Supporting Information

Unsupported Nanoporous Gold Catalyst for Highly Selective Hydrogenation of Quinolines

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General Information. GC-MS analysis was performed on an Agilent 6890N GC interfaced to an Agilent 5973 mass-selective detector (30 m x 0.25 mm capillary column, HP-5MS). Scanning electron microscope (SEM) observation was carried out using a JEOL JSM-6500F instrument operated at an accelerating voltage of 30 kV. TEM characterization was performed using a JEM-2100F TEM (JEOL, 200 kV) equipped with double spherical aberration (Cs) correctors for both the probe-forming and image-forming lenses. ^1H NMR and ^{13}C NMR spectra were recorded on JEOL JNM AL 400 (400 MHz) spectrometers. ^1H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of CDCl_3 at 7.26 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broadened), and coupling constants (Hz). ^{13}C NMR spectra were recorded on JEOL JNM AL 400 (100.5 MHz) spectrometers with complete proton decoupling, and chemical shift reported in ppm (δ) relative to the central line of triplet for CDCl_3 at 77 ppm. Column chromatography was carried out employing silica gel 60 N (spherical, neutral, 40~100 μm , KANTO Chemical Co.). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F254 (Merck).

Materials. The hydrosilanes and substituted quinolines are commercially available, which are used as received. Au (99.99%) and Ag (99.99%) are purchased from Tanaka Kikinzoku Hanbai K.K. and Mitsuwa's Pure Chemicals, respectively. 2-Propylquinoline **1f**,^{1a} **1i**^{1b} and **1j**^{1c} were prepared following the reported literature.¹ **2i** was identified by ^1H NMR comparing with the literature reported.² Structures of **2a**,³ **2b**,³ **2c**,³ **2d**,³ **2e**,⁴ **1f**,⁵ **2f**,² **2g**,² **2h**,⁶ **2i**,² and **2j**⁹ were determined by comparing with the reported authentic compounds. Nanoporous gold (AuNPore)⁷ and nanoporous silver (AgNPore)⁸ was fabricated following the reported method.

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SEM images and EDX spectra of AuNPore catalyst

Figure S1. (a) EDX analysis of fresh AuNPore, Au₉₈Ag₂. (b) SEM image of after 5th cycle.

SEM images and EDX spectra of AgNPore catalyst

Figure S2. (a) SEM image and EDX analysis of fresh AgNPore, Ag₈₈Al₁₂.

Representative procedure for the AuNPore-catalyzed hydrogenation of **1a** (Tables 1, entry 1)

To a toluene solution (1 M, 0.5 mL) of AuNPore (2 mol%) were added **1a** (0.5 mmol), H₂O (1.5 mmol) and PhMe₂SiH (1.25 mmol) subsequently at room temperature. The reaction mixture was stirred at 80 °C for 24 hours and was monitored by GC-MS analysis. The AuNPore catalyst was recovered by filtration, and washed by diethyl ether. The recovered AuNPore catalyst was washed with acetone and dried under vacuum. After concentration, the residue was purified with a silica gel chromatography to afford **2a** in 86% yield.

Reaction procedure for the hydrogenation of isoquinoline (**1i**) (eq 4)

To a toluene solution (1 M, 0.5 mL) of AuNPore (2 mol%) were added **1i** (0.5 mmol), H₂O (2.0 mmol) and PhMe₂SiH (2.0 mmol) subsequently at room temperature. The reaction mixture was stirred at 80 °C for 26 hours and was monitored by GC-MS analysis. The AuNPore catalyst was recovered by filtration, and washed by diethyl ether. The recovered AuNPore catalyst was washed with acetone and dried under vacuum. After concentration, the residue showed that the corresponding **2i**² was observed in 73% ¹H NMR yield using CH₂Br₂ as an internal standard together with small amount of the recovered isoquinoline in 10% yield.

Deuterium-labeling experiment

To a toluene solution (1 M, 0.5 mL) of AuNPore (2 mol%) were added **1a** (0.5 mmol), D₂O (1.5 mmol) and PhMe₂SiH (1.25 mmol) subsequently at room temperature. The reaction mixture was stirred at 80 °C for 24 hours and was monitored by GC-MS analysis. The AuNPore catalyst was recovered by filtration, and washed by diethyl ether. After concentration, the residue showed that the 3-position deuterated corresponding product **2a'** was obtained in 60% NMR yield containing 100% D and **1a** was recovered in 28% yield.

Figure 1. ^1H NMR chart of Deuterium-labeling experiment for the reaction of quinoline with PhMe_2SiH and D_2O under standard conditions.

Leaching experiments

Quinoline **1a** was treated with PhMe_2SiH and water in the presence of AuNPore catalyst (2 mol%) in toluene at $80\text{ }^\circ\text{C}$. After 8 h, a part of supernatant was transferred to the other reaction vessel and **2a** was produced in 51% ^1H NMR yield at this time. The supernatant was continuously heated at $80\text{ }^\circ\text{C}$ in the absence of the catalyst for 16 h, affording **2a** in 51% ^1H NMR yield. In contrast, the residual containing the AuNPore catalyst was completed in 16 h, giving **2a** in 90% ^1H NMR yield.

Synthesis of starting material

2-propylquinoline (**1f**)¹

To a stirred solution of 2-methylquinoline (10.0 mmol) in ether at $0\text{ }^\circ\text{C}$ was added $n\text{-BuLi}$ (12.0 mmol, 1.62 M in hexane). After stirring 1.5 h at room temperature, $\text{CH}_3\text{CH}_2\text{I}$ (15.0 mmol) was added at $0\text{ }^\circ\text{C}$. The resulting mixture was stirred at room temperature for 3 h. Water (10 mL) was added, and the product was extracted with ethyl acetate (30 mL $\times$ 3). The combined organic layer was dried over sodium sulfate, and concentrated in vacuo. Silica gel column purification afforded 2-propylquinoline.

Analytical data of (**1** and **2**)

1,2,3,4-tetrahydroquinoline (**2a**)³

^1H NMR (400 MHz, CDCl_3) δ 7.00-6.95 (m, 2H), 6.64-6.60 (m, 1H), 6.50-6.48 (m, 1H), 3.81 (br, 1H), 3.31 (t, $J = 5.6\text{ Hz}$, 2H), 2.79 (t, $J = 6.4\text{ Hz}$, 2H), 1.99-1.93 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.6, 129.3, 126.6, 121.3, 116.8, 114.0, 41.9, 26.9, 22.1;

2-methyl-1,2,3,4-tetrahydroquinoline (**2b**)³

^1H NMR (400 MHz, CDCl_3) δ 7.02-6.99 (m, 2H), 6.66-6.63 (m, 1H), 6.51 (d, J = 8.4 Hz, 1H), 3.72 (br, 1H), 3.47-3.40 (m, 1H), 2.92-2.74 (m, 2H), 2.00-1.94 (m, 1H), 1.68-1.58 (m, 1H), 1.25 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.6, 129.1, 126.5, 120.9, 116.8, 113.8, 47.1, 30.1, 26.6, 22.6;

3-methyl-1,2,3,4-tetrahydroquinoline (2c)³

^1H NMR (400 MHz, CDCl_3) δ 7.00-6.95 (m, 2H), 6.62 (t, J = 7.2 Hz, 1H), 6.50 (d, J = 8.0 Hz, 1H), 3.84 (br, 1H), 3.30-3.26 (m, 1H), 2.91 (t, J = 10.4 Hz, 1H), 2.82-2.72 (m, 1H), 2.48-2.42 (m, 1H), 2.12-2.04 (m, 1H), 1.07 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.1, 129.4, 126.5, 121.0, 116.8, 113.7, 48.8, 35.5, 27.2, 19.0;

8-methyl-1,2,3,4-tetrahydroquinoline (2d)³

^1H NMR (400 MHz, CDCl_3) δ 6.95 (dd, J = 8.0 Hz, 10.0 Hz, 2H), 6.64 (t, J = 7.2 Hz, 1H), 3.71 (br, 1H), 3.45 (t, J = 5.6 Hz, 2H), 2.88 (t, J = 6.4 Hz, 2H), 2.16 (s, 3H), 2.06-2.00 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.5, 127.6, 127.2, 121.0, 120.6, 116.2, 42.2, 27.2, 22.1, 17.1;

3,6-dimethyl-1,2,3,4-tetrahydroquinoline (2e)⁴

^1H NMR (400 MHz, CDCl_3) δ 6.79 (d, J = 7.6 Hz, 2H), 6.42 (d, J = 7.6 Hz, 1H), 3.42-3.34 (m, 1H), 2.88-2.68 (m, 2H), 2.22 (s, 3H), 1.96-1.90 (m, 1H), 1.65-1.55 (m, 1H), 1.22 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.3, 129.7, 127.1, 126.1, 121.1, 114.1, 47.3, 30.4, 26.6, 22.6, 20.4;

2-propylquinoline (1f)⁵

^1H NMR (400 MHz, CDCl_3) δ 8.04-8.00 (m, 2H), 7.72 (d, J = 8.0 Hz, 1H), 7.66-7.62 (m, 1H), 7.46-7.43 (m, 1H), 7.27-7.24 (m, 1H), 2.95-2.90 (m, 2H), 1.86-1.77 (m, 2H), 0.99 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.7, 147.7, 136.0, 129.1, 128.7, 127.3, 126.6, 125.5, 121.2, 41.3, 23.3, 14.0;

2-propyl-1,2,3,4-tetrahydroquinoline (2f) ²

^1H NMR (400 MHz, CDCl_3) δ 7.03-6.99 (m, 2H), 6.67-6.63 (m, 1H), 6.52 (dd, J = 8.4 Hz, 1.2 Hz, 1H), 3.64 (br, 1H), 3.32-3.27 (m, 1H), 2.91-2.75 (m, 2H), 2.04-1.98 (m, 1H), 1.70-1.45 (m, 5H), 1.02 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.5, 129.1, 126.5, 121.2, 116.7, 113.9, 51.2, 38.8, 28.1, 26.4, 18.9, 14.2;

2-phenyl-1,2,3,4-tetrahydroquinoline (2g) ²

^1H NMR (400 MHz, CDCl_3) δ 7.36-7.20 (m, 5H), 6.99-6.95 (m, 2H), 6.61 (dd, J = 7.6, 7.6 Hz, 1H), 6.49 (d, J = 8.4 Hz, 1H), 4.40 (d, J = 9.2 Hz, 1H), 4.00 (s, 1H), 2.93-2.85 (m, 1H), 2.73-2.68 (m, 1H), 2.11-2.06 (m, 1H), 2.00-1.91 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.6, 144.6, 129.1, 128.4, 127.3, 126.7, 126.4, 120.7, 117.0, 113.8, 56.2, 31.0, 26.4;

6-chloro-1,2,3,4-tetrahydroquinoline (2h) ⁶

^1H NMR (400 MHz, CDCl_3) δ 6.93-6.90 (m, 2H), 6.38 (d, J = 8.4 Hz, 1H), 3.71 (br, 1H), 3.28 (t, J = 5.6 Hz, 2H), 2.73 (t, J = 6.4 Hz, 2H), 1.95-1.89 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.1, 128.8, 126.3, 122.6, 120.8, 114.9, 41.7, 26.8, 21.7;

2,3-Methyl-1,2,3,4-tetrahydroquinoline (2i) ²

Syn : *anti* = 2.5 : 1; ^1H NMR (400 MHz, CDCl_3) δ 7.00-6.96 (m, 2H, for *syn* and *anti* isomers), 6.64-6.60 (m, 1H), 6.49 (d, J = 8.0 Hz, 1H, for *syn* and *anti* isomers), 3.71 (br, 1H, for *syn* and *anti* isomers), 3.55 (bs, 1H, for *syn* and *anti* isomers), 3.46 (dq, J = 6.4, 3.2 Hz, 1H, for *syn* isomer), 3.01 (m, 1H, for *anti* isomer), 2.92 (dd, J = 16.5, 5.2 Hz, 1H, for *syn* isomer), 2.75 (dd, J = 16.0, 4.8 Hz, 1H, for *anti* isomer), 2.50 (dd, J = 5.6 Hz, 1H, for *syn* isomer), 2.50 (m, 1H, for *anti* isomer), 2.10-2.00 (m, 1H, for *syn* isomer), 1.70-1.58 (m, 1H,

for *anti* isomer), 1.22 (d, $J = 6.4$ Hz, 3H, for *anti* isomer), 1.13 (d, $J = 6.8$ Hz, 3H, for *syn* isomer), 1.04 (d, $J = 6.4$ Hz, 3H, for *anti* isomer), 0.96 (d, $J = 6.8$ Hz, 3H, for *syn* isomer); ^{13}C NMR (100 MHz, CDCl_3) *syn* isomer: δ 143.7, 128.9, 126.4, 121.1, 116.6, 113.3, 49.9, 33.8, 30.5, 18.1, 14.4; *anti* isomer: 144.3, 128.9, 126.5, 121.2, 116.6, 113.3, 53.2, 35.5, 33.5, 20.8, 18.3;

2-Phenethyl-1,2,3,4-tetrahydroquinoline (2j)⁹

^1H NMR (400 MHz, CDCl_3) δ 7.32-7.19 (m, 5H), 6.98-6.94 (m, 2H), 6.61 (dd, $J = 7.6, 7.6$ Hz, 1H), 6.46 (d, $J = 8.4$ Hz, 1H), 3.81 (bs, 1H), 3.33-3.28 (m, 1H), 2.82-2.73 (m, 4H), 2.04-1.97 (m, 1H), 1.87-1.82 (m, 2H), 1.73-1.66 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.3, 141.7, 129.1, 128.4, 128.2, 126.6, 125.8, 121.2, 116.9, 114.0, 51.1, 38.2, 32.2, 28.0, 26.2;

^1H and ^{13}C NMR spectra