Supporting Information
for DOI: 10.1055/s-0030-1259548
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Supporting Information

Domino Ligand-Free Copper-Catalyzed Synthesis of Polysubstituted Indoles.

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Contents Page

1 General Information and Procedure for Indole Synthesis S1
2 Characterization Data of the Products S2-S9
3 Scans of \(^1\)H and \(^{13}\)C NMR Spectra S10-S47

General Information. 2-Haloanilines, Cu\(_2\)O powder <5 micron (97%), Cs\(_2\)CO\(_3\), and K\(_3\)PO\(_4\) were purchased from Aldrich and used without further purification. The column chromatography was performed with Rankem silica gel (60-120 mesh). NMR spectra (400 MHz for \(^1\)H and 100 MHz for \(^{13}\)C) were recorded using DRX-400 Varian spectrometer using CDCl\(_3\) and DMSO-d\(_6\) as solvent and Me\(_4\)Si as internal standard. Chemical shifts (\(\delta\)) are reported in ppm and spin-spin coupling constants (\(J\)) are given in Hz. Melting points were determined using Buchi B-540 melting point apparatus and are uncorrected. FT-IR spectra were recorded using Perkin Elmer IR spectroscopy. Elemental analyses were recorded using Perkin Elmer CHNS analyzer.

General Procedure for Synthesis of Indoles: An oven-dried 10 mL round bottom flask was charged with 2-haloaniline (1 mmol), 1,3-dicarbonylcompound (1.2 mmol), Cu\(_2\)O (10 mol %), Cs\(_2\)CO\(_3\) (1 mmol), DMSO:H\(_2\)O (3:1, 1 mL) and the mixture was stirred at 100 °C under nitrogen atmosphere. The progress of the reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was cooled to room temperature and diluted with ethyl acetate (15 mL). The resulting solution was washed with brine (3 mL) and water (2 x 3 mL). Drying
(Na₂SO₄) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using (10-20%) ethyl acetate in hexane as eluent.

Characterization Data of Products:

Methyl-2-methyl-1H-indole-3-carboxylate (1a): Light yellow solid; mp 165-166 °C (lit. mp 164-166 °C); yield 81%; ¹H NMR (400 MHz, CDCl₃) δ 8.44 (br s, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.30-7.16 (m, 3H), 3.92 (s, 3H), 2.73 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃:DMSO-d₆ (3:1)) δ 166.1, 144.5, 134.6, 126.8, 121.3, 120.7, 120.4, 110.6, 102.9, 50.1, 13.6 ppm; FT-IR (KBr) 3291, 3269, 2946, 2923, 2851, 1666, 1547, 1489, 1456, 1440, 1332, 1270, 1199, 1116, 1091, 1015 cm⁻¹. Anal. Calcd. for C₁₁H₁₁NO₂: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.77; H, 5.84; N, 7.44.

Methyl-5-chloro-2-methyl-1H-indole-3-carboxylate (1b): Light brown solid; mp 173-174 °C; yield 80%; ¹H NMR (400 MHz, CDCl₃) δ 8.38 (br s, 1H), 8.06 (s, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.16 (dd, J = 8.4, 2.0 Hz, 1H), 3.94 (s, 3H) 2.74 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃:DMSO-d₆ (3:1)) δ 166.2, 146.1, 133.3, 128.3, 126.8, 121.9, 120.4, 111.9, 103.4, 50.7, 14.1 ppm; FT-IR (KBr) 3290, 2947, 2857, 1662, 1462, 1437, 1294, 1196, 1103 cm⁻¹. Anal. Calcd. for C₁₁H₁₀ClNO₂: C, 59.07; H, 4.51; N, 6.26. Found: C, 59.00; H, 4.48; N, 6.22.
**Methyl 2,5-dimethyl-1H-indole-3-carboxylate (1c):** White solid; mp 168-169 °C; yield 83%; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.33 (br s, 1H), 7.86 (s, 1H), 7.17 (d, \(J = 8.0\) Hz, 1H), 7.00 (d, \(J = 9.2\) Hz, 1H), 3.91 (s, 3H), 2.70 (s, 3H), 2.45 (s, 3H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.1, 144.6, 133.0, 131.2, 127.5, 123.9, 120.9, 110.5, 103.7, 50.9, 21.8, 14.3 ppm; FT-IR (KBr) 3305, 3005, 2943, 2857, 1673, 1541, 1473, 1445, 1421, 1334, 1299, 1276, 1210, 1191, 1157, 1095 cm\(^{-1}\).

1: Anal. Calcd. for C\(_{12}\)H\(_{13}\)NO\(_2\): C, 70.92; H, 6.45; N, 6.89. Found: C, 70.86; H, 6.43; N, 6.93.

![Methyl 2,5-dimethyl-1H-indole-3-carboxylate (1c)](image)

**Methyl 2,5,7-trimethyl-1H-indole-3-carboxylate (1d):** White solid; mp 196-198 °C; yield 81%; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.18 (br s, 1H), 7.70 (s, 1H), 6.82 (s, 1H), 3.91 (s, 3H), 2.72 (s, 3H), 2.42 (s, 6H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.9, 144.5, 132.6, 130.8, 127.1, 124.3, 119.8, 118.2, 103.5, 50.6, 21.5, 16.6, 14.1 ppm; FT-IR (KBr) 3306, 3000, 2953, 2914, 2851, 1649, 1477, 1456, 1380, 1365, 1309, 1293, 1238, 1226, 1193, 1147, 1109, 1083 cm\(^{-1}\). Anal. Calcd. for C\(_{13}\)H\(_{15}\)NO\(_2\): C, 71.87; H, 6.96; N, 6.45. Found: C, 71.81; H, 6.98; N, 6.41.

![Methyl 2,5,7-trimethyl-1H-indole-3-carboxylate (1d)](image)

**Methyl-2,5,6-trimethyl-1H-indole-3-carboxylate (1e):** White solid; mp 207-208 °C; yield 78%; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.15 (br s, 1H), 7.81 (s, 1H), 7.04 (s, 1H), 3.90 (s, 3H), 2.69 (s, 3H), 2.35 (s, 3H), 2.32 (s, 3H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\):DMSO-d\(_6\) (3:1)) \(\delta\) 166.8, 143.8, 133.7, 130.7, 129.8, 125.5, 121.0, 111.3, 103.1, 50.5, 20.2, 20.1, 14.1 ppm; FT-IR (KBr) 3294, 2956, 2917, 2851, 1659, 1468, 1418, 1208, 1118, 1089 cm\(^{-1}\). Anal. Calcd. for C\(_{13}\)H\(_{15}\)NO\(_2\): C, 71.87; H, 6.96; N, 6.45. Found: C, 71.82; H, 6.94; N, 6.42.
Ethyl 2-methyl-1H-indol-3-carboxylate** (1f):** White solid; mp 134-136 °C (lit. 2 mp 135-136 °C); yield 87%; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.38 (br s, 1H), 8.10 (d, $J$ = 7.6 Hz, 1H), 7.31-7.17 (m, 3H), 4.40 (q, $J$ = 6.8 Hz, 2H), 2.75 (s, 3H), 1.45 (t, $J$ = 6.8 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.6, 144.5, 134.8, 127.4, 122.4, 121.8, 121.3, 110.9, 104.5, 59.8, 14.7, 14.3 ppm; FT-IR (KBr) 3305, 2976, 2926, 1658, 1548, 1458, 1334, 1274, 1199, 1122, 1093, 1016 cm$^{-1}$. Anal. Calcd. for C$_{12}$H$_{13}$NO$_2$: C, 70.92; H, 6.45; N, 6.89. Found: C, 70.87; H, 6.42; N, 6.93.

Ethyl 2-phenyl-1H-indol-3-carboxylate** (1g):** White solid; mp 157-158 °C (lit. 2 mp 156-158 °C); yield 69%; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.85 (br s, 1H), 8.11 (d, $J$ = 7.2 Hz, 1H), 7.50-7.47 (m, 2H), 7.26-7.25 (m, 3H), 7.21-7.11 (m, 3H), 4.14 (q, $J$ = 6.8 Hz, 2H), 1.18 (t, $J$ = 7.2 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.8, 144.9, 135.4, 132.2, 129.8, 129.2, 128.2, 127.8, 123.2, 122.2, 122.1, 111.4, 104.6, 59.9, 14.4 ppm; FT-IR (KBr) 3307, 2976, 2926, 1658, 1548, 1334, 1274, 1199, 1122, 1093, 1016 cm$^{-1}$. Anal. Calcd. for C$_{17}$H$_{15}$NO$_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.89; H, 5.68; N, 5.22.

1-(2-Methyl-1H-indol-3-yl)ethanone (1h): Light yellow solid; mp 201-202 ºC (lit. 3 mp 200-201 ºC); yield 84%; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.49 (br s, 1H), 8.01 (d, $J$ = 8.4 Hz, 1H),
7.32 (d, J = 7.6 Hz, 1H), 7.26-7.20 (m, 2H), 2.76 (s, 3H), 2.66 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$; DMSO-d$_6$ (3:1)) δ 193.9, 144.2, 134.7, 126.7, 123.7, 121.5, 121.2, 120.3, 110.9, 30.7, 14.9 ppm; FT-IR (KBr) 3453, 3428, 2928, 1615, 1580, 1456, 1437, 1261, 1100, 1067, 1020 cm$^{-1}$. Anal. Calcd. for C$_{11}$H$_{11}$NO: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.21; H, 6.37; N, 8.05.

![Chemical Structure](image)

**1-(5-Chloro-2-methyl-1H-indol-3-yl)ethanone (1i):** Light brown solid; mp 264-265 °C; yield 90%; $^1$H NMR (400 MHz, DMSO-d$_6$) δ 12.00 (br s, 1H), 8.04 (d, J = 2.0 Hz, 1H), 7.37 (d, J = 8.4 Hz, 1H), 7.15 (dd, J = 8.4, 2.0 Hz, 1H), 2.68 (s, 3H), 2.49 (s, 3H) ppm; $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ 192.9, 145.6, 133.2, 128.2, 126.0, 121.7, 119.9, 113.3, 112.6, 30.6, 15.0 ppm; FT-IR (KBr) 3205, 3181, 2989, 1621, 1610, 1574, 1456, 1447, 1418, 1386, 1263, 1200, 1055, 1024 cm$^{-1}$. Anal. Calcd. for C$_{11}$H$_{10}$ClNO: C, 63.62; H, 4.85; N, 6.75. Found: C, 63.58; H, 4.86; N, 6.71.

![Chemical Structure](image)

**1-(2,5-Dimethyl-1H-indol-3-yl)ethanone (1j):** Yellow solid; mp 236-238 °C; yield 76%; $^1$H NMR (400 MHz, DMSO-d$_6$) δ 11.68 (br s, 1H), 7.79 (s, 1H), 7.21 (d, J = 8.0 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 2.63 (s, 3H), 2.47 (s, 3H), 2.37 (s, 3H) ppm; $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ 192.9, 144.1, 132.9, 129.9, 127.2, 123.1, 120.5, 117.8, 110.8, 30.9, 21.4, 15.0 ppm; FT-IR (KBr) 3214, 3187, 3051, 2917, 2857, 1724, 1621, 1608, 1585, 1452, 1419, 1217, 1071, 1028 cm$^{-1}$. Anal. Calcd. for C$_{12}$H$_{13}$NO: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.95; H, 6.98; N, 7.53.
1-(2-Methyl-5-nitro-1\textit{H}-indol-3-yl)ethanone (1k): Brown solid; mp 281-283 °C; yield 66%; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 11.55 (s, 1H), 8.48 (s, 1H), 7.52 (d, $J = 8.8$ Hz, 1H), 6.92 (dd, $J = 8.8$, 2.4 Hz, 1H), 2.26 (s, 3H), 2.10 (s, 3H) ppm; $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 193.9, 148.2, 142.6, 138.3, 126.7, 117.8, 117.4, 115.1, 111.9, 30.8, 15.3 ppm; FT-IR (KBr) 3200, 3075, 2958, 2925, 2855, 1732, 1615, 1582, 1541, 1514, 1468, 1419, 1333, 1264, 1202, 1186, 1122, 1077, 1021 cm$^{-1}$. Anal. Calcd. for C$_{11}$H$_{10}$N$_2$O$_3$: C, 60.55; H, 4.62; N, 12.84. Found: C, 60.51; H, 4.59; N, 12.89.

![Structure of 1-(2-Methyl-5-nitro-1\textit{H}-indol-3-yl)ethanone](image1)

1-(2,5,7-Trimethyl-1\textit{H}-indol-3-yl)ethanone (1l): Yellow solid; mp 225-226 °C; yield 88%; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 11.53 (s, 1H), 7.64 (s, 1H), 6.76 (s, 1H), 2.67 (s, 3H), 2.48 (s, 3H), 2.42 (s, 3H), 2.35 (s, 3H) ppm; $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 193.0, 143.9, 132.5, 129.9, 126.9, 123.9, 119.9, 118.1, 113.6, 30.9, 21.4, 16.6, 14.9 ppm; FT-IR (KBr) 3200, 3131, 3053, 2956, 2918, 2851, 1732, 1606, 1593, 1453, 1421, 1295, 1068, 1020 cm$^{-1}$. Anal. Calcd. for C$_{13}$H$_{15}$NO: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.53; H, 7.53; N, 6.93.

![Structure of 1-(2,5,7-Trimethyl-1\textit{H}-indol-3-yl)ethanone](image2)

1-(2,5,6-Trimethyl-1\textit{H}-indol-3-yl)ethanone (1m): Yellow solid; mp 257-258 °C; yield 82%; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 11.58 (br s, 1H), 7.77 (s, 1H), 7.12 (s, 1H), 2.63 (s, 3H), 2.48 (s, 3H), 2.29 (s, 3H), 2.28 (s, 3H) ppm; $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 192.8, 143.2, 133.6, 130.0, 129.2, 123.8, 120.9, 118.5, 111.4, 30.8, 20.0, 19.9, 14.9 ppm; FT-IR (KBr) 3208, 3175, 3137, 3087, 2962, 2917, 2851, 1725, 1716, 1609, 1572, 1457, 1415, 1385, 1261, 1208, 1163, 1102, 1067, 1018 cm$^{-1}$. Anal. Calcd. for C$_{13}$H$_{15}$NO: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.52; H, 7.48; N, 6.91.
2,2-Dimethyl-2,3-dihydro-1H-carbazol-4(9H)-one \(^4\) (1n): White solid; mp 194-195 °C (lit. \(^4\) mp 195-196 °C); yield 85%; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.12 (br s, 1H), 8.22 (d, \(J = 8.0\) Hz, 1H), 7.37 (d, \(J = 8.4\) Hz, 1H), 7.27-7.21 (m, 2H), 2.84 (s, 2H), 2.47 (s, 2H), 1.15 (s, 6H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\):DMSO-d\(_6\) (3:1)) \(\delta\) 193.3, 150.9, 136.3, 124.6, 122.4, 121.7, 120.7, 111.2, 52.2, 37.0, 35.4, 28.4 ppm; FT-IR (KBr) 3217, 3186, 2959, 2926, 2868, 1624, 1612, 1471, 1456, 1100, 1059 cm\(^{-1}\). Anal. Calcd. for C\(_{14}\)H\(_{15}\)NO: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.78; H, 7.07; N, 6.61.

2-Methyl-N-p-tolyl-1H-indol-3-carboxamide (1o): Light yellow solid; mp 205-206 °C; yield 91%; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.51 (s, 1H), 7.78 (d, \(J = 7.6\) Hz, 1H), 7.66 (s, 1H), 7.52 (d, \(J = 6.8\) Hz, 2H), 7.35 (dd, \(J = 6.8, 2.0\) Hz, 1H), 7.26-7.16 (m, 4H), 2.74 (s, 3H), 2.34 (s, 3H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\):DMSO-d\(_6\) (3:1)) \(\delta\) 164.4, 141.0, 136.1, 134.8, 132.5, 128.9, 125.5, 121.1, 120.3, 119.8, 118.3, 111.1, 107.5, 20.4, 13.1 ppm; FT-IR (KBr) 3257, 3054, 2919, 2851, 1608, 1552, 1518, 1494, 1456, 1421, 1403, 1326, 1240, 1198, 1119, 1083, 1021 cm\(^{-1}\). Anal. Calcd. for C\(_{17}\)H\(_{16}\)N\(_2\)O: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.18; H, 6.08; N, 10.65.
5-Chloro-2-Methyl-N-p-tolyl-1H-indol-3-carboxamide (1p): Grey solid; mp 232-234 °C; yield 90%; $^1$H NMR (400 MHz, DMSO-d$_6$) δ 11.75 (s, 1H), 9.55 (s, 1H), 7.70 (s, 1H), 7.60 (d, J = 8.8 Hz, 1H), 7.37 (d, J = 8.8 Hz, 1H), 7.13 (m, 3H), 2.61 (s, 3H), 2.28 (s, 3H) ppm; $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ 163.6, 141.1, 137.2, 133.2, 131.9, 128.9, 127.6, 124.7, 121.1, 120.0, 118.8, 112.5, 108.6, 20.5, 13.2 ppm; FT-IR (KBr) 3280, 3252, 3225, 3032, 2921, 2851, 1602, 1573, 1518, 1496, 1469, 1427, 1241, 1199, 1097, 1066, 1019 cm$^{-1}$. Anal. Calcd. for C$_{17}$H$_{15}$ClN$_2$O: C, 68.34; H, 5.06; N, 9.38. Found: C, 68.42; H, 5.08; N, 9.33.

![5-Chloro-2-Methyl-N-p-tolyl-1H-indol-3-carboxamide](image)

2-Methyl-5-nitro-N-p-tolyl-1H-indol-3-carboxamide (1q): Deep brown solid; mp 232-233 °C; yield 62%; $^1$H NMR (400 MHz, DMSO-d$_6$) δ 12.24 (s, 1H), 9.76 (s, 1H), 8.63 (s, 1H), 8.03 (d, J = 8.8 Hz, 1H), 7.60 (d, J = 6.8 Hz, 2H), 7.55 (d, J = 8.8 Hz, 1H), 7.15 (d, J = 7.2 Hz, 2H), 2.65 (s, 3H), 2.29 (s, 3H) ppm; $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ 163.6, 143.6, 142.0, 138.7, 137.5, 132.9, 129.7, 126.6, 120.8, 117.5, 116.9, 112.2, 111.5, 21.2, 13.9 ppm; FT-IR (KBr) 3295, 2960, 2924, 2854, 1740, 1634, 1597, 1519, 1509, 1478, 1462, 1422, 1401, 1330, 1313, 1297, 1261, 1241, 1196, 1099, 1064, 1023 cm$^{-1}$. Anal. Calcd. for C$_{17}$H$_{15}$N$_3$O$_3$: C, 66.01; H, 4.89; N, 13.58. Found: C, 65.94; H, 4.87; N, 13.63.

![2-Methyl-5-nitro-N-p-tolyl-1H-indol-3-carboxamide](image)

2,5,7-Trimethyl-N-p-tolyl-1H-indol-3-carboxamide (1r): Light brown solid; mp 217-218 °C; yield 89%; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.15 (s, 1H), 7.63 (s, 1H), 7.50 (d, J = 7.6 Hz, 2H),...
7.38 (s, 1H), 7.15 (d, J = 8.4 Hz, 2H), 6.85 (s, 1H), 2.74 (s, 3H), 2.45 (s, 3H), 2.44 (s, 3H), 2.33 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$:DMSO-d$_6$ (3:1)) δ 164.8, 141.8, 136.2, 133.0, 132.8, 130.5, 129.4, 125.5, 124.0, 120.6, 120.0, 115.7, 107.6, 21.6, 20.8, 16.8, 13.6 ppm; FT-IR (KBr) 3422, 3199, 2919, 2856, 1637, 1607, 1593, 1516, 1456, 1402, 1310, 1245, 1233, 1160, 1152, 1105, 1018 cm$^{-1}$. Anal. Calcd. for C$_{19}$H$_{20}$N$_2$O: C, 78.05; H, 6.89; N, 9.58. Found: C, 78.00; H, 6.86; N, 9.55.

![Chemical structure](image)

**2,5,6-Trimethyl-N-p-tolyl-1H-indol-3-carboxamide (1s):** Light brown solid; mp 227-228 °C; yield 82%; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.16 (s, 1H), 7.62 (s, 1H), 7.50 (d, J = 7.2 Hz, 3H), 7.15 (d, J = 8.0 Hz, 2H), 7.11 (s, 1H), 2.70 (s, 3H), 2.36 (s, 3H), 2.34 (s, 3H), 2.33 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$:DMSO-d$_6$ (3:1)) δ 164.5, 140.3, 136.2, 133.7, 132.3, 129.9, 128.9, 123.8, 119.7, 118.6, 111.5, 106.8, 20.5, 19.9, 19.8, 13.2 ppm; FT-IR (KBr) 3403, 3269, 2917, 2857, 1633, 1621, 1593, 1542, 1515, 1494, 1448, 1402, 1309, 1262, 1238, 1196, 1173, 1115, 1023 cm$^{-1}$. Anal. Calcd. for C$_{19}$H$_{20}$N$_2$O: C, 78.05; H, 6.89; N, 9.58. Found: C, 77.98; H, 6.85; N, 9.60.

**References**
