



# Synthesis, catalytic activity and recycle of novel dimeric salen-Mn(III) complexes in asymmetric epoxidation

Liu Xinwen<sup>a,b</sup>, Tang Ning<sup>a,\*</sup>, Liu Weisheng<sup>a</sup>, Tan Minyu<sup>a</sup>

<sup>a</sup> College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China

<sup>b</sup> Department of Chemistry, Tianshui Normal University, Tianshui 741000, China

Received 26 September 2003; received in revised form 20 November 2003; accepted 20 November 2003

## Abstract

Novel chiral dimeric salen-Mn complexes were synthesized and their catalytic effects in asymmetric epoxidation of non-functionalized alkenes were investigated. The study was undertaken using a dimeric catalyst to establish whether high enantioselectivity could be achieved just like its active monomer, and whether the bigger complex could be efficiently recovered and reused by a simple controlling solvent system. The result showed that high activity and enantioselectivity were achieved. The dimeric complex formation enhanced the catalyst's reactivity and stability without compromising its enantioselectivity. Catalyst **3a**, unlike its monomer, could be easily recovered and reused for several cycles under the mild reaction conditions before a marked decline in yield and ee was observed.

© 2003 Elsevier B.V. All rights reserved.

**Keywords:** Dimeric complex; Catalytic epoxidation; Enantioselectivity; Recycle; Synthesis

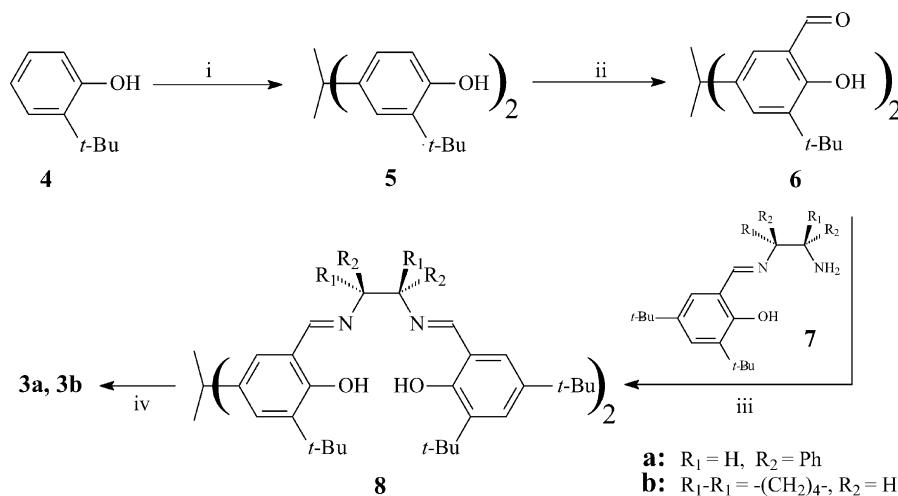
## 1. Introduction

Since Jacobsen designed and synthesized the first chiral C<sub>2</sub>-asymmetric salen-type complex in the 1990s, a large number of chiral Schiff-base complexes have been developed as catalysts for various asymmetric reactions [1–3]. With regard to environmental legislation and economical consideration, the synthesis of catalysts that can be easily recovered and provide high selectivity while producing low levels of waste is highly desirable [4]. The Jacobsen salen-Mn catalysts, with a simple structure (monomer) and lighter molecular weights, have emerged as efficient and practical catalysts for asymmetric epoxidation of *cis*-alkenes [5], for example **1** and **2** (Scheme 2) that bear *t*-butyl groups at the C3 (3') and C5 (5') positions have been commercially excellent catalysts. However, it has been established that the salen-Mn catalysts are unstable under prolonged oxidative condition and cannot be recovered and recycled [6]. In practice, the steric and electronic properties of the salen framework, composed of two salicylaldehyde units and a chiral diamine, can be tuned by altering the substituents on

either portion. Therefore, many reports have afterward appeared describing studies of structurally varied complexes [7]. For example, some macrocycle complexes and multinuclear complexes reported contain several active centers [8]. But these efforts to improve catalysts' reactivity or recyclability have succeeded less often as a result of unsuitable or unstable catalyst structure [9]. While homogeneous catalysis often provides the best results in achieving high levels of enantioselectivity, heterogeneous catalysis offers the advantages of simplified product purification and the potential for recycling the catalyst. In order to be recovered for reuse, a number of supported catalysts with big molecular weights have been synthesized and studied. Among them, the salen monomer was incorporated to support by many methods including non-covalent immobilization, inorganic graft, copolymerization or polymer attachment, etc. [10]. Pozzi et al. fluoros biphase systems (FAB) was also one of the interesting attempts about separation and recycling techniques [11]. These supported catalysts, however, generally involved complicated synthesis or high costs and their uses have produced varied results including lower conversion, poor selectivity, narrow range of use, and even limited recyclability [12]. Indeed, making material precipitate by the control of solvent is still the most convenient and economical method for both product isolation and catalyst recovery.

\* Corresponding author. Tel.: +86-931-8912582/8626264;  
fax: +86-931-8912582.

E-mail address: [liuxw9391@163.com](mailto:liuxw9391@163.com) (T. Ning).



Scheme 1. Reagents and conditions: (i) catalyst,  $\text{H}_2\text{SO}_4$ , acetone; (ii) hexamethylenetetramine, acetic acid, 33% $\text{H}_2\text{SO}_4$ ,  $\Delta$ ; (iii) EtOH, reflux; (iv)  $\text{Mn}(\text{OAc})_2/\text{LiCl}$ ,  $\text{CH}_2\text{Cl}_2$ , EtOH.

We had expected that increasing the number of active metal sites on the catalyst would result in high activity or reactivity and help substrate turnover. Conversely appropriately increasing the molecular weight of catalyst would lower its solubility with a wider solvent selection, thus aid product isolation and catalyst recovery. Therefore, two dimeric salen-Mn(III) complexes (**3a** and **3b**, Scheme 2) were designed and synthesized. The immediate goals of our studies were to evaluate the effect of new dimeric catalysts on the enantioselectivity and to further determine the extent of its recovery and recycling in different solvent systems.

## 2. Results and discussion

### 2.1. Synthesis of dimeric Mn(III)-Schiff-base complexes

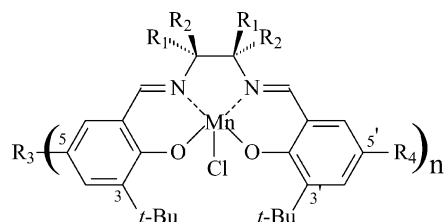
The synthesis route for chiral dimeric complexes **3a** and **3b** is shown in Scheme 1. The procedure includes initial preparation of 5,5-isopropylidene-bis-salicylaldehyde **6** by aldolization from *o*-*t*-butyl-bis-phenol-A **5**, followed by a condensation of **6** with the chiral half-units **7**, which were synthesized by condensation from 3,5-disubstituted-sali-

cyaldehyde and (*S,S*)-1,2-diphenylethylenediamine or (*R,R*)-1,2-cyclohexanediamine, final metallation with Mn(II) salt.

### 2.2. The effect of dimeric catalysts on epoxidation

Complexes **3a** and **3b** were then used as catalysts in epoxidation of styrene (A), *cis*- $\beta$ -methyl-styrene (B) and 6-cyano-2,2-dimethylchromene (C). The monomer **1** was also examined as a comparison. Two model oxidation systems (*m*-CPBA/NMO/ $\text{CH}_2\text{Cl}_2$  homogeneous system and NaClO/PPNA/ $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$  binary media system) were selectively employed as oxidant conditions. The results from the epoxidation of these substrates are shown in Table 1.

All reactions proceeded smoothly and afforded high yields and enantioselectivity. However, the terminal-olefin styrene gave somewhat moderate ee's. The possibility for partial epoxide ring opening with subsequent kinetic resolution cannot be ruled out [13]. Two kinds of oxidants afforded almost identical yields and ee's as to most of the substrates. The NaClO system resulted in longer reaction times (e.g. at 0 °C reaction time extend to 2 h, while under the *m*-CPBM system the reaction was generally completed in 15 min) (entries 5, 8 and 10). In the *m*-CPBA/NMO/ $\text{CH}_2\text{Cl}_2$  system, lowering the temperature from 0 to -20 °C had practically no effect on the ee of the epoxide but had a minor affect on the increase of conversion (entries 1 and 2). Further lowering of the temperature to -78 °C resulted in retardation of the reaction rate and only a slight increase in ee (entry 3). For the same catalyst, the effect of asymmetric epoxidation gradually improved in the order of substrates from A, B to C. Particularly useful values (yield, ee) were obtained for electron-rich substrate C (entries 11–13). We also saw the difference in reactivity between 1,2-diphenylethylenediamine- and 1,2-diaminocyclohexane-derived catalysts (**3a** versus **3b**). While catalyst **3b** produced slightly better results compared



- 1:**  $n=1, R_1=\text{H}, R_2=\text{Ph}, R_3=R_4=t\text{-Bu}$ .  
**2:**  $n=1, R_1-R_1=-(\text{CH}_2)_4-, R_2=\text{H}, R_3=R_4=\text{Me}$ .  
**3a:**  $n=2, R_1=\text{H}, R_2=\text{Ph}, R_3=\text{CH}(\text{CH}_3)_2-, R_4=t\text{-Bu}$ .  
**3b:**  $n=2, R_1-R_1=-(\text{CH}_2)_4-, R_2=\text{H}, R_3=\text{CH}(\text{CH}_3)_2-, R_4=t\text{-Bu}$ .

Scheme 2.

Table 1

Epoxidation of styrene, *cis*- $\beta$ -methyl-styrene and 6-cyano-2,2-dimethylchromene using catalyst **3a**, **3b** and **1**<sup>a</sup>

Entry	Alkene <sup>b</sup>	Catalyst	Oxidant	Temperature (°C)	Time (min)	Yield (%) <sup>c</sup>	ee (%) <sup>d</sup>	Configuration
1	A	<b>3a</b>	<i>m</i> -CPBA	0	10	73	55	<i>S</i>
2	A	<b>3a</b>	<i>m</i> -CPBA	−20	15	76	56	<i>S</i>
3	A	<b>3a</b>	<i>m</i> -CPBA	−78	20	75	57	<i>S</i>
4	A	<b>3b</b>	<i>m</i> -CPBA	−30	20	70	51	<i>R</i>
5	A	<b>3b</b>	NaClO	0	120	68	47	<i>R</i>
6	B	<b>1</b>	<i>m</i> -CPBA	−20	30	81	82	1 <i>S</i> , 2 <i>R</i>
7	B	<b>3a</b>	<i>m</i> -CPBA	−20	15	83	83	1 <i>S</i> , 2 <i>R</i>
8	B	<b>3a</b>	NaClO	0	100	79	76	1 <i>S</i> , 2 <i>R</i>
9	B	<b>3b</b>	<i>m</i> -CPBA	−20	25	81	78	1 <i>R</i> , 2 <i>S</i>
10	B	<b>3b</b>	NaClO	0	120	77	81	1 <i>R</i> , 2 <i>S</i>
11	C	<b>1</b>	<i>m</i> -CPBA	−20	25	91	94	3 <i>S</i> , 4 <i>S</i>
12	C	<b>3a</b>	<i>m</i> -CPBA	−20	15	93	92	3 <i>S</i> , 4 <i>S</i>
13	C	<b>3b</b>	<i>m</i> -CPBA	−20	15	92	94	3 <i>R</i> , 4 <i>R</i>

<sup>a</sup> Reaction were carried out in CH<sub>2</sub>Cl<sub>2</sub> using *m*-CPBA as oxidant with a molar ratio of substrate:catalyst:oxidant:NMO = 1:0.025 (0.05 for **1**):2:5, or using NaClO as oxidant and 4-phenylpyridine N-oxide as additive.

<sup>b</sup> A: styrene, B: *cis*- $\beta$ -methyl-styrene, C: 6-cyano-2,2-dimethylchromene.

<sup>c</sup> Determined by GC.

<sup>d</sup> Determined by GLC.

to **3a** for C, catalyst **3a** gave higher values of ee's and yields than **3b** gave for else substrates. As compared with Jacobsen complex **1**, **3a** is also a better catalyst to afford more excellent conversions although they showed a similar level of asymmetric induction (entries 6–7 and 11–12).

In practice, it was found that most of the above catalytic reactions were finished in less than 15 min. However, the reactions using Jacobsen's monomeric catalyst would close after 25 min. As expected, the dimeric complexes showed enhanced activity and the results indicate that the two metal centers were not working in isolation but had some synergistic interaction.

In order to compare the efficiency between mono- and dimeric catalysts (**1** and **3a**) with different loadings, a further examination was carried out. The results are shown in Table 2. We found the lowest level of efficient loading was 1 mol% (**3a**) or 2.5 mol% (**1**). When catalyst loading was increased from 1 to 5 mol% the reaction rate was acceler-

ated obviously, and for **3a** the yields of epoxide rose greatly from 53 to 83% at the second minute. The reaction was finished after 7 min using 2.5 mol% dimeric catalyst **3a**, but for monomer **1** the reaction was finished after more than 30 min under the same reaction condition. When catalyst loading was increased to 5.0 mol%, maximum conversion occurred within 2 min for **3a** but more than 15 min for **1**. We also found the enantioselectivity of reactions was independent of the loading level of the catalyst and always high, even in the presence of only 0.5 mol% of the catalyst. This result was fully consistent with that of monomer reported previously [14].

### 2.3. The recovery and recycling of dimeric catalyst

At first using *m*-CPBA as the oxidant, the recovery and recycling of catalyst **3a** was investigated in both homogeneous and heterogeneous reactions. In practice, this dimeric catalyst was found to be less soluble than its monomer. It could be easily precipitated from hexane, ether, even EtOAc and EtOH, but soluble in CH<sub>2</sub>Cl<sub>2</sub>, DMF and CH<sub>3</sub>CN. For catalyst **3a**, we chose soluble CH<sub>2</sub>Cl<sub>2</sub> as homogeneous reaction solvent and difficult-soluble ether as the heterogeneous reaction medium. In the former system, the catalyst was recovered by adding sufficient hexane to reaction mixture and was filtrated, while in the latter system the catalyst was recovered through direct filtration of the suspension. The filter cake was washed with aq. NaOH (1 M) and water then dried for reuse in the next run. The results for the multi-recycle epoxidation of *cis*- $\beta$ -methyl-styrene are shown in Table 3.

It was interesting to note that in general recycles, the conversions of epoxide were more steady but showed a significant drop in ee's under heterogeneous catalytic reactions while in homogeneous reaction, the values of ee's only had a slight decrease but a quickly reducing change in yields. It was also noteworthy that recycling under two

Table 2

Yield (%) (ee%) of epoxide of *cis*- $\beta$ -methyl-styrene with different loading of catalysts in CH<sub>2</sub>Cl<sub>2</sub> at different time<sup>a</sup>

	Time (min)				
	2	7	15	30	60
Catalyst <b>3a</b> (mol%)					
1.0	53 (82) <sup>b</sup>	74 (83)	80	82	83
2.5	81 (83)	83 (82)	83 (83)	83 (82)	–
5.0	83 (83)	83	84	–	–
Catalyst <b>3a</b> (mol%)					
1.0	38	56	68	72	–
2.5	39	69	78	82	82
5.0	64	76	82	83	–

<sup>a</sup> Reaction were carried out in CH<sub>2</sub>Cl<sub>2</sub> at −20 °C using *m*-CPBA as oxidant with a molar ratio of substrate:catalyst:*m*-CPBA:NMO = 1:0.01–0.05:2:5.

<sup>b</sup> Values in parentheses are ee(%) determined at correlative time.

Table 3

Catalyst **3a**'s recyclability in different-phase epoxidation of *cis*- $\beta$ -methyl-styrene at  $-20^\circ\text{C}$ 

Reaction	Homogeneous ( <i>m</i> -CPBA/CH <sub>2</sub> Cl <sub>2</sub> )					Heterogeneous ( <i>m</i> -CPBA/ether)				
	1	2	3	4	5	1	2	3	4	5
Run	1	2	3	4	5	1	2	3	4	5
Yield (%)	80	71	63	56	49	79	74	70	67	64
ee (%)	83	82	80	77	72	78	74	69	63	58
Time (min)	15	15	20	25	30	15	20	25	30	40

reaction types could be successfully repeated about 2–3 times at temperatures  $0^\circ\text{C}$  or lower. At room temperature or higher, however, the efficiency of recycling would, especially for homogeneous catalysis, sharply worsen with rapidly decreasing ee's and yields. One possible reason is that low temperatures would prevent or slow catalyst degradation [13]. The oxidative degradation or soluble loss of the catalyst in a homogeneous reaction was heavier than in a heterogeneous reaction. It is apparent from the results that the solvent systems can influence the efficiency of catalyst recycling. This also indicates that the insoluble nature of the catalyst does not obviously affect the rate of epoxidation.

Then the recycling of catalyst **3a** was conducted under binary solvent systems (*m*-CPBA/CH<sub>2</sub>Cl<sub>2</sub>/ether and NaClO/H<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub> biphasic system). In the first system, ether was slowly dropped into a previous solution of mixture of catalyst, alkene and NMO in CH<sub>2</sub>Cl<sub>2</sub> until the solution just became slightly turbid and then *m*-CPBA was added in. The results are shown in Table 4.

Under NaClO/H<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub> system, **3a** could be used in a second reaction with light loss of both ee and yield for the epoxidation of *cis*- $\beta$ -methyl-styrene. After the first recycle, unfortunately, precipitation resulted in a pale-color gummy solid that led to poor results in further recycles. It was exciting to find that under the *m*-CPBA/CH<sub>2</sub>Cl<sub>2</sub>/ether biphasic system, catalyst **3a** could be effectively used for 4–5 times without a significant drop in selectivity and without an unacceptable yield. Further attempts to recycle, however, resulted in poor results of both conversion and enantioselectivity. The NaClO oxidative system was not more robust than *m*-CPBA system, possibly due to the loss of more manganese in the base solution. The studies indicate that the reaction conditions play a fundamental role in the extent of catalysis and recycles.

While monomeric salen-Mn catalysts are generally difficult to recover and recycle [6] the bigger dimeric catalyst **3a** can be recovered and reused for several recycles. Obvi-

ously, catalyst **3a**'s repeatability or stability is better and its recyclability is even superior to polymer-supported catalysts which generally involve complicated synthesis or high costs as noted previously [12].

In conclusion, the new dimeric Mn(III)-Schiff-base complexes have been synthesized and successfully used in the asymmetric epoxidation of unfunctionalized alkenes examined in this investigation. Complex **3a** is a superior catalyst with higher catalytic activity and asymmetric inductivity. The quickened reaction and high activity indicates that two metal centers of dimeric catalyst are working under synergistic interaction. The dimeric catalyst also shows better repeatability and stability than monomer. Multiple recycles of the dimeric catalyst have been carried in different phase reactions. Complex **3a** can be efficiently used for as many as five cycles under the biphasic reaction system used. The activity of the recycled catalyst gradually decreased during each successive use, possibly due to minor catalyst's degradation or soluble loss during the reaction. Choosing a heavier catalyst or semi-soluble oxidation condition can be an efficient and desirable way to aid catalyst recovery and reuse.

### 3. Experiment

#### 3.1. Generation

<sup>1</sup>H NMR spectra were obtained at 200 MHz on Bruker DRX-200 spectrometer using CDCl<sub>3</sub> as solvent. IR spectra were recorded on Nicolet NEXUS 670 FT-IR spectrometer. FAB-MS was acquired on MASPEC II System mass spectrometer. Elemental analyses were performed on Elementar VarioEL instrument in the Analysis and Test Center of Lanzhou University. Chiral half-units **7a–b** were prepared by reference to literature [15,16]. Catalyst **1** was prepared as indicated in the literature [17]. (*S, S*)-1,2-Diphenylethylenediamine and (*R, R*)-1,

Table 4

Catalyst **3a**'s recyclability in binary solvent oxidation systems

Reaction	<i>m</i> -CPBA/CH <sub>2</sub> Cl <sub>2</sub> /ether, $-20^\circ\text{C}$					NaClO/H <sub>2</sub> O/CH <sub>2</sub> Cl <sub>2</sub> , $0^\circ\text{C}$				
	1	2	3	4	5	1	2	3	4	5
Run	1	2	3	4	5	1	2	3	4	5
Yield (%)	80	77	74	70	65	78	67	48	24	–
ee (%)	82	81	80	78	73	76	71	64	56	43
Time (min)	15	20	25	30	40	100	120	200	250	360

2-cyclohexanediamine were purchased from the Likai Chiral Technique Company Ltd. in Chengdu.

### 3.2. Synthesis of 2,2-di-*t*-butylbisphenol-A **5** [18]

Acetone (3.0 ml, 0.04 mol) was dropped into a mixture of *o*-*t*-butyl-benzene phenol (0.08 mol), catalyst H<sub>2</sub>SO<sub>4</sub> (78%, 5 ml) and additional catalyst in 15 ml methylbenzene under continuous stirring, and the temperature was confined below 35 °C. The mixture continued to be stirred for 2 h with a higher temperature between 35 and 40 °C. Then the mixture was poured into 40 ml cold water and stood for several hours. The precipitation was filtered and washed with cold water till the filter-liquor showed with no acid reaction. After being dried, the crude product was recrystallized in EtOH to give white needle crystal (yield 64%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.28 (18H, s), 1.38 (6H, s), 4.95 (2H, s), 6.50–7.35 (6H, m) ppm.

### 3.3. Synthesis of 5,5-isopropylidene-3,3-di-*t*-butyl-bissalicylaldehyde (**6**)

The general preparation was referenced partially to literature [16]. A mixture of 2,2-di-*t*-butylbisphenol A (0.012 mol) and 6.8 g hexamethylenetetramine in 16 ml acetic acid was heated slowly to 130 °C while being stirred and refluxed for 2 h and then cooled to 75 °C. After adding 16 ml 33% H<sub>2</sub>SO<sub>4</sub> and being refluxed 1 h at 105–110 °C, the mixture was cooled back to room temperature and extracted with ether. The extract was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed. The residue was purified by silica gel column chromatography to give yellow semi-solid product. Yield 57%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.35 (18H, s), 1.60 (6H, s), 7.35–7.38 (2H, d), 7.60–7.63 (2H, d), 9.89 (2H, s), 11.66 (2H, s) ppm.

### 3.4. Synthesis of Schiff-base ligands (**8a–b**)

The general preparation was referenced to literature [19]. A solution of mono-imine **7** (1.0 mmol) and bis-salicylaldehyde **6** (0.5 mmol) in dry EtOH (20 ml) was refluxed for 5–7 h. The resulting solution, after being concentrated, precipitated out the desired chiral ligand. The residue was purified by silica gel column chromatography (eluent hexane–EtOAc) to give **8**.

**8a** was prepared from **6** and **7a**, yellow foam-solid. Yield 75%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.26 (18H, s), 1.44 (36H, s), 1.60 (6H, s), 4.78 (4H, s), 6.76–7.30 (28H, m), 8.40 (4H, s), 13.63 (bs, 4H exchangeable with D<sub>2</sub>O) ppm. FAB-MS *m/z*: 1217.87 (*M* + 1)<sup>+</sup> (FM 1216). Anal. calcd. for C<sub>83</sub>H<sub>100</sub>N<sub>4</sub>O<sub>4</sub>: C, 81.87; H, 8.28; N, 4.60%. Found: C, 81.64; H, 8.37; N, 4.46%.

**8b** was prepared from **6** and **7b**, yellow foam-solid. Yield 80%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.24 (18H, s), 1.42 (36H, s), 1.55 (6H, s), 1.57–2.26 (16H, m), 3.22 (4H, s), 6.78 (4H, s), 7.10 (4H, s), 8.24 (4H, s), 13.76 (bs, 4H exchangeable with D<sub>2</sub>O) ppm. FAB-MS *m/z*: 1021.56 (*M* + 1)<sup>+</sup> (FM 1020).

Anal. calcd. for C<sub>67</sub>H<sub>96</sub>N<sub>4</sub>O<sub>4</sub>: C, 78.78; H, 9.47; N, 5.48%. Found: C, 79.03; H, 9.33; N, 5.51%.

### 3.5. Synthesis of Mn (III)-Schiff-base complexes (**3a–b**)

A mixture of **8a** or **8b** (1 mmol, in CH<sub>2</sub>Cl<sub>2</sub>) and Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O (2.1 mmol, in EtOH) was stirred under reflux under nitrogen atmosphere for 5–6 h. Solid LiCl·H<sub>2</sub>O (5 mmol) was added and the mixture was further refluxed for 3 h while exposed to air. The solvent was removed, and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The extract was washed with water and brine and concentrated partially. After an addition of hexane, the precipitation was filtered and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> to afford dark brown complex **3a** or **3b**.

**3a**, yield 93%, Anal. calcd. for C<sub>83</sub>H<sub>100</sub>Cl<sub>2</sub>Mn<sub>2</sub>N<sub>4</sub>O<sub>6</sub>: C, 69.69; H, 7.05; N, 3.92; Mn, 7.68%. Found: C, 69.58; H, 7.02; N, 3.97; Mn, 7.45%. IR (KBr): 3447, 3056, 3027, 2949, 2922, 2866, 1614, 1533, 1465, 1442, 1380, 1319, 1279, 1216, 1188, 1100, 1025, 969, 870, 738, 701, 633, 521 cm<sup>-1</sup>. Λ<sub>M</sub> (MeOH): 3 mho cm<sup>-1</sup> mol<sup>-1</sup>.

**3b**, Yield 88%. Anal. calcd. for C<sub>67</sub>H<sub>96</sub>Cl<sub>2</sub>Mn<sub>2</sub>N<sub>4</sub>O<sub>6</sub>: C, 65.20; H, 7.84; N, 4.54; Mn, 8.90%. Found: C, 66.50; H, 7.75; N, 4.63; Mn, 9.22%. IR (KBr): 3438, 3024, 3002, 2952, 2923, 2865, 1610, 1538, 1472, 1442, 1388, 1338, 1302, 1268, 1220, 1178, 1089, 1024, 937, 829, 758, 686, 565 cm<sup>-1</sup>. Λ<sub>M</sub> (MeOH): 5 mho cm<sup>-1</sup> mol<sup>-1</sup>.

### 3.6. General procedure in epoxidation reactions

For *m*-CPBA system, enantioselective epoxidation was carried out with a minor modification to the reported procedure [20]. A solution containing catalyst **3a** (2.5 mmol%), alkene (0.5 mmol) and NMO (2.5 mmol) in dichloromethane (or, ether) was cooled to desired temperature (–78–0 °C). The pre-cooled solid *m*-CPBA (1.0 mmol) was portion-wise added with stirring. The reaction process was monitored by GC. After completion of the reaction, the mixture was concentrated and diluted with hexane. The precipitated catalyst was recovered by filtration, washed with 1 M NaOH and dried to reuse. The organic phase was separated and washed with water then with brine, dried over anhydrous sodium sulphate and concentrated. The residue was purified by flash chromatography on silica gel to offer the epoxide.

For NaClO system, the epoxidation was carried out according to the literature [21]. To a cooled (0 °C) solution of catalyst **3a** (2.5 mmol%), substrate (0.5 mmol) and 4-phenylpyridine N-oxide (0.5 mmol) in dichloromethane, a pre-cooled solution of 13% NaClO (1.0 mmol, pH 11) was portion-wise added. After completion of the reaction, the mixture was diluted with dichloromethane and water. The organic phase separated, was washed with water, brine, and then concentrated. The catalyst was separated by precipitation with hexane to be reused. The organic solvent was removed and the residue was purified to determine the ee.

## Acknowledgements

Financial assistance from the National Natural Science Foundation (Grant No. 30170228) is greatly acknowledged.

## References

- [1] L. Canali, D.C. Sherrington, *Chem. Soc. Rev.* 28 (1999) 85.
- [2] (a) S.E. Schaus, J. Branalt, E.N. Jacobsen, *J. Org. Chem.* 63 (1998) 403;  
(b) Y.N. Ito, T. Katsuki, *Bull. Chem. Soc. Jpn.* 72 (1999) 603;  
(c) C. Bolm, F. Bienewald, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 2640.
- [3] (a) D.A. Cogan, G. Liu, K. Kim, B.J. Backes, J.A. Ellman, *J. Am. Chem. Soc.* 120 (1998) 8011;  
(b) D.A. Annis, E.N. Jacobsen, *J. Am. Chem. Soc.* 121 (1999) 4147.
- [4] J.S. Rafalt, J.H. Clark, *Catal. Today* 57 (2000) 33.
- [5] (a) W. Zhang, J.L. Loebach, S.R. Wilson, E.N. Jacobsen, *J. Am. Chem. Soc.* 112 (1990) 2801–2803;  
(b) E.N. Jacobsen, W. Zhang, M.L. Guler, *J. Am. Chem. Soc.* 113 (1991) 6703–6704, and 7063–7064;  
(c) L. Deng, E.N. Jacobsen, *J. Org. Chem.* 57 (1992) 4320.
- [6] S.H. Zhao, P.R. Ortiz, B.A. Keys, K.G. Davenport, *Tetrahedron Lett.* 37 (1996) 2725.
- [7] (a) N. Hosoya, A. Hatayama, R. Irie, H. Sasaki, T. Katsuki, *Tetrahedron* 50 (1994) 4311;  
(b) D.E. De Vos, P.A. Jacobs, *Catal. Today* 57 (2000) 105–114.
- [8] (a) H.-L. Shyu, H.-H. Wei, Y. Wang, *Inorg. Acta* 290 (1999) 8.;  
(b) S.H. Zhao, P.R. Ortiz, B.A. Keys, K.G. Davenport, *Tetrahedron Lett.* 37 (1996) 2725.
- [9] D. Das, C.P. Cheng, *J. Chem. Soc., Dalton Trans.* (2000) 1081–1086.
- [10] (a) S. Ogunwumi, T. Bein, *Chem. Commun.* (1997) 901;  
(b) G.-J. Kim, J.-H. Shin, *Tetrahedron Lett.* 40 (1999) 6827;  
(c) F. Minutolo, D. Pini, A. Petri, P. Salvadori, *Tetrahedron: Asymm.* 7 (1996) 2293;  
(d) M.D. Angelino, P.E.J. Laibinis, *Polym. Sci. A: Polym. Chem.* 37 (1999) 3888.
- [11] G. Pozzi, F. Cinato, F. Montanari, S. Quici, *Chem. Commun.* (1998) 877.
- [12] T.S. Reger, K.D. Janda, *J. Am. Chem. Soc.* 122 (2000) 6929–6930.
- [13] Pekka Pietikäinen, *Tetrahedron* 56 (2000) 417–424.
- [14] M.H. Wu, E.N. Jacobsen, in: E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), *Comprehensive Asymmetric Catalysis*, Springer, 1999, p. 649.
- [15] R.I. Kureshy, N.H. Khan, S.H.R. Abdi, S.T. Patel, R.V. Jasra, *Tetrahedron: Asymm.* 12 (2001) 433–437.
- [16] J.F. Larrow, E.N. Jacobsen, *J. Org. Chem.* 59 (1994) 1939.
- [17] P. Pietikäinen, *Tetrahedron* 54 (1998) 4319.
- [18] G.C. Zhang, Z. Tan, *The Refined Experiment of Organic Synthesis*, Lanzhou University, 2002, p. 207.
- [19] W. Zhang, E.N. Jacobsen, *J. Org. Chem.* 56 (1991) 2296.
- [20] M. Palucki, G.J. Mc Cormick, E.N. Jacobsen, *Tetrahedron Lett.* 36 (1995) 5457–5460.
- [21] H. Sasaki, R. Irie, T. Hamada, K. Susuki, T. Katsuki, *Tetrahedron* 41 (1994) 11827.