

# Encapsulation of a chiral Mn<sup>III</sup>(salen) complex in ordered mesoporous silicas: an approach towards heterogenizing asymmetric epoxidation catalysts for non-functionalized alkenes

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**Abstract**—Two immobilized chiral Mn<sup>III</sup>(salen) complexes covalently anchored on modified MCM-41 (50 Å) and SBA-15 (75 Å) were prepared using 3-aminopropyltriethoxysilane as a reactive surface modifier to afford comparable or even higher enantioselectivity than homogeneous catalysts for the enantioselective epoxidation of a series of smaller to bulkier alkenes. The catalyst immobilized in silica with larger pore diameters was found to be more active. Compared to homogeneous catalysts, the heterogenized catalysts are more stable and can be recycled four times with retention of enantioselectivity.  
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## 1. Introduction

Homogeneous catalysts usually display higher activities and enantioselectivities than heterogeneous catalysts for enantioselective catalytic reactions. However, the product separation and catalyst recovery is difficult for homogeneous systems.<sup>1</sup> An immobilized enantioselective catalytic system is one of the most promising strategies to produce single optically active enantiomers due to easy separation and recycling of the catalyst.<sup>2</sup> One general way to transform a homogeneous catalytic reaction into heterogeneous process involves anchoring of active catalytic sites on a solid support by a linker group. Such immobilization of Mn<sup>III</sup>(salen) complexes also effectively prevents the formation of inactive dimeric or polymeric  $\mu$ -oxo intermediate species through isolation of the active metal sites.<sup>3</sup> Several papers have recently appeared on the immobilization of chiral Mn<sup>III</sup>(salen) complexes onto solid supports such as organic polymers<sup>4–6</sup> and inorganic solids of various porosity<sup>2b,7–12</sup> with moderate to excellent results

for epoxidation of non-functionalized alkenes. The solid chiral catalysts accommodated in the pores or cavities of the porous materials show differences in reactivity and enantioselectivity of the epoxidation reaction.<sup>2b,8,10</sup> It is, therefore, intuitive to graft the active metal complex onto solid supports of varied pore sizes to examine the influence of surface and pores on catalytic activity and enantioselectivity (confinement effect) of the Mn<sup>III</sup>(salen) complex without losing its merits. Mesoporous materials have received extensive attention due to their ordered pore structure, good thermal stability, large surface area and ease of modification by utilizing the available surface silanol groups for the anchoring of a homogeneous catalyst.<sup>13</sup> Herein, we have synthesized the siliceous MCM-41 and SBA-15 to immobilize the chiral Mn<sup>III</sup>(salen) complex **1** using 3-aminopropyltriethoxysilane (APTES) as a reactive surface modifier. The immobilized catalysts **1a** (complex **1** supported on MCM-41) and **1b** (complex **1** supported on SBA-15) lead to markedly higher ee for 4-chlorostyrene (69–71%) than the homogeneous complex **1** and other reported immobilized Mn<sup>III</sup>(salen) complexes<sup>8,14</sup> anchored on MCM-41. Furthermore, catalysts **1a** and **1b** epoxidized bulkier alkenes with high chiral induction (up to 96%) and the catalysts are reusable for up to four cycles.

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## 2. Results and discussion

### 2.1. Synthesis and characterization of catalysts

The preparation of immobilized catalysts, **1a** and **1b**, was carried out by covalent grafting of preformed, well characterized Mn<sup>III</sup>(salen) complex **1** onto APTES modified MCM-41 (pore diameter 50 Å) and SBA-15 (pore diameter 75 Å), respectively (Scheme 1). To make the catalytic environment of immobilized complexes **1a** and **1b** analogous to that of homogeneous system, the grafting of complex **1** was done through the 5th position of salen ligand **4**. The functionalization of calcined MCM-41 **5** and SBA-15 **5'** was performed by their interaction with APTES **6** in toluene under reflux condition. Functionalized MCM-41 **7** and SBA-15 **7'**, which were thus obtained, interacted with **1** to give the immobilized complexes **1a** and **1b**, respectively. The immobilized complexes were repeatedly extracted with CH<sub>2</sub>Cl<sub>2</sub> in order to ensure the elimination of any physically bounded Mn<sup>III</sup>(salen) complex from the silica matrix.

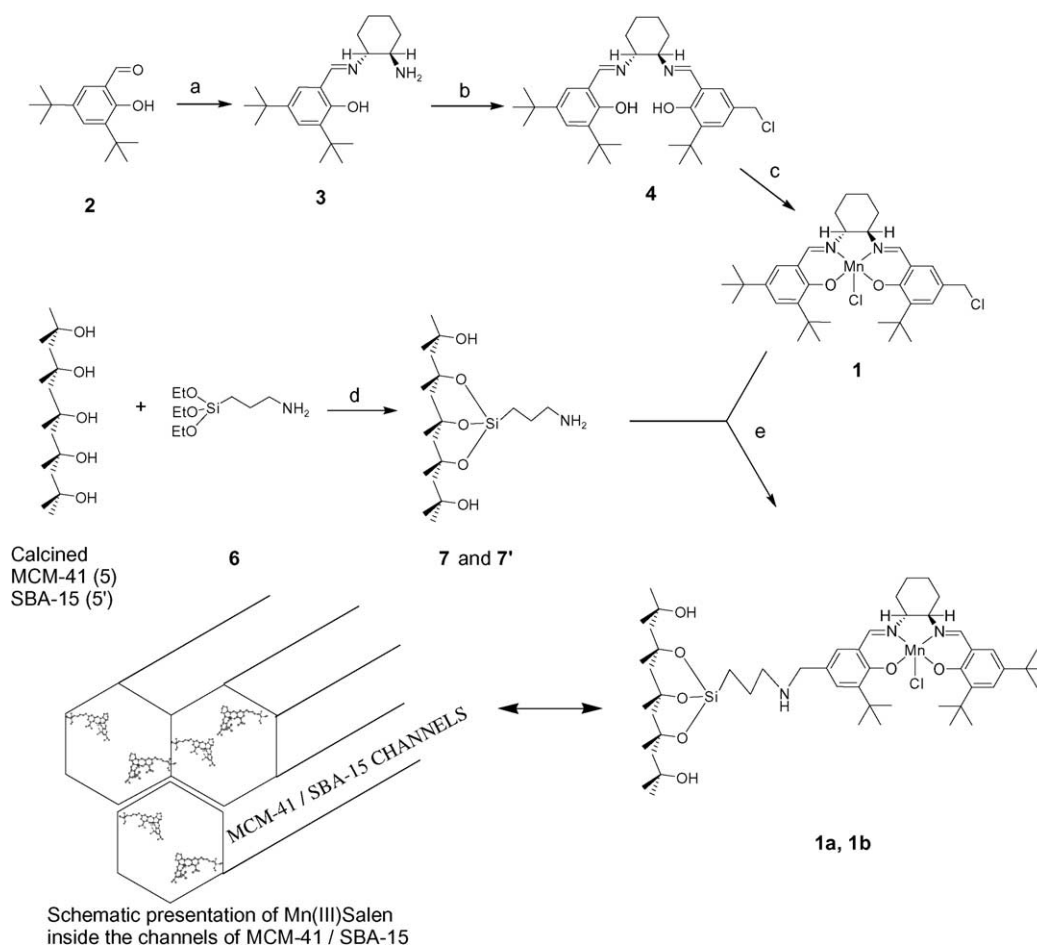
The immobilized catalysts **1a** and **1b** were characterized by FTIR, solid reflectance spectroscopy, microanalysis, inductive coupled plasma atomic emission (ICP), N<sub>2</sub>

adsorption–desorption isotherm, X-ray powder diffraction, SEM and TEM, which evidenced the effective complex immobilization with a catalyst loading in the range 23–25 mg/100 mg (data are given in the Experimental).

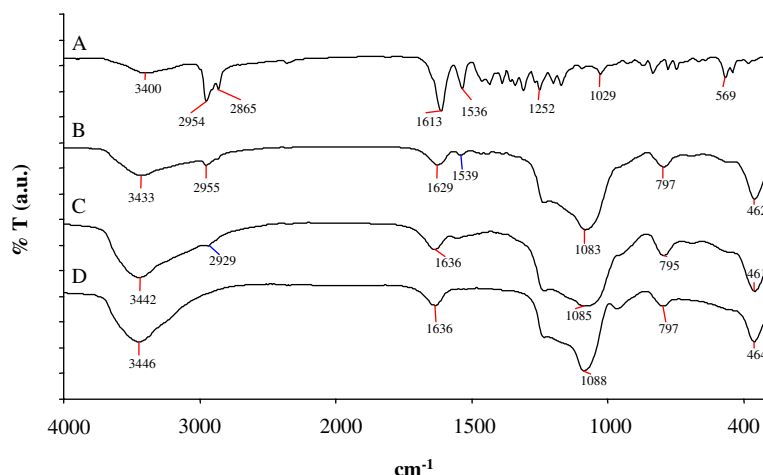
FTIR spectra of complexes **1a** and **1b** were in good agreement with the expected chemical structure of the organic moieties. In particular, the formation of the immobilized complexes **1a** and **1b** was confirmed by the presence of bands near 2954 and 1536 cm<sup>-1</sup> due to  $\nu(\text{CH}_2)$  of the propyl arm of the silylating agent and  $\nu(\text{H}-\text{C}=\text{N})$  of the azomethine group, respectively. These bands were absent in IR spectra of MCM-41 **5** and SBA-15 **5'** (Fig. 1).

Solid reflectance UV–vis spectra also supported the successful immobilization of the complexes as the characteristic charge transfer and d–d transition bands<sup>8</sup> near 425 and 520 nm of homogeneous Mn<sup>III</sup>(salen) complex **1** are present as broad bands for immobilized complexes **1a** and **1b** (Fig. 2). The virgin silica materials do not show any band in these regions.

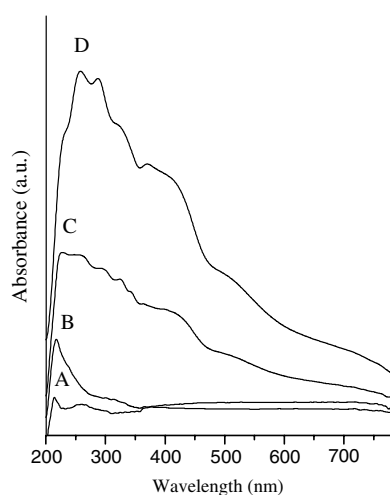
To further confirm that salen complex **1** was grafted on modified MCM-41 and SBA-15, complexes **1a** and **1b**



**Scheme 1.** The synthesis of immobilized catalyst on MCM-41 and SBA-15 (a) resolved (1*R*,2*R*)-diamino cyclohexane, CHCl<sub>3</sub>, 0 °C; (b) 5-chloromethyl *tert*-butyl-salicylaldehyde, dry MeOH, reflux, 24 h; (c) Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O, LiCl, dry EtOH, reflux, 12 h; (d) and (e) toluene, reflux, 24 h.



**Figure 1.** Representative IR spectra of calcined SBA-15 (D), aminopropyl modified SBA-15 (C), immobilized  $\text{Mn}^{\text{III}}(\text{salen})$  complex **1b** on surface modified SBA-15 (B),  $\text{Mn}^{\text{III}}(\text{salen})$  complex **1** (A).

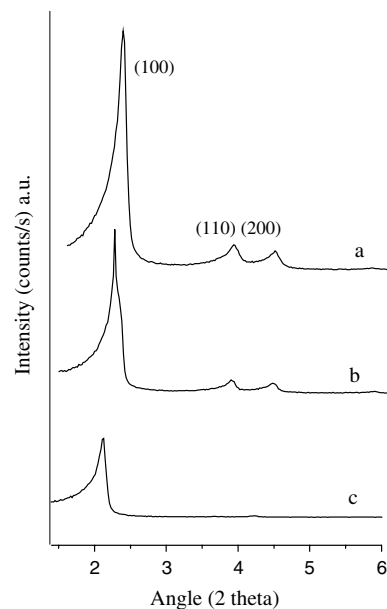


**Figure 2.** Solid reflectance UV-vis spectra of calcined MCM-41 (A), aminopropyl modified MCM-41 (B), immobilized  $\text{Mn}^{\text{III}}(\text{salen})$  complex **1a** (C),  $\text{Mn}^{\text{III}}(\text{salen})$  complex **1** (D).

were dissolved in HF solution and the resulting mass extracted with  $\text{CH}_2\text{Cl}_2$ . After complete removal of the solvent, the resulting brown mass was analyzed by UV-vis and IR spectroscopy, which showed the presence of  $\text{Mn}^{\text{III}}(\text{salen})$  complex **1**. These observations are consistent with that reported for the immobilization of salen on siliceous material.<sup>14</sup>

X-ray powdered diffraction patterns of MCM-41 and SBA-15 show three well-resolved peaks indexed to 100, 110 and 200 reflections (a) of hexagonal space group  $p6mm$ . The mesoporous structure of these supports remain undisturbed as the immobilized complexes **1a** and **1b** are bonded on their surface. This was confirmed by monitoring the X-ray diffraction at each step of immobilization (Fig. 3).

TEM images for calcined MCM-41 and SBA-15 showed two-dimensional hexagonal structures ( $p6mm$ )<sup>15</sup> that remained unaffected on immobilization of complex **1**



**Figure 3.** (a) Representative XRPD patterns of calcined MCM-41, (b) aminopropyl modified MCM-41, (c) immobilized complex **1a**.

thus confirming the retention of the physical structure of the siliceous material (Fig. 4).

The BET surface area, pore diameter, pore volume and microanalysis of calcined MCM-41, SBA-15 and immobilized complexes are given in Table 1 suggesting that complex **1** is present inside the pores of the support material.

## 2.2. Asymmetric catalytic epoxidation

Six representative non-functionalized alkenes 4-chlorostyrene, indene, 2,2-dimethylchromene, 6-cyano-2,2-dimethylchromene, spiro[cyclohexane-1,2'-[2H][1]chromene] and 6-methoxy-2,2-dimethylchromene were studied with these immobilized catalysts for asymmetric epoxidation. To compare the epoxidation capability of

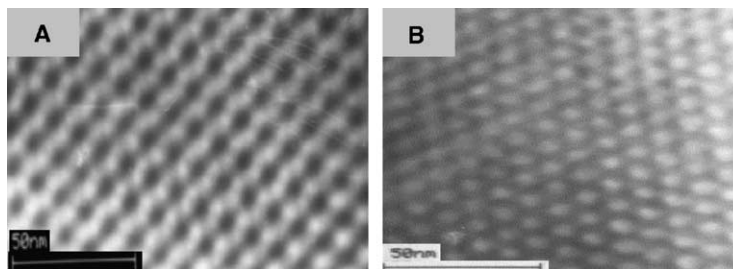


Figure 4. Representative TEM images of calcined SBA-15 (A) and complex **1b** (B).

Table 1. Physico-chemical characterization data of MCM-41, SBA-15, aminopropyl modified MCM-41 (**7**) and SBA-15 (**7'**) and immobilized complexes **1a**, **1b**

Compound	Mn loading/mg/100 mg	BJH pore diameter (Å)	Total pore volume (cm <sup>3</sup> /g)	BET surface area (m <sup>2</sup> /g)	C/N ratio
<b>1</b>	—	—	—	—	14.13
MCM-41	—	50.0	1.041	825	—
<b>7</b>	—	35.0	0.416	477	4.03
<b>1a</b>	23	19.0	0.129	332	10.2
SBA-15	—	75.0	1.229	743	—
<b>7'</b>	—	65.0	0.651	342	4.08
<b>1b</b>	25	52.0	0.401	245	10.10

the heterogeneous catalyst, complex **1** was used as a reference catalyst for the epoxidation of all the alkenes under homogeneous conditions. The asymmetric epoxidation of the alkenes were carried out with complexes **1**, **1a** and **1b** (5 mol % with respect to substrate) in dichloromethane at 0 °C using NaOCl as oxidant and the data summarized in Table 2. The immobilized catalysts **1a** and **1b** are active (yields; 90–99%) and enantioselective (ee, 69–96%). Complex **1** under homogeneous conditions also showed similar activity (yields; 94–100%) and enantioselectivity (ee; 46–98%) with these substrates, suggesting that the local environment around the active catalytic site is not unchanged on immobilization. Furthermore, compared to the homogeneous system (8 h), the time taken for the completion of the epoxidation reaction increases only marginally under the heterogeneous system (10 h), predictably due to slower diffusion<sup>2b</sup> of the reactant and the oxidant molecules into the mesopores of MCM-41 and SBA-15. Remarkably, when 4-chlorostyrene was used as a substrate with immobilized catalysts **1a** and **1b**, there was a significant improvement in enantioselectivity (ee, 69–71%; entries 2 and 3) over the homogeneous system (ee, 46%; entry 1). Similar results were obtained with MCM-41 supported chiral Mn<sup>III</sup> and Cr<sup>III</sup>(salen) complexes for the epoxidation of chlorostyrene,<sup>16</sup>  $\alpha$ -methylstyrene<sup>2b</sup> and *cis*- $\beta$ -methylstyrene.<sup>10b</sup> The increase in ee is mainly attributed to the unique spatial environment constituted by the chiral catalyst and mesopores of MCM-41 and SBA-15. MCM-41 and SBA-15 alone showed negligible catalytic activity towards the epoxidation of 4-chlorostyrene as the representative substrate (2%, entries 4 and 5) suggesting that the supported materials are not responsible for epoxidation reaction. In general, SBA-15 supported catalyst **1b**, where the pore size is larger, performed better than MCM-41 supported catalyst **1a**, as evident from their TOF values.

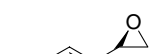
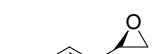
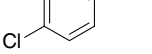
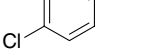
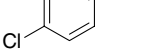
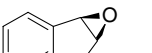
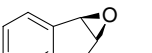
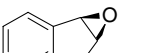
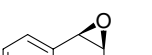
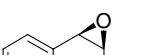
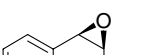
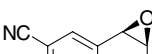
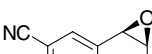
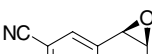
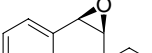
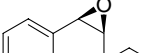
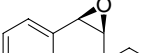
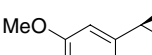
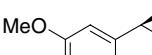
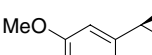
The solid catalysts were filtered, washed thoroughly with distilled water, methanol and CH<sub>2</sub>Cl<sub>2</sub> and then used for the next cycle. The aqueous and organic layers of the filtrate were tested for the presence of manganese by ICP. As there was no trace of manganese in the filtrate, it was concluded that Mn<sup>III</sup>(salen) is intact on the solid support and that no leaching took place during the epoxidation reaction.

Recycling experiments were conducted with recovered immobilized Mn<sup>III</sup>(salen) complexes **1a** and **1b** for the epoxidation of 2,2-dimethylchromene, as a representative substrate. The data are summarized in Table 3 and show only a marginal decrease in activity in subsequent epoxidation runs, however, the enantioselectivity remains unchanged. The characterization of the recycled catalyst (by FTIR spectra, XRPD and CHN analysis) also suggests partial degradation of the catalyst along with entrapment of some of the reactants within the mesopores that cause a gradual slow down of the epoxidation reaction in the successive recycle runs. These observations are in agreement with earlier reports based on immobilized Mn<sup>III</sup>(salen) system.<sup>8</sup>

### 3. Conclusion

Chiral Mn<sup>III</sup>(salen) complexes were immobilized onto mesoporous solids namely, MCM-41 and SBA-15, and used for the enantioselective epoxidation of various alkenes. The immobilized complexes are stable, recyclable and give comparable or even higher ees (e.g., 4-chlorostyrene) than homogeneous catalysts. The SBA-15 based catalyst, which had a larger pore diameter, was found to be more active than the MCM-41 based Mn<sup>III</sup>(salen) catalyst.

**Table 2.** Product yields, ee and TOF for enantioselective epoxidation<sup>a</sup> of non-functionalized alkenes catalyzed by **1**, **1a** and **1b**

Entry	Catalyst	Product	Yield (%) <sup>b</sup>	ee (%) <sup>c</sup>	TOF <sup>d</sup> × 10 <sup>-4</sup>	Config.
1	<b>1<sup>f</sup></b>		100	46	6.94	<i>R</i>
2	<b>1a</b>		98	69	5.44	<i>R</i>
3	<b>1b</b>		99	71	5.50	<i>R</i>
4	MCM-41		2 <sup>e</sup>	—	—	—
5	SBA-15		2 <sup>e</sup>	—	—	—
6	<b>1<sup>f</sup></b>		96	86	6.66	1 <i>R</i> ,2 <i>S</i>
7	<b>1a</b>		96	82	5.33	1 <i>R</i> ,2 <i>S</i>
8	<b>1b</b>		99	84	5.50	1 <i>R</i> ,2 <i>S</i>
9	<b>1<sup>f</sup></b>		99	98	6.87	3 <i>R</i> ,4 <i>R</i>
10	<b>1a</b>		98	94	6.80	3 <i>R</i> ,4 <i>R</i>
11	<b>1b</b>		99	96	5.50	3 <i>R</i> ,4 <i>R</i>
12	<b>1<sup>f</sup></b>		98	92	6.80	3 <i>R</i> ,4 <i>R</i>
13	<b>1a</b>		93	89	5.16	3 <i>R</i> ,4 <i>R</i>
14	<b>1b</b>		97	88	5.38	3 <i>R</i> ,4 <i>R</i>
15	<b>1<sup>f</sup></b>		94	82	6.52	3 <i>R</i> ,4 <i>R</i>
16	<b>1a</b>		90	78	5.00	3 <i>R</i> ,4 <i>R</i>
17	<b>1b</b>		92	77	5.11	3 <i>R</i> ,4 <i>R</i>
18	<b>1<sup>f</sup></b>		97	85	6.73	3 <i>R</i> ,4 <i>R</i>
19	<b>1a</b>		92	81	5.11	3 <i>R</i> ,4 <i>R</i>
20	<b>1b</b>		96	82	5.33	3 <i>R</i> ,4 <i>R</i>

<sup>a</sup> Reactions were performed in CH<sub>2</sub>Cl<sub>2</sub> (4 ml) with catalyst 0.05 mmol, substrate 1.00 mmol, NaOCl 2.75 mmol.

<sup>b</sup> Isolated yield.

<sup>c</sup> By <sup>1</sup>H NMR using chiral shift reagent (+)-Eu(hfc)<sub>3</sub>/chiral capillary column GTA type/chiral HPLC column OB, OD, OJ.

<sup>d</sup> Turn over frequency is calculated by the expression [product]/[catalyst] × time, s<sup>-1</sup>.

<sup>e</sup> Conversion, not isolated yield.

<sup>f</sup> Reaction time was 8 h under homogeneous reaction condition while it was 10 h with catalyst **1a** and **1b**.

**Table 3.** Recycling data for enantioselective epoxidation<sup>a</sup> of 2,2-dimethyl chromene as a representative substrate using immobilized catalysts **1a** and **1b**

Run	Catalyst	Yield (%)	ee <sup>b</sup>	TOF × 10 <sup>-4</sup>
1	<b>1a (1b)</b>	98 (99)	94 (96)	5.44 (5.50)
2	<b>1a (1b)</b>	95 (97)	94 (96)	5.27 (5.38)
3	<b>1a (1b)</b>	91 (93)	94 (96)	5.06 (5.17)
4	<b>1a (1b)</b>	91 (92)	94 (95)	5.06 (5.11)

<sup>a</sup> Reactions were performed in CH<sub>2</sub>Cl<sub>2</sub> (4 ml) with the recovered catalyst, substrate 1.00 mmol, NaOCl 2.75 mmol for 10 h.

<sup>b</sup> By chiral HPLC column, Chiralcel OD.

## 4. Experimental

### 4.1. General

(1*R*,2*R*)-Diaminocyclohexane was resolved from the technical grade *cis-trans* mixture (Aldrich). Indene (IND) and 4-chlorostyrene (4CSTR) were passed through a pad of neutral alumina before use. 2,2-Dimethylchromene (CR), 6-cyano-2,2-dimethylchromene (CNCR), 6-methoxy-2,2-dimethylchromene (MCR) and spiro[cyclohexane-1,2'-(2*H*)[1]chromene] (CYCR) were synthesized by reported procedures.<sup>17</sup> All the solvents used were purified by known methods.<sup>18</sup> MCM-41 was synthesized by using cetyl pyridinium chloride as a structure directing agent while for SBA-15 synthe-

sis, amphiphilic triblock copolymer P123 was used in the reported procedure.<sup>11</sup> Gas chromatography (Shimadzu GC 14B) was used for the determination of purity, time and conversions. Enantiomeric excesses of the resultant epoxides were determined by <sup>1</sup>H NMR using chiral shift reagent (+)-Eu(hfc)<sub>3</sub>, which were further confirmed by HPLC (Shimadzu SCL-10AVP) using a DAICEL Chiralcel columns OJ/OB for IND, OD for CR, CNCR, MCR, CYCR, 4CSTR and by GC using Astec GTA chiral column (30 m) for 4CSTR. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a 200 and 50 MHz spectrometer (Bruker, F113V). The IR spectra were recorded on a Perkin-Elmer Spectrum GX spectrophotometer in KBr/Nujol mull. Electronic spectra were recorded on a Varian UV-vis-NIR CARY 500 SCAN Spectrophotometer. Diffuse reflectance spectra were obtained from a UV-vis-NIR Scanning Spectrophotometer UV-3101 PC. Microanalysis was done on a Perkin-Elmer model 2400 CHNS analyzer. Inductive coupled plasma spectrometer (Perkin-Elmer Instrument, Optical Emission spectrometer, Optima 2000 DV) was used for Mn estimation. X-ray powder diffraction patterns of the samples were recorded on a Philips X'Pert MPD diffractometer. BET surface area was determined using N<sub>2</sub> sorption data measured at 77 K using volumetric adsorption set-up (Micromeritics ASAP-2010, USA). The pore diameter of the samples was determined from the Barret, Joyner and Halenda (BJH) method. TEM analysis was accomplished by



transmission electron microscope (TEM) Philips Tecnai 20. SEM analysis of the sample was done by scanning electron microscope model LEO 1430 VP.

#### 4.2. Preparation of 3-aminopropylsilyl-functionalized MCM-41 **7** and SBA-15 **7'**

A suspension of APTES (4.56 g, 20.63 mmol) and 10 g of calcined MCM-41/SBA-15 in 90 ml of toluene was heated at reflux with stirring under an inert atmosphere for 24 h. The resulting masses were cooled to 25–30 °C and filtered. The solids were filtered, washed successively with dry toluene, diethyl ether and dried under vacuum at ambient temperature. The dried material was subjected to Soxhlet extraction with dry dichloromethane for 24 h. Finally, solids **7** and **7'** were dried at 50–55 °C under vacuum for 8 h. The characterization was accomplished by microanalysis (Table 1), IR-, diffuse reflectance UV–vis. Spectroscopy, XRPD, nitrogen sorption studies. IR (KBr) for **7**: 461, 795, 1085, 1636, 2929, 3442 cm<sup>-1</sup>. Diffuse reflectance UV–vis: 240, 335 nm; IR (KBr) for **7'**: 460, 795, 1080, 1636, 2922, 3446 cm<sup>-1</sup>. Diffuse reflectance UV–vis: 270, 340, 375 nm.

#### 4.3. Synthesis of unsymmetrical Mn<sup>III</sup>(salen) complex **1**

Chiral catalyst **1** was obtained through the synthetic sequence given in Scheme 1 as follows: (1*R*,2*R*)-(–)-*N*-(2-hydroxy-3,5-di-*tert*-butylbenzaldehyde)-1-amino-2-cyclohexaneimine **3**<sup>19</sup> was condensed with 5-chloromethyl-3-*tert*-butylsalicylaldehyde<sup>20</sup> in dry methanol to form an unsymmetrical chiral salen based ligand **4**, which on complexation with Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O/LiCl gave complex **1**. Yield (80–82%), Anal. Calcd for C<sub>33</sub>H<sub>47</sub>ClN<sub>2</sub>O<sub>2</sub>: C, 73.54; H, 8.73; N, 5.20. Found: C, 73.48; H, 8.73; N, 5.17; IR (KBr) 3411, 2957, 2863, 1629, 1597, 1470, 1441, 1390, 1361, 1272, 1251, 1204, 1172, 1095, 1044,

878, 827, 712, 644, 590 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ ppm 1.23 (18H, s), 1.42 (9H, s), 1.47–2.10 (m, 8H), 3.30–3.48 (2H, m), 4.56 (s, 2H), 6.85 (d, 1H, *J* = 1.9 Hz), 7.05 (d, *J* = 2.0 Hz), 7.43 (d, 1H, *J* = 2.2 Hz), 7.52 (d, 1H, *J* = 2.2 Hz), 8.32 (1H, s), 8.44 (1H, s), 13.50 (br s, 1H), 14.48 (1H, br s); <sup>13</sup>C{<sup>1</sup>H}, δ ppm 24.2, 24.8, 26.2, 29.3, 29.6, 29.8, 33.9, 34.1, 35.2, 45.8, 72.3, 78.1, 116.8, 118.2, 122.4, 126.4, 127.4, 127.6, 136.2, 139.8, 157.9, 161.5, 164.8, 165.7; Complex **1** yield 90%; IR (KBr): 3400, 2954, 2865, 1613, 1536, 1252, 1029, 569 cm<sup>-1</sup>; UV–vis (CH<sub>2</sub>Cl<sub>2</sub>) 284, 416, 422, 399, 320, 284 nm; [α]<sub>D</sub><sup>30</sup> = +663 (c 0.04 g, 0.064 mmol/100 ml, CH<sub>2</sub>Cl<sub>2</sub>).

#### 4.4. Immobilization of unsymmetrical Mn<sup>III</sup>(salen) complex **1** on aminopropyl-functionalized MCM-41 **7** and SBA-15 **7'**

The unsymmetrical Mn<sup>III</sup>(salen) complex **1** (352.4 mg, 0.562 mmol) in dry toluene (10 ml) was refluxed with surface modified MCM-41/SBA-15 **7/7'** (1 g) for 48 h under an inert atmosphere. The immobilized catalyst **1a/1b** was filtered, washed thoroughly with dry toluene, diethyl ether and extracted repeatedly with methanol and dichloromethane on a Soxhlet extractor until the washings become colourless. All the washings were combined, the solvent evaporated and the residue dissolved in toluene (10 ml). The difference of the initial and final concentration was measured by UV–vis spectroscopy and gave the amount of complex covalently bonded on modified MCM-41 **7** and SBA-15 **7'**. The characterization of chiral Mn<sup>III</sup>(salen) catalysts **1a** and **1b** immobilized on MCM-41/SBA-15 was accomplished by microanalysis (Table 1). Complex **1a** yield 90%; IR (KBr): 3433, 2955, 1629, 1539, 1083, 797, 462 cm<sup>-1</sup>. Solid reflectance UV–vis 240, 335, 425, 520 nm. Complex **1b** yield 89%; IR (KBr) 3426, 2957, 1614, 1540, 1082, 801, 462 cm<sup>-1</sup>. Solid reflectance UV–vis

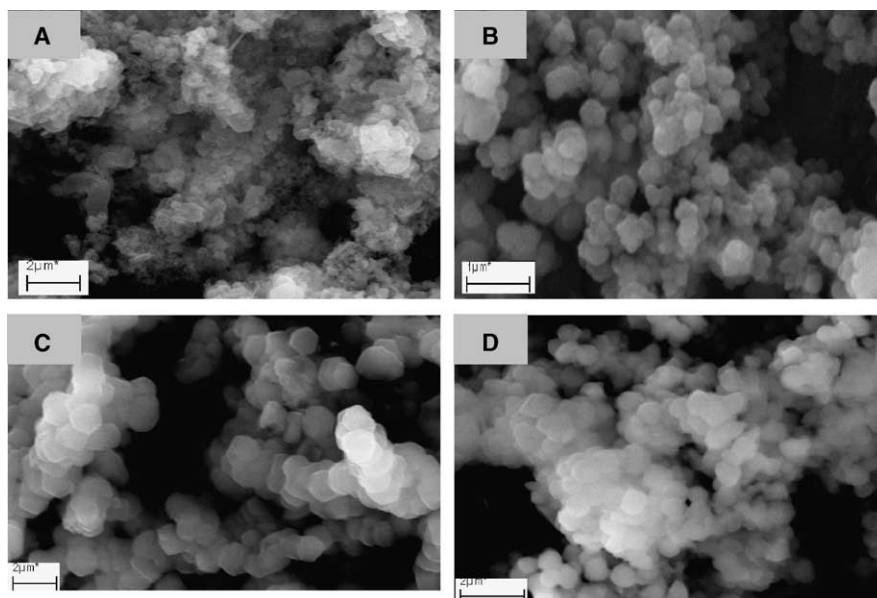
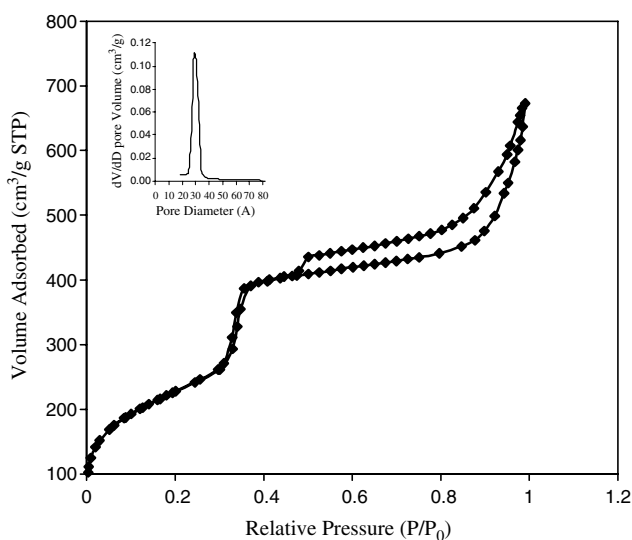


Figure 5. SEM micrograph of MCM-41 and SBA-15 samples (A) calcined MCM-41, (B) complex **1a**, (C) calcined SBA-15, (D) complex **1b**.

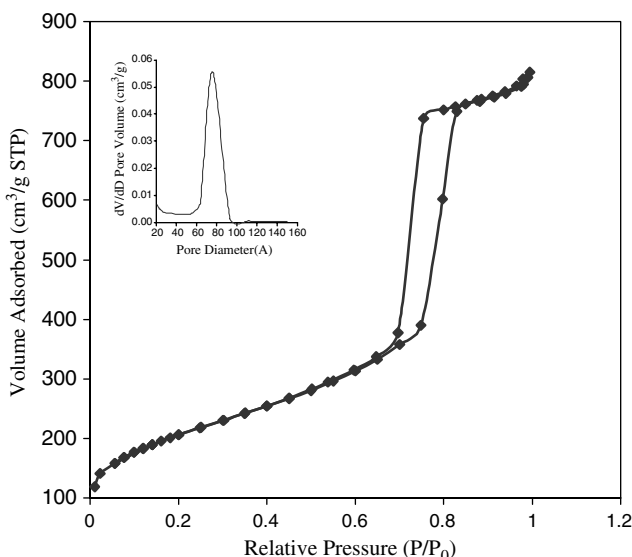
270, 340, 435, 510 nm. Solid reflectance spectroscopy (DRS), IR-, XRPD, ICP, SEM, TEM and N<sub>2</sub> sorption studies and data are shown in Figures 5–8.

#### 4.4.1. Enantioselective epoxidation of non-functionalized alkenes.

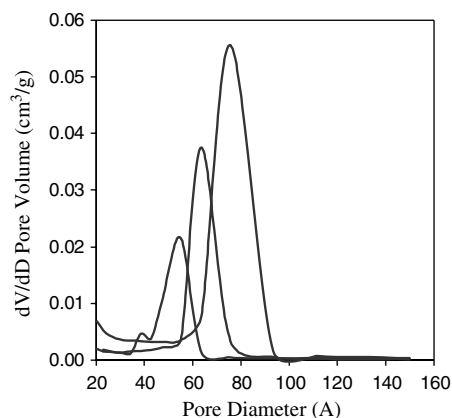
Enantioselective epoxidation reactions were carried out using the catalysts **1**, **1a** and **1b** (0.05 mmol) with 4-chlorostyrene, indene, 2,2-dimethylchromene, 6-cyano-2,2-dimethylchromene, 6-methoxy-2,2-dimethylchromene and spiro[cyclohexane-1,2'-[2H][1]chromene] (1 mmol) as substrates in 1/4 ml of dichloromethane with buffered NaOCl (2.75 mmol) (pH 11.5) as an oxidant under homogeneous/heterogeneous reaction condition. The addition of NaOCl was carried out in five equal portions at 0 °C. The epoxidation reaction was monitored by GC with *n*-tridecane (0.1 mmol) as the



**Figure 6.** N<sub>2</sub> adsorption–desorption isotherms and BJH pore size distribution curves of calcined MCM-41.



**Figure 7.** N<sub>2</sub> adsorption–desorption isotherms and BJH pore size distribution curves of calcined SBA-15.



**Figure 8.** N<sub>2</sub> adsorption pore diameter and relative pore volume of calcined SBA-15 (a), aminopropyl modified SBA-15 (b), immobilized complex **1b** (c).

GLC internal standard for product quantification. After completion of the reaction, the immobilized catalysts **1a** and **1b** were separated by centrifugation, washed thoroughly with water, methanol, dichloromethane and dried for re-use experiments.

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