

**Transition Metal- and Solvent-Free *anti*-Markovnikov Selective Protoboration of Alkenes with *Bis*(pinacolato)diboron**

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## I. General Information

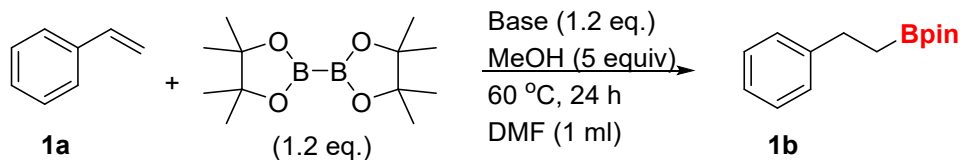
Unless otherwise noted all the reactions are performed in nitrogen filled KIYON glove box or using standard Schlenk technique. All reagents were purchased from Avra, BLDpharm, SDFCL or Aldrich and were used as received.  $\text{CDCl}_3$  was purchased from Cambridge Isotope Laboratories and were dried using molecular sieves and deoxygenated using the freeze pump-thaw method. Commercially available, pre-coated TLC sheets ALUGRAM® Xtra Sil G/UV254 was purchased from MACHEREY-NAGEL GmbH & Co. The removal of solvent was performed on a rotary evaporator in vacuum at a maximum temperature of 40 °C. All NMR spectra were recorded at ambient temperature using a Bruker Avance 500 NMR spectrometer ( $^1\text{H}$ , 500 MHz;  $^{13}\text{C}$ , 126 MHz;  $^{11}\text{B}$ , 160 MHz) or Bruker Avance 400 NMR spectrometer ( $^1\text{H}$ , 400 MHz;  $^{13}\text{C}$ , 100 MHz;  $^{11}\text{B}$ , 128 MHz).  $^1\text{H}$  NMR chemical shifts are reported relative to TMS and were referenced *via* residual proton resonances of the corresponding deuterated solvent ( $\text{CDCl}_3$ : 7.26 ppm,  $\text{C}_6\text{D}_6$ : 7.16 ppm), whereas  $^{13}\text{C}$  NMR spectra are reported relative to TMS using the carbon signals of the deuterated solvent ( $\text{CDCl}_3$ : 77.16 ppm,  $\text{C}_6\text{D}_6$ : 128.06 ppm).  $^{11}\text{B}$  NMR signals were quoted relative to  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ . All  $^{11}\text{B}$  and  $^{13}\text{C}$  NMR spectra were broad-band  $^1\text{H}$  decoupled. GC-MS data were acquired using SHIMADZU GC-MS QP 2010SE system. High resolution mass spectrometry was performed on Micromass Q-TOF Micro instrument.

## II. Optimization of the Reaction Conditions for the Alkenes Protoboration

### Experimental Procedures for Examples Described in Table 1 and 2.

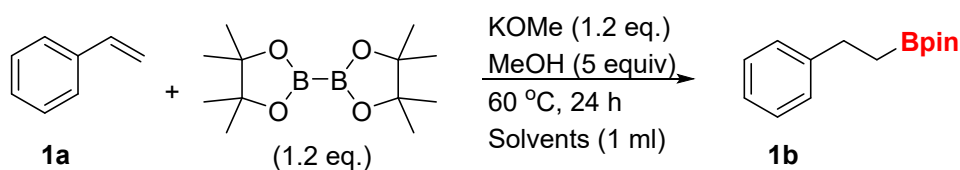
In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, styrene (**1a**, 0.25 mmol, 26 mg), B<sub>2</sub>pin<sub>2</sub> (1.2 equiv, 0.3 mmol, 76 mg), base (1.2 equiv, 0.3 mmol) MeOH (5 equiv.) and solvent (1 mL) were added. The reaction mixture was stirred at indicated time and temperature. The crude reaction was dissolved in Et<sub>2</sub>O (10 mL) and then transferred to a separatory funnel followed by the addition of H<sub>2</sub>O (10 mL). The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et<sub>2</sub>O (3 x 5 mL). The combined organics were dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated. In the concentrated crude reaction mixture nitromethane was added as an internal standard. The product yield was determined by <sup>1</sup>H NMR spectroscopy using nitromethane as an internal standard.

**Table S1:** Screening of the Lewis-base for the protoboration of styrene (**1a**).<sup>a</sup>



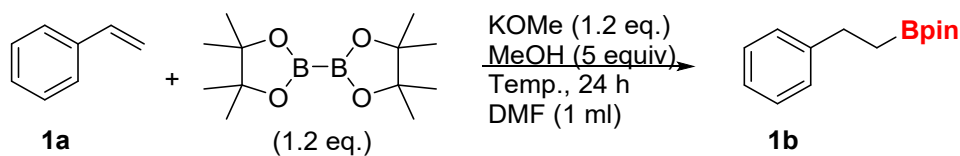
Entry	Solvent	B <sub>2</sub> pin <sub>2</sub>	Base (1.2 equiv)	Temp. (°C)	Time (h)	Yield (%) <sup>b</sup>
1	DMF	1.2 equiv.	NaOMe	60	24	71
2	DMF	1.2 equiv.	NaO <sup>t</sup> Bu	60	24	75
3	DMF	1.2 equiv.	KO <sup>t</sup> Bu	60	24	74
4	DMF	1.2 equiv.	LiO <sup>t</sup> Bu	60	24	83
5	DMF	1.2 equiv.	KOMe	60	24	96
6	DMF	1.2 equiv.	-	60	24	0
7	DMF	1.2 equiv.	50 mol%	60	24	69
8	DMF	1.2 equiv.	30 mol%	60	24	68
9	DMF	1.2 equiv.	20 mol%	60	24	61
10	DMF	1.2 equiv.	10 mol%	60	24	70

<sup>a</sup>Reaction condition: 0.25 mmol **1a**, B<sub>2</sub>pin<sub>2</sub> (1.2 equiv.), base (1.2 equiv.), MeOH (5 equiv.) DMF (1 mL) for 24 h at 60 °C. <sup>b</sup>Yields were determined by <sup>1</sup>H NMR analysis using nitromethane as an internal standard.

**Table S2:** Screening of the solvents for the protoboration of styrene (**1a**).<sup>a</sup>

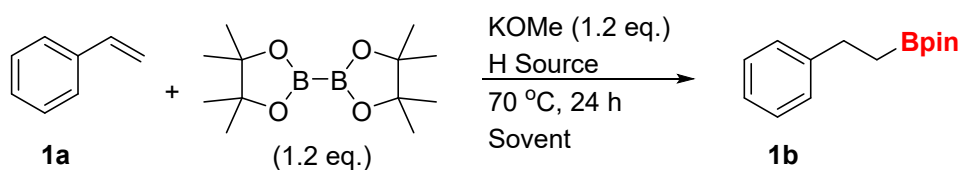
Entry	Solvent	Base	Temp (°C)	Time (h)	Yield (%) <sup>b</sup>
1	Acetonitrile	KOMe	60	24	83
2	DMF	KOMe	60	24	96
3	Toluene	KOMe	60	24	29
4	THF	KOMe	60	24	23
5	DMAc	KOMe	60	24	84

<sup>a</sup>Reaction condition: 0.25 mmol **1a**,  $B_2pin_2$  (1.2 equiv.), KOMe (1.2 equiv.), MeOH (5 equiv.) solvent (1 mL) for 24 h at 60 °C. <sup>b</sup>Yields were determined by <sup>1</sup>H NMR analysis, using nitromethane as an internal standard.

**Table S3:** Screening of temperature for the protoboration of styrene (**1a**).<sup>a</sup>

Entry	Solvent	Base	Temp (°C)	Time (h)	Yield (%) <sup>b</sup>
1	DMF	KOMe	RT	24	72
2	DMF	KOMe	40	24	71
3	DMF	KOMe	70	24	98
4	DMF	KOMe	80	24	88

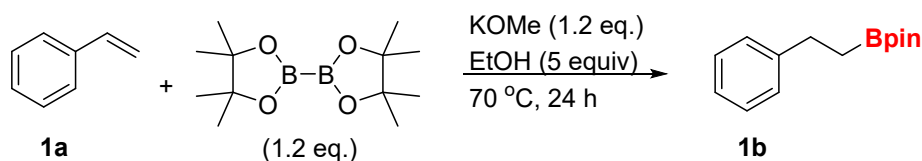
<sup>a</sup>Reaction condition: 0.25 mmol **1a**,  $B_2pin_2$  (1.2 equiv.), KOMe (1.2 equiv.), MeOH (5 equiv.) DMF (1 mL) for 24 h at indicated temperature. <sup>b</sup>Yields were determined by <sup>1</sup>H NMR analysis, using nitromethane as an internal standard.

**Table S4:** Control experiments for the protoboration of styrene (**1a**).<sup>a</sup>

Entry	Solvent	Methanol	Ethanol	Time (h)	Yield (%) <sup>b</sup>
1	DMF	-	-	24	82%
2	-	-	-	24	3%
3	-	5 equiv.	-	24	>99
4	-	-	5 equiv.	24	>99
5	-	-	0.5 mL (excess)	24	75%

<sup>a</sup>Reaction condition: 0.25 mmol **1a**,  $B_2pin_2$  (1.2 equiv.), KOMe (1.2 equiv.), additive, solvent for 24 h at 70 °C.

<sup>b</sup>Yields were determined by <sup>1</sup>H NMR analysis, using nitromethane as an internal standard.

**Table S5:** Screening of base under neat conditions for the protoboration of styrene (**1a**).<sup>a</sup>

Entry	Ethanol	Base	Temp (°C)	Time (h)	Yield (%) <sup>b</sup>
1	5 equiv.	$CS_2CO_3$	70	24	71
2	5 equiv.	$K_3PO_4$	70	24	21 <sup>c</sup>
3	5 equiv.	$K_2CO_3$	70	24	34 <sup>d</sup>

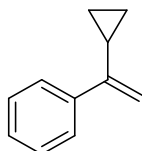
<sup>a</sup>Reaction condition: 0.25 mmol **1a**,  $B_2pin_2$  (1.2 equiv.), base (1.2 equiv.), EtOH (5 equiv.) for 24 h at 70 °C.

<sup>b</sup>Yields were determined by <sup>1</sup>H NMR analysis, using nitromethane as an internal standard. <sup>c</sup>71% of styrene diboration product was detected by GC-MS. <sup>d</sup>57% styrene diboration product was detected by GC-MS.

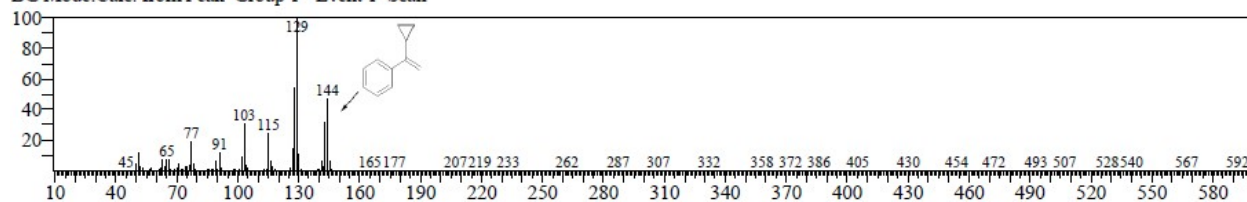
### III. Substrate Synthesis

#### *Procedure for the preparation of (1-cyclopropylvinyl)benzene (27a).*<sup>1</sup>

Under a nitrogen atmosphere, to an anhydrous THF (13 mL) solution of methyltriphenylphosphonium bromide (2.1 g, 6 mmol) at 0 °C, n-butyl lithium (2.4 mL, 2.5 M in hexane, 6 mmol) was added dropwise and the mixture was stirred for 1 h. To the above reaction mixture cyclopropyl(phenyl)methanone (730 mg; 5 mmol) was added and stirred at room temperature for another 3 h. After completion of the reaction, the solvent was evaporated and the residue was purified by column chromatography to afford (1-cyclopropylvinyl)benzene (**27a**) as a colorless oil (620 mg, 86% yield).



Line#:1 R.Time:5.895(Scan#:560) MassPeaks:355  
RawMode:Averaged 5.890-5.900(559-561) BasePeak:129.10(1021216)  
BG Mode:Calc. from Peak Group 1 - Event 1 Scan

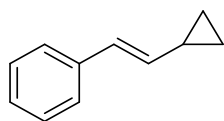


GC-MS analysis of (1-cyclopropylvinyl)benzene

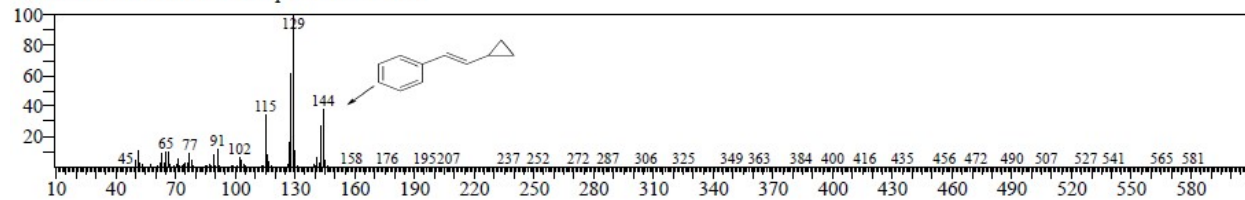
#### *Procedure for the preparation of (2-cyclopropylvinyl)benzene (28a)*<sup>2,3</sup>

Under a nitrogen atmosphere, to an anhydrous THF (13 mL) solution of benzyl-triphenylphosphonium bromide (5.0 g, 11.5 mmol) at 0 °C, n-butyl lithium (4.6 mL, 2.5 M in hexane, 11.5 mmol) was added dropwise and the mixture was stirred for 1 h. To the above reaction mixture cyclopropanecarboxaldehyde (0.81 g, 11.5 mmol) was added and stirred at room temperature for another 3 h. After completion of the reaction, the solvent was evaporated and the residue was purified by column chromatography to afford (2-cyclopropylvinyl)benzene (**28a**) as a colorless oil (1.19 g, 72% yield).

**(2-Cyclopropylvinyl)benzene (28a):**



Line#1 R.Time:6.060(Scan#:593) MassPeaks:338  
RawMode:Averaged 6.055-6.065(592-594) BasePeak:129.10(609875)  
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



GC-MS analysis of (2-cyclopropylvinyl)benzene

## IV. Substrate Scope of Alkenes Protoboration Reaction

### Experimental Procedure for Examples Described in Table 3.

**General Procedure A.** In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, alkene (0.25 mmol), B<sub>2</sub>pin<sub>2</sub> (1.2 equiv., 0.3 mmol, 76 mg), KOMe (1.2 equiv, 0.3 mmol, 21 mg) and EtOH (5 equiv., 57  $\mu$ L) were added and the reaction mixture was stirred vigorously at 70 °C for 24 h. The crude reaction mixture was dissolved in Et<sub>2</sub>O (5 mL) and passed through a plug of Celite. The solvent was removed in vacuum, and nitromethane was added as an internal standard. The product yield was determined from <sup>1</sup>H NMR.

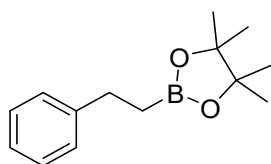
**General Procedure B.** In case of solid substrate, in a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, alkene (0.25 mmol), B<sub>2</sub>pin<sub>2</sub> (1.2 equiv., 0.3 mmol, 76 mg), KOMe (1.2 equiv, 0.3 mmol, 21 mg), EtOH (5 equiv., 57  $\mu$ L), and DMF (1 mL) were added and the reaction mixture was stirred vigorously at 70 °C for 24 h. The crude reaction mixture was dissolved in Et<sub>2</sub>O (10 mL) and then transferred to a separatory funnel followed by the addition of H<sub>2</sub>O (10 mL). The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et<sub>2</sub>O (3 x 10 mL). The combined organics were dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated. The product yield was determined from <sup>1</sup>H NMR using nitromethane as an internal standard.

**General Procedure C.** In a 15 mL thick-walled reaction tube equipped with a magnetic stirring bar, alkene (1 mmol), B<sub>2</sub>pin<sub>2</sub> (1.2 equiv, 1.2 mmol, 76 mg), KOMe (1.2 equiv, 1.2 mmol, 21 mg) and EtOH (5 equiv.) were added and the reaction mixture was stirred vigorously at 70 °C for 24 h. The crude reaction mixture was dissolved in Et<sub>2</sub>O (10 mL) and passed through a plug of Celite. The solvent was removed in vacuum, and the residue was purified by column chromatography.



**General Procedure D.** In case of solid substrate, in a 15 mL thick-walled reaction tube equipped with a magnetic stirring bar, alkene (1 mmol), B<sub>2</sub>pin<sub>2</sub> (1.2 equiv, 1.2 mmol, 76 mg), KOMe (1.2 equiv, 1.2 mmol, 21 mg), EtOH (5 equiv.), and DMF (5 mL) were added and the reaction mixture was stirred vigorously at 70 °C for 24 h. The crude reaction was dissolved in Et<sub>2</sub>O (20 mL) and then transferred to a separatory funnel followed by the addition of H<sub>2</sub>O (20 mL). The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et<sub>2</sub>O (3 x 15 mL). The combined organics were dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated. The residue was purified by column chromatography.

#### 4,4,5,5-Tetramethyl-2-phenethyl-1,3,2-dioxaborolane (**1b**)<sup>4</sup>



Following general procedure C, a colorless liquid in 85% yield (197 mg) from styrene (**1a**, 104 mg, 1 mmol) was obtained.

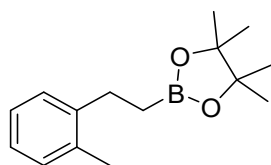
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.27-7.19 (m, 4H), 7.16-7.12 (m, 1H), 2.74 (t, *J* = 15 Hz, 2H), 1.21 (s, 12H), 1.13 (t, *J* = 15 Hz, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 144.3, 128.0, 127.9, 125.4, 83.0, 29.9, 24.7, 13.2.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 33.87.

GC-MS: *m/z* 232 (M<sup>+</sup>).

#### 4,4,5,5-Tetramethyl-2-(2-methylphenethyl)-1,3,2-dioxaborolane (**2b**)<sup>5</sup>



Following general procedure C, a colorless liquid in 84% yield (204 mg) from 1-methyl-2-vinylbenzene (**2a**, 118 mg, 1 mmol) was obtained.

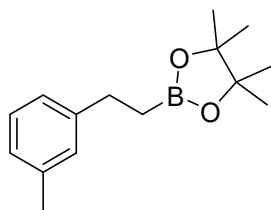
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.10 (t, *J* = 7.5 Hz, 1H), 7.03-6.96 (m, 3H), 2.63 (t, *J* = 10 Hz, 2H), 2.22 (s, 3H), 1.14 (s, 12H), 1.02 (t, *J* = 7.5 Hz, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 142.5, 135.8, 130.0, 128.1, 125.9, 125.7, 83.1, 27.2, 24.9, 19.3, 11.7.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>): δ 34.05.

GC-MS: *m/z* 246 (M<sup>+</sup>).

#### 4,4,5,5-tetramethyl-2-(3-methylphenethyl)-1,3,2-dioxaborolane (3b)<sup>5</sup>



Following general procedure C, a colorless liquid in 85% yield (209 mg) from 1-methyl-3-vinylbenzene (**3a**, 118 mg, 1 mmol) was obtained.

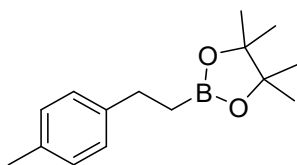
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.18 (t, *J* = 7.5 Hz, 1H), 7.08 – 7.03 (m, 2H), 6.99 (d, *J* = 7.4 Hz, 1H), 2.75 (t, *J* = 8.1 Hz, 2H), 2.34 (s, 3H), 1.25 (d, *J* = 1.0 Hz, 12H), 1.16 (t, *J* = 8.1 Hz, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 144.4, 137.6, 128.8, 128.1, 126.2, 125.0, 83.0, 29.9, 24.8, 21.4, 13.2.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 33.98.

GC-MS: *m/z* 246 (M<sup>+</sup>).

#### 4,4,5,5-Tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane (4b)<sup>4</sup>



Following general procedure C, a colorless liquid in 75% yield (184 mg) from 1-methyl-4-vinylbenzene (**4a**, 118 mg, 1 mmol) was obtained.

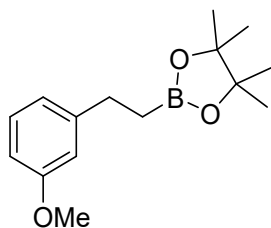
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.13-7.03 (m, 4H), 2.72-2.69 (m, 2H), 2.29 (s, 3H), 1.22 (s, 12H), 1.13-1.10 (m, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 141.4, 134.8, 128.9, 127.8, 83.0, 29.5, 24.8, 21.0, 13.2.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 34.00.

GC-MS: *m/z* 246 (M<sup>+</sup>).

### 2-(3-Methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5b**)<sup>4</sup>



Following general procedure C, a colorless liquid in 82% yield (214 mg) from 1-methoxy-3-vinylbenzene (**5a**, 134 mg, 1 mmol) was obtained.

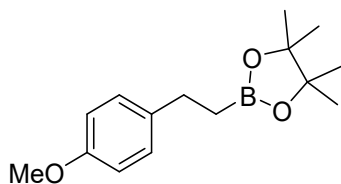
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.18 (t, *J* = 15 Hz, 1H), 6.85 – 6.77 (m, 2H), 6.71 (dd, *J* = 8, 2.5 Hz, 1H), 3.78 (s, 3H), 2.73 (t, *J* = 15 Hz, 2H), 1.23 (s, 12H), 1.15 (t, *J* = 10 Hz, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 159.5, 146.1, 129.1, 120.4, 113.6, 111.0, 83.1, 55.0, 30.0, 24.8, 13.0.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 33.90.

GC-MS: *m/z* 262 (M<sup>+</sup>).

### 2-(4-Methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6b**)<sup>5</sup>



Following general procedure C, a colorless liquid in 71% yield (186 mg) from 1-methoxy-4-vinylbenzene (**6a**, 134 mg, 1 mmol) was obtained.

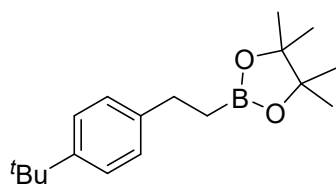
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.13 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 3.78 (s, 3H), 2.69 (t, *J* = 7.5 Hz, 2H), 1.22 (s, 12H), 1.11 (t, *J* = 7.5 Hz, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 157.5, 136.5, 128.8, 113.6, 83.0, 55.2, 29.0, 24.8, 13.2.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 34.23.

GC-MS: *m/z* 262 (M<sup>+</sup>).

## 2-(4-(Tert-butyl)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7b)<sup>4</sup>



Following general procedure C, a colorless liquid in 59% yield (169 mg) from 1-(tert-butyl)-4-vinylbenzene (**7a**, 160 mg, 1 mmol) was obtained.

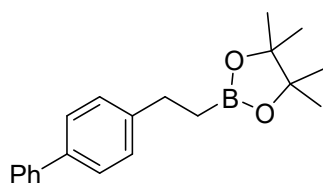
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.31 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 2.74 (t, *J* = 15 Hz, 2H), 1.33 (s, 9H), 1.25 (s, 12H), 1.16 (t, *J* = 15 Hz, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 148.2, 141.3, 127.6, 125.0, 83.0, 34.3, 31.4, 29.4, 24.8, 13.0.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 33.71.

GC-MS: *m/z* 288 (M<sup>+</sup>).

## 2-(2-([1,1'-Biphenyl]-4-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8b)<sup>4</sup>



Following general procedure D, a white solid in 84% yield (258 mg) from 4-vinyl-1,1'-biphenyl (**8a**, 180 mg, 1 mmol) was obtained.

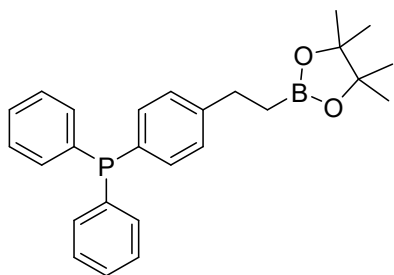
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 7.8 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.31-7.25 (m, 3H), 2.77 (t, *J* = 8.1 Hz, 2H), 1.20 (s, 12H), 1.16 (t, *J* = 8.2 Hz, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 143.6, 141.2, 138.5, 128.7, 128.4, 127.0, 126.9, 126.9, 83.1, 29.6, 24.8, 13.0.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 33.18.

GC-MS: *m/z* 308 (M<sup>+</sup>).

## Diphenyl(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)phosphane (9b)



Following general procedure **D**, a light yellow liquid in 92% yield (382 mg) from diphenyl(4-vinylphenyl)phosphane (**9a**, 288 mg, 1 mmol) was obtained.

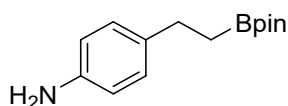
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 – 7.24 (m, 10H), 7.23 – 7.16 (m, 4H), 2.74 (t,  $J = 8.0$  Hz, 2H), 1.17 (s, 12H), 1.15 – 1.11 (m, 2H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  145.3, 137.7 (d,  $J = 11.0$  Hz), 134.3 – 133.2 (m), 128.6 – 128.4 (m), 83.1, 29.8, 24.9, 15.4.

$^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ )  $\delta$  34.60.

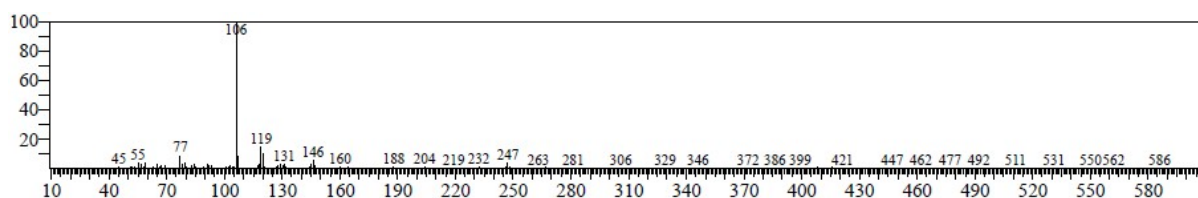
GC-MS:  $m/z$  416 ( $\text{M}^+$ ).

## 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)aniline (10b)

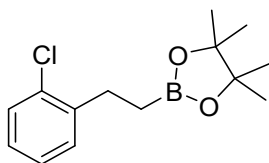


Following general procedure A. The GC-MS analysis of the reaction mixture showed the formation of **10b**.

GC-MS:  $m/z$  247 ( $\text{M}^+$ ), 232 ( $\text{M}^+ - \text{CH}_3$ )



## 2-(2-Chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11b**)<sup>6</sup>



Following general procedure C, a colorless liquid in 87% yield (231 mg) from 1-chloro-2-vinylbenzene (**11a**, 138 mg, 1 mmol) was obtained.

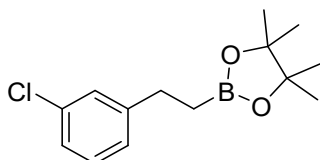
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.22 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.18 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.08 (td, *J* = 7.5, 1.3 Hz, 1H), 7.01 (td, *J* = 7.6, 1.7 Hz, 1H), 2.76 (t, *J* = 7.5 Hz, 2H), 1.15 (s, 12H), 1.10 – 1.04 (m, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 140.7, 132.8, 128.7, 128.2, 125.9, 125.5, 82.1, 26.7, 23.7, 10.2.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>): δ 33.73.

GC-MS: *m/z* 266 (M<sup>+</sup>).

## 2-(3-Chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**12b**)<sup>6</sup>



Following general procedure C, a colorless liquid in 84% yield (223 mg) from 1-chloro-3-vinylbenzene (**12a**, 138 mg, 1 mmol) was obtained.

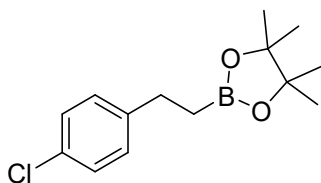
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.21 (s, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.13 – 7.06 (m, 2H), 2.72 (t, *J* = 8.0 Hz, 2H), 1.20 (s, 12H), 1.12 (t, *J* = 8.0 Hz, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 146.4, 133.8, 129.4, 128.2, 126.2, 125.6, 83.1, 29.7, 24.8, 12.9.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 34.23.

GC-MS: *m/z* 266 (M<sup>+</sup>).

## 2-(4-Chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**13b**)<sup>6</sup>



Following general procedure C, a colorless liquid in 83% yield (220 mg) from 1-chloro-4-vinylbenzene (**13a**, 138 mg, 1 mmol) was obtained.

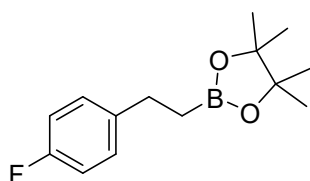
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.12 (d, *J* = 5 Hz, 2H), 7.05 (d, *J* = 10 Hz, 2H), 2.62 (t, *J* = 7.5 Hz, 2H), 1.12 (s, 12H), 1.03 (t, *J* = 7.5 Hz, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 142.8, 131.1, 129.4, 128.2, 83.1, 29.3, 24.8, 12.9.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>): δ 33.80.

GC-MS: *m/z* 266 (M<sup>+</sup>).

## 2-(4-Fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**14b**)<sup>7</sup>



Following general procedure C, a colorless liquid in 82% yield (205 mg) from 1-fluoro-4-vinylbenzene (**14a**, 122 mg, 1 mmol) was obtained.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.18-7.13 (m, 2H), 6.96 – 6.89 (m, 2H), 2.71 (t, *J* = 8.1 Hz, 2H), 1.21 (s, 12H), 1.17 – 1.08 (m, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 162.1 (d, *J* = 242.6 Hz), 139.9 (d, *J* = 3.1 Hz), 129.3 (d, *J* = 7.7 Hz), 114.8 (d, *J* = 21.0 Hz), 83.1, 29.1, 24.7, 13.1.

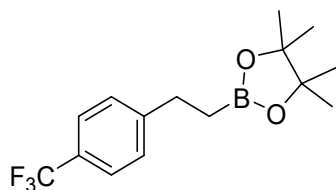
<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 33.92.

<sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -118.37.

GC-MS: *m/z* 250 (M<sup>+</sup>).



#### 4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenethyl)-1,3,2-dioxaborolane (**15b**)<sup>7</sup>



Following general procedure C, a colorless liquid in 80% yield (240 mg) from 1-(trifluoromethyl)-4-vinylbenzene (**15a**, 172 mg, 1 mmol) was obtained.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.51 (d, *J* = 8.1 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 2.80 (t, *J* = 8.1 Hz, 1H), 1.21 (s, 6H), 1.17-1.13 (m, 1H).

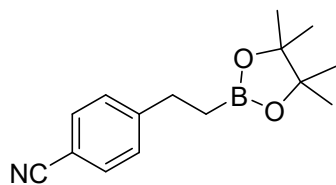
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 148.5, 128.3, 125.1 (q, *J* = 3.8 Hz), 83.2, 29.8, 24.7, 12.6.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 33.66.

<sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -62.25.

GC-MS: *m/z* 300 (M<sup>+</sup>).

#### 4-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzotrile (**16b**)<sup>4</sup>



Following general procedure C, a colorless liquid in 81% yield (208 mg) from 4-vinylbenzotrile (**16a**, 129 mg, 1 mmol) was obtained.

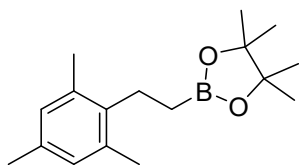
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 2.80 (t, *J* = 8.0 Hz, 2H), 1.21 (s, 12H), 1.13 (t, *J* = 15 Hz, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 150.0, 131.9, 128.8, 119.1, 109.3, 83.2, 30.1, 24.7, 12.4.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 33.74.

GC-MS: *m/z* 257 (M<sup>+</sup>).

#### 4,4,5,5-Tetramethyl-2-(2,4,6-trimethylphenethyl)-1,3,2-dioxaborolane (17b)<sup>4</sup>



Following general procedure C, a light yellow liquid in 32% yield (87 mg) from 1,3,5-trimethyl-2-vinylbenzene (**17a**, 146 mg, 1 mmol) was obtained.

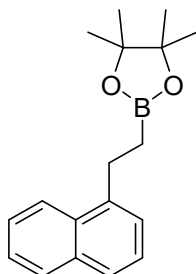
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.82 (s, 2H), 2.72 – 2.63 (m, 2H), 2.27 (d, *J* = 28.0 Hz, 9H), 1.28 (s, 12H), 1.00 – 0.92 (m, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 138.5, 135.6, 134.6, 128.8, 83.0, 24.8, 23.2, 20.7, 19.6. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 34.16.

GC-MS: *m/z* 274 (M<sup>+</sup>).

#### 4,4,5,5-Tetramethyl-2-(2-(naphthalen-1-yl)ethyl)-1,3,2-dioxaborolane (18b)<sup>8</sup>



Following general procedure C, a colorless liquid in 87% yield (220 mg) from 1-vinylnaphthalene (**18a**, 154 mg, 1 mmol) was obtained.

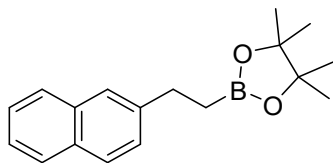
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.06 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.63 (dd, *J* = 7.7, 5.6 Hz, 1H), 7.42 (dt, *J* = 20.5, 7.1 Hz, 2H), 7.37 – 7.30 (m, 2H), 3.20 (t, *J* = 10 Hz, 2H), 1.28 (t, *J* = 7.5 Hz, 2H), 1.18 (s, 12H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 139.4, 132.8, 130.8, 127.6, 125.3, 124.6, 124.5, 124.3, 124.0, 122.9, 82.1, 26.0, 23.8, 11.4.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>): δ 33.93.

GC-MS:  $m/z$  282 ( $M^+$ ).

#### 4,4,5,5-Tetramethyl-2-(2-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane (**19b**)<sup>5</sup>



Following general procedure **D**, a colorless liquid in 83% yield (210 mg) from 2-vinylnaphthalene (**19a**, 154 mg, 1 mmol) was obtained.

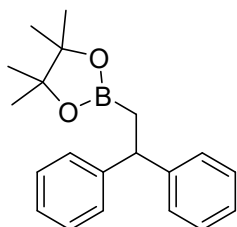
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.83-7.78 (m, 3H), 7.69 (s, 1H), 7.50 – 7.39 (m, 3H), 2.97 (t,  $J$  = 8.1 Hz, 2H), 1.31 – 1.27 (m, 2H), 1.25 (s, 12H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  142.0, 133.7, 131.9, 127.5 (dd,  $J$  = 34.9, 17.8 Hz), 125.7 (d,  $J$  = 3.0 Hz), 124.9, 30.2, 24.8, 12.9.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  34.14.

GC-MS:  $m/z$  282 ( $M^+$ ).

#### 2-(2,2-diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**20b**)<sup>4</sup>



Following general procedure **C**, a colorless liquid in 21% yield (64 mg) from ethene-1,1-diyldibenzene (**20a**, 180 mg, 1 mmol) was obtained.

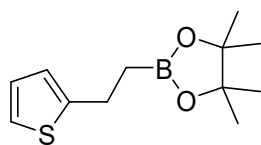
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.28 – 7.20 (m, 8H), 7.15-7.09 (m, 2H), 4.28 (t,  $J$  = 8.4 Hz, 1H), 1.60 (dd,  $J$  = 8.5, 1.9 Hz, 2H), 1.05 (d,  $J$  = 1.7 Hz, 12H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  146.6, 128.2, 127.7, 125.9, 83.1, 46.5, 24.6, 19.2.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  33.25.

GC-MS:  $m/z$  308 ( $M^+$ ).

#### 4,4,5,5-Tetramethyl-2-(2-(thiophen-2-yl)ethyl)-1,3,2-dioxaborolane (**21b**)<sup>7</sup>



Following general procedure C, a light yellow liquid in 81% yield (192 mg) from 2-vinylthiophene (**21a**, 110 mg, 1 mmol) was obtained.

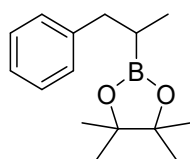
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.07 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.89 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.82 – 6.78 (m, 1H), 2.97 (t, *J* = 15 Hz, 2H), 1.29 – 1.21 (m, 14H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 147.7, 126.5, 123.4, 122.6, 83.1, 24.8, 24.3, 14.1.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 34.04.

GC-MS: *m/z* 238 (M<sup>+</sup>).

#### 4,4,5,5-Tetramethyl-2-(1-phenylpropan-2-yl)-1,3,2-dioxaborolane (**22b**)<sup>4</sup>



Following general procedure C, a colorless liquid in 28% yield (68 mg) from (E)-prop-1-en-1-ylbenzene (**22a**, 118 mg, 1 mmol) was obtained.

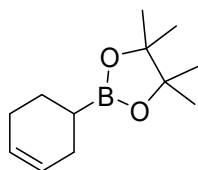
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.25 – 7.13 (m, 5H), 2.80 (dd, *J* = 13.6, 7.5 Hz, 1H), 2.54 (dd, *J* = 13.6, 8.4 Hz, 1H), 1.37 (dq, *J* = 14.8, 7.3 Hz, 1H), 1.18 (d, *J* = 5.7 Hz, 12H), 0.96 (d, *J* = 7.4 Hz, 3H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 142.3, 128.9, 128.0, 125.5, 82.9, 38.9, 24.8, 24.7, 24.7, 15.2.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 33.91.

GC-MS: *m/z* 246 (M<sup>+</sup>).

### 2-(Cyclohex-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**23b**)<sup>9</sup>



Following general procedure C, a colorless liquid in 68% yield (141 mg) from cyclohexa-1,3-diene (**23a**, 80 mg, 1 mmol) was obtained.

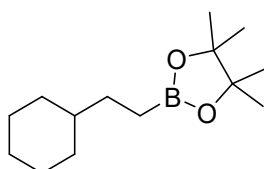
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.01 – 5.60 (m, 2H), 2.37 – 1.93 (m, 4H), 1.73 – 1.47 (m, 3H), 1.21 (s, 12H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 127.5, 127.0, 82.9, 26.2, 25.2, 24.7, 24.7, 23.8. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 34.18.

GC-MS: m/z 208 (M<sup>+</sup>).

### 2-(2-Cyclohexylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**24b**)<sup>4</sup>



Following general procedure C, a colourless liquid in 82% yield (206 mg) from vinylcyclohexane (**24a**, 110 mg, 1 mmol) was obtained.

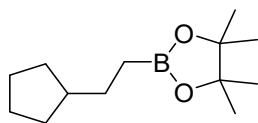
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.65 (dd, J = 30.3, 9.6 Hz, 6H), 1.24 (s, 12H), 1.13 – 0.98 (m, 5H), 0.95 – 0.86 (m, 2H), 0.85-0.71 (m, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 82.6, 41.4, 32.1, 31.9, 26.8, 26.7, 24.9, 24.8, 24.6, 9.6.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 34.56

GC-MS: m/z 238 (M<sup>+</sup>).

## 2-(2-Cyclopentylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**25b**)<sup>10</sup>



Following general procedure C, a colourless liquid in 84% yield (188 mg) from vinylcyclopentane (**26a**, 96 mg, 1 mmol) was obtained.

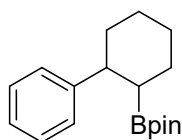
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.76 – 1.65 (m, 2H), 1.50 (s, 2H), 1.44 – 1.39 (m, 2H), 1.17 (t, *J* = 7.6 Hz, 14H), 1.08 (d, *J* = 7.0 Hz, 2H), 0.97 – 0.92 (m, 1H), 0.79 (t, *J* = 9.1 Hz, 2H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 82.65 (d, *J* = 14.0 Hz), 43.76, 31.74 (d, *J* = 16.4 Hz), 25.29 (d, *J* = 37.4 Hz), 24.88, 24.70 (d, *J* = 8.7 Hz), 11.51.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 33.79.

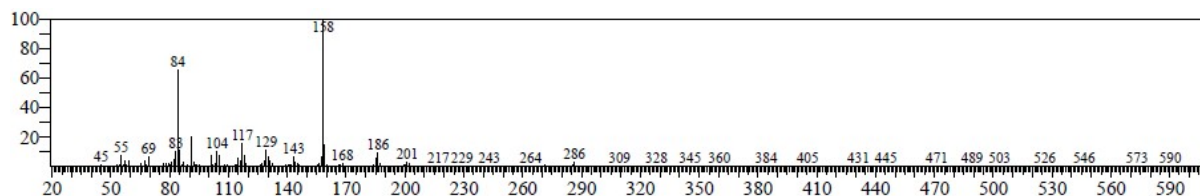
GC-MS: *m/z* 224 (M<sup>+</sup>).

## 4,4,5,5-tetramethyl-2-(2-phenylcyclohexyl)-1,3,2-dioxaborolane (**26b**)

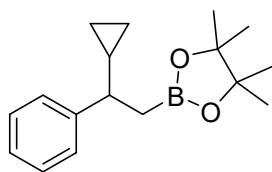


Following general procedure A. The GC-MS analysis of the reaction mixture showed the product formation.

GC-MS: *m/z* 286 (M<sup>+</sup>), 271 (M<sup>+</sup>-CH<sub>3</sub>)



## 2-(2-Cyclopropyl-2-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (27b)<sup>11</sup>



Following general procedure C, a colorless liquid in 58% yield (157 mg) from (1-cyclopropylvinyl)benzene (**27a**, 144 mg, 1 mmol) was obtained.

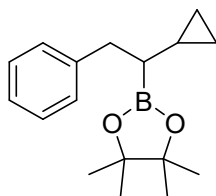
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.15 – 7.09 (m, 4H), 7.05 – 7.00 (m, 1H), 1.99 (dd, J = 16.4, 8.7 Hz, 1H), 1.19 (dd, J = 7.8, 3.8 Hz, 1H), 0.98 (s, 6H), 0.97 (s, 6H), 0.92 – 0.68 (m, 2H), 0.43 – 0.36 (m, 1H), 0.22 (ddd, J = 8.7, 7.6, 4.9 Hz, 1H), 0.16 (td, J = 9.3, 5.0 Hz, 1H), -0.01 (td, J = 9.5, 5.1 Hz, 1H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 147.40, 128.05, 127.29, 125.80, 82.97, 46.35, 24.79, 24.66, 19.80, 5.39, 4.42. signal of carbon directly bonded to boron was not detected because of quadrupolar relaxation.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 33.21.

GC-MS: m/z 272 (M<sup>+</sup>).

## 2-(1-Cyclopropyl-2-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (28b)<sup>12</sup>



Following general procedure C, a colorless liquid in 46% yield (125 mg) from (E)-(2-cyclopropylvinyl)benzene (**28a**, 144 mg, 1 mmol) was obtained.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.09 – 7.04 (m, 4H), 7.00 – 6.95 (m, 1H), 2.71 – 2.60 (m, 2H), 1.00 (s, 6H), 0.98 (s, 6H), 0.67 – 0.53 (m, 2H), 0.31 – 0.19 (m, 2H), 0.03 – -0.04 (m, 1H), -0.09 – -0.18 (m, 1H).

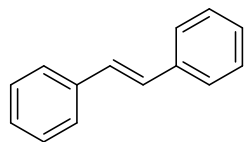
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 142.39, 128.89, 127.98, 83.01, 37.69, 34.16, 24.71, 24.65, 12.67, 5.33, 3.63.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 33.02.

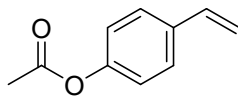
GC-MS: m/z 272 (M<sup>+</sup>).

## V. List of Unsuccessful Substrates

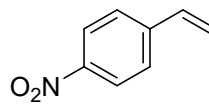
A complete list of unsuccessful alkene substrates for the KOMe-mediated protoboration reaction.



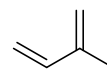
Yield : 0%



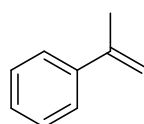
Yield : 0%



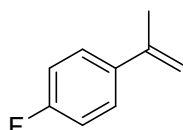
Yield : 0%



Yield : Mixture



Yield : 0%



Yield : 0%

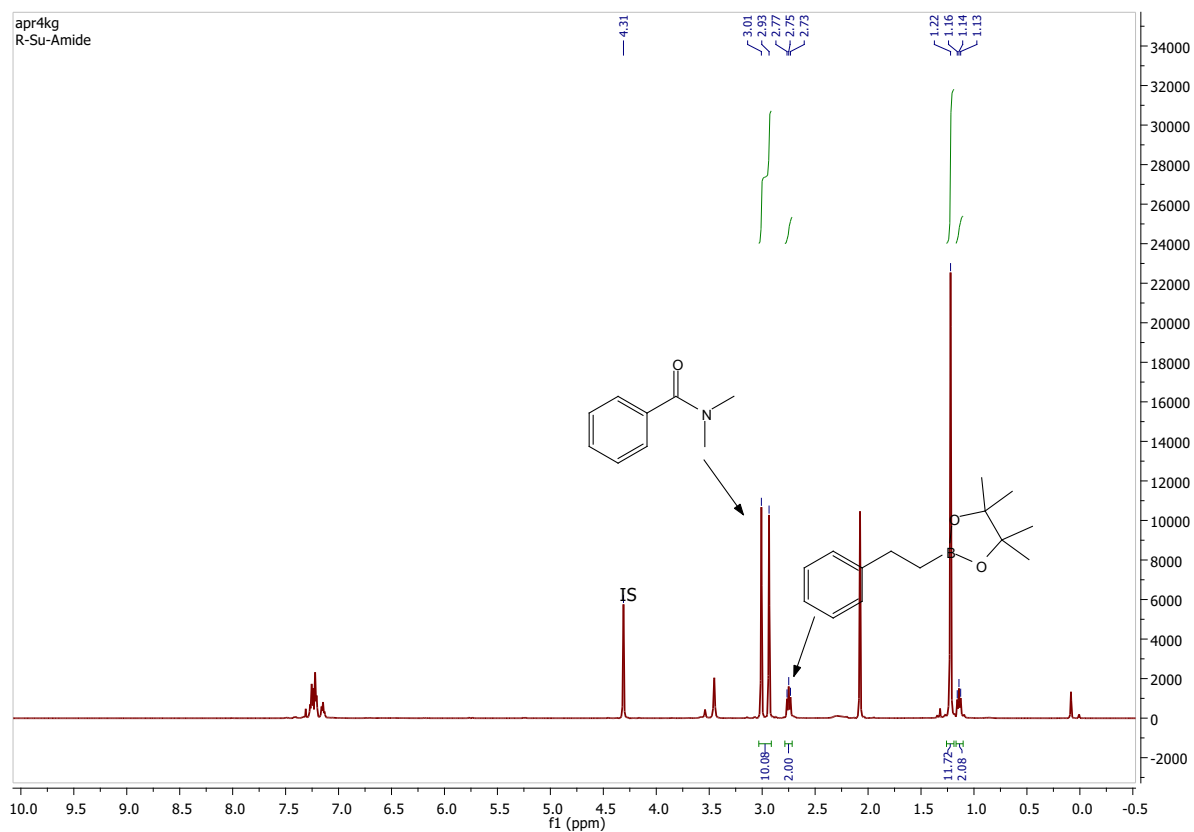
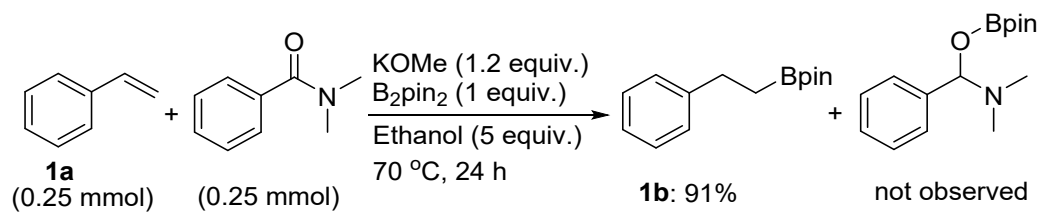


## VI. Chemoselectivity Experiments

### *Chemoselectivity Experiments.*

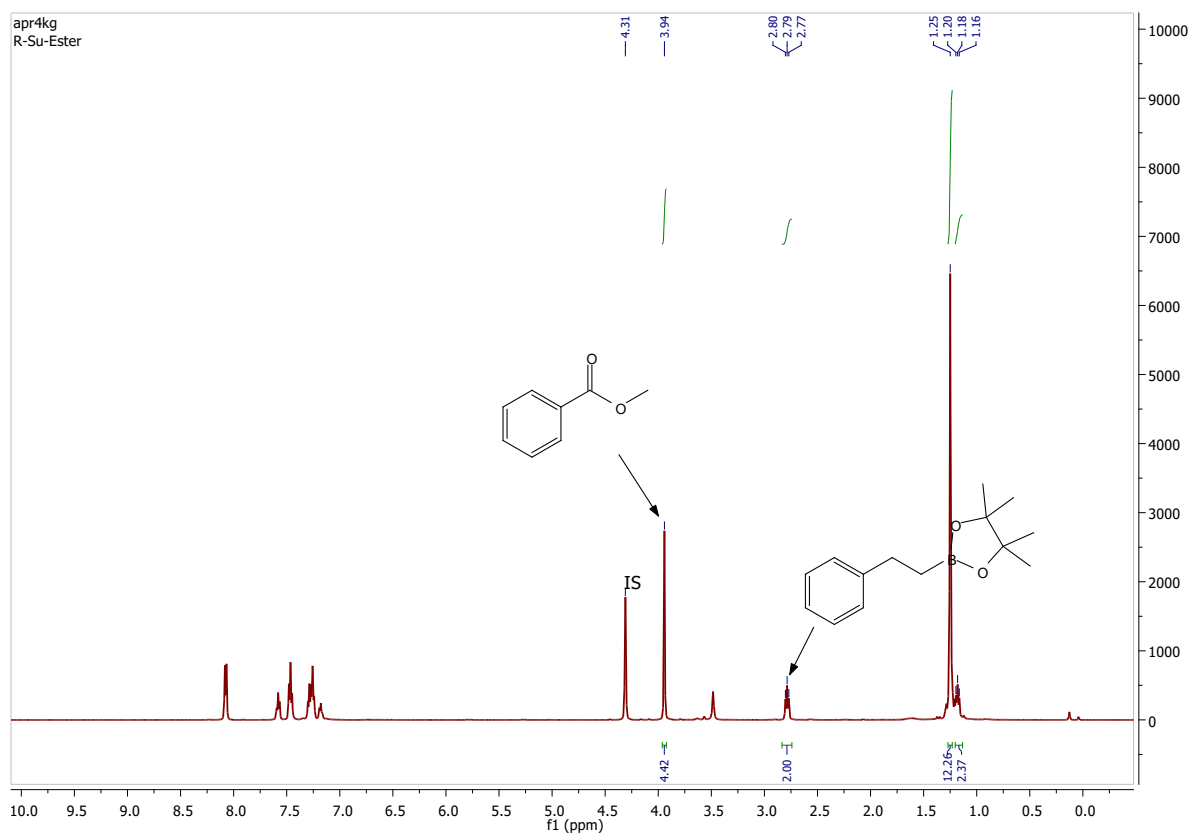
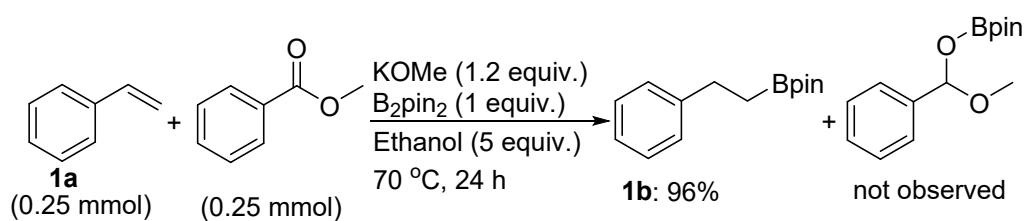
In N<sub>2</sub> atmosphere, a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, KOMe (1.2 equiv, 21 mg, 0.3 mmol), B<sub>2</sub>pin<sub>2</sub> (1.2 equiv, 76 mg, 0.3 mmol), EtOH (5 equiv, 57  $\mu$ L), styrene (**1a**; 0.25 mmol) and *N,N*-dimethylbenzamide/methyl benzoate (0.25 mmol) were added and the reaction mixture was stirred vigorously at 70 °C for 24 h. The reaction mixture was then diluted with Et<sub>2</sub>O (2 mL) and filtered through a plug of celite ( $\emptyset$  3 mm x 8 mm) with copious washing (Et<sub>2</sub>O). The solvents were removed *in vacuo*, and the ratio of the desired product by determined by <sup>1</sup>H NMR spectroscopy using nitromethane as an internal standard.

### Reaction between styrene (**1a**) and *N,N*-dimethylbenzamide:



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of reaction mixture of **1a** and *N,N*-dimethylbenzamide.

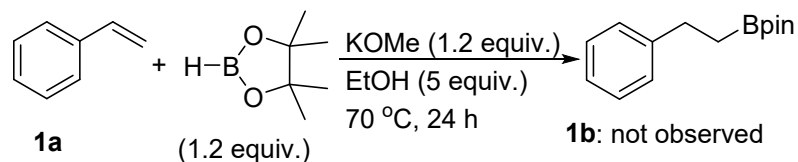
Reaction between equimolar amounts of **1a** and methyl benzoate:



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of reaction mixture of **1a** and methyl benzoate.

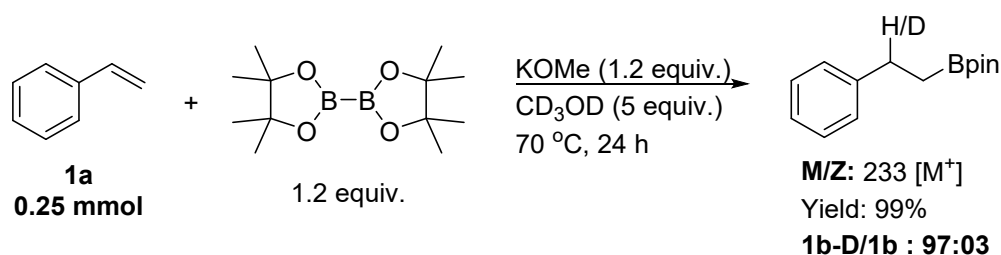
## VII. Mechanistic investigations

### Protoboration of styrene (**1a**) with HBpin:



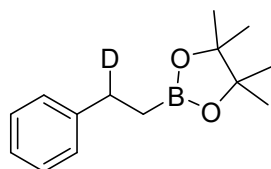
In nitrogen atmosphere, a glass vial equipped with magnetic stirring bar, styrene (**1a**, 0.25 mmol, 26.03 mg), HBpin (1.2 equiv, 38 mg, 0.3 mmol), KOMe (1.2 equiv, 21 mg, 0.3 mmol) and EtOH (57  $\mu$ l; 5 equiv.) were added and reaction mixture was kept under stirring for 24 h at 70 °C. The crude reaction mixture was dissolved in Et<sub>2</sub>O (10 mL) and passed through a plug of celite. The solvent was removed in vacuo, and nitromethane was added as an internal standard. The product yield was determined from <sup>1</sup>H NMR.

## Isotope Labelling Experiment



In N<sub>2</sub> atmosphere a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, styrene (**1a**, 26 mg, 0.25 mmol), B<sub>2</sub>pin<sub>2</sub> (1.2 equiv, 76 mg, 0.3 mmol), KOMe (1.2 equiv, 21 mg, 0.3 mmol), DMF (1 mL), CD<sub>3</sub>OD (5 equiv, 42 μL), were added and the reaction was stirred vigorously at 70 °C temperature for 24 h. The crude reaction mixture was dissolved in Et<sub>2</sub>O (10 mL) and passed through a plug of celite. The solvent was removed in vacuo, and obtained product was determined by GC-MS and <sup>1</sup>H NMR spectroscopy. The protoboration product was formed in 99% (of which ca. 97% was deuterated, determined by <sup>1</sup>H NMR analysis).

### 4,4,5,5-Tetramethyl-2-(2-phenylethyl-2-d)-1,3,2-dioxaborolane (**1b-D**)<sup>4</sup>

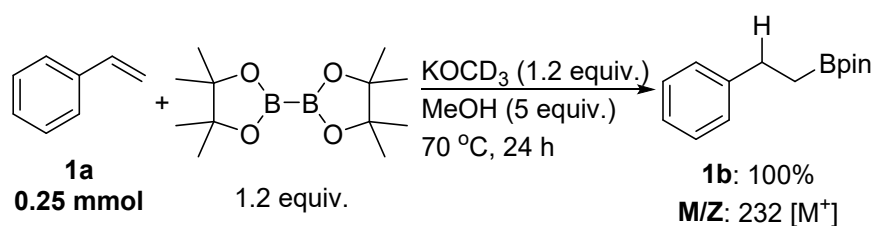


<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.33-6.94 (m, 5H), 2.92-2.74 (m), 2.73-2.52 (m, 1H), 1.13 (s, 12H), 1.05 (d, *J* = 7.5 Hz, 2H).

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 34.02.

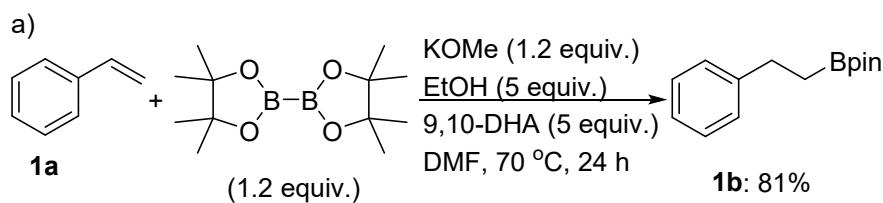
GC-MS: *m/z* 233 (M<sup>+</sup>).

### Protoboration of styrene (**1a**) in the presence of KOCD<sub>3</sub> as promoter:



In N<sub>2</sub> atmosphere a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, styrene (**1a**, 26 mg, 0.25 mmol), B<sub>2</sub>pin<sub>2</sub> (1.2 equiv, 76 mg, 0.3 mmol), KOCD<sub>3</sub> (1.2 equiv, 22 mg, 0.3 mmol), CH<sub>3</sub>OH (2.0 equiv, 50 μL, 1.25 mmol), were added and the reaction was stirred vigorously at 70 °C temperature for 24 h. The crude reaction mixture was dissolved in Et<sub>2</sub>O (10 mL) and passed through a plug of celite. The solvent was removed in vacuo, and obtained product was characterised by GC-MS and <sup>1</sup>H NMR spectroscopy. The protoboration product was not detected by GC-MS analysis.

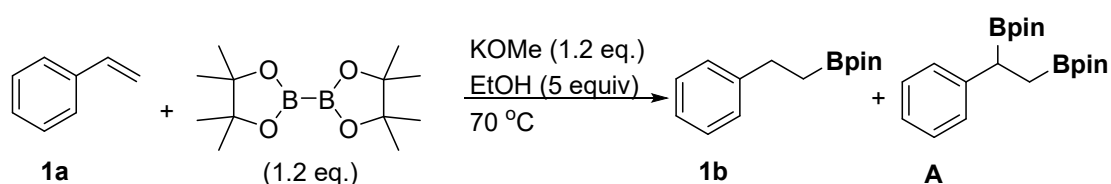
### Radical Scavenging Experiments



In nitrogen atmosphere, a glass vial equipped with magnetic stirring bar, styrene (**1a**, 0.25 mmol, 26.03 mg), B<sub>2</sub>pin<sub>2</sub> (1.2 equiv, 76 mg, 0.3 mmol), KOMe (1.2 equiv, 21 mg, 0.3 mmol), EtOH (57 μL; 5 equiv) and 5 equiv. of 9,10-dihydroanthracene (225.3 mg) were added, followed by 2.5 mL of DMF and reaction mixture was kept under stirring for 24 h at 70 °C. The crude reaction was dissolved in Et<sub>2</sub>O (20 mL) and then transferred to a separatory funnel followed by the addition of H<sub>2</sub>O (20 mL). The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et<sub>2</sub>O (3 x 10 mL). The combined organics were dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated. An internal standard nitromethane was added to the residue. The yield of the product was determined by <sup>1</sup>H NMR spectroscopy.

### Time dependence experimental procedure for the protoboration of **1a** under neat conditions.

In a 15 mL thick-walled reaction tube equipped with a magnetic stirring bar, styrene (**1a**, 104 mg, 1 mmol), B<sub>2</sub>pin<sub>2</sub> (1.2 equiv, 1.2 mmol, 76 mg), KOMe (1.2 equiv, 1.2 mmol, 21 mg) and EtOH (5 equiv.) were added and the reaction mixture was stirred vigorously at 70 °C. 50 μL samples were periodically withdrawn from the crude reaction mixture in an N<sub>2</sub> atmosphere. The product yield was determined by GC-MS.

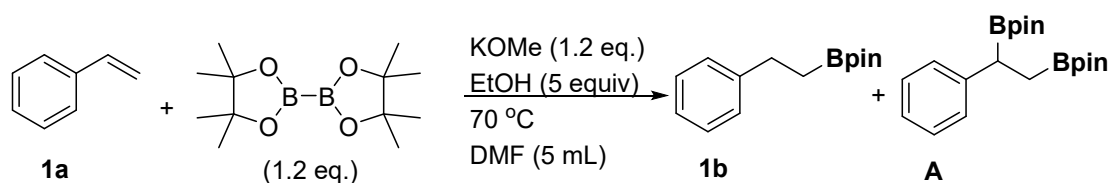


Entry	Ethanol	Base	Time	Yield <b>1b</b> (%)	Yield <b>A</b> (%)
1	5 equiv.	KOMe	10 min.	70	6
2	5 equiv.	KOMe	20 min.	78	5
3	5 equiv.	KOMe	30 min	81	3
4	5 equiv.	KOMe	40 min.	90	trace
5	5 equiv.	KOMe	2 h	97	0
6	5 equiv.	KOMe	4 h	>99	0

<sup>a</sup>Reaction condition: 1 mmol **1a**, B<sub>2</sub>pin<sub>2</sub> (1.2 equiv.), base (1.2 equiv.), EtOH (5 equiv.) at 70 °C.

### Time dependence experimental procedure for the protoboration of **1a** in DMF solvent.

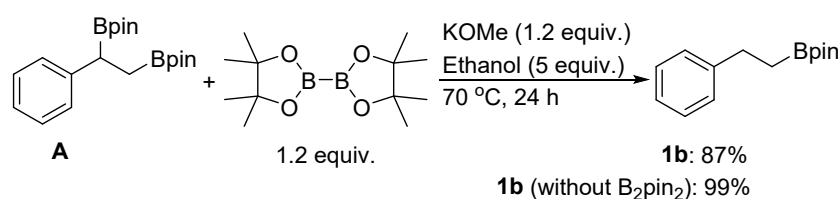
In a 15 mL thick-walled reaction tube equipped with a magnetic stirring bar, styrene (**1a**, 104 mg, 1 mmol), B<sub>2</sub>pin<sub>2</sub> (1.2 equiv, 1.2 mmol, 76 mg), KOMe (1.2 equiv, 1.2 mmol, 21 mg), EtOH (5 equiv.) and DMF (5 mL) were added and the reaction mixture was stirred vigorously at 70 °C. 50 μL samples were periodically withdrawn from the crude reaction mixture in an N<sub>2</sub> atmosphere. The product yield was determined by GC-MS.



Entry	Ethanol	Base	Time	Yield <b>1b</b> (%)	Yield <b>A</b> (%)
1	5 equiv.	KOMe	30 min.	38	0
2	5 equiv.	KOMe	1 h	63	0
3	5 equiv.	KOMe	2 h	74	0
4	5 equiv.	KOMe	3 h	87	0
5	5 equiv.	KOMe	7 h	92	0
6	5 equiv.	KOMe	16 h	98	0
7	5 equiv.	KOMe	24 h	>99	0

<sup>a</sup>Reaction condition: 1 mmol **1a**, B<sub>2</sub>pin<sub>2</sub> (1.2 equiv.), base (1.2 equiv.), EtOH (5 equiv.) at 70 °C in DMF (5 mL).

To gain insight into the mechanism, diboronate ester (**A**) was synthesized according to the literature procedure.<sup>13a</sup> Based on the literature report, **A** can be easily formed from alkene with B<sub>2</sub>pin<sub>2</sub> under basic conditions.<sup>13</sup> Therefore, **A** can be considered a possible intermediate in the synthesis of alkyl boronate ester (**1b**) from alkene. When **A** was subjected to our standard reaction conditions, the desired product **1b** was obtained in 87% yield (Scheme S1). Further reaction in the absence of B<sub>2</sub>pin<sub>2</sub> afforded a quantitative yield of **1b**. These results suggested that **A** might be the intermediate in this transformation, and the alkyl boronate ester may be formed *via* tandem diboration and protodeboronation processes.<sup>13b</sup> However, when the styrene (**1a**) protoboration reaction in the presence of KOMe and EtOH at 70 °C in DMF was monitored by GC-MS analysis, intermediate **A** was not observed, which exclude the possibility of the intermediacy of **A** in this reaction.



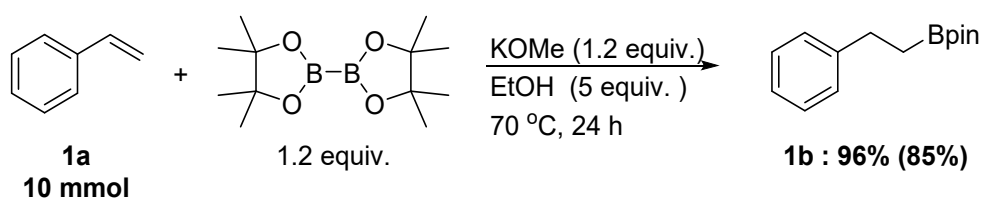
**Scheme S1.** Control experiment.



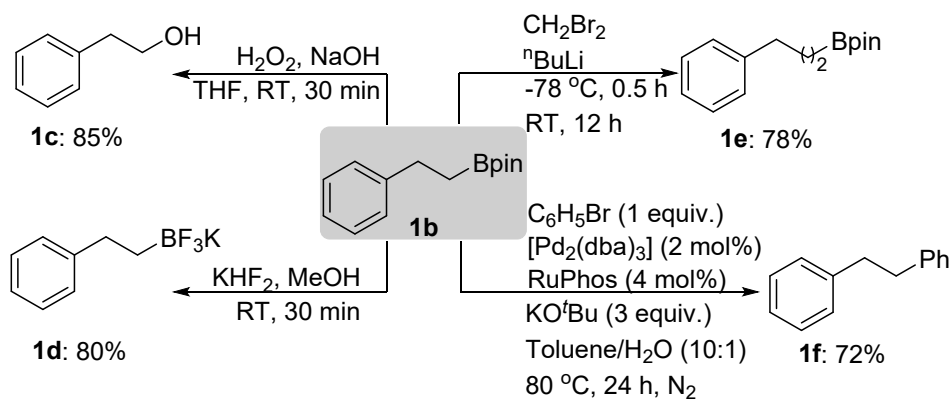
## VIII. Synthetic Application

### Gram Scale Reaction

In a glovebox, to an oven-dried 100 mL round bottom flask equipped with a magnetic stirring bar, styrene (**1a**; 1.04 g; 10 mmol), KOMe (841 mg, 1.2 equiv., 12 mmol), B<sub>2</sub>pin<sub>2</sub> (3.04 g, 1.2 equiv., 12 mmol) and EtOH (2.28 mL, 5 equiv.) were added and the reaction mixture was stirred vigorously at 70 °C for 24 h. The crude reaction mixture was dissolved in Et<sub>2</sub>O (50 mL) and passed through a plug of Celite. The solvent was removed in vacuum, and the residue was purified by column chromatography to give 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane (**1b**; 1.97 g, 85%) as a colourless oil.



### Conversion of Alkyl Boronate Ester (**1b**) into **1c-1f**<sup>4,6,14</sup>

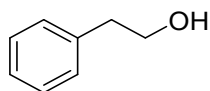


### Conversion of Alkyl Boronate Ester (**1b**) into 2-phenylethan-1-ol (**1c**)<sup>4</sup>

To a solution of **1b** (232.1 mg, 1 mmol) generated *in situ* from styrene in THF (10 mL) was added with NaOH (3M aq., 1 mL, 3 mmol). The mixture was then cooled to -30 °C and H<sub>2</sub>O<sub>2</sub> (30% aq., 0.3 mL, 3 mmol) was added drop wise in 5 minutes. The cooling bath was removed and the reaction mixture was warmed up to room temperature and stirred for 30 minutes. Then the reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in

vacuo to give product **1c** as colourless oil (103 mg, 85%). The corresponding alcohol was identified by  $^1\text{H}$  and  $^{13}\text{C}$  NMR.

#### 2-Phenylethan-1-ol (**1c**)<sup>4</sup>



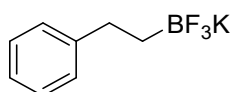
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 – 7.30 (m, 2H), 7.26 – 7.22 (m, 3H), 3.86 (t,  $J = 6.6$  Hz, 2H), 2.87 (t,  $J = 6.6$  Hz, 2H), 1.58 (s, 1H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  138.4, 129.0, 128.5, 126.44, 63.6, 39.1.

#### Conversion of Alkyl Boronate Ester (**1b**) into Potassium trifluoro (phenethyl) borate (**1d**)<sup>4</sup>

The boronate ester **1b** (232.1 mg, 1.0 mmol) generated *in situ* from styrene was dissolved in methanol (5 mL).  $\text{KHF}_2$  (4.5M aq., 1 mL, 4.5 mmol) was added dropwise to the solution. The reaction mixture was stirred at 25 °C for 30 minutes. The solvent was removed in vacuo, and the solid residue was triturated with dry acetone (5 mL). The liquid phase was carefully decanted, and the residual inorganic salts were washed twice with additional acetone. The combined solution was concentrated in vacuo to obtain white solids. The solid was then washed with  $\text{Et}_2\text{O}$  and dried under vacuum to give the desired product **1d** as white solid (169 mg, 82%). The corresponding salt was analysed by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{11}\text{B}$  and  $^{19}\text{F}$  NMR.

#### Trifluoro(phenethyl)-14-borane, potassium salt (**1d**)<sup>4</sup>



$^1\text{H}$  NMR (500 MHz, DMSO):  $\delta$  7.21 – 7.04 (m, 5H), 2.44 (t,  $J = 15$  Hz, 2H), 0.32 (s, 2H).

$^{13}\text{C}$  NMR (126 MHz, DMSO):  $\delta$  148.4, 128.3, 128.1, 124.8, 32.5.

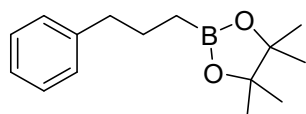
$^{11}\text{B}$  NMR (160 MHz, DMSO):  $\delta$  4.5.

$^{19}\text{F}$  NMR (471 MHz, DMSO):  $\delta$  -137.8.

### Conversion of Alkyl Boronate Ester (**1b**) into 4,4,5,5-tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (**1e**)<sup>6</sup>

To a flame-dried 10 mL Schlenk tube were added **1b** (232 mg, 1 mmol, 1.0 eq.), THF (5.0 mL), and CH<sub>2</sub>Br<sub>2</sub> (513 mg, 3 mmol, 3.0 eq.) in a glovebox. After it was sealed and taken out of the glovebox, the reaction mixture was cooled to -78 °C, and then nBuLi (2.8 mmol, 2.8 eq.) was added dropwise under an N<sub>2</sub> atmosphere. The reaction was stirred at -78 °C for 30 minutes before it was allowed to warm to room temperature and stirred for 3 hours. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (saturated aqueous solution, 10 mL) was added, and the reaction mixture was extracted with Et<sub>2</sub>O (3 × 10 mL). The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure, and the residue was purified by column chromatography to give 4,4,5,5-tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (**1e**; 191 mg, 78%) as a colourless oil. The product **1e** was identified by <sup>1</sup>H, <sup>13</sup>C and <sup>11</sup>B NMR and GC-MS analysis. GC-MS: m/z 246.

### 4,4,5,5-tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (**1e**)<sup>6</sup>



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.28 – 7.23 (m, 2H), 7.19 – 7.13 (m, 3H), 2.60 (t, J = 15 Hz, 2H), 1.78 – 1.66 (m, 2H), 1.24 (s, 12H), 0.82 (t, J = 15 Hz, 2H).

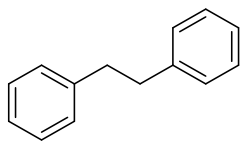
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 142.6, 128.5, 128.1, 125.5, 82.8, 38.5, 24.7, 20.9, 14.1.

<sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>): δ 34.07.

### Conversion of alkyl boronate ester (**1b**) into 1,2-diphenylethane (**1f**)<sup>14</sup>

Under air, Pd<sub>2</sub>(dba)<sub>3</sub> (36 mg, 0.04 mmol), KO<sup>t</sup>Bu (672.0 mg, 6 mmol), and RuPhos (37 mg, 0.08 mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon. Toluene (6 mL), H<sub>2</sub>O (0.6 mL), chlorobenzene (224 mg, 2 mmol), and **1b** (464 mg, 2 mmol, 1.0 equiv) were added to the Schlenk tube by syringe. The resulting reaction mixture stirred vigorously at 80 °C for 24 h. The reaction mixture was filtered through celite and washed with EtOAc (15×15 mL). The solution was combined and the volatiles were removed under vacuum. The residue was purified by column chromatography to obtain 1,2-diphenylethane (**1f**; 282 mg, 72%) and characterised by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

**1,2-Diphenylethane (1f)<sup>14</sup>**



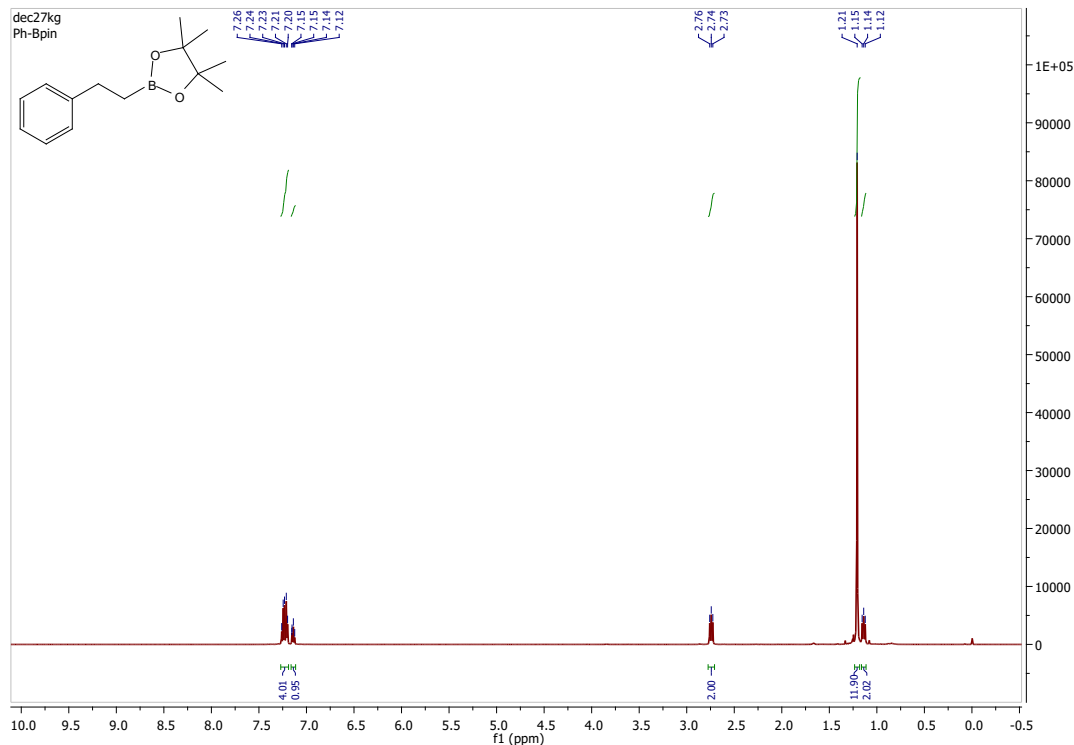
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.64-7.58 (m, 4H), 7.55-7.48 (m, 6H), 3.25 (d, J = 3.9 Hz, 4H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 142.1, 128.8, 128.7, 126.3, 38.3.

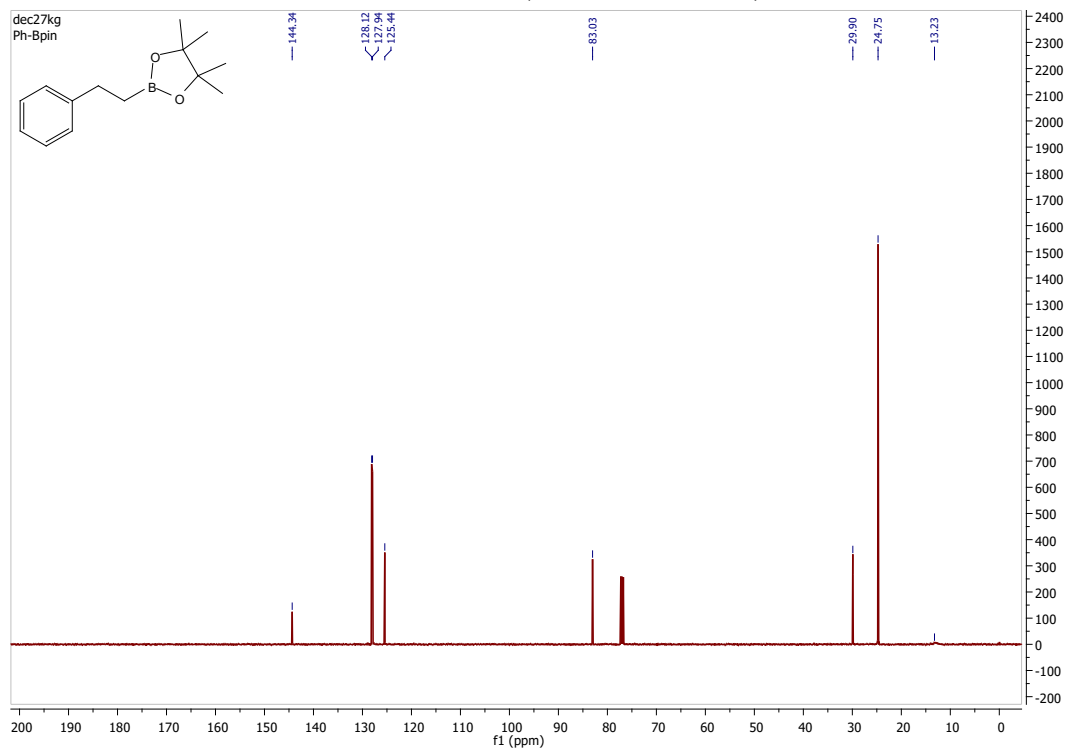
## IX. NMR Spectra of Alkene protoboration Products

**Note:** Resonances denoted by (#) corresponds to solvent/grease. Resonance at  $\delta = 1.56$  corresponds to H<sub>2</sub>O and peak at  $\delta = 0.07$  corresponds to silicone grease.

### 4,4,5,5-Tetramethyl-2-phenethyl-1,3,2-dioxaborolane (**1b**)<sup>4</sup>

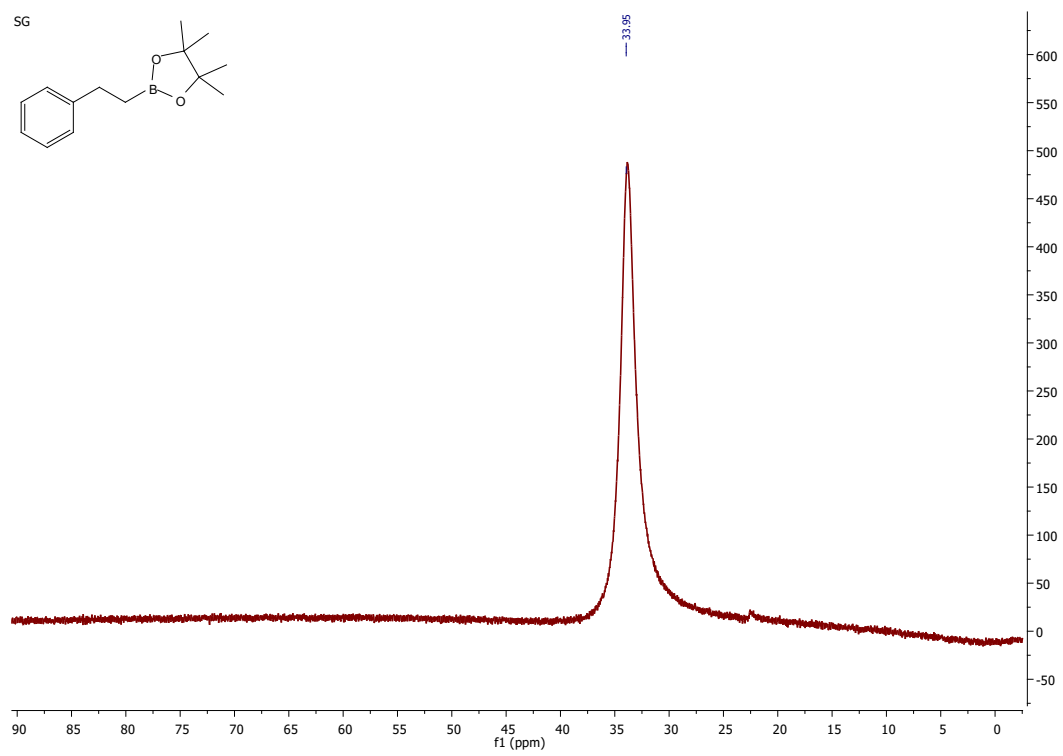
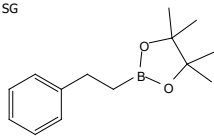


<sup>1</sup>H NMR of **1b** (500 MHz, CDCl<sub>3</sub>)



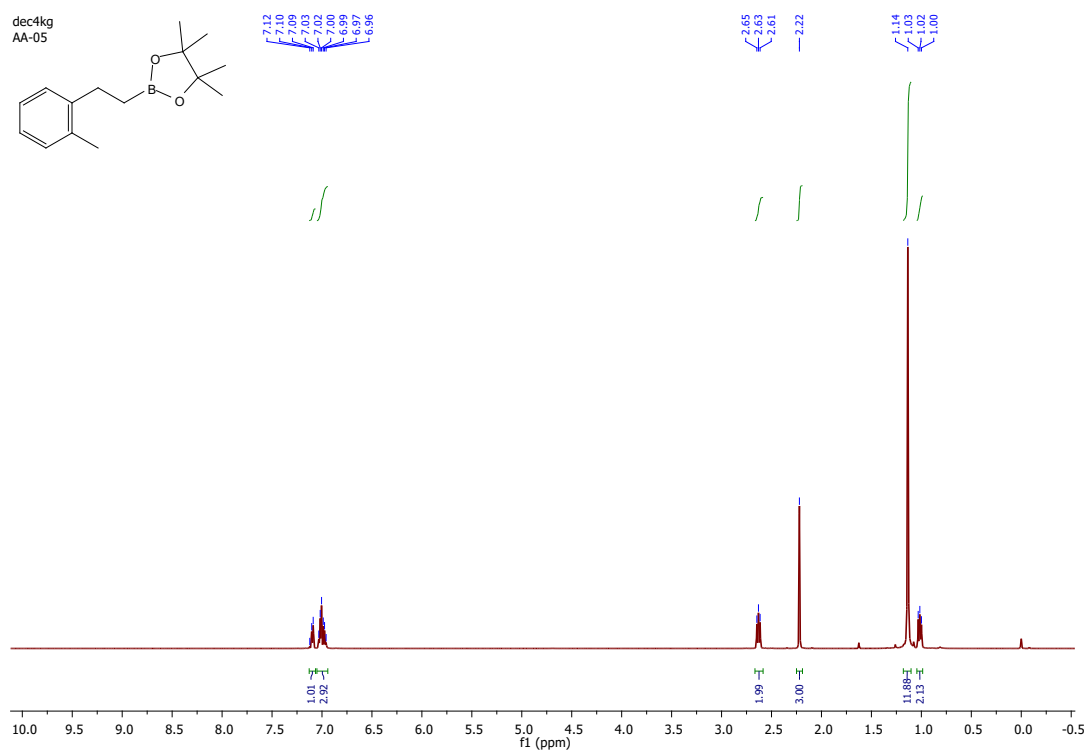
<sup>13</sup>C NMR of **1b** (126 MHz, CDCl<sub>3</sub>)

SG

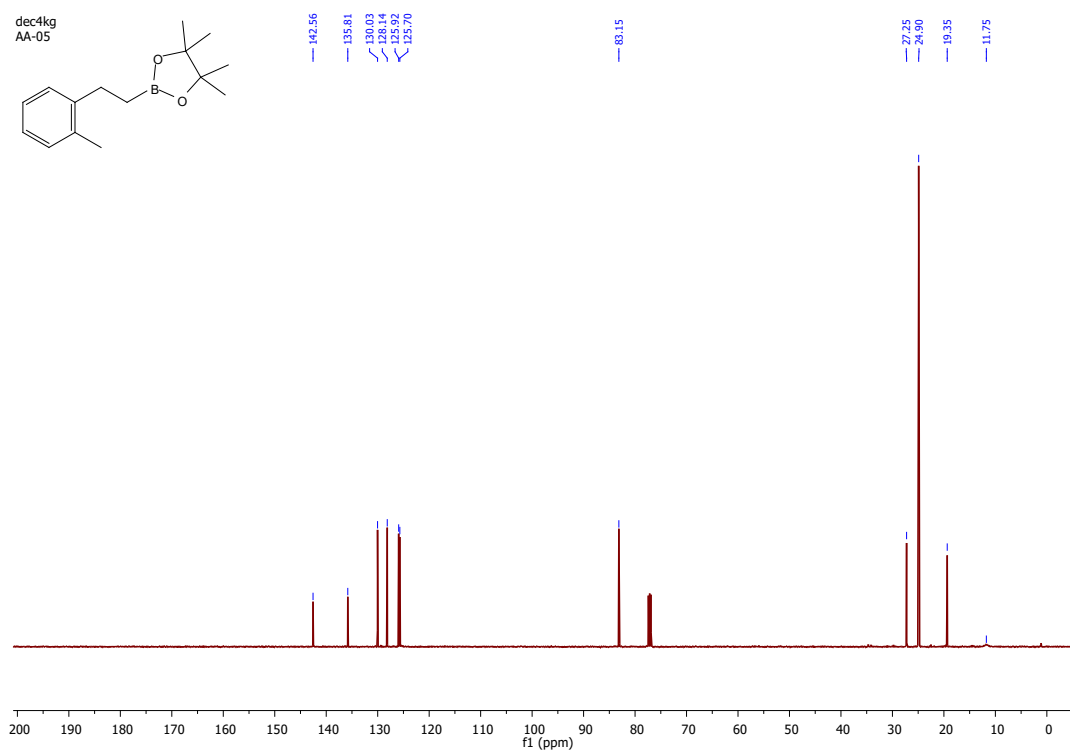


$^{11}\text{B}$  NMR of **1b** (160 MHz,  $\text{CDCl}_3$ )

# 4,4,5,5-Tetramethyl-2-(2-methylphenethyl)-1,3,2-dioxaborolane (**2b**)<sup>5</sup>

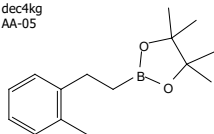


<sup>1</sup>H NMR of **2b** (500 MHz, CDCl<sub>3</sub>)

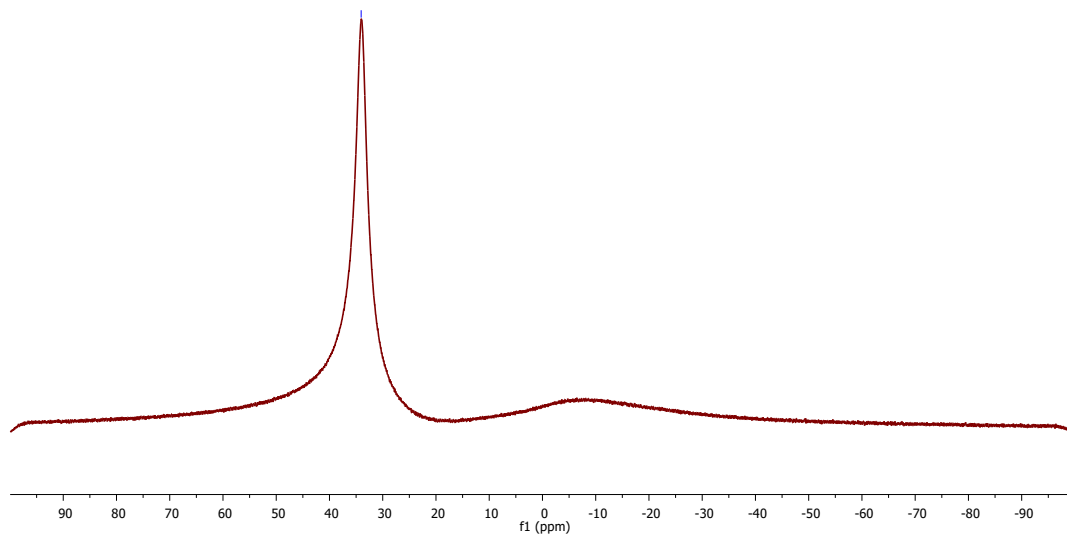


<sup>13</sup>C NMR of **2b** (126 MHz, CDCl<sub>3</sub>)

dec4kg  
AA-05



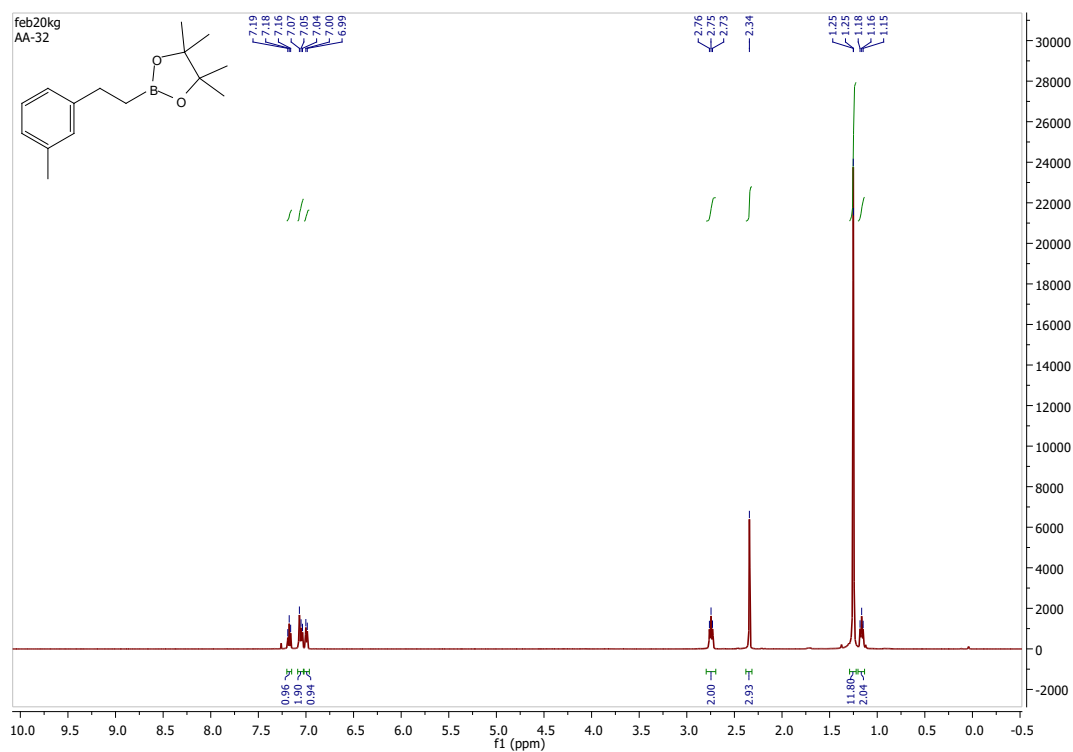
34.05



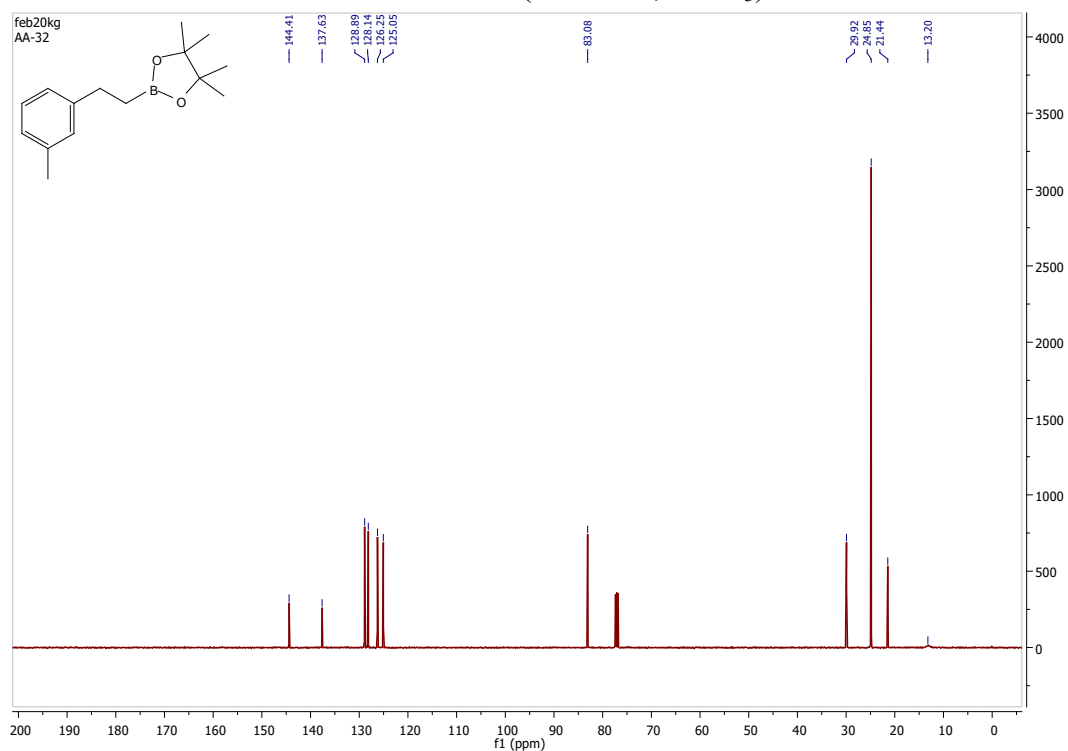
$^{11}\text{B}$  NMR of **2b** (160 MHz,  $\text{CDCl}_3$ )



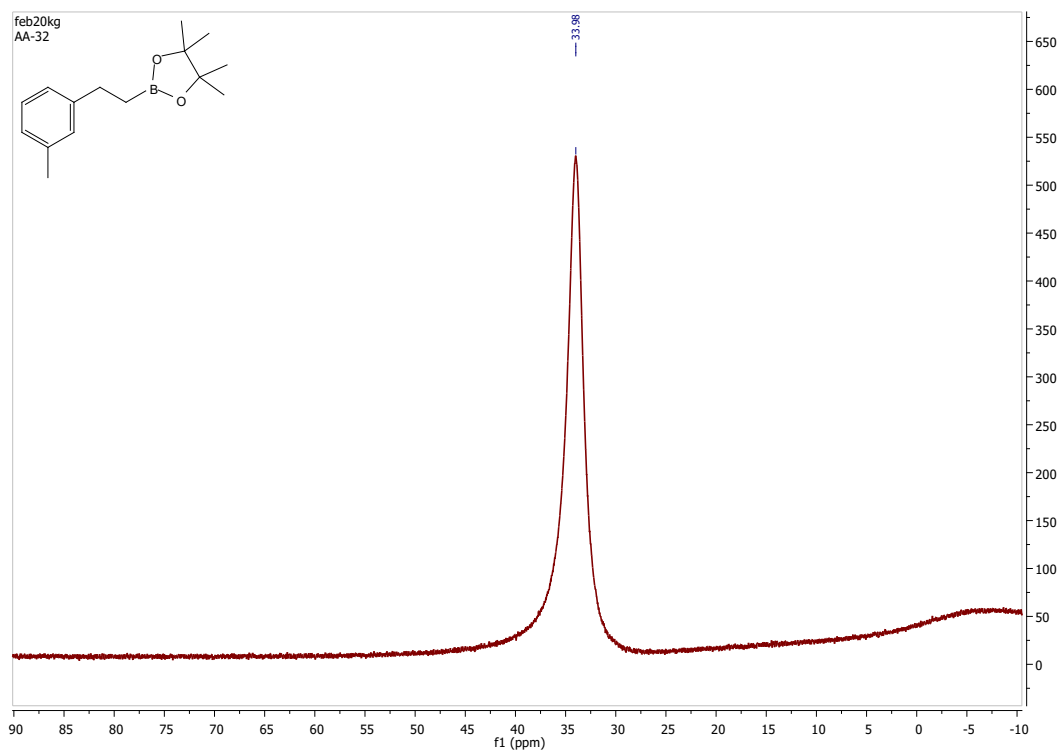
# 4,4,5,5-Tetramethyl-2-(3-methylphenethyl)-1,3,2-dioxaborolane (**3b**)<sup>5</sup>



<sup>1</sup>H NMR of **3b** (500 MHz, CDCl<sub>3</sub>)

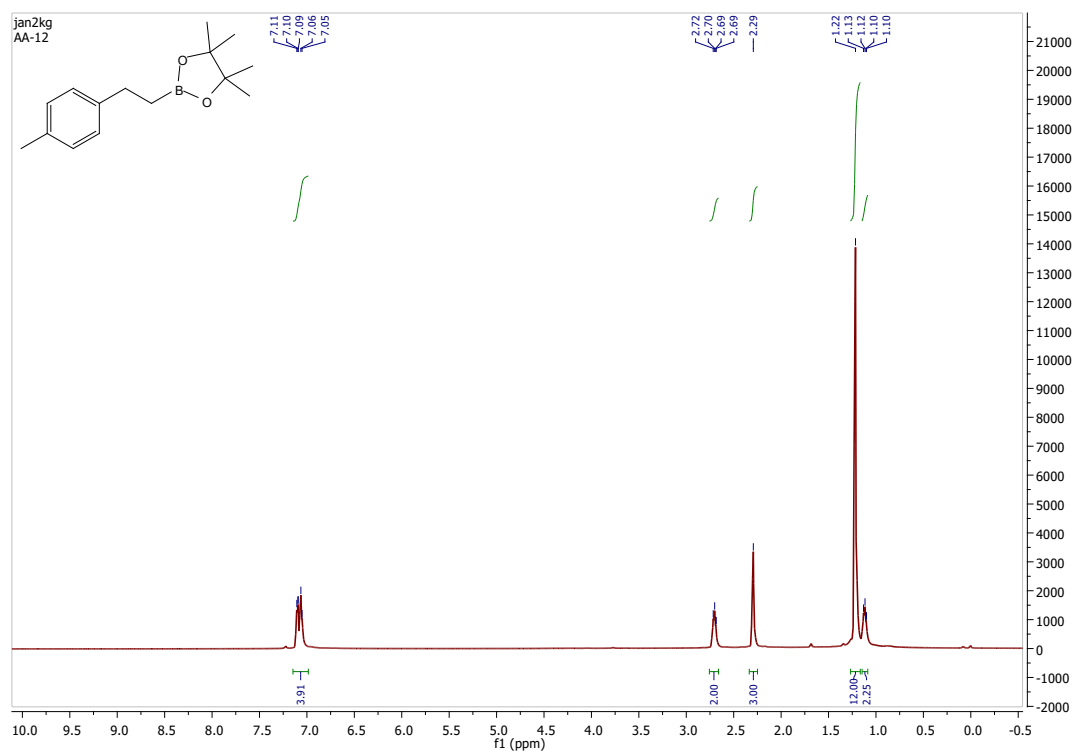


<sup>13</sup>C NMR of **3b** (126 MHz, CDCl<sub>3</sub>)

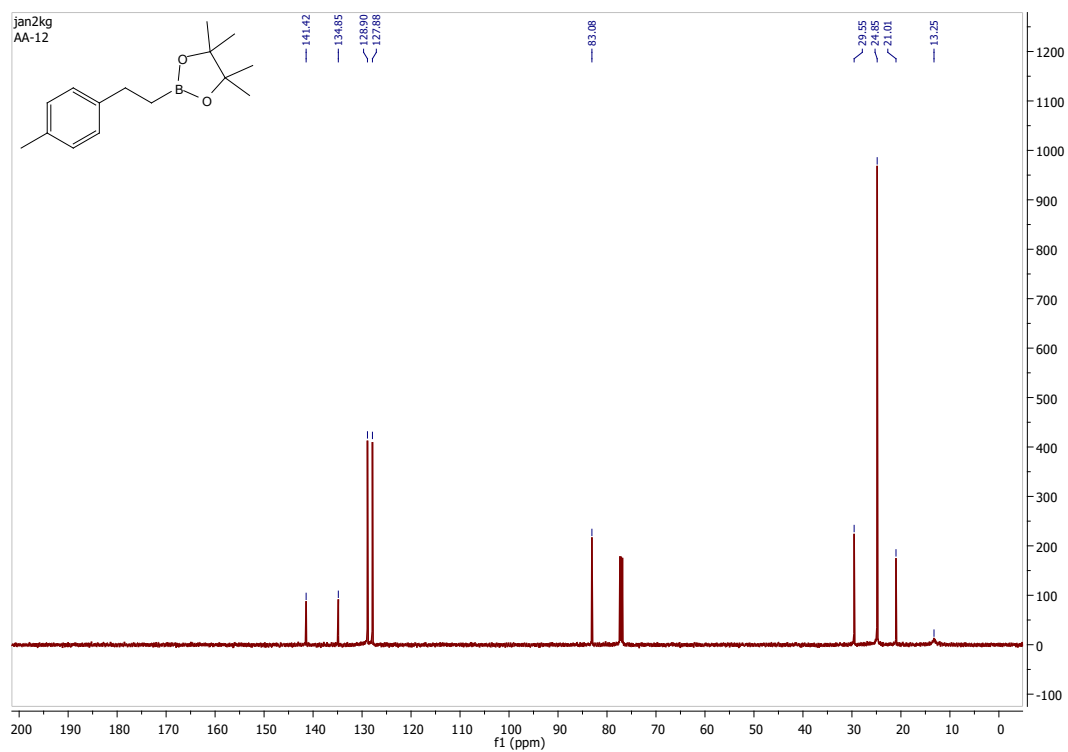


$^{11}\text{B}$  NMR of **3b** (160 MHz,  $\text{CDCl}_3$ )

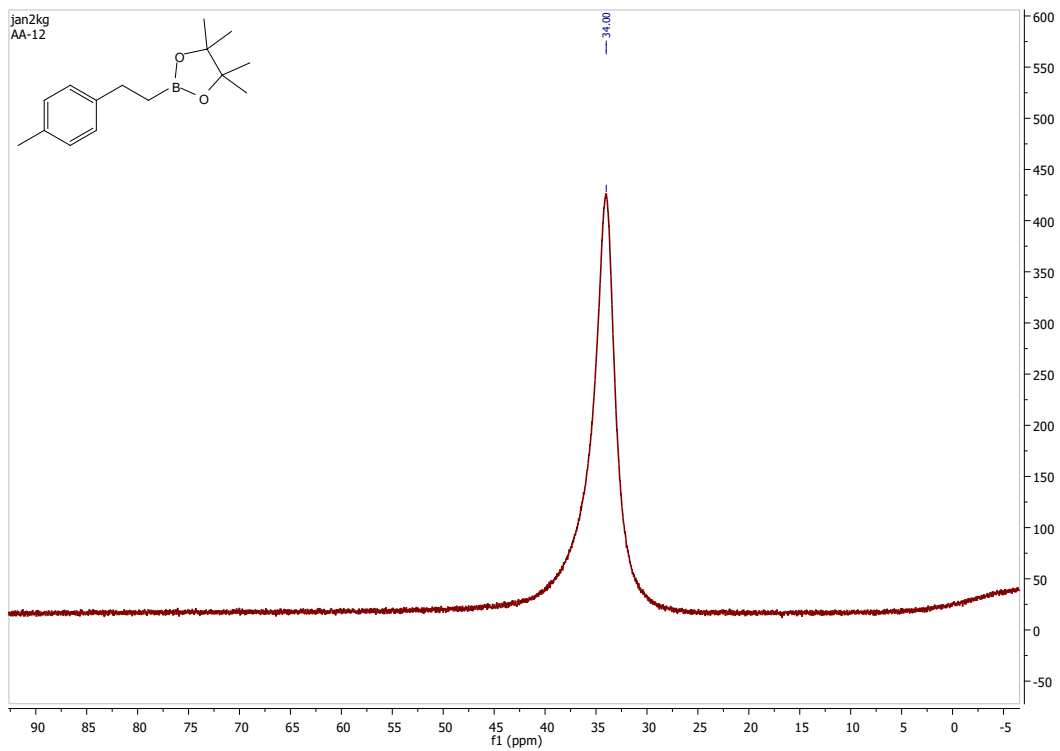
### 4,4,5,5-Tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane (**4b**)<sup>4</sup>



<sup>1</sup>H NMR of **4b** (500 MHz, CDCl<sub>3</sub>)

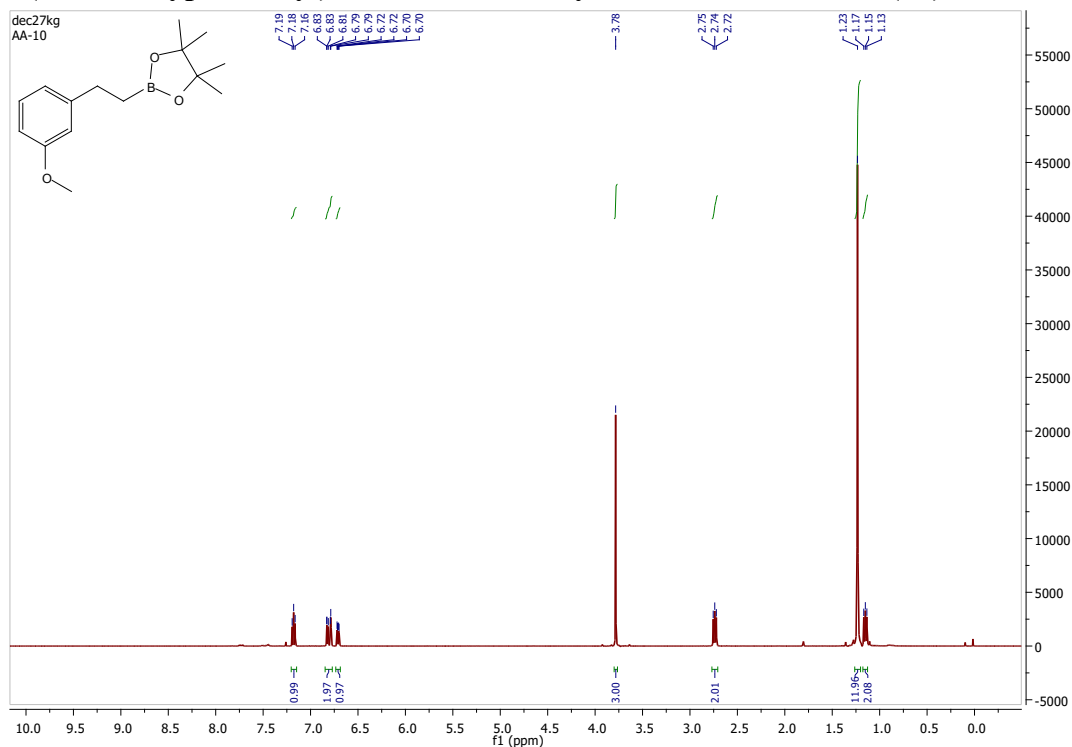


<sup>13</sup>C NMR of **4b** (126 MHz, CDCl<sub>3</sub>)

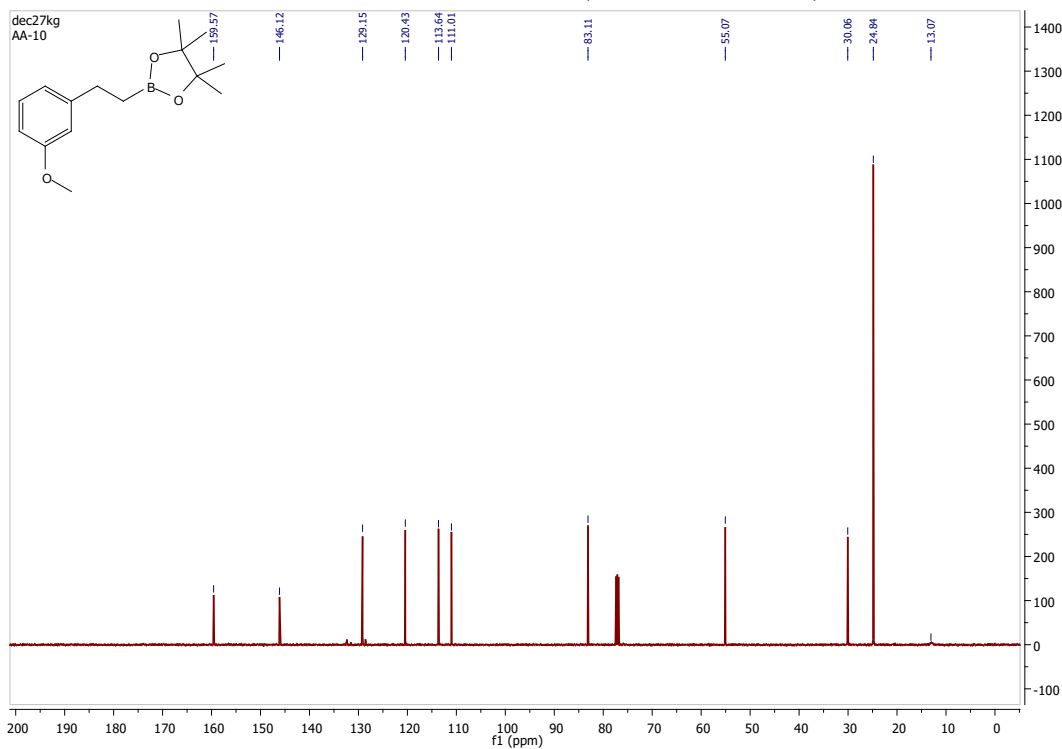


$^{11}\text{B}$  NMR of **4b** (160 MHz,  $\text{CDCl}_3$ )

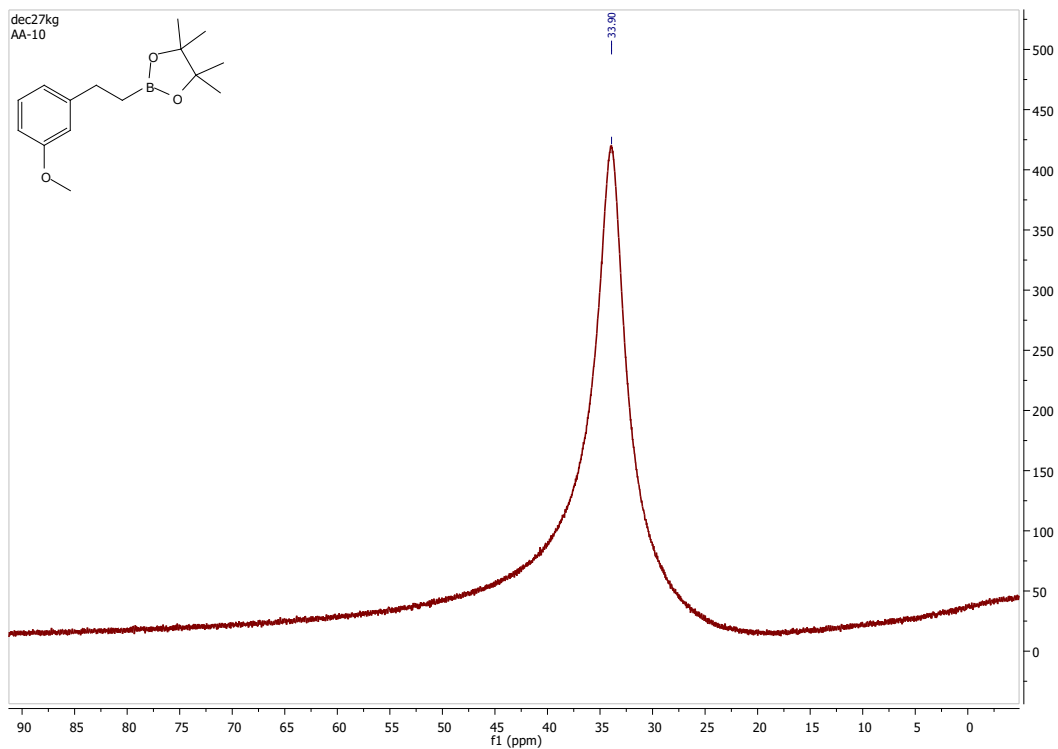
## 2-(3-Methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5b**)<sup>4</sup>



<sup>1</sup>H NMR of **5b** (500 MHz, CDCl<sub>3</sub>)

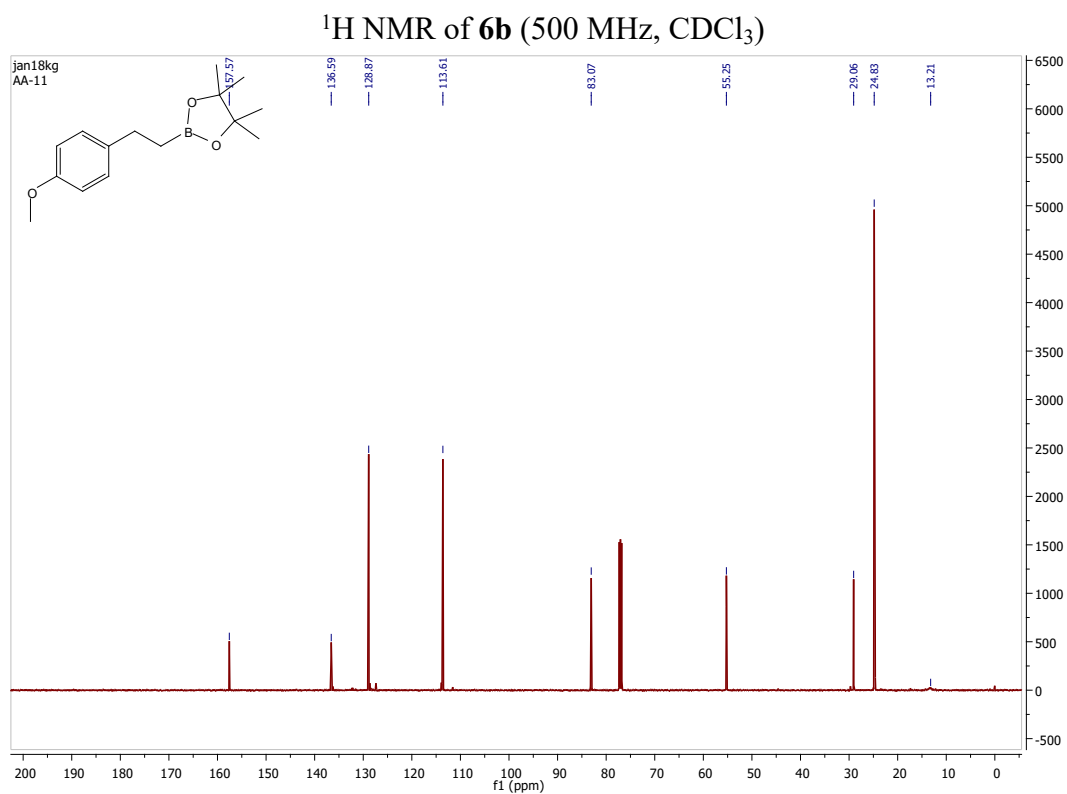
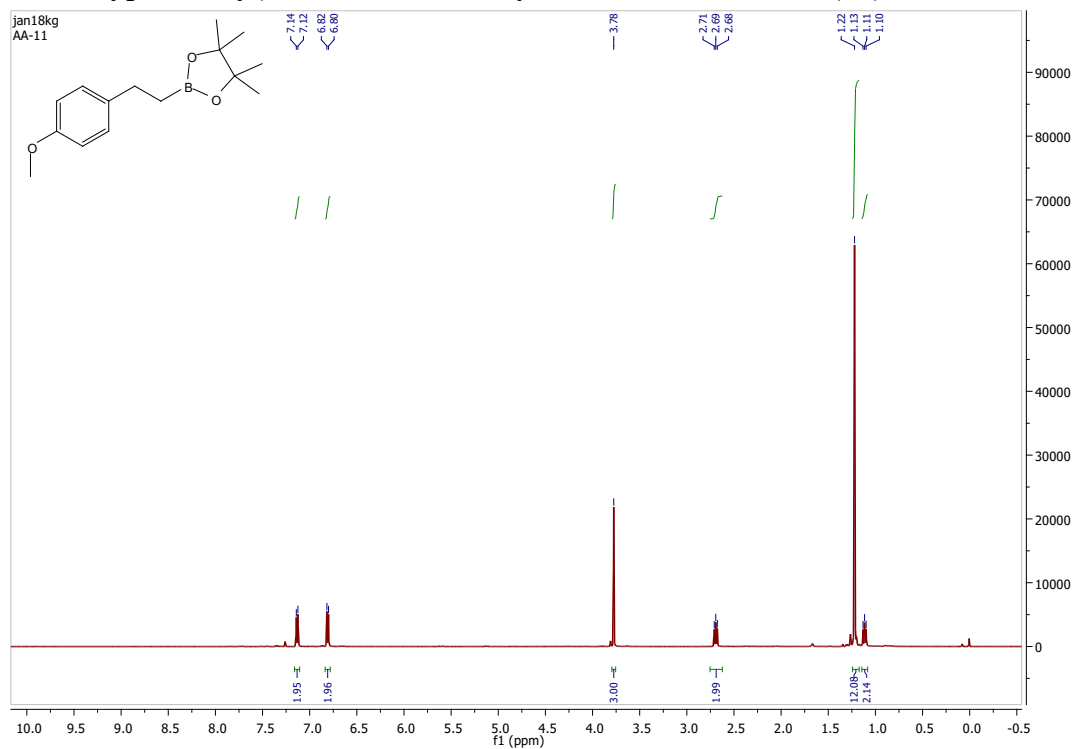


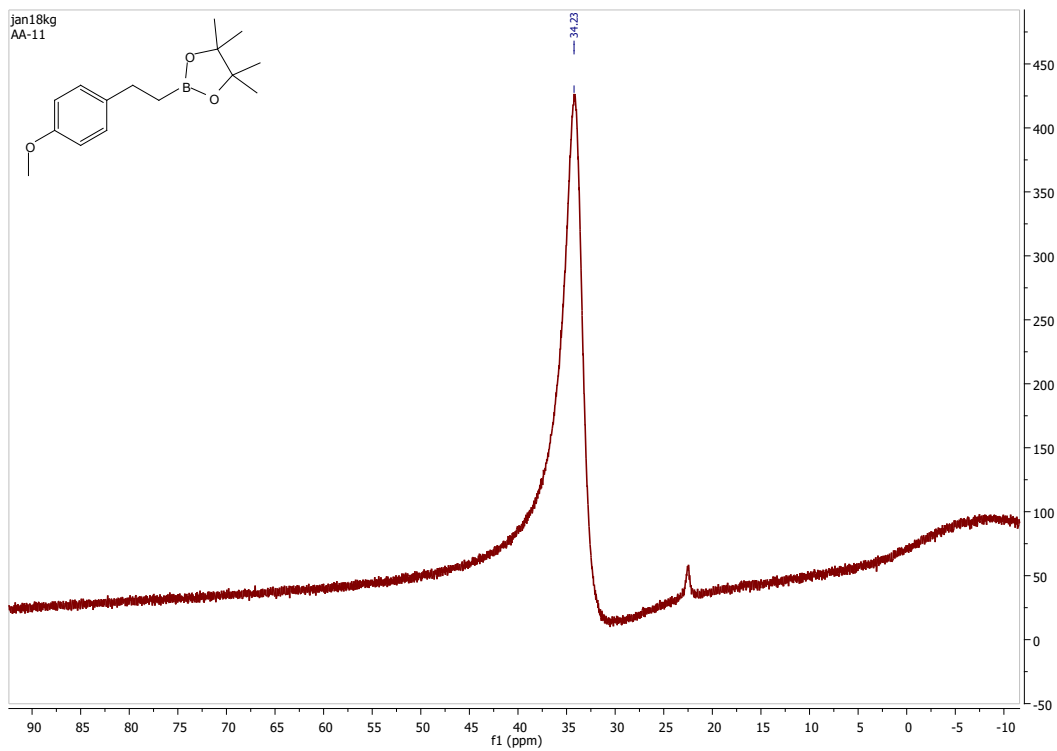
<sup>13</sup>C NMR of **5b** (126 MHz, CDCl<sub>3</sub>)



$^{11}\text{B}$  NMR of **5b** (160 MHz,  $\text{CDCl}_3$ )

## 2-(4-Methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6b**)<sup>5</sup>

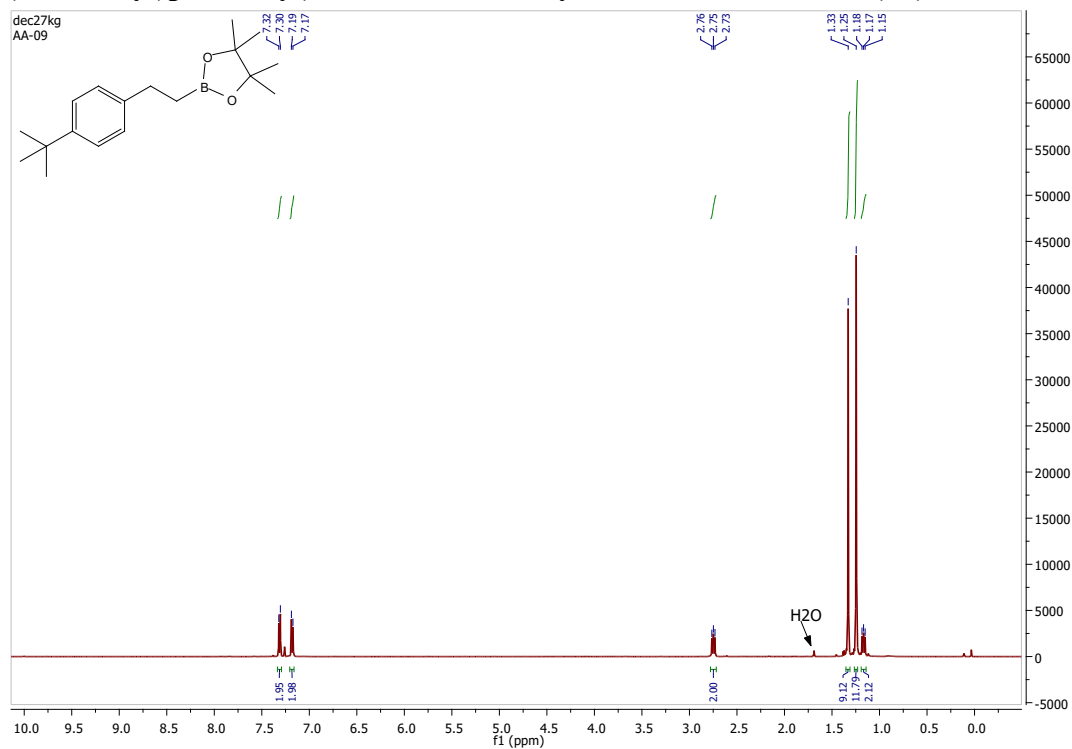




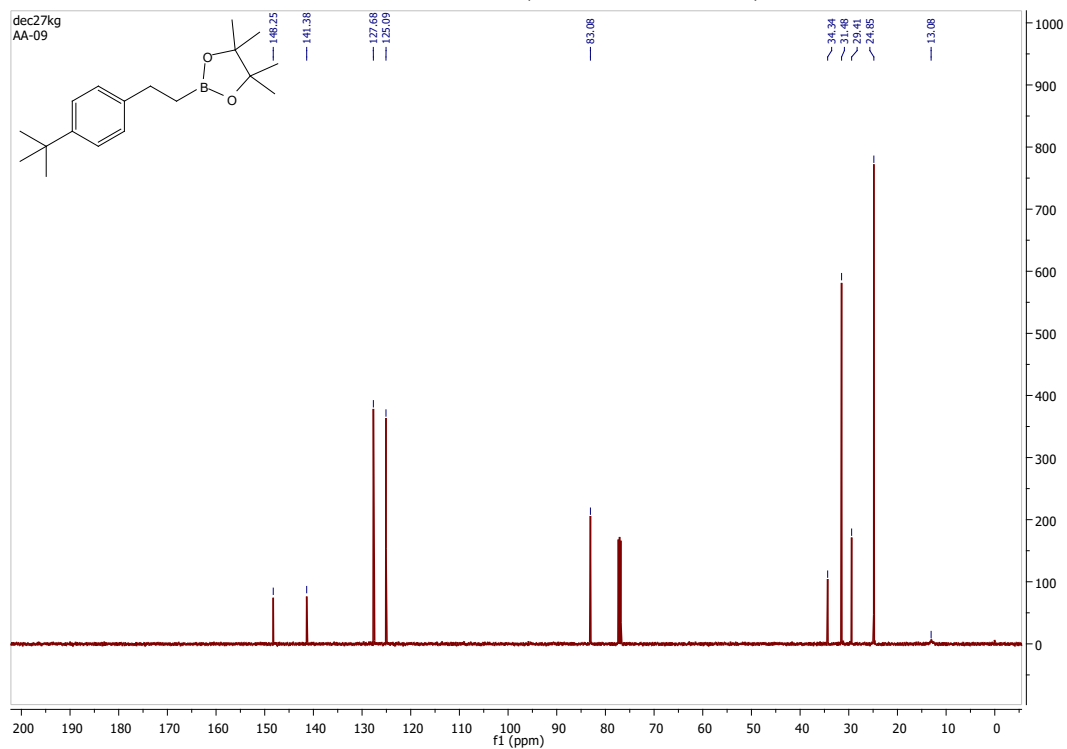
$^{11}\text{B}$  NMR of **6b** (160 MHz,  $\text{CDCl}_3$ )



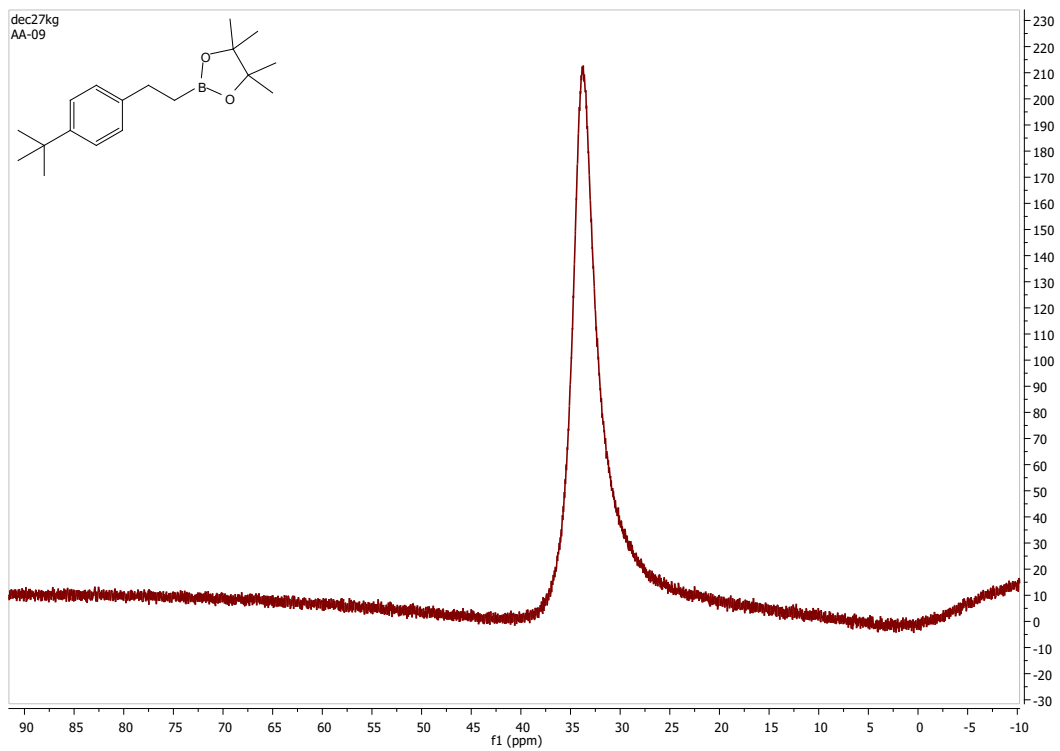
## 2-(4-(Tert-butyl)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**7b**)<sup>4</sup>



<sup>1</sup>H NMR of **7b** (500 MHz, CDCl<sub>3</sub>)

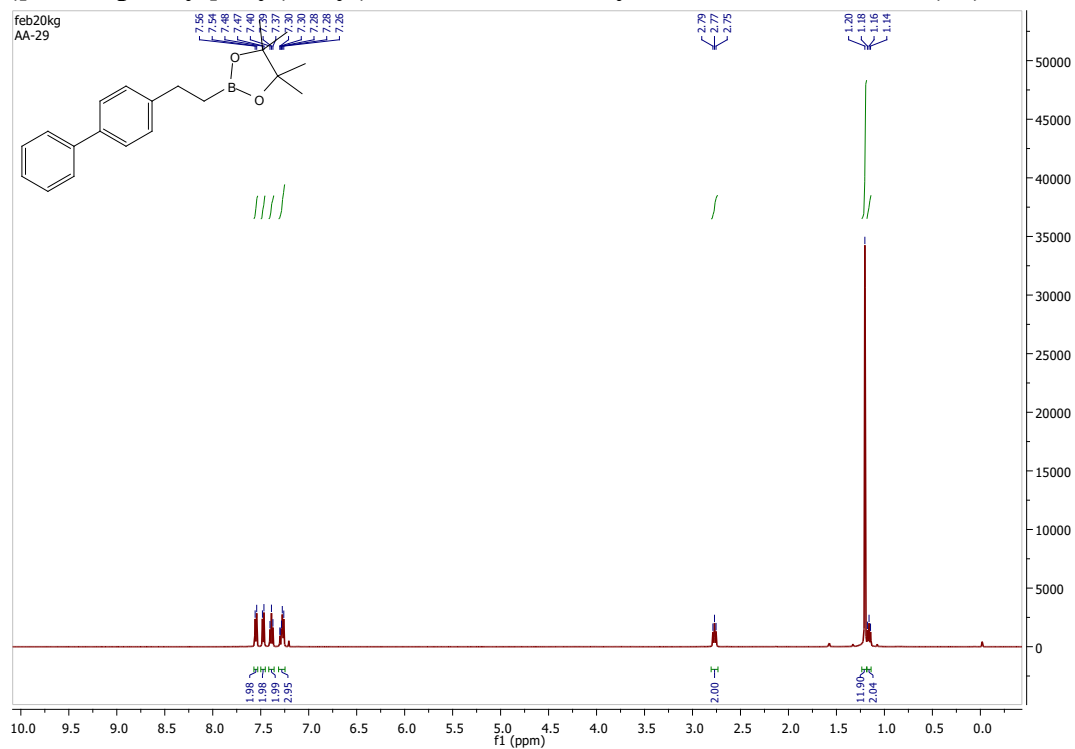


<sup>13</sup>C NMR of **7b** (126 MHz, CDCl<sub>3</sub>)

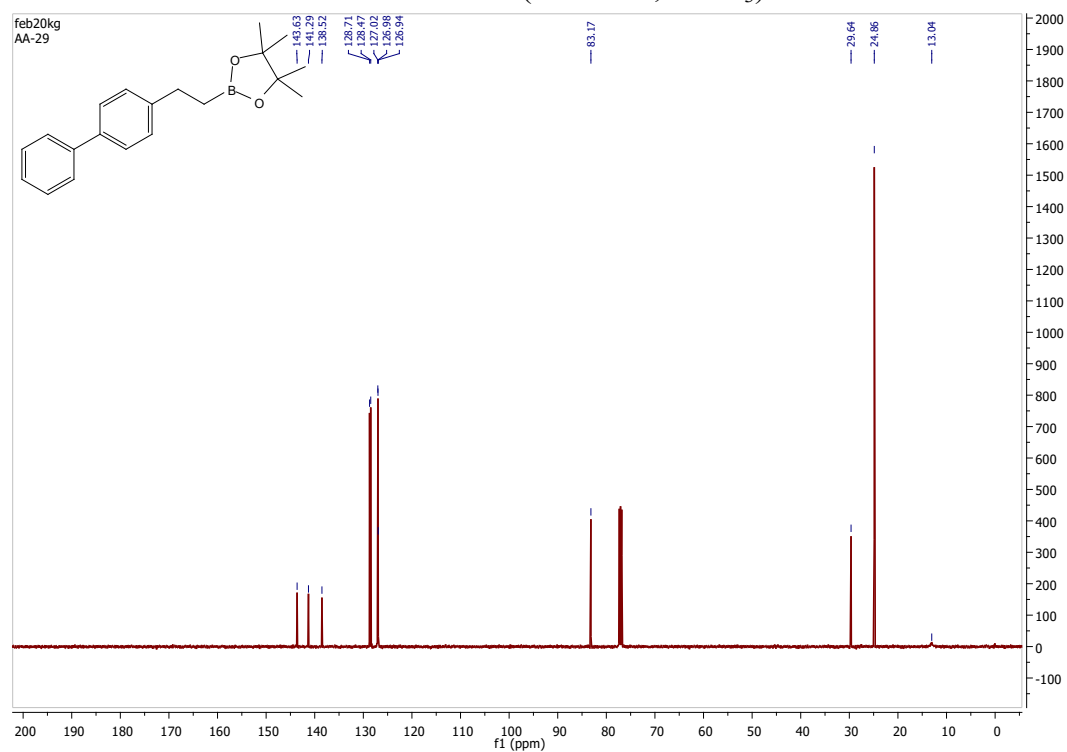


$^{11}\text{B}$  NMR of **7b** (160 MHz,  $\text{CDCl}_3$ )

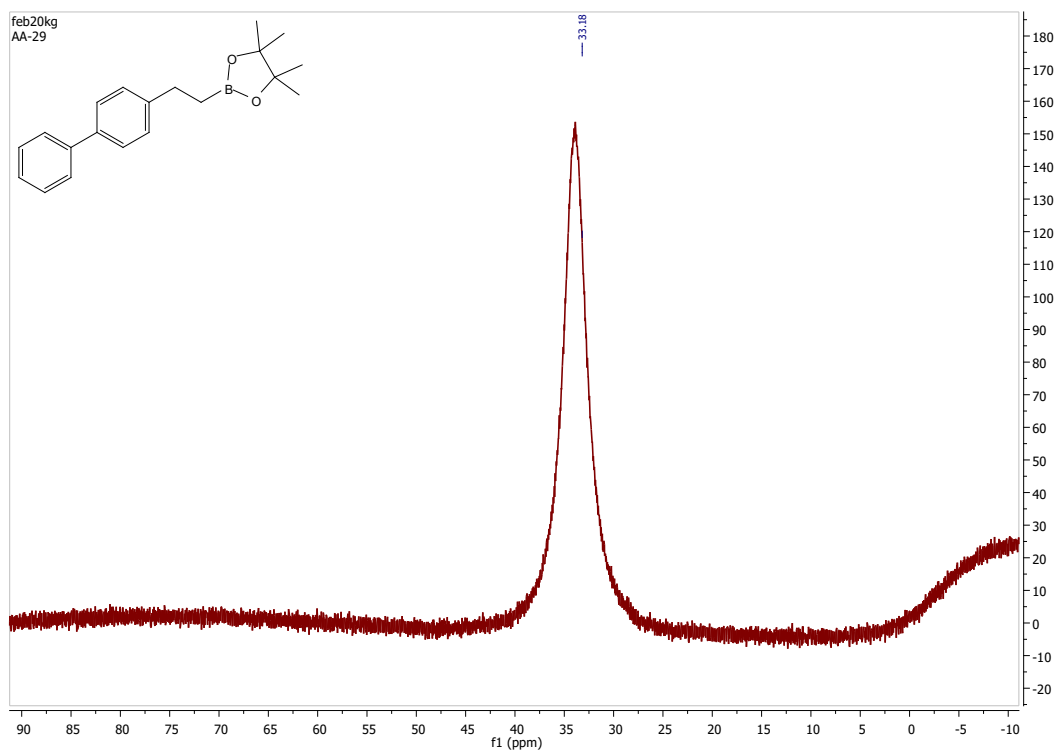
## 2-(2-([1,1'-Biphenyl]-4-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**8b**)<sup>4</sup>



<sup>1</sup>H NMR of **8b** (500 MHz, CDCl<sub>3</sub>)

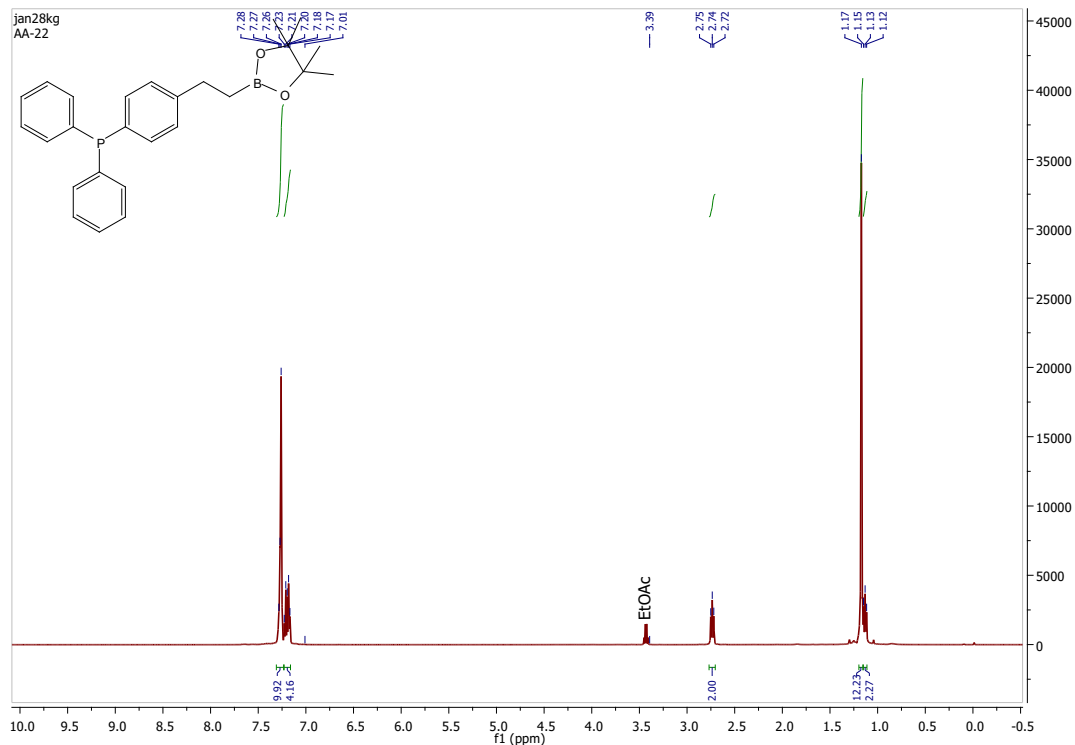


<sup>13</sup>C NMR of **8b** (126 MHz, CDCl<sub>3</sub>)

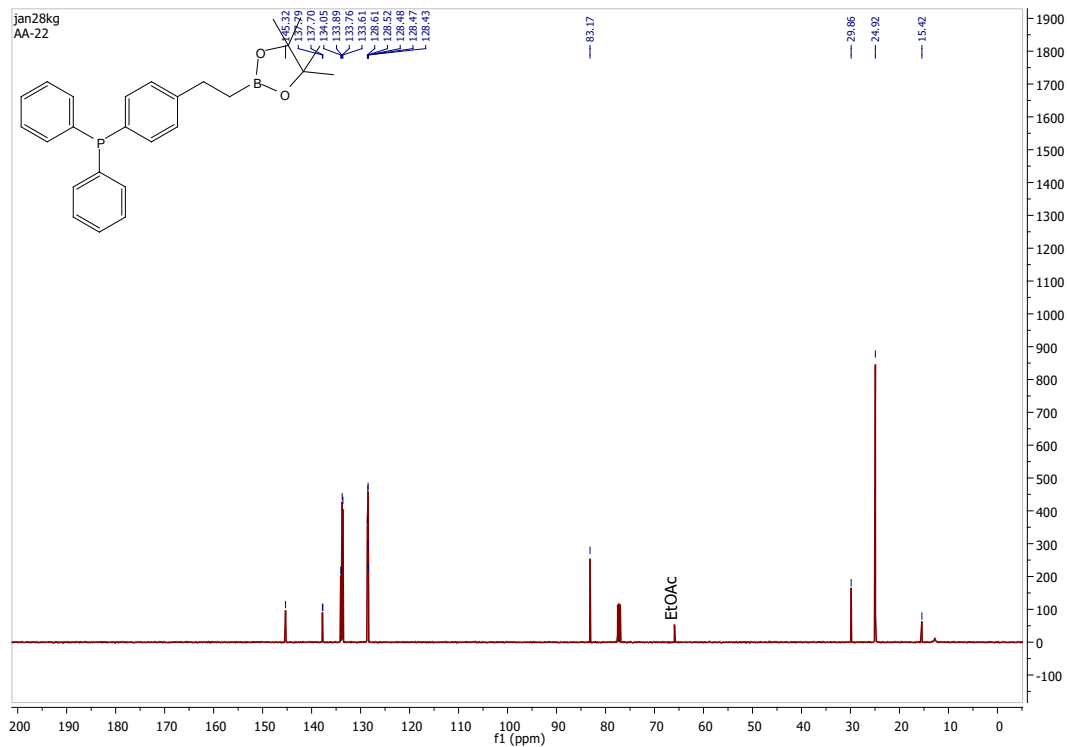


$^{11}\text{B}$  NMR of **8b** (160 MHz,  $\text{CDCl}_3$ )

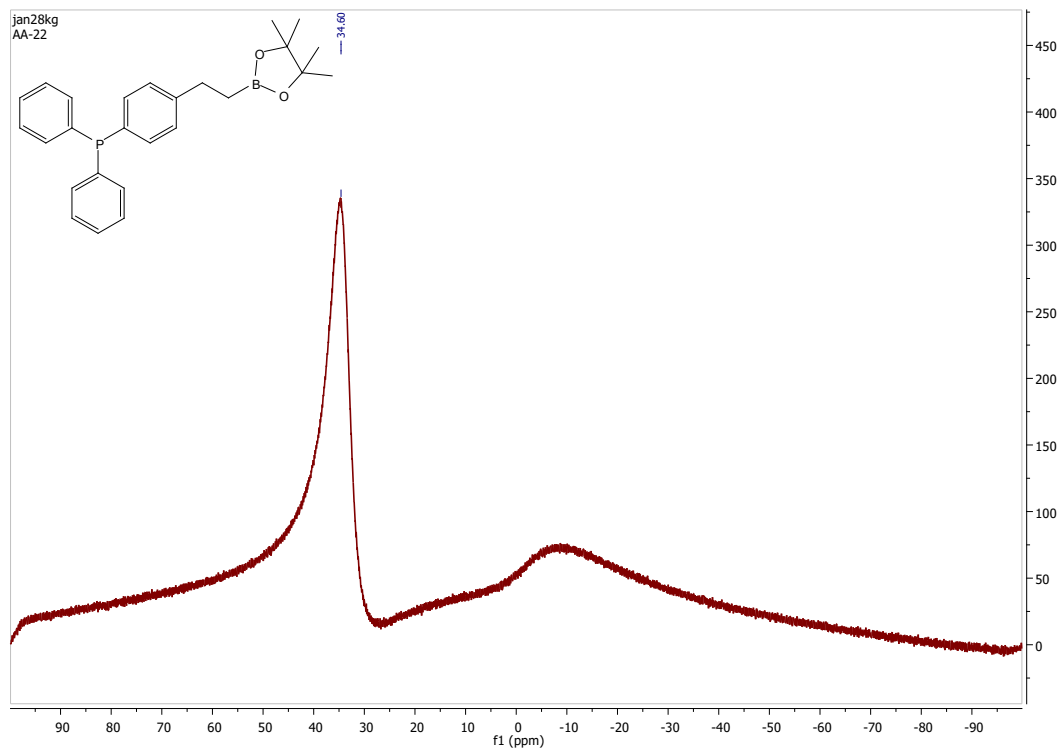
# Diphenyl(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)phosphane (9b)



<sup>1</sup>H NMR of **9b** (500 MHz, CDCl<sub>3</sub>)

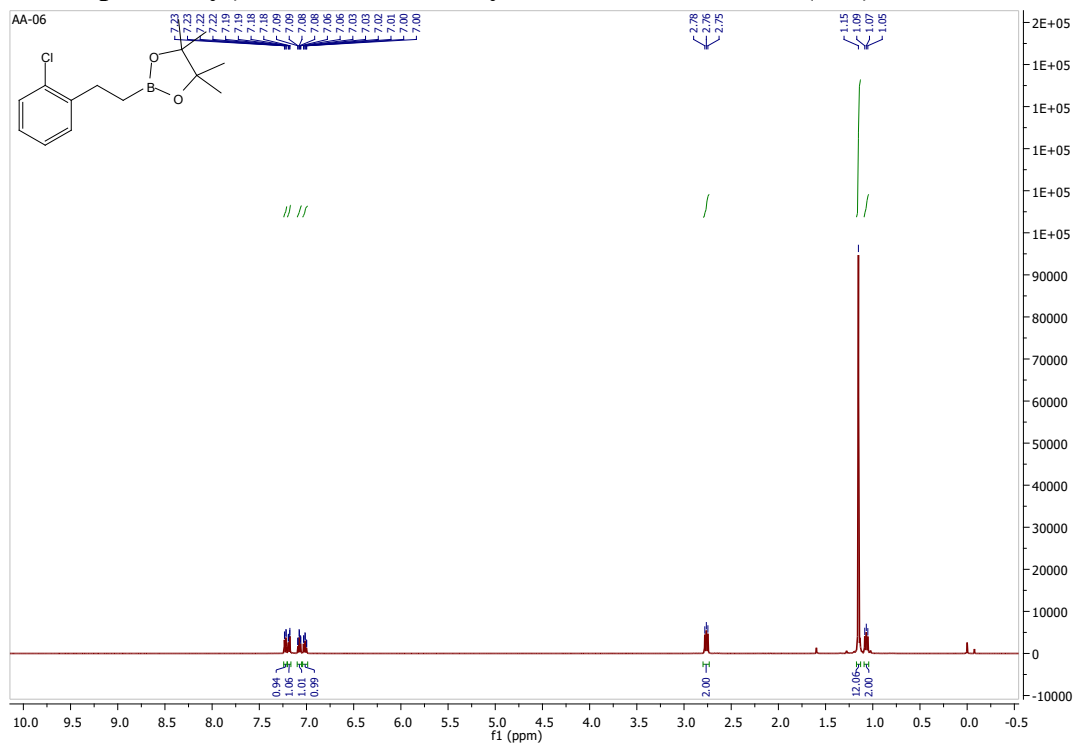


<sup>13</sup>C NMR of **9b** (126 MHz, CDCl<sub>3</sub>)

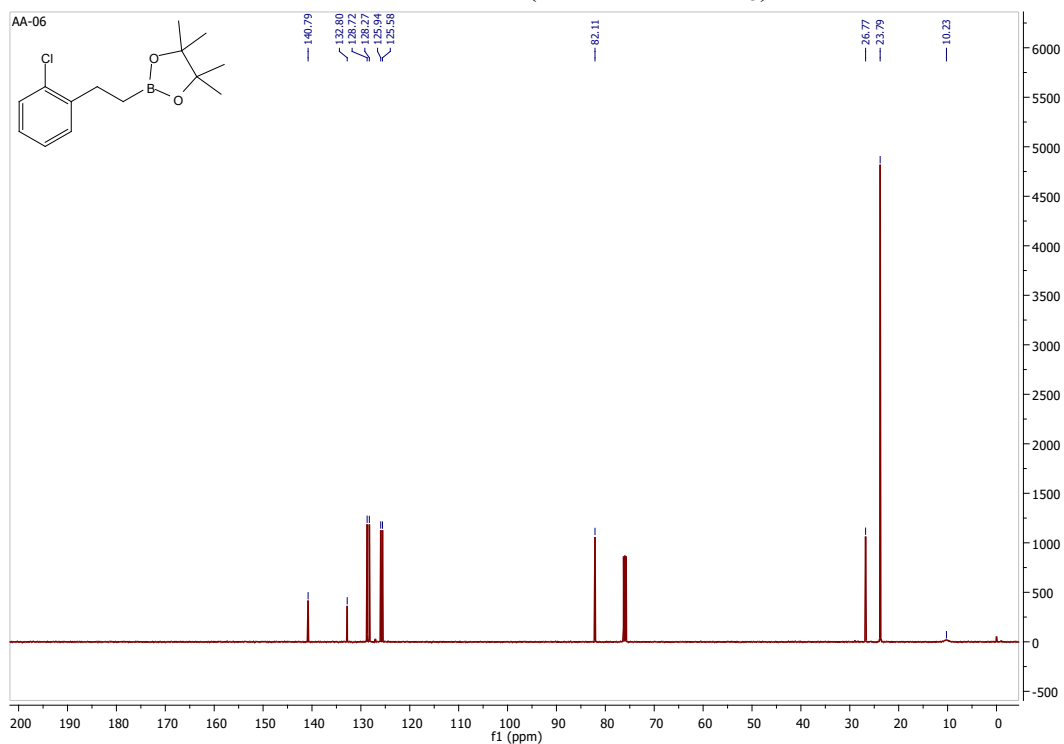


$^{11}\text{B}$  NMR of **9b** (160 MHz,  $\text{CDCl}_3$ )

## 2-(2-Chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11b**)<sup>6</sup>

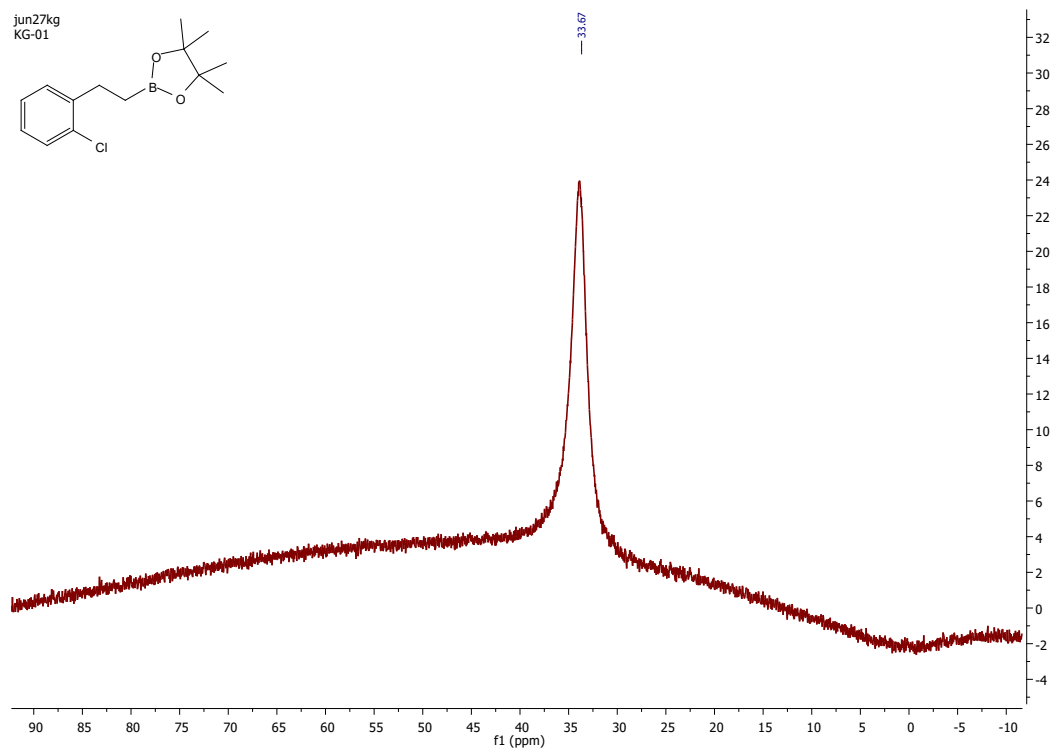
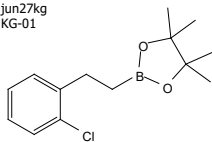


<sup>1</sup>H NMR of **11b** (500 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR of **11b** (126 MHz, CDCl<sub>3</sub>)

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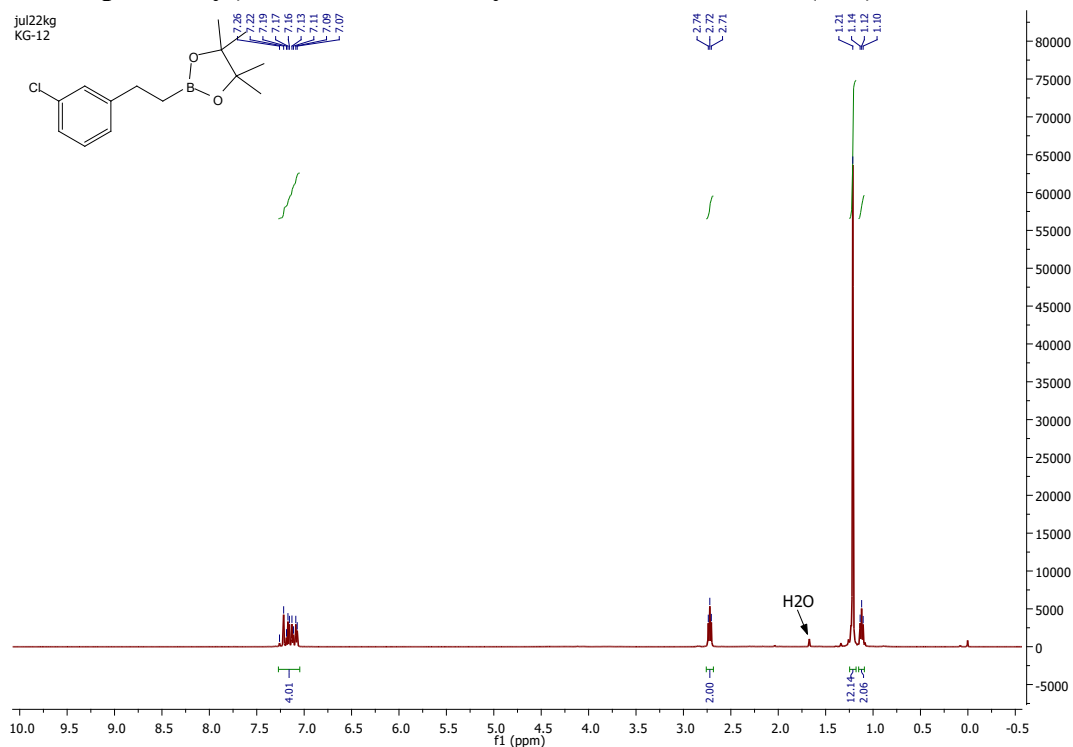


NMR of **11b** (160 MHz, CDCl<sub>3</sub>)

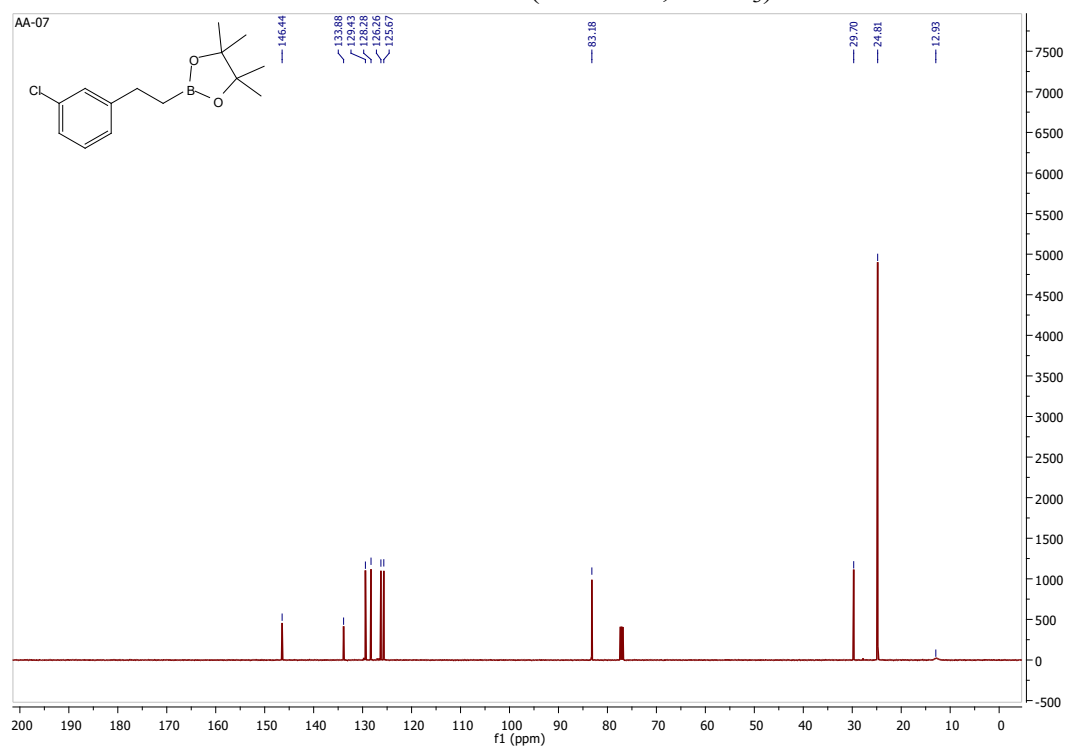
<sup>11</sup>B



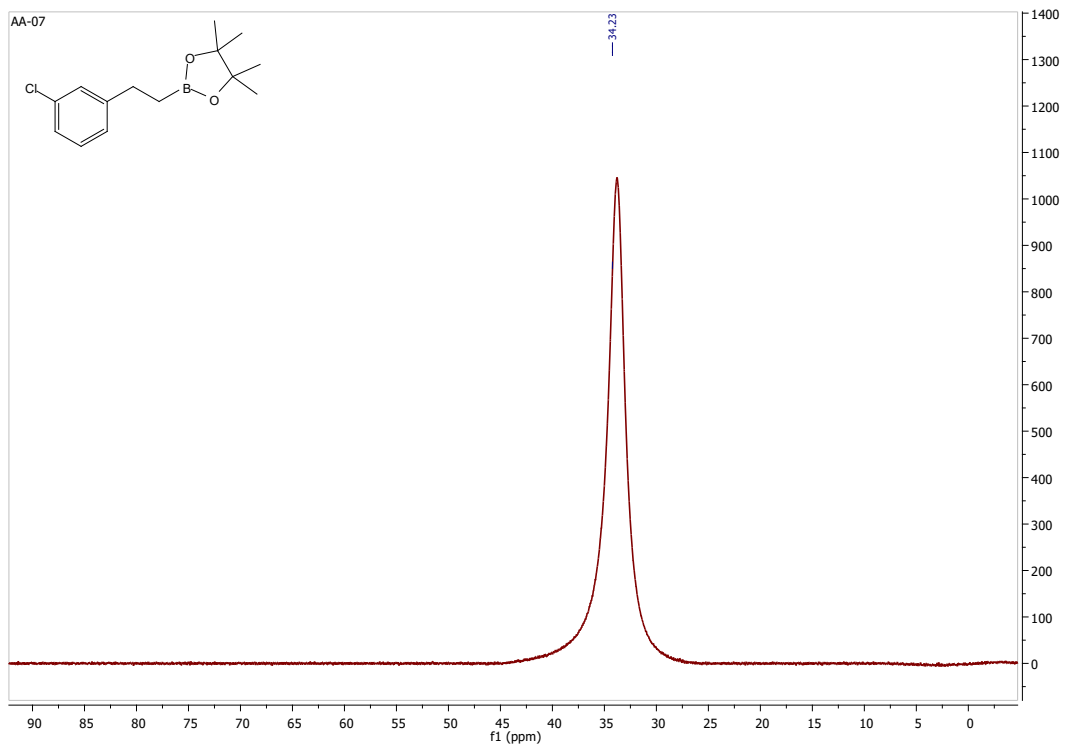
## 2-(3-Chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**12b**)<sup>6</sup>



<sup>1</sup>H NMR of **12b** (500 MHz, CDCl<sub>3</sub>)

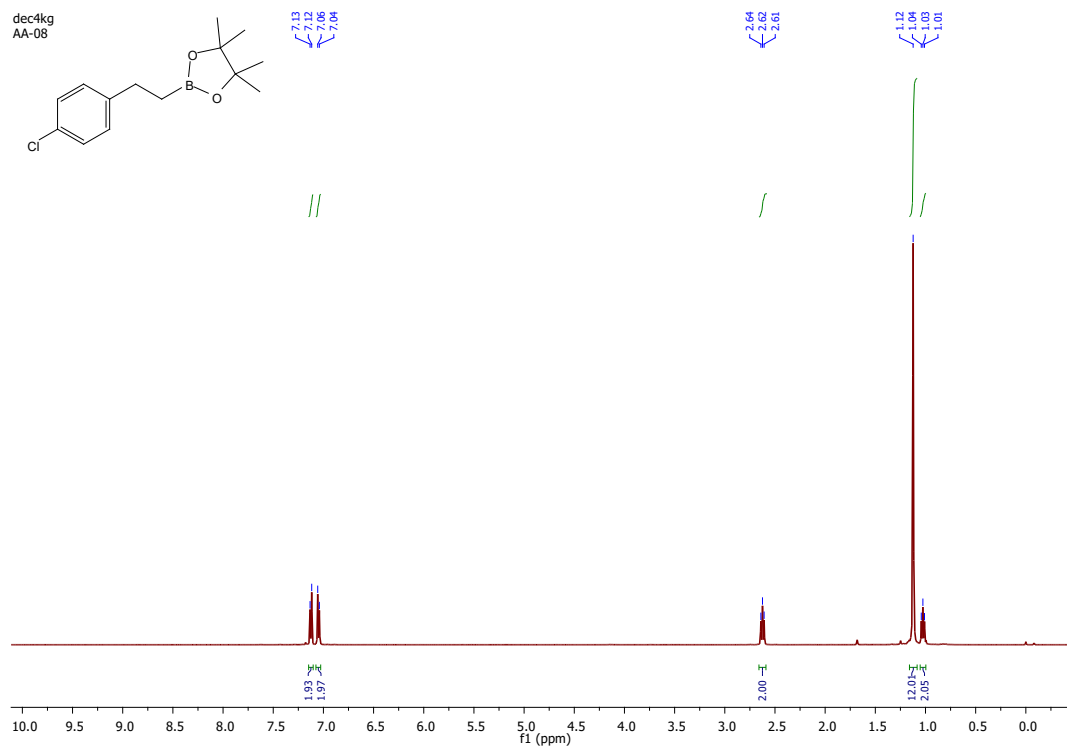


<sup>13</sup>C NMR of **12b** (126 MHz, CDCl<sub>3</sub>)

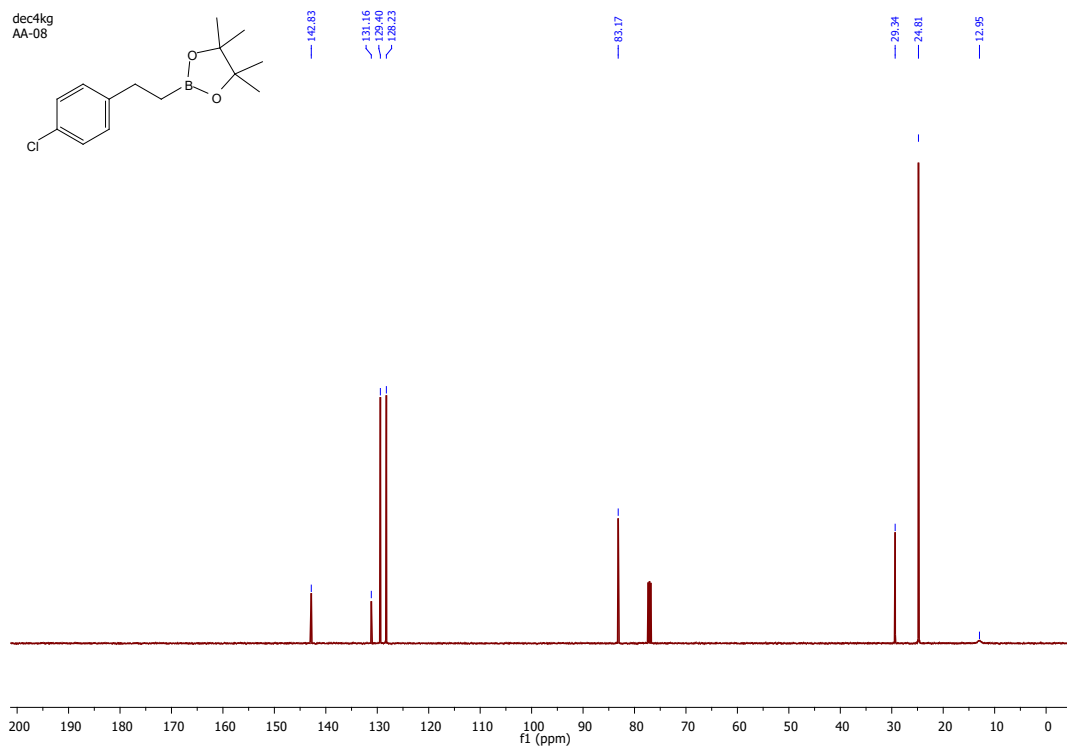


$^{11}\text{B}$  NMR of **12b** (160 MHz,  $\text{CDCl}_3$ )

## 2-(4-Chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**13b**)<sup>4</sup>

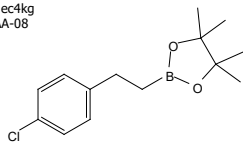


### <sup>1</sup>H NMR of **13b** (500 MHz, CDCl<sub>3</sub>)

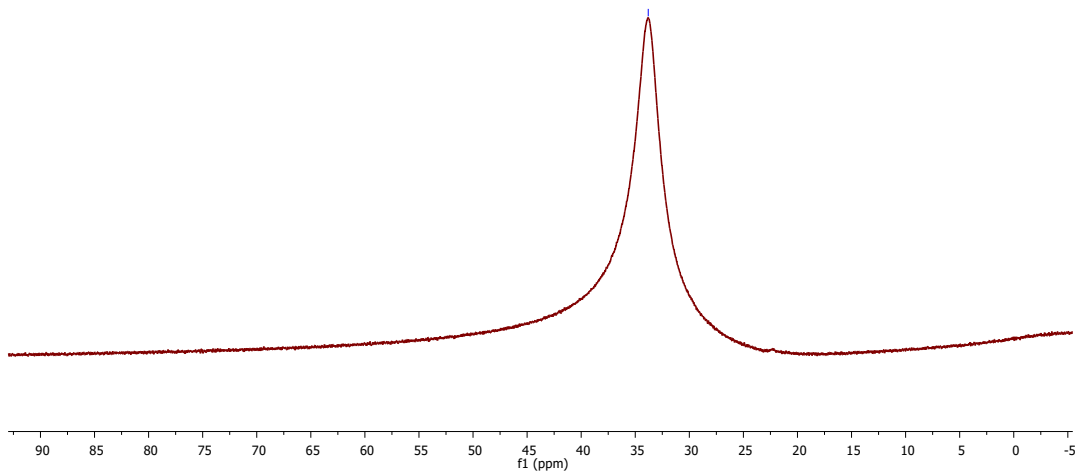


### <sup>13</sup>C NMR of **13b** (126 MHz, CDCl<sub>3</sub>)

dec4kg  
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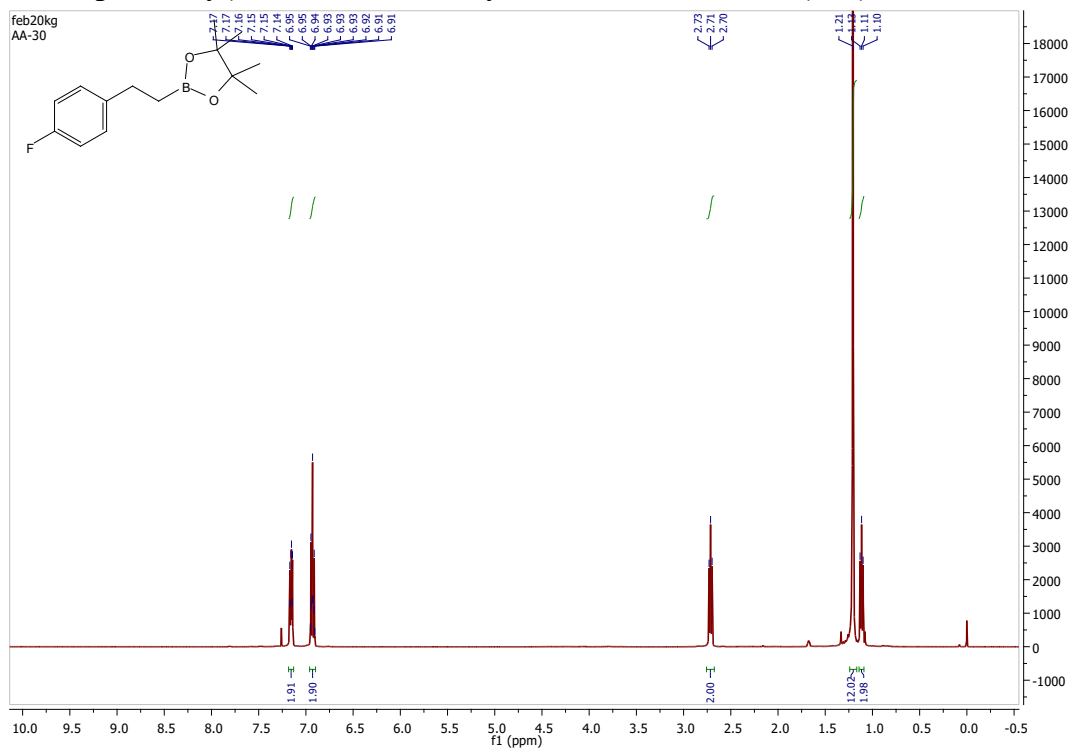


33.80

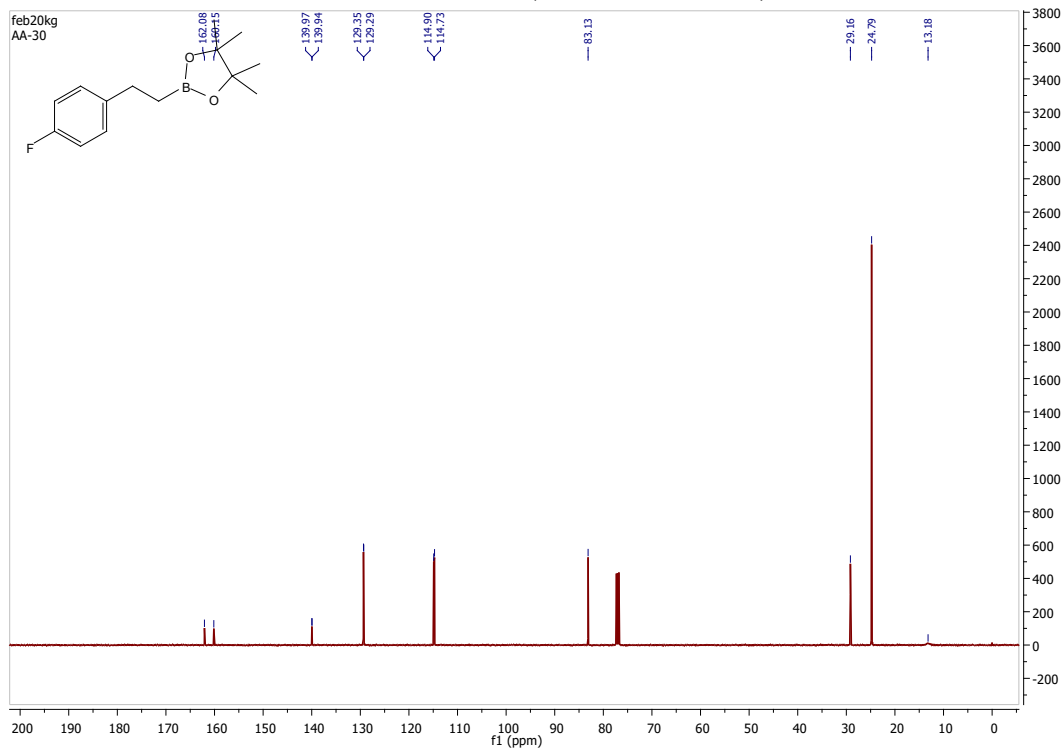


$^{11}\text{B}$  NMR of **13b** (160 MHz,  $\text{CDCl}_3$ )

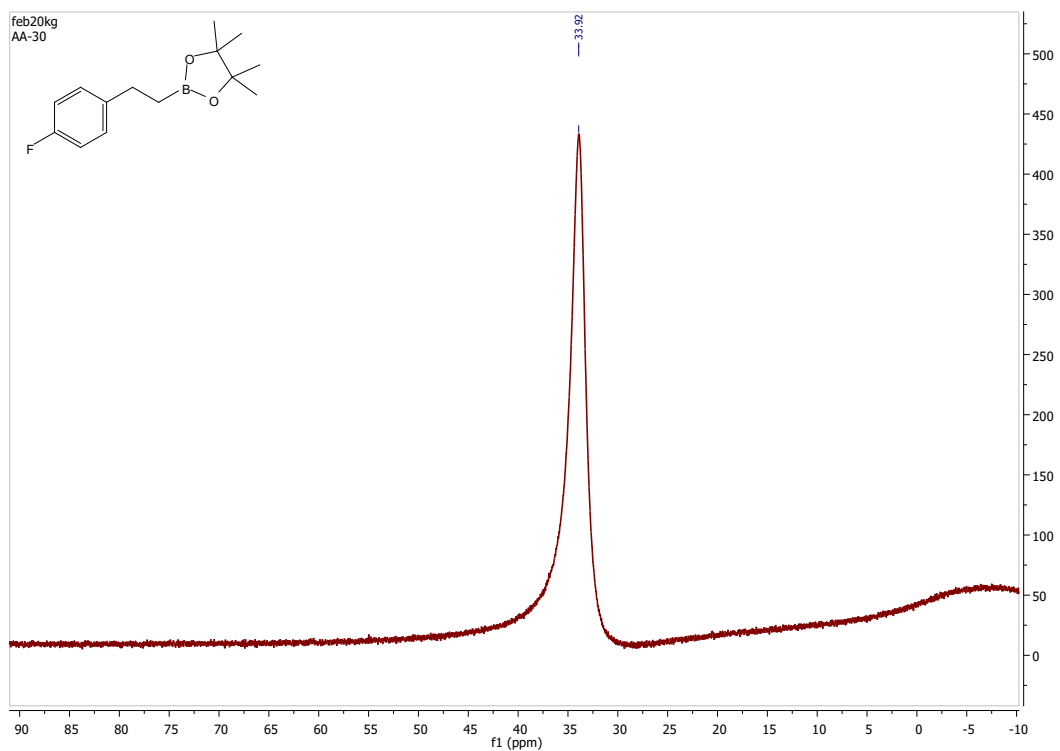
## 2-(4-Fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**14b**)<sup>6</sup>



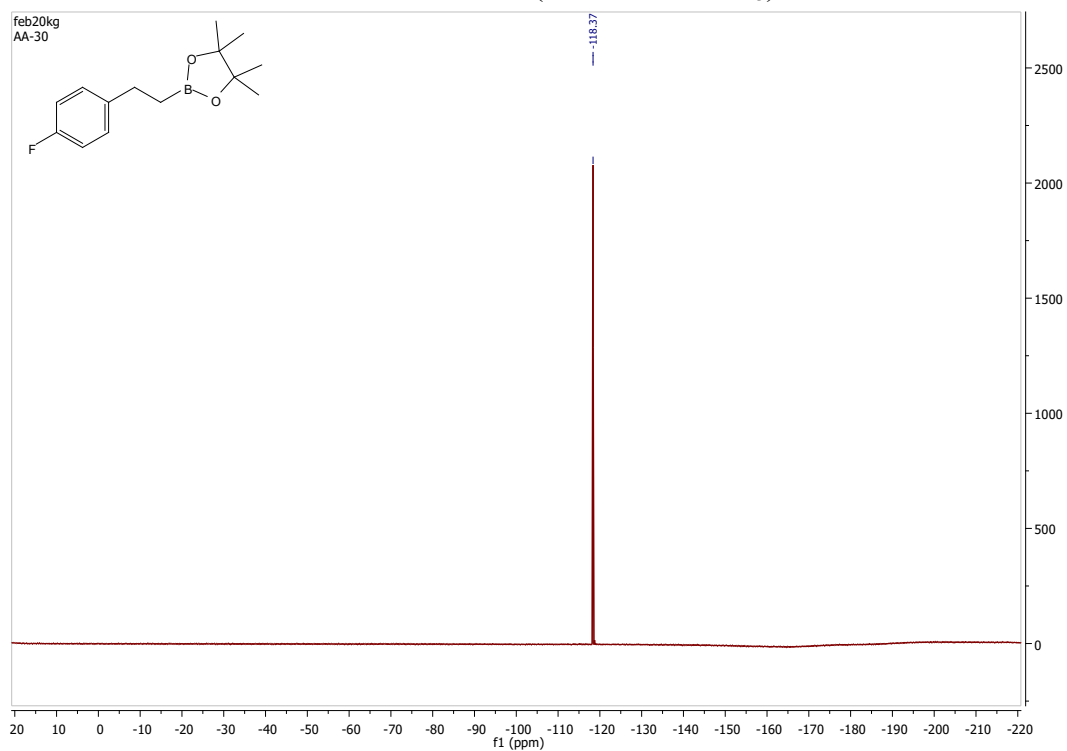
<sup>1</sup>H NMR of **14b** (500 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR of **14b** (126 MHz, CDCl<sub>3</sub>)

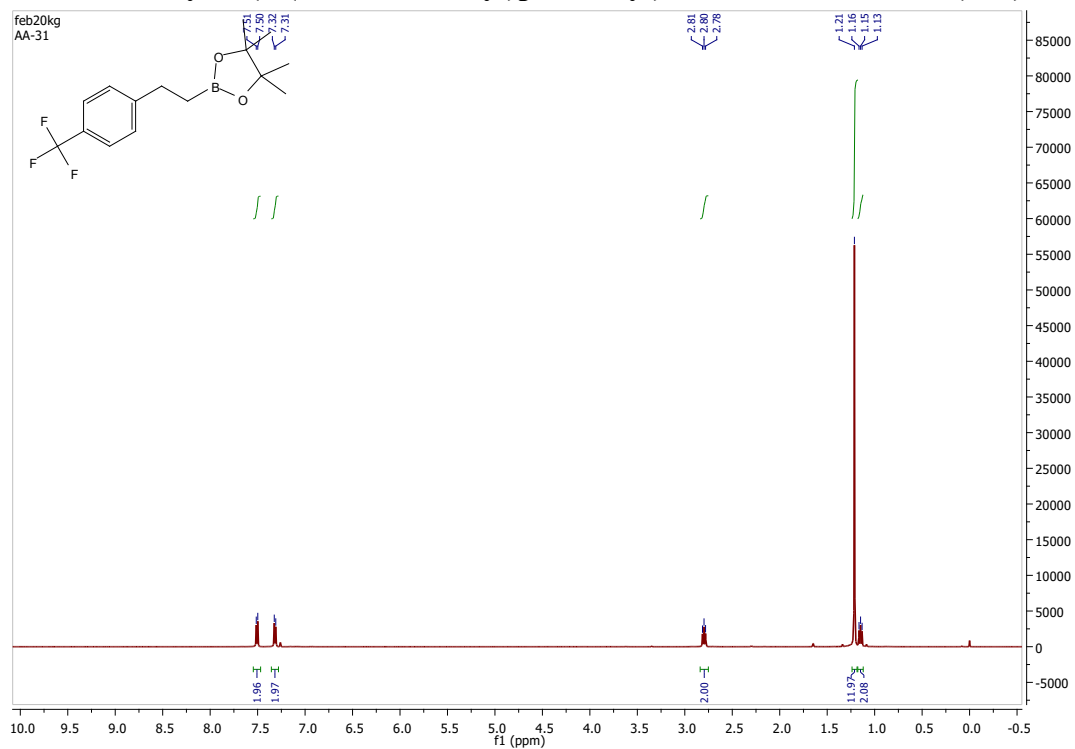


$^{11}\text{B}$  NMR of **14b** (160 MHz,  $\text{CDCl}_3$ )

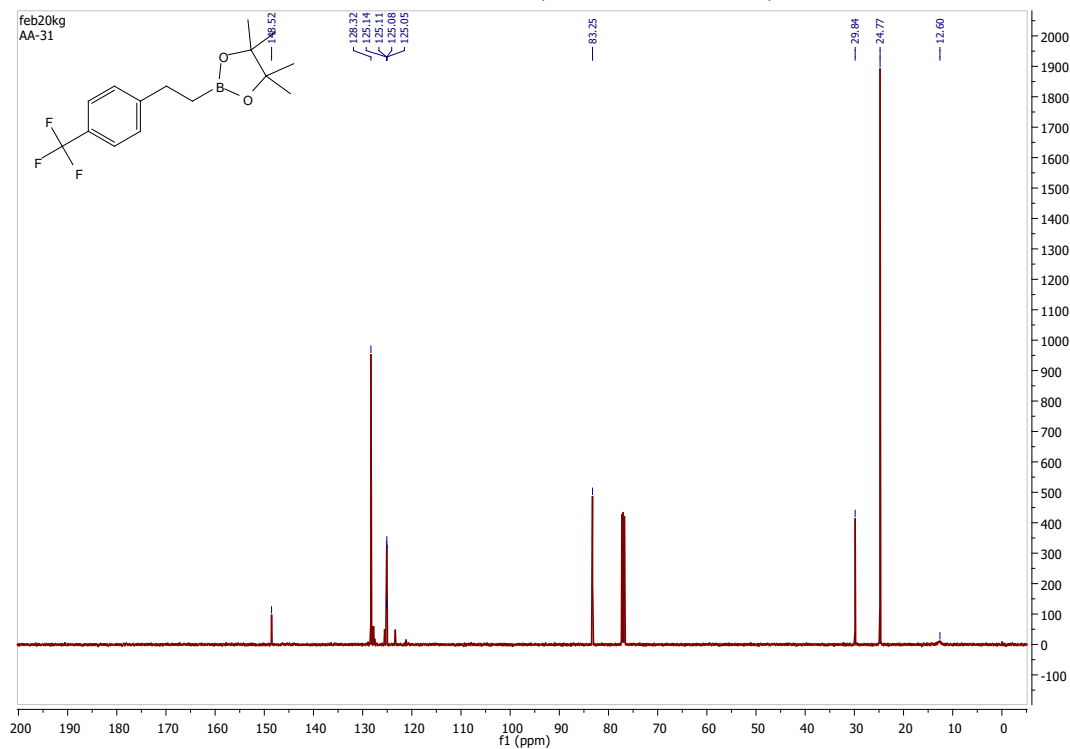


$^{19}\text{F}$  NMR of **14b** (471 MHz,  $\text{CDCl}_3$ )

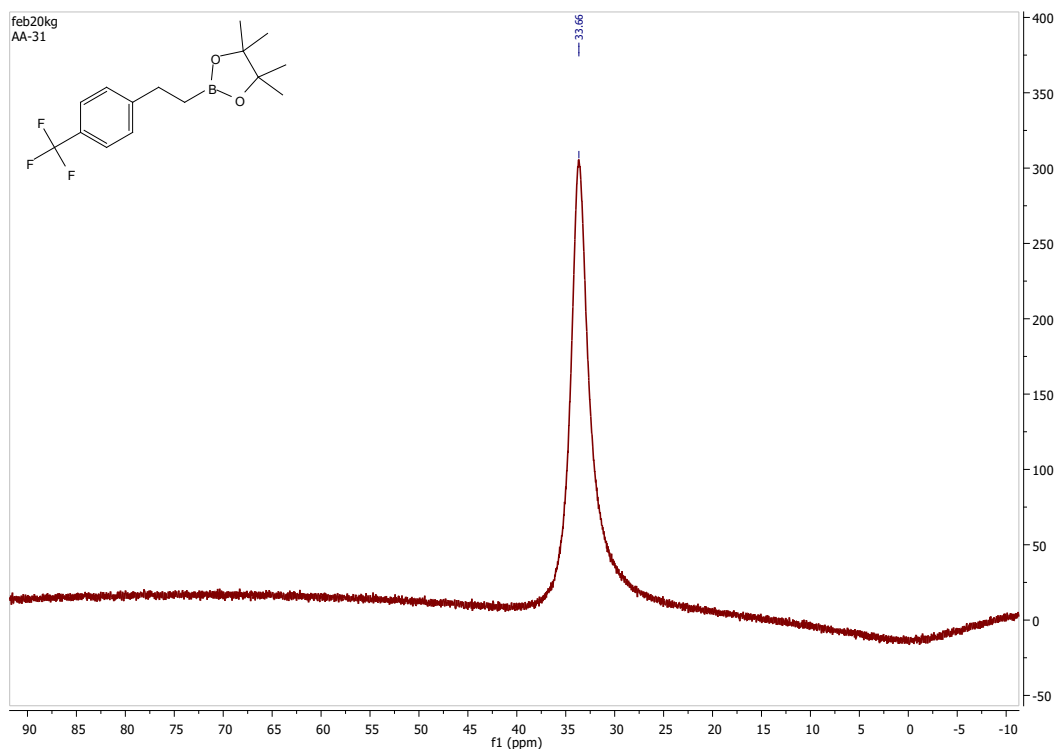
# 4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenethyl)-1,3,2-dioxaborolane (**15b**)<sup>7</sup>



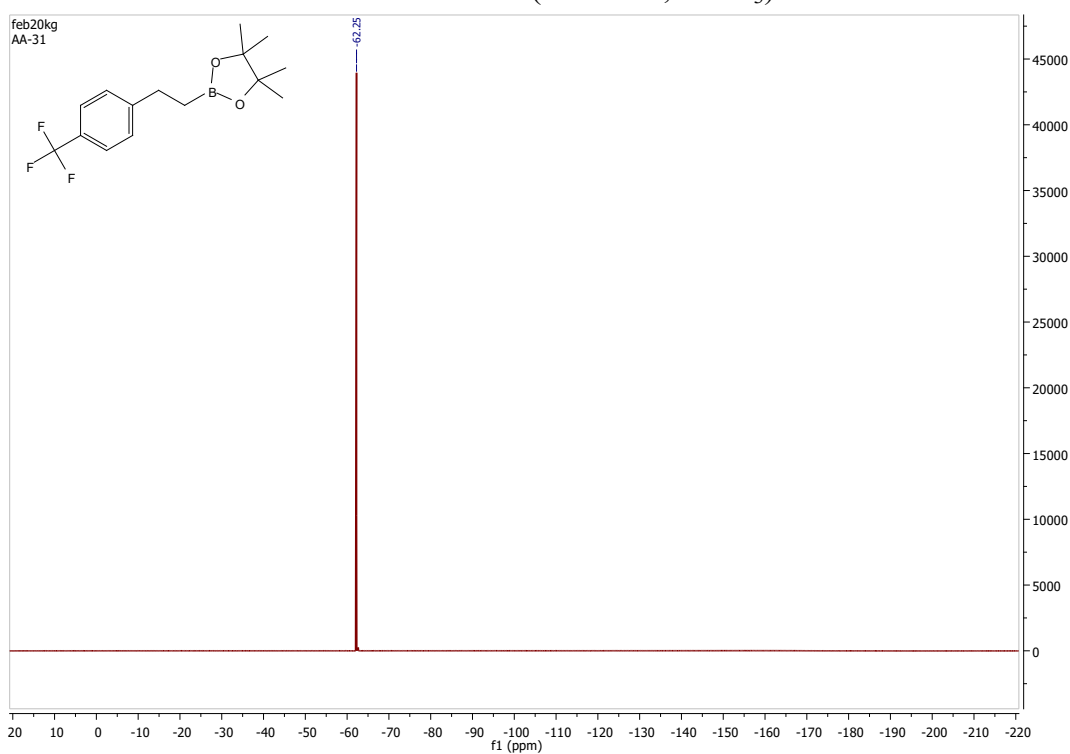
<sup>1</sup>H NMR of **15b** (500 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR of **15b** (126 MHz, CDCl<sub>3</sub>)



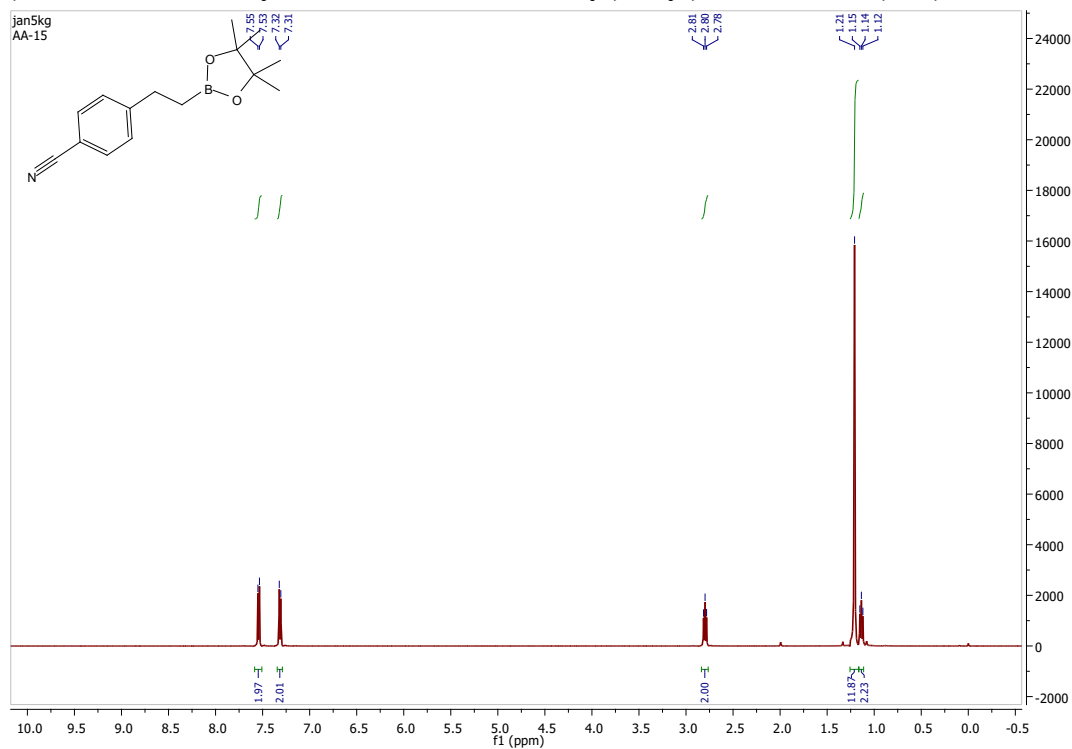
$^{11}\text{B}$  NMR of **15b** (160 MHz,  $\text{CDCl}_3$ )



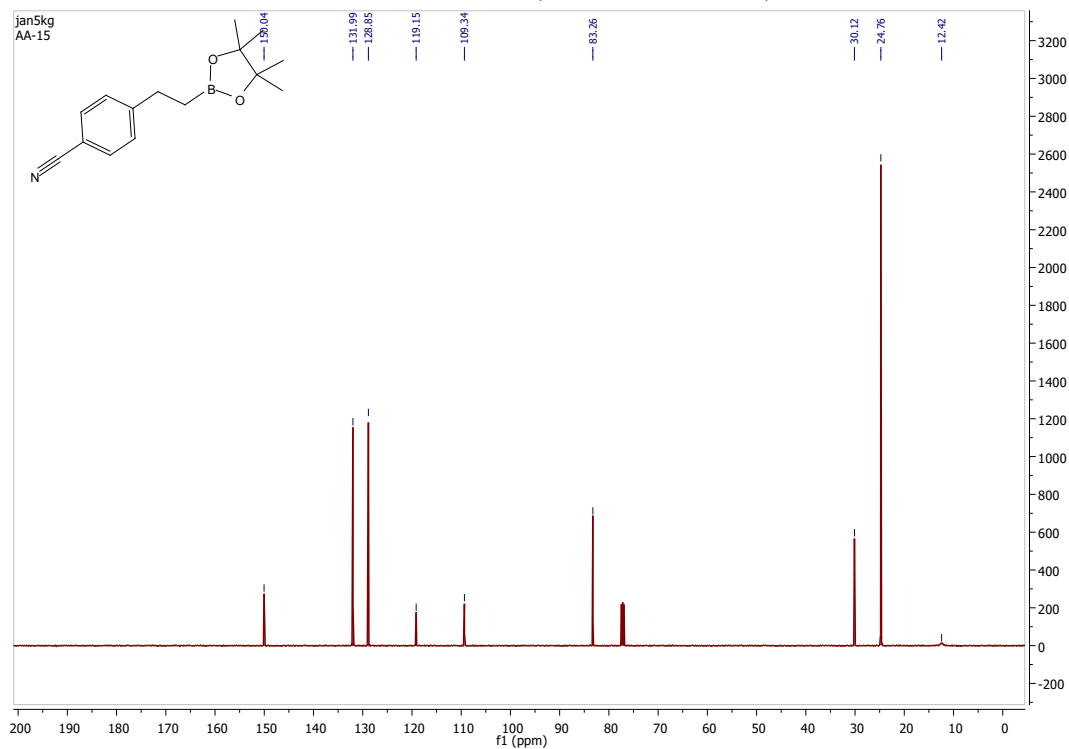
$^{19}\text{F}$  NMR of **15b** (471 MHz,  $\text{CDCl}_3$ )



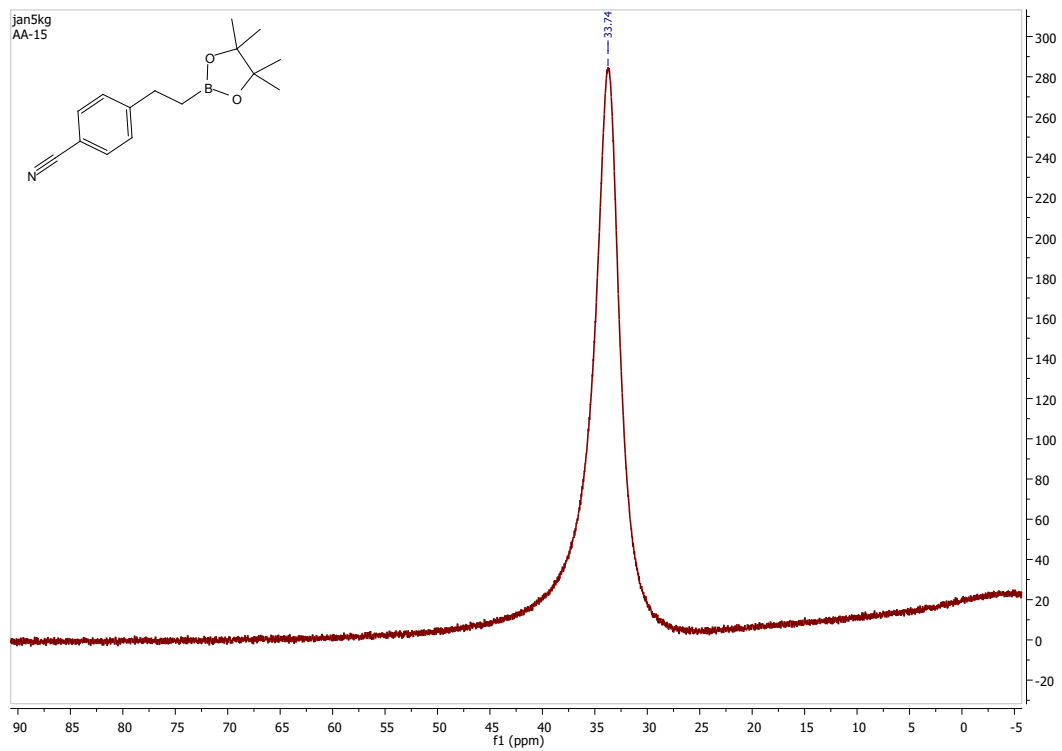
### 4-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (**16b**)<sup>4</sup>



<sup>1</sup>H NMR of **16b** (500 MHz, CDCl<sub>3</sub>)

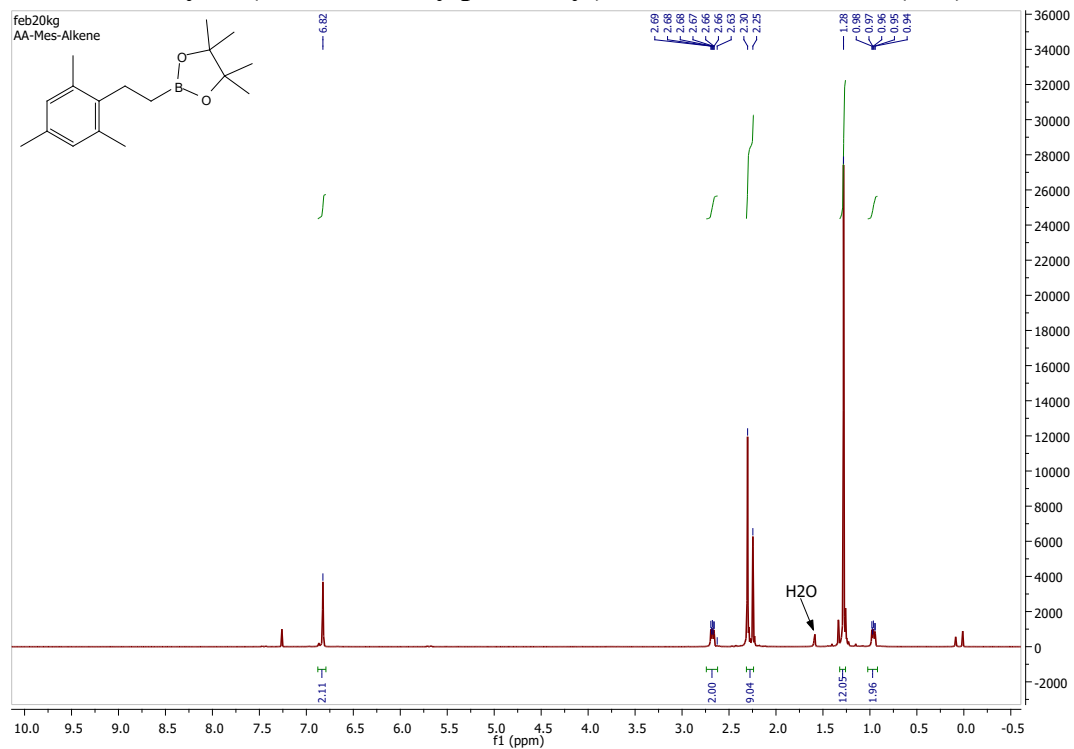


<sup>13</sup>C NMR of **16b** (126 MHz, CDCl<sub>3</sub>)

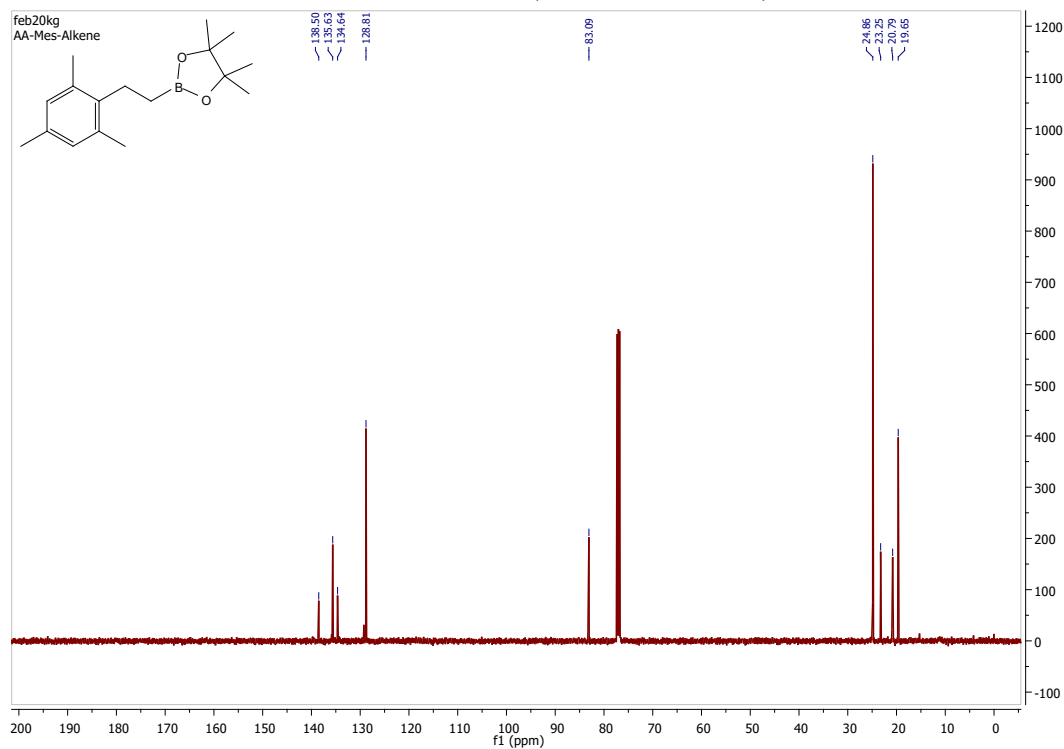


$^{11}\text{B}$  NMR of **16b** (160 MHz,  $\text{CDCl}_3$ )

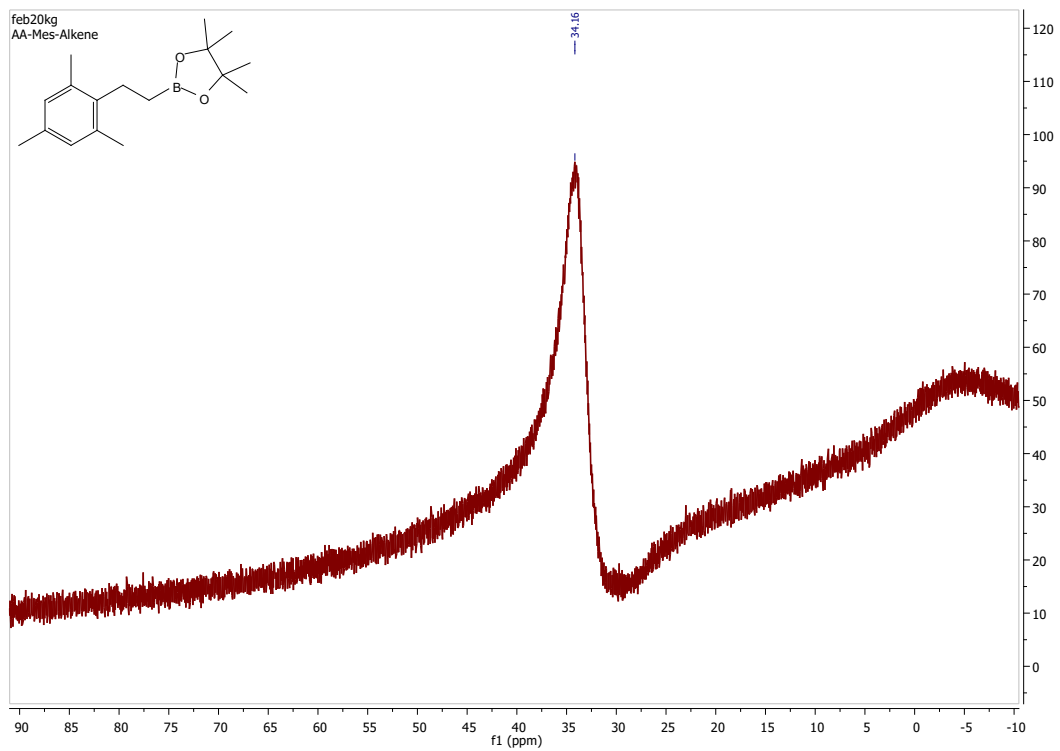
# 4,4,5,5-Tetramethyl-2-(2,4,6-trimethylphenethyl)-1,3,2-dioxaborolane (**17b**)<sup>4</sup>



<sup>1</sup>H NMR of **17b** (500 MHz, CDCl<sub>3</sub>)

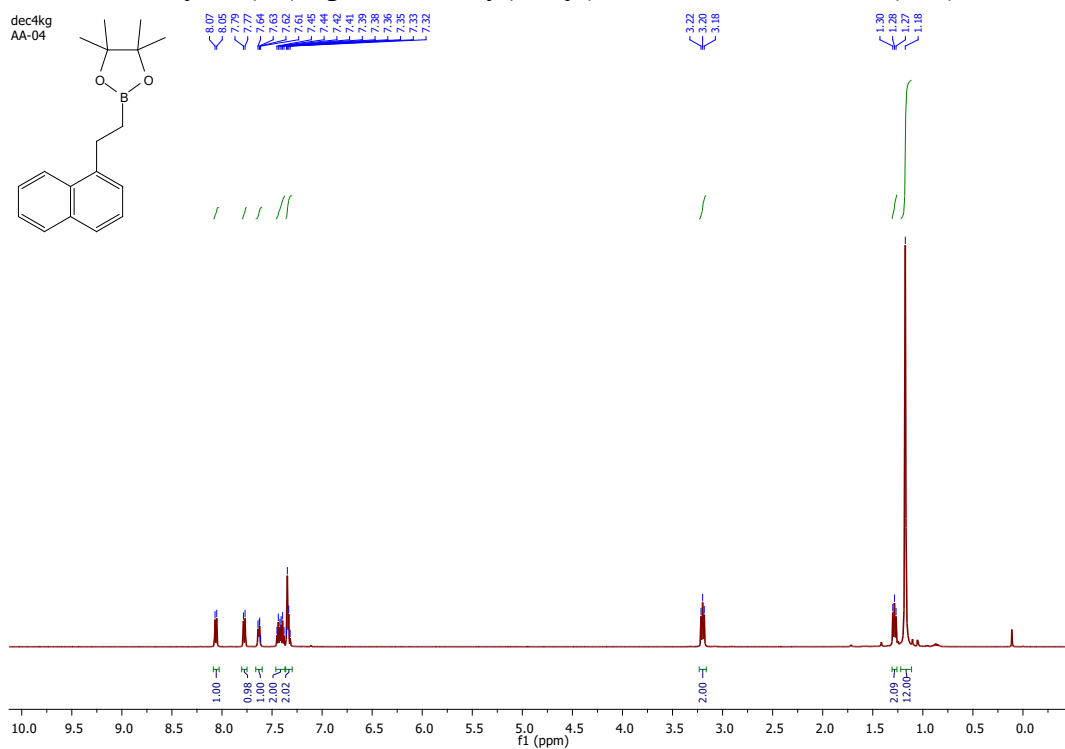


<sup>13</sup>C NMR of **17b** (126 MHz, CDCl<sub>3</sub>)

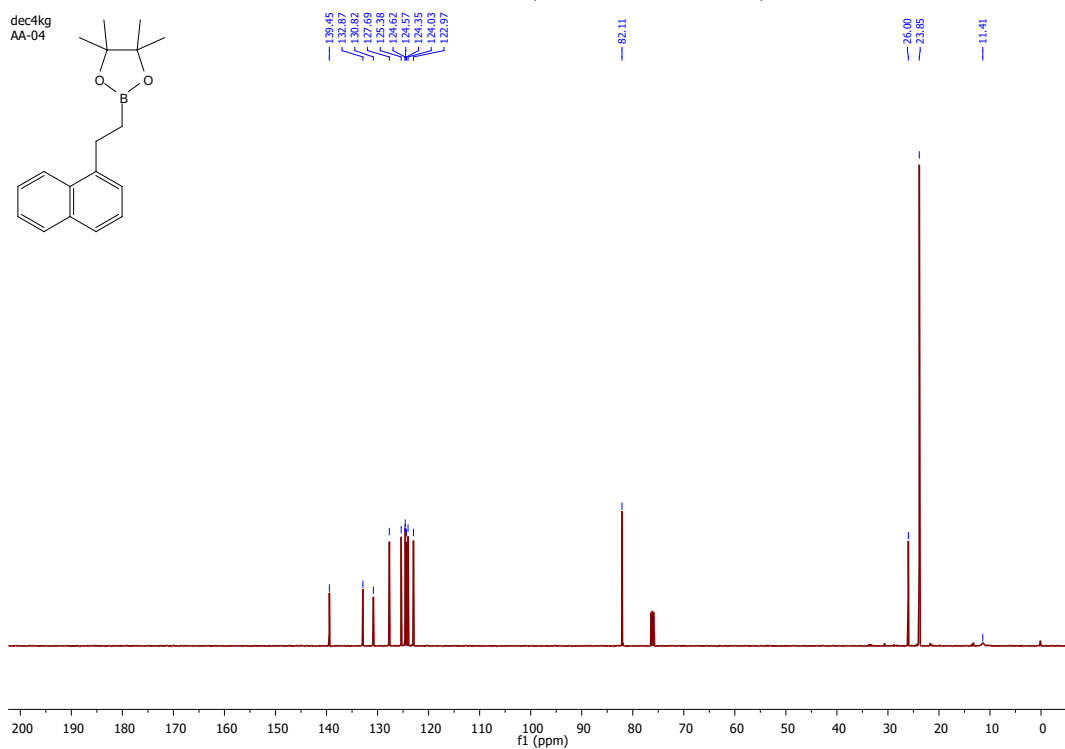


$^{11}\text{B}$  NMR of **17b** (160 MHz,  $\text{CDCl}_3$ )

# 4,4,5,5-Tetramethyl-2-(2-(naphthalen-1-yl)ethyl)-1,3,2-dioxaborolane (**18b**)<sup>8</sup>

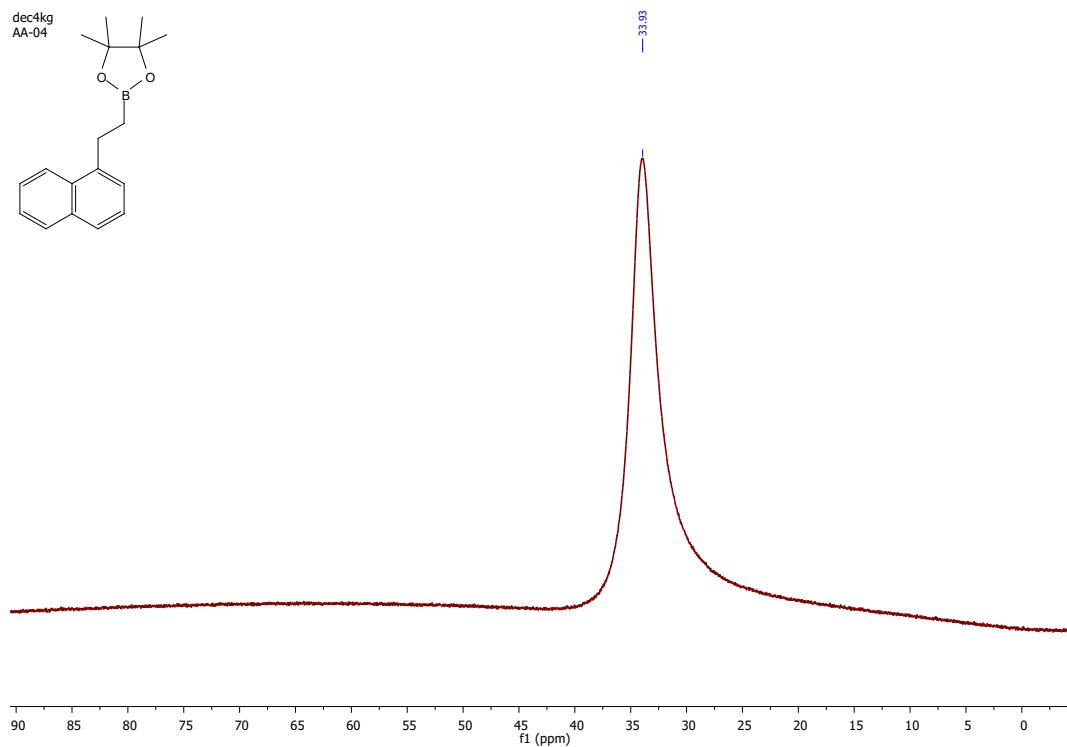
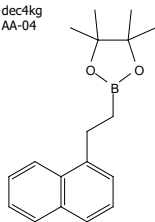


<sup>1</sup>H NMR of **18b** (500 MHz, CDCl<sub>3</sub>)



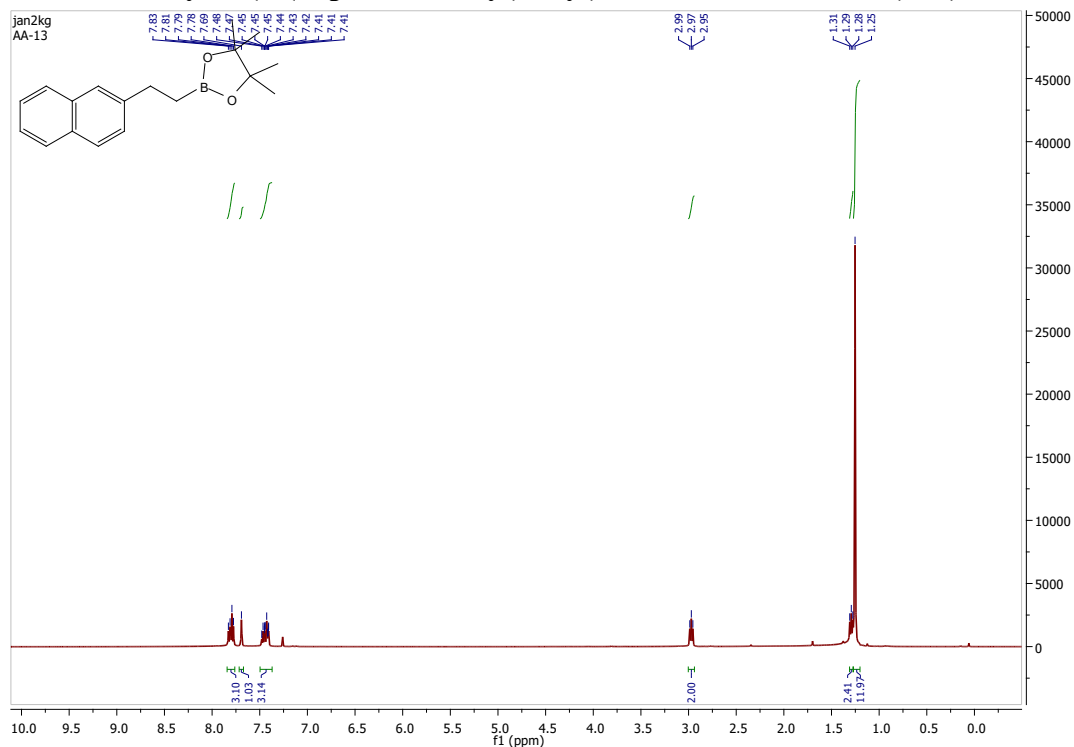
<sup>13</sup>C NMR of **18b** (126 MHz, CDCl<sub>3</sub>)

dec4kg  
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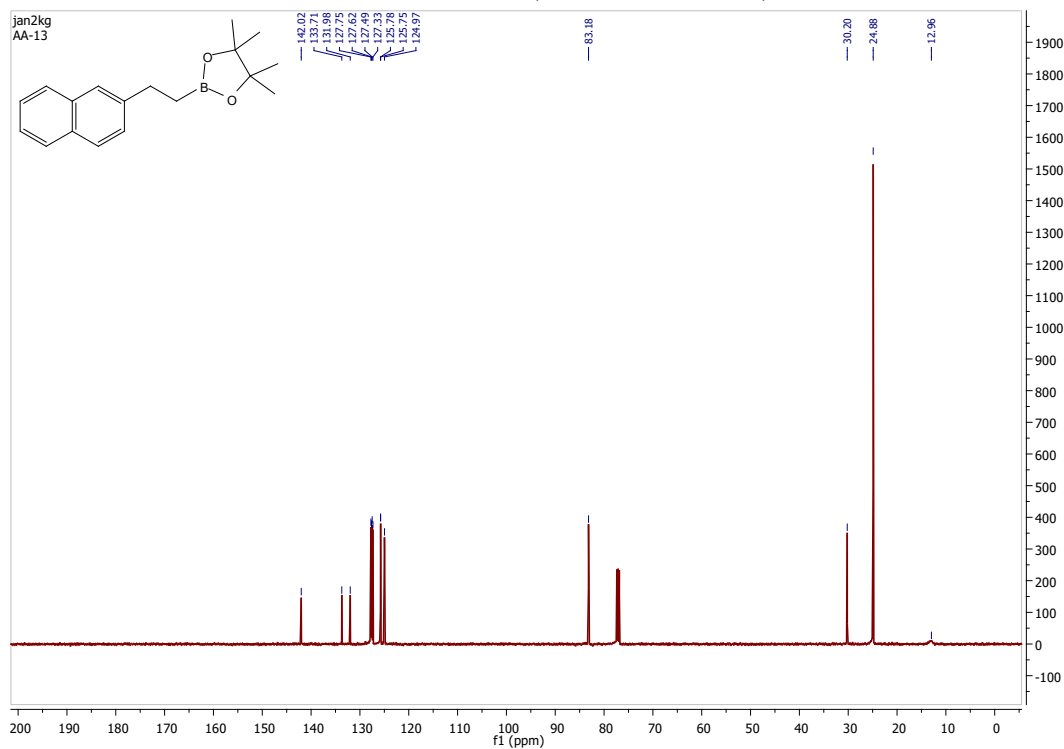


$^{11}\text{B}$  NMR of **18b** (160 MHz,  $\text{CDCl}_3$ )

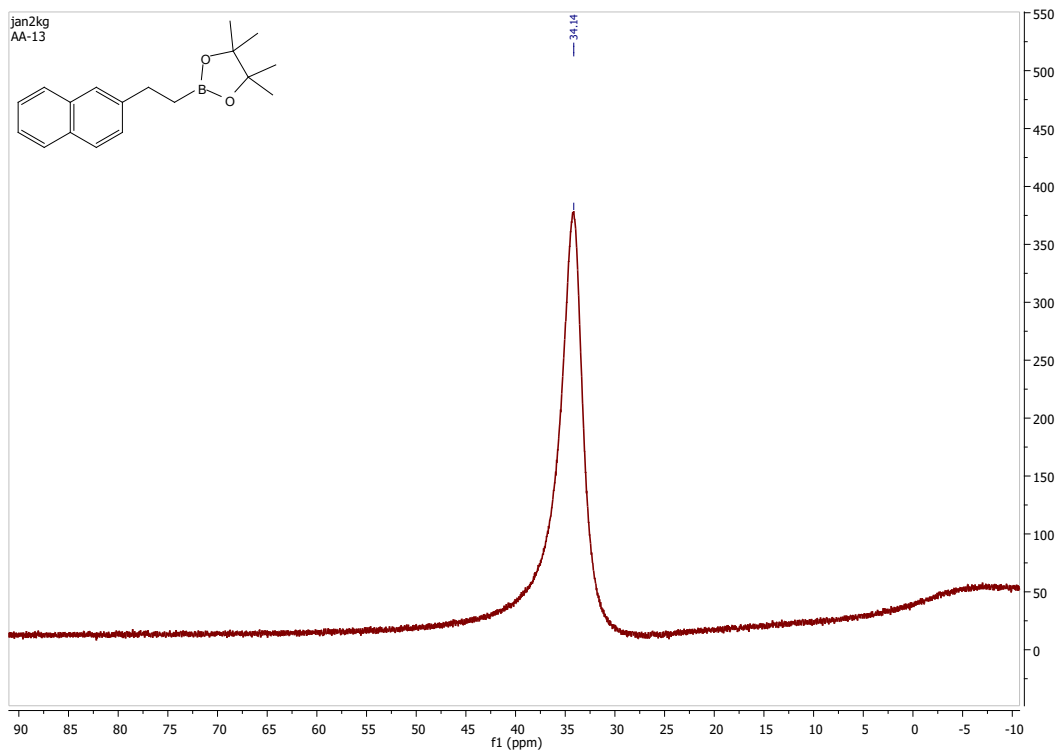
# 4,4,5,5-Tetramethyl-2-(2-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane (**19b**)<sup>5</sup>



<sup>1</sup>H NMR of **19b** (500 MHz, CDCl<sub>3</sub>)



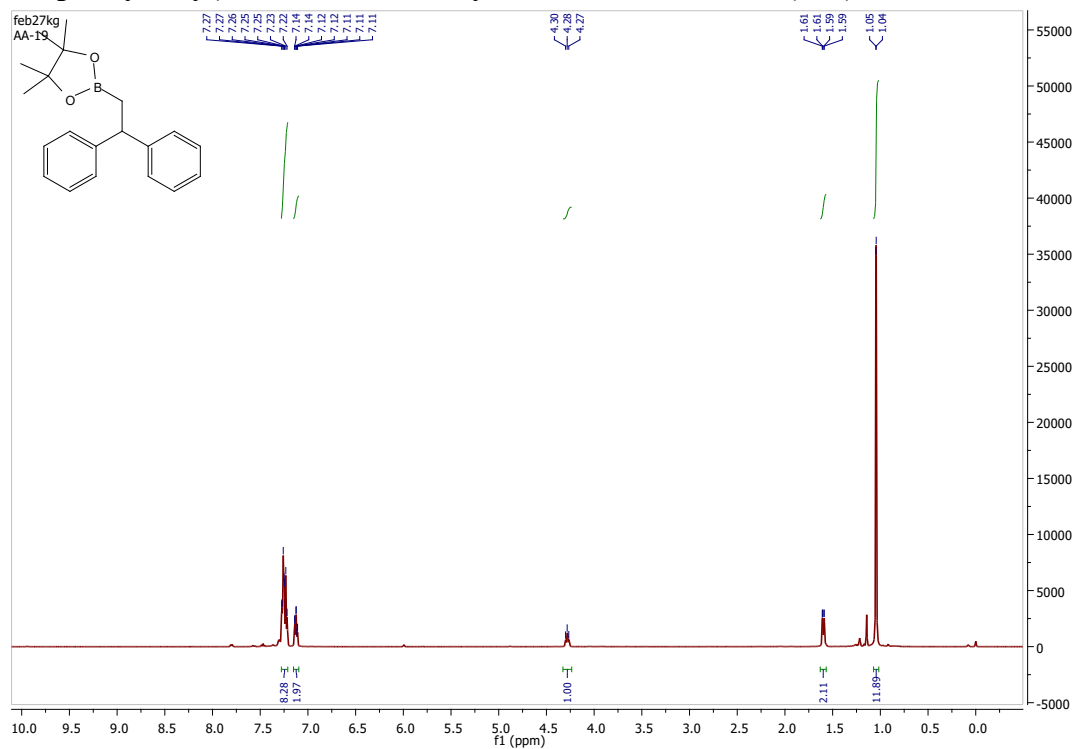
<sup>13</sup>C NMR of **19b** (126 MHz, CDCl<sub>3</sub>)



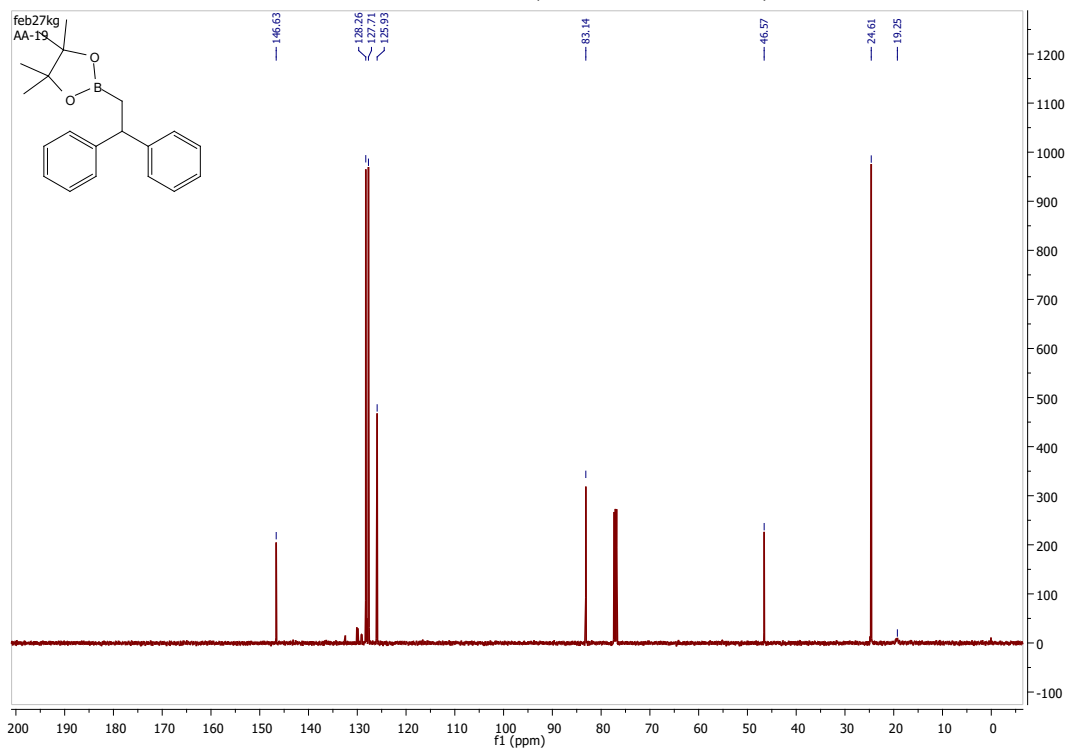
$^{11}\text{B}$  NMR of **19b** (160 MHz,  $\text{CDCl}_3$ )



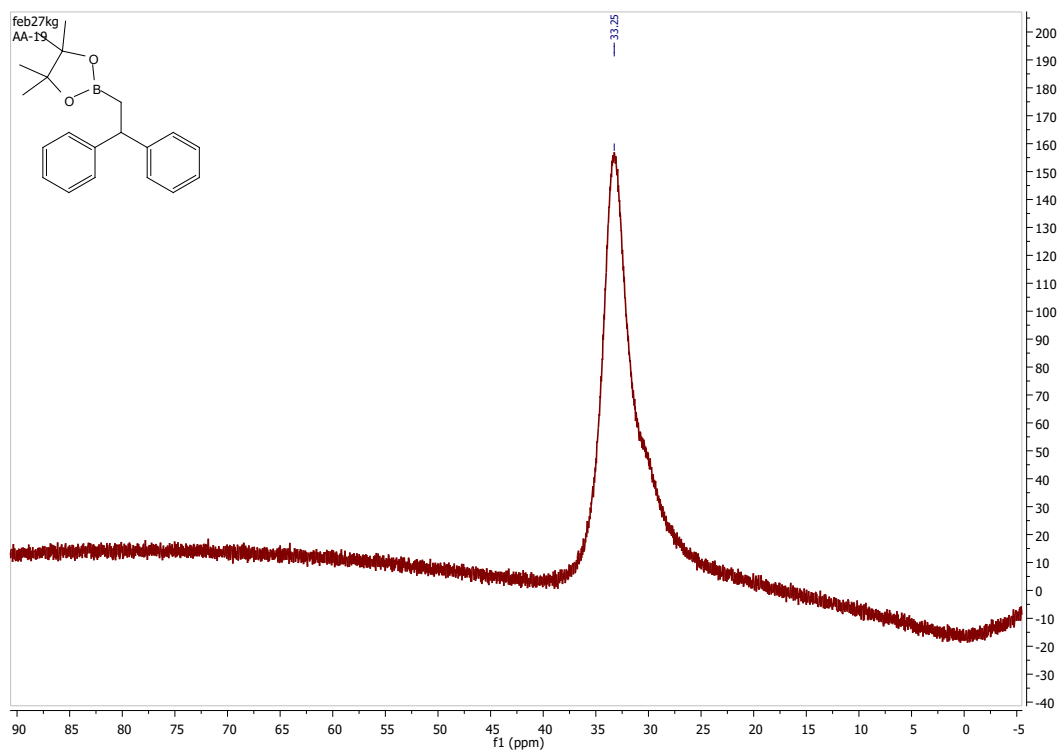
## 2-(2,2-diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**20b**)<sup>4</sup>



<sup>1</sup>H NMR of **20b** (500 MHz, CDCl<sub>3</sub>)

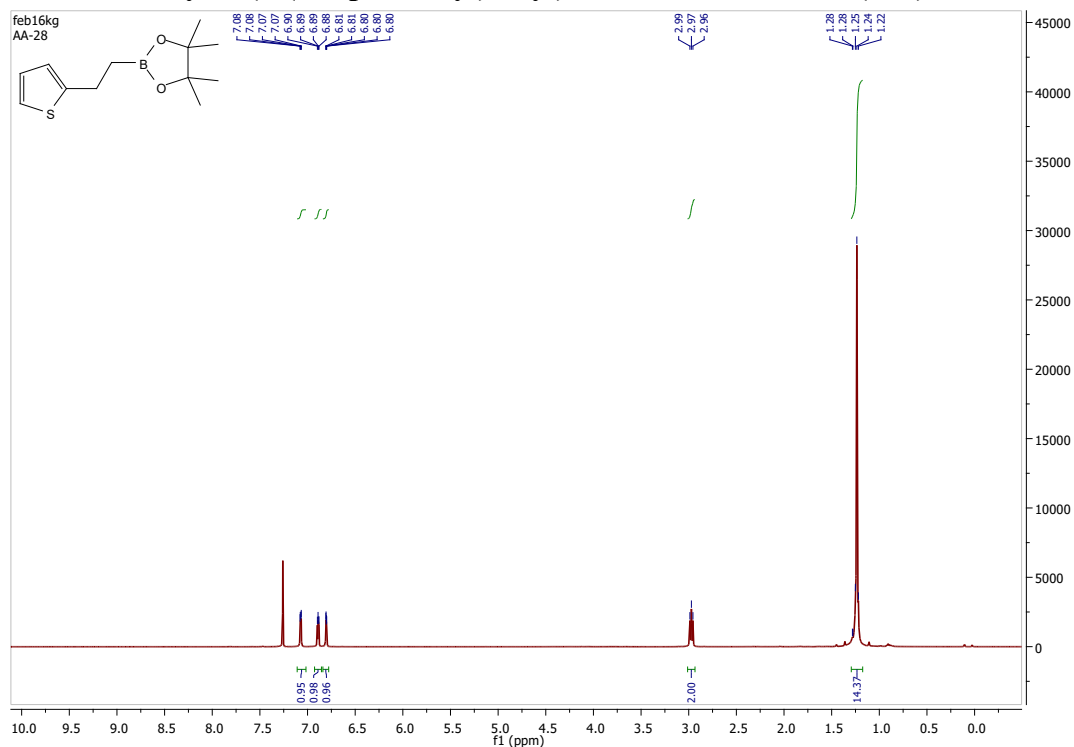


<sup>13</sup>C NMR of **20b** (126 MHz, CDCl<sub>3</sub>)

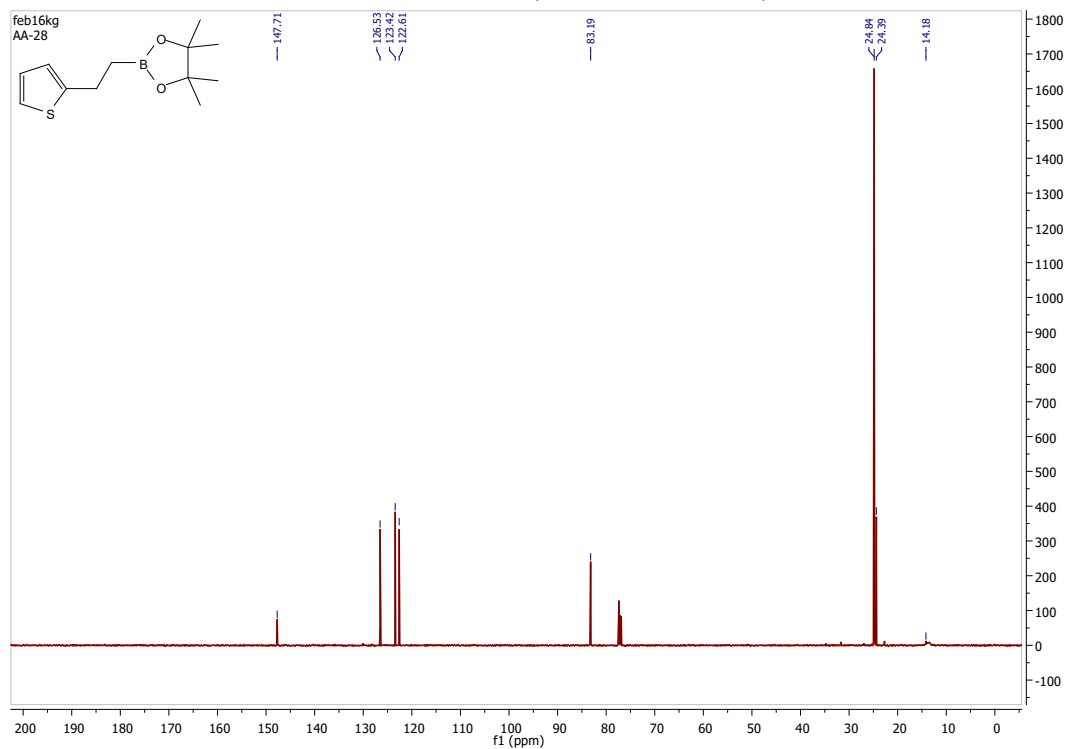


$^{11}\text{B}$  NMR of **20b** (160 MHz,  $\text{CDCl}_3$ )

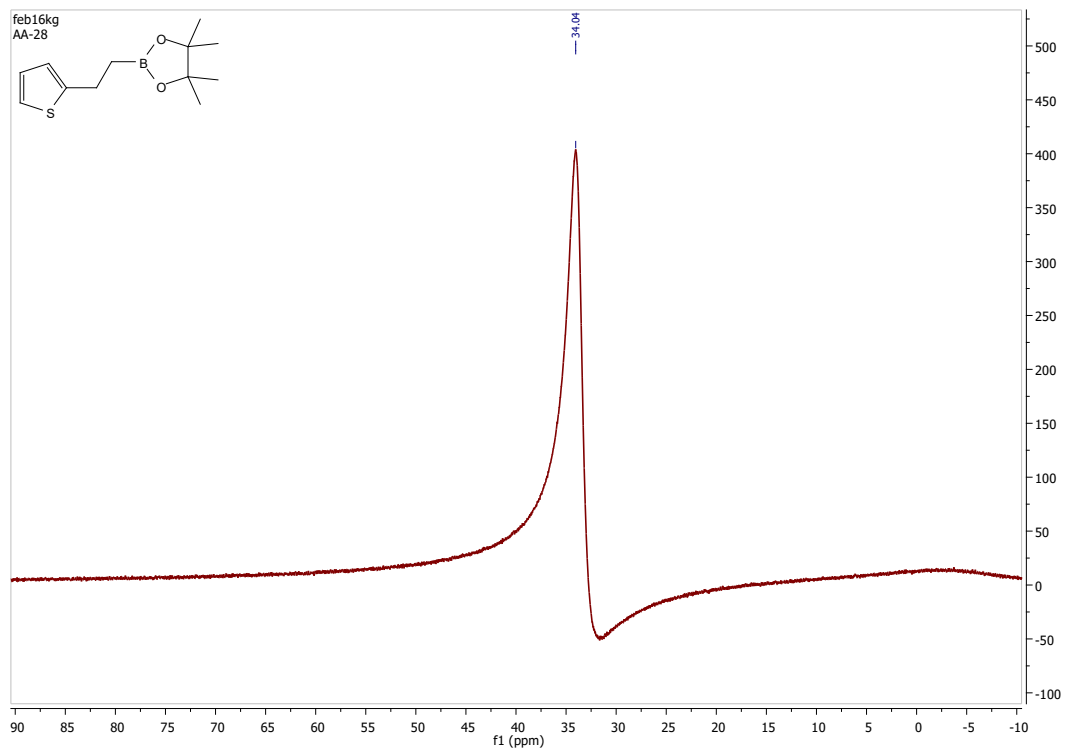
# 4,4,5,5-Tetramethyl-2-(2-(thiophen-2-yl)ethyl)-1,3,2-dioxaborolane (**21b**)<sup>7</sup>



<sup>1</sup>H NMR of **21b** (500 MHz, CDCl<sub>3</sub>)

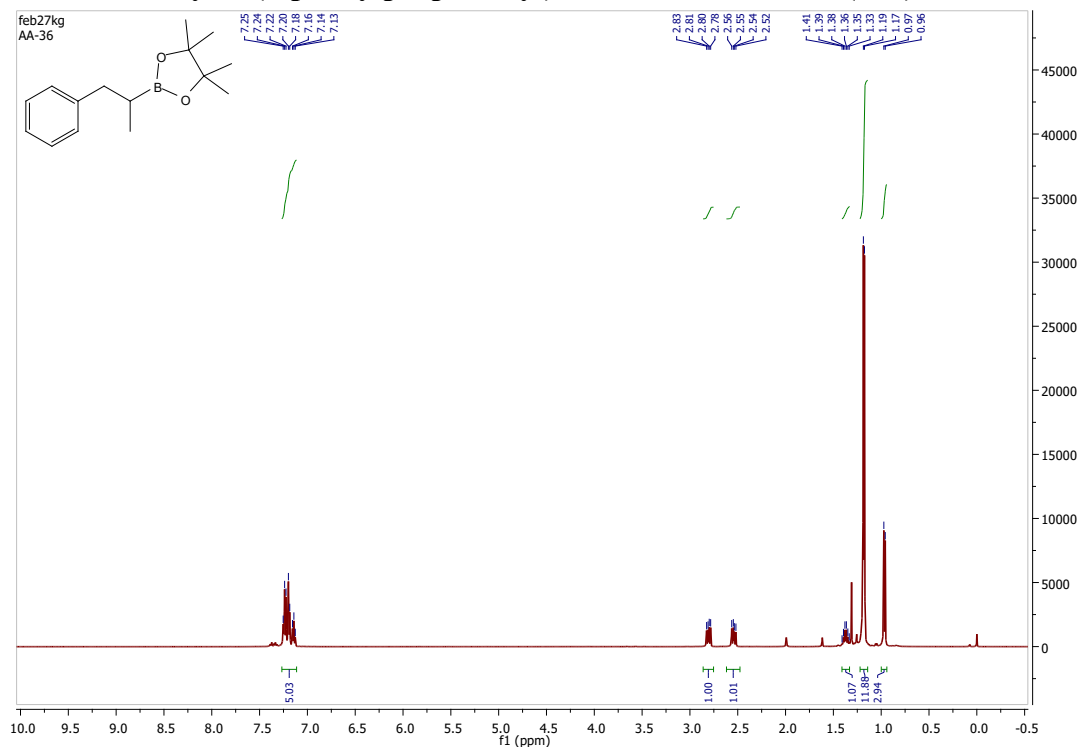


<sup>13</sup>C NMR of **21b** (126 MHz, CDCl<sub>3</sub>)

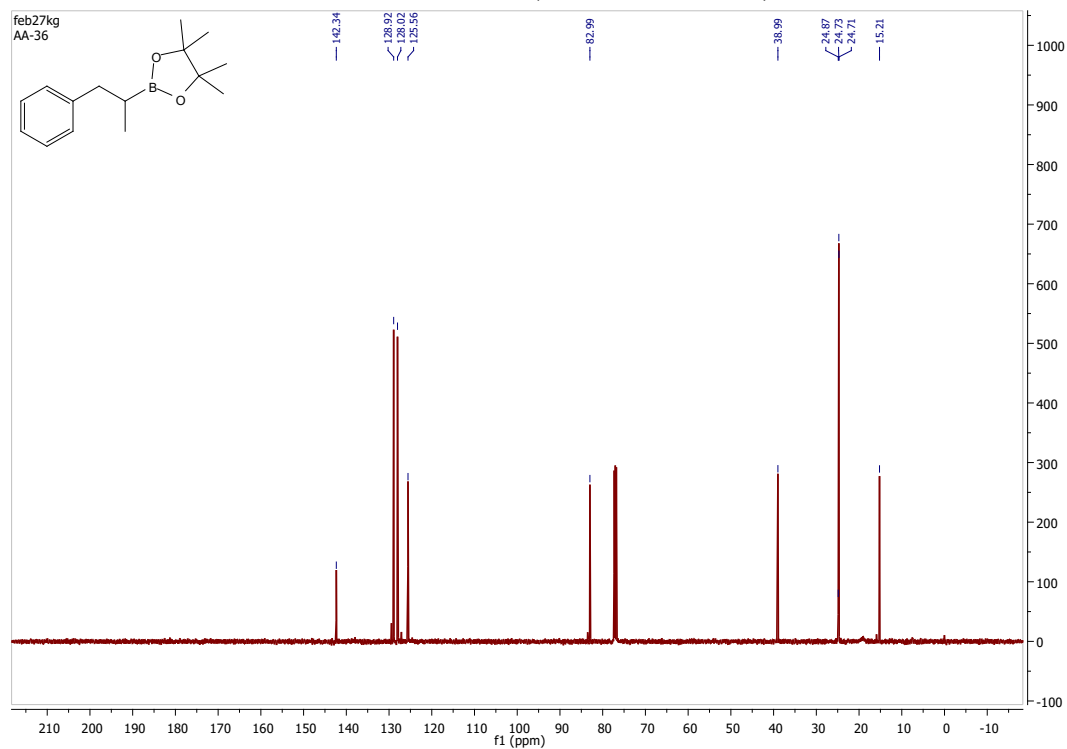


$^{11}\text{B}$  NMR of **21b** (160 MHz,  $\text{CDCl}_3$ )

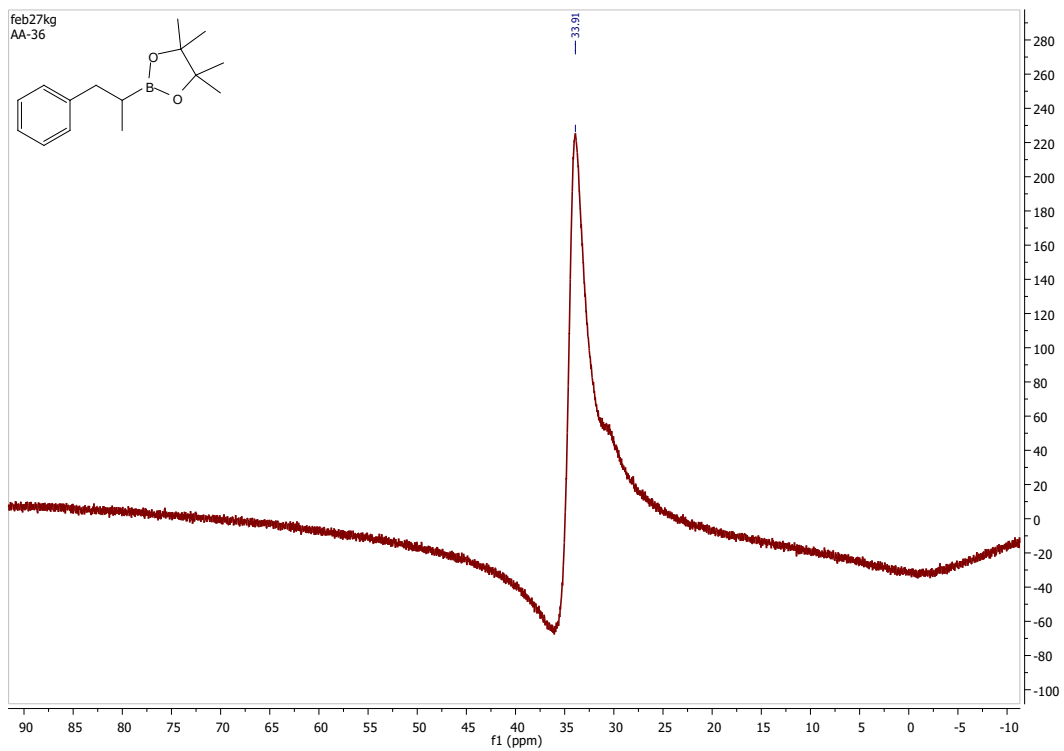
# 4,4,5,5-Tetramethyl-2-(1-phenylpropan-2-yl)-1,3,2-dioxaborolane (**22b**)<sup>4</sup>



<sup>1</sup>H NMR of **22b** (500 MHz, CDCl<sub>3</sub>)

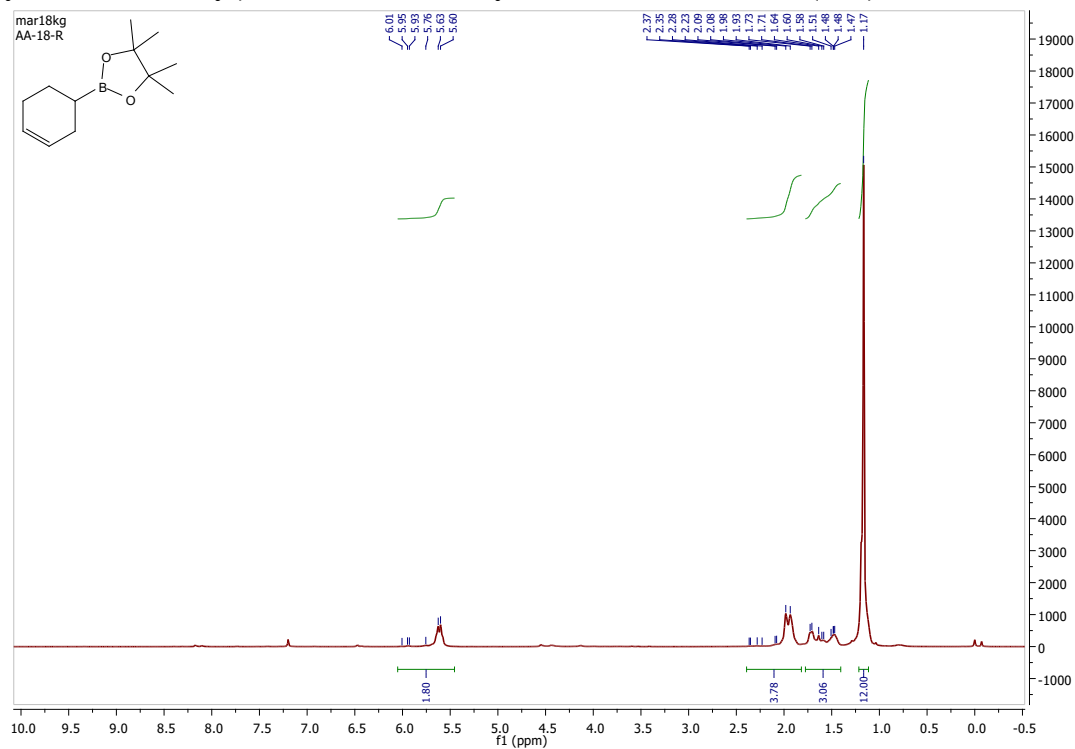


<sup>13</sup>C NMR of **22b** (126 MHz, CDCl<sub>3</sub>)

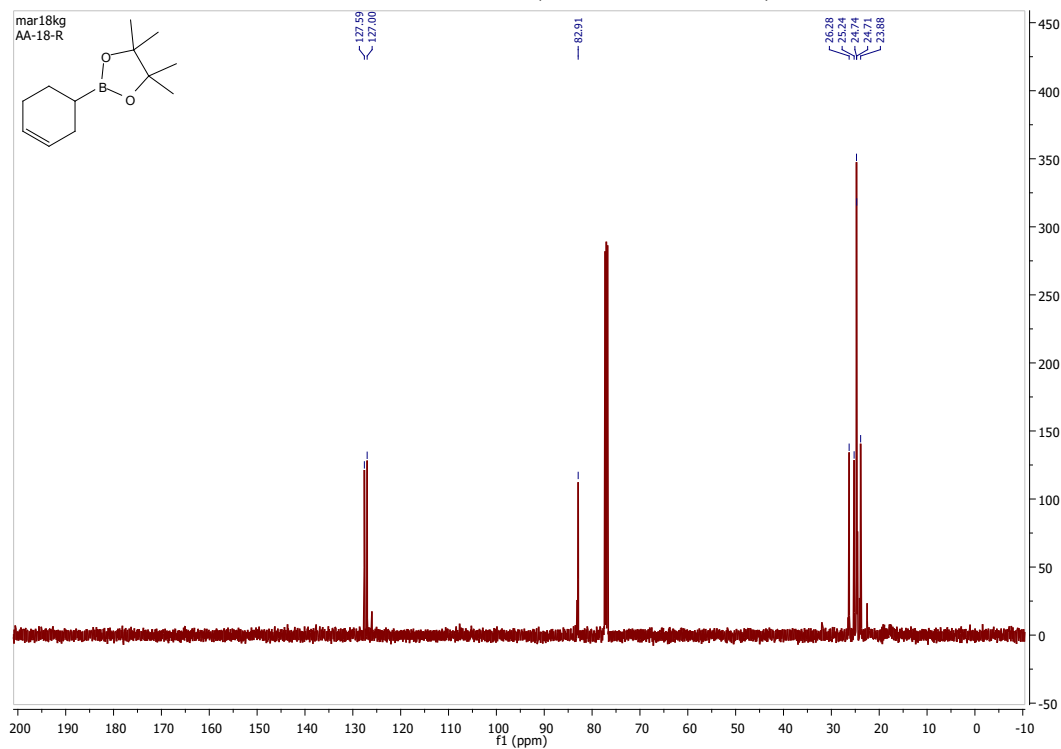


$^{11}\text{B}$  NMR of **22b** (160 MHz,  $\text{CDCl}_3$ )

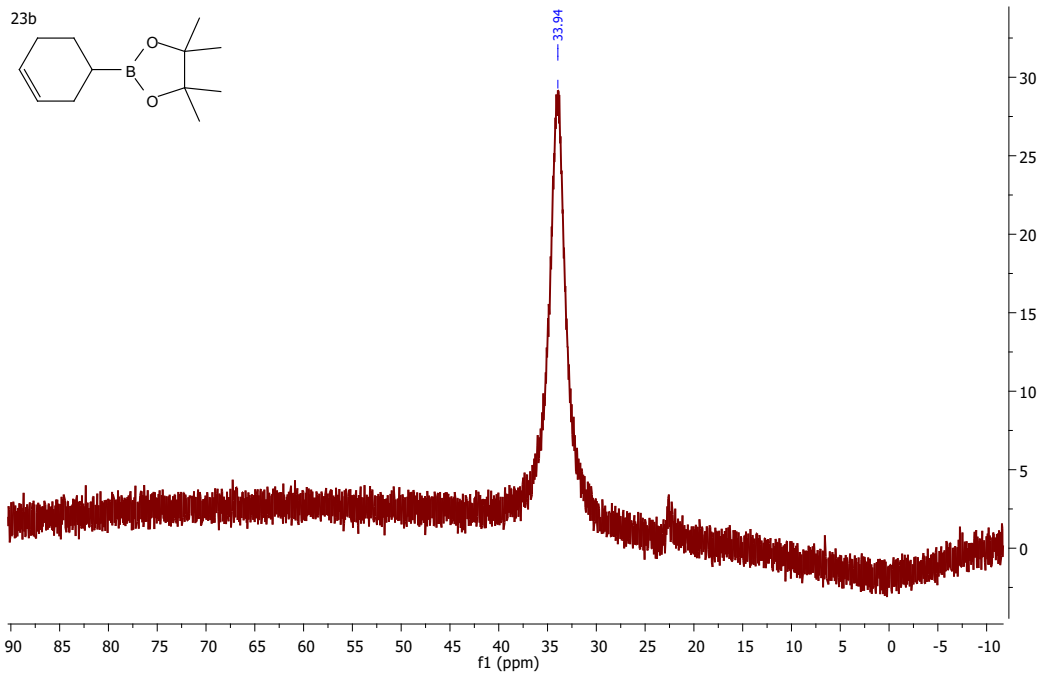
## 2-(Cyclohex-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**23b**)<sup>9</sup>



<sup>1</sup>H NMR of **23b** (500 MHz, CDCl<sub>3</sub>)



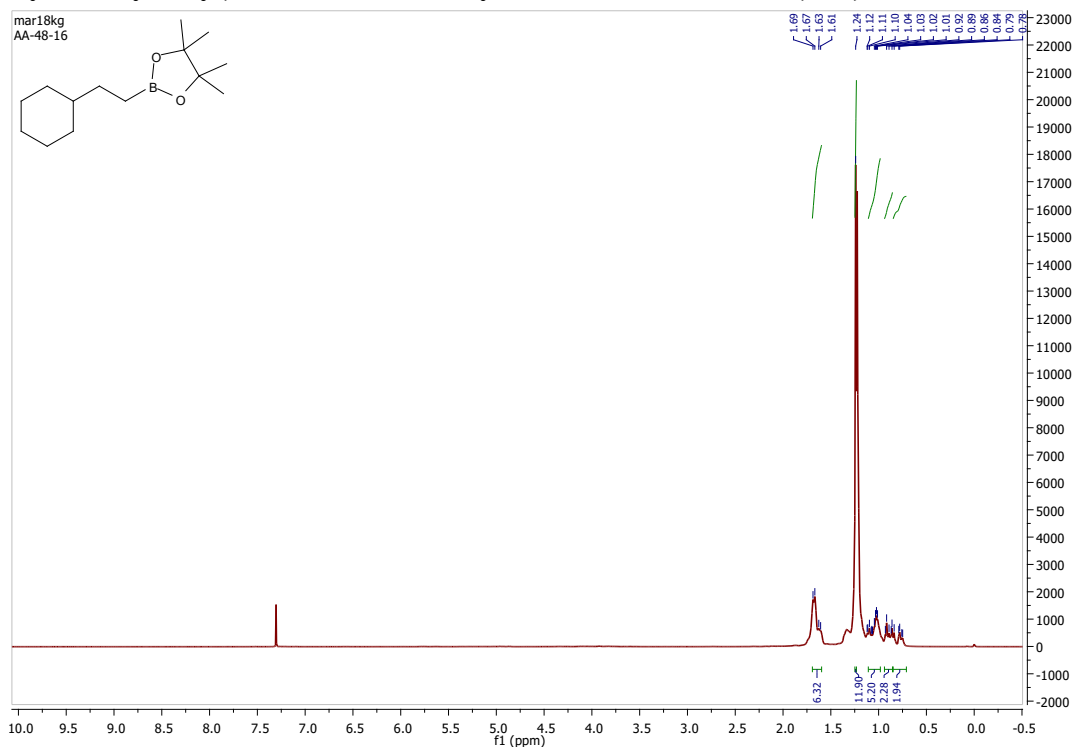
<sup>13</sup>C NMR of **23b** (126 MHz, CDCl<sub>3</sub>)



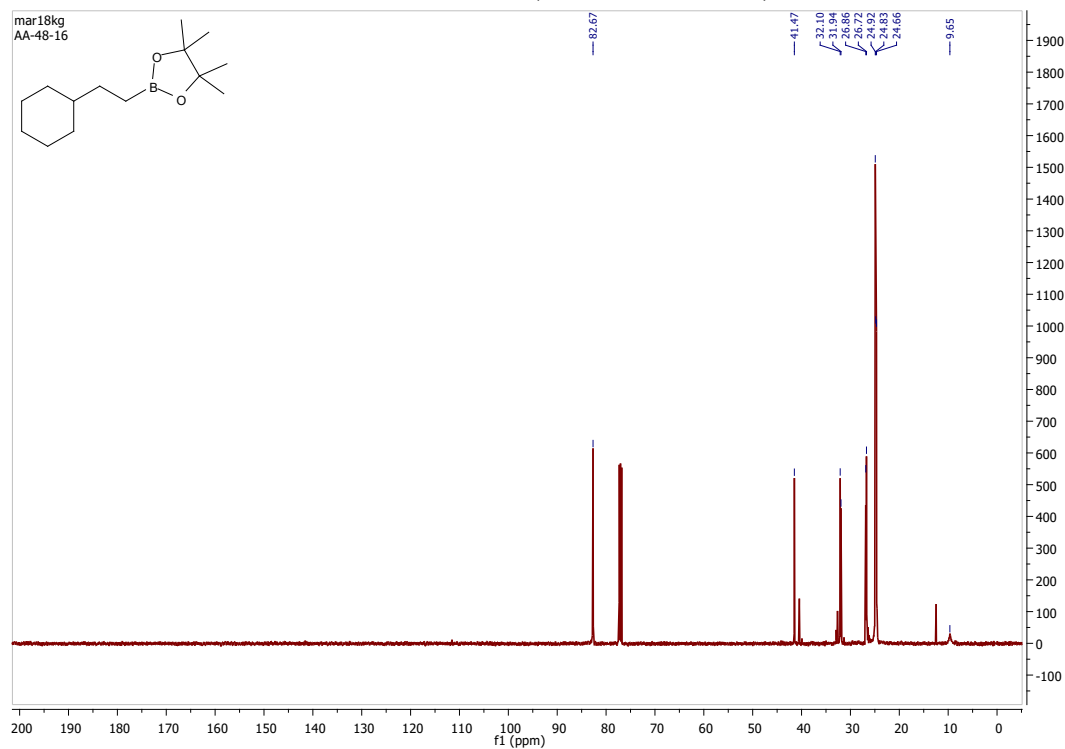
$^{11}\text{B}$  NMR of **23b** (160 MHz,  $\text{CDCl}_3$ )



## 2-(2-Cyclohexylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**24b**)<sup>4</sup>

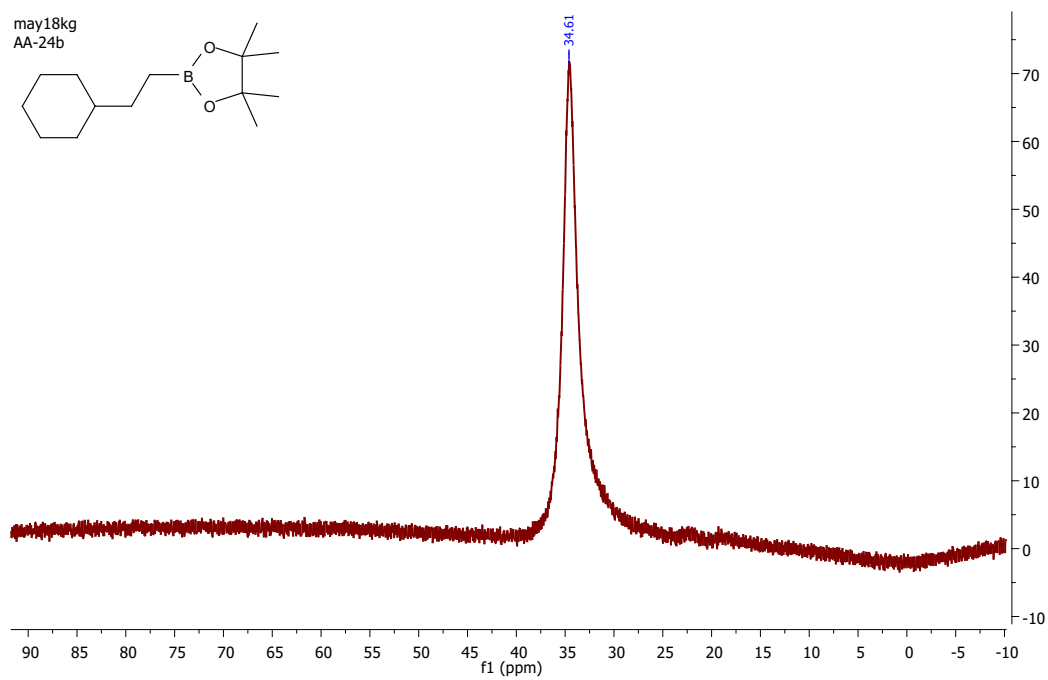
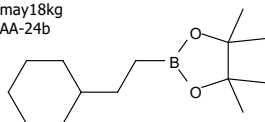


<sup>1</sup>H NMR of **24b** (500 MHz, CDCl<sub>3</sub>)



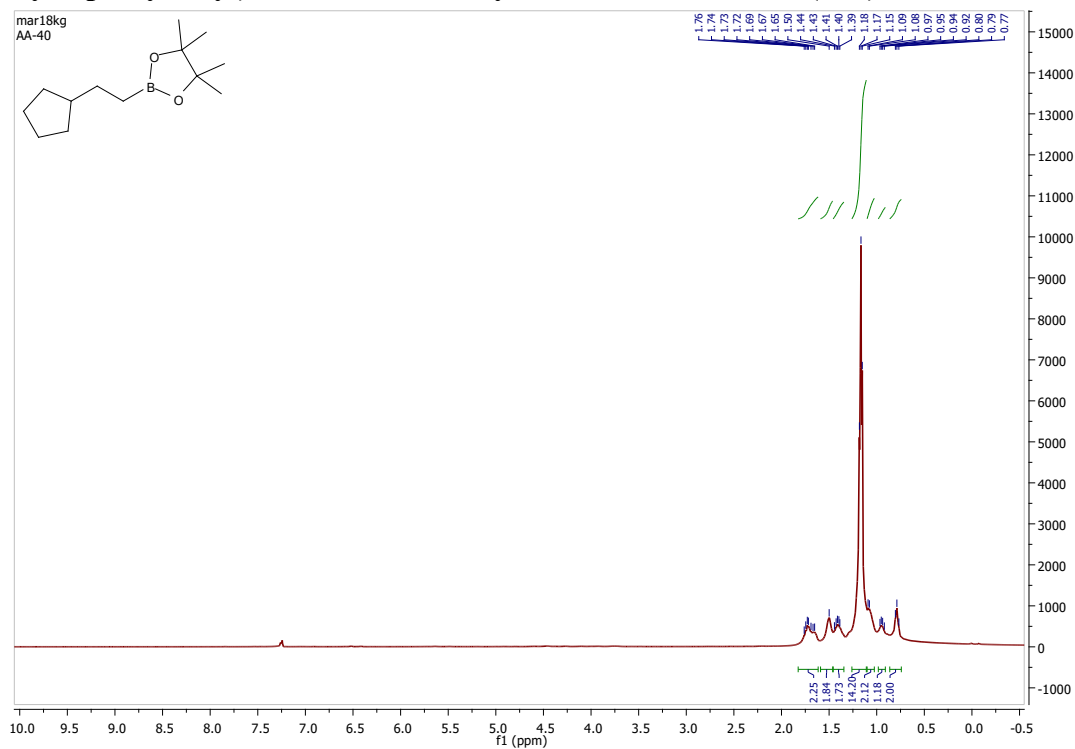
<sup>13</sup>C NMR of **24b** (126 MHz, CDCl<sub>3</sub>)

may18kg  
AA-24b

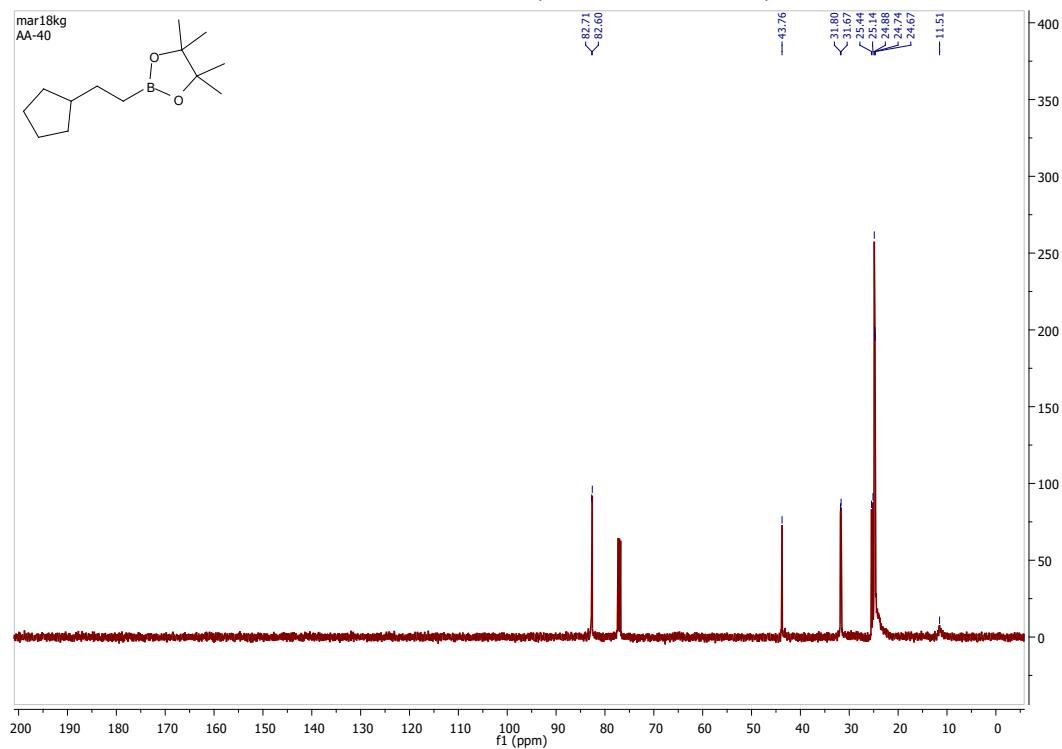


$^{11}\text{B}$  NMR of **24b** (160 MHz,  $\text{CDCl}_3$ )

## 2-(2-Cyclopentylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**25b**)<sup>10</sup>

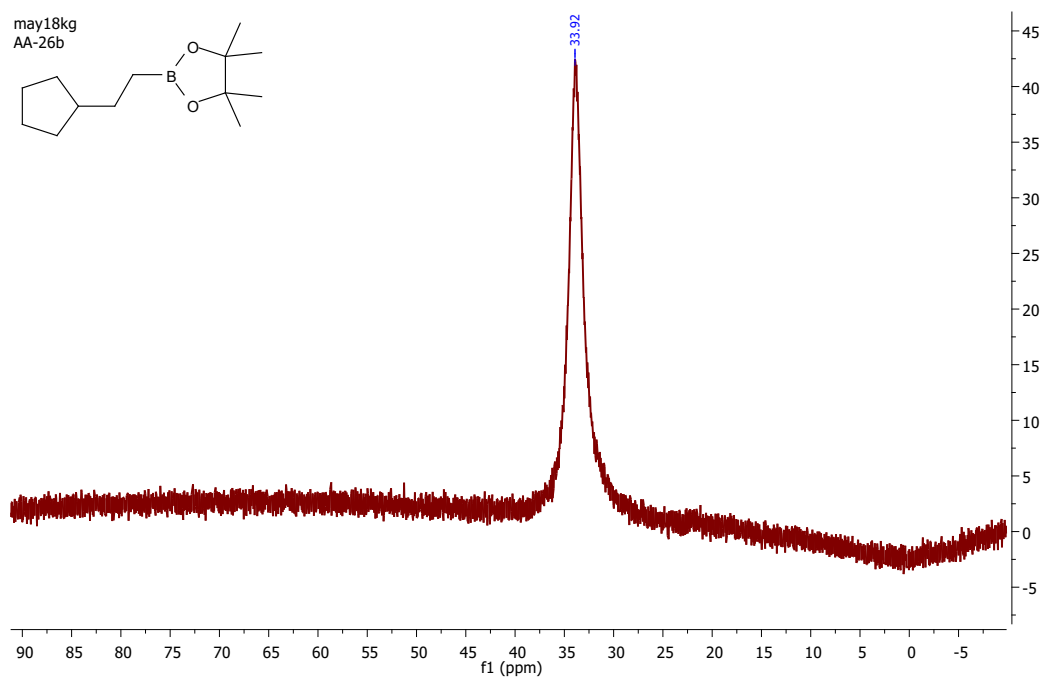
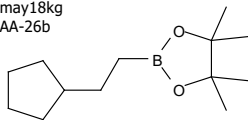


<sup>1</sup>H NMR of **25b** (500 MHz, CDCl<sub>3</sub>)



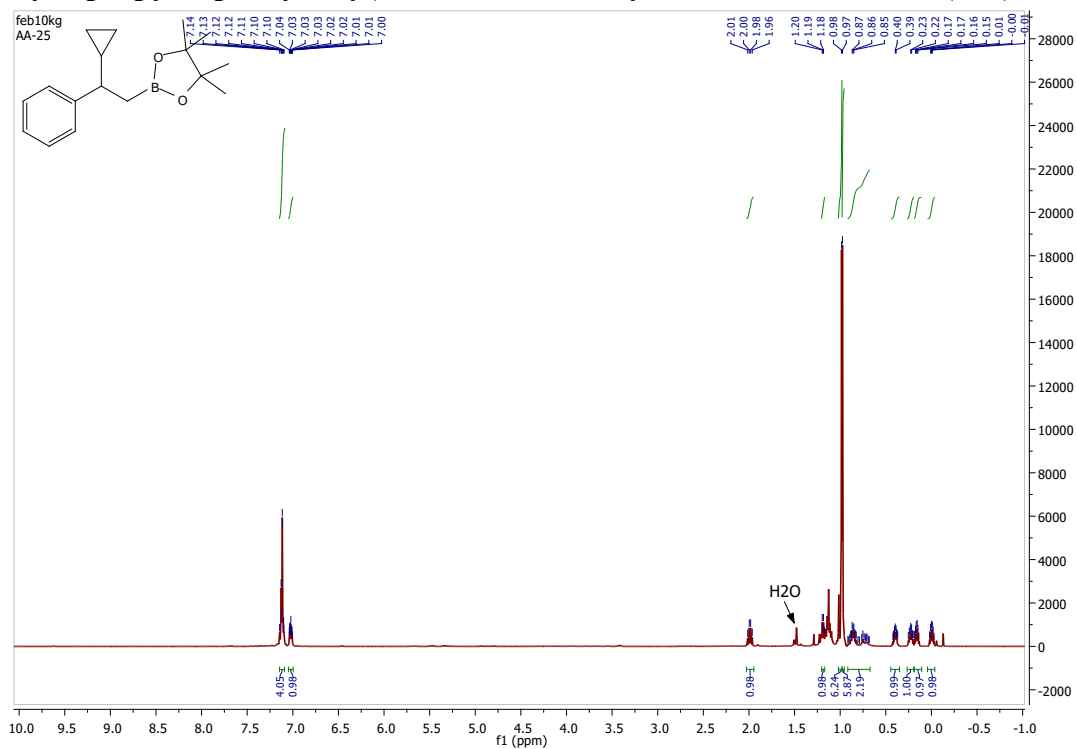
<sup>13</sup>C NMR of **25b** (126 MHz, CDCl<sub>3</sub>)

may18kg  
AA-26b

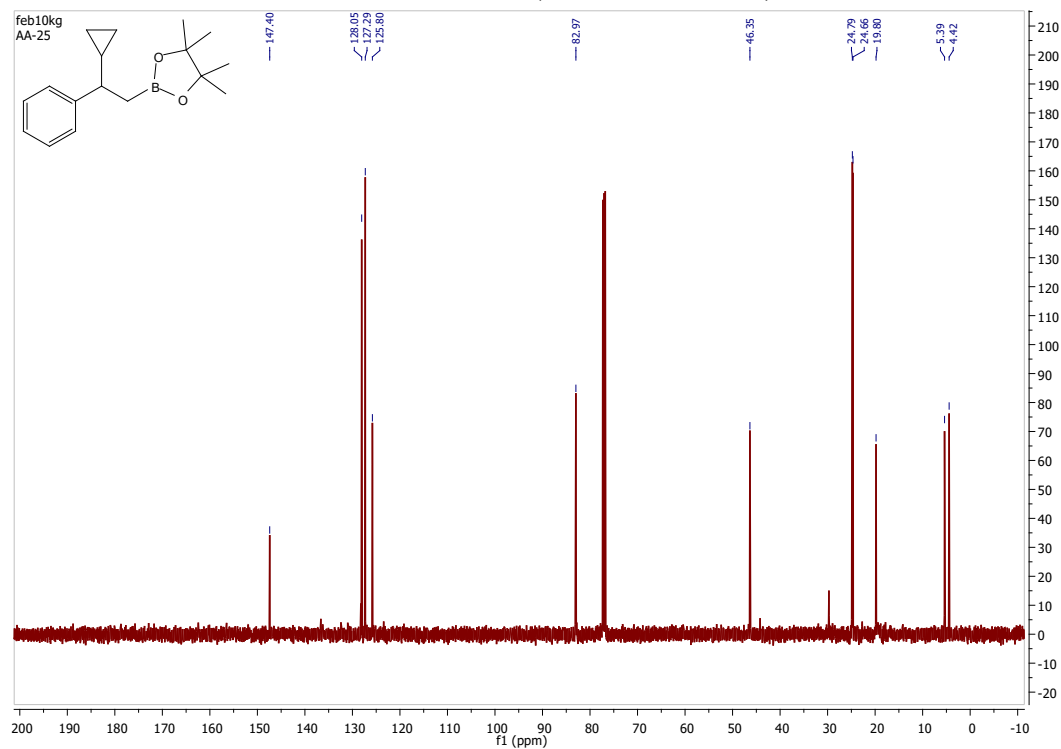


$^{11}\text{B}$  NMR of **25b** (160 MHz,  $\text{CDCl}_3$ )

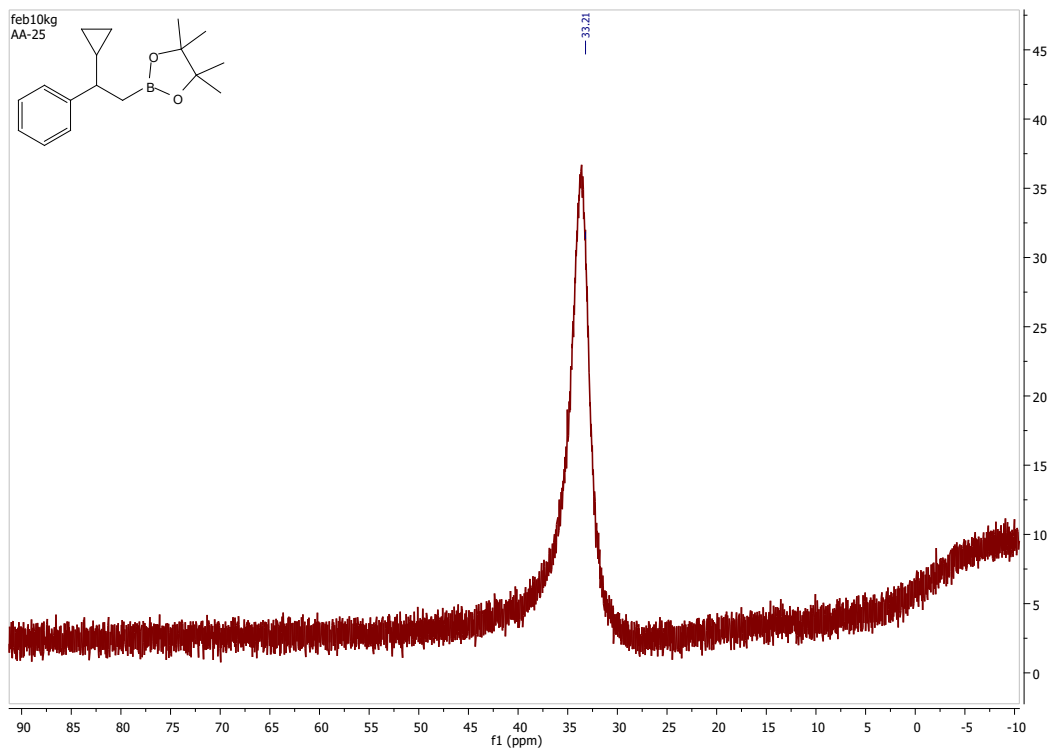
## 2-(2-Cyclopropyl-2-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**27b**)<sup>11</sup>



<sup>1</sup>H NMR of **27b** (500 MHz, CDCl<sub>3</sub>)

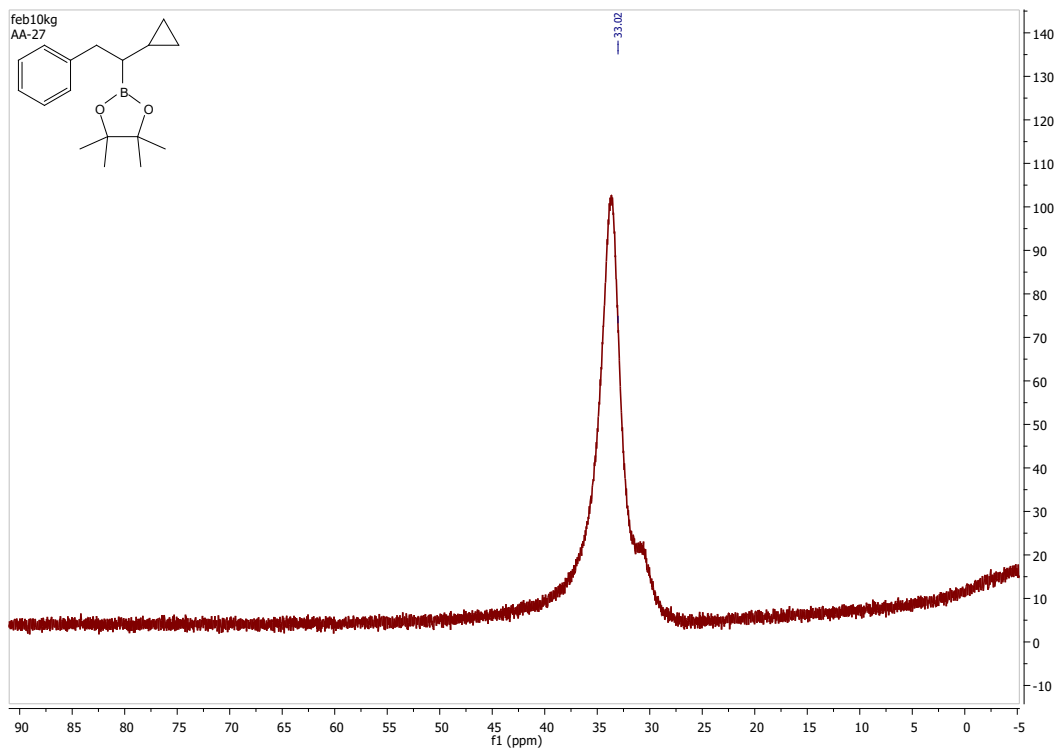


<sup>13</sup>C NMR of **27b** (126 MHz, CDCl<sub>3</sub>)



$^{11}\text{B}$  NMR of **27b** (160 MHz,  $\text{CDCl}_3$ )

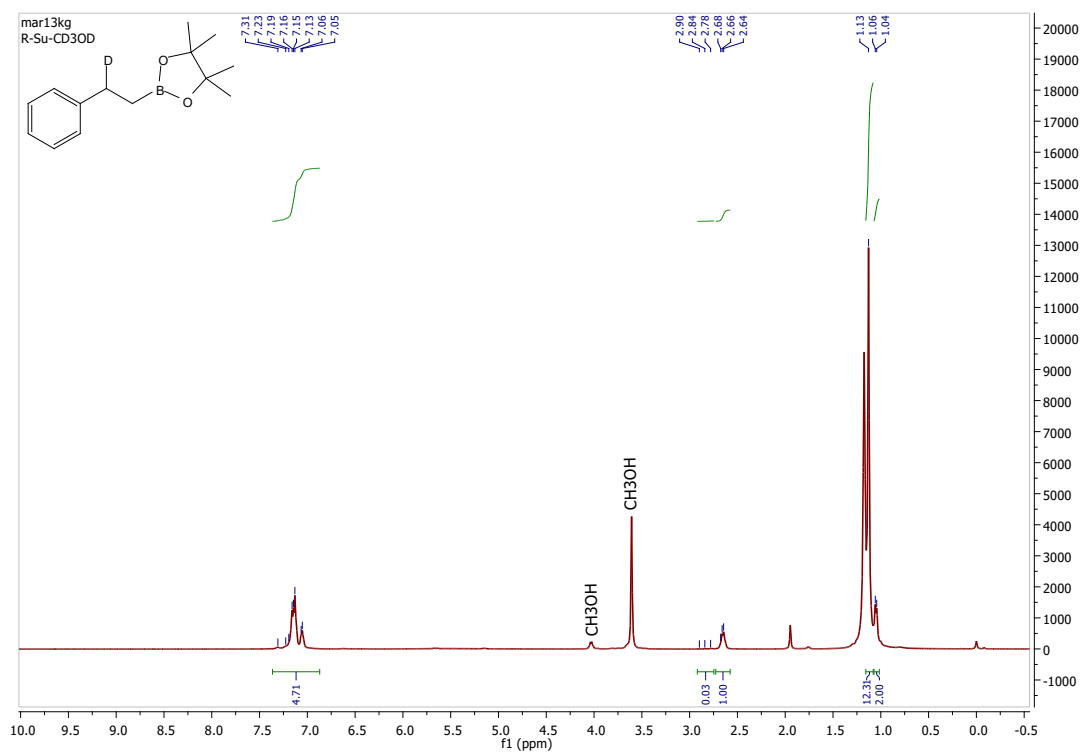




$^{11}\text{B}$  NMR of **28b** (160 MHz,  $\text{CDCl}_3$ )

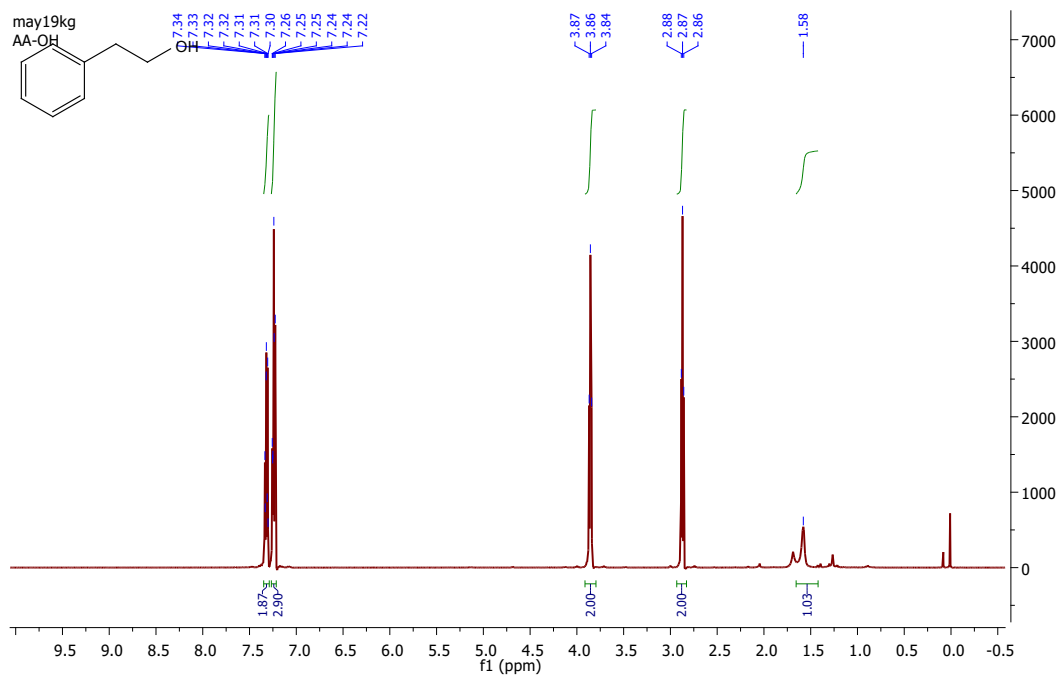


# 4,4,5,5-Tetramethyl-2-(2-phenylethyl-2-d)-1,3,2-dioxaborolane (**1b-D**)<sup>4</sup>

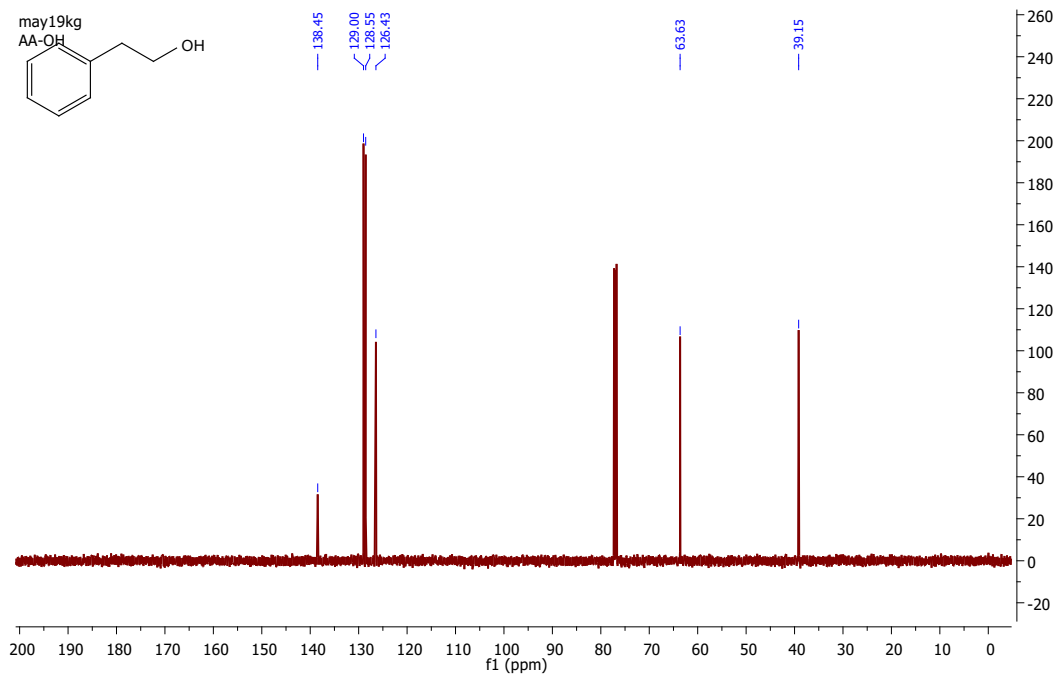


<sup>1</sup>H NMR of **1b-D** (500 MHz, CDCl<sub>3</sub>)

### 2-phenylethan-1-ol (1c)<sup>4</sup>

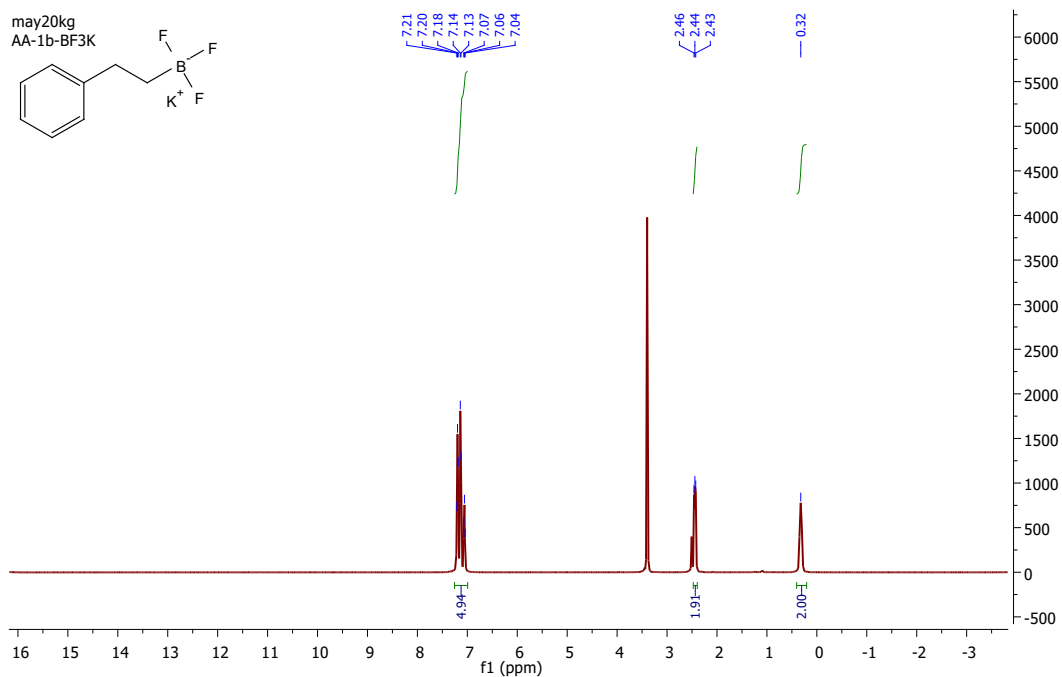


<sup>1</sup>H NMR of **1c** (500 MHz, CDCl<sub>3</sub>)

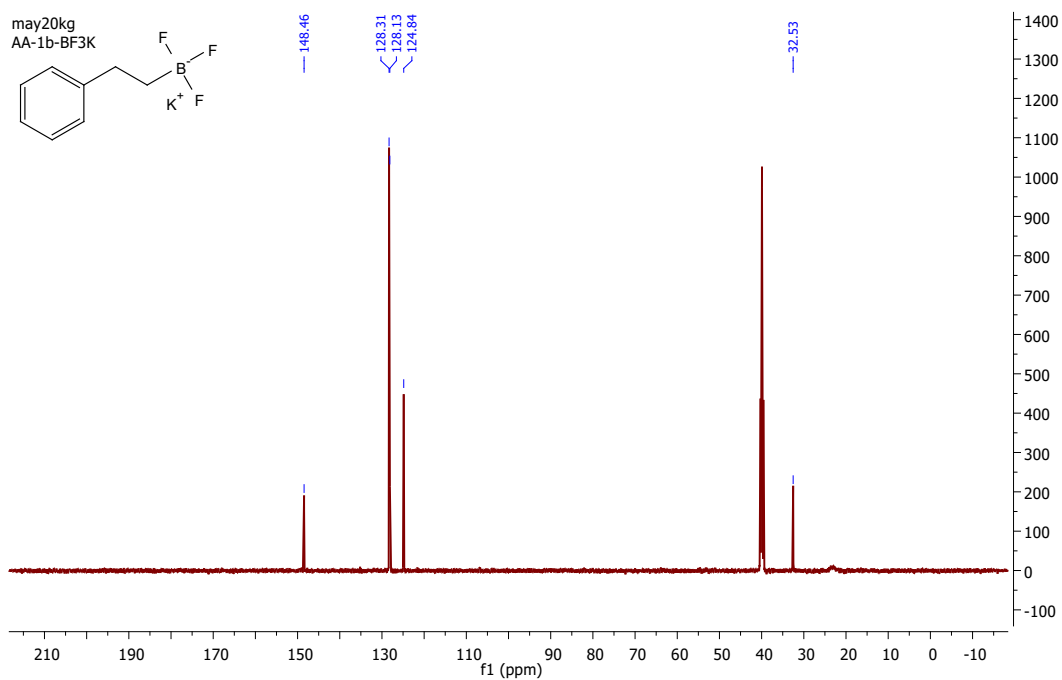


<sup>13</sup>C NMR of **1c** (500 MHz, CDCl<sub>3</sub>)

# Potassium 2-phenylethyltrifluoroborate (**1d**)<sup>4</sup>

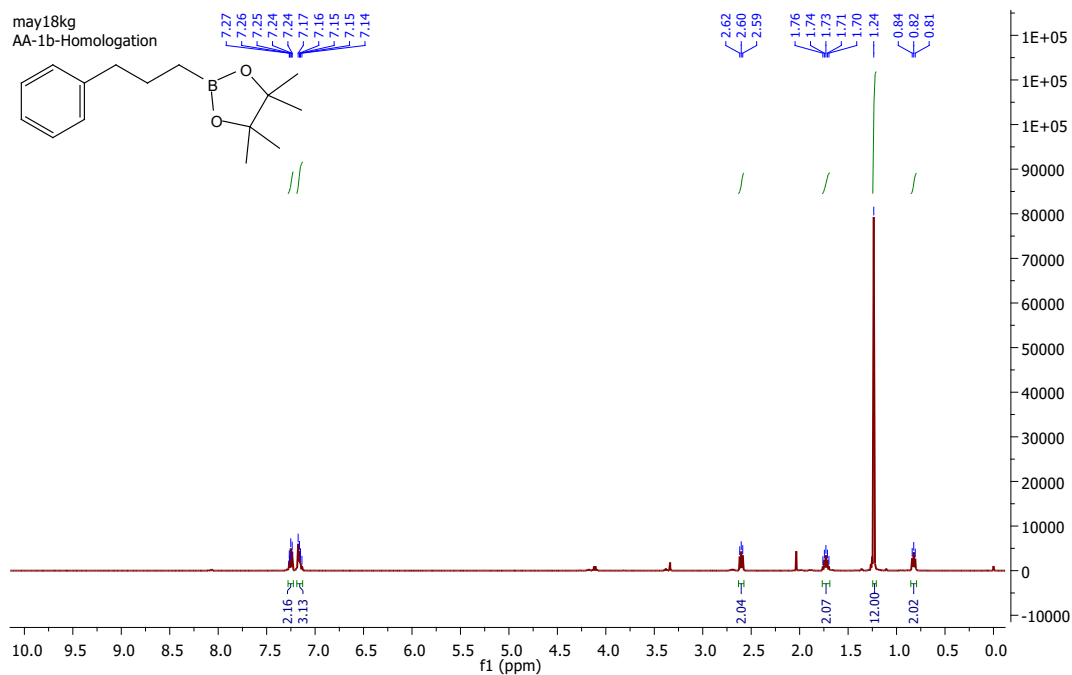


<sup>1</sup>H NMR of **1d** (500 MHz, DMSO-d<sub>6</sub>)

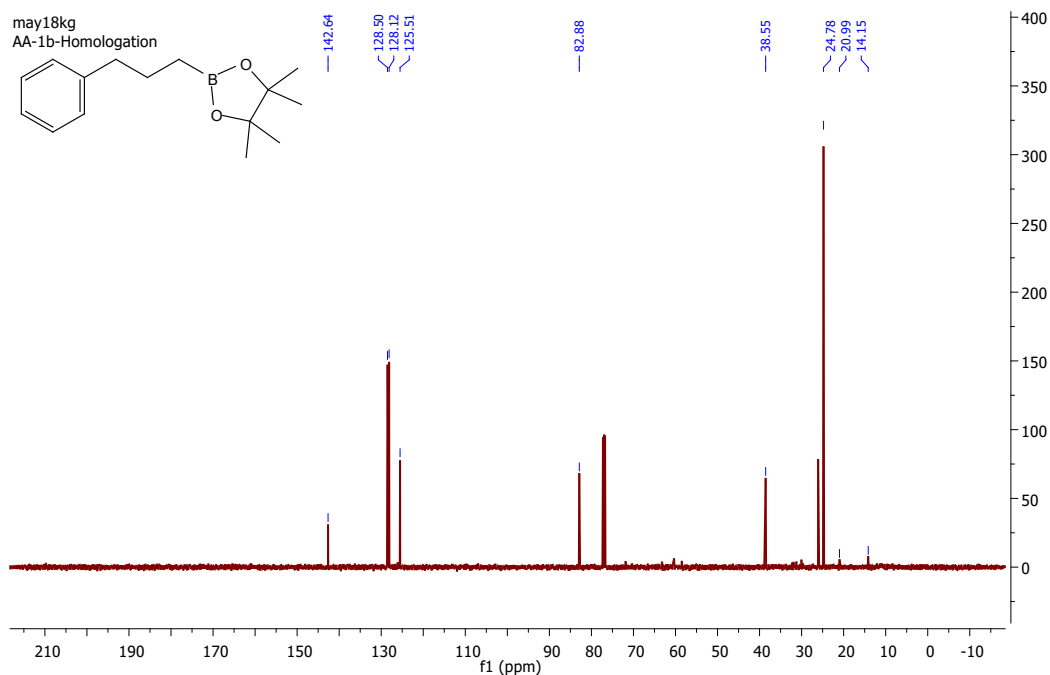


<sup>13</sup>C NMR of **1d** (126 MHz, DMSO-d<sub>6</sub>)

### 4,4,5,5-Tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (**1e**)<sup>6</sup>

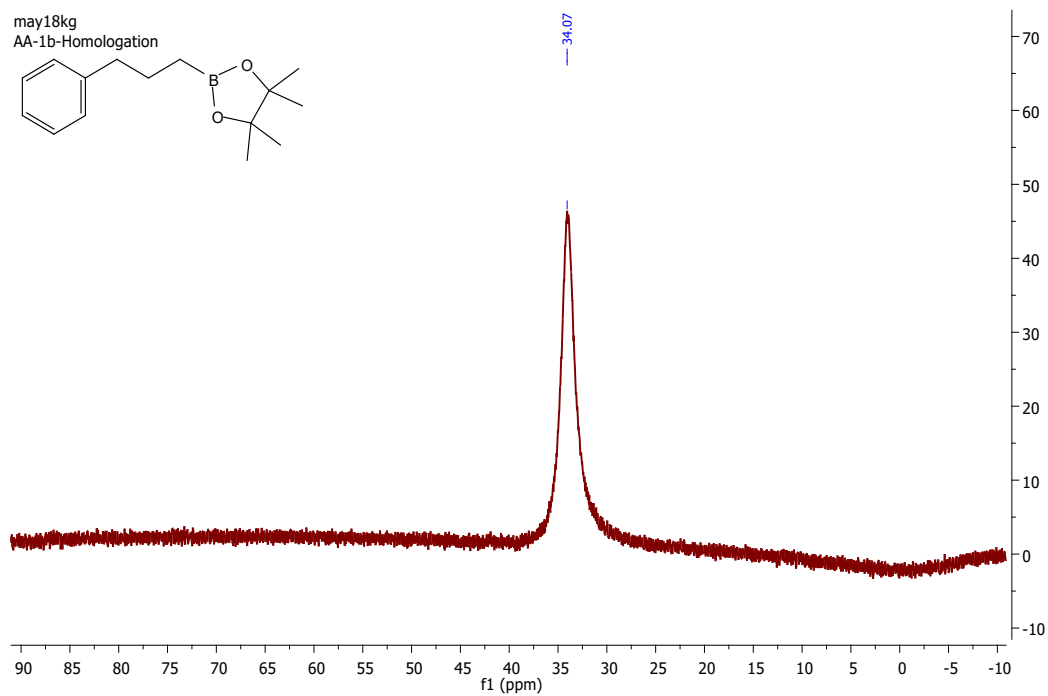
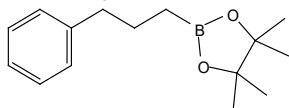


<sup>1</sup>H NMR of **1e** (500 MHz, CDCl<sub>3</sub>)



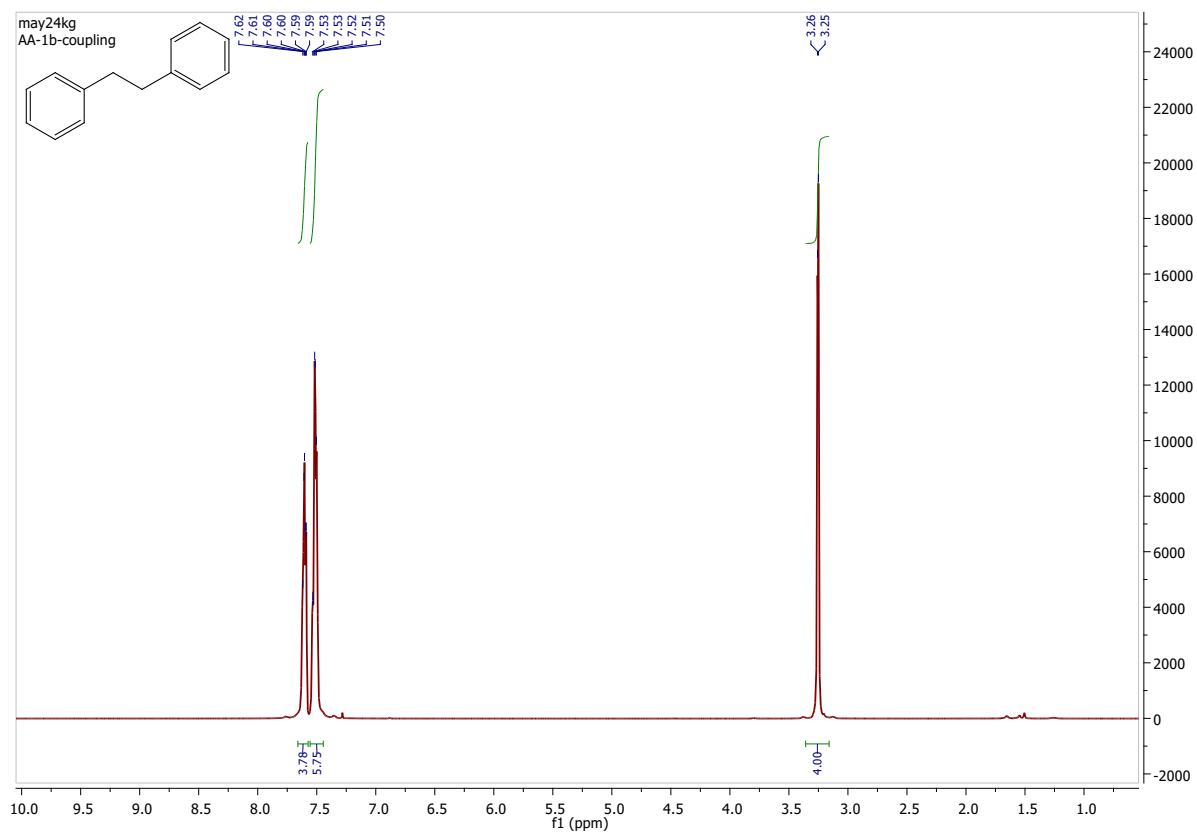
<sup>13</sup>C NMR of **1e** (126 MHz, CDCl<sub>3</sub>)

may18kg  
AA-1b-Homologation

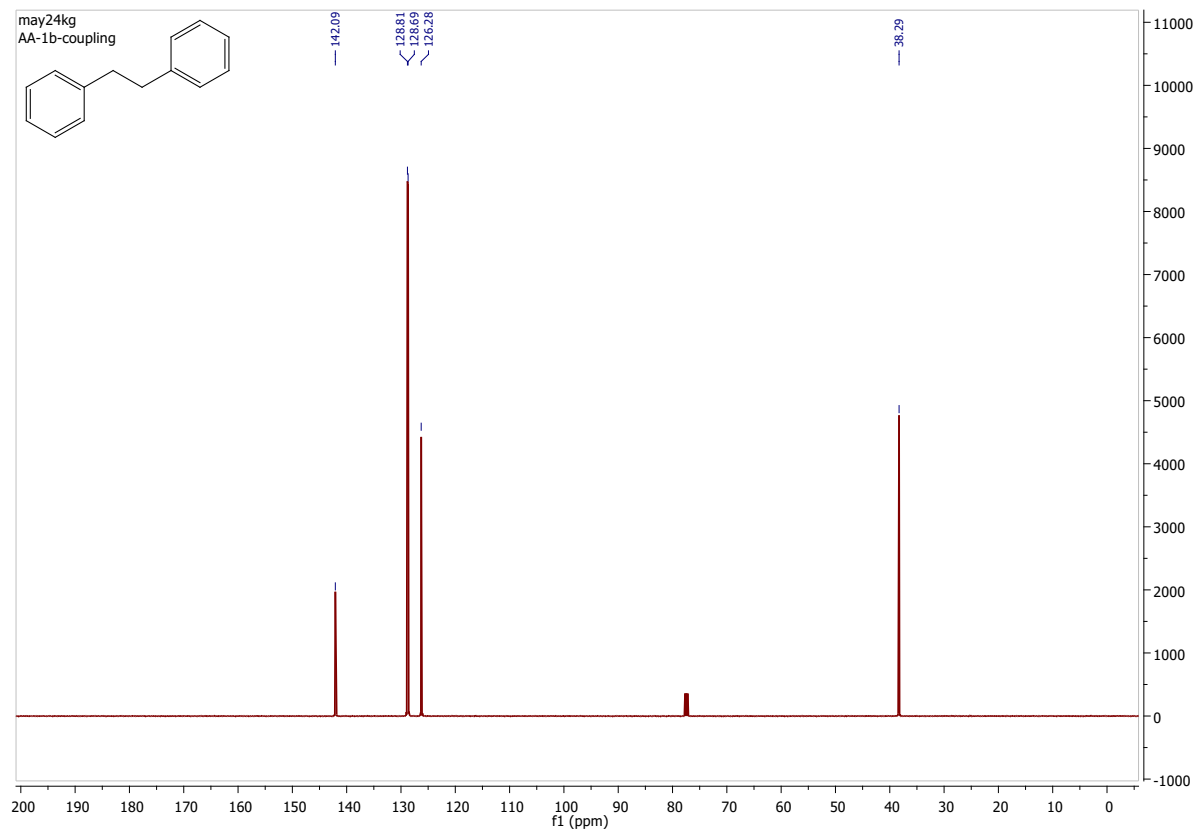


$^{11}\text{B}$  NMR of **1e** (160 MHz,  $\text{CDCl}_3$ )

# 1,2-Diphenylethane (1f)<sup>14</sup>



<sup>1</sup>H NMR of **1f** (500 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR of **1f** (126 MHz, CDCl<sub>3</sub>)

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