Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

CeO_2-nanocubes as efficient and selective catalysts for the hydroboration of carbonyl groups

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I. General Information

All reagents were purchased from TCI, SDFCL or Aldrich and were used as received. The ceria precursor $Ce(NO_3)_3 \cdot 6H_2O$ was purchased from TCI. 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] CeO_2 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 Advance 400 NMR spectrometer (^{1}H, 400 MHz; ^{13}C, 100 MHz; ^{11}B, 128 MHz). ^{1}H NMR chemical shifts are reported relative to TMS and were referenced *via* residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm, C_6D_6: 7.16 ppm) 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 CeO_2 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. TEM was carried out using FEI Tecnai T20 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 CeO_2 nanoparticles.[1b] To obtain CeO_2 nano-cubes, a hydrothermal process was employed. $Ce(NO_3)_3 \cdot 6H_2O$ (4 mmol) and NaOH (480 mmol) were dissolved in 10 mL and 70 mL of distilled water, respectively. Then both the solution was mixed and stirred for 30 min at room temperature to get purple slurry. Subsequently, the slurry was transferred into a 100 mL Teflon-lined stainless autoclave and heated at 180 °C for 24 h to obtain nano-cubes. After the hydrothermal treatment, the precipitates were separated by filtration, washed with distilled water and ethanol several times. After drying at 80 °C for 1 day, the products were calcined at 600 °C for 5 h to get a yellow product. The CeO_2 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).

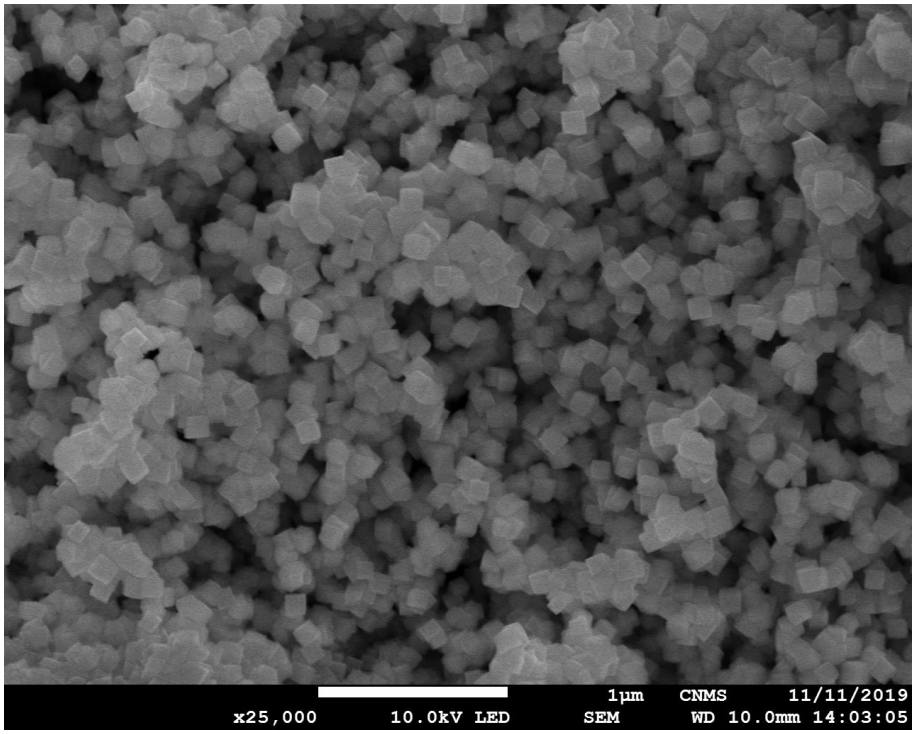
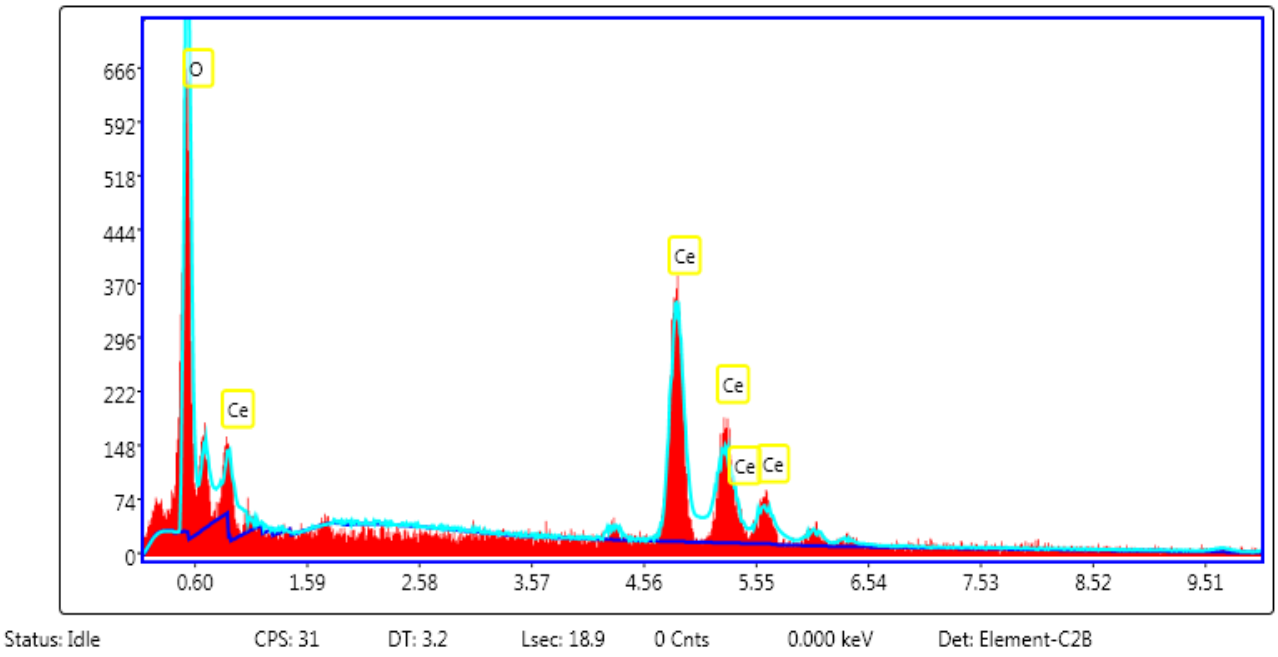


Figure S1. FESEM image of CeO_2 nanoparticles.



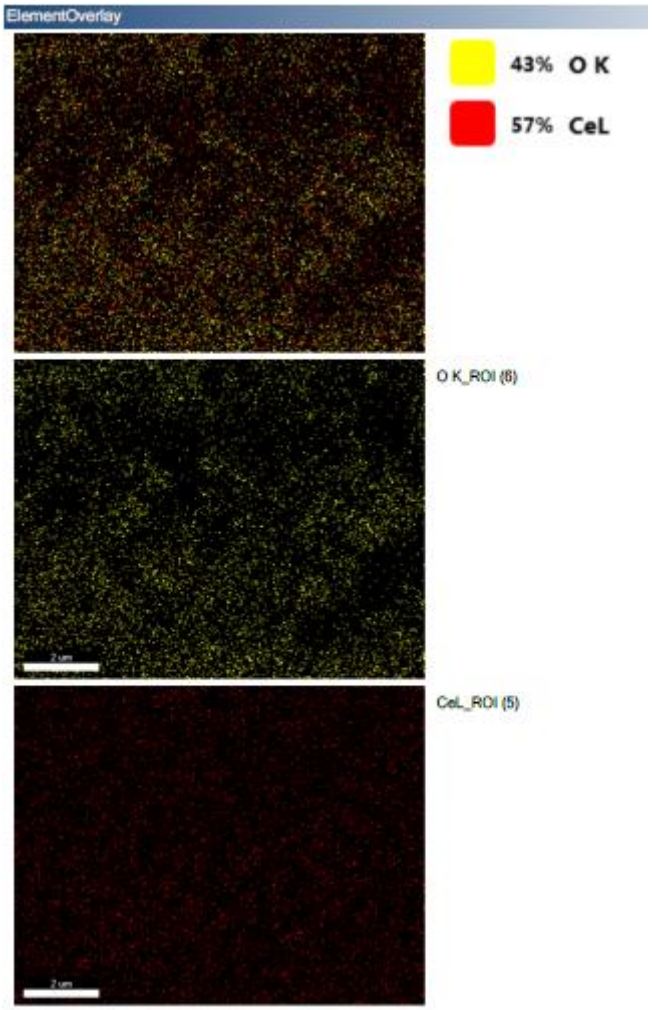
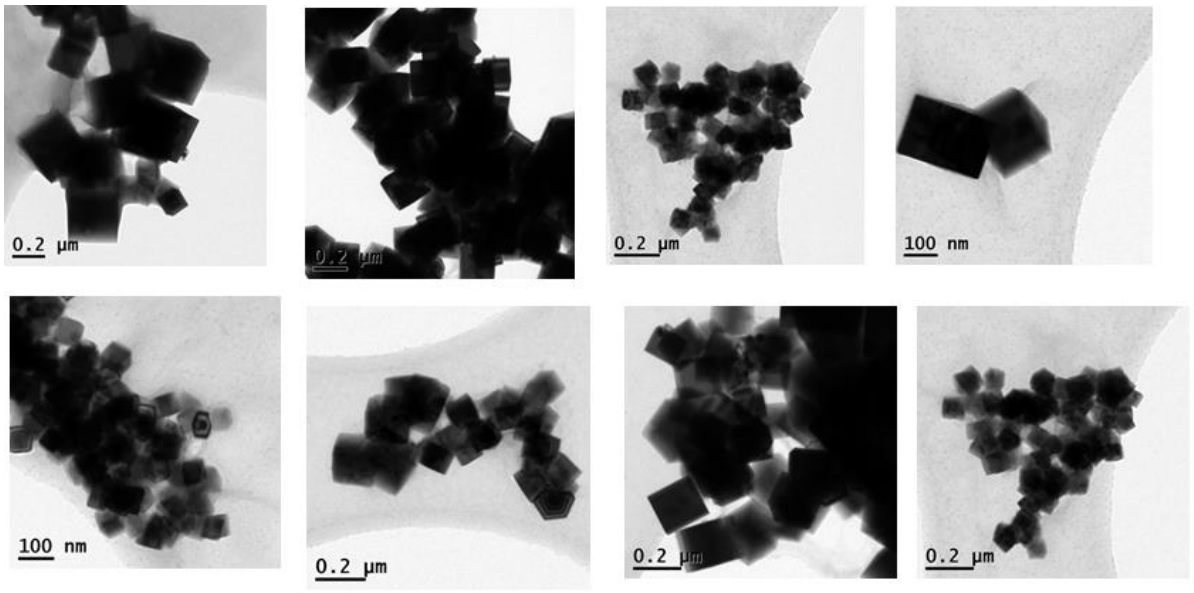
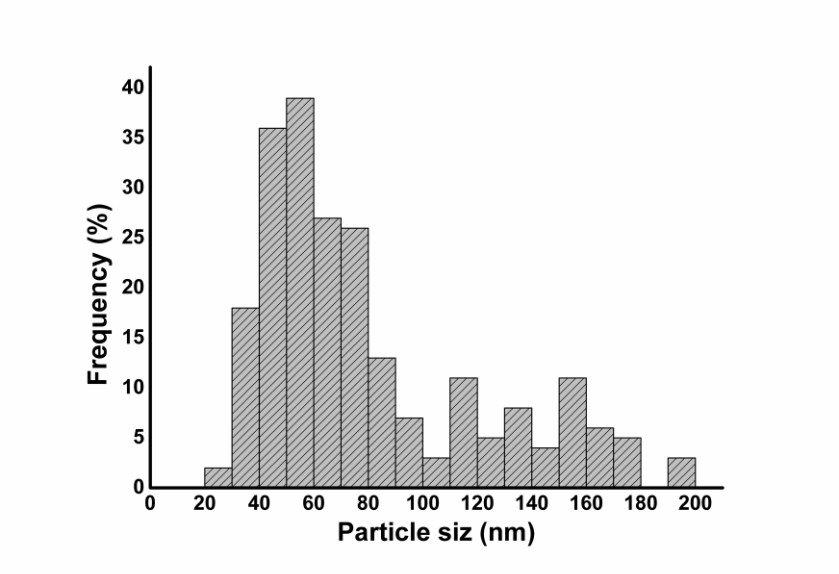


Figure S2. EDX spectrum and overlay map of CeO_2 nanoparticles.

TEM images and particle size distributions of CeO_2 NPs



a)



c)

Figure S3. a) TEM images of CeO_2 nanoparticles. b) Particle size distribution chart of CeO_2 nanoparticles.

The TEM analysis of CeO_2 nanoparticles (Figure S3) shows that the nanoparticles were having particle size in the range of 20-200 nm and an average particle size of ~55 nm.

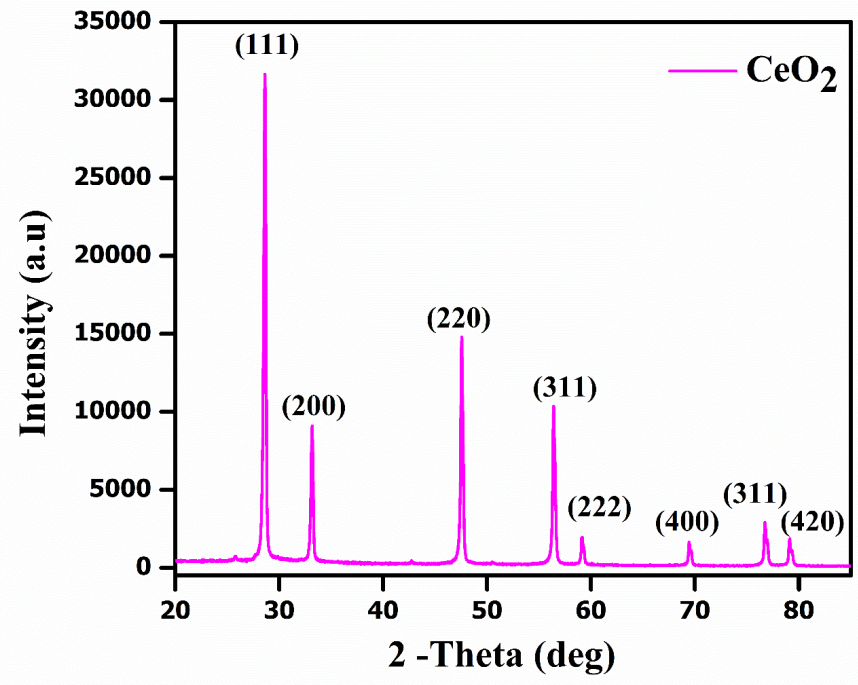


Figure S4. Powder XRD pattern of CeO_2 nanoparticles.

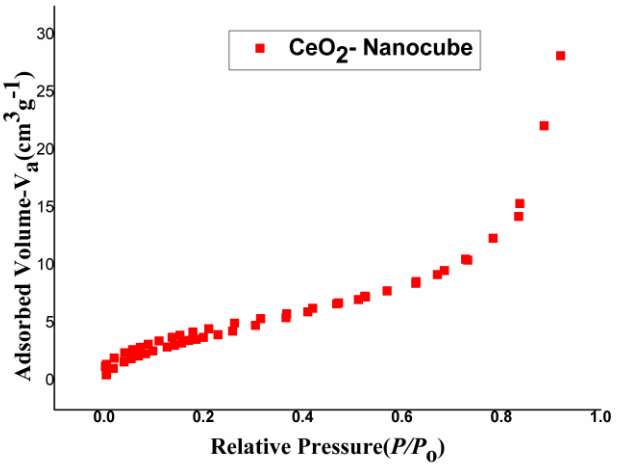


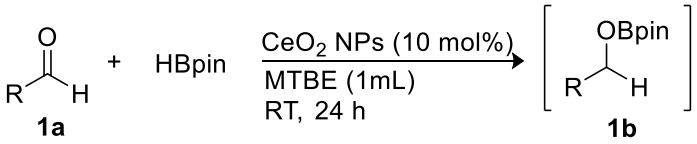
Figure S5. BET analysis of CeO_2 nanoparticles.

BET analysis results based on the N_2 adsorption desorption isotherms, depicted in Figure S5. It was seen that of CeO_2 nanoparticles possesses a BET surface area of 23 m^2 g^{-1}.

Experimental procedures for examples described in Table 1.

In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, CeO_2-catalyst (0.025 mmol), HBpin (0.33 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 ^1H NMR spectroscopy using nitromethane as an internal standard.

Table S1: Effect of different equivalents of HBpin on the CeO_2 nanoparticles catalysed hydroboration of benzaldehyde (**1a**).[a]



Entry	Catalyst (mol %)	Time (h)	HBpin (equiv)	Solvent (1 mL)	Yield (%)[b]
1	CeO_2 NPs (10)	24	1.0	MTBE	72
2	CeO_2 NPs (10)	24	1.1	MTBE	86
3	CeO_2 NPs (10)	24	1.2	MTBE	97
4	CeO_2 NPs (10)	24	1.3	MTBE	>99

[a] Reaction conditions: benzaldehyde (0.25 mmol), CeO_2 NPs (10 mol %, 4 mg), HBpin, MTBE (1 mL), at room temperature for 24 h. [b] Yields were determined by ^1H NMR, using nitromethane as an internal standard.

General procedure of hydroboration of aldehydes (examples described in Table 2).

In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, CeO_2 NPs (10 mol %, 4 mg, 0.0250 mmol), HBpin (1.3 equiv, 47 µL, 0.33 mmol), MTBE (1 mL) and aldehyde (0.25 mmol) were added and the reaction was stirred vigorously at room temperature for 24 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.

General procedure of hydroboration of ketones (examples described in Table 3).

In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, CeO_2 NPs (10 mol %, 4 mg, 0.0250 mmol), HBpin (1.3 equiv, 47 µL, 0.33 mmol), MTBE (1 mL) and ketone (0.25 mmol) were added and the reaction mixture was stirred vigorously at 50 °C for 24 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.

Experimental procedures for catalytic conversion of aldehydes/ketones to 1º/2º alcohols:

General procedure A. In a 50 mL round bottom flask equipped with a magnetic stirring bar, CeO_2 (10 mol %, 0.1 mmol, 17 mg), HBpin (1.3 mmol, 188 µL), MTBE (4 mL) and aldehyde (1.0 mmol) were added. The resulting reaction mixture was stirred vigorously at room temperature for 24 h (for ketone 50 °C, 24 h). 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 product. The crude residue was purified by silica gel column chromatography using a mixture of hexane and ethyl acetate as eluent and characterized by ^1H and ^{13}C NMR spectroscopy.

General procedure B. 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 *vacuo* and the residue was purified by silica gel column chromatography using a mixture of hexane and ethyl acetate as eluent.

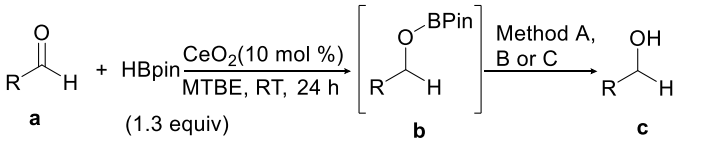
General procedure C. The resulted borate ester reaction mixture was exposed to the air and was stirred at room temperature for 14-16 h, for the quantitative conversion to corresponding alcohol. The organic layer was extracted with dichloromethane (3 x 10 mL) and was removed by vacuum to get the crude product. 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.

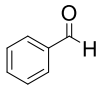
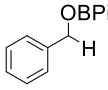
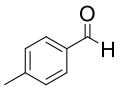
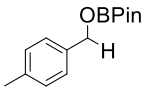
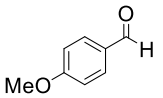
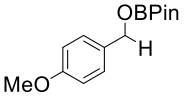
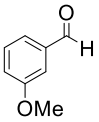
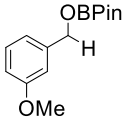
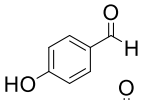
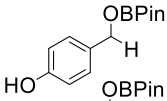
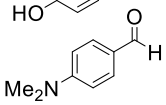
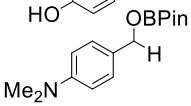
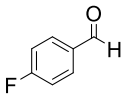
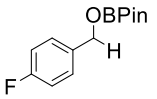
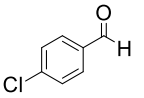
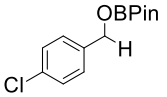
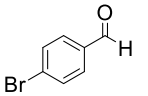
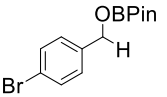
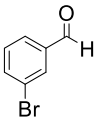
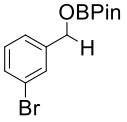
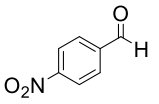
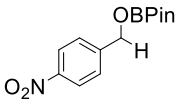
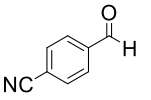
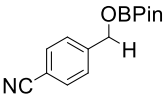
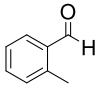
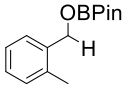
General procedure for preparative scale reactions.

In a 100 mL round bottom flask equipped with a magnetic stirring bar, CeO_2 (10 mol %, 0.5 mmol, 86 mg), HBpin (1.3 equiv, 6.5 mmol, 0.9 mL), MTBE (10 mL) and aldehyde (5.0 mmol) were added. The resulting reaction mixture was stirred vigorously at room temperature for 24 h. 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 (**9a**, 0.925 gm, 5 mmol), 2-methylbenzaldehyde (**13a**, 0.6 gm, 5 mmol) and 1-naphthaldehyde (**17a**, 0.781 gm, 5 mmol) gave the desired alcohols in good yields (**9c**: 0.795 g, 86%; **13c**: 0.452 g, 75% and **17c**: 0.492 g, 63%).

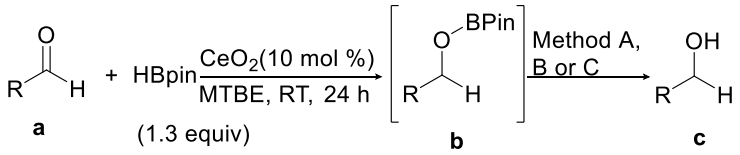
Table S2a. Hydroboration of aldehydes catalysed by CeO_2 NPs.[a]

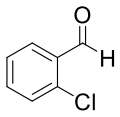
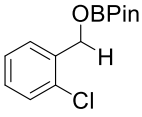
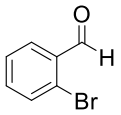
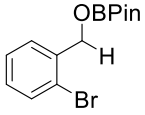
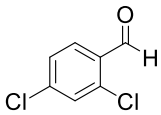
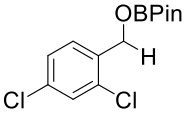
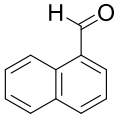
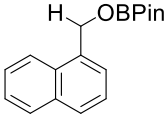
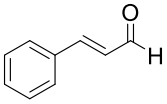
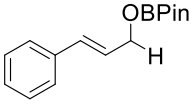
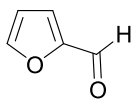
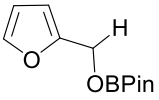
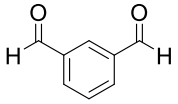
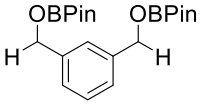
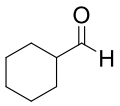
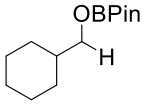
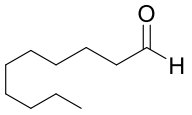
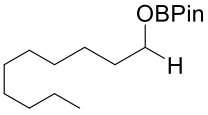


Entry	Aldehyde	Borate ester	Yield (%)[b] (1° alcohol (%))[c]
1			**1b**: >99[b] **1c:** (89)[c]
2			**2b**: >99[b] **2c:** (81)[c]
3			**3b**: >99[b] **3c**: 96[b] (90)[c]
4			**4b**: 93[b] **4c:** 89[b] (79)[c]
5			**5b**: 84[b]
6			**6b**: 96[b]
7			**7b**: >99[b] **7c:** (85)[c]
8			**8b**: >99[b] **8c:** 98[b] (87)[c]
9			**9b**: >99[b] **9c:** (82)[c]
10			**10b**: >99[b] **10c:** 96[b] (78)[c]
11			**11b**: 86[b] **11c:** 84[b] (70)[c]
12			**12b**: >99[b] **12c:** (80)[c]
13			**13b**: >99[b] **13c:** (84)[c]

[a] Reaction conditions: Aldehyde (1.0 mmol), CeO_2 NPs (10 mol %, 0.1 mmol, 17 mg), HBpin (1.3 mmol, 188 μL) and MTBE (2 mL), at room temperature for 24 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.

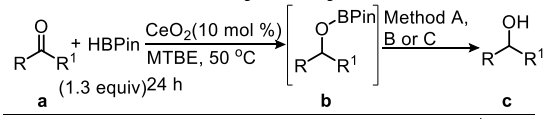
Table S2b. Hydroboration of aldehydes catalysed by CeO_2 NPs.[a]

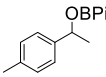
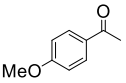
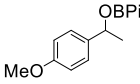
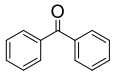
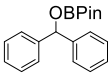
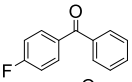
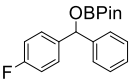
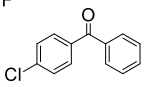
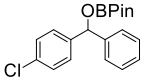
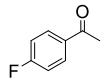
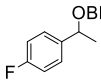
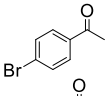
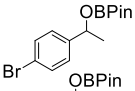
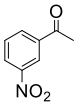
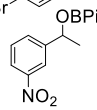
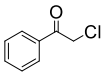
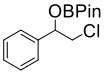
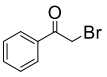
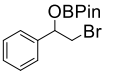
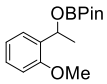
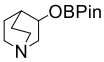
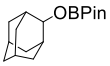
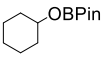
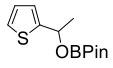


Entry	Aldehyde	Borate ester	Yield (%)[b] (1° alcohol (%))[c]
14			**14b**: >99[b]
15			**15b**: >99[b]
16			**16b**: >99[b]
17			**17b**: >99[b] **17c:** (88)[c]
18			**18b**: 74[b] **18c:** 72[b] (59)[c]
19			**19b**: 73[b]
20			**20b**:[d] 88[b] **20c:** (73)[c]
21			**21b**: >99[b]
22			**22b**: 85[b] **22c:** (80)[c]

[a] Reaction conditions: Aldehyde (1.0 mmol), CeO_2 NPs (10 mol %, 0.1 mmol, 17.2 mg), HBpin (1.3 mmol, 188μL) and MTBE (2 mL), at room temperature for 24 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 2.6. equiv of HBpin.

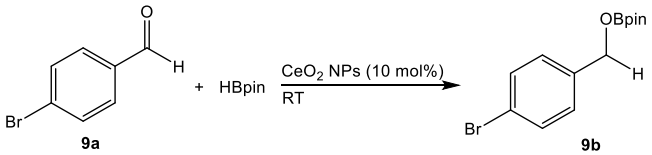
Table S3. Hydroboration of ketones catalysed by CeO_2 NPs.[a]



Entry	Ketone	Borate ester	Yield (%)[b] (2° alcohol yield (%))[c]
23			**23b:** >98[b] **23c:** (80)[c]
24			**24b:** 85[b] **24c:** 83[b] (72)[c]
25			**25b:** 87[b] **25c:** (78)[c]
26			**26b:** >99[b] **26c:** (89)[c]
27			**27b:** >99[b]
28			**28b:** >99[b]
29			**29b:** 97[b] **29c:** 94[b] (75)[c]
30			**30b:** 93[b] **30c:** 87[b] (71)[c]
31			**31b:** 53[b] **31c:** (41)[c]
32			**32b:** 72[b] **32c:** (58)[c]
33			**33b:** 61[b] **33c:** 60[b] (37)[c]
34			**34b:** 72[b] **34c:** 59[b] (56)[c]
35			**35b:** 58[b]
36			**36b:** 84[b]
37			**37b:** 61[b]
38			**38b:** 86[b]

[a] Reaction conditions: ketone (1.0 mmol), CeO_2 NPs (10 mol %, 0.01 mmol, 17.2 mg), HBpin (1.3 mmol, 188 μL) and MTBE (2 mL), at 50 °C for 24 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.

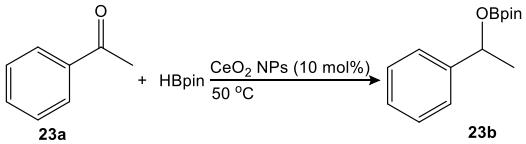
Table S4. Solvent effect on the CeO_2 nanoparticle catalysed hydroboration of 4-bromobenzaldehyde (**7a**).[a]



Entry	Catalyst (mol%)	Temperature (°C)	Time (h)	HBpin (equiv)	Solvent (1 mL)	Product Yield (%)[b]
1	CeO_2 (10)	RT	24	1.3	MTBE	>99
2	CeO_2 (10)	RT	24	1.3	-	83
3	-	RT	24	1.3	-	15

[a] Reactions were carried out using 0.25 mmol of **9a** (1 equiv), 1.3 equiv of HBpin (0.33 mmol) in 1 mL of MTBE at room temperature unless otherwise stated. [b] Yield was determined by ^{1}H NMR analysis, using nitromethane as an internal standard.

Table S5. Solvent effect on the CeO_2 nanoparticle catalysed hydroboration of acetophenone (**23a**).[a]

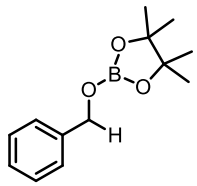


Entry	Catalyst (mol%)	Temperature (°C)	Time (h)	HBpin (equiv)	Solvent (1 mL)	Product Yield (%)[b]
1	CeO_2 NPs (10)	50 °C	24	1.3	MTBE	98
2	CeO_2 NPs (10)	50 °C	24	1.3	-	74

[a] Reactions were carried out using 0.25 mmol of **23a** (1 equiv), 1.3 equiv of HBpin (0.33 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.

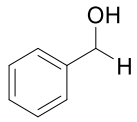
III. Spectroscopic Data of Hydroboration Products and Related Alcohols

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



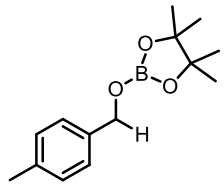
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.41-7.28 (m, 5H), 4.97 (s, 2H), 1.31 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.2.

Phenylmethanol (**1c**).[2,4]



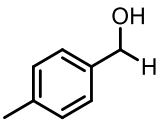
Following General procedure A. Colourless oil. Yield: 89% (96 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.26-7.19 (m, 5H), 4.46 (s, 2H), 3.55 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 140.8, 128.3, 127.4, 127.0, 79.37, 64.6.

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



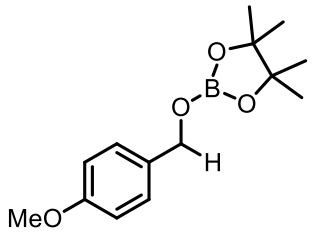
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.28 (d, *J* = 8 Hz, 2H), 7.18 (d, *J* = 8 Hz, 2H), 4.92 (s, 2H), 2.37 (s, 3H), 1.30 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.1.

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



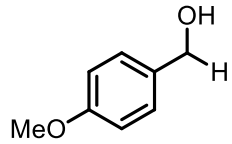
Following General procedure A. Colourless oil. Yield: 81% (99 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.27 (d, *J* = 8 Hz, 2H), 7.19 (d, *J* = 8 Hz, 2H), 4.65 (s, 2H), 2.38 (s, 3H), 1.89 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 138.0, 137.4, 129.3, 127.2, 65.3, 21.2.

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



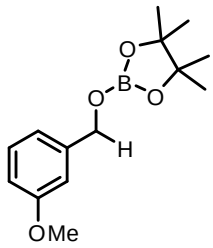
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.30 (d, *J* = 8 Hz, 2H), 6.89 (d, *J* = 8 Hz, 2H), 4.87 (s, 2H), 3.82 (s, 3H), 1.29 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.3.

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



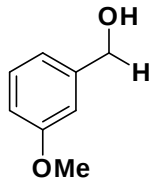
Following General procedure A. Colourless oil. Yield: 90% (125 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.24 (d, *J* = 8 Hz, 2H), 6.87 (d, *J* = 8 Hz, 2H), 4.52 (s, 2H), 3.78 (s, 3H), 3.47 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 158.8, 133.1, 128.5, 113.7, 64.3, 55.1.

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



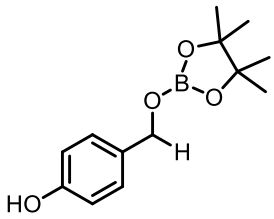
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.26 (br, 1H), 6.95–6.84 (m, 3H), 4.94 (s, 2H), 3.82 (s, 3H), 1.30 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.3.

(3-Methoxyphenyl)methanol (4c).[2,7]



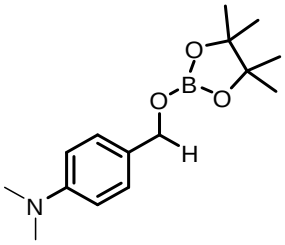
Following General procedure A. A colorless oil. Yield: 79% (108 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.29-7.25 (m, 1H), 6.93-6.91 (m, 2H), 6.85-6.82 (m, 1H), 4.59 (s, 2H), 3.79 (s, 3H), 3.37 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 159.6, 142.6, 129.4, 119.0, 112.9, 112.1, 64.6, 55.0.

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



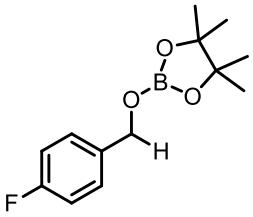
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.20 (d, J = 8 Hz, 2H), 6.81 (d, J = 8 Hz, 2H), 4.84 (s, 2H), 1.28 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.2.

N,N-Dimethyl-4-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)aniline

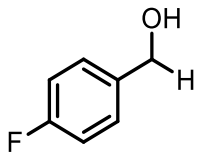


(Table 2, 6b).[8] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.25 (d, *J* = 8 Hz, 2H), 6.74 (d, *J* = 8 Hz, 2H), 4.85 (s, 2H), 2.97 (s, 6H), 1.30 (s, 12H). ^{11}B (128 MHz, $CDCl_3$, ppm): δ 22.3.

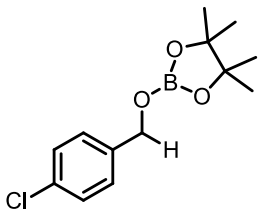
2-((4-Fluorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 7b).[2,7] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.36-7.31 (m, 2H), 7.06-7.01 (m, 2H), 4.90 (s, 2H), 1.29 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.3.



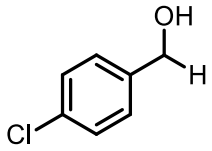
(4–Fluorophenyl)methanol (7c).[2,5] Following General procedure A. Colourless oil. Yield: 85% (107 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.21-7.19 (m, 2H), 6.95-6.91 (m, 2H), 4.50 (s, 2H), 2.42 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 162.4 (d, $J_{C–F}$ = 244 Hz), 136.5 (d, $J_{C–F}$ = 3 Hz), 128.8 (d, $J_{C–F}$ = 8 Hz), 115.5 (d, $J_{C–F}$ = 20 Hz), 64.5.



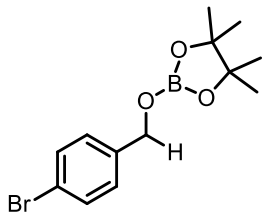
2-((4-Chlorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 8b).[2,3] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.30-7.29 (m, 4H), 4.89 (s, 2H), 1.27 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.3.



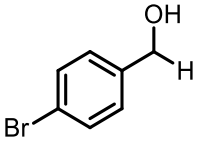
(4–Chlorophenyl)methanol (8c).[2,7] Following General procedure A. White solid. Yield: 87% (126 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.29-7.24 (m, 4H), 4.59 (s, 2H), 2.42 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 139.3, 133.3, 128.7, 128.3, 64.4.



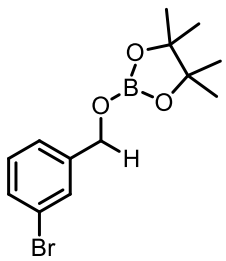
2-((4-Bromobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 9b).[2,6] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.46 (d, *J* = 8 Hz, 2H), 7.23 (d, *J* = 8 Hz, 2H), 4.87 (s, 2H), 1.27 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.3.



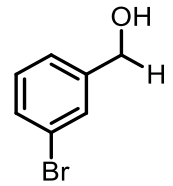
(4–Bromophenyl)methanol (9c).[2,5] Following General procedure A. White solid. Yield: 82% (154 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.44 (d, *J* = 8 Hz, 2H), 7.15 (m, 2H), 4.55 (s, 2H), 2.60 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 139.7, 131.6, 128.6**,** 121.4, 64.4.



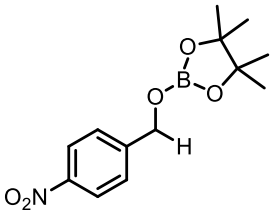
2-((3-Bromobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 10b).[2,6] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.54 (br, 1H), 7.42-7.27 (m, 3H), 4.91 (s, 2H), 1.29 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.3.



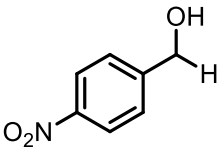
(3-Bromophenyl)methanol (10c).[2,7] Following General procedure A. Colourless oil. Yield: 78% (146 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.45 (br, 1H), 7.38-7.37 (m, 1H), 7.20-7.06 (m, 2H), 4.55 (s, 2H), 2.94 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 143.1, 130.7, 130.5, 129.9, 125.4, 122.6, 64.2.



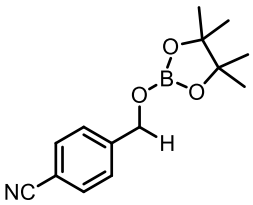
4,4,5,5-Tetramethyl-2-((4-nitrobenzyl)oxy)-1,3,2-dioxaborolane (Table 2, 11b).[2,3] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.20 (d, *J* = 8 Hz, 2H), 7.51 (d, *J* = 8 Hz, 2H), 5.03 (s, 2H), 1.28 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.0.



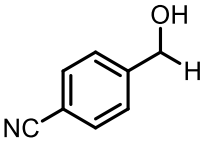
(4-Nitrophenyl)methanol (11c).[2,9] Following General procedure B. Brown crystalline solid. Yield: 70% (107 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.19 (d, *J* = 8 Hz, 2H), 7.51 (d, *J* = 8 Hz, 2H), 4.82 (s, 2H), 2.36 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.3, 147.3, 127.1, 123.8, 64.0.



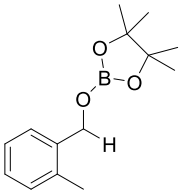
4-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzonitrile (Table 2, 12b).[2,6] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.62 (d, *J* = 8 Hz, 2H), 7.44 (d, *J* = 8 Hz, 2H), 4.97 (s, 2H), 1.26 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.3.



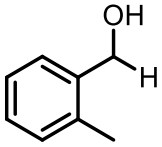
4-(Hydroxymethyl)benzonitrile (12c).[2,7] Following General procedure B. White crystalline solid. Yield: 80% (105 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.56 (d, *J* = 8 Hz, 2H), 7.42 (d, *J* = 8 Hz, 2H), 4.69 (s, 2H), 3.58 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 146.6, 132.2, 127.0, 118.9, 110.6, 63.8.



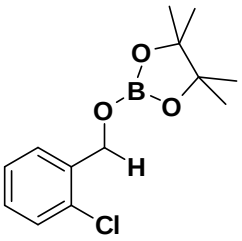
4,4,5,5-Tetramethyl-2-((2-methylbenzyl)oxy)-1,3,2-dioxaborolane (Table 2, 13b).[2,10] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.45 (br, 1H), 7.25-7.21 (m, 3H), 5.0 (s, 2H), 2.38 (s, 3H), 1.33 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.3.



***o*-Tolylmethanol (13c)**.[2,11] Following General procedure A. Colourless oil. Yield: 84% (103 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.31-7.30 (m, 1H), 7.19-7.15 (m, 3H), 4.58 (s, 2H), 2.58 (br, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 138.8, 136.0, 130.3, 127.7, 127.5, 126.0, 63.2, 18.6.

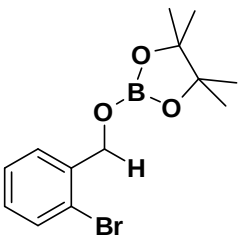


4,4,5,5-Tetramethyl-2-((2-Chlorobenzyl)oxy)-1,3,2-dioxaborolane (Table 2, 14b).[2,10]



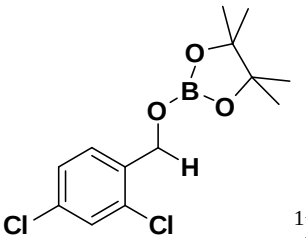
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.52 (br, 1H), 7.37-7.21 (m, 3H), 5.03 (s, 2H), 1.28 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.3.

4,4,5,5-Tetramethyl-2-((2-Bromobenzyl)oxy)-1,3,2-dioxaborolane (Table 2, 15b).[12]



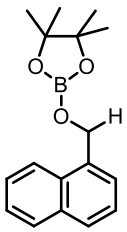
^{1}H NMR 400 MHz, $CDCl_3$, ppm): δ 7.51 (br, 1H), 7.34-7.12 (m, 3H), 4.98 (s, 2H), 1.28 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.4.

4,4,5,5-Tetramethyl-2-((2,4-Dichlorobenzyl)oxy)-1,3,2-dioxaborolane (Table 2, 16b).[13]



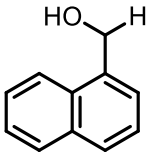
^{1}H NMR 400 MHz, $CDCl_3$, ppm): δ 7.47-7.35 (br, 1H), 7.35-7.34 (m, 1H), 7.28-7.24 (m, 1H), 4.97 (s, 2H), 1.28 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.3. ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 137.0, 135.5, 133.6, 132.9, 128.9, 83.3, 63.6, 24.8.

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

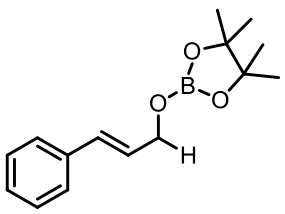


^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.12-8.10 (m, 1H), 7.93-7.90 (m, 1H), 7.86-7.64 (m, 1H), 7.57-7.49 (m, 4H), 5.47 (s, 2H), 1.34 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.4.

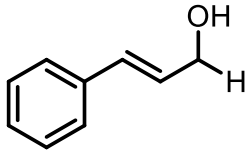
Naphthalen-2-ylmethanol (17c).[2,14] Following General procedure A. Colourless oil. Yield: 88% (140 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.12-8.10 (m, 1H), 7.91-7.89 (m, 1H), 7.84-7.82 (m, 1H), 7.57-7.44 (m, 4H), 5.11 (s, 2H), 2.19 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 136.3, 133.8, 131.2, 128.7, 128.6, 126.4, 125.9, 125.4, 125.3, 123.7, 63.6.



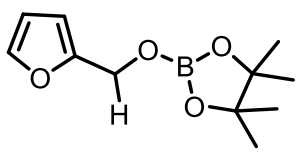
2-(Cinnamyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 18b).[2,6] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.46-7.13 (m, 5H), 6.64 (d, *J* = 16 Hz, 1H), 6.31 (dt, *J* = 16, 6 Hz, 1H), 4.56 (d, *J* = 6 Hz, 2H), 1.30 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.2.



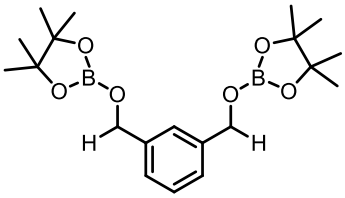
3-Phenyl-2-propene-1-ol (18c).[2,14] Following General procedure B. Colourless oil. Yield: 59% (80 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.35-7.34 (m, 2H), 7.29-7.27 (m, 2H), 7.23-7.20 (m, 1H), 6.57 (d, *J* = 16 Hz, 1H), 6.32 (dt, *J* = 16, 6 Hz, 1H), 4.27 (d, *J* = 6 Hz, 2H), 2.41 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 136.7, 131.1, 128.7, 128.5, 127.7, 126.5, 63.5.



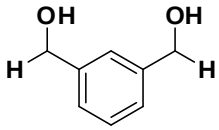
2-(Furan-2-ylmethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 19b).[2,6] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.37 (br, 1H), 6.31 (br, 2H), 4.82 (s, 2H), 1.27 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 152.7, 142.5, 110.6, 108.4, 83.2, 59.2, 24.4. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.3.



1,3-*Bis*(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzene (Table2, 20b).[2,3] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.36-7.30 (m, 4H), 4.95 (s, 4H), 1.29 (s, 24H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.0.

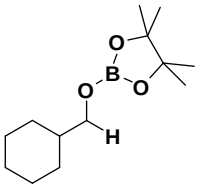


1,3-Phenylenedimethanol (Table 2, 20c).[2,14]



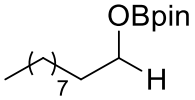
Following General procedure A. A colorless oil. Yield: 73% (100 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38-7.36 (m, 2H), 7.31-7.28 (m, 2H), 4.68 (s, 4H), 2.53 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 141.2, 128.7, 126.2, 125.6, 64.9.

2-(Cyclohexyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 21b).[12]

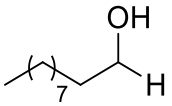


^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.63 (d, *J* = 7 Hz, 2H), 1.73-1.47 (m, 6H), 1.24 (s, 12H), 1.18-1.08 (m, 3H), 0.97-0.89 (m, 2H) ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.3.

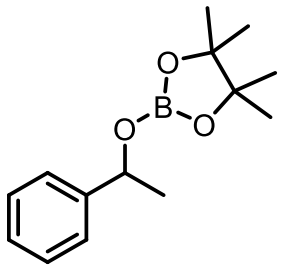
2-(Decyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 22b).[2,4] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.74 (t, *J* = 7 Hz, 2H), 1.62-1.53 (m, 2H), 1.26 (br, 26H), 0.87 (t, *J* = 7 Hz, 3H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.2.



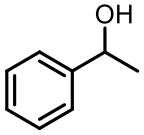
Decan-1-ol (22c).[2,4] Following General procedure B. Colorless oil. Yield: 80% (127 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.59 (t, *J* = 6 Hz, 2H), 2.73 (br, 1H), 1.55-1.52 (m, 2H), 1.26-1.24 (m, 14H), 0.87 (t, *J* = 6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 62.8, 32.7, 31.9, 29.7, 29.6, 29.5, 29.4, 25.8, 22.7, 14.1.



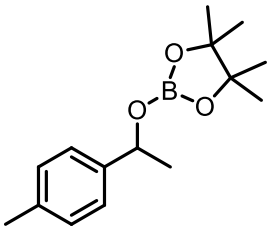
4,4,5,5-Tetramethyl-2-(1-phenylethoxy)-1,3,2-dioxaborolane (Table 3, 23b).[2,3] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.41-7.27 (m, 5H), 5.28 (q, *J* = 6 Hz, 1H), 1.53 (d, *J* = 8 Hz, 3H), 1.28 (s, 6H), 1.25 (s, 6H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.1.



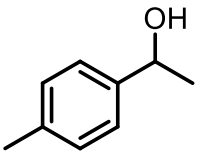
1-Phenylethanol (23c).[2,4] Following General procedure A. Colourless oil. Yield: 80% (91 mg) ^{1}H NMR (400 MHz, CDCl3): δ 7.40-7.35 (m, 4H), 7.32-7.28 (m, 1H), 4.90 (q, *J* = 6.5 Hz, 1H), 2.13 (br, 1H), 1.51 (d, *J* = 4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 128.5, 127.5, 125.5, 70.4, 25.2.



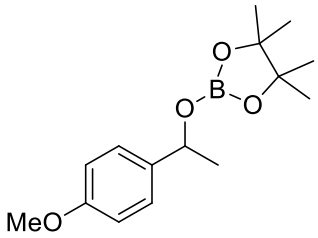
4,4,5,5-Tetramethyl-2-(1-(p-tolyl)ethoxy)-1,3,2-dioxaborolane (Table 3, 24b).[2,3] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.27 (d, *J* = 8 Hz, 2H), 7.16 (d, *J* = 8 Hz, 2H), 5.25 (q, *J* = 6 Hz, 1H), 2.36 (s, 3H), 1.51 (d, *J* = 8 Hz, 3H), 1.29 (s, 6H), 1.28 (s, 6H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.1.



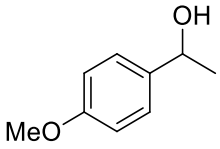
1-(*p*-Tolyl)ethanol (24c).[2,4] Following General procedure B. Colourless oil. Yield: 72% (96 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.29 (d, *J* = 6.4 Hz, 2H), 7.18 (d, *J* = 6.5 Hz, 2H), 4.88 (q, *J* = 6 Hz, 1H), 2.37 (s, 3H), 1.93 (s, 1H), 1.50 (d, *J* = 8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 143.0, 137.2, 129.2, 125.4, 70.3, 25.1, 21.2.



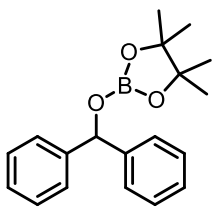
2-(1-(4-Methoxyphenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 25b).[2,3] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.32 (d, *J* = 8 Hz, 2H), 6.88 (d, *J* = 8 Hz, 2H), 5.24 (q, *J* = 6 Hz, 1H), 3.81 (s, 3H), 1.50 (d, *J* = 4 Hz, 3H), 1.26 (s, 6H), 1.23 (s, 6H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.3.



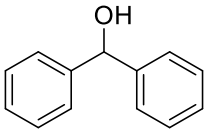
1-(4-Methoxyphenyl)ethanol (Table 3, 25c).[2] Following General procedure B. Colorless oil. Yield: 78% (118 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.33-7.31 (m, 2H), 6.93-6.90 (m, 2H), 4.85 (q, *J* = 6 Hz, 1H), 3.83 (s, 3H), 2.56 (br, 1H), 1.50 (d, *J* = 4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 158.9, 138.1, 126.7, 113.8, 69.8, 55.2, 25.0.



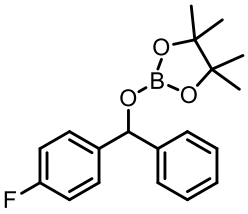
2-(Benzhydryloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 26b).[2,6] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.51-7.50 (m, 4H), 7.42-7.39 (m, 4H), 7.35-7.32 (m, 2H), 6.31 (s, 1H), 1.31(s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.4.



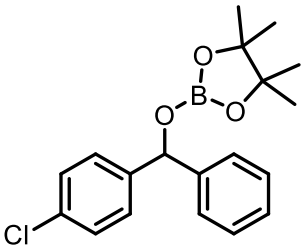
Diphenylmethanol (Table 3, 26c).[2] Following General procedure B. White solid. Yield: 89% (162 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.17-7.07 (m, 10H), 5.48 (s, 1H), 3.20 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 143.7, 128.3, 127.3, 126.5, 75.8.



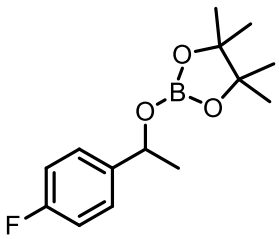
2-((4-Fluorophenyl)(phenyl)methoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 27b). [2,6] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.45-7.07 (m, 9H), 6.26 (s, 1H), 1.29 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.4.



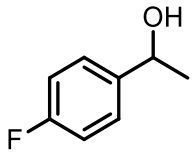
2-((4-Chlorophenyl)(phenyl)methoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 28b).[2,6] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.42-7.35 (m, 9H), 6.22 (s, 1H), 1.27 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.4. ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 142.6, 141.7, 133.1, 128.4, 128.4, 128.0, 127.5, 126.4, 62.2, 83.1, 24.6, 24.4.



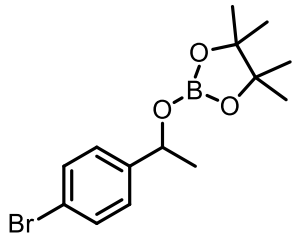
2-(1-(4-Fluorophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 29b).[2,14] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.35 (m, 2H), 7.03-6.99 (m, 2H), 5.24 (q, *J* = 6 Hz, 1H), 1.48 (d, *J* = 8 Hz, 3H), 1.26 (s, 6H), 1.23 (s, 6H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.1.



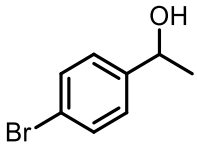
1-(4-Fluorophenyl)ethanol (29c).[2,14] Following General procedure A. Colorless oil. Yield: 75% (105 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.35-7.32 (m, 2H), 7.06-7.02 (m, 2H), 4.86 (q, *J* = 6 Hz, 1H), 2.35 (s, 1H), 1.48 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 162.2 (d, *J* = 245 Hz), 141.6, 127.1 (d, *J* = 8 Hz), 115.3 (d, *J* = 21 Hz), 69.8, 25.3.



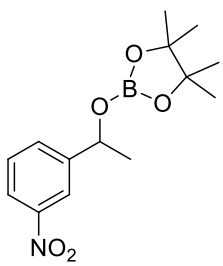
2-(1-(4-Bromophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 30b).[2,3] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.46 (m, 2H), 7.27 (m, 2H), 5.22 (br, 1H), 1.49 (br, 3H), 1.26 (s, 6H), 1.24 (s, 6H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.1.



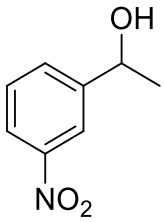
1-(4-Bromophenyl)ethanol (30c).[2,10] Following General procedure C. The 87% yield of **30c** was determined by ^{1}H NMR spectroscopy, using nitromethane as an internal standard. Colourless oil. Yield: 71% (142 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.42 (d, *J* = 8 Hz, 2H), 7.17 (d, *J* = 8 Hz, 2H), 4.77 (q, *J* = 6 Hz, 1H), 2.70 (br, 1H), 1.40 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 144.8, 131.5, 127.2, 121.13, 69.7, 25.2.



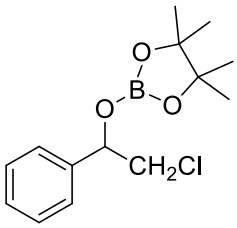
4,4,5,5-Tetramethyl-2-(1-(3-nitrophenyl)ethoxy)-1,3,2-dioxaborolane (Table 3, 31b).[2] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.22 (s, 1H), 8.10-8.08 (m, 1H), 7.70-7.68 (m, 1H), 7.51-7.49 (m, 1H), 5.32 (q, *J* = 6.4 Hz, 1H), 1.52 (d, *J* = 6.5 Hz, 3H), 1.24 (s, 6H), 1.21 (s, 6H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.4.



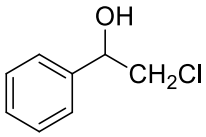
1-(3-Nitrophenyl)ethanol (31c).[2] Following General procedure B. Brown solid. Yield: 41% (67 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.22 (s, 1H), 8.09 (d, *J* = 8 Hz, 1H), 7.70 (d, *J* = 8 Hz, 1H), 7.51 (t, *J* = 8 Hz, 1H), 5.00 (q, *J* = 6.4 Hz, 1H), 2.80 (s, 1H), 1.52 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.3, 148.0, 131.7, 129.4, 122.3, 120.4, 69.3, 25.4.



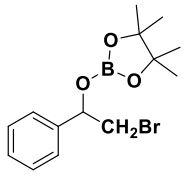
2-(2-Chloro-1-phenylethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 32b).[2,15] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.37-7.34 (m, 5H), 5.26 (m, 1H), 3.63 (m, 2H), 1.25 (s, 6H), 1.22 (s, 6H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.3.



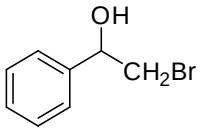
2-Chloro-1-phenylethan-1-ol (32c).[2,16] Following General procedure A. Colorless oil. Yield: 58% (89 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.39-7.34 (m, 5H), 4.91-4.88 (m, 1H), 3.74 (dd, *J* = 11.3, 3.6 Hz, 1H), 3.65 (dd, *J* = 11.3, 8.6 Hz, 1H), 2.82 (s, 1H).^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 140.0, 128.7, 128.5, 126.1, 74.1, 50.8.



2-(2-Bromo-1-phenylethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 33b).[2,15] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.40-7.32 (m, 5H), 5.33 (m, 1H), 3.56 (m, 2H), 1.28 (s, 6H), 1.25 (s, 6H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.4.

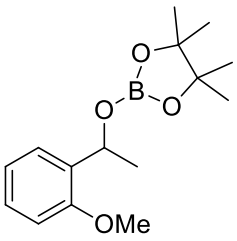


2-Bromo-1-phenylethan-1-ol (33c).[2,16]



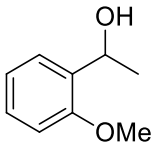
Following General procedure C. The 60% yield of **33c** was determined by ^{1}H NMR spectroscopy, using nitromethane as an internal standard. Colorless oil. Yield: 37% (57 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.39-7.34 (m, 5H), 4.94-4.90 (m, 1H), 3.64 (dd, *J* = 11.3, 3.6 Hz, 1H), 3.55 (dd, *J* = 11.3, 8.6 Hz, 1H), 2.78 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 140.4, 128.6, 128.4, 126.04, 73.7, 39.9.

2-(1-(2-Methoxyphenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 34b).[2]



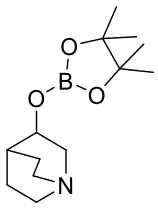
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.56 (d, *J* = 8 Hz, 1H), 7.26-7.22 (m, 1H), 7.00-6.97 (m, 1H), 6.86 (d, *J* = 8 Hz, 1H), 5.61 (q, *J* = 6.3 Hz, 1H), 3.84 (s, 3H), 1.48 (d, *J* = 6 Hz, 3H), 1.28 (s, 6H), 1.26 (s, 6H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.3.

1-(2-Methoxyphenyl)ethanol (34c).[2,17] Following General procedure C. The 59% yield of

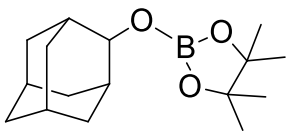


34c was determined by ^{1}H NMR spectroscopy, using nitromethane as an internal standard. Colorless oil. Yield: 56% (84 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.43-7.41 (m, 1H), 7.33-7.29 (m, 1H), 7.05-7.01 (m, 1H), 7.01-6.92 (m, 1H), 5.17 (q, *J* = 6 Hz, 1H), 3.90 (s, 3H), 3.10 (s, 1H), 1.56 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 156.4, 133.5, 128.1, 126.02, 120.7, 110.3, 66.1, 55.2, 22.9.

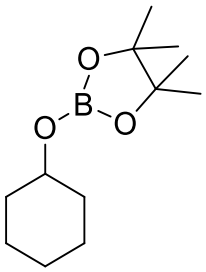
3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-2-yloxy)quinuclidine (Table 3, 35b).[18] ^{1}H NMR: δ 3.72 (br, 1H), 2.91-2.62 (m, 6H), 1.96-1.30 (m, 5H), 1.23 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.0.



2-(Adamantan-2-yloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 36b).[18] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.19 (m, 1H), 2.13-1.45 (m, 14H), 1.25 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 21.9. ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 81.2, 71.7, 48.1, 36.5, 35.2, 25.7, 23.5.

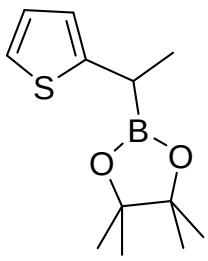


2-(Cyclohexyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 37b).[18] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.97 (m, 1H), 1.88-1.31 (m, 10H), 1.24 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 21.8. ^{13}C NMR (100 MHz, $CDCl_3$): δ 82.4, 72.6, 34.2, 25.4, 24.5, 23.8.



2-(Thiophene-2-yloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 38b).[12]

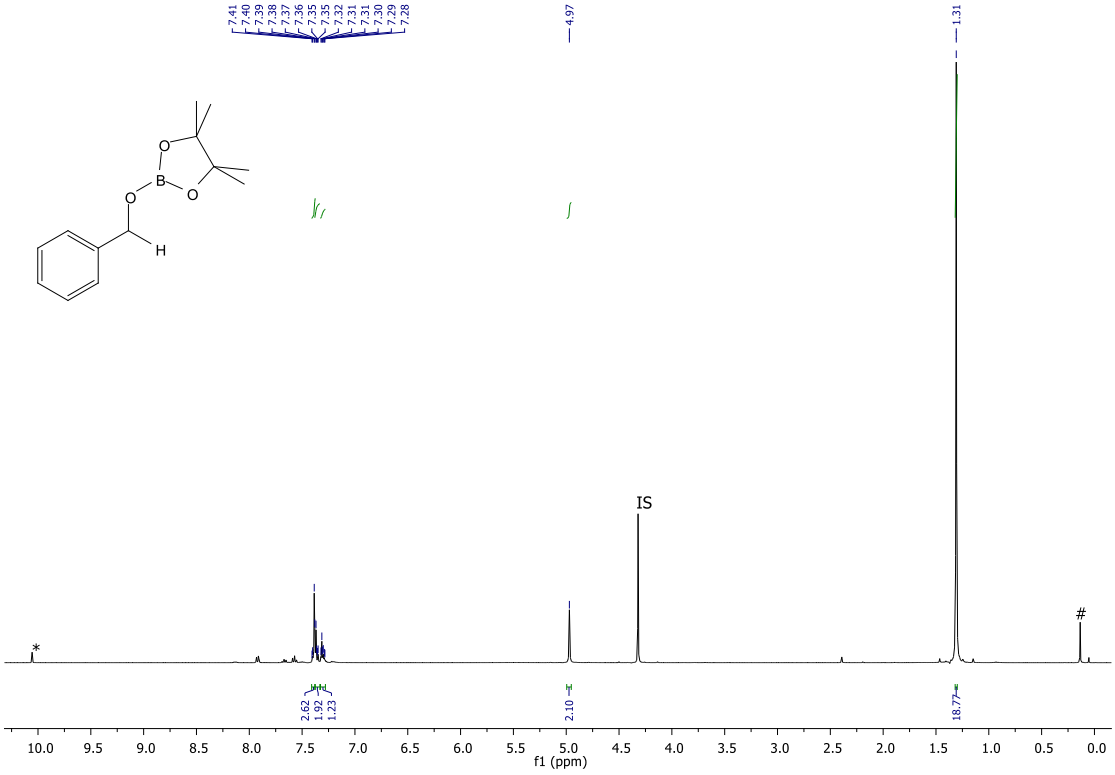
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.37 (br, 1H), 7.22-6.98 (br, 2H), 5.51 (br, 1H), 1.62 (br, 3H), 1.27 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 152.7, 142.5, 110.6, 108.4, 83.2, 59.2, 24.4. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.1. ^{13}C NMR (100MHz, $CDCl_3$, ppm): 148.2, 126.5, 124.2, 123.3, 82.9, 68.7, 25.2, 24.5.



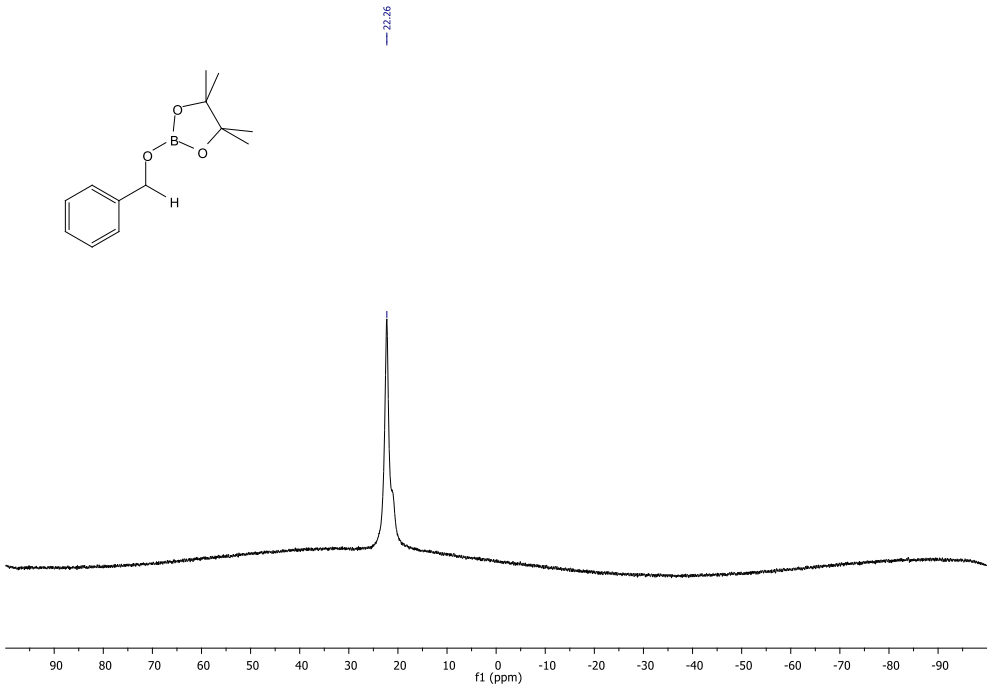
IV. NMR Spectra of Hydroboration Products and Related Alcohols

***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 (#). In the ^{11}B NMR spectra of few substrates, aside from the signal for borate ester (δ = 22 ppm), a broad signal corresponded to B_2pin_3, pinBOBpin, and/or HOBpin, was observed at δ = 21 ppm (overlapped with borate ester signal).[19,20]

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

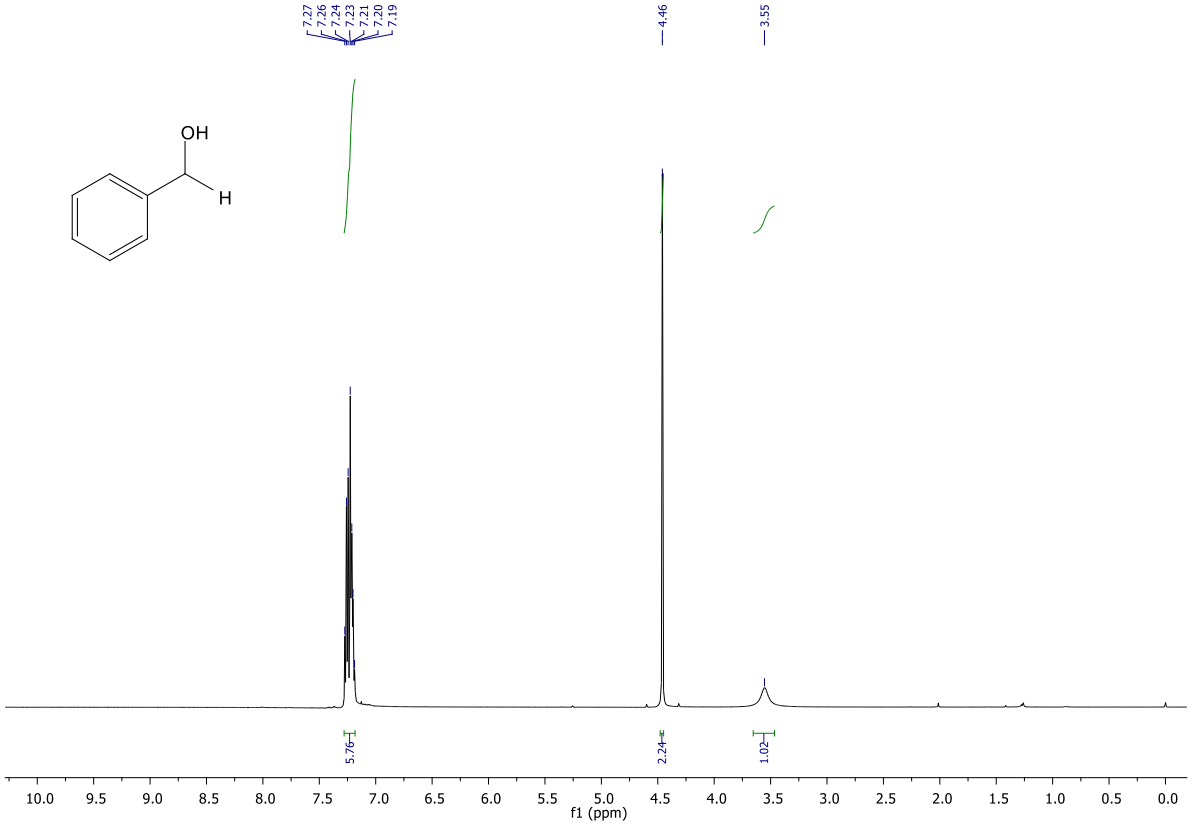


^{1}H NMR of **1b** (400 MHz, $CDCl_3$)

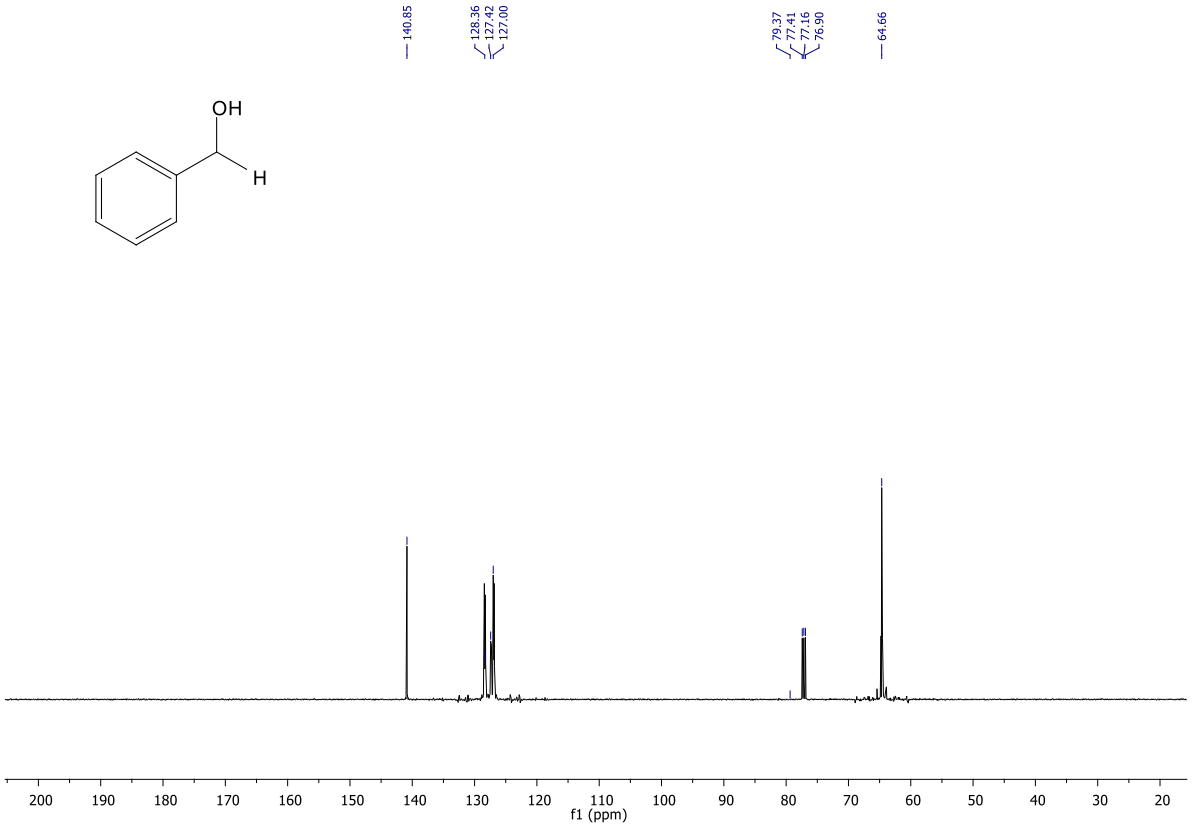


^{11}B NMR of **1b** (128 MHz, $CDCl_3$)

Phenylmethanol (**1c**).[2,4]

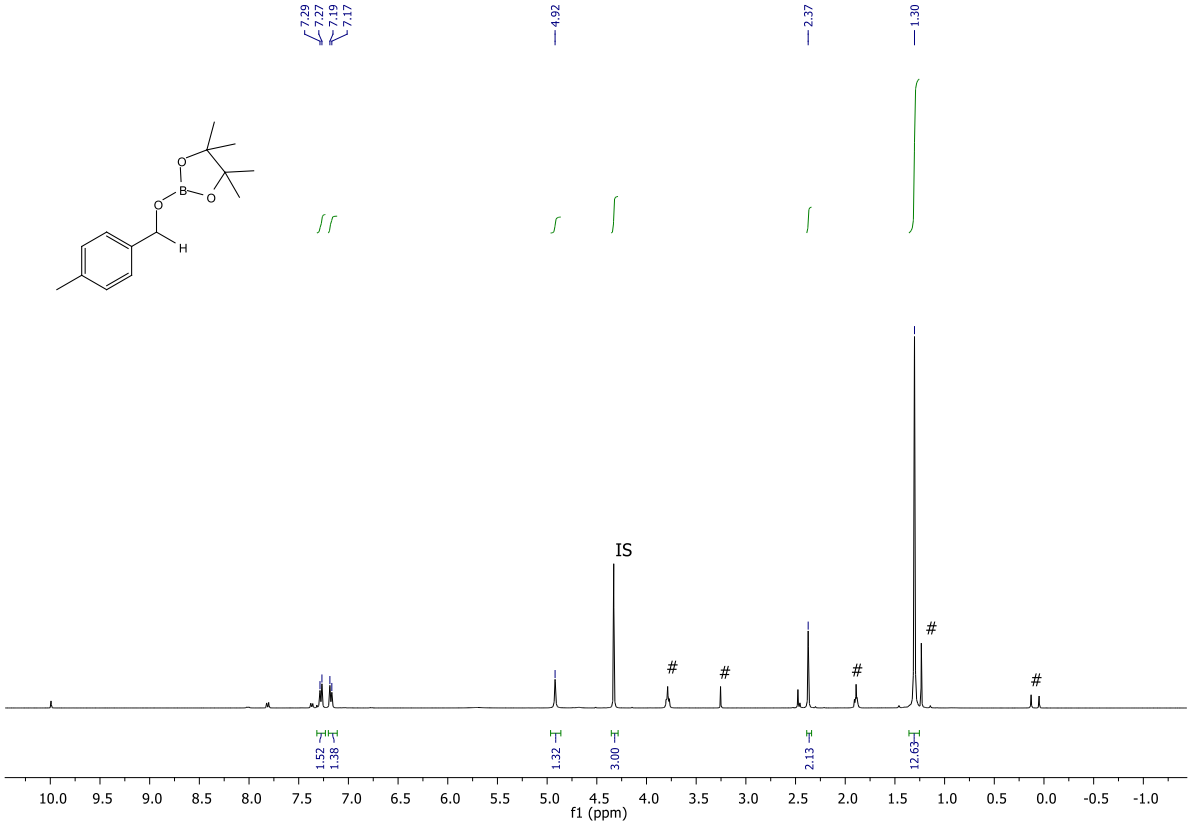


^{1}H NMR of **1c** (400 MHz, $CDCl_3$)

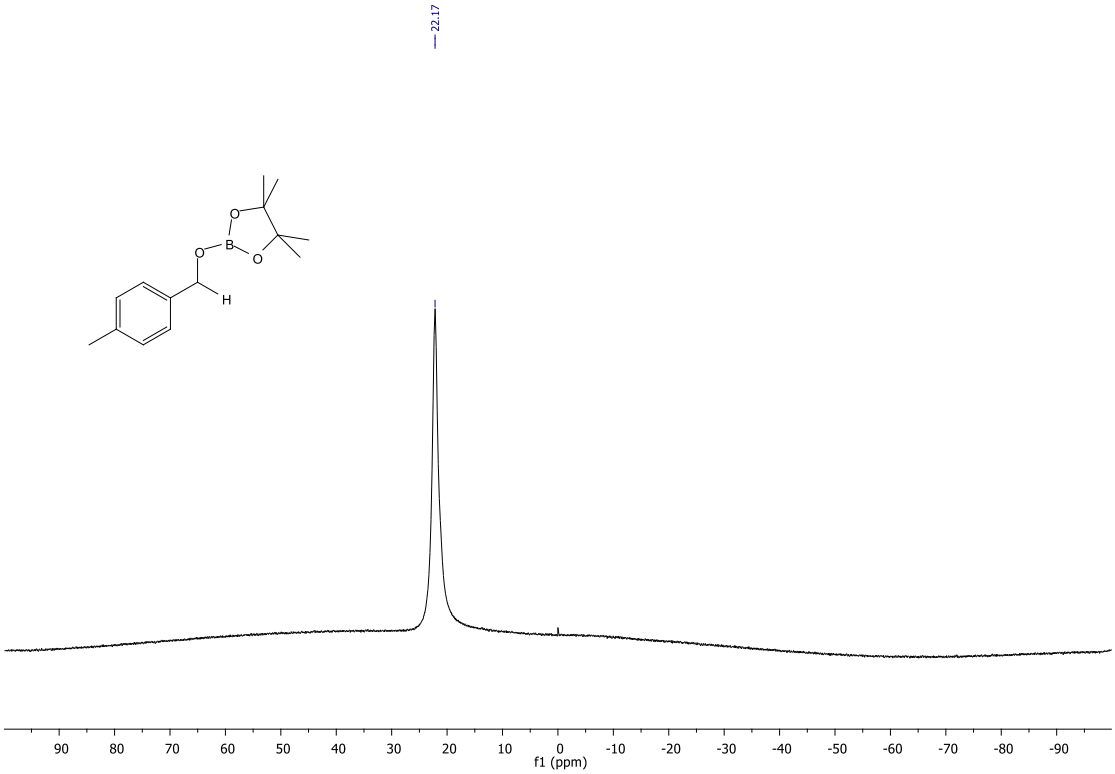


^{13}C NMR of **1c** (100 MHz, $CDCl_3$)

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

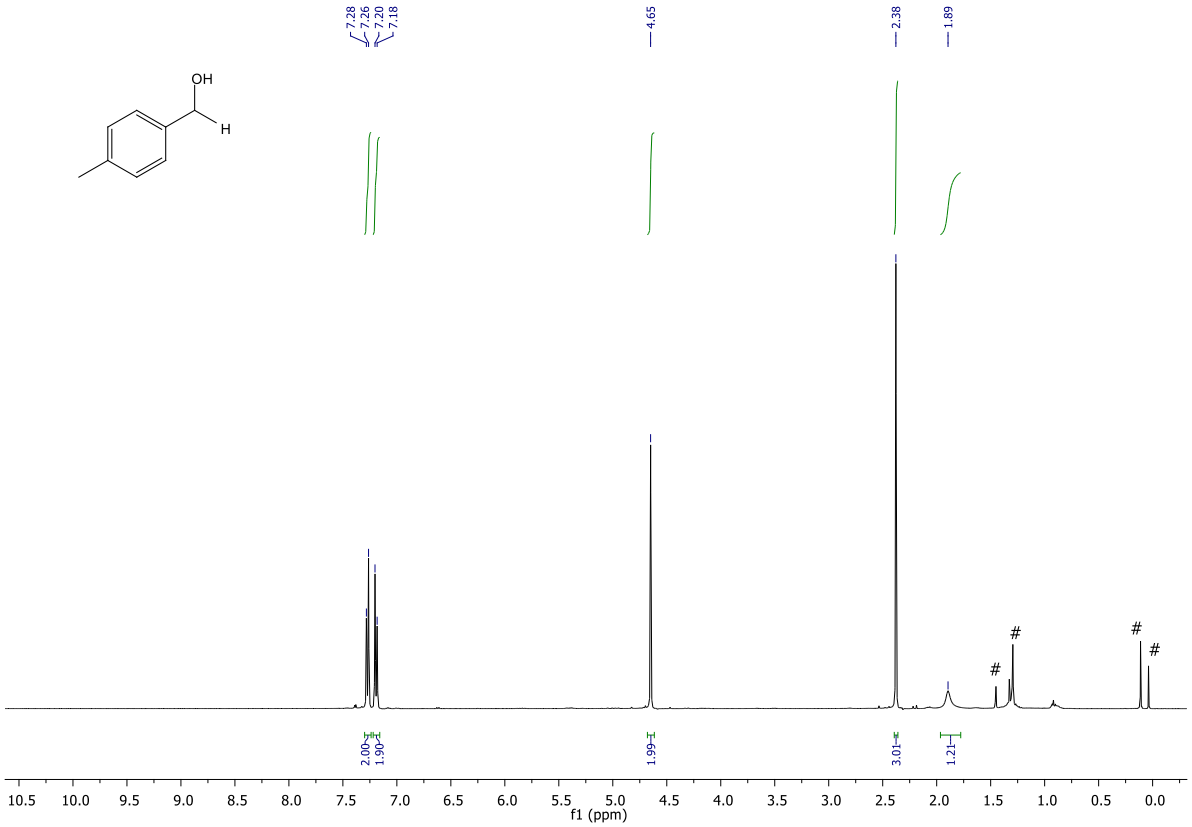


^{1}H NMR of **2b** (400 MHz, $CDCl_3$)

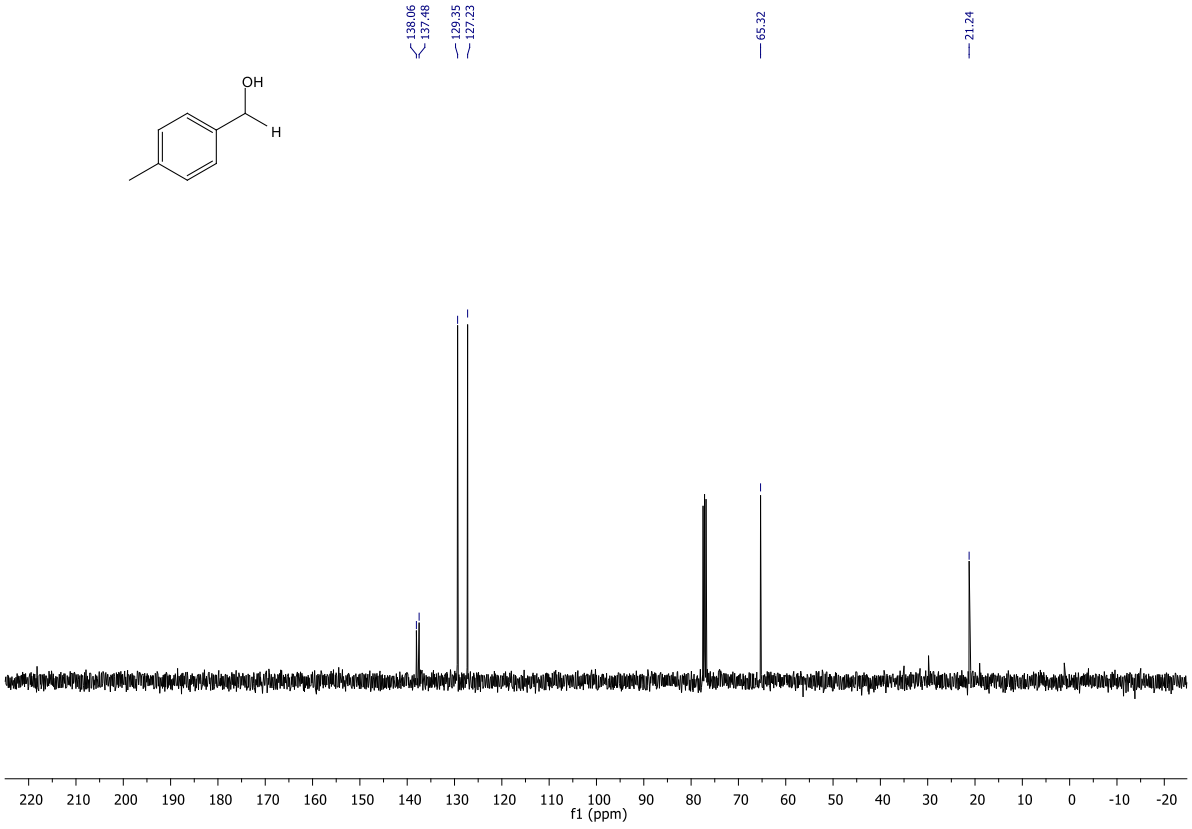


^{11}B NMR of **2b** (128 MHz, $CDCl_3$)

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

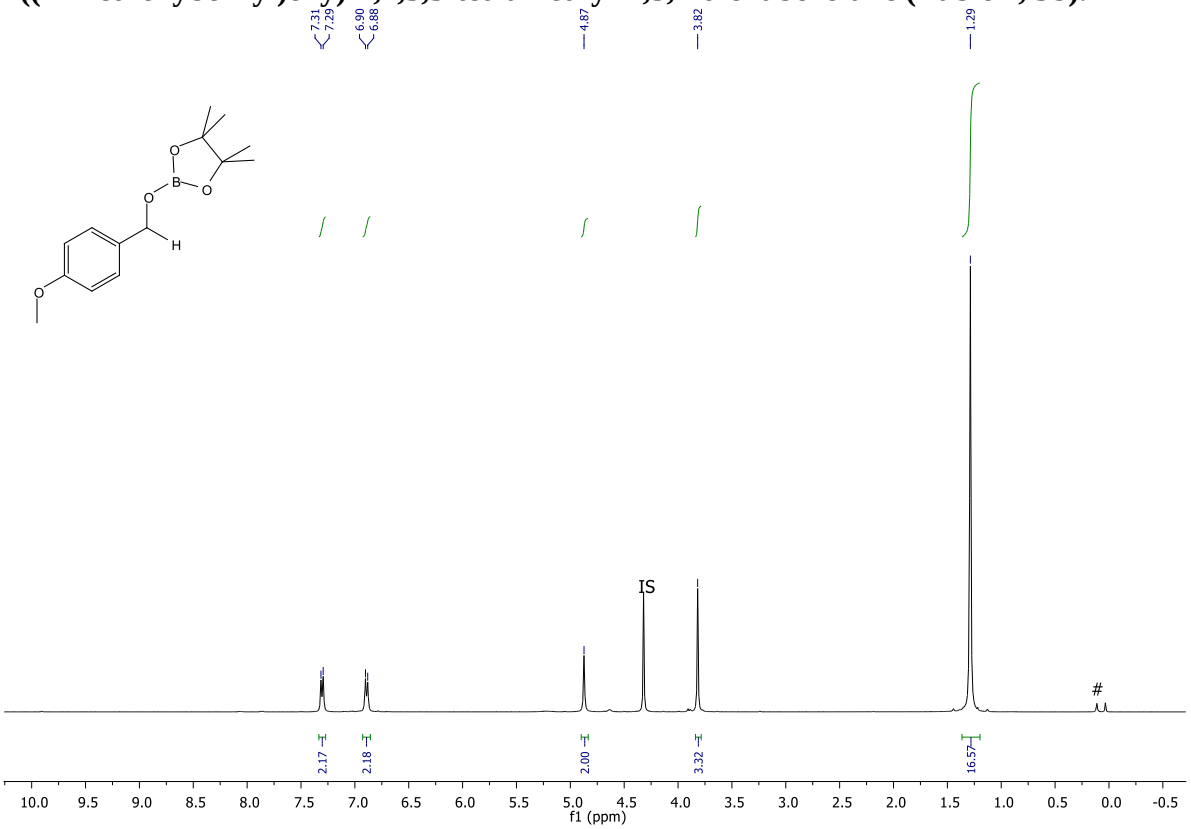


^{1}H NMR of **2c** (400 MHz, $CDCl_3$)

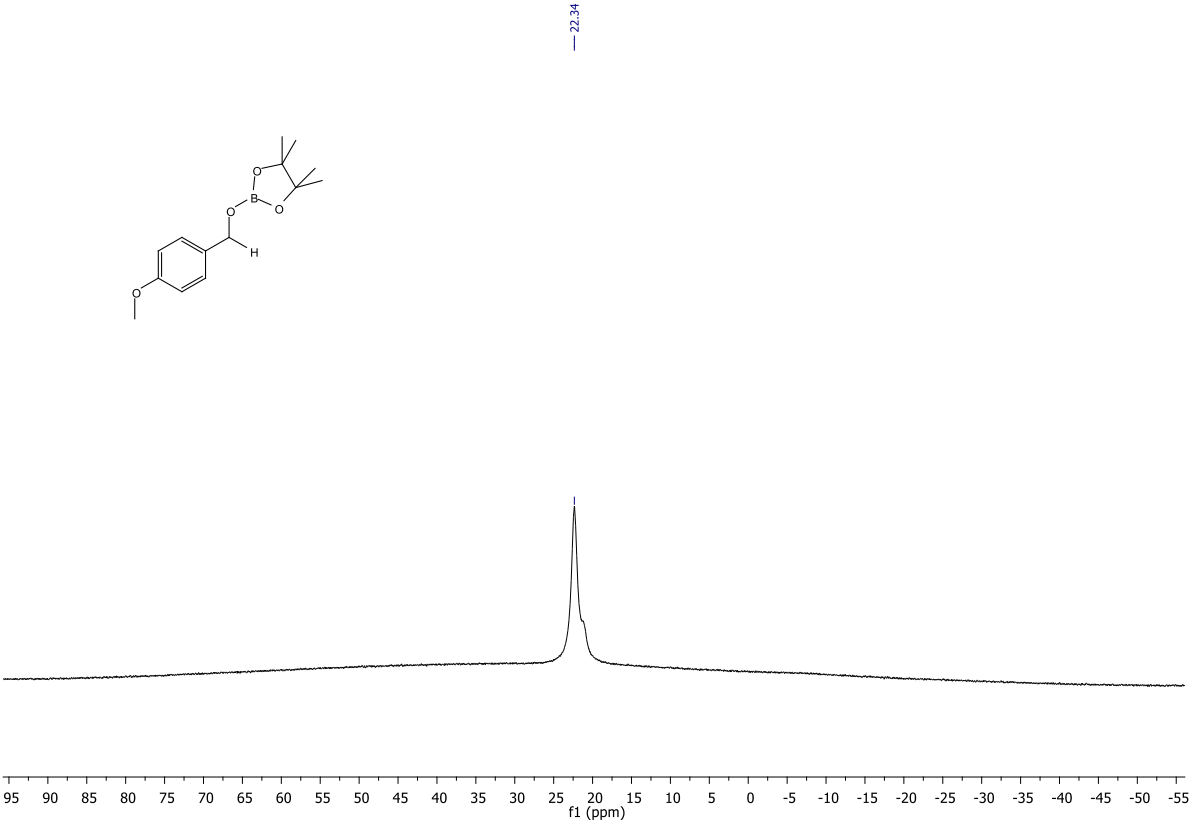


^{13}C NMR of **2c** (100 MHz, $CDCl_3$)

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

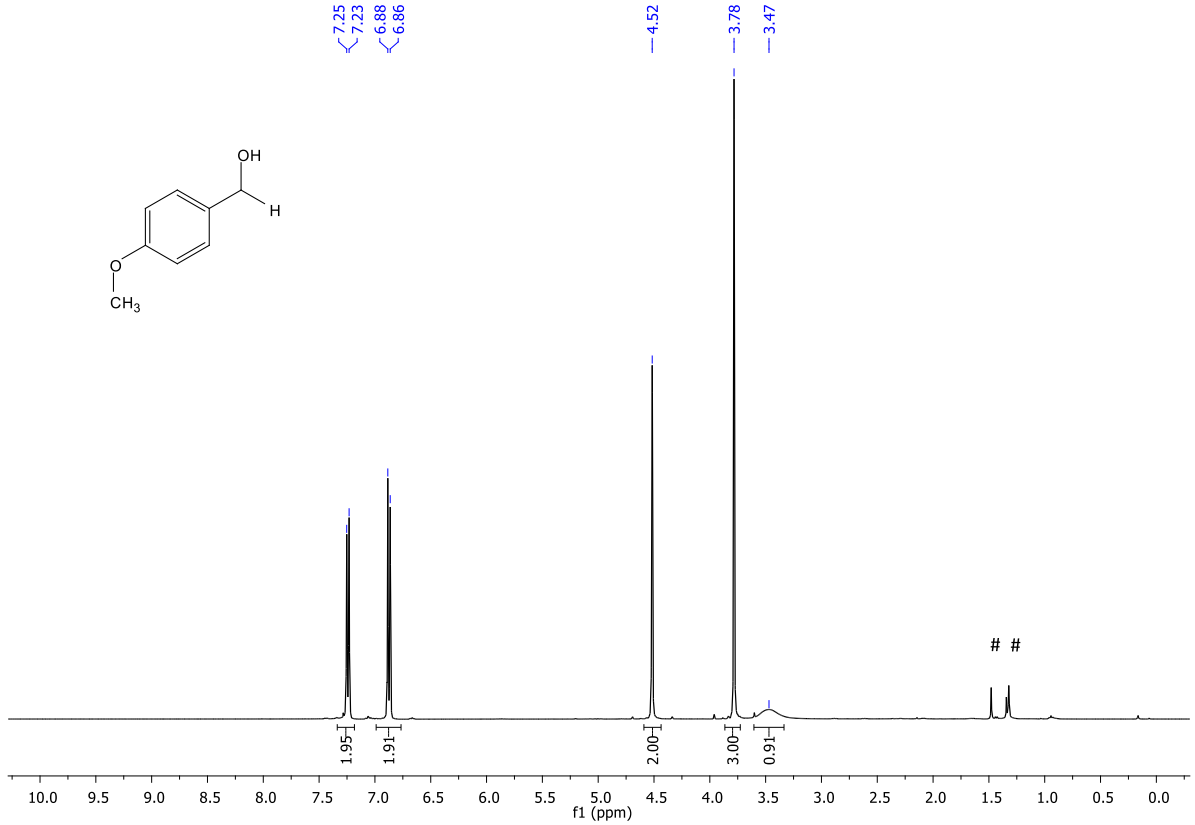


^{1}H NMR of **3b** (400 MHz, $CDCl_3$)

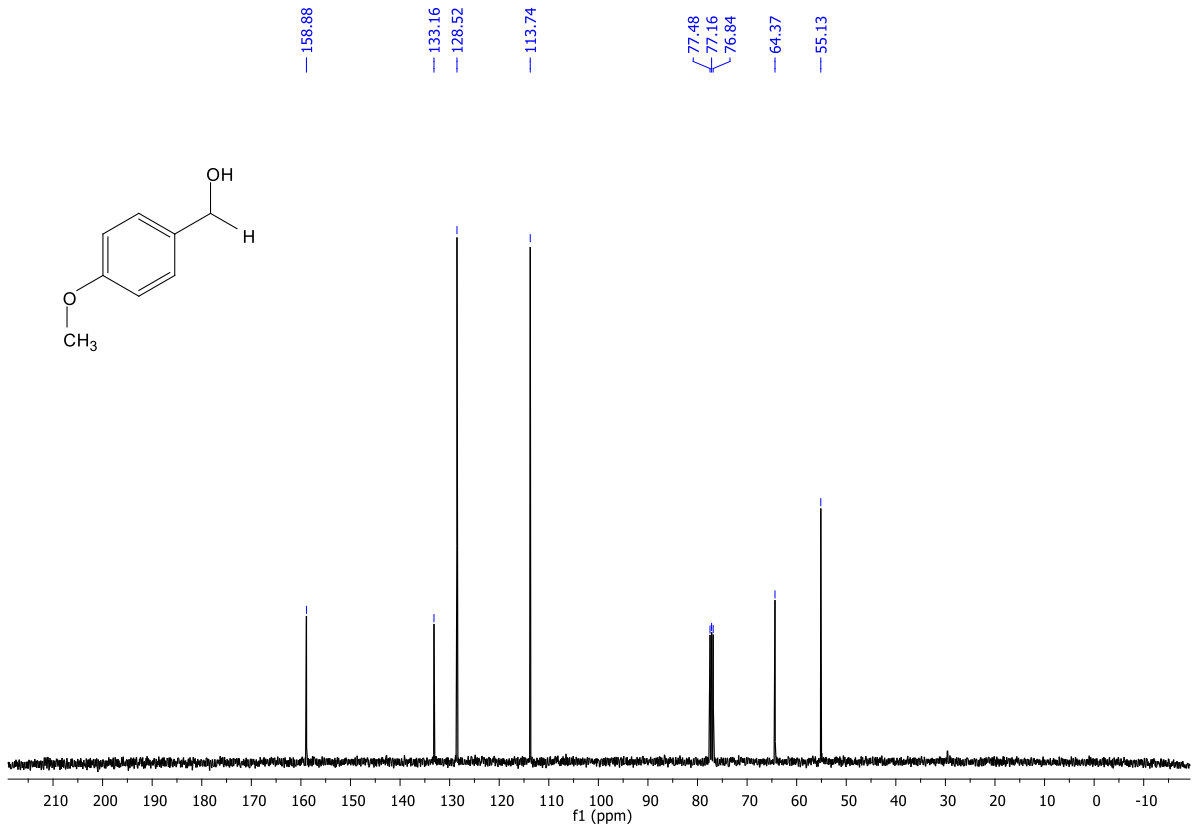


^{11}B NMR of **3b** (128 MHz, $CDCl_3$)

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

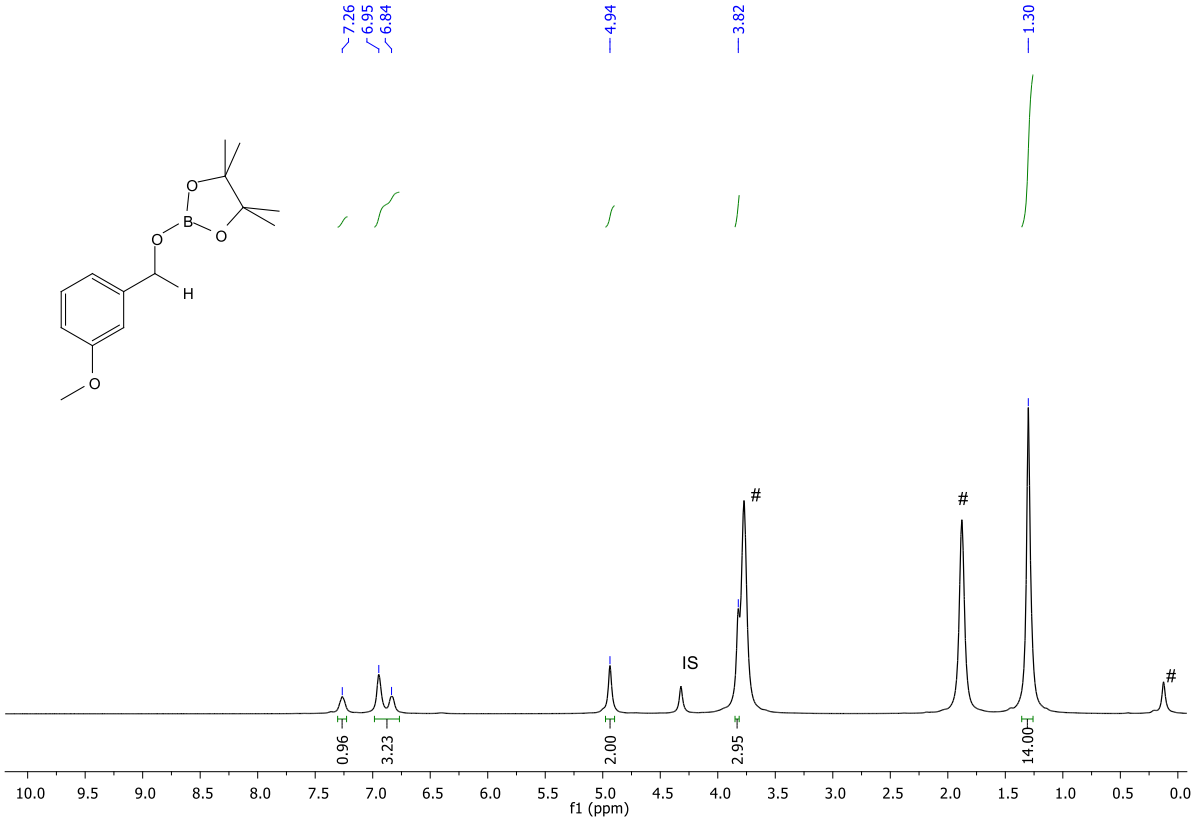


^{1}H NMR of **3c** (400 MHz, $CDCl_3$)

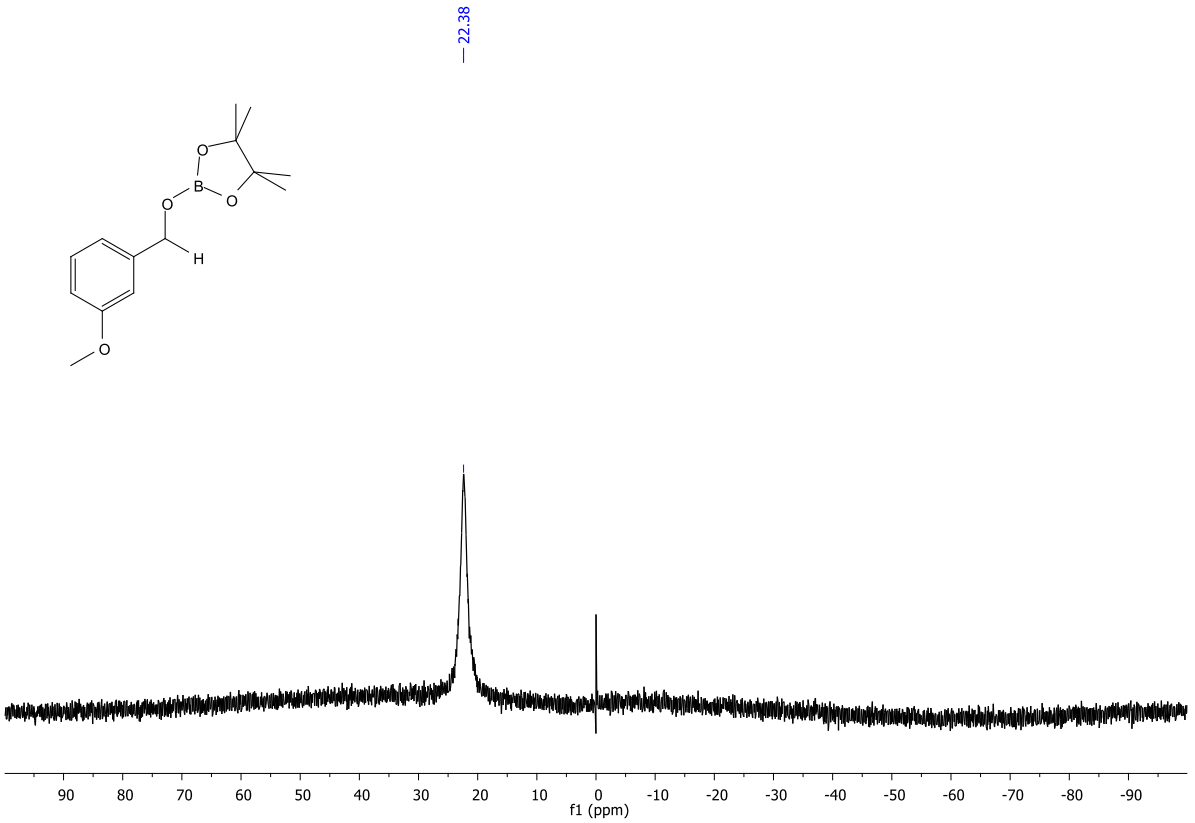


^{13}C NMR of **3c** (100 MHz, $CDCl_3$)

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

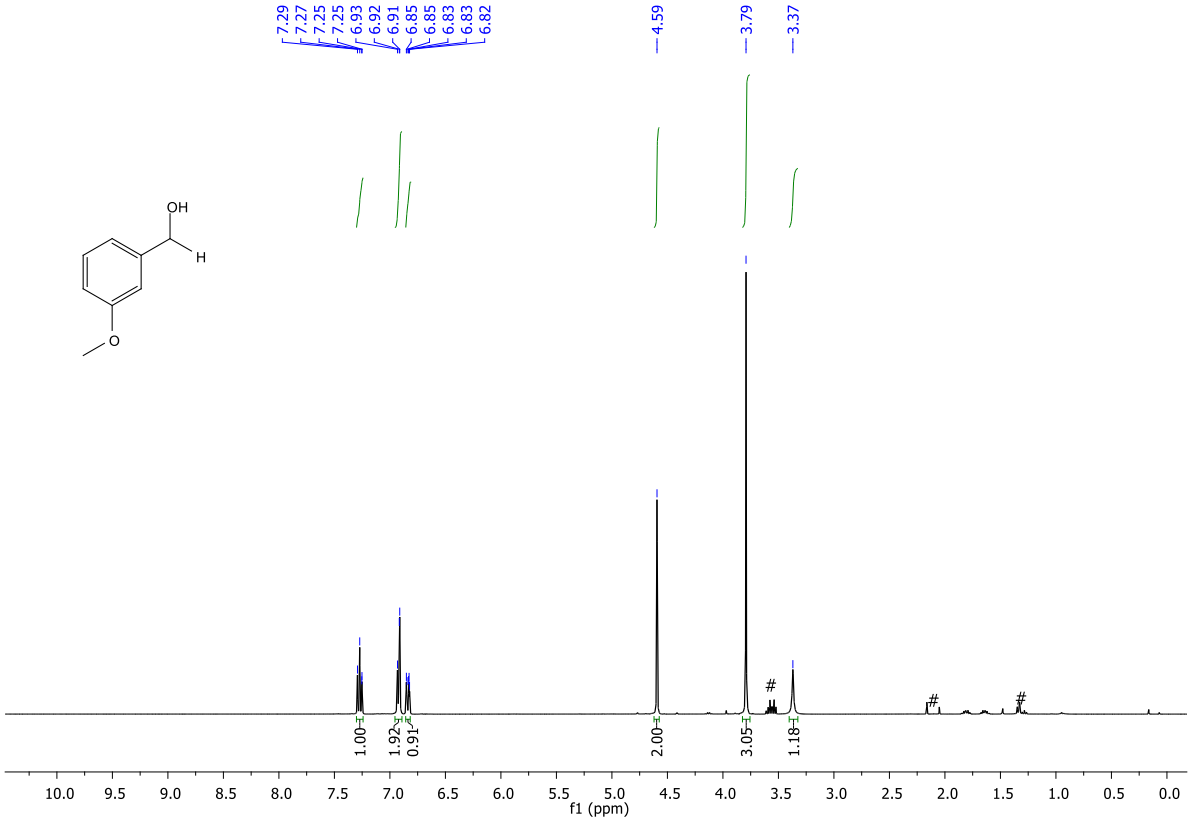


^{1}H NMR of **4b** (400 MHz, $CDCl_3$)

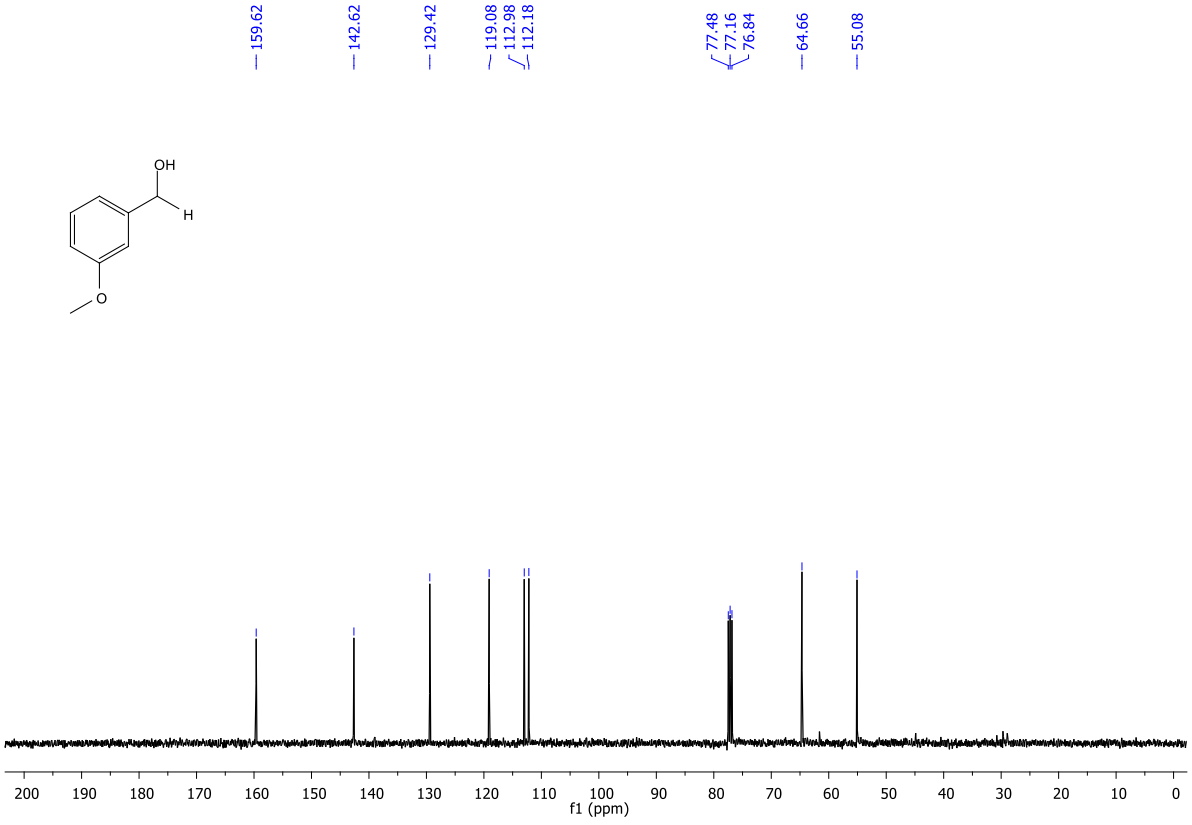


^{11}B NMR of **4b** (128 MHz, $CDCl_3$)

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

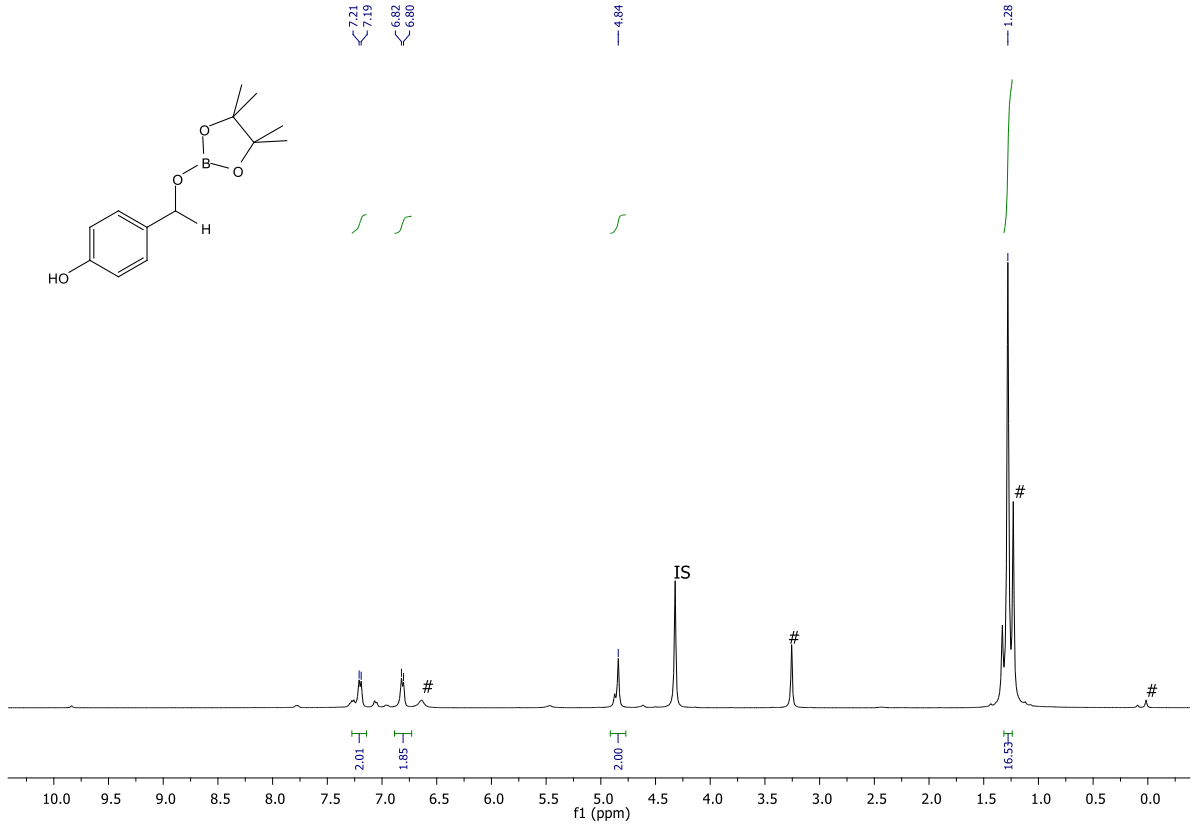


^{1}H NMR of **4c** (400 MHz, $CDCl_3$)

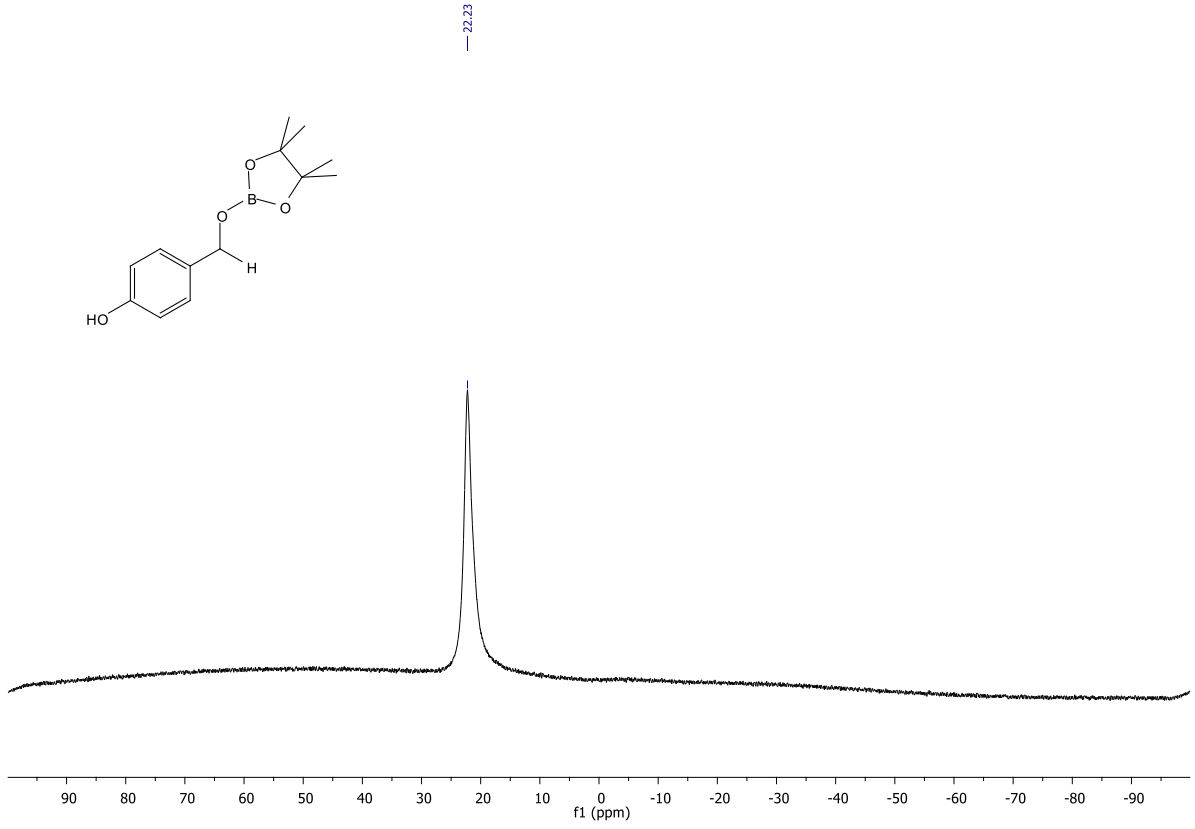


^{13}C NMR of **4c** (100 MHz, $CDCl_3$)

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

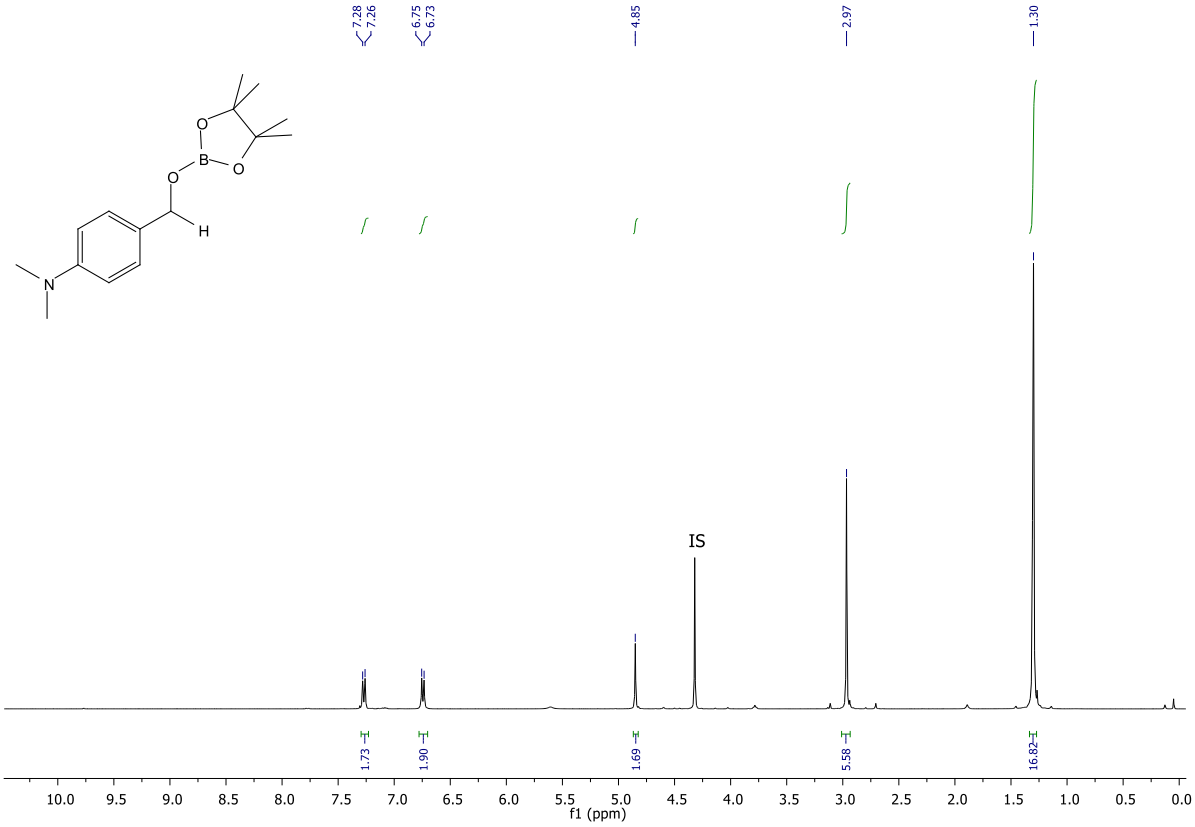


^{1}H NMR of **5b** (400 MHz, $CDCl_3$)

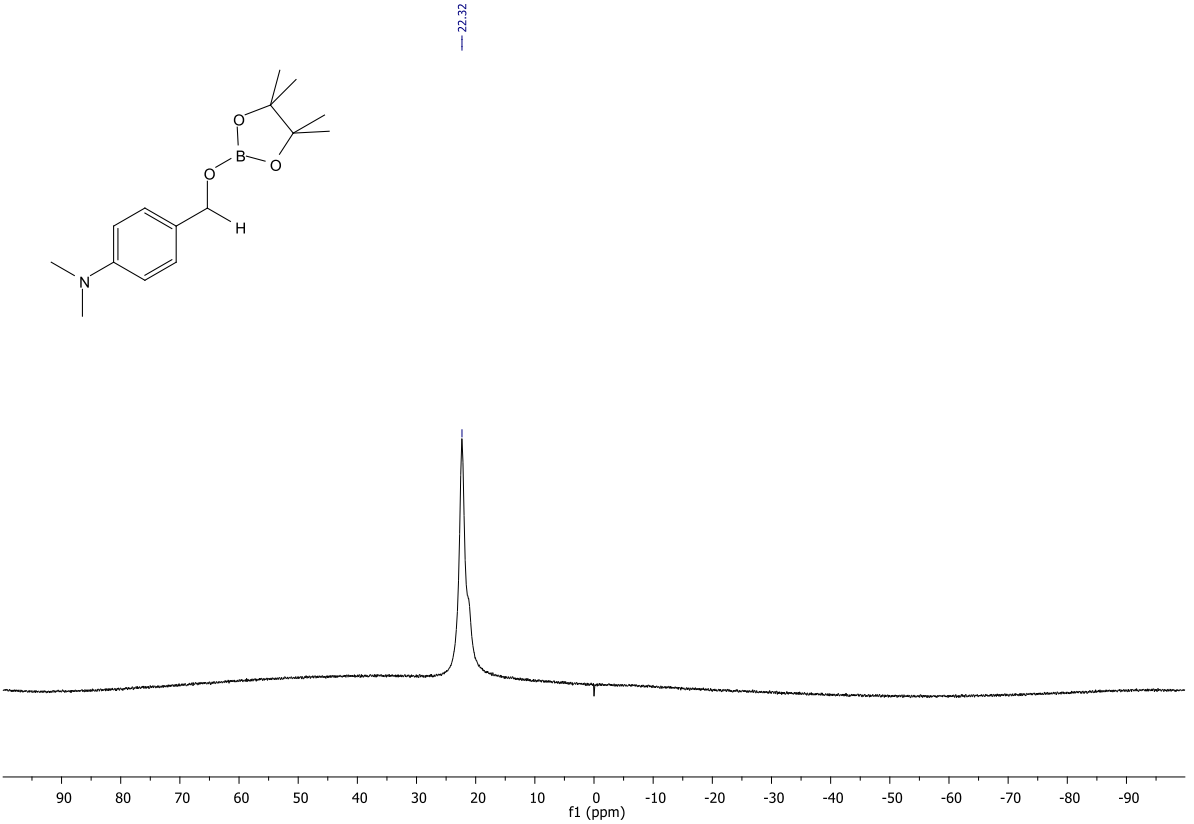


^{11}B NMR of **5b** (128 MHz, $CDCl_3$)

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

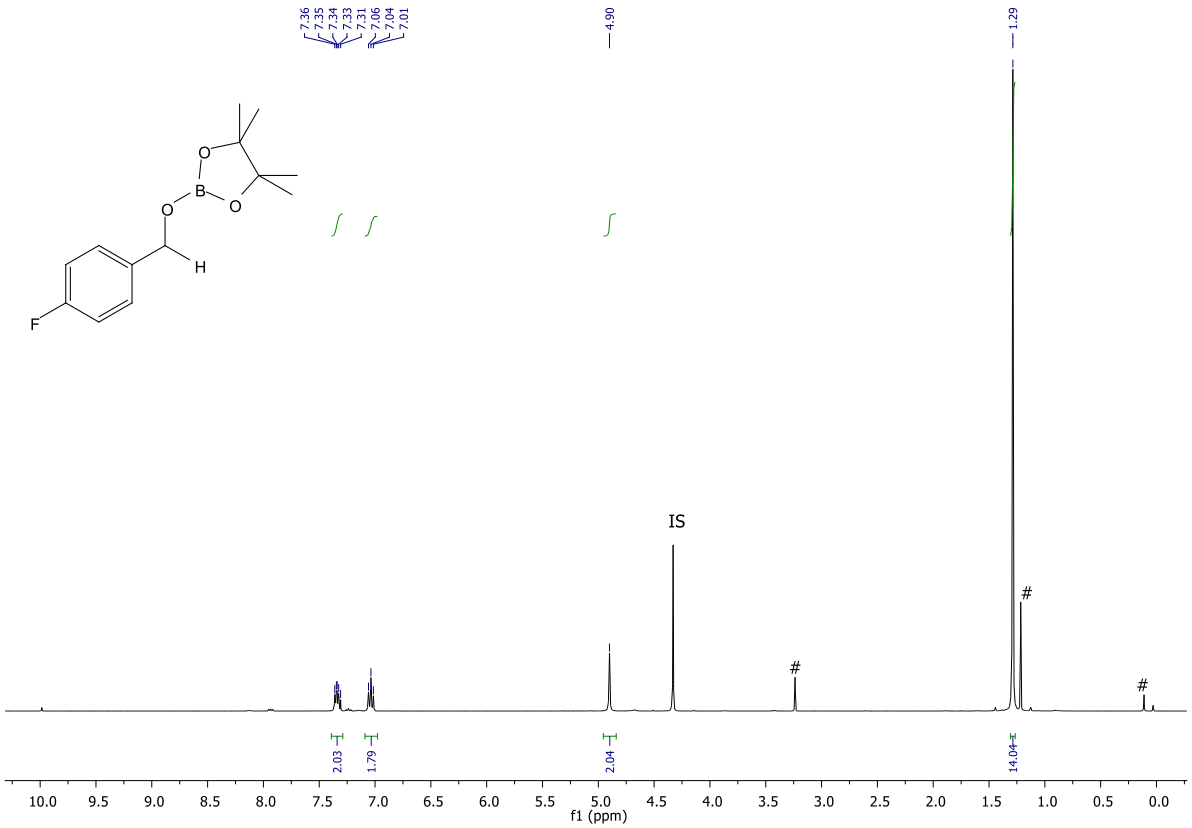


^{1}H NMR of **6b** (400 MHz, $CDCl_3$)

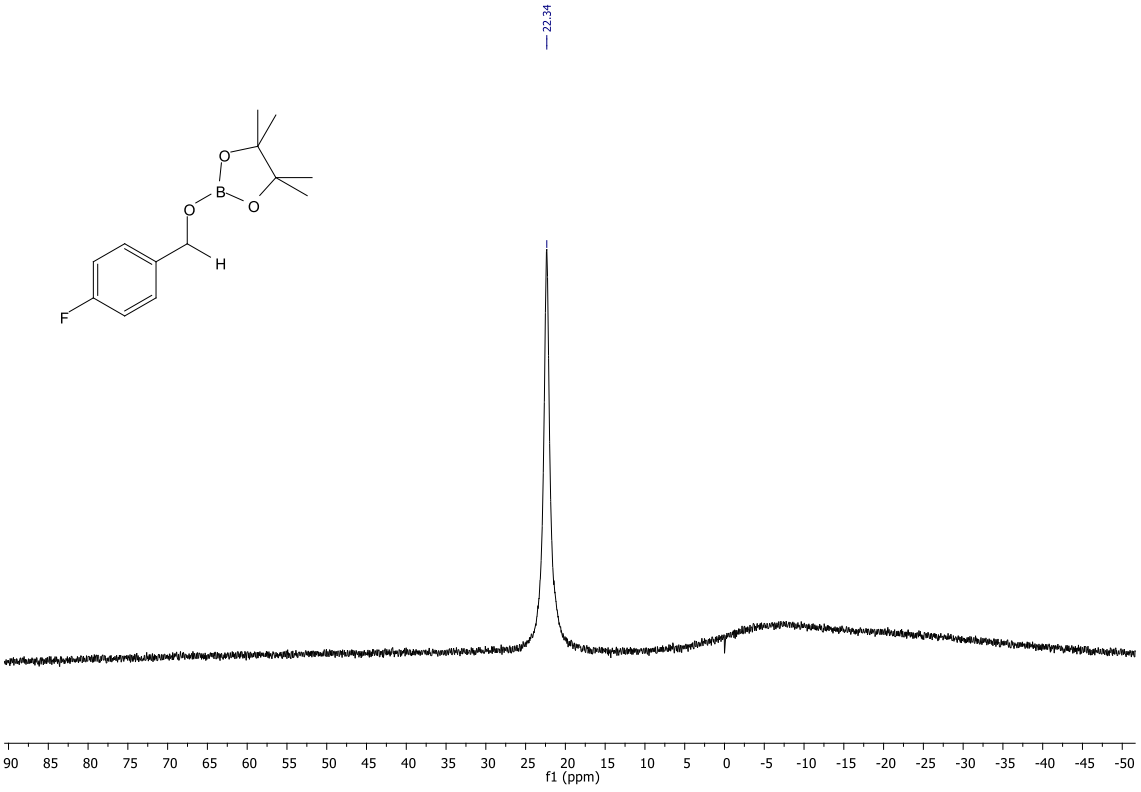


^{11}B NMR of **6b** (128 MHz, $CDCl_3$)

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

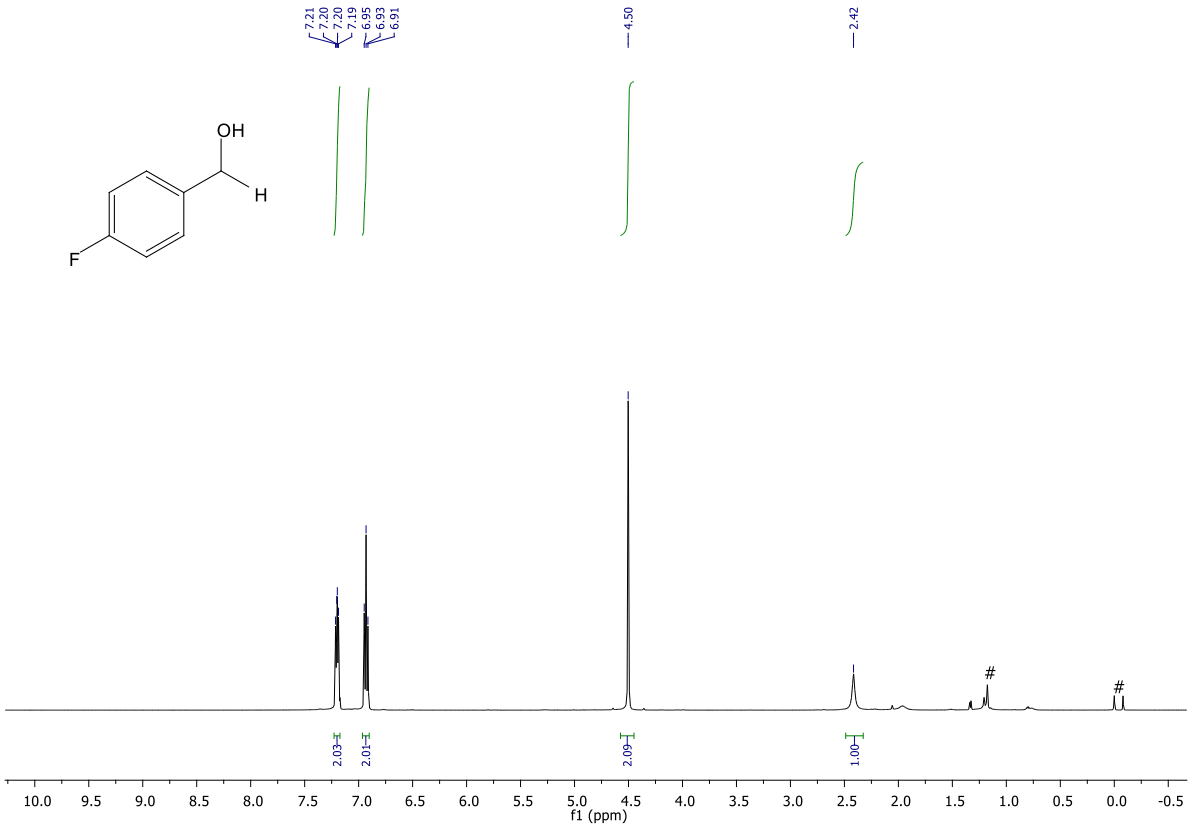


^{1}H NMR of **7b** (400 MHz, $CDCl_3$)

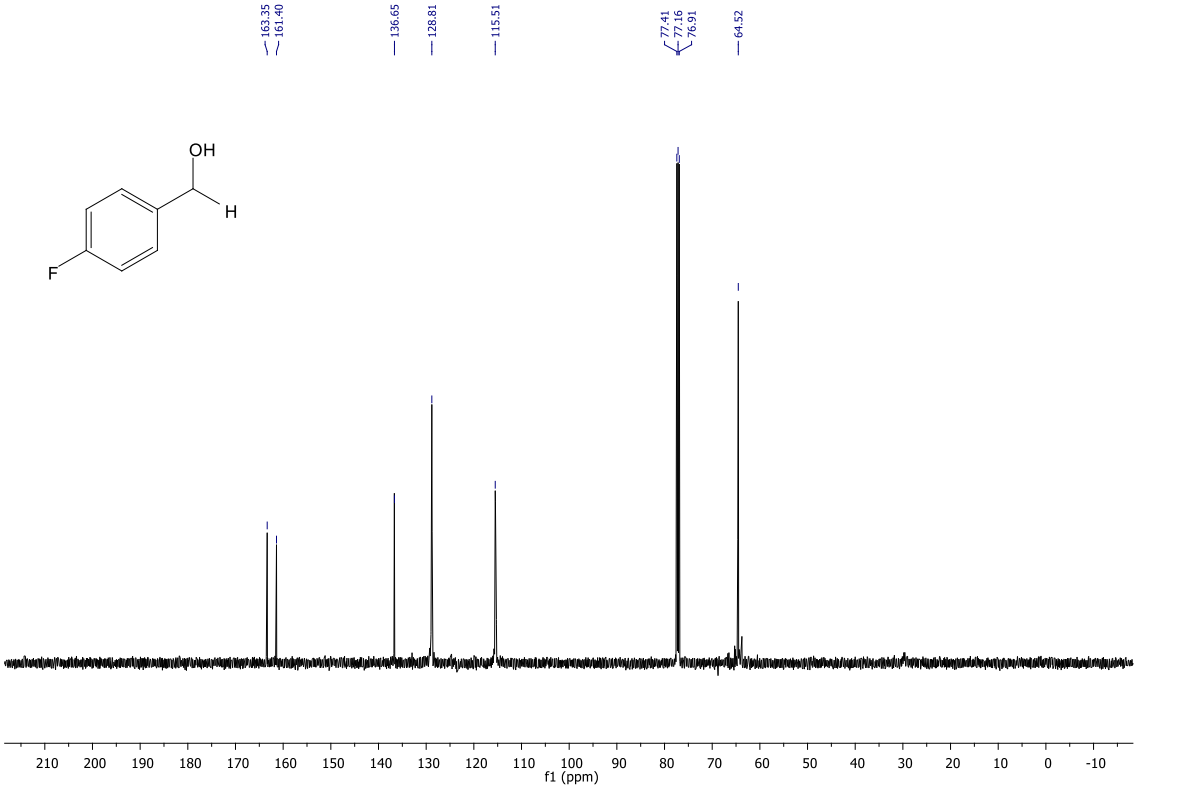


^{11}B NMR of **7b** (128 MHz, $CDCl_3$)

(4–Fluorophenyl)methanol (7c).[2,5]

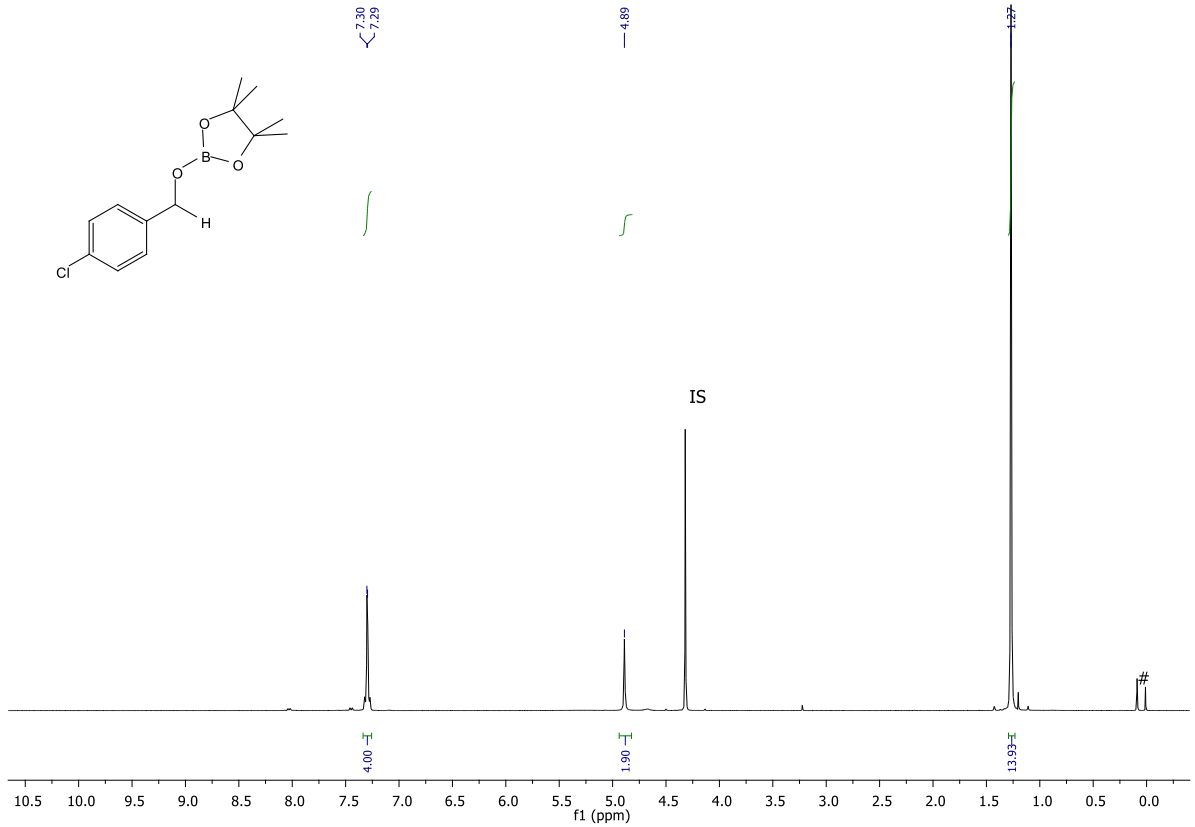


^{1}H NMR of **7c** (400 MHz, $CDCl_3$)

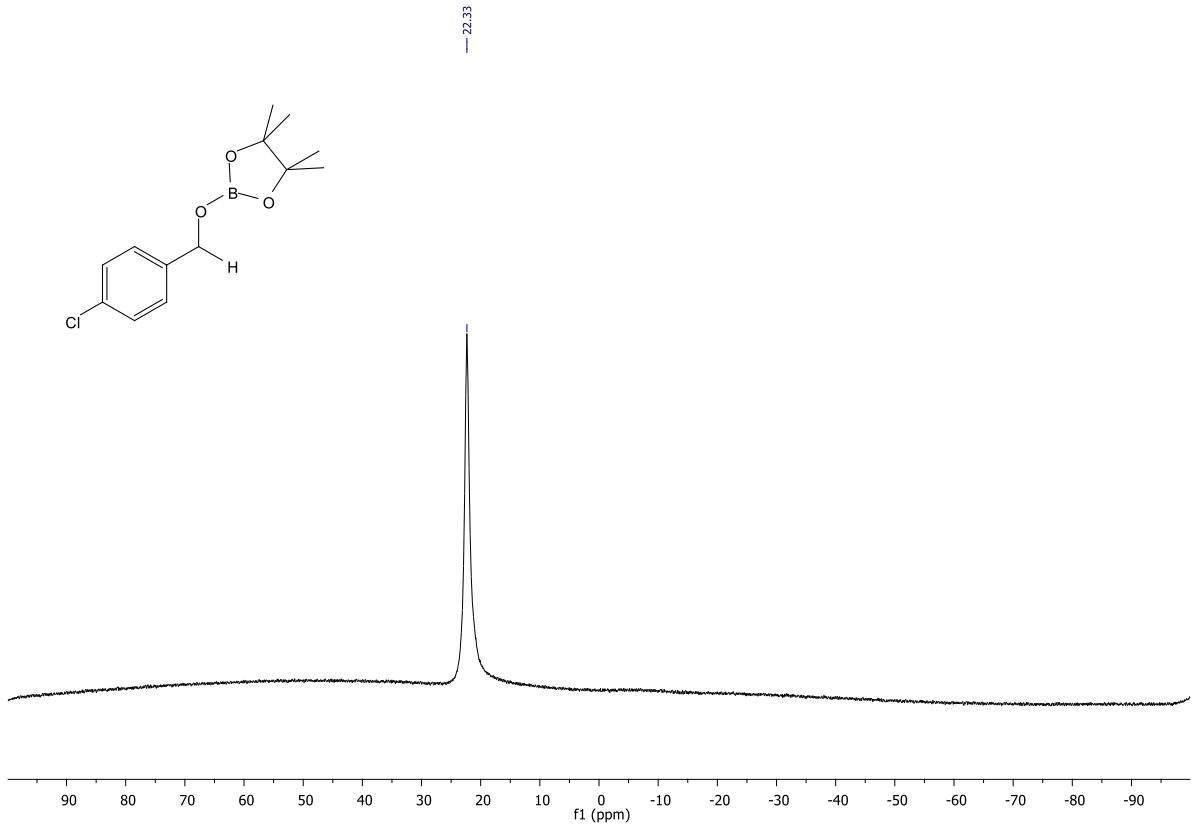


^{13}C NMR of **7c** (100 MHz, $CDCl_3$)

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

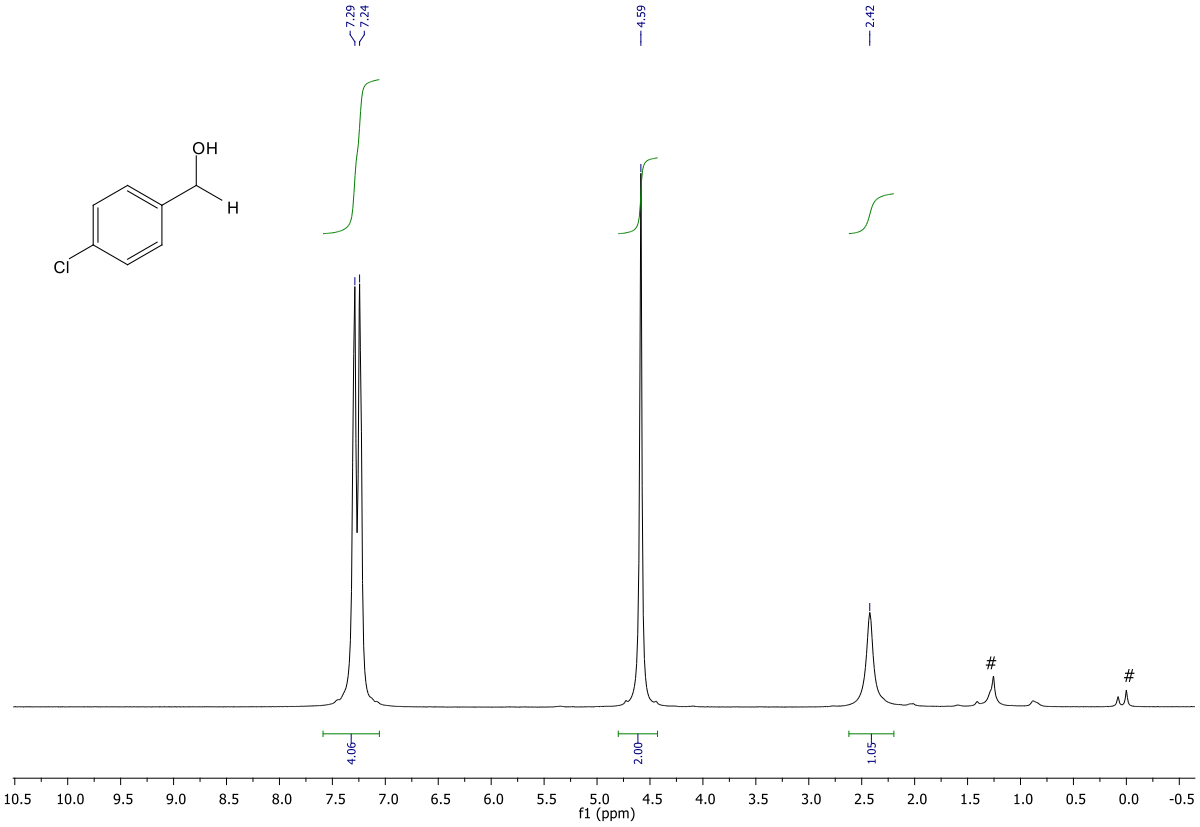


^{1}H NMR of **8b** (400 MHz, $CDCl_3$)

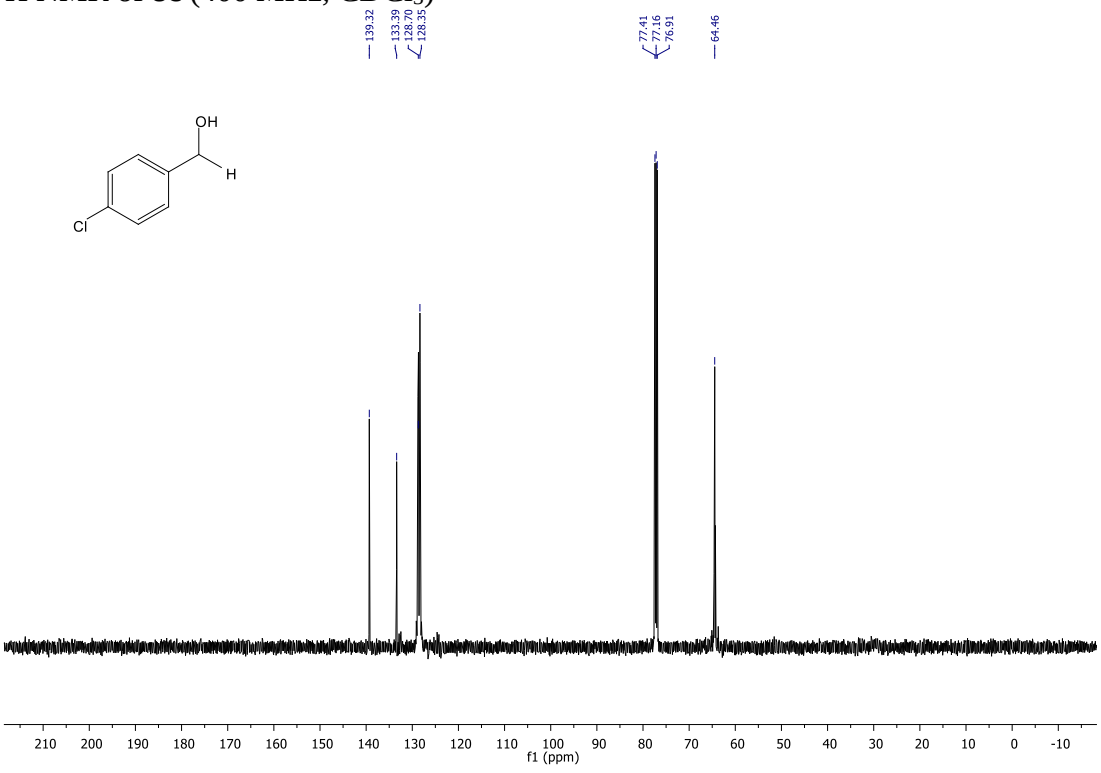


^{11}B NMR of **8b** (128 MHz, $CDCl_3$)

(4–Chlorophenyl)methanol (8c).[2]

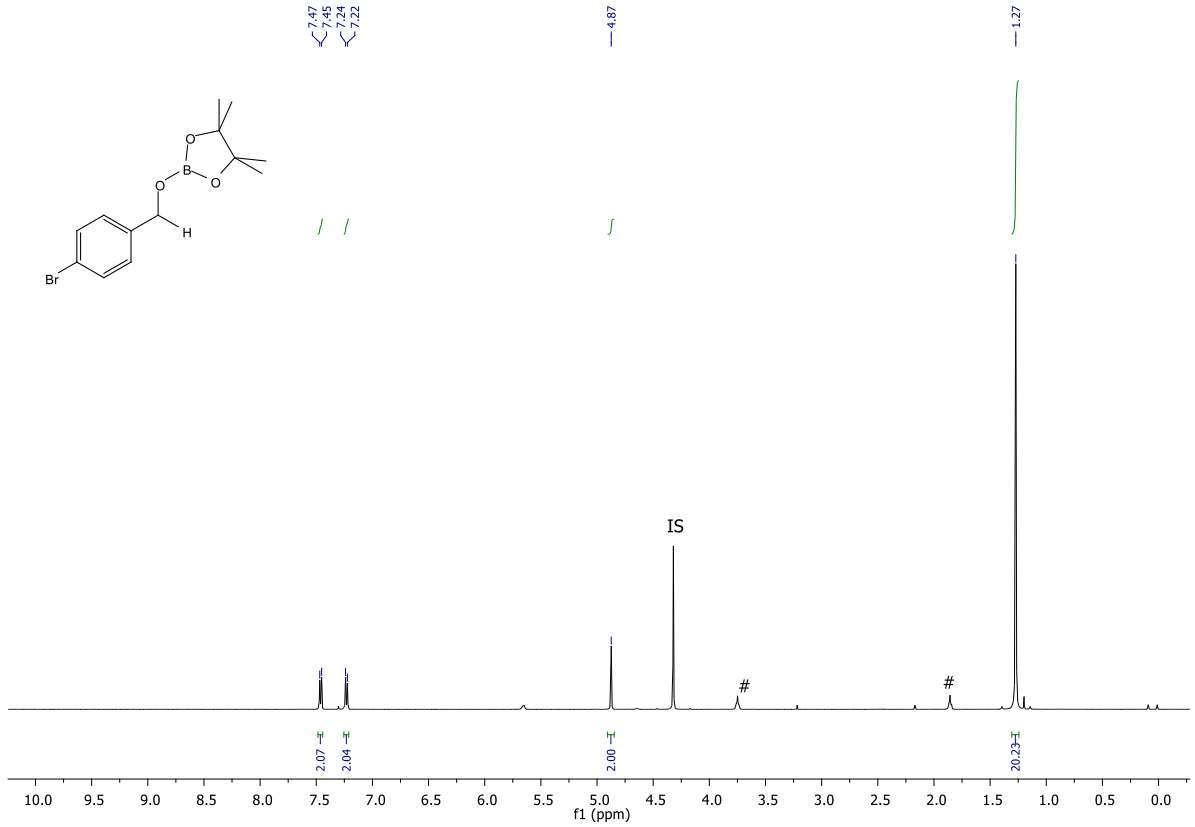


^{1}H NMR of **8c** (400 MHz, $CDCl_3$)

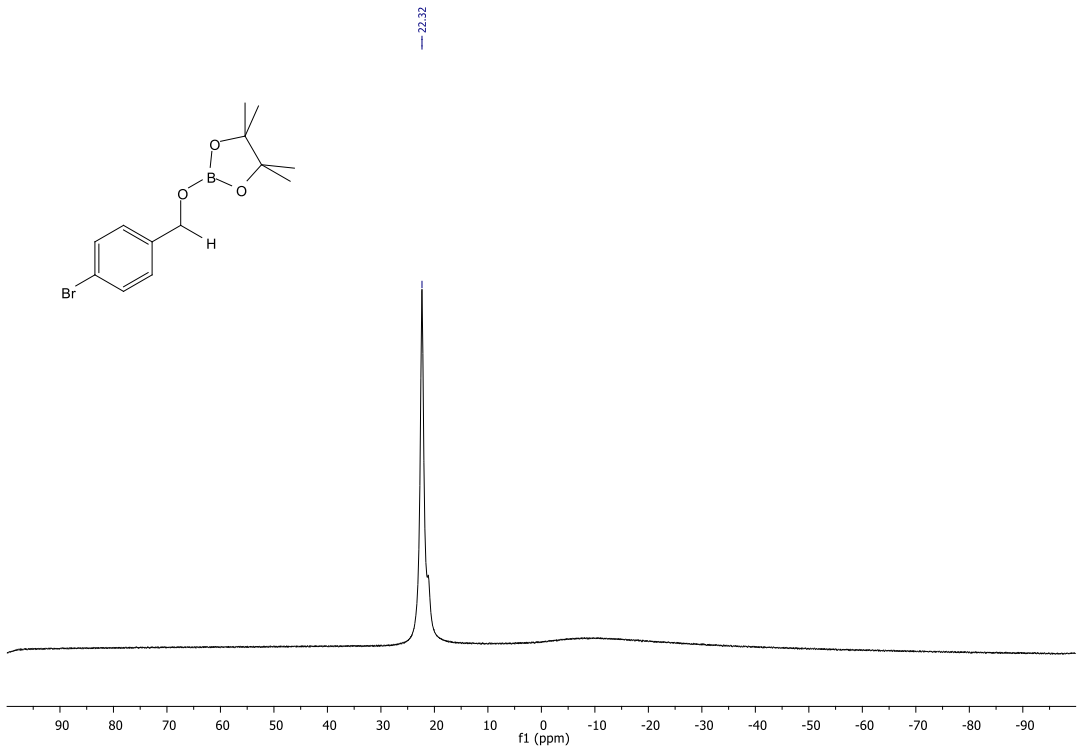


^{13}C NMR of **8c** (100 MHz, $CDCl_3$)

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

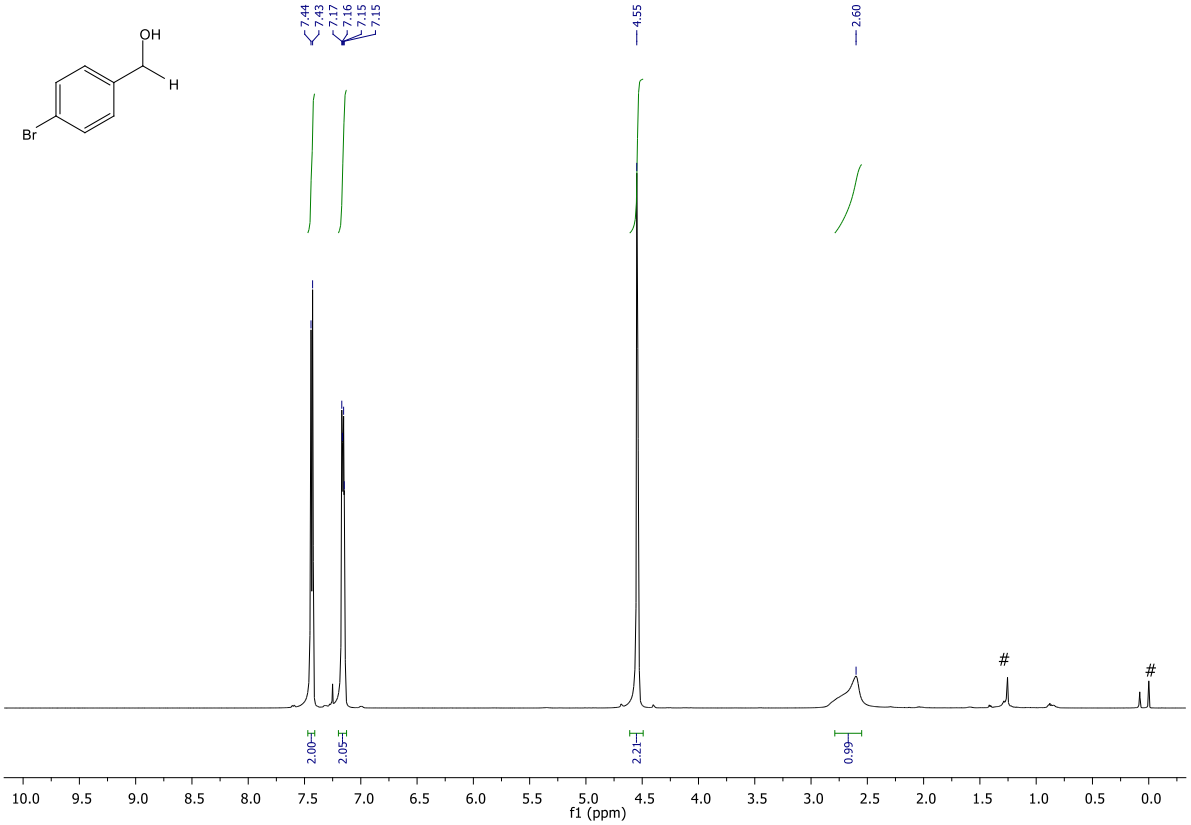


^{1}H NMR of **9b** (400 MHz, $CDCl_3$)

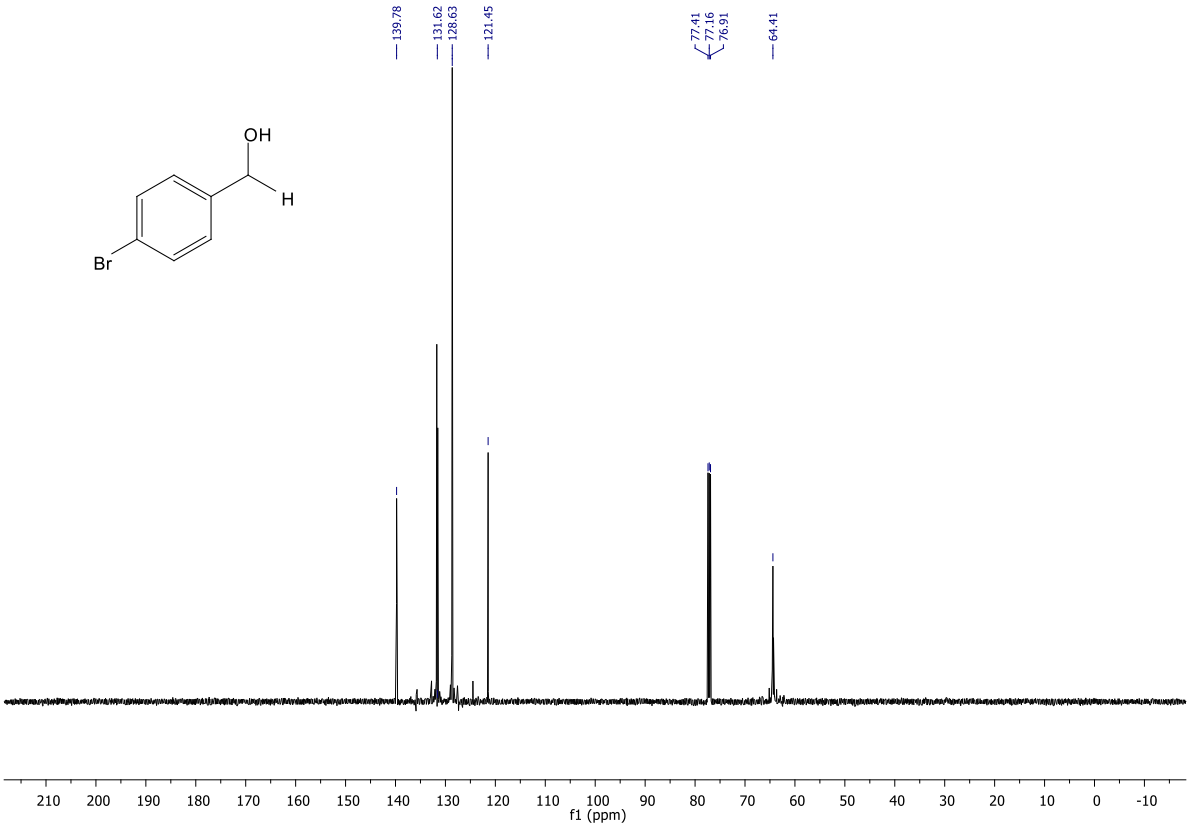


^{11}B NMR of **9b** (128 MHz, $CDCl_3$)

(4–Bromophenyl)methanol (9c).[2,5]

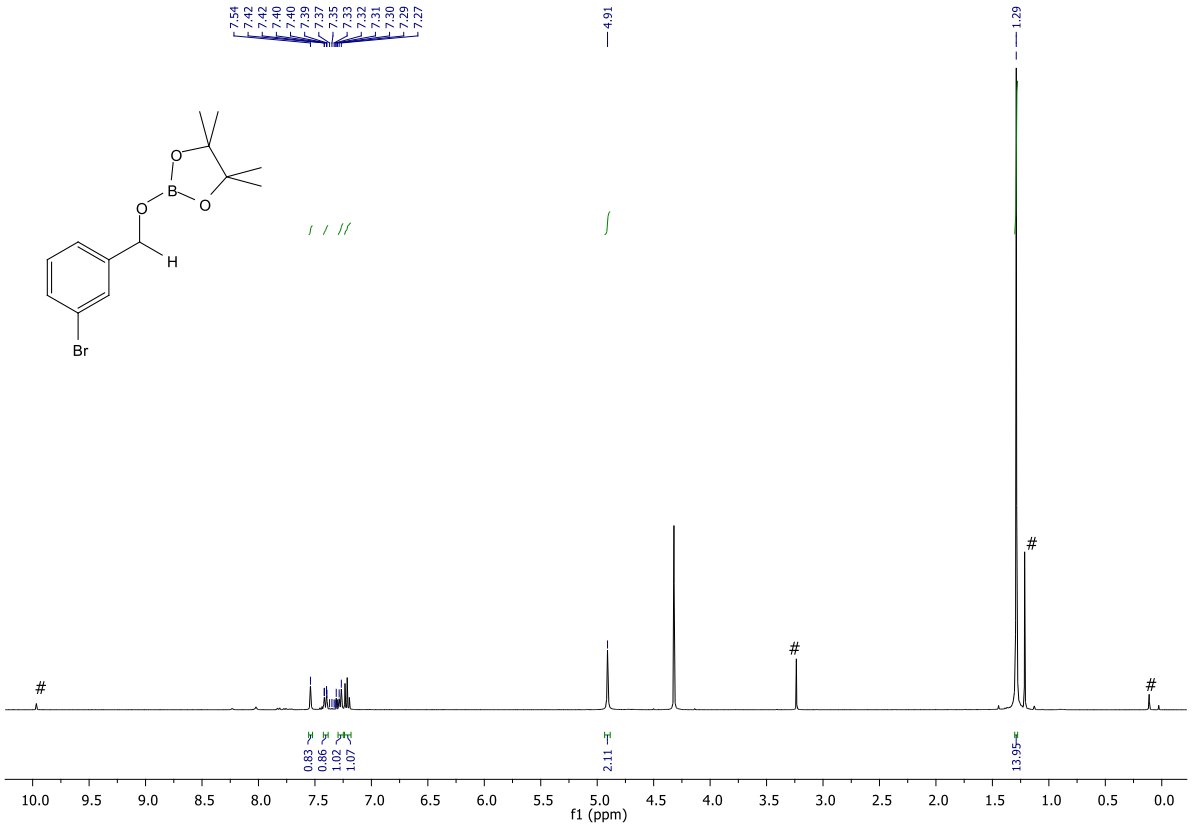


^{1}H NMR of **9c** (400 MHz, $CDCl_3$)

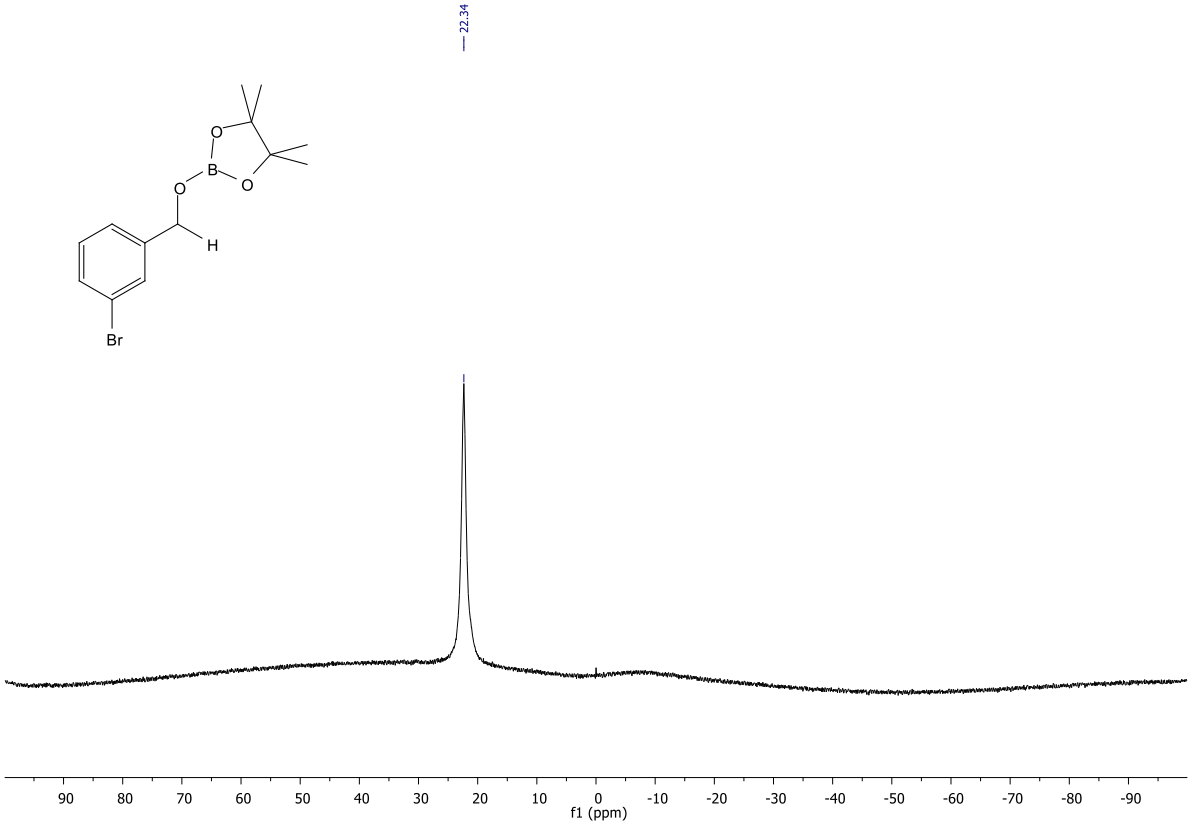


^{13}C NMR of **9c** (100 MHz, $CDCl_3$)

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

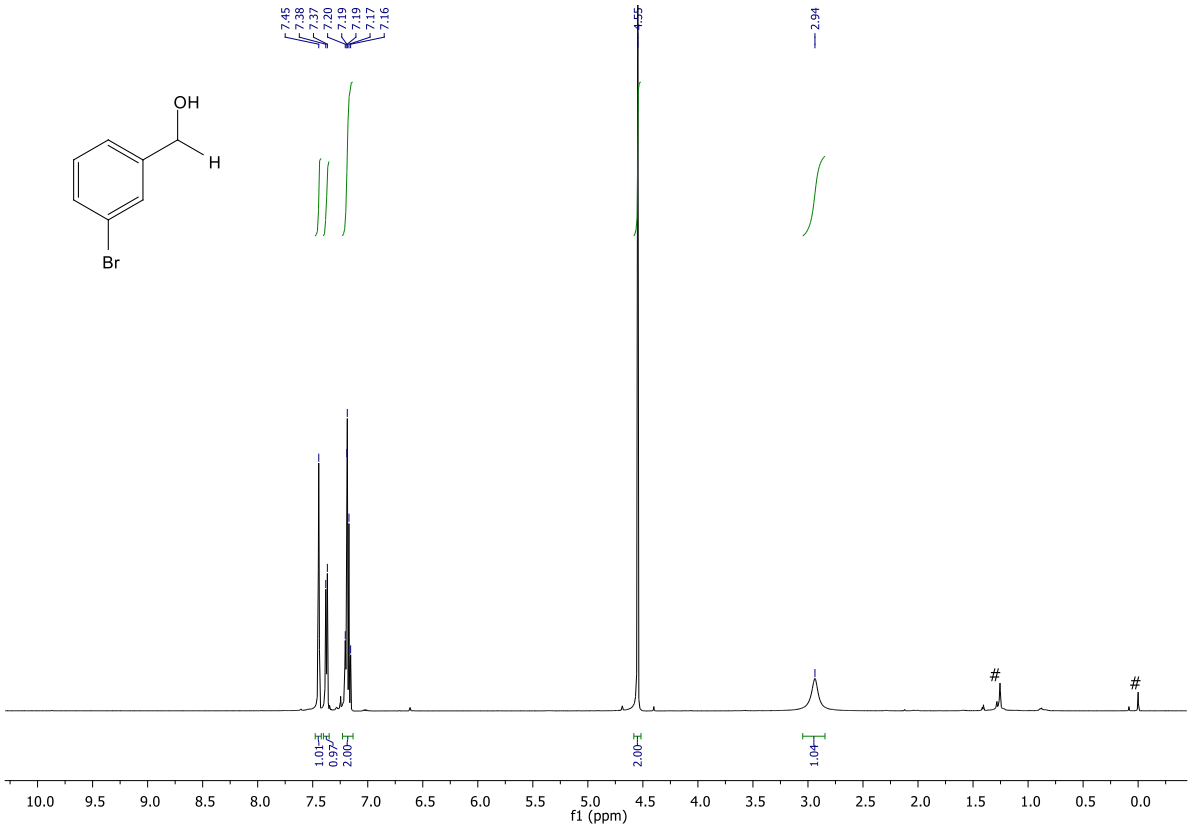


^{1}H NMR of **10b** (400 MHz, $CDCl_3$)

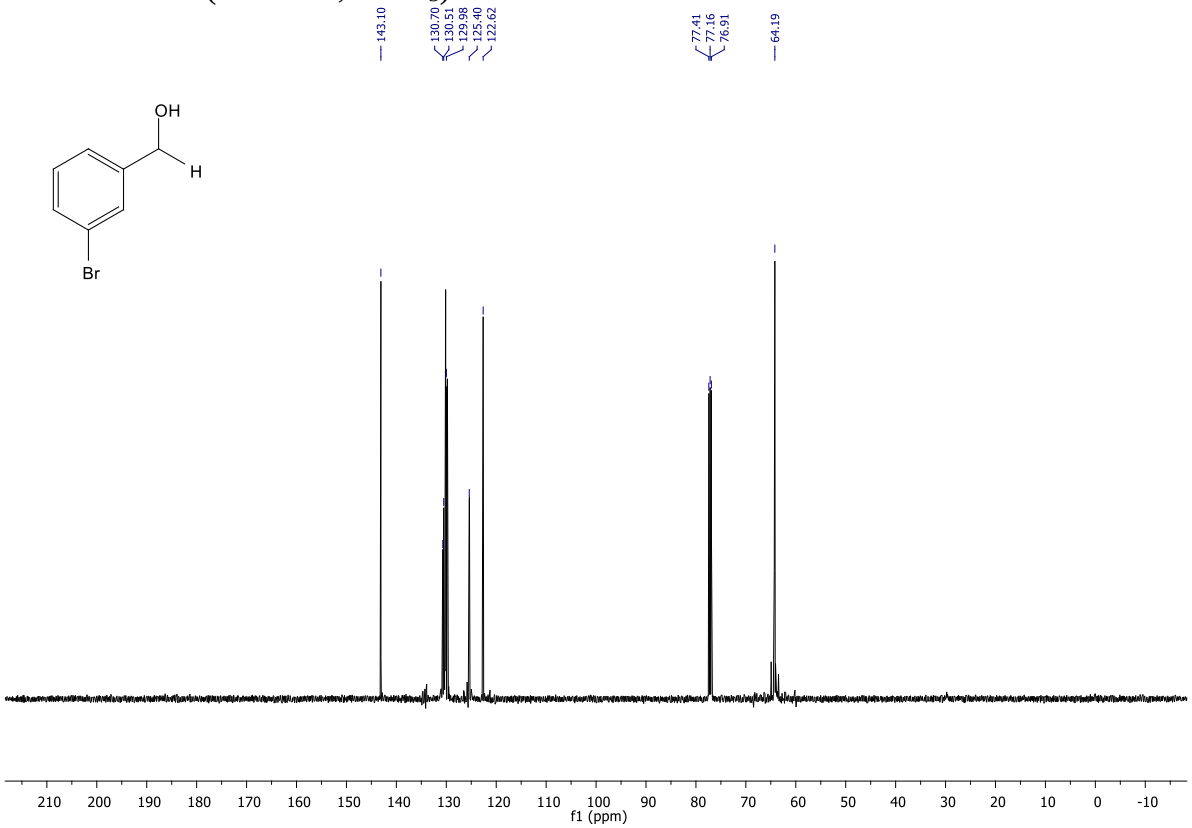


^{11}B NMR of **10b** (128 MHz, $CDCl_3$)

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

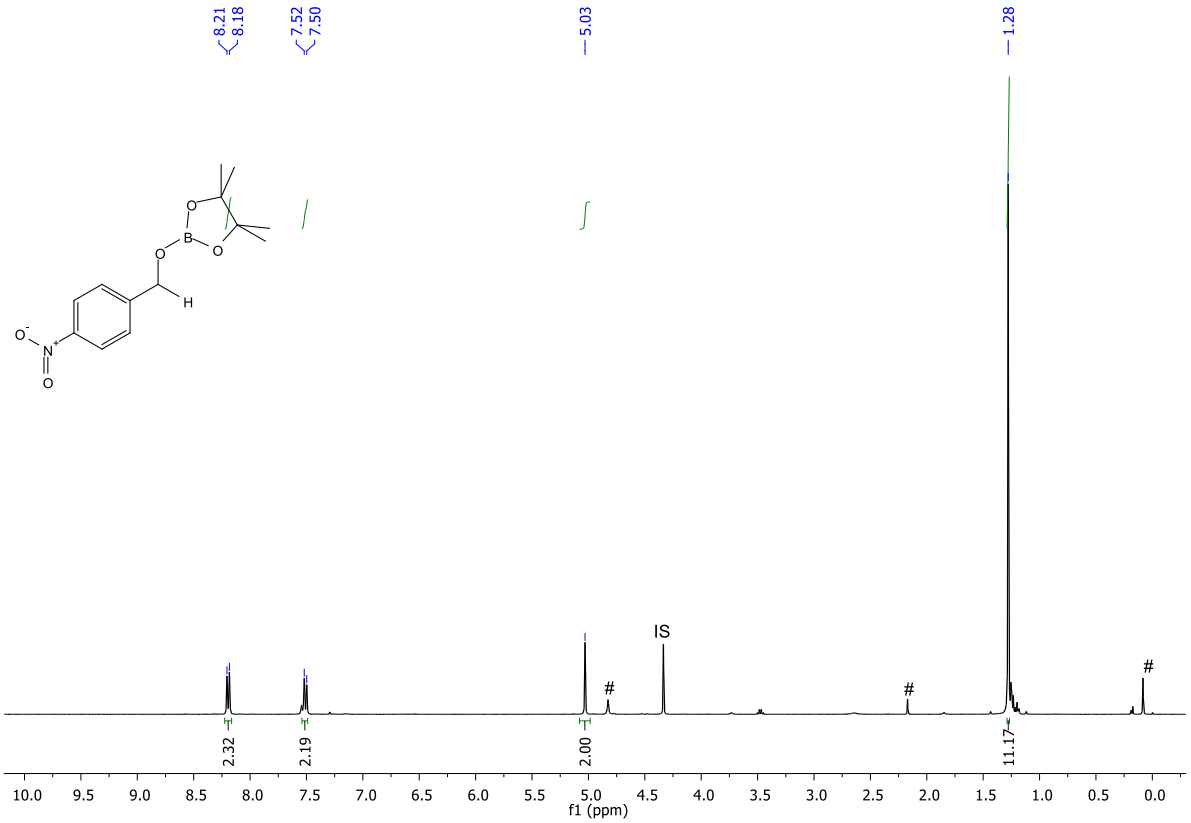


^{1}H NMR of **10c** (400 MHz, $CDCl_3$)

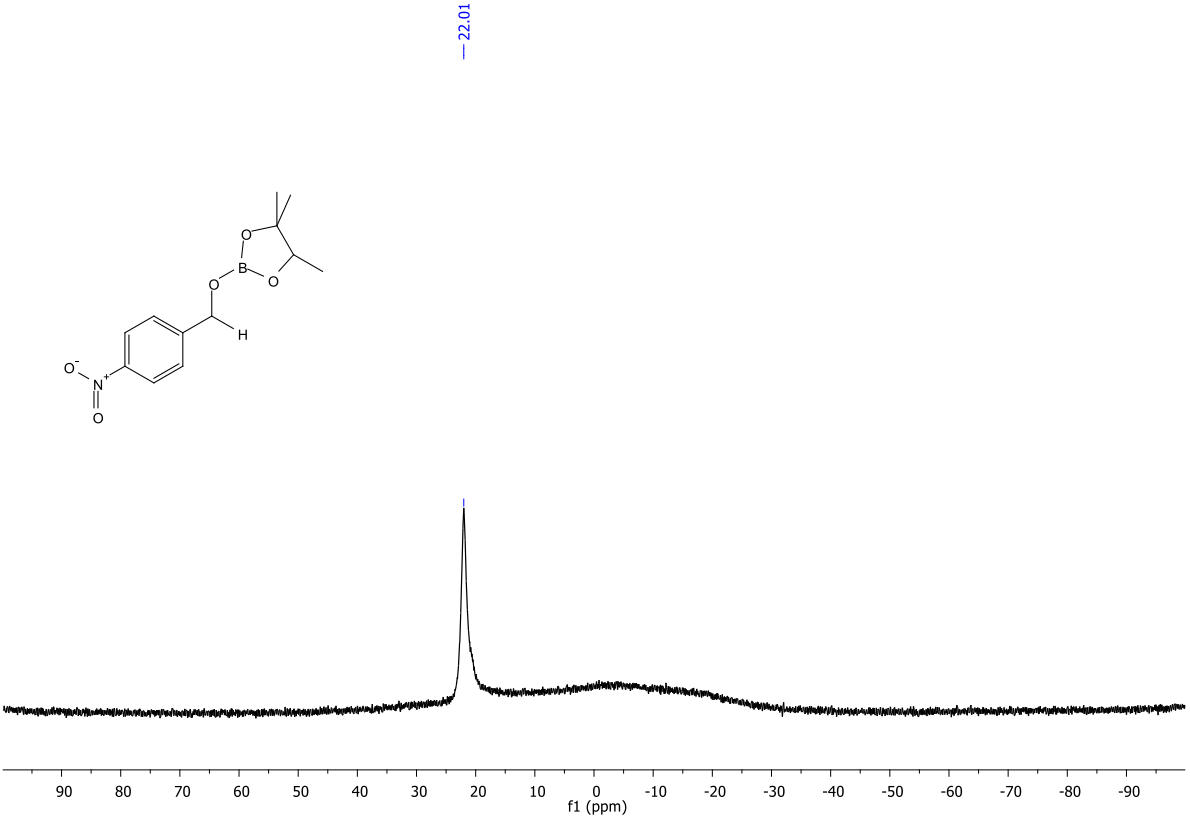


^{13}C NMR of **10c** (100 MHz, $CDCl_3$)

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

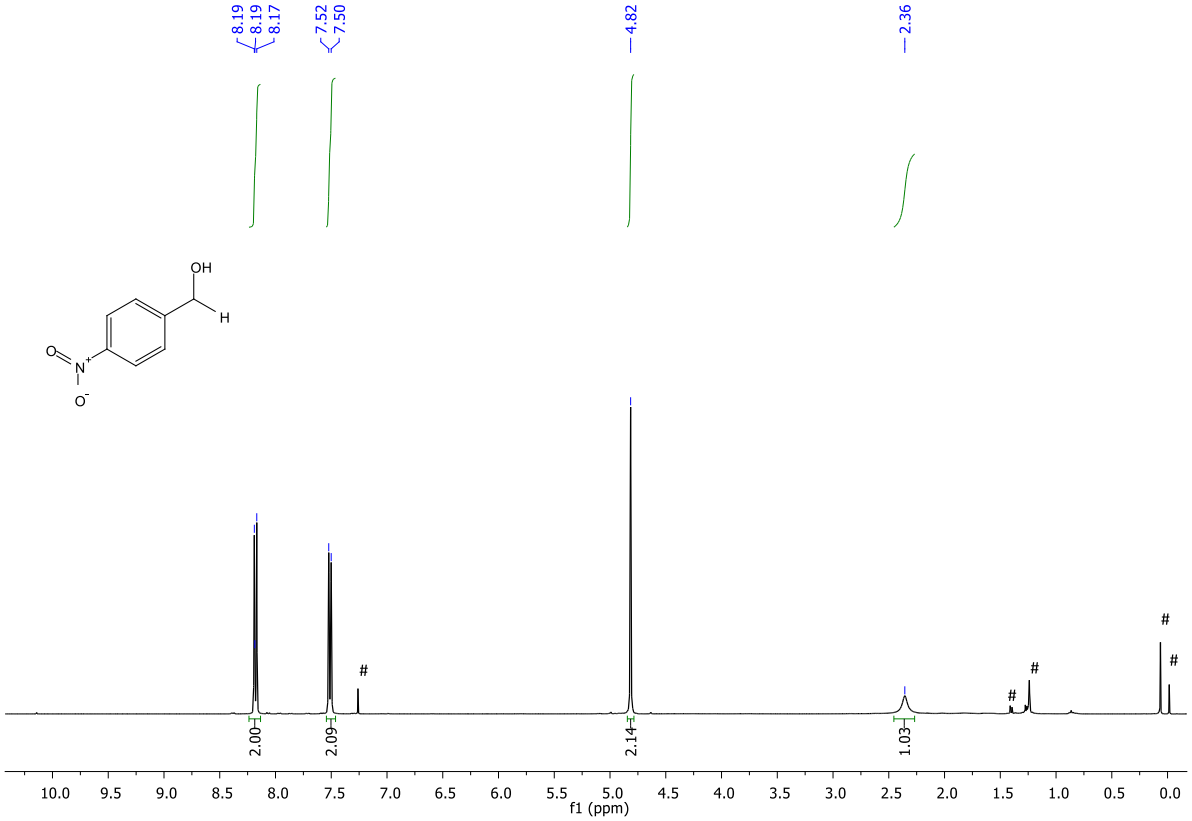


^{1}H NMR of **11b** (400 MHz, $CDCl_3$)

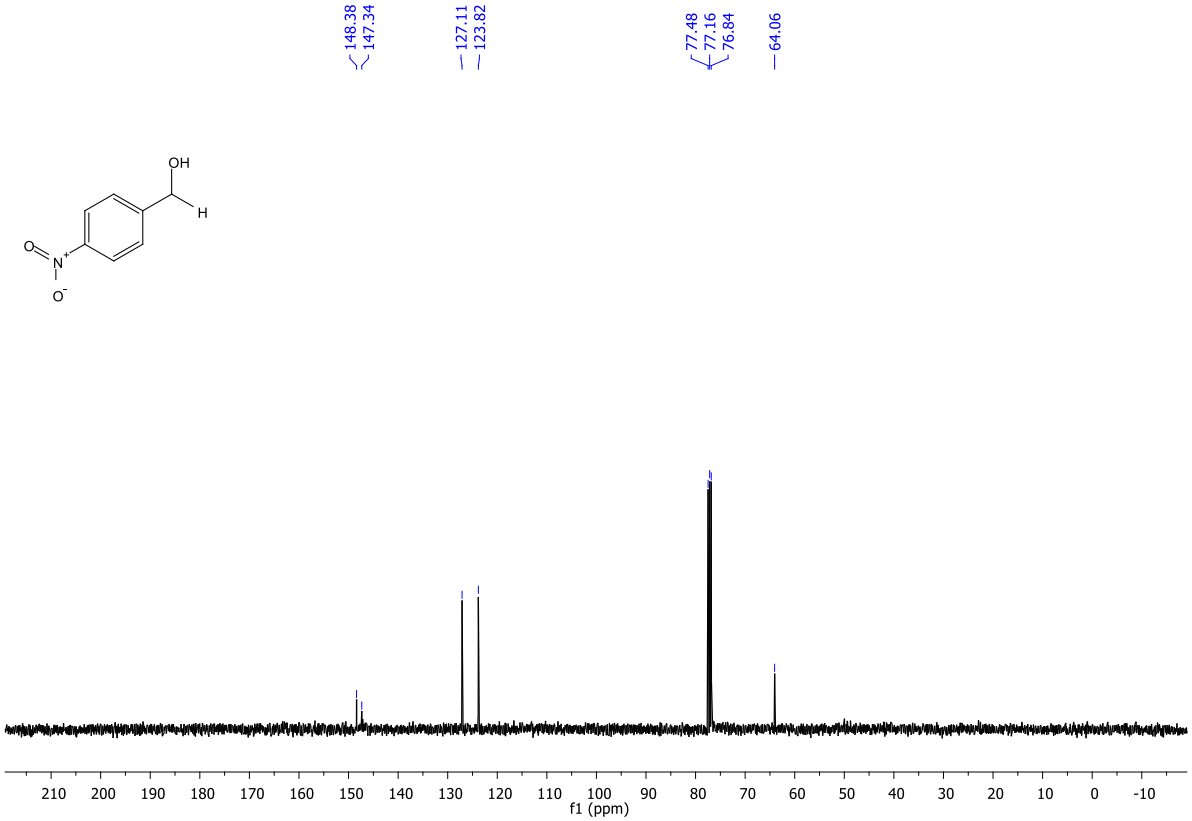


^{11}B NMR of **11b** (128 MHz, $CDCl_3$)

(4-Nitrophenyl)methanol (11c).[2]

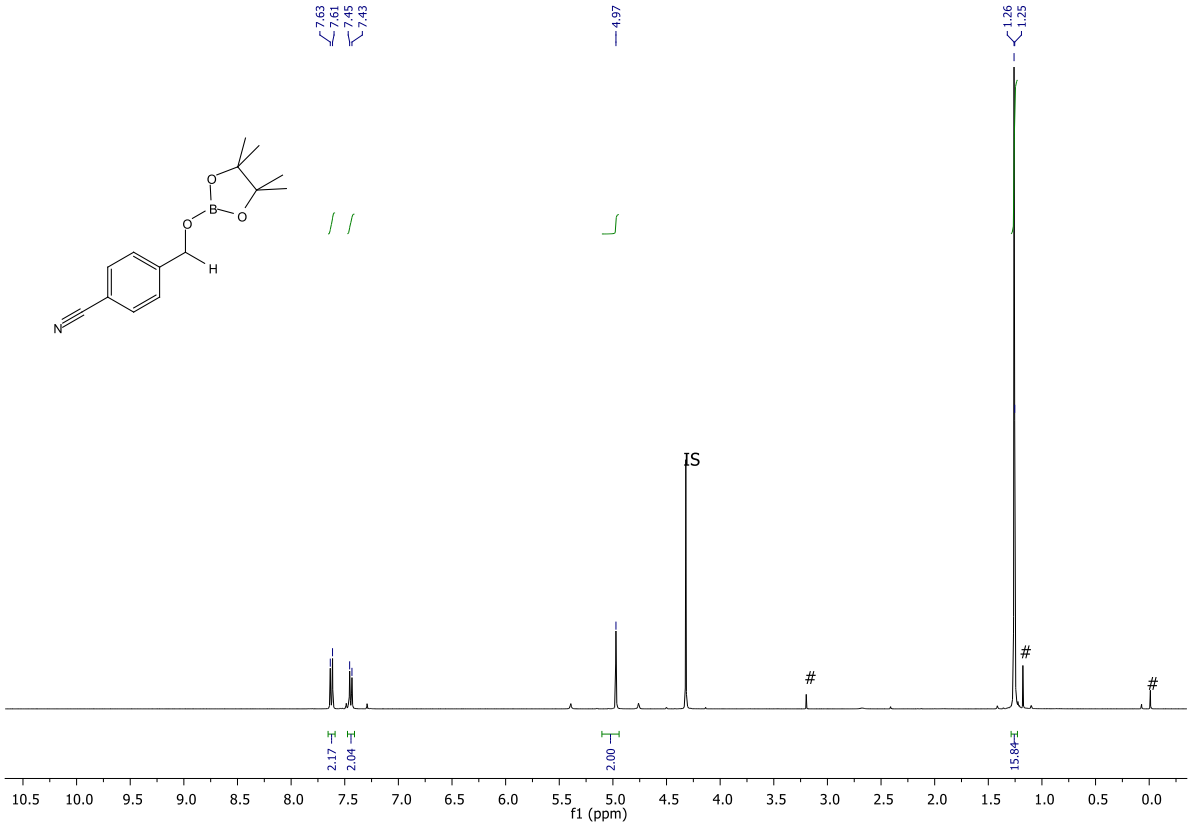


^{1}H NMR of **11c** (400 MHz, $CDCl_3$)

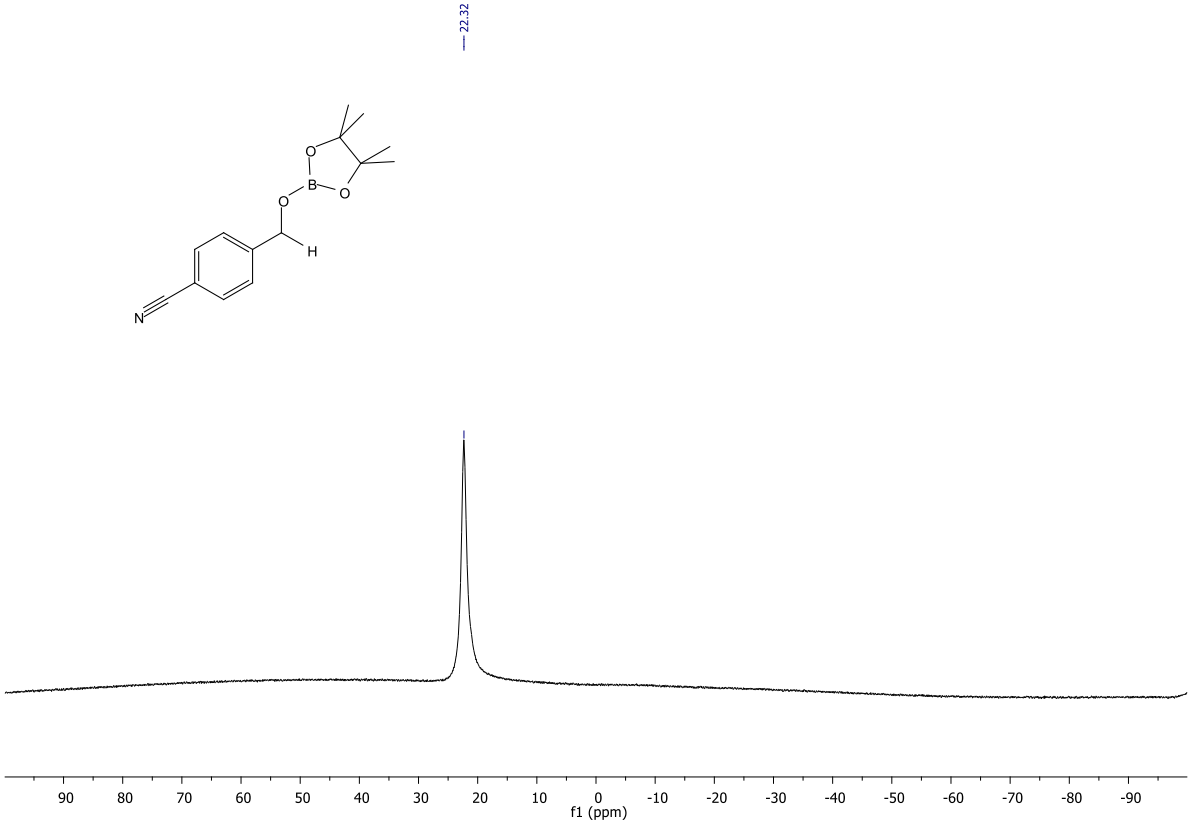


^{13}C NMR of **11c** (100 MHz, $CDCl_3$)

4-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzonitrile (Table 2, 12b).[2,6]

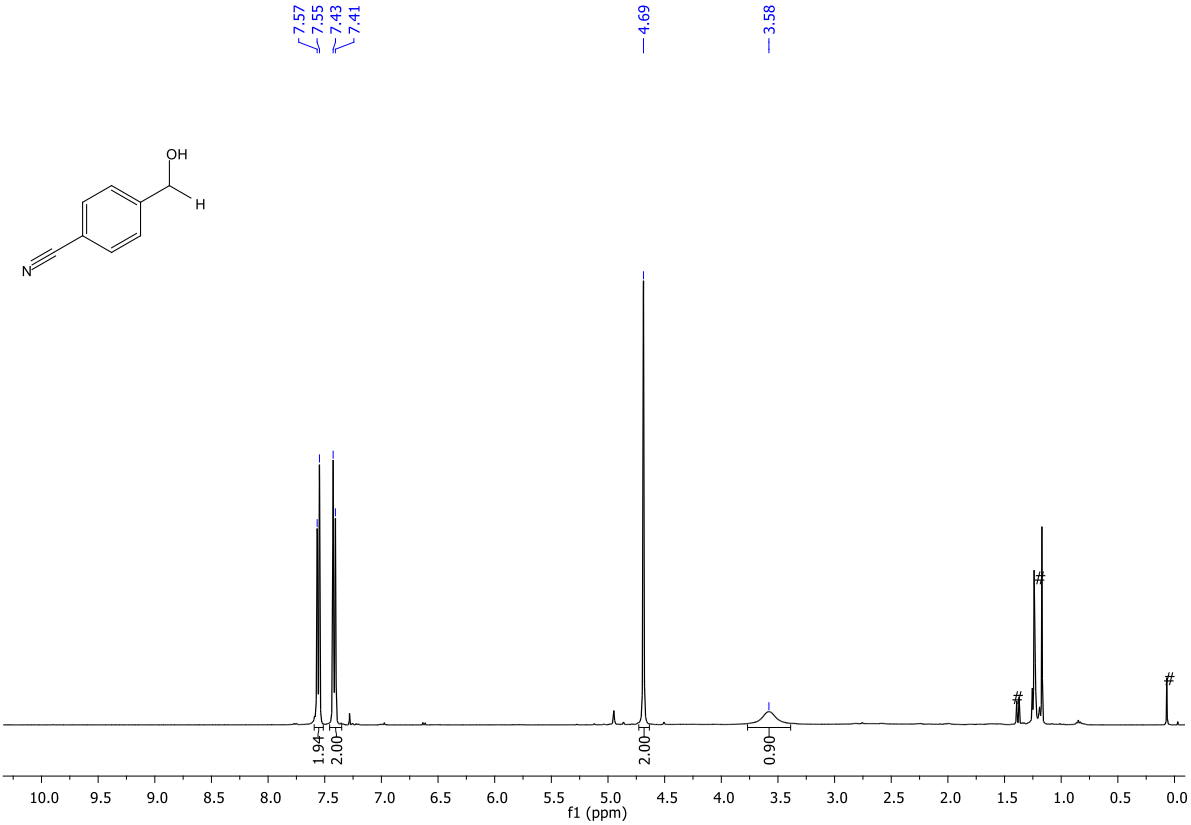


^{1}H NMR of **12b** (400 MHz, $CDCl_3$)

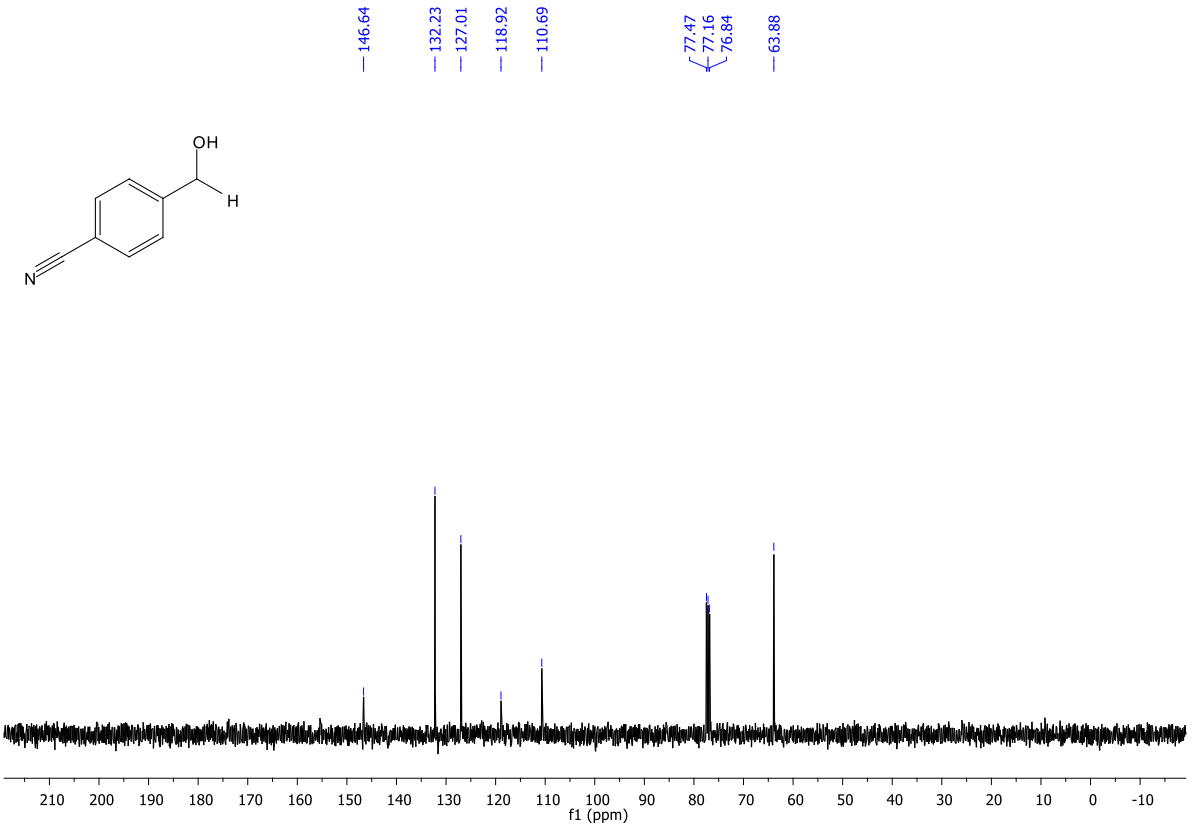


^{11}B NMR of **12b** (128 MHz, $CDCl_3$)

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

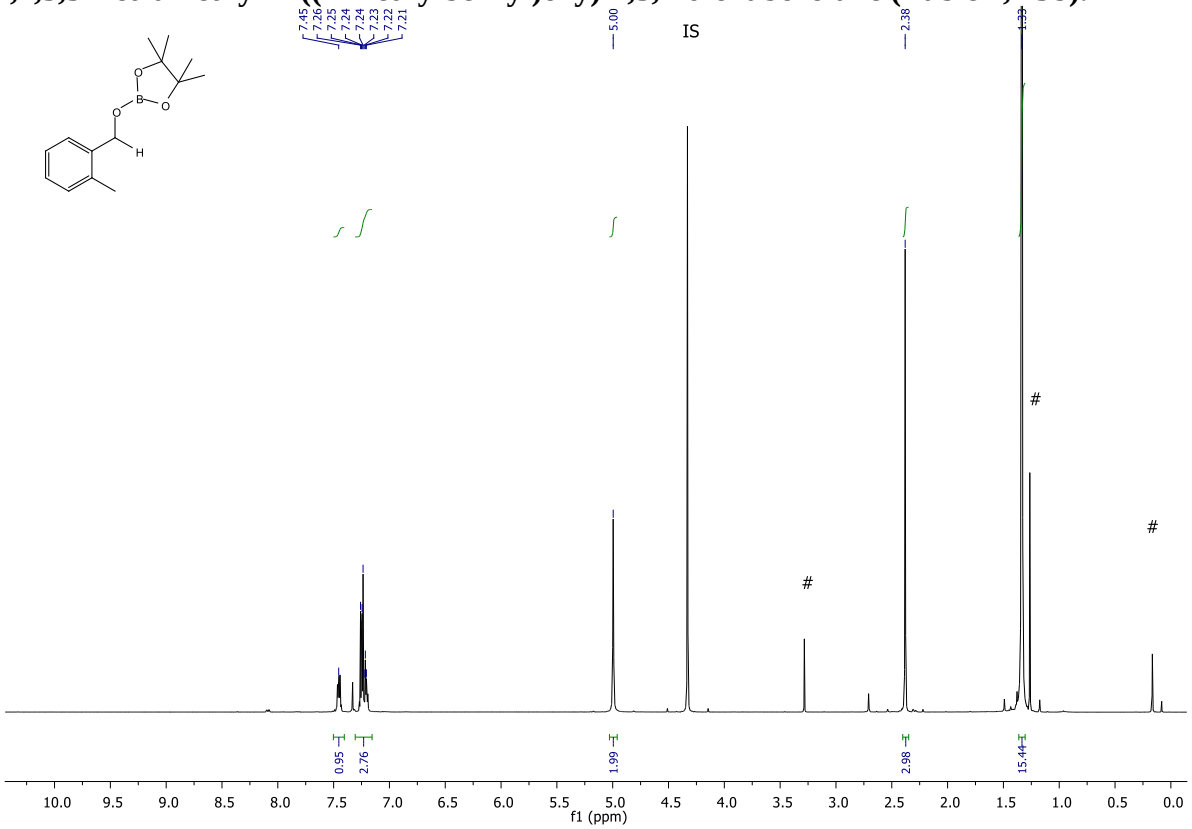


^{1}H NMR of **12c** (400 MHz, $CDCl_3$)

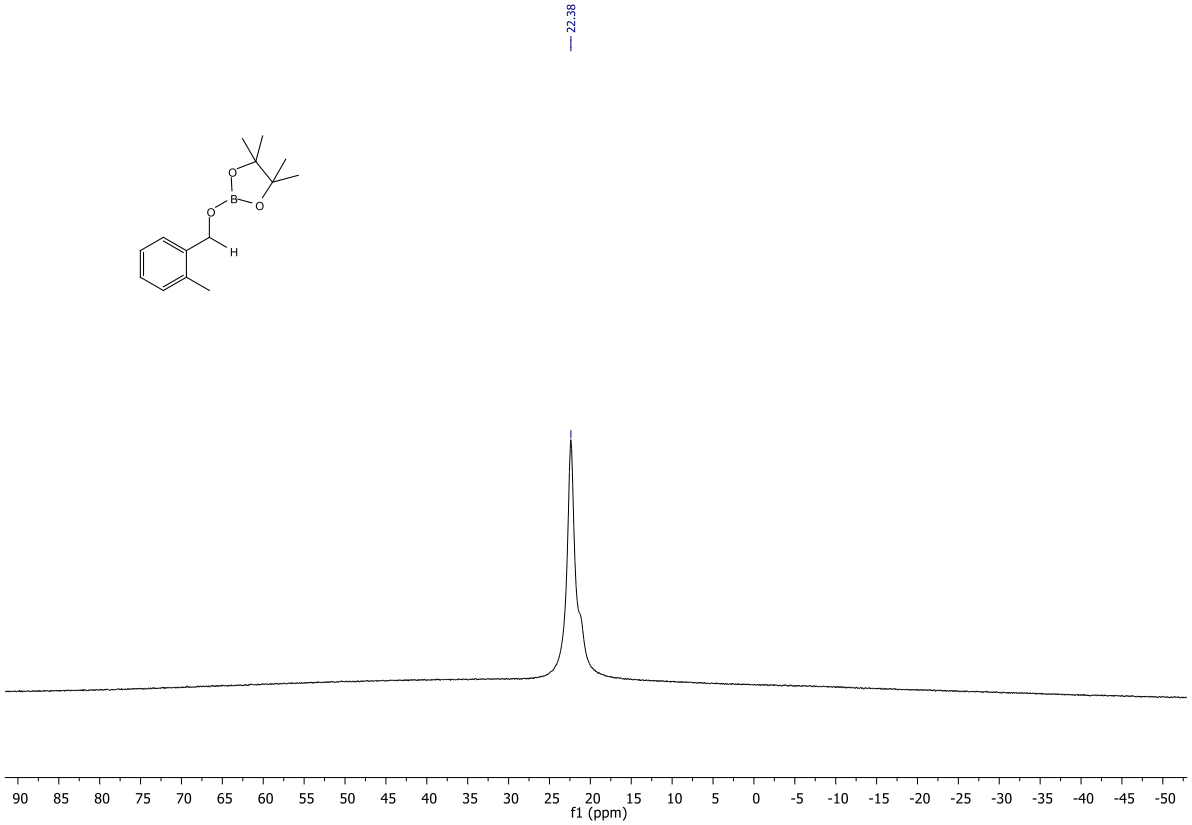


^{13}C NMR of **12c** (100 MHz, $CDCl_3$)

4,4,5,5-Tetramethyl-2-((2-methylbenzyl)oxy)-1,3,2-dioxaborolane (Table 2, 13b).[2]

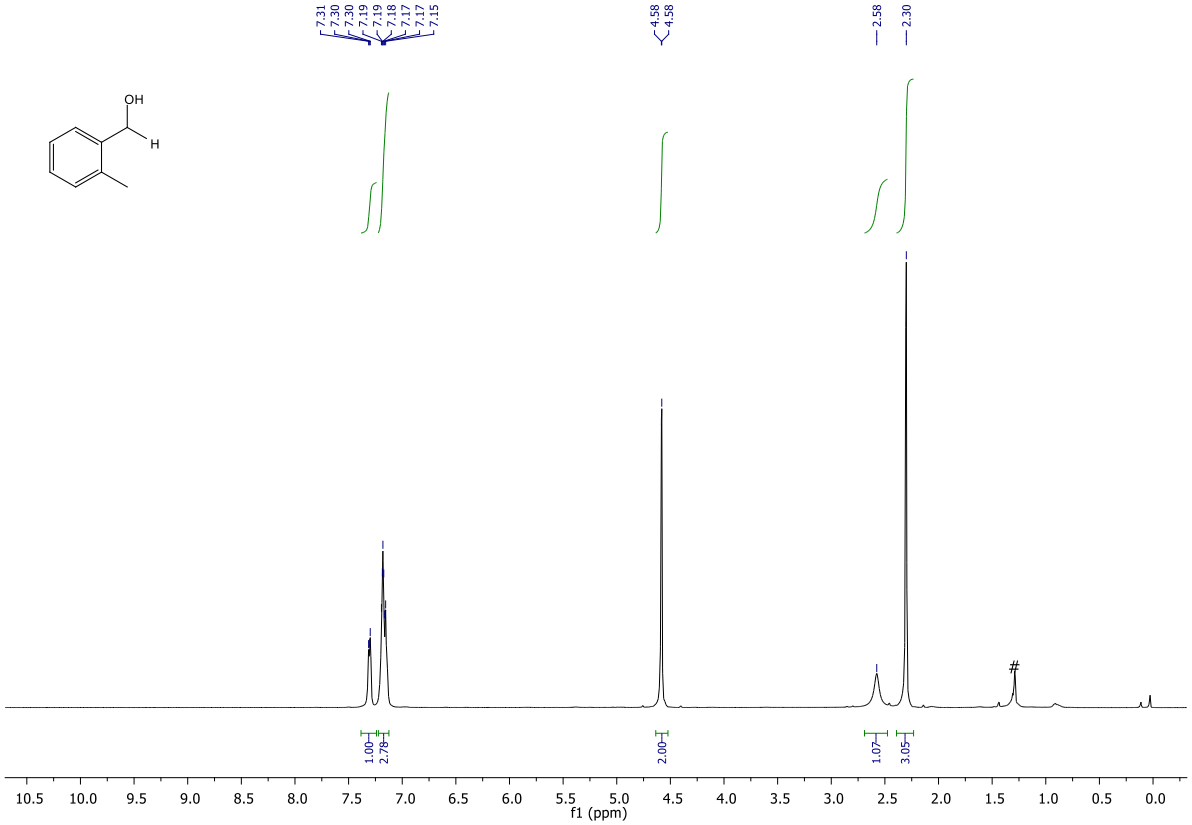


^{1}H NMR of **13b** (400 MHz, $CDCl_3$)

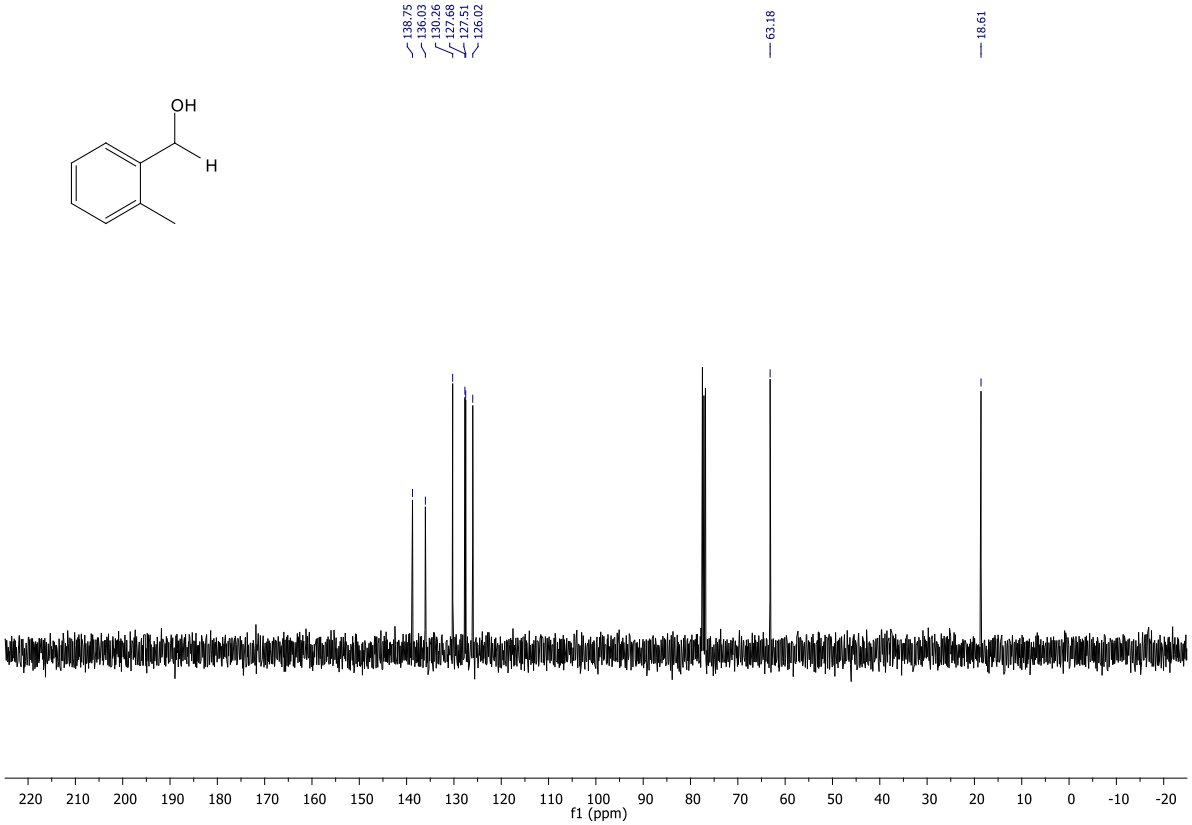


^{11}B NMR of **13b** (128 MHz, $CDCl_3$)

***o*-Tolylmethanol (13c).**[2]

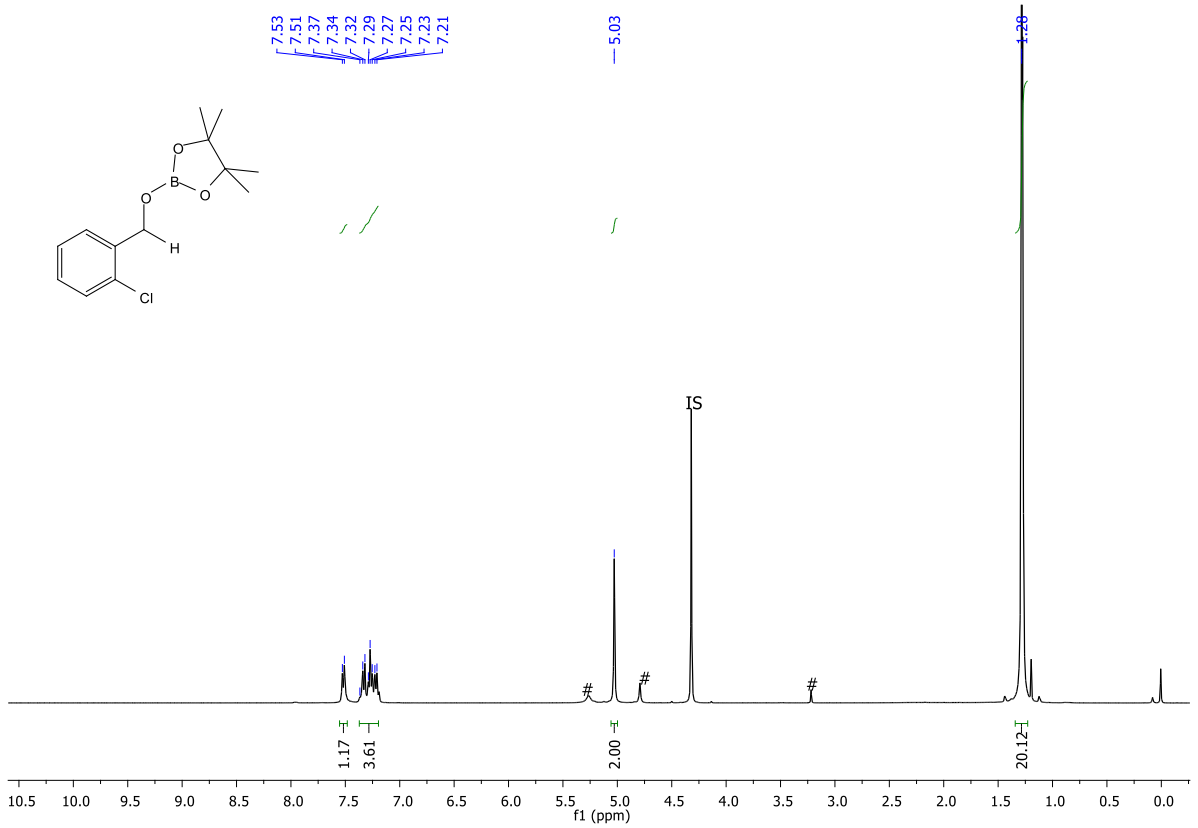


^{1}H NMR of **13c** (400 MHz, $CDCl_3$)

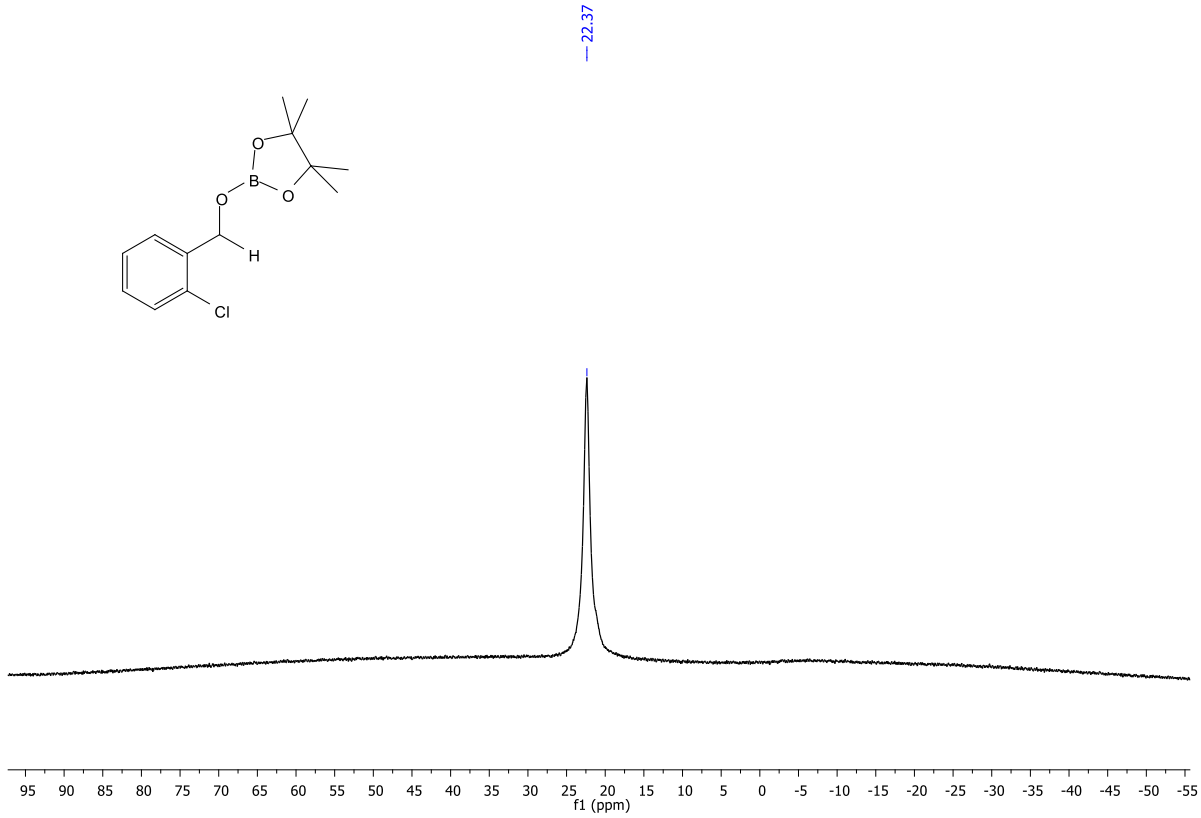


^{13}C NMR of **13c** (100 MHz, $CDCl_3$)

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

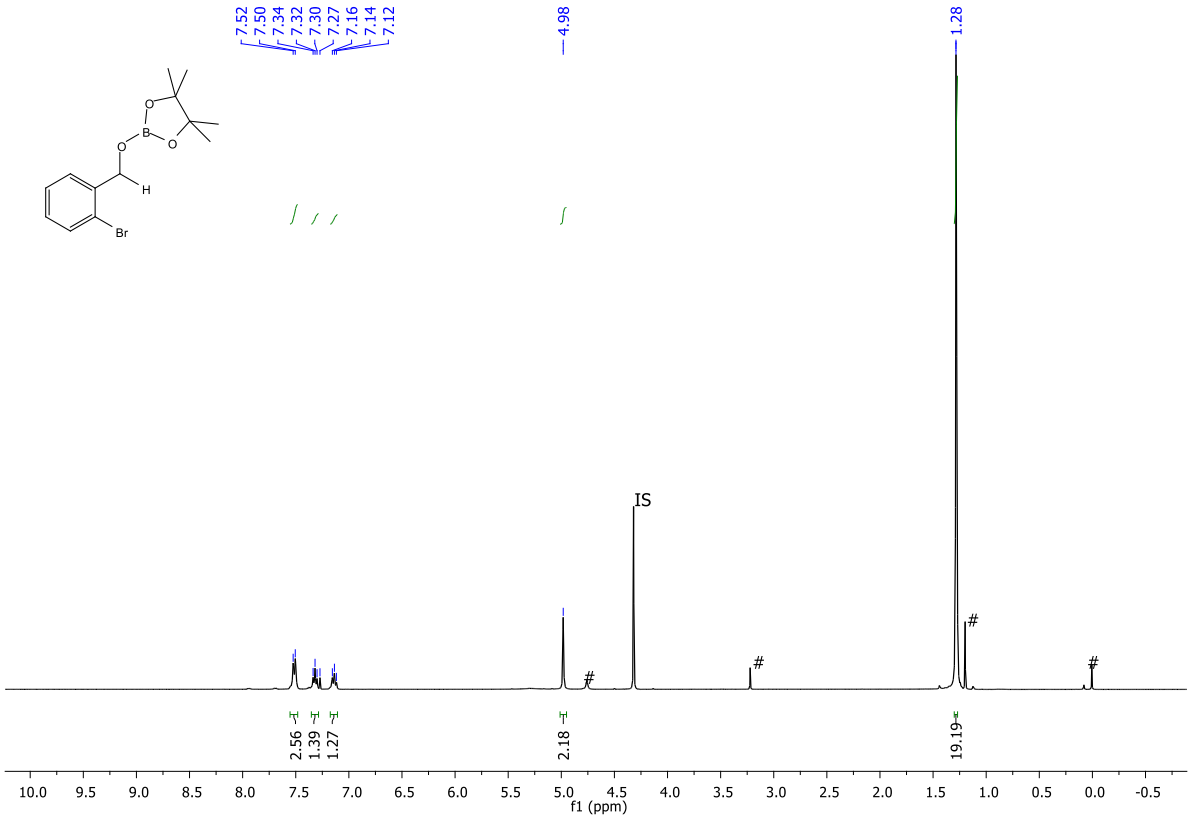


^{1}H NMR of **14b** (400 MHz, $CDCl_3$)

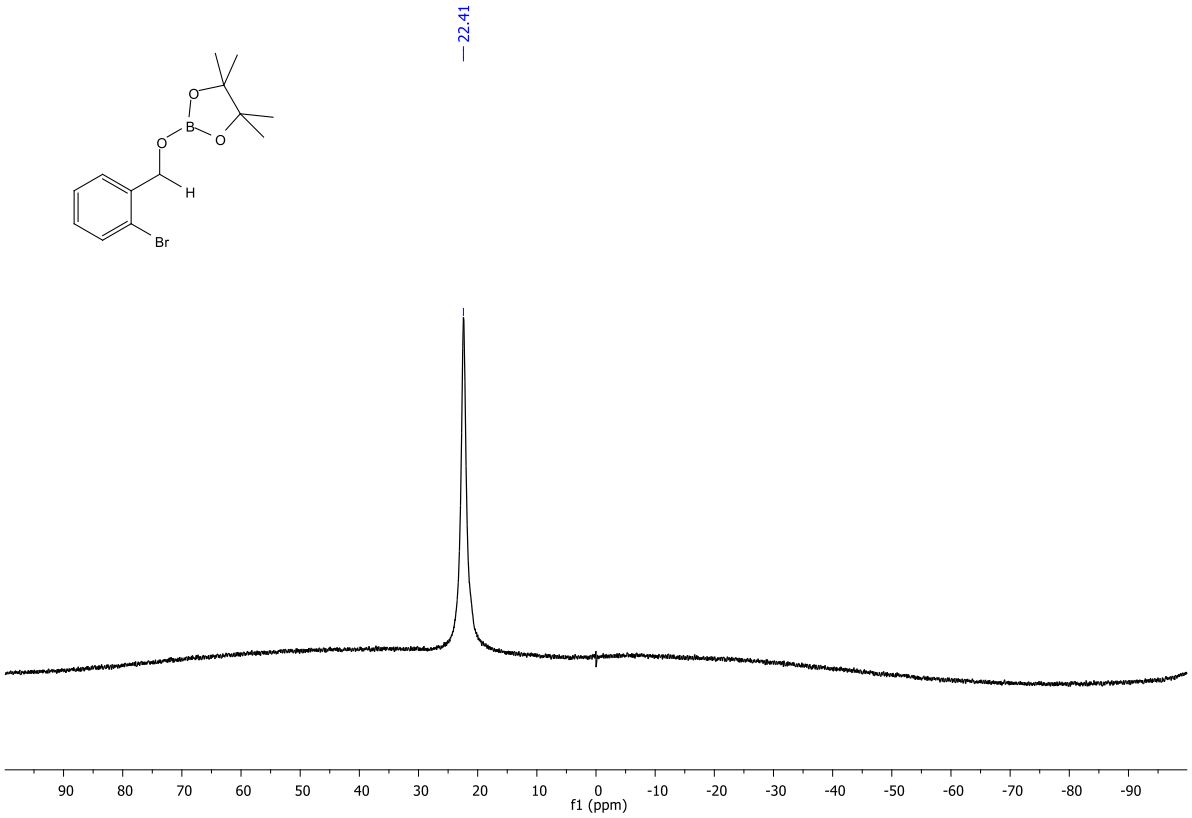


^{11}B NMR of **14b** (128 MHz, $CDCl_3$)

4,4,5,5-Tetramethyl-2-((2-Bromobenzyl)oxy)-1,3,2-dioxaborolane (Table 2, 15b).[12]

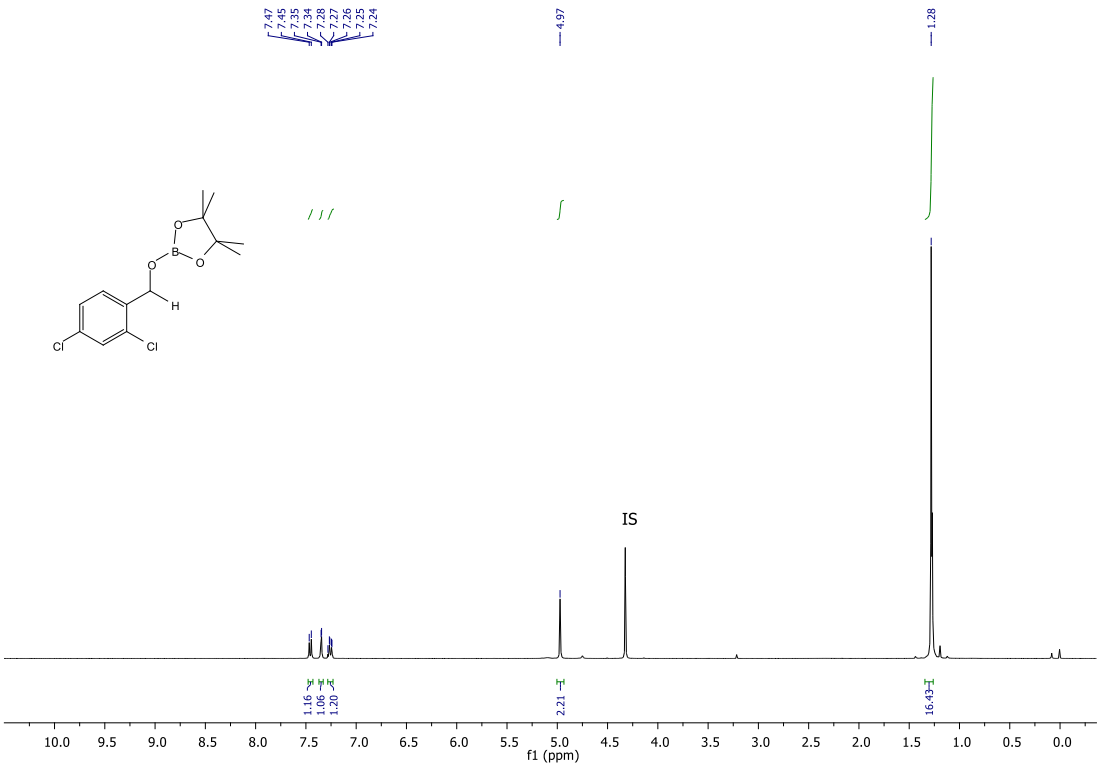


^{1}H NMR of **15b** (400 MHz, $CDCl_3$)

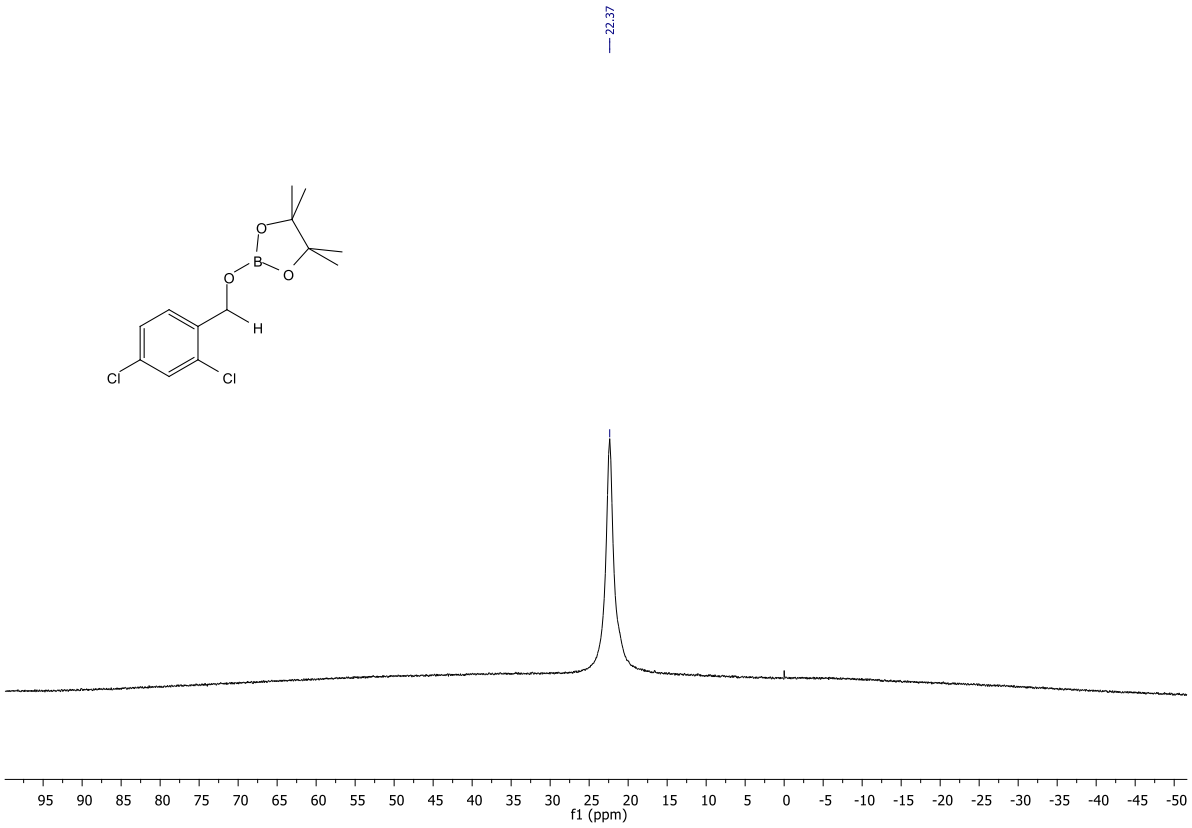


^{11}B NMR of **15b** (128 MHz, $CDCl_3$)

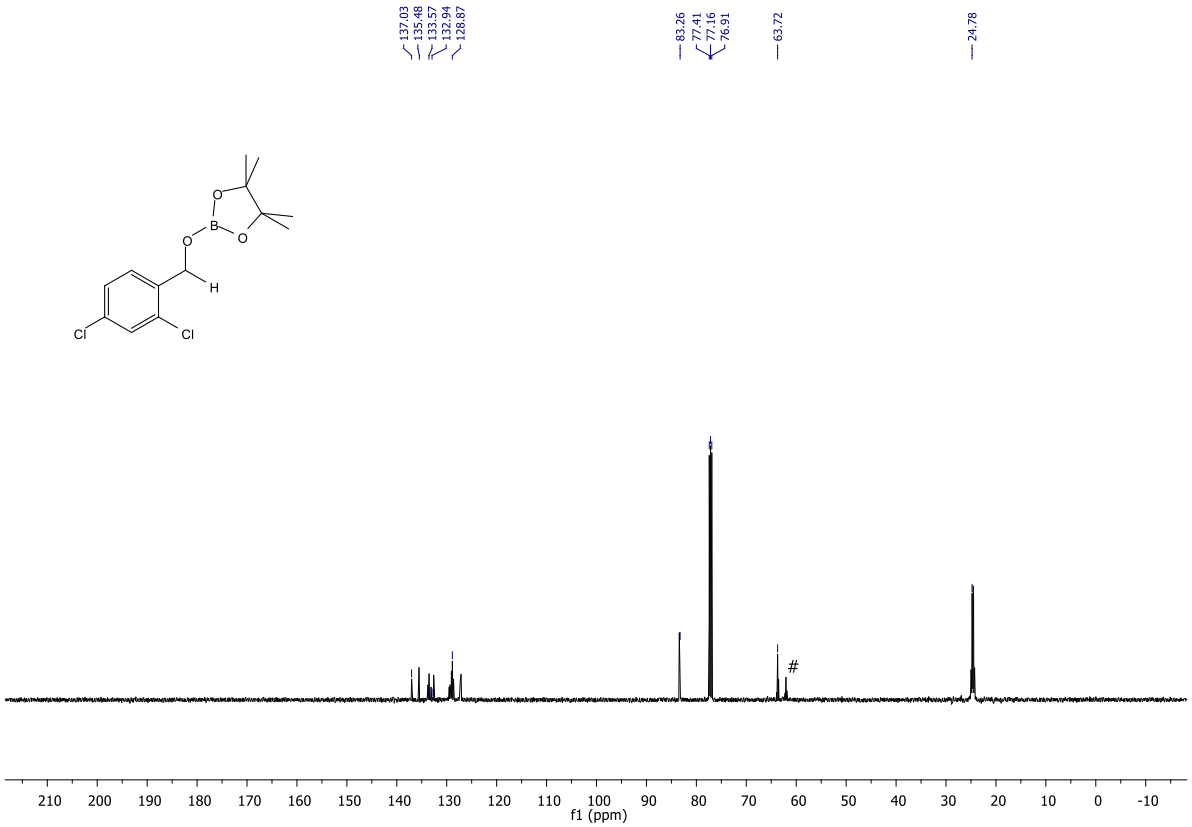
4,4,5,5-Tetramethyl-2-((2,4-Dichlorobenzyl)oxy)-1,3,2-dioxaborolane (Table 2, 16b).[13]



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

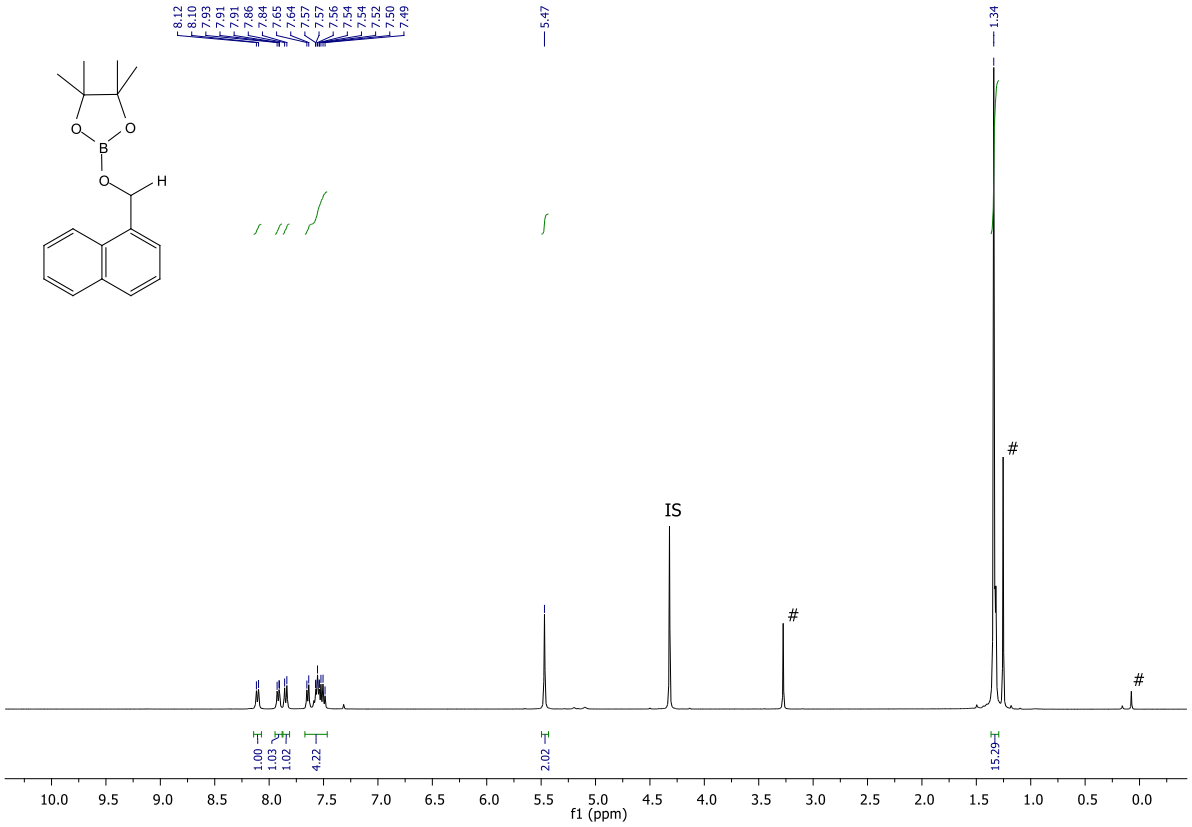


^{11}B NMR of **16b** (128 MHz, $CDCl_3$)

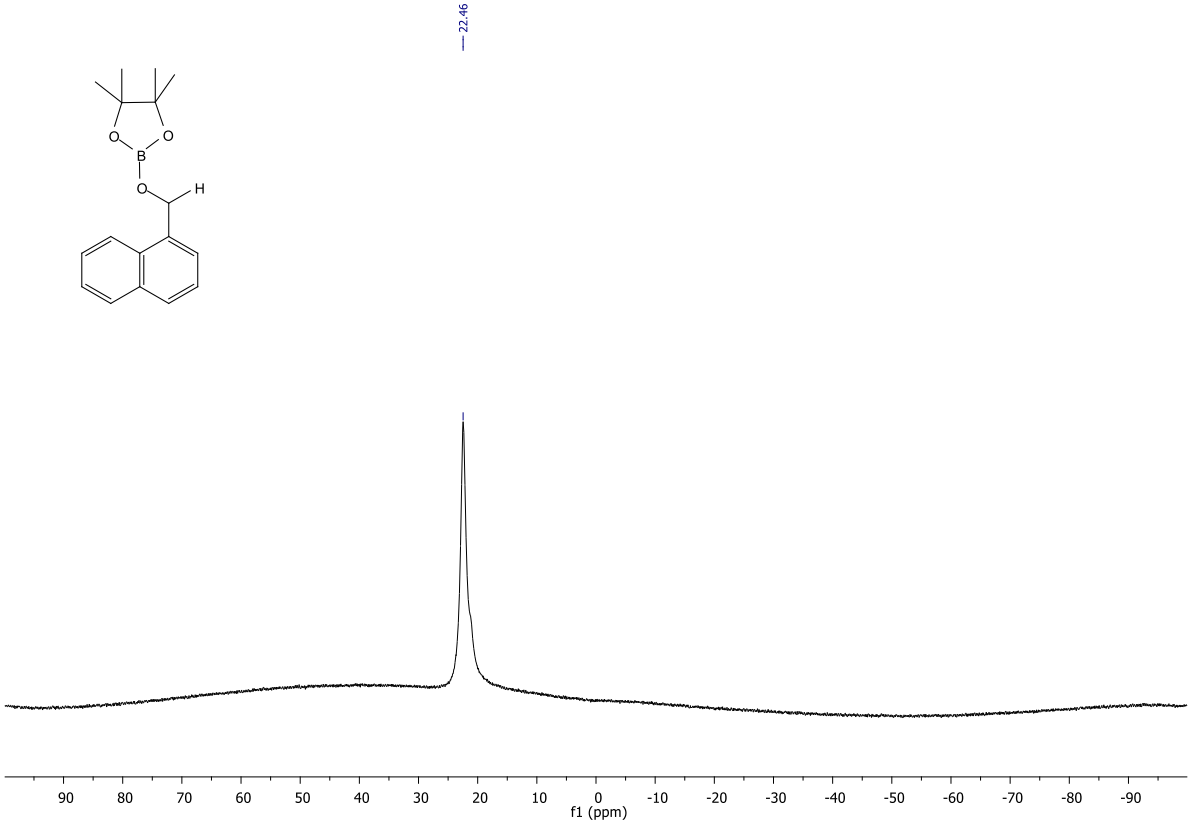


^{13}C NMR of **16b** (100 MHz, $CDCl_3$)

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

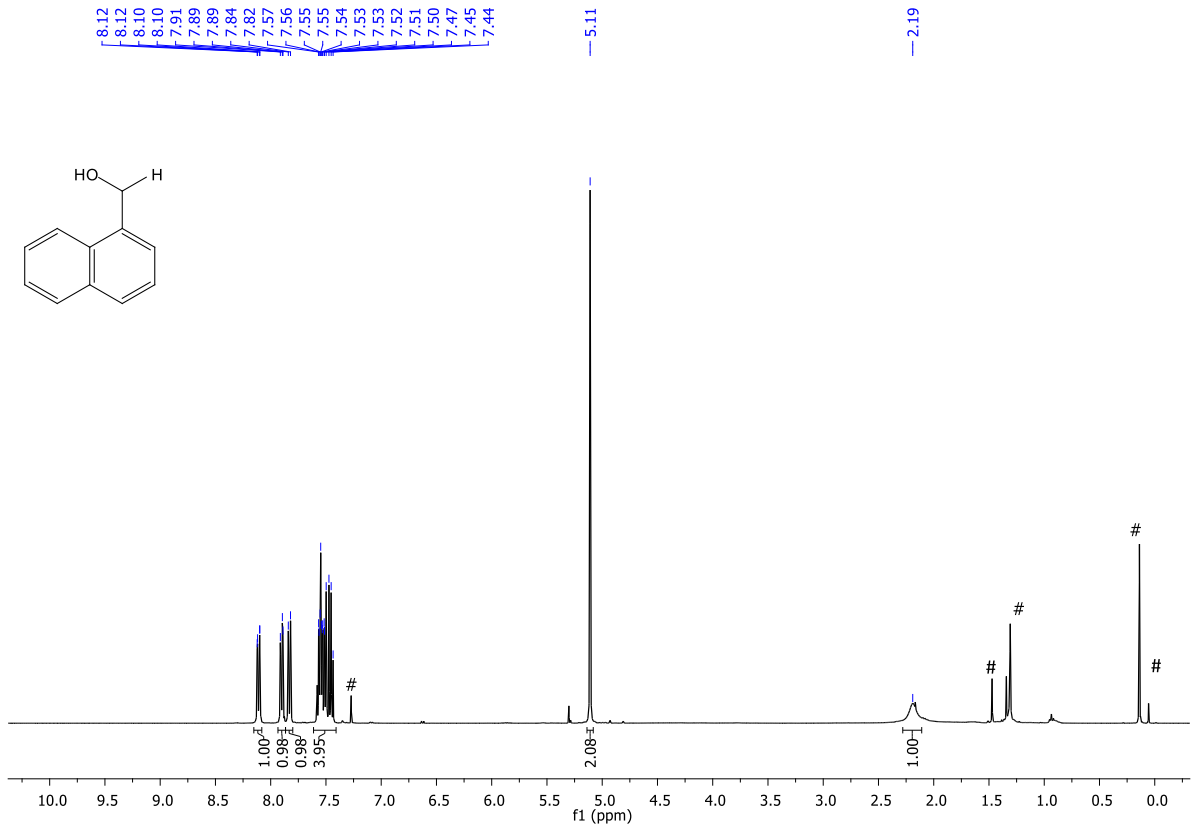


^{1}H NMR of **17b** (400 MHz, $CDCl_3$)

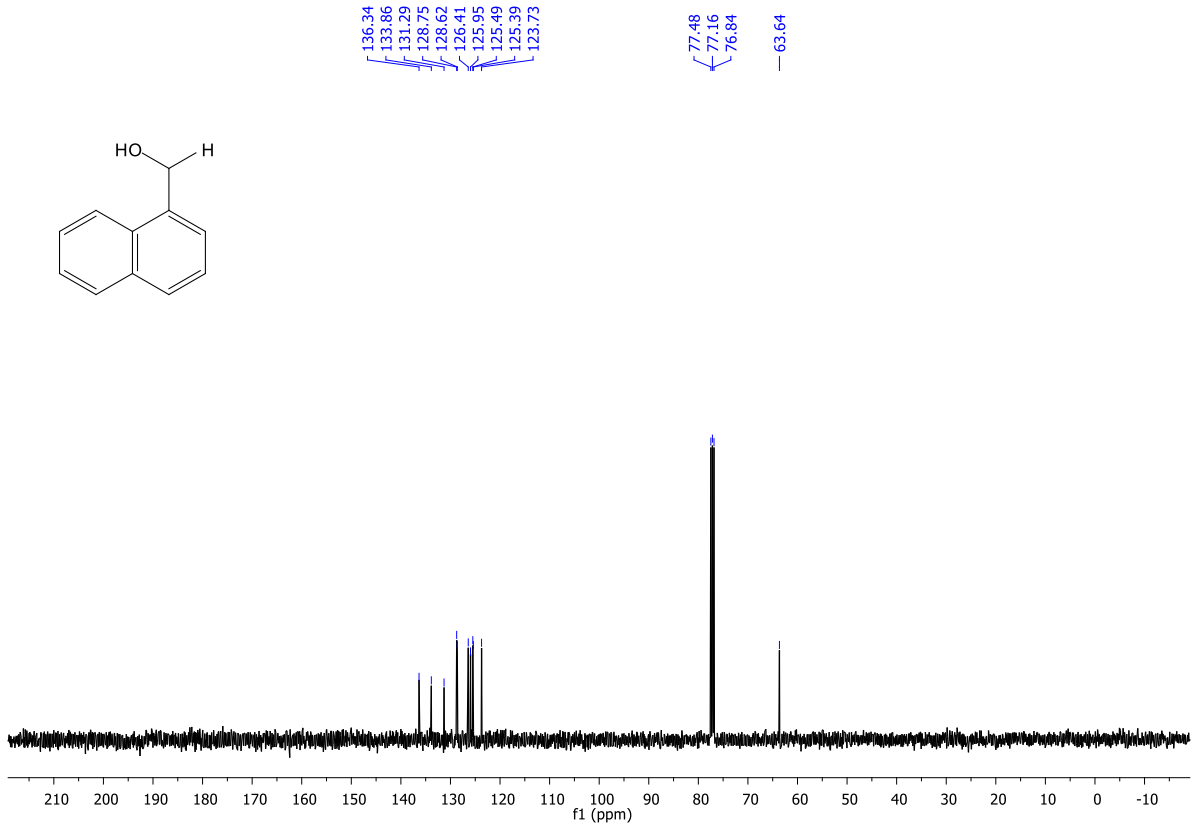


^{11}B NMR of **17b** (128 MHz, $CDCl_3$)

Naphthalen-1-ylmethanol (17c).[2]

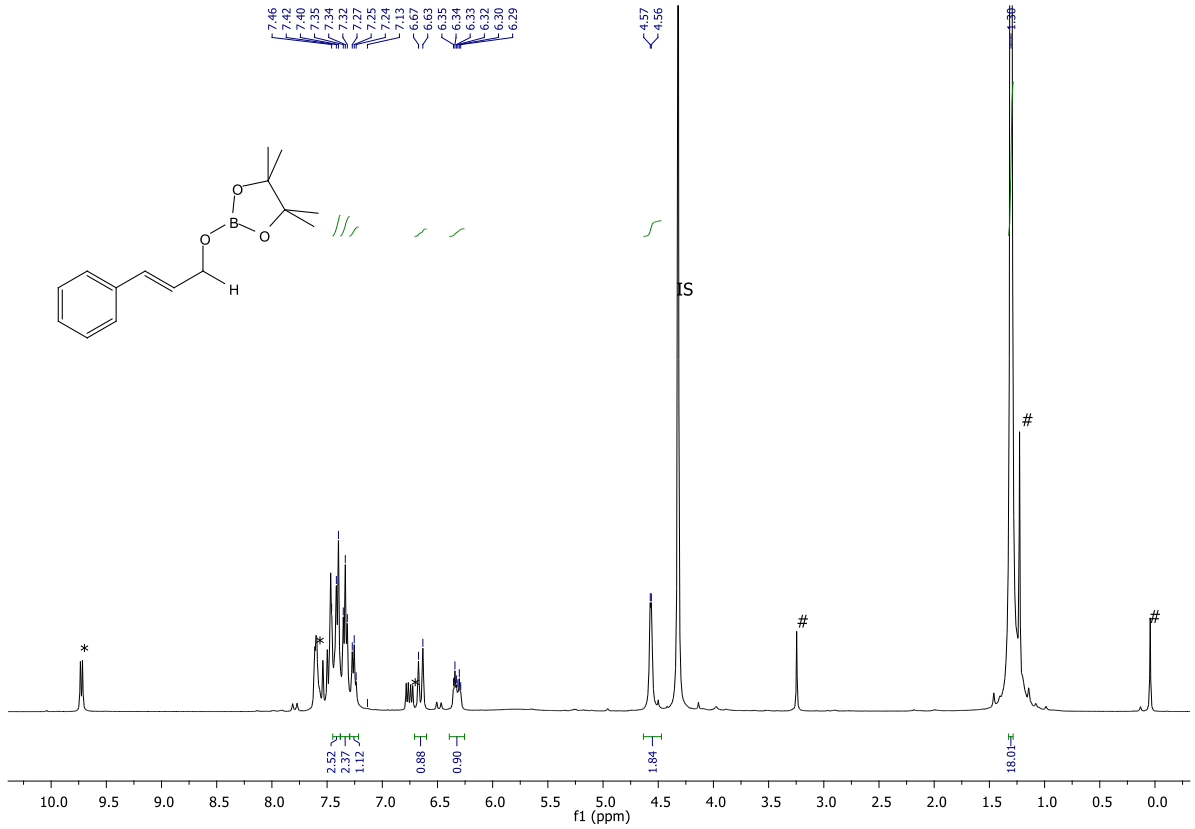


^{1}H NMR of **17c** (400 MHz, $CDCl_3$)

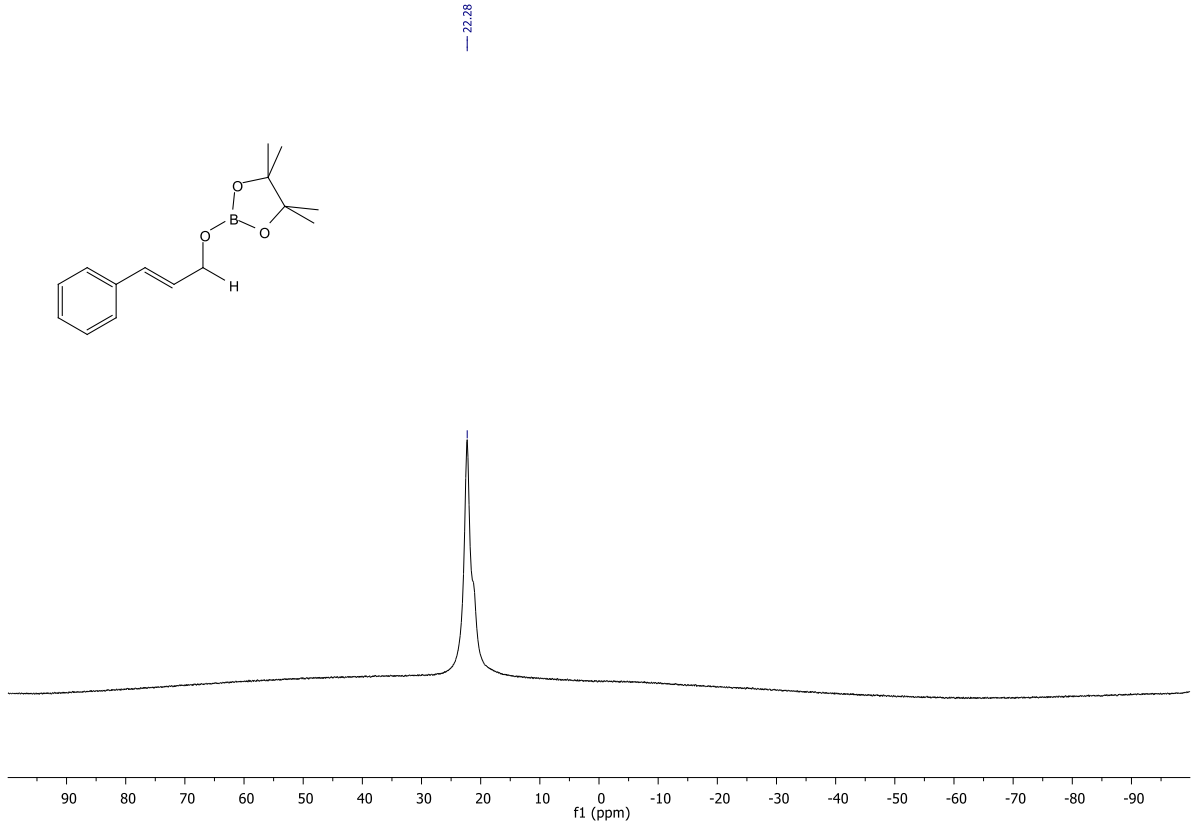


^{13}C NMR of **17c** (100 MHz, $CDCl_3$)

2-(Cinnamyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 18b).[2,6]

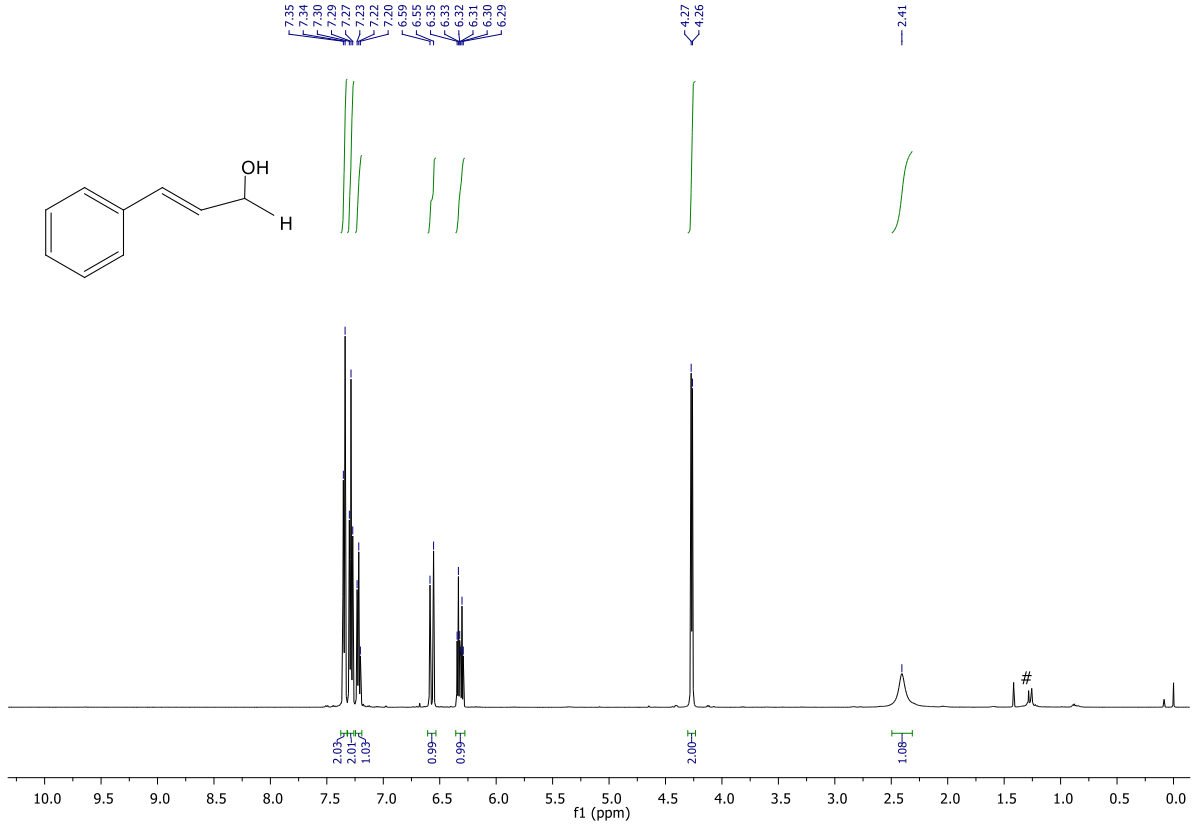


^{1}H NMR of **18b** (400 MHz, $CDCl_3$)

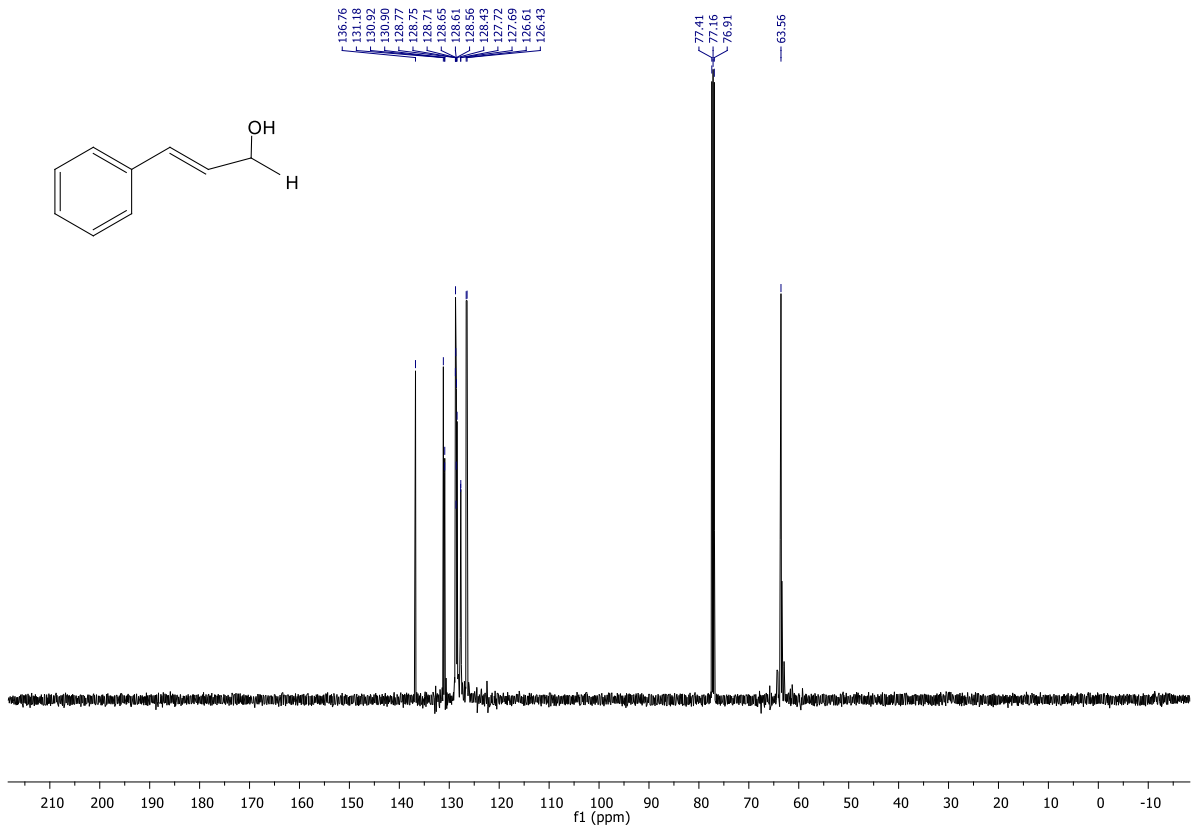


^{11}B NMR of **18b** (128 MHz, $CDCl_3$)

3-Phenyl-2-propene-1-ol (18c).[2]

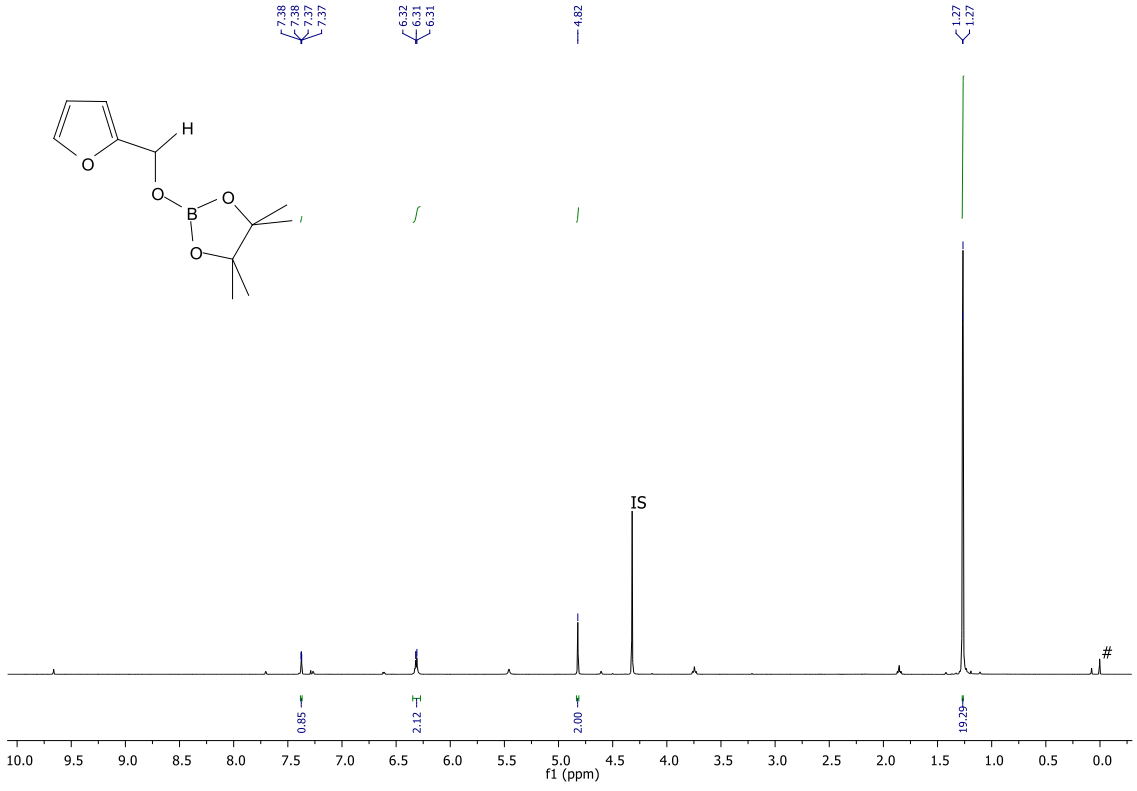


^{1}H NMR of **18c** (400 MHz, $CDCl_3$)

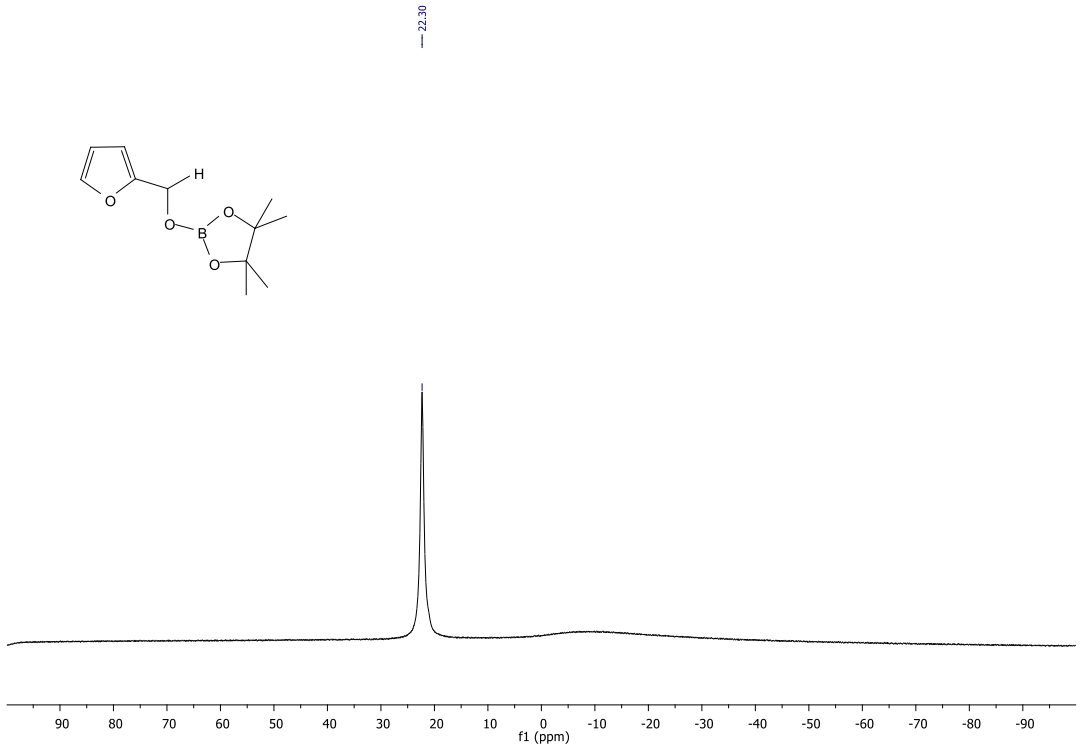


^{13}C NMR of **18c** (100 MHz, $CDCl_3$)

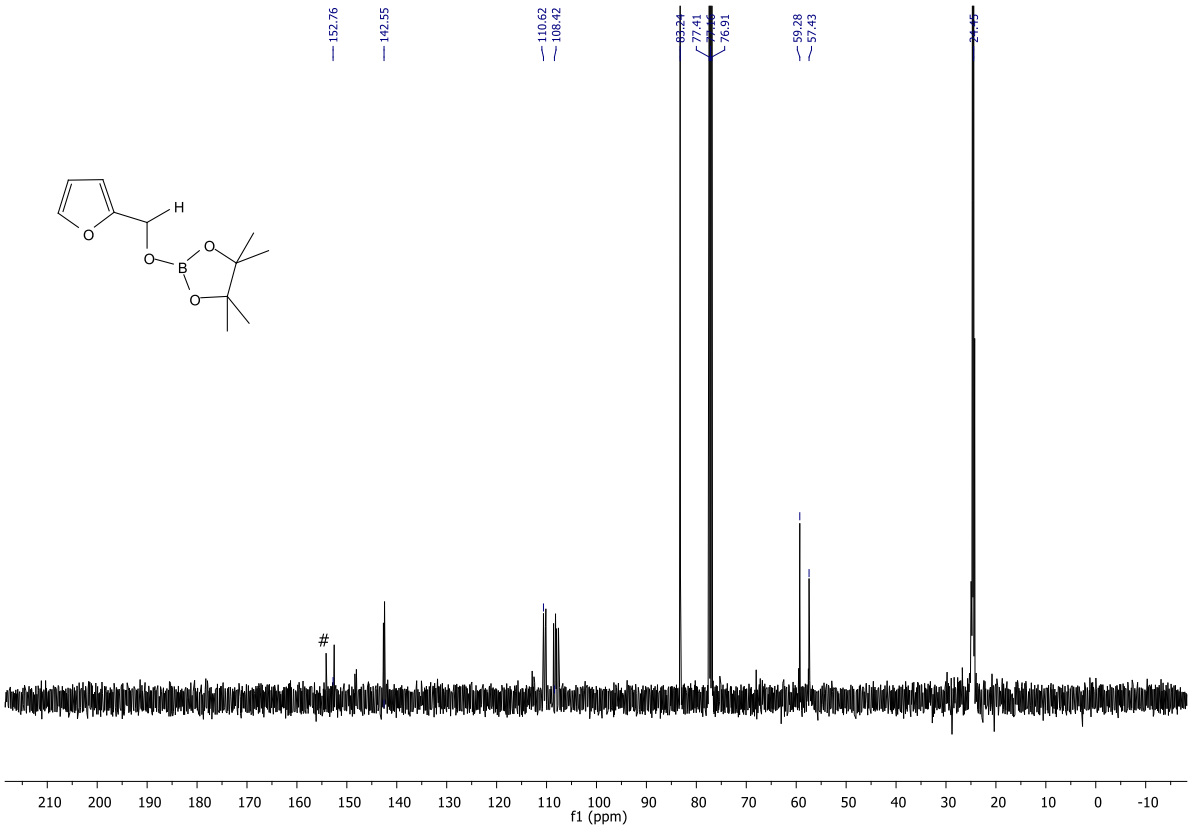
2-(Furan-2-ylmethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 19b).[2,6]



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

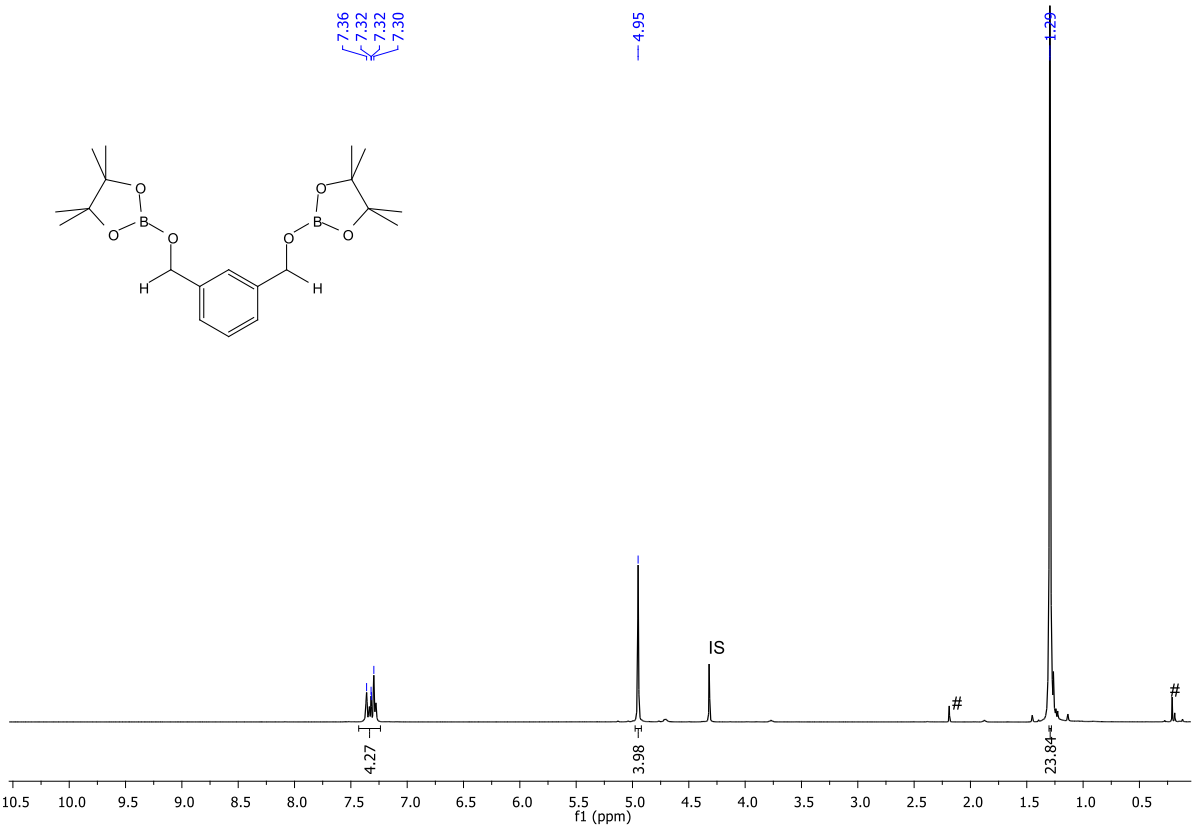


^{11}B NMR of **19b** (128 MHz, $CDCl_3$)

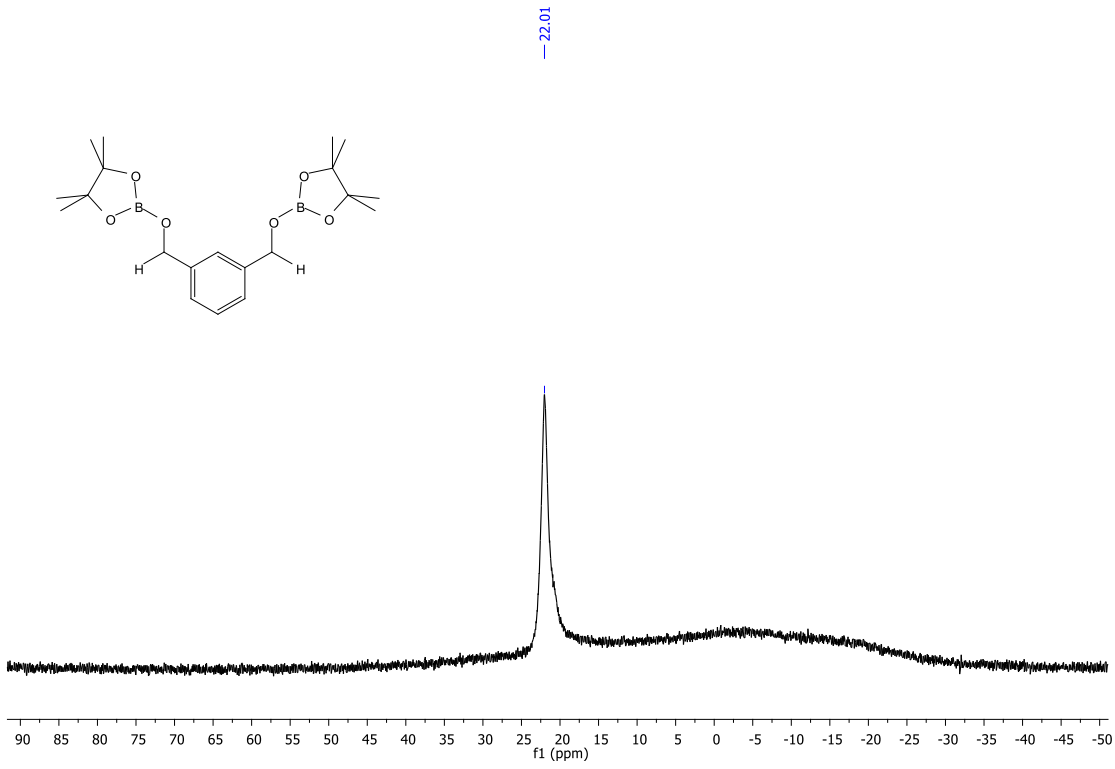


^{13}C NMR of **19b** (100 MHz, $CDCl_3$)

1,3-bis(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzene (Table 2, 20b).[2,3]

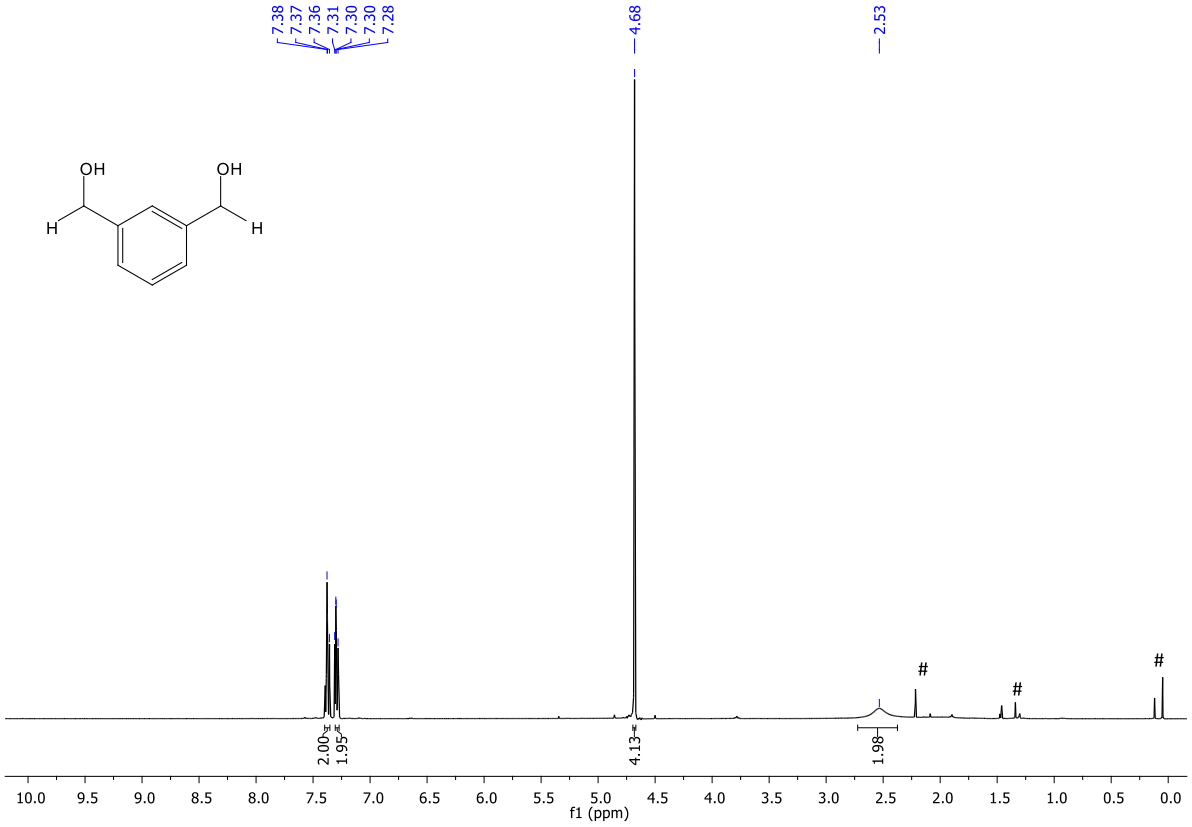


^{1}H NMR of **20b** (400 MHz, $CDCl_3$)

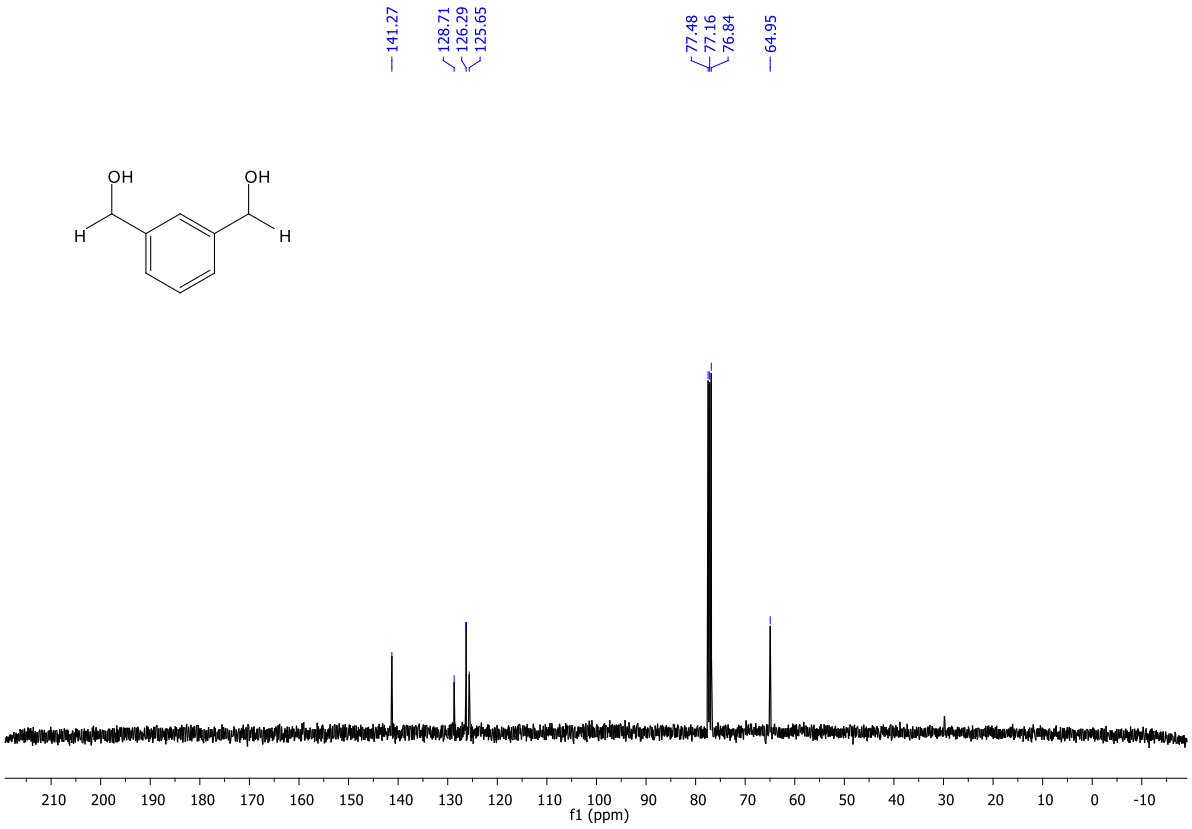


^{11}B NMR of **20b** (128 MHz, $CDCl_3$)

1,3-Phenylenedimethanol (**20c**)

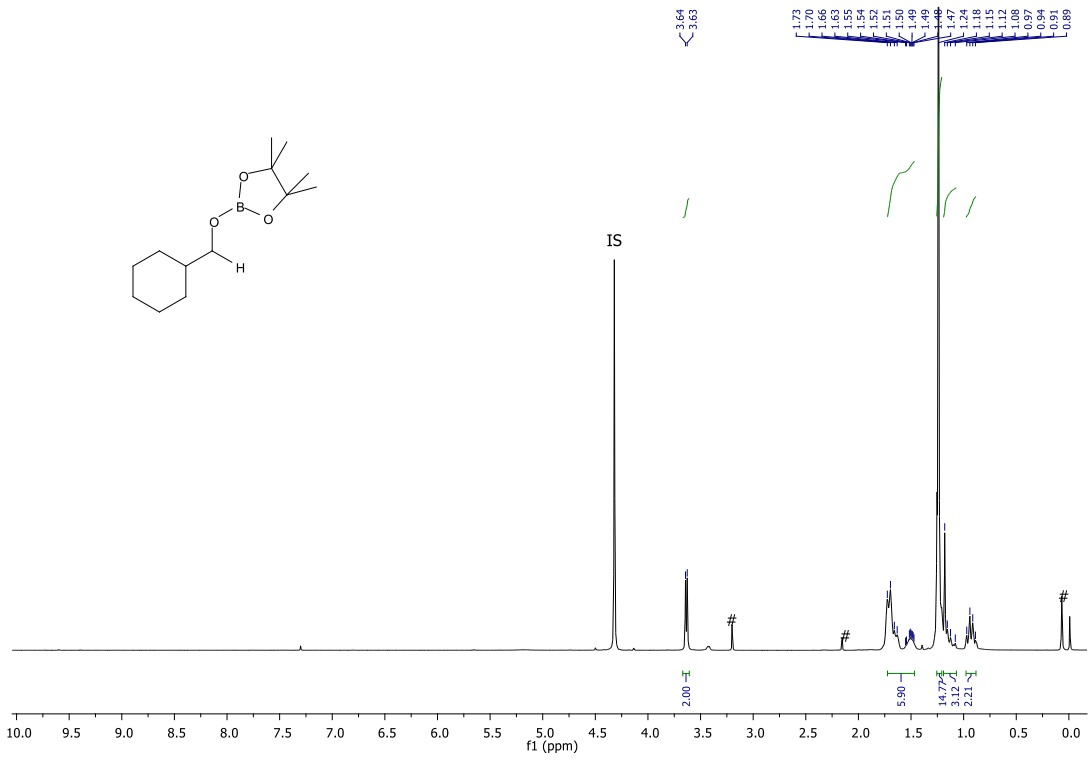


^{1}H NMR of **20c** (400 MHz, $CDCl_3$)

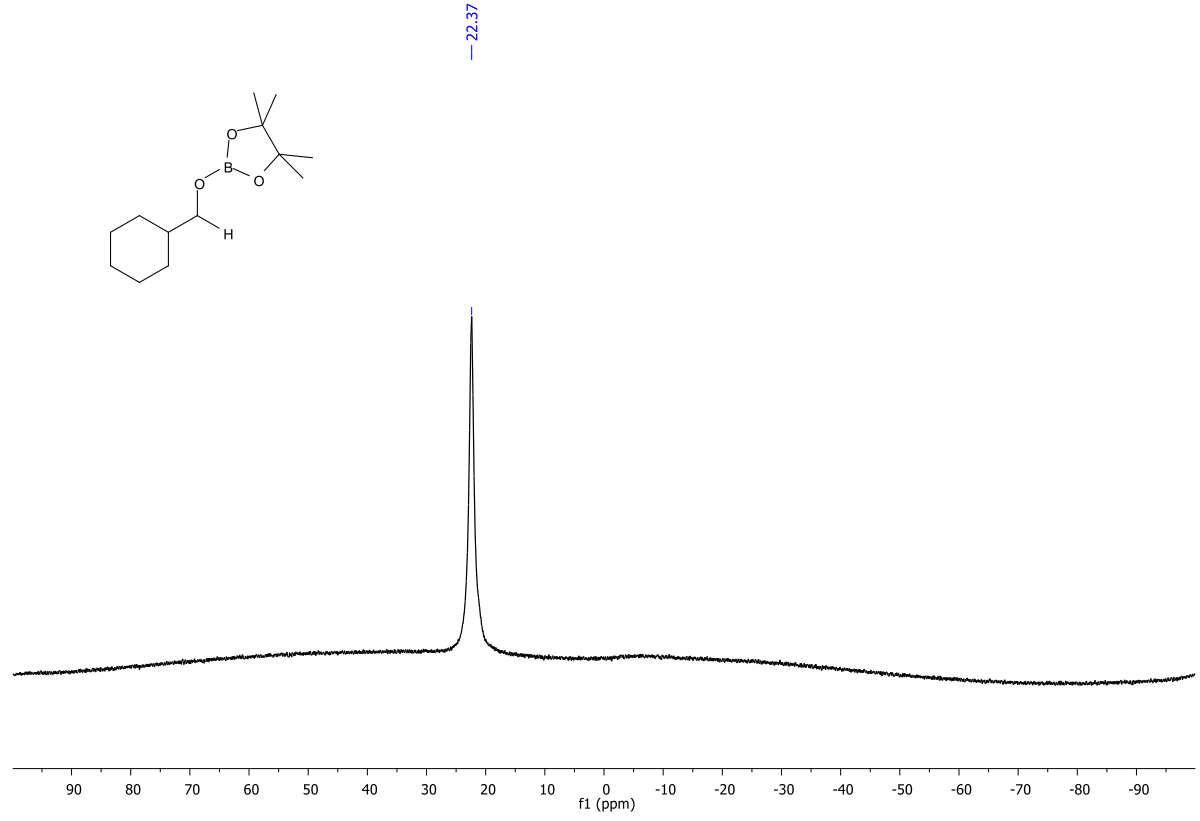


^{13}C NMR of **20b** (100 MHz, $CDCl_3$

2-(Cyclohexyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 21b).[12]

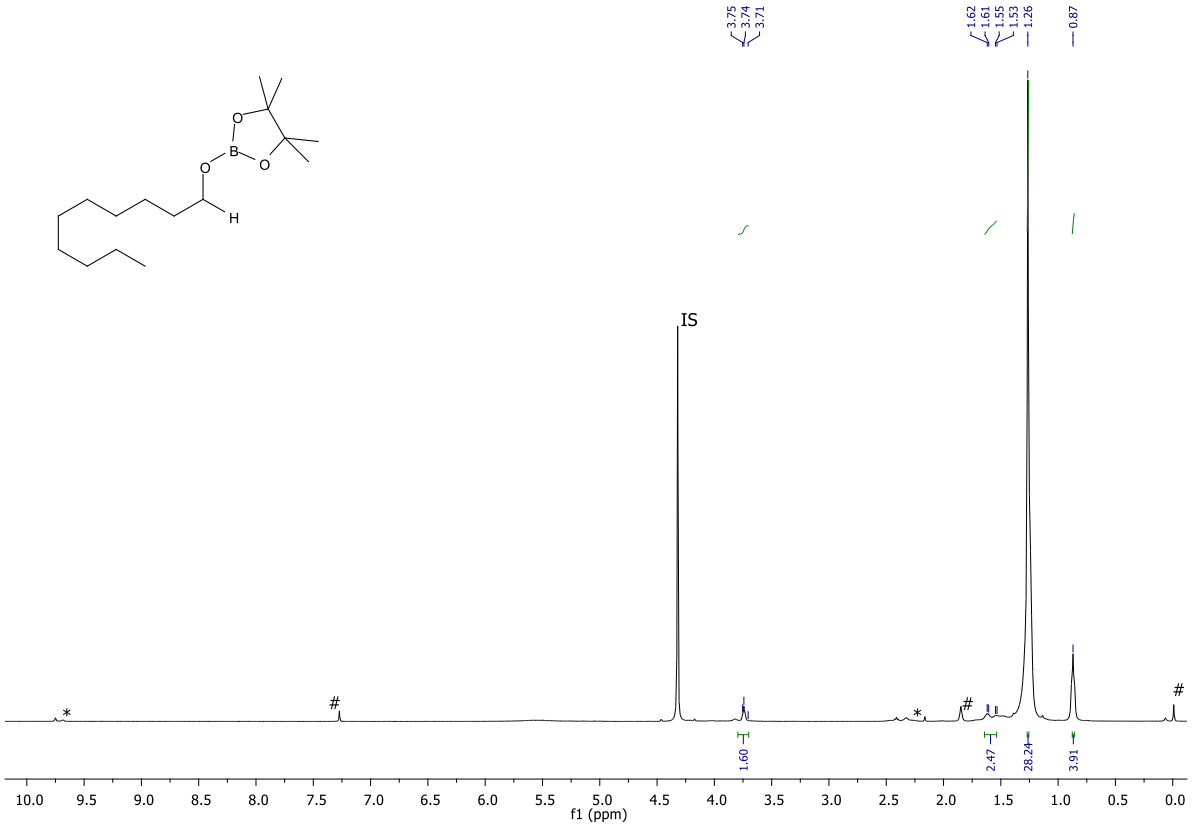


^{1}H NMR of **21b** (400 MHz, $CDCl_3$)

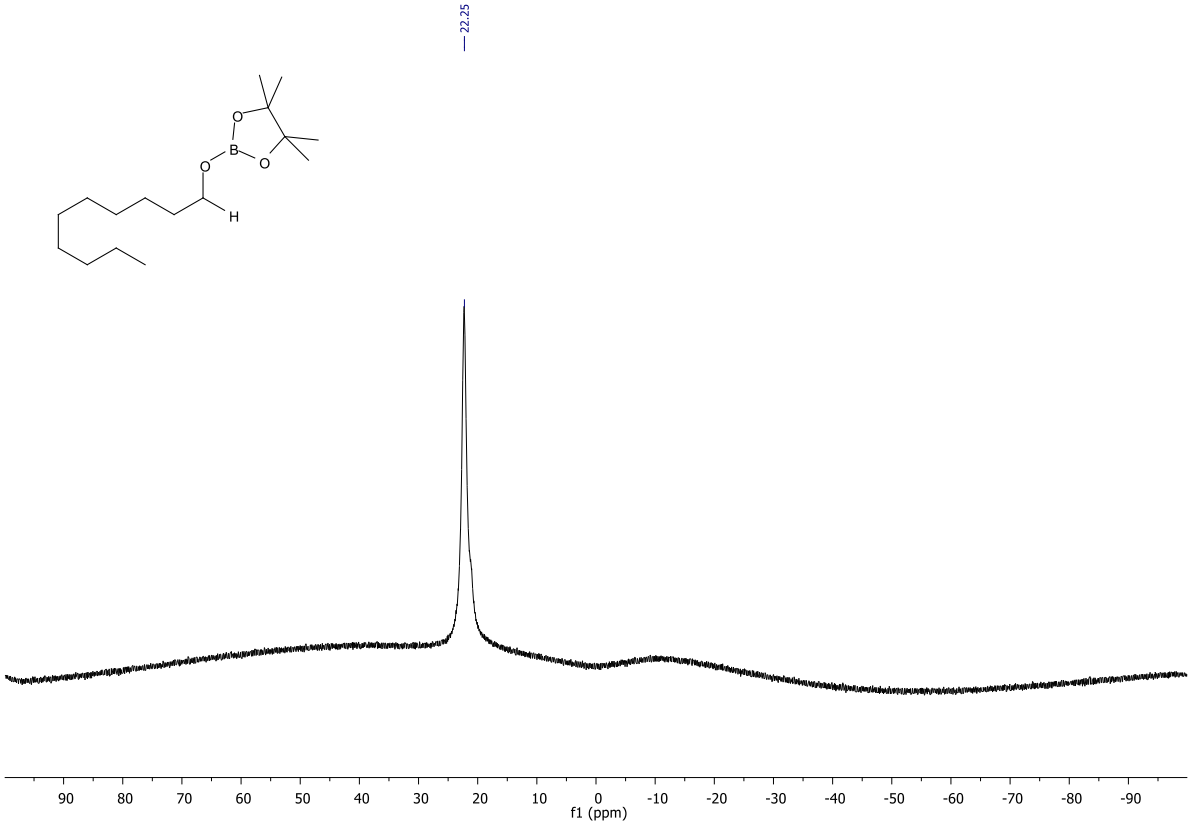


^{11}B NMR of **21b** (128 MHz, $CDCl_3$)

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

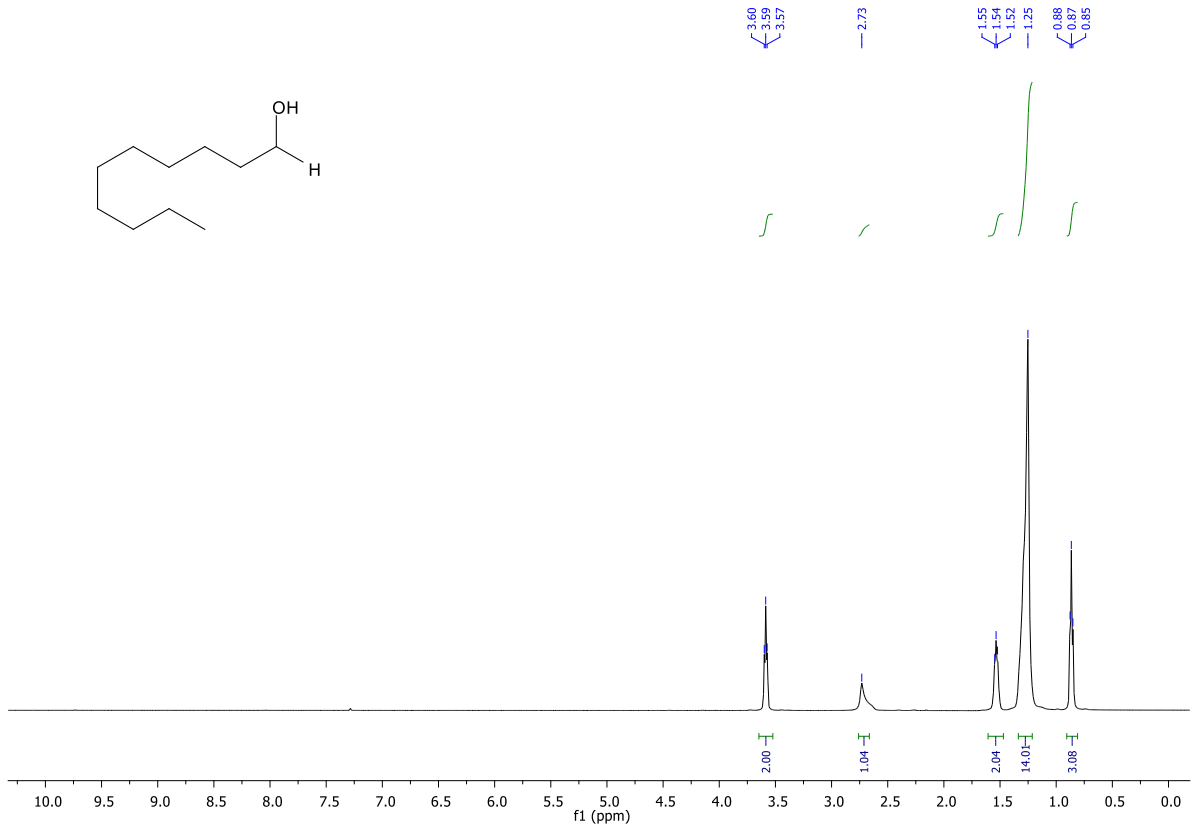


^{1}H NMR of **22b** (400 MHz, $CDCl_3$)

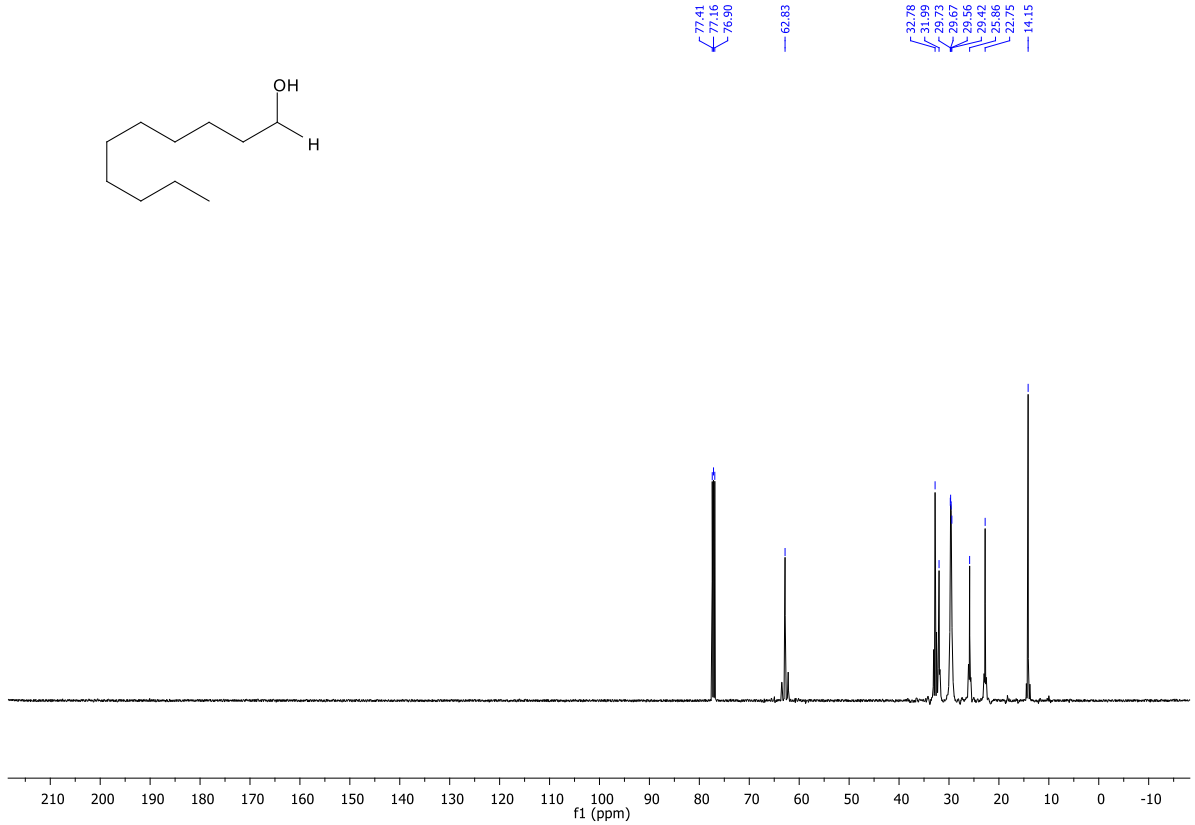


^{11}B NMR of **22b** (128 MHz, $CDCl_3$)

Decan-1-ol (22c).[2,4]

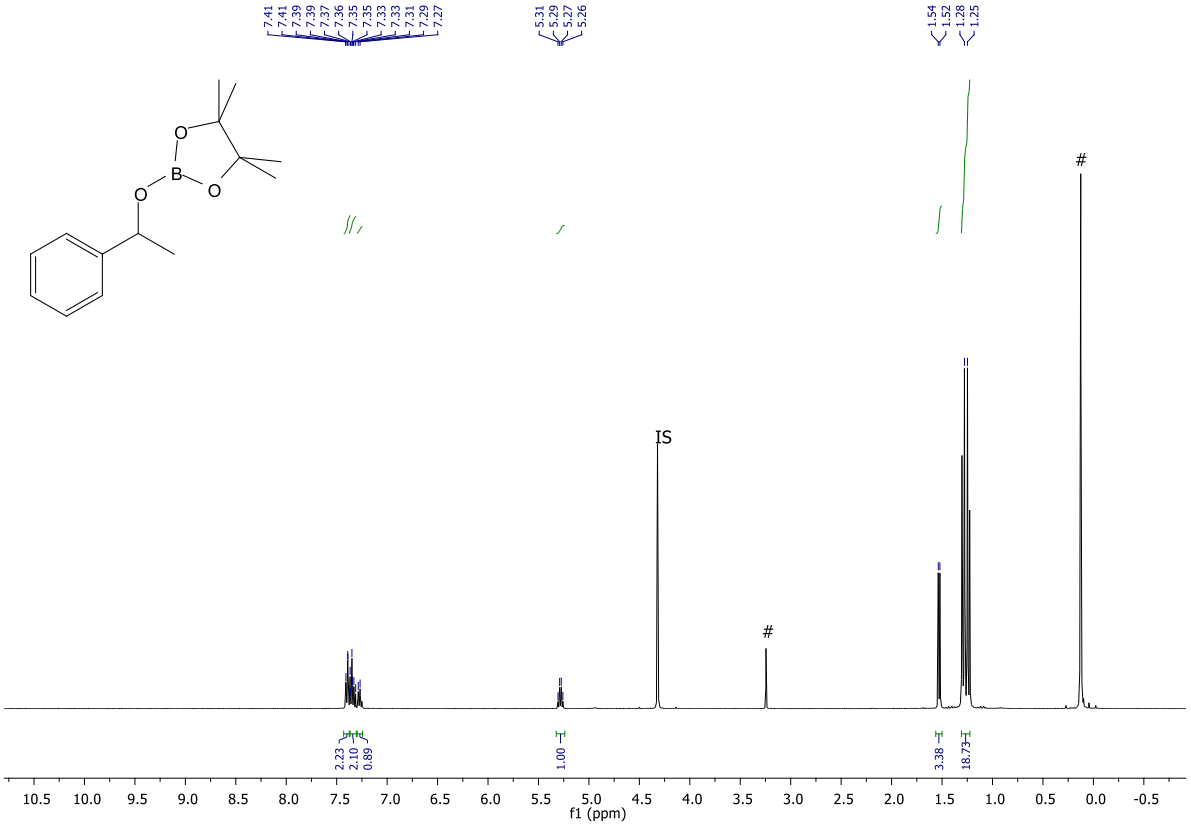


^{1}H NMR of **22c** (400 MHz, $CDCl_3$)

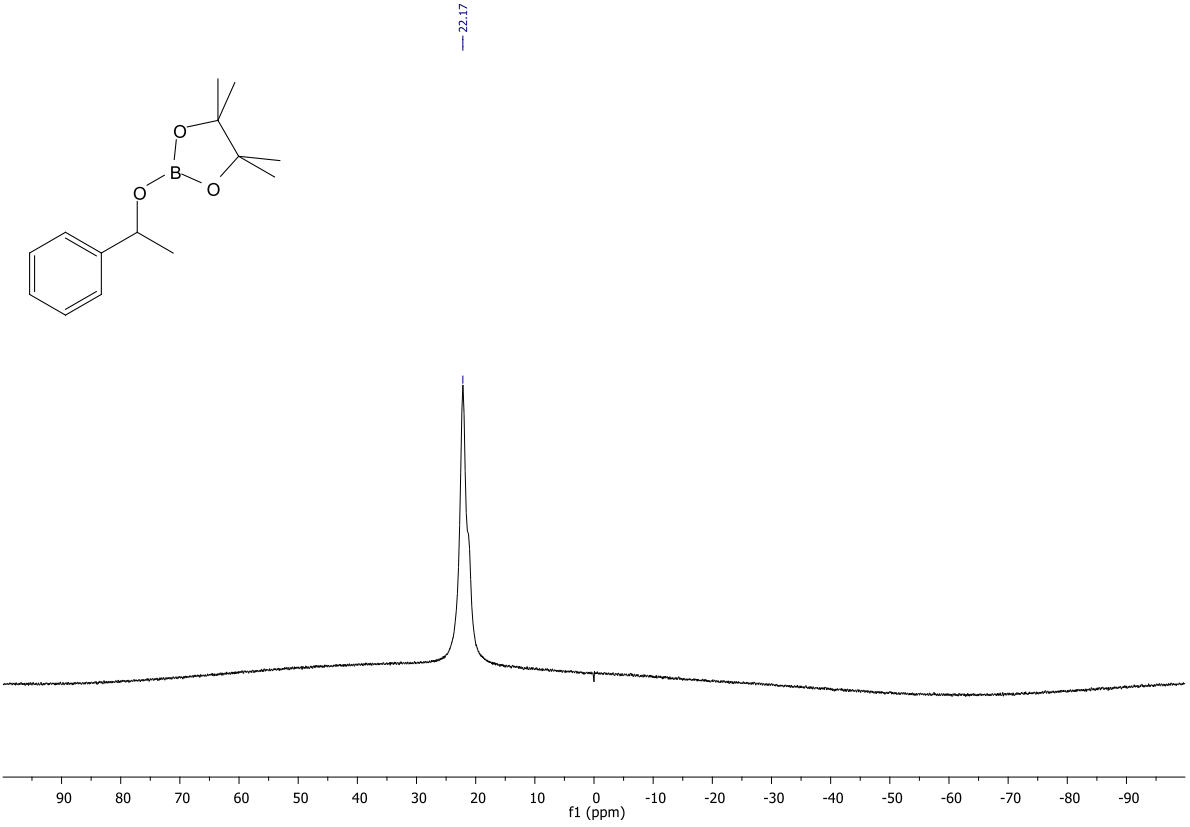


^{13}C NMR of **22c** (100 MHz, $CDCl_3$)

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

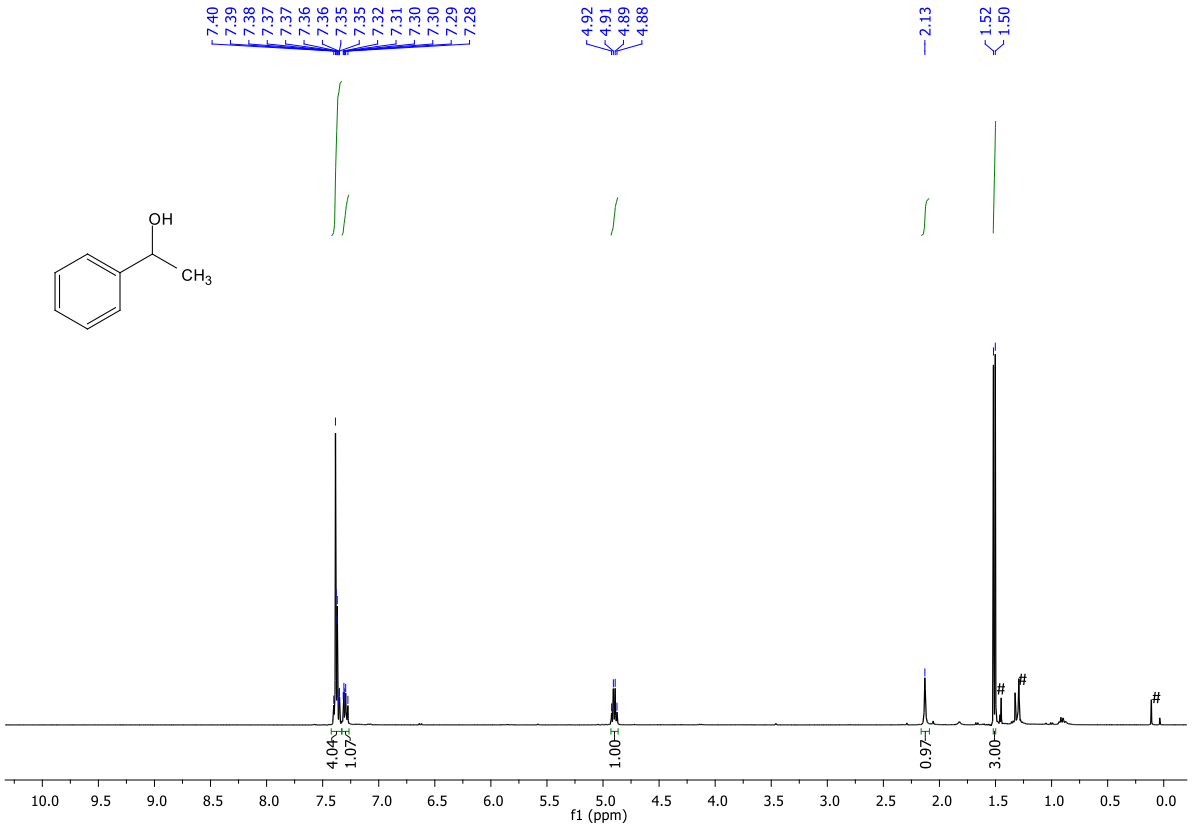


^{1}H NMR of **23b** (400 MHz, $CDCl_3$)

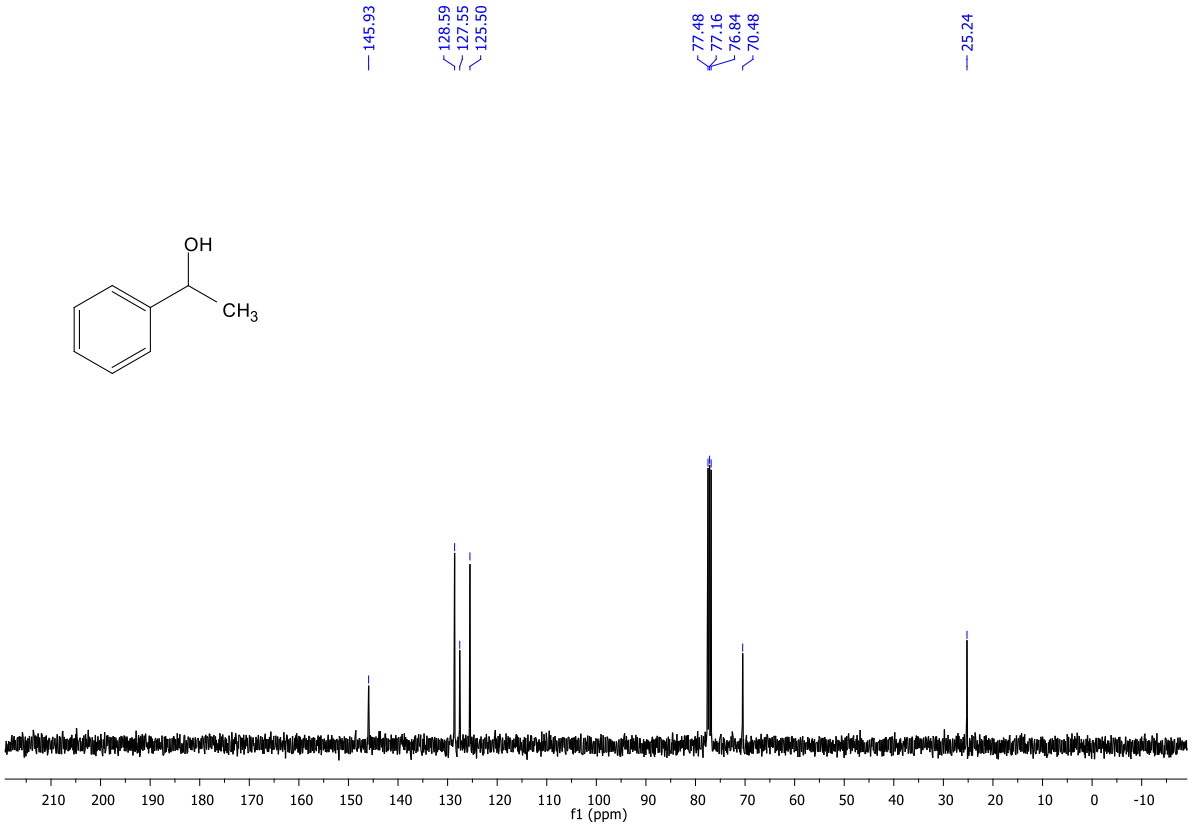


^{11}B NMR of **23b** (128 MHz, $CDCl_3$)

1-Phenylethanol (23c).[2,4]

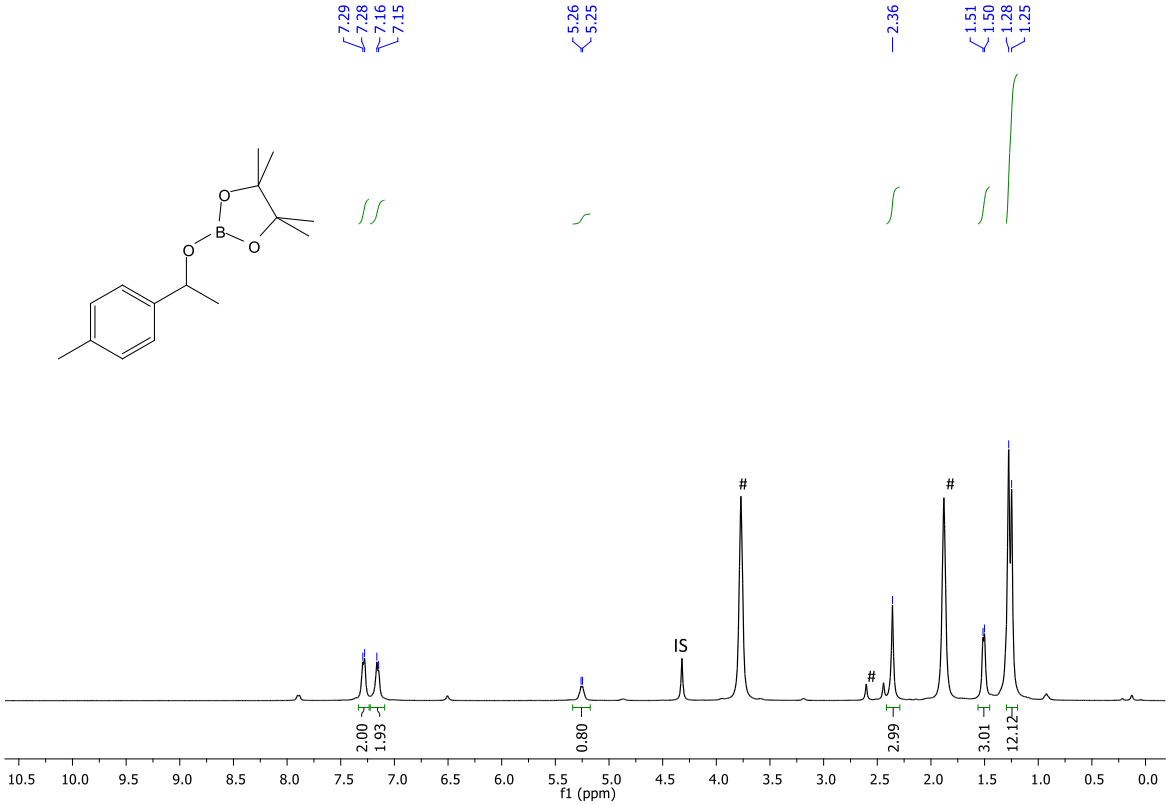


^{1}H NMR of **23c** (400 MHz, $CDCl_3$)

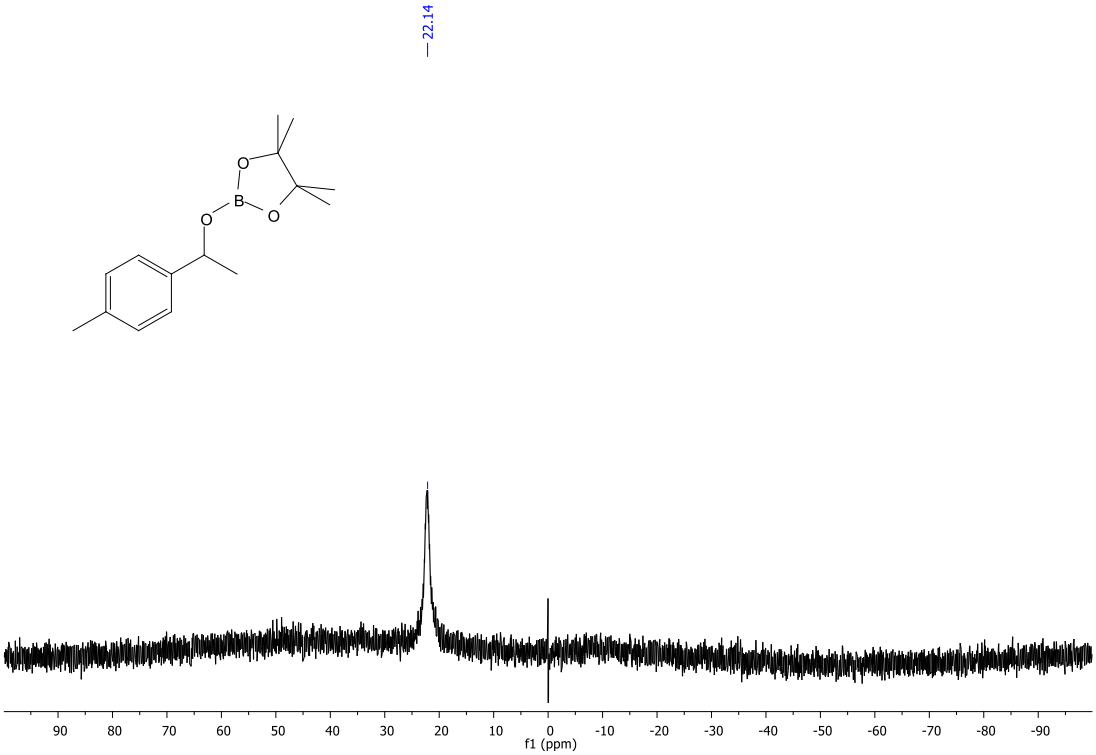


^{13}C NMR of **23c** (100 MHz, $CDCl_3$)

4,4,5,5-Tetramethyl-2-(1-(p-tolyl)ethoxy)-1,3,2-dioxaborolane (Table 3, 24b).[2,3]

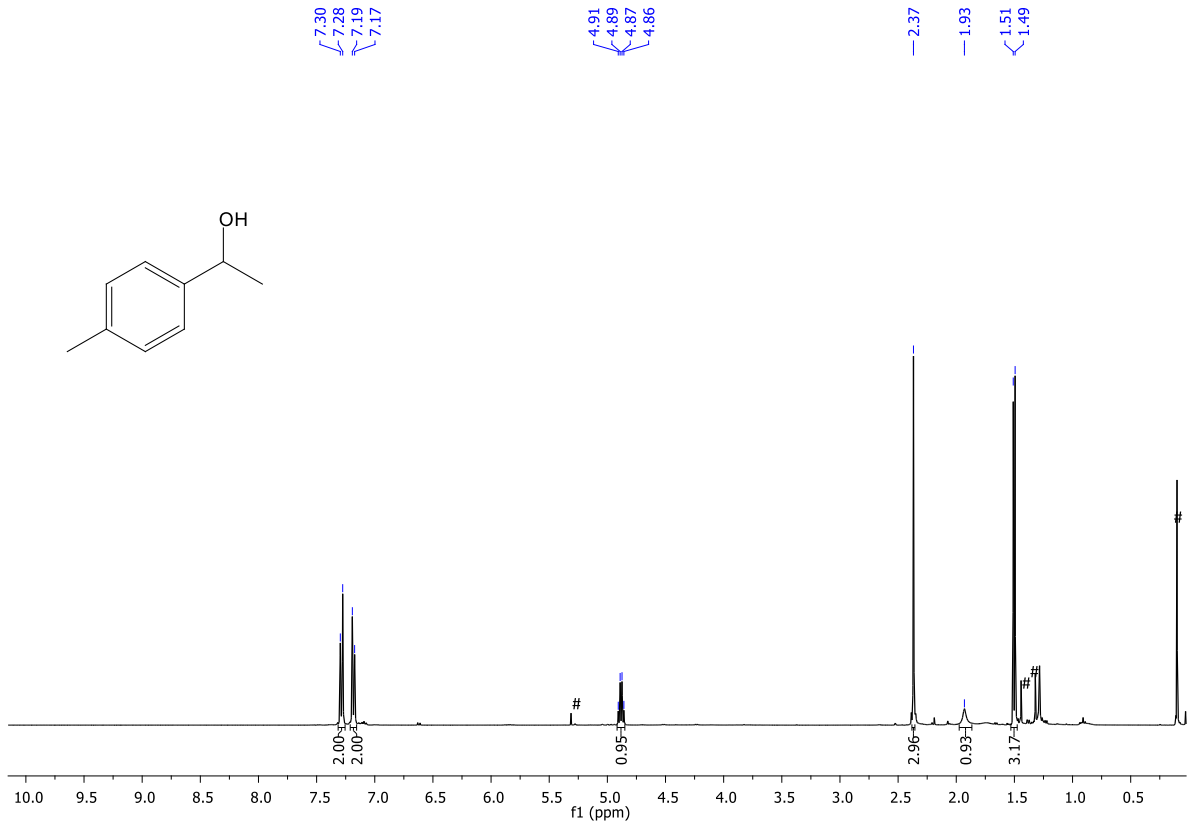


^{1}H NMR of **24b** (400 MHz, $CDCl_3$)

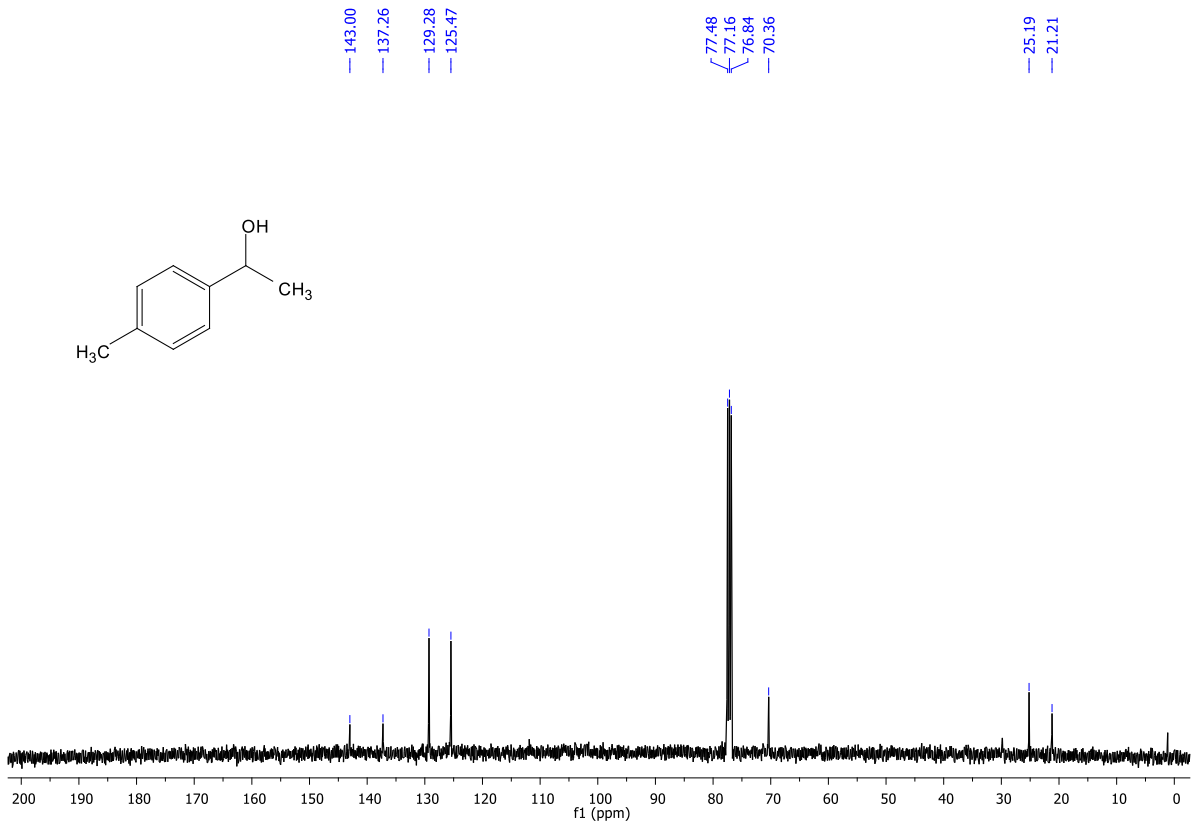


^{11}B NMR of **24b** (128 MHz, $CDCl_3$)

1-(p-Tolyl)ethanol (24c).[2,4]

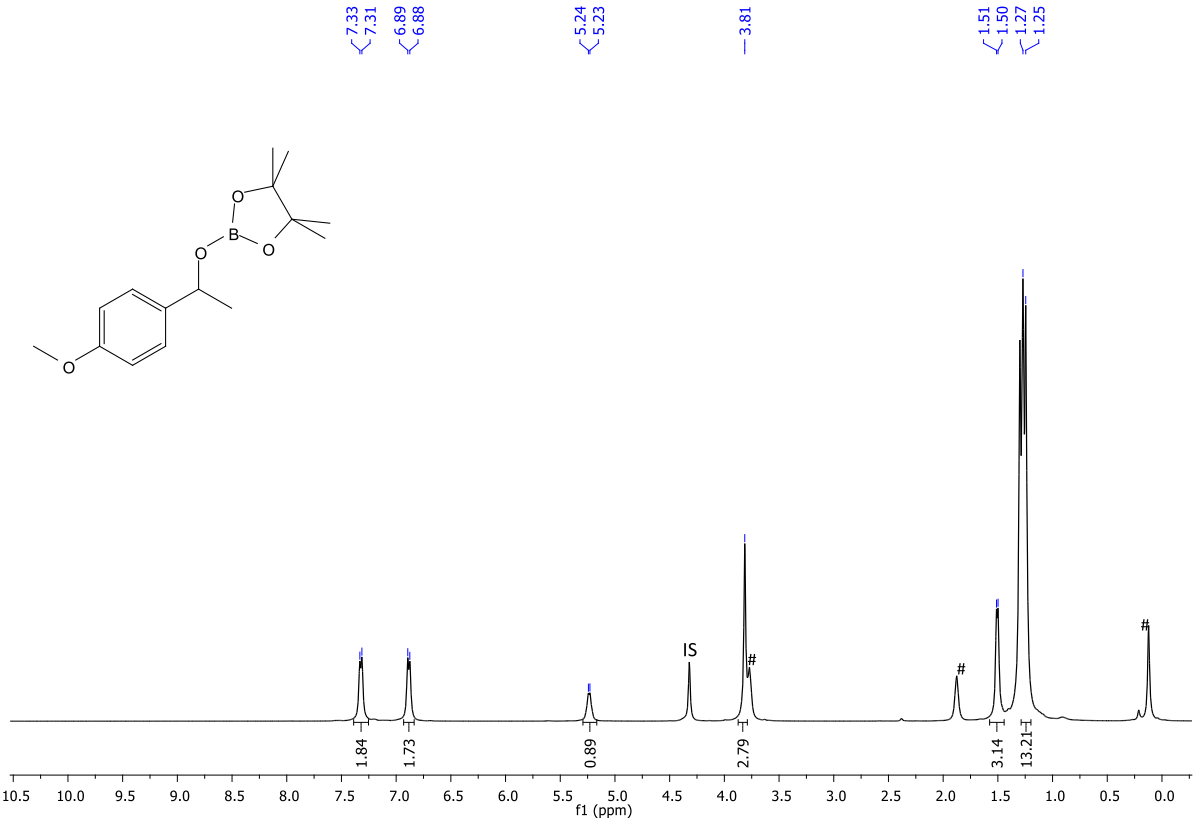


^{1}H NMR of **24c** (400 MHz, $CDCl_3$)

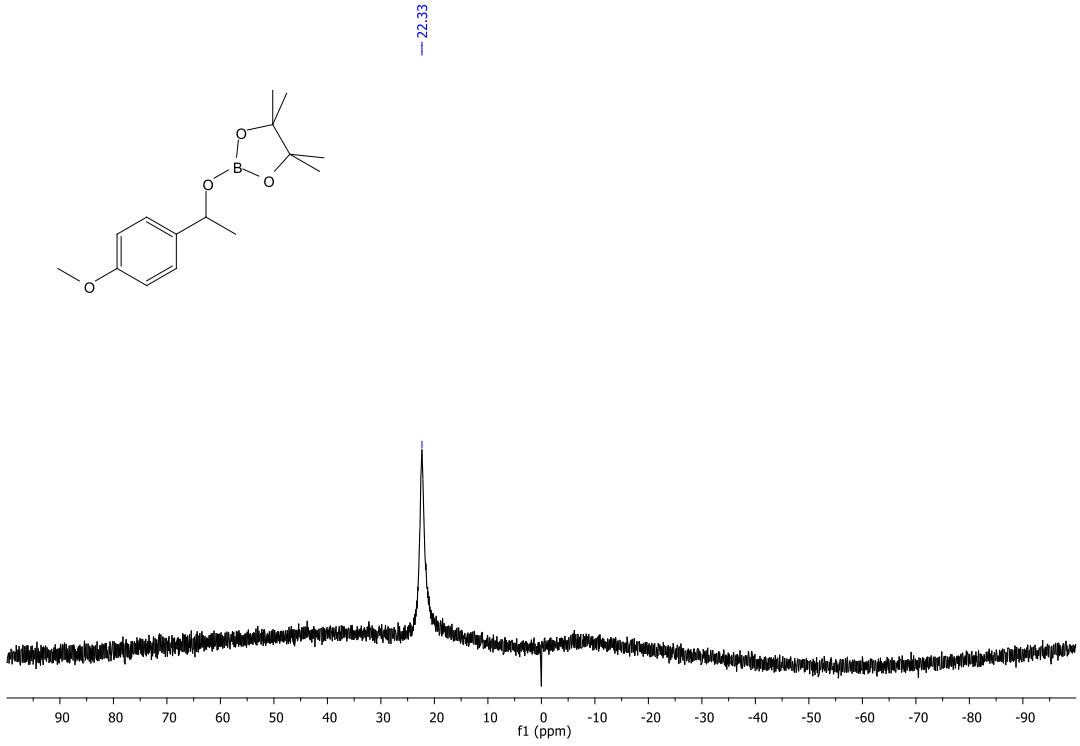


^{13}C NMR of **24c** (100 MHz, $CDCl_3$)

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

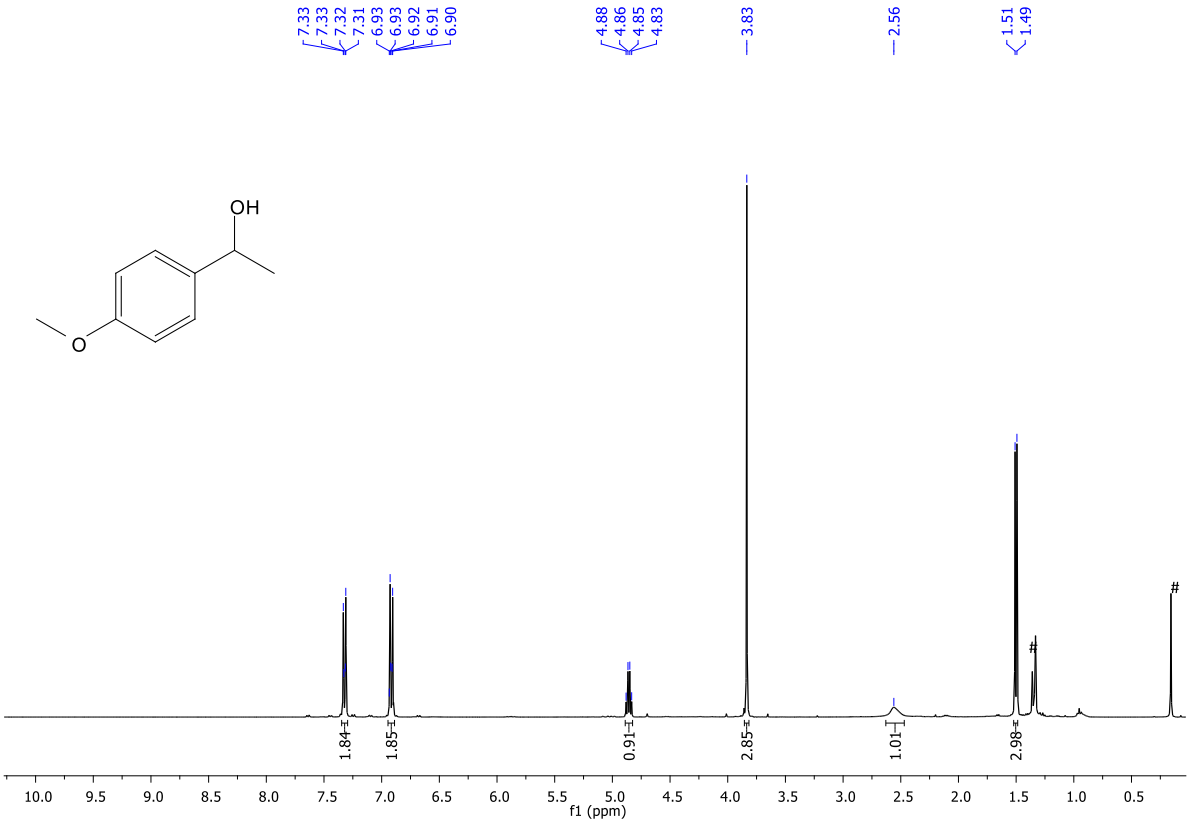


^{1}H NMR of **25b** (400 MHz, $CDCl_3$)

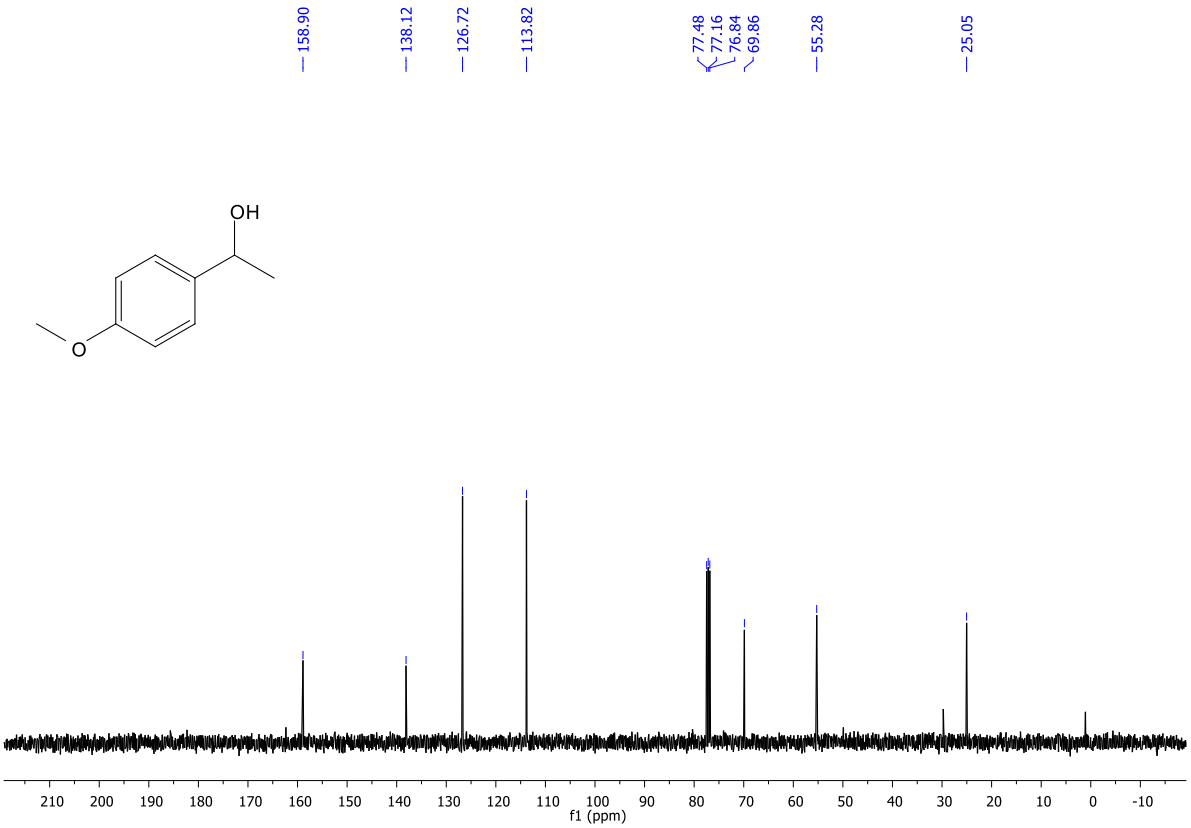


^{11}B NMR of **25b** (128 MHz, $CDCl_3$)

1-(4-Methoxyphenyl)ethanol (Table 3, 25c).[2]

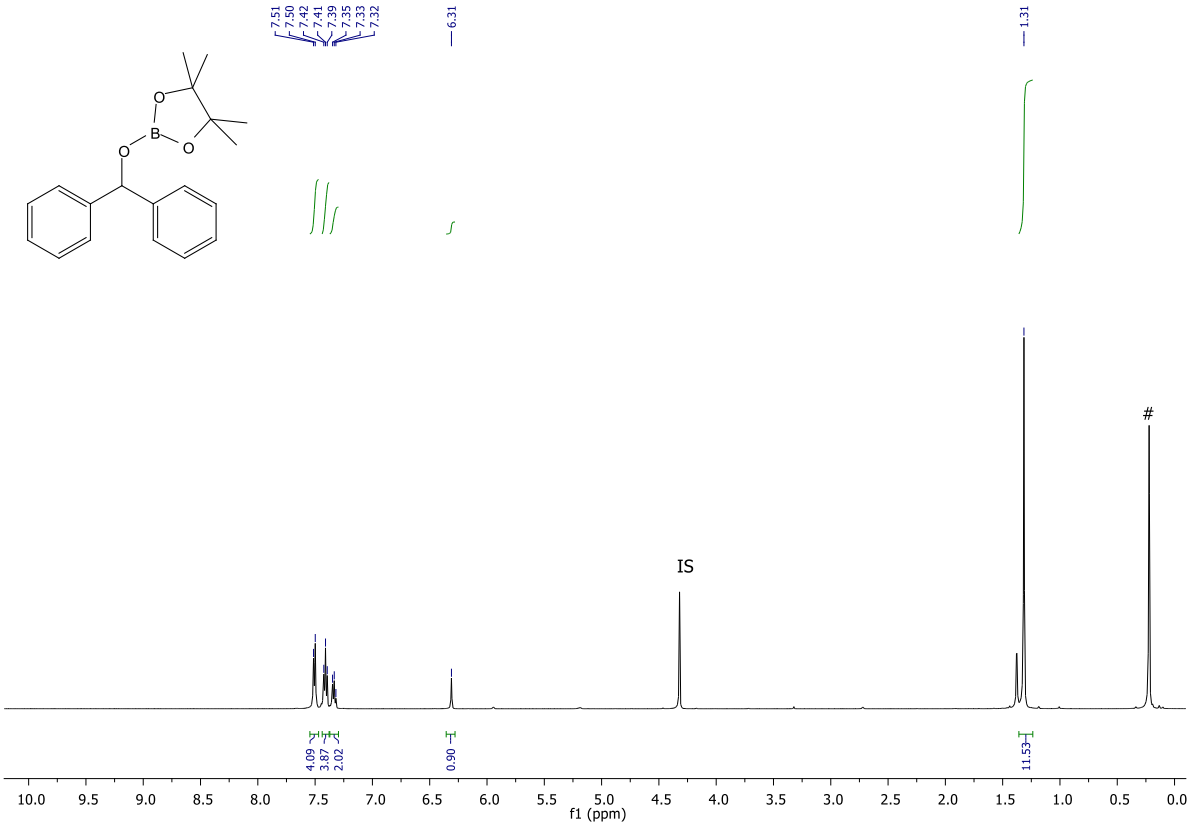


^{1}H NMR of **25c** (400 MHz, $CDCl_3$)

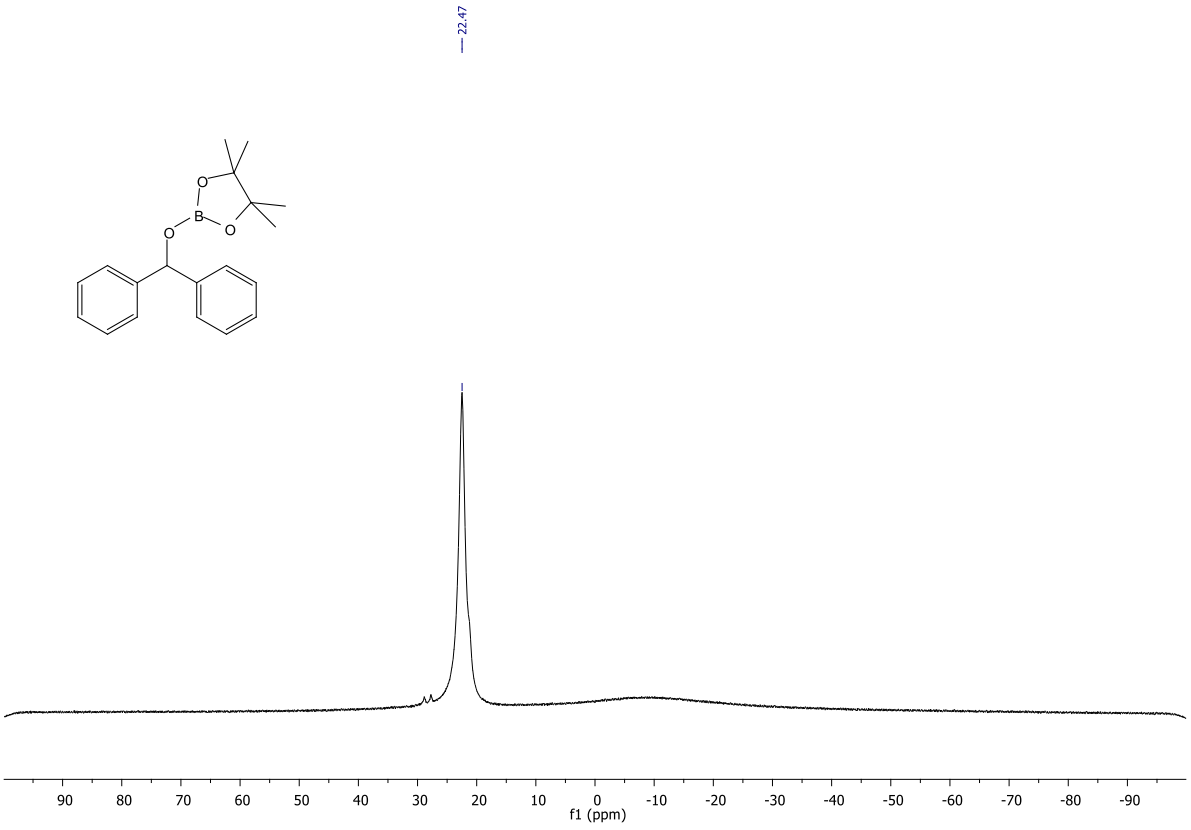


^{13}C NMR of **25c** (100 MHz, $CDCl_3$)

2-(Benzhydryloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 26b).[2,6]

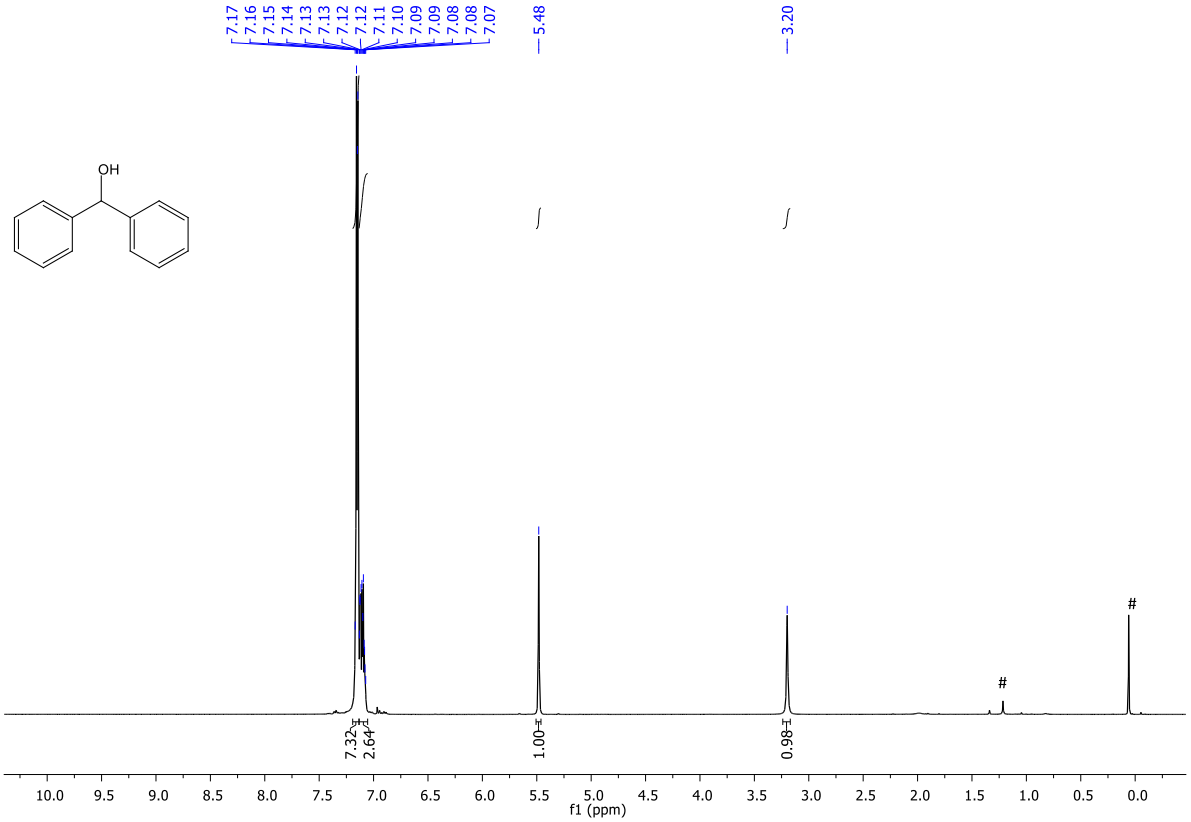


^{1}H NMR of **26b** (400 MHz, $CDCl_3$)

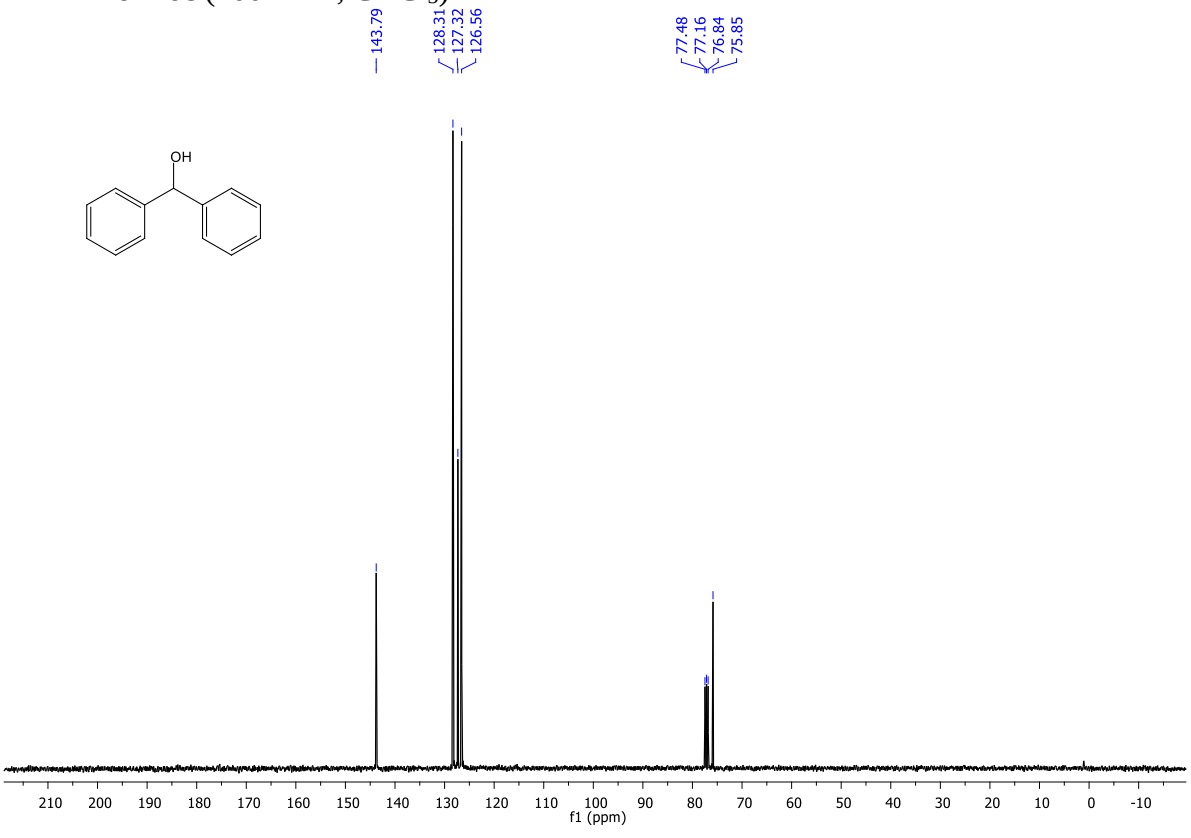


^{11}B NMR of **26b** (128 MHz, $CDCl_3$)

Diphenylmethanol (Table 3, 26c).[2]

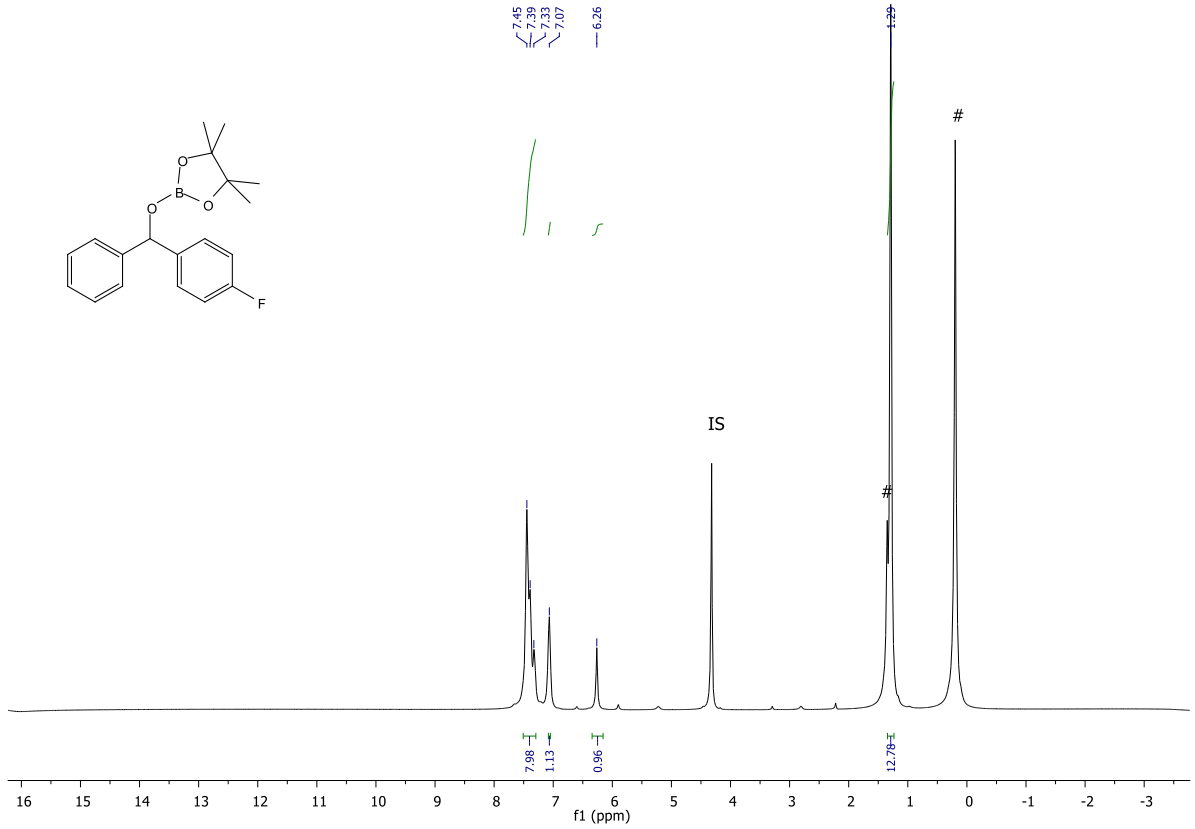


^{1}H NMR of **26c** (400 MHz, $CDCl_3$)

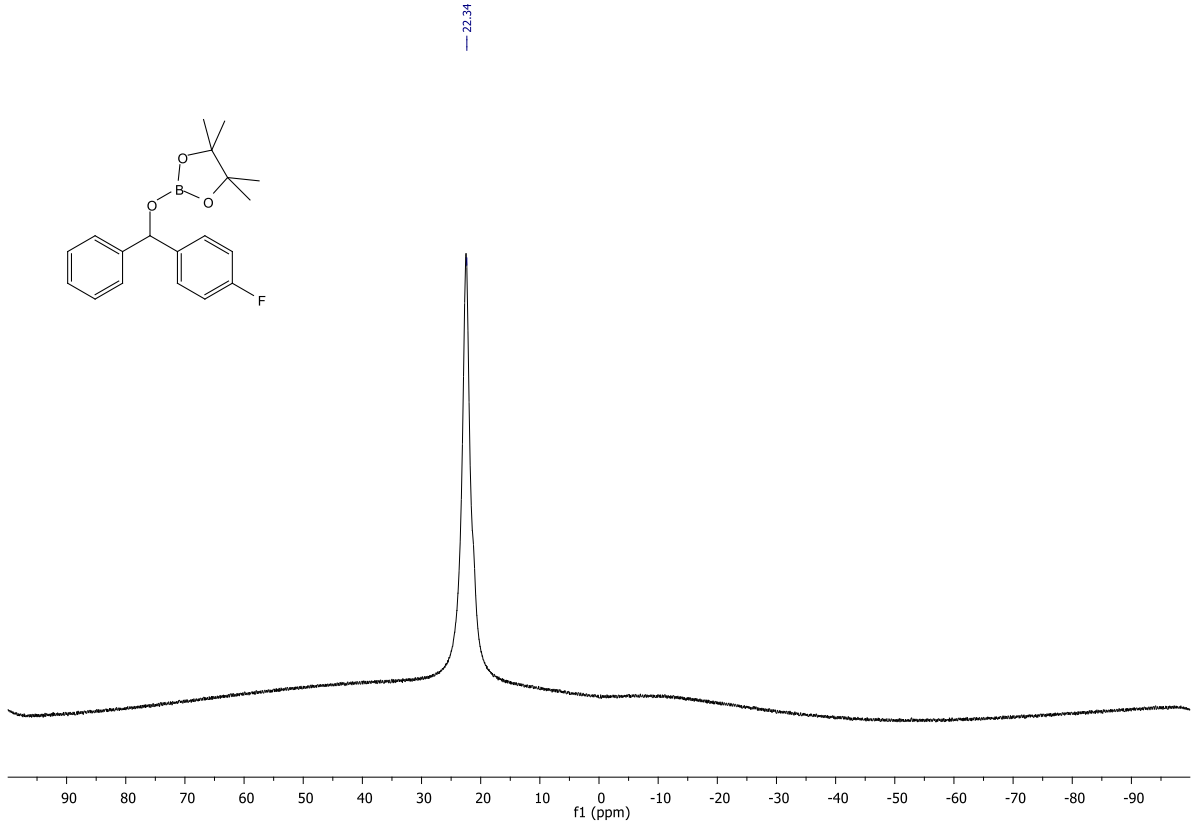


^{13}C NMR of **26c** (100 MHz, $CDCl_3$)

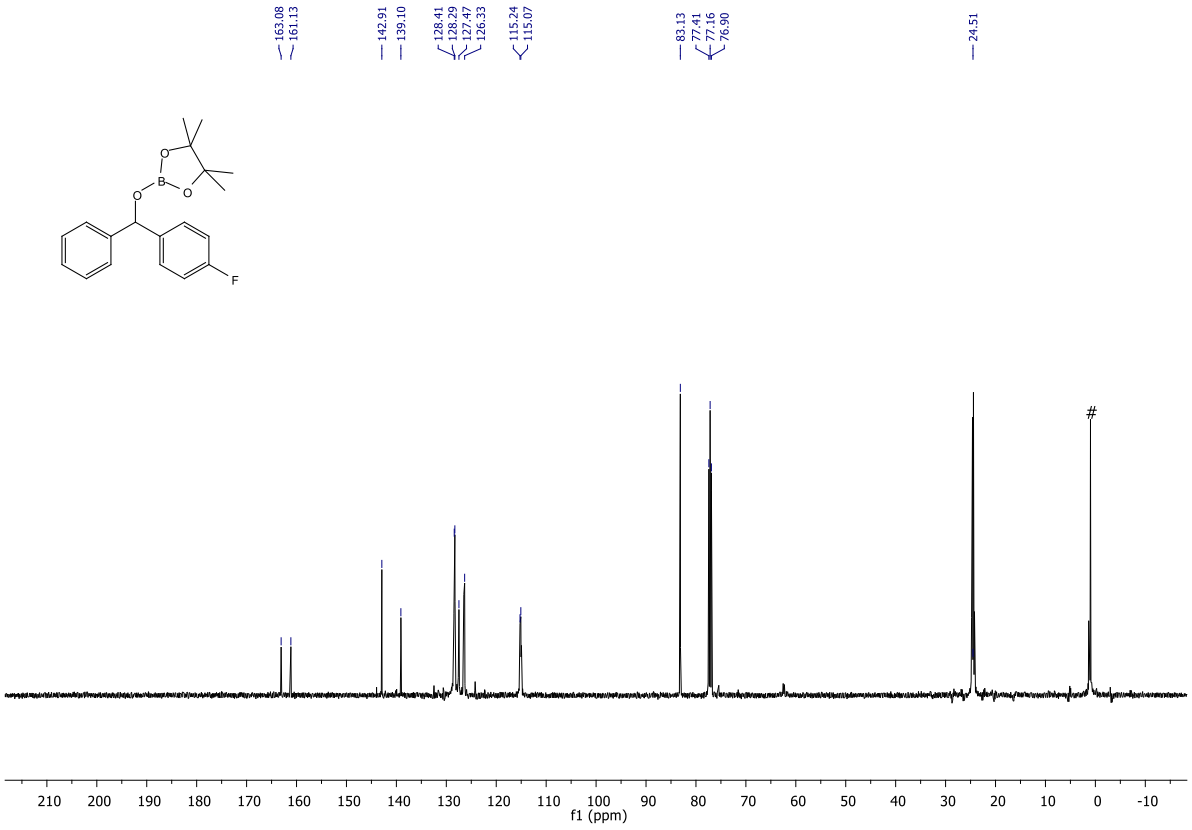
2-((4-Fluorophenyl)(phenyl)methoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 27b).[2]



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

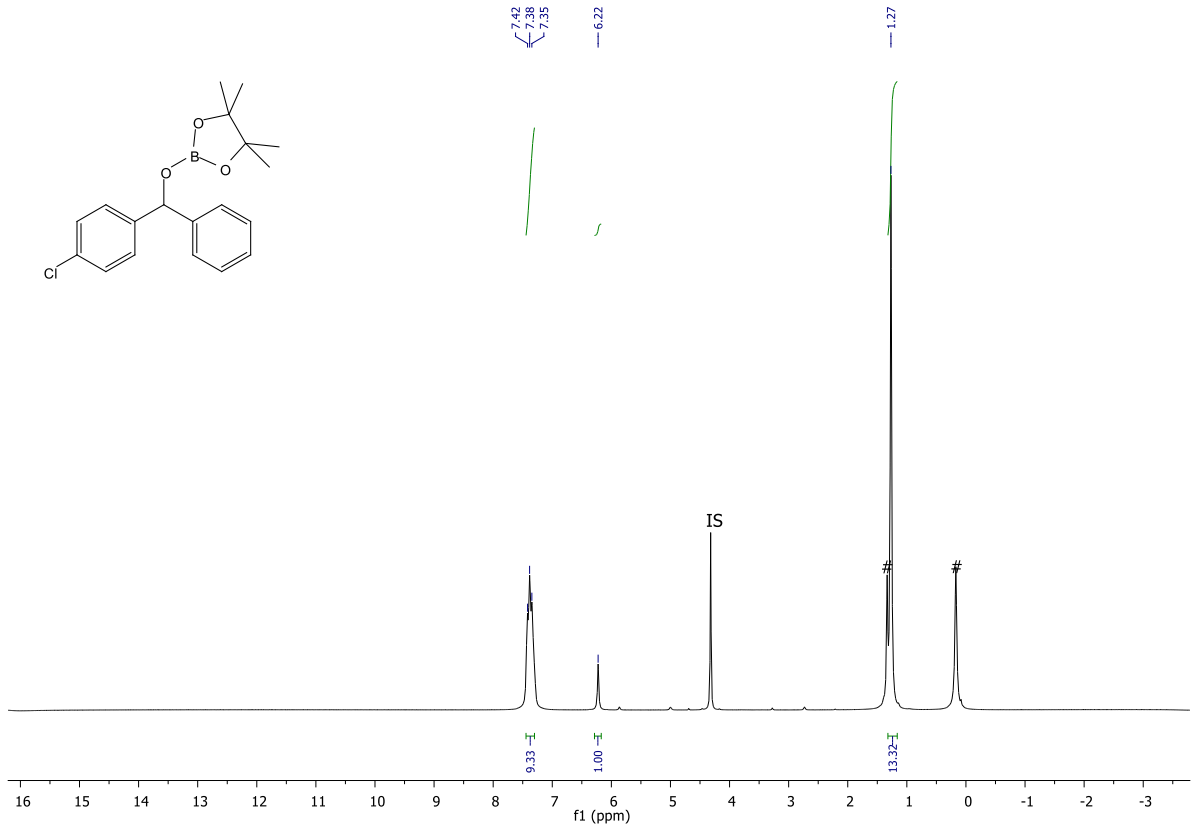


^{11}B NMR of **27b** (128 MHz, $CDCl_3$)

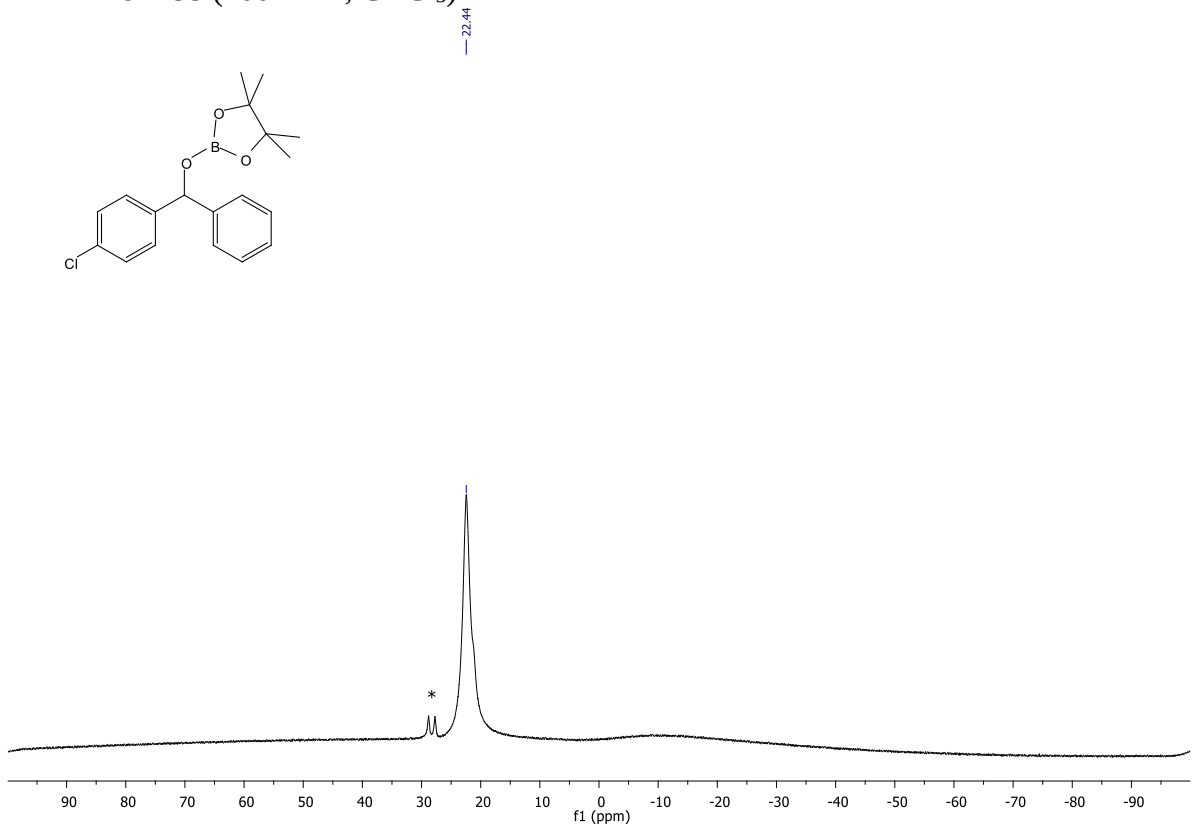


^{13}C NMR of **27b** (100 MHz, $CDCl_3$)

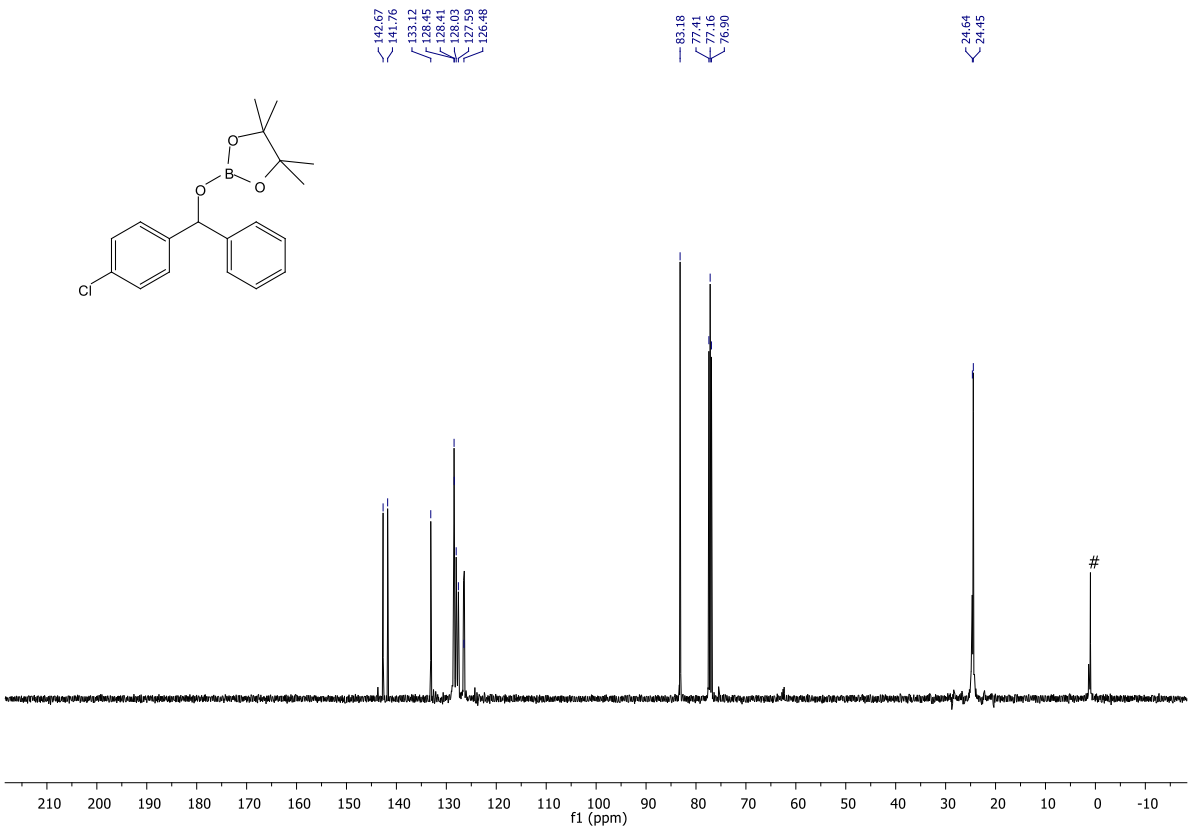
2-((4-Chlorophenyl)(phenyl)methoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 28b).[2]



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

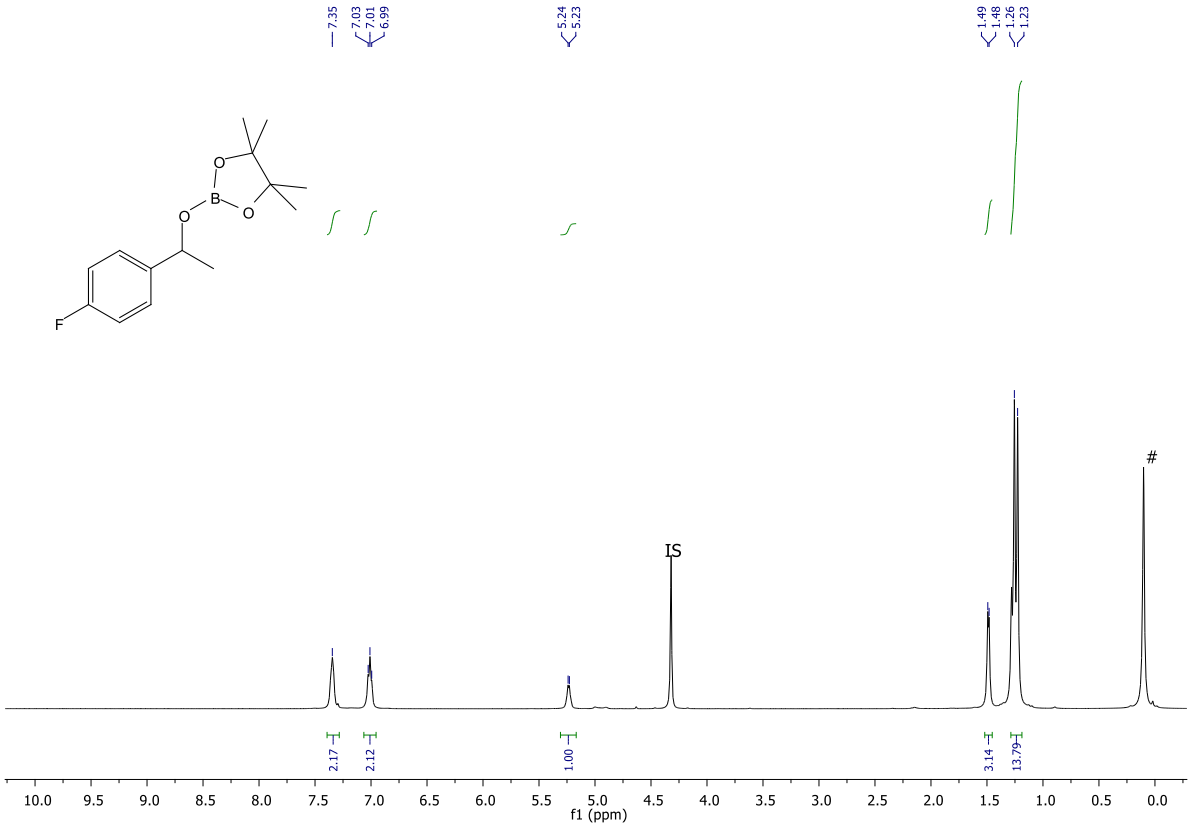


^{11}B NMR of **28b** (128 MHz, $CDCl_3$)

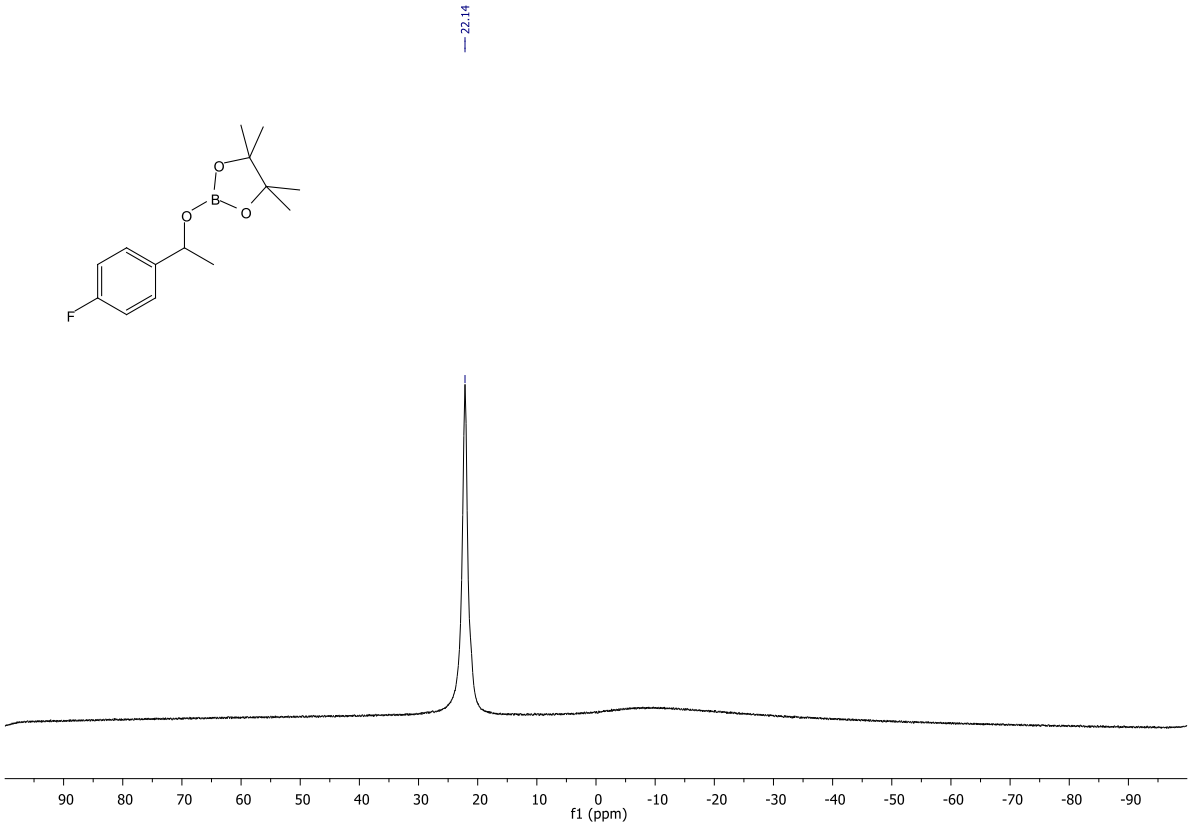


^{13}C NMR of **28b** (100 MHz, $CDCl_3$)

2-(1-(4-Fluorophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 29b).[2,14]

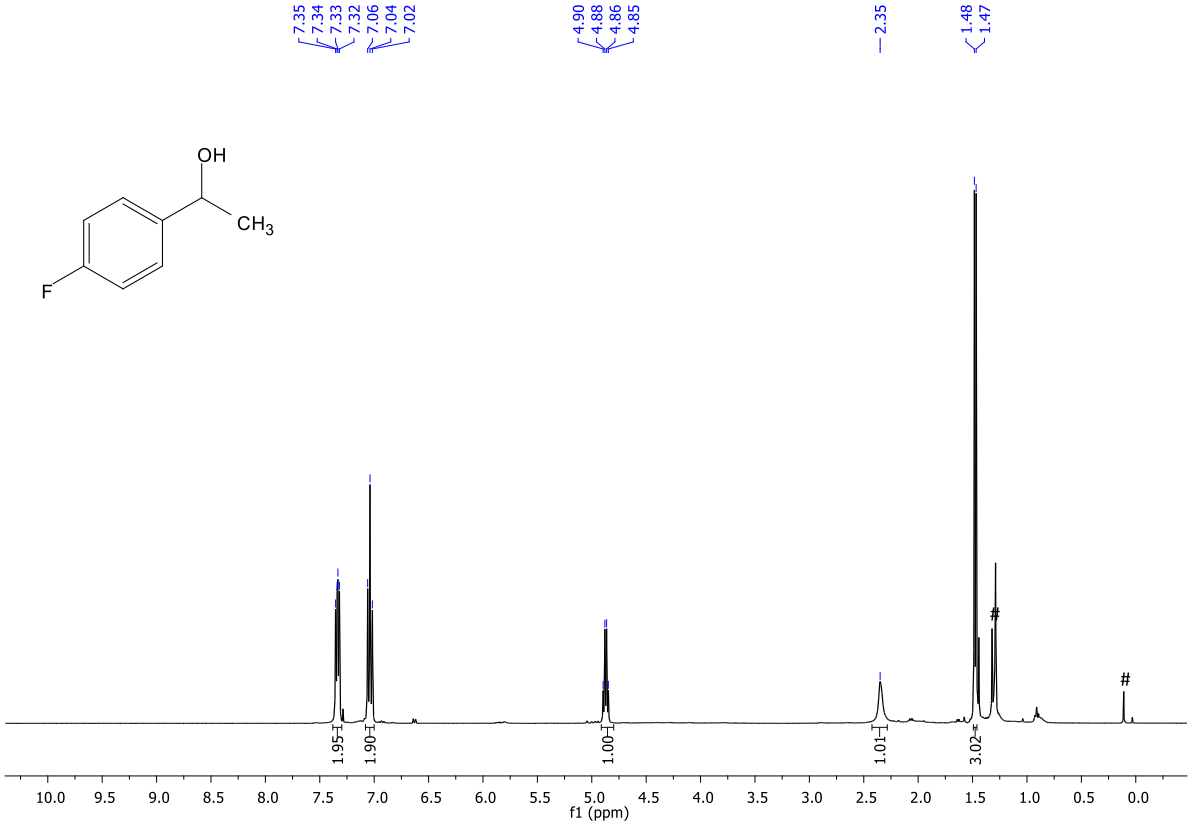


^{1}H NMR of **29b** (400 MHz, $CDCl_3$)

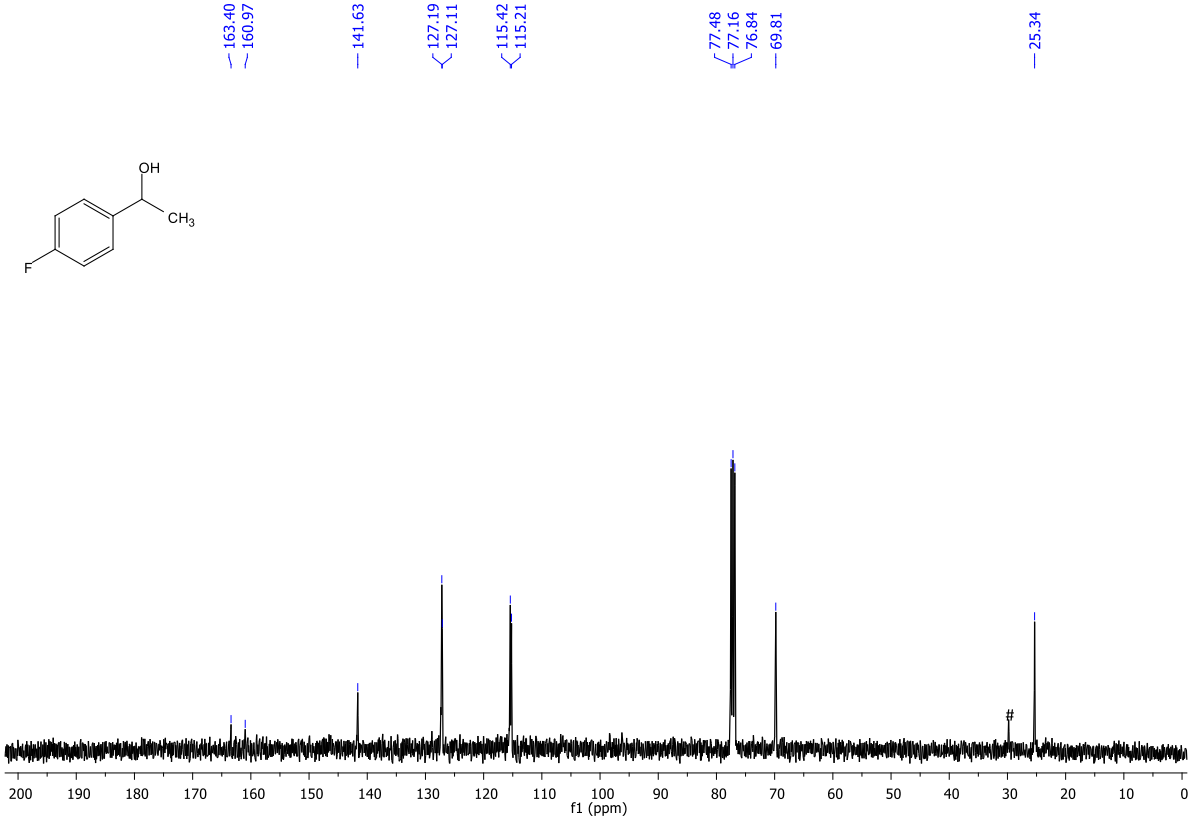


^{11}B NMR of **29b** (128 MHz, $CDCl_3$)

1-(4-Fluorophenyl)ethanol (29c).[2,14]

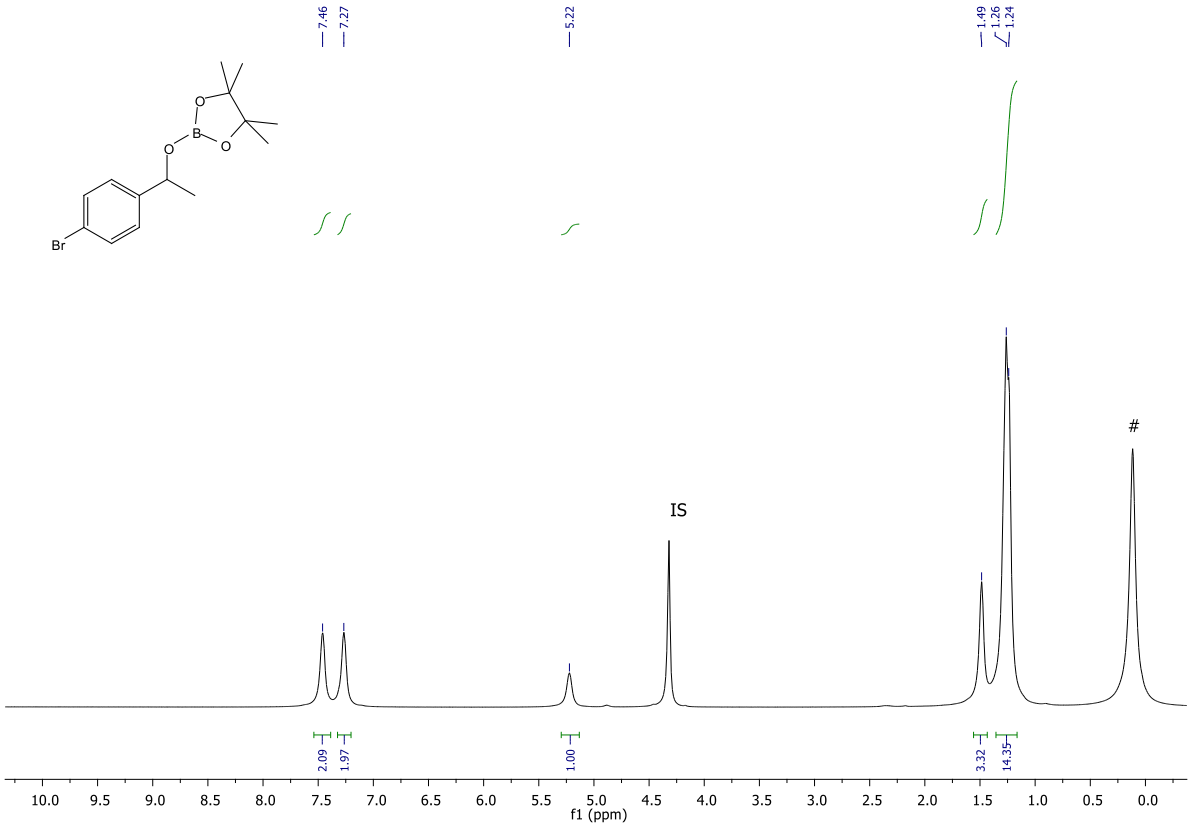


^{1}H NMR of **29c** (400 MHz, $CDCl_3$)

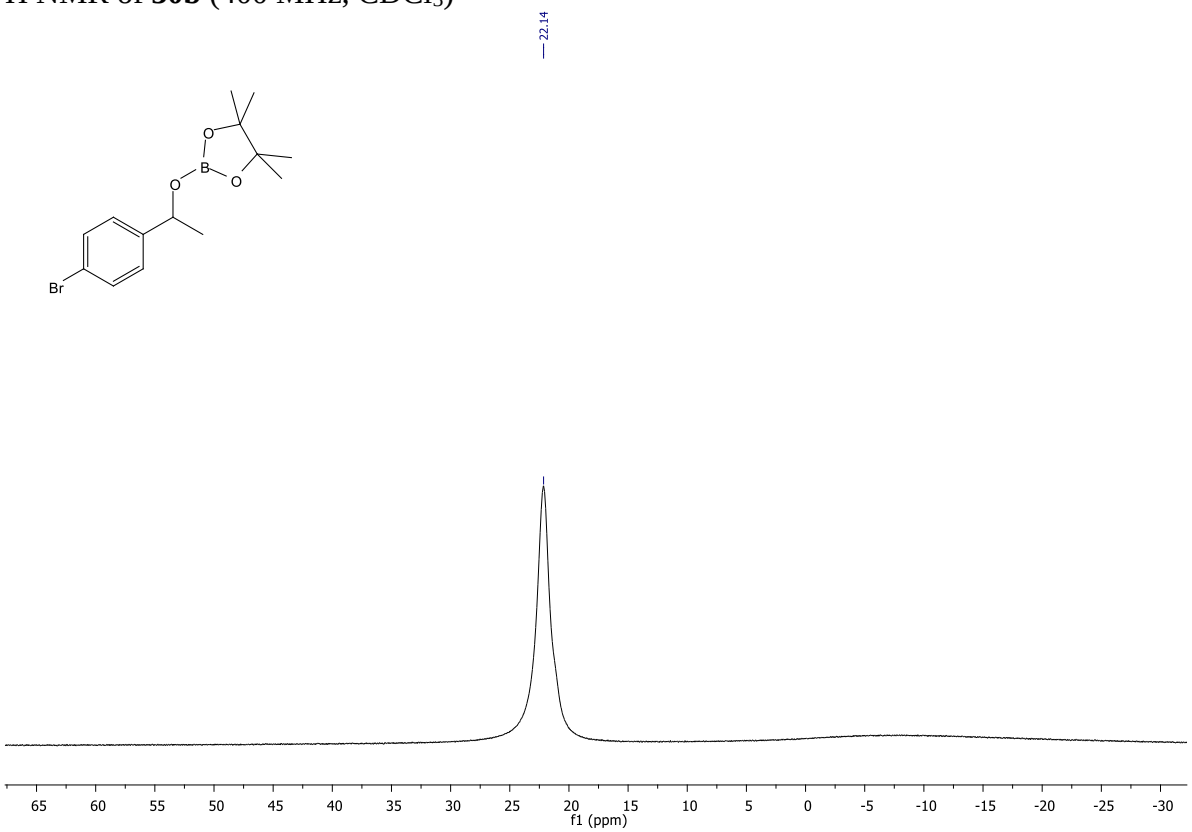


^{13}C NMR of **29c** (100 MHz, $CDCl_3$)

2-(1-(4-Bromophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 30b).[2,3]

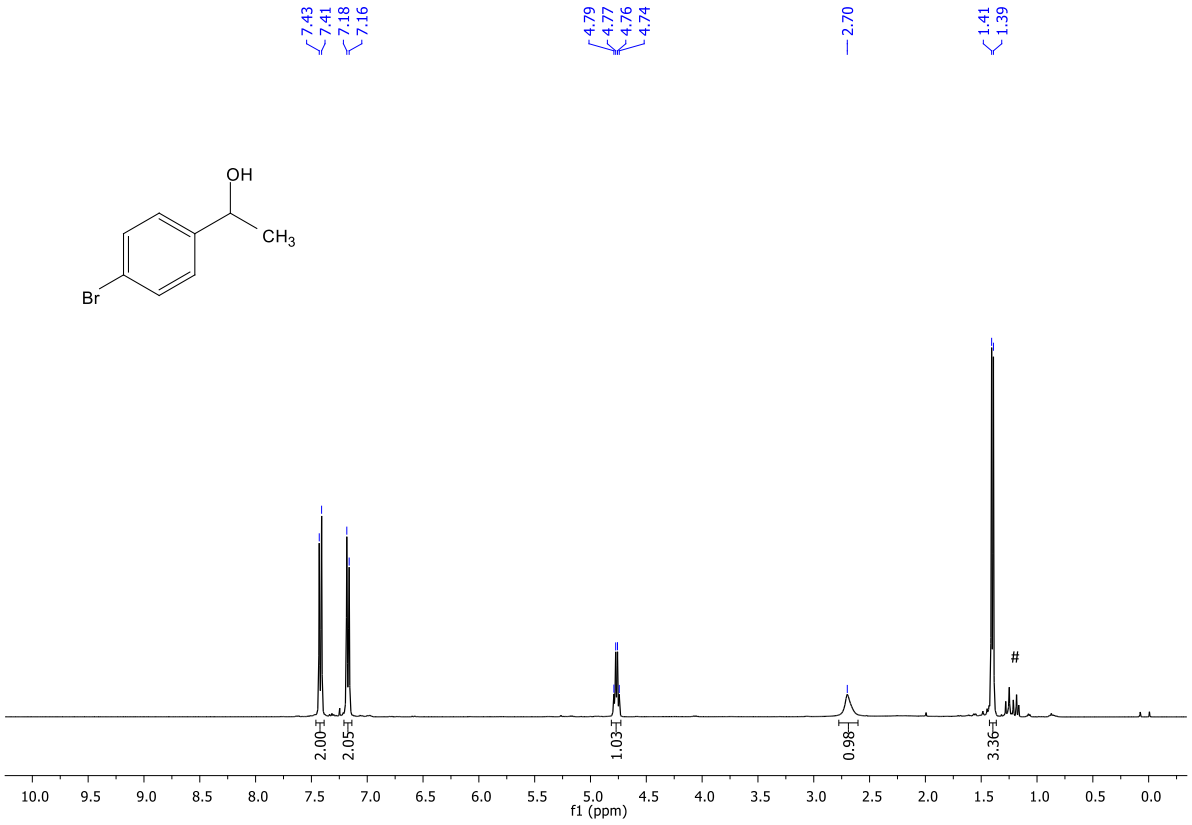


^{1}H NMR of **30b** (400 MHz, $CDCl_3$)

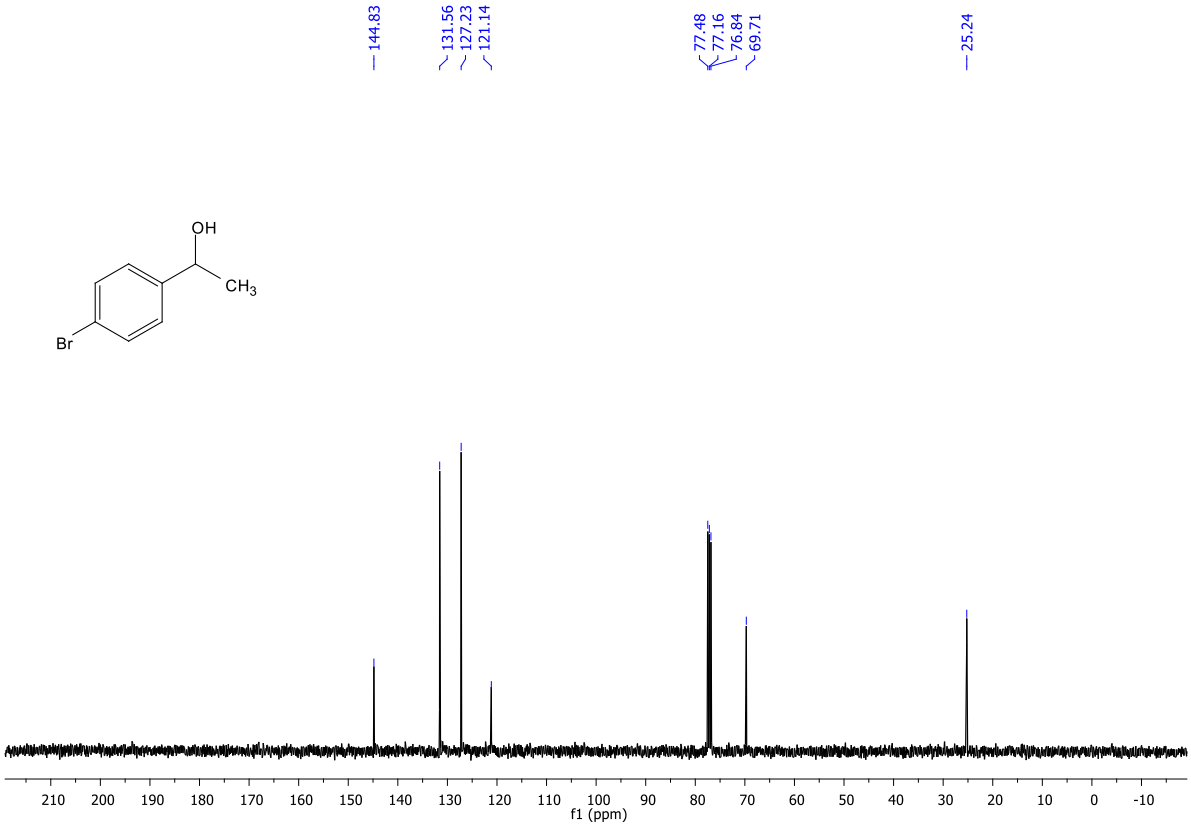


^{11}B NMR of **30b** (128 MHz, $CDCl_3$)

1-(4-Bromophenyl)ethanol (30c).[2]

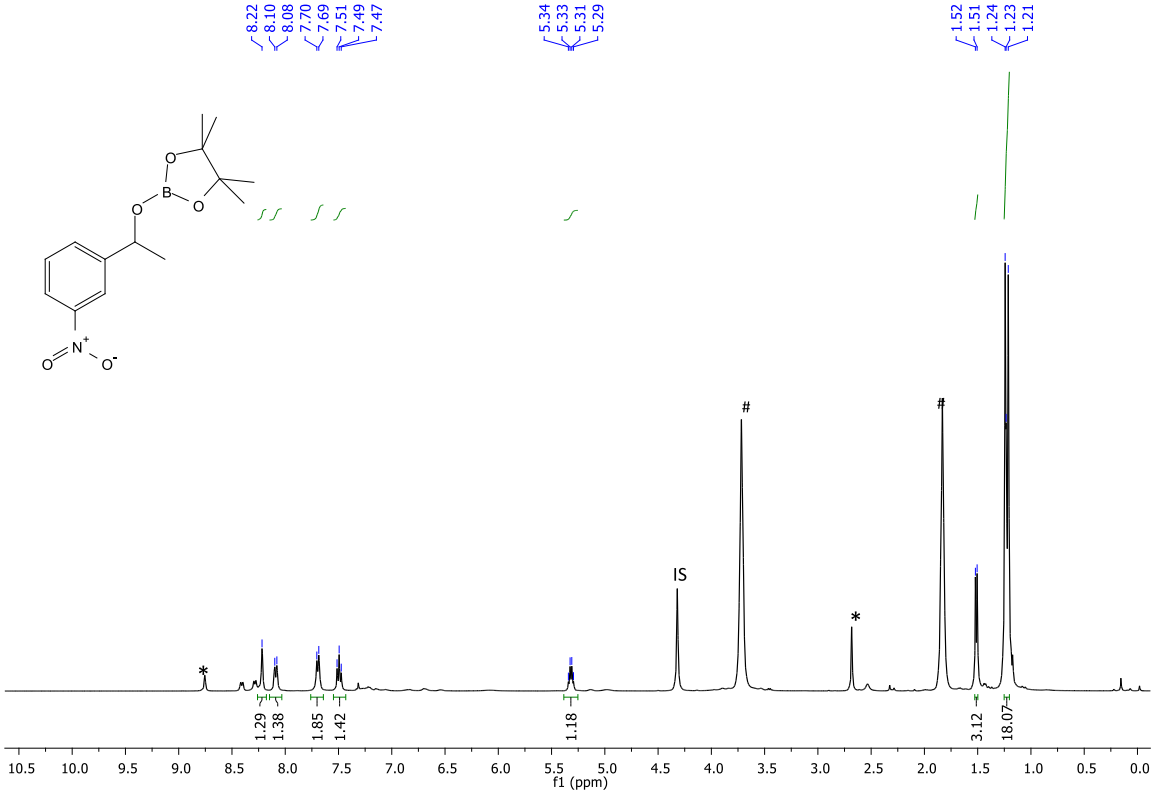


^{1}H NMR of **30c** (400 MHz, $CDCl_3$)

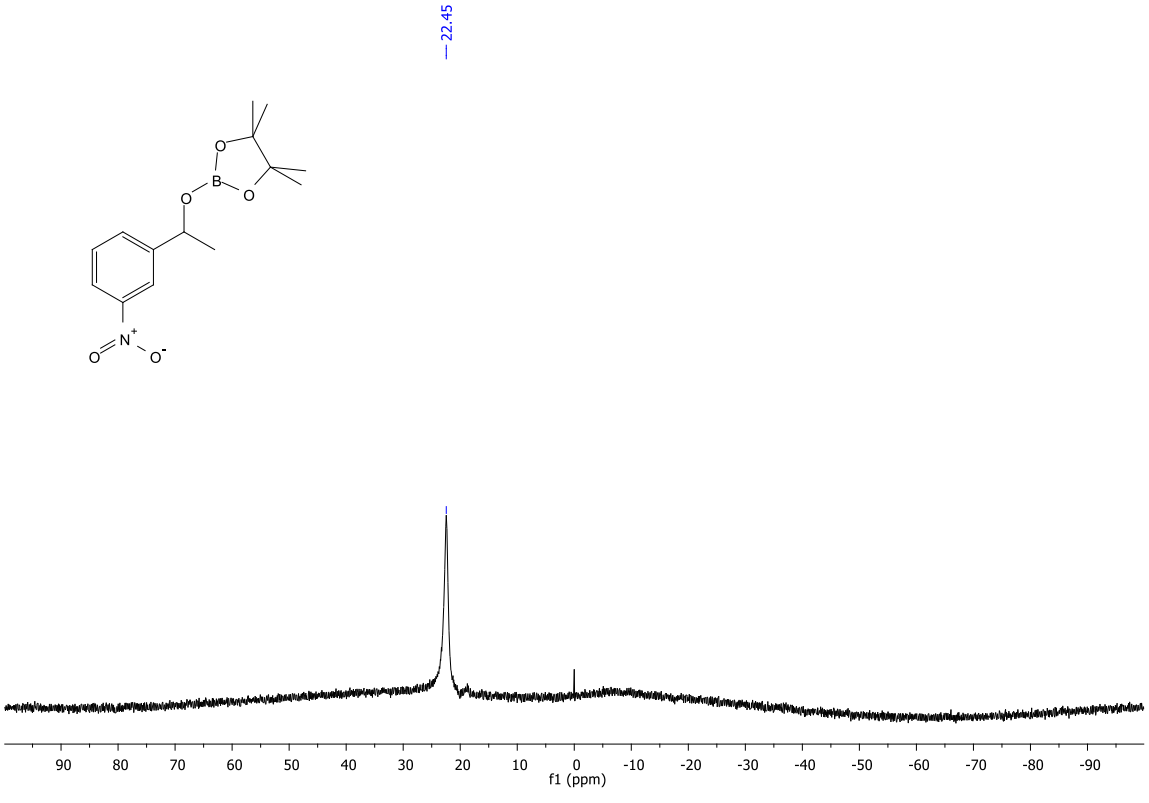


^{13}C NMR of **30c** (100 MHz, $CDCl_3$)

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

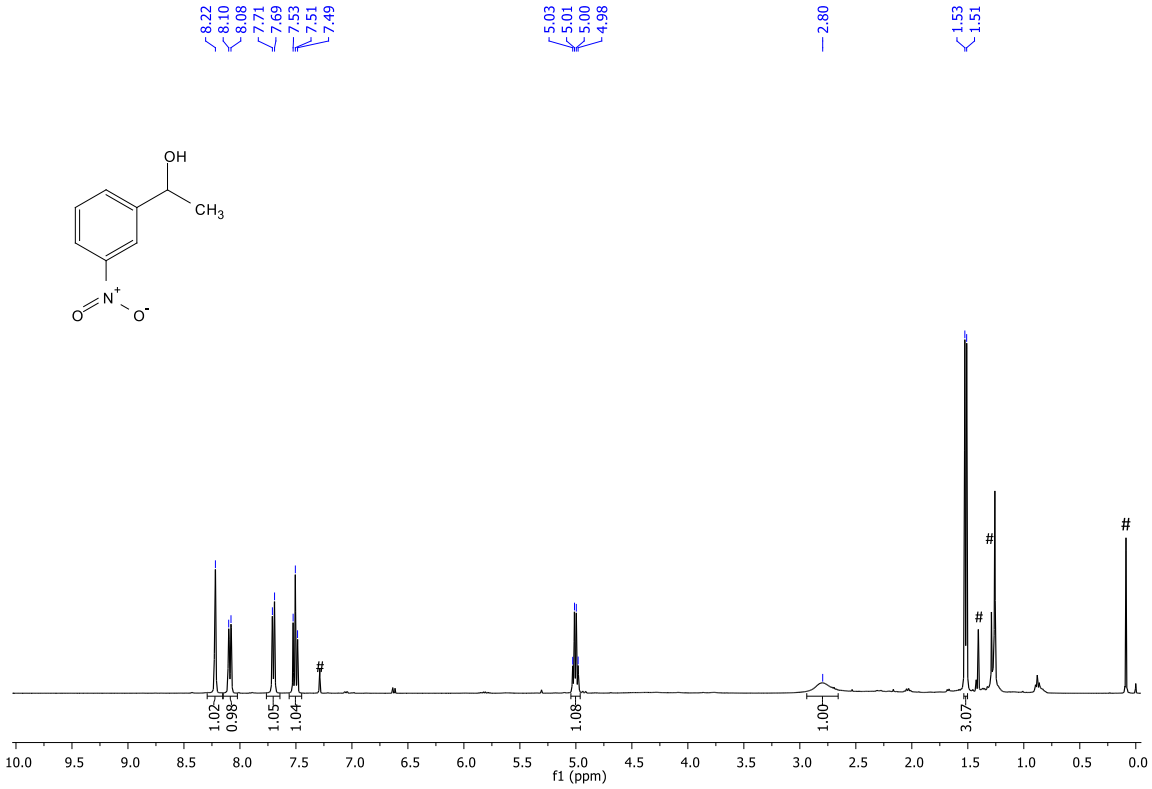


^{1}H NMR of **31b** (400 MHz, $CDCl_3$)

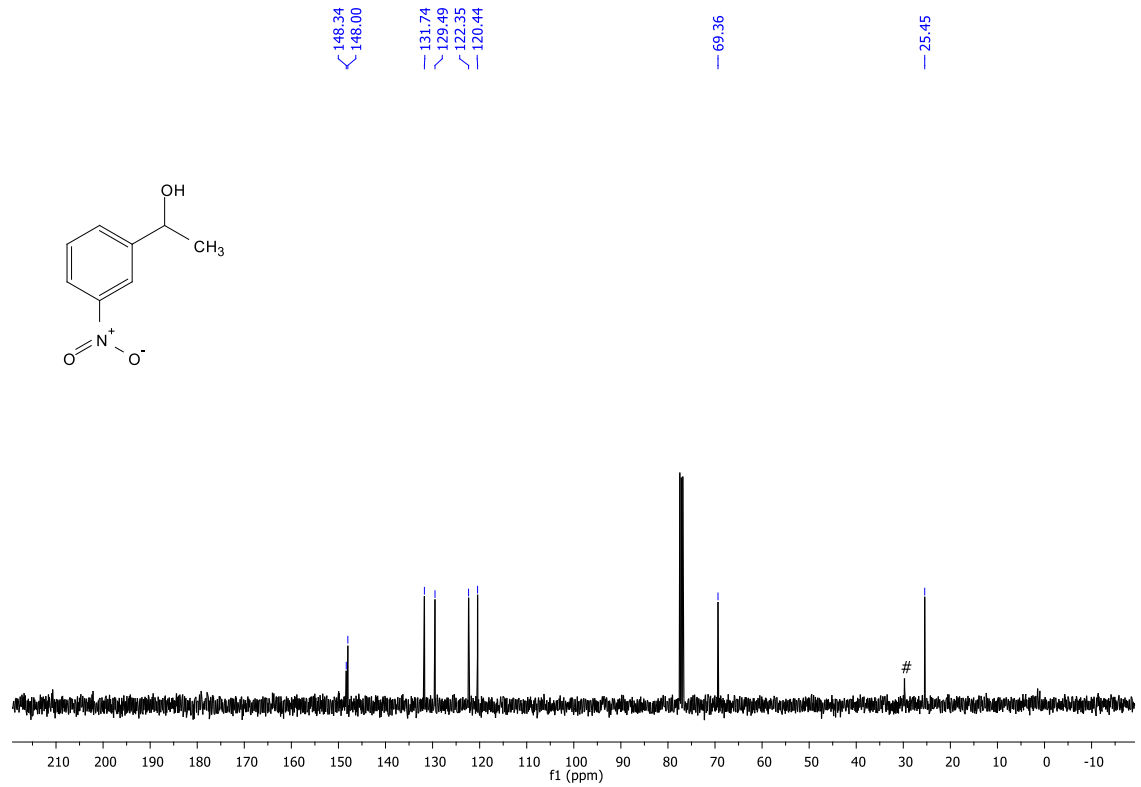


^{11}B NMR of **31b** (128 MHz, $CDCl_3$)

1-(3-Nitrophenyl)ethanol (31c).[2]

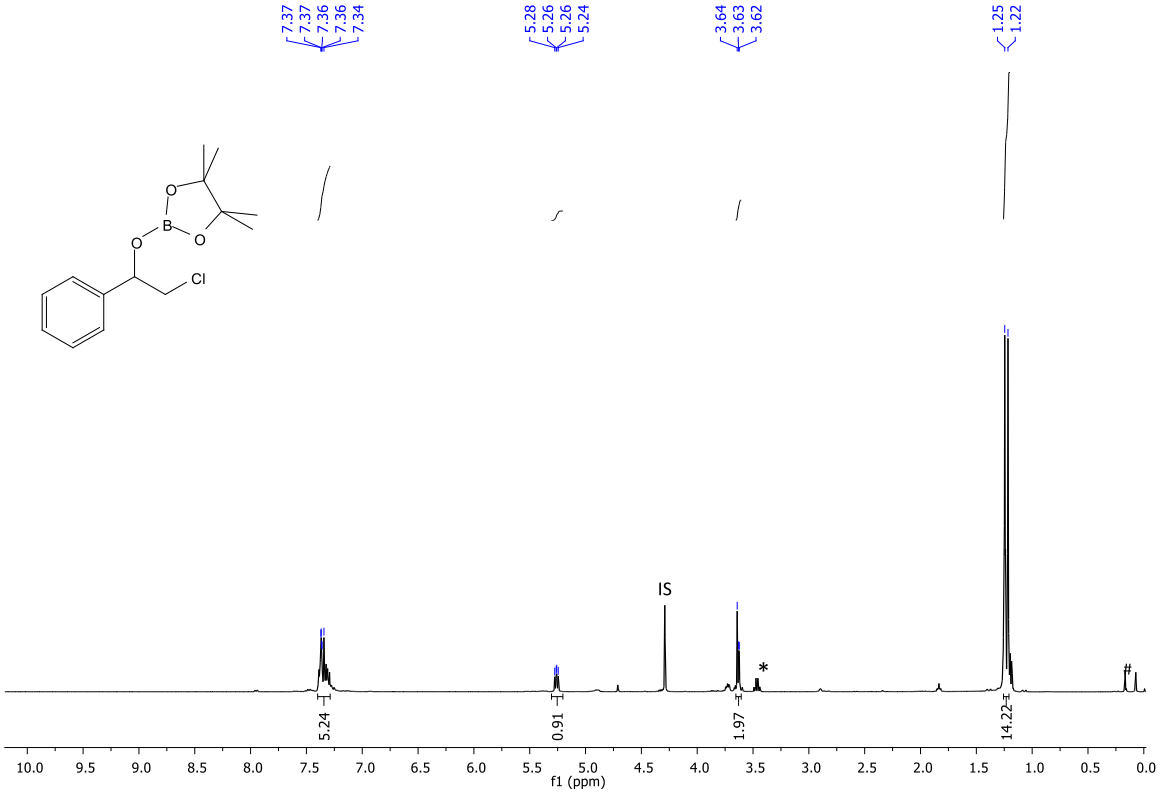


^{1}H NMR of **31c** (400 MHz, $CDCl_3$)

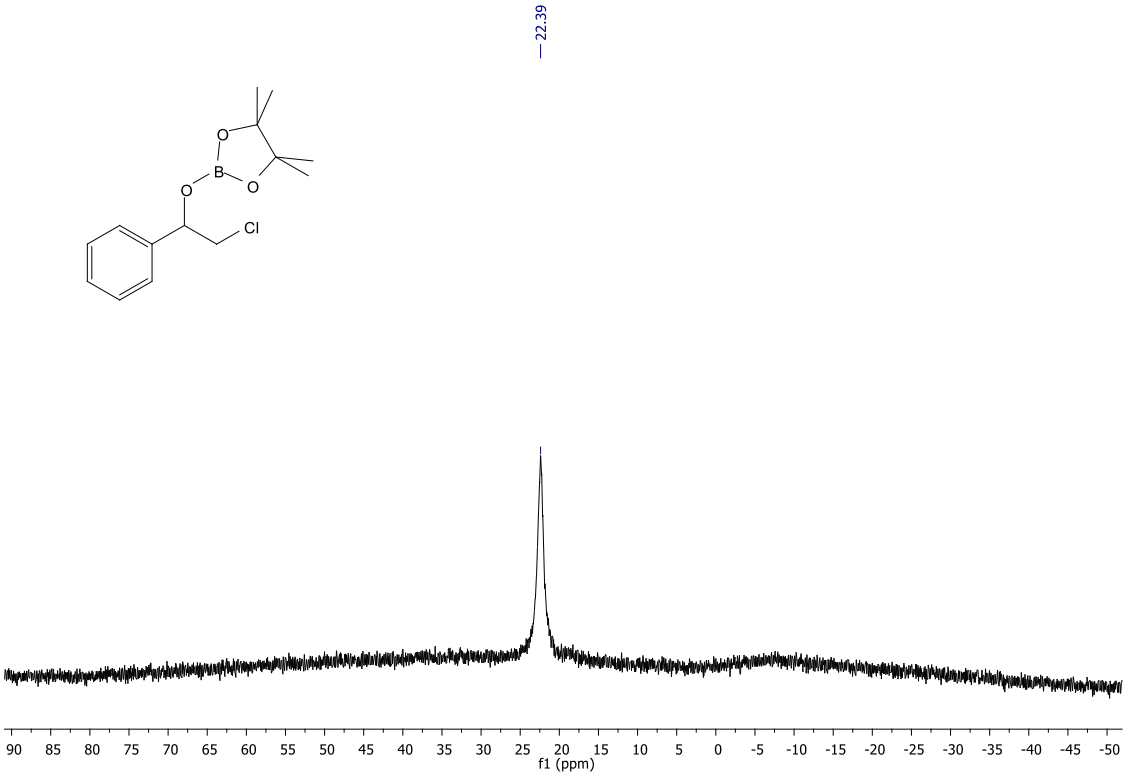


^{13}C NMR of **31c** (100 MHz, $CDCl_3$)

2-(2-Chloro-1-phenylethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 32b).[2,14]

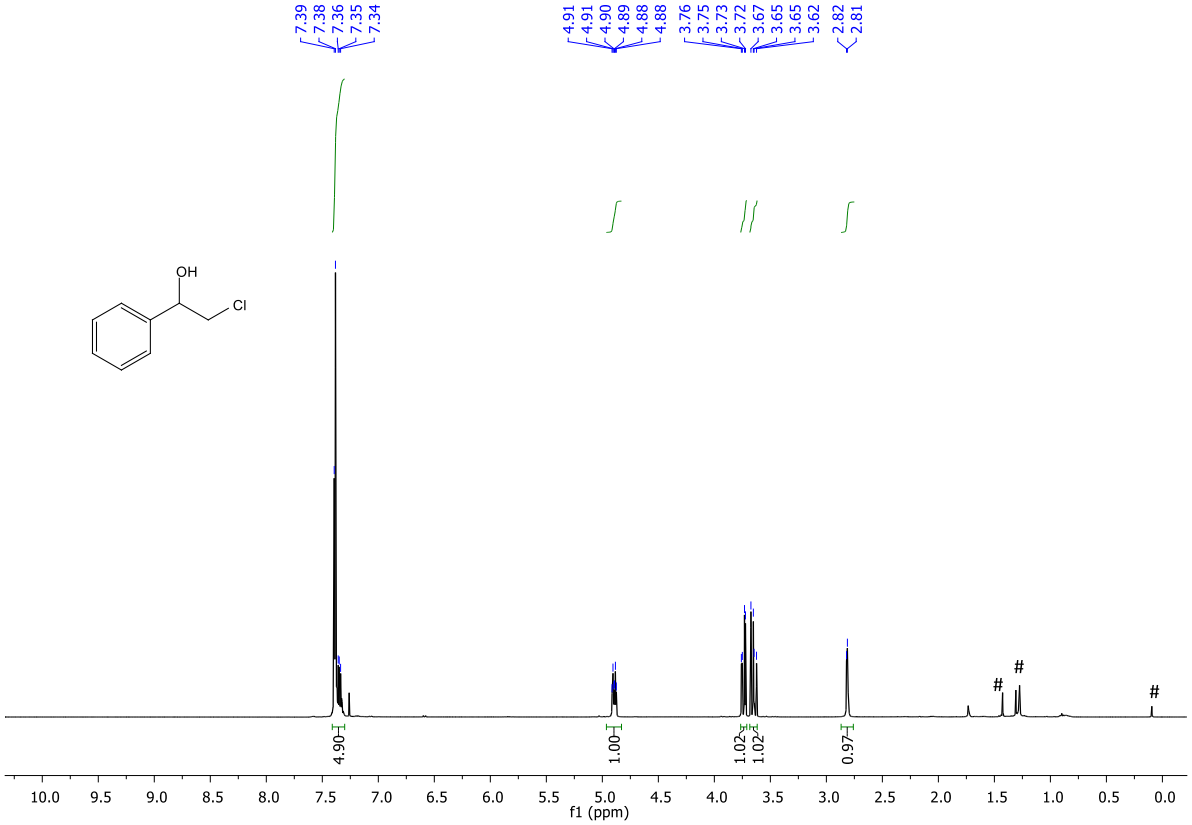


^{1}H NMR of **32b** (400 MHz, $CDCl_3$)

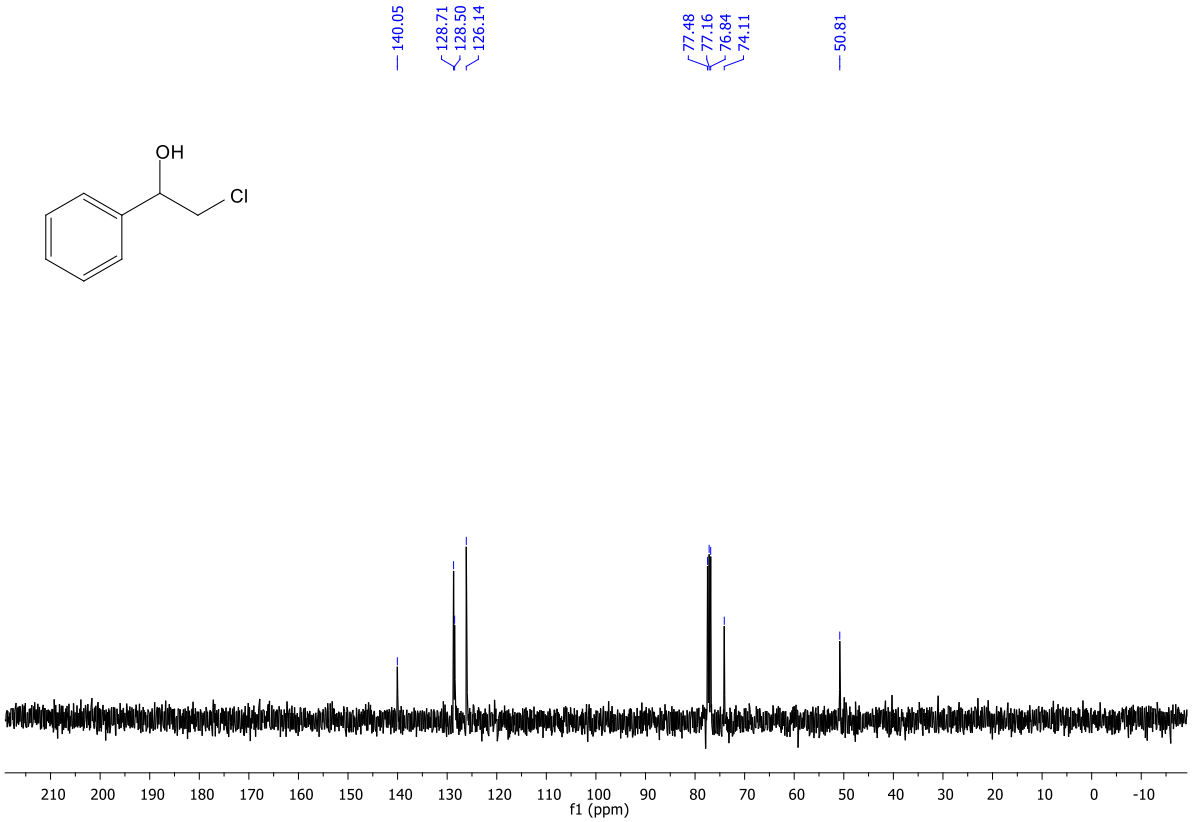


^{11}B NMR of **32b** (128 MHz, $CDCl_3$)

2-Chloro-1-phenylethan-1-ol (32c).[2,16]

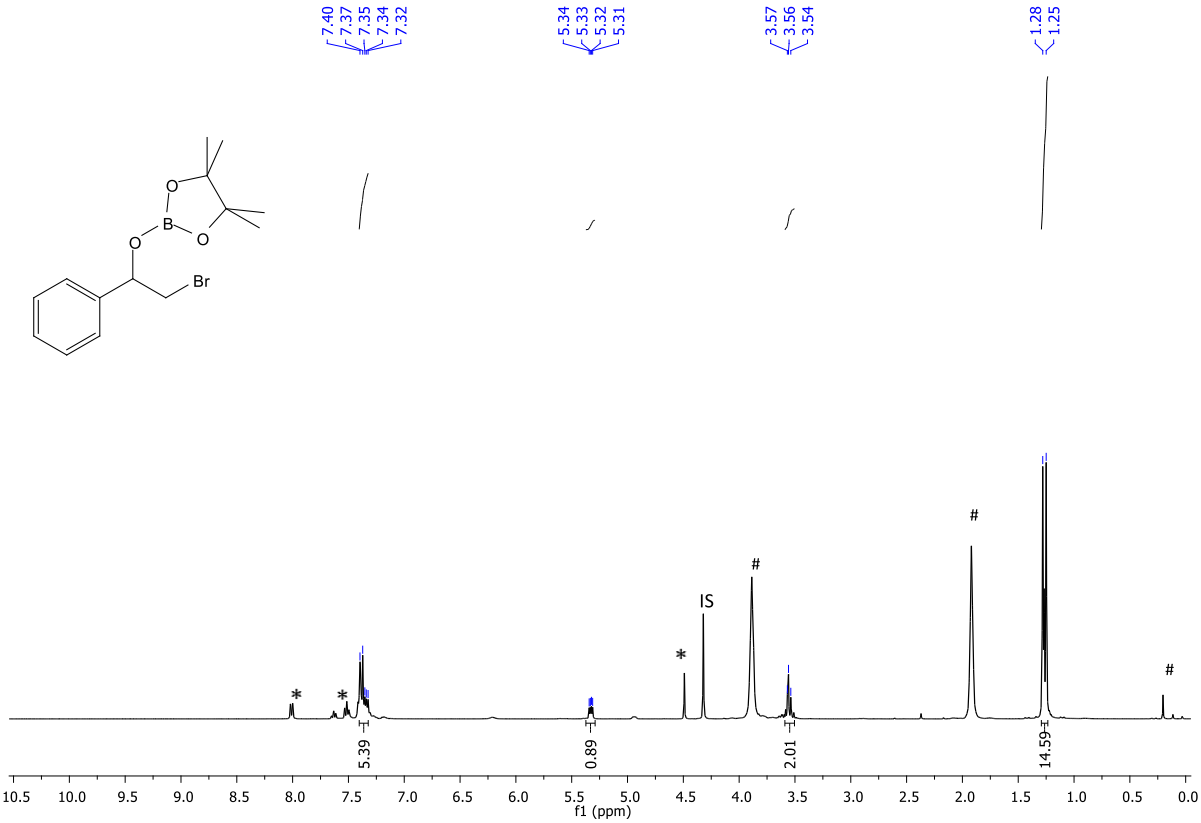


^{1}H NMR of **32c** (400 MHz, $CDCl_3$)

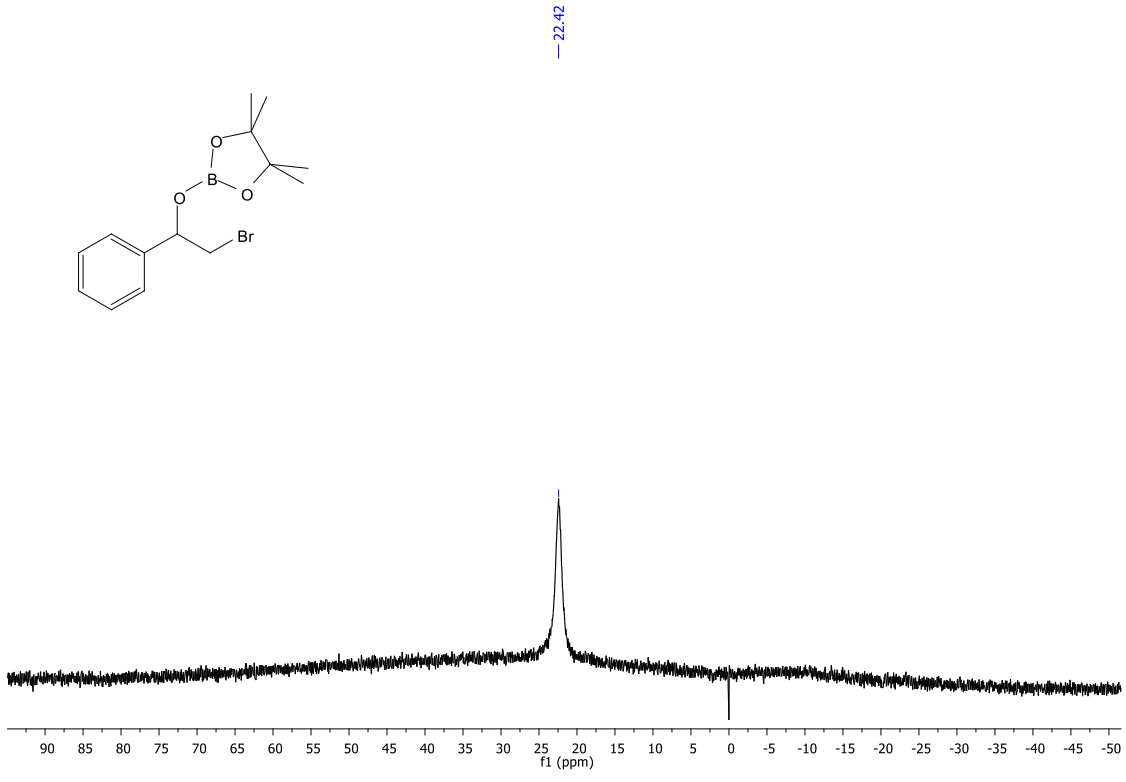


^{13}C NMR of **32c** (100 MHz, $CDCl_3$)

2-(2-Bromo-1-phenylethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 33b).[2,15]

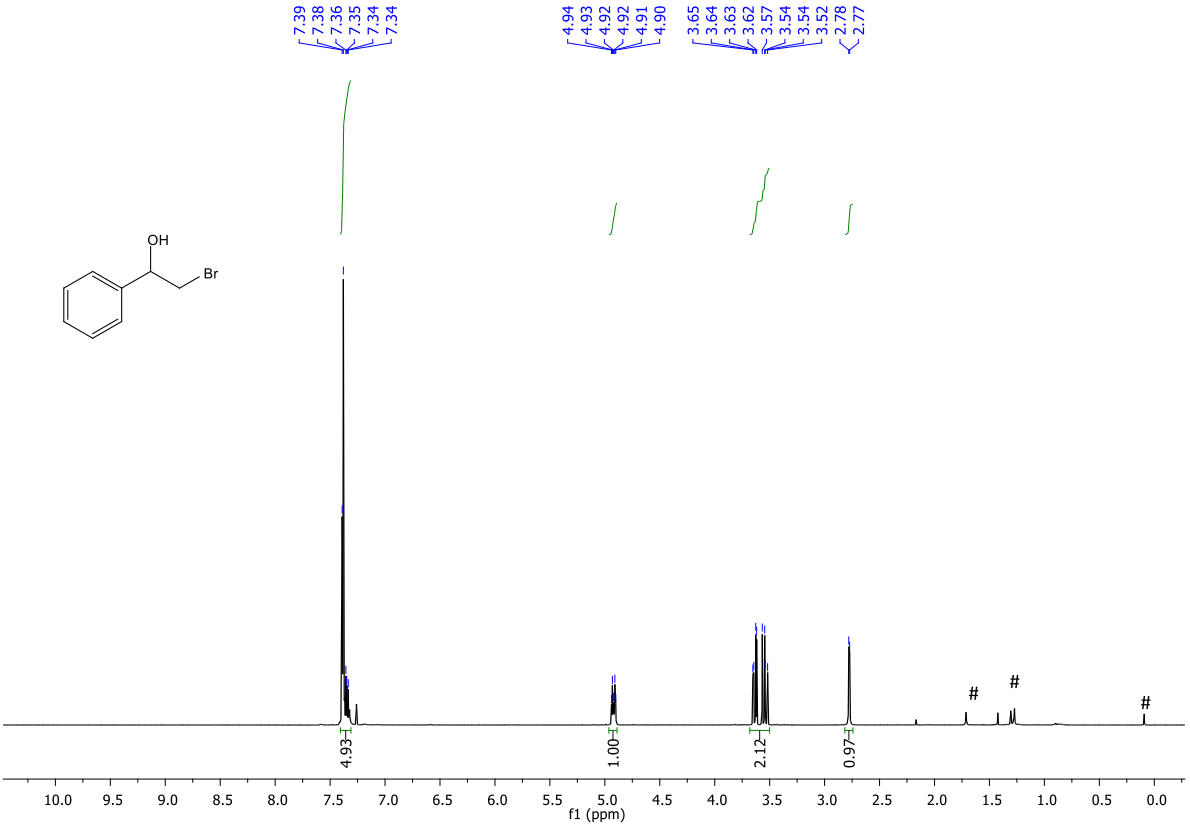


^{1}H NMR of **33b** (400 MHz, $CDCl_3$)

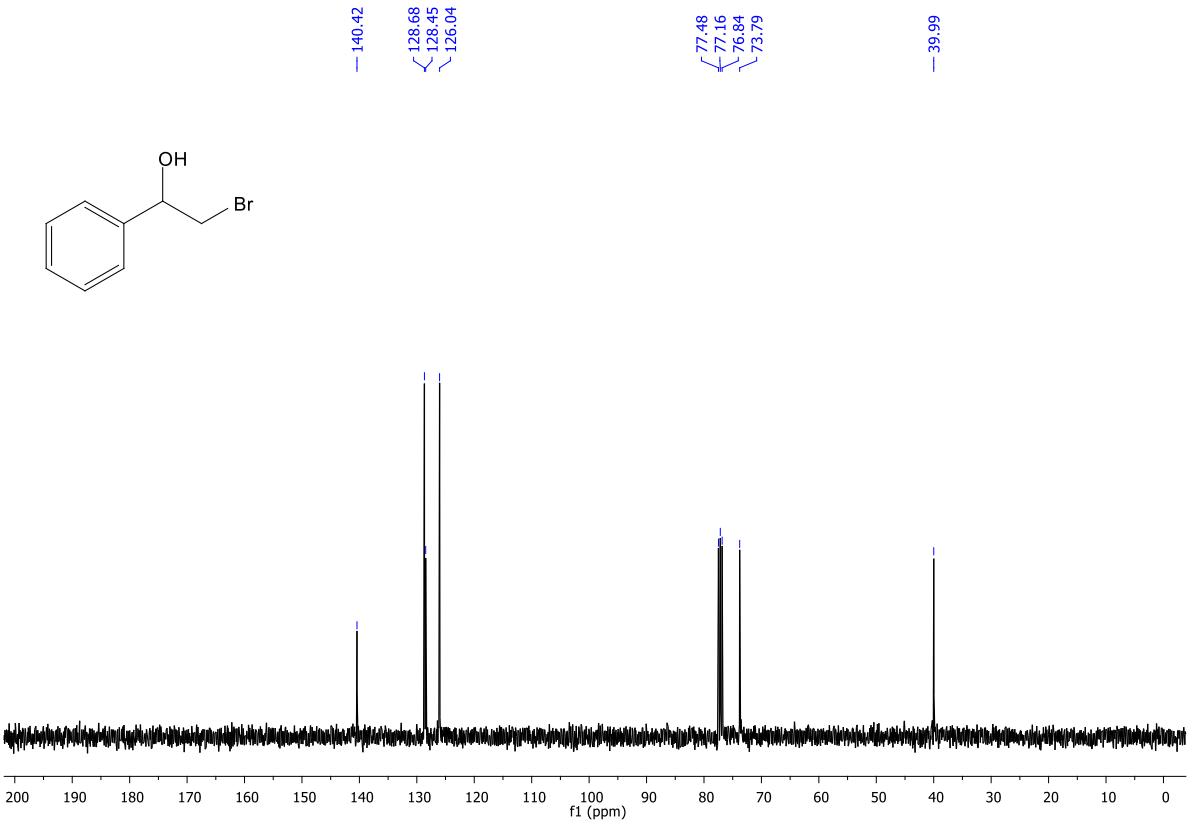


^{11}B NMR of **33b** (128 MHz, $CDCl_3$)

2-Bromo-1-phenylethan-1-ol (33c).[2,16]

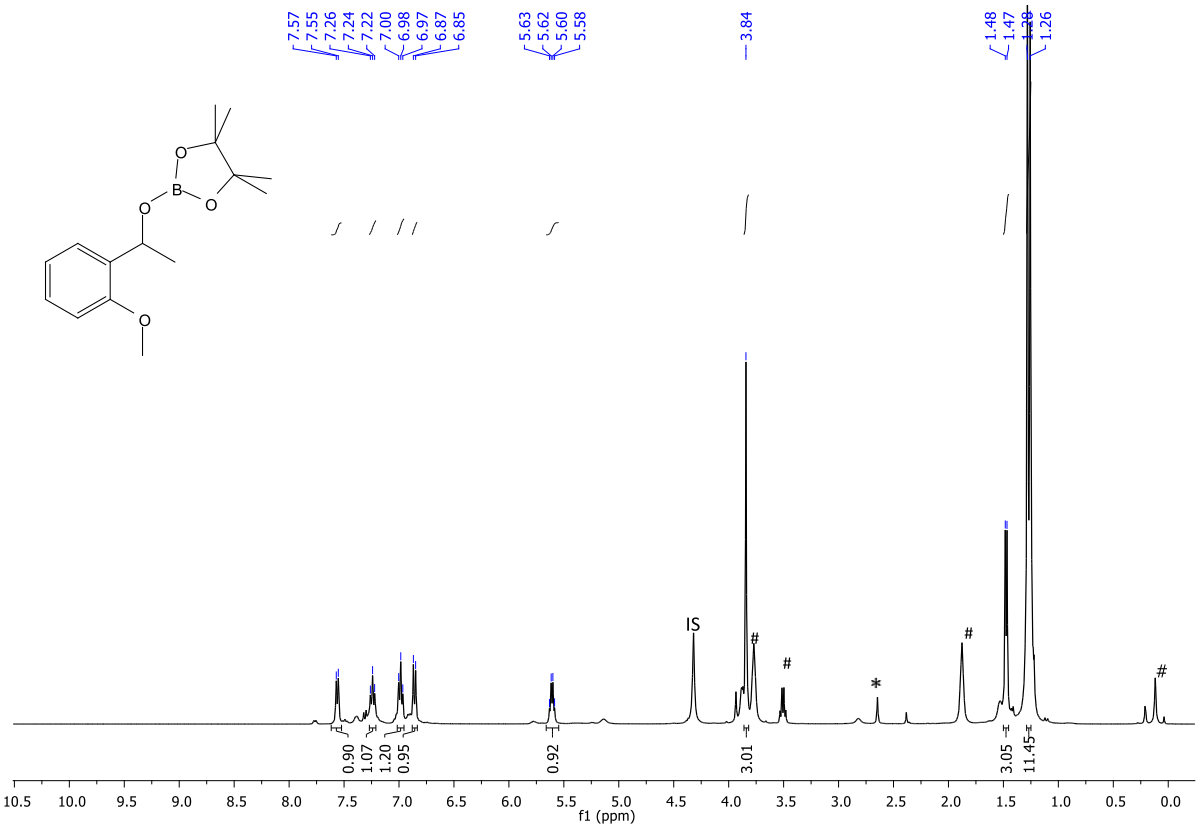


^{1}H NMR of **33c** (400 MHz, $CDCl_3$)

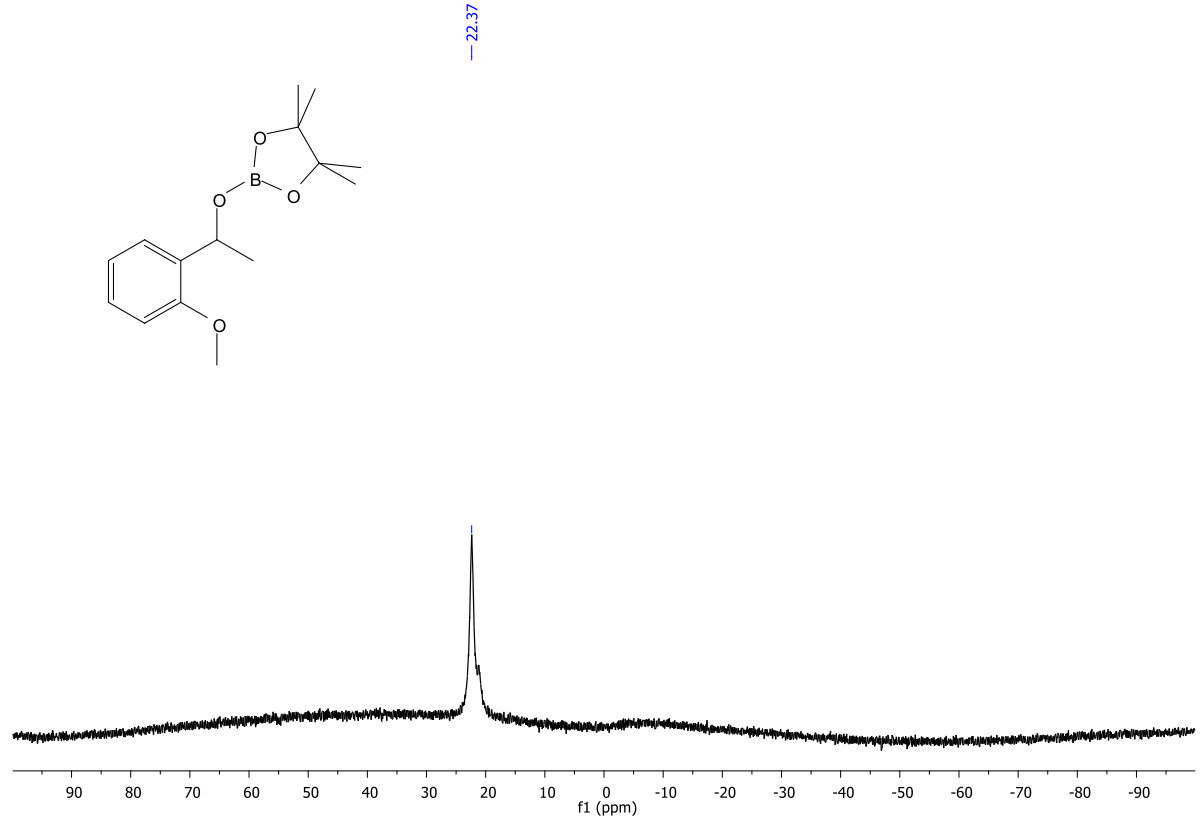


^{13}C NMR of **33c** (100 MHz, $CDCl_3$)

2-(1-(2-Methoxyphenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 34b).[2]

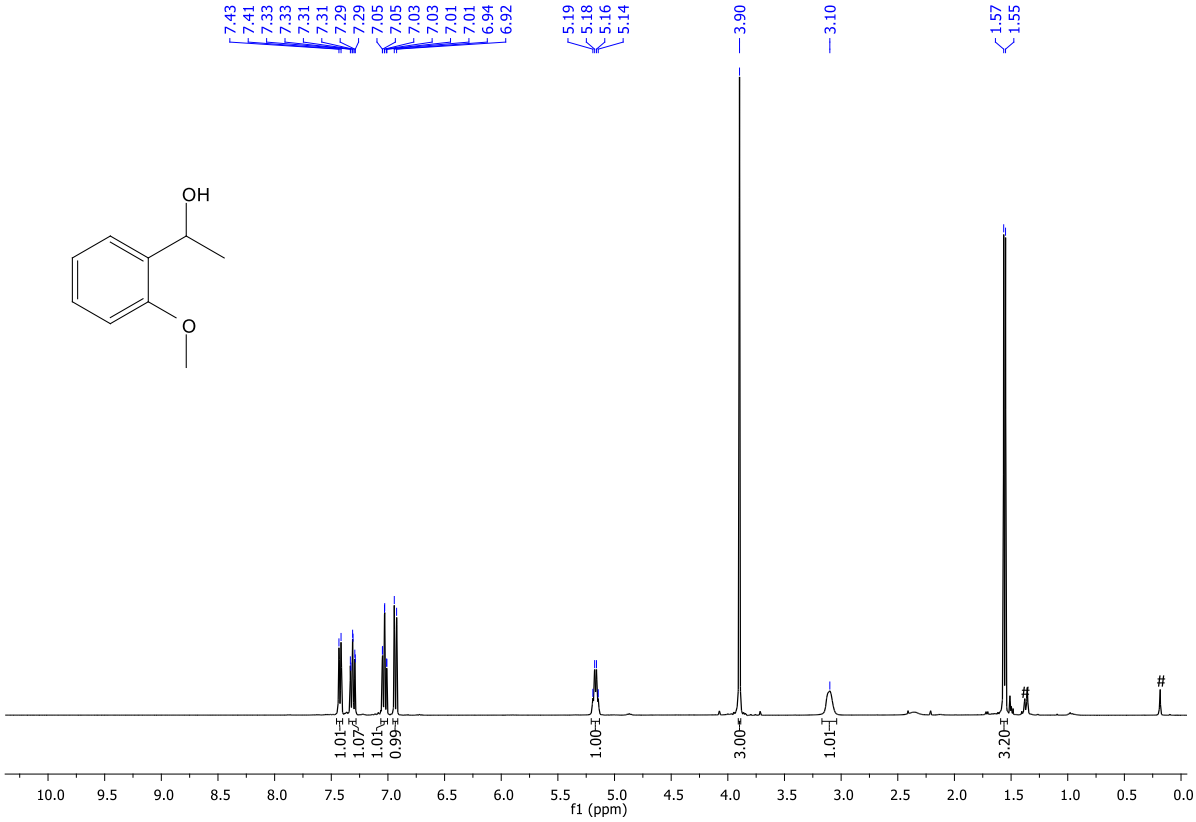


^{1}H NMR of **34b** (400 MHz, $CDCl_3$)

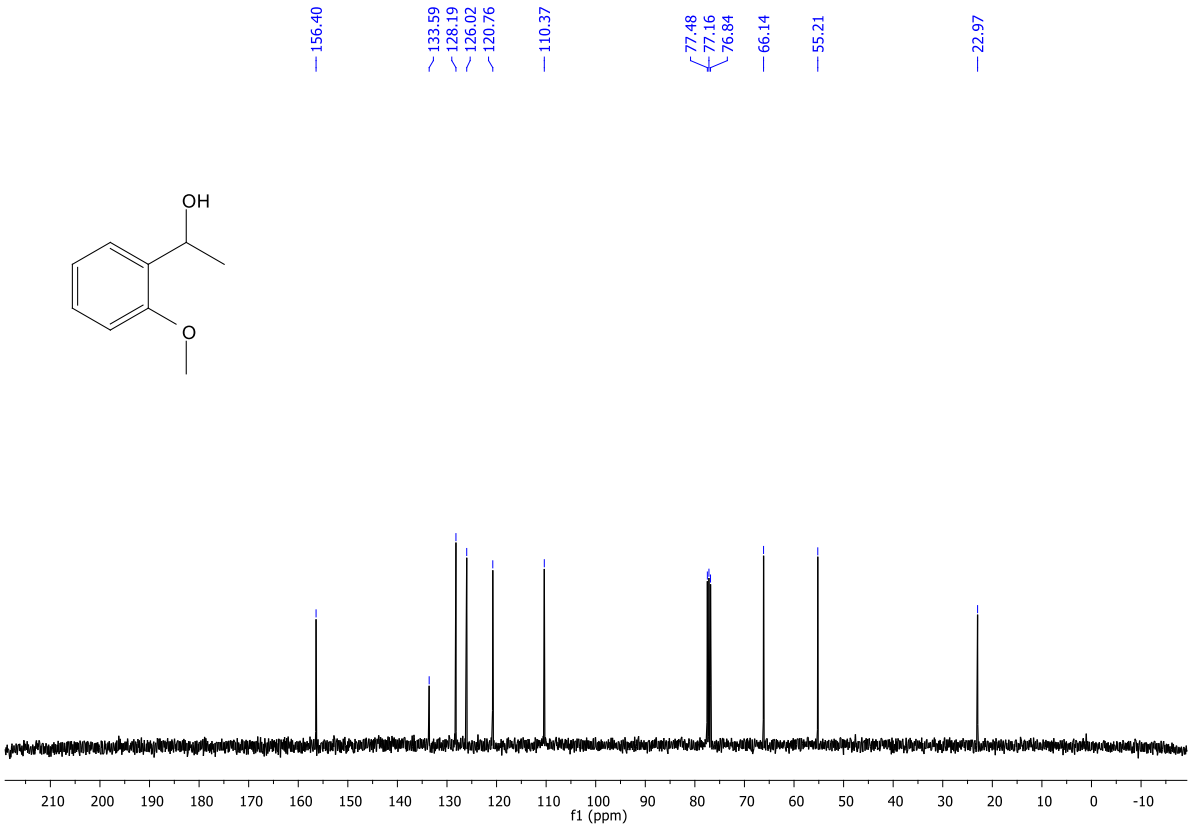


^{11}B NMR of **34b** (128 MHz, $CDCl_3$)

1-(2-Methoxyphenyl)ethanol (34c).[2,17]

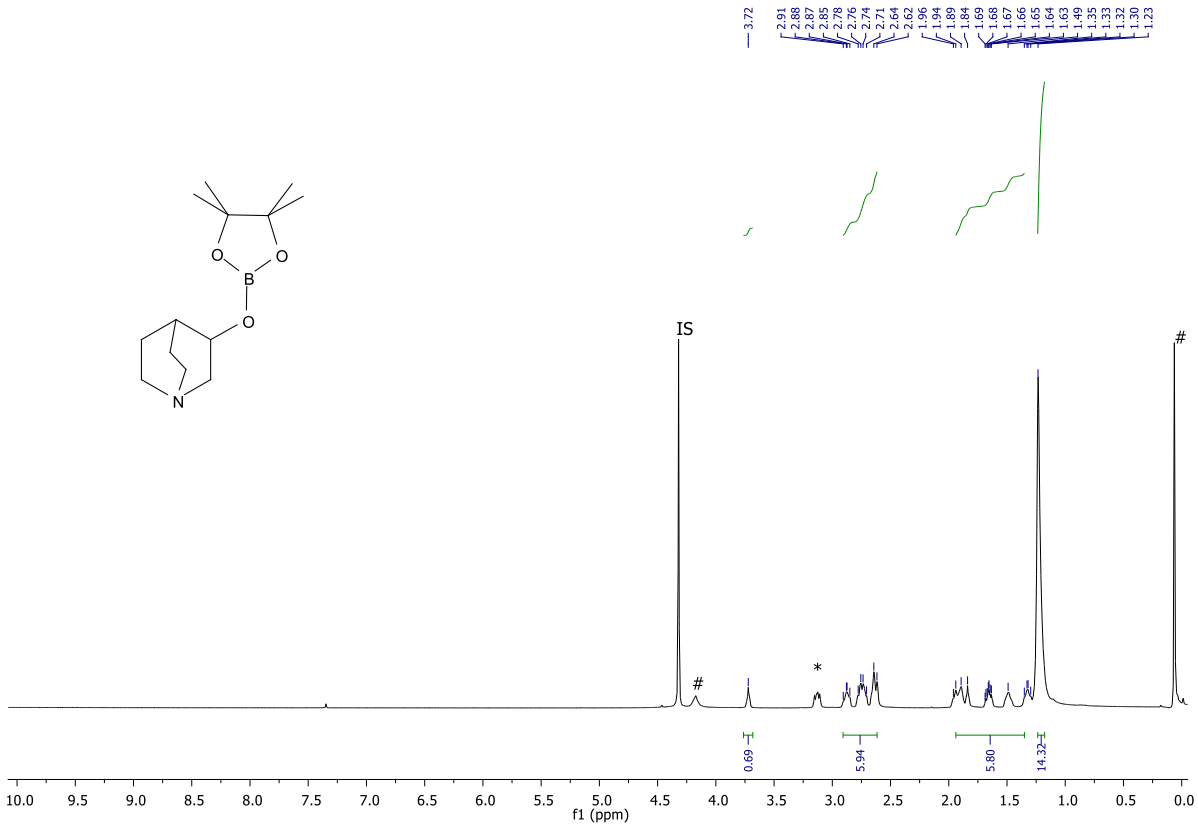


^{1}H NMR of **34c** (400 MHz, $CDCl_3$)

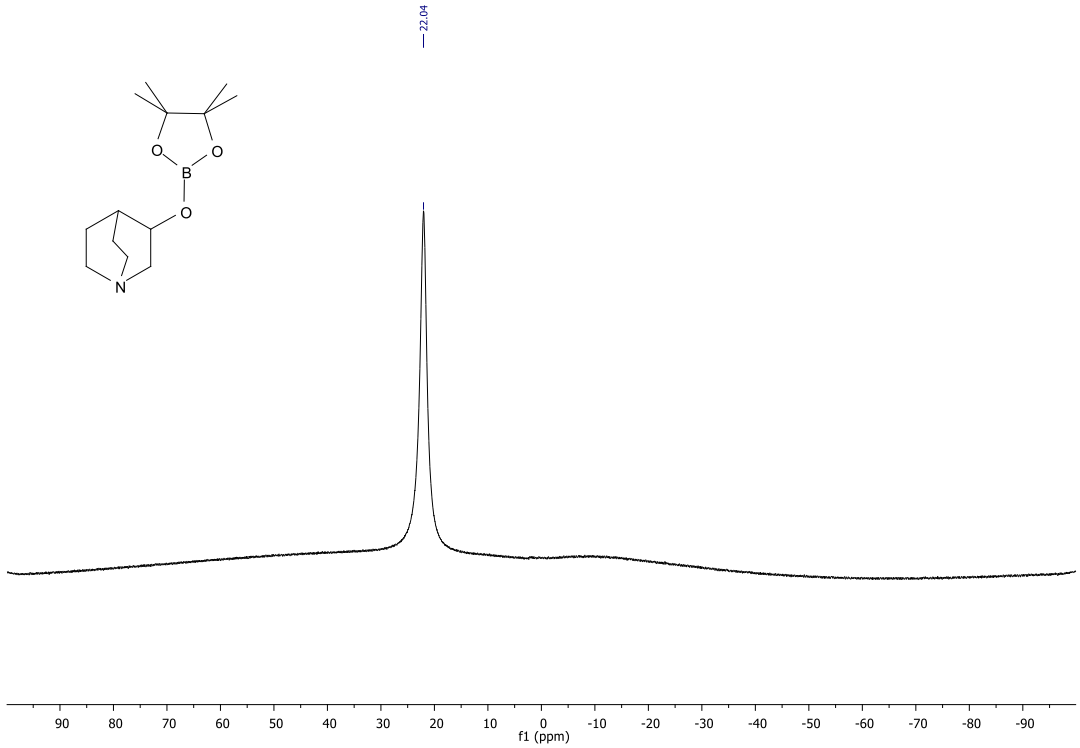


^{13}C NMR of **34c** (100 MHz, $CDCl_3$)

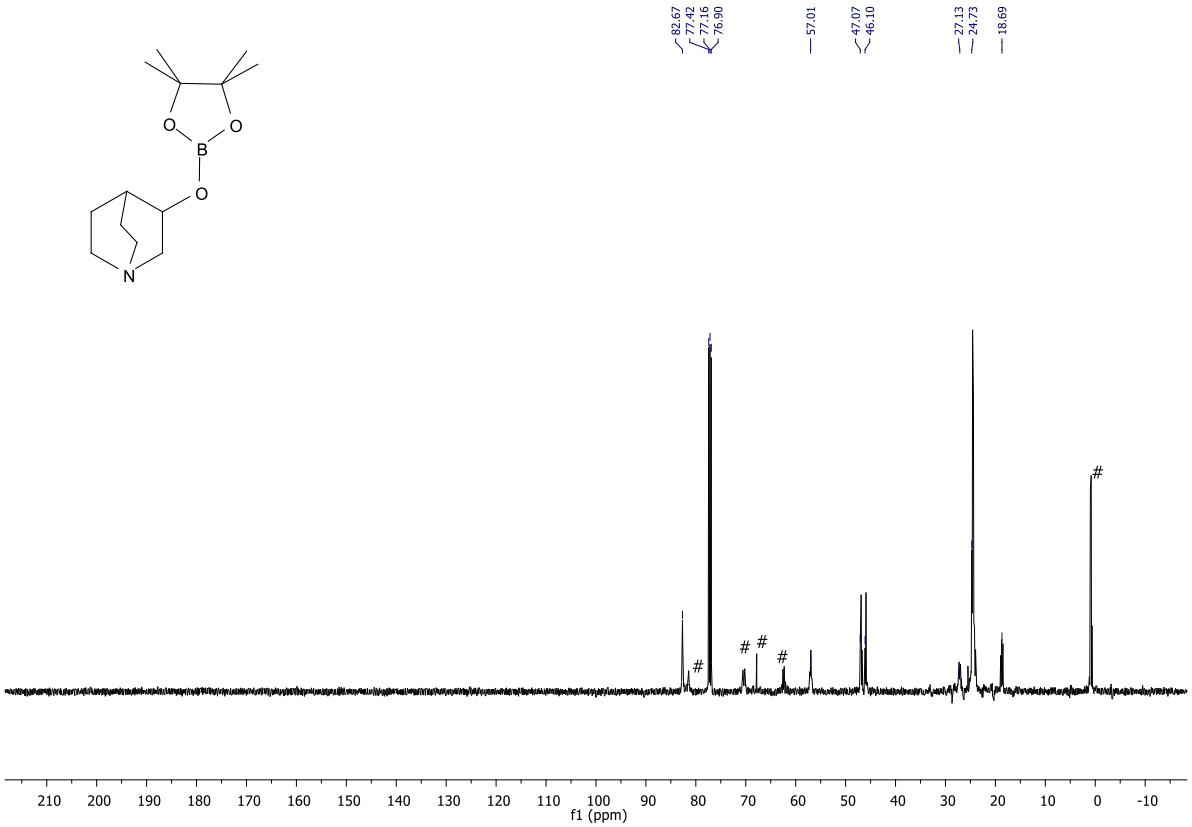
3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yloxy)quinuclidine (Table 3, 35b).[18]



^{1}H NMR of **35b** (400 MHz, $CDCl_3$)

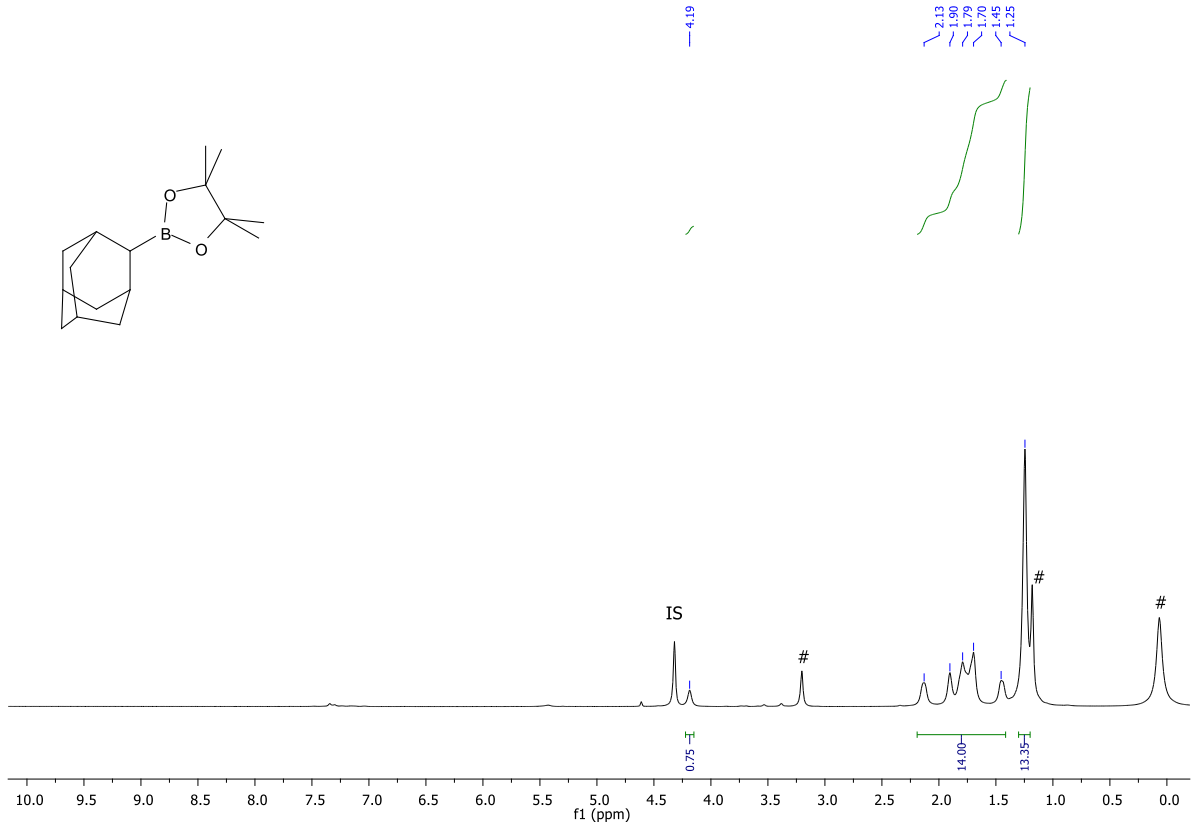


^{11}B NMR of **35b** (128 MHz, $CDCl_3$)

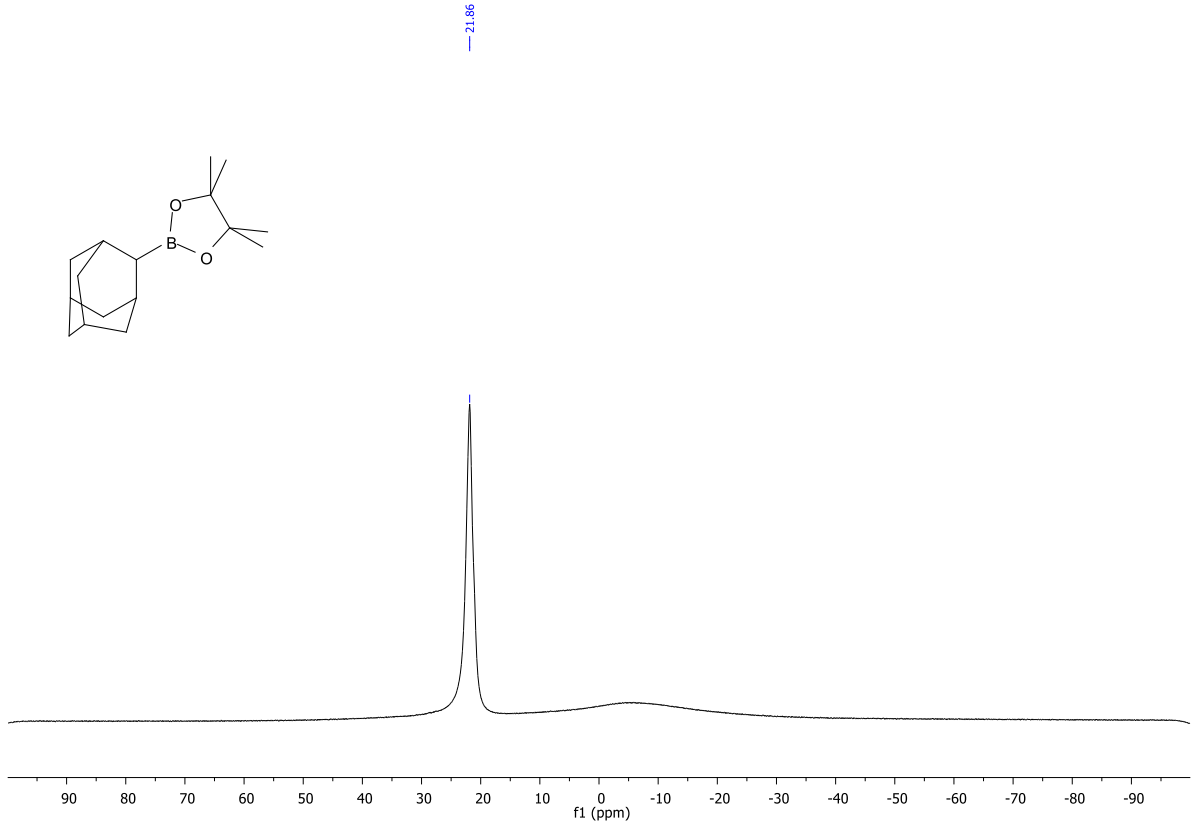


^{13}C NMR of **35b** (100 MHz, $CDCl_3$)

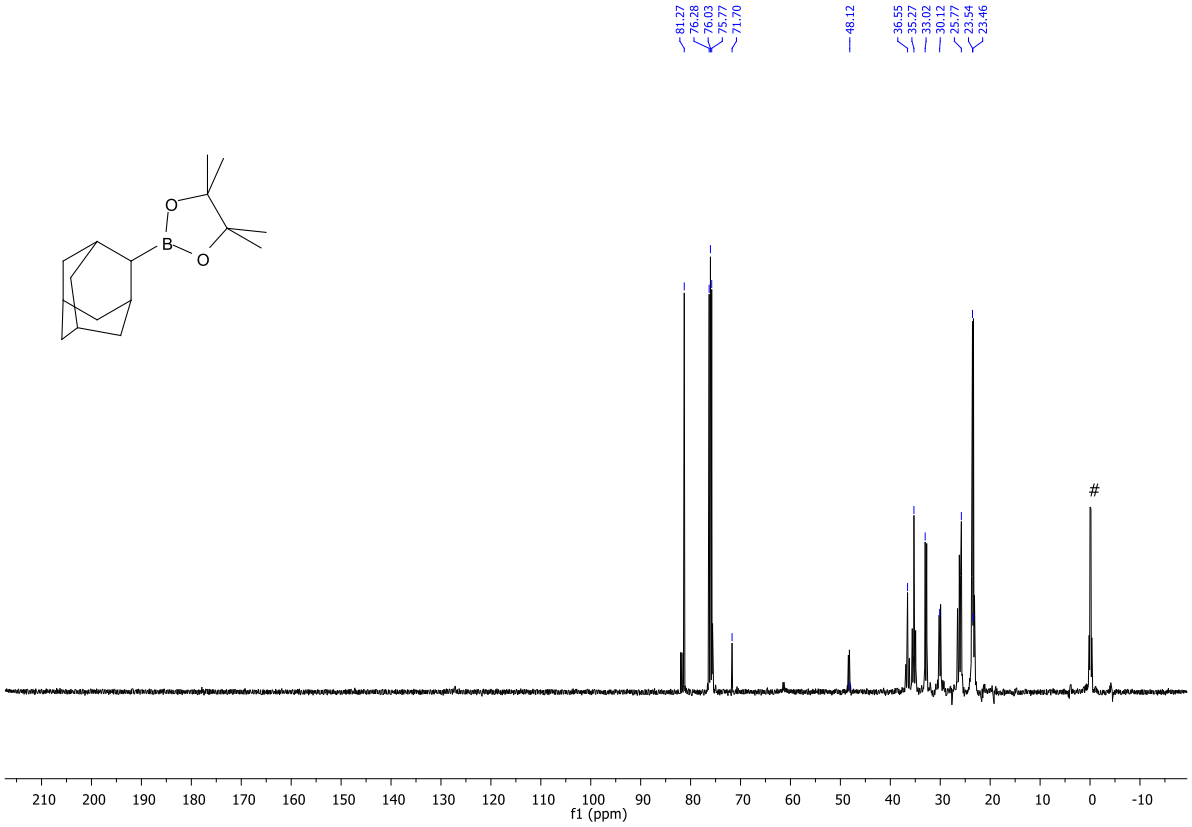
2-(Adamantan-2-yloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 36b).[18]



^{1}H NMR of **36b** (400 MHz, $CDCl_3$)

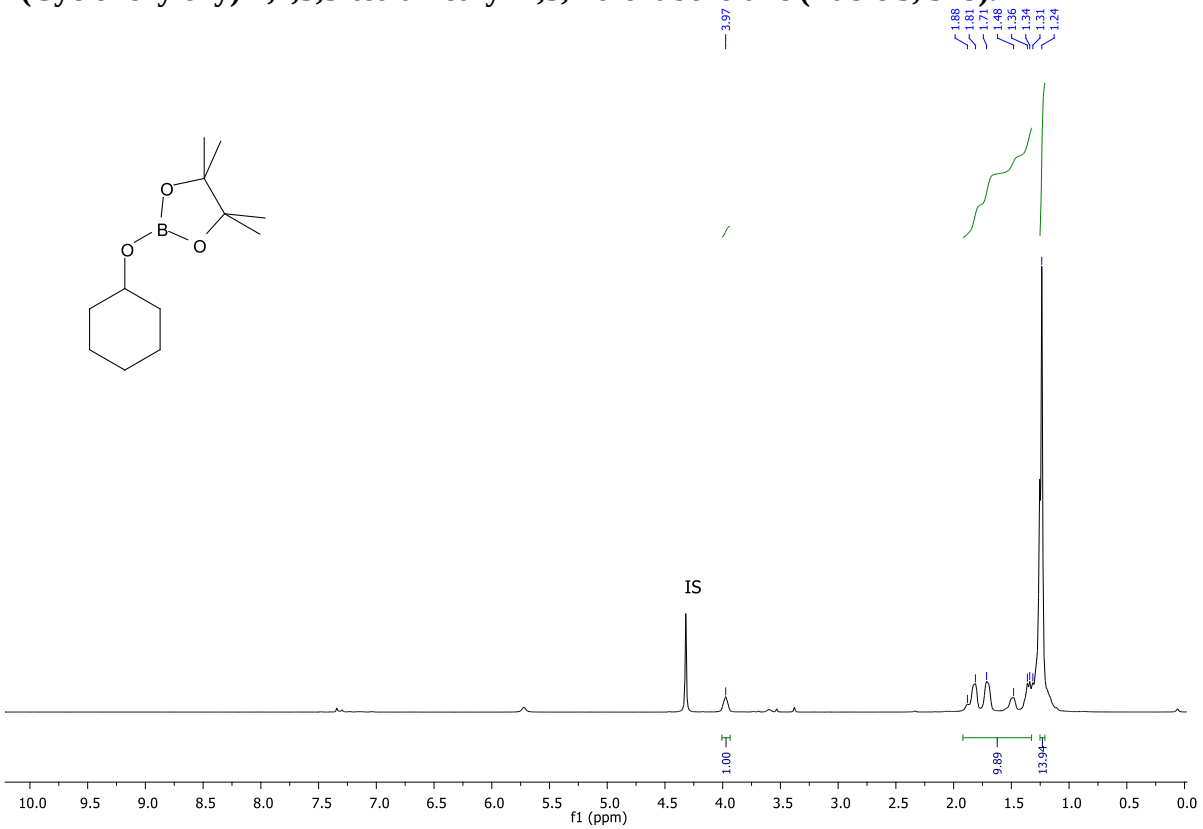


^{11}B NMR of **36b** (128 MHz, $CDCl_3$)

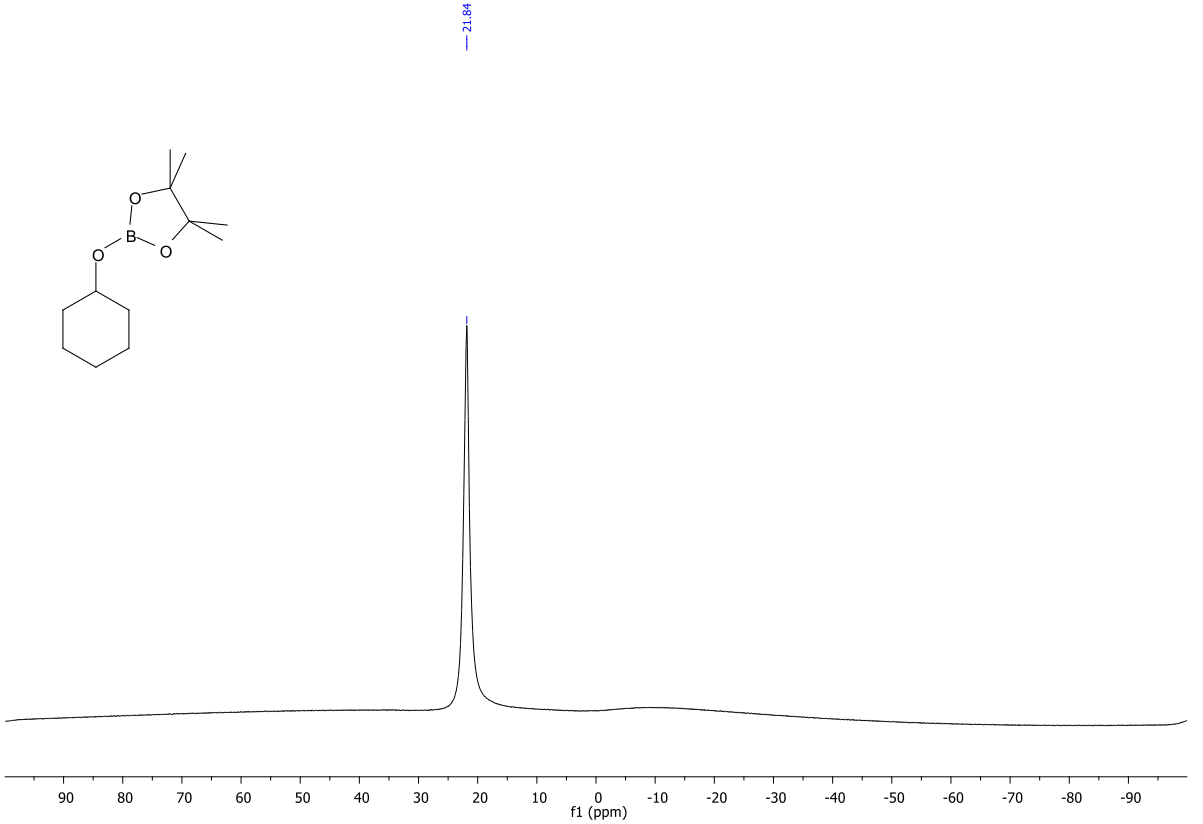


^{13}C NMR of **36b** (100 MHz, $CDCl_3$)

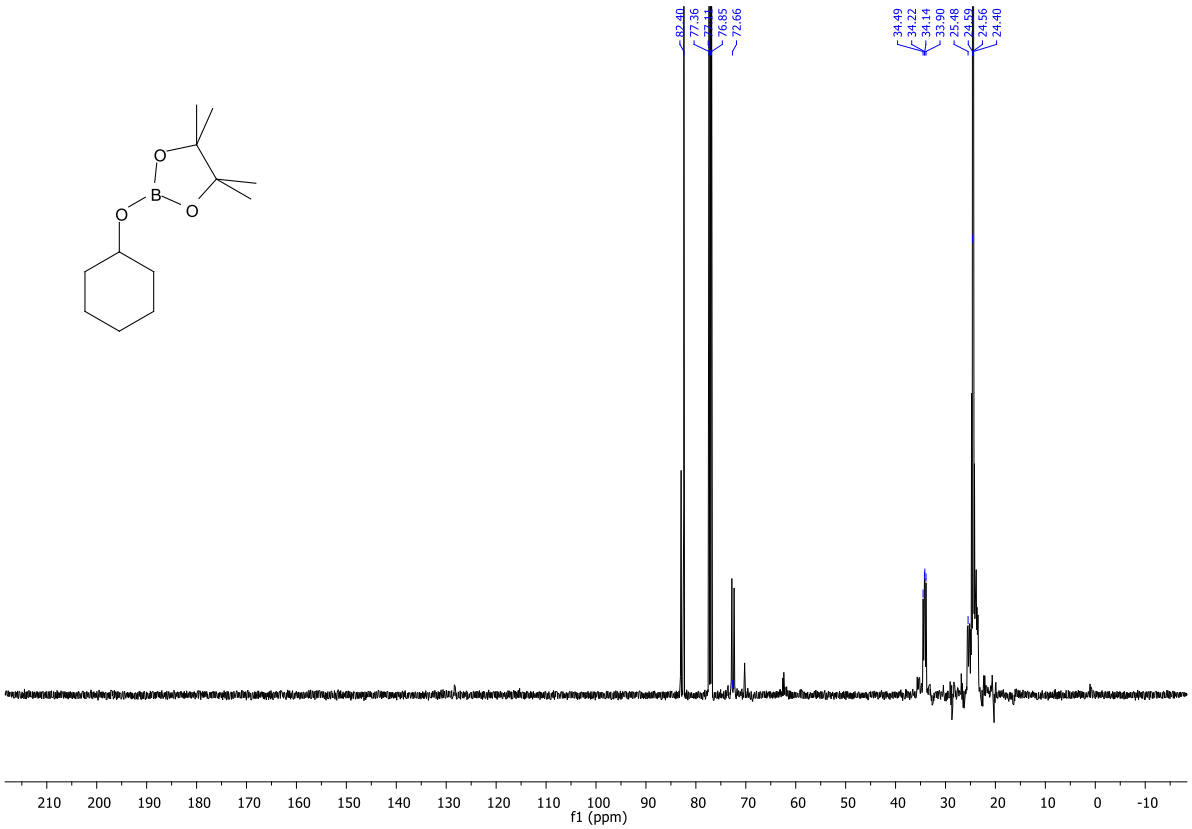
2-(Cyclohexyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, 37b).[18]



^{1}H NMR of **37b** (400 MHz, $CDCl_3$)

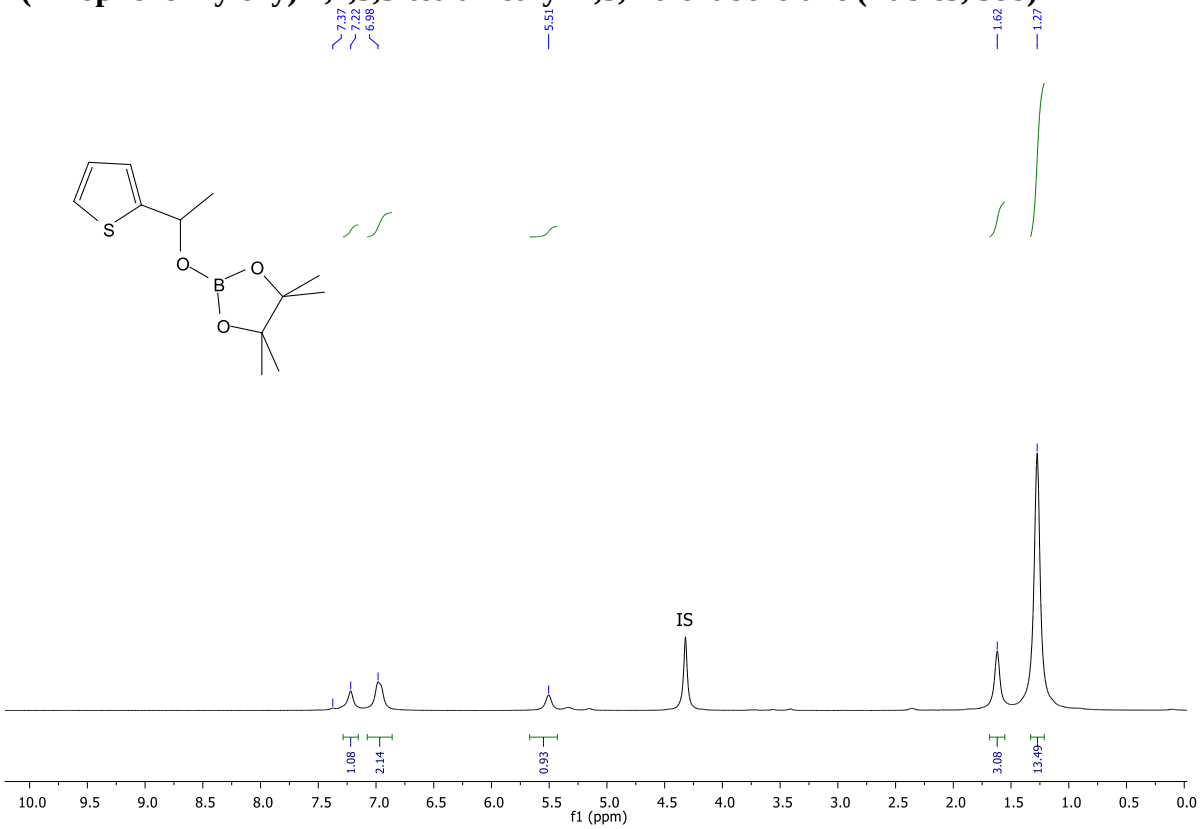


^{11}B NMR of **37b** (128 MHz, $CDCl_3$)

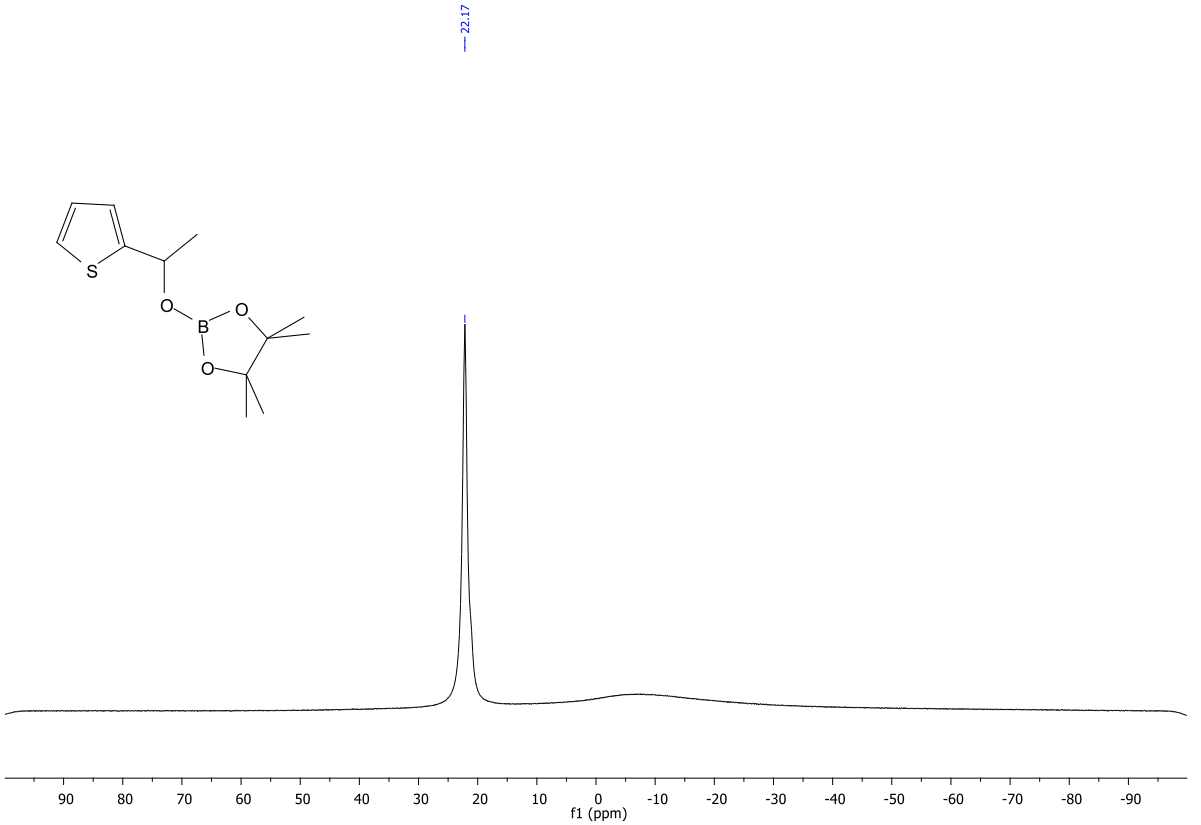


^{13}C NMR of **37b** (100 MHz, $CDCl_3$)

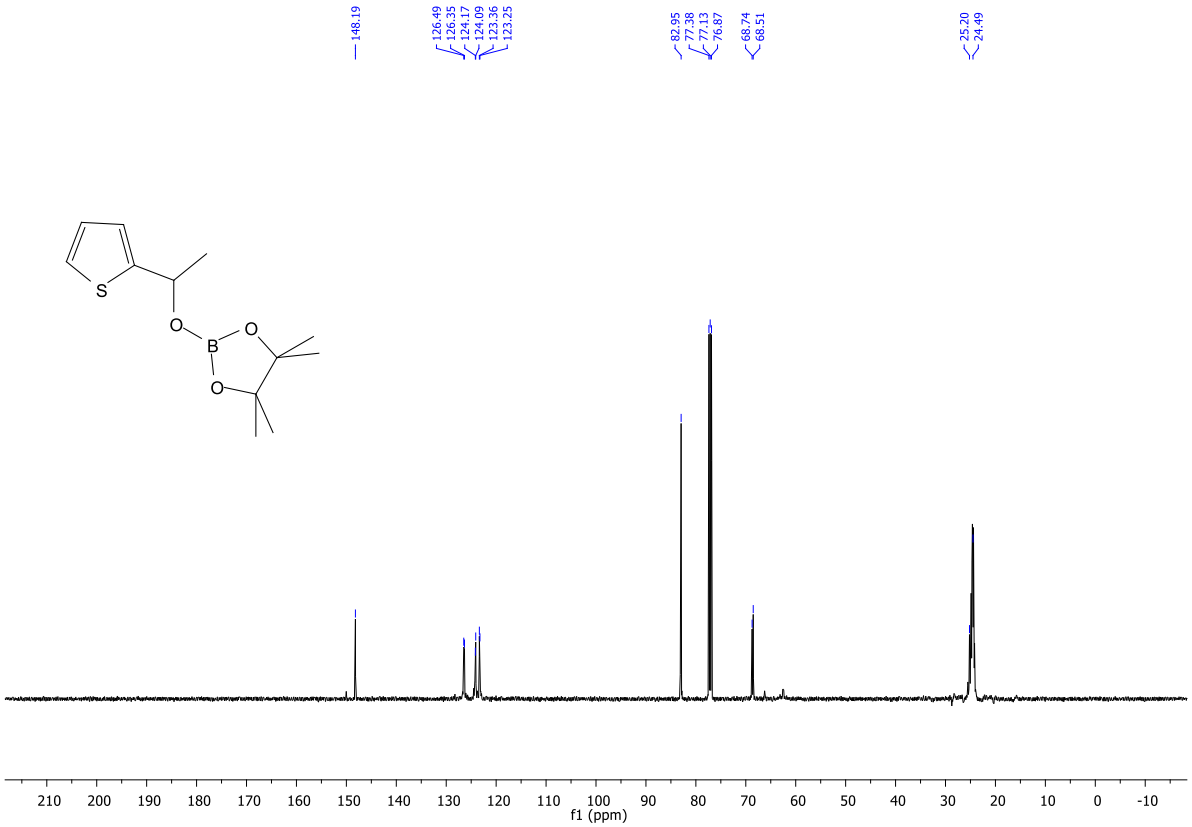
2-(Thiophene-2-yloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table3, 38b)[12]



^{1}H NMR of **38b** (400 MHz, $CDCl_3$)



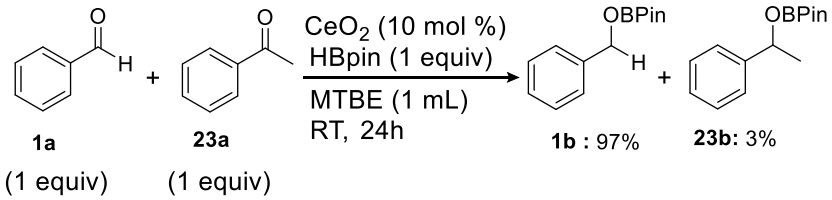
^{11}B NMR of **38b** (128MHz, $CDCl_3$)



^{13}C NMR of **38b** (100 MHz, $CDCl_3$)

V. Competitive Chemoselective Hydroboration Reactions

Experimental Procedure for the Examples Described in Scheme 1: In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, CeO_2 NPs (10 mol %, 4 mg, 0.0250 mmol), HBpin (1.0 equiv, 36 µL, 0.25 mmol), MTBE (1 mL), aldehyde (0.25 mmol) and ketone (0.25 mmol) were added, and the reaction was stirred vigorously at room temperature for 24 h (for ketone at 50 °C). 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.



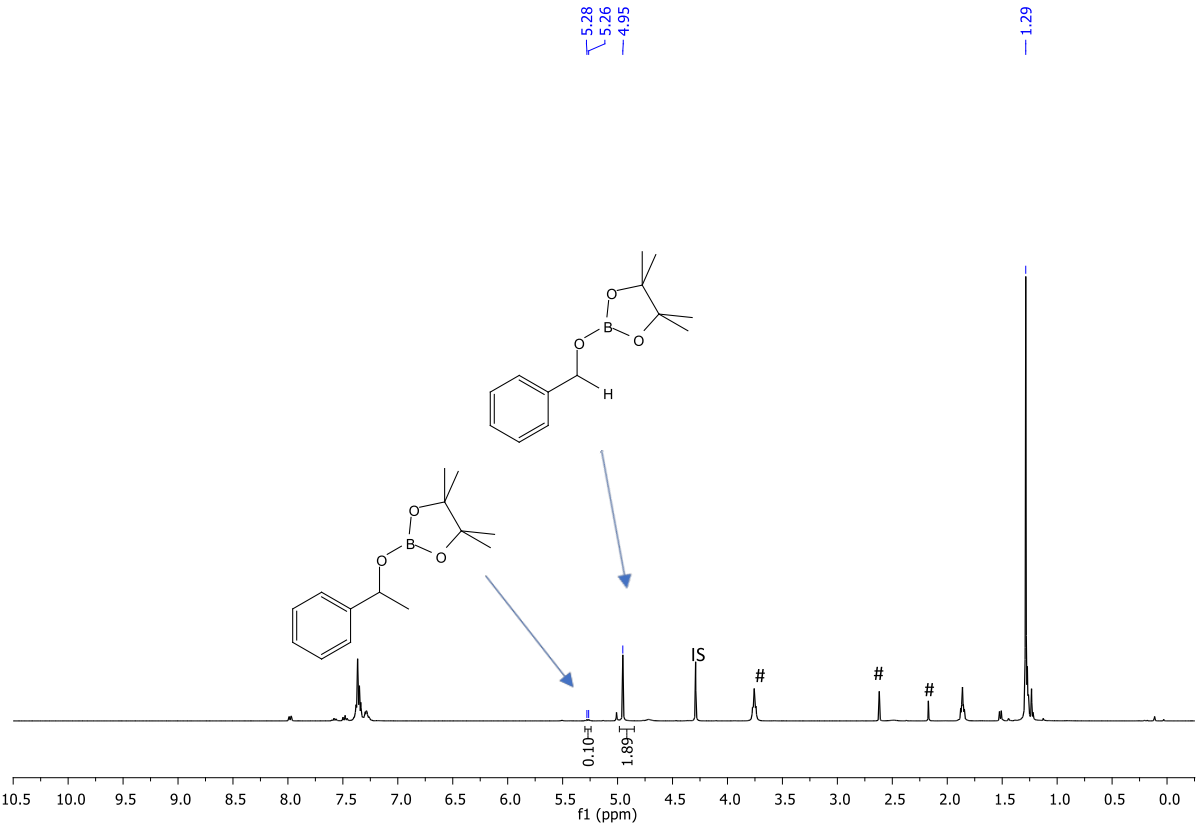


Figure S6. ^1H NMR spectra of competitive hydroboration reaction between benzaldehyde (**1a**) and acetophenone (**23a**).

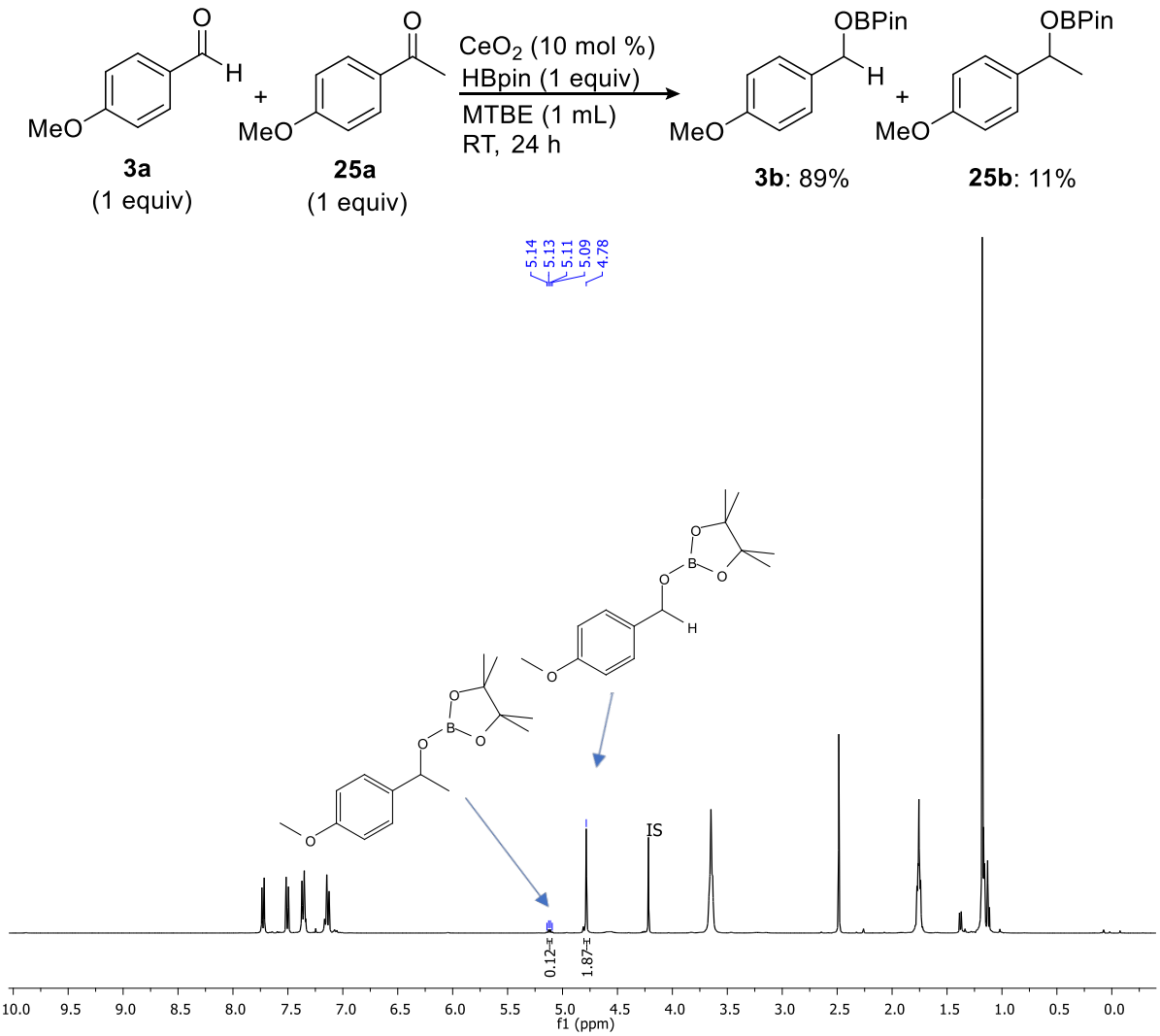


Figure S7. ^{1}H NMR spectra of competitive hydroboration reaction between 4-methoxybenzaldehyde (**3a**) and 1-(4-methoxyphenyl)ethanone (**25a**).

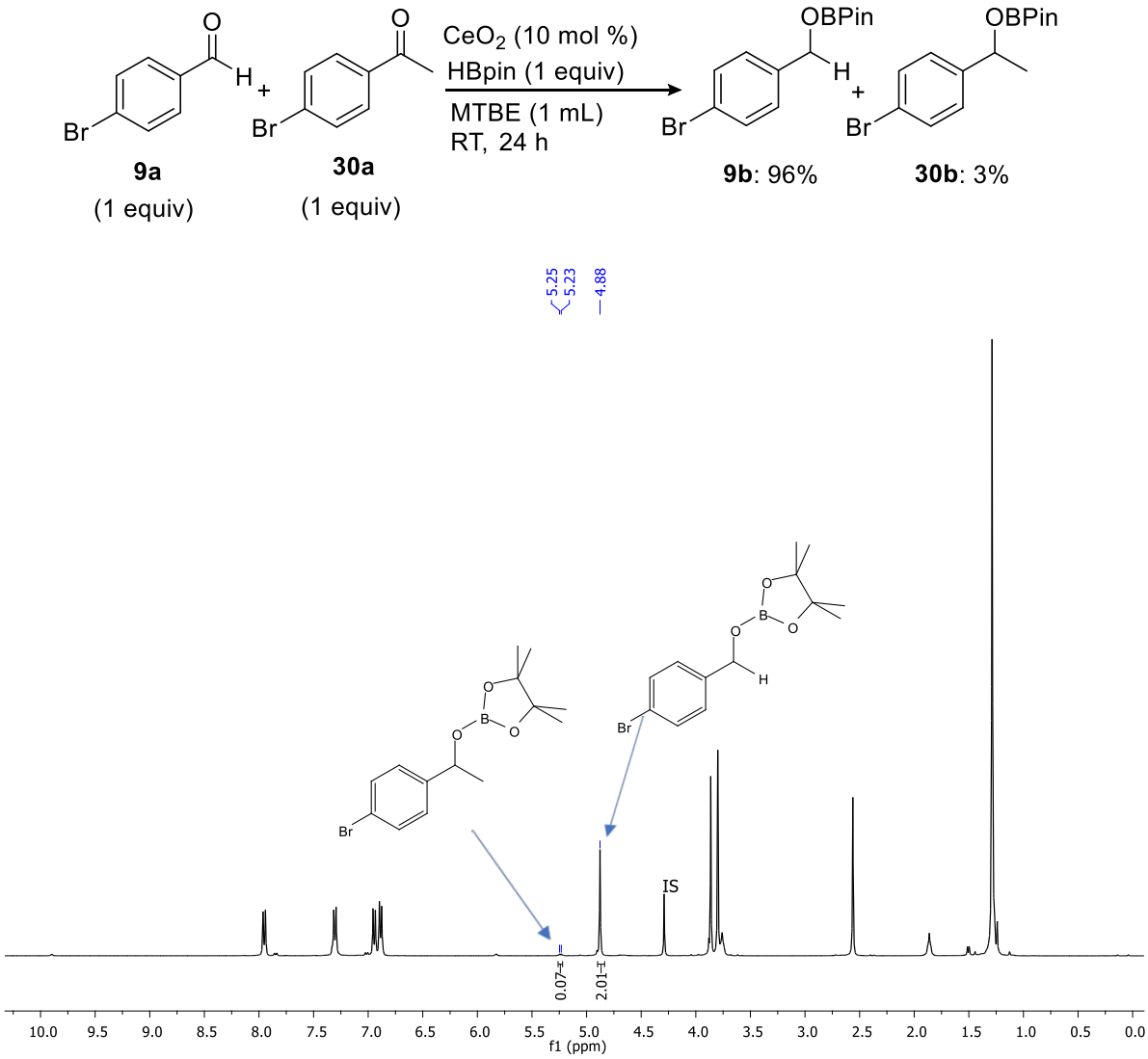


Figure S8. ^{1}H NMR spectra of competitive hydroboration reaction between 4-bromolbenzaldehyde (**9a**) and 1-(4-bromophenyl)ethenone (**30a**).

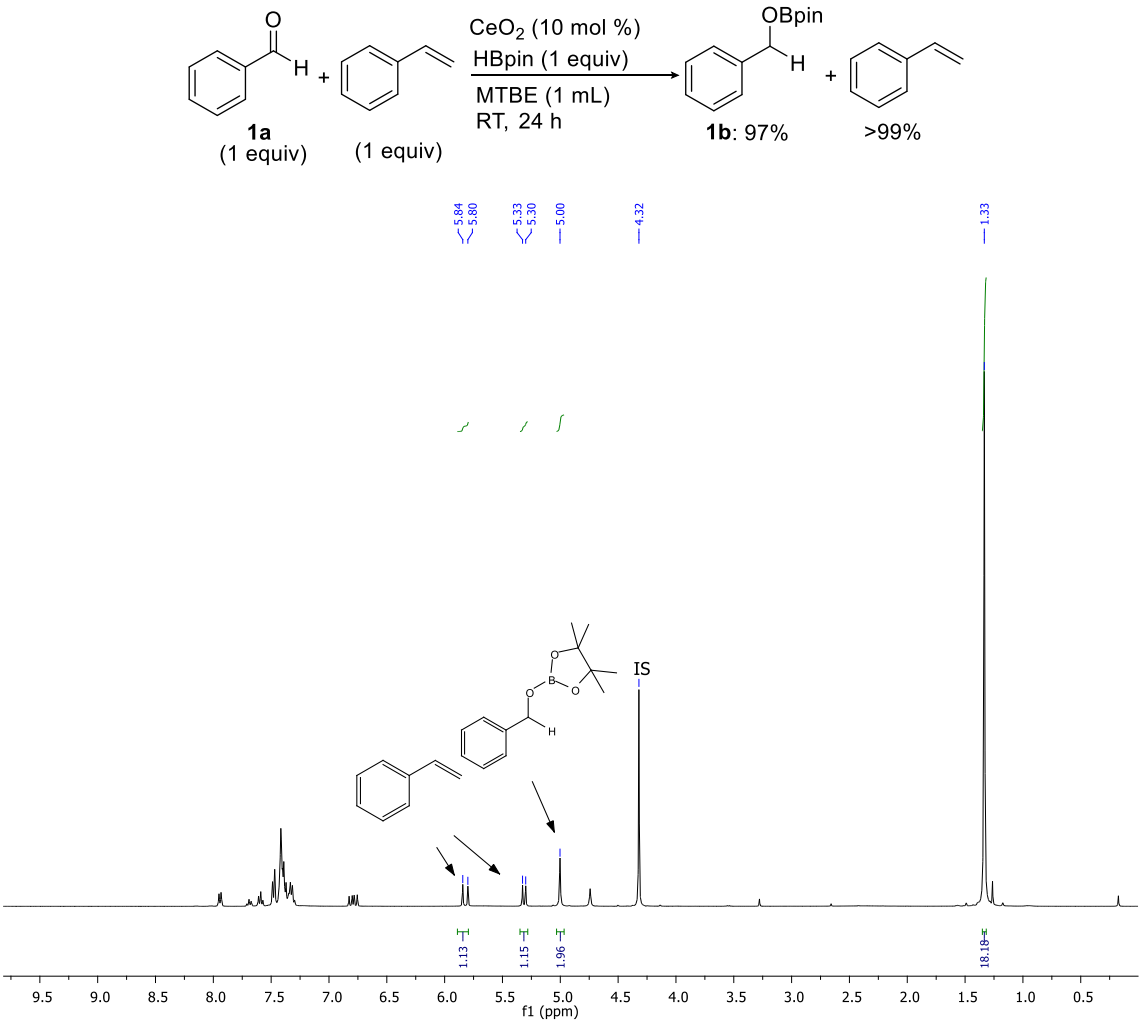


Figure S9. ^{1}H NMR spectra of competitive hydroboration reaction between benzaldehyde (**1a**) and styrene.

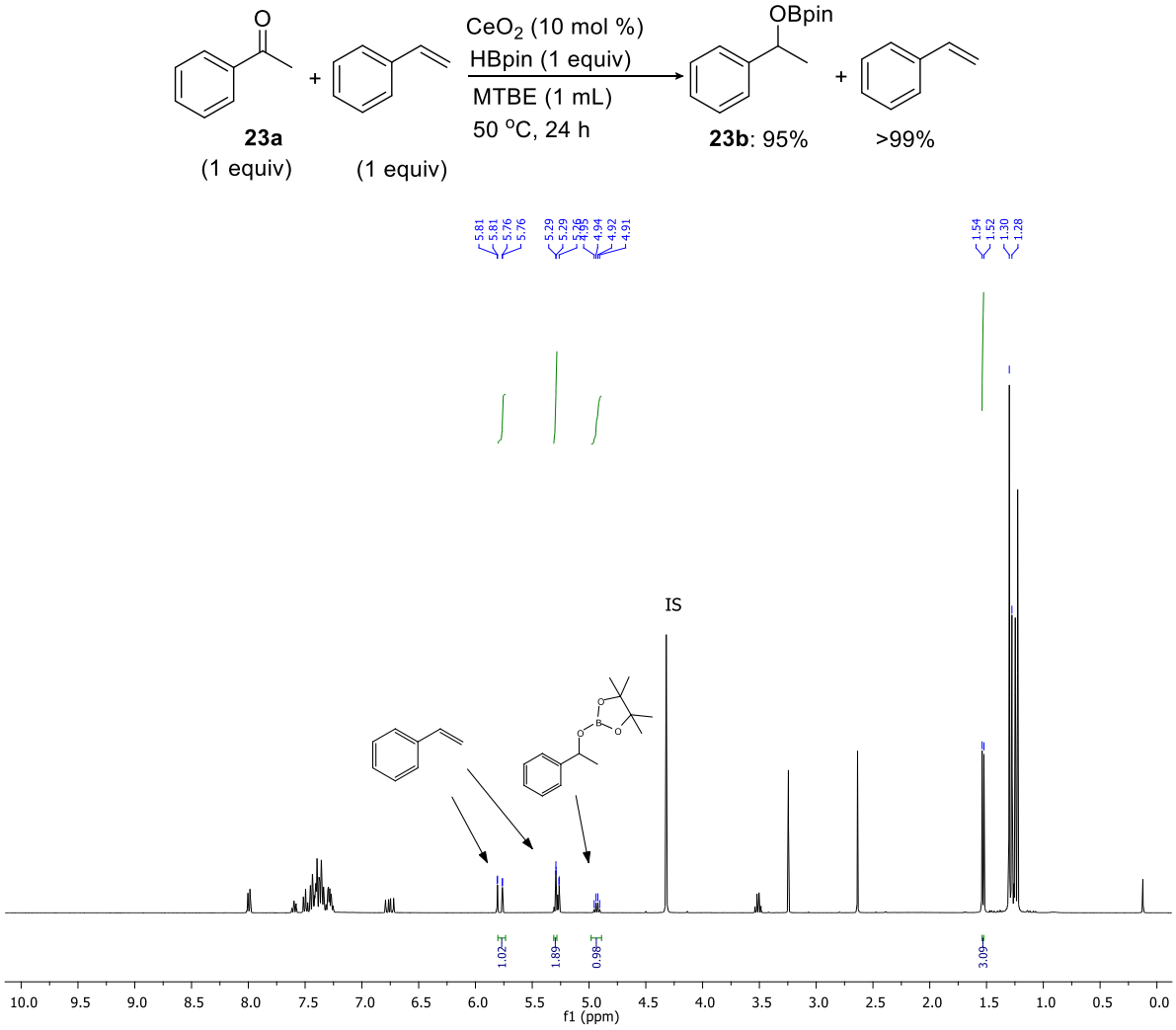


Figure S10. ^{1}H NMR spectra of competitive hydroboration reaction between acetophenone (**23a**) and styrene.

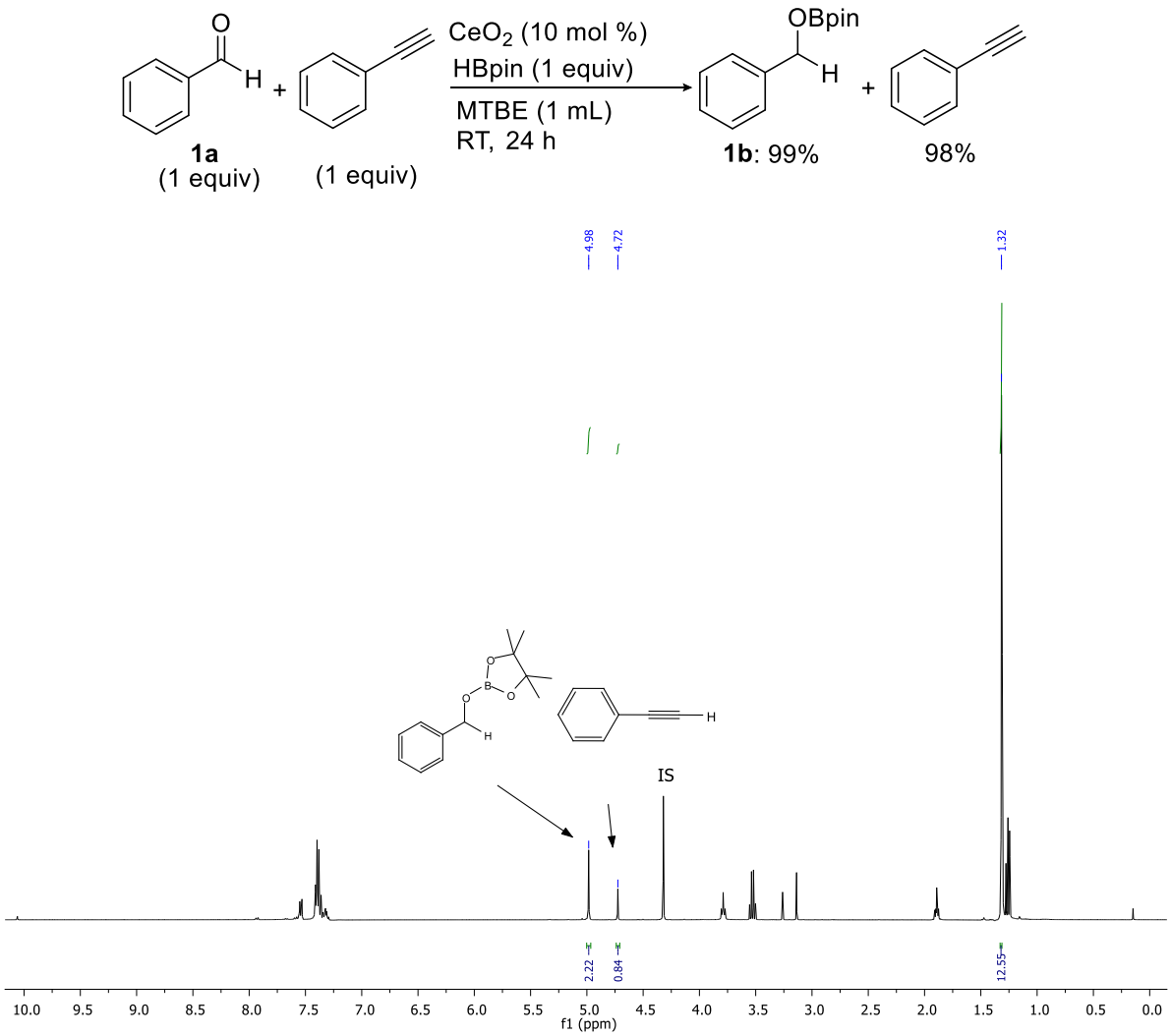


Figure S11. ^{1}H NMR spectra of competitive hydroboration reaction between benzaldehyde (**1a**) and phenylacetylene.

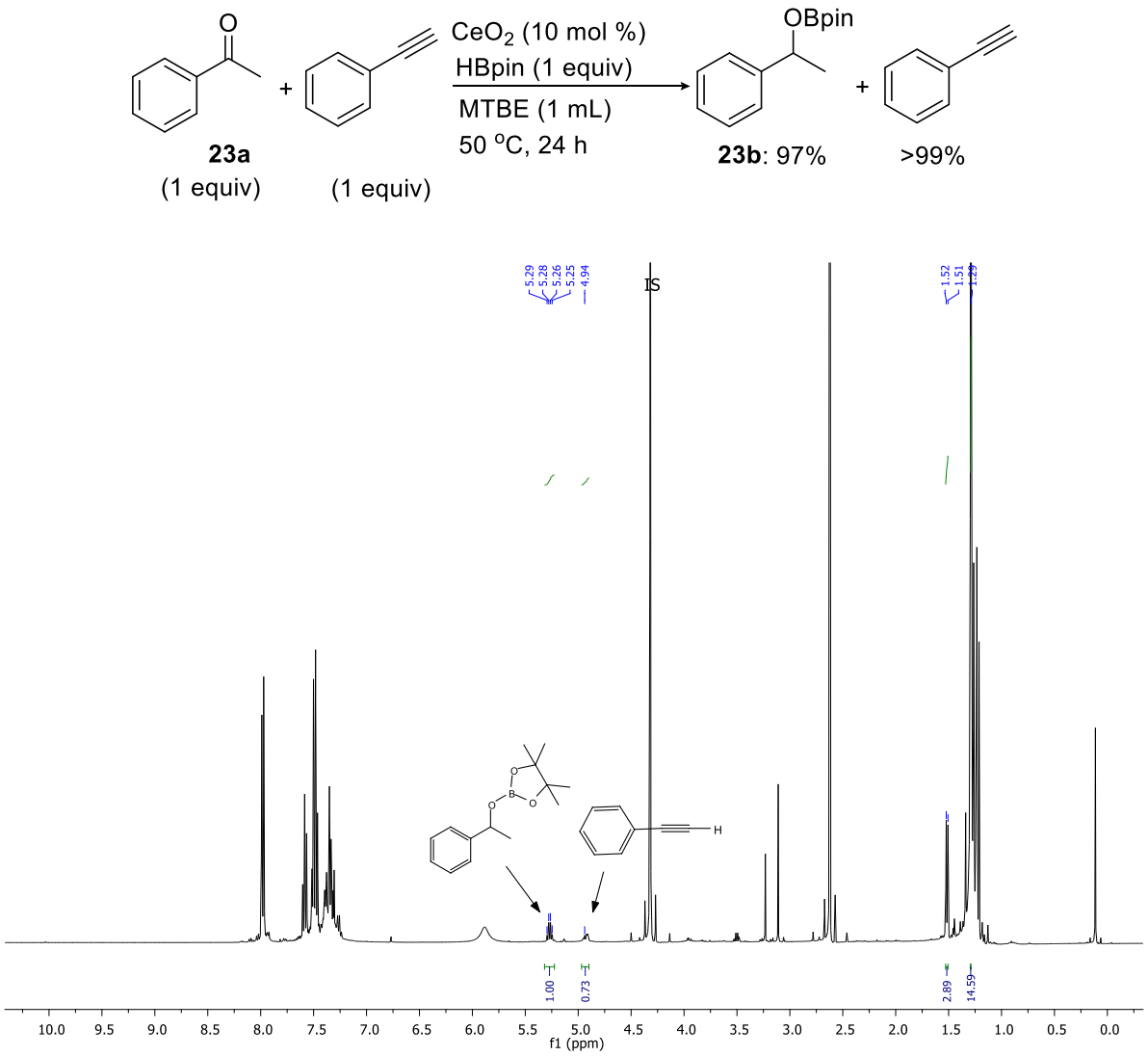


Figure S12. ^{1}H NMR spectra of competitive hydroboration reaction between acetophenone (**23a**) and phenylacetylene.

Experimental Procedure for the Examples Described in Scheme 2: In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, CeO_2 NPs (10 mol %, 4 mg, 0.0250 mmol), HBpin (1.0 equiv, 36 µL, 0.25 mmol), MTBE (1 mL) and substrate (0.25 mmol) were added and the reaction was stirred vigorously at room temperature for 24 h (for ketone at 50 °C). 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.

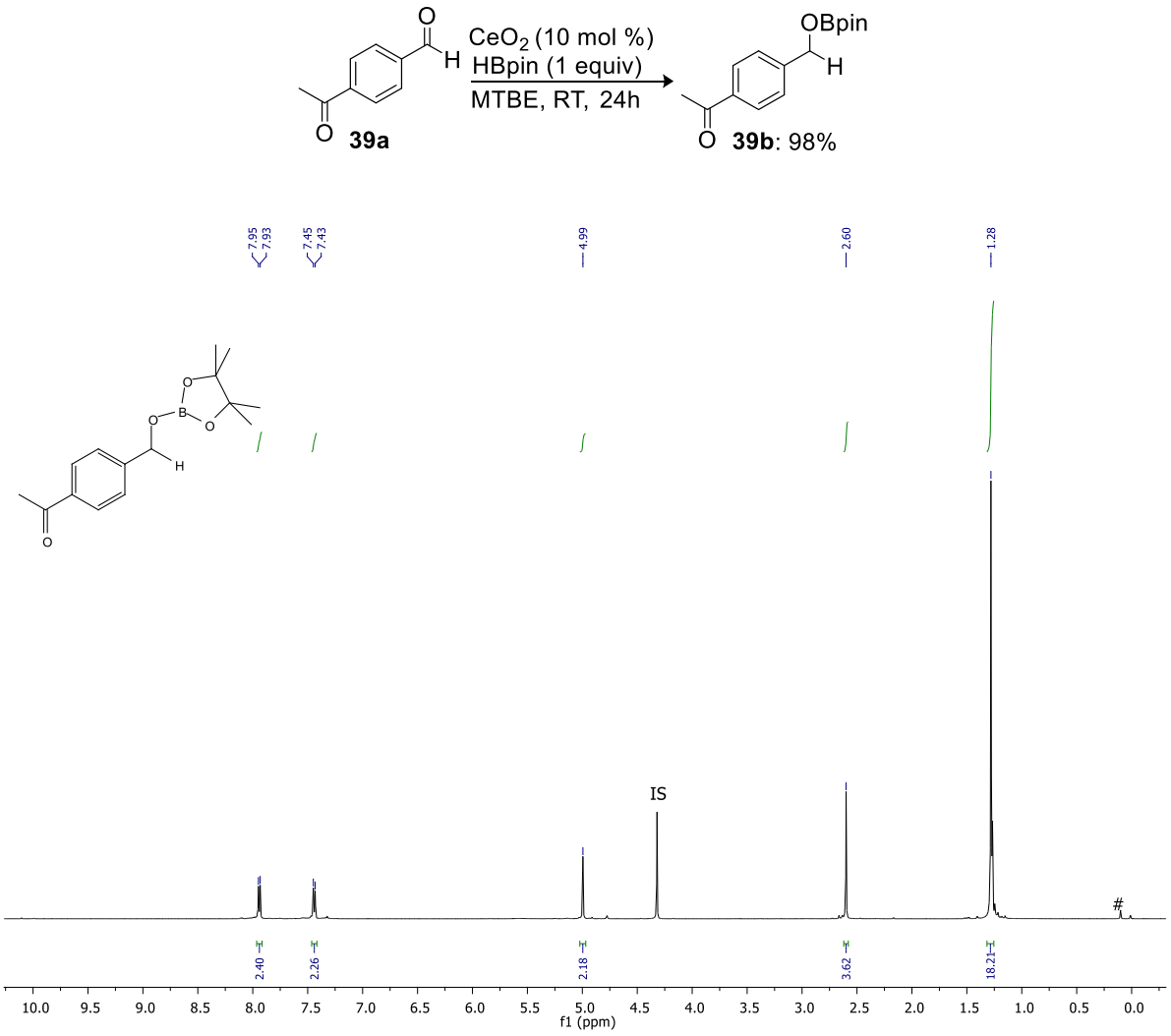


Figure S13. ^1H NMR spectra of intramolecular competitive hydroboration reaction of 4-acetylbenzaldehyde (**39a**).

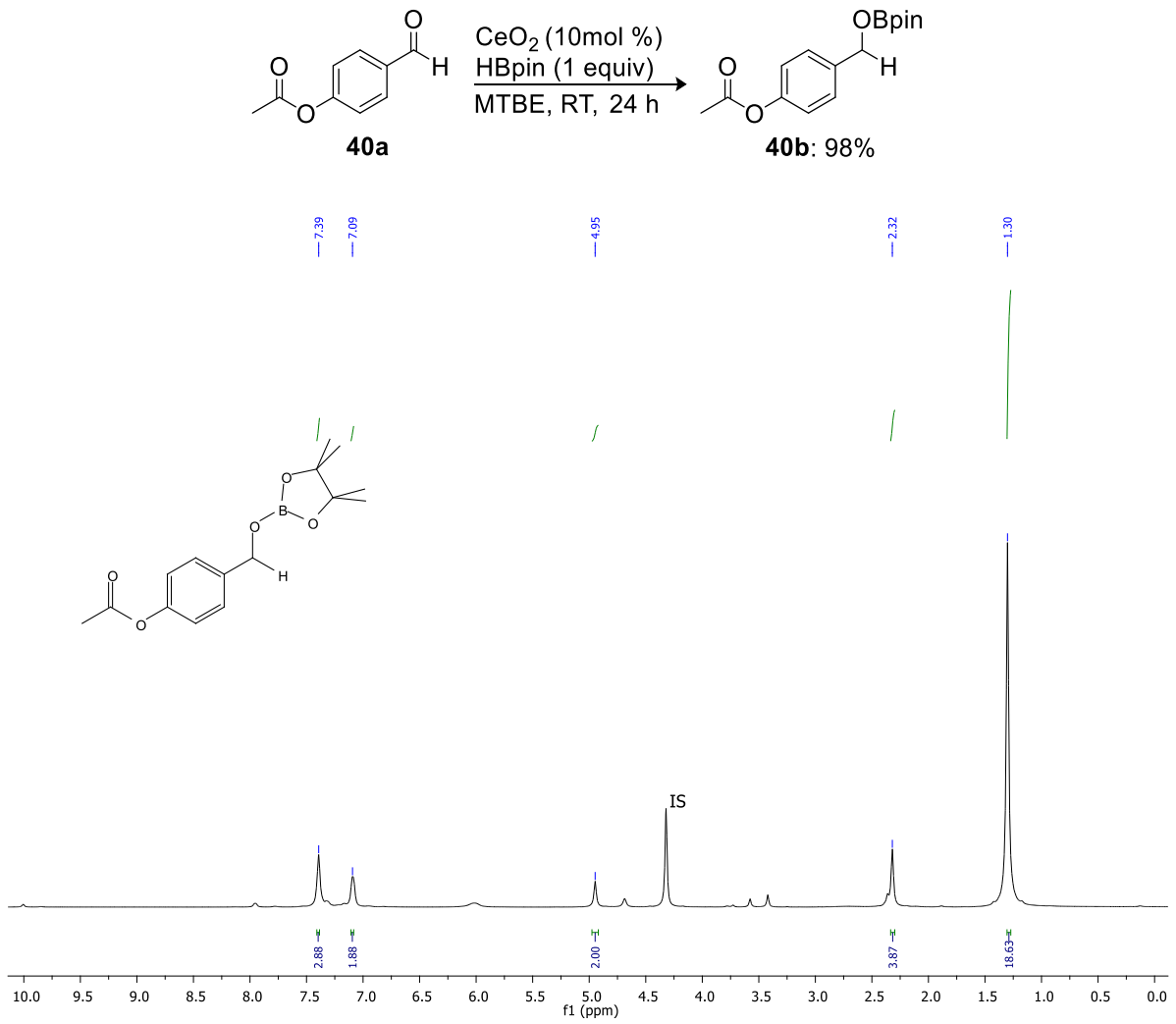


Figure S14. ^{1}H NMR spectra of intramolecular competitive hydroboration reaction of 4-formylphenyl acetate (**40a**).

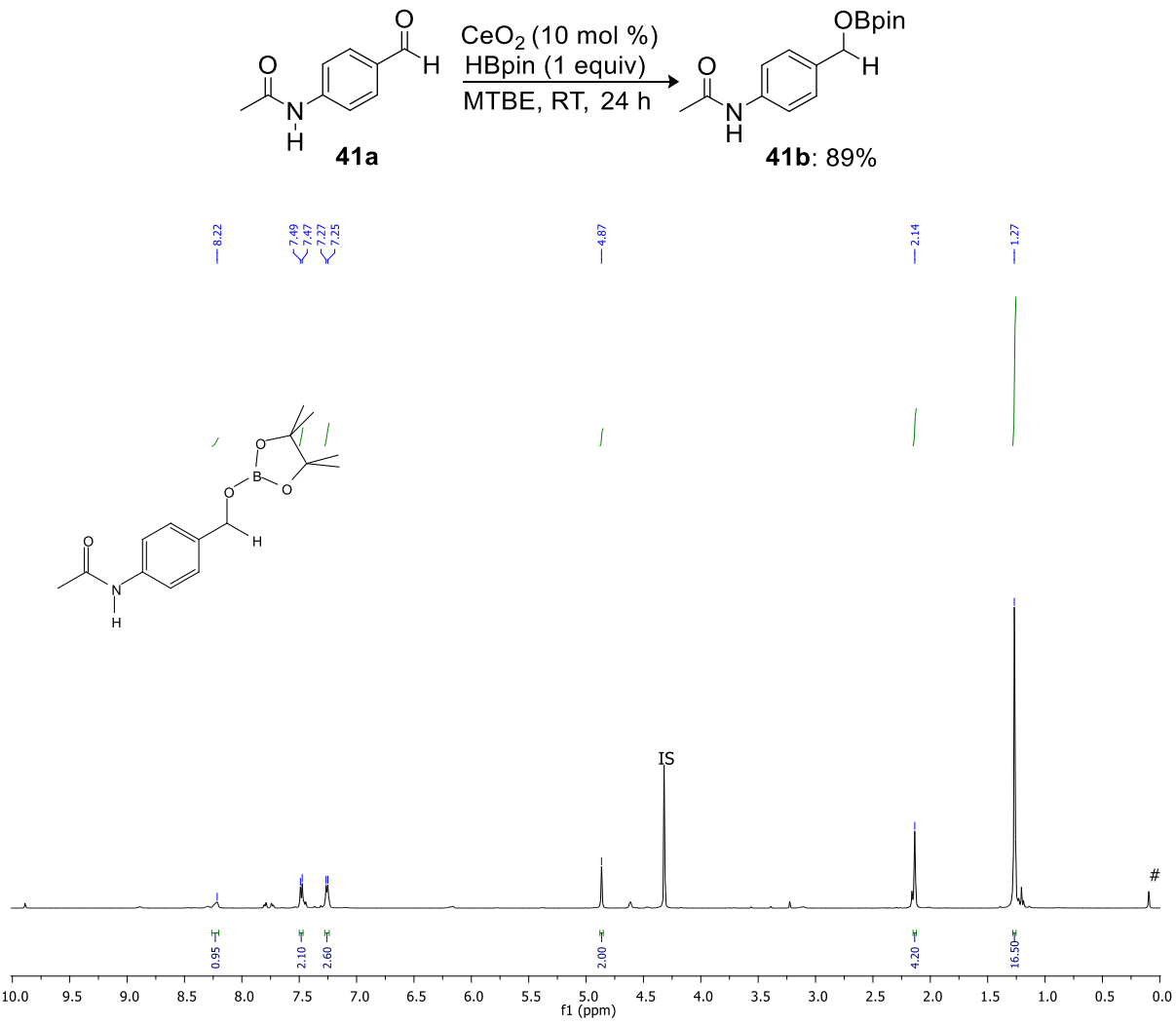


Figure S15. ^{1}H NMR spectra of intramolecular competitive hydroboration reaction of N-(4-formylphenyl)acetamide (**41a**).

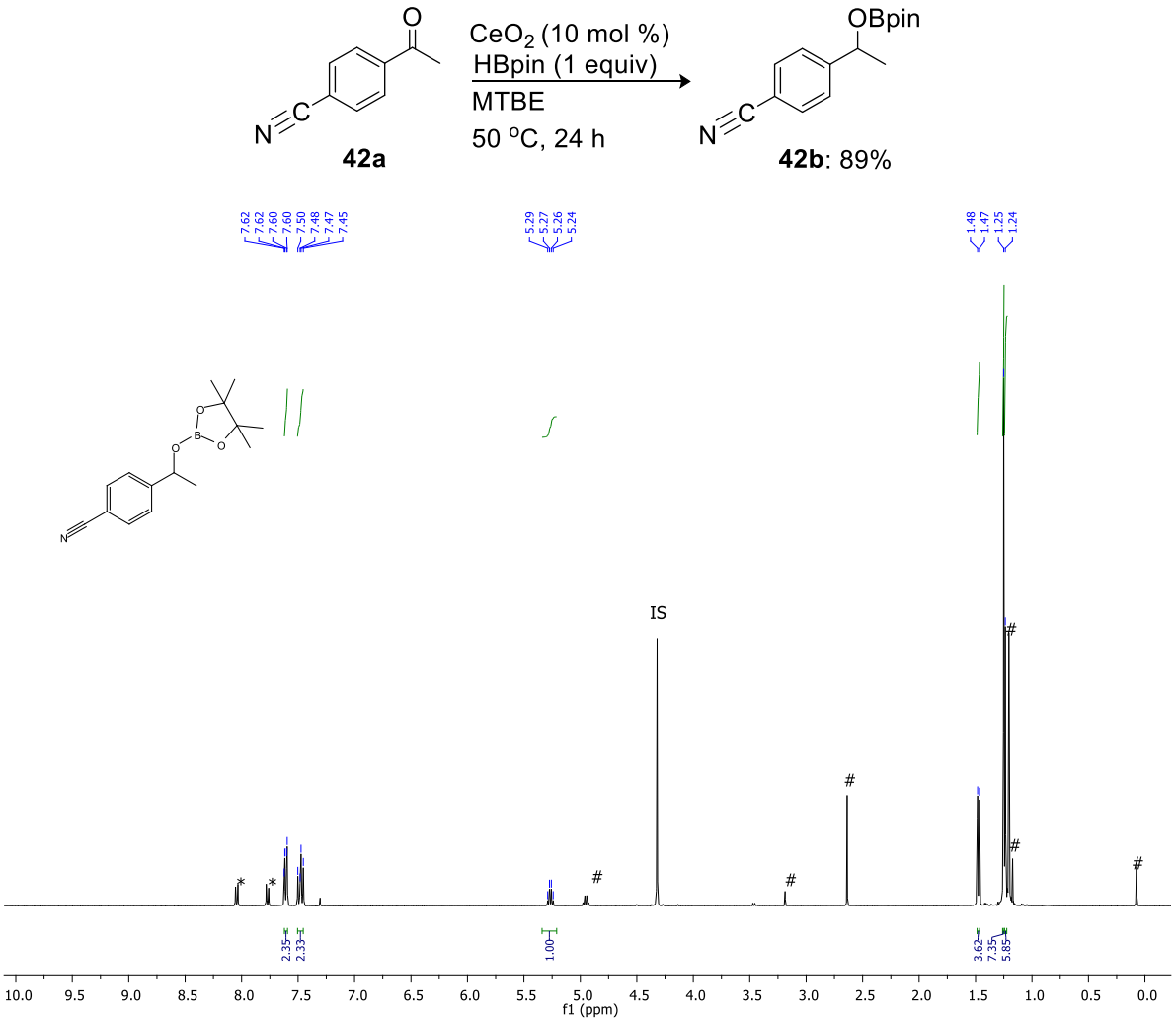


Figure S16. ^{1}H NMR spectra of intramolecular competitive hydroboration reaction of 4-acetylbenzonitrile (**42a**).

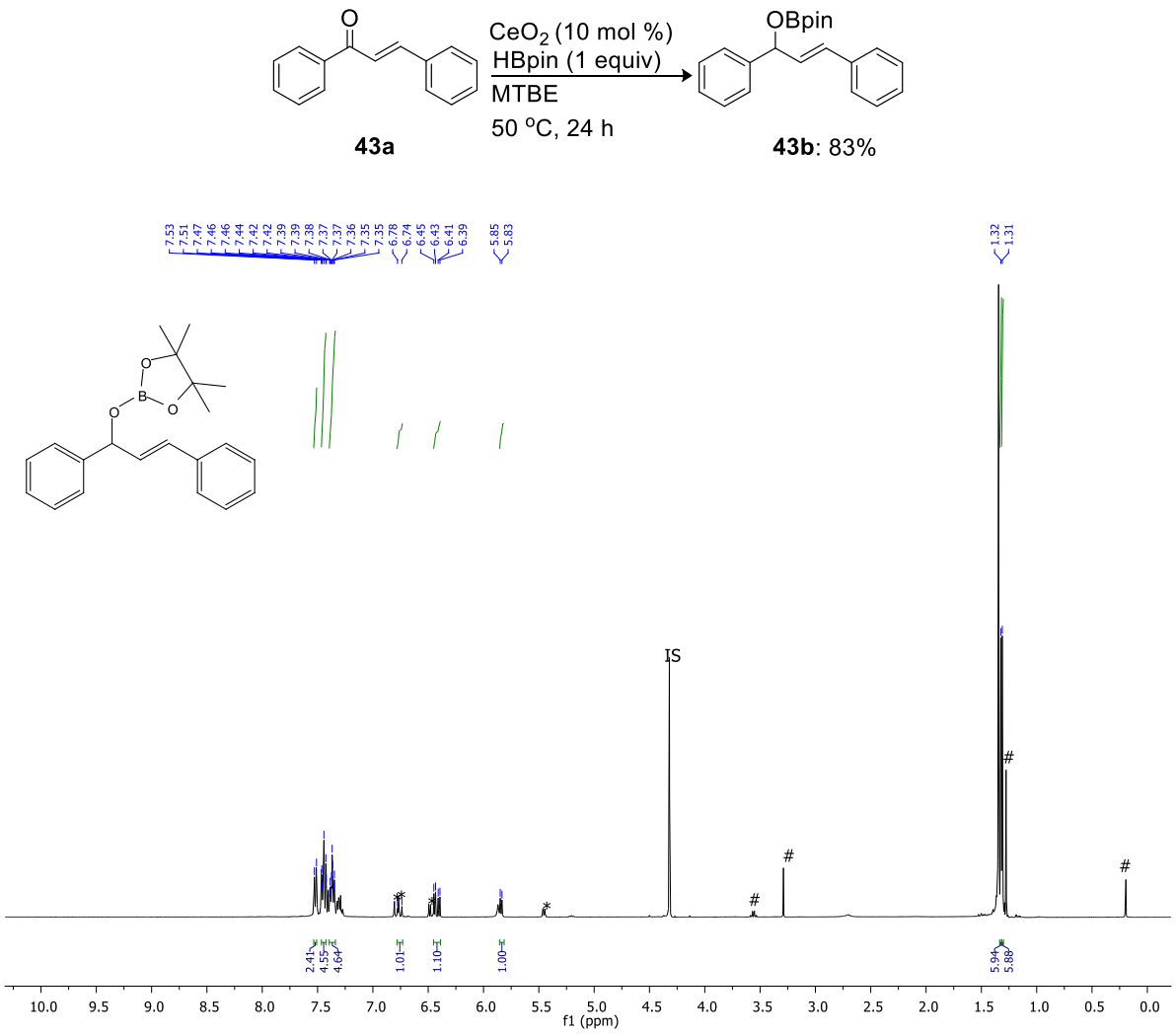


Figure S17. ^{1}H NMR spectra of intramolecular competitive hydroboration reaction of (*E*)-chalcone (**43a**).

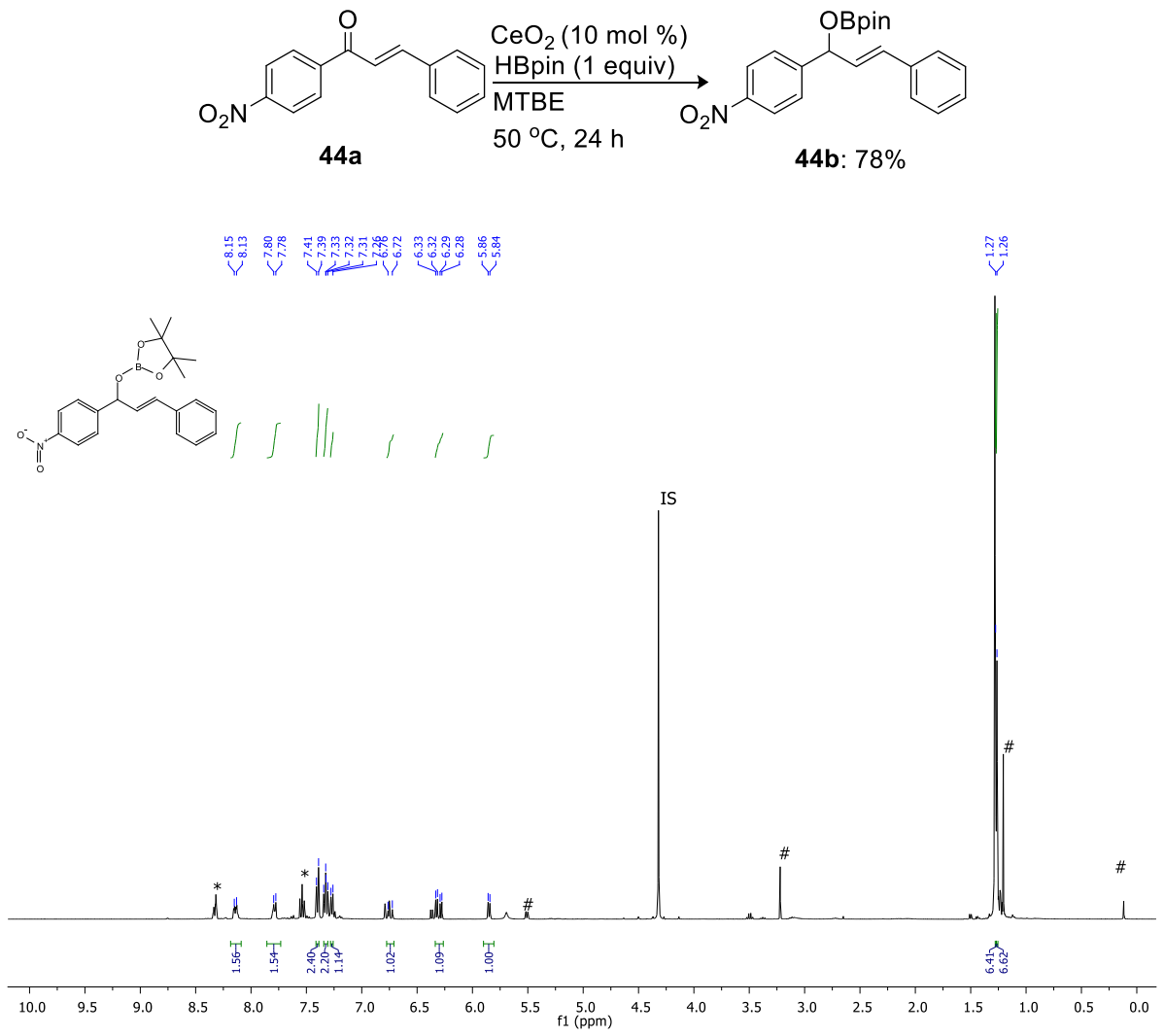
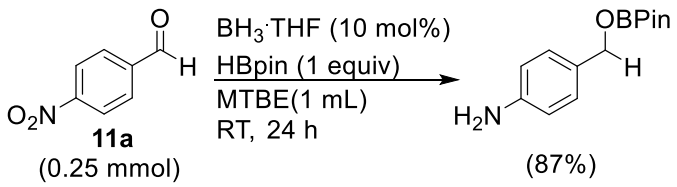


Figure S18. [1]H NMR spectra of intramolecular competitive hydroboration reaction of (*E*)-1-(4-nitrophenyl)-3-phenylprop-2-en-1-one (**44a**).

Experimental Procedure for BH_3 Mediated Reduction: In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, BH_3·THF (10 mol %, 0.0250 mmol), HBpin (1.0 equiv, 36 µL, 0.25 mmol), MTBE (1 mL) and substrate (0.25 mmol) were added, and the reaction was stirred vigorously at room temperature for 24 h (for ketone at 50 °C). 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.

A). The BH_3 mediated carbonyl hydroboration of 4-nitrobenzaldehyde (**11a**) having both NO_2 and C=O groups gave reduction at the carbonyl part as well as nitro group.



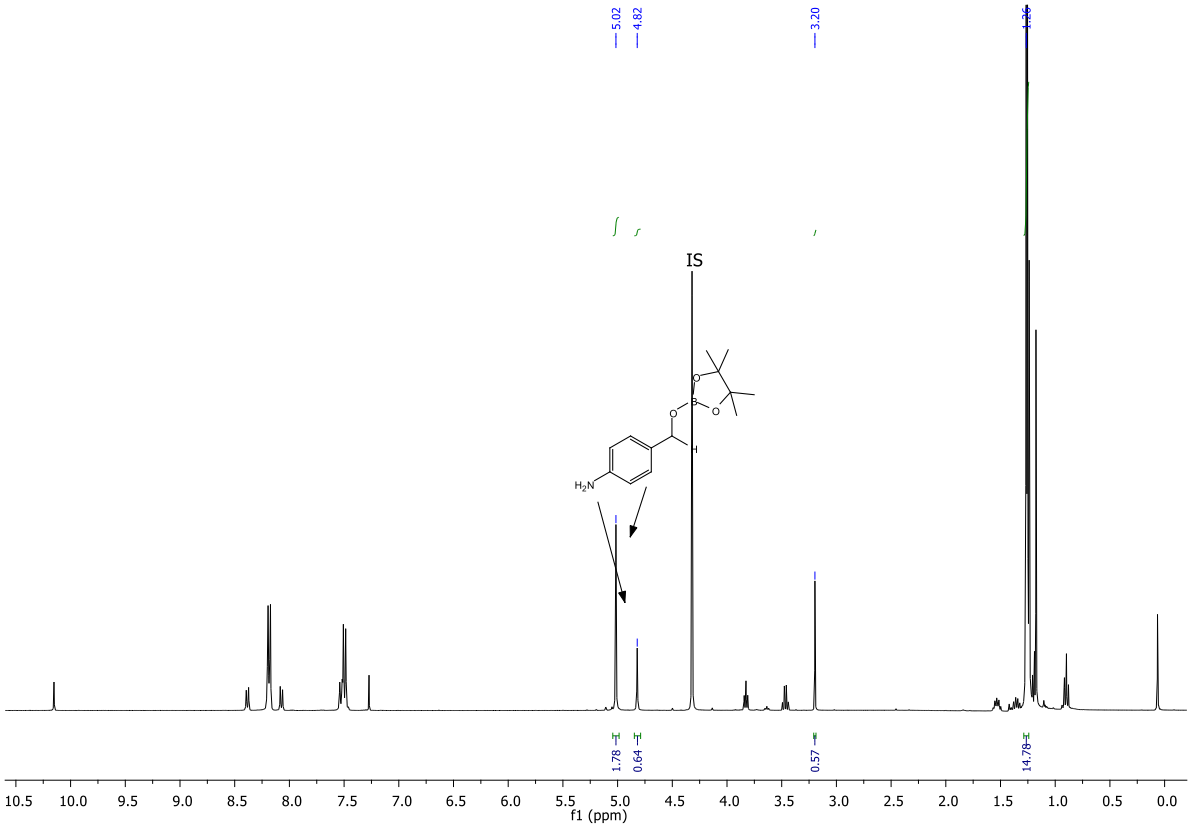


Figure S19. ^1H NMR spectra of intramolecular competitive hydroboration reaction of 4-nitrobenzaldehyde (**11a**) catalyse by BH_3·THF.

B). The intermolecular selectivity experiments were performed using BH_3 as a catalyst. The equimolar amounts of benzaldehyde (**1a**) and styrene with HBpin in the presence of BH_3·THF catalyst gave both aldehyde (**1b**: 48%) and styrene hydroboration (52%) products.

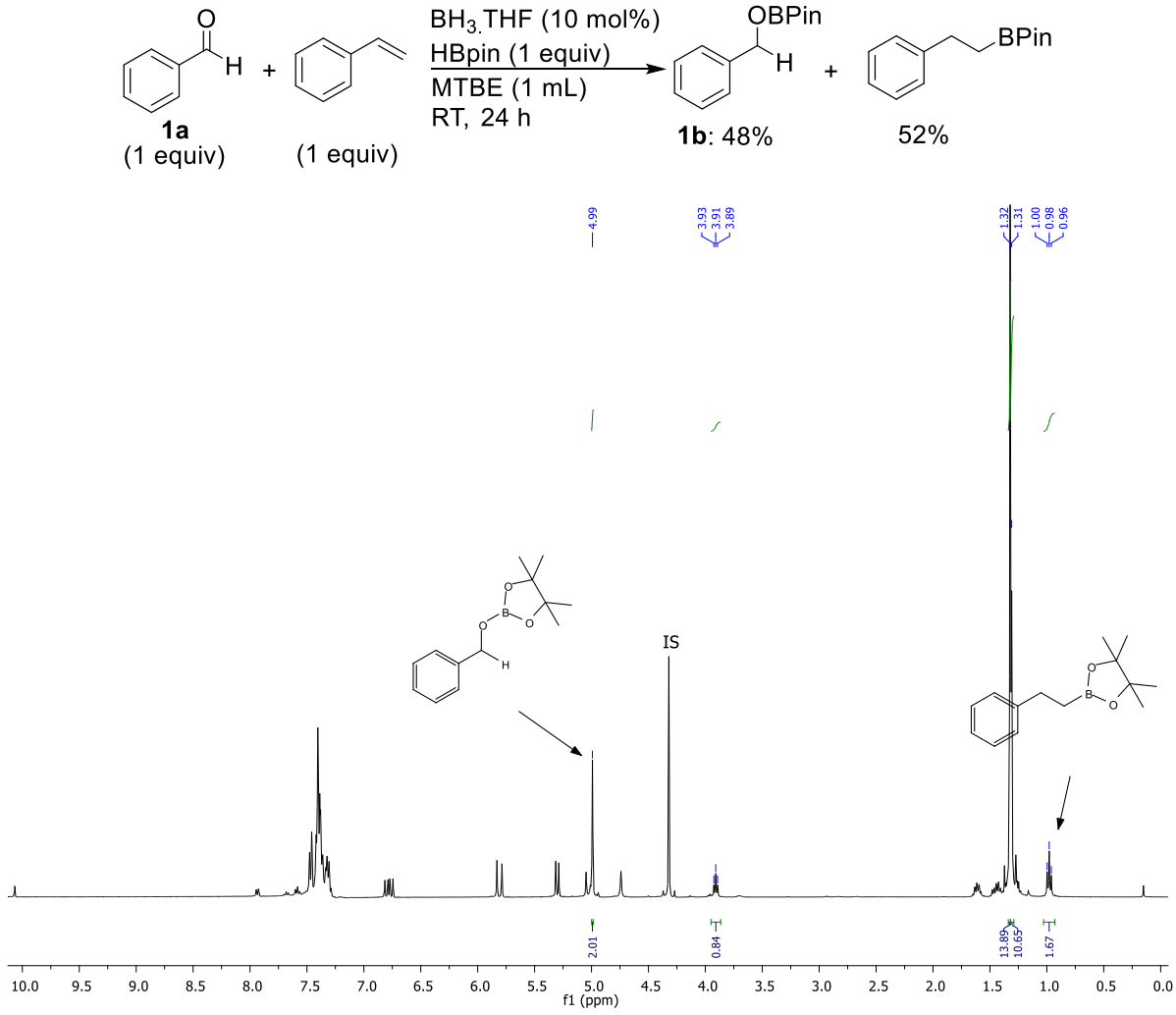
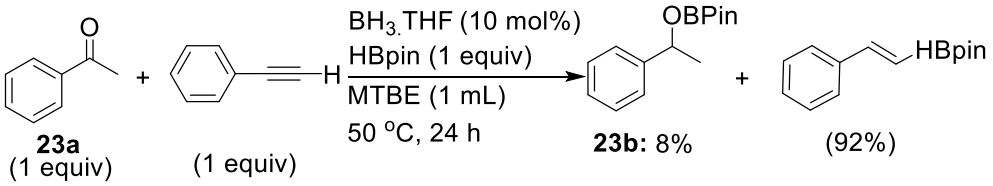


Figure S20. ^{1}H NMR spectra of intermolecular competitive hydroboration reaction between benzaldehyde (**1a**) and styrene catalyse by BH_3·THF.

C). The intermolecular selectivity experiments were performed using BH_3 as a catalyst. The reaction between stoichiometric amounts of acetophenone, phenylacetylene and HBpin gave 8% ketone hydroboration and 92% alkyne hydroboration products.



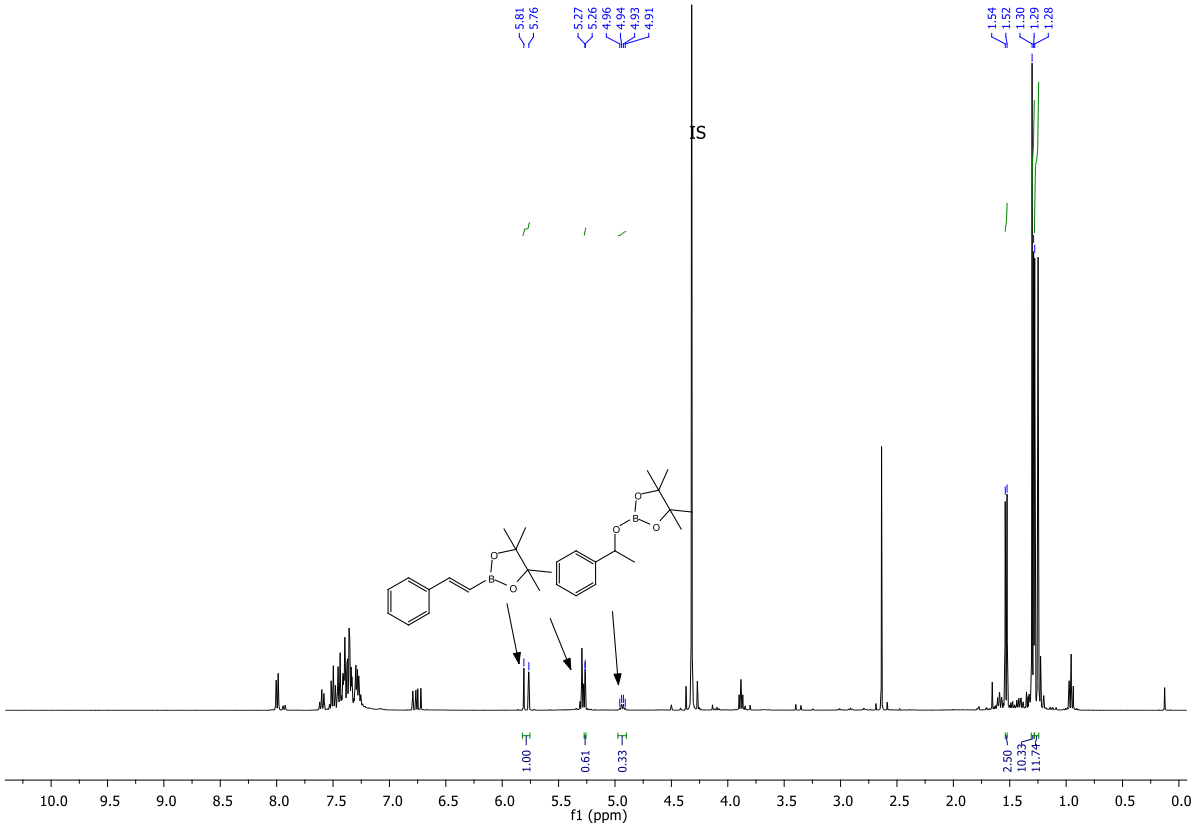
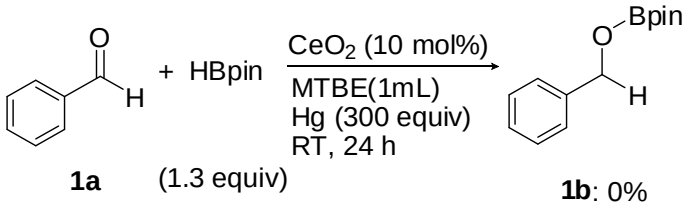


Figure S21. ^{1}H NMR spectra of intermolecular competitive hydroboration reaction between acetophenone (**23a**) and phenylacetylene catalyse by BH_3·THF.

VI. Mechanistic Investigations

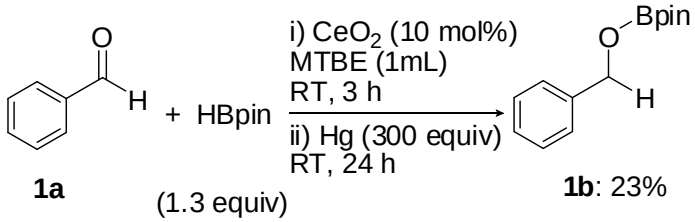
Mercury Poisoning Experiments.

a) In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, CeO_2 NPs (10 mol %, 4 mg, 0.0250 mmol), HBpin (1.3equiv, 48 μL, 0.33 mmol), methyl-*tert*-butyl ether (1 mL), benzaldehyde (**1a**, 0.25 mmol, 20 μL) and Hg (300 equiv) were added, and the reaction was stirred vigorously at room temperature for 24 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.



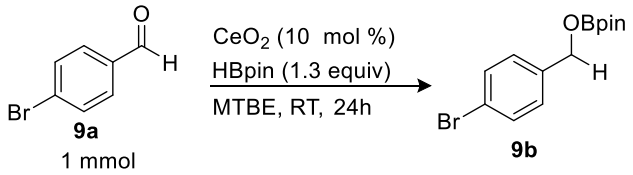
1a (1.3 equiv) **1b**: 0%

b) In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, CeO_2 NPs (10 mol %, 4 mg, 0.025 mmol), HBpin (1.3 equiv, 48 μL, 0.33 mmol), methyl-*tert*-butyl ether (1 mL) and benzaldehyde (**1a**, 0.25 mmol, 20 μL) were added, and the reaction was stirred vigorously at room temperature for 3 h. After 3 h reaction process, the reaction was interrupted and 300 equiv of Hg was added. After stirring for about 24 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 (1.3 equiv) **1b**: 23%

Recyclability Experiment for Hydroboration of 4-bromobenzaldehyde (9a).



In a 50 mL round bottom flask equipped with a magnetic stirring bar, 10 mol% of CeO_2 (5 mol %, 0.1 mmol, 17 mg), HBpin (1.3 mmol, 192 μL), methyl-tert-butyl ether (4 mL) and 4-bromobenzaldehyde (**9a**, 1.0 mmol, 185 mg) were added. The resulting reaction mixture was stirred vigorously at room temperature for 24 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 CeO_2 NPs was charged into 50 mL round bottom flask equipped with a magnetic stirring bar, to which additional HBpin (1.3 mmol, 192 μL), methyl-*tert*-butyl ether (4 mL) and 4-bromobenzaldehyde (**9a**, 1.0 mmol, 185 mg) were added. The resulting reaction mixture was stirred vigorously at room temperature for 24 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 (1.3 mmol, 192 μL) and methyl-*tert*-butyl ether (4 mL) added to the separated CeO_2 NPs. The combined organic extracts were analyzed by ^{1}H NMR spectroscopy using nitromethane as an internal standard. The results of 10 recycling experiments are summarized in Figure S12.

Yields: 1st cycle = >99%, 2nd cycle = >99%, 3rd cycle = 90%, 4th cycle = 87 %, 5th cycle = 85%, 6th cycle = 85%, 7th cycle = 84%, 8th cycle = 83%, 9th cycle = 81 %, 10th cycle =78%.

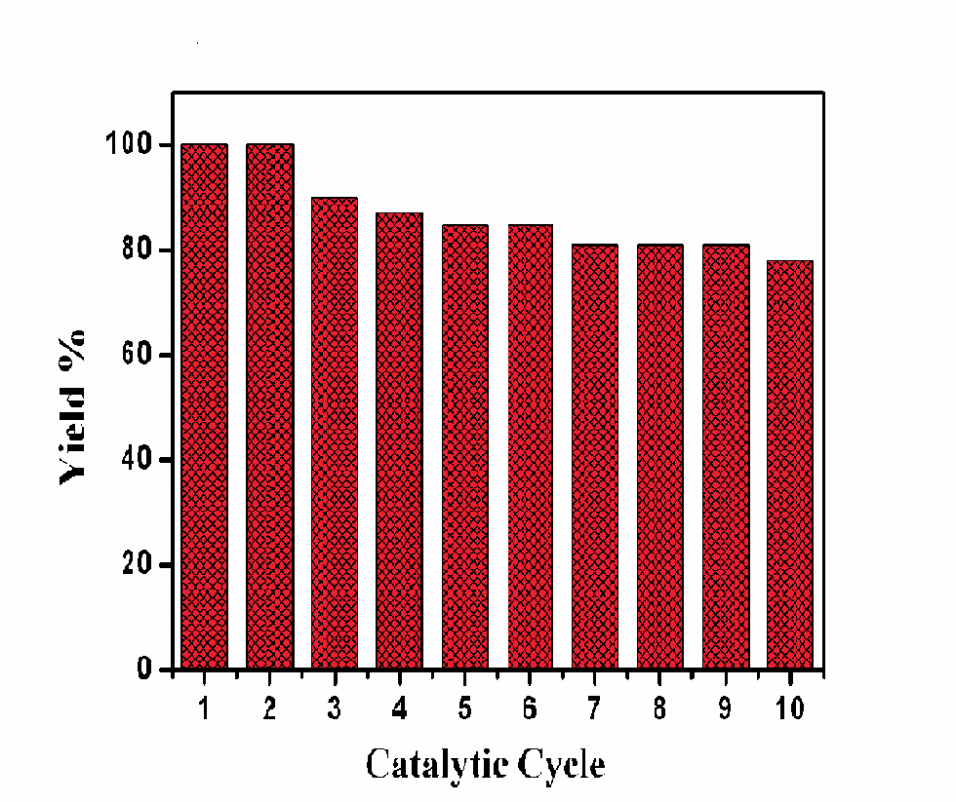


Figure S22.^{1}H NMR yields (%) of borate ester at different cycles in the recyclability experiment for CeO_2 NPs catalysed hydroboration of 4-bromobenzaldehyde.

Gratifyingly, when the recovered catalyst, after the 2nd cycle of the reaction, was calcined at 600 °C for 2 h, and has been used as a catalyst for the hydroboration of 4-bromobenzaldehyde (**9a**) under standard reaction conditions gave the desire borate ester **9b** in 99% yield confirmed by ^{1}H NMR spectroscopy.

Furthermore, when the recovered catalyst, after the 10th cycle of the reaction was calcined at 600 °C for 2 h, and has been used as a catalyst for the hydroboration of **9a** also gave the desire borate ester **9b** in 99% yield.

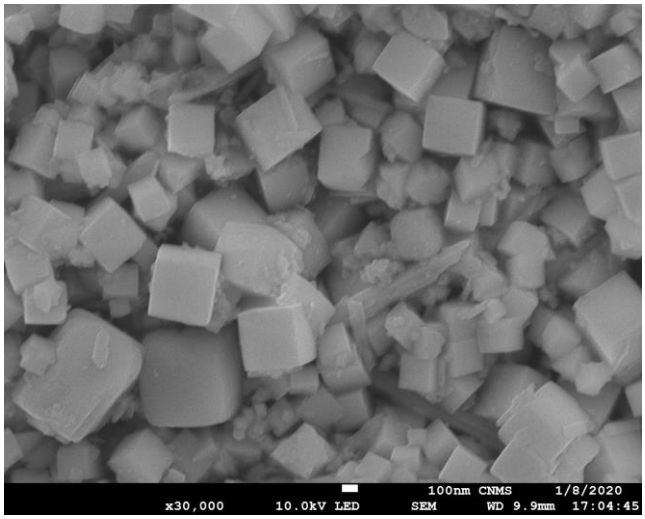


Figure S23. FE-SEM images of calcined CeO_2 nanoparticles, recovered after 10 catalytic cycles.

The calcined CeO_2 nanoparticles recovered after 10 catalytic cycles were characterized by field emission scanning electron microscopy (FESEM, Figure S13). The FESEM images demonstrated that the morphology of nanoparticles is intact.

Stoichiometric reaction of CeO_2 NPs with benzaldehyde and HBpin.

Monitoring by FT-IR spectroscopy:

Several stoichiometric experiments were performed to gain insight into the hydroboration mechanism. In an argon-filled glovebox, the CeO_2 NPs (21 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 S14). The FT-IR analysis of CeO_2 NPs shows strong absorption peak at 469 cm^{-1}, can be attributed to the Ce–O band vibrations (Figure S14a). The FT-IR analysis of benzaldehyde shows strong absorption peak at 1701 cm^{-1} is due to the CO stretching frequency (Figure S14b). The FT-IR spectrum of the reaction mixture of CeO_2 and benzaldehyde shows shift in the absorption band correspond to the Ce–O vibration as well as in the CO stretching frequency towards lower wavenumber indicating interaction between CeO_2 NPs catalyst and benzaldehyde substrate (Figure S14c)

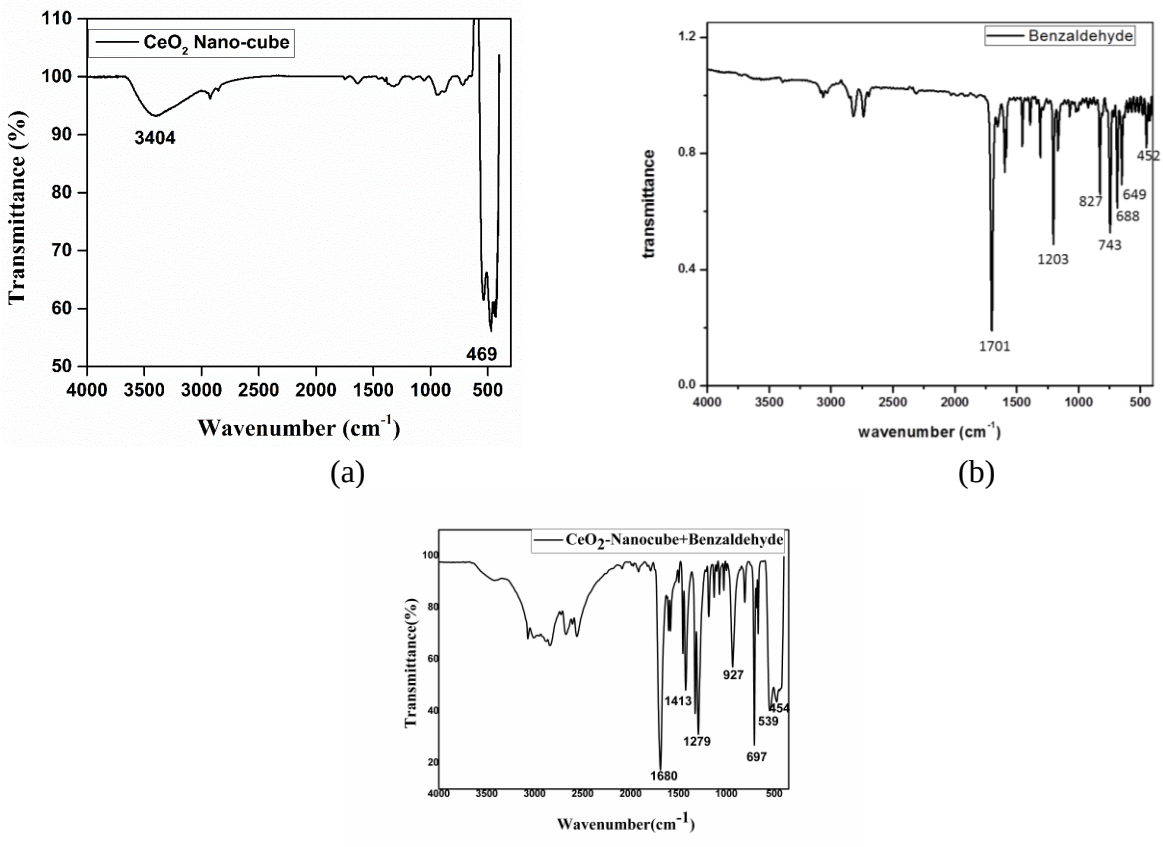
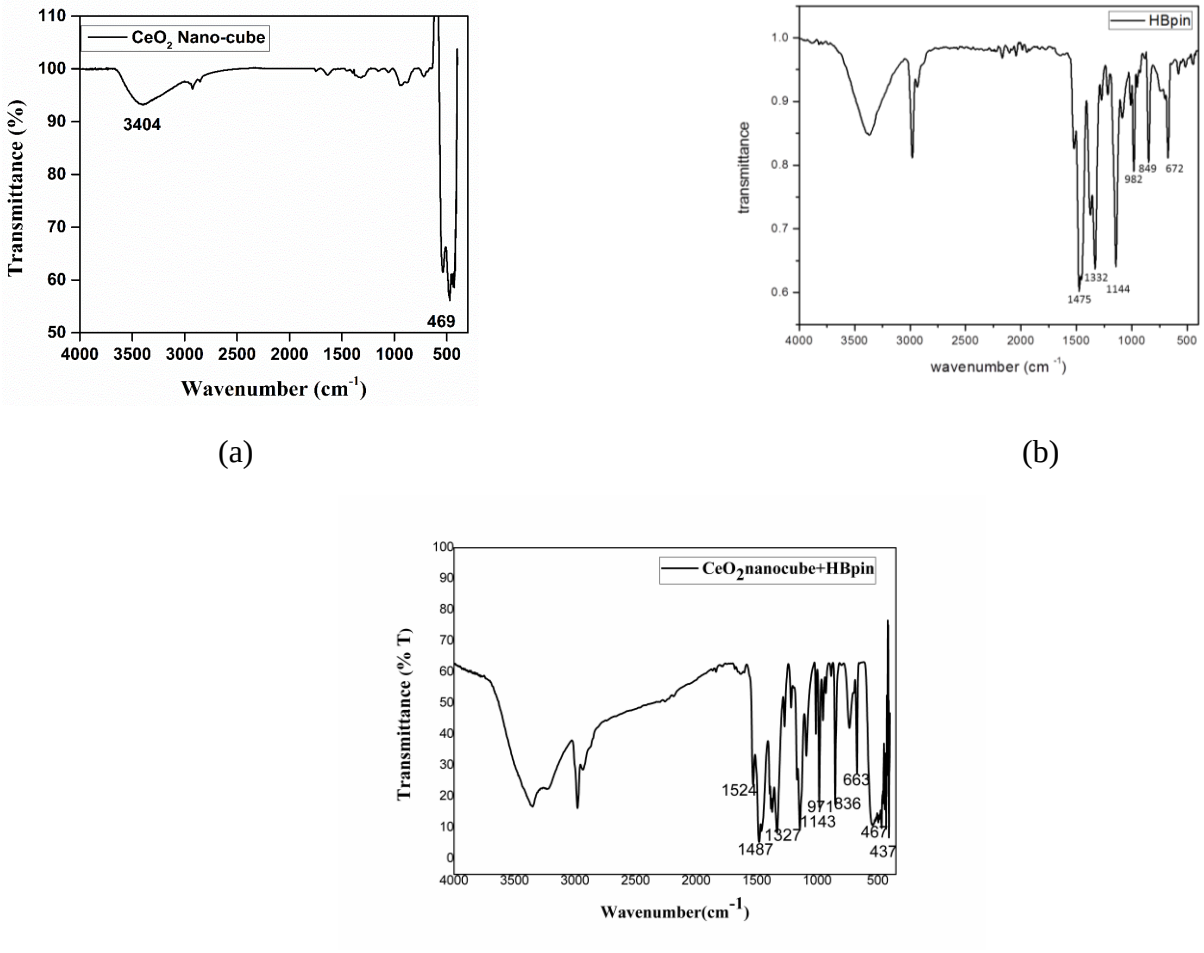


Figure S24. IR spectra of: (a) CeO_2; (b) C_6H_5CHO and (c) CeO_2 + C_6H_5CHO.

In an argon-filled glove box, the CeO_2 NPs (21 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 S15). The FT-IR spectrum of the reaction mixture does not show shift in the absorption band correspond to the Ce–O vibration, indicating no interaction between CeO_2 and HBpin (Figure S15c).



(a) (b)

(c)

Figure S25. IR spectra of: (a) CeO_2; (b) HBpin and (c) CeO_2+ HBpin.

At this point we cannot speculate on the detailed mechanism of the catalytic reaction. However, based on the previous reports[21] and our experimental results, a plausible mechanism for the hydroboration of aldehydes and ketones is proposed. In the first step, the

CeO_2 NPs polarises the carbonyl oxygen moiety to give an active catalytic species.[22] In the next step, a nucleophilic attack occurs on the electron-deficient carbonyl carbon atom by the incoming hydride of HBpin, leading to the formation of the four-membered transition state, which undergoes σ bond metathesis reaction, followed by reaction with another molecule of carbonyl substrate gives borate ester and regenerate the catalytic active species (Figure 16).

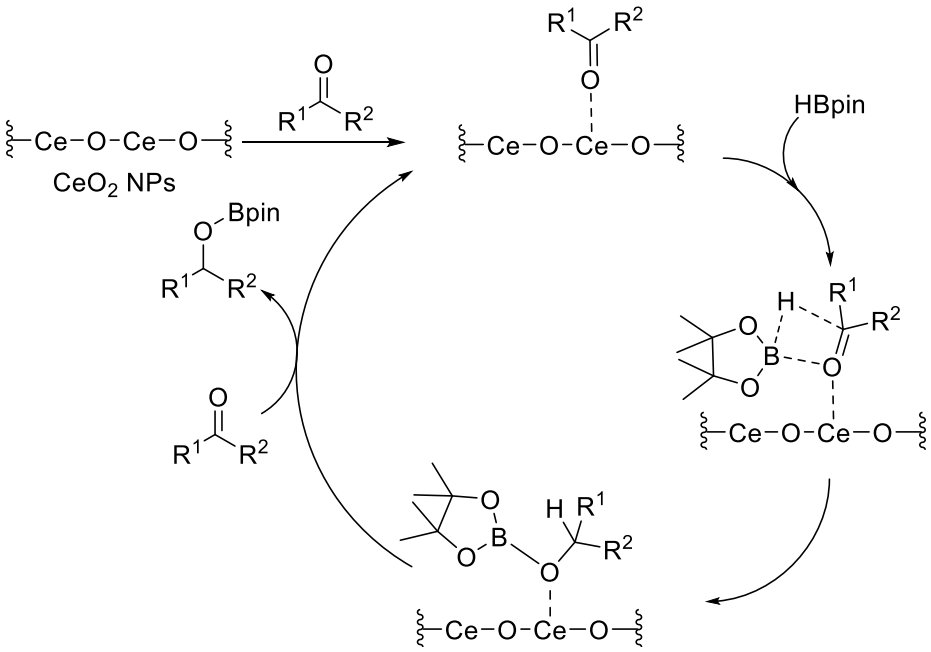


Figure 26. Possible schematic representation of carbonyl interaction with CeO_2 NPs with the formation of borate ester.

VII. References

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