## **Electronic Supplementary Information**

# Promoted Activity of Cr(Salen) in Nanoreactor for Kinetic Resolution of Terminal Epoxides

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# Experimental

#### **Reagents and materials**

Pluronic	P123	copolymer	$(EO_{20}PO_{70}EO_{20}),$	pluronic	copolymer	F127
(EO <sub>106</sub> PO <sub>70</sub>	<sub>0</sub> EO <sub>106</sub> ),		propyltrimetho	oxysilane		and

(R,R)-N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminochromium(III) chloride [Cr(Salen)] were purchased from Sigma-Aldrich Company Ltd and were used without any further purification. All the epoxide and azidotrimethylsilane (TMSN<sub>3</sub>) were obtained from Alfa Aesar Company. Other reagents were obtained from Shanghai Chemical Reagent. Inc., of Chinese Medicine Group. Azidotrimethylsilane and epoxides were distilled from CaH<sub>2</sub> prior to use.

The mesoporous silicas with cage-like pore structure, FDU-12, was synthesized according to the literature method.<sup>1</sup> A typical synthesis procedure was as follows: 4.0 g of F127 and 10 g of KCl were dissolved in 240 mL of 2 M HCl, then 8.8 g of TMB was added and the mixture was stirred at 15  $^{\circ}$ C for 24 h in a capped container. 16.4 g of TEOS was added to the above reaction mixture, and the reaction mixture was kept under stirring for 24 h at 15  $^{\circ}$ C before being transferred to an autoclave and kept at 100  $^{\circ}$ C for 24 h. The solid product was collected by filtration and dried at 100  $^{\circ}$ C. Then FDU-12-as made was obtained. FDU-12 with inner surface covered with a layer of carbon species was denoted as FDU-C, which was synthesized by carbonization of FDU-12-as made in nitrogen at 500  $^{\circ}$ C for 4h.

#### Encapsulation of Cr(Salen) in the nanocages of FDU-C

A typical procedure for encapsulation of Cr(Salen) in the nanocages of FDU-C using pyridine as silylation catalyst is a modified method as reported previously<sup>2-3</sup>. FDU-C with cage-like porous structure (0.5 g, evacuated at 398 K for 6 h) was dispersed in dichloromethane (3 mL) containing the desired amounts of Cr(Salen) (50 to 150 mg). After stirring the mixture at 313 K for 24 h under Ar, CH<sub>2</sub>Cl<sub>2</sub> was removed by evaporation. The resultant solid was dispersed in dried hexane (1.0 mL) containing anhydrous pyridine (0.70 mL) and propyltrimethoxysilane (984 mg). After refluxing the mixture for 24 h under Ar, the resultant solid was isolated by filtration, washed thoroughly with CH<sub>2</sub>Cl<sub>2</sub>. The resultant solid catalyst was dried in vacuum and denoted as Cr(salen) 2py@FDU-C.

#### Synthesis of Cr(Salen)py

0.2 mL of pyridine was added in the solution containing 200 mg Cr(Salen) in 5mL CH<sub>2</sub>Cl<sub>2</sub>. After stirring the mixture at 293 K for 6 h, the solvent was removed by evaporation at about 323 K.

# Kinetic resolution of terminal epoxides via asymmetric ring opening (ARO) with TMSN<sub>3</sub>

A 10 mL flask was charged with solid catalyst followed by addition of epoxide (2 mmol). After the suspension was stirred for 10 min, TMSN<sub>3</sub> (132  $\mu$ L, 1 mmol) was added via syringe. After the reaction mixture was stirred for certain time, about 90 mg of octane (internal standard) and 5 mL CH<sub>2</sub>Cl<sub>2</sub> was added to the reaction mixture. The solid catalyst was separated by centrifugalization and washed with 5 mL CH<sub>2</sub>Cl<sub>2</sub>

twice. The filtration was collected and analyzed by an Agilent 7890N GC equipped with chiral capillary column (Beta DEX 120 capillary column).

In the case of recycle, the solid catalyst was separated by filtration after reaction, washed thoroughly with  $CH_2Cl_2$ , dried under vacuum for 4 h and directly used for the next cycle.

#### **Characterization**

N<sub>2</sub> sorption isotherms were carried out on a Micromeritics ASAP 2020 volumetric adsorption analyzer after the samples were outgassed at 393 K for 6 h. FT-IR spectra were collected with a Nicolet Nexus 470 IR spectrometer. All the mass spectra were recorded using a Micromass Q-Tof (Micromass, Wythenshawe, Waters) mass spectrometer equipped with an orthogonal electrospray source (Z-spray) operated in positive ion mode, and the data were acquired using Masslynx software (version 4.1). PEG1000 was used for mass calibration for a calibration range of m/z 100-2000. The ESI capillary voltage was maintained between 2.5 and 3.5 kV, and the cone voltage was kept at 5-10 V. EPR (electron paramagnetic resonance) spectra were recorded on a Bruker A200 spectrometer at 9.4 GHz and 298 K.

#### **Results and Discussions**

Samples	BET Surface Area	Pore volume	Pore Size	
	m²/g	$cm^3/g^a$	$nm^b$	
FDU-12	721	0.73	18.2	
FDU-C	622	0.61	17.5	
Cr(Salen)py@FDU-C <sup>c</sup>	284	0.38	16.5	

Table S1 The textural parameters of FDU-12 and FDU-C

<sup>a</sup> Estimated from the amounts adsorbed at a relative pressure (P/P<sub>0</sub>) of 0.99. <sup>b</sup> the pore size distribution calculated from the N<sub>2</sub> adsorption branch using the BJH method. <sup>c</sup> Cr(Salen)py@FDU-C with Cr content of 0.76 wt% and N content of 0.85 wt% (Cr/pyridine=2.15).

**Table S2** Kinetic resolution of terminal epoxides via ARO with  $TMSN_3$  on the solid nanoreactor with different concentration of Cr(Salen)py in the nanocages<sup>a</sup>

	+SiN <sub>3</sub>		+	0
	,	1		2
Cr content	number of	conversion	ee value of 2	TOF
[wt%] <sup>b</sup>	Cr(Salen) in	[%]	[%]	$[h^{-1}]$
	$5 \times 5 \times 5$ nm <sup>3</sup>			
0.085	2.6	11	64	64
0.17	5	27	87	98
0.49	15	41	90	140
0.76	23	>49	91	170

<sup>a</sup> The reactions were performed at S/C=1000 in the presence of 1,2-epoxyhexane of 20 mmol and TMSN<sub>3</sub> of 10 mmol at room temperature for 8 h. <sup>b</sup> Obtained from the difference between the initial Cr(Salen) added and the filtrate after silylation.

Table S3 The kinetic resolution of terminal epoxides via ARO with TMSN\_3 using Cr(Salen)py@FDU-C  $(0.76wt\% Cr)^a$ 

o, , /	Cr(Salen)py	Cr(Salen)py@FDU-C(0,76wt% Cr)			
$R^{+}$	$-N_3$	S/C=1000	<sup>™</sup> N <sub>3</sub> R		
Expoxide	Time / h	Conversion / %	Ee value / %		
$\frown \!\!\!\! \bullet$	6	51	91		
	10	46	90		
	40	42	81		
	13	46	76		
Eto O	24	36	76		
<sup>a</sup> The reactions w	ere performed	at S/C=1000 in	the presence of		
1,2-epoxyhexane of 2 mmol and TMSN <sub>3</sub> of 1 mmol at room temperature.					



Fig. S1 Raman spectrum of FDU-C.



Fig. S2 TG analysis of FDU-C.



Fig. S3 TEM images of (a) FDU-12 and (b) Cr(Salen)py@FDU-C (0.76 wt% of Cr)



**Fig. S4** Kinetic plots of the kinetic resolution of 1,2-epoxyhexane via asymmetric ring opening with  $TMSN_3$  over solid catalysts Cr(Salen)py@FDU-C with different content of Cr (a) 0.085 wt%, (b) 0.17 wt%, (c) 0.49 wt% and (d) 0.76 wt%.

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