Cine Substitution of Arenes using the Aryl Carbamate as a Removable Directing Group

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Materials and Methods. Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of nitrogen using anhydrous solvents (either freshly distilled or passed through activated alumina columns). Unless otherwise stated, commercially obtained reagents were used as received. $\text{NiCl}_2(\text{PCy}_3)_2$ was obtained from Strem Chemicals, 1,1,3,3-tetramethyldisiloxane (TMDSO) was obtained from Sigma Aldrich and potassium phosphate was obtained from VWR (manufactured by Acros Organics). Reaction temperatures were controlled using an IKAmag temperature modulator, and unless stated otherwise, reactions were performed at room temperature (rt, approximately 23 °C). Thin-layer chromatography (TLC) was conducted with EMD gel 60 F254 pre-coated plates (0.25 mm) and visualized using a combination of UV, anisaldehyde, ceric ammonium molybdate, iodine, vanillin, and potassium permanganate staining. Silicycle Siliacflash P60 (particle size 0.040–0.063 mm) was used for flash column chromatography. ¹H NMR spectra were recorded on Bruker spectrometers (at 300, 400, 500, 600 MHz) and are reported relative to deuterated solvent signals. Data for ¹H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ¹³C NMR spectra were recorded on Bruker Spectrometers (at 125 MHz). Data for ¹³C NMR spectra are reported in terms of chemical shift. ¹⁹F NMR (at 300, 400 MHz) spectra are reported in terms of chemical shift. IR spectra were recorded on a Perkin-Elmer 100 spectrometer and are reported in terms of frequency of absorption (cm⁻¹). Melting points are uncorrected and were obtained on a Laboratory Devices Mel-Temp II instrument. High resolution mass spectra were obtained from both the UC Los Angeles and Irvine Mass Spectrometry Facility.

Experimental Procedures.

A. Synthesis of Aryl Carbamate Substrates

Note: Supporting information for the synthesis of the aryl carbamates shown in Figures 2–5 have previously been reported,¹ with the exception of the carbamates **SI-2**, **SI-4**, **SI-6**, **SI-8**, **SI-10**, **SI-13**, **4a**, **4b**, **4c**, **7**, **8**, and **9**.

4a. To a solution of carbamate **3**¹ (0.1 g, 0.448 mmol, 1.0 equiv) and TMEDA (0.087 mL, 0.582 mmol, 1.3 equiv) in THF (2.2 mL) at -78°C was added *sec*-BuLi (0.525 mL, 0.582 mmol, 1.3 equiv) over 15 min. After stirring for 1 h, ClC(O)NEt₂ (0.074 mL, 0.582 mmol, 1.3 equiv) was added over 10 min. The reaction was stirred at -78°C for 1 h, allowed to warm to 23°C , and then quenched with saturated aqueous NH₄Cl (5 mL). The reaction mixture was diluted with H₂O (5 mL) and EtOAc (10 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over MgSO₄ and concentrated under reduced pressure. The crude residue was purified by flash chromatography (3:1 Hexanes:EtOAc) to yield amide product **4a** (0.118 g, 82% yield) as a light yellow oil. *R*_f 0.12 (3:1 Hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃): δ 7.12 (d, *J* = 9.0, 1H), 6.90 (dd, *J* = 9.0, 3.0, 1H), 6.78 (d, *J* = 3.0, 1H), 3.80 (s, 3H), 3.74 (as, 1H), 3.44–3.23 (m, 6H), 3.13 (as, 1H), 1.21 (atd, *J* = 7.0, 1.5, 6H), 1.17 (t, *J* = 7.0, 3H), 1.07 (t, *J* = 7.0, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 167.4, 156.6, 153.9, 140.8, 131.3, 124.3, 115.0, 111.5, 55.7, 42.8, 42.2, 42.0, 38.6, 14.2, 13.9, 13.4, 12.7; IR (film): 2973, 2936, 1714, 1634, 1197, 1152 cm⁻¹; HRMS-ESI (*m/z*) [*M* + *H*]⁺ calcd for C₁₇H₂₆N₂O₄H, 323.1971; found, 323.1971.

4b. To a solution of carbamate **3**¹ (0.1 g, 0.448 mmol, 1.0 equiv) and TMEDA (0.087 mL, 0.582 mmol, 1.3 equiv) in THF (2.2 mL) at -78°C was added *sec*-BuLi (0.525 mL, 0.582 mmol, 1.3 equiv) over 15 min. After stirring for 1 h, Et_3SiCl (0.098 mL, 0.582 mmol, 1.3 equiv) was added over 10 min. The reaction was stirred at -78°C for 1 h, allowed to warm to 23°C , and then quenched with saturated aqueous NH_4Cl (5 mL). The reaction mixture was diluted with H_2O (5 mL) and EtOAc (10 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over MgSO_4 and concentrated under reduced pressure. The crude residue was purified by flash chromatography (20:1 Hexanes:EtOAc) to yield silyl product **4b** (0.107 g, 71% yield) as a clear oil. R_f 0.52 (3:1 Hexanes:EtOAc); ^1H NMR (400 MHz, CDCl_3): δ 6.97–6.87 (m, 3H), 3.81 (s, 3H), 3.47 (q, $J = 6.8$, 2H), 3.40 (q, $J = 7.2$, 2H), 1.25 (t, $J = 7.2$, 3H), 1.19 (t, $J = 6.8$, 6H), 0.96 (at, $J = 8.0$, 9H), 0.81 (aq, $J = 8.0$, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 156.5, 155.3, 150.0, 123.3, 119.8, 118.4, 83.7, 55.8, 42.1, 41.7, 25.0, 14.2, 13.6; IR (film): 2954, 2876, 1715, 1264, 1186, 1153 cm^{-1} ; HRMS-ESI (m/z) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{31}\text{NO}_3\text{SiH}$, 338.2151; found, 338.2153.

4c. To a solution of carbamate **3**¹ (0.1 g, 0.448 mmol, 1.0 equiv) and TMEDA (0.087 mL, 0.582 mmol, 1.3 equiv) in THF (2.2 mL) at -78°C was added *sec*-BuLi (0.525 mL, 0.582 mmol, 1.3 equiv) over 15 min. After stirring for 1 h, trimethylborate (0.065 mL, 0.582 mmol, 1.3 equiv) was added over 10 min. The reaction was stirred at -78°C for 1 h, allowed to warm to 23°C , and then quenched with saturated aqueous NH_4Cl (5 mL). The reaction mixture was diluted with H_2O (5 mL) and EtOAc (10 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over MgSO_4 and concentrated under reduced

pressure. The crude residue was dissolved in MeOH (30 ml) with pinacol (0.069 g, 0.582 mmol), concentrated in vacuo, and purified by flash chromatography (5:1 Hexanes:EtOAc) to yield pinacolborane product **4c** (0.105 g, 67% yield) as a clear oil. R_f 0.44 (3:1 Hexanes:EtOAc); ^1H NMR (500 MHz, CDCl_3): δ 7.27 (ad, $J = 3.0$, 1H), 6.99–6.95 (m, 2H), 3.50 (q, $J = 7.0$, 2H), 3.38 (q, $J = 7.0$, 2H), 1.31 (s, 12H), 1.29 (t, $J = 7.5$, 3H), 1.20 (t, $J = 7.0$, 9H); ^{13}C NMR (125 MHz, CDCl_3): δ 156.3, 154.9, 150.2, 130.1, 123.2, 121.1, 114.9, 55.7, 41.9, 41.5, 14.3, 13.4, 7.6, 3.5; IR (film): 2977, 2935, 1712, 1410, 1194, 1156 cm^{-1} ; HRMS-ESI (m/z) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{28}\text{BNO}_5\text{H}$, 350.2142; found, 350.2144.

Amide Carbamate 7. To a solution of indole carbamate **6**² (1.5 g, 6.09 mmol, 1.0 equiv) and TMEDA (1.0 mL, 6.70 mmol, 1.1 equiv) in THF (30 mL) at $-78\text{ }^\circ\text{C}$ was added *sec*-BuLi (6.0 mL, 6.70 mmol, 1.1 equiv) over 15 min. After stirring for 45 min the reaction was allowed to warm to $23\text{ }^\circ\text{C}$ and stirred for 3 h. The reaction was quenched with H_2O (30 mL) and EtOAc (100 mL). The layers were separated and the aqueous layer was extracted with EtOAc (4 x 100 mL). The combined organic layers were washed with brine (50 mL), dried over MgSO_4 and concentrated under reduced pressure. The crude residue was purified by flash chromatography (7:1 $\rightarrow$ 5:1 $\rightarrow$ 4:1 $\rightarrow$ 2:1 $\rightarrow$ 1:1 $\rightarrow$ 1:2 Hexanes:Acetone) to yield the amide hydroxyindole product **SI-1** (0.980 g, 65% yield) as a colorless amorphous solid. R_f 0.13 (5:1 Hexanes:Acetone); ^1H NMR (500 MHz, CDCl_3): δ 7.33 (d, $J = 8.5$, 1H), 7.23 (at, $J = 7.5$, 1H), 7.07–7.09 (m, 2H), 6.44 (dd, $J = 0.5$, 3.0, 1H), 3.81 (s, 3H), 3.65 (as, 2H), 3.22 (as, 2H), 1.31 (as, 3H), 1.02 (as, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 170.9, 136.9, 129.7, 129.7, 125.6, 121.4, 117.2, 109.9, 99.9, 43.2, 38.9, 33.1, 14.6, 13.3; IR (film): 3160, 1596, 1577, 1309, 1255 cm^{-1} ; HRMS-ESI (m/z) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_2\text{H}$, 247.1447; found, 247.1448.

A round bottom flask was charged with NaH (0.175 g, 4.38 mmol, 1.2 equiv, 60% dispersion in oil). A solution of amide hydroxyindole **SI-1** (0.90 g, 3.65 mmol, 1 equiv) in DME (15 mL) and DMSO (5 mL) was warmed to $50\text{ }^\circ\text{C}$ to fully dissolve the amide hydroxyindole. The homogeneous solution was added dropwise via cannula to the sodium hydride. Diethylcarbamoyl chloride (0.44 mL, 3.47 mmol, 0.95 equiv) was then added dropwise to the reaction vessel. The reaction was stirred for 41

h. The reaction was diluted with H₂O (25 mL) and EtOAc (25 mL) and the layers were separated. The aqueous layer was extracted with EtOAc (3 x 500 mL). The combined organic layers were then washed with H₂O (2 x 50 mL) and brine (50 mL), dried over MgSO₄, and evaporated to dryness. The crude residue was purified by flash chromatography (6:1 → 4:1 Hexanes:Acetone) to yield amide carbamate **7** (0.700 g, 58% yield) as a yellow oil. *R*_f 0.31 (4:1 Hexanes:Acetone); ¹H NMR (500 MHz, CDCl₃): δ 7.25 (d, *J* = 5.0, 1H), 7.06–7.05 (m, 2H), 6.36 (d, *J* = 3.0, 1H), 3.79 (s, 3H), 3.72 (sextet, *J* = 7.0, 1H), 3.53 (sextet, *J* = 7.0, 1H), 3.50–3.31 (m, 4H), 3.28 (sextet, *J* = 7.0, 1H), 3.11 (sextet, *J* = 7.0, 1H), 1.27 (t, *J* = 7.0, 3H), 1.23 (t, *J* = 7.0, 3H), 1.17 (t, *J* = 7.0, 3H), 0.98 (t, *J* = 7.0, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 167.2, 154.7, 140.6, 134.4, 130.2, 125.8, 121.8, 117.4, 109.9, 100.0, 43.0, 42.2, 42.1, 38.5, 33.3, 14.3, 14.2, 13.6, 13.1; IR (film): 2974, 1714, 1632, 1417, 1220, 1160 cm⁻¹; HRMS-ESI (*m/z*) [*M* + H]⁺ calcd for C₁₉H₂₇N₃O₃H, 346.2131; found, 346.2130.

Methyl Carbamate 8. To a solution of indole carbamate **6**² (1.0 g, 4.06 mmol, 1.0 equiv) and TMEDA (0.67 mL, 4.47 mmol, 1.1 equiv) in THF (20 mL) at –78 °C was added *sec*-BuLi (3.6 mL, 4.47 mmol, 1.1 equiv) over 15 min. After stirring for 1 h, methyl iodide (0.30 mL, 4.87 mmol, 1.2 equiv) was added dropwise over 1 min and stirred for 1 h. The reaction was allowed to warm to 23 °C over 1 h and quenched with saturated aqueous NH₄Cl (10 mL). The reaction mixture was diluted with H₂O (20 mL) and EtOAc (30 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with brine (30 mL), dried over MgSO₄ and concentrated under reduced pressure. The crude residue was purified by flash chromatography (7:1 → 5:1 Hexanes:EtOAc) to afford the methyl carbamate **8** (0.80 g, 76% yield) as a white solid. *R*_f 0.30 (5:1 Hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃): δ 7.11 (d, *J* = 8.5, 1H), 7.03 (d, *J* = 3.0, 1H), 6.94 (d, *J* = 8.5, 1H), 6.46 (d, *J* = 3.0, 1H), 3.76 (s, 3H), 3.51 (ad, *J* = 6.0, 2H), 3.41 (ad, *J* = 6.0, 2H), 2.37 (s, 3H), 1.30 (as, 3H), 1.21 (as, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 155.1, 142.8, 134.3, 129.3, 129.1, 121.6, 116.8, 107.1, 99.9, 42.2, 41.9, 33.2, 17.4, 14.5, 12.7; IR (film): 2972, 1708, 1467, 1418, 1218, 1159 cm⁻¹; HRMS-ESI (*m/z*) [*M* + Na]⁺ calcd for C₁₅H₂₀N₂O₂Na, 283.1422; found, 283.1420.

Silyl Carbamate 9. To a solution of indole carbamate **6**² (1.0 g, 4.06 mmol, 1.0 equiv) and TMEDA (0.67 mL, 4.47 mmol, 1.1 equiv) in THF (20 mL) at $-78\text{ }^{\circ}\text{C}$ was added *sec*-BuLi (3.6 mL, 4.47 mmol, 1.1 equiv) over 15 min. After stirring for 1 h, Me_3SiCl (0.67 mL, 4.87 mmol, 1.2 equiv) was added dropwise over 1 min and stirred for 2 h. The reaction was allowed to warm to $23\text{ }^{\circ}\text{C}$ over 20 min and then quenched with saturated aqueous NH_4Cl (10 mL) and H_2O (10 mL). The aqueous layer was extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with brine (30 mL), dried over MgSO_4 and concentrated under reduced pressure. The crude residue was purified by flash chromatography (19:1 $\rightarrow$ 9:1 $\rightarrow$ 5:1 Hexanes:EtOAc) to yield silyl carbamate product **9** (0.933 g, 72% yield) as an off-white solid. R_f 0.20 (5:1 Hexanes:EtOAc); ^1H NMR (500 MHz, CDCl_3): δ 7.30 (d, $J = 8.5$, 1H), 7.09 (d, $J = 3.0$, 1H), 6.88 (d, $J = 8.5$, 1H), 6.64 (dd, $J = 3.0$, 0.5, 1H), 3.78 (s, 3H), 3.52 (q, $J = 7.0$, 2H), 3.42 (q, $J = 7.0$, 2H), 1.28 (t, $J = 7.0$, 3H), 1.21 (q, $J = 7.0$, 3H), 0.42 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3): δ 155.6, 150.4, 133.7, 132.7, 129.3, 122.2, 116.9, 111.1, 102.6, 41.8, 41.5, 33.2, 14.4, 14.5, 1.1; IR (film): 2972, 1707, 1601, 1401, 1210, 1157 cm^{-1} ; HRMS-ESI (m/z) $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{17}\text{H}_{26}\text{N}_2\text{O}_2\text{ASiNa}$, 341.1661; found, 341.1660.

SI-2. To a solution of indole carbamate **6**² (1.0 g, 4.06 mmol, 1.0 equiv) and TMEDA (0.67 mL, 4.47 mmol, 1.1 equiv) in THF (20 mL) at $-78\text{ }^{\circ}\text{C}$ was added *sec*-BuLi (4.0 mL, 4.47 mmol, 1.1 equiv) over 15 min. After stirring for 45 min, trimethylborate (0.54 mL, 4.87 mmol, 1.2 equiv) was added dropwise and stirred for 1.5 h. The reaction was allowed to warm to $23\text{ }^{\circ}\text{C}$ over 30 min and then quenched with saturated aqueous NH_4Cl (15 mL) and a drop of H_2O . The reaction mixture was diluted with H_2O (30 mL) and EtOAc (30 mL). The layers were separated and the aqueous layer extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with brine (30 mL), dried over MgSO_4 and concentrated under reduced pressure. The crude product was dissolved in dry MeOH (40 mL) and pinacol (0.53g, 4.47 mmol, 1.1 equiv) was added. The solution was evaporated to dryness

over 10 min. The crude residue was purified by flash chromatography (15:1 Hexanes:Acetone) to generate boronic ester indole carbamate product **SI-2** (1.08 g, 71% yield) as a yellow oil. R_f 0.25 (5:1 Hexanes:Acetone); ^1H NMR (500 MHz, CDCl_3): δ 7.33 (d, $J = 9.0$, 1H), 7.07 (d, $J = 3.0$, 1H), 6.94–6.92 (m, 2H), 3.77 (s, 3H), 3.54 (q, $J = 7.0$, 2H), 3.40 (q, $J = 7.0$, 2H), 1.34 (s, 12H), 1.33–1.29 (m, 3H), 1.20 (t, $J = 6.0$, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 155.8, 150.8, 138.0, 134.1, 133.8, 130.0, 129.2, 125.4, 116.7, 112.3, 103.5, 83.1, 42.0, 41.6, 33.1, 25.2, 25.0, 21.6, 14.3, 13.7; IR (film): 2976, 2933, 1709, 1412, 1275, 1214, 1162 cm^{-1} ; HRMS-ESI (m/z) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{29}\text{BN}_2\text{O}_4\text{H}$, 373.2303; found, 373.2305.

SI-4. A round bottom flask was charged with NaH (0.60 g, 14.98 mmol, 2.4 equiv, 60% dispersion in oil). A solution of 1,5-dihydroxynaphthalene (**SI-3**) (1.0 g, 6.24 mmol, 1 equiv) in DME (25 mL) was added dropwise via cannula to the sodium hydride. Diethylcarbamoyl chloride (1.50 mL, 11.86 mmol, 1.9 equiv) was then added dropwise to the reaction vessel. The reaction was allowed to stir for 20 h. The volatiles were removed under reduced pressure and then EtOAc (30 mL) and H_2O (20 mL) were added. The layers were separated, and the organic layer was washed successively with 1 M KOH (20 mL) and H_2O (20 mL). The combined aqueous layers were extracted with EtOAc (3 x 50 mL). The combined organic layers were then washed with brine (10 mL), dried over MgSO_4 , and concentrated under reduced pressure. The crude residue was purified by flash chromatography (5:1 Benzene: Et_2O) to yield biscarbamate naphthalene **SI-4** as a red amorphous solid (0.50 g, 22% yield). R_f 0.30 (5:1 Benzene: Et_2O); ^1H NMR (500 MHz, CDCl_3): δ 7.79 (d, $J = 8.5$, 2H), 7.45 (t, $J = 8.0$, 2H), 7.31 (d, $J = 7.5$, 2H), 3.61 (q, $J = 7.0$, 4H), 3.45 (q, $J = 7.0$, 4H), 1.38 (t, $J = 7.0$, 6H), 1.25 (t, $J = 7.0$, 6H); ^{13}C NMR (125 MHz, CDCl_3): δ 154.2, 147.6, 129.0, 126.0, 118.8, 118.6, 42.5, 42.2, 14.6, 13.6; IR (film): 2975, 1709, 1394, 1242, 1153 cm^{-1} ; HRMS-ESI (m/z) $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_4\text{Na}$, 381.1790; found, 381.1790.

SI-6. A 50 mL round bottom flask was charged with $\text{Pd}(\text{OAc})_2$ (83.0 mg, 0.37 mmol, 10 mol%), BINAP (0.24 g, 0.40 mmol, 11 mol%), anhydrous powdered NaOtBu (0.59 g, 5.14 mmol, 1.4 equiv), bromide **SI-5**³ (1.0 g, 3.67 mmol, 1 equiv), morpholine (0.39 mL, 4.4 mmol, 1.2 equiv) and a magnetic stir bar, all in a glove box. Subsequently, toluene (15 mL) that had been rigorously sparged with N_2 was added. The vessel was sealed under an atmosphere of argon and then heated at 80 °C for 24 h. After cooling the reaction vessel to 23 °C, the crude mixture was diluted with Et_2O (10 mL), filtered over a plug of celite with additional Et_2O (10 mL) and concentrated under reduced pressure. The crude residue was purified by flash chromatography (5:1 Hexanes: EtOAc) to yield aminated carbamate **SI-6** (0.7835 g, 77% yield) as a gray amorphous solid. R_f 0.10 (5:1 Hexanes: EtOAc); ^1H NMR (500 MHz, CDCl_3): δ 7.02 (d, $J = 9.0$, 2H), 6.89 (d, $J = 9.0$, 2H), 3.85 (t, $J = 4.5$, 4H), 3.42–3.38 (m, 4H), 3.10 (t, $J = 4.5$, 4H), 1.24–1.19 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3): δ 154.8, 154.8, 148.9, 145.1, 122.4, 116.8, 67.1, 50.2, 42.3, 41.9, 14.4, 13.5; IR (film): 2971, 2834, 1713, 1512, 1418, 1210 cm^{-1} ; HRMS-ESI (m/z) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{22}\text{N}_2\text{O}_3\text{H}$, 279.1709; found, 279.1710.

SI-8. A round bottom flask was charged with NaH (0.88 g, 21.92 mmol, 1.2 equiv, 60% dispersion in oil). A solution of dihydrobenzofuranol **SI-7** (3.0 mL, 18.27 mmol, 1 equiv) in DME (40 mL) was added dropwise via cannula to the sodium hydride. A solution of diethylcarbamoyl chloride (2.2 mL, 17.36 mmol, 0.95 equiv) in DME (30 mL) was then added dropwise via cannula to the reaction vessel. The reaction was stirred at 23 °C for 45 h. The volatiles were removed under reduced pressure and then Et_2O (30 mL) and H_2O (20 mL) were added. The layers were separated and the organic layer was washed successively with 1 M KOH (20 mL) and H_2O (20 mL). The combined aqueous layers were extracted with Et_2O (3 x 20 mL). The combined organic layers were then washed with brine (20 mL), dried over MgSO_4 , and evaporated to dryness. The crude residue was purified by flash chromatography

(7:1 Hexanes:EtOAc) to yield carbamate **SI-8** as a clear oil (1.0 g, 92% yield). R_f 0.4 (Benzene); ^1H NMR (400 MHz, CDCl_3): δ 6.95 (dd, $J = 7.5, 1.5$, 1H), 6.91 (ad, $J = 8.0$, 1H), 6.76 (at, $J = 7.5$, 1H), 3.44–3.38 (m, 4H), 3.01 (s, 2H), 1.47 (s, 6H), 1.26–1.20 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3): δ 153.8, 150.6, 135.4, 129.3, 121.9, 121.8, 119.9, 87.8, 43.1, 42.3, 42.1, 28.2, 14.1, 13.4; IR (film): 2974, 2934, 1718, 1416, 1152, 1052 cm^{-1} ; HRMS-ESI (m/z) $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{21}\text{NO}_3\text{Na}$, 286.1419; found, 286.1420.

SI-10. A round bottom flask was charged with NaH (122 mg, 3.04 mmol, 1.2 equiv, 60% dispersion in oil). A solution of 2-hydroxycarbazole **SI-9** (500 mg, 2.54 mmol, 1 equiv) in DME (10 mL) was added dropwise via cannula to the sodium hydride. Diethylcarbamoyl chloride (0.31 mL, 2.41 mmol, 0.95 equiv) was then added dropwise to the reaction vessel. The reaction was stirred at 23 °C for 13 h. The reaction was diluted with H_2O (10 mL) and the volatiles were removed under reduced pressure. EtOAc (30 mL) and H_2O (20 mL) were added and the layers were separated. The organic layer was washed successively with 1 M KOH (20 mL) and H_2O (20 mL). The combined aqueous layers were extracted with EtOAc (3 x 30 mL). The combined organic layers were then washed with brine (20 mL), dried over MgSO_4 , and concentrated under reduced pressure. The crude residue was purified by flash chromatography (2:1 Hexanes:EtOAc) to generate carbazole carbamate **SI-10** as a white solid (0.643 g, 90% yield). R_f 0.15 (5:1 Hexanes:EtOAc); ^1H NMR (500 MHz, CDCl_3): δ 8.06 (d, $J = 8.0$, 1H), 8.04 (d, $J = 8.5$, 1H), 7.46–7.44 (m, 1H), 7.39 (d, $J = 8.0$, 1H), 7.25–7.21 (m, 2H), 6.99 (dd, $J = 8.5, 2.0$, 1H), 3.81 (s, 3H), 3.52 (q, $J = 7.0$, 2H), 3.44 (q, $J = 7.0$, 2H), 1.32 (t, $J = 7.0$, 3H), 1.25 (t, $J = 7.0$, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 154.8, 150.3, 141.6, 141.6, 125.4, 122.7, 120.7, 120.3, 120.2, 119.2, 113.3, 108.5, 102.2, 42.4, 42.0, 29.4, 14.5, 13.6; IR (film): 3055, 2978, 1710, 1602, 1417, 1266, 1154 cm^{-1} ; HRMS-ESI (m/z) $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_2\text{Na}$, 319.1422; found, 319.1421.

SI-13. A round bottom flask was charged with NaH (0.188 g, 4.70 mmol, 1.2 equiv, 60% dispersion in oil). A solution of phenol **SI-11** (0.43 mL, 6.24 mmol, 1 equiv) in DME (7 mL) was added dropwise via cannula to the sodium hydride. A solution of diethylcarbamoyl chloride (0.47 mL, 3.73 mmol, 0.95 equiv) in DME (9 mL) was then added dropwise via cannula to the reaction vessel. The reaction was stirred at 64 °C for 1.5 h. The reaction was stopped and cooled to 23 °C. The volatiles were removed under reduced pressure and then Et₂O (30 mL) and H₂O (20 mL) were added. The layers were separated, and the organic layer was washed successively with 1 M KOH (20 mL) and H₂O (20 mL). The combined aqueous layers were extracted with Et₂O (3 x 20 mL). The combined organic layers were then washed with brine (20 mL), dried over MgSO₄, and evaporated to dryness. The crude residue was purified by flash chromatography (7:1 Hexanes:EtOAc) to yield carbamate **SI-12** (1.0 g, 87% yield) as a clear oil. Spectral data match those previously reported.⁴

A 20 mL scintillation vial was charged with a magnetic stir bar, K₃PO₄ (2.2 mL, 2 M aqueous) and toluene (4.3 mL) and the biphasic solution was sparged with N₂ for 1 h. To the solution was added bromide **SI-12** (250 mg, 0.86 mmol, 1 equiv), phenylboronic acid (126 mg, 1.03 mmol, 1.2 equiv) and Pd(PPh₃)₄ (149 mg, 0.13 mmol, 15 mol%) and the resulting mixture was sparged with N₂ for 10 min. The vial was sealed with a Teflon-coated screw-cap and heated at 90 °C for 18 h. After cooling to 23 °C, CH₂Cl₂ (10 mL) and Na₂SO₄ were added and the mixture was allowed to stand for 30 min. The crude mixture was then filtered over silica and concentrated under reduced pressure. The crude residue was purified by flash chromatography (15:1 → 10:1 Hexanes: EtOAc) to yield fluorobiphenyl carbamate **SI-13** (140 mg, 92% yield) as a clear oil. *R*_f 0.05 (Hexanes); ¹H NMR (500 MHz, CDCl₃): δ 7.56–7.51 (m, 2H), 7.46–7.41 (m, 2H), 7.38–7.31 (m, 3H), 7.26 (t, *J* = 8.0, 1H), 3.48 (q, *J* = 7.0, 2H), 3.42 (q, *J* = 7.0, 2H), 1.29 (t, *J* = 7.0, 3H), 1.23 (t, *J* = 7.0, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 155.6, 153.7, 153.3, 134.0, 139.9, 139.6, 128.9, 127.7, 127.1, 124.4, 122.8, 115.2, 115.1, 42.6, 42.1, 14.1, 13.3; IR (film): 2976, 1714, 1471, 1367, 1141 cm⁻¹; HRMS-ESI (*m/z*) [M + H]⁺ calcd for C₁₇H₁₈FNO₂H, 288.1400; found 288.1399.

B. Reduction of Aryl Carbamates

Representative Procedure (reduction of naphthylcarbamate SI-14, Figure 5 is used as an example). Naphthalene (18, Figure 5). A 4-mL vial was charged with anhydrous powdered K_3PO_4 (0.379 g, 1.8 mmol, 4.5 equiv) and a magnetic stir bar. The vial and contents were flame-dried under reduced pressure, then allowed to cool under N_2 . Naphthyl carbamate **SI-14** (96.8 mg, 0.4 mmol, 1 equiv) and $\text{NiCl}_2(\text{PCy}_3)_2$ (13.8 mg, 0.02 mmol, 5 mol%) were added. Subsequently, tetramethyldisiloxane (TMDSO) (0.17 mL, 1.0 mmol, 2.5 equiv) and toluene (1.5 mL) were added. The septum cap was replaced with a Teflon-lined screw cap. The heterogeneous mixture was stirred at 115 $^\circ\text{C}$ for 15 h. The reaction vessel was cooled to 23 $^\circ\text{C}$. The reaction mixture was diluted with EtOAc (5 mL), filtered over a pad of celite (eluted with an additional 5 mL of EtOAc), and evaporated to dryness. The crude residue was purified by flash chromatography (100% Hexanes) to yield deoxygenated product **18** (47.2 mg, 92% yield) as a white amorphous solid. R_f 0.52 (100% Hexanes). Spectral data match those previously reported.⁵

Any modifications of the conditions shown in this representative procedure are specified in the following schemes, which depict all of the results shown in Figures 2, 3, 4, and 5.

Amide 5a (Figure 2). Purification by flash chromatography (3:1 Hexanes:EtOAc) generated deoxygenated product **5a** (91% yield) as a clear oil. R_f 0.28 (1:1 Hexanes:EtOAc). Spectral data match those previously reported.⁶

Silane 5b (Figure 2). Purification by flash chromatography (19:1 Hexanes:EtOAc) generated deoxygenated product **5b** (91% yield) as a clear oil. R_f 0.44 (19:1 Hexanes:EtOAc). Spectral data match those previously reported.⁷

Boronic Ester 5c (Figure 2). Purification by flash chromatography (19:1 Hexanes:EtOAc) afforded deoxygenated product **5c** (77% yield) as a clear oil. R_f 0.30 (19:1 Hexanes:EtOAc). Spectral data match those previously reported.⁸

Amide Indole 10 (Figure 3). Purification by flash chromatography (7:1 Hexanes:Acetone) yielded deoxygenated product **10** (58% yield) as a pale green solid. R_f 0.09 (5:1 Hexanes:EtOAc); ^1H NMR (500 MHz, CDCl_3): δ 7.33 (ad, $J = 8.5$, 1H), 7.22 (at, $J = 7.5$, 1H), 7.09–7.07 (m, 2H), 6.44 (dd, $J = 3.0$, 0.5, 1H), 3.81 (s, 3H), 3.65 (as, 2H), 3.22 (as, 2H), 1.31 (as, 3H), 1.02 (as, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 170.9, 136.9, 129.7, 129.7, 125.6, 121.4, 117.2, 109.9, 99.9, 43.2, 38.9, 33.1, 14.6, 13.3; IR (film): 2972, 1624, 1427, 1288, 1113 cm^{-1} ; HRMS-ESI (m/z) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{18}\text{N}_2\text{OH}$, 231.1497; found, 231.1495.

Methylindole 11 (Figure 3). Purification by flash chromatography (20:1 Hexanes:EtOAc) generated deoxygenated product **11** (75% yield) as a light yellow liquid. R_f 0.42 (20:1 Hexanes:EtOAc). Spectral data match those previously reported.¹⁴

Silylindole 12 (Figure 3). Purification by flash chromatography (5:1 Hexanes:EtOAc) yielded deoxygenated product **12** (92% yield) as a pale green solid. R_f 0.47 (5:1 Hexanes:EtOAc); ^1H NMR (500 MHz, CDCl_3): δ 7.36 (ad, $J = 8.0$, 1H), 7.29–7.22 (m, 2H), 7.11 (d, $J = 3.5$, 1H), 6.62 (dd, $J = 2.5$, 1.0, 1H), 3.87 (s, 3H), 0.41 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3): δ 135.6, 132.4, 132.2, 128.7, 125.4, 121.2, 110.4, 102.1, 32.9, 0.42; IR (film): 3044, 2956, 1518, 1406, 1248 cm^{-1} ; HRMS-ESI (m/z) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{17}\text{NSiH}$, 204.1208; found, 204.1213.

Boronic Ester Indole 13 (Figure 4). Purification by flash chromatography (10:1 Hexanes:EtOAc) generated deoxygenated product **13** (87% yield) as a white solid. R_f 0.37 (10:1 Hexanes:EtOAc). Spectral data match those previously reported.⁹

Naphthalene (18, Figure 5). Purification by flash chromatography (100% Hexanes) yielded deoxygenated product **18** (82% yield) as a white amorphous solid. R_f 0.52 (100% Hexanes). Spectral data match those previously reported.⁵

Phenanthrene (19, Figure 5). Purification by flash chromatography (100% Hexanes) afforded deoxygenated product **19** (81% yield) as a white amorphous solid. R_f 0.35 (100% Hexanes). Spectral data match those previously reported.⁵

Naphthyl Ester 20 (Figure 5). Purification by flash chromatography (9:1 Hexanes:EtOAc) afforded deoxygenated product **20** (91% yield) as a white amorphous solid. R_f 0.37 (9:1 Hexanes:EtOAc). Spectral data match those previously reported.⁵

Naphthyl Ether 21 (Figure 5). Purification by flash chromatography (19:1 Hexanes:EtOAc) afforded deoxygenated product **21** (79% yield) as a white solid. R_f 0.48 (19:1 Hexanes:EtOAc). Spectral data match those previously reported.¹⁰

Arylamine 22 (Figure 5). Purification by flash chromatography (9:1 Hexanes:EtOAc) afforded deoxygenated product **22** (90% yield) as a white amorphous solid. R_f 0.29 (9:1 Hexanes:EtOAc). Spectral data match those previously reported.¹¹

Estrone 23 (Figure 5). Purification by flash chromatography (10:1 Hexanes:EtOAc) generated deoxygenated product **23** (87% yield) a white solid. R_f 0.48 (10:1 Hexanes:EtOAc). Spectral data match those previously reported.¹²

Dihydrobenzofuran 24 (Figure 5). Purification by flash chromatography (10:1 Hexanes:EtOAc) afforded deoxygenated product **24** (86% yield) as a pale yellow oil. R_f 0.52 (10:1 Benzene:Et₂O). Spectral data match those previously reported.¹³

Indole 25 (Figure 5). Purification by flash chromatography (7:1 Hexanes:EtOAc) yielded deoxygenated product **25** (79% yield) as a light yellow liquid. R_f 0.53 (7:1 Hexanes:EtOAc). Spectral data match those previously reported.¹⁴

Carbazole 26 (Figure 5). Purification by flash chromatography (10:1 Hexanes:EtOAc) yielded deoxygenated product **26** (93% yield) as a white solid. R_f 0.48 (10:1 Hexanes:EtOAc). Spectral data match those previously reported.⁵

Biphenyl (27, Figure 5). Purification by flash chromatography (9:1 Hexanes:EtOAc) afforded deoxygenated product **27** (93% yield) as a white solid. R_f 0.62 (9:1 Hexanes:EtOAc). Spectral data match those previously reported.⁵

Flurobiphenyl (28, Figure 5). Purification by flash chromatography (100% Hexanes) yielded deoxygenated product **28** (85% yield) as a white amorphous solid. R_f 0.50 (100% Hexanes). Spectral data match those previously reported.¹⁵

C. Cross Coupling Approaches to Ipso and Cine Substituted Products

5-Morpholine Indole 14. A 20 mL scintillation vial was charged with Ni(cod)_2 (27.5 mg, 0.1 mmol, 20 mol%), $\text{SIPr}\cdot\text{HCl}$ (85.4 mg, 0.2 mmol, 40 mol%), anhydrous powdered NaOtBu (105.7 mg, 1.1 mmol, 2.2 equiv), and a magnetic stir bar, all in a glove box. Subsequently, a solution of carbamate substrate **6** (123.2 mg, 0.50 mmol, 1 equiv) and morpholine (79.0 μL , 0.9 mmol, 1.8 equiv) in dioxane (2.5 mL) was added. The vessel was removed from the glove box and then heated to 80 °C for 3 h. After cooling the reaction vessel to 23 °C and concentrating under reduced pressure, the crude residue was loaded onto a silica gel column (2.5 x 10 cm) and purified by flash chromatography (6:1:1 Benzene: Et_2O : CH_2Cl_2) to yield aminated product **14** (47.6 mg, 55% yield) as a white solid. R_f 0.21 (10:1:1 Benzene: Et_2O : CH_2Cl_2). Spectral data match those previously reported.¹¹

5-Phenylindole 15. A 4-mL vial was charged with anhydrous powdered K_3PO_4 (611 mg, 2.88 mmol, 7.2 equiv) and a magnetic stir bar. The vial and the contents were flame-dried under reduced pressure and then allowed to cool under N_2 . Phenyl boronic acid (195 mg, 1.6 mmol, 4.5 equiv), $\text{NiCl}_2(\text{PCy}_3)_2$ (27.6 mg, 0.04 mmol, 10 mol%), and indole carbamate **6** (98.5 mg, 0.4 mmol, 1 equiv) were added. The vial was then evacuated and backfilled with N_2 . Toluene (1.4 mL) was added and the vial was sealed with a Teflon-lined screw cap and stirred at 23 °C for 1 h. The heterogeneous mixture was then heated at 120 °C for 14 h. The reaction vessel was allowed to cool to 23 °C. The mixture was diluted with EtOAc (5 mL) and filtered over a pad of silica (eluted with an additional 5 mL of EtOAc). The crude residue was purified by flash chromatography (20:1 Hexanes: EtOAc) to yield coupled product

15 (88.0 mg, 70% yield) as a white solid. R_f 0.53 (5:1 Hexanes:EtOAc). Spectral data match those previously reported.^{1a}

4-Morpholine Indole 16. A 4-mL dram vial equipped with a magnetic stir bar was flame-dried under reduced pressure and backfilled with N_2 . After cooling to 23°C , the indole boronic ester **13** (0.050 g, 0.194 mmol, 1 equiv) and copper acetate (0.212g, 1.167 mmol, 6 equiv) were added to the vial. Morpholine (0.050 mL, 0.583 mmol, 3 equiv), pyridine (0.063 mL, 0.778 mmol, 4 equiv) and CH_2Cl_2 (0.5 mL) were then added to the solids. The septum cap was replaced with a Teflon-coated cap and the reaction was stirred at 55°C for 2 d. The reaction vessel was removed from the heating block and cooled to 23°C . The solution was loaded directly onto a silica gel column and purified by flash chromatography (5:1 hexanes:EtOAc) to yield 4-morpholine indole **16** (0.025g, 60% yield) as a light yellow solid. R_f 0.42 (5:1 Hexanes:EtOAc); ^1H NMR (500 MHz, CDCl_3): δ 7.17 (t, $J = 8.0$, 1H), 7.04 (d, $J = 8.0$, 1H), 7.02 (d, $J = 3.0$, 1H), 6.61 (d, $J = 8.0$, 1H), 6.48 (d, $J = 3.0$, 1H), 3.9 (t, $J = 5.0$, 4H), 3.79 (s, 3H), 3.26 (t, $J = 5.0$, 4H); ^{13}C NMR (125 MHz, CDCl_3): δ 145.8, 138.0, 127.5, 122.4, 121.7, 106.3, 104.5, 99.5, 67.8, 52.0, 33.2; IR (film): 2963, 2858, 1575, 1498, 1235, 1117 cm^{-1} ; HRMS-ESI (m/z) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{16}\text{N}_2\text{OH}$, 217.1341; found, 217.1347.

4-Phenylindole 17. A 20 mL scintillation vial was charged with a magnetic stir bar, K_3PO_4 (3 mL, 2 M aqueous) and toluene (1.5 mL). The biphasic solution was then sparged with N_2 for 1 h. To the solution was added indole boronic ester **13** (150 mg, 0.583 mmol, 1 equiv), phenylboronic acid (123

mg, 1.167 mmol, 2 equiv) and Pd(PPh₃)₄ (101 mg, 0.088 mmol, 15 mol%) and the resulting mixture was sparged with N₂ for 10 min. The vial was sealed with a Teflon-coated screw-cap and heated at 90 °C for 14 h. After cooling to 23 °C, CH₂Cl₂ (5 mL) and Na₂SO₄ were added and the mixture was allowed to stand for 30 min. The crude mixture was then filtered over silica and concentrated under reduced pressure. The crude residue was purified by flash chromatography (7:1 Hexanes:EtOAc) to yield 4-phenylindole **17** as a light yellow oil (112 mg, 92% yield). R_f 0.41 (7:1 Hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃): δ 7.72 (d, *J* = 7.5, 2H), 7.50 (t, *J* = 7.5, 2H), 7.40–7.32 (m, 3H), 7.22 (dd, *J* = 6.5, 1.5, 1H), 7.12 (d, *J* = 3.5, 1H), 6.80 (d, *J* = 3.0, 1H) 3.85 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 141.4, 137.2, 134.5, 129.2, 128.8, 128.5, 127.0, 126.7, 121.9, 119.3, 108.5, 100.4, 32.8; IR (film): 3053, 2909, 1603, 1513, 1413, 1286 cm⁻¹; HRMS-ESI (*m/z*) [M + H]⁺ calcd for C₁₅H₁₃NOH, 208.1126; found 208.1128.

D. References

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¹H NMR Spectra

fault proton paramete

7.870
7.864
7.858
7.851
7.504
7.497
7.491
7.485
7.269

Current Data Parameters
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PROCNO 1

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fault proton paramete

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PROCNO 1

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LB 0.30 Hz
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fault proton paramete

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6.897
6.883

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SSB 0
LB 1.00 Hz
GB 0
PC 1.00

fault proton paramete

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7.373
7.438
7.454
7.468
7.599
7.614
7.616

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PROCNO 1

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PL1 0.00 dB
SFO1 500.330020 MHz

F2 – Processing parameters
SI 32768
SF 500.3300280 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

3.920
3.911
3.901
3.755
3.144
3.135
3.125

7.262
7.245
7.162
7.157
7.015
7.009
7.005
6.992
6.987
6.410
6.404

fault proton paramete

^{13}C NMR Spectra