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Enantioselective Epoxidation of Electron-Deficient Alkenes Catalyzed by Manganese Complexes with Chiral N4 Ligands Derived from Rigid Chiral Diamines

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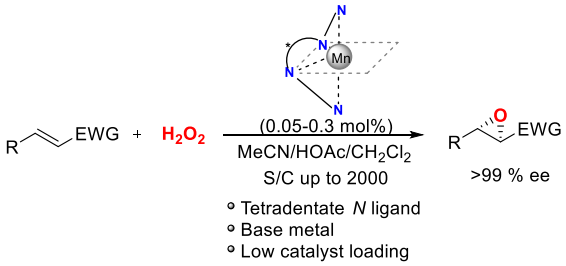
Abstract. A series of tetradentate sp^2N/sp^3N hybrid chiral N4 ligands derived from rigid chiral diamines were synthesized, which enabled the first Mn-catalyzed enantioselective epoxidation of electron-deficient alkenes with H_2O_2 as an oxidant. The reaction furnishes enantiomerically pure epoxy amides, epoxy ketones as well as epoxy esters in good yields and excellent enantioselectivities (up to 99.9% ee) with lower catalyst loading. Preliminary studies on structure-activity relationship demonstrated that maintaining comparatively lower electron-donating ability of the sp^3-N and relatively higher electron-donating ability of sp^2-N of the N4 ligands is beneficial to getting higher activity and selectivity, thus providing us a new view to understand epoxidation with H_2O_2.

Keywords: enantioselective epoxidation; alkenes; manganese; chiral N4 ligand; hydrogen peroxide

Enantioselective epoxidation of C-C double bond with chiral catalysts in the presence of oxidants provides an easy and direct access to optically active epoxides and their derivatives, which has reached a very high level of development leading to a vast number of enantiomerically pure epoxy molecules.[1] However, a limited number of methods have been developed so far for the selective epoxidation of alkenyl amides,[2] yet the resulting chiral epoxy amides are versatile starting materials for the synthesis of functional molecules.[3] Shibasaki and co-workers realized the enantioselective epoxidation of α,β-unsaturated amides in the presence of chiral lanthanide catalysts,[2] but a large amount of environmentally unfriendly TBHP and high catalyst loading (5-10 mol%) were required for achieving high enantioselectivity, which significantly reduced the appeal of this elegant catalytic epoxidation process and hindered large-scale applications. Hence, an efficient and practical catalytic system enabling the environment-benign H_2O_2 to be used as the oxidant and allowing the asymmetric epoxidation to proceed with low catalyst loading is highly desirable. Herein, we reported a new type of tetradentate sp^2N/sp^3N hybrid chiral N4 ligands derived from rigid chiral diamines with lower electron-donating ability, which enabled us to establish a highly efficient manganese catalytic system for enantioselective epoxidation of alkenyl amides, enones as well as α,β-unsaturated esters with H_2O_2 as an oxidant (Scheme 1).



Scheme 1. Mn-catalyzed enantioselective epoxidation of electron-deficient alkenes.

The chiral ligand plays a definitive role cooperated with the central metal in asymmetric reactions catalyzed by metal-complexes. Finely tuning the electron-donating ability of the coordinative atoms of ligands often revolutionizes the catalytic performance in terms of reactivity, selectivity and productivity.[4] Bio-inspired manganese complexes ligated with tetradentate sp^2N/sp^3N hybrid chiral N4 ligand have been identified as effective catalysts for the enantioselective epoxidation of enones and α,β-unsaturated esters.[5] However, very few such kind of catalysts were utilized for epoxidation of the recalcitrant alkenyl amides due to their low reactivity. A critical step in this type of catalysis relies on the ability of the high-valent electrophilic oxidizing

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species LMn=O to transfer the O-atom to the C-C double bond to allow the catalyst turnover with enantioselectivity.[6] It is widely appreciated that appropriate modulation of the electron-donating ability of the four sp^2N/sp^3N-atoms of the N4 ligand could effectively tune the electrophilicity of the active Mn-oxo species to facilitate the O-atom transfer and ensure high enantioselectivity. Since the coordinated sp^2N-atom usually could exert stronger influence on the electron properties of central-metal than that of sp^3N-atom, almost all of the documented works on modifying chiral Mn-N4 catalysts focused on the modulation of sp^2N moiety by introducing strongly electron-donating groups to improve the interaction of the sp^2N-atom with the central metal.[5,6] However, even the strongest electron-donating group NMe_2 was introduced in the backbone of sp^2N, the electron-donating ability of the sp^2N-atom still could not meet the requirement for fulfilling the reactivity of some formidable substrates. In this context, we envisioned that appropriate attenuation of the donating ability of the sp^3N-atom might enhance the interaction of the sp^2N-atom of N4 ligand with the central metal to improve the electrophilicity of the corresponding active species. In this regard, the benzene-fused chiral diamine 1,1'-biisoindoline (named BIDN) developed by our own group appeared to be a suitable diamine precursor for the chiral N4 ligand. Our previous work suggested that the presence of fused benzene ring in BIDN not only made it more rigid, but also could attenuate the electron-donating ability of the sp^3N-atom due to its π-electron acceptability.[7] Inspired by the unique nature of this chiral diamine, we anticipated that it could be evolved into a new class of unique chiral N4 ligands for Mn-catalyzed epoxidation by combination of this chiral backbone and an achiral privileged pyridine or benzoimidazole, in which the lower electron-donating ability of the sp^3N-atom in BIDN might enhance the interaction of pyridine or benzoimidazole sp^2N-atom with central metal to craft an effective chiral environment.

The development of chiral diamines into a series of chiral N4 ligands **1** and **2** was successfully achieved in one step from the chiral diamine BIDN and the corresponding 2-(chloromethyl)pyridines or N-substituted 2-(chloromethyl)benzoimidazoles (Scheme 2). The corresponding Mn(II)-complexes were obtained in high yields by stirring the mixture of ligands and $Mn(OTf)_2$ in CH_3CN at room temperature overnight. The solid-state structures of [Mn(**2a**)$(OTf)_2$] and [Mn(**2e**)$(OTf)_2$] were confirmed by X-ray analysis of their single crystals recrystallized from Et_2O/CH_3CN and Et_2O/CH_2Cl_2 solvent system, respectively. The X-ray structures of these two complexes revealed that the chiral N4 ligand is bound to a manganese center in a *cis*-α configuration with two sp^2N-atoms coordinated to the metal center trans to each other and the two triflate groups bind at the two remaining coordination sites that are *cis* to each other (Figure 2).[8] In the structure of [Mn(**2e**)$(OTf)_2$], the metal bonds to the benzoimidazole sp^2N-atoms [2.168Å, 2.155Å] are significantly shorter than those to the amino sp^3N-atoms [2.363Å, 2.361Å] as a consequence of the sp^2-hybridization of the benzimidazole N-atom and the metal-benzoimidazole π-interaction. Moreover, the bond length of the two Mn-Nsp^3 bonds is the longest, but the bond length of the two Mn-Nsp^2 bonds is the shortest in all of the reported chiral Mn-N4 complexes for catalytic epoxidation (see SI). These results confirmed our hypothesis that decreasing the electron-donating ability of sp^3N-atom of the chiral N4 ligands could indeed enhance the interaction of sp^2N-atom with the central metal. To further validate this concept, the benzene-fused chiral diamine unit in ligand **2e** was replaced by the commonly used chiral bipyrrolidine to give the chiral N4 ligand **2i** and the corresponding [Mn(**2i**)$(OTf)_2$]. Confirmation of the solid-state structure of the Mn-complex was obtained from single crystal X-ray diffraction studies (Figure 1).[8] As expected, the bond length [2.250Å, 2.213Å] of the two Mn-Nsp^2 bonds is much longer than that of [Mn(**2e**)$(OTf)_2$], but the bond length [2.322Å, 2.316Å] of the two Mn-Nsp^3 bonds is shorter than that of [Mn(**2e**)$(OTf)_2$]. This observation is most likely resulted from the stronger electron-donating ability of the sp^3N-atom in bipyrrolidine than that of BIDN.

Scheme 2. Synthesis of the chiral ligands.

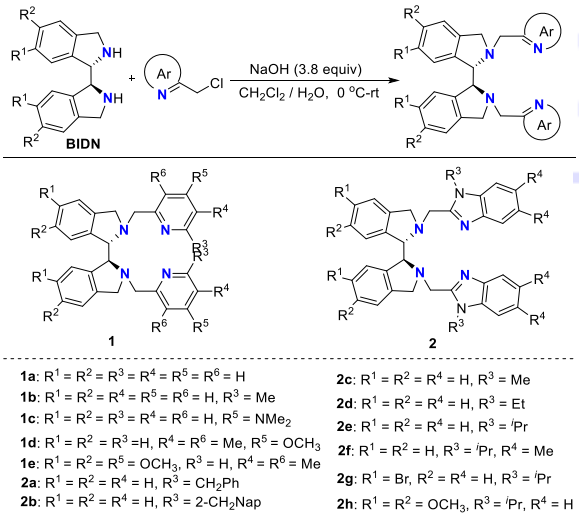
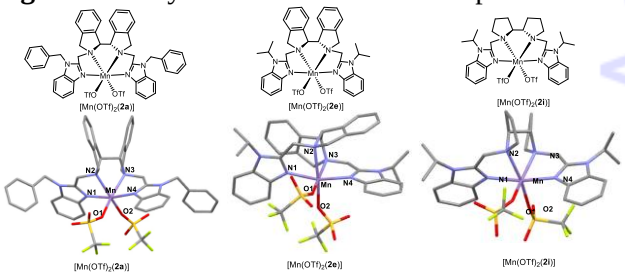


Figure 1. X-ray structure of Mn-N4 complexes.



Encouraged by the successful preparation of the chiral ligands and their corresponding manganese complexes, we examined the enantioselective epoxidation with *N*,*N*-dibenzylcinnamamide **3a** as a model substrate for identifying an effective chiral

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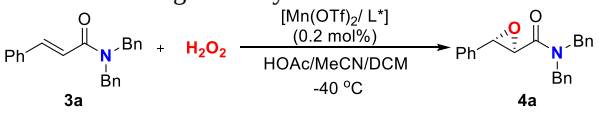
catalyst. The reaction was carried out in the presence of 0.2 mol% of catalyst under acidic condition at -40 °C for 35 min with H_2O_2 as the sole oxidant. To our delight, the asymmetric epoxidation of **3a** proceeded smoothly in the presence of manganese complex ligated with **1a**, affording the desired product **4a** in 66% isolated yield with 90.9% ee (Table 1, entry 1). This prompted us to assess other chiral N4 ligands, and we found that both the yield and enantioselectivity were affected significantly by the steric bulk and electron-donating ability of the chiral N4 ligands. For the pyridine-derived ligand **1**, the reaction was virtually stopped when a methyl group was introduced into the *ortho*-position of the pyridine-ring presumably due to steric hindrance (Table 1, entry 2). In addition, when electron-donating groups were introduced at the *para*-position (R^5) of the pyridine, both the yield and selectivity were improved (Table 1, entry 3). Interestingly, the ligands **1e** and **2h** bearing two electron-donating methoxy groups in the fused benzene ring of diamine

Table 1. Screening of catalyst[a]



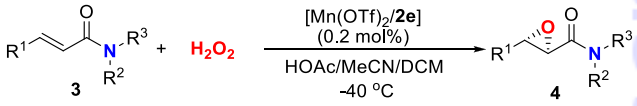
Entry	Ligand	Yield (%)	ee (%)
1	**1a**	66	90.9
2	**1b**	NR	-
3	**1c**	85	94.9
4	**1d**	87	59.9
5	**1e**	NR	-
6	**2a**	75	98.0
7	**2b**	35	35.4
8	**2c**	86	93.5
9	**2d**	85	95.4
10	**2e**	87	98.5
11	**2f**	81	99.6
12	**2g**	68	97.6
13	**2h**	NR	-
14	**2i**	69	81.0

[a] Reaction conditions: the reaction was conducted in HOAc/MeCN/DCM (0.6 mL/1.2 mL/0.2 mL) with **1a** (0.3 mmol) and [Mn(OTf)2L*] (0.2 mol%) at -40 °C, and H_2O_2 (1.2 equiv., 1 M in MeCN, 50% H_2O_2) was added dropwise through a syringe pump for 30 min, and additional 5 min of stirring was allowed, isolated yields, ee values were determined by HPLC.

backbone were unable to catalyze the reaction (Table 1, entries 5 and 13). These results indicated that maintaining comparatively lower electron-donating ability of the sp^3N-atom and relatively higher electron-donating ability of sp^2N-atom was beneficial to getting higher activity and selectivity, which confirmed our hypothesis that electrophilicity of the reactive Mn-species. This tendency was further confirmed by comparing the catalytic performance of ligand **2e** with **2f** (99.6% ee (**2f**) vs 98.5% ee (**2e**)). The ligand **2f** contains two electron-donating groups in the arene-ring of benzoimidazole moiety, giving the corresponding product with higher enantioselectivity (99.6% ee, Table 1, entry 11). Finally, among the series of catalysts examined, excellent results were observed with the Mn-complexes ligated with **2e** and **2f** (Table 1, entries 10 and 11). As expected, the Mn-complex derived from chiral ligand **2i** exhibited lower reactivity and selectivity (Table 1, entry 14).

Having identified the best catalyst and with the optimal reaction conditions in hand, the scope of this enantioselective epoxidation was investigated in the presence of manganese complexes ligated with **2e** or **2f** as a chiral ligand. As summarized in Table 2, various types of cinnamamides were found to be applicable for the reaction with low catalyst loading (0.3-0.05 mol%). Electronically and sterically diverse

Table 2. Screening of catalyst[a]



Entry	R^1	R^2	R^3	Yield (%)	ee (%)
1[b]	C_6H_5	Bn	Bn	**4a** (81)	99.6
2	C_6H_5	*t*-Bu	H	**4b** (85)	98.2
3	C_6H_5	cyclohexyl	H	**4c** (83)	95.1
4[b]	C_6H_5	Bn	H	**4d** (86)	97.2
5[c]	C_6H_5	CH_3	H	**4e** (82)	97.1
6[d]	C_6H_5	H	H	**4f** (80)	97.7
7[b]	C_6H_5	C_6H_5	CH_3	**4g** (81)	97.1
8	C_6H_5	*i*-Pr	*i*-Pr	**4h** (86)	99.1
9	C_6H_5	$(CH_2)_4$		**4i** (83)	95.7
10[b]	C_6H_5	$(CH_2)_5$		**4j** (81)	96.7
11	4-$CH_3C_6H_4$	Bn	Bn	**4k** (85)	98.4
12	4-BrC_6H_4	Bn	Bn	**4l** (79)	99.4
13	4-ClC_6H_4	Bn	Bn	**4m** (83)	99.4
14	3-$CH_3C_6H_4$	Bn	Bn	**4n** (84)	99.0
15	2-$CH_3C_6H_4$	Bn	Bn	**4o** (80)	97.7
16[e]	3-ClC_6H_4	Bn	Bn	**4p** (83)	98.9
17[e]	2-ClC_6H_4	Bn	Bn	**4q** (82)	95.6
18	3,4-$(CH_3)_2C_6H_3$	Bn	Bn	**4r** (83)	97.7
19	3,4-$Cl_2C_6H_3$	Bn	Bn	**4s** (87)	94.5
20[f]	C_6H_5	Bn	Bn	**4a** (81)	99.5

[a] Unless noted, the reaction was conducted in HOAc/MeCN/CH_2Cl_2 (0.6 mL/1.2 mL/0.2 mL) with **3** (0.3 mmol) and [Mn(OTf)2/**2e**] (0.2 mol%) at -40 °C, and 360 µL H_2O_2 (1.2 equiv., 1 M in MeCN, 50% H_2O_2) was added dropwise through a syringe pump for 30 min, and additional 5 min of stirring was allowed. Isolated yields and ee values were determined by HPLC. The absolute configuration was determined by comparison of the optical rotation with reported data.

[b] Using [Mn(OTf)2/**2f**] as a catalyst.

[c] The reaction was conducted in HOAc/MeCN/CH_2Cl_2 (2.0 mL/4.0 mL/1.0 mL) with **3e** (1.0 mmol) and [Mn(OTf)2/**2e**] (0.2 mol%) at -30 °C, H_2O_2 (1.2 equiv., 1 M in MeCN, 50% H_2O_2).

[d] The reaction was conducted in HOAc/MeCN/CH_2Cl_2 (1.0 mL/2.0 mL/0.3 mL) with **3f** (1.0 mmol) and [Mn(OTf)2/**2e**] (0.2 mol%) at -30 °C, and 1.2 mL H_2O_2 (1.2 equiv., 1 M in MeCN, 50% H_2O_2).

[e] [Mn(OTf)2/**2e**] (0.3 mol%).

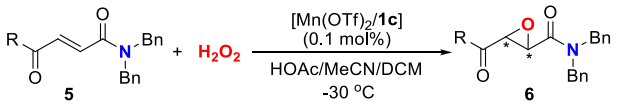
[f] [Mn(OTf)2/**2f**] (0.05 mol%), -25 °C.

cinnamamides all participated smoothly to provide the targets **4a-4s** in high yields with excellent

enantioselectivities. The protocol can be extended to primary and secondary amides and this enables highly enantioselective epoxidation of α,β-unsaturated amides with different substituents at the nitrogen atom, giving the corresponding epoxides in high yields with excellent enantioselectivities (Table 2, entries 2-6). These epoxides can be used directly as key intermediates for the synthesis of a number of natural products and bioactive molecules.[9] Furthermore, the electronic and steric effects on aromatic ring of cinnamamides were investigated, and we found that the reactions proceeded in high yields with excellent enantioselectivities in the presence of both electron-deficient and electron-rich aromatic systems (94.5-99.4% ee, Table 2, entries 11-19). Typical functional groups, such as chloro, and bromo, are also tolerated well under the reaction conditions. Importantly, the successful preparation of **4l**, **4m**, **4p**, **4q** and **4s** with intact bromine and chlorine provides a good opportunity for further formation of carbon-carbon or carbon-heteroatom bonds by transition-metal-catalyzed coupling and other reactions. Significantly, the reaction is effectively catalyzed with 0.05 mol% of the catalyst within 35 min, which represents the lowest catalyst/substrate ratio and one of the fastest catalytic system for enantioselective epoxidation of alkenyl amides (Table 2, entry 20).

Encouraged by the above results, we turned our attention to the more electron-deficient unsaturated ketoamides. The reactions were conducted at -30 °C for 35 min in the presence of H_2O_2 with **1c** as the best chiral ligand. As summarized in Table 3, the results shown that α,β-unsaturated ketoamides **5** were smoothly epoxidized to afford the corresponding chiral epoxy amides **6** in moderate yields with nearly perfect enantioselectivities (ee values range from 98.3% to 99.9% ee) in the presence of 0.1 mol% chiral Mn-catalyst. Electron-donating substituents as well as electron-withdrawing groups at the *para* position of the phenyl ring exerted little impact on the reactivity and selectivity (Table 3, entries 1-4).

Table 3. Substrate scope of unsaturated ketoamides[a]

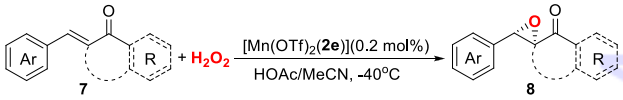


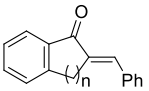
Entry	R	Yield (%)	ee (%)
1	C_6H_5	**6a** (53)	98.3
2	4-$CH_3C_6H_4$	**6b**(46)	99.5
3	4-BrC_6H_4	**6c**(48)	99.9
4	4-ClC_6H_4	**6d** (51)	99.4

[a] All reactions were conducted in HOAc/MeCN/CH_2Cl_2 (0.6 mL/1.2 mL/0.2 mL) with **5** (0.3 mmol) and [$Mn(OTf)_2$/**1c**] (0.1 mol%) at -30 °C, and 360 μL of H_2O_2 (1.2 equiv., 1 M in MeCN, 50% H_2O_2) were added dropwise via a syringe pump for 30 minutes, and additional 5 minutes of stirring was allowed; isolated yields and ee values were determined by HPLC.

With the success of the Mn-catalysed epoxidation as a means to provide chiral epoxy compounds with an amide functionality and to further explore the catalytic behavior of these new chiral Mn-N4 catalytic systems, we decided to move forwards to the synthesis of epoxy compounds with a ketone or ester functionality. As shown in Table 4, a variety of enones were could be efficiently converted to the desired products in good to excellent yields (71% to 92% yields) and enantioselectivities (up to 99% ee) with $Mn(OTf)_2$(**2e**) as a catalyst under the optimized reaction conditions. Excellent performance was observed when electron-donating or electron-withdrawing substituents were introduced in the aromatic rings of enones (Table 4, entries 2-14). Moreover, the sterically hindered enone **7o** could also be smoothly transformed to the corresponding epoxide in good yield with excellent enantioselectivity (96 % ee). However, no desired reaction occurred for substrates bearing oxidation sensitive groups (such as thioether and hydroxyl) on the phenyl ring of the alkene. For the epoxidation of cinnamic ester **7p**, a good yield was achieved but only moderate ee value (62% ee) was observed (Table 4, entry 16). Furthermore, the cyclic enones (Table 4, entries 17-18) were epoxidized with high yields and excellent enantioselectivities (96-99% ee). Unfortunately, no desired epoxy product was observed when cinnamaldehyde was subjected to the standard reaction conditions.

Table 4. Substrate scope of enones[a]



Entry	Ar	R	Yield (%)	ee (%)
1	C_6H_5	C_6H_5	**8a** (85)	96
2	4-$CH_3C_6H_4$	C_6H_5	**8b** (72)	93
3[b]	4-FC_6H_4	C_6H_5	**8c** (90)	93
4[b]	4-ClC_6H_4	C_6H_5	**8d** (91)	95
5[b]	4-BrC_6H_4	C_6H_5	**8e** (92)	95
6[b]	3-ClC_6H_4	C_6H_5	**8f** (80)	95
7	2-ClC_6H_4	C_6H_5	**8g** (92)	82
8[c]	2-naphthyl	C_6H_5	**8h** (84)	82
9[b]	C_6H_5	4-$CH_3OC_6H_4$	**8i** (85)	93
10[b]	C_6H_5	4-*i*-BuC_6H_4	**8j** (71)	93
11[b]	C_6H_5	4-ClC_6H_4	**8k** (89)	93
12[b]	C_6H_5	4-BrC_6H_4	**8l** (89)	92
13	C_6H_5	2-$CH_3OC_6H_4$	**8m** (85)	94
14	C_6H_5	2-ClC_6H_4	**8n** (88)	96
15[d]	C_6H_5	*t*-Bu	**8o** (84)	96
16	C_6H_5	C_6H_5O	**8p** (77)	62
17[b]		n = 1	**8q** (82)	99
18[b]		n= 2	**8r** (84)	96

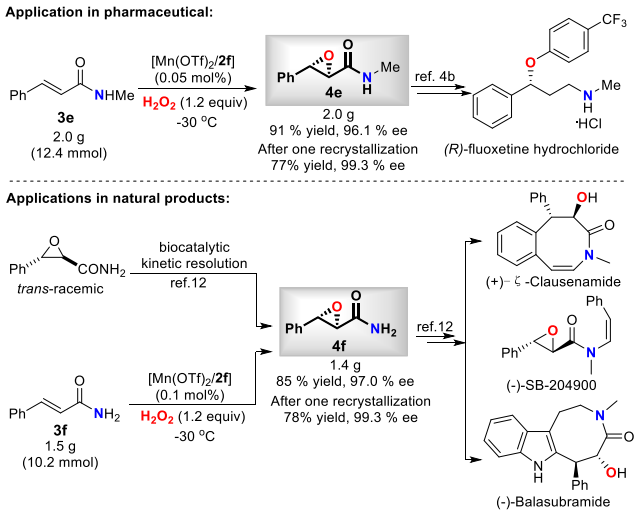
[a] Unless noted, the reaction was conducted in HOAc/MeCN (0.3 mL/0.6 mL) with **7** (0.3 mmol) and [$Mn(OTf)_2$(**2e**)] (0.2 mol%) at -40 °C, and H_2O_2 (1.2 equiv, 1 M in MeCN, 50% H_2O_2) was added dropwise through a syringe pump for 30 min, and additional 5 min of stirring was allowed; isolated yields and ee values were determined by HPLC.

[b] CH_2Cl_2 (0.2 mL) was added.

[c] 0 °C, [$Mn(OTf)_2$(**2e**)] (0.3 mol%), and CH_2Cl_2 (0.2 mL) was added.

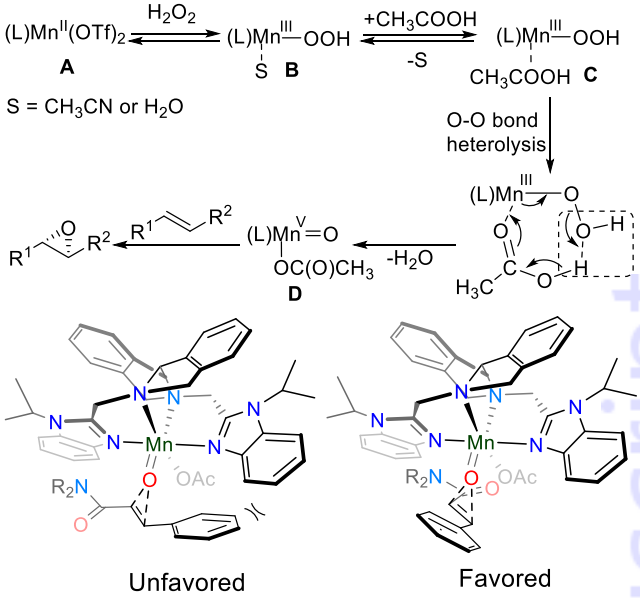
[d] [$Mn(OTf)_2$(**2e**)] (0.3 mol%).

In order to evaluate the practicability and synthetic utility of this Mn-catalyzed epoxidation process, the reactions of **3e** and **3f** with H_2O_2 were carried out on a gram scale in the presence of 0.05 mol% and 0.1 mol% of catalyst at -30 °C with a reaction time of 2 h and 3 h, respectively. As expected, the reactions underwent smoothly to afford the corresponding (*2R,3S*)-N-methyl-3-phenyloxirane-2-carboxamide **4e** and (*2R,3S*)-3-phenyloxirane-2-carboxamide **4f** in high yields with excellent enantioselectivities (S/C = 2000 and 1000, 96.1 and 97.0% ee, respectively). The ee value can be upgraded to 99% by crystallization from CH_2Cl_2/hexane to produce **4e** and **4f** in high yields. The product **4e** could be converted to the (*R*)-fluoxetine according to the method reported by Shibasaki and co-workers.[2e] On the other hand, the product **4f**, which previously prepared by bio-catalytic kinetic resolution, is a key intermediate toward a wide range of natural products. For example, the (+)-ζ-Clausenamide, (-)-SB-204900 and (-)-Balasubramide (Scheme 3) could be easily prepared from **4f** by using the reported method.[9]



Scheme 3. (*2R,3S*)-3-phenyloxirane-2-carboxamide **4e** and (*2R,3S*)-N-methyl-3-phenyloxirane-2-carboxamide **4f** as versatile synthons in organic synthesis.

On the basis of the above results and previous reports,[6] a plausible reaction mechanism was proposed (Scheme 4). The manganese complex Mn(L)(OTf)$_2$ **A** is initially converted to the intermediate **B** in the presence of H_2O_2. Subsequently, the active Mn=O complex **D** is formed via acid-assisted heterolytic cleavage of the O-O bond of intermediate **C**. The active species **D** epoxidizes the olefins to the corresponding products. On the basis of understanding the X-ray structure of the manganese complex [Mn(OTf)$_2$**2e**], we supposed that when the cinnamamide approaches to the Mn=O species, the oxygen should capture the double bond from the *Si*, *Si*-face of the alkene delivering the corresponding epoxy amides with *2R,3S*-configuration. In contrast, the *Re*, *Re*-face attack model would lead to large steric hindrance between two phenyl rings that come from the substrate and ligand, respectively.



Scheme 4. Proposed reaction mechanism and transition state for epoxidation of alkene.

In summary, a novel class of sp^{2}N/sp^{3}N hybrid chiral N4 ligands derived from rigid chiral diamines as well as the corresponding chiral Mn-complexes were designed and synthesized. The structures of these Mn-N4 complexes were confirmed by X-ray analysis and identified as effective catalysts for the enantioselective epoxidation of electron-deficient alkenes with H_2O_2 as an oxidant. The established catalytic system has a broad generality for epoxidation of electron-deficient alkenes with a nearly stoichiometric amount of H_2O_2 and low catalyst loading (0.05 mol%). A large number of chiral α,β-epoxy amides, ketones and esters were afforded in high yields with excellent enantioselectivities (up to 99.9% ee). Conceptually, it is shown that the catalytic behavior of these chiral Mn-complexes for asymmetric epoxidation could be modulated by finely tuning the electron-donating ability of the sp^{3}N-atoms of the chiral N4 ligands. Therefore, we anticipate that the present results should significantly expand the range of possibilities in designing catalysts not only for oxidation but also for many other reactions.

Experimental Section

General procedure for enantioselective epoxidation

To an oven-dried Schlenk tube equipped with a stir bar was added alkenyl amide (**3a** 0.3 mmol), manganese complexes (0.2 mol%), HOAc (0.6 mL), DCM (0.2 mL) and MeCN (1.2 mL) under nitrogen atmosphere. The reaction mixture

was allowed to stir at room temperature for 5 minutes and then cooled to -40 ºC. H_2O_2 (0.36 mmol, 50% H_2O_2, 1M in MeCN) was added by syringe pump for 30 minutes, and an additional 5 minutes of stirring was allowed at -40 ºC. The resulting mixture was quenched with Et_3N (1.0 mL) at -40 °C, and purified directly by flash column chromatography on silica gel and eluted with EtOAc/petroleum ether/DCM (1/3/1 to 1/10/1) to afford the chiral α,β-epoxy amides.

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[8] CCDC 1475364 ([Mn(**2a**)OTf_2]), 1475388 ([Mn(**2e**)OTf_2]) and 1486425 ([Mn(**2i**)OTf_2]) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Enantioselective Epoxidation of Electron-Deficient Alkenes Catalyzed by Manganese Complexes with Chiral N4 Ligands Derived from Rigid Chiral Diamines

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