Iridium-Catalyzed, Silyl-Directed Borylation of Nitrogen-Containing Heterocycles

Supporting Information

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Experimental Information

General Procedures. All reactions were conducted under an argon or nitrogen atmosphere in flame-dried glassware or in an Innovative Technologies drybox. Dry and degassed solvents were used unless otherwise noted. Column chromatography was performed using Silicycle silica gel. Analytical thin-layer chromatography was performed on glass plates coated with silica gel (Silicycle, 60 A pore size, 40-64 um particle size) impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by ultraviolet light and staining solution of *p*-anisaldehyde or $KMNO_4$.

Materials. [Ru(*p*-cymene)Cl_2]$_2$ was obtained from Strem Chemicals and used as received. [Ir(cod)Cl]$_2$ and [Ir(cod)OMe]$_2$ were obtained from Johnson Matthey and used as received. 4,4'-di-*tert*-butylbipyridine was obtained from Aldrich Chemicals and used as received. B_2pin_2 was obtained from Allychem and used as received. HBpin was obtained from Aldrich Chemicals and distilled before use. Et_2SiH_2 was obtained from Aldrich Chemicals or Alfa Aesar and used as received. Et_3N was obtained from Fisher Scientific and used as received. Dimethylchlorosilane was obtained from Gelest and used as received. NaH was obtained as a 60% suspension in mineral oil and washed with pentane and dried before use. All indoles and nitrogen heterocycles were obtained from Aldrich Chemicals, Alfa Aesar, TCI America or Acros and used as received. Pd(dba)$_2$ was prepared using standard methods.[1] Bromobenzene, cinnamyl acetate, PPh_3, K_3PO_4, $CuCl_2$, $CuBr_2$ and methyl 2-bromobenzoate were obtained from Aldrich and used as received. KF was obtained from Acros and used as received. Methyl 6-bromo-1,3-

[1] Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.

benzodioxole-5-carboxylate was prepared from 6-bromopiperonal (purchased from Aldrich) using the method of McDonald, et. al.[2]

Instruments. ^{1}H NMR spectra were recorded on a 500 MHz Varian instrument (126 MHz for ^{13}C). ^{11}B NMR spectra were recorded on a 300 MHz Varian instrument. Chemical shifts are reported in parts per million relative to residual protiated solvent (7.26 ppm for $CDCl_3$ and 7.15 for C_6D_6). In general, the carbon bonded to boron the heterocycle borylation products could not be observed via ^{13}C NMR spectroscopy. This is consistent with previous reports of 7-borylindole compounds.[3] GC-MS data were obtained on an Agilient 6890-N GC system containing an Alltech EC-1 capillary column and an Agilient 5973 mass selective detector. Elemental analyses were conducted by the University of Illinois at Urbana-Champaign Microanalysis Laboratory or Robertson Microlit Laboratories (Madison, NJ, USA).

General procedures for the silyl-directed borylation of indoles.

Borylation of *N*-diethylsilylindoles (Procedure 1)

Inside a glove box, $[Ru(p\text{-cymene})Cl_2]_2$ (6.0 mg, 0.01 mmol, 0.01 equiv), the indole (1.00 mmol, 1.00 equiv), diethylsilane (132 mg, 1.50 mmol, 1.50 equiv) and toluene (0.5 mL) were added to a dry vial. The mixture was stirred for 2-12 h until GC analysis showed

[2] McDonald, C.; Holcomb, H.; Kennedy, K.; Kirkpatrick, E.; Leathers, T.; Vanemon, P. *J. Org. Chem.* **1989**, *54*, 1213.
[3] Paul, S.; Chotana, G. A.; Holmes, D.; Reichle, R. C.; Maleczka, R. E.; Smith, M. R. *J. Am. Chem. Soc.* **2006**, *128*, 15552.; Hartung, C. G.; Fecher, A.; Chapell, B.; Snieckus, V. *Org. Lett.* **2003**, *5*, 1899.

full conversion of the indole to the *N*-silylindole. The volatile materials were removed under vacuum. $[Ir(cod)Cl]_2$ (1.7 mg, 0.0025 mmol, 0.0025 equiv), dtbpy (1.4 mg, 0.0050 mmol, 0.0050 equiv), B_2pin_2 (254 mg, 1.00 mmol, 1.00 equiv), HBpin (0.008 mL, 0.05 mmol, 0.05 equiv), and THF (1 mL) were added to the vial, and the reaction mixture was heated at 80 °C. GC analysis indicated full conversion of the *N*-diethylsilylindole after 4-16 h. The reaction mixture was cooled to room temperature. The volatile materials were removed from the reaction mixture under high vacuum at 40 °C. The reaction mixture was dissolved in 2 mL of THF, and 0.5 mL of 3 M NaOAc (aq) was added. The mixture was stirred at room temperature for 4-6 h. Upon complete desilylation, as assayed by GC, the reaction mixture was diluted with Et_2O and H_2O. The aqueous layer was separated and extracted with Et_2O. The combined organic layers were washed with brine. The organic layer was dried with $MgSO_4$, filtered and concentrated under vacuum. Column chromatography eluting under the conditions described below for each example afforded pure product.

Borylation of *N*-dimethylsilylindoles (Procedure 2)

Inside a glove box, triethylamine (160 mg, 1.50 mmol, 1.50 equiv), the indole (1.00 mmol, 1.00 equiv), dimethylchlorosilane (144 mg, 1.50 mmol, 1.50 equiv) and THF (2 mL) were added to a dry vial. The mixture was stirred at room temperature for 4-6 h until GC analysis showed full conversion of the indole to the *N*-silylindole. The reaction mixture was filtered through Celite, and the volatile materials were removed under vacuum. $[Ir(cod)Cl]_2$ (1.7 mg, 0.0025 mmol, 0.0025 equiv), dtbpy (1.4 mg, 0.0050 mmol, 0.0050 equiv), B_2pin_2 (254 mg, 1.00 mmol, 1.00 equiv), HBpin (0.008 mL, 0.05

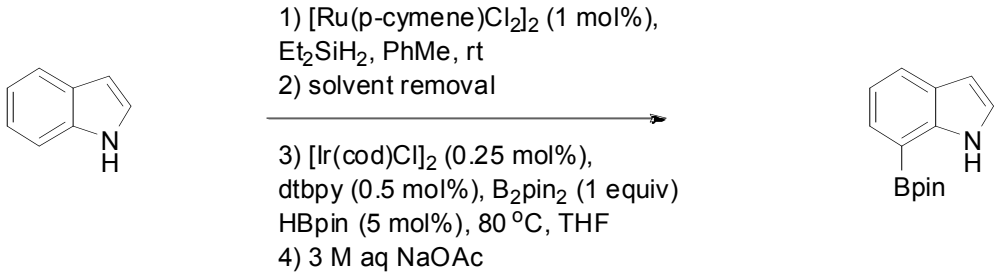
mmol, 0.05 equiv), and THF (1 mL) were added to the vial, and the reaction mixture was heated at 80 °C. GC analysis indicated full conversion of the *N*-dimethylsilylindole after 4-16 h. The reaction mixture was cooled to room temperature. The volatile materials were removed from the reaction mixture under high vacuum at 40 °C. The reaction mixture was dissolved in 2 mL of THF, and 1 mL of saturated $NaHCO_3$ (aq) was added. The mixture was stirred at room temperature for 6 h. Upon complete desilylation as assayed using GC analysis, the reaction mixture was diluted with Et_2O and H_2O. The aqueous layer was separated and extracted with Et_2O. The combined organic layers were washed with brine. The organic layer was dried with $MgSO_4$, filtered and concentrated under vacuum. Column chromatography, eluting under the conditions described below for each example, afforded pure product.

Borylation of *N*-diethylsilylindoles without use of a glovebox (Procedure 3)

$[Ru(p\text{-cymene})Cl_2]_2$ (6.0 mg, 0.010 mmol, 0.010 equiv) and 3-methyl indole (131 mg, 1.00 mmol, 1.00 equiv) were added to a dry glass reaction vessel equipped with a side arm and a vacuum valve and sealed under N_2. The vessel was evacuated and filled with N_2 three times. Under a positive flow of N_2, a mixture of diethylsilane (132 mg, 1.50 mmol, 1.50 equiv) and toluene (0.5 mL) were added. The vessel was sealed and stirred for 12 h when GC analysis showed full conversion of the indole to the *N*-silylindole. The volatile materials were removed under vacuum. $[Ir(cod)Cl]_2$ (1.7 mg, 0.0025 mmol, 0.0025 equiv), dtbpy (1.4 mg, 0.0050 mmol, 0.0050 equiv), and B_2pin_2 (254 mg, 1.00 mmol, 1.00 equiv) were added to the vessel. The vessel was evacuated and refilled with N_2 three times. Under a positive flow of N_2, a mixture of HBpin (0.008 mL, 0.05 mmol,

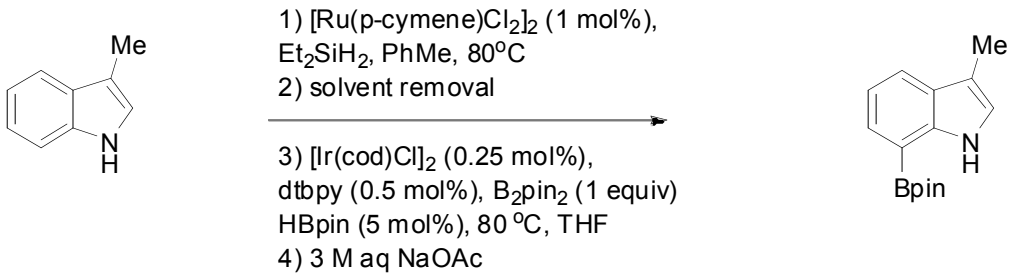
0.05 equiv), and THF (1 mL) was added to the reaction mixture. The vessel was sealed, and the reaction mixture was heated at 80 °C. GC analysis indicated full conversion of the *N*-diethylsilylindole after 12 h. The reaction mixture was cooled to room temperature. The volatile materials were removed from the reaction mixture under high vacuum at 40 °C. The reaction mixture was dissolved in 2 mL of THF, and 0.5 mL of 3 M NaOAc (aq) was added. The mixture was stirred at room temperature for 6 h. Upon complete desilylation, as assayed by GC, the reaction mixture was diluted with Et_2O and H_2O. The aqueous layer was separated and extracted with Et_2O. The combined organic layers were washed with brine. The organic layer was dried with $MgSO_4$, filtered and concentrated under vacuum. Column chromatography (90:10 hexanes:ethyl acetate) afforded 143 mg (56%) of the 3-methyl-7-boronic ester product.

Specific Experimental Procedures for the Borylation of Indoles



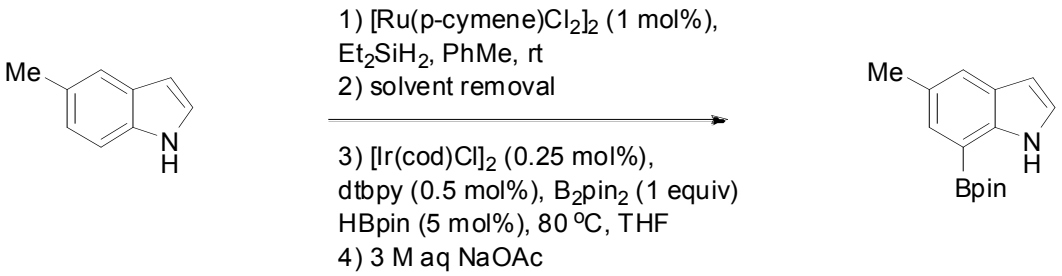
Borylation of indole. Inside a glove box, [Ru(*p*-cymene)Cl_2]$_2$ (6.0 mg, 0.010 mmol, 0.010 equiv), indole (117 mg, 1.00 mmol, 1.00 equiv), diethylsilane (132 mg, 1.50 mmol, 1.50 equiv) and toluene (0.5 mL) were added to a dry vial. The mixture was stirred at room temperature for 2 h, at which time, GC analysis showed full conversion of the indole to the *N*-silylindole. The volatile materials were removed under vacuum. [Ir(cod)Cl]$_2$ (1.7 mg, 0.0025 mmol, 0.0025 equiv), dtbpy (1.4 mg, 0.0050 mmol, 0.005

equiv), B_2pin_2 (254 mg, 1.00 mmol, 1.00 equiv), HBpin (0.008 mL, 0.05 mmol, 0.05 equiv), and THF (1 mL) were added to the vial, and the reaction mixture was heated at 80 °C. After 4 h, GC analysis indicated full conversion of the *N*-diethylsilylindole. The reaction mixture was cooled to room temperature. The volatile materials were removed from the reaction mixture under high vacuum at 40 °C. The reaction mixture was dissolved in 2 mL of THF, and 0.5 mL of 3 M NaOAc (aq) was added. The mixture was stirred at room temperature for 6 h. Upon complete desilylation, the reaction mixture was diluted with Et_2O and H_2O. The aqueous layer was separated and extracted with Et_2O. The combined organic layers were washed with brine. The organic layer was dried with $MgSO_4$, filtered and concentrated under vacuum. Column chromatography (85:15 hexanes:ethyl acetate) afforded the known product[2] judged to be pure by NMR spectroscopy (160 mg, 66%). ^{1}H NMR (499 MHz, $CDCl_3$) δ 9.27 (s, 1H), 7.80 (d, J = 7.9, 1H), 7.68 (d, J = 7.0, 1H), 7.29 (t, J = 2.7, 1H), 7.16 (t, J = 7.4, 1H), 6.57 (m, 1H), 1.42 (s, 12H). ^{13}C NMR (126 MHz, CDCl3) δ 141.20, 129.47, 127.02, 124.50, 124.30, 119.55, 102.20, 83.95, 25.25. ^{11}B NMR (300MHz, $CDCl_3$): δ 31.3.



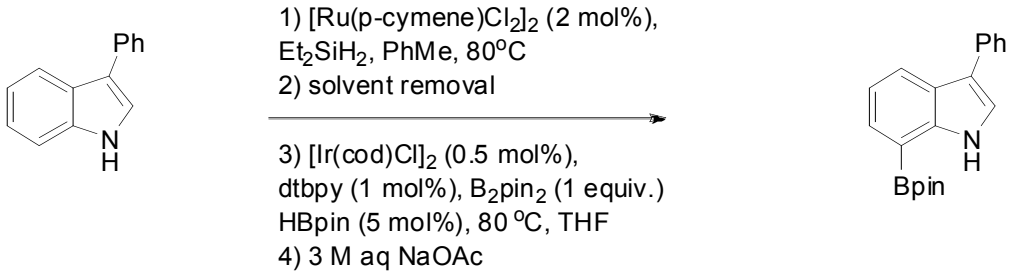
Borylation of 3-methylindole. Inside a glove box, [Ru(*p*-cymene)Cl_2]$_2$ (6.0 mg, 0.010 mmol, 0.010 equiv), 3-methylindole (131 mg, 1.00 mmol, 1.00 equiv), diethylsilane (132 mg, 1.50 mmol, 1.50 equiv) and toluene (0.5 mL) were added to a dry vial. The mixture

was stirred at 80 °C for 12 h, at which time GC analysis showed full conversion of the indole. The volatile materials were removed under vacuum. $[Ir(cod)Cl]_2$ (1.7 mg, 0.0025 mmol, 0.0025 equiv), dtbpy (1.4 mg, 0.0050 mmol, 0.0050 equiv), B_2pin_2 (254 mg, 1.00 mmol, 1.00 equiv), HBpin (0.008 mL, 0.05 mmol, 0.05 equiv), and THF (1 mL) were added to the vial, and the reaction mixture was heated at 80 °C. After 6 h, GC analysis indicated full conversion of the *N*-diethylsilylindole. The reaction mixture was cooled to room temperature. The volatile materials were removed from the reaction mixture under high vacuum at 40 °C. The reaction mixture was dissolved in 2 mL of THF, and 0.5 mL of 3 M NaOAc (aq) was added. The mixture was stirred at room temperature for 6 h. Upon complete desilylation, the reaction mixture was diluted with Et_2O and H_2O. The aqueous layer was separated and extracted with Et_2O. The combined organic layers were washed with brine. The organic layer was dried with $MgSO_4$, filtered and concentrated under vacuum. Column chromatography (90:10 hexanes:ethyl acetate) afforded analytically pure product (156 mg, 61%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.74 (d, J = 7.8, 1H), 7.68 (dd, J = 0.9, 7.1, 1H), 7.17 (dd, J = 7.1, 7.8, 1H), 7.05 (d, J = 0.9, 1H), 2.38 (s, 3H), 1.42 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.68, 129.34, 127.43, 122.61, 121.75, 118.78, 111.28, 83.96, 25.25, 9.93. ^{11}B NMR (300MHz, $CDCl_3$): δ 31.6. Anal Calcd. for $C_{15}H_{20}BNO_2$: C, 70.0; H, 7.84; N, 5.45; found: C, 69.6; H, 7.96; N, 5.48.



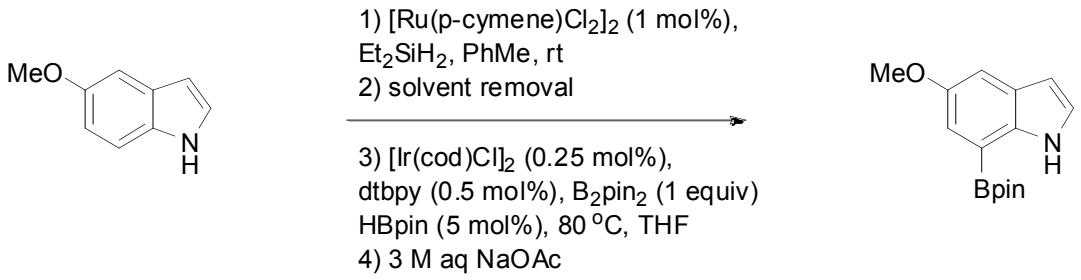
Borylation of 5-methylindole. Inside a glove box, [Ru(*p*-cymene)Cl_2]$_2$ (6.0 mg, 0.010 mmol, 0.010 equiv), 5-methylindole (131 mg, 1.00 mmol, 1.00 equiv), diethylsilane (132 mg, 1.50 mmol, 1.50 equiv) and toluene (0.5 mL) were added to a dry vial. The mixture was stirred at 80 °C for. After 12 h, at which time, GC analysis indicated that the indole was fully conversion of the indole to *N*-diethylsilylindole. The volatile materials were removed under vacuum. [Ir(cod)Cl]$_2$ (1.7 mg, 0.0025 mmol, 0.0025 equiv), dtbpy (1.4 mg, 0.0050 mmol, 0.0050 equiv), B_2pin_2 (254 mg, 1.00 mmol, 1.00 equiv), HBpin (0.008 mL, 0.05 mmol, 0.05 equiv), and THF (1 mL) were added to the vial, and the reaction mixture was heated at 80 °C. After 4 h, GC analysis indicated full conversion of the *N*-diethylsilylindole. The reaction mixture was cooled to room temperature. The volatile materials were removed from the reaction mixture under high vacuum at 40 °C. The reaction mixture was dissolved in 2 mL of THF, and 0.5 mL of 3 M NaOAc (aq) was added. The mixture was stirred at room temperature for 4 h. Upon complete desilylation, the reaction mixture was diluted with Et_2O and H_2O. The aqueous layer was separated and extracted with Et_2O. The combined organic layers were washed with brine. The organic layer was dried with $MgSO_4$, filtered and concentrated under vacuum. Column chromatography (90:10 hexanes:ethyl acetate) afforded analytically pure product (156 mg, 61%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.20 (s, 1H), 7.64 (s, 1H), 7.58 (s, 1H), 7.28 (t, J = 2.7, 1H), 6.54 (d, J = 2.7, 1H), 2.53 (s, 3H), 1.46 (s, 12H). ^{13}C NMR (126 MHz,

$CDCl_3$) δ 139.69, 130.87, 128.59, 127.47, 124.47, 124.41, 101.71, 84.06, 25.28, 21.56. ^{11}B NMR (300MHz, $CDCl_3$): δ 31.8. Anal Calcd. for $C_{15}H_{20}BNO_2$: C, 70.0; H, 7.84; N, 5.45; found: C, 70.2; H, 8.02; N, 5.49.



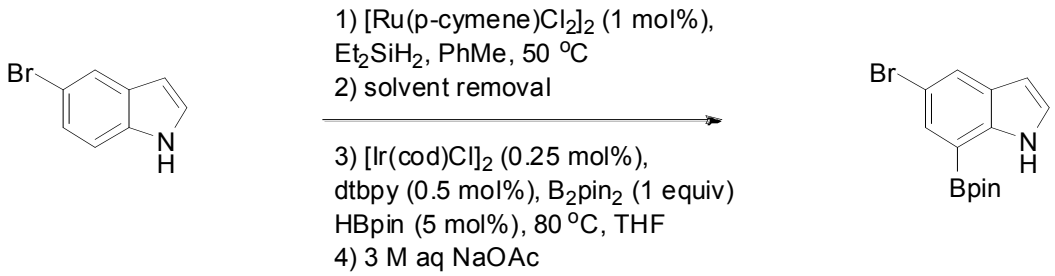
Borylation of 3-phenylindole. Inside a glove box, [Ru(*p*-cymene)Cl_2]$_2$ (12 mg, 0.020 mmol, 0.020 equiv), 3-phenylindole (197 mg, 1.00 mmol, 1.00 equiv), diethylsilane (132 mg, 1.50 mmol) and toluene (0.5 mL) were added to a dry vial. The mixture was stirred at 80 °C for 16 h, at which time GC-MS analysis showed full conversion of 3-phenylindole. The volatile materials were removed under vacuum. [Ir(cod)Cl]$_2$ (3.4 mg, 0.0050 mmol, 0.050 equiv), dtbpy (2.7 mg, 0.010 mmol, 0.010 equiv), B_2pin_2 (254 mg, 1.00 mmol, 1.00 equiv), HBpin (0.008 mL, 0.05 mmol, 0.05 equiv), and THF (2.0 mL) were added to the vial, and the reaction mixture was heated at 80 °C. After 12 h, GC-MS analysis indicated full conversion of the *N*-diethylsilyl-3-phenylindole. The reaction mixture was cooled to room temperature. The volatile materials were removed from the reaction mixture under high vacuum at 40 °C. The reaction mixture was dissolved in 2 mL of THF, and 0.5 mL of 3 M NaOAc (aq) was added. The mixture was stirred at room temperature for 4 h. Upon complete desilylation, the reaction mixture was diluted with Et_2O and H_2O. The aqueous layer was separated and extracted with Et_2O. The combined organic layers were washed with brine. The organic layer was dried with $MgSO_4$, filtered

and concentrated under vacuum. Column chromatography (90:10 hexanes:ethyl acetate) afforded analytically pure product (140 mg, 44%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.41 (s, 1H), 8.13 (d, J = 8.0, 1H), 7.77 (d, J = 7.0, 1H), 7.73 (d, J = 7.5, 2H), 7.49 (m, 3H), 7.33 (t, J = 7.4, 1H), 7.27 (t, J = 7.5, 1H), 1.45 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.11, 136.09, 129.93, 129.02, 127.76, 126.09, 124.97, 123.64, 122.04, 120.09, 118.06, 84.18, 25.28. ^{11}B NMR (300MHz, $CDCl_3$): δ 31.6. Anal Calcd. for $C_{20}H_{22}BNO_2$: C, 75.25; H, 6.95; N, 4.39; found: C, 75.29; H, 6.70; N, 4.16.



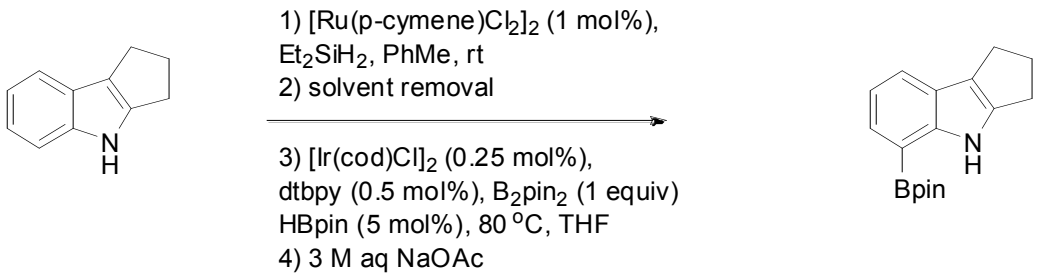
Borylation of 5-methoxyindole. Inside a glove box, [Ru(*p*-cymene)Cl_2]$_2$ (6.0 mg, 0.010 mmol, 0.010 equiv), 5-methoxyindole (148 mg, 1.00 mmol, 1.00 equiv), diethylsilane (132 mg, 1.50 mmol, 1.50 equiv) and toluene (0.5 mL) were added to a dry vial. The mixture was stirred at room temperature for 6 h, at which time GC analysis showed full conversion of the indole. The volatile materials were removed under vacuum. [Ir(cod)Cl]$_2$ (1.7 mg, 0.0025 mmol, 0.0025 equiv), dtbpy (1.4 mg, 0.0050 mmol, 0.0050 equiv), B_2pin_2 (254 mg, 1.00 mmol, 1.00 equiv), HBpin (0.008 mL, 0.05 mmol, 0.05 equiv), and THF (1 mL) were added to the vial, and the reaction mixture was heated at 80 °C. After 6 h, GC analysis indicated full conversion of the *N*-diethylsilylindole. The reaction mixture was cooled to room temperature. The volatile materials were removed from the reaction mixture under high vacuum at 40 °C. The

reaction mixture was dissolved in 2 mL of THF, and 0.5 mL of 3 M NaOAc (aq) was added. The mixture was stirred at room temperature for 4 h. Upon complete desilylation, the reaction mixture was diluted with Et_2O and H_2O. The aqueous layer was separated and extracted with Et_2O. The combined organic layers were washed with brine. The organic layer was dried with $MgSO_4$, filtered and concentrated under vacuum. Column chromatography (85:15 hexanes:ethyl acetate) afforded analytically pure product (160 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.15 (s, 1H), 7.36 (d, J = 2.4, 1H), 7.31 (d, J = 2.3, 1H), 7.28 (t, J = 2.7, 1H), 6.51 (dd, J = 2.3, 2.9, 1H), 3.90 (s, 3H), 1.42 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.03, 136.72, 127.87, 125.17, 118.05, 107.81, 101.77, 84.17, 56.48, 25.24. ^{11}B NMR (300MHz, $CDCl_3$): δ 31.8. Anal Calcd. for $C_{15}H_{20}BNO_3$: C, 65.96; H, 7.38; N, 5.13; found: C, 65.70; H, 7.63; N, 4.95.



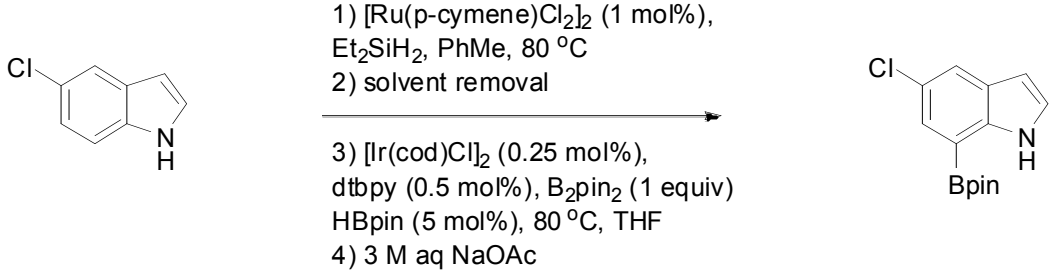
Borylation of 5-bromoindole. Inside a glove box, [Ru(*p*-cymene)Cl_2]$_2$ (6.0 mg, 0.010 mmol, 0.010 equiv), 5-bromoindole (197 mg, 1.00 mmol, 1.00 equiv), diethylsilane (132 mg, 1.50 mmol, 1.50 equiv) and toluene (0.5 mL) were added to a dry vial. The mixture was stirred at 50 °C for 12 h, at which time GC analysis showed full conversion of the indole. The volatile materials were removed under vacuum. [Ir(cod)Cl]$_2$ (1.7 mg, 0.0025 mmol, 0.0025 equiv), dtbpy (1.4 mg, 0.0050 mmol, 0.0050 equiv), B_2pin_2 (254 mg, 1.00 mmol, 1.00 equiv), HBpin (0.008 mL, 0.05 mmol, 0.05 equiv), and THF (1 mL) were

added to the vial, and the reaction mixture was heated at 80 °C. After 6 h, GC analysis indicated full conversion of the *N*-diethylsilylindole. The reaction mixture was cooled to room temperature. The volatile materials were removed from the reaction mixture under high vacuum at 40 °C. The reaction mixture was dissolved in 2 mL of THF, and 0.5 mL of 3 M NaOAc (aq) was added. The mixture was stirred at room temperature for 4 h. Upon complete desilylation, the reaction mixture was diluted with Et_2O and H_2O. The aqueous layer was separated and extracted with Et_2O. The combined organic layers were washed with brine. The organic layer was dried with $MgSO_4$, filtered and concentrated under vacuum. Column chromatography (85:15 hexanes:ethyl acetate) afforded analytically pure product (175 mg, 55%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.23 (s, 1H), 7.88 (d, J = 1.7, 1H), 7.73 (d, J = 1.8, 1H), 7.27 (m, 1H), 6.49 (m, 1H), 1.40 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.74, 131.61, 129.00, 126.66, 125.55, 113.15, 101.82, 84.43, 25.22. ^{11}B NMR (300MHz, $CDCl_3$): δ 31.8. Anal Calcd. for $C_{14}H_{17}BBrNO_2$: C, 52.22; H, 5.32; N, 4.35; found: C, 52.16; H, 5.52; N, 3.96.

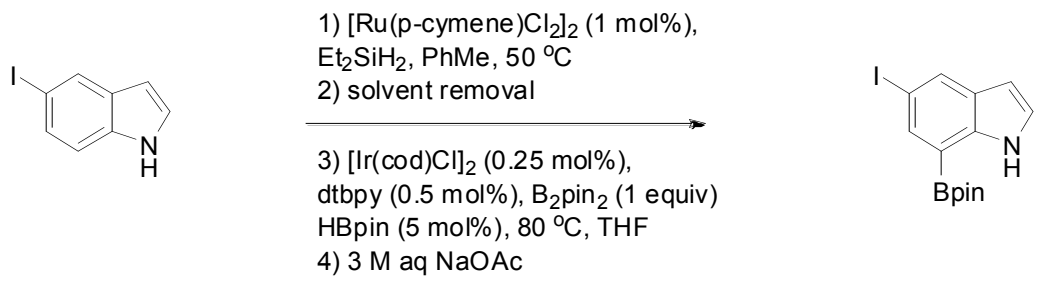


Borylation of 1,2,3,4-Tetrahydrocyclopentindole. Inside a glove box, [Ru(*p*-cymene)Cl_2]$_2$ (6.0 mg, 0.010 mmol, 0.010 equiv), 1,2,3,4-Tetrahydrocyclopentindole (158 mg, 1.00 mmol, 1.00 equiv), diethylsilane (132 mg, 1.50 mmol, 1.50 equiv) and toluene (0.5 mL) were added to a dry vial. The mixture was stirred at room temperature

for 6 h, at which time GC analysis showed full conversion of the indole. The volatile materials were removed under vacuum. $[Ir(cod)Cl]_2$ (1.7 mg, 0.0025 mmol, 0.0025 equiv), dtbpy (1.4 mg, 0.0050 mmol, 0.0050 equiv), B_2pin_2 (254 mg, 1.00 mmol, 1.00 equiv), HBpin (0.008 mL, 0.05 mmol, 0.05 equiv), and THF (1 mL) were added to the vial, and the reaction mixture was heated at 80 °C. After 8 h, GC analysis indicated full conversion of the *N*-diethylsilylindole. The reaction mixture was cooled to room temperature. The volatile materials were removed from the reaction mixture under high vacuum at 40 °C. The reaction mixture was dissolved in 2 mL of THF, and 0.5 mL of 3 M NaOAc (aq) was added. The mixture was stirred at room temperature for 4 h. Upon complete desilylation, the reaction mixture was diluted with Et_2O and H_2O. The aqueous layer was separated and extracted with Et_2O. The combined organic layers were washed with brine. The organic layer was dried with $MgSO_4$, filtered and concentrated under vacuum. Column chromatography (90:10 hexanes:ethyl acetate) afforded the known product[2] judged to be pure by NMR spectroscopy (179 mg, 64%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.63 (d, J = 2.4, 1H), 7.62 (d, J = 1.3, 1H), 7.16 (t, J = 7.4, 1H), 2.98 (t, J = 7.1, 2H), 2.90 (t, J = 6.9, 2H), 2.60 (m, 2H), 1.45 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.64, 144.00, 127.86, 123.93, 122.22, 119.30, 119.12, 84.00, 29.06, 26.32, 25.27, 24.75. ^{11}B NMR (300MHz, $CDCl_3$): δ 31.8.

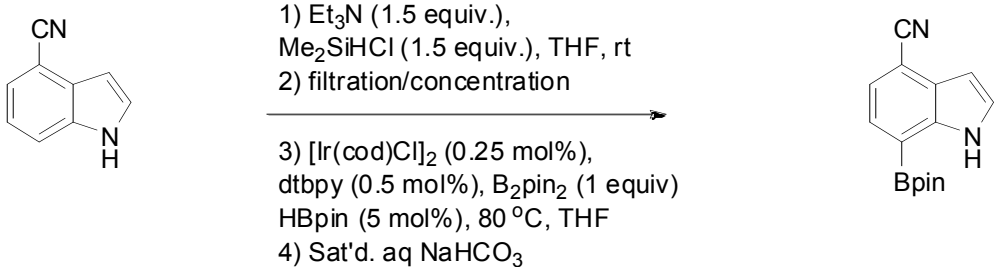


Borylation of 5-chloroindole. Inside a glove box, [Ru(*p*-cymene)Cl_2]$_2$ (6.0 mg, 0.010 mmol), 5-chloroindole (151 mg, 1.00 mmol, 1.00 equiv), diethylsilane (132 mg, 1.50 mmol, 1.50 equiv) and toluene (0.5 mL) were added to a dry vial. The mixture was stirred at 80 °C for 2 h, at which time GC-MS analysis showed full conversion of 5-chloroindole. The volatile materials were removed under vacuum. [Ir(cod)Cl]$_2$ (1.7 mg, 0.0025 mmol, 0.0025 equiv), dtbpy (1.4 mg, 0.0050 mmol, 0.0050 equiv), B_2pin_2 (254 mg, 1.00 mmol, 1.00 equiv), HBpin (0.008 mL, 0.05 mmol, 0.05 equiv), and THF (1 mL) were added to the vial, and the reaction mixture was heated at 80 °C. After 4 h, GC analysis indicated full conversion of the *N*-diethylsilylindole. The reaction mixture was cooled to room temperature. The volatile materials were removed from the reaction mixture under high vacuum at 40 °C. The reaction mixture was dissolved in 2 mL of THF, and 0.5 mL of 3 M NaOAc (aq) was added. The mixture was stirred at room temperature for 4 h. Upon complete desilylation, the reaction mixture was diluted with Et_2O and H_2O. The aqueous layer was separated and extracted with Et_2O. The combined organic layers were washed with brine. The organic layer was dried with $MgSO_4$, filtered and concentrated under vacuum. Column chromatography (90:10 hexanes:ethyl acetate) afforded analytically pure product (176 mg, 64%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.24 (s, 1H), 7.74 (d, J = 1.8, 1H), 7.63 (d, J = 1.9, 1H), 7.30 (m, 1H), 6.51 (m, 1H), 1.41 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.55, 129.08, 128.40, 125.75, 125.48, 123.62, 101.92, 84.44, 25.23. ^{11}B NMR (300MHz, $CDCl_3$): δ 31.4. Anal Calcd. for $C_{14}H_{17}BClNO_2$: C, 60.58; H, 6.17; N, 5.05; found: C, 60.53; H, 6.32; N, 4.97.



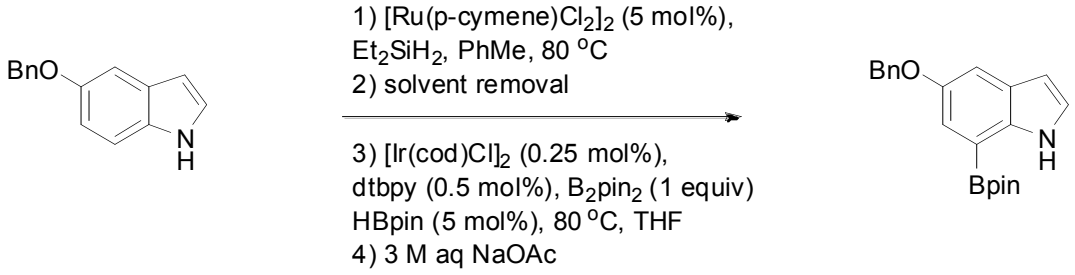
Borylation of 5-iodoindole. Inside a glove box, [Ru(*p*-cymene)Cl_2]$_2$ (12.0 mg, 0.020 mmol, 0.020 equiv), 5-iodoindole (243 mg, 1.00 mmol, 1.00 equiv), diethylsilane (132 mg, 1.50 mmol, 1.50 equiv) and toluene (0.5 mL) were added to a dry vial. The mixture was stirred at 50 °C for 2 h, at which time GC-MS analysis showed full conversion of 5-chloroindole. The volatile materials were removed under vacuum. . [Ir(cod)Cl]$_2$ (1.7 mg, 0.0025 mmol, 0.0025 equiv), dtbpy (1.4 mg, 0.0050 mmol, 0.0050 equiv), B_2pin_2 (254 mg, 1.00 mmol, 1.00 equiv), HBpin (0.008 mL, 0.05 mmol, 0.05 equiv), and THF (1 mL) were added to the vial, and the reaction mixture was heated at 80 °C. After 4 h, GC analysis indicated full conversion of the *N*-diethylsilylindole. The reaction mixture was cooled to room temperature. The volatile materials were removed from the reaction mixture under high vacuum at 40 °C. The reaction mixture was dissolved in 2 mL of THF, and 0.5 mL of an aqueous solution of 3 M NaOAc was added. The mixture was stirred at room temperature for 4 h. Upon complete desilylation, the reaction mixture was diluted with Et_2O and H_2O. The aqueous layer was separated and extracted with Et_2O. The combined organic layers were washed with brine. The organic layer was dried with $MgSO_4$, filtered and concentrated under vacuum. Column chromatography (90:10 hexanes:ethyl acetate) afforded analytically pure product (210 mg, 57%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.25 (s, 1H), 8.12 (s, 1H), 7.93 (d, J = 1.5, 1H), 7.24 (m, 1H), 6.49 (m, 1H), 1.41 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.15, 137.11, 132.90, 129.83,

129.48, 125.24, 101.59, 84.45, 25.25. ^{11}B NMR (300MHz, $CDCl_3$): δ 32.5. Anal Calcd. for $C_{14}H_{17}BINO_2$: C, 45.57; H, 4.64; N, 3.80; found: C, 45.28; H, 4.44; N, 3.88.



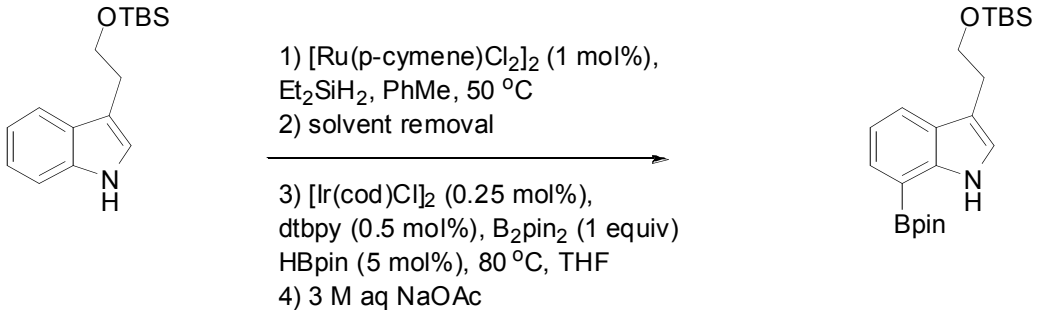
Borylation of 4-cyanoindole. Inside a glove box, triethylamine (160 mg, 1.50 mmol, 1.50 equiv), 4-cyanoindole (142 mg, 1.00 mmol, 1.00 equiv), dimethylchlorosilane (144 mg, 1.50 mmol, 1.50 equiv) and THF (2 mL) were added to a dry vial. The mixture was stirred at room temperature for 6 h, at which time GC analysis showed full conversion of the indole. The reaction mixture was filtered through Celite and the volatile materials were removed under vacuum. $[Ir(cod)Cl]_2$ (1.7 mg, 0.0025 mmol, 0.0025 equiv), dtbpy (1.4 mg, 0.0050 mmol, 0.0050 equiv), B_2pin_2 (254 mg, 1.00 mmol, 1.00 equiv), HBpin (0.008 mL, 0.05 mmol, 0.05 equiv), and THF (1 mL) were added to the vial, and the reaction mixture was heated at 80 °C. After 16 h, GC analysis indicated full conversion of the *N*-dimethylsilylindole. The reaction mixture was cooled to room temperature. The volatile materials were removed from the reaction mixture under high vacuum at 40 °C. The reaction mixture was dissolved in 2 mL of THF, and 1 mL of saturated $NaHCO_3$ (aq) was added. The mixture was stirred at room temperature for 6 h. Upon complete desilylation, the reaction mixture was diluted with Et_2O and H_2O. The aqueous layer was separated and extracted with Et_2O. The combined organic layers were washed with brine. The organic layer was dried with $MgSO_4$, filtered and concentrated under vacuum.

Column chromatography (75:25 hexanes:ethyl acetate) afforded analytically pure product (120 mg, 49%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.49 (s, 1H), 7.65 (d, J = 7.3, 1H), 7.46 (d, J = 7.3, 1H), 7.44 (t, J = 2.7, 1H), 6.76 (m, 1H), 1.41 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.86, 128.47, 128.27, 127.12, 124.45, 119.03, 105.81, 101.28, 84.77, 25.22. ^{11}B NMR (300MHz, $CDCl_3$): δ 31.9. Anal Calcd. for $C_{15}H_{17}BN_2O_2$: C, 67.19; H, 6.39; N, 10.45; found: C, 67.14; H, 6.37; N, 10.05



Borylation of 5-benzyloxylindole. Inside a glove box, [Ru(*p*-cymene)Cl_2]$_2$ (30 mg, 0.050 mmol, 0.05 equiv), 5-benzyloxyindole (223 mg, 1.00 mmol, 1.00 equiv), diethylsilane (132 mg, 1.50 mmol) and toluene (0.5 mL) were added to a dry vial. The mixture was stirred at 80 °C for 12 h, at which time GC-MS analysis showed full conversion of 5-benzyloxyindole. The volatile materials were removed under vacuum. [Ir(cod)Cl]$_2$ (1.7 mg, 0.0025 mmol, 0.025 equiv), dtbpy (1.4 mg, 0.0050 mmol, 0.0050 equiv), B_2pin_2 (254 mg, 1.00 mmol, 1.00 equiv), HBpin (0.008 mL, 0.05 mmol, 0.05 equiv), and THF (1.0 mL) were added to the vial, and the reaction mixture was heated at 80 °C. After 6 h, GC-MS analysis indicated full conversion of the *N*-diethylsilyl-5-benzyloxyindole. The reaction mixture was cooled to room temperature. The volatile materials were removed from the reaction mixture under high vacuum at 40 °C. The reaction mixture was dissolved in 2 mL of THF, and 0.5 mL of 3 M NaOAc (aq) was

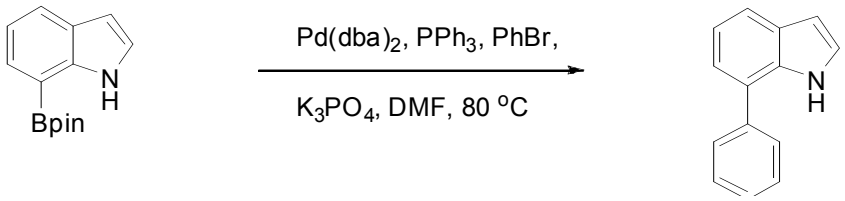
added. The mixture was stirred at room temperature for 4 h. Upon complete desilylation, the reaction mixture was diluted with Et_2O and H_2O. The aqueous layer was separated and extracted with Et_2O. The combined organic layers were washed with brine. The organic layer was dried with $MgSO_4$, filtered and concentrated under vacuum. Column chromatography (90:10 hexanes:ethyl acetate) afforded analytically pure product (183 mg, 53%). ^{1}H NMR (500 MHz, CDCl3) δ 9.14 (s, 1H), 7.51 (d, J = 7.5, 3H), 7.47 (d, J = 2.4, 1H), 7.41 (t, J = 7.5, 3H), 7.37 (d, J = 2.4, 1H), 7.35 (d, J = 7.3, 1H), 7.27 (t, J = 2.7, 1H), 6.50 (dd, J = 2.3, 3.0, 1H), 5.16 (s, 2H), 1.42 (s, 12H). ^{13}C NMR (126 MHz, CDCl3) δ 153.22, 138.16, 136.85, 128.76, 127.87, 127.81, 127.70, 125.14, 119.20, 109.20, 101.88, 84.31, 71.42, 25.26. ^{11}B NMR (300MHz, $CDCl_3$): δ 31.6. Anal Calcd. for $C_{21}H_{24}BNO_3$: C, 72.2; H, 6.9; N, 4.0; found: C, 72.0; H, 6.5; N, 3.7.



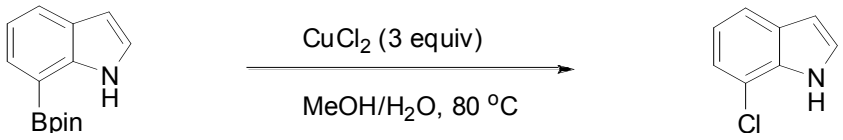
Borylation of 3-(2-(*tert*-butyldimethylsilyloxy)ethyl)indole. Inside a glove box, [Ru(*p*-cymene)Cl_2]$_2$ (6.0 mg, 0.010 mmol, 0.010 equiv), 3-(2-(*tert*-butyldimethylsilyloxy)ethyl)indole (275 mg, 1.00 mmol, 1.00 equiv), diethylsilane (132 mg, 1.50 mmol, 1.50 equiv) and toluene (0.5 mL) were added to a dry vial. The mixture was stirred at 50 °C for 12 h, at which time GC-MS analysis showed full conversion of 3-(2-(*tert*-butyldimethylsilyloxy)ethyl)indole. The volatile materials were removed under vacuum. [Ir(cod)Cl]$_2$ (1.7 mg, 0.0025 mmol, 0.0025 equiv), dtbpy (1.4 mg, 0.0050

mmol, 0.0050 equiv), B_2pin_2 (254 mg, 1.00 mmol, 1.00 equiv), HBpin (0.008 mL, 0.05 mmol, 0.05 equiv), and THF (1.0 mL) were added to the vial, and the reaction mixture was heated at 80 °C. After 6 h, GC-MS analysis indicated full conversion of the *N*-diethylsilyl-3-(2-(*tert*-butyldimethylsilyloxy)ethyl)indole. The reaction mixture was cooled to room temperature. The volatile materials were removed from the reaction mixture under high vacuum at 40 °C. The reaction mixture was dissolved in 2 mL of THF, and 0.5 mL of 3 M NaOAc (aq) was added. The mixture was stirred at room temperature for 4 h. Upon complete desilylation, the reaction mixture was diluted with Et_2O and H_2O. The aqueous layer was separated and extracted with Et_2O. The combined organic layers were washed with brine. The organic layer was dried with $MgSO_4$, filtered and concentrated under vacuum. Column chromatography (90:10 hexanes:ethyl acetate) afforded analytically pure product (193 mg, 48%). ^{1}H NMR (499 MHz, $CDCl_3$) δ 9.10 (s, 1H), 7.80 (d, J = 7.8, 1H), 7.71 (d, J = 6.9, 1H), 7.19 (t, J = 7.4, 1H), 7.15 (s, 1H), 3.94 (t, J = 7.4, 2H), 3.07 (t, J = 7.4, 2H), 1.44 (s, 12H), 0.98 (s, 9H), 0.11 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.58, 129.44, 126.93, 122.72, 122.24, 118.97, 112.82, 84.00, 64.38, 29.37, 26.30, 25.26, 18.67, -4.96. ^{11}B NMR (300MHz, $CDCl_3$): δ 32.5. Anal Calcd. for $C_{16}H_{20}BNO_4$: C, 65.82; H, 9.04; N, 3.49; found: C, 65.86; H, 9.18; N, 3.47.

Specific Experimental Procedures for Functionalization of 7-borylindoles



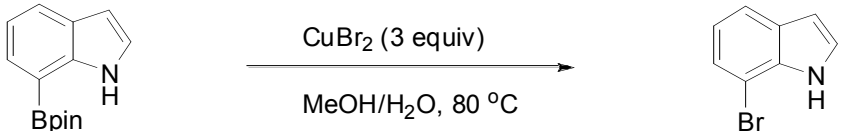
Suzuki-Miyaura Coupling of 7-borylindole with bromobenzene. 7-borylindole (243 mg, 1.00 mmol, 1.00 equiv), $Pd(dba)_2$ (28.8 mg, 0.050 mmol, 0.050 equiv), PPh_3 (52.4 mg, 0.200 mmol, 0.200 equiv), K_3PO_4 (640 mg, 3.00 mmol, 3.00 equiv), bromobenzene (220 mg, 1.40 mmol, 1.40 equiv) and DMF (4 mL) were added to a dry vial. The reaction mixture was heated at 80 °C for 10 h. The reaction mixture was cooled to room temperature, filtered through Celite, washing with Et_2O. The filtrate was concentrated. Column chromatography (80:20 hexanes:ethyl acetate) afforded the known product[4] judged to be pure by NMR spectroscopy (169 mg, 88%). ^{1}H NMR (499 MHz, $CDCl_3$): δ 8.48 (s, 1H), 7.77 (dd, J = 4.1, 4.7, 1H), 7.73 (d, J = 8.2, 2H), 7.60 (t, J = 7.6, 2H), 7.51 (t, J = 7.4, 1H), 7.34 (t, J = 5.0, 2H), 7.21 (d, J = 2.0, 1H), 6.73 (d, J = 4.3, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.64, 134.05, 129.47, 128.66, 128.54, 127.73, 125.97, 124.81, 122.23, 120.64, 120.39, 103.31.



Chlorination of 7-borylindole. 7-borylindole (243 mg, 1.00 mmol, 1.00 equiv) was dissolved in MeOH (12 mL). $CuCl_2$ (mg, 3.00 mmol, 3.00 equiv) was dissolved in H_2O (12 mL). The aqueous $CuCl_2$ solution was added to the MeOH solution, and the mixture was heated at 80 °C for 4 h. The reaction mixture was cooled to room temperature and diluted with Et_2O. The layers were separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried with $MgSO_4$, filtered and concentrated under vacuum. Column chromatography (80:20 hexanes:ethyl acetate)

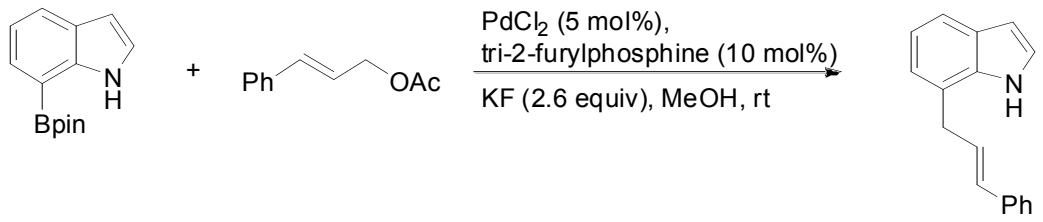
[4] Molander, G. A.; Biolatto, B. *J. Org. Chem.* **2003**, *68*, 4302.

afforded the known product[5] judged to be pure by NMR spectroscopy (113 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.56 (d, J = 7.9, 1H), 7.26 (d, J = 2.5, 1H), 7.21 (d, J = 7.6, 1H), 7.07 (t, J = 7.8, 1H), 6.61 (d, J = 4.3, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.38, 129.54, 124.98, 121.56, 120.81, 119.58, 116.81, 103.92.



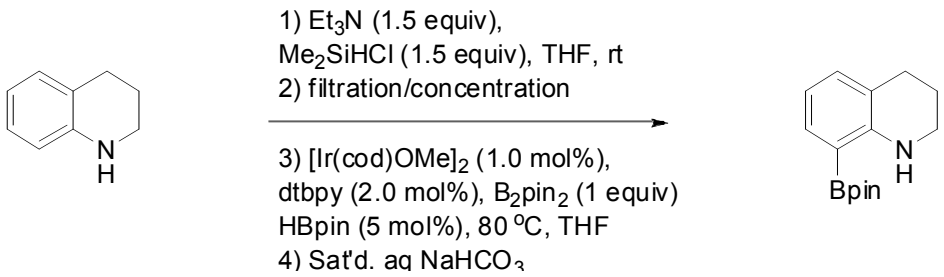
Bromination of 7-borylindole. 7-borylindole (243 mg, 1.00 mmol, 1.00 equiv) was dissolved in MeOH (12 mL). $CuBr_2$ (670 mg, 3.00 mmol, 3.00 equiv) was dissolved in H_2O (12 mL). The aqueous $CuBr_2$ solution was added to the MeOH solution and the mixture was heated at 80 °C for 4 h. The reactions mixture was cooled to room temperature and diluted with Et_2O. The layers were separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried with $MgSO_4$, filtered and concentrated under vacuum. Column chromatography (80:20 hexanes:ethyl acetate) afforded the known product[6] judged to be pure by NMR spectroscopy (78 mg, 40%). ^{1}H NMR (499 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.63 (d, J = 7.9, 1H), 7.40 (d, J = 7.6, 1H), 7.26 (m, 1H), 7.05 (t, J = 7.7, 1H), 6.70 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.84, 129.26, 124.96, 124.59, 121.26, 120.22, 104.91, 104.11.

[5] Bratulescu, G. *Tetrahedron Lett.* **2008**, *49*, 984.
[6] Smith, A. B.; Kurti, L.; Davulcu, A. H.; Cho, Y. S.; Ohmoto, K. *J.Org. Chem.* **2007**, *72*, 4611.



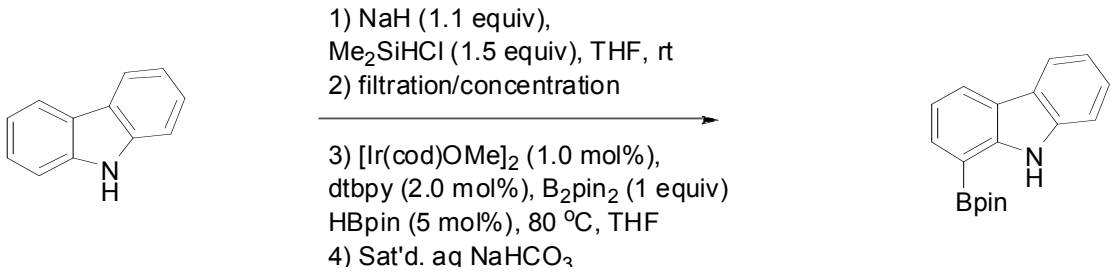
Allylation of 7-borylindole. $PdCl_2$ (7.0 mg, 0.039 mmol, 0.05 equiv), tri-2-furylphosphine (18 mg, 0.078 mmol, 0.10 equiv), 7-borylindole (243 mg, 1.00 mmol, 1.30 equiv), cinnamyl acetate (136 mg, 0.770 mmol, 1.00 equiv), KF (118 mg, 2.00 mmol, 2.6 equiv), and MeOH (4 mL) were added to a dry vial. The reaction was stirred at room temperature. After 24 h, GC analysis indicated full consumption of cinnamyl acetate. The reaction mixture was diluted with EtOAc and filtered through silica gel. The reaction mixture was concentrated under vacuum. Column chromatography (95:5 hexanes:ethyl acetate) afforded analytically pure product (121 mg, 52%). ^{1}H NMR (499 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.67 (d, J = 7.7, 1H), 7.43 (d, J = 7.7, 2H), 7.38 (t, J = 7.6, 2H), 7.31 (t, J = 7.2, 1H), 7.18 (dt, J = 7.3, 17.1, 3H), 6.66 (dd, J = 6.2, 9.4, 2H), 6.58 – 6.45 (m, 1H), 3.86 (d, J = 6.5, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.32, 135.47, 131.61, 128.91, 128.65, 128.29, 127.69, 126.48, 124.42, 122.51, 122.44, 120.34, 119.58, 103.16, 36.19. Anal Calcd. for $C_{17}H_{15}N$: C, 87.52; H, 6.48; N, 6.00; found: C, 87.27; H, 6.28; N, 5.93.

Specific Experimental Procedures for Borylation of other Nitrogen-Containing Heterocycles



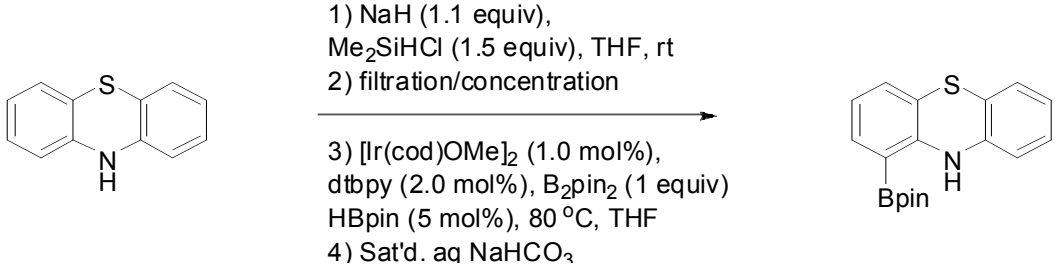
Borylation of 1,2,3,4-tetrahydroquinoline. Inside a glove box, triethylamine (160 mg, 1.50 mmol, 1.50 equiv), 1,2,3,4-tetrahydroquinoline (133 mg, 1.00 mmol, 1.00 equiv), dimethylchlorosilane (144 mg, 1.50 mmol, 1.50 equiv) and THF (2 mL) were added to a dry vial. The mixture was stirred at room temperature for 6 h, at which time GC analysis showed full conversion of the 1,2,3,4-tetrahydroquinoline. The reaction mixture was filtered through Celite, and the volatile materials were removed under vacuum. $[Ir(cod)OMe]_2$ (6.8 mg, 0.010 mmol, 0.010 equiv), dtbpy (5.6 mg, 0.020 mmol, 0.020 equiv), B_2pin_2 (254 mg, 1.00 mmol, 1.00 equiv), HBpin (0.008 mL, 0.05 mmol, 0.05 equiv), and THF (1 mL) were added to the vial, and the reaction mixture was heated at 80 °C. GC analysis indicated full conversion of the *N*-dimethylsilyltetrahydroquinoline. The reaction mixture was cooled to room temperature. The volatile materials were removed from the reaction mixture under high vacuum at 40 °C. The reaction mixture was dissolved in 2 mL of THF, and 1 mL of saturated $NaHCO_3$ (aq) was added. The mixture was stirred at room temperature for 6 h. Upon complete desilylation, the reaction mixture was diluted with Et_2O and H_2O. The aqueous layer was separated and extracted with Et_2O. The combined organic layers were washed with brine. The organic layer was

dried with $MgSO_4$, filtered, and concentrated under vacuum. Column chromatography (90:10 hexanes:ethyl acetate) afforded analytically pure product (64 mg, 40%). ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.44 (d, J = 7.4, 1H), 6.99 (d, J = 7.2, 1H), 6.50 (t, J = 7.3, 1H), 5.84 (s, 1H), 3.36 (m, 2H), 2.75 (t, J = 6.4, 2H), 1.91 (m, 2H), 1.32 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.58, 135.15, 133.08, 120.46, 115.11, 83.58, 41.81, 27.79, 25.11, 21.80. ^{11}B NMR (300MHz, $CDCl_3$): δ 33.3. Anal Calcd. for $C_{15}H_{22}BNO_2$: C, 69.52; H, 8.56; N, 5.40; found: C, 69.50; H, 8.68; N, 5.13.



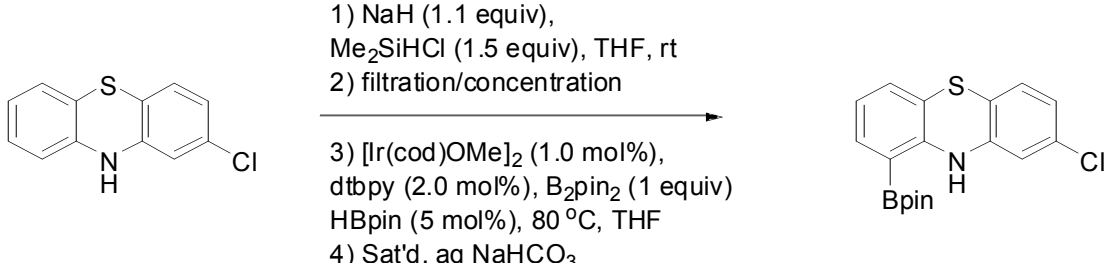
Borylation of carbazole. Inside a glove box, carbazole (168 mg, 1.00 mmol, 1.00 equiv), NaH (27 mg, 1.1 mmol, 1.1 equiv), and THF (2 mL) were added to a dry vial. The mixture was stirred at room temperature for 2 h. Dimethylchlorosilane (144 mg, 1.50 mmol, 1.50 equiv) was added. The mixture was stirred at room temperature for 10 h, at which time GC analysis showed full conversion of the carbazole. The reaction mixture was filtered through Celite, and the volatile materials were removed under vacuum. $[Ir(cod)OMe]_2$ (6.8 mg, 0.010 mmol, 0.010 equiv), dtbpy (5.6 mg, 0.020 mmol, 0.020 equiv), B_2pin_2 (254 mg, 1.00 mmol, 1.00 equiv), HBpin (0.008 mL, 0.05 mmol, 0.05 equiv), and THF (1 mL) were added to the vial, and the reaction mixture was heated at 80 °C. GC analysis indicated full conversion of the *N*-dimethylsilylcarbazole. The reaction mixture was cooled to room temperature. The volatile materials were removed

from the reaction mixture under high vacuum at 40 °C. The reaction mixture was dissolved in 2 mL of THF, and 1 mL of saturated $NaHCO_3$ (aq) was added. The mixture was stirred at room temperature for 6 h. Upon complete desilylation, the reaction mixture was diluted with Et_2O and H_2O. The aqueous layer was separated and extracted with Et_2O. The combined organic layers were washed with brine. The organic layer was dried with $MgSO_4$, filtered, and concentrated under vacuum. Column chromatography (90:10 hexanes:ethyl acetate) afforded analytically pure product (138 mg, 47%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.23 (d, J = 7.5, 1H), 8.12 (t, J = 7.0, 2H), 7.91 (d, J = 7.0, 1H), 7.55 (d, J = 8.0, 1H), 7.50 – 7.37 (m, 2H), 7.28 (dd, J = 7.3, 14.7, 3H), 1.47 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.30, 139.57, 133.08, 125.98, 123.94, 123.14, 122.53, 120.54, 119.39, 118.98, 110.82, 84.27, 25.30. Anal Calcd. for $C_{18}H_{20}BNO_2$: C, 73.74; H, 6.88; N, 4.78; found: C, 73.66; H, 7.10; N, 4.78.



Borylation of phenothiazine. Inside a glove box, phenothiazine (199 mg, 1.00 mmol, 1.00 equiv), NaH (27 mg, 1.1 mmol, 1.1 equiv), and THF (2 mL) were added to a dry vial. The mixture was stirred at room temperature for 2 h. Dimethylchlorosilane (144 mg, 1.50 mmol, 1.50 equiv) was added, and the mixture was stirred at room temperature for 10 h. The reaction mixture was filtered and concentrated, washing with Et_2O. $[Ir(cod)OMe]_2$ (6.8 mg, 0.010 mmol, 0.010 equiv), dtbpy (5.6 mg, 0.020 mmol, 0.020

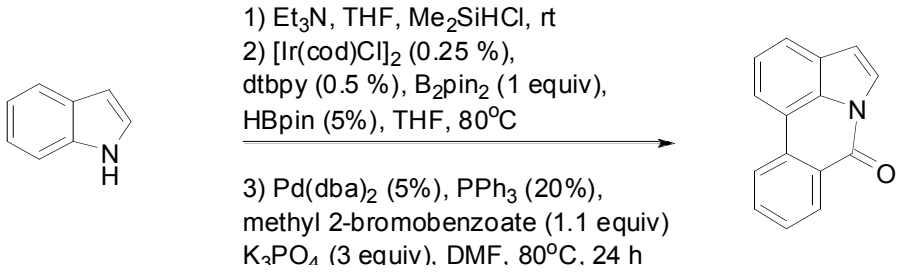
equiv), B_2pin_2 (254 mg, 1.00 mmol, 1.00 equiv), HBpin (0.008 mL, 0.05 mmol, 0.05 equiv), and THF (1 mL) were added to the vial.. The reaction mixture was heated at 80 °C for 24 h, at which time GC analysis indicated full conversion of the *N*-dimethylsilyl-phenothiazine. The reaction mixture was cooled to room temperature. The volatile materials were removed from the reaction mixture under high vacuum at 40 °C. Column chromatography (90:10 hexanes:ethyl acetate) afforded analytically pure product (208 mg, 64%). ^{1}H NMR (499 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.48 (d, 1H), 7.09 (d, J = 7.5, 1H), 7.01 (m, 2H), 6.82 (ddd, J = 4.6, 9.1, 10.5, 2H), 6.58 (d, J = 7.8, 1H), 1.41 (s, J = 1.6, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.95, 142.23, 135.02, 130.42, 127.49, 126.86, 122.71, 121.72, 118.55, 118.27, 115.01, 84.48, 25.21. ^{11}B NMR (300MHz, $CDCl_3$): δ 31.7. Anal Calcd. for $C_{18}H_{20}BNO_2S$: C, 66.47; H, 6.20; N, 4.31; found: C, 66.22; H, 6.19; N, 4.38.



Borylation of 2-chlorophenothiazine. Inside a glove box, 2-chlorophenothiazine (234 mg, 1.00 mmol, 1.00 equiv), NaH (27 mg, 1.1 mmol, 1.1 equiv), and THF (2 mL) were added to a dry vial. The mixture was stirred at room temperature for 2 h. Dimethylchlorosilane (144 mg, 1.50 mmol, 1.50 equiv) was added, and the mixture was stirred at room temperature for 10 h. The reaction mixture was filtered and concentrated, washing with Et_2O. $[Ir(cod)OMe]_2$ (6.8 mg, 0.010 mmol, 0.010 equiv), dtbpy (5.6 mg,

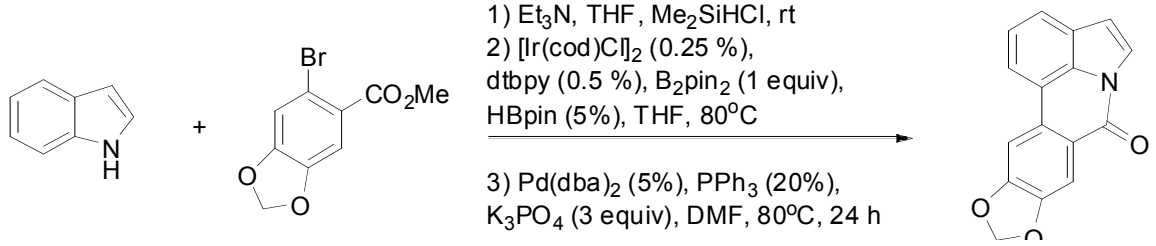
0.020 mmol, 0.020 equiv), B_2pin_2 (254 mg, 1.00 mmol, 1.00 equiv), HBpin (0.008 mL, 0.05 mmol, 0.05 equiv), and THF (1 mL) were added to the vial.. The reaction mixture was heated at 80 °C for 24 h, at which time GC analysis indicated full conversion of the *N*-dimethylsilyl-2-chlorophenothiazine. The reaction mixture was cooled to room temperature. The volatile materials were removed from the reaction mixture under high vacuum at 40 °C. The reaction mixture was dissolved in 2 mL of THF, and 1 mL of saturated $NaHCO_3$ (aq) was added. The mixture was stirred at room temperature for 6 h. Upon complete desilylation, the reaction mixture was diluted with Et_2O and H_2O. The aqueous layer was separated and extracted with Et_2O. The combined organic layers were washed with brine. The organic layer was dried with $MgSO_4$, filtered and concentrated under vacuum. Column chromatography (90:10 hexanes:ethyl acetate) afforded analytically pure product (314 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.46 (dd, J = 1.2, 7.4, 1H), 7.04 (d, J = 8.4, 1H), 6.80 (m, 3H), 6.50 (d, J = 1.9, 1H), 1.39 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.04, 143.30, 135.15, 132.96, 130.39, 127.47, 122.41, 122.21, 117.86, 117.11, 114.81, 84.64, 25.19. ^{11}B NMR (300MHz, $CDCl_3$): δ 31.8. Anal Calcd. for $C_{18}H_{19}BNO_2SCl$: C, 60.11; H, 5.632 N, 3.89 found: C, 60.34; H, 5.49; N, 4.10.

Specific Experimental Procedures for Synthesis of Pyrrolophenanthridone Alkaloids



Synthesis of core of pyrrolophenanthridone alkaloids. Inside a glove box, triethylamine (160 mg, 1.50 mmol, 1.50 equiv), indole (117 mg, 1.00 mmol, 1.00 equiv), dimethylchlorosilane (144 mg, 1.50 mmol, 1.50 equiv) and THF (2 mL) were added to a dry vial. The mixture was stirred at room temperature for 6 h, at which time GC analysis showed full conversion of the indole. The reaction mixture was filtered through Celite, and the volatile materials were removed under vacuum. $[Ir(cod)Cl]_2$ (1.7 mg, 0.0025 mmol, 0.0025 equiv), dtbpy (1.4 mg, 0.0050 mmol, 0.0050 equiv), B_2pin_2 (254 mg, 1.00 mmol, 1.00 equiv), HBpin (0.008 mL, 0.05 mmol, 0.05 equiv), and THF (1 mL) were added to the vial.. The reaction mixture was heated at 80 °C for 6 h, at which time GC analysis indicated full conversion of the *N*-dimethylsilylindole. The reaction mixture was cooled to room temperature. The volatile materials were removed from the reaction mixture under high vacuum. $Pd(dba)_2$ (30 mg, 0.050 mmol, 0.050 equiv), PPh_3 (52 mg, 0.20 mmol, 0.20 equiv), methyl 2-bromobenzoate (255 mg, 1.20 mmol, 1.20 equiv), K_3PO_4 (638 mg, 3.00 mmol, 3.00 equiv) and DMF (4 mL) were added to the reaction mixture. The reaction mixture was heated to 80 ^oC for 24 h. The reaction was filtered through Celite, washed with EtOAc, and concentrated under vacuum. Column chromatography (80:20 hexanes:ethyl acetate) afforded the known product[3] judged to be

pure by NMR spectroscopy (130 mg, 60%). ^{1}H NMR (499 MHz, $CDCl_3$) δ 8.58 (d, J = 8.0, 1H), 8.22 (d, J = 7.9, 1H), 8.03 (d, J = 3.6, 1H), 7.97 (d, J = 7.7, 1H), 7.75 (m, 2H), 7.58 (t, J = 7.6, 1H), 7.44 (t, J = 7.7, 1H), 6.89 (d, J = 3.6, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.93, 134.65, 133.28, 131.64, 129.73, 128.65, 128.29, 127.22, 124.26, 123.59, 123.12, 122.83, 118.77, 116.80, 111.27.

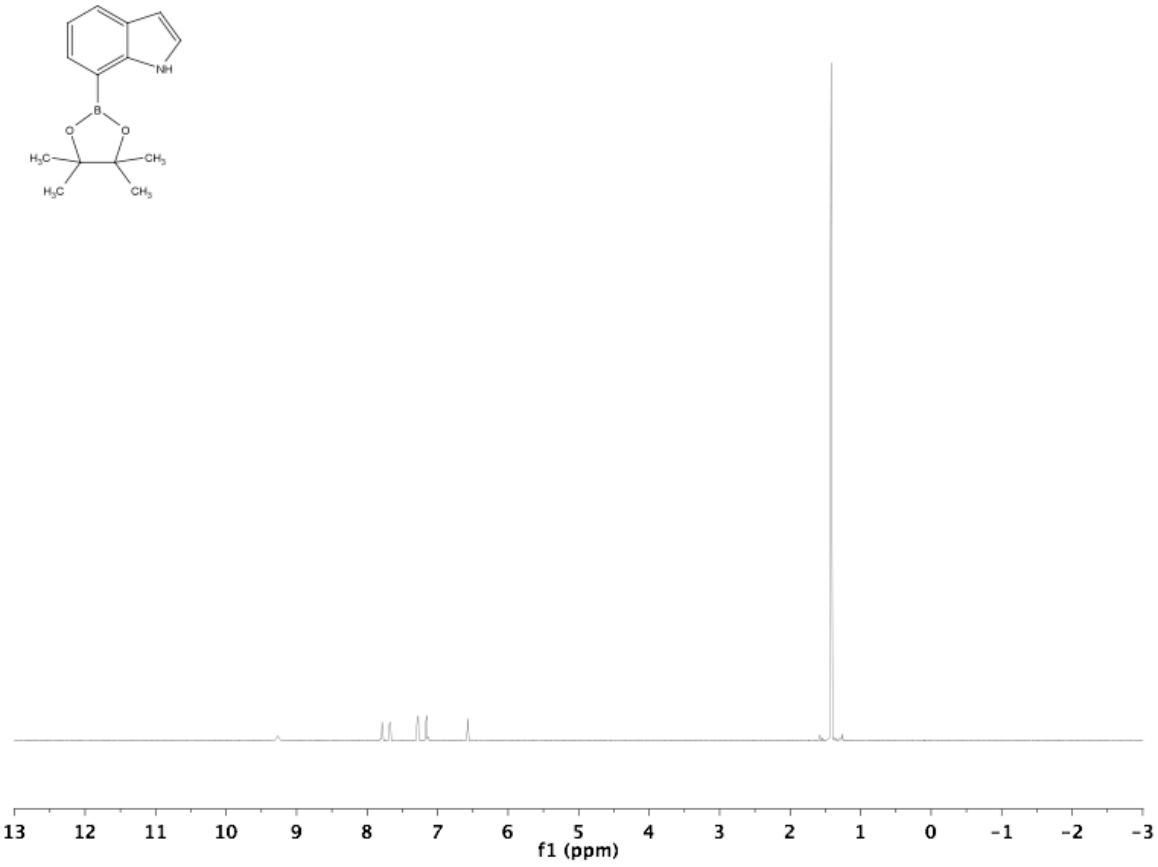


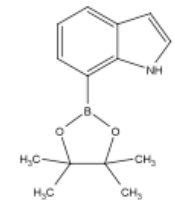
Synthesis of Hippadine. Inside a glove box, triethylamine (37 mg, 0.36 mmol, 1.5 equiv), indole (28 mg, 0.24 mmol, 1 equiv), dimethylchlorosilane (34 mg, 0.36 mmol, 1.5 equiv) and THF (0.5 mL) were added to a dry vial. The mixture was stirred at room temperature for 6 h, at which time GC analysis showed full conversion of the indole. The reaction mixture was filtered through Celite, and the volatile materials were removed under vacuum. $[Ir(cod)Cl]_2$ (0.4 mg, 0.0006 mmol, 0.003 equiv), dtbpy (0.3 mg, 0.001 mmol, 0.005 equiv), B_2pin_2 (61 mg, 0.24 mmol, 1.0 equiv), HBpin (0.001 mL, 0.01 mmol, 0.05 equiv), and THF (0.4 mL) were added to the vial. The reaction mixture was heated at 80 °C for 6 h, at which time GC analysis indicated full conversion of the *N*-dimethylsilylindole. The reaction mixture was cooled to room temperature. The volatile materials were removed from the reaction mixture under high vacuum. $Pd(dba)_2$ (7.2 mg, 0.012 mmol, 0.05 equiv), PPh_3 (12.4 mg, 0.048 mmol, 0.20 equiv), methyl 6-bromo-1,3-

benzodioxole-5-carboxylate (68 mg, 0.26 mmol, 1.10 equiv), K_3PO_4 (153 mg, 0.717 mmol, 3.00 equiv) and DMF (1 mL) were added to the reaction mixture. The reaction mixture was heated at 80 °C for 24 h. The reaction was filtered through Celite, washed with EtOAc, and concentrated under vacuum. Column chromatography (80:20 hexanes:ethyl acetate) afforded the known product[7] judged to be pure by NMR spectroscopy (30 mg, 48%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 3.5, 1H), 7.94 (s, 1H), 7.87 (d, J = 7.6, 1H), 7.73 (d, J = 7.6, 1H), 7.60 (s, 1H), 7.45 (t, J = 7.7, 1H), 6.88 (d, J = 3.5, 1H), 6.15 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.35, 152.73, 148.72, 131.69, 131.10, 128.69, 124.15, 123.69, 122.84, 122.64, 118.54, 116.76, 110.98, 108.15, 102.57, 101.86.

[7] Ganton, M. D.; Kerr, M. A. *Org. Lett.* **2005**, *7*, 4777.

Selected ^{1}H and ^{13}C NMR Spectra

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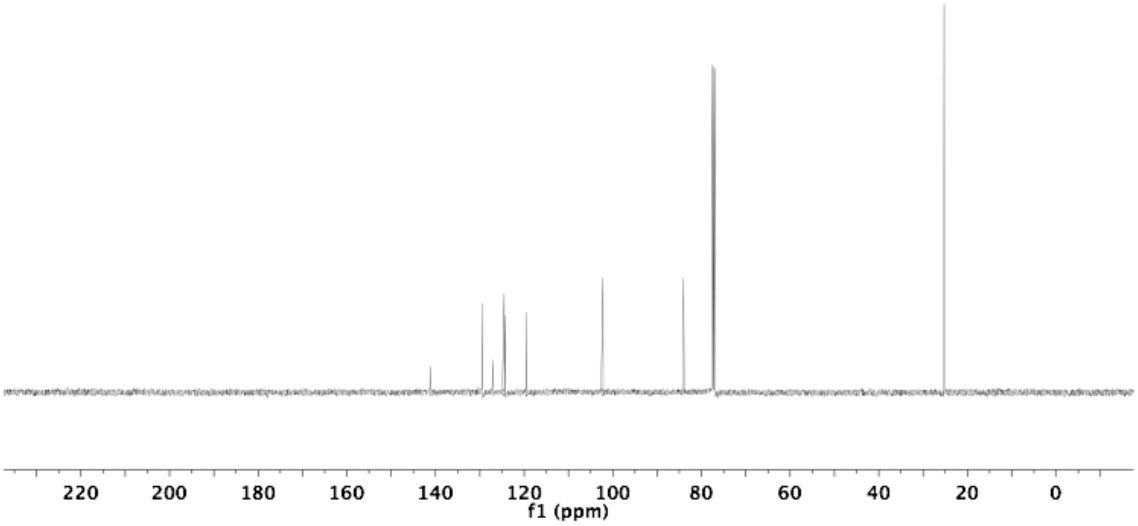
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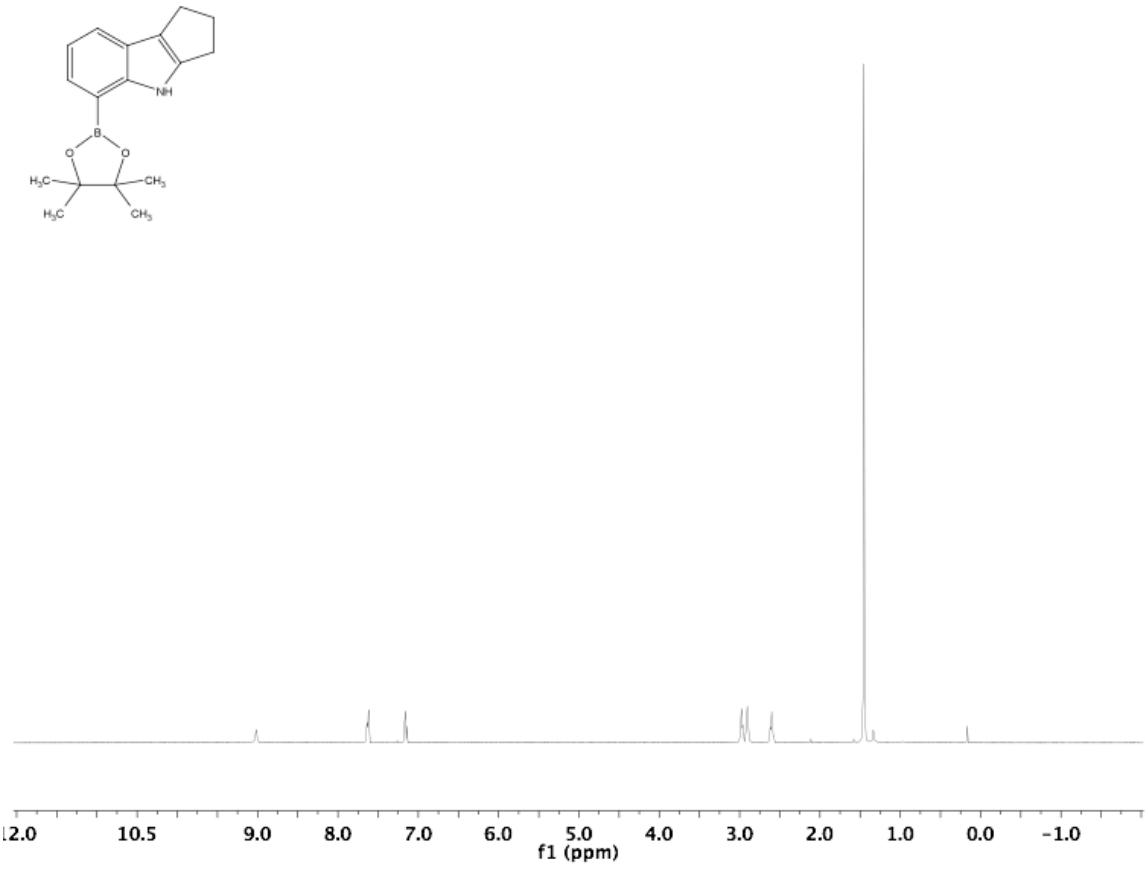
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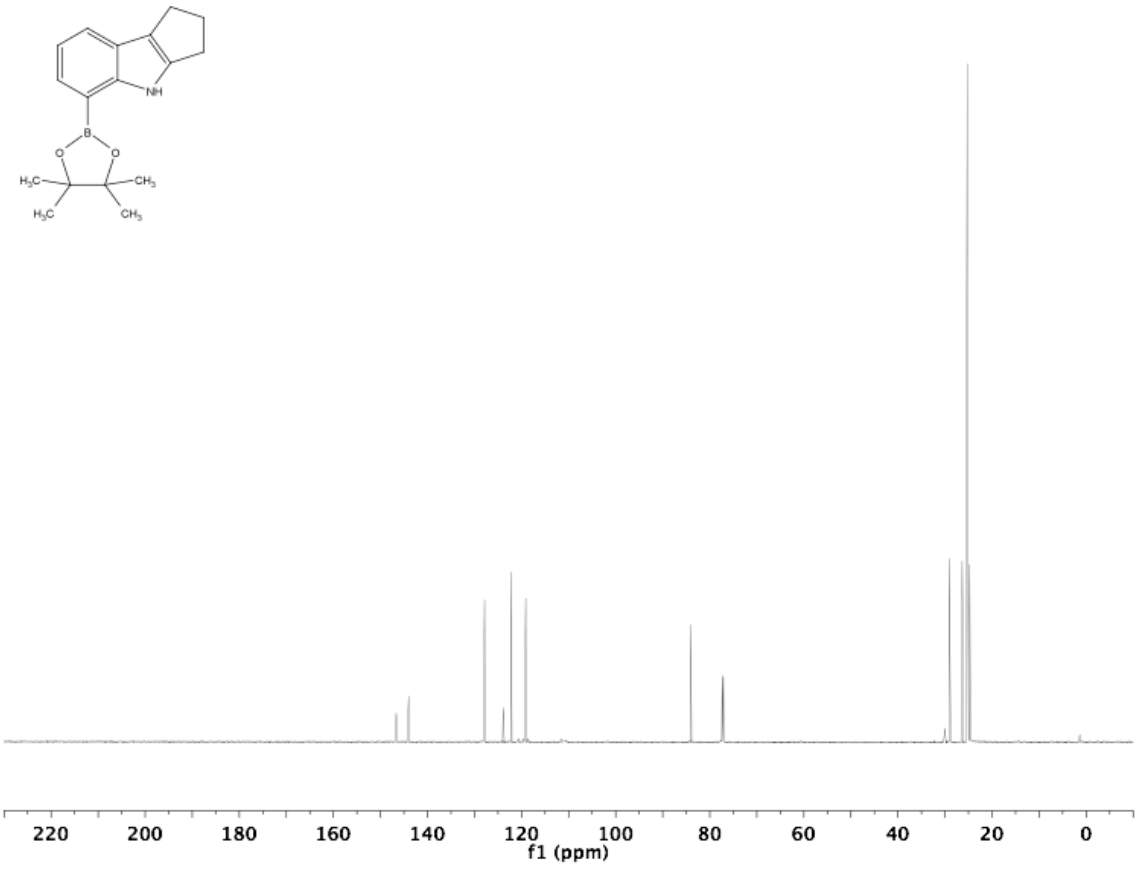
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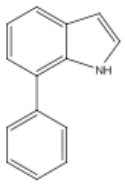
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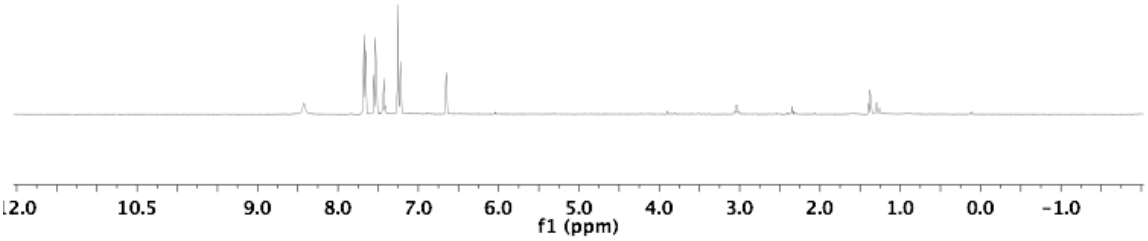
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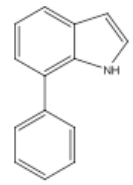
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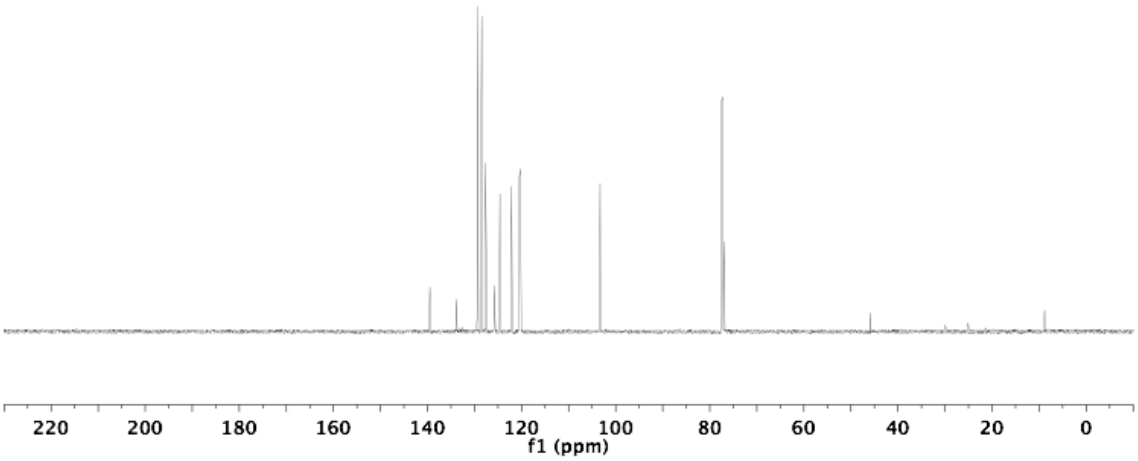
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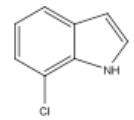
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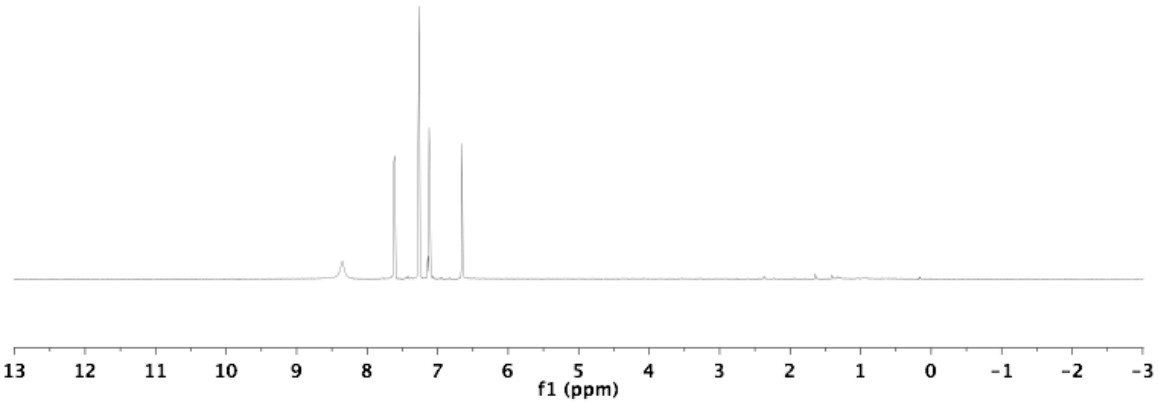
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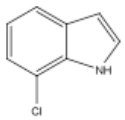
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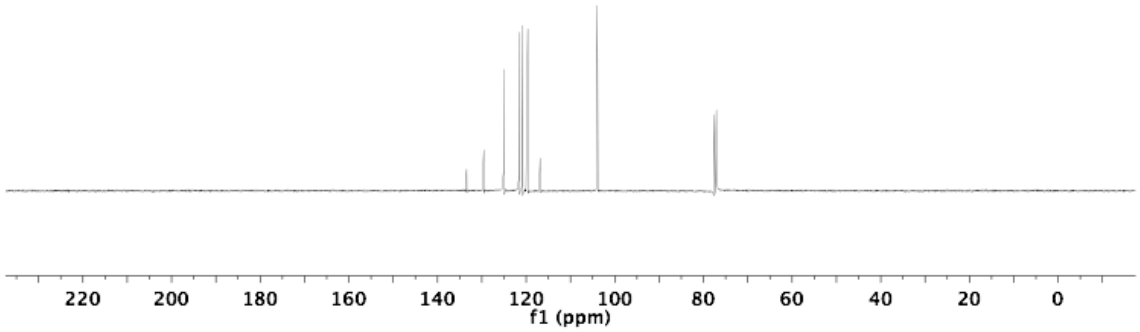
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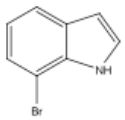
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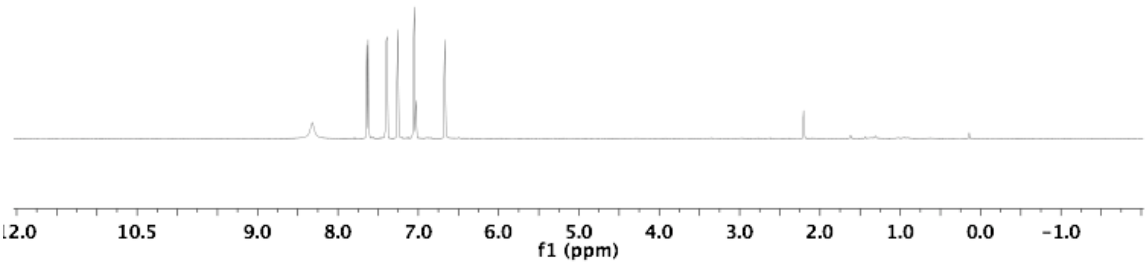
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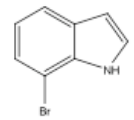
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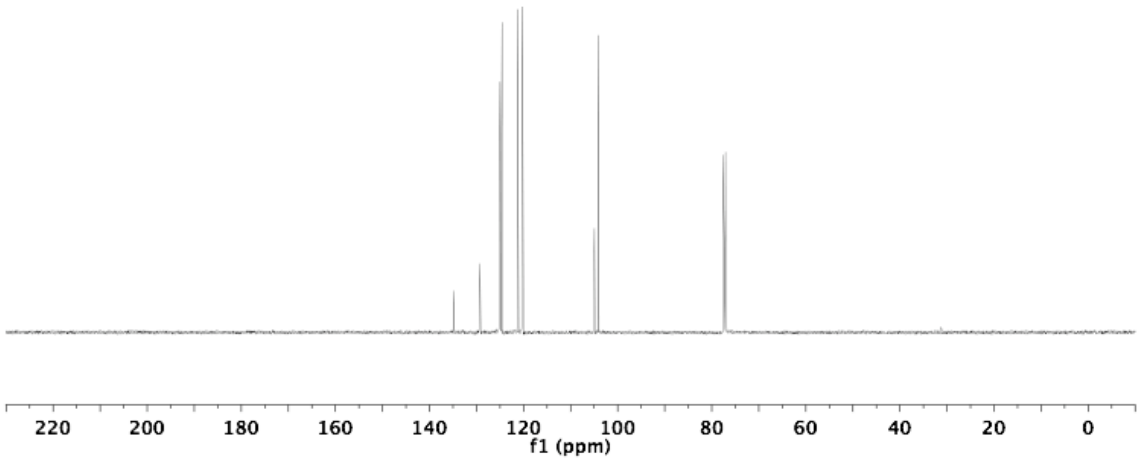
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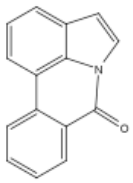
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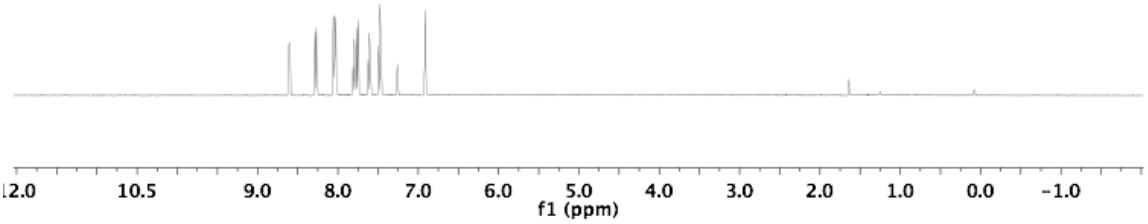
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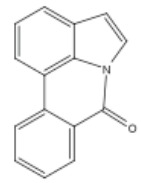
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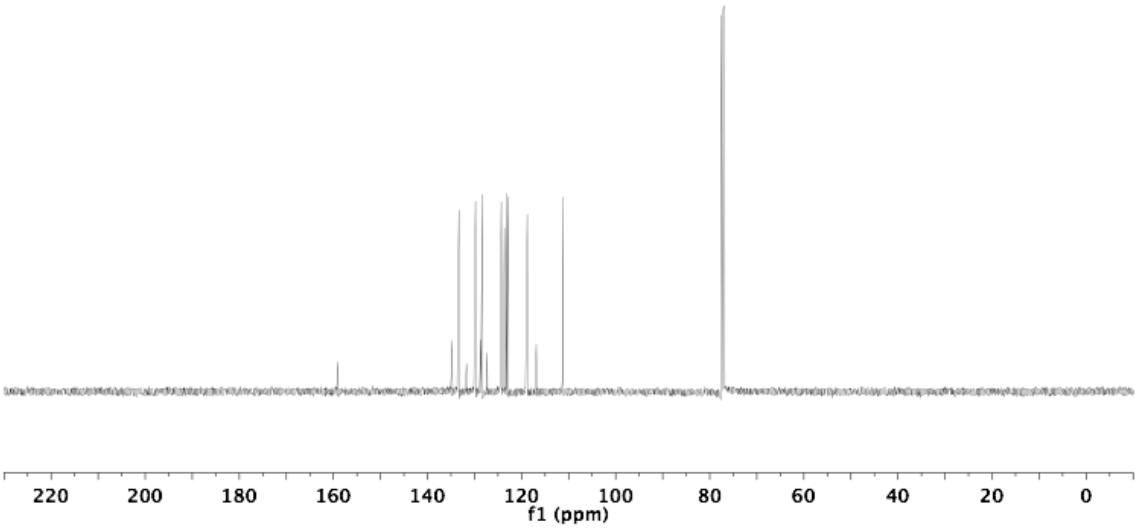
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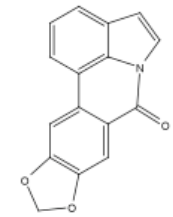
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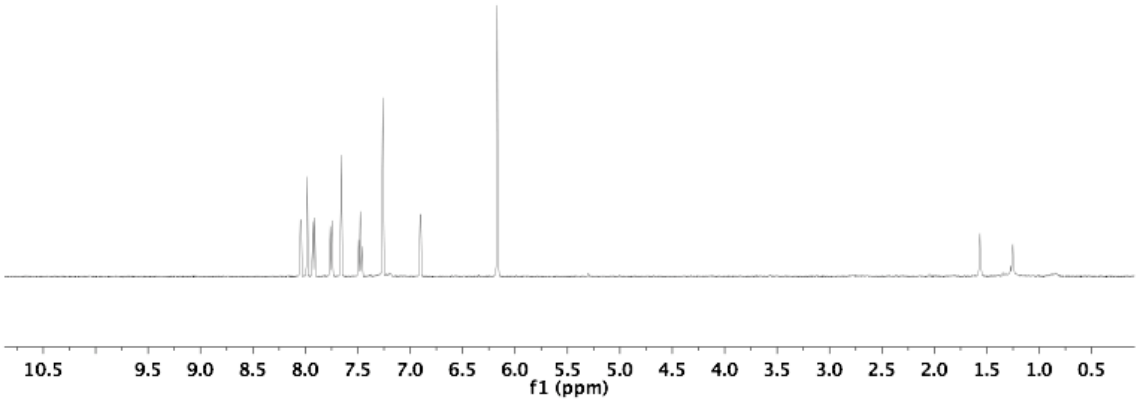
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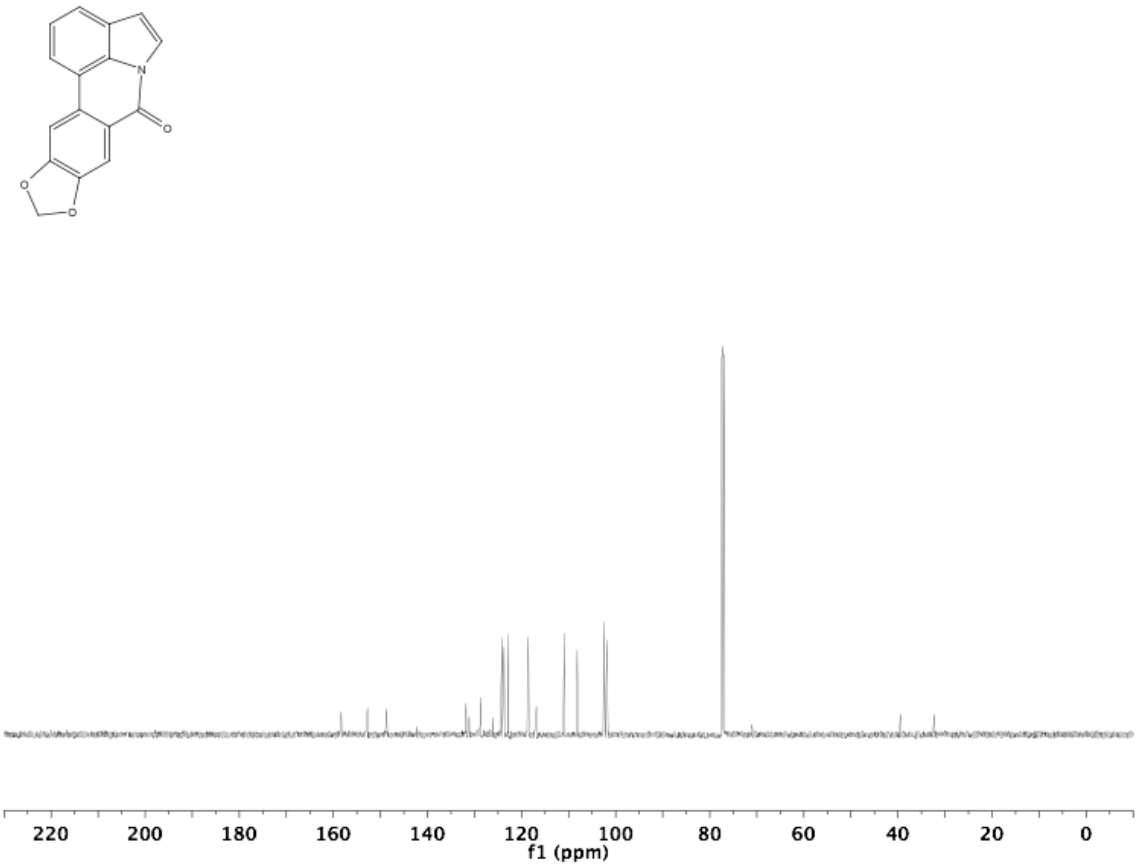
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