

## Experimental section

### *Materials and methods:*

Ethanol employed in the work was distilled before use. All the other solvents and reagents were used as received from commercial sources unless otherwise stated.  $^1\text{H}$  NMR spectra were recorded on Bruker DRX300 spectrometer. IR spectra were recorded on NICOLET NEXUS870. Products were identified using a 6820 gas chromatograph (GC) with an Agilent Technologies HP-Innowax (30 m $\times$ 0.32 mm $\times$ 0.5  $\mu\text{m}$ ). XRD data were collected with  $\text{Cu}_{\text{K}\alpha}$  radiation on Bruker C8 ADVANCE. ESR spectrums were determined on Bruker EMX-10/12. Elemental analysis was carried out using a Leeman Plasma Spec (I) ICP-ES and a P-E 2400 CHN elemental analyzer.

### *Synthesis of 2,2,6,6-tetramethyl-1-oxyl-piperidin-4-yl 2-chloroacetate 1:*

The TEMPO base IL was prepared according the method proposed by Miao [1] with some modifications.

To a stirred solution of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4.3 g, 25 mmol) and chloroacetic acid (2.0 g, 25 mmol) in  $\text{CH}_2\text{Cl}_2$  (40 mL) at 0  $^\circ\text{C}$  under argon, DCC (5.15 g, 25 mmol) and DMAP (0.75 g, 6.25 mmol), dissolved in  $\text{CH}_2\text{Cl}_2$  (40 mL) were dropwise added. And the mixture was stirred for 12 h at room temperature. After reaction, the precipitate was filtered, and the filtrate was washed with 1M HCl (25 mL), saturated  $\text{NaHCO}_3$  (50 mL) and brine (50 mL). The organic phase was dried over  $\text{MgSO}_4$ , and evaporated under reduced pressure. Further purification went through a short flash chromatography (the eluent: EtOAc-petroleum ether 1:10) providing 2,2,6,6-tetramethyl-1-oxyl-piperidin-4-yl 2-chloroacetate (**1**) as a red powder.

### *Synthesis of TEMPO based IL 2:*

1-methylimidazole (0.46 g, 5.6 mmol) was added to a solution of **1** (1.00 g, 4 mmol) in MeCN (30 mL), and the resulting mixture was stirred for 48 h at 80  $^\circ\text{C}$ . The final solution was evaporated under reduced pressure to remove about half the solvent, followed by the addition of diethyl ether to get a precipitate. Then the solid was filtered and washed with acetone, diethyl ether, respectively to give **2** as a light red powder;

### *Synthesis of difunctionalized IL 3:*

$\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  was prepared according to the procedure in literature [2]. **2** (0.63 g, 2 mmol) was dissolved in 50 mL of deionized water, and  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  (0.70 g, 0.4 mmol) was dissolved in 30 mL of deionized water. The solution of **2** was added dropwise into the  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  solution, yielding a yellowish green precipitate. The resulting suspension was stirred for 2 h at room temperature, and the solid product was separated by filtration, washed with deionized water, and then dried overnight at 50  $^\circ\text{C}$ .

### *Synthesis of magnetic silica supported IL 3 (IL/SMNP):*

The magnetic nanoparticles (MNP) were synthesized by chemical co-precipitation method [3]. The procedure of silica coating follows a method reported in ref. [4].

SMNP supported IL was also prepared by a co-precipitation method. One gram of carrier (SMNP,  $\text{SiO}_2$ , or  $\text{Al}_2\text{O}_3$ ) was dispersed in 50 mL of deionized water and sonicated for 15 min. Then **2** (0.105 g) was added dropwise to the slurry and stirred for 1 h, followed by the dropwise addition of 30 mL  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  solution (0.112 g). The resulting slurry was stirred for another 2 h at room temperature, and the solid product was separated by filtration, washed with deionized water, and then dried overnight at 50  $^\circ\text{C}$ .

### *General procedure for aerobic oxidation of alcohols:*

Reactions were carried out in 50 mL glass pressure tubes. IL/SMNP (0.01 mmol) was dispersed in toluene (15 mL) and sonicated for 15 min followed by the addition of alcohol (1 mmol). Oxygen was introduced to the tube to a pressure of 2 atm and the pressure tube was placed in an oil bath thermostated at 80  $^\circ\text{C}$ . When the reaction was finished, the catalyst was recovered by simply applying an external magnetic field and the crude product was analyzed by GC.

**4-Nitrobenzaldehyde:** Light yellow acicular crystals, mp 105-106.8 $^\circ\text{C}$ ,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$ =8.08 (d,

$^3J_{H,H} = 4.35$  Hz, 2 H), 8.39 (d,  $^3J_{H,H} = 4.35$  Hz, 2 H), 10.16 (s, 1 H);  $^{13}C \{^1H\}$  NMR ( $CDCl_3$ , 75 MHz):  $\delta = 124.2, 130.4, 140.0, 151.1, 190.2$ .

**Cinnamaldehyde:** Light yellow liquid,  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta = 6.69-6.77$  (m, 1 H), 7.43-7.47 (m, 4 H), 7.52-7.59 (m, 2 H), 9.71 (d,  $^3J_{H,H} = 3.9$  Hz, 1 H);  $^{13}C \{^1H\}$  NMR ( $CDCl_3$ , 75 MHz):  $\delta = 128.5, 128.6, 129.1, 131.3, 134.0, 152.8, 193.8$ .

**Acetophenone:** Light yellow liquid,  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta = 2.60$  (s, 3 H), 7.46 (t,  $^3J_{H,H} = 7.7$  Hz, 2 H), 7.56 (t,  $^3J_{H,H} = 7.5$  Hz, 1 H), 7.96 (d,  $^3J_{H,H} = 7.8$  Hz, 2 H);  $^{13}C \{^1H\}$  NMR ( $CDCl_3$ , 100.6 MHz):  $\delta = 26.5, 128.2, 128.5, 133.0, 137.1, 198.1$ .

**Benzophenone:** White crystals, mp 47-48.8°C,  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta = 7.48$  (t,  $^3J_{H,H} = 7.9$  Hz, 4 H), 7.58 (t,  $^3J_{H,H} = 7.9$  Hz, 2 H), 7.81 (t,  $^3J_{H,H} = 5.7$  Hz, 4 H);  $^{13}C \{^1H\}$  NMR (75 MHz,  $CDCl_3$ ):  $\delta = 128.3, 130.1, 132.4, 137.6, 196.7$ .

Table S1 The elementary analysis data of IL 3.

IL 3	Elemental analysis wt %					
	C	H	N	Mo	V	P
observed	26.05	3.68	6.70	30.80	3.24	1.01
calcd	26.22	3.76	6.56	29.97	3.18	0.97

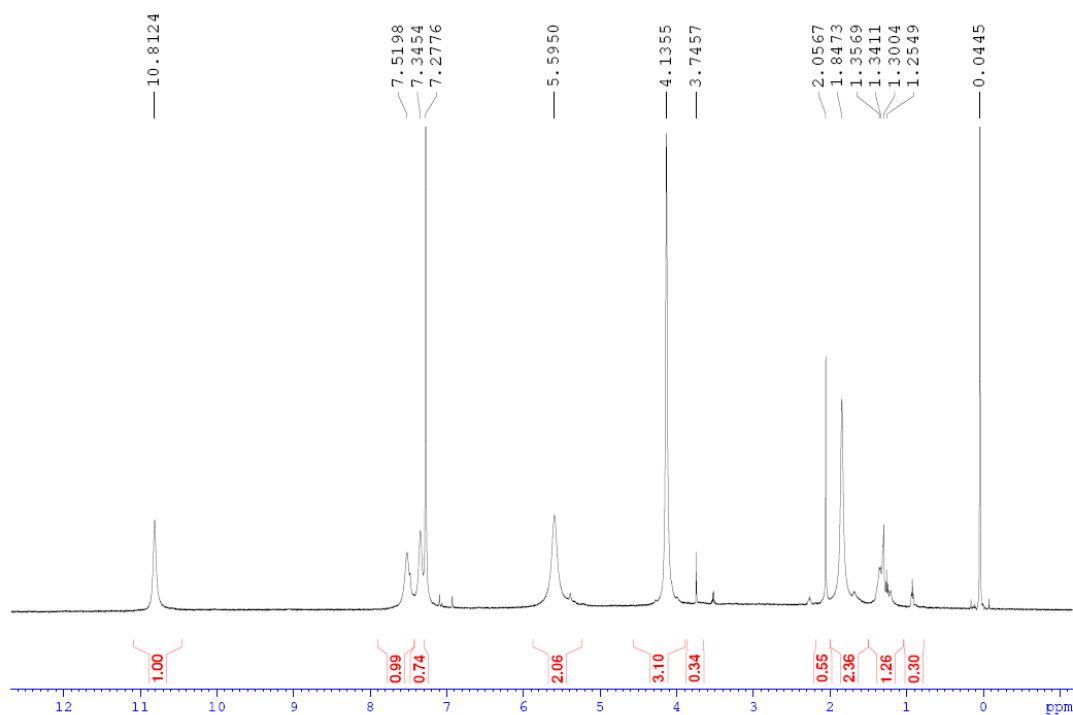


Figure S1  $^1H$ NMR of 2,2,6,6-tetramethyl-1-oxyl-piperidin-4-yl 2-chloroacetate 1

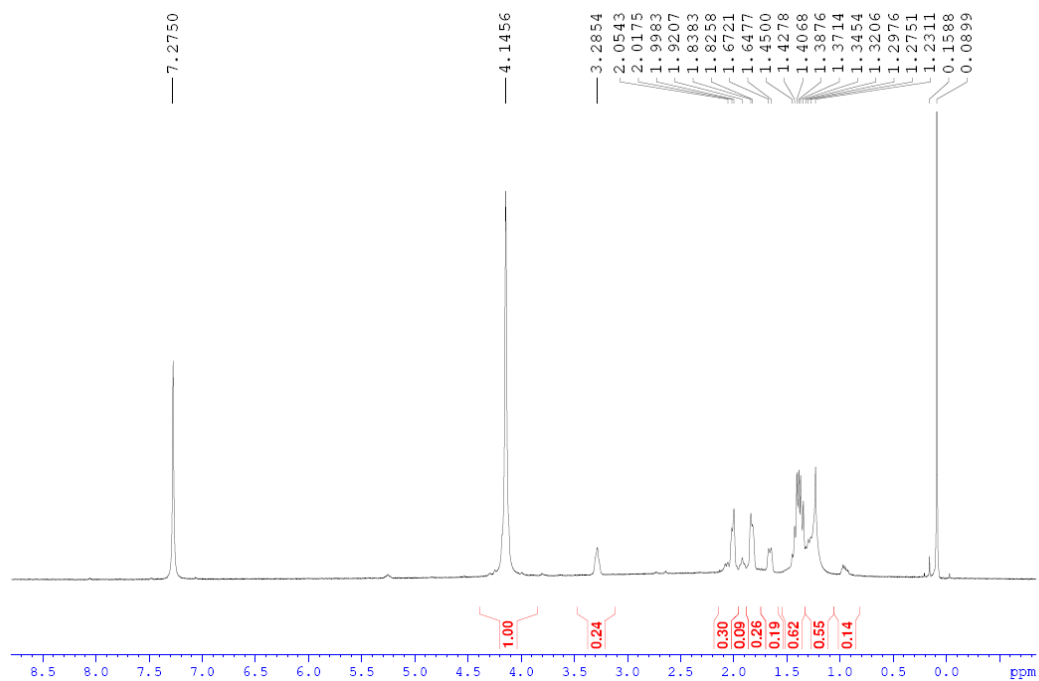


Figure S2  $^1\text{H}$ NMR of TEMPO based IL 2

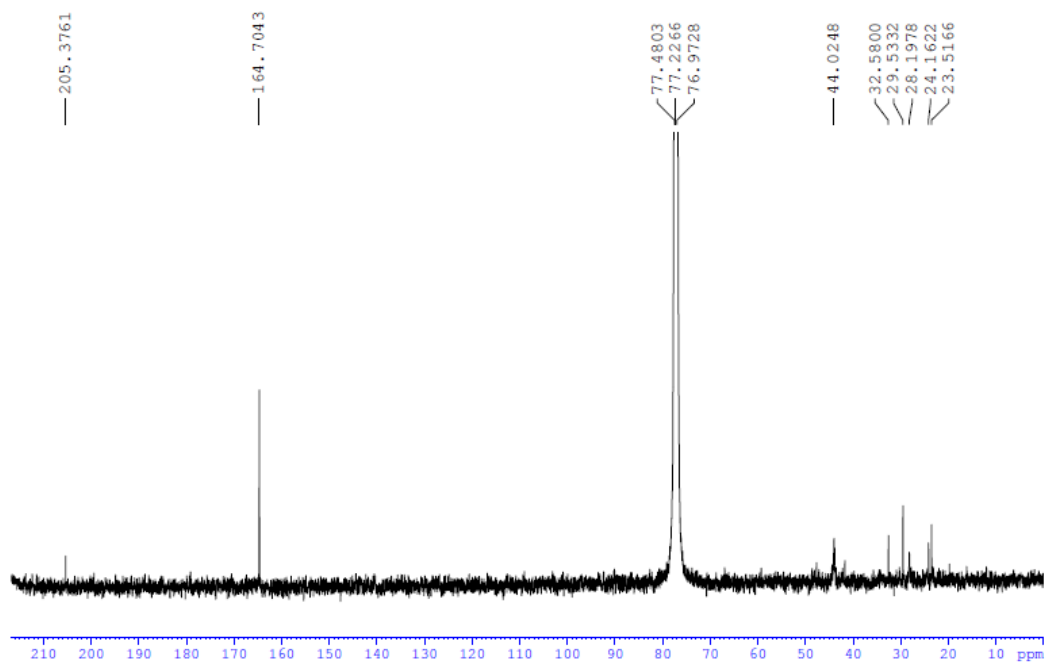


Figure S3  $^{13}\text{C}$ NMR of 2,2,6,6-tetramethyl-1-oxyl-piperidin-4-yl 2-chloroacetate 1

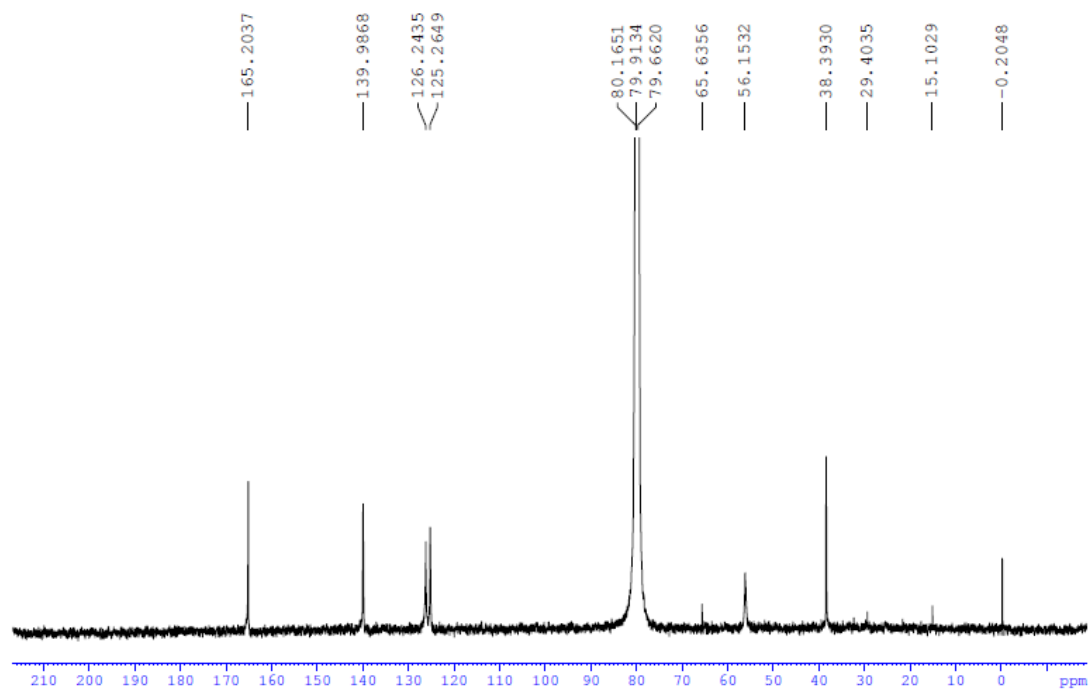
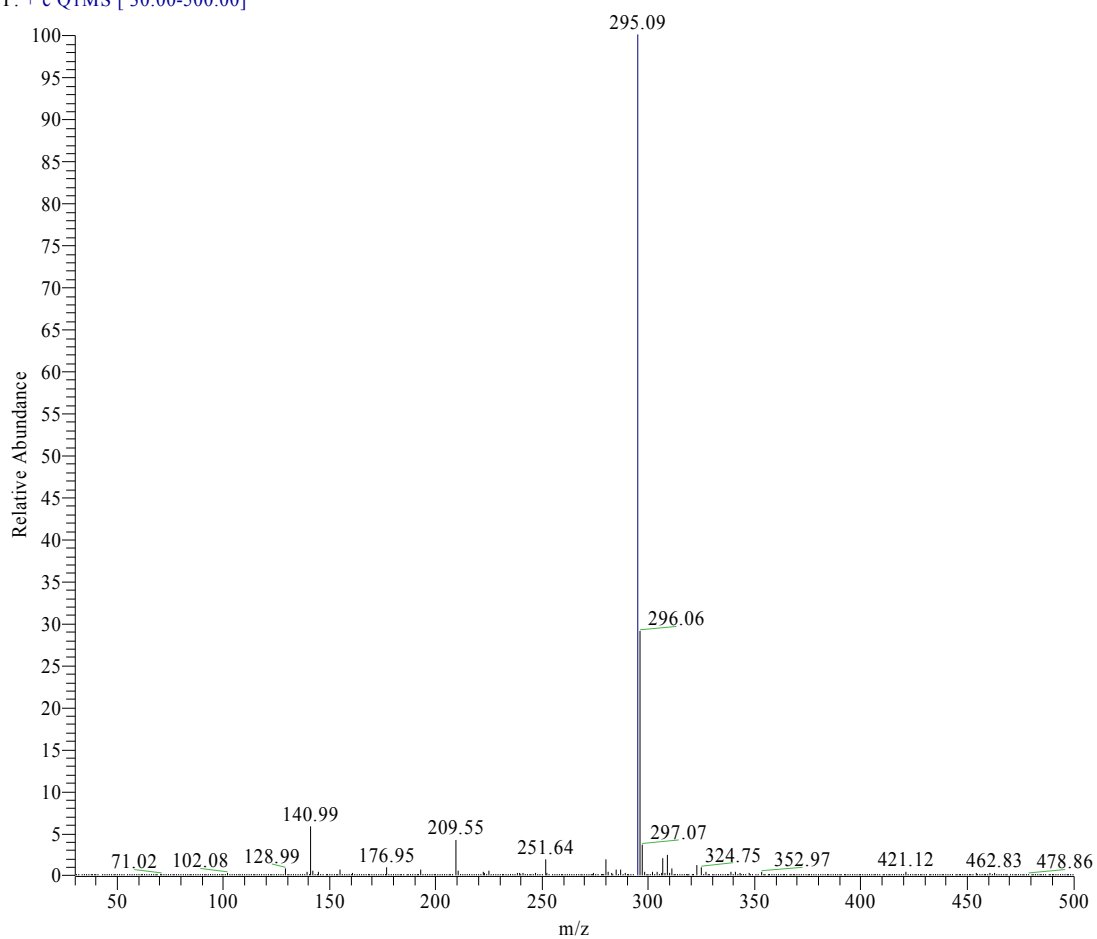


Figure S4  $^{13}\text{C}$ NMR of TEMPO based IL 2

201203-13-wpch #6 RT: 0.06 AV: 1 NL: 3.27E8  
T: + c Q1MS [ 30.00-500.00]



201203-13-wpch #19 RT: 0.22 AV: 1 NL: 2.51E8  
T: + c Full ms2 295.00@-10.00 [ 30.00-300.00]

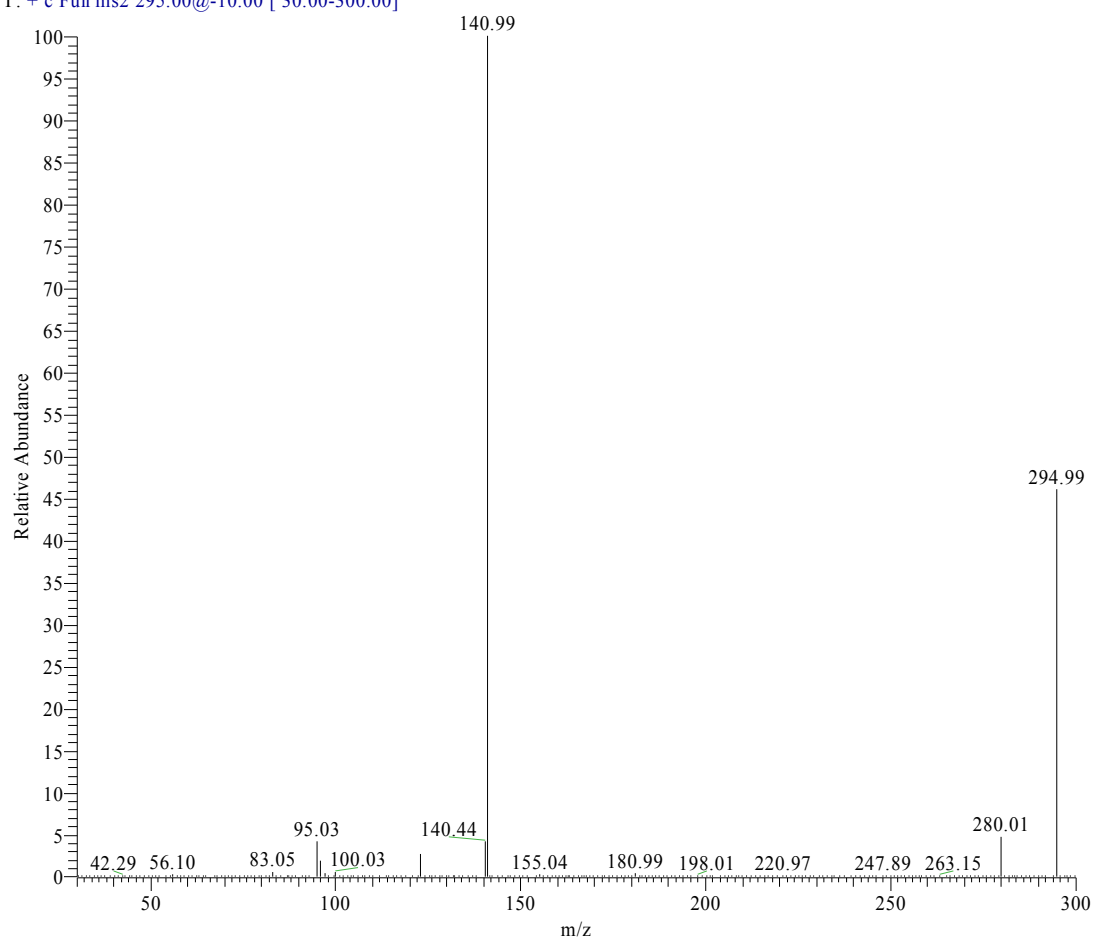


Figure S5 MS of IL 2

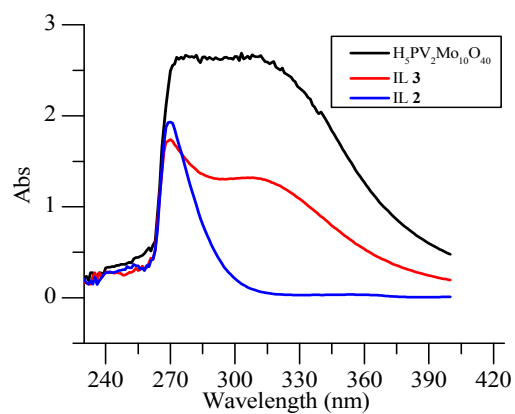


Figure S6 UV spectra of IL 2, IL 3 and  $H_5PV_2Mo_{10}O_{40}$

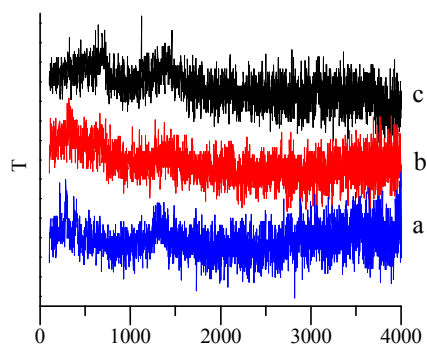


Figure S7 Raman Raman spectrum of (a) MNP; (b) SMNP and (c) IL/SMNP

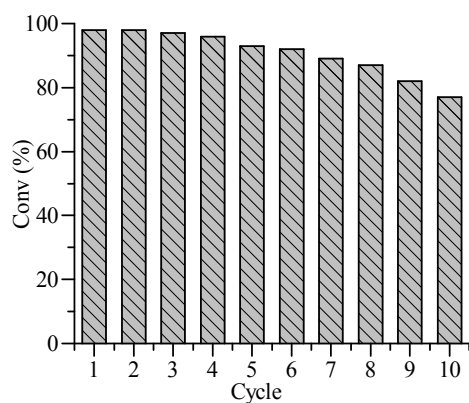


Figure S8 The recycling study of IL/SMNP. Reaction conditions: 2 mmol benzyl alcohol, 1 mmol IL/SMNP (20 wt% loading IL), toluene (15 mL), 2 atm O<sub>2</sub>, 80 °C.

Table S1 XRF analyze of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> SMNPs (w %)

Items	contents	Items	contents
Fe <sub>2</sub> O <sub>3</sub>	50.16	Al <sub>2</sub> O <sub>3</sub>	0.081
SiO <sub>2</sub>	47.54	CaO	0.064
Na <sub>2</sub> O	1.24	ZnO	0.040
P <sub>2</sub> O <sub>5</sub>	0.54	PbO	0.039
Cl	0.18	Cr <sub>2</sub> O <sub>3</sub>	0.012
MnO	0.13		

References:

- 1 C. X. Miao, L. N. He, J. Q. Wang and J. L. Wang, *Adv. Synth. Catal.*, 2009, **351**, 2209-2216.
- 2 G. A. Tsigdinos and C. J. Hallada, *Inorg. Chem.*, 1968, **7**, 437-441.
- 3 Z. G. Peng, K. Hidajat, and M. S. Uddin, *J. Colloid Interface Sci.*, 2004, **271**, 277-283.
- 4 B. Karimi and E. Farhangi, *Chem.-Eur. J.*, 2011, **17**, 6056-6060.