Journal of Molecular Catalysis A: Chemical 366 (2013) 380–389

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Organic carbonates as solvents in macrocyclic Mn(III) salen catalyzed asymmetric epoxidation of non-functionalized olefins

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ARTICLE INFO

Article history:
Received 29 June 2012
Received in revised form 18 October 2012
Accepted 20 October 2012
Available online 30 October 2012

Keywords:
Asymmetric epoxidation
Organic carbonate
Macrocyclic Mn(III) salen complex

ABSTRACT

Organic carbonates, e.g., dimethyl carbonate and propylene carbonate were used as reaction media in enantioselective epoxidation of non-functionalized alkenes by using a series of chiral macrocyclic Mn(III) salen complexes (5 mol%) as catalyst with pyridine *N*-oxide as an axial base. This protocol worked effectively with urea hydrogen peroxide, as well as sodium hypochlorite as oxidants to give respective epoxides in high yields and ee (up to >91% in selected cases). Furthermore kinetic studies of the catalytic epoxidation reaction in dimethyl carbonate:methanol (optimized solvent mixture) with urea hydrogen peroxide as an oxidant showed first order dependence on catalyst and oxidant whereas it is zero order for the substrate, styrene.

1. Introduction

The correct choice of solvent is one of the central problems in the synthetic chemistry, for in many cases the physical and toxicological properties of a solvent have a pivotal influence on its use both in the laboratory and industrial scale [1]. A case in study here is the classic chiral Mn(III) salen catalyst that has shown high enantioselectivity for the asymmetric epoxidation of prochiral alkenes under homogeneous condition. Invariably, dichloromethane is used as preferred solvent for this reaction particularly with the oxidant NaOCl [2]. Notwithstanding environmental implications; very high catalyst solubility in this solvent also poses challenges in catalyst recyclability [2–4]. To make Mn(III) salen catalyst recyclable, strategies like its immobilization on organic polymers [5], inorganic supports [6–8], encapsulation in zeolite cavities [9], physical entrapment in siloxane membranes [10], tuneable solubility and multiphase methods have been reported. In the past, the ecologically sensible media have been used, notable among these are water [11–13], fluorinated hydrocarbons [14], supercritical CO_2 [15–18], and ionic liquids [19,20]. To our best knowledge there are no reports on the use of organic carbonates as solvent in asymmetric epoxidation reaction. Organic carbonates are polar aprotic solvents, which are noncorrosive, nontoxic and biodegradable, hence are safer, and environment friendly alternatives to conventionally used CH_2Cl_2 (DCM), tetrahydrofuran (THF) and other hazardous aromatic solvents [21,22]. For the present study we have employed our earlier reported macrocyclic Mn(III) salen complexes **1**, **2** [23] and two new but closely related complexes **3** and **4** for the epoxidation of several prochiral olefins in organic carbonates as reaction media using pyridine *N*-oxide (Py*N*O) as an axial ligand. This protocol worked equally well with sodium hypochlorite (NaOCl) and urea hydrogen peroxide (UHP) as oxidants in our initial exploratory experiment. However, due to the environment friendly nature of UHP, it was studied in detail. The present study revealed that dimethyl carbonate (DMC) could be a suitable replacement for chlorinated solvents like CH_2Cl_2 and gave comparable conversions (>99%) and enantioselectivities (ee, up to 91%) in the epoxidation of styrene, *cis*-β-methyl styrene, Indene and chromenes. Additionally, the use of DMC over DCM has allowed easy catalyst separation due to relatively lower catalyst solubility in the former solvent.

2. Experimental

2.1. Materials and methods

Indene and styrene (both from Fluka) were passed through a pad of neutral alumina before use. (*1R*,*2R*)-(+)-1,2-diphenyl-1,2-ethanediamine, (*1S*,*2S*)-(+)-1,2-diaminocyclohexane and 1-butyl-3-methylimidazolium hexaflurophosphate (BMIM-PF_6) were procured from Sigma–Aldrich. All chromenes [24,25] and

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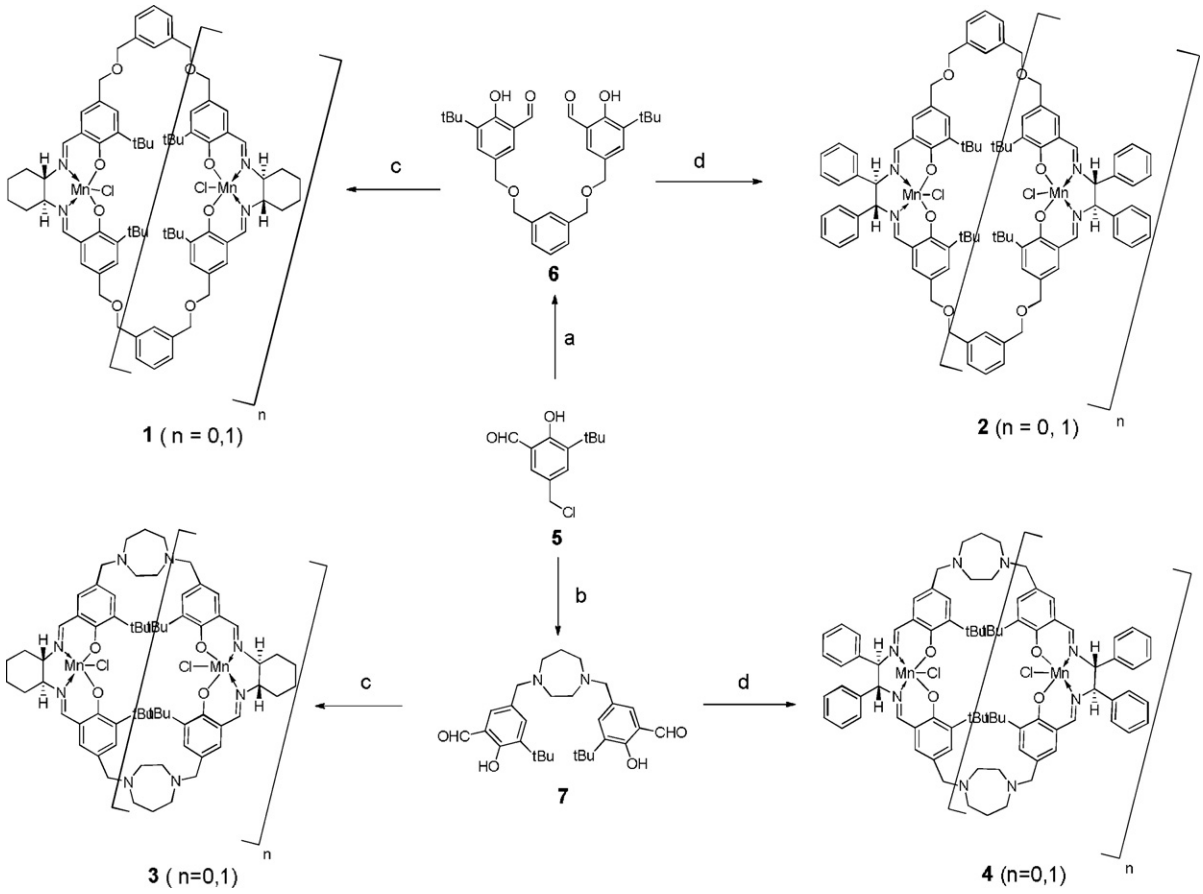
http://dx.doi.org/10.1016/j.molcata.2012.10.021



Scheme 1. Reaction conditions: (a) NaH, THF, 0 °C; (b) dry toluene, reflux; 2 h; (c) Step I: (*1S,2S*)-(+)-1,2-cyclohexane diamine, THF, RT, 2 h; Step II: $Mn(CH_3COO)_2{\cdot}4H_2O$, MeOH, LiCl; (d) Step I: (*1R,2R*)-(+)-1,2-diphenylethylene diamine, THF, RT, 2 h; Step II: $Mn(CH_3COO)_2{\cdot}4H_2O$, MeOH, LiCl.

3-*tert*-butyl-5-(chloromethyl)-2-hydroxy benzaldehyde were synthesized according to the reported procedures [26]. All the solvents were purified before use [27]. Analytical reagent grade propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC) (all from Spectrochem Pvt. Ltd., India), manganese acetate (SD Fine Chem. Ltd., India), NaOCl (14% aqueous solution, National Chemicals, India) and UHP (Merck) were used as received. Racemic epoxides were synthesized from their corresponding alkenes by racemic [Mn(III) (salen) Cl] complex and were purified by flash column chromatography. All the melting points reported here were determined on Thermo Scientific MET-TEMP (Model No. 1002D) and were uncorrected. Optical rotations of chiral intermediates and the chiral complexes were recorded on an automatic polarimeter (Digipol 78, Rudolph) instrument. Microanalysis of the products was carried out on a vario MICRO cube (Elementar) CHNS analyzer. The ^1H NMR and ^{13}C NMR spectra were recorded on Bruker 200 MHz or 500 MHz instruments at ambient temperature. The chemical shifts are reported in ppm relative to TMS ($\delta = 0.00$) for ^1H NMR and relative to the central $CDCl_3$ resonance ($\delta = 77.0$) for ^{13}C NMR. FT-IR spectra were recorded on Perkin Elmer Spectrum GX spectrophotometer in KBr window. Electronic spectra of chiral macrocyclic Mn(III) salen complexes were recorded in (1:1) DMC:MeOH on a Shimadzu UV-Vis-NIR spectrophotometer (Serial No. A108446). TOFF mass of the catalysts and intermediates were determined on a Micromass Q-TOF-micro instrument. The purity of the solvents, alkenes and analysis of the epoxide product were determined by gas chromatography (GC) using a Shimadzu GC 2010 instrument with a Bruker Factor four capillary column VF-1ms (15 m long, 0.25 mm inner diameter, 0.25 μm density of film) equipped with an FID detector. Ultrapure nitrogen was the carrier gas (rate 30 ml/min). Injection port and detector temperature were kept at 200 °C. For the product analysis of styrene, *cis*-β-methyl styrene and indene the column temperature was programmed at 70–140 °C, while for chromene it was kept at 140 °C (isothermal). Synthetic standard of the products were used to determine the conversions by comparing the peak height and area. Flash column chromatography (FCC) was carried out using neutral alumina (Grade-1). Enantiomeric excesses (ee) of the indene oxide and chromenes were determined by HPLC (Shimadzu SCL-10AVP) using Daicel Chiralpak OD or OB column with 2-propanol/hexane as eluent. Enantiomeric excess of styrene and *cis*-β-methyl styrene were determined by gas chromatography using a Shimadzu GC 2010 instrument with a Supelco Astec Chiral DEX™ G-TA column. The following abbreviations were used to designate NMR chemical shift multiplicities: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad; coupling constants are given in Hertz (Hz). The NMR data of known compounds are in aggrement with literature values [28,29]. Optical rotations are reported as follow: $[\alpha]_D^t$ (*c* in g per 100 mL, $CHCl_3$). HPLC and GC traces of product epoxides were compared with their respective racemic samples. The complexes **1**, **2** and **3**, **4** were prepared via intermediate dialdehydes **6** [23] and **7** respectively according to Scheme 1.

2.2. Synthesis of 5,5′-((1,4-diazepane-1,4-diyl)-bis-(methylene))-bis-(3-tert-butyl)-2-hydroxybenzaldehyde
7

1,4-Diazacycloheptane (0.88 g, 8.8 mmol) was added to a solution of 3-(*tert*-butyl)-5-(chloromethyl)-2-hydroxybenzaldehyde **5** (4.0 g, 17.6 mmol) in dry toluene (20 mL) at room temperature. The

reaction mixture was heated at 60 °C for 2 h and then cooled to room temperature. The white solid which was precipitated out was separated by centrifugation. The white solid was taken in ethyl acetate (50 mL) and treated with saturated $NaHCO_3$ solution (5 mL). The organic layer was repeatedly washed sequentially with water (5 × 20 mL) and brine (2 × 50 mL), dried over anhydrous $MgSO_4$ and the solvent was removed completely under reduced pressure to get a light brown viscous liquid. Yield: 3.80 g, 90%; FT-IR (KBr) γ_{max}/cm^{-1}: 3436, 2924, 1647, 1517, 1459, 1023, 670, 464; ^1H NMR ($CDCl_3$, 200 MHz) δ, ppm: 11.70 (s, 2H), 9.85 (s, 2H), 7.51 (d, J = 1.8 Hz, 2H), 7.35 (d, J = 1.4 Hz, 2H), 3.62 (s, 4H), 2.74 (t, J = 5.8 Hz, 4H), 2.67 (s, 4H), 1.88–1.76 (m, 2H), 1.42 (s, 18H); ^{13}C ($CDCl_3$, 125 MHz), δ, ppm: 196.67, 159.73, 137.53, 134.41, 131.08, 129.68, 119.82, 61.29, 54.55, 53.58, 34.33, 28.79, 27.25; TOFMAS (ES^+) (m/z): 481.54 (M+H); Anal. Calcd. for $C_{29}H_{40}N_2O_4$: C, 72.47; H, 8.39; N, 5.83. Found: C, 72.24; H, 8.25; N, 5.92.

2.3. Synthesis of ligand 3′

Dialdehyde **7** (0.55 g, 1.1 mmol) was taken in dry THF (0.5 mL) to which (*1S,2S*)-(+)-diamino cyclohexane (0.125 g, 1.1 mmol) dissolved in dry THF (1 mL) was added and the reaction mixture was stirred for 2–3 h at room temperature. THF was removed from the resulting pale yellow solution under reduced pressure. The residue was washed with methanol and then dried in vacuum to get bright yellow product. Yield: 0.59 g, 93%; m.p.: 122–124 °C; FT-IR (KBr) γ_{max}/cm^{-1}: 3427, 2934, 2862, 1628, 1443, 1360, 1265, 1206, 1158, 1097, 1029, 874, 801, 703, 420; ^1H ($CDCl_3$, 500 MHz) δ, ppm: 13.78 (s, 2H), 8.27 (s, 2H), 7.19 (s, 2H), 6.97 (s, 2H), 3.48 (s, 4H), 3.31 (t, J = 3 Hz, 2H), 2.64 (s, 4H), 2.6 (s, 4H), 1.95–1.71 (m, 10H), 1.38 (s, 18H); ^{13}C ($CDCl_3$, 125 MHz) δ, ppm: 165.53, 159.20, 136.73, 130.02, 129.85, 128.35, 118.23, 72.35, 62.06, 54.99, 53.91, 34.74, 33.18, 29.48, 27.53, 24.31; $[\alpha]_D^{24}$ = +97 (c = 0.8, $CHCl_3$); TOFMAS (ES^+) (m/z): 559.64 (M+H, 90%); 1118.3 (M+H, 10%); Anal. Calcd. for $C_{35}H_{50}N_4O_2$: C, 75.23; H, 9.02; N, 10.03. Found: C, 75.02; H, 8.89; N, 9.83.

2.4. Synthesis of ligand 4′

Solution of dialdehyde **7** (0.55 g, 1.1 mmol) in dry THF (0.5 mL) and (*1R,2R*)-(+)-1,2-diphenylethylene diamine (0.230 g, 1.1 mmol) in dry THF (1 mL) were mixed and the resultant solution was stirred for 6–7 h at room temperature. THF was removed from the resulting solution under reduced pressure. The yellow residue thus obtained was washed with methanol and then dried under vacuum to get bright yellow residue. Yield: 0.600 g, 80%; m.p.: 190–194 °C; FT-IR (KBr) γ_{max}/cm^{-1}: 3426, 2949, 1625, 1445, 1265, 1158, 1029, 767, 699, 573; ^1H NMR ($CDCl_3$, 500 MHz) δ, ppm: 13.63 (s, 2H), 8.31 (s, 2H), 7.18 (s, br, 12H), 6.92 (s, 2H), 4.69 (s, 2H), 3.43 (s, 4H), 2.58 (s, 4H), 2.54 (s, 4H), 1.50 (s, 2H), 1.38 (s, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ, ppm: 166.95, 159.12, 139.63, 136.78, 130.37, 130.08, 128.58, 128.31, 128.05, 127.49, 118.19, 80.12, 62.06, 55.11, 53.91, 34.78, 29.44, 27.59; $[\alpha]_D^{24}$ = −28 (c = 0.8, $CHCl_3$); TOFMAS (ES^+) m/z: 673.54 (M+OH, 55%), 1330.08 (M+OH, 45%); Anal. Calcd. For $C_{86}H_{104}N_8O_4$: C, 78.62; H, 7.98; N, 8.53. Found: C, 78.52; H, 7.81; N, 8.40.

2.5. Synthesis of complexes 3 and 4

Ligand **3′**/**4′** (0.54 mmol) was dissolved in DCM:MeOH (6 mL, 1:1) in a three necked round bottom flask under nitrogen to which $Mn(CH_3COO)_2{\cdot}4H_2O$ (0.140 g, 0.55 mmol) was added and the reaction mixture was stirred for 6 h at 60 °C. After bringing the reaction mixture at RT, LiCl (0.057 g, 1.37 mmol) was added and was further stirred for 4 h under aerobic condition. The solvent from the reaction mixture was removed under reduced pressure and the residue was extracted in ethyl acetate (EtOAc). The organic layer was washed successively with water, brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to get dark brown residue that was used directly as catalyst without further purification.

3; Yield: 0.33 g, 94%; m.p.: >240 °C; FT-IR (KBr) $\gamma_{max/}cm^{-1}$: 3422, 2930, 2860, 1613, 1540, 1432, 1388, 1339, 1309, 1236, 1202, 1165, 1027, 826, 567; Cl-TOFMAS (ES^+) m/z: 611.65 (92%), 1257.31 (8%); $[\alpha]_D^{24}$ = +1015 (c = 0.02, $CHCl_3$); Anal. Calcd. for $C_{35}H_{48}ClMnN_4O_2$: C, 64.96; H, 7.48; N, 8.66. Found: C, 64.84; H, 7.32; N, 8.53.

4; Yield: 0.31 g, 92%; m.p.: >250 °C; FT-IR (KBr) γ_{max}/cm^{-1}: 3426, 2927, 1610, 1538, 1454, 1307, 1161, 1027, 697, 568, 466; $[\alpha]_D^{24}$ = −173 (c = 0.02, $CHCl_3$); Cl-TOFMAS (ES^+) m/z: 710.38 (53%); 1453.69 (47%); Anal. Calcd. for $C_{86}H_{100}Cl_2Mn_2N_8O_4$: C, 69.30; H, 6.76; N, 7.52. Found: C, 69.21; H, 6.6; N, 7.41.

2.6. General epoxidation reaction procedure

2.6.1. UHP oxidant system

Catalyst **1**/**2**/**3**/**4** (5 mol%) was dissolved in (1:1) DMC:MeOH (1 mL) to which pyridine *N*-oxide (Py*N*O) (11.5 mg, 0.12 mmol) and *n*-dodecane (7.5 mg as an internal standard) were added. The resulting solution was stirred for 10–15 min at room temperature. The desired olefin (0.625 mmol) was added to the above mixture and the reaction temperature was brought to 5 °C. UHP (144.8 mg, 1.5 mmol, in four equal portions) was added to the above mixture under stirring. The progress of the reaction was monitored on gas chromatography (GC). After the completion of the reaction, catalyst was separated from the product epoxides by precipitation with hexane (2 mL) and was used as such for further catalytic runs. Epoxides were purified by flash chromatography through neutral alumina using ethyl acetate and hexane (9:1) as eluent.

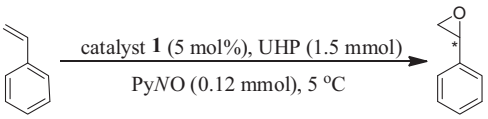
2.6.2. NaOCl oxidant system

Catalyst **1** (5 mol%) was dissolved in DMC (1 mL) to which pyridine *N*-oxide (Py*N*O) (11.5 mg, 0.12 mmol) and *n*-dodecane (7.5 mg as an internal standard) and the resulting solution was stirred for 10–15 min at room temperature. The desired olefin (0.625 mmol) was added to the above mixture and reaction temperature was brought to 5 °C. To the above mixture, buffered NaOCl (pH 11.3; 1.5 mmol) was added in drop wise manner over 1 h and the reaction was monitored by GC. After the reaction, the organic layer was separated, washed with water, brine and finally dried over anhydrous Na_2SO_4. The catalyst was separated from the product epoxide by precipitation with hexane (2 mL) and used as such for further catalytic runs. The evaporation of the solvent under reduced pressure yielded the crude epoxide which was purified by flash chromatography through neutral alumina using ethyl acetate and hexane (9:1) as eluent.

3. Results and discussion

Solvents play an important role in a chemical transformation. It determine the interactions between reaction partners; consequently have direct bearing on mode and stability of the transition states and intermediates, which is reflected in reaction outcome, i.e. conversion and selectivity [23]. Due to this reason exploring newer solvent systems for new and even well-known reactions has become an important area of research. Since, solvents often constitute major volume of reactions; their selection should therefore be based on parameters, e.g., easy recovery, reuse, safety, and more importantly acceptability to the environment health. Among the new generation of solvents ionic liquids and organic carbonates are vigorously promoted for carrying out various organic transformations, as most of them fall under the category of "green" solvents. In the present study our focus was on utilizing these solvents for

Table 1
Screening of solvent with catalyst **1** at 5 °C.



Entry[a]	Solvent	Conv. (%)[c]	*t* (h)	ee (%)[d]
1	DMC	10	6	27
2	DMC:MeOH[b]	>99	6	40
3	PC:MeOH[b]	>99	7	30
4	DEC:MeOH[b]	>99	7	36
5	BMIM-PF_6:MeOH[b]	>99	12	31
6	DCM:MeOH[b]	>99	2	34
7	MeOH	70	6	25

[a] Reaction condition: catalyst **1** (5 mol%, 1 mL solvent), styrene (0.625 mmol), pyridine *N*-oxide (0.12 mmol), UHP (1.5 mmol) at 5 °C.
[b] Solvent: 1:1 (v/v).
[c] Determined on GC.
[d] Chiral capillary column GTA-type.

the enantioselective epoxidation of non-functionalized olefins with macrocyclic Mn(III) salen complexes **1**–**4** as catalyst (Scheme 1) and UHP as a non-chlorine oxidant. For the sake of comparison, the present epoxidation protocol was also studied with conventionally used oxidant NaOCl (Table 4). Complexes **1** and **2** were earlier reported [23] whereas; structurally similar complexes **3** and **4** are new and were synthesized according to the Scheme 1. The synthesis of complexes **3** and **4** is simpler as their respective ligands **3′** and **4′** were obtained directly in high purity without the use of column chromatography as compared to the synthesis of ligands **1′** and **2′** that required short silica gel column chromatography for their purification.

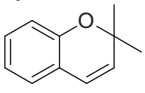
3.1. Screening of solvent

Our systematic study was initiated by exploring the epoxidation of styrene (as a model substrate) in several organic carbonates (propylene carbonate, DMC, diethyl carbonate) with **1** as a test catalyst in the presence of Py*N*O as an axial base and UHP as an oxidant at 5 °C. However, under this condition the reaction was found to be too sluggish (Table 1, entry 1). Considering the viscous nature of DMC at 5 °C (m.p. of DMC is 2–4 °C) and also low solubility of UHP in DMC and other organic carbonates, next we conducted the epoxidation reaction in 1:1 binary mixture of DMC/PC/DEC and MeOH as solvent. There was a significant improvement in the reaction performance with these combinations of solvents however; DMC fared slightly better than DEC (entries 2 and 4) in terms of conversion and enantioselectivity, followed by the performance of PC which imparted considerably lower ee in the product (entry 3). The epoxidation reaction in BMIM-PF_6:MeOH (1:1) was rather very slow and the enantioselectivity was noticeably lower as compare to DMC (entry 5). For the sake of comparison, conventionally used solvent system CH_2Cl_2+MeOH (1:1), which is known for its suitability in the enantioselective epoxidation with Mn(III) salen catalysts was also studied that gave the product in high yield with catalyst **1** in short time at 5 °C albeit with slightly lower ee (entry 6). In view of the above DMC:MeOH (1:1) was taken as preferred solvent system to optimize various other reaction parameters for this reaction. It is to be noted here that neat MeOH as reaction medium gave the product styrene oxide with low conversions (70% in 6 h) and considerably lower ee (25%) (entry 7).

3.2. Screening of catalysts and oxidants

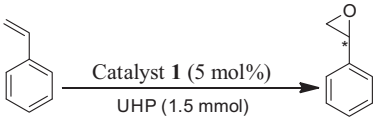
All the complexes **1**–**4** were found to be very active (conversions >99%, Table 2) for the epoxidation of styrene and chromenes as substrates in DMC:MeOH (1:1) as reaction medium. However, complexes with phenyl groups on diamine collar have shown higher enantioselectivity (entries, 2 and 4) than complexes derived from 1,2-diaminocyclohexane (entries 1 and 3) for the substrate styrene, which is in line with the earlier report [23]. However, such a difference in enantioselectivity was not observed in the case of substrate chromene (entries 6–9). The reactivity and enantioselectivity of the complexes **3** and **4** were at par with the complexes **1** and **2** under the identical condition (entries, 1–4 and 6–9). Under the similar condition original Jacobsen's Mn(III) salen complex (based on which we designed our catalyst **1**) gave similar enantioselectivity in the case of styrene but with slightly lower conversion (90%) in 6 h (entry

Table 2
Screening of catalysts and oxidants.

Entry	Oxidant	Catalyst	Substrate	Conv. (%)[e]	*t* (h)	ee (%)	TOF ($\times 10^{-3}$ s^{-1})[h]
1[a]	UHP	**1**	Styrene	>99	6	40[f] (*S*)	0.92
2[a]	UHP	**2**	Styrene	>99	7	51[f] (*R*)	0.78
3[a]	UHP	**3**	Styrene	>99	7	38[f] (*S*)	0.78
4[a]	UHP	**4**	Styrene	>99	6	49[f] (*R*)	0.92
5[a]	UHP	Jacobsen's catalyst	Styrene	90	6	40[f] (*S*)	0.83
6[a]	UHP	**1**		>99	12	80[g] (*3S,4S*)	0.45
7[a]	UHP	**2**		>99	11	84[g] (*3R,4R*)	0.50
8[a]	UHP	**3**		>99	13	80[g] (*3S,4S*)	0.42
9[a]	UHP	**4**		>99	10	83[g] (*3R,4R*)	0.55
10[a]	UHP	Absence of catalyst	Styrene	0	18	0[f]	–
11[b]	30% H_2O_2	**1**	Styrene	60	8	40[f](*S*)	0.42
12[b]	Buffer NaOCl	**1**	Styrene	>99	6	40[f] (*S*)	0.92
13[c]	UHP	**1**	Styrene	>99	7	39[f] (*S*)	0.78
14[d]	UHP	**1**	Styrene	>99	3	35[f] (*S*)	1.8

[a] Reaction condition: catalyst (5 mol% in 1 mL DMC:MeOH), substrate (0.625 mmol), pyridine *N*-oxide (0.12 mmol), oxidant (1.5 mmol) at 5 °C.
[b] Reaction condition: catalyst (5 mol% in 1 mL DMC), substrate (0.625 mmol), pyridine *N*-oxide (0.12 mmol), oxidant (1.5 mmol) at 5 °C.
[c] Reaction condition: catalyst (2.5 mol% in 1 mL DMC:MeOH), substrate (0.625 mmol), pyridine *N*-oxide (0.12 mmol), oxidant (1.5 mmol) at 5 °C.
[d] Reaction condition: catalyst (10 mol% in 1 mL DMC:MeOH), substrate (0.625 mmol), pyridine *N*-oxide (0.12 mmol), oxidant (1.5 mmol) at 5 °C.
[e] Determined on GC.
[f] Chiral capillary column GTA-type.
[g] Chiral HPLC OD column.
[h] Turn over frequency is calculated by the expression [product]/[catalyst] × time (s^{-1}).

Table 3
Epoxidation of styrene using catalyst **1** at different temperature and *N*-oxide.



Entry	Temp. (°C)	Conv. (%)[c]	*t* (h)	ee (%)[d]
1[a]	0	>99	7	42
2[a]	5	>99	6	40
3[a]	10	>99	5	35
4[a]	20	>99	4	32
5[a]	40	>99[e]	2	28
6[b]	5	>99	7	40

[a] Reaction condition: catalyst (5 mol%, 1 mL DMC:MeOH), styrene (0.625 mmol), pyridine *N*-oxide (0.12 mmol), UHP (1.5 mmol).
[b] Catalyst (5 mol%, 1 mL DMC:MeOH), styrene (0.625 mmol), 4-phenyl pyridine *N*-oxide (0.12 mmol), UHP (1.5 mmol).
[c] Determined on GC.
[d] Chiral capillary column GTA-type.
[e] With ~5% benzaldehyde formation.

5). In the absence of a catalyst, the epoxidation of styrene does not take place even for prolonged time (18 h, entry 10).

For the oxidants, like buffered NaOCl (pH 11.3) or aqueous H_2O_2 (30%), the catalytic run was carried out in neat DMC. The complex **1** is partially soluble in pure PC/DEC or DMC, but after the addition of requisite amount of Py*N*O and substrate under stirring, a clear brown solution of the reaction mixture was obtained within few minutes at room temperature. On using H_2O_2 (30%) as an oxidant with catalyst **1** (Table 2, entry 11) the epoxidation of styrene is rather slow (conversion 60% in 8 h) but the ee (40%) of the product was similar to the value obtained with UHP. Further, as the epoxidation reaction of olefin progressed, color of the reaction mixture changed from dark brown to light brown, indicating that H_2O_2 is causing the degradation of the complex. The use of NaOCl (entry 12) as an oxidant gave similar performance with that of UHP for the epoxidation reaction but UHP was studied in greater details for its environmental benefits.

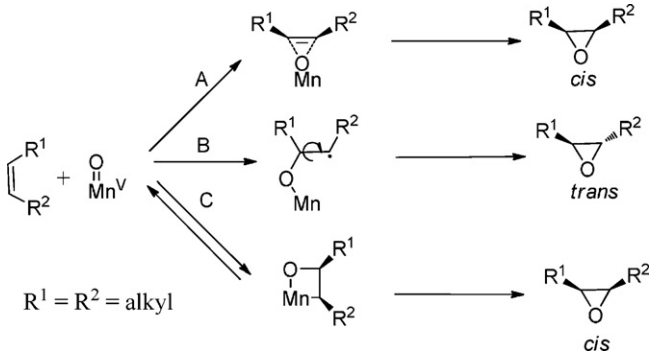
After finding the suitability of the UHP as an oxidant, we next optimized loading of the catalyst **1** using styrene as a test substrate at 5 °C. A decrease (2.5 mol%, entry 13) or increase (10 mol%, entry 14) in the catalyst loading had caused some lowering in the ee of the product while conversion remained same albeit with some increase and decrease in the reaction time respectively.

3.3. Effect of temperature and N-oxides

Epoxidation of styrene in DMC:MeOH with catalyst **1** and Py*N*O as an axial base, over a temperature range of 0–40 °C (Table 3, entries 1–5) revealed that 5 °C reaction temperature is suitable in all respects like conversion (>99%), time (6 h) and ee (40%). Expectedly, at relatively higher temperature, e.g. at 40 °C the reaction is faster but showed drastic decrease in the product ee (28%) with the formation of benzaldehyde (5%) as side product (entry 5). Changing the axial base from hydrophilic Py*N*O to hydrophobic 4-PhPy*N*O (entry 6) gave no advantage, in fact it took little longer (7 h) to give comparable conversion and ee.

3.4. Asymmetric epoxidation of various olefins

In view of the comparable results obtained with NaOCl (Table 2, entry 12) as an oxidant vis-à-vis UHP, the enantioselective epoxidation of various olefins was studied using representative catalyst **1** and the results are summarized in Table 4. However, all the four catalysts **1**–**4** were tested with the UHP as an oxidant at 5 °C in DMC:MeOH mixture for the epoxidation of various olefins (Table 5).



Scheme 2. Three mechanisms for oxygen transfer: (A) concerted, (B) via radicals, (C) via manganaoxetane intermediates.

Both, the oxidants studied here gave comparable performance with our previously reported results obtained with two of these catalysts (**1** and **2**) in CH_2Cl_2 as solvent at 0 °C with NaOCl as an oxidant [23].

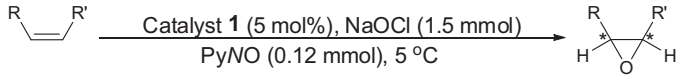
Since the reactivity and enantioselectivity pattern remained almost same, it can be concluded that the transition states during oxygen atom transfer from oxidant → catalyst → substrates in the case of present solvent system remained same as reported earlier [6]. For instance reactivity order follows styrene > *cis*-β-methyl styrene > indene > chromenes, that is to say smaller olefins react faster than bulkier olefins (Table 5). But, available experimental data (earlier and present studies) show that enantioselective epoxidation of the small alkenes remains low even for numerous substituted salen catalysts having variable steric and electronic features. However, larger olefins (predominantly *cis*) showed better enantioselectivity, possibly due to their multiple interactions with the critical chirality regions of the catalyst [30].

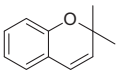
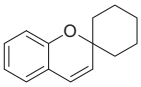
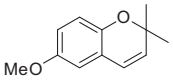
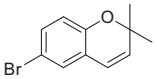
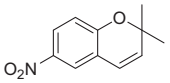
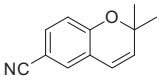
The case of epoxidation of *cis*-β-methyl styrene was of particular importance as it gives mechanistic insight as well as served as a model substrate for the synthesis of taxol side chain and calcium channel antagonist Diltiazem. With the present protocol epoxidation of *cis*-β-methyl styrene produced predominantly *cis* epoxide (E/Z ratio; 93:7) with 78% ee; however the ee (39%) of the *trans* epoxide was much lower, but at par with earlier reported Mn(III) salen catalysts [31,32]. The fact that there is the formation of *trans* product, although to a lesser extent (7%), the oxygen atom transfer from intermediate Mn=O to the substrate is not entirely through concerted mechanism or through the formation of manganaoxetane intermediate and the contribution of radical mechanism is not entirely ruled out (Scheme 2) [31–33]. It is worth mentioning here that we have not observed the formation of aldehydes with styrene or *cis*-β-methyl styrene epoxidation under our optimized reaction condition with these catalysts. Moreover, performance of these catalysts was not much affected by the presence of electron donating and withdrawing substituents and sterically demanding group in various chromenes used in the present study. In all the cases catalysts gave the respective products in high yields (89–98%) and enantio-induction (ee, 80–91%). After the completion of the epoxidation reaction, the organic carbonate (DMC) was quantitatively retrieved from the reaction mixture by fractional distillation, which showed no change in its chemical properties (checked by NMR, Fig. S1), which in turn showed its inertness in the oxidizing environment used here and also demonstrated that it is neither taking part nor interfering in the epoxidation reaction (Table 2, entry 10) [34].

3.4.1. Reaction kinetics

To understand the mechanism of the epoxidation reaction in DMC:MeOH (1:1) medium, the kinetics of epoxidation of styrene as a representative substrate was investigated using catalyst **1** in the

Table 4
Asymmetric epoxidation of alkenes catalyzed by **1** with NaOCl as an oxidant in DMC.



Entry[a]	Substrate	Conv. (%)[b]	*t* (h)	ee (%)	Configuration	TOF ($\times 10^{-3}$ s^{-1})[g]
1		>99	6	40[c]	*S*	0.92
2		>99	6	74[d]	*1S,2R*	0.92
3		>99	7	81[e]	*1S,2R*	0.78
4		94	12	83[f]	*3S,4S*	0.43
5		92	12	82[f]	*3S,4S*	0.42
6		93	12	90[f]	*3S,4S*	0.42
7		92	12	86[f]	*3S,4S*	0.42
8		89	12	80[f]	*3S,4S*	0.41
9		88	12	89[f]	*3S,4S*	0.40

[a] Reaction condition: catalyst (5 mol%, 1 mL DMC), substrate (0.625 mmol), pyridine *N*-oxide (0.12 mmol), buffer NaOCl (pH 11.3, 1.5 mmol) at 5 °C.
[b] Determined on GC.
[c] Chiral capillary column GTA-type.
[d] ee of *cis* epoxide measured on chiral capillary column GTA-type, ration of (*E*:*Z*) epoxide 89:11.
[e] Chiral HPLC OB column.
[f] Chiral HPLC OD column.
[g] Turn over frequency is calculated by the expression [product]/[catalyst] × time (s^{-1}).

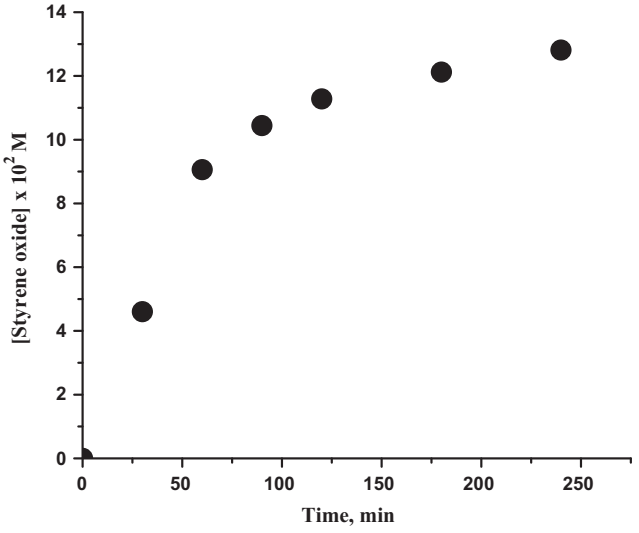


Fig. 1. Time dependent plot of the formation of styrene oxide at 5 °C with the catalyst **1** in 1 mL DMC:MeOH (1:1), [substrate] = 0.1393 M, [catalyst] = 0.00875 M, [oxidant] = 0.805 M.

presence of Py*N*O as an axial base with UHP as oxidant, as a function of the concentrations of the catalyst and styrene at 5 °C (Table 6). In all the kinetic runs, the plot for formation of styrene epoxide with time was found to be linear in the initial stage of the reaction, which attained saturation near completion (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 with time. During kinetic studies DMC:MeOH solvent mixture behaved just like any other solvent in asymmetric epoxidation reaction.

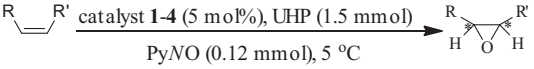
3.4.2. Rate determination with respect to catalyst concentration

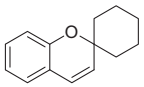
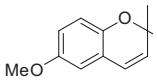
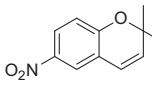
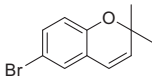
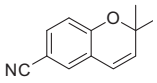
The kinetic data for the epoxidation of styrene with various concentration of catalyst with constant concentration of Py*N*O, styrene and UHP at 5 °C gave straight line for the rate constant (k_{obs}) versus catalyst concentration plot with unit slope ($d \log k_{obs}/d \log$ [catalyst] = ~1, Fig. 2) suggesting that the epoxidation of styrene is first order with respect to the concentrations of the catalyst.

3.4.3. Rate determination with respect to oxidant (UHP) concentration

Similarly for the epoxidation of styrene with various concentration of oxidant (UHP) with constant concentration of catalyst **1** the k_{obs} versus the concentration of oxidant ($d \log k_{obs}/d$

Table 5
Asymmetric epoxidation of alkenes catalyzed by **1–4** with UHP as an oxidant in DMC:MeOH.



Entry[a]	Catalyst	Substrate	Conv. (%)[b]	*t* (h)	ee (%)	Configuration	TOF ($\times 10^{-3}$ s^{-1})[l]
1	**1**		>99	7	74[c]	*1S,2R*	0.78
2	**2**		>99	6	78[d]	*1R,2S*	0.91
3	**3**		>99	6	75[e]	*1S,2R*	0.91
4	**4**		>99	7	77[f]	*1R,2S*	0.78
5	**1**		>99	8	76[g]	*1S,2R*	0.68
6	**2**		>99	7	81[g]	*1R,2S*	0.78
7	**3**		94	8	77[g]	*1S,2R*	0.44
8	**4**		92	7	80[g]	*1R,2S*	0.43
9	**1**		94	12	80[h]	*3S,4S*	0.44
10	**2**		90	12	81[h]	*3R,4R*	0.42
11	**3**		89	12	80[h]	*3S,4S*	0.41
12	**4**		91	12	82[h]	*3R,4R*	0.42
13	**1**		98	12	91[h]	*3S,4S*	0.45
14	**2**		93	12	80[h]	*3R,4R*	0.43
15	**3**		90	12	88[h]	*3S,4S*	0.42
16	**4**		94	12	82[h]	*3R,4R*	0.44
17	**1**		92	12	82[h]	*3S,4S*	0.43
18	**2**		94	12	84[h]	*3R,4R*	0.44
19	**3**		90	12	80[h]	*3S,4S*	0.42
20	**4**		85	12	83[h]	*3R,4R*	0.39
21	**1**		90	12	82[h]	*3S,4S*	0.42
22	**2**		92	12	87[h]	*3R,4R*	0.43
23	**3**		84	12	85[h]	*3S,4S*	0.39
24	**4**		90	12	86[h]	*3R,4R*	0.42
25	**1**		93	12	86[h]	*3S,4S*	0.43
26	**2**		90	12	91[h]	*3R,4R*	0.42
27	**3**		91	12	88[h]	*3S,4S*	0.42
28	**4**		89	12	90[h]	*3R,4R*	0.41

[a] Reaction condition: catalyst (5 mol% in 1 mL DMC:MeOH), substrate (0.625 mmol), pyridine *N*-oxide (0.12 mmol), UHP (1.5 mmol) at 5 °C.
[b] Determined on GC.
[c] ee of *cis* epoxide measured on chiral capillary column GTA-type, ration of (*E*:*Z*) epoxide 87:13.
[d] ee of *cis* epoxide measured on chiral capillary column GTA-type, ration of (*E*:*Z*) epoxide 93:7.
[e] ee of *cis* epoxide measured on chiral capillary column GTA-type, ration of (*E*:*Z*) epoxide 89:11.
[f] ee of *cis* epoxide measured on chiral capillary column GTA-type, ration of (*E*:*Z*) epoxide 92:8.
[g] Chiral HPLC OB column.
[h] Chiral HPLC OD column.
[l] Turn over frequency is calculated by the expression [product]/[catalyst] × time (s^{-1}).

log[oxidant] ~ 1, Fig. 3) showed first order dependence of the reaction of the oxidant concentration.

3.4.4. Rate determination with respect to substrate (styrene) concentration

Substrate concentration was varied from 13.93 to 27.87×10^{-2} M with constant catalyst concentration **1** and UHP at 5 °C. Zero-order dependence was observed for the initial concentration of styrene ($13.93–27.87 \times 10^{-2}$ M) at constant concentration of the other reactants. Overall rate of the reaction was dependent on the concentration of the catalyst and oxidant; and was second order. Based on the kinetic measurements and product distribution, Scheme 2 represents the probable mechanism. The literature [35] establishes that Py*N*O occupies the axial position in the Mn(III) salen complex, and that resulting complex react with the oxidant to form an oxo intermediate (L*Mn = O, L* = chiral macrocyclic ligand) in the rate determining step. The formation of the (L*Mn = O) complex is proposed on the basis of spectroscopic measurement as well as our kinetic results, which show first order dependence on the catalyst and oxidant concentrations. The

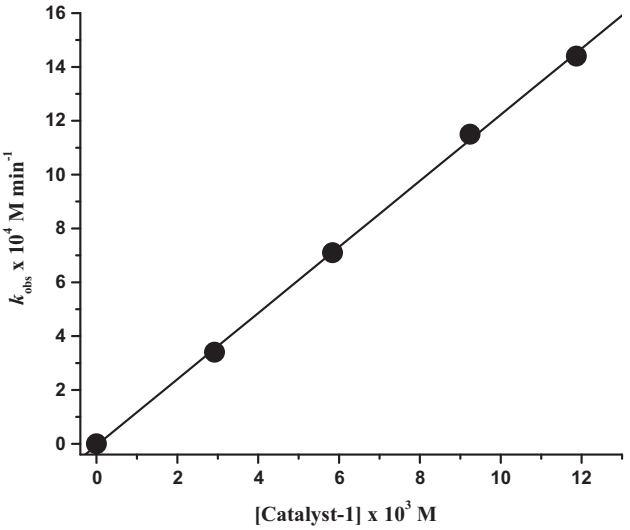


Fig. 2. Linear dependence of k_{obs} on the catalyst **1** concentration at 5 °C, [substrate] = 13.93×10^{-2} M, [oxidant] = 8.05×10^{-1} M, 1 mL DMC:MeOH (1:1).

alkene interacts with (L*Mn = O) and probably follows the route of manganaoxetane formation [33,36] (enantioselective pathway C, Scheme 2) to selectively give the epoxide and the catalyst L*Mn in its original form. However, in the absence of absolute chiral induction with the substrate, formation of a radical intermediate coupled with C—C bond rotation (B) is possibly responsible for the drop in product ee. To demonstrate the occurrence of this pathway *cis*-*β*-methyl styrene was used as a substrate that resulted in the formation of *cis* as well as *trans* epoxide [37]. Since, in the present reaction the product was predominantly *cis* (Table 5, entry 2, 93%), the contribution pathway B should be small. Spectroscopic study shows the formation of L*Mn = O as a catalytically active species in the Mn(III) salen catalyzed epoxidation of alkenes. Fig. 4 shows a stepwise overlay of UV–Vis spectra for the complex **1** with Py*N*O (X), oxidant (Y) and substrate styrene (Z) in DMC:MeOH at 5 °C. The spectrum of the catalyst **1**, showed a peak at 406 nm (X), which is typical of axially coordinated Py*N*O Mn(III) salen complexes [38]. Upon the addition of UHP as the oxidant the solution turns dark brown; and a new absorption band develops around 550 nm (Y). The maximum of which obscured by the tailing of the strongly absorbing species at $\lambda > 550$ nm. This band is assigned for the

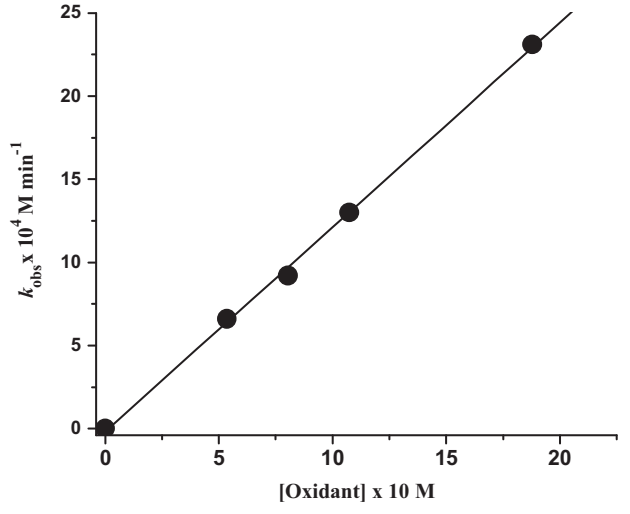


Fig. 3. Plot of k_{obs} versus [oxidant] with catalyst **1** using styrene as substrate at 5 °C, [catalyst] = 8.75×10^{-3} M, [substrate] = 13.93×10^{-2} M, 1 mL DMC:MeOH (1:1).

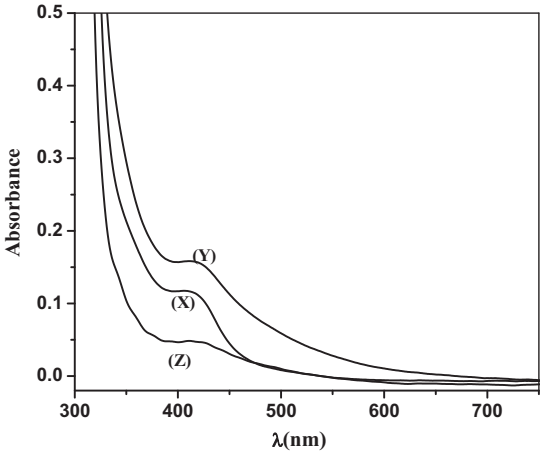


Fig. 4. UV–Vis spectra with 4.9×10^{-5} M solution of catalyst **1** in dimethyl carbonate:MeOH (1:1) with Py*N*O (X), with oxidant, UHP (Y), on addition of substrate [styrene] (Z).

formation of Mn=O intermediate. The same has been reported earlier with UHP [39], NaOCl [40] and other oxidants such as PhIO, *t*-BuOOOH [41]. After the addition of the substrate, in this case styrene, a spectrum (Z) appeared which closely resemble to the original complex **1** (X). This spectral changes further support our proposition for the formation of Mn=O species in the catalytic cycle and is consistent with earlier reports on Mn(III) salen complexes [41,42].

3.5. Recycling

All the catalysts **1**–**4** were probed for their reusability in the epoxidation of styrene with UHP as an oxidant under the optimized reaction condition. After the first catalytic run, the macrocyclic complexes were precipitated out from the reaction mixture by the addition of hexane. The precipitated complexes were washed with hexane and water, dried in vacuum, and used in for the subsequent catalytic run without further purification. The catalysts **1** and **2** were recovered (with some physical loss) but the recovery of catalysts **3** and **4** was comparatively poor may be due to the presence of N linkers, which made these catalysts having greater affinity toward water. As a result, these catalysts were not fully recovered at the stage where the reaction mixture was subjected to washing with water in order to remove urea and other water soluble impurities. The recyclability data for the catalysts **2** and **4** are given in Figs. 5 and 6 respectively, which showed the

Table 6
Dependence of rate of the reaction on the catalyst, substrate and oxidant concentration for asymmetric epoxidation reaction at 5 °C in DMC:MeOH.

[Catalyst] × 10^3 M	[Substrate] × 10^2 M	[Oxidant] × 10 M	k_{obs} (×10^4 M min^{-1})
Effect of substrate concentration			
	13.93		9.6
8.75	20.90	8.05	9.4
	27.87		9.3
Effect of oxidant concentration			
		5.36	6.6
		8.05	9.2
8.75	13.93	10.74	13.0
		18.79	23.1
Effect of catalyst concentration			
2.92			3.4
5.84	13.93	8.05	7.1
9.24			11.5
11.87			14.4

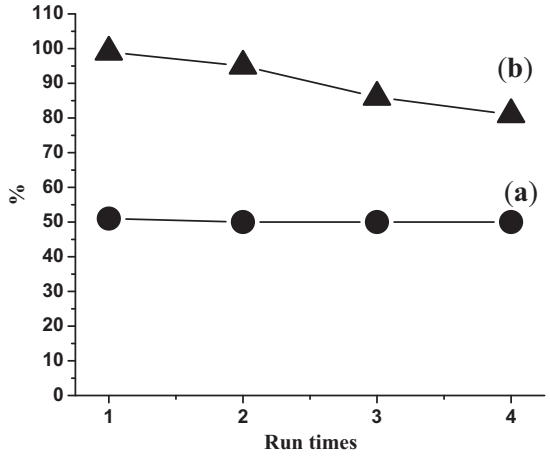


Fig. 5. The reuse of catalyst **2** in the asymmetric epoxidation of styrene with UHP/Py*NO* as oxidant system at 5 °C (a: ee value; b: conversion).

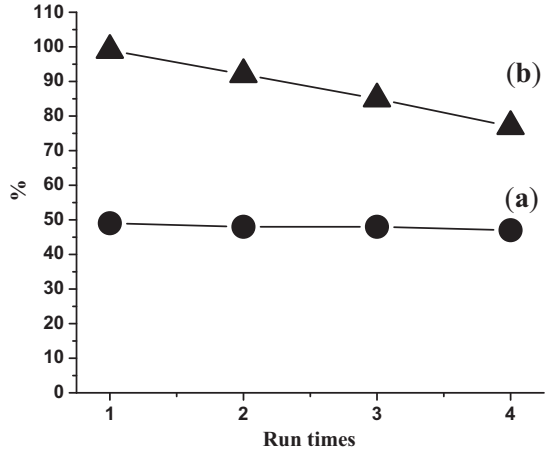


Fig. 6. The reuse of catalyst **4** in the asymmetric epoxidation of styrene with UHP/Py*NO* as oxidant system at 5 °C (a: ee value; b: conversion).

performance at par with the fresh catalyst in term of enantioselectivity, but showed gradual decrease in the conversion (greater decrease in the case of the catalyst **4**) due to physical loss during catalyst recovery process. The fairly similar enantioselectivity indicated that these catalysts are quite stable under the epoxidation condition used in the present study. The FT-IR spectrum of the initial catalysts **2**–**4** and the recycled catalysts (after 4th cycle) were given in the supporting information which clearly shows integrity of the catalyst after four catalytic cycles in this mixture solvent system and oxidant Figs. S2 and S3 (see supporting information).

4. Conclusions

The present study illustrates the feasibility of organic carbonates like DMC as an environment friendly alternative to the conventionally used chlorinated solvents in asymmetric epoxidation of non-functionalized alkenes to give the product epoxides in reasonably good yield and enantioselectivity. The easily synthesizable novel macrocyclic Mn(III) salen complexes **3** and **4** which are analog of **1** and **2** were also equally active in asymmetric epoxidation of non-functionalized alkenes.

Acknowledgements

Authors thank CSIR-Network project and DST for financial support and analytical division of CSIR-CSMCRI for their valuable support. We thank Dr. Asif A. Dabbawala for valuable discussions.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2012.10.021.

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