

## Supplementary Material

### Transition-Metal-Free Synthesis of Pinacol Arylboronate: Regioselective Boronation of 1, 3 disubstituted benzenes

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<b>General Experimental Methods</b> .....	S1
<b>Experimental Procedures</b> .....	S1
<b>Characterization data of Compounds</b> .....	S2
<b><sup>1</sup>H, <sup>13</sup>C NMR, <sup>19</sup>F NMR Spectra</b> .....	S5

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**General Experimental Methods.** THF was heated at reflux over sodium benzophenone ketyl before use. All reactions were carried out under N<sub>2</sub> atmosphere using oven dried glassware. NMR spectra were recorded with Bruker Advance II at 400 MHz for <sup>1</sup>H, 100 MHz for <sup>13</sup>C NMR, 396 MHz for <sup>19</sup>F NMR, and chemical shifts are given in parts per million. LC-MS (ESI-API) analyses was carried out with an Agilent 1100 LC/MSD Trap mass spectrometer. GC-MS(EI) analyses was carried out with a Thermo Fisher DSQ apparatus (70 eV) with ions given in m/z, **High-resolution mass spectra were recorded on an IT-TOF of Shimadzu mass spectrometer.**

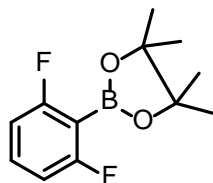
**General procedure for metalation-boration of 1,3-disubstituted benzene:**

**Method A:** To an oven-dried 100 mL flask was added 1,3-disubstituted benzene (3.0 mmol), TMEDA (1.1 equiv., 3.3 mmol), DIPA (5% equiv., 0.16 mmol) and THF (10.0 mL). The solution was cooled to -78 °C for 10 min and then *n*-BuLi (1.1 equiv., 3.3 mmol) was added dropwise. The mixture was kept at this temperature for 1.5 hour; B<sub>2</sub>Pin<sub>2</sub> (1.5 equiv., 4.5 mmol) was added and the mixture was further stirred for another half an hour at -78 °C. The mixture was allowed to warm up to room temperature for 1-12 h, followed by the addition of saturated NH<sub>4</sub>Cl-H<sub>2</sub>O solution (5 mL); extraction three times with ethyl acetate (10 mL×3). The combined organic layers were dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated in vacuo. The regioselectivity of the crude product was confirmed by <sup>19</sup>F NMR or by LC/MS and then subjected to flash chromatography to obtain the desired products which were characterized by <sup>1</sup>H NMR, <sup>19</sup>F NMR, <sup>13</sup>C NMR spectral data and LC/MS analyses.

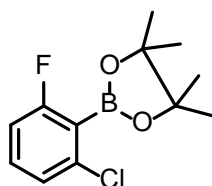
**Method B:**

Similar to method A, the electrophilic reagent was changed to *i*-PrOBPin. The mixture was dealt with the same as in method A.

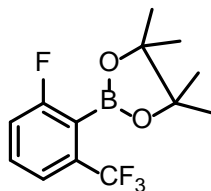
## Characterization data of compounds



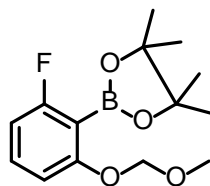
**1b.** Yellow solid, m.p.: 50.1-51.8 °C .  $^1\text{H}$  NMR ( 400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 ( m, 1H ), 6.86 ( t,  $J$  = 8.0 Hz, 2H), 1.41 (s, 12H),  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.8,165.3, 133.1, 111.1, 84.3, 77.0, 24.8 ,  $^{19}\text{F}$  NMR ( 376 MHz,  $\text{CDCl}_3$ )  $\delta$  -100.66 . HRMS (ESI)  $\text{C}_{12}\text{H}_{16}\text{BF}_2\text{O}_2$   $[\text{M}+\text{H}]^+$  calcd. 241.1133, found 241.1211.



**2b.** Yellow solid, m.p.: 68.3-69.6 °C.  $^1\text{H}$  NMR ( 400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.29 (m, 1H), 7.15 (d,  $J$  = 8.0 Hz, 1H) , 6.94 (t,  $J$  = 8.0 Hz, 1H ) 1.43 ( s, 12H ),  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.7, 164.2, 138.4, 131.9, 124.7,113.2, 84.8, 77.0, 24.7  $^{19}\text{F}$  NMR ( 376 MHz,  $\text{CDCl}_3$ )  $\delta$  -102.64. HRMS (ESI)  $\text{C}_{12}\text{H}_{16}\text{BClFO}_2$   $[\text{M}+\text{H}]^+$  calcd. 257.0838, found 257.0895.

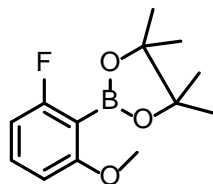


**3b.** Yellow Oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (m, 2H), 7.22 (d,  $J$  = 8.0 Hz, H), 1.42 (s, 12H),  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  131.54, 131.45, 121.26, 118.36, 118.12, 85.07, 24.63.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -59.94 (3F), -103.13 (F). HRMS (ESI)  $\text{C}_{13}\text{H}_{16}\text{BF}_4\text{O}_2$   $[\text{M}+\text{H}]^+$  calcd.291.1101, found 291.1168.

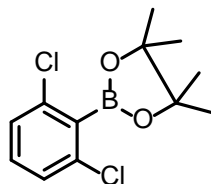


**4b.** Yellow solid, m.p.: 96.3-97.2 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27 (m, 1H), 6.82 (d,  $J$  = 8.4 Hz, 1H), 6.70 (t,  $J$  = 8.0 Hz, 1H), 5.18 (s, 2H), 3.49 (s, 3H), 1.40 (s,

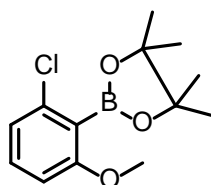
12H),  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.4, 164.9, 161.3, 161.2, 132.1, 109.6, 94.6, 83.5, 77.0, 56.6, 25.0.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -103.88. EI-MS:  $m/z$  = 281.87 (20%).



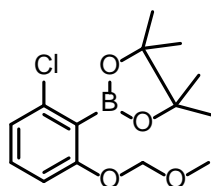
**5b.** Yellow solid, m.p.: 68.6-70.1 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  /ppm, 7.29 (m, 1H), 6.64 (m, 2H), 1.41 (s, 12H),  $^{13}\text{C}$  NMR(100 MHz,  $\text{CDCl}_3$ ):  $\delta$  /ppm, 167.5, 165.1, 164.0, 132.1, 107.7, 105.8, 84.1, 77.0, 56.0, 24.7.  $^{19}\text{F}$  NMR ( 376 MHz,  $\text{CDCl}_3$  )  $\delta$ -104.17 . HRMS (ESI)  $\text{C}_{13}\text{H}_{19}\text{BFO}_3$   $[\text{M}+\text{H}]^+$  calcd.253.1333, found 253.1400.



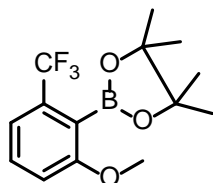
**6b.** Yellow solid. m.p.: 78.5-79.6 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 (s, 3H), 1.45 (s, 12H),  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.1, 131.2, 126.8, 85.0, 77.0, 24.8. ESI-MS:  $[\text{M}+\text{Na}]^+$ , 295.1. HRMS (ESI)  $\text{C}_{12}\text{H}_{16}\text{BCl}_2\text{O}_2$   $[\text{M}+\text{H}]^+$  calcd.273.0542, found 273.0610.



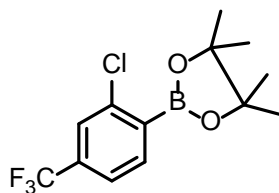
**7b.** Yellow solid, m.p.:78.4-79.7 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 (d,  $J$  = 8.0 Hz, 1H), 6.93 (d,  $J$  = 8.0 Hz, 1H), 6.72 (d,  $J$  = 8.4 Hz, 1H) , 3.8 (s, 3H), 1.42 (s, 12H),  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.1, 137.8, 132.6, 131.3, 121.2, 108.0, 84.4, 77.0, 55.8, 24.7. HRMS (ESI)  $\text{C}_{13}\text{H}_{19}\text{BClO}_3$   $[\text{M}+\text{H}]^+$  calcd. 269.1038, found 269.1101.



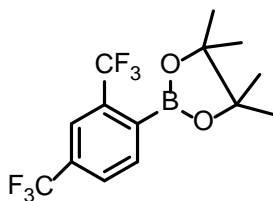
**8b.** Yellow solid, m.p.: 100.6-101.3°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.22 (t, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 5.16 (s, 2H), 3.48 (s, 3H), 1.42 (s, 12H), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.4, 137.7, 131.2, 122.2, 111.6, 94.3, 77.0, 56.1, 29.7, 24.7. EI-MS: *m/z* = 297.83(20%).



**9b.** Yellow Oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 3.85 (s, 3H), 1.41 (s, 12H), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 24.6, 55.9, 77.0, 84.5, 112.9, 117.7, 130.8, 134.4, 162.7. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -63.24. HRMS (ESI) C<sub>14</sub>H<sub>19</sub>BF<sub>3</sub>O<sub>3</sub> [M+H]<sup>+</sup> calcd. 303.1301, found 303.1365.



**10c.** Yellow Oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.63 (s, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 1.40 (s, 12H), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 140.1, 136.8, 133.9, 133.5, 126.1, 122.4, 84.6, 77.0, 24.8. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -63.21. ESI-MS: [M+H]<sup>+</sup>, 306.9.

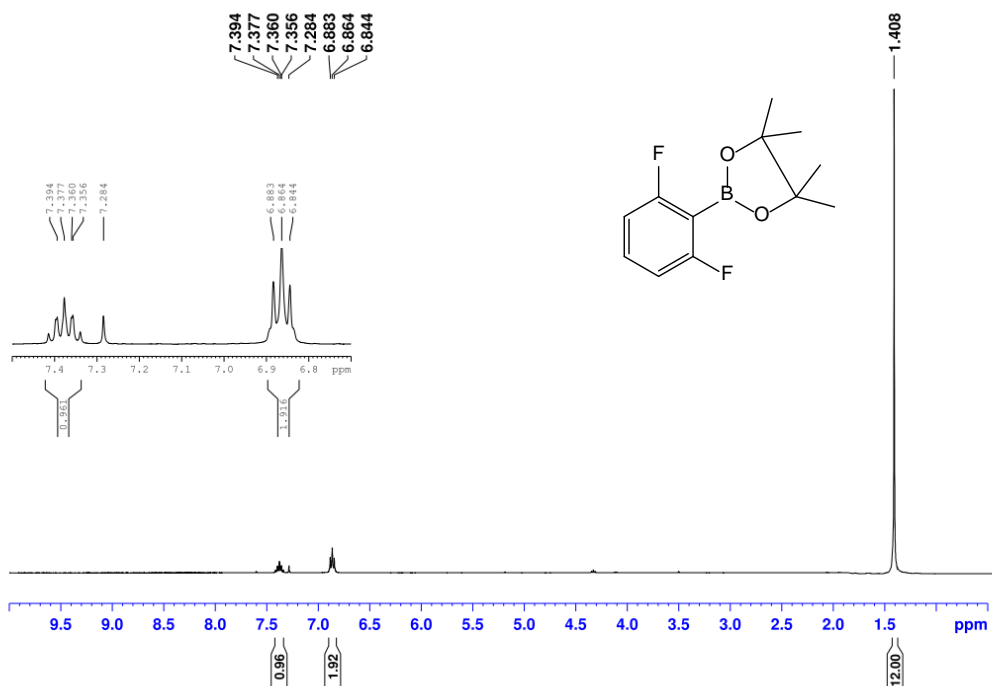


**11c.** Yellow Oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 1.40 (s, 12H), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 24.6, 77.0, 85.0, 122.2, 124.9, 127.3, 132.2, 134.7, 135.5. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -60.13, -63.27. ESI-MS: [M+Na]<sup>+</sup>, 363.1.

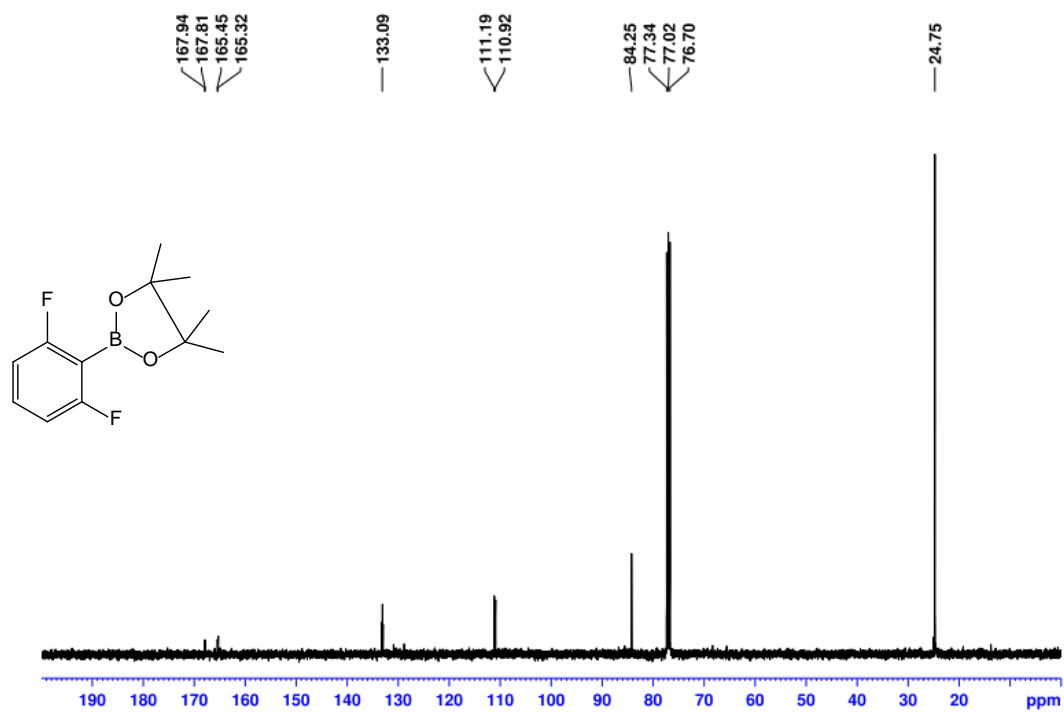
# $^1\text{H}$ , $^{13}\text{C}$ NMR, $^{19}\text{F}$ NMR Spectra

1b:

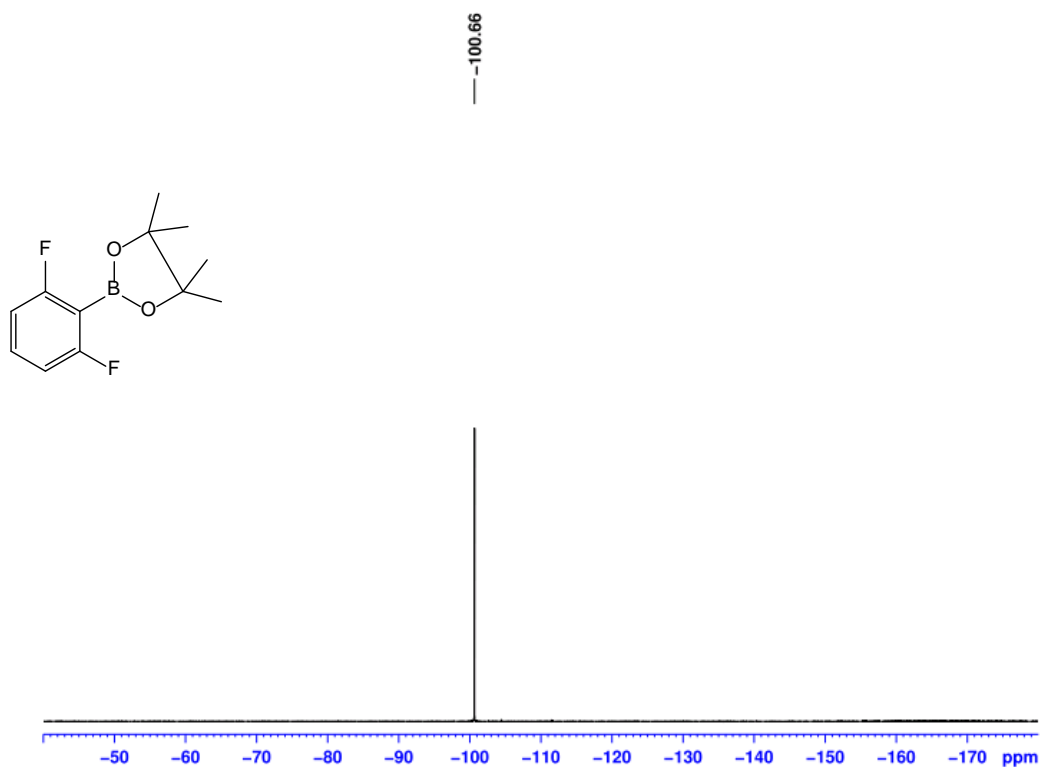
$^1\text{H}$  NMR



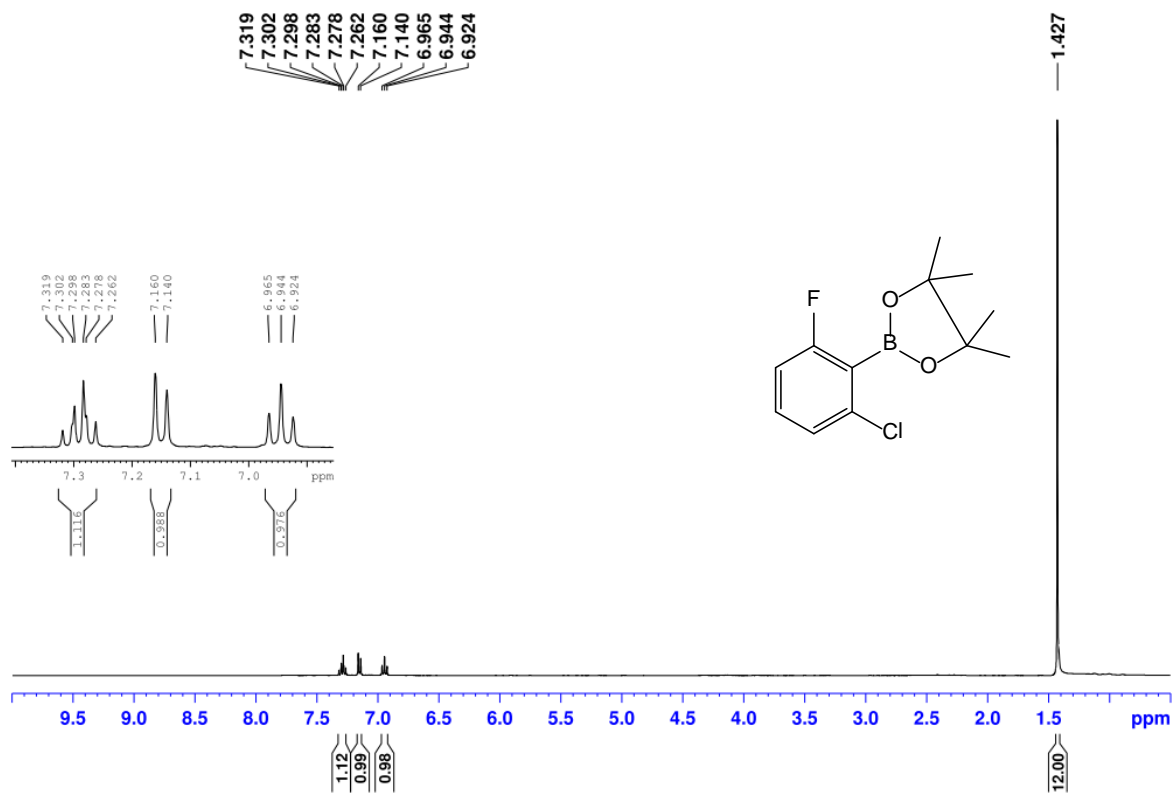
$^{13}\text{C}$  NMR



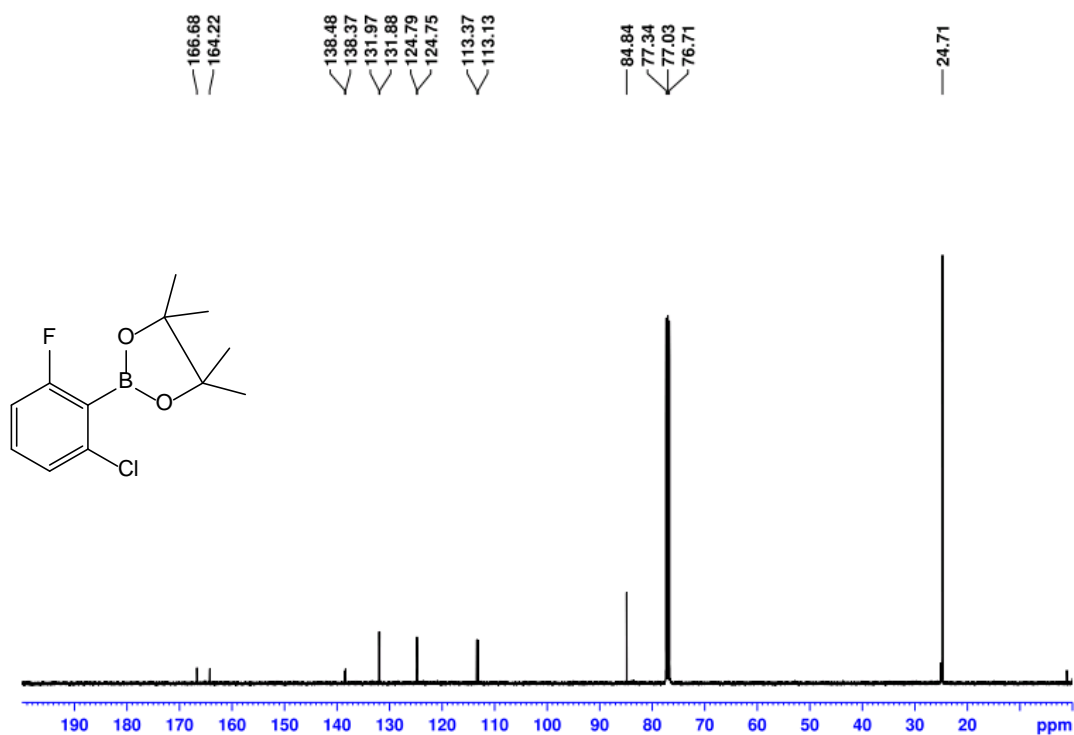
# <sup>19</sup>F NMR



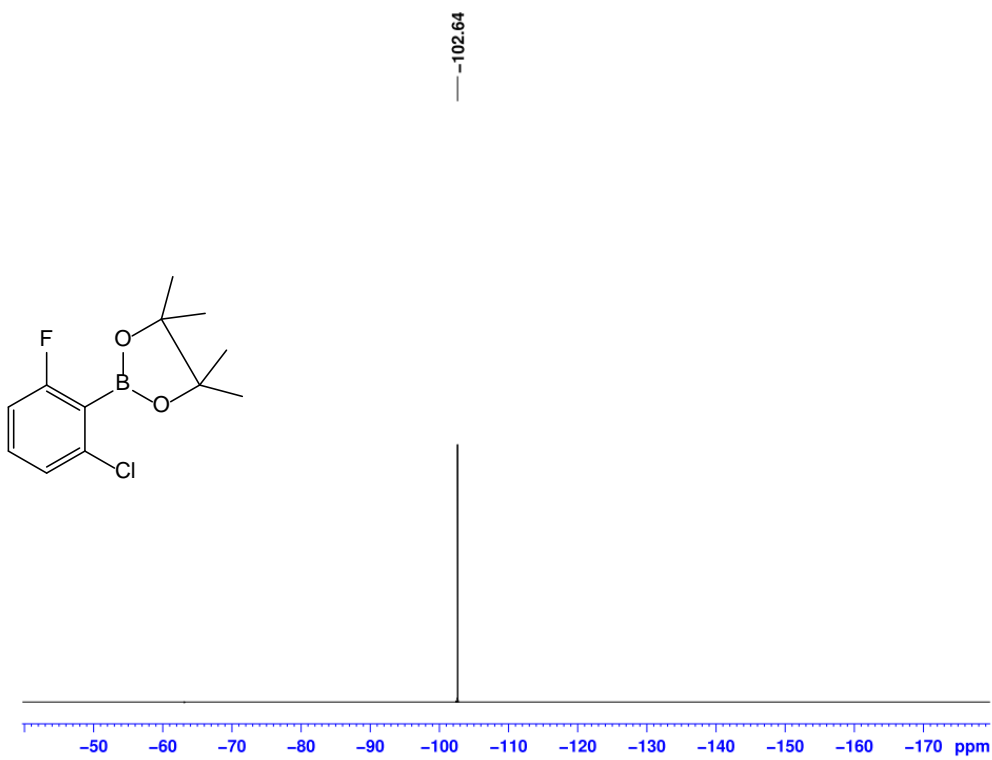
# 2b: <sup>1</sup>H NMR



# <sup>13</sup>C NMR

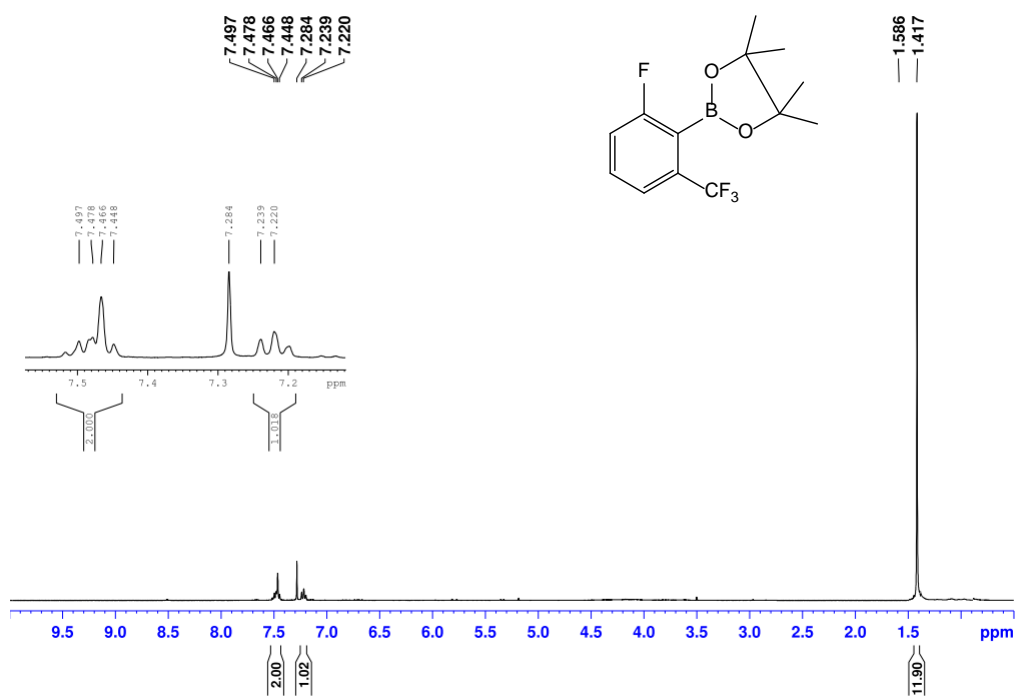


# <sup>19</sup>F NMR

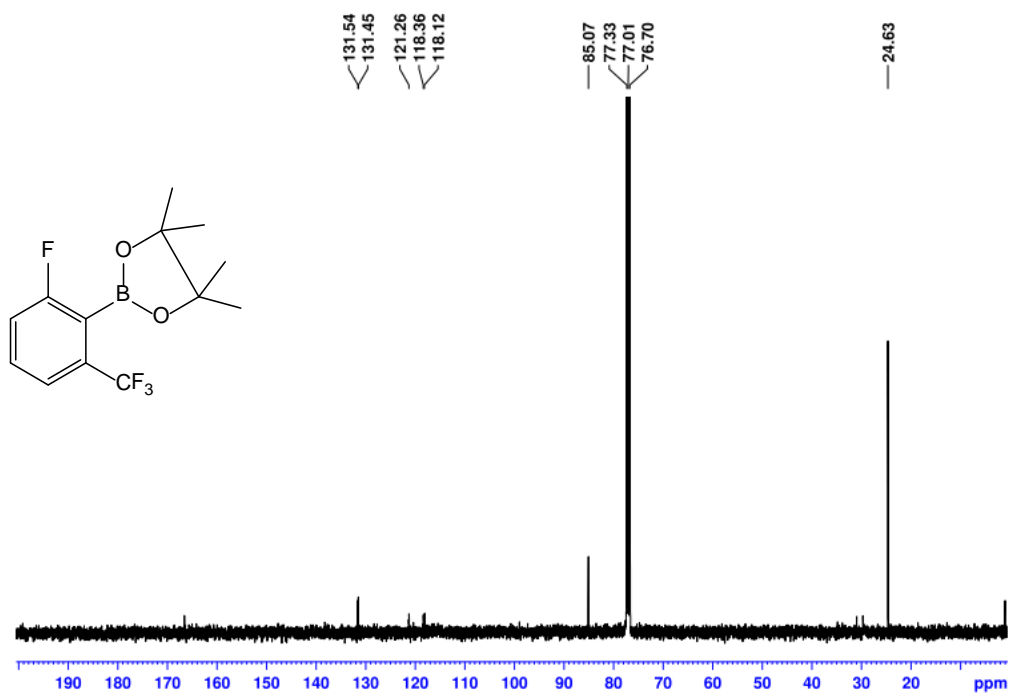




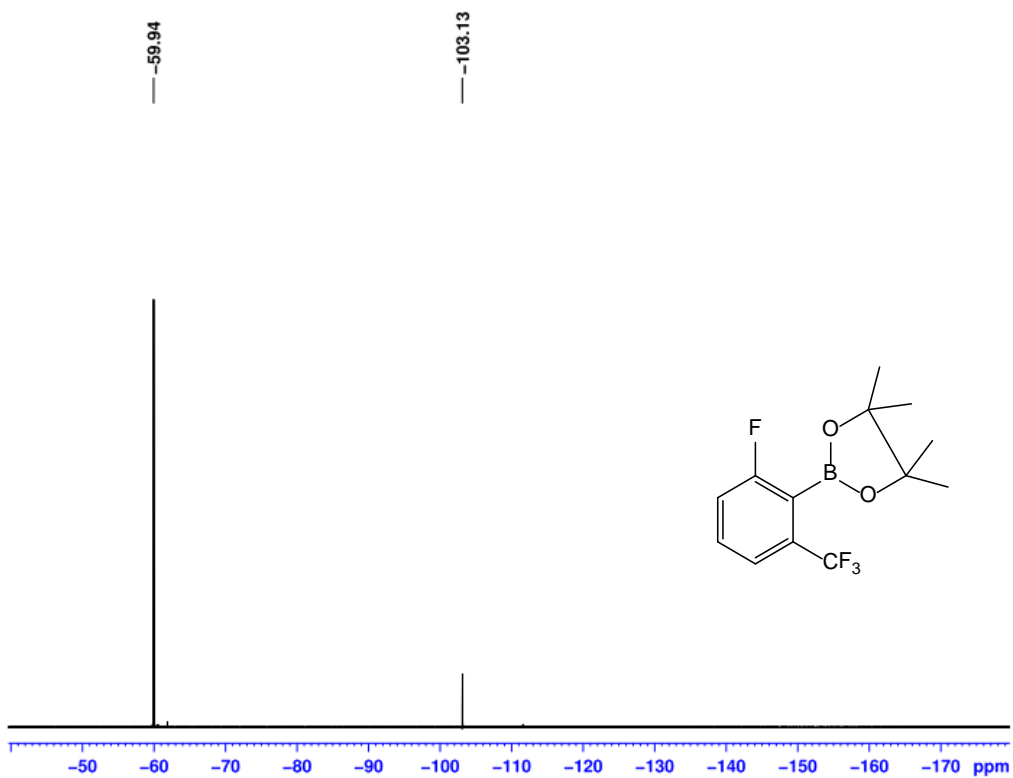
3b:  
<sup>1</sup>H NMR



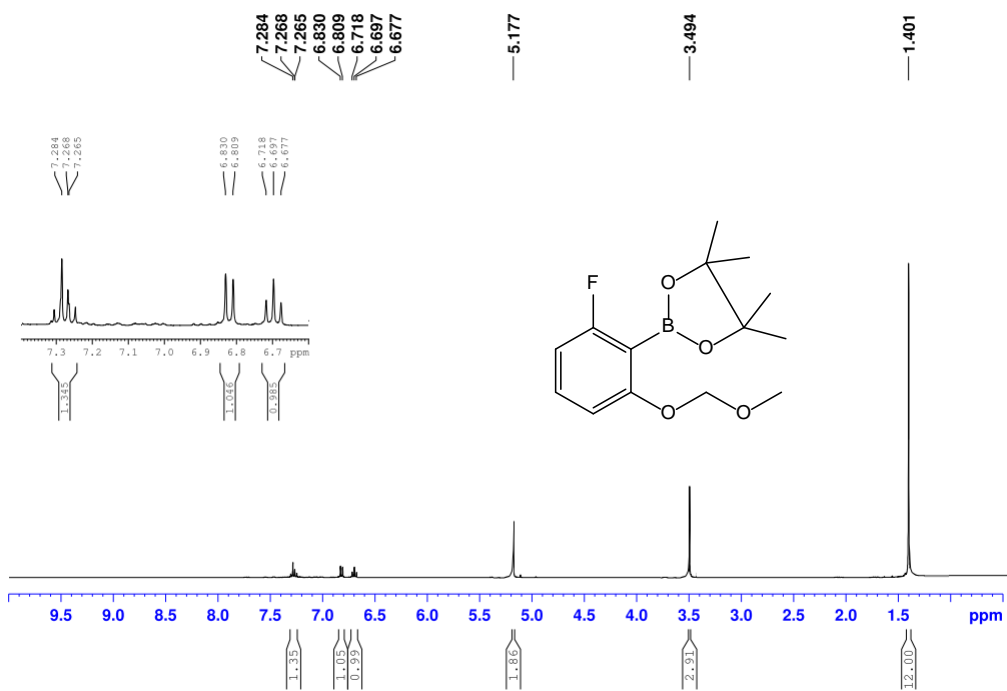
<sup>13</sup>C NMR



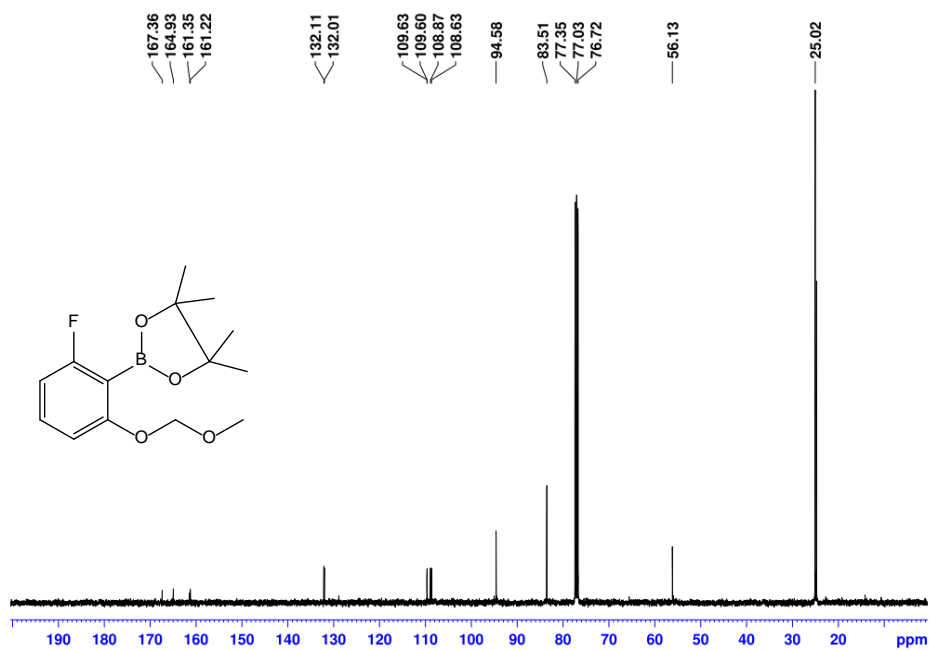
# <sup>19</sup>F NMR



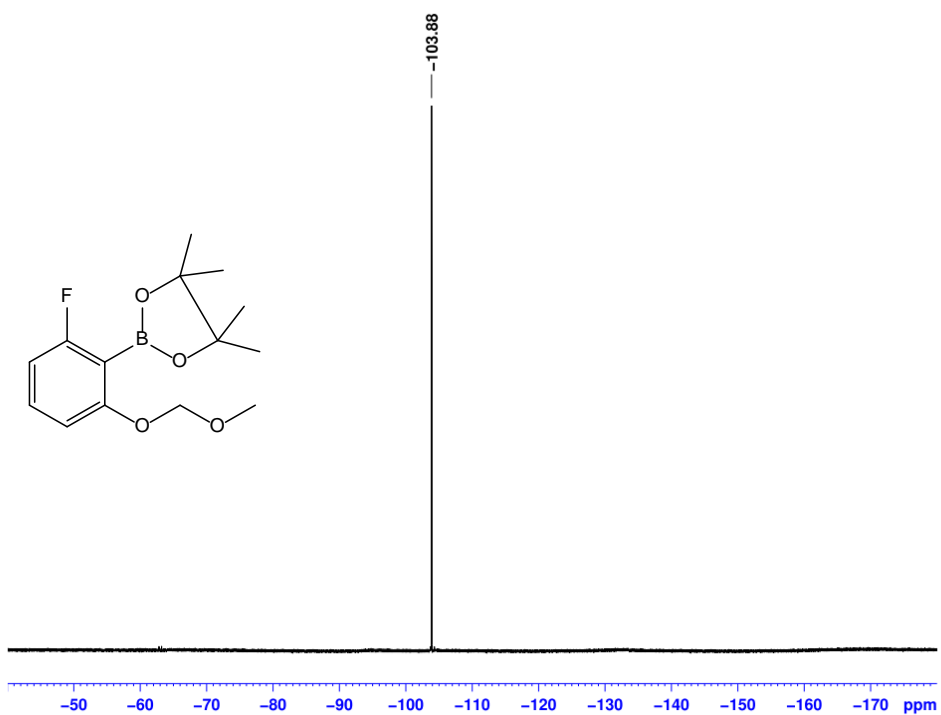
# 4b: <sup>1</sup>H NMR



# <sup>13</sup>C NMR



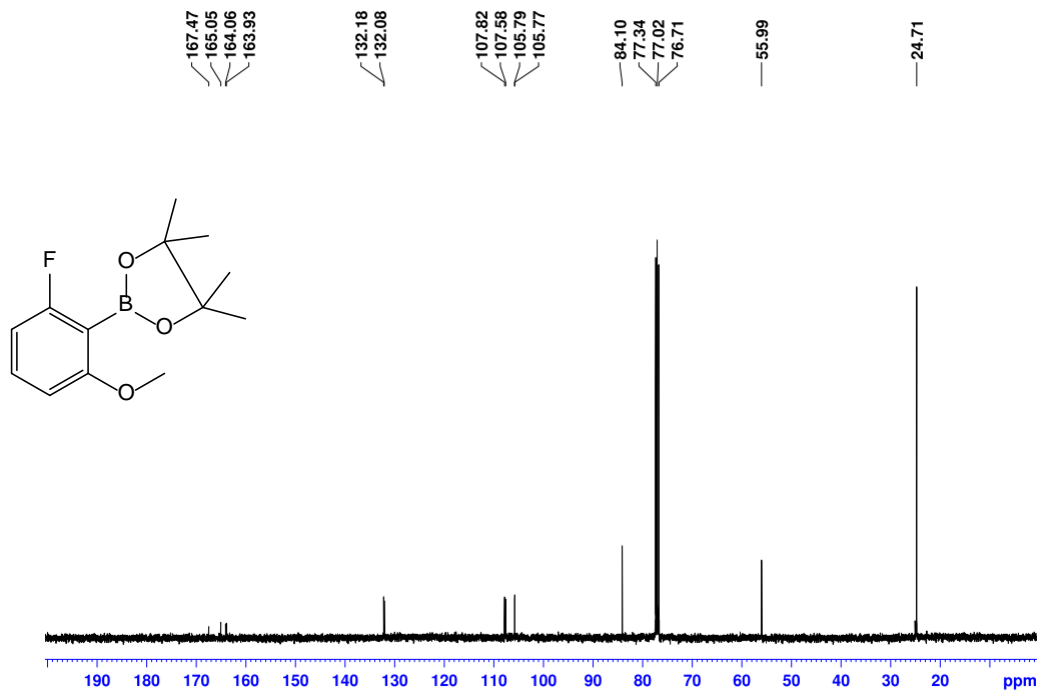
# <sup>19</sup>F NMR



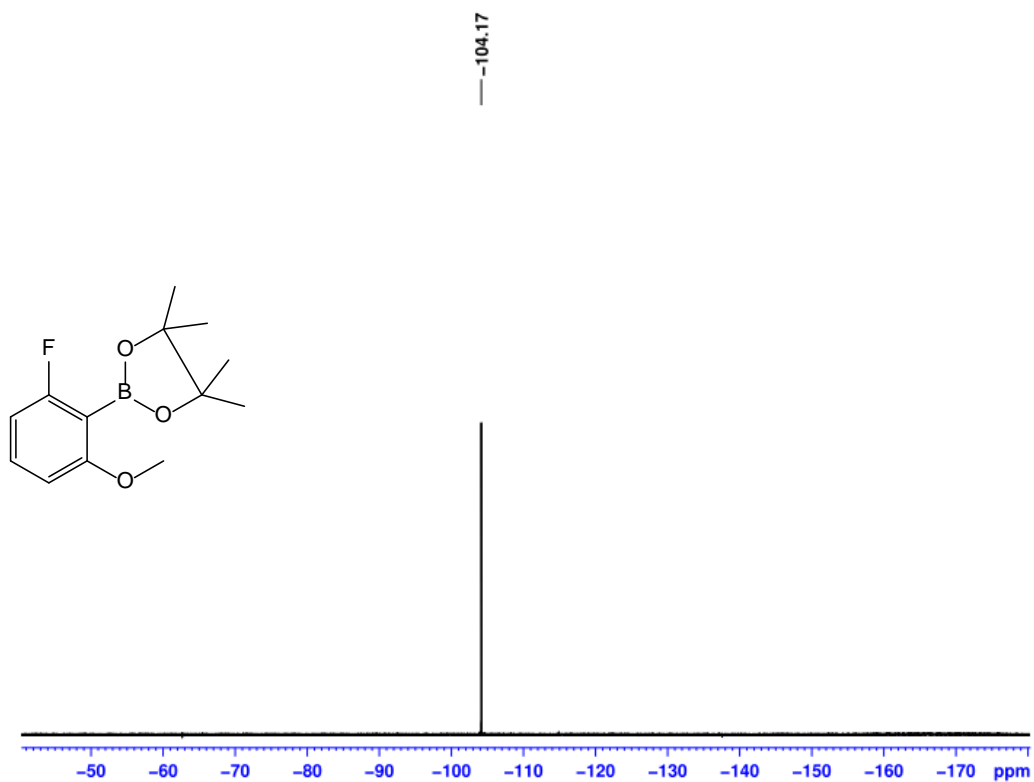
5b:  
<sup>1</sup>H NMR



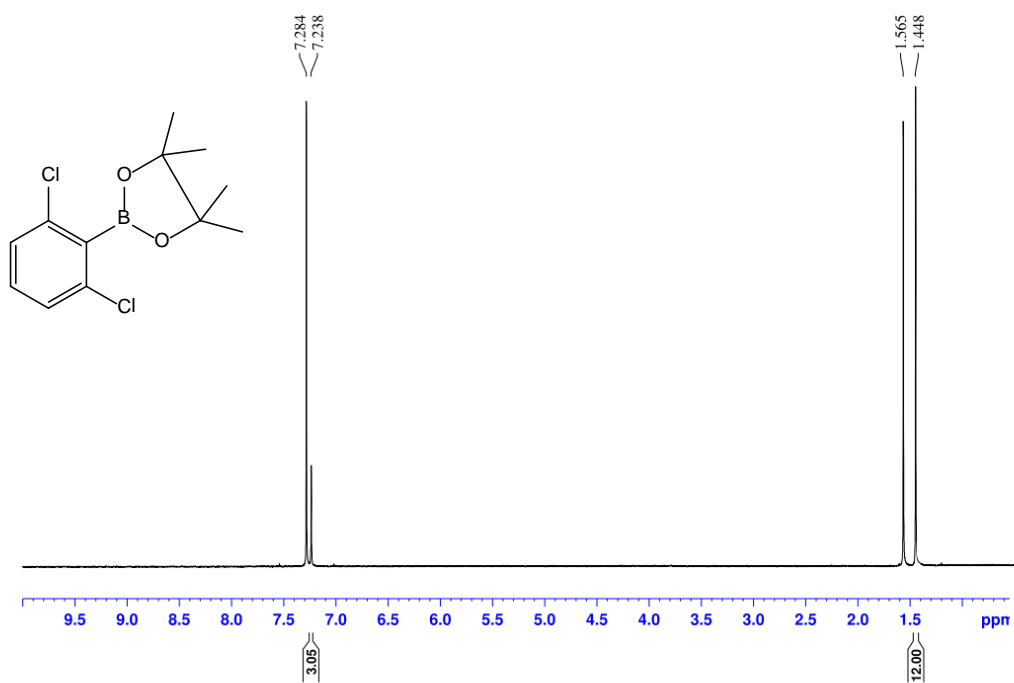
<sup>13</sup>C NMR



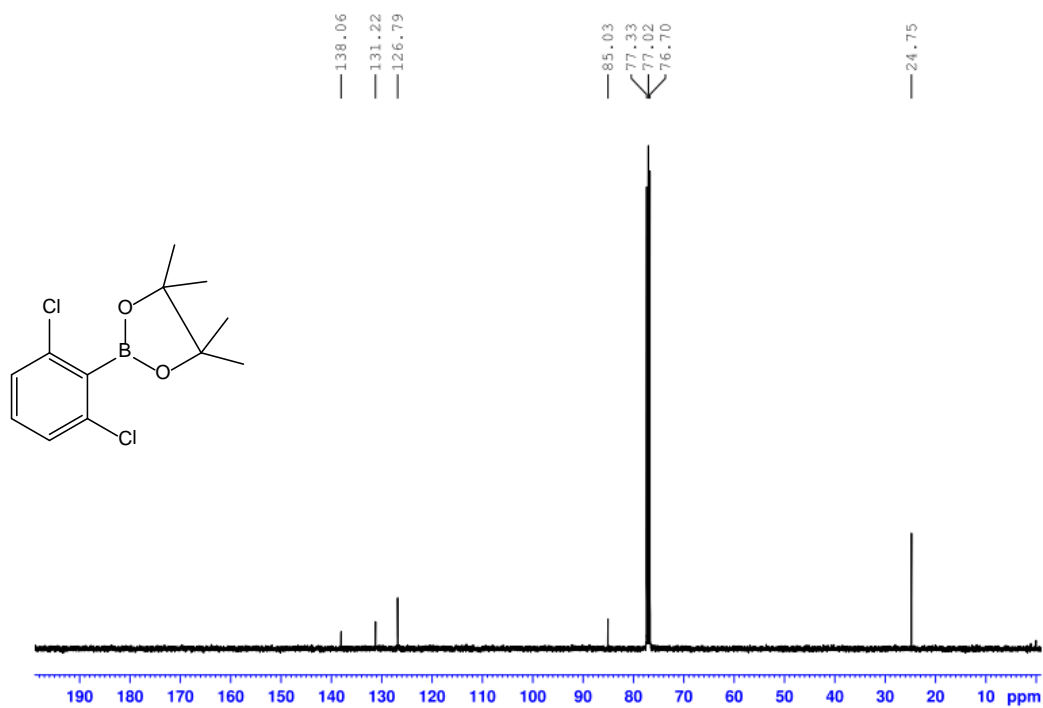
# $^{19}\text{F}$ NMR



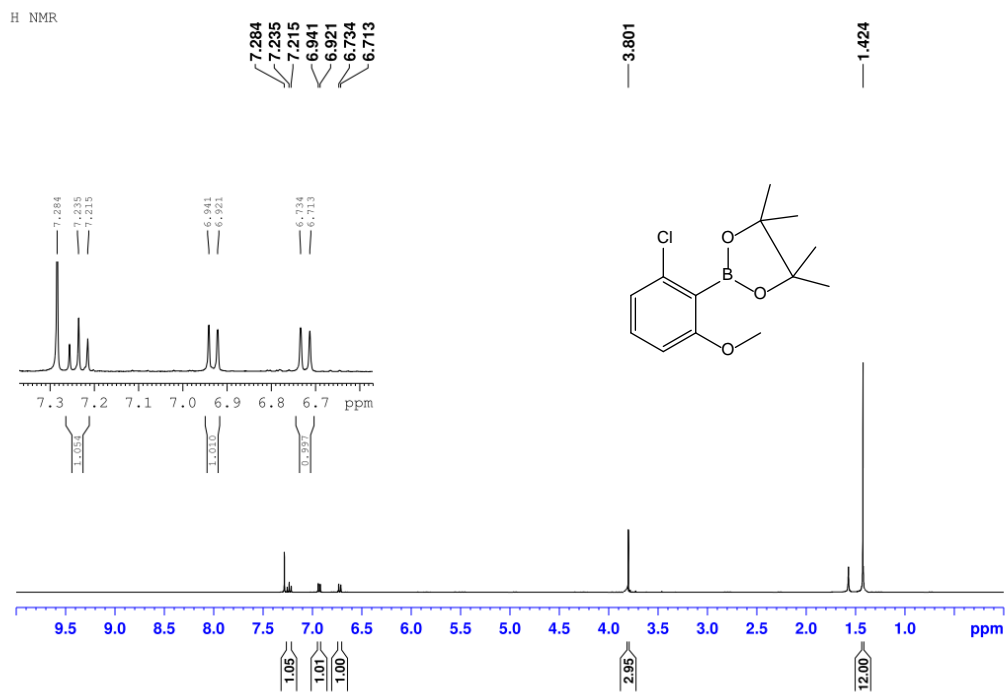
# 6b: $^1\text{H}$ NMR



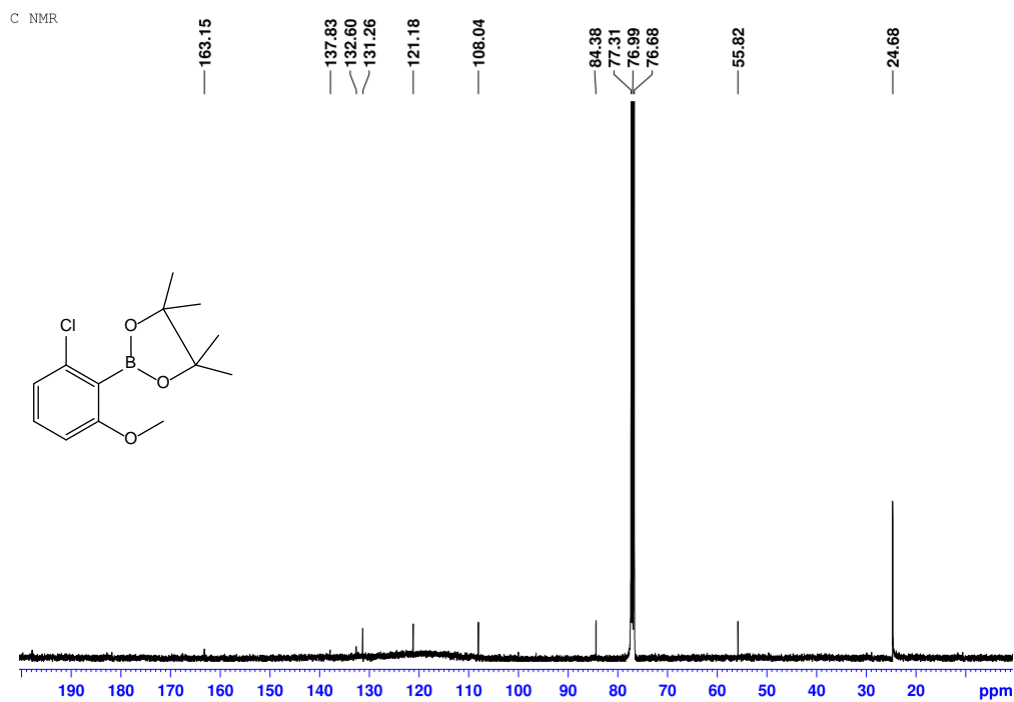
# <sup>13</sup>C NMR



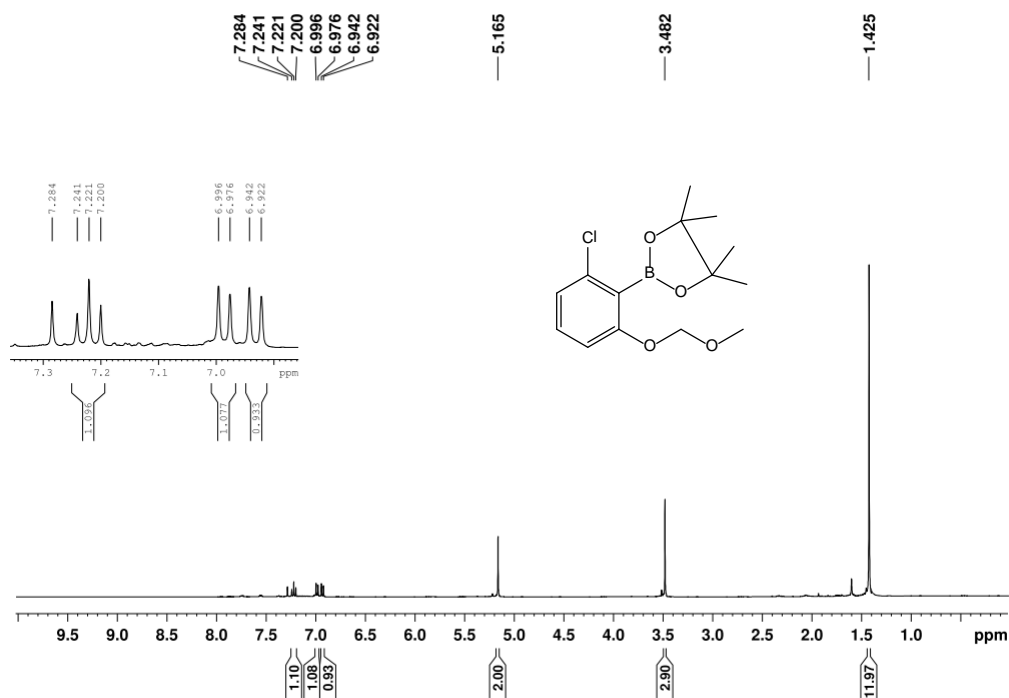
# 7b: <sup>1</sup>H NMR



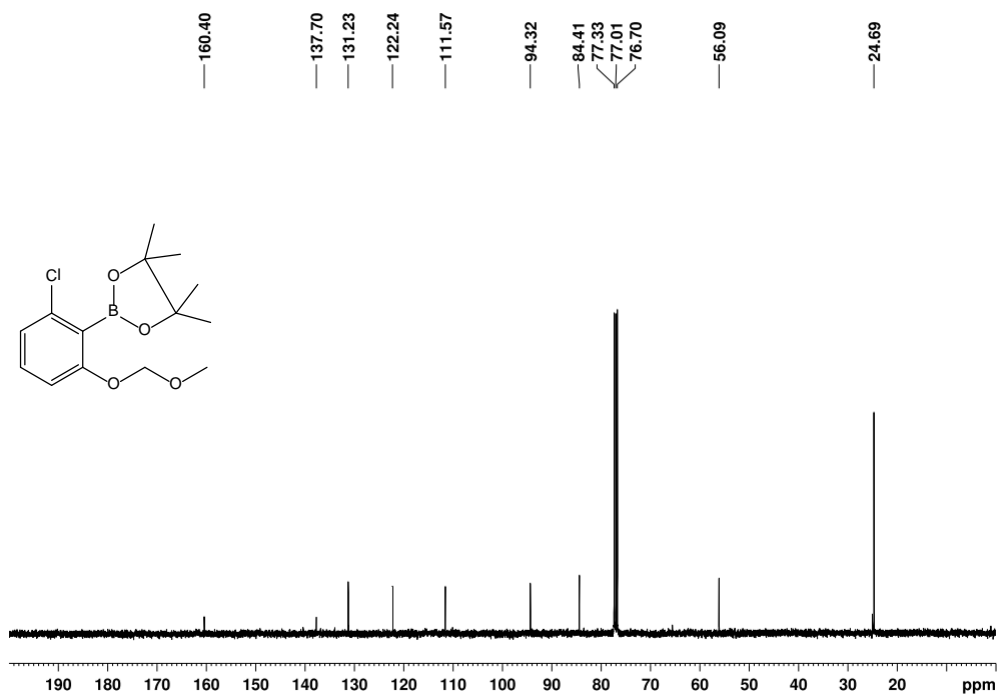
# <sup>13</sup>C NMR



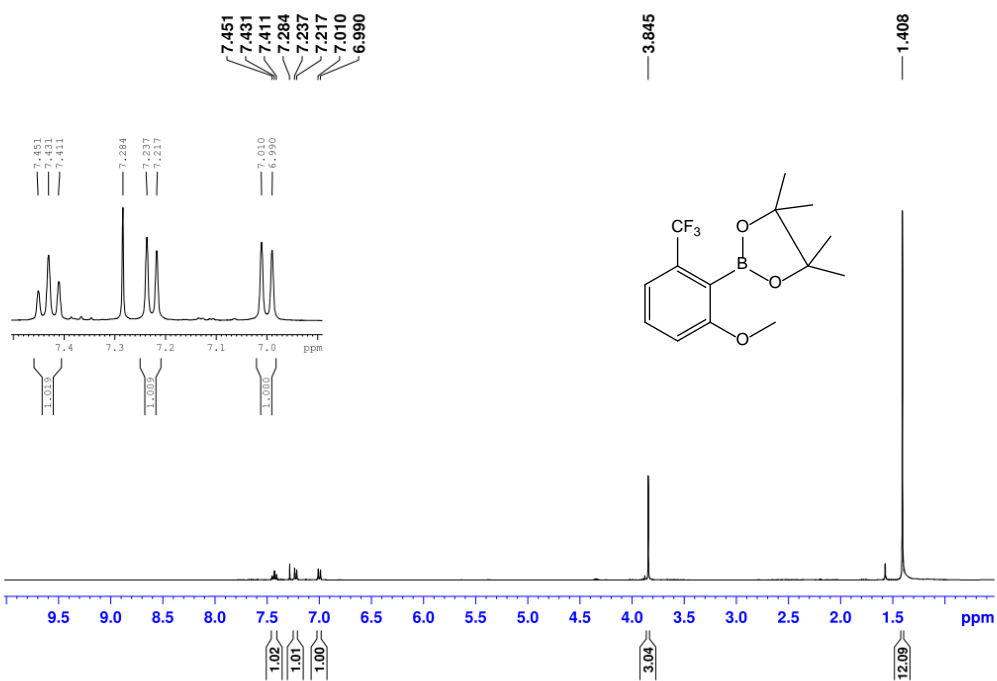
# 8b: <sup>1</sup>H NMR



# <sup>13</sup>C NMR

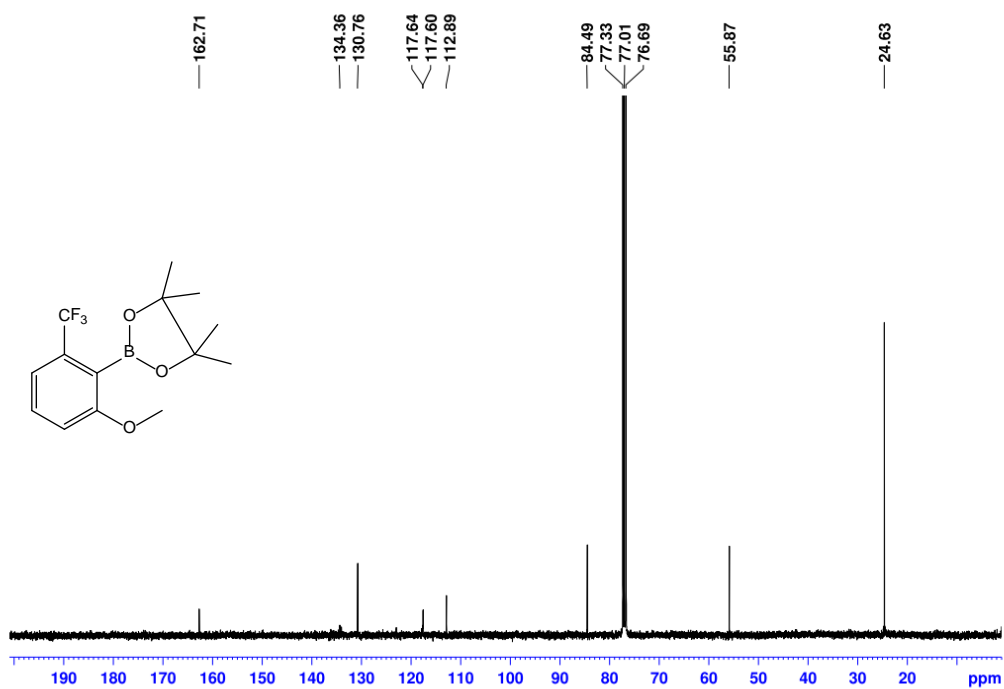


# 9b: <sup>1</sup>H NMR





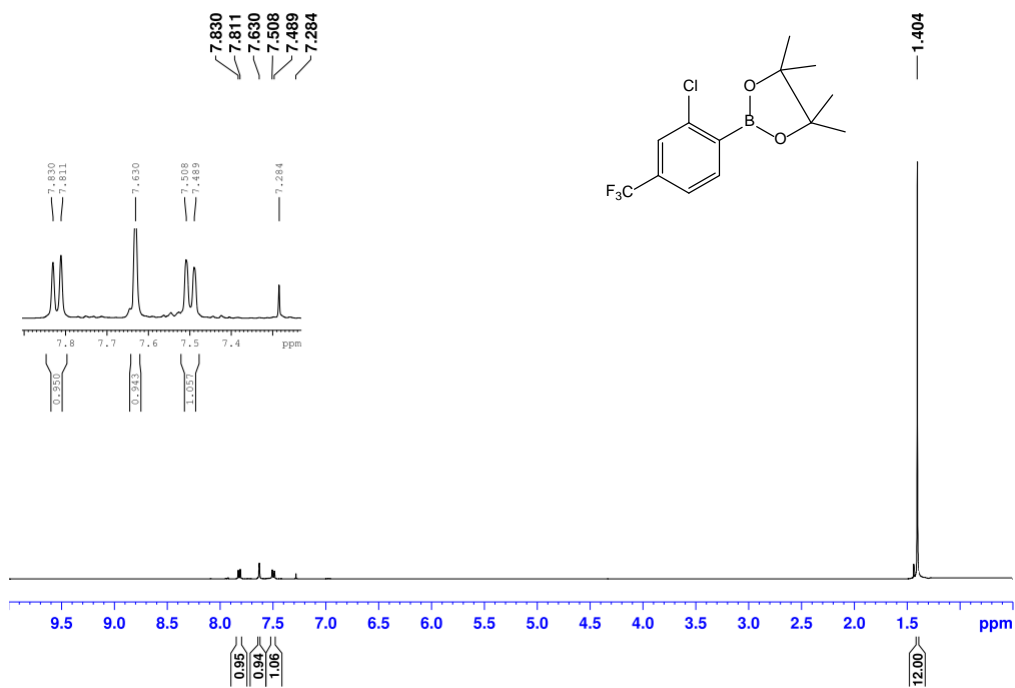
# <sup>13</sup>C NMR



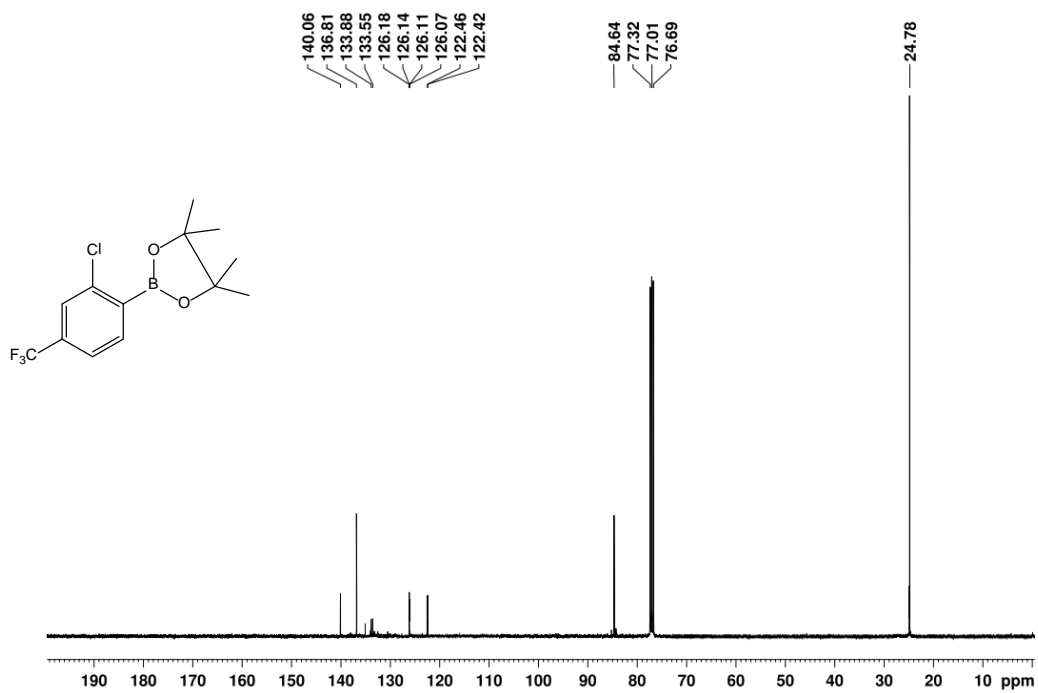
# <sup>19</sup>F NMR



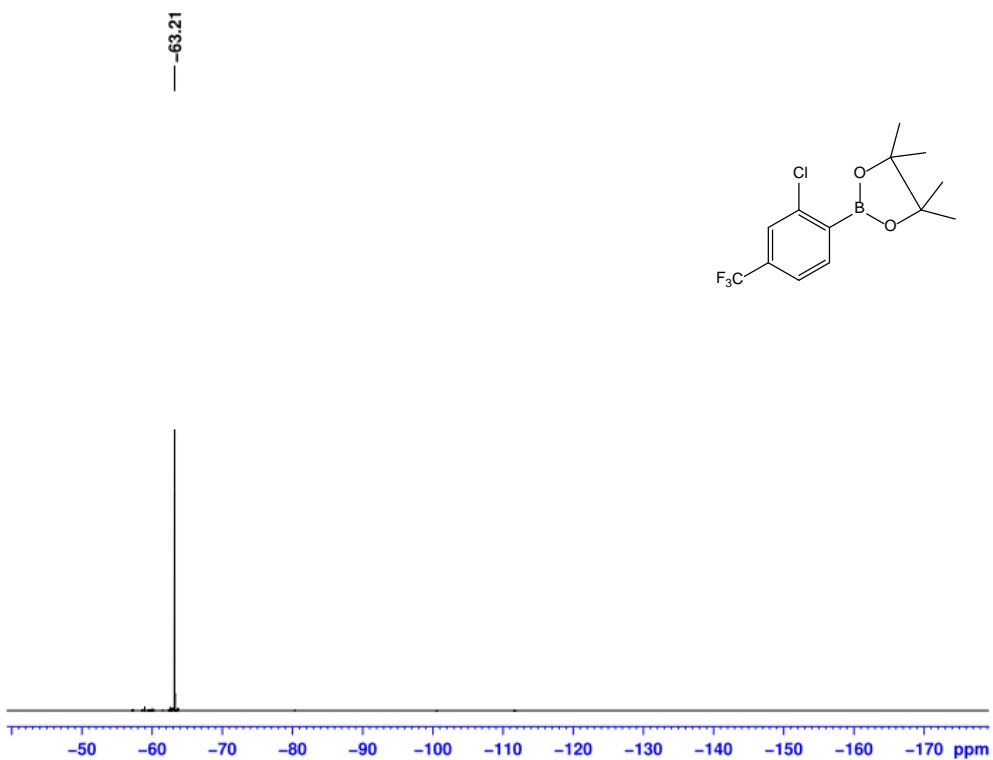
10c:  
<sup>1</sup>H NMR



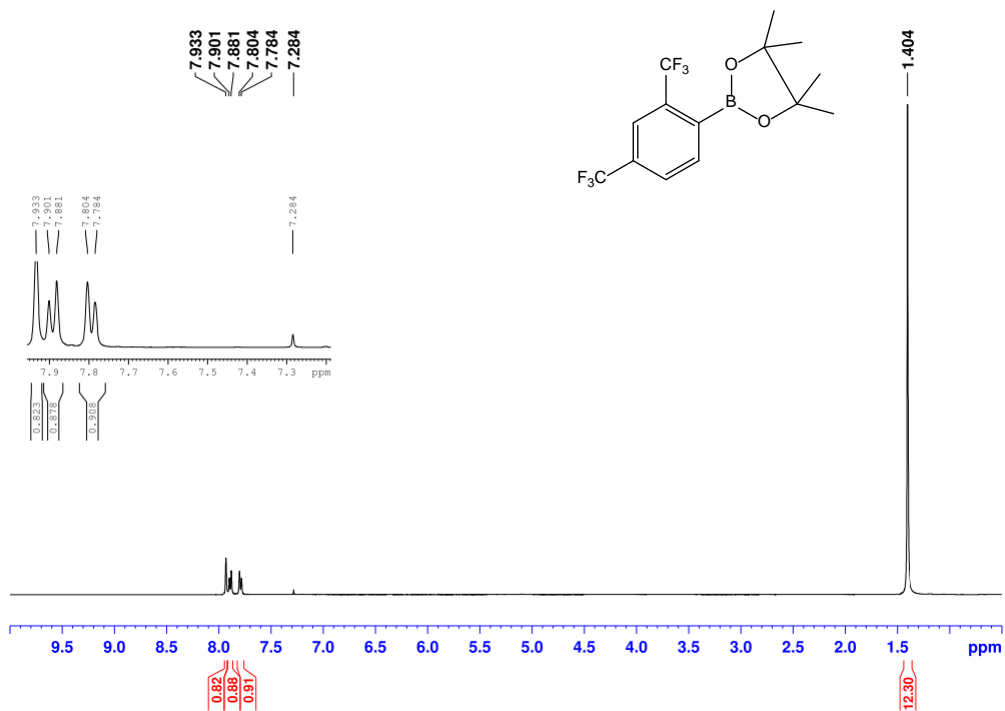
<sup>13</sup>C NMR



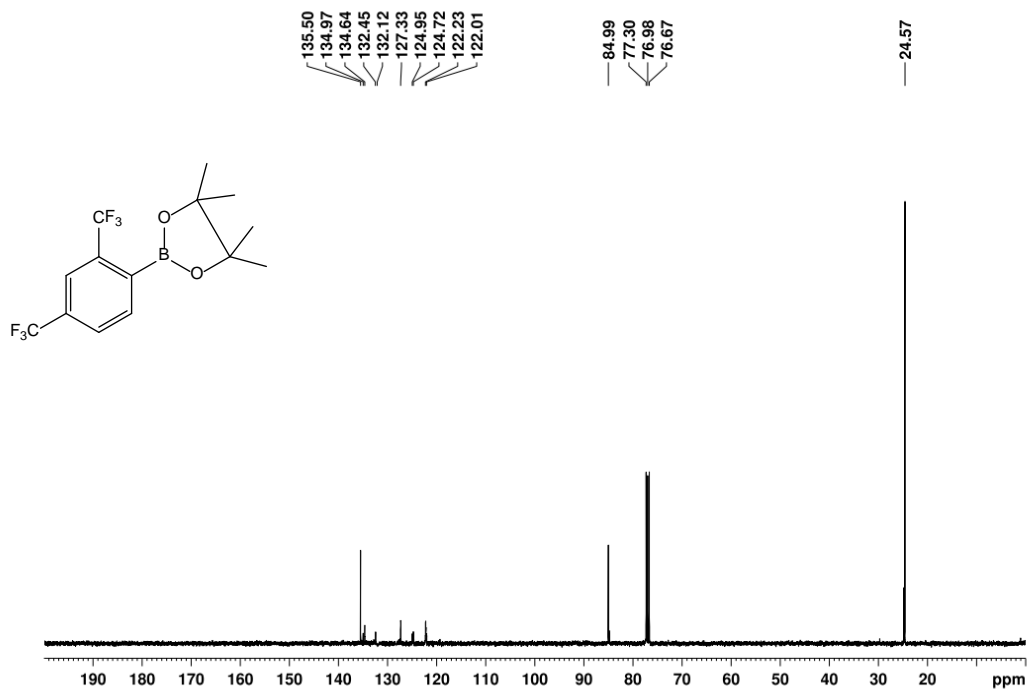
# <sup>19</sup>F NMR



# 11c: <sup>1</sup>H NMR



# <sup>13</sup>C NMR



# <sup>19</sup>F NMR

