

Supplementary Information

Materials

SiO₂, Al₂O₃, MgO, Pr₆O₁₁ and Urea were the commercial products of Tianjin Kermel Chemical Reagent Co., Ltd., H₂AuCl₄ were purchased from Aladdin Chemistry Co., Ltd. α -bromo acetophenone (98%), phenol and guaiacol were purchased from Alfa Aesar.

Preparation of 2-phenoxyacetophenone and 2-phenyloxy-1-phenylethanol

2-Phenoxy-1-phenylethanol (PP-one) was synthesized by a modified procedure published in literature[1]. Typically, 2-bromo-1-phenylethanol (11.8 g, 49 mmol) and phenol (8 g, 85 mmol) were dissolved in 250 mL acetone, mixed with K₂CO₃ (12.3 g, 89 mmol) and refluxed at 343K for 12h. After cooling down to room temperature, K₂CO₃ was separated by filtration. Then, the product was obtained by recrystallization from ethanol.

2-Phenoxy-1-phenylethanol (PP-ol) was synthesized by selective reduction of the carbonyl group in 2-phenoxy-1-phenylethanol. 2-Phenoxy-1-phenylethanol (1.5 g, 6.8 mmol) was first dissolved in 35 mL mixture of tetrahydrofuran and water (4/1, v/v). NaBH₄, which was used as a reductant, was added into the solution and the solution was then stirred at room temperature for 6 h. A saturated solution of ammonium chloride (50 mL) followed by 50 mL water was added into the reaction mixture. Then, the product was extracted by ethyl ether, washed with saturated NaCl and recrystallized from ethanol. Similar procedures were also employed for the synthesis of other β -O-4 lignin model compounds.

Product analysis

Gas Chromatography-Mass Spectrometer (GC-MS):

Analysis of samples was performed on an Agilent 7697A GC equipped with a 5977B MS. Sample compounds were separated using a 30 m \times 0.25 mm \times 0.10 μ m DB-5HT column (Agilent). Each sample was placed on an auto-sampler (Agilent) and injected at a volume of 1 μ L into the GC/MS (Agilent). The GC/MS method consisted of a front inlet temperature of 300 °C, MS transfer line temperature of 300 °C. A starting temperature of 40 °C was held for 5 minutes and then ramped at 10 °C min⁻¹

to a temperature of 180 °C, then continued at a ramped rate of 15 °C min⁻¹ to 250 °C and held for 10 minutes.

High performance liquid chromatography (HPLC):

Reaction mixture was analyzed using Shimazu LC-20A make HPLC system equipped with autosampler, C18 column (7 mm, 8×300 mm) and differential refractive index detector (RID) detector (50 °C). CH₃OH: H₂O (9:11 v/v) was used as a mobile phase with a flow rate of 1 mL/min. The identification of compounds in the reaction mixture was done by injecting standards.

Table S1. Physicochemical properties of catalysts.

Catalyst	Au loading(wt%) ^a	S _{BET} /m ² g ⁻¹	D _{pore} ^b /nm	V _{pore} ^b /cm ³ g ⁻¹
SiO ₂	–	152.1	19.2	0.92
Al ₂ O ₃	–	180.7	8.7	0.57
Pr ₆ O ₁₁	–	72	10.6	0.38
CeO ₂	–	68.7	10	0.22
Au/SiO ₂	0.94	164.4	22.3	0.91
Au/Al ₂ O ₃	0.91	187.4	9.7	0.55
Au/Pr ₆ O ₁₁	0.73	88	12.6	0.35
Au/CeO ₂	0.88	53	12.1	0.21

^a Metal loading determined by ICP-AES.

^b Obtained from P/P0 = 0.99.

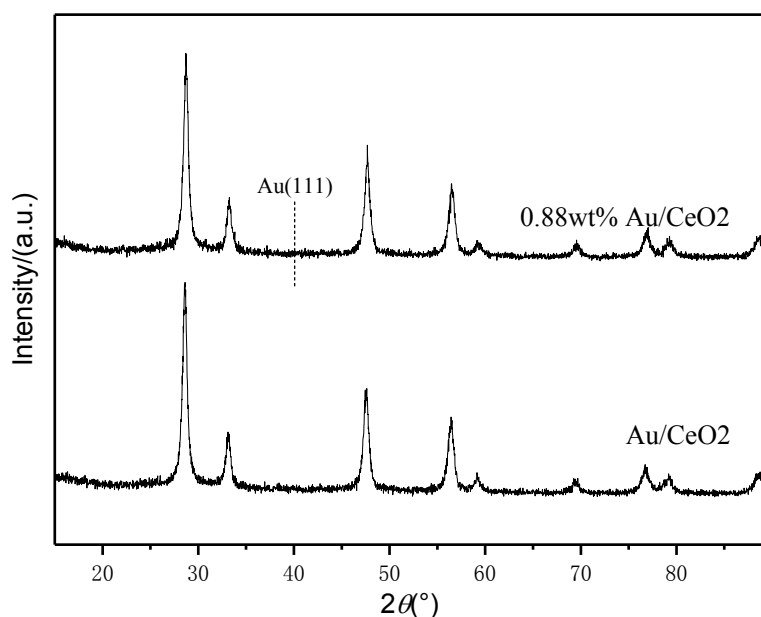


Fig.S1 XRD patterns of CeO₂ and 0.88wt% Au/CeO₂

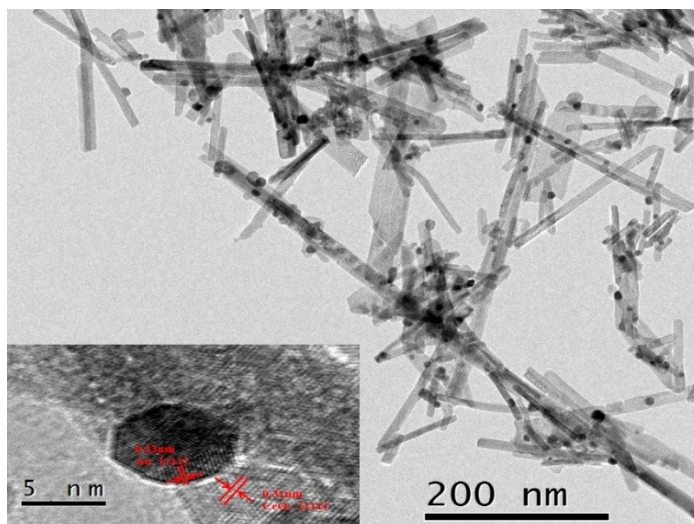


Fig. S2 TEM of Au/CeO₂

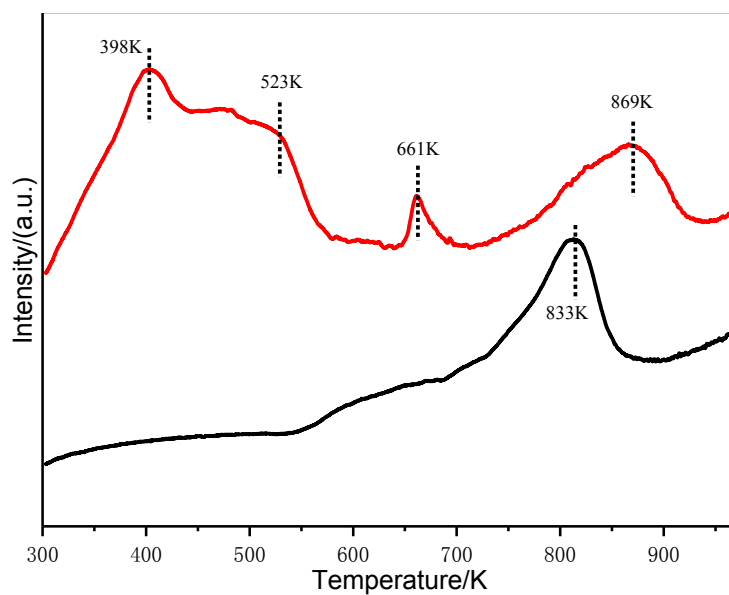


Fig.S3 H₂-TPR profiles of the CeO₂ and Au/CeO₂

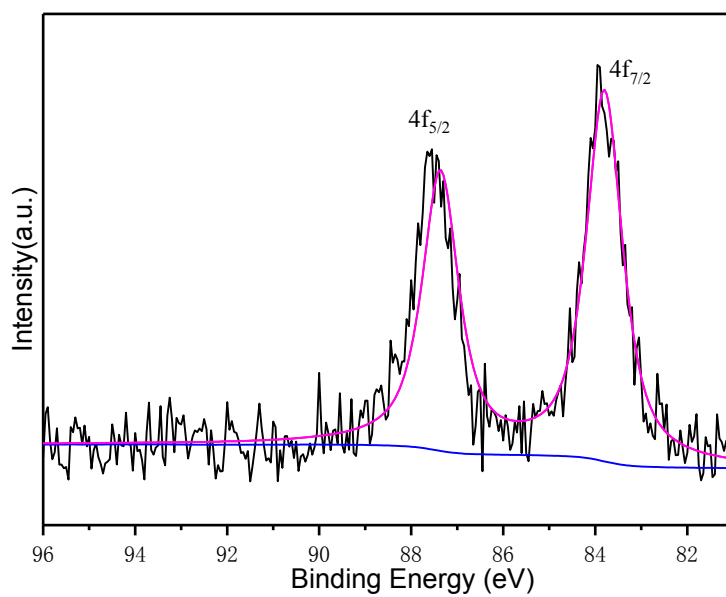


Fig. S4 XPS analysis of Au/CeO₂ samples.

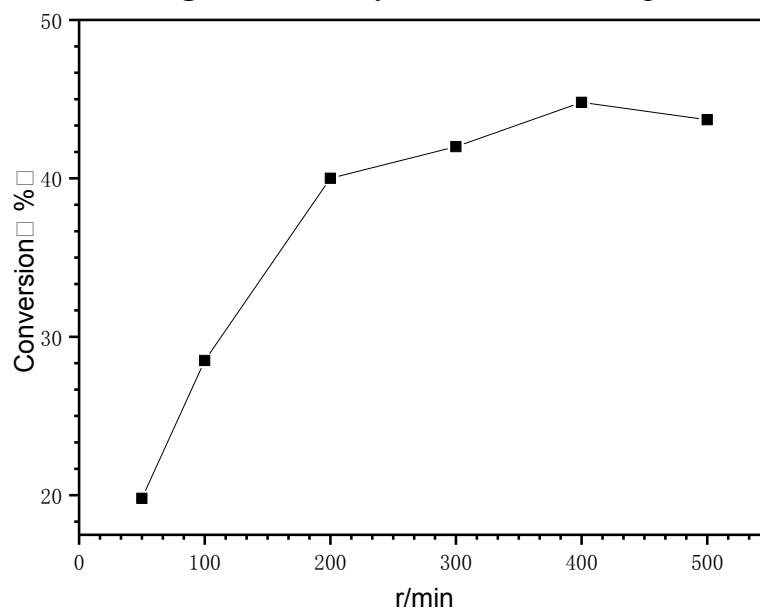


Fig.S5 the conversion of 2-phenoxy-1-phenylethanol as a function of stirring speed. Experimental conditions: substrate, 0.1 g (0.47 mmol); catalyst, 0.1 g; MeOH, 25 mL; O₂, 1 MPa; 453K; 1 h.

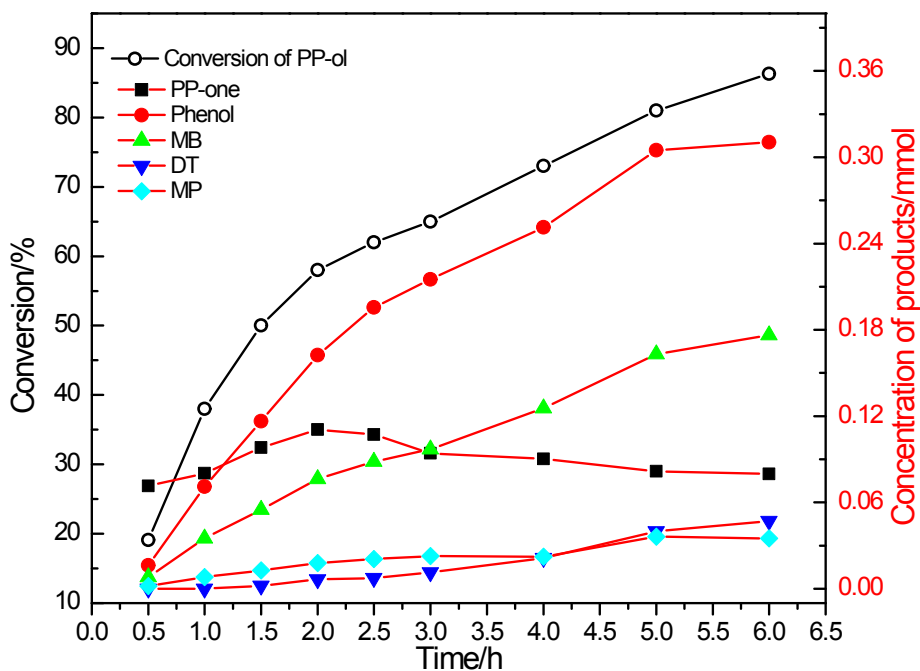


Fig. S6 Time course for the oxidation of PP-ol catalyzed by Au/CeO₂. (A) PP-ol conversion. (B) Concentration of products. Reaction conditions: 0.1 g (0.47 mmol); catalyst, 20 mg; CH₃OH, 25 mL; O₂, 1 MPa; 453 K.

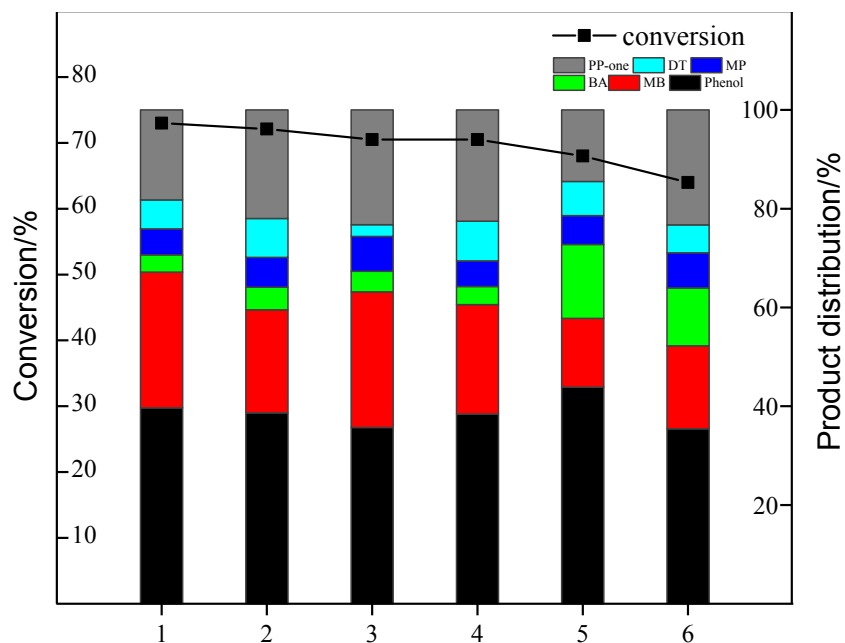


Fig. S7 Cycling tests on Au/CeO₂. Reaction conditions: 0.47 mmol of substrate, 20 mg of Au/CeO₂, 25 mL of methanol, 453K, 4 h, 1 MPa of O₂.

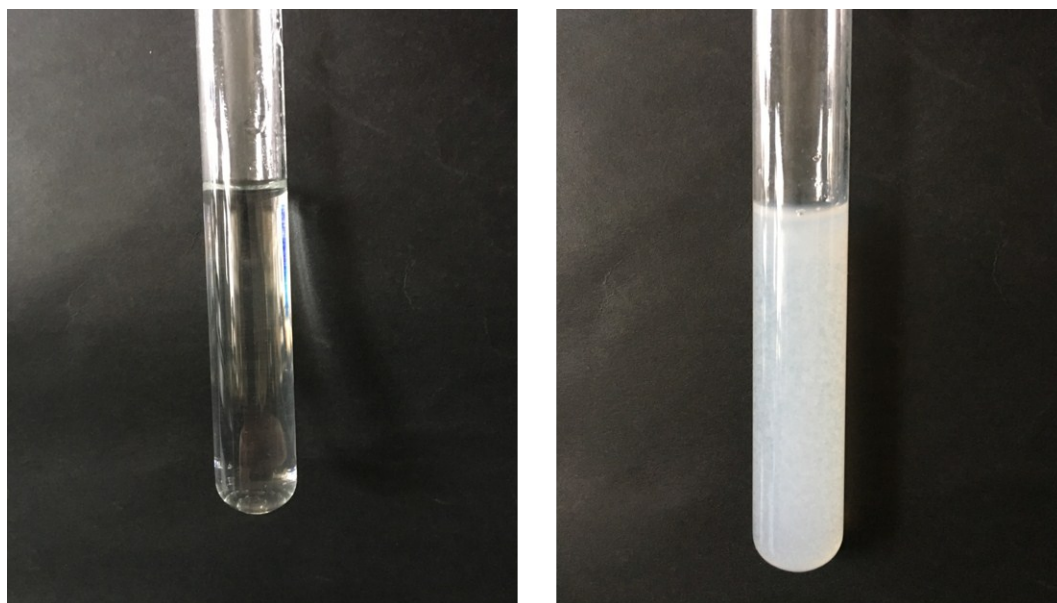


Fig.S8 Limewater images before (left) and after (right) introduction of the reaction gas phase. The limewater was cloudy, indicating the generation of CO₂ during the reaction.

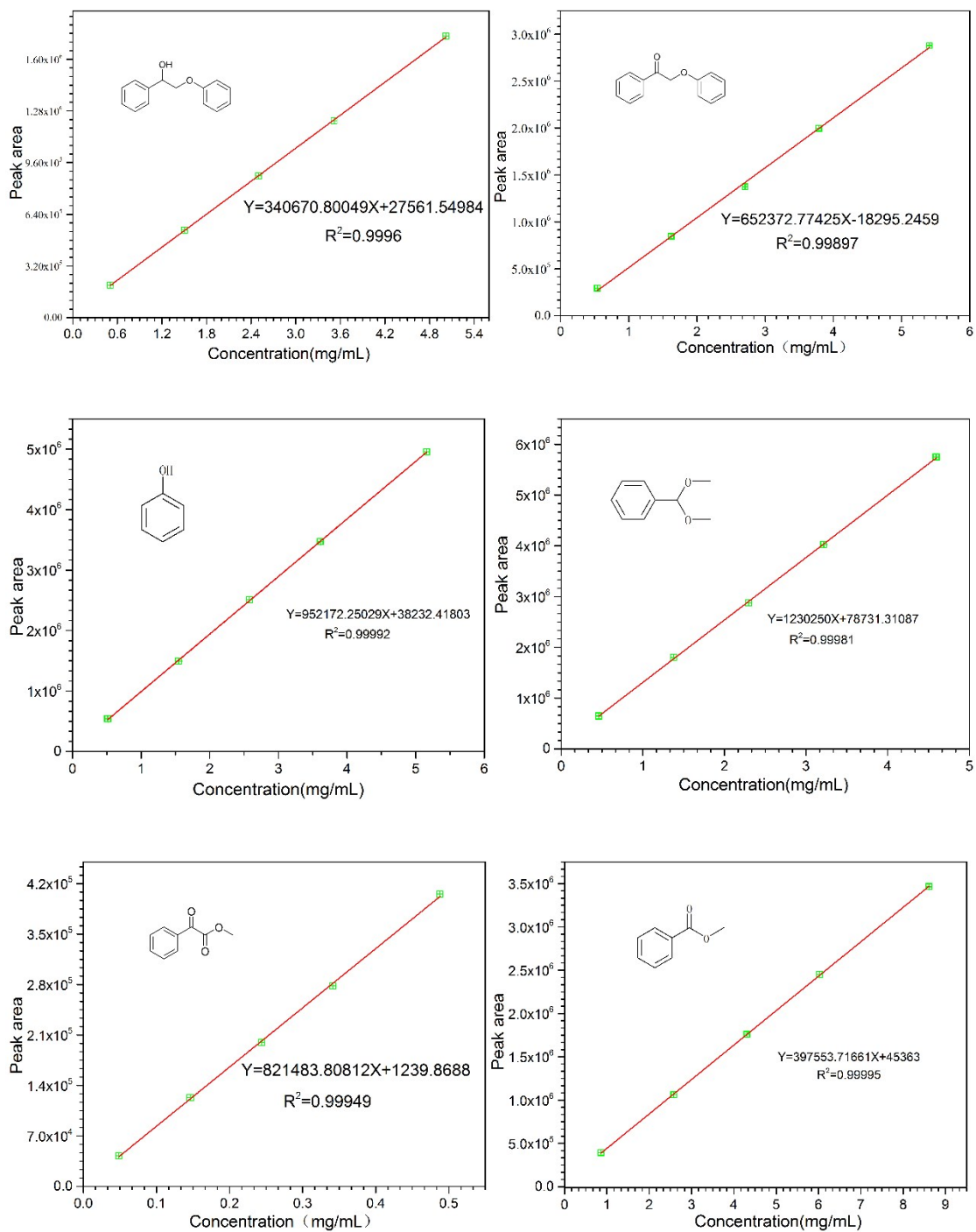


Fig. S9 HPLC quantitative analysis standard curves

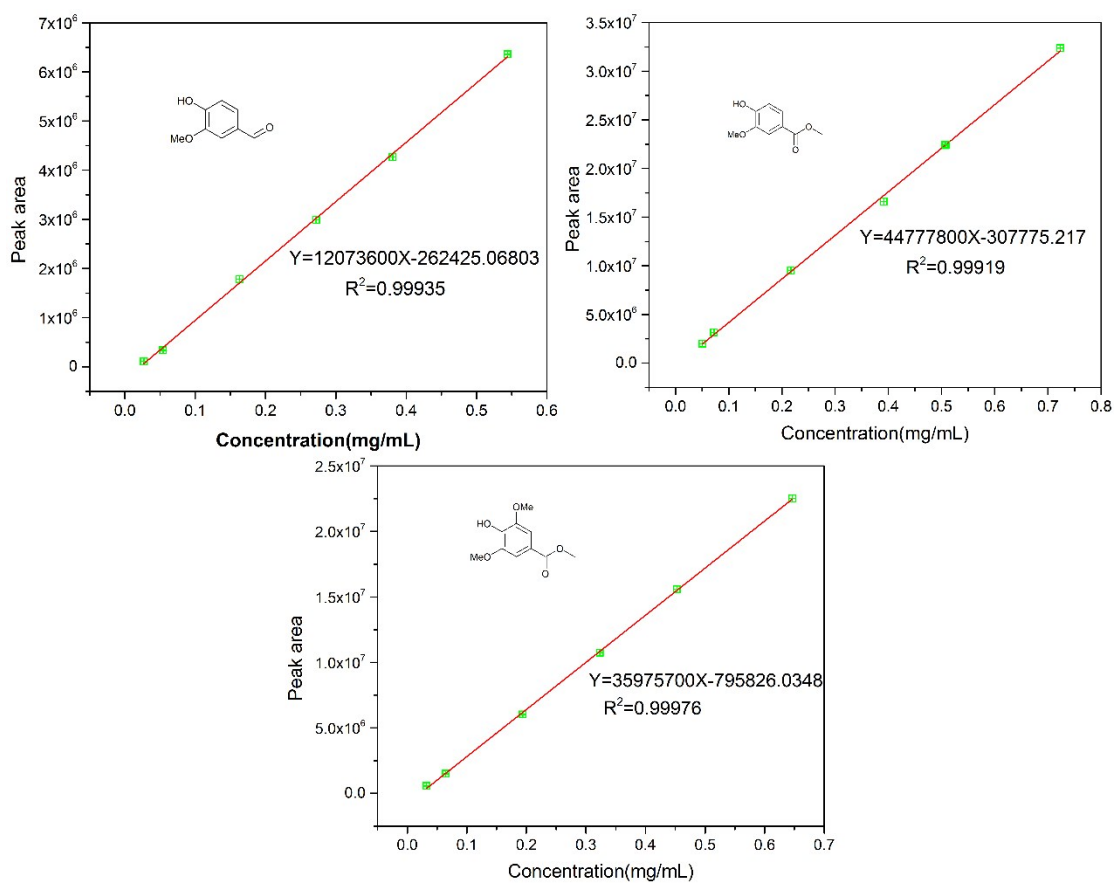


Fig.S10 GC-MS quantitative analysis standard curves

[1] W. Deng, H. Zhang, X. Wu, R. Li, Q. Zhang, Y. Wang, Green chemistry. 17 (2015) 5009-5018.