**Ir-Catalyzed Functionalization of 2-Substituted Indoles at the 7-Position:
Nitrogen-Directed Aromatic Borylation**

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General Methods:

All commercially available chemicals were used as received unless otherwise indicated. Pinacolborane (HBPin) was generously supplied by BASF. Bis(η^4 -1,5-cyclooctadiene)-di- μ -methoxy-diiridium(I) [Ir(OMe)(COD)]₂ was prepared per the literature procedure.¹ 2-Trimethylsilylindole was prepared per the literature procedure.² Solid substrates were sublimed under vacuum and liquid substrates were purified by distillation. Pinacolborane (HBPin) was distilled before use. *n*-Hexane was refluxed over sodium, distilled, and degassed. Tetrahydrofuran was obtained from a dry still packed with activated alumina and degassed before use. Silica gel was purchased from EMD™ (230-400 Mesh).

All reactions were monitored by GC-FID (Varian CP-3800; column type: WCOT Fused silica 30m × 0.25mm ID coating CP-SIL 8 CB). GC-FID method: 70 °C, 2 min.; 20 °C/min, 9 min.; 250 °C, 20 min.; All reported yields are for isolated materials.

^1H and ^{13}C NMR spectra were recorded on a Varian Inova-300 (300.11 and 75.47 MHz respectively), Varian VXR-500 or Varian Unity-500-Plus spectrometer (499.74 and 125.67 MHz respectively) and referenced to residual solvent signals (7.24 ppm and 77.0 ppm for CDCl_3 , respectively). ^{11}B spectra were recorded on a Varian VXR-300 operating at 96.29 MHz and were referenced to neat $\text{BF}_3\cdot\text{Et}_2\text{O}$ as the external standard. All coupling constants are apparent J values measured at the indicated field strengths. All 2-dimensional experiments were run using z -axis pulse field gradients. Elemental analyses were performed at Michigan State University using a Perkin Elmer Series II 2400 CHNS/O Analyzer. GC-MS data were obtained using a Varian Saturn 2200 GC/MS (column type: WCOT Fused silica 30m $\times$ 0.25mm ID coating CP-SIL 8 CB). High-resolution mass spectra were obtained at the Mass Spectrometry Core of the Research Technology Support Facility (RTSF) at Michigan State University. Melting points were measured on a MEL-TEMP[®] capillary melting apparatus and are uncorrected.

General Procedure

Unless otherwise specified, all reactions followed this general procedure. The Ir-catalyst was generated by a modified literature protocol,³ where in a glove box, a Schlenk flask, equipped with a magnetic stirring bar, was charged with the corresponding indole (1 mmol, 1 equiv). Two separate test tubes were charged with $[\text{Ir}(\text{OMe})(\text{COD})]_2$ (10 mg, 0.015 mmol, 3 mol % Ir) and $d^t\text{bpy}$ (8 mg, 0.03 mmol, 3 mol %). Excess HBPIn (1.5 to 2 equiv) was added to the $[\text{Ir}(\text{OMe})(\text{COD})]_2$ test tube. n -Hexane (1 mL) was added to the $d^t\text{bpy}$ containing test tube in order to dissolve the $d^t\text{bpy}$. The $d^t\text{bpy}$ solution

was then mixed with the [Ir(OMe)(COD)]₂ and HBPIn mixture. After mixing for one minute, the resulting solution was transferred to the Schlenk flask containing the indole substrate. Additional *n*-hexane (2 × 1 mL) was used to wash the test tubes and the washings were transferred to the Schlenk flask. The flask was stoppered, brought out of the glove box, and attached to a Schlenk line in hood. The Schlenk flask was placed under N₂ and heated in a 60 °C oil bath. The reaction was monitored by GC FID/MS. After completion of the reaction, the volatile materials were removed on a rotary evaporator. The crude material was dissolved in CH₂Cl₂ and passed through a short plug of silica to afford the corresponding 7-borylated indole. Small amounts of impurities, if present, were removed by crystallization or column chromatography. Regiochemistry of the borylated products was assigned by NMR spectroscopy (¹H, ¹³C, gHMQC, gHMBC).

Experimental Details and Spectroscopic Data:

Table 1, Entry 1: Borylation of 2-methylindole.

The general procedure was applied to 2-methylindole (262 mg, 2.00 mmol, 1 equiv) and HBPin (435 μ L, 384 mg, 3.00 mmol, 1.50 equiv) at 60 $^{\circ}$ C for 4 h. The product was isolated as colorless oil (201 mg, 78% yield). ^1H NMR (CDCl_3 , 300 MHz): δ 8.85 (br s, 1 H, H_a), 7.62 (d, J = 7.8 Hz, 1 H, H_e), 7.55 (dd, J = 7.2, 1.2 Hz, 1 H, H_c), 7.06 (dd, J = 7.8, 7.2 Hz, 1 H, H_d), 6.21-6.19 (m, 1 H, H_b), 2.48 (d, J = 0.9 Hz, 3 H, CH_3), 1.39 (br s, 12 H, CH_3 of BPin); ^{13}C NMR $\{^1\text{H}\}$ (CDCl_3 , 75 MHz): δ 141.3 (C), 134.9 (C), 128.0 (CH), 127.9 (C), 123.0 (CH), 118.9 (CH), 99.8 (CH), 83.6 (2 C), 24.8 (4 CH_3 of BPin), 13.7 (CH_3); ^{11}B NMR (CDCl_3 , 96 MHz): δ 31.6; FT-IR (neat) $\tilde{\nu}_{\text{max}}$: 3451, 2978, 1604, 1560, 1493, 1431, 1371, 1277, 1136, 974, 850, 802, 752, 679, 636 cm^{-1} ; GC-MS (EI) m/z (% relative intensity): M^+ 257 (100), 200 (24); Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{BNO}_2$: C, 70.06; H, 7.84; N, 5.45. Found: C, 69.68; H, 8.07; N, 5.28.

Figure 1: ¹H spectrum of 2-methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-indole.

Figure 2: ¹³C spectrum of 2-methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-indole.

Table 1, Entry 2: Borylation of 5-chloro-2-methylindole.

The general procedure was applied to 5-chloro-2-methylindole (166 mg, 1.00 mmol, 1 equiv) and HBPin (218 μ L, 192 mg, 1.50 mmol, 1.50 equiv) at room temperature for 20 h. The product was isolated as a white solid (264 mg, 91% yield, mp 106-110 $^{\circ}$ C). ^1H NMR (CDCl_3 , 500 MHz): δ 8.82 (br s, 1 H, H_a), 7.55 (d, $J = 1.9$ Hz, 1 H, $H_{c/d}$), 7.49 (d, $J = 1.9$ Hz, 1 H, $H_{c/d}$), 6.14 (m, 1 H, H_b), 2.47 (d, $J = 0.7$ Hz, 3 H, CH_3), 1.39 (br s, 12 H, CH_3 of BPin); ^{13}C NMR $\{^1\text{H}\}$ (CDCl_3 , 75 MHz): δ 139.7 (C), 136.7 (C), 129.5 (C), 127.6 (CH), 125.0 (C), 122.3 (CH), 99.6 (CH), 84.2 (2 C), 25.0 (4 CH_3 of BPin), 14.0 (CH_3); ^{11}B NMR (CDCl_3 , 96 MHz): δ 31.0; FT-IR (neat) $\tilde{\nu}_{\text{max}}$: 3443, 2978, 1558, 1464, 1427, 1387, 1130, 952, 881, 850, 758, 679, 640 cm^{-1} ; GC-MS (EI) m/z (% relative intensity): M^+ 291 (100), 234 (63), 191 (33); Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{BClINO}_2$: C, 61.79; H, 6.57; N, 4.80. Found: C, 62.06; H, 6.89; N, 4.78.

Figure 3: ^1H spectrum of 5-chloro-2-methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-indole.

Figure 4: ^{13}C spectrum of 5-chloro-2-methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-indole.

Table 1, Entry 3: Borylation of 5-methoxy-2-methylindole.

The general procedure was applied to 5-methoxy-2-methylindole (161 mg, 1.00 mmol, 1 equiv) and HBPIn (218 μ L, 192 mg, 1.50 mmol, 1.50 equiv) at 60 $^{\circ}$ C for 4 h to give the borylated product (274 mg, 95%) and 3% starting indole. Crystallization from hexanes at -30 $^{\circ}$ C afforded the desired product as a white solid (253 mg, 88% yield, mp 72-74 $^{\circ}$ C). ^1H NMR (CDCl_3 , 500 MHz): δ 8.72 (br s, 1 H, H_a), 7.21 (d, J = 2.4 Hz, 1 H, $H_{c/d}$), 7.16 (d, J = 2.44, 1 H, $H_{c/d}$), 6.14 (m, 1 H, H_b), 3.86 (s, 3 H, OCH_3) 2.47 (d, J = 0.7 Hz, 3 H, CH_3), 1.39 (br s, 12 H, CH_3 of BPin); ^{13}C NMR $\{^1\text{H}\}$ (CDCl_3 , 75 MHz): δ 153.6 (C), 136.8 (C), 135.9 (C), 128.8 (C), 115.8 (CH), 107.1 (CH), 99.4 (CH), 83.8 (2 C), 56.2 (OCH_3), 24.9 (4 CH_3 of BPin), 13.9 (CH_3); ^{11}B NMR (CDCl_3 , 96 MHz): δ 31.3; FT-IR (neat) $\tilde{\nu}_{\text{max}}$: 3455, 2980, 1483, 1373, 1326, 1282, 1217, 1126, 1041, 852, 752 cm^{-1} ; GC-MS (EI) m/z (% relative intensity): M^+ 287 (100), 187 (42); Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{BNO}_3$: C, 66.92; H, 7.72; N, 4.88. Found: C, 66.68; H, 7.56; N, 4.86.

Figure 5: ^1H spectrum of 5-methoxy-2-methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-indole.

Figure 6: ^{13}C spectrum of 5-methoxy-2-methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-indole.

Table 1, Entry 4: Borylation of ethyl indole-2-carboxylate.

The general procedure was applied to ethyl indole-2-carboxylate (189 mg, 1.00 mmol, 1 equiv) and HBPin (218 μ L, 192 mg, 1.50 mmol, 1.50 equiv) at 60 $^{\circ}$ C for 1 h. The product was isolated as a white solid (274 mg, 87% yield, mp 82-84 $^{\circ}$ C). ^1H NMR (CDCl_3 , 500 MHz): δ 9.69 (br s, 1 H, H_a), 7.80-7.77 (m, 1 H, H_c), 7.76 (dd, J = 7.0, 1.2 Hz, 1 H, H_e), 7.20 (d, J = 2.2 Hz, 1 H, H_b), 7.19-7.14 (dd, J = 8.1, 7.1 Hz, 1 H, H_d), 4.40 (q, J = 7.2 Hz, 2 H, CH_2CH_3), 1.41 (t, J = 7.2 Hz, 3 H, CH_2CH_3), 1.39 (br s, 12 H, CH_3 of BPin); ^{13}C NMR $\{^1\text{H}\}$ (CDCl_3 , 75 MHz): δ 162.0 (C=O), 141.6 (C), 132.7 (CH), 127.4 (C), 126.4 (C), 126.0 (CH), 120.3 (CH), 108.1 (CH), 84.0 (2 C), 60.8 (CH_2), 24.9 (4 CH_3 of BPin), 14.3 (CH_3); ^{11}B NMR (CDCl_3 , 96 MHz): δ 31.3; FT-IR (neat) $\tilde{\nu}_{\text{max}}$: 3449, 2982, 1711, 1593, 1535, 1421, 1371, 1290, 1232, 1132, 976, 850, 752, 677 cm^{-1} ; GC-MS (EI) m/z (% relative intensity): M^+ 315 (100), 258 (49), 230 (14), 215 (17), 169(23). Anal. Calcd for $\text{C}_{17}\text{H}_{22}\text{BNO}_4$; C, 64.78; H, 7.04; N, 4.44. Found: C, 64.45; H, 7.20; N, 4.62.

Table 1, Entry 5: Borylation of ethyl 5-chloroindole-2-carboxylate.

The general procedure was applied to ethyl 5-chloroindole-2-carboxylate (224 mg, 1.00 mmol, 1 equiv) and HBPIn (290 μ L, 256 mg, 2.00 mmol, 2.00 equiv) at 60 $^{\circ}$ C for 6 h. The product was isolated as a white solid (290 mg, 83% yield, mp 112-114 $^{\circ}$ C). ^1H NMR (CDCl_3 , 500 MHz): δ 9.64 (s, 1 H, H_a), 7.73 (dd, J = 2.1, 0.7 Hz, 1 H, H_c) 7.69 (d, J = 2.1 Hz, 1 H, H_d), 7.11 (d, J = 2.3 Hz, 1 H, H_b), 4.40 (q, J = 7.1 Hz, 2 H, CH_2CH_3), 1.41 (t, J = 7.1 Hz, 3 H, CH_2CH_3), 1.38 (s, 12 H, CH_3 of BPIn); ^{13}C NMR { ^1H } (CDCl_3 , 125 MHz): δ 161.6 (C=O), 139.7 (C), 132.5 (CH), 128.6 (C), 127.5 (C), 126.2 (C), 124.8 (CH), 107.3 (CH), 84.4 (2 C), 61.0 (CH_2), 24.8 (4 CH_3 of BPIn), 14.3 (CH_3); ^{11}B NMR (CDCl_3 , 96 MHz): δ 30.9; FT-IR (neat) $\tilde{\nu}_{\text{max}}$: 3449, 1709, 1641, 1300, 1233, 1142, 851, 752, 713, 677 cm^{-1} ; GC-MS (EI) m/z (% relative intensity): M^+ 349 (100), 351 (32), 334 (14), 292 (63); Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{BClNO}_4$: C, 58.40; H, 6.05; N, 4.01. Found: C, 58.15; H, 5.79; N, 4.33.

Table 1, Entry 6: Borylation of ethyl 5-methoxyindole-2-carboxylate.

The general procedure was applied to ethyl 5-methoxyindole-2-carboxylate (219 mg, 1.00 mmol, 1 equiv) and HBPIn (290 μ L, 256 mg, 2.00 mmol, 2.00 equiv) at 60 $^{\circ}$ C for 3 h. The product was isolated as a white solid (282 mg, 82% yield, mp 79 $^{\circ}$ C). ^1H NMR (CDCl_3 , 500 MHz): δ 9.56 (br s, 1 H, H_a), 7.44 (d, J = 2.4 Hz, 1 H, H_d), 7.20 (dd, J = 2.4, 0.5 Hz, 1 H, H_c), 7.11 (d, J = 2.3 Hz, 1 H, H_b), 4.40 (q, J = 7.2 Hz, 2 H, CH_2CH_3), 3.83 (s, 3 H, OCH_3), 1.41 (t, J = 7.2 Hz, 3 H, CH_2CH_3), 1.38 (br s, 12 H, CH_3 of BPin); ^{13}C NMR { ^1H } (CDCl_3 , 125 MHz): δ 162.0 (C=O), 154.3 (C), 137.1 (C), 127.8 (C), 127.1 (C), 122.9 (CH), 107.5 (CH), 107.3 (CH), 84.1 (2 C), 60.7 (CH_2), 55.9 (OCH_3), 24.9 (4 CH_3 of BPin), 14.3 (CH_3); ^{11}B NMR (CDCl_3 , 96 MHz): δ 31.0; FT-IR (neat) $\tilde{\nu}_{\text{max}}$: 3453, 2978, 1705, 1597, 1533, 1446, 1421, 1230, 1213, 1140, 1039, 850, 752 cm^{-1} ; GC-MS (EI) m/z (% relative intensity): M^+ 345 (100), 330 (5), 299 (26), 245 (8), 213 (9), 199 (14); Anal. Calcd for $\text{C}_{18}\text{H}_{24}\text{BNO}_5$: C, 62.63; H, 7.01; N, 4.06. Found: C, 62.69; H, 7.18; N, 4.20.

Table 1, Entry 7: Borylation of ethyl 2-methylindole-3-carboxylate.

The general procedure was applied to ethyl 2-methylindole-3-carboxylate (203 mg, 1.00 mmol, 1 equiv) and B₂Pin₂ (254 mg, 1.00 mmol, 1.00 equiv, 2.00 equiv of boron) at 60 °C for 18 h. Column chromatography (hexanes/ethyl acetate 90:10) furnished the desired product as a white solid (210 mg, 64% yield, mp 96-98 °C). ¹H NMR (CDCl₃, 500 MHz): δ 9.23 (br s, 1 H, H_a), 8.19 (m, 1 H, H_{b/d}), 7.61 (dd, *J* = 7.1, 1.2 Hz, 1 H, H_{b/d}), 7.20 (dd, *J* = 8.0, 7.1 Hz, 1 H, H_c), 4.38 (q, *J* = 7.2 Hz, 2 H, CH₂CH₃), 2.78 (s, 3 H, CH₃), 1.43 (t, *J* = 7.2 Hz, 3 H, CH₂CH₃), 1.39 (br s, 12 H, CH₃ of BPin); ¹³C NMR {¹H} (CDCl₃, 125 MHz): δ 166.1 (C=O), 143.8 (C), 139.8 (C), 129.4 (CH), 126.2 (C), 124.8 (CH), 121.2 (CH), 104.2 (C), 84.0 (2 C), 59.3 (CH₂), 25.0 (4 CH₃ of BPin), 14.6 (CH₃), 14.3 (CH₃); ¹¹B NMR (CDCl₃, 96 MHz): δ 31.3; FT-IR (neat) $\tilde{\nu}_{\text{max}}$: 3429, 2978, 1689, 1591, 1549, 1495, 1373, 1278, 1132, 1093, 846, 804, 756, 680, 652 cm⁻¹; GC-MS (EI) *m/z* (% relative intensity): M⁺ 329 (100), 314 (4), 300 (9), 284 (16), 272 (21), 184 (18); Anal. Calcd for C₁₈H₂₄BNO₄: C, 65.67; H, 7.35; N, 4.25. Found: C, 65.47; H, 7.42; N, 4.58.

Figure 13: ^1H spectrum of ethyl 2-methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-indole-3-carboxylate.

Figure 14: ^{13}C spectrum of ethyl 2-methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-indole-3-carboxylate.

Table 1, Entry 8: Borylation of methyl 4-methoxy-2-indolecarboxylate.

The general procedure was applied to methyl 4-methoxy-2-indolecarboxylate (205 mg, 1.00 mmol, 1 equiv) and HBPin (218 μ L, 192 mg, 1.50 mmol, 1.50 equiv) at 60 $^{\circ}$ C for 8 h, except the starting material was weighed out in test tube and transferred into Schlenk flask by dissolving it into DME (1 mL). The product was isolated as a white solid (261 mg, 79% yield, mp 118-120 $^{\circ}$ C). ^1H NMR (CDCl_3 , 500 MHz): δ 9.66 (br s, 1 H, H_a), 7.73 (d, J = 7.8 Hz, 1 H, H_d), 7.33 (d, J = 2.2 Hz, 1 H, H_b), 6.51 (d, J = 7.8 Hz, 1 H, H_c), 3.95 (s, 3 H, CH_3), 3.92 (s, 3 H, CH_3), 1.38 (br s, 12 H, CH_3 of BPin); ^{13}C NMR [^1H] (CDCl_3 , 125 MHz): δ 162.3 (C=O), 157.6 (C), 143.2 (C), 135.0 (CH), 125.6 (C), 117.7 (C), 106.1 (CH), 100.0 (CH), 83.7 (2 C), 55.2 (CH_3), 51.7 (CH_3), 24.8 (4 CH_3 of BPin); ^{11}B NMR (CDCl_3 , 96 MHz): δ 31.3; FT-IR (neat) $\tilde{\nu}_{\text{max}}$: 3445, 2978, 2841, 1711, 1593, 1531, 1439, 1371, 1182, 1117, 1080, 979, 854, 756, 677 cm^{-1} ; GC-MS (EI) m/z (% relative intensity): M^+ 331 (100), 316 (6), 299 (15), 274 (9), 231 (16), 199 (18); Anal. Calcd for $\text{C}_{17}\text{H}_{22}\text{BNO}_5$: C, 61.65; H, 6.70; N, 4.23. Found: C, 61.58; H, 6.89; N, 4.17.

Figure 15: ^1H spectrum of methyl 7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-4-methoxy-2-indolecarboxylate.

Figure 16: ^{13}C spectrum of methyl 7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-4-methoxy-2-indolecarboxylate.

Table 1, Entry 9: Borylation of N,N-diethylindole-2-carboxamide.

The general procedure was applied to N,N-diethylindole-2-carboxamide (108 mg, 0.5 mmol, 1 equiv) except B₂Pin₂ (127 mg, 0.5 mmol, 2.0 equiv of B) was used instead of HBPIn as borylating agent. The reaction was stirred at 60 °C for 2.5 h. Eluting with CH₂Cl₂ through a short silica plug buffered with 2% triethylamine purified the crude and the product was isolated as yellow oil which solidified upon standing (154 mg, 90 % yield, mp 108-110 °C). ¹H NMR ((CD₃)₂SO, 500 MHz): δ 9.83 (br s, 1 H, H_a), 7.80 (d, *J* = 7.9 Hz, 1 H, H_{c/e}), 7.58 (d, *J* = 8.0 Hz, 1 H, H_{c/e}), 7.11 (t, *J* = 7.9, 1 H, H_d), 6.89 (d, *J* = 2.2 Hz, 1 H, H_b), 3.62 (q, *J* = 7.0 Hz, 4 H, CH₂CH₃), 1.37 (br s, 12 H, CH₃ of BPin), 1.24 (t, *J* = 7.0 Hz, 6 H, CH₂CH₃); ¹³C NMR {¹H} ((CD₃)₂SO, 125 MHz): δ 161.0 (C), 139.1 (C), 130.6 (C), 129.3 (CH), 126.5 (CH), 125.1 (C), 119.4 (CH), 103.3 (CH), 83.5 (2 C), 41.2 (2 CH₂ of CH₂CH₃), 24.3 (4 CH₃ of BPin), 13.1 (2 CH₃ of CH₂CH₃); ¹¹B NMR (CDCl₃, 96 MHz): δ 31.7; FT-IR (neat) $\tilde{\nu}_{\text{max}}$: 3441, 2978, 1616, 1527, 1433, 1369, 1288, 1130, 979, 748, 679 cm⁻¹; GC-MS (EI) *m/z* (% relative intensity): M⁺ 342 (100), 270 (67), 243 (79), 186 (22), 170 (54), 142 (12); HRMS (EI): *m/z* 343.2193 [(M+H)⁺; Calcd for C₁₉H₂₈BN₂O₃: 343.2195].

Figure 17: ^1H spectrum of N,N-diethyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-indole-2-carboxamide.

Figure 18: ^{13}C spectrum of N,N-diethyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-indole-2-carboxamide.

Table 1, Entry 10: Borylation of 1,2,3,4-tetrahydrocyclopent[*b*]indole.

The general procedure was applied to 1,2,3,4-tetrahydrocyclopent[*b*]indole (157 mg, 1.00 mmol, 1 equiv) and HBPin (290 μ L, 256 mg, 2.00 mmol, 2.00 equiv) at 60 °C for 36 h. Column chromatography (hexanes/ethyl acetate 90:10) furnished the desired product as a white solid (127 mg, 45% yield, mp 135 °C). ^1H NMR (CDCl_3 , 500 MHz): δ 8.96 (s, 1 H, H_a), 7.58 (d, $J = 7.7$ Hz, 1 H, H_d), 7.57 (d, $J = 7.1$ Hz, 1 H, H_b), 7.1 (dd, $J = 7.8, 7.2$ Hz, 1 H, H_c), 2.96-2.91 (m, 2 H, CH_2), 2.87-2.83 (m, 2 H, CH_2), 2.58-2.52 (m, 2 H, CH_2), 1.41 (s, 12 H, CH_3 of BPin); ^{13}C NMR $\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ 146.3 (C), 143.7 (C), 127.5 (CH), 123.6 (C), 121.9 (CH), 119 (C), 118.8 (CH), 83.7 (2 C), 28.7 (CH $_2$), 26.0 (CH $_2$), 24.9 (4 CH_3 of BPin), 24.4 (CH $_2$); ^{11}B NMR (CDCl_3 , 96 MHz): δ 31.3; FT-IR (neat) $\tilde{\nu}_{\text{max}}$: 3453, 3018, 2982, 1414, 1265, 1215, 1136, 929, 848, 767, 669, 623, 509 cm^{-1} ; GC-MS (EI) m/z (% relative intensity): M^+ 283 (100), 226 (26), 183 (33); HRMS (EI): m/z 283.1743 [M^+]; calcd for $\text{C}_{17}\text{H}_{22}\text{NO}_2\text{B}$: 283.1744].

Figure 19: ^1H spectrum of 7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-1,2,3,4-tetrahydrocyclopent[b]indole.

Figure 20: ^{13}C spectrum of 7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-1,2,3,4-tetrahydrocyclopent[b]indole.

Table 1, Entry 11: Borylation of 2-trimethylsilanylindole.

The general procedure was applied to 2-trimethylsilylindole² (189 mg, 1.00 mmol, 1 equiv) and HBPin (290 μ L, 192 mg, 2.00 mmol, 2.00 equiv) at 60 °C for 1 h. The product was isolated as light yellow solid (238 mg, 76% yield, mp 100-102 °C). ¹H NMR (CDCl₃, 300 MHz): δ 9.25 (br s, 1 H, *H_a*), 7.79 (d, *J* = 7.8 Hz, 1 H, *H_{c/e}*), 7.67 (d, *J* = 7.1 Hz, 1 H, *H_{c/e}*), 7.13 (dd, *J* = 7.8, 7.1 Hz, 1 H, *H_d*), 6.76 (d, *J* = 2.2 Hz, 1 H, *H_b*), 1.43 (br s, 12 H, CH₃ of BPin), 0.40 (br s, 9 H, CH₃ of SiMe₃); ¹³C NMR {¹H} (CDCl₃, 75 MHz): δ 143.7 (C), 137.9 (C), 129.5 (CH), 127.7 (C), 124.1 (CH), 119.2 (CH), 110.5 (CH), 83.7 (2 C), 24.9 (4 CH₃ of BPin), -1.1 (3 CH₃ of SiMe₃); ¹¹B NMR (CDCl₃, 96 MHz): δ 31.4; FT-IR (neat) $\tilde{\nu}_{\text{max}}$: 3453, 3052, 2978, 1595, 1423, 1368, 1130, 1107, 952, 869, 754, 679 cm⁻¹; GC-MS (EI) *m/z* (% relative intensity): M⁺ 315 (100), 301 (27); HRMS (EI): *m/z* 315.1828 [(M⁺); Calcd for C₁₇H₂₆BNO₂Si: 315.1826].

Figure 21: ^1H spectrum of 7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2-trimethylsilanylindole.

Figure 22: ^{13}C spectrum of 7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2-trimethylsilanylindole.

Table 1, Entry 12: Borylation of 2-phenylindole.

The general procedure was applied to 2-phenylindole (193 mg, 1.00 mmol, 1 equiv) and HBPin (218 μ L, 192 mg, 1.50 mmol, 1.5 equiv) at 60 $^{\circ}$ C for 3 h. The product was isolated as white solid (219 mg, 69% yield, mp 120-121 $^{\circ}$ C). Small amounts of two isomeric diborylated products were also observed by GC-FID. ^1H NMR (CDCl_3 , 500 MHz): δ 9.47 (br s, 1 H, H_a), 7.76 (d, J = 7.8 Hz, 1 H, $H_{f/h}$), 7.71 (d, J = 8.4 Hz, 2 H, H_b), 7.67 (d, J = 7.1 Hz, 1 H, $H_{f/h}$), 7.47 (dd, J = 8.4, 7.4 Hz, 2 H, H_c), 7.35 (t, J = 7.4 Hz, 1 H, H_d), 7.15 (dd, J = 7.1, 7.8 Hz, 1 H, H_g), 6.83 (d, J = 2.3 Hz, 1 H, H_e), 1.44 (br s, 12 H, CH_3 of BPin); ^{13}C NMR $\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ 142.1 (C), 137.6 (C), 132.6 (C), 129.5 (CH), 128.9 (2 CH), 128.2 (C), 127.6 (CH), 125.2 (2 CH), 124.1 (CH), 119.7 (CH), 99.3 (CH), 83.9 (2 C), 25.0 (4 CH_3 of BPin); ^{11}B NMR (CDCl_3 , 96 MHz): δ 31.7; FT-IR (neat) $\tilde{\nu}_{\text{max}}$: 3451, 3055, 2978, 1601, 1498, 1429, 1371, 1323, 1288, 1196, 1145, 1138, 976, 850, 750, 677, 615, 518 cm^{-1} ; GC-MS (EI) m/z (% relative intensity): M^+ 319 (100), 219 (26); HRMS (EI): m/z 319.1745 [M^+]; calcd for $\text{C}_{20}\text{H}_{22}\text{BNO}_2$: 319.1744].

Figure 23: ¹H spectrum of 7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2-phenylindole.

Figure 24: ¹³C spectrum of 7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2-phenylindole.

Table 1, Entry 13: Diborylation of indole.

The general procedure was applied to indole (234 mg, 2.00 mmol, 1 equiv) and HBPin (638 μ L, 563 mg, 4.40 mmol, 2.20 equiv) using 2 mol % [Ir] catalyst loading at 60 $^{\circ}$ C for 4 h. After cooling to room temperature, the reaction contents were transferred to a vial. The mother liquor was removed via pipette and the remaining solid was washed with hexanes (2×1 mL). The off-white solid diborylated product (372 mg) was dried under high vacuum. The ^1H NMR spectrum of this solid showed the product to be free of impurities. The washings and the mother liquor were combined, volatile materials were removed under reduced pressure, and the crude mixture was eluted with CH_2Cl_2 through a plug of silica gel to afford additional diborylated product as a white solid (293 mg). Combined yield (665 mg, 90%, mp 147-148 $^{\circ}$ C). ^1H NMR (CDCl_3 , 500 MHz): δ 9.34 (br s, 1 H, H_a), 7.76 (dt, $J = 7.9, 1.0$ Hz, 1 H, H_c), 7.68 (dd, $J = 7.0, 1.2$ Hz, 1 H, H_e), 7.10 (d, $J = 2.1$ Hz, 1 H, H_b), 7.08 (dd, $J = 7.9, 7.0$ Hz, 1 H, H_d), 1.40 (br s, 12 H, CH_3 of BPin), 1.37 (br s, 12 H, CH_3 of BPin); ^{13}C NMR $\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ 143.1 (C, $C7a$), 131.3 (CH, $C6$), 127.3 (C, $C3a$), 125.1 (CH, $C4$), 119.3 (CH, $C5$), 113.8 (CH, $C3$), 84.0 (2 C), 83.8 (2 C), 25.0 (4 CH_3 of BPin), 24.8 (4 CH_3 of BPin); ^{11}B NMR (CDCl_3 , 96 MHz): δ 30.1; FT-IR (neat) $\tilde{\nu}_{\text{max}}$: 3455, 2978, 1593, 1543, 1371, 1327, 1302, 1262, 1143, 1130, 970, 854, 819, 756, 700, 679 cm^{-1} ; GC-MS (EI) m/z (% relative intensity): M^+ 369

(100), 312 (4), 285 (7), 269 (4), 254 (2), 226 (2), 212 (4), 184 (3), 169 (3); Anal. Calcd for $C_{20}H_{29}B_2NO_4$: C, 65.09; H, 7.92; N, 3.80. Found: C, 65.24; H, 8.05; N, 3.65.

1H , ^{13}C NMR, gHMQC and gHMBC spectroscopy (pages S8-S9) showed the single diborylated product to be 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-indole as follows. The 1H NMR spectrum showed that proton H_d is ortho coupled to protons H_c and H_e . This ruled out the possibility of second borylation taking place on C5 or C6. Hence the second borylation took place either at C4 or C7. gHMQC spectrum showed that proton H_b (which is coupled to NH proton H_a) is attached to C3 at 113.8 ppm. C3 showed a three bond cross peak to proton H_c in the gHMBC spectrum. This could only be possible if proton H_c is attached to C4. This ruled out the possibility of second borylation taking place at C4. In the ^{13}C spectrum of starting indole (and mono borylated indole), carbon C7 is present at 111 ppm. A sharp resonance for C7 was not seen in the ^{13}C NMR spectrum of the diborylated product due to broadening from and coupling with boron. Instead quaternary carbon C7 was observed as a broad hump at 111 ppm in the ^{13}C spectrum of diborylated product. A three bond cross peak from C7 to proton H_d in the gHMBC spectrum was seen as expected for the C7 borylated isomer. Three cross peaks from quaternary carbon C8 to protons H_b , H_c and H_e and one cross peak from quaternary carbon C9 to proton H_d in the gHMBC spectrum were also consistent with the second borylation taking place at C7.

Diborylation of indole (using (Ind)Ir(COD) and dmpe at 150 °C).

In a glove box, a Schlenk flask, equipped with a magnetic stirring bar, was charged with indole (234 mg, 2.00 mmol, 1 equiv). (Ind)Ir(COD) (8 mg, 0.02 mmol, 2.00 mol% Ir) and dmpe (3 mg, 0.02 mmol, 2.00 mol%) were weighed in separate test tubes. Excess HBPin (870 μ L, 768 mg, 6.00 mmol, 3.00 equiv) was used to dissolve the (Ind)Ir(COD) and dmpe, and the resulting solution was transferred to the Schlenk flask. The flask was stoppered, removed from the glove box, and heated at 150 °C for 1 h. The crude material was dissolved in CH₂Cl₂ and passed through a plug of silica to remove HBPin byproducts. Crystallization from hexane at -80 °C afforded the desired diborylated product as a white solid (516 mg, 70% yield, mp 147-148 °C).

Figure 27: gHMQC spectrum of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-indole.

Figure 28: gHMBC spectrum of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-indole.

Table 1, Entry 14: Diborylation of 4-cyanoindole.

The general procedure was applied to 4-cyanoindole (142 mg, 1.00 mmol, 1 equiv) and HBPIn (363 μ L, 320 mg, 2.5 mmol, 2.5 equiv) at 60 $^{\circ}$ C for 10 h. The product was isolated as white solid (362 mg, 92% yield, mp 158-160 $^{\circ}$ C). ^1H NMR (CDCl_3 , 300 MHz): δ 9.50 (br s, 1 H, H_a), 7.67 (d, J = 7.3 Hz, 1 H, $H_{c/d}$), 7.42 (d, J = 7.3 Hz, 1 H, $H_{c/d}$), 7.29 (d, J = 2.2, 1 H, H_b), 1.40 (br s, 12 H, CH_3 of BPin), 1.37 (br s, 12 H, CH_3 of BPin); ^{13}C NMR $\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ 142.6 (C), 129.9 (CH), 128.1 (C), 124.4 (CH), 118.4 (C), 112 (CH), 106.4 (C), 85.5 (2 C), 84.5 (2 C), 24.9 (4 CH_3 of BPin), 24.8 (4 CH_3 of BPin); ^{11}B NMR (CDCl_3 , 96 MHz): δ 29.9; FT-IR (neat) $\tilde{\nu}_{\text{max}}$: 3445, 2980, 2936, 2218, 1545, 1373, 1332, 1296, 1142, 972, 852, 775, 704, 680 cm^{-1} ; GC-MS (EI) m/z (% relative intensity): M^+ 394 (100), 379 (8) 337 (16), 309 (10) 294 (7); HRMS (EI): m/z 394.2234 [M^+]; Calcd for $\text{C}_{21}\text{H}_{28}\text{B}_2\text{N}_2\text{O}_4$: 394.2235].

Figure 29: ¹H spectrum of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-4-cyanoindole.

Figure 30: ¹³C spectrum of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-4-cyanoindole.

Desilylation of 7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2-trimethylsilanylindole.

Desilylation of 7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-2-trimethylsilylindole was carried out as per literature procedure with slight modification.⁴ The silyl compound (157 mg, 0.5mmol) was dissolved in 1 M tetrabutylammonium fluoride (TBAF) in THF (3 mL). The solution was stirred at 60 °C for 21 h until analysis by GC-FID indicated the absence of starting material. Water (10 mL) was added, and the mixture was extracted with ether (10 mL × 3). The combined ether layer was dried over MgSO₄, and the solvent was removed under reduced pressure. The residue was further purified by eluting with CH₂Cl₂ through a plug of silica gel to afford 7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-indole as a white solid (107 mg, 88% yield, mp 83-85 °C). ¹H NMR (CDCl₃, 500 MHz): δ 9.24 (br s, 1 H, H_a), 7.78 (d, *J* = 7.8 Hz, 1 H, H_{d/f}), 7.66 (d, *J* = 6.9 Hz, 1 H, H_{d/f}), 7.26 (t, *J* = 2.8 Hz, 1 H, H_b), 7.13 (dd, *J* = 7.8, 6.9 Hz, 1 H, H_e), 6.55 (m, 1 H, H_c), 1.39 (br s, 12 H, CH₃ of BPin); ¹³C NMR {¹H} (CDCl₃, 125 MHz): δ 140.9 (C), 129.2 (CH), 126.7 (C), 124.2 (CH), 124.0 (CH), 119.3 (CH), 101.9 (CH), 83.8 (2 C), 24.9 (4 CH₃ of BPin); ¹¹B NMR (CDCl₃, 96 MHz): δ 31.3; FT-IR (neat) $\tilde{\nu}_{\text{max}}$: 3453, 2978, 1635, 1512, 1429, 1369, 1331, 1294, 1130, 974, 798, 729, 679 cm⁻¹; GC-MS (EI) *m/z* (% relative intensity): M⁺ 243 (100), 186 (33), 170 (3), 143 (7); HRMS (EI): *m/z* 243.1431 [(M⁺); Calcd for C₁₄H₁₈BNO₂: 243.1432].

Figure 31: ^1H spectrum of 7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-indole.

Figure 32: ^{13}C spectrum of 7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-indole.

Monoborylation of Benzofuran.

Borylation of benzofuran was carried out using a slightly modified literature procedure.^{3,5} In a glove box $[\text{Ir}(\text{OMe})(\text{COD})]_2$ (10 mg, 0.015 mmol, 3 mol % Ir) and $d^4\text{bpy}$ (8 mg, 0.03 mmol, 3 mol %) were weighed in separate test tubes. HBPIn (175 μL , 154 mg, 1.20 mmol, 1.20 equiv) was added to the $[\text{Ir}(\text{OMe})(\text{COD})]_2$ containing test tube. *n*-Hexane (1 mL) was added to the $d^4\text{bpy}$ containing test tube in order to dissolve the $d^4\text{bpy}$. The $d^4\text{bpy}$ solution was then mixed with the $[\text{Ir}(\text{OMe})(\text{COD})]_2$ and HBPIn mixture. The resulting solution was transferred to a 20 mL scintillation vial equipped with a magnetic stirring bar. Additional *n*-hexane (2×1 mL) was used to wash the test tubes and the washings were transferred to the scintillation vial. Benzofuran (108 μL , 118 mg, 1.00 mmol, 1 equiv) was then added to the scintillation vial and the reaction mixture was stirred at room temperature for 30 minutes. GC-FID showed 100% consumption of the starting benzofuran. The ratio of the 2-borylated and 3-borylated benzofuran at the end of reaction was 97.5 : 2.5 as judged by GC-FID. Volatile materials were removed on a rotary evaporator. The crude material was dissolved in CH_2Cl_2 and passed through a short plug of silica to afford the monoborylated product mixture (199 mg, 82% yield). The minor isomer (2.5% by GC-FID) was not observed by NMR. The following data are for the major (2-borylated) isomer. ^1H NMR (CDCl_3 , 300 MHz): δ 7.58-7.62 (m, 1 H, H_b), 7.55 (dd, $J = 8.3, 0.7$ Hz, 1 H, H_e), 7.38 (d, $J = 1.0$ Hz, 1 H, H_a), 7.28-7.34 (m, 1 H, H_d), 7.20 (dt, $J = 7.8$ Hz, 1.0 Hz, 1 H, H_c), 1.36 (s, 12 H, CH_3 of BPin); ^{13}C NMR $\{^1\text{H}\}$

(CDCl₃, 75 MHz): δ 157.5 (C, *C7a*), 127.5 (C, *C3a*), 125.9 (CH, *C6*), 122.7 (CH, *C5*), 121.8 (CH, *C4*), 119.5 (CH, *C3*), 111.9 (CH, *C7*), 84.6 (2 C), 24.7 (4 CH₃ of BPin); ¹¹B NMR (CDCl₃, 96 MHz): δ 28.1; FT-IR (neat) $\tilde{\nu}_{\text{max}}$: 3065, 2991, 2978, 2936, 1566, 1361, 1327, 1138, 1068, 962, 852, 831, 819, 756, 748, 692 cm⁻¹; GC-MS (EI) *m/z* (% relative intensity): M⁺ 244 (52), 245 (9), 243 (14), 229 (11), 201 (100), 159 (16), 158 (17), 144 (19); Anal. Calcd for C₁₄H₁₇BO₃: C, 68.89; H, 7.02. Found: C, 68.82; H, 7.35.

Figure 33: ¹H spectrum of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-benzofuran.

Figure 34: ¹³C spectrum of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-benzofuran.

Borylation of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-benzofuran.

In a glove box 2-borylated benzofuran (containing 2.5% 3-borylated isomer by GC-FID) from the previous reaction (488 mg, 2.00 mmol, 2.00 equiv), $[\text{Ir}(\text{OMe})(\text{COD})]_2$ (10 mg, 0.015 mmol, 3 mol % Ir), and $d^4\text{bpy}$ (8 mg, 0.03 mmol, 3 mol %) were weighed in separate test tubes. HBPin (145 μL , 128 mg, 1.00 mmol, 1 equiv) was added to the $[\text{Ir}(\text{OMe})(\text{COD})]_2$ containing test tube. *n*-Hexane (1 mL) was added to the $d^4\text{bpy}$ containing test tube in order to dissolve the $d^4\text{bpy}$. The $d^4\text{bpy}$ solution was then mixed with $[\text{Ir}(\text{OMe})(\text{COD})]_2$ and HBPin mixture. The resulting solution was transferred to a 20 mL scintillation vial equipped with a magnetic stirring bar. To this vial was added the *n*-hexane solution (1 mL) of the monoborylated benzofuran. Additional *n*-hexane (1 mL) was used to wash the test tubes and the washings were transferred to the scintillation vial. The reaction mixture was stirred at room temperature. The reaction was stopped after 7 hours to minimize any conversion of diborylated products in to triborylated products. Six diborylated products were observed by GC-FID, their GC retention times and percentage of the isomer mixture are given in the following table.

Isomer	A	B	C	D	E	F
GC ret. Time (min)	14.54	14.81	15.71	15.92	17.06	17.58
GC Percentage	64.5	3.4	4.2	7.5	3.9	16.6

After the reaction was stopped, the volatile materials were removed on a rotary evaporator. Gradient column chromatography (hexanes:CH₂Cl₂ 50:50→ hexanes:CH₂Cl₂ 0:100) was used to isolate the major diborylated product (136 mg, 37%, GC-FID retention time 14.54 min). This fraction was of $\approx$ 92% isomeric purity by GC-FID. Crystallization from *n*-hexanes at -80 °C afforded the pure diborylated product as a white solid (90 mg, 24% yield, mp 161-162 °C). ¹H, ¹³C NMR, gHMQC and gHMBC spectroscopy showed this major diborylated isomer to be 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-benzofuran. ¹H NMR (CDCl₃, 500 MHz): δ 7.77 (dd, *J* = 7.2, 1.3 Hz, 1 H, *H_d*), 7.70 (dd, *J* = 7.8, 1.3 Hz, 1 H, *H_b*), 7.36 (s, 1 H, *H_a*), 7.21 (dd, *J* = 7.8, 7.2 Hz, 1 H, *H_c*), 1.40 (s, 12 H, CH₃ of BPin), 1.35 (s, 12 H, CH₃ of BPin); ¹³C NMR {¹H} (CDCl₃, 125 MHz): δ 161.5 (C, *C7a*), 133.4 (CH, *C6*), 127.0 (C, *C3a*), 125.1 (CH, *C4*), 122.2 (CH, *C5*), 119.5 (CH, *C3*), 84.4 (2 C), 84.0 (2 C), 24.9 (4 CH₃ of BPin), 24.8 (4 CH₃ of BPin); ¹¹B NMR (CDCl₃, 96 MHz): δ 30.6; FT-IR (neat) $\tilde{\nu}_{\text{max}}$: 3063, 2980, 2934, 1608, 1591, 1570, 1487, 1363, 1338, 1307, 1165, 1143, 1130, 1072, 980, 922, 850, 760, 694, 679 cm⁻¹; GC-MS (EI) *m/z* (% relative intensity): *M*⁺ 370 (100), 371 (20), 369 (48), 355 (5), 284 (20), 270 (8), 227 (40); Anal. Calcd for C₂₀H₂₈B₂O₅: C, 64.91; H, 7.63. Found: C, 64.64; H, 7.98.

Another fraction from the column was obtained (21.0 mg) which was significantly enriched in isomer **F** ($\approx$ 66 % by GC-FID. retention time 17.58 min). This sample was

sufficiently enriched in isomer **F** to identify and assign its regiochemistry by NMR. ^1H , ^{13}C NMR, gHMQC and gHMBC spectroscopy showed this minor diborylated isomer **F** (GC-FID retention time 17.58 min) to be 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-benzofuran. ^1H NMR (CDCl_3 , 500 MHz): δ 7.96 (d, $J = 0.9$ Hz, 1 H, H_h), 7.65 (dd, $J = 7.8, 0.7$ Hz, 1 H, H_g), 7.60 (dd, $J = 7.8, 0.7$ Hz, 1 H, H_f), 7.37 (d, $J = 1.1$ Hz 1 H, H_e), 1.37 (s, 12 H, CH_3 of BPin), 1.34 (s, 12 H, CH_3 of BPin); ^{13}C NMR $\{^1\text{H}\}$ (CDCl_3 , 125 MHz): δ 157.4 (C, $C7a'$), 130.1 (C, $C3a'$), 128.7 (CH, $C5'$), 121.2 (CH, $C4'$), 119.6 (CH, $C3'$), 118.1 (CH, $C7'$), 84.7 (2 C), 83.8 (2 C), 24.9 (4 CH_3 of BPin), 24.8 (4 CH_3 of BPin).

Unreacted 2-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-benzofuran was also recovered (277 mg, 57%).

Figure 35: ^1H spectrum of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-benzofuran.

Figure 36: ^{13}C spectrum of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-benzofuran.

Figure 37: gHMQC spectrum of 2,7-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-benzofuran.

Figure 38: gHMBC spectrum of 2,7-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-benzofuran.

One-pot borylation/Suzuki coupling of ethyl 5-methoxyindole-2-carboxylate.

The general borylation procedure was applied to ethyl 5-methoxyindole-2-carboxylate (219 mg, 1.00 mmol, 1 equiv) and HBPIn (290 μ L, 256 mg, 2.00 mmol, 2.00 equiv) at 60 $^{\circ}$ C for 3 h. The GC-FID showed 100% consumption of the starting indole. The reaction mixture was pumped down under high vacuum for 1 h to remove the volatile materials. The Schlenk flask was brought into the glove box, where Pd(PPh₃)₄ (12 mg, 1 mol %), 5-bromo-*m*-xylene (163 μ L, 222 mg, 1.20 equiv), and DME (3 mL) were added. The Schlenk flask was then brought out of the glove box and attached to a Schlenk line. K₃PO₄·nH₂O (319 mg, 1.50 equiv) was added under N₂ counter flow to the Schlenk flask. The flask was stoppered and the mixture was heated at 80 $^{\circ}$ C for 2 h. The flask was cooled down to room temperature and 5 mL of water were added to the reaction mixture. The reaction mixture was extracted with ether (10 mL $\times$ 3). The combined ether extractions were washed with brine (10 mL), followed by water (10 mL), dried over MgSO₄ before being concentrated under reduced pressure on a rotary evaporator. Column chromatography (CH₂Cl₂) furnished the desired product as a white solid (280 mg, 87% yield, R_f = 0.6, mp 125-126 $^{\circ}$ C). ¹H NMR (CDCl₃, 300 MHz): δ 8.89 (br s, 1 H, H_a), 7.22-7.21 (m, 2 H, H_e), 7.18 (d, J = 2.2 Hz, 1 H, H_{c/d}), 7.07-7.06 (m, 1 H, H_f), 7.04 (d, J = 2.2 Hz, 1 H, H_{c/d}), 7.00 (d, J = 2.4 Hz, 1 H, H_b), 4.40 (q, J = 7.1 Hz, 2 H, CH₂CH₃), 3.87 (s, 3 H, OCH₃), 2.40 (s, 6 H, CH₃ of xylene), 1.40 (t, J = 7.1 Hz, 3 H, CH₂CH₃); ¹³C NMR {¹H} (CDCl₃, 75 MHz): δ 161.9 (C), 155.1 (C), 138.9 (2 C), 138.0 (C), 130.6 (C),

129.7 (CH), 128.3 (C), 128.1 (C), 127.7 (C), 125.9 (CH), 116.2 (CH), 108.5 (CH), 101.9 (CH), 60.9 (CH₂), 55.8 (OCH₃), 21.4 (2 CH₃), 14.4 (CH₃); FT-IR (neat) $\tilde{\nu}_{\text{max}}$: 3470, 3306, 2982, 2938, 1694, 1599, 1536, 1464, 1425, 1373, 1321, 1233, 1203, 1161, 1024, 847, 773, 748, 710, 664 cm⁻¹; GC-MS (EI) m/z (% relative intensity): M⁺ 323 (100), 324 (22), 278 (35), 234 (23), 190 (4); Anal. Calcd for C₂₀H₂₁NO₃: C, 74.28; H, 6.55; N, 4.33. Found: C, 74.00; H, 6.78; N, 4.29.

Figure 39: ^1H spectrum of Suzuki product of ethyl 5-methoxy-7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-indole-2-carboxylate.

Figure 40: ^{13}C spectrum of Suzuki product of ethyl 5-methoxy-7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-indole-2-carboxylate.

One-pot borylation/Suzuki coupling of 2-methylindole.

The general borylation procedure was applied to 2-methylindole (131 mg, 1.00 mmol, 1 equiv) and HBPin (218 μ L, 192 mg, 1.50 mmol, 1.50 equiv) at 60 °C for 10 h. The GC-FID showed 97% consumption of the starting indole. The reaction mixture was pumped down under high vacuum for 1 h to remove the volatile materials. The Schlenk flask was brought into the glove box, where Pd(PPh₃)₄ (23 mg, 2 mol %), 3-bromopyridine (116 μ L, 190 mg, 1.20 equiv), and DME (3 mL) were added. The Schlenk flask was then brought out of the glove box and attached to a Schlenk line. K₃PO₄·nH₂O (319 mg, 1.50 equiv) was added under N₂ counter flow to the Schlenk flask. The flask was stoppered and the mixture was heated at 80 °C for 4 h. The flask was cooled down to room temperature and 5 mL of water were added to the reaction mixture. The reaction mixture was extracted with ether (10 mL $\times$ 3). The combined ether extractions were washed with brine (10 mL), followed by water (10 mL), dried over MgSO₄ before being concentrated under reduced pressure on a rotary evaporator. Column chromatography (CH₂Cl₂ containing 2% triethylamine) furnished the desired product as a light yellow solid (170 mg, 82% yield, R_f = 0.3, mp 158-160 °C). ¹H NMR (CDCl₃, 500 MHz): δ 9.10 (br s, 1 H, H_a), 8.94 (dd, *J* = 2.2, 0.7 Hz, 1 H, H_f), 8.54 (dd, *J* = 4.9, 1.0 Hz, 1 H, H_g), 7.88 (ddd, *J* = 7.8, 2.3, 1.7 Hz, 1 H, H_i), 7.54 (dt, *J* = 7.8, 0.8 Hz, 1 H, H_c), 7.40 (ddd, *J* = 7.8, 4.9, 0.8 Hz, 1 H, H_g), 7.16 (dd, *J* = 7.8, 7.3 Hz, 1 H, H_d), 7.08 (dd, *J* = 7.3, 1.0 Hz, 1 H, H_e), 6.29 (m, 1H, H_b), 2.43 (s, 3 H, CH₃); ¹³C NMR {¹H} (CDCl₃, 125

MHz): δ 149.2 (CH), 148.3 (CH), 136.0 (C), 135.7 (CH), 135.4 (C), 133.9 (C), 129.7 (C), 124.0 (CH), 121.2 (CH), 121.1 (C), 120.2 (CH), 119.8 (CH), 101.0 (CH), 13.7 (CH₃); FT-IR (neat) $\tilde{\nu}_{\text{max}}$: 3200, 2916, 2850, 1574, 1539, 1412, 1280, 1140, 1028, 797, 738, 712 cm⁻¹; GC-MS (EI) m/z (% relative intensity): M⁺ 208 (100), 193 (3), 180 (9), 166 (2), 152 (4); Anal. Calcd for C₁₄H₁₂N₂: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.10; H, 5.98; N, 13.27. HRMS (FAB): m/z 209.1080 [(M+1)⁺]; Calcd for C₁₄H₁₃N₂: 209.10788].

Figure 41: ¹H spectrum of Suzuki product of 2-methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-indole.

Figure 42: ¹³C spectrum of Suzuki product of 2-methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-indole.

Isomer	A	B	C
GC Ret. Time (Min)	19.50	21.60	22.50
GC Percentage	20	58	22

Isomer B: (GC retention time 21.6 min) ^1H , ^{13}C NMR, gHMQC and gHMBC spectroscopy showed this major diborylated isomer **B** to be 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-N-methylindole. ^1H NMR (C_6D_6 , 500 MHz): δ 8.27 (s, 1 H, H_d), 8.08 (d, $J = 7.9$ Hz, 1 H, H_c), 7.70 (dd, $J = 7.9, 0.9$ Hz, 1 H, H_b), 7.51 (d, $J = 0.9$ Hz, 1 H, H_a),

3.66 (s, 3 H, CH₃), 1.19 (s, 12 H, CH₃ of BPin), 1.06 (s, 12 H, CH₃ of BPin), ¹H NMR (CDCl₃, 500 MHz): δ 7.84 (d, *J* = 0.7 Hz, 1 H, H_d), 7.62 (dd, *J* = 8.0, 1.0 Hz, 1 H, H_{b/c}), 7.49 (dd, *J* = 8.0, 1.0 Hz, 1 H, H_{b/c}), 7.09 (d, *J* = 0.7 Hz, 1 H, H_a), 3.99 (s, 3 H, CH₃), 1.36 (s, 12 H, CH₃ of BPin), 1.35 (s, 12 H, CH₃ of BPin); ¹³C NMR {¹H} (C₆D₆, 125 MHz): δ 140.6 (C, C7a), 131.1 (C, C3a), 125.9 (CH, C5), 121.5 (CH, C4), 117.8 (CH, C7), 115.3 (CH, C3), 83.6 (2 C), 83.5 (2 C), 25.1 (4 CH₃ of BPin), 24.8 (4 CH₃ of BPin).

Isomer C: (GC retention time 22.5 min) ¹H spectroscopy showed this minor diborylated isomer **C** to be 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-N-methylindole. ¹H NMR (CDCl₃, 500 MHz): δ 8.14 (s, 1 H, H_f), 7.67 (dd, *J* = 8.3, 1.0 Hz, 1 H, H_{g/h}), 7.30 (d, *J* = 8.3 Hz, 1 H, H_{g/h}), 7.12 (d, *J* = 1.0 Hz, 1 H, H_e), 3.94 (s, 3 H, CH₃), 1.34 (s, 24 H, CH₃ of BPin).

Fraction significantly enriched in isomer A was not obtained. Pure samples of isomer B and C were not obtained.

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