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Reusable chiral macrocyclic Mn(III) salen complexes for enantioselective epoxidation of nonfunctionalized alkenes

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ABSTRACT

A series of new chiral monomeric and dimeric macrocyclic Mn(III) salen complexes **1**–**4** with trigol linker were synthesized, characterized (by microanalysis, IR spectroscopy, UV–vis. spectroscopy, optical rotation, and mass spectrometry), and used as catalysts in the enantioselective epoxidation of styrene, *cis* β-methyl styrene, indene, and chromenes in the presence of several *N*-oxides as an axial base and NaOCl as an oxidant at 0 °C. With the use of chiral dimeric macrocyclic catalyst **3** (2.5 mol%), enantio-pure epoxides were achieved in excellent yields (>99%) and enantioselectivities (ee up to 98% in selected cases). The recycling was demonstrated with complex **4** (recyclable up to six cycles studied with retention of enantioselectivity) in the asymmetric epoxidation of styrene. The kinetic investigation with complex **4** for the epoxidation of styrene as the representative substrate showed the first-order dependence on the catalyst and the oxidant but independent on the initial concentration of the substrate.

1. Introduction

The design and development of chiral catalysts that can lead to enantioselectivity in the epoxidation of nonfunctionalized alkenes for the formation of enantio-pure epoxides constitutes a major challenge in asymmetric synthesis [1–20]. In this context, considerable success has been achieved in the asymmetric epoxidation of nonfunctionalized alkenes catalyzed by various chiral catalysts [13–17], noteworthy among them are chiral Mn(III) salen complexes initially developed by Jacobsen and Katsuki [6,7,9–11,18–20]. Meunier and co-workers reported multi-step synthesis of macrocyclic version of the chiral Mn(III) salen complexes to catalyze enantioselective epoxidation of *cis*-olefins [21,22] and also attempted catalyst recycling with limited success. Moreover, the creation of macrocycle was through polyether linker at 3,3′ positions of salicylidine moiety that made the synthesis of macrocycle complicated. Although excellent activity and enantioselectivity was achieved with Mn(III) salen complexes, recyclability of the expensive chiral catalysts remains an important and challenging goal to cut down the high production cost of desired enantio-pure epoxides. To address this issue, heterogeneous chiral catalysts were developed by anchoring chiral Mn(III) salen complexes on polymer supports [23,24], inorganic solid supports of varied porosity [23,25–37], polysiloxane membranes [38], and in ionic liquids [39,40]. Alternatively, homogeneous catalysts were also made recyclable [41–43] by manipulating the solubility of the catalyst such that the catalysis is performed under the homogeneous condition, but in a post-catalytic step, the catalyst is precipitated out by the addition of a solvent in which the catalyst is insoluble. In this context, our group has earlier reported the straightforward synthesis of chiral macrocyclic salen ligands linked through 1,3-phenylene-bis-(methylene)-bis-(oxy) moiety at 5,5′ positions of salen unit [44]. The Mn(III) complexes of these macrocyclic salen ligands performed well in enantioselective epoxidation of nonfunctionalized alkenes under biphasic reaction condition in the presence of Py*N*O an axial base at 0 °C. Still, only 2 recycle runs were possible with these catalysts. It would not be out of context to mention here the high solubility of Jacobsen's Mn(III) salen complex (soluble even in hexanes) due to moderate molecular weight and highly hydrophobic character. Keeping these facts in mind, we have designed new monomeric and dimeric macrocyclic Mn(III) salen complexes **1**–**4** of relatively high molecular weights incorporating a flexible and hydrophilic trigol linker through 5,5′ positions of salen. These catalysts were used for enantioselective epoxidation of representative nonfunctionalized alkenes viz., styrene, *cis* β-methyl styrene, indene, and chromenes using NaOCl as an oxidant in the presence of Py*N*O as an axial base at 0 °C. Excellent yield (up to 99%) of epoxides with high chiral induction (ee 98%) was achieved in the case of 6-cyano-2,2-dimethylchromene. In order to understand the mechanism of epoxidation reaction, kinetic investigations were carried out using complex **4** as a catalyst and styrene as a representative substrate with NaOCl as an oxidant in the presence of Py*N*O at 0 °C. The kinetic profile

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obtained has shown first-order dependence on concentrations of catalyst and oxidant and independent on initial concentration of the substrate. Based on kinetic, catalytic, and experimental evidence, a probable mechanism of the epoxidation reaction is suggested.

2. Experimental

2.1. Methods and materials

Manganese acetate (SD Fine Chem. Ltd.), 1*S*,2*S*-(−)-1,2-diphenylethane-1,2-diamine and 1*S*,2*S*-(+)-1,2-diaminocyclohexane (Sigma Aldrich) were used as received. Indene and styrene (Fluka) were passed through a bed of neutral alumina before use. All chromenes were synthesized according to the reported procedures [45,46]. All the solvents were purified prior to use [47]. 3-*t*-Bu-5-chloromethyl-2-hydroxy benzaldehyde was synthesized by the reported procedure [48]. Trigol bis-aldehyde **c** was prepared by our earlier reported method [49].

Microanalysis of the intermediates, ligands, and catalysts was carried out on a Perkin Elmer 2400 CHNS analyzer. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 200 MHz or 500 MHz spectrometer at ambient temperature using TMS as an internal standard. FTIR spectra were recorded on a Perkin Elmer Spectrum GX spectrophotometer as KBr pellet. Electronic spectra of chiral macrocyclic Mn(III) salen complexes were recorded in methanol and dichloromethane on a Varian Cary 500 Scan UV–vis.–NIR spectrophotometer. Optical rotations of chiral intermediates and chiral complexes were recorded on an automatic polarimeter (digipol 78, Rudolph) instrument. All the melting points reported here were determined on a Mettler Toledo-FB62 and were uncorrected. High-resolution mass spectra were obtained with a LC–MS (Q-TOFF) LC (Waters), MS (Micromass), MALDI-TOF, Model make Ultra flex TOF/TOF, Burker Daltonics, Germany instruments. For product purification, flash chromatography was performed 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 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 used as carrier gas (rate 30 mL/min). Injection port and detector temperature was kept at 200 °C. For the product analysis of styrene and indene, the column temperature was programmed at 70–140 °C, while 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 of styrene oxide was determined on GC using a chiral capillary column (Chiraldex GTA). For the chromenes and indene epoxides, the ees were determined on HPLC (Shimadzu SCL-10AVP) by using a Chiralcel column (OD and OB).

2.2. Synthesis of chiral monomeric macrocyclic salen ligands *1′* and *2′*

In a single-necked 50 mL round-bottom flask bis-aldehyde **c** (0.72 g, 1.5 mmol) was taken in dry MeOH (10 mL) and was stirred at 0 °C, and a solution of 1*S*,2*S*-(+)-1,2-diaminocyclohexane (0.18 g,1.6 mmol)/1*S*, 2*S*-(−)-1,2-diphenylethane-1,2-diamine (0.34 g,1.6 mmol) in dry MeOH (5 mL) was added drop wise to the above solution. After complete addition, the resulting solution was further stirred at room temperature. After an interval of 12 h, solvent was completely removed under reduced pressure, and the bright yellow solid was extracted with dichloromethane (50 mL). The organic layer was washed with water (3 × 50 mL) and with brine (3 × 50 mL) and finally dried over anhydrous Na_2SO_4. After removal of dichloromethane under reduced pressure, the chiral ligands **1′** and **2′** purified by silica gel column chromatography (100–200 mesh) in 20% (EtOAc: Hexane) resulted in yellowish solid monomeric macrocyclic ligands, **1′** and **2′**.

1′: Yield 85%. m.p. 104 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.44 (18 H, s), 1.73–1.91 (8H, m), 3.23–3.25 (2H, m), 3.31–3.33 (4H, m), 3.51–3.62 (8H, m), 4.19 (2H, d, J = 11), 4.43 (2H, d, J = 11), 6.72 (2H, s), 7.27 (2H, s), 8.07 (2H, s), 11.78 (2H, br) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 24.3, 29.4, 32.7, 34.8, 68.5, 69.2, 70.7, 72.3, 76.4, 118.3, 127.3, 129.8, 137.4, 160.0, 166.2 ppm. FT-IR (KBr): ν 3432, 2942, 2863, 2359, 1629, 1558, 1442, 1387, 1259, 1212, 1099, 970, 845, 768, 728, 668, 594 cm^{-1}. $[\alpha]_D^{27} = +195^\circ$ (c = 0.052, CH_2Cl_2). Anal. Calcd. for $C_{36}H_{52}N_2O_6$: C, 71.02; H, 8.61; N, 4.60. Found C, 71.0; H, 8.58; N, 4.58. TOF-MS (ESI+): m/z Calcd. for [$C_{36}H_{52}N_2O_6$] 608.81, Found 610.2 [M+H].

2′: Yield 90%. m.p. 98 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.46 (18H, s), 3.30–3.36 (4H, m), 3.57–3.68 (8H, m), 4.19 (2H, d, J = 10), 4.47 (2H, d, J = 10), 4.56 (2H, s), 6.72 (2H, d, J = 1.8), 7.18–7.30 (12H, m), 8.24 (2H, s), 13.86 (2H, br) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): 29.5, 33.9, 69.0, 70.8, 72.5, 78.6, 118.3, 127.5, 128.3, 128.4, 129.2, 137.4, 139.8, 160.1, 166.8 ppm. IR (KBr): ν 3452, 2929, 2865, 1626, 1553, 1440, 1263, 1096, 848, 726, 585, 464 cm^{-1}. $[\alpha]_D^{27} = -136^\circ$ (c = 0.206, $CHCl_3$). Anal. Calcd. for $C_{44}H_{54}N_2O_6$ C, 74.76; H, 7.70; N, 3.96. Found C, 74.73; H, 7.68; N, 3.93. TOF-MS (ESI+): m/z Calcd. for [$C_{44}H_{54}N_2O_6$] 706.91, Found 708.45 [M+H].

2.3. Synthesis of chiral dimeric macrocyclic salen ligands *3′* and *4′*

Bis-aldehyde **c** (0.53 g,1.1 mmol) in dry THF (1.2 mL) was taken in a single-necked 50 mL round-bottom flask to which the solution of 1*S*,2*S*-(+)-1,2-diaminocyclohexane (0.14 g,1.2 mmol)/1*S*,2*S*-(−)-1,2-diphenylethane-1,2-diamine (0.27 g, 1.2 mmol) in dry THF (0.6 mL) was added slowly and the resultant solutions were stirred at room temperature. After completion of the reaction (2 h) checked on TLC, the solvent was removed completely under reduced pressure. The bright yellow solids were extracted with dichloromethane (50 mL), and the organic layer was washed with water (3 × 50 mL), brine (3 × 50 mL) and finally dried over anhydrous Na_2SO_4. After removal of dichloromethane under reduced pressure, the chiral dimeric macrocyclic ligands **3′** and **4′** were purified by silica gel chromatography (100–200 mesh) with a EtOAc-to-Hexane of 3:2.

3′: Yield 96%. m.p. 76 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.38 (36H, s),1.67–1.93 (16H, m), 3.32 (4H, m), 3.55 (8H, t, J = 5), 3.61 (16H, t, J = 7), 4.37 (8H, s), 6.97 (4H, s), 7.20 (4H, s), 8.26 (4H, s), 13.86 (4H, br) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 25.0, 31.0, 34.7, 70.7, 72.2, 74.0, 74.8, 79.0, 119.8, 128.7, 131.2, 138.8, 161.6, 167.0 ppm; FT-IR (KBr): ν 3424, 2934, 2863, 2361, 1628, 1537, 1446, 1384, 1317, 1239, 1098, 940, 868, 785, 671, 563, 420 cm^{-1}. $[\alpha]_D^{27} = +171^\circ$ (c = 0.052, CH_2Cl_2). Anal. Calcd. for $C_{72}H_{104}N_4O_{12}$ C, 71.02; H, 8.61; N, 4.60. Found C, 71.05; H, 8.63; N, 4.62. MALDI-TOF: m/z Calcd. for [$C_{72}H_{104}N_4O_{12}$] 1217.62, Found 1218.19 [M+H].

4′: Yield 93%. m.p. 95 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.40 (36H, s), 3.53–3.63 (24H, m), 4.37 (8H, s), 4.71 (4H, s), 6.97 (4H, s), 7.19–7.29 (24H, m), 8.32 (4H, s), 13.78 (4H, br) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): 29.3, 34.8, 69.1, 70.6, 73.1, 80.0, 118.1, 127.6, 128.1, 128.3, 129.8, 137.3, 139.5, 159.9, 166.7 ppm. FT-IR (KBr): ν 3452, 2952, 2865, 2361, 1626, 1446, 1386, 1357, 1320, 1266, 1208, 1100, 1035, 936, 871, 801, 775, 573 cm^{-1}. $[\alpha]_D^{27} = -305^\circ$ (c = 0.108, $CHCl_3$). Anal. Calcd. for $C_{88}H_{108}N_4O_{12}$ C, 74.76; H, 7.70; N, 3.96. Found C, 74.75; H, 7.73; N, 3.98. MALDI-TOF: m/z Calcd. for [$C_{88}H_{108}N_4O_{12}$] 1413.82, Found 1414.19 [M+H].

2.4. Synthesis of chiral monomeric and dimeric macrocyclic Mn(III) salen complexes (1–4)

The chiral monomeric/dimeric macrocyclic salen ligands **1′**/**2′** (1 mmol) or **3′**/**4′** (0.5 mmol) were dissolved in 30 mL methanol to which $Mn(CH_3COO)_2{\cdot}4H_2O$ (294 mg; 1.2 mmol) was added in an inert atmosphere, and the reaction mixture was refluxed for 6 h. After completion of the reaction (checked on TLC), the reaction mixture was cooled to room temperature, lithium chloride (127 mg; 3 mmol) was added, and the mixture was further stirred for 3 h exposed to 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 anhydrous Na_2SO_4. After complete removal of the solvent, the desired complexes **1**–**4** were obtained as brown solid.

1: Yield 0.66 g, 95%. m.p. > 200 °C. IR (KBr): cm^{-1} 3434(br), 2928(s), 2859(s), 1616 (s), 1540 (s), 1435 (sh), 1386 (s), 1340 (w), 1304 (w), 1263 (w), 1234 (w), 1203 (m), 1162 (m), 1071 (w), 1024 (w), 826 (w), 785 (w), 663 (w), 563 (w), 483 (w), 420 (w). UV–vis. (MeOH), λ_{max} (nm) 402, 315, 256, 230. $[\alpha]_D^{27} = 880^\circ$ (c = 0.011, $CHCl_3$). Anal. Calcd. for $C_{36}H_{50}MnN_2O_6Cl$: C, 62.02, H, 7.23, N, 4.02, Found: C 62.04, H 7.26, N, 4.05. LC–MS: m/z Calcd. for $[C_{36}H_{50}ClMnN_2O_6]$ 696.27, Found 661.38 [M−Cl].

2: Yield 0.73 g, 92%. m.p. > 200 °C. IR (KBr): cm^{-1} 3434 (br), 2931 (s), 2860 (s), 1615 (s), 1540 (s), 1439 (sh), 1386 (s), 1340 (w), 1304 (w), 1265 (w), 1237 (w), 1201 (m), 1165 (m), 1069 (w), 1026 (w), 826 (w), 783 (w), 667 (w), 570 (w), 483 (w), 420 (w). UV–vis. (MeOH), λ_{max} (nm) 402, 291, 255, 228. $[\alpha]_D^{27} = 630^\circ$ (c = 0.011, $CHCl_3$). Anal. Calcd. for $C_{44}H_{52}MnN_2O_6Cl$: C, 66.45, H, 6.59, N, 3.52, Found C 66.42, H 6.56, N, 3.49. LC–MS: m/z Calcd. for $[C_{44}H_{52}ClMnN_2O_6]$ 794.29, Found: 759.60 [M−Cl].

3: Yield 1.3 g, 93%. m.p. > 200 °C. IR (KBr): cm^{-1} 3438 (br), 2935 (s), 2862 (s), 1614 (s), 1541 (s), 1437 (sh), 1387 (s), 1341 (w), 1306 (w), 1265 (w), 1238 (w), 1201 (m), 1162 (m), 1090 (w), 1026 (w), 824 (w), 781 (w), 663 (w), 564 (w), 484 (w), 421 (w). UV–vis. (MeOH), λ_{max} (nm) 405, 297, 259, 230. $[\alpha]_D^{27} = 1356^\circ$ (c = 0.01, $CHCl_3$). Anal. Calcd. for $C_{72}H_{100}Mn_2N_4O_{12}Cl_2$: C, 62.02, H, 7.23, N, 4.02, Found C 62.00, H 7.19, N, 4.00.LC–MS: m/z Calcd. for $[C_{72}H_{100}Cl_2Mn_2N_4O_{12}]$ 1392.55, Found: 1357.96 [M−Cl].

4: Yield 1.48 g, 93%. m.p. > 200 °C. IR (KBr): cm^{-1} 3438 (br), 2919 (s), 2865 (s), 1613 (s), 1541 (s), 1456 (sh), 1387 (s), 1342 (w), 1306 (w), 1265 (w), 1235 (w), 1202 (m), 1163 (m), 1090 (w), 1023 (w), 824 (w), 775 (w), 671 (w), 572 (w), 484 (w), 421 (w). UV–vis. (MeOH), λ_{max} (nm) 418, 341, 259, 230. $[\alpha]_D^{27} = 749^\circ$ (c = 0.075, $CHCl_3$). Anal. Calcd. for $C_{88}H_{104}Mn_2N_4O_{12}Cl_2$: C66.45, H, 6.59, N, 3.52, Found: C 66.4 3, H 6.52, N, 3.5 4. LC–MS: m/z Calcd. for $[C_{88}H_{104}Cl_2Mn_2N_4O_{12}]$ 1588.58, Found 1553.61 [M−Cl].

2.5. General procedure for enantioselective epoxidation of nonfunctionalized alkenes using NaOCl as an oxidant

Enantioselective epoxidation reactions of different alkenes viz. styrene (STR), *cis* β-methyl styrene, indene (IND), 2,2-dimethylchromene (CHR), 6-cyano-2,2-dimethylchromene (CN-CHR), 6-nitro-2,2-dimethylchromene (NO_2-CHR), 6-methoxy-2,2-dimethylchromene (MeO-CHR), and spiro[cyclohexane-1,2-[2H][1] chromene] (Cy-CHR) (0.625 mmol) were performed using complexes **1**–**4** (1–5 mol%) as catalyst in dichloromethane (1 mL) in the presence of Py*N*O (6 mg, 0.063 mmol) as an axial base and buffered (pH 11.3) NaOCl (1.5 mmol added in 4 equal parts) as an oxidant at 0 °C. The progress of the reaction was monitored by GC analysis of the products using *n-tri*-decane (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 hexane and was used as such for further catalytic runs. Epoxides were purified by flash chromatography through a bed of neutral alumina using ethyl acetate and hexane (9:1) as eluent, and their enantiomeric excess (ee) was determined.

2.6. Recycling of the catalyst 2 and 4

At the end of the catalytic run (checked on GC), the organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was washed with water (3 × 50 mL) and brine (3 × 50 mL) and dried over anhydrous Na_2SO_4. After partial removal of CH_2Cl_2, the catalysts **2** and **4** were precipitated out from the solution by the addition of 20 mL hexane (Table 1, entry 17), dried and kept in a desiccator for further use.

2.7. Kinetic study

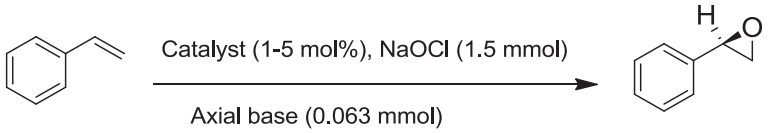
The catalyst **4** (0.20×10^{-2}–1.0×10^{-2} M) in 1.5 mL CH_2Cl_2 was stirred with Py*N*O (2×10^{-2} M) and styrene (10×10^{-2}–25×10^{-2} M) at 0 °C; the resulting solution was treated with NaOCl (40×10^{-2}–90×10^{-2} M) and stirred constantly. To determine the rates of epoxidation, aliquots were drawn from the reaction mixture on a regular interval, quenched with triphenylphosphine, and analyzed on GC.

3. Results and discussion

Chiral monomeric and dimeric macrocyclic Mn(III) salen complexes **1**–**4** were prepared as shown in Scheme 1. Thus, in a stepwise manner, 3-*t*-butyl salicylaldehyde was chloromethylated to give **a** [48], which on reaction with trigol **b** gave trigol bis-aldehyde **c** in the presence of NaH [49]. The compound **c** on condensation with equimolar quantities of diamines (1*S*,2*S*-(+)-1,2-diaminocyclohexane/1*S*,2*S*-(−)-1,2-diphenylethane-1,2-diamine) gave the ligands **1′**–**4′** in good yields with sufficient purity. It is worth mentioning that when condensation reaction was carried out in MeOH exclusively monomeric ligands **1′** and **2′**, while in THF entirely dimeric macrocyclic ligands **3′** and **4′** were formed. Complexation of the ligands **1′**–**4′** was done with Mn(II) acetate under refluxing condition in an inert atmosphere in MeOH. The addition of LiCl under aerobic reaction condition at RT to the above reaction mixture provided monomeric and dimeric macrocyclic Mn(III) salen complexes **1**–**4** in excellent yields.

Styrene (0.625 mmol) was used as a test substrate to evaluate the efficacy of catalysts **1**–**4** (5–2.5 mol%) in the asymmetric epoxidation reaction using Py*N*O as an axial base and NaOCl as an oxidant at 0 °C. It can be seen from entries 1–4 of Table 1 that dimeric complexes **3** and **4** are more reactive and enantioselective than complexes **1** and **2** at similar metal loading. This increase in reactivity and enantioselectivity can be attributed to the increase in active catalytic sites, which may be working in cooperation. This phenomenon of cooperation has been reported earlier by us and other groups for epoxidation [41–43,50] and other catalytic reactions [49,51]. However, among these the dimeric macrocyclic salen complex **4** performed better (conversion, >99% in 4 h; ee, 70%) than rest of the complexes **1**–**3**. Therefore, next we used this catalyst to optimize the reaction parameters such as catalyst loading, temperature, and solvent variations for asymmetric epoxidation of styrene as representative substrate with NaOCl as an oxidant. A decrease in catalyst loadings (entries 5 and 6) from the test-loading (entry 4) under similar reaction condition resulted in lowering of reaction rates and enantioselectivity. Whereas, an increase in the catalyst loading (5 mol%, entry 7) led to no observable improvement in the catalyst performance except for a decrease in reaction time. Hence, 2.5 mol% catalyst loading was taken as

Table 1
Screening of the catalysts **1**–**4**[a] for enantioselective epoxidation of styrene and optimization of the reaction conditions.



Entry	Catalyst	Catalyst loading	Axial base	Solvent	Time (h)	Yield (%)[b]	ee (%)[c]	TOF × 10^{-3} s^{-1}[e]
1	**1**	5	Py*N*O	CH_2Cl_2	6	>99	54[d]	0.93
2	**2**	5	Py*N*O	CH_2Cl_2	7	>99	62[d]	0.79
3	**3**	2.5	Py*N*O	CH_2Cl_2	3	>99	62[d]	3.70
4	**4**	2.5	Py*N*O	CH_2Cl_2	4	>99	70[d]	2.78
5	**4**	1	Py*N*O	CH_2Cl_2	4	72	58[d]	5
6	**4**	1.5	Py*N*O	CH_2Cl_2	4	80	63[d]	3.70
7	**4**	5	Py*N*O	CH_2Cl_2	3	>99	70[d]	1.85
8[¥]	**4**	2.5	Py*N*O	CH_2Cl_2	3	>99	52[d]	3.70
9[≠]	**4**	2.5	Py*N*O	CH_2Cl_2	1	>99	28[d]	11.11
10	**4**	2.5	Py*N*O	$CHCl_3$	3.5	>99	65[d]	3.17
11	**4**	2.5	Py*N*O	Toluene + $CHCl_3$	8	85	52[d]	1.18
12	**4**	2.5	Py*N*O	MeOH	6	>99	54[d]	1.85
13	**4**	2.5	PPy*N*O	CH_2Cl_2	3	>99	70[d]	3.70
14	**4**	2.5	PPPy*N*O	CH_2Cl_2	3	>99	70[d]	3.70
15	**4**	2.5	NMO	CH_2Cl_2	2.5	96	55[d]	4.27
16	**4**	2.5	–	CH_2Cl_2	12	31	32[d]	0.29
17[f]	**4**	2.5	Py*N*O	CH_2Cl_2	5	>99	70[d]	2.22

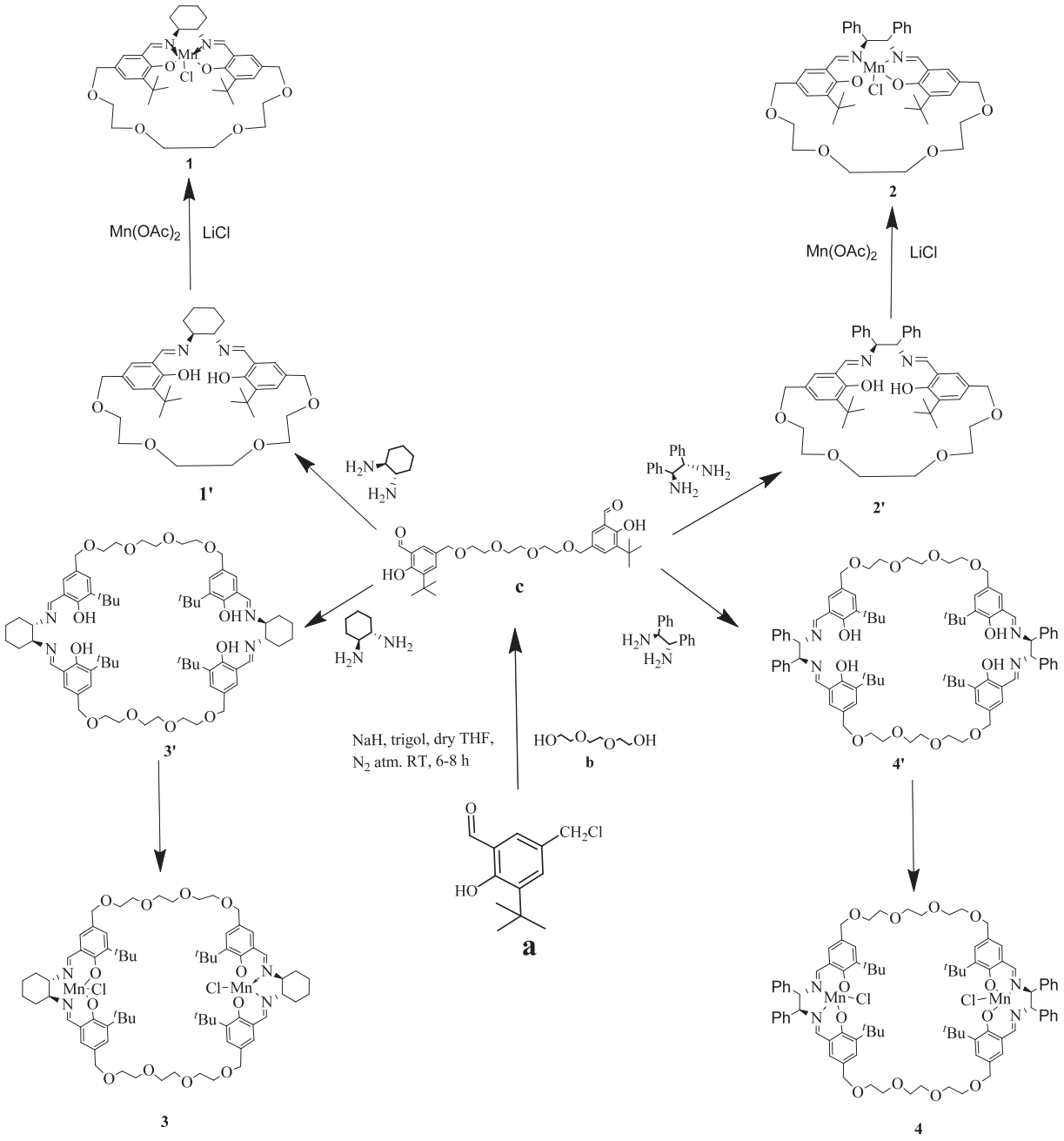
[a] Reaction condition: catalyst (1–5 mol% in 1 ml CH_2Cl_2), substrate (0.625 mmol), pyridine-*N*-oxide (0.063 mmol), NaOCl (1.5 mmol), reaction temp. 0 °C (¥ reaction temp. 10 °C, ≠ reaction temp. RT).
[b] Determined on GC.
[c] Chiral capillary column GTA-type.
[d] Epoxide configuration *S*.
[e] Turnover frequency is calculated by the expression [product]/[catalyst] × time (s^{-1}).
[f] Reaction condition: catalyst **4** (2.5 mol% in 20 ml CH_2Cl_2), substrate (10 mmol), pyridine-*N*-oxide (1 mmol), NaOCl (25 mmol), reaction temp. 0 °C.

optimum for varying reaction temperature from 0 °C to RT. As expected, there was a marked drop in the product ee on increasing the reaction temperature (entries 8 and 9). Having optimized catalyst loading (2.5 mol%) and reaction temperature (0 °C), variation in solvent was attempted as its effect on the reactivity and enantioselectivity of epoxidation reaction is well documented [23,52]. Accordingly, the epoxidation reaction was conducted in different solvents viz., $CHCl_3$, toluene + $CHCl_3$, and MeOH (entries 10–12). However, best results were obtained with the use of CH_2Cl_2 as solvent, which was used in our subsequent studies as preferred solvent (Fig. 1).

It is well-known in literature that the addition of pyridine-*N*-oxide derivatives in Mn(III) salen-based catalysts, employing NaOCl as an oxidant, improves both catalyst turnover and enantioselectivity [41]. The rationale behind this improvement is based on dual role of *N*-oxide, (a) *N*-oxides help in stabilizing the reactive Mn^V = O species and prevents the formation of Mn–O–Mn species, which is catalytically inactive [53] and (b) hydrophobic *N*-oxides viz., 4-phenylpyridine-*N*-oxide (4-PPy*N*O), and 4-(3-phenylpropyl) pyridine-*N*-oxide (4-PPPy*N*O) help in transporting HOCl from aqueous phase to the organic phase [54] where the catalyst and substrate actually reside. This led us to study the above mentioned axial bases and hydrophilic pyridine-*N*-oxide (Py*N*O) and *N*-methyl morpholine-*N*-oxide (NMO) for the epoxidation of styrene in dichloromethane with catalyst **4** (Table 1, entries 13–15) and NaOCl as an oxidant at 0 °C. Both 4-PPy*N*O and 4-PPPy*N*O worked well (reaction took 3 h to give the similar results); however, the results showed that there is no apparent advantage over the simple and inexpensive Py*N*O (Fig. 1). The reason behind this finding may be attributed to the introduction of trigol linkage in these macrocyclic Mn(III) complexes, which makes them relatively more hydrophilic and thus residing at the interface of organic and aqueous phase. In the event of this, the requirement of HOCl transportation to the organic phase is minimized, consequently, even hydrophilic Py*N*O is good enough for this catalytic system. This finding is in consonance with the earlier reported Mn(III) salen complexes [41,42]. Nevertheless, the use of Py*N*O in the epoxidation reaction is essential as its absence gave the product styrene oxide in 31% yield and 32% ee in 12 h (Table 1, entry 16).

The above optimization study was carried out by using styrene as a model substrate with catalyst **4** having 1,2-diphenylethane-1,2-diamine collar, which is known to give better ee in the product styrene oxide as compared to the catalysts with 1,2-diaminocyclohexane collar. However, for the substrates like chromenes [48] and indene [42], the salen catalysts with 1,2-diaminocyclohexane collar often work better. Due to this reason, we used the above optimized reaction condition in the epoxidation of chromenes and indene with all the catalysts **1**–**4** (Table 2). In all the cases, nearly quantitative yield of epoxides was obtained in 5.5–15 h, where the reactions were significantly faster and more enantioselective for dimeric complexes **3** and **4** as compared to their monomeric counterparts **1** and **2**. However, difference in the enantioselectivities obtained with the catalysts having 1,2-diaminocyclohexane and 1,2-diphenylethane-1,2-diamine collar remained within 1–4%. This shows that there is no significant role of the diamine collar in imparting enantio-induction in the product for the present catalyst design (Fig. 2). In terms of product configuration, the trend obtained with catalyst **1**–**4** followed the similar trend obtained for Jacobsen's catalyst. However, dimeric catalysts **3** and **4** were significantly better (entries 19 and 20; yield, >99%; ee, 96–98%) in terms of reactivity and enantioselectivity than Jacobsen's catalyst (entry 21; yield, 62%; ee, 92%) as exemplified with the cyano-chromene epoxidation reaction under similar metal loading and other reaction conditions.

To better demonstrate the applicability of this protocol at higher scale (~15 times than catalyst screening scale), styrene (10 mmol) epoxidation was conducted with catalyst **4** under the optimized reaction conditions (Table 1, entry 17). The reaction at this scale gave similar product yield and ee in 5 h as compared to 4 h taken at 0.625 mmol scale of styrene (Table 1, entry 4).



Scheme 1. Schematic representation for synthesis of catalyst **1**–**4**.

Catalyst recyclability experiments were conducted on a 10 mmol scale of styrene with catalyst **4** (2.5 mol%) with NaOCl as an oxidant in the presence of Py*N*O as an axial base in dichloromethane at 0 °C. After the catalytic run, the solvent was reduced to ca. one-fourth and the complex **4** was precipitated out by the addition of excess of *n*-hexane. The precipitated catalyst was washed thoroughly with hexane, dried in vacuum, stored under dry and inert atmosphere, and used as such for the subsequent catalytic run without further purification. The recovered catalyst worked well for the epoxidation of styrene in the same manner as that of the fresh catalyst. The recycling data as given in Table 3 suggest that the recovered catalyst **4** is stable and worked well for six cycles without significant loss in performance. However, there was some physical loss (~1–2% per recycle) of catalyst, and the amount of styrene was adjusted accordingly. This recycling protocol was also applied for the monomeric catalyst **2**. However, the recovery of the monomeric catalyst after the first cycle was only ~80% possibly due to its relatively higher solubility in *n*-hexane. Besides, after 3rd catalytic cycle, there was a change in catalyst color (from reddish brown to light brown) with marked decrease in product yield and ee, suggesting the relatively poor stability of monomeric complex under the epoxidation reaction condition than its dimeric counterpart.

In order to understand the mechanism of the epoxidation reaction, the kinetics of epoxidation of styrene as a representative substrate was investigated using catalyst **4** in the presence of Py*N*O as an axial base with NaOCl, as a function of the concentrations of catalysts, oxidant, and styrene at 0 °C. In all the kinetic runs, the plots for formation of styrene epoxide with time were found to be linear in the initial stage of the reaction, which attained

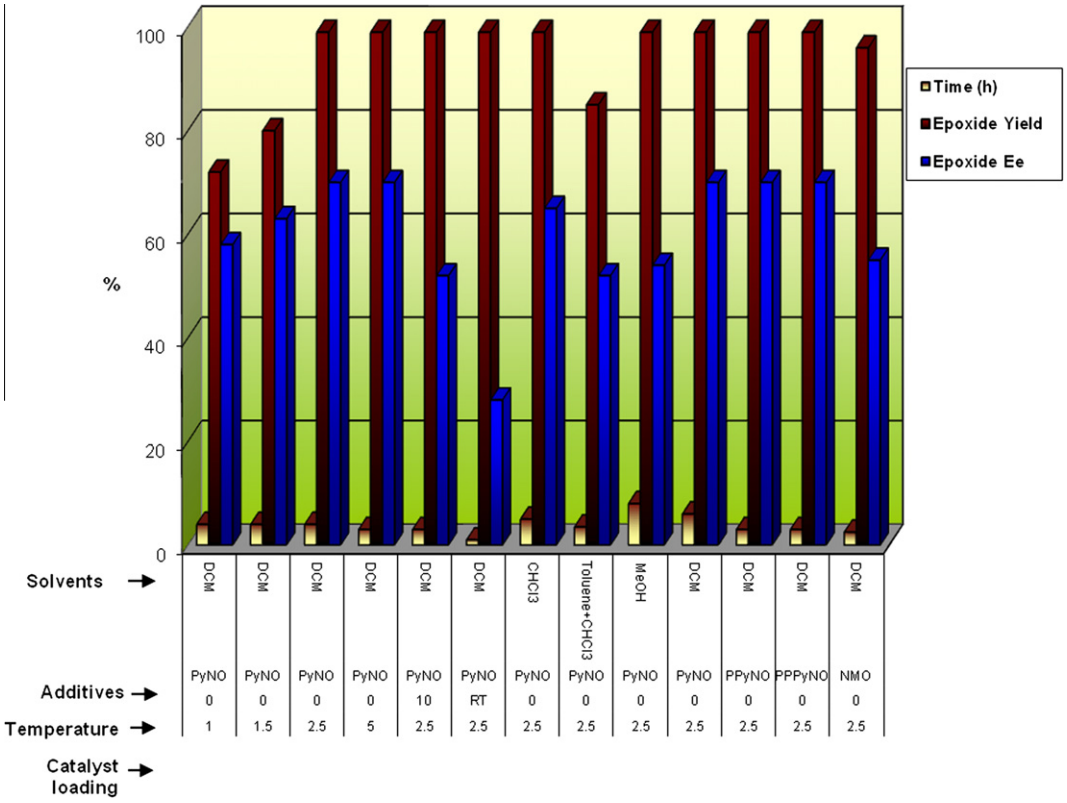
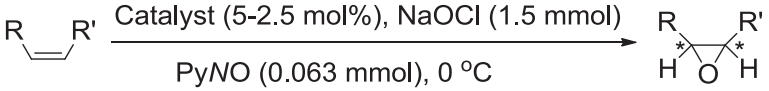


Fig. 1. Optimization of reaction conditions for enantioselective epoxidation of styrene with complex **4**.

Table 2
Product yield and ee data for the epoxidation of nonfunctionalized alkenes catalyzed by complexes **1–4**.[a]



Entry	Catalyst	Substrate	% Yield[b]	Time (h)	ee (%)	TOF × 10^{-3} s^{-1}[e]
1(2)	**1(2)***	IND[f]	>99(>99)	10(11)	84(82)[c]	0.56(0.51)
3(4)	**3(4)**≠		>99(>99)	7(7.5)	89(92)[c]	1.59(1.48)
5(6)	**1(2)***	CHR[g]	>99(>99)	14(14)	92(88)[d]	0.40(0.40)
7(8)	**3(4)**≠		>99(>99)	10(10)	94(90)[d]	1.11(1.11)
9(10)	**1(2)***	Cy-CHR[g]	>99(>99)	15(15)	85(87)[d]	0.37(0.37)
11(12)	**3(4)**≠		>99(>99)	10(10)	93(91)[d]	1.11(1.11)
13(14)	**1(2)***	MeO-CHR[g]	>99(>99)	15(15)	85(84)[d]	0.37(0.37)
15(16)	**3(4)**≠		>99(>99)	10(10)	93(95)[d]	1.11(1.11)
17(18)	**1(2)***	CN-CHR[g]	>99(>99)	10(10)	93(89)[d]	0.56(0.56)
19(20)	**3(4)**≠		>99(>99)	5.5(6)	98(96)[d]	2.02(1.85)
21	**Jacobsen***[h]	CN-CHR[g]	62	10	92[d]	0.34
22	**4**#	*cis*-β-Me sty[j]	>99[i]	8	93[b]	1.39

[a] Reaction condition: *catalyst loading (5 mol%), ≠ catalyst loading (2.5 mol%) in 1 ml CH_2Cl_2, substrate (0.625 mmol), pyridine-*N*-oxide (0.063 mmol), NaOCl (1.5 mmol).
[b] Determined on GC.
[c] Chiral HPLC OB column.
[d] Chiral HPLC OD column.
[e] Turnover frequency is calculated by the expression [product]/[catalyst] × time (s^{-1}).
[f] Product configuration: 1*S*,2*R*.
[g] Product configuration: 3*S*,4*S*.
[h] With (1*S*,2*S*)-1,2-diaminocyclohexane collar.
[i] Ratio of (E/Z) epoxide 17:83.
[j] *cis*-β-Me sty = *cis*-β-methyl styrene.

saturation near completion giving >99% styrene epoxide (Fig. 3). Based on these results, the initial rate constants k_{obs} (up to the linear portion of the graph) were determined by the amount of epoxide formed with respect to time.

3.1. Dependence of the reaction rate on catalyst concentration

The epoxidation of styrene was studied by conducting the epoxidation reaction at different concentrations (over a range of

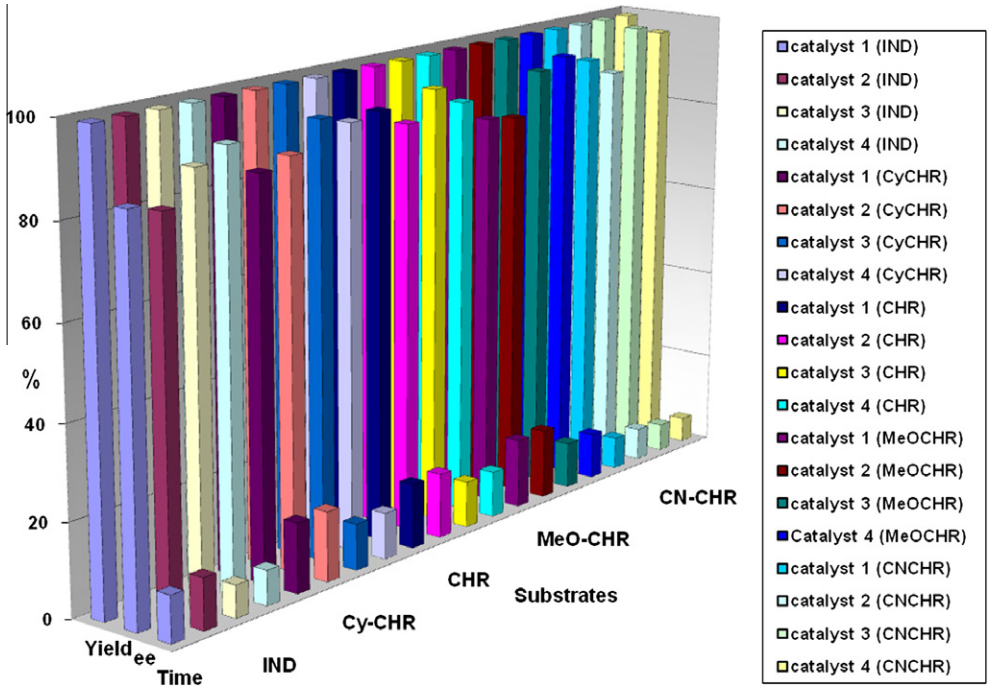


Fig. 2. Yield [%] and ee [%] of chiral epoxides with the catalysts **1**–**4**.

Table 3
Recyclability data of catalyst **4** in the enantioselective synthesis of styrene oxide using NaOCl as an oxidant and Py*NO* as an axial base.[a]

Run	Time (h)	Yield (%)	ee (%)
1	5	>99	70
2	5	>99	70
3	5	98	70
4	5	98	70
5	5	96	70
6	5	95	70

[a] Reaction condition: catalyst **4** (2.5 mol% in 20 ml CH_2Cl_2), substrate (10 mmol), pyridine-*N*-oxide (1 mmol), NaOCl (25 mmol), reaction temp. 0 °C.

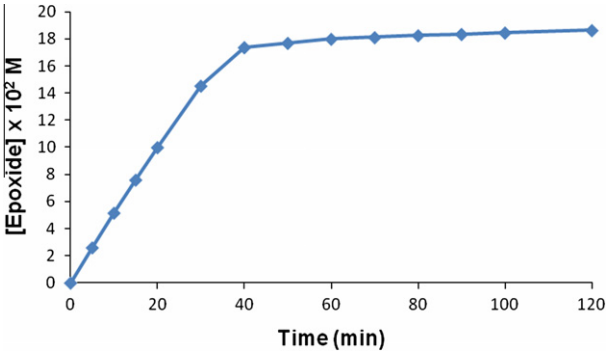


Fig. 3. Time-dependence plot of the formation of epoxide at 0 °C, [catalyst] = 0.005 M, [oxidant] = 0.8 M, and [styrene] = 0.2 M.

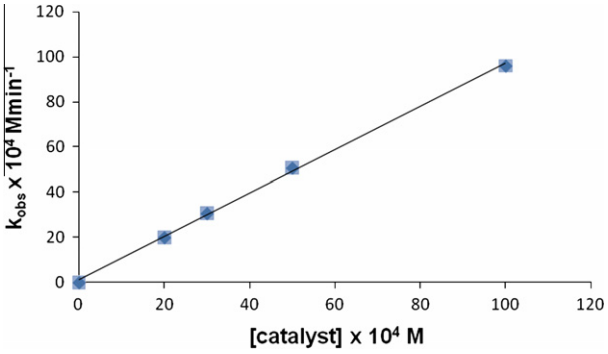


Fig. 4. Plot of catalyst concentration versus k_{obs} at 0 °C, [styrene] = 0.2 M, [oxidant] = 0.8 M.

Table 4
Dependence of the catalyst concentration for the epoxidation of styrene at 0 °C, [styrene] = 0.2 M, [oxidant] = 0.8 M, [Py*NO*] = 0.02 M.

[Catalyst] × 10^4 M	k_{obs} × 10^4 M min^{-1}
20	20.00
30	30.67
50	50.67
100	96.00

0.002–0.01 M) of catalyst **4**, keeping the concentrations of oxidant and styrene constant. A linear increase in the styrene epoxide formation was observed with an increase in the initial concentration of the catalyst **4**. The plot of the rate (k_{obs}) of the styrene epoxide formation versus the concentration of the catalyst **4** passed through the origin (Fig. 4), indicating the absolute necessity of the catalyst for the reaction to proceed under the experimental condition. On the other hand, the plot of the log k_{obs} versus log[catalyst] were found to be linear with unit slopes (d log k_{obs}/d log[catalyst]) ~1) that clearly indicated the first-order dependence of the rate of the epoxidation reaction with respect to the concentration of the catalyst **4**. The kinetic data of the catalyst dependence for the epoxidation of styrene are given in Table 4.

3.2. Dependence of the reaction rate on the concentration of oxidant

The effect of concentration of the oxidant on the rate of epoxidation of styrene was evaluated by varying oxidant concentration

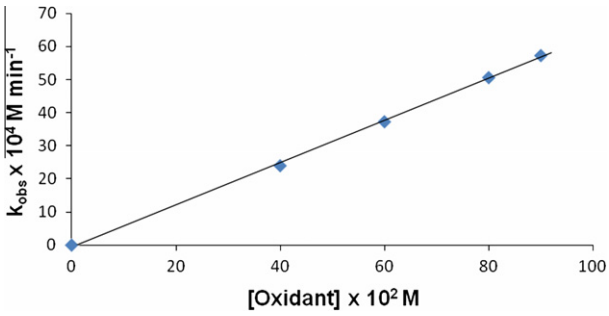


Fig. 5. Plot of oxidant concentration versus k_{obs} at 0 °C, [styrene] = 0.2 M, [catalyst] = 0.005 M.

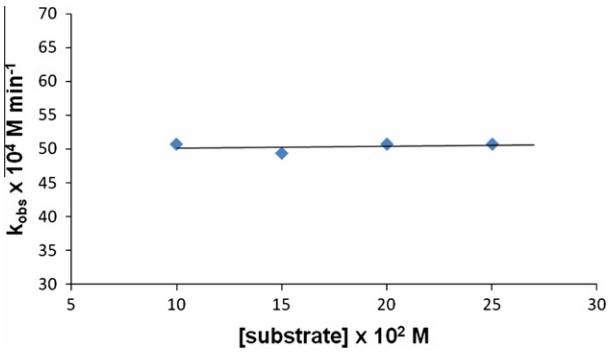


Fig. 6. Plot of substrate concentration versus k_{obs} at 0 °C, [catalyst] = 0.005 M, [oxidant] = 0.8 M.

Table 5
Dependence of the oxidant concentration for the epoxidation of styrene at 0 °C, [styrene] = 0.2 M, [catalyst] = 0.005 M, [Py*NO*] = 0.02 M.

[Oxidant] M	$k_{obs} \times 10^4$ M min^{-1}
0.4	24.00
0.6	37.33
0.8	50.67
0.9	57.33

Table 6
Dependence of the k_{obs} on the concentration of styrene at 0 °C, [catalyst] = 0.005 M, [oxidant] = 0.8 M, [Py*NO*] = 0.02 M.

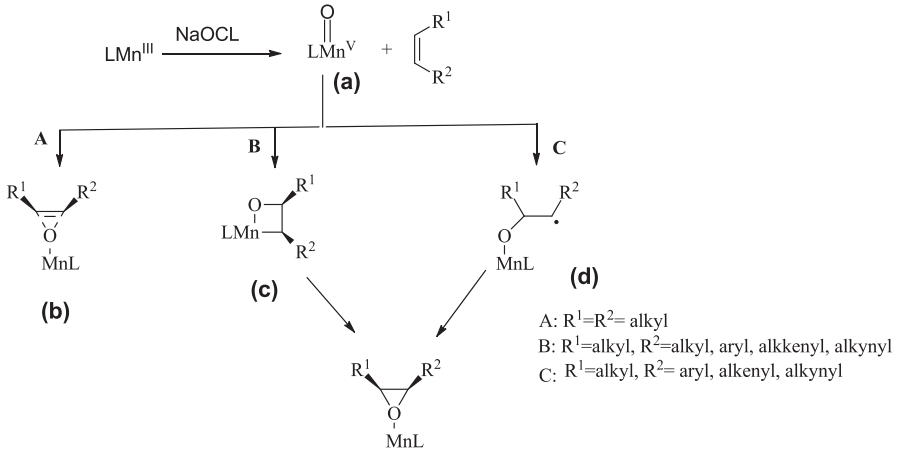
[Styrene] M	$k_{obs} \times 10^4$ M min^{-1}
0.10	50.67
0.15	49.33
0.20	50.67
0.25	50.67

over a range of 0.4–0.9 M, whereas the substrate and the catalyst concentration was kept fixed at 0.2 M and 0.005 M, respectively. Under the employed reaction concentration rate of the epoxidation increased linearly with an increase in initial concentration of oxidant (Fig. 5). The plot of the rate constant versus oxidant concentration further confirmed the first-order dependence of rate constant with oxidant concentration (d log k_{obs}/d log [oxidant] ~1) (Table 5).

3.3. Dependence of the reaction rate on the concentration of alkene

Kinetic experiments were conducted at different initial concentrations of styrene (Table 6) ranging from 0.1 M to 0.25 M, by keeping the other reaction parameters constant indicated a zero-order dependence of rate of the reaction with initial concentration of styrene (Fig. 6). The tendency of following zero-order kinetics during catalytic epoxidation of alkenes in terms of higher alkene concentrations has been reported earlier in Mn(III) salen-catalyzed epoxidation of nonfunctionalized alkenes using NaOCl [55], HOCl [56], and UHP as oxidants [57]. Possibly, at higher concentrations of the alkenes, the major contribution of the epoxidation reaction is toward the formation of epoxide from the alkene and contribution toward the side reaction is negligible. It is only at lower concentrations of the alkenes, the side reaction becomes significant. Under our experimental conditions, styrene epoxide was the only product, further supporting the zero-order dependence in styrene concentration at reasonably high concentrations.

On the basis of kinetics and experimental results, a probable mechanism for the epoxidation of alkene is proposed (Scheme 2) where the catalyst first gets oxidized by the oxidant, NaOCl to form an oxo complex $LMn^{V}=O$ (intermediate **a**) at the rate-determining step. According to Scheme 2, the epoxidation reaction may proceed via concerted oxygen atom attack (intermediate **b**, path A) or oxametalla-oxetane formation (intermediate **c**, Path B) to give selectively epoxide and the catalyst LMn^{III} back in its original form. The radical pathway C via an intermediate **d** has been proposed to be absent or insignificant (for the test substrate styrene) as there was no aldehyde formation [58] under our epoxidation reaction conditions. To further verify this statement, *cis*-β-methyl styrene



Scheme 2. Probable mechanisms for the chiral macrocyclic Mn(III) salen-catalyzed epoxidation: (A) concerted reaction; (B) reaction via metalla-oxetane intermediate; (C) reaction via a radical intermediate.

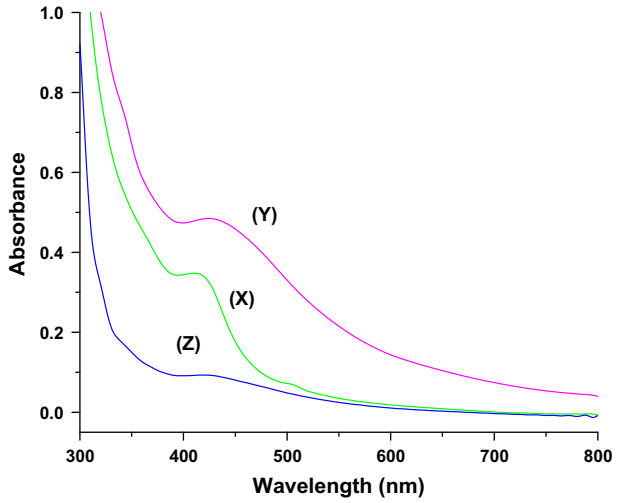


Fig. 7. UV–vis. spectra with 0.2 mM solution of **4** in CH_2Cl_2 with Py*N*O (**X**), with oxidant (**Y**), on addition of substrate, styrene (**Z**).

was used as a substrate for the epoxidation reaction using catalyst **4** under the optimized reaction condition. The (*E*/*Z*)-epoxide ratio of 17:83 (entry 22, Table 2), however, suggests that radical pathway cannot be entirely ruled out [59,60].

The spectroscopic investigations were carried out to further strengthen the assumption for the formation of $LMn^V=O$ as catalytically active species in Mn(III) salen-catalyzed epoxidation of alkene. A stepwise overlay of UV–vis. spectra for complex **4** in CH_2Cl_2 at 0 °C is shown in Fig. 7. Wherein (**X**) is the spectrum of catalyst **4** with Py*N*O, which shows a peak at 415 nm typically observed for Mn(III) salen systems [61]. The color of the solution changes to dark brown on addition of the oxidant–NaOCl to this solution with concomitant development of a new absorption band centered around 500 nm, (**Y**) the maximum of which is obscured by the tailing of strongly absorbing species at $\lambda > 500$ nm. This band is commonly reported with other oxidants like PhIO and *t*-BuOOOH as well [61] and is attributed to the formation of oxo complex $LMn^V=O$ (**Y**). After the addition of the substrate (styrene), it gave spectrum (**Z**) similar to the original complex **4** (**X**). These events support our assumption that $LMn^V=O$ species is involved at oxygen atom transfer stage and is consistent with earlier reports on Mn(III) salen complexes [55,61].

4. Conclusion

In conclusion, we have designed chiral monomeric and dimeric macrocyclic Mn(III) salen complexes with ether linkage at 5,5′ positions of the salen unit. These complexes worked very well as catalysts in the enantioselective epoxidation of nonfunctionalized alkenes with NaOCl as oxidants in the presence of inexpensive Py*N*O as an axial base at 0 °C. Among these complexes, the catalyst **4** was recycled six times with the retention of ee for the epoxidation of styrene with NaOCl as an oxidant. The catalyst **4** also gave similar performance at relatively higher scale of the styrene (~10 mmol) epoxidation.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jcat.2011.10.011.

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