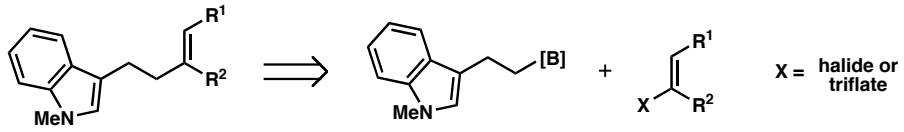
APPENDIX FOUR

The Synthesis of C-3β Functionalized Indoles via a Hydroboration/Suzuki-Miyaura Coupling Sequence

A4.1 Introduction

Indoles are important structural moieties in a number of biologically relevant compounds.[1] The development of synthetic methods involving indole-containing compounds remains an active area of research.[1a,2] During the course of our studies on the palladium-catalyzed oxidative annulation of indoles,[3] it became necessary to synthesize substrates with olefin tethers at the C-3 position. Specifically, we desired compounds where the indole tethers had olefins attached to the β carbon. We envisioned that indoles of this type could arise via sp^2-sp^3 palladium-catalyzed cross coupling chemistry. The Suzuki-Miyaura reaction has proven widely effective in the construction of carbon-carbon bonds.[4] We anticipated that a sequence consisting of a hydroboration of a 3-vinyl indole followed by a palladium-catalyzed cross coupling with a halide or triflate would afford the desired indole products (Scheme A4.1.1).

Scheme A4.1.1



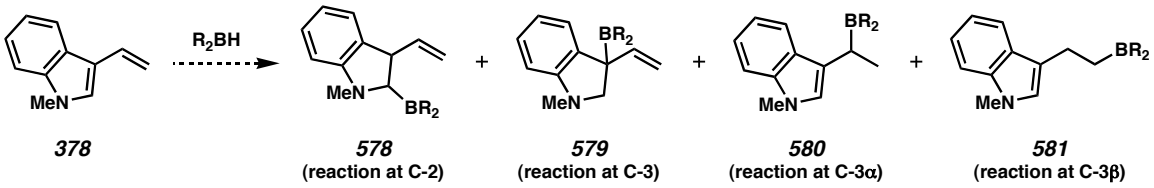
575 ***576*** ***577***

A4.2 Reaction Development

A4.2.1 Regioselectivity of Hydroboration

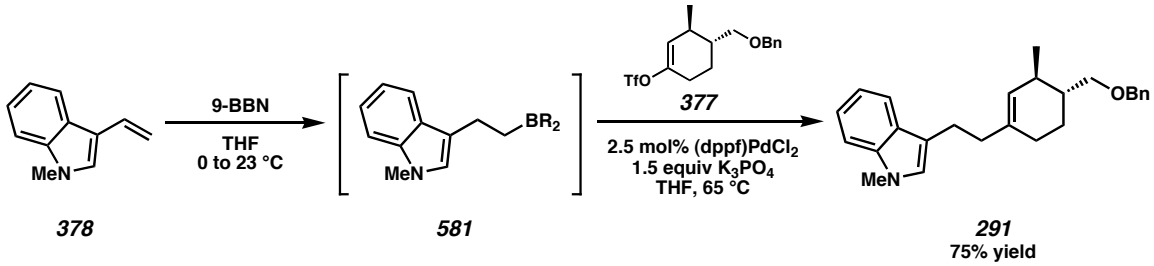
The regioselectivity of a hydroboration on a vinyl indole compound was uncertain at the beginning of this study. Styrenyl compounds generally react with hydroborating agents to afford compounds with boron substitution at the terminal (β) position. The hydroboration of more electron-rich heteroarenes, however, could potentially be complicated by the numerous nucleophilic sites. It could be envisioned that the hydroboration of *N*-methyl-3-vinyl indole could result in boron substitution at four different sites, C-2, C-3, C-3α, and C-3β, the desired location (Scheme A4.2.1).

Scheme A4.2.1



In the event, the hydroboration/Suzuki-Miyaura coupling sequence proved to be remarkably effective. Starting with *N*-methyl-3-vinyl indole (**378**), hydroboration with 9-BBN afforded B-alkyl intermediate **581**, which was treated with triflate **377** under standard Suzuki-Miyaura coupling conditions.[5] After the reaction was complete, analysis of the crude material revealed that there was only one compound present arising from boron substitution at C-3β. No products arising from hydroboration at any other sites on **378** were observed. This outcome is strongly suggestive that the regioselectivity of the hydroboration event was extremely high for the terminal position of the vinyl group.

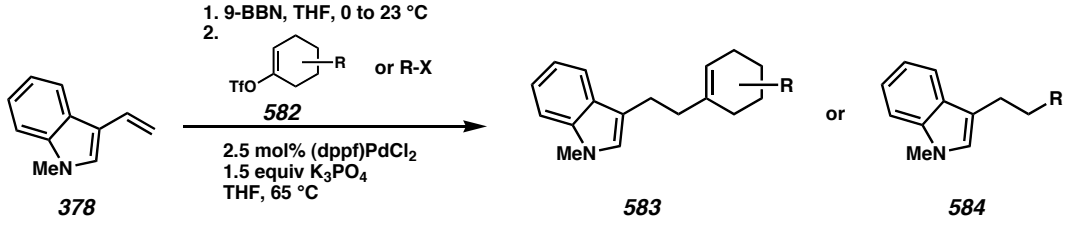
Scheme A4.2.2



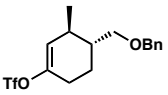
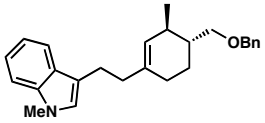
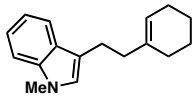
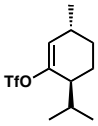
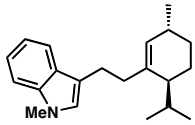
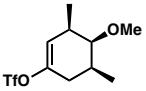
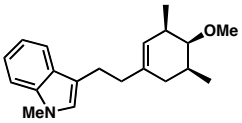
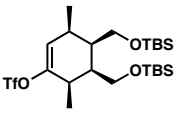
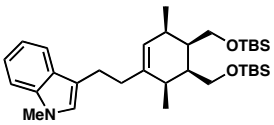
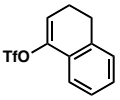
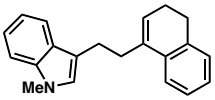
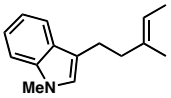
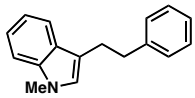
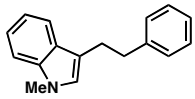
A4.2.2 Applications of the Hydroboration/Suzuki-Miyaura Coupling Sequence

A variety of C-3β substituted indoles can be synthesized via this hydroboration/Suzuki-Miyaura method (Table A4.2.1). Triflates derived from cyclohexanone derivatives are efficient coupling partners for this reaction (entries 1-6). Vinyl and aryl halides are also viable substrates for the construction of C-3β substituted indoles (entries 7-9).

Table A4.2.1. The synthesis of C-3β substituted indoles via a hydroboration/Suzuki-Miyaura coupling sequence.



378 ***583*** ***584***

entry	triflate or R-X		product		yield (%)[a]
1		***377***		***291***	75
2		***585***		***586***	46
3		***587***		***588***	56
4		***589***		***590***	61
5		***591***		***592***	73
6[b]		***593***		***594***	72
7		***369***		***26***	57
8[b]		***595***		***596***	63
9[b]		***597***		***596***	56

[a] Yields listed are isolated. [b] See footnote 6.

A general procedure is as follows: 9-BBN dimer (203 mg, 0.830 mmol) was dissolved in THF (1.66 mL) at 23 °C under an argon atmosphere. Once fully in solution, it was cooled to 0 °C, and to the solution was added a solution of indole **378** (261 mg, 1.66 mmol) in THF (1.66 mL). The reaction mixture was warmed to 23 °C and stirred for 3 h. To the solution was then added a solution of triflate **377** (552 mg, 1.51 mmol) in THF (7.55 mL), (dppf)$PdCl_2$ (30.8 mg, 0.0378 mmol), and K_3PO_4 (482 mg, 2.27 mmol), and the reaction was heated to 65 °C. After 5 h, the reaction was cooled to 23 °C and quenched with 1 mL NaOH (3.0 M aq.) and 1 mL 30% H_2O_2, and the resulting mixture was stirred 1 h. The mixture was then partitioned between Et_2O (50 mL) and water (40 mL), and the aqueous phase was extracted with Et_2O (1 x 50 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Purification of the residue by flash chromatography (2:1 → 1:1 hexanes/CH_2Cl_2 eluent) afforded Suzuki product **291** (467 mg, 75% yield, R_F = 0.20 in 4:1 hexanes/CH_2Cl_2) as a colorless oil.

A4.3 Conclusion

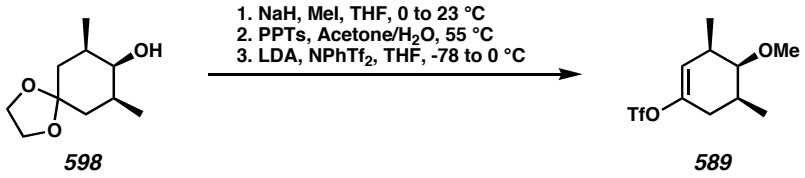
In summary, a hydroboration/Suzuki-Miyaura method was utilized to functionalize 3-vinyl indoles. An array of indole-containing compounds arising from triflates or halides can be synthesized via this protocol. It is anticipated that this method could be applied to the synthesis of a number of biologically interesting compounds featuring the indole nucleus.

A4.4 Experimental Section

A4.4.1 Materials and Methods

Unless stated otherwise, reactions were conducted in flame-dried glassware under a nitrogen atmosphere with dry solvents (either freshly distilled or passed through activated alumina columns). All commercially obtained reagents were used as received. Reaction temperatures were controlled by an IKAmag temperature modulator. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized via UV, anisaldehyde, and potassium permanganate staining. ICN silica gel (particle size 0.032-0.063 mm) was used for flash column chromatography. ^{1}H spectra were recorded on a Varian Mercury 300 (at 300 MHz) and are reported relative to Me_4Si (δ 0.0). Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C spectra were recorded on a Varian Mercury 300 (at 75 MHz) and are reported relative to Me_4Si (δ 0.0). Data for ^{13}C NMR spectra are reported in terms of chemical shift. IR spectra were recorded on a Perkin Elmer Spectrum BX FT-IR spectrometer and are reported in frequency of absorption (cm^{-1}). High resolution mass spectra were obtained from the California Institute of Technology Mass Spectral Facility. All chemicals were purchased from the Sigma-Aldrich Chemical Company, Milwaukee, WI.

A4.4.2 Triflate Synthesis

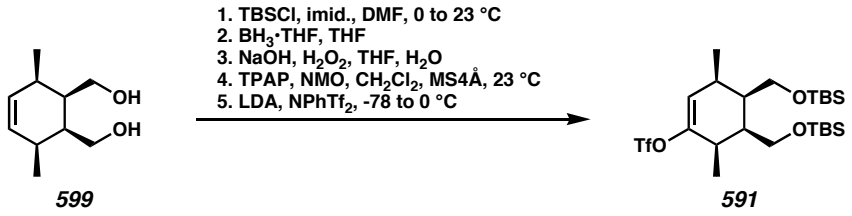


598 *589*

Triflate 589. To a solution of alcohol **598**[7] (286 mg, 1.54 mmol) in 6.16 mL THF at 0 °C was added NaH (123 mg, 60% dispersion in mineral oil, 3.08 mmol). The mixture was stirred for 5 min, then allowed to warm to 23 °C and stirred for 1 h. The reaction mixture was then cooled to 0 °C, and MeI (144 μl, 2.31 mmol) was introduced. The mixture was allowed to warm to 23 °C and maintained at room temperature for 3 h. The reaction was then cooled to 0 °C, quenched with saturated NH_4Cl (40 mL), and extracted with Et_2O (2 x 75 mL). The organic phases were combined, washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Purification of the residue by flash chromatography (9:1 hexanes/EtOAc eluent) afforded the methyl ether (241 mg, 78% yield, R_F = 0.49 in 4:1 hexanes/EtOAc) as a colorless oil.

To a solution of the methyl ether (282 mg, 1.41 mmol) in acetone (12.7 mL) and H_2O (1.41 mL) was added PPTs (106 mg, 0.423 mmol). The mixture was heated to 55 °C and stirred. After 4.5 h, the mixture was cooled to room temperature, and the acetone was removed by rotary evaporation. The residue was partitioned between Et_2O (75 mL) and saturated $NaHCO_3$ (50 mL). The organic phase was washed with brine, dried over $MgSO_4$, and concentrated to an oil. The residue was purified by flash chromatography (6:1 hexanes/EtOAc eluent) to afford the ketone (157 mg, 71% yield, R_F = 0.41 in 4:1 hexanes/EtOAc) as a colorless oil.

To a solution of LDA (1.20 mmol) in 1.20 mL THF at –78 °C was added a solution of the ketone (157 mg, 1.00 mmol) in 1.00 mL THF dropwise over 1 min. The reaction mixture was maintained at –78 °C for 3 h, then a solution of $NPhTf_2$ (393 mg, 1.10 mmol) in 1.10 mL THF was added via cannula. The mixture was allowed to warm to 0 °C and maintained for 3 h. The reaction was then quenched with saturated NH_4Cl (30 mL) and extracted with Et_2O (2 x 50 mL). The organic phases were combined, washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Purification of the residue by flash chromatography (9:1 hexanes/EtOAc eluent) afforded triflate **589** (211 mg, 73% yield, R_F = 0.43 in 9:1 hexanes/EtOAc) as a yellow oil. **Triflate 589**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.38 (br s, 1H), 3.49 (s, 3H), 3.12 (m, 1H), 2.61-2.51 (m, 1H), 2.34-2.12 (comp m, 2H), 2.04-1.91 (m, 1H), 1.14 (d, *J* = 7.5 Hz, 3H), 1.10 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.2, 120.6, 118.7 (q, *J* = 318.2 Hz), 82.1, 62.2, 36.5, 35.1, 31.3, 18.1, 16.6; IR (film) 1417, 1246, 1210, 1145, 1096, 919 cm^{-1}; HRMS (EI$^+$) *m/z* calc'd for $[C_{10}H_{15}O_4F_3S]^+$: 288.0643, found 288.0633.



Triflate 591. To a solution of diol **599**[8] (316 mg, 1.86 mmol) in 3.72 mL DMF at 0 °C was added imidazole (317 mg, 4.65 mmol), then TBSCl (589 mg, 3.91 mmol). The mixture was allowed to warm to 23 °C and stirred for 4 h. The reaction was then quenched with water (30 mL) and extracted with Et_2O (2 x 75 mL). The combined organic phases were washed with 1 N HCl (2 x 30 mL) and then brine, dried over

$MgSO_4$, and concentrated in vacuo. The residue was purified by flash chromatography (25:1 hexanes/EtOAc eluent) to provide the bis(silyl ether) (571 mg, 77% yield, R_F = 0.90 in 4:1 hexanes/EtOAc) as a colorless oil.

To a solution of the bis(silyl ether) (571 mg, 1.43 mmol) in 14.3 mL THF at 0 °C was added BH_3•THF (2.00 mL, 1.0 M in THF, 2.00 mmol) dropwise. The reaction mixture was allowed to warm to 23 °C and stirred for 3 h. The mixture was then cooled to 0 °C, and aq. NaOH (5.72 mL, 15% w/v) and H_2O_2 (3.97 mL, 30% in H_2O) were added sequentially. The reaction mixture was allowed to warm to 23 °C and stirred 18 h. The mixture was then quenched by addition of 230 mg sodium metabisulfite, stirred 15 min, and partitioned between Et_2O (100 mL) and brine (50 mL). The aqueous layer was extracted with Et_2O (2 x 40 mL), and the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resulting alcohol (581 mg, 97% yield, R_F = 0.16 in 9:1 hexanes/EtOAc) was sufficiently pure to carry on to the next reaction.

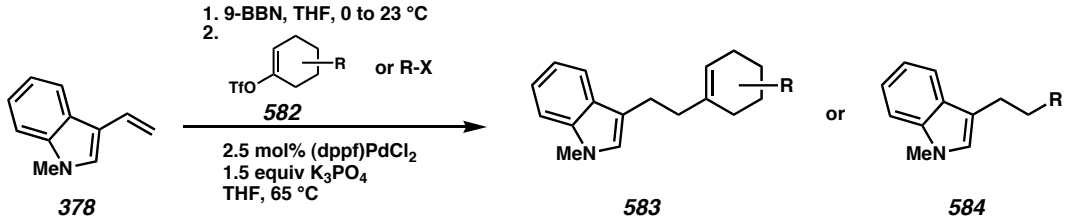
To a solution of the alcohol (581 mg, 1.39 mmol) in CH_2Cl_2 (2.78 mL) at 23 °C was added MS4Å (695 mg, 500 mg/mmol), then NMO (245 mg, 2.09 mmol). The resulting suspension was stirred for 15 min, and then TPAP (24.4 mg, 0.0695 mmol) was added. The mixture was stirred for 10 min, then diluted with CH_2Cl_2 (30 mL) and filtered through a plug of SiO_2 (1 x 5 cm, CH_2Cl_2 eluent). The filtrate was concentrated to an oil, which was purified by flash chromatography (19:1 hexanes/EtOAc eluent) to afford the ketone (521 mg, 90% yield, R_F = 0.40 in 9:1 hexanes/EtOAc) as a colorless oil.

To a solution of LDA (0.656 mmol) in 656 μl THF at –78 °C was added a solution of the ketone (227 mg, 0.547 mmol) in 547 μl THF dropwise over 1 min. The

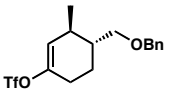
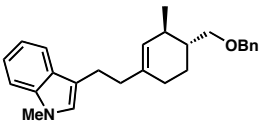
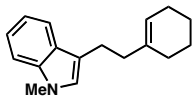
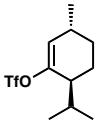
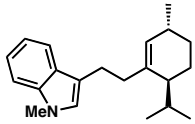
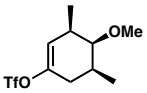
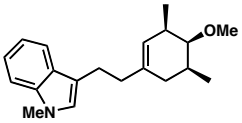
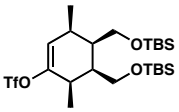
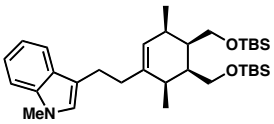
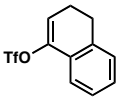
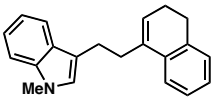
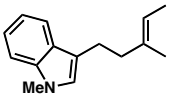
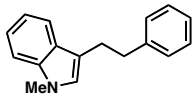
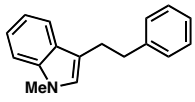
reaction mixture was maintained at –78 °C for 3 h, then a solution of $NPhTf_2$ (215 mg, 0.602 mmol) in 602 μl THF was added via cannula. The mixture was allowed to warm to 0 °C and maintained for 3 h. The reaction was then quenched with saturated NH_4Cl (25 mL) and extracted with Et_2O (2 x 50 mL). The organic phases were combined, washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Purification of the residue by flash chromatography (29:1 hexanes/EtOAc eluent) afforded triflate **591** (201 mg, 67% yield, R_F = 0.70 in 9:1 hexanes/EtOAc) as a yellow oil. **Triflate 591**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.50 (m, 1H), 3.88 (dd, *J* = 8.7, 10.5 Hz, 1H), 3.70-3.55 (comp m, 3H), 2.80-2.65 (comp m, 2H), 2.24-2.16 (m, 1H), 2.05-1.98 (m, 1H), 1.09 (d, *J* = 7.2 Hz, 3H), 1.07 (d, *J* = 7.5 Hz, 3H), 0.89 (app.s, 18H), 0.05 (s, 6H), 0.03 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.2, 122.5, 118.7 (q, J = 317.9 Hz), 62.6, 60.9, 44.8, 41.6, 34.0, 33.6, 26.1, 18.4, 18.3, 17.9, 12.8, -5.2, -5.2, -5.3, -5.3; IR (film) 2956, 2931, 1418, 1249, 1210, 1146, 1087, 838 cm^{-1}; HRMS (FAB$^+$) *m/z* calc'd for $[C_{23}H_{46}O_5SSi_2F_3]^+$: 547.2557, found 547.2562.

A4.4.3 Hydroboration/Suzuki-Miyaura Couplings

Table A4.2.1 (reproduced)



378 ***583*** ***584***

entry	triflate or R-X		product		yield (%)
1		***377***		***291***	75
2		***585***		***586***	46
3		***587***		***588***	56
4		***589***		***590***	61
5		***591***		***592***	73
6		***593***		***594***	72
7		***369***		***26***	57
8		***595***		***596***	63
9		***597***		***596***	56

General Procedure for the Hydroboration/Suzuki Cross-Coupling Sequence for Table A4.2.1. Entry 1 is used as an example. 9-BBN dimer (203 mg, 0.830 mmol) was dissolved in THF (1.66 mL) at 23 °C under an argon atmosphere. Once fully in solution, it was cooled to 0 °C, and to the solution was added a solution of indole **378** (261 mg, 1.66 mmol) in THF (1.66 mL). The reaction mixture was warmed to 23 °C and stirred for 3 h. To the solution was then added a solution of triflate **377** (552 mg, 1.51 mmol) in THF (7.55 mL), (dppf)$PdCl_2$ (30.8 mg, 0.0378 mmol), and K_3PO_4 (482 mg, 2.27 mmol), and the reaction was heated to 65 °C. After 5 h, the reaction was cooled to 23 °C and quenched with 1 mL NaOH (3.0 M aq.) and 1 mL 30% H_2O_2, and the resulting mixture was stirred 1 h. The mixture was then partitioned between Et_2O (50 mL) and water (40 mL), and the aqueous phase was extracted with Et_2O (1 x 50 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Purification of the residue by flash chromatography (2:1 → 1:1 hexanes/CH_2Cl_2 eluent) afforded Suzuki product **291** (467 mg, 75% yield, R_F = 0.20 in 4:1 hexanes/CH_2Cl_2) as a clear oil. (See Chapter 4.7.2 for characterization data.)

Indole 586 (Entry 2). Starting from triflate **585**[9] (179 mg, 0.778 mmol), purification by flash chromatography (9:1 hexanes/CH_2Cl_2 eluent) afforded indole **586** in 46% yield (85 mg, R_F = 0.51 in 9:1 hexanes/EtOAc) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.24 (app.t, *J* = 8.1 Hz, 1H), 7.13 (app.t, *J* = 8.1 Hz, 1H), 6.86 (s, 1H), 5.53 (br s, 1H), 3.76 (s, 3H), 2.88 (app.t, *J* = 7.8 Hz, 2H), 2.36 (app.t, *J* = 7.8 Hz, 2H), 2.08-2.04 (comp m, 4H), 1.73-1.58 (comp m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.2, 137.2, 128.1, 126.1, 121.6, 121.1, 119.2, 118.6, 115.6,

109.3, 39.1, 32.7, 28.7, 25.5, 23.9, 23.3, 22.8; IR (film) 2923, 2360, 736 cm^{-1}; HRMS (EI^+) *m/z* calc'd for $[C_{17}H_{21}N]^+$: 239.1674, found 239.1679.

Indole 588 (Entry 3). Starting from triflate **587**[10] (245 mg, 0.856 mmol), purification by flash chromatography (9:1 hexanes/CH_2Cl_2 eluent) afforded indole **588** in 56% yield (143 mg, R_F = 0.54 in 9:1 hexanes/EtOAc) as a yellow oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.1 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.24 (app.t, *J* = 8.1 Hz, 1H), 7.13 (app.t, *J* = 8.1 Hz, 1H), 6.87 (s, 1H), 5.42 (br s, 1H), 3.76 (s, 3H), 2.94 (ddd, *J* = 5.1, 10.8, 14.7 Hz, 1H), 2.75 (ddd, *J* = 6.3, 10.2, 14.4 Hz, 1H), 2.49-2.06 (comp m, 5H), 1.86-1.69 (comp m, 2H), 1.40-1.27 (m, 1H), 1.09-1.01 (m, 1H), 0.99 (d, *J* = 6.6 Hz, 3H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.75 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.7, 137.2, 130.9, 128.1, 126.1, 121.6, 119.2, 118.7, 115.7, 109.3, 42.3, 36.0, 32.7, 31.8, 31.1, 27.8, 24.2, 22.6, 22.0, 21.1, 16.1; IR (film) 2954, 2926, 1472, 736 cm^{-1}; HRMS (EI^+) *m/z* calc'd for $[C_{21}H_{29}N]^+$: 295.2300, found 295.2309.

Indole 590 (Entry 4). Starting from triflate **589** (211 mg, 0.732 mmol), purification by flash chromatography (3:2 hexanes/CH_2Cl_2 eluent) afforded indole **590** in 61% yield (132 mg, R_F = 0.43 in 9:1 hexanes/EtOAc) as a brown oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.22 (app.t, *J* = 7.8 Hz, 1H), 7.11 (app.t, *J* = 7.8 Hz, 1H), 6.85 (s, 1H), 5.15 (br s, 1H), 3.74 (s, 3H), 3.54 (s, 3H), 3.18 (m, 1H), 2.94-2.83 (comp m, 2H), 2.46-2.26 (comp m, 3H), 2.04-1.94 (comp m, 2H), 1.91-1.81 (m, 1H), 1.11 (d, *J* = 7.2 Hz, 3H), 1.10 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.3, 137.1, 128.1, 126.2, 124.0, 121.5, 119.2, 118.6, 115.5, 109.2, 84.2, 62.0, 38.2,

37.0, 34.5, 32.8, 32.7, 23.6, 18.9, 17.4; IR (film) 2928, 1470, 1101, 737 cm^{-1}; HRMS (EI^+) *m/z* calc'd for $[C_{20}H_{27}NO]^+$: 297.2093, found 297.2101.

Indole 592 (Entry 5). Starting from triflate **591** (201 mg, 0.368 mmol), purification by flash chromatography (12:1 → 6:1 hexanes/CH_2Cl_2 eluent) afforded indole **592** in 73% yield (148 mg, R_F = 0.55 in 9:1 hexanes/EtOAc) as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.23 (app.t, *J* = 8.4 Hz, 1H), 7.11 (app.t, *J* = 7.8 Hz, 1H), 6.84 (s, 1H), 5.22 (br s, 1H), 3.90 (dd, *J* = 8.4, 10.2 Hz, 1H), 3.75 (s, 3H), 3.72-3.57 (comp m, 3H), 2.97-2.88 (m, 1H), 2.84-2.74 (m, 1H), 2.52-2.36 (comp m, 4H), 2.11-2.00 (comp m, 2H), 1.01 (app.d, *J* = 7.5 Hz, 6H), 0.92 (s, 9H), 0.91 (s, 9H), 0.08 (s, 6H), 0.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.7, 137.2, 128.1, 126.4, 126.1, 121.6, 119.3, 118.7, 115.7, 109.3, 64.1, 61.5, 45.1, 42.5, 36.0, 34.8, 33.2, 32.8, 26.2, 26.2, 24.3, 18.9, 18.5, 18.3, 14.6, -5.1, -5.1, -5.2, -5.2; IR (film) 2955, 2929, 1086, 836, 774 cm^{-1}; HRMS (FAB^+) *m/z* calc'd for $[C_{33}H_{57}NO_2Si_2]^+$: 555.3928, found 555.3919.

Indole 594 (Entry 6). Starting from triflate **593**[11] (150 mg, 0.539 mmol), purification by flash chromatography (9:1 hexanes/CH_2Cl_2 eluent) afforded indole **594** in 73% yield (111 mg, R_F = 0.45 in 9:1 hexanes/EtOAc) as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.28-7.18 (comp m, 4H), 7.13 (app.t, *J* = 7.8 Hz, 1H), 6.89 (s, 1H), 5.95 (t, *J* = 4.5 Hz, 1H), 3.77 (s, 3H), 3.05-2.99 (comp m, 2H), 2.89-2.83 (comp m, 2H), 2.79 (app.t, *J* = 8.4 Hz, 2H), 2.32-2.25 (comp m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2, 137.0, 136.6, 135.2, 128.1,

127.9, 126.8, 126.6, 126.2, 125.2, 122.8, 121.7, 119.3, 118.8, 115.4, 109.3, 33.9, 32.8, 28.7, 24.6, 23.3; IR (film) 2930, 1485, 736 cm^{-1}; HRMS (EI^+) *m/z* calc'd for $[C_{21}H_{21}N]^+$: 287.1674, found 287.1678.

Indole 26 (Entry 7). Starting from 2-bromo-2-butene (47.1 μl, 0.463 mmol), purification by flash chromatography (9:1 hexanes/CH_2Cl_2 eluent) afforded indole **26** in 57% yield (56.6 mg, R_F = 0.54 in 9:1 hexanes/EtOAc) as a colorless oil. (See Chapter 4.7.2 for characterization data.)

Indole 596 (Entry 8). Starting from bromobenzene (48.8 μl, 0.463 mmol), purification by flash chromatography (9:1 hexanes/CH_2Cl_2 eluent) afforded indole **596** in 63% yield (69.0 mg, R_F = 0.48 in 9:1 hexanes/EtOAc) as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 1H), 7.38-7.25 (comp m, 7H), 7.16 (app.t, *J* = 7.5 Hz, 1H), 6.83 (s, 1H), 3.76 (s, 3H), 3.15-3.03 (comp m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.7, 137.2, 128.7, 128.5, 128.0, 126.3, 126.0, 121.7, 119.2, 118.8, 114.9, 109.3, 37.0, 32.7, 27.4; IR (film) 738, 699 cm^{-1}; HRMS (EI^+) *m/z* calc'd for $[C_{17}H_{17}N]^+$: 235.1361, found 235.1366.

Indole 596 (Entry 9). Starting from iodobenzene (51.8 μl, 0.463 mmol), purification by flash chromatography (9:1 hexanes/CH_2Cl_2 eluent) afforded indole **596** in 56% yield (60.5 mg, R_F = 0.43 in 9:1 hexanes/EtOAc) as a colorless oil.

A4.5 Notes and References

(1) (a) Sundberg, R. J. *The Chemistry of Indoles*; Academic Press: New York, 1970. (b) *The Monoterpenoid Indole Alkaloids*; Saxton, J. E., Ed.; The Chemistry of Heterocyclic Compounds, Vol. 25, Part 4; Wiley & Sons: New York, 1983. (c) *Monoterpenoid Indole Alkaloids*; Saxton, J. E., Ed.; The Chemistry of Heterocyclic Compounds, Vol. 25, Supplement to Part 4; Wiley & Sons: Chichester, U. K., 1994.

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(5) The conditions for the palladium-catalyzed coupling were derived from a procedure described by Suzuki et al. See, Oh-e, T.; Miyaura, N.; Suzuki, A. *J. Org. Chem*. **1993**, *58*, 2201-2208.

(6) A minor amount (~5%) of the coupling product arising from boron substitution at C-3α was observed.

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APPENDIX FIVE

Notebook Cross-Reference

The following notebook cross-reference has been included to facilitate access to the original spectroscopic data obtained for the compounds presented in this thesis. For each compound, both hardcopy and electronic characterization folders have been created that contain copies of the original ^{1}H NMR, ^{13}C NMR, and IR spectra. All notebooks and spectral data are stored in the Stoltz archives.

Table A5.1 Compounds Appearing in Chapter 3: Palladium-Catalyzed Aerobic Wacker Cyclizations and the Formal Total Synthesis of Cephalotaxine

Compound	^{1}H NMR	^{13}C NMR	IR
204	EMF-VI-289	EMF-VI-289	EMF-VI-289
205	EMF-XXVII-101	EMF-XXVII-101	EMF-XXVII-101
207	EMF-VII-299	EMF-VII-299	EMF-VII-299
208	EMF-IX-143	EMF-IX-143	EMF-IX-143

Table A5.2 Compounds Appearing in Chapter 4:

C-H Bond Functionalizations with Palladium(II): Intramolecular

Annulations of Arenes

Compound	^{1}H NMR	^{13}C NMR	IR
26	EMF-X-135	EMF-X-135	EMF-X-135
267	EMF-X-133	EMF-X-133	EMF-X-133
269	EMF-XIV-227	EMF-XIV-227	EMF-XIV-227
271	EMF-XIV-231	EMF-XIV-231	EMF-XIV-231
273	EMF-XIV-273	EMF-XIV-273	EMF-XIV-273
275	EMF-IX-293	EMF-IX-293	EMF-IX-293
277	EMF-XI-269	EMF-XI-269	EMF-XI-269
279	EMF-XII-59	EMF-XII-59	EMF-XII-59
281	EMF-XI-101	EMF-XI-101	EMF-XI-101
283	EMF-X-225	EMF-X-225	EMF-X-225
285	EMF-XIV-303	EMF-XIV-303	EMF-XIV-303
287	EMF-XIV-239	EMF-XIV-239	EMF-XIV-239
289	EMF-XIII-263	EMF-XIII-263	EMF-XIII-263
377	EMF-XX-155	EMF-XX-155	EMF-XX-155
291	EMF-XV-115	EMF-XV-115	EMF-XV-115
298	EMF-XVII-223	EMF-XVII-223	EMF-XVII-223
27	EMF-XI-279	EMF-XI-279	EMF-XI-279
268	EMF-XII-71	EMF-XII-71	EMF-XII-71
270	EMF-XIV-167	EMF-XIV-167	EMF-XIV-167
272	EMF-XIV-269	EMF-XIV-269	EMF-XIV-269
274	EMF-XIV-281	EMF-XIV-281	EMF-XIV-281
276	EMF-XII-81	EMF-XII-81	EMF-XII-81
278	EMF-XII-63	EMF-XII-63	EMF-XII-63
280	EMF-XII-93	EMF-XII-93	EMF-XII-93

Compound	1H NMR	13C NMR	IR
282	EMF-XIII-297	EMF-XIII-297	EMF-XIII-297
284	EMF-XII-135	EMF-XII-135	EMF-XII-135
286	EMF-XIV-165	EMF-XIV-165	EMF-XIV-165
288	EMF-XIV-237	EMF-XIV-237	EMF-XIV-237
290	EMF-XIV-25	EMF-XIV-25	EMF-XIV-25
297	EMF-XV-113	EMF-XV-139	EMF-XV-139

Table A5.3 Compounds Appearing in Chapter 5:

Further Investigations into Palladium(II)-Catalyzed Asymmetric Oxidative Heterocyclizations

Compound	^{1}H NMR	^{13}C NMR	IR
413	EMF-XXIII-217	EMF-XXIII-217	EMF-XXIII-217
415	EMF-XXIV-65	EMF-XXIV-65	EMF-XXIV-65
416	EMF-XXIV-85	EMF-XXIV-85	EMF-XXIV-85
417	EMF-XXIV-87	EMF-XXIV-87	EMF-XXIV-87
422	EMF-XXIII-107	EMF-XXIII-107	EMF-XXIII-107
427	EMF-XXII-303	EMF-XXII-303	EMF-XXII-303
431	EMF-XXIII-103	EMF-XXIII-103	EMF-XXIII-103
434	EMF-XXIII-177	EMF-XXIII-177	EMF-XXIII-177
435	EMF-XXVII-99	EMF-XXVI-273	EMF-XXVI-273
480	EMF-XVII-59	EMF-XVII-59	EMF-XVII-59
(*E*)-406	EMF-XIX-49	EMF-XIX-49	EMF-XIX-49
(*Z*)-406	EMF-XIX-229	EMF-XIX-229	EMF-XIX-229
409	EMF-XX-289	EMF-XX-289	EMF-XX-289
443	EMF-XXII-171	EMF-XXII-171	EMF-XXII-171

Compound	^{1}H NMR	^{13}C NMR	IR
444	EMF-XXII-203	EMF-XXII-203	EMF-XXII-203
449	EMF-XXI-277	EMF-XXI-277	EMF-XXI-277
451	EMF-XXII-51	EMF-XXII-51	EMF-XXII-51
454	EMF-XXII-31	EMF-XXII-31	EMF-XXII-31
456	EMF-XXII-111	EMF-XXII-111	EMF-XXII-111
458	EMF-XXII-215	EMF-XXII-215	EMF-XXII-215
460	EMF-XXII-255	EMF-XXII-255	EMF-XXII-255
462	EMF-XXIII-29	EMF-XXIII-29	EMF-XXIII-29
464	EMF-XXIII-37	EMF-XXIII-37	EMF-XXIII-37
466	EMF-XXI-295	EMF-XXI-295	EMF-XXI-295
468	EMF-XXIII-261	EMF-XXIII-261	EMF-XXIII-261
470	EMF-XXIII-289	EMF-XXIII-289	EMF-XXIII-289
474	EMF-XIX-197	EMF-XIX-197	EMF-XIX-197
487	EMF-XXI-173	EMF-XXI-173	EMF-XXI-173
490	EMF-XXVII-81	EMF-XXVII-81	EMF-XXVII-81
505	EMF-XXI-115	EMF-XXI-115	EMF-XXI-115
410	EMF-XXVII-73	EMF-XXVII-73	EMF-XXVII-73
469	EMF-XXVII-59	EMF-XXVII-59	EMF-XXVII-59
471	EMF-XXVII-61	EMF-XXVII-61	EMF-XXVII-61
508	EMF-XXVII-77	EMF-XXVII-77	EMF-XXVII-77
573	EMF-XXVII-89	EMF-XXVII-89	EMF-XXVII-89
511	EMF-XXVII-93	EMF-XXVII-93	EMF-XXVII-93
451	EMF-XXVI-237	EMF-XXVI-237	EMF-XXVI-237
446	EMF-XXVI-249	EMF-XXVI-249	EMF-XXVI-249
448	EMF-XXVI-243	EMF-XXVI-243	EMF-XXVI-243
453	EMF-XXVI-269	EMF-XXVI-269	EMF-XXVI-269
455	EMF-XXVI-265	EMF-XXVI-265	EMF-XXVI-265
457	EMF-XXVI-257	EMF-XXVI-257	EMF-XXVI-257

Compound	^{1}H NMR	^{13}C NMR	IR
459	EMF-XXVI-259	EMF-XXVI-259	EMF-XXVI-259
461	EMF-XXVI-261	EMF-XXVI-261	EMF-XXVI-261
463	EMF-XXVI-253	EMF-XXVI-253	EMF-XXVI-253
465	EMF-XXVI-267	EMF-XXVI-267	EMF-XXVI-267
489	EMF-XXVII-27	EMF-XXVII-27	EMF-XXVII-27
488	EMF-XXVI-301	EMF-XXVI-301	EMF-XXVI-301

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ABOUT THE AUTHOR

Eric Matthew Ferreira was born on March 16, 1978 in Gilroy, California (The Garlic Capital of the World). He was the second child (behind sister Andrea) of Phil and Marna Ferreira. Shortly thereafter, the family moved to Sonora, California, nestled in the foothills of the Sierra Nevada, where Eric was raised for the next seventeen years. Eric attended Sonora High School, where he played on the tennis team and was a trumpet player in the Golden Regiment and in the jazz band. He also spent significant amounts of time not wanting to be in Sonora.

Desperate to accomplish this goal, he set out for college across the country to the Massachusetts Institute of Technology in Cambridge, Massachusetts. Although he initially was interested in biomedical engineering, he quickly became excited about chemistry. His first research experience was a summer stint at Oregon State University in Corvallis, where he studied food chemistry in the laboratories of Ronald Wrolstad. Later at MIT, he became very interested in organometallic chemistry. He spent over a year in the laboratories of Stephen Buchwald, working on both palladium and copper catalysis. He also was a member of the lightweight crew team (one of the eleven teams in the elite Eastern Sprints league), which pretty much meant he had no time to do anything else. He graduated in 2000 with an S.B. in Chemistry with a concentration in writing.

He then moved to Pasadena, California to pursue Ph.D. studies at the California Institute of Technology. He received his degree in 2005 for his work in palladium-catalyzed oxidation chemistry. He will begin postdoctoral studies later in 2005 at Stanford University under the direction of Professor Barry Trost.