Supporting Information

Synthesis of indoles via dehydrogenative N-heterocyclization by supported platinum catalysts

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NMR and GC/MS analysis

¹H and ¹³C NMR spectra for synthesized compounds were assigned and reproduced to the corresponding literature. ¹H and ¹³C NMR specta were recorded using at ambient temperature on JEOL-ECX 600 operating at 600.17 and 150.92 MHz, respectively with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and *d*-solvent (CDCl₃)peaks respectively. Abbreviations used in the NMR experiments: s, singlet d, doublet; t, triplet; q, quartet; m, multiplet. GC-MS spectra was taken by SHIMADZU QP2010.

Indole:1

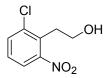


¹H NMR (600.17 MHz, CDCl₃, TMS): δ 7.91 (brs, 1H), 7.64 (d, J = 8.28 Hz, 1H), 7.31 (d, J = 8.22 Hz, 1H), 7.19-7.16 (m, 1H), 7.13-7.09 (m, 2H), 6.53 (d, J = 2.04 Hz, 1H); ¹³C NMR (150.92 MHz, CDCl₃) δ 135.65, 127.73, 124.12, 121.90, 120.66, 119.74, 111.01, 102.45; GC-MS m/e 117.055.

4-Chloro-1*H*-indole:¹

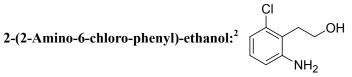


¹H NMR (600.17 MHz, CDCl₃, TMS): δ 8.25 (brs, 1H), 7.29 (d, *J* = 7.56 Hz, 1H), 7.25-7.22 (m, 1H), 7.13-7.09 (m, 2H), 7.13-7.09 (m, 2H), 6.66 (t like d, *J* = 3.42 Hz, 1H); ¹³C NMR (150.92 MHz, CDCl₃) δ 136.42, 126.73, 126.12, 124.63, 122.57, 119.57, 109.62, 101.35; GC-MS m/e 151.020.



2-(2-Chloro-6-nitro-phenyl)-ethanol:²

A typical reaction procedure is described for the synthesis of 2-(2-Chloro-6-nitro-phenyl)-ethanol. 2-chloro-6 nitro toluene (6.3 g, 36.5 mmol), paraformaldehyde (91 mmol), DMSO (20 mL), and Triton B (Benzenetrimethylammonium hydroxide, 40% solution of MeOH, 1.0 mL), were placed in a 100-mL three necked round bottomed flask equiped with a reflux condenser. The reaction mixture was stirred for 8 h at 90°C. Then the reaction mixture was quenched with saturated NH₄Cl solution, the organic compounds were extracted with ehtylacetate. The combined organic layers were washed with brine and dried over Na₂SO₄. After removal of the solvent, the residue was subjected to column chromatography (*n*-hexane:AcOEt = 4:1) to give 2-(2-Chloro-6-nitro-phenyl)-ethanol (88%). Mp 60-61 °C (*n*-hexane/AcOEt), light yellowish solid; ¹H NMR δ 7.70 (dd, 1H, J = 7.2, 1.2 Hz, 1H), 7.62 (dd, 1H, J = 7.2, 1.0 Hz, 1H), 7.33 (t, J = 8.10 Hz, 1H), 3.94 (t, J = 6.8 Hz, 2H), 3.27 (t, J = 6.8 Hz, 2H), 2.01 (brs, 1H); ¹³C NMR δ 151.97, 136.64, 133.74, 130.99, 127.90, 122.90, 61.07, 32.62; GC-MS m/e 201.02.



A typical reaction procedure is described for the synthesis of 2-(2-amino-6-chloro-phenyl)-ethanol. 2-(2-Chloro-6-nitro-phenyl)-ethanol (2.016 g, 10 mmol), Pd/C (5 wt %, 1 mol%), ethylacetate (5.0 mL) were placed in a 100-mL round bottomed flask equiped with a Hydrogen balloon. The reaction mixture was stirred for 6 h at room temperature. Then the catalyst was filtered off and after removal of the solvent, the residue was purified by column chromatography (*n*-hexane:AcOEt = 3:1) to give 2-(2-amino-6-chloro-phenyl)-ethanol (90%).

References

1. K. Fujita, K. Yamamoto and R. Yamaguchi, Org. Lett., 2002, 4, 2691.

2. Y. Tsuji, S. Kotachi, K. Huh and Y. Watanabe, J. Org. Chem., 1990, 55, 580.