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A Mononuclear Manganese Complex of a Tetradentate Nitrogen Ligand – Synthesis, Characterizations, and Application in the Asymmetric Epoxidation of Olefins

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A new chiral manganese complex (**C1**) bearing a tetradentate nitrogen ligand containing chiral bipyrrolidine and benzimidazole moieties was prepared. The structure of **C1** was confirmed by ESI-MS and crystallography. This manganese complex is an active catalyst for the asymmetric epoxidation of various olefins with excellent conversion (up to 99 %) and high enantiomeric excess (up to 96 % *ee*) with hydrogen peroxide as the oxidant in the presence of 2-ethylhexanoic acid or acetic acid. Compared with previous structurally similar manganese complexes with different diamine backbones (**C2**, cyclohexanediamine; **C3**, diamine from L-proline), **C1** showed improved asymmetric induction, especially for simple olefins such as styrene derivatives and substituted chromene. The possible reasons for the improvement of the *ee* values are discussed in the text on the basis of the crystal structures of the manganese complexes.

Introduction

The catalytic asymmetric epoxidation of olefins is one of the most important chemical transformations, because the resulting epoxides are highly useful structural motifs or versatile intermediates for organic synthesis.[1] The seminal studies of enantioselective epoxidation were started in the late 1970s, and one of the major breakthroughs came in the early 1980s with the discovery and development of the Sharpless titanium-catalyzed asymmetric epoxidation of allylic alcohols.[2] Afterwards, substantial progress was made in the development of catalysts for the asymmetric epoxidation of a broad range of unfunctionalized olefins. Among these methods, the Mn–salen-catalyzed asymmetric epoxidation reaction, which was developed independently by Jacobsen[3] and Katsuki,[1a,4] in particular, has drawn more attention. In consideration of these pioneering achievements, growing interests and efforts were dedicated to manganese-catalyzed epoxidation, owing to the low toxicity, commercial availability, and biological role of manganese in enzyme-catalyzed redox processes.[5] Thus, numerous manganese complexes coordinated with well-designed polydentate nitrogen-donating ligands, mainly based on enantiopure polyamine backbones such as chiral triazacyclononane,[6] cyclohexanediamine,[7] amino-acid-derived amines,[8] and bipyrrolidine,[9] were synthesized, characterized, and intensively studied.

Within these versatile bioinspired manganese complexes, the rational modification to the ligands, including the manipulation of the steric and electronic properties of the N donors, led to dramatic changes of the efficiency and enantioselectivity of the catalyst. An early example was the improvement made by Costas and co-workers, who achieved better-defined chiral pockets[7f] by appending pinene to the 4- and 5-positions of the two pyridine rings of the ligand *N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyridylmethyl)cyclohexane-*trans*-1,2-diamine (MCP; Figure 1, **1** and **3**);[7a] further, they demonstrated that electron-rich groups such as dimethylamine at the 4-position of the pyridine ring could improve the *ee* values and reduce the amount of carboxylic acid required to a substoichiometric level (Figure 1, **7**).[9d] Very recently, Bryliakov et al. also undertook a systematic investigation of the steric and electronic impacts of the functional groups on the pyridine rings of (*S*,*S*)-bipyrrolidine-derived manganese catalysts in the epoxidation of electron-deficient alkenes (Figure 1, **8**).[9e] In addition, Pfaltz et al.[10] creatively prepared a series of manganese complexes of N,N,N,N ligands containing chiral oxazoline rings rather than pyridine rings (Figure 1, **2**). As steric constraints are generated by the substituents at the oxazoline rings, different coordination modes existed in these metal complexes, but the enantioselectivities were relatively low (21 %*ee* for *trans*-β-methylstyrene). Similarly, Gao et al.[11] developed a highly efficient asymmetric epoxidation with

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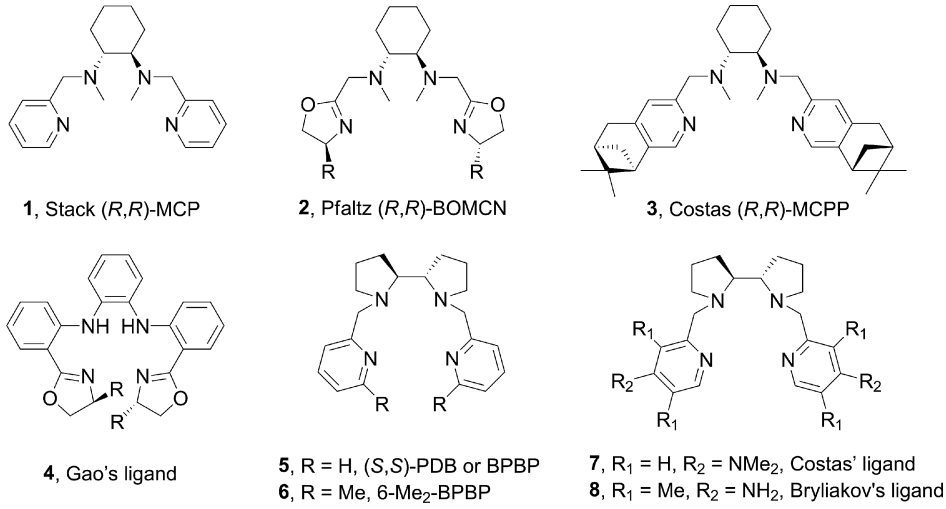


Figure 1. Structures of previously synthesized tetradentate nitrogen ligands.

manganese catalysts generated in situ from a porphyrin-inspired ligand, which consisted of chiral oxazoline rings and an achiral *o*-phenylenediamine moiety (Figure 1, **4**).

On the other hand, Shul'pin et al.[12] reported that the carboxylic acid cocatalysts had an indispensable influence on the initial reaction rate and the final selectivity of the Mn-catalyzed alkene epoxidation through kinetic studies. Recently, Bryliakov et al. and Costas et al. found that the employment of a bulkier acid such as 2-ethylhexanoic acid (EHA) could successfully lead to a dramatic increase of enantioselectivity relative to that with acetic acid (AA) for asymmetric epoxidation.[9a,9c–9e]

In 2009, our group devised and synthesized a family of MCP-related manganese complexes with bulky aromatic rings at the two 2-pyridylmethyl positions;[7c] these complexes effectively increased the *ee* values for the epoxidation of various α,β-enones under mild conditions. From another aspect, we made one more modification by replacing the chiral cyclohexanediamine moiety of MCP with an L-proline-derived diamine, and the newly-prepared C_1-symmetric manganese complex presented higher asymmetric induction for chalcones.[8a] On this basis, we further modified this C_1-symmetric complex by switching the pyridine rings to benzimidazole moieties (homolog of **L3**, Figure 2), and great improvements to both the efficiency [turnover frequency (TOF) = 59000 h^{-1}] and the enantiomeric excesses (up to 95% *ee*)[8b] were achieved for the asymmetric epoxidation compared with those for the two examples mentioned above. In addition, the use of a C_2-symmetric manganese catalyst bearing a cyclohexanediamine–benzimidazole ligand (**L2**, Figure 2) also afforded high enantioselectivities for chalcones.[7g]

The chiral bipyrrolidine framework was first used in asymmetric catalysis by Hirama for the osmylation of alkenes.[13] White and Chen reported that the iron(II) complex [Fe(*S*,*S*-PDB)$(MeCN)_2$][SbF_6]$_2$ based on a bipyrrolidine moiety could efficiently catalyze aliphatic C–H or methylene oxidation (Figure 1, **5**).[14] Que et al. also demonstrated

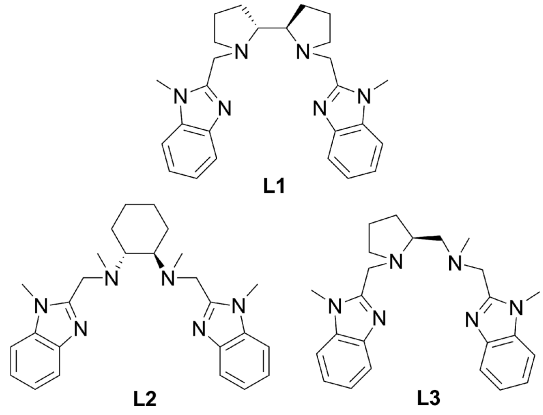


Figure 2. Ligands studied in this work.

that a 6-Me_2-BPBP iron complex could promote the asymmetric *cis*-dihydroxylation of alkenes with up to 97%*ee* (Figure 1, **6**).[15] Subsequently, several manganese catalysts containing tetradentate aminopyridine ligands derived from bipyrrolidine showed improved asymmetric inductions in the epoxidation compared with the manganese catalysts bearing chiral cyclohexanediamines.[9] As mentioned above, the N,N,N,N ligands with a bipyrrolidine backbone had enjoyed increasing use in target-oriented synthesis. To develop even more efficient bioinspired catalysts, the N,N,N,N ligand-merging bipyrrolidine and benzimidazole moieties is considered to be an ideal choice for the Mn-catalyzed asymmetric epoxidation of olefins. Herein, we present the synthesis of such a ligand, **L1**, containing bipyrrolidine and benzimidazole moieties, its manganese complex, and investigations of the performance for the epoxidation of olefins. Furthermore, we make comparisons of the asymmetric epoxidation abilities of the three manganese complexes containing bipyrrolidine, cyclohexanediamine,[7g] and the diamine from L-proline.[16]

Results and Discussion

The ligand **L1** could be readily prepared in good yield through the direct alkylation of (*R*,*R*)-bipyrrolidine with 2-chloromethyl-1-methylbenzimidazole according to a conventional method.[7g,8b] The corresponding manganese complex **C1** was synthesized by reacting equimolar amounts of ligand **L1** and $Mn(OTf)_2$ (OTf = trifluoromethanesulfonate), and the single-crystal X-ray structure of the acetonitrile solvate of Mn(**L1**)$(OTf)_2$ was determined (Figure 3, **C1**).

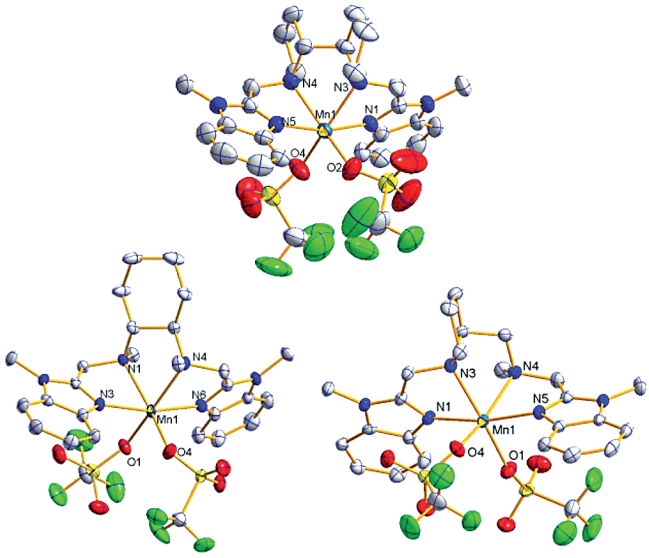
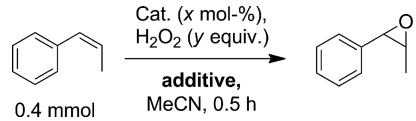


Figure 3. Molecular structures of the Mn^{II} complexes **C1** (top), **C2** (left), and **C3** (right) with key atoms labeled. The hydrogen atoms have been omitted for clarity.

The structure reveals that the ligand **L1** adopts a *cis*-α conformation around the distorted octahedral manganese center, in which the nitrogen atoms of the two benzimidazole donors are *trans* to each other.[17] The same patterns are also found in the structures of the related complexes **C2**[7g] and **C3**[16] with different diamine backbones. In **C1**, the Mn–N (benzimidazole donors) bonds tilt into the vacant space between Mn1–N4 and Mn1–O4. The N1–Mn1–N5 angle is significantly distorted [166.73(12)°] from the 180° associated with an ideal octahedral coordination. The distortion of **C1** is larger than those of **C2** [168.46(10)°] and **C3** [168.44(10)°] as a result of the more-rigid bipyrrolidine framework.[7g,16] It is worth mentioning here that the geometrical distortion manifested in the N1–Mn1–N5 angle (benzimidazole donors) is also larger than that of aminopyridine manganese complex featuring a bipyrrolidine moiety [N4–Mn1–N1, 171.94(9)°].[9a] As shown in Table S1, the Mn–N bond lengths of **C1** are apparently close to those found in **C2** and **C3**, except that the Mn–N5 bond length in **C3** is slightly shorter (by ca. 0.02–0.03 Å) owing to its C_1-symmetric nature. For **C1**, the Mn–N bond lengths of the bipyrrolidine nitrogen atoms [Mn–N(3) = 2.304(3) and Mn–N(4) = 2.325(3) Å] are clearly longer than those of the benzimidazole nitrogen atoms N(1) and N(2) [both are 2.215(3) Å], consistent with those of the analogs **C2** and **C3**.[7g,16]

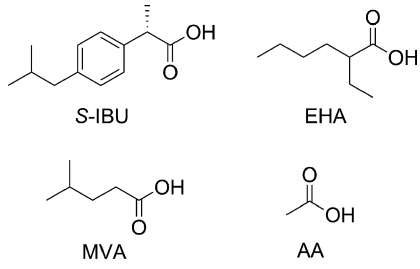
On the basis of the discoveries of Bryliakov et al.[9c] and Costas et al.,[9d] we first explored the new catalyst **C1** in the asymmetric epoxidation of *cis*-β-methylstyrene with EHA as the additive and hydrogen peroxide as the oxidant. Gratifyingly, full conversion and a high *ee* (73%) were achieved with 1.0 mol-% of catalyst and 3.0 equiv. of EHA in half an hour at –20 °C (Table 1, Entry 2). The same results could also be obtained with a 0.3 mol-% catalyst loading (Table 1, Entries 3 and 4). In addition, several carboxylic acids such as AA, (*S*)-ibuprofen [(*S*)-IBU], and 4-methylvaleric acid (MVA) were also evaluated, but EHA was the most efficient for conversion and enantioselectivity (Table 1, Entries 5–8). The optimal conditions were then established, and the highest *ee* (81%) was accomplished with 2.0 equiv. of EHA and 1.2 equiv. of H_2O_2 at –30 °C (Table 1, Entries 9–11). However, under the optimized conditions, the analogous manganese complexes **C2** and **C3** with different diamines presented poorer activities both in conversion and in asymmet-

Table 1. Screening the reaction conditions with *cis*-β-methylstyrene.[a]



0.4 mmol

Entry	Catalyst [*x*]	H_2O_2 [*y*]	Additive [equiv.]	*T* [°C]	Conv./GC yield [%]	*ee* [%]
1	**C1** (1.0)	1.6	–	–20	trace	–
2	**C1** (1.0)	1.6	EHA (3.0)	–20	99/89	73
3	**C1** (0.3)	1.6	EHA (3.0)	–20	99/88	73
4	**C1** (0.2)	1.6	EHA (3.0)	–20	55/50	73
5	**C1** (0.3)	1.6	EHA (3.0)	–30	97/87	81
6	**C1** (0.3)	1.6	(*S*)-IBU (3.0)	–30	80/68	45
7	**C1** (0.3)	1.6	AA (3.0)	–30	69/52	60
8	**C1** (0.3)	1.6	MVA (3.0)	–30	99/83	65
9	**C1** (0.3)	1.6	EHA (1.5)	–30	78/66	81
10	**C1** (0.3)	1.6	EHA (2.0)	–30	99/89	81
11	**C1** (0.3)	1.2	EHA (2.0)	–30	99/89	81
12	**C2** (0.3)	1.2	EHA (2.0)	–30	70/40	75
13	**C3** (0.3)	1.2	EHA (2.0)	–30	25/15	74
14	**C2** (0.3)	1.6	EHA (2.0)	–30	85/54	75
15	**C3** (0.3)	1.6	EHA (2.0)	–30	52/41	74
16	**C3** (1.0)	1.6	EHA (3.0)	–20	99/90	69



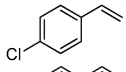
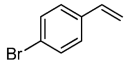
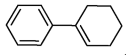
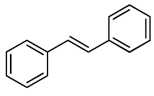
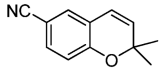
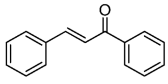
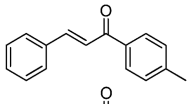
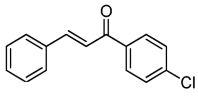
[a] Reaction conditions: hydrogen peroxide (50% aqueous solution) diluted with MeCN (0.5 mL) was delivered through a syringe pump over 0.5 h to a stirred solution of catalyst (0.2–1.0 mol-%), carboxylic acid (1.5–3.0 equiv.), internal standard (decane), and substrate (0.4 mmol) in MeCN (1.0 mL) in the air.

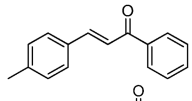
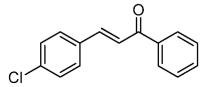
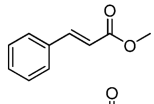
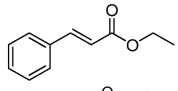
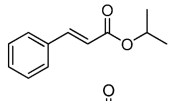
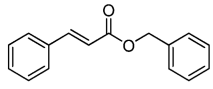
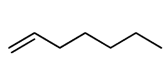
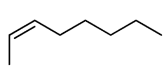
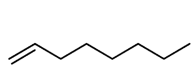
ric induction (Table 1, Entries 12 and 13). The substrate could be fully epoxidized only when larger amounts of the catalysts, oxidants, and additives were employed (Table 1, Entries 14–16).

To test the applicability of this manganese catalyst, a broad range of olefins, including aromatic alkenes, unfunctionalized aliphatic alkenes, and electron-deficient α,β-unsaturated ketones and esters, were studied under the optimal conditions. In most cases, the asymmetric epoxidation proceeded rapidly with good-to-excellent conversion, selectivity, and enantioselectivity in the presence of small amounts of carboxylic acid (<5 equiv.). For example, styrene was epoxidized with high conversions and a good *ee* of 56% (Table 2, Entries 2 and 3), which was even a little higher than the value we reported previously.[7c,7g] However, for the reaction of 4-Cl- and 4-Br-substituted styrenes, more catalyst was needed, but moderate *ee* values were achieved because of the electronegative halogen groups (Table 2, Entries 4 and 5). For other styrene derivatives such as cyclic 1-phenyl-1-cyclohexene, very low *ee* values (12%) were detected even though excellent conversion and selectivity were achieved (Table 2, Entry 6); *trans*-stilbene was transformed into the epoxide with 50% yield and 36%*ee* (Table 2, Entry 7) in the presence of 5.0 equiv. of AA (almost no reaction with EHA). On the contrary, for the asymmetric epoxidation of 2,2-dimethyl-2*H*-chromene-6-carbonitrile, 75%*ee* was obtained with AA, which was nearly consistent with the results with **C2** and **C3** under the same conditions. However, high yields (90%) and excellent *ee* values (93%) were obtained with the bulkier EHA (Table 2, Entries 8 and 9), which was the carboxylic acid chosen by Costas et al.[9d] and Bryliakov et al.[9e]

For α,β-unsaturated ketones, similarly, a slightly higher *ee* was gained for chalcone with EHA than with AA, but a

Table 2. Asymmetric epoxidation of olefins with H_2O_2 and catalyst **C1**.[a]

Entry	Substrate	Conv./Select. [%]	Isolated yield [%]	*ee* [%]
1		99/93	–	81
2		85/93	–	56
3[b]		99/93	–	56
4[c]		99/94	–	39
5[c]		–	75	36
6		99/92	–	12
7[d]		–	50	36
8[e]		–	49	75
9		–	90	93
10[f]			49	82
11[g]			23	81
12[c]		–	72	96
13[d]		–	92	90
14[d]		–	88	88
15[d]		–	53	84

Entry	Substrate	Conv./Select. [%]	Isolated yield [%]	*ee* [%]
16[d]		–	81	91
17[d]		–	51	91
18[d]		–	94	45
19[d]		–	92	57
20[d]		–	93	67
21[d]		–	85	63
22[h]		99/99	–	20
23[i]		99/99	–	25
24		99/99	–	5
25[e]		99/99	–	2
26[h]		99/99	–	5
27[i]		99/99	–	8
28[h]		99/99	–	4
29[i]		99/99	–	5
30[h]		99/99	–	5
31[i]		99/99	–	6

[a] Unless stated, the reaction conditions are: cat. (**C1**, 0.3 mol-%), EHA (2 equiv.), and H_2O_2 (1.2 equiv.) in MeCN at –30 °C for 0.5 h. [b] EHA (3 equiv.), 1 h. [c] Cat. (**C1**, 0.6 mol-%), EHA (3 equiv.), H_2O_2 (1.6 equiv.), 1 h. [d] HOAc (5 equiv.), H_2O_2 (2 equiv.), 1 h. [e] HOAc (2 equiv.). [f] Cat. (**C2**, 0.3 mol-%). [g] Cat. (**C3**, 0.3 mol-%). [h] Cat. (**C1**, 1.5 mol-%), EHA (3 equiv.), H_2O_2 (2 equiv.). [i] Cat. (**C1**, 0.3 mol-%), HOAc (3 equiv.), H_2O_2 (1.6 equiv.).

larger catalyst loading was required (Table 2, Entries 12 and 13). Substrates bearing electron-donating groups such as *para*-Me on the phenyl rings on the olefin or carbonyl side, both presented high α,β-epoxy ketone yields and *ee* values (up to 96%). Meanwhile, electron-withdrawing groups such as *para*-Cl had an undesirable impact on the yields; however, the stereocontrol was not bad (Table 2, Entries 14–17). Furthermore, trace amounts of product were formed in the epoxidation of methyl cinnamate even with 5 equiv. of EHA. Thus, AA was employed, and good yields (close to 90%) were obtained, and the *ee* values increased slightly in the order *i*Pr > Bn > Et > Me (Table 2, Entries 18–21).

Fortunately, this manganese complex was also an active catalyst for aliphatic olefins with full conversions and epoxide selectivities (Table 2, Entries 22–31). Surprisingly, relatively large amounts of catalyst (1.5 mol-%) were required with EHA as the additive, probably because of the steric effect of this bulkier acid. In contrast, the epoxidation proceeded smoothly in the presence of 3.0 equiv. of AA with only 0.3 mol-% of catalyst loading. However, the fairly low enantioselectivities are a tough problem that remains to be resolved.

In addition, with respect to the role of the additive in manganese-catalyzed asymmetric epoxidation systems, Talsi et al. concluded by the EPR analysis that the acid might act as an auxiliary ligand in the possible intermediate [(**5**)Mn^{V}=O] in the enantioselectivity-determining step.[9c] Compared with those for manganese catalyst systems, the accounts of the effect of the acid in iron-catalyzed oxidations seem to be relatively extensive,[18] and an acid-assisted mechanism[19] has already been proposed. Very recently, Que et al.[20] synthesized and fully characterized a low-spin acylperoxoiron(III) intermediate, of which the degradation product was assigned to be an oxoiron(V) species and the true powerful oxidant. Their findings were suggested to apply to other non-heme iron models[9b,21] and will perhaps be quite helpful in further understanding the synergistic cooperation of carboxylic acids with non-heme manganese catalysts.

Conclusions

A new chiral manganese complex of a N,N,N,N ligand with a bipyrrolidine and benzimidazole framework has been synthesized and characterized. This manganese complex exhibits good control of asymmetric induction (up to 96% *ee*) in the asymmetric epoxidation of various olefins, including α,β-unsaturated olefins and aromatic olefins, with 2.0–5.0 equiv. of EHA or AA as the additive and 1.2–2.0 equiv. of H_2O_2 as the oxidant. Nevertheless, the enantioselectivities for simple aliphatic alkenes are very low, although the conversions and selectivities for epoxidation are excellent. Further studies on the reaction mechanism as well as the development of even more efficient non-heme systems for oxidations are underway in our laboratory.

Experimental Section

General: All chemicals were purchased from commercial sources and used as received, unless noted otherwise. Anhydrous solvents were purified by standard methods.[22] The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance III 400 MHz spectrometer. The ^{1}H and ^{13}C NMR spectroscopic chemical shifts (δ) are given in ppm relative to tetramethylsilane as an internal standard or to the solvent signal (for ^{1}H: $CDCl_3$, δ = 7.26 ppm). The ESI-MS spectra were collected with a Bruker Daltonics micrOTOF-Q^{II} mass spectrometer. Optical rotations were recorded with a Perkin–Elmer 341 polarimeter (sodium lamp, 1 dm cuvette, *c* in g/100 mL, 20 °C). GC analysis for *ee* values and yields were performed with an Agilent 6820GC instrument with a Beta dex™ 120 column or a 7890 GC instrument with a CP-Chirasil-Dex CB column. HPLC analysis for *ee* values was performed with a Waters-Breeze system (2487 Dual λ Absorbance Detector and 1525 Binary HPLC Pump). Chiralpak OD, OB, OJ, AS, and IC columns were purchased from Daicel Chemical Industries, Ltd. The X-ray crystallographic data were collected with a Bruker SMART CCD1000 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 296(2) K.

Synthesis of the Ligand L1 and Complexes C1-C3: The ligand **L1** and the corresponding Mn^{II} complex **C1** were synthesized from (*R*,*R*)-bipyrrolidine by the same procedures as we reported previously.[8b] Complexes **C2**[7g] and **C3**[16] were prepared according to our previous methods.

Ligand L1: Yield 0.9 g, 70%. $[\alpha]_D^{20}$ = –23 (*c* = 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (dd, *J* = 6.3, 1.9 Hz, 2 H), 7.33–7.20 (m, 6 H), 4.24 (d, *J* = 13.3 Hz, 2 H), 3.79 (s, 6 H), 3.65 (d, *J* = 11.6 Hz, 2 H), 2.86 (s, 2 H), 2.74 (s, 2 H), 2.34 (d, *J* = 3.4 Hz, 2 H), 1.90–1.55 (m, 8 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.4, 142.2, 136.2, 122.4, 121.9, 119.6, 109.0, 65.3, 55.5, 52.5, 29.9, 26.3, 24.0 ppm. HRMS (ESI): calcd. for $C_{26}H_{33}N_6$ $[M + H]^+$ 429.2767; found 429.2793.

Complex C1: HRMS (ESI-MS): calcd. for $C_{27}H_{32}F_3MnN_6O_3S$ $[M – OTf]^+$ 632.1589; found 632.1605. X-ray-quality crystals were grown from the layer interface between diethyl ether and MeCN. CCDC-979540 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for the Asymmetric Epoxidation of *cis*-β-Methylstyrene: A MeCN (1.0 mL) solution of the substrate (0.4 mmol), catalyst (0.3 mol-%), and carboxylic acid (1.5–3.0 equiv.) was prepared in a 10 mL flask at room temperature. Then, a H_2O_2 solution (1.2–1.6 equiv., diluted from a 50% aqueous solution in 0.5 mL of MeCN) was added with a syringe pump over 30 min with stirring at –20 or –30 °C. At this point, decane was added to the mixture as an internal standard. The reaction was quenched with a saturated $NaHCO_3$ aqueous solution and a saturated $Na_2S_2O_3$ aqueous solution and then extracted with diethyl ether; the yields and *ee* values were determined by GC analysis. The enantiomeric purity was determined with an Agilent 6820 GC instrument with a Beta dex™ 120 column (80 °C isothermal for 2 min, 3 °C/min, 170 °C for 5 min, t_r = 25.449 and 25.793 min).

General Procedure for the Asymmetric Epoxidation of 2,2-Dimethyl-2*H*-chromene-6-carbonitrile: A MeCN (1.0 mL) solution of the substrate (0.4 mmol), catalyst (0.3 mol-%), and carboxylic acid (2 equiv.) was prepared in a 10 mL flask at room temperature. Then, a H_2O_2 solution (1.2 equiv., diluted from a 50% aqueous solution in 0.5 mL of MeCN) was added with a syringe pump over

30 min with stirring at –30 °C. The reaction was quenched with a saturated $NaHCO_3$ aqueous solution and a saturated $Na_2S_2O_3$ aqueous solution and then extracted with diethyl ether. The solvent was evaporated, and the residue was purified by column chromatography (petroleum ether/ethyl acetate 30:1) to give the corresponding epoxide 2,2-dimethyl-2,7b-dihydro-1a*H*-oxireno[2,3-*c*]chromene-6-carbonitrile as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, J = 2.0 Hz, 1 H), 7.53 (dd, J = 8.5, 2.1 Hz, 1 H), 6.87 (d, J = 8.5 Hz, 1 H), 3.91 (d, J = 4.3 Hz, 1 H), 3.54 (d, J = 4.4 Hz, 1 H), 1.60 (s, 3 H), 1.30 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.5, 134.4, 133.8, 121.1, 119.0, 118.7, 104.3, 74.7, 62.3, 49.8, 25.5, 23.0 ppm. The enantiomeric purity was determined by HPLC (Chiralcel OD-H, 25 °C, hexane/2-propanol 90:10, flow rate: 1 mL/min, 254 nm, t_r = 10.72 and 12.92 min).

Supporting Information (see footnote on the first page of this article): Crystal analysis, characterization data, copies of HPLC, GC and NMR spectra.

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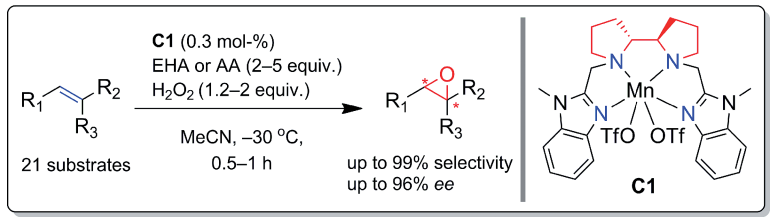

A chiral manganese complex bearing a tetradentate nitrogen ligand with chiral bipyrrolidine and benzimidazole moieties is an active catalyst for the asymmetric epoxidation of various olefins with excellent conversions (up to 99%) and up to 96% *ee* with hydrogen peroxide as the oxidant in the presence of 2-ethylhexanoic acid or acetic acid.

