

Supporting Information

Synthesis of indoles and polycyclic amides via ruthenium(II)-catalyzed C–H activation and annulation

Hui Lin,^a Shuai-Shuai Li^a and Lin Dong^{*a}

Key Laboratory of Drug-Targeting and Drug Delivery System of the Education Ministry,
West China School of Pharmacy, Sichuan University, Chengdu 610041, China

E-mail: dongl@scu.edu.cn

- 1. General Methods**
- 2. General Procedure for Synthesis of Indoles, Polycyclic Amides and
Characterization Data**
- 3. NMR Spectra of Indoles and Polycyclic Amides**

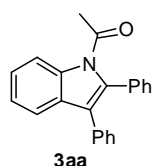
1. General methods

NMR data were obtained for ^1H at 400 MHz or 600 MHz, and for ^{13}C at 100 MHz or 151 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in CDCl_3 solution. ESI HRMS was recorded on a Waters SYNAPT G2 and Water XEVO G2 Q-ToF. UV detection was monitored at 220 nm. TLC was performed on glass-backed silica plates. Column chromatography was performed on silica gel (200-300 mesh), eluting with ethyl acetate and petroleum ether. *N*-phenylacetamide, benzamide and alkynes were commercially available.

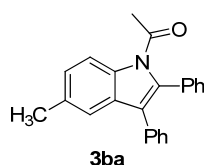
2. General Procedure for Synthesis of Indoles, Polycyclic Amides and Characterization Data

N-phenylacetamide **1a** (13.5 mg, 0.1 mmol), diphenylacetylene **2a** (8.9 mg, 0.05 mmol), $[\text{RuCl}_2(p\text{-cymene})]_2$ (1.5 mg, 5 mmol %), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (6.0 mg, 0.6 equiv) and $\text{CH}_3\text{SO}_2\text{OAc}$ (3.0 mg, 0.3 equiv) were stirred in toluene (0.6 mL) at 110 °C for 12 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:20) to give the product **3aa** as a white solid (13.5 mg, 87%).¹

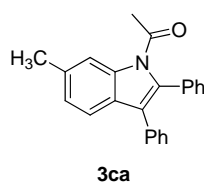
Benzamides **4a** (6.1 mg, 0.05 mmol), diphenylacetylene **2a** (31.2 mg, 0.175 mmol), $[\text{RuCl}_2(p\text{-cymene})]_2$ (2.3 mg, 7.5 mmol %), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (22.0 mg, 2.2 equiv) and Na_2CO_3 (10.6 mg, 2.0 equiv) were stirred in chlorobenzene (0.5 mL) at 110 °C for 16 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:30) to give the product **5aa** as a yellow solid (10.2mg, 43%).²



1-(2,3-diphenyl-1*H*-indol-1-yl)ethanone (**3aa**). 12 h, 87% yield, white solid; m.p. 148.7-150.2 °C; IR (KBr): $\nu = 3053, 2922, 2851, 1694, 1612, 1512, 1448, 1307 \text{ cm}^{-1}$. ^1H NMR (400 MHz, CDCl_3) δ 8.46 (d, $J = 8.0$ Hz, 1H), 7.56 (d, $J = 7.6$ Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 1H), 7.37~7.32 (m, 5H), 7.30~7.25 (m, 4H), 7.24~7.21 (m, 2H), 2.00 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 171.6, 136.8, 135.0, 133.1, 132.9, 130.8, 130.1, 129.3, 128.6, 128.2, 126.9, 125.5, 123.8, 123.4, 119.6, 116.2, 27.9 ppm. ESI HRMS: calcd. for $\text{C}_{22}\text{H}_{17}\text{NO}+\text{H}$ 312.1388, found 312.1384.

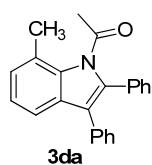


1-(5-methyl-2,3-diphenyl-1*H*-indol-1-yl)ethanone (**3ba**). 12 h, 76% yield, pale yellow solid; m.p. 182.0-183.8 °C; IR (KBr): $\nu = 3057, 2921, 2856, 1693, 1608, 1512, 1462, 1311 \text{ cm}^{-1}$. ^1H NMR (400 MHz, CDCl_3) δ 8.34 (d, $J = 8.4$ Hz, 1H), 7.34~7.39 (m, 6H), 7.27~7.20 (m, 6H), 2.43 (s, 3H), 1.99 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 171.4, 135.1, 135.1, 133.4, 133.2, 133.1, 130.8, 130.1, 129.5, 128.6, 128.2, 126.9, 126.8, 123.3, 119.4, 116.0, 27.9, 21.4 ppm. ESI HRMS: calcd. for $\text{C}_{23}\text{H}_{19}\text{NO}+\text{H}$ 326.1545, found 326.1547.

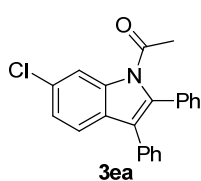


1-(6-methyl-2,3-diphenyl-1*H*-indol-1-yl)ethanone (**3ca**). 12 h, 64% yield, pale yellow solid; m.p. 129.1-130.5°C; IR (KBr): $\nu = 3059, 2920, 2854, 1693, 1614, 1512, 1480, 1311 \text{ cm}^{-1}$. ^1H NMR (400 MHz, CDCl_3) δ 8.29 (s, 1H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.34 (s, 5H), 7.30~7.25 (m, 3H), 7.23~7.20 (m, 2H), 7.13 (d, $J = 8.0$ Hz, 1H), 2.53 (s, 3H), 1.98 (s, 3H) ppm. ^{13}C NMR (151 MHz, CDCl_3) δ 171.4, 136.9, 135.4, 134.1, 133.0, 132.8, 130.5, 129.7, 128.3, 128.2, 127.9, 126.8, 126.6, 124.9, 123.0, 118.9,

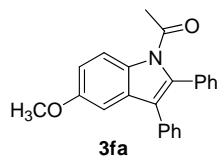
116.0, 27.7, 21.8 ppm. ESI HRMS: calcd. for C₂₃H₁₉NO+Na 348.1364, found 348.1362.



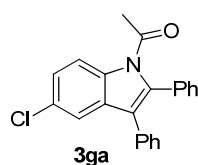
1-(7-methyl-2,3-diphenyl-1*H*-indol-1-yl)ethanone (**3da**). 12 h, 50% yield. pale yellow solid; m.p. 130.1-132.9 °C; IR (KBr): $\nu = 3044, 2925, 2853, 1707, 1617, 1542, 1512, 1446, 1283 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, $J = 7.2 \text{ Hz}$, 1H), 7.35 (s, 5H), 7.30~7.16 (m, 7H), 2.44 (s, 3H), 2.06 (s, 3H) ppm. ¹³C NMR (151 MHz, CDCl₃) δ 172.9, 135.2, 134.8, 133.2, 132.1, 130.6, 129.8, 129.8, 128.4, 128.3, 127.9, 127.3, 126.4, 124.3, 123.0, 121.0, 117.3, 28.4, 21.1 ppm. ESI HRMS: calcd. for C₂₃H₁₉NO+H 326.1545, found 326.1554.



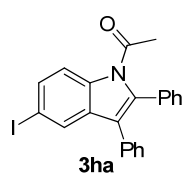
1-(6-chloro-2,3-diphenyl-1*H*-indol-1-yl)ethanone (**3ea**). 12 h, 70% yield, yellow solid; m.p. 139.2-141.3 °C; IR (KBr): $\nu = 3024, 2925, 2854, 1702, 1602, 1561, 1513, 1456, 1306 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃) δ 8.52 (s, 1H), 7.46 (d, $J = 8.0 \text{ Hz}$, 1H), 7.39~7.36 (m, 3H), 7.35~7.32 (m, 2H), 7.30~7.26 (m, 4H), 7.20~7.18 (m, 2H), 1.99 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 171.5, 137.0, 135.4, 132.6, 132.5, 131.4, 130.7, 129.9, 128.9, 128.7, 128.4, 127.8, 127.2, 124.3, 123.0, 120.3, 116.5, 27.8 ppm. ESI HRMS: calcd. for C₂₂H₁₆ClNO+Na 368.0818, found 368.0811, 370.0796.



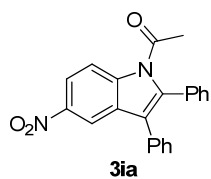
1-(5-methoxy-2,3-diphenyl-1*H*-indol-1-yl)ethanone (**3fa**). 12 h, 59% yield, pale orange solid; m.p. 186.3-188.5 °C; IR (KBr): $\nu = 3005, 2958, 2930, 2832, 1692, 1606, 1544, 1512, 1468, 1370, 1297 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃) δ 8.39 (d, $J = 8.8 \text{ Hz}$, 1H), 7.36~7.31 (m, 5H), 7.29~7.24 (m, 3H), 7.22~7.19 (m, 2H), 7.03~6.99 (m, 2H), 3.82 (s, 3H), 1.98 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 171.2, 156.7, 135.7, 133.1, 133.0, 131.6, 130.8, 130.2, 130.0, 128.6, 128.6, 128.3, 126.9, 123.3, 117.3, 113.9, 102.2, 55.8, 27.8 ppm. ESI HRMS: calcd. for C₂₃H₁₉NO₂+H 342.1494, found 342.1511.



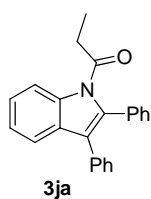
1-(5-chloro-2,3-diphenyl-1*H*-indol-1-yl)ethanone (**3ga**). 12 h, 77% yield, pale yellow solid; m.p. 208.9-210.6 °C; IR (KBr): $\nu = 3059, 2927, 2855, 1700, 1597, 1513, 1445, 1305 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃) δ 8.39 (d, $J = 8.8 \text{ Hz}$, 1H), 7.50 (s, 1H), 7.38~7.34 (m, 6H), 7.30~7.26 (m, 3H), 7.18 (d, $J = 6.4 \text{ Hz}$, 2H), 1.98 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 171.4, 136.2, 135.1, 132.5, 132.4, 130.7, 130.6, 129.9, 129.4, 128.9, 128.7, 128.4, 127.2, 125.6, 122.7, 119.1, 117.4, 27.8 ppm. ESI HRMS: calcd. for C₂₂H₁₆ClNO+Na 368.0818, found 368.0821, 370.0804.



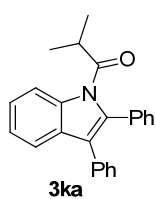
1-(5-iodo-2,3-diphenyl-1*H*-indol-1-yl)ethanone (**3ha**). 12 h, 83% yield, pale yellow solid; m.p. 223.9-225.4 °C; IR (KBr): $\nu = 3055, 2930, 1698, 1603, 1578, 1515, 1441, 1301 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, $J = 8.8 \text{ Hz}$, 1H), 7.86 (s, 1H), 7.68~7.66 (m, 1H), 7.38~7.37 (m, 3H), 7.34~7.31 (m, 3H), 7.29~7.25 (m, 2H), 7.19~7.17 (m, 2H), 1.98 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 171.5, 136.1, 135.7, 133.9, 132.4, 132.4, 131.6, 130.7, 130.0, 128.9, 128.7, 128.4, 128.3, 127.2, 122.3, 118.2, 87.8, 27.9 ppm. ESI HRMS: calcd. for C₂₂H₁₆I NO+Na 460.0174, found 460.0177.



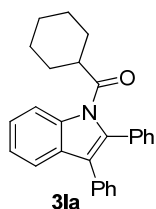
1-(5-nitro-2,3-diphenyl-1H-indol-1-yl)ethanone (**3ia**). 12 h, 34% yield, yellow solid; m.p. 152.9-154.6 °C; IR (KBr): $\nu = 3061, 2922, 2851, 1715, 1611, 1575, 1519, 1445, 1336, 1295 \text{ cm}^{-1}$. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.52 (d, $J = 9.2 \text{ Hz}$, 1H), 8.45 (s, 1H), 8.29~8.26 (m, 1H), 7.42~7.39 (m, 3H), 7.38~7.36 (m, 2H), 7.35~7.31 (m, 3H), 7.22~7.20 (m, 2H), 2.03 (s, 3H) ppm. $^{13}\text{C NMR}$ (100MHz, CDCl_3) δ 171.6, 144.4, 139.6, 137.7, 131.8, 131.6, 130.6, 129.9, 129.4, 129.3, 128.9, 128.7, 127.7, 123.5, 120.6, 116.3, 116.0, 27.9 ppm. ESI HRMS: calcd. for $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_3+\text{Na}$ 379.1059, found 379.1053.



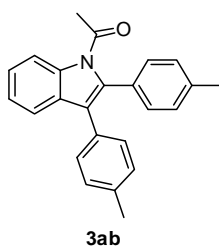
1-(2,3-diphenyl-1H-indol-1-yl)propan-1-one (**3ja**). 12 h, 50% yield, pale yellow solid; m.p. 145.4-147.5 °C; IR (KBr): $\nu = 3063, 2984, 2937, 2875, 1696, 1609, 1565, 1485, 1447, 1274 \text{ cm}^{-1}$. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.41 (d, $J = 8.4 \text{ Hz}$, 1H), 7.56 (d, $J = 7.6 \text{ Hz}$, 1H), 7.42~7.39 (m, 1H), 7.36~7.32 (m, 5H), 7.29~7.25 (m, 4H), 7.22~7.20 (m, 2H), 2.20 (q, $J = 7.2 \text{ Hz}$, 2H), 1.02 (t, $J = 7.6 \text{ Hz}$, 3H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 175.8, 136.8, 134.8, 133.2, 133.1, 130.6, 130.1, 129.2, 128.6, 128.5, 128.2, 126.9, 125.4, 123.6, 123.1, 119.6, 115.8, 33.2, 9.4 ppm. ESI HRMS: calcd. for $\text{C}_{23}\text{H}_{19}\text{NO}+\text{Na}$ 348.1364, found 348.1373.



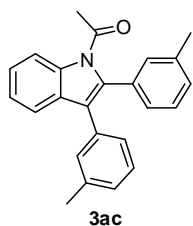
1-(2,3-diphenyl-1H-indol-1-yl)-2-methylpropan-1-one (**3ka**). 12 h, 40% yield, pale yellow solid; m.p. 123.2-125.0 °C; IR (KBr): $\nu = 3023, 2966, 2929, 2871, 1697, 1617, 1564, 1511, 1447, 1272 \text{ cm}^{-1}$. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.20 (d, $J = 8.0 \text{ Hz}$, 1H), 7.57 (d, $J = 7.6 \text{ Hz}$, 1H), 7.40~7.28 (m, 10H), 7.26~7.22 (m, 2H), 2.55~2.48 (m, 1H), 0.97 (d, $J = 6.8 \text{ Hz}$, 6H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 180.1, 137.0, 134.5, 133.4, 132.8, 130.2, 130.1, 129.1, 128.6, 128.4, 128.3, 126.9, 125.2, 123.3, 122.3, 119.6, 114.8, 37.2, 19.0 ppm. ESI HRMS: calcd. for $\text{C}_{24}\text{H}_{21}\text{NO}+\text{Na}$ 362.1521, found 362.1524.



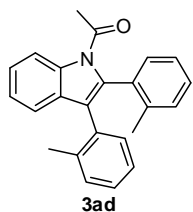
cyclohexyl(2,3-diphenyl-1H-indol-1-yl)methanone (**3la**). 12 h, 75% yield, pale yellow solid; m.p. 142.3-143.9 °C; IR (KBr): $\nu = 3053, 2929, 2849, 1699, 1604, 1562, 1507, 1447, 1312 \text{ cm}^{-1}$. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.25 (d, $J = 8.4 \text{ Hz}$, 1H), 7.57 (d, $J = 7.6 \text{ Hz}$, 1H), 7.39~7.23 (m, 12H), 2.15 (t, $J = 7.2 \text{ Hz}$, 1H), 1.63~1.56 (m, 3H), 1.48~1.34 (m, 4H), 1.08 (q, $J = 12.8 \text{ Hz}$, 1H), 0.69 (q, $J = 12.8 \text{ Hz}$, 2H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 178.7, 136.9, 134.7, 133.3, 133.0, 130.3, 130.1, 129.0, 128.6, 128.4, 128.2, 126.8, 125.1, 123.3, 122.3, 119.5, 115.1, 46.7, 29.1, 25.5, 25.4 ppm. ESI HRMS: calcd. for $\text{C}_{27}\text{H}_{25}\text{NO}+\text{Na}$ 402.1834, found 402.1834.



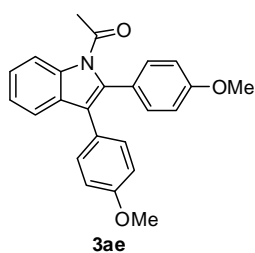
1-(2,3-di-p-tolyl-1H-indol-1-yl)ethanone (**3ab**). 12 h, 71% yield, white solid; m.p. 170.0-171.8 °C; IR (KBr): $\nu = 3016, 2939, 2861, 1687, 1590, 1504, 1448, 1311 \text{ cm}^{-1}$. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.44 (d, $J = 8.4 \text{ Hz}$, 1H), 7.54 (d, $J = 7.6 \text{ Hz}$, 1H), 7.39 (t, $J = 7.6 \text{ Hz}$, 1H), 7.30~7.25 (m, 1H), 7.23~7.21 (m, 2H), 7.17~7.13 (m, 2H), 7.11~7.09 (m, 4H), 2.37 (s, 3H), 2.33 (s, 3H), 1.99 (s, 3H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.7, 138.5, 136.8, 136.5, 135.0, 130.6, 130.1, 130.0, 129.9, 129.5, 129.3, 129.0, 125.3, 123.7, 123.0, 119.5, 116.2, 28.0, 21.4, 21.2 ppm. ESI HRMS: calcd. for $\text{C}_{24}\text{H}_{21}\text{NO}+\text{H}$ 340.1701, found 340.1700.



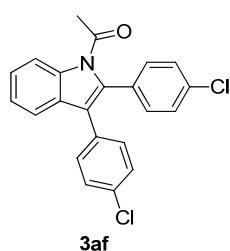
1-(2,3-di-m-tolyl-1H-indol-1-yl)ethanone (**3ac**). 12 h, 77% yield, pale yellow oil; IR (KBr): $\nu = 3033, 2961, 2860, 1695, 1608, 1515, 1449, 1307 \text{ cm}^{-1}$. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.45 (d, $J = 8.0 \text{ Hz}$, 1H), 7.56 (d, $J = 7.6 \text{ Hz}$, 1H), 7.39 (t, $J = 7.6 \text{ Hz}$, 1H), 7.29 (t, $J = 7.2 \text{ Hz}$, 1H), 7.25~7.21 (m, 1H), 7.18~7.12 (m, 4H), 7.08~7.04 (m, 2H), 6.99 (d, $J = 7.6 \text{ Hz}$, 1H), 2.32 (s, 3H), 2.29 (s, 3H), 2.00 (s, 3H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.7, 137.2, 136.6, 135.7, 134.1, 132.0, 131.9, 130.3, 129.7, 128.3, 128.3, 127.4, 127.0, 126.9, 126.6, 126.1, 124.3, 122.7, 122.2, 118.6, 115.1, 26.9, 20.4, 20.3 ppm. ESI HRMS: calcd. for $\text{C}_{24}\text{H}_{21}\text{NO}+\text{Na}$ 362.1521, found 362.1520.



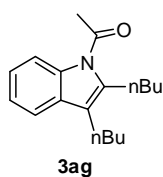
1-(2,3-di-o-tolyl-1H-indol-1-yl)ethanone (**3ad**). 12 h, 80% yield, pale yellow solid; m.p. 85.1-86.9 °C; IR (KBr): $\nu = 3034, 2952, 2860, 1695, 1606, 1516, 1448, 1307 \text{ cm}^{-1}$. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.45 (d, $J = 8.0 \text{ Hz}$, 1H), 7.56 (d, $J = 7.6 \text{ Hz}$, 1H), 7.42~7.38 (m, 1H), 7.31~7.28 (m, 1H), 7.25~7.21 (m, 1H), 7.18~7.12 (m, 4H), 7.08~7.05 (m, 2H), 6.99 (d, $J = 7.6 \text{ Hz}$, 1H), 2.32 (s, 3H), 2.29 (s, 3H), 2.00 (s, 3H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.8, 138.2, 137.7, 136.8, 135.1, 133.0, 132.9, 131.4, 130.7, 129.4, 129.4, 128.4, 128.1, 127.9, 127.7, 127.1, 125.4, 123.7, 123.3, 119.6, 116.2, 27.9, 21.5, 21.4 ppm. ESI HRMS: calcd. for $\text{C}_{24}\text{H}_{21}\text{NO}+\text{Na}$ 362.1521, found 362.1521.



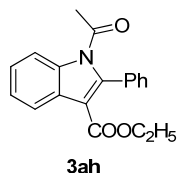
1-(2,3-bis(4-methoxyphenyl)-1H-indol-1-yl)ethanone (**3ae**). 12 h, 80% yield, pale yellow solid; m.p. 148.6-150.1 °C; IR (KBr): $\nu = 3066, 2955, 2837, 1701, 1610, 1568, 1504, 1451, 1300, 1249 \text{ cm}^{-1}$. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.45 (d, $J = 8.4 \text{ Hz}$, 1H), 7.54 (d, $J = 7.6 \text{ Hz}$, 1H), 7.39 (t, $J = 7.6 \text{ Hz}$, 1H), 7.30 (d, $J = 7.6 \text{ Hz}$, 1H), 7.27~7.23 (m, 2H), 7.15 (d, $J = 8.4 \text{ Hz}$, 2H), 6.89 (d, $J = 8.4 \text{ Hz}$, 2H), 6.84 (d, $J = 8.4 \text{ Hz}$, 2H), 3.83 (s, 3H), 3.80 (s, 3H), 2.01 (s, 3H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.7, 159.8, 158.4, 136.7, 134.6, 132.0, 131.1, 129.5, 125.4, 125.3, 125.2, 123.7, 122.7, 119.4, 116.2, 114.1, 113.8, 55.3, 55.2, 27.3 ppm. ESI HRMS: calcd. for $\text{C}_{24}\text{H}_{21}\text{NO}_3+\text{Na}$ 394.1419, found 394.1423.



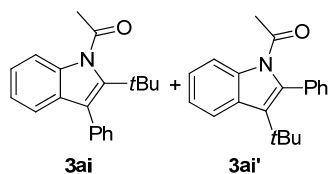
1-(2,3-bis(4-chlorophenyl)-1H-indol-1-yl)ethanone (**3af**). 12 h, 59% yield, pale yellow solid; m.p. 204.2-205.8 °C; IR (KBr): $\nu = 3062, 2957, 2853, 1698, 1598, 1557, 1447, 1301 \text{ cm}^{-1}$. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.41 (d, $J = 8.4 \text{ Hz}$, 1H), 7.49 (d, $J = 7.6 \text{ Hz}$, 1H), 7.40 (t, $J = 7.6 \text{ Hz}$, 1H), 7.38~7.36 (m, 2H), 7.33~7.30 (m, 2H), 7.28~7.25 (m, 3H), 7.13 (d, $J = 8.0 \text{ Hz}$, 2H), 2.06 (s, 3H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.0, 136.8, 135.0, 133.9, 133.2, 131.9, 131.3, 131.2, 129.1, 128.9, 128.7, 125.9, 124.0, 122.7, 119.4, 116.2, 28.1 ppm. ESI HRMS: calcd. for $\text{C}_{22}\text{H}_{15}\text{Cl}_2\text{NO}+\text{Na}$ 402.0428, found 402.0443, 404.0373.



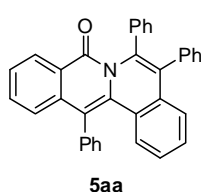
1-(2,3-dibutyl-1H-indol-1-yl)ethanone (**3ag**). 12 h, 33% yield, yellow oil; IR (KBr): $\nu = 3048, 2957, 2930, 2863, 1703, 1602, 1578, 1518, 1460, 1311 \text{ cm}^{-1}$. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76~7.74 (m, 1H), 7.49~7.47 (m, 1H), 7.25~7.22 (m, 2H), 2.98 (t, $J = 7.6 \text{ Hz}$, 2H), 2.76 (s, 3H), 2.64 (t, $J = 7.6 \text{ Hz}$, 2H), 1.62~1.52 (m, 4H), 1.44~1.37 (m, 4H), 0.97~0.93 (m, 6H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.0, 138.3, 135.7, 130.9, 123.3, 122.6, 120.1, 118.7, 114.5, 32.5, 32.4, 27.7, 26.8, 23.7, 22.9, 22.8, 14.0, 13.9 ppm. ESI HRMS: calcd. For $\text{C}_{18}\text{H}_{25}\text{NO}+\text{Na}$ 294.1834, found 294.1840.



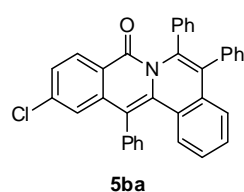
ethyl 1-acetyl-2-phenyl-1H-indole-3-carboxylate (**3ah**). 12 h, 26% yield, pale yellow solid; m.p. 104.5-106.1 °C; IR (KBr): $\nu = 3057, 2987, 2945, 2897, 1796, 1707, 1608, 1555, 1515, 1446, 1290, 1240, 1178 \text{ cm}^{-1}$. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.32 (d, $J = 7.2 \text{ Hz}$, 1H), 8.23~8.20 (m, 1H), 7.51~7.48 (m, 5H), 7.42~7.40 (m, 2H), 4.20 (q, $J = 7.6 \text{ Hz}$, 2H), 1.92 (s, 3H), 1.16 (t, $J = 7.6 \text{ Hz}$, 3H) ppm. $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 171.7, 164.2, 143.6, 136.2, 132.6, 130.4, 129.5, 128.3, 126.9, 125.7, 124.5, 121.7, 115.6, 112.4, 60.1, 27.8, 14.0 ppm. ESI HRMS: calcd. for $\text{C}_{19}\text{H}_{17}\text{NO}_3 + \text{Na}$ 330.1106, found 330.1102.



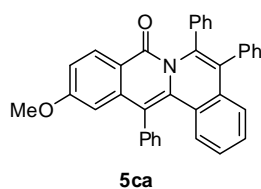
1-(2-(tert-butyl)-3-phenyl-1H-indol-1-yl)ethanone (**3ai**); 1-(3-(tert-butyl)-2-phenyl-1H-indol-1-yl)ethanone (**3ai'**); (**3ai**:**3ai'** = **17**:**1**). 12 h, 45% yield, pale yellow solid; m.p. 86.3-87.9 °C; IR (KBr): $\nu = 3060, 2994, 2963, 2918, 2864, 1713, 1584, 1516, 1454, 1295 \text{ cm}^{-1}$. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ **3ai**: 7.48~7.12 (m, 9H), 2.87 (s, 3H), 1.34 (s, 9H) ppm; **3ai'**: 8.44 (d, $J = 8.0 \text{ Hz}$, 1H), 7.86 (d, $J = 8.0 \text{ Hz}$, 1H), 7.48~7.12 (m, 7H), 1.50 (s, 3H), 1.25 (s, 9H) ppm. $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 174.9, 145.5, 136.5, 134.8, 131.4, 130.8, 128.2, 127.1, 123.6, 123.0, 121.8, 119.8, 111.4, 35.2, 32.1, 31.1, 29.9, 28.3 ppm.¹



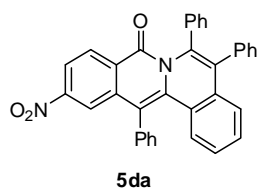
5,6,13-triphenyl-8H-isoquinolino[3,2-a]isoquinolin-8-one (**5aa**). 16 h, 43% yield, yellow solid; m.p. 296.5-297.9 °C; IR(KBr): $\nu = 3021, 1673, 1595, 1540, 1477, 1309 \text{ cm}^{-1}$. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.26 (d, $J = 8.0 \text{ Hz}$, 1H), 7.62~7.58 (m, 1H), 7.56~7.53 (m, 5H), 7.44 (t, $J = 7.6 \text{ Hz}$, 1H), 7.35 (d, $J = 8.0 \text{ Hz}$, 1H), 7.28~7.20 (m, 3H), 7.18~7.12 (m, 5H), 7.08 (s, 5H), 6.88 (t, $J = 7.6 \text{ Hz}$, 1H) ppm. $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 162.2, 138.6, 137.1, 137.1, 136.2, 136.1, 133.8, 133.0, 132.3, 132.1, 131.4, 129.6, 129.0, 128.8, 128.4, 128.1, 127.9, 127.6, 127.4, 127.1, 126.9, 126.8, 126.6, 126.4, 126.3, 125.8, 125.6, 125.5, 116.9 ppm. ESI HRMS: calcd. for $\text{C}_{35}\text{H}_{23}\text{NO} + \text{Na}$ 496.1677, found 496.1674



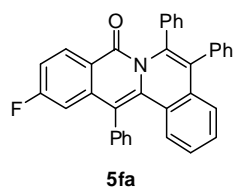
11-chloro-5,6,13-triphenyl-8H-isoquinolino[3,2-a]isoquinolin-8-one (**5ba**). 16 h, 56% yield, yellow solid; m.p. 334.2-336.1 °C; IR (KBr): $\nu = 3025, 1667, 1591, 1529, 1449, 1317 \text{ cm}^{-1}$. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.19 (d, $J = 8.4 \text{ Hz}$, 1H), 7.58~7.50 (m, 5H), 7.38 (d, $J = 8.4 \text{ Hz}$, 1H), 7.32~7.23 (m, 4H), 7.19~7.11 (m, 5H), 7.08 (s, 5H), 6.89 (t, $J = 7.6 \text{ Hz}$, 1H) ppm. $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 161.5, 139.0, 138.4, 137.9, 136.9, 136.0, 135.9, 135.2, 133.1, 132.0, 131.3, 129.9, 129.3, 129.1, 128.8, 128.8, 128.4, 127.9, 127.2, 127.2, 127.0, 126.9, 126.9, 126.8, 126.4, 125.7, 124.8, 123.9, 115.8. ESI HRMS: calcd. for $\text{C}_{35}\text{H}_{22}\text{ClNO} + \text{H}$ 508.1468, found 508.1468, 510.1452.



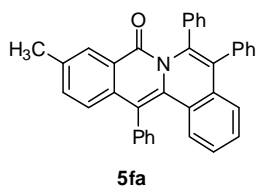
11-methoxy-5,6,13-triphenyl-8H-isoquinolino[3,2-a]isoquinolin-8-one (**5ca**). 16 h, 40% yield, yellow solid; m.p. 301.6-303.1 °C; IR (KBr): $\nu = 3021, 2938, 2839, 1670, 1604, 1540, 1475, 1279, 1217 \text{ cm}^{-1}$. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.19 (d, $J = 8.8 \text{ Hz}$, 1H), 7.54~7.50 (m, 5H), 7.27~7.21 (m, 3H), 7.16~7.09 (m, 5H), 7.06 (s, 5H), 7.03~7.00 (m, 1H), 6.86 (t, $J = 8.0 \text{ Hz}$, 1H), 6.71 (d, $J = 2.4 \text{ Hz}$, 1H), 3.75 (s, 3H) ppm. $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 162.9, 161.7, 139.2, 138.7, 137.3, 136.3, 136.2, 134.6, 133.2, 132.1, 131.5, 129.7, 129.7, 129.1, 128.8, 128.5, 128.1, 127.9, 127.5, 127.1, 126.9, 126.7, 126.3, 126.2, 125.6, 119.9, 116.6, 115.1, 107.5, 55.3 ppm. ESI HRMS: calcd. for $\text{C}_{36}\text{H}_{25}\text{NO}_2 + \text{Na}$ 526.1783, found 526.1780.



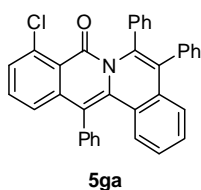
11-nitro-5,6,13-triphenyl-8*H*-isoquinolino[3,2-*a*]isoquinolin-8-one (**5da**). 16 h, 35% yield, red solid; m.p. 348.5-349.7 °C; IR (KBr): $\nu = 3026, 1666, 1605, 1578, 1519, 1456, 1340, 1293 \text{ cm}^{-1}$. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.38 (d, $J = 8.4 \text{ Hz}$, 1H), 8.22 (s, 1H), 8.15 (d, $J = 8.4 \text{ Hz}$, 1H), 7.61~7.57 (m, 3H), 7.52~7.50 (m, 2H), 7.29~7.20 (m, 4H), 7.17~7.15 (m, 4H), 7.09 (s, 5H), 6.93 (t, $J = 7.2 \text{ Hz}$, 1H) ppm. $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 160.8, 150.3, 137.7, 137.2, 136.4, 136.0, 135.8, 135.6, 133.1, 131.8, 131.2, 130.2, 129.4, 129.3, 129.2, 128.9, 128.8, 128.4, 128.0, 127.8, 127.3, 127.2, 127.1, 126.7, 126.6, 125.9, 121.2, 119.7, 116.3 ppm. ESI HRMS: calcd. for $\text{C}_{35}\text{H}_{22}\text{N}_2\text{O}_3+\text{H}$ 519.1709, found 519.1705.



11-fluoro-5,6,13-triphenyl-8*H*-isoquinolino[3,2-*a*]isoquinolin-8-one (**5fa**). 16 h, 42% yield, yellow solid; m.p. 298.2-300.0 °C; IR (KBr): $\nu = 3024, 1673, 1614, 1580, 1490, 1399, 1286 \text{ cm}^{-1}$. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.25 (dd, $J = 6.4, 8.4 \text{ Hz}$, 1H), 7.59~7.53 (m, 3H), 7.51~7.49 (m, 2H), 7.28~7.21 (m, 3H), 7.19~7.12 (m, 6H), 7.08 (s, 5H), 6.98~6.95 (m, 1H), 6.89 (t, $J = 7.6 \text{ Hz}$, 1H) ppm. $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 165.4(d, $J_{\text{C-F}} = 252 \text{ Hz}$), 161.4, 139.6 (d, $J_{\text{C-F}} = 10.0 \text{ Hz}$), 138.2, 137.0, 136.1, 136.0, 135.2, 133.2, 132.0, 131.4, 130.7 (d, $J_{\text{C-F}} = 10.0 \text{ Hz}$), 129.9, 129.1, 128.8, 128.8, 128.4, 127.9, 127.2, 127.1, 127.0, 126.9, 126.8, 126.4, 125.7, 122.3, 116.2, 115.0 (d, $J_{\text{C-F}} = 24.0 \text{ Hz}$), 110.6 (d, $J = 24.0 \text{ Hz}$) ppm. ESI HRMS: calcd. for $\text{C}_{35}\text{H}_{22}\text{FNO}+\text{Na}$ 514.1583, found 514.1581.



10-methyl-5,6,13-triphenyl-8*H*-isoquinolino[3,2-*a*]isoquinolin-8-one (**5fa**). 16 h, 36% yield, yellow solid; m.p. 252.1-253.5 °C; IR (KBr): $\nu = 3025, 2923, 2852, 1669, 1606, 1537, 1467, 1326 \text{ cm}^{-1}$. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.07 (s, 1H), 7.57~7.50 (m, 5H), 7.46~7.42 (m, 1H), 7.26~7.20 (m, 5H), 7.17~7.11 (m, 4H), 7.07 (s, 5H), 8.87 (t, $J = 7.6 \text{ Hz}$, 1H), 2.45 (s, 3H) ppm. $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 162.2, 138.7, 137.2, 136.7, 136.2, 136.2, 134.8, 133.8, 132.9, 132.9, 132.1, 131.4, 129.6, 128.9, 128.8, 128.2, 128.0, 127.9, 127.8, 127.1, 127.0, 126.9, 126.7, 126.6, 126.2, 125.7, 125.6, 125.6, 117.0, 21.3 ppm. ESI HRMS: calcd. for $\text{C}_{36}\text{H}_{25}\text{NO}+\text{K}$ 526.1573, found 526.1573.



9-chloro-5,6,13-triphenyl-8*H*-isoquinolino[3,2-*a*]isoquinolin-8-one (**5ga**). 16 h, 18% yield, yellow solid; m.p. 229.7-230.6 °C; IR (KBr): $\nu = 3024, 1689, 1581, 1528, 1447, 1294 \text{ cm}^{-1}$. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.58~7.52 (m, 3H), 7.46~7.36 (m, 4H), 7.29~7.21 (m, 3H), 7.18~7.09 (m, 10H), 7.04~7.02 (m, 1H), 6.88 (t, $J = 7.2 \text{ Hz}$, 1H) ppm. $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 161.5, 140.3, 138.7, 136.5, 136.4, 136.0, 134.3, 133.8, 133.4, 132.0, 131.4, 131.3, 129.8, 129.0, 128.9, 128.7, 128.5, 128.1, 127.9, 127.4, 127.1, 127.0, 126.6, 126.2, 125.8, 125.5, 124.4, 122.2, 114.7 ppm. ESI HRMS: calcd. for $\text{C}_{35}\text{H}_{22}\text{ClNO}+\text{Na}$ 530.1288, found 530.1271, 532.1256.

References

- 1 Y. Hoshino, Y. Shibata, K. Tanaka. *Adv. Synth. Catal.* **2014**, *356*, 1577.
- 2 B. Li, H.-L. Feng, N.-C. Wang, J.-F. Ma, H.-B. Song, S.-S. Xu, B.-Q. Wang. *Chem.-Eur. J.* **2012**, *18*, 12873.

3. NMR Spectra of Indoles and Polycyclic Amides

