# Boc Groups as Protectors and Directors for Ir-Catalyzed C-H Borylation of Heterocycles

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## Supporting Information

**Table of Contents:**



**List of Figures:**

**General Methods:**

Pinacolborane (HBPin) and $B_2Pin_2$ was generously supplied by BASF. Bis($\eta^4$-1,5-cyclooctadiene)-di-$\mu$-methoxy-diiridium(I) $[Ir(OMe)(COD)]_2$ was prepared per the literature procedure.[1] 4,4′-Di-*t*-butyl-2,2′-bipyridine (d$^t$bpy) was purchased from Aldrich. Materials that are commercially available were purchased and protected per literature procedure.[2,3] 2-Methylpyrrole and 6-azaindole were prepared per literature procedure[4] and Boc protected. All substrates were purified by column chromatography or passing through a plug of alumina. Pinacolborane (HBPin) was distilled before use. *n*-Hexane, diethylether and MTBE were refluxed over sodium benzophenone, distilled, and degassed. Tetrahydrofuran was obtained from a dry still packed with activated alumina and degassed before use.

All reactions were monitored by GC-FID. GC-FID method: 70 °C, 2 min.; 20 °C/min, 9 min.; 250 °C, 10 or 20 min. All reported yields are for isolated materials.

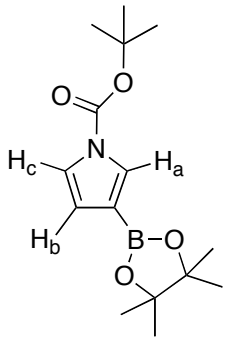
$^1$H NMR spectra were recorded at 300.11 or 499.74 MHz and $^{13}$C NMR spectra were recorded at 75.47 or 125.67 MHz. The $^1$H and $^{13}$C NMR spectra were referenced to residual solvent signals (7.24 ppm and 77.0 ppm for $CDCl_3$, respectively). $^{11}$B NMR spectra were recorded at 96.29 MHz and were referenced to neat $BF_3{\cdot}Et_2O$ as the external standard. All coupling constants are apparent *J* values measured at the indicated field strengths. Melting points are uncorrected. Optical rotation was recorded at the sodium D line.

**General Procedure:**

Unless otherwise specified, all reactions followed this general procedure. The Ir-catalyst was generated by a modified literature protocol,[5] where in a glove box, a Schlenk flask, equipped with a magnetic stirring bar, was charged with the corresponding substrate (1 mmol, 1 equiv). Two separate test tubes were charged with $[Ir(OMe)(COD)]_2$ (10 mg, 0.015 mmol, 3 mol % Ir) and d$^t$bpy (8 mg, 0.03 mmol, 3 mol %). Excess HBPin (1.1 to 2 equiv) was added to the $[Ir(OMe)(COD)]_2$ containing test tube. Solvent (1 mL) was added to the d$^t$bpy containing test tube in order to dissolve the d$^t$bpy. The d$^t$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. Additional solvent ($2 \times 1$ 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 a fume hood. The Schlenk flask was placed under $N_2$ and the reaction was carried out at the specified temperature. 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 purified by column chromatography or dissolved in $CH_2Cl_2$ and passed through a plug of silica. Evaporation of solvent afforded the product.

**Experimental Details and Spectroscopic Data:**

**Table 1, Entry 1: Borylation of N-Boc pyrrole.**




The general procedure was applied to N-Boc pyrrole (1003 mg, 6.00 mmol, 1 equiv) and HBPin (1088 μL, 960 mg, 7.50 mmol, 1.25 equiv) at 55 °C for 13 h. The product was isolated as a white solid (1587 mg, 90% yield, mp 83-85 °C). $^{1}$H NMR ($CDCl_3$, 500 MHz): δ 7.62-7.61 (t, $J$ = 1.7 Hz, 1 H, $H_a$), 7.24-7.23 (dd, $J$ = 3.2, 2.1 Hz, 1H, $H_c$), 6.45-6.44 (dd, $J$ = 3.2, 1.5 Hz, 1 H, $H_b$), 1.56 (br s, 9 H, C$H_3$ of $^{t}$Bu), 1.30 (br s, 12 H, C$H_3$ of BPin); $^{13}$C NMR {$^{1}$H} ($CDCl_3$, 125 MHz): δ 148.6 (C=O), 128.8 (CH), 120.7 (CH), 116.2 (CH), 83.8 (C), 83.3 (C), 28.0 (3 $CH_3$ of $^{t}$Bu), 24.8 (4 $CH_3$ of BPin); $^{11}$B NMR ($CDCl_3$, 96 MHz): δ 30.2; FT-IR (neat) $\tilde{\nu}_{max}$: 3150, 2980, 2934, 1748, 1563, 1491, 1372, 1329, 1292, 1217, 1183, 1144, 1067, 976, 936, 857, 775, 691 cm$^{-1}$; GC-MS (EI) *m/z* (% relative intensity): $M^+$ 293 (13), 237 (55), 194 (39), 193 (35), 178 (76), 107 (100), 57 (14); Anal. Calc'd for $C_{15}H_{24}BNO_4$: C, 61.45; H, 8.25; N, 4.78. Found: C, 61.68; H, 8.53; N, 4.70.

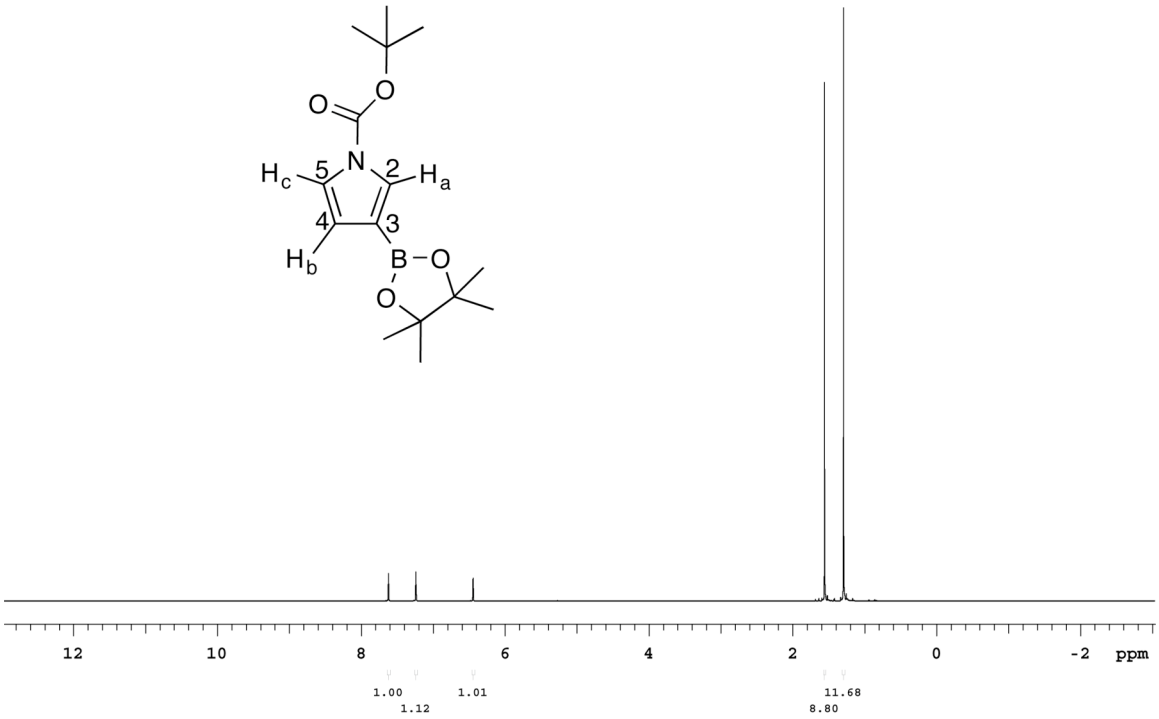



**Figure 1:** $^{1}$H spectrum of N-Boc-3-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)pyrrole.

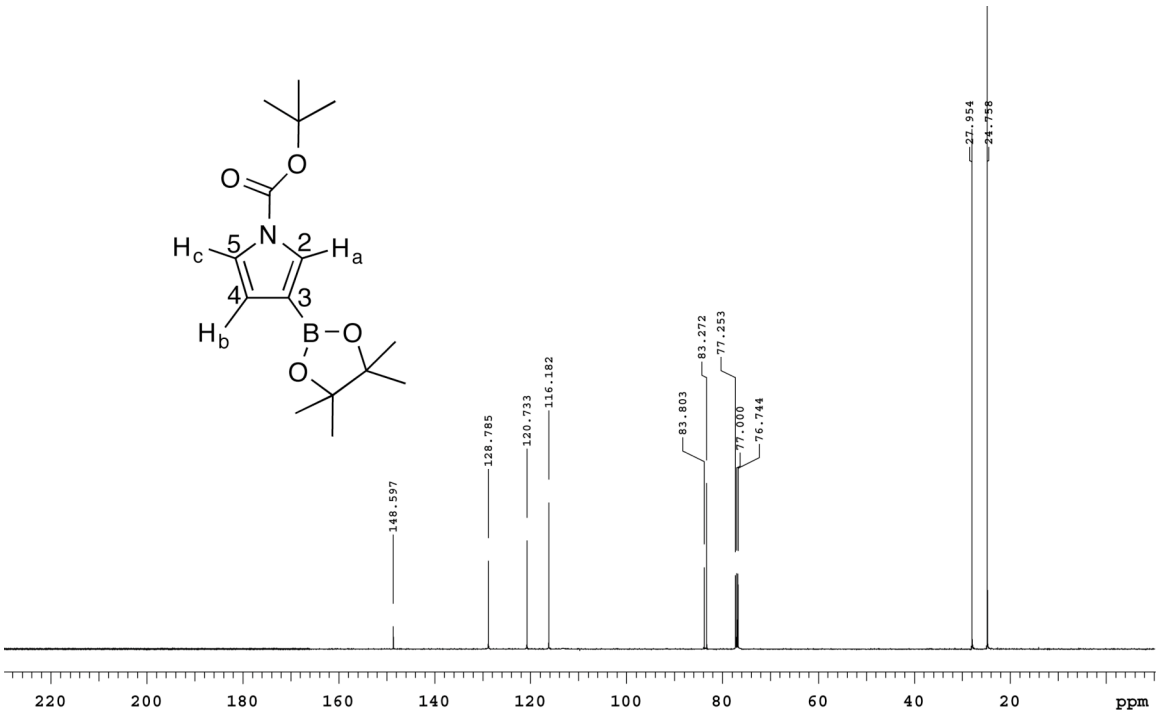
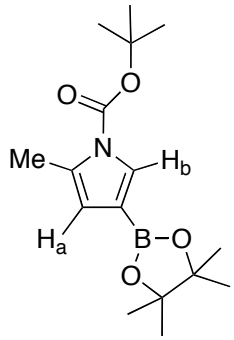



**Figure 2:** $^{13}$C spectrum of N-Boc-3-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)pyrrole.

**Table 1, Entry 2: Borylation of N-Boc-2-methylpyrrole.**




The general procedure was applied to N-Boc-2-methylpyrrole (181 mg, 1.00 mmol, 1 equiv) and HBPin (218 μL, 192 mg, 1.50 mmol, 1.50 equiv) at 60 °C for 6 h. The product was isolated as a white solid (253 mg, 82% yield, mp 68-70 °C). $^{1}$H NMR ($CDCl_3$, 500 MHz): δ 7.57 (d, $J$ = 2.0 Hz, 1 H, $H_b$), 6.15-6.14 (m, 1 H, $H_a$), 2.39 (d, 1.2 Hz, 3 H, C$H_3$), 1.55 (br s, 9 H, C$H_3$ of $^{t}$Bu), 1.29 (br s, 12 H, C$H_3$ of BPin); $^{13}$C NMR {$^{1}$H} ($CDCl_3$, 125 MHz): δ 149.4 (C=O), 132.5 (C), 129.6 (CH), 115.9 (CH), 83.5 (C), 83.2 (C), 28.0 (3 $CH_3$ of $^{t}$Bu), 24.7 (4 $CH_3$ of BPin), 15.1 ($CH_3$); $^{11}$B NMR ($CDCl_3$, 96 MHz): δ 30.2; FT-IR (neat) $\tilde{\nu}_{max}$: 2980, 2930, 1748, 1586, 1532, 1399, 1372, 1318, 1296, 1271, 1256, 1221, 1190, 1165, 1144, 1105, 1078, 970, 855, 774, 708, 691 cm$^{-1}$; GC-MS (EI) *m/z* (% relative intensity): $M^+$ 307 (23), 251 (100), 207 (48), 192 (37), 121 (49), 57 (13); Anal. Calc'd for $C_{16}H_{26}BNO_4$: C, 62.56; H, 8.53; N, 4.56. Found: C, 62.58; H, 8.46; N, 4.46.

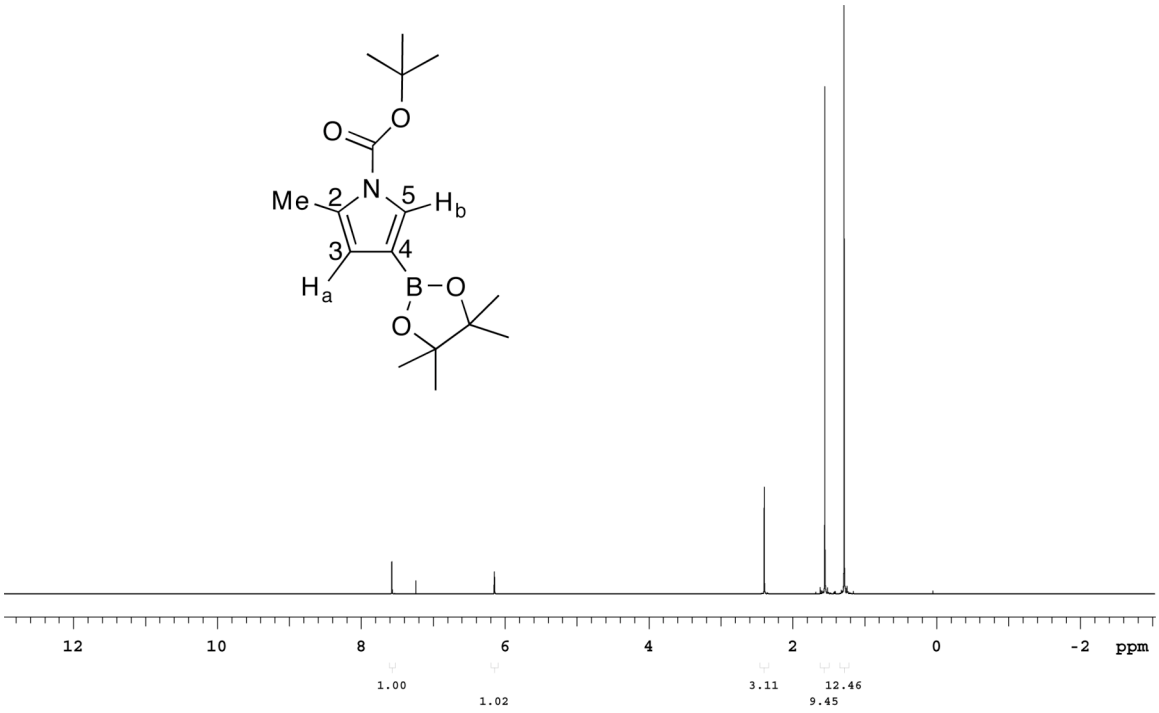



**Figure 3:** $^{1}H$ spectrum of N-Boc-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)pyrrole.

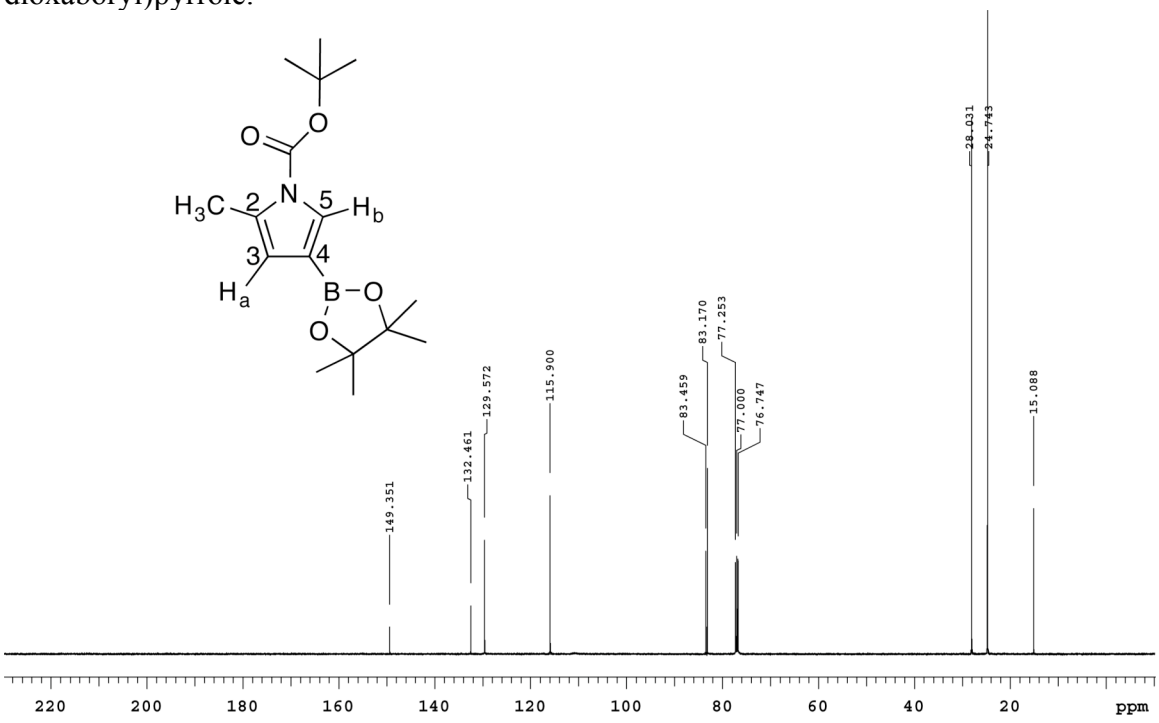
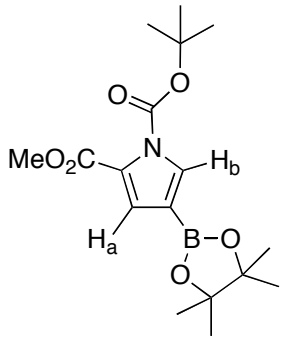



**Figure 4:** $^{13}C$ spectrum of N-Boc-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)pyrrole.

**Table 1, Entry 3: Borylation of N-Boc-methyl-2-pyrrolecarboxylate.**




The general procedure was applied to N-Boc-methyl-2-pyrrole carboxylate (450 mg, 2.00 mmol, 1 equiv) and HBPin (348 μL, 307 mg, 2.40 mmol, 1.20 equiv) at room temperature for 5 h. The product was isolated as a white solid (524 mg, 75% yield, mp 109-110 °C). $^{1}$H NMR ($CDCl_3$, 500 MHz): δ 7.65 (d, $J$ = 1.7 Hz, 1 H, $H_b$), 7.08 (d, $J$ = 1.7 Hz, 1 H, $H_a$), 3.79 (s, 3 H, C$H_3$), 1.54 (br s, 9 H, C$H_3$ of $^{t}$Bu), 1.27 (br s, 12 H, C$H_3$ of BPin); $^{13}$C NMR {$^{1}$H} ($CDCl_3$, 125 MHz): δ 161.1 (C=O), 148.0 (C=O), 134.7 (CH), 126.0 (C), 125.6 (CH), 84.9 (C), 83.5 (C), 51.8 ($CH_3$), 27.6 (3 $CH_3$ of $^{t}$Bu), 24.7 (4 $CH_3$ of BPin); $^{11}$B NMR ($CDCl_3$, 96 MHz): δ 29.9; FT-IR (neat) $\tilde{\nu}_{max}$: 2980, 1755, 1730, 1570, 1483, 1435, 1391, 1373, 1314, 1283, 1252, 1213, 1142, 106, 970, 957, 851, 775, 760, 706, 689 cm$^{-1}$; GC-MS (EI) *m/z* (% relative intensity): $(M-100)^+$ 251 (100), 236 (49), 208 (45), 165 (52), 152 (40), 151 (42), 120 (35), 94 (13); Anal. Calc'd for $C_{17}H_{26}BNO_6$: C, 58.14; H, 7.46; N, 3.99. Found: C, 57.84; H, 7.68; N, 3.98.

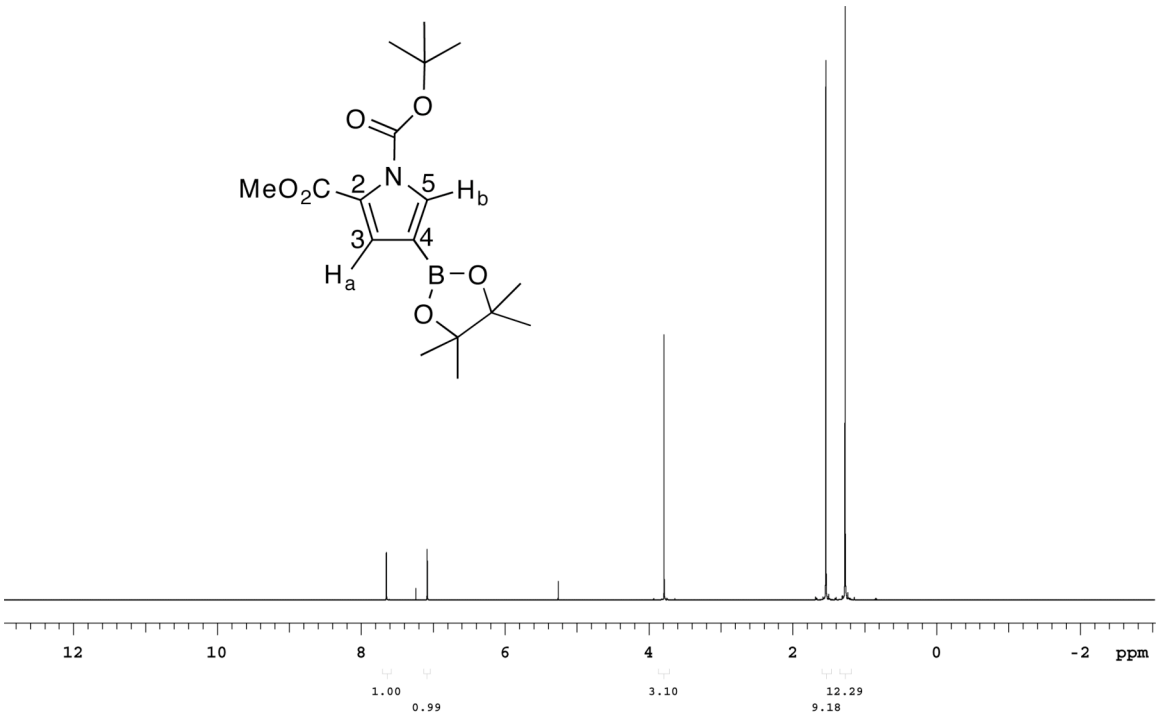



**Figure 5:** $^{1}H$ spectrum of N-Boc-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)pyrrolecarboxylate.

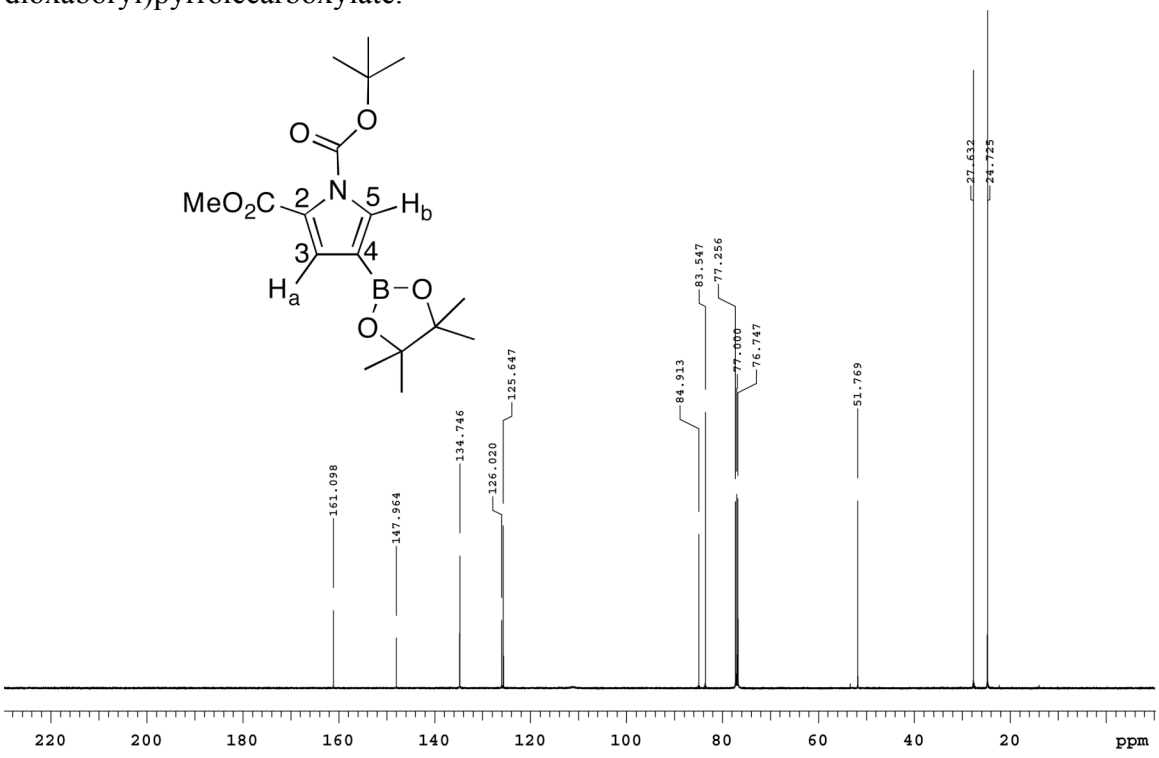
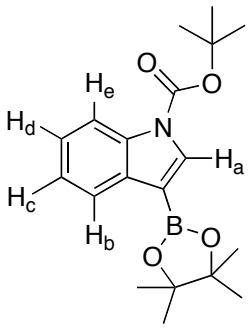



**Figure 6:** $^{13}C$ spectrum of N-Boc-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)pyrrolecarboxylate.

**Table 1, Entry 4: Borylation of N-Boc indole.**




The general procedure was applied to N-Boc indole (1085 mg, 5.00 mmol, 1 equiv) and HBPin (1451 μL, 1280 mg, 10.00 mmol, 2.00 equiv) at 60 °C for 8 h. The product was isolated as a white solid (1113 mg, 65% yield, mp 100-102 °C). $^{1}$H NMR ($CDCl_3$, 500 MHz): δ 8.16-8.14 (d, *J*= 8.1 Hz, 1 H, $H_e$), 8.00 (s, 1 H, $H_a$), 7.98-7.96 (m, 1 H, $H_b$), 7.31-7.23 (m, 2 H, $H_c$ , $H_d$), 1.65 (br s, 9 H, C$H_3$ of $^t$Bu), 1.36 (br s, 12 H, C$H_3$ of BPin); $^{13}$C NMR {$^{1}$H} ($CDCl_3$, 125 MHz): δ 149.4 (C=O), 136.1 (C), 135.2 (CH), 133.5 (C), 124.2 (CH), 122.9 (CH), 122.6 (CH), 114.9 (CH), 83.8 (C), 83.3 (C), 28.2 (3 $CH_3$ of $^t$Bu), 24.9 (4 $CH_3$ of BPin); $^{11}$B NMR ($CDCl_3$, 96 MHz): δ 30.4; FT-IR (neat) $\tilde{\nu}_{max}$: 3054, 2978, 2934, 1740, 1555, 1478, 1453, 1402, 1372, 1339, 1318, 1246, 1208, 1140, 1111, 1061, 986, 857, 766, 748 cm$^{-1}$; GC-MS (EI) *m/z* (% relative intensity): $(M-100)^+$ 243 (100), 228 (28), 157 (14), 143 (17); Anal. Calc'd for $C_{19}H_{26}BNO_4$: C, 66.49; H, 7.64; N, 4.08. Found: C, 66.70; H, 7.64; N, 3.95.

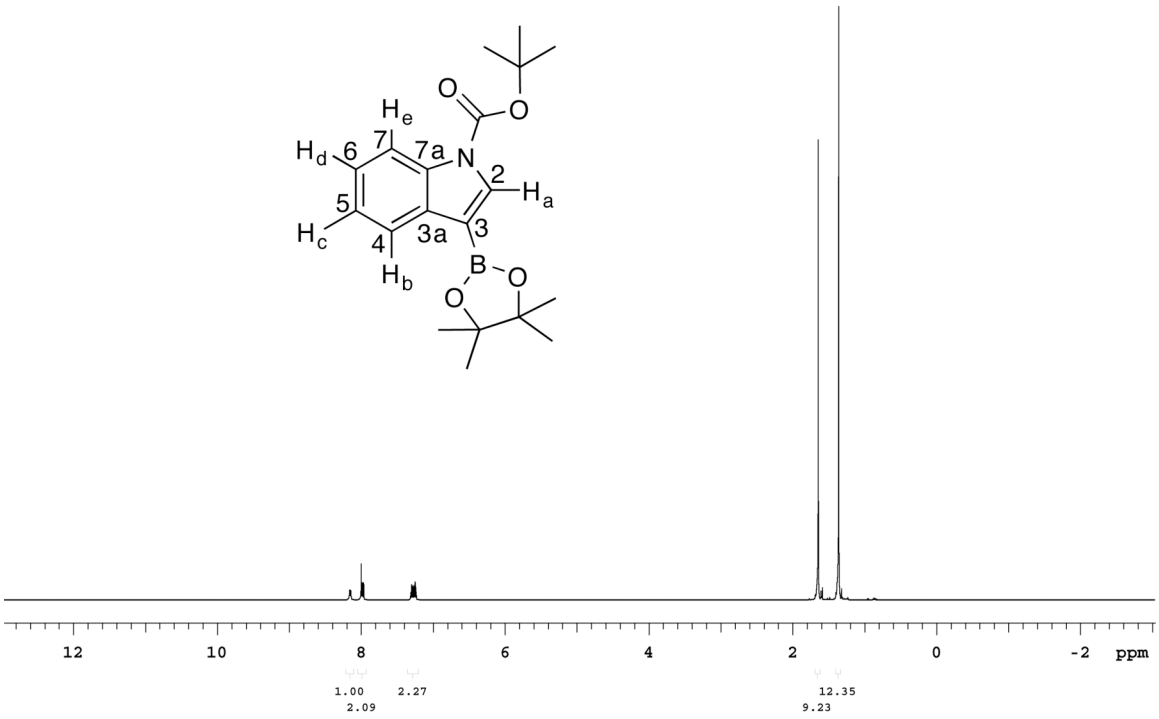



**Figure 7:** $^{1}H$ spectrum of N-Boc-3-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)indole.

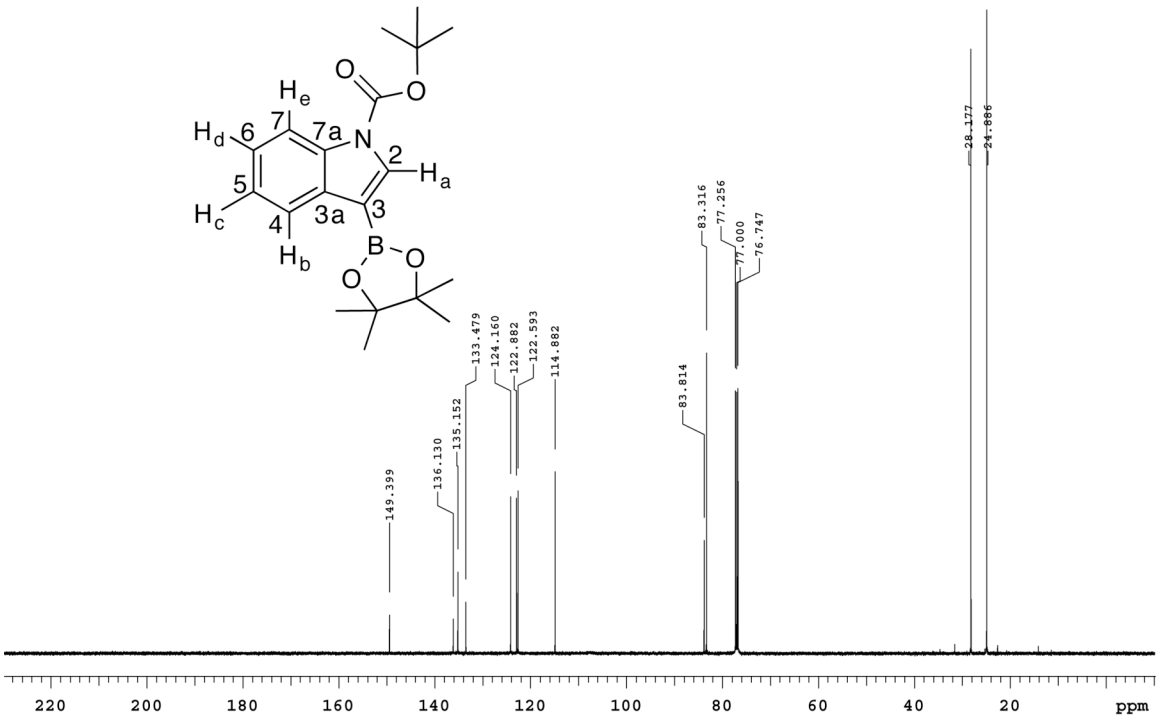
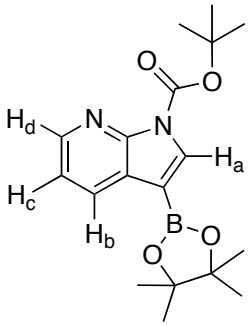



**Figure 8:** $^{13}C$ spectrum of N-Boc-3-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)indole.

**Table 1, Entry 5: Borylation of N-Boc-7-azaindole.**




The general procedure was applied to N-Boc-7-azaindole (218 mg, 1.00 mmol, 1 equiv) and HBPin (160 μL, 141 mg, 1.10 mmol, 1.10 equiv) at room temperature for 5 h. The product was isolated as a white solid (193 mg, 56% yield, mp 115-117 °C). $^{1}$H NMR ($CDCl_3$, 500 MHz): δ 8.46-8.45 (dd, $J$ = 4.9, 1.7 Hz, 1 H, $H_d$), 8.22-8.20 (dd, $J$ = 7.8, 1.7 Hz, 1 H, $H_b$), 8.01 (br s, 1 H, $H_a$), 7.18-7.16 (dd $J$ = 7.8, 4.6 Hz, 1 H, $H_c$), 1.62 (br s, 9 H, C$H_3$ of $^t$Bu), 1.33 (br s, 12 H, C$H_3$ of BPin); $^{13}$C NMR {$^{1}$H} ($CDCl_3$, 125 MHz): δ 149.3 (C=O), 147.6 (C), 145.1 (CH), 135.4 (CH), 130.9 (CH), 126.1 (C), 118.8 (CH), 84.3 (C), 83.5 (C), 28.1 (3 $CH_3$ of $^t$Bu), 24.8 (4 $CH_3$ of BPin); $^{11}$B NMR ($CDCl_3$, 96 MHz): δ 30.2; FT-IR (neat) $\tilde{\nu}_{max}$: 2980, 2934, 1763, 1736, 1599, 1547, 1477, 1418, 1372, 1316, 1285, 1267, 1248, 1211, 1142, 1107, 1069, 984, 858, 775, 681 cm$^{-1}$; GC-MS (EI) *m/z* (% relative intensity): $(M-100)^+$ 244 (100), 229 (38), 187 (35), 158 (37), 144 (46) 117 (11); Anal. Calc'd for $C_{18}H_{25}BN_2O_4$: C, 62.81; H, 7.32; N, 8.14. Found: C, 63.18; H, 7.59; N, 8.09.

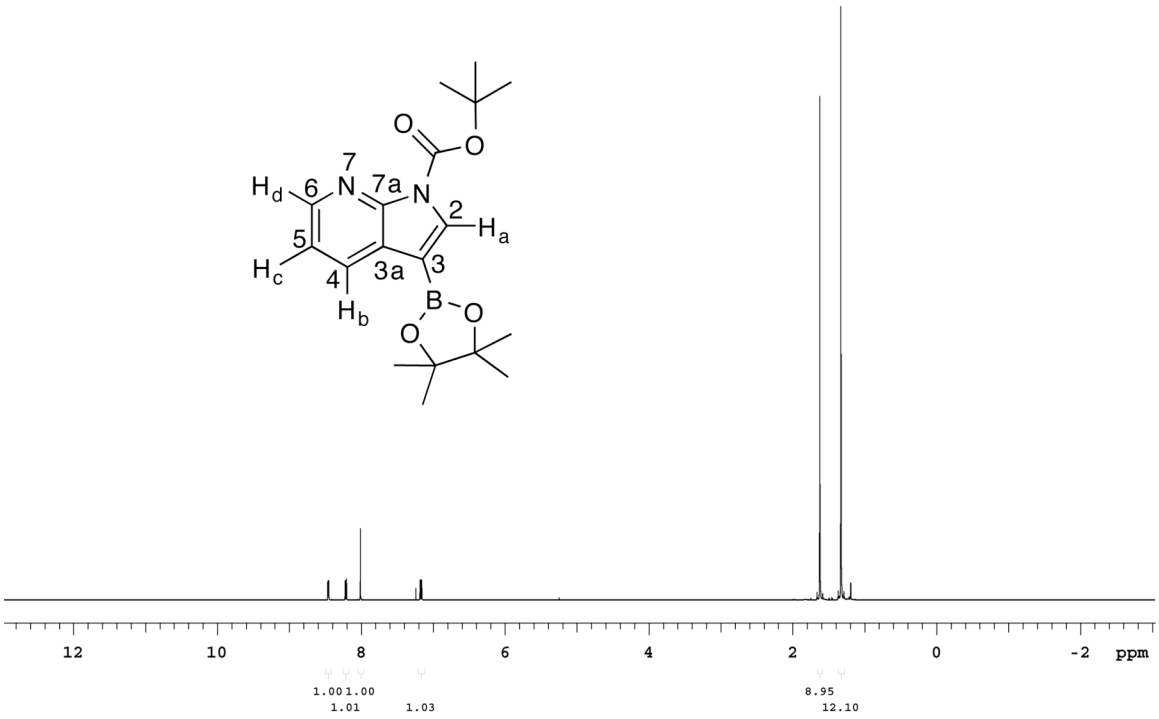



**Figure 9:** $^{1}$H spectrum of N-Boc-3-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-7-azaindole.

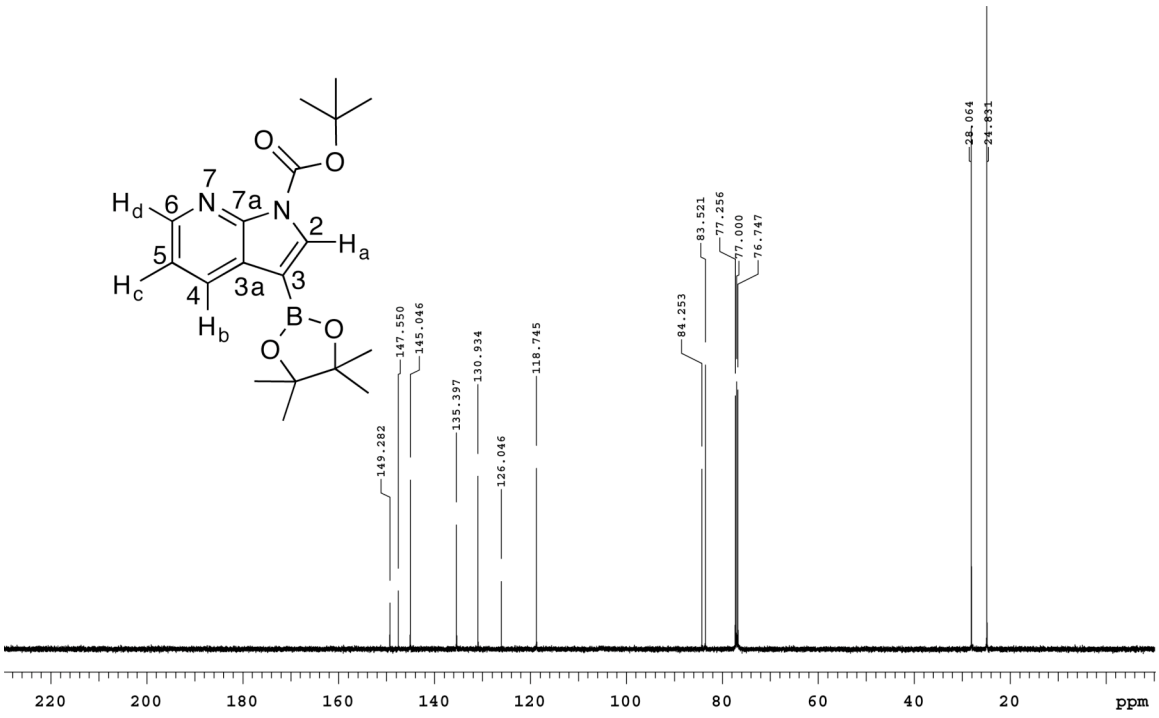
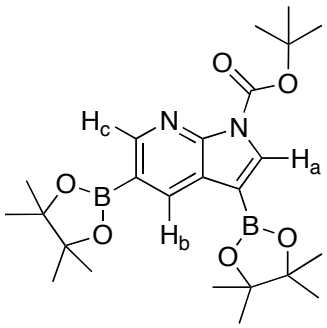



**Figure 10:** $^{13}$C spectrum of N-Boc-3-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-7-azaindole.

**Table 1, Entry 6: Diborylation of N-Boc-7-azaindole.**




The general procedure was applied to N-Boc-7-azaindole (218 mg, 1.00 mmol, 1 equiv) and HBPin (508 μL, 448 mg, 3.50 mmol, 3.50 equiv) at room temperature for 96 h. The product from plug with $CH_2Cl_2$ was not pure, so recrystallized from $CH_2Cl_2$/Hexane (1 : 2) as a pale yellow solid (253 mg, 54% yield, mp 176-178 °C). $^1$H NMR ($CDCl_3$, 500 MHz): δ 8.82 (d, $J$ = 1.7 Hz, 1 H, $H_c$), 8.54 (d, $J$ = 1.5 Hz, 1 H, $H_b$), 8.01 (s, 1 H, $H_a$), 1.63 (br s, 9 H, C$H_3$ of $^t$Bu), 1.35-1.34 (2 overlapping singlets, 24 H, C$H_3$ of BPin); $^{13}$C NMR {$^1$H} ($CDCl_3$, 125 MHz): δ 151.5 (CH), 151.1 (C), 147.5 (C), 137.4 (CH), 135.7 (CH), 125.2 (C), 84.3 (C), 83.9 (C), 83.6 (C), 28.1 (3 $CH_3$ of $^t$Bu), 24.85 (4 $CH_3$ of BPin), 24.84 (4 $CH_3$ of BPin); $^{11}$B NMR ($CDCl_3$, 96 MHz): δ 30.9; FT-IR (neat) $\tilde{\nu}_{max}$: 2980, 2934, 1765, 1738, 1543, 1476, 1418, 1372, 1341, 1306, 1246, 1142, 853, 698 cm$^{-1}$; GC-MS (EI) *m/z* (% relative intensity): $(M-100)^+$ 370 (100), 355 (13), 313 (10), 285 (45), 271 (14), 171 (10); Anal. Calc'd for $C_{24}H_{36}B_2N_2O_6$: C, 61.31; H, 7.72; N, 5.96. Found: C, 61.55; H, 7.90; N, 6.03.

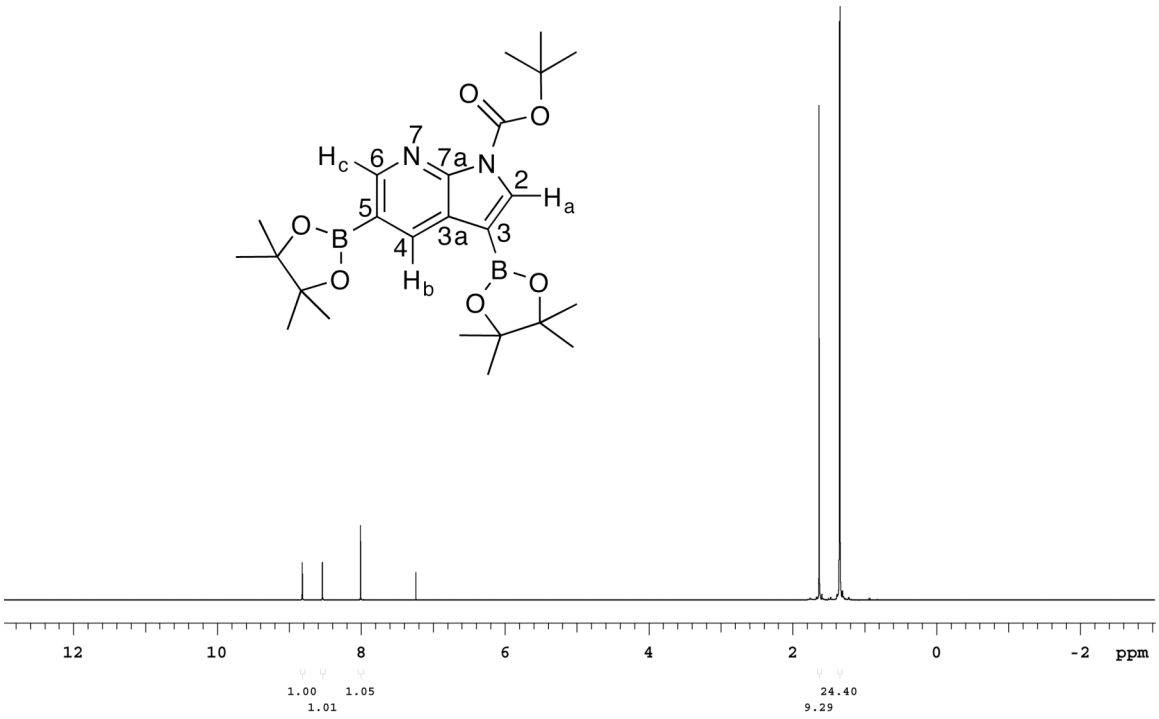



**Figure 11:** $^{1}H$ spectrum of N-Boc-3,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-7-azaindole.

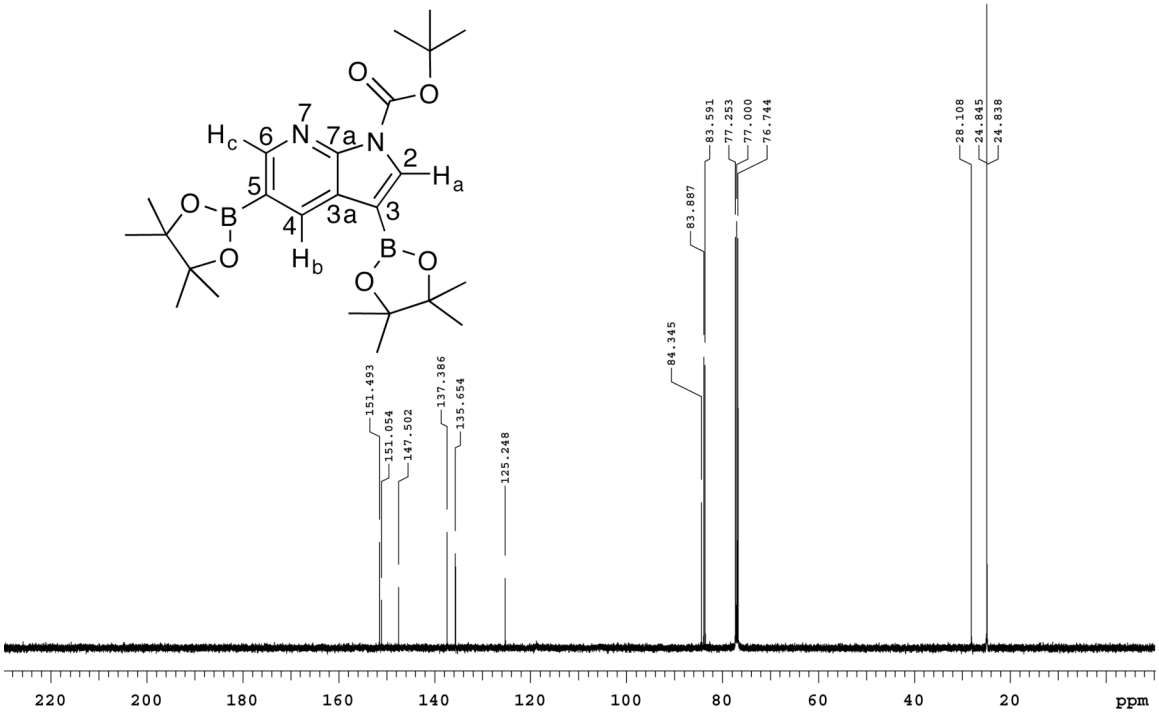
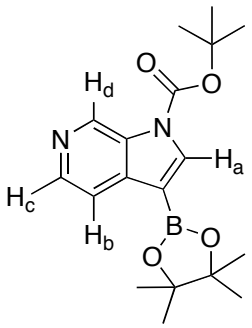



**Figure 12:** $^{13}C$ spectrum of N-Boc-3,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-7-azaindole.

**Table 1, Entry 7: Borylation of N-Boc-6-azaindole.**




The general procedure was applied to N-Boc-6-azaindole (218 mg, 1.00 mmol, 1 equiv) and HBPin (218 μL, 192 mg, 1.50 mmol, 1.50 equiv) at 55 °C for 20 h (80% conversion). The product was isolated as a white solid (48 mg, 14% yield, mp 114-124 °C). $^{1}$H NMR ($CDCl_3$, 500 MHz): δ 9.37 (br s, 1 H, $H_d$), 8.40-8.39 (d, $J$ = 5.4 Hz, 1 H, $H_c$), 8.09 (br s, 1 H, $H_a$), 7.85-7.84 (dd, $J$ = 5.4, 0.7 Hz, 1 H, $H_b$), 1.66 (br s, 9 H, C$H_3$ of $^{t}$Bu), 1.34 (br s, 12 H, C$H_3$ of BPin); $^{13}$C NMR {$^{1}$H} ($CDCl_3$, 125 MHz): δ 148.6 (C=O), 142.3 (CH), 139.3 (C), 137.9 (CH), 137.2 (CH), 133.1 (C), 117.1 (CH), 85.1 (C), 83.6 (C), 28.1 (3 $CH_3$ of $^{t}$Bu), 24.9 (4 $CH_3$ of BPin); $^{11}$B NMR ($CDCl_3$, 96 MHz): δ 30.0; FT-IR (neat) $\tilde{\nu}_{max}$: 3137, 2980, 2934, 1746, 1599, 1568, 1545, 1464, 1439, 1400, 1372, 1327, 1310, 1252, 1213, 1138, 1069, 1038, 857, 831, 735 cm$^{-1}$; GC-MS (EI) *m/z* (% relative intensity): $(M-100)^+$ 244 (100), 229 (60), 207 (11), 158 (28), 144 (62), 118 (17), 91 (10); Anal. Calc'd for $C_{18}H_{25}BN_2O_4$: C, 62.81; H, 7.32; N, 8.14. Found: C, 63.13; H, 7.72; N, 8.06.

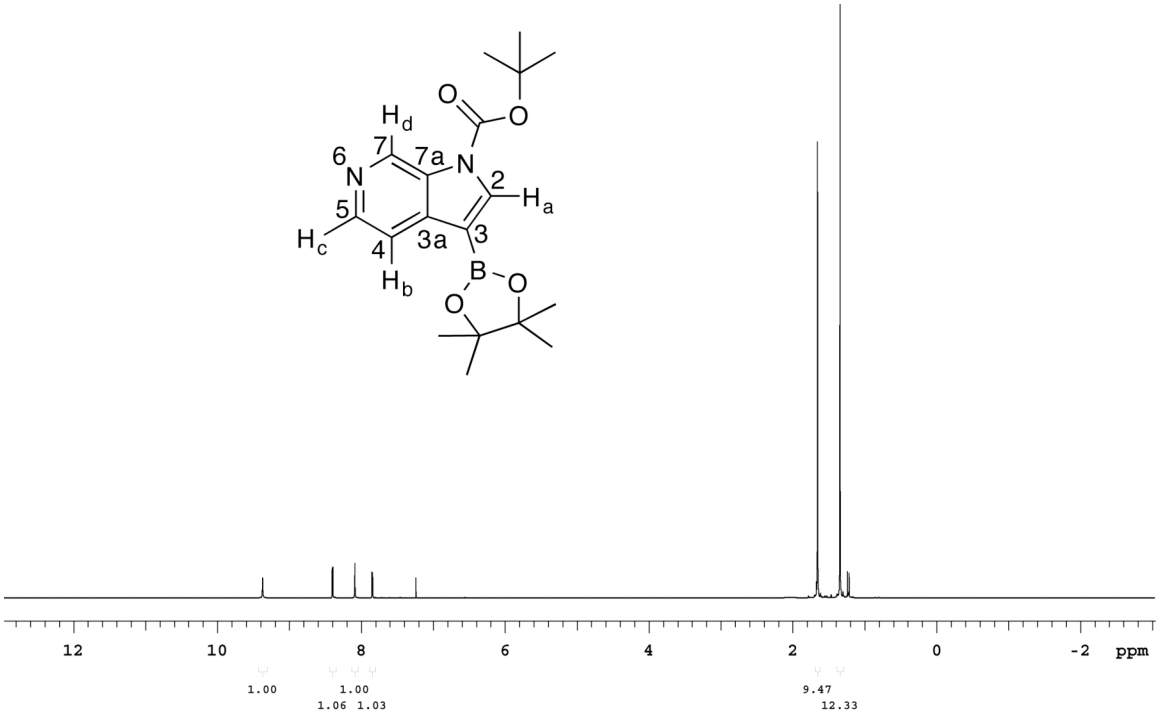



**Figure 13:** $^{1}H$ spectrum of N-Boc-3-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-6-azaindole.

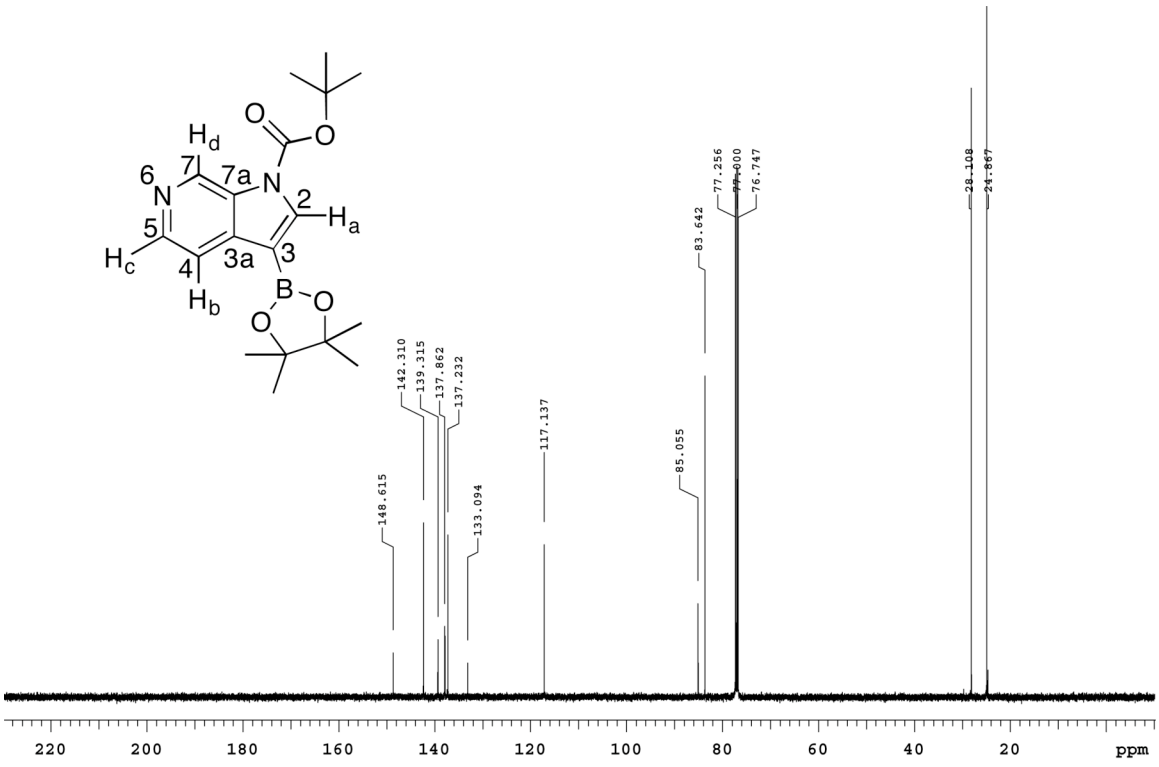
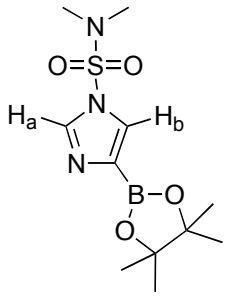



**Figure 14:** $^{13}C$ spectrum of N-Boc-3-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-6-azaindole.

**Table 1, Entry 9: Borylation of N,N-dimethylimidazole-1-sulfonamide.**



The general procedure was applied to N,N-dimethylimidazole-1-sulfonamide (175 mg, 1.00 mmol, 1 equiv) and $B_2Pin_2$ (254 mg, 1.00 mmol, 1 equiv) at room temperature for 65 h. The crude reaction mixture was washed with pentane, 3 mL portions, until the washings were colorless. The product was isolated as an off white solid (249 mg, 82% yield, mp 118-122 °C). $^1$H NMR ($CDCl_3$, 500 MHz): δ 7.95 (d, $J$ = 1.2 Hz, 1 H, $H_a$), 7.66 (d, $J$ = 1.2 Hz, 1 H, $H_b$), 2.83 (s, 6 H, C$H_3$ of $NMe_2$), 1.32 (br s, 12 H, C$H_3$ of BPin); $^{13}$C NMR {$^1$H} ($CDCl_3$, 125 MHz): δ 137.9 (CH), 126.9 (CH), 84.2 (C), 38.2 (2 $CH_3$ of $NMe_2$), 24.8 (4 $CH_3$ of BPin); $^{11}$B NMR ($CDCl_3$, 96 MHz): δ 29.0; FT-IR (neat) $\tilde{\nu}_{max}$: 2980, 2884, 1543, 1474, 1393, 1299, 1177, 1132, 1065, 966, 729 cm$^{-1}$; GC-MS (EI) *m/z* (% relative intensity): 301 (68), 300 (24), 286 (28), 202 (20), 193 (100), 192 (28), 149 (22), 135 (52), 109 (30), 108 (42), 95 (19), 43 (25); Anal. Calc'd for $C_{11}H_{20}BN_3O_4S$: C, 43.87; H, 6.69; N, 13.95. Found: C, 44.03; H, 7.08; N, 14.12.

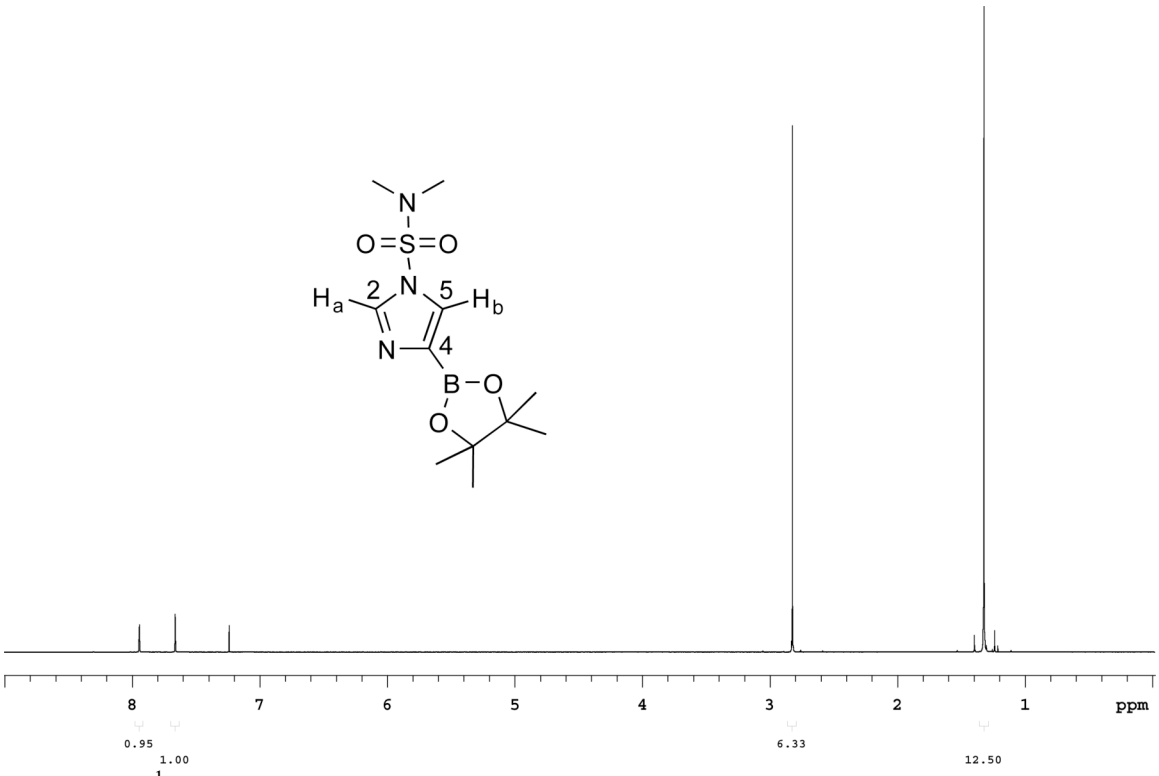



**Figure 15:** $^{1}$H spectrum of N,N-dimethylsulfonamide-4-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)imidazole.

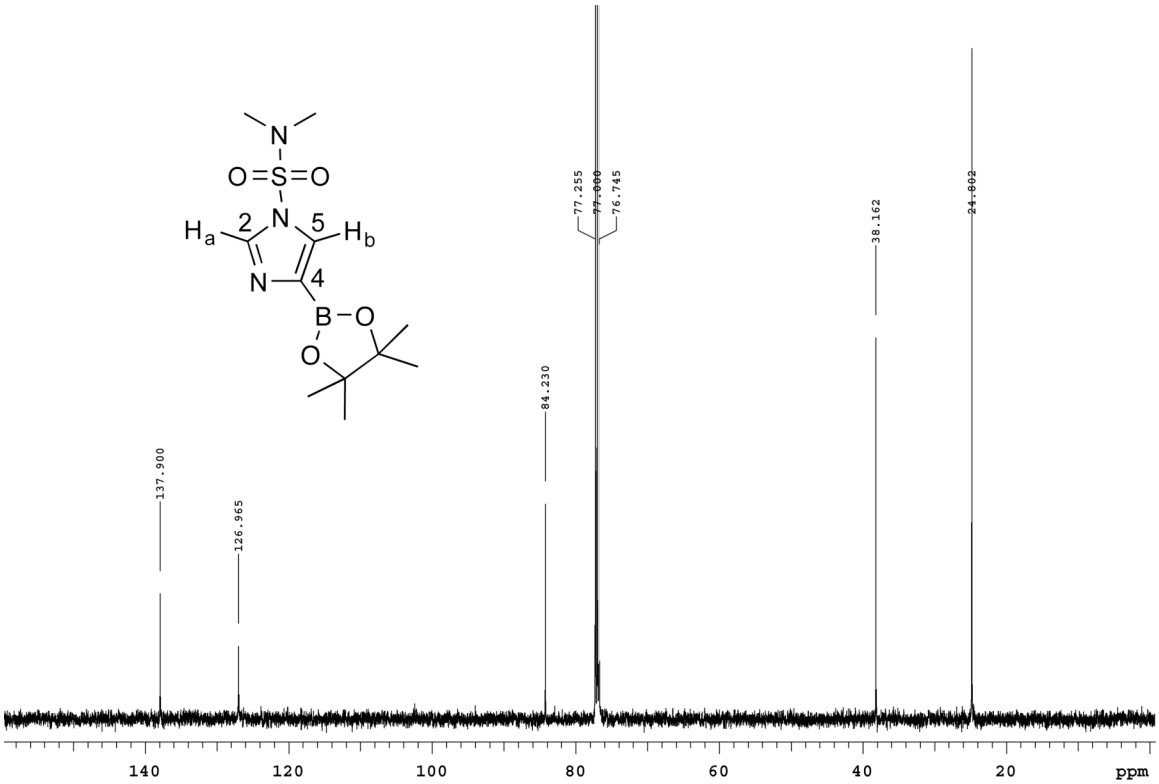
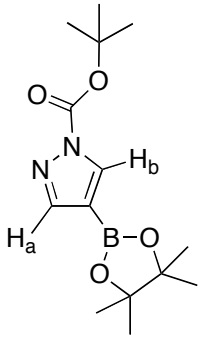



**Figure 16:** $^{13}$C spectrum of N,N-dimethylsulfonamide-4-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)imidazole.

**Table 1, Entry 10: Borylation of N-Boc pyrazole.**




The general procedure was applied to N-Boc pyrazole (168 mg, 1.00 mmol, 1 equiv) and HBPin (218 μL, 192 mg, 1.50 mmol, 1.5 equiv) at room temperature for 90 min. The product was isolated as a pale yellow solid (223 mg, 76% yield, mp 84-86 °C). $^{1}$H NMR ($CDCl_3$, 500 MHz): δ 8.34 (d, $J$ = 0.7 Hz, 1 H, $H_b$), 7.88 (d, $J$ = 0.6 Hz, 1H, $H_a$), 1.60 (br s, 9 H, C$H_3$ of $^t$Bu), 1.29 (br s, 12 H, C$H_3$ of BPin); $^{13}$C NMR {$^{1}$H} ($CDCl_3$, 125 MHz): δ 148.6 (CH), 147.2 (C=O), 137.7 (CH), 85.5 (C), 83.8 (C), 27.9 (3 $CH_3$ of $^t$Bu), 24.7 (4 $CH_3$ of BPin); $^{11}$B NMR ($CDCl_3$, 96 MHz): δ 29.2; FT-IR (neat) $\tilde{\nu}_{max}$: 2980, 1748, 1572, 1393, 1372, 1318, 1289, 1277, 1256, 1144, 1092, 982, 959, 857, 845, 772, 696 cm$^{-1}$; GC-MS (EI) *m/z* (% relative intensity): $(M\text{-}99)^+$ 195 (88), 194 (25), 179 (100), 178 (25), 151 (8), 95 (35), 43 (12); Anal. Calc'd for $C_{14}H_{23}BN_2O_4$: C, 57.16; H, 7.88; N, 9.52. Found: C, 57.56; H, 7.90; N, 9.75.

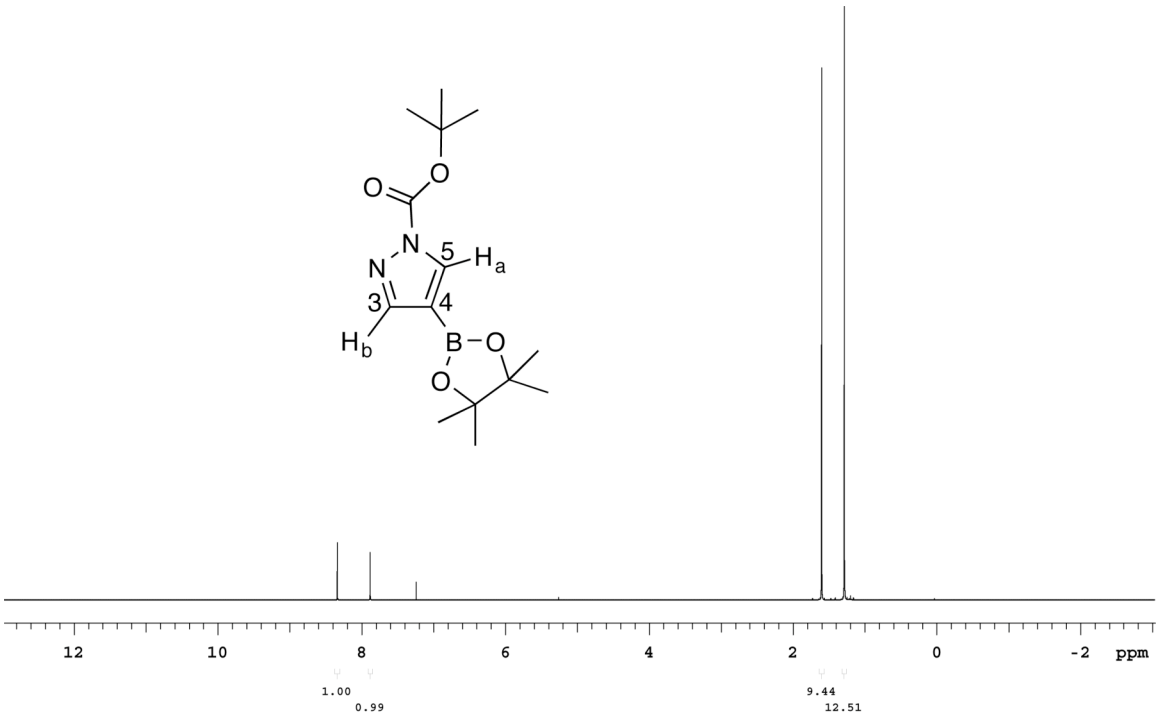



**Figure 17:** $^{1}$H spectrum of N-Boc-4-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-pyrazole.

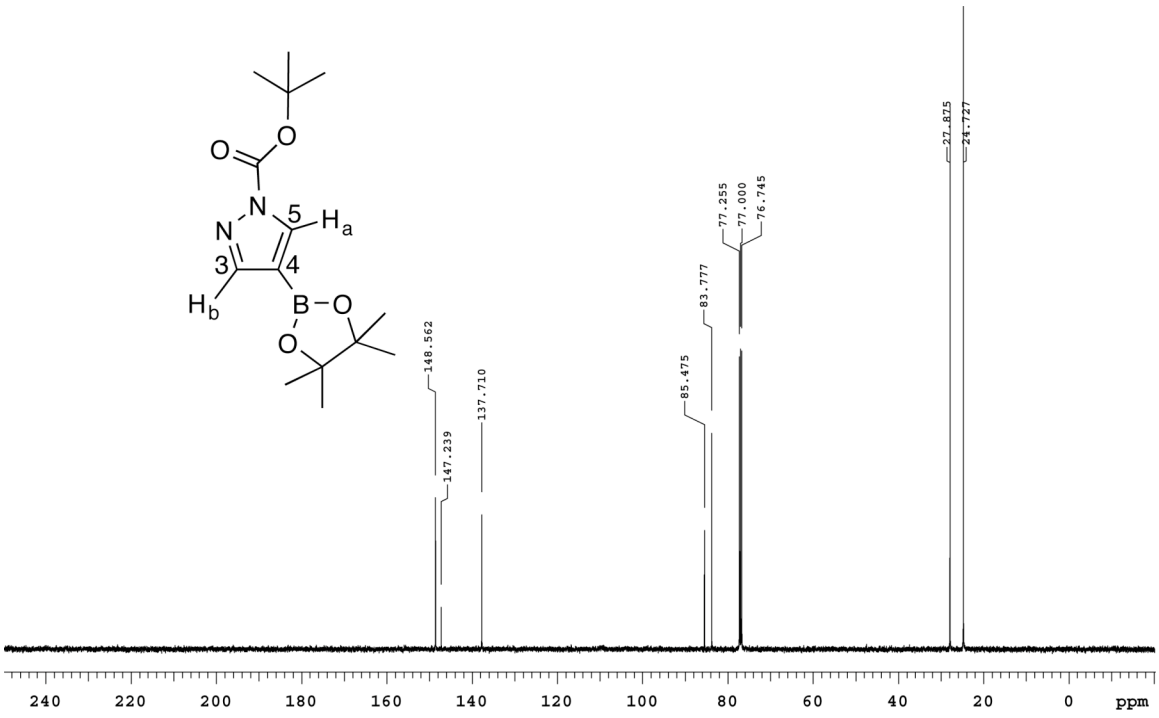
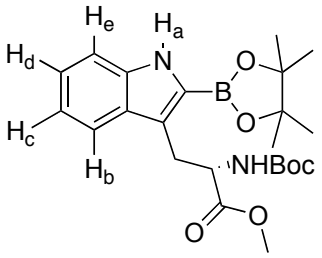



**Figure 18:** $^{13}$C spectrum of N-Boc-4-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-pyrazole.

**Table 1,Entry 11: Monoborylation of Boc-L-tryptophan methyl ester.**




In a glove box, the Boc-L-tryptophan methyl ester (159 mg, 0.5 mmol, 1 equiv) was weighed in a 20 mL vial and dissolved in 10 mL of methyl *tert*-butyl ether. Two separate test tubes were charged with $[Ir(OMe)(COD)]_2$ (10 mg, 0.015 mmol, 6 mol % Ir) and d$^t$bpy (8 mg, 0.03 mmol, 6 mol %). HBPin (15 μL, 0.2 equiv) was added to the $[Ir(OMe)(COD)]_2$ test tube. Methyl *tert*-butyl ether (1 mL) was added to the d$^t$bpy containing test tube in order to dissolve the d$^t$bpy. The d$^t$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 20 mL reaction vial containing the Boc-L-tryptophan methyl ester. Additional methyl *tert*-butyl ether (2 × 1 mL) was used to wash the test tubes and the washings were transferred to the reaction vial. $B_2Pin_2$ (127 mg, 0.5 mmol, 1 equiv) was weighed in a test tube and was transferred to the reaction vial by dissolving in methyl *tert*-butyl ether (5 mL). The reaction vial was stirred at room temperature inside the glove box. The reaction was monitored by TLC. The reaction was stopped after 45 minutes. Volatile materials were removed on a rotary evaporator. The ratio of starting indole substrate to monoborylated product to diborylated product was 0.42:1.0:0.05 by $^1$H NMR of the crude reaction mixture. The crude material was dissolved in $CH_2Cl_2$ (2 mL) and placed on a silica column. Column chromatography (silica gel, hexanes/ethyl acetate 3:1, $R_f$ 0.3) gave three fractions. The first fraction (13 mg) was 1:1 mixture of mono and

diborylated products. The second fraction (95 mg, 43% yield based on starting indole used) was pure monoborylated product. The third fraction was recovered unreacted starting indole substrate (50 mg). The monoborylated product in the second fraction was obtained as a white solid (95 mg, 63% yield based on recovered starting indole, mp 183-185 °C). The monoborylated product exists as 80:20 mixture of two amide rotamers at room temperature by $^{1}$H NMR. Different $^{1}$H NMR peaks for the two amide rotamers coalesce at 70 °C in $C_6D_6$. Regiochemistry of the monoborylated product was assigned by NMR spectroscopy. $^{1}$H NMR ($CDCl_3$, 300 MHz): δ 8.48 (br s, 1 H, N-H), 7.66 (d, $J$ = 8.1 Hz, 1 H), 7.32 (d, $J$ = 8.1 Hz, 1 H), 7.19-7.24 (dt, $J$ = 7.5, 1.0 Hz, 1 H), 7.07-7.12 (dt, $J$ = 7.5, 1.0 Hz, 1 H), 5.94 – 5.56 (d, $J$ = 7.1 Hz, 1 H, N-H both rotamers), 4.32-4.38 (m, 1 H both rotamers), 3.71 (s, 3 H), 3.27-3.45 (m, 2H), 1.39 (br s, 6 H, 2 $CH_3$ of BPin), 1.37 (br s, 6 H, 2 $CH_3$ of BPin), 1.18-1.34 (br, 9 H, $CH_3$ of Boc); $^{13}$C NMR {$^{1}$H} ($CDCl_3$, 75 MHz): δ 173.4 (C=O), 155.6 (C=O), 138.3 (CH), 128.0 (C), 124.0 (CH), 123.3 (C), 119.7 (CH), 119.5 (C), 111.4 (CH), 84.5 (2 C), 79.2 (C), 55.2 (CH), 51.9 ($OCH_3$), 28.3 ($CH_3$ of Boc), 27.6 ($CH_2$), 24.9 (2 $CH_3$ of BPin), 24.7 (2 $CH_3$ of BPin); $^{11}$B NMR ($CDCl_3$, 96 MHz): δ 29.4; FT-IR (neat) $\tilde{\nu}_{max}$: 3379, 2978, 1718, 1550, 1516, 1390, 1325, 1267, 1169, 1112, 856, 744 cm$^{-1}$; GC-MS (EI) *m/z* (% relative intensity): $M^+$ 444 (0.97), 370 (0.52), 344 (0.40), 327 (0.73), 285 (1.3), 256 (100), 155 (35.2); $[\alpha]^{20}_{D}$ +14.3 (*c* 0.7, $CH_2Cl_2$); Anal. Calc'd for $C_{23}H_{33}BN_2O_6$: C, 62.17; H, 7.49; N, 6.30. Found: C, 62.84; H, 7.88; N, 6.11; HRMS (EI): *m/z* 444.2433 [($M^+$; Calc'd for $C_{23}H_{33}BN_2O_6$: 444.2432].

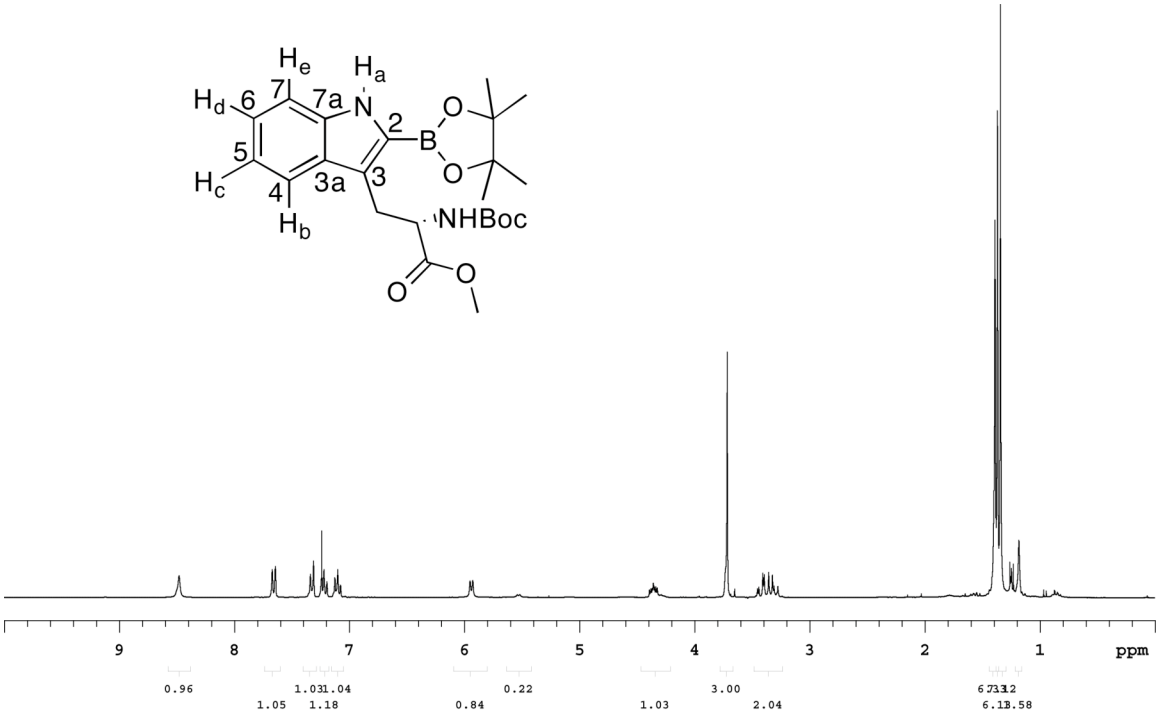



**Figure 19:** $^{1}H$ spectrum of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-Boc-L-tryptophan methyl ester.

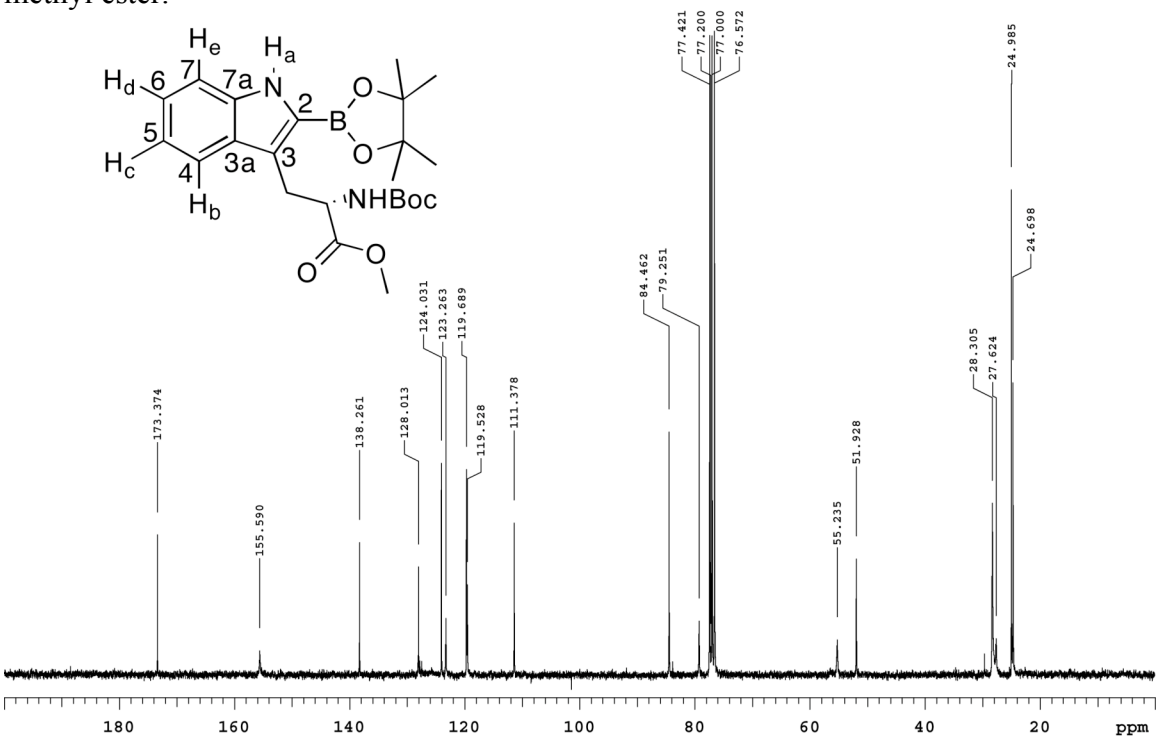
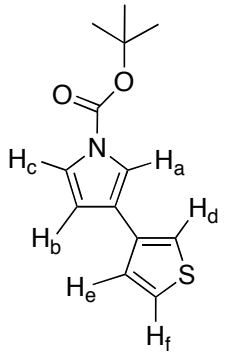



**Figure 20:** $^{13}C$ spectrum of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-Boc-L-tryptophan methyl ester.

**Scheme 1: One-pot borylation/C-C cross-coupling of N-Boc pyrrole with 3-chlorothiophene.**




The general borylation procedure was applied to N-Boc pyrrole (167 µL, 167 mg, 1.00 mmol, 1 equiv) and HBPin (217 µL, 192 mg, 1.50 mmol, 1.50 equiv) at 60 °C for 30 h. The GC-FID showed 100% consumption of the starting material. The reaction mixture was pumped down under high vacuum for 2 h to remove the volatile materials. The Schlenk flask was brought into the glove box, where $Pd_2dba_3$ (9.2 mg, 0.01 mmol), XPhos (19.1 mg, 0.04 mmol) and powdered, anhydrous $K_3PO_4$ (425 mg, 2.00 mmol, 2.0 equiv) were added. The Schlenk tube was sealed and brought out of the glove box. The Schlenk tube was opened under argon and was capped with a rubber septum. The Schlenk tube was then evacuated and backfilled with argon (this sequence was carried out two times). *t*-Amyl alcohol (2.00 mL) and 3-chlorothiophene (93 µL, 119 mg, 1.00 mmol, 1.0 equiv) were added via syringe through the septum. The septum was then replaced with a Teflon screwcap and flushed with argon twice as mentioned previously. The Schlenk tube was then sealed and heated at 80 °C for 48 h. At this point the reaction mixture was allowed to cool to room temperature. The reaction solution was then filtered through a thin pad of silica gel (eluting with ethyl acetate) and the eluent was concentrated under reduced pressure. The crude material so obtained was purified via

flash chromatography on silica gel (5% EtOAc/Hexanes) to provide the Suzuki product as a pale yellow solid (189 mg, 76% yield, mp 49-51 °C). $^{1}$H NMR ($CDCl_3$, 300 MHz): δ 7.40-7.39 (t, $J$ = 1.7 Hz, 1 H, $H_a$), 7.32-7.30 (dd, $J$ = 4.9, 2.9 Hz, 1H, $H_f$), 7.27-7.23 (m, 3H, $H_c$, $H_d$, $H_e$), 6.45-6.43 (dd, $J$ = 3.2, 1.7 Hz, 1 H, $H_b$), 1.60 (br s, 9 H, C$H_3$ of $^{t}$Bu); $^{13}$C NMR {$^{1}$H} ($CDCl_3$, 125 MHz): δ 148.8 (C=O), 135.6 (C), 125.9 (2xCH), 123.2 (C), 120.8 (CH), 118.6 (CH), 115.6 (CH), 110.8 (CH), 83.8 (C), 27.9 (3 $CH_3$ of $^{t}$Bu); FT-IR (neat) $\tilde{\nu}_{max}$: 3144, 3108, 2980, 2934, 1742, 1489, 1412, 1372, 1345, 1327, 1314, 1271, 1258, 1227, 1161, 1146, 1078, 974, 851, 770 cm$^{-1}$; GC-MS (EI) *m/z* (% relative intensity): $M^+$ 249 (3), 193 (100), 149 (68), 148 (26), 121 (20), 57 (33); Anal. Calc'd for $C_{13}H_{15}NO_2S$: C, 62.62; H, 6.06; N, 5.62. Found: C, 62.53; H, 5.99; N, 5.52.

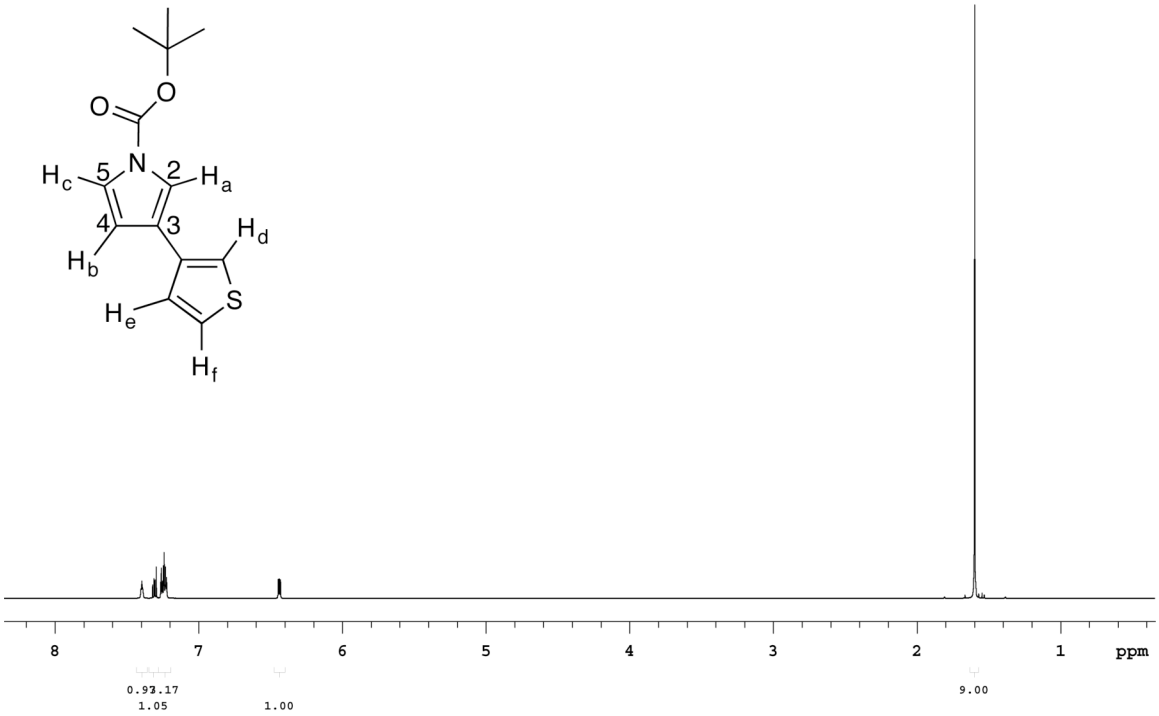



**Figure 21:** $^{1}H$ spectrum of N-Boc-3-(3′-thiophene)-pyrrole.

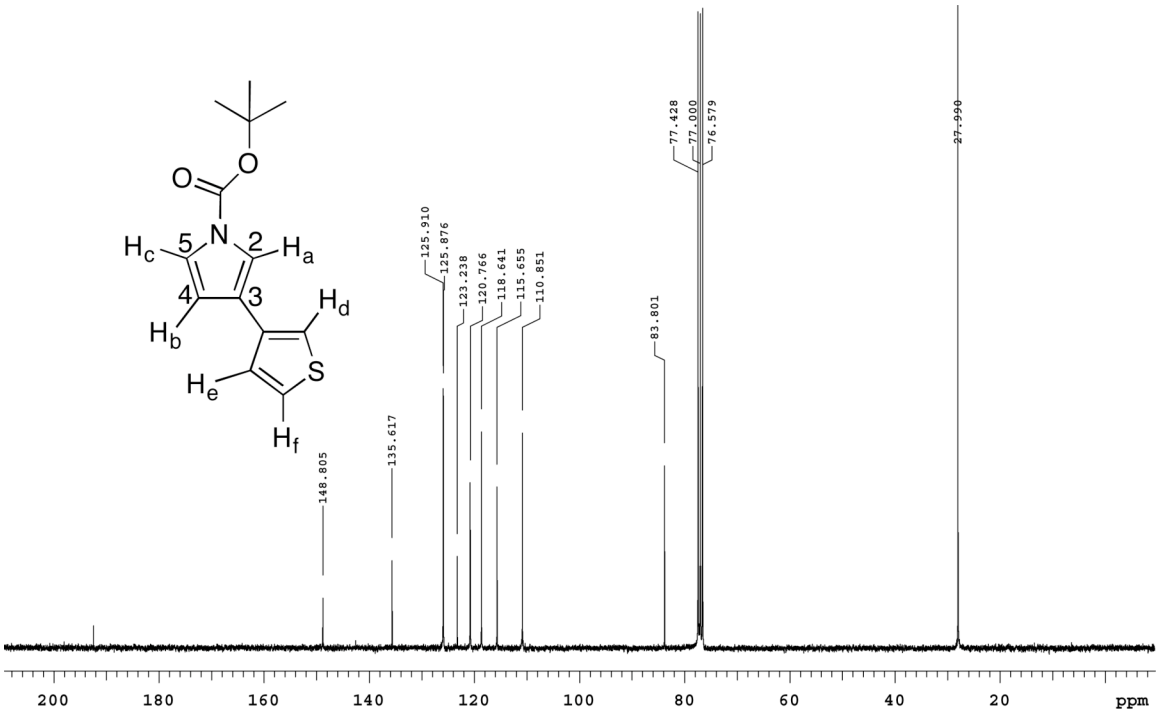
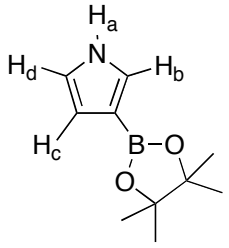



**Figure 22:** $^{13}C$ spectrum of N-Boc-3-(3′-thiophene)-pyrrole.

**General Procedure for Boc Deprotection**

Unless otherwise specified, all reactions followed this general procedure. A Schlenk flask, equipped with a magnetic stirring bar, was charged with the substrate and heated in air at specified temperature until bubbling ceases. The crude material was dissolved in $CH_2Cl_2$ and passed through a plug of silica. Evaporation of solvent afforded the product.

**Table 2, Entry 1: Deprotection of N-Boc-3-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)pyrrole.**




The general procedure for deprotection was applied to N-Boc-3-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)pyrrole (2930 mg, 10.00 mmol) at 180 °C for 35 min. The product was isolated as a white solid (1548 mg, 80% yield, mp 102-104 °C). $^1$H NMR ($CDCl_3$, 500 MHz): δ 8.61 (br s, 1 H, $H_a$), 7.24-7.22 (ddd, $J$ =1.5, 1.7, 2.7 Hz, 1 H, $H_b$), 6.83-6.81 (dd, $J$ =1.7, 2.5 Hz, 1 H, $H_d$), 6.55-6.54 (ddd, $J$ =1.5, 2.5, 2.6 Hz, 1 H, $H_c$), 1.31 (br s, 12 H, C$H_3$ of BPin); $^{13}$C NMR {$^1$H} ($CDCl_3$, 125 MHz): δ 127.0 (CH), 118.6 (CH), 113.8 (CH), 82.9 (C), 24.8 (4 $CH_3$ of BPin); $^{11}$B NMR ($CDCl_3$, 96 MHz): δ 30.6; FT-IR (neat) $\tilde{\nu}_{max}$: 3372, 3121, 2980, 2930, 1549, 1495, 1429, 1418, 1383, 1371, 1318, 1291, 1165, 1140, 1107, 966, 930, 860, 737, 691, 592 cm$^{-1}$; GC-MS (EI) *m/z* (% relative intensity): $M^+$ 193 (100), 178 (20), 150 (9), 107 (21); Anal. Calc'd for $C_{10}H_{16}BNO_2$: C, 62.22; H, 8.35; N, 7.26. Found: C, 62.46; H, 8.35; N, 7.35.

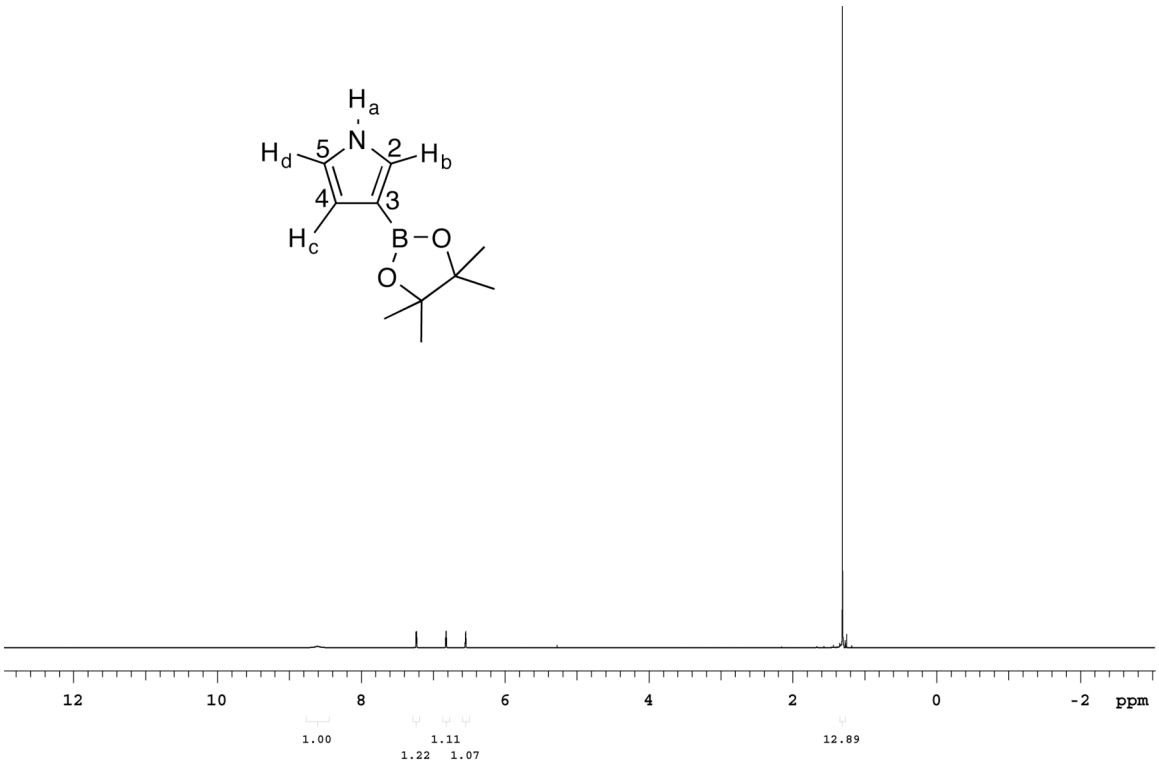



**Figure 23:** [1]H spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-pyrrole.

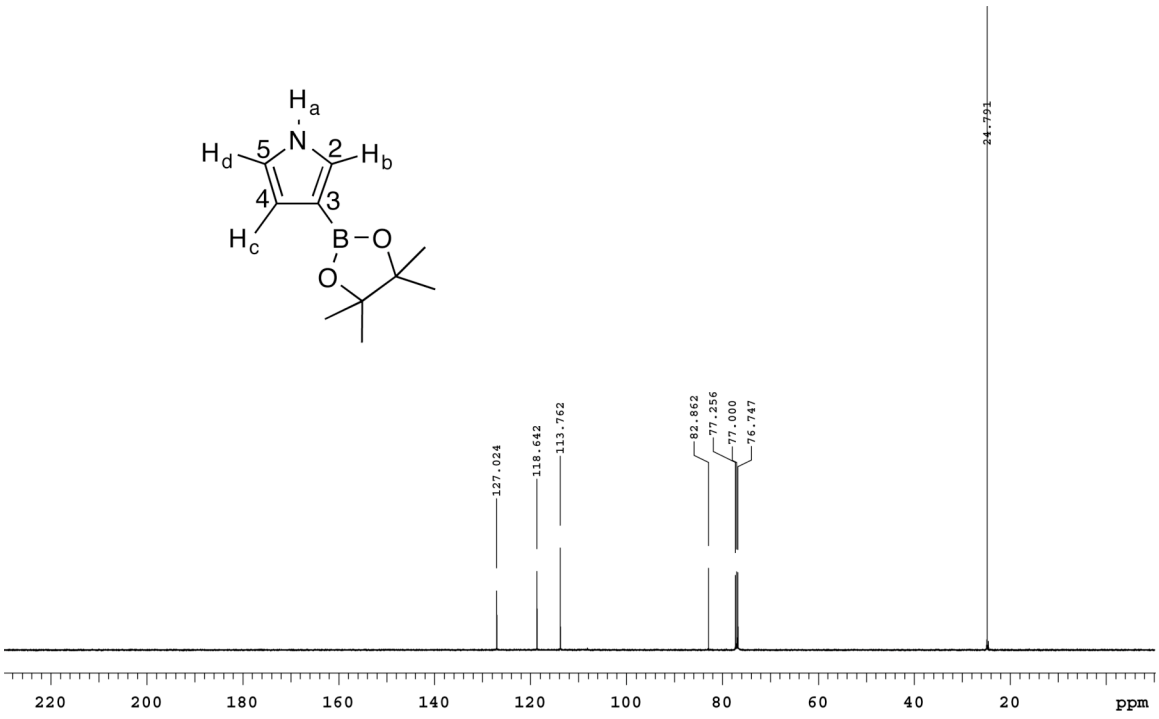
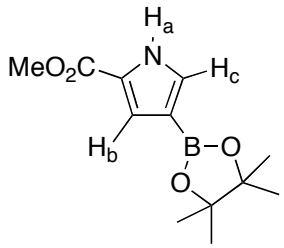


**Figure 24:** $^{13}C$ spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-pyrrole

**Table 2, Entry 2: Deprotection of N-Boc-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)pyrrole carboxylate.**




The general procedure for deprotection was applied to N-Boc-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)pyrrolecarboxylate (150 mg, 0.43 mmol) at 180 °C for 18 min. The product was isolated as a white solid (82 mg, 76% yield, mp 133-135 °C). $^1H$ NMR ($CDCl_3$, 500 MHz): δ 9.42 (br s, 1 H, *$H_a$*), 7.32-7.31 (dd, *J*= 2.9, 1.5 Hz, 1 H, *$H_c$* ), 7.22-7.21 (dd, *J*= 2.4, 1.5 Hz, 1 H, *$H_b$*), 3.82 (s, 3 H, $CH_3$), 1.29 (br s, 12 H, C*$H_3$* of BPin) ;$^{13}C$ NMR {$^1H$} ($CDCl_3$, 125 MHz): δ 161.6 (C=O), 130.9 (CH), 123.9 (C), 121.2 (CH), 83.2 (C), 51.5 ($CH_3$), 24.8 (4 $CH_3$ of BPin); $^{11}B$ NMR ($CDCl_3$, 96 MHz): δ 30.2; FT-IR (neat) $\tilde{\nu}_{max}$: 3308, 2978, 1707, 1564, 1499, 1443, 1363, 1284, 1271, 1211, 1144, 1078, 968, 857, 772, 743, 691 $cm^{-1}$; GC-MS (EI) *m/z* (% relative intensity): $M^+$ 251 (100), 236 (25), 208 (29), 176 (18), 165 (27), 152 (7), 150 (8), 120 (9); Anal. Calc'd for $C_{12}H_{18}BNO_4$: C, 57.40; H, 7.23; N, 5.58. Found: C, 57.19; H, 7.37; N, 5.51.

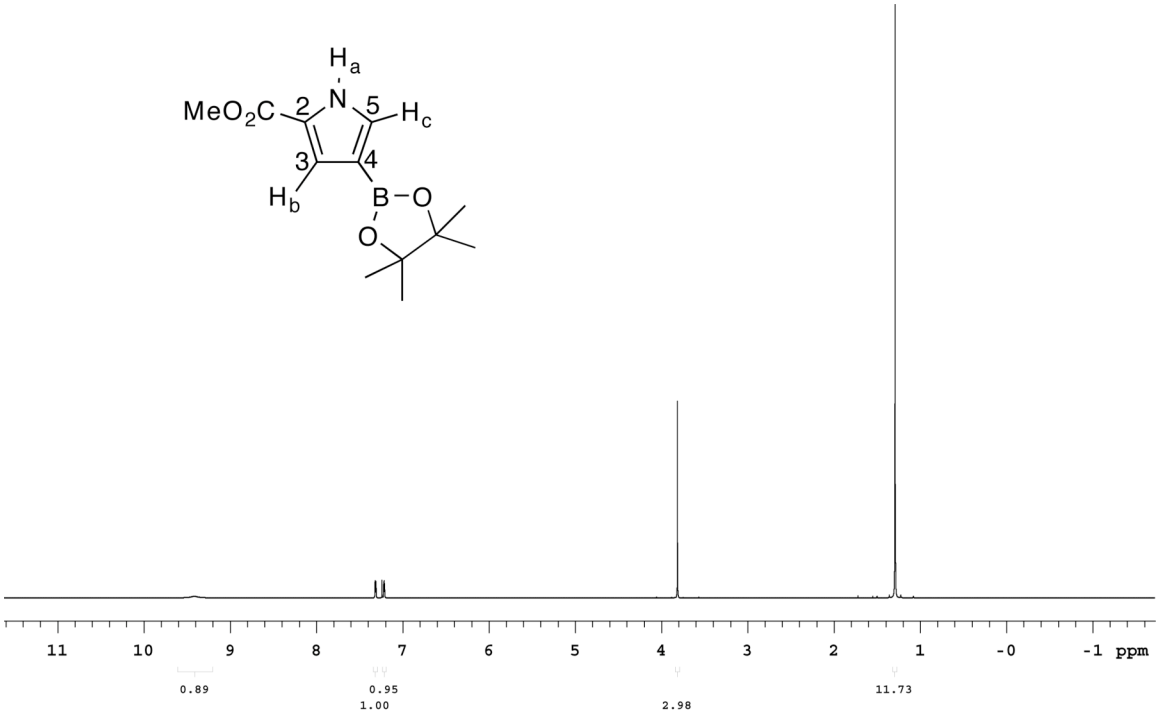



**Figure 25:** $^{1}H$ spectrum of 2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-pyrrole carboxylate.

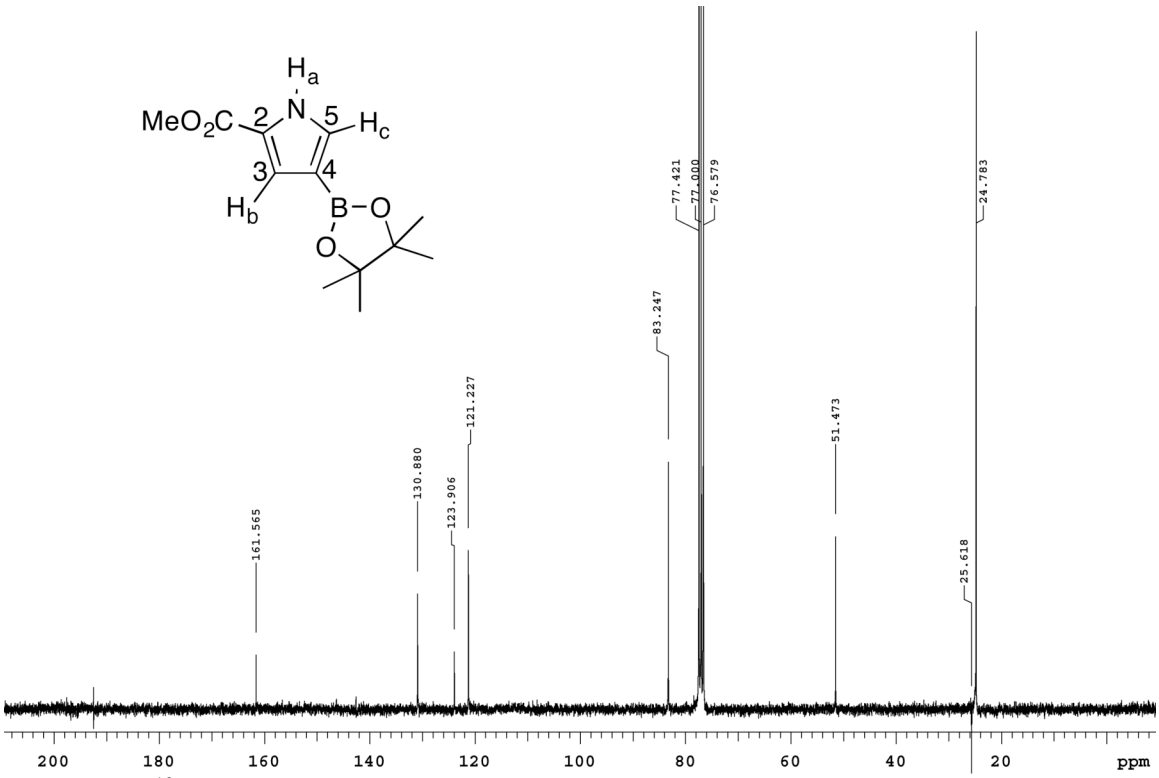
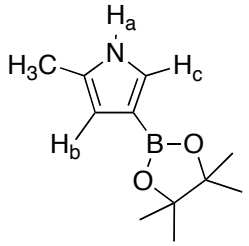



**Figure 26:** $^{13}C$ spectrum of 2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-pyrrole carboxylate.

**Table 2, Entry 3: Deprotection of N-Boc-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)pyrrole.**




The general procedure for deprotection was applied to N-Boc-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)pyrrole (100 mg, 0.33 mmol) at 140 °C for 16 h. The product was isolated as a white solid (49 mg, 72% yield, mp 102-108 °C). $^{1}$H NMR ($CDCl_3$, 500 MHz): δ 8.11 (br s, 1 H, *H*$_a$), 7.10-7.08 (dd, *J* = 2.4, 1.7 Hz, 1 H, *H*$_c$), 6.18-6.17 (m, 1 H, *H*$_b$), 2.25 (d, *J* = 0.7 Hz, 3 H, C*H*$_3$), 1.29 (br s, 12 H, C*H*$_3$ of BPin); $^{13}$C NMR {$^{1}$H} ($CDCl_3$, 125 MHz): δ 128.6 (C), 125.9 (CH), 111.2 (CH), 82.7 (C), 24.8 (4 $CH_3$ of BPin), 12.6 ($CH_3$); $^{11}$B NMR ($CDCl_3$, 96 MHz): δ 30.6; FT-IR (neat) $\tilde{\nu}_{max}$: 3362, 2977, 2926, 1582, 1522, 1458, 1391, 1374, 1291, 1212, 1148, 1130, 970, 943, 858, 816, 708, 691 cm$^{-1}$; GC-MS (EI) *m/z* (% relative intensity): $M^+$ 207 (100), 192 (16), 121 (19), 106(13); Anal. Calc'd for $C_{11}H_{18}BNO_2$: C, 63.80; H, 8.76; N, 6.76. Found: C, 63.80; H, 9.03; N, 6.59.

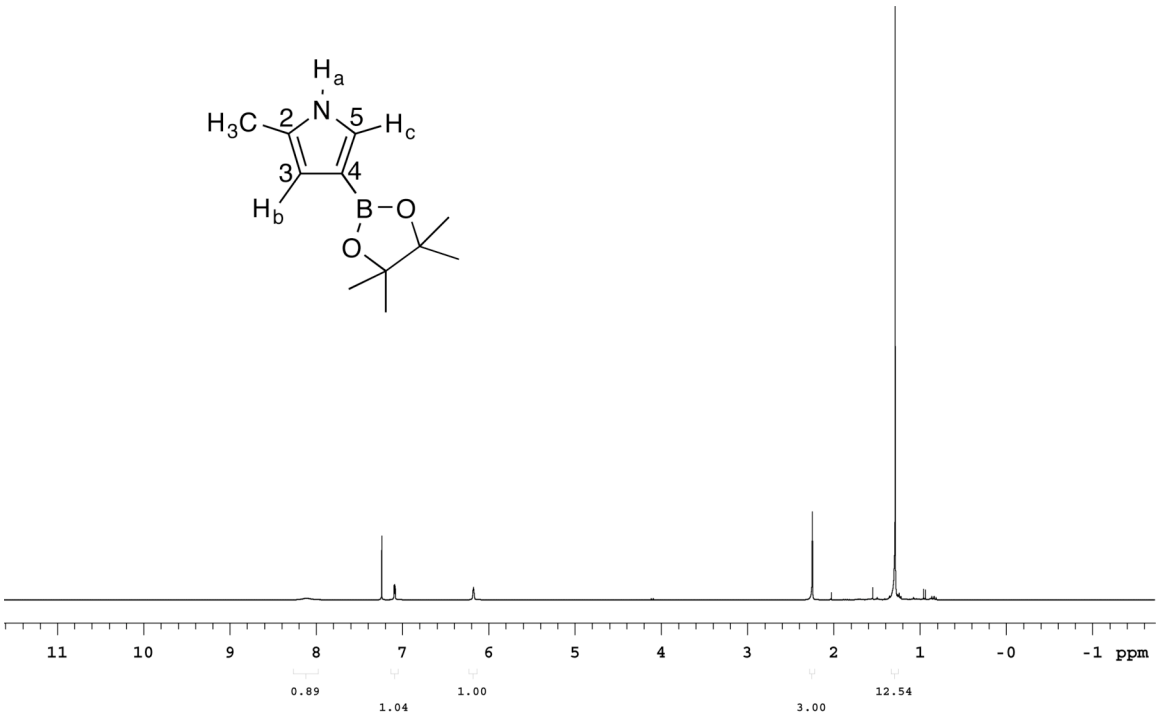



**Figure 27:** $^{1}$H spectrum of 2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-pyrrole.

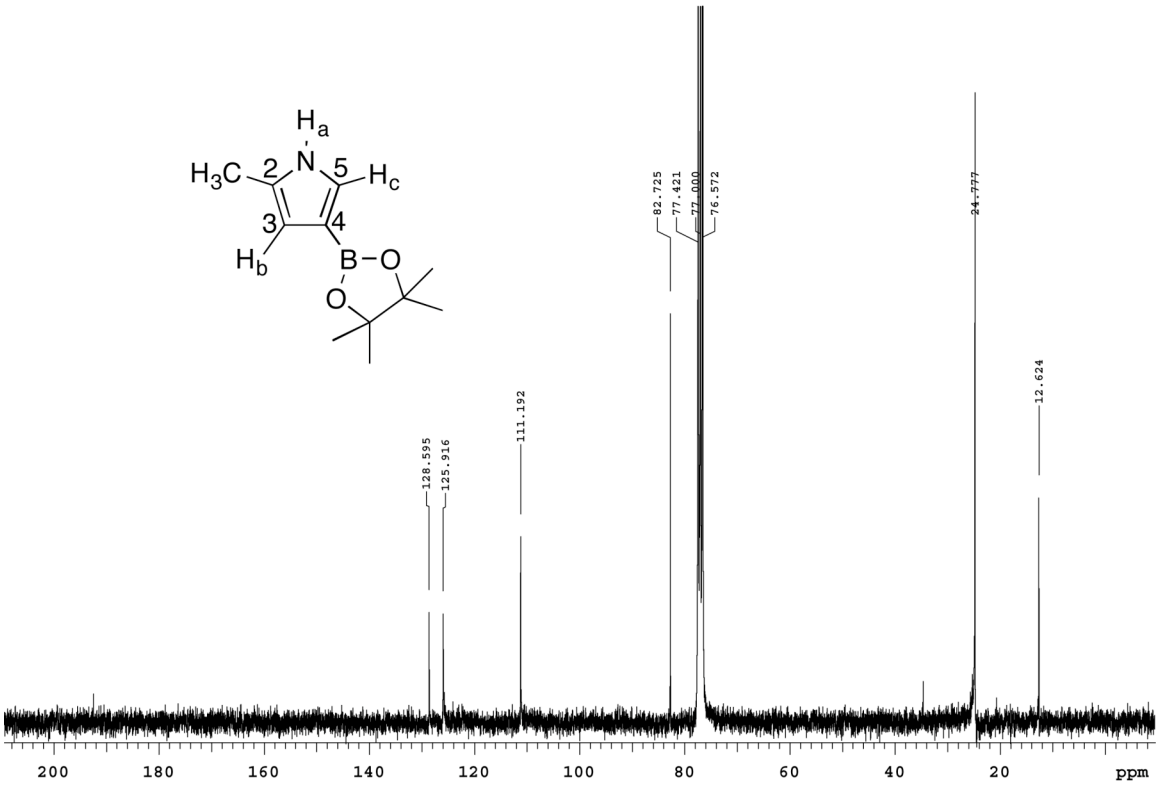
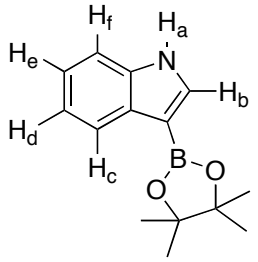



**Figure 28:** $^{13}$C spectrum of 2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-pyrrole.

**Table 2, Entry 4: Deprotection of N-Boc-3-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)indole.**




The general procedure for deprotection was applied to N-Boc-3-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)indole (1000 mg, 2.92 mmol) at 180 °C for 45 min. The product was isolated as a white solid (453 mg, 64% yield, mp 163-165 °C). $^{1}$H NMR ($CDCl_3$, 500 MHz): δ 8.49 (br s, 1 H, $H_a$), 8.08-8.06 (m, 1 H, $H_c$/$H_f$ ), 7.61-7.60 (d, $J$= 2.5 Hz, 1 H, $H_b$), 7.36-7.34 (m, 1 H, $H_c$/$H_f$ ), 7.21-7.16 (m, 2 H, $H_d$ , $H_e$), 1.37 (br s, 12 H, C$H_3$ of BPin) ;$^{13}$C NMR {$^{1}$H} ($CDCl_3$, 125 MHz): δ 136.7 (C), 133.9 (CH), 131.6 (C), 122.5 (CH), 122.2 (CH), 120.5 (CH), 110.9 (CH), 82.9 (C), 24.9 (4 $CH_3$ of BPin); $^{11}$B NMR ($CDCl_3$, 96 MHz): δ 30.5; FT-IR (neat) $\tilde{\nu}_{max}$: 3413, 2980, 2932, 1484, 1458, 1439, 1335, 1138, 1032, 851,768, 743, 671 cm$^{-1}$; GC-MS (EI) *m/z* (% relative intensity): $M^+$ 243 (100), 228 (49), 157 (24), 143 (48), 117 (16); Anal. Calc'd for $C_{14}H_{18}BNO_2$: C, 69.17; H, 7.46; N, 5.76. Found: C, 69.40; H, 7.51; N, 5.73.

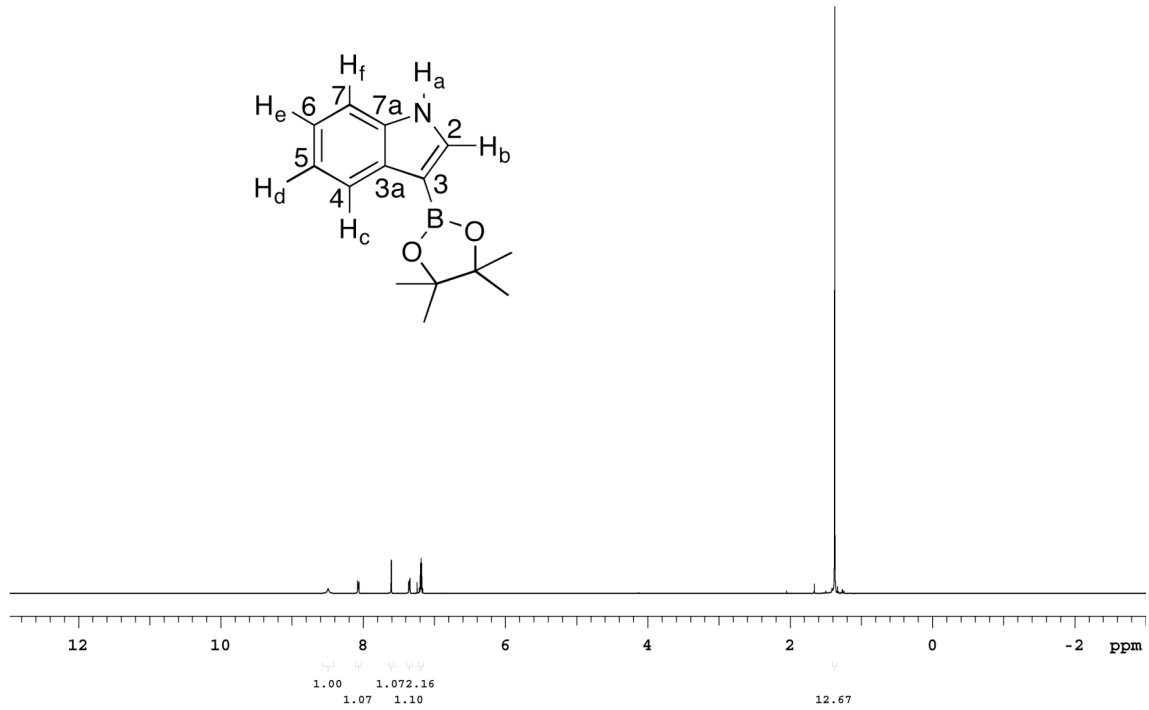



**Figure 29:** $^{1}H$ spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-indole.

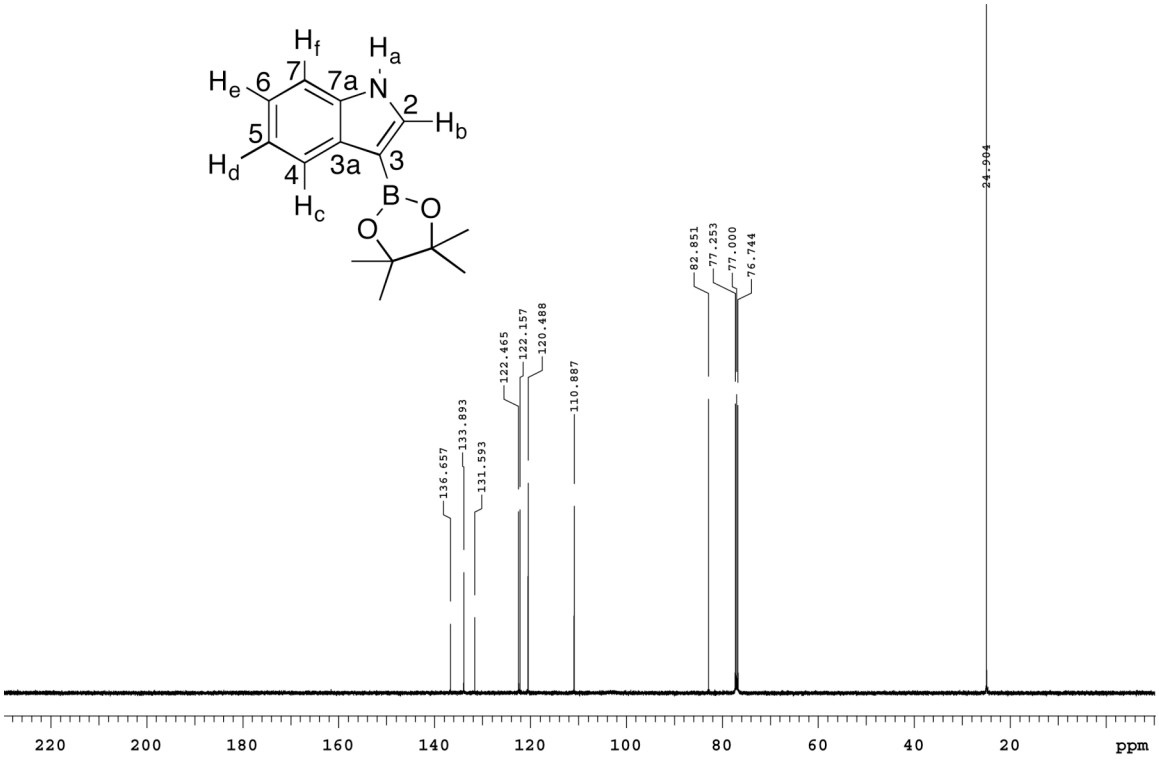
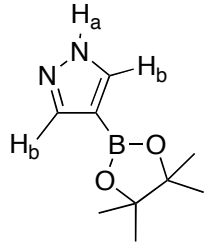



**Figure 30:** $^{13}C$ spectrum of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-indole.

**Table 2, Entry 5: Deprotection of N-Boc-4-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)pyrazole.**




The general procedure for deprotection was applied to N-Boc-3-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)pyrazole (294 mg, 1.00 mmol) at 180 °C for 5 min. The product was isolated as a pale yellow solid (140 mg, 72% yield, mp 147-149 °C). $^{1}$H NMR ($CDCl_3$, 300 MHz): δ 11.96 (br s, 1 H, *H*$_a$), 7.88 (s, 2H, *H*$_b$), 1.29 (br s, 12 H, C*H*$_3$ of BPin); $^{13}$C NMR {$^{1}$H} ($CDCl_3$, 125 MHz): δ 140.2 (CH), 83.3 (C), 24.7 (4 $CH_3$ of BPin); $^{11}$B NMR ($CDCl_3$, 96 MHz): δ 29.7; FT-IR (neat) $\tilde{\nu}_{max}$: 3231, 2977, 1564, 1495, 1424, 1393, 1333, 1283, 1235, 1214, 1140, 978, 943, 857, 710, 696 cm$^{-1}$; GC-MS (EI) *m/z* (% relative intensity): 195 (79), 194 (21), 179 (100), 178 (25), 151 (8), 137 (10), 95 (35), 43 (15); Anal. Calc'd for $C_9H_{15}BN_2O_2$: C, 55.71; H, 7.79; N, 14.44. Found: C, 55.67; H, 7.74; N, 14.61.

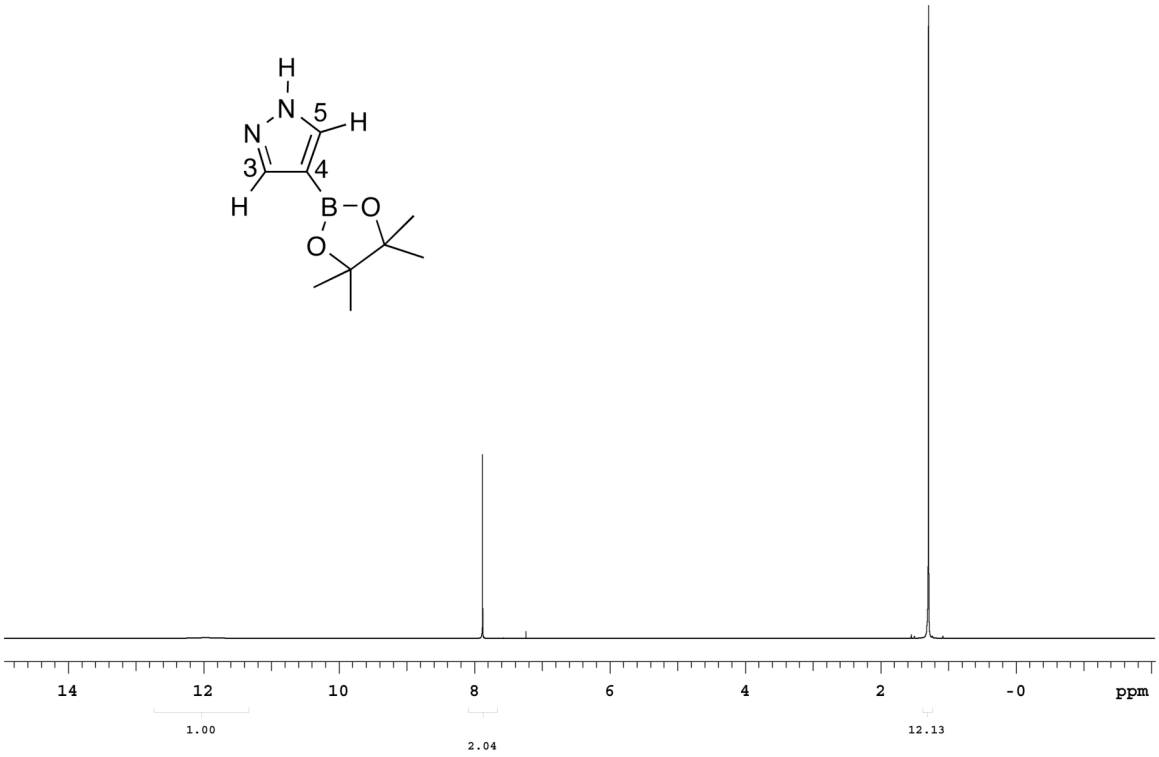



**Figure 31:** $^{1}H$ spectrum of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-pyrazole.

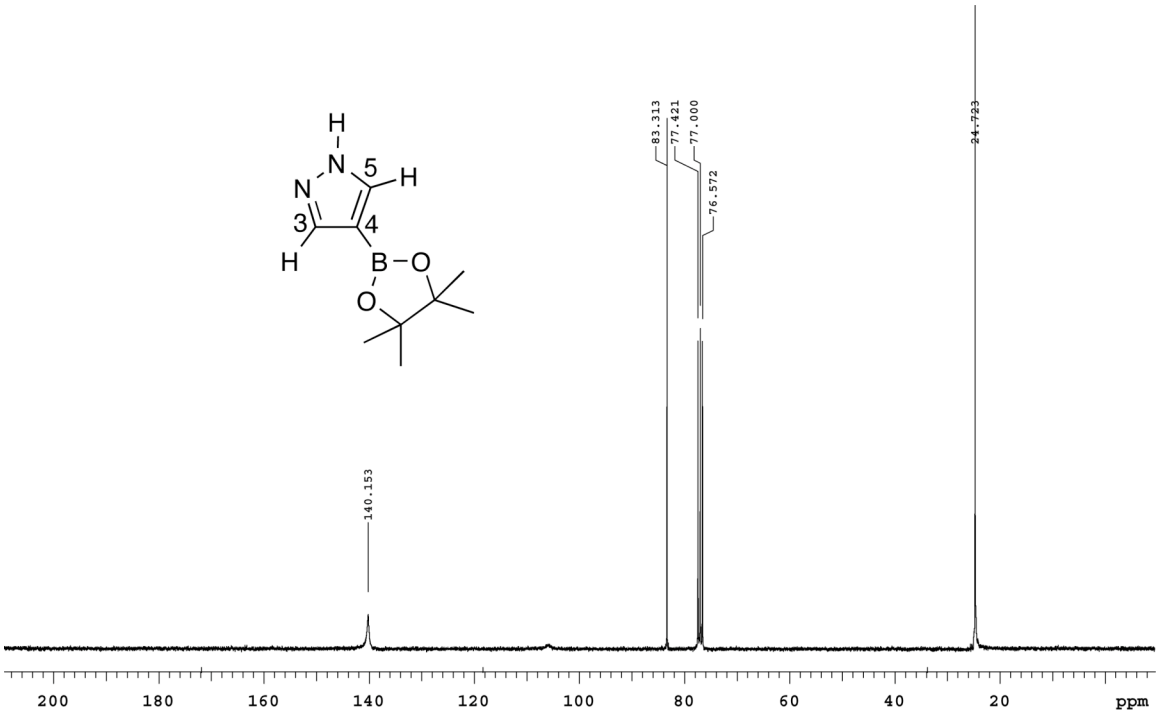



**Figure 32:** $^{13}C$ spectrum of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)-pyrazole.

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