

## Supporting Information

# Phenalenyl-based Nickel Catalyst for Hydroboration of Olefins under Ambient Conditions

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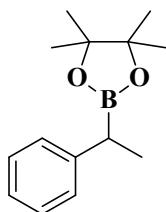
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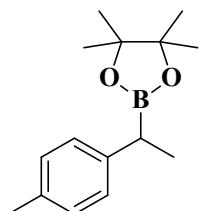
## Spectroscopic data of products in catalytic hydroboration of vinylarenes

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



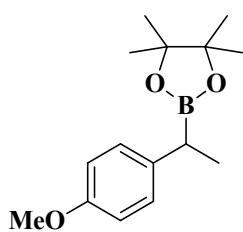
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.29–7.7.17 (m, 4H), 7.16–7.13 (m, 1H), 2.44 (q, *J* = 7.5 Hz, 1H), 1.36 (d, *J* = 7.5 Hz, 3H), 1.21 (d, *J* = 5.3 Hz, 12H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ 144.9 (C<sub>q</sub>), 128.2 (CH), 127.7 (CH), 125.0 (CH), 83.2 (C<sub>q</sub>), 24.6 (CH), 24.5 (CH<sub>3</sub>), 17.0 (CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ 33.59 ppm.

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



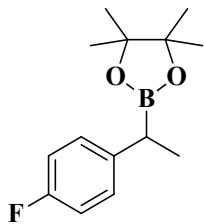
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ 7.12 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 2.38 (q, *J* = 7.5 Hz, 1H), 2.30 (s, 3H), 1.32 (d, *J* = 7.5 Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ 141.8 (C<sub>q</sub>), 134.37 (C<sub>q</sub>), 129.0 (CH), 127.6 (CH), 83.2 (C<sub>q</sub>), 24.6 (CH), 24.5 (CH<sub>3</sub>), 20.9 (CH<sub>3</sub>), 17.2 (CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ 33.6 ppm.

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



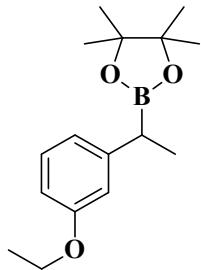
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ 7.14 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 3.78 (s, 3H), 2.38 (q, *J* = 7.5 Hz, 1 H), 1.29 (d, *J* = 7.5 Hz, 3H), 1.20 (d, *J* = 5.3 Hz, 12H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ 157.2 (C<sub>q</sub>), 137.0 (C<sub>q</sub>), 128.6 (CH), 113.7 (CH), 83.2 (C<sub>q</sub>), 55.1 (CH<sub>3</sub>), 24.6 (CH), 24.5 (CH<sub>3</sub>), 17.3 (CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ 33.55 ppm.

**2-(1-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane<sup>3</sup>**



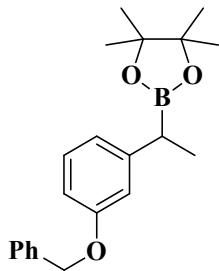
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ 7.18–7.15 (m, 2H), 6.96–6.92 (m, 2H), 2.42 (q, *J* = 7.5 Hz, 1H), 1.32 (d, *J* = 7.5 Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ 161.8, (d, *J* = 126.9 Hz, C<sub>q</sub>), 140.5 (C<sub>q</sub>), 129.0 (d, *J* = 7.5 Hz, CH), 115.0 (d, *J* = 20 Hz, CH), 83.3 (C<sub>q</sub>), 24.6 (CH), 24.5 (CH<sub>3</sub>), 17.1 (CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ 33.5 ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -118.9 ppm.

**2-(1-(3-ethoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane**



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.17 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.11 (td, *J* = 7.9, 1.6 Hz, 1H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 4.04 (qd, *J* = 7.0, 2.7 Hz, 2H), 2.55 (q, *J* = 7.5 Hz, 1H), 1.42 (t, *J* = 7.0 Hz, 3H), 1.30 (d, *J* = 7.6 Hz, 3H), 1.23 (d, *J* = 3.4 Hz, 12H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ 156.2 (C<sub>q</sub>), 134.1 (C<sub>q</sub>), 128.7 (CH), 126.0 (CH), 120.5 (CH), 110.8 (CH), 82.9 (C<sub>q</sub>), 63.3 (CH<sub>2</sub>), 24.7 (CH), 24.6 (CH<sub>3</sub>), 15.1 (CH<sub>3</sub>), 14.9 (CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ 34.0 ppm. ESI-MS: (m/z): calcd for C<sub>16</sub>H<sub>25</sub>BNO<sub>3</sub>H, [M+H]<sup>+</sup>: 277.1975; found, 277.1972.

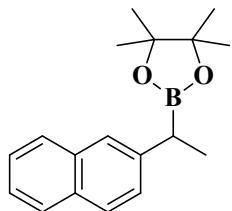
**2-(1-(3-(benzyloxy)phenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane**



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.49 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.23 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.16 – 7.09 (m, 1H), 6.94 (td, *J* = 7.5, 0.9 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 5.12 (s, 2H), 2.65 (q, *J* = 7.5 Hz, 1H), 1.38 (d, *J* = 7.5 Hz, 3H), 1.13 (s, 12H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ 155.9 (C<sub>q</sub>), 137.4 (C<sub>q</sub>), 134.1 (C<sub>q</sub>), 128.4 (CH), 128.3 (CH), 126.9 (CH), 126.1 (CH), 120.9 (CH), 111.1 (CH), 83.0

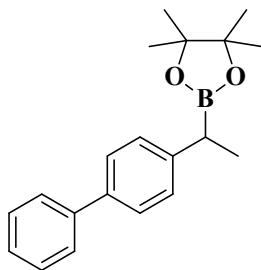
(C<sub>q</sub>), 69.6 (CH<sub>2</sub>), 24.6 (CH), 24.5 (CH<sub>3</sub>), 15.16 (CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ 34.0 ppm. ESI-MS: (m/z): calcd for C<sub>21</sub>H<sub>27</sub>BO<sub>3</sub>H, [M+H]<sup>+</sup>: 339.2132; found, 339.2128.

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



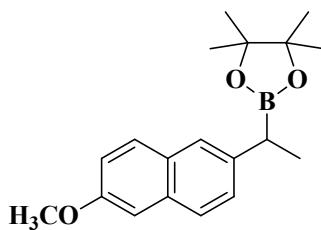
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ 7.80–7.74 (m, 3H), 7.65 (s, 1H), 7.45–7.37 (m, 3H), 2.63 (q, *J* = 7.5 Hz, 1H), 1.43 (d, *J* = 7.5 Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ 142.7 (C<sub>q</sub>), 134.0 (C<sub>q</sub>), 131.8 (C<sub>q</sub>), 127.8 (CH), 127.6 (CH), 127.5 (CH), 127.3 (CH), 125.8 (CH), 125.4 (CH), 124.9 (CH), 83.5 (C<sub>q</sub>), 24.8 (CH), 24.7 (CH<sub>3</sub>), 17.0 (CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ 34.49 ppm.

#### **2-(1-(biphenyl-4-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane<sup>1</sup>**



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ 7.60–7.58 (m, 2H), 7.52–7.50 (m, 2H), 7.43–7.40 (m, 2H), 7.32–7.29 (m, 3H), 2.48 (q, *J* = 7.6 Hz, 1H), 1.37 (d, *J* = 7.6 Hz, 3H), 1.23 (s, 6H), 1.21 (s, 6H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ 144.1 (C<sub>q</sub>), 141.2 (C<sub>q</sub>), 137.9 (C<sub>q</sub>), 128.6 (CH), 128.1 (CH), 127.0 (CH), 126.9 (CH), 126.8 (CH), 83.3 (C<sub>q</sub>), 24.6 (CH), 24.6 (CH<sub>3</sub>), 17.0 (CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ 33.58 ppm.

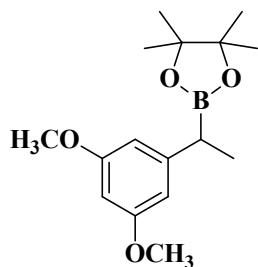
#### **2-(1-(6-methoxynaphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane<sup>4</sup>**



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ 7.69–7.65 (m, 2H), 7.59 (m, 1H), 7.38–7.35 (m, 1H), 7.13–7.1 (m, 2H), 3.92 (s, 3H), 2.60 (q, *J* = 4.8 Hz, 1H), 1.43 (d, *J* = 4.8 Hz, 3H), 1.22 (s, 6H), 1.21 (s, 6H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ 156.9 (C<sub>q</sub>), 140.2 (C<sub>q</sub>), 132.6 (C<sub>q</sub>), 129.3 (C<sub>q</sub>), 128.9 (CH), 127.6 (CH),

126.5 (CH), 125.1 (CH), 118.3 (CH), 105.6 (CH), 83.3 (C<sub>q</sub>), 55.2 (CH<sub>3</sub>), 24.6 (CH), 24.5 (CH<sub>3</sub>), 16.9 (CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ 33.37 ppm.

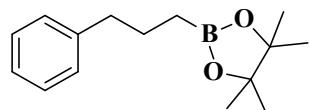
### **2-(1-(3,5-dimethoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane**



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ 6.40 (s, 2H), 6.26 (s, 1H), 3.77 (s, 6H), 2.38 (q, *J* = 7.5 Hz, 1H), 1.30 (d, *J* = 7.5 Hz, 3H), 1.22 (s, 6H), 1.21 (s, 6H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ 160.6 (C<sub>q</sub>), 147.4 (C<sub>q</sub>), 105.9 (CH), 97.4 (CH), 83.3 (C<sub>q</sub>), 55.1(CH<sub>3</sub>), 24.6 (CH), 24.6 (CH<sub>3</sub>), 16.9 (CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ 33.4 ppm. ESI-MS: (m/z): calcd for C<sub>16</sub>H<sub>25</sub>BO<sub>4</sub>H, [M+H]<sup>+</sup>: 293.1924; found, 293.1929.

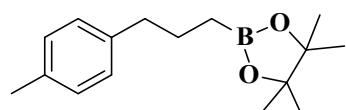
### **Spectroscopic data of products in catalytic hydroboration of aliphatic alkenes.**

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



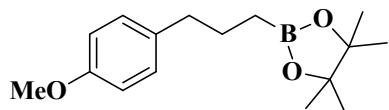
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ 7.25 (d, *J* = 7.3 Hz, 2H), 7.18 – 7.16 (m, 3H), 2.61 (t, *J* = 7.7 Hz, 2H), 1.77 – 1.69 (m, 2H), 1.24 (s, 12H), 0.83 (t, *J* = 7.9 Hz, 2H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ 142.7 (C<sub>q</sub>), 128.5 (CH), 128.1 (CH), 125.5 (CH), 82.9 (C<sub>q</sub>), 38.5 (CH<sub>2</sub>), 26.0 (CH<sub>2</sub>CH<sub>2</sub>), 24.8 (CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ 34.1 ppm.

#### **4,4,5,5-tetramethyl-2-(3-p-tolylpropyl)-1,3,2-dioxaborolane**



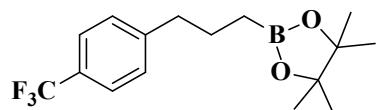
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ 7.07 (s, 4H), 2.58 – 2.55 (m, 2H), 2.30 (s, 3H), 1.74 – 1.67 (m, 2H), 1.24 (d, *J* = 6.0 Hz, 12H), 0.81 (t, *J* = 7.9 Hz, 2H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ 139.6 (C<sub>q</sub>), 134.9 (C<sub>q</sub>), 128.8 (CH), 128.4 (CH), 82.91 (C<sub>q</sub>), 38.1 (CH<sub>2</sub>), 26.2 (CH<sub>2</sub>CH<sub>2</sub>), 24.8 (CH<sub>3</sub>), 20.9 (CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ 34.1 ppm. ESI-MS: (m/z): calcd for C<sub>16</sub>H<sub>25</sub>BNaO<sub>2</sub>, [M+Na]<sup>+</sup>: 283.1845; found, 283.1841.

**2-(3-(4-Methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane<sup>6</sup>**



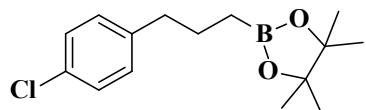
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ 7.09 (d, *J* = 8.2, 2H), 6.81 (d, *J* = 8.2, 2H), 3.78 (s, 2H), 2.55 (t, *J* = 7.6, 2H), 1.72–1.68 (m, 2H), 1.24 (s, 12H), 0.81 (t, *J* = 8.0, 2H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ 157.6 (C<sub>q</sub>), 134.8 (C<sub>q</sub>), 129.3 (CH), 113.6 (CH), 82.9 (C<sub>q</sub>), 55.2 (CH<sub>3</sub>), 37.6 (CH<sub>2</sub>), 26.2 (CH<sub>2</sub>CH<sub>2</sub>), 24.8 (CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ 34.08 ppm.

**4,4,5,5-Tetramethyl-2-(3-(4-trifluoromethylphenyl)propyl)-1,3,2-dioxaborolane<sup>6</sup>**



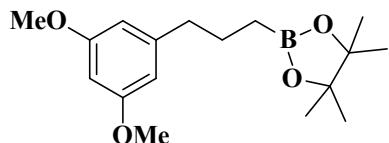
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.27 (m, 2H), 2.66 (t, *J* = 7.7 Hz, 2H), 1.78–1.70 (m, 2H), 1.24 (s, 12H), 0.82 (t, *J* = 7.8 Hz, 2H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ 146.7 (C<sub>q</sub>), 128.8 (CH), 128.1 (q, *J*<sub>C-F</sub> = 32.2, C<sub>q</sub>) 125.1 (q, *J*<sub>C-F</sub> = 3.8, CH), 124.0 (q, *J*<sub>C-F</sub> = 271.6, CF<sub>3</sub>), 83.0 (C<sub>q</sub>), 38.2 (CH<sub>2</sub>), 25.7 (CH<sub>2</sub>CH<sub>2</sub>), 24.8 (CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ 34.0 ppm. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -62.1 ppm.

**2-(3-(4-chlorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane**



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ 7.24–7.18 (m, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 2.57 (t, *J* = 7.7 Hz, 2H), 1.73–1.66 (m, 2H), 1.24 (s, 12H), 0.80 (t, *J* = 7.9 Hz, 2H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ 141.0 (C<sub>q</sub>), 131.2 (C<sub>q</sub>), 129.8 (CH), 128.2 (CH), 82.9 (C<sub>q</sub>), 37.8 (CH<sub>2</sub>), 25.9 (CH<sub>2</sub>CH<sub>2</sub>), 24.8 (CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ 34.0 ppm. ESI-MS: (m/z): calcd for C<sub>15</sub>H<sub>22</sub>BClNaO<sub>2</sub>, [M+Na]<sup>+</sup>: 303.1299; found, 303.1295.

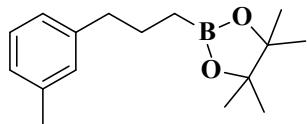
**2-(3-(3,5-dimethoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane**



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ 6.34 (d, *J* = 2.0 Hz, 2H), 6.29 (s, 1H), 3.77 (s, 6H), 2.55 (t, *J* = 7.7 Hz, 2H), 1.77–1.65 (m, 2H), 1.24 (s, 12H), 0.82 (t, *J* = 7.9 Hz, 2H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ 160.6 (C<sub>q</sub>), 145.1 (C<sub>q</sub>), 106.6 (CH), 97.7 (CH), 82.8 (C<sub>q</sub>), 55.2 (CH<sub>3</sub>), 38.9 (CH<sub>2</sub>), 25.8 (CH<sub>2</sub>CH<sub>2</sub>),

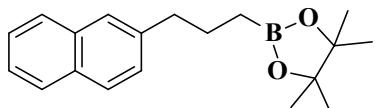
24.8 (CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ 34.14 ppm. ESI-MS: (m/z): calcd for C<sub>17</sub>H<sub>27</sub>BNaO<sub>4</sub>, [M+Na]<sup>+</sup>: 329.1900; found, 329.1906.

#### 4,4,5,5-tetramethyl-2-(3-m-tolylpropyl)-1,3,2-dioxaborolane



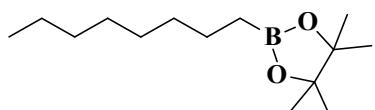
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ 7.15 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 4.6 Hz, 2H), 6.97 (s, 1H), 2.57 (t, *J* = 7.7 Hz, 2H), 2.32 (s, 3H), 1.72 (m, 2H), 1.24 (s, 12H), 0.83 (t, *J* = 7.9 Hz, 2H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ 142.6 (C<sub>q</sub>), 137.6 (C<sub>q</sub>), 129.3 (CH), 128.0 (CH), 126.2 (CH), 125.5 (CH), 82.9 (C<sub>q</sub>), 38.5 (CH<sub>2</sub>), 26.0 (CH<sub>2</sub>CH<sub>2</sub>), 24.8 (CH<sub>3</sub>), 21.3 (CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ 34.1 ppm. ESI-MS: (m/z): calcd for C<sub>16</sub>H<sub>25</sub>BNaO<sub>2</sub>, [M+Na]<sup>+</sup>: 283.1845; found, 283.1841.

#### 4,4,5,5-tetramethyl-2-(3-(naphthalen-2-yl)propyl)-1,3,2-dioxaborolane<sup>7</sup>



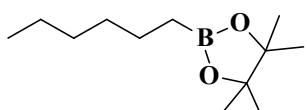
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ 7.78–7.73 (m, 3H), 7.62 (s, 1H), 7.46–7.38 (m, 2H), 7.34 (d, *J* = 8.3 Hz, 1H), 2.79 (t, *J* = 7.7 Hz, 2H), 1.87–1.79 (m, 1H), 1.24 (s, 12H), 0.88 (t, *J* = 7.8 Hz, 2H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ 140.2 (C<sub>q</sub>), 133.6 (C<sub>q</sub>), 131.9 (C<sub>q</sub>), 127.6 (CH), 127.5 (CH), 127.5 (CH), 127.4 (CH), 126.4 (CH), 125.7 (CH), 124.9 (CH), 82.9 (C<sub>q</sub>), 38.6 (CH<sub>2</sub>), 25.9 (CH<sub>2</sub>CH<sub>2</sub>), 24.8 (CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ 34.11 ppm.

#### 4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane<sup>8</sup>

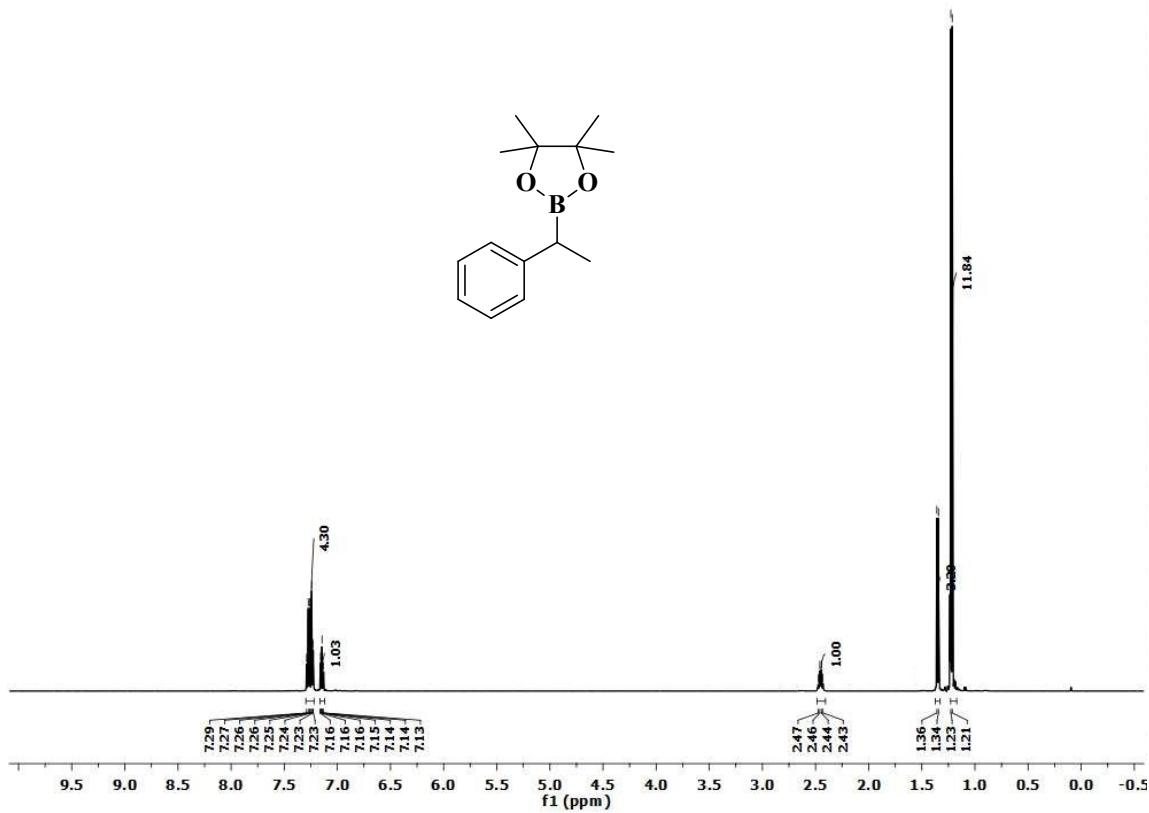


<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ 1.43 – 1.34 (m, 2H), 1.29 – 1.24 (m, 22H), 0.86 (q, *J* = 6.6 Hz, 3H), 0.76 (t, *J* = 7.8 Hz, 2H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ 82.8 (C<sub>q</sub>), 32.4 (CH<sub>2</sub>), 31.9 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 29.2 (CH<sub>2</sub>), 24.8 (CH<sub>3</sub>), 24.0 (CH<sub>2</sub>), 22.6 (CH<sub>2</sub>CH<sub>2</sub>), 14.1 (CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ 34.17 ppm.

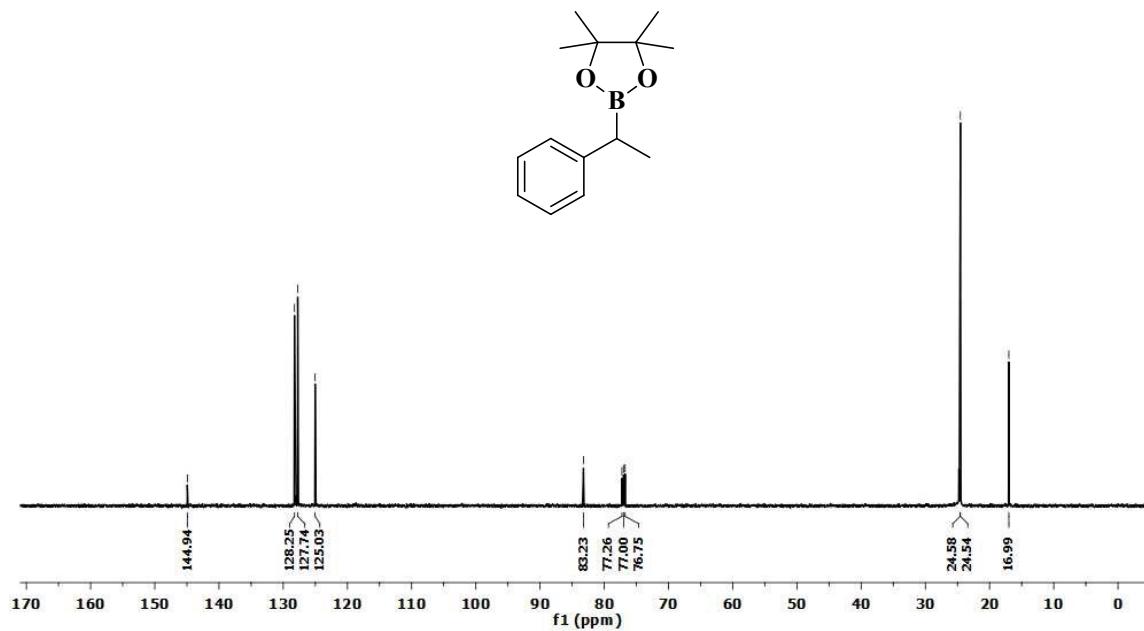
#### 2-hexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane<sup>6</sup>



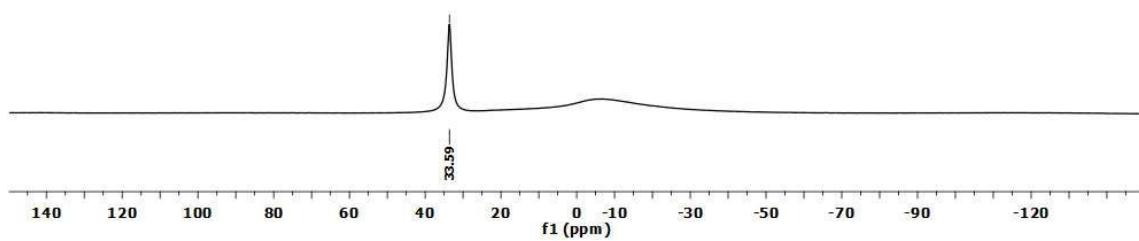
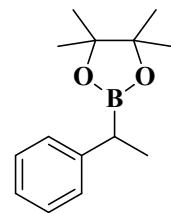
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ 1.41–1.39 (m, 2H), 1.31 – 1.24 (m, 18H), 0.86 (t, *J* = 6.8 Hz, 3H), 0.76 (t, *J* = 7.7 Hz, 2H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ 82.8 (C<sub>q</sub>), 32.1 (CH<sub>2</sub>), 31.6 (CH<sub>2</sub>), 24.7 (CH<sub>3</sub>), 23.9 (CH<sub>2</sub>), 22.5 (CH<sub>2</sub>CH<sub>2</sub>), 14.0 (CH<sub>3</sub>) ppm. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ 34.16 ppm



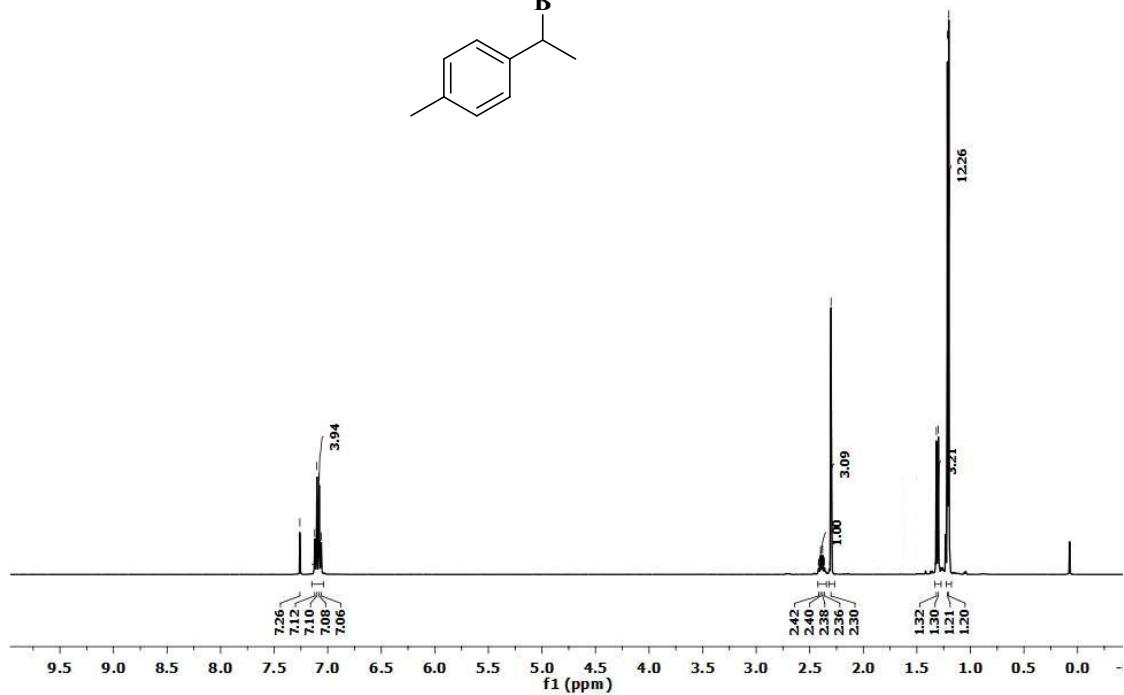
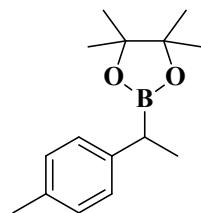
**Figure S1.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of 4,4,5,5-tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane



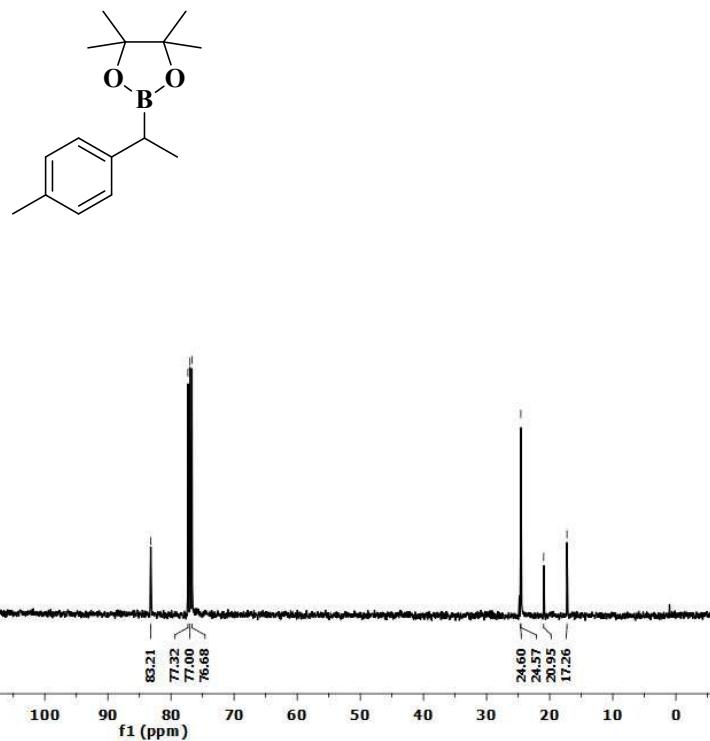
**Figure S2.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) of 4,4,5,5-tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane



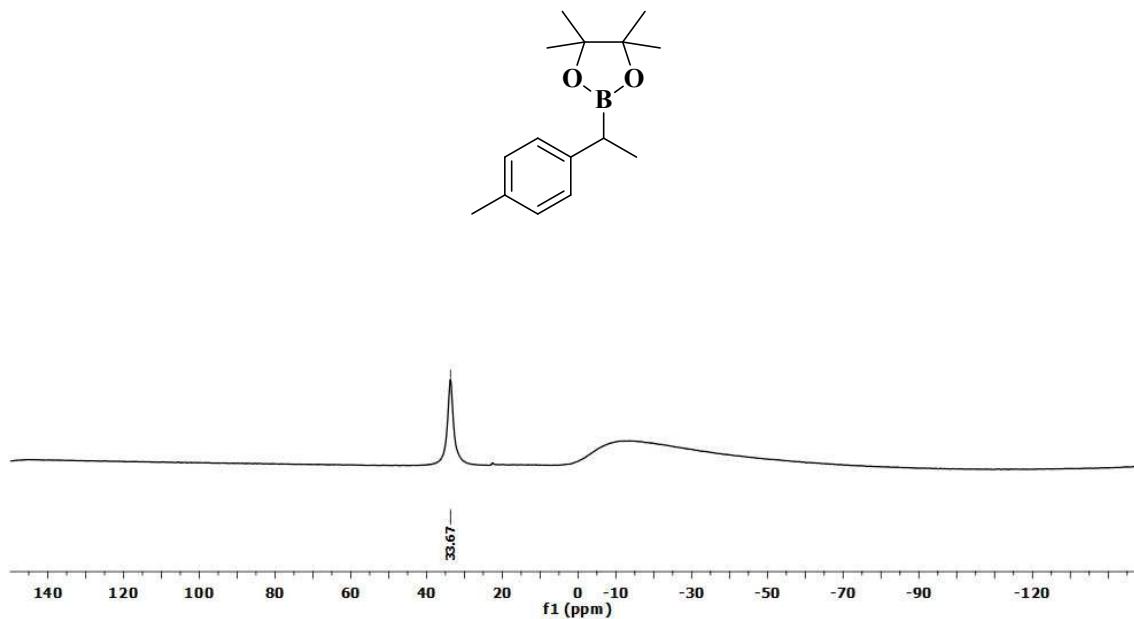
**Figure S3.**  $^{11}\text{B}$  NMR spectrum ( $\text{CDCl}_3$ ) of 4,4,5,5-tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane



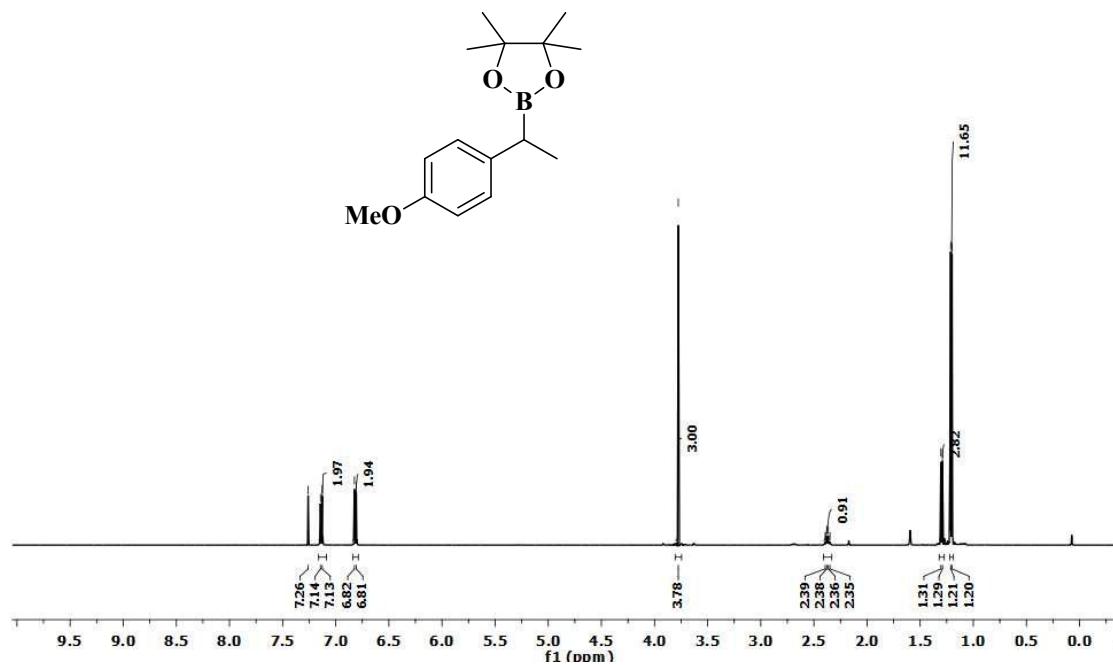
**Figure S4.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of 4,4,5,5-tetramethyl-2-(1-*p*-tolylethyl)-1,3,2 dioxaborolane.



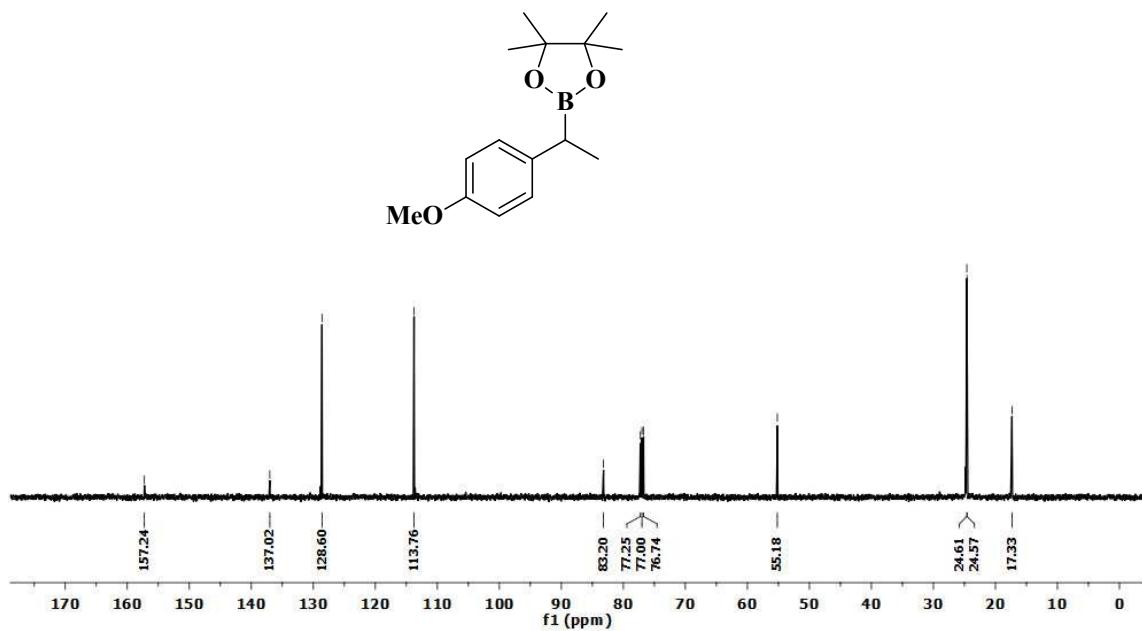
**Figure S5.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) of 4,4,5,5-tetramethyl-2-(1-*p*-tolylethyl)-1,3,2 dioxaborolane.



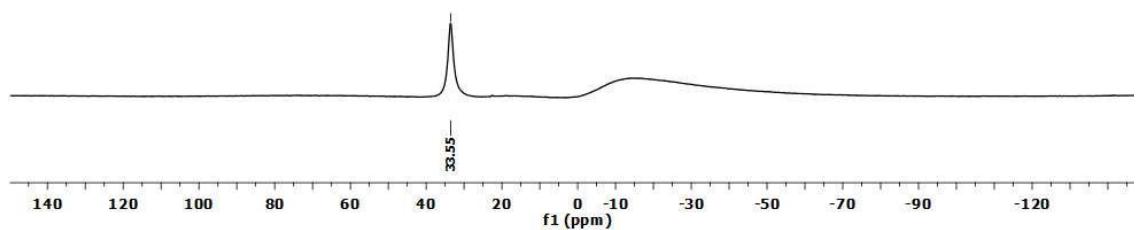
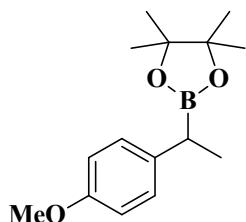
**Figure S6.**  $^{11}\text{B}$  NMR spectrum ( $\text{CDCl}_3$ ) of 4,4,5,5-tetramethyl-2-(1-*p*-tolylethyl)-1,3,2 dioxaborolane



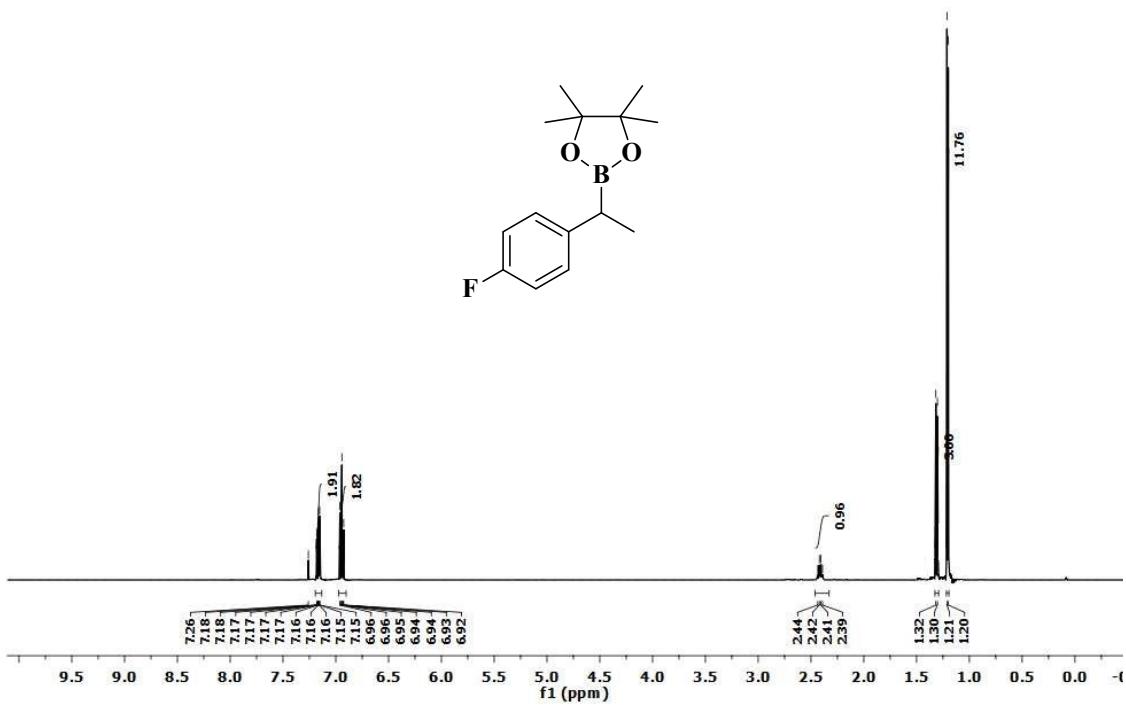
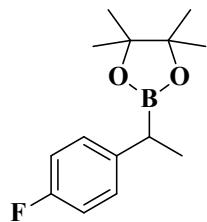
**Figure S7.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(1-(4-methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



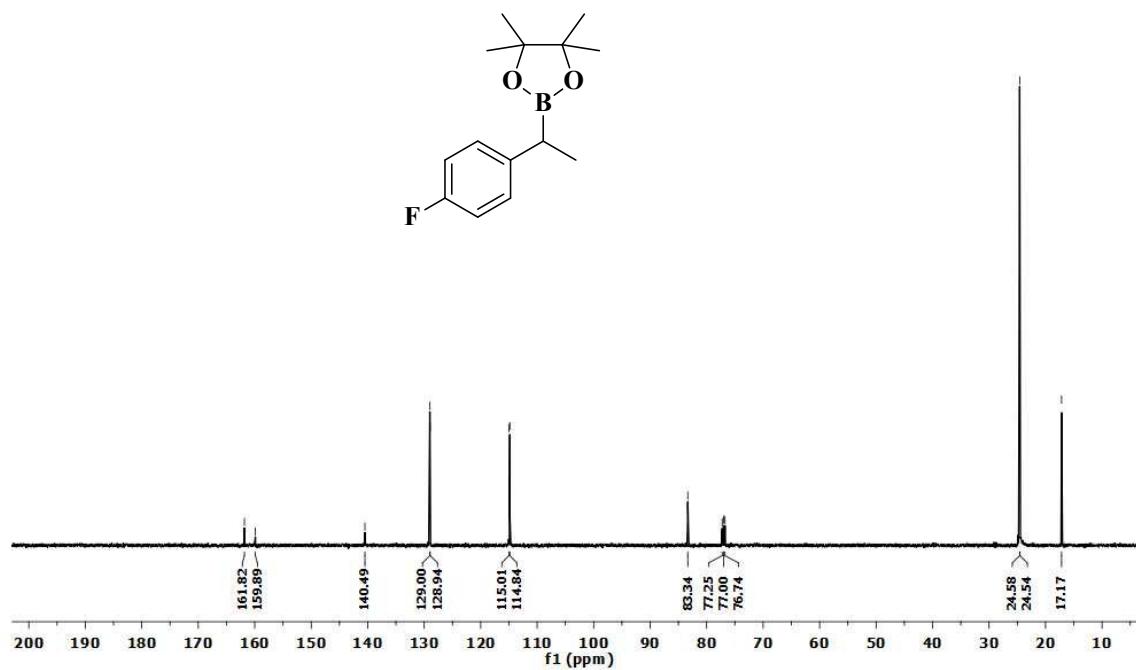
**Figure S8.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(1-(4-methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



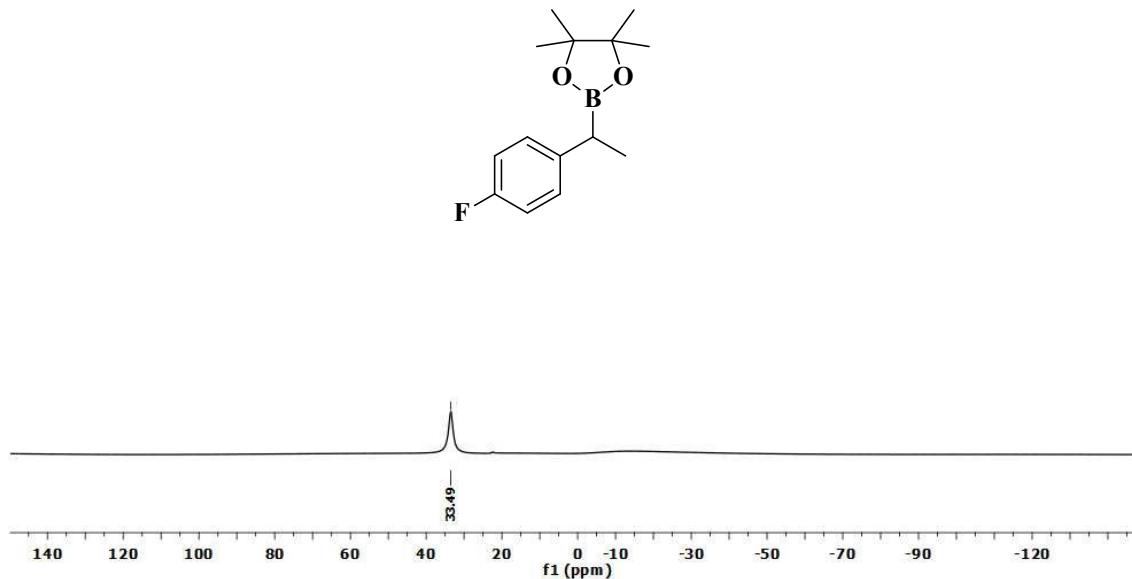
**Figure S9.**  $^{11}\text{B}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(1-(4-methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



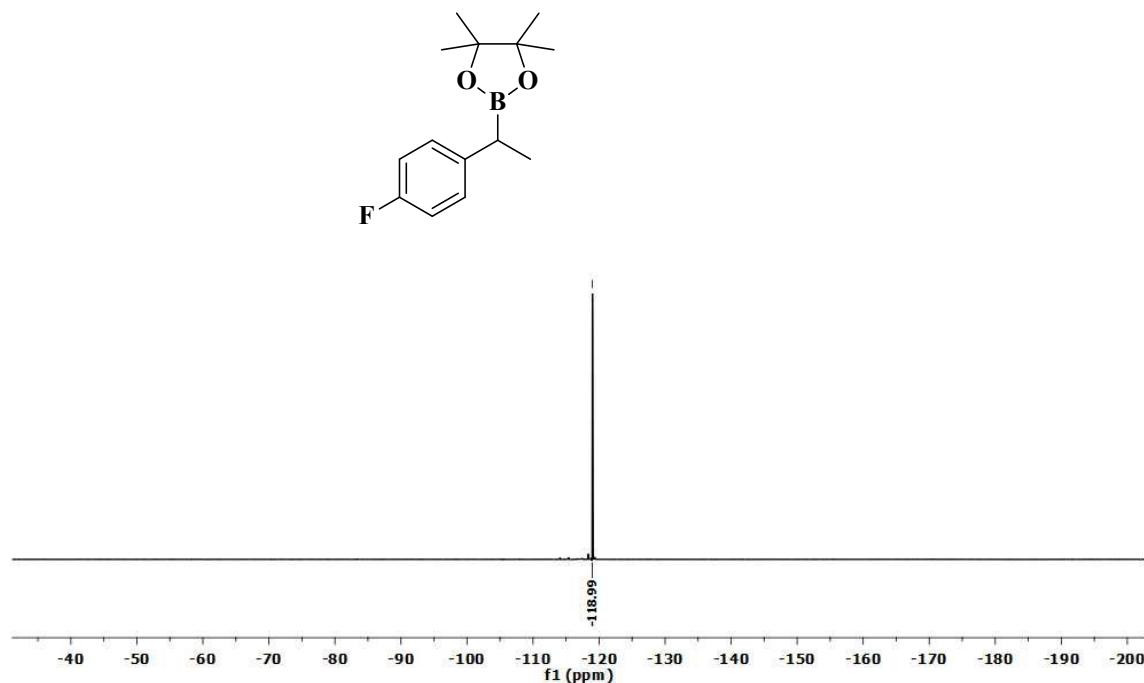
**Figure S10.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(1-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



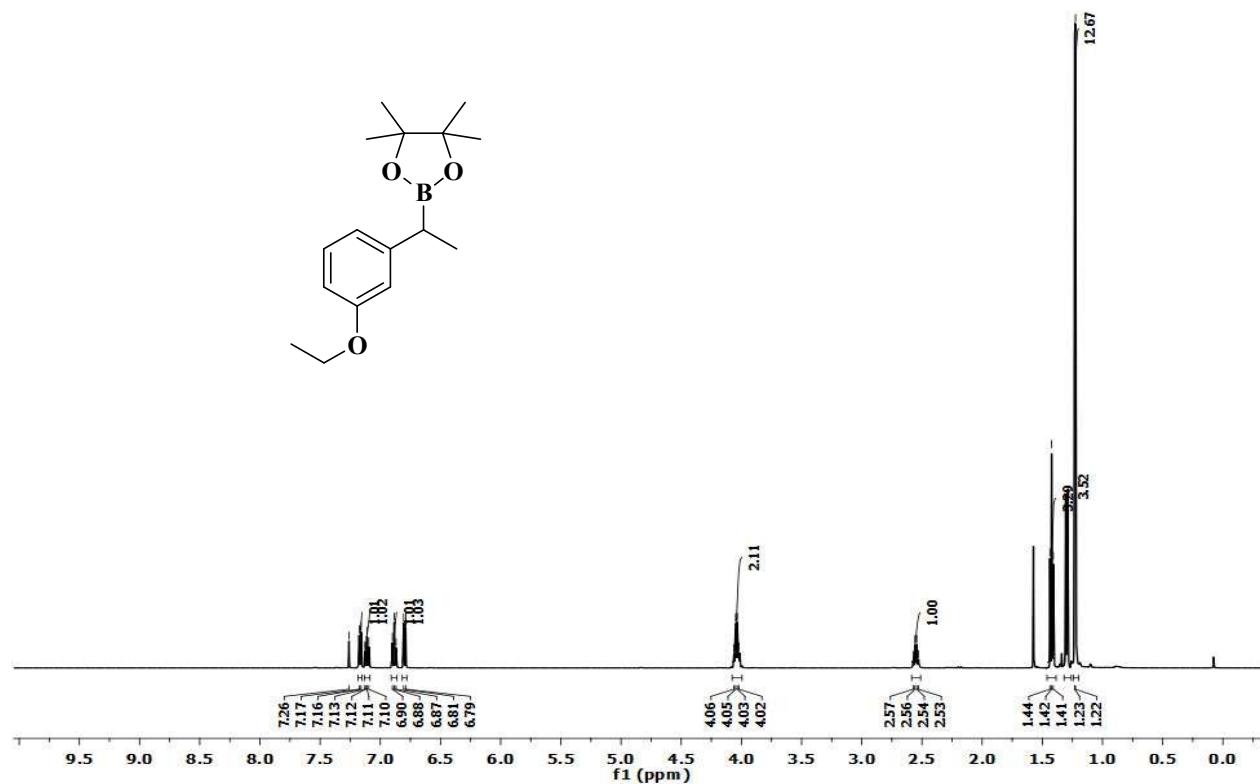
**Figure S11.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(1-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



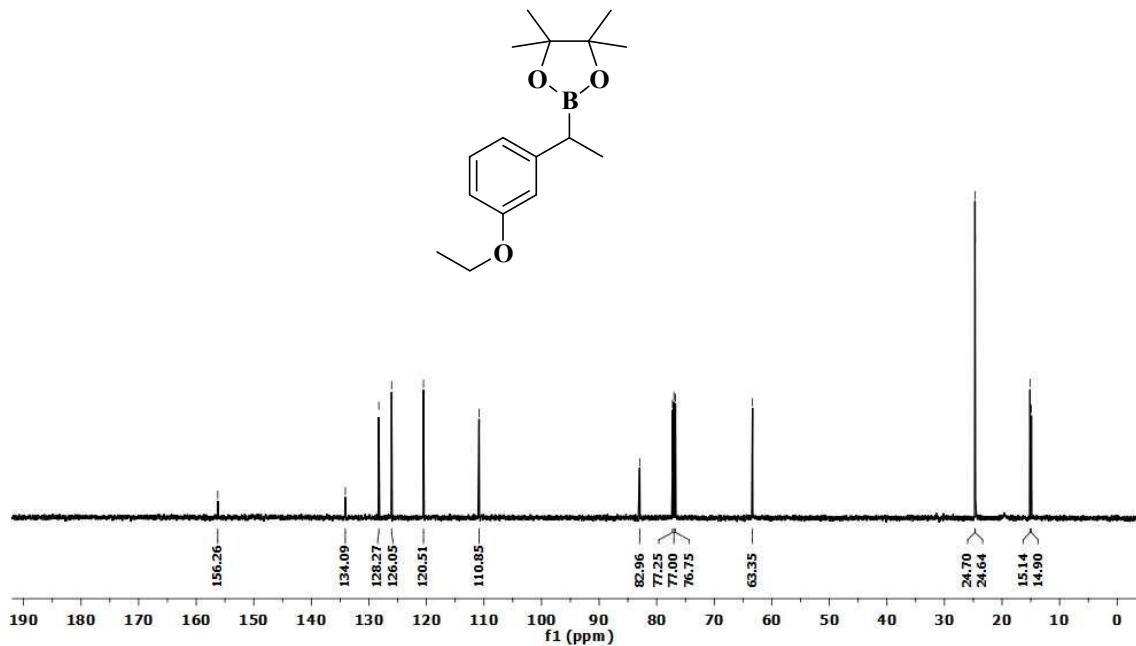
**Figure S12.**  $^{11}\text{B}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(1-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



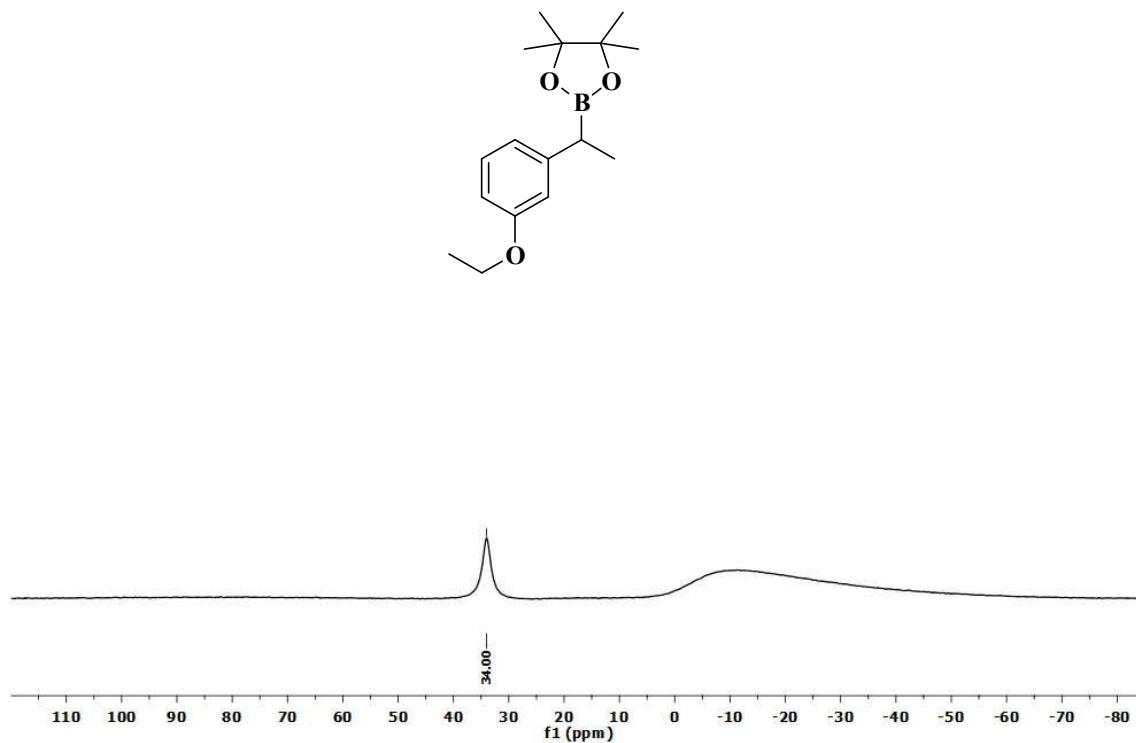
**Figure S13.**  $^{19}\text{F}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(1-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



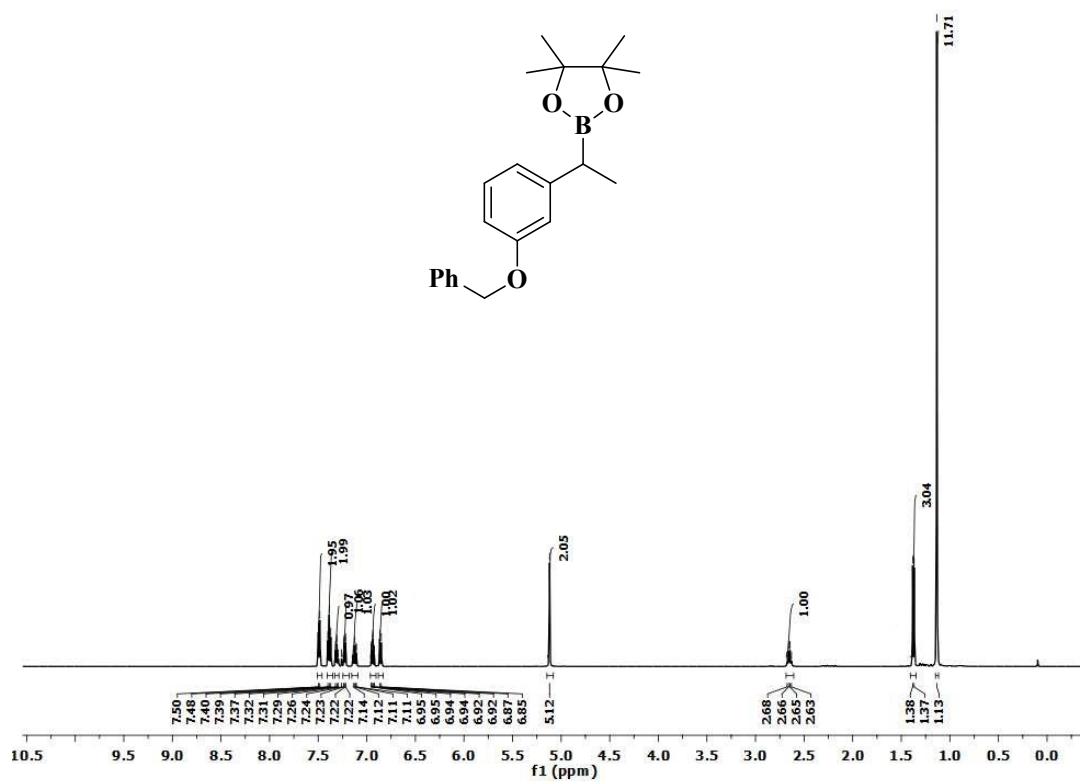
**Figure S14.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(1-(3-ethoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



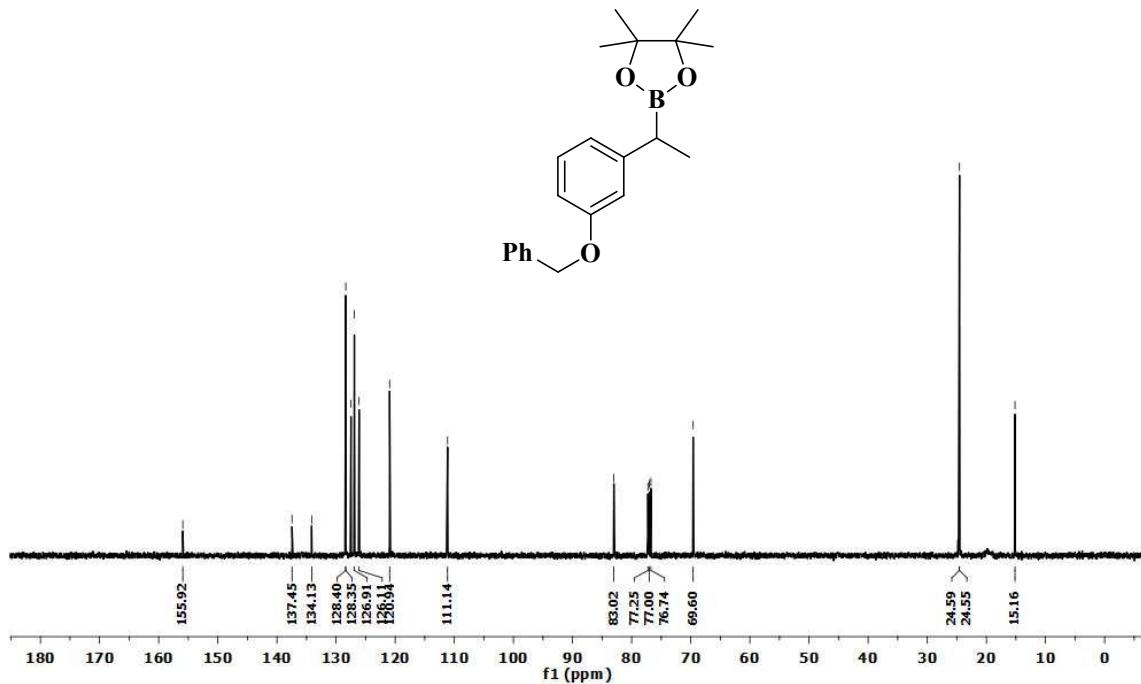
**Figure S15.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(1-(3-ethoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



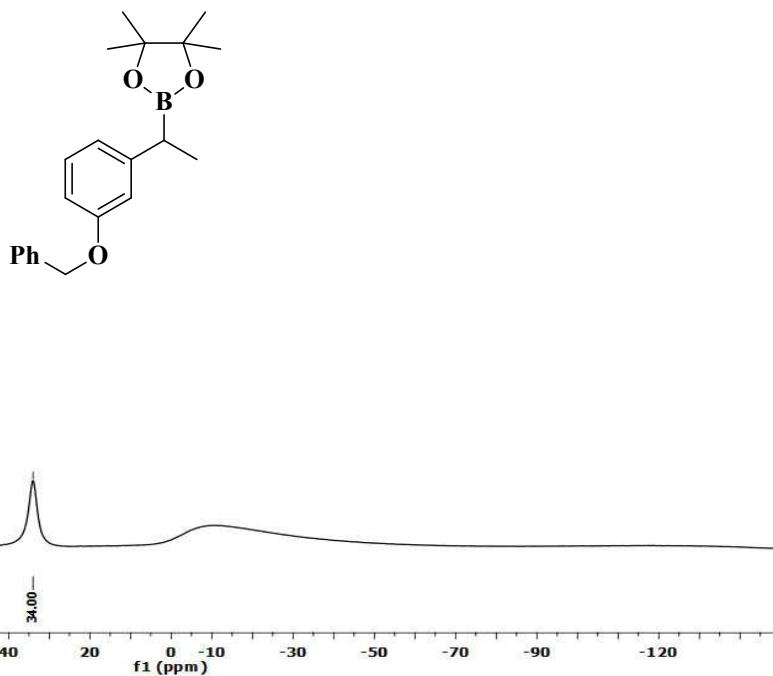
**Figure S16.**  $^{11}\text{B}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(1-(3-ethoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



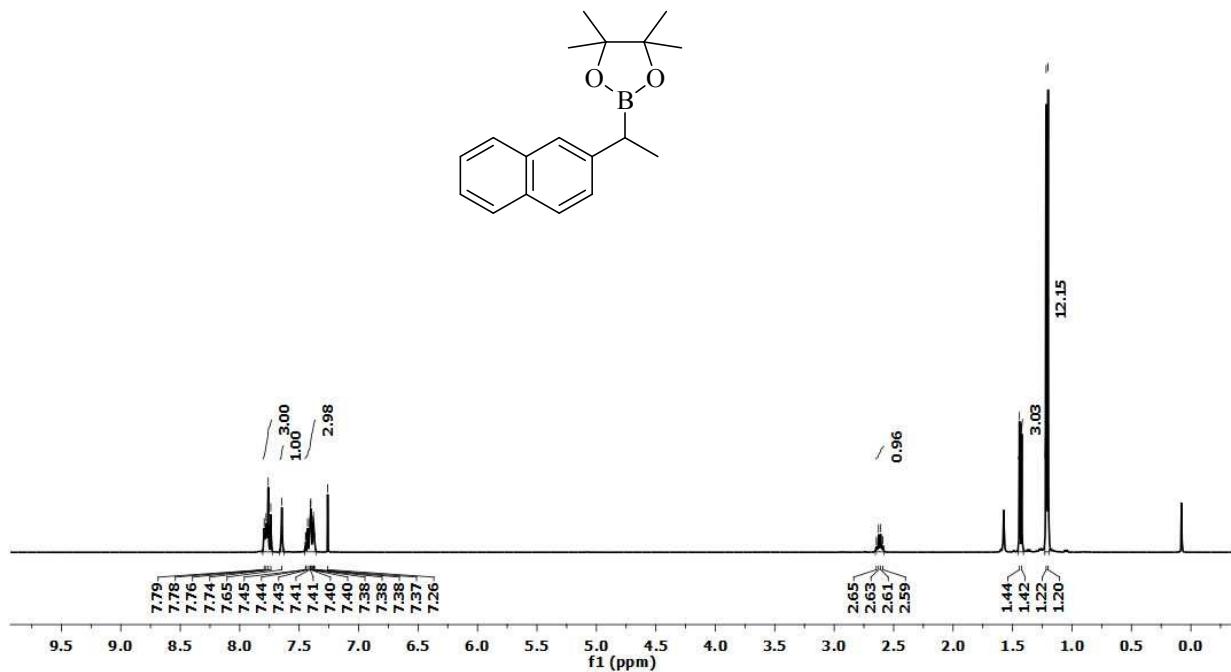
**Figure S17.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(1-(3-(benzyloxy)phenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



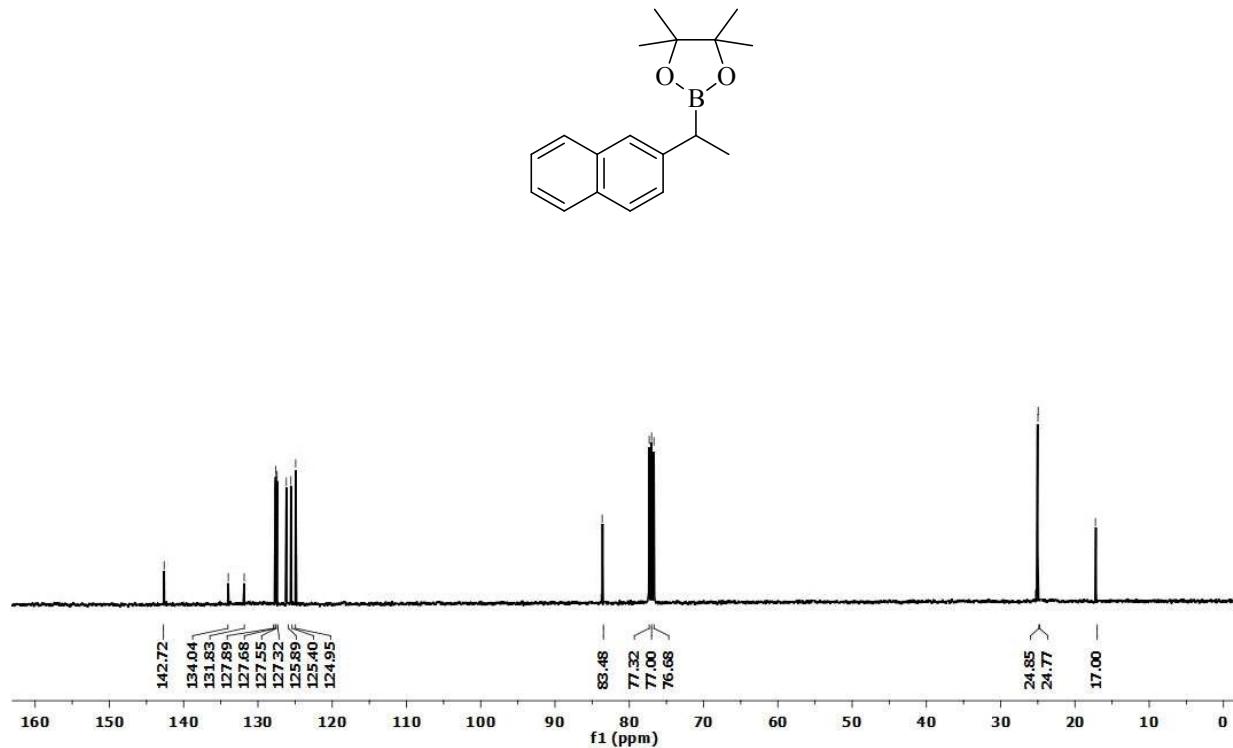
**Figure S18.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(1-(3-(benzyloxy)phenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



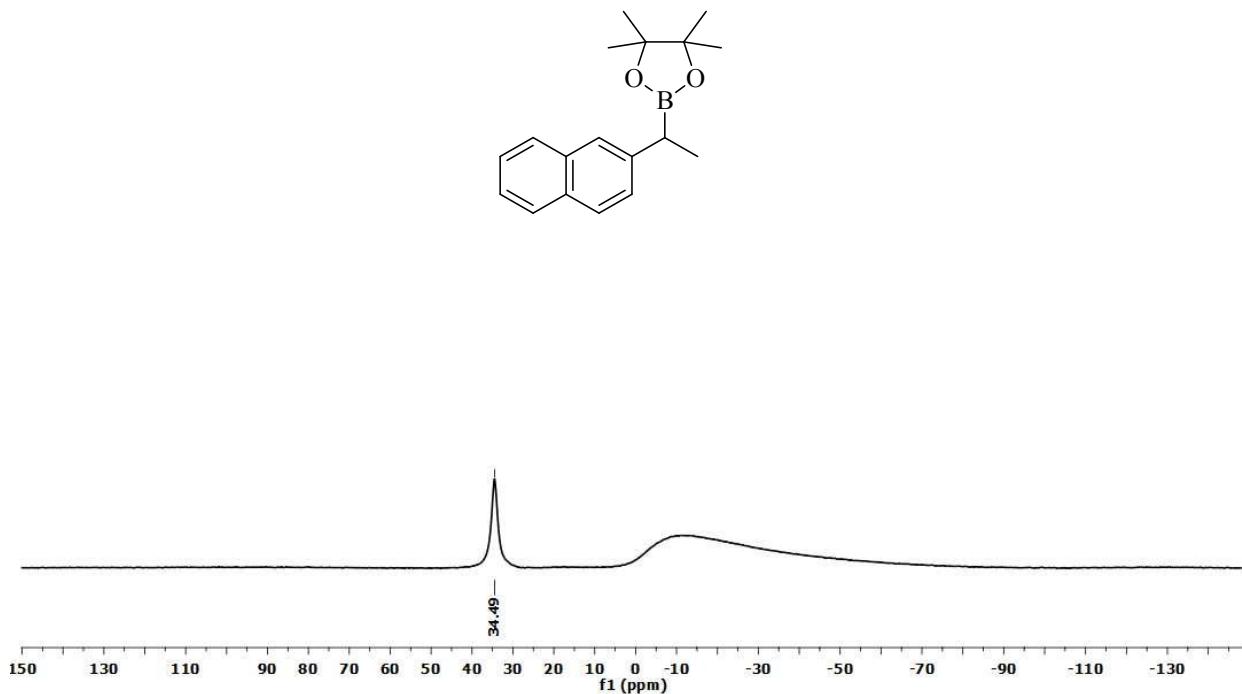
**Figure S19.**  $^{11}\text{B}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(1-(3-(benzyloxy)phenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



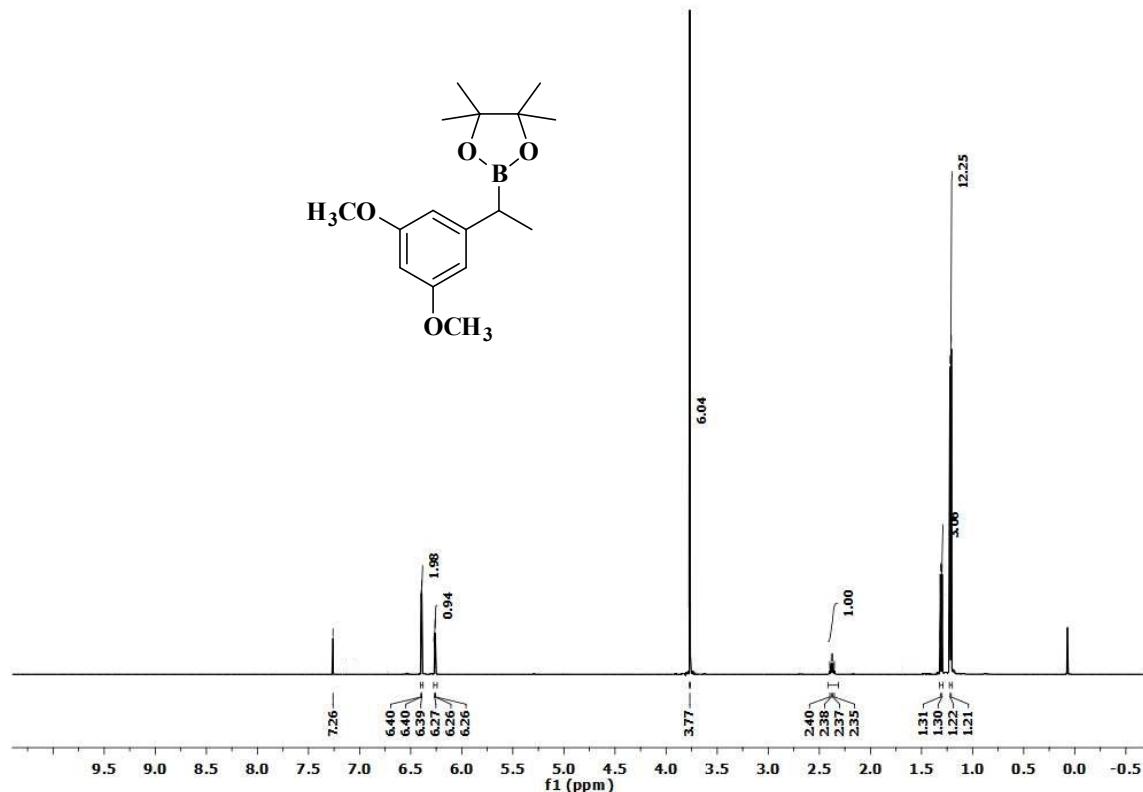
**Figure S20.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of 4,4,5,5-tetramethyl-2-(1-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane.



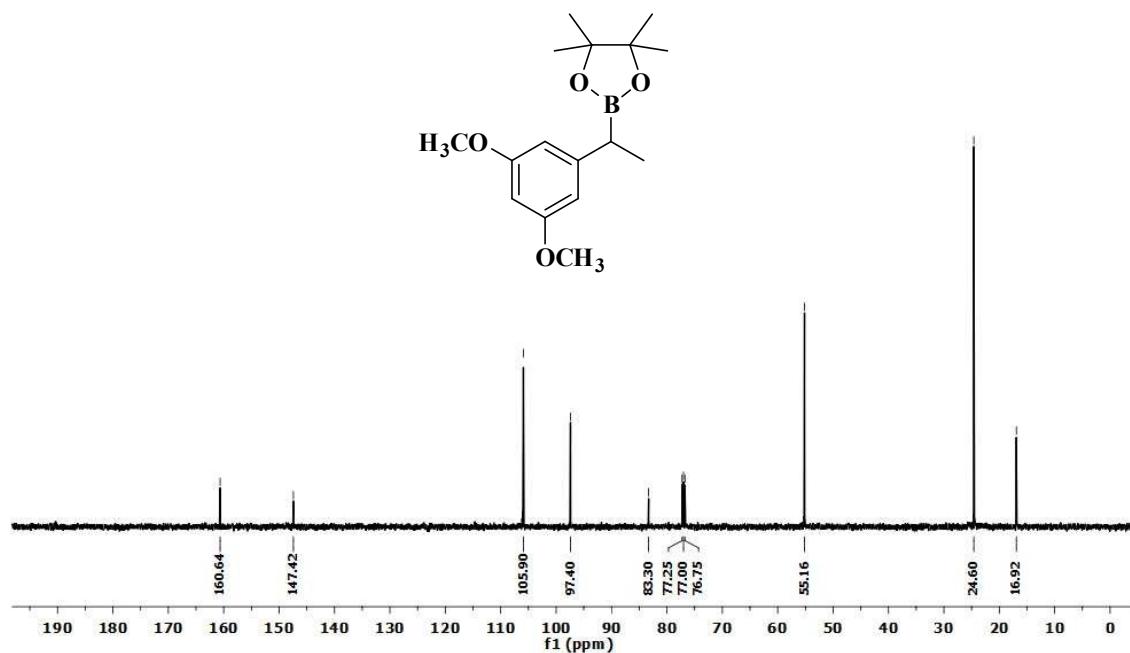
**Figure S21.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) of 4,4,5,5-tetramethyl-2-(1-naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane.



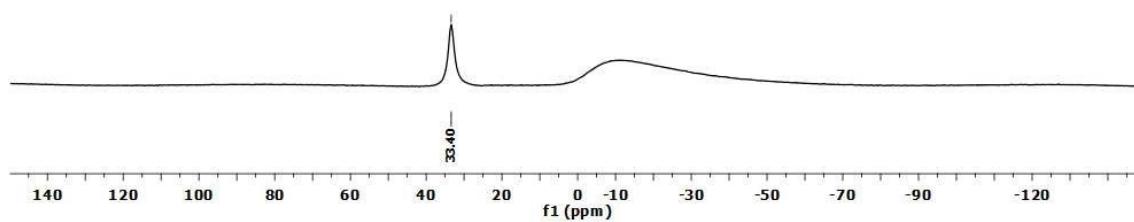
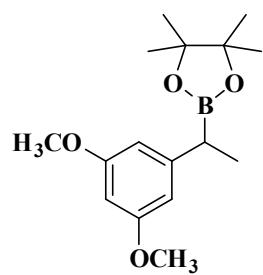
**Figure S22.**  $^{11}\text{B}$  NMR spectrum ( $\text{CDCl}_3$ ) of 4,4,5,5-tetramethyl-2-(1-naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane.



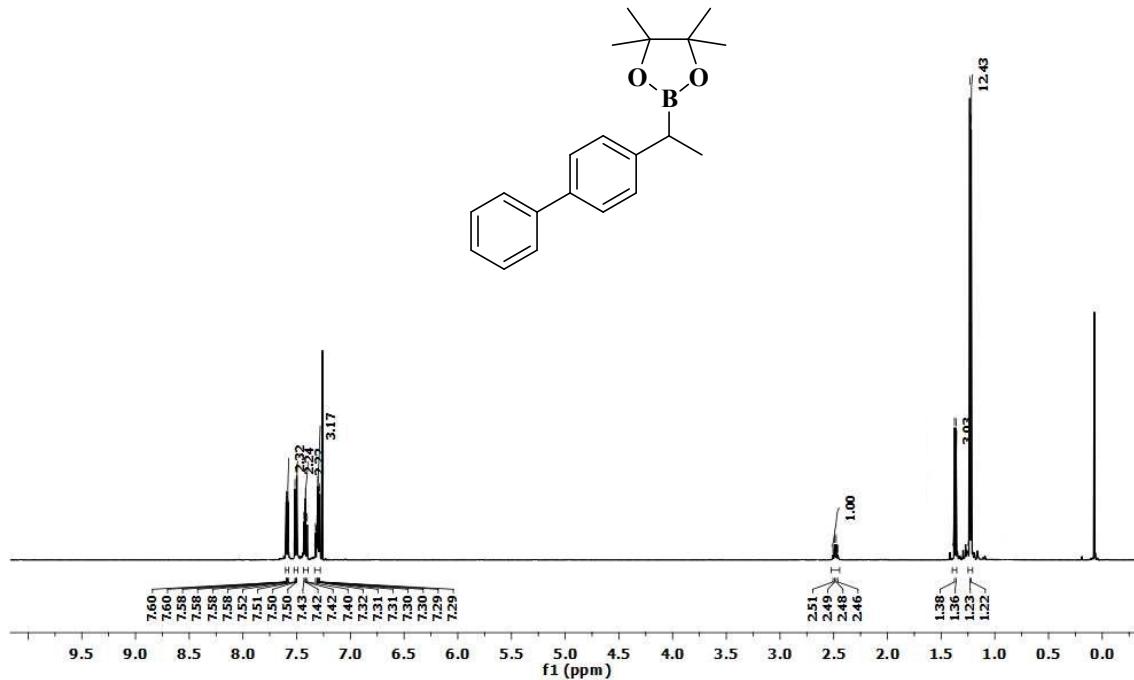
**Figure S23.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(1-(3,5-dimethoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



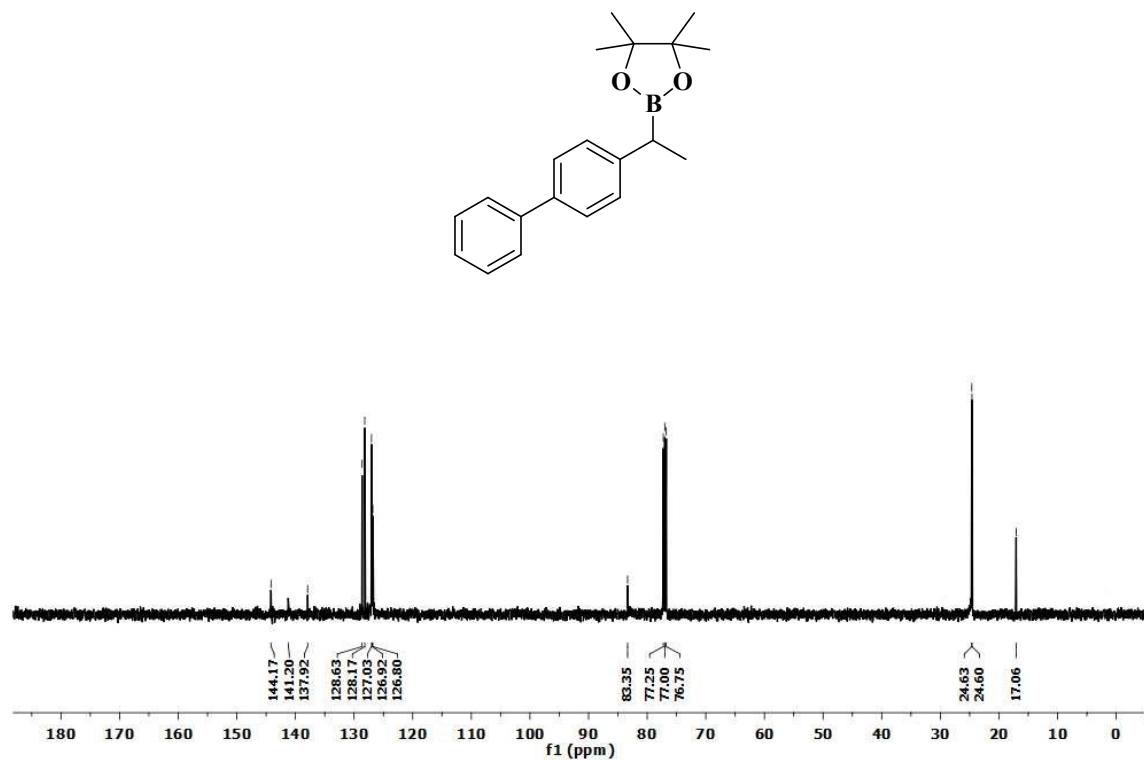
**Figure S24.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(1-(3,5-dimethoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



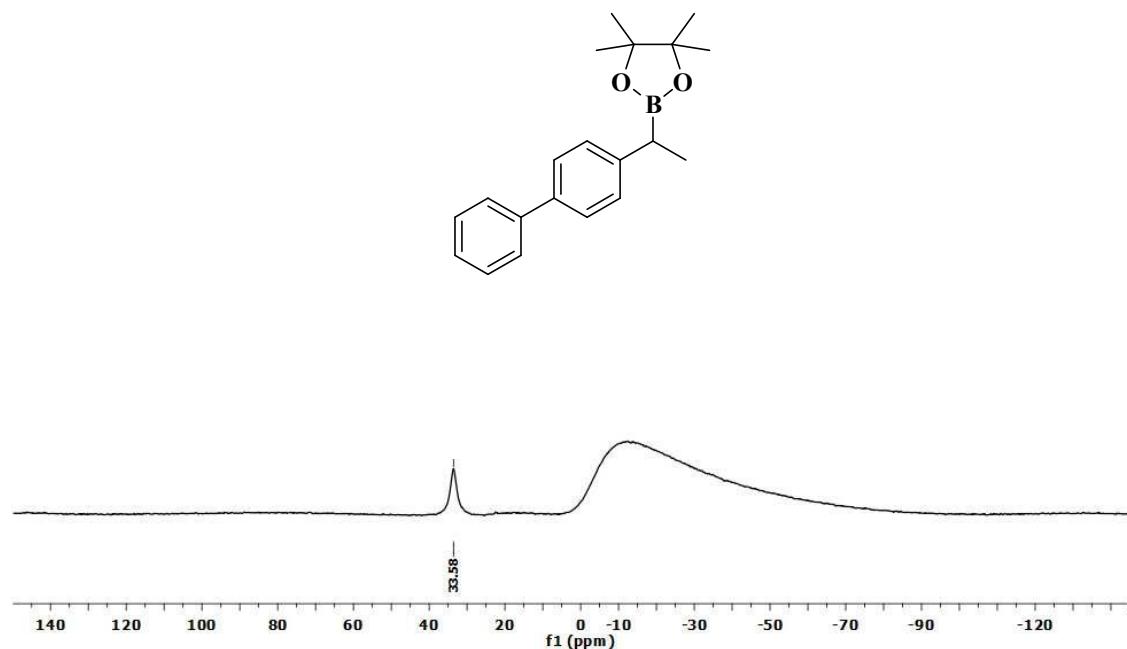
**Figure S25.**  $^{11}\text{B}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(1-(3,5-dimethoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



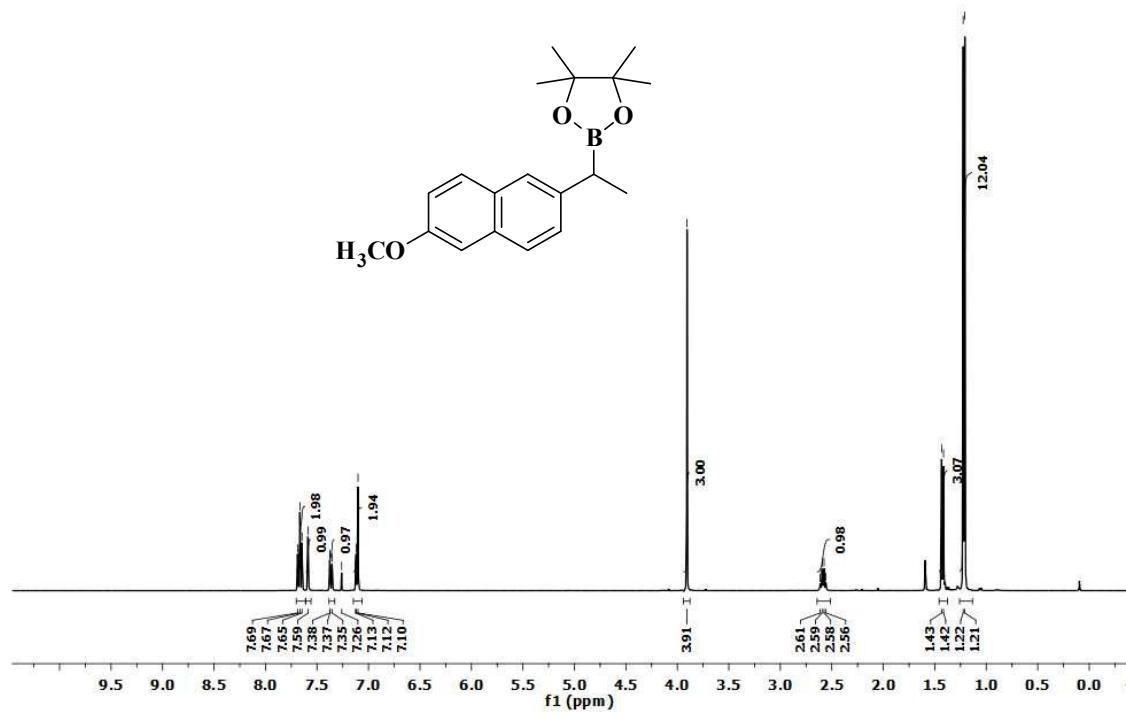
**Figure S26.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(1-(biphenyl-4-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



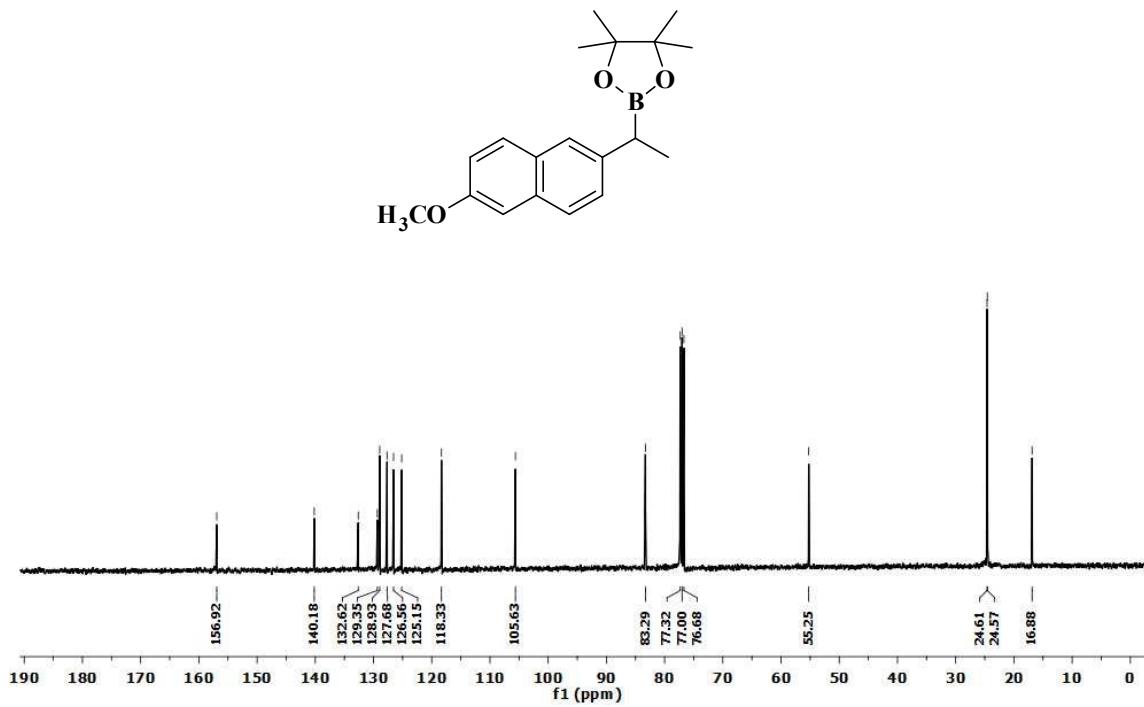
**Figure S27.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(1-(biphenyl-4-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



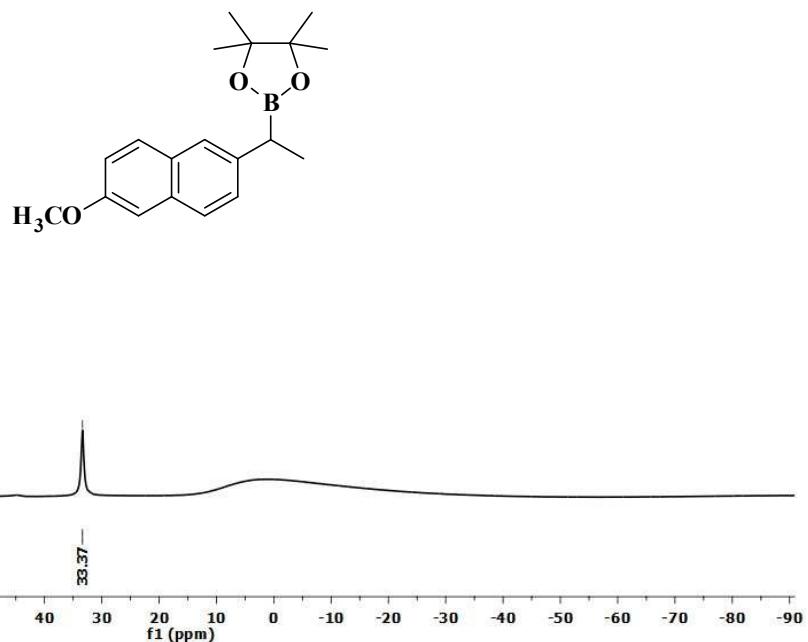
**Figure S28.**  $^{11}\text{B}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(1-(biphenyl-4-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



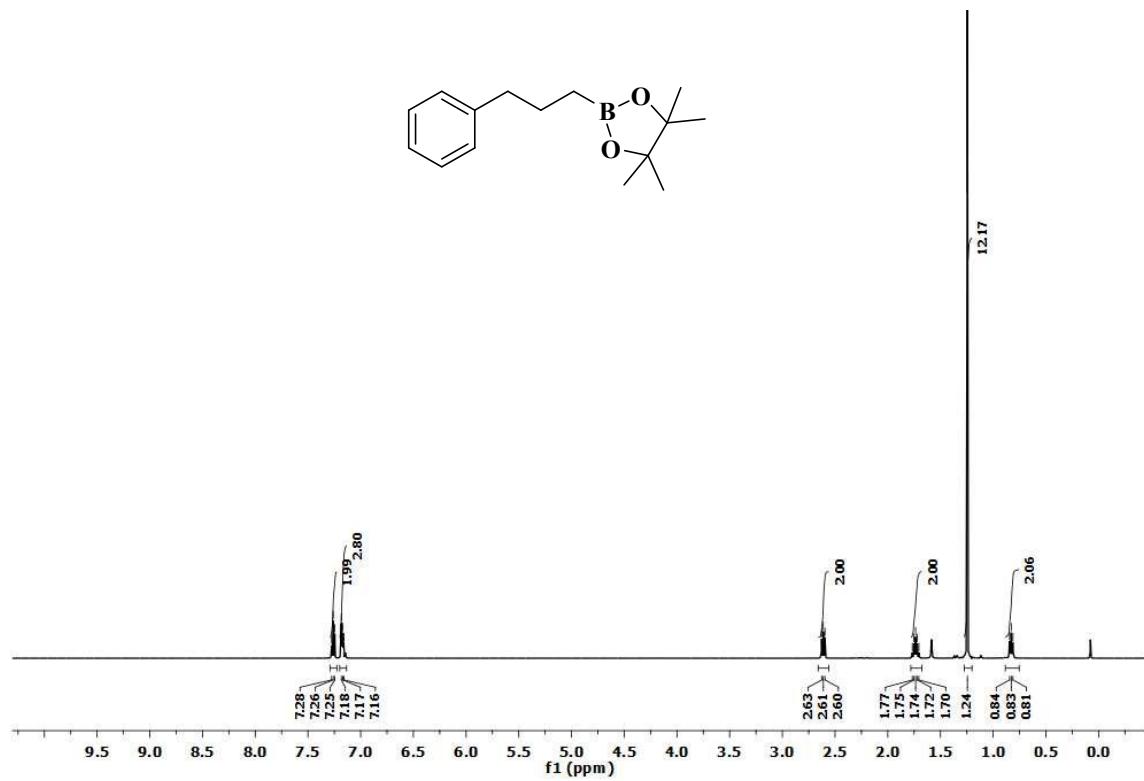
**Figure S29.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(1-(6-methoxynaphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



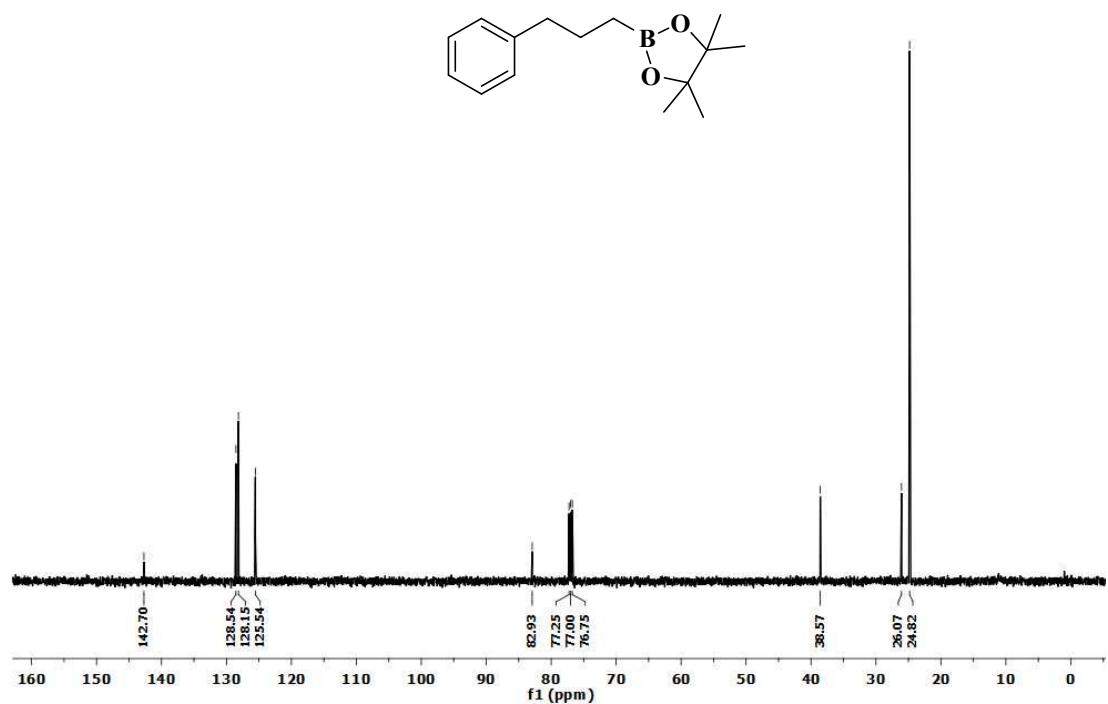
**Figure S30.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(1-(6-methoxynaphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



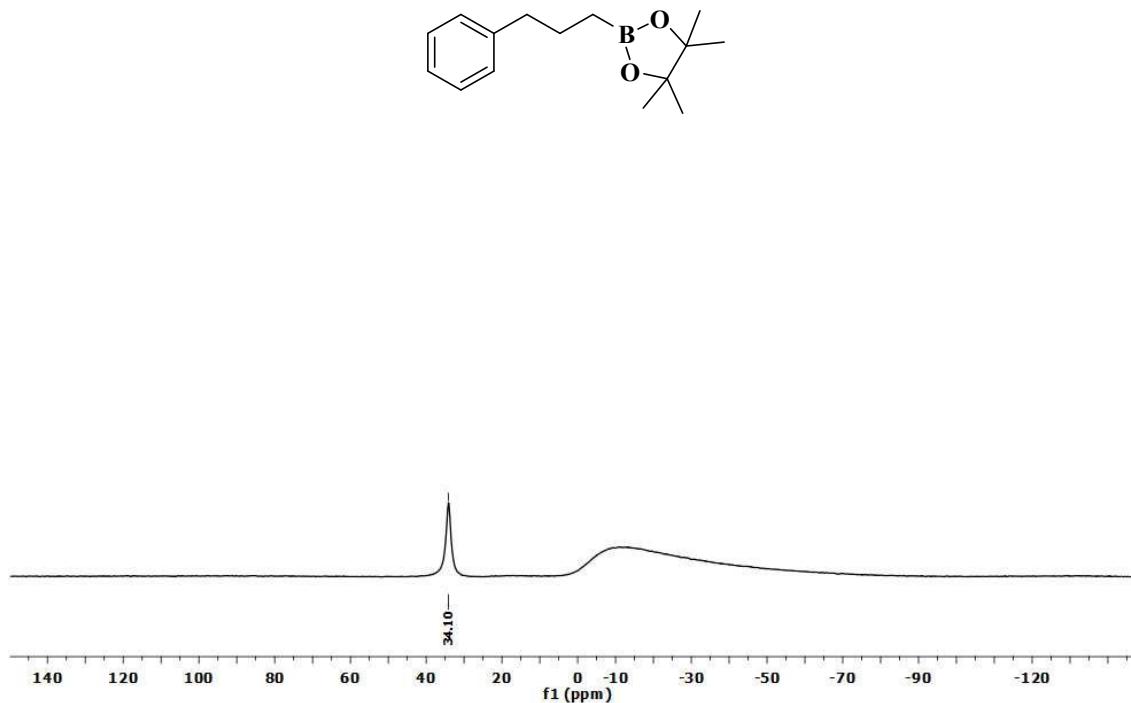
**Figure S31.**  $^{11}\text{B}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(1-(6-methoxynaphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



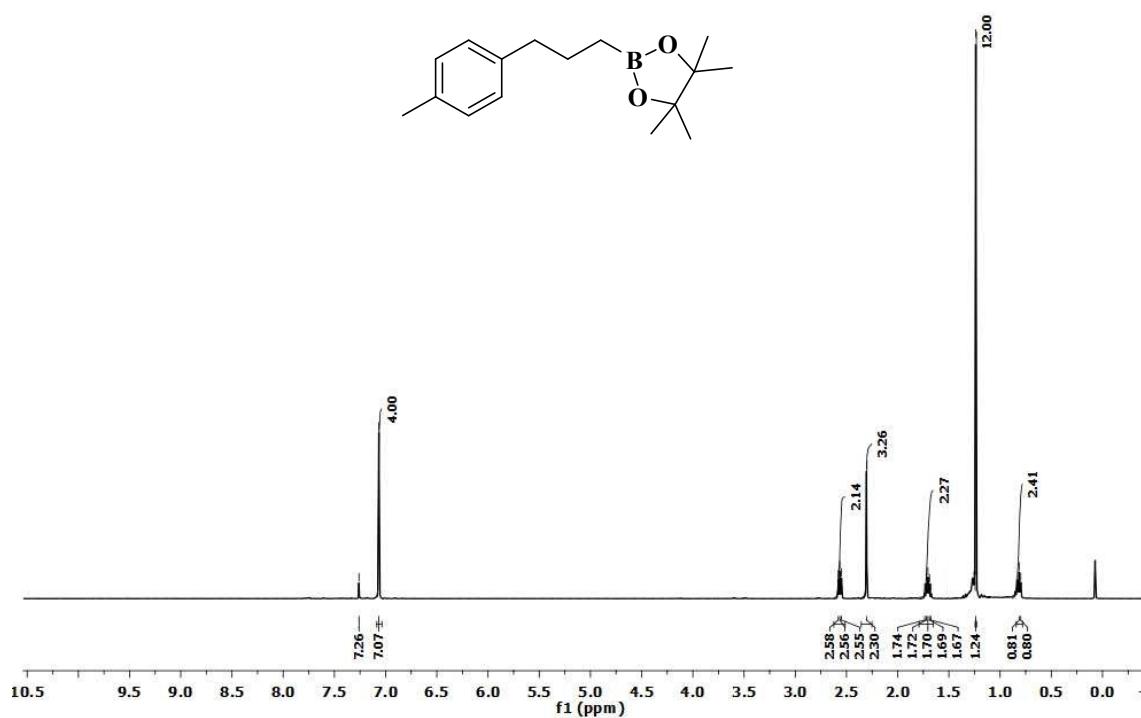
**Figure S32.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(3-Phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



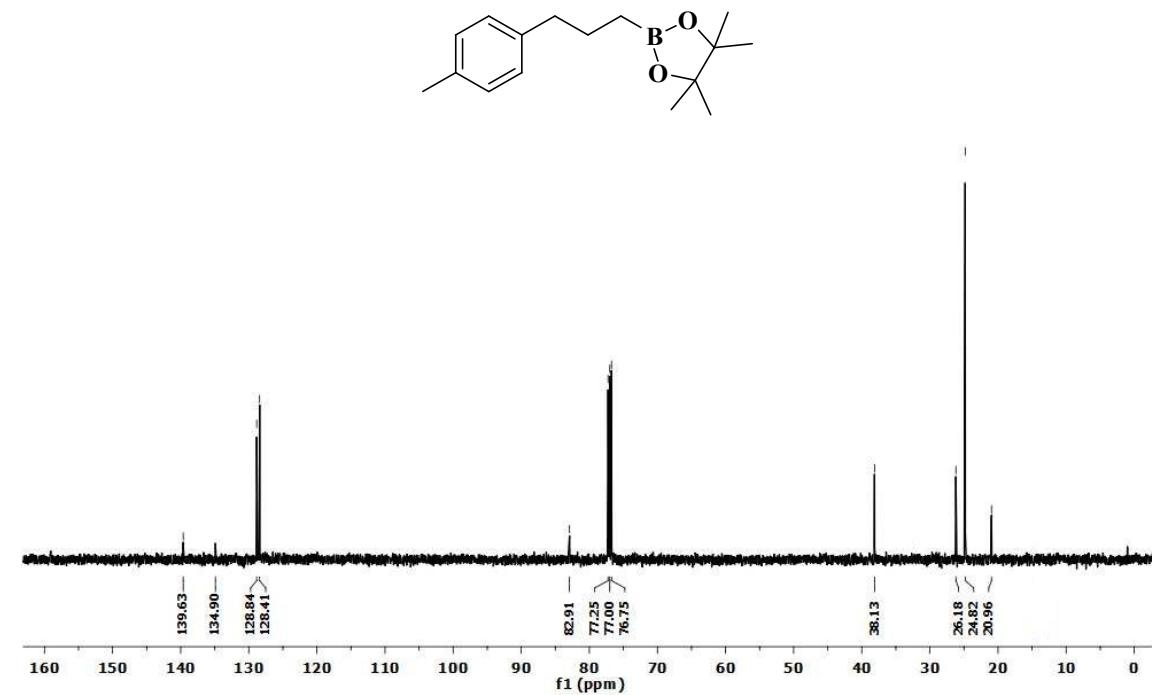
**Figure S33.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(3-Phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



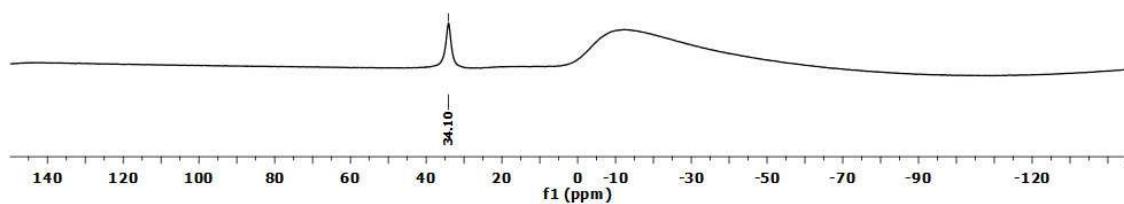
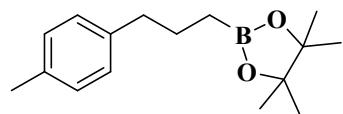
**Figure S34.**  $^{11}\text{B}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(3-Phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



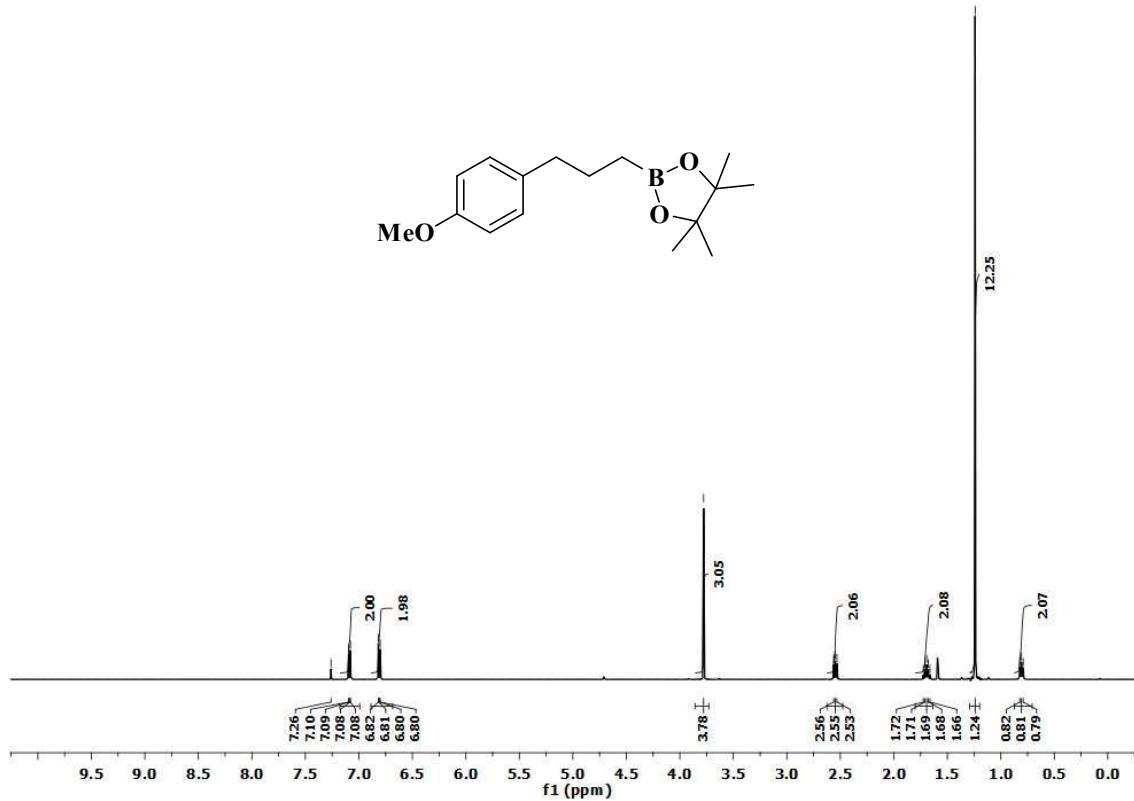
**Figure S35.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of 4,4,5,5-tetramethyl-2-(3-p-tolylpropyl)-1,3,2-dioxaborolane.



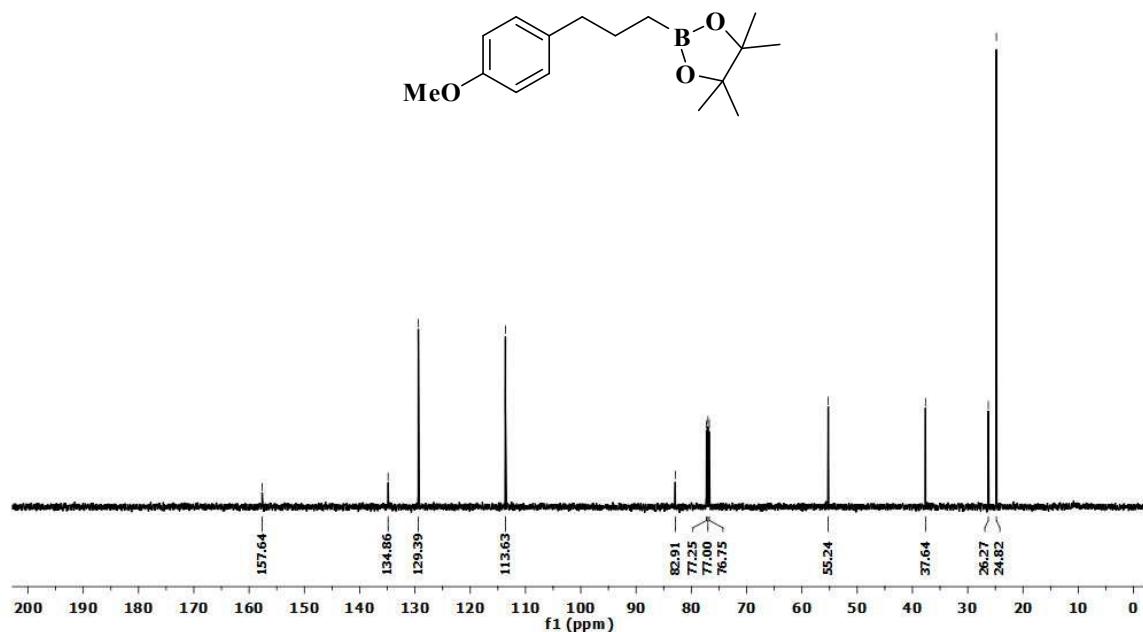
**Figure S36.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) of 4,4,5,5-tetramethyl-2-(3-p-tolylpropyl)-1,3,2-dioxaborolane.



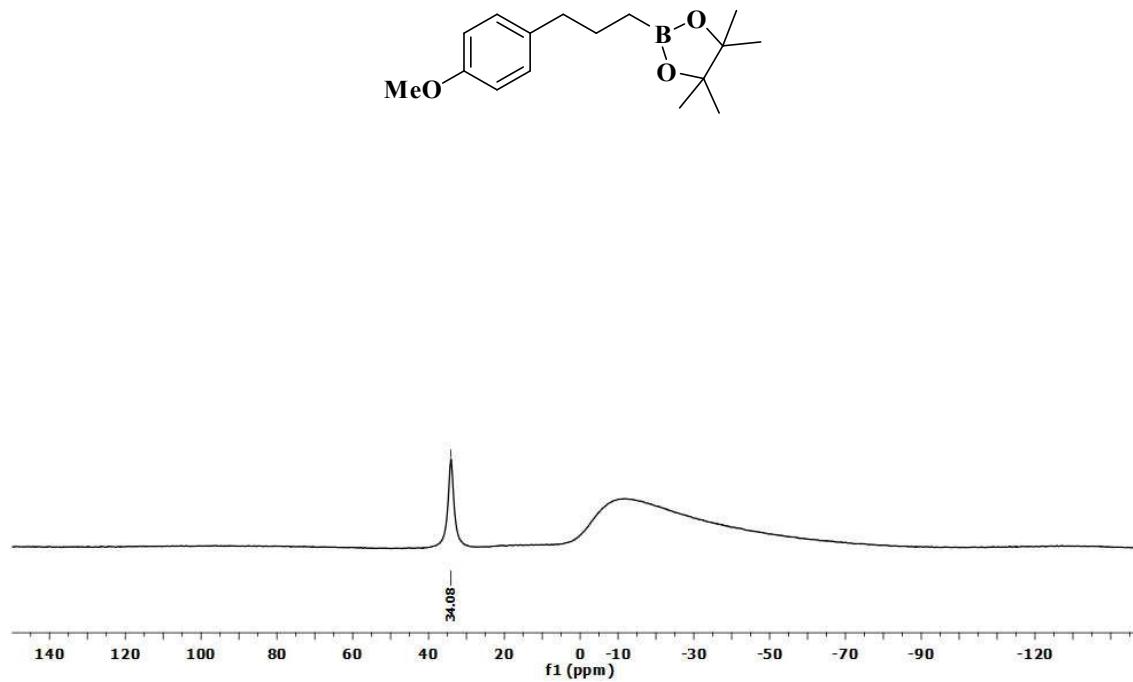
**Figure S37.**  $^{11}\text{B}$  NMR spectrum ( $\text{CDCl}_3$ ) of 4,4,5,5-tetramethyl-2-(3-p-tolylpropyl)-1,3,2-dioxaborolane.



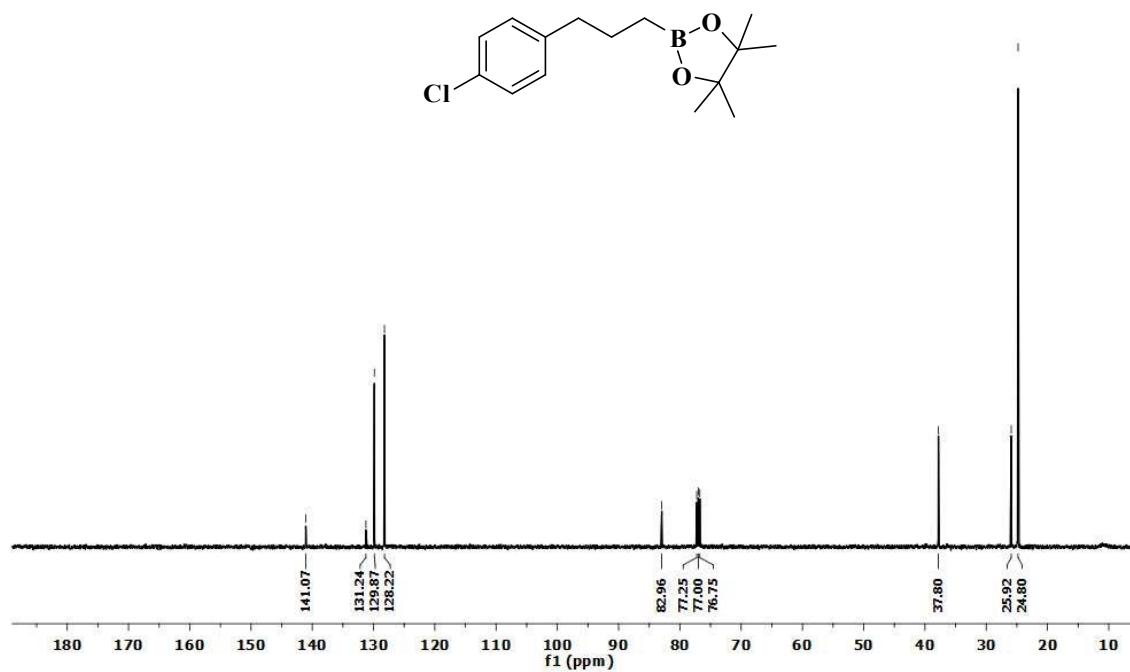
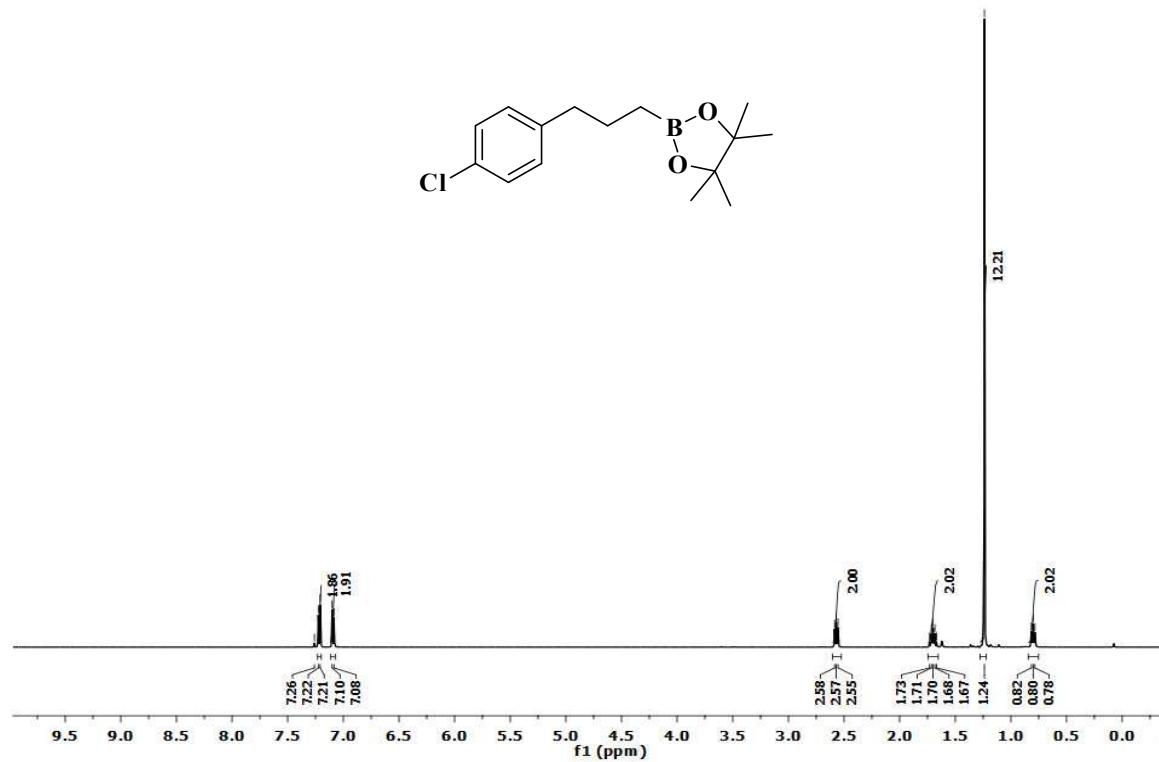
**Figure S38.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(3-(4-Methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

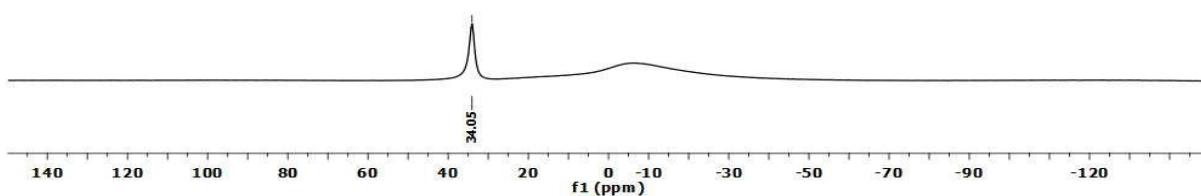
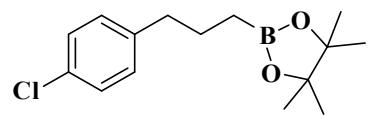


**Figure S39.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(3-(4-Methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

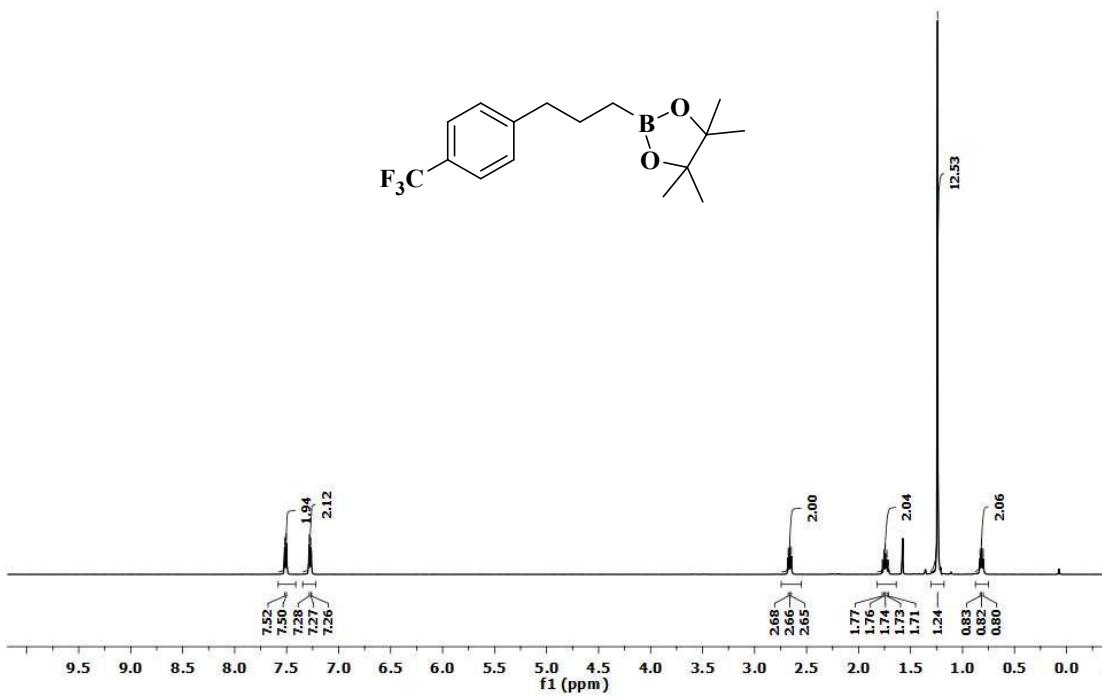
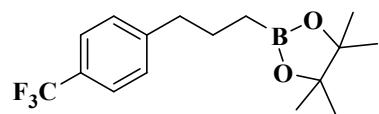


**Figure S40.**  $^{11}\text{B}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(3-(4-Methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

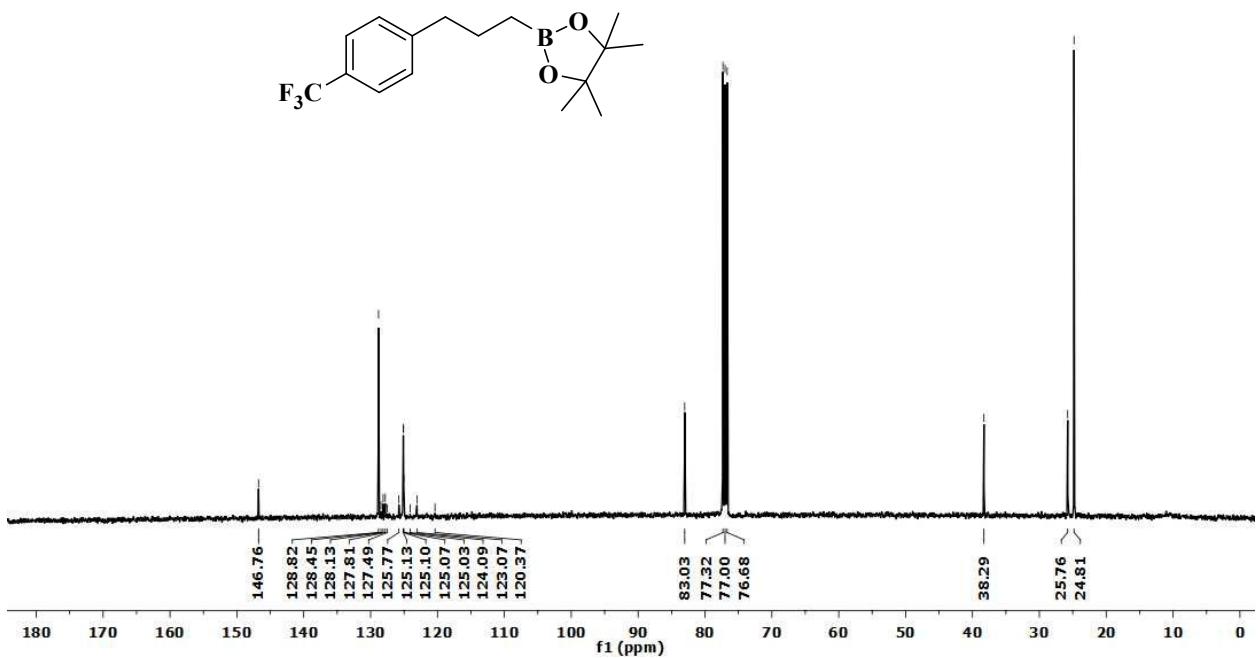




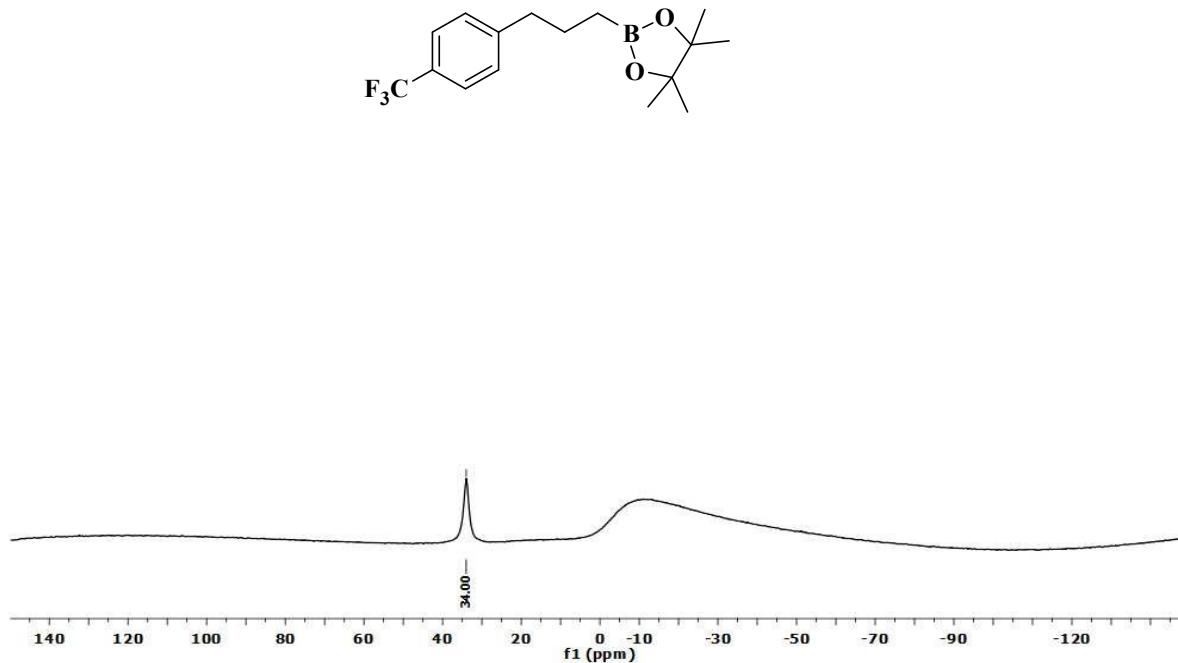
**Figure S43.**  $^{11}\text{B}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(3-(4-chlorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



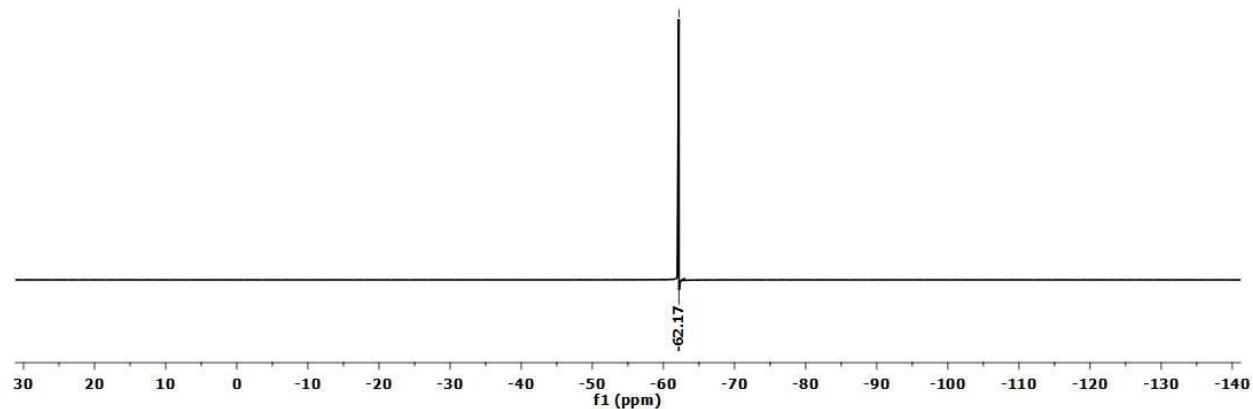
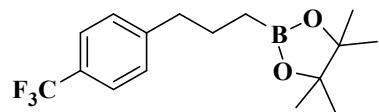
**Figure S44.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of 4,4,5,5-Tetramethyl-2-(3-(4-trifluoromethylphenyl)propyl)-1,3,2-dioxaborolane.



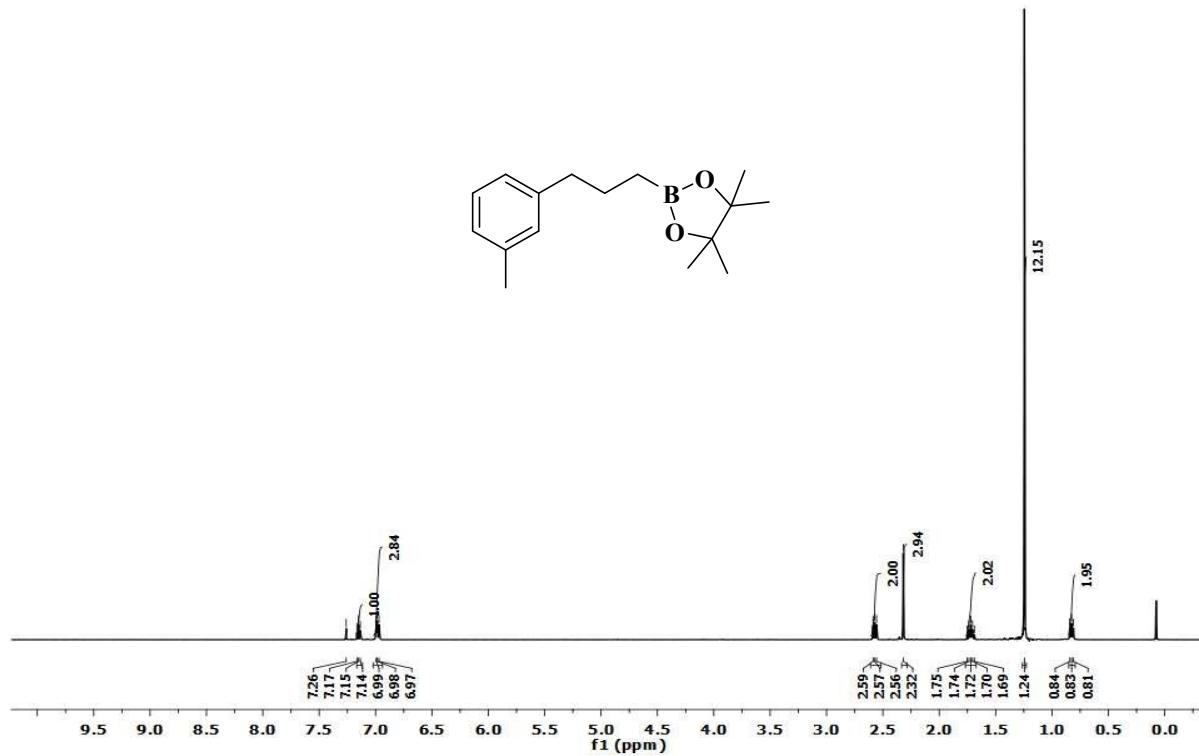
**Figure S45.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) of 4,4,5,5-Tetramethyl-2-(3-(4-trifluoromethylphenyl)propyl)-1,3,2-dioxaborolane.



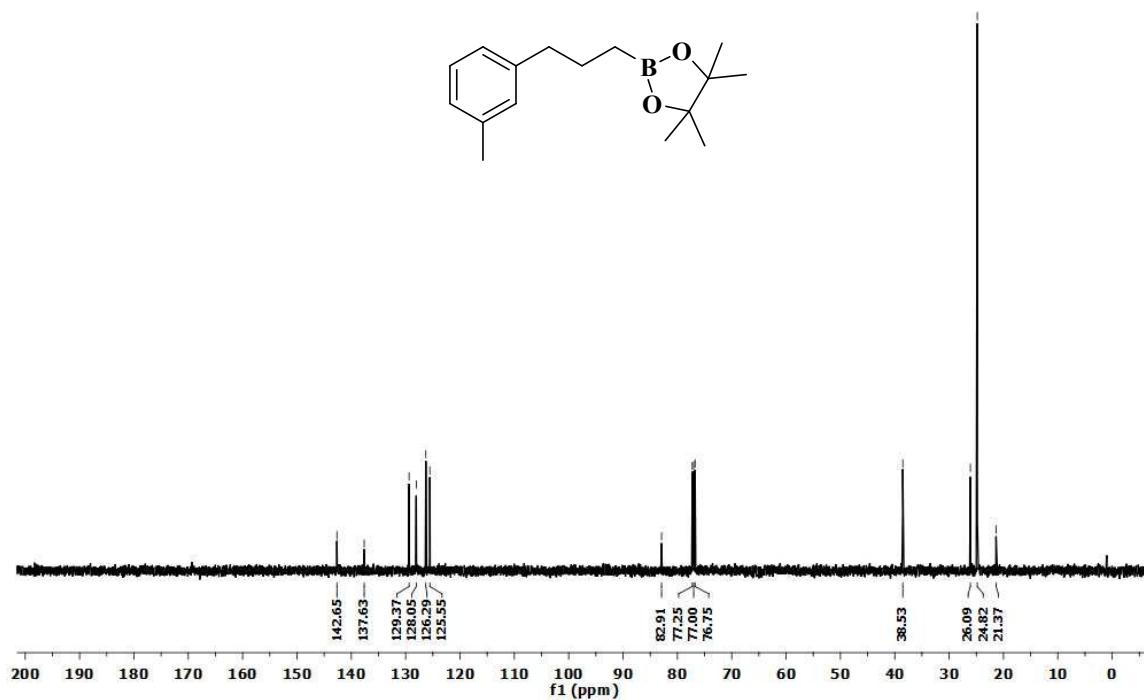
**Figure S46.**  $^{11}\text{B}$  NMR spectrum ( $\text{CDCl}_3$ ) of 4,4,5,5-Tetramethyl-2-(3-(4-trifluoromethylphenyl)propyl)-1,3,2-dioxaborolane.



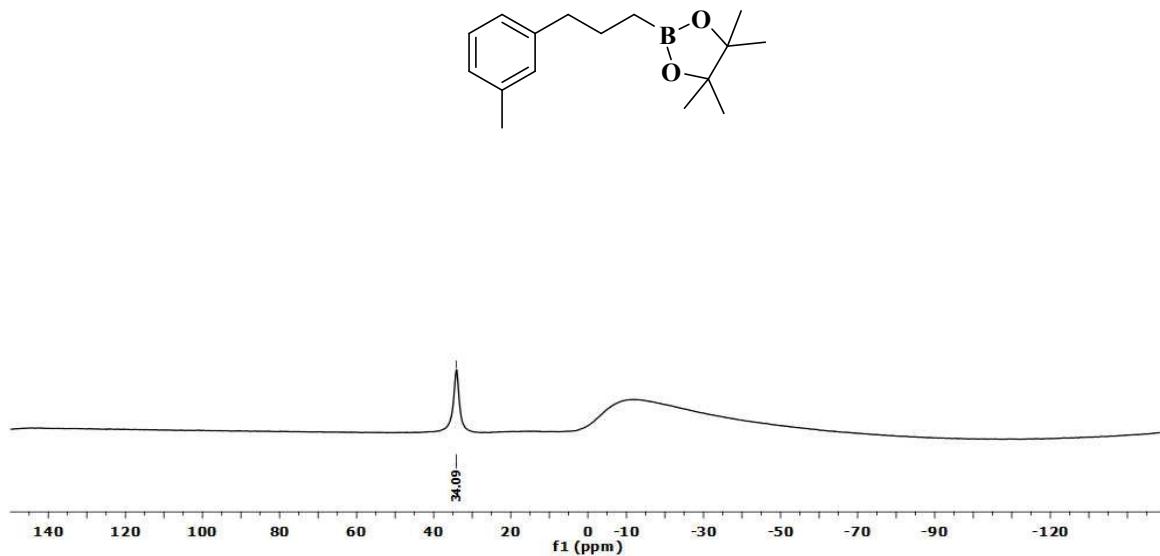
**Figure S47.** <sup>19</sup>F NMR spectrum (CDCl<sub>3</sub>) of 4,4,5,5-Tetramethyl-2-(3-(4-trifluoromethylphenyl)propyl)-1,3,2-dioxaborolane



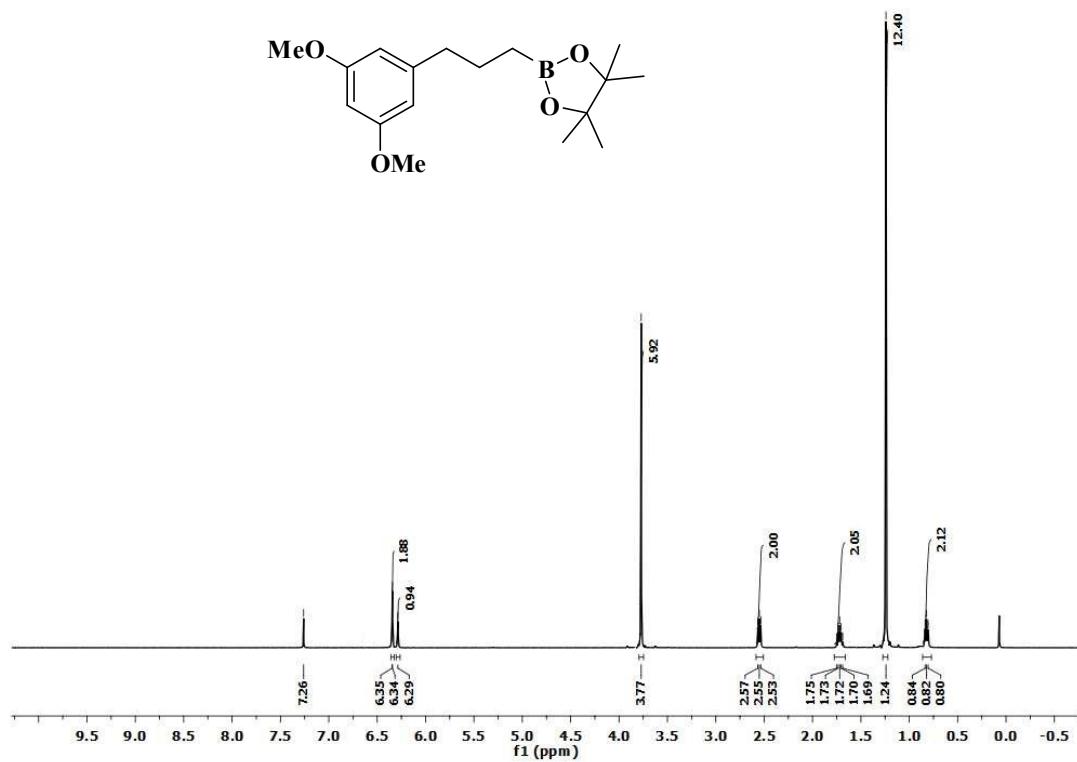
**Figure S48.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of 4,4,5,5-tetramethyl-2-(3-m-tolylpropyl)-1,3,2-dioxaborolane.



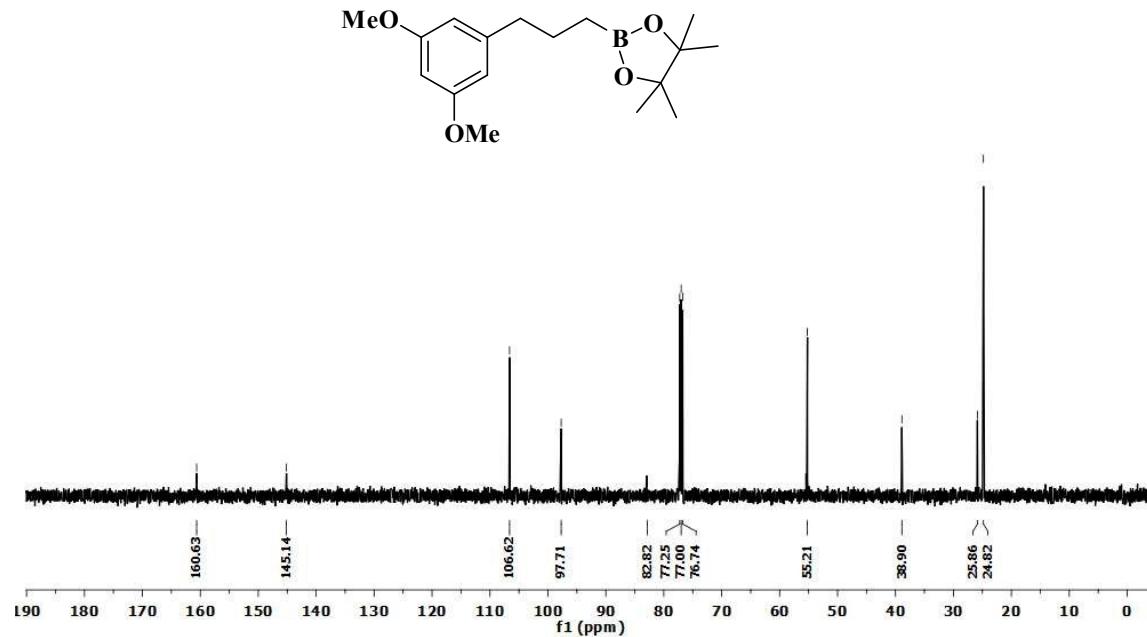
**Figure S49.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) of 4,4,5,5-tetramethyl-2-(3-m-tolylpropyl)-1,3,2-dioxaborolane.



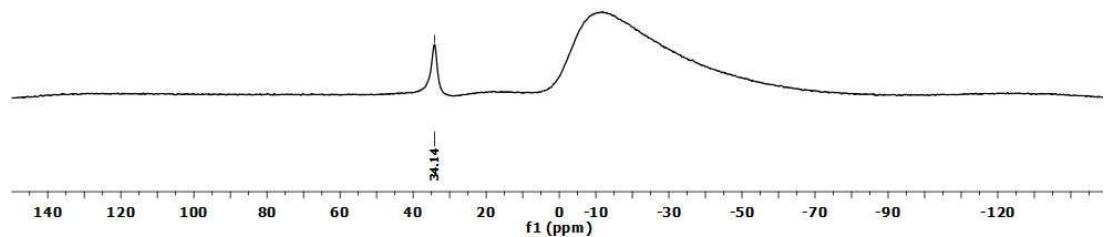
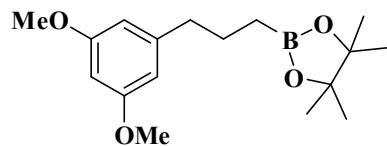
**Figure S50.**  $^{11}\text{B}$  NMR spectrum ( $\text{CDCl}_3$ ) of 4,4,5,5-tetramethyl-2-(3-m-tolylpropyl)-1,3,2-dioxaborolane.



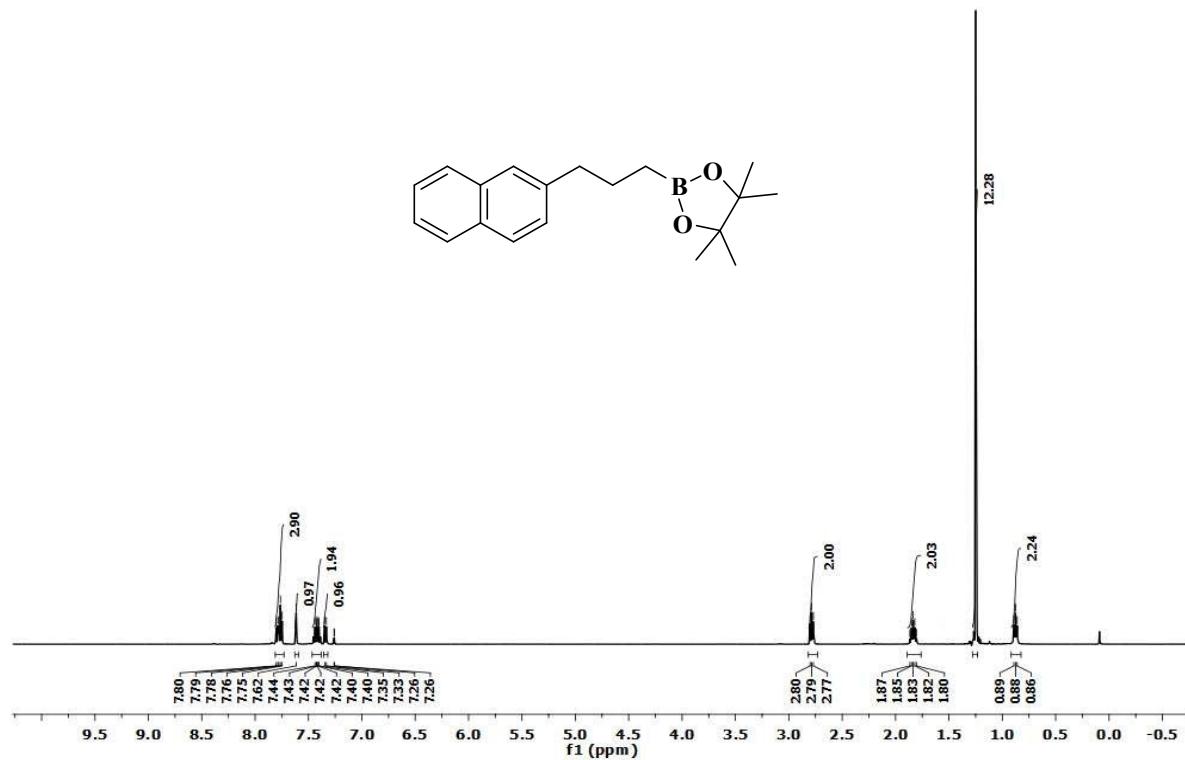
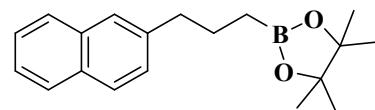
**Figure S51.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(3,5-dimethoxyphenyl)propyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



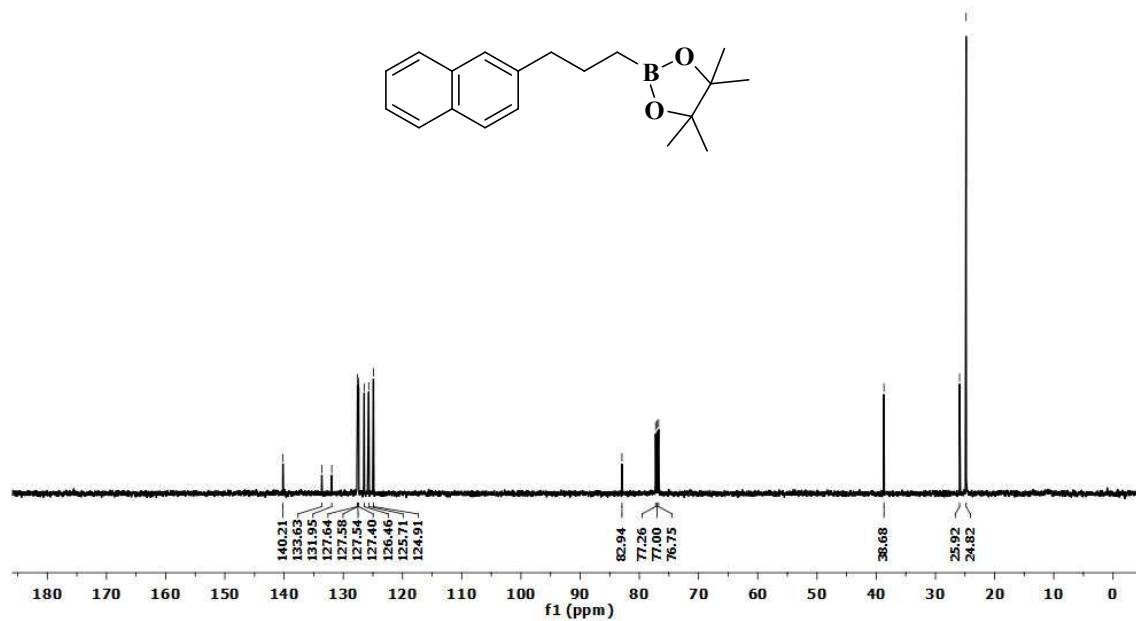
**Figure S52.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(3,5-dimethoxyphenyl)propyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



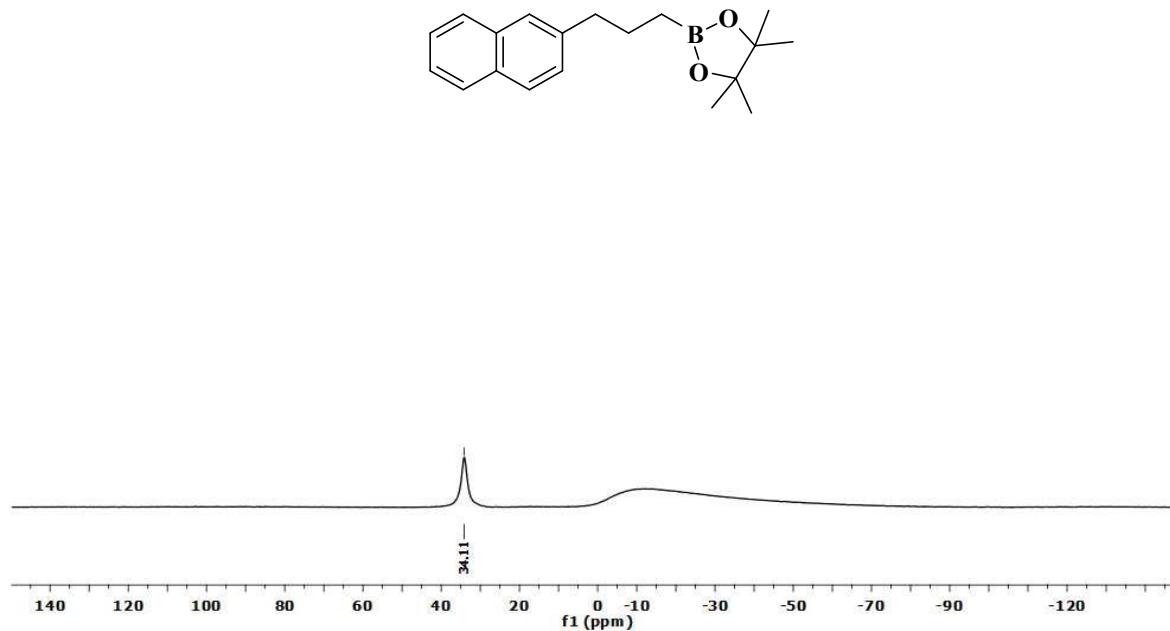
**Figure S53.**  $^{11}\text{B}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-(3,5-dimethoxyphenyl)propyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



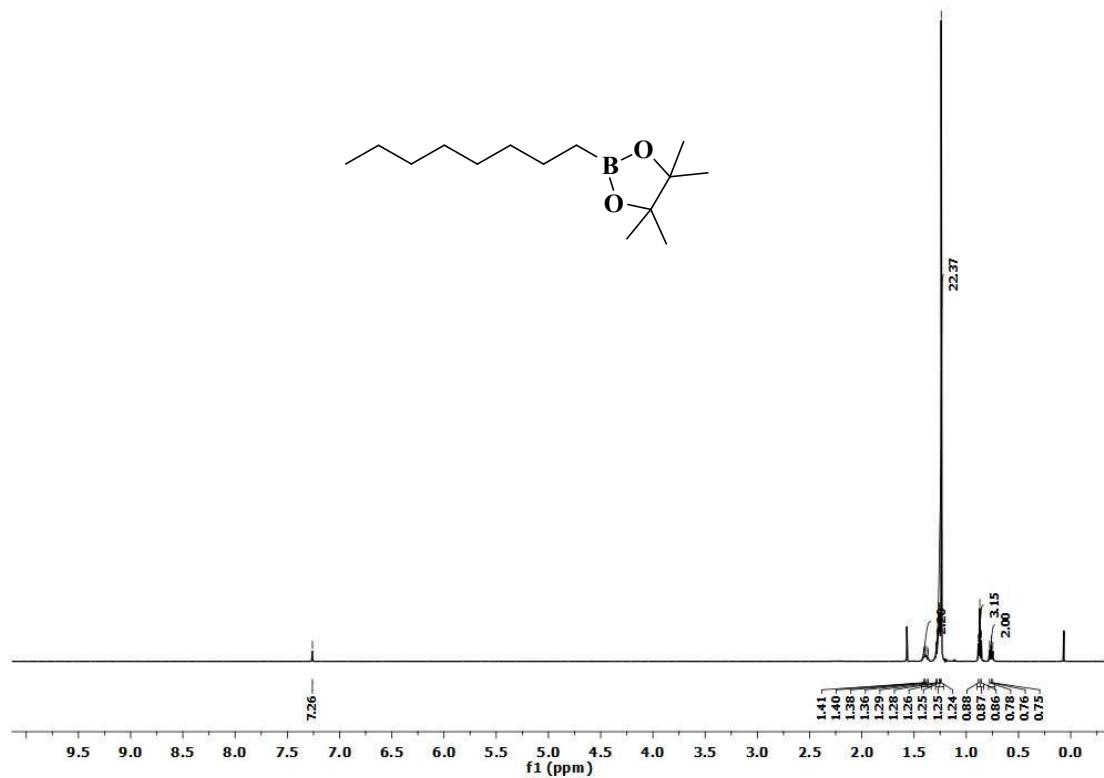
**Figure S54.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of 4,4,5,5-tetramethyl-2-(3-(naphthalen-2-yl)propyl)-1,3,2-dioxaborolane.



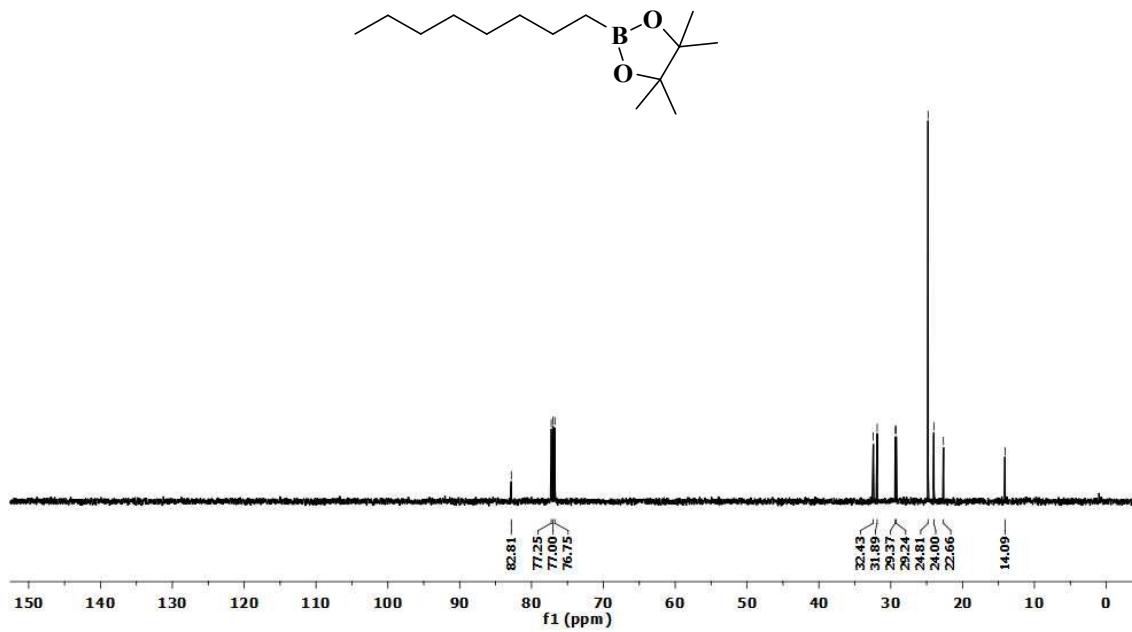
**Figure S55.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) of 4,4,5,5-tetramethyl-2-(3-(naphthalen-2-yl)propyl)-1,3,2-dioxaborolane.



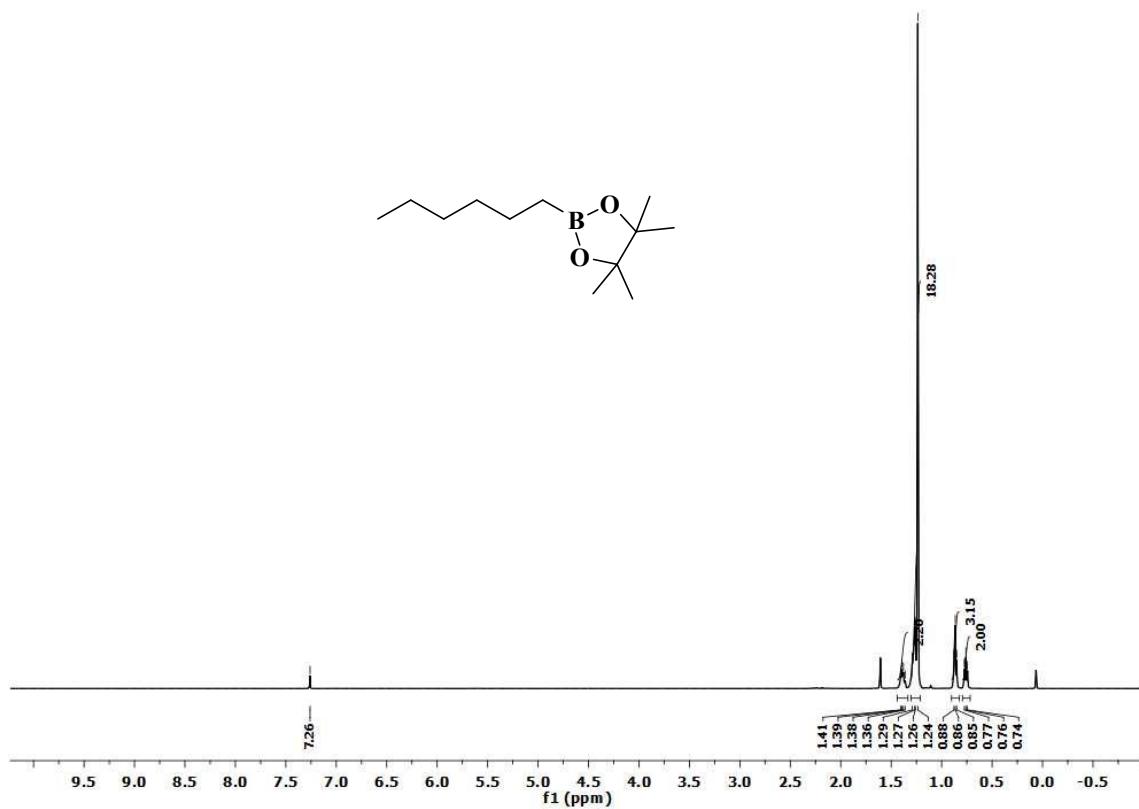
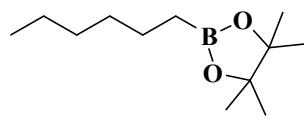
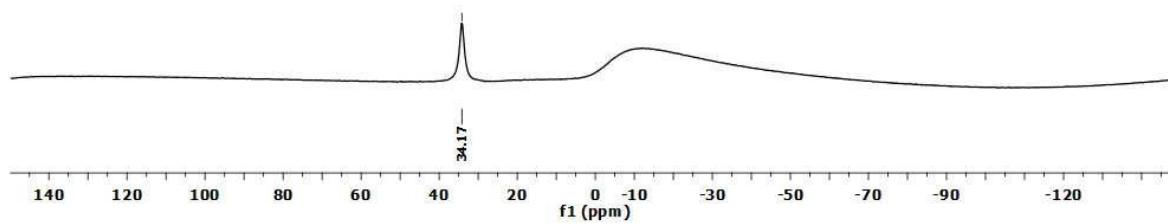
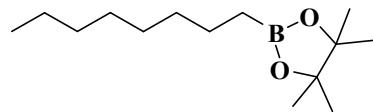
**Figure S56.**  $^{11}\text{B}$  NMR spectrum ( $\text{CDCl}_3$ ) of 4,4,5,5-tetramethyl-2-(3-(naphthalen-2-yl)propyl)-1,3,2-dioxaborolane.

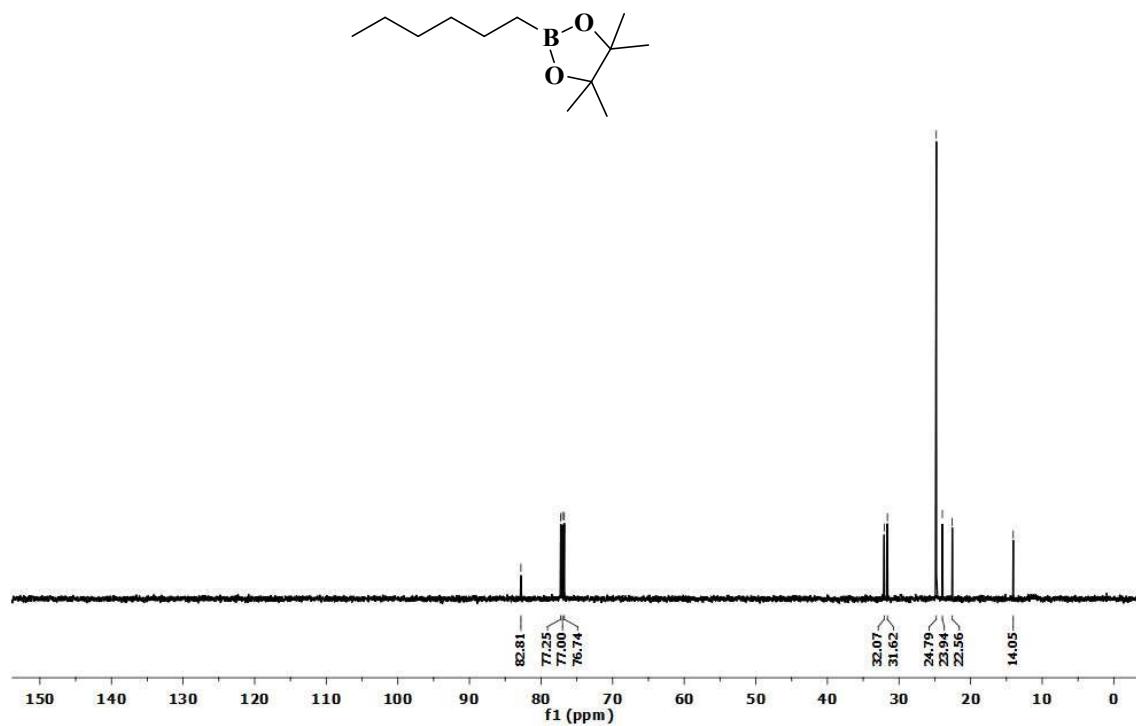


**Figure S57.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of 4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane.

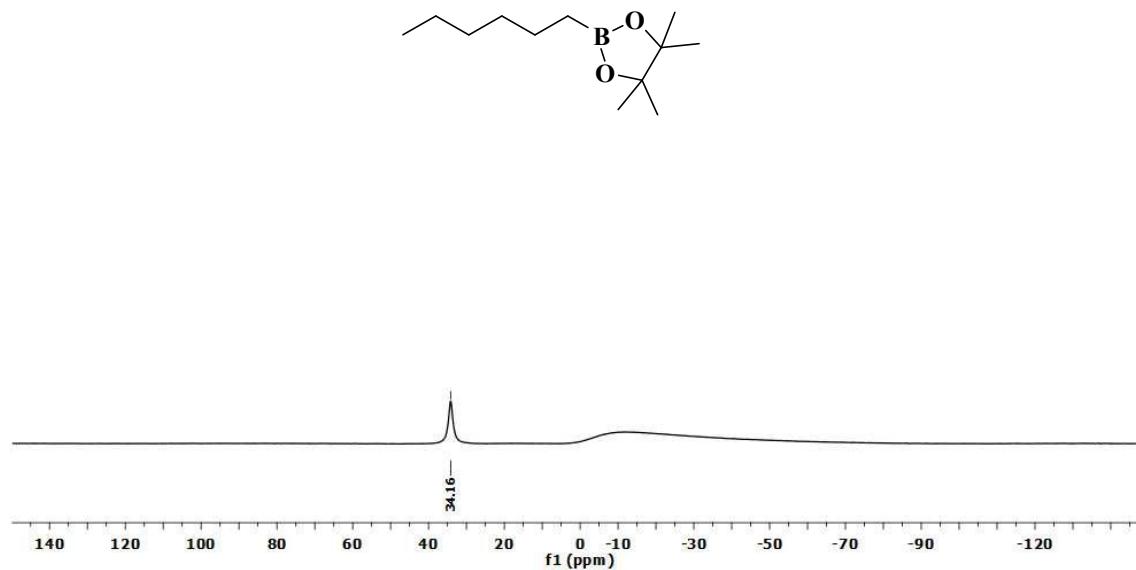


**Figure S58.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) of 4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane

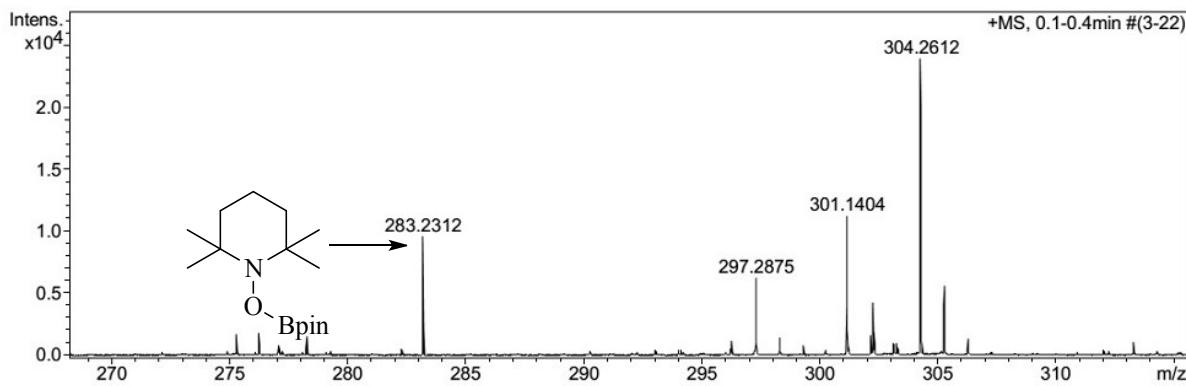




**Figure S61.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-hexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



**Figure S62.**  $^{11}\text{B}$  NMR spectrum ( $\text{CDCl}_3$ ) of 2-hexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



**Figure S63.** HRMS spectrum of reaction mixture showing formation of **4**

**References:**

1. J. Huang, W. Yan, C. Tan, W. Wu and H. Jiang, *Chem. Commun.*, 2018, **54**, 1770-1773
2. A. Chen, L. Ren and C. M. Crudden, *J. Org. Chem.* 1999, **64**, 9704–9710.
3. S. R. Tamang, D. Bedi, S. Shafiei-Haghghi, C. R. Smith, C. Crawford and M. Findlater, *Org. Lett.*, 2018, **20**, 6695–6700
4. C. M. Crudden, Y. B. Hleba and A. C. Chen, *J. Am. Chem. Soc.*, 2004, **126**, 9200-9201
5. L. Zhang, Z. Zuo, X. Leng and Z. Huang, *Angew. Chem. Int. Ed.*, 2014, **53**, 2696-2700.
6. J. Zheng, J.-B. Sortais and C. Darcel, *ChemCatChem*, 2014, **6**, 763–766
7. L. Guo, X. Liu, C. Baumann and M. Rueping, *Angew. Chem. Int. Ed.*, 2016, **55**, 15415–15419
8. J. V. Obligacion and P. J. Chirik, *Org. Lett.*, 2013, **15**, 2680-2683.