Supplemental Material

A New β-Carbolinone Synthesis Using a Rh(II) Promoted [3+2]-Cycloaddition and Pd(0) Cross-Coupling/Heck Cyclization Chemistry

*Joel M. Harris[†] and Albert Padwa**
Department of Chemistry, Emory University, Atlanta, GA 30322

Supplementary Material

Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70eV. Unless otherwise noted, all reactions were performed in flame dried glassware under an atmosphere of dry nitrogen. Solutions were evaporated under reduced pressure with a rotary evaporator and the residue was chromatographed on a silica gel column using an ethyl acetate-hexane mixture as the eluent unless specified otherwise.

General Procedure for Pd-Catalyzed Couplings of Pyridone Triflates and Anilines/Amide/Carbamate. A flame-dried 10 mL round bottom flask was charged with *tris*(dibenzylideneacetone), dipalladium(0) (4.0 mg, 0.005 mmol, 2.5 mol %), Xantphos (10 mg, 0.02 mmol, 10 mol %), pyridone **21** (0.05 g, 0.18 mmol), and Cs_2CO_3 (0.09 g, 0.27 mmol). The solid reactants were dissolved in 5 mL of dioxane and the appropriate aniline derivative (25 *u*L, 0.27 mmol) was added to the flask. The flask was capped with a condensor and kept under an atmosphere of argon. The reaction was heated at 100 ^{o}C for 1-2 h or until the starting triflate had been completely consumed as judged by TLC. The reaction mixture was then cooled to room temperature, diluted with ethyl acetate, filtered through a pad of celite and concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica gel or florisil to give the 2,3-dihydro-1*H*-indolizin-5-one.

6-Phenylamino-2,3-dihydro-1*H*-indolizin-5-one (15). Recrystallization from hexane gave a cream colored solid; mp 166-168 ^{o}C; IR (thin film) 1645, 1596, 1560, 1497, 1235, and 1143 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.20 (m, 2H), 3.03 (t, 2H, *J* = 7.2

Hz), 4.20 (t, 2H, *J* = 7.2 Hz), 6.06 (d, 1H, *J* = 7.2 Hz), 6.86 (brs, 1H), 6.95 (t, 1H, *J* = 7.8 Hz), 7.11 (d, 1H, *J* = 7.2 Hz), 7.15 (d, 2H, *J* = 7.8 Hz), and 7.29 (t, 2H, *J* = 7.8 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 22.2, 30.7, 48.8, 100.9, 111.9, 118.7, 121.4, 129.2, 131.9, 137.4, 141.7, and 157.3; FAB HRMS Calcd for $[(C_{14}H_{14}N_2O)+Li]^+$: 233.1266. Found 233.1273.

6-(4-Methoxy-phenylamino)-2,3-dihydro-1*H*-indolizin-5-one (16). Recrystallization from hexane gave a tan solid: mp 148-150 °C; IR (KBr) 1645, 1596, 1581, 1440, 1233, 1179, and 1030 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.18 (m, 2H), 3.00 (t, 2H, *J* = 7.2 Hz), 3.79 (s, 3H), 4.18 (t, 2H, *J* = 7.2 Hz), 6.02 (d, 1H, *J* = 7.8 Hz), 6.60 (brs, 1H), 6.84 (d, 1H, *J* = 7.8 Hz), 6.86 (d, 2H, *J* = 9.0 Hz), and 7.10 (d, 2H, *J* = 9.0 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 22.3, 30.6, 48.7, 55.5, 101.0, 110.0, 114.6, 122.2, 133.5, 134.7, 136.4, 155.1, and 156.9; Anal. Calcd. For $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29; N, 10.93. Found: C, 70.05; H, 6.29; N, 10.77.

6-(4-Nitro-phenylamino)-2,3-dihydro-1*H*-indolizin-5-one (17). Recrystallization from ethyl acetate gave a pale yellow solid: mp 238-240 °C; IR (KBr) 1643, 1582, 1558, 1471, 1365, and 1111 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.24 (m, 2H), 3.09 (t, 2H, *J* = 7.2 Hz), 4.21 (t, 2H, *J* = 7.2 Hz), 6.18 (d, 1H, *J* = 7.2 Hz), 7.11 (d, 2H, *J* = 9.0 Hz), 7.32 (d, 1H, *J* = 7.2 Hz), 7.38 (brs, 1H), and 8.15 (d, 2H, *J* = 9.0 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 22.0, 31.1, 49.2, 100.6, 115.2, 118.0, 126.0, 128.8, 140.2, 141.4, 148.2, and 157.3; Anal. Calcd. For $C_{14}H_{13}N_3O_3$: C, 61.99; H, 4.83; N, 15.49. Found: C, 61.62; H, 4.84; N, 15.22.

6-(3,5-Dimethoxy-phenylamino)-2,3-dihydro-1*H*-indolizin-5-one (18) was obtained as a pale yellow oil; IR (thin film) 1646, 1600, 1519, 1441, 1194, and 1160 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.19 (m, 2H), 3.02 (t, 2H, *J* = 7.2 Hz), 3.76 (s, 6H), 4.17 (t, 2H, *J* = 7.2 Hz), 6.06 (d, 1H, *J* = 7.8 Hz), 6.08 (s, 1H), 6.31 (s, 2H), 6.85 (brs, 1H), and 7.15 (d, 1H, *J* = 7.8 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 22.2, 30.7, 48.9, 55.2, 93.3, 96.8, 100.9, 113.2, 131.3, 137.7, 143.6, 157.1, and 161.4; FAB HRMS Calcd for $[(C_{16}H_{18}N_2O_3)+Li]^+$: 293.1477. Found 293.1478.

6-(2-Trifluoromethyl-phenylamino)-2,3-dihydro-1*H*-indolizin-5-one (19) was obtained as a pale yellow oil; IR (thin film) 1651, 1603, 1580, 1522, 1462, 1166, and 1041 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.21 (m, 2H), 3.04 (t, 2H, *J* = 7.2 Hz), 4.20 (t, 2H, *J* = 7.2 Hz), 6.07 (d, 1H, *J* = 7.2 Hz), 7.00 (t, 1H, *J* = 7.8 Hz), 7.07 (d, 1H, *J* = 7.2 Hz), 7.14 (brs, 1H), 7.43 (t, 1H, *J* = 7.8 Hz), 7.49 (d, 1H, *J* = 7.8 Hz), and 7.59 (d, 1H, *J* = 7.8 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 22.2, 30.9, 48.9, 100.5, 114.2, 120.2, 120.9, 124.3 (q, 1C, *J* = 317.7 Hz), 127.0, 127.1, 131.1, 132.5, 139.1, 140.2, 157.3; FAB HRMS Calcd for $[(C_{15}H_{13}F_3N_2O)]^+$: 294.0980. Found 294.0969.

6-(Pyridin-2-ylamino)-2,3-dihydro-1*H*-indolizin-5-one (20). Recrystallization from hexane gave a white solid: mp 208-210 °C; IR (KBr), 1644, 1601, 1571, 1481, 1422, 1368, and 1157 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.18 (m, 2H), 3.04 (t, 2H, *J* = 7.2 Hz), 4.18 (t, 2H, *J* = 7.2 Hz), 6.17 (d, 1H, *J* = 7.2 Hz), 6.77 (dd, 1H, *J* = 7.8 and 4.2 Hz), 6.74 (d, 1H, *J* = 7.8 Hz), 7.47 (ddd, 1H, *J* = 8.4, 7.8, and 1.8 Hz), 7.68 (brs, 1H), 8.23 (d, 1H, *J* = 4.2 Hz), and 8.52 (d, 1H, *J* = 7.8 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 22.1, 30.8, 49.0, 101.5, 111.7, 114.8, 118.2, 129.2, 137.0, 138.6, 147.4, 155.2, 156.9.

6-(2-Bromo-phenylamino)-2,3-dihydro-1*H*-indolizin-5-one (21). Recrystallization from hexane gave a white solid: mp 125-127 °C; IR (KBr) 1649, 1586, 1519, 1440, 1365, 1275, 1181, and 1022 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.21 (m, 2H), 3.04 (t, 2H, *J* = 7.2 Hz), 4.21 (t, 2H, *J* = 7.2 Hz), 6.08 (d, 1H, *J* = 7.8 Hz), 6.79 (t, 1H, *J* = 7.8 Hz), 7.10 (d, 1H, *J* = 7.8 Hz), 7.18 (brs, 1H), 7.23 (t, 1H, *J* = 7.2 Hz), 7.37 (d, 1H, *J* = 7.8 Hz), and 7.56 (d, 1H, *J* = 7.8 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 22.2, 30.9, 48.9, 100.6, 113.9, 114.5, 117.5, 121.9, 127.9, 130.9, 133.3, 138.8, 139.7, 157.3; Anal. Calcd. For $C_{14}H_{13}BrN_2O$: C, 55.10; H, 4.29; N, 9.18. Found: C, 55.05; H, 4.27; N, 8.98.**6-Benzylamino-2,3-dihydro-1*H*-indolizin-5-one (22)** was obtained as a pale yellow oil; IR (thin film) 1646, 1590, 1485, 1453, 1379, and 1223 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.15 (m, 2H), 2.96 (t, 2H, *J* = 7.2 Hz), 4.14 (t, 2H, *J* = 7.2 Hz), 4.32 (s, 2H), 5.25 (brs, 1H), 5.98 (d, 1H, *J* = 7.2 Hz), 6.15 (d, 1H, *J* = 7.2 Hz), and 7.24-7.38 (m, 5H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 22.4, 30.5, 47.7, 48.5, 101.4, 108.5, 127.1, 127.2, 128.5, 135.0,

136.5, 138.8, 156.8; FAB HRMS Calcd for $[(C_{15}H_{16}N_2O)+Li]^+$: 247.1423. Found 247.1412.

***N*-(5-Oxo-1,2,3,5-tetrahydro-indolizin-6-yl)-benzamide (23).** Recrystallization from hexane gave a white solid: mp 140-142 °C; IR (KBr) 1647, 1593, 1522, 1489, 1280, 1186, and 1031 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.23 (m, 2H), 3.09 (t, 2H, *J* = 7.2 Hz), 4.20 (t, 2H, *J* = 7.2 Hz), 6.22 (d, 1H, *J* = 7.6 Hz), 7.50 (m, 3H), 7.92 (m, 2H), 8.55 (d, 1H, *J* = 7.6 Hz), and 9.08 (brs, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.9, 31.1, 49.1, 101.4, 123.3, 126.8, 127.1, 128.7, 131.8, 134.4, 142.7, 156.7, 165.6.

(5-Oxo-1,2,3,5-tetrahydro-indolizin-6-yl)-carbamic Acid Benzyl Ester (24) was obtained as a pale yellow oil; IR (thin film) 1716, 1647, 1581, 1533, 1448, 1362, 1211, and 1065 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.19 (m, 2H), 3.04 (t, 2H, *J* = 7.2 Hz), 4.15 (t, 2H, *J* = 7.2 Hz), 5.19 (s, 2H), 6.14 (d, 1H, *J* = 7.2 Hz), 7.32-7.41 (m, 5H), 7.75 (brs, 1H), and 8.02 (d, 1H, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.9, 31.1, 49.0, 66.9, 101.0, 121.1, 126.7, 128.1, 128.2, 128.5, 136.0, 141.7, 153.4, 156.2; FAB HRMS Calcd for $[(C_{16}H_{16}N_2O_3)+Li]^+$: 291.1232. Found 291.1318.

5-Oxo-6-phenylamino-1,2,3,5-tetrahydro-indolizine-8-carboxylic Acid Methyl Ester. Recrystallization from hexane gave a white solid: mp 170-172 °C; IR (KBr) 1708, 1632, 1590, 1435, 1382, 1181, and 1098 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.23 (m, 2H), 3.48 (t, 2H, *J* = 7.2 Hz), 3.83 (s, 3H), 4.22 (t, 2H, *J* = 7.2 Hz), 6.82 (s, 1H), 7.00 (d, 1H, *J* = 7.2 Hz), 7.19 (d, 2H, *J* = 7.8 Hz), 7.33 (t, 2H, *J* = 8.4 Hz), and 7.62 (s, 1H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 21.3, 32.8, 49.3, 51.7, 105.6, 110.5, 119.1, 122.0, 129.4, 131.5, 141.1, 144.8, 157.6, and 165.8; Anal. Calcd. For $C_{16}H_{16}N_2O_5$: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.19; H, 5.70; N, 9.64.

6-(4-Methoxy-phenylamino)-5-oxo-1,2,3,5-tetrahydro-indolizine-8-carboxylic Acid Methyl Ester was obtained as a pale yellow oil; IR (KBr) 1701, 1636, 1602, 1592, 1440, 1375, and 1098 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.22 (m, 2H), 3.45 (t, 2H, *J* = 7.2 Hz), 3.80 (s, 3H), 4.22 (t, 2H, *J* = 7.2 Hz), 6.57 (s, 1H), 6.90 (d, 2H, *J* = 9.0 Hz), 7.13 (d,

2H, *J* = 9.0 Hz), and 7.34 (t, 2H, *J* = 8.4 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 21.4, 32.7, 49.2, 51.7, 55.5, 105.8, 108.7, 114.7, 122.6, 134.0, 143.9, 155.5, and 165.9.

6-(4-Nitro-phenylamino)-5-oxo-1,2,3,5-tetrahydro-indolizine-8-carboxylic Acid Methyl Ester. Recrystallization from ethyl acetate gave a yelllow solid: mp 232-235 °C; IR (KBr) 1719, 1637, 1596, 1485, 1328, 1268, and 1110 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.27 (m, 2H), 3.53 (t, 2H, *J* = 7.2 Hz), 3.87 (s, 3H), 4.24 (t, 2H, *J* = 7.2 Hz), 7.17 (d, 2H, *J* = 9.0 Hz), 7.35 (s, 1H), 7.84 (s, 1H), and 8.17 (d, 2H, *J* = 9.0 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 21.1, 33.1, 49.6, 52.0, 105.3, 115.7, 116.4, 126.0, 128.5, 140.7, 147.5, 148.1, 157.6, and 165.2.

6-(3,5-Dimethoxy-phenylamino)-5-oxo-1,2,3,5-tetrahydro-indolizine-8-carboxylic Acid Methyl Ester was obtained as a pale yellow oil; IR (thin film) 1711, 1638, 1598, 1377, 1216, 1098, and 1068 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.24 (m, 2H), 3.49 (t, 2H, *J* = 7.2 Hz), 3.79 (s, 6H), 3.83 (s, 3H), 4.22 (t, 2H, *J* = 7.2 Hz), 6.13 (t, 1H, *J* = 1.8 Hz), 6.35 (d, 2H, *J* = 1.8 Hz), 6.79 (s, 1H), and 7.68 (s, 1H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 21.3, 32.8, 49.3, 51.8, 55.3, 94.2, 97.3, 105.6, 111.8, 131.1, 143.0, 145.1, 157.6, 161.5, and 165.8.

5-Oxo-6-(2-trifluoromethyl-phenylamino)-1,2,3,5-tetrahydro-indolizine-8-carboxylic Acid Methyl Ester was obtained as a pale yellow oil; IR (thin film) 1711, 1642, 1585, 1526, 1439, 1274, 1094, and 1035 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.25 (m, 2H), 3.50 (t, 2H, *J* = 7.8 Hz), 3.82 (s, 3H), 4.24 (t, 2H, *J* = 7.8 Hz), 7.08 (dd, 1H, *J* = 8.4 and 6.6 Hz), 7.52 (m, 2H), 7.57 (s, 1H), and 7.63 (d, 1H, *J* = 8.4 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 21.3, 33.0, 49.3, 51.8, 105.3, 112.4, 120.3, 121.8, 124.0 (q, 1C, *J* = 336 Hz), 127.1, 127.2, 131.0, 132.8, 139.5, 146.2, 157.7, and 165.7.

5-Oxo-6-(pyridin-2-ylamino)-1,2,3,5-tetrahydro-indolizine-8-carboxylic Acid Methyl Ester. Recrystallization from ethyl acetate gave a yellow solid: mp 213-215 °C; IR (KBr) 1707, 1635, 1602, 1523, 1378, 1195, and 1095 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.24 (m, 2H), 3.51 (t, 2H, *J* = 7.8 Hz), 3.88 (s, 3H), 4.22 (t, 2H, *J* = 7.8 Hz), 6.78 (m, 2H), 7.52 (ddd,1H, *J* = 9.0 and 1.8 Hz), 7.59 (brs, 1H), 8.31 (d, 1H, *J* = 4.8 Hz), and

9.00 (s, 1H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 21.2, 32.9, 49.4, 51.8, 106.0, 111.6, 115.3, 117.0, 128.7, 137.2, 146.1, 147.7, 154.8, 157.5, and 166.0.

6-(2-Bromo-phenylamino)-5-oxo-1,2,3,5-tetrahydro-indolizine-8-carboxylic Acid Methyl Ester. Recrystallization from hexane gave a white solid: mp 134-136 °C; IR (KBr) 1709, 1639, 1522, 1413, 1269, and 1094 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.25 (m, 2H), 3.49 (t, 2H, *J* = 7.2 Hz), 3.84 (s, 3H), 4.24 (t, 2H, *J* = 7.2 Hz), 6.85 (ddd, 1H, *J* = 7.8, 7.2, and 1.8 Hz), 7.16 (brs, 1H), 7.30 (ddd, 1H, *J* = 7.8, 7.2, and 1.8 Hz), 7.44 (dd, 1H, *J* = 7.8 and 1.8 Hz), 7.58 (dd, 1H, *J* = 8.4 and 1.8 Hz), and 7.62 (s, 1H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 21.2, 32.9, 49.3, 51.8, 105.3, 112.2, 114.8, 118.1, 122.6, 128.2, 130.5, 133.3, 139.1, 146.0, 157.7, and 165.7; Anal. Calcd. For $C_{16}H_{15}BrN_2O_3$: C, 52.91; H, 4.16; N, 7.71. Found: C, 52.71; H, 4.18; N, 7.54.

8-Benzenesulfonyl-6-phenylamino-2,3-dihydro-1*H*-indolizin-5-one was obtained as a pale yellow oil; IR (thin film) 1638, 1589, 1520, 1446, 1150, and 1072 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.23 (m, 2H), 3.42 (t, 2H, *J* = 7.2 Hz), 4.17 (t, 2H, *J* = 7.2 Hz), 6.91 (brs, 1H), 7.06 (t, 1H, *J* = 7.8 Hz), 7.16 (d, 2H, *J* = 7.8 Hz), 7.36 (t, 2H, *J* = 7.8 Hz), 7.49 (s, 1H), 7.55 (m, 3H), and 7.87 (d, 2H, *J* = 8.4 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 21.4, 31.5, 49.4, 107.3, 116.1, 119.4, 122.8, 126.9, 128.5, 129.3, 129.6, 132.5, 140.3, 141.1, 141.9, and 157.1.

8-Benzenesulfonyl-6-(4-methoxy-phenylamino)-2,3-dihydro-1*H*-indolizin-5-one was obtained as a pale yellow oil; IR (thin film) 1636, 1599, 1306, 1151, and 1101 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.21 (m, 2H), 3.39 (t, 2H, *J* = 7.2 Hz), 4.16 (t, 2H, *J* = 7.2 Hz), 6.68 (s, 1H), 6.92 (d, 1H, *J* = 8.4 Hz), 7.11 (d, 1H, *J* = 8.4 Hz), 7.23 (s, 1H), 7.51 (m, 1H), 7.58 (m, 1H), and 7.84 (d, 1H, *J* = 7.2 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 21.5, 31.4, 49.3, 55.6, 105.7, 114.9, 116.3, 122.7, 126.9, 128.3, 129.2, 133.1, 134.1, 140.2, 142.0, 156.0, and 156.9.

8-Benzenesulfonyl-6-(4-nitro-phenylamino)-2,3-dihydro-1*H*-indolizin-5-one was obtained as a pale yellow oil; IR (thin film) 1637, 1593, 1562, 1479, 1321, 1301, and 1112 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.27 (m, 2H), 3.47 (t, 2H, *J* = 7.2 Hz), 4.20 (t, 2H, *J* = 7.2 Hz), 7.17 (d, 2H, *J* = 9.0 Hz), 7.35 (brs, 1H), 7.57 (t, 2H, *J* = 7.8 Hz), 7.64 (t,

1H, *J* = 7.8 Hz), 7.90 (d, 2H, *J* = 7.8 Hz), and 8.23 (d, 2H, *J* = 9.0 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 21.2, 31.8, 49.7, 112.7, 116.0, 116.3, 126.1, 127.0, 129.5, 129.8, 133.5, 141.4, 141.6, 144.4, 146.6, and 157.0.

8-Benzenesulfonyl-6-(3,5-dimethoxy-phenylamino)-2,3-dihydro-1*H*-indolizin-5-one was obtained as a pale yellow oil; IR (thin film) 1638, 1596, 1565, 1480, 1319, 1152, and 1069 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.23 (m, 2H), 3.44 (t, 2H, *J* = 7.2 Hz), 3.79 (s, 6H), 4.16 (t, 2H, *J* = 7.2 Hz), 6.17 (s, 1H), 6.32 (s, 2H), 6.86 (s, 1H), 7.52 (t, 2H, *J* = 7.2 Hz), 7.55 (s, 1H), 7.59 (t, 1H, *J* = 7.2 Hz), and 7.88 (d, 2H, *J* = 7.8 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 21.4, 31.6, 49.4, 55.3, 95.1, 97.6, 108.7, 116.2, 126.9, 129.3, 132.2, 133.2, 141.3, 141.9, 142.1, 157.0, and 161.6.

8-Benzenesulfonyl-6-(2-trifluoromethyl-phenylamino)-2,3-dihydro-1*H*-indolizin-5-one was obtained as a pale yellow oil; IR (thin film) 1644, 1609, 1585, 1461, 1321, 1152, and 1036 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.24 (m, 2H), 3.41 (t, 2H, *J* = 7.2 Hz), 4.19 (t, 2H, *J* = 7.2 Hz), 7.16 (m, 2H), 7.42 (s, 1H), 7.53 (m, 4H), 7.60 (t, 1H, *J* = 7.8 Hz), 7.66 (d, 1H, *J* = 7.8 Hz), and 7.84 (m, 2H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 21.4, 31.6, 49.4, 108.9, 115.8, 120.9, 121.6, 122.8, 124.0 (q, 1C, *J* = 317.7 Hz), 126.9, 127.3, 129.4, 132.2, 133.0, 133.3, 138.7, 141.8, 142.6, and 157.0.

8-Benzenesulfonyl-6-(pyridin-2-ylamino)-2,3-dihydro-1*H*-indolizin-5-one. Recrystallization from hexane gave a white solid: mp 218-220 ^{o}C; IR (KBr) 1642, 1591, 1520, 1475, 1317, and 1150 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.23 (m, 2H), 3.46 (t, 2H, *J* = 7.2 Hz), 4.21 (t, 2H, *J* = 7.2 Hz), 6.76 (d, 1H, *J* = 9.0 Hz), 6.81 (dd, 1H, *J* = 7.2 and 5.4 Hz), 7.52 (m, 3H), 7.58 (m, 1H), 7.63 (brs, 1H), 7.96 (d, 2H, *J* = 7.8 Hz), 8.33 (dd, 1H, *J* = 4.8 and 1.8 Hz) and 9.11 (s, 1H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 21.2, 31.7, 49.5, 111.7, 114.6, 115.8, 116.6, 127.1, 129.2, 129.7, 133.1, 137.2, 142.0, 142.3, 147.8, 154.4, and 156.9.

1,2,3,6-Tetrahydro-indolizino[6,7-*b*]indol-5-one (26). A flame-dried 20 mL heavy-walled pyrex tube was charged with $Pd(PPh_3)_4$ (0.03 g, 0.02 mmol, 10 mol %), pyridone **21** (0.07 g, 0.23 mmol), and Cs_2CO_3 (0.11 g, 0.34 mmol). The solid reactants were dissolved in 4 mL of dioxane and the tube was sealed with a teflon screw cap. The

reaction was heated at 110 °C for 24 h in an oil bath. The reaction mixture was cooled to room temperature, diluted with ethyl acetate, filtered through a pad of celite, and concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica gel to give β-carbolinone **26** (0.03 g, 0.15 mmol) in 65% yield. Recrystallization from hexane gave a white solid: mp 170-172 °C; IR (KBr) 1661, 1594, 1566, 1301, and 1255 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.31 (m, 2H), 3.21 (t, 2H, *J* = 7.2 Hz), 4.35 (t, 2H, *J* = 7.2 Hz), 6.87 (s, 1H), 7.22 (t, 1H, *J* = 7.8 Hz), 7.45 (t, 1H, *J* = 7.2 Hz), 7.58 (d, 1H, *J* = 8.4 Hz), 7.92 (d, 1H, *J* = 7.8 Hz), and 10.09 (brs, 1H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 22.8, 31.1, 48.1, 95.7, 112.4, 119.8, 121.2, 122.2, 126.4 (2C), 126.8, 139.7, 140.2, and 159.5; FAB HRMS Calcd for $[(C_{14}H_{12}N_2O)+Li]^+$: 231.1110. Found 231.1109.

5-Oxo-2,3,5,6-tetrahydro-1*H*-indolizino[6,7-*b*]indole-11-carboxylic Acid Methyl Ester (27). A flame-dried 20 mL heavy-walled pyrex tube was charged with $Pd(PPh_3)_4$ (0.06 g, 0.05 mmol, 10 mol %), pyridone **25** (0.18 g, 0.5 mmol), and Cs_2CO_3 (0.24 g, 0.74 mmol). The solid reactants were dissolved in 5 mL of dioxane and the tube was sealed with a teflon screw cap. The reaction was heated at 110 °C for 24 h in an oil bath. The reaction mixture was cooled to room temperature, diluted with ethyl acetate, filtered through a pad of celite, and concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica gel to give β-carbolinone **27** (0.09 g, 0.3 mmol) in 65% yield. Recrystallization from hexane gave a white solid: mp >250 °C; IR (KBr) 1707, 1655, 1555, 1383, 1307, and 1143 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6) δ 2.19 (m, 2H), 3.45 (t, 2H, *J* = 7.2 Hz), 3.94 (s, 3H), 4.18 (t, 2H, *J* = 7.2 Hz), 7.14 (ddd, 1H, *J* = 8.4 and 2.4 Hz), 7.40 (ddd, 1H, *J* = 8.4 and 2.4 Hz), 7.51 (d, 1H, *J* = 8.4 Hz), 8.35 (d, 1H, *J* = 8.4 Hz), and 12.18 (brs, 1H); ^{13}C-NMR (150 MHz, DMSO-d_6) δ 21.5, 32.2, 49.4, 52.1, 102.1, 112.0, 113.1, 119.0, 120.1, 121.2, 125.3, 126.7, 140.0, 147.3, 154.0, and 166.5; FAB HRMS Calcd for $[(C_{16}H_{14}N_2O_3)+Li]^+$: 289.1164. Found 289.1151.