

## Cyclic boronium and borenium cations derived from borabenzene-pyridine

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**General Procedures.** All manipulations were performed under argon atmosphere using standard glovebox and Schlenk techniques. Toluene and *n*-hexane solvents were dried and purified by passing through activated alumina and Q5 columns.<sup>1</sup> Methylene dichloride was dried and distilled from CaH<sub>2</sub>. Pyridine was purchased from Aldrich Chemical Co. and distilled prior to use. Pyridine hydrochloride was prepared by adding a solution of HCl in Et<sub>2</sub>O to pyridine in Et<sub>2</sub>O at room temperature. A white precipitate forms immediately, which was washed with Et<sub>2</sub>O and dried under vacuum. 1-chloro-2-(trimethylsilyl)-4-(isopropyl)boracyclohexa-2,5-diene<sup>2</sup>, borabenzene lutidine<sup>3</sup>, borabenzene pyridine<sup>3</sup> **1a**, and TIB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>4</sup> were prepared according to reported procedures. 1-chloro-2-(trimethylsilyl)-4-(methyl)boracyclohexa-2,5-diene was prepared according to the synthetic procedure reported for 1-chloro-2-(trimethylsilyl)-4-(isopropyl)boracyclohexa-2,5-diene.<sup>2</sup>

All NMR spectra were performed in dry, oxygen-free CD<sub>2</sub>Cl<sub>2</sub> or CDCl<sub>3</sub>. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, DEPT-135, <sup>11</sup>B, COSY and HMQC NMR experiments were recorded on a Bruker DRX-400 spectrometer. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were calibrated using signals from the solvent and are reported downfield from SiMe<sub>4</sub>, whereas <sup>11</sup>B NMR spectra are referenced to external BF<sub>3</sub>·OEt<sub>2</sub>.

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Mass spectra were recorded on Esquire 3000, Kratos MS80RFA or Micromass VG7070 spectrometers. The pattern of boron-containing ions was compared with theoretical values.

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**Synthesis of 1b.** Pyridine (227 mg, 0.23 mL, 2.87 mmol) was added dropwise to a stirred solution of 1-chloro-2-(trimethylsilyl)-4-(isopropyl)boracyclohexa-2,5-diene (650 mg, 2.87 mmol) in 10 mL toluene at room temperature. The solution was stirred for 1 h at room temperature, and the volatiles were removed under vacuum. The resulting solid was slurried in *n*-hexane, sonicated, and filtered to collect an orange solid (422 mg, 75%). Suitable crystals for X-ray diffraction study were grown by cooling a solution of **1b** in CH<sub>2</sub>Cl<sub>2</sub> at -35 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): δ 1.27 (d, 6H, CH<sub>3</sub>-<sup>*i*</sup>Pr, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz), 2.87 (sept., 1H, CH-<sup>*i*</sup>Pr, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz), 6.63 (d, 2H, BCHCH, <sup>3</sup>J<sub>HH</sub> = 10.7 Hz), 7.34 (d, 2H, BCHCH, <sup>3</sup>J<sub>HH</sub> = 10.4 Hz), 7.68 (dd, 2H, C<sub>6</sub>H<sub>5</sub>-*meta*, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz), 8.01 (t, 1H, C<sub>6</sub>H<sub>5</sub>-*para*, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz), 9.00 (d, 2H, C<sub>6</sub>H<sub>5</sub>-*ortho*, <sup>3</sup>J<sub>HH</sub> = 5.4 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz): δ 25.60 (s, CH<sub>3</sub>-<sup>*i*</sup>Pr), 35.30 (s, CH-<sup>*i*</sup>Pr), 118.99 (s, br, BCHCH), 126.86 (s, C<sub>6</sub>H<sub>5</sub>-*meta*), 133.66 (s, BCHCH), 136.18 (s, C-*ipso*), 140.46 (s, C<sub>6</sub>H<sub>5</sub>-*para*), 144.54 (s, C<sub>6</sub>H<sub>5</sub>-*ortho*). <sup>11</sup>B NMR (CD<sub>2</sub>Cl<sub>2</sub>, 128 MHz): δ 31.80 (s). EI-MS: m/z: 197 [M<sup>+</sup>], 182 [M<sup>+</sup> - CH<sub>3</sub>], 154 [M<sup>+</sup> - CH(CH<sub>3</sub>)<sub>2</sub>]. EI-HRMS: 197.13644 (calcd 197.13758 amu, C<sub>13</sub>H<sub>16</sub><sup>11</sup>BN).

**Synthesis of 1c.** Pyridine (0.77 g, 0.79 mL, 9.74 mmol) was added dropwise to a stirred solution of 1-chloro-2-(trimethylsilyl)-4-(methyl)boracyclohexa-2,5-diene (1.95 g, 9.82 mmol) in 50 mL hexane at room temperature. The solution was stirred for 1 h at room temperature, and the volatiles were removed under vacuum. The resulting solid was slurried in *n*-hexane, sonicated, and filtered to collect an orange solid (1.53 g, 92%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): δ 2.36 (s, 3H, CH<sub>3</sub>), 6.62 (d, 2H, BCHCHC(Me), <sup>3</sup>J<sub>HH</sub> = 10.6 Hz), 7.30 (d, br, 2H, BCHCHC(Me), <sup>3</sup>J<sub>HH</sub> = 10.1 Hz), 7.64 (m, 2H, C<sub>6</sub>H<sub>5</sub>-*meta*), 7.98 (dt,

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1H,  $C_6H_5$ -*para*,  $^3J_{HH} = 7.8$  Hz,  $^4J_{HH} = 1.4$  Hz), 8.97 (dd, 2H,  $C_6H_5$ -*ortho*,  $^3J_{HH} = 6.7$  Hz,  $^4J_{HH} = 1.4$  Hz).  $^{13}C\{^1H\}$  NMR ( $CD_2Cl_2$ , 100 MHz):  $\delta$  22.28 (s,  $CH_3$ ), 119.14 (d, br, BCHCHC(Me),  $^1J_{BC} = 83.8$  Hz), 124.16 (s, *C-ipso*), 126.83 (s,  $C_6H_5$ -*meta*), 136.25 (s, BCHCHC(Me)), 140.38 (s,  $C_6H_5$ -*para*), 144.44 (s,  $C_6H_5$ -*ortho*).  $^{11}B$  NMR ( $CD_2Cl_2$ , 128 MHz):  $\delta$  31.58 (s). EI-MS: m/z: 169 [ $M^+$ ], 90 [ $M^+ - C_6H_5N$ ]. EI-HRMS: 169.10475 (calcd 169.10628 amu,  $C_{11}H_{12}^{11}BN$ ).

**Synthesis of [2a]Cl and [3a]Cl.** A suspension of pyridine hydrochloride (149 mg, 1.29 mmol) in 5 mL of  $CH_2Cl_2$  was added dropwise to a solution of borabenzene pyridine (200 mg, 1.29 mmol) in 5 mL of  $CH_2Cl_2$  at room temperature. The solution was stirred for 15 min at room temperature, and the volatiles were removed under vacuum to leave 348 mg (100 %) of a white solid. The compound was obtained as a 1:1 mixture of two regioisomers. Cooling a solution containing [2a]Cl and [3a]Cl in  $CH_2Cl_2$  at  $-35$  °C gave suitable crystals for X-ray diffraction study of the 2,5-isomer [3a]Cl.  $^1H$  NMR ( $CD_2Cl_2$ , 400 MHz,  $-30$  °C):  $\delta$  **2a** 1.93 (dd, br, 2H,  $BCH_2CHCH$ ,  $^3J_{HH} = 4.4$  Hz,  $^4J_{HH} = 1.4$  Hz), 5.76 (m, 1H,  $BCH_2CHCH$ ), 5.85 (m, 1H,  $BCH_2CHCH$ ), 6.29 (d, 1H,  $BCHCHCH$ ,  $^3J_{HH} = 12.0$  Hz), 6.50 (dd, 1H,  $BCHCHCH$ ,  $^3J_{HH} = 12.5$  Hz,  $^3J_{HH} = 4.8$  Hz), 7.90 (m, 4H,  $C_5H_5N$ -*meta*), 8.30 (m, 2H,  $C_5H_5N$ -*para*), 8.74 or 8.89 (m, 4H,  $C_5H_5N$ -*ortho*). **3a** 2.77 (s, br, 2H,  $BCHCHCH_2$ ), 6.27 (d,  $BCHCHCH_2$ ,  $^3J_{HH} = 12.5$  Hz), 6.55 (d, br,  $BCHCHCH_2$ ,  $^3J_{HH} = 12.5$  Hz), 7.90 (m, 4H,  $C_5H_5N$ -*meta*), 8.30 (m, 2H,  $C_5H_5N$ -*para*), 8.74 or 8.89 (m, 4H,  $C_5H_5N$ -*ortho*).  $^{13}C\{^1H\}$  NMR ( $CD_2Cl_2$ , 100 MHz,  $-30$  °C):  $\delta$  **2a** 22.10 (s, br,  $BCH_2CHCH$ ), 125.11 (s,  $BCH_2CHCH$ ), 127.01 or 127.14 (s,  $C_5H_5N$ -*meta*), 129.27 (s,  $BCH_2CHCH$ ), 136.48 (s,  $BCHCHCH$ ), 143.05 or 143.17 (s,  $C_5H_5N$ -*para*), 144.95 (s,  $C_5H_5N$ -*ortho*). **3a** 32.08 (s,  $BCHCHCH_2$ ), 127.01 or 127.14 (s,  $C_5H_5N$ -*meta*), 130.30 (s, br,  $BCHCHCH_2$ ), 140.13 (s,  $BCHCHCH_2$ ), 143.05 or 143.17 (s,  $C_5H_5N$ -*para*), 144.95 (s,  $C_5H_5N$ -*ortho*).  $^{11}B$  NMR ( $CD_2Cl_2$ , 128 MHz,  $-30$  °C):  $\delta$  **2a** 4.82 (s), **3a** 0.36 (s). ESI-MS<sub>pos</sub>: m/z: 156 [**2a,3a** -  $C_5H_5N$ ] $^+$ , 77 [**2a,3a** -  $2C_5H_5N$ ] $^+$ .

**Synthesis of [2b]Cl.** A suspension of pyridine hydrochloride (59 mg, 0.51 mmol) in 2 mL of  $CH_2Cl_2$  was added dropwise to a solution of **1b** (100 mg, 0.51 mmol) in 4 mL of  $CH_2Cl_2$  at room temperature. The solution was stirred for 15 min at room temperature,

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and the volatiles were removed under vacuum to leave 158 mg (100 %) of a white solid.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz,  $-50\text{ }^\circ\text{C}$ ):  $\delta$  0.89 (d, 6H,  $\text{CH}_3$ -*i*Pr,  $^3J_{\text{HH}} = 6.8$  Hz), 1.92 (d, 2H,  $\text{BCH}_2\text{CHC}$ (*i*Pr),  $^3J_{\text{HH}} = 4.6$  Hz), 2.21 (sept., 1H,  $\text{CH}$ -*i*Pr,  $^3J_{\text{HH}} = 6.7$  Hz), 5.60 (t, 1H,  $\text{BCH}_2\text{CHC}$ (*i*Pr),  $^3J_{\text{HH}} = 4.8$  Hz), 6.21 (d, 1H,  $\text{BCHCHC}$ (*i*Pr),  $^3J_{\text{HH}} = 12.4$  Hz), 6.57 (d, 1H,  $\text{BCHCHC}$ (*i*Pr),  $^3J_{\text{HH}} = 12.4$  Hz), 7.88 (dd, 4H,  $\text{C}_5\text{H}_5\text{N}$ -*meta*,  $^3J_{\text{HH}} = 6.8$  Hz), 8.27 (t, 2H,  $\text{C}_5\text{H}_5\text{N}$ -*para*,  $^3J_{\text{HH}} = 7.7$  Hz), 8.71 (d, 4H,  $\text{C}_5\text{H}_5\text{N}$ -*ortho*,  $^3J_{\text{HH}} = 5.4$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100 MHz,  $-50\text{ }^\circ\text{C}$ ):  $\delta$  21.17 (s,  $\text{CH}_3$ -*i*Pr), 22.11 (s, br,  $\text{BCH}_2\text{CHC}$ (*i*Pr)), 33.41 (s,  $\text{CH}$ -*i*Pr), 120.24 (s,  $\text{BCH}_2\text{CHC}$ (*i*Pr)), 127.20 (s,  $\text{C}_5\text{H}_5\text{N}$ -*meta*), 130.63 (s, br,  $\text{BCHCHC}$ (*i*Pr)), 139.63 (s,  $\text{BCHCHC}$ (*i*Pr)), 142.41 (s,  $\text{BCHCHC}$ (*i*Pr)), 143.35 (s,  $\text{C}_5\text{H}_5\text{N}$ -*para*), 144.92 (s,  $\text{C}_5\text{H}_5\text{N}$ -*ortho*).  $^{11}\text{B}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 128 MHz,  $-50\text{ }^\circ\text{C}$ ):  $\delta$  5.10 (s, br). ESI-MS<sub>pos</sub>: m/z: 198 [**2b** -  $\text{C}_5\text{H}_5\text{N}$ ]<sup>+</sup>, 156 [ $\text{C}_5\text{H}_6\text{B}$ - $\text{C}_5\text{H}_5\text{N}$ ]<sup>+</sup>.

**Synthesis of 4a and 5a.** A solution of borabenzene pyridine (100 mg, 0.64 mmol) in 6 mL  $\text{CH}_2\text{Cl}_2$  was treated with HCl gas (23 mg, 63 mmol) at  $-78\text{ }^\circ\text{C}$ . The color of the solution changed immediately from orange to colorless. After 10 min the volatiles were removed in vacuum to leave 123 mg (100 %) of a colorless oil. The compound was obtained as a 1:1 mixture of two regioisomers.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 400 MHz,  $25\text{ }^\circ\text{C}$ ):  $\delta$  **4a** AB spin system: A 1.61 (d, br, 1H,  $\text{BCH}_2\text{CHCH}$ ,  $^2J_{\text{HH}} = 19.3$  Hz), B 2.34 (d, br, 1H,  $\text{BCH}_2\text{CHCH}$ ,  $^2J_{\text{HH}} = 19.3$  Hz), 6.03 (m, 1H,  $\text{BCHCHCH}$ ), 6.28 (d, 1H,  $\text{BCHCHCH}$ ,  $^3J_{\text{HH}} = 12.0$  Hz), 6.29 (d, br, 1H,  $\text{BCH}_2\text{CHCH}$ ,  $^3J_{\text{HH}} = 12.2$  Hz), 6.61 (m, 1H,  $\text{BCH}_2\text{CHCH}$ , overlapping with the ortho protons from pyridine), 6.63 (dd, 2H,  $\text{C}_5\text{H}_5\text{N}$ -*meta*,  $^3J_{\text{HH}} = 7.0$  Hz), 7.99 (t, 1H,  $\text{C}_5\text{H}_5\text{N}$ -*para*,  $^3J_{\text{HH}} = 7.6$  Hz), 8.58 (d, 2H,  $\text{C}_5\text{H}_5\text{N}$ -*ortho*,  $^3J_{\text{HH}} = 5.2$  Hz). **5a** 2.83 (d, br, 2H,  $\text{BCHCHCH}_2$ ,  $^3J_{\text{HH}} = 10.6$  Hz), 6.03 (m,  $\text{BCHCHCH}_2$ ), 6.30 (dt,  $\text{BCHCHCH}_2$ ,  $^3J_{\text{HH}} = 12.4$  Hz,  $^4J_{\text{HH}} = 1.7$  Hz), 6.63 (dd, 2H,  $\text{C}_5\text{H}_5\text{N}$ -*meta*,  $^3J_{\text{HH}} = 7.0$  Hz), 7.99 (t, 1H,  $\text{C}_5\text{H}_5\text{N}$ -*para*,  $^3J_{\text{HH}} = 7.6$  Hz), 8.63 (s, br, 2H,  $\text{C}_5\text{H}_5\text{N}$ -*ortho*).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 100 MHz,  $25\text{ }^\circ\text{C}$ ):  $\delta$  **4a** 28.61 (s, br,  $\text{BCH}_2\text{CHCH}$ ), 125.37 (s,  $\text{C}_5\text{H}_5\text{N}$ -*meta*), 125.68 (s,  $\text{BCHCHCH}$ ), 133.60 (s,  $\text{BCHCHCH}$ ), 135.36 (s,  $\text{BCH}_2\text{CHCH}$ ), 136.37 (s, br,  $\text{BCHCHCH}$ ), 140.64 (s,  $\text{C}_5\text{H}_5\text{N}$ -*para*), 144.47 (s,  $\text{C}_5\text{H}_5\text{N}$ -*ortho*). **5a** 32.74 (s,  $\text{BCHCHCH}_2$ ), 130.57 (s, br,  $\text{BCHCHCH}_2$ ), 136.38 (s, br,  $\text{BCHCHCH}_2$ ), 125.37 (s,  $\text{C}_5\text{H}_5\text{N}$ -*meta*), 140.64 (s,  $\text{C}_5\text{H}_5\text{N}$ -*para*), 144.85 (s,  $\text{C}_5\text{H}_5\text{N}$ -*ortho*).  $^{11}\text{B}$  NMR ( $\text{C}_6\text{D}_6$ , 128 MHz,  $25\text{ }^\circ\text{C}$ ):  $\delta$  **4a** 4.89 (s), **5a** 1.13 (s). EI-MS: m/z: 112 [**4a,5a** -  $\text{C}_5\text{H}_5\text{N}$ ]<sup>+</sup>, 79 [ $\text{C}_5\text{H}_5\text{N}$ ]<sup>+</sup>.

**Synthesis of 4b.** A solution of **1b** (105 mg, 0.53 mmol) in 8 mL CH<sub>2</sub>Cl<sub>2</sub> was treated with HCl gas (22 mg, 60 mmol) at -78 °C. The color of the solution changed immediately from orange to colorless. After 10 min the volatiles were removed in vacuum to leave 124 mg (100 %) of a colorless oil. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 25 °C): δ 1.19 (d, 6H, CH<sub>3</sub>-<sup>i</sup>Pr, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz), 1.71 (d, br, 2H, BCH<sub>2</sub>CHC(<sup>i</sup>Pr), <sup>3</sup>J<sub>HH</sub> = 15.1 Hz), 2.47 (sept., 1H, CH-<sup>i</sup>Pr, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz), 5.83 (s, br, 1H, BCH<sub>2</sub>CHC(<sup>i</sup>Pr)), 6.46 (d, 1H, BCHCHC(<sup>i</sup>Pr), <sup>3</sup>J<sub>HH</sub> = 12.2 Hz), 6.64 (dd, 2H, C<sub>5</sub>H<sub>5</sub>N-*meta*, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz), 6.70 (d, 1H, BCHCHC(<sup>i</sup>Pr), <sup>3</sup>J<sub>HH</sub> = 11.9 Hz), 6.99 (t, 1H, C<sub>5</sub>H<sub>5</sub>N-*para*, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz), 8.69 (d, br, 2H, C<sub>5</sub>H<sub>5</sub>N-*ortho*, <sup>3</sup>J<sub>HH</sub> = 4.5 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 100 MHz, 25 °C): δ 22.21 (s, br, CH<sub>3</sub>-<sup>i</sup>Pr), 22.31 (s, br, CH<sub>3</sub>-<sup>i</sup>Pr), 28.13 (s, br, BCH<sub>2</sub>CHC(<sup>i</sup>Pr)), 34.66 (s, CH-<sup>i</sup>Pr), 122.05 (s, BCH<sub>2</sub>CHC(<sup>i</sup>Pr)), 125.19 (s, C<sub>5</sub>H<sub>5</sub>N-*meta*), 136.05 (s, BCHCHC(<sup>i</sup>Pr)), 136.99 (s, br, BCHCHC(<sup>i</sup>Pr)), 140.41 (s, C<sub>5</sub>H<sub>5</sub>N-*para*), 142.11 (s, BCHCHC(<sup>i</sup>Pr)), 144.47 (s, br, C<sub>5</sub>H<sub>5</sub>N-*ortho*). <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>, 128 MHz, 25 °C): δ 5.08 (s, br). EI-MS: m/z: 119 [**4b** - C<sub>5</sub>H<sub>5</sub>N, - Cl]<sup>+</sup>, 104 [**4b** - C<sub>5</sub>H<sub>5</sub>N, - Cl, -CH<sub>3</sub>]<sup>+</sup>, 79 [C<sub>5</sub>H<sub>5</sub>N]<sup>+</sup>.

**Synthesis of 4c.** A solution of **1c** (150 mg, 0.88 mmol) in 10 mL CH<sub>2</sub>Cl<sub>2</sub> was treated with HCl gas (32 mg, 0.88 mmol) at -78 °C. The color of the solution changed immediately from orange to colorless. After 10 min the volatiles were removed in vacuum to leave 182 mg (100 %) of a colorless oil. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, 25 °C): δ AB spin system: A 1.46 (d, br., 1H, BCH<sub>2</sub>CHC(CH<sub>3</sub>), <sup>2</sup>J<sub>HH</sub> = 18.8 Hz), B 1.88 (d, br., 1H, BCH<sub>2</sub>CHC(CH<sub>3</sub>), <sup>2</sup>J<sub>HH</sub> = 18.8 Hz), 1.76 (m, 3H, BCH<sub>2</sub>CHC(CH<sub>3</sub>)), 5.57 (s, br, 1H, BCH<sub>2</sub>CHC(CH<sub>3</sub>)), 6.00 (d, 1H, BCHCHC(CH<sub>3</sub>), <sup>3</sup>J<sub>HH</sub> = 12.0 Hz), 6.31 (d, br., 1H, BCHCHC(CH<sub>3</sub>), <sup>3</sup>J<sub>HH</sub> = 12.0 Hz), 7.66 (dd, 2H, C<sub>5</sub>H<sub>5</sub>N-*meta*, <sup>3</sup>J<sub>HH</sub> = 7.08 Hz), 8.08 (t, 1H, C<sub>5</sub>H<sub>5</sub>N-*para*, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz), 8.89 (d, br, 2H, C<sub>5</sub>H<sub>5</sub>N-*ortho*, <sup>3</sup>J<sub>HH</sub> = 5.2 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz, 25 °C): δ 22.72 (s, br, BCH<sub>2</sub>CHC(CH<sub>3</sub>)), 27.49 (s, br, BCH<sub>2</sub>CHC(CH<sub>3</sub>)), 124.63 (s, BCH<sub>2</sub>CHC(CH<sub>3</sub>)), 126.27 (s, C<sub>5</sub>H<sub>5</sub>N-*meta*), 131.82 (s, BCHCHC(CH<sub>3</sub>)), 136.22 (s, br, BCHCHC(CH<sub>3</sub>)), 138.14 (s, BCHCHC(CH<sub>3</sub>)), 141.83 (s, C<sub>5</sub>H<sub>5</sub>N-*para*), 145.26 (s, C<sub>5</sub>H<sub>5</sub>N-*ortho*). <sup>11</sup>B NMR (CD<sub>2</sub>Cl<sub>2</sub>, 128 MHz, 25 °C): δ 4.75 (s, br). EI-MS: m/z: 170 [**4c** - Cl]<sup>+</sup>, 126 [**4c** - C<sub>5</sub>H<sub>5</sub>N]<sup>+</sup>, 111 [**4c** - C<sub>5</sub>H<sub>5</sub>N, - CH<sub>3</sub>]<sup>+</sup>, 79 [C<sub>5</sub>H<sub>5</sub>N]<sup>+</sup>.

**Synthesis of 6a and 7a.** A solution of TIB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> (203 mg, 0.23 mmol) in 5 mL CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to a solution containing a mixture of **4a** and **5a** (44 mg, 0.23 mmol) in 4 mL CH<sub>2</sub>Cl<sub>2</sub> and stirred for 10 min at room temperature. The white precipitate of TiCl<sub>4</sub> was removed by filtration. The compound was obtained as a mixture of 2,5- and 2,4-isomers in 9:1 ratio, after recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane: yield 123 mg (64 %). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, 25 °C): δ **7a** 3.78 (m, 2H, BCHCHCH<sub>2</sub>), 7.01 (dt, 2H, BCHCHCH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 12.0 Hz, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz), 8.21 (m, 4H, BCHCHCH<sub>2</sub> + C<sub>5</sub>H<sub>5</sub>N-*meta*), 8.73 (m, C<sub>5</sub>H<sub>5</sub>N-*para*), 9.1 (d, 2H, C<sub>5</sub>H<sub>5</sub>N-*ortho*, <sup>3</sup>J<sub>HH</sub> = 5.3 Hz). **6a** 2.89 (d, br, 2H, BCH<sub>2</sub>CHCH, <sup>3</sup>J<sub>HH</sub> = 3.5 Hz), 6.09 (dt, 1H, BCH<sub>2</sub>CHCH, <sup>3</sup>J<sub>HH</sub> = 1.7 Hz, <sup>3</sup>J<sub>HH</sub> = 12.7 Hz), 6.73 (d, br, 1H, BCHCHCH, <sup>3</sup>J<sub>HH</sub> = 12.2 Hz), 6.93 (1H, BCHCHCH, <sup>3</sup>J<sub>HH</sub> = 11.9 Hz), 8.27 (m, 2H, C<sub>5</sub>H<sub>5</sub>N-*meta*, partially overlapping with the C<sub>5</sub>H<sub>5</sub>N-*meta* signal of **7a**), 8.78 (m, 2H, C<sub>5</sub>H<sub>5</sub>N-*para*, partially overlapping with the C<sub>5</sub>H<sub>5</sub>N-*para* signal of **7a**), 9.02 (d, 2H, C<sub>5</sub>H<sub>5</sub>N-*ortho*, <sup>3</sup>J<sub>HH</sub> = 5.2 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz, 25 °C): **7a** δ 40.47 (s, BCHCHCH<sub>2</sub>), 124.81 (s, br, BCHCHCH<sub>2</sub>), 128.18 (s, *C-ipso*), 129.24 (s, C<sub>5</sub>H<sub>5</sub>N-*meta*), 136.90 (d, br, C<sub>6</sub>F<sub>5</sub>-*meta*, <sup>1</sup>J<sub>CF</sub> = 244.9 Hz), 138.82 (d, C<sub>6</sub>F<sub>5</sub>-*para*, <sup>1</sup>J<sub>CF</sub> = 244.0 Hz), 146.09 (s, C<sub>5</sub>H<sub>5</sub>N-*ortho*), 148.10 (d, C<sub>6</sub>F<sub>5</sub>-*ortho*, <sup>1</sup>J<sub>CF</sub> = 239.0 Hz), 150.15 (s, C<sub>5</sub>H<sub>5</sub>N-*para*), 168.77 (s, BCHCHCH<sub>2</sub>) signals for the **6a** isomer were not detected. <sup>11</sup>B NMR (CD<sub>2</sub>Cl<sub>2</sub>, 128 MHz, 25 °C): **7a** δ -17.43 (s, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>) 45.52 (s, br, BC<sub>5</sub>H<sub>5</sub>) **6a** δ -17.43 (s, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>) 57.24 (s, br, BC<sub>5</sub>H<sub>5</sub>). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 282 MHz, 25 °C): δ -167.20 (dd, C<sub>6</sub>F<sub>5</sub>-*meta*, <sup>3</sup>J<sub>FF</sub> = 28.2 Hz), -163.3 (t, C<sub>6</sub>F<sub>5</sub>-*para*, <sup>3</sup>J<sub>FF</sub> = 28.2 Hz), -133.00 (s, br, C<sub>6</sub>F<sub>5</sub>-*ortho*). ESI-MS<sub>pos</sub>: m/z: 156 [**6a,7a** - B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>+</sup>, 80 [C<sub>6</sub>N<sub>5</sub>H]<sup>+</sup>. ESI-MS<sub>neg</sub>: m/z: 679 [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>.

**Synthesis of 6b.** A solution of TIB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> (113 mg, 0.13 mmol) in 4 mL CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to a solution of **4b** (30 mg, 0.13 mmol) in 2 mL CH<sub>2</sub>Cl<sub>2</sub> and the mixture stirred for 10 min at room temperature. The white precipitate of TiCl<sub>4</sub> was removed by filtration. **6b** was obtained as a white crystalline solid by layering a CH<sub>2</sub>Cl<sub>2</sub> solution with hexane and allowing the two solvents to diffuse: yield 88 mg (78 %). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, 25 °C): δ 1.21 (d, 6H, CH<sub>3</sub>-<sup>*i*</sup>Pr, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz), 2.75 (sept., 1H, CH-<sup>*i*</sup>Pr, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz), 2.85 (d, 2H, BCH<sub>2</sub>CHC(<sup>*i*</sup>Pr), <sup>3</sup>J<sub>HH</sub> = 4.1 Hz), 6.74 (s, br, 1H, BCH<sub>2</sub>CHC(<sup>*i*</sup>Pr)),

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6.92 (d, 1H, BCHCHC(<sup>i</sup>Pr), <sup>3</sup>J<sub>HH</sub> = 12.2 Hz), 8.21 (dd, 2H, C<sub>5</sub>H<sub>5</sub>N-*meta*, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz), 8.30 (d, br, 1H, BCHCHC(<sup>i</sup>Pr), <sup>3</sup>J<sub>HH</sub> = 11.8 Hz), 8.71 (dt, 1H, C<sub>5</sub>H<sub>5</sub>N-*para*, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, <sup>4</sup>J<sub>HH</sub> = 1.5 Hz), 9.1 (d, br, 2H, C<sub>5</sub>H<sub>5</sub>N-*ortho*, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz, 25 °C): δ 21.90 (s, CH<sub>3</sub>-<sup>i</sup>Pr), 27.52 (s, br, BCH<sub>2</sub>CHC(<sup>i</sup>Pr)), 33.97 (s, CH-<sup>i</sup>Pr), 124.28 (s, br, BCHCHC(<sup>i</sup>Pr)), 128.79 (s, C<sub>5</sub>H<sub>5</sub>N-*meta*), 134.80 (s, BCH<sub>2</sub>CHC(<sup>i</sup>Pr)), 136.27 (d, C<sub>6</sub>F<sub>5</sub>-*meta*, <sup>1</sup>J<sub>CF</sub> = 245.6 Hz), 138.22 (d, C<sub>6</sub>F<sub>5</sub>-*para*, <sup>1</sup>J<sub>CF</sub> = 244.2 Hz), 145.11 (s, C<sub>5</sub>H<sub>5</sub>N-*ortho*), 146.35 (s, *C-ipso*), 148.10 (d, C<sub>6</sub>F<sub>5</sub>-*ortho*, <sup>1</sup>J<sub>CF</sub> = 242.3 Hz), 149.79 (s, C<sub>5</sub>H<sub>5</sub>N-*para*), 167.55 (s, BCHCHC(<sup>i</sup>Pr)), 172.48 (s, *C-ipso*). <sup>11</sup>B NMR (CD<sub>2</sub>Cl<sub>2</sub>, 128 MHz, 25 °C): δ -17.28 (s, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>) 56.56 (s, br, BC<sub>5</sub>H<sub>5</sub>). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 282 MHz, 25 °C): δ -167.30 (dd, C<sub>6</sub>F<sub>5</sub>- *meta*, <sup>3</sup>J<sub>FF</sub> = 28.2 Hz), -163.4 (t, C<sub>6</sub>F<sub>5</sub>- *para*, <sup>3</sup>J<sub>FF</sub> = 28.2 Hz), -133.00 (s, br, C<sub>6</sub>F<sub>5</sub>- *ortho*). ESI-MS<sub>pos</sub>: m/z: 198 [**6b** - B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>+</sup>, 156 [**6b**- B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>, -CH(CH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. ESI-MS<sub>neg</sub>: m/z: 679 [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>.

**Synthesis of 6c.** A solution of TIB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> (176 mg, 0.20 mmol) in 4 mL CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to a solution of **4c** (41 mg, 0.20 mmol) in 2 mL CH<sub>2</sub>Cl<sub>2</sub> and the mixture stirred for 10 min at room temperature. The white precipitate of TiCl<sub>4</sub> was removed by filtration. **6c** was obtained as colorless crystals by layering a CH<sub>2</sub>Cl<sub>2</sub> solution with hexane and allowing the two solvents to diffuse: yield 122 mg (72 %). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, 25 °C): δ 2.18 (m, 3H, CH<sub>3</sub>), 2.83 (d, br, 2H, BCH<sub>2</sub>CHC(CH<sub>3</sub>)), <sup>3</sup>J<sub>HH</sub> = 2.2 Hz), 6.73 (s, br, 1H, BCH<sub>2</sub>CHC(CH<sub>3</sub>)), 6.88 (d, 1H, BCHCHC(CH<sub>3</sub>), <sup>3</sup>J<sub>HH</sub> = 12.0 Hz), 8.14 (d, br, 1H, BCHCHC(CH<sub>3</sub>), <sup>3</sup>J<sub>HH</sub> = 12.0 Hz), 8.18 (m, 2H, C<sub>5</sub>H<sub>5</sub>N-*meta*), 8.70 (dt, 1H, C<sub>5</sub>H<sub>5</sub>N-*para*, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, <sup>4</sup>J<sub>HH</sub> = 1.5 Hz), 9.01 (dd, br, 2H, C<sub>5</sub>H<sub>5</sub>N-*ortho*, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, <sup>4</sup>J<sub>HH</sub> = 1.4 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz, 25 °C): δ 21.85 (s, CH<sub>3</sub>), 28.68 (s, br, BCH<sub>2</sub>CHC(CH<sub>3</sub>)), 124.86 (s, br, BCHCHC(CH<sub>3</sub>)), 129.37 (s, C<sub>5</sub>H<sub>5</sub>N-*meta*), 139.91 (d, C<sub>6</sub>F<sub>5</sub>-*meta*, <sup>1</sup>J<sub>CF</sub> = 244.2 Hz), 137.67 (s, BCH<sub>2</sub>CHC(CH<sub>3</sub>)), 138.86 (d, C<sub>6</sub>F<sub>5</sub>-*para*, <sup>1</sup>J<sub>CF</sub> = 237.7 Hz), 145.71 (s, C<sub>5</sub>H<sub>5</sub>N-*ortho*), 148.73 (d, C<sub>6</sub>F<sub>5</sub>-*ortho*, <sup>1</sup>J<sub>CF</sub> = 240.3 Hz), 150.39 (s, C<sub>5</sub>H<sub>5</sub>N-*para*), 169.67 (s, BCHCHC(CH<sub>3</sub>)), *C-ipso* was not detected. <sup>11</sup>B NMR (CD<sub>2</sub>Cl<sub>2</sub>, 128 MHz, 25 °C): δ -17.43 (s, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), 56.39 (s, br, BC<sub>5</sub>H<sub>5</sub>). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 282 MHz, 25 °C): δ -167.20 (dd, C<sub>6</sub>F<sub>5</sub>- *meta*, <sup>3</sup>J<sub>FF</sub> = 28.2 Hz), -163.3 (t, C<sub>6</sub>F<sub>5</sub>- *para*, <sup>3</sup>J<sub>FF</sub> = 28.2 Hz), -133.00 (s, br, C<sub>6</sub>F<sub>5</sub>- *ortho*). ESI-MS<sub>pos</sub>: m/z: 170 [**6c** - B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>+</sup>, 155 [**6c**-

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$B(C_6F_5)_4$ ,  $-CH_3]^+$ , 91 [**6c**-  $B(C_6F_5)_4$ ,  $-NC_6H_5]^+$ , 80 [ $HNC_6H_5]^+$ . ESI-MS<sub>neg</sub>: m/z: 679 [ $B(C_6F_5)_4$ ].

**Synthesis of [2a][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and [3a][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>].** TIB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> (114 mg, 0.13 mmol) in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to a solution containing a mixture of [**2a**]Cl and [**3a**]Cl (35 mg, 0.13 mmol) in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> at room temperature. The solution was stirred for 15 min at room temperature. The white precipitate of TiCl<sub>4</sub> was removed by filtration and the volatiles were removed under vacuum to leave 118 mg (100 %) of a white solid. The compound was obtained as a mixture of 2,5- and 2,4-isomers in 2:1 ratio. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, 25 °C): δ [**2a**][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] 1.97 (d, br, 2H, BCH<sub>2</sub>CHCH, <sup>3</sup>J<sub>HH</sub> = 2.2 Hz), 6.04 (m, 2H, BCH<sub>2</sub>CHCH + BCH<sub>2</sub>CHCH), 6.67 (m, 1H, BCHCHCH overlapping with signals from [**3a**][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]), 6.86 (dd, 1H, BCHCHCH, <sup>3</sup>J<sub>HH</sub> = 10.7 Hz, <sup>4</sup>J<sub>HH</sub> = 1.0 Hz), 7.81 (m, 4H, C<sub>5</sub>H<sub>5</sub>N-*meta*), 8.28 (m, 2H, C<sub>5</sub>H<sub>5</sub>N-*para*), 8.45 (m, 4H, C<sub>5</sub>H<sub>5</sub>N-*ortho*). [**3a**][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] 2.93 (m, 2H, BCHCHCH<sub>2</sub>), 6.09 (dt, BCHCHCH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 12.7 Hz, <sup>4</sup>J<sub>HH</sub> = 2.0 Hz), 6.7 (d, br, BCHCHCH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 12.4 Hz), 7.81 (m, 4H, C<sub>5</sub>H<sub>5</sub>N-*meta*), 8.28 (m, 2H, C<sub>5</sub>H<sub>5</sub>N-*para*), 8.45 (m, 4H, C<sub>5</sub>H<sub>5</sub>N-*ortho*). <sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz, 25 °C): δ [**2a**][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] 24.60 (s, br, BCH<sub>2</sub>CHCH), 126.69 (s, BCH<sub>2</sub>CHCH), 128.23 (s, C<sub>5</sub>H<sub>5</sub>N-*meta*), 129.58 (s, BCH<sub>2</sub>CHCH), 136.91 (d, br, C<sub>6</sub>F<sub>5</sub>-*meta*, <sup>1</sup>J<sub>CF</sub> = 244.3 Hz), 138.85 (d, C<sub>6</sub>F<sub>5</sub>-*para*, <sup>1</sup>J<sub>CF</sub> = 243.9 Hz), 139.00 (s, BCHCHCH), 144.45 (s, C<sub>5</sub>H<sub>5</sub>N-*para*), 145.06 (s, C<sub>5</sub>H<sub>5</sub>N-*ortho*), 148.75 (d, C<sub>6</sub>F<sub>5</sub>-*ortho*, <sup>1</sup>J<sub>CF</sub> = 238.4 Hz). [**3a**][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] 33.32 (s, BCHCHCH<sub>2</sub>), 124.27 (s, br, BCHCHCH<sub>2</sub>), 127.65 (s, C<sub>6</sub>F<sub>5</sub>-*ipso*), 128.15 (s, C<sub>5</sub>H<sub>5</sub>N-*meta*), 136.91 (d, br, C<sub>6</sub>F<sub>5</sub>-*meta*, <sup>1</sup>J<sub>CF</sub> = 244.3 Hz), 138.85 (d, C<sub>6</sub>F<sub>5</sub>-*para*, <sup>1</sup>J<sub>CF</sub> = 243.9 Hz), 142.70 (s, BCHCHCH<sub>2</sub>), 144.09 (s, C<sub>5</sub>H<sub>5</sub>N-*para*), 145.50 (s, C<sub>5</sub>H<sub>5</sub>N-*ortho*), 148.75 (d, C<sub>6</sub>F<sub>5</sub>-*ortho*, <sup>1</sup>J<sub>CF</sub> = 238.4 Hz). <sup>11</sup>B NMR (CD<sub>2</sub>Cl<sub>2</sub>, 128 MHz, 25 °C): δ [**2a**][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] δ -17.43 (s, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), 5.09 (s, br, BC<sub>5</sub>H<sub>5</sub>). [**3a**][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] δ -17.43 (s, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), 1.27 (s, br, BC<sub>5</sub>H<sub>5</sub>). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 282 MHz, 25 °C): δ -167.20 (dd, C<sub>6</sub>F<sub>5</sub>-*meta*, <sup>3</sup>J<sub>FF</sub> = 28.2 Hz), -163.3 (t, C<sub>6</sub>F<sub>5</sub>-*para*, <sup>3</sup>J<sub>FF</sub> = 28.2 Hz), -133.00 (s, br, C<sub>6</sub>F<sub>5</sub>-*ortho*). ESI-MS<sub>pos</sub>: m/z: 156 [**2a,3a** - C<sub>6</sub>N<sub>5</sub>]<sup>+</sup>, 80 [C<sub>6</sub>N<sub>5</sub>H]<sup>+</sup>, 77 [**2a,3a** - 2 C<sub>6</sub>N<sub>5</sub>]<sup>+</sup>. ESI-MS<sub>neg</sub>: m/z: 679 [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>].



# Supplementary Material (ESI) for Chemical Communications  
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**Synthesis of [2b][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>].** TIB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> (99 mg, 0.11 mmol) in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to a solution of **3** (35 mg, 0.11 mmol) in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> at room temperature. The solution was stirred for 15 min at room temperature. The white precipitate of TiCl<sub>4</sub> was removed by filtration and the volatiles were removed under vacuum to leave 107 mg (100 %) of a white solid. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>Br, 300 MHz, 25 °C): δ 0.97 (d, 6H, CH<sub>3</sub>-<sup>i</sup>Pr, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz), 1.58 (d, br, 2H, BCH<sub>2</sub>CHC(<sup>i</sup>Pr), <sup>3</sup>J<sub>HH</sub> = 4.5 Hz), 2.23 (sept., 1H, CH-<sup>i</sup>Pr, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz), 5.58 (s, br, 1H, BCH<sub>2</sub>CHC(<sup>i</sup>Pr)), 5.77 (d, 1H, BCHCHC(<sup>i</sup>Pr), <sup>3</sup>J<sub>HH</sub> = 12.3 Hz), 6.56 (d, 1H, BCHCHC(<sup>i</sup>Pr), <sup>3</sup>J<sub>HH</sub> = 12.3 Hz), 7.06 (dd, 4H, C<sub>5</sub>H<sub>5</sub>N-*meta*, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz), 7.48 (t, 2H, C<sub>5</sub>H<sub>5</sub>N-*para*, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz), 7.92 (d, br, 4H, C<sub>5</sub>H<sub>5</sub>N-*ortho*, <sup>3</sup>J<sub>HH</sub> = 5.5 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>5</sub>Br, 75 MHz, 25 °C): δ 21.41 (s, CH<sub>3</sub>-<sup>i</sup>Pr), 22.60 (s, br, BCH<sub>2</sub>CHC(<sup>i</sup>Pr)), 33.64 (s, CH-<sup>i</sup>Pr), 119.94 (s, BCH<sub>2</sub>CHC(<sup>i</sup>Pr)), 126.62 (s, C<sub>5</sub>H<sub>5</sub>N-*meta*), 129.63 (s, BCHCHC(<sup>i</sup>Pr), buried under the signal of C<sub>6</sub>D<sub>5</sub>Br), 136.30 (d, C<sub>6</sub>F<sub>5</sub>-*meta*, <sup>1</sup>J<sub>CF</sub> = 242.0 Hz), 138.18 (d, C<sub>6</sub>F<sub>5</sub>-*para*, <sup>1</sup>J<sub>CF</sub> = 246.3 Hz), 140.72 (s, BCHCHC(<sup>i</sup>Pr)), 142.67 (s, C<sub>5</sub>H<sub>5</sub>N-*para*), 143.18 (s, *C-ipso*), 143.59 (s, C<sub>5</sub>H<sub>5</sub>N-*ortho*), 143.97 (s, *C-ipso*), 148.35 (d, C<sub>6</sub>F<sub>5</sub>-*ortho*, <sup>1</sup>J<sub>CF</sub> = 241.9 Hz). <sup>11</sup>B NMR (C<sub>6</sub>D<sub>5</sub>Br, 96 MHz, 25 °C): δ -16.99 (s, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), 5.13 (s, br, BC<sub>5</sub>H<sub>5</sub>). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 282 MHz, 25 °C): δ -167.30 (dd, C<sub>6</sub>F<sub>5</sub>-*meta*, <sup>3</sup>J<sub>FF</sub> = 28.2 Hz), -163.4 (t, C<sub>6</sub>F<sub>5</sub>-*para*, <sup>3</sup>J<sub>FF</sub> = 28.2 Hz), -133.00 (s, br, C<sub>6</sub>F<sub>5</sub>-*ortho*). ESI-MS<sub>pos</sub>: m/z: 198 [**2b** - Py]<sup>+</sup>, 156 [**2b** - Py, - C(CH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. ESI-MS<sub>neg</sub>: m/z: 679 [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>.