

Dicationic chiral Mn(III) salen complex exchanged in the interlayers of montmorillonite clay: a heterogeneous enantioselective catalyst for epoxidation of nonfunctionalized alkenes

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Abstract

Dicationic chiral Mn^{III} salen complexes **1–4** were prepared from the reaction of 1*S*,2*S*-(+)-1,2-diaminocyclohexane/1*S*,2*S*-(–)-diphenyldiamine with 2-hydroxy-3-*t*-Bu-5-(triisooctylaminomethyl) benzaldehyde chloride/2-hydroxy-3-*t*-Bu-5-(triethylaminomethyl) benzaldehyde chloride and were exchanged in montmorillonite clay to give supported complexes **1'–4'**. Enantioselective epoxidation of styrene, indene, and 2,2-dimethyl-6-nitro chromene mediated by **1–4** complexes (0.4–2 mol%) as catalysts in the presence of pyridine *N*-O as axial base with NaOCl as an oxidant gave quantitative epoxide yield (> 99%) under biphasic homogeneous conditions. On employment of catalysts **1'–4'** under similar epoxidation condition, the epoxide selectivity in the case of styrene was found to be in the range 68–74%. However, there was a significant enhancement in ee (69–70%) compared to its homogeneous catalysts **1–4** (ee; 41–52%). Importantly, for the bulkier substrates like indene and chromene the selectivity were comparable both in homogeneous and heterogeneous system, probably due to the flexible T–O–T layers of clay allowing greater accessibility to the Mn^{III} salen residing between the layers of clay. Further, the catalyst **1'–4'** could be recovered easily and recycled efficiently several times by a simple separation method.

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1. Introduction

There is considerable commercial interest in the immobilization of catalysts on solid supports, since the active materials thus prepared are very easy to handle, retrieve, and recycle compared to their homogeneous counterpart [1]. Mn^{III} salen complexes have proven activity and selectivity for enantioselective epoxidation of nonfunctionalized alkenes under homogeneous conditions [2–5]. Various immobilization strategies for Mn^{III} salen complexes involving multistep surface modification of the support and its binding with the catalytically active complex are reported in the literature [6–9]. These methods include covalent and coordinated covalent binding to organic polymers [6,7], ion exchange resins [10], polymeric membranes [11], mesoporous silica [12], molecular sieves [13,14], layered double hydrox-

ides [15,16], ion exchange into the intracrystalline space of zeolite Y, AlMCM-41 [17,18], and encapsulation in zeolite using ship-in-a-bottle methodology [19]. Although immobilization has sometimes shown increases in the activity of homogeneous catalysts [20,21], it is often accompanied by a decrease in enantioselectivity, which is a problem commonly encountered with heterogenization of homogeneous asymmetric catalyst. Nevertheless a beneficial effect of support on enantioselectivity has also been reported [22].

Clays, due to their large surface area and cation exchange capacity, have considerable potential as catalytic materials for various type of reactions, such as acid catalysis [23,24], hydrogenation [17], dihydroxylation [15,16], and Heck reaction [25]. Montmorillonite types of clay, due to their lamellar structure, can be utilized to support suitably tailored complexes by ion-exchange mechanisms [26,27]. In the present study, we are reporting synthesis of Mn^{III} salen complexes in dicationic form and their immobilization between the layers of the montmorillonite type of clay by a simple cation

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exchange process. These supported complexes **1'–4'**, when used as catalysts for the epoxidation of styrene, showed a significant enhancement in enantiomeric excess (ee) for styrene epoxide (69–70%) compared to that obtained in homogeneous systems (41–52%). Further, complexes **1'–4'** worked well even for bulkier alkenes such as indene and 6-nitro-2,2-dimethylchromene vis-à-vis other solid supports such as MCM-41 containing Mn^{III} salen complex, which failed to epoxidize bulkier and nonplanar substrates [12].

2. Experimental methods

All the solvents used were purified by known procedures [28]. Indene and styrene were passed through a pad of neutral alumina before use. Montmorillonite-type clay used was from the Rajasthan region of India and was upgraded and activated at 120 °C prior to use, with cation exchange capacity 83 meq/100 g. 2,2-Dimethyl-6-nitrochromene was synthesized by a reported method [29]. The purity of the solvent, alkenes, and analysis of the products epoxide was determined by gas chromatography (GC) using a Shimadzu GC 14B having a stainless-steel column (2 m long, 3 mm i.d., 4 mm o.d.) packed with 5% SE30 (mesh size 60–80) and FID detector. For styrene and indene, column temperature was programmed between 70 and 150 °C, while for chromene it was held at 150 °C isothermal. Nitrogen was used as carrier gas (30 ml/min) at injection temperature 200 °C. A synthetic standard of the product was used to determine yields by comparison of peak height and area. The ee for styrene oxide was determined by GC chiral capillary column GTA. For chromene and indene epoxides, ee were determined by ¹H NMR using the chiral shift reagent Eu(hfc)₃, as well as HPLC (Shimadzu SCL-10AVP) using Chiralcel column OJ/OB.

¹H NMR spectra were recorded in CDCl₃ (Bruker F113V 200 MHz). The IR spectra were recorded on a Perkin–Elmer Spectrum GX spectrophotometer in a KBr/nujol mull. Electronic spectra were recorded in dichloromethane on a Hewlett–Packard diode array spectrophotometer Model 8452A. Microanalysis of the complex was done on a CHNS analyzer, Perkin–Elmer model 2400. Molar conductance

was measured at room temperature on a Digisun Electronic DI909 conductivity bridge. The optical rotation was measured in dichloromethane on a Atago, Japan polarimeter. A Perkin–Elmer inductively coupled plasma spectrometer (ICP), Model ICP Optima 3300 RL, was used for Mn estimation. Powdered X-ray diffraction patterns of the samples were recorded in a Philips X'pert MPD diffractometer using Cu-K_α (40 kV, 40 mA) radiation with step size and step time of curved Cu-K_α monochromator under identical conditions. BET surface area was calculated using N₂ adsorption data at 77 K. The pore diameters of the samples were determined using the adsorption as well as the desorption branch of the isotherm employing the Barret, Joyner, and Halenda (BJH) method.

2.1. Synthesis of metal complex catalysts

2.1.1. Synthesis of QATBS-1 and QATBS-2

Complexes **1–4** and their precursors were synthesized as follows: Trialkylamine (2 mmol) in 20 ml dry benzene was added dropwise to a stirred solution of **CMTBS** (2 mmol, 20 ml) in dry benzene. The resulting hazy solution was allowed to stir or reflux for 27 or 36 h for **QATBS-1** or **QATBS-2**, respectively. After the completion of the reaction the solvent was removed to yield the respective quaternary aldehyde. The products were characterized by microanalysis, IR, and ¹H NMR. The data are given as supplementary material.

2.1.2. Synthesis of chiral Schiff base ligand **5–8**

To an ethanolic solution of **QATBS-1/QATBS-2** (2 mmol, 2 equivalent, 10 ml) was added an ethanolic solution of (1*S*,2*S*)-(+)-1,2-diaminocyclohexane/(1*S*,2*S*)-(–)-diphenyldiaminoethane (1 mmol, 1 equivalent, 10 ml) and the resulting mixture was allowed to reflux for 7–8 h. The progress of the reaction was monitored on TLC. The solvent was partially removed under reduced pressure on a rotary evaporator and the yellow product of **5–8** was precipitated by hexane. The analytical data for these ligands are given in Table 1. ¹H NMR data are supplied as supplemental material.

Table 1
Physicochemical characterisation data of the complexes **1–4** and **1'–4'**

Compound	M.P. (°C)	Yield (%)	[α] _D ²⁷ (MeOH)	Mn loading (mmol/g)	BJH pore diameter (Å)	Total pore volume (cc m ³ /g)	BET surface area (m ² /g)	Microanalysis, found (calcd) (%)		
								C	H	N
1	218	90	−105.41 (<i>c</i> = 0.28)	–	–	–	–	72.44 (72.50)	9.94 (9.98)	3.89 (3.93)
2	210	91	+81.36 (<i>c</i> = 0.24)	–	–	–	–	70.56 (70.62)	10.49 (10.56)	4.20 (4.23)
3	204	92	−106.89 (<i>c</i> = 0.18)	–	–	–	–	69.35 (69.40)	8.04 (8.10)	6.42 (6.48)
4	235	88	+59.56 (<i>c</i> = 0.16)	–	–	–	–	61.30 (61.35)	8.22 (8.28)	6.80 (6.82)
1'	–	–	–	0.017	94	0.106	87	2.54	1.76	0.13
2'	–	–	–	0.022	91	0.102	66	2.37	1.72	0.14
3'	–	–	–	0.015	367	0.021	7	2.26	0.98	0.24
4'	–	–	–	0.020	90	0.095	72	2.43	0.85	0.26

2.1.3. Synthesis of chiral Mn(III) Schiff base complexes 1–4

An ethanolic solution of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (4 mmol, 10 ml) was added to a solution of **5–8** (2 mmol, 25 ml) in absolute ethanol under N_2 . The resulting brown mixture was refluxed for 7–8 h, cooled to room temperature, followed by addition of solid LiCl (6 mmol), and stirred for an additional 4 h, while the reaction mixture was exposed to air. The resulting mass was filtered and the solvent was removed from the filtrate on a rota evaporator. The resulting residue was extracted with dichloromethane (100 ml) and the organic phase was washed with water and dried over anhydrous Na_2SO_4 . The drying agent was removed by filtration and the solution was concentrated to yield the desired complex which was precipitated by the addition of hexane. The % yield, m.p., CHN analysis, and optical rotation, are given in Table 1. Molar conductance, configuration, UV/vis, and IR spectroscopic data are given as supplemental material.

2.1.4. Synthesis of the supported catalysts 1'–4'

An ethanolic 100-ml solution of the complexes **1–4** (0.004 mmol) was stirred for 48 h with preactivated clay (4 g). The loaded samples **1'–4'** were centrifuged, washed thoroughly, and extracted repeatedly with ethanol and CH_2Cl_2 on Soxhlet extractor till the washing become colorless. All the washings were combined and solvent was evaporated till the solution attained the original volume. The difference of initial and final concentrations as measured by UV–vis spectroscopy gave the amount of complex loaded into the interlayer of the clay. The characterization of the samples, **1'–4'**, was done by microanalysis, ICP, pore size determination, total pore diameter, BET surface area (Table 1), XRD, and IR- and diffuse reflectance UV spectroscopy. The data are given as supplemental material.

2.2. Enantioselective epoxidation of nonfunctionalized alkenes under homogeneous and heterogeneous conditions

In a typical enantioselective epoxidation run 2 mol% of the complex **1–4/1'–4'** was used as catalyst with 6-nitro-2,2-dimethylchromene, styrene, and indene (1.29 mmol) as substrate in 1 ml/5 ml of dichloromethane in the presence of pyridine *N*-oxide (PyN-O) (0.13 mmol) using NaOCl (2.75 mmol, added in four equal portions) as an oxidant at 0 °C under homogeneous/heterogeneous conditions. The progress of the epoxidation reaction was monitored on GC with *n*-tridecane (0.1 mmol) as GLC internal standard for product quantification. In the case of a homogeneous reaction, after completion of the reaction the solvent was removed and the product was separated by a short column of silica gel (60–120 mesh) using hexane:dichloromethane as eluent. For clay-immobilized catalysts the reaction mixture was centrifuged to isolate the product.

3. Results and discussion

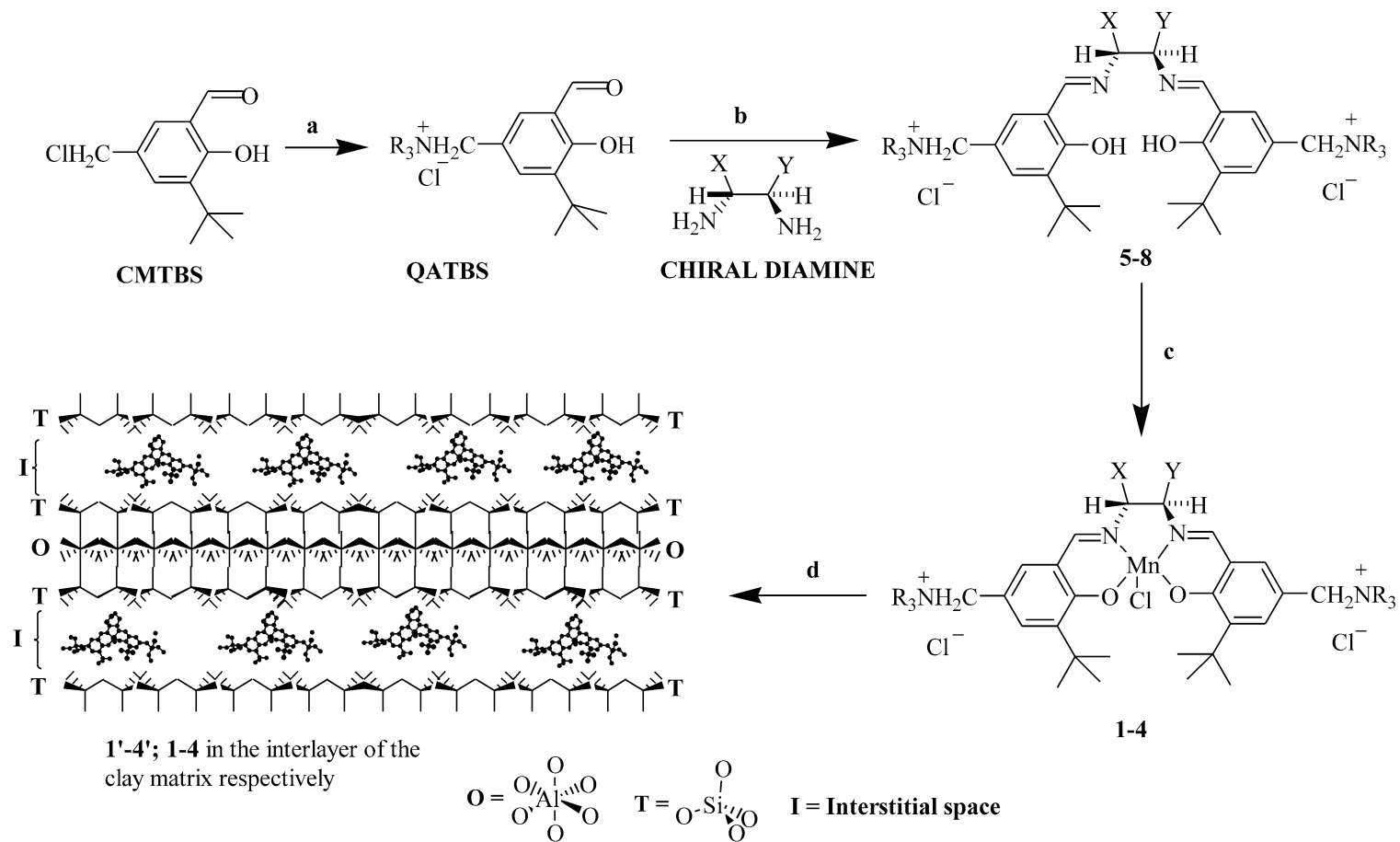
Complexes **1–4** and their respective clay-supported complexes **1'–4'** were prepared by the synthetic strategy shown in Scheme 1. Consequently, 3-*t*-Bu-5-(chloromethyl)-2-hydroxybenzaldehyde **CMTBS** was prepared from 3-*t*-Bu-2-hydroxy benzaldehyde by the reported method [30]. **CMTBS**, on interaction with an appropriate tertiary amine, viz., triisooctylamine, triethylamine, yielded the quaternary ammonium salt of salicylaldehyde, **QATBS-1** and **QATBS-2**. Condensation of appropriate **QATB-S** with diamine, viz., (+)-(1*S*,2*S*)-1,2-diaminocyclohexane/(–)-(1*S*,2*S*)-1,2-diphenyl 1,2-diaminoethane in a 2:1 molar ratio, gave the chiral salen ligands **5–8**, which were then complexed with manganese to give the chiral complexes **1–4**. These complexes were exchanged with a montmorillonite type of clay to give the complexes **1'–4'**.

The characterization of the clay-exchanged complexes **1'–4'** was done by comparing their spectroscopic features with those of the nonsupported complexes **1–4**. The loading of the complexes corresponds to 0.016–0.022 mmol/g of clay as determined by spectrophotometry and ICP. The C/N ratio was in good agreement with the theoretical value and data are given as supplementary materials. The diffuse reflectance UV spectra of the solid supported complexes **1'–4'** were similar to those of the complexes **1–4** in EtOH with a shoulder near 430–439 nm.

Representative IR spectra of the complexes **4** and **4'** and clay itself are shown in Fig. 1. The presence of IR bands at 2962 and 2865 cm^{-1} ($\text{C}_{\text{aliph}}\text{-H}$) and a broad but pronounced band in the range 1750–1550 cm^{-1} in complex **4'** indicate the presence of complex **4** in the clay matrix.

The XRD diffractogram of clay and clay-supported complexes **1'–4'** indicates that clay structure is retained during loading of the metal complex.

Pore diameter calculated from N_2 adsorption data shows an increase of 13–17 Å in **1'**, **2'**, and **4'** on exchange of the metal complexes with clay (Table 1). This increase in basal spacing of the clay is due to the exchange of the Mn^{III} salen into the interlayer space between T–O–T layers. However, in complex **3'** there is an abrupt increase in pore diameter. BET surface area calculated using adsorption data in the pressure range 0.0–0.21 shows a decrease of 16–37 m^2/g on impregnation of catalysts in the interlayer of clay (Table 1). The same decrease was also seen in the total pore volume of the sample estimated on the basis of the amount of N_2 adsorbed at a relative pressure of about 1. However, a sharp decrease in BET surface area and pore volume is seen when complex **3'** is loaded in clay (Table 1). This may be due to the rigid placement of the complex **3'** in the interlayer of clay at a temperature of 77 K, at which nitrogen adsorption is measured and kinetics of adsorption is substantially reduced due to the blocking of the pore. However, at a reaction temperature of 0 °C, the complex **3'** (Table 2) is in a more flexible position and allows reactant and product to diffuse through the interlayer of clay and interact with active reaction sites.



1 and 5; X = Y = Ph, R = *isooctyl*; **2 and 6** = X---Y = $-(\text{CH}_2)_4-$, R = *isooctyl* **3** and **7;** X = Y = Ph, R = ethyl, **4 and 8;** X = Y = $-(\text{CH}_2)_4-$, R = ethyl,

Scheme 1. *Reagents and conditions:* (a) triisooctylamine/triethylamine, benzene, reflux, 6 h, 95–97%; (b) (1*S*,2*S*)-(–)-1,2-diphenyldiamine, (1*S*,2*S*)-(+)-1,2-diaminocyclohexane abs. EtOH, reflux, 7–8 h, 90–94%; (c) (1) $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, EtOH, N_2 , reflux, 7–8 h (2) LiCl, rt, 4 h, 88–92%; (d) EtOH, stirred, 48 h, rt.

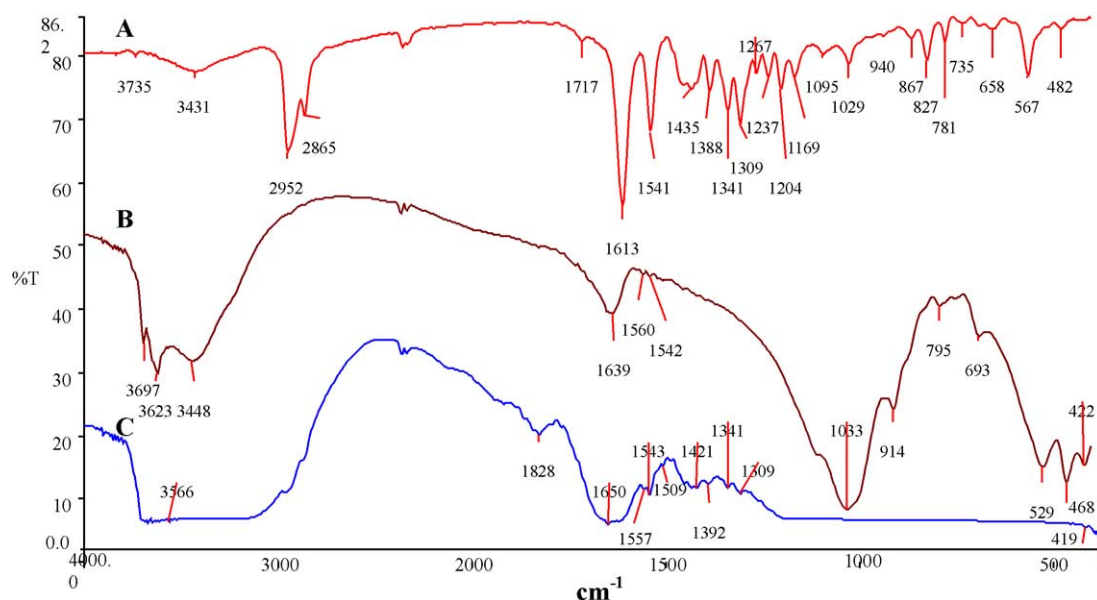


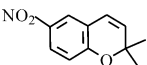


Fig. 1. IR spectra: (A) complex **4**; (B) montmorillonite clay; (C) complex **4'**.

Table 2

Product yields, Ees, and TOF for enantioselective epoxidation^a of nonfunctionalized alkenes catalyzed by **1–4** and **1'–4'**

Entry	Catalyst	Substrate	Time (h)	Yield (%) ^b	ee (%) ^c	TOF ^j × 10 ⁻³	
1 (2)	1 (1')		4.0 (7.0)	> 99 (70)	45 (70) ^d	3.55 (1.41)	
3 (4)	2 (2')		4.5 (8.0)	99 (72)	44 (69) ^d	3.13 (1.29)	
5 (6)	3 (3')		4.0 (24)	> 99 (68)	52 (70) ^d	3.55 (0.41)	
7 (8)	4 (4')		4.5 (24)	> 99 (74)	> 41 (69) ^d	3.13 (0.60)	
(9)	(clay) ^e		24	3	–	–	
(10)	(1') ^f		12	16	16	–	
(11)	(1') ^g		12	70	70	0.82	
12 (13)	1 (1')			4.0 (10)	> 99 (99)	68 (65) ^h	3.55 (1.37)
14 (15)	2 (2')			5.0 (9.0)	> 99 (99)	67 (62) ^h	2.82 (1.56)
16 (17)	3 (3')			4.0 (7.0)	98 (99)	59 (50) ^h	3.50 (2.02)
18 (19)	4 (4')			4.0 (10)	99 (99)	72 (69) ^h	3.55 (1.41)
20 (21)	1 (1')		0.5 (8)	99 (99)	> 99 (89) ⁱ	28.66 (1.77)	
22 (23)	2 (2')		4.5 (9)	99 (99)	> 99 (99) ⁱ	3.13 (1.56)	
24 (25)	3 (3')		5.5 (12)	99 (99)	84 (90) ⁱ	2.59 (1.17)	
26 (27)	4 (4')		5.0 (8.0)	99 (99)	89 (91) ⁱ	2.82 (1.77)	

Results in parentheses are for the heterogeneous system.

^a Reactions were performed in CH₂Cl₂ (1 ml/5 ml) with catalyst 2 mol%, substrate 1.29 mmol, pyridine *N*-oxide 0.13 mmol, NaOCl 2.75 mmol.

^b Isolated epoxide.

^c By ¹H NMR using chiral shift reagent (+)Eu(hfc)₃/chiral capillary column GTA type/chiral HPLC column OJ,OB.

^d Epoxide configuration *S*.

^e Clay without Mn^{III} salen.

^f Catalytic run without py*N*-O.

^g Catalyst loading 0.4 mol%.

^h Epoxide configuration *1S,2R*.

ⁱ Epoxide configuration *3S,4S*.

^j Turnover frequency is calculated by the expression [product]/[catalyst] × time s⁻¹.

The catalytic activity of the complexes **1–4** and **1'–4'** was determined for enantioselective epoxidation of styrene, indene, and 2,2-dimethyl-6-nitrochromene in the presence of Py*N*-O using NaOCl as oxidant. Product yields, ee, and turnover frequency are presented in Table 2. Excellent yields

(> 99%) were obtained with all alkenes under homogeneous and heterogeneous conditions except for styrene (68–74%) (entries 2, 4, 6, and 8) with these complexes and reactions are remarkably faster in the case of a homogeneous system (0.5–5.5 h) than in a heterogeneous system (7–24 h) (entries

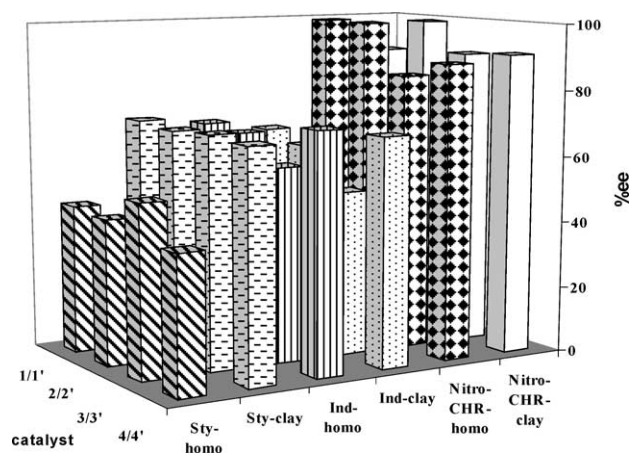


Fig. 2. 3D view showing the %ee of alkene oxides obtained with catalysts 1–4 and 1'–4'.

given in parentheses). This may be due to the slow diffusion of the reactant to the active catalytic sites in the confined media of a solid matrix [12]. Nevertheless, the ee obtained with styrene is remarkably higher (69–70%) (entries 2, 4, 6, 8) in the case of a heterogeneous system than in that of a homogeneous system (entries 1, 2, 3, 4), and this increase in ee is mainly attributed to the unique spatial environment of the complex in a confined medium. The similar increase in ee for α -methylstyrene (from 56 to 72%) was also reported earlier for an Mn^{III} salen complex immobilized on MCM-41 [20]. Further, Mn^{III} salen complex on other inorganic solid support were found to be inactive for bulkier or nonplanar substrates such as 1-phenylcyclohexene [12], but the complexes 1'–4' were active and enantioselective for the bulkier substrates like indene (entries 13, 15, 17, 19) and 2,2-dimethyl-6-nitrochromene (entries 21, 23, 25, 27) (Fig. 2). This is probably due to the flexible T–O–T layers of the clay, which adjust to allow even the bulkier substrate to diffuse in the clay interlayer space. The comparative results of catalysts 1–4 under the homogeneous system and 1'–4' with immobilized catalysts show that the transition states in both cases are similar.

A control reaction with the unloaded clay carried out under identical condition (entry 9) with styrene as substrate gave 2–3% styrene oxide in 24 h, indicating that clay alone is not responsible for the epoxidation. Further, in the absence of pyridine *N*-oxide (entry 10), the catalyst 1' took 12 h to epoxidize styrene (yield, 16%; ee, 16%), suggesting that the presence of PyN–O is essential for both catalyst stability and selectivity. The role of PyN–O as an axial base has been established earlier by other authors [31] and by us [30] and is reported to facilitate the formation of catalytically active $Mn=O$ species during the catalytic cycle while favoring the enantioselectivity. A minimum of 0.4% of the catalyst 1' is required for the epoxidation of styrene (conversion 70%) in 12 h with no loss of enantioselection (entry 11). A further reduction in catalyst-to-substrate ratio reduces the efficiency and selectivity of the reaction drastically.

Table 3

Data for enantioselective epoxidation of styrene for recycling of the catalyst 1'

Run	Entry	Time (h)	Conversion (%)	ee (%)	Configuration
1	28	7	70	70	<i>S</i>
2	29	9	69	70	<i>S</i>
3	30	12	68	69	<i>S</i>
4	31	16	69	70	<i>S</i>

The catalyst 1' was recycled four times (entries 29–31) for the epoxidation of styrene and results are presented in Table 3. It is evident from the results that the reaction time to achieve complete conversion is increased in subsequent cycles; however, no loss in enantioselectivity was observed for at least four cycles. The recycling ability and spectroscopic characterization of recycled catalyst confirmed our conviction that the dicationic complex 1' is strongly held within the negatively charged layer of clay and does not leach out during the epoxidation reaction.

In order to characterize the recycled catalyst 1' (after one cycle), FTIR spectra, XRD, and CHN analysis were done for the recovered complex after one catalytic run, which suggests the partial degradation of the complex and the entrapment of reactant in the pores of clay matrix. These observations are in consonance with earlier reports on immobilized systems [32]. As far as the configuration of the product epoxide is concerned, the *S* form of the catalyst resulted in the formation of the *S* form of the product in excess.

4. Conclusion

Efficient immobilized dicationic chiral Mn^{III} salen complexes were developed by an exchange process in the interlayer of a montmorillonite type of clay and were used for enantioselective epoxidation of styrene, indene, and 6-nitro-2,2-dimethyl chromene. Excellent conversions and epoxide selectivity (> 99%) were obtained with all alkenes except for styrene. However, in the case of styrene, significantly higher ee (69–70%) in the product epoxide was obtained with supported catalyst. The significant enhancement in ee of styrene oxide compared to its homogeneous counterpart was attributed to the unique spatial environment of the confined medium. Further, due to flexible T–O–T layers of clay, the supported catalysts were active and selective even for the bulkier substrates such as indene and nitrochromene.

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