"Click" tetradentate ligands†

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A series of triazole-based N4 tetradenate ligands **1a–d** are efficiently synthesized using Cu^{I}-catalyzed azide-alkyne "click" strategy and are readily coordinated to many metal ions (*e.g.* Mn^{II}, Ni^{II}, Zn^{II} and Fe^{II}). The X-ray structures of the resultant metal-complexes (**4a–d**, **5a**, **6a** and **7a**) reveal an octahedral mononuclear structure with two co-ligands bonded in *cis* sites and the two triazoles as nitrogen donors to the metal center. The Mn^{II}-complexes (**4a–d**) show efficient catalytic activities in the epoxidation of various aliphatic terminal olefins with peracetic acid, and feature with low catalyst loading, fast conversion and high yields.

Introduction

Tetradentate ligands have been widely used in coordination, biological, synthetic, and supramolecular chemistry, as well as in the development of sensors and molecular switches.[1] Among those, N4 tetradentate ligands have been extensively used for the construction of various metal-coordination complexes used as bioinspired non-heme catalysts for many important and challenging catalytic processes.[2,3] The key features of these catalysts, including activity, selectivity, and stability are dictated by the steric and electronic properties of these ligands coordinated to the metal.[4] Consequently, ligand variation becomes the most powerful tool in the optimization of these catalysts, and most efforts in the area of catalysis have been put into the design of novel suitable ligands. Still, there is limited access to N4 tetradentate ligands, and most of them are based on a pyridyl-framework,[5] such as tpa,[6] mep[7] and pbp[3b,8] as shown in Fig. 1. The limited modification methods for the pyridyl-framework result in the limited synthetic variations of these N4 tetradentate ligands. Thus it is necessary to develop a novel non-pyridyl-based N4 tetradentate ligand system and an efficient construction method for such a system.

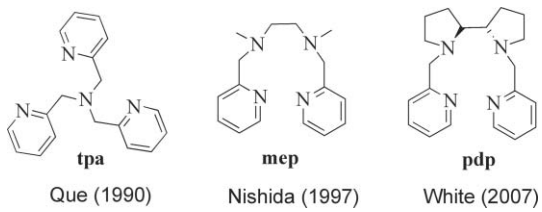


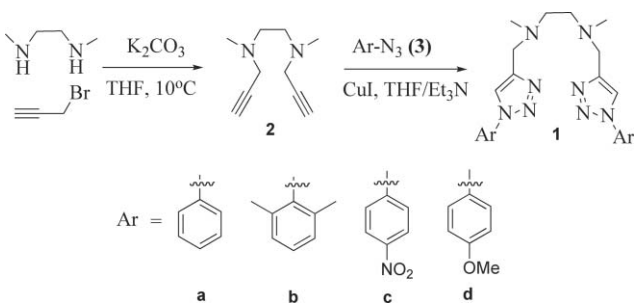
Fig. 1 Examples of N4 tetradentate ligands.

We were attracted to the Cu^{I}-catalyzed cycloaddition of azides and terminal alkynes known as "click chemistry" by Sharpless *et al.*,[9] and the 1,2,3-triazoles from this "click" reaction. "Click" reaction has been widely used in organic synthesis and features with high yields, high efficiency, mild reaction conditions, and simple work-up procedures.[10] The resulting 1,2,3-triazole itself has attracted growing interest[11,12] in the design of tridentate pincer-type ligands.[11b-c,12a] Clearly, the "click" strategy could be an ideal method for achieving non-pyridyl-based N4 tetradentate ligands, since its application to various commercially or readily available azides and alkynes will result in a wide variety of tetradentate ligands.

Herein, we report the "click" syntheses of triazole-based N4 tetradentate ligands **1a–d**, and the X-ray structures of their metal complexes **4a–d**, **5a**, **6a** and **7a**. To demonstrate the application of our non-pyridyl-based ligands in catalysis, their manganese (Mn^{II}) complexes **4a–d** have been used in the epoxidation of various terminal aliphatic olefins with peracetic acid, in which these complexes show good catalytic activities, and feature with low catalyst loading, fast conversion and high yields.

Results and discussion

Ligands **1a–d** were synthesized in 57–71% overall yield by treating acetylene **2** with aromatic azides **3a–d** in a one-pot two-step procedure as shown in Scheme 1. The syntheses of these ligands are readily scaled up to the multigram scale without column chromatography using readily available aromatic azides **3** as starting materials.[13] The triazole unit of these ligands offers an alternative framework to that pyridyl-based traditional framework, and can easily be used for further functionalization.



Scheme 1 Synthesis of ligands **1a–d**.

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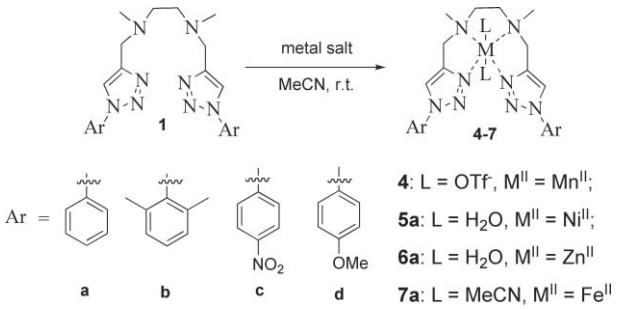
To demonstrate the good coordination properties of nitrogen in these ligands, ligand **1a** was initially studied. It readily coordinated to Mn^{II}, Ni^{II}, Zn^{II} and Fe^{II} metal ions as shown in Scheme 2, and generated the corresponding metal complexes **4a–7a** in 77, 42, 53 and 82% yields respectively. Complexes **4a–7a** were characterized by MS, elemental and X-ray structure analyses.[14] Their X-ray structures reveal an octahedral mononuclear structure with the two triazoles as nitrogen donors to the metal center and two co-ligands ($CF_3SO_3^-$ for **4a**, H_2O for **5a–6a** and MeCN for **7a**) bonded in *cis* sites as shown in Fig. 2. The bond lengths of the triazole-N_3 nitrogen's to Mn^{II}, Ni^{II}, Zn^{II} and Fe^{II} are 2.29, 2.09, 2.12 and 2.15 Å respectively, similar to those in the pyridyl-based metal-complexes.[15]



Scheme 2 Synthesis of metal complexes **4a–7a**.

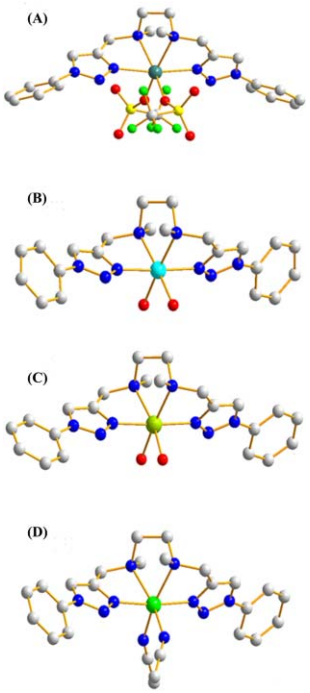


Fig. 2 X-Ray structures of catalysts **4a–6a**. (A): $[Mn^{II}(CF_3SO_3)_2(\mathbf{1a})]$ (**4a**); (B): $[Ni^{II}(H_2O)_2(\mathbf{1a})](ClO_4)_2$ (**5a**); (C): $[Zn^{II}(H_2O)_2(\mathbf{1a})](ClO_4)_2$ (**6a**) and (D): $[Fe^{II}(MeCN)_2(\mathbf{1a})]$ (**7a**). Hydrogen atoms and non-coordinating solvent molecules have been omitted for clarity. Average M–N (triazole) lengths [Å]: for **4a**, 2.29; for **5a**, 2.09; for **6a**, 2.12 and for **7a**, 2.15 Å. C grey, N blue, O red, S yellow, F bright-green, M^{II} dark green, Ni^{II} light blue, Zn^{II} light green and Fe^{II} green.

Ligands **1b–d** exhibit similar coordination properties to these metal ions and smoothly generated complexes **4b–d** in 60–87% yields. Complexes **4b–d** were characterized by MS, elemental and X-ray analyses.[14] The X-ray structures of complexes **4a–d**, shown in Fig. 2 and Fig. 3, are similar to the pyridyl-based complex $[Mn^{II}(R,R\text{-mcp})(CF_3SO_3)_2]$[4b] in which the average bond length of the pyridyl-nitrogen to Mn^{II} is 2.25 Å. Complex **4d** exhibits a relatively shorter average bond length (2.22 Å) between Mn^{II} and the triazole-N_3 nitrogen compared to those of **4a** (2.29 Å), **4b** (2.29 Å) and **4c** (2.30 Å). This difference may be due to the electron-donating effect from methoxy-substituents in complex **4d**.

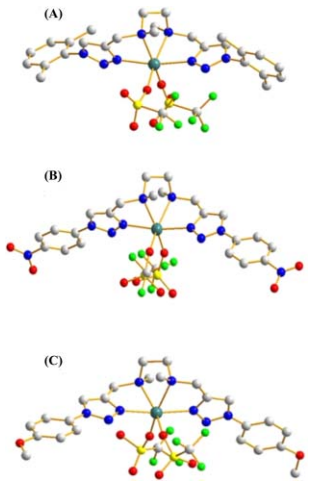
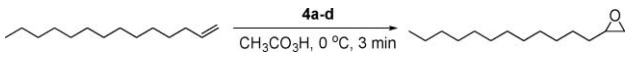


Fig. 3 X-Ray structures of catalysts **4b**, **4c** and **4d**. (A): $[Mn^{II}(CF_3SO_3)_2(\mathbf{1b})]$ (**4b**); (B): $[Mn^{II}(CF_3SO_3)_2(\mathbf{1c})]$ (**4c**) and (C): $[Mn^{II}(CF_3SO_3)_2(\mathbf{1d})]$ (**4d**). Hydrogen atoms and non-coordinating solvent molecules have been omitted for clarity. Average Mn–N (triazole) lengths [Å]: for **4b**, 2.29; for **4c**, 2.30 and for **4d**, 2.22. C gray, Mn dark-green, N blue, O red, S yellow and F bright-green.

The facile access to these triazole-based N4 tetradentate ligands opens a way to the rapid and convenient construction of a variety of metal complexes and the screening of their catalytic properties. We are attracted to the catalytic epoxidation of terminal olefins, because the resulting 1,2-epoxides are extremely versatile starting materials for the syntheses of more complicated molecules while the reaction itself remains challenging due to the relatively electron-deficient nature of these olefins.[16] Recently, Stack, Costas and Que have disclosed several efficient catalysts[4b,5b,17] based on the pyridyl-fragment for the epoxidation of terminal olefins. With metal complexes of ligands **1a–d** in hand, and to exemplify the advantages of these resultant ligands, we investigated the catalytic activities of their Mn^{II}-complexes **4a–d** in the epoxidation of terminal olefins.

The initial screening of the catalytic activities of these complexes in the epoxidization of terminal olefins was performed on 1-tetradecene with peracetic acid as the oxidant. Typically, two equivalents of peracetic acid (8–10%) is slowly added into the system containing the catalyst, and the results are summarized in Table 1. Complexes **4a–d** are powerful catalysts in the epoxidization of 1-tetradecene. With 2 mol% catalyst loading, complexes **4a–4d** were able to generate the desired 1,2-epoxytetradecane in 79%–89% conversion respectively within 3 min (entries 1–4

Table 1 Epoxidation reactivity of catalysts **4a–d**[a]

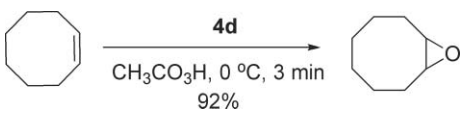


Entries	Catalyst	Catalyst loading (%)	Conversion (%)
1	**4a**	2	81[b]
2	**4b**	2	82[b]
3	**4c**	2	71[b]
4	**4d**	2	89[b]
5	**4d**	2	98[c]
6	**4d**	0.5	81[c]
7	**4d**	0.1	67[c]
8	**4d**	0.1	75[c,d]
9	**4d**	0.5	87[c,e]
10	**4d**	0.5	90[c,f]
11	**4d**	0.5	98[c,d]

[a] Performed with 1-tetradecene (5.0 mmol), catalyst (2.5 mmol% for 0.5% catalyst loading), CH_3CO_3H (7.65 g, 10% CH_3CO_3H, 10.0 mmol); reaction temperature 0 °C, reaction time: 3 min. Results are the average of at least three runs. [b] Addition of CH_3CO_3H over 10 min. [c] Addition of CH_3CO_3H over 30 min. [d] CH_3CN–CH_2Cl_2 = 1/1 (v/v) was used as solvent. [e] CH_3CN–CH_2Cl_2 = 10/1 (v/v) was used as solvent. [f] CH_3CN–CH_2Cl_2 = 5/1 (v/v) was used as solvent.

in Table 1). Catalyst **4d** based on ligand **1d** with more electron-rich triazole rings, shows the highest catalytic activity (entry 4 in Table 1), giving comparable catalytic performance to that of $[Mn^{II}(mep)(CF_3SO_3)_2]$.[4b] Although 1-tetradecene is rapidly expoxidized with 0.1 mol% catalyst loading of **4d** (entry 8 in Table 1), it generally requires 0.5 mol% catalyst loading with the slight modification of the reaction conditions to achieve the complete conversion of 1-tetradecene (entry 11 in Table 1).

To test the versatility of catalyst **4d** in the epoxidation of olefins, the optimized reaction conditions were further applied to other aliphatic terminal olefins and the results are summarized in Table 2. The epoxidations are generally accomplished at 0.5 mol% catalyst loading of **4d**. Catalyst **4d** showed good catalytic activity towards various terminal olefins studied. At either 0 °C or room temperature within 3 min, the desired epoxidation products were generated in high isolated yields (79–94%). There are few reports about the epoxidation of these long-chain aliphatic terminal olefins, such as 1-tetradecene, 1-hexadecene and 1-octadecene (entries 3–5 in Table 2) associated with their low solubility in MeCN. The usage of the mixture solvent (MeCN–CH_2Cl_2) in our system is able to improve the solubility of these long chain olefins and leads to good epoxidation yields. Catalyst **4d** also shows well catalytic performance in the epoxidation of internal olefin, for example cyclooctene (92% isolated yield) as shown in Scheme 3.

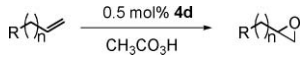


Scheme 3 Catalytic epoxidation of cyclooctene.

Conclusions

In summary, we have developed a conceptually new approach for the synthesis of a series of triazole-based N4 tetradentate ligands using the "click-chemistry" method. These ligands have good coordination properties to many metal ions, and provide great opportunities for the efficient screening of a broad range of organometallic catalysts. These advantages are exemplified here by applying their Mn^{II} complexes **4a–d** for the efficient catalytic epoxidation of various aliphatic terminal olefins. Extending this synthetic strategy to the synthesis of various nitrogen donor ligands, including chiral N4 tetradentate ligands and their metal complexes for further applications in the selective or asymmetrical oxidation of aliphatic C–H bonds are currently under way.

Table 2 Epoxidation reactivity of catalyst **4d** for various terminal olefins[a]



Entries	R	*n*	Isolated yield (%)
1	Me	7	93[b]
2	Me	9	94
3	Me	11	89
4	Me	13	83[c]
5	Me	15	79[c]
6	MeOC(O)	8	89[b]
7	EtOC(O)	8	91[b]

[a] Performed with olefins (5.0 mmol) and catalyst **4d** (2.5×10^{-2} mmol) in 9 mL CH_2Cl_2–CH_3CN (v/v = 1/1); CH_3CO_3H (7.65 g, 10%, 10.0 mmol) was added over 30 min; reaction time: 3 min; reaction temperature: 0 °C unless noted otherwise. Results are the average of at least three runs. [b] MeCN (9 mL) was used as solvent. [c] Reaction was performed at room temperature.

Experimental

General

Reagents were purchased as reagent-grade and used without further purification unless otherwise stated. Solvents were used as received from commercial suppliers unless noted otherwise. Acetonitrile was distilled over CaH_2. THF was freshly distilled from sodium benzophenone ketyl. All olefin substrates used were purchased from a commercial source. Peracetic acid (8–10%) was prepared according to the literature.[18] All reactions were performed in oven-dried or flame-dried glassware unless otherwise stated, and were monitored by TLC using 0.25 mm silica gel plates with UV indicator (60F-254) or I_2 vapor. Reactions involving light-sensitive compounds such as CuI were carried out wrapped in foil. ^{1}H- and ^{13}C-NMR are obtained on an AV-300 Bruker spectrometer at 298 K; chemical shifts (δ) are reported in δ [ppm] relative to $CDCl_3$ (7.26 ppm, ^{1}H; 77.3 ppm, ^{13}C) or DMSO-d_6 (2.50 ppm, ^{1}H; 40.5 ppm, ^{13}C); coupling constants J are given in [Hz] and the multiplicities are expressed as follows: s = singlet, d = doublet, t = triplet, m = multiplet. ESI-MS spectra were obtained on Agilent-6220. Elemental analysis was obtained on VarioEL III.

Syntheses

***N*,*N*-dimethyl-*N*,*N*-di(prop-2-ynyl)ethane-1,2-diamine 2.** To *N*,*N*-dimethylethanamine (370 mg, 4.2 mmol) in dry DMF (5 mL) at 10 °C was added anhydrous potassium carbonate (1.73 g, 12.5 mmol) in one portion, and propargyl bromide (1.01 g, 8.5 mmol) in DMF (5 mL) dropwise over 1 h. After stirring at 10 °C for 8 h, the reaction mixture was filtered off, and the solid was washed with DMF (2 × 3 mL). Organic layers were combined, poured into water (100 mL), extracted with DCM (3 × 30 mL),

washed with water (3 × 100 mL), and dried over anhydrous $MgSO_4$. Solvent was removed under reduced pressure, and the pure **2** was obtained as a yellow oil in 92% yield (634 mg) from column chromatography (silica gel, EtOAc/petroleum ether = 1/2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.32 (s, 4H), 2.47 (s, 4H), 2.24 (s, 6H), 2.16 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 78.1, 73.3, 52.5, 45.3, 41.6.

One-pot syntheses of ligands 1. To *N*,*N*-dimethylethanamine (502 mg, 5.7 mmol) in THF (5 mL) at 10 °C was added anhydrous potassium carbonate (2.35 g, 17.0 mmol) in one portion, and propargyl bromide (1.35 g, 11.4 mmol) in THF (5 mL) dropwise over 1 h. After stirring at 10 °C for 8 h, the reaction mixture was filtered off and washed with THF (2 × 2.5 mL). Organic layers were combined and poured into aromatic azides **3a–d** (17 mmol, generated according to the literature[13]) in THF (15 mL). To the reaction mixture was added CuI (1.10 g, 5.7 mmol) and triethylamine (2 mL), and was stirred at room temperature in the dark for 24 h according to TLC. The reaction mixture was diluted with aqueous $NH_3{\cdot}H_2O$ (100 mL, 5%), extracted with DCM (3 × 50 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuum to obtain a crude oil residue. It was washed with petroleum ether (3 × 30 mL) to give the desired analytical pure products **1a–d** as light brown powers.

Ligand ***1a***. As described in the general procedure (66% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (s, 2H), 7.62 (d, J = 9 Hz, 4H), 7.36–7.31 (m, 4H), 7.27–7.25 (m, 2H), 3.68 (s, 4H), 2.53 (s, 4H), 2.18 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.7, 136.8, 129.6, 128.5, 121.3, 120.2, 54.0, 52.1, 42.2. HRMS: calcd. for $C_{22}H_{27}N_8$ $[M + H]^+$ 403.2358, found 403.2361. Anal. calcd. for $C_{22}H_{26}N_8$: C, 65.65; H, 6.51; N, 27.84. found: C, 65.38; H, 6.48; N, 27.79.

Ligand ***1b***. As described in the general procedure (58% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (s, 2H), 7.32 (t, J = 7.5 Hz, 7.8 Hz, 2H), 7.16 (d, J = 7.5 Hz, 4H), 3.92 (s, 4H), 2.75 (s, 4H), 2.36 (s, 6H), 1.97 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.4, 135.9, 135.3, 130.0, 128.7, 125.1, 53.6, 52.4, 42.0, 16.8. HRMS: calcd. for $C_{26}H_{35}N_8$ $[M + H]^+$ 459.2985, found 459.3029. Anal. calcd. for $C_{26}H_{34}N_8$: C, 68.09; H, 7.47; N, 24.43. found: C, 67.92; H, 7.18; N, 24.71.

Ligand ***1c***. As described in the general procedure (71% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.40 (d, J = 7.8 Hz, 4H), 8.26 (s, 2H), 8.02 (d, J = 8.6 Hz, 4H), 3.84 (s, 4H), 2.68 (s, 4H), 2.34 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.1, 146.1, 141.1, 125.5, 121.2, 120.3, 54.2, 52.3, 42.5. HRMS: calcd. for $C_{22}H_{24}N_{10}O_4$ $[M]^+$ 492.1982, found 492.1962. Anal. calcd. for $C_{22}H_{24}N_{10}O_4$: C, 53.65; H, 4.91; N, 28.44. found: C, 53.37; H, 4.76; N, 28.69.

Ligand ***1d***. As described in the general procedure (57% yield). ^{1}H NMR (300 MHz, $CDCl_3$): 7.93 (s, 2H), 7.63 (d, J = 8.6 Hz, 4H), 7.00 (d, J = 8.3 Hz, 4H), 3.85 (s, 6H), 3.82 (s, 4H), 2.67 (t, 4H), 2.34 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 159.6, 145.1, 130.5, 121.9, 121.0, 114.7, 55.5, 54.3, 52.5, 42.5. HRMS: calcd. for $C_{24}H_{30}N_8O_2$ $[M]^+$ 492.2492, found 492.2497. Anal. calcd. for $C_{24}H_{30}N_8O_2$: C, 62.32; H, 6.54; N, 24.23. found: C, 62.08; H, 6.25; N, 24.47.

Complex 4a. To ligand **1a** (403 mg, 1.0 mmol) in MeCN (6 mL) was added $Mn^{II}(CF_3SO_3)_2$ (353 mg, 1.0 mmol).[19,20] The resulting homogeneous solution was vigorous stirred for 24 h, and Et_2O was carefully layered on the top of the solution. Crystals were obtained over 12 h and washed with cold Et_2O to yield a light colour crystal **4a** in 77% yield (584 mg). X-Ray quality crystals were obtained by slow diffusion of Et_2O into its concentrated MeCN solution. HRMS: calcd. for $C_{22}H_{26}N_8Mn$ m/z 228.5830, found 228.5857. Anal. calcd. for $C_{24}H_{26}F_6MnN_8O_6S_2$: C, 38.15; H, 3.47; N, 14.83. found: C, 38.03; H, 3.51; N, 14.63.

Complex 4b. Following the procedure for **4a** but replacing **1a** with **1b** (458 mg, 1.0 mmol) (64% yield). X-Ray quality crystals were obtained by slow diffusion of Et_2O into its concentrated MeCN solution. HRMS: calcd. for $C_{26}H_{34}MnN_8$ m/z 256.7793, found 256.7771. Anal. calcd. for $C_{28}H_{34}F_6MnN_8O_6S_2$: C, 41.43; H, 4.22; N, 13.81. found: C, 41.77; H, 4.31; N, 14.20.

Complex 4c. Following the procedure for **4a** but replacing **1a** with **1c** (493 mg, 1.0 mmol) (60% yield). X-Ray quality crystals were obtained by slow diffusion of Et_2O into its concentrated MeCN solution. HRMS: calcd. for $C_{22}H_{24}MnN_{10}O_4$ m/z 273.6812, found 273.6793. Anal. calcd. for $C_{24}H_{24}F_6MnN_{10}O_{10}S_2$: C, 34.09; H, 2.86; N, 16.56; found: C, 34.31; H, 3.11; N, 16.70.

Complex 4d. Following the procedure for **4a** but replacing **1a** with **1d** (463 mg, 1.0 mmol) (87% yield). X-Ray quality crystals were obtained by slow diffusion of Et_2O into its concentrated MeCN solution. HRMS: calcd. for $C_{24}H_{30}MnN_8O_2$ m/z 258.5936, found 258.5901. Anal. calcd. for $C_{26}H_{30}F_6MnN_8O_8S_2$: C, 38.29; H, 3.71; N, 13.74; found: C, 38.57; H, 3.98; N, 13.88.

Complex 5a. To **1a** (403 mg, 1.0 mmol) in MeCN (6 mL) was added $Ni^{II}(ClO_4)_2{\cdot}H_2O$ (366 mg, 1.0 mmol), and a homogeneous solution was obtained. After vigorous stirring for 24 h, the reaction mixture was concentrated *in vacuo*, MeOH was added, Et_2O was carefully layered on the solution, crystals were obtained over 12 h and washed with cold Et_2O to yield complex **5a** in 40% yield (276 mg). X-Ray quality crystals were obtained by slow diffusion of Et_2O into its concentrated MeCN solution. HRMS: calcd. for $C_{22}H_{26}N_8Ni$ m/z 230.0817, found 230.0819. Anal. calcd. for $C_{22}H_{30}Cl_2N_8NiO_{10}$: C, 37.96; H, 4.34; N, 16.10; found: C, 37.78; H, 4.29; N, 15.93.

Complex 6a. To **1a** (403 mg, 1.0 mmol) in MeCN (6 mL) was added $Zn^{II}(ClO_4)_2{\cdot}H_2O$(372 mg, 1.0 mmol), and a homogeneous solution was obtained. After vigorous stirring for 24 h, Et_2O was carefully layered on the solution. Crystals were obtained over 12 h and washed with cold Et_2O to yield a light colour crystal **6a** in 53% (373 mg) yield. X-Ray quality crystals were obtained by slow diffusion of Et_2O into its concentrated MeCN solution. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.08 (s, 2H), 8.01–7.98 (m, 4H), 7.71–7.65 (m, 6H), 4.11–3.94 (m, 4H), 2.73 (s, 4H), 2.51 (s, 6H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 144.0, 136.6, 130.6, 130.4, 123.3, 121.1, 52.3, 42.9, 39.1. HRMS: calcd. for $C_{22}H_{25}N_8Zn$ $[M - H]^+$ 465.1494, found 465.1578; calcd. for $C_{22}H_{25}N_8Zn$ m/z 233.0786, found 233.0810. Anal. calcd. for $C_{22}H_{30}Cl_2N_8ZnO_{10}$: C, 37.60; H, 4.30; N, 15.94; found: C, 37.24; H, 4.41; N, 15.72.

Complex 7a. Using a one-pot two-step procedure (82% overall yield), to ligand **1a** (500 mg, 1.2 mmol) in CH_3CN (7 mL) was added $Fe^{II}Cl_2{\cdot}4H_2O$ (247 mg, 1.2 mmol) at room temperature under argon. With the addition of $Fe^{II}Cl_2{\cdot}4H_2O$, a bright orange precipitate instantly formed. After continuous stirring for 24 h, Et_2O was added until no more precipitate formed. After removing solvent, the precipitate was washed thoroughly with ether (5 × 3 mL), and dried under argon over night to yield the complex

Table 3 Details of structure determination, refinement, and experimental parameters for complexes **4a–7a**

	4a	**5a**	**6a**	**7a**
Formula	$C_{24}H_{26}F_6MnN_8O_6S_2$	$C_{22}H_{38}Cl_2N_8NiO_{13}$	$C_{22}H_{30}Cl_2N_8O_{10}Zn$	$C_{26}H_{32}F_{12}FeN_{10}Sb_2$
Formula wt	755.59	752.21	702.81	1011.97
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$C2/c$	$C2/c$	$P2_1/c$	$Pcca$
Crystal size/mm	0.30 × 0.20 × 0.20	0.40 × 0.20 × 0.20	0.50 × 0.30 × 0.20	0.45 × 0.25 × 0.20
a/Å	19.148(7)	7.899(5)	16.1160(12)	30.139(5)
b/Å	8.570(3)	18.312(5)	11.5326(8)	11.190(5)
c/Å	20.170(7)	22.243(5)	18.0774(13)	22.140(5)
α/°	90.00	90.00	90.00	90.000(5)
β/°	106.082(4)	92.183(5)	113.0980(10)	90.000(5)
γ/°	90.00	90.00	90.00	90.000(5)
V/Å^3	3180.3(19)	3215(2)	3090.5(4)	7467(4)
Z	4	4	4	8
D_c/mg m^{-3}	1.578	1.554	1.510	1.800
μ/mm^{-1}	0.634	0.844	1.031	1.914
F(000)	1540	1568	1448	3952
θ range/°	2.10–25.00	1.83–25.00	1.37–25.00	1.82–25.00
Reflns. collected	10 989	11 242	21 604	33 857
Reflns. unique	2802	2837	5453	6584
Parameters	243	211	400	467
Goodness-of-fit on F^2	1.017	1.146	1.087	1.232
R_1, wR_2 [$I > 2\sigma(I)$]	0.0308, 0.0825	0.1030, 0.2926	0.0442, 0.1330	0.0840, 0.2089
R_1, wR_2 [all data]	0.0400, 0.0891	0.1643, 0.3436	0.0545, 0.1426	0.1685, 0.2509
Max, min $\Delta\rho$/e Å^{-3}	0.329, –0.269	1.215, –0.616	1.303, –0.459	1.300, –1.595

1a·FeCl$_2$ in 82% yield (538 mg) (HRMS: calcd. for $C_{22}H_{26}N_8FeCl$ [M – Cl]$^+$ 493.1318, found 493.1332.) which was directly used to react with $AgSbF_6$ (703 mg, 2.1 mmol) in CH_3CN (14 mL) in dark under argon to generate complex **7a**. After stirring for 24 h, the reaction mixture was filtered through Celite three times. Organic layers were combined, filtered through filter paper and concentrated to give complex **7a** (645 mg) as a light colour solid. HRMS: calcd. for $C_{22}H_{26}N_8Fe$ m/z 229.0815, found 229.0821. Anal. calcd. for $C_{26}H_{32}F_{12}FeN_{10}Sb_2·H_2O$: C, 30.32; H, 3.33; N, 13.60. found: C, 30.21; H, 3.42; N, 13.71.

X-Ray crystallography

Crystallographic data for complexes **4–7a** are shown in Table 3, and those for **4b–d** are shown in Table 4. X-Ray quality crystals were obtained by slow diffusion of Et_2O into concentrated MeCN solution of the corresponding complexes. The vial containing this solution was placed, loosely capped, to promote the crystallization upon ether diffusion.

A suitable crystal was chosen and mounted on a glass fiber using grease. Data were collected using a Bruker SMART APEX-2 diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at room temperature. Cell parameters were retrieved using SMART[21] software and refined using SAINT on all observed reflections. The determination of unit cell parameters and data collections were performed with Mo Kα radiation (λ) at 0.71073 Å. Data reduction was performed using the SAINT software,[22] which corrects for Lp and decay. The structure was solved by the direct method using the SHELXS-97[23] program and refined by least squares method on F^2, SHELXL-97,[24] incorporated in SHELXTL V5.10.[25] Unit cell dimensions were obtained with least-squares refinements, and all structures were solved by direct methods with SHELXL-97. The other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms were added theoretically and riding on the concerned atoms.

Catalytic properties

General procedure for epoxidation reactions. At 0 °C, to the olefin (5.0 mmol) in MeCN (5 mL) was added catalyst **4a–d** (0.5-10 mmol%) in MeCN in one portion, and CH_3CO_3H (7.65 g, 10%, 10.0 mmol) over 5 or 30 min. The reaction mixture was stirred at 0 °C for 3 min, quenched with Et_3N, diluted with H_2O (50 mL), and extracted with pentane (2 × 40 mL) or petroleum ether (boiling point: 30–40 °C) (2 × 40 mL) depending on the volatility of the products. Organic layers were combined, washed sequentially with H_2O (2 × 50 mL) and saturated $NaHCO_3$ (1 × 40 mL), dried over anhydrous K_2CO_3, filtered, and carefully concentrated in vacuum in an ice bath.

1,2-Epoxydecane[21]. 1-Decene (745 mg, 94% pure, 5.0 mmol) in 5 mL CH_3CN; catalyst **4d** (21 mg, 2.5 × 10^{-2} mmol) in 4 mL CH_3CN; CH_3CO_3H (7.65 g, 10%, 10.0 mmol) was added over 30 min; reaction time: 3 min; reaction temperature: 0 °C; workup using pentane (2 × 50 mL). Three trials provided the product in 93% isolated average yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.88 (m, 1H), 2.74 (t, J = 5.0 Hz, 1H), 2.46 (dd, J = 3.0 and 5.5 Hz, 1H), 1.55–1.27 (m, 14H), 0.87 (t, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.6, 47.4, 32.7, 32.1, 29.74, 29.67, 29.4, 26.2, 22.9, 14.3.

1,2-Epoxydodecane[21]. 1-Dodecene (852 mg, 5.0 mmol) in 4.5 mL CH_2Cl_2; catalyst **4d** (21 mg, 2.5 × 10^{-2} mmol) in 4.5 mL CH_3CN; CH_3CO_3H (7.65 g, 10%, 10.0 mmol) was added over 30 min; reaction time: 3 min; reaction temperature: 0 °C; workup using petroleum ether (boiling point: 30–40 °C) (2 × 50 mL). Three trials provided the product in 94% isolated average yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.90 (m, 1H), 2.72 (dd, J = 4.0 and 5.0 Hz,

Table 4 Details of structure determination, refinement, and experimental parameters for complexes **4b–4d**

	4b	**4c**	**4d**
Formula	$C_{28}H_{34}F_6MnN_8O_6S_2$	$C_{24}H_{24}F_6MnN_{10}O_{10}S_2$	$C_{28}H_{33}F_6MnN_9O_8S_2$
Formula wt	811.67	845.59	856.69
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	*Pc*	*P*21/*n*	*Pbca*
Crystal size/mm	0.45× 0.15 × 0.15	0.25× 0.20 × 0.20	0.50× 0.30 × 0.20
a/Å	10.3766(19)	9.0524(11)	19.677(5)
b/Å	21.576(4)	26.257(3)	14.929(5)
c/Å	9.2436(17)	15.0307(18)	25.509(5)
α/°	90.00	90.00	90.000(5)
β/°	115.806(2)	97.368(2)	90.000(5)
γ/°	90.00	90.00	90.000(5)
V/Å^3	1863.2(6)	3543.2(7)	7493(3)
Z	2	4	8
D_c/mg m^{-3}	1.441	1.585	1.519
μ/mm^{-1}	0.546	0.588	0.552
F(000)	828	1716	3512
θ range/°	1.89–25.00	1.57–26.00	1.60–25.00
Reflns. collected	12744	26327	51351
Reflns. unique	5635	6890	6611
Parameters	530	480	489
Goodness-of-fit on F^2	1.073	0.968	1.044
R_1, wR_2 [$I > 2\sigma(I)$]	0.0627, 0.1931	0.0620, 0.1519	0.0865, 0.2497
R_1, wR_2 [all data]	0.0655, 0.1966	0.1406, 0.1813	0.1199, 0.2868
Max, min Δ*ρ*/e Å^{-3}	0.418, –0.356	0.356, –0.365	1.700, –1.600

1H), 2.43 (dd, J = 2.6 and 5.0 Hz, 1H), 1.51–1.24 (m, 18H), 0.88 (t, J = 7.0 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 58.3, 52.7, 47.4, 32.7, 32.1, 29.8, 29.78, 29.70, 29.5, 26.2, 22.9, 14.4.

1,2-Epoxytetradane[26]. 1-Tetradecene (1.04 g, 94% pure, 5.0 mmol) in 4.5 mL CH_2Cl_2; catalyst **4d** (21 mg, 2.5 × 10^{-2} mmol) in 4 mL CH_3CN; CH_3CO_3H (7.65 g, 10%, 10.0 mmol) was added over 30 min; reaction time: 3 min; reaction temperature: 0 °C; workup using petroleum ether (boiling point: 30–40 °C) (2 × 50 mL). Three trials provided the product in 89% isolated average yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.89 (m, 1H), 2.72 (dd, J = 4.2 and 5.0 Hz, 1H), 2.44 (dd, J = 3.0 and 5.1 Hz, 1H), 1.52–1.24 (m, 22H), 0.88 (t, J = 6.8 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.4, 47.1, 32.5, 31.9, 29.7, 29.65, 29.64, 29.56, 29.55, 29.5, 29.4, 29.0, 22.7, 14.1.

1,2-Epoxyhexadecane[27]. 1-Hexadecene (1.19 g, 94% pure, 5.0 mmol) in 4.5 mL CH_2Cl_2; catalyst **4d** (21 mg, 2.5 × 10^{-2} mmol) in 4.5 mL CH_3CN; CH_3CO_3H (7.65 g, 10%, 10.0 mmol) was added over 30 min; reaction time: 3 min; reaction temperature: room temperature; workup using petroleum ether (boiling point: 30–40 °C) (2 × 50 mL). Three trials provided the product in 83% isolated average yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.91–2.86 (m, 1H), 2.74 (dd, J = 3.7 and 5.2 Hz, 1H), 2.47 (dd, J = 2.2, 5.2 Hz, 1H), 1.51–1.26 (m, 26H), 0.88 (t, J = 6.8 Hz, 3 H). ^{13}C (75 MHz, $CDCl_3$) δ 52.3, 47.1, 32.5, 32.0, 29.7, 29.6 (several overlapped peaks), 29.4, 25.9, 22.7, 14.1.

1,2-Epoxyoctadecane[28]. 1-Octadecene (1.40 g, 90% pure, 5.0 mmol) in 4.5 mL CH_2Cl_2; catalyst **4d** (21 mg, 2.5 × 10^{-2} mmol) in 4.5 mL CH_3CN; CH_3CO_3H (7.65 g, 10%, 10.0 mmol) was added over 30 min; reaction time: 3 min; reaction temperature: room temperature; workup using petroleum ether (boiling point: 30–40 °C) (2 × 50 mL). Three trials provided the product in 79% isolated average yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.91 (m, 1H), 2.75 (dd, J = 3.3 and 4.9 Hz, 1H), 2.47 (dd, J = 4.2 and 5.1 Hz, 1H), 1.51–1.19 (m, 30H), 0.88 (t, J = 7.0 Hz, 3 H).

Methyl 9-(oxiran-2-yl)nonanoate[29]. Methyl 10-undecenoate (1.0 g, 5.0 mmol) in 4.5 mL CH_3CN; catalyst **4d** (21 mg, 2.5 × 10^{-2} mmol) in 4.5 mL CH_3CN; CH_3CO_3H (7.65 g, 10%, 10.0 mmol) was added over 30 min; reaction time: 3 min; reaction temperature: 0 °C; workup using petroleum ether (boiling point: 30–40 °C) (2 × 50 mL). Three trials provided the product in 89% isolated average yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.62 (s, 3H), 2.89 (m, 1H), 2.71 (dd, J = 4.2, 4.7 Hz, 1H), 2.45 (m, 1H), 2.28 (t, J = 7.4 Hz, 2H), 1.59–1.21 (m, 14H). ^{13}C (75 MHz, $CDCl_3$) δ 174.3, 51.4, 52.5, 47.2, 34.1, 32.5, 29.3, 29.2, 29.1, 29.0, 25.9, 24.9. ESI-MS m/z 214 $[M + H]^+$.

Ethyl 9-(oxiran-2-yl)nonanoate[29]. Ethyl 10-undecenoate (1.10 g, 5.0 mmol) in 4.5 mL CH_3CN; catalyst **4d** (21 mg, 2.5 × 10^{-2} mmol) in 4.5 mL CH_3CN; CH_3CO_3H: (7.65 g, 10%, 10.0 mmol) was added over 30 min; reaction time: 3 min; reaction temperature: 0 °C; workup using petroleum ether (boiling point: 30–40 °C) (2 × 50 mL). Three trials provided the product in 91% isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.11 (t, J = 7.1 Hz, 2H), 2.88 (m, 1H), 2.72 (dd, J = 4.1, 4.8 Hz, 1H), 2.44 (m, 1H), 2.27 (t, J = 7.3 Hz, 2H), 1.60–1.23 (m, 14H), 1.21 (t, J = 7.0 Hz, 3H).

1,2-Epoxycyclooctene[4b]. Cyclooctene (550 mg, 5.0 mmol) in 9.0 mL MeCN; catalyst **4d** (21 mg, 2.5 × 10^{-2} mmol) in 5 mL MeCN; CH_3CO_3H (7.6 g, 10%, 10.0 mmol) was added over 30 min; reaction time: 3 min; reaction temperature 0 °C; workup using pentane (2 × 40 mL). Three trials provided the product in 92% isolated average yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.87–2.83 (m, 2H), 2.12–2.08 (m, 2H), 1.56–1.22 (m, 10H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.6, 26.5, 26.3, 25.6.

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