Supporting Information

Ruthenium-catalyzed Oxidative Dearomatization of Indoles for the Construction of C2-Quaternary Indolin-3-ones

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General: The chemical shifts for ¹H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard. The chemical shifts for ¹³C NMR were recorded in ppm downfield using the central peak of d-dimethyl sulfoxide (39.6 ppm) or d-chloroform (77.23 ppm) as the internal standard. Coupling constants (J) are reported in Hz and refer to apparent peak multiplications. Flash column chromatography was performed on silica gel (200-300 mesh). TLC analysis was performed using glass-backed plates coated with 0.2 mm silica.

Materials: All commercially available reagents were used without further purification. The starting materials 1a-1o are commercially available.

2. The Typical Procedure for Ru-Catalyzed Oxidative Dearomatization of Indoles
A mixture of indole 1 (0.50 mmol), NaIO₄ (107 mg, 0.50 mmol, 1.0 equiv) and RuCl₃·3H₂O (6.5 mg, 0.025 mmol, 5.0 mol%) in CH₃CN (3 mL) was added into a Schlenk flask (25 mL) and stirred at room temperature. The mixture was stirred at 70 °C until the reaction was finished. Then the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (petroleum ether/ethyl acetate 10:1 to 5:1).

2-phenyl-2-(2-phenyl-1H-indol-3-yl)indolin-3-one (2a). Yield: 97%, 97.0 mg, yellow solid, mp 220-223 °C. ¹H NMR (500 MHz, DMSO) δ 11.34 (s, 1H), 8.33 (s, 1H), 7.51 (dd, J = 8.3, 7.1 Hz, 1H), 7.39-7.33 (m, 3H), 7.25 (d, J = 7.7 Hz, 1H), 7.16-7.11 (m, 3H), 7.06-7.01 (m, 6H), 6.98 (d, J = 8.3 Hz, 1H), 6.78-6.69 (m, 2H), 6.61 (d, J = 8.0 Hz, 1H); ¹³C NMR (126 MHz, DMSO) δ 200.5, 160.1, 139.8, 138.0, 137.5, 135.8, 133.2, 129.5, 127.6, 127.4, 127.0, 124.4, 121.2, 120.3, 118.7, 118.5, 117.5, 111.9, 111.3, 111.0, 71.2; IR (neat): ν_{max} 3058, 3025, 2910, 1696, 1618, 1470, 1439, 1074, 1026, 919, 742 cm⁻¹; HRMS (ESI) m/z: Calcd for C₂₈H₂₀N₂ONa: 423.1473 [M+Na]⁺; found: 423.1477.
2-((p-tolyl)-2-(p-tolyl)-1H-indol-3-yl)indolin-3-one (2b). Yield: 85%, 90.6 mg, yellow solid, mp 233-235 °C. $^1$H NMR (500 MHz, DMSO) $\delta$ 11.25 (s, 1H), 8.26 (s, 1H), 7.49-7.47 (m, 1H), 7.32 (d, $J = 8.1$ Hz, 1H), 7.25-7.20 (m, 2H), 7.02-6.99 (m, 2H), 6.95 (d, $J = 8.2$ Hz, 1H), 6.86 (t, $J = 8.2$ Hz, 4H), 6.75-6.68 (m, 3H), 6.61 (d, $J = 7.8$ Hz, 1H), 6.57 (d, $J = 8.2$ Hz, 1H), 2.21 (s, 3H), 2.15 (s, 3H). $^{13}$C NMR (126 MHz, DMSO) $\delta$ 200.5, 159.9, 137.8, 137.3, 136.9, 136.5, 136.1, 135.7, 130.4, 129.4, 128.2, 127.6, 127.0, 124.4, 121.0, 120.3, 118.6, 117.3, 111.8, 111.1, 110.8, 71.0, 20.8, 20.5; IR (neat): $\nu_{max}$ 3055, 2912, 1682, 1629, 1471, 1439, 1336, 1187, 1026, 968, 749 cm$^{-1}$; HRMS (ESI) m/z: Calcd for C$_{30}$H$_{24}$N$_2$O$_2$Na: 451.1786 [M+Na]$^+$; found: 451.1791.

2-((4-ethylphenyl)-2-(4-ethylphenyl)-1H-indol-3-yl)indolin-3-one (2c). Yield: 75%, 85.6 mg, yellow solid, mp 237-239 °C. $^1$H NMR (500 MHz, DMSO) $\delta$
MHz, DMSO) δ 11.29 (s, 1H), 8.32 (s, 1H), 7.53 (dd, J = 8.3, 7.1 Hz, 1H), 7.36 (d, J = 8.1 Hz, 1H), 7.30 (d, J = 8.3 Hz, 3H), 7.08-7.03 (m, 3H), 6.99 (d, J = 8.2 Hz, 1H), 6.89 (t, J = 8.1 Hz, 4H), 6.72-6.78 (m, 2H), 6.67 (d, J = 8.2 Hz, 1H), 2.53-2.44 (m, 4H), 1.15-1.05 (m, 6H). 13C NMR (126 MHz, DMSO) δ 200.8, 160.1, 142.7, 142.4, 138.2, 137.4, 136.8, 135.7, 130.5, 129.5, 127.4, 127.1, 126.9, 126.4, 124.4, 121.0, 120.2, 118.6, 118.4, 117.4, 111.8, 111.2, 111.0, 71.0, 27.9, 27.7, 15.7; IR (neat): νmax 3053, 2922, 1716, 1692, 1619, 1501, 1433, 1074, 812, 759 cm⁻¹; HRMS (ESI) m/z: Calcd for C32H28N2O4Na: 479.2099 [M+Na]+; found: 479.2093.

2-(4-fluorophenyl)-2-(2-(4-fluorophenyl)-1H-indol-3-yl)indolin-3-one (2d). Yield: 85%, 92.6 mg, yellow solid, mp 231-233 °C. 1H NMR (500 MHz, DMSO) δ 11.40 (s, 1H), 8.38 (s, 1H), 7.54-7.51 (m, 1H), 7.39-7.31 (m, 4H), 7.19-7.16 (m, 2H), 7.04 (dd, J = 11.6, 4.5 Hz, 1H), 6.98 (d, J = 8.3 Hz, 1H), 6.92-6.73 (m, 6H), 6.67 (d, J = 8.1 Hz, 1H). 13C NMR (126 MHz, DMSO) δ 201.2, 162.9, 160.9, 160.7, 138.2, 137.5, 136.1, 132.2, 129.9, 129.5, 127.4, 124.9, 121.8, 120.5, 119.4, 118.6, 118.3, 114.8, 114.6, 114.3, 112.4, 111.8, 71.0, 40.5, 40.2, 40.0, 39.8, 39.6, 39.5. 19F NMR (470 MHz, DMSO) δ -114.40 (m), -116.04 (m); IR (neat): νmax 3052, 2911, 1676, 1630, 1501, 1438, 1325, 1189, 968, 808, 761 cm⁻¹;
HRMS (ESI) m/z: Calcd for C_{28}H_{18}F_{2}N_{2}O_{Na}: 459.1285 [M+Na]^+; found: 459.1286.

2-methyl-2-(2-methyl-1H-indol-3-yl)indolin-3-one (2e). Yield: 85%, 59.0 mg, yellow solid, mp 151–153 °C. $^1$H NMR (500 MHz, DMSO) $\delta$ 10.88 (s, 1H), 7.72 (s, 1H), 7.50-7.44 (m, 2H), 7.22 (dd, $J = 12.0, 8.1$ Hz, 2H), 6.95-6.91 (m, 1H), 6.87 (d, $J = 8.3$ Hz, 1H), 6.78 (dd, $J = 8.1, 7.1$, 1H), 6.72-6.69 (m, 1H), 2.39 (s, 3H), 1.73 (s, 3H). $^{13}$C NMR (126 MHz, DMSO) $\delta$ 203.9, 150.0, 137.5, 134.7, 133.0, 127.2, 124.4, 120.0, 119.4, 118.4, 117.7, 117.0, 111.8, 110.5, 108.5, 66.3, 40.0, 39.8, 39.7, 39.5, 39.3, 39.2, 39.0, 24.4, 14.0; IR (neat): $\nu_{\text{max}}$ 3025, 2920, 1693, 1620, 1492, 1435, 1317, 1074, 1040, 920, 870, 819, 743, 702 cm$^{-1}$; HRMS (ESI) m/z: Calcd for C_{18}H_{16}N_{2}O_{Na}: 299.1160 [M+Na]^+; found: 299.1164.

2-(2,5-dimethyl-1H-indol-3-yl)-2,5-dimethylindolin-3-one (2f). Yield: 82%, 62.0 mg, yellow solid, mp 159-161 °C. $^1$H NMR (400 MHz, DMSO) $\delta$ 10.73 (s, 1H), 7.44 (s, 1H), 7.32 (d, $J = 8.4$ Hz, 1H), 7.25 (s, 1H), 7.10 (d, $J = 8.4$ Hz, 2H), 6.81 (d, $J = 8.3$ Hz, 1H), 6.76 (d, $J = 8.5$ Hz, 1H), 2.32 (s, 3H), 2.23 (s, 3H), 2.22 (s, 3H), 1.72 (s, 3H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 204.4, 159.0, 139.2, 133.5, 133.2, 127.9, 126.8, 126.2,
123.9, 121.8, 119.8, 118.3, 112.3, 110.6, 108.7, 67.1, 25.0, 22.0, 20.6, 14.4; IR (neat): \( \nu_{\text{max}} \) 3034, 2969, 2914, 2868, 1681, 1632, 1492, 1441, 1332, 1187, 1073, 1041, 968, 867, 798, 674 cm\(^{-1}\); HRMS (ESI) m/z: Calcd for \( \text{C}_{20}\text{H}_{20}\text{N}_{2}\text{O}_{3} \text{Na} \): 359.1372 \([\text{M+Na}]^+\); found: 359.1377.

5-methoxy-2-(5-methoxy-2-methyl-1H-indol-3-yl)-2-methylindolin-3-one (2g). Yield: 67%, 56.7 mg, yellow solid, mp 176-178 °C. \(^1\)H NMR (500 MHz, DMSO) \( \delta \) 10.69 (s, 1H), 7.30 (s, 1H), 7.20 (dd, \( J = 8.8, 2.7 \) Hz, 1H), 7.10-7.08 (m, 1H), 6.93 (d, \( J = 2.7 \) Hz, 1H), 6.88 (dd, \( J = 8.8, 0.5 \) Hz, 1H), 6.66 (d, \( J = 2.3 \) Hz, 1H), 6.59-6.57 (m, 1H), 3.71 (s, 3H), 3.51 (s, 3H), 2.37 (s, 3H), 1.70 (s, 3H). \(^{13}\)C NMR (126 MHz, DMSO) \( \delta \) 204.3, 156.2, 152.6, 151.7, 133.8, 129.9, 127.8, 127.5, 117.8, 113.5, 110.9, 109.2, 108.5, 104.4, 102.3, 67.2, 55.5, 54.9, 24.4, 14.2; IR (neat): \( \nu_{\text{max}} \) 3069, 3005, 2940, 2912, 2836, 1639, 1605, 1494, 1439, 1282, 1243, 1074, 1029, 920, 862, 840 cm\(^{-1}\); HRMS (ESI) m/z: Calcd for \( \text{C}_{20}\text{H}_{20}\text{N}_{2}\text{O}_{3}\text{Na} \): 359.1372 \([\text{M+Na}]^+\); found: 359.1377.
5-chloro-2-(5-chloro-2-methyl-1H-indol-3-yl)-2-methyldolin-3-one (2h). Yield: 79%, 67.8 mg, yellow solid, mp 180–182 °C. \(^1\)H NMR (500 MHz, DMSO) \(\delta\) 7.95 (s, 1H), 7.48 (dd, \(J = 8.7, 2.3\) Hz, 1H), 7.42 (d, \(J = 2.0\) Hz, 1H), 7.29 (d, \(J = 1.9\) Hz, 1H), 7.22 (d, \(J = 8.6\) Hz, 1H), 6.93 (dd, \(J = 8.6, 2.2\) Hz, 2H), 2.39 (s, 3H), 1.73 (s, 3H). \(^{13}\)C NMR (126 MHz, DMSO) \(\delta\) 202.5, 158.3, 137.2, 135.1, 133.2, 128.0, 123.4, 123.1, 120.9, 119.9, 118.5, 113.5, 111.9, 108.0, 79.2, 78.9, 78.6, 67.0, 40.0, 39.8, 39.7, 39.5, 39.3, 39.2, 39.0, 24.1, 14.0; IR (neat): \(\nu_{\text{max}}\) 3076, 3020, 2981, 2909, 1720, 1638, 1474, 1444, 1330, 1053, 921, 752 cm\(^{-1}\); HRMS (ESI) m/z: Calcd for C\(_{18}\)H\(_{14}\)Cl\(_2\)N\(_2\)O\(_2\)Na: 367.0381 [M]\(^+\); found: 367.0384.

![](image)

1-methyl-2-(1-methyl-2-phenyl-1H-indol-3-yl)-2-phenylindolin-3-one (2i). Yield: 87%, 93.1 mg, yellow solid, mp 235-237 °C (lit.\(^3\) mp. = 230-233 °C). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.40-7.10 (m, 12H), 6.91-6.86 (m, 2H), 6.79 (d, \(J = 7.6\) Hz, 1H), 6.62 (d, \(J = 8.1\) Hz, 1H), 6.56-6.50 (m, 2H), 3.43 (s, 3H), 2.76 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 200.1, 159.4, 140.0, 138.5, 137.2, 136.8, 131.4, 130.7, 128.3, 127.6, 127.0, 125.2, 121.9, 121.6, 119.5, 116.4, 109.8, 109.5, 107.8, 76.2, 30.6, 29.7; IR (neat): \(\nu_{\text{max}}\) 3059, 2924, 1704, 1615, 1491, 1467, 1446, 1371, 1321, 1160, 978, 740, 701 cm\(^{-1}\); HRMS (ESI) (ESI) m/z: Calcd for C\(_{30}\)H\(_{24}\)N\(_2\)O\(_2\): 451.1786 [M+Na]\(^+\); found: 451.1781.
1-ethyl-2-(1-ethyl-2-phenyl-1H-indol-3-yl)-2-phenylindolin-3-one (2j). Yield: 82%, 93.8 mg, yellow solid, mp 167-169 °C. $^1$H NMR (500 MHz, DMSO) $\delta$ 7.49-7.43 (m, 2H), 7.25-7.24 (m, 7H), 7.10-7.06 (m, 2H), 6.97 (m, 3H), 6.78 (t, $J = 7.2$ Hz, 1H), 6.68 (d, $J = 8.3$ Hz, 1H), 6.56-6.50 (m, 2H), 3.88 (q, $J = 7.2$ Hz, 2H), 3.58-3.53 (m, 1H), 3.04-3.02 (m, 1H), 1.02 (t, $J = 7.1$ Hz, 3H), 0.47 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (126 MHz, DMSO) $\delta$ 199.2, 158.1, 139.2, 137.9, 135.8, 131.5, 131.3, 130.5, 128.9, 128.7, 128.4, 128.1, 127.9, 127.4, 124.8, 121.7, 119.5, 118.8, 116.6, 110.6, 110.1, 108.9, 75.9, 38.4, 38.3, 15.5, 13.0; IR (neat): $\nu_{\text{max}}$ 3006, 2941, 2910, 2836, 1686, 1631, 1605, 1495, 1440, 1243, 1185, 1028, 969, 864 cm$^{-1}$; HRMS (ESI) m/z: Calcd for C$_{32}$H$_{28}$N$_2$O$_3$: 479.2099 [M+Na]$^+$; found: 479.2102.

2-(1,2-dimethyl-1H-indol-3-yl)-1,2-dimethyldindolin-3-one (2k). Yield: 81%, 61.7 mg, yellow solid, mp 160–162 °C (lit.$^3$ mp. = 153-155 °C). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.67 (dd, $J = 7.7$, 0.6 Hz, 1H), 7.54-7.50 (m, 1H), 7.43 (d, $J = 8.1$ Hz, 1H), 7.24-7.22 (m, 1H), 7.13-7.09 (m, 1H), 6.98-6.94 (m, 1H), 6.78-6.72 (m, 2H), 3.61 (s, 3H), 2.86 (s, 3H), 2.27 (s, 3H), 1.89 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 203.8, 158.9, 137.7,
136.8, 135.6, 127.3, 125.5, 120.7, 119.6, 118.4, 116.8, 109.0, 108.1, 106.7, 100.0, 71.2, 29.5, 27.8, 22.0, 11.9; IR (neat): $\nu_{\text{max}}$ 3077, 3002, 2935, 2909, 2839, 1692, 1619, 1508, 1464, 1439, 1381, 1259, 1219, 1165, 1075, 1032, 967, 924, 852, 801 cm$^{-1}$; HRMS (ESI) m/z: Calcd for C$_{20}$H$_{20}$N$_2$O$_2$Na: 327.1473 [M+Na]$^+$; found: 327.1471.
3. Copy of NMR for the Oxidative Dearomatization Products