mg, 1.25 mmol) were mixed and the reaction mixture was analyzed by FT-IR spectroscopy (Figure S16). The FT-IR spectrum of the reaction mixture shows shift in the absorption band correspond to the Fe–O vibration towards lower wavenumber indicating interaction between Fe_2O_3 and HBpin (Figure S16-c)

(a)



(b)



(c)

Figure S16. IR spectra of: (a) Fe_2O_3; (b) HBpin and (c) Fe_2O_3 + HBpin.

VII. References

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