

Highly Efficient Construction of Benzene Ring in Carbazoles by Palladium-Catalyzed *Endo*-mode Oxidative Cyclization of 3-(3'-Alkenyl)indoles

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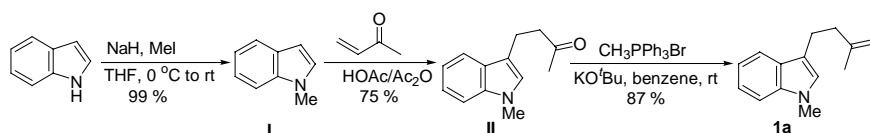
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Materials and Methods

Palladium acetate was used as purchased from Aldrich. BQ was recrystallized from petroleum ether (90-120 °C). All solvents were dried and distilled before use according to the standard methods. NMR spectra were recorded on a Varian Mercury V \square 300 spectrometer. Infrared spectra were obtained on a Bio-Rad FTS-185 machine. Mass spectra were provided on Agilent 5973 or Agilent 1100 machines. Elemental analyses were carried out on Elementar Vario EL instruments. All melting points were uncorrected.

Synthesis of Indole Substrates:

1-Methyl-3-(3'-methylbut-3'-enyl)indole (1a):



Methylation of indole was done according to the literature procedure.¹ To a solution of indole (5.86 g, 50 mmol) in THF (150 mL) at 0 °C was added NaH (3.00 g, 60 % dispersion in mineral oil, 75 mmol). The heterogeneous mixture was stirred at 0 °C for 15 minutes and 1h at room temperature. The mixture was then cooled to 0 °C, treated with iodomethane (4.17 mL, 67 mmol), and allow to warm to room temperature. After 30 minutes, the reaction mixture was cooled to 0 °C, quenched with saturated NH₄Cl (200 mL), and extracted with ether (3 x 50 mL). The organic layers were combined, washed with brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The resulting oil was purified by flash chromatography (eluent: petroleum ether/EtOAc 10:1) to provide indole I (6.49 g, 99 % yield) as a colorless oil. **Indole I:**

^1H NMR (300 MHz, CDCl_3): δ 7.63 (d, $J = 7.5$ Hz, 1 H), 7.33 (d, $J = 7.8$ Hz, 1 H), 7.25-7.08 (m, 2 H), 7.05 (d, $J = 3.3$ Hz, 1 H), 6.48 (d, $J = 2.7$ Hz, 1 H), 3.79 (s, 3 H); IR (neat): ν 3055, 2926, 1614, 1514, 1317, 1243, 1079, 740 cm^{-1} ; MS (EI): m/z : 131 (M^+ , 100), 130, 128, 116, 103, 89.

Conjugate addition of **indole I** was done according to the literature procedure.²

Indole I (1.31 g, 10 mmol) was dissolved in glacial acetic acid (6 mL), 2 mL of acetic anhydride was added, then 2.50 mL (30 mmol) of methyl vinyl ketone. The solution was allowed to stand at room temperature for 5 minutes and then heated to 90 °C for 30 min. The initial yellow solution turned dark brown. It was cooled in ice water, quenched with water (20 mL), cautiously neutralized with solid NaHCO_3 , and extracted with ether (3 x 20 mL). The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4 , and concentrated in vacuo. The resulting oil was purified by flash chromatography (eluent: petroleum ether/EtOAc 5:1) to provide indole **II** (1.51g, 75 % yield) as a pale yellow oil. **Indole II**: ^1H NMR (300 MHz, CDCl_3): δ 7.57 (d, $J = 7.8$ Hz, 1 H), 7.28-7.22 (m, 2 H), 7.13-7.10 (m, 1 H), 6.85 (s, 1 H), 3.73 (s, 3 H), 3.04 (t, $J = 6.9$ Hz, 2 H), 2.83 (t, $J = 6.9$ Hz, 2 H), 2.14 (s, 3 H); IR (neat): ν 3055, 2922, 1716, 1616, 1474, 1326, 1162, 741 cm^{-1} ; MS (EI): m/z : 201 (M^+ , 158, 144 (100), 128, 115, 103, 89, 77.

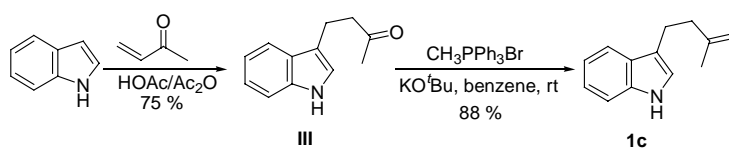
The Wittig reaction of **indole II** was done according to the literature procedure.³

To a flask containing 3.57 g (10 mmol) of methyl triphenylphosphonium bromide and 1.12 g (10 mmol) of potassium *tert*-butoxide at 0 °C was added 10 mL of benzene. The suspension was stirred for 15 min at 0 °C and 1h at room temperature. The resulting

bright yellow solution was cooled to 0 °C, and **indole II** (1.61 g, 8 mmol) in benzene (5 mL) was added. After being stirred at room temperature for 4h, the mixture was cooled to 0 °C, quenched with water (10 mL), and extracted with ether (3 x 30 mL). The organic layers were combined, washed with brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The resulting oil was purified by flash chromatography (eluent: petroleum ether/EtOAc 20:1) to provide **1a** (1.39 g, 87 % yield) as a colorless oil.

1-Methyl-3-(3'-methylbut-3'-enyl)indole (1a): ¹H NMR (300 MHz, CDCl₃): δ 7.60 (d, *J* = 7.8 Hz, 1 H), 7.30-7.19 (m, 2 H), 7.13-7.07 (m, 1 H), 6.85 (s, 1 H), 4.77 (s, 2 H), 3.74 (s, 3 H), 2.92-2.87 (m, 2 H), 2.45-2.39 (m, 2 H), 1.81 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 145.9, 136.8, 127.7, 125.8, 121.3, 118.9, 118.4, 114.8, 109.9, 109.0, 77.4, 77.0, 76.6, 38.4, 32.5, 23.4, 22.6; IR (neat): ν 3056, 2935, 1649, 1616, 1484, 1473, 1376, 1325, 886, 738 cm⁻¹; MS (EI): *m/z*: 199 (M⁺), 144 (100), 128, 115, 103, 77; HRMS: Calcd for C₁₄H₁₇N (M⁺ + Na) 222.1253, found 222.1265.

3-(3'-Methylbut-3'-enyl)indole (1c):



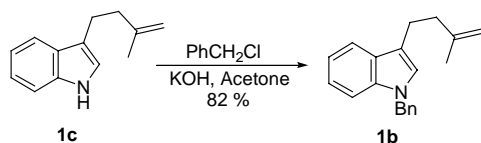
Conjugate additions of indole was done according to the literature procedure.²

Indole (1.17 g, 10 mmol) was dissolved in glacial acetic acid (6 mL), 2 mL of acetic anhydride was added, then 2.5 mL (30 mmol) of methyl vinyl ketone. The solution was allowed to stand at room temperature for 5 minutes and then heated to 90 °C for 30 min. The initial yellow solution turned dark brown. It was cooled with ice, 50 mL of water was added and, after standing for a few minutes, the precipitate was filtered and

washing with water. The crude product was recrystallized from benzene-petroleum ether (30-60 °C) to provide **III** (1.40 g, 75 % yield) as pale yellow needles. **Indole III**: m.p. 89-90 °C (lit.² m.p. 93-94 °C); ¹H NMR (300 MHz, CDCl₃): δ 7.96 (br s, 1 H), 7.59 (d, *J* = 8.7 Hz, 1 H), 7.38-7.35 (m, 1 H), 7.23-7.10 (m, 2 H), 7.00 (s, 1 H), 3.08-3.03 (m, 2 H), 2.85 (t, *J* = 7.5 Hz, 2 H), 2.16 (s, 3 H); IR (KBr): ν 3323, 3059, 1702, 1620, 1575, 1458, 1352, 1165, 739 cm⁻¹; MS (EI): *m/z*: 187 (M⁺), 144, 130 (100), 115, 103, 77.

3-(3'-Methylbut-3'-enyl)indole (**1c**) was isolated in 88 % yield as a white solid from **III** and methyl triphenylphosphonium bromide employing a procedure similar to that used for synthesizing **1a**. **3-(3'-Methylbut-3'-enyl)indole (1c)**: m.p. 60-62 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.87 (br s, 1 H), 7.63-7.61 (m, 1H), 7.36-7.33 (m, 1 H), 7.24-7.09 (m, 2 H), 6.99-6.98 (m, 1 H), 4.77 (s, 2 H), 2.93-2.88 (m, 2 H), 2.46-2.41 (m, 2 H), 1.81 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 145.9, 136.2, 127.4, 121.8, 121.0, 119.1, 118.8, 116.5, 111.0, 110.0, 38.2, 23.5, 22.6; IR (KBr): ν 3398, 3074, 1647, 1618, 1456, 1093, 885, 743 cm⁻¹; MS (EI): *m/z*: 185 (M⁺), 149, 130 (100), 103, 91, 77; Anal. Calcd for C₁₃H₁₅N: C, 84.28; H, 8.16; N, 7.56. Found C, 84.27; H, 8.07; N, 7.38.

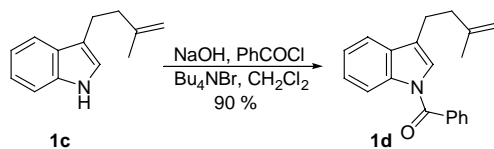
1-Benzyl-3-(3'-methylbut-3'-enyl)indole (1b):



Benylation of indole **1c** was done according to the literature procedure.⁴ To an acetone solution (3 mL) of **1c** (0.19 g, 1 mmol) is added powdered potassium hydroxide (0.28 g, 5 mmol) with cooling. After few minutes, benzyl chloride (0.23 mL, 2 mmol)

was added to the acetone solution with vigorous stirring and the reaction mixture was stirred for 2h. Insoluble materials are removed by filtration and acetone is concentrated in vacuo. Then 10 mL of water is added to the residue and the mixture was extracted with ether (3 x 10 mL). The organic layers were combined, washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The resulting oil was purified by flash chromatography (eluent: petroleum ether/EtOAc 20:1) to provide **1b** (0.23 g, 82 % yield) as a colorless oil. **1-Benzyl-3-(3'-methylbut-3'-enyl)indole (1b)**: ¹H NMR (300 MHz, CDCl₃): δ 7.63 (dd, *J* = 7.5, 0.6 Hz, 1 H), 7.29-7.08 (m, 8 H), 6.92 (s, 1 H), 5.27 (s, 2 H), 4.76 (s, 2 H), 2.93-2.88 (m, 2 H), 2.45-2.40 (m, 2 H), 1.80 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 145.9, 137.8, 136.6, 128.6, 128.1, 127.4, 126.6, 125.3, 121.6, 119.0, 118.8, 115.6, 110.0, 109.5, 49.7, 38.3, 23.5, 22.6; IR (neat): ν 3067, 2933, 1649, 1614, 1467, 1454, 1329, 1181, 886, 738 cm⁻¹; MS (EI): *m/z*: 275 (M⁺), 220, 91 (100), 65, 55; Anal. Calcd for C₂₀H₂₁N: C, 87.23; H, 7.69; N, 5.09. Found: C, 86.97; H, 7.89; N, 5.18.

1-Benzoyl-3-(3'-methylbut-3'-enyl)indole (1d):

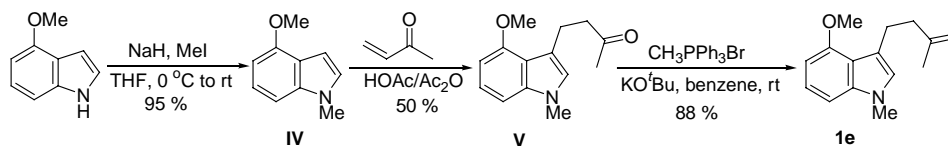


Benzoylation of indole **1c** was done according to the literature procedure.^[5] To a stirred suspension of **1c** (0.17 g, 0.91 mmol), powdered NaOH (0.11 g, 2.7 mmol), and ⁿBu₄NBr (4.3 mg) in dry methylene chloride (5 mL) was added 0.20 mL (1.7 mmol) of benzoyl chloride. During addition, the reaction was cooled with ice. After 1.5h stirring, water (10 mL) was added and the reaction mixture was extracted with CH₂Cl₂. The

extracts were combined, washed with brine, dried over anhydrous Na_2SO_4 , and concentrated in vacuo. The resulting oil was purified by flash chromatography (eluent: petroleum ether/EtOAc 20:1) to provide **1d** (0.24 g, 90 % yield) as a colorless oil.

1-benzoyl-3-(3'-methylbut-3'-enyl)indole (1d): ^1H NMR (300 MHz, CDCl_3): δ 8.38 (d, $J = 7.5$ Hz, 1 H), 7.74-7.71 (m, 2 H), 7.61-7.51 (m, 4 H), 7.39-7.33 (m, 2 H), 7.08 (s, 1 H), 4.77 (s, 1 H), 4.73 (s, 1 H), 2.84-2.79 (m, 2 H), 2.41-2.36 (m, 2 H), 1.78 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 168.4, 145.0, 136.3, 134.9, 131.7, 131.0, 129.0, 128.5, 125.0, 123.9, 123.7, 122.2, 118.9, 116.5, 110.5, 37.0, 23.2, 22.4; IR (neat): ν 3068, 2968, 2934, 2855, 1684, 1649, 1453, 1333, 1215, 874, 749 cm^{-1} ; MS (EI): m/z : 289 (M^+), 234, 105 (100), 77, 51; HRMS: Calcd for $\text{C}_{20}\text{H}_{20}\text{NO}$ ($\text{M}^+ + \text{H}$) 290.1540, found 290.1541.

4-Methoxy-1-methyl-3-(3'-methylbut-3'-enyl)indole (1e):



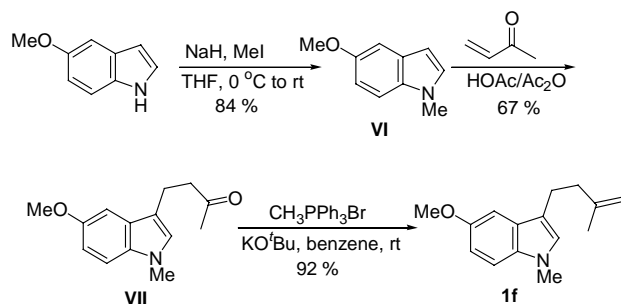
4-Methoxy-1-methylindole (**IV**) was isolated in 95 % yield as a solid from 4-Methoxyindole and iodomethane employing a procedure similar to that used to synthesize **I**. **Indole IV**: m.p. 87-88 $^{\circ}\text{C}$ (lit.⁶ m.p. 88 $^{\circ}\text{C}$); ^1H NMR (300 MHz, CDCl_3): δ 7.15 (dd, $J_1 = J_2 = 8.1$ Hz, 1 H), 6.97-6.95 (m, 2 H), 6.58 (d, $J = 2.7$ Hz, 1 H), 6.53 (d, $J = 7.8$ Hz, 1 H), 3.96 (s, 3 H), 3.77 (s, 3 H); IR (KBr): ν 3099, 2841, 1613, 1581, 1501, 1259, 1059, 736 cm^{-1} ; MS (EI): m/z : 161 (M^+ , 100), 146, 130, 118, 103, 91, 77.

Indole **V** was isolated in 50 % yield as a pale yellow oil from indole **IV** and methyl vinyl ketone employing a procedure similar to that used to synthesize **II**.

Indole V: ^1H NMR (300 MHz, CDCl_3): δ 7.11 (dd, $J_1 = J_2 = 8.1$ Hz, 1 H), 6.88 (d, $J = 7.8$ Hz, 1 H), 6.70 (s, 1 H), 6.48 (d, $J = 7.8$ Hz, 1 H), 3.91 (s, 3 H), 3.68 (s, 3 H), 3.11 (t, $J = 7.2$ Hz, 2 H), 2.82 (t, $J = 7.2$ Hz, 2 H), 2.13 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 209.6, 154.6, 138.7, 125.2, 122.3, 117.2, 114.1, 102.5, 98.8, 55.1, 45.9, 32.7, 30.0, 21.2; IR (neat): ν 2931, 2839, 1712, 1613, 1581, 1501, 1325, 1258, 731 cm^{-1} ; MS (EI): m/z : 231 (M^+), 188, 174 (100), 144, 131, 77, 43; HRMS: Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_2\text{Na}$ ($\text{M}^+ + \text{Na}$) 254.1152, found 254.1161.

4-Methoxy-1-methyl-3-(3'-methylbut-3'-enyl)indole **1e** was isolated in 88 % yield as a clear oil from **V** and methyl triphenylphosphonium bromide employing a procedure similar to that used for synthesizing **1a**. **4-Methoxy-1-methyl-3-(3'-methylbut-3'-enyl)indole (1e):** ^1H NMR (300 MHz, CDCl_3): δ 7.10 (dd, $J_1 = J_2 = 8.1$ Hz, 1 H), 6.88 (d, $J = 8.1$ Hz, 1 H), 6.70 (s, 1 H), 6.47 (d, $J = 7.8$ Hz, 1 H), 4.76 (s, 1 H), 4.74 (s, 1 H), 3.91 (s, 3 H), 3.69 (s, 3 H), 3.02-2.96 (m, 2 H), 2.42-2.36 (m, 2 H), 1.82 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 154.9, 146.7, 138.7, 124.6, 122.2, 117.5, 115.7, 109.5, 102.5, 98.8, 55.0, 40.1, 32.7, 25.6, 22.6; IR (neat): ν 3072, 1648, 1613, 1583, 1500, 1467, 1257, 1097, 885, 728 cm^{-1} ; MS (EI): m/z : 229 (M^+), 174 (100), 144, 131, 115, 103, 77; HRMS: Calcd for $\text{C}_{15}\text{H}_{19}\text{NONa}$ ($\text{M}^+ + \text{Na}$) 252.1359, found 252.1371.

5-Methoxy-1-methyl-3-(3'-methylbut-3'-enyl)indole (1f):



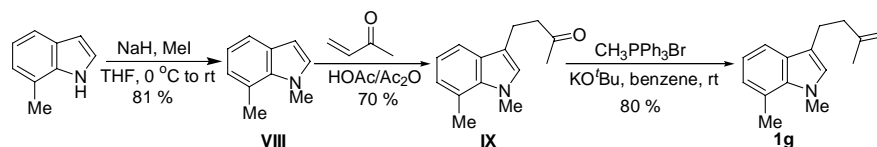
5-Methoxy-1-methylindole (**VI**) was isolated in 84 % yield as a solid from 5-Methoxyindole and iodomethane employing a procedure similar to that used for synthesizing **I**. **Indole VI**: m.p. 100-102 °C (lit.⁷ m.p. 103-104 °C); ¹H NMR (300 MHz, CDCl₃): δ 7.21 (d, *J* = 8.7 Hz, 1 H), 7.09 (d, *J* = 2.7 Hz, 1 H), 7.02 (d, *J* = 3.3 Hz, 1 H), 6.89 (dd, *J* = 9.0, 2.4 Hz, 1 H), 6.41-6.39 (m, 1 H), 3.85 (s, 3 H), 3.77 (s, 3 H); IR (KBr): ν 3131, 3105, 2952, 1863, 1622, 1497, 1151, 1025, 803, 726 cm⁻¹; MS (EI): *m/z*: 161 (M⁺, 100), 146, 118, 91, 77, 51.

Indole **VII** was isolated in 67 % yield as a solid from **VI** and methyl vinyl ketone employing a procedure similar to that used for synthesizing **II**. **Indole VII**: m.p. 76-78 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.18 (d, *J* = 9.0 Hz, 1 H), 7.01 (d, *J* = 2.4 Hz, 1 H), 6.88 (dd, *J* = 8.7, 2.4 Hz, 1 H), 6.82 (s, 1 H), 3.87 (s, 3 H), 3.70 (s, 3 H), 3.02-2.97 (m, 2 H), 2.82 (t, *J* = 7.5 Hz, 2 H), 2.15 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 208.8, 153.6, 132.3, 127.7, 126.9, 113.0, 111.6, 109.9, 100.5, 55.9, 44.1, 32.7, 30.0, 19.1; IR (KBr): ν 3111, 3072, 2999, 1709, 1621, 1582, 1495, 1218, 797 cm⁻¹; MS (EI): *m/z*: 231(M⁺), 188, 174 (100), 159, 131, 77, 43; Anal. Calcd for C₁₄H₁₇NO₂: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.54; H, 7.43; N, 6.30.

4-Methoxy-1-methyl-3-(3'-methylbut-3'-enyl)indole (**1f**) was isolated in 92 % yield as a colorless oil from **VII** and methyl triphenylphosphonium bromide employing a procedure similar to that used for synthesizing **1a**. **5-Methoxy-1-methyl-3-(3'-methylbut-3'-enyl)indole (1f)**: ¹H NMR (300 MHz, CDCl₃): δ 7.17 (d, *J* = 8.7 Hz, 1 H), 7.03 (d, *J* = 2.7 Hz, 1 H), 6.88 (dd, *J* = 9.0, 2.7 Hz, 1 H), 6.82 (s, 1 H), 4.78 (s, 2 H), 3.87 (s, 3 H), 3.71 (s, 3 H), 2.88-2.83 (m, 2 H),

2.43-2.38 (m, 2 H), 1.81 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 153.5, 146.0, 132.4, 128.0, 126.5, 114.3, 111.5, 109.9, 109.8, 100.9, 56.0, 38.2, 32.7, 23.4, 22.6; IR (neat): ν 3074, 2937, 1648, 1622, 1579, 1493, 1226, 1064, 886, 790 cm^{-1} ; MS (EI): m/z : 229 (M^+), 174 (100), 159, 131, 116, 89, 77; Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}$: C, 78.56; H, 8.35; N, 6.11. Found: C, 78.40; H, 8.28; N, 6.17.

1,7-Dimethyl-3-(3'-methylbut-3'-enyl)indole (1g):



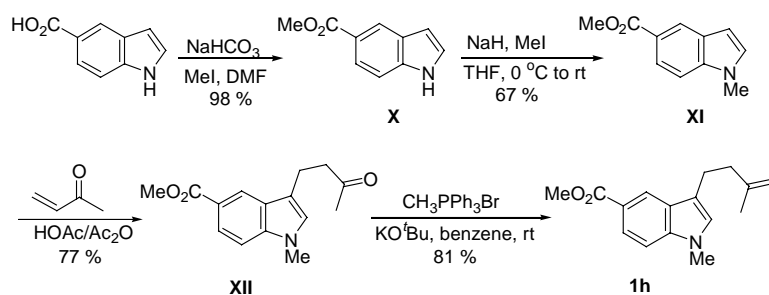
1,7-Dimethylindole (**VIII**) was isolated in 81 % yield as a solid from 7-methylindole and iodomethane employing a procedure similar to that used for synthesizing **I**. **Indole VIII**: m.p. 77-79 °C (lit.⁸ m.p. 78 °C); ^1H NMR (300 MHz, CDCl_3): δ 7.44 (d, $J = 7.8$ Hz, 1 H), 6.98-6.88 (m, 3 H), 6.42 (d, $J = 3.0$ Hz, 1 H), 4.06 (s, 3 H), 2.77 (s, 3 H); IR (KBr): ν 3050, 3028, 2965, 2926, 1890, 1684, 1494, 1458, 1314, 1086, 779, 711 cm^{-1} ; MS (EI): m/z : 145 (M^+ , 100), 130, 115, 103, 91, 82.

Indole **IX** was isolated in 70 % yield as a pale yellow oil from **VIII** and methyl vinyl ketone employing a procedure similar to that used for synthesizing **II**. **Indole IX**: ^1H NMR (300 MHz, CDCl_3): δ 7.39 (d, $J = 7.2$ Hz, 1 H), 6.99-6.89 (m, 2 H), 6.72 (s, 1 H), 3.99 (s, 3 H), 2.99 (t, $J = 7.5$ Hz, 2 H), 2.81 (t, $J = 7.5$ Hz, 2 H), 2.74 (s, 3 H), 2.14 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 208.4, 135.4, 128.4, 127.7, 123.9, 121.0, 118.7, 116.5, 113.0, 43.9, 36.1, 29.7, 19.4, 18.9; IR (neat): ν 3039, 2901, 1714, 1603, 1466, 1318, 1166, 744 cm^{-1} ; MS (EI): m/z : 215 (M^+), 158 (100), 143, 128, 115, 91; HRMS: Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}$: 215.1310, found 215.1306.

1,7-Dimethyl-3-(3'-methylbut-3'-enyl)indole **1g** was isolated in 80 % yield as a colorless oil from **IX** and methyl triphenylphosphonium bromide employing a procedure similar to that used for synthesizing **1a**.

1,7-Dimethyl-3-(3'-methylbut-3'-enyl) indol (1g): ^1H NMR (300 MHz, CDCl_3): δ 7.42 (d, $J = 7.8$ Hz, 1 H), 6.98-6.88 (m, 2 H), 6.73 (s, 1 H), 4.77 (s, 2 H), 4.00 (s, 3 H), 2.87-2.82 (m, 2 H), 2.75 (s, 3 H), 2.42-2.37 (m, 2 H), 1.80 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 146.0, 135.6, 128.9, 117.6, 124.1, 121.1, 118.8, 117.0, 114.6, 109.9, 38.3, 36.3, 23.3, 22.6, 19.6; IR (neat): ν 3073, 3045, 2929, 1649, 1606, 1586, 1460, 1407, 1318, 886, 780, 741 cm^{-1} ; MS (EI): m/z : 213 (M^+), 158 (100), 143, 115, 91, 77; HRMS: Calcd for $\text{C}_{15}\text{H}_{19}\text{N}$: 213.1517, found 213.1508.

Methyl 1-methyl-3-(3'-methylbut-3'-enyl)indole-5-carboxylate (1h):



Esterification of indole-5-carboxylic acid was done according to the literature procedure.⁹ A mixture of indole-5-carboxylic acid (0.50 g, 3.1 mmol), powdered NaHCO_3 (1.04 g, 12.4 mmol), and iodomethane (1.26 mL, 20.1 mmol) in DMF (3.5 mL) was stirred for 72 h under nitrogen. The reaction mixture was diluted with water (20 mL) and extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with aqueous NaHCO_3 and brine, dried over anhydrous Na_2SO_4 , and concentrated in vacuo. The resulting oil was purified by flash chromatography (eluent:

petroleum ether/EtOAc 20:1) to provide **X** (532 mg, 98 % yield) as a solid. **Indole X**: m.p. 122-124 °C (lit.⁹ 127-128 °C); ¹H NMR (300 MHz, CDCl₃): δ 8.43 (s, 1 H), 8.42 (s, 1 H), 7.92 (d, *J* = 8.7 Hz, 1 H), 7.41 (d, *J* = 8.4 Hz, 1 H), 7.28-7.26 (m, 1 H), 6.67 (s, 1 H), 3.94 (s, 3 H); IR (KBr): ν 3319, 3111, 2951, 1695, 1612, 1511, 1291, 1274, 758 cm⁻¹; MS (EI): *m/z*: 175 (M⁺), 144 (100), 116, 89, 63.

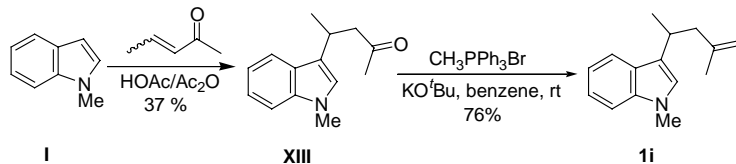
Indole **XI** was isolated in 67 % yield as a solid from **X** and iodomethane employing a procedure similar to that used for synthesizing **I**. **Indole XI**: m.p. 104-104.5 °C (lit.¹⁰ 105-106 °C); ¹H NMR (300 MHz, CDCl₃): δ 8.40-8.39 (m, 1 H), 7.93 (dd, *J* = 8.7, 1.8 Hz, 1 H), 7.33 (d, *J* = 8.4 Hz, 1 H), 7.11 (d, *J* = 3.0 Hz, 1 H), 6.59-6.58 (m, 1 H), 3.93 (s, 3 H), 3.83 (s, 3 H); IR (KBr): ν 3104, 3022, 2947, 1707, 1612, 1571, 1309, 972, 762 cm⁻¹; MS (EI): *m/z*: 189 (M⁺), 158 (100), 130, 115, 103, 77.

Indole **XII** was isolated in 77 % yield as a solid from **XI** and methyl vinyl ketone employing a procedure similar to that used for synthesizing **II**. **Indole XII**: m.p. 83-85 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.34 (dd, *J*₁ = *J*₂ = 0.9 Hz, 1 H), 7.92 (dd, *J* = 8.4, 1.5 Hz, 1 H), 7.29 (s, 1 H), 6.91 (s, 1 H), 3.94 (s, 3 H), 3.76 (s, 3 H), 3.06 (t, *J* = 7.2 Hz, 2 H), 2.84 (t, *J* = 7.2 Hz, 2 H), 2.15 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 208.3, 168.2, 139.4, 127.8, 127.1, 122.9, 121.7, 120.7, 115.4, 108.8, 51.8, 44.1, 32.7, 30.0, 18.9; IR (KBr): ν 2947, 2922, 1710, 1615, 1460, 1288, 1247, 767 cm⁻¹; MS (EI): *m/z*: 259 (M⁺), 228, 202 (100), 184, 157, 143, 115, 77; Anal. Calcd for C₁₅H₁₇NO₃: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.41; H, 6.59; N, 5.25.

Methyl 1-Methyl-3-(3'-methylbut-3'-enyl)indole-5-carboxylate (**1h**) was isolated

in 81 % yield as a colorless oil from **XII** and methyl triphenylphosphonium bromide employing a procedure similar to that used for synthesizing **1a**. **Methyl 1-Methyl-3-(3'-methylbut-3'-enyl)indole-5-carboxylate (1h)**: ^1H NMR (300 MHz, CDCl_3): δ 8.36 (d, $J = 1.5$ Hz, 1 H), 7.92 (dd, $J = 8.7, 1.8$ Hz, 1 H), 7.27 (d, $J = 8.1$ Hz, 1 H), 6.90 (s, 1 H), 4.78 (s, 1 H), 4.77 (s, 1 H), 3.94 (s, 3 H), 3.76 (s, 3 H), 2.95-2.89 (m, 2 H), 2.45-2.39 (m, 2 H), 1.81 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 168.3, 145.5, 139.3, 127.4, 127.2, 122.8, 122.0, 120.5, 116.8, 110.1, 108.7, 51.7, 38.2, 32.7, 23.1, 22.6; IR (neat): ν 3071, 2948, 2854, 1710, 1649, 1616, 1312, 1101, 770 cm^{-1} ; MS (EI): m/z : 257 (M^+), 226, 202 (100), 143, 115; Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_2$: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.55; H, 7.45; N, 5.52.

1-Methyl-3-(1',3'-Dimethylbut-3'-enyl)indole (1i):



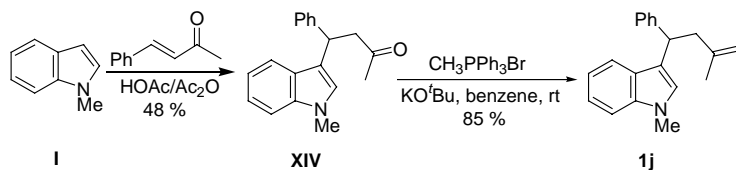
Conjugate addition of **indole I** was done according to the literature procedure.²

Indole I (1.31 g, 10 mmol) was dissolved in glacial acetic acid (6 mL), 2 mL of acetic anhydride was added, then 1.01 g (12 mmol) of pent-3-en-2-one. The solution was allowed to stand at room temperature for 5 minutes and then heated to 90 °C for 30 min. The initial yellow solution turned dark brown. It was cooled in ice-water, quenched with water (20 mL), cautiously neutralized with solid NaHCO_3 , and extracted with ether (3 x 20 mL). The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4 , and concentrated in vacuo. The resulting oil was purified by flash chromatography (eluent: petroleum ether/EtOAc 5:1) to provide **XIII** (0.80 g, 37 %

yield) as a pale yellow oil. **Indole XIII**: $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.66 (d, $J = 8.1$ Hz, 1 H), 7.32-7.22 (m, 2 H), 7.16-7.10 (m, 1 H), 6.85 (s, 1 H), 3.75 (s, 3 H), 3.69-3.62 (m, 1 H), 2.95 (dd, $J = 16.2, 6.0$ Hz, 1 H), 2.77 (dd, $J = 16.2, 8.4$ Hz, 1 H), 2.12 (s, 3 H), 1.40 (d, $J = 6.9$ Hz, 3 H); IR (neat): ν 3054, 2962, 1714, 1615, 741 cm^{-1} ; MS (EI): m/z : 215 (M^+), 158 (100).

1-Methyl-3-(1',3'-dimethylbut-3'-enyl)indole (**1i**) was isolated in 76 % yield as a pale yellow oil from **XIII** and methyl triphenylphosphonium bromide employing a procedure similar to that used for synthesizing **1a**. **1-Methyl-3-(1',3'-dimethylbut-3'-enyl)indole (1i)**: $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.66-7.62 (m, 1 H), 7.27-7.17 (m, 2 H), 7.11-7.06 (m, 1 H), 6.79 (s, 1 H), 4.76 (s, 1 H), 4.72 (s, 1 H), 3.69 (s, 3 H), 3.28-3.21 (m, 1 H), 2.57 (dd, $J = 13.8, 5.4$ Hz, 1 H), 2.28-2.21 (m, 1 H), 1.76 (s, 3 H), 1.30 (d, $J = 6.9$ Hz, 3 H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 144.6, 137.1, 127.1, 124.7, 121.4, 121.0, 119.3, 118.4, 111.7, 109.2, 46.3, 32.5, 28.6, 22.3, 20.8; IR (neat): ν 2963, 1646, 1615, 738 cm^{-1} ; MS (EI): m/z : 213 (M^+), 158 (100); HRMS: Calcd for $\text{C}_{15}\text{H}_{20}\text{N}$ ($\text{M}^+ + \text{H}$) 214.1590, found 214.1598.

1-Methyl-3-(1'-phenyl-3'-methylbut-3'-enyl)indole (1j):



Conjugate addition of **indole I** was done according to the literature procedure.²

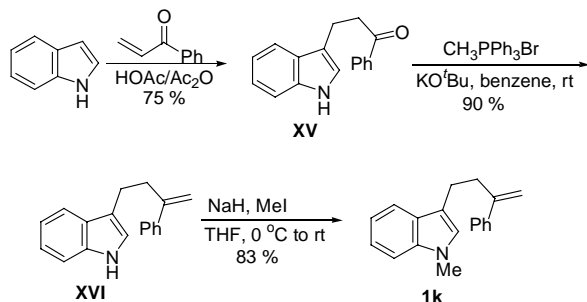
Indole I (1.31 g, 10 mmol) was dissolved in glacial acetic acid (6 mL), 2 mL of acetic anhydride was added, and then 1.78 g (12 mmol) of 4-phenylbut-3-en-2-one was added. The solution was allowed to stand at room temperature for 5 minutes and then

heated to 90 °C for 30 min. The initial yellow solution turned dark brown. It was cooled in ice water, quenched with water (20 mL), cautiously neutralized with solid NaHCO₃, and extracted with ether (3 x 20 mL). The organic layers were combined, washed with brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The resulting oil was purified by flash chromatography (eluent: petroleum ether/EtOAc 5:1) to provide **XIV** (1.33 g, 48 % yield) as a pale yellow oil. **Indole XIV**: ¹H NMR (300 MHz, CDCl₃): δ 7.44-7.41 (m, 1 H), 7.33-7.14 (m, 7 H), 7.04-6.99 (m, 1 H), 6.83 (s, 1 H), 4.82 (t, *J* = 7.8 Hz, 1 H), 3.75 (s, 3 H), 3.25 (dd, *J* = 15.9, 7.5 Hz, 1 H), 3.15 (dd, *J* = 15.9, 7.5 Hz, 1 H), 2.07 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 207.6, 144.0, 137.2, 128.4, 127.6, 126.8, 126.3, 126.1, 121.7, 119.4, 118.8, 117.2, 109.2, 50.4, 38.3, 32.7, 30.3; IR (neat): ν 3058, 3028, 1714, 1614, 1602, 1548, 1156, 741, 703 cm⁻¹; MS (EI): *m/z*: 277 (M⁺), 234, 220 (100), 204, 178, 77; HRMS: Calcd for C₁₉H₁₉NONa (M⁺ + Na) 300.1359, found 300.1365.

1-Methyl-3-(1'-phenyl-3'-methylbut-3'-enyl)indole **1j** was isolated in 85 % yield as a pale yellow oil from **XIV** and methyl triphenylphosphonium bromide employing a procedure similar to that used for synthesizing **1a**. **1-Methyl-3-(1'-phenyl-3'-methylbut-3'-enyl)indole (1j)**: ¹H NMR (300 MHz, CDCl₃): δ 7.46-7.44 (m, 1 H), 7.31-7.12 (m, 7 H), 7.03-6.98 (m, 1 H), 6.86 (s, 1 H), 4.69-4.64 (m, 2 H), 4.43 (t, *J* = 7.8 Hz, 1 H), 3.73 (s, 3 H), 2.92 (dd, *J* = 14.4, 7.2 Hz, 1 H), 2.73 (dd, *J* = 14.4, 8.7 Hz, 1 H), 1.72 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 145.0, 143.8, 137.1, 128.2, 127.9, 127.3, 126.0, 125.9, 121.4, 119.4, 118.6, 118.3, 112.2, 109.1, 44.6, 41.0, 32.6, 22.5; IR (neat): ν 3059, 3027, 2932, 1649, 1546, 1484, 1374, 1154, 888, 739, 701 cm⁻¹; MS (EI):

m/z : 275 (M^+), 220 (100), 204, 178, 152, 77; HRMS: Calcd for $C_{20}H_{22}N$ ($M^+ + H$)
276.1747, found 276.1743.

1-Methyl-3-(3'-phenylbut-3'-enyl)indole (1k):



Indole **XV** was isolated in 75 % yield as pale yellow needles from indole and phenyl vinyl ketone¹¹ employing a procedure similar to that used for synthesizing **III**.

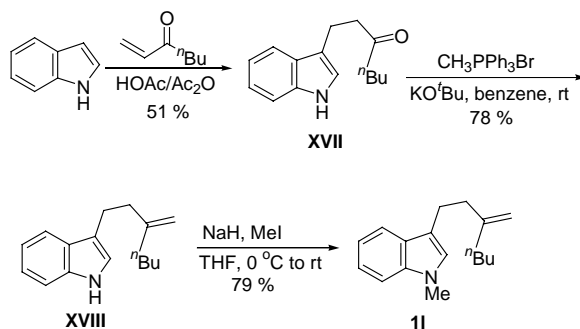
Indole XV: m.p. 122-124 °C, (lit.¹² 126-127 °C); ¹H NMR (300 MHz, CDCl₃): δ 7.99-7.95 (m, 3 H), 7.65 (d, $J = 7.5$ Hz, 1 H), 7.58-7.52 (m, 1 H), 7.47-7.42 (m, 2 H), 7.39-7.36 (m, 1 H), 7.23-7.11 (m, 2 H), 7.06 (d, $J = 2.1$ Hz, 1 H), 3.43-3.38 (m, 2 H), 3.25-3.20 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃): δ 200.0, 136.9, 136.2, 133.0, 128.5, 128.0, 127.1, 121.9, 121.6, 119.2, 118.6, 115.2, 111.2, 39.3, 19.6; IR (KBr): ν 3317, 3059, 2909, 1672, 1619, 1597, 1284, 747, 736 cm⁻¹; MS (EI): m/z : 249 (M^+), 144, 130 (100), 117, 105, 77; Anal. Calcd for C₁₇H₁₅NO: C, 81.90; H, 6.06; N, 5.62. Found: C, 82.01; H, 6.12; N, 5.48.

3-(3'-Phenylbut-3'-enyl)indole **XVI** was isolated in 90 % yield as a white solid from **XV** and methyl triphenylphosphonium bromide employing a procedure similar to that used for synthesizing **1a**. **Indole XVI**: m.p. 80-82 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.92 (br s, 1 H), 7.60 (d, $J = 7.8$ Hz, 1 H), 7.47 (d, $J = 7.8$ Hz, 2 H), 7.38-7.09 (m, 6 H), 6.98 (d, $J = 2.1$ Hz, 1 H), 5.33 (s, 1 H), 5.13 (s, 1 H), 2.93 (s, 4 H); ¹³C NMR (75

MHz, CDCl₃): δ 148.2, 141.1, 136.2, 128.3, 127.4, 127.3, 126.1, 121.8, 121.1, 119.1, 118.8, 116.2, 112.5, 111.0, 35.8, 24.2; IR (KBr): ν 3425, 3399, 2903, 1625, 1618, 1457, 1089, 898, 743 cm⁻¹; MS (EI): m/z : 247 (M⁺), 130 (100), 115, 103, 91, 77; Anal. Calcd for C₁₈H₁₇N: C, 87.41; H, 6.93; N, 5.66. Found: C, 87.31; H, 6.62; N, 5.48.

1-Methyl-3-(3'-phenylbut-3'-enyl)indole (**1k**) was isolated in 83 % yield as a colorless oil from **XVI** and iodomethane employing a procedure similar to that used for synthesizing **1**. **1-Methyl-3-(3'-phenylbut-3'-enyl)indole (1k)**: ¹H NMR (300 MHz, CDCl₃): δ 7.58 (d, J = 8.1 Hz, 1 H), 7.49-7.46 (m, 2 H), 7.38-7.19 (m, 5 H), 7.09 (dd, $J_1 = J_2 = 7.5$ Hz, 1 H), 6.83 (s, 1 H), 5.33 (d, J = 1.2 Hz, 1 H), 5.13 (s, 1 H), 3.74 (s, 3 H), 2.91 (s, 4 H); ¹³C NMR (75 MHz, CDCl₃): δ 148.3, 141.2, 136.9, 128.3, 127.8, 127.3, 126.1, 126.0, 121.4, 118.9, 118.5, 114.7, 112.4, 109.1, 36.2, 32.5, 24.2; IR (neat): ν 3055, 3028, 2933, 1627, 1617, 1600, 1326, 1248, 1151, 896, 739 cm⁻¹; MS (EI): m/z : 261 (M⁺), 157, 144 (100), 115, 91, 77; Anal. Calcd for C₁₉H₁₉N: C, 87.31; H, 7.33; N, 5.36. Found: C, 87.57; H, 7.20; N, 5.33.

1-Methyl-3-(3'-butylbut-3'-enyl)indole (**1l**):



Indole **XVII** was isolated in 51 % yield as a solid from indole and butyl vinyl ketone¹³ employing a procedure similar to that used for synthesizing **III**. **Indole XVII**: m.p. 86-88 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.95 (br s, 1 H), 7.60 (d, J = 7.8 Hz, 1

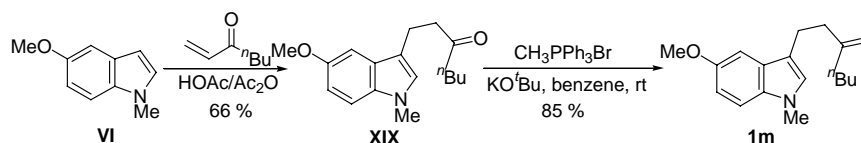
H), 7.36 (d, $J = 8.1$ Hz, 1 H), 7.22-7.10 (m, 2 H), 6.99 (d, $J = 2.1$ Hz, 1 H), 3.08-3.03 (m, 2 H), 2.84-2.80 (m, 2 H), 2.42-2.37 (m, 2 H), 1.59-1.49 (m, 2 H), 1.34-1.22 (m, 2 H), 0.88 (t, $J = 7.5$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 211.4, 136.2, 127.1, 121.9, 121.5, 119.1, 118.6, 115.1, 111.1, 43.0, 42.7, 25.8, 22.2, 19.3, 13.8; IR (KBr): ν 3324, 2953, 2930, 1702, 1621, 1458, 1414, 1221, 732 cm^{-1} ; MS (EI): m/z : 229 (M^+), 172, 144, 130 (100), 115, 103, 77; Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}$: C, 78.56; H, 8.35; N, 6.11. Found: C, 78.63; H, 8.34; N, 6.10.

3-(3'-butylbut-3'-enyl)indole **XVIII** was isolated in 78 % yield as a colorless oil from **XVII** and methyl triphenylphosphonium bromide employing a procedure similar to that used for synthesizing **1a**. **Indole XVIII**: ^1H NMR (300 MHz, CDCl_3): δ 7.90 (br s, 1 H), 7.63-7.61 (m, 1 H), 7.36 (d, $J = 7.8$ Hz, 1 H), 7.22-7.09 (m, 2 H), 7.00-6.99 (m, 1 H), 4.82 (s, 1 H), 4.78 (s, 1 H), 2.93-2.87 (m, 2 H), 2.46-2.41 (m, 2 H), 2.10 (t, $J = 7.5$ Hz, 2 H), 1.51-1.30 (m, 4 H), 0.92 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 150.0, 136.2, 127.4, 121.8, 121.0, 119.1, 118.8, 116.5, 111.0, 108.8, 36.4, 36.0, 30.0, 23.7, 22.5, 14.0; IR (neat): ν 3421, 3059, 2957, 2930, 1645, 1619, 1457, 1092, 888, 741 cm^{-1} ; MS (EI): m/z : 227 (M^+), 130 (100), 115, 103, 77; Anal. Calcd for $\text{C}_{16}\text{H}_{21}\text{N}$: C, 84.53; H, 9.31; N, 6.16. Found: C, 84.36; H, 9.28; N, 6.12.

1-Methyl-3-(3'-butylbut-3'-enyl)indole (**II**) was isolated in 79 % yield as a colorless oil from **XVIII** and iodomethane employing a procedure similar to that used for synthesizing **1**. **1-Methyl-3-(3'-butylbut-3'-enyl)indole (II)**: ^1H NMR (300 MHz, CDCl_3): δ 7.62-7.59 (m, 1 H), 7.30-7.19 (m, 2 H), 7.13-7.07 (m, 1 H), 6.85 (s, 1 H), 4.82-4.78 (m, 2 H), 3.74 (s, 3 H), 2.91-2.86 (m, 2 H), 2.44-2.39 (m, 2 H), 2.12-2.08 (m,

2 H), 1.48-1.29 (m, 4 H), 0.91 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 150.1, 136.9, 127.8, 125.9, 121.4, 118.9, 118.5, 115.1, 109.1, 108.7, 36.7, 36.0, 32.5, 30.0, 23.6, 22.5, 14.0; IR (neat): ν 2956, 2930, 2858, 1645, 1616, 1473, 1326, 886, 737 cm^{-1} ; MS (EI): m/z : 241 (M^+), 182, 144 (100), 115, 103, 77; Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{N}$: C, 84.59; H, 9.60; N, 5.80. Found: C, 84.37; H, 9.54; N, 5.84.

1-Methyl-3-(3'-butylbut-3'-enyl)-5-methoxyindole (1m);



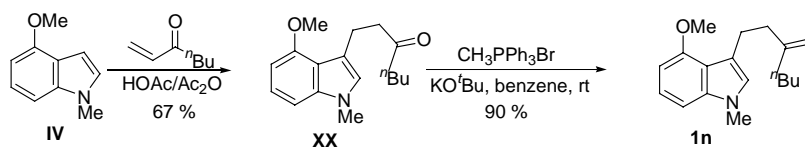
Indole **XIX** was isolated in 66 % yield as a pale yellow oil from indole **VI** and butyl vinyl ketone employing a procedure similar to that used for synthesizing **III**.

Indole **XIX**: ^1H NMR (300 MHz, CDCl_3): δ 7.17 (d, $J = 8.7$ Hz, 1 H), 7.00 (d, $J = 2.4$ Hz, 1 H), 6.88 (dd, $J = 8.7, 2.4$ Hz, 1 H), 6.80 (s, 1H), 3.87 (s, 3 H), 3.70 (s, 3H), 2.99 (t, $J = 7.5$ Hz, 2 H), 2.78 (t, $J = 7.5$ Hz, 2 H), 2.39 (t, $J = 7.5$ Hz, 2 H), 1.60-1.50 (m, 2 H), 1.35-1.22 (m, 2 H), 0.88 (t, $J = 7.5$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 211.1, 153.6, 132.3, 127.7, 126.9, 113.2, 111.6, 109.9, 100.7, 55.9, 43.1, 42.6, 32.6, 25.8, 22.2, 19.2, 13.8; IR (neat): ν 2957, 2873, 1710, 1622, 1579, 1492, 1226, 1058, 792 cm^{-1} ; MS (EI): m/z : 273 (M^+), 188, 174 (100), 159, 131, 103, 77; HRMS: Calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_2$: 273.1729, found 273.1721.

1-Methyl-3-(3'-butylbut-3'-enyl)-5-methoxyindole **1m** was isolated in 85 % yield as a colorless oil from **XIX** and methyl triphenylphosphonium bromide employing a procedure similar to that used for synthesizing **1a**. Indole **1m**: ^1H NMR (300 MHz, CDCl_3): δ 7.17 (d, $J = 8.7$ Hz, 1 H), 7.03 (d, $J = 2.1$ Hz, 1 H), 6.88 (dd, $J =$

9.0, 2.4 Hz, 1 H), 6.82 (s, 1 H), 4.82 (s, 1 H), 4.79 (s, 1 H), 3.87 (s, 3 H), 3.71 (s, 3 H), 2.87-2.82 (m, 2 H), 2.43-2.37 (m, 2 H), 2.13-2.08 (m, 2 H), 1.51-1.40 (m, 2 H), 1.40-1.28 (m, 2 H), 0.91 (t, $J = 7.5$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 153.5, 150.0, 132.4, 128.0, 126.5, 114.5, 111.5, 109.8, 108.7, 100.9, 55.9, 36.5, 36.0, 32.6, 30.0, 23.6, 22.5, 14.0; IR (neat): ν 3078, 2930, 1644, 1622, 1580, 1493, 1226, 1062, 885, 789 cm^{-1} ; MS (EI): m/z : 271 (M^+), 174 (100), 159, 131, 104, 77; HRMS: Calcd for $\text{C}_{18}\text{H}_{25}\text{NO}$: 271.1936, found 271.1932.

1-Methyl-3-(3'-butylbut-3'-enyl)-4-methoxyindole (**1n**):



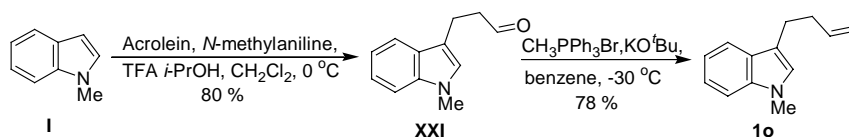
Indole **XX** was isolated in 67 % yield as a pale yellow oil from **indole IV** and butyl vinyl ketone employing a procedure similar to that used for synthesizing **III**.

Indole XX: ^1H NMR (300 MHz, CDCl_3): δ 7.11 (dd, $J_1 = J_2 = 8.1$ Hz, 1 H), 6.88 (d, $J = 8.1$ Hz, 1 H), 6.70 (s, 1H), 6.48 (d, $J = 7.5$ Hz, 1 H), 3.91 (s, 3 H), 3.67 (s, 3 H), 3.10 (t, $J = 7.5$ Hz, 2 H), 2.80 (t, $J = 7.5$ Hz, 2 H), 2.38 (t, $J = 7.5$ Hz, 2 H), 1.57-1.49 (m, 2 H), 1.35-1.22 (m, 2 H), 0.88 (t, $J = 7.5$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 211.7, 154.6, 138.7, 125.1, 122.2, 117.3, 114.2, 102.5, 98.8, 55.0, 44.9, 42.5, 32.5, 25.9, 22.2, 21.2, 13.8; IR (neat): ν 2937, 2922, 1710, 1613, 1582, 1501, 1257, 1100, 730 cm^{-1} ; MS (EI): m/z : 273 (M^+), 188, 174 (100), 144, 131, 77; HRMS: Calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_2$: 273.1729, found 273.1743.

1-Methyl-3-(3'-butylbut-3'-enyl)-4-methoxyindole (**1n**) was isolated in 90 % yield as a colorless oil from **XX** and methyl triphenylphosphonium bromide employing

a procedure similar to that used for synthesizing **1a**. Indole **1n**: ^1H NMR (300 MHz, CDCl_3): δ 7.10 (dd, $J = 8.1, 7.8$ Hz, 1 H), 6.88 (d, $J = 8.1$ Hz, 1 H), 6.70 (s, 1H), 6.47 (d, $J = 7.8$ Hz, 1 H), 4.80 (s, 1 H), 4.75 (s, 1 H), 3.91 (s, 3 H), 3.69 (s, 3 H), 3.00-2.95 (m, 2 H), 2.41-2.36 (m, 2 H), 2.11 (t, $J = 7.5$ Hz, 2 H), 1.50-1.30 (m, 4 H), 0.92 (t, $J = 7.5$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 154.8, 150.6, 138.7, 124.6, 122.1, 117.5, 115.8, 108.4, 102.4, 98.7, 54.9, 38.4, 36.0, 32.5, 30.0, 25.8, 22.5, 14.0; IR (neat): ν 3073, 2930, 1644, 1613, 1583, 1500, 1257, 1095, 727 cm^{-1} ; MS (EI): m/z : 271 (M^+), 174 (100), 144, 131, 103, 77; HRMS: Calcd for $\text{C}_{18}\text{H}_{26}\text{NO}$ ($\text{M}^+ + \text{H}$) 272.2009, found 272.2015.

1-Methyl-3-but-3'-enylindole (**1o**):

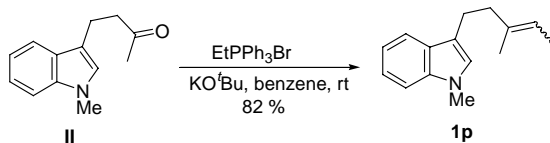


Indole **XXI** was done according to the literature procedure.¹ To a solution of acrolein (9.24 mL, 141 mmol) in 85:15 $\text{CH}_2\text{Cl}_2/i\text{-PrOH}$ (94 mL) at rt was added *N*-methylaniline (0.36 mL, 3.3 mmol) and trifluoroacetic acid (0.25 mL, 3.3 mmol). The resulting solution was cooled to 0 °C, and indole **I** (6.17g, 47 mmol) was added dropwise. The reaction was stirred at 0 °C for 4h, then filtered through a pad of silica gel (5 x 6 cm, eluent: Et_2O), and the filtrate was concentrated in vacuo. Purification by flash chromatography (eluent: petroleum ether/ EtOAc 6:1) provided aldehyde **XXI** (7.04 g, 80 % yield) as a yellow oil. **Aldehyde XXI**: ^1H NMR (300 MHz, CDCl_3): δ 9.83 (t, $J = 1.5$ Hz, 1 H), 7.56 (dd, $J = 7.8, 0.9$ Hz, 1 H), 7.31-7.23 (m, 2 H), 7.41-7.11 (m, 1 H), 6.84 (s, 1 H), 3.73 (s, 3 H), 3.10 (t, $J = 7.2$ Hz, 2 H), 2.86-2.80 (m, 2 H); IR

(neat): ν 3422, 3055, 2917, 2725, 1724, 1616, 1474, 1377, 1326, 742 cm^{-1} ; MS (EI): m/z : 187 (M^+), 144 (100), 131, 115, 109, 77.

At a lower reaction temperature, 1-Methyl-3-but-3'-enylindole (**1o**) was isolated in 78 % yield as a colorless oil from the reaction of **XXI** and methyl triphenylphosphonium bromide employing a procedure similar to that used for synthesizing **1a**. **1-Methyl-3-but-3'-enylindole (1o)**: ^1H NMR (300 MHz, CDCl_3): δ 7.60 (d, $J = 8.1$ Hz, 1 H), 7.30-7.19 (m, 2 H), 7.10 (ddd, $J_1 = J_2 = 7.8$ Hz, $J_3 = 0.9$ Hz, 1 H), 6.84 (s, 1 H), 5.99-5.89 (m, 1 H), 5.12-4.97 (m, 2 H), 3.74 (s, 3 H), 2.84 (t, $J = 7.5$ Hz, 2 H), 2.50-2.42 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3): δ 138.8, 136.9, 127.8, 126.0, 121.3, 118.9, 118.5, 114.6, 114.6, 109.1, 34.5, 32.4, 24.6; IR (neat): ν 3057, 2916, 2848, 1641, 1616, 1555, 1473, 1324, 911, 738 cm^{-1} ; MS (EI): m/z : 185 (M^+), 144 (100), 128, 115, 102, 77; Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{N}$: C, 84.28; H, 8.16; N, 7.56. Found C, 84.33; H, 8.30; N, 7.65.

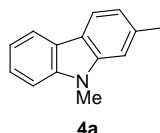
1-Methyl-3-(3'-methylpent-3'-enyl)indole (1p)¹:



The Wittig reaction of **indole II** was done according to the literature procedure.¹ To a flask containing 3.71 g (10 mmol) of ethyl triphenylphosphonium bromide and 1.12 g (10 mmol) of potassium *tert*-butoxide at 0 °C was added 30 mL of benzene. The suspension was stirred for 15 min at 0 °C and 1h at room temperature. The resulting red solution was cooled to 0 °C, **indole II** (1.01 g, 5 mmol) in benzene (20 mL) was added and the solution was heated to 75 °C. After stirring for 6h, the mixture was cooled to 0

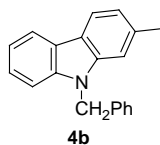
°C, quenched with water/NH₄Cl (20 mL, 1:1), and extracted with ether (3 x 30 mL). The organic layers were combined, washed with brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The resulting oil was purified by flash chromatography (eluent: petroleum ether/EtOAc 20:1) to provide **1p**¹ (0.87 g, 82 % yield) as a colorless oil. **1-Methyl-3-(3'-methylpent-3'-enyl)indole (1p)**: ¹H NMR (300 MHz, CDCl₃): δ 7.63-7.58 (m, 1 H), 7.33-7.19 (m, 2 H), 7.12-7.09 (m, 1 H), 6.85 (s, 0.5 H), 6.83 (s, 0.5 H), 5.33-5.23 (m, 1 H), 3.74 (s, 1.5 H), 3.73 (s, 1.5 H), 2.86-2.78 (m, 2 H), 2.44-2.34 (m, 2 H), 1.78-1.76 (m, 1.5 H), 1.70 (s, 1.5 H), 1.61-1.54 (m, 3 H); IR (neat): ν 3055, 3028, 2917, 1616, 1555, 1473, 738 cm⁻¹; MS (EI): *m/z*: 213 (M⁺), 144 (100), 128, 102, 77.

General Procedure for the Pd-Catalyzed Oxidative Cyclization of 3-(3'-Alkenyl)indoles. A dried schlenk tube was charged with Pd(OAc)₂ (5.6 mg, 0.025 mmol), *p*-benzoquinone (113.5 mg, 1.05 mmol), toluene (2 mL) and HOAc (1 mL) under nitrogen. A solution of substrate (0.5 mmol) in toluene (2 mL) was then added to the mixture, and the solution was stirred and heated at 80 °C for 8 hours. After concentrating the solvent in vacuo, 5 mL of acetone and some 100-mesh silica gel was added to the residue. The acetone was removed in vacuo and the residue was purified by flash chromatography (eluent: petroleum ether/EtOAc 50:1) to provide the product.

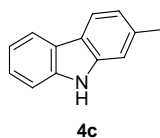


4a: m.p. 86-88 °C (lit.¹⁴ m.p. 88-88.5 °C); ¹H NMR (300 MHz, CDCl₃): δ 8.04 (d, *J* = 7.8 Hz, 1 H), 7.96 (d, *J* = 8.1 Hz, 1 H), 7.46-7.41 (m, 1 H), 7.35 (d, *J* = 8.7 Hz, 1 H),

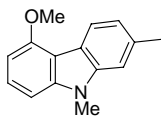
7.23-7.07 (m, 2 H), 7.05 (d, $J = 7.8$ Hz, 1 H), 3.82 (s, 3 H), 2.57 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 141.4, 141.0, 135.8, 125.0, 122.8, 120.4, 120.3, 120.0, 119.9, 118.6, 108.6, 108.2, 28.9, 22.2; IR (KBr): ν 2916, 1630, 1599, 1468, 1321, 1247, 803, 745, 724 cm^{-1} ; MS (EI): m/z : 195 (M^+ , 100), 179, 165, 152, 97, 77.



4b: m.p. 123-125 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3): δ 8.07 (d, $J = 5.1$ Hz, 1 H), 7.99 (d, $J = 7.8$ Hz, 1 H), 7.40-7.05 (m, 10 H), 5.47 (s, 2 H), 2.50 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 141.1, 140.6, 137.2, 136.0, 128.7, 127.3, 126.3, 125.3, 123.1, 120.72, 120.68, 120.04, 120.01, 119.1, 109.0, 108.8, 46.3, 22.2; IR (KBr): ν 3028, 2917, 1629, 1599, 1330, 1171, 807, 725 cm^{-1} ; MS (EI): m/z : 271 (M^+), 220, 194, 180, 91 (100), 77; Anal. Calcd for $\text{C}_{20}\text{H}_{17}\text{N}$: C, 88.52; H, 6.31; N, 5.16. Found: C, 88.56; H, 6.34; N, 5.05.

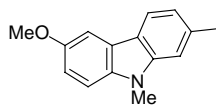


4c: m.p. 254-255 $^{\circ}\text{C}$ (lit.¹⁵ m.p. 258-260 $^{\circ}\text{C}$); ^1H NMR (300 MHz, CDCl_3): δ 10.23 (br s, 1 H), 8.06-8.03 (m, 1 H), 7.97 (d, $J = 7.8$ Hz, 1 H), 7.48-7.45 (m, 1 H), 7.36-7.30 (m, 2 H), 7.17-7.11 (m, 1 H), 7.03-7.00 (m, 1 H), 2.48 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 141.3, 140.8, 136.1, 125.7, 123.9, 121.5, 121.0, 120.4, 120.3, 119.3, 111.6, 111.4, 21.9; IR (KBr): ν 3400, 2914, 1886, 1631, 1608, 1461, 1439, 1327, 808, 727 cm^{-1} ; MS (EI): m/z : 181 (M^+ , 100), 178, 152, 127, 90, 77; Anal. Calcd for $\text{C}_{13}\text{H}_{11}\text{N}$: C, 86.15; H, 6.12; N, 7.73. Found: C, 85.94; H, 6.18; N, 7.57.



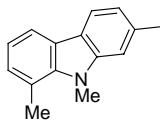
4e

4e: m.p. 128-130 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.19 (d, $J = 8.1$ Hz, 1 H), 7.36 (dd, $J_1 = J_2 = 8.1$ Hz, 1 H), 7.17 (s, 1 H), 7.06 (d, $J = 7.8$ Hz, 1 H), 7.00 (d, $J = 8.4$ Hz, 1 H), 6.67 (d, $J = 8.1$ Hz, 1 H), 4.07 (s, 3 H), 3.80 (s, 3 H), 2.57 (s, 3 H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 155.9, 142.4, 140.6, 134.7, 125.8, 122.6, 120.5, 119.7, 111.8, 108.1, 101.4, 99.9, 55.4, 29.1, 22.2; IR (KBr): ν 3002, 2965, 2839, 1629, 1602, 1465, 1267, 1047, 807, 746, 718 cm^{-1} ; MS (EI): m/z : 225 (M^+ , 100), 210, 182, 167, 152, 140, 112, 77; HRMS: Calcd for $\text{C}_{15}\text{H}_{16}\text{NO}$ ($\text{M}^+ + \text{H}$) 226.1226, found 226.1229.



4f

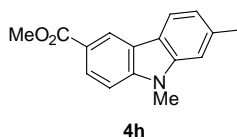
4f: m.p. 94-96 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.91 (d, $J = 7.8$ Hz, 1 H), 7.54 (d, $J = 2.1$ Hz, 1 H), 7.24 (s, 1 H), 7.15 (s, 1 H), 7.07 (dd, $J = 8.7, 2.4$ Hz, 1 H), 7.01 (dd, $J = 7.8, 0.6$ Hz, 1 H), 3.92 (s, 3 H), 3.76 (s, 3 H), 2.55 (s, 3 H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 153.4, 141.9, 136.0, 135.7, 123.1, 120.2, 119.9, 119.8, 114.0, 108.9, 108.7, 103.1, 56.1, 29.0, 22.2; IR (KBr): ν 2993, 2918, 1629, 1610, 1579, 1486, 1206, 805 cm^{-1} ; MS (EI): m/z : 225 (M^+), 210 (100), 182, 167, 139, 113, 91; Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{NO}$: C, 79.97; H, 6.71; N, 6.22. Found: C, 80.11; H, 6.66; N, 6.09.



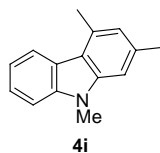
4g

4g: m.p. 98-100 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.94-7.88 (m, 2 H), 7.17-7.03 (m, 4 H), 4.08 (s, 3H), 2.85 (s, 3H), 2.56 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 142.0,

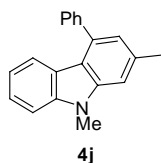
139.6, 135.5, 128.2, 123.5, 120.6, 120.3, 120.2, 119.5, 118.8, 117.8, 108.7, 31.9, 22.2, 20.2; IR (KBr): ν 3017, 2909, 1624, 1593, 1460, 1404, 1236, 808, 783 cm^{-1} ; MS (EI): m/z : 209 (M^+ , 100), 194, 179, 165, 104, 77; Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{N}$: C, 86.08; H, 7.22; N, 6.69. Found: C, 85.79; H, 7.17; N, 6.62.



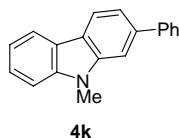
4h: m.p. 129-131 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3): δ 8.77 (dd, $J_1 = J_2 = 0.6$ Hz, 1 H), 8.15 (dd, $J = 8.7, 1.5$ Hz, 1 H), 8.01 (d, $J = 7.8$ Hz, 1 H), 7.36 (d, $J = 8.7$ Hz, 1 H), 7.22 (s, 1 H), 7.12 (d, $J = 7.8$ Hz, 1 H), 3.97 (s, 3 H), 3.84 (s, 3 H), 2.58 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 168.0, 143.5, 141.9, 136.6, 126.7, 122.5, 122.3, 121.3, 120.5, 120.2, 109.0, 107.7, 51.8, 29.1, 22.2; IR (KBr): ν 1862, 1714, 1630, 1600, 1256, 1101, 973, 759 cm^{-1} ; MS (EI): m/z : 253 (M^+ , 100), 222, 194, 179, 152, 111; Anal. Calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_2$: C, 75.87; H, 5.97; N, 5.53; found: C, 75.56; H, 6.03; N, 5.32; HRMS: Calcd for $\text{C}_{16}\text{H}_{16}\text{NO}_2$ ($\text{M}^+ + \text{H}$) 254.1176, found 254.1179.



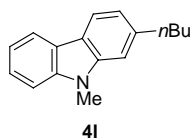
4i: m.p. 129-130 $^{\circ}\text{C}$ (lit.¹⁶ 133-134 $^{\circ}\text{C}$); ^1H NMR (300 MHz, CDCl_3): δ 8.14 (d, $J = 7.5$ Hz, 1 H), 7.44-7.37 (m, 2 H), 7.25-7.22 (m, 1 H), 7.06 (s, 1 H), 6.85 (s, 1 H), 3.80 (s, 3 H), 2.84 (s, 3 H), 2.53 (s, 3 H); IR (KBr): ν 2917, 1623, 1600 cm^{-1} ; MS (EI): m/z : 209 (M^+ , 100), 194.



4j: m.p. 95-97 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.64-7.45 (m, 6 H), 7.38-7.36 (m, 2 H), 7.25-7.21 (m, 1 H), 6.95-6.94 (m, 2 H), 3.86 (s, 3 H), 2.59 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 141.7, 141.3, 141.2, 137.3, 135.6, 129.1, 128.3, 127.4, 125.0, 122.4, 122.1, 121.9, 118.3, 117.9, 108.1, 107.6, 29.0, 22.1; IR (KBr): ν 3041, 3024, 2918, 1621, 1598, 1472, 1321, 1116, 842, 701 cm⁻¹; MS (EI): *m/z*: 271 (M⁺, 100), 255, 194, 127, 120, 77; HRMS: Calcd for C₂₀H₁₈N (M⁺ + H) 272.1434, found 272.1432.

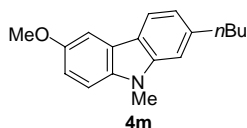


4k: m.p. 140-142 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.12 (dd, *J*₁ = *J*₂ = 8.1 Hz, 2 H), 7.74 (dd, *J* = 8.1, 0.6 Hz, 2 H), 7.59 (s, 1 H), 7.51-7.37 (m, 6 H), 7.27-7.22 (m, 1 H), 3.89 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 142.2, 141.5, 139.2, 128.7, 127.6, 127.0, 125.7, 122.5, 122.0, 120.5, 120.3, 119.0, 118.6, 108.4, 107.0, 29.1; IR (KBr): ν 3051, 2922, 1893, 1627, 1599, 1454, 1324, 1248, 755, 744 cm⁻¹; MS (EI): *m/z*: 257 (M⁺, 100), 228, 164, 128; HRMS: Calcd for C₁₉H₁₆N (M⁺ + H) 258.1277, found 258.1282.

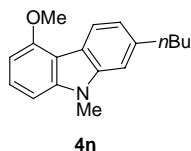


4l: Oil. ¹H NMR (300 MHz, CDCl₃): δ 8.06-8.03 (m, 1 H), 7.98 (d, *J* = 8.1 Hz, 1 H), 7.46-7.34 (m, 2 H), 7.23-7.17 (m, 2 H), 7.07 (dd, *J* = 8.1, 1.5 Hz, 1 H), 3.81 (s, 3 H), 2.82 (t, *J* = 8.1 Hz, 2 H), 1.76-1.66 (m, 2 H), 1.45-1.38 (m, 2 H), 0.96 (t, *J* = 7.5 Hz, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 141.4, 141.1, 141.0, 125.1, 122.8, 120.7, 120.0, 119.8, 118.7, 108.2, 108.0, 36.5, 34.3, 29.0, 22.5, 14.0; IR (neat): ν 2956, 2929, 2858, 1631, 1604, 1469, 1322, 1249, 744, 725 cm⁻¹; MS (EI): *m/z*: 237 (M⁺), 194 (100), 179,

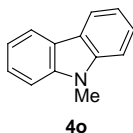
165, 152, 115; HRMS: Calcd for C₁₇H₂₀N (M⁺ + H) 238.1590, found 238.1597.



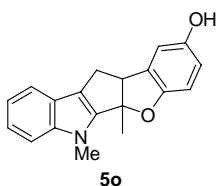
4m: m.p. 59-61 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.93 (d, *J* = 8.1 Hz, 1 H), 7.54 (d, *J* = 2.7 Hz, 1 H), 7.27 (d, *J* = 7.2 Hz, 1 H), 7.16 (s, 1H), 7.08 (dd, *J* = 8.7, 2.7 Hz, 1 H), 7.03 (d, *J* = 8.1 Hz, 1 H), 3.93 (s, 3 H), 3.80 (s, 3 H), 2.81 (t, *J* = 7.8 Hz, 2 H), 1.76-1.66 (m, 2 H), 1.48-1.35 (m, 2 H), 0.96 (t, *J* = 7.5 Hz, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 153.5, 141.9, 141.0, 136.2, 123.1, 120.5, 119.9, 119.3, 114.0, 108.9, 108.0, 103.2, 56.1, 36.5, 34.2, 29.0, 22.5, 14.0; IR (KBr): ν 2956, 2927, 2855, 1630, 1582, 1490, 1209, 1176, 1058, 1028, 805 cm⁻¹; MS (EI): *m/z*: 267 (M⁺, 100), 252, 224, 209, 181, 166, 113, 91; HRMS: Calcd for C₁₈H₂₁NO: 267.1623, found 267.1613.



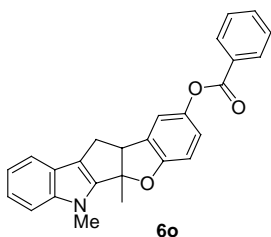
4n: m.p. 98-100 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.20 (d, *J* = 8.1 Hz, 1 H), 7.36 (dd, *J* = 8.4, 7.8 Hz, 1 H), 7.17 (s, 1H), 7.07 (d, *J* = 8.1 Hz, 1 H), 7.00 (d, *J* = 8.1 Hz, 1 H), 6.67 (d, *J* = 8.1 Hz, 1 H), 4.07 (s, 3 H), 3.82 (s, 3 H), 2.81 (t, *J* = 7.8 Hz, 2 H), 1.74-1.66 (m, 2 H), 1.45-1.37 (m, 2 H), 0.95 (t, *J* = 7.5 Hz, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 156.0, 142.5, 140.6, 140.0, 125.8, 122.6, 120.0, 119.99, 111.9, 107.4, 101.4, 99.9, 55.3, 36.5, 34.3, 29.1, 22.5, 14.0; IR (KBr): ν 3070, 3030, 2956, 2931, 1883, 1604, 1582, 1466, 1269, 1103, 1048, 814, 751, 719 cm⁻¹; MS (EI): *m/z*: 267 (M⁺), 224 (100), 209, 194, 181, 166, 113, 77; Anal. Calcd for C₁₈H₂₁NO: C, 80.86; H, 7.92; N, 5.24. Found: C, 80.75; H, 7.77; N, 5.12.



4o: m.p. 88-90 °C (lit.¹⁷ m.p. 86-89 °C); ¹H NMR (300 MHz, CDCl₃): δ 7.09 (d, *J* = 7.8 Hz, 2 H), 7.50-7.20 (m, 6 H), 3.82 (s, 3 H); IR (KBr): ν 2924, 1628, 1598, 1467, 1323, 1247, 745, 720 cm⁻¹; MS (EI): *m/z*: 181 (M⁺, 100), 180, 166, 152, 140, 90, 77.

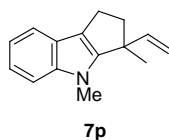


5o: Oil. ¹H NMR (300 MHz, CDCl₃): δ 7.44 (d, *J* = 7.5 Hz, 1 H), 7.29-7.26 (m, 1 H), 7.21-7.16 (m, 1 H), 7.06 (dd, *J*₁ = *J*₂ = 7.5 Hz, 1 H), 6.74 (s, 1 H), 6.56 (s, 2 H), 4.52 (br s, 1 H), 4.20 (d, *J* = 7.2 Hz, 1 H), 4.34 (s, 3 H), 3.99 (dd, *J* = 14.7, 7.5 Hz, 1 H), 3.00 (d, *J* = 14.7 Hz, 1 H), 1.90 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 152.3, 149.7, 143.8, 142.5, 136.7, 123.4, 121.7, 119.5, 119.2, 117.8, 115.0, 111.8, 109.9, 109.7, 92.8, 58.7, 30.8, 30.3, 24.6; IR (neat): ν 3381, 3051, 2970, 2925, 2249, 1702, 1614, 1488, 1469, 1218, 740 cm⁻¹; MS (ESI): *m/z*: 292 (M⁺ + H); HRMS: Calcd for C₁₉H₁₈NO₂ (M⁺ + H) 292.1332, found 292.1325.



Benzoylation of **5o** was done according to the literature procedure.¹⁸ To an ice-cold solution of **5o** (14 mg, 0.05 mmol), triethylamine (13.9 μL, 0.1 mmol) in dichloromethane (3 mL) was added benzoyl chloride (11.6 μL, 0.1 mmol). After being

stirred at room temperature for 1h, 10 mL of water was added and the mixture was extracted with CH₂Cl₂ (3 x 10 mL). The organic layers were combined, washed with brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The resulting oil was purified by TLC (eluent: petroleum ether/EtOAc 5:1) to provide **6o** (16 mg, 83 % yield) as a solid which was recrystallized from ethanol-hexane. **6o**: ¹H NMR (300 MHz, CDCl₃): δ 8.18 (dd, *J* = 8.4, 1.5 Hz, 2 H), 7.63-7.60 (m, 1 H), 7.53-7.43 (m, 3 H), 7.31-7.18 (m, 2 H), 7.11-7.05 (m, 2 H), 6.92 (dd, *J* = 9.6, 2.4 Hz, 1 H), 6.74 (d, *J* = 8.4 Hz, 1 H), 4.29 (d, *J* = 7.5 Hz, 1 H), 3.86 (s, 3 H), 3.42 (dd, *J* = 14.7, 7.2 Hz, 1 H), 3.05 (dd, *J* = 14.7, 1.2 Hz, 1 H), 1.94 (s, 3 H); IR (neat): ν 2921, 2858, 1736, 1601, 1479, 1379, 1211, 1056, 1025, 708 cm⁻¹; MS (EI): *m/z*: 395 (M⁺, 100), 380, 290, 218, 168, 105; HRMS: Calcd for C₂₆H₂₁NO₃Na (M⁺ + Na) 418.1414, found 418.1404. Deposit number of **6o** from Crystallographic Data Centre: CCDC 277361.



7p¹: Oil. ¹H NMR (300 MHz, CDCl₃): δ 7.47-7.44 (m, 1 H), 7.26-7.23 (m, 1 H), 7.17-7.12 (m, 1 H), 7.10-7.05 (m, 1 H), 6.08 (dd, *J* = 17.4, 10.2 Hz, 1 H), 5.07-4.94 (m, 2 H), 3.63 (s, 3 H), 2.82 (t, *J* = 6.9 Hz, 2 H), 2.55-2.47 (m, 1 H), 2.39-2.30 (m, 1 H), 1.48 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 148.7, 145.1, 141.6, 123.9, 120.2, 118.9, 118.7, 117.3, 111.8, 109.3, 46.2, 46.0, 30.0, 23.7, 22.5; IR (neat): ν 3082, 3054, 2932, 2856, 1635, 1614, 1562, 1466, 1376, 738 cm⁻¹; MS (EI): *m/z*: 211 (M⁺), 196 (100), 181, 168, 128, 152, 97, 77.

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