

## Supporting Information to

### Neopentylglycolborylation of Aryl Mesylates and Tosylates Catalysed by Ni-Based Mixed Ligand Systems Activated with Zn

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## 1. Supporting data

**Table ST1.** Comparison of  $\text{NiCl}_2(\text{dppp})/\text{dppf}$ -Catalyzed Neopentyl-glycolborylation of Aryl Tosylates with and without Zn

entry	substrate	time (h)	0.05 equiv $\text{NiCl}_2(\text{dppp})/0.1$ equiv dppf/ (2 equiv Zn)		time (h)	convn <sup>a</sup> /yield <sup>b,c</sup> (%)
			convn <sup>a</sup> (%)	yield <sup>b</sup> (%)		
1	<chem>TsOc1ccccc1</chem>	42	22 / 22 (11) <sup>d</sup>		2	100 / 100 (83)
2	<chem>CC1=CC=C(C=C1)S(=O)(=O)c2ccccc2</chem>	48	95 / 95 (83)		1	100 / 100 (83)
3	<chem>TsOc1ccccc1C(=O)OCC</chem>	25	59 / 59 (50)		1	100 / 100 (81)
4	<chem>TsOc1ccccc1C(=O)OC</chem>	19	53 / 53		1	100 / 100 (84)
5	<chem>TsOc1ccccc1C(=O)OCC</chem>	20	49 / 33 (25) <sup>d</sup>		1	100 / 88 (75)
6	<chem>TsOc1ccccc1C#N</chem>	25	91 / 91 (82)		2	100 / 100 (80)
7	<chem>TsOc1ccccc1OC</chem>	19	19 / 19		3	100 / 100 (90)
8	<chem>TsOc1ccccc1C</chem>	41	16 / 16		4	100 / 100 (73)
9	<chem>TsOc1ccccc1C(C)C</chem>	89	65 / 65		2	100 / 100 (91)
10	<chem>TsOc1ccccc1C(C)C(C)C</chem>	20	3 / 3		20	100 / 93 (67)

<sup>a</sup> Conversion calculated from GC. <sup>b</sup> Yield determined by GC. Isolated yield in parentheses. <sup>c</sup> 2 equiv of Zn powder were used. <sup>d</sup> Isolated as solid trifluoroborates since the corresponding boronates are liquid.

## 2. Materials

1,3-Bis(diphenylphosphino)propane, *p*-toluenesulfonyl chloride,  $\text{KHF}_2$ ,  $\text{PTol}_3$ , phenol, 4-hydroxybenzonitrile, and 4-fluorophenol were used as received from Aldrich. 1,1'-Bis(diphenylphosphino)ferrocene, 99%, and  $\text{Ni}(\text{COD})_2$  were used as received from Strem Chemicals. 2-Fluorophenol and 3-methoxyphenol were used as received from Lancaster. Borane dimethylsulfide complex,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , methanesulfonyl chloride, toluenesulfonyl chloride, methyl 4-hydroxybenzoate, methyl 3-hydroxybenzoate, *m*-cresol, *p*-cresol, 4-methoxyphenol and 3,5-dimethoxyphenol were used as received from Acros. *o*-Cresol was used as received from Alfa Aesar. Naphtalen-2-ol was used as received from Kodak. Ethanol was used as received from Decon Laboratories. Methyl 2-hydroxybenzoate,  $\text{MgSO}_4$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NaCl}$ ,  $\text{NaHCO}_3$ , dichloromethane, acetone, ethyl acetate, hexanes, and methanol were all used as received from Fisher. Neopentylglycol from Acros was recrystallized from dichloromethane prior to use. Triphenylphosphine from Acros was recrystallized from hexanes prior to use. Toluene, triethylamine (ACS reagent grade), pyridine (ACS reagent grade) and dichloromethane from Fisher were distilled over  $\text{CaH}_2$  and stored under nitrogen prior to use. Deuterated solvents were obtained from Cambridge Isotope Labs.  $\text{NiCl}_2(\text{dppp})$  was synthesized according to a literature procedure<sup>1</sup>.

## 3. Instrumentation

<sup>1</sup>H NMR (500 MHz) and <sup>13</sup>C NMR (125 MHz) spectra were recorded using TMS as internal standard. A GC coupled with an FID detector and column HP 19091J-413 (5%-phenyl)-methylpolysiloxane 30m Length 0.32mm internal diameter was used to follow the reaction conversions and to assess purity of final compounds complementary to the NMR technique. The crude reaction mixtures were diluted with THF stabilized with BHT (3%), which was used as internal standard for GC analysis.

<sup>1</sup> Van Hecke, G. R.; Horrocks, W. D. *Inorg. Chem.* **1966**, 5, 1968.

#### 4. List of Abbreviations

$\text{BH}_3\bullet\text{DMS}$	borane dimethylsulfide complex
DCM	dichloromethane
dppp	1,3-bis(diphenylphosphino)propane
dppf	1,1'-bis(diphenylphosphino)ferrocene
$\text{PTol}_3$	tri- <i>p</i> -tolylphosphine
$\text{PPh}_3$	triphenylphosphine
$\text{NiCl}_2(\text{dppp})$	(1,3-bis(diphenylphosphino)propane) nickel(II) chloride

#### 5. General Synthetic Procedures

All reactions were performed in oven dried 25 mL Schlenk tubes with rubber septa tops under an  $\text{N}_2$  atmosphere. Commercially available air sensitive reagents and neopentylglycolborane generated *in situ* were transferred via syringe. Silica Gel (Flash) Chromatography was performed using silica gel (60 Å pore size, 230-400 Mesh, 40-64  $\mu\text{m}$  particle size, SiliCycle). Thin Layer Chromatography was carried out on pre-coated aluminum plates (silica gel with F254 indicator; layer thickness 200  $\mu\text{m}$ ; particle size 2-25  $\mu\text{m}$ ; pore size 60 Å, SIGMA-Aldrich).

#### General Procedure for the Synthesis of Aryl Mesylates or Aryl Tosylates

The aryl mesylates and tosylates were prepared according to literature procedures<sup>2</sup> and their spectral data and melting points are in agreement with the literature values.<sup>2,3,4,5</sup>

To an oven dried round bottom flask equipped with a stirring bar and nitrogen blanket was added the appropriate phenol ( $3.8 \times 10^{-2}$  mol) and freshly distilled dichloromethane (31mL) along with anhydrous pyridine (15g, 0.19 mol) and the reaction mixture was cooled to 0°C in an ice and water bath. Methanesulfonyl chloride ( $4.56 \times 10^{-2}$  mol) was added dropwise with stirring while toluenesulfonyl chloride is a solid and was added prior in the reaction flask. The reaction was allowed to proceed with stirring in the ice water bath for 4 hours after which the ice water bath was removed and the reaction was allowed to warm to room temperature and continued until complete consumption of the starting material was observed by TLC. The reaction was quenched by addition of water (40 mL) and the organic phase was separated. The aqueous phase was further extracted with dichloromethane (3 x 20mL) and all the organic layers were combined and washed successively with 15% HCl (2 x 20 mL) and Brine (3 x 20mL) then dried over  $\text{MgSO}_4$ . Following filtration the solvent was removed under reduced pressure and purified by column chromatography or recrystallization.

**Phenyl Methanesulfonate** The crude product was purified by column chromatography using dichloromethane as eluent to yield the product as white crystals, 5.75 g (82% yield), mp 60 °C (lit<sup>6</sup> 60 - 62 °C).

<sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (t, 1H), 7.33 (t, 1H), 7.29 (d, 1H), 3.13 (s, 3H).

**Naphthalen-2-yl Methanesulfonate** Purification by flash chromatography using dichloromethane afforded the title compound as a pale yellow powder, 6.09 g (85% yield), mp 103 °C (lit<sup>7</sup> 103 - 104 °C).

<sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (d, 1H), 7.90 - 7.85 (m, 2H), 7.78 (d, 1H), 7.59 - 7.52 (m, 2H), 7.42 (dd, 1H), 3.20 (s, 3H).

**Methyl 4-((Methysulfonyl)oxy)benzoate** Recrystallization from methanol afforded white crystals, 5.30 g (72.1% yield), mp 90 °C (lit<sup>2</sup> 89 - 90 °C).

<sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (d, 2H), 7.36 (d, 2H), 3.93 (s, 3H), 3.19 (s, 3H).

**Methyl 3-((Methysulfonyl)oxy)benzoate** The crude product was purified by column chromatography using DCM as eluent to yield the product as white crystals, 5.58g (80% yield), mp 73 °C (lit<sup>2</sup> 70 - 72 °C).

<sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (t,  $J = 0.9$ , 1H), 7.93 (s, 1H), 7.51 (d,  $J = 4.9$ , 1.2, 2H), 3.94 (s, 3H), 3.19 (s, 3H).

<sup>2</sup> Percec, V.; Bae, J.-Y.; Zhao, M.; Hill, D. H. *J. Org. Chem.* **1995**, *60*, 176.

<sup>3</sup> Barbero, M.; Degani, I.; Dughera, S.; Fochi, R.; Perracino, P. *Synthesis* **1999**, *1*, 90.

<sup>4</sup> Carnahan Jr., J. C.; Closson, W. D.; Ganson, J. R.; Juckett, D. A. Quaal, K. S. *J. Am. Chem. Soc.* **1976**, *98*, 2526.

<sup>5</sup> Zim, D.; Lando, V. R.; Dupont, J.; Monteiro, A. L. *Org. Lett.* **2001**, *3*, 3049.

<sup>6</sup> Kaboardin, B.; Abedi, Y. *Synthesis* **2009**, *12*, 2025.

<sup>7</sup> Latimer, P. H.; Bost, R. W. *J. Org. Chem.* **1940**, *5*, 24.

**Methyl 2-((Methylsulfonyl)oxy)benzoate** Purification by flash chromatography using dichloromethane as the eluent afforded the title compound as a slightly yellow oil, 2.37 g (33.6% yield). The spectral data are in agreement with the literature values.<sup>2</sup>

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.97 (dd, J = 7.8, 1.7, 1H), 7.57 (ddd, J = 8.2, 7.4, 1.8, 1H), 7.43 (dd, J = 8.2, 1.0, 1H), 7.37 (td, J = 7.7, 1.1, 1H), 3.91 (s, 3H), 3.26 (s, 3H).

**4-Cyanophenyl Methanesulfonate** The crude product was recrystallized from methanol to yield white crystals, 5.83g (83% yield), mp 92 °C (lit<sup>2</sup> 89 - 90 °C).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 (t, 1H), 7.33 (t, 1H), 7.29 (d, 1H), 3.13 (s, 3H).

**4-Fluorophenyl Methanesulfonate** The crude product was purified by silica gel chromatography (dichloromethane) to yield the product as colorless oil, 6.28 g (87% yield). The spectral data are in agreement with the literature values.<sup>2</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.27 (m, 2H), 7.11 (m, 2H), 3.13 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  162.42 (d, J = 247 Hz), 145.18 (d, J = 3 Hz), 124.03 (d, J = 9 Hz), 117.09 (d, J = 24 Hz), 37.51.

**2-Fluorophenyl Methanesulfonate** The crude product was purified by silica gel chromatography (dichloromethane) to yield the product as a colorless oil, 6.36 g (88% yield). The spectral data are in agreement with the literature values.<sup>3</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.39 (t, J = 7.8 Hz, 1H), 7.31 (m, 1H), 7.22 (m, 2H), 3.20 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  155.55 (d, J = 250Hz), 136.97 (d, J = 12 Hz), 128.94 (d, J = 7 Hz), 125.48 (d, J = 3 Hz), 125.31 (d, J = 4 Hz), 117.62 (d, J = 18 Hz), 38.34.

**p-Tolyl Methanesulfonate** Purification by flash chromatography using dichloromethane as the eluent afforded the title compound as a white crystalline powder, 5.74 g (80.0% yield), 48 – 49 °C (lit<sup>6</sup> 47 – 49 °C).

<sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>)  $\delta$  7.24 – 7.14 (m, J = 8.8, 7.5, 4H), 3.12 (s, 3H), 2.37 (s, 3H).

**m-Tolyl Methanesulfonate** Purification by flash chromatography using dichloromethane afforded the title compound as a colorless oil, 5.62 g (80.5% yield). The spectral data are in agreement with the literature values.<sup>3</sup>

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.33 – 7.26 (m, J = 15.4, 7.5, 1H), 7.15 (d, J = 7.7, 1H), 7.12 – 7.07 (m, 2H), 3.13 (s, 3H), 2.39 (s, 3H).

**o-Tolyl Methanesulfonate** The crude product was purified by silica gel chromatography using dichloromethane to yield the product as colorless oil, 5.23 g (74% yield). The spectral data are in agreement with the literature values.<sup>2</sup>

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.28 (m, 2H), 7.22 (m, 2H), 3.17 (s, 3H), 2.36 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  148.12, 132.16, 131.55, 127.54, 122.29, 38.31, 16.86.

**4-Methoxyphenyl Methanesulfonate** Purification by flash chromatography using dichloromethane/ethylacetate 5/1 afforded the title compound as a white crystalline powder, 6.2 g (87.8% yield), mp 80 °C (lit<sup>2</sup> 78 – 80 °C).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.21 (d, J = 9.1, 2H), 6.91 (d, J = 9.1, 2H), 3.81 (s, 3H), 3.11 (s, 3H).

#### Phenyl 4-Methylbenzenesulfonate

Purification by flash chromatography using dichloromethane affording white crystals, 5.4 g (76 % yield), mp 95 °C (lit<sup>8</sup> 95 – 96 °C).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.70 (d, J = 8.3, 2H), 7.30 (d, J = 8.0, 2H), 7.28 (d, J = 7.9, 1H), 7.24 (t, J = 7.1, 1H), 6.98 (d, J = 7.3, 2H), 2.45 (s, 3H).

#### Naphthalen-2-yl 4-Methylbenzenesulfonate

Purification by flash chromatography using dichloromethane affording yellow pale crystals, 5.6 g (80 % yield), mp 124 °C (lit<sup>9</sup> 125 – 126 °C).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.84 – 7.78 (m, 1H), 7.77 – 7.70 (m, 4H), 7.52 – 7.45 (m, 3H), 7.29 (d, J = 8.0, 2H), 7.10 (dd, J = 8.9, 1H), 2.44 (s, 3H).

#### Methyl 4-(Tosyloxy)benzoate

<sup>8</sup> Roberts, J. D.; Chambers, V. C. *J. Am. Chem. Soc.* **1951**, 73, 5034.

<sup>9</sup> Balasubramanian, V.; Baliah, V. *J. Indian Chem. Soc.* **1959**, 36, 391.

Purification by recrystallization from acetone afforded white crystals, 5.4 g (77% yield), mp 88 – 89 °C (lit<sup>2</sup> 85 – 86 °C).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.98 (d, J = 8.8, 2H), 7.71 (d, J = 8.3, 2H), 7.32 (d, J = 8.1, 2H), 7.07 (d, J = 8.9, 2H), 3.91 (s, 3H), 2.46 (s, 3H).

#### **Methyl 3-(Tosyloxy)benzoate**

Purification by flash chromatography using dichloromethane affording an oily liquid, 5.1 g (78 % yield). The spectral data are in agreement with the literature values.<sup>10</sup>

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.93 (d, J = 7.8, 1H), 7.71 (d, J = 8.4, 2H), 7.66 (s, 1H), 7.37 (t, J = 8.0, 1H), 7.32 (d, J = 8.0, 2H), 7.19 (d, J = 8.2, 2.4, 1.0, 1H), 3.89 (s, 4H), 2.45 (s, 3H).

#### **Methyl 2-(Tosyloxy)benzoate**

Purification by recrystallization from methanol affording white crystals, 4.8 g (67% yield), mp 89 – 90 °C (lit<sup>5</sup> 89 – 90 °C).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.88 (d, J = 7.8, 1H), 7.73 (d, J = 8.3, 2H), 7.47 (td, J = 7.5, 1H), 7.38 – 7.28 (m, 3H), 7.10 (d, J = 8.2, 1H), 3.80 (s, 3H), 2.45 (s, 3H).

#### **4-Cyanophenyl 4-Methylbenzenesulfonate**

Purification by recrystallization from methanol affording white crystals, 5 g (70% yield), mp 85 – 88 °C (lit<sup>5</sup> 84 – 86 °C).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.74 (d, J = 17.6, 16.0, 2H), 7.63 (d, 2H), 7.35 (d, J = 8.1, 2H), 7.20 – 7.07 (m, 2H), 2.47 (s, 3H).

#### **4-Methoxyphenyl 4-Methylbenzenesulfonate**

Purification by flash chromatography using dichloromethane : ethyl acetate (5 : 1) as the eluent afforded a white crystalline powder, 5.6 g (83% yield), mp 69 – 71 °C (lit<sup>5</sup> 69 – 71 °C).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.69 (d, J = 8.3, 2H), 7.30 (d, J = 8.1, 2H), 6.88 (d, J = 9.1, 2H), 6.76 (d, J = 9.1, 2H), 3.76 (s, 3H), 2.44 (s, 3H).

#### **p-Tolyl 4-Methylbenzenesulfonate**

Purification by flash chromatography using dichloromethane as white powder, 5.4 g (76% yield), mp 59 – 60 °C (lit<sup>15</sup> 58 – 60 °C).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.88 (dd, J = 7.8, 1H), 7.73 (d, J = 8.3, 2H), 7.47 (td, J = 7.5, 1H), 7.37 – 7.28 (m, J = 11.9, 8.1, 3H), 7.10 (d, J = 8.2, 1H), 3.80 (s, 3H), 2.45 (s, 3H).

#### **m-Tolyl 4-Methylbenzenesulfonate**

Purification by flash chromatography using dichloromethane as the eluent afforded the title compound as a white crystalline powder, 5.2 g (73% yield), mp 62 °C (lit<sup>5</sup> 60 – 62 °C).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.71 (d, J = 8.2, 2H), 7.30 (d, J = 8.0, 2H), 7.13 (t, J = 7.9, 1H), 7.04 (d, J = 7.6, 1H), 6.85 (s, 1H), 6.71 (d, J = 8.1, 1H), 2.44 (s, 3H), 2.29 (s, 3H).

#### ***o*-Tolyl 4-Methylbenzenesulfonate**

Purification by flash chromatography using dichloromethane as the eluent afforded the product as white crystals, 4.9 g (70%), mp 60 °C (lit<sup>5</sup> 59 – 60 °C).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.73 (d, J = 8.3, 2H), 7.31 (d, J = 8.0, 2H), 7.18 – 7.06 (m, 3H), 6.99 (d, 1H), 2.44 (s, 3H), 2.07 (s, 3H).

#### **General Procedure for Neopentylglycolborylation**

To an oven dried 25mL Schlenk tube was added NiCl<sub>2</sub>(dppp) (0.081g, 1.5x10<sup>-4</sup> mol) and dpff (0.166g, 3x10<sup>-4</sup> mol) along with the appropriate aryl mesylate or tosylate(3x10<sup>-3</sup> mol). The mesylate, catalyst and ligand were degassed by pumping and backfilling with nitrogen three times. Toluene was added to the reaction mixture (5mL) along with Et<sub>3</sub>N (1.26 mL 9x10<sup>-3</sup> mol). Neopentylglycol borane was added dropwise to the reaction mixture. The reaction was

<sup>10</sup> Huang, X.; Anderson, K. W.; Zim, D.; Jiang, L.; Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, 125, 6653.

allowed to heat and proceed at 100 °C with stirring under an inert atmosphere until complete consumption of the starting material was observed by GC analysis. The reaction was then quenched with addition of NH<sub>4</sub>Cl (50 mL) and extracted with ethyl acetate (3x25mL). The organic fractions were combined and dried over MgSO<sub>4</sub>. Following filtration the solvent was removed under reduced pressure and the crude reaction mixture immediately passed through a plug of silica gel with DCM eluent to remove traces of Ni catalyst and salts before further purification on silica gel with appropriate eluent. The neopentylglycolboronates were reported previously as final products resulted from neopentylglycolborylation of aryl halides.<sup>11</sup>

### General Procedure for Neopentylglycolborylation in the Presence of Zn

To an oven dried 25mL Schlenk tube was added NiCl<sub>2</sub>(dppp) (0.081g, 1.5x10<sup>-4</sup> mol), dppf (0.166g, 3x10<sup>-4</sup> mol) and zinc dust (0.389g 6x10<sup>-3</sup> mol) along with the appropriate aryl mesylate or tosylate (3x10<sup>-3</sup> mol). The mesylate, catalyst and ligand were degassed by pumping and backfilling with nitrogen three times. Toluene was added to the reaction mixture (5mL) along with Et<sub>3</sub>N (1.26 mL 9x10<sup>-3</sup> mol). Neopentylglycol borane was added dropwise to the reaction mixture and the reaction heated to 100°C. The reaction was allowed to proceed at 100 °C with stirring under an inert atmosphere until complete consumption of the starting material was observed by GC analysis. The reaction mixture was filtered to remove the zinc dust and the precipitate washed with ethyl acetate (3x10mL). The filtrate was then quenched with addition of NH<sub>4</sub>Cl (50 mL) extracted with ethyl acetate (3x25mL). The organic fractions were combined and dried over MgSO<sub>4</sub>. Following filtration the solvent was removed under reduced pressure and the crude reaction mixture was immediately passed through a plug of silica gel with DCM eluent to remove traces of Ni catalyst and salts before further purification on silica gel with appropriate eluent.

### General Procedure for the Synthesis of Aryl Trifluoroborates

The potassium trifluoroborates were prepared from the corresponding crude boronic esters according to literature procedures.<sup>12</sup> In a nalgene bottle were added a stir bar and the crude boronic ester (5 mmol, 1 equiv) dissolved in 12 ml MeOH : H<sub>2</sub>O (2:1). KHF<sub>2</sub> (15 mmol, 3 equiv) was added one portion over the reaction mixture and the reaction mixture was stirred at room temperature overnight. The reaction mixture was transferred to a round bottom flask and concentrated by rotary evaporation. The crude product was recrystallized from acetone to yield the corresponding aryl trifluoroborate.

**5,5-Dimethyl-2-phenyl-1,3,2-dioxaborinane (Table 1, entry 1).** Purification by flash chromatography with gradient of hexanes : ethyl acetate; white powder, 0.55 g (97% yield), mp 64 – 67 °C (lit<sup>13</sup> 62 – 66 °C).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.83 (dd, J = 7.9, 1.2, 2H), 7.48 – 7.42 (m, 1H), 7.40 – 7.35 (m, 2H), 3.80 (s, 4H), 1.05 (s, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 133.74, 130.58, 127.48, 72.22, 31.64, 21.82.

**5,5-Dimethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborinane (Table 1, entry 2).** Purification by flash chromatography on silica gel with hexanes : ethyl acetate (8 : 1) and recrystallized from MeOH giving a white powder, 0.7 g (95% yield), mp 100 -103 °C. The spectral data are in agreement with the literature values.<sup>14</sup>

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.36 (s, 1H), 7.98 – 7.69 (m, 4H), 7.55 – 7.39 (m, 2H), 3.85 (s, 4H), 1.07 (s, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 134.94, 129.83, 128.57, 127.55, 126.68, 126.51, 125.48, 72.33, 31.86, 21.85.

**Methyl 4-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (Table 1, entry 3).** Purified by column chromatography on silica gel with DCM and recrystallized from MeOH; white crystals, 0.67 g (88% yield), mp 114 °C (lit<sup>11</sup> 113 – 114 °C).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.01 (d, J = 8.1, 2H), 7.87 (d, J = 8.1, 2H), 3.93 (s, 3H), 3.79 (s, 4H), 1.04 (s, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 167.23, 133.67, 131.71, 128.41, 72.28, 51.99, 31.80, 21.79.

**Methyl 3-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (Table 1, entry 4).** Purification by flash chromatography (hexanes : ethyl acetate) afforded a white wax, mp 69 – 73 °C (lit<sup>15</sup> 70 – 72 °C). 0.66g (87% yield); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.47 (s, 1H), 8.09 (d, J = 7.7, 1H), 7.98 (d, J = 7.4, 1H), 7.43 (t, J = 7.3, 1H), 3.91 (s,

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<sup>12</sup> Molander, G. A.; Biolatto, B. *J. Org. Chem.* **2003**, *68*(11), 4302.

<sup>13</sup> Chaumeil, H.; Signorella, S.; Le Drian, C. *Tetrahedron*, **2000**, *56*, 9655.

<sup>14</sup> Ukai, K.; Aoki, M.; Takaya, J.; Iwasawa, N. *J. Am. Chem. Soc.* **2006**, *128*, 8706.

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3H), 3.79 (s, 4H), 1.03 (s, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  167.29, 138.22, 134.89, 131.64, 129.29, 129.10, 127.55, 72.25, 52.27, 31.77, 21.77, 8.50.

**Methyl 2-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (Table 1 entry 5).** The crude product was purified by silica gel chromatography (8 hexanes: 1 dichloromethane) to yield the product as colorless oil (0.56 g, 75%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (dd,  $J = 7.8, 0.8$  Hz, 1H), 7.51 (m, 2H), 7.40 (dt,  $J = 7.8, 2.4$  Hz, 1H), 3.92 (s, 3H), 3.80 (s, 4H), 1.11 (s, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.44, 133.09, 132.29, 131.63, 128.96, 128.72, 72.87, 52.70, 32.15, 22.39.

**4-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)benzonitrile (Table 1, entry 6).** The crude product was purified by silica gel chromatography on silica gel with dichloromethane, mp 124 – 125 °C (lit<sup>16</sup> 123–125 °C).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (d,  $J = 8.2$ , 2H), 7.61 (d,  $J = 8.3$ , 2H), 3.78 (s, 4H), 1.03 (s, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  134.14, 130.91, 119.03, 113.81, 72.31, 31.80, 21.73.

**2-(4-Fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (Table 1 entry 7).** The crude product was purified by silica gel chromatography (10 hexanes: 1 ethyl acetate) to yield the product as white crystals (0.55 g, 88%), mp 64–67°C (lit.<sup>17</sup> 65–67°C).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (dd,  $J = 8.5, 5.1$  Hz, 2H), 7.06 (m, 2H), 3.77 (s, 4H), 1.03 (s, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  164.61 (d,  $J = 250$  Hz), 136.80 (d,  $J = 8$  Hz), 115.43 (d,  $J = 20$  Hz), 73.08, 32.64, 22.65.

**2-(2-Fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (Table 1 entry 8).** The crude product was purified by silica gel chromatography (10 hexanes: 1 ethyl acetate) to yield the product as yellowish crystals (0.47 g, 75%), mp 37–40°C (lit.<sup>18</sup> 40°C).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (dt,  $J = 6.8, 1.7$  Hz, 1H), 7.41 (m, 1H), 7.13 (t,  $J = 7.3$  Hz, 1H), 7.02 (t,  $J = 8.8$  Hz, 1H), 3.80 (s, 4H), 1.04 (s, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  168.43 (d,  $J = 250$  Hz), 136.50 (d,  $J = 8$  Hz), 132.86 (d,  $J = 9$  Hz), 123.80 (d,  $J = 3$  Hz), 115.74 (d,  $J = 24$  Hz), 72.75, 32.13, 22.17.

**Potassium Trifluoro(2-fluorophenyl)borate (Table 1 entry 8).** The crude product was recrystallized from acetone to yield the product as white powder (0.06 g, 13%), mp >250°C (lit.<sup>19</sup> 304–305°C).  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-d}_6$ )  $\delta$  7.34 (t,  $J = 6.5$  Hz, 1H), 7.06 (q,  $J = 6.5$  Hz, 1H), 6.90 (t,  $J = 6.9$  Hz, 1H), 6.78 (t,  $J = 8.5$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-d}_6$ )  $\delta$  166.61 (d,  $J = 240$  Hz), 134.20 (dd,  $J = 13, 2$  Hz), 127.24 (d,  $J = 8$  Hz), 122.47, 113.80 (d,  $J = 26$  Hz).

**5,5-Dimethyl-2-(*p*-tolyl)-1,3,2-dioxaborinane (Table 1, entry 9).** The crude product was purified by column chromatography with hexanes: ethyl acetate (4:1) giving 0.57 g (95 % yield) of white crystals, mp 93 – 94 °C (lit<sup>20</sup> 92 – 95 °C).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J = 7.9$ , 2H), 7.21 (d,  $J = 7.6$ , 2H), 3.88 – 3.68 (m, 4H), 2.45 – 2.35 (m, 3H), 1.05 (s, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  140.59, 133.84, 128.33, 72.20, 30.26, 21.83, 21.58.

**5,5-Dimethyl-2-(*m*-tolyl)-1,3,2-dioxaborinane (Table 1, entry 10).**

Purification by column chromatography with hexane : ethyl acetate (4:1), yellowish powder, 0.61 g (98% yield), mp 85 – 87 °C. The spectral data are in agreement with the literature values.<sup>21</sup>

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 – 7.56 (m, 2H), 7.30 – 7.22 (m, 2H), 3.78 (s,  $J = 9.2, 4$  H), 2.35 (s,  $J = 22.6, 3$  H), 1.04 (s, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  136.81, 134.38, 131.36, 130.78, 127.46, 72.22, 53.33, 31.78, 21.80, 21.27.

**5,5-Dimethyl-2-(*o*-tolyl)-1,3,2-dioxaborinane (Table 1 entry 12).** The crude product was purified by silica gel chromatography (10 hexanes: 1 ethyl acetate) to yield the product as colorless oil (0.47 g, 77%). The spectral data are in agreement with the literature values.<sup>11</sup>  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (d,  $J = 7.3$  Hz, 1H), 7.27 (dt,  $J = 7.4, 1.4$  Hz, 1H), 7.14 (t,  $J = 7.5$  Hz, 2H), 3.74 (s, 4H), 2.50 (s, 3H), 1.00 (s, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  144.10, 135.03, 130.20, 130.12, 124.83, 72.42, 31.79, 22.58, 22.03.

**2-(4-Methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (Table 1, entry 13).** Purification by flash chromatography (hexanes : ethyl acetate 4:1) afforded 0.64 g (95%) yield of white powder, mp 59 °C (lit<sup>11</sup> 57 – 58

<sup>16</sup> Commercially available from COMBI-BLOCKS, Inc., San Diego, CA [http://www.combi-blocks.com/cgi-bin/cbp.cgi?MY\\_ACTION=msds&MY\\_CATA\\_NUM=NE-2264](http://www.combi-blocks.com/cgi-bin/cbp.cgi?MY_ACTION=msds&MY_CATA_NUM=NE-2264) (accessed January 18, 2010).

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<sup>19</sup> Vedejs, E.; Chapman, R. W.; Fields, S. C.; Lin, S.; Schrimpf, M. R. *J. Org. Chem.* **1995**, 60(10), 3020.

<sup>20</sup> Yasuike, S. *Chem. Lett.* **2006**, 35, 1402.

<sup>21</sup> Gardiner, S. J.; Smith, B. D.; Duggan, P. J.; Karpa, M. J.; Griffin, G. J. *Tetrahedron*, **1999**, 55, 2857.

°C).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (d,  $J$  = 8.7, 2H), 6.90 (d,  $J$  = 8.7, 2H), 3.83 (s, 3H), 3.76 (s, 4H), 1.02 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  161.68, 135.44, 113.05, 72.15, 54.93, 31.78, 21.81.

**2-(3-Methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (Table 1, entry 14).** Purification by flash chromatography (dichloromethane) afforded 0.58g (86% yield), mp 69 - 72 °C (lit<sup>22</sup> 68 - 71°C).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (d,  $J$  = 7.2, 1H), 7.36 (d,  $J$  = 2.6, 1H), 7.29 (dd,  $J$  = 13.5, 6.0, 1H), 6.99 (ddd,  $J$  = 8.2, 2.7, 0.9, 1H), 3.84 (s, 3H), 3.78 (s, 4H), 1.04 (s, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  158.95, 128.66, 126.17, 117.85, 117.14, 72.23, 55.06, 31.78, 21.81.

**2-(3,5-Dimethoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (Table 1, entry 15).** Purification by column chromatography on silica gel with hexanes : ethyl acetate (4 : 1), white powder 0.57 g (75% yield), mp 115 °C (lit<sup>11</sup> 114 - 115 °C).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.98 (s, 2H), 6.56 (d,  $J$  = 2.0, 1H), 3.83 (s, 6H), 3.78 (s, 4H), 1.04 (s, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  160.27, 110.70, 103.82, 72.23, 55.22, 31.76, 21.80.

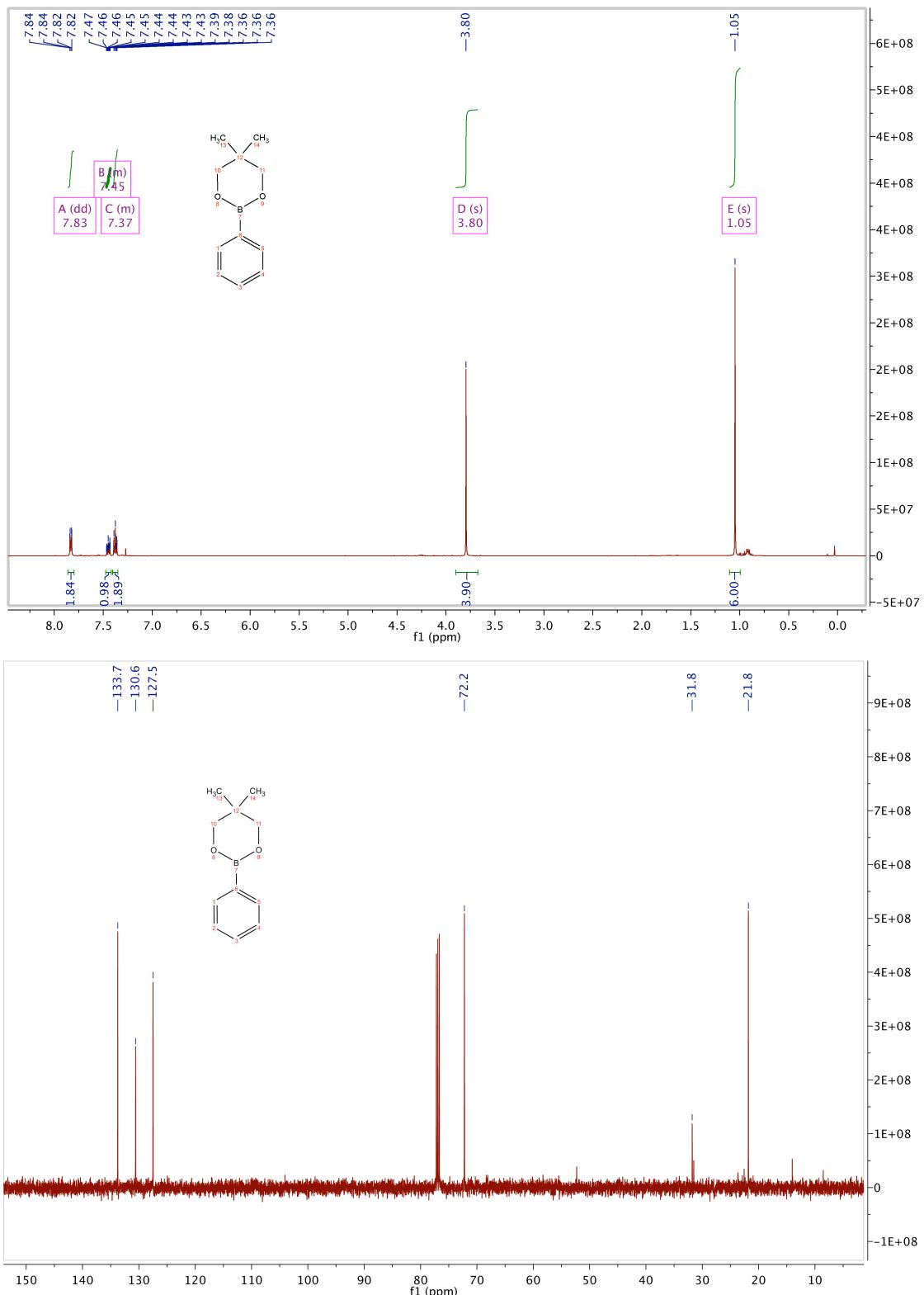
**2-(2-Methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (Table 1 entry 16).** The crude product was purified by silica gel chromatography (10 hexanes: 1 ethyl acetate) to yield the product as white solid, 0.55 g (83% yield), mp 37 - 41 °C (lit<sup>13</sup> 41 °C).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (dd,  $J$  = 7.2, 1.7 Hz, 1H), 7.37 (dt,  $J$  = 7.8, 1.8 Hz, 1H), 6.95 (dt,  $J$  = 7.3, 0.7 Hz, 1H), 6.87 (d,  $J$  = 8.3 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 4H), 1.04 (s, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  163.96, 136.10, 131.97, 120.55, 110.72, 72.81, 56.03, 32.08, 22.22.

**Trifluoro(2-methoxyphenyl)borate (Table 1 entry 16).** The crude product was recrystallized from acetone to yield the product as white powder (0.16 g, 33%). mp >250°C (lit.<sup>23</sup> >230°C).  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-d}_6$ )  $\delta$  7.30 (d,  $J$  = 6.6 Hz, 1H), 7.03 (d,  $J$  = 7.4 Hz, 1H), 6.70 (m, 2H), 3.61 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-d}_6$ )  $\delta$  162.46, 131.15, 126.62, 119.14, 109.62, 54.71.

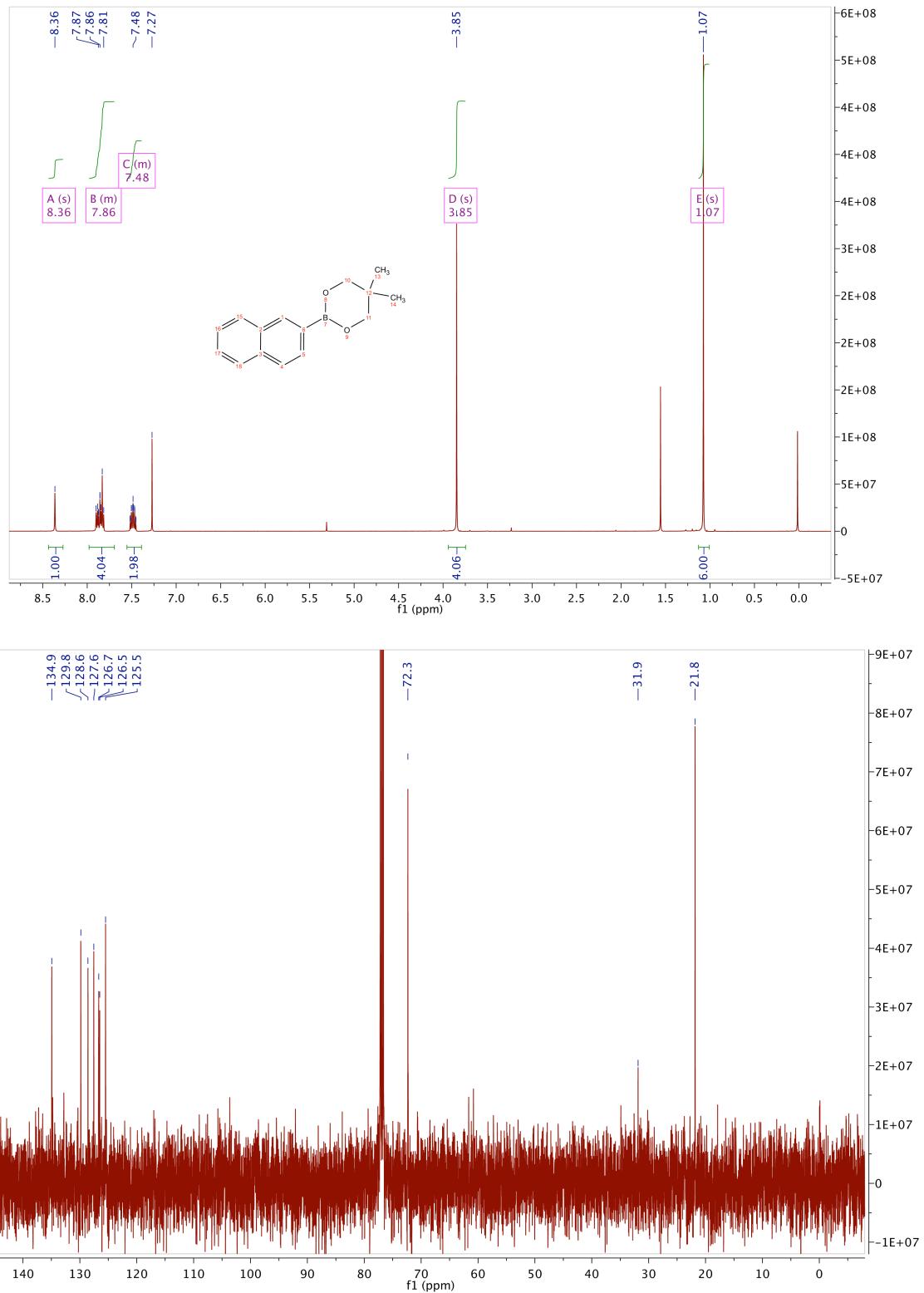
<sup>22</sup> Schnuerch, M. *Green Chem.* **2007**, 9, 139.

<sup>23</sup> Yuen, A. K. L.; Hutton, C. A. *Tet. Let.* **2005**, 46(46), 7899.

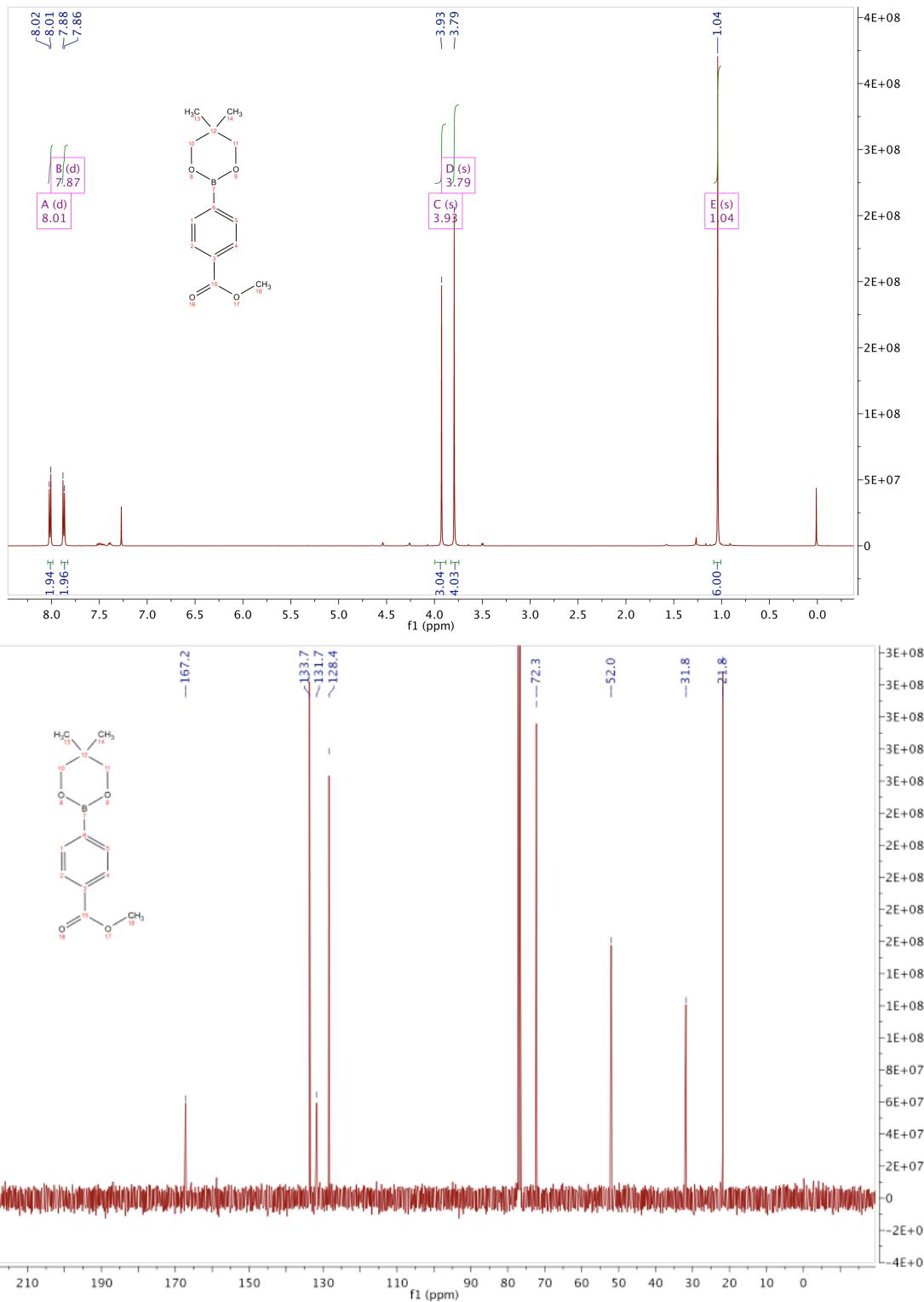
## 6. Characterization of Neopentylglycolboronates



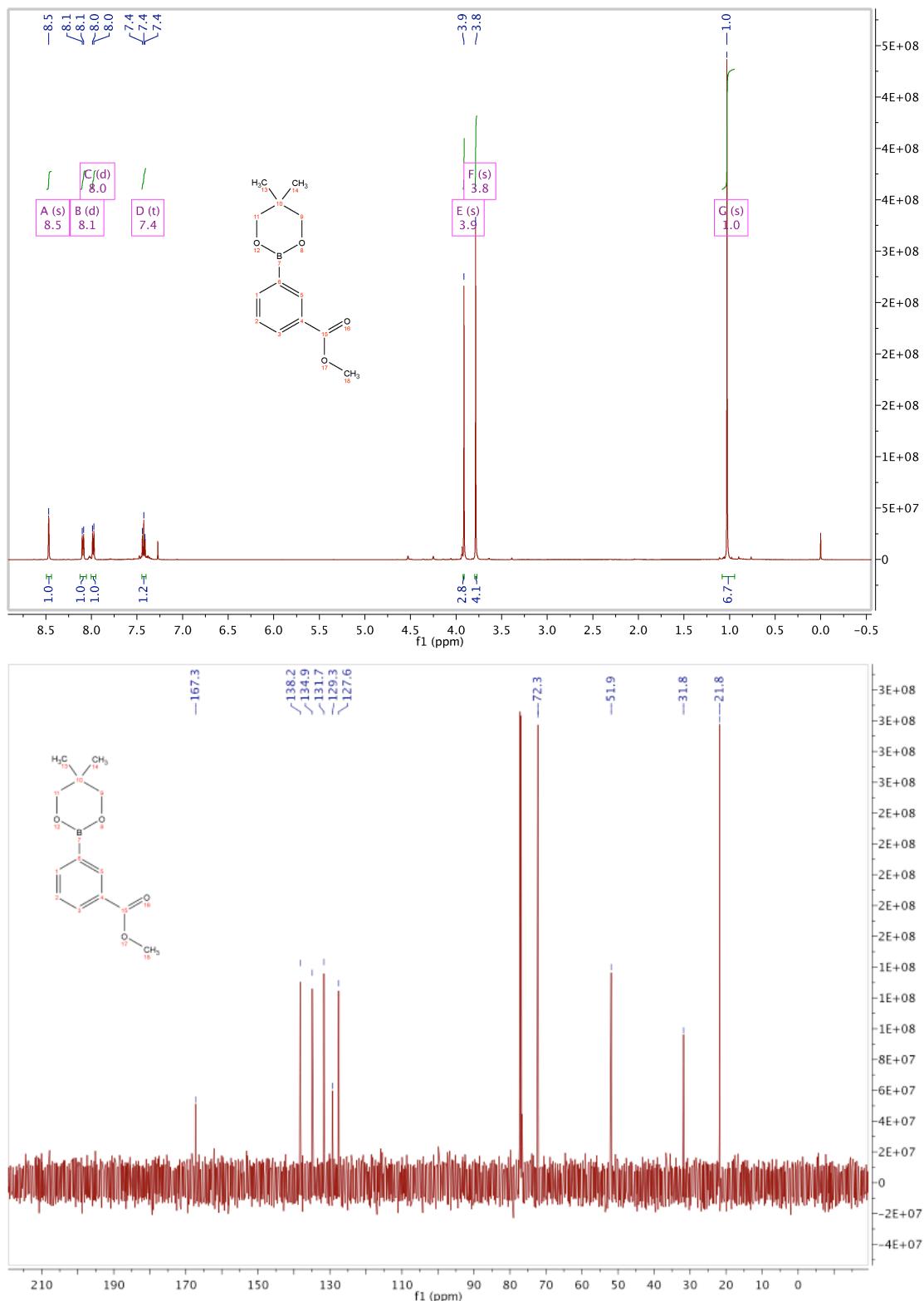
**Figure SF1.** <sup>1</sup>H-NMR (500 MHz) and <sup>13</sup>C-NMR (125 MHz) spectra of 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane in CDCl<sub>3</sub>.



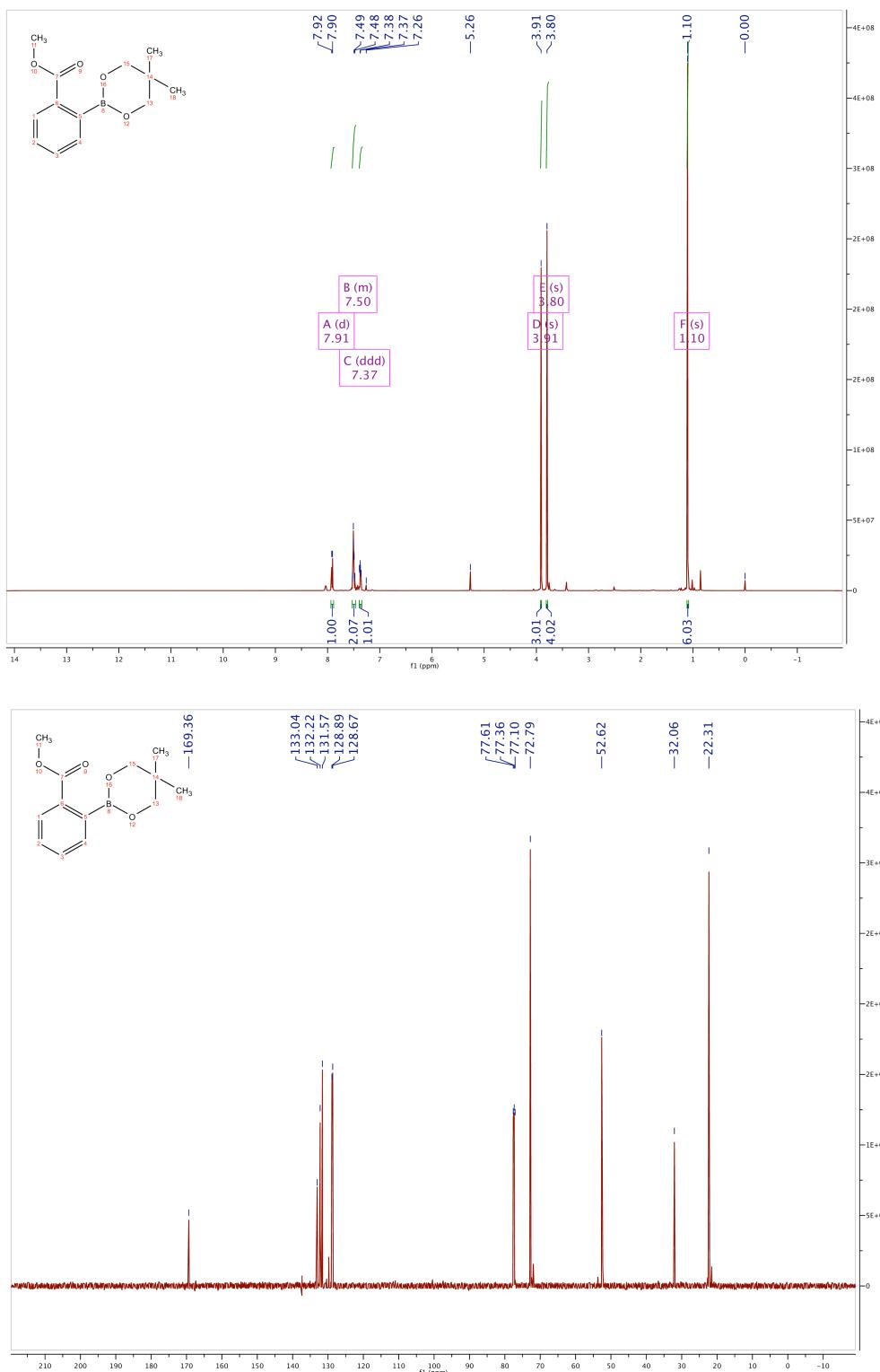
**Figure SF2.**  $^1\text{H}$ -NMR (500 MHz) and  $^{13}\text{C}$ -NMR (125 MHz) spectra of 5,5-dimethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborinane in  $\text{CDCl}_3$ .



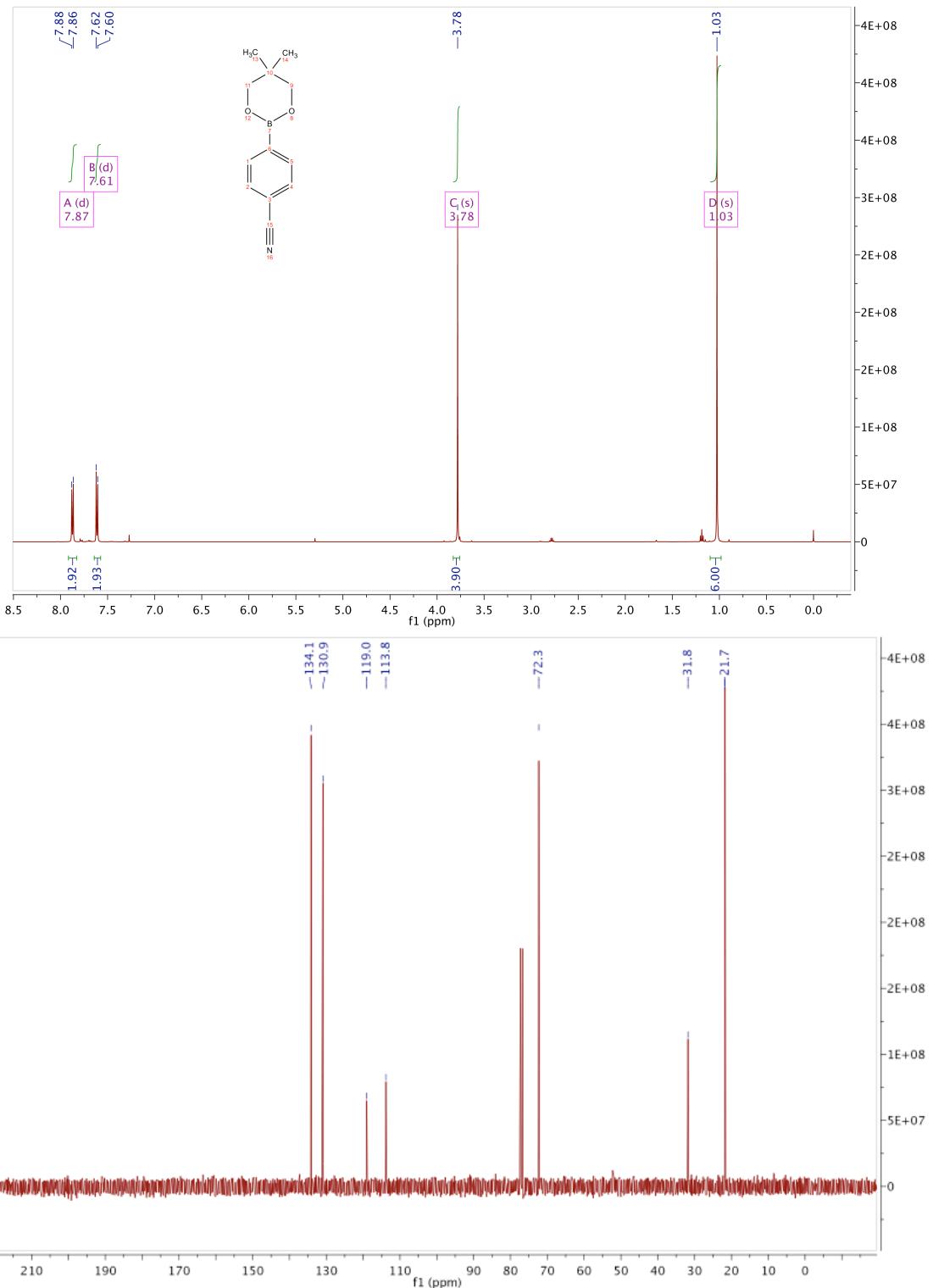
**Figure SF3.**  $^1\text{H}$ -NMR (500 MHz) and  $^{13}\text{C}$ -NMR (125 MHz) spectra of methyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate in  $\text{CDCl}_3$ .



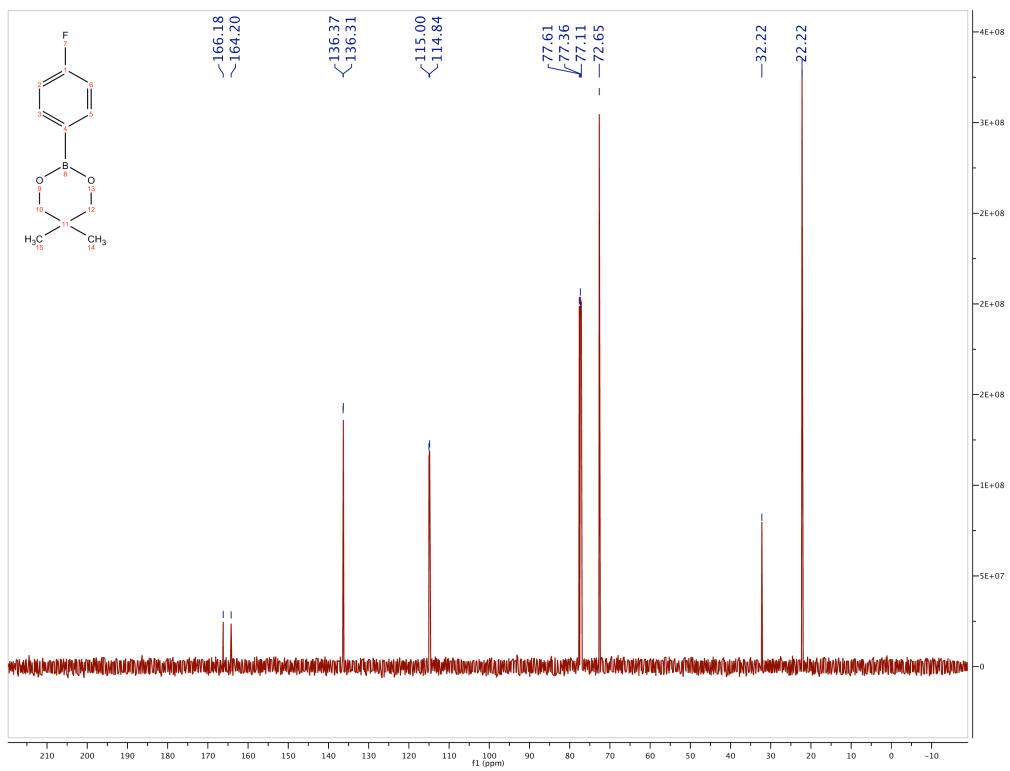
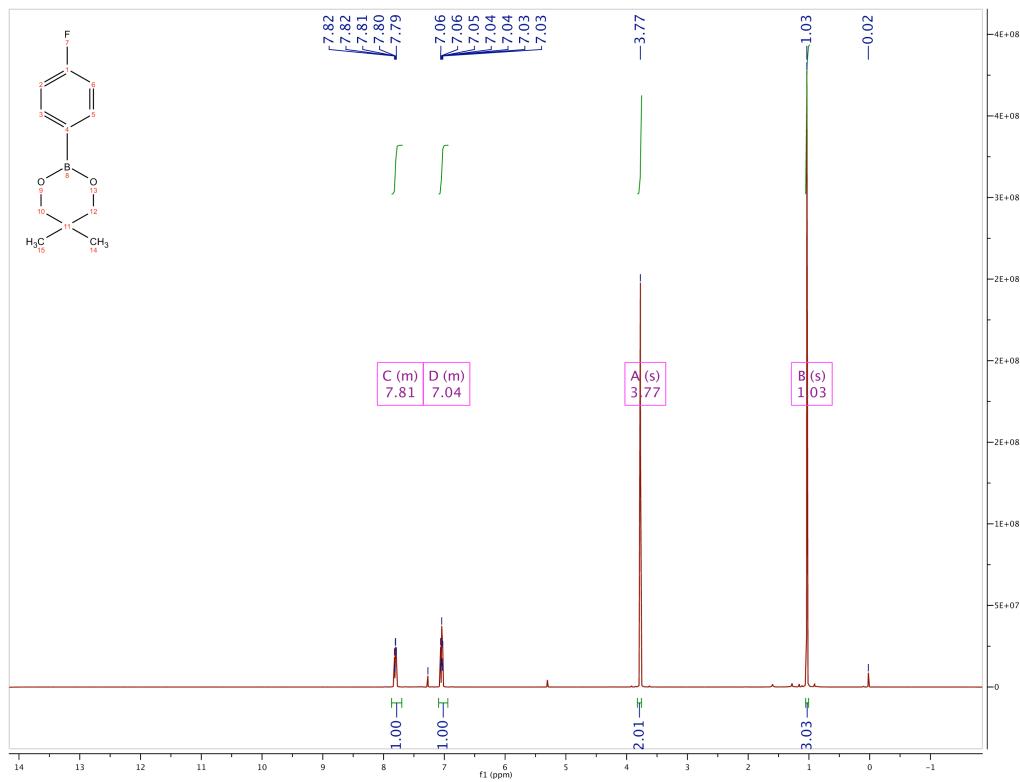
**Figure SF4.**  $^1\text{H}$ -NMR (500 MHz) and  $^{13}\text{C}$ -NMR (125 MHz) spectra of methyl 3-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate in  $\text{CDCl}_3$ .



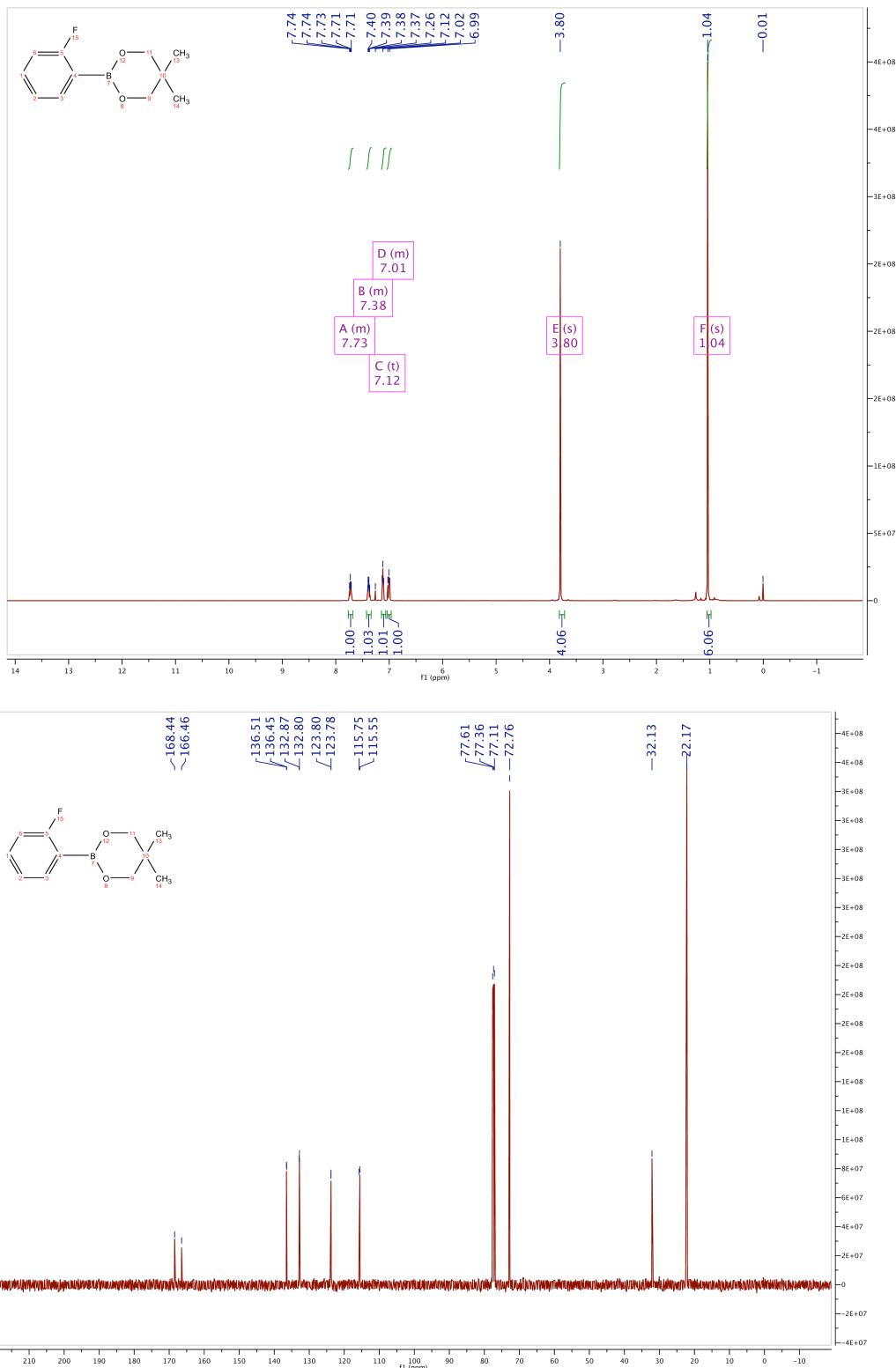
**Figure SF5.**  $^1\text{H}$ -NMR (500 MHz) and  $^{13}\text{C}$ -NMR (125 MHz) spectra of methyl 2-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate in  $\text{CDCl}_3$ .



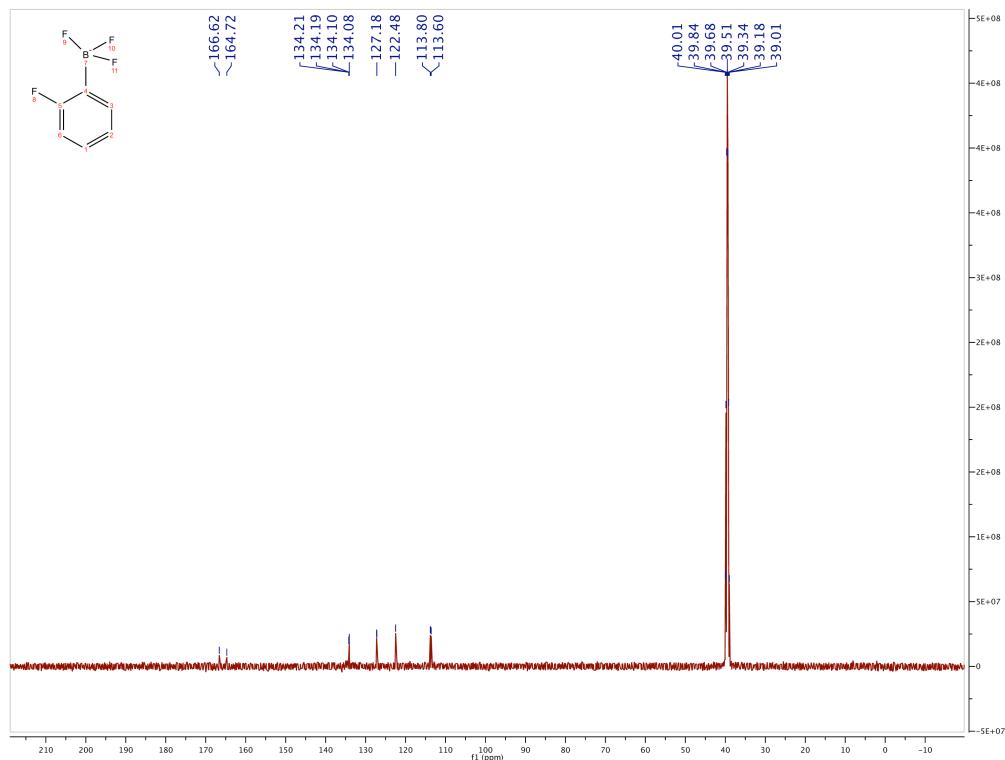
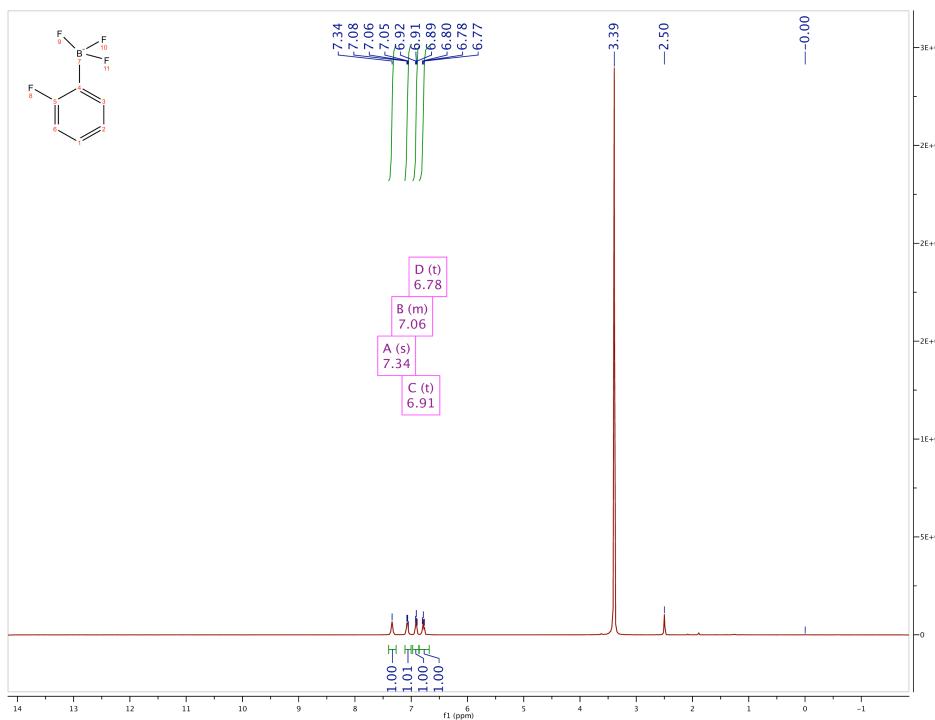
**Figure SF6.**  $^1\text{H}$ -NMR (500 MHz) and  $^{13}\text{C}$ -NMR (125 MHz) spectra of 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzonitrile in  $\text{CDCl}_3$ .



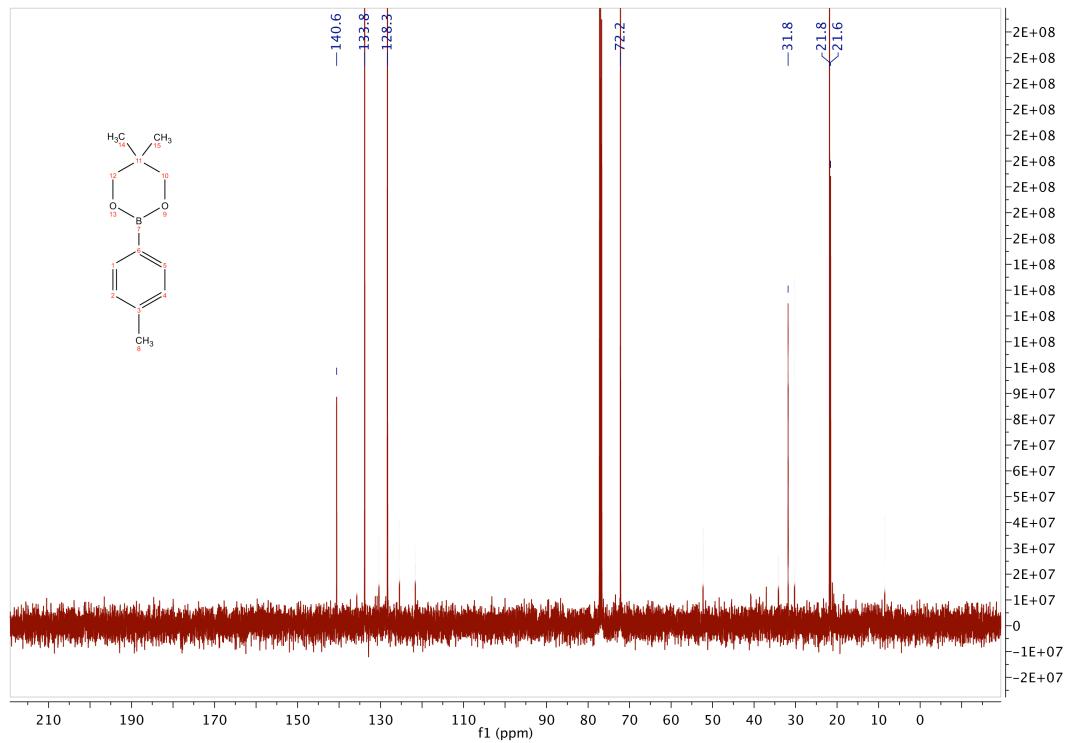
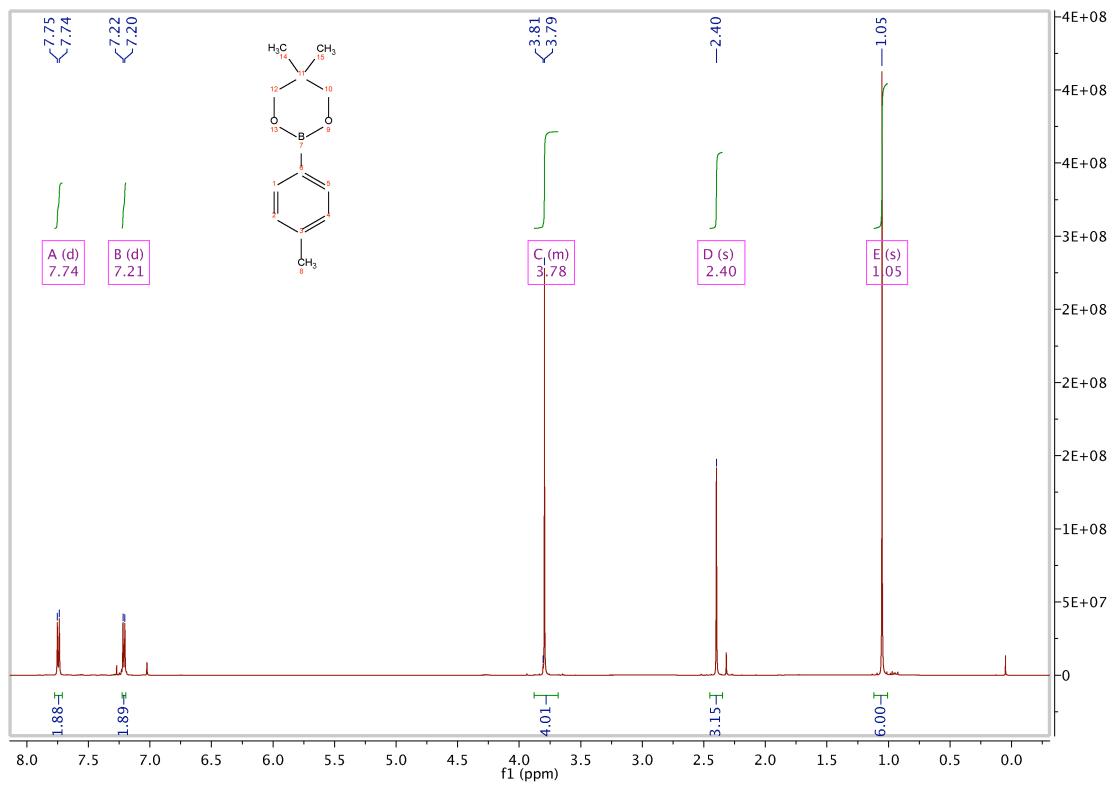
**Figure SF7.**  $^1\text{H}$ -NMR (500 MHz) and  $^{13}\text{C}$ -NMR (125 MHz) spectra of 2-(4-fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane in  $\text{CDCl}_3$ .



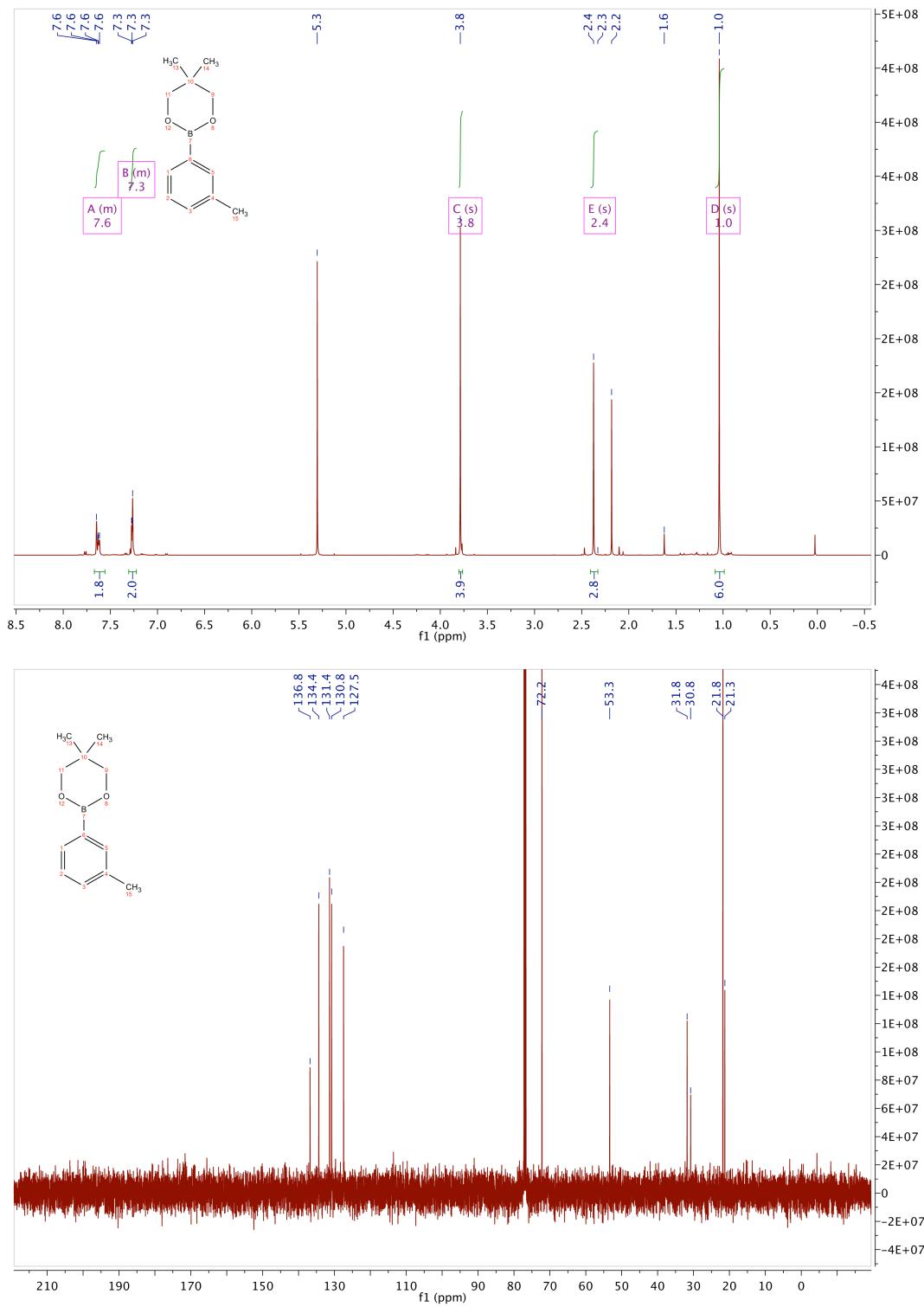
**Figure SF8.**  $^1\text{H}$ -NMR (500 MHz) and  $^{13}\text{C}$ -NMR (125 MHz) spectra of 2-(2-fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane in  $\text{CDCl}_3$ .



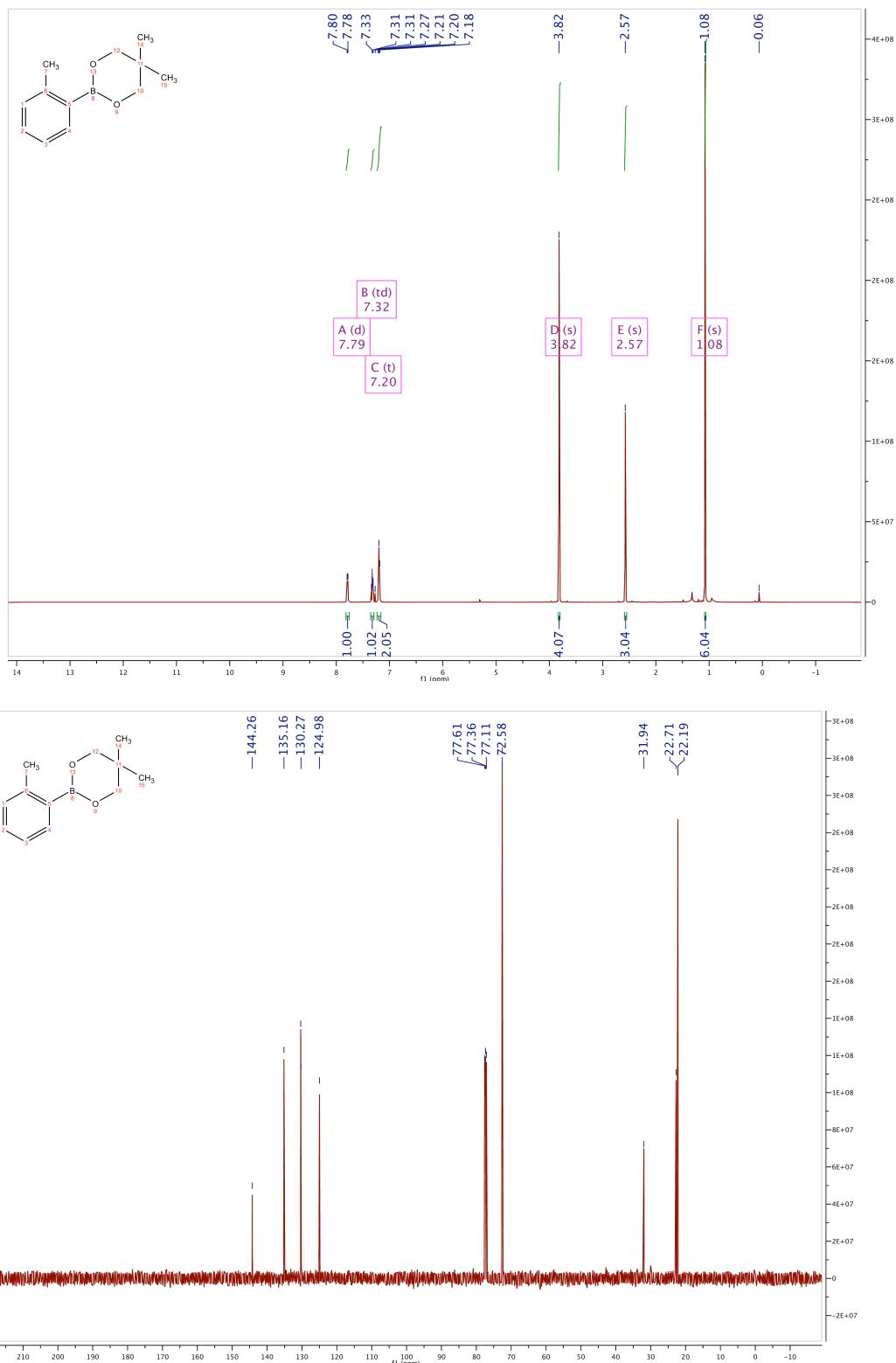
**Figure SF9.**  $^1\text{H}$ -NMR (500 MHz) and  $^{13}\text{C}$ -NMR (125 MHz) spectra of potassium trifluoro(2-fluorophenyl) borate in  $\text{DMSO}-d_6$ .



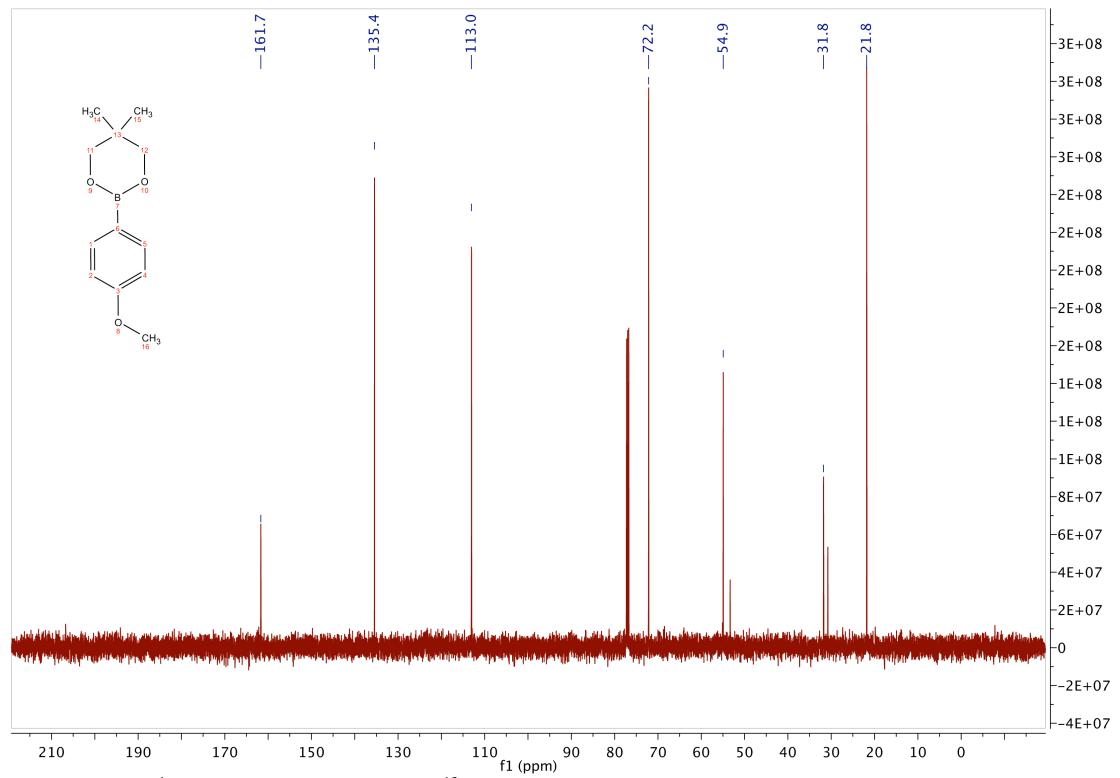
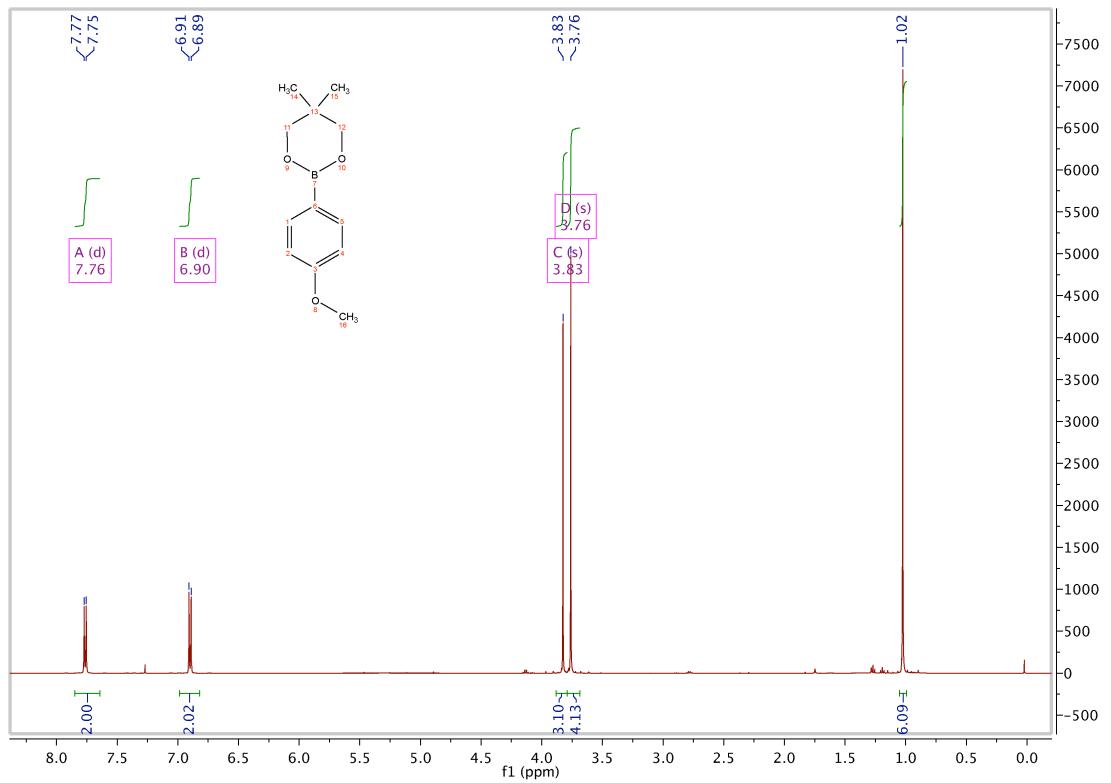
**Figure SF10.** <sup>1</sup>H-NMR (500 MHz) and <sup>13</sup>C-NMR (125 MHz) spectra of 5,5-dimethyl-2-(p-tolyl)-1,3,2-dioxaborinane in CDCl<sub>3</sub>.



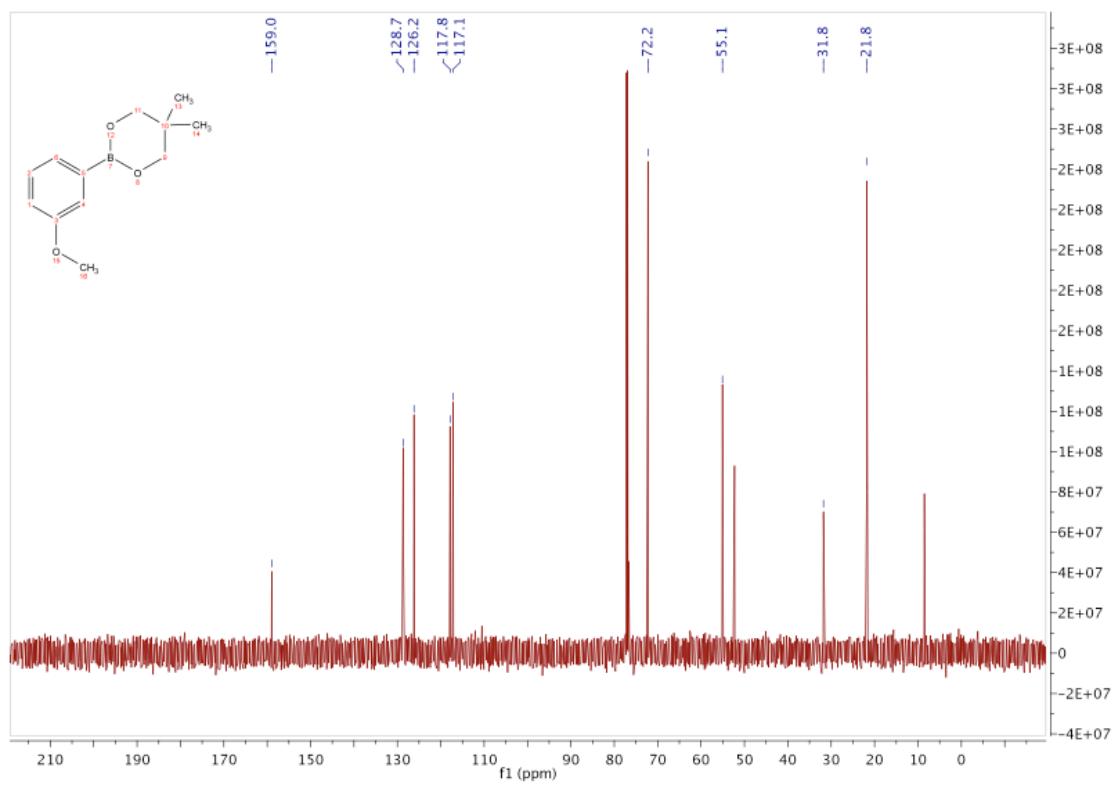
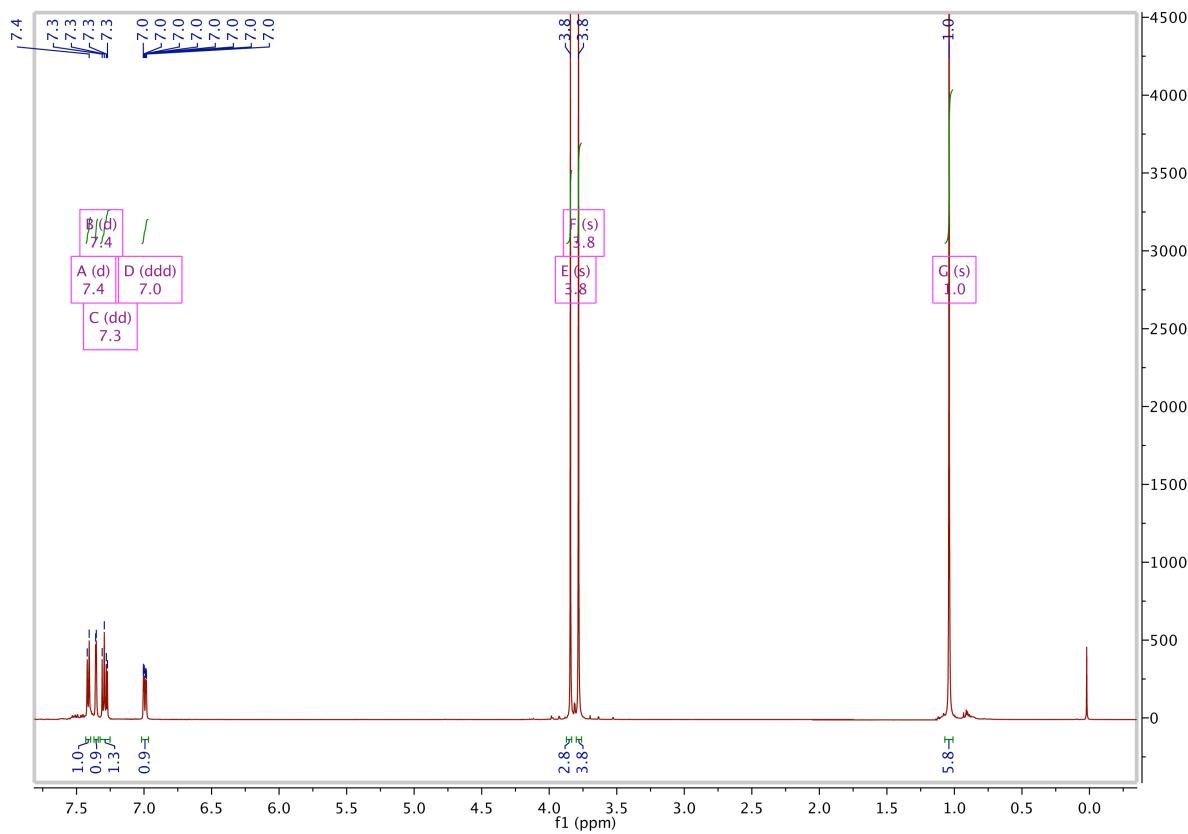
**Figure SF11.**  $^1\text{H-NMR}$  (500 MHz) and  $^{13}\text{C-NMR}$  (125 MHz) spectra of 5,5-dimethyl-2-(*m*-tolyl)-1,3,2-dioxaborinane in  $\text{CDCl}_3$ .



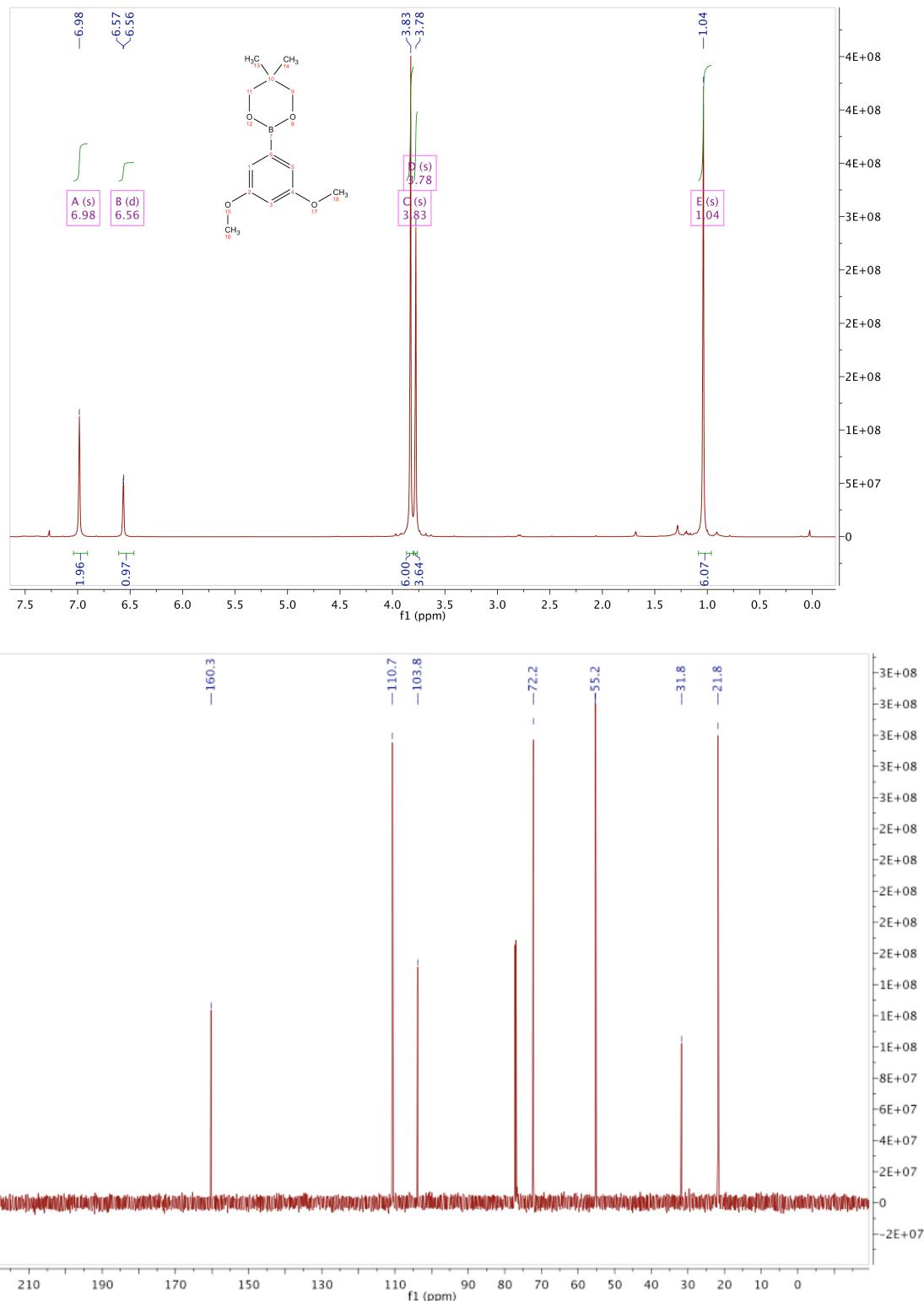
**Figure SF12.**  $^1\text{H-NMR}$  (500 MHz) and  $^{13}\text{C-NMR}$  (125 MHz) spectra of 5,5-dimethyl-2-(*o*-tolyl)-1,3,2-dioxaborinane in  $\text{CDCl}_3$ .



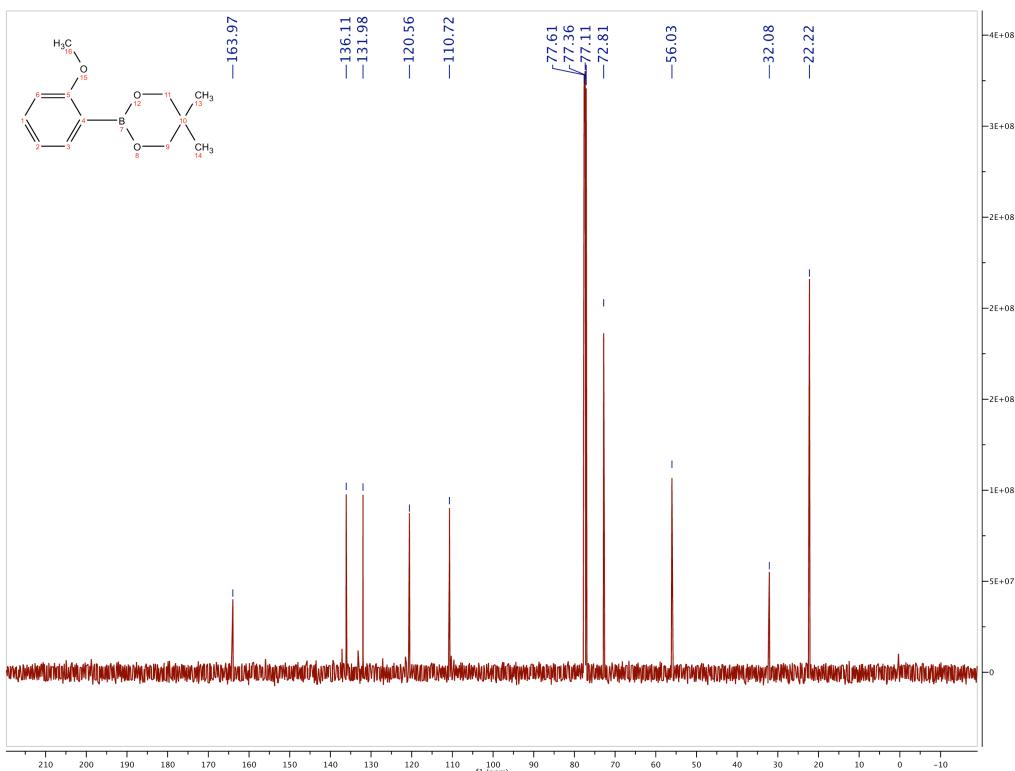
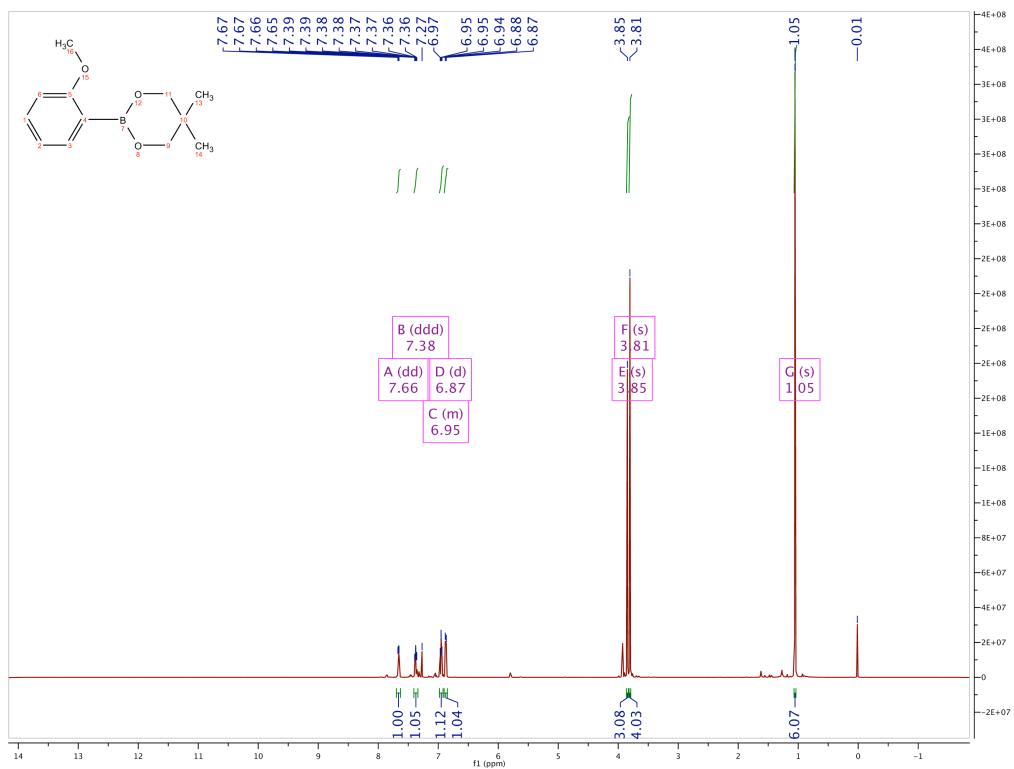
**Figure SF13.** <sup>1</sup>H-NMR (500 MHz) and <sup>13</sup>C-NMR (125 MHz) spectra of 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane in CDCl<sub>3</sub>.



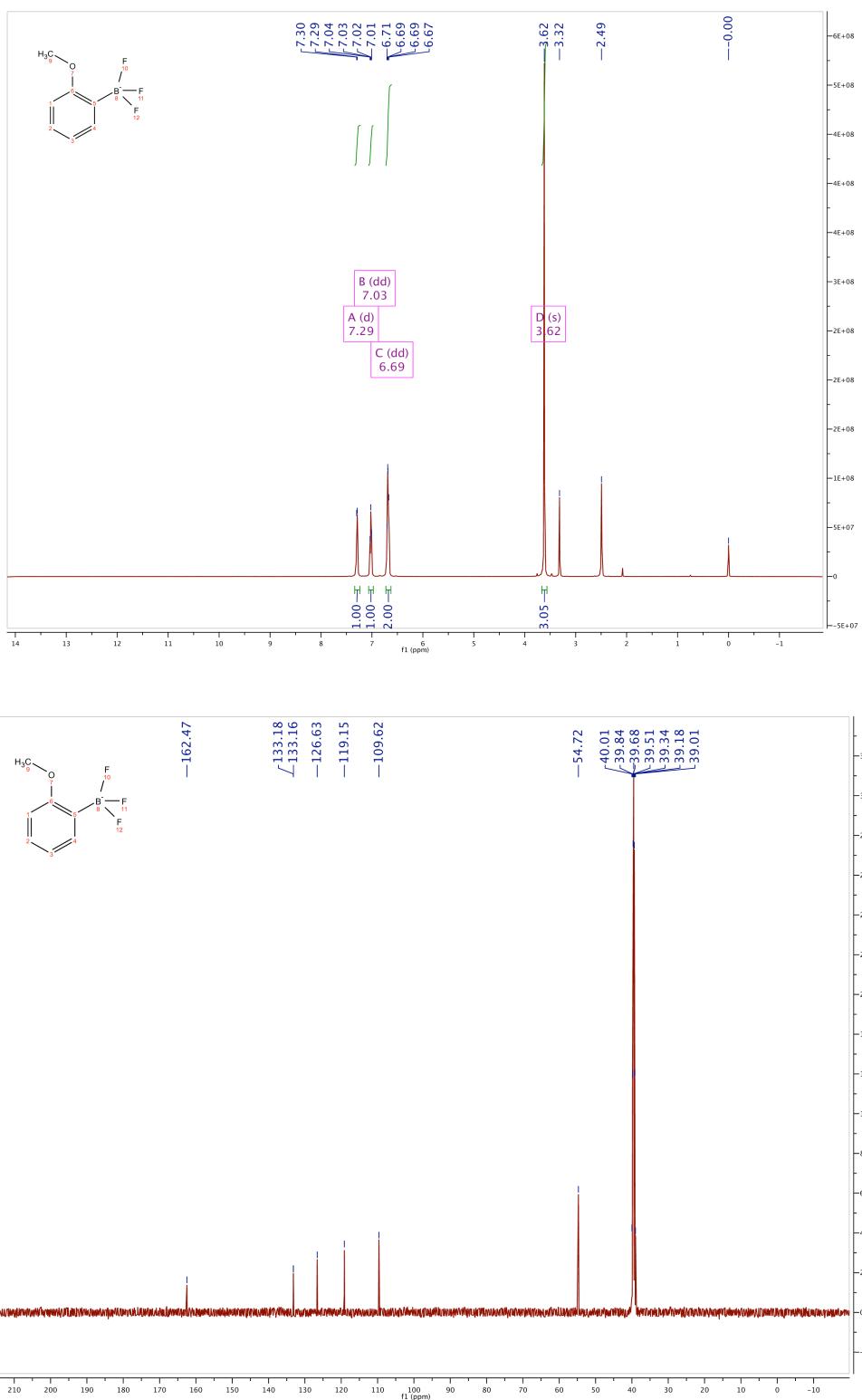
**Figure SF14.**  $^1\text{H}$ -NMR (500 MHz) and  $^{13}\text{C}$ -NMR (125 MHz) spectra of 2-(3-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane in  $\text{CDCl}_3$ .



**Figure SF15.**  $^1\text{H}$ -NMR (500 MHz) and  $^{13}\text{C}$ -NMR (125 MHz) spectra of 2-(3,5-dimethoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane in  $\text{CDCl}_3$ .



**Figure SF16.** <sup>1</sup>H-NMR (500 MHz) and <sup>13</sup>C-NMR (125 MHz) spectra of 2-(2-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane in CDCl<sub>3</sub>.



**Figure SF17.**  $^1\text{H}$ -NMR (500 MHz) and  $^{13}\text{C}$ -NMR (125 MHz) spectra of potassium trifluoro(2-methoxyphenyl)borate in  $\text{DMSO}-d_6$ .