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Mn^{II} complexes with tetradentate N_4 ligands: Highly efficient catalysts for the epoxidation of olefins with H_2O_2

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ABSTRACT

A series of Mn-complexes with tetradentate N_4 ligands, introducing aromatic groups into 2-pyridylmethyl positions of N,N′-dimethyl-N,N′-bis(2-pyridylmethyl)ethane-1,2-diamine (***mep***), N,N′-dimethyl-N,N′-bis(2-pyridylmethyl)cyclohexane-*trans*-diamine (***mcp***), have been synthesized and applied for epoxidation of olefins using H_2O_2 as the oxidant. The Mn-complexes still possessed an octahedral mononuclear structure in a *cis*-α topology. These complexes showed good regioselectivity, high yields and turnover frequency (even up to 228,000 h^{-1}) with low catalyst loading (0.1–0.01 mol%) for epoxidation of a family of olefins (including internal aromatic olefins, internal and terminal aliphatic olefins and diolefins).

1. Introduction

Olefin epoxidation constitutes a very important reaction in organic synthesis because epoxides are valuable building blocks for a number of subsequent transformations [1–4]. Many efforts have been dedicated to the development of metal-catalyzed epoxidation reaction effectively [5–8]. Notable in the non-heme iron area is the report of Fe^{II} with ***mep*** (N,N′-dimethyl-N,N′-bis(2-pyridylmethyl)ethane-1,2-diamine), that performs rapid, efficient epoxidations of terminal olefins using H_2O_2 as the oxidant in the presence of acetic acid [9]. On the other hand, manganese complexes have been also attracting significant attention [10], especially after the breakthroughs of asymmetric epoxidation of unfunctionalized olefins catalyzed by Mn(III)-salen complexes developed by Jacobsen and Katsuki groups [11–14]. In recent years, Stack and co-workers developed Mn^{II} complexes bearing tridentate and tetradentate nitrogen based ligands (***mcp***, N,N′-dimethyl-N,N′-bis(2-pyridylmethyl)cyclohexane-*trans*-diamine)in combination with peracetic acid as very fast and efficient epoxidation system [15,16]. Subsequently, Costas and co-workers exploited a series of $Mn^{II}(PyTACN)(CF_3SO_3)_2$ complexes which exhibited excellent activity and selectivity in epoxidation of olefins [17,18]. $[Mn_2(DMEGqu)_2(\mu\text{-}CF_3SO_3)_2(CF_3SO_3)_2(H_2O)_2]$ (DMEGqu = *N*-(1,3-dimethylimidazolidin-2-ylidene)quinolin-8-amine) also showed moderate catalytic activity in the epoxidation of the terminal alkene, such as 1-octene [19]. Recently, our group has successfully developed a series of Mn^{II} complexes of chiral tetradentate nitrogen ligands derived from ***mcp*** that could efficiently epoxidize electron-deficient olefins with nearly full conversion and up to 89% ee using hydrogen peroxide as the oxidant in the presence of AcOH [20]. Later, Bryliakov et al. prepared a series of Mn-complexes based on ***mcp*** template and investigated their performance in the epoxidation of olefins with various oxidants (peroxycarboxylic acids, alkyl hydroperoxides, iodosylarenes, etc.) [21,22]. Base on above mentioned, Mn-complexes based on tetradentate nitrogen ligands have exhibited good performance in the epoxidation. Taking into account the selectivity and efficiency of the catalysts, however, the development of highly efficient catalysts is still in high demand.

As a part of our ongoing interest in the developing novel catalysts for oxidation reaction [20,23–26], herein we reported the synthesis of tetradentate N_4 ligands and their corresponding Mn-complexes by introducing aromatic groups into 2-pyridylmethyl positions derived from various diamine backbones (Scheme 1) and investigated their performance in the epoxidation. To our delighted, the simply prepared manganese complexes **C1** and **C3** derived from ***mep*** and ***mcp*** could efficiently epoxidize a family of

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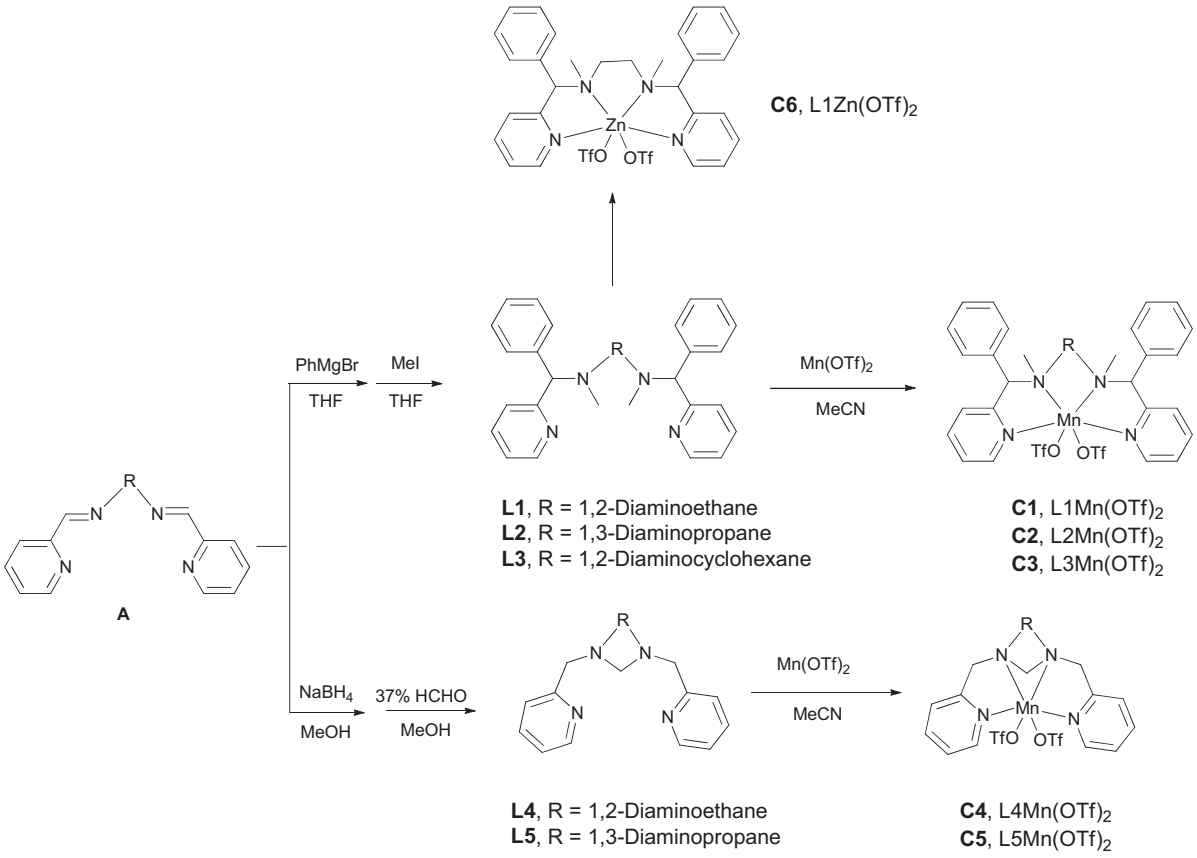


Scheme 1. Synthesis of ligands **L1**–**L5** and complexes **C1**–**C6**.

olefins (including internal aromatic olefins, internal and terminal aliphatic olefins and diolefins) with 0.1–0.01 mol% catalyst loading within 5 min using hydrogen peroxide as the terminal oxidant. The turnover frequency (TOF) can be reached up to 228,000 h^{-1}.

2. Experimental

2.1. General

The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. HRMS were obtained on a Bruker Daltonics micrOTOF-Q^{II} mass spectrometer. X-ray crystallographic data were collected on a Bruker SMART CCD1000 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 298(2) K. GC analysis was performed on Agilent 6820 or 7890A equipment. Column chromatography was generally performed on silica gel (200–300 mesh) and TLC inspections were on silica gel GF254 plates.

All reactions were carried out under argon in dried glassware. All chemicals and solvents were used as received unless otherwise stated. Tetrahydrofuran, ethyl ether (Na, benzophenone), acetonitrile (CaH_2) were distilled under argon prior to use.

2.2. Synthetic procedure and characterization of *L1*–*L5* and *C1*–*C6*

A solution of ligand **A** (0.48 g, 2 mmol) in THF was added dropwise to a vigorously stirred Grignard reagent (10 mmol) in THF (20 mL) at room temperature and then the reaction mixture was stirred at same temperature for 12 h. Saturated NH_4Cl was added to quench the reaction. After that, the mixture was extracted with CH_2Cl_2 and organic phase was dried over anhydrous Na_2SO_4 and concentrated in vacuo to yield the product as a brown solid. To a solution of the brown solid in THF (15 mL) was added NaH (ca. 60% in oil, 0.32 g, 8 mmol) at 0 °C. After stirring for 1 h, MeI (3.0 mmol) was added to the mixture and stirred for 12 h. The reaction mixture was quenched by saturated NH_4Cl and extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4. The crude product was purified by chromatography on silica gel to afford yellow solids in 70% isolated yields **L1** [20,27]. And the synthetic procedure of **L2** or **L3** was the same as the procedure for **L1**, both are yellow solid in 65% yield, 85% yield respectively.

For the synthesis of ***L4***: $NaBH_4$ (2.48 g, 10 mmol) was added into the compound **A** (5 mmol) dissolved in MeOH (50 mL), and the mixture was stirred for 30 min at room temperature. Aqueous HCl (3 M, 15 mL) was added slowly with stirring, and then the MeOH was removed in vacuo. Aqueous NaOH (20%) was added until the solution reached pH > 10. After that, the product was extracted with CH_2Cl_2, washed with H_2O and brine (50 mL), and then dried over Na_2SO_4. Following filtration and concentration, the diamine was obtained as yellow oil. Then, the oil was dissolved in absolute methanol (10 mL). 37% aqueous formaldehyde solution diluted with methanol (2 mL) was added, and the mixture was stirred for 6 h at 45 °C. Finally, the product was concentrated in vacuo and purified by chromatography on silica gel to give yellow oil **L4** in 90% yield. And the synthetic procedure of **L5** was the same with **L4**, **L5** was obtained as yellow oil in 87% yield.

Complex **1** (**C1**): Under argon atmosphere, $Mn(OTf)_2$ (0.1 mmol) was added into a stirred solution of ligand **1** (0.1 mmol) in acetonitrile (2.0 mL). The mixture was stirred for 12 h and then was concentrated in vacuo to yield the product as a brown powder. The powder was washed with cold Et_2O and dried in vacuo. Crystals of **C1** suitable for X-ray diffraction was obtained by slow diffusion of

Et_2O into its concentrated MeCN solution. And the synthetic procedures of **C2–C6** were the same with procedure for **C1**. CCDC 754024, 808616 and 808615 contain the supplementary crystallographic data of **C1**, **C5** and **C6** for this paper respectively. Crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

L1 ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.48 (d, J = 4.8 Hz, 2H, ArH), 7.60–7.52 (m, 4H, ArH), 7.44 (d, J = 7.6 Hz, 4H, ArH), 7.28–7.24 (m, 4H, ArH), 7.19 (t, J = 7.6 Hz, 2H, ArH), 7.09–7.06 (m, 2H, ArH), 4.52 (s, 2H, CH), 2.63–2.52 (m, 4H, CH_2), 2.06 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.8, 149.0, 141.8, 136.5, 128.4, 128.2, 127.1, 122.1, 121.8, 77.8, 53.1, 41.1.

L2 ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.48 (dd, J_1 = 0.8 Hz, J_2 = 4.8 Hz, 2H, ArH), 7.59–7.54 (m, 2H, ArH), 7.42 (q, J = 8.0 Hz, 6H, ArH), 7.27–7.23 (m, 4H, ArH), 7.18 (t, J = 7.2 Hz, 2H, ArH), 7.08–7.05 (m, 2H, ArH), 4.48 (s, 2H, CH), 2.40–2.23 (m, 4H, CH_2), 2.13 (s, 6H, CH_3), 1.74 (t, J = 7.2 Hz, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.9, 148.9, 141.8, 136.5, 128.4, 128.3, 127.1, 122.1, 121.8, 77.7, 53.3, 40.2, 24.0.

L3 [20] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.48 (dd, J_1 = 0.8 Hz, J_2 = 4.8 Hz, 2H, ArH), 7.90 (d, J = 8.0 Hz, 2H, ArH), 7.76–7.72 (m, 2H, ArH), 7.49 (d, J = 7.2 Hz, 4H, ArH), 7.26 (t, J = 8.0 Hz, 4H, ArH), 7.21–7.17 (m, 2H, ArH), 7.14–7.11 (m, 2H, ArH), 5.02 (s, 2H, CH), 2.58 (dd, J_1 = 3.2 Hz, J_2 = 6.0 Hz, 2H, CH), 2.19 (s, 6H, CH_3), 1.78 (d, J = 12.8 Hz, 2H, CH_2), 1.51 (t, J = 3.6 Hz, 2H, CH_2), 1.09 (d, J = 8.8 Hz, 2H, CH_2), 0.78 (d, J = 9.6 Hz, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.3, 149.0, 141.4, 136.5, 129.0, 128.3, 127.1, 121.9, 121.7, 75.4, 59.9, 34.2, 25.4, 25.0.

L4 ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (d, J = 4.8 Hz, 2H, ArH), 7.65 (t, J = 7.6 Hz, 2H, ArH), 7.46 (d, J = 8.0 Hz, 2H, ArH), 7.17–7.14 (m, 2H, ArH), 3.91 (s, 4H, CH_2), 3.61 (s, 2H, CH_2), 2.95 (s, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1, 149.1, 136.6, 122.7, 122.0, 76.6, 61.1, 52.5.

L5 ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (dd, J_1 = 0.4 Hz, J_2 = 4.8 Hz, 2H, ArH), 7.61 (t, J = 7.6 Hz, 2H, ArH), 7.47 (d, J = 7.6 Hz, 2H, ArH), 7.14–7.11 (m, 2H, ArH), 3.75 (s, 4H, CH_2), 3.35 (s, 2H, CH_2), 2.66 (t, J = 5.2 Hz, 4H, CH_2), 1.76 (t, J = 4.8 Hz, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8, 148.9, 136.4, 123.0, 121.9, 75.4, 60.8, 52.3, 22.7.

C6 ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.19 (d, J = 4.8 Hz, 2H, ArH), 7.91 (t, J = 7.6 Hz, 2H, ArH), 7.66–7.57 (m, 4H, ArH), 7.56–7.48 (m, 4H, ArH), 7.43 (t, J = 7.6 Hz, 2H, ArH), 7.21 (d, J = 8.0 Hz, 2H, ArH), 7.10 (d, J = 7.6 Hz, 2H, ArH), 5.92 (s, 2H, CH), 2.85 (d, J = 10.4 Hz, 2H, CH_2), 2.40 (s, 6H, CH_3), 1.97 (d, J = 10.4 Hz, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.4, 148.9, 140.2, 134.8, 131.1, 129.8, 129.5, 128.8, 128.6, 125.7, 124.8, 71.2, 48.6, 40.1.

C1 HRMS: calcd. for $C_{29}H_{30}F_3MnN_4O_3S$ m/z 626.1371, found 626.1358. Anal. calcd. For $C_{30}H_{30}F_6MnN_4O_6S_2{\cdot}2H_2O$: C, 44.39; H, 4.22; N, 6.90. Found: C, 44.71; H, 3.89; N, 6.99.

C2 HRMS: calcd. for $C_{30}H_{32}F_3MnN_4O_3S$ m/z 640.1528, found 640.1523. Anal. calcd. For $C_{31}H_{32}F_6MnN_4O_6S_2{\cdot}1.5H_2O$: C, 45.59; H, 4.32; N, 6.86. Found: C, 45.74; H, 4.16; N, 6.74.

C3 HRMS: calcd. for $C_{33}H_{36}F_3MnN_4O_3S$ m/z 680.1841, found 680.1847. Anal. calcd. For $C_{34}H_{36}F_6MnN_4O_6S_2{\cdot}0.9H_2O$: C, 48.27; H, 4.50; N, 6.62. Found: C, 48.60; H, 4.48; N, 6.74.

C4 HRMS: calcd. for $C_{16}H_{18}F_3MnN_4O_3S$ m/z 458.0432, found 458.0419. Anal. calcd. For $C_{17}H_{18}F_6MnN_4O_6S_2{\cdot}2H_2O$: C, 31.73; H, 3.45; N, 8.71. Found: C, 31.38; H, 3.20; N, 8.36.

C5 HRMS: calcd. for $C_{17}H_{20}F_3MnN_4O_3S$ m/z 472.0589, found 472.0576. Anal. calcd. For $C_{18}H_{20}F_6MnN_4O_6S_2{\cdot}2H_2O$: C, 32.88; H, 3.68; N, 8.52. Found: C, 32.98; H, 3.35; N, 8.42.

2.3. General procedure for epoxidation reactions with H_2O_2 as oxidant

To a mixture of the substrate (2.0 mmol), nitrobenzene (0.20 mmol), catalyst 0.1 mol%, and acetic acid (20 mmol, 10.0 equiv) in 1.5 mL CH_3CN under Ar atmosphere was added dropwise 1.3 equiv of 30% H_2O_2 dissolved in CH_3CN 1:1 (V:V) over a period of 30 min. And 5 extra minutes of stirring was allowed at 0 °C. Then the reaction mixture was quenched by saturated Na_2CO_3 and extracted with Et_2O. The corresponding epoxides and the side-products were determined by GC–MS. Yields were further determined by GC using nitrobenzene as internal standard.

2.4. General procedure for epoxidation reactions with AcOOH as oxidant

To a mixture of the substrate (1.0 mmol), nitrobenzene (0.20 mmol), and catalyst 0.25 mol% in 1.5 mL CH_3CN under Ar atmosphere was rapidly added 1.2 equiv of 8% AcOOH. And 5 extra min of stirring was allowed at room temperature. Then the reaction mixture was quenched by saturated Na_2CO_3 and extracted with Et_2O. The corresponding epoxides and the side-products were determined by GC–MS. Yields were further determined by GC using nitrobenzene as internal standard.

3. Results and discussion

According to our previous reported methods [20], the ligands **L1**–**L3** can be prepared in good yields through Grignard reaction and subsequent methylation with MeI from compound **A**. And the ligands L**4** and **L5** were synthesized with about 90% yields as shown in Scheme 1 from compound **A** through reduction with NaBH4 and cyclization with 37% aqueous formaldehyde solution [28]. Additionally, the corresponding Mn- or Zn-complexes **1**–**6** (**C1**–**C6**) were prepared by reactions of $Mn(OTf)_2$ or $Zn(OTf)_2$ with equivalent of ligands in acetonitrile and then treated with diethyl ether. All the complexes were obtained in nearly quantitive yields.

It has been known that linear tetradentate N_2Py_2 ligands can coordinate to an octahedral Mn^{II} center in three possible topologies (*cis*-α, *cis*-β, and *trans*) depending on the way they wrap around the metal center [29,30]. The solid state structures of metal-complexes could be established by X-ray analysis. For the present complexes, crystals of **C1**, **C5** and **C6** for suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into their MeCN solution. Then the data were collected using a Bruker APEX-II CCD and the structures were solved by the direct method using the SHELX-97 program. The crystallographic data for **C1**, **C5** and **C6** were listed in Table 1 and the crystal structures of the three metal-complexes were shown in Fig. 1.

The result revealed that **C1** possessed a distorted octahedral mononuclear structure with the ligands adopting a *cis*-α topology. The two pyridine rings as nitrogen donors to the metal center are disposed in *trans* position. The Zn-complex **C6** also adopted a *cis*-α topology. Interestingly, **C5** formed a seven-coordinate structure in topology containing an acetonitrile molecule because of a loose spatial environment correspondingly. Importantly, the bond lengths of Mn—N reflect the different electronic effect of coordination atoms and also influence the catalytic activity of the metal complexes. And the results in Table 2 showed that the bond lengths of Mn1 to the pyridyl nitrogens for **C1**, **C3** [20] and **C5** are noticeably shorter than to the aliphatic amine nitrogens. The average bond length of pyridyl nitrogens and Mn atom for complex **C1** is 2.22 Å, similar with the previous reported complex **C3** [20]. For the seven-coordinate Mn-complex **C5**, all the lengths of Mn—N bond are longer than those of $[Mn^{II}(mcp)(CF_3SO_3)_2]$, **C1** and **C3**, due to the additional coordinated acetonitrile [15].

The NMR spectra of Zn^{II} complex can reveal considerable information about the structure of complex with N_4 ligand [31]. The Zn^{II} complex of **L1** (**C6**) was prepared in order to study the stability of complex in solution. X-ray structure of **C6** indicates that ligand also coordinates the zinc center in a *cis*-α topology (Fig. 1).

Table 1
Details of structure determination, refinement, and experimental parameters for **C1**, **C5** and **C6**.

	L1–Mn·0.5MeCN	L5–Mn	L1–Zn·0.5MeCN
Formula	$C_{31}H_{31.5}F_6MnN_{4.5}O_6S_2$	$C_{20}H_{23}F_6MnN_5O_6S_2$	$C_{31}H_{31.5}F_6ZnN_{4.5}O_6S_2$
Formula	796.17	662.49	806.60
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*P*21/*n*	*P*21/*c*	*P*21/*n*
Crystal size/mm	0.32 × 0.28 × 0.26	0.32 × 0.30 × 0.22	0.46 × 0.42 × 0.39
a/Å	9.0508(9)	19.473(17)	9.0415(4)
b/Å	25.808(2)	8.876(7)	25.6007(10)
c/Å	16.1004(18)	16.687(16)	16.0329(7)
α/°	90	90	90
β/°	105.693(11)	105.24(4)	105.841(2)
γ/°	90	90	90
V/Å^3	3629.0(6)	2783(4)	3570.2(3)
Z	4	4	4
Dc/mg m^{-3}	1.457	1.581	1.501
m/mm^{-1}	0.557	0.709	0.884
F(000)	1632	1348	1652
*θ*range/°	1.53–25.50	2.17–24.20	1.54–25.50
Reflns. collected	19,502	12,485	19,156
Reflns. unique	6725	4333	6638
Parameters	575	362	555
Goodness-of-fit on F^2	1.024	1.012	1.045
R1,wR2	0.0543, 0.1410	0.0909, 0.2192	0.0445, 0.1127
R1,wR2 [all data]	0.0804, 0.1620	0.1834, 0.2637	0.0635, 0.1239
Largest diff. peak and hole [e Å^{-3}]	0.542, −0.395	0.627, −0.708	0.410, −0.913

The ^{1}H NMR spectrum indicates that there is only one isomer in solution even at room temperature (5.92 ppm. S, 2H. Fig. 2, also see Figure S1 in the supplementary data for details). Taking into account the NMR spectra and X-ray structure, the Zn^{II} complex **C6** still retain its ligand topology in solution. The result also suggests that the corresponding Mn-complex seems to adopt a *cis*-α topology in solution.

Que et al. have determined that iron with N_4 ligands could catalyze in situ formation of AcOOH from H_2O_2 and AcOH [32]. Costas and our group also explored H_2O_2/AcOH system for the epoxidation of olefins [16,20]. And in preliminary studies we evaluated the catalytic property of **C1**–**C5** in the epoxidation of 1-octene with H_2O_2 as terminal oxidant (1.5 equiv) in the presence of acetic acid (10.0 equiv). Fortunately, **C1** and **C3** exhibited excellent catalytic activities affording the corresponding epoxides in 99% yields (Table 3, entries 1, 3). However, the catalytic activities of other complexes were very low (entries 2, 4, 5). Subsequently, reaction conditions were screened using **C1** as model catalyst and the results were summarized in Table 4. Obviously, acetic acid loading has significant influence on the catalytic activity. When acetic acid loading increased to 10.0 equiv, high yield was achieved with 0.1 mol% catalyst loading (Table 4, entry 5). According to the previous reports, acetic acid may enhance the electrophilicity of the peroxide moiety or assist heterolytic O—O bond cleavage of the Mn peroxide intermediate [17,18]. And the optimal conditions are as follow: 0.1 mol% **C1**, 1.3 equiv of H_2O_2, 10.0 equiv of CH_3COOH, 0 °C for 5 min.

To demonstrate the versatility of the reaction system, **C1** and **C3** were applied to the epoxidation of a series of olefins substrates, such as internal aromatic olefins, internal and terminal aliphatic olefins and diolefins. The results were shown in Table 5. Fortunately, a broad of olefins were rapidly epoxidized in high conversions and yields. The activities of terminal aliphatic olefins were almost not influenced by the steric hindrance and chain length (Table 5, entries 1–9), especially using **C3** as the catalyst with TOF even up to 228,000 h^{-1} (entry 6). Additionally, steric hindrance and chain length also did not affect the activities of internal aliphatic olefins (entries 10–14). Besides, the epoxidation of aromatic olefins such as 1, 2-diphenylethene and methyl cinnamate was also accomplished with good yield and high selectivity employing **C3** as catalyst (entries 15, 16). However, slight low yields were obtained using **C1** as catalyst. The epoxidation of electron-deficient

Table 3
Reactivity of complexes in epoxidation of 1-octene.[a]

Entry	Complex	Yield[b]/%
1	**C1**	99
2	**C2**	<10
3	**C3**	99
4	**C4**	<10
5	**C5**	<10

[a] Reaction conditions: alkene (1.0 mmol), complex (0.5 mol%) and CH_3COOH (10.0 equiv) dissolved in 1.5 mL CH_3CN, and 30% H_2O_2 (1.5 equiv) dissolved in CH_3CN (V:V = 1:1) was added at 0 °C over a period of 30 min, and the mixture was stirred for additional 30 min.
[b] Determined by GC using nitrobenzene as internal standard.

Table 2
Selected bond lengths and angles for **C1**, **C3** and **C5**.

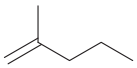
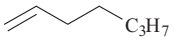
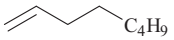
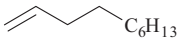
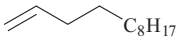
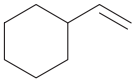
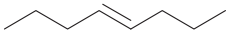
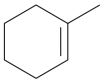
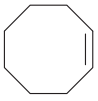
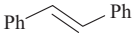
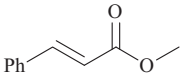
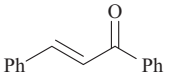
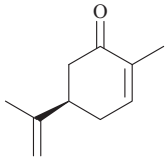
	C1	C3	C5
Mn1–N1/Å	2.225	2.241	2.343
Mn1–N2/Å	2.284	2.287	2.425
Mn1–N3/Å	2.311	2.287	2.408
Mn1–N4/Å	2.216	2.241	2.273
Mn1–O1/Å	2.13[a]	2.17	2.219
Mn1–O2/Å	2.20[b]	2.17	2.244
N1–Mn1–N4/°	171	165	89
N2–Mn1–N3/°	81	82	58
O–Mn1–O/°	90	92	86

Table 4
Screening of reaction conditions in the epoxidation of 1-octene.[a]

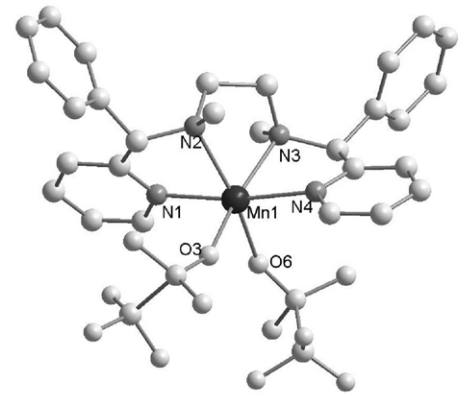
Entry	**C1**/mol%	H_2O_2/equiv	CH_3CO_2H/equiv	*T*/min	Yield[b]/%
1	0.25	1.5	1.0	30	2
2	0.25	1.5	5.0	30	78
3	0.25	1.5	10.0	30	99
4	0.25	1.3	10.0	30	96
5	0.1	1.3	10.0	30	92
6	0.1	1.3	10.0	5.0	90

[a] Reaction conditions: alkene (2.0 mmol), **C1** (0.1–0.25 mol%) and CH_3COOH (1.0–10.0 equiv) dissolved in 1.5 mL CH_3CN, 30% H_2O_2 (1.3–1.5 equiv) dissolved in CH_3CN (V:V = 1:1) was added at 0 °C over a period of 30 min.
[b] Determined by GC using nitrobenzene as internal standard.

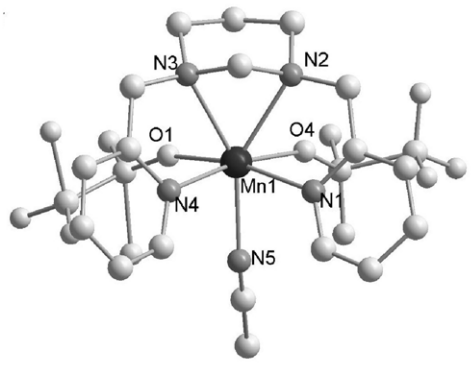
Table 5
Epoxidations of different substrates using **C1** and **C3**.[a]

Entry	Alkenes	Cat./mol%	H_2O_2/equiv	**C1** Conv./yield[b]/%	**C3** Conv./yield[b]/%
1		0.1	1.3	97/92	99/99
2		0.1	1.3	96/94	99/98
3		0.1	1.3	92/90	99/97
4		0.01	1.3	–[c]	56/54
5		0.01	1.3	–[c]	64/60[d]
6		0.01	1.3	–[c]	40/38[e]
7		0.1	1.3	94/91	99/97
8		0.1	1.3	89/87	99/95
9		0.1	1.3	89/89	99/99
10		0.1	1.3	96/94	97/88
11		0.1	1.3	100/95	100/92
12		0.1	1.3	100/75	100/80
13		0.1	1.3	97/96	97/96
14		0.1	1.3	100/97	100/95
15		0.1	1.3	57/55[f,g]	100/99/90[g,h]
16		0.1	1.3	74/70[h,i]	97/94/87[h]
17		0.1	1.3	90/88/85[h]	100/99/96[h]
18		0.1	1.3	90/88/88[h]	95/91/90[h]
19		0.1	3.0	94/92/90[h]	100/96/94[h]
20[j]		0.25	1.2	92/90/88[h]	97/92/89[h]
21[j]		0.25	3.0	96/90/88[h]	99/94/92[h]

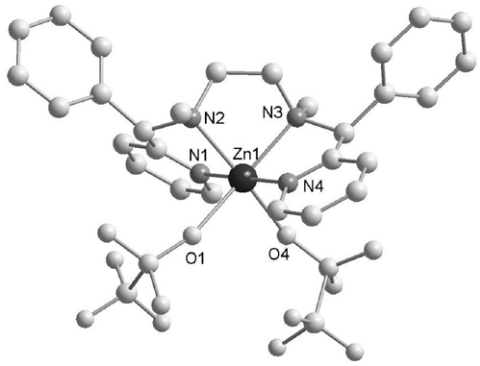
[a] Reaction conditions: alkene (2.0 mmol), complex (0.1 mol%) and CH_3COOH (10.0 equiv) dissolved in 1.5 mL CH_3CN, 30% H_2O_2 (1.3 equiv) dissolved in CH_3CN (V:V = 1:1) was added dropwise at 0 °C over a period of 30 min and 5 extra min of stirring were allowed.
[b] Yields determined by GC using nitrobenzene as internal standard.
[c] "–" means that the reaction was not carried out.
[d] H_2O_2 dissolved in CH_3CN (V:V = 1:1) was added dropwise at 0 °C in 60 min.
[e] H_2O_2 dissolved in CH_3CN (V:V = 1:1) is added dropwise at 0 °C rapidly and total reaction time is 1 min, and the corresponding TOF was up to 228,000 h^{-1}.
[f] **C1** 0.5 mol%.
[g] Dissolved in 15 mL CH_3CN.
[h] Isolated yields.
[i] **C1** 0.25 mol%.
[j] Reaction conditions: alkene (1.0 mmol) and complex (0.25 mol%) dissolved in 1.5 mL CH_3CN, 8% AcOOH (1.2–3.0 equiv) added at room temperature in one time and stirred for 5 min.



C1



C5



C6

Fig. 1. X-ray structures of **C1**, **C5** and **C6** (hydrogen atoms are omitted for clarity).

olefins such as chalcone also proceeded well with good yield and selectivity (entry 17).

Importantly, an excellent regioselectivity of **C1** or **C3** was also demonstrated by the monoepoxidations of the terminal olefin site of R(−)-carvone (entries 18–21). Different from the previous report [15], the same monoepoxide was attained when the amount of hydrogen peroxide (entries 18–19) or peracetic acid [33] (entries 20–21) was increased to 3.0 equiv of R(−)-carvone. Furthermore, a 1:1 mole mixture of cyclooctene and *trans*-4-octene was used in the present catalytic system to testify the regioselectivity (Table S1). Interestingly, excellent results were obtained using **C3** as the catalyst (yields of cyclooctene epoxide and *trans*-4-octene epoxide were 65% and 4.6% respectively). However,

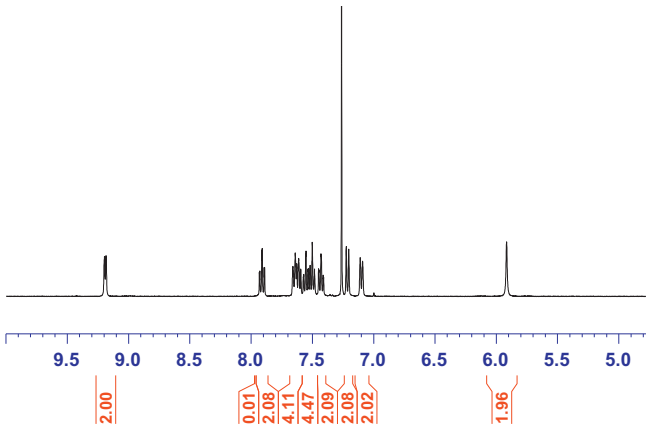


Fig. 2. ^{1}H NMR spectrum of $Zn^{II}L_1(CF_3SO_3)_2$ in $CDCl_3$ at ambient temperature.

the regioselectivity of **C1** or Mn complex with ***mep*** ligand was poorer than that of **C3**. We presumed that the phenyl group introduced into the 2-pyridylmethyl positions of ***mep*** and ***mcp*** changed the steric hindrance and electronic effect, which was beneficial for achieving perfectly selective monoepoxidation in the epoxidation of R(−)-carvone. Additionally, the addition time of hydrogen peroxide was examined and the yield just increased a little when the time was prolonged to 60 min (Table 5, entry 5). The efficiency of these Mn-complexes also was tested. The hydrogen peroxide was added one-offly with 0.01 mol% catalyst loading, the yield reached 38% within 1 min. And the TOF was 228,000 h^{-1} (Table 5, entry 6).

4. Conclusion

In summary, the present work describes an efficient approach for the synthesis of a family of N_4 tetradentate ligands and their corresponding Mn^{II} complexes which provided opportunities for the screening of a broad range of epoxidation catalysts. And the influence of the topologies of the ligands including the steric hindrance and the electronic effect on the catalytic activities was systematically examined, which provided important information for designing new efficient ligand. Fortunately, **C1** and **C3** exhibited excellent selectivity, high yields and TOF with low catalyst loading (0.1–0.01 mol%) for epoxidation of a family of olefins, including internal aromatic olefins, internal and terminal aliphatic olefins and diolefins. Notably, the TOF was even up to 228,000 h^{-1}. And diolefins R(−)-carvone could be epoxidized with excellent regioselectivity using H_2O_2 or AcOOH as the terminal oxidant. Further developing new synthetic strategy toward the nitrogen ligands and further mechanistic studying on these highly active systems are currently underway.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.11.024.

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