

## Electronic Supplementary Information

### Superparamagnetic core-shell radical polymer brushes as efficient catalysts for the oxidation of alcohols to aldehydes and ketones

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## 1. Materials

Iron(III) chloride (FeCl<sub>3</sub>, 98%) and tetraethoxysilane (TEOS, 98%) were obtained from Riedel-de Hën (Germany) and Fluka (Milwaukee, WI, USA), respectively. 2,2,6,6-Tetramethylpiperinyl methacrylate (TMPM, 98%) and but-3-en-1-ol were obtained from Tokyo Chemical Industry (TCI, Tokyo, Japan). 2-Bromo-2-methylpropionyl bromide (98%), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in xylene (~2% Pt), copper(I) bromide (CuBr, 99.999%), N,N,N',N'',N'''-pentamethyldiethylenetriamine (PMDETA, 99+%), 2-(2-(benzyloxy)ethoxy)ethanol (97%), 3-methyl-4-nitrophenylmethanol (98%), cyclohexanol (99%), and ethylene glycol (99.5%) were purchased from Sigma-Aldrich. 1-Butanol (99.5%), 4-methylpentan-2-ol (97%), methylene chloride (99.9%), and hydrochloric acid (HCl, 37%) were obtained from Merck (Darmstadt, Germany). 1-Octanol (99.5%) was purchased from Shimakyu Chemicals (Osaka, Japan). 2-Ethylhexan-1-ol was purchased from Janssen Chemicals (Beerse, Belgium). Benzyl alcohol was purchased from Alfa Aesar (Ward Hill, MA). Sodium acetate (95%, anhydrous) was purchased from Osaka Chemicals (Osaka, Japan). Trichlorosilane (>98%), sodium bicarbonate (99.5%), potassium bromide (99%), and magnesium sulfate (99%, anhydrous) were purchased from Showa Chemicals (Tokyo, Japan). Acetone (99%), ethanol (95%), toluene (99.9%) and sodium hypochlorite (6% aqueous solution) were purchased from Echo Chemicals (Miaoli, Taiwan). Ammonia (28-30% aqueous solution) was purchased from J. T. Baker (Phillipsburg, NJ, USA). 3-Chloroperoxybenzoic acid (*m*CPBA, 70~75%) was purchased from Acros Organics (Geel, Belgium). Except for *m*CPBA, all chemicals were used as received. *m*CPBA was recrystallized in methanol.<sup>1</sup> The surface initiator, (4-(2-bromo-2-methyl)propionyloxy)butyltrichlorosilane (BMPBTS), was synthesized according to the previous paper.<sup>2</sup>

### References:

1. V. K. Aggarwal, Z. Gultekin, R. S. Grainger, H. Adams and P. L. Spargo, *J. Chem. Soc. Perkin Trans. 1*, 1998, 2771.
2. Y.-H. Wang, M.-K. Hung, C.-H. Lin, H.-C. Lin and J.-T. Lee, *Chem. Commun.*, 2011, 47, 1249.

## 2. Instruments

The surface morphology of nanoparticles was observed by a field emission scanning electron microscope (FESEM, JEOL JSM-6700F) using an accelerating voltage of 10 kV. The transmission Fourier transform infrared spectroscopy (FTIR) spectra were measured by a Perkin-Elmer spectrum 100 FTIR spectrometer with a resolution of 4  $\text{cm}^{-1}$ . The percentage of the PTMA brushes was determined by means of a thermogravimetric analysis (TGA) with a Perkin-Elmer TGA 4000 analyzer in an atmosphere of air at a heating rate of 10  $^{\circ}\text{C min}^{-1}$  from 50 to 800 $^{\circ}\text{C}$ .  $^1\text{H-NMR}$  spectra were acquired using a 300 MHz NMR Bruker spectrometer. The chemical composition of nanoparticles and the oxidation state of elements were measured by loading nanoparticles on gold coated silicon wafers then performing the X-ray photoelectron spectroscopy (XPS, ULVAC-PHI, PHI Quantera SXM) with a focused monochromatic Al  $\text{K}_{\alpha}$  radiation (1486.6 eV). Electron paramagnetic resonance (EPR) spectrum was measured on a Bruker EMX-10 spectrometer. The percentage of carbon (C), hydrogen (H), and nitrogen (N) in the  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  core-shell PTMA brush catalyst was determined by an elemental analyzer (Elementar vario EL III CHN-OS Rapid). The structure of the  $\text{Fe}_3\text{O}_4$  nanoparticles and the  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  core-shell nanoparticles was performed by powder X-ray diffraction (XRD) using a Bruker D8. The thickness of the  $\text{SiO}_2$  layer of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  core-shell nanoparticles was observed by a transmission electron microscope (TEM, JEOL JEM-2010) using an accelerating voltage of 200 kV.

### **3. Preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell PTMA brushes**

Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles were modified with a surface initiator, BMPBTS, and the subsequent surface-initiated polymerization of TPM on Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles was carried out by atom transfer radical polymerization (ATRP) to graft PTMPM brushes on the nanoparticles. The PTMPM brushes were oxidized by *m*CPBA in dichloromethane to give Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell PTMA brushes. The detail synthesis processes of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell PTMA brushes are shown below.

#### ***Synthesis of Fe<sub>3</sub>O<sub>4</sub> nanoparticles***

Iron(III) chloride (FeCl<sub>3</sub>, 1.62 g) was dissolved in ethylene glycol (EG, 100 mL), and then sodium acetate (7.24 g) was added into the EG solution. The above solution was sealed in an autoclave. The autoclave was heated at 200 °C for 8 h to form Fe<sub>3</sub>O<sub>4</sub> nanoparticles, and then was naturally cooled to room temperature. Using a magnet to separate Fe<sub>3</sub>O<sub>4</sub> nanoparticles from the mixture solution. The Fe<sub>3</sub>O<sub>4</sub> nanoparticles were redispersed in DI water and recovered by the magnet twice. Followed by washing with ethanol for three times, the the Fe<sub>3</sub>O<sub>4</sub> nanoparticles were dreid in a vacuum oven at 60°C for 8 h.

#### ***Synthesis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell nanoparticles***

The Fe<sub>3</sub>O<sub>4</sub> nanoparticles (0.1 g) were dispersed in a 0.1 M HCl<sub>(aq)</sub> (50 mL), and then were ultrasinicated for 10 min. After the ultrasonication, the Fe<sub>3</sub>O<sub>4</sub> nanoparticles were collected by a magnet. The the nanopaticles were washed with DI water twice. Then, the nanoparitcles were dispersed in a 20 mL DI water. The nanoparitcle dispersion was added with ethanol (80 mL) and ammonium hydroxide solution (1 mL). Next, TEOS (32 μL) was slowly added in the nanoparticle solution with a mechanical stirring. After 6 h reaction, the resulting Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles were washed with ethanol for three times. Finally, the nanoparticles were dreid in a vacuum oven at 60°C for 8 h.

### ***Attachment of surface initiator on Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles***

The Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles (0.41 g) were dispersed in toluene (10 mL) solution of BMPBTS (100 μL) at room temperature for 5 h. Then, the initiator-attached Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles were washed and ultrasonicated in acetone for 10 minutes three times. Finally, the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles were dried in a vacuum oven at 60°C for 8 h.

### ***Surface-initiated ATRP of TPM on Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell nanoparticles***

PMDETA (31 μL) was dissolved in a 10-mL cosolvent of acetone/water (= 4/1, v/v). The solution was sealed in a flask and degassed by three freeze-pump-thaw cycles. The above solution was transferred *via* a cannula into a degassed flask containing CuBr (7.2 mg) as a catalyst. Finally, the above solution of was transferred by a cannula into a degassed container containing the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles (408.2 mg) and TPM (1.1267 g). The polymerization was carried out under a nitrogen atmosphere at 60°C for 1 h to give PTMPM brushes. The Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell PTMPM brushes were rinsed and ultrasonicated with acetone and then dried in a vacuum oven at 60°C for 8 h.

### ***Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell PTMA brushes: Oxidation of PTMPM brushes***

Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell PTMPM brushes (392.6 mg) were dispersed in a 20 mL dichloromethane solution of *m*CPBA (192.2 g) at room temperature for 10 minutes to give the PTMA brush. The resulting Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell PTMA (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PTMA) brushes were ultrasonicated with acetone for three times and then dried in a vacuum oven at 60°C for 8 h.

### ***Oxidation of alcohols using Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell PTMA brushes as a catalyst***

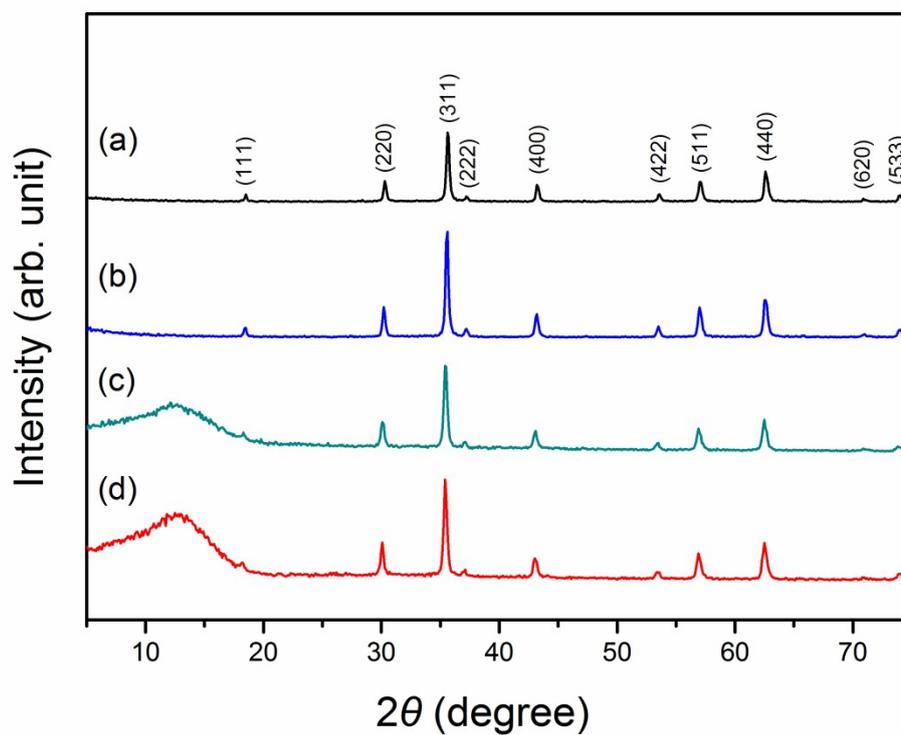
Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PTMA (2.6 mg) were dispersed in a 1.5 mL dichloromethane solution of KBr (9.5 mg) and alcohol (The molar ratio of alcohol and TEMPO is 100 to 1.). A 3-mL aqueous solution of NaClO (pH value was adjusted to 9.33 by adding 1 M NaHCO<sub>3</sub> aqueous solution) was dropwise added to above solution at 0°C. The organic layer was dried by anhydrous

MgSO<sub>4</sub>, and then was concentrated. The conversion was measured by <sup>1</sup>H-NMR spectroscopy.

***Recovery of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell PTMA brushes catalyst***

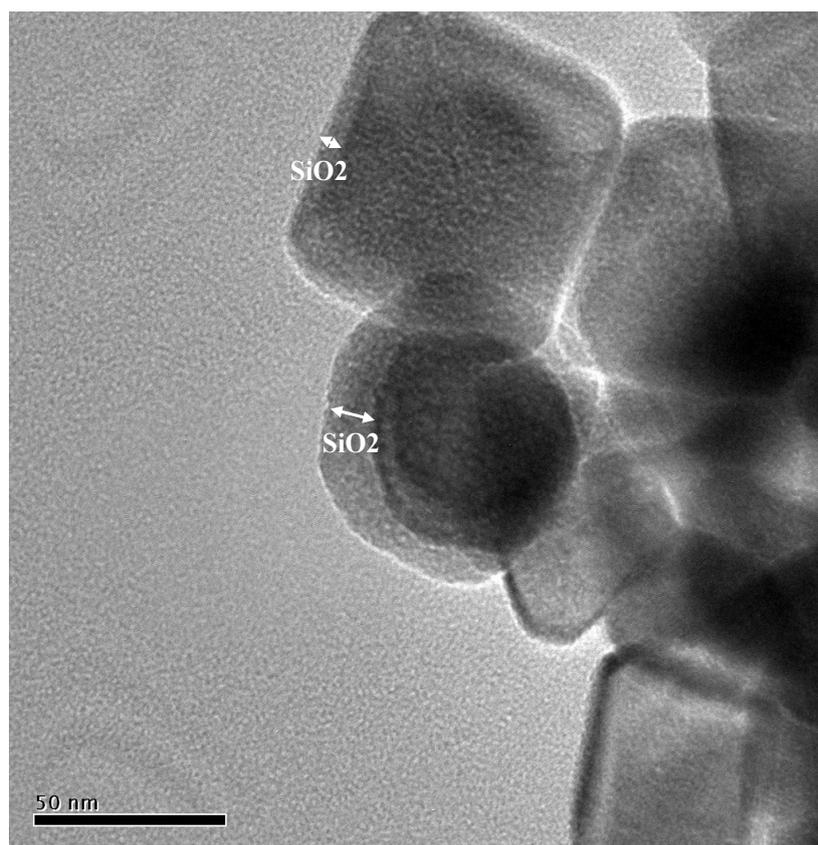
For the recovery of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PTMA, the reaction mixture was added with ethanol (to reduce emulsification), and the catalyst was recovered with a magnet. The recovered catalyst was washed by DI water and ethanol sequentially for three times. Finally, the catalyst was dried using vacuum pump at 60°C for 8 h.

## 4. XRD

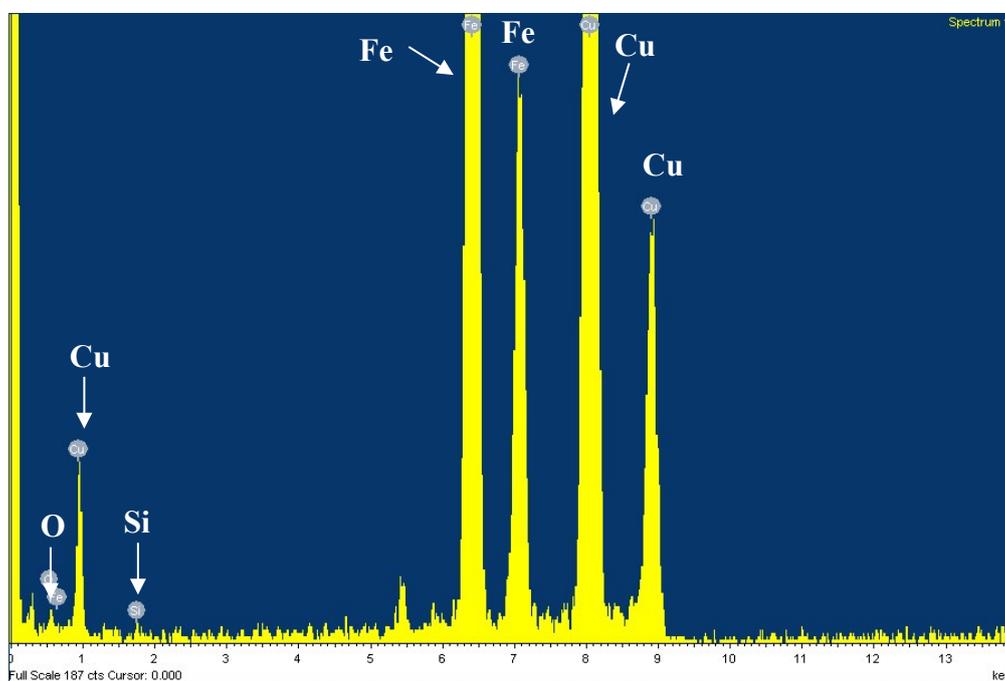


**Fig. S1** XRD patterns of (a)  $\text{Fe}_3\text{O}_4$  nanoparticles, (b)  $\text{Fe}_3\text{O}_4@SiO_2$  nanoparticles, (c)  $\text{Fe}_3\text{O}_4@SiO_2$  core-shell PTMA brush, and (d)  $\text{Fe}_3\text{O}_4@SiO_2$  core-shell PTMA brush after catalyzing the oxidation of benzyl alcohol.

## 5. TEM



**Fig. S2** TEM image of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles.



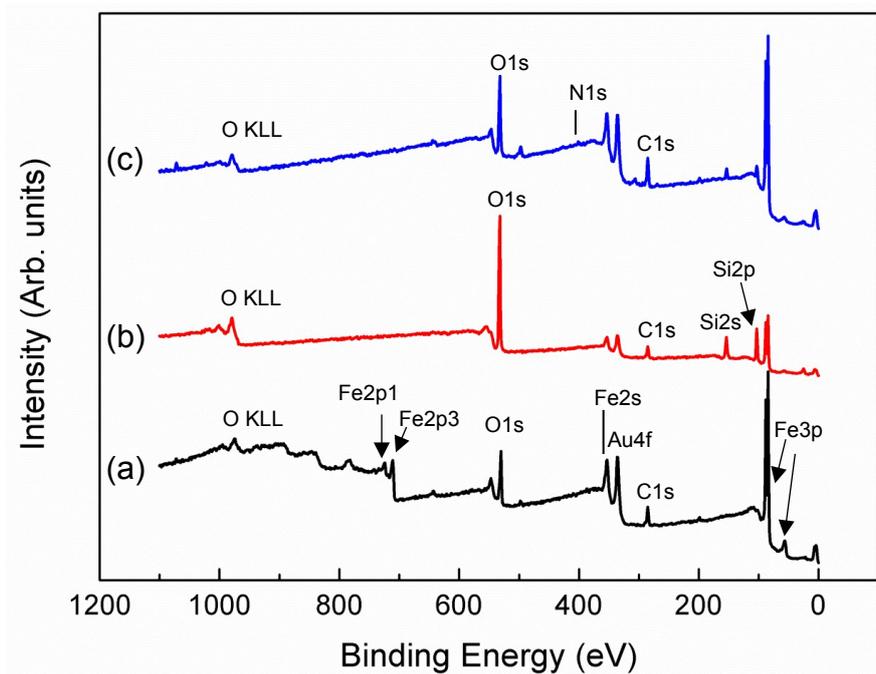
**Fig. S3** EDS of the above TEM image of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles.

**Table S1** Atomic concentration of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles obtained by EDS

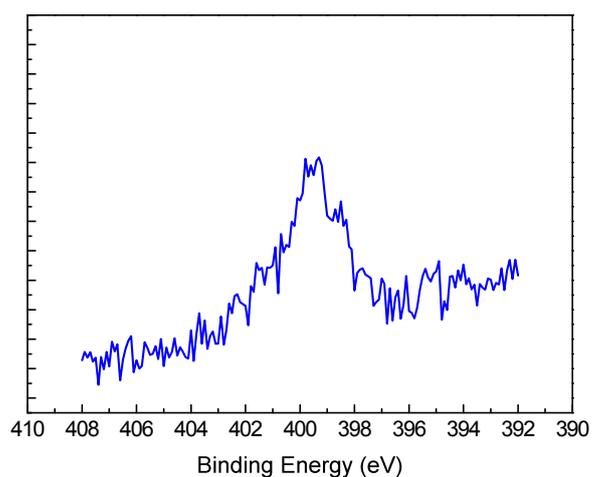
<b>Elements</b>	<b>Atomic %</b>
O K	20.43
Si K	2.64
Fe K	25.76
Cu K*	51.17

\* Contributed from Cu grid.

## 6. XPS



**Fig. S4** XPS survey spectra of (a) Fe<sub>3</sub>O<sub>4</sub> nanoparticles, (b) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles, and (c) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell PTMA brush.



**Fig. S5** XPS spectra for binding energy N1s of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell PTMA brush.

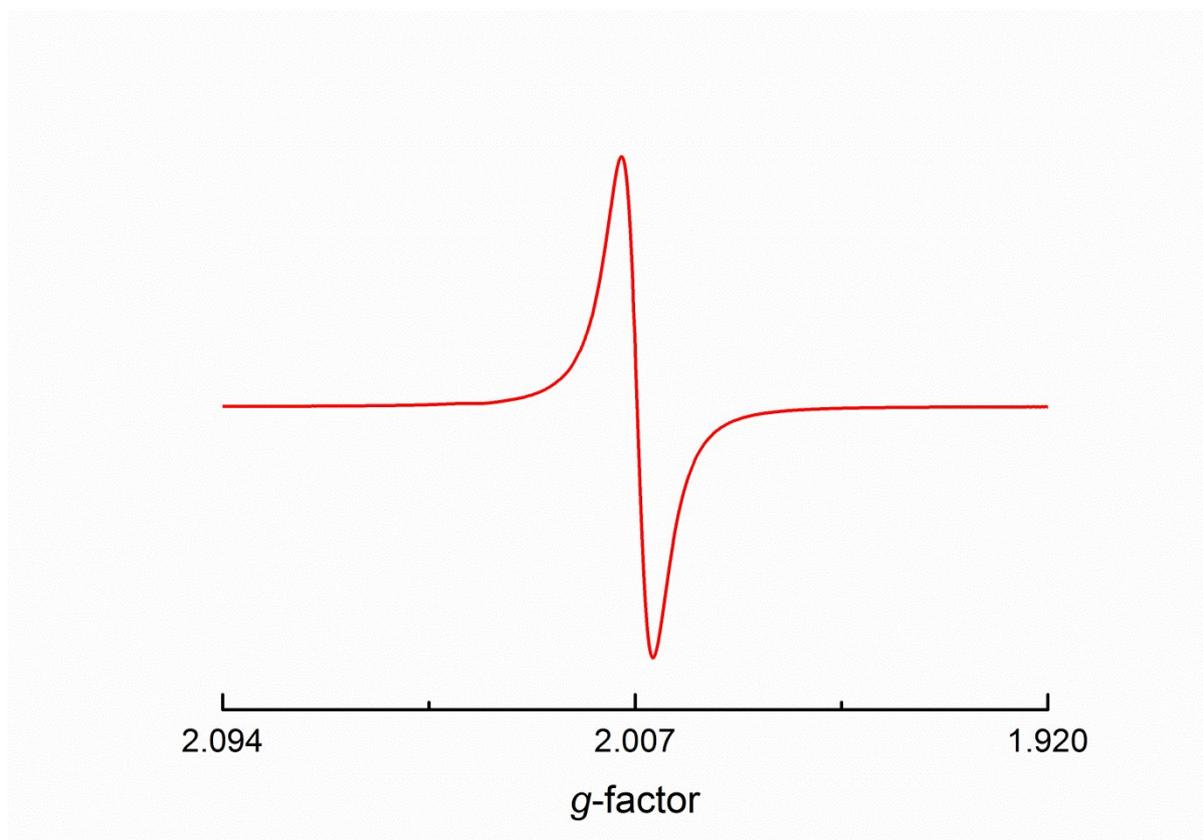
**Table S2** Atomic concentration obtained by XPS.

	C1s	N1s	O1s	Si2p	Fe2p
Fe <sub>3</sub> O <sub>4</sub>	30.83	-	47.24	-	21.94
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub>	12.66	-	60.78	26.45	0.11
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -PTMA Brush	39.14	2.42	40.50	17.82	0.12

**Table S3** Atomic weight percentage analyzed by an elemental analyzer.

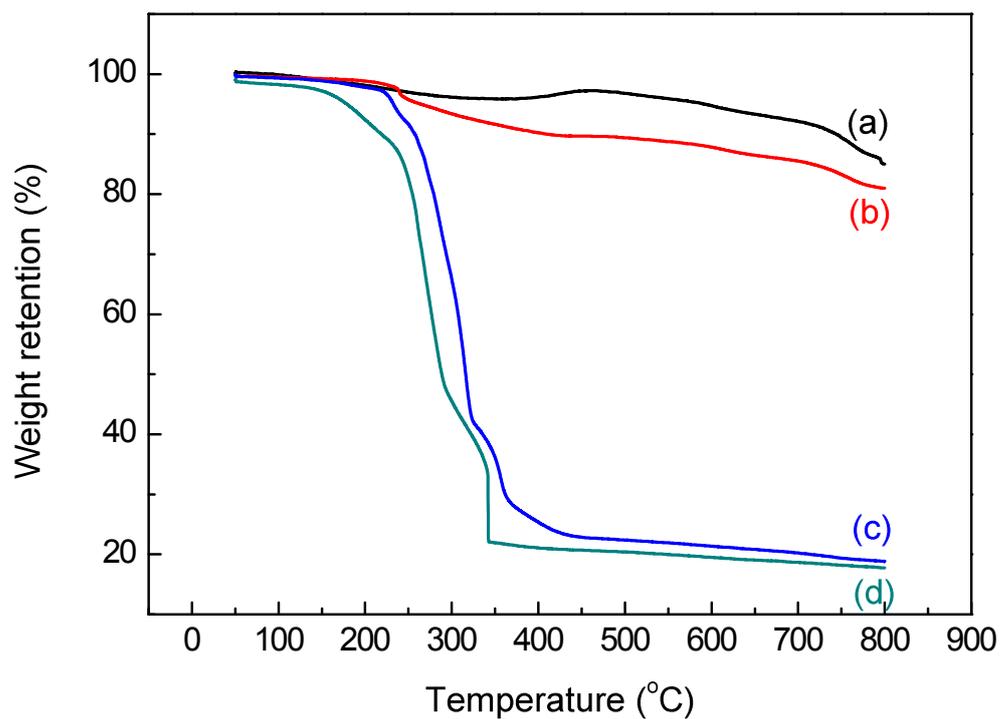
	Weight percentage (%)		
	C	H	N
Measurement	47.98	6.39	3.18

## 7. EPR



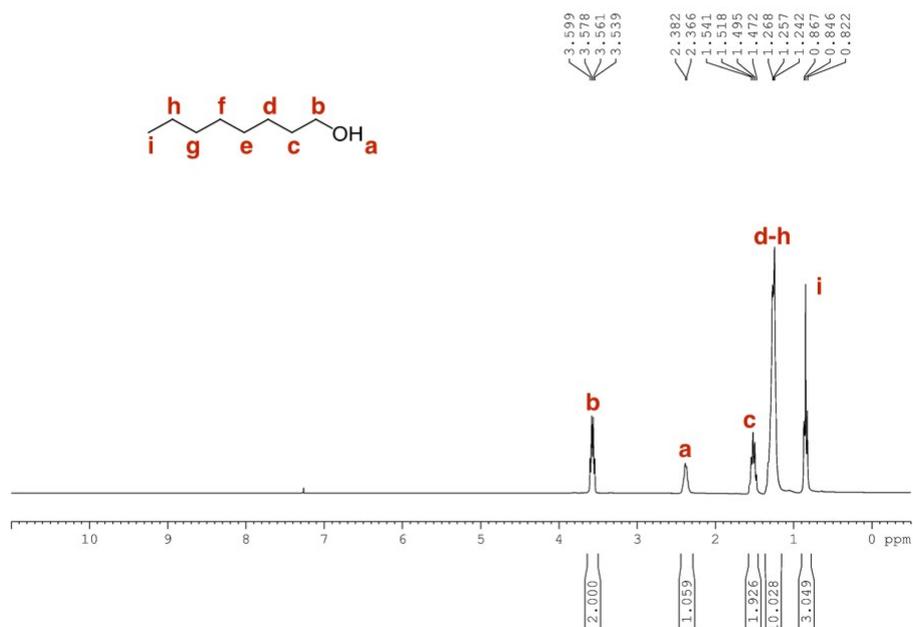
**Fig. S6** EPR spectrum of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  core-shell PTMA brush.

## 8. TGA

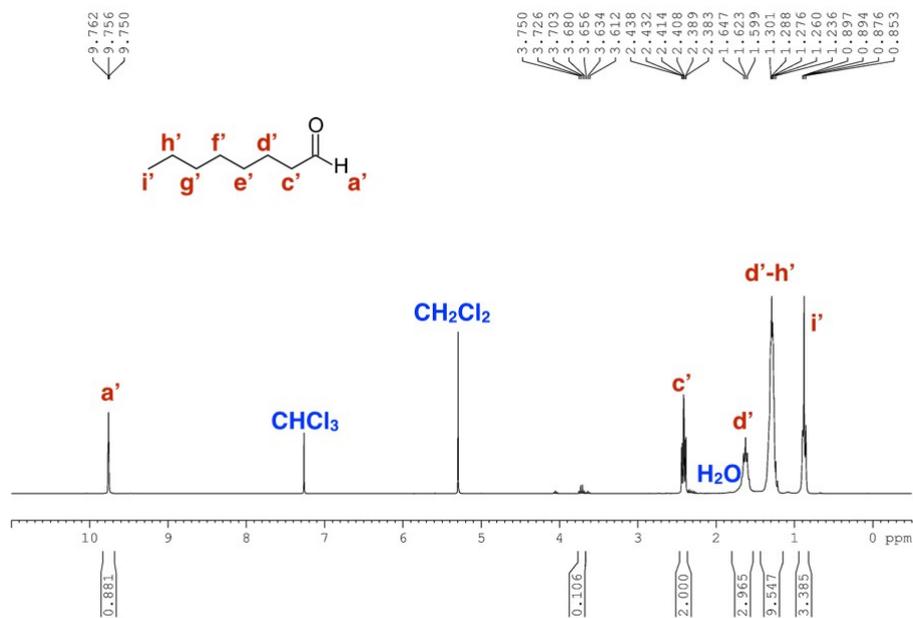


**Fig. S7** TGA curves for (a) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles, (b) surface initiator-modified Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles, (c) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell PTMPM brushes, and (d) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell PTMA brushes.

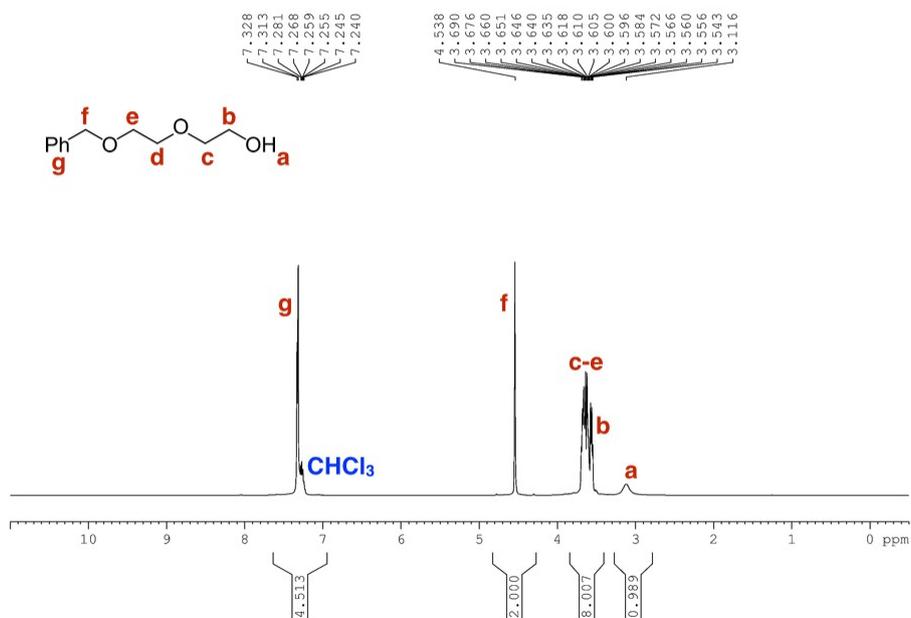




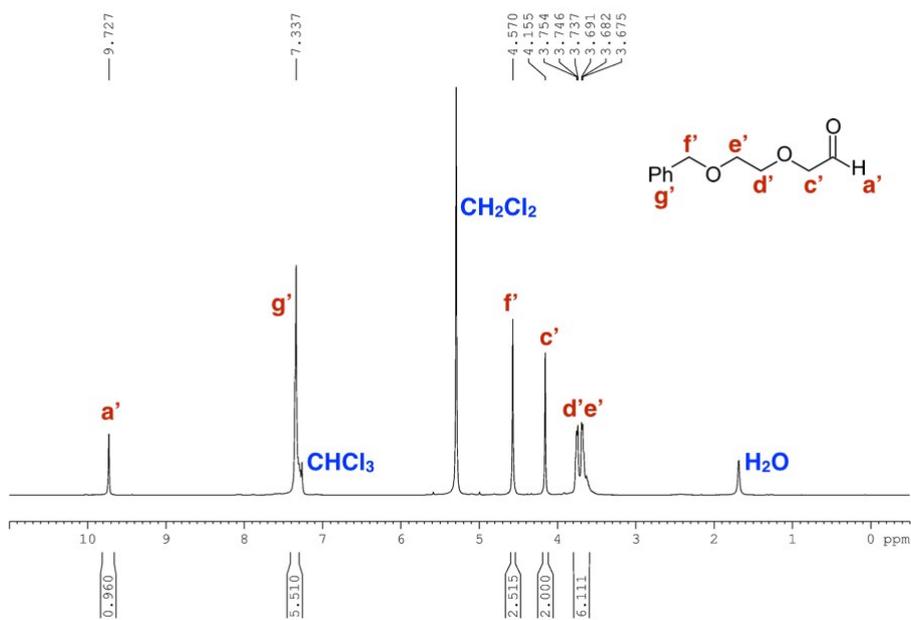
**Fig. S10** <sup>1</sup>H-NMR spectrum of 1-octanol.



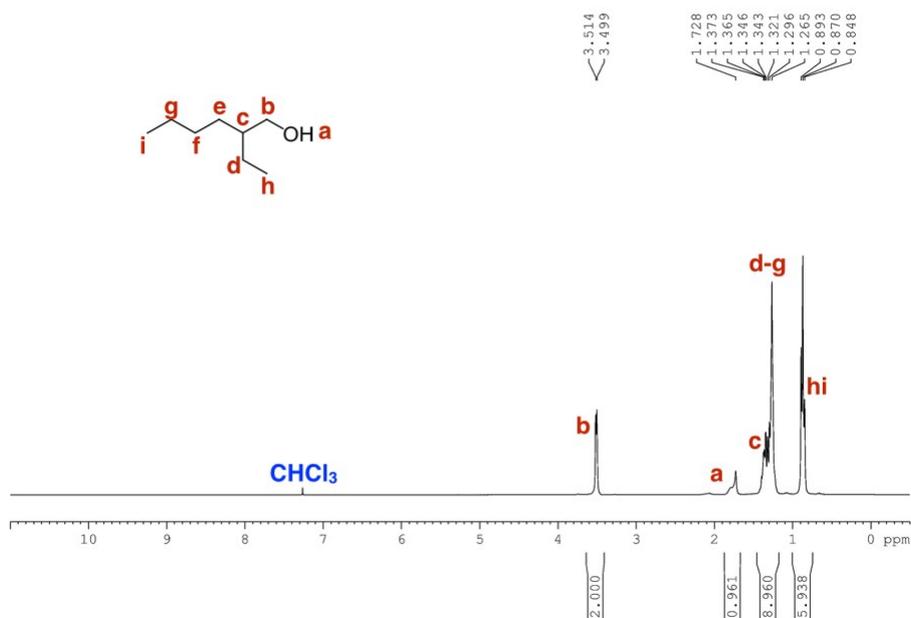
**Fig. S11** <sup>1</sup>H-NMR spectrum of oxidized 1-octanol catalyzed by Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PTMA.



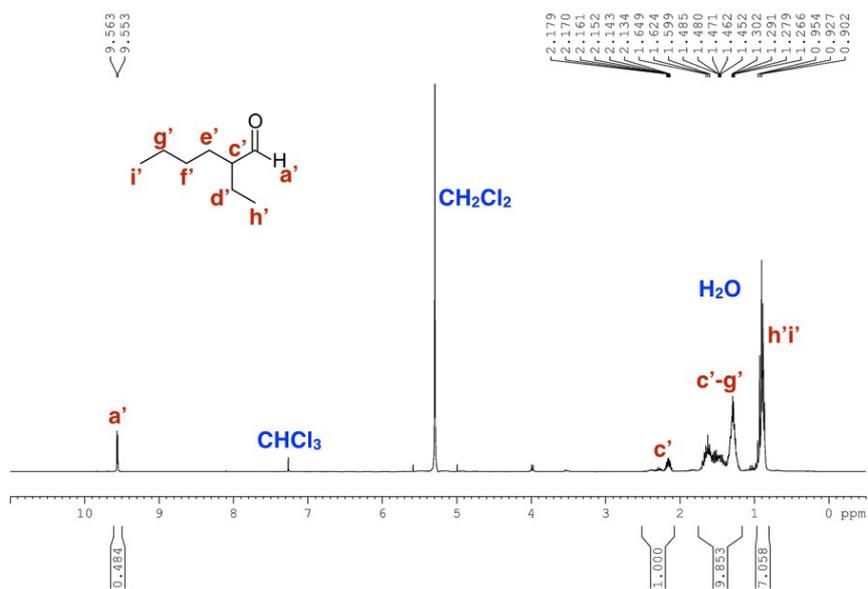
**Fig. S12**  $^1\text{H-NMR}$  spectrum of 2-(2-(benzyloxy)ethoxy)ethanol.



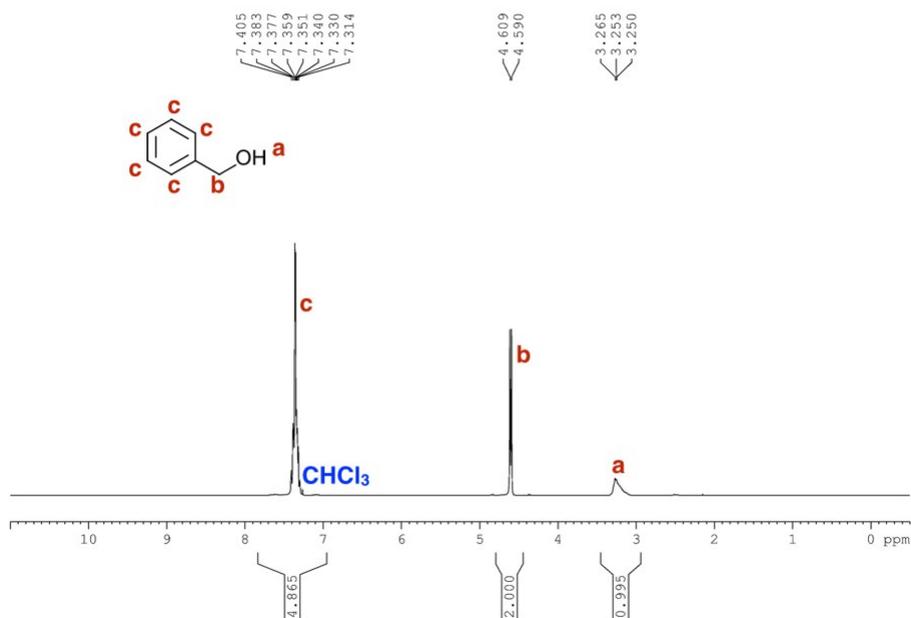
**Fig. S13**  $^1\text{H-NMR}$  spectrum of oxidized 2-(2-(benzyloxy)ethoxy)ethanol catalyzed by  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-PTMA}$ .



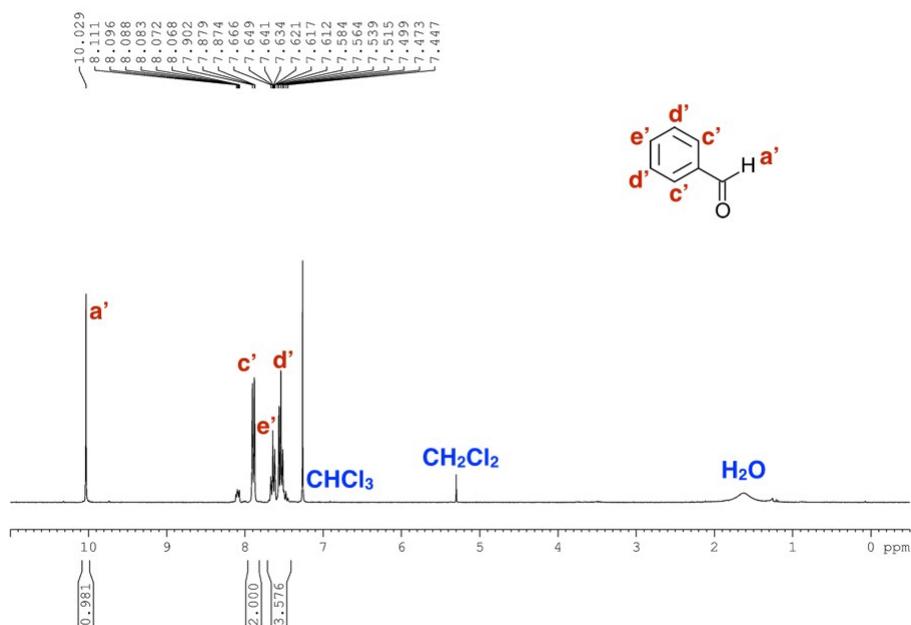
**Fig. S14** <sup>1</sup>H-NMR spectrum of 2-ethylhexan-1-ol.



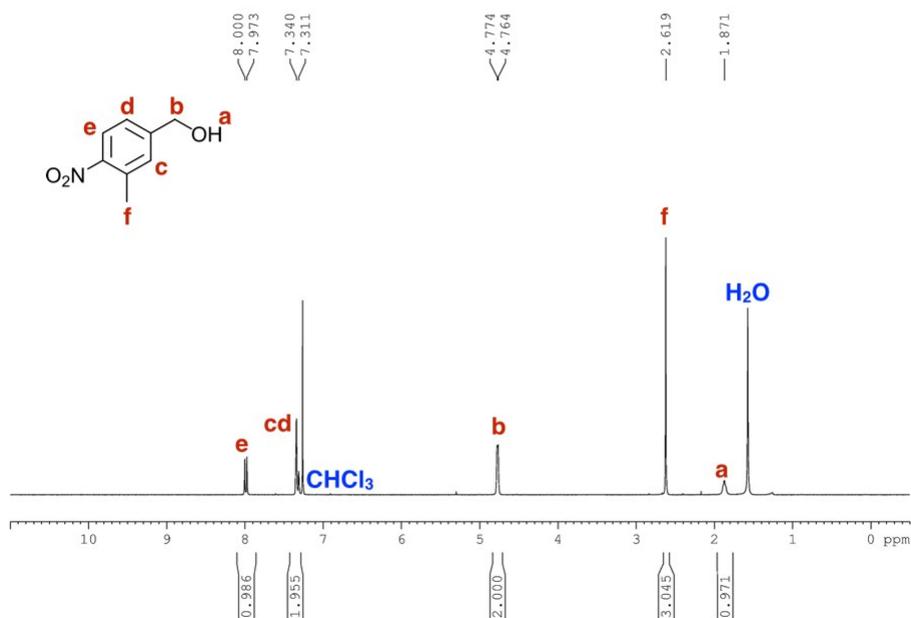
**Fig. S15** <sup>1</sup>H-NMR spectrum of oxidized 2-ethylhexan-1-ol catalyzed by Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PTMA.



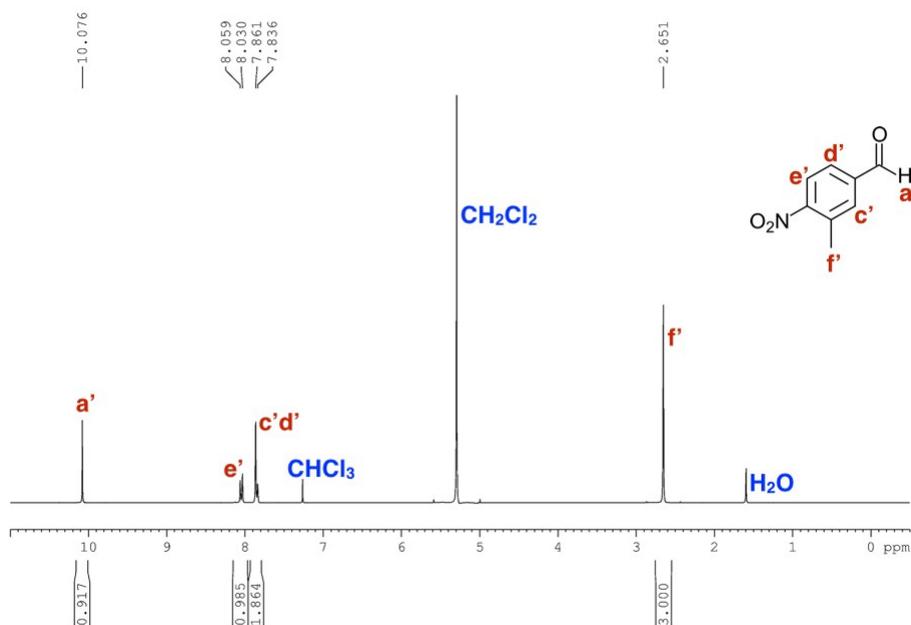
**Fig. S16** <sup>1</sup>H-NMR spectrum of benzyl alcohol.



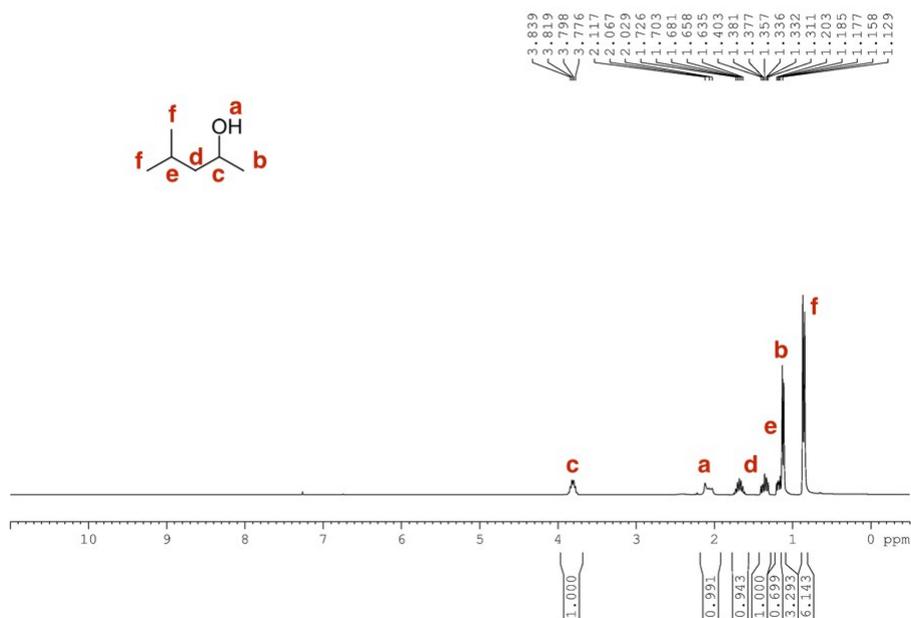
**Fig. S17** <sup>1</sup>H-NMR spectrum of oxidized benzyl alcohol catalyzed by Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PTMA.



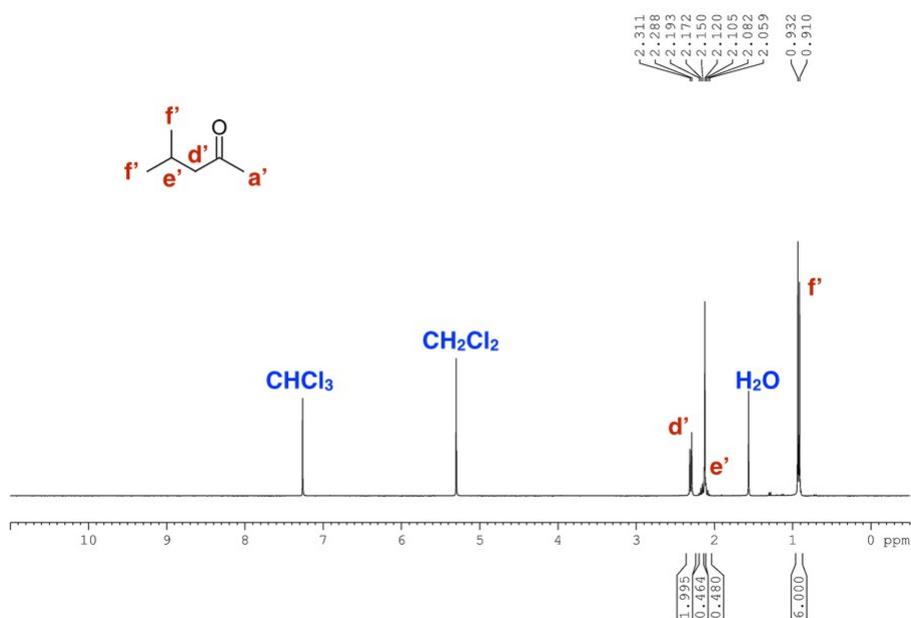
**Fig. S18** <sup>1</sup>H-NMR spectrum of (3-methyl-4-nitrophenyl)methanol.



**Fig. S19** <sup>1</sup>H-NMR spectrum of oxidized (3-methyl-4-nitrophenyl)methanol catalyzed by Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PTMA.



**Fig. S20** <sup>1</sup>H-NMR spectrum of 4-methylpentan-2-ol.



**Fig. S21** <sup>1</sup>H-NMR spectrum of oxidized 4-methylpentan-2-ol catalyzed by Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PTMA.

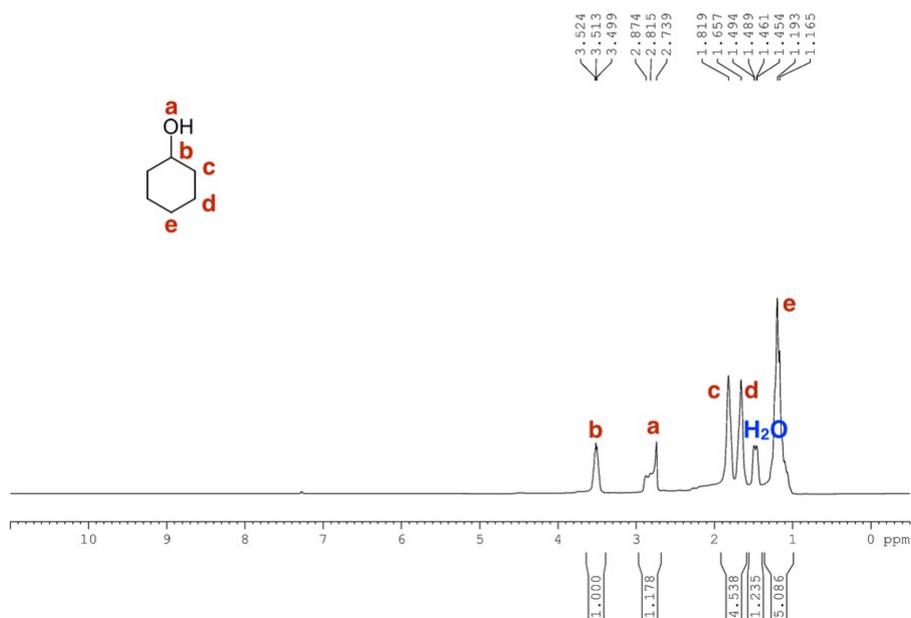


Fig. S22 <sup>1</sup>H-NMR spectrum of cyclohexanol.

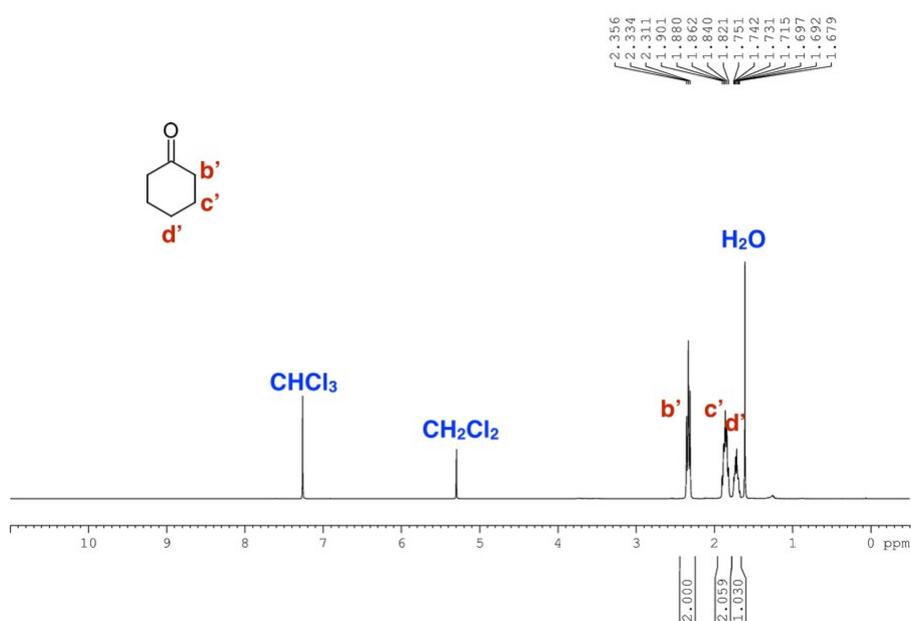


Fig. S23 <sup>1</sup>H-NMR spectrum of oxidized cyclohexanol catalyzed by Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PTMA.