Supporting Information

Chemoselective reduction of α,β - unsaturated aldehydes using unsupported nanoporous gold catalyst

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1. General Information

Thin layer chromatography (TLC) was carried out on SiO₂ (silica gel 60 F254, Merck). Solvents were obtained and used without further purification. Silanes and aldehydes are commercially available. ¹H and ¹³C NMR spectra were recorded on either a Varian Inova-400 spectrometer (400 MHz for ¹H, 100 MHz for ¹³C) a Bruker Avance II-400 spectrometer (400 MHz for ¹H, 100 MHz for ¹³C); d_6 -DMSO and CDCl₃ with internal standard TMS were used as a solvent. The chemical shifts are reported in ppm downfield (δ) from TMS, the coupling constants *J* are given in Hz. The peak patterns are indicated as follows: bs, broad singlet; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

2. Fabrication of AuNPore Catalyst

An alloy of Au/Ag (30/70, in at. %) was prepared by melting Au (99.99%) and Ag (99.99%) in electric arc-melting furnace under Ar atmosphere. The resultant alloy was rolled down to thickness of 80-100 μ m. The thin plate was cut into 3 x 3 mm square pieces. These pieces (50.0 mg) were treated with 70 wt. % nitric acid (2.8 mL) in conical flask and were shaken for one hour after every five minute interval. The conical flask was then kept for 24 hours at room temperature to provide the nanoporous structure by selective de-alloying of silver. The resultant pieces were successively washed with pure water and acetone. Vacuum drying of these pieces gave the nanoporous gold (22.3 mg) and its composition was found to be Au₉₇Ag₃ by calculation from the weight loss of the silver.

3. Procedure for Reduction of α,β -Unsaturated Aldehydes



Representative procedure for reduction of **1a**: To acetonitrile solution (1.5 mL) were added AuNPore (2 mol%), cinnamaldehyde **1a** (0.5 mmol), Et₃SiH (1.5 mmol), Et₃N (0.25 mmol) and H₂O (3.0 mmol) successively at room temperature in a V-shaped reactor. The reaction mixture was stirred at 70 °C for 24 h and was monitored by Thin Layer Chromatography (TLC). Later, the solution was taken out from the V-shaped reactor with the help of pipette and the reactor was washed three times with acetone. Collective organic solution was evaporated to give crude

product, which was purified by silica gel column chromatography using a 3:1 mixture of pet ether and ethyl acetate as an eluent to give pure product 2a, in 73% yield.

(*E*)-3-phenylprop-2-en-1-ol (2a)

_{OH} ¹H NMR (CDCl₃, 400 MHz) δ : 7.37 (d, J = 7.6 Hz, 2H), 7.31 (t, J=7.2 Hz, 2H),

7.26-7.24(m, 1H), 6.60 (d, J = 15.6 Hz, 1H), 6.35 (dt, J = 16.0, 5.6 Hz, 1H), 4.31 (d, J = 5.6 Hz, 2H), 1.83 (br s, 1H, OH).

(*E*)-3-(p-tolyl)prop-2-en-1-ol (2b)



(*E*)-3-(m-tolyl)prop-2-en-1-ol (2c)



¹H NMR (CDCl₃, 400 MHz) δ : 7.23-7.17 (m, 3H), 7.06 (d, J = 6.8 Hz, 1H), 6.58 (d, J = 16.0 Hz, 1H), 6.36 (dt, J = 15.6, 6.0 Hz, 1H), 4.31 (d, J = 5.6 Hz, 2H), 2.34 (s, 3H), 1.70 (br s, 1H, OH).

(*E*)-3-(4-methoxyphenyl)prop-2-en-1-ol (2d)



¹H NMR (CDCl₃, 400 MHz) δ : 7.35-7.31 (m, 2H), 6.87-6.85 (m, 2H), 6.56 (d, J = 15.6 Hz, 1H), 6.24 (dt, J = 16.0, 6.0 Hz, 1H), 4.30 (dd, J = 5.6, 0.8 Hz, 2H), 3.81 (s, 3H), 1.81 (br s, 1H, OH).

(E)-3-(3-methoxyphenyl)prop-2-en-1-ol (2e)

OH ¹H NMR (CDCl₃, 400 MHz) δ : 7.23-7.21 (m, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.92 (s, 1H), 6.80 (dd, J = 8.0, 2.4 Hz, 1H), 6.59 (d, J = 15.6 Hz, 1H), 6.36 (dt, J = 16.0, 5.6 Hz, 1H), 4.32 (d, J = 5.6 Hz, 2H), 3.81 (s, 3H), 1.70 (br s, 1H, OH).

(E)-3-(2-methoxyphenyl)prop-2-en-1-ol (2f)

 $\stackrel{\text{IH NMR (CDCl}_3, 400 \text{ MHz})}{\circ} \delta: 7.44 \text{ (dd, } J = 7.6, 1.6 \text{ Hz}, 1\text{H}\text{)}, 7.24-7.21 \text{ (m, 1H)}, 6.95-6.91 \text{ (m, 2H)}, 6.87 \text{ (d, } J = 8.4 \text{ Hz}, 1\text{H}\text{)}, 6.39 \text{ (dt, } J = 16.0, 5.6 \text{ Hz}, 1\text{H}\text{)}, 4.33 \text{ (d, } J = 5.2 \text{ Hz}, 2\text{H}\text{)}, 3.85 \text{ (s, 3H)}, 1.50 \text{ (br s, 1H, OH)}.$

(E)-4-(3-hydroxyprop-1-en-1-yl)phenol (2g)

HO HO HING (DMSO-d₆
$$\delta$$
, 400 MHz) δ : 9.40 (s, 1H, OH), 7.23-7.21 (m, 2H), 6.72-6.70 (m, 2H), 6.41 (d, $J = 16.0$ Hz, 1H), 6.12 (dt, $J = 16.0$, 5.2 Hz, 1H), 4.72 (t, $J=5.6$ Hz, 1H), 4.07 (td, $J=5.6$, 1.6 Hz, 2H).

(E)-3-(3-hydroxyprop-1-en-1-yl)phenol (2h)



¹H NMR (DMSO-d₆ δ , 400 MHz) δ : 7.19 (t, *J*=8.0 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.87-6.86 (m, 1H), 6.74-6.72 (m, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 6.34 (dt, *J* = 16.0, 5.6 Hz, 1H), 5.04 (br s, 1H, OH), 4.32-4.31 (m, 2H), 1.50 (br s, 1H, OH).

(E)-3-(4-bromophenyl)prop-2-en-1-ol (2i)



¹H NMR (CDCl₃, 400 MHz) δ : 7.44 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 6.56 (d, J = 16.0 Hz, 1H), 6.35 (dt, J = 16.0, 7.6 Hz, 1H), 4.32 (t, J = 5.6 Hz, 2H), 1.97 (t, J = 5.6 Hz, 1H, OH).

(E)-3-(4-fluorophenyl)prop-2-en-1-ol (2j)



¹H NMR (CDCl₃, 400 MHz) δ : 7.27-7.24 (m, 4H), 6.51 (d, J = 15.6 Hz, 1H), 6.31-6.24 (m, 1H), 4.26 (d, J = 5.2 Hz, 2H), 2.90 (br s, 1H, OH).

(E)-3-(3-(trifluoromethyl)phenyl)prop-2-en-1-ol (2k)



¹H NMR (CDCl₃, 400 MHz) δ : 7.61 (s, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H),7.41 (t, J=7.6 Hz, 1H), 6.64 (d, J = 16.0 Hz, 1H), 6.43 (dt, J = 15.6, 5.6 Hz, 1H), 4.35 (d, J = 5.2 Hz, 2H), 1.97 (br s, 1H, OH).

(E)-2-methyl-3-phenylprop-2-en-1-ol (2m)

(E)-2-benzylideneheptan-1-ol (2n)

4. Deuterium Labeling in the Reduction of Cinnamaldehyde



To acetonitrile solution (1.5 mL) were added AuNPore (2 mol%), cinnamaldehyde **1a** (0.5 mmol), PhMe₂SiD (1.5 mmol), Et₃N (0.25 mmol) and H₂O (3.0 mmol) successively at room temperature in a V-shaped reactor. The reaction mixture was stirred at 70 °C for 24 h and was monitored by Thin Layer Chromatography (TLC). Later, the solution was taken out from the V-shaped reactor with the help of pipette and the reactor was washed three times with acetone. Collective organic solution was evaporated to give crude product, which was purified by silica gel column chromatography using a 3 : 1 mixture of pet ether and ethyl acetate as an eluent to give pure product 2**a'**, in 50% yield; ¹H NMR (CDCl₃, 400 MHz) δ : 7.40- 7.37 (m, 2H), 7.33- 7.30 (m, 2H), 7.26-7.22(m, 1H), 6.60 (dd, *J* = 16.0, 0.8 Hz, 1H), 6.35 (m, 1H), 4.31-4.29 (m, 1H), 2.08 (br s, 1H, OH); ¹³C NMR (CDCl₃, 100 MHz) δ : 136.7, 131.2, 128.6, 127.7, 126.5, 63.5.

5. NMR Spectra's of Products

















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