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Catalytic asymmetric epoxidation of non-functionalised alkenes using polymeric Mn(III) Salen as catalysts and NaOCl as oxidant

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Abstract

Polymeric chiral Mn(III) Salen complexes **1a**, **1b** were synthesised by the interaction of 1*S*,2*S*-(+)-l,2-diaminocyclohexane, 1*R*,2*R*-(+)-l,2-diphenyl ethylenediamine with 5,5′-methylene-di-3-*tert*-butylsalicylaldehyde. Number of repetitive units and molecular weight of the polymeric ligands were found to be between 10 and 12 and $M_n = \sim 5200$ and ~ 5400, respectively by VPO. Enantioselective epoxidation of chromenes, indene and styrene mediated by complexes **1a** and **1b** (2 mol%) as catalyst using NaOCl as an oxidant gave >99% epoxide yields except for cyclochromene where the yield is in the range of 50–61% in 2.5–12 h. The enantiomeric excess (ee) for the product epoxide was found to be in the range of 75 to >99%, except for styrene (ee, 32–56%). The catalysts were easily recovered by precipitation and were re-used up to five times with some loss of activity while there was no loss of enantioselectivity in the product epoxide. The effect of axial bases, oxidants and phase transfer reagents on activity and enantioselectivity of the catalytic system was also studied.

Keywords: Polymeric; Mn(III) Salen; Enantioselective; Epoxidation; Non-functionalised alkenes

1. Introduction

To obtain high chiral induction in the synthesis of chiral building blocks for pharmaceutical and fine chemicals, the designing of a chiral catalyst and its reusability is of utmost important [1–3]. Chiral Mn (III) Salen complexes have been reported to give high enantioselectivity in the epoxidation of *cis* and cyclic alkenes in presence of 4-phenyl pyridine N-oxide (4-PhPyNO) using NaOCl as oxidant under homogeneous biphasic reaction condition [4–7] but separation and recycling of the catalyst is problematic. Attempts were made to develop supported Mn(III) Salen complexes using organic polymer [8,9], polymeric membrane [10] encapsulation in zeolite [11] and inorganic supported catalyst [12–14] so as to minimise the degradation of the catalyst, allowing easy recovery and re-usability of the catalyst for a number of cycles. We have earlier reported recyclable dimeric catalyst [15–17] by means of simultaneous increase in the molecular weight and active sites in the catalyst. These catalysts showed lower solubility in non-polar solvents and could be easily recovered from catalytic reaction mixture by precipitation and could be used in subsequent catalytic runs. Herein, we report polymeric chiral Mn(III) Salen complexes **1a** and **1b** derived from 1*S*,2*S*-(+)-1,2-diaminocyclohexane, 1*R*,2*R*-(+)-l,2-diphenyl ethylenediamine with 5,5′-methylene di-3-*tert*-butylsalicylaldehyde. These complexes were used as catalyst for the enantioselective epoxidation of styrene, indene and chromenes in presence of pyridine-N-oxide (PyNO) as an axial base and NaOCl as oxidant and were recycled several times.

2. Experimental

2.1. Materials and methods

Manganese acetate from s.d. Fine Chemical, indene and styrene were passed through a pad of neutral alumina before use. 2,2-Dimethylchromene and its substituted derivatives were synthesised by known method [18]. All the solvents were purified by reported method [19].

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Microanalysis of the ligands and metal complexes was carried out on Perkin-Elmer CHN Analyzer 2400. ^{1}H NMR spectra were recorded in $CDCl_3$ (Bruker F113V 200 MHz). FTIR spectra were recorded on Perkin-Elmer Spectrum GX spectrophotometer in KBr/nujol mull. Electronic spectra were recorded in dichloromethane on Hewlett-Packard Diode Array spectrophotometer Model 8452A. Molar conductance was measured at room temperature on Digisun Electronic Conductivity Bridge DI-909. The optical rotation was measured in dichloromethane on Polarimeter Atago, Japan. CD spectra were recorded on Jasco machine J-720. Melting points were determined with capillary apparatus and are unconnected.

The purity of solvents, alkenes and analysis of the products epoxide was determined by gas chromatography (GC) using 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. Ultrapure nitrogen was used as carrier gas with flow rate 30 ml/min and injection port temperature was kept at 200 °C. For styrene and indene, column temperature was programmed between 70 and 150 °C while for chromene it was held at 150 °C isothermal. Synthetic standard of the product was used to determine yields by comparison of peak height and area. Ee for styrene oxide was determined by GC chiral capillary column GTA. For chromenes and indene epoxides, ee were determined by ^{1}H NMR using chiral shift reagent Eu(hfc)$_3$, as well as HPLC (Shimadzu SCL-10AVP) using Chiralcel column OD, OJ/OB.

Synthesis of 5,5′-methylene-di-3-*tert*-butylsalicylaldehyde **2** was carried out by the procedure reported earlier [16].

*2.2. Synthesis of poly[(S,S)-N,N′-bis-{3-(1,1-dimethylethyl)-5-methylene salicylidine}cyclohexene-1,2-diamine] **1′a** and poly[(R,R)-N,N′-bis{3-(1,1-dimethylethyl)-5-methylene salicylidine}1,2-diphenyl-1,2-ethylene diamine] **1′b***

5,5′-Methylene-di-3-*tert*-butylsalicylaldehyde **2** (0.002 mol) in ethanol was refluxed with 1*S*,2*S*-(+)-1,2-cyclohexanediamine and 1*R*,2*R*-(+)-1,2-diphenyl ethylenediamine (0.002 mol) in dichloromethane for 6–8 h. Partial removal of the solvent and addition of hexane precipitated out the desired chiral ligands **1′a** and **1′b**. These ligands were recrystallised with ethanol and characterised by microanalysis, IR, ^{1}H NMR and Vapour Pressure Osmometry (VPO). **1′a**: Yield: 84%; Anal. Calcd. for $C_{29}H_{40}$ N_2O_2: C, 77.64; H, 8.98; N, 6.24%. Found: C, 77.52; H, 8.93; N, 6.20%. IR (KBr) cm^{-1} 1620 ν(H–C=N), ^{1}H NMR ($CDCl_3$, 200 MHz) δ ppm; 13.77 (bs, 2H, OH), 8.21 (s, 2H, azomethine), 6.74 (d, 2H, aromatic, $J_m = 2$ Hz), 7.05 (d, 2H, aromatic, $J_m = 2$ Hz), 3.68 (s, 2H, methylene), 3.29 (bm, 2H, asymmetric), 1.87 (m, 8H, cyclohexane), 1.36 (s, 8H, *t*-butyl); ($M_n = \sim 5400$, $n = \sim 12$). **1′b**: Yield: 85%, mp: 220 °C; Anal. Calcd. for $C_{37}H_{40}N_2O_2$: C, 82.83; H, 6.90; N, 4.82%. Found: C, 82.75; H, 6.85; N, 4.76%. IR (KBr), (H–C=N) 1630 cm^{-1}, ^{1}H NMR ($CDCl_3$, 200 MHz) 6 ppm 13.56 (bs, 2H, OH), 8.22 (s, 2H, azomethine), 7.13 (bs, 10H, phenyl), 7.03 (d, 2H, aromatic), 6.67 (d, 2H, aromatic), 4.64 (s, 2H, methylene), 3.66 (s, 2H, asymmetric), 1.34 (s, 18H, *t*-butyl); ($M_n = 5200$, $n = \sim 10$).

*2.3. Synthesis of poly[(S,S)-N,N′-bis{3-(1,1-dimethylethyl)-5-methylene salicylidine}cyclohexene-1,2-diaminato(2-)manganese(III)chloride] **1a** and poly[(R,R)-N,N′-bis{3-(1,1-dimethyl ethyl)-5-methylene-salicylidine} 1,2-diphenyl-1,2-ethane diaminato(2-)manganese(III)] **1b***

Chiral Schiff bases **1′a** and **1′b** (0.001 mol) was dissolved in CH_2Cl_2 while manganese acetate (0.002 mol) was taken in CH_3OH and the two solutions were mixed and refluxed under an inert atmosphere for 8–10 h. The reaction mixture was cooled to room temperature, solid lithium chloride (0.006 mol) was added and was further stirred for 5 h, while exposed to the air and filtered. The solvent was removed from the filtrate and the residue was extracted with dichloromethane. The organic layer was washed with water, brine and dried over anhydrous sodium sulfate. On partial removal of the solvent, the desired complexes **1a** and **1b** were precipitated on addition of petroleum ether (40–60). **1a**: Yield: 90%; Anal. Calcd. for $C_{29}H_{39}$ ClN_2O_3Mn: C, 62.87; H, 7.09; N, 5.05%. Found: C, 62.80; H, 7.03; N, 5.02%; IR (KBr) cm^{-1} 3431 (br), 2947 (s), 2865 (s), 1612 (s), 1538 (s), 1421 (sh), 1388 (m), 1342 (s), 1309 (s), 1285 (sh), 1238 (sh), 1201 (m), 1170 (m), 1100 (w), 1030 (m), 940 (w), 833 (m), 780 (w); UV-Vis: (CH_2Cl_2) $\lambda_{\max}$ (ε) 196 (3092), 206 (3778), 218 (4904), 224 (4618), 238 (16,116), 248 (16,823), 260 (18,545), 278 (16,782), 290 (16,243), 326 (14,187), 412 (4527), 416 (4517), 424 (4513), 484 (1932), 602 (516); CD: (CH_2Cl_2) $\lambda_{\max}$ ($\Delta\varepsilon$), 340 (+23), 445 (+10), 570 (+2), 600 (+3), 650 (−2), 680 (+2); $[\alpha]_{\mathrm{D}}^{30} = +188$ ($c = 0.05$, CH_2Cl_2); Configuration (*S*); Λ_{M} (MeOH) 4 mho cm^{-1} mol^{-1}; **1b**: Yield: 90%; Anal. Calcd. for $C_{37}H_{40}$ ClN_2O_3Mn: C, 69.91; H, 5.86; N, 4.07%. Found: C, 69.86; H, 5.83; N, 4.04%; IR (KBr), 3446 (br), 2957 (s), 2869 (s), 1605 (s), 1536 (s), 1456 (sh), 1418 (s), 1388 (m), 1346 (s), 1309 (s), 1285 (sh), 1238 (sh), 1201 (m), 1170 (m), 1100 (w), 1030 (m), 940 (w), 831 (m), 780 (w), 731 (w); UV-Vis: (CH_2Cl_2) $\lambda_{\max}$ (ε) 206 (3658), 220 (4851), 238 (16,342), 242 (16,881), 264 (179,755), 266 (17,674), 280 (17,485), 296 (17,168), 316 (15,602), 328 (15,602), 416 (4695), 412 (47,416), 448 (5011), 490 (2248); CD: (CH_2Cl_2) $\lambda_{\max}$ ($\Delta\varepsilon$), 340 (−23), 440 (−4.5), 580 (+3), 610 (+6), 650 (+8), 680 (+9); $[\alpha]_{\mathrm{D}}^{30} = +793$ ($c = 0.06$, CH_2Cl_2); Configuration (R); Λ_{M} (MeOH) 6 mho cm^{-1} mol^{-1}.

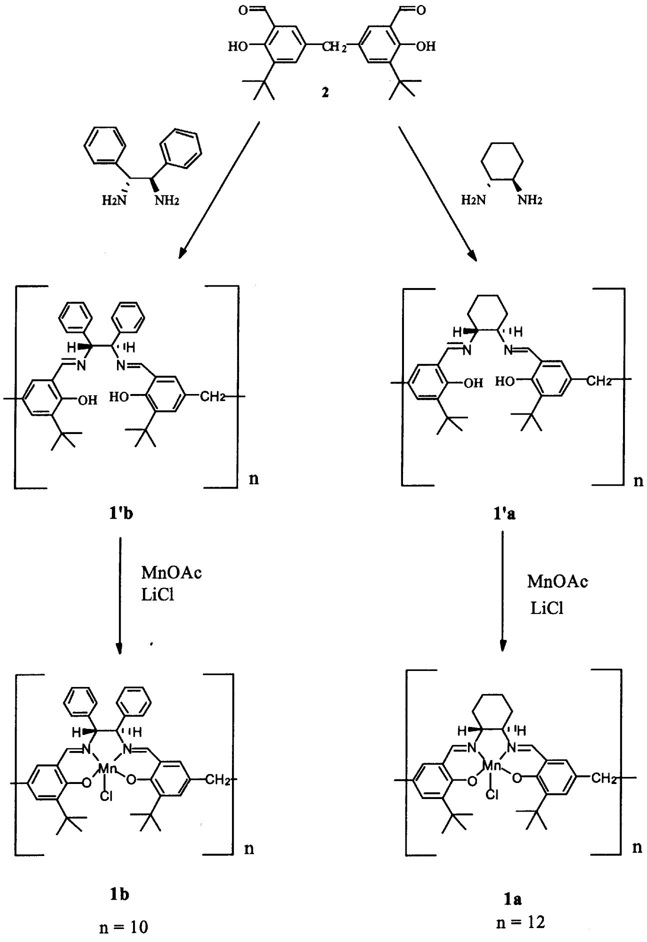
2.4. Enantioselective epoxidation of non-functionalised alkenes

Enantioselective epoxidation reactions were performed according to the procedure reported earlier [20].

Accordingly, 2 mol% of the complex **1a** and **1b** (based on monomeric unit of Mn(III) Salen), appropriate alkene (1.29 mmol) and PyNO (0.2 mmol) were stirred in 1 ml dichloromethane and the oxidant NaOCl (2.75 mmol) was added in four equal portions at 0 °C. The progress of the epoxidation reaction was monitored on GC. After completion of reaction the organic layer was washed with water, dried over sodium sulfate and the catalyst was precipitated out from the solution by the addition of hexane and was kept for subsequent use without further purification.

3. Results and discussion

Polymeric Mn(III) Salen complexes **1a** and **1b** were synthesised by condensation of 1*S*,2*S*-(+)-1,2-cyclohexanediamine/1*R*,2*R*-(+)-1,2-diphenyl ethylenediamine with 5,5′-methylene-di-3-*tert*-butylsalicylaldehyde in 1:2 molar ratio in $CHCl_3$ followed by insertion of manganese (Scheme 1). ^{1}H NMR and IR showed absence of aldehyde group in the ligands **1′a** and **1′b**. The average molecular weight of **1′a** and **1′b** as measured by vapour pressure osmometry (VPO) was $\sim$5400 ($M_n = \sim$5400, $n = \sim$12) and $\sim$5200 ($M_n = \sim$5200, $n = \sim$10), respectively. Microanalysis of ligands further confirms the structure of the ligands as depicted in Scheme 1.



Scheme 1. Synthesis of the complexes **1a** and **1b**.

3.1. Enantioselective epoxidation of non-functionalised alkenes

The epoxidation reaction catalysed by poly Mn(III) Salen complexes **1a** and **1b** conducted in dichloromethane using styrene, indene, 2,2-dimethylchromene, 6-cyano-2,2-dimethylchromene, 6-nitro-2,2-dimethylchromene, 6-methoxy-2,2-dimethylchromene and spiro[cyclohexane-l,2′-[2H][1]]chromene gave epoxides in quantitative yields with NaOCl as oxidant in presence of PyNO as axial base except for cyclochromene which gave corresponding epoxide yield in the range of 50–61% in 2.5–10 h. Product yield, ee and turn over frequency (TOF) for the complexes **1a** and **1b** are given in Table 1. The catalytic reaction is observed to be faster in case of 6-nitro 2,2-dimethylchromene (entries 14 and 15) as shown by TOF (Fig. 1). The best chiral induction (ee $>$ 99%) was found in the case of electron deficient nitro- and cyanochromene (entries 11, 12, 14 and 15). The catalyst **1b** was observed to give the high ee (89%) for 6-methoxy-2,2-dimethylchromene (entry 10). However, the ees were not encouraging (32–56%) in the case of styrene; nevertheless the catalyst **1b** gave higher ees than **1a**. In all the catalytic runs the configuration of product is the same as that of the catalyst.

To compare the efficiency of the catalysts **1a** and **1b** (2 mol% of Mn(III) Salen unit) with that of monomeric Jacobsen's complex (**J**) (2 mol%), epoxidation of 6-cyano-2,2-dimethylchromene was conducted using these catalysts in presence of PyNO under similar reaction conditions, which gave >99% conversion with >99% ees in 5.5–6 h (Table 1, entries 11, 12) while Jacobsen's catalyst gave 60% conversion and 92% ees in 9 h (entry 13). The enhanced activity of the polymeric catalyst **1a** and **1b** may be attributed to the increase in the active reaction sites that are functioning in synergy.

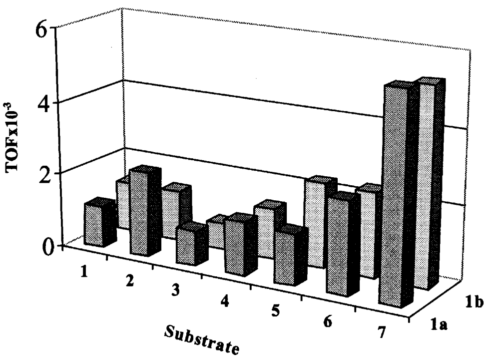
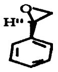
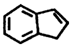
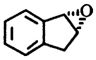
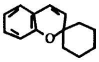
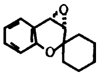
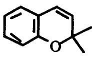
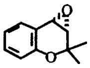
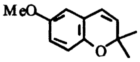
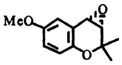
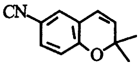
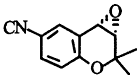
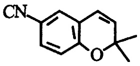
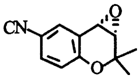
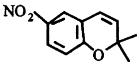
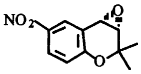


Fig. 1. 3D view showing TOF vs. substrates (1) styrene (2) indene (3) cyclochromene (4) chromene, (5) methoxychromene (6) cyanochromene and (7) nitrochromene with catalysts **1a** and **1b**.

Table 1
Data for enantioselective epoxidation of non-functionalised alkenes catalysed by polymeric complexes **1a**, **1b** in presence of PyNO with NaOCl as oxidant

Entry	Catalyst	Substrate	Product	Yield[a] (%)	Time (h)	ee[b] (%)	[i]TOF × 10^{-3}
1 (2)	**1a** (**1b**)			>99 (>99)	10 (12)	32[c] (56)[d]	1.37 (1.14)
3 (4)	**1a** (**1b**)			>99 (>99)	10 (6)	78[e] (79)[f]	1.37 (2.29)
5 (6)	**1a** (**1b**)			50 (61)	10 (9)	78[g] (82)[h]	0.70 (0.95)
7 (8)	**1a** (**1b**)			>99 (>99)	10 (9.5)	75[g] (77)[h]	1.37 (1.45)
9 (10)	**1a** (**1b**)			>99 (>99)	6 (10)	82[g] (89)[h]	2.29 (1.37)
11 (12)	**1a** (**1b**)			>99 (>99)	6 (5.5)	99[g] (99)[h]	2.29 (2.50)
13	Jacobsen Mn(III) Salen (**J**)			66	9	92[g]	0.95
14 (15)	**1a** (**1b**)			>99 (>99)	2.6 (2.5)	99[g] (99)[h]	5.30 (5.51)

Reactions conditions: catalyst (2 mol% in 1 ml CH_2Cl_2), substrate (1.29 mmol), pyridine N-oxide (0.13 mmol), NaOCl (2.75 mmol).

[a] Determined on GC.

[b] Chiral capillary column GTA-type/by ^{1}H NMR using chiral shift reagent (+)Eu(hfc)$_3$/chiral HPLC column OJ, OD, OB.

[c] Epoxide configuration, *S*.

[d] Epoxide configuration, *R*.

[e] Epoxide configuration, 1*S*,2*R*.

[f] Epoxide configuration 1*R*,2*S*.

[g] Epoxide configuration, 3*S*,4*S*.

[h] Epoxide configuration, 3*R*,4*R*.

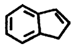
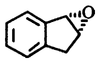
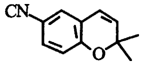
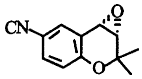
[i] Turnover frequency is calculated by the expression [product]/[catalyst] × time (s^{-1}).

Various O coordinating axial bases have been reported to increase the activity and stability of the Mn(III) Salen complexes for the epoxidation of non-functionalised alkenes using NaOCl as an oxidant [20]. In the case of complexes **1a** and **1b** the effect of axial bases namely, PyNO, 4-PhPyNO, 4-(3-phenyl propyl pyridine N-oxide) (4-PPPyNO), 4-methyl morpholine *N*-oxide, (NMO) and dimethyl sulphoxide, (DMSO) in the epoxidation of styrene, indene and 6-cyano-2,2-dimethylchromene was studied and data are given in Table 2. With water-insoluble axial bases, viz., 4-PhPyNO and 4-PPPyNO the time period for completion of the epoxidation reaction decreases from 10 to 1.5 h (entries 18–21, 26–29, 34–37) as compared to water-soluble PyNO, however, there was no change in enantioselectivity. This observation is in consonance with that reported for dimeric Mn(III) Salen complexes [15] and polymeric Mn(III) Salen complex reported by Yao et al. [21]. Whereas, in case of NMO (entries 16, 17, 24, 25, 32, 33) and DMSO (entries 22, 23, 30, 31, 38, 39) as axial base the reaction is slow and does not complete even after 24 h.

Furthermore, the recovery and reusability of the catalyst was studied. After the completion of the epoxidation reaction the organic phase of the reaction mixture was washed with water, brine, concentrated and the catalyst was precipitated by hexane. The recovered catalyst was used as such without purification (dried under vacuum before use) for the subsequent catalytic runs and the whole process was repeated five times (Table 3). The activity of the recycled catalyst gradually decreased upon successive use possibly due to minor degradation under epoxidation conditions and/or weight loss during recovery process of the catalyst **1a** and **1b**. The retention of ee suggests that there is no apparent change in the catalyst structure during epoxidation reaction.

The epoxidation reaction with NaOCl as an oxidant is a biphasic reaction therefore, we thought it would be appropriate to study the effect of various commercially available phase transfer catalysts viz., tetrabutylamminium bromide (TBAB), tetrabutylammonium hexaflurophosphate (TBAHFP), tetraethylammonium hydroxide (TEAH), tetrabutylammonium tetrafluoroborate (TBATFB) and cetyltrimethylammonium bromide (CTAB) in the epoxidation of styrene as representative substrate with catalyst **1a** and **1b** under the similar reaction conditions. The results are summarised in the Table 4. The epoxidation of styrene with catalyst **1a** and **1b** in absence of a phase transfer catalyst takes 10–12 h (Table 1, entries 1 and 2) while with the

Table 2
Data for enantioselective epoxidation of styrene, indene and 6-cyano-2,2-dimethylchromene catalysed by complexes **1a**, **1b** in presence of different axial bases with NaOCl as oxidant

Entry	Substrate	Product	Axial base	Conversion (%)	Time (h)	ee (%)	TOF × 10^{-3}
16 (17)			NMO	79 (50)	24 (24)	28 (40)	0.41 (0.29)
18 (19)			4-PhPyNO	>99 (>99)	8 (8)	31 (58)	1.71 (1.71)
20 (21)			4-PPPyNO	>99 (>99)	2 (6)	30.5 (57)	6.87 (2.29)
1 (2)			PyNO	>99 (>99)	10 (12)	32 (55)	1.37 (1.14)
22 (23)			DMSO	60 (40)	24 (24)	33 (55)	0.35 (0.23)
24 (25)			NMO	70 (80)	15 (15)	67 (49)	0.65 (0.74)
26 (27)			4-PhPyNO	>99 (>99)	2.5 (3)	77 (71)	5.50 (4.58)
28 (29)			4-PPPyNO	>99 (>99)	3.5 (2.5)	76 (63)	3.93 (5.50)
3 (4)			PyNO	>99 (>99)	10 (6)	78 (69)	1.37 (2.29)
30 (31)			DMSO	50 (25)	16 (16)	70 (63)	0.43 (0.22)
32 (33)			NMO	51 (51)	8.5 (7.5)	83 (81)	0.83 (0.94)
34 (35)			4-PhPyNO	>99 (99)	1.5 (2)	100 (100)	9.16 (6.87)
36 (37)			4-PPPyNO	>99 (99)	1.5 (3.5)	100 (100)	0.92 (3.93)
11 (12)			PyNO	>99 (99)	6 (5.5)	100 (100)	2.29 (2.50)
38 (39)			DMSO	73 (53)	9.5 (9)	81 (82)	1.07 (0.86)

Results given in parenthesis are for the catalyst **1b**.

Table 3
Data for enantioselective epoxidation of styrene with recycled catalysts **1a** and **1b** in presence of PyNO as axial base with NaOCl

Catalytic cycle	Time (h)	Conversion (%)	ee (%)
1	10 (12)	>99 (>99)	32 (55)
2	10 (12)	95 (92)	31 (54)
3	12 (14)	75 (72)	31 (55)
4	17 (19)	60 (59)	31 (54)
5	20 (24)	40 (39)	31 (55)

Results given in parenthesis are for the catalyst **1b**.

Table 4
Data for enantioselective epoxidation of styrene in presence of phase transfer catalyst catalysed by **1a**, **1b** in presence of axial base PyNO

Entry	Phase transfer catalyst	Time (h)	Conversion (%)	ee[a] (%)
40 (41)	TBAB	3 (2.5)	>99 (>99)	30 (49)
42 (43)	TBAHFP	7 (6)	80 (68)	28 (56)
44 (45)	TEAH	24 (24)	9 (12)	–
46 (47)	TBATFB	3 (3.5)	>99 (>99)	31 (55)
48 (49)	CTAB	3 (3.5)	>99 (>99)	32 (56)

[a] Determined on chiral GC column. Configuration of styrene oxide was same as that of catalyst results given in parenthesis are for the catalyst **1b**.

use of TBAB, TBATFB and CTAB as phase transfer catalyst the reaction completes within 3–3.5 h (entries 40, 41, 46–49) with marginal change in ees. However, TBAHFP is less effective (entries 42, 43) and TEAH adversely affected the epoxidation reaction (entries 44,45).

4. Conclusion

In conclusion, the polymeric chiral Mn(III) Salen complexes **1a** and **1b** worked very well as epoxidation catalyst with all non-functionalised alkenes in the presence of PyNO with NaOCl as an oxidant. Water insoluble substituted pyridine N-oxides were found to be more effective axial base than water-soluble pyridine N-oxide. Certain phase transfer catalysts quicken the epoxidation reaction. The polymeric Mn(III) Salen complexes used in the present study can be easily separated from the reaction system and re-used effectively.

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