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Enantioselective epoxidation of nonfunctionalized alkenes catalyzed by recyclable new homochiral bis-diamine-bridged bi-Mn(salen) complexes

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Three new homochiral bis-diamine-bridged bi-Mn(salen) complexes were synthesized. Their catalysis on asymmetric epoxidation of α -methylstyrene, styrene and indene was studied with NaClO and *m*-CPBA as oxidants respectively. This homogeneous catalyst exhibited comparable catalytic activity and enantioselectivity to the Jacobsen's catalyst in the asymmetric epoxidation of unfunctionalized olefins. Furthermore, the catalyst could be conveniently recovered and reused at least five times without significant losses of both activity and enantioselectivity. Specially, it also could be efficiently used in large-scale reactions with superior catalytic disposition being maintained at the same level, which provided the potential for the applications in industry. The effect of axial bases, temperature and solvent on activity and enantioselectivity of the catalytic system were also studied.

homochiral bi-Mn(salen) complex, enantioselective, asymmetric epoxidation, unfunctionalized olefins

1 Introduction

Asymmetric epoxidation of unfunctionalized olefins is highly significant in synthesis of chiral epoxides which are versatile intermediates in the pharmaceutical and various fine chemicals fields. It's still a challenge to get the excellent enantioselectivity epoxides in high yields. Recently, chiral salen Mn (III) complexes have been reported to give high enantioselectivity in the epoxidation of unfunctionalized olefins. Among them, Jacobsen's catalyst and its analogues showed prominent advantages [1]. However, decomposition of the catalyst and formation of inactive dimeric μ -oxo-Mn(VI) [2] lead to the problems of separation and recyclability of the catalyst, which limited the practical applications of chiral Mn(III) salen catalysts in both synthetic chemistry and industrial processes. To address the issue, significant effort has been made to "heterogenize" the Jacobsen chiral salen Mn(III) complex, such as grafting chiral Mn(salen)Cl complexes monomeric catalyst systems onto organic polymers [3], inorganic supports clays [4], MCM-41 [5], SBA-15 [6], activated silica [7], zeolites [8] and organic polymer-inorganic hybrid phosphate-phosphonate materials [9-17]. Unfortunately, although the immobilized catalysts showed the advantages of easy separation and reusing, significant gaps still existed in the scope of these methodologies. First, compared with the homogeneous counterparts, the immobilized complexes generally need some modifications of the supports which lead to the complicated synthesis and high costs. Second, the leaching of salen Mn(III) complexes during reaction is often troublesome. Third, most of modified catalysts are less efficient than their corresponding unmodified catalysts, partly, because of the inaccessibility of the reagents to the active centers in the

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heterogeneous reaction [18]. Thus, the development of a novel class of catalyst with high activity, enantioselectivity and easily separation from the reaction mixture is highly desirable. As we known, appropriately increased the molecular weight of the catalysts could lower their solubility in certain solvents, thus opening a door for product isolation and catalyst recovery [19]. Additionally, increasing the catalytically active metal centers of the catalysts could enhance the catalytic activities and recover the catalyst easily [20, 21]. Recently, a great number of dimeric [22-25] and polymeric homochiral Mn(III) salen complexes [26-28], linked through side chain as homogenous catalysts, have been reported. These dimeric or polymeric complexes, with increased number of active reaction sites, showed higher activities and turnover frequency compared with their corresponding monomeric counterparts. Unfortunately, the enantioselectivity was disappointed and the synthesized steps were still problems. Zhang et al. [29] have reported that axial coordination of the catalyst could improve the enantioselectivities in the asymmetric epoxidation of unfunctionalized olefins. According to this, we herein designed and synthesized a series of bis-diamine-bridged bi-Mn(salen) complexes as homogeneous catalysts (Scheme 1). The prepared catalysts displayed superior catalytic activities and enantioselectivities in the asymmetric epoxidation of α -methylstyrene and indene with *m*-CPBA and NaClO as

the oxidants, especially for α -methylstyrene showed conv. up to 99% and ee up to 99%. And the catalyst could be easily recovered and reused five times without significant losses of both activity and enantioselectivity. Furthermore, it could also be efficiently used in large-scale reactions with the enantioselectivity being maintained at the same level, which provided the potential for applications in industry.

2 Experimental

2.1 Materials and methods

(1R,2R)-(-)-1,2-Diaminocyclohexane, indene, α -methylstyrene, *n*-nonane, *N*-methylmorpholine *N*-oxide (NMO), *m*-chloroperbenzoic acid (*m*-CPBA), NaClO and 4-PPNO were supplied by Alfa Aesar. Other commercially available chemicals were laboratory-grade reagents from local suppliers and used as supplied without further purification. Chiral salen ligand and chiral homogeneous catalyst salen Mn(III) were synthesized according to the standard literature procedures [30].

FT-IR spectra were recorded from KBr pellets using a Bruker RFS100/S spectrophotometer (USA) and diffuse reflectance UV-Vis spectra of the solid samples were recorded in the spectrophotometer with an integrating sphere using BaSO₄ as standard. ¹H NMR and ¹³C NMR were per-



Scheme 1 Synthesis of bis-diamine-bridged bi-Mn(salen) complexes (3a-3c).

formed on AV-300 NMR instrument at ambient temperature of 300 and 121 MHz. All of the chemical shifts were reported downfield in ppm relative to the hydrogen resonance of TMS. The conversions (with *n*-nonane as internal standard) and the ee values were analyzed by gas chromatography (GC) with a Shimadzu GC2010 (Japan) instrument equipped using a chiral column (HP19091G-B233, 30 m × 25 μ m × 0.25 m) and FID detector, injector 230 °C, detector 230 °C. The column temperature was in the range of 80–150 °C.

2.2 Synthesis of bis-diamine-bridged bi-Mn(salen) complexes

1,4-Bis(bromomethyl)-2,3,5,6-tetramethylbenzene (1)

1,2,4,5-Tetramethylbenzene (8.04 g, 6.0 mmol), paraformaldehyde (5.4 g, 180 mmol, 3 equiv) and potassium bromide (23.42 g, 180 mmol, 3 equiv) were mixed with 80 mL acetic acid at room temperature. Then the mixed solution of 10 mL concentrated sulfuric acid (180 mmol, 3 equiv) and 10 mL acetic acid (180 mmol, 3 equiv) was added dropwise. The solution was vigorously stirred with mechanical agitation overnight at 95 °C. The grey solid was collected by filtration and extracted with CH₂Cl₂. The yellow solid was obtained by evaporation of the filtrate under reduced pressure. The crude product was crystallized by ethyl acetate to obtain white needle crystal **1** in a yield of 87%. ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 2.33 (s, 12H), 4.60 (s, 4H); ¹³C NMR (75 MHz, CDCl₃): δ = 134.4, 133.8, 30.7, 15.6; IR (KBr, cm⁻¹): v = 2921.2, 1618.8, 1433.4, 507.4 cm⁻¹.

C2-symmetrical bis-diamine ligands (2a-2c)

Diamine (25 mmol, 2.5 equiv) and sodium hydroxide (1 g, 25 mmol, 2.5 equiv) in 50 mL absolute THF, and 1,4bis(bromomethyl)-2,3,5,6-tetramethylbenzene (3.17 g, 10 mmol) in 20 mL absolute THF was added dropwise. The mixture was then vigorously stirred for 24 h at 65 °C under N₂ protection. After cooled to room temperature, the precipitate was filtered off, washed with ethanol, distilled water, Na₂CO₃ (5%), respectively, and the product **2** was obtain after dried under vacuum.

2a: Yield 82%; ¹H NMR (300 MHz, DMSO-*d*₆): δ (ppm) 2.22 (s, 12H), 4.00 (s, 4H), 4.47 (s, 6H), 6.37–6.62 (m, 8H); IR (KBr, cm⁻¹): v = 3427, 3391, 3348(N–H), 2969, 2894, 2874(C–H), 1612, 1501(–C₆H₅), 1350–1241(C–N), 810(N–H) cm⁻¹; Anal. Calcd. for C₂₄H₃₀N₄: C, 76.97; H, 8.07; N, 14.96%. Found: C, 76.94; H, 8.03; N, 14.94%.

2b: Yield 85%; ¹H NMR (300 MHz, DMSO-*d*₆): δ (ppm) 2.22 (s, 12H), 4.05 (s, 4H), 4.73 (s, 4H), 4.93 (s, 2H), 6.01 (m, 6H), 6.74 (t, *J* = 6.2 Hz, 2H); IR (KBr, cm⁻¹): *v* = 3418, 3378, 3309(N–H), 2982, 2869(C–H), 1612, 1501 (–C₆H₅), 1360–1241(C–N), 810(N–H) cm⁻¹ (in Figure S1); Anal. Calcd. for C₃₆H₃₀N₄: C, 82.09; H, 7.27; N, 10.64%. Found: C, 82.06; H, 7.25; N, 10.61%.

2c: Yield 88%; ¹H NMR (300 MHz, DMSO-*d*₆): δ (ppm) 2.25 (s, 12H), 4.15 (s, 4H), 5.01 (s, 4H), 5.33 (s, 2H), 6.60 (d, *J*=9.0 Hz, 4H), 6.74 (d, *J*=6.2 Hz, 4H), 7.24 (d, *J*=9.0 Hz, 4H), 7.30 (d, *J*=6.2 Hz, 4H); IR (KBr, cm⁻¹): *v* = 3391, 3324, 3210(N-H), 2982, 2920, 2860(C-H), 1609, 1508(-C₆H₅), 1384–1349(C-N), 825(N-H) cm⁻¹; Anal. Calcd. for C₂₄H₃₀N₄: C, 76.97; H, 8.07; N, 14.96%. Found: C, 76.95; H, 8.04; N, 14.95%.

Bis-diamine-bridged bi-Mn(salen) complexes (3a-3c)

Bis-diamine derivative axially coordinated ligands 2a-2c (1.5 mmol), chiral Jacobsen's catalyst (4.5 mmol, 3 equiv) and NaOH (4.5 mmol) in THF (25 mL) was vigorously stirred for 24 h under reflux. The dark brown powder was collected by filtration and washed thoroughly with ethanol, and deionized water respectively, then dissolved in CH₂Cl₂, filtrated, and the filtrate was collected, evaporated under reduced pressure, dried under vacuum.

3a: Yield 90%; IR (KBr, cm⁻¹): v = 3393(N-H), 2914, 2871(C–H), 1630(C=N), 1605, 1510(-C₆H₅), 1350–1245 (C–N), 820(N–H), 519(Mn–O) cm⁻¹ (Figure S1 in the Supporting Information); UV-Vis: (CH₂Cl₂) λ_{max} 330, 421, 503; Anal. Calcd. for C₉₆H₁₃₂Mn₂N₈O₄: C, 73.35; H, 8.46; N, 7.13%. Found: C, 73.31; H, 8.44; N, 7.10%.

3b: Yield 84%; IR (KBr, cm⁻¹): v = 3410(N-H), 2982, 2864(C-H), 1630(C=N), 1613 1502(-C₆H₅), 1350–1239 (C-N), 809(N-H), 505(Mn-O) cm⁻¹ (Figure S1); UV-Vis: (CH₂Cl₂) λ_{max} 340, 429, 512 (Figure S2 in the Supporting Information); Anal. Calcd. for C₁₀₈H₁₄₀Mn₂N₈O₄: C, 75.23; H, 8.18; N, 6.50%. Found: C, 75.20; H, 8.15; N, 6.48%.

3c: Yield 86%; IR (KBr, cm⁻¹): v = 3397(N-H), 2923, 2868(C–H), 1629(C=N), 1607, 1501(–C₆H₅), 1349–1250 (C–N), 872(N–H), 510(Mn–O) cm⁻¹ (Figure S1); UV-Vis: (CH₂Cl₂) λ_{max} 321, 415, 496. Anal. Calcd. for C₉₆H₁₃₂Mn₂N₈O₄: C, 73.35; H, 8.46; N, 7.13%. Found: C, 73.32; H, 8.43; N, 7.11%.

2.3 Synthesis of arylamine modified chiral salen Mn(III) catalyst 4

The arylamine modified chiral salen Mn(III) catalyst were prepared according to similar procedure to bis-diaminebridged bi-Mn(Salen) catalysts [16] (Scheme 2).

2.4 General procedures for enantioselective epoxidation

All catalytic reactions were performed under laboratory atmosphere. The course of the product formation was monitored by GC analysis. A working model of the bis-diaminebridged bi-Mn(salen) complex was showed in Figure 1. Epoxidation of olefins were carried out in two methods.

Method A. A solution of 1.0 mmol of olefin in 4.0 mL of CH_2Cl_2 , the homogeneous diamine-bridged bi-Mn(salen)



Scheme 2 Synthesis of arylamine modified chiral salen Mn(III) catalyst 4.



Figure 1 A working model of diamine-bridged dimeric Mn(salen) complex.

complexes **3a–3c** (0.015 mmol), *n*-nonane (internal standard, 1 mmol) and 4-PPNO (0.50 mmol) was cooled to the desired temperature. Pre-cooled NaClO solution (3.7 mL, 2.0 mmol, 0.55 M, pH = 11.3) was added to the solution. When the reaction was completed (as monitored by TLC), the phases were separated and the aqueous layer was extracted with CH_2Cl_2 (2.0 mL × 3). The combined organic layers were washed with brine (2.0 mL × 3) and dried over anhydrous Na₂SO₄. The conversion and ee values of the epoxide were determined by GC.

Method B. A solution of 1.0 mmol of olefin, the homogeneous diamine-bridged bi-Mn(salen) complexes 3a-3c(0.015 mmol), *n*-nonane (internal standard, 1 mmol) and NMO (*N*-methylmorpholine *N*-oxide) (5.0 mmol) in 4 mL CH₂Cl₂, was cooled to the appropriate temperature, after which pre-cooled solid *m*-CPBA (2.0 mmol) was added in portions over 5 minutes. When the reaction was completed (as monitored by TLC), NaOH (4 mL, 1.0 M) was added, the phases were separated and the aqueous layer was extracted with CH₂Cl₂ (2.0 mL × 3). The combined organic layers were washed with brine (2 mL × 2) and dried over anhydrous Na₂SO₄. The conversion and ee values of the epoxide were determined by GC.

2.5 Recycling of the bis-diamine-bridged bi-Mn(salen) complexes

In a typical recycle experiment, the equal volume of hexane

was added to the reaction mixture after the reactions. Thereafter, the organic phase was separated, and the catalyst was washed with hexane and deionized water, and dried over vacuum at 60 °C for subsequent use without further purification.

2.6 Large-scale asymmetric epoxidation

4b R = $-PhNH_2$

In order to see the catalyst's potential industrial applications, we performed large-scale asymmetric epoxidation reactions. The amount of reagents was α -methylstyrene (25 mmol), *n*-nonane (12.5 mmol), catalyst **3b** (0.375 mmol), NaClO (92.5 ml, 50 mmol, 0.55 M, pH = 11.3), 4-PPNO (12.5 mmol). The organic layer was dried over sodium sulfate. The catalyst was precipitated out from the solution by adding hexane and kept for subsequent use without further purification. The conversion and ee values of the epoxide were determined by GC.

3 Results and discussion

3.1 Asymmetric epoxidation of non-functionalized olefins catalyzed by 3a–3c with *m*-CPBA and NaClO as oxidants

Enantioselective epoxidations of indene, styrene, α -methylstyrene by the prepared catalysts 3a-3c were studied with m-CPBA/NMO or NaClO/PPNO as an oxidant system in CH₂Cl₂ at defined temperature. Jacobsen's catalyst and monomer chiral salen Mn(III) catalysts 4a-4b were also examined for comparison purposes. Conversions and enantiomeric excess values were determined by gas chromatography. The results were presented in Table 1. As described in Table 1, in the two oxidant system, the bi-Mn(salen) catalysts showed higher conversions and ee values than Jacobsen's catalyst 2 and the monomeric catalysts 4a and 4b in the asymmetric epoxidation of indene, styrene and α-methylstyrene under identical reaction conditions. For example, in the m-CPBA/NMO oxidant system, 98% conversion and 99% ee were obtained in the asymmetric epoxidation of indene. In the NaClO/PPNO oxidant system, 99% conversion and 94% ee were obtained in the asymmetric epoxidation of a-methylstyrene (Figure S3 in the Supporting Infor-

Table 1	Asymmetric e	poxidation of	f alkenes c	talyzed by	y 3a–3c with m-	-CPBA ^a) and NaClO ^b) as oxidants
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Entry	Substrate	Catalyst	Oxidant	<i>T</i> (°C)	Time (h)	Conv. (%)	ee (%) ^{c)}
1	2-methylstyrene	Jacobsen	m-CPBA/NMO	-20	4	95	57
2	2-methylstyrene	4 a	m-CPBA/NMO	-20	4	97	64
3	2-methylstyrene	4b	m-CPBA/NMO	-20	4	95	72
4	2-methylstyrene	3a	m-CPBA/NMO	-20	4	96	85
5	2-methylstyrene	3a	m-CPBA	-20	4	78	53
6	2-methylstyrene	3b	m-CPBA/NMO	-20	4	98	90
7	2-methylstyrene	3c	m-CPBA/NMO	-20	4	99	92
8	2-methylstyrene	Jacobsen	NaClO/PPNO	20	6	90	47
9	2-methylstyrene	3a	NaClO/PPNO	20	6	95	89
10	2-methylstyrene	3a	NaClO	20	6	67	52
11	2-methylstyrene	3b	NaClO/PPNO	20	6	97	90
12	2-methylstyrene	3c	NaClO/PPNO	20	6	99	94
13	indene	Jacobsen	m-CPBA/NMO	-20	4	92	65
14	indene	4 a	m-CPBA/NMO	-20	4	90	78
15	indene	4b	m-CPBA/NMO	-20	4	92	72
16	indene	3a	m-CPBA/NMO	-20	4	93	87
17	indene	3b	m-CPBA/NMO	-20	4	95	90
18	indene	3c	m-CPBA/NMO	-20	4	98	99
19	indene	Jacobsen	NaClO/PPNO	20	6	90	72
20	indene	3a	NaClO/PPNO	20	6	92	80
21	indene	3b	NaClO/PPNO	20	6	94	87
22	indene	3c	NaClO/PPNO	20	6	97	91
23	styrene	Jacobsen	m-CPBA/NMO	-20	4	87	31
24	styrene	4 a	m-CPBA/NMO	-20	4	86	35
25	styrene	4b	m-CPBA/NMO	-20	4	90	42
26	styrene	3a	m-CPBA/NMO	-20	4	92	45
27	styrene	3b	m-CPBA/NMO	-20	4	98	50
28	styrene	3c	m-CPBA/NMO	-20	4	99	62
29	styrene	Jacobsen	NaClO/PPNO	20	6	84	42
30	styrene	3a	NaClO/PPNO	20	6	88	51
31	styrene	3b	NaClO/PPNO	20	6	90	55
32	styrene	3c	NaClO/PPNO	20	6	93	67

a) Reactions were carried out at desired temperature in CH₂Cl₂ (4 mL) with alkene (1.0 mmol), *m*-CPBA(2.0 mmol), NMO (5.0 mmol, if necessary), nonane (internal standard, 1.0 mmol) and catalysts (0.015 mmol). The conversion and the ee value were determined by GC with chiral capillary columns (HP19091G-B233, 30 m × 25 μ m × 0.25 μ m); b) reactions were carried out at desired temperature in CH₂Cl₂ (4 mL) with alkene (1.0 mmol), NaClO (3.7 ml, 2.0 mmol, 0.55 M, pH = 11.3), 4-PPNO (0.5 mmol, if necessary), nonane (internal standard, 0.5 mmol) and catalysts (0.015 mmol). The conversion and the ee value were determined by GC with chiral capillary columns (HP19091G-B233, 30 m × 25 μ m × 0.25 μ m); c) (*S*)-form.

mation). However, Hu et al. [31] reported that the ethyldiamine-bridged bi-Mn(salen) complexes catalyzed enantioselective epoxidation of a-methylstyrene only got 33% yield and had no enantiomeric excess values. The results were also better than the previously reported -CH2- linked dimeric Mn(III) salen complex [24] with the ee values only 20–30% for epoxidation of α -methylstyrene. To the best of our knowledge, the highest ee value of α -methylstyrene is 78% known from the literatures [5] with heterogeneous Mn(salen) catalysts immobilized in inorganic support via multi-step grafting. The excellent results in this text were due to the increased local concentration of the active sites for the bis-diamine-bridged bi-Mn(salen) complexes, and the cooperative interaction [18, 21] between the two metal centers presented in the catalysts that were not working in isolation. Moreover, diamine group in bis-diamine-bridged bi-Mn(salen) complexes can facilitate the electron transfer between the

Mn(salen) complexes [31]. Meanwhile, the monomeric catalysts **4a** and **4b** also showed higher ee values than the Jacobsen's catalyst with the same level of conversions. Based on above, it indicates that the rigid linker, coordination method and increased active metal centers were devoted to the increase of ee values. Moreover, catalyst **3c** got the better results than **3a** and **3b** in both the two oxidation systems. It was probably due that the axial coordinating ligand **2c** has stronger electron-donating character than **2a** and **2b**, and the olefins can approach to the Mn-oxo center more expediently with the increase of linkage lengths. The same results were also obtained by Li *et al.* [32].

Chiral Mn(III) salen complexes are sensitive to the choice of the solvent and it has been reported [33] that 15 mol% monomeric Jacobsen catalyst loading resulted in cyanochromene epoxide yield 67%, ee's 85% in 15 min and yield 61%, ee's 19.8% in 12 h in acetonitrile and CH_2Cl_2 respectively. In view of this, the effect of solvents using complex **3b** as catalyst in the epoxidation of indene was studied (Table 2). The considerable decrease of enantioselectivity caused by the use of toluene and hexane as solvents may be due to the polarity of these solvents in comparison with dichloromethane. Acetonitrile and tetrahydrofuran which moderately dissolves complex **3b**, can take part in coordination on the Mn centre, competing with indene coordination, hence leading to the lower yields observed compared with dichloromethane as solvent. The solvent dichloromethane dissolves complex **3b** completely yielded 94% conversion with 87% ee's. Hence, dichloromethane turned out to be the most suitable solvent for the present epoxidation studies.

We further researched the effect of the temperature for the epoxidation of α -methylstyrene using *m*-CPBA as the oxidant (Table 3). A decrease of reaction temperature from 0 to -78 °C led to the decrease of the conversion from 99 to 90%. However, an increase of enantioselectivity (86% to 99%) was observed, which was consistent with the conclusion reported in reference [25]. The reaction rate was decreased with the decrease of temperature.

It is well known that the axial base acts as an additional donor ligand by forming a strong bond with the transitionmeter center, which endows it with a dual role in activating the catalyst and stabilizing the oxo intermediate [34, 35]. The effects of various axial bases, such as PyNO, NMO, 4-PhPyNO and 4-PPPyNO, as well as their different amounts on the asymmetric epoxidation of indene in the presence of the complex 3b were investigated and the results were listed in Table 4. As expected, a rather low yield of the epoxide with a relatively low enantioselectivity was obtained in the absence of additive axial base (entry 1), whereas the addition of axial base led to the increase of the yield and enantioselectivity of the epoxide (entries 2-9), suggesting that the presence of axial base is essential to the asymmetric epoxidation of indene. Also, the amount of various axial bases had a crucial influence on the yield and enantioselectivity of the epoxide. In general, with an increased amount of the axial base, the yield of the epoxide reached a maximum level then decreased and the enantioselectivity increased until a constant level was reached (entries 2-6). When adding 1 mmol of 4-PhPyNO or 4-PPPyNO in the reaction system, the maximum yield and enantioselectivity of target product was obtained (entries 8, 9). An excess of axial base would lower the activity of the catalyst, thus resulting in a decrease of the yield of target product, but with no effect on the enantioselectivity. As a result, adding 0.5 mmol 4-PPNO to the NaClO oxidant system could obtain the best results.

3.2 The recycling of the chiral bi-Mn(salen) complexes

We are also interested in recycling the catalysts in the ee's of the epoxidation. It was found that the bi-Mn(salen) com-

Table 2 Data for the enantioselective epoxidation of indene with NaClO^{a)} catalyzed by the catalyst **3b** using different solvents at 20 °C

Entry	Solvent	Time (h)	Con. (%)	ee (%) ^{b)}
1	toluene	6	89	45
2	hexane	6	72	36
3	THF	6	46	69
4	CH3CN	6	28	76
5	DCM	6	94	87

a) The reactions were carried out using the same method with Table 1. The conversion and the ee value were determined by GC with chiral capillary columns (HP19091G-B233, 30 m × 25 μ m × 0.25 μ m); b) (*S*)-form.

Table 3 Effect of temperature on epoxidation of indene with *m*-CPBA ^{a)} catalyzed by the catalyst **3b**

Entry	<i>T</i> (°C)	Time (h)	Conv. (%)	ee (%) ^{b)}
1	0	4	99	86
2	-20	5	98	90
3	-40	7	95	93
4	-78	10	90	99

a) Reactions were carried out at desired temperature in CH_2Cl_2 (4 mL) with alkene (1.0 mmol), *m*-CPBA(2.0 mmol), NMO (5.0 mmol), nonane (internal standard, 1.0 mmol) and catalysts (0.015 mmol). The conversion and the ee value were determined by GC with chiral capillary columns (HP19091G-B233, 30 m × 25 µm × 0.25 µm); b) (*S*)-form.

Table 4 Effect of donor ligands on the on epoxidation of indene withNaClO $^{a)}$ catalyzed by the catalyst **3b** at 20 °C

Entry	Axial base (mmol)	ee (%) ^{b)}	Conv. (%)
1	-	48	65
2	4-PPNO(0.2)	74	86
3	4-PPNO(0.5)	87	94
4	4-PPNO(1.0)	85	92
5	4-PPNO(1.5)	86	87
6	4-PPNO(2.0)	88	75
7	PyNO (0.5) ^{c)}	58	89
8	4-PhPyNO (1) c)	74	78
9	4-PPPyNO (1) ^{c)}	82	84

a) Reactions were carried out at desired temperature in CH₂Cl₂ (4 mL) with alkene (1.0 mmol), NaClO (3.7 ml, 2.0 mmol, 0.55 M, pH = 11.3), different axial base, nonane (internal standard, 0.5 mmol) and catalysts (0.015 mmol). The conversion and the ee value were determined by GC with chiral capillary columns (HP19091G-B233, 30 m × 25 μ m × 0.25 μ m). b) (*S*)-form; c) the optimum amount.

plexes were very soluble in dichloromethane, but almost insoluble in hexanes and diethyl ether. Based on the solubility of our bi-Mn(salen) complexes mentioned above, the catalysts was precipitated in hexane for recovery from the concentrated reaction mixture (Figure 2). The solid can be conveniently isolated by filtration, and then dissolved in dichloromethane for another reaction. Experimental study of the recovery and recyclability was conducted using complex **3b** as the catalyst, the epoxidation of α -methylstyrene with aqueous NaClO/4-PPNO as an oxidant under optimized reaction conditions.

Despite the possible loss of catalyst during the recovery

and reuse process, the recycling experiments were successfully carried out up to five times. The recycling data were listed in Table 5. As can be seen, 87% conversion and 86% ee value were obtained in the fifth reaction with only a small decrease in catalytic activity compared to the fresh catalyst. Slightly decreased conversion and ee values were attributed to the minor physical losses of the catalyst in the post-epoxidation work up. The amount of Mn in catalyst **3b** was calculated by AAS after five runs. The result indicated that 15% of the Jacobsen salen Mn gradually degradated from the catalyst **3b** under the epoxidation conditions.

3.3 Large-scale asymmetric epoxidation reaction

We further performed various proportions of large-scale asymmetric epoxidation reactions with α -methylstyrene as a model substrate using NaClO/PPNO as oxidation system. The large-scale experiments proceeded smoothly under the same procedure with the experimental-scale. As can be seen from the results summarized in Table 6, delightfully, the conversion and enantioselectivity maintained at the same



Figure 2 (a) The catalytic system; (b) separation of the catalyst.

Table 5 Recycling of complex **3b** for asymmetric epoxidation of α -methylstyrene using NaClO/4-PPNO as oxidant^{a)}

Run	ee (%) ^{b)}	Conv. (%)
Fresh	90	97
2	90	96
3	89	93
4	87	90
5	86	87

a) Reactions were carried out at desired temperature in CH₂Cl₂ (4 mL) with α -methylstyrene (1.0 mmol), NaClO (3.7 ml, 2.0 mmol, 0.55 M, pH = 11.3), 4-PPNO (0.5 mmol), nonane (internal standard, 0.5 mmol) and catalyst 3b (0.015 mmol) at 20 °C for 6 h; b) (*S*)-form.

Table 6 Large-scale asymmetric epoxidation reaction of α-methylstyrene ^{a)}

Entry	Time (h)	Conv. (%)	ee (%) ^{d)}
1 ^{b)}	6	97	92
2 ^{c)}	6	95	90

a) Same as in Table 2; b) the usage amounts of reagents were α -methylstyrene (25 mmol), *n*-nonane (12.5 mmol), catalyst **3b** (0.375 mmol), NaClO (92.5 ml, 50 mmol, 0.55 M, pH = 11.3), 4-PPNO (12.5 mmol) at 20 °C for 6 h; c) the usage amounts of reagents were α -methylstyrene (50 mmol), *n*-nonane (25 mmol), heterogeneous catalyst **3b** (0.75 mmol), NaClO (185 ml, 100 mmol, 0.55 M, pH = 11.3), 4-PPNO (25 mmol) at 20 °C for 6 h; d) (*S*)-form.

level for the large-scale reactions under the corresponding condition although the large scale was 25 or 50 times bigger than the experimental scale.

4 Conclusions

In summary, three new bis-diamine-bridged bi-Mn(salen) complexes have been synthesized and characterized. They were efficient catalysts for asymmetric epoxidation of un-functionalized alkenes with good-to-excellent chemical yields and enantioselectivity. Moreover, those catalysts were relatively stable, could be recycled five times in the asymmetric epoxidation reactions, and could also be efficiently used in large-scale reactions with the enantioselectivity being maintained at the same level, which provided the potential for applications in industry.

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