

Supplementary information

Ni^{II}-Containing L-glutamic acid cross-linked chitosan anchored on Fe₃O₄/f-MWCNT: A sustainable catalyst for the green reduction and one-pot two-step reductive Schotten–Baumann-type acetylation of nitroarenes

Hossein Mousavi*, Behzad Zeynizadeh and Morteza Hasanpour Galehban

Department of Organic Chemistry, Faculty of Chemistry, Urmia University, Urmia, Iran.

E-mail: 1hossein.mousavi@gmail.com

S1. Experimental

S1.1. Preparation of the hybrid Fe₃O₄/f-MWCNT-CS-Glu/Ni^{II} nanocomposite

The hybrid Fe₃O₄/f-MWCNT-CS-Glu/Ni^{II} nanocomposite was prepared accurately through our previous research paper.¹¹

S1.2. General procedure for the reduction of nitroarenes to aryl amines catalyzed by the as-prepared Fe₃O₄/f-MWCNT-CS-Glu/Ni^{II} nanocomposite

As a representative example, in a round-bottom flask (10 mL) equipped with a magnetic stirrer, a mixture of PhNO₂ (1 mmol) and H₂O (3 mL) was prepared. Then, 5 mg of the as-prepared Fe₃O₄/f-MWCNT-CS-Glu/Ni^{II} nanocomposite was added, and the mixture was stirred. At the next step, NaBH₄ (2 mmol) was added, and the resulting mixture was continuously stirred at 60 °C for four minutes. After the completion of the reaction, the mentioned Ni^{II}-containing catalytic system was separated from the reaction pot using an external magnet. The reaction mixture was extracted with ethyl acetate (EtOAc) (2 × 5 mL) and then dried over anhydrous sodium sulfate (Na₂SO₄). Lastly, the solvent was evaporated under reduced pressure to afford the pure liquid aniline in 98% yield.

S1.2.1. Aniline

FT-IR (KBr) ν_{\max} 3430, 3356, 3216, 3071, 2924, 2854, 2768, 1618, 1497, 1276, 1173, 1052, 994, 754, 690, 501 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ_{H} 7.28–7.16 (m, 2H, –Ph), 6.83–6.70 (m, 2H, –Ph), 3.60 (s, 2H, –NH₂); ¹³C NMR (75 MHz, CDCl₃) δ_{C} 146.34, 129.31, 118.60, 115.16.

S1.3. General procedure for the one-pot two-step reductive Schotten–Baumann-type acetylation of nitroarenes catalyzed by Fe₃O₄/f-MWCNT-CS-Glu/Ni^{II} nanocomposite

As an example, in a round-bottom flask (10 mL) equipped with a magnetic stirrer, a mixture of PhNO₂ (1 mmol) and H₂O (3 mL) was prepared, and then, 5 mg of the as-prepared Fe₃O₄/f-MWCNT-CS-Glu/Ni^{II} nanocomposite was added, and the mixture was stirred. At the next step, NaBH₄ (2 mmol) was added, and the resulting mixture was continuously stirred at 60 °C for four minutes. After completion of the reduction step, acetic anhydride (Ac₂O) (1 mmol) was added to the reaction mixture, followed by stirring for further one minute at the same temperature conditions. After the completion of the acetylation reaction, the mentioned Ni^{II}-containing catalytic system was separated from the reaction pot using an external magnet. The reaction

mixture was extracted with ethyl acetate (EtOAc) (2×5 mL) and then dried over anhydrous sodium sulfate (Na_2SO_4). Lastly, the solvent was evaporated under reduced pressure to afford the pure acetanilide in 97% yield.

S1.3.1. *N*-phenylacetamide

FT-IR (KBr) ν_{max} 3299, 3195, 3128, 2927, 1663, 1605, 1521, 1380, 1310, 1255, 1021, 815, 750, 610, 499 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ_{H} 7.52 (s, 1H, $-\text{NH}-$), 7.49–7.27 (m, 4H, Ph), 7.11 (t, $J = 7.2$ Hz, 1H, Ph), 2.18 (s, 3H, $-\text{CH}_3$).