

## Supporting Information

### **A Simple and Efficient *in situ* Generated Ruthenium Catalyst for Chemoselective Transfer Hydrogenation of Nitroarenes: Kinetic and Mechanistic Studies and Comparison with Iridium Systems**

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**Text S1: General Procedure for Optimization of Amount of NaO<sup>t</sup>Pr:**

Eight identical TH experiments of nitroarenes were conducted in parallel following the outlined procedure with varying amount of NaO<sup>t</sup>Pr (0, 10, 20, 30, 40, 50, 60, 70 and 80 mol% with respect to catalyst). All the reactions were carried out at 110°C (oil bath Temp) and the progress was monitored after 5 hours by gas chromatography. All the reactions were repeated three times and the average data were plotted as yield of aniline (%) vs amount of NaO<sup>t</sup>Pr (mol%) (Fig. 1).

**Text S2: General Procedure for Only NaO<sup>t</sup>Pr Catalysed TH of Nitrobenzene:**

In a screw cap tube nitrobenzene (123 mg, 1 mmol), NaO<sup>t</sup>Pr (32.8 mg, 0.4 mmol), toluene (as internal standard) and 10 mL dry isopropanol were taken under argon atmosphere. The mixture was heated to reflux at 110°C (oil bath Temp). The conversion and product selectivity were determined by gas chromatography at different time interval. The reaction was repeated three times and an average data were plotted as conversion (%) vs time (minute) (Fig. 5).

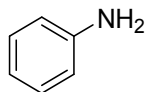
**Text S3: Performance Comparison of Ruthenium and Iridium Catalyst in the TH Experiment of Nitrobenzene:**

Two identical TH experiments of nitroarenes were conducted in parallel following the outlined procedure, one with Ru-catalyst and other with Ir-catalyst. Both the reaction tubes were heated at 110°C (oil bath Temp) and the progress of the reaction was monitored at different time interval by gas chromatography. The reactions were repeated three times and an average data for both catalyst were plotted as yield of aniline (%) vs time (minute) (Fig. 7).

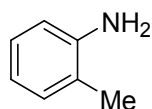
**Text S4: General Procedure for Influence of External Amine on TH of Nitrobenzene with Ru-catalyst:**

Two identical TH experiments of nitrobenzene were conducted in parallel following the outlined procedure, one acted as a control reaction. Under argon atmosphere 4-methoxy aniline (1 eq.) was added to one of the reaction tube whereas the other one keep in same argon condition. Both the tubes were heated at 110 °C in the oil bath and the progress of the reaction was monitored after 1 hour and 5 hours by gas chromatography. The yield of aniline with and without externally added 4-methoxy aniline were shown in Scheme 3.

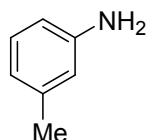
### Characterisation of products:



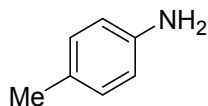
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.17 (t, *J*<sub>H,H</sub> = 7.75 Hz, 2H), 6.77 (t, *J*<sub>H,H</sub> = 7.45 Hz, 1H), 6.69 (d, *J*<sub>H,H</sub> = 7.51 Hz, 2H), 3.95 (br s, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 146.42, 129.38, 118.68, 115.23



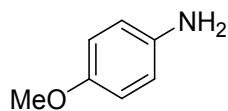
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.04 (t, *J*<sub>H,H</sub> = 7.63 Hz, 1H), 6.59 (d, *J*<sub>H,H</sub> = 7.54 Hz, 1H), 6.53-6.48 (m, 2H), 3.47 (br s, 2H), 2.26 (s, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 141, 129.25, 123.45, 119.72, 116.13, 112.46, 21.49



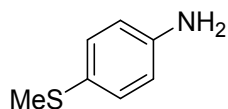
<sup>1</sup>H NMR (400 MHz, DMSO-D<sub>6</sub>): δ = 6.83 (t, *J*<sub>H,H</sub> = 7.64 Hz, 1H), 6.33-6.25 (m, 3H), 4.86 (br s, 2H), 2.10 (s, 3H). <sup>13</sup>C NMR (125 MHz, DMSO-D<sub>6</sub>): δ = 149.02, 138.22, 129.20, 117.07, 115.05, 111.68, 21.74



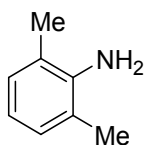
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 6.96 (d, *J*<sub>H,H</sub> = 7.88 Hz, 2H), 6.61 (d, *J*<sub>H,H</sub> = 8.36 Hz, 2H), 3.35 (br s, 2H), 2.20 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 143.81, 129.83, 127.92, 115.37, 20.68



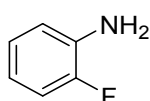
<sup>1</sup>H NMR (400 MHz, DMSO-D<sub>6</sub>): δ = 6.74 (d, *J*<sub>H,H</sub> = 8.84 Hz, 2H), 6.65 (d, *J*<sub>H,H</sub> = 9.0 Hz, 2H), 3.73 (s, 3H), 3.31 (br s, 2H). <sup>13</sup>C NMR (125 MHz, DMSO-D<sub>6</sub>): δ = 152.90, 139.77, 116.62, 115.02, 55.82



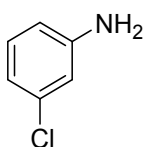
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.17(\text{d}, J_{\text{H,H}} = 8.48 \text{ Hz}, 2\text{H}), 6.62(\text{d}, J_{\text{H,H}} = 8.63 \text{ Hz}, 2\text{H}), 3.59(\text{br s}, 2\text{H}), 2.40(\text{s}, 2\text{H})$ .  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 145.15, 131.16, 125.93, 115.83, 18.88$



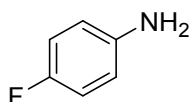
$^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta = 6.98(\text{d}, J_{\text{H,H}} = 7.42 \text{ Hz}, 2\text{H}), 6.68(\text{t}, J_{\text{H,H}} = 7.68 \text{ Hz}, 1\text{H}), 3.57(\text{br s}, 2\text{H}), 2.21(\text{s}, 6\text{H})$ .  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 142.81, 128.36, 121.82, 118.12, 17.73$



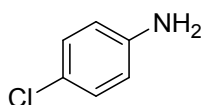
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.76(\text{d}, J_{\text{H,H}} = 7.25 \text{ Hz}, 1\text{H}), 7.47(\text{t}, J_{\text{H,H}} = 7.47 \text{ Hz}, 1\text{H}), 7.06(\text{d}, J_{\text{H,H}} = 8.35\text{Hz}, 1\text{H}), 6.98(\text{t}, J_{\text{H,H}} = 7.65 \text{ Hz}, 1\text{H})$ .  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 151.34, 136.99, 133.63, 125.51, 120.16, 116.21$



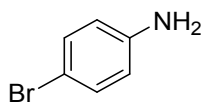
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.05(\text{t}, J_{\text{H,H}} = 7.92 \text{ Hz}, 1\text{H}), 6.71(\text{d}, J_{\text{H,H}} = 7.86 \text{ Hz}, 1\text{H}), 6.66(\text{t}, J_{\text{H,H}} = 2.21 \text{ Hz}, 1\text{H}), 6.54\text{-}6.51(\text{m}, 1\text{H}), 3.67(\text{br s}, 2\text{H})$ .  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 147.74, 134.92, 130.42, 118.53, 115.01, 113.29$



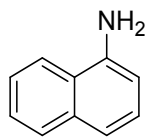
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.17(\text{d}, J_{\text{H,H}} = 9.30 \text{ Hz}, 2\text{H}), 6.9(\text{m}, J_{\text{H,H}} = 9.20 \text{ Hz}, 2\text{H})$ .  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 158.76, 121.58, 110.88, 66.51$



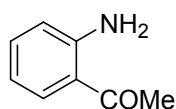
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.08(\text{d}, J_{\text{H,H}} = 8.72 \text{ Hz}, 2\text{H}), 6.59(\text{d}, J_{\text{H,H}} = 8.68 \text{ Hz}, 2\text{H}), 3.64(\text{br s}, 2\text{H})$ .  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 145.0, 129.19, 123.27, 116.30$



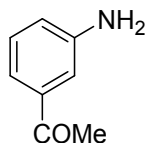
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.22 (d,  $J_{\text{H,H}} = 8.28$  Hz, 2H), 6.54 (d,  $J_{\text{H,H}} = 8.28$  Hz, 2H), 3.58 (br s, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 145.53, 132.09, 116.81, 110.25



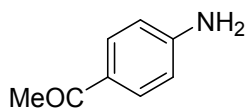
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.83-7.78 (m, 2H), 7.47-7.45 (m, 2H), 7.33-7.25 (m, 2H), 6.78 (dd,  $J_{\text{H,H}} = 6.95$  Hz,  $J_{\text{H,H}} = 1.2$  Hz, 1H), 4.14 (br s, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 139.60, 131.98, 126.08, 123.85, 123.35, 122.37, 121.24, 118.30, 116.53, 107.23



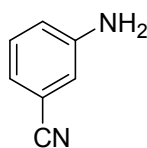
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.69 (dd,  $J_{\text{H,H}} = 8.32$  Hz,  $J_{\text{H,H}} = 1.48$  Hz, 2H), 7.26-7.22 (m, 1H), 6.65-6.60 (m, 2H), 6.26 (br s, 2H), 2.55 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 200.84, 150.37, 134.46, 132.12, 118.32, 117.29, 115.81, 27.94



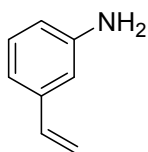
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.32 (d,  $J_{\text{H,H}} = 7.65$  Hz, 1H), 7.26-7.21 (m, 2H), 6.87 (dd,  $J_{\text{H,H}} = 8.05$  Hz,  $J_{\text{H,H}} = 1.95$  Hz, 1H), 2.03 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 198.46, 146.69, 139.58, 129.50, 119.75, 119.02, 114.15, 29.76



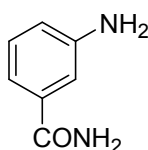
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.80 (d,  $J_{\text{H,H}} = 8.6$  Hz, 2H), 6.64 (d,  $J_{\text{H,H}} = 8.5$  Hz, 2H), 4.11 (br s, 2H), 2.49 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 191.78, 146.40, 126.12, 123.27, 109.05, 21.40



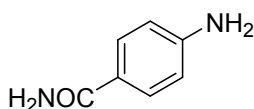
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.10 (t,  $J_{\text{H,H}} = 7.9$  Hz, 1H), 6.90 (d,  $J_{\text{H,H}} = 7.55$  Hz, 1H), 6.78 (s, 1H), 6.75 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 146.97, 130.13, 122.12, 119.27, 117.54, 113.04



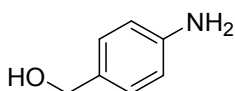
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.13(t,  $J_{\text{H,H}}$  = 7.70 Hz, 1H), 6.84 (d,  $J_{\text{H,H}}$  = 7.61 Hz, 1H), 6.75 (t,  $J_{\text{H,H}}$  = 1.95 Hz, 1H), 6.67-6.59(m, 2H), 5.72-5.69(d,  $J_{\text{H,H}}$  = 17.3 Hz 1H), 5.22(d,  $J_{\text{H,H}}$  = 10.95 Hz, 1H), 3.52(br s, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 146.52, 138.83, 137.13, 129.49, 117.10, 114.92, 113.65, 112.90



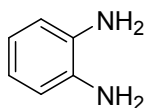
$^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  = 7.68 (s, 1H), 7.07-7.00 (m, 3H), 6.94 (d,  $J_{\text{H,H}}$  = 7.75 Hz, 1H), 6.65(d,  $J_{\text{H,H}}$  = 9.15 Hz, 1H), 5.13(br s, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  = 169.34, 149.06, 135.66, 129.09, 117.08, 115.27, 113.62



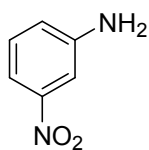
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  = 7.54 (d,  $J_{\text{H,H}}$  = 8.60 Hz, 2H), 6.78 (br s, 4H), 6.48 (d,  $J_{\text{H,H}}$  = 8.64 Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  = 168.64, 152.23, 129.64, 121.31, 112.96



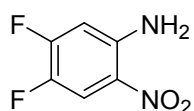
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.15 (d,  $J_{\text{H,H}}$  = 8.15 Hz, 2H), 6.67 (d,  $J_{\text{H,H}}$  = 8.25 Hz, 2H), 4.55 (s, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 146.13, 131.10, 128.88, 115.20, 65.43



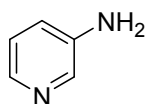
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 6.73-6.68 (m, 4H), 3.32(br s, 4H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 130.10, 115.62, 112.12



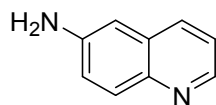
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.57$  (dd,  $J_{\text{H,H}} = 8.05$  Hz,  $J_{\text{H,H}} = 2.1$  Hz, 1H), 7.48 (t,  $J_{\text{H,H}} = 2.15$  Hz, 1H), 7.26 (t,  $J_{\text{H,H}} = 8.12$  Hz, 1H), 6.94 (dd,  $J_{\text{H,H}} = 8.05$  Hz,  $J_{\text{H,H}} = 2.25$  Hz, 1H), 2.40 (br s, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 158.14, 147.49, 130.0, 120.68, 113.26, 109.12$



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.72$  (d,  $J_{\text{H,H}} = 7.95$  Hz, 1H), 6.93 (d,  $J_{\text{H,H}} = 12.4$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 160.01, 157.84, 157.18, 135.67, 124.91, 104.62$



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.08$  (d,  $J_{\text{H,H}} = 2.64$  Hz, 1H), 7.99 (dd,  $J_{\text{H,H}} = 4.6$  Hz,  $J_{\text{HH}} = 1.22$  Hz, 1H), 7.06-7.02 (m, 1H), 6.96-6.93 (m, 1H), 3.60 (br s, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 142.57, 140.08, 137.55, 123.79, 121.54$



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.64$  (d,  $J_{\text{H,H}} = 4.01$  Hz, 1H), 7.89 (t,  $J_{\text{H,H}} = 9.65$  Hz, 2H), 7.25 (t,  $J_{\text{H,H}} = 4.80$  Hz, 1H), 7.14 (dd,  $J_{\text{H,H}} = 9.07$  Hz,  $J_{\text{H,H}} = 2.65$  Hz, 1H), 6.88 (d,  $J_{\text{H,H}} = 2.5$  Hz, 1H), 3.84 (br s, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 146.83, 144.72, 143.48, 133.90, 130.58, 129.89, 121.67, 121.46, 107.49$



# Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Amines

