Supplementary Material (ESI) for Green Chemistry

Supporting Information for

Synergistic effect of vanadium-phosphorus promoted benzylic alcohols oxidation with molecular oxygen in water

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1. General Equipments and Materials

All experiments were carried out in a closed glass-lined stainless steel autoclave equipped with a magnetic stirring, a pressure gauge and automatic temperature control apparatus.

Veratryl alcohol is obtained from Alfa Aesar, and TEMPO from Acros Organics; All other alcohols were commercial available and used as received.

$VOSO_4 \cdot xH_2O$ (USP28) was dried at 120 ^oC overnight. The content of lattice water is about 5% measured by TG. V_2O_5 and H_3PO_4 (85%) are analytic reagents. $VOPO_4$, VPO and $VOHPO_4$ were prepared and characterization according to previous literature (pp.4, ESI).[1-4]

2. Synthesis and Characterization of Catalysts

Synthesis of $VOPO_4 \cdot 2H_2O$: [1, 2] The $VOPO_4 \cdot 2H_2O$ was prepared by reacting V_2O_5 (5.0 g) with 85% H_3PO_4 (24 mL) in water (120 mL) under reflux with continuous stirring for 24 h. The yellow solid was then recovered by filtration, washed with distilled water (25 mL) and followed by acetone (25 mL). It was dried at 110 ^oC for overnight. Finally 4.48 g yellow product was received.

Synthesis of VPO (vanadium phosphorus oxide): [3] V_2O_5 (5 g) was refluxed and agitated by mechanic stirrer in a mixture of isobutanol (16 mL) and benzyl alcohol (8 mL) for 12 h, then 7 g of 85% H_3PO_4 (P/V=1.1) was added and refluxed for further 6 h to give a light green precipitate. The precipitate was filtered off, dried at 110 ^oC overnight and then calcined in air at 400 ^oC for 4 h. Finally, 8.8 g green powder was received.

Synthesis of $VOHPO_4 \cdot 0.5H_2O$:[4] V_2O_5 (6 g) and 85% H_3PO_4 (9 g) were refluxed in isobutanol (125 mL) for 16 h. The solid was recovered by filtration, washed with isobutanol (100 mL) and ethanol (100 mL), refluxed with water (10 mL/g) for 3 h, filtered immediately and dried. (120 ^oC, 16 h).

Characterization of Catalysts (Fig. 4-6): X-ray diffraction analysis was performed using a Rigaku D/Max 3400 powder diffraction system with a Cu-Kα radiation running at 40 kV/200 mA in the 2θ range of 10^{o}(or 5^{o}) to 80^{o}.

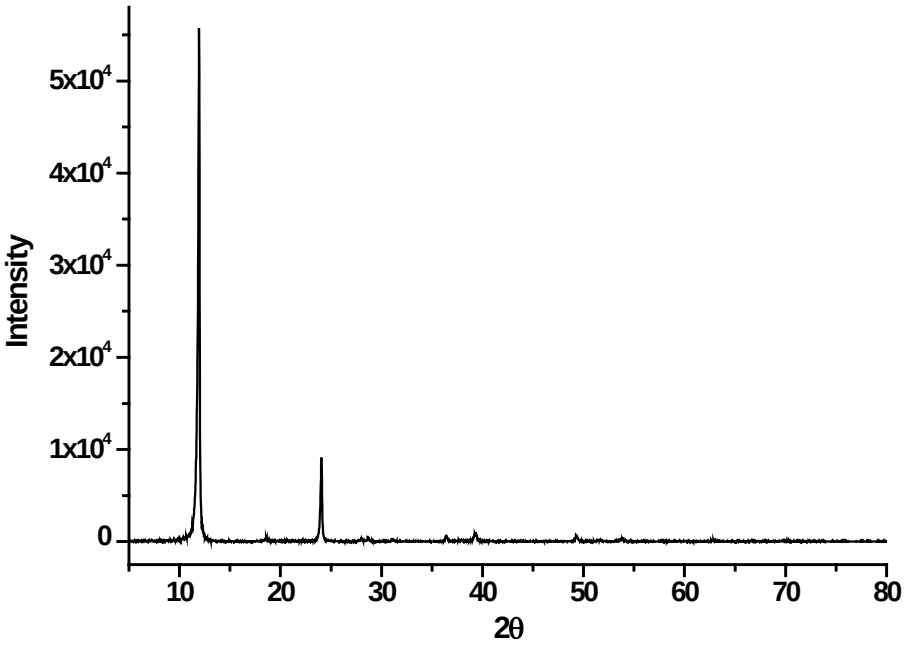

Fig. 4 XRD pattern of $VOPO_4 \cdot 2H_2O$.

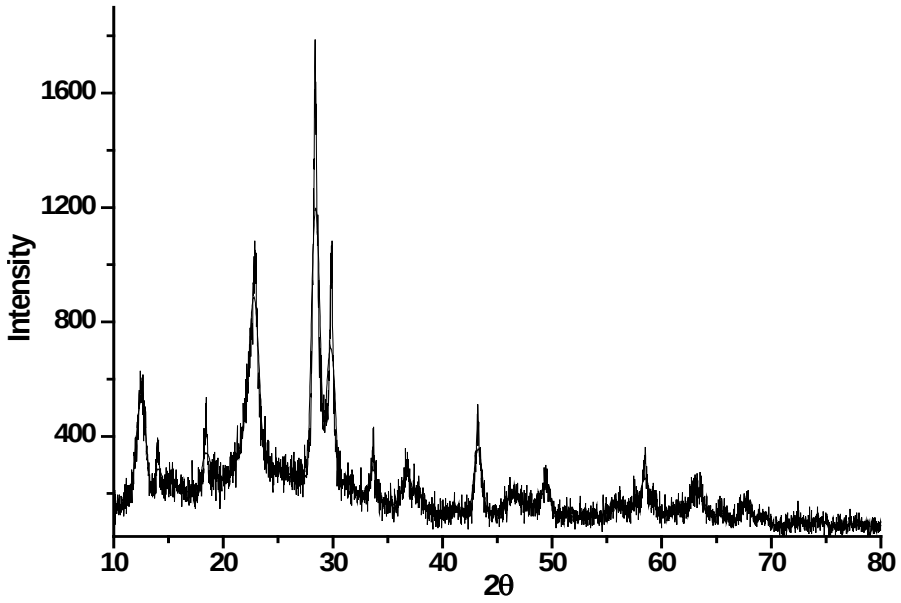

Fig. 5 XRD pattern of VPO.

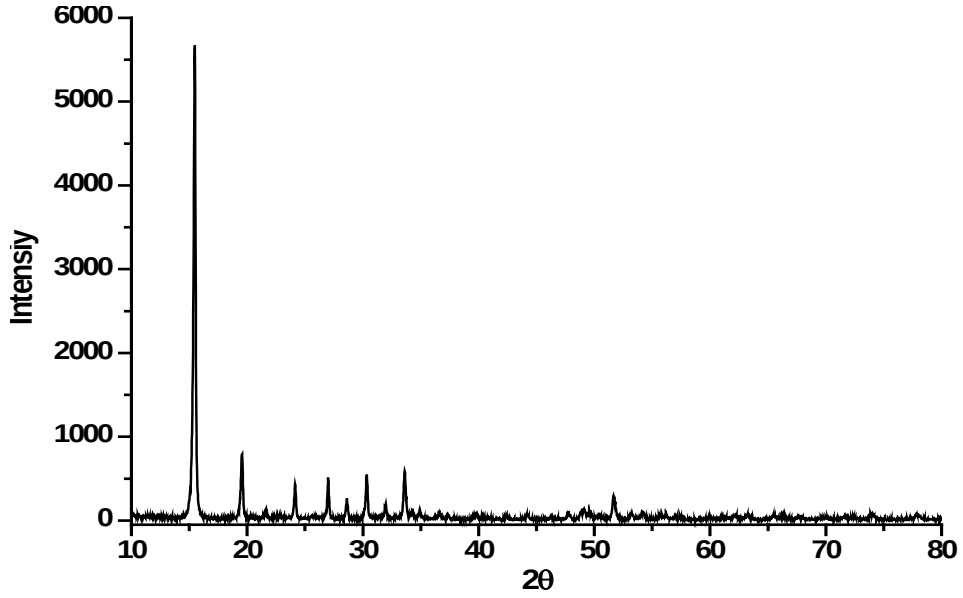

Fig. 6 XRD pattern of $VOHPO_4 \cdot 0.5H_2O$.

References:

(1) T. Nakato, Y. Furumi, N. Terao and T. Okuhara, *J. Mater. Chem.*, 2000, **10**, 737-743.

(2) H. Imai, Y. Kamiya and T. Okuhara, *J. Catal.*, 2007, **251**, 195-203.

(3) U. R. Pillai and E. Sahle-Demessie, *New J. Chem.*, 2003, **27**, 525-528.

(4) F. J. C. Sanchez, R. P. K. Wells, C. Rhodes, J. K. Bartley, C. J. Kiely and G. J. Hutchings, *Phys. Chem. Chem. Phys.*, 2001, **3**, 4122-4128.

3. Typical Procedure for Oxidation

Take experiment 2 (Fig. 1 in the main text) for an example: **V**$OPO_4 \cdot 2H_2O$ (24.75 mg, 0.125 mmol), TEMPO (19.50 mg, 0.125 mmol) and veratryl alcohol (420 mg, 2.5 mmol) were added into the autoclave followed by 5 mL H_2O. After the autoclave was closed, oxygen was charged to 0.4 MPa. It was heated to 80 ^oC within 20 min. After 4 h (heating period is not included), the autoclave was cooled to room temperature and carefully depressurized to normal pressure. The products were extracted using 3×4 mL CH_2Cl_2. The conversion and selectivity were determined by GC without any purification.

4. GC Measurements

Gas chromatography measurements were conducted using Agilent 4890D GC with a flame ionization detector. PEG-20M capillary column was used for separation of aliphatic alcohols and their products; HP-5 capillary column for benzylic alcohols and their produts. TEMPO and 2,2,6,6-tetramethylpiperidine were also detected by GC. Conversions and selectivities are based on the gas chromatography with area normalization. All product were confirmed by *GC-MS with Agilent 6890N GC/5973 MS detector*.

5. ^{51}V and ^{31}P NMR Spectra

^{51}V NMR spectra were recorded at 105.20 MHz on a Bruker 400 MHz spectrometer at 25 ^{o}C. $VOCl_3$ was used as an external reference for chemical shifts (0 ppm). D_2O sealed in a capillary was used for NMR lock. The parameters were as follows: sweep width, 100 kHz; acquisition time, 0.082 s; pulse width, 8.0 μs.

^{31}P NMR spectra were recorded on the same spectrometer as the ^{51}V NMR spectra, at 162.0 MHz. The ^{31}P NMR chemical shifts were given relative to 85% H_3PO_4 (0 ppm). The parameters were as follows: sweep width, 45.5 KHz; acquisition time, 0.36 s; pulse width, 8.0 μs.

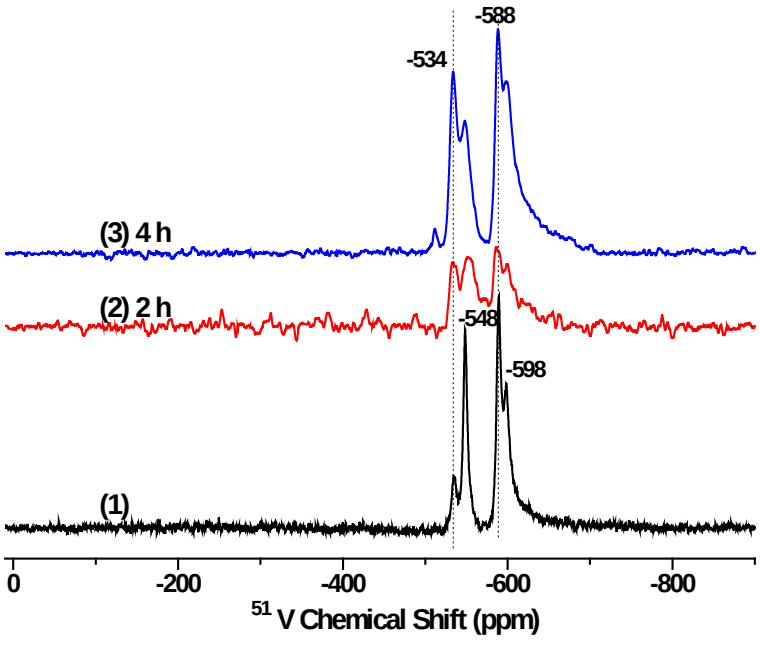

Fig. 7 ^{51}V NMR spectra recorded after different time.

(1) $VOPO_4$ aqueous solution.

25 mg $VOPO_4 \cdot 2H_2O$ was dissolved in 5 mL H_2O.

(2) t=2 h. Conversion: 83.5%

Reaction conditions: 2.5 mmol veratryl alcohol, 0.125 mmol $VOPO_4$, 0.125 mmol TEMPO, 5 mL H_2O, 80 ^oC, 0.4 MPa O_2. Then it was cooled and ^{51}V and ^{31}P NMR was recorded.

(3) t=4 h. Conversion: 100%

Reaction conditions were as (2) except reaction time.

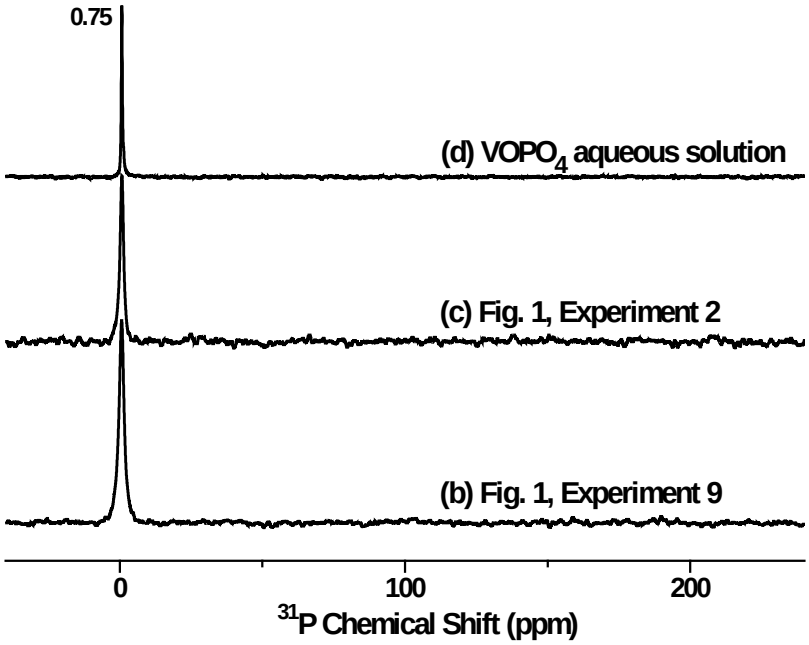

Fig. 8 ^{31}P NMR spectra for different aqueous solution

6. pH Measurements

pH measurements were performed using a pH meter (PHS-3C) at 25±1 ^{o}C.

I 25 mg $VOPO_4 \cdot 2H_2O$ was dissolved in 5 mL H_2O, pH=2.07

II 21 mg $VOSO_4 \cdot xH_2O$ was dissolved in 5 mL H_2O, pH=3.08

III 22 mg $VOHPO_4 \cdot 0.5H_2O$ was added into 5 mL H_2O (partially dissolved in 5 mL H_2O at 25 ^{o}C), pH=3.11

7. Stoichiometric Reactions

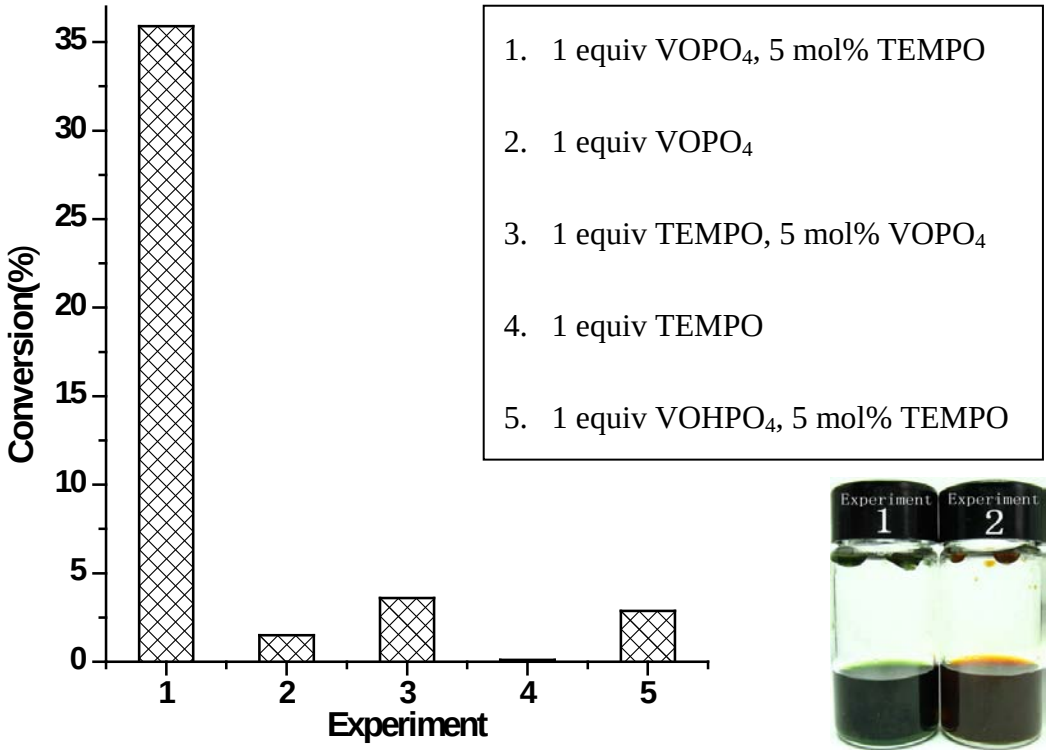

Fig. 9 Reaction of veratryl alcohol with stoichiometric different compounds

Reaction conditions: 0.5 mmol veratryl alcohol, 5 mL H_2O, N_2, room temperature, 4 h.

8. Detection of V^{IV} Species by EPR

Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker spectrometer at X-band, with a field modulation of 100 kHz. The magnetic field was scanned from 280 to 400 mT. The microwave frequency was kept at 9.401 GHz. The temperature was 20±2 ^{o}C.

Sample A: 25 mg $VOPO_4 \cdot 2H_2O$ was dissolved in 5 mL H_2O.

Sample B: 10 mg TEMPO was added to **A** (parallel sample**)**, and it was stirred at room temperature for 5 h under N_2.

Sample C: 100 mg veratryl alcohol was added to **B** (parallel sample**)**, and the mixture was stirred at room temperature for 10 h under N_2.

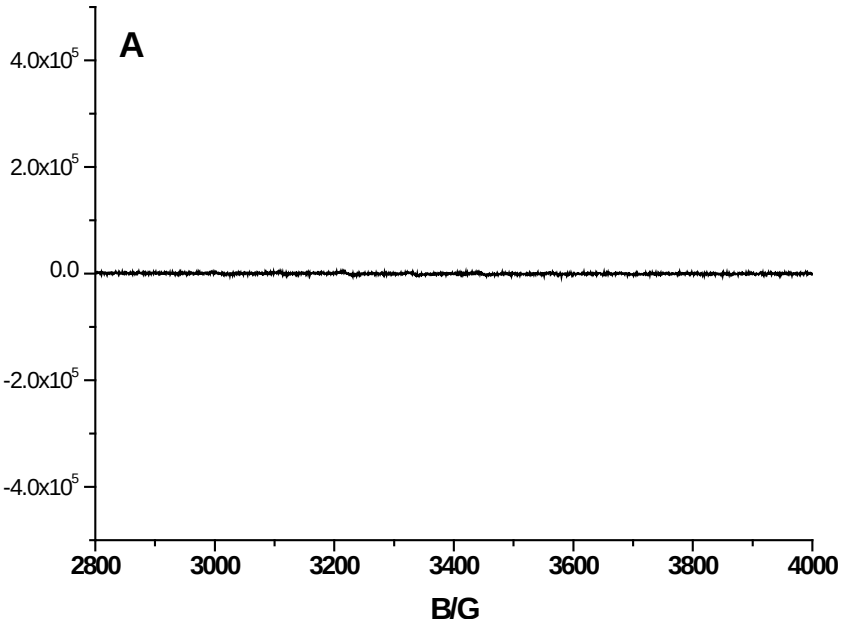

Fig. 10 EPR of $VOPO_4$ aqueous solution (Sample **A**).

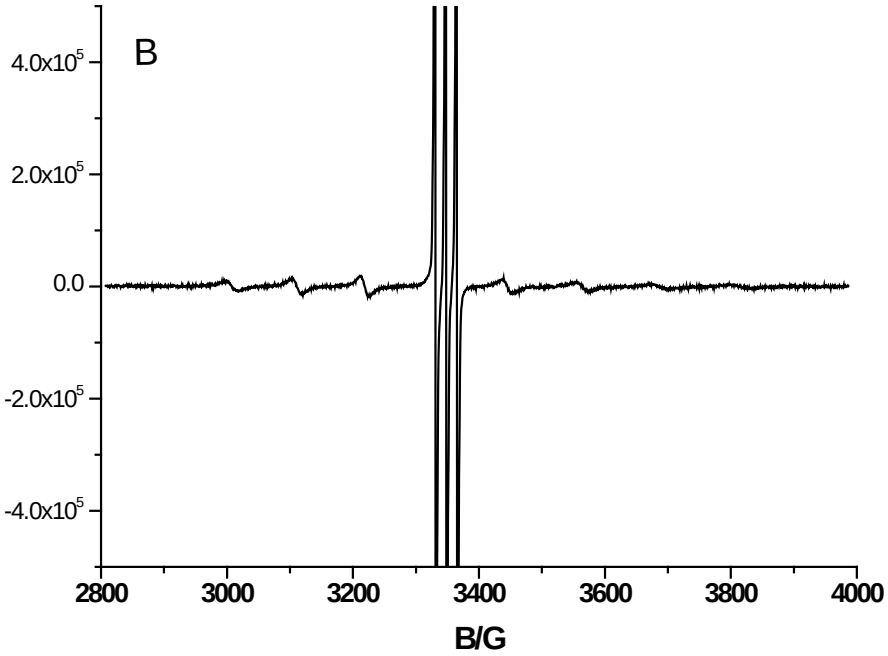

Fig. 11 EPR of Sample **B**.

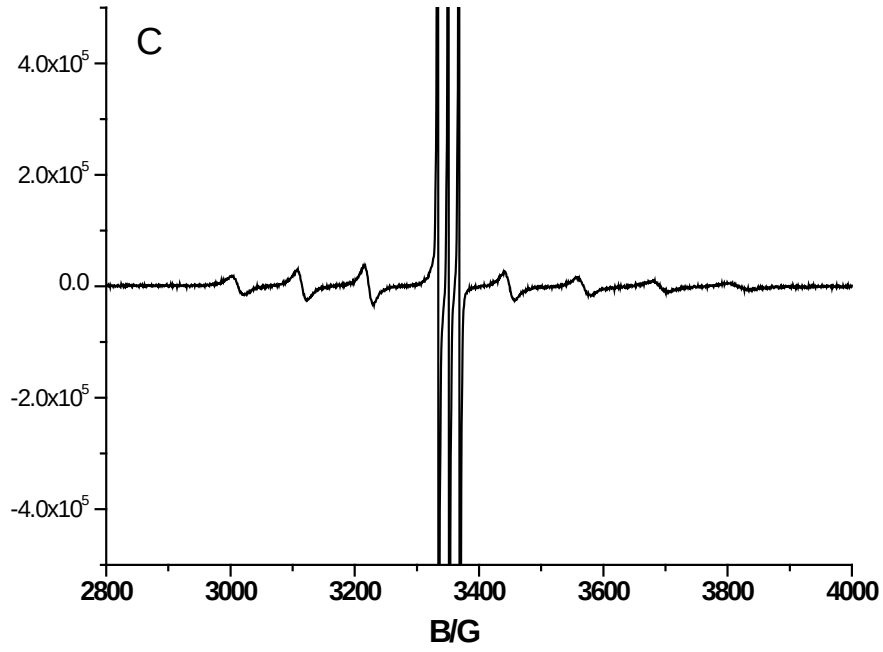

Fig. 12 EPR of Sample **C**.

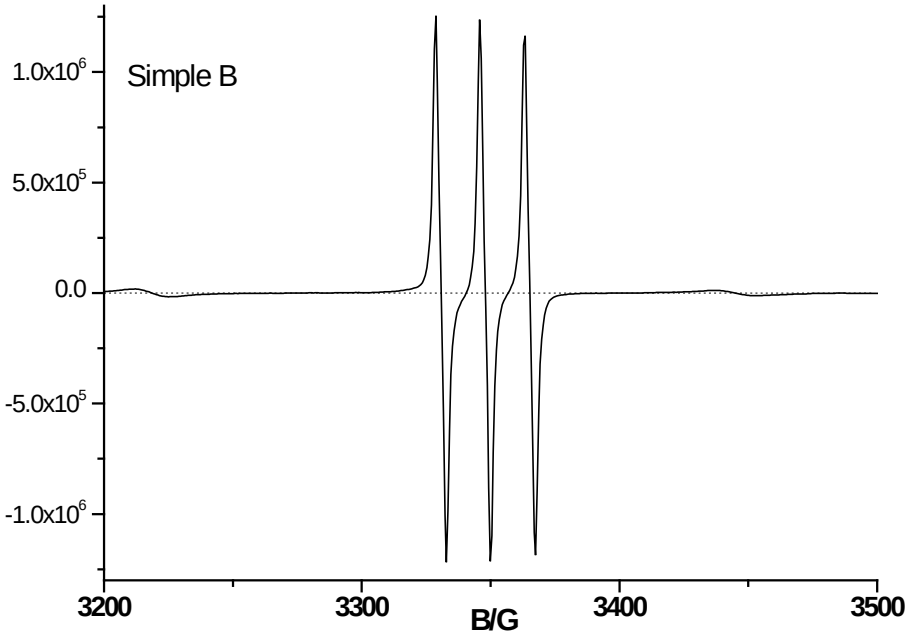

Fig. 13 EPR spectrum of TEMPO remaining in Sample **B**.

9. GC Chromatogram and ^{1}H, ^{13}C NMR Spectra

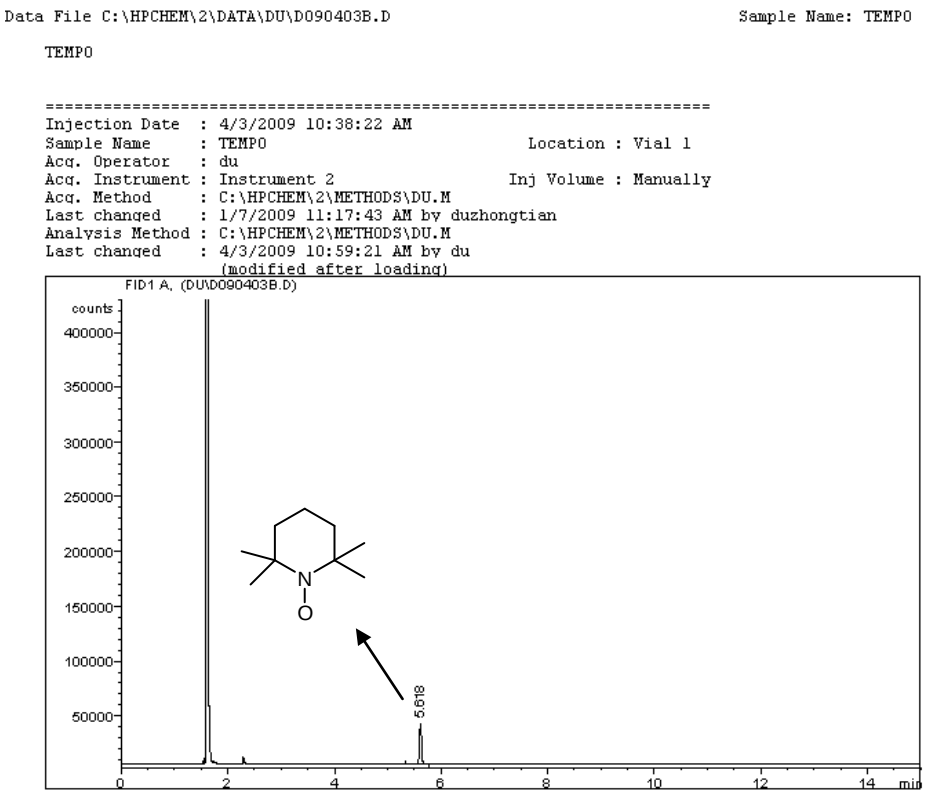

Fig. 14 GC chromatogram of **TEMPO**

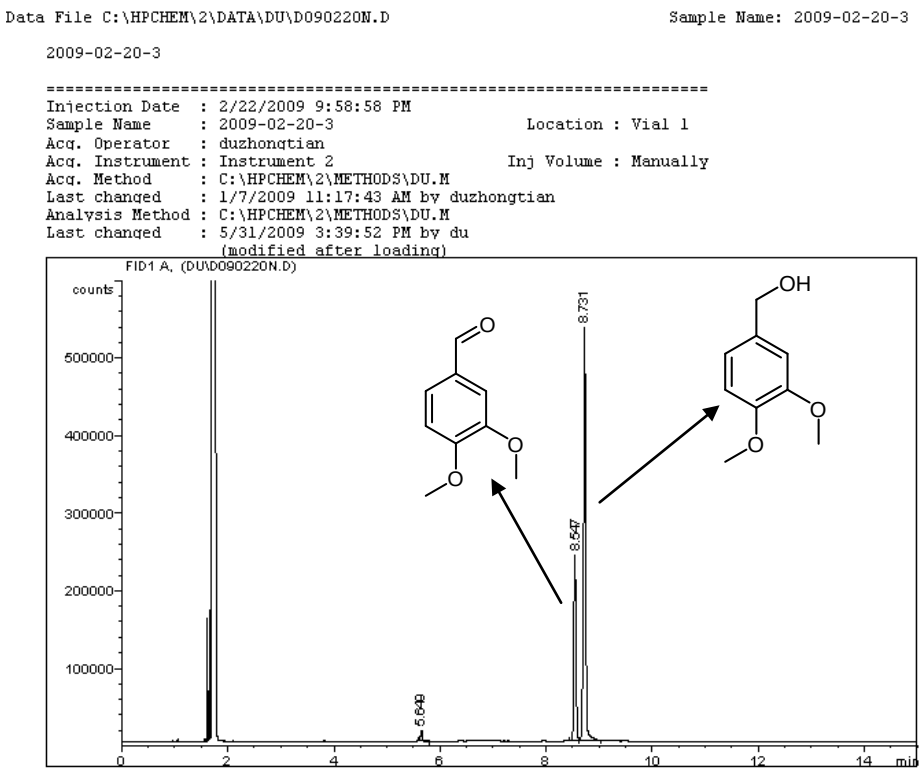

Fig. 15 GC chromatogram of the reaction mixture (**Fig. 1, experiment 5** in the main text)

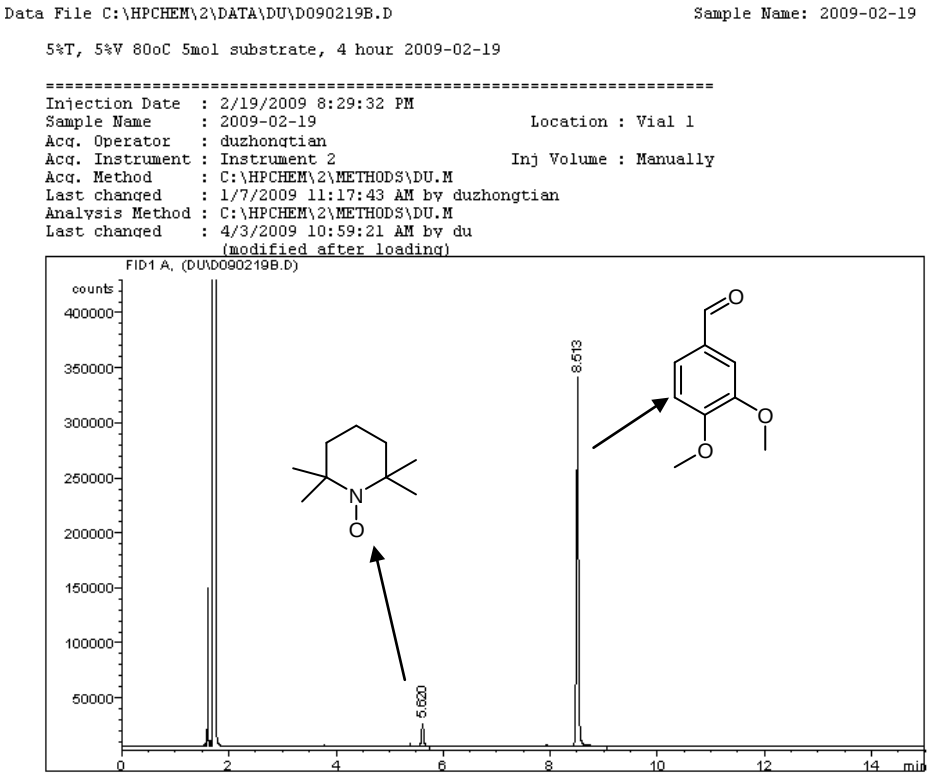

Fig. 16 GC chromatogram of the reaction mixture (**Table 1, Entry 1** in the main text)

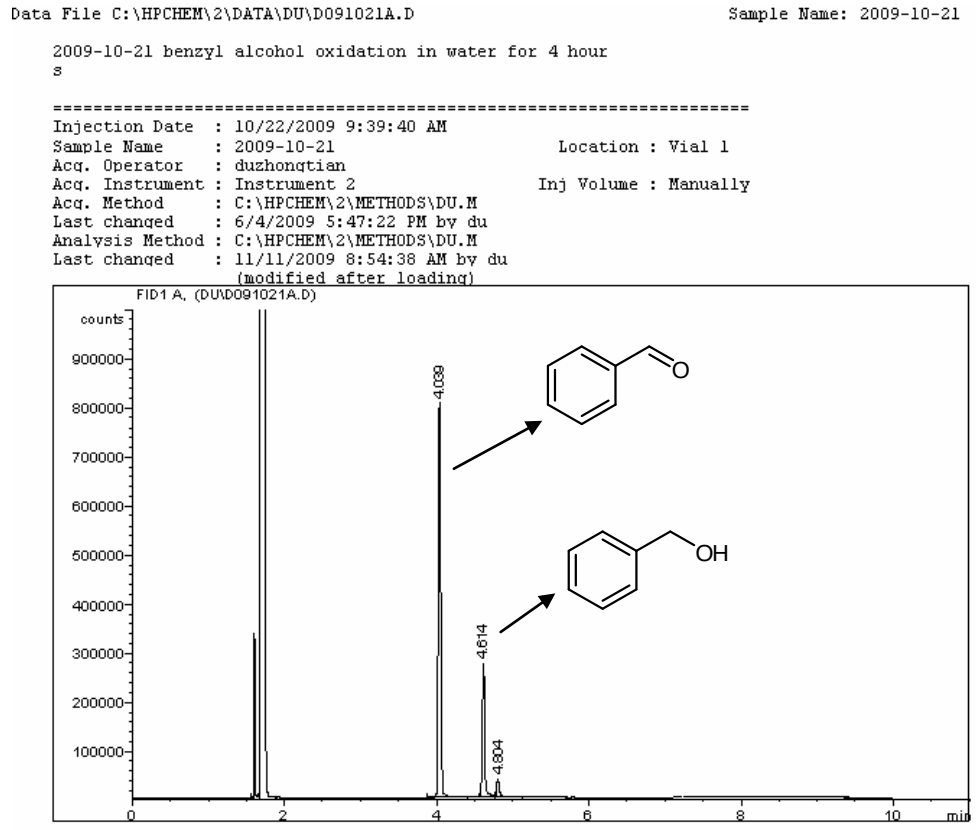

Fig. 17 GC chromatogram of the reaction mixture (**Table 1, Entry 2** in the main text)

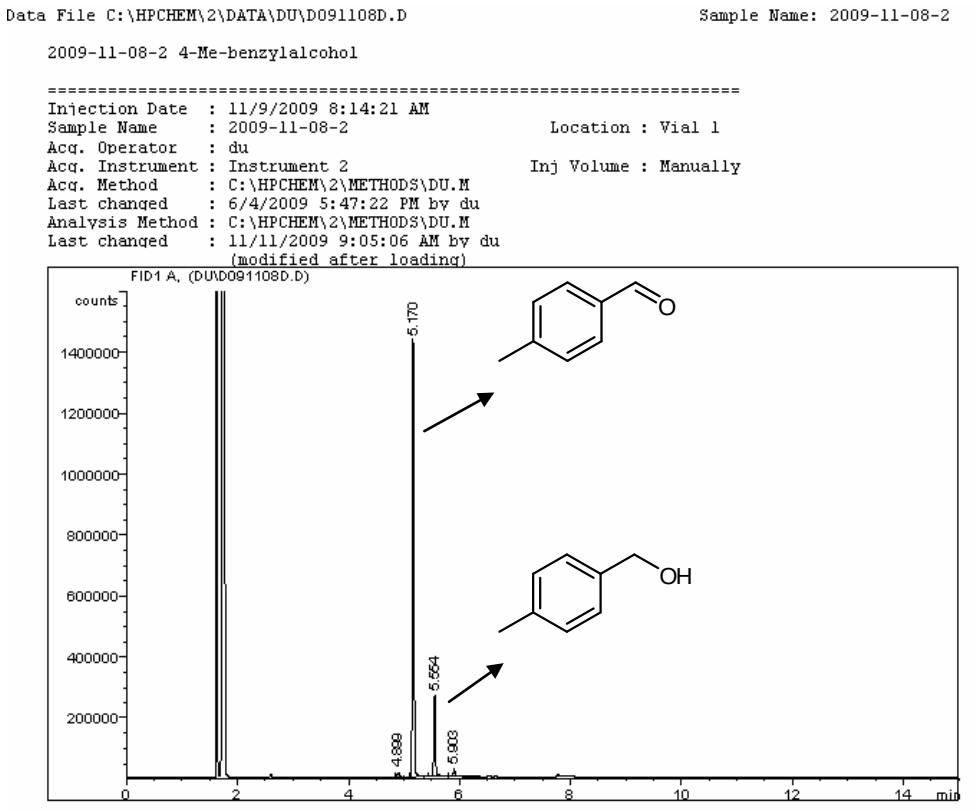

Fig. 18 GC chromatogram of the reaction mixture (**Table 1, Entry 3** in main text)

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2009-11-10 2-Me-PhOH

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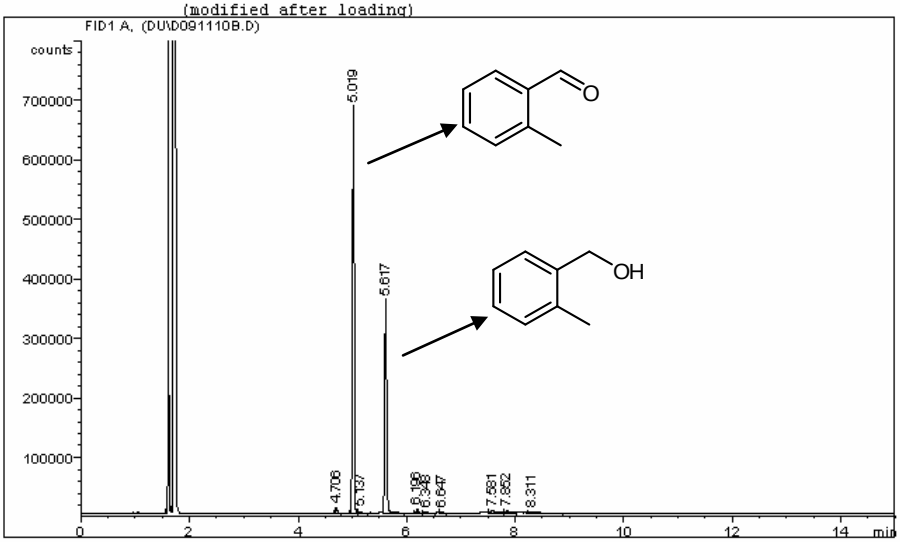

Fig. 19 GC chromatogram of the reaction mixture (**Table 1, Entry 4** in main text)

Data File C:\HPCHEM\2\DATA\DU\D090415B.D Sample Name: 2009-04-15-1

2009-04-15-1 3-methoxyl-

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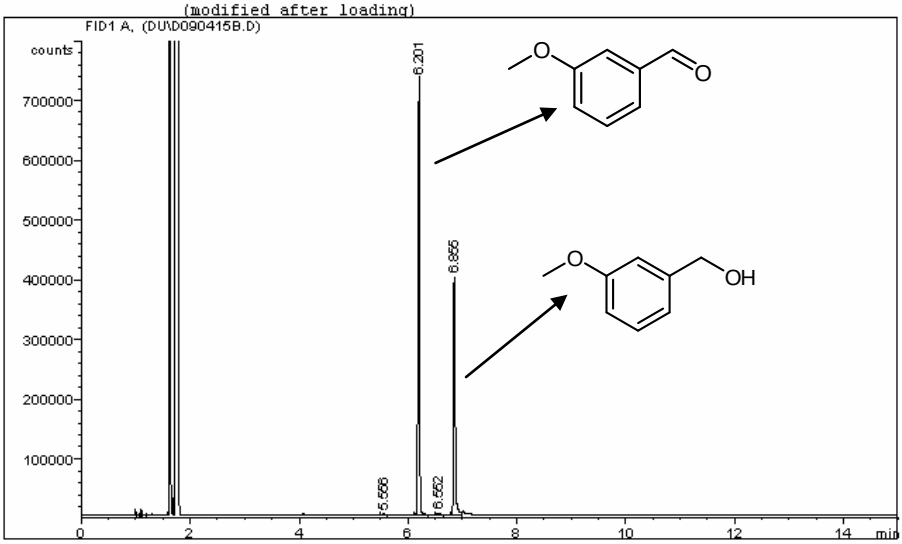

Fig. 20 GC chromatogram of the reaction mixture (**Table 1, Entry 5** in main text)

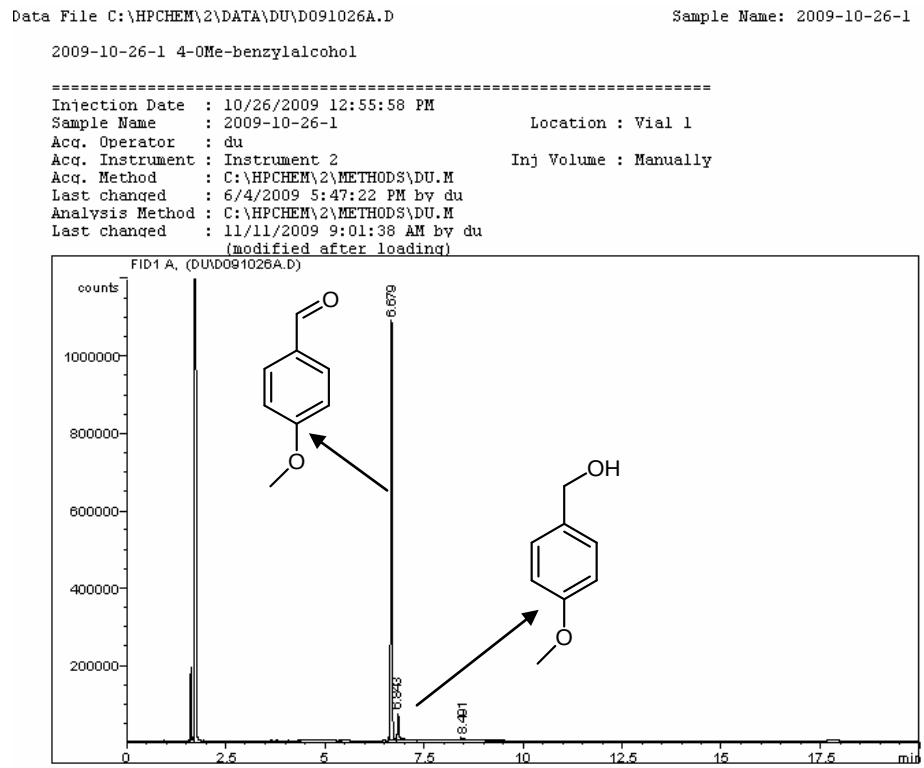

Fig. 21 GC chromatogram of the reaction mixture (**Table 1, Entry 6** in main text)

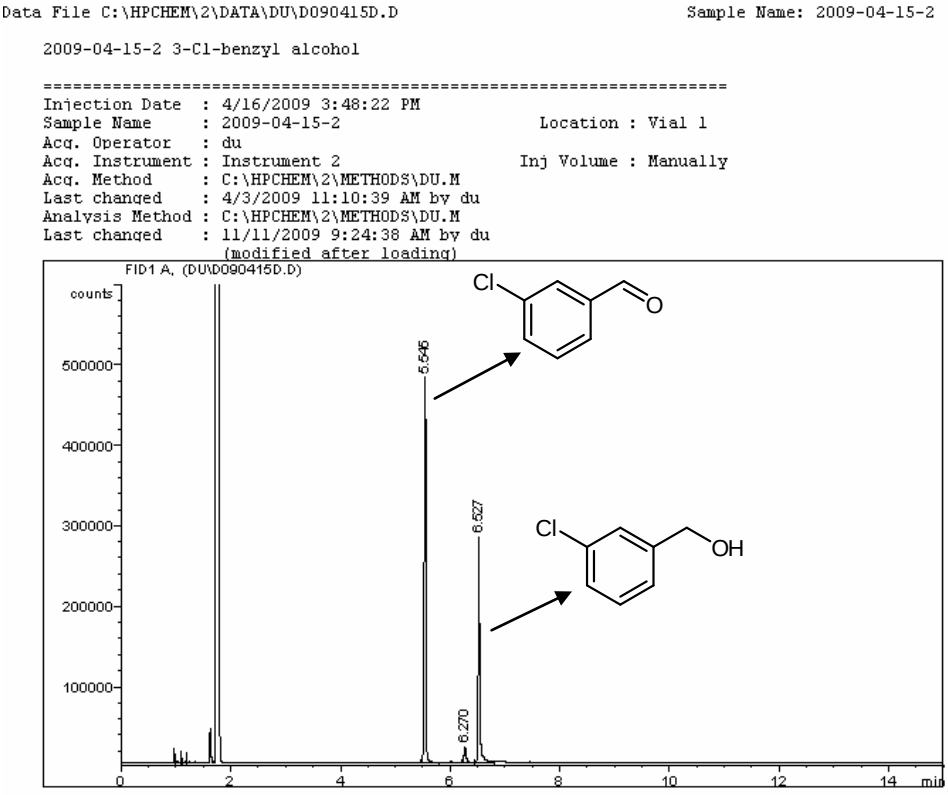

Fig. 22 GC chromatogram of the reaction mixture (**Table 1, Entry 7** in main text)

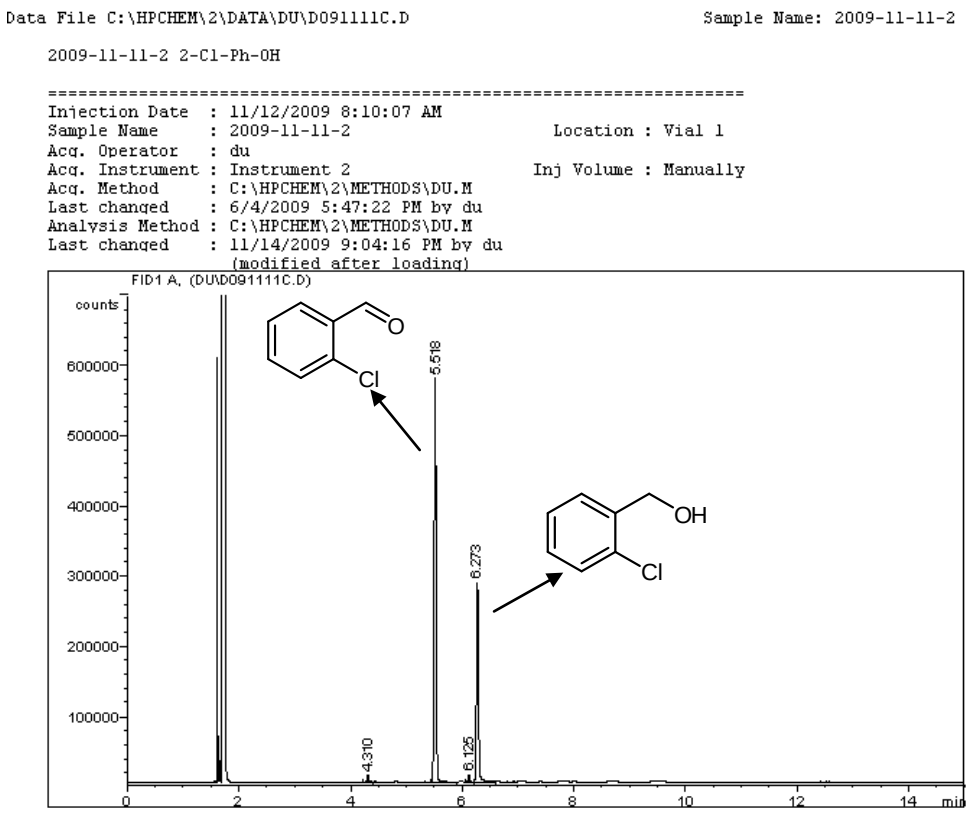

Fig. 23 GC chromatogram of the reaction mixture (**Table 1, Entry 8** in main text)

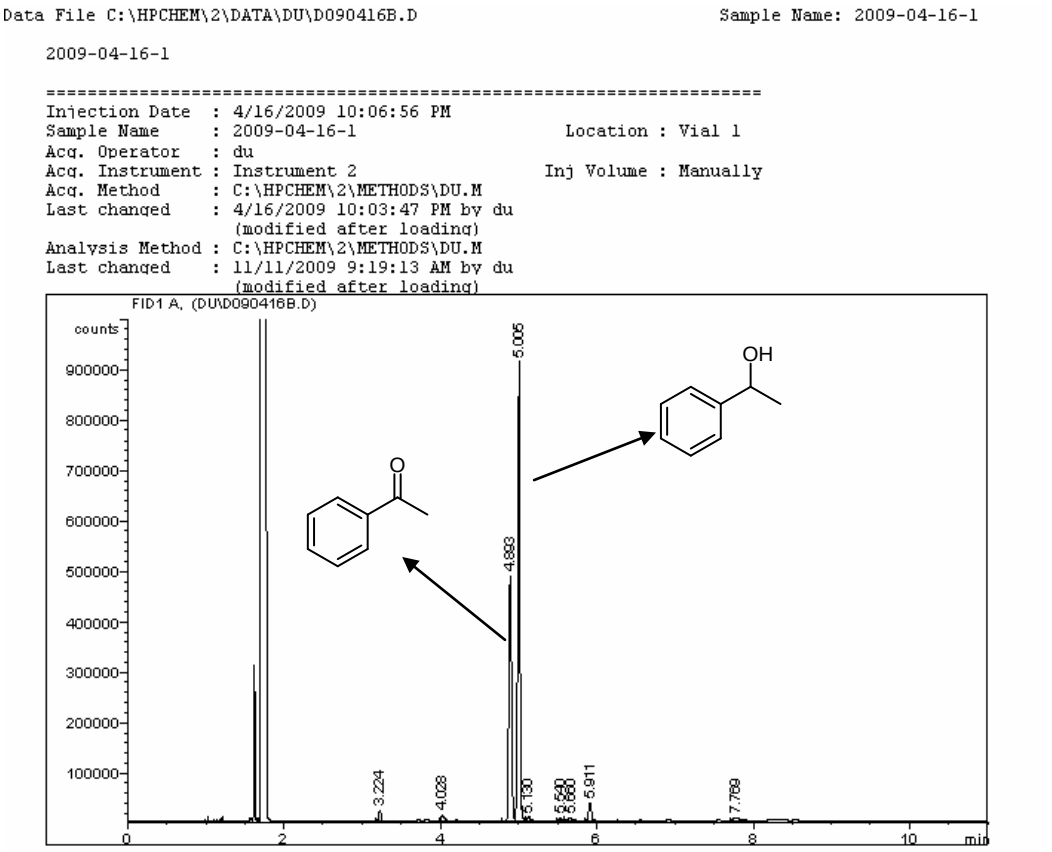

Fig. 24 GC chromatogram of the reaction mixture (**Table 1, Entry 9** in main text)

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2009-10-28-2

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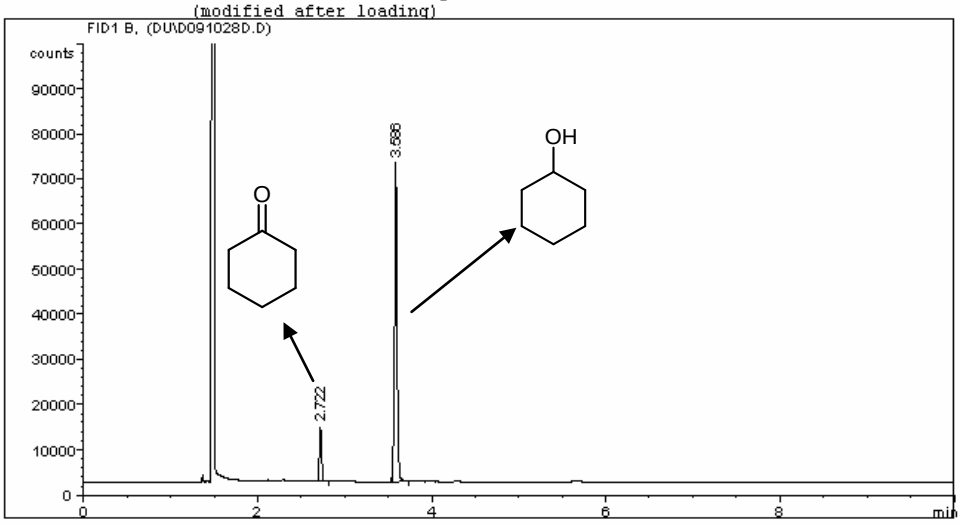

Fig. 25 GC chromatogram of the reaction mixture (**Table 1, Entry 10** in main text)

Data File C:\HPCHEM\2\DATA\DU\D091026C.D Sample Name: 2009-10-26-2

2009-10-26-2 acetone as products water as solvent

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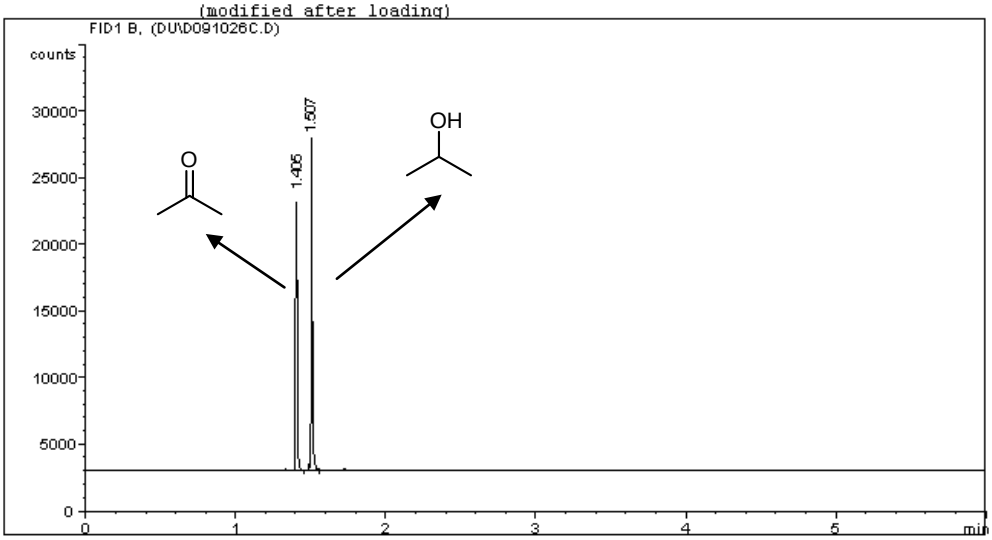

Fig. 26 GC chromatogram of the reaction mixture (**Table 1, Entry 11** in main text)

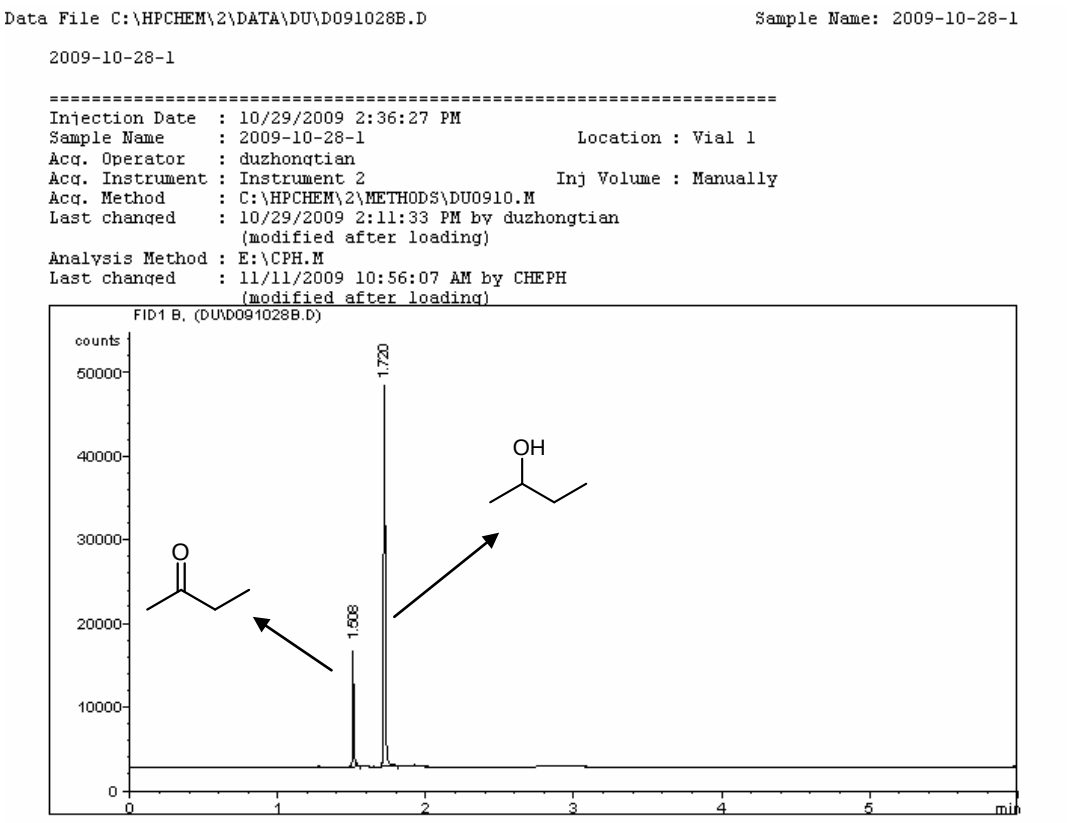

Fig. 27 GC chromatogram of the reaction mixture (**Table 1, Entry 12** in main text)

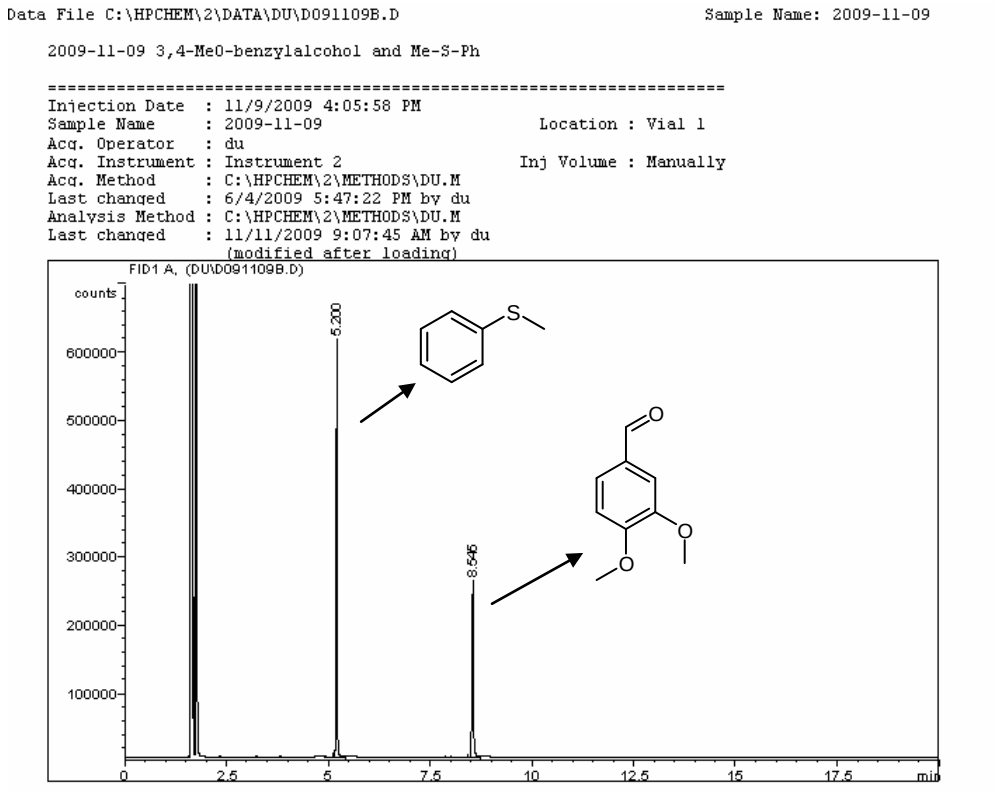

Fig. 28 GC chromatogram of the reaction mixture (**Table 1, Entry 13** in the main text)

NMR (DMSO-d_6) of Isolated Veratraldehyde

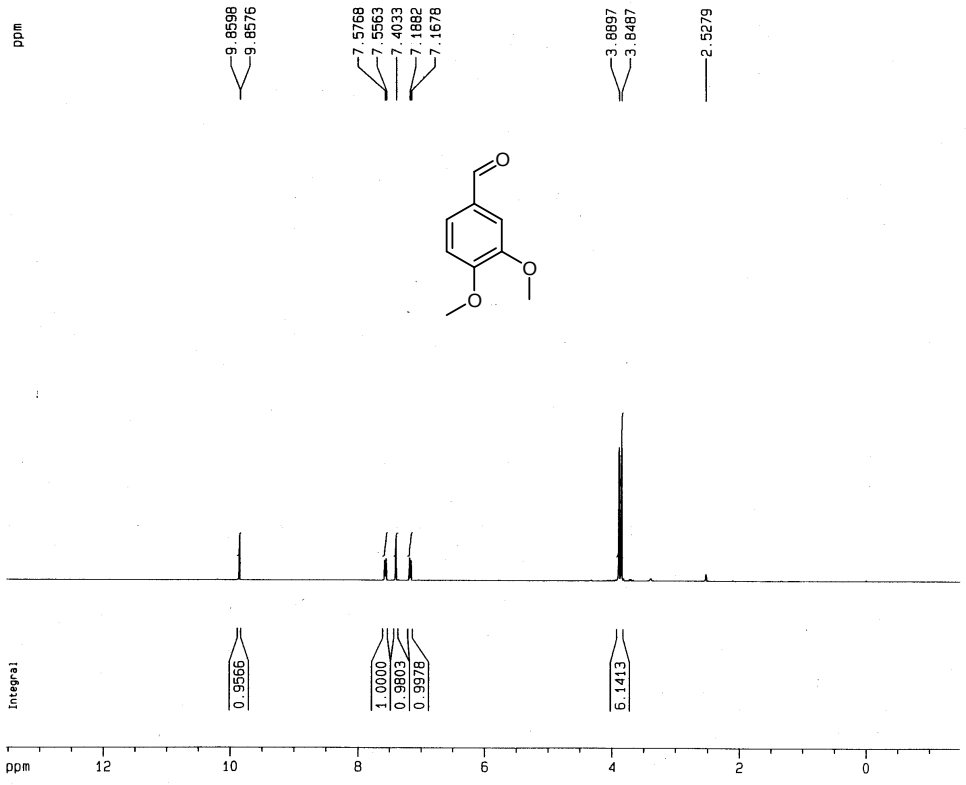

Fig. 29 ^{1}H NMR of veratraldehyde.

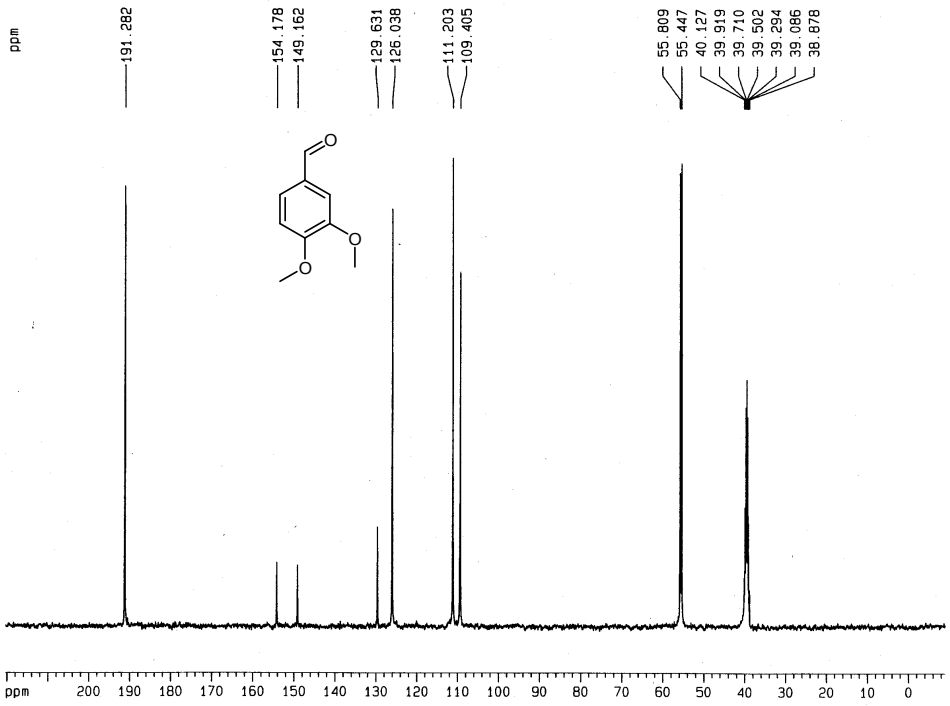

Fig. 30 ^{13}C NMR of veratraldehyde