

Electronic Supporting Information for:

**The Hydroboration of  $\alpha$ -diimines**

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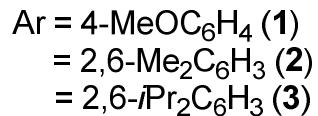
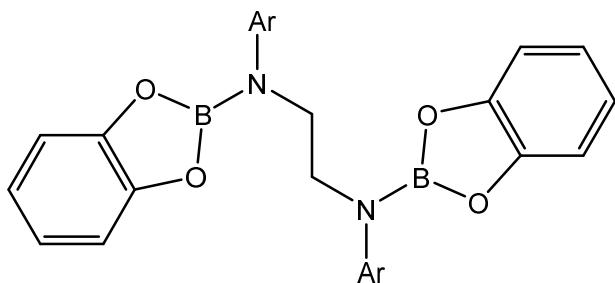
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**Experimental Section.** Reagents and solvents used were obtained from Aldrich Chemicals.  $\alpha$ -Diimines were prepared by condensation of aniline derivatives with glyoxal or 2,3-butanedione. NMR spectra were recorded on a JEOL JNM-GSX400 FT NMR ( $^1\text{H}$ : 400 MHz;  $^{11}\text{B}$ : 128 MHz;  $^{13}\text{C}$ : 100 MHz) spectrometer. Chemical shifts ( $\delta$ ) are reported in ppm [relative to residual solvent peaks ( $^1\text{H}$  and  $^{13}\text{C}$ ) or external  $\text{BF}_3\text{OEt}_2$  ( $^{11}\text{B}$ )]. Multiplicities are reported as singlet (s), doublet (d), triplet (t), multiplet (m). Melting points were measured uncorrected with a Stuart SMP30 apparatus. Elemental analyses for C, H, and N were carried out at the University of Windsor. All reactions were carried out under an atmosphere of dinitrogen.

**General Procedure for bis-Hydroboration Products 1-3.** Catecholborane (50 mg, 0.42 mmol, 2.1 eq) was added to diimine (0.20 mmol) in toluene. Following 4 hours of stirring, the solvent was removed in vacuo and the residue washed with hexanes (3 x 5 mL).



$N^1,N^2\text{-Bis(benzo}[d][1,3,2]\text{dioxaborol-2-yl)\text{-}N^1,N^2\text{-bis(4-methoxyphenyl)ethane-1,2-diamine (1)}$

\*Note: The  $^{11}\text{B}$  NMR spectrum of the crude reaction mixture shows a resonance at 21.1 ppm in addition to the signal corresponding to **1**, suggesting that  $\text{BO}_3$  environment(s) are also present in solution, possibly  $\text{B}_2\text{cat}_3$  ((cat) $\text{B}$ (cat) $\text{B}$ (cat)) or (diamino) $\text{B}$ (cat) $\text{B}$ (cat).

Yield: 60 mg (59%, 0.12 mmol). M.P. = 180°C (decomp). Anal. calc. for  $\text{C}_{28}\text{H}_{26}\text{N}_2\text{B}_2\text{O}_6$  (508.14 g/mol) (%): C 66.18, H 5.16, N 5.51. Found: C 66.35, H 5.04, N 5.28.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 3.78 (s, 4H), 3.79 (s, 6H), 6.82 (d,  $J$  = 9.2 Hz, 4H), 6.91-7.01 (m, 8H, cat), 7.05 (d,  $J$  = 8.7 Hz, 4H).  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$ : 24.5 (br).  $^{13}\text{C}\{{}^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 48.6, 55.5, 111.7, 114.3, 121.9, 125.6, 137.1, 148.7, 156.5.

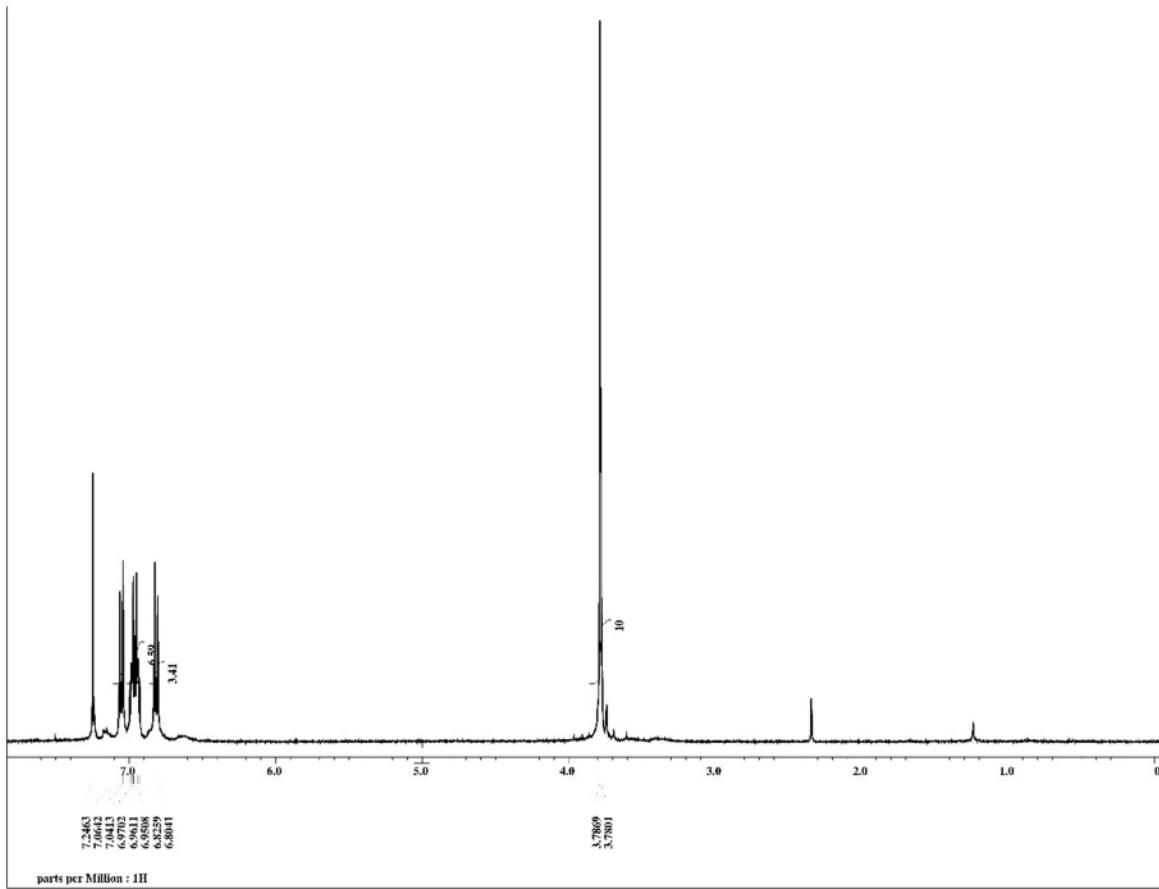


Figure S1.  $^1\text{H}$  NMR of  $N^1,N^2$ -bis(benzo[*d*][1,3,2]dioxaborol-2-yl)- $N^1,N^2$ -bis(4-methoxyphenyl)ethane-1,2-diamine (**1**) in  $\text{CDCl}_3$ .

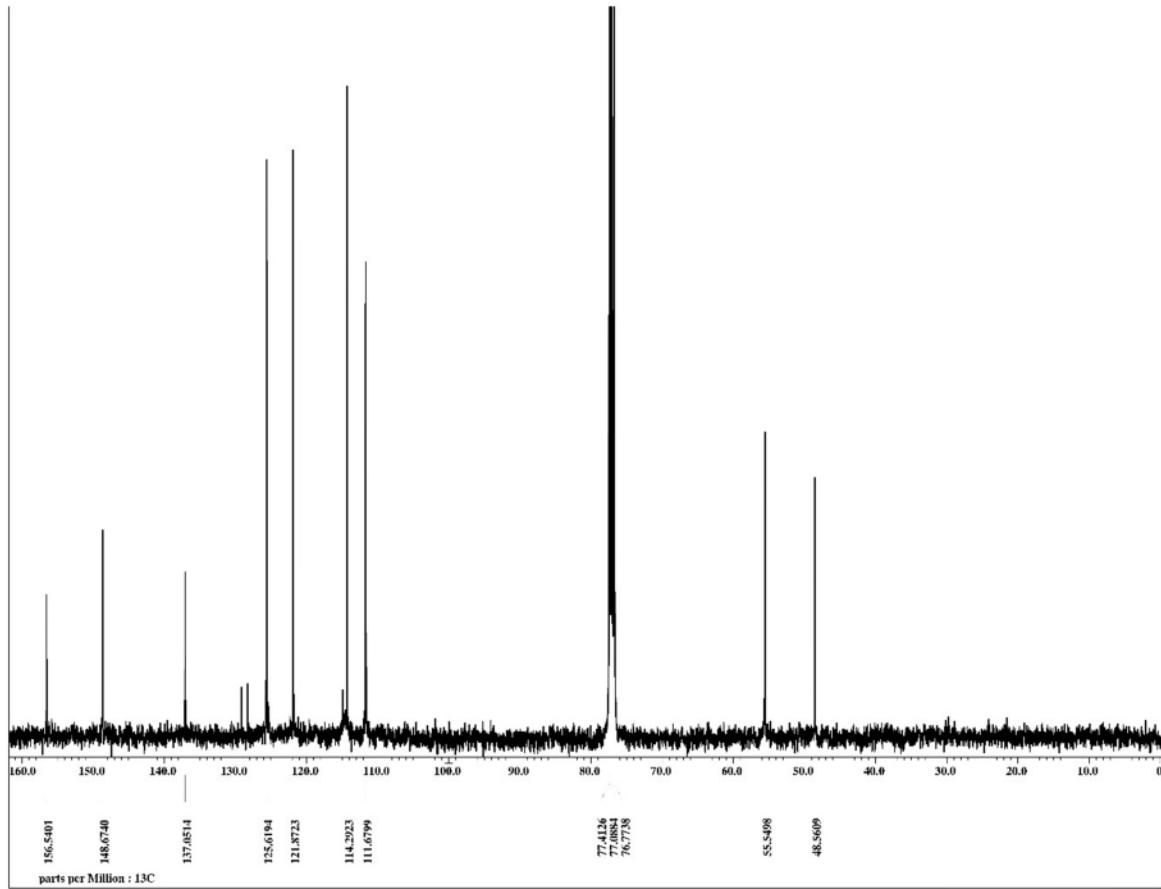


Figure S2.  $^{13}\text{C}$  NMR of  $N^1,N^2$ -bis(benzo[*d*][1,3,2]dioxaborol-2-yl)- $N^1,N^2$ -bis(4-methoxyphenyl)ethane-1,2-diamine (**1**) in  $\text{CDCl}_3$ .

$N^1,N^2$ -Bis(benzo[*d*][1,3,2]dioxaborol-2-yl)- $N^1,N^2$ -bis(2,6-dimethylphenyl)ethane-1,2-diamine (**2**)

Yield: 80 mg (79%, 0.16 mmol). M.P. = 147-149 (decomp). Anal. calc. Anal. calc. for  $\text{C}_{30}\text{H}_{30}\text{N}_2\text{B}_2\text{O}_4 \cdot 1/4 \text{CH}_2\text{Cl}_2$  (525.43 g/mol) (%): C 69.15, H 5.85, N 5.33. Found: C 69.72, H 5.57, N 5.00.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.23 (s, 12H), 3.62 (s, 4H), 6.95 (br s, 4H, cat), 6.98 (br s, 4H, cat), 7.11 (s, 4H), 7.20 (br, 1H), 7.35 (br, 1H).  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$ : 22.5 (br).  $^{13}\text{C}^{\{1\text{H}\}}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 18.8, 49.1, 111.7, 121.8, 126.7, 128.9, 136.1, 141.2, 149.0.

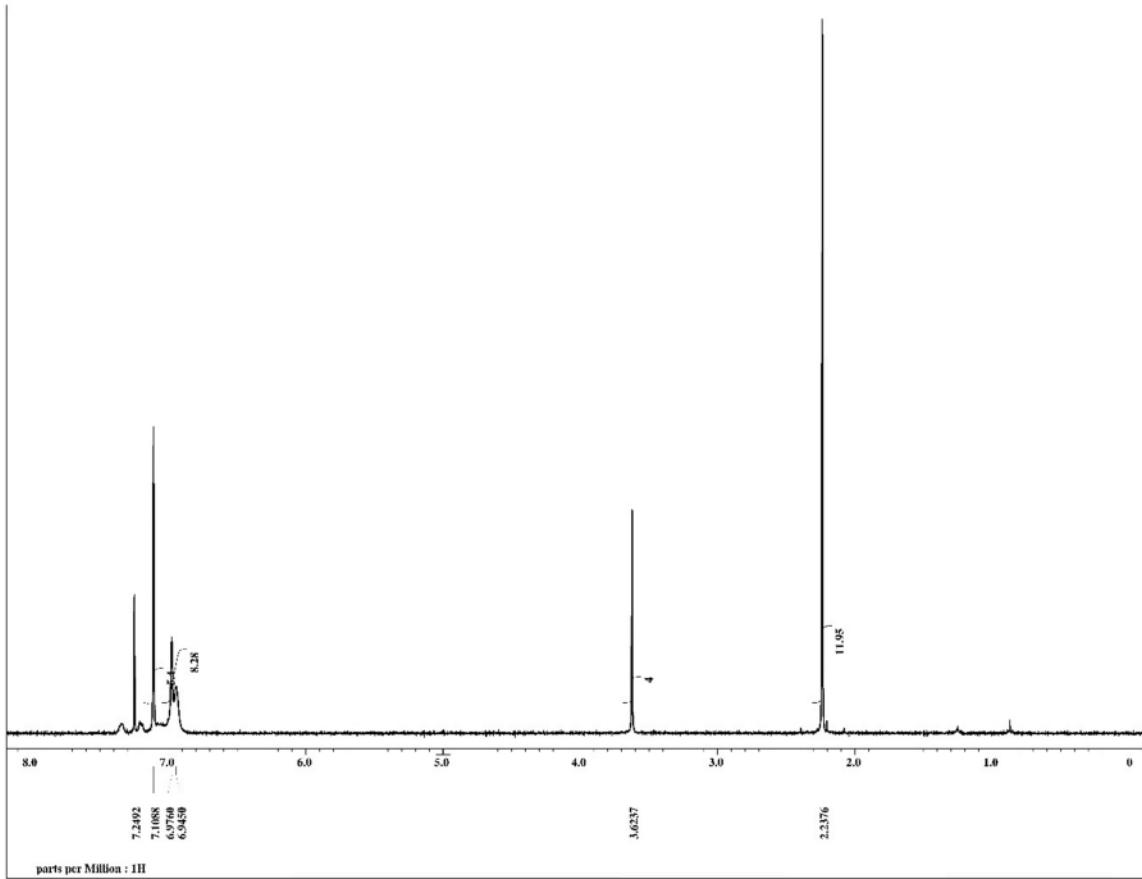
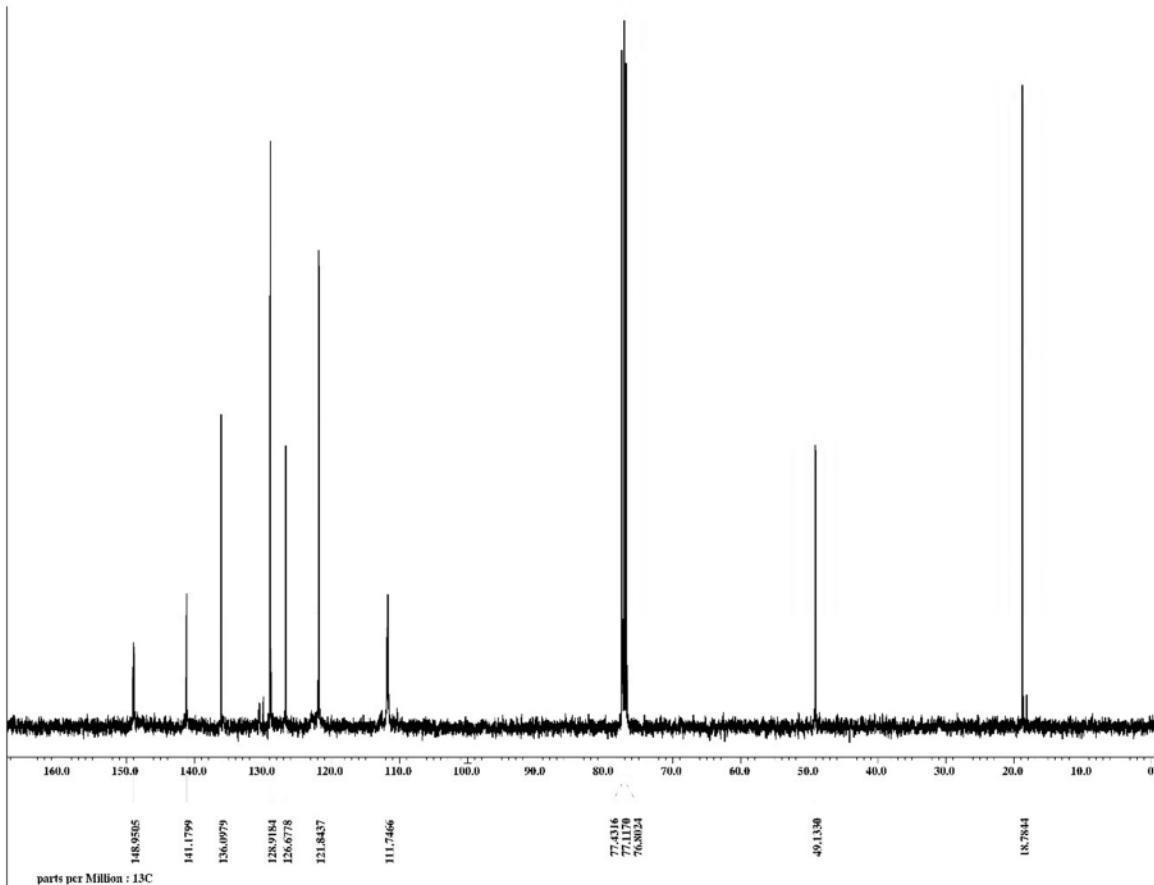


Figure S3. <sup>1</sup>H NMR of *N*<sup>1</sup>,*N*<sup>2</sup>-bis(benzo[*d*][1,3,2]dioxaborol-2-yl)-*N*<sup>1</sup>,*N*<sup>2</sup>-bis(2,6-dimethylphenyl)ethane-1,2-diamine (**2**) in CDCl<sub>3</sub>.



*Figure S4.*  $^{13}\text{C}$  NMR of  $N^1,N^2\text{-bis}(\text{benzo}[d][1,3,2]\text{dioxaborol-2-yl})\text{-}N^1,N^2\text{-bis}(2,6\text{-dimethylphenyl})\text{ethane-1,2-diamine}$  (**2**) in  $\text{CDCl}_3$ .

$N^1,N^2\text{-Bis}(\text{benzo}[d][1,3,2]\text{dioxaborol-2-yl})\text{-}N^1,N^2\text{-bis}(2,6\text{-diisopropylphenyl})\text{ethane-1,2-diamine}$  (**3**)

Yield: 104 mg (84%, 0.169 mmol). M.P. = 170°C (decomp). Anal. calc. for  $\text{C}_{38}\text{H}_{46}\text{N}_2\text{B}_2\text{O}_4$  (616.42 g/mol) (%): C 74.04, H 7.52, N 4.54. Found: C 73.98, H 7.53, N 4.52.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.10 (d,  $J$  = 6.9 Hz, 12H), 1.19 (d,  $J$  = 6.9 Hz, 12H), 3.19 (sept,  $J$  = 6.9 Hz, 4H), 3.64 (s, 4H), 6.93 (br s, 6H, cat), 7.17 (d,  $J$  = 7.8 Hz, 4H, *m*-CH), 7.28 (t,  $J$  = 7.8 Hz, 2H, *p*-CH).  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$ : 24.6 (br).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 23.8, 25.0, 28.2, 50.3, 111.7, 121.8, 124.3, 127.6, 137.8, 146.7, 148.9.

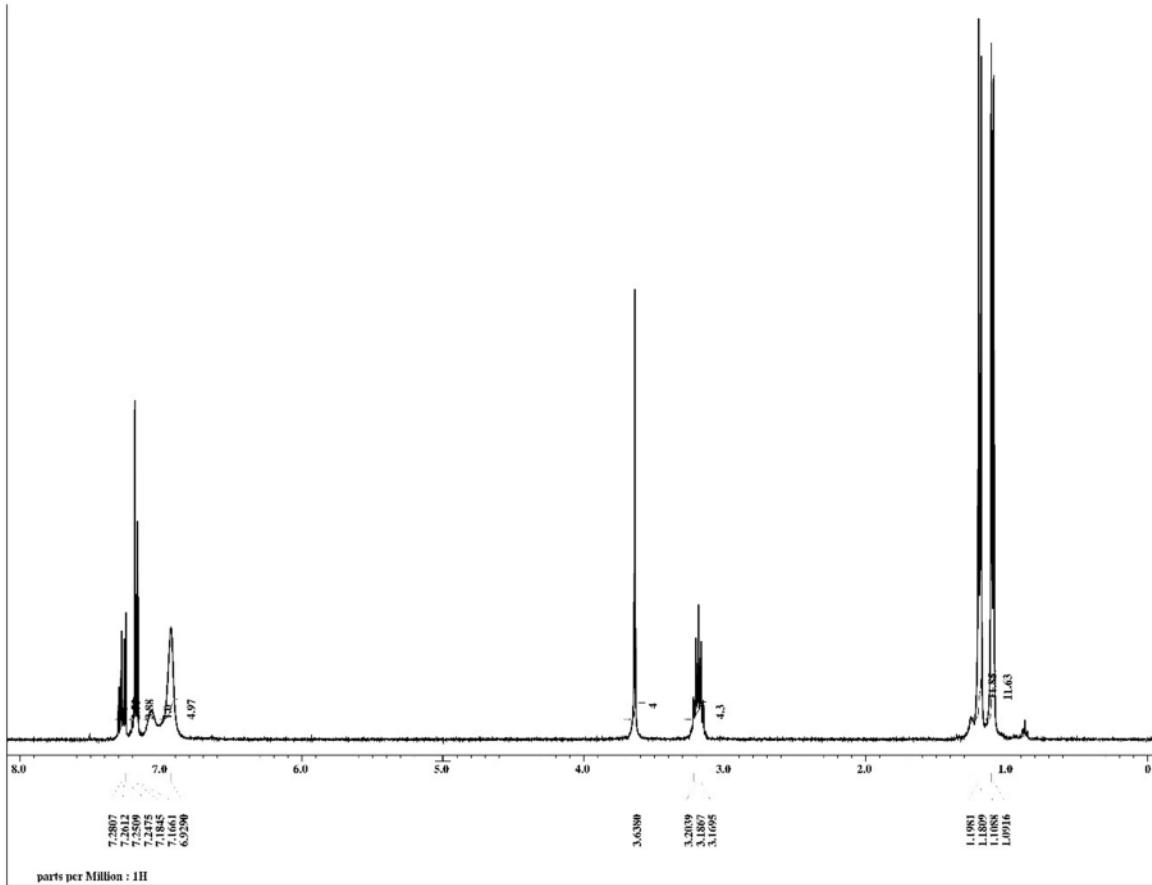


Figure S5.  $^1\text{H}$  NMR of  $N^1,N^2$ -bis(benzo[*d*][1,3,2]dioxaborol-2-yl)- $N^1,N^2$ -bis(2,6-diisopropylphenyl)ethane-1,2-diamine (**3**) in  $\text{CDCl}_3$ .

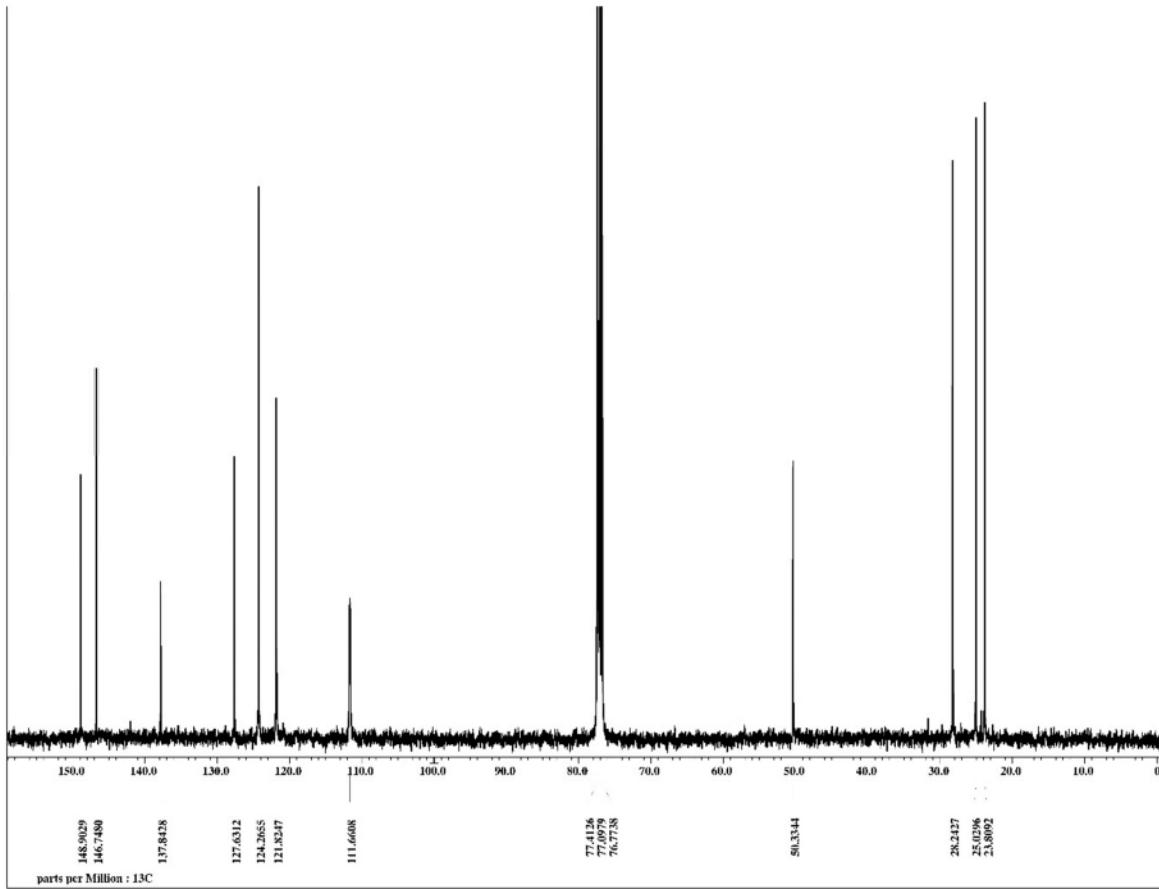
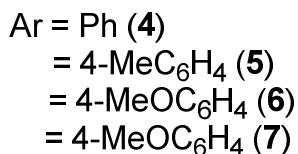
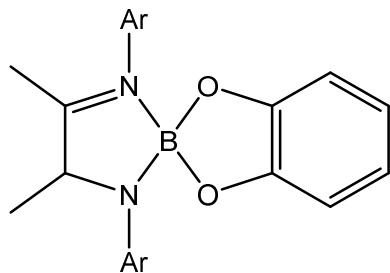


Figure S6.  $^{13}\text{C}$  NMR of  $N^1,N^2\text{-bis}(\text{benzo}[d][1,3,2]\text{dioxaborol-2-yl})\text{-}N^1,N^2\text{-bis}(2,6\text{-diisopropylphenyl})\text{ethane-1,2-diamine}$  (**3**) in  $\text{CDCl}_3$ .

**General Procedure for the Synthesis of 4-7.** To 100 mg of diimine (0.34-0.42 mmol) in 10 mL of diethyl ether was added 1-1 mg catecholborane (0.37-0.47 mmol, 1.1 equivalents). Following 4 hours of stirring the mixture was filtered and the precipitate was washed with diethyl ether (3x5 mL) and dried *in vacuo*.



4',5'-Dimethyl-1',3'-diphenyl-1',5'-dihydrospiro[benzo[*d*][1,3,2]dioxaborole-2,2'-[1,3,2]diazaborol]-3'-ium-9-uide (**4**)

Yield: 86 mg (57%, 0.24 mmol). M.P. = 128°C (decomp). Anal. calc. for  $\text{C}_{22}\text{H}_{21}\text{N}_2\text{BO}_2 \bullet 1/4 \text{Et}_2\text{O}$  (374.76 g/mol) (%): C 73.71, H 6.32, N 7.48. Found: C 73.42, H 6.27, N 7.46.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.66 (d,  $J = 6.9$  Hz, 3H), 2.23 (s, 3H), 4.83 (q,  $J = 6.9$  Hz, 1H), 6.53-6.60 (ov m, 5H), 6.63-6.69 (m 2H), 7.10 (t,  $J = 8.2$  Hz, 2H), 7.19 (d,  $J = 7.8$  Hz, 2H), 7.27-7.33 (ov m, 3H).  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$ : 11.5 (br).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 16.0, 17.3, 59.6, 109.3, 109.5, 114.9, 117.1, 119.0, 124.0, 129.1, 129.2, 129.5, 137.2, 144.9, 151.2, 151.7, 187.0.

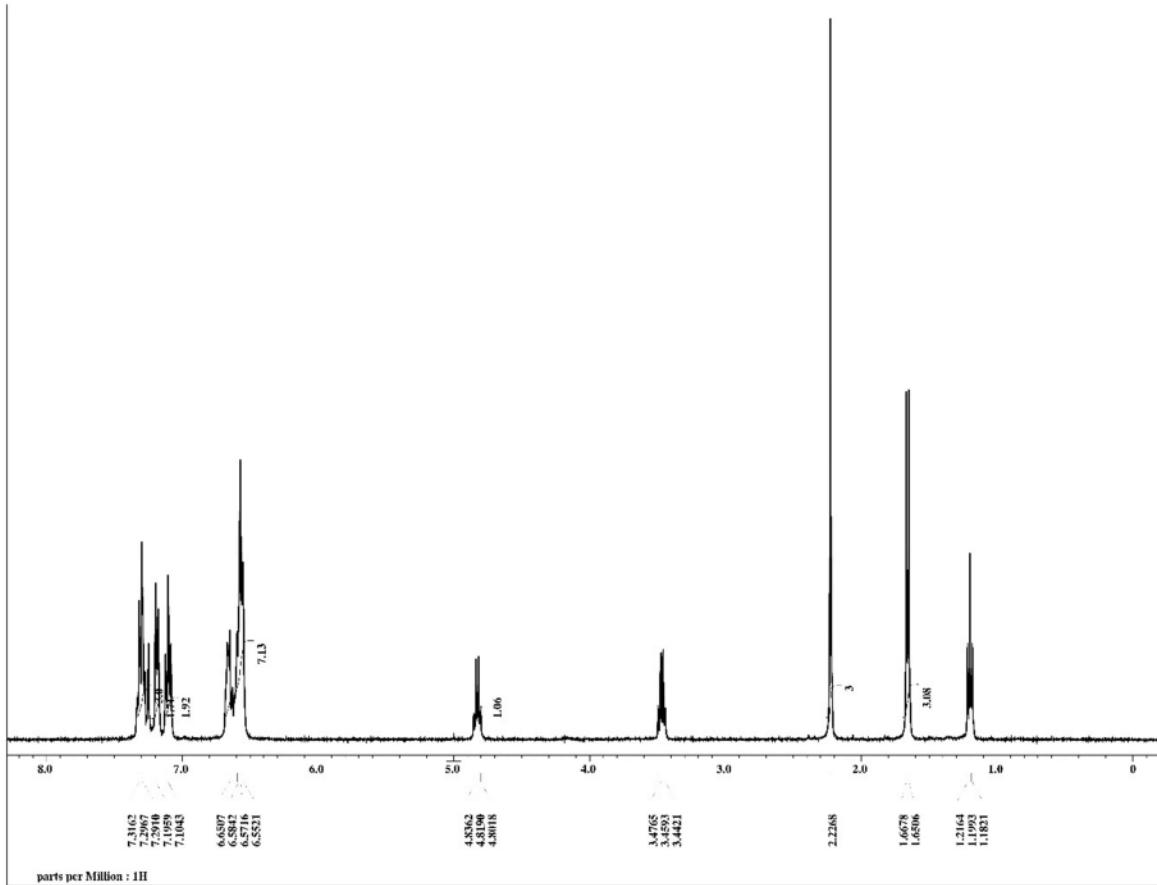
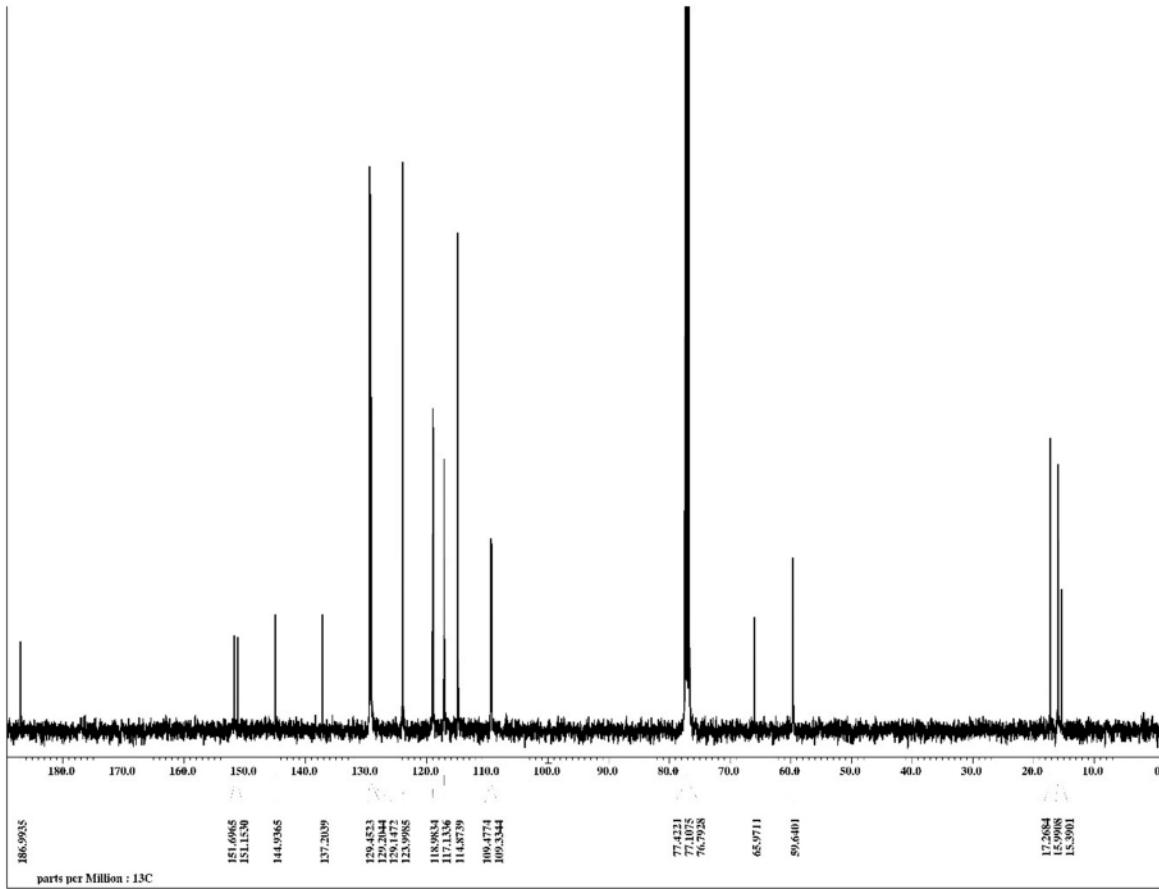


Figure S7.  $^1\text{H}$  NMR of 4',5'-dimethyl-1',3'-diphenyl-1',5'-dihydrospiro[benzo[*d*][1,3,2]dioxaborole-2,2'-[1,3,2]diazaborol]-3'-ium-9-uide (**4**) in  $\text{CDCl}_3$ .



*Figure S8.*  $^{13}\text{C}$  NMR of 4',5'-dimethyl-1',3'-diphenyl-1',5'-dihydrospiro[benzo[*d*][1,3,2]dioxaborole-2,2'-[1,3,2]diazaborol]-3'-ium-9-uide (**4**) in  $\text{CDCl}_3$ .

4',5'-Dimethyl-1',3'-di-*p*-tolyl-1',5'-dihydrospiro[benzo[*d*][1,3,2]dioxaborole-2,2'-[1,3,2]diazaborol]-3'-ium-9-uide (**5**)

Yield: 92 mg (63%, 0.24 mmol). M.P. = 160°C (decomp). Anal. calc. for  $\text{C}_{24}\text{H}_{25}\text{N}_2\text{BO}_2$  (384.29 g/mol) (%): C 75.01, H 6.56, N 7.29. Found: C 74.48, H 6.55, N 7.17.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.62 (d,  $J$  = 6.9 Hz, 3H), 2.17 (s, 3H), 2.21 (s, 3H), 2.26 (s, 3H), 4.81 (q,  $J$  = 6.9 Hz, 1H), 6.48 (d,  $J$  = 8.2 Hz, 2H), 6.55-6.58 (ov m, 3H), 6.67 (d,  $J$  = 6.0 Hz, 1H), 6.91 (d,  $J$  = 8.2 Hz, 2H), 7.08 (ov m, 4H).  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$ : 11.6 (br).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 16.0, 17.1, 20.5, 21.2, 59.7, 109.2, 109.4, 115.1, 118.9, 123.8, 129.7, 130.1, 130.2, 134.7, 139.1, 150.6, 151.2, 151.9, 187.1.

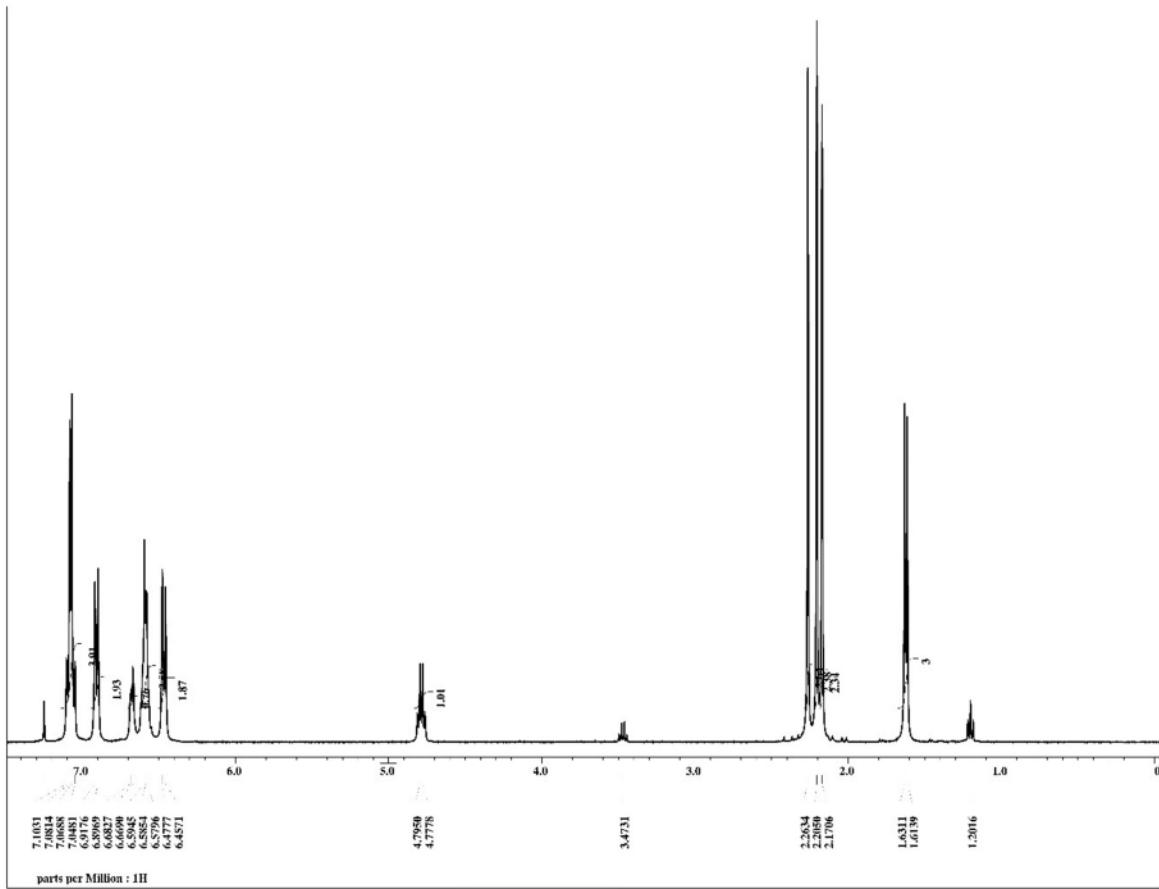


Figure S9.  $^1\text{H}$  NMR of 4',5'-dimethyl-1',3'-di-*p*-tolyl-1',5'-dihydrospiro[benzo[*d*][1,3,2]dioxaborole-2,2'-[1,3,2]diazaborol]-3'-ium-9-uide (**5**) in  $\text{CDCl}_3$ .

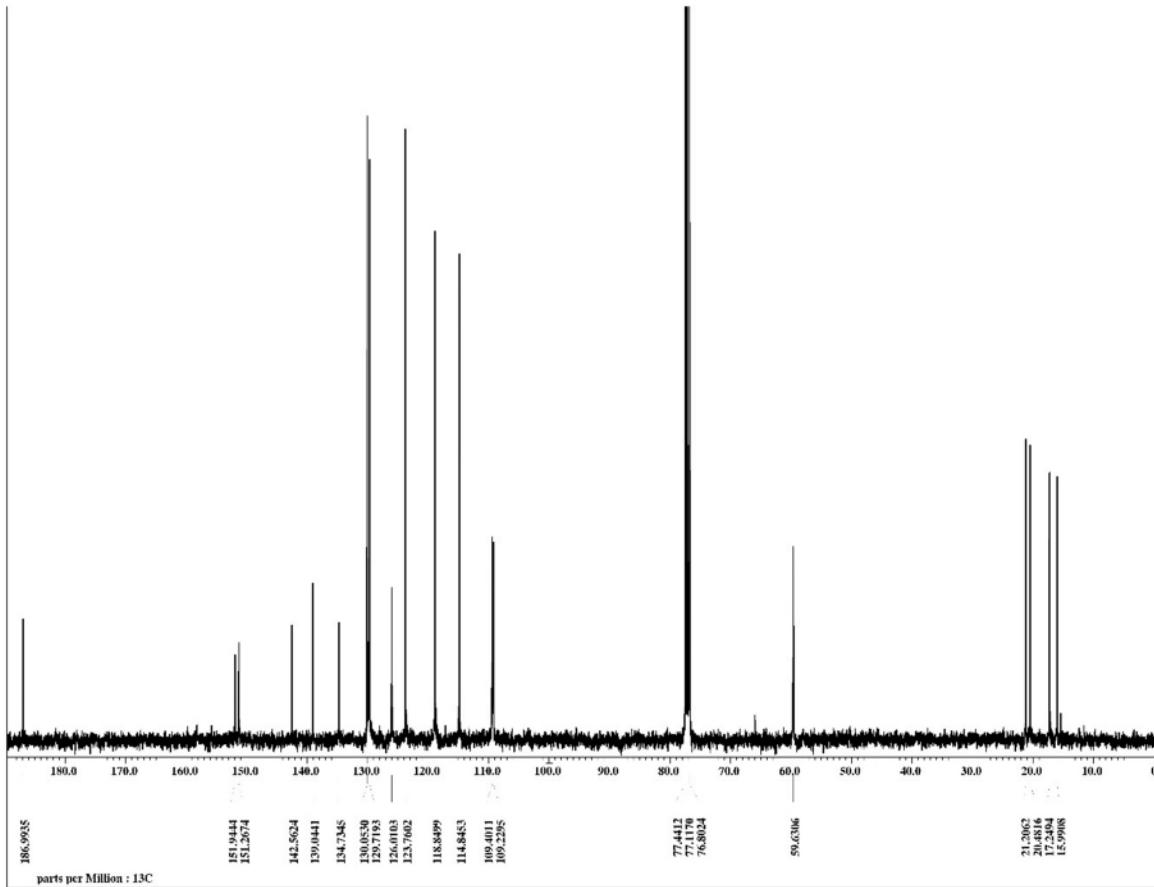


Figure S10.  $^{13}\text{C}$  NMR of 4',5'-dimethyl-1',3'-di-*p*-tolyl-1',5'-dihydrospiro[benzo[*d*][1,3,2]dioxaborole-2,2'-[1,3,2]diazaborol]-3'-ium-9-uide (**5**) in  $\text{CDCl}_3$ .

1',3'-bis(4-methoxyphenyl)-4',5'-dimethyl-1',5'-dihydrospiro[benzo[*d*][1,3,2]dioxaborole-2,2'-[1,3,2]diazaborol]-3'-ium-9-uide (**6**)

Yield: 110 mg (78%, 0.26 mmol). M.P. = 115°C (decomp). Anal. calc. for  $\text{C}_{24}\text{H}_{25}\text{N}_2\text{BO}_4$  (416.28 g/mol) (%): C 69.25, H 6.05, N 6.73. Found: C 68.58, H 6.22, N 6.64.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.60 (d,  $J$  = 6.8 Hz, 3H), 2.22 (s, 3H), 3.68 (s, 3H), 3.73 (s, 3H), 4.76 (q,  $J$  = 6.8 Hz, 1H), 6.50 (d,  $J$  = 9.2 Hz, 2H), 6.55-6.61 (ov m, 3H), 6.70 (m, 3H), 6.79 (d,  $J$  = 8.5 Hz, 2H), 7.11 (d,  $J$  = 8.7 Hz, 2H).  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$ : 11.5 (br).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 16.0, 17.3, 55.4, 55.8, 59.8, 109.2, 109.4, 114.6, 115.0, 115.6, 118.9, 125.2, 130.0, 139.0, 151.2, 151.5, 151.9, 159.7, 187.0.

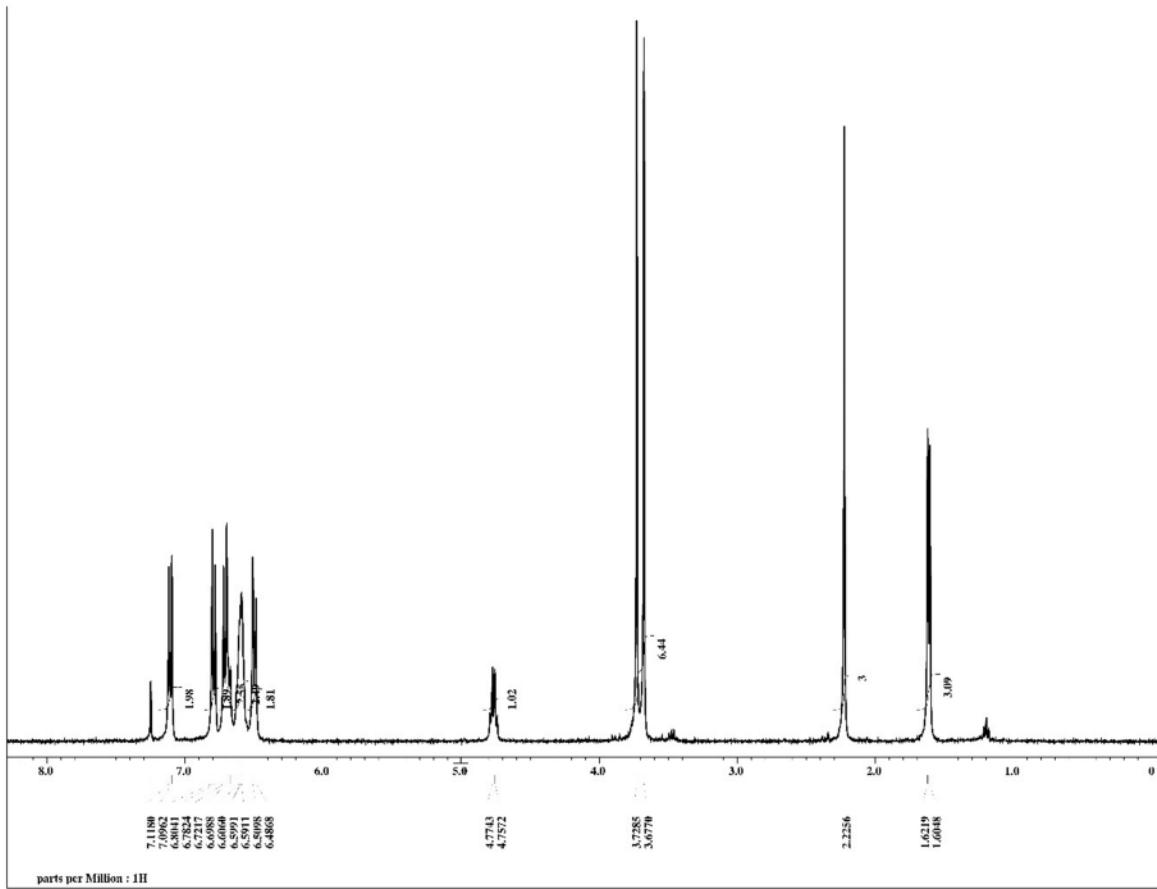
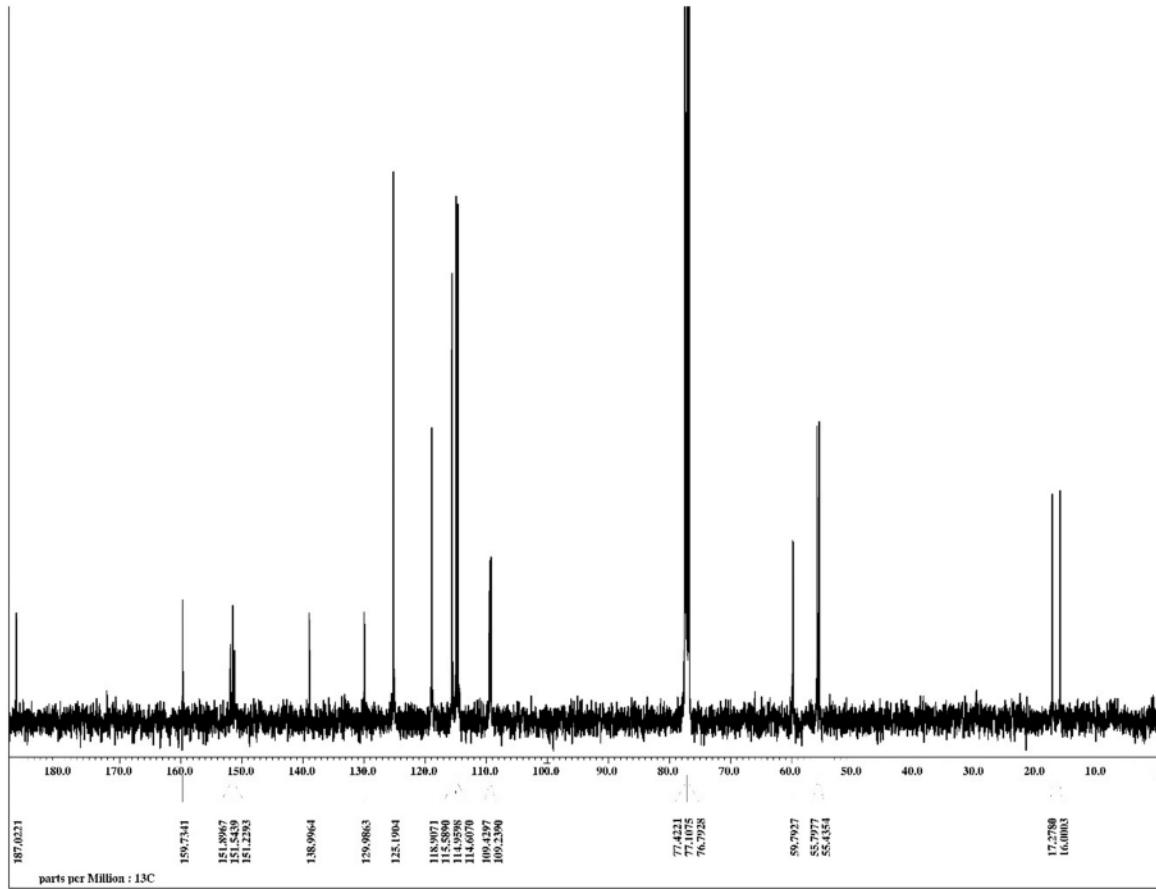


Figure S11.  $^1\text{H}$  NMR of 1',3'-bis(4-methoxyphenyl)-4',5'-dimethyl-1',5'-dihydrospiro[benzo[d][1,3,2]dioxaborole-2,2'-[1,3,2]diazaborol]-3'-ium-9-uide (**6**) in  $\text{CDCl}_3$ .



*Figure S12.*  $^{13}\text{C}$  NMR of 1',3'-bis(4-methoxyphenyl)-4',5'-dimethyl-1',5'-dihydrospiro[benzo[d][1,3,2]dioxaborole-2,2'-[1,3,2]diazaborol]-3'-ium-9-uide (**6**) in  $\text{CDCl}_3$ .

1',3'-bis(4-fluorophenyl)-4',5'-dimethyl-1',5'-dihydrospiro[benzo[d][1,3,2]dioxaborole-2,2'-[1,3,2]diazaborol]-3'-ium-9-uide (**7**)

Yield: 86 mg (60%, 0.22 mmol). M.P. = 120°C (decomp). Anal. calc. for  $\text{C}_{22}\text{H}_{19}\text{N}_2\text{BO}_4\text{F}_2$  (392.21 g/mol) (%): C 67.37, H 4.88, N 7.14. Found: C 67.04, H 4.97, N 7.12.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.63 (d,  $J$  = 6.9 Hz, 3H), 2.25 (s, 3H), 4.78 (q,  $J$  = 6.9 Hz, 1H), 6.47 (m, 2H), 6.58-6.62 (ov m, 3H), 6.68 (br, 1H), 6.82 (t,  $J$  = 8.7 Hz, 2H), 7.01 (t,  $J$  = 8.2 Hz, 2H), 7.18 (m, 2H).  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$ : 11.6 (br).  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 16.0, 17.1, 59.9, 109.4, 109.6, 115.4 (d,  $J_{\text{C}-\text{F}}$  = 10 Hz), 115.7 (d,  $J_{\text{C}-\text{F}}$  = 28 Hz), 116.7 (d,  $J_{\text{C}-\text{F}}$  = 29 Hz), 119.3, 125.9 (d,  $J_{\text{C}-\text{F}}$  = 12 Hz), 133.0 (d,  $J_{\text{C}-\text{F}}$  = 1.1 Hz), 141.0, 150.9, 151.5, 156.9, 163.8, 187.4.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -111.2 (t,  $J$  = 7.9 Hz), -128.7 (br).

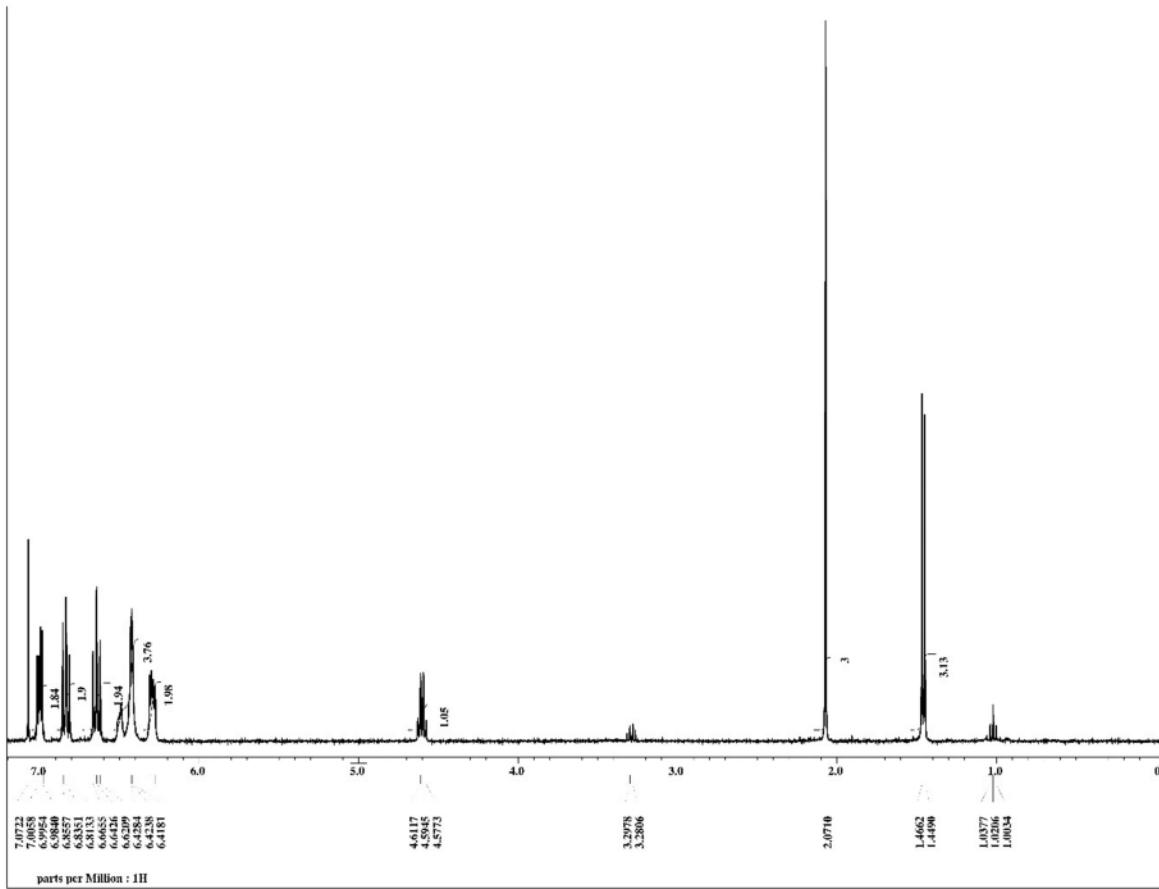


Figure S13.  $^1\text{H}$  NMR of 1',3'-bis(4-fluorophenyl)-4',5'-dimethyl-1',5'-dihydrospiro[benzo[*d*][1,3,2]dioxaborole-2,2'-[1,3,2]diazaborol]-3'-ium-9-uide (**7**) in  $\text{CDCl}_3$ .

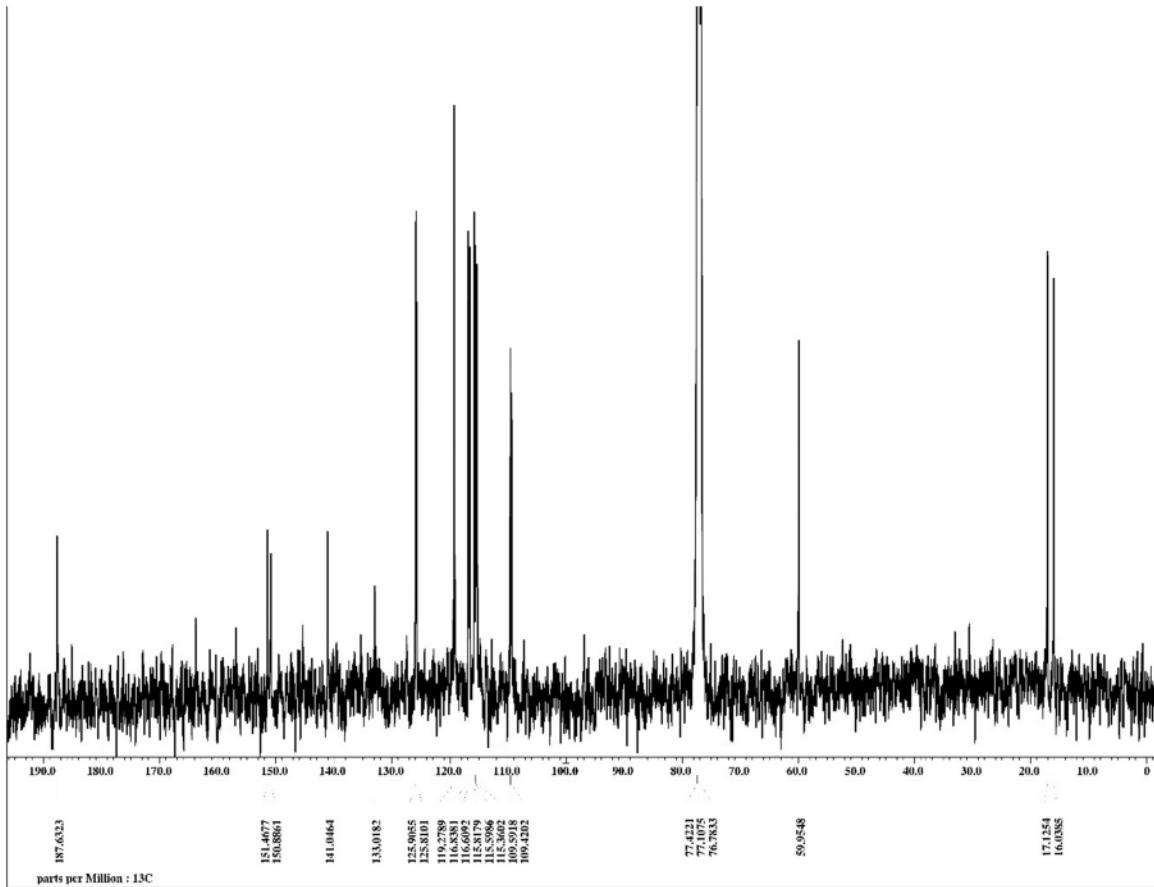


Figure S14.  $^{13}\text{C}$  NMR of 1',3'-bis(4-fluorophenyl)-4',5'-dimethyl-1',5'-dihydrospiro[benzo[d][1,3,2]dioxaborole-2,2'-[1,3,2]diazaborol]-3'-ium-9-uide (**7**) in  $\text{CDCl}_3$ .

### X-Ray Crystallography

Crystals were grown from dilute Et<sub>2</sub>O solutions. Single crystals were coated with Paratone-N oil, mounted using a polyimide MicroMount and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using  $\omega$  and  $\phi$  scans with a scan width of 0.3 ° and 10 s exposure times. The detector distance was 5 cm. The data were reduced (SAINT)<sup>1</sup> and corrected for absorption (SADABS).<sup>2</sup> The structure was solved by direct methods and refined by full-matrix least squares on F2(SHELXTL)<sup>3</sup>. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and refined using a riding model.

1 SAINT 7.23A, 2006, Bruker AXS, Inc., Madison, Wisconsin, USA.

2 SADABS 2008, George Sheldrick, 2008, Bruker AXS, Inc., Madison, Wisconsin, USA.

3 Sheldrick, G.M. (2008). SHELXTL. Acta Cryst. A64, 112-122.

**Table 1.** Crystallographic Data-Collection Parameters

| Complex                                | <b>3</b>   | <b>6</b>   | <b>7</b>  |
|--|--|--|---|
| Formula                                | C <sub>38</sub> H <sub>46</sub> B <sub>2</sub> N <sub>2</sub> O <sub>4</sub> | C <sub>24</sub> H <sub>25</sub> BN <sub>2</sub> O <sub>4</sub> | C <sub>22</sub> H <sub>19</sub> BF <sub>2</sub> N <sub>2</sub> O <sub>4</sub> |
| Molecular weight                       | 616.39   | 416.27   | 392.20  |
| Crystal system                         | Monoclinic   | Monoclinic   | Monoclinic  |
| Space group                            | C2/c   | P2(1)/c  | P2(1)/c   |
| a/Å                                    | 28.1959(14)  | 10.4891(3)   | 9.9992(4)   |
| b/Å                                    | 11.5570(6)   | 8.8508(3)  | 8.9229(4)   |
| c/Å                                    | 22.0519(11)  | 22.8286(7)   | 21.8330(8)  |
| $\alpha/^\circ$                        | 90   | 90   | 90  |
| $\beta/^\circ$                         | 101.603(2)   | 91.108(2)  | 99.004(2)   |
| $\gamma/^\circ$                        | 90   | 90   | 90  |
| V/Å <sup>3</sup>                       | 7039.0(6)  | 2118.94(11)  | 1923.98(14)   |
| Z                                      | 8  | 4  | 4   |
| $\rho_{\text{calc.}}/\text{Mg m}^{-3}$ | 1.163  | 1.305  | 1.354   |
| Crystal size/mm <sup>3</sup>           | 0.518 x 0.24 x 0.16  | 0.22 x 0.13 x 0.124  | 0.24 x 0.231 x 0.09   |
| Temp/K                                 | 170.0  | 169.99   | 169.84  |

| Radiation                                      | Mo- $K_{\alpha}$ ( $\lambda=0.71073$<br>Å) | Cu- $K_{\alpha}$ ( $\lambda=1.54178$<br>Å) | Cu- $K_{\alpha}$ ( $\lambda=1.54178$<br>Å) |
|--|--|--|--|
| $\mu/\text{mm}^{-1}$                           | 0.074                                      | 0.713                                      | 0.828                                      |
| Total reflections                              | 115455                                     | 40528                                      | 41998                                      |
| Total unique reflections                       | 7826                                       | 4028                                       | 3925                                       |
| No. of variables                               | 423  | 284  | 264  |
| $\theta$ Range/°                               | 2.95 to 27.21                              | 3.873 to 70.129                            | 4.1 to 74.852                              |
| Largest difference peak/hole/e Å <sup>-3</sup> | 0.20 and -0.20                             | 0.24 and -0.27                             | 0.33 and -0.43                             |
| S (GoF) on F <sup>2</sup>                      | 1.089                                      | 1.046                                      | 1.052                                      |
| R1 <sup>a</sup> ( $I>2\sigma(I)$ )             | 0.0491                                     | 0.0453                                     | 0.0578                                     |
| wR2 <sup>b</sup> (all data)                    | 0.1062                                     | 0.1289                                     | 0.1652                                     |

<sup>a</sup>)  $R1 = \sum|F_o - F_c| / \sum|F_o|$ . <sup>b</sup>)  $wR2 = (\sum[w(F_o^2 - F_c^2)^2] / \sum[wF_o^4])^{1/2}$ , where  $w = 1/[\sigma^2(F_o^2) + (0.0559 \cdot P)^2 + (0.0350 \cdot P)]$  (1),  $1/[\sigma^2(F_o^2) + (0.497 \cdot P)^2 + (1.8527 \cdot P)]$  (3), where  $P = (\max(F_o^2, 0) + 2 \cdot F_c^2)/3$ .