Synthesis of N-aryl-1-aminoindoles via intermolecular redox amination

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Supporting information

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General Information:
All reactions were run in flame-dried glassware under argon atmosphere using standard Schlenk techniques or in an inert atmosphere glove box and 1-dram sealed pressure vials. Commercially available reagents and solvents were used without additional purification unless otherwise stated. Indolines1 and nitrosobenzenes2 were prepared according to literature procedures. Compound purification was effected by flash chromatography using 230 × 400 mesh, 60 Å porosity silica. 1H NMR and 13C NMR spectra were obtained on a Bruker Avance 400 or a Bruker Avance 500 DRX spectrometer and referenced to residual protio solvent signals (most spectra were taken using a QNP Cryoprobe). Structural assignments are based on 1H, 13C, DEPT-135, COSY, HSQC and IR spectroscopies. Mass Spectrometry was run using EI or ESI techniques.
Procedure for the intermolecular redox amination reactions:

\[
\text{Indoline} + \text{Nitrosobenzene} \rightarrow \text{Product} \quad \text{PhCO}_2\text{H} (30 \text{ mol\%})
\]

Toluene (0.5 M), 110 °C, 1h

A: To a mixture of indoline (59.58 mg, 0.5 mmol) and 30 mol% benzoic acid (18.32 mg, 0.15 mmol) in dry toluene (0.2 mL), nitrosobenzene (53.56 mg, 0.5 mmol) in 0.8 mL dry toluene was added dropwise over 1 hour at 110 °C via a septum-sealed pressure vial. After heating in an aluminum block for 1 hour, completion of the reaction was indicated via TLC analysis. At this point, the reaction mixture was passed through a pad of silica gel and the product was isolated by flash column chromatography using silica gel as the stationary phase and 95:5 hexane:ethyl acetate as the eluent. 83 mg (80%) of the product \(N\)-phenyl-\(1H\)-indol-1-amine (1a) was obtained as an oil.

B: To 5-nitroindoline (164.16 mg, 1.0 mmol) and 30 mol% of benzoic acid (18.32 mg, 0.15 mmol) nitrosobenzene (53.56 mg, 0.5 mmol) in 1.0 mL of dry toluene was added to a pressure vial equipped with a septum. The mixture was heated in an aluminum block for 1 hour, at which point completion of reaction was indicated via TLC. The reaction mixture was then passed through a short pad of silica gel and the product was isolated by flash column chromatography using silica gel as the stationary phase and 95:5 hexane:ethyl acetate as the eluent. 63 mg (50%) of the product 5-nitro-\(N\)-phenyl-\(1H\)-indol-1-amine (1k) was obtained as a yellow oil.

Procedure for the one-pot synthesis of \(N\)-amino indolines:

\[
\text{Aniline} + \text{Ph}_2\text{Se}_2 (5 \text{ mol\%}) + \text{PhCO}_2\text{H} (30 \text{ mol\%})
\]

Toluene, RT, 2 h

Indoline, 110 °C, 1 h

\(X = H \quad 67\% (1a)\)

\(X = \text{OMe} \quad 66\% (1h)\)

To aniline (93.13 mg, 1.0 mmol), \(\text{Ph}_2\text{Se}_2\) (15.6 mg, 0.05 mmol) was added followed by 35% aq. hydrogen peroxide (146µL, 1.5 mmol) in 1.0 mL of dry toluene. The solution was stirred in a
pressure vial at room temperature for 2 hours. After 2 hours, indoline (59.58 mg, 0.5 mmol) and benzoic acid (18.32 mg, 0.15 mmol) were added and the resulting mixture was heated in an aluminum block for 1 hour or until completion of the reaction was indicated by TLC. The reaction mixture was passed through a short pad of silica gel and the product was isolated by flash column chromatography using silica gel as the stationary phase and 95:5 hexane:ethyl acetate as the eluent. 70 mg (67%) of the product \( N \)-phenyl-1\( H \)-indol-1-amine (1a) was obtained as a slightly red oil.

References:


Spectroscopic Data of compounds for 1a-1l & 2a-2e:

\( N \)-Phenyl-1\( H \)-indol-1-amine (1a): Prepared following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as a reddish liquid; IR (neat): \( \nu \)max 3327, 3053, 1601, 1495, 1473, 1458, 1327, 1090, 1215, 742, 692 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.68 (d, \( J = 7.0 \) Hz, 1H), 7.29 (d, \( J = 8.2 \) Hz, 1H), 7.22-7.16 (m, 5H), 6.92 (t, \( J = 7.5 \) Hz, 1H), 6.60 (s, 1H), 6.56 (dd, \( J = 3.3, 0.7 \) Hz, 1H), 6.52 (dd, \( J = 8.6, 0.9 \) Hz, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 147.3, 135.8, 129.4, 128.6, 126.6, 122.4, 121.2, 121.1, 120.3, 112.6, 109.4, 100.7. HRMS m/z 207.0906 (M − H\(^+\)), calcd for C\(_{14}\)H\(_{11}\)N\(_2\) 207.0922.

2-Methyl-\( N \)-phenyl-1\( H \)-indol-1-amine (1b): Prepared following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as a white solid; IR (neat): \( \nu \)max 3333, 2918, 2361, 1601, 1497, 1456, 1325, 1242, 746, 692 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.56 – 7.54 (m, 1H), 7.18 (dt, \( J = 11.8, 5.9 \) Hz, 3H), 7.11 – 7.09 (m, 2H), 6.68 (t, \( J = 7.5 \) Hz, 1H), 6.47 (dd, \( J = 9.0, 1.0 \) Hz, 2H), 6.44 (s, 1H), 6.30 (t, \( J = 1.0 \) Hz, 1H), 2.34 (s, 3H). \(^{13}\)C NMR (126 MHz,
CDCl$_3$ δ 146.8, 137.6, 135.5, 129.6, 126.0, 121.2, 120.8, 120.3, 119.9, 112.5, 108.8, 98.7, 11.4. HRMS m/z 221.1053 (M – H$^+$), calcd for C$_{15}$H$_{13}$N$_2$ 221.1079.

3-Methyl-N-phenyl-1H-indol-1-amine (1c): Prepared following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as a white solid; IR (neat): $\nu_{\text{max}}$ 3327, 3053, 2916, 1497, 1458, 1306, 1227, 1111, 1009, 743, 692 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.62 (d, $J$ = 7.9 Hz, 1H), 7.26 (d, $J$ = 8.2 Hz, 1H), 7.18 (dt, $J$ = 15.9, 7.2 Hz, 4H), 6.96 (d, $J$ = 1.0 Hz, 1H), 6.49 (t, $J$ = 7.4 Hz, 1H), 6.52 (dd, $J$ = 8.6, 1.0 Hz, 3H). 13C NMR (126 MHz, CDCl$_3$) δ 147.4, 136.1, 129.1, 126.9, 126.0, 122.3, 121.0, 119.7, 119.0, 112.6, 110.1, 109.2, 9.6. HRMS m/z 221.1052 (M – H$^+$), calcd for C$_{15}$H$_{13}$N$_2$ 221.1079.

5-Methyl-N-phenyl-1H-indol-1-amine (1d): Prepared following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as a white solid; IR (neat): $\nu_{\text{max}}$ 3323, 2901, 1495, 1472, 1331, 1246, 1209, 1150, 1090, 1045, 796, 752, 692 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.46 (s, 1H), 7.20 (dd, $J$ = 8.5, 7.4 Hz, 2H), 7.16 (dd, $J$ = 5.8, 2.5 Hz, 2H), 7.02 (d, $J$ = 8.3 Hz, 1H), 6.91 (t, $J$ = 7.8 Hz, 1H), 6.57 (s, 1H), 6.51 (d, $J$ = 9.4 Hz, 2H), 6.47 (d, $J$ = 4.0 Hz, 1H), 2.47 (s, 3H). 13C NMR (126 MHz, CDCl$_3$) δ 147.4, 134.1, 129.6, 129.3, 128.7, 126.9, 124.0, 121.1, 120.8, 112.6, 109.1, 100.2, 21.4. HRMS m/z 221.1052 (M – H$^+$), calcd for C$_{15}$H$_{13}$N$_2$ 221.1079.

5-Bromo-N-phenyl-1H-indol-1-amine (1e): Prepared following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as a white solid; IR (neat): $\nu_{\text{max}}$ 3329, 1601, 1495, 1458, 1325, 1207, 1092, 1043, 895, 798, 750, 692 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.68 (d, $J$ = 1.6 Hz, 1H), 7.16 (dd, $J$ = 8.7, 1.8 Hz, 1H), 7.12 – 7.07 (m, 3H), 7.04 (d, $J$ = 8.6 Hz, 1H), 6.82 (t, $J$ = 7.4 Hz, 1H), 6.46 (s, 1H), 6.38 – 6.37 (m, 3H). 13C NMR (126 MHz, CDCl$_3$) δ 146.9, 134.5, 129.8, 129.4, 128.1, 125.3, 123.5, 121.4, 113.6, 112.6, 110.9, 100.4. HRMS m/z 285.0017 (M – H$^+$), calcd for C$_{14}$H$_{10}$N$_2$Br 285.0027.
1-(1-(Phenylamino)-1H-indol-5-yl)ethanone (1f): Prepared following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as a yellow liquid; IR (neat): $v_{\text{max}}$ 3325, 3128, 2959, 1603, 1560, 1495, 1302, 1229, 970, 822, 753 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.20 (d, $J$ = 1.5 Hz, 1H), 7.72 (d, $J$ = 8.6 Hz, 1H), 7.20 (d, $J$ = 8.6 Hz, 1H), 7.15 – 7.14 (m, 1H), 7.10 (dd, $J$ = 8.5, 7.5 Hz, 2H), 6.82 (t, $J$ = 7.4 Hz, 2H), 6.54 (d, $J$ = 3.3 Hz, 1H), 6.41 (d, $J$ = 7.7 Hz, 2H), 2.54 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 198.3, 146.9, 138.6, 130.4, 130.2, 129.4, 126.0, 123.2, 122.7, 121.4, 112.7, 109.4, 102.6, 26.6. HRMS m/z 251.1182 (M + H$^+$), calcd for C$_{16}$H$_{15}$N$_2$O 251.1184.

N-Phenyl-1H-benzo[g]indol-1-amine (1g): Prepared following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as a white solid; IR (neat): $v_{\text{max}}$ 3335, 1603, 1485, 1402, 1354, 1236, 806, 750, 687 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.73 (d, $J$ = 8.3 Hz, 1H), 7.98 (d, $J$ = 7.6 Hz, 1H), 7.76 (d, $J$ = 8.6 Hz, 1H), 7.62 (d, $J$ = 8.6 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.22 (t, $J$ = 7.5 Hz, 2H), 7.07 (d, $J$ = 3.2 Hz, 1H), 6.94 (t, $J$ = 7.4 Hz, 1H), 6.71 (d, $J$ = 3.2 Hz, 1H), 6.64 (s, 1H), 6.52 (d, $J$ = 7.9 Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 147.1, 131.3, 129.5, 129.0, 128.5, 127.2, 125.5, 124.0, 122.7, 122.1, 121.6, 121.3, 121.2, 120.8, 112.9, 102.8. HRMS m/z 259.1208 (M + H$^+$), calcd for C$_{18}$H$_{15}$N$_2$ 259.1235.

5-Methoxy-N-phenyl-1H-indol-1-amine (1h): Prepared following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as a white solid; IR (neat): $v_{\text{max}}$ 3319, 1603, 1497, 1473, 1252, 1232, 1148, 1028, 752, 692 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.18 (dd, $J$ = 24.5, 18.9, 10.2 Hz, 5H), 6.91 (t, $J$ = 7.4 Hz, 1H), 6.85 (dd, $J$ = 8.8, 2.3 Hz, 1H), 6.59 (s, 1H), 6.51 (d, $J$ = 8.5 Hz, 2H), 6.47 (d, $J$ = 3.2 Hz, 1H), 3.87 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 154.6, 147.4, 130.9, 129.3, 129.2, 127.0, 121.1, 112.6, 110.2, 102.8, 100.3, 55.8. HRMS m/z 237.1004 (M – H$^+$), calcd for C$_{15}$H$_{13}$N$_2$O 237.1028.
**N^1-Phenyl-1H-indole-1,5-diamine (1i):** Prepared following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as a yellow solid; IR (neat): \( \nu_{\text{max}} \), 3400, 3327, 3211, 2959, 2359, 1603, 1495, 1474, 1242, 1215, 1153, 800, 750, 619 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.19 (dd, \( J = 8.5, 7.4 \) Hz, 2H), 7.12 (d, \( J = 3.3 \) Hz, 1H), 7.05 (d, \( J = 8.5 \) Hz, 1H), 6.94 (d, \( J = 2.1 \) Hz, 1H), 6.89 (t, \( J = 6.4 \) Hz, 1H), 6.63 (dd, \( J = 8.5, 2.1 \) Hz, 1H), 6.59 (s, 1H), 6.51 (dd, \( J = 8.6, 0.9 \) Hz, 2H), 6.35 (dd, \( J = 3.3, 0.8 \) Hz, 1H), 3.47 (s, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 147.5, 140.1, 130.5, 129.3, 129.1, 127.6, 121.0, 113.1, 112.6, 110.0, 105.9, 99.5. HRMS m/z 222.1056 (M\(^-\)H\(^+\)), calcd for C\(_{14}\)H\(_{12}\)N\(_3\) 222.1031.

**6-Methoxy-N-phenyl-1H-indol-1-amine (1j):** Prepared following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as a white solid; IR (neat): \( \nu_{\text{max}} \), 3323, 1601, 1493, 1286, 1231, 1084, 1043, 933, 752, 692, 635 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.53 (d, \( J = 8.6 \) Hz, 1H), 7.22 (dd, \( J = 8.5, 7.5 \) Hz, 2H), 7.07 (d, \( J = 3.3 \) Hz, 1H), 6.92 (t, \( J = 7.4 \) Hz, 1H), 6.84 (dd, \( J = 8.6, 2.3 \) Hz, 1H), 6.79 (d, \( J = 2.2 \) Hz, 1H), 6.51 (dd, \( J = 15.8, 6.0 \) Hz, 4H), 3.79 (s, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 156.8, 147.2, 136.9, 129.4, 127.2, 121.7, 121.1, 120.4, 112.7, 110.5, 101.0, 92.6, 55.5. HRMS m/z 237.1006 (M\(^-\)H\(^+\)), calcd for C\(_{15}\)H\(_{13}\)N\(_2\)O 237.1028.

**5-Nitro-N-phenyl-1H-indol-1-amine (1k):** Prepared following the procedure B and purified by column chromatography using EtOAc/hexane and isolated as a yellow liquid; IR (neat): \( \nu_{\text{max}} \), 3323, 1603, 1578, 1514, 1497, 1205, 1327, 1067, 897, 743, 692, 602 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.63 (s, 1H), 8.12 (d, \( J = 9.0 \) Hz, 1H), 7.39 (dd, \( J = 9.1, 6.2 \) Hz, 2H), 7.26 (dd, \( J = 8.5, 7.5 \) Hz, 2H), 6.99 (t, \( J = 7.4 \) Hz, 1H), 6.82 (s, 1H), 6.77 (d, \( J = 3.4 \) Hz, 1H), 6.55 (dd, \( J = 8.6, 0.9 \) Hz, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 146.4, 142.4, 139.1, 131.7, 129.6, 125.6, 122.0, 118.3, 118.2, 112.8, 109.6, 103.5. HRMS m/z 252.0757 (M\(^-\)H\(^+\)), calcd for C\(_{14}\)H\(_{10}\)N\(_3\)O\(_2\) 252.0773.
6-Nitro-N-phenyl-1H-indol-1-amine (1l): Prepared following the procedure B and purified by column chromatography using EtOAc/hexane and isolated as a yellow solid; IR (neat): \( \nu_{\text{max}} \) 3319, 1603, 1514, 1495, 1400, 1333, 1211, 1119, 1061, 752, 692, 625 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.28 (d, \( J = 2.0 \) Hz, 1H), 8.02 (dd, \( J = 8.7 \), 2.1 Hz, 1H), 7.68 (d, \( J = 8.8 \) Hz, 1H), 7.49 (d, \( J = 3.3 \) Hz, 1H), 7.22 (dd, \( J = 8.6 \), 7.5 Hz, 2H), 6.95 (t, \( J = 6.9 \) Hz, 1H), 6.87 (s, 1H), 6.66 (dd, \( J = 3.3 \), 0.9 Hz, 1H), 6.52 (dd, \( J = 8.6 \), 1.0 Hz, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 146.6, 143.7, 134.8, 134.3, 131.0, 129.5, 121.9, 121.1, 115.8, 112.7, 106.4, 101.9. HRMS m/z 252.0773 (M – H\(^+\)), calcd for C\(_{14}\)H\(_{10}\)N\(_3\)O\(_2\) 252.0773.

\( N-(o\text{-Tolyl})-1H\text{-indol-1-amine (2a):} \): Prepared following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as a white solid; IR (neat): \( \nu_{\text{max}} \) 3331, 3051, 1600, 1514, 1495, 1402, 1346, 1327, 1238, 1067, 808, 746, 688 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.57 (dd, \( J = 6.8 \), 1.4 Hz, 1H), 7.14 (dd, \( J = 7.8 \), 1.4 Hz, 1H), 7.11 – 7.05 (m, 4H), 6.87 (t, \( J = 7.0 \) Hz, 1H), 6.74 (t, \( J = 7.4 \) Hz, 1H), 6.47 (dd, \( J = 3.3 \), 0.8 Hz, 1H), 6.43 (s, 1H), 5.94 (d, \( J = 8.1 \) Hz, 1H), 2.26 (s, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 145.0, 135.8, 130.5, 128.8, 127.3, 126.6, 122.4, 121.4, 121.1, 120.8, 120.3, 111.9, 109.3, 100.8, 17.1. HRMS m/z 221.1060 (M – H\(^+\)), calcd for C\(_{15}\)H\(_{13}\)N\(_2\) 221.1079.

5-Methoxy-N-(o-tolyl)-1H-indol-1-amine (2b): Prepared following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as a white solid; IR (neat): \( \nu_{\text{max}} \) 3342, 2935, 1622, 1589, 1472, 1283, 1236, 1148, 1030, 800, 752, 625 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.18 (d, \( J = 3.3 \) Hz, 1H), 7.16 (d, \( J = 7.4 \) Hz, 1H), 7.12 (d, \( J = 9.3 \) Hz, 2H), 6.98 (t, \( J = 7.7 \) Hz, 1H), 6.85 (dd, \( J = 14.0 \), 5.1 Hz, 2H), 6.52 (s, 1H), 6.49 (d, \( J = 3.2 \) Hz, 1H), 6.04 (d, \( J = 8.0 \) Hz, 1H), 3.87 (s, 3H), 2.36 (s, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 154.6, 145.1, 130.9, 130.4, 129.3, 127.3, 126.9, 121.3, 120.7, 112.6, 111.8, 110.1, 102.7, 100.2, 55.8, 17.1. HRMS m/z 251.1154 (M – H\(^+\)), calcd for C\(_{16}\)H\(_{15}\)N\(_2\)O 251.1184.
N\(^1\)-(1H-Indol-1-yl)-N\(^4\),N\(^4\)-dimethylbenzene-1,4-diamine (2c): Prepared following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as a yellow liquid; IR (neat): \(\nu_{\text{max}}\) 3312, 2795, 1516, 1453, 1327, 1215, 1124, 1086, 945, 816, 743 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.64 (d, \(J = 7.6\) Hz, 1H), 7.33 (d, \(J = 7.3\) Hz, 1H), 7.22 (d, \(J = 3.3\) Hz, 1H), 7.19 – 7.16 (m, 1H), 7.13 (td, \(J = 7.5, 1.1\) Hz, 1H), 6.67 – 6.64 (m, 2H), 6.53 – 6.50 (m, 3H), 6.42 (s, 1H), 2.84 (s, 6H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 146.5, 138.6, 136.0, 128.7, 126.5, 122.2, 120.9, 120.1, 114.5, 109.5, 100.3, 41.5. HRMS m/z 250.1320 (M – H\(^+\)), calcd for C\(_{16}\)H\(_{16}\)N\(_3\) 250.1344.

4-((1H-Indol-1-yl)amino)benzonitrile (2d): Prepared following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as a white solid; IR (neat): \(\nu_{\text{max}}\) 3302, 2222, 1607, 1510, 1456, 1258, 1217, 1173, 829, 762, 744, 546 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.67 (dd, \(J = 8.3, 1.4\) Hz, 1H), 7.45 (d, \(J = 8.8\) Hz, 2H), 7.22 – 7.17 (m, 3H), 7.14 (d, \(J = 3.4\) Hz, 1H), 6.98 (s, 1H), 6.59 (d, \(J = 3.4\) Hz, 1H), 6.50 (d, \(J = 8.8\) Hz, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 150.7, 135.3, 133.9, 128.0, 126.6, 122.9, 121.4, 120.9, 119.3, 112.3, 109.0, 103.5, 101.9. HRMS m/z 232.0877 (M – H\(^+\)), calcd for C\(_{15}\)H\(_{10}\)N\(_3\) 232.0875.

N-(4-Nitrophenyl)-1H-indol-1-amine (2e): Prepared following the procedure A and purified by column chromatography using EtOAc/hexane and isolated as a yellow solid; IR (neat): \(\nu_{\text{max}}\) 3329, 2359, 2341, 1597, 1501, 1329, 1261, 1217, 1113, 839, 762, 743 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.07 (d, \(J = 9.3\) Hz, 2H), 7.70 – 7.68 (m, 1H), 7.24 – 7.18 (m, 3H), 7.15 (d, \(J = 3.4\) Hz, 1H), 7.13 (s, 1H), 6.61 (d, \(J = 3.3\) Hz, 1H), 6.48 (d, \(J = 9.1\) Hz, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 152.5, 141.2, 135.3, 133.9, 128.0, 126.6, 123.0, 121.4, 121.0, 111.4, 109.0, 102.1. HRMS m/z 252.0754 (M – H\(^+\)), calcd for C\(_{14}\)H\(_{10}\)N\(_3\)O\(_2\) 252.0773.
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