Synthesis of Indoles via 6 π -Electrocyclic Ring Closures of Enecarbamates

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Buta-1,3-dienyl-[2-(trimethylsilyl)ethoxymethyl]carbamic acid *tert*-butyl ester. To a suspension of sodium hydride (426 mg, 10.7 mmol) in THF (48 mL) at 0 °C was added buta-1,3-dienylcarbamic acid *tert*-butyl ester (1.64 g, 9.69 mmol) in THF (5 mL) dropwise over 5 min. The mixture was stirred at 0 °C for 20 min. To the resulting solution was added SEMCl (1.80 mL, 10.2 mmol). The solution was warmed to rt and stirred 2 h. The mixture was quenched with saturated aqueous NH₄Cl and extracted with ether. The combined extracts were dried (Na₂SO₄) and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 20) provided the carbamate as a colorless oil (2.70 g, 93%); ¹H NMR (200 MHz, CDCl₃) δ 0.02 (s, 9 H), 0.94 (ddd, J = 2.7, 7.2, 8.2 Hz, 2 H), 1.51 (s, 9 H), 3.56 (ddd, J = 2.7, 7.2, 8.2 Hz, 2 H), 4.93 (dd, J = 1.7, 10.2 Hz, 1 H), 5.03 (s, 2 H), 5.09 (dd, J = 1.7, 16.9 Hz, 1 H), 5.91 (dd, J = 10.6, 14.3 Hz, 1 H), 6.31 (dt, J = 10.4, 16.9 Hz, 1 H), 7.02 (m, 1 H); ¹³C NMR (50 MHz, CDCl₃) δ -1.5, 17.8, 28.1, 65.3, 74.2, 81.7, 112.3, 113.3, 130.4, 135.4, 152.6; IR (neat)

2954, 1715, 1645 cm^{-1} ; HRMS (MH^+) calcd for $\text{C}_{15}\text{H}_{30}\text{NO}_3\text{Si}$ 300.1990, found 300.2002.

1-(Tributylstannyl)buta-1,3-dienyl-[2-(trimethylsilyl)ethoxymethyl]carbamic acid *tert*-butyl ester. To a solution of the enecarbamate (2.70 g, 9.01 mmol) in THF (90 mL) at $-78\text{ }^{\circ}\text{C}$ was added TMEDA (1.36 mL, 9.01 mmol) followed by *n*-BuLi (2.5 M in hexane, 4.33 mL, 10.8 mmol) dropwise over 10 min. The mixture was warmed to $-60\text{ }^{\circ}\text{C}$ and stirred for 1 h. To the resulting solution was added Bu_3SnCl (3.06 mL, 11.3 mmol). The solution was warmed to $0\text{ }^{\circ}\text{C}$ over 2 h. The mixture was quenched with brine and extracted with hexanes. The combined extracts were dried (Na_2SO_4) and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 3 : 97) afforded the stannane (mixture of amide rotamers) as a colorless oil (3.98 g, 75%); ^1H NMR (200 MHz, CDCl_3) δ 0.02 (s, 9 H), 0.88 (t, $J = 7.3\text{ Hz}$, 9 H), 0.94 (m, 8 H), 1.25 – 1.71 (m, 12 H), 1.47 (s, 9 H), 3.58 (br t, $J = 8.3\text{ Hz}$, 2 H), 4.88 (s, 2 H), 5.03 – 5.27 (m, 2 H), 6.37 (m, 1 H), 6.83 (br d, $J = 10.7\text{ Hz}$, 1 H), ^{13}C NMR (50 MHz, CDCl_3 , amide rotamers) δ -1.4, 12.4, 13.5 (minor), 13.6 (major), 17.4 (major), 18.2 (minor), 26.1 (minor), 26.8 (major), 27.3 (minor), 27.9 (major), 29.1, 65.5, 78.8, 80.6, 116.6, 133.1, 136.1, 153.1, 154.2; IR (neat) 2955, 1689, 1619 cm^{-1} ; HRMS (MH^+) calcd for $\text{C}_{27}\text{H}_{56}\text{NO}_3\text{SiSn}$ 590.3046, found 590.3068.

1-(Tributylstannyl)buta-1,3-dienylcarbamic acid *tert*-butyl ester (1). To a solution of the stannane (3.00 g, 5.10 mmol) in acetone (50 mL) at 0 °C was added 48% aqueous HF (5 mL) dropwise. The resulting solution was stirred at 0 °C for 45 min. The mixture was quenched with saturated aqueous NaHCO₃ and extracted with ether. The combined extracts were dried (Na₂SO₄) and concentrated to afford the crude N-hydroxymethyl amide. The N-hydroxymethyl amide was then dissolved in MeOH (50 mL) and concentrated aqueous NH₄OH (15 mL) was added. The mixture was stirred at rt for 30 min. The solution was quenched with saturated aqueous NH₄Cl and extracted with ether. The combined extracts were dried (Na₂SO₄) and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 3 : 97) afforded carbamate **1** as a colorless oil (1.61 g, 69%); ¹H NMR (200 MHz, CDCl₃) δ 0.89 (t, *J* = 7.1 Hz, 9 H), 1.01 (br t, *J* = 8.1 Hz, 6 H), 1.32 (hextet, *J* = 7.1 Hz, 6 H), 1.45 (s, 9 H), 1.40 – 1.60 (m, 6 H), 4.91 (d, *J* = 9.5 Hz, 1 H), 5.02 (d, *J* = 16.9 Hz, 1 H), 6.25 – 6.50 (m, 2 H), 6.33 (s, 1 H); ¹³C NMR (50 MHz, CDCl₃) δ 13.1, 13.7, 27.3, 28.2, 29.0, 80.0, 114.0, 126.1, 135.9, 145.4, 153.9; IR (neat) 3304, 2956, 1712, 1617 cm⁻¹; HRMS (MH⁺) calcd for C₂₁H₄₂NO₂Sn 460.2232, found 460.2228.

1-(6-Oxocyclohex-1-enyl)buta-1,3-dienylcarbamic acid *tert*-butyl ester (2). To a solution of 2-iodocyclohex-2-enone (346 mg, 1.56 mmol) and stannane **1** (650 mg, 1.42 mmol) in THF (14 mL) was added CuI (67.5 mg, 0.35 mmol) and Pd(PPh₃)₄ (49.2 mg, 0.043 mmol). The mixture was stirred at 50 °C for 3 h. The solution was filtered through a plug of silica-gel, washed with ether, and concentrated. Purification by silica-gel chromatography (ether-CH₂Cl₂, 3 : 97) provided triene **2** as a colorless oil (301 mg, 81%); ¹H NMR (300 MHz, CDCl₃) δ 1.42 (s, 9 H), 2.07 (p, *J* = 6.3 Hz, 2 H), 2.45 – 2.56 (m, 4 H), 4.91 (dd, *J* = 1.6, 10.1 Hz, 1 H), 5.15 (dd, *J* = 1.6, 16.7 Hz, 1 H), 6.22 (s, 1 H), 6.25 (ddd, *J* = 10.1, 11.0, 16.7 Hz, 1 H), 6.46 (d, *J* = 11.0 Hz, 1 H), 6.98 (t, *J* = 4.2 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 22.5, 26.1, 28.2, 38.4, 80.2, 115.4, 117.0, 132.7, 133.4, 135.0, 151.6, 152.4, 197.8; IR (neat) 3325, 2977, 1732, 1710 cm⁻¹; HRMS (MH⁺) calcd for C₁₅H₂₂NO₃ 264.1594, found 264.1586.

8-Oxo-5,6,7,8-tetrahydronaphthalen-1-ylcarbamic acid *tert*-butyl ester (4). A solution of triene **2** (301 mg, 1.14 mmol) in toluene (23 mL) was heated at reflux for 1 h. The resulting solution was cooled to rt and DDQ (311 mg, 1.37 mmol) was added. The

mixture was stirred at 50 °C for 6 h. The solution was quenched with saturated aqueous NaHCO₃ and extracted with ether. The combined extracts were washed with saturated aqueous NaHCO₃, dried (Na₂SO₄), and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 9) provided the protected aniline **4** as a white solid: mp 84 – 86 °C (271 mg, 91%); ¹H NMR (300 MHz, CDCl₃) δ 1.52 (s, 9 H), 2.06 (p, *J* = 6.3 Hz, 2 H), 2.67 (t, *J* = 6.3 Hz, 2 H), 2.95 (t, *J* = 6.3 Hz, 2 H), 6.83 (dd, *J* = 1.0, 7.6 Hz, 1 H), 7.40 (dd, *J* = 7.6, 8.4 Hz, 1 H), 8.31 (dd, *J* = 1.0, 8.4 Hz, 1 H), 11.40 (s, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 22.7, 28.3, 31.0, 40.7, 80.3, 116.6, 118.0, 121.5, 134.8, 142.8, 145.9, 153.2, 202.7; IR (neat) 3213, 2976, 1727, 1650 cm⁻¹; HRMS (MH⁺) calcd for C₁₅H₂₀NO₃ 262.1438, found 262.1453.

8-Amino-3,4-dihydro-2 *H*-naphthalen-1-one. To a solution of carbamate **4** (250 mg, 0.96 mmol) in CH₂Cl₂ (9.6 mL) at –50 °C was added TFA (147 μL, 1.91 mmol). The solution was warmed to rt over 30 min and stirred for 3 h. The mixture was quenched with saturated aqueous NaHCO₃ and extracted with CH₂Cl₂. The combined extracts were dried (Na₂SO₄) and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 9) provided a white solid: mp 77 – 79 °C (145 mg, 94%); ¹H NMR (360 MHz, CDCl₃) δ 2.02 (p, *J* = 6.3 Hz, 2 H), 2.61 (t, *J* = 6.3 Hz, 2 H),

2.86 (t, $J = 6.3$ Hz, 2 H), 6.44 (d, $J = 7.3$ Hz, 1 H), 6.45 (br s, 2 H), 6.47 (d, $J = 8.3$ Hz, 1 H), 7.14 (dd, $J = 7.3, 8.3$ Hz, 1 H); ^{13}C NMR (90 MHz, CDCl_3) δ 22.9, 30.9, 40.3, 114.5, 115.4, 115.8, 134.2, 145.9, 151.1, 201.2; IR (neat) 3436, 3326, 2940, 1638, 1606 cm^{-1} ; HRMS (MH^+) calcd for $\text{C}_{10}\text{H}_{12}\text{NO}$ 162.0913, found 162.0903.

1-(4,5-Dihydro-3H-benzo[cd]indol-1-yl)ethanone (6). To a solution of the aniline (56.7 mg, 0.35 mmol) in MeOH (4 mL) at 0 °C was added NaOAc (57.7 mg, 0.70 mmol), glacial acetic acid (80.5 μL , 1.41 mmol), glyoxylic acid monohydrate (48.6 mg, 0.53 mmol), and NaCNBH_3 (24.3 mg, 0.39 mmol). The solution was warmed slowly to rt over 1 h. The mixture was then filtered through a plug of silica gel and washed with 1% glacial acetic acid in ethyl acetate. The solution was then washed with brine, dried (Na_2SO_4), and concentrated to afford the crude carboxylic acid 5, which was used without further purification. ^1H NMR (300 MHz, d^6 -Acetone) δ 1.99 (p, $J = 6.2$ Hz, 2 H), 2.57 (t, $J = 6.2$ Hz, 2 H), 2.87 (t, $J = 6.2$ Hz, 2 H), 4.07 (d, $J = 5.1$ Hz, 2 H), 6.47 (d, $J = 7.4$ Hz, 1 H), 6.49 (d, $J = 8.4$ Hz, 1 H), 7.26 (dd, $J = 7.4, 8.4$ Hz, 1 H), 9.56 (br s, 1 H). To the crude carboxylic acid 5 was added a solution of acetic anhydride (3.5 mL) and Et_3N (490 μL , 3.52 mmol). The mixture was heated to reflux for 30 min. The resulting solution was concentrated *in vacuo*. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 :

9) afforded the N-acetylindole **6** (mixture of amide rotamers) as a colorless oil (54.2 mg, 77%); ^1H NMR (400 MHz, CDCl_3) δ 2.04 (pentet, $J = 6.1$ Hz, 2 H), 2.60 (s, 3 H), 2.80 (t, $J = 6.1$ Hz, 2 H), 2.90 (t, $J = 6.1$, 2 H), 7.02 (d, $J = 7.3$ Hz, 1 H), 7.06 (br s, 1 H), 7.26 (t, $J = 7.3$ Hz, 1 H), 8.06 (br s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 21.7, 23.8, 24.0, 27.0, 114.0, 118.0, 120.2, 120.8, 125.6, 129.5, 132.3, 133.9, 168.5; IR (neat) 2930, 1697, 1642 cm^{-1} ; HRMS (MH^+) calcd for $\text{C}_{13}\text{H}_{14}\text{NO}$ 200.1069, found 200.1064. The N-acetyl group was then removed to obtain cleaner spectra without broadening due to amide rotamers. Treatment of the N-acetylindole **6** with K_2CO_3 (75.2 mg, 0.54) in MeOH (3 mL) at rt for 1 h, upon workup, afforded the corresponding deprotected indole in quantitative yield as a white solid: mp 46 – 48 $^\circ\text{C}$ (42.7 mg, quantitative); ^1H NMR (360 MHz, CDCl_3) δ 2.07 (p, $J = 6.2$ Hz, 2 H), 2.87 (t, $J = 6.2$ Hz, 2 H), 2.95 (t, $J = 6.2$ Hz, 2 H), 6.84 (d, $J = 6.8$ Hz, 1 H), 6.85 (s, 1 H), 7.11 (dd, $J = 6.8$, 8.1 Hz, 1 H), 7.16 (d, $J = 8.1$ Hz, 1 H), 7.79 (br s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 21.9, 24.6, 27.5, 108.0, 113.9, 115.8, 117.1, 122.6, 127.2, 132.3, 133.9; IR (neat) 3410, 2924 cm^{-1} ; HRMS (MH^+) calcd for $\text{C}_{11}\text{H}_{12}\text{N}$ 158.0964, found 158.0949.

1-(8-Oxocyclooct-1-enyl)buta-1,3-dienylcarbamic acid *tert*-butyl ester (7). To a solution of 2-bromocyclooct-2-enone (160 mg, 0.79 mmol) and stannane **1** (300 mg, 0.65 mmol) in THF (7 mL)

was added CuI (31.2 mg, 0.16 mmol) and Pd(PPh₃)₄ (37.8 mg, 0.033 mmol). The mixture was stirred at reflux for 3 h. The solution was filtered through a plug of silica-gel, washed with ether, and concentrated. Purification by silica-gel chromatography (ether-CH₂Cl₂, 1 : 99) provided triene **7** as a colorless oil (166 mg, 87%); ¹H NMR (400 MHz, CDCl₃) δ 1.44 (s, 9 H), 1.66 (br pentet, *J* = 2.9 Hz, 4 H), 1.98 (m, 2 H), 2.38 (m, 2 H), 2.55 (m, 2 H), 4.94 (dd, *J* = 1.9, 10.1 Hz, 1 H), 5.18 (dd, *J* = 1.9, 16.8 Hz, 1 H), 6.15 (t, *J* = 5.1 Hz, 1 H), 6.53 (ddd, *J* = 10.1 11.0, 16.8 Hz, 1 H), 6.55 (s, 1 H), 6.75 (d, *J* = 11.0 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 21.9, 22.2, 28.0, 28.6, 29.8, 43.7, 80.3, 115.1, 115.3, 133.2, 133.3, 134.8, 140.4, 152.5, 210.3; IR (neat) 3354, 2931, 1721 cm⁻¹.

10-Oxo-5,6,7,8,9,10-hexahydrobenzocycloocten-1-yl)carbamic acid *tert*-butyl ester (8). A solution of triene **7** (109 mg, 0.37 mmol) in toluene (7.4 mL) was heated at reflux for 2 h. The resulting solution was cooled to rt and DDQ (101 mg, 0.45 mmol) was added. The mixture was stirred at 70 °C for 3 h. The solution was quenched with saturated aqueous NaHCO₃ and extracted with ether. The combined extracts were washed with saturated aqueous NaHCO₃, dried (Na₂SO₄), and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 9) provided the protected aniline **8** as a colorless oil (93.9 mg,

87%); ^1H NMR (200 MHz, CDCl_3) δ 1.48 (s, 9 H), 1.61 (m, 2 H), 1.78 (m, 4 H), 2.79 (m, 4 H), 6.88 (d, $J = 7.7$ Hz, 1 H), 7.29 (t, $J = 8.0$ Hz, 1 H), 7.62 (s, 1 H), 7.86 (d, $J = 8.2$ Hz, 1 H); ^{13}C NMR (50 MHz, CDCl_3) δ 23.5, 27.3, 28.3, 28.5, 33.6, 46.7, 80.5, 119.4, 125.0, 130.0, 130.7, 134.8, 140.3, 153.1, 212.2; IR (neat) 3307, 2931, 1730, 1690 cm^{-1} ; HRMS (MH^+) calcd for $\text{C}_{17}\text{H}_{24}\text{NO}_3$ 290.1751, found 290.1773.

4-Amino-7,8,9,10-tetrahydro-6H-benzocycloocten-5-one. To a solution of carbamate **8** (64.6 mg, 0.22 mmol) in CH_2Cl_2 (4 mL) at -50 $^\circ\text{C}$ was added TFA (86 μL , 1.12 mmol). The solution was warmed to rt over 30 min and stirred for 3 h. The mixture was quenched with saturated aqueous NaHCO_3 and extracted with CH_2Cl_2 . The combined extracts were dried (Na_2SO_4) and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 4) provided a colorless oil (40.8 mg, 97%); ^1H NMR (200 MHz, CDCl_3) δ 1.48 – 1.61 (m, 2 H), 1.69 – 1.90 (m, 4 H), 2.92 (t, $J = 6.8$ Hz, 2 H), 2.95 (t, $J = 6.1$ Hz, 2 H), 5.20 (br s, 2 H), 6.51 (d, $J = 7.5$ Hz, 1 H), 6.55 (d, $J = 7.5$ Hz, 1 H), 7.10 (t, $J = 7.5$ Hz, 1 H); ^{13}C NMR (50 MHz, CDCl_3) δ 24.2, 25.4, 28.4, 35.0, 45.3, 115.3, 120.1, 123.7, 131.8, 142.3, 147.2, 209.7; IR (neat) 3448, 3342, 2926, 1678, 1604 cm^{-1} ; HRMS (MH^+) calcd for $\text{C}_{12}\text{H}_{16}\text{NO}$ 190.1226, found 190.1217.

1-(7,8,9,10-Tetrahydro-6H-2-aza-cycloocta[cd]inden-2-yl)-ethanone (9). To a solution of the aniline (21.2 mg, 0.11 mmol) in MeOH (2 mL) at 0 °C was added NaOAc (18.4 mg, 0.22 mmol), glacial acetic acid (26 μ L, 0.45 mmol), glyoxylic acid monohydrate (25.8 mg, 0.28 mmol), and NaCNBH₃ (7.7 mg, 0.12 mmol). The solution was warmed slowly to rt over 1 h. The mixture was then filtered through a plug of silica gel and washed with 1% glacial acetic acid in ethyl acetate. The solution was then washed with brine, dried (Na₂SO₄), and concentrated to afford the crude carboxylic acid, which was used without further purification. To the crude carboxylic acid was added a solution of acetic anhydride (1.1 mL) and Et₃N (156 μ L, 1.12 mmol). The mixture was heated to reflux for 30 min. The resulting solution was concentrated *in vacuo*. Purification by silica-gel chromatography (ethyl acetate-hexane, 3 : 17) afforded the N-acetylindole **9** (mixture of amide rotamers) as a colorless oil (19.2 mg, 75%); ¹H NMR (300 MHz, CDCl₃) δ 1.36 – 1.46 (m, 2 H), 1.77 – 1.88 (m, 4 H), 2.60 (s, 3 H), 3.00 (t, *J* = 7.1 Hz, 2 H), 3.14 (t, *J* = 6.9 Hz, 2 H), 6.97 (d, *J* = 7.3 Hz, 1 H), 7.11 (s, 1 H), 7.24 (dd, *J* = 7.3, 8.3 Hz, 1 H), 8.30 (d, *J* = 8.3 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 22.6, 24.1, 25.4, 29.1, 29.5, 32.3, 114.6, 121.7, 123.3, 124.4, 125.4, 131.6, 134.5, 135.6, 168.3; IR (neat) 2929, 1704 cm⁻¹; HRMS (MH⁺) calcd for C₁₅H₁₈NO 228.1388, found 228.1391.

1-(5-Oxo-8,9-dihydro-5*H*-benzocyclohepten-6-yl)buta-1,3-dienylcarbamate *tert*-butyl ester (10). To a solution of the above iodide (186 mg, 0.65 mmol) and stannane **1** (300 mg, 0.65 mmol) in DMF (8 mL) was added CuI (31.2 mg, 0.16 mmol) and Pd(PPh₃)₄ (37.8 mg, 0.033 mmol). The mixture was stirred at rt for 30 min. The solution was quenched with water and extracted with ether. The combined extracts were washed with water, dried (Na₂SO₄), and concentrated. Purification by silica-gel chromatography (ether-CH₂Cl₂, 1 : 99) provided triene **10** as a colorless oil (185 mg, 87%); ¹H NMR 400 MHz, CDCl₃) δ 1.41 (s, 9 H), 2.69 (m, 2 H), 3.04 (br t, *J* = 6.0 Hz, 2 H), 4.89 (dd, *J* = 1.8, 9.9 Hz, 1 H), 5.13 (dd, *J* = 1.8, 16.4 Hz, 1 H), 6.30 (dt, *J* = 10.4, 16.4 Hz, 1 H), 6.33 (s, 1 H), 6.39 (d, *J* = 11.0 Hz, 1 H), 6.78 (t, *J* = 5.0 Hz, 1 H), 7.16 (d, *J* = 7.5 Hz, 1 H), 7.27 (dt, *J* = 1.2, 7.7 Hz, 1 H), 7.38 (dt, *J* = 1.2, 7.5 Hz, 1 H), 7.59 (dd, *J* = 1.2, 7.7 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 28.1, 30.2, 33.4, 80.0, 115.0, 116.4, 126.5, 126.7, 128.1, 129.4, 131.8, 132.9, 136.8, 138.6, 140.9, 148.3, 152.3, 194.8; IR (neat) 3328, 2976, 1722, 1643 cm⁻¹; HRMS (MH⁺) calcd for C₂₀H₂₄NO₃ 326.1751, found 326.1768.

5-Oxo-10,11-dihydro-5*H*-dibenzo[*a,d*]cyclohepten-4-ylcarbamic acid *tert*-butyl ester (11). A solution of triene **10** (164 mg, 0.50 mmol) in toluene (10 mL) was heated at reflux for 2 h. The resulting solution was cooled to rt and DDQ (137 mg, 0.60 mmol) was added. The mixture was stirred at 70 °C for 3 h. The solution was quenched with saturated aqueous NaHCO₃ and extracted with ether. The combined extracts were washed with saturated aqueous NaHCO₃, dried (Na₂SO₄), and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 9) provided the protected aniline **11** as a colorless oil (151 mg, 93%); ¹H NMR (300 MHz, CDCl₃) δ 1.51 (s, 9 H), 3.08 (m, 2 H), 3.23 (m, 2 H), 6.89 (d, *J* = 7.5 Hz, 1 H), 7.20 (d, *J* = 7.5 Hz, 1 H), 7.29 – 7.38 (m, 2 H), 7.44 (dt, *J* = 1.5, 7.5 Hz, 1 H), 8.05 (d, *J* = 8.4 Hz, 1 H), 8.09 (dd, *J* = 1.5, 7.9 Hz, 1 H), 8.63 (s, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 28.2, 34.0, 35.2, 80.4, 119.1, 122.2, 126.3, 128.9, 130.3, 131.2, 131.9, 132.7, 137.5, 138.0, 140.5, 142.3, 153.0, 198.5; IR (neat) 3381, 2978, 1729, 1638 cm⁻¹; HRMS (MH⁺) calcd for C₂₀H₂₂NO₃ 324.1594, found 324.1619.

4-Amino-10,11-dihydro-dibenzo[*a,d*]cyclohepten-5-one. To a solution of carbamate **11** (119 mg, 0.37 mmol) in CH₂Cl₂ (8 mL) at -50 °C was added TFA (141 μL, 1.84 mmol). The solution was warmed to rt over 30 min and stirred for 3 h. The mixture was quenched with saturated aqueous NaHCO₃ and extracted with CH₂Cl₂. The combined extracts were dried (Na₂SO₄) and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 3 : 20) provided a colorless oil (77.9 mg, 95%); ¹H NMR (400 MHz, CDCl₃) δ 3.09 (m, 2 H), 3.19 (m, 2 H), 5.51 (s, 2 H), 6.52 (d, *J* = 7.3 Hz, 1 H), 6.57 (d, *J* = 8.2 Hz, 1 H), 7.12 (dd, *J* = 7.3, 8.2 Hz, 1 H), 7.18 (d, *J* = 7.6 Hz, 1 H), 7.31 (dt, *J* = 1.2, 7.6 Hz, 1 H), 7.40 (dt, *J* = 1.5, 7.6 Hz, 1 H), 8.05 (dd, *J* = 1.5, 7.6 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 35.0, 35.3, 115.4, 117.5, 122.6, 126.2, 129.2, 131.0, 131.9, 132.4, 139.4, 141.7, 142.7, 148.9, 197.5; IR (neat) 3472, 3366, 2931, 1607 cm⁻¹; HRMS (MH⁺) calcd for C₁₅H₁₄NO 224.1070, found 224.1076.

1-(6,7-Dihydro-2-aza-dibenzo[*cd,h*]azulen-2-yl)ethanone (12). To a solution of the aniline (50.5 mg, 0.23 mmol) in MeOH (4

mL) at 0 °C was added NaOAc (37.1 mg, 0.45 mmol), glacial acetic acid (51.8 μ L, 0.90 mmol), glyoxylic acid monohydrate (52.0 mg, 0.57 mmol), and NaCNBH₃ (15.6 mg, 0.25 mmol). The solution was warmed slowly to rt over 1 h. The mixture was then filtered through a plug of silica gel and washed with 1% glacial acetic acid in ethyl acetate. The solution was then washed with brine, dried (Na₂SO₄), and concentrated to afford the crude carboxylic acid, which was used without further purification. To the crude carboxylic acid was added a solution of acetic anhydride (2.3 mL) and Et₃N (315 μ L, 2.26 mmol). The mixture was heated to reflux for 30 min. The resulting solution was concentrated *in vacuo*. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 9) afforded the N-acetylindole **12** (mixture of amide rotamers) as a white solid: mp 144 – 147 °C (49.6 mg, 84%); ¹H NMR (400 MHz, CDCl₃) δ 2.72 (s, 3 H), 3.16 (m, 2 H), 3.22 (m, 2 H), 7.08 (d, *J* = 7.4 Hz, 1 H), 7.22 – 7.32 (m, 4 H), 7.69 (d, *J* = 7.7 Hz, 1 H), 7.70 (s, 1 H), 8.35 (d, *J* = 8.2 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 24.2, 34.1, 36.4, 114.3, 120.8, 123.2, 123.5, 125.0, 126.6, 126.9, 127.3, 127.4, 130.4, 132.5, 136.3, 137.0, 141.2, 168.5; IR (neat) 2928, 1703 cm⁻¹; HRMS (MH⁺) calcd for C₁₈H₁₆NO 262.1226, found 262.1225.

Penta-1,3-dienylcarbamic acid *tert*-butyl ester. To a solution of sorbic acid (10.0 g, 89.2 mmol) in acetone (45 mL) was added *i*-Pr₂NEt (19.4 mL, 111 mmol). The solution was cooled to 0 °C and

ethyl chloroformate (8.70 mL, 91.0 mmol) in acetone (25 mL) was added over 5 min. The mixture was stirred at 0 °C for 30 min. To the resulting solution at 0 °C was added NaN₃ (11.6 g, 178 mmol) in H₂O (25 mL) dropwise over 5 min. The solution was stirred at 0 °C for 30 min. The resulting mixture was quenched with H₂O and extracted with toluene. The combined extracts were dried (Na₂SO₄) and concentrated to approximately 80 mL of toluene containing the acyl azide. To a solution of *t*-BuOH (25.6 mL, 268 mmol) and BHT (79 mg, 0.36 mmol) in toluene (45 mL) at 110 °C was added the crude acyl azide solution dropwise over 20 min. The resulting solution was refluxed for 3 h, cooled to rt, and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 9) afforded a yellow solid: mp 57 – 59 °C (12.3 g, 75%); ¹H NMR (200 MHz, CDCl₃) δ 1.46 (s, 9 H), 1.72 (dd, *J* = 1.3, 6.7 Hz, 3 H), 5.35 – 5.65 (m, 2 H), 5.95 (ddd, *J* = 1.3, 10.5, 15.1 Hz, 1 H), 6.21 (m, 1 H), 6.58 (br t, *J* = 12.8 Hz, 1 H); ¹³C NMR (50 MHz, CDCl₃) δ 18.0, 28.1, 80.3, 110.7, 124.7, 125.4, 128.8, 152.7; IR (neat) 3351, 2975, 1691, 1662, 1638 cm⁻¹; HRMS (MH⁺) calcd for C₁₀H₁₈NO₂ 184.1332, found 184.1347.

Penta-1,3-dienyl-[2-(trimethylsilyl)ethoxymethyl]carbamic acid *tert*-butyl ester. To a suspension of sodium hydride (720 mg, 18.0 mmol) in THF (82 mL) at 0 °C was added penta-1,3-dienylcarbamic acid *tert*-butyl ester (3.00 g, 16.4 mmol) in THF (10

mL) dropwise over 5 min. The mixture was stirred at 0 °C for 20 min. To the resulting solution was added SEMCl (3.19 mL, 18.0 mmol). The solution was warmed to rt and stirred 2 h. The mixture was quenched with saturated aqueous NH₄Cl and extracted with ether. The combined extracts were dried (Na₂SO₄) and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 20) provided a colorless oil (4.79 g, 93%); ¹H NMR (200 MHz, CDCl₃) δ 0.00 (s, 9 H), 0.93 (t, *J* = 8.3 Hz, 2 H), 1.50 (s, 9 H), 1.74 (d, *J* = 6.6 Hz, 3 H), 3.54 (t, *J* = 8.3 Hz, 2 H), 5.01 (s, 2 H), 5.56 (m, 1 H), 5.80 – 6.08 (m, 2 H), 6.91 (m, 1 H); ¹³C NMR (50 MHz, CDCl₃) δ -1.5, 17.8, 18.0, 28.0, 65.1, 74.2, 81.3, 112.0, 125.4, 127.7, 129.5, 152.7; IR (neat) 2954, 1713, 1657, 1626 cm⁻¹; HRMS (MH⁺) calcd for C₁₆H₃₂NO₃Si 314.2146, found 314.2160.

1-(Tributylstannyl)penta-1,3-dienyl-[2-(trimethylsilyl)ethoxymethyl]carbamic acid *tert*-butyl ester. To a solution of the enecarbamate (3.20 g, 10.2 mmol) in THF (100 mL) at -78 °C was added TMEDA (1.54 mL, 10.2 mmol) followed by *n*-BuLi (2.5 M in hexane, 5.72 mL, 14.3 mmol) dropwise over 10 min. The mixture was warmed to -60 °C and stirred for 1 h. To the resulting solution was added Bu₃SnCl (4.15 mL, 15.3 mmol). The solution was warmed to 0 °C over 2 h. The mixture was quenched with brine and extracted with hexanes. The combined extracts were dried (Na₂SO₄) and concentrated. Purification by

silica-gel chromatography (ethyl acetate-hexane, 3 : 97) afforded the stannane (mixture of amide rotamers) as a colorless oil (4.69 g, 76%); ^1H NMR (200 MHz, CDCl_3) δ 0.01 (s, 9 H), 0.90 (t, $J = 7.3$ Hz, 9 H), 0.91 – 1.00 (m, 8 H), 1.31 (hextet, $J = 7.3$ Hz, 6 H), 1.48 (s, 9 H), 1.52 (m, 6 H), 1.77 (d, $J = 6.1$ Hz, 3 H), 3.57 (t, $J = 8.5$ Hz, 2 H), 4.85 (br s, 2 H), 5.65 (m, 1 H), 6.03 (m, 1 H), 6.79 (br, d, $J = 11.1$ Hz, 1 H); ^{13}C NMR (50 MHz, CDCl_3 , amide rotamers) δ -1.4, 12.2 (minor), 13.6 (major), 18.2 (minor), 18.3 (major), 27.3, 28.3, 28.9, 32.0, 35.5, 65.4 (major), 67.1 (minor), 78.9, 80.3, 128.9, 130.5, 133.4, 149.4, 154.2; IR (neat) 2955, 1688 cm^{-1} ; HRMS (MH^+) calcd for $\text{C}_{28}\text{H}_{58}\text{NO}_3\text{SiSn}$ 604.3203, found 604.3180.

1-(Tributylstannyl)penta-1,3-dienylcarbamic acid *tert*-butyl ester. To a solution of the stannane (6.00 g, 9.96 mmol) in acetone (200 mL) at 0 °C was added 48% aqueous HF (19.9 mL) dropwise. The resulting solution was stirred at 0 °C for 1 h. The mixture was quenched with saturated aqueous NaHCO_3 and extracted with ether. The combined extracts were dried (Na_2SO_4) and concentrated to afford the crude N-hydroxymethyl amide. The N-hydroxymethyl amide was then dissolved in MeOH (100 mL) and concentrated aqueous NH_4OH (25 mL) was added. The mixture was stirred at rt for 30 min. The solution was quenched with saturated aqueous NH_4Cl and extracted with ether. The combined extracts were dried (Na_2SO_4) and concentrated. Purification by silica-gel

chromatography (ethyl acetate-hexane, 3 : 97) afforded a colorless oil (3.28 g, 70%); ^1H NMR (200 MHz, CDCl_3) δ 0.89 (t, $J = 7.2$ Hz, 9 H), 0.96 (m, 6 H), 1.32 (hextet, $J = 7.2$ Hz, 6 H), 1.46 (s, 9 H), 1.49 – 1.54 (m, 6 H), 1.75 (dd, $J = 1.4, 6.7$ Hz, 3 H), 5.51 (dq, $J = 6.7, 14.5$ Hz, 1 H), 6.08 (dd, $J = 10.8, 14.5$ Hz, 1 H), 6.25 (s, 1 H), 6.30 (d, $J = 10.8$ Hz, 1 H); ^{13}C NMR (50 MHz, CDCl_3) δ 13.0, 13.7, 18.3, 27.4, 28.3, 29.0, 79.8, 126.0, 126.5, 130.2, 141.6, 154.0; IR (neat) 3294, 2956, 1760, 1704 cm^{-1} .

1-(6-Oxocyclohex-1-enyl)penta-1,3-dienylcarbamate *tert*-butyl ester (13). To a solution of 2-iodocyclohex-2-enone (169 mg, 0.76 mmol) and the above stannane (300 mg, 0.63 mmol) in THF (7.5 mL) was added CuI (30.2 mg, 0.16 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (36.7 mg, 0.032 mmol). The mixture was stirred at 50 °C for 3 h. The solution was filtered through a plug of silica-gel, washed with ether, and concentrated. Purification by silica-gel chromatography (ether- CH_2Cl_2 , 3 : 97) provided triene 13 as a colorless oil (180 mg, 85%); ^1H NMR (300 MHz, CDCl_3) δ 1.39 (s, 9 H), 1.68 (dd, $J = 1.5, 6.7$ Hz, 3 H), 2.04 (m, 2 H), 2.47 (m, 4 H), 5.61 (dq, $J = 6.7, 15.0$ Hz, 1 H), 5.90 (ddq, $J = 1.5, 10.8, 15.0$ Hz, 1 H), 6.18 (s, 1 H), 6.33 (d, $J = 10.8$ Hz, 1 H), 6.94 (t, $J = 4.1$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 18.5, 22.6, 26.1, 28.2, 38.4, 79.9, 124.9, 125.0, 127.0, 128.3, 130.3,

135.3, 151.2, 198.0; IR (neat) 3319, 2978, 1721, 1678, 1612 cm^{-1} ; HRMS (MH^+) calcd for $\text{C}_{16}\text{H}_{24}\text{NO}_3$ 278.1751, found 278.1749.

4-Methyl-8-oxo-5,6,7,8-tetrahydronaphthalen-1-ylcarbamic acid *tert*-butyl ester (14). A solution of triene **13** (120 mg, 0.43 mmol) in toluene (8.5 mL) was heated at reflux for 2 h. The resulting solution was cooled to rt and DDQ (144 mg, 0.52 mmol) was added. The mixture was stirred at 50 $^{\circ}\text{C}$ for 4 h. The solution was quenched with saturated aqueous NaHCO_3 and extracted with ether. The combined extracts were washed with saturated aqueous NaHCO_3 , dried (Na_2SO_4), and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 9) provided the protected aniline **14** as a colorless oil (107 mg, 90%); ^1H NMR (300 MHz, CDCl_3) δ 1.51 (s, 9 H), 2.07 (pentet, $J = 6.3$ Hz, 2 H), 2.22 (s, 3 H), 2.65 (t, $J = 6.3$ Hz, 2 H), 2.83 (t, $J = 6.3$ Hz, 2 H), 7.29 (d, $J = 8.7$ Hz, 1 H), 8.21 (d, $J = 8.7$ Hz, 1 H), 11.34 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 19.4, 22.0, 27.5, 28.3, 40.4, 80.1, 116.2, 118.3, 128.5, 136.5, 140.8, 143.5, 153.3, 203.2; IR (neat) 3217, 2931, 1726, 1650 cm^{-1} ; HRMS (MH^+) calcd for $\text{C}_{16}\text{H}_{22}\text{NO}_3$ 276.1594, found 276.1576.

8-Amino-5-methyl-3,4-dihydro-2H-naphthalen-1-one. To a solution of carbamate **14** (95.0 mg, 0.34 mmol) in CH₂Cl₂ (7 mL) at –50 °C was added TFA (266 µL, 3.45 mmol). The solution was warmed to rt over 30 min and stirred for 3 h. The mixture was quenched with saturated aqueous NaHCO₃ and extracted with CH₂Cl₂. The combined extracts were dried (Na₂SO₄) and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 4) provided a white solid: mp 84 – 85 °C (58.9 mg, 98%); ¹H NMR (300 MHz, CDCl₃) δ 2.05 (pentet, *J* = 6.1 Hz, 2 H), 2.15 (s, 3 H), 2.61 (t, *J* = 6.1 Hz, 2 H), 2.78 (t, *J* = 6.1 Hz, 2 H), 6.32 (s, 2 H), 6.44 (d, *J* = 8.4 Hz, 1 H), 7.06 (d, *J* = 8.4 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 19.0, 22.2, 27.5, 40.1, 114.2, 115.7, 122.5, 136.4, 143.1, 149.5, 201.6; IR (neat) 3422, 3330, 2944, 1630, 1609 cm⁻¹; HRMS (MH⁺) calcd for C₁₁H₁₄NO 176.1070, found 176.1055.

1-(6-Methyl-4,5-dihydro-3H-benzo[*cd*]indol-1-yl)ethanone (15). To a solution of the aniline (20.0 mg, 0.11 mmol) in MeOH (2 mL) at 0 °C was added NaOAc (18.7 mg, 0.23 mmol), glacial acetic acid (26 µL, 0.46 mmol), glyoxylic acid monohydrate (26.3 mg, 0.29 mmol), and NaCNBH₃ (7.9 mg, 0.13 mmol). The solution was

warmed slowly to rt over 1 h. The mixture was then filtered through a plug of silica gel and washed with 1% glacial acetic acid in ethyl acetate. The solution was then washed with brine, dried (Na_2SO_4), and concentrated to afford the crude carboxylic acid, which was used without further purification. To the crude carboxylic acid was added a solution of acetic anhydride (1.1 mL) and Et_3N (159 μL , 1.14 mmol). The mixture was heated to reflux for 30 min. The resulting solution was concentrated *in vacuo*. Purification by silica-gel chromatography (ethyl acetate-hexane, 3 : 20) afforded the N-acetylindole **15** (mixture of amide rotamers) as a colorless oil (17.2 mg, 71%); ^1H NMR (300 MHz, CDCl_3 , amide rotamers) δ 2.04 (pentet, $J = 6.0$ Hz, 2 H), 2.33 (s, 3 H), 2.59 (s, 3 H), 2.76 (m, 2 H), 2.81 (t, $J = 6.0$ Hz, 2 H), 7.03 (br m, 1 H), 7.11 (d, $J = 8.4$ Hz, 1 H), 7.76 (br, m, 1 H); HRMS (MH^+) calcd for $\text{C}_{14}\text{H}_{16}\text{NO}$ 214.1226, found 214.1242. The N-acetyl group was then removed to obtain cleaner spectra without broadening due to amide rotamers. Treatment of the N-acetylindole **15** with K_2CO_3 (22.3 mg, 0.16) in MeOH (3 mL) at rt for 1 h, upon workup, afforded the corresponding deprotected indole in quantitative yield as a colorless oil (13.8 mg, quantitative); ^1H NMR (300 MHz, CDCl_3) δ 2.07 (pentet, $J = 6.1$ Hz, 2 H), 2.34 (s, 3 H), 2.80 – 2.88 (m, 4 H), 6.82 (s, 1 H), 6.97 (d, $J = 8.1$ Hz, 1 H), 7.07 (d, $J = 8.1$ Hz, 1 H), 7.69 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 17.3, 21.6, 24.4, 25.0, 107.6, 113.6, 117.2, 123.6, 124.8, 127.3, 129.5, 132.6; IR (neat) 3401, 2928 cm^{-1} .

1-(2-Methyl-6-oxocyclohex-1-enyl)buta-1,3-dienylcarbamic acid *tert*-butyl ester. To a solution of the above iodide (185 mg, 0.79 mmol) and stannane **1** (300 mg, 0.65 mmol) in THF (8 mL) was added CuI (31.2 mg, 0.16 mmol) and Pd(PPh₃)₄ (37.8 mg, 0.033 mmol). The mixture was stirred at 50 °C for 3 h. The solution was filtered through a plug of silica-gel, washed with ether, and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 4) provided the triene as a white solid: mp 136 – 138 °C (184 mg, 84%); ¹H NMR (300 MHz, CDCl₃) δ 1.42 (s, 9 H), 1.93 (s, 3 H), 2.01 (m, 2 H), 2.40 – 2.47 (m, 4 H), 4.89 (dd, *J* = 1.9, 10.2 Hz, 1 H), 5.12 (dd, *J* = 1.9, 16.9 Hz, 1 H), 5.89 (s, 1 H), 5.95 (ddd, *J* = 10.2, 11.0, 16.9 Hz, 1 H), 6.58 (d, *J* = 11.0 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 21.9, 22.5, 28.2, 32.2, 37.6, 80.1, 115.2, 116.3, 131.4, 132.1, 132.8, 152.3, 161.3, 197.1; IR (neat) 3306, 2928, 1723, 1660, 1623 cm⁻¹; HRMS (MH⁺) calcd for C₁₆H₂₄NO₃ 278.1751, found 278.1754.

4-Methyl-8-oxo-5,6,7,8-tetrahydronaphthalen-1-ylcarbamic acid *tert*-butyl ester (14**).** A solution of the triene (94.2 mg, 0.34 mmol) in toluene (6.8 mL) was heated at 150 °C in a sealed tube for

6 h. The resulting solution was cooled to rt, transferred to a flask, and DDQ (116 mg, 0.51 mmol) was then added. The mixture was stirred at 110 °C for 3 h. The solution was quenched with saturated aqueous NaHCO₃ and extracted with ether. The combined extracts were washed with saturated aqueous NaHCO₃, dried (Na₂SO₄), and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 9) provided the protected aniline **14** as a colorless oil (82.9 mg, 89%).

Buta-1,3-dienylmethylcarbamic acid *tert*-butyl ester. To a suspension of sodium hydride (624 mg, 15.6 mmol) in THF (130 mL) at 0 °C was added buta-1,3-dienylcarbamic acid *tert*-butyl ester (2.20 g, 13.0 mmol) in THF (5 mL) dropwise over 5 min. The mixture was stirred at 0 °C for 20 min. To the resulting solution was added MeI (1.21 mL, 19.5 mmol). The solution was warmed to rt and stirred 2 h. The mixture was quenched with saturated aqueous NH₄Cl and extracted with ether. The combined extracts were dried (Na₂SO₄) and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 20) provided a colorless oil (2.19 g, 92%); ¹H NMR (360 MHz, CDCl₃) δ 1.46 (s, 9 H), 2.99 (s, 3 H), 4.83 (d, *J* = 10.2 Hz, 1 H), 5.00 (d, *J* = 16.6 Hz, 1 H), 5.47 (dd, *J* = 10.2, 14.1 Hz, 1 H), 6.27 (dt, *J* = 10.2, 16.6 Hz, 1 H), 7.23 (m, 1 H); ¹³C NMR (90 MHz, CDCl₃) δ 28.1, 30.3, 81.2, 109.7, 112.3, 132.1,

135.4, 152.6; IR (neat) 2954, 1714, 1643 cm^{-1} ; HRMS (MH^+) calcd for $\text{C}_{10}\text{H}_{18}\text{NO}_2$ 184.1332, found 184.1339.

Methyl-1-(tributylstannyl)buta-1,3-dienylcarbamate *tert*-butyl ester. To a solution of the dienamide (2.00 g, 10.9 mmol) in THF (110 mL) at $-78\text{ }^{\circ}\text{C}$ was added TMEDA (1.65 mL, 10.9 mmol) followed by *n*-BuLi (2.5 M in hexane, 5.24 mL, 13.1 mmol) dropwise over 10 min. The mixture was warmed to $-60\text{ }^{\circ}\text{C}$ and stirred for 1 h. To the resulting solution was added Bu_3SnCl (3.55 mL, 13.1 mmol). The solution was warmed to $0\text{ }^{\circ}\text{C}$ over 2 h. The mixture was quenched with brine and extracted with hexanes. The combined extracts were dried (Na_2SO_4) and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 99) afforded the stannane (mixture of amide rotamers) as a colorless oil (3.97 g, 77%); ^1H NMR (360 MHz, CDCl_3) δ 0.89 (t, $J = 7.3\text{ Hz}$, 9 H), 0.95 (m, 6 H), 1.33 (hextet, $J = 7.3\text{ Hz}$, 6 H), 1.47 (s, 9 H), 1.50 (m, 6 H), 3.10 (s, 3 H), 4.95-5.18 (m, 2 H), 6.32-6.55 (m, 2 H); ^{13}C NMR (50 MHz, CDCl_3 , amide rotamers) δ 13.2 (minor), 13.7 (major), 26.8 (minor), 27.4 (major), 28.0 (minor), 28.4 (major), 28.8, 29.0 (minor), 29.2 (major), 35.1, 80.3, 115.1, 129.2, 136.4, 154.5, 154.7; IR (neat) 2929, 1682, 1616 cm^{-1} ; HRMS (MH^+) calcd for $\text{C}_{22}\text{H}_{44}\text{NO}_2\text{Sn}$ 474.2389, found 474.2385.

Methyl-1-(6-oxocyclohex-1-enyl)buta-1,3-dienylcarbamic acid *tert*-butyl ester (16). To a solution of 2-iodocyclohex-2-enone (181 mg, 0.82 mmol) and the stannane (350 mg, 0.74 mmol) in DMF (8 mL) was added CuI (35.3 mg, 0.19 mmol) and Pd(PPh₃)₄ (25.7 mg, 0.022 mmol). The mixture was stirred at rt for 8 h. The solution was quenched with saturated aqueous NaCl and extracted with ether. The combined extracts were washed with water, dried (Na₂SO₄), and concentrated. Purification by silica-gel chromatography (ether-CH₂Cl₂, 3 : 97) provided triene **16** (mixture of amide rotamers) as a colorless oil (189 mg, 92%); ¹H NMR (300 MHz, CDCl₃) δ 1.38 (s, 9 H), 2.06 (pentet, *J* = 6.1 Hz, 2 H), 2.48 (m, 4 H), 3.16 (s, 3 H), 5.05 (dd, *J* = 1.7, 9.8 Hz, 1 H), 5.22 (dd, *J* = 1.7, 16.7, 1 H), 6.06 (d, *J* = 11.0 Hz, 1 H), 6.25 (m, 1 H), 6.91 (t, *J* = 4.3 Hz, 1 H); ¹³C NMR (50 MHz, CDCl₃) δ 22.7, 26.1, 28.3, 37.8, 38.6, 79.9, 117.4, 125.9, 132.8, 136.6, 139.9, 150.3, 154.2, 197.0; IR (neat) 2975, 1699, 1624 cm⁻¹; HRMS (MH⁺) calcd for C₁₆H₂₄NO₃ 278.1751, found 278.1753.

Methyl-(8-oxo-5,6,7,8-tetrahydronaphthalen-1-yl)carbamic acid *tert*-butyl ester (17). A solution of triene **16** (121 mg, 0.43

mmol) in toluene (8.7 mL) was heated at reflux for 3 h. The resulting solution was concentrated to afford the crude cyclohexadiene. The residue was diluted with dioxane (8.7 mL) and DDQ (128 mg, 0.57 mmol) was added. The mixture was stirred at rt for 16 h. The solution was quenched with saturated aqueous NaHCO₃ and extracted with ether. The combined extracts were washed with saturated aqueous NaHCO₃, dried (Na₂SO₄), and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 4) provided the protected aniline **17** (mixture of amide rotamers) as a colorless oil (106 mg, 88%); ¹H NMR (300 MHz, CDCl₃, amide rotamers) δ 1.27 (s, major, 9 H), 1.50 (s, minor, 9 H), 2.10 (m, 2 H), 2.62 (m, 2 H), 2.94 (m, 2 H), 3.14 (s, minor, 3 H), 3.16 (s, major, 3 H), 7.04 (d, major, *J* = 7.7 Hz, 1 H), 7.10 (d, minor, *J* = 7.7 Hz, 1 H), 7.16 (d, *J* = 7.7 Hz, 1 H), 7.40 (m, 1 H); ¹³C NMR (75 MHz, CDCl₃, amide rotamers) δ 22.8 (minor), 22.9 (major), 28.2 (major), 28.4 (minor), 30.4 (minor), 30.5 (major), 37.1 (major), 37.7 (minor), 40.2 (minor), 40.4 (major), 79.3 (major), 80.1 (minor), 127.4 (major), 127.5 (minor), 127.8 (major), 127.9 (minor), 129.0 (major), 129.4 (minor), 132.9 (major), 133.2 (minor), 143.4 (minor), 143.6 (major), 145.6 (major), 146.1 (minor), 154.4 (major), 155.4 (minor), 197.2 (major), 197.6 (minor); IR (neat) 2966, 1702, 1590 cm⁻¹; HRMS (MH⁺) calcd for C₁₆H₂₂NO₃ 276.1594, found 276.1576.

8-Methylamino-3,4-dihydro-2H-naphthalen-1-one. To a solution of carbamate **17** (80.4 mg, 0.29 mmol) in CH₂Cl₂ (6 mL) at – 50 °C was added TFA (113 μL, 1.46 mmol). The solution was warmed to rt over 30 min and stirred for 2 h. The mixture was quenched with saturated aqueous NaHCO₃ and extracted with CH₂Cl₂. The combined extracts were dried (Na₂SO₄) and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 3 : 20) provided a colorless oil (47.7 mg, 93%); ¹H NMR (300 MHz, CDCl₃) δ 2.02 (pentet, *J* = 6.3 Hz, 2 H), 2.62 (t, *J* = 6.3 Hz, 2 H), 2.87 (t, *J* = 6.3 Hz, 2 H), 2.90 (d, *J* = 5.1 Hz, 3 H), 6.41 (d, *J* = 7.3 Hz, 1 H), 6.52 (d, *J* = 8.5 Hz, 1 H), 7.26 (t, *J* = 7.8 Hz, 1 H), 9.13 (br s, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 23.0, 29.4, 31.2, 40.4, 108.7, 114.3, 114.7, 134.9, 146.5, 152.8, 201.2; IR (neat) 3292, 2934, 1629, 1579 cm^{–1}; HRMS (MH⁺) calcd for C₁₁H₁₄NO 176.1070, found 176.1063.

1-Methyl-1,3,4,5-tetrahydrobenzo[cd]indole (18). To a solution of the aniline (40.0 mg, 0.23 mmol) in DMF (2 mL) at rt was added methyl iodoacetate (137 mg, 0.68 mmol) and K₂CO₃ (95.0 mg, 0.68 mmol). The mixture was heated at 100 °C for 12 h. The solution was quenched with saturated aqueous NH₄Cl and extracted

with ether. The combined extracts were washed with brine, dried (Na_2SO_4), and concentrated. Purification by silica-gel chromatography (ether- CH_2Cl_2 , 3 : 97) provided the ester as a colorless oil (40.1 mg, 71%); ^1H NMR (200 MHz, CDCl_3) δ 2.01 (pentet, $J = 6.1$ Hz, 2 H), 2.61 (t, $J = 6.1$ Hz, 2 H), 2.89 (t, $J = 6.1$ Hz, 2 H), 3.00 (s, 3 H), 3.75 (s, 3 H), 3.86 (s, 2 H), 6.72 (d, $J = 7.5$ Hz, 1 H), 6.85 (d, $J = 8.5$ Hz, 1 H), 7.29 (t, $J = 7.9$ Hz, 1 H).

To a solution of ester (25.0 mg, 0.10 mmol) in MeOH (1 mL) was added 4 M aqueous NaOH (500 μL). The mixture was stirred at rt for 2 h. The resulting solution was acidified with 2 M HCl and extracted with ethyl acetate. The combined extracts were dried (Na_2SO_4) and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 19) afforded indole **18** as a colorless oil (16.1 mg, 93%); ^1H NMR (300 MHz, CDCl_3) δ 2.06 (pentet, $J = 6.2$ Hz, 2 H), 2.85 (t, $J = 6.2$ Hz, 2 H), 2.94 (t, $J = 6.2$ Hz, 2 H), 3.75 (s, 3 H), 6.70 (s, 1 H), 6.81 (dd, $J = 1.0, 6.7$ Hz, 1 H), 7.08 (d, $J = 8.2$ Hz, 1 H), 7.14 (dd, $J = 6.7, 8.2$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 21.8, 24.7, 27.5, 32.6, 106.2, 112.6, 115.1, 122.0, 122.2, 127.5, 132.4, 134.9; IR (neat) 2924, 1610 cm^{-1} ; HRMS (MH^+) calcd for $\text{C}_{12}\text{H}_{14}\text{N}$ 172.1121, found 172.1110.

8-Oxo-5,6,7,8-tetrahydronaphthalen-1-ylaminophenylacetic acid methyl ester (20). To a solution of aniline **19** (34.8 mg,

0.22 mmol) in DMF (2 mL) at rt was added methyl α -bromophenylacetate (203 μ L, 1.30 mmol) and K_2CO_3 (89.5 mg, 0.65 mmol). The mixture was heated at 110 $^{\circ}C$ for 8 h. The solution was quenched with saturated aqueous NH_4Cl and extracted with ether. The combined extracts were washed with brine, dried (Na_2SO_4), and concentrated. Purification by silica-gel chromatography (CH_2Cl_2) provided ester **20** as a colorless oil (38.5 mg, 59%); 1H NMR (300 MHz, $CDCl_3$) δ 2.05 (pentet, $J = 6.4$ Hz, 2 H), 2.68 (t, $J = 6.4$ Hz, 2 H), 2.88 (t, $J = 6.4$ Hz, 2 H), 3.74 (s, 3 H), 5.17 (d, $J = 6.1$ Hz, 1 H), 6.27 (d, $J = 8.6$ Hz, 1 H), 6.45 (d, $J = 7.5$ Hz, 1 H), 7.14 (br t, $J = 7.8$ Hz, 1 H), 7.30 – 7.41 (m, 3 H), 7.50 (m, 2 H), 10.31 (d, $J = 6.1$ Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.9, 31.2, 40.4, 52.8, 60.5, 109.8, 115.7, 127.2, 127.7, 128.4, 128.9, 134.8, 137.1, 146.7, 149.5, 171.4, 201.5; IR (neat) 3260, 2951, 1745, 1635 cm^{-1} ; HRMS (MH^+) calcd for $C_{19}H_{20}NO_3$ 310.1438, found 310.1418.

2-Phenyl-1,3,4,5-tetrahydrobenzo[*cd*]indole (21). To a solution of ester **20** (28.1 mg, 0.091 mmol) in MeOH (2 mL) was added 4 M aqueous NaOH (1 mL). The mixture was stirred at rt for 2 h. The resulting solution was acidified with 2 M HCl and extracted with ethyl acetate. The combined extracts were dried (Na_2SO_4) and concentrated to afford the crude carboxylic acid, which was used immediately without further purification. To the crude carboxylic

acid was added a solution of acetic anhydride (1 mL) and Et₃N (127 μ L, 0.91 mmol). The mixture was heated to reflux for 30 min. The resulting solution was concentrated *in vacuo*. Purification by silica-gel chromatography (CH₂Cl₂-hexane, 1 : 1) afforded the indole **21** as a colorless oil (16.5 mg, 78%); ¹H NMR (300 MHz, CDCl₃) δ 2.11 (pentet, *J* = 6.1 Hz, 2 H), 2.97 (t, *J* = 6.1 Hz, 2 H), 3.07 (t, *J* = 6.1 Hz, 2 H), 6.85 (dd, *J* = 1.0, 6.8 Hz, 1 H), 7.12 (dd, *J* = 6.8, 8.1 Hz, 1 H), 7.18 (d, *J* = 8.1 Hz, 1 H), 7.28 (m, 1 H), 7.46 (t, *J* = 7.5 Hz, 2 H), 7.59 (m, 2 H), 8.03 (s, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 23.2, 24.6, 27.5, 107.8, 111.6, 116.3, 123.0, 126.1, 126.7, 128.8, 128.9, 130.3, 132.6, 133.3, 134.2; IR (neat) 3417, 2925, 1602 cm⁻¹; HRMS (MH⁺) calcd for C₁₇H₁₆N 234.1283, found 234.1289.

1-(1-Acetyl-2-phenylvinyl)buta-1,3-dienylcarbamic acid tert-butyl ester (22). To a solution of the above bromide (177 mg, 0.79 mmol) and stannane **1** (300 mg, 0.65 mmol) in THF (6.5 mL) was added CuI (31.2 mg, 0.16 mmol) and Pd(PPh₃)₄ (37.8 mg, 0.033 mmol). The mixture was stirred at 65 °C for 4 h. The solution was filtered through a plug of silica-gel, washed with ether, and concentrated. Purification by silica-gel chromatography (ether-CH₂Cl₂, 3 : 97) provided triene **22** as a colorless oil (185 mg, 90%); ¹H NMR (300 MHz, CDCl₃) δ 1.41 (s, 9 H), 2.36 (s, 3 H), 4.88 (dd, *J* = 1.9, 10.3 Hz, 1 H), 5.13 (dd, *J* = 1.9, 16.3 Hz, 1 H), 6.10 (ddd, *J* =

10.3, 11.2, 16.3 Hz, 1 H), 6.14 (s, 1 H), 6.64 (d, $J = 11.2$ Hz, 1 H), 7.28 - 7.37 (m, 3 H), 7.55 - 7.66 (m, 3 H); ^{13}C NMR (75 MHz, CDCl_3) δ 26.9, 28.0, 80.8, 116.3, 116.4, 128.6, 130.2, 130.6, 131.9, 132.2, 133.6, 133.9, 140.7, 152.6, 197.9; IR (neat) 3325, 2978, 1718 cm^{-1} ; HRMS (MH^+) calcd for $\text{C}_{19}\text{H}_{24}\text{NO}_3$ 314.1751, found 314.1773.

2-Acetyl-3-phenyl-1H-indole-1-carboxylic acid *tert*-butyl ester (23). A solution of triene **22** (173 mg, 0.55 mmol) in toluene (5.5 mL) was heated at 150 °C in a sealed tube for 2 h. The resulting solution was cooled to rt, transferred to a flask, and DDQ (150 mg, 0.66 mmol) was then added. The mixture was stirred at 70 °C for 16 h. The solution was quenched with saturated aqueous NaHCO_3 and extracted with ether. The combined extracts were washed with saturated aqueous NaHCO_3 , dried (Na_2SO_4), and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 9) provided the protected aniline **23** as a white solid: mp 113 - 115 °C (152 mg, 89%); ^1H NMR (300 MHz, CDCl_3) δ 1.51 (s, 9 H), 1.83 (s, 3 H), 7.07 (dd, $J = 1.1, 7.6$ Hz, 1 H), 7.30 - 7.36 (m, 2 H), 7.39 - 7.47 (m, 4 H), 8.16 (dd, $J = 1.1, 8.4$ Hz, 1 H), 8.41 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 28.2, 32.3, 80.6, 119.6, 124.4, 128.1, 128.8, 128.9, 131.0, 132.2, 136.2, 141.0, 141.5, 153.0, 206.9; IR (neat) 3378, 2978, 1732, 1668 cm^{-1} ; HRMS (MH^+) calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_3$ 312.1594, found 312.1614

1-(3-Aminobiphenyl-2-yl)ethanone. To a solution of carbamate **23** (110 mg, 0.35 mmol) in CH₂Cl₂ (7 mL) at -50 °C was added TFA (272 μL, 3.53 mmol). The solution was warmed to rt over 30 min and stirred for 2 h. The mixture was quenched with saturated aqueous NaHCO₃ and extracted with CH₂Cl₂. The combined extracts were dried (Na₂SO₄) and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 4) provided a colorless oil (72.0 mg, 96%); ¹H NMR (360 MHz, CDCl₃) δ 1.79 (s, 3 H), 5.03 (s, 2 H), 6.69 (dd, *J* = 1.1, 8.1 Hz, 1 H), 6.71 (dd, *J* = 1.1, 7.5 Hz, 1 H), 7.22 (dd, *J* = 7.5, 8.1 Hz, 1 H), 7.33 - 7.45 (m, 5 H); ¹³C NMR (50 MHz, CDCl₃) δ 32.0, 115.8, 119.6, 123.7, 127.8, 128.6, 128.9, 131.3, 142.0, 143.0, 146.2, 206.1; IR (neat) 3476, 3370, 2923, 1660, 1602 cm⁻¹; HRMS (MH⁺) calcd for C₁₄H₁₄NO 212.1070, found 212.1054.

1-(3-Methyl-4-phenylindol-1-yl)ethanone (24). To a solution of the aniline (43.8 mg, 0.21 mmol) in MeOH (4 mL) at 0 °C was added NaOAc (34.0 mg, 0.41 mmol), glacial acetic acid (47 μL, 0.83 mmol), glyoxylic acid monohydrate (47.7 mg, 0.52 mmol), and NaCNBH₃ (14.3 mg, 0.23 mmol). The solution was warmed slowly to rt over 1 h. The mixture was then filtered through a plug of silica gel and washed with 1% glacial acetic acid in ethyl acetate. The

solution was then washed with brine, dried (Na_2SO_4), and concentrated to afford the crude carboxylic acid, which was used without further purification. To the crude carboxylic acid was added a solution of acetic anhydride (2.1 mL) and Et_3N (289 μL , 2.07 mmol). The mixture was heated to reflux for 30 min. The resulting solution was concentrated *in vacuo*. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 9) afforded the N-acetylindole **24** as a white solid: mp 114 – 116 °C (46.6 mg, 90%); ^1H NMR (300 MHz, CDCl_3) δ 1.76 (d, J = 1.6 Hz, 3 H), 2.61 (s, 3 H), 7.15 (d, J = 7.4 Hz, 1 H), 7.17 (s, 1 H), 7.37 – 7.45 (m, 6 H), 8.52 (d, J = 8.3 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 12.9, 24.1, 115.6, 118.8, 123.4, 124.7, 125.2, 127.1, 127.5, 128.3, 129.7, 136.0, 136.4, 140.6, 168.2; IR (neat) 2924, 1705, 1604 cm^{-1} ; HRMS (MH^+) calcd for $\text{C}_{17}\text{H}_{16}\text{NO}$ 250.1226, found 250.1251.

1-(1-Acetyl-2-methylpropenyl)buta-1,3-dienylcarbamic acid *tert*-butyl ester (25**)**. To a solution of the above iodide (176 mg, 0.79 mmol) and stannane **1** (300 mg, 0.65 mmol) in THF (8 mL) was added CuI (31.2 mg, 0.16 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (37.8 mg, 0.033 mmol). The mixture was stirred at 50 °C for 3 h. The solution was filtered through a plug of silica-gel, washed with ether, and concentrated. Purification by silica-gel chromatography (ether- CH_2Cl_2 , 1 : 99) provided triene **25** as a colorless oil (154 mg, 88%); ^1H NMR (200 MHz, CDCl_3) δ 1.45 (s, 9 H), 1.81 (s, 3 H), 2.06 (s, 3 H),

2.20 (s, 3 H), 4.96 (dd, $J = 1.6, 10.3$ Hz, 1 H), 5.19 (dd, $J = 1.6, 16.8$ Hz, 1 H), 5.82 (s, 1 H), 6.15 (ddd, $J = 10.3, 11.1, 16.8$ Hz, 1 H), 6.77 (d, $J = 11.1$ Hz, 1 H); ^{13}C NMR (50 MHz, CDCl_3) δ 22.2, 23.8, 28.2, 29.6, 80.7, 115.7, 116.1, 132.4, 133.0, 133.6, 150.2, 152.0, 200.6; IR (neat) 3320, 2978, 1718, 1684, 1653 cm^{-1} ; HRMS (MH^+) calcd for $\text{C}_{15}\text{H}_{24}\text{NO}_3$ 266.1751, found 266.1734.

2-Acetyl-3,5-dimethylphenylcarbamic acid *tert*-butyl ester (28). A solution of triene **25** (145 mg, 0.55 mmol) in toluene (5.5 mL) was heated at 150 °C in a sealed tube for 6 h. The resulting solution was cooled to rt, transferred to a flask, and DDQ (161 mg, 0.71 mmol) was then added. The mixture was stirred at 60 °C for 2 h. The solution was quenched with saturated aqueous NaHCO_3 and extracted with ether. The combined extracts were washed with saturated aqueous NaHCO_3 , dried (Na_2SO_4), and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 4) provided the protected aniline **28** as a colorless oil (95.2 mg, 66%); ^1H NMR (300 MHz, CDCl_3) δ 1.49 (s, 9 H), 2.32 (s, 3 H), 2.36 (s, 3 H), 2.50 (s, 3 H), 6.72 (s, 1 H), 7.70 (s, 1 H), 7.93 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 21.3, 21.5, 28.3, 32.5, 80.4, 119.4, 126.7, 128.3, 135.1, 135.7, 141.3, 153.1, 206.4; IR (neat) 3322, 2977, 1729, 1613 cm^{-1} ; HRMS (MH^+) calcd for $\text{C}_{15}\text{H}_{22}\text{NO}_3$ 264.1594, found 264.1586.

1-(2-Amino-4,6-dimethylphenyl)ethanone. To a solution of carbamate **28** (96.1 mg, 0.36 mmol) in CH₂Cl₂ (7 mL) at -50 °C was added TFA (141 μL, 1.82 mmol). The solution was warmed to rt over 30 min and stirred for 3 h. The mixture was quenched with saturated aqueous NaHCO₃ and extracted with CH₂Cl₂. The combined extracts were dried (Na₂SO₄) and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 4) provided a colorless oil (56.8 mg, 95%); ¹H NMR (200 MHz, CDCl₃) δ 2.21 (s, 3 H), 2.38 (s, 3 H), 2.51 (s, 3 H), 4.87 (br s, 2 H), 6.35 (s, 1 H), 6.38 (s, 1 H); ¹³C NMR (50 MHz, CDCl₃) δ 21.2, 22.3, 32.7, 115.1, 121.8, 122.6, 136.9, 141.8, 146.6, 205.2; IR (neat) 3460, 3365, 2920, 1613 cm⁻¹; HRMS (MH⁺) calcd for C₁₀H₁₄NO 164.1070, found 164.1063.

1-(3,4,6-Trimethylindol-1-yl)ethanone (29). To a solution of the aniline (28.5 mg, 0.17 mmol) in MeOH (2 mL) at 0 °C was added NaOAc (28.6 mg, 0.35 mmol), glacial acetic acid (40.0 μL, 0.70 mmol), glyoxylic acid monohydrate (40.2 mg, 0.44 mmol), and NaCNBH₃ (12.1 mg, 0.19 mmol). The solution was warmed slowly to rt over 1 h. The mixture was then filtered through a plug of silica gel and washed with 1% glacial acetic acid in ethyl acetate. The

solution was then washed with brine, dried (Na_2SO_4), and concentrated to afford the crude carboxylic acid, which was used without further purification. To the crude carboxylic acid was added a solution of acetic anhydride (1.7 mL) and Et_3N (243 μL , 1.75 mmol). The mixture was heated to reflux for 30 min. The resulting solution was concentrated *in vacuo*. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 9) afforded the N-acetylindole **29** as a colorless oil (30.4 mg, 87%); ^1H NMR (300 MHz, CDCl_3) δ 2.42 (s, 3 H), 2.43 (s, 3 H), 2.56 (s, 3 H), 2.62 (s, 3 H), 6.85 (s, 1 H), 7.05 (s, 1 H), 8.15 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.4, 19.7, 21.7, 24.1, 114.7, 119.2, 122.0, 126.7, 127.1, 130.6, 135.2, 136.9, 168.2; IR (neat) 2919, 1693, 1608 cm^{-1} ; HRMS (MH^+) calcd for $\text{C}_{13}\text{H}_{16}\text{NO}$ 202.1226, found 202.1217.

5-(1-*tert*-Butoxycarbonylamino-1,3-dienyl)-4-oxo-3,4-dihydro-2H-pyridine-1-carboxylic acid phenyl ester (30). To a solution of the above iodide (170 mg, 0.50 mmol) and stannane (234 mg, 0.50 mmol) in THF (5 mL) was added CuI (23.6 mg, 0.12 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (28.7 mg, 0.025 mmol). The mixture was stirred at 50 $^\circ\text{C}$ for 3 h. The solution was filtered through a plug of silica-gel, washed with ether, and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 3 : 7) provided triene **30** (mixture of amide rotamers) as a colorless oil (154 mg,

78%); ^1H NMR (300 MHz, CDCl_3) δ 1.42 (s, 9 H), 1.73 (d, J = 6.6 Hz, 3 H), 2.75 (t, J = 7.2 Hz, 2 H), 4.22 (m, 2 H), 5.69 (dq, J = 6.6, 14.9 Hz, 1 H), 6.02 (br dd, J = 10.9, 14.9 Hz, 1 H), 6.25 (s, 1 H), 6.38 (d, J = 10.9 Hz, 1 H), 7.17 (d, J = 9.1 Hz, 2 H), 7.29 (t, J = 9.1 Hz, 1 H), 7.41 (t, J = 9.1 Hz, 2 H), 8.03 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.5, 18.5, 28.1, 35.6, 80.0, 118.7, 121.2, 121.6, 126.4, 126.6, 127.8, 128.9, 129.6, 143.3, 150.3, 151.1, 152.8, 191.5; IR (neat) 3331, 2974, 1737, 1720, 1678, 1609 cm^{-1} ; HRMS (MH^+) $\text{C}_{22}\text{H}_{27}\text{N}_2\text{O}_5$ 399.1915, found 399.1944.

5-*tert*-Butoxycarbonylamino-8-methyl-4-oxo-3,4-dihydro-2*H*-quinoline-1-carboxylic acid phenyl ester (31). A solution of triene **30** (109 mg, 0.27 mmol) in toluene (6 mL) was heated at reflux for 2 h. The resulting solution was cooled to rt and DDQ (74 mg, 0.33 mmol) was added. The mixture was stirred at 50 °C for 4 h. The solution was quenched with saturated aqueous NaHCO_3 and extracted with ether. The combined extracts were washed with saturated aqueous NaHCO_3 , dried (Na_2SO_4), and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 3 : 20) provided the protected aniline **31** (mixture of amide rotamers) as a colorless oil (93.1 mg, 87%); ^1H NMR (300 MHz, CDCl_3 , amide rotamers) δ 1.53 (s, 9 H), 2.32 (s, 3 H), 2.73 and 3.10 (m, 2 H), 3.63 and 4.71 (m, 2 H), 7.19 (m, 2 H), 7.23 (d, J = 8.7 Hz, 1 H), 7.38 (m, 3

H), 8.30 (d, $J = 8.7$ Hz, 1 H), 11.00 (s, 1 H); ^{13}C NMR (50 MHz, CDCl_3) δ 17.9, 28.3, 40.4, 45.3, 80.7, 114.2, 117.3, 121.3, 125.8, 126.9, 129.4, 138.0, 140.6, 141.8, 150.9, 153.0, 154.4, 198.9; IR (neat) 3260, 2977, 1725, 1654 cm^{-1} ; HRMS (MNH_4^+) calcd for $\text{C}_{22}\text{H}_{28}\text{N}_3\text{O}_5$ 414.2024, found 414.1995.

5-Amino-8-methyl-4-oxo-3,4-dihydro-2H-quinoline-1-carboxylic acid phenyl ester. To a solution of carbamate **31** (75.5 mg, 0.19 mmol) in CH_2Cl_2 (4 mL) at -50 $^\circ\text{C}$ was added TFA (73.4 μL , 0.95 mmol). The solution was warmed to rt over 30 min and stirred for 3 h. The mixture was quenched with saturated aqueous NaHCO_3 and extracted with CH_2Cl_2 . The combined extracts were dried (Na_2SO_4) and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 4) provided the aniline (mixture of amide rotamers) as a colorless oil (54.0 mg, 96%); ^1H NMR (200 MHz, CDCl_3 , amide rotamers) δ 2.23 (s, 3 H), 2.66 and 3.04 (m, 2 H), 3.57 and 4.70 (m, 2 H), 6.38 (s, 2 H), 6.51 (d, $J = 8.6$ Hz, 1 H), 7.03 – 7.25 (m, 3 H), 7.14 (d, $J = 8.6$ Hz, 1 H), 7.37 (br t, $J = 7.4$ Hz, 2 H); ^{13}C NMR (50 MHz, CDCl_3) δ 17.6, 39.8, 45.4, 111.0, 115.3, 120.8, 121.4, 125.6, 129.3, 137.7, 141.1, 149.3, 151.1, 197.5; IR (neat) 3448, 3330, 2931, 1716, 1645 cm^{-1} ; HRMS (MH^+) calcd for $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}_3$ 297.1234, found 297.1239.

1-Acetyl-6-methyl-3,4-dihydro-1H-pyrrolo[4,3,2-de]quinoline-5-carboxylic acid phenyl ester (32). To a solution of the aniline (29.2 mg, 0.099 mmol) in MeOH (2 mL) at 0 °C was added NaOAc (16 mg, 0.20 mmol), glacial acetic acid (23 μ L, 0.39 mmol), glyoxylic acid monohydrate (23 mg, 0.29 mmol), and NaCNBH₃ (6.8 mg, 0.11 mmol). The solution was warmed slowly to rt over 1 h. The mixture was then filtered through a plug of silica gel and washed with 1% glacial acetic acid in ethyl acetate. The solution was then washed with brine, dried (Na₂SO₄), and concentrated to afford the crude carboxylic acid, which was used without further purification. To the crude carboxylic acid was added a solution of acetic anhydride (1 mL) and Et₃N (137 μ L, 0.99 mmol). The mixture was heated to reflux for 30 min. The resulting solution was concentrated *in vacuo*. Purification by silica-gel chromatography (ethyl acetate-hexane, 3 : 7) afforded the N-acetylindole **32** (mixture of amide rotamers) as a colorless oil (25.4 mg, 77%); ¹H NMR (400 MHz, CDCl₃) δ 2.41 (s, 3 H), 2.62 (s, 3 H), 3.01 (br m, 2 H), 3.48 – 4.95 (br m, 2 H), 7.08 – 7.25 (m, 5 H), 7.37 (t, *J* = 7.9 Hz, 2 H), 7.97 (br s, 1 H). The N-acetyl group was then removed to obtain cleaner spectra without broadening due to amide rotamers. Treatment of the N-acetylindole **32** with K₂CO₃ (21 mg, 0.15) in MeOH (3 mL) at rt for 1 h, upon workup, afforded the corresponding deprotected indole (mixture of amide rotamers) in quantitative yield as a colorless oil (22.2 mg, quantitative); ¹H NMR

(300 MHz, CDCl₃, amide rotamers) δ 2.41 (s, 3 H), 3.06 (br m, 2 H), 3.70 – 5.17 (br m, 2 H), 6.89 (d, J = 1.6 Hz, 1 H), 7.03 (d, J = 8.3 Hz, 1 H), 7.12 (d, J = 8.3 Hz, 1 H), 7.13 – 7.24 (m, 3 H), 7.36 (t, J = 7.8 Hz, 2 H), 7.91 (br s, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 18.2, 23.2, 47.5, 108.2, 110.3, 118.2, 121.6, 121.7, 122.4, 125.3, 126.3, 129.0, 129.3, 130.6, 132.8, 151.4; IR (neat) 3355, 2923, 1708, 1602 cm⁻¹; HRMS (MH⁺) calcd for C₁₈H₁₇N₂O₂ 293.1285, found 293.1292.

4-Formyl-2,3-dihydropyrrole-1-carboxylic acid *tert*-butyl ester. To a solution of DMF (9.07 mL, 117 mmol) in CH₂Cl₂ (27 mL) at 0 °C was added oxalyl chloride (949 μ L, 10.9 mmol) dropwise. The solution was stirred at 0 °C for 10 min. To the resultant white suspension was added the enecarbamate (1.54 g, 9.07 mmol) shown above in CH₂Cl₂ (9 mL). The solution was warmed to rt and stirred for 1 h. The mixture was quenched with saturated aqueous Na₂CO₃ (40 mL) and stirred vigorously for 1 h. The resultant solution was extracted with CH₂Cl₂, dried (Na₂SO₄) and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 10) provided the aldehyde (mixture of amide rotamers) as a white solid: mp 62 – 63 °C (1.71 g, 95%); ¹H NMR (400 MHz, CDCl₃) δ 1.49 (s, 9 H), 2.81 (t, J = 9.3 Hz, 2 H), 3.88 (t, J = 9.3 Hz, 2 H), 7.47 (m, 1 H), 9.54 (s, 1 H); ¹³C NMR (50 MHz, CDCl₃) δ 24.7, 28.0, 47.1, 82.5, 124.7, 147.5, 151.8, 185.6; IR (neat) 2977, 1718, 1659, 1609 cm⁻¹; HRMS (MH⁺) calcd for C₁₀H₁₆NO₃ 198.1125, found 198.1125.

4-Vinyl-2,3-dihydropyrrole-1-carboxylic acid *tert*-butyl ester. To a solution of the aldehyde (1.88 g, 9.53 mmol) in ether (38 mL) at 0 °C was added (trimethylsilyl)methylmagnesium chloride (1.0 M in THF, 14.3 mL, 14.3 mmol) dropwise. The solution was stirred at 0 °C for 1.5 h. The resultant solution was cooled to –78 °C and acetic acid (2.76 mL, 47.7 mmol) was added dropwise. The solution was warmed to –40 °C over 30 min. The mixture was quenched with saturated NaHCO₃ and extracted with CH₂Cl₂. The combined extracts were dried (Na₂SO₄) and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 40) gave the diene (mixture of amide rotamers) as a colorless oil (1.47 g, 79%); ¹H NMR (300 MHz, d₆-acetone) δ 1.45 (s, 9 H), 2.69 (m, 2 H), 3.73 (m, 2 H), 4.89 (m, 2 H), 6.62 (m, 2 H); ¹³C NMR (75 MHz, d₆-acetone, amide rotamers) δ 27.7, 28.4, 46.1 (major), 46.5 (minor), 80.4, , 111.2 (minor), 111.4 (major), 122.6, 129.6, 131.7, 151.6 (major), 152.2 (minor); IR (neat) 2976, 1704, 1634 cm⁻¹; HRMS (MH⁺) calcd for C₁₁H₁₈NO₂ 196.1332, found 196.1337.

5-(Trimethylstannyl)-4-vinyl-2,3-dihydropyrrole-1-carboxylic acid *tert*-butyl ester. To a solution of the diene (1.19 g, 6.09 mmol) in THF (27 mL) at –30 °C was added *n*-BuLi (2.5 M in hexane, 2.68 mL, 6.70 mmol) dropwise over 5 min. The solution was stirred at –30 °C for 20 min. To the resulting solution

was added trimethyltin chloride (1.0 M in THF, 6.70 mL, 6.70 mmol) dropwise over 5 min. The solution was warmed to rt over 30 min. The mixture was quenched with saturated NaHCO₃ and extracted with ether. The combined extracts were dried (Na₂SO₄) and concentrated to afford the stannane (mixture of amide rotamers) as a yellow oil (1.84 g, 84%); ¹H NMR (400 MHz, CDCl₃) δ 0.25 (s, 9 H), 1.46 (s, 9 H), 2.76 (t, *J* = 9.3 Hz, 2 H), 3.71 (t, *J* = 9.3 Hz, 2 H), 4.86 (d, *J* = 17.1 Hz, 1 H), 4.93 (d, *J* = 10.6 Hz, 1 H), 6.74 (dd, *J* = 10.6, 17.1 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ -4.7, 28.3, 30.1, 46.1, 80.0, 110.8, 132.8, 133.0, 145.4, 153.4; IR (neat) 2977, 1683, 1614 cm⁻¹; HRMS (MH⁺) calcd for C₁₄H₂₆NO₂Sn 360.0980, found 360.0974.

5-(3,3-Dimethyl-6-oxocyclohex-1-enyl)-4-vinyl-2,3-dihydropyrrole-1-carboxylic acid *tert*-butyl ester (33). To a solution of 2-iodo-4,4-dimethylcyclohexeneone (183 mg, 0.73 mmol) and the above stannane (219 mg, 0.61 mmol) in THF (6 mL) was added CuI (29.1 mg, 0.15 mmol) and Pd(PPh₃)₄ (35.3 mg, 0.031 mmol). The mixture was stirred at 50 °C for 3 h. The solution was filtered through a plug of silica-gel, washed with ether, and concentrated. Purification by silica-gel chromatography (ether-CH₂Cl₂, 3 : 97) provided triene **33** (mixture of amide rotamers) as a colorless oil (158 mg, 82%); ¹H NMR (200 MHz, CDCl₃) δ 1.23 (s, 6 H), 1.40 (s, 9 H), 1.93 (t, *J* = 6.8 Hz, 2 H), 2.57 (m, 2 H), 2.67 (t, *J* =

9.3 Hz, 2 H), 3.84 (t, $J = 9.3$ Hz, 2 H), 4.87 (dd, $J = 1.4, 7.8$ Hz, 1 H), 4.95 (s, 1 H), 6.35 (m, 1 H), 6.39 (s, 1 H); ^{13}C NMR (50 MHz, CDCl_3) δ 27.4, 27.8, 28.3, 33.1, 34.4, 35.7, 46.6, 80.0, 111.3, 121.6, 130.1, 130.4, 136.7, 151.4, 156.1, 196.8; IR (neat) 2961, 1690 cm^{-1} ; HRMS (MH^+) calcd for $\text{C}_{19}\text{H}_{28}\text{NO}_3$ 318.2064, found 318.2085.

6,6-Dimethyl-9-oxo-2,3,6,7,8,9-hexahydrobenzo[*g*]indole-1-carboxylic acid *tert*-butyl ester (34). A solution of triene **33** (113 mg, 0.35 mmol) in toluene (7 mL) was heated at reflux for 12 h. The resulting solution was cooled to rt and DDQ (80.5 mg, 0.35 mmol) was added. The mixture was stirred at rt for 6 h. The solution was quenched with saturated aqueous NaHCO_3 and extracted with ether. The combined extracts were washed with saturated aqueous NaHCO_3 , dried (Na_2SO_4), and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 4) provided the protected aniline **34** as a colorless oil (96.2 mg, 86%); ^1H NMR (200 MHz, CDCl_3) δ 1.32 (s, 6 H), 1.48 (s, 9 H), 1.98 (t, $J = 6.6$ Hz, 2 H), 2.72 (t, $J = 6.6$ Hz, 2 H), 2.97 (t, $J = 8.1$ Hz, 2 H), 4.14 (t, $J = 8.1$ Hz, 2 H), 7.02 (d, $J = 7.8$ Hz, 1 H), 7.25 (d, $J = 7.8$ Hz, 1 H); ^{13}C NMR (50 MHz, CDCl_3) δ 27.9, 28.3, 29.7, 34.3, 35.7, 36.7, 50.3, 80.8, 120.4, 122.9, 128.1, 132.6, 141.5, 150.9, 153.0, 197.8; IR (neat) 2963, 1686 cm^{-1} ; HRMS (MH^+) calcd for $\text{C}_{19}\text{H}_{26}\text{NO}_3$ 316.1907, found 316.1919.

6,6-Dimethyl-1,2,3,6,7,8-hexahydrobenzo[*g*]indol-9-one. To a solution of carbamate **34** (90.0 mg, 0.29 mmol) in CH₂Cl₂ (6 mL) at -50 °C was added TFA (110 μL, 1.43 mmol). The solution was warmed to rt over 30 min and stirred for 3 h. The mixture was quenched with saturated aqueous NaHCO₃ and extracted with CH₂Cl₂. The combined extracts were dried (Na₂SO₄) and concentrated. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 4) provided a colorless oil (58.1 mg, 94%); ¹H NMR (200 MHz, CDCl₃) δ 1.32 (s, 6 H), 1.91 (t, *J* = 6.7 Hz, 2 H), 2.65 (t, *J* = 6.7 Hz, 2 H), 2.99 (t, *J* = 8.5 Hz, 2 H), 3.75 (t, *J* = 8.5 Hz, 2 H), 6.50 (d, *J* = 7.4 Hz, 1 H), 7.11 (d, *J* = 7.4 Hz, 1 H), 7.30 (br s, 1 H); ¹³C NMR (50 MHz, CDCl₃) δ 27.5, 29.8, 33.7, 35.2, 37.2, 46.9, 111.7, 111.9, 128.8, 128.9, 150.5, 154.6, 199.7; IR (neat) 3390, 2918, 1641 cm⁻¹; HRMS (MH⁺) calcd for C₁₄H₁₈NO 216.1383, found 216.1365.

6,6-Dimethyl-1,4,5,6-tetrahydro-2*H*-2a-azacyclopenta-[*bc*]acenaphthylene (52). To a solution of the aniline (42.0 mg, 0.20 mmol) in DMF (2 mL) at rt was added methyl iodoacetate (117 mg, 0.59 mmol) and K₂CO₃ (81 mg, 0.59 mmol). The mixture was heated at 100 °C for 16 h. The solution was quenched with

saturated aqueous NH_4Cl and extracted with ether. The combined extracts were washed with brine, dried (Na_2SO_4), and concentrated. The residue was filtered through a plug of silica-gel, washed with ether- CH_2Cl_2 (3 : 97), and concentrated to afford the crude methyl ester, which was used without further purification; ^1H NMR (200 MHz, CDCl_3) δ 1.29 (s, 6 H), 1.90 (t, $J = 6.9$ Hz, 2 H), 2.61 (t, $J = 6.9$ Hz, 2 H), 3.04 (t, $J = 8.8$ Hz, 2 H), 3.73 (t, $J = 8.8$ Hz, 2 H), 3.76 (s, 3 H), 3.99 (s, 2 H), 6.69 (d, $J = 7.6$ Hz, 1 H), 7.13 (d, $J = 7.6$ Hz, 1 H). The crude methyl ester was dissolved in MeOH (2 mL) and 4 M aqueous NaOH (1 mL) was added. The solution was stirred at rt for 2 h. The resulting mixture was acidified with 2 M aqueous HCl and extracted with ethyl acetate. The combined extracts were dried (Na_2SO_4) and concentrated to afford the crude carboxylic acid, which was used immediately without further purification. To the crude carboxylic acid was added a solution of acetic anhydride (2 mL) and Et_3N (272 μL , 1.95 mmol). The mixture was heated to reflux for 30 min. The resulting solution was concentrated *in vacuo*. Purification by silica-gel chromatography (ethyl acetate-hexane, 1 : 19) afforded the indole **35** as a white solid: mp 130 – 132 $^\circ\text{C}$ (27.8 mg, 67% 3 steps); ^1H NMR (300 MHz, CDCl_3) δ 1.36 (s, 6 H), 1.85 (t, $J = 6.0$ Hz, 2 H), 2.90 (t, $J = 6.0$ Hz, 2 H), 3.73 (t, $J = 6.7$ Hz, 2 H), 4.39 (t, $J = 6.7$ Hz, 2 H), 6.73 (d, $J = 6.8$ Hz, 1 H), 6.76 (s, 1 H), 6.85 (d, $J = 6.8$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 20.6, 28.4, 34.6, 35.3, 41.9, 52.3, 113.1, 116.5, 119.3, 119.9, 121.1, 121.8, 139.7, 149.7; IR (neat) 2916, 1614 cm^{-1} ; HRMS (MH^+) calcd for $\text{C}_{15}\text{H}_{18}\text{N}$ 212.1434, found 212.1430.