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# Enantioselective epoxidation of nonfunctionalized alkenes catalyzed by recyclable new homochiral dimeric Mn(III) salen complexes

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**Abstract**

Two recyclable dimeric $Mn^{III}$ salen complexes with geminal methyl groups on the linking carbon atom at the 5,5′ position of the salen units were synthesized. They gave a high epoxide yield (> 99%) and enantiomeric excess up to > 99% in 2 to 11 h at 2 mol% catalyst loading in the enantioselective epoxidation of nonfunctionalized alkenes using NaOCl as the oxidant in the presence of Py N–O as the axial base. The epoxidation reaction was successful even at a catalyst loading of 0.4 mol%, but the reaction took longer. The catalyst was recovered easily and recycled five times in a simple separation process. To understand the mechanism of the catalytic reaction, the kinetic investigation was carried out with different concentrations of the catalyst, the oxidant, and the substrate and with styrene as the representative substrate. The epoxidation of styrene was first order with respect to the catalyst and the oxidant but did not depend on the initial concentration of the substrate. An appropriate mechanism of the epoxidation reaction is proposed.


*Keywords:* Enantioselective; Homochiral; Dimeric $Mn^{III}$ salen; Nonfunctionalized alkenes; Kinetics; Mechanism; NaOCl

## 1. Introduction

Significant progress has been made in the design and synthesis of homogeneous metal complexes with chiral ligands. They are used as enantioselective catalysts for diverse applications [1,2]. However, separation of the catalyst from the reaction mixture and reuse are still problematic [3]. To address this issue, several groups have tried to immobilize $Mn^{III}$ salen complexes on polymer supports [4–6], on zeolites, clays, or siloxane membranes [7,8], on ordered mesoporous silica like MCM-41 [9–12], and in ionic liquids [13]. Although the immobilized catalysts can be separated, the catalytic efficiency was lower than that of $Mn^{III}$ salen complexes under homogeneous conditions. We reported [14] an alternative strategy: the solubility of the catalyst was decreased by increasing its molecular weight, thereby making it easier to isolate the product and recover the catalyst. In an attempt to develop an efficient recyclable catalyst for the enantioselective epoxidation of nonfunctionalized alkenes, we used new, recyclable dimeric $Mn^{III}$ salen complexes in which the two $Mn^{III}$ salen units are linked by a carbon atom with geminal methyl groups. These catalysts were recovered easily after precipitation with hexane. They were reused several times and their activity and enantioselectivity were higher than those of dimeric $Mn^{III}$ salen [14,15], polymeric $Mn^{III}$ salen [16,17], and monomeric Jacobsen $Mn^{III}$ salen complexes [18–20]. Furthermore, kinetic investigations were carried out to elucidate the mechanism of the epoxidation reaction with the dimeric complexes as catalysts and styrene as the representative substrate.

## 2. Experimental methods

Manganese acetate (SD Fine Chem. Ltd.), indene, and styrene (both from Fluka) were passed through a pad of neutral alumina before use. (*1R,2R*)-(−)-cyclohexanediamine was resolved from a technical grade *cis–trans* mixture according to procedure in Ref. [21]. Synthesis of **3** (Scheme 1) was carried out according to a modified procedure [22]. 2,2-Dimethylchromene and its derivatives were synthesized

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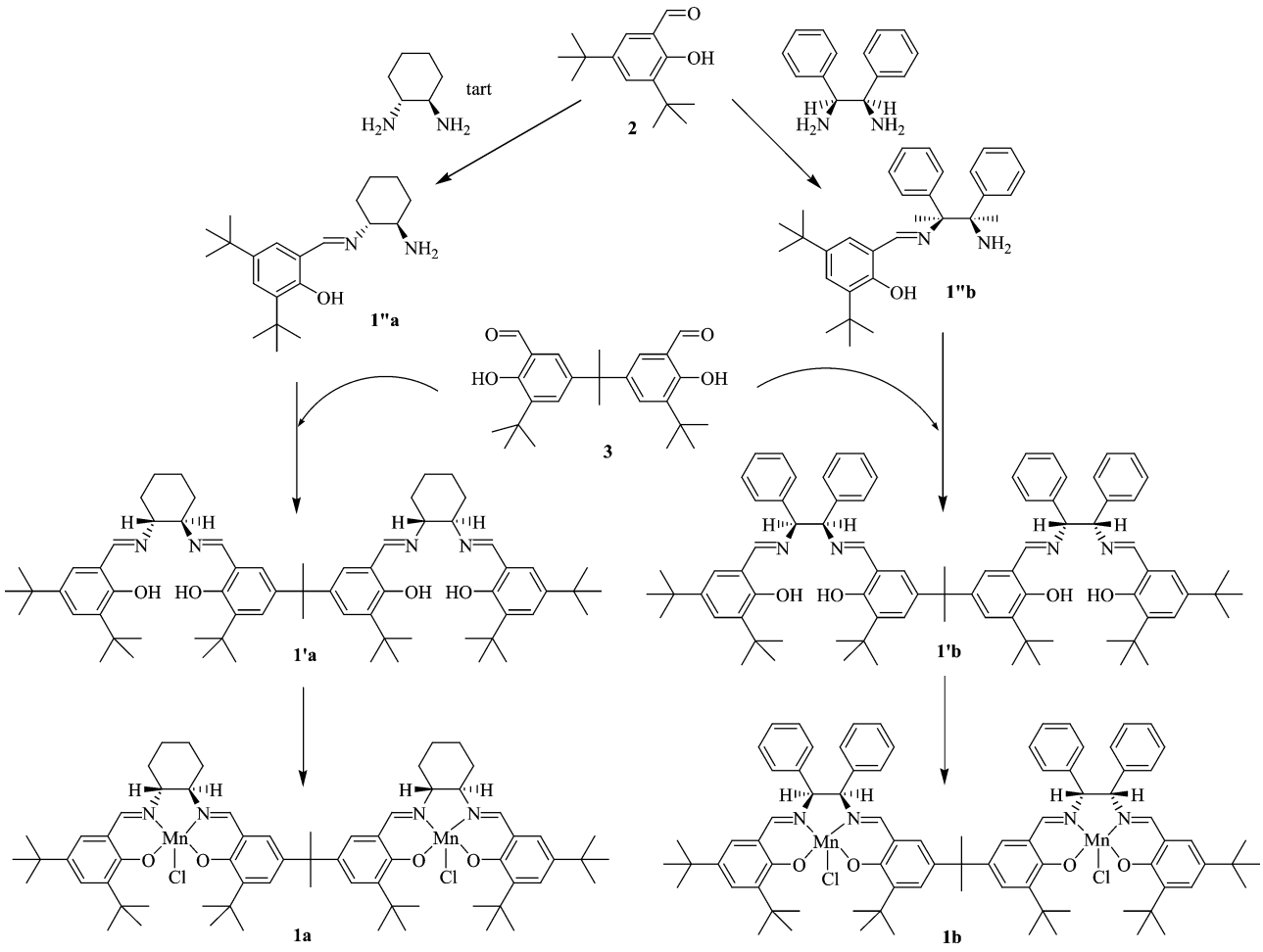



Scheme 1. Synthesis of complexes **1a** and **1b**.

as described in Ref. [23]. All the solvents were purified before use [24].

Microanalysis of the catalyst was carried out on Perkin Elmer CHN Analyzer 2400. $^1$H NMR spectra of the dimeric ligands were recorded in $CDCl_3$ (Bruker F113V, 200 MHz). FTIR spectra were recorded on a Perkin Elmer Spectrum GX spectrophotometer in a KBr/nujol mull. Electronic spectra of the dimeric complexes were recorded in dichloromethane on a Hewlett-Packard Diode Array spectrophotometer (Model 8452A). Molar conductance was measured at room temperature on a Digisun Electronic Conductivity Bridge DI-909 instrument. The optical rotation in dichloromethane was measured on an Atago polarimeter, (Japan). The melting points were determined with a capillary apparatus and are reported without correction.

The purity of the solvent and alkenes and the analysis of the epoxide product were determined by gas chromatography (GC) using 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 an FID detector. Ultrapure nitrogen was the carrier gas (rate 30 ml/min) and the injection port temperature was 200 °C. The temperature of the column for styrene and indene was 70 to 150 °C, while for chromene the isothermal temperature was 150 °C. Synthetic standards of the products were used to determine conversions by comparing the peak height and area. The ee of styrene oxide was determined by GC on a chiral capillary column (Chiraldex GTA). For the chromenes and indene epoxides, the ee was determined by $^1$H NMR using the chiral shift reagent $Eu(hfc)_3$ and by HPLC (Shimadzu SCL-10AVP) using a Chiralcel column (OD, OJ/OB).

Scheme 1 and the following section describe, the complete synthesis of complexes **1a** and **1b**, used as catalysts.

### *2.1. Synthesis of 5,5′-di-tert-butyl-6,6′-dihydroxy-3,3′-(propane-2,2-diyl)dibenzaldehyde 3*

A solution consisting of 2,2′-di-*tert*-butyl-4,4′-(propane-2,2-diyl)diphenol (32.6 mmol), $SnCl_4$ (19.5 mmol), 2,6-lutidine (78.1 mmol), and 200 ml toluene was stirred in a nitrogen atmosphere at room temperature for 45 min. Paraformaldehyde (260 mmol) was then added and the mixture heated while refluxing. The progress of the reaction was monitored by TLC. The reaction mixture was cooled to room temperature and 200 ml water and 200 ml diethyl ether

were added. The resulting emulsion was filtered through a pad of celite, the organic layer was washed with water and brine and dried over anhydrous sodium sulfate. A light yellow solid (mp 130 °C) of 5,5′-di-*tert*-butyl-6,6′-dihydroxy-3,3′-(propane-2,2-diyl)dibenzaldehyde **3** was obtained (85% yield), which was purified by flash column chromatography using hexane: ethyl acetate (95:5) as an eluent. Anal. calcd. for $C_{25}H_{32}O_4$: C, 75.82; H, 8.14; N, 3.93. Found: C, 75.79; H, 8.09; N, 3.89%: $^1$H NMR ($CDCl_3$, 200 MHz); $\delta$ ppm 11.72 (s, 2H, OH), 9.84 (s, 2H, HCO), 7.30 (bs, 4H, aromatic), 1.70 (s, 6H, methyl), 1.34 (s, 18H, *tert*-butyl): IR (KBr), cm$^{-1}$; 3473, 2963, 2870, 1646.

The synthesis of N-(2-hydroxy-3,5-di-*tert*-butylbenzaldehyde)-1-amino-2-cyclohexaneimine (**1″a**) was carried out according to the method in Ref. [15].

### *2.2. Synthesis of N-(2-hydroxy-3,5-di-tert-butylbenzaldehyde)-1-amino-1,2-diphenylethaneimine (**1″b**)*

3,5-Di-*tert*-butylsalicylaldehyde **2** (0.001 mol) dissolved in 10 mL chloroform reacted slowly with 0.001 mol of *1S,2S*-(−)-1,2-diphenylethylenediamine in 50 mL of cold chloroform; the reaction mixture was stirred for 48 h at 0 °C. The progress of the reaction was checked on TLC using a hexane:ethyl acetate (9:1) mixture. **1″b**: Yield 89%: anal. calcd. for $C_{29}H_{36}N_2O$: C, 81.32; H, 8.40; N, 6.53. Found: C, 81.25; H, 8.36; N, 6.48%: $^1$H NMR. ($CDCl_3$, 200 MHz): $\delta$ ppm 13.60 (s, 1H, OH exchangeable with $D_2O$), 8.46 (s, 1H, H–C=N), 6.87–7.30 (bs, 12H, aromatic), 4.72 (d, 1H), 4.29–4.44, (q, 1H), 1.66 (2H, s, br), $NH_2$ proton $D_2O$ exchangeable) 1.47 (9H, s), 1.29 (9H, s): IR (KBr), cm$^{-1}$ 3448, 2958, 2868, 1626, 1598, 1453, 1414, 1391, 1249, 1173, 1047, 879.

### *2.3. Synthesis of 5,5-(2′,2′-dimethylpropane)-di-[(R,R)-{N-(3-tert-butylsalicylidine)-N′-(3′,5′-di-tert-butylsalicylidine)}-1,2-cyclohexanediamine] (**1′a**) and 5,5-(2′,2′-dimethylpropane)-di-[(S,S)-{N-(3-tert-butylsalicylidine)-N′-(3′,5′-di-tert-butylsalicylidine)}-1,2-diphenylethylene diamine (**1′b**)*

A solution of **1″a**/**1″b** (0.002 mol) in dichloromethane and 5,5′-di-*tert*-butyl-6,6′-dihydroxy-3,3′-(propane-2,2-diyl)dibenzaldehyde **3** (0.001 mol) in ethanol was refluxed for 6 to 8 h. The progress of the reaction was checked on TLC. After completion of the reaction the resulting solution was concentrated to give the desired ligands **1′a**/**1′b**. Yield, 89%: **1′a**: anal. calcd. for $C_{67}H_{96}N_4O_4$: C, 78.78; H, 9.47; N, 5.48. Found: C, 78.50; H, 9.30; N, 5.38%: IR (KBr): 1628 cm$^{-1}$ $\nu$(H–C=N); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta$ ppm 13.70 (bs, 4H exchangeable with $D_2O$, OH), 8.29 (s, 4H, HCN), 7.25 (s, 4H, aromatic), 6.97 (s, 4H, aromatic), 3.29 (m, 4H), 1.90 (s, 6H), 1.40 (s, 36H), 1.23 (s, 18H): $[\alpha]_D^{27} = -238$ ($c = 0.10$, $CH_2Cl_2$).

**1′b**: anal. calcd. for $C_{83}H_{100}N_4O_4$: C, 81.87; H, 8.28; N, 4.26. Found: C, 81.69; H, 8.18; N, 4.23%; IR (KBr): 1626 cm$^{-1}$ $\nu$(H–C=N); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta$ ppm 13.58 (bs, 4H exchangeable with $D_2O$, OH), 8.31 (s, 4H, HCN), 7.25 (s, 4H, aromatic), 7. 17 (s, 10H), 6.97 (s, 4H, aromatic), 4.72 (s, 4H), 1.42 (s, 36H), 1.22 (s, 18H): $[\alpha]_D^{27} = -327$ ($c = 0.12$, $CH_2Cl_2$).

### *2.4. Synthesis of 5,5-(2′,2′-dimethylpropane)-di-[(R,R)-{N-(3-tert-butylsalicylidine)-N′-(3′,5′-di-tert-butylsalicylidine)}-1,2-cyclohexanediaminato(2-)manganese(III) chloride (**1a**) and 5,5-(2′,2′-dimethylpropane)-di-[(S,S)-{N-(3-tert-butylsalicylidine)-N′-(3′,5′-di-tert-butylsalicylidine)}-1,2-di-phenylethylenediaminato(2-)manganese (III) chloride (**1b**)*

The dimeric homochiral Schiff base (**1′a**) and (**1′b**) (0.001 mol) was dissolved in 40 mL dichloromethane:methanol (1:1) and 0.002 mol $Mn(CH_3COO)_2 \cdot 4H_2O$ was added in an inert atmosphere. The reaction mixture was refluxed for 8 h and the reaction was monitored by TLC using hexane:ethyl acetate (6:4) as the mobile solvent. The reaction mixture was cooled to room temperature, lithium chloride (0.006 mol) was added, and the mixture was stirred for 5 h in air and 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 sodium sulfate. After partial removal of the solvent the desired complexes **1a** and **1b** were precipitated upon the addition of petroleum ether (40–60). **1a**: Yield 80%, anal. calcd. for $C_{67}H_{92}Mn_2N_4O_4\,Cl_2$: C, 67.16; H, 7.74; N, 5.92. Found: C, 67.01; H, 7.68; N, 5.85: IR (KBr) (cm$^{-1}$) 3476 (br), 2957 (s), 2865 (s), 1612 (s), 1587 (s), 1528 (s), 1440 (sh), 1388 (w), 1328 (w), 1274 (w), 1241 (w), 1215 (m), 1176 (m), 1136 (w), 1011 (w), 879 (w): UV–vis. ($CH_2Cl_2$), $\lambda_{max}(\in)$, 506 (2740), 436 (6510), 321 (22040), 239 (59700): $\Lambda_M$(MeOH): 5 $\Omega^{-1}$ cm$^{-1}$ mol$^{-1}$: $[\alpha]_D^{27} = -88$ ($c = 0.11$, $CH_2Cl_2$).

**1b**: Yield 80%, anal. calcd. for $C_{84}H_{96}Cl_2Mn_2N_4O_4$; C, 71.49; H, 7.08; N, 4.02. Found; C, 71.18; H, 7.05; N, 3.95: IR (KBr) (cm$^{-1}$): 3471 (br), 2957 (s), 2869 (s), 1606 (s), 1534 (s), 1456 (sh), 1429 (s), 1388, 1311 (s), 1249 (s), 1177 (m), 1135 (w), 1027 (w), 850 (w): UV–vis: ($CH_2Cl_2$), $\lambda_{max}(\in)$ (nm) 328 (73085), 442 (23550), 509 (8270), 535 (6611): $\Lambda_M$(MeOH): 6 $\Omega^{-1}$ cm$^{-1}$ mol$^{-1}$: $[\alpha]_D^{27} = -139.8$ ($c = 0.14$, $CH_2Cl_2$).

### *2.5. Enantioselective epoxidation of nonfunctionalized alkenes*

Enantioselective epoxidation reactions were performed using 2 mol% of complexes **1a** and **1b** with 2,2-dimethylchromene (CR), 6-cyano-2,2-dimethylchromene (CNCR), 6-methoxy-2,2-dimethylchromene (MeOCR), spiro[cyclohexane-1,2′-[2H][1]chromene] (CyCR), indene (IND), and styrene (STR) (1.29 mmol) was the substrates. One milliliter of dichloromethane was added in the presence of Py N–O (0.13 mmol) as an axial ligand using buffered NaOCl (2.75 mmol) (pH 11.3) as an oxidant and added in four equal portions at 0 °C. The epoxidation reaction was monitored

by GC with n-*tri*decane (0.1 mmol) as the GLC internal standard for product quantification. After the reaction, the product was extracted with $CH_2Cl_2$, washed with water, and dried over sodium sulfate. The catalyst was separated from the product epoxide by precipitation with 2 mL hexane and used as such for further catalytic runs.

### *2.6. Epoxidation reaction for kinetic measurements*

The catalysts **1a** and **1b** ($0.20 \times 10^{-2}$–$0.84 \times 10^{-2}$ M) in 1 mL $CH_2Cl_2$ were stirred with Py N–O ($2.09 \times 10^{-2}$ M) and STR ($10.41 \times 10^{-2}$–$41.64 \times 10^{-2}$ M) at 0 °C; the resulting solution was treated with NaOCl ($22.49 \times 10^{-2}$–$89.96 \times 10^{-2}$ M) and stirred constantly. To determine the rates of epoxidation, aliquots were drawn from the reaction mixture every 2 min, quenched with triphenylphosphine, and analyzed on GC.

## 3. Results and discussion

Product yield and ee data (Table 1) show that complexes **1a** and **1b** exhibit excellent epoxidation activity (> 99% conversion to epoxide) with all the substrates (entries 1–12) after 2 to 11 h and gave > 99% ees with chromenes having the polar substituents, MeOCR (entries 7, 8) and CNCR (entries 9, 10). The ee was moderate to good for IND (entries 1, 2), (CyCR) (entries 3, 4), and CR (entries 5, 6). At −5 °C the epoxidation of IND took a longer time to reach completion but the ee was higher (Table 1, entries 1*, 2*). Complex **1b** (entry 2) induced higher enantioselectivity for STR than for **1a**, while the over all performance of catalyst **1a** was better than **1b** for most of the alkenes (Table 1). Furthermore, the epoxidation reaction was faster for all the alkenes with improved enantioinduction except in case of the electron-deficient CNCR where the reaction was slower than that of the previously reported dimeric $Mn^{III}$ complex (**B**) [14] (Table 1). The increase in enantioselectivity is attributed to two methyl groups on the linking carbon atom of the homochiral dimeric complexes **1a**, **1b** which may cause the substrate to follow a chiral path; in the case of the previously reported dimer [14] there were two hydrogen atoms on the linking carbon atom. In all catalytic runs, the configuration of the dominant enantiomer of the product was the same as that of the catalyst.

A *tertiary* carbon-linked polysalen–$Mn^{III}$ complex (4 mol%) was reported [16] to give 86% yield and 37% ee for styrene oxide using 4-phenylpyridine *N*-oxide (20 mol%); the catalyst was recycled several times without loss of enantioselectivity. The dimeric version of this catalyst (complex **1a**) gave > 99% conversion and 47% ee with styrene as the substrate under similar reaction conditions as with Py N–O (5 mol%) (entry 11).

We compared the catalytic activity of the monomeric [18–20] and dimeric $Mn^{III}$ salen complex **1a**, by conducting experiments to determine the epoxidation of styrene. The

Table 1
Product yields and ee for enantioselective epoxidation[a] of nonfunctionalized alkenes catalyzed by complexes **1a** and **1b** with pyridine N–O and NaOCl as oxidants

| Entry | Catalyst | Substrate | Yield[b] (%) | Time (h) | ee[c] (%) | TOF × $10^{-3}$ [k] |
|---|---|---|---|---|---|---|
| 1 (2) | **1a** (**1b**) | IND | > 99 (> 99) | 2 (5) | 77[d] (66)[e] | 6.87 (2.75) |
| 1* (2*)[l] | | | | 3 (6) | 87[d] (71)[e] | |
| 3 (4) | **1a** (**1b**) | CyCR | > 99 (96) | 11 (7) | 91[f] (96)[g] | 1.25 (1.90) |
| 5 (6) | **1a** (**1b**) | CR | > 99 (> 99) | 5 (5.5) | 83[f] (88)[g] | 2.75 (2.50) |
| 7 (8) | **1a** (**1b**) | MeOCR | > 99 (> 99) | 4 (5) | 99[f] (99)[g] | 3.43 (2.75) |
| 9 (10) | **1a** (**1b**) | CNCR | > 99 (> 99) | 5 (6) | 99[f] (99)[g] | 2.75 (2.29) |
| 11 (12) | **1a** (**1b**) | STR | > 99 (> 99) | 3 (3) | 47[h] (62)[i] | 4.58 (4.58) |
| 13 | **A**[j] | STR | 92 | 11 | 48[h] | 1.16 |
| 14 | **B**[j] | STR | > 99 | 7.5 | 35[h] | 1.83 |
| 15 | **1a**[j] | STR | > 99 | 3.5 | 47[h] | 3.92 |

[a] 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).
[b] Determined on GC.
[c] Chiral capillary column GTA-type/By $^1$H NMR using chiral shift reagent (+)Eu(hfc)$_3$/chiral HPLC column OJ, OD, OB.
[d] Epoxide configuration, *1R,2S*.
[e] Epoxide configuration, *1S,2R*.
[f] Epoxide configuration, *3R,4R*.
[g] Epoxide configuration, *3S,4S*.
[h] Epoxide configuration, *R*.
[i] Epoxide configuration, *S*.
[j] Catalyst (1 mol%).
[k] Turnover frequency is calculated by the expression, [product]/([catalyst] × time) ($s^{-1}$).
[l] 1* (2*) reaction conducted at −5 °C.

Jacobsen catalyst (**A**) (2 mol%), the –$CH_2$– linked dimeric complex (**B**) (1 mol%) [14], and the $CH_3$–C–$CH_3$-linked complex **1a** (1 mol%) were reacted under identical reaction conditions; pyridine *N*-oxide (5 mol%) was the axial base and NaOCl the oxidant. These catalysts gave epoxide conversions of 92%; (ee 48%) in 9 h (Table 1, entry 13), > 99% (ee 35%) in 7.5 h (entry 14), and > 99% (ee 47%) in 3.5 h (entry 15), respectively. Moreover, the initial rate constants, $k_{obs}$, during the initial 2 h of this reaction suggest that the two catalytic units do not operate in isolation but interact. The cause of this behavior is unknown.

The literature shows that axial bases have a pronounced effect on the reactivity and selectivity of the enantioselective epoxidation reaction. In the case of chiral monomeric $Mn^{III}$ salen complexes, 4-phenylpyridine *N*-oxide (4-PhPyNO) is reported to (a) stabilize the formation of catalytically active metal oxo species and (b) act as a phase-transfer reagent in transporting HOCl from the aqueous to the organic phase under biphasic reaction conditions. We therefore studied the effect of axial bases such as 4-(3-phenylpropyl)pyridine *N*-oxide (4-PPPyNO), 4-PhPyNO, and DMSO on the epoxidation of STR as a model substrate in dichloromethane using

Table 2
Effect of different axial bases on enantioselective epoxidation of (STR) catalyzed by complexes **1a** and **1b** with NaOCl

| Entry | Catalyst | Axial base | Conversion (%) | Time (h) | ee (%) | TOF × $10^{-3}$ |
|---|---|---|---|---|---|---|
| 16 | **1b** | — | 20 | 7 | 52 | 0.39 |
| 17 (18) | **1a** (**1b**) | PyNO | > 99 (> 99) | 3 (3) | 47 (62) | 4.62 (4.62) |
| 19 (20) | **1a** (**1b**) | 4-PhPyNO | > 99 (> 99) | 2.5 (2.5) | 45 (61) | 5.50 (5.50) |
| 21 (22) | **1a** (**1b**) | 4-PPPyNO | > 99 (> 99) | 2 (1.6) | 46 (60) | 6.87 (8.59) |
| 23 (24) | **1a** (**1b**) | DMSO | 50 (80) | 6 (5) | 46 (57) | 1.16 (2.22) |
| 25 | — | PyNO | — | 24 | — | — |

Table 3
Effect of solvent on epoxidation of styrene using catalyst **1b** in the presence of Py N–O as axial base

| Solvent | Time (h) | Conversion (%) | ee |
|---|---|---|---|
| $CH_2Cl_2$ | 3 | > 99 | 62 |
| $CH_3OH$ | 6 | > 99 | 36 |
| $CH_3CN$ | 2.5 | > 99 | 46 |
| $CH_3COOC_2H_5$ | 4 | > 99 | 57 |

catalysts **1a** and **1b** (Table 2). Of all the axial bases used, 4-PPPyNO had the highest turnover frequency with catalysts **1a** and **1b** (entries 21, 22) followed by 4-PhPyNO (entries 19, 20), and Py N–O (entries 17, 18) while DMSO (23, 24) was least effective. We reported the same trend with the dimeric catalyst [14], which is in agreement with the $Mn^{III}$ salen complexes [25]. In the absence of an axial base the conversion of STR was only 20% after 7 h (entry 16) (Table 2), indicating a significant contribution of the axial bases in the catalytic reactions. Furthermore, the epoxidation of STR in the presence of Py N–O (no catalyst added) with NaOCl did not occur (entry 25).

The choice of solvent has a significant effect on the activity and the selectivity of the chiral $Mn^{III}$ salen complexes [26,27]. We studied the effect of various solvents on the epoxidation of STR using complex **1b** as a representative catalyst (Table 3). Although complete conversion to the product epoxide was achieved in all cases, the solvent dichloromethane had the best effect on the reaction time and enantioselectivity.

The recovered catalysts, **1a** and **1b**, were reused with the NaOCl and Py N–O system with STR as the substrate (Table 4). After each use, the catalyst was precipitated from the reaction mixture by the addition of hexane. In subsequent catalytic runs, the precipitated catalyst, dried in vacuum, was used without further purification. However, the epoxidation reaction proceeded only after the addition of fresh Py N–O (axial base). Furthermore, the activity of the recycled catalyst after successive epoxidation indicates degradation of the catalyst and/or physical loss during the recovery process. However, the ee of the product did not decrease.

To understand the mechanism of the epoxidation reaction, kinetic investigations were carried out with a representative

Table 4
Enantioselective epoxidation of (STR) with recycled catalysts **1a** and **1b** and PyNO as the axial base with NaOCl

| Run | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Time (h) | 3 (3) | 5.5 (5) | 7 (8) | 8 (9) | 10 (12) |
| Conversion | 100 (99) | 100 (99) | 80 (99) | 70 (60) | 62 (50) |
| ee | 47 (62) | 47 (59) | 47 (60) | 47 (59) | 47 (59) |

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

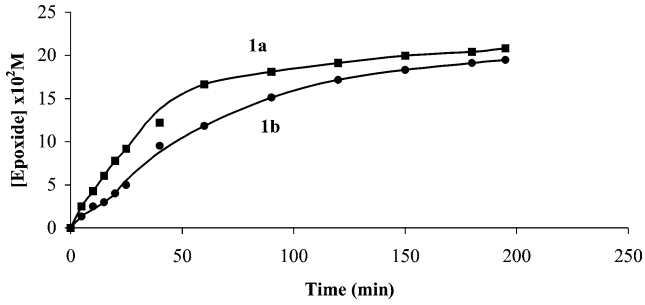



Fig. 1. Time-dependent plot of the formation of epoxide at 0 °C for catalysts **1a** and **1b** [catalyst] = $0.42 \times 10^{-2}$ M, [STR] = $20.82 \times 10^{-2}$ M, [oxidant] = $89.96 \times 10^{-2}$ M.

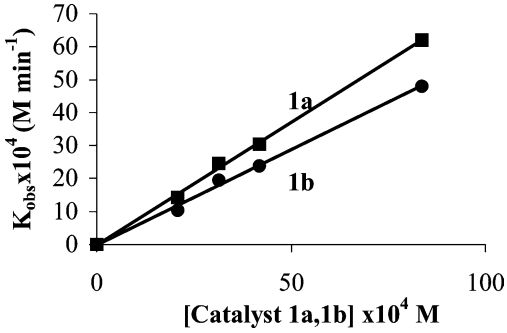



Fig. 2. Plot of catalysts [**1a**, **1b**] versus $k_{obs}$ at 0 °C, [STR] = $20.82 \times 10^{-2}$ M and [oxidant] = $89.96 \times 10^{-2}$ M.

substrate, STR, and catalysts **1a** and **1b** in the presence of NaOCl as the oxidant and Py N–O as the axial base; the concentrations of the catalysts, the oxidant, and STR were varied. At the beginning of epoxidation reaction, the kinetic runs showed a liner plot; saturation was achieved by the end of the reaction (Fig. 1). Based on these results the initial rate constants $k_{obs}$ (up to the linear portion of the graph) were determined by estimating the amount of epoxide formed by the end of the reaction.

The kinetic data for the epoxidation of STR with various concentrations of catalysts **1a** and **1b** gave linear plots of the $\log k_{obs}$ versus log[catalyst], with unit slopes ($d \log k_{obs}/d \log[\text{catalyst}] = 1$) suggesting that the epoxidation of STR is first order with respect to the concentrations of the catalysts (Fig. 2). Further, the plots of the rate constants ($k_{obs}$) versus the concentration of oxidant ($d \log k_{obs}/d \log[\text{oxidant}] \sim 1$) also showed first-order dependence of the reaction on the oxidant concentration (Fig. 3). Whereas, zero-order dependence was observed for the initial concentration of STR ($10.41–41.64 \times 10^{-2}$ M) at

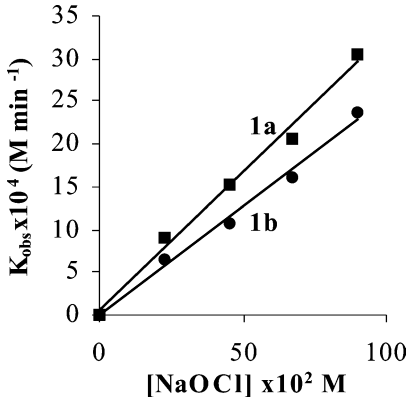
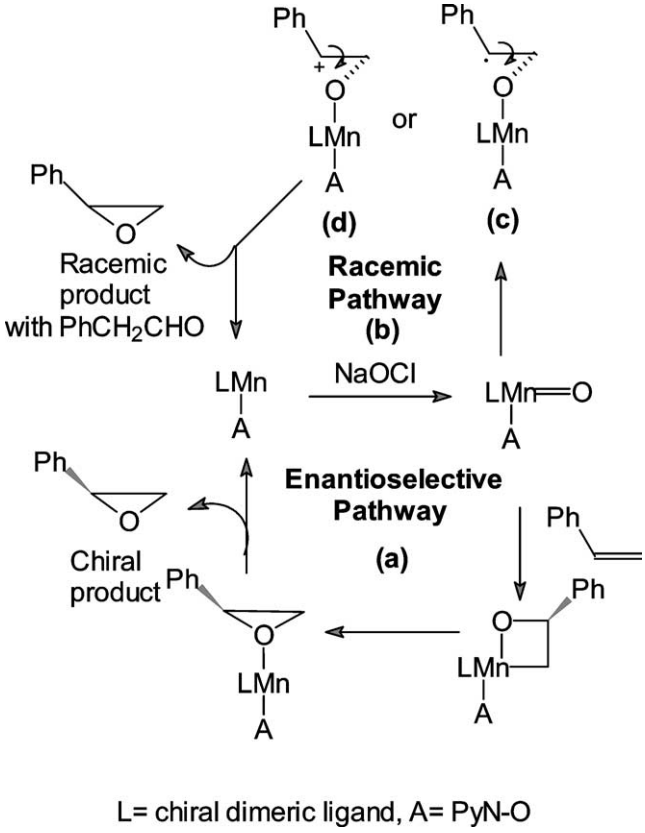



Fig. 3. Plot showing linear dependence of $k_{obs}$ with respect to the concentration of oxidant for epoxidation of styrene at 0 °C, [**1a**, **1b**] = $0.42 \times 10^{-2}$ M and [STR] = $20.82 \times 10^{-2}$ M.




Scheme 2. Proposed mechanism for Mn(III) salen complexes **1a** and **1b**.

constant concentration of the other reactants and the physical conditions. Zero-order kinetics in the catalytic epoxidation of alkenes at higher alkene concentrations and a first-order dependence for alkene at lower concentrations [30,31] have been reported for the $Mn^{III}$ salen complexes as catalysts and NaOCl [28] and HOCl [29] as oxidants. In our kinetic runs, neat styrene epoxide was found without side products, supporting the zero-order dependence on substrate at reasonably high concentrations.

Based on the kinetic measurements and product distribution, Scheme 2 represents the probable mechanism. The

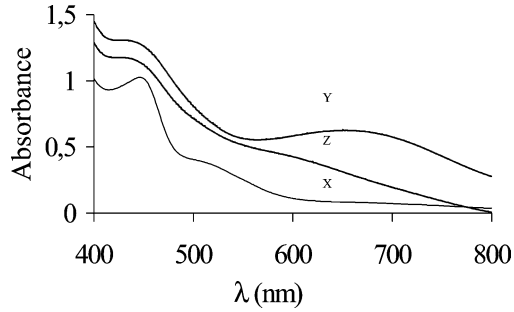



Fig. 4. UV–vis spectra with 0.2 mM solution of **1b** in $CH_2Cl_2$ with Py N–O (**X**), with oxidant (**Y**), on addition of substrate (STR) (**Z**).

literature [32] establishes that Py N–O (A) occupies the axial position in the $Mn^{III}$ salen complex, and that the resulting complex reacts with the oxidant to form an oxo complex, (L(A)Mn=O) in the rate-determining step. The formation of the (L(A)Mn=O) complex is proposed on the basis of spectroscopic measurements as well as on our kinetic results, which show first-order dependence on the catalyst and oxidant concentrations. The interaction of alkene with the oxo complex occurs relatively fast to selectively yield the epoxide through oxygen atom transfer at the olefinic bond. The alkene interacts with (L(A)Mn=O) and probably follows the route of manganaoxetane formation [33], (enantioselective pathway **a**, Scheme 2) to selectively give the epoxide and the catalyst (L(A)Mn) in its original form. However, in the absence of absolute chiral induction with the substrate STR, the racemic pathway (**b**) through the formation of a radical intermediate (**c**), which is largely responsible for the racemization due to the rotation of the C–C bond, cannot be ruled out. This pathway has been proposed especially in the case of conjugated alkenes, resulting in *cis*/*trans* isomerization [34]. Racemization may also occur via a radical pathway, which may result in the formation of a carbocationic intermediate (**d**), which is largely responsible for the formation of an aldehyde [35]. In all our catalytic epoxidation reactions, the formation of epoxide only (with almost absolute enantioinduction in case of substituted chromenes) and the absence of aldehyde suggest that pathway (**a**) is probably operative in this system.

Spectroscopic investigations were carried out to show the formation of (L(A)Mn=O) as a catalytically active species in the $Mn^{III}$ salen-catalyzed epoxidation of alkene. Fig. 4 shows a stepwise overlay of UV–vis spectra for complex **1b** in $CH_2Cl_2$ at 0 °C. (**X**) is the spectrum of catalyst **1b** with Py N–O, with a peak at 515 nm, typical of $Mn^{III}$ salen complexes [36]. Upon the addition of NaOCl as the oxidant to this solution, the solution becomes dark brown, and a new absorption band develops around 650 nm; this is commonly reported with NaOCl [35] and other oxidants such as PhIO, *t*-BuOOOH [36]. This spectral change is attributed to the formation of (L(A)Mn=O) (**Y**). After the addition of the substrate STR, a spectrum (**Z**), appeared which is similar to the original complex **1b** (**X**). This supports our observation that the L(A)Mn=O species is involved in the oxygen atom

transfer and is consistent with earlier reports on $Mn^{III}$ salen complexes [28,36].

## 4. Conclusion

We found new recyclable homochiral dimeric $Mn^{III}$ salen complexes, in which two $Mn^{III}$ salen units are linked by a carbon atom bearing geminal methyl groups. These complexes were used as epoxidation catalysts for nonfunctionalized alkenes. Excellent conversions were obtained for all the alkenes, but $> 99\%$ chiral induction was obtained only with the methoxy and cyano chromenes. The catalysts were reused up to five times without purification, the reactivity of the catalyst decreased gradually with successive use, possibly due to physical loss and degradation of catalyst **1a**/**1b** during recovery and epoxidation. The catalyst loading was reduced by more than half without having an adverse effect on the activity and selectivity, suggesting that the two units in the dimer work together. The kinetic investigations of a representative substrate STR show first-order dependence on the concentrations of the catalysts **1a** and **1b**, the oxidant, but no dependence on the initial substrate concentration. During epoxidation, the catalysts oxidized to form catalytically active (L(A)Mn=O) species in the rate-determining step; which, upon interaction with alkene, selectively give the epoxide product with moderate to high chiral induction through the formation of a manganaoxetane intermediate.

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