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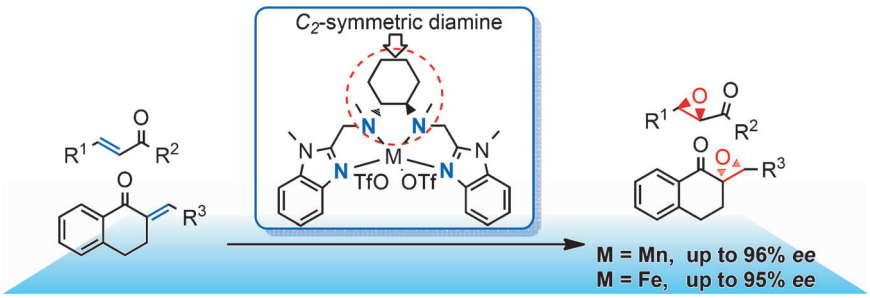

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Bioinspired Manganese and Iron Complexes with Tetradentate N Ligands for the Asymmetric Epoxidation of Olefins

Asymmetric barrier overtaken! The manganese and iron complexes with the tetradentate N ligand (1*R*,2*R*)-*N*,*N*′-dimethyl-*N*,*N*′-bis(1-methyl-2-benzimidazolylmethyl)cyclohexane-1,2-diamine have been synthesized and characterized. These complexes are active catalysts for the asymmetric epoxidation of olefins, which resulted in up to 96% *ee*.

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Bioinspired Manganese and Iron Complexes with Tetradentate N Ligands for the Asymmetric Epoxidation of Olefins

Xiaoe Wang,[a, b] Chengxia Miao,[a] Shoufeng Wang,[a] Chungu Xia,[a] and Wei Sun*[a]

The manganese and iron complexes with the tetradentate N ligand (1*R*,2*R*)-*N*,*N*′-dimethyl-*N*,*N*′-bis(1-methyl-2-benzimidazolylmethyl)cyclohexane-1,2-diamine have been synthesized and characterized. The crystal structure of the manganese complex demonstrates a *cis*-α configuration. Both the manganese and iron complexes are active catalysts for the asymmetric epoxidation of olefins with H_2O_2 as an oxidant and acetic acid as an additive. Up to 96% *ee* was observed for the epoxidation of α,β-unsaturated ketones at −20 °C.

Introduction

The use of ligands based on a chiral vicinal diamine backbone is an established strategy for chiral induction in metal-catalyzed oxidations.[1] Of the oxidation reactions, the asymmetric epoxidation of olefins is one of the most important transformations in organic synthesis because the resulting enantiomerically enriched epoxides are highly useful intermediates and building blocks in chemical or pharmaceutical industry.[2] The manganese and iron centers supported by the nonheme ligands have attracted intense interests because of their high efficiency in various oxidation reactions.[3,4] Pioneering studies by Jacobsen and co-workers demonstrated that the iron(II)-*N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyridylmethyl)ethylene-1,2-diamine complex could efficiently promote the epoxidation of various aliphatic olefins.[3a] Then, Stack and co-workers described that the manganese complex of the MCP (MCP = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyridylmethyl)cyclohexane-1,2-diamine) ligand could act as an efficient catalyst for the epoxidation of olefins with peracetic acid as an oxidant.[5] Costas et al. prepared a novel family of manganese complexes with chiral pinene-appended tetradentate ligands derived from *R*,*R*-MCP and the complexes demonstrated only up to 46% *ee* in the epoxidation of selected alkenes with peracetic acid as an oxidant.[6] Pfaltz and co-workers synthesized two classes of tetradentate chiral diaminobisoxazoline ligands and studied the catalytic activity of the corresponding manganese complexes in the enantioselective epoxidation; however, the enantioselectivities were still modest.[7] In 2009, a series of manganese complexes with ligands were designed and synthesized by our group by introducing aromatic groups at the 2-pyridylmethyl positions of *R*,*R*-MCP and relatively high enantioselectivities (up to 89% *ee*) were achieved in the epoxidation of α,β-enones with 1 mol% catalyst loading.[8] Then, Bryliakov et al. reported a series of chiral nonheme aminopyridinylmanganese(II) complexes for efficiently catalyzing enantioselective olefin oxidation to the corresponding epoxides with high yields and enantioselectivities (up to 93% *ee*).[9] However, an example referring to chiral N_4 iron complexes for the asymmetric epoxidation was rare. We and Bryliakov et al. reported the corresponding iron complexes using different ligands for the asymmetric epoxidation that resulted in 87 and 86% *ee*, respectively.[9c,10] Although significant progress has been made using iron or manganese complexes with chiral N_4 ligands, the attainment of high enantioselectivity (>90% *ee*) remains a formidable challenge in the asymmetric epoxidation of olefins, especially for the iron-catalyzed asymmetric epoxidation.

Generally, this type of N_4 ligands is composed of sp^2 N donors of pyridine and two chiral sp^3 N donors of the diamine backbone. The rational tuning of the sp^2 N donors or chiral sp^3 N donors has shown an increase both in the reactivity and in the selectivity for the bioinspired oxidation (Figure 1).[3,6,8] For example, the use of ligands (*S*,*S*-BPBP and *S*,*S*,*R*-BPBPP) derived from the bipyrrolidine backbone increases the regioselectivity or enantioselectivity of the catalysts in the aliphatic C–H oxidation, asymmetric *cis*-dihydroxylation, and asymmetric epoxidation.[3e–h,9b,c,11] Our group recently reported the synthesis of Fe^{II} or Mn^{II} complexes with the C_1-symmetric tetradentate N ligand (*S*-PEB), which consisted of more rigid chiral diamine template derived from L-proline and two benzimidazole donors, and the asymmetric epoxidation of various olefins that resulted in up to 98% or 95% *ee*.[12]

We synthesized an easily available ligand, (1*R*,2*R*)-*N*,*N*′-dimethyl-*N*,*N*′-bis(1-methyl-2-benzimidazolylmethyl)cyclohexane-1,2-diamine (*R*,*R*-MCMB), and described the new nonheme

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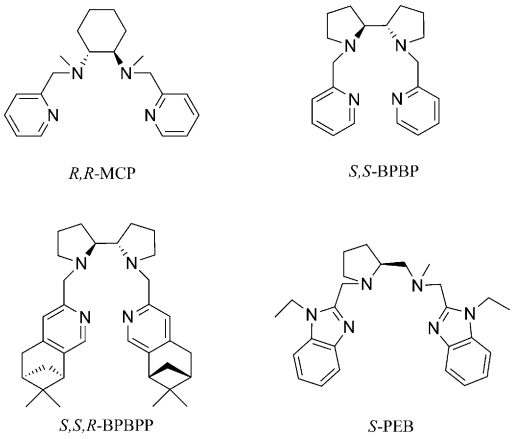


Figure 1. Selected N_4 ligands for the bioinspired oxidation.

manganese and iron complexes (Figure 2), which proved to be highly active and enantioselective catalyst for the epoxidation of olefins with H_2O_2 as an oxidant and acetic acid as an additive.

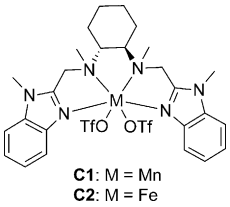
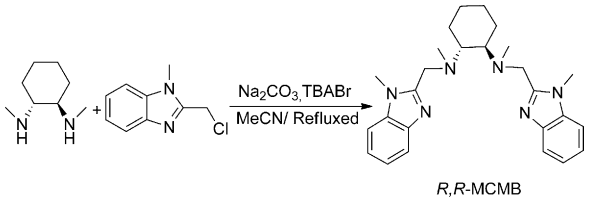


Figure 2. Chiral metal (M = Mn, Fe) complexes of (1*R*,2*R*)-*N*,*N*′-dimethyl-*N*,*N*′-bis(1-methyl-2-benzimidazolylmethyl)cyclohexane-1,2-diamine.

Results and Discussion

Synthesis of ligand and manganese and iron complexes

The *R*,*R*-MCMB ligand can be prepared easily in good yield through the direct alkylation of the (1*R*,2*R*)-*N*,*N*-dimethylcyclohexane-1,2-diamine with 2-chloromethyl-1-methyl-benzimidazole (Scheme 1). The [Mn(*R*,*R*-MCMB)$(OTf)_2$] (**C1**) complex was prepared by mixing MeCN solutions of *R*,*R*-MCMB and $Mn(OTf)_2$. The Fe(*R*,*R*-MCMB)$(OTf)_2$ (**C2**) complex resulted from the reaction of Fe(*R*,*R*-MCMB)Cl_2 with silver trifluoromethanesulfonate. Both the Mn^{II} and Fe^{II} products were characterized by elemental analysis and ESIMS. The complex **C1** has also been characterized by X-ray crystal structure determination (CCDC 898685).[13] In the crystal structure of **C1**, the tetradentate ligand coordinates to the metal in a *cis*-α conformation, in which the two benzimidazole rings are *trans* to each other and the two triflate anions are *cis* to each other (Figure 3). The Mn–N (benzimidazole) bond lengths of **C1** are 2.221(3) and 2.244(3) Å, respectively. These lengths are longer than those of Mn–N (benzimidazole) bonds in the Mn^{II}-*S*-PEB$(OTf)_2$ complex (2.202(4) Å).[12b] Compared to the Mn^{II}-MCP$(OTf)_2$ complex [Mn–N (pyridine): 2.216(4) and 2.199(4) Å], these Mn–N bond lengths of **C1** are longer.[5a]



Scheme 1. Synthesis of the (1*R*,2*R*)-*N*,*N*′-dimethyl-*N*,*N*′-bis(1-methyl-2-benzimidazolylmethyl)cyclohexane-1,2-diamine ligand.

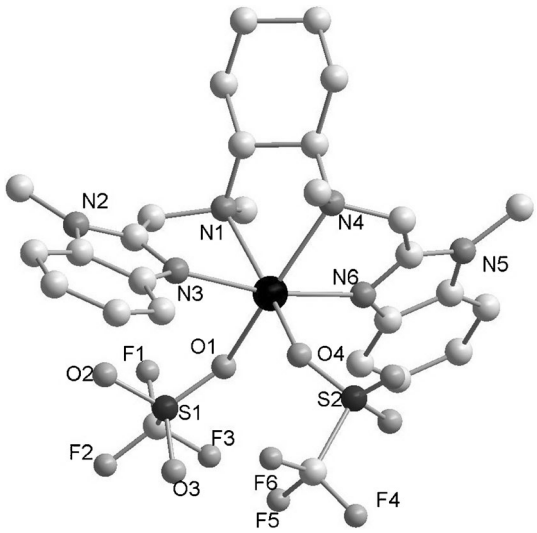
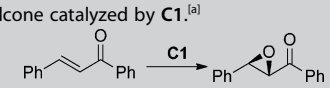


Figure 3. X-ray structure of **C1** (hydrogen atoms are omitted for clarity).

Catalytic activity testing

The exploratory experiments were started by testing this protocol, and the results of the screening and optimizing conditions, with chalcone as the model substrate and the manganese complex **C1** as the catalyst are summarized in Table 1. A

Table 1. Optimization of the reaction conditions for the asymmetric epoxidation of chalcone catalyzed by **C1**.[a]

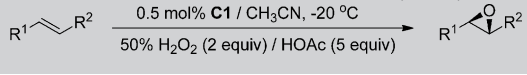


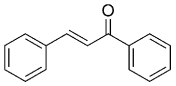
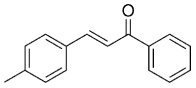
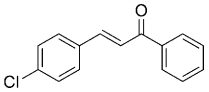
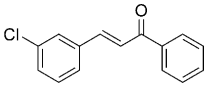
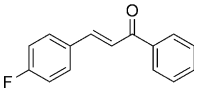
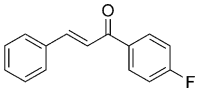
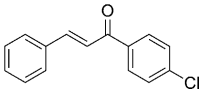
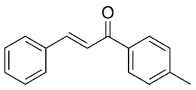
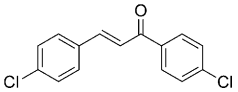
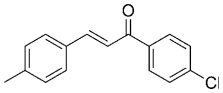
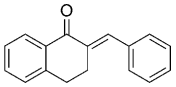
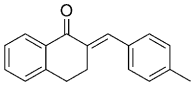
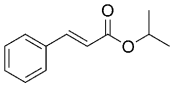
Entry	Catalyst [mol%]	*T* [°C]	HOAc [equiv.]	H_2O_2 [equiv.]	Yield [%][b]	*ee* [%][c]
1	1	RT	5	6	71	82
2	1	−20	5	2	89	89
3	0.5	−20	5	2	93	91
4	0.2	−20	5	2	62	83
5	0.5	−20	5	1.5	61	90
6	0.5	−30	5	2	94	90
7	0.5	−20	14	2	94	90

[a] Reaction conditions: 2 equiv. of 50% H_2O_2 diluted with 0.5 mL of CH_3CN was added with a syringe pump for an hour to a stirred solution of the catalyst **C1** (1.25×10^{-3} mmol, 0.5 mol%), HOAc (1.25 mmol), and substrate (0.25 mmol) in 1.0 mL of CH_3CN at −20 °C under argon, and then the mixture was stirred for an additional hour; [b] Isolated yield; [c] Determined from HPLC analysis (see the Supporting Information for details).

total of 82% *ee* and 71% yield could be obtained by using 5 equiv. of acetic acid, 6 equiv. of 50% H_2O_2 with respect to the substrate, and 1 mol% manganese complex as the catalyst at room temperature (Table 1, entry 1), and 89% *ee* could be obtained by lowering the temperature to −20 °C even by using 2 equiv. of 50% H_2O_2 (entry 2). Then, the catalyst loading was investigated. The asymmetric induction of epoxidation achieved 91% *ee* with 0.5 mol% catalyst **C1** at −20 °C (entry 3). Further lowering of the catalyst loading led to the decrease in enantioselectivity and yield (entry 4). In addition, the yield would evidently reduce but with similar enantioselectivity when the dosage of H_2O_2 was reduced from 2 to 1.5 equiv. (entry 3 vs. entry 5). The same results were obtained on conducting the reaction at −30 °C (entry 3 vs. entry 6). There is clearly no effect of the increase in acetic acid from 5 to 14 equiv. on the *ee* and yield (entry 3 vs. entry 7).

Table 2. Enantioselective epoxidation of olefins catalyzed by **C1**.[a]



Entry	Substrate	Yield [%][b]	*ee* [%][c]
1		93	91
2		75	91
3		96	94
4		96	96
5		91	95
6		97	84
7		83	79
8		91	90
9		95	96
10		37	75
11		61	54
12		54	84
13		79	71
14[d]		91	39

[a] Reaction conditions: 2 equiv. of 50% H_2O_2 diluted with 0.5 mL of CH_3CN was added with a syringe pump for an hour to a stirred solution of the catalyst **C1** (1.25×10^{-3} mmol, 0.5 mol%), HOAc (1.25 mmol), and substrate (0.25 mmol) in 1.0 mL of CH_3CN at −20 °C under argon, and then the mixture was stirred for an additional hour; [b] Isolated yield; [c] Determined from HPLC analysis (see the Supporting Information for details); [d] The yield and *ee* were determined from GC analysis.

The scope of the reaction was studied under the optimized conditions (Table 1, entry 3). As shown in Table 2, the epoxidation of various chalcone derivatives with aqueous H_2O_2 and acetic acid gave the corresponding α,β-epoxyketone in good yields and enantioselectivities.[14] For the substrates bearing either electron-donating or electron-withdrawing groups on the phenyl ring of the olefin side, more than 90% *ee* and 90% yields were obtained (Table 2, entries 3–5); however, for the substrate with the *p*-Me group at the phenyl ring, only a 75% yield was obtained (entry 2). In contrast, only substitution by the *p*-Me group on the phenyl ring of the carbonyl side led to 90% *ee* and 91% yield (entry 8), and other chalcones with electron-withdrawing groups on the phenyl ring of the carbonyl side transformed to the desired epoxides in approximately 80% *ee* (entries 6 and 7). The electronic property of the substituents on both sides has a significant effect on the stereocontrol and yield for the present C_2-symmetric manganese complex. The substrate with the *p*-Cl group on both phenyl rings gave 95% yield and 96% *ee* (entry 9). The outcome is better than that for the Mn^{II}-*S*-PEB$(OTf)_2$ complex.[12b] However, for the *p*-Me- and *p*-Cl-substituted substrates, only a 37% yield was obtained (entry 10). Presumably, the diversity in the reactivity and enantioselectivity for the C_2-symmetric Mn(*R*,*R*-MCMB)OTf_2 and C_1-symmetric Mn^{II}-*S*-PEB$(OTf)_2$ complexes attributes to the nature of the complexes.[12b] With trisubstituted α,β-unsaturated ketones as substrates, only moderate yields and 54–84% *ee* were obtained (entries 11 and 12). In addition, isopropyl cinnamate resulted in 79% yield and 71% *ee* (entry 13). For the epoxidation of styrene, a good yield was achieved but with a 39% *ee* (entry 14). Unfortunately, low *ee* values were generated by using aliphatic olefins such as 1-octene and vinylcyclohexane as the substrates, although they were completely transformed into epoxides (see the Supporting Information).

Subsequently, the activity of the corresponding iron complex **C2** was also tested (Table 3). A total of 89% *ee* and 72% yield were observed with the 2 mol% catalyst **C2**, 5 equiv. of acetic acid, and 1.2 equiv. of H_2O_2 at −20 °C (Table 3, entry 1). The *ee* and yield could be increased to 93 and 87%, respectively, by increasing the amount of H_2O_2 to 1.5 equiv. (entry 2), and an increase in the H_2O_2 amount to 2 equiv. led to an increase in the yield to 94% (entry 3). The reaction proceeded uneventfully in the presence of 3 equiv. of acetic acid, even though with slightly lower levels of enantioselectivity and yield (entry 3 vs. entry 4). Overall, the present iron system based on the *R*,*R*-

Table 3. Optimization of the reaction conditions for the asymmetric epoxidation of chalcone catalyzed by **C2**.[a]

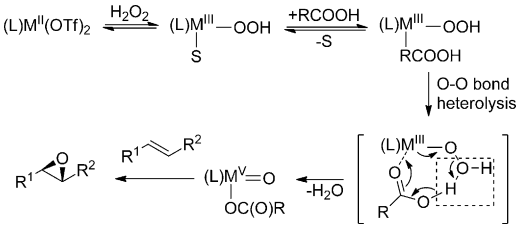
Entry	Catalyst [mol%]	*T* [°C]	HOAc [equiv.]	H_2O_2 [equiv.]	Yield [%][b]	*ee* [%][c]
1	2	−20	5	1.2	72	89
2	2	−20	5	1.5	87	93
3	2	−20	5	2	94	93
4	2	−20	3	2	83	90

[a] Reaction conditions: 2 equiv. of 50% H_2O_2 diluted with 0.5 mL of CH_3CN was added with a syringe pump for an hour to a stirred solution of the catalyst **C2** (1.25×10^{-3} mmol, 0.5 mol%), HOAc (1.25 mmol), and substrate (0.25 mmol) in 1.0 mL of CH_3CN at −20 °C under argon, and then the mixture was stirred for an additional hour; [b] Isolated yield; [c] Determined from HPLC analysis (see the Supporting Information for details).

MCMB ligand demonstrates reactivity and enantioselectivity comparable with those of the Fe^{II}-*S*-PEB$(OTf)_2$ complex.[12a]

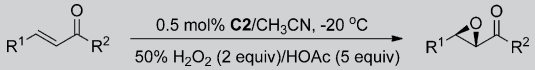
To demonstrate the substrate scope of the nonheme iron-catalyzed epoxidation, a series of chalcone derivatives as well as trisubstituted cyclic enones were evaluated under optimized conditions. In most cases, the reaction gave the corresponding α,β-epoxyketones in good yields and enantioselectivities (Table 4). For the trisubstituted cyclic enones, only the substrate without any substituent gave 77% yield and 91% *ee* (entry 7). With the *p*-Me–Ph-substituted substrate, the corresponding epoxides were isolated in poor yields (entry 8). For this type of substrate, the steric bulk represented by this *p*-Me–Ph group could potentially hinder the oxidation catalyzed by the Fe(*R*,*R*-MCMB)OTf_2 catalyst. However, this substrate is a good candidate for forming the α,β-epoxyketones promoted by the C_1-symmetric Fe^{II}-*S*-PEB$(OTf)_2$ complex.[12a]

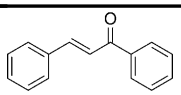
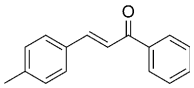
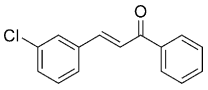
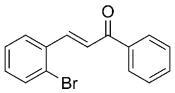
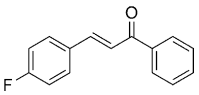
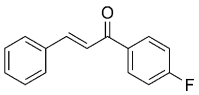
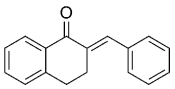
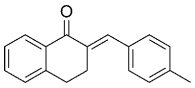
The oxidation mechanisms catalyzed by manganese or iron complexes with N_4 ligands have recently made significant progress using acetic acid as an additive. On the basis of the electron paramagnetic resonance spectroscopy and enantioselectivity studies on the epoxidation in the presence of various carboxylic acids, Bryliakov et al. proposed a reasonable mechanism, which is shown in Scheme 2.[9c] For the present catalytic system for the epoxidation, acetic acid is essential to achieve epoxidation activity. As shown in Scheme 2, the presence of acetic acid would facilitate the heterolysis of the O–O bond of the intermediate (M^{III}-OOH).[3d] Costas et al. trapped the active oxoiron(V) species in a related catalyst system based on the iron complex with N_4 ligands.[15] In our recent work, when the



Scheme 2. Proposed mechanism for the epoxidation catalyzed by the nonheme manganese or iron complex.

Table 4. Enantioselective epoxidation of chalcone derivatives catalyzed by **C2**.[a]



Entry	Substrate	Yield [%][b]	*ee* [%][c]
1		94	93
2		71	87
3		76	95
4		93	91
5		81	93
6		85	87
7		77	91
8		40	75

[a] Reaction conditions: 2 equiv. of 50% H_2O_2 diluted with 0.5 mL of CH_3CN was added with a syringe pump over an hour to a stirred solution of the catalyst **C2** (5×10^{-3} mmol, 2 mol%), HOAc (1.25 mmol), and substrate (0.25 mmol) in 1.0 mL of CH_3CN at −20 °C under argon, and then the mixture was stirred for an additional hour; [b] Isolated yield; [c] Determined from HPLC analysis (see the Supporting Information for details).

asymmetric epoxidation of chalcone was performed in the presence of excess of $H_2{}^{18}O$, the ^{18}O labeling epoxide products were observed in both manganese and iron complex catalytic systems.[10,12] These results indicate that high-valent M=O species are involved as the active oxidant in the catalytic process.[3d,15,16]

Conclusions

In summary, we synthesized a chiral C_2-symmetric tetradentate N ligands from the easily available cyclohexane-1,2-diamine and 2-chloromethyl-1-methyl-benzimidazole. The corresponding manganese and iron complexes could serve as efficient and enantioselective catalysts in the epoxidation with H_2O_2 as an oxidant. Notably, when the pyridine moieties of the *N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyridylmethyl)cyclohexane-1,2-diamine ligand are replaced with benzimidazoles, the resulting *R*,*R*-MCMB ligand demonstrates much higher enantioselectivity (up to 96% *ee*) with its manganese and iron complexes catalyzing the asymmetric epoxidation of olefins. Further studies on the ap-

plication of this N_4 ligand in other new reactions are in progress.

Experimental Section

General remarks

The ^1H and ^{13}C NMR spectra were recorded by using a Bruker Avance III 400 MHz NMR spectrometer. The GC–MS spectra were recorded by using an Agilent 6890/5973 GC–MS spectrometer. The HRMS (ESI) spectra were determined by using a Bruker Daltonics micrOTOF-QII mass spectrometer. X-ray crystallographic data were collected by using a Bruker SMART CCD 1000 diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) at 150(2) K. HPLC analysis was performed by using a Waters Breeze system with a 2487 Dual λ absorbance detector and a 1525 Binary HPLC pump. Chiralpak OD, AD, OJ, AS, and OB columns were purchased from Daicel Chemical Industries, Ltd. GC analysis was performed by using an Agilent 7890A GC with a CP-Chirasil-Dex CB column. Column chromatography was performed on silica gel (200–300 mesh), and TLC inspections were performed on silica gel GF254 plates. All reactions were performed under argon in dried glassware. All chemicals and solvents were used as received unless otherwise stated. Diethyl ether (Na/benzophenone) and acetonitrile (CaH_2) were distilled under argon before use. 2-Chloromethyl-benzimidazole was synthesized by using the modified literature method.[17]

General method for the synthesis of the *R,R*-MCMB ligand

2-Chloromethyl-1-methyl-benzimidazole (2 mmol), (1*R*,2*R*)-*N*,*N*-dimethylcyclohexane-1,2-diamine (1 mmol), and anhydrous acetonitrile (10 mL) were mixed in a 25 mL flask. Then, anhydrous Na_2CO_3 (0.87 g) and tetrabutylammonium bromide (0.04 g) were added directly as solids and the resulting mixture was heated to reflux for 24 h under argon. After cooling to RT, the mixture was filtered and the filter cake was washed with CH_2Cl_2. The combined filtrates were evaporated under reduced pressure. To the resulting residue, NaOH (1 M, 8.75 mL) was added and the mixture was extracted with CH_2Cl_2 (4×15 mL). The combined organic layer was washed successively with saturated aqueous solutions of $NaHCO_3$, NaCl, and finally H_2O. The organic layers were dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure; the crude product was purified by using chromatography on silica gel (PET/EtOAc 2:1) to afford the desired ligand *R,R*-MCMB.

81% yield; yellow solid; $[\alpha]_D^{20} = +12.8$ ($c = 0.5$ in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 7.74$–7.72 (m, 2H), 7.27–7.25 (m, 6H), 3.94 (s, 4H), 3.79 (m, 6H), 2.68 (s, 2H), 2.14 (s, 6H), 2.02 (d, 2H, $J = 10.9$ Hz), 1.79 (d, $J = 6.7$ Hz, 2H), 1.27–1.15 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta = 152.5$, 142.3, 136.4, 122.4, 121.8, 119.6, 109.1, 62.7, 51.7, 35.8, 29.9, 25.6, 24.0 ppm; HRMS (ESI): *m/z*: calcd for $C_{26}H_{34}N_6$: 431.2922 $[M+H]^+$; found: 431.2918.

General method for the preparation and characterization of the manganese complex C1 and iron complex C2

Under argon, $Mn(CF_3SO_3)_2$ (0.10 mmol) was added to a stirred solution of the chiral ligand *R,R*-MCMB (0.10 mmol) in acetonitrile (3 mL). The reaction mixture was stirred for 12 h and dried under vacuum to yield the manganese complex **C1**. Crystals suitable for XRD were grown through vapor diffusion of ether into a saturated solution of the manganese complex in MeCN.

$[Mn^{II}(R,R\text{-MCMB})(CF_3SO_3)_2]$: HRMS (ESI): *m/z*: calcd for $C_{27}H_{34}F_3MnN_6O_3S$: 634.1740 $[M-OTf]^+$; found: 634.1759; elemental analysis calcd (%) for $C_{28}H_{34}F_6MnN_6O_6S_2 \cdot H_2O$: C 41.95, H 4.53, N 10.48; found: C 41.67, H 4.40, N 10.34.

Under argon, $FeCl_2 \cdot 4H_2O$ (49.4 mg, 0.25 mmol, 1 equiv.) was added to a stirred solution of the chiral ligand *R,R*-MCMB (108 mg, 0.25 mmol, 1 equiv.) in acetonitrile (3 mL) at RT. The reaction mixture was stirred for 24 h, and diethyl ether was added to the solution to completely precipitate out the bright orange solid. The solvent was decanted out of the flask with a pipette, and the solids were washed thoroughly with ether thrice and dried under vacuum to yield the $Fe(R,R\text{-MCMB})(Cl)_2$ complex. A flame-dried 10 mL flask was charged with $Fe(R,R\text{-MCMB})(Cl)_2$ (0.21 mmol) suspended in acetonitrile (4 mL) under argon. Silver trifluoromethanesulfonate (106 mg, 0.42 mmol, 2 equiv.) was weighed under argon and then added to the vigorously stirred heterogeneous mixture. The flask was covered with the aluminum foil to protect the silver salts from light. After 24 h, the reaction mixture was filtered through a 0.2 μm LC PVDF filter (HPLC certified) twice to ensure no silver salts remained; the solvent was removed under vacuum to yield the iron complex **C2**.

$[Fe^{II}(R,R\text{-MCMB})(CF_3SO_3)_2]$: HRMS (ESI): *m/z*: calcd for $C_{27}H_{34}F_3FeN_6O_3S$: 635.1709 $[M-OTf]^+$; found: 635.1715; elemental analysis calcd (%) for $C_{28}H_{34}F_6FeN_6O_6S_2 \cdot 1.5\,H_2O$: C 41.44, H 4.60, N 10.35; found C 41.45, H 4.73, N 10.18.

Representative method for the manganese-catalyzed asymmetric epoxidation of olefins

Under argon, the catalyst **C1** (1.0 mL, 1.25×10^{-3} mmol, 0.979 mg mL^{-1} in MeCN), substrate (0.25 mmol), and AcOH (1.25 mmol, 75 mg, 5 equiv.) were added to a 10 mL flask and the solution was stirred for 2 min at RT. Then the mixture was cooled to −20 °C; 50% H_2O_2 (0.5 mmol, diluted with 0.5 mL MeCN, 2 equiv.) was added dropwise with a syringe pump for an hour; and the mixture was stirred at −20 °C for an hour. The crude product was purified by using chromatography on silica gel (PET/EtOAc 50:1) to afford the epoxide product.

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Keywords: asymmetric epoxidation · iron · manganese · N_4 ligand · olefin

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