

# Construction of 3-Oxyindoles via Hypervalent Iodine Mediated Tandem Cyclization Acetoxylation of *o*-Acyl Anilines

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## **Supporting Information**

1. General experimental methods (S2)
2. General experimental procedure and characterization data. (S2-S7)
3. Copies of  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra of products (S8-S51)

### General experimental methods:

Flash column chromatography was performed using silica gel (60-Å pore size, 32–63 µm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr (house vacuum) at 25–35 °C. Commercial reagents and solvents were used as received. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale.

### Representative experimental procedure:

The mixture of **1a** (61 mg, 0.2 mmol), PhI(OAc)<sub>2</sub> (193 mg, 0.6 mmol), and NaOAc (16 mg, 0.2 mmol) in dioxane (1 mL) was treated with Bu<sub>4</sub>NI (185 mg, 0.5 mmol). The reaction was allowed to stir at 25 °C for 1 h. Upon completion by TLC, the reaction mixture was quenched with saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (25 mL), and extracted by ethyl acetate (25 mL x 3). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (15% ethyl acetate in hexanes) to provide 2-methyl-3-oxo-1-tosylindolin-2-yl acetate **3a** in 89% yield.

**2-methyl-3-oxo-1-tosylindolin-2-yl acetate 3a:** white solid, m.p. 159-162°C: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 8.2 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.18 (t, *J* = 8.1 Hz, 1H), 2.39 (s, 3H), 1.86 (s, 3H), 1.81 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 193.8, 168.4, 150.3, 144.9, 137.5, 137.3, 129.9, 126.8, 124.8, 123.7, 121.4, 114.3, 90.6, 22.5, 21.6, 20.1; IR (KBr) cm<sup>-1</sup>: 3021, 2835, 2765, 1751, 1684, 1653, 1616, 1506; HRMS *m/z* calcd for C<sub>18</sub>H<sub>17</sub>O<sub>5</sub>NSNa ([M+Na]<sup>+</sup>): 382.0725, found 382.0719.

**2,5-dimethyl-3-oxo-1-tosylindolin-2-yl acetate 3g:** white solid, m.p. 146-147°C: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.83 (d, *J* = 8.3 Hz, 1 H), 7.78 (d, *J* = 8.2 Hz, 2 H), 7.52 (s, 1H), 7.46 (d, *J* = 8.3 Hz, 1 H), 7.26 (d, *J* = 8.3 Hz, 2 H), 2.39 (s, 3 H), 2.35 (s, 3 H), 1.82 (s, 3 H), 1.80 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 193.8, 168.3, 148.4, 144.7, 138.5, 137.4, 133.7, 129.9, 126.8, 124.5, 121.4, 114.1, 90.7, 22.5, 21.4 20.6, 20.2; IR (KBr) cm<sup>-1</sup>: 3010, 2828, 2799, 1749, 1720, 1635, 1538; HRMS *m/z* calcd for C<sub>17</sub>H<sub>17</sub>O<sub>3</sub>NSNa ([M+Na]<sup>+</sup>): 338.0827, found 338.0826.

**5-isopropyl-2-methyl-3-oxo-1-tosylindolin-2-yl acetate 3h:** white solid, m.p. 150-151°C:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79-7.85 (m, 3 H), 7.59 (s, 1 H), 7.53 (d,  $J = 8.3$  Hz, 1 H), 7.27 (d,  $J = 8.3$  Hz, 2 H), 2.93 (m, 1 H), 2.39 (s, 3 H), 1.83 (s, 3 H), 1.82 (s, 3 H), 1.24 (d,  $J = 6.8$  Hz, 6 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  194.0, 168.4, 148.5, 144.8, 144.6, 137.4, 136.5, 129.9, 126.8, 121.8, 121.4, 114.1, 90.9, 33.4, 23.9, 22.5, 21.6, 20.2; IR (KBr)  $\text{cm}^{-1}$ : 3205, 2820, 2793, 2722, 1740, 1640, 1472, 1380; HRMS  $m/z$  calcd for  $\text{C}_{21}\text{H}_{23}\text{O}_5\text{NSNa}$  ( $[\text{M}+\text{Na}]^+$ ): 424.1195, found 424.1187.

**5-methoxy-2-methyl-3-oxo-1-tosylindolin-2-yl acetate 3i:** white solid, m.p. 157-158°C:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J = 8.8$  Hz, 1 H), 7.77 (d,  $J = 8.2$  Hz, 2 H), 7.23-7.27 (m, 3 H), 7.16 (s, 1 H), 3.81 (s, 3 H), 2.39 (s, 3 H), 1.81 (s, 3 H), 1.80 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  193.9, 168.3, 156.3, 144.8, 144.7, 137.4, 129.9, 126.7, 126.2, 122.0, 115.6, 105.8, 90.9, 55.9, 22.5, 21.6, 20.2; IR (KBr)  $\text{cm}^{-1}$ : 3105, 2905, 2852, 1748, 1617, 1478, 1375; HRMS  $m/z$  calcd for  $\text{C}_{19}\text{H}_{19}\text{O}_6\text{NSNa}$  ( $[\text{M}+\text{Na}]^+$ ): 412.0831, found 412.0824.

**5-chloro-2-methyl-3-oxo-1-tosylindolin-2-yl acetate 3j:** white solid, m.p. 158-160°C:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (d,  $J = 8.7$  Hz, 1 H), 7.77 (d,  $J = 8.3$  Hz, 2 H), 7.68 (s, 1 H), 7.59 (d,  $J = 8.7$  Hz, 1 H), 7.28 (d,  $J = 8.3$  Hz, 2 H), 2.40 (s, 3 H), 1.83 (s, 3 H), 1.79 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  192.7, 168.4, 148.6, 145.2, 137.1, 137.1, 130.0, 129.5, 126.8, 124.3, 122.7, 115.6, 90.8, 22.5, 21.7, 20.1; IR (KBr)  $\text{cm}^{-1}$ : 3120, 2830, 2750, 2605, 1740, 1640, 1452; HRMS  $m/z$  calcd for  $\text{C}_{18}\text{H}_{16}\text{O}_5\text{ClNSNa}$  ( $[\text{M}+\text{Na}]^+$ ): 416.0335, found 416.0322.

**5-bromo-2-methyl-3-oxo-1-tosylindolin-2-yl acetate 3k:** white solid, m.p. 155-156°C:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (d,  $J = 8.8$  Hz, 1 H), 7.83 (s, 1 H), 7.76 (d,  $J = 8.2$  Hz, 2 H), 7.73 (d,  $J = 8.7$  Hz, 1 H), 7.27 (d,  $J = 8.3$  Hz, 2 H), 2.40 (s, 3 H), 1.82 (s, 3 H), 1.79 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  192.5, 168.4, 149.1, 145.2, 139.9, 137.0, 130.0, 127.3, 126.8, 123.1, 116.6, 116.0, 90.7, 22.4, 21.7, 20.0; IR (KBr)  $\text{cm}^{-1}$ : 3105, 2790, 2782, 1765, 1650, 1430; HRMS  $m/z$  calcd for  $\text{C}_{18}\text{H}_{16}\text{O}_5\text{BrNSNa}$  ( $[\text{M}+\text{Na}]^+$ ): 459.9830, found 459.9824.

**3-oxo-1-tosylindolin-2-yl acetate 3l:** white solid, m.p. 154-156°C:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J = 8.2$  Hz, 1 H), 7.78 (d,  $J = 8.2$  Hz, 2 H), 7.64-7.71 (m, 2 H), 7.29 (d,  $J = 8.3$  Hz, 2 H), 7.21 (t,  $J = 7.3$  Hz, 1 H), 6.20 (s, 1 H), 2.39 (s, 3 H), 2.19 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  191.3, 169.1, 152.1, 145.6, 138.1, 133.8, 130.3, 127.5, 125.1, 124.8, 122.2, 115.8, 79.6

21.7, 20.6; IR (KBr)  $\text{cm}^{-1}$ : 3032, 2836, 2788, 2671, 1756, 1734, 1540, 1469; HRMS  $m/z$  calcd for  $\text{C}_{17}\text{H}_{15}\text{O}_5\text{NSNa}$  ( $[\text{M}+\text{Na}]^+$ ): 368.0569, found 368.0568.

**2-benzyl-5-methyl-3-oxo-1-tosylindolin-2-yl acetate 3m**: white solid, m.p. 171-172°C:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72-7.77 (m, 3 H), 7.12-7.31 (m, 6 H), 7.05-7.11 (m, 3 H), 4.09 (d,  $J = 12.9$  Hz, 1 H), 3.36 (d,  $J = 13.2$  Hz, 1 H), 2.37 (s, 3 H), 2.21 (s, 3 H), 1.69 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  194.0, 167.9, 149.2, 144.6, 138.1, 137.6, 133.1, 131.2, 130.9, 129.7, 128.0, 127.2, 126.5, 123.5, 122.7, 113.3, 93.0, 41.6, 21.5, 20.4, 20.2; IR (KBr)  $\text{cm}^{-1}$ : 3055, 2980, 2870, 2605, 1740, 1690, 1430, 1240; HRMS  $m/z$  calcd for  $\text{C}_{25}\text{H}_{23}\text{O}_5\text{NSNa}$  ( $[\text{M}+\text{Na}]^+$ ): 472.1195, found 472.1176.

**2,5-dimethyl-1-tosylindolin-3-one 2g**: white solid, m.p. 143-144°C :  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 8.2$  Hz, 1 H), 7.63 (d,  $J = 8.2$  Hz, 2 H), 7.50 (d,  $J = 8.3$  Hz, 2 H), 7.21 (d,  $J = 8.2$  Hz, 2 H), 3.93 (q,  $J = 6.8$  Hz, 1 H), 2.35 (s, 6 H), 1.65 (d,  $J = 6.8$  Hz, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.7, 151.0, 144.9, 138.6, 134.7, 133.4, 130.0, 127.3, 124.3, 116.8, 63.7, 21.6, 20.7, 18.0; IR (KBr)  $\text{cm}^{-1}$ : 3049, 2840, 2773, 2689, 1720, 1683, 1506; HRMS  $m/z$  calcd for  $\text{C}_{17}\text{H}_{17}\text{O}_3\text{NSNa}$  ( $[\text{M}+\text{Na}]^+$ ): 338.0827, found 338.0826.

**Diethyl-2-(2-(4-methylphenylsulfonamido)benzoyl)-3-phenylcyclopropane-1,1-dicarboxylate 4n**: colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  11.04 (s, 1 H), 8.12 (d,  $J = 8.3$  Hz, 1 H), 7.70-7.72 (m, 3 H), 7.49 (t,  $J = 7.3$  Hz, 1 H), 7.28 (t,  $J = 7.3$  Hz, 2 H), 7.14-7.26 (m, 6 H), 4.07-4.10 (m, 2 H), 3.95-4.01 (m, 3 H), 3.81 (d,  $J = 7.3$  Hz, 1 H), 2.29 (s, 3 H), 1.05 (t,  $J = 7.3$  Hz, 3 H), 0.96 (t,  $J = 7.3$  Hz, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.0, 165.7, 165.4, 144.0, 140.0, 136.4, 135.4, 133.0, 131.9, 129.7, 128.5, 127.9, 127.4, 123.2, 122.7, 119.5, 62.2, 62.1, 46.5, 36.0, 35.8, 21.5, 13.9, 13.8; IR (KBr)  $\text{cm}^{-1}$ : 3430, 3020, 2960, 2850, 1760, 1735, 1680, 1660, 1480, 1260, 1240; HRMS  $m/z$  calcd for  $\text{C}_{29}\text{H}_{29}\text{O}_7\text{NSNa}$  ( $[\text{M}+\text{Na}]^+$ ): 558.1562, found 558.1546.

**2-phenyl-1-tosylindolin-3-one 5a**: white solid, m.p. 132-133°C:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (d,  $J = 8.3$  Hz, 1H), 7.72 (t,  $J = 8.2$  Hz, 1 H), 7.64 (d,  $J = 7.8$  Hz, 1 H), 7.57 (d,  $J = 8.3$  Hz, 2 H), 7.31-7.35 (m, 5 H), 7.18-7.23 (m, 3 H), 5.02 (s, 1 H), 2.36 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.7, 153.6, 145.0, 137.5, 134.5, 134.1, 130.0, 128.9, 128.6, 127.3, 127.0, 125.3,

124.7, 123.8, 116.5, 70.2, 21.6; IR (KBr)  $\text{cm}^{-1}$ : 3050, 2940, 2860, 2750, 1730, 1460; HRMS  $m/z$  calcd for  $\text{C}_{21}\text{H}_{17}\text{O}_3\text{NSNa}$  ( $[\text{M}+\text{Na}]^+$ ): 386.0827, found 386.0828.

**2-o-tolyl-1-tosylindolin-3-one 5b-1** and **2-p-tolyl-1-tosylindolin-3-one 5b-2**: white solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 (d,  $J = 8.2$  Hz, 1 H), 7.63-7.74 (m, 2 H), 7.53-7.58 (m, 2 H), 7.17-7.25 (m, 5 H), 7.01-7.14 (m, 2 H), 5.33 (s, 0.4 H), 4.98 (s, 0.6 H), 2.41 (s, 1.2 H), 2.35 (s, 3 H), 2.32 (s, 1.8 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.0, 196.0, 153.6, 145.0, 138.5, 137.5, 137.4, 136.6, 134.3, 134.1, 133.1, 131.5, 131.2, 129.9, 129.9, 129.6, 128.5, 127.3, 127.2, 127.0, 126.3, 125.3, 125.1, 124.6, 124.5, 123.8, 116.5, 116.2, 70.1, 67.9, 21.6, 21.3, 19.8; IR (KBr)  $\text{cm}^{-1}$ : 3105, 2980, 2850, 1740, 1650, 1450; HRMS  $m/z$  calcd for  $\text{C}_{22}\text{H}_{19}\text{O}_3\text{NSNa}$  ( $[\text{M}+\text{Na}]^+$ ): 400.0983, found 400.0983.

**2-(2-methoxyphenyl)-1-tosylindolin-3-one 5c-1** and **2-(4-methoxyphenyl)-1-tosylindolin-3-one 5c-2**: white solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d,  $J = 8.2$  Hz, 0.3 H), 8.05 (d,  $J = 8.2$  Hz, 0.7 H), 7.63-7.72 (m, 2.3 H), 7.56 (d,  $J = 8.2$  Hz, 0.7 H), 7.44 (d,  $J = 8.2$  Hz, 1.3 H), 7.35 (d,  $J = 7.3$  Hz, 0.7 H), 7.29 (m, 0.7 H), 7.17-7.26 (m, 3.2 H), 6.97 (t,  $J = 7.8$  Hz, 0.7 H), 6.85 (d,  $J = 8.8$  Hz, 0.7 H), 6.66 (d,  $J = 8.2$  Hz, 0.7 H), 5.20 (s, 0.7 H), 4.99 (s, 0.3 H), 3.78 (s, 2 H), 3.33 (s, 1 H), 2.35 (s, 1 H), 2.34 (s, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.8, 196.2, 159.8, 157.2, 153.6, 152.8, 145.0, 144.3, 137.5, 136.8, 135.0, 134.2, 132.2, 130.4, 129.9, 129.6, 128.4, 127.3, 127.0, 126.6, 125.3, 124.6, 124.3, 123.7, 123.3, 120.9, 116.4, 115.6, 114.3, 111.2, 69.8, 67.7, 55.4, 55.2, 21.6; IR (KBr)  $\text{cm}^{-1}$ : 3020, 2905, 2870, 2705, 2650, 1740, 1705, 1640, 1450, 1405, 1270; HRMS  $m/z$  calcd for  $\text{C}_{22}\text{H}_{19}\text{O}_4\text{NSNa}$  ( $[\text{M}+\text{Na}]^+$ ): 416.0932, found 416.0923.

**2-(2,5-dimethylphenyl)-1-tosylindolin-3-one 5d**: white solid, m.p. 128-130 °C:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (d,  $J = 8.3$  Hz, 1 H), 7.72 (t,  $J = 7.3$  Hz, 1 H), 7.67 (d,  $J = 7.3$  Hz, 1 H), 7.51 (d,  $J = 8.3$  Hz, 2 H), 7.22 (t,  $J = 7.3$  Hz, 1 H), 7.17 (d,  $J = 7.8$  Hz, 2 H), 7.07 (d,  $J = 7.8$  Hz, 1 H), 6.97 (d,  $J = 7.3$  Hz, 1 H), 6.67 (s, 1H), 5.33 (s, 1H), 2.38 (s, 3 H), 2.36 (s, 3 H), 2.11 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.2, 153.7, 144.8, 137.4, 135.7, 134.7, 133.6, 132.6, 131.1, 129.8, 129.3, 127.6, 127.2, 125.1, 124.3, 123.8, 116.0, 67.9, 21.6, 20.8, 19.3; IR (KBr)  $\text{cm}^{-1}$ : 3040, 2950, 2835, 2760, 1720, 1605, 1430; HRMS  $m/z$  calcd for  $\text{C}_{23}\text{H}_{21}\text{O}_3\text{NSNa}$  ( $[\text{M}+\text{Na}]^+$ ): 414.1140, found 414.1136.

**2-(2,5-dimethoxyphenyl)-1-tosylindolin-3-one 5e:** white solid, m.p. 150-151°C:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (d,  $J = 8.8$  Hz, 1 H), 7.69 (d,  $J = 7.3$  Hz, 2 H), 7.48 (d,  $J = 8.3$  Hz, 2 H), 7.19 (t,  $J = 7.3$  Hz, 1 H), 7.14 (d,  $J = 7.8$  Hz, 2 H), 6.80-6.86 (m, 2 H), 6.65 (d,  $J = 8.8$  Hz, 1 H), 5.20 (s, 1 H), 3.76 (s, 3 H), 3.37 (s, 3 H), 2.34 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.5, 153.6, 152.9, 151.5, 144.4, 136.9, 134.9, 129.6, 127.1, 124.5, 124.4, 123.8, 117.3, 115.7, 115.0, 112.6, 67.3, 56.0, 55.8, 21.6; IR (KBr)  $\text{cm}^{-1}$ : 3030, 2850, 2765, 2722, 1705, 1650, 1470, 1250; HRMS  $m/z$  calcd for  $\text{C}_{23}\text{H}_{21}\text{O}_5\text{NSNa}$  ( $[\text{M}+\text{Na}]^+$ ): 446.1038, found 446.1033.

**2-(2,3-dimethylphenyl)-1-tosylindolin-3-one 5f-1** and **2-(3,4-dimethylphenyl)-1-tosylindolin-3-one 5f-2:** white solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (d,  $J = 8.2$  Hz, 1 H), 7.63-7.73 (m, 2 H), 7.51-7.57 (m, 2 H), 7.16-7.23 (m, 3 H), 7.05-7.10 (m, 2 H), 6.94-7.01 (m, 1 H), 5.38 (s, 0.2 H), 4.96 (s, 0.8 H), 2.35 (s, 2.4 H), 2.27 (s, 0.6 H), 2.22 (s, 4.8 H), 2.18 (s, 1.2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.1, 196.1, 153.6, 153.5, 144.9, 137.7, 137.5, 137.4, 137.2, 135.2, 134.2, 132.8, 131.8, 130.3, 130.1, 129.9, 128.0, 127.3, 127.2, 125.8, 125.3, 125.1, 124.7, 124.5, 124.4, 123.8, 116.4, 116.2, 70.2, 70.2, 21.6, 20.9, 19.9, 19.6, 15.6; IR (KBr)  $\text{cm}^{-1}$ : 3032, 2952, 2870, 2705, 1730, 1640, 1605, 1430; HRMS  $m/z$  calcd for  $\text{C}_{23}\text{H}_{21}\text{O}_3\text{NSNa}$  ( $[\text{M}+\text{Na}]^+$ ): 414.1140, found 414.1126.

**2-(3,4-dimethoxyphenyl)-1-tosylindolin-3-one 5g:** white solid, m.p. 140-141°C:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 (d,  $J = 8.7$  Hz, 1 H), 7.72 (td,  $J = 8.2, 1.4$  Hz, 1 H), 7.66 (d,  $J = 7.8$  Hz, 1 H), 7.56 (d,  $J = 8.7$  Hz, 2 H), 7.18-7.24 (m, 3 H), 6.93 (dd,  $J = 8.2, 1.4$  Hz, 1 H), 6.82 (d,  $J = 8.2$  Hz, 1 H), 6.73 (s, 1 H), 5.00 (s, 1 H), 3.86 (s, 3 H), 3.77 (s, 3 H), 2.36 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.0, 153.5, 149.3, 149.2, 145.0, 137.6, 134.3, 129.9, 127.3, 126.6, 125.3, 124.6, 123.7, 119.8, 116.4, 111.2, 109.8, 70.0, 56.0, 55.9, 21.6; IR (KBr)  $\text{cm}^{-1}$ : 3050, 2950, 2850, 2705, 1740, 1650, 1405, 1296; HRMS  $m/z$  calcd for  $\text{C}_{23}\text{H}_{21}\text{O}_5\text{NSNa}$  ( $[\text{M}+\text{Na}]^+$ ): 446.1038, found 446.1022.

**2-mesityl-1-tosylindolin-3-one 5h:** white solid, m.p. 135-136°C:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (d,  $J = 8.2$  Hz, 1 H), 7.68-7.73 (m, 2 H), 7.45 (d,  $J = 8.2$  Hz, 2 H), 7.20 (t,  $J = 7.3$  Hz, 1 H), 7.12 (d,  $J = 8.2$  Hz, 2 H), 6.95 (s, 1 H), 6.58 (s, 1 H), 5.55 (s, 1 H), 2.58 (s, 3 H), 2.35 (s, 3 H), 2.25 (s, 3 H), 1.53 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.7, 152.9, 144.6, 139.1, 138.3, 137.3, 137.1, 135.0, 130.4, 129.6, 128.4, 127.1, 124.5, 124.2, 124.0, 116.0, 67.3, 21.6, 21.0, 20.9,

20.7; IR (KBr)  $\text{cm}^{-1}$ : 3016, 2890, 2750, 1730, 1630, 1450; HRMS  $m/z$  calcd for  $\text{C}_{24}\text{H}_{23}\text{O}_3\text{NSNa}$  ( $[\text{M}+\text{Na}]^+$ ): 428.1296, found 428.1304.

**1-tosyl-2-(2, 4, 6-trimethoxyphenyl) indolin-3-one 5i**: white solid, m.p. 152-153°C:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 (d,  $J = 8.2$  Hz, 1 H), 7.66-7.68 (m, 2 H), 7.60 (d,  $J = 8.3$  Hz, 2 H), 7.16-7.18 (m, 3 H), 6.21 (s, 1 H), 5.87 (s, 1 H), 5.49 (s, 1 H), 3.97 (s, 3 H), 3.79 (s, 3 H), 3.18 (s, 3 H), 2.35 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.2, 162.1, 160.5, 159.1, 152.7, 144.2, 136.4, 134.7, 129.5, 127.3, 125.0, 123.7, 123.4, 115.9, 105.0, 91.0, 90.9, 61.8, 56.2, 55.4, 55.2, 21.6; IR (KBr)  $\text{cm}^{-1}$ : 3025, 2930, 2875, 1750, 1635, 1620, 1405, 1205; HRMS  $m/z$  calcd for  $\text{C}_{24}\text{H}_{23}\text{O}_6\text{NSNa}$  ( $[\text{M}+\text{Na}]^+$ ): 476.1144, found 476.1153.

**2-(5-bromo-2-methoxyphenyl)-1-tosylindolin-3-one 5j**: white solid, m.p. 156-157°C:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (d,  $J = 8.2$  Hz, 1 H), 7.67-7.72 (m, 2 H), 7.52 (d,  $J = 8.2$  Hz, 2 H), 7.35 (t,  $J = 8.8$  Hz, 2 H), 7.21 (t,  $J = 7.3$  Hz, 1 H), 7.16 (d,  $J = 8.3$  Hz, 2 H), 6.61 (d,  $J = 8.8$  Hz, 1 H), 5.19 (s, 1 H), 3.46 (s, 3 H), 2.35 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.9, 156.5, 153.0, 144.8, 137.1, 134.5, 133.7, 132.9, 129.7, 127.1, 125.5, 124.5, 124.2, 124.1, 115.9, 113.0, 112.9, 66.3, 55.7, 21.6; IR (KBr)  $\text{cm}^{-1}$ : 3010, 2835, 2790, 1705, 1630, 1420, 1230; HRMS  $m/z$  calcd for  $\text{C}_{22}\text{H}_{18}\text{O}_4\text{NSBrNa}$  ( $[\text{M}+\text{Na}]^+$ ): 494.0038, found 494.0035.

**2-(2-chlorophenyl)-1-tosylindolin-3-one 5k-1** and **2-(4-chlorophenyl)-1-tosylindolin-3-one 5k-2**: white solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 (d,  $J = 8.3$  Hz, 0.3 H), 8.12 (d,  $J = 8.7$  Hz, 0.7 H), 7.57-7.75 (m, 4.7 H), 7.28-7.30 (m, 3 H), 7.20-7.26 (m, 3.3 H), 5.47 (s, 0.3 H), 4.96 (s, 0.7 H), 2.37 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.2, 194.6, 153.6, 153.6, 145.3, 145.2, 137.7, 137.5, 134.6, 133.9, 133.8, 133.6, 133.0, 132.9, 130.1, 130.1, 130.0, 129.8, 129.1, 128.4, 127.4, 127.3, 127.2, 125.4, 125.1, 124.9, 124.7, 123.8, 123.5, 116.6, 116.4, 69.4, 67.5, 21.6; IR (KBr)  $\text{cm}^{-1}$ : 3046, 2952, 2870, 2740, 1750, 1690, 1632, 1405; HRMS  $m/z$  calcd for  $\text{C}_{21}\text{H}_{16}\text{O}_3\text{NClNa}$  ( $[\text{M}+\text{Na}]^+$ ): 420.0437, found 420.0421.

**2-(2,5-dimethylphenyl)-3H-indol-3-one 6**: red oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ , 7.52-7.60 (m, 3 H), 7.42 (d,  $J = 7.3$  Hz, 1 H), 7.26 (t,  $J = 7.3$  Hz, 1 H), 7.19-7.20 (m, 2 H), 2.55 (s, 3 H), 2.37 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  193.4, 164.5, 160.2, 136.7, 136.5, 135.2, 131.7, 131.6, 131.5, 128.6, 128.4, 124.8, 122.2, 122.1, 21.2, 21.0; IR (KBr)  $\text{cm}^{-1}$ : 3120, 3020, 2830, 1760, 1640, 1580; HRMS  $m/z$  calcd for  $\text{C}_{16}\text{H}_{14}\text{ON}$  ( $[\text{M}+\text{H}]^+$ ): 236.1075, found 236.1076.



































































































