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Enantioselective epoxidation of olefins catalyzed by chiral dimeric and partially water-soluble monomeric salen-Mn(III) complexes in the presence of novel co-catalysts

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Abstract

New chiral salen-Mn(III) complexes analogous to Jacobsen's catalyst ([(*R*,*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminato(2-)]manganese(III)chloride) have been synthesized and employed in the enantioselective epoxidation of non-functionalized alkenes. Two dimeric chiral salen-Mn(III) complexes proved to be effective catalysts in the asymmetric epoxidation of some cyclic alkenes, and the two other monomeric chiral salen-Mn(III) catalysts should have certain inherent phase-transfer capability during the epoxidation because of their weak water-solubility. Based on a new synergetic strategy of catalysts with their corresponding co-catalysts, pyridine *N*-oxide and Fujita's porous coordination polymer were used as co-catalyst. In particular, Fujita's porous coordination polymer ($\{[Cd(4,4'\text{-bpy})_2](NO_3)_2\}_\infty$) accelerated epoxidation without depressing the chiral induction as well as conversions in the fresh catalytic cycle. In general, moderate to high enantioselectivity and acceptable yields were achieved when NaClO was used as oxidant under CH_2Cl_2/H_2O biphasic media in the presence of these co-catalysts. Additionally, the recovery and recycling of one dimeric salen-Mn(III) complex were tested in order to further apprehend the effects of different co-catalysts on the alkene epoxidations.

Keywords: Enantioselective epoxidation; Co-catalyst; Phase-transfer; Porous coordination polymer; Salen-Mn(III)

1. Introduction

Epoxides are versatile synthetic intermediates that can be readily converted into a large variety of useful compounds by means of regioselective ring opening [1]. Therefore, the design of new chiral catalysts for enantioselective epoxidation of alkenes constitutes an important strategy for the synthesis of chiral pharmaceuticals and fine chemicals [2]. Among several catalytic systems, the Jacobsen epoxidation had emerged as a powerful method for the asymmetric oxidation of unfunctionalized olefins [3], and Katsuki and co-workers had developed another set of manganese Schiff-base complexes containing two extra stereogenic axes in the C-3 and C-3′ positions of the aryl groups as the asymmetric epoxidation catalysts [4]. Due to their availability, lower cost and nontoxic property, the use of chiral manganese Schiff-base complexes is of increasing interest in asymmetric epoxidation. Soon after these key findings, a number of reports appeared describing efforts to expand this system. These approaches can be roughly grouped into several categories: (1) homogeneous catalysis [5]; (2) kinetic resolution [6]; (3) immobilization in zeolites, clays, siloxane membranes and other inorganic supports such as silica, MCM-41 and conducting surface [7]; (4) polymer-supported catalysts [8]; (5) soluble macromolecules [9]; (6) fluorous biphase system (FBS) [10]; (7) ionic liquid [11]; (8) photo-oxidation [12]; (9) theoretical research [13]. It is also interesting to note that co-catalysts play an important role in the Jacobsen epoxidation. As is known, the organic co-catalyst appears to coordinate to the unsaturated Mn(III) species emerging from a first catalytic cycle and prevent this reacting with active Mn(V) oxo species to produce catalytically inactive μ-oxo-Mn(IV) dimmer [14]. It was reported that the use of 4-phenyl pyridine *N*-oxide (PPNO)[15], 4-phenylpropyl pyridine *N*-oxide (PPPNO) [16], methylmorphline-*N*-oxide (NMO) [17] and imidazole compounds [18] etc. could stabilize the catalytically active intermediate species Mn(V)-

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oxo. Nevertheless, chiral quaternary ammonium salts [19] and carboxylate salts [20] are also perfect co-catalysts. Among the co-catalysts used in the Mn(salen) catalyzed epoxidation systems, the presence of lipophilic PPPNO in the asymmetric epoxidation of indene catalyzed by Jacobsen's catalyst provided high enantioselectivity and rate acceleration [16]. However, PPPNO is expensive and get degraded gradually during the epoxidation procedure [16], and its lipophilic property would make the extraction of epoxides inconveniently. Consequently, there is still room for improvement in terms of economical acceptability of co-catalyst.

We supposed that a successful salen-Mn(III) catalyzed asymmetric alkene epoxidation is an effective combination of metal complexes with their corresponding co-catalysts. Therefore, in order to substitute expensive proximal ligands such as PPNO and PPPNO with more available co-catalysts, two dimeric Mn(III) salen complexes and two monomeric Mn(III) salen complexes containing hydrophilic groups have been prepared and employed as epoxidation catalysts. It was estimated that increasing the molecular weight of the catalyst would lower its solubility, facilitating product isolation and catalyst recovery. Additionally, increasing the number of active metal centers on the catalyst would result in increased catalytic activity and promote substrates turnover [5a]. Furthermore, multiple metal centers are not working in isolation but have some synergetic interaction [5a,21,22]. Therefore, the stabilizing effect of proximal ligands should become marginal in this catalytic system, and water-soluble pyridine *N*-oxide was selected as co-catalyst subsequently. Since the transportation of HOCl from water to oil phase is required for the classical salen-Mn(III) catalyzed epoxidation [16], and the average salen-Mn(III) complexes cannot be dissolved in water, the design and preparation of water-soluble salen-Mn(III) complexes become an attractive target. Additionally, the stabilizing effect of hydrophilic PNO can also be anticipated herein, possibly because PNO could stabilize the catalytically active intermediate species Mn(V)-oxo in the water phase. Based on these points and economical acceptability of PNO [23,24], the effect of PNO on salen-Mn(III) catalyzed alkene epoxidation deserved more attention. In our attempts to explore new co-catalysts suitable to be used in Jacobsen epoxidation system, Fujita's porous coordination polymer ($\{[Cd(4,4'\text{-bpy})_2](NO_3)_2\}_\infty$) was found to be an effective one under biphasic oxidation condition (H_2O/CH_2Cl_2, NaClO as terminal oxidant). Fujita et al. described the preparation, clathration ability and catalysis of a two-dimensional square network material ($\{[Cd(4,4'\text{-bpy})_2](NO_3)_2\}_\infty$) [25]. A unique character of this easily prepared coordination polymer is its heterogeneous catalysis for the cyanosilylation of aldehydes. The reaction is apparently promoted by this polymer because no reaction took place with powered $Cd(NO_3)_2$ or 4,4′-bipyridine alone or with the supernatant liquid of a CH_2Cl_2 suspension of the polymer. Furthermore, different aldehydes as substrates gave adducts in different yields: 77% (benzaldehyde), 40% (2-tolualdehyde), 19% (3-tolualdehyde), 62% (α-naphthaldehyde), 84% (β-naphthaldehyde), 0% (9-anthraldehyde) [25]. Hence, the cyanosilylation of aldehydes catalyzed by Fujita's polymer is selective to the sizes of different substrates. We supposed this polymer would also activate some alkenes of certain size under typical Jacobsen epoxidation media. Therefore, this polymer was first introduced as co-catalyst into the alkene epoxidation system. Our strategy to investigate the effect of Fujita's polymer under salen-Mn(III) epoxidation system was performed in a step-wise manner. At first, Fujita's porous coordination polymer ($\{[Cd(4,4'\text{-bpy})_2]\ (NO_3)_2\}_\infty$) was prepared and used as catalyst for the epoxidation in the absence of any Mn(III) salen complexes when NaClO was selected as terminal oxidant. Subsequently, we examined the catalysis of different chiral Mn(III) salen complexes in the presence of pyridine *N*-oxide and Fujita's polymer as co-catalyst, respectively. In order to further apprehend the effect of the two co-catalysts on alkene epoxidation, the recycling experiments were also performed when catalyst **2b** was selected as catalyst. The immediate goals of this work were: (1) to evaluate the catalytic abilities of the combination of dimeric salen-Mn(III) complexes with PNO or Fujita's polymer in alkene epoxidation; (2) to examine the recyclability of dimeric salen-Mn(III) catalyst in the presence of different co-catalysts and (3) to investigate the inherent phase-transfer capability of partially water-soluble monomeric salen-Mn(III) catalysts by using PNO and Fujita's polymer as co-catalysts.

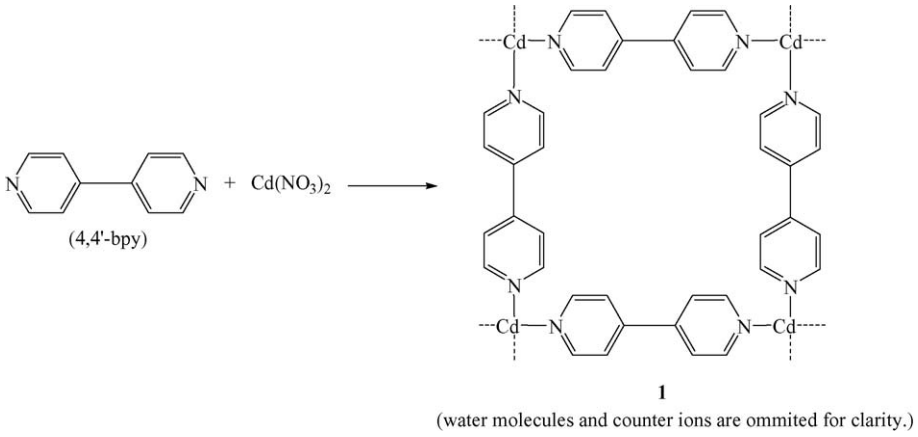
2. Results and discussion

2.1. Synthesis and catalysis of $\{[Cd(4,4'\text{-bpy})_2](NO_3)_2\}_\infty$

This porous coordination polymer was synthesized according to the literature method [25] as shown in Scheme 1. When $Cd(NO_3)_2{\cdot}4H_2O$ was treated with 4,4′-bpy·$2H_2O$ (1–2 M equiv.) in H_2O-EtOH at room temperature, colorless crystals easily grew within 1 week. Elemental analysis and X-ray crystallography supported the formation of the square network material [25]. In practice, we found that this polymer was almost insoluble in dichloromethane and water. Based on the solubility of Fujita's polymer, it was estimated that the porous structure of this polymer will be retained under CH_2Cl_2/H_2O biphasic reaction media at low temperature. To test the catalytic properties of Fujita's polymer, we performed the epoxidation of styrene and indene catalyzed by this polymer (catalyst loading is 20 mol%) in dichloromethane using buffered NaClO (pH 11.3) as oxidant at 0 °C in the absence of salen-Mn(III) complexes. In these two blank experiments, no considerable epoxidation was observed under the above reaction conditions.

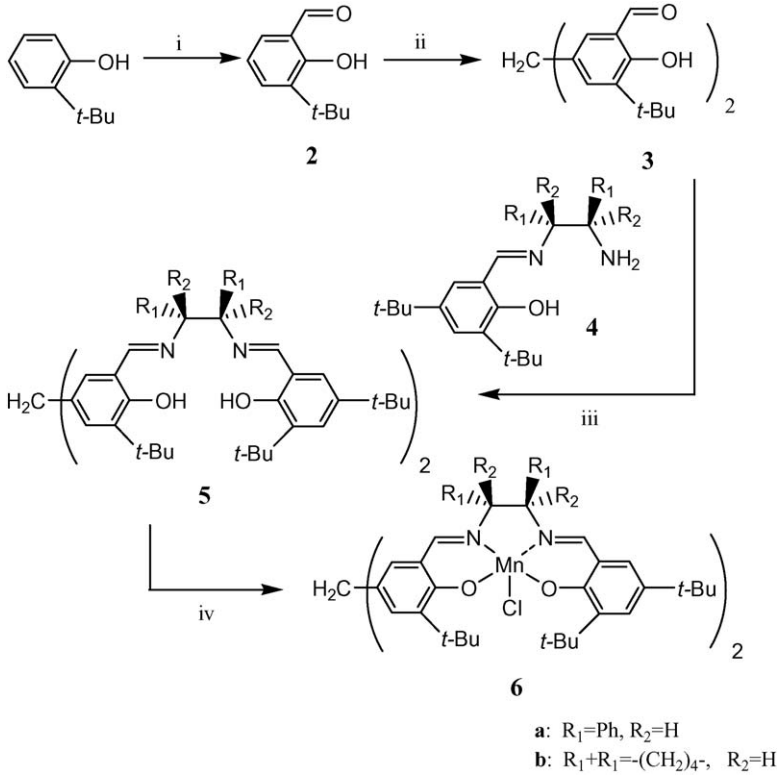
2.2. Synthesis and catalysis of dimeric salen-Mn(III) complexes

The synthesis route for chiral dimeric complexes **6a** and **6b** is shown in Scheme 2. The synthetic procedure includes initial preparation of 5,5′-methylene-di-3-*tert*-butylsalicylaldehyde (**3**) as a connecting matrix by treating 3-*tert*-butyl-2-hydroxybenzaldehyde (**2**) with trioxane and sulfuric acid in an acetic acid solution, followed by a condensation of **3** with the chiral half-units **4**, which were synthesized by condensation of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde with (*R*,*R*)-1,2-diphenylethylenediamine or (*R*,*R*)-1,2-cyclohexanediamine,



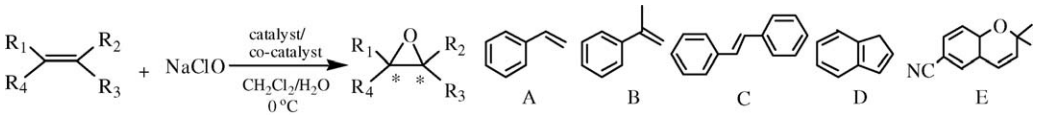
Scheme 1. Synthesis of Fujita's porous coordination polymer ($\{[Cd(4,4'\text{-bpy})_2](NO_3)_2\}_\infty$).

final metallation with Mn(II) salt. Complexes **6a** and **6b** were then used as catalysts in epoxidation of styrene (A), α-methylstyrene (B), *trans*-stilbene (C), indene (D) and 6-cyano-2,2-dimethylchromene (E). All asymmetric epoxidations were performed using NaClO as terminal oxidant under CH_2Cl_2/H_2O biphasic reaction conditions at 0 °C. Pyridine *N*-oxide and Fujita's polymer were used as co-catalysts, respectively. The catalytic results are summarized in Table 1. For all the substrates the reaction proceeded smoothly, and good conversions were reached in the range of 30 min to 4 h. In general, dimeric salen-Mn(III) derived from chiral diaminocyclohexane (**6b**) afforded higher enantioselectivity on alkene epoxidation than it's analogue **6a**. When PNO was selected as co-catalyst, although the enantioselectivitives found in the epoxidation of styrene, α-methylstyrene and *trans*-stilbene were modest (Table 1, entries 1–6), significantly improved ee values were observed with indene and 6-cyano-2,2-dimethylchromene (Table 1, entries 7–10). On the other hand, when Fujita's polymer was selected as co-catalyst, all epoxidations were somewhat accelerated. The exact role of Fujita's polymer as co-catalyst during epoxidation is not clear. Possibly, its porous structure will effectively prevent the formation of inactive μ-oxo-Mn(IV) species, so the epoxidation was obviously accelerated. At the same time, the addition of Fujita's polymer would not suppress the chiral



Scheme 2. Reagents and conditions: (i) anhydrous $SnCl_4$, 2,6-dimethylpyridine, paraform-aldehyde, toluene, N_2; (ii) trioxane in glacial acetic acid, conc. H_2SO_4, 90–95 °C, N_2; (iii) EtOH, reflux; (iv) $Mn(OAc)_2{\cdot}4H_2O$, $LiCl{\cdot}H_2O$, EtOH.

Table 1
Epoxidation of non-functionalized alkenes catalyzed by complexes **6a** and **6b** in the presence of different co-catalysts[a]



Entry	Alkene[b]	Catalyst	ee[c] (%) (yield[d] (%), time[e] (h))		Configuration[g]
			PNO	Polymer[f]	
1	A	**6a**	25 (85, 3.5)	10 (80, 1.5)	*R*-(+)
2	A	**6b**	31 (73, 2.5)	32 (85, 1.5)	*R*-(+)
3	B	**6a**	16 (72, 2.5)	21 (64, 1.5)	*R*-(+)
4	B	**6b**	33 (60, 2.5)	27 (69, 1.0)	*R*-(+)
5	C	**6a**	5 (88, 4.0)	3 (72, 2.0)	1*R*,2*R*-(+)
6	C	**6b**	10 (81, 4.0)	12 (76, 2.0)	1*R*,2*R*-(+)
7	D	**6a**	62 (75, 2.5)	53 (82, 0.5)	1*R*,2*S*-(−)
8	D	**6b**	69 (79, 2.5)	62 (86, 0.5)	1*R*,2*S*-(−)
9	E	**6a**	86 (77, 3.5)	83 (82, 3.5)	3*R*,4*R*-(+)
10	E	**6b**	93 (91, 3.5)	90 (89, 3.5)	3*R*,4*R*-(+)

[a] Reaction conditions: substrate (2 mmol), catalyst (6 mol%), co-catalyst (for PNO, 15 mol%; for Fujita's polymer, 20 mol%), NaClO (4 mmol).
[b] A, styrene; B, α-methylstyrene; C, *trans*-stilbene; D, indene; E, 6-cyano-2,2-dimethylchromene.
[c] Determined by HPLC over a chiral OD-H column.
[d] Yield of the isolated epoxide.
[e] Monitored by TLC every other half an hour.
[f] Fujita's porous coordination polymer ($\{[Cd(4,4'\text{-bpy})_2](NO_3)_2\}_\infty$).
[g] Absolute configuration of major enantiomers which were determined by comparison of the sign of $[\alpha]_D$ to the literature values.

induction. If we compare the performance of these catalyts with that of standard Jacobsen's catalyst [26–28], dimeric manganese salen complexes showed satisfactory reactivity but lower enantioselectivity on epoxidation. Taking into account four criteria of constructing immobilized Jacobsen's catalyst, promoted by Canali et al. [8c], we hypothesized that two reactive centers on the catalyst would affect the chiral induction because of their much shorter distance.

2.3. Recovery and recycling of dimeric salen-Mn(III) complex (*6b*)

To further investigate the synergetic effect of dimeric salen-Mn(III) complexes with different co-catalysts, we also conducted recycling the catalyst **6b** in the presence of PNO and Fujita's polymer as co-catalysts, respectively. In practice, the catalyst **6b** can be recovered easily by *n*-hexane from the concentrated reaction mixture. Therefore, it makes the recycling of dimeric salen-Mn(III) complex possible. Table 2 lists the two recycling systems (two times) using dimeric **6b** as catalyst with 6-cyano-2,2-dimethylchromene as substrate: NaClO/PNO (the former system) and NaClO/Fujita's polymer (the latter system) were used as oxidants, respectively. In the former system, 86% yield was achieved in the last reaction with only a minor decrease in the enantioselectivity compared to the first run (cycle fresh catalyst versus cycle 2, in Table 2). In the latter system, the catalytic combination (**6b**/NaClO/Fujita's polymer) were degraded gradually in term of activity as well as chiral induction although the co-catalyst loading was increased step by step. Considering the importance of donor ligands [14] and the gradual decomposition of Mn(III) salen complexes during epoxidation [9a], we suspected that the porous polymer could not prevent the gradual decomposition of dimeric salen-Mn(III) in epoxidation, possibly because of no obviously coordinating atoms on it. The sharp decrease in enantioselectivity maybe due to the partial decomposition of the dimeric complex (one manganese ion leaching from the dimeric matrix to afford an unsymmetrical monomeric salen-Mn(III) complexes).

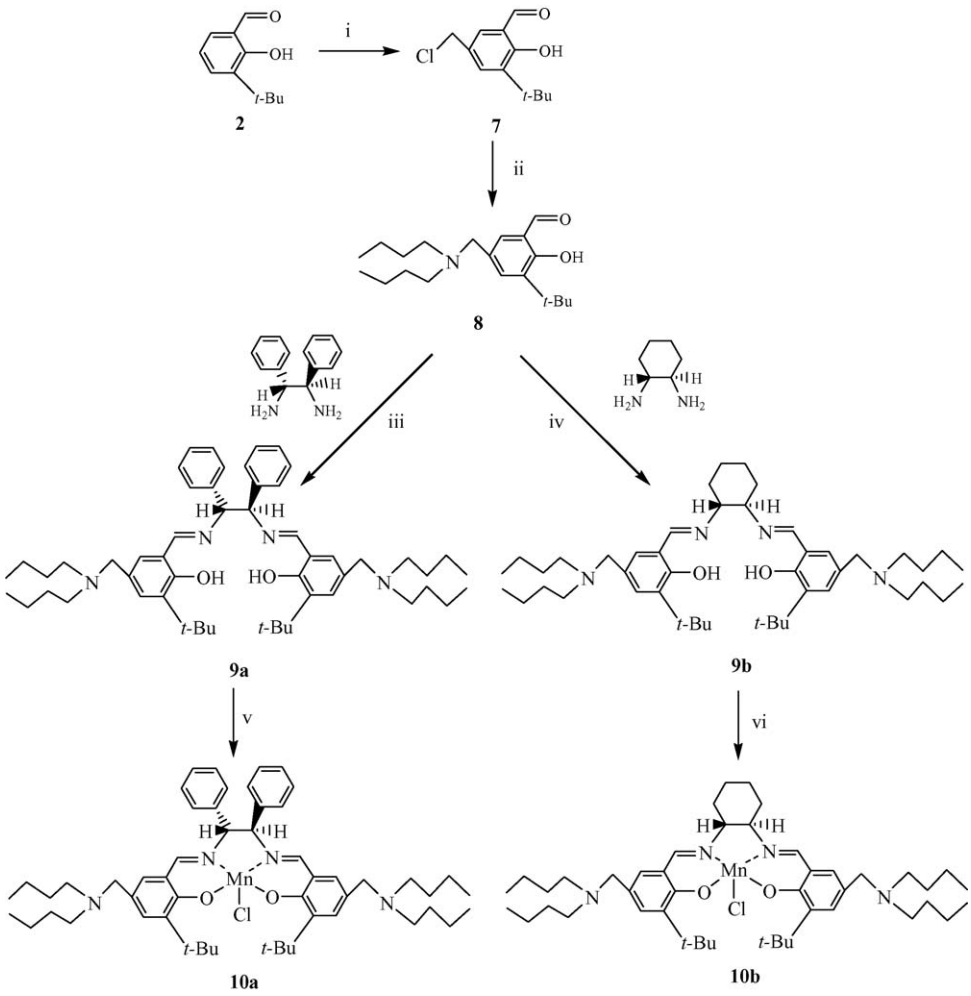
2.4. Synthesis and catalysis of weakly water-soluble monomeric salen-Mn(III) complexes

For this study, salen-manganese(III) complexes were synthesized according to Scheme 3. Two kinds of chiral salen ligand

Table 2
The recycling experiment for the enantioselective epoxidation of 6-cyano-2,2-dimethylchromene using NaClO/PNO and NaClO/Fujita's polymer as oxidants respectively catalyzed by complex **6b**[a]

Oxidant	NaClO/PNO			NaClO/Fujita's polymer		
	Cycle fresh	Cycle 1	Cycle 2	Cycle fresh	Cycle 1	Cycle 2
Yield (%)	91	89	86	89	81	47
ee (%)	93	93	90	90	76	75
Time (h)	3.5	4.5	5.5	3.5	5.0	7.0

After the total conversion, the organic phase was separated, washed with saturated NaCl solution (2 × 15 mL) and then dried over $MgSO_4$. The solution was concentrated partially and *n*-hexane (5 mL) was added to precipitate the catalyst. The solid was isolated by centrifugation and washed with *n*-hexane (2 × 2 mL), then dissolved in dichloromethane for the next cycle.
[a] Reaction conditions: substrate, 2 mmol; catalyst, 6 mol%; co-catalyst for PNO, 15 mol%; for Fujita's polymer, 20 mol%; NaClO, 4 mmol.



Scheme 3. Reagents and conditions: (i) paraformaldehyde, conc. HCl, tetrabutylammonium bromide, 40 °C, 72 h, 91%; (ii) *N*,*N*-dibutylamine, toluene, Et_3N, 85–90 °C, 7 h, 82%; (iii) (1*R*,2*R*)-(+)-diphenyldiamine, EtOH, reflux, 6 h; (iv) monotartarate salt of (1*R*,2*R*)-(−)-diaminocyclohexane, K_2CO_3, EtOH/H_2O, reflux, 8 h; (v) (1) $Mn(OAc)_2{\cdot}4H_2O$, EtOH, N_2, reflux, 4 h, (2) $LiCl{\cdot}H_2O$, rt, 3 h, 75%; (vi) (1) $Mn(OAc)_2{\cdot}4H_2O$, EtOH, N_2, reflux, 4 h, (2) $LiCl{\cdot}H_2O$, rt, 3 h, 72%.

(**9a** and **9b**) were prepared by the condensation of 2-hydroxyl-3-*t*-butyl-5-(*N*,*N*-dibutylmethylene)benzaldehyde **8** with 1*R*,2*R*-(+)-diphenyldiamine and 1*R*,2*R*-(−)-cyclohexanediamine, respectively. Finally, ligands **9a** and **9b** were complexed with manganese to give chloro-(*R*,*R*)-[[2,2′]-(1,2-diphenyl-1,2-ethanediyl)bis(nitrilomethylidyne)]bis[4-(methylene-*N*,*N*-dibutylamino)-6-(1,1-dimethyl)phenolato]-[*N*,*N*′,*O*,*O*′]-manganese(III) **10a** and chloro-(*R*,*R*)-[[2,2′]-(1,2-cyclohexanediyl-1,2-ethanediyl)bis(nitrilomethylidyne)]bis[4-(methylene-*N*,*N*-dibutylamino)-6-(1,1-dimethyl)phenolato]-[*N*,*N*′,*O*,*O*′]-manganese(III) **10b**, respectively. More exactly, in a step-wise manner, 3-*t*-butylsalicylaldehyde **2** was chloromethylated [29], and then reacted with *N*,*N*-dibutylamine to afford 2-hydroxy-3-*t*-butyl-5-(*N*,*N*-dibutylmethylene)benzaldehyde **8** in a high yield. Connecting 3-*t*-butyl-5-chloromethyl-2-hydroxylbenzaldehyde **7** with *N*,*N*-dibutylamine is a typical Mannich reaction [30]. Employing triethylamine as base to absorb hydrochloride is an appropriate method for obtaining the air-stable intermediate **8** [31]. The catalytic results obtained are shown in Table 3. According to these data, the addition of pyridine *N*-oxide remarkably enhanced asymmetric induction as well as chemical yields (entries 7 and 8). Substituting Fujita's porous coordination polymer for PNO as co-catalyst accelerated the epoxidation obviously in some cases. Interestingly, in the epoxidation of indene with Fujita's polymer as co-catalyst, catalyst **10b** afforded a comparatively high enantioselectivity and conversion (entry 6, ee values up to 81%, 79% yield). In practice, when the epoxidation was over, biphasic systems appeared gradually after magnetic stirring was discontinued. The upper water phase turned slightly yellow, possibly owing to the inherent phase-transfer capability of **10a** and **10b** with methylene aminoalkyl groups on their salicylaldehyde moieties.

3. Experimental

3.1. General remarks

Chemicals were obtained from commercial resources or prepared in our laboratories. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-200 spectrometer in $CDCl_3$ as the solvent and TMS as internal standard. IR spectra were obtained on a Nicolet NEXUS 670 FT-IR spec-

Table 3
Asymmetric alkene epoxidation catalyzed by complexes **10a** and **10b** in the presence of different co-catalysts[a]

Entry	Substrate[b]	Catalyst	ee[c] (%) (yield[d] (%), time[e] (h))		Configuration[g]
			PNO	Polymer[f]	
1	A	**10a**	77 (88, 5.0)	65 (71, 5.0)	*R*-(+)
2	A	**10b**	82 (63, 5.0)	64 (67, 5.0)	*R*-(+)
3	B	**10a**	54 (84, 5.0)	42 (77, 3.5)	*R*-(+)
4	B	**10b**	67 (83, 5.0)	65 (81, 3.5)	*R*-(+)
5	D	**10a**	72 (69, 5.0)	69 (72, 2.0)	1*R*,2*S*-(−)
6	D	**10b**	83 (85. 5.0)	81 (79, 2.0)	1*R*,2*S*-(−)
7	E	**10a**	89 (86, 6.0)	81 (82, 6.0)	3*R*,4*R*-(+)
8	E	**10b**	92 (88, 6.0)	89 (78, 6.0)	3*R*,4*R*-(+)

[a] Reaction conditions: substrate, 2 mmol; catalyst, 10 mol%; co-catalyst for PNO, 15 mol%; for Fujita's polymer, 20 mol%; NaClO, 4 mmol.
[b] A, styrene; B, α-methylstyrene; D, indene; E, 6-cyano-2,2-dimethylchromene.
[c] Determined by HPLC over a chiral OD-H column.
[d] Yield of the isolated epoxide.
[e] Monitored by TLC every other half an hour.
[f] Fujita's porous coordination polymer ($\{[Cd(4,4'\text{-bpy})_2](NO_3)_2\}_\infty$).
[g] Absolute configuration of major enantiomers which were determined by comparison of the sign of $[\alpha]_D$ to the literature values.

trometer. FAB-MS were acquired on a MASPEC II System mass spectrometer. Elemental analyses were performed on an Elementar VarioEL instrument in the Instrumental Analysis and Research Center of Lanzhou University. TLC was conducted on glass plates coated with silica gel $60F_{254}$. Optical rotations were measured with a Perkin-Elmer-341 high sensitive polarimeter. Chiral stationary phase column was Daicel Chiralcel OD-H manufactured by Daicel Chemical industries Ltd. (hexane:*i*-PrOH = 100:1). HPLC analysis were carried out on a Shimadzu instrument (system controller: LC-10AT VP; UV–vis detector: SPD-10A VP, 260 nm UV detection; flow rate is 1.0 mL/min; column pressure: 37–40 kg f/cm^2). The 3,5-di-*tert*-butyl-2-hydroxyl-benzaldehyde[32], (*R*,*R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt [32], 3-*tert*-butyl-2-hydroxy-benzaldehyde (**2**) [29], 5,5′-methylene-di-3-*tert*-butylsalicylaldehyde (**3**) [7c], and (1*R*,2*R*)-*N*-(2-hydroxyl-3,4-di-*tert*-butylbenzaldehyde)-1-amino-2-cyclohexeneimine (**4b**) [5a], 3-*t*-butyl-5-chloromethyl-2-hydroxylbenzaldehyde (**7**) [29] had been prepared according to the literature. The final metallation of free ligands **5a** and **5b** with manganese salts is a typical procedure [5b].

3.2. Synthesis and characterization of Fujita's porous coordination polymer ($\{[Cd(4,4'\text{-bpy})_2](NO_3)_2\}_\infty$)

The synthetic procedure was carried out according to the reported method [30]. An aqueous solution (8 mL) of $Cd(NO_3)_2{\cdot}4H_2O$ (1.0 mmol) and an ethanol solution (2 mL) of 4,4′-bpy·$2H_2O$ (2.0 mmol) were combined under magnetic stirring. The initially formed precipitate was filtered, and the clear filtrate was allowed to stand at room temperature. The colorless crystals will form within 1 week upon the slow evaporation of solvent. The crystals were collected by decanting the remaining solvent followed by washing with CH_2Cl_2 (35% yield). Elemental analysis is satisfactory with the reported data [25]. Anal. calcd. for $C_{20}H_{16}CdN_4O_6{\cdot}H_2O$ ($[Cd(4,4'\text{-bpy})_2](NO_3)_2{\cdot}H_2O$): C, 42.38; H, 3.20; N, 14.83; Found: C, 42.19; H, 3.22; N, 14.70 [25].

3.3. Synthesis of 5,5′-methylene-di-3-tert-butylsalicylaldehyde (*3*)

The synthetic procedure was carried out according to the reported method [7c]. Yellow solid (75% yield); m.p. 100–102 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ_H, ppm: 1.40 (18H, s, C(CH_3)$_3$), 3.93 (2H, s, methylene), 7.14–7.37 (4H, m, Ar*H*), 9.81 (2H, s, C*H*O), 11.75 (2H, s, O*H*); FAB-MS *m/z*: 369.3 $(M+1)^+$ (calcd. for M^+ 368) [7c].

3.4. Synthesis of (1R,2R)-N-(3,5-di-tert-butylsalicylidene)-1,2-diphenylethylene-diamine (*4a*)

The reported procedure included the argon atmosphere protection and the utilization of molecular sieve (3 Å) [7j]. The chiral half-unit **4a** can also be formed from 3,5-di-*tert*-butylsalicylaldehyde and an excess 1*R*,2*R*-(+)-diphenyldiamine at low temperature. A solution of 3,5-di-*tert*-butylsalicylaldehyde (0.50 g, 2.1 mmol) in ethanol (50 mL) was added slowly to a solution of 1*R*,2*R*-(+)-diphenyldiamine (0.80 g, 3.8 mmol) in ethanol (8 mL) under vigorous stirring at 0 °C. The yellow mixture was stirred vigorously for 1 h at 0 °C, and then stored at 0 °C for 48 h. The solvent was removed under reduced pressure, and the crude solid was purified by flash chromatography (SiO_2, petroleum ether/EtOAc = 10:1) to generate a yellow solid (0.68 g, 76%). ^{1}H NMR (200 MHz, $CDCl_3$) δ_H, ppm: 1.29 (9H, s, C(CH_3)$_3$), 1.48 (9H, s, C(CH_3)$_3$), 1.62 (2H, s, NH_2), 4.31 (1H, d, J = 8 Hz, C*H*), 4.42 (1H, d, J = 8 Hz, C*H*), 7.09 (1H, d, J = 2 Hz, Ar*H*), 7.13–7.21 (10H, m, Ar*H*), 7.39 (1H, d, J = 3 Hz, Ar*H*), 8.46 (1H, s, C*H*N), 13.57 (1H, s, O*H*). FAB-MS *m/z*: 429.2 $(M+1)^+$ (calcd. for M^+ 428) [7j].

3.5. Synthesis of 5,5-methylenedi-[(R,R)-{N-(3-tert-butyl salicylidine)-N′-(3′,5′-di-tert-butylsalicy lidene)}-1,2-diphenylethylenediamine] (*5a*)

A solution of (1*R*,2*R*)-*N*-(3,5-di-*tert*-butylsalicylidene)-1,2-diphenylethylenediamine (**4a**) (0.51 g; 1.2 mmol) in ethanol

(10 mL) was added to a solution of 5,5′-methylene-di-3-*tert*-butyl-salicylaldehyde (**3**) (0.22 g, 0.6 mmol) in ethanol (10 mL). The stirred mixture was heated at reflux (75–80 °C) for 8 h before heating and stirring were discontinued. The solvent was removed under reduced pressure, and the crude solid was purified by flash chromatography (SiO_2, petroleum ether/EtOAc = 15:1) to generate a yellow solid (0.65 g, 90%). ^{1}H NMR (200 MHz, $CDCl_3$) δ_H, ppm: 1.29 (18H, s, C(C*H*$_3$)$_3$), 1.53 (36H, s, C(C*H*$_3$)$_3$), 3.92 (2H, s, methylene), 4.72 (4H, s, C*H*), 6.76–7.58 (28H, m, Ar*H*), 8.39 (4H, s, C*H*N), 13.57 (4H, bs, O*H*); ^{13}C NMR (50 MHz, $CDCl_3$) δ_C, ppm: 29.4, 31.4, 34.9, 40.2, 76.4, 117.8, 118.4, 126.3, 127.9, 128.2, 131.2, 137.0, 137.4, 139.6, 139.9, 157.9, 166.8; FT-IR (KBr) ν, cm^{-1}: 2600–2800 (br, w, ArO–H), 1626 (vs, C=N), 1269 (m, Ar–OH); FAB-MS *m/z*: 1189.8 $(M+1)^+$ (calcd. for M^+ 1188). Anal. calcd. for $C_{81}H_{96}N_4O_4$: C, 81.77; H, 8.13; N, 4.71; Found: C, 81.82; H, 8.21; N, 4.99.

*3.6. Synthesis of 5,5-methylenedi-[(R,R-{N-(3-tert-butylsalicylidine)-N′-(3′,5′-di-tert-butyl-salicylidene)}-1,2-diphenylethylenediaminato(2-)manganese(III) chloride] (**6a**)*

A mixture of **5a** (1 mmol, in CH_2Cl_2) and $Mn(OAc)_2{\cdot}4H_2O$ (3 mmol, in hot EtOH) was stirred to reflux under nitrogen atmosphere for 4 h. Solid $LiCl{\cdot}H_2O$ (6 mmol) was added and the resulting mixture was further refluxed for 2 h while exposed to air. The solvent was removed under reduced pressure, and the residue was extracted with CH_2Cl_2. The extract was washed cautiously with water, then brine, dried over anhydrous Na_2SO_4, and then concentrated to leave a dark brown powders. Yield is 95%. Anal. calcd. for $C_{81}H_{92}Cl_2Mn_2N_4O_4$: C, 71.21; H, 7.03; N, 4.10; Found: C, 71.45; H, 6.85; N, 3.92; FT-IR (KBr) ν, cm^{-1}: 1612 (vs, C=N), 1251 (m, Ar–OMn).

*3.7. Synthesis of (1R,2R)-N-(2-hydroxyl-3,4-di-tert-butylbenzaldehyde)-1-amino-2-cyclo-hexeneimine (**4b**)*

The synthetic procedure was carried out according to the reported method [5a]. Yellow solid (57% yield). ^{1}H NMR (200 MHz, $CDCl_3$) δ_H, ppm: 1.23 (9H, s, C(C*H*$_3$)$_3$), 1.41 (9H, s, C(C*H*$_3$)$_3$), 1.57–2.25 (10H, m, C*H*$_2$), 3.37 (2H, s, N*H*$_2$), 6.89 (1H, s, Ar*H*), 7.27 (1H, s, Ar*H*), 13.71 (1H, s, O*H*). Anal. calcd. for $C_{21}H_{34}N_2O$: C, 76.31; H, 10.37; N, 8.48. Found: C, 76.24; H, 10.33; N, 8.41.

*3.8. Synthesis of 5,5-methylene di-[(R,R)-{N-(3-tert-butylsalicylidine)-N′-(3′,5′-di-tert-butylsalic-ylidene)}-1,2-cyclohexanediamine] (**5b**)*

The synthetic procedure was carried out according to the reported method [5a]. Yellow solid (87% yield). ^{1}H NMR (200 MHz, $CDCl_3$) δ_H, ppm: 1.23 ((18H, s, C(C*H*$_3$)$_3$), 1.41 (36H, s, C(C*H*$_3$)$_3$), 1.54–2.06 (16H, m, C*H*$_2$), 3.29 (4H, s, C*H*), 3.69 (2H, s, methylene), 6.74 (4H, s, Ar*H*), 7.05 (4H, s, Ar*H*), 8.21 (4H, s, C*H*N), 13.68 (4H, bs, O*H*); FT-IR (KBr) ν, cm^{-1}: 2600–2800 (br, w, ArO–H), 1622 (vs, C=N), 1268 (m, Ar–OH); FAB-MS *m/z*: 993.3 $(M+1)^+$ (calcd. for M^+ 992). Anal. calcd. for $C_{65}H_{92}N_4O_4$: C, 78.58; H, 9.34; N, 5.64; Found: C, 78.32; H, 9.31; N, 5.55 [5a].

*3.9. Synthesis of 5,5-methylenedi-[(R,R)-{N-(3-tert-butylsalicylidine)-N′-(3′,5′-di-tert-butylsalicylidene)-1,2-cyclohexanediaminato(2-)manganese(III)chloride] (**6b**)*

The synthetic procedure was carried out according to the reported method [5a]. A dark brown powder. Yield is 92%. Anal. calcd. for $C_{65}H_{88}Cl_2Mn_2N_4O_4$: C, 67.81; H, 8.06; N, 4.87; Found: C, 67.57; H, 8.10; N, 4.82; FT-IR (KBr) ν, cm^{-1}: 1614 (vs, C=N), 1250 (m, Ar–OMn).

*3.10. Synthesis of 2-hydroxyl-3-t-butyl-5-(N,N-dibutylmethylene)benzaldehyde (**8**)*

A stirred mixture of 3-*t*-butyl-5-chloromethyl-2-hydroxyl-benzaldehyde **7** (4.49 g, 19.9 mmol), *N*,*N*-dibutylamine (2.57 g, 19.9 mmol), and triethylamine (3.02 g, 29.8 mmol) in freshly distilled toluene (50 mL) was heated to 85–90 °C for 7 h. After the evaporation of the solvent under reduced pressure, water (100 mL) was poured into the residue. The solution was then extracted with dichloromethane (3 × 30 mL). The organic layer was washed with brine (50 mL), dried over $MgSO_4$, concentrated and purified through flash chromatography (SiO_2, petroleum ether–EtOAc = 20:1) to generate a yellow liquid (5.21 g, 82%). ^{1}H NMR (200 MHz, $CDCl_3$) δ_H, ppm: 0.87 (6H, t, J = 7Hz, C*H*$_3$), 1.24–1.48 (8H, m, C*H*$_2$), 1.42 (9H, s, C(C*H*$_3$)$_3$), 2.40 (4H, t, J = 7Hz, C*H*$_2$), 3.49 (2H, s, methylene), 7.33 (1H, s, Ar*H*), 7.52 (1H, s, Ar*H*), 9.86 (1H, s, C*H*O), 11.71 (1H, s, ArOH); ^{13}C NMR (50 MHz, $CDCl_3$) δ_C, ppm: 14.0, 20.5, 29.2, 29.3, 29.5, 53.4, 57.9, 131.0, 131.4, 135.0, 137.8, 160.1, 197.1; FAB-MS *m/z*: 319 (M^+) (calcd. for M^+ 319).

*3.11. Synthesis of (R,R)-N,N′-[2,2′-bis(notrilomethylidyne)]bis[4-(methylene-N,N′-dibutylamino)-6-(1,1-dimethylethyl)phenolato]-1,2-diphenydilamine (**9a**)*

A stirred mixture of compound **8** (2 mmol) and 1*R*,2*R*-(+)-diphenyldiamine (1 mmol) in EtOH (15 mL) was heated to reflux for 8 h. After the removal of the solvent under reduced pressure, the crude product was purified by flash chromatography (petroleum ether/EtOAc = 10:1) to yield **9a** as a yellow oil (89%). ^{1}H NMR (200 MHz, $CDCl_3$) δ_H, ppm: 0.84 (12H, t, J = 7Hz, C*H*$_3$), 1.16–1.30 (16H, m, C*H*$_2$), 1.42 (18H, s, C(C*H*$_3$)$_3$), 2.32 (8H, t, J = 7Hz, C*H*$_2$), 3.38 (4H, s, C*H*$_2$), 4.73 (2H, s, C*H*), 6.93 (4H, s, Ar*H*), 7.23 (10H, s, Ar*H*), 8.35 (2H, s, C*H*N), 13.66 (2H, s, ArOH); ^{13}C NMR (50 MHz, $CDCl_3$) δ_C, ppm: 14.0, 20.6, 29.2, 29.4, 34.7, 53.2, 58.0, 80.2, 127.4, 128.0, 128.3, 128.9, 130.0, 130.6, 136.7, 139.7, 159.1, 166.9; FT-IR (KBr) ν, cm^{-1}: 2600–2800 (br, w, ArO–H), 1627 (vs, C=N), 1264 (m, Ar–OH); FAB-MS *m/z*: 815.5 $(M+1)^+$ (calcd. for M^+ 814). Anal. calcd. for $C_{54}H_{78}N_4O_2$: C, 79.61; H, 9.58; N, 6.88; Found: C, 79.35; H, 9.50; N, 6.79.

3.12. Synthesis of chloro-(R,R)-[2,2′-(1,2-diphenyl-1,2-ethanediyl)bis(nitrilomethylidyne)]bis[4-(methylene-N,N-dibutylamino)-6-(1,1-dimethyl)phenolato]-[N,N′,O,O′]manganese(III) (**10a**)

A mixture of the ligand **9a** (0.48 mmol) and $Mn(OAc)_2{\cdot}4H_2O$ (0.72 mmol) in dry EtOH (8 mL) was refluxed under nitrogen atmosphere for 4 h. Solid $LiCl{\cdot}H_2O$ (2 mmol) was added and the mixture was further refluxed for 3 h in air. The solvent was removed, and the residue was extracted with CH_2Cl_2. The extract was washed with water and brine, dried over $NaSO_4$ and concentrated to afford **10a** as a dark brown powder (75% yield). Anal. calcd. for $C_{54}H_{76}ClMnN_4O_2$: C, 71.80; H, 8.42; N, 6.20; Found: C, 71.57; H, 8.10; N, 6.32; FT-IR (KBr) ν, cm^{-1}: 1613 (vs, C=N), 1232 (m, Ar–OMn).

3.13. Synthesis of (R,R)-N,N′-[2,2′-bis(nitrilomethylidyne)] bis[4-(methylene-N,N′-dibutylami-no)-6-(1,1-dimethylethyl)phenolato]-1,2-cyclohexanediamine (**9b**)

A mixture of (*R*,*R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt (7.57 mmol), K_2CO_3 (15.15 mmol), and distilled water (10 mL) was stirred until dissolution was achieved, and then ethanol (40 mL) was added. The resulting cloudy mixture was heated to reflux (80–85 °C), and a solution of compound **8** (15.15 mmol) in ethanol (20 mL) was added. The yellow slurry was stirred under reflux for 8 h. After the removal of the solvent under reduced pressure, the crude product was purified by flash chromatography (petroleum ether/EtOAc 20:1) to yield **9a** as an dark yellow oil (77% yield). ^{1}H NMR (200 MHz, $CDCl_3$) δ_H, ppm: 0.88 (12H, t, J = 6Hz, C*H*$_3$), 1.40 (18H, s, C(C*H*$_3$)$_3$), 1.20–1.93 (24H, m, C*H*$_2$), 2.33 (8H, t, J = 6Hz, C*H*$_2$), 3.39 (2H, m, C*H*), 3.71 (4H, s, C*H*$_2$), 6.79 (2H, s, Ar*H*), 7.23 (2H, s, Ar*H*), 8.29 (2H, s, C*H*N), 13.77 (2H, s, ArOH); ^{13}C NMR (50 MHz, $CDCl_3$) δ_C, ppm: 14.1, 20.5, 24.3, 28.6, 29.3, 29.5, 33.2, 53.3, 58.1, 72.4, 127.1, 129.0, 129.2, 136.6, 165.6. FT-IR (KBr) ν, cm^{-1}: 2600–2800 (br, w, ArO–H), 1628 (vs, C=N), 1265 (m, Ar–OH); FAB-MS *m/z*: 716 (M^+) (calcd. for M^+ 716). Anal. calcd. for $C_{46}H_{76}N_4O_2$: C, 77.09; H, 10.61; N, 7.82; Found: C, 77.35; H, 10.12; N, 7.79.

3.14. Synthesis of chloro-(R,R)-[2,2′-(1,2-cyclohexanediyl-1,2-ethanediyl)bis(nitrilomethylidyne)]bis[4-(methylene-N,N-dibutylamino)-6-(1,1-dimethyl)phenolato]-[N,N′,O,O′]manganese(III) (**10b**)

Complex **10b** was prepared according to the synthetic procedure of **10a**. A dark brown solid (72% yield). Anal. calcd. for $C_{46}H_{78}ClMnN_4O_4$ ($C_{46}H_{74}ClMnN_4O_2{\cdot}2H_2O$): C, 65.68; H, 8.80; N, 6.66; Found: C, 65.79; H, 8.51; N, 6.39; FT-IR (KBr) ν, cm^{-1}: 3414 (w, H_2O), 1613 (vs, C=N), 1234 (m, Ar–OMn).

3.15. General procedure in epoxidation reactions

The epoxidation was carried out with some modification to the reported method [5b]. About 4 mL Na_2HPO_4 (0.05 mol/L) was combined with 10 mL 13% NaClO solution, then the pH of the mixture was adjust to 11.3 by instillation of 1 mol/L HCl and 1 mol/L NaOH solutions. The mixture was stirred vigorously at 0 °C and monitored by TLC before a pre-cooled solution of catalyst (for dimeric complexes, 0.12 mmol; for monomeric complexes, 0.20 mmol), 2 mmol substrate and 15–20 mmol co-catalyst in CH_2Cl_2 (4 mL) was added. After completion of the reaction, the mixture was diluted with CH_2Cl_2 (20 mL). The organic layer was separated, washed with water and brine, then dried over $MgSO_4$. The dimeric catalysts can be precipitated by adding *n*-hexane after partial concentrating the solvent. Centrifugation would afford the precipitated catalyst to be reused. After the total removal of the solvent under reduced pressure, the crude product was purified by flash chromatography (SiO_2, petroleum ether/CH_2Cl_2 = 2:1) to yield the epoxides.

4. Conclusions

In conclusion, these dimeric and monomeric salen-Mn(III) complexes were developed by a facile step-wise procedure. The combination of dimeric salen-Mn(III) complexes with available pyridine *N*-oxide proved effective in cyclic alkene epoxidation reactions. Furthermore, the utilization of porous coordination polymer accelerated the alkene epoxidation in some cases without depressing the enantioselectivity and conversions in the fresh cycles. However, the recycling experiment was unsuccessful, possibly because the porous structure cannot prevent the gradual decomposition of dimeric salen-Mn(III) catalyst. The inherent phase-transfer capability of weakly water-soluble monomeric salen-Mn(III) complexes had been revealed through the catalytic effect of their collaboration with different co-catalysts and the color change on the upper water layer at the end of epoxidation. This work may emphasize a combinational strategy to apprehend the asymmetric alkene epoxidation reactions and encourage more attempts to explore new effective co-catalysts.

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