Supporting Information**Highly Selective Aerobic Oxidation of Alcohol
Catalyzed by Gold(I) Complex with Anionic Ligand**

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General: All reagents were obtained commercially and used without further purification unless otherwise noted. Flash chromatographic purification of products was performed on silica gel 200-300 mesh. Thin-layer chromatography (TLC) was visualized with UV light (254 and 365 nm) or by iodine vapor staining. Proton nuclear magnetic resonance (^1H NMR) spectra were acquired on a Varian YH200/300, and carbon nuclear magnetic resonance (^{13}C NMR) spectra were acquired on a Varian YH200, respectively, and are referenced internally according to residual protio solvent signals or internal TMS standard. Data for ^1H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet), integration, coupling constant (Hz). Data for ^{13}C NMR are reported in terms of chemical shift (δ , ppm). Infrared resonance (IR) spectra were acquired on a Nicolet AVATAR 330. Electron spray mass spectrascopy (ESI) was acquired on a LCQ DECA XPplus (Thermo Finnigan). Low-resolution mass spectra were obtained from the Mass Spectrometry Facility, Peking University.

General Methods

Oxidation of benzyl alcohol with AuCl and neocuprione as catalyst and O₂ as oxidant.

11.0 mg of neocuprione (0.05 mmol) and 12.0 mg of gold(I) chloride were dissolved into 4 mL of distilled water. 108 mg of benzyl alcohol was added via syringe under N₂. After the addition, the reaction mixture was degassed three times and refilled with O₂. The reaction mixture was heated to 90 °C and stirred for 24 h. The reaction was extracted with ether and the yield and conversion was determined by GC with the use of *n*-decane as internal standard. GC spectroscopy showed us the conversion and yield are around 30%.

Preparation of Li-3 solution in hexanes.

Preparation of 0.25 mol/L of Li-3 solution in hexanes: 418 mg of **3** (1.0 mmol) was dissolved in 3.375 mL of dry hexanes and 0.625 mL of *n*-BuLi solution (1.6 mmol/L in hexanes, 1.0mmol) was added by syringe under N₂. After the addition, the reaction mixture was stirred at room temperature for additional 2 h. The solution was stored for the direct use of next step.

Oxidation of alcohols with AuCl and Li-3 as catalyst and TBHP or H₂O₂ as oxidants

12.0 mg of gold(I) chloride (0.05 mmol), 0.50 mL of **3** solution (prepared as above, 0.25 mol/L in hexanes, 0.063 mmol) were added into flame-dried Schlenk flask under nitrogen. After additional 2 min, 4 mL of freshly distilled toluene was added and the mixture became pale yellow. 1 mmol of benzyl alcohol **1a** was added quickly followed by the addition of 2 mL of TBHP solution (1.0 mol/L in toluene) and the colour of mixture was change to purple immediately. The mixture was heated to 90 °C and stirred for 24 h. and monitored by GC until the reaction was complete. All of conversions and yields of products were determined by GC with the use of decane as internal standard.

Oxidation of alcohols with AuCl and Li-3 as catalyst and O₂ as oxidant

("Caution! This oxidation reaction might occasionally lead to explosions due to this relatively harsh condition.")

12.0 mg of gold(I) chloride (0.05 mmol), 0.50 mL of **3** solution (prepared as above, 0.25 mol/L in hexanes, 0.063 mmol) were added into flame-dried Schlenk flask under

nitrogen. After additional 2 min, 4 mL of freshly distilled toluene was added and the mixture became pale yellow. 1 mmol of benzyl alcohol **1a** was added quickly and the colour of mixture was change to purple immediately. The mixture was degassed three times and refilled with O₂ under bubble pressure. The mixture was heated to 90 °C and stirred for the proper time and monitored by GC until the reaction was complete. Some of conversions and yields of products were determined by GC with the use of decane as internal standard. Some of the products were purified by flashchromatography with proper eluents.

Benzaldehyde (2a): ¹H NMR (200 MHz, CDCl₃) δ 10.01 (s , 1 H) , 7.90-7.85 (m, 2 H) , 7.63-7.52 (m ,3 H); ¹³C NMR(75 MHz, CDCl₃) δ 192.3, 136.6, 134.4, 129.6, 129.0; MS (m/e, EI): 106(M⁺); IR (film): 1700 cm⁻¹.

4-Bromobenzaldehyde (2e). ¹H NMR (200 MHz, CDCl₃) δ 7.73 (m, 4 H), 10.02 (s, 1 H); NMR (75 MHz, CDCl₃) δ 129.2, 130.5(2 C), 131.9, 134.7, 190.3; IR (KBr) 1687 cm⁻¹.

2-naphthaldehyde (2f): ¹H NMR (200 MHz, CDCl₃) δ 10.16 (s , 1 H) , 8.34-7.58 (m , 7 H); ¹³C NMR (200M Hz, CDCl₃) δ 192.2, 134.6, 134.5, 132.4, 129.5, 129.1, 129.1, 128.0, 127.1, 122.9, 122.8; MS (m/e, EI): 156(M⁺); IR (KBr): 1691 cm⁻¹.

E-Cinnamaldehyde (2g): ¹H NMR (200 MHz, CDCl₃) δ 9.65 (s , 1 H) , 7.54-7.50 (m , 2 H); 7.43-7.37 (m, 3H), 6.69 (d, *J* = 16.2 Hz, 1H), 6.65 (d, *J* = 16.2 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 193.3, 152.4, 133.7, 131.0, 128.9, 128.3, 128.2; MS (m/e, EI): 132 (M⁺); IR (KBr): 1696 cm⁻¹.

Acetophenone (2h): ¹H NMR (200 MHz, CDCl₃) δ 7.98-7.93 (m, 2 H), 7.56-7.41 (m, 3 H), 2.59 (s, 3 H); ¹³C NMR (75M Hz, CDCl₃) δ 198.0, 137.0, 133.0, 128.2, 128.2, 26.5; MS (m/e, EI): 120(M⁺); IR (KBr): 1683 cm⁻¹.

Phenyl vinyl ketone(2i): ^1H NMR (300 MHz, CDCl_3) δ 7.95 (d, $J = 7.22$ Hz, 2H), 7.57-7.60 (m, 1H), 7.47 (t, $J = 3.64$ Hz, 2H), 7.17 (dd, $J = 17.17, 10.59$ Hz, 1H), 6.45 (d, $J = 17.1$ Hz, 1H), 5.94 (d, $J = 8.95$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.105, 137.28, 133.00, 132.39, 130.23, 128.71, 128.63; MS (m/e, EI) 132 (M^+); IR (film) 1671 cm^{-1} .

Benzophenone (2j): ^1H NMR (200 MHz, CDCl_3) δ 7.83-7.78 (m, 4H), 7.59-7.48 (m, 6H); ^{13}C NMR (200 MHz, CDCl_3) δ 196.3, 137.9, 132.4, 130.1, 128.3; MS (m/e, EI): 182(M^+); IR (KBr): 1658 cm^{-1} .

4-nitrophenylethanone (2k): ^1H NMR (300 MHz, CDCl_3) for 8.33 (d, $J = 9.0$ Hz, 2H), 8.12 (d, $J = 9.0$ Hz, 2H), 2.69 (s, 3H); MS (m/e, EI): 165 (M^+); IR (KBr): 1640 cm^{-1} .

4-*t*-Butyl-cyclohexanone (2n): ^1H NMR (200 MHz, CDCl_3) δ 2.44-2.26 (m, 4 H), 2.15-2.01 (m, 2 H); 1.55-1.38 (m, 3H), 0.92 (s, 9H); ^{13}C NMR (200 MHz, CDCl_3) δ 212.9, 47.1, 41.7, 32.8, 28.0; MS (m/e, EI): 154 (M^+); IR (KBr): 1726 cm^{-1} .

Supporting Scheme 1.

(a) (b) (c)
Scheme 1. Photograph on colour change of alcohol oxidation catalyzed by gold(I)-**3** complex. (1) A solution of gold(I)-**3** complex with 1:1 ratio. (b) Benzyl alcohol was added and the colour of mixture was changed to purple immediately. (c) Nothing happened when dioxygen was streamed into a solution gold(I)-**3** complex.

ESI study on mechanism:

In reaction system, gold species was showed very obviously with ESI mass spectroscopy after two hours.