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Self-Supported Chiral Polymeric Mn^{III} Salen Complexes as Highly Active and Recyclable Catalysts for Epoxidation of Nonfunctionalized Olefins

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A series of self-supported chiral polymeric Mn^{III} *N*,*N*′-ethylenebis(salicylimine) (salen) complexes were synthesized through metalation of the corresponding salen ligands obtained by condensation of several bis/tris-aldehydes with (1*R*,2*R*)-1,2-diaminocyclohexane. Upon employment in the asymmetric epoxidation reaction of nonfunctionalized olefins, all complexes showed enhanced activity and enantioselectivity relative to the classical Jacobsen's monomeric salen complex. However, 1,3,5-triazole-based polymeric Mn^{III} salen complex **7** was noticeably preferred over others owing to its ability to render higher enantioselectivity at the expense of lower catalyst loading. Furthermore, complex **7** was recycled and reused in eight recycling experiments with marginal loss in catalytic activity.

Introduction

Chiral epoxides are of great industrial worth as stereospecific ring opening of these leads to the synthesis of numerous biologically and pharmaceutically significant compounds.[1] Amid the numerous synthetic methods described in the literature for the procurement of chiral epoxides,[2] the Mn^{III} *N*,*N*′-ethylenebis(salicylimine) (salen) complex-catalyzed asymmetric epoxidation developed by Jacobsen et al.[3] and Katsuki et al.[4] at its infancy is one of the most significant ones. Despite the high catalytic activity obtained with the former catalytic systems for asymmetric epoxidation of nonfunctionalized olefins, there is still much room for improvement in terms of catalyst loading, reaction time, and recyclability. The expensive nature of the chiral catalysts enforced the scientific community worldwide to be certain about the maximum utilization of a good catalytic system. In this direction substantial research work has been performed for the design and synthesis of recyclable chiral Mn^{III} salen complexes, which was achieved in both homogeneous and heterogeneous conditions. For recyclability of the catalyst under homogeneous reaction conditions, several dimeric,[5] oligomeric,[6] and polymeric[7] versions of Jacobsen's monomeric salen system have been tested, which could be precipitated out from the reaction mass in a postcatalytic workup with the addition of a nonpolar solvent such as hexanes and could subsequently be reused. Ionic liquids also featured as an alternative solvent medium to ensure better recyclability of the catalyst under homogeneous reaction conditions only.[8] Alternatively, immobilization of the homogeneous Mn^{III} salen complex was accomplished by using several solid supports, such as mesoporous silica,[9] zirconium phosphate,[10] zeolite,[9a, 11] polyoxometalate,[12] polymers,[13] and membranes.[14] Both of these techniques for catalyst recyclability have their own merits and demerits. Heterogeneous complexes, despite showing preference over homogeneous recyclable catalytic systems in terms of ease of recycling and product separation, still lack the reactivity and enantioselectivity obtained for the product epoxide, which are often less than those for the monomeric Jacobsen system possibly because of the confinement effect.[15] Hence, a catalytic system that can improve on the catalytic activity as well as rendering higher enantioselectivity at the expense of lower catalyst loading, along with a very high degree of reusability without sacrificing its catalytic activity, is always desirable.

Recently, chiral metal–organic polymers have gathered a lot of attention as an alternative strategy for catalyst recyclability owing to the enhanced activity and enantioselectivity relative to their monomeric counterparts. In this direction, we have also reported several polymeric chiral ligands based on some chiral as well as nonchiral bridging precursors.[16] Herein, we have employed Mn^{III} salen complexes with various ditopic/tritopic linkers, namely, methylene **a**, piperazine **b**, trigol **c**, (*R*)/(*S*)/racemic 1,1′-bi-2-naphthol (BINOL, **d**–**f**), and triazine-piperazine linker **g** (Figure 1), on the ligands in the asymmetric epoxidation of nonfunctionalized olefins in the presence of an oxygen donor to give chiral epoxides in high yield and enantioselectivity with eight times catalyst recyclability.

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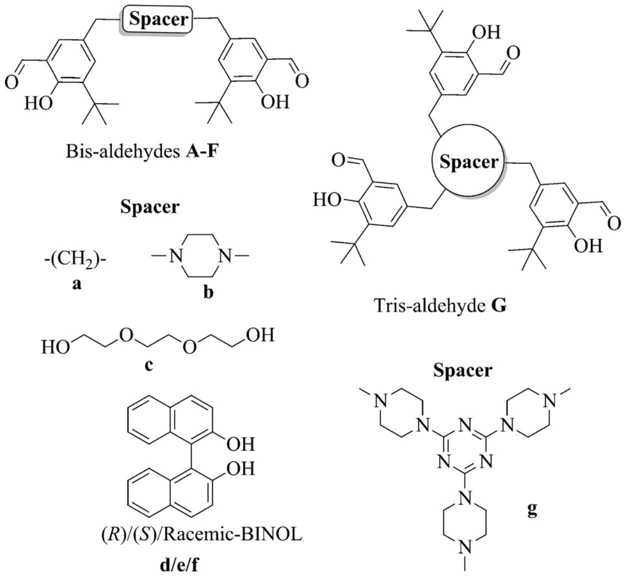


Figure 1. General structures of the bis- and tris-aldehydes (**A**–**G**).

Results and Discussion

In the quest for developing highly recyclable self-supported chiral polymeric Mn^{III} salen complexes for asymmetric epoxidation of nonfunctionalized olefins, initially we have synthesized a group of bis- and tris-aldehydes (**A**–**G**; Figure 1) by the treatment of 3-*tert*-butyl-5-chloromethyl salicylaldehyde with several diamines/diols/triamines as per previously reported procedures.[16] After the successful synthesis of different bis/tris-aldehydes, these were condensed with (1*R*,2*R*)-1,2-diaminocyclohexane to obtain the polymeric salen ligands **1′**–**7′** that have linker molecules of dissimilar length and geometry (see the Supporting Information).

Subsequently, all of these ligands were characterized by suitable spectroscopic methods, namely UV/Vis, IR, and NMR, together with elemental analysis and gel permeation chromatography (see the Supporting Information), and were subjected to metalation with $Mn(OAc)_2{\cdot}4H_2O$ under a nitrogen atmosphere followed by aerobic oxidation in the presence of LiCl to isolate complexes **1**–**7** as brown solids (Figure 2). The successful syntheses of these complexes were further confirmed by IR spectroscopy, elemental analysis, and inductively coupled plasma analysis for absolute detection of metal content (see the Supporting Information).

To determine the effect of the linker molecule on the activity of the above synthesized chiral polymeric Mn^{III} salen complexes, all of them were screened in the asymmetric epoxidation of nonfunctionalized olefins by using indene as a model substrate under identical reaction conditions. Preliminary results indicated a better reactivity and enantioselectivity with all of the complexes **1**–**7** than with classical Jacobsen's system **8** (Table 1) under the present reaction conditions.

The greater activity of the polymeric salen complexes was perhaps governed by the creation of a supramolecular assembly by each of the monomeric building units responsible for the polymeric network. Further, when we assessed the results

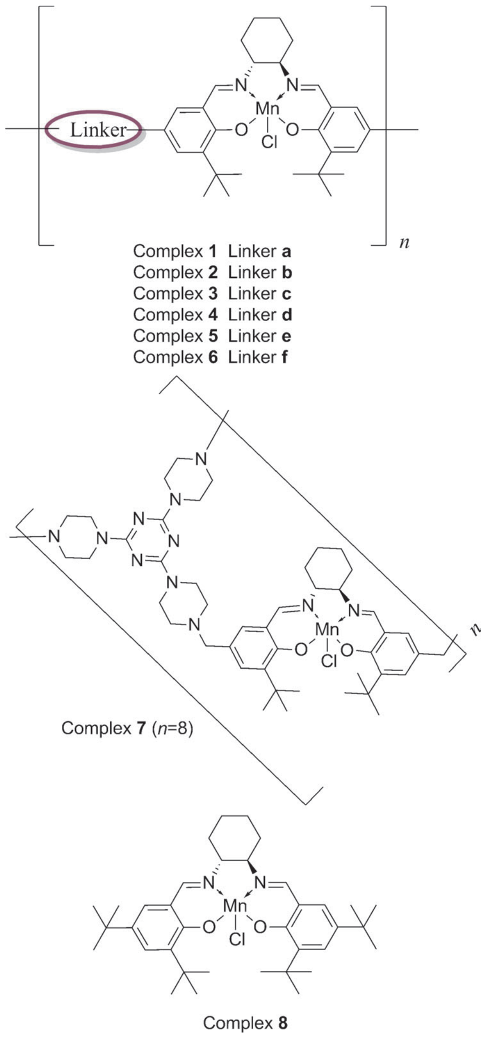
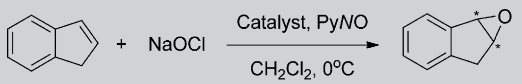


Figure 2. General structures of the polymeric (**1**–**7**) and monomeric Mn^{III} salen (**8**) complexes.

Table 1. Screening of catalysts for the asymmetric epoxidation of indene.[a]



Complex	*t* [h]	Yield [%][b]	*ee* [%][c,d]	TOF [$\times 10^{-3}$ s^{-1}][e]
1	8	> 99	78	1.73
2	8	> 99	79	1.73
3	6	> 99	88	2.31
4	12	95	79	1.10
5	12	92	80	1.06
6	12	92	70	1.06
7	5	> 99	92	2.78
8	12	90	75	1.04

[a] Reaction conditions: indene (1 mmol), pyridine *N*-oxide (Py*N*O; 0.1 mmol), catalyst (0.02 mmol), NaOCl (2.5 mmol), CH_2Cl_2 (1 mL), 0 °C. [b] Determined by GC analysis. [c] Determined by HPLC on a chiral stationary phase (Chiralcel OB column). [d] Epoxide configuration is 1*R*,2*S*. [e] Turnover frequency (TOF) is calculated by the expression [product]/[catalyst] × time (s^{-1}).

obtained for asymmetric epoxidation of indene with complexes **1**–**6**, which have ditopic bridging linkers, a general trend in reactivity and enantioselectivity was obtained with the length and the extension angle of the linker molecule. For instance, in the case of polymeric Mn^{III} salen complexes with linear bridging linkers, an increase in the length of the linker led to higher activity and enantioselectivity (Table 1, entries 1–3). This also resulted in better activity for the polymeric Mn^{III} salen complex based on trigol linker (complex **3**) relative to the complexes obtained with the use of a methylene (complex **1**) or piperazine (complex **2**) group as the linker. However, the use of the BINOL moiety as the bridging linker led to a decrease in the reactivity of the corresponding manganese complexes and the reaction required a much longer time for completion, which may be attributed to the deleterious effect on the electronic environment of one of the active metal centers on the other (Table 1, entries 4–6). A similar type of phenomenon was also observed by Ding et al.[17] with the use of a supramolecular version of Shibasaki's La–BINOL complex, in which reduction of the extension angle in the bridge led to lower activity and enantioselectivity. However, differing from their report, we have not observed any drop in enantioselectivity except in the case of the achiral BINOL moiety (Table 1, entry 6), in which the existence of a random twist in the supramolecular structure owing to the presence of an equimolar mixture of both enantiomers of BINOL could be the decisive factor.[16a] Nevertheless, unlike our former report on asymmetric aminolytic kinetic resolution of terminal epoxide,[16a] no assistive effect of the external chirality from the BINOL moiety was shown here, which might be a result of the absence of a bimetallic reaction mechanism in the case of asymmetric epoxidation of nonfunctionalized olefins in the presence of an oxygen donor.

Next, on moving from a ditopic bridging linker to a tritopic one, that is, salen ligand derived from a tris-aldehyde grown on a triazine-piperazine linker, we found a significant increase in both reactivity and enantioselectivity for the production of chiral epoxides (Table 1, entry 7). This observation was in concordance with the report of Ding et al.[17] in which it was witnessed that a polymeric complex based on a tritopic ligand with large linker was also able to produce high reactivity and enantioselectivity. A similar type of effect, namely an increase in catalytic activity with an increase in the length of the linker molecule, was also observed by our group[18] as well as by Fu et al.[9e] for immobilized Mn^{III} salen complexes on solid porous materials. In our present study, complex **7** has a fairly large linker of triazine-piperazine, which separates the two reactive metal centers by a distance that might be suitable for both catalyst activity and the formation of a supramolecular assembly. Besides, distinct from the previous report by Gothelf et al.[7c] on the asymmetric epoxidation of nonfunctionalized olefins by using a polymeric Mn^{III} salen complex grown on a tris-aldehyde, we have found greater activity and enantioselectivity with our polymeric complex **7** (Figure 3) at the expense of lower catalyst loading. The reason behind the enhanced activity of the present complex is perhaps owing to its better solubility in the reaction medium, which in turn results in more access to each and every single active metal center of the polymer network, unlike in the former report in which the cross-linked polymeric Mn^{III} complex was not soluble in the reaction medium.

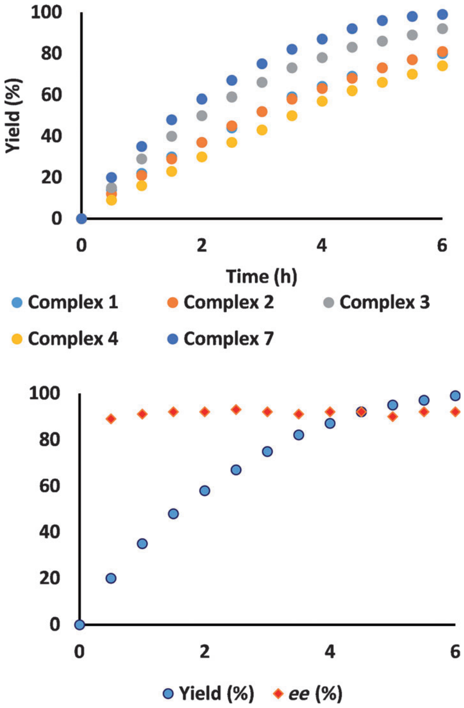


Figure 3. Comparison of the catalytic activity of the polymeric complexes in the formation of indene oxide (top) and formation of indene oxide with respect to time using complex **7** (bottom).

Having identified complex **7** as the catalyst of choice, the optimization of reaction conditions, such as choice of oxidants, axial bases, catalyst loading, solvents, and temperature, was investigated for the asymmetric epoxidation of indene as a model substrate, as these parameters are known to influence the yield and enantioselectivity of the product. First, we screened several oxidants, namely NaOCl, urea–hydrogen peroxide (UHP), *t*BuOOH, *meta*-chloroperbenzoic acid (*m*CPBA), iodosylbenzene (PhIO), and oxone, for the enantioselective epoxidation of indene (Figure 4). In the case of UHP, *t*BuOOH, and oxone, a similar level of enantioselectivity was observed; how-

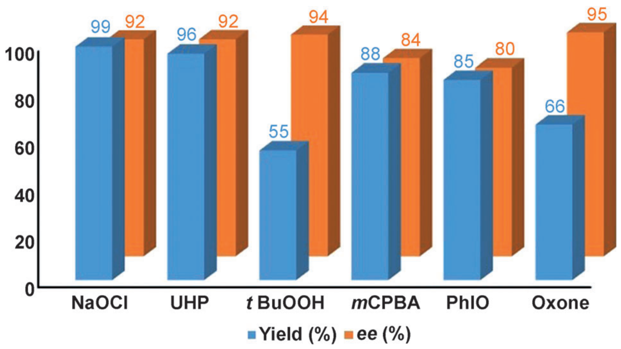


Figure 4. Screening of oxidants for the catalytic oxidation of indene using complex **7** as catalyst.

ever, there was a significant drop in the formation of epoxide when *t*BuOOH and oxone were used as oxidants. On conducting the epoxidation reaction of indene with *m*CPBA and PhIO, both enantiomeric excess and yield were inferior compared with those of NaOCl and UHP.

Thereafter, we varied the catalyst loading from 0.5 to 2 mol% with respect to indene (Figure 5) and found that 1 mol% of the catalyst is sufficient to give 99% yield with 92% enantioselectivity of indene epoxide with NaOCl as the oxidant. Temperature plays a crucial role in the enantiomeric excess (*ee*) of the products in most of the asymmetric organic transformations including the asymmetric epoxidation reaction. Hence, the enantioselective epoxidation reaction was studied in a temperature range from 0 °C to room temperature (Figure 6), and 0 °C was found to be optimum in terms of yield and enantioselectivity of the product.

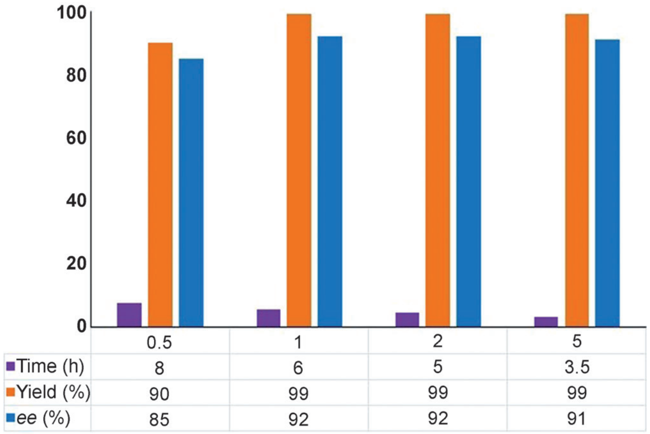


Figure 5. Variation of catalyst loading in the asymmetric epoxidation of indene using complex **7**.

It is well known that axial bases have a pronounced effect on the reactivity and selectivity of the enantioselective epoxidation reaction. Under the present reaction conditions we were able to attain good catalytic activity using inexpensive water-soluble Py*N*O as an axial base (Figure 7, top). The use of an expensive and hydrophobic version of Py*N*O, such as 4-phenyl Py*N*O (PPyNO) or 4-phenyl propyl Py*N*O (PPPyNO), gave similar activity and enantioselectivity, albeit in less reaction time owing to better transportation of active oxidant HOCl, generated in situ from the aqueous layer to the organic layer. Henceforth, for the subsequent catalytic studies we zeroed upon Py*N*O as an optimal axial base (Figure 7, top). Different solvents were explored for the epoxidation reaction of indene using dichloromethane (CH_2Cl_2), chloroform, toluene, methanol, acetonitrile, and CH_2Cl_2/methanol mixture. The data in Figure 7 (bottom) clearly show that CH_2Cl_2 is the solvent of choice.

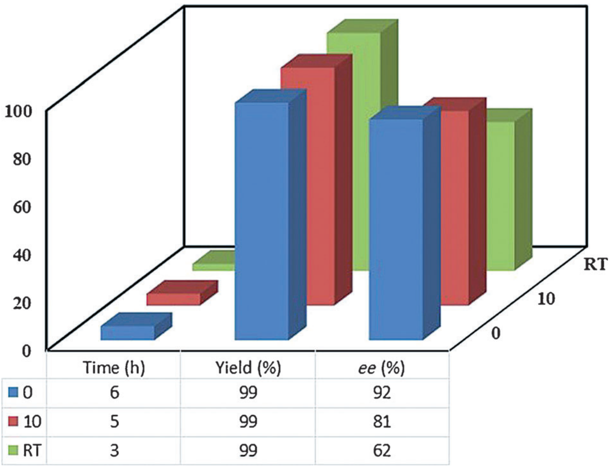


Figure 6. Variation of reaction temperature in the asymmetric epoxidation of indene using complex **7**.

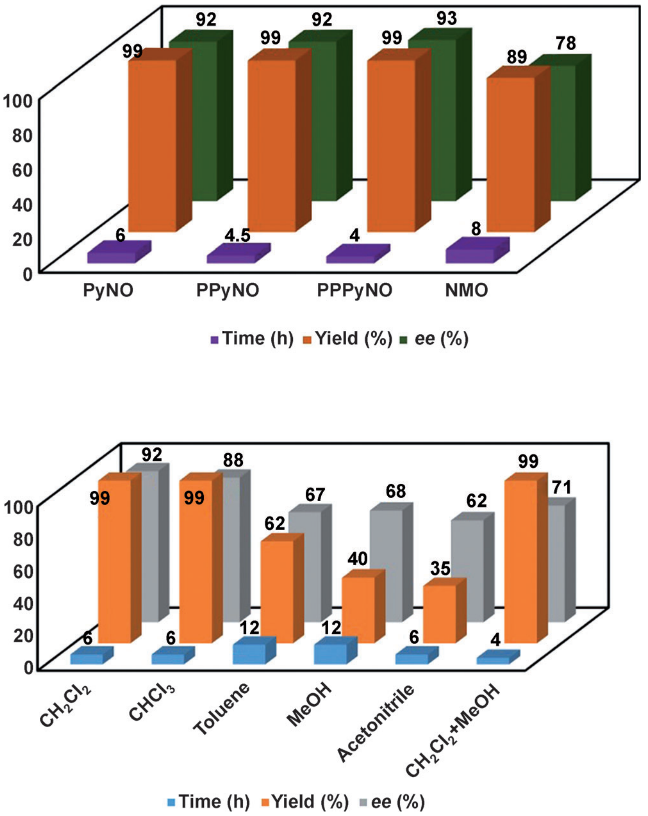
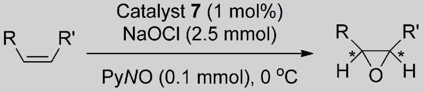
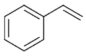
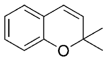
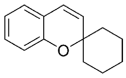
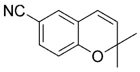
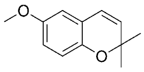
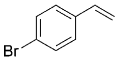
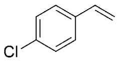
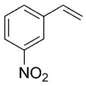
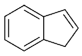


Figure 7. Variation of the axial base (top) and solvent (bottom) in the asymmetric epoxidation of indene using complex **7**. Reaction conditions: indene (1 mmol), axial base (0.1 mmol), catalyst (0.01 mmol), NaOCl (2.5 mmol), solvent (1 mL), 0 °C. NMO = *N*-methylmorpholine *N*-oxide.

Once all the reaction parameters governing the asymmetric epoxidation reaction were established, next we performed asymmetric epoxidation of other nonfunctionalized olefins, that is, styrene and simple or substituted chromenes, by using polymeric Mn^{III} salen complex **7** under optimized reaction conditions (Table 2, entries 1–6). All the above substrates except styrene performed well with quantitative yields and 90–99% enantioselectivity for the product epoxides in 5–8 hours. Despite enantioselective epoxidation of styrene with complex **7** giving styrene oxide in quantitative yield, still only a moderate enantioselectivity (60% *ee*) was obtained in this case (Table 2,

Table 2. Variation of substrate in the asymmetric epoxidation of nonfunctionalized olefins using complex **7**.[a]



Entry	Substrate	*t* [h]	Yield [%][b]	*ee* [%]	TOF [$\times 10^{-3}$ s^{-1}][c]
1		4.5	>99	60[d]	6.17
2		6	>99	95[e]	4.63
3		8	>99	94[e]	3.47
4		8	>99	99[e]	3.47
5		5	>99	92[e]	5.55
6		6	92	52[f]	4.26
7		6	95	54[f]	4.40
8		8	90	33[g]	3.12
9[h]		5	90[i]	91[j]	5.00

[a] Reaction conditions: substrate (1 mmol), Py*NO* (0.1 mmol), catalyst **7** (0.01 mmol), NaOCl (2.5 mmol), CH_2Cl_2 (1 mL), 0 °C. [b] Determined by GC analysis. [c] Turnover frequency is calculated by the expression [product]/[catalyst] × time (s^{-1}). [d] Determined by HPLC analysis on a chiral stationary phase (chiral capillary column GTA type). Epoxide configuration is *R*. [e] Determined by HPLC analysis on a chiral stationary phase (Chiralcel OD column). Epoxide configuration is 3*R*,4*R*. [f] Determined by HPLC analysis on a chiral stationary phase (Chiralcel AS-H column). Epoxide configuration *R*. [g] Determined by HPLC analysis on a chiral stationary phase (Chiralcel IA column). Epoxide configuration is *R*. [h] Reaction scale of 10 mmol. [i] Yield of isolated product. [j] Determined by HPLC analysis on a chiral stationary phase (Chiralcel OB column). Epoxide configuration is 1*R*,2*S*.

entry 1). The *ee* values were particularly encouraging for bulkier alkenes such as chromene and its derivatives (Table 2, entries 2–5). A better enantioselectivity was obtained when there was an electron-withdrawing group present in the chromene moiety at the 6-position (Table 2, entry 4), whereas an electron-donating group at the same place resulted in little decrease in *ee* value (Table 2, entry 5). To show the practical applicability of the catalytic system, we performed asymmetric epoxidation of indene at a larger reaction scale (10 mmol) to obtain the corresponding product indene oxide in high yield of isolated material (90 %) and enantioselectivity (91 %), which further supports the robustness of the present catalytic system (Table 2, entry 6).

Chiral catalysts are expensive in nature so it is desirable to check for their recyclability if possible. We also subjected our best catalytic system, that is, complex **7**, to the study of reusability and found that the activity of the catalyst remained constant for four consecutive cycles. However, on proceeding further there was a visible drop in both yield and enantioselectivity of the product epoxides (Figure 8). This is probably a result of oxidative degradation of the complex, which was also reflected in the change of catalyst color from dark brown to light brown. On the contrary, when we utilized the same catalytic system for the study of recyclability under single-phase reaction conditions using UHP adduct as an oxidant, the catalyst could be recycled eight times without any significant loss in catalytic activity or enantioselectivity (Figure 8).

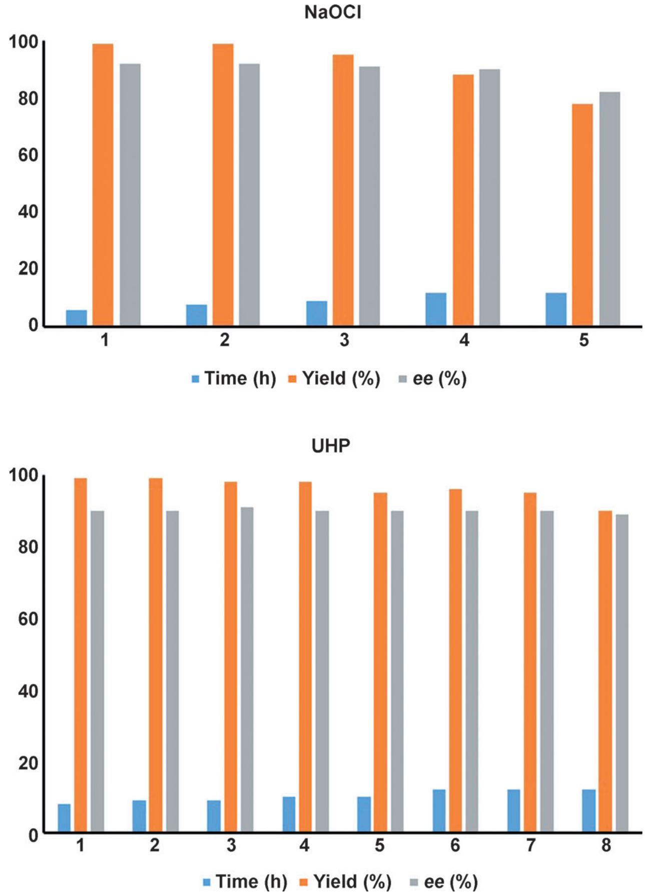
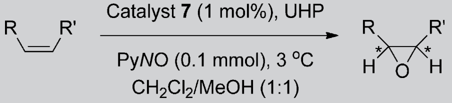
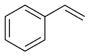
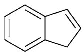
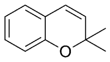
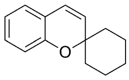
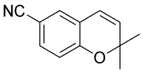
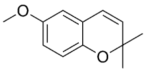


Figure 8. Study of catalyst recyclability in the asymmetric epoxidation of indene with complex **7** using NaOCl (top) and UHP (bottom) as oxidant.

After obtaining better recyclability of complex **7** using UHP as an oxidant, next we explored the efficacy of complex **7** for the asymmetric epoxidation of all the above tested nonfunctionalized olefins by using the same oxidant in the presence of Py*NO* as an axial base at 3 °C and 1:1 CH_2Cl_2/MeOH as reaction medium; the results are summarized in Table 3 (entries 1–6). From turnover frequency (TOF) calculations it is apparent that the asymmetric epoxidation reaction was relatively slower with UHP as an oxidant than with NaOCl, with almost parallel enantioselectivity values obtained in both cases, which was in tandem with our earlier report.[19]

Table 3. Enantioselective epoxidation of nonfunctionalized olefins with complex **7** using urea–hydrogen peroxide (UHP) as an oxidant.[a]



Entry	Substrate	*t* [h]	Yield [%][b]	*ee* [%]	TOF [×10^{-3} s^{-1}][c]
1		8	> 99	58[d]	3.47
2		8	> 99	90[e]	3.47
3		10	96	92[f]	2.67
4		10	90	92[f]	2.50
5		10	88	94[f]	2.44
6		10	92	90[f]	2.55

[a] Reaction conditions: substrate (1 mmol), Py*NO* (0.1 mmol), catalyst (0.01 mmol), UHP (1.5 mmol), CH_2Cl_2 (1 mL), 3 °C. [b] Determined by GC analysis. [c] Turnover frequency is calculated by the expression [product]/[catalyst] × time (s^{-1}). [d] Determined by HPLC analysis on a chiral stationary phase (Chiral capillary column GTA type). Epoxide configuration is *R*. [e] Determined by HPLC analysis on a chiral stationary phase (Chiralcel OB column). Epoxide configuration is 1*R*,2*S*. [f] Determined by HPLC analysis on a chiral stationary phase (Chiralcel OD column). Epoxide configuration is 1*R*,2*S*.

Conclusion

We have synthesized a series of self-supported polymeric Mn^{III} salen complexes based on several bis/tris-aldehydes and employed them for the asymmetric epoxidation of nonfunctionalized olefins with different oxidants under homogeneous conditions. A systematic evaluation has been done on the effect of the linker molecule joining the salen units on the outcome of the asymmetric epoxidation reaction. The Mn^{III} salen complex based on triazole linker was found to be most effective in terms of activity and enantioselectivity when NaOCl was used as oxidant. Further, this complex was recycled several times under the described reaction conditions without any loss in activity and enantioselectivity in the presence of urea–hydrogen peroxide and NaOCl as oxidants.

Experimental Section

Methods and materials

Manganese acetate (SD Fine Chem. Ltd.) and (1*R*,2*R*)-(−)-1,2-diaminocyclohexane (Sigma Aldrich) were used as received. Indene and styrene (Fluka) were passed through a bed of neutral alumina before use. All the chromenes used in the present study were synthesized according to literature reports.[20] All the solvents were purified by distillation prior to use.[21] 3-*tert*-Butyl-5-chloromethyl salicylaldehyde was synthesized by the previously known method.[22] The bis-[16a,c] and tris-aldehydes[16b] (**A**–**G**), used for the synthesis of polymeric ligands, were prepared as per our earlier reports. Microanalysis of the intermediates, ligands, and catalysts was performed on a PerkinElmer 2400 CHNS analyzer. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 200 MHz or 500 MHz spectrometer at ambient temperature with reference to TMS. FTIR spectra were recorded on a PerkinElmer Spectrum GX spectrophotometer with samples as KBr pellets. Electronic spectra of the polymeric Mn^{III} salen complexes were recorded in dichloromethane on a Varian Cary 500 Scan UV/Vis–near-IR spectrophotometer. Optical rotations of chiral intermediates and chiral complexes were recorded on an automatic polarimeter (Digipol 78, Rudolph). High-resolution mass spectra were obtained with LC-MS (Q-TOF) LC (Waters), MS (Micromass), MALDI-TOF, and Ultraflex TOF/TOF instruments (Bruker Daltonics, Germany). The product epoxides were purified with flash chromatography using silica gel 60–200 mesh purchased from SD Fine Chemicals Limited, Mumbai (India). The purity of the solvents and alkenes and the analysis of the epoxide product were determined by gas chromatography (GC) on a Shimadzu GC 14B instrument with a stainless-steel column (2 m long, 3 mm inner diameter, 4 mm outer diameter) packed with 5 % SE30 (mesh size 60–80) and equipped with a flame ionization detector. Ultrapure nitrogen was used as carrier gas (rate 30 mL min^{-1}). The injection port and detector temperature was kept at 200 °C. For the product analysis of styrene and indene, the column temperature was programmed at 70 to 140 °C, whereas for chromenes it was kept at 140 °C (isothermal). Synthetic standards of the products were used to determine the conversions by comparing the peak height and area. The *ee* value of styrene oxide was determined by GC using a chiral capillary column (Chiraldex GTA). For the chromenes and indene epoxides, the *ee* values were determined by HPLC (Shimadzu SCL-10AVP) on a Chiralcel column (OD and OB).

General method for preparation of polymeric salen ligands

The polymeric salen ligands based on several bis/tris-aldehydes (**A**–**G**) were prepared as per earlier reported procedure.[16a–c] In a typical procedure, a solution of (1*R*,2*R*)-1,2-diaminocyclohexane and a solution of a suitable bis/tris-aldehyde were taken together in an appropriate molar ratio and the resulting mixture was heated at reflux until the disappearance of the starting aldehyde, as observed by TLC. Subsequently, the solvent was evaporated and the yellow mass thus obtained was dissolved in CH_2Cl_2 and washed thoroughly with water and brine. The organic layer was separated and removal of the solvent under reduced pressure gave the polymeric salen ligands **1′**–**7′** as yellow solids.

General method for preparation of polymeric Mn^{III} salen complexes

$Mn(CH_3COO)_2 \cdot 4H_2O$ (490 mg, 2 mmol) was added to a solution of a polymeric salen ligand (**1′**–**7′**; 1 mmol with respect to monomeric unit) in CH_2Cl_2/methanol mixture (30 mL, 1:1) under an inert atmosphere, and the resulting mixture was heated at reflux for 6–8 h. After completion of the reaction, the mixture was cooled to room temperature, lithium chloride (170 mg, 4 mmol) was added, and the mixture was further stirred for 3 h with exposure to air and then filtered. The solvent was removed from the filtrate and the residue was extracted with dichloromethane. The organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. After complete removal of the solvent the desired complexes **1**–**7** were obtained as brown solids.

General procedure for enantioselective epoxidation of non-functionalized olefins using NaOCl as an oxidant

Enantioselective epoxidation reactions of different olefins, namely styrene, indene, 2,2-dimethylchromene, 6-cyano-2,2-dimethylchromene, 6-nitro-2,2-dimethylchromene, 6-methoxy-2,2-dimethylchromene, and spiro[cyclohexane-1,2-[2*H*][1]chromene] (1 mmol), were performed using complexes **1**–**7** (0.5–5 mol %) as catalyst in dichloromethane (1 mL) in the presence of Py*N*O (10 mg, 0.1 mmol) as an axial base and buffered (pH 11.3) NaOCl (2.5 mmol added in four equal parts) as an oxidant at 0 °C. The progress of the reaction was monitored by GC analysis of the products using *n*-tridecane (0.1 mmol) as the GLC internal standard.

After completion of the reaction, the product chiral epoxide of the respective alkene was extracted with CH_2Cl_2, washed with water, and dried over Na_2SO_4. The catalyst was separated from the product by precipitation with hexanes, washed several times with hexanes/ethyl acetate (90:10), dried, and reused for further catalytic runs. Epoxides were purified by flash chromatography through a bed of neutral alumina by using ethyl acetate/hexanes (9:1) as eluent and their *ee* values were determined.

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Keywords: asymmetric catalysis · epoxidation · manganese · olefins · recyclability

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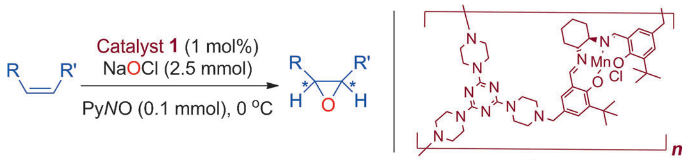
Self-Supported Chiral Polymeric Mn^{III} Salen Complexes as Highly Active and Recyclable Catalysts for Epoxidation of Nonfunctionalized Olefins



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In the long run: Self-supported chiral polymeric Mn^{III} complexes have been evaluated in the asymmetric epoxidation of nonfunctionalized olefins, to obtain epoxides in good yield and enantioselectivity with a high degree of catalyst recyclability (see scheme; Py*N*O = pyridine *N*-oxide). A correlation between linker length and catalyst activity was established from experimental evidence.