

1 *Supplementary Materials*

# 2 **Enhanced Selective Production of Carbonyl Products** 3 **for Aerobic Oxidation of Benzylic Alcohols over** 4 **Mesoporous Fe<sub>2</sub>O<sub>3</sub> Supported Gold Nanoparticles**

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## 11 **1. Materials**

12 Ordered KIT-6 mesoporous silica was purchased from XFNano Co. Ltd, Nanjing, China. The  
13 following chemicals were purchased from the Sinopharm Chemical Reagent Co. Ltd, Shanghai,  
14 China and used as received: iron(III) nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O), sodium hydroxide (>  
15 99%), toluene (anhydrous, > 99% GC assay), urea (> 99%), dodecane (anhydrous, > 99% GC assay).  
16 Gold chloride trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O, > 99.9%), diphenyl ether (> 99% GC assay), cyclohexanol (>  
17 99% GC assay), cinnamic alcohol (> 99% GC assay), 1-phenylethanol (> 99% GC assay) and benzyl  
18 alcohol (> 99% GC assay) were purchased from Aladdin Co. Ltd, Shanghai, China and used without  
19 further purification. Purified water (EASypure II, resistivity:18.2 MΩ·cm<sup>-1</sup>) were also received and  
20 used without further purification. For synthesis of benzylic alcohol, and related lignin model  
21 compounds, 4-hydroxy-3-methoxy- $\alpha$ -methylbenzyl alcohol, 4'-methylacetophenone, 4'-  
22 methoxyacetophenone, 4'-bromoacetophenone, 3',4'-dimethoxyacetophenone, cyclopropyl phenyl  
23 ketone, benzophenone, 2-bromo-4'-methoxyacetophenone, guaiacol, sodium borohydride and p-  
24 toluenesulfonyl chloride were purchased from Aladdin Co. Ltd, Shanghai, China and used without  
25 further purification.

## 26 **2. General synthetic procedure for benzylic alcohols**

27 Related benzylic alcohol was synthesized via reduction of the corresponding ketones. The  
28 appropriate ketone (1 mmol) was dissolved in THF: MeOH (v/v=1:1, 50 mL). Sodium borohydride  
29 (3.5 mmol) was added into the reaction mixture at 0 °C. After stirring overnight, the reaction mixture  
30 was concentrated and diluted with deionized water (200 mL). The mixture was extracted with  
31 dichloromethane (50 mL) and combined organic extracts were dried over anhydrous MgSO<sub>4</sub> and  
32 concentrated in vacuum. Resulting products were analyzed by means of GC-MS. Yields were higher  
33 than 95% in all cases.

## 34 **3. General synthesis procedure of $\beta$ -O-4 linkage lignin model compounds**

### 35 *3.1. Synthesis of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)-ethanone (product 4)*

36 2-Bromo-4'-methoxyacetophenone (22 g, 0.11 mol) was added to a solution of K<sub>2</sub>CO<sub>3</sub> (20 g, 0.14  
37 mol) and guaiacol (16 g, 0.13 mol) in acetone (100 mL). After stirring at reflux condition overnight,  
38 the reaction mixture was filtered and dried over anhydrous MgSO<sub>4</sub>. The crude product was  
39 recrystallized from EtOAc/hexanes giving product 4. Yield: 27.6 g (93%) [1].

40 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.03-8.01 (dd, J= 8.8, 1.4 Hz, 2H), 6.97-6.84 (m, 6H), 5.29 (s, 2H),  
41 3.89 (s, 3H), 3.88 (s, 3H).

42 <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  193.1, 163.9, 155.8, 149.7, 147.6, 130.5, 127.7, 122.3, 120.8, 114.7,  
43 113.9, 112.1, 71.9, 55.9, 55.5.

### 44 3.2. Synthesis of 3-hydroxy-2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)-1-propanone (product 2)

45 Product 4 (5 g, 18 mmol) was added into a stirred suspension of  $K_2CO_3$  (2.8 g, 20 mmol) in a 1:1  
46 mixture of ethanol/acetone (100 mL) solution. Aqueous formaldehyde solution (37 wt.%) (0.82 mL,  
47 11 mmol) was added and stirred overnight and concentrated in vacuo to give a yellow oil. After  
48 subjected to column chromatography on silica gel (DCM: ethyl acetate, v/v=6:1), the crude product  
49 was to give a yellow-colored oil, which was crystallized from ethanol to give a pale yellow solid.  
50 Yield: 4.3 g (78%) [2].

51  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.08-8.05 (dd,  $J$ = 9.4, 2.0 Hz, 2H), 6.97-6.80 (m, 6H), 5.39-5.37 (t,  
52  $J$ = 5.2 Hz, 1H), 4.06 -4.05 (d,  $J$ = 5.4 Hz, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 3.17 (s, 1H).

53  $^{13}C$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  199.9, 188.9, 162.9, 131.2, 127.9, 123.4, 121.2, 118.1, 113.9, 112.3,  
54 84.5, 63.6, 55.8, 55.5.

### 55 3.3. Synthesis of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)-1,3-propanediol (product 1)

56 Product 2 (1.5 g, 5 mmol) was dissolved in THF: MeOH (v/v=2:1, 30 mL). Sodium borohydride  
57 (0.4 g, 10 mmol) was added in portions under stirring at 0 °C. After stirring overnight at room  
58 temperature, the reaction mixture was concentrated in vacuo and diluted with 20 mL deionized water.  
59 The mixture was extracted with dichloromethane (3-15 mL) and dried over anhydrous  $MgSO_4$ . The  
60 crude product was subjected to column chromatography on silica gel (DCM: ethyl acetate, v/v=4:1)  
61 to give a yellow oil. Yield: 1.18 g (84%).

62  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.36-7.24 (ddd,  $J$ = 13.5, 8.5, 1.7 Hz, 2H), 7.11-7.01 (m, 2H), 6.91-  
63 6.86 (m, 4H), 4.97 (s, 1H), 4.13 -4.01 (m, 1H), 3.88 (s, 3H), 3.77 (s, 3H), 3.5 (m, 1H).

64  $^{13}C$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  162.9, 151.7, 147.8, 147.1, 128.5, 127.5, 124.5, 121.8, 121.1,  
65 114.1, 113.9, 112.3, 87.5, 72.6, 60.8, 56.0, 55.4.

### 66 3.4. Synthesis of 1-(4-methoxyphenyl)-2-(2-methoxyphenoxy)-2-propen-1-one (product 3)

67 Product 2 (1.5 g, 5 mmol) dissolved into a DCM (30 mL) solution and  $Et_3N$  (2.0 mL, 14 mmol)  
68 was stirred at 30 °C prior to the addition of p-toluenesulfonyl chloride (1.43 g, 7.5 mmol). After  
69 stirring overnight, diluted with additional DCM (20 mL), washed with deionized water (2×20 mL),  
70 dried over anhydrous  $MgSO_4$ . The crude product was purified via column chromatography (DCM:  
71 ethyl acetate, v/v= 1:1) giving a yellow oil. Yield: 0.83 g (74%) [3].

72  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.31-8.29 (dd,  $J$ = 8.5, 2.7 Hz, 2H), 8.11-8.03 (m 2H), 7.96-7.93 (dd,  
73 8.2, 2.2 Hz, 1H), 7.56-7.54 (dd,  $J$ = 8.3, 2.2 Hz, 2H), 6.96-6.87(m, 2H), 5.19-5.18 (d,  $J$ = 2.20 Hz, 1H), 4.72-  
74 4.71 (d,  $J$ = 2.13 Hz, 1H), 3.90 (s, 3H), 3.85 (s, 3H).

75  $^{13}C$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  169.3, 163.1, 162.6, 151.3, 151.1, 142.9, 132.9, 132.4, 122.3,  
76 113.7, 113.2, 112.2, 101.8, 55.5, 55.1.

### 77 3.5. Synthesis of (2-methoxyphenyl)-4-methoxybenzoate (product 7)

78 p-Anisic acid (4.9 g, 0.032 mol) was added to a solution of oxalyl chloride (4.35 g, 0.035 mol) in  
79 DCM (100 mL). After stirring overnight at room temperature, the mixture was concentrated in vacuo  
80 to give yellow colored oil. DCM (50 mL) was added to redissolve the mixture to which guaiacol (4.003  
81 g, mmol) was added. After stirring for 4 h, the reaction mixture was washed with deionized water (2  
82 ×20 mL) and the organic extract was dried over anhydrous  $MgSO_4$  to give a clear colored oil. The  
83 crude product was recrystallized from ethanol giving a white crystalline solid. Yield: 6.85 g (83%) [4].

84  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.2-8.16 (dd,  $J$ = 8.8, 1.8 Hz, 2H), 7.25-7.20 (t,  $J$ = 6.5 Hz, 1H), 7.15-  
85 7.13 (dd,  $J$ = 6.6, 1.6 Hz, 1H), 7.02-6.96 (m, 4H), 3.88 (s, 1H), 3.81 (s, 1H).

86  $^{13}C$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  164.5, 163.8, 163.0, 151.5, 140.1, 132.4, 132.1, 126.8, 123.1,  
87 121.8, 120.8, 113.8, 112.5, 55.9, 55.5.

88  $^1H$  and  $^{13}C$  NMR spectra were obtained with Bruker 400 MHz spectrometer with  
89 tetramethylsilane used as the internal reference.

## 90 4. Synthesis and methods

91 The mesoporous Fe<sub>2</sub>O<sub>3</sub> supported gold nanoparticles (Au/meso-Fe<sub>2</sub>O<sub>3</sub>) was synthesized with  
92 hard template method. For typical synthesis processes, 0.6 g KIT-6 was dispersed in 5 mL toluene by  
93 sufficient stirring and evenly dispersed, then 1.1543 g Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were added dropwise and  
94 refluxed for 6 h at 70 °C. Then the solid mixture was filtrated, dried at 70 °C and calcined at 600 °C  
95 with heating rate of 1 °C·min<sup>-1</sup> for 3 h. Finally, the resulting material was dissolved in 2 mol·L<sup>-1</sup> NaOH  
96 and continuously stirred for 24 h at 40 °C. After washing and vacuum drying, the obtained  
97 mesoporous Fe<sub>2</sub>O<sub>3</sub> was denoted as meso-Fe<sub>2</sub>O<sub>3</sub>. Then 1 g of meso-Fe<sub>2</sub>O<sub>3</sub> was added into 80 mL of  
98 water and stirred for 1 h. 10 mL of 0.0025 mol/L H<sub>2</sub>AuCl<sub>4</sub> solution was added into above solution and  
99 stirred for another 1 h. After adding 0.9 g of urea into above mixture, the mixture was heated to 80  
100 °C and continue stirred for 8 h. After centrifuging and washing, the precipitate is vacuum dried at 60  
101 °C and reduced at 120 °C for 3 h in H<sub>2</sub> flow (50 mL/min), which was denoted as Au/meso-Fe<sub>2</sub>O<sub>3</sub>.

102 Oxidation reaction of benzylic alcohols was conducted in a 50 mL 3-neck round-bottom flask,  
103 employing the substrate (1 mmol), iron-based catalyst 100 mg and dodecane (1 mmol) in 10 mL of  
104 diphenyl ether under flowing air (30 mL·min<sup>-1</sup>) at 120 °C and 500 rpm stirring. The aliquots were  
105 taken periodically and analyzed by GC (Shimadzu 2010 GC-FID, Agilent HP-5, 0.320 mm inner  
106 diameter, 30 m long, 0.25 μm film thickness) using dodecane as internal standard.

## 107 5. Catalysts characterizations

108 The morphology and structure of mesoporous templates and catalysts were observed using a  
109 scanning electron microscope (SEM, JSM-7000F) equipped with energy-dispersive X-ray  
110 spectroscopy (EDS) at 20 kV and a transmission electron microscope (TEM, JEM 2100, 200 kV). Prior  
111 to the recording, samples were prepared by suspension in ethanol, assisted by sonication and  
112 followed by deposition on a copper grid-supported carbon film. The average cluster size was  
113 obtained by counting 80 metal particles. Low and high angle XRD patterns were recorded using a  
114 Bruker D8 diffractometer (Cu Kα radiation with a λ of 1.54 Å). Average particle sizes of Ni in the  
115 catalysts were calculated using the Debye–Scherrer equation. Textural properties of the samples were  
116 determined by N<sub>2</sub> physisorption isotherms using a Micromeritics ASAP 2020 automated system.  
117 Surface areas of the catalysts were calculated by BET method, and pore volume and average pore  
118 diameter were determined by the BJH method. The content and leaching of gold were determined by  
119 ICP method (Varian Instruments).

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