Supporting Information

Magnetically Separable Palladium Catalyst for Highly Selective Epoxide Hydrogenolysis under Mild Conditions

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Experimental Procedures

Synthesis of Catalyst 1: Pd(OAc)₂ (115 mg, 0.512 mmol) and THF (1.00 mL) were added to a 50 mL round bottom flask. The mixture was stirred at 23 °C for 10 min in the air. Al(O-sec-Bu)₃ (4.00 g, 16.2 mmol) and 2-butanol (1.00 mL) were added to the reaction mixture and the mixture was heated at 50 °C for 20 min in the air. Magnetite nanoparticles (100 mg) dispersed in ethanol (2.00 mL) were added to the resulting black suspension. The mixture was stirred for 10 min at 50 °C. Then, water (3.00 mL) was added to form black gel. The gel was isolated by filtration, washed with acetone, and dried at 120 °C for 5 h to give dark brown powder **1** (1.37 g; 3.66 wt% of Pd and 2.74 wt% of Fe).

Synthesis of Iron oxide nanoparticles:^[1] FeCl₃·6H₂O (540 mg, 2.00 mmol), ethylene glycol (16.0 g) were added to a 100 mL round bottom flask equipped with condenser. The mixture was stirred at room temperature for 10 min in the air. Sodium acetate (1.60 g) and poly(ethylene glycol) (M_n = 400; 400 mg) were added to the reaction mixture and the mixture was heated at 200 °C for 6 h in the air and allowed to cool to room temperature. The black nanoparticles were isolated by centrifugation and washed several times with ethanol, and dried under reduced pressure to give iron oxide nanoparticles as black powder (182 mg).

Hydrogenolysis of Epichlorohydrin: Epichlorohydrin (92 mg, 1.0 mmol) and **1** (58 mg, 2.0 mol % Pd) were added in ethyl acetate (2.0

mL). The mixture was stirred for 4 h at room temperature under hydrogen balloon. The catalyst was magnetically separated by using an external magnet, and washed five times with ethyl acetate, and then dried in the air for reuse. The yield was determined by GC analysis.

Recycling of 1 for the Hydrogenolysis of Epichlorohydrin^a

Cycle	1-5	6-10	11-15	16-21	22	23	24	25
Conv _n (%) ^b	64 ^c	64 ^c	66 ^c	64 ^c	95 ^d	97 ^d	94 ^d	96 ^d

^a The reaction was performed on 1.0 mmol of epichlorohydrin dissolved in 2.0 mL of EtOAc with 2.0 mol % Pd at 23 °C under hydrogen balloon. ^b Determined by GC. ^c Average yield after 1.5 h. ^d After 4 h.

Magnetization Curve for 1 Measured at 300 K

Photographs of Reaction Mixture

(a) The reaction mixture during the hydrogenolysis. (b) The reaction mixture after the hydrogenolysis and an external magnet.

NMR Data for the Products of Epoxide Hydrogenolysis

1,2-Diphenylethanol^[2]

^1H NMR (CDCl_3) δ 7.14 – 7.31 (10H, m), 4.80 – 4.84 (1H, m), 2.90 – 3.01 (2H, m), 2.09 (1H, s); ^{13}C NMR (CDCl_3) δ 144.0, 138.2, 129.7, 128.6, 128.5, 127.7, 126.7, 126.1, 75.4, 46.2.

Ethyl 1-2-Hydroxy-3-phenylpropionate^[3]

^1H NMR (CDCl_3) δ 7.18 – 7.30 (5H, m), 4.39 (1H, s), 4.14 – 4.21 (2H, m), 3.06 – 3.12 (1H, m), 2.91 – 2.98 (2H, m), 1.22 – 1.26 (3H, t, J = 7.2 Hz); ^{13}C NMR (CDCl_3) δ 174.2, 136.5, 129.6, 128.4, 126.8, 71.3, 61.7, 40.6, 14.2.

3-Phenylpropane-1,2-diol^[4]

^1H NMR (CDCl_3) δ 7.15 – 7.29 (5H, m), 3.80 – 3.84 (1H, m), 3.35 – 3.57 (4H, m), 2.66 – 2.68 (2H, d, J = 6.8 Hz); ^{13}C NMR (CDCl_3) δ

138.0, 129.5, 129.4, 128.6, 126.6, 73.2, 66.0, 39.8.

1-Phenoxy-2-propanol^[5]

^1H NMR (CDCl_3) δ 7.22 – 7.30 (2H, m), 6.87 – 6.97 (3H, m), 4.15 – 4.19 (1H, m), 3.74 – 3.92 (2H, m), 2.71 (1H, s), 1.25 – 1.27 (3H, d, J = 6.4 Hz); ^{13}C NMR (CDCl_3) δ 158.6, 129.6, 121.2, 114.6, 73.3, 66.3, 18.9.

NMR spectra of 1,2-Diphenylethanol

NMR spectra of Ethyl 2-Hydroxy-3-phenylpropionate

NMR spectra of 3-Phenylpropane-1,2-diol

NMR spectra of 1-Phenoxy-2-propanol

GC Data for Epoxides and the Products of Epoxide Hydrogenolysis

Entry 1 of Table 1

Entry 2 of Table 2

Entry 5 of Table 2

Entry 6 of Table 2

Entry 8 of Table 2

Entry 9 of Table 2

Entry 10 of Table 2

Entry 11 of Table 2

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