Supporting Information

A Mild Approach for the Synthesis of Indoles from $N$-(2-Iodo-Aryl)-Formamides and Phenylacetylene by a Cu(I) and Pd-Catalyzed Cascade Process

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2. General remarks

CuI and Pd(OAc)$_2$ catalyzed cascade reactions were carried out with dry and distilled DMF, and Et$_3$N solvents. All yields were calculated after column chromatography purification using Silica gel (60-120 mesh) purchased from Rankem, India. Bruker-200 (200 MHz) and Bruker-400 (400 MHz) were used to record $^1$H and $^{13}$C NMR spectra using CDCl$_3$ and d$_6$-DMSO solvents. $^1$H and $^{13}$C NMR data of compounds are reported by using the following abbreviations: chemical shifts, multiplicity (s = singlet, d = doublet, m = multiplet, dd = doublet of doublet), coupling constant (Hz) and for $^{13}$C $\delta$ is in ppm. Open capillaries were used to determine melting points and are uncorrected.

3. 1. General procedure for the synthesis of 4:

PBr$_3$ (0.26 mL, 2.7 mmol), DMF (0.23 mL, 3 mmol), and CHCl$_3$ (0.80 mL) were placed in a two necked round-bottomed flask fitted with guard tube. Next, the reaction mixture was allowed to cool to 0 $^0$C and stirred for 0.5 h. After formation of colorless solid complex, $\sigma$-iodoaniline 1 (1 mmol) in CHCl$_3$ (5 mL) was added to it and allowed the reaction mixture to stir at r.t. for another 1-2 h. Upon completion of the reaction, a solution of saturated NaHCO$_3$ was added slowly into the reaction mixture, followed by extraction with DCM (3 x 20 mL). The combined organic layer was dried over Na$_2$SO$_4$ and concentrated in vacuum to get crude product which was then purified through column chromatography by using silica gel (60-120 mesh) and pet ether : EtOAc (5:1) as eluent.

3. 2. General procedure for the synthesis of indoles 5:

To a DMF (5 mL) solution of a mixture containing 4 (1mmol), phenylacetylene 2 (1.010 mmol), and PCy$_3$ (0.25 mmol) placed in a two necked round-bottomed flask fitted with condenser, Et$_3$N (7 equiv), Pd(OAc)$_2$ (5 mol%), and CuI (10 mol%) were added and the reaction mixture was allowed to stir at 110 $^0$C under argon atmosphere. The progress of the reaction was monitored by TLC. Upon completion of the reaction, the mixture was allowed to cool to r.t, diluted with water, followed by extractions with EtOAc (3 x 20 mL). The combined organic layers was dried over Na$_2$SO$_4$ and concentrated in vacuum to get crude product which was then purified through
column chromatography by using silica gel (60-120 mesh) and pet ether: EtOAc (10:1) as eluent.

4. Spectral data:

4.1. N-(2-Iodo-4, 6-dimethyl-phenyl)-formamide 4b:

Brown oil; \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta = 7.37\) (s, 1H), 7.06 (s, 1H), 6.81 (s, 1H), 2.12 (s, 3H), 2.06 (s, 3H); \(^1\)C NMR (50 MHz, CDCl\(_3\)) \(\delta = 154.8, 149.7, 136.7, 133.3, 131.2, 130.5, 94.9, 20.2, 19.8\); Anal. Calcd. for C\(_9\)H\(_{10}\)INO: C, 39.30; H, 3.66; N, 5.09%. Found: C, 39.24; H, 3.75; N, 5.02%.

4.2.1. 5-Methyl-2-phenyl-1H-indole 5a:

White solid; mp 210-211 °C (lit\(^1\) 211-213 °C); \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta = 8.11\) (s, 1H), 7.56-7.52 (m, 2H), 7.36-7.14 (m, 5H), 6.93 (d, \(J = 8.2\) Hz, 1H), 6.65 (d, \(J = 1.4\) Hz, 1H), 2.36 (s, 3H); \(^1\)C NMR (50 MHz, CDCl\(_3\)) \(\delta = 138.1, 135.3, 132.7, 129.7, 129.6, 129.2, 127.8, 125.2, 124.2, 120.5, 110.8, 99.7, 21.7\); Anal. Calcd. for C\(_{15}\)H\(_{13}\)N: C, 86.92; H, 6.32; N, 6.76%. Found: C, 86.84; H, 6.41; N, 6.70%.

4.2.2. 5, 7-Dimethyl-2-phenyl-1H-indole 5b:

White solid; mp 88-89 °C; \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta = 7.97\) (s, 1H), 7.57-7.53 (m, 2H), 7.35-7.31 (m, 2H), 7.21 (d, \(J = 8.4\) Hz, 1H), 7.16 (s, 1H), 6.73 (s, 1H), 6.64 (d, \(J = 2.2\) Hz, 1H), 2.38 (s, 3H), 2.32 (s, 3H); \(^1\)C NMR (50 MHz, CDCl\(_3\)) \(\delta = 137.9, 135.0, 132.9, 129.8, 129.3, 129.1, 127.7, 125.3, 124.9, 119.9, 118.2, 100.3, 21.6, 16.8\); Anal. Calcd. for C\(_{14}\)H\(_{13}\)N: C, 86.84; H, 6.83; N, 6.33%. Found: C, 86.77; H, 6.91; N, 6.26%.

4.2.3. 5-Bromo-2-phenyl-1H-indole 5c:

White solid; mp 195-196 °C (lit\(^2\) 196-197 °C); \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta = 8.38\) (s, 1H), 7.75 (s, 1H), 7.64 (d, \(J = 7.2\) Hz, 2H), 7.48-7.41 (m, 3H), 7.36 (d, \(J = 6.6\) Hz, 2H), 6.75 (s, 1H); \(^1\)C NMR (50 MHz, CDCl\(_3\)) \(\delta = 139.3, 135.6, 132.0, 131.2, 129.3, 128.3, 125.5, 125.3, 123.3, 113.6, 112.5, 99.6\); Anal. Calcd. for C\(_{14}\)H\(_{10}\)BrN: C,
61.79; H, 3.70; N, 5.15%. Found: C, 61.69; H, 3.79; N, 5.09%.

4.2.4. 5-Chloro-2-phenyl-1H-indole 5d:

White solid; mp 196-197 °C (lit3 196-197 °C); 1H NMR (400 MHz, CDCl3) δ = 8.38 (s, 1H), 7.65-7.63 (m, 2H), 7.59 (s, 1H), 7.51-7.40 (m, 2H), 7.37-7.22 (m, 2H), 7.15(dd, J = 8.8, 2.0 Hz, 1H), 6.76 (d, J = 1.6 Hz, 1H); 13C NMR (50 MHz, CDCl3) δ = 139.5, 135.4, 132.1, 130.6, 129.3, 128.3, 126.1, 125.4, 122.8, 120.2, 112.1, 99.8; Anal. Calcd. for C14H10ClN: C, 73.85; H, 4.43; N, 6.15%. Found: C, 73.78; H, 4.52; N, 6.09%.

4.2.5. 5, 6-Dichloro-2-phenyl-1H-indole 5e:

White solid; mp 140 °C; 1H NMR (400 MHz, CDCl3) +1 drop DMSO- d6 δ = 10.55 (s, 1H), 7.74-7.65 (m, 2H), 7.56 (s, 1H), 7.45 (s, 1H), 7.36-7.33 (m, 2H), 7.26-722 (m, 1H), 6.62 (s, 1H); 13C NMR (50 MHz, CDCl3) +1 drop DMSO- d6 δ = 140.4, 136.2, 132.0, 128.9, 128.1, 125.6, 125.1, 123.5, 121.1, 112.7, 98.6; Anal. Calcd. for C14H6Cl2N: C, 64.15; H, 3.46; N, 5.34%. Found: C, 64.05; H, 3.54; N, 5.28%.

4.2.6. 5-Fluoro-2-phenyl-1H-indole 5f:

White solid; mp 178 °C; 1H NMR (200 MHz, CDCl3) δ = 8.24 (s, 1H), 7.55 (d, J = 7.6 Hz, 2H), 7.39-7.32 (m, 2H), 7.28-7.16 (m, 3H), 6.89-6.81 (m, 1H), 6.69 (s, 1H); 13C NMR (50 MHz, CDCl3) δ = 158.4 (d, 1Jc,F = 233.0 Hz), 139.8, 133.5, 132.2, 129.8 (d, 1Jc,F = 10.5 Hz), 129.3, 128.2, 125.4, 111.7 (d, 2Jc,F = 9.5 Hz), 110.8 (d, 2Jc,F = 26.5 Hz), 105.5 (d, 2Jc,F = 23.5 Hz), 100.2 (d, 4Jc,F = 4.5 Hz); Anal. Calcd. for C14H10FN: C, 79.60; H, 4.77; N, 6.63%. Found: C, 79.54; H, 4.83; N, 6.58%.

4.2.7. 5-Nitro-2-phenyl-1H-indole 5g:

Yellow solid; mp 198-199 °C (lit4 199-200 °C); 1H NMR (200 MHz, CDCl3) +1 drop DMSO- d6 δ = 12.07 (s, 1H), 8.46 (s, 1H), 7.94 (dd, J = 9.0, 2.2 Hz, 1H), 7.81 (d, J = 7.4 Hz, 2H), 7.49-7.37 (m, 3H), 7.32 (d, J = 7.2 Hz, 1H), 6.99 (s, 1H); 13C NMR (50 MHz, CDCl3) +1 drop DMSO- d6 δ = 141.6, 141.5, 140.5, 131.4, 128.9, 128.3, 128.2, 125.6, 117.2, 117.1, 111.2, 100.6; Anal. Calcd. for C14H10N2O2: C, 70.58; H, 4.23; N, 11.76%. Found: C, 70.52; H, 4.29; N, 11.69%.
5. References


6. NMR Spectra

$^1$H NMR Spectrum (200 MHz in CDCl$_3$) of compound 4b:

![NMR Spectrum](image)

$^{13}$C NMR (50 MHz in CDCl$_3$) of compound 4b:

![NMR Spectrum](image)
$^1$H NMR Spectrum (200 MHz in CDCl$_3$) of compound 5a:

$^{13}$C NMR (50 MHz in CDCl$_3$) of compound 5a:
$^1$H NMR Spectrum (200 MHz in CDCl$_3$) of compound 5b:

$^{13}$C NMR (50 MHz in CDCl$_3$) of compound 5b:
$^1$H NMR Spectrum (200 MHz in CDCl$_3$) of compound 5c:

$^{13}$C NMR (50 MHz in CDCl$_3$) of compound 5c:
$^1$H NMR Spectrum (400 MHz in CDCl$_3$) of compound 5d:

$^{13}$C NMR (50 MHz in CDCl$_3$) of compound 5d:
$^1$H NMR Spectrum (400 MHz in CDCl$_3$ +1 drop DMSO- $d_6$) of compound 5e:

![NMR Spectrum](image)

$^{13}$C NMR (50 MHz in CDCl$_3$ +1 drop DMSO- $d_6$) of compound 5e:

![NMR Spectrum](image)
$^1\text{H}$ NMR Spectrum (200 MHz in CDCl$_3$) of compound 5f:

$^{13}\text{C}$ NMR (50 MHz in CDCl$_3$) of compound 5f:
$^1$H NMR Spectrum (200 MHz in CDCl$_3$+1 drop DMSO- d$_6$) of compound 5g:

$^{13}$C NMR (50 MHz in CDCl$_3$+1 drop DMSO- d$_6$) of compound 5g: