# Supporting Information for:

## "Intermolecular Insertion Reactions of Azides Into 9-

## Borafluorenes to Generate 9,10-B,N-Phenanthrenes"

Sam Yruegas, Jesse J. Martinez, and Caleb D. Martin\*

Baylor University, Department of Chemistry and Biochemistry, One Bear Place #97348, Waco,

TX 76798

E-mail: caleb\_d\_martin@baylor.edu

# Table of Contents

Experimental details.	S3
Multinuclear NMR spectra for <b>3Cl</b>	S13
Multinuclear NMR spectra for <b>8Cl</b>	S15
FT-IR spectrum of <b>8CI</b>	S20
Multinuclear NMR spectra for <b>9Ph</b>	S21
FT-IR spectrum of <b>9Ph</b>	S26
Multinuclear NMR spectra for <b>10Cl</b>	S27
FT-IR spectrum of <b>10Cl</b>	S32
Multinuclear NMR spectra for <b>10Ph</b>	S33
FT-IR spectrum of <b>10Ph</b>	S38
Multinuclear NMR spectra for <b>8Ph</b>	\$39
FT-IR spectrum of <b>8Ph</b>	S44
Gutmann-Beckett Studies	S45
UV-Vis and Fluorescence Studies	S54
X-ray crystallographic details	S56
References	S59

#### **EXPERIMENTAL SECTION**

General Considerations. All manipulations were performed under an inert atmosphere in a nitrogen-filled MBraun Unilab glove box. Solvents were purchased from commercial sources as anhydrous grade, dried further using a JC Meyer Solvent System with dual columns packed with solvent-appropriate drying agents and stored over molecular sieves. 9,9-dimethyl-9stannafluorene and **3Ph** were prepared according to the literature procedures.<sup>1</sup> 2'-2'dibromobiphenyl was purchased from Ark Pharm, boron trichloride in hexanes (1M) from Acros Organics, triethylphosphine oxide from Alfa Aesar, dichlorophenylborane from Beantown Chemicals, azidobenzene from Enamine, and 1-azidoadamantane and phenyllithium in dibutyl ether (1.8 M) from Sigma Aldrich, respectively. All reagents were used as received. CDCl<sub>3</sub> for NMR spectroscopy was purchased from Cambridge Isotope Laboratories and dried by stirring for 3 days over CaH<sub>2</sub>, distilled, and stored over 4 Å molecular sieves. Multinuclear NMR spectra were recorded on Bruker 400 or 600 MHz spectrometers. FT-IR spectra were recorded on a Bruker Alpha ATR FT-IR spectrometer on solid samples. High resolution mass spectra (HRMS) were collected at the University of Texas at Austin Mass Spectrometry Center on a Micromass Autospec Ultima spectrometer using CI. Melting points were measured with a Thomas Hoover Uni-melt capillary melting point apparatus and are uncorrected. UV-Vis spectra were recorded using an Agilent 8453 UV-Vis spectrophotometer. Fluorescence spectra were recorded on a Cary Eclipse fluorescence spectrophotometer with excitation at the absorbance  $\lambda_{max}$ . Solutions were prepared in a N<sub>2</sub> filled glovebox and measured in screw capped quartz cuvettes for both UV-Vis and fluorescence. Single crystal X-ray diffraction data were collected on a Bruker Apex II-CCD detector using Mo-K<sub>a</sub> radiation ( $\lambda$  = 0.71073 Å). Crystals were selected under paratone oil,

mounted on micromounts, and immediately placed in a cold stream of  $N_2$ . Structures were solved and refined using SHELXTL and figures produced using OLEX2.<sup>2,3</sup> Note: The following synthesis is adapted from the previous preparation of **3Ph** by Piers and coworkers.<sup>1</sup> In our hands, this route was higher yielding than the prior synthesis for **3CI** by going through the corresponding 9,9-dimethyl-9-stannafluorene, an air-stable intermediate, instead of the lithiation route which was found to be exceedingly sensitive.<sup>4</sup>



Synthesis of 3CI: A solution of 9,9-dimethyl-9-stannafluorene (2.56 g, 8.51 mmol) in toluene (50 mL) was cooled to 0°C upon which BCl<sub>3</sub> in hexanes (1 M, 8.5 mL, 8.51 mmol) was added dropwise over 10 min. The reaction mixture was then stirred for 14 h at 23°C. The volatiles were removed *in vacuo* to give an orange powder. The Me<sub>2</sub>SnCl<sub>2</sub> by-product was removed by sublimation (40°C, 0.2 Torr) and the resultant yellow residue was crystallized in *n*-pentane to give bright yellow crystals of **3CI**.

**Yield**: 1.24 g, 73%

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.55 (d, J = 12.0 Hz, 2H), 7.38-7.34 (m, 4H), 7.15 (td, J = 12.0, 6.0 Hz, 2H)

<sup>11</sup>B{<sup>1</sup>H} NMR (193 MHz, CDCl<sub>3</sub>): δ 63.8 (br)

The spectroscopic data matches the literature values.<sup>4,5</sup>



*vacuo*. The residue was washed with hexanes (3 x 2 mL) and dried *in vacuo* to give **8CI** as a yellow powder. Single crystals for X-ray diffraction studies were grown from a *n*-pentane solution of **8CI** by vapor diffusion into toluene.

**Yield**: 0.272 g, 74%

**m.p.** 92-94°C

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.54-8.41 (m, 2H), 8.39 (d, *J* = 8.0 Hz, 1H), 7.82 (td, *J* = 8.0, 1.2 Hz, 1H), 7.61-7.55 (m, 4H), 7.52-7.48 (m, 1H), 7.31-7.29 (m, 2H), 7.25-7.23 (m, 1H), 6.82-6.78 (m, 1H)

<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>): δ 143.00, 141.95, 139.08, 135.14, 132.32, 129.97, 129.21, 128.26, 127.86, 126.99, 124.19, 123.67, 122.32, 122.22, 118.90

<sup>11</sup>B{<sup>1</sup>H} NMR (193 MHz, CDCl<sub>3</sub>): δ 35.5 (br)

**FT-IR** (cm<sup>-1</sup>(ranked intensity)): 1591(12), 1481(7), 1444(9), 1363(8), 1281(15), 1259(3), 1170(11), 950(6), 752(1), 739(13), 721(4), 698(2), 598(5), 560(10), 429(14)

HRMS (CI<sup>+</sup>) for C<sub>18</sub>H<sub>13</sub>BCIN [*M*<sup>+</sup>], calcd: 289.0829; found 289.0829

**UV-Vis** (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  (329 nm):  $\epsilon$  = 11,100 Lmol<sup>-1</sup> cm<sup>-1</sup>, (318 nm):  $\epsilon$  = 7,700 Lmol<sup>-1</sup> cm<sup>-1</sup>; **Fluorescence** (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{em}$  352 nm; Stokes shift (CH<sub>2</sub>Cl<sub>2</sub>) 23 nm (2,000 cm<sup>-1</sup>).



Synthesis of **9Ph**: A solution of azidobenzene (0.145 g, 1.22 mmol) in toluene (1 mL) was added to a toluene solution (1 mL) of **3Ph** (0.293 g, 1.22 mmol) and stirred for 2 d at 23°C. The solvent was removed *in vacuo* to yield a yellow residue. The residue was washed with *n*-pentane (3 x 2 mL) and dried *in vacuo* 

to give **9Ph** as a yellow powder (the estimated purity by <sup>1</sup>H NMR 90%). Single crystals for X-ray diffraction studies were grown from a dichloromethane solution of **9Ph** by vapor diffusion into toluene.

Yield: 0.312 g, 71%

**m.p.** 120-121°C

<sup>1</sup>**H NMR** (600 MHz, C<sub>6</sub>D<sub>6</sub>): δ 8.31 (d, *J* = 12.0 Hz, 1H), 8.27 (d, *J* = 6.0 Hz, 1H), 7.71-7.68 (m, 2H), 7.52 (t, *J* = 6.0, 1H), 7.29 (t, *J* = 6.0, 1H), 7.24-7.19 (m, 6H), 7.16-7.15 (m, 2H), 7.09 (t, *J* = 6.0, 2H), 7.04-6.99 (m, 2H)

<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>): 148.24, 138.89, 138.74, 138.48, 137.63, 133.02, 131.90, 131.41, 130.91, 129.73, 129.22, 128.49, 127.92, 127.24, 126.92, 126.53, 124.09, 123.83, 123.34, 122.93, 122.15, 121.94, 119.01, 116.49

<sup>11</sup>B{<sup>1</sup>H} NMR (193 MHz, CDCl<sub>3</sub>): δ 36.9 (br)

**FT-IR** (cm<sup>-1</sup>(ranked intensity)): 1598(13), 1481(7), 1429(9), 1291(11), 1229(3), 1140(12), 1002(4), 771(8), 745(1), 718(5), 705(2), 685(6), 638(15), 564(14), 516(10)

**HRMS** (Cl<sup>+</sup>) for C<sub>24</sub>H<sub>18</sub>BN<sub>3</sub> [*M*<sup>+</sup>], calcd 359.1593; found 359.1597

**UV-Vis** (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  (319 nm):  $\epsilon$  = 24,300 Lmol<sup>-1</sup> cm<sup>-1</sup>;

**Fluorescence** (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{em}$  357 nm; Stokes shift (CH<sub>2</sub>Cl<sub>2</sub>) 38 nm (3,400 cm<sup>-1</sup>).



*vacuo* to give **10** as an off-white powder. Single crystals for X-ray diffraction studies were grown from a dichloromethane solution of **10Cl** by vapor diffusion into hexanes.

Yield: 0.028 g, 54%

**m.p.** 117-118°C

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.22 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 8.07 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.73-7.66 (m, 2H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.27-7.22 (m, 1H), 7.18 (m, 1H), 2.50 (s, 6H), 2.19 (s, 3H), 1.73 (q, *J* = 12.0 Hz, 6H)

<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>): δ 140.00, 139.33, 133.65, 132.05, 128.01, 126.49, 125.26, 124.75, 123.73, 121.79, 61.28, 43.14, 36.48, 30.92

<sup>11</sup>B{<sup>1</sup>H} NMR (193 MHz, CDCl<sub>3</sub>): δ 40.0 (br)

**FT-IR** (cm<sup>-1</sup>(ranked intensity)): 2905(4), 1597(9), 1478(11), 1441(14), 1333(15), 1304(6), 1230(2), 1176(12), 1137(13), 1065(7), 948(8), 888(10), 759(5), 741(1), 616(3)

HRMS (CI<sup>+</sup>) for C<sub>22</sub>H<sub>23</sub>BCIN [*M*<sup>+</sup>], calcd 347.1612; found 347.1608

**UV-Vis** (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  (328 nm):  $\epsilon$  = 3,700 Lmol<sup>-1</sup> cm<sup>-1</sup>; **Fluorescence** (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{em}$  353 nm; Stokes shift (CH<sub>2</sub>Cl<sub>2</sub>) 25 nm (2,200 cm<sup>-1</sup>). Synthesis of **10Ph**: A solution of 1-azidoadamantane (0.037 g, 0.21 mmol) in toluene (1 mL) was added to a toluene solution (1 mL) of **3Ph** (0.050 g, 0.21 mmol) in a pressure tube and heated for 5 d at 110°C, after which the solvent was removed *in vacuo*. The yellow residue was washed with acetonitrile (3 x 2 mL) and dried *in vacuo* to give **10Ph** as an off-white powder. Single crystals for X-ray diffraction studies were

grown from a dichloromethane solution of **10Ph** by vapor diffusion into hexanes.

Yield: 0.052 g, 64%

**m.p.** 178-179°C.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.26 (d, J = 12.0 Hz, 1H), 8.21 (d, J = 12.0 Hz, 1H), 8.06 (d, J = 6.0 Hz, 1H), 7.89 (d, J = 12.0 Hz, 1H), 7.65 (t, J = 6.0 Hz, 1H), 7.59 (d, J = 12.0 Hz, 2H), 7.43 (t, J = 6.0 Hz, 2H), 7.39-7.36 (m, 2H), 7.32 (t, J = 6.0 Hz, 1H), 7.22 (t, J = 6.0 Hz, 1H), 2.26 (s, 6H), 2.01 (s, 3H), 1.54 (q, J = 12.0 Hz, 6H);

<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>): δ 145.02, 141.06, 139.03, 137.10, 135.54, 132.60, 131.07, 130.40, 128.27, 127.32, 127.16, 125.92, 125.41, 124.67, 123.51, 121.63, 121.19, 61.74, 44.72, 36.38, 30.79;

<sup>11</sup>B{<sup>1</sup>H} NMR (193 MHz, CDCl<sub>3</sub>): δ 42.1 (br);

**FT-IR** (cm<sup>-1</sup>(ranked intensity)): 2903(3), 1596(10), 1482(6), 1427(8), 1305(12), 1257(2), 1062(5), 936(14), 906(9), 785(13), 745(1), 729(7), 704(4), 632(11), 580(15);

HRMS (CI<sup>+</sup>) for C<sub>28</sub>H<sub>28</sub>BN [*M*<sup>+</sup>], calcd 389.2314; found 389.2315

**UV-Vis** (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  (331 nm):  $\epsilon$  = 8,200 Lmol<sup>-1</sup> cm<sup>-1</sup>;

**Fluorescence** (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{em}$  357 nm; Stokes shift (CH<sub>2</sub>Cl<sub>2</sub>) 26 nm (2,200 cm<sup>-1</sup>).



the cold bath was removed and the solution warmed to 23°C and stirred 3 h. The volatiles were removed *in vacuo* and the resultant orange residue was washed with hexanes (3 x 10 mL), filtered, and dried *in vacuo* to give **8Ph** as a yellow powder. Single crystals for X-ray diffraction studies were grown from a dichloromethane solution of **8Ph** by vapor diffusion into toluene.

Yield: 0.248 g, 73%

**m.p** 176-178°C.

<sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>): δ 8.58-8.55 (m, 2H), 7.87 (d, *J* = 6.0 Hz, 1H), 7.78 (t, *J* = 6.0 Hz, 1H), 7.45 (t, *J* = 6.0 Hz, 1H), 7.33-7.30 (m, 4H), 7.25-7.24 (m, 3H), 7.18 (m, 3H), 7.13 (d, *J* = 6.0 Hz, 2H), 6.94-6.91 (m, 1H)

<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>): δ 144.29, 142.00, 138.89, 137.64, 133.02, 131.42, 129.73, 129.23, 127.92, 126.96, 126.93, 126.43, 124.22, 124.09, 121.98, 121.94, 119.01

<sup>11</sup>B{<sup>1</sup>H} NMR (193 MHz, CDCl<sub>3</sub>): δ 39.3 (br)

**FT-IR** (cm<sup>-1</sup>(ranked intensity)): 1594(8), 1552(13), 1483(5), 1427(10), 1352(7),1323(9), 1298(3), 1023(14), 751(2), 742(15), 724(4), 697(1), 653(11), 619(6), 577(12)

HRMS (CI<sup>+</sup>) for C<sub>24</sub>H<sub>18</sub>BN [*M*<sup>+</sup>], calcd 331.1532; found 331.1534

**UV-Vis** (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  (331 nm):  $\epsilon$  = 12,500 Lmol<sup>-1</sup> cm<sup>-1</sup>, (319 nm):  $\epsilon$  = 11,300 Lmol<sup>-1</sup> cm<sup>-1</sup>; **Fluorescence** (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{em}$  355 nm; Stokes shift (CH<sub>2</sub>Cl<sub>2</sub>) 24 nm (2,100 cm<sup>-1</sup>). Figure S-1: <sup>1</sup>H NMR spectrum of **3Cl** in CDCl<sub>3</sub>.



Figure S-2: <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of **3CI** in CDCl<sub>3</sub>.

















## Figure S-6: Expansion of ${}^{13}C{}^{1}H$ NMR spectrum of **8Cl** in CDCl<sub>3</sub> (aryl region).

Figure S-7: <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of **8CI** in CDCl<sub>3.</sub>





Figure S-8: FT-IR spectrum of **8CI**.

\*

Figure S-9: <sup>1</sup>H NMR spectrum of **9Ph** in  $C_6D_6$ .









Figure S-11: <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **9Ph** in CDCl<sub>3.</sub>



Figure S-12: Expansion of  ${}^{13}C{}^{1}H$  NMR spectrum of **9Ph** in CDCl<sub>3</sub> (aryl region).

151 150 149 148 147 146 145 144 143 142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116

Figure S-13: <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of **9Ph** in CDCl<sub>3.</sub>



Figure S-14: FT-IR spectrum of **9Ph**.













Figure S-17: <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **10Cl** in CDCl<sub>3</sub> (\*grease).

Figure S-18: Expansion of  ${}^{13}C{}^{1}H$  NMR spectrum of **10Cl** in CDCl<sub>3</sub> (aryl region).



150 149 148 147 146 145 144 143 142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116 115 114 113 112 111 11





Figure S-20: FT-IR spectrum of **10CI**.



Figure S-21: <sup>1</sup>H NMR spectrum of **10Ph** in  $CDCl_3$  (\*grease).









Figure S-23: <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **10Ph** in CDCl<sub>3</sub> (\*grease).



Figure S-24: Expansion of  ${}^{13}C{}^{1}H$  NMR spectrum of **10Ph** in CDCl<sub>3</sub> (aryl region).

Figure S-25:  ${}^{11}B{}^{1}H{}$  NMR spectrum of **10Ph** in CDCl<sub>3.</sub>

---42.13









Figure S-27: <sup>1</sup>H NMR spectrum of **8Ph** in CDCl<sub>3</sub> (\*CH<sub>2</sub>Cl<sub>2</sub>).













## Figure S-30: Expansion of ${}^{13}C{}^{1}H$ NMR spectrum of **8Ph** in CDCl<sub>3</sub> (aryl region).

.51 150 149 148 147 146 145 144 143 142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116 115 114





Figure S-32: FT-IR spectrum of **8Ph**.



#### **Gutmann-Beckett Studies**

For the Gutmann–Beckett studies, samples were prepared in a 1:1 stoichiometric ratio of Lewis acid/Et<sub>3</sub>PO. Subsequent <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy was done in  $C_6D_6$ . Samples were prepared in a glovebox under a nitrogen atmosphere. Single crystals for X-ray diffraction studies were grown from a dichloromethane solution of the adduct by vapor diffusion into hexanes.



<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.68 (d, J = 6.0 Hz, 2H), δ 7.25 (d, J = 6.0 Hz, 1H), 7.11-7.00 (m, 12H),
6.91-6.86 (m, 8H), 6.79 (t, J = 6.0 Hz, 2H, 1.72 (dq, J = 18.0, 6.0 Hz, 6H), 1.04 (dt, J = 18.0, 6.0 Hz, 9H)

<sup>31</sup>P{<sup>1</sup>H} NMR (243 MHz, C<sub>6</sub>D<sub>6</sub>): δ 76.6 (br)

<sup>11</sup>B{<sup>1</sup>H} NMR (193 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.4 (br)



<sup>1</sup>**H NMR** (600 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.84 (d, *J* = 6.0 Hz, 2H), 7.81 (d, *J* = 6.0 Hz, 2H), 7.67 (d, *J* = 6.0 Hz, 2H), 7.42-7.39 (m, 2H), 7.35-7.32 (m, 2H), 7.27-7.23 (m, 3H), 0.85-0.82 (m, 6H), 0.40-0.28 (m, 9H)

<sup>31</sup>P{<sup>1</sup>H} NMR (243 MHz, C<sub>6</sub>D<sub>6</sub>): δ 74.1 (br)

<sup>11</sup>B{<sup>1</sup>H} NMR (193 MHz, C<sub>6</sub>D<sub>6</sub>): δ 6.0 (br)

## Figure S-33: <sup>1</sup>H NMR spectrum of **1Ph'OPEt<sub>3</sub>** in $CDCl_3$ (\*CH<sub>2</sub>Cl<sub>2</sub>).





Figure S-34: Expansion of <sup>1</sup>H NMR spectrum of **1Ph'OPEt<sub>3</sub>** in CDCl<sub>3 (</sub>\*CH<sub>2</sub>Cl<sub>2</sub>, aryl region).

Figure S-35: <sup>31</sup>P NMR spectrum of **1Ph'OPEt<sub>3</sub>** in  $C_6D_6$ .

140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240



Figure S-36: <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of **1Ph'OPEt<sub>3</sub>** in C<sub>6</sub>D<sub>6</sub>.



Figure S-37: <sup>1</sup>H NMR spectrum of **3Ph'OPEt<sub>3</sub>** in  $C_6D_6$ .







Figure S-39: <sup>31</sup>P NMR spectrum of **3Ph<sup>•</sup>OPEt<sub>3</sub>** in  $C_6D_6$ .

140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240



Figure S-40: <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of **3Ph<sup>•</sup>OPEt<sub>3</sub>** in  $C_6D_6$ .



### **UV-Vis and Fluorescence Studies**

Figure S-41: Normalized absorption spectra of **8Cl**, **8Ph**, **9Ph**, **10Cl**, and **10Ph**, in CH<sub>2</sub>Cl<sub>2</sub> under an N<sub>2</sub> atmosphere (spectra have their respective  $\lambda_{max}$  listed above their respective peaks).



9Ph



Figure S-42: Normalized emission spectra of **8Cl**, **8Ph**, **9Ph**, **10Cl**, and **10Ph** in  $CH_2Cl_2$  under an  $N_2$  atmosphere (all emission spectra excited at their respective  $\lambda_{max}$  and correspondingly labeled).





### X-ray crystallographic details

	8Cl	9Ph	10Cl	10Ph	8Ph	1Ph'OPEt₃	3Ph <sup>.</sup> OPEt₃
CCDC	1819488	1819489	1819490	1819491	1819492	1819493	1819494
Empirical	C <sub>18</sub> H <sub>13</sub> BCIN	$C_{24}H_{18}BN_3$	$C_{22}H_{23}BCIN$	$C_{28}H_{28}BN$	$C_{24}H_{18}BN$	$C_{40}H_{40}BOP$	$C_{24}H_{28}BOP$
formula							
FW (g/mol)	289.55	359.22	347.67	389.32	331.20	578.50	374.24
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Tetragonal	Monoclinic	Monoclinic
Space group	P21/n	P-1	P21/c	P21/c	I41/a	P21/n	Pn
<i>a</i> (Å)	11.4311(11)	8.3238(12)	13.679(15)	15.8892(14)	26.7935(17)	9.0948(3)	9.8145(9)
<i>b</i> (Å)	7.5161(6)	9.5871(14)	12.5898(13)	12.4193(10)	26.7935(17)	36.1717(13)	15.5763(15)
<i>c</i> (Å)	17.3831(16)	11.8893(15)	10.2613(10)	11.0719(9)	9.9207(13)	10.2433(4)	13.7943(13)
lpha (deg)	90	83.315(4)	90	90	90	90	90
eta (deg)	101.691(3)	81.252(4)	97.732(3)	104.771(3)	90	110.991(2)	90.023(3)
$\gamma$ (deg)	90	76.743(5)	90	90	90	90	90
<i>V</i> (ų)	1462.5(2)	909.5(2)	1751.1(3)	2112.6(3)	7122.0(13)	3146.2(2)	2108.8(3)
Ζ	4	2	4	4	16	4	4
<i>D</i> <sub>c</sub> (mg m <sup>-3</sup> )	1.315	1.312	1.319	1.224	1.236	1.221	1.179
radiation, $\lambda$ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
temp (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
R1[I>2σI] <sup>a</sup>	0.0481	0.0640	0.0433	0.0499	0.0928	0.0445	0.0492
$wR2(F^2)^a$	0.1053	0.1861	0.1221	0.1109	0.2264	0.1197	0.1104
GOF ( <i>S</i> ) <sup><i>a</i></sup>	1.046	1.153	1.147	1.042	1.221	1.110	1.025

Table S-1: Crystallographic data for 8-10, 1Ph'OPEt<sub>3</sub>, and 3Ph'OPEt<sub>3</sub>.

 $^{a} R1(F[I > 2(I)]) = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|; wR2(F^{2} [all data]) = [w(F_{o}^{2} - F_{c}^{2})^{2}]^{1/2}; S(all data) = [w(F_{o}^{2} - F_{c}^{2})^{2}/(n - p)]^{1/2} (n = no. of data; p = no. of parameters varied; w = 1/[^{2}(F_{o}^{2}) + (aP)^{2} + bP]$  where  $P = (F_{o}^{2} + 2F_{c}^{2})/3$  and a and b are constants suggested by the refinement program.

Figure S-43: Solid-state structure of **8Ph**. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms have been omitted for clarity.



*Note*: Similar boron heterocycles bearing phenyl groups on boron and nitrogen atoms within the ring have shown disorder. Therefore, the bond distances and bond angles are not discussed in detail. However, the structure confirms the identity of **8Ph**. The disorder was modeled using EADP on both boron and nitrogen atoms.

Figure S-44: Solid-state structures of **1Ph'OPEt**<sub>3</sub> and **3Ph'OPEt**<sub>3</sub>. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms have been omitted for clarity.



#### References

1. Romero, P. E.; Piers, W. E.; Decker, S. A.; Chau, D.; Woo, T. K.; Parvez, M., Organometallics, **2003**, *22*, 1266.

2. Sheldrick, G. M. Acta Crystallogr. 2008, A64, 112.

3. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K, and Puschmann, H., J. Appl. Crystallogr., 2009, 42, 339.

4. Biswas, S.; Oppel, I. M.; Bettinger, H. F., Inorg. Chem., 2010, 49, 4499.

5. Müller, M.; Maichle-Mössmer, C.; Bettinger, H. F., Angew. Chem. Int. Ed., 2014, 53, 9380.