Supplementary Material (ESI) for Green Chemistry
This journal is © The Royal Society of Chemistry 2006

# Simple and eco-friendly reduction of nitroarenes to the corresponding aromatic amines using polymer-supported hydrazine hydrate over iron oxide hydroxide catalyst

Qixun Shi, Rongwen Lu,* Kun Jin, Zhuxia Zhang and Defeng Zhao

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, P. R. China. Fax: +86 411 88993800; Tel.: +86 411 88993829; E-mail: lurw@dlut.edu.cn

## SUPPORTING INFORMATION

Contents:



## 1. Experimental details and powder X-ray diffraction pattern of iron oxide hydroxide catalyst

Powder X-ray diffraction measurement was carried out on a Rigaku D/Max 2400 instrument.

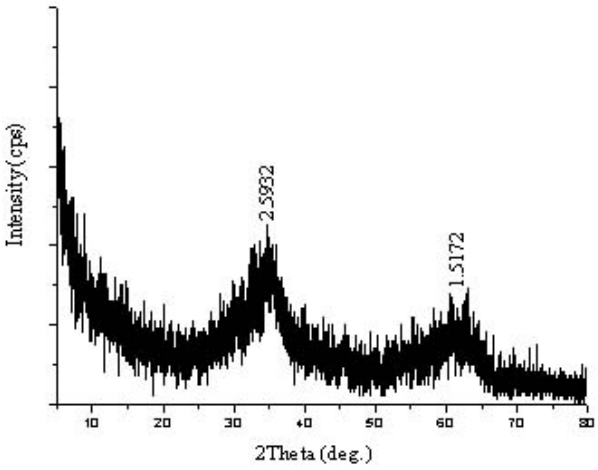
### (1) Preparation of iron oxide hydroxide catalyst

80 mL of 2 mol/L NaOH were added dropwise into an aqueous solution of 13.8 g $FeCl_3.6H_2O$ dissolved in 850 mL of distilled water under vigorous mechanical stirring. After the addition, the pH of mother liquor was 7-8. Then the suspension was heated to 60 °C and maintained at this temperature for 12 h. The solid formed was filtered, washed with deionized water and dried at 50 °C for one whole day. Afterwards, the dried product was milled to a fine powder.

### (2) Powder X-ray diffraction pattern of iron oxide hydroxide catalyst

Powder X-ray diffraction pattern of iron oxide hydroxide catalyst was given below

This journal is © The Royal Society of Chemistry 2006




## 2. Analytical data for products

$^1$H NMR spectra was measured on a Varian INOVA 400 M NMR instrument with TMS as an internal standard. MS was recorded on a HP 6890GC/5973MSD or HP 1100LC-MSD instrument. Spectral properties of products were given below

**Aniline (entry 1).** $^1$H NMR (DMSO-$d_6$, 400 MHz): δ 7.07 (2H, t, J=7.2 Hz, Ar-H), 6.65 (2H, d, J=7.2 Hz, Ar-H), 6.56 (1H, t, J=7.2 Hz, Ar-H), 4.99 (2H, s, -$NH_2$); MS: *m/z* 93 ($M^{+\cdot}$).

**2-Methyl-aniline (entry 2).** $^1$H NMR (DMSO-$d_6$, 400 MHz): δ 6.99-7.03 (2H, m, Ar-H), 6.75 (1H, d, J=7.6 Hz, Ar-H), 6.60 (1H, t, J=7.6 Hz, Ar-H), 4.75 (2H, s, -$NH_2$), 2.16 (3H, s, -$CH_3$); MS (API-ES): *m/z* 108 $[M+H]^+$.

**3-Methyl-aniline (entry 3).** $^1$H NMR (DMSO-$d_6$, 400 MHz): δ 6.94 (1H, t, J=7.6 Hz, Ar-H), 6.45 (1H, s, Ar-H), 6.44 (1H, d, J=8.0 Hz, Ar-H), 6.38 (1H, d, J=6.8 Hz, Ar-H), 4.90 (2H, s, -$NH_2$), 2.20 (3H, s, -$CH_3$); MS (API-ES): *m/z* 108 $[M+H]^+$.

**4-Methyl-aniline (entry 4).** $^1$H NMR (DMSO-$d_6$, 400 MHz): δ 6.82 (2H, d, J=8.0 Hz, Ar-H), 6.48 (2H, d, J=8.0 Hz, Ar-H), 4.77 (2H, s, -$NH_2$), 2.13 (3H, s, -$CH_3$); MS (API-ES): *m/z* 108 $[M+H]^+$.

**2-Chloro-aniline (entry 5).** $^1$H NMR (DMSO-$d_6$, 400 MHz): δ 7.20 (1H, d, J=7.6 Hz, Ar-H), 7.03 (1H, t, J=7.0 Hz, Ar-H), 6.86 (1H, d, J=7.4 Hz, Ar-H), 6.56 (1H, t, J=7.6 Hz, Ar-H), 5.30 (2H, s, -$NH_2$); MS: *m/z* 127 ($M^{+\cdot}$).

**3-Chloro-aniline (entry 6).** $^1$H NMR (DMSO-$d_6$, 400 MHz): δ 7.00 (1H, t, J=8.0 Hz, Ar-H), 6.64 (1H, s, Ar-H), 6.53 (1H, d, J=8.4 Hz, Ar-H), 6.51 (1H, d, J=8.4 Hz, Ar-H), 5.35 (2H, s, -$NH_2$); MS: *m/z* 127 ($M^{+\cdot}$).

**4-Chloro-aniline (entry 7).** $^1$H NMR (DMSO-$d_6$, 400 MHz): δ 7.01 (2H, d, J=8.8 Hz, Ar-H), 6.55 (2H, d, J=8.8 Hz, Ar-H), 5.22 (2H, s, -$NH_2$); MS: *m/z* 127 ($M^{+\cdot}$).

**3,4-Dichloro-aniline (entry 8).** $^1$H NMR (DMSO-$d_6$, 400 MHz): δ 7.17 (1H, d, J=8.8 Hz, Ar-H), 6.73 (1H, s, Ar-H), 6.51 (1H, d, J=8.6 Hz, Ar-H), 5.54 (2H, s, -$NH_2$); MS (API-ES): *m/z* 162 $[M+H]^+$.

**2-Amino-phenol (entry 9).** $^1$H NMR (DMSO-$d_6$, 400 MHz): δ 6.64 (1H, d, J=7.6 Hz, Ar-H), 6.58 (1H, t, J=7.6 Hz, Ar-H), 6.53 (1H, d, J=7.2 Hz, Ar-H), 6.40 (1H, t, J=7.6 Hz, Ar-H), 8.94 (1H, s, -OH), 4.46 (2H, s, -$NH_2$); MS: *m/z* 109 ($M^{+\cdot}$).

**Benzene-1,2-diamine (entry 10).** $^1$H NMR (DMSO-$d_6$, 400 MHz): δ 6.49-6.51 (2H, m, Ar-H), 6.37-6.39 (2H, m, Ar-H), 4.38 (4H, s, -$NH_2$); MS: *m/z* 108 ($M^{+\cdot}$).

**Benzene-1,3-diamine (entry 11).** $^1$H NMR (DMSO-$d_6$, 400 MHz): δ 6.64 (1H, t, J=7.6 Hz, Ar-H),

This journal is © The Royal Society of Chemistry 2006

5.78 (3H, t, J=8.4 Hz, Ar-H), 4.64 (4H, s, $-NH_2$); MS: *m/z* 108 ($M^{+\cdot}$).

**Benzene-1,4-diamine (entry 12).** $^1$H NMR (DMSO-$d_6$, 400 MHz): δ 6.35 (4H, s, Ar-H), 4.17 (4H, s, $-NH_2$); MS: *m/z* 108 ($M^{+\cdot}$).

**4-Methoxy-aniline (entry 13).** $^1$H NMR (DMSO-$d_6$, 400 MHz): δ 6.64 (2H, d, J=8.8 Hz, Ar-H), 6.52 (2H, d, J=8.4 Hz, Ar-H), 4.58 (2H, s, $-NH_2$), 3.61 (3H, s, $-OCH_3$); MS: *m/z* 123 ($M^{+\cdot}$).

**4-Amino-benzoic acid ethyl ester (entry 14).** $^1$H NMR (DMSO-$d_6$, 400 MHz): δ 7.63 (2H, d, J=8.4 Hz, Ar-H), 6.55 (2H, d, J=8.8 Hz, Ar-H), 5.95 (2H, s, $-NH_2$), 4.19 (2H, q, J=7.2 Hz, $-CH_2-$), 1.26 (3H, t, J=6.8 Hz, $-CH_3$); MS (API-ES): *m/z* 166 $[M+H]^+$, 188 $[M+Na]^+$.