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# **Electronic Supplementary Information**

# Planarized *B*,*N*-Phenylated Dibenzoazaborine with a Carbazole Substructure: Electronic Impact of the Structural Constraint

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#### 1. Experimental Details

General Procedures. Melting points (mp) or decomposition temperatures were determined with a Yanaco MP-S3 instrument.  ${}^{1}H$ ,  ${}^{13}C{}^{1}H$ , and  ${}^{11}B{}^{1}H$  NMR spectra were recorded with a JEOL AL-400 spectrometer in CDCl<sub>3</sub> and acetone- $d_6$  (400 MHz for <sup>1</sup>H, 100 MHz for <sup>13</sup>C, and 128 MHz for <sup>11</sup>B).  $^{13}C{^{1}H}$  and  $^{11}B{^{1}H}$  NMR spectra were also measured with a JEOL A-400 spectrometer in CDCl<sub>3</sub> (100 MHz for <sup>13</sup>C and 128 MHz for <sup>11</sup>B). The chemical shifts in <sup>1</sup>H NMR spectra are reported in  $\delta$ ppm using the residual proton of the solvents,  $\delta$ 7.26 in CDCl<sub>3</sub> and  $\delta$ 2.05 in acetone- $d_6$ , as an internal standard and those in  ${}^{13}C$  NMR spectra are reported using the solvent signals of CDCl<sub>3</sub> ( $\delta$  77.16), and acetone- $d_6$  ( $\delta$  29.84) as an internal standard. The chemical shifts in <sup>11</sup>B NMR spectra are reported using BF<sub>3</sub>·OEt<sub>2</sub> ( $\delta$  0.00) as an external standard. Mass spectra were measured with a Bruker micrOTOF Focus spectrometry system with the ionization method of APCI. Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thickness of silica gel 60F<sub>254</sub> (Merck). Column chromatography was performed using PSQ100B or PSQ60B (Fuji Silvsia Chemicals). Recycling preparative gel permeation chromatography (GPC) was performed using LC-918 equipped with polystyrene gel columns (JAIGEL 1H and 2H, Japan Analytical Industry) using chloroform as an eluent. Anhydrous THF, Et<sub>2</sub>O, toluene, and CH<sub>2</sub>Cl<sub>2</sub> were purchased from Kanto Chemicals or FUJIFILM Wako Pure Chemical Corporation, and further purified by Glass Contour 2-Bromo-1,3-di(propen-2-yl)benzene,1 dimethyl Solvent Systems. [2,6-di(propen-2yl)phenyl]boronate,<sup>2</sup> dimethyl (2,4,6-trimethylphenyl)boronate,<sup>3</sup> and compound 5<sup>4</sup> were prepared according to the literature methods. All reactions were carried out under a nitrogen atmosphere.

Scheme S1



**Bis(2-bromophenyl)phenylamine (S1).** A mixture of bis(2-bromophenyl)amine (2.17 g, 6.64 mmol), iodobenzene (10.9 g, 53.4 mmol), copper(I) iodide (630 mg, 3.31 mmol), and potassium carbonate (9.17 g, 66.4 mmol) was heated at 200 °C for 23 h. After cooling to room temperature, CH<sub>2</sub>Cl<sub>2</sub> was added to the mixture, which was then filtered through a pad of Celite<sup>®</sup> using CH<sub>2</sub>Cl<sub>2</sub> as an eluent. After water was added to the filtrate, the organic layer was separated and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The combined organic layer was washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated under a reduced pressure. The crude product was subjected to silica gel column chromatography (hexane,  $R_f = 0.11$ ) and further purified by recrystallization from hexane to give 1.82 g (4.50 mmol) of **S1** in 68% yield as white solids: mp 98.0–99.0 °C; <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>)  $\delta$  6.64–6.67 (m, 2H), 6.93–6.98 (m, 1H), 7.12–7.18 (m, 4H), 7.21-7.25 (m, 2H), 7.38 (td, *J*<sub>HH</sub> = 8.0 Hz, 1.2 Hz, 2H), 7.68 (dd, *J*<sub>HH</sub> = 8.0 Hz, 1.2 Hz, 2H); <sup>13</sup>C NMR (100 MHz, acetone-*d*<sub>6</sub>)  $\delta$  121.6, 122.57, 122.60, 127.6, 129.6, 129.9, 130.4, 135.4, 146.4, 148.4; HRMS (APCI) *m/z* calcd for C<sub>18</sub>H<sub>13</sub><sup>79</sup>Br<sub>2</sub>N[*M*]<sup>+</sup> 400.9409, found: 400.9414.

B-(2,4,6-Trimethylphenyl)-N-phenyl-5,10-dihydro-dibenzo-1,4-azaborine (2). To a solution of bis(2-bromophenyl)phenylamine S1 (408 mg, 1.01 mmol) in anhydrous Et<sub>2</sub>O (25 mL) was added t-BuLi (1.53 M in pentane, 2.90 mL, 4.44 mmol) dropwise at -78 °C. After stirring at 0 °C for 3 h, a solution of dimethyl (2,4,6-trimethylphenyl)boronate (219 mg, 1.14 mmol) in anhydrous Et<sub>2</sub>O (3.0 mL) was added to the mixture at the same temperature. The mixture was warmed to room temperature and stirred at reflux for 13 h. After a saturated aqueous solution of NH<sub>4</sub>Cl was added, the organic layer was separated and the aqueous laver was extracted with Et<sub>2</sub>O three times. The combined organic laver was washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated under a reduced pressure. The crude product was subjected to silica gel column chromatography (hexane/CH<sub>2</sub>Cl<sub>2</sub> 5/1,  $R_f = 0.37$ ) and further purified by recrystallization from hexane to give 295 mg (0.790 mmol) of 2 in 78% yield as white solids: mp. 233.5-234.5 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.04 (s, 6H), 2.42 (s, 3H), 6.84 (d,  $J_{HH} = 8.8$  Hz, 2H), 6.98 (s, 2H), 7.10 (t,  $J_{HH} = 7.2$  Hz, 2H), 7.42 (d,  $J_{HH} = 8.0$  Hz, 2H), 7.48–7.52 (m, 2H), 7.64 (t,  $J_{HH}$  = 7.2 Hz, 1H), 7.71–7.74 (m, 2H), 7.88 (dd,  $J_{HH}$  = 7.4 Hz, 1.2 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ21.5, 23.4, 117.1, 119.8, 127.0, 129.0, 130.5, 131.1, 132.9, 136.5, 137.1, 139.5, 141.8, 146.8, two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  54.0; HRMS (APCI) m/z calcd for C<sub>27</sub>H<sub>24</sub><sup>11</sup>BN[*M*]<sup>+</sup> 373.1996, found: 373.1995.

B-[2,6-di(propen-2yl)phenyl]-N-phenyl-5,10-dihydro-dibenzo-1,4-azaborine (S2). To a solution of S1 (811 mg, 2.01 mmol) in anhydrous  $Et_2O$  (50 mL) was added *t*-BuLi (1.53 M in pentane, 5.80 mL, 8.87 mmol) dropwise at -78 °C. After stirring at 0 °C for 2 h, a solution of dimethyl [2,6di(propen-2-yl)phenyl]boronate (541 mg, 2.35 mmol) in anhydrous Et<sub>2</sub>O (5.0 mL) was added to the mixture at the same temperature. The mixture was warmed to room temperature and stirred at reflux for 33 h. After a saturated aqueous solution of NH<sub>4</sub>Cl was added, the organic layer was separated and the aqueous layer was extracted with Et<sub>2</sub>O three times. The combined organic layer was washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated under a reduced pressure. The crude product was subjected to silica gel column chromatography (hexane/CH<sub>2</sub>Cl<sub>2</sub> 10/3,  $R_f = 0.43$ ) and further purified by preparative GPC (CHCl<sub>3</sub>) to give 529 mg (1.29 mmol) of **S2** in 64% yield as white solids: mp. 199.0–200.0 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.89 (s, 6H), 4.52 (s, 2H), 4.66 (s, 2H), 6.73 (d,  $J_{HH}$  = 8.8 Hz, 2H), 7.05 (t, *J*<sub>HH</sub> = 7.2 Hz, 2H), 7.34–7.45 (m, 7H), 7.62 (t, *J*<sub>HH</sub> = 7.2 Hz, 1H), 7.70 (t, *J*<sub>HH</sub> = 7.2 Hz, 2H), 7.89 (d,  $J_{HH}$  = 7.2 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  24.7, 116.7, 117.2, 119.4, 125.5, 126.9, 128.9, 130.7, 131.0, 132.1, 137.2, 142.1, 146.3, 147.4, 147.7, two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  50.7; HRMS (APCI) *m/z* calcd for C<sub>30</sub>H<sub>26</sub><sup>11</sup>BN[*M*]<sup>+</sup> 411.2153, found: 411.2161.

**Compound 4.** A mixutre of **S2** (210 mg, 0.511 mmol) and Sc(OTf)<sub>3</sub> (255 mg, 0.517 mmol) in anhydrous 1,2-dichloroethane (125 mL) was stirred at reflux for 15 h. After water was added, the organic layer was separated and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The combined organic layer was washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated under a reduced pressure. The crude product was purified through silica gel column chromatography (hexane/CH<sub>2</sub>Cl<sub>2</sub> 3/1,  $R_f$ = 0.42) to give 91.3 mg (0.222 mmol) of **4** in 43% yield as pale yellow solids: mp. 265.0–266.0 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.83 (s, 12H), 6.58 (d,  $J_{HH}$  = 8.0 Hz, 2H), 7.40–7.44 (m, 4H), 7.56 (t,  $J_{HH}$  = 8.0 Hz, 2H), 7.62 (d,  $J_{HH}$  = 7.6 Hz, 1H), 7.66–7.72 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  35.0, 43.2, 113.0, 117.9, 123.9, 128.8, 130.6, 131.0, 131.8, 132.8, 142.1, 146.6, 154.8, 156.1, two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  39.2; HRMS (APCI) m/z calcd for C<sub>30</sub>H<sub>27</sub><sup>11</sup>BN[M+H]<sup>+</sup> 412.2231, found: 412.2226.

Scheme S2



**Compound 3.** To a solution of **5** (151 mg, 0.503 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (3.0 mL) was added BBr<sub>3</sub> (100  $\mu$ L, 0.26 g, 1.04 mmol) and stirred at room temperature for 5.5 h. After removal of volatiles under a reduced pressure at 50 °C, the resulting mixture was resolved into anhydrous toluene (3.0 mL). A THF solution of MesMgBr (0.51 M, 1.20 mL, 0.61 mmol) was then added to the mixture at 0°C. After stirring at room temperature for 25 h, a saturated aqueous solution of NH<sub>4</sub>Cl was added to the mixture. The organic layer was separated and the aqueous layer was extracted with Et<sub>2</sub>O three times. The combined organic layer was washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated under a reduced pressure. The crude product was purified through silica gel column chromatography (hexane/CH<sub>2</sub>Cl<sub>2</sub> 5/1,  $R_f = 0.41$ ) to give 158 mg (0.426 mmol) of 4 in 85% yield as pale yellow solids: mp. 138.0–139.0 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.02 (s, 6H), 2.43 (s, 3H), 6.99 (s, 2H), 7.33 (t,  $J_{HH} = 7.2$  Hz, 1H), 7.49 (t,  $J_{HH} = 7.3$  Hz, 1H), 7.56 (t,  $J_{HH} = 7.3$  Hz, 1H), 7.63–7.67 (m, 1H), 7.89– 7.93 (m, 1H), 7.99–8.06 (m, 2H), 8.28 (d, *J*<sub>HH</sub> = 8.0 Hz, 1H), 8.46 (dd, *J*<sub>HH</sub> = 7.4 Hz, 1.2 H<sub>Z</sub>, 1H), 8.54 (d,  $J_{HH}$  = 8.4 Hz, 1H), 8.73 (d,  $J_{HH}$  = 8.4 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  21.5, 23.5, 114.8, 115.9, 121.3, 121.9, 122.2, 122.8, 124.0, 125.2, 127.09, 127.11, 127.3, 134.0, 135.1, 137.0, 139.0, 139.3, 140.2, 142.1, 143.7, three signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  56.2; HRMS (APCI) m/zcalcd for  $C_{27}H_{22}^{11}BN[M]^+$  371.1840, found: 371.1833.

**Compound 7.** To a solution of **5** (1.20 g, 4.01 mmol) in anhydrous  $CH_2Cl_2$  (20 mL) was added BBr<sub>3</sub> (1.00 mL, 2.64 g, 10.5 mmol) at room temperature. After stirring at the same temperature for 4.5 h, the volatiles were removed under a reduced pressure at 50 °C. The resulting mixture was dissolved into anhydrous toluene (7 mL), followed by addition of a toluene solution of 2,6-di(propen-2-

yl)phenyllithium at 0 °C, which was prepared from 2-bromo-1,3-di(propen-2-yl)benzene (1.08 g, 4.56 mmol) and *n*-BuLi (1.6 M in hexane, 3.00 mL, 4.80 mmol) in toluene (11 mL).<sup>1</sup> After stirring at 50 °C for 20 h, a saturated aqueous solution of NH<sub>4</sub>Cl was added. The organic layer was separated and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The crude product was passed through a pad of silica gel using CH<sub>2</sub>Cl<sub>2</sub> as an eluent and purified by preparative GPC (CHCl<sub>3</sub>) to give 1.24 g (3.02 mmol) of 7 in 75% yield as yellow solids: mp. 188.0–189.0 °C; <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>)  $\delta$  1.92 (s, 6H), 4.41 (s, 2H), 4.55 (s, 2H), 7.36–7.53 (m, 5H), 7.60 (t, *J*<sub>HH</sub> = 7.6 Hz, 1H), 7.91–7.96 (m, 2H), 8.02 (d, *J*<sub>HH</sub> = 7.4 Hz, 1H), 8.41 (d, *J*<sub>HH</sub> = 8.0 Hz, 1H), 8.56 (d, *J*<sub>HH</sub> = 7.6 Hz, 1H), 8.68 (d, *J*<sub>HH</sub> = 8.0 Hz, 1H), 8.81 (d, *J*<sub>HH</sub> = 8.0 Hz, 1H), 13°C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  24.5, 114.6, 115.6, 117.9, 121.2, 121.6, 121.9, 122.4, 123.5, 124.1, 125.5, 127.00, 127.04, 127.3, 133.0, 134.3, 138.7, 140.0, 141.8, 143.2, 147.3, 147.7, three signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$ 54.2; HRMS (APCI) *m/z* calcd for C<sub>30</sub>H<sub>24</sub><sup>11</sup>BN[*M*]<sup>+</sup> 409.1996, found: 409.2016.

**Compound 1**. A mixture of 7 (208 mg, 0.508 mmol) and Sc(OTf)<sub>3</sub> (282 g, 0.572 mmol) in anhydrous 1,2-dichloroethane (250 mL) was stirred at 60 °C for 3 h. After a saturated aqueous solution of NaHCO<sub>3</sub> was added, the organic layer was separated and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under a reduced pressure. The crude product was purified through silica gel column chromatography (hexane/CH<sub>2</sub>Cl<sub>2</sub> 1/1,  $R_f$ = 0.68) and further purified by preparative GPC (CHCl<sub>3</sub>) to give 174 mg (0.426 mmol) of **1** in 84% yield as yellow solids: mp. 210.0–211.0 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.87 (s, 6H), 1.89 (s, 6H), 7.45 (t,  $J_{HH}$  = 7.6 Hz, 1H), 7.62 (t,  $J_{HH}$  = 7.6 Hz, 1H), 7.66–7.74 (m, 4H), 7.81 (d,  $J_{HH}$  = 8.0 Hz, 1H), 7.97 (t,  $J_{HH}$  = 8.0 Hz, 1H), 8.25 (d,  $J_{HH}$  = 7.6 Hz, 1H), 8.45–8.50 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  33.9, 34.5, 43.4, 44.5, 112.9, 114.3, 119.3, 119.8, 120.7, 121.3, 122.0, 123.8, 124.5, 124.9, 126.5, 127.0, 132.6, 133.8, 141.2, 141.9, 143.5, 154.5, 155.0, 156.7, 158.3, three signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  38.4; HRMS (APCI) *m/z* calcd for C<sub>30</sub>H<sub>24</sub><sup>11</sup>BN[*M*]<sup>+</sup> 409.1996, found: 409.1989.

Scheme S3



**Compound 8.** To a solution of **1** (408 mg, 0.996 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (6 mL) was added *N*bromosuccinimide (195 mg, 1.10 mmol) portionwise at 0 °C under air. After stirring for 22 h at room temperature, another amount of *N*-bromosuccinimide (41.4 mg, 0.233 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) were added to the mixture. After stirring for 28 h, water was added to the mixture, and the organic layer was separated. The aueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/ CH<sub>2</sub>Cl<sub>2</sub> 15/1, *R*<sub>f</sub> = 0.13) and a mixture containing **8** was further purified by preparative GPC (CHCl<sub>3</sub>) to give 258 mg (0.528 mmol) of **8** in 53% yield as yellow solids: mp. 297.5–298.5 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.87 (s, 6H), 1.88 (s, 6H), 7.67–7.74 (m, 5H), 7.82 (d, *J*<sub>HH</sub> = 8.0 Hz, 1H), 7.98 (t, *J*<sub>HH</sub> = 8.0 Hz, 1H), 8.33–8.42 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  33.8, 34.5, 43.5, 44.5, 112.8, 115.0, 115.5, 118.6, 119.7, 121.1, 123.9, 124.1, 124.6, 125.2, 128.91, 128.98, 132.8, 133.9, 139.8, 142.2, 143.2, 155.0, 155.4, 156.7, 158.5, three signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  42.0; HRMS (APCI) *m/z* calcd for C<sub>30</sub>H<sub>23</sub><sup>11</sup>B<sup>79</sup>BrN[*M*]<sup>+</sup> 487.1101, found; 487.1120.

**Compound 9.** A mixture of **8** (48.6 mg, 99.5 µmol), 4-*tert*-butylphenylboronic acid (20.2 mg, 113 µmol), tetrakis(triphenylphosphine)palladium(0) (20.1 mg, 17.4 µmol), 2.0 M aqueous solution of potassium carbonate (0.30 mL) in degassed toluene (2.0 mL) was stirred at 70 °C for 35.5 h. After cooling to room temperature, a saturated aqueous solution of NH<sub>4</sub>Cl was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with Et<sub>2</sub>O three times. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The crude product was passed through a pad of silica gel using CH<sub>2</sub>Cl<sub>2</sub> as an eluent and purified by preparative GPC to give 50.1 mg (92.5 µmol) of **9** in 93% yield as yellow solids: mp. 161.0–162.0 °C (decomp.) ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.42 (s, 9H), 1.88 (s, 6H), 1.90 (s, 6H), 7.56 (d, *J*<sub>HH</sub> = 8.4 Hz, 2H), 7.67–7.76 (m, 6H), 7.81–7.87 (m, 2H), 7.99 (t, *J*<sub>HH</sub> = 8.0 Hz, 1H), 8.45–8.53 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  31.6, 33.9, 34.5, 34.7, 43.4, 44.5, 112.9, 114.5, 119.4, 119.5, 119.9, 120.8,

123.9, 124.5, 125.0, 125.6, 126.0, 127.0, 127.6, 132.7, 133.8, 135.1, 138.5, 140.4, 142.3, 143.4, 150.2, 154.6, 155.0, 156.8, 158.3, three signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  62.1; HRMS (APCI) *m/z* calcd for C<sub>40</sub>H<sub>36</sub><sup>11</sup>BN[*M*]<sup>+</sup> 541.2935, found: 541.2945.

## 2. X-ray Crystallographic Analysis

Structural analysis of 1. Single crystal of 1 suitable for X-ray crystallographic analysis was obtained by vapor diffusion of hexane into a CHCl<sub>3</sub> solution of 1. Intensity data were collected at 123 K on a Rigaku Single Crystal X-ray diffractometer equipped with FR-X generator, Varimax optics, and PILATUS 200K photon counting detector with MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). Total 40864 reflections were measured at the maximum  $2\theta$  angle of 55°, of which 4915 were independent reflections ( $R_{int} = 0.0465$ ). The structure was solved by direct methods (SHELXL-2017/1)<sup>5</sup> and refined by full-matrix least-squares procedure on  $F^2$  for all reflections (SHELXL-2017/1)<sup>5</sup>. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: C<sub>30</sub>H<sub>24</sub>BN, FW = 409.31, crystal size 0.50 × 0.40 × 0.40 mm<sup>3</sup>, *orthorhombic*, *P*bca, a = 10.6779(2) Å, b = 10.8890(2) Å, c = 36.8908(7) Å, V = 4289.35(14) Å<sup>3</sup>, Z =8, D = 1.268 g cm<sup>-3</sup>. The refinement converged to  $R_1$  [ $I > 2\sigma(I)$ ] = 0.0416, w $R_2$  (all data) = 0.1119, GOF = 1.026.

Structural analysis of 4. Single crystal of 4 suitable for X-ray crystallographic analysis was obtained by vapor diffusion of hexane into a CHCl<sub>3</sub> solution of 4. Intensity data were collected at 123 K on a Rigaku Single Crystal X-ray diffractometer equipped with FR-X generator, Varimax optics, and PILATUS 200K photon counting detector with MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). Total 26152 reflections were measured at the maximum  $2\theta$  angle of 55°, of which 9162 were independent reflections ( $R_{int} = 0.0269$ ). The structure was solved by direct methods (SHELXL-2017/1)<sup>5</sup> and refined by full-matrix least-squares procedure on  $F^2$  for all reflections (SHELXL-2017/1)<sup>5</sup>. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: C<sub>31</sub>H<sub>27</sub>BCl<sub>3</sub>N, FW = 530.69, crystal size 0.20 × 0.15 × 0.15 mm<sup>3</sup>, *monoclinic*, Cc, a = 26.0787(16) Å, b = 18.5482(5) Å, c = 11.0330(5) Å,  $\beta = 103.001(6)^\circ$ , V =5200.0(4) Å<sup>3</sup>, Z = 8, D = 1.356 g cm<sup>-3</sup>. The refinement converged to  $R_1$  [ $I > 2\sigma(I)$ ] = 0.0450, w $R_2$  (all data) = 0.1112, GOF = 1.014.



**Figure S1.** Crystal structure of **1** (50% probability for thermal ellipsoids). Hydrogen atoms are omitted for clarity.



**Figure S2.** Crystal structure of **4** (50% probability for thermal ellipsoids). Hydrogen atoms are omitted for clarity.

	•	•	2
B1C1	1.494(5)	B2-C31	1.491(5)
B1-C18	1.498(5)	B2-C48	1.493(5)
B1-C19	1.516(5)	B2-C49	1.518(5)
C6-N1	1.408(4)	C36–N2	1.406(5)
N1-C7	1.443(4)	N2-C37	1.443(5)
N1-C13	1.402(4)	N2-C43	1.406(4)
C1-B1-C18	118.4(3)	C31-B2-C48	119.0(3)
C1-B1-C19	121.0(3)	C31-B2-C49	120.6(3)
C18-B1-C19	120.6(3)	C48-B2-C49	120.4(3)

Table S1 Selected Bond Lengths (Å) and Angles (°) in the Crystal Structure of 4

## 3. Cyclic Voltammetry

*Methods.* Cyclic voltammetry (CV) was performed on an ALS/chi-617A electrochemical analyzer. The CV cell was consisted of a glassy carbon electrode, a Pt wire counter electrode, and an Ag/AgNO<sub>3</sub> reference electrode. The measurements were carried out under an argon atmosphere using a THF or CH<sub>2</sub>Cl<sub>2</sub> solution of sample with a concentration of 1 mM and 0.1 M tetrabutylammonium hexafluorophosphate (n-Bu<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup>) as a supporting electrolyte with a scan rate of 100 mV s<sup>-1</sup>. The potentials were calibrated with ferrocene as an internal standard.



**Figure S3.** Cyclic voltammograms of 1–4 and 9 at a scan rate of 100 mV s<sup>-1</sup> in THF (reduction) and in CH<sub>2</sub>Cl<sub>2</sub> (oxidation).

## 4. Photophysical Properties

*Methods.* UV-vis absorption and fluorescence spectra were measured with a Shimadzu UV-3600 Plus spectrometer and a JASCO FP-8500 spectrofluorometer, respectively, using dilute sample solutions in a 1 cm square quartz cuvette. Absolute Fluorescence quantum yields were determined with a Hamamatsu Photonics C-9920-02 calibrated integrating sphere system. Time resolved fluorescence spectra were measured with a Hamamatsu picosecond fluorescence measurement system C4780.

Compound	${\cal P}_{ m F}{}^a$	$\tau$ [ns]	$k_{\rm r}  [{ m s}^{-1}]^b$	$k_{ m nr}  [ m s^{-1}]^c$
1	0.82	5.5	$1.5 \times 10^{8}$	$3.3  imes 10^7$
2	$0.96^{d}$	7.7	$1.2 \times 10^{8}$	$5.2 \times 10^{6}$
3	0.72	7.3	$9.9  imes 10^7$	$3.9 \times 10^{7}$
4	0.95	6.2	$1.5  imes 10^8$	$8.0 imes10^6$

Table S2 Fluorescence Quantum Yields, Lifetimes, and Decay Rate Constants for 1-4 in THF

<sup>*a*</sup> Absolute fluorescence quantum yields determined by a calibrated integrating sphere system within  $\pm 3\%$  error.  $\lambda_{ex} = 380$  nm. <sup>*b*</sup> Radiative decay rate constant. <sup>*c*</sup> Nonradiative decay rate constant. <sup>*d*</sup>  $\lambda_{ex} = 360$  nm.

#### 5. Chemical Oxidation

*Methods.* In a Schlenk flask equipped with J-Young stopcock, to a dilute solution of **9** in dried and degassed  $CH_2Cl_2$  (~10<sup>-4</sup> M) was added an excess amount of nitrosonium hexafluoroantimonate under an argon atmosphere. The thus generated radical cation was directly employed for the UV-vis-NIR absorption measurement. UV-vis-NIR absorption spectra were recorded with a Shimadzu UV-3600 Plus spectrometer in a 1 mm-thickness quartz cuvette equipped with J-Young stopcock.  $CH_2Cl_2$  was distilled over calcium hydride and degassed by freeze-pump-thaw cycles prior to use.

#### 6. Theoretical Calculations

*Computational method.* Theoretical calculations were conducted using the Gaussian 16 program.<sup>6</sup> TD-DFT calculations of **1**–**4** and **9** were performed at the B3LYP/6-31G(d) level for the optimized geometries obtained at the same level. TD-DFT calculation of  $1^{++}$  and  $9^{++}$  were carried out at the UB3LYP/6-31+G(d) level including the effect of solvents by PCM model. Nucleus independent chemical shift (NICS) calculations were carried out at the B3LYP/6-31G(d) level for the optimized structures of **1**–**4** at the B3LYP/6-31G(d). The Cartesian coordinates are listed in Tables S4–S10.

In order to elucidate the effect of the structural constraint around the boron atom, the difference between **2** and *B*,*N*-phenyl-substituted dibenzoazaborine **S3** was theoretically compared according to the litelature method.<sup>2,7</sup> The result is summarized in Figure S9, and **S3**' represents a model compound where the alignment of the *B*-phenyl group changed from orthogonal (**S3**) to parallel relative to the dibenzoazaborin scaffold.



**Figure S5.** The NICS(1) values for the optimized structures of **1**–**4** calculated at the B3LYP/6-31G(d) level. Chemical shifts are given in ppm.



**Figure S6.** Kohn–Sham molecular orbitals of **9** in the neutral state, calculated at the B3LYP/6-31G(d) level.



**Figure S7.** Spin density distributions of  $1^{++}$  and  $9^{++}$  in CH<sub>2</sub>Cl<sub>2</sub> calculated at the UB3LYP/6-31+G(d) level.



Figure S8. Kohn–Sham molecular orbitals of  $9^+$  in CH<sub>2</sub>Cl<sub>2</sub> calculated at the UB3LYP/6-31+G(d) level.



**Figure S9.** Energy diagram and Kohn–Sham HOMOs and LUMOs for **S3**, **S3**', and **4** at the B3LYP/6-31G(d) level of theory. The results of TD-DFT calculations are also shown.

excited state	transition energy [eV] <sup>a</sup>	main CI coefficient	$f^{b}$
		$0.84724$ : HOMO( $\beta$ ) $\rightarrow$ SOMO( $\beta$ )	
1	0.69 (1793)	0.36609: HOMO–1( $\beta$ ) $\rightarrow$ SOMO( $\beta$ )	0.0463
		$0.34731$ : HOMO $-2(\beta) \rightarrow \text{SOMO}(\beta)$	
r	1 12 (1105)	$-0.44580$ : HOMO( $\beta$ ) $\rightarrow$ SOMO( $\beta$ )	0 2021
2	1.12 (1105)	0.86644: HOMO–1( $\beta$ ) $\rightarrow$ SOMO( $\beta$ )	0.3921
		$-0.26227$ : HOMO( $\beta$ ) $\rightarrow$ SOMO( $\beta$ )	
3	1.22 (1020)	$-0.28454$ : HOMO $-1(\beta) \rightarrow \text{SOMO}(\beta)$	0.1359
		0.91667: HOMO– $2(\beta) \rightarrow \text{SOMO}(\beta)$	

**Table S3** Excited Energies of  $9^{+}$  in CH<sub>2</sub>Cl<sub>2</sub> calculated at the UB3LYP/6-31+G(d) level.

<sup>a</sup> Corresponding wavelength (nm) is shown in parenthesis. <sup>b</sup> Oscillator strength.

Table S4 Cartesian Coordinates of 1 Calculated at the B3LYP/6-31G(d) Level

atom	x	у	Ζ	atom	x	у	Ζ
В	-0.00075298	0.94979596	0.00000000	Н	-0.01427291	5.19606911	-2.14294250
С	-1.29508231	0.12581103	0.00000000	С	-0.00418643	3.25721491	-1.21404934
С	-2.57434558	0.73220746	0.00000000	Ν	0.00107003	-1.95927743	0.00000000
Н	-2.6153593	1.8183962	0.00000000	С	-0.0071188	2.52804468	-2.54220084
С	-3.74595566	-0.00353052	0.00000000	Н	0.8735553	1.88201238	-2.64853783
Н	-4.71425773	0.48884166	0.00000000	Н	-0.00895502	3.23017338	-3.38248177
С	-3.66091827	-1.40462584	0.00000000	Н	-0.88778466	1.88144044	-2.64499791
Н	-4.56798492	-2.0042343	0.00000000	С	-0.0071188	2.52804468	2.54220084
С	-2.43405661	-2.04797868	0.00000000	Н	0.8735553	1.88201238	2.64853783
Н	-2.40428332	-3.13016306	0.00000000	Н	-0.88778466	1.88144044	2.64499791
С	-1.2351216	-1.29621204	0.00000000	Н	-0.00895502	3.23017338	3.38248177
С	1.29463246	0.1274376	0.00000000	С	0.02135982	6.88863755	0.00000000
С	1.23647811	-1.29467103	0.00000000	Н	1.05156777	7.27061356	0.00000000
С	2.43639841	-2.04488822	0.00000000	Н	-0.47482708	7.29955046	0.88621982
Н	2.40804433	-3.12709921	0.00000000	Н	-0.47482708	7.29955046	-0.88621982
С	3.66243337	-1.39995527	0.00000000	С	0.00186383	-3.40246962	0.00000000
Н	4.57027763	-1.99838592	0.00000000	С	0.00218748	-4.09854939	-1.21142549
С	3.74566687	0.001243	0.00000000	Н	0.00187893	-3.54189499	-2.14382062
Н	4.71334396	0.49484918	0.00000000	С	0.00292746	-5.49428032	-1.20913132
С	2.57311176	0.73546339	0.00000000	Н	0.00320014	-6.03432438	-2.15182439
Н	2.61269152	1.82170051	0.00000000	С	0.0033118	-6.19322022	0.00000000
С	-0.00138352	2.53296257	0.00000000	Н	0.00388328	-7.27967498	0.00000000
С	-0.00418643	3.25721491	1.21404934	С	0.00292746	-5.49428032	1.20913132
С	-0.00841734	4.65617671	1.19701650	Н	0.00320014	-6.03432438	2.15182439
Н	-0.01427291	5.19606911	2.14294250	С	0.00218748	-4.09854939	1.21142549
С	-0.00705063	5.37741999	0.00000000	Н	0.00187893	-3.54189499	2.14382062
С	-0.00841734	4.65617671	-1.19701650				

 Table S5 Cartesian Coordinates of 2 Calculated at the B3LYP/6-31G(d) Level

atom	x	у	Z	atom	x	у	Z
В	-0.92166434	0.05955952	-0.04002753	Н	-5.01001338	-0.46021955	2.32058841
С	-0.21868126	1.44162036	-0.02818941	С	-3.13993662	-0.21136398	1.29069248
С	-0.97698328	2.63398952	-0.04849184	Ν	1.98689936	0.40226811	-0.03333841
Н	-2.0581875	2.54333208	0.01392351	С	-2.34032542	-0.15782716	2.57643396
С	-0.3968621	3.88798145	-0.16480397	Н	-2.98901198	-0.24873557	3.45376243
Н	-1.00927996	4.78498259	-0.17730402	Н	-1.78586107	0.78479276	2.66781679
С	0.99316511	3.97554574	-0.30183558	Н	-1.59987078	-0.96656373	2.62459502
Н	1.46789036	4.94304618	-0.44429103	С	-2.62549257	-0.06075446	-2.49979073
С	1.78684236	2.83598503	-0.27518311	Н	-1.87179399	-0.84331853	-2.65282854
Н	2.84788649	2.937053	-0.44593976	Н	-2.11245125	0.90118168	-2.62663639
С	1.20347829	1.56779816	-0.09692853	Н	-3.36603405	-0.15004436	-3.30127949
С	0.03498239	-1.13667885	-0.16421911	С	-6.81201871	-0.58017791	0.27198172
С	1.41028536	-0.86155125	-0.13112117	Н	-7.11396053	-1.13786778	1.16533872
С	2.41465551	-1.85331893	-0.16419416	Н	-7.21288292	-1.10186779	-0.60403395
С	2.03204813	-3.18748697	-0.27402962	Н	-7.30693248	0.39954999	0.31962446
Н	2.7783017	-3.97719166	-0.31025833	С	3.39226241	0.22611025	0.08242659
С	0.66611661	-3.50498027	-0.32805739	С	4.42076731	1.13501998	0.34993352
Н	0.36482987	-4.54571064	-0.40816472	Н	4.23500303	2.1826163	0.53842973
С	-0.30465191	-2.50474188	-0.26462442	С	5.72927767	0.65391949	0.42974009
Н	-1.35712474	-2.7758908	-0.28631447	Н	6.53135548	1.35708873	0.63595228

С	-2.49062832	-0.10453336	0.03960529	С	6.02448412	-0.70472328	0.26407717
С	-3.27461758	-0.16941521	-1.134935	Н	7.0533699	-1.04680589	0.32724469
С	-4.66096484	-0.33347083	-1.04268901	С	4.9976771	-1.61960933	0.04605926
Н	-5.24862995	-0.38414853	-1.95820542	Н	5.21263225	-2.68077399	-0.04719418
С	-5.30977346	-0.43538239	0.19088749	С	3.68117057	-1.1613609	-0.03241801
С	-4.52781152	-0.37528948	1.34778696				

Table S6 Cartesian Coordinates of 3 Calculated at the B3LYP/6-31G(d) Level

atom	x	у	Z	atom	x	у	Z
В	-0.00000047	-0.78926008	0.00000000	С	-2.59630012	-2.25466033	0.00000000
С	-1.29493948	-0.01933395	0.00000000	С	3.37994886	-2.69516778	1.26885710
С	-1.24528757	1.39887822	0.00000000	Н	3.50837786	-3.78173367	1.29700002
С	1.24515936	1.39894332	0.00000000	Н	2.84478147	-2.39403155	2.17565819
С	1.29489568	-0.01926489	0.00000000	Н	4.37531365	-2.2406877	1.29650580
С	-2.44946181	2.12960148	0.00000000	С	3.37994886	-2.69516778	-1.26885710
Н	-2.45211374	3.21249833	0.00000000	Н	3.50837786	-3.78173367	-1.29700002
С	-3.65361818	1.43769371	0.00000000	Н	4.37531365	-2.2406877	-1.29650580
Н	-4.58173895	2.00444378	0.00000000	Н	2.84478147	-2.39403155	-2.17565819
Н	-4.68152065	-0.44420911	0.00000000	С	-3.37988301	-2.6952843	1.26885658
С	-3.70904961	0.03861473	0.00000000	Н	-2.84468382	-2.39420705	2.17565845
С	-2.5293716	-0.70804102	0.00000000	Н	-3.50839186	-3.78183846	1.29697527
С	2.44926738	2.12975352	0.00000000	Н	-4.37521589	-2.24072915	1.29652628
Н	2.45183296	3.21265513	0.00000000	С	-3.37988301	-2.6952843	-1.26885658
С	3.65347139	1.43792565	0.00000000	Н	-3.50839186	-3.78183846	-1.29697527
Н	4.58154903	2.00474621	0.00000000	Н	-2.84468382	-2.39420705	-2.17565845
С	3.70899565	0.03885169	0.00000000	Н	-4.37521589	-2.24072915	-1.29652628
Н	4.68149895	-0.44390238	0.00000000	Ν	-0.00007423	2.05899629	0.00000000
С	2.529367	-0.70789544	0.00000000	С	-0.00006206	3.50015835	0.00000000
С	0.00004225	-2.30970984	0.00000000	С	-0.00002944	4.19761837	-1.21105908
С	1.23508216	-2.99454433	0.00000000	Н	-0.00003549	3.64097565	-2.14349090
С	1.21462209	-4.39460471	0.00000000	С	-0.00000451	5.59340114	-1.20904483
Н	2.13703928	-4.96847958	0.00000000	Н	0.00001028	6.13338112	-2.15184417
С	0.00013409	-5.08032604	0.00000000	С	0.00000293	6.29245789	0.00000000
Н	0.00017045	-6.1678848	0.00000000	Н	0.00002435	7.37895525	0.00000000
С	-1.21439667	-4.39468087	0.00000000	С	-0.00000451	5.59340114	1.20904483
Н	-2.13677144	-4.96861992	0.00000000	Н	0.00001028	6.13338112	2.15184417
С	-1.23495569	-2.99461636	0.00000000	С	-0.00002944	4.19761837	1.21105908
С	2.59637889	-2.25452483	0.00000000	Н	-0.00003549	3.64097565	2.14349090

Table S7 Cartesian Coordinates of 4 Calculated at the B3LYP/6-31G(d) Level

atom	x	у	Z	atom	x	У	Z
В	0.23817058	-1.07604993	-0.04750682	С	-1.58469538	-2.85737590	-0.02322870
С	0.23817058	-1.07604993	-0.04750682	С	-2.74358638	2.22014836	0.04198836
С	-0.26383997	1.45383689	-0.00893500	С	-1.79919982	-3.74504320	1.23455284
С	1.13842475	1.72335298	-0.07058672	Н	-2.82564071	-4.12166363	1.28449761
С	1.57481754	-0.69491905	-0.05732059	Н	-1.60193150	-3.17485233	2.14836982
Ν	2.03424515	0.62455466	-0.02842541	Н	-1.12681127	-4.60906272	1.22236383
С	1.56476123	3.05163442	-0.20437664	С	-1.87323366	-3.69665792	-1.29940249
Н	2.60387083	3.30831050	-0.34134762	Н	-2.90081636	-4.07369706	-1.30270692
С	0.61502209	4.07073531	-0.21269231	Н	-1.20040880	-4.55844235	-1.35975655
Н	0.95649960	5.09815298	-0.31199070	Н	-1.73067556	-3.09133156	-2.20069549
С	-0.75378699	3.81496003	-0.10922493	С	-3.28322505	2.89647180	1.33414695
Н	-1.44222308	4.65433903	-0.11527627	Н	-4.36982799	2.78842602	1.41038855
С	-1.21545485	2.49662884	-0.02627561	Н	-3.05172457	3.96637567	1.34631484
С	-0.09801978	-2.43757752	-0.05837928	Н	-2.83431574	2.44224819	2.22375184
С	0.95610123	-3.37204567	-0.09144963	С	-3.40385929	2.88251149	-1.20063373
Н	0.74721537	-4.43817012	-0.10471870	Н	-3.03312479	2.42505687	-2.12395294
С	2.30145658	-2.96917602	-0.09748634	Н	-3.18810342	3.95444574	-1.24311912
Н	3.08059085	-3.72746615	-0.11455542	Н	-4.49144502	2.76410468	-1.17777963
С	2.63601233	-1.60994670	-0.07198172	С	3.45238145	0.55661715	0.02935682
С	-2.24007136	-0.31991294	0.03202272	С	3.84759287	-0.81496363	-0.02370726
С	-2.61439492	-1.68614707	0.02812691	С	5.19943546	-1.16228248	0.01273590
С	-3.98290417	-1.97811271	0.06931064	Н	5.49346766	-2.20760920	-0.03187898
Н	-4.33804510	-3.00487332	0.06835030	С	6.15997916	-0.16001144	0.12063538
С	-4.92376898	-0.94677513	0.11384680	Н	7.21466651	-0.41802975	0.14966393
Н	-5.98203272	-1.19492436	0.14863251	С	5.76637521	1.18035226	0.21197951
С	-4.53726188	0.39436015	0.11096412	Η	6.51952165	1.95552733	0.32318202
Н	-5.30772851	1.15977050	0.14266801	С	4.42148456	1.55416632	0.17374220
С	-3.17889806	0.73088684	0.06487117	Н	4.16766678	2.59727681	0.29306848

atom	x	у	Z	atom	x	у	Z
В	3.43247453	0.0216147	0.00006377	Н	7.42976859	-2.33759753	1.08727767
С	2.31470044	1.01234739	0.08232424	Н	6.25775841	-3.65829452	1.13560714
С	3.07724204	-1.45002124	-0.01573059	Н	5.9538352	-2.17304016	2.0524436
С	1.711452	-1.86595541	0.04994695	С	6.2165763	-2.53946333	-1.41747824
С	1.02537731	0.49376791	0.09620161	Н	5.7131957	-2.11556703	-2.29277507
Ν	0.70576642	-0.86613978	0.04335366	Н	6.09857544	-3.62724125	-1.45232197
С	1.42654256	-3.23440559	0.15009496	Н	7.28497924	-2.31616952	-1.50002934
Н	0.4206206	-3.60147714	0.28368709	С	-0.71114457	-0.94472937	0.00488974
С	2.47726054	-4.14871715	0.12587501	С	-1.24787109	0.37519326	0.08709957
Н	2.24556959	-5.20839736	0.19961283	С	-2.62579885	0.58325668	0.07788392
С	3.81108401	-3.74889862	0.02093575	Н	-3.01783453	1.59197839	0.17316605
Н	4.58321113	-4.5117636	0.00116318	С	-3.50598962	-0.50144779	-0.03197808
С	4.13228258	-2.38799411	-0.03211942	С	-2.95471184	-1.79284064	-0.15147207
С	2.50715106	2.4010141	0.12101353	Н	-3.62145219	-2.63863633	-0.29118056
С	1.36177551	3.21924563	0.18477393	С	-1.58111411	-2.02922364	-0.13987656
Н	1.45851793	4.30080615	0.22059801	Н	-1.23094151	-3.0404201	-0.28801517
С	0.06579458	2.67799924	0.19430141	С	-4.97586754	-0.29820378	-0.03992887
Н	-0.78792639	3.3500881	0.2362836	С	-5.55887291	0.80875375	-0.67217401
С	-0.12525227	1.29224486	0.14163561	Н	-4.92608717	1.52140669	-1.19454803
С	4.85722026	0.52097172	-0.03374895	С	-6.94100249	1.00001081	-0.67518984
С	5.08714355	1.91845768	-0.00287466	Н	-7.33573861	1.87084267	-1.18713612
С	6.41725979	2.35247381	-0.04923333	С	-7.80980443	0.09485652	-0.05111582
Н	6.66346384	3.41046719	-0.02862981	С	-7.22048455	-1.01465597	0.57931177
С	7.45989894	1.42608833	-0.12433283	Н	-7.84716212	-1.74348638	1.08650327
Н	8.48613354	1.78398683	-0.16246359	С	-5.8431863	-1.20844406	0.58788394
С	7.2152622	0.05215317	-0.14798865	Н	-5.43028855	-2.06607046	1.11239243
Н	8.06090724	-0.62776115	-0.20338436	С	-9.33853162	0.27102542	-0.03436196
С	5.89994659	-0.42522839	-0.09816113	С	-10.00563172	-0.94816848	-0.7146551
С	3.94153816	2.97441757	0.08250576	Н	-9.68351037	-1.03918887	-1.7582652
С	5.62244794	-1.95199724	-0.10587526	Н	-11.09743562	-0.84195048	-0.70333947
С	4.15465343	3.81274292	1.37400425	Н	-9.75704103	-1.88539658	-0.20581159
Н	5.13759954	4.29428727	1.37695908	С	-9.7900646	1.54164923	-0.77913804
Н	4.08500923	3.17747893	2.26319416	Н	-9.49845253	1.52098283	-1.83540093
Н	3.39685214	4.59862671	1.45851273	Н	-9.3743756	2.44928342	-0.32685146
С	4.04881806	3.9053125	-1.15766037	Н	-10.88215526	1.62400153	-0.73991215
Н	5.02976579	4.38813323	-1.20817432	С	-9.82938474	0.37137183	1.42969491
Н	3.29008532	4.69382184	-1.12105458	Н	-9.37893203	1.23289112	1.93568952
Н	3.90233385	3.33648699	-2.08181966	Н	-9.57622783	-0.52414294	2.00679398
С	6.36064216	-2.56904981	1.11600351	Н	-10.91949829	0.49047823	1.45971504

Table S8 Cartesian Coordinates of 9 Calculated at the B3LYP/6-31G(d) Level

Table S9 Cartesian Coordinates of  $1^{+}$  in CH<sub>2</sub>Cl<sub>2</sub> Calculated at the UB3LYP/6-31+G(d) Level

atom	x	У	z	atom	x	У	z
В	-0.78413384	0.02131939	0.00610983	С	-1.61140364	-2.85823363	-0.03338308
С	0.22173865	-1.0921579	-0.05619138	С	-2.7170734	2.24221714	0.05042197
С	-0.25922487	1.44690227	-0.01840032	С	-1.8226625	-3.77646339	1.20531153
С	1.15017107	1.70229632	-0.09817381	Н	-2.85160382	-4.14517257	1.24668966
С	1.56165318	-0.7212709	-0.07152962	Н	-1.6153811	-3.23314775	2.13353103
Ν	2.02493376	0.60269664	-0.03695124	Н	-1.16177044	-4.6481077	1.1626586
С	1.6028391	3.02575137	-0.27647907	С	-1.91415135	-3.66859549	-1.3284849
Н	2.64064471	3.262541	-0.45085449	Н	-2.94567459	-4.03304254	-1.32630649
С	0.66883188	4.05802457	-0.28453721	Н	-1.25374664	-4.5382205	-1.40684079
Н	1.0165077	5.07811246	-0.41576295	Н	-1.77166471	-3.04730335	-2.21924607
С	-0.70121242	3.81275311	-0.146829	С	-3.23042702	2.94905201	1.34092959
Н	-1.3774801	4.66098112	-0.15238543	Н	-4.31706556	2.85607264	1.42341725
С	-1.19186273	2.4910016	-0.03771138	Н	-2.98917612	4.01650575	1.32966013
С	-0.12570555	-2.44634925	-0.07256108	Н	-2.77927385	2.50348255	2.23396132
С	0.93373751	-3.3820257	-0.12157328	С	-3.37978105	2.90323934	-1.19621364
Н	0.72632477	-4.44748213	-0.14433745	Н	-3.02427639	2.43367691	-2.11969088
С	2.29049468	-2.98813038	-0.13211743	Н	-3.15809125	3.97323058	-1.24682677
Н	3.06112859	-3.75283635	-0.16041494	Н	-4.4671214	2.79477981	-1.15464106
С	2.62336856	-1.63402271	-0.09632359	С	3.45061915	0.53542408	0.04235856
С	-2.24269637	-0.30844122	0.04623861	С	3.84400939	-0.83329028	-0.03355911
С	-2.62795529	-1.67855203	0.04662318	С	5.18658963	-1.17834393	0.01509424
С	-3.99773561	-1.9527337	0.11229357	Н	5.49428984	-2.21748405	-0.04835839
Н	-4.3714818	-2.97203682	0.11640383	С	6.1464029	-0.16092355	0.16541201
С	-4.92485212	-0.90450923	0.17490536	Н	7.19999682	-0.41964034	0.20449437
Н	-5.98451271	-1.14160796	0.22841436	С	5.75319161	1.17251612	0.29239812
С	-4.52928188	0.43769315	0.16455754	Н	6.49957109	1.94562867	0.44401872
Н	-5.29618302	1.20509104	0.20878287	С	4.40112466	1.54019511	0.24460841
С	-3.17008509	0.76103359	0.09293794	Н	4.14020611	2.57616705	0.40160668

atom	x	y	Z	atom	x	V	Z
В	3.42474504	0.02945688	0.00023796	С	6.36226790	-2.52159347	-1.17657967
С	3.06494981	-1.44656604	-0.04891797	Н	5.97343968	-2.08576004	-2.10336662
С	2.46153790	-4.14320733	-0.34677942	Н	6.26351983	-3.60913075	-1.24145855
С	1.70133206	-1.86512434	-0.16014517	Н	7.42962418	-2.29159009	-1.11327976
С	4.11698576	-2.37872561	-0.05935009	С	6.17232264	-2.60964964	1.35480626
С	3.79031329	-3.74291074	-0.18805683	Н	7.24037182	-2.39650896	1.45852293
С	1.41136367	-3.22567773	-0.34739440	Н	6.05150909	-3.69725375	1.33293360
Н	4.56124547	-4.50642111	-0.19048054	Н	5.65865065	-2.22496863	2.24262068
Н	0.41163541	-3.58690035	-0.53074947	С	4.00975140	3.87582039	1.31392404
Н	2.23501625	-5.19618993	-0.48612817	Н	4.98939924	4.35578746	1.39557739
С	2.30292455	1.02661903	-0.06926429	Н	3.84597895	3.27639488	2.21615005
С	0.04826208	2.69250434	-0.14982439	Н	3.25392150	4.66720226	1.28646731
С	2.49767494	2.41725222	-0.04980714	С	4.16566163	3.87617017	-1.21826657
С	1.01726428	0.51660404	-0.12323927	Н	4.11509425	3.27705988	-2.13403496
С	-0.13172917	1.30629664	-0.15115474	Н	5.14772437	4.35662353	-1.17780733
С	1.34950369	3.23331186	-0.10139808	Н	3.41087098	4.66651904	-1.28372297
Н	1.44062405	4.31531026	-0.09427860	С	-4.95040435	-0.34494186	0.01628210
Н	-0.80391263	3.36570629	-0.17572698	С	-7.78826739	0.04224761	0.06629140
С	4.83909573	0.52328535	0.07813813	С	-5.55111025	0.78828991	-0.58468462
С	7.43799783	1.41812427	0.26002789	С	-5.81174983	-1.27554794	0.64059040
С	5.88142369	-0.43221732	0.12622320	С	-7.18825956	-1.07965432	0.66919868
С	5.06876678	1.92637195	0.10654185	С	-6.92579981	0.96617559	-0.56457159
С	6.39826005	2.35365624	0.19831423	Н	-4.93873586	1.51756293	-1.10529779
С	7.19519088	0.04140227	0.22426930	Н	-5.40191423	-2.14501100	1.14430052
Н	6.65257719	3.40900574	0.22424866	Н	-7.79809363	-1.81638312	1.17893234
Н	8.04208424	-0.63664744	0.27062900	Н	-7.33734710	1.84183534	-1.05696648
Н	8.46319657	1.77273923	0.33416894	С	-9.30344960	0.28424653	0.07265155
N	0.69143134	-0.86590579	-0.11608429	С	-10.07536797	-0.82481476	0.81353101
С	-0.69951886	-0.95180018	-0.07255300	Н	-9.93394662	-1.80621456	0.34587874
С	-3.49995742	-0.53968549	-0.00741437	Н	-11.14727412	-0.59944664	0.78732279
С	-1.25355218	0.37510141	-0.13115320	Н	-9.77990725	-0.89754060	1.86677683
С	-1.56324822	-2.05680906	0.07517769	С	-9.81530810	0.33991188	-1.38950118
С	-2.92933823	-1.83720419	0.10425173	Н	-9.62102845	-0.60520773	-1.91008886
С	-2.61828315	0.57067107	-0.11785060	Н	-9.34190613	1.14557802	-1.96045278
Н	-1.20337659	-3.06778212	0.19196964	Н	-10.89752664	0.51644951	-1.39675170
Н	-3.57905374	-2.69989931	0.19483671	С	-9.60161590	1.63523300	0.77176767
Н	-3.01386058	1.57998388	-0.14544526	H	-9.12323792	2.47761897	0.26096148
C	5.60330342	-1.95526560	0.06067622	H	-9.25262197	1.62537720	1.8110/010
C	3.92851985	2.98837277	0.03801255	Н	-10.68276810	1.81852025	0.77745349

Table S10 Cartesian Coordinates of 9<sup>-+</sup> in CH<sub>2</sub>Cl<sub>2</sub> Calculated at the UB3LYP/6-31+G(d) Level

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# 8. NMR Spectra

Figure S10. <sup>1</sup>H NMR spectrum of S1 (400 MHz, acetone- $d_6$ ).



Figure S11. <sup>13</sup>C{H} NMR spectrum of S1 (100 MHz, acetone- $d_6$ ).



Figure S12. <sup>1</sup>H NMR spectrum of 2 (400 MHz, CDCl<sub>3</sub>).



Figure S13.  $^{13}C{H}$  NMR spectrum of 2 (100 MHz, CDCl<sub>3</sub>).



Figure S14. <sup>11</sup>B{H} NMR spectrum of 2 (128 MHz, CDCl<sub>3</sub>).



Figure S15. <sup>1</sup>H NMR spectrum of S2 (400 MHz, CDCl<sub>3</sub>).



Figure S16. <sup>13</sup>C{H} NMR spectrum of S2 (100 MHz, CDCl<sub>3</sub>).



Figure S17. <sup>11</sup>B{H} NMR spectrum of S2 (128 MHz, CDCl<sub>3</sub>).



Figure S18. <sup>1</sup>H NMR spectrum of 4 (400 MHz, CDCl<sub>3</sub>).



Figure S19.  $^{13}C\{H\}$  NMR spectrum of 4 (100 MHz, CDCl<sub>3</sub>).



Figure S20. <sup>11</sup>B{H} NMR spectrum of 4 (128 MHz, CDCl<sub>3</sub>).



Figure S21. <sup>1</sup>H NMR spectrum of 3 (400 MHz, CDCl<sub>3</sub>).



Figure S22.  $^{13}C{H}$  NMR spectrum of 3 (100 MHz, CDCl<sub>3</sub>).



**Figure S23.** <sup>11</sup>B{H} NMR spectrum of **3** (128 MHz, CDCl<sub>3</sub>).



Figure S24. <sup>1</sup>H NMR spectrum of 7 (400 MHz, acetone-*d*<sub>6</sub>).



Figure S25.  $^{13}C{H}$  NMR spectrum of 7 (100 MHz, CDCl<sub>3</sub>).



Figure S26. <sup>11</sup>B{H} NMR spectrum of 7 (128 MHz, CDCl<sub>3</sub>).



Figure S27. <sup>1</sup>H NMR spectrum of 1 (400 MHz, CDCl<sub>3</sub>).



Figure S28.  $^{13}C{H}$  NMR spectrum of 1 (100 MHz, CDCl<sub>3</sub>).



Figure S29.  $^{11}B{H}$  NMR spectrum of 1 (128 MHz, CDCl<sub>3</sub>).



Figure S30. <sup>1</sup>H NMR spectrum of 8 (400 MHz, CDCl<sub>3</sub>).



Figure S31.  $^{13}C{H}$  NMR spectrum of 8 (100 MHz, CDCl<sub>3</sub>).



**Figure S32.** <sup>11</sup>B{H} NMR spectrum of **8** (128 MHz, CDCl<sub>3</sub>).



Figure S33. <sup>1</sup>H NMR spectrum of 9 (400 MHz, CDCl<sub>3</sub>).



Figure S34.  $^{13}C{H}$  NMR spectrum of 9 (100 MHz, CDCl<sub>3</sub>).



Figure S35.  $^{11}B{H}$  NMR spectrum of 9 (128 MHz, CDCl<sub>3</sub>).