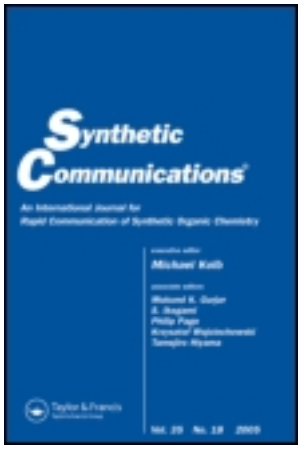

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A Homogeneous Chiral Manganese(III)-Salphe Catalyst for Enantioselective Epoxidation of Olefins

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A HOMOGENEOUS CHIRAL MANGANESE(III)–SALPHE CATALYST FOR ENANTIOSELECTIVE EPOXIDATION OF OLEFINS

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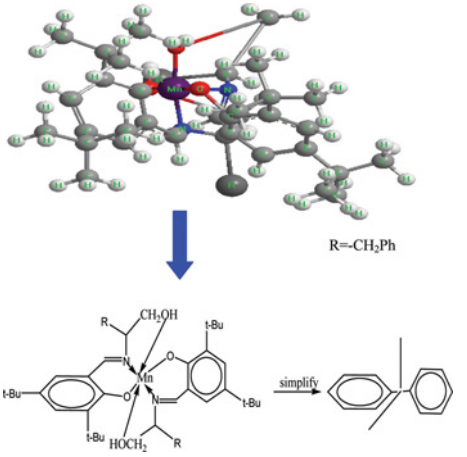
GRAPHICAL ABSTRACT



Abstract *A new chiral Mn(III)–Salphe catalyst was synthesized from natural amino acid (R)-phenylalanine and 3,5-di-*tert*-butyl-hydroxybenzaldehyde and applied to the asymmetric epoxidations of unfunctionalized olefins in ionic liquids. Satisfactory enantioselectivities (79% < ee < 93%) and good yields were achieved when NaClO was used as oxidant. We found that both the pH value (11.3) and reaction temperature (15°C) were crucial for the epoxidation reactions. In our reaction system, NH_4OAc was unnecessary. We proposed that alcoholic hydroxyls in the Mn(III)–Salphe compound played the role of axial ligand. However, the reaction time was longer than when using Jacobsen's catalyst because of the structure of the Mn(III)–Salphe compound, in which coordination geometries by the two alcoholic hydroxyls with certain angles affected the substrate approaching the Mn(V) = 0*

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center. The chiral ligand was characterized by the combination of infrared, ultraviolet, and visible spectra and ^1H *NMR.*

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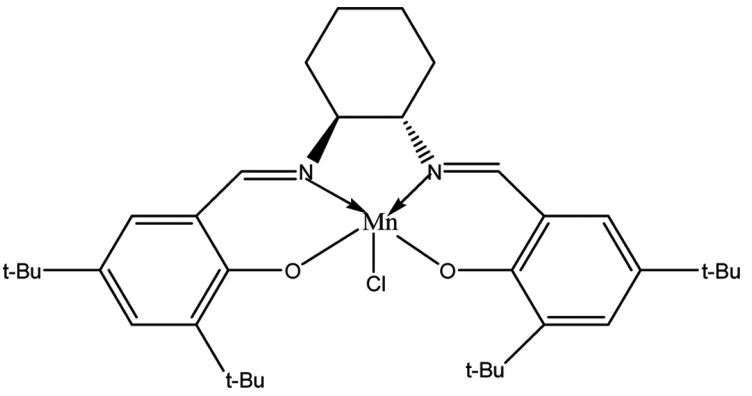
Keywords Chiral Mn(III)–salphe; enantioselective epoxidation; ionic liquid; olefins; (R)-phenylalanine

INTRODUCTION

Chiral epoxides are valuable fine chemicals and important synthetic intermediates because of their high regio- and stereoselective ring-opening reactions.[1–7] Since Jacobsen's work in 1990 (Scheme 1), chiral Mn(III)–Salen compounds had emerged as highly efficient catalysts for the enantioselective epoxidation of unfunctionalized olefins, giving rise to optically active epoxides. Then, the research topics about these chiral Mn(III)–Salen species have attracted many chemists' attention to design and synthesis of new salen ligands and the rationale of the asymmetric induction from steric and electronic effects of the catalyst structure.[8–10] In these reports, almost of chiral Mn(III)–Salen catalysts used the chiral diamines (such as 1,2-diaminocyclohexane and 1,2-diphenylethane-1,2-diamine) as the chiral source. However, the chiral diamines are usually expensive and unavailable.

At the molecular level nature is chiral. So, naturally occurring compounds almost always exist in two enantiomeric forms. Thus, our studies had focused on the natural amino acids, which are optically pure and commercially available. In this work, natural amino acids were designed as the source of chiral factors in Salen-type systems. The chiral moiety of the Mn(III)–Salen catalyst played a significant role in the asymmetric epoxidation reactions. Catalysts with different chiral fragments showed different enantioselectivity and enantiofacial selection, resulting in reversed enantioselectivity in some cases. The present work aimed to synthesize a new chiral Mn(III)–Salen-like-type ligand by incorporating the transition metal manganese into the Schiff base compound derived from salicylaldehyde and amino acid. To

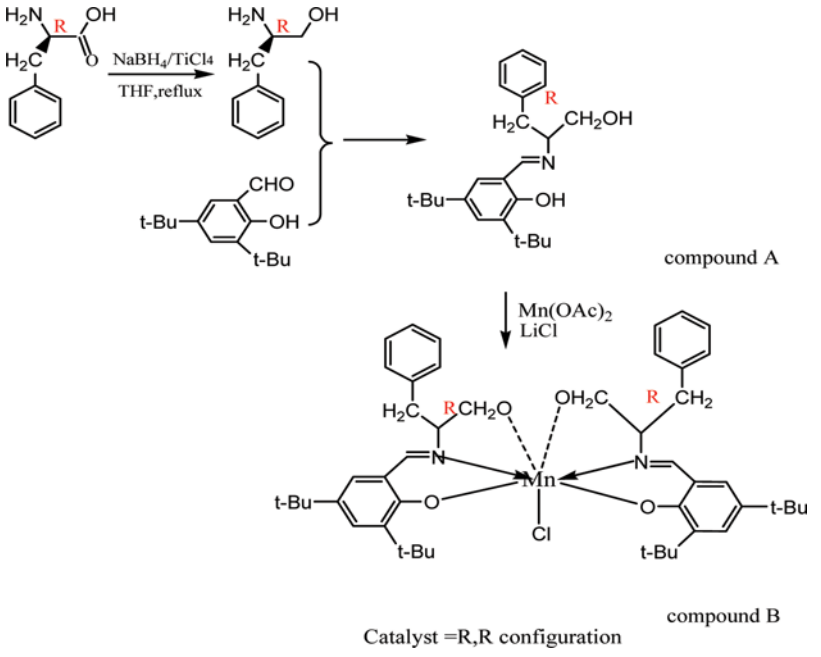


Scheme 1. Structure of Jacobsen catalyst.

mimic the porphyrin ring of natural enzymes, (R)-phenylalanine and (R)-tyrosine containing benzene groups were selected as the chiral precursor of ligands. However, (R)-tyrosine containing a phenolic hydroxyl has little acidity, which may affect the acid-sensitive epoxides in asymmetric synthesis. Meanwhile, the easily avaliable and natural characteristics of (R)-phenylalanine make it ideal as a chiral precursor introduced into the molecular structures of the catalysts, so (R)-phenylalanine was chosen as the starting material. The new ligand was designated as Salphe, and its metal compound as Mn(III)-Salphe.

So far only a few reports about the synthesis and applications of Schiff base ligands derived from chiral amino acids have been publishied. Mao et al.[11] synthesized a series of novel Schiff base complexs from arginine having two kinds of asymmetric $-NH_2$, which have been proven to be efficient catalysts for the asymmetirc oxidation of β-isophorone. Ando et al.[12] reported a amino acid–Schiff base complex of oxovanadium(IV) and applied it to the oxidation of sulfide, but it furnished the sulfoxide in poor enantiomeric excess (5–20%).

In our research, we introduced the chiral (R)-phenylalanine building blocks into the catalyst molecules by forming Schiff base between amino group ($-NH_2$) of the phenylalanine and aldehyde (–CHO) of salicyaldehyde (Scheme 2) in the hope of obtaining chiral catalysts with generally good activity and enantioselectivity. Herein, we report the preparation of Mn(III)–Salphe complex, its physicochemical properties such as infrared (IR) ultraviolet (UV), and ^1H NMR spectra, and its application in the epoxidation of unfunctional alkenes.



Scheme 2. Route for preparation of chiral Mn(III)–Salphe catalyst. (Figure is provided in color online.)

RESULTS AND DISCUSSION

To obtain more details on the structure of the Mn(III)-Salphe, the FT-IR and UV-Vis spectra of the Mn(III) complex had been measured and compared with the chiral ligand and the known Jacobsen catalyst.

FT-IR Spectra

The vibration of the imine group (C=N) of the ligand A (Fig. 1a) was observed at 1627 cm^{-1}, while it was shifted to a lower frequency at 1615 cm^{-1} in the complex B (Fig. 1b). The result indicated that the nitrogen atom of the imine group had already coordinated to the manganese ion. The new band at 460 cm^{-1} of the complex B was associated with the Mn–N bond. In the FT-IR spectrum of the ligand A, the band at 1198 cm^{-1} was ascribed to the phenolic C–O stretching vibration. Meanwhile, a similar band was found at 1175 cm^{-1} in the spectra of the complex B. The (C–O) frequency shift toward lower values was attributed to the coordination action between oxygen and manganese ion.

UV-Vis Spectra

The UV-vis electronic spectra of the neat complex B (b) and Jacobsen catalyst (a) are shown in Fig. 2. It could be seen that the chiral complex B demonstrated broad peaks near 433 nm and at around 508 nm, which were identical with those of Jacobsen catalyst. It confirmed that the Mn(III)–Salphe complex was formed. The peak of chiral Mn(III)–Salphe at 433 nm was assigned to charge-transfer transitions

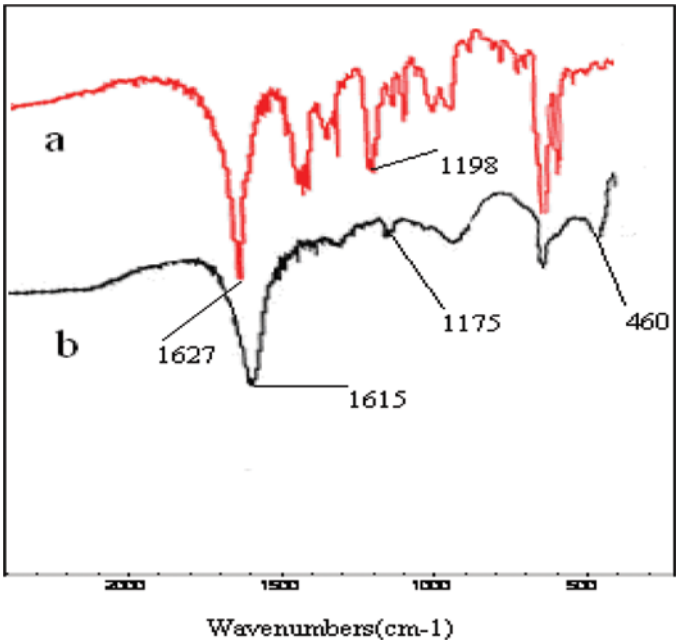


Figure 1. FT-IR spectra of the ligand A(a) and the complex B(b). (Figure is provided in color online.)

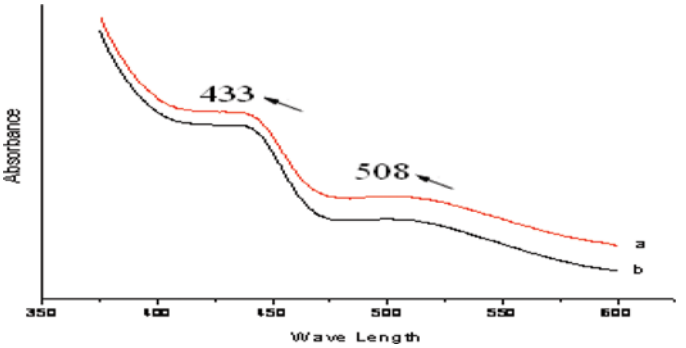


Figure 2. UV-vis spectra of the Jacobsen catalyst (a) and chiral Mn(III)–Salphe (b). (Figure is provided in color online.)

between the metal and ligand. Meanwhile the other characteristic absorption peak at 508 nm was assigned to the d–d transitions of manganese in the Mn(III)–Salphe compound.[13]

Optimization of pH and Reaction Temperature

According to the literature, the epoxidation conditions were not identical when the different Mn(III)–Salen catalysts were used.[14–20] To clarify the effect of this new Mn(III)–Salphe catalyst, our preliminary experiments were run under the following conditions: 2 mmol of styrene, 10 mol% of Mn(III)–Salphe catalyst, 20 mol% of NH_4OAc, $NaOCl/Na_2HPO_4$ buffer solution (pH 11.3), and 4 ml of $BMImPF_6$, at 0 °C. To get the best results, different pH values (10.0, 10.5, 11.3, 12.0, and 12.5)

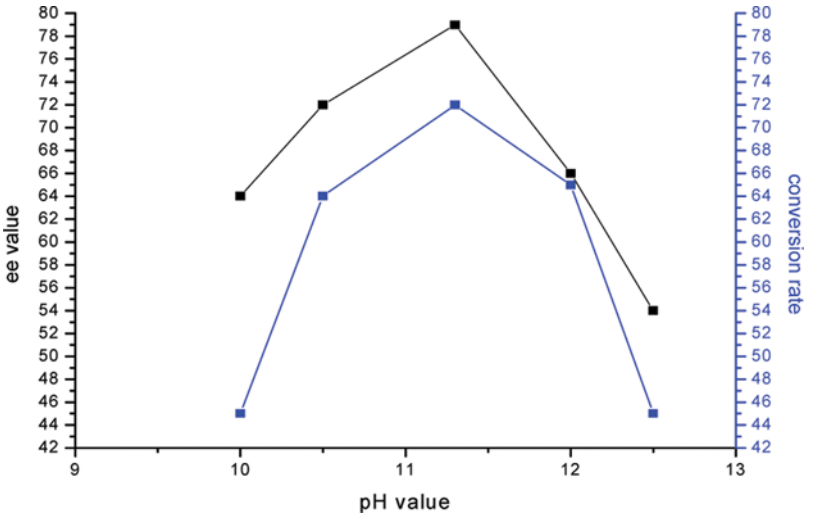


Figure 3. Effect of pH for *ee* value (black line, ≤79%) and conversion rate (blue line, ≤72%). (Figure is provided in color online.)

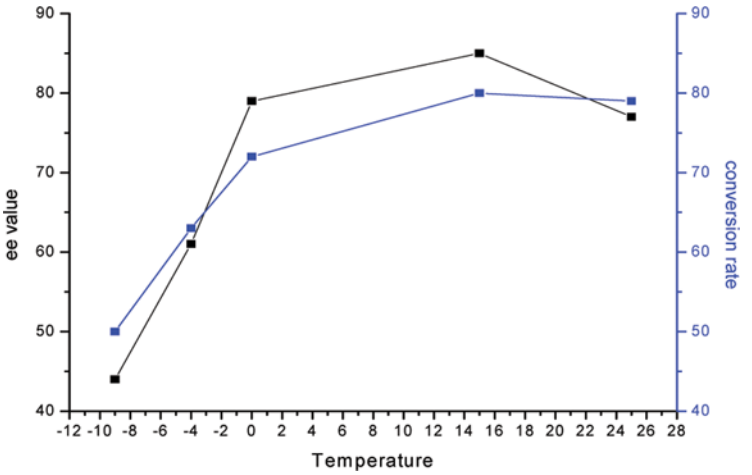


Figure 4. Effect of reaction temperature for *ee* value (black line, ≤85%) and conversion rate (blue line, ≤80%). (Figure is provided in color online.)

and temperature (−9 °C, −4 °C, 0 °C, 15 °C, and 25 °C) were investigated respectively. The results are shown in Figs. 3 and 4.

In Fig. 3, it is obvious that the pH value of NaOCl/Na_2HPO_4 buffer greatly impacted both the conversion rate and the *ee* value. When the pH value of NaOCl/Na_2HPO_4 buffer solution was 11.3, the greatest *ee* value and conversion rate of epoxides were obtained. Because the oxidation reaction first occured in the aqueous phase and produced HOCl as a weak acid (pKa = 7.54[21]), HOCl was transferred to the organic phase to participate in the epoxidation reaction. If the pH value was too high, less formation of HOCl and low conversion rate of substrate occurred. On the other hand, if the pH value was too low, a large quantity of HOCl received, which resulted in poor yield and poor enantioselective of olefin epoxides. So, pH 11.30 was the optimal value. Furthermore, the choice of reaction temperature was also very important. In Fig. 4, it is clear that the greatest *ee* value and conversion rate of epoxides were given at 15 °C. When the temperature was increased to 25 °C, the enantioselectivity decreased. The reason was that the temperature caused the olefins to approach the catalyst.[22]

Effect of Ammonium Acetate

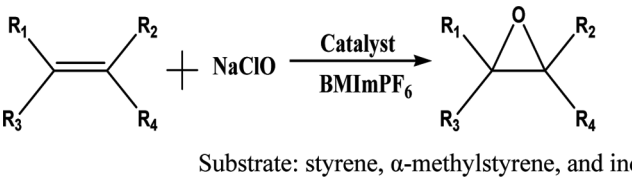
In the study of catalytic mechanism of olefin epoxidation by the Mn(III)-Salen catalysts, it was found that adding axial ligands (such as the pyridine nitrogen oxides and salt ammonium acetate) could increase the reaction rate and enantioselectivity, because the axial ligand *trans* to the oxygen atom of Mn(V) = O compound reduced the Lewis acidity of Mn(III)–Salen compound in order to inhibit the acid-sensitive epoxides decomposition.[23] In view of the difference of our new catalyst, whether NH_4OAc was important for the asymetric epoxidation of styrene was investigated. Overall, all reactions proceeded smoothly within 6 h. *Ee* valus of epoxides in three cycles were respectively 87%, 85%, and 81% in the presence of NH_4OAc and respectively 86%, 83%, and 79% in the absence of NH_4OAc. The results showed that the NH_4OAc was not necessary. We proposed that the oxgen atom of the alcoholic

hydroxyl group in the Mn(III)–Salphe complex could also coordinate to the manganese center so as to stabilize the Mn(V)oxo compound in the epoxidation process. The alcoholic hydroxyl group played a role of axial ligand instead of the NH_4OAc. From the economic standpoint, our new catalyst is more attractive than others.

Catalytic Performances

In preliminary experiments, enantioselective epoxidation reactions were performed according to our established procedure[24] (Scheme 3). When the reaction was finished, the reaction mixture was extracted with *n*-hexane for obtaining epoxides. After separation, ionic liquid $BMImPF_6$, including catalysts, could be recycled. To evaluate our new Mn(III)–Salphe catalyst, Jacobsen catalyst was also used for the same reactions. Table 1 summarized the catalytic performance of our Mn(III)–Salphe catalyst and Jacobsen catalyst in the asymetric epoxidation of styrene, α-methylstyrene, and indene.[25]

Under the optimized reaction conditions, the Mn(III)–Salphe catalyst showed excellent reaction activities and enantioselectivities in the asymetric epoxidation of various unfunctionalized olefins (Table 1, entries 2, 4, and 6). The chiral induction effects of this new Mn(III)–Salphe catalyst are similar to those of the Jacobsen catalysts. For styrene, α-methylstyrene, and indene, the epoxidation reactions proceeded smoothly and gave the desired products in 89–92% yields with good to excellent enantioselectivities (86% to 93%) respectively (cycle 1). To check the recyclability of the catalytic system, it was separated from the reaction mixture by extraction of n-hexane and reused for further epoxidation reactions. All of those substrates were examined and gave good yields and acceptable *ee* values (cycles 2, and 3). The results showed that the catalytic system is still active but with little detriment to yield and *ee* value after being recycled three times. Then, the n-hexane extractant was detected by FT-IR and its spectroscopy showed the characteristic absorption peak of the Mn(III)–Salphe catalyst in the second and third cycles. It means that a little bit of Mn(III)–Salphe catalyst was lost during the extraction. However, it was evident that the reaction time using Mn(III)–Salphe as catalyst was longer than with the Jacobsen catalyst. This was related to the hindered structure of the Mn(III)–Salphe compound, which affected the substrate approached to Mn(III) = O center. By computational chemistry methods, the optimal conformation of Mn(III)–Salphe was obtained by Gaussian03 in Fig. 5, which showed that manganese atom retained coordination geometries in which one side of ligand chains was coordinated with a phenolate and an imine nitrogen in the equatorial plane, and the other side was coordinated in the oblique plane. Meanwhile, the two hydroxyls of animo acid were coordinated in the axial position of each plane. In other words, there was a big stereospecific blockade close to the manganese



Scheme 3. Enantioselective epoxidation of olefins in $BMImPF_6$.

Table 1. Epoxidations catalyzed by Jacobsen's catalyst and Mn(III)–Salphe catalyst with the ionic liquids as reaction media[a]

Entry[b]	Substrate[c]	Catalyst	*ee*[d](%) (yield[e](%), time[f] (h))		
			Cycle 1	Cycle 2	Cycle 3
1	Styrene	Jacobsen	89 (93, 2)	88 (90, 2)	85 (86, 2)
2		Mn(III)–Salphe	86 (89, 6)	83 (86, 6)	79 (80, 6)
3	α-Methylstyrene	Jacobsen	91 (94, 2)	91 (92, 2)	89 (88, 2)
4		Mn(III)–Salphe	87 (90, 6)	86 (87, 6)	83 (83, 6)
5	Indene	Jacobsen	94 (95, 2)	92 (93, 2)	89 (90, 2)
6		Mn(III)–Salphe	93 (92, 6)	90 (89, 6)	86 (85, 6)

[a]Reaction conditions: substrate (2 mmol), catalyst (0.2 mmol, 10 mol%), NaClO (5.8 mmol).
[b]All entries in this article were numbered consecutively in spite of the table numbers.
[c]A, styrene; B, α-methylstyrene; C, indene.
[d]Determined by HPLC over a chiral OD–H column after comparing the retention times with those of three racemic epoxide samples.
[e]Yield of the isolated epoxide.
[f]Monitored by TLC.

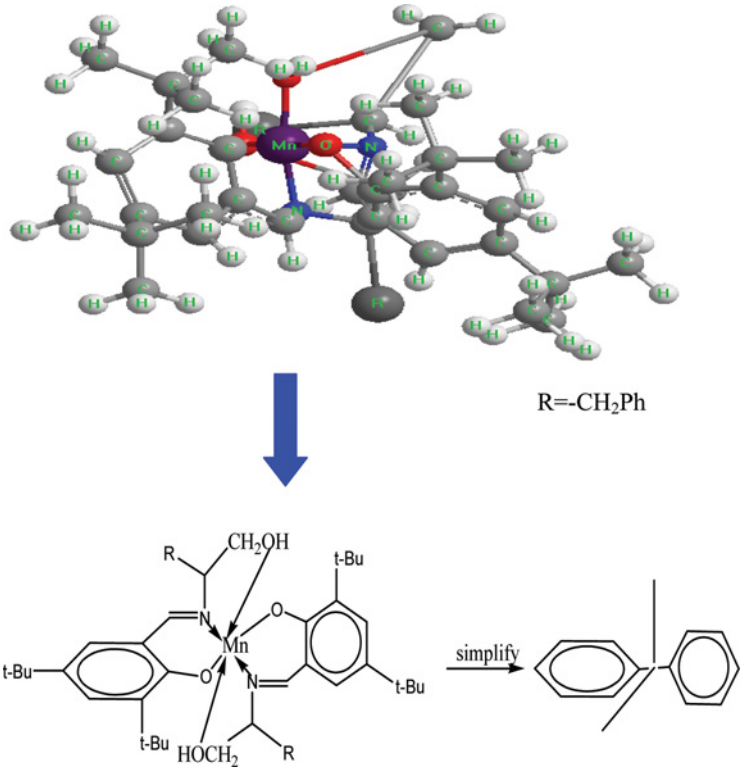


Figure 5. Optimal configuration of catalyst. (Figure is provided in color online.)

atom, so it should be more difficult for the substrate to approach the Mn(III) = O center, which resulted in the low rate of reaction and long reaction time for the enantioselective epoxidation. However, after the oxidant NaClO interacted with the manganese atom, the substrate from the direction of the chiral amino acid approached the Mn(III) = O center to form the reaction intermediate, and the close proximity was a benefit for the asymmetric selectivity.

CONCLUSIONS

In this work, Mn(III)–Salphe catalyst was synthesized by introducing chiral (R)-phenylalanine into the catalyst molecules via forming imino group and applied to the asymmetric epoxidations of olefins. The optimization reaction conditions were that pH was 11.3 and reaction temperature was 15 °C. Meanwhile, the NH_4OAc was unnecessary in the epoxidation reactions because alcoholic hydroxyl in the Mn(III)–Salphe complex stabilized the Mn(V)oxo intermediate instead of it. The activity and chiral induction effect of the Mn(III)–Salphe catalyst were satisfactory except for the longer reaction time. It was related to the structure of Mn(III)–Salphe with coordination geometries by the two ligands with certain angles, which affected the substrate approaching to Mn(V) = O center from the direction of the chiral amino acid. The experiment provided a theoretical basis for further studying the catalytic mechanism of the Mn(III)-Salen compound.

EXPERIMENTAL

Materials and Methods

1,2-Diaminocyclohexane, 3,5-di-*tert*-butyl-hydroxybenzaldehyde, and titanium tetrachloride were obtained from Alfa Aesar. (R)-Phenylalanine, L(+)-tartaric acid, manganese acetate, and lithium chloride were laboratory-grade reagents from local suppliers. Jacobsen's catalyst was synthesized according to the literature procedure.[26] All other chemicals were reagent grade and used as received.

The UV-vis and FT-IR spectra of some samples were recorded from 200 to 800 nm on a UV-3310 spectrophotometer and from 400 to 4000 cm^{-1} on a Nicolet Avatar 330 FT-IR instrument (using KBr pellets), respectively. Elemental analyses were performed on an Elementar VarioEL instrument in the Instrumental Analysis and Research Center of Xi'an Jiaotong University. High-resolution mass spectrometry (HRMS) operating conditions were as follows: ion source: electric impact ionization (EI), positive; electric energy: 55 eV; source temperature: 250 °C; detection mode: ion detector (ID); accelerative voltage: 5000 V; and mass resolution: 10000, tuned by FC43. ^1H NMR spectra of the samples were recorded with a Bruker-400 spectrometer using tetramethylsilane (TMS) as an internal reference. The chiral stationary phase column was a Daicel Chiralcel OD-H manufactured by Daicel Chemical Industries Ltd., and the associated high-performance liquid chromatographic (HPLC) analysis was carried out on a Shimadzu Instrument (system controller: LC-10AT VP; UV-vis detector: SPD-10A VP). The reaction products were analyzed by HPLC, containing UV detection wavelength: 254 nm; eluent agent: n-hexane/i-PrOH, 99/1, v/v; flow rate: 0.8 ml/min; column pressure: 2.0–3.0 MPa, and column temperature: 25 °C).

Preparation of Catalysts

A 1000-ml, three-necked flask equipped with a mechanical stirrer, a reflux condensor, and an addition funnel was charged with 166 mmol $NaBH_4$, 55 mmol (R)-phenylalanine, and 220 ml THF. The resulting mixture was cooled to 0 °C, and 60 mmol $TiCl_4$ was added in a steady stream over 30 min under stirring. Meanwhile the reaction produced hydrogen and continued overnight at room temperature. The stirred solution was heated to reflux for 3 h until no gas evolved and was cooled to room temperature. Then 200 ml ether was added. In the ice bath, the reaction was terminated by adding an appropriate amount of water. NaOH 150 ml, was added and stirred for 30 min. The organic layer was separated, dried over Na_2SO_4, and concentrated under reduced pressure. The final product, (R)-2-amino-3-phenyl-1-propanol, was recrystallized from toluene (7.14, yield: 86%) (mp 90–91 °C). FT-IR (KBr) v: 3366, 3299, 3123, 3081, 2941, 2920, 2878, 2842, 2825, 1579, 1495, 1463, 1338, 1122, 1092, 1070, 994, 975, 965, 906, 837, 704 665 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ ppm 2.52 (d, 1H, 3-H), 2.79(d, 1H, 3-H), 3.08–3.14 (m, 1H, 2-H) 3.38 (d, 1H, 1-H), 3.63 (d, 1H, 1-H), 7.18–7.32 (m, 5H, PhH). Anal. calcd. for $C_9H_{13}NO$: C, 71.52; H, 8.61; N, 9.27, Found: C, 71.69; H, 8.48; N, 9.23.

A mixture of 3,5-di-*tert*-butylsalicylaldehyde (1.17 g, 5 mmol) and (R)-2-amino-3-phenyl-1-propanol (0.585 g, 5 mmol) in EtOH (10 ml) was stirred for 24 h at the room temperature. Evaporation of the solvent afforded a residue that was purified on column chromatography (5% hexane/ethyl acetate) to give compound A, {2,4-di-*tert*-butyl-6-((1-hydroxy-3-phenylpropan-2-ylimino)methyl)phenol} (1.53 g, yield: 92%) as yellow liquid. (bp159–161 °C). FT-IR (KBr): *v*: 3680, 3670, 3120, 2910, 1660, 1627, 1510, 1280, 710, 680, 330 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ ppm 8.18 (s, 1 H), 7.28 (s, 1 H), 7.21 (d, 2 H), 7.18 (s, 1 H), 7.12 (d, 2 H), 7.08 (s, 1 H), 3.72 (d, 2H), 3.60 (m, 1 H), 2.99 (d, 2H), 1.45 (q, 18 H). Anal. calcd. for $C_{24}H_{33}NO_2$: C, 78.47; H, 8.99; N, 3.81. Found: C,78.56; H, 8.75; N, 3.74.

The preparation of catalyst is outlined in Scheme 2. Under vigorous stirring, 15 ml of dry ethanol containing 5 mmol of manganese acetate was added dropwise to 15 ml of dry ethanol solution containing 8 mmol of chiral compound A under nitrogen protection. The mixture was refluxed for 5 h, and then 10 ml of ethanol containing 24 mmol of lithium chloride was added to the mixture under stirring for 3 h. After heating and nitrogen addition were discontinued, the crude product was collected by evaporation of the solvent under reduced pressure, redissolved in dichloromethane (50 ml), washed with deionized water (2×15 ml) and brine (10 ml), and then filtered. The catalyst (compound B) was obtained and dried under vacuum (0.77 g, yield: 85%(mp 135–136 °C). FT-IR (KBr) *v*: 3520, 3120, 3040, 2610, 1615, 1540, 1490, 1280, 1175, 990, 460, 310 cm^{-1}; UV–vis (CH_2Cl_2): 508, 433, 327 nm. Anal. calcd. for $C_{48}H_{64}N_2O_4MnCl$: C, 70.03; H, 7.78; N, 3.40. Found: C, 70.14; H, 7.58; N, 3.37. Meanwhile the HRMS analysis of compound B was made. Anal. calcd. for $C_{48}H_{64}N_2O_4MnCl$: 820.3779. Found: 820.3783. The results of HRMS and EA analysis for the Mncomplex were almost the same, which proved the structure of complex. A goal to prepare single crystals of the Mn(III)–Salphe compound for x-ray diffraction measurements has been unsuccessful.

Enantioselective Epoxidation of Unfunctionalized Olefins

Enantioselective epoxidation reactions were performed according to the procedure established by our group[24] as follows. First, 2 mmol of unfunctionalized olefins (styrene, α-methylstyrene, and indene) and 0.4 mmol of axial base NH_4OAc (20 mol% based on the mol of the olefins) were added to 4 ml of reaction medium (1-n-butyl-3-methylimidazolium hexafluorophosphate, $BMImPF_6$) containing 0.2 mmol of catalyst (10 mol% based on the mol of the olefins) under stirring. A solution of Na_2HPO_4 (0.05 mol/L) was added to a precooled solution of aqueous NaClO (0.58 mol/L) as an oxidant, and then pH value of the mixed solution was accurately adjusted to a desirable amount by slow instillation of HCl (1 mol/L) and NaOH (1 mol/L) solutions. The mixture was kept at the appointed temperature. After the reaction was finished, 20 ml of *n*-hexane was directly added to the reaction mixture, and then a triphase system was formed: organic phase (*n*-hexane phase, upper layer), water phase (middle layer), and ionic liquid phase (the bottom). The *n*-hexane phase was separated and concentrated under reduced pressure, and then the residue was purified by column chromatography (SiO_2, petroleum ether/CH_2Cl_2, 2/1, *v*/*v*). On the other hand, the ionic liquid including catalyst was also separated for recycling.

SUPPLEMENTARY MATERIAL

A list of HPLC chromatograms of the epoxide products of styrene, α-methylstyrene, and indene in Table 1 is available online.

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