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Synthesis of new binol based [1+1] macrocyclic chiral manganese(III) Schiff bases as catalysts for asymmetric epoxidation

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ABSTRACT

A series of new chiral binol based [1+1] macrocyclic Schiff bases have been synthesized in high yields in short reaction times via cyclo-condensation of dialdehydes with long tethers and chiral diamines. Macrocyclic Mn(salen) complexes containing N_2O_2 salen units incorporated with spacers of increased tether lengths were synthesized and characterized. The newly synthesized catalyst system was successfully employed for the enantioselective epoxidation of unfunctionalized olefins with high yields and good enantioselectivity.

1. Introduction

In biologically active compounds, chiral epoxides are very important for the synthesis of enantiomerically pure complex molecules.[1] Catalytic asymmetric epoxidation is a useful technique for the synthesis of chiral compounds because chiral catalysts can act as enzymes to induce chirality in the molecules.[2] The development of chiral catalysts capable of inducing asymmetric centers with high efficiency has always been an important task for asymmetric synthesis. A wide variety of highly selective asymmetric reactions catalyzed by chiral (salen) metal complexes have been reported on over the past decade.[3] Salen ligands are among the most synthetically accessible frameworks for asymmetric catalysts because their structures can be readily tuned. Chiral salen ligands have been demonstrated to be effective for a wide variety of asymmetric transformations catalyzed by different metals.[4] The simplicity of this ligand, the high enantioselectivity, and the broad substrate generality have attracted the attention of many chemists toward the commercial development of their use in asymmetric synthesis.

Recently our group developed a new method for the synthesis of [1+1],[5] [2+2],[6] [3+3][7] and [6+6][8] chiral polyimine macrocycles using cyclic as well as acyclic chiral diamine salts with achiral and chiral dialdehydes. Under microwave reaction conditions, these reactions are very rapid.

Herein we report the synthesis of new chiral [1+1] macrocyclic Schiff bases and chiral binol based [1+1] macrocyclic manganese–salen complexes. The catalytic activities of these new chiral complexes were evaluated in the asymmetric epoxidation of prochiral alkenes using sodium hypochlorite and *m*-chloro perbenzoic acid as oxidants.

2. Results and discussion

2.1. Synthesis and characterization of the ligands

The conformational bias offered by dialdehydes is a key factor in deciding which macrocycle formed during self condensation with chiral diamines. The dialdehyde component should adopt a conformation, which favors the formation of a [1+1] macrocycle over higher order macrocycles.[9] This requirement can be achieved by the use of dialdehydes containing a long tether between the aldehyde groups. As an initial effort, bisbinaphthyl aldehyde, tethered using a diester group, was used for the reaction. The (*S*)-bisbinaphthyl aldehydes **5**–**7** were synthesized from the corresponding enantiomerically pure (*S*)-1,1′-bi-2-naphthol **1** according to Scheme 1. Treatment of **1** with NaH and then with methoxymethyl (MOM) chloride gave MOM protected (*S*)-2,2′-bis(methoxymethoxy)1,1′-binaphthyl **2**. Direct *ortho*-lithiation using *n*-BuLi followed by the addition of DMF gave (*S*)-2,2′-bis(methoxymethoxy)1,1′-binaphthyl-3-carbaldehyde **3**.[10] Deprotection of the MOM protecting group using 5% HCl/MeOH gave compound **4** with 82% yield. Condensation of compound **4** in succinic acid using EDC·HCl as the coupling agent afforded (*S*)-bisbinaphthyl aldehyde **5** in over 73% yield. In order to study the effect of the tether length of the dialdehyde upon macrocyclization, compound **6** and compound **7** were synthesized in an analogous manner using glutaric and adipic acid as a linker in preference to succinic acid.

In an attempt to synthesize bis((*S*)-3′-formyl-2′-hydroxyl-1,1′-binapthyl-2-yl) malonate via the condensation of malonic acid and (*S*)-2,2′-dihydroxy-1,1′-binaphthyl-3-carbaldehyde **4** with (1-(3-dimethylaminopropyl)-3-ethyl carbodiimide (EDCI) using dimethylaminopyridne (DMAP) in dichloromethane compound (*S*)-3′-formyl-2′hydroxy-1,1′-binaphthyl-2-yl acetate **8** was formed over

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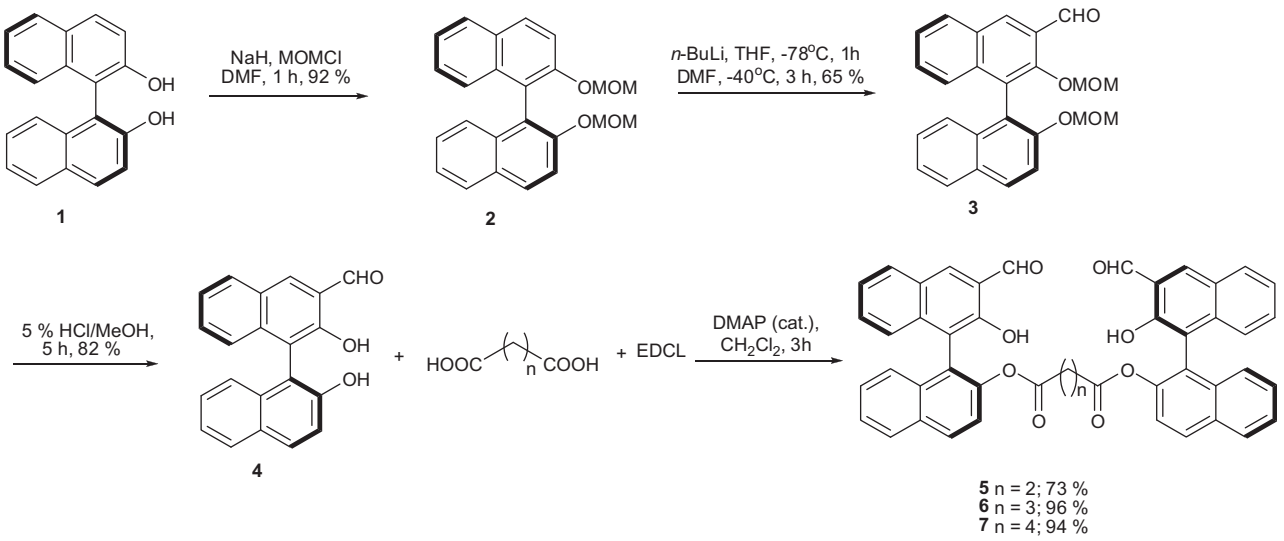
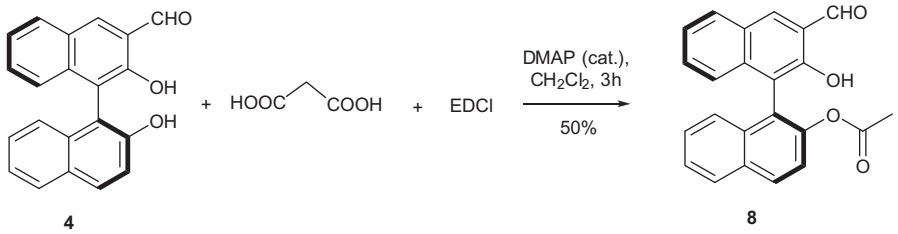


Scheme 1. General procedure for the synthesis of diester linked bisbinaphthyl aldehydes.

50% yield, which was confirmed by analytical techniques (NMR, ESI mass, and single crystal XRD) (Scheme 2). This result is in line with the known chemistry that under basic conditions, diacids undergo decarboxylation to give the corresponding mono-condensed product. The ORTEP representation of compound **8** is shown in Figure 1 with 30% probability displacement ellipsoids.[11]

Microwave irradiation of a mixture of bisbinaphthyl aldehydes **5**, **6**, and **8** and chiral diamines **9**, **10**, and **11** in the presence of potassium carbonate afforded chiral [1+1] macrocyclic imines in 5 min in good yields. The cyclocondensation does not require any anhydrous or dilute reaction conditions for macrocycle synthesis. Moreover, salts of chiral diamines were employed for the macrocycle synthesis instead of the widely employed enantiopure diamines; the results are summarized in Table 1 (Scheme 3).

The [1+1] macrocycle formed exclusively in higher yield and was free from linear oligomers or higher macrocycles during the cyclocondensation of compound **5** with (1*R*,2*R*)-diammoniumcyclohexane mono-(+)-tartrate **9**[12] (Table 1, entry 1). The tether length was found to have little effect on the yield or the nature of the macrocyclization. Accordingly, compounds **6** and **7** upon reaction with **9** gave the [1+1] macrocycle in >90% yield (Table 1,



Scheme 2. Synthesis of (*S*)-2′-formyl-3′-hydroxy-1,1′-binaphthyl-2-yl acetate.

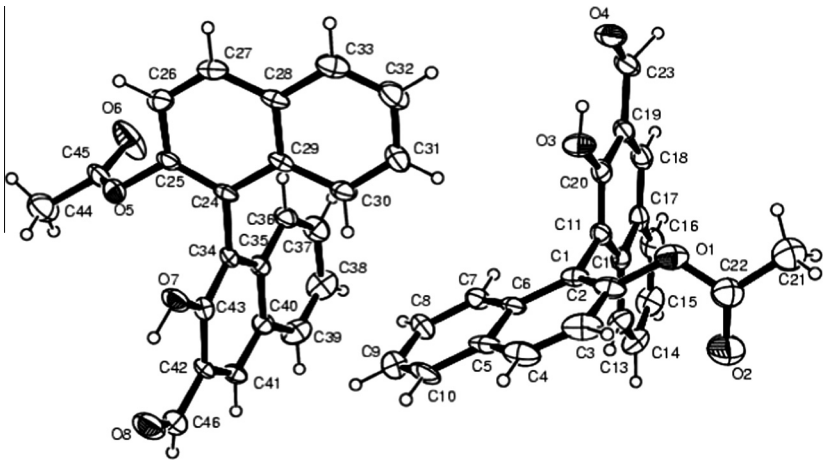
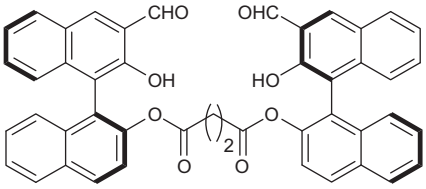
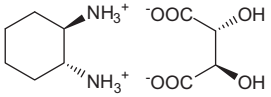
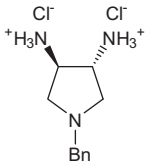
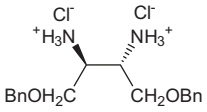
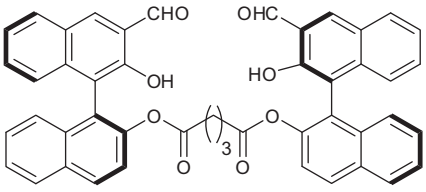
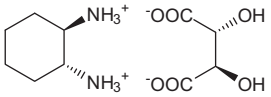
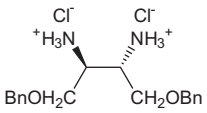
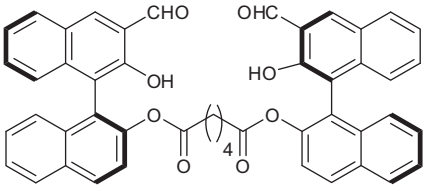
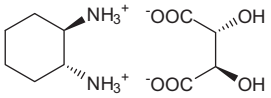
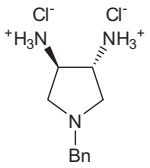
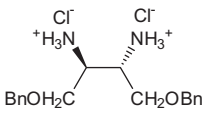
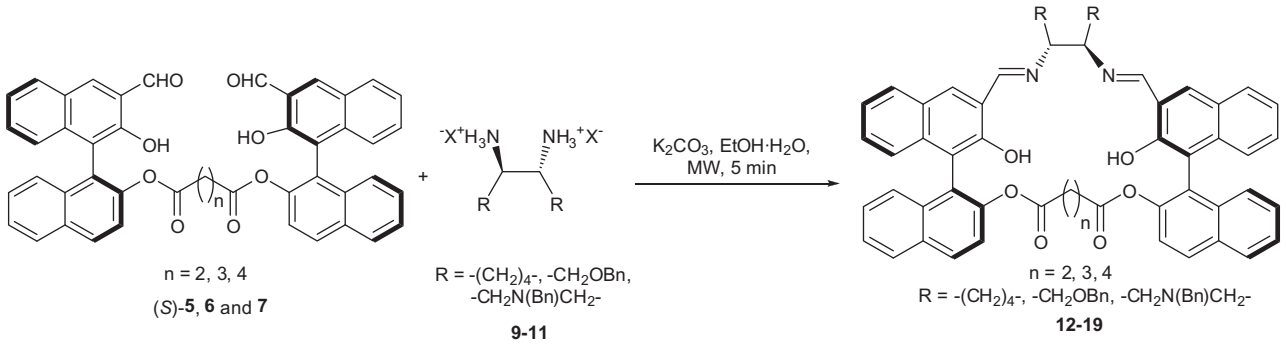


Figure 1. ORTEP representation of (*S*)-2′-formyl-3′-hydroxy-1,1′-binaphthyl-2-yl acetate **8**.

Table 1
[1+1] Cyclocondensation of bisbinaphthyl aldehydes with chiral diamine salts

Entry	Bis(hydroxyaldehyde)	Chiral diamine	[n+n]	*m/z*	Yield (%)
1	 **5**	 **9**	[1+1] **12**	788.4	97
2		 **10**	[1+1] **13**	866	89
3		 **11**	[1+1] **14**	947	78
4	 **6**	 **9**	[1+1] **15**	802.9	94
5		 **11**	[1+1] **16**	989	91
6	 **7**	 **9**	[1+1] **17**	816.5	96
7		 **10**	[1+1] **18**	894	84
8		 **11**	[1+1] **19**	1003	89

entries 4 and 6). Chiral diamines with different dihedral angles, such as (1,4-bis(benzyloxy)-2,3-diaminobutane hydrochloride[13] **10** and (2*R*,3*R*)-1,4bis(benzyloxy)-2,3-diaminobutane hydrochloride[14] **11**, displayed reactivity similar to **9** forming [1+1] macrocycles in 78–89% yields (Table 1, entries 2, 3, 5, 7, and 8). In all cases, the MALDI-TOF mass spectra revealed a single peak corresponding to the molecular ion of the macrocycle. Figure 2 shows the MALDI-TOF mass spectra of macrocycle **12** and **17**. Similarly, all of the macrocyclic imines displayed the predicted spectroscopic features, most importantly one set of NMR signals indicating a highly symmetric structure. The ^{1}H NMR of the [1+1] macrocycles derived from **7** and chiral diamines **9**–**11** displayed noteworthy features. In all three macrocycles, two signals each of one proton intensity appeared at negative δ with respect to TMS. These two signals, corresponding to the four protons of the tether, were comparatively deshielded (approximately −0.2 to −0.5 ppm) in macrocycles derived from **6** to **9**–**11** while the two protons of the tether resonated at approximately 0.7–1.0 ppm. These data indicated that the structure of the macrocycles from bisbinaphthyl aldehydes **7** and **6** is more twisted than that of the macrocycles from **5**.



Scheme 3. [1+1] Cyclocondensation between dialdehydes with spacers and chiral diamines.

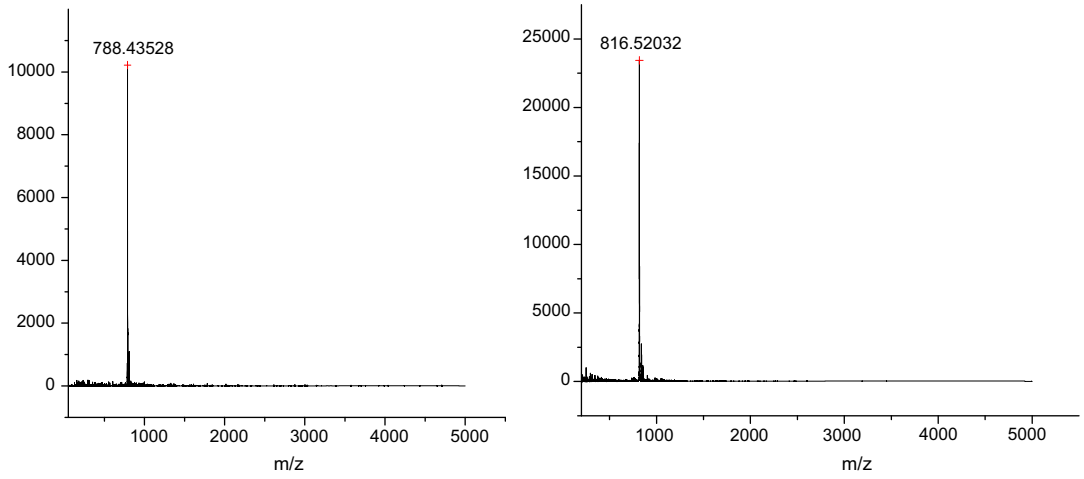
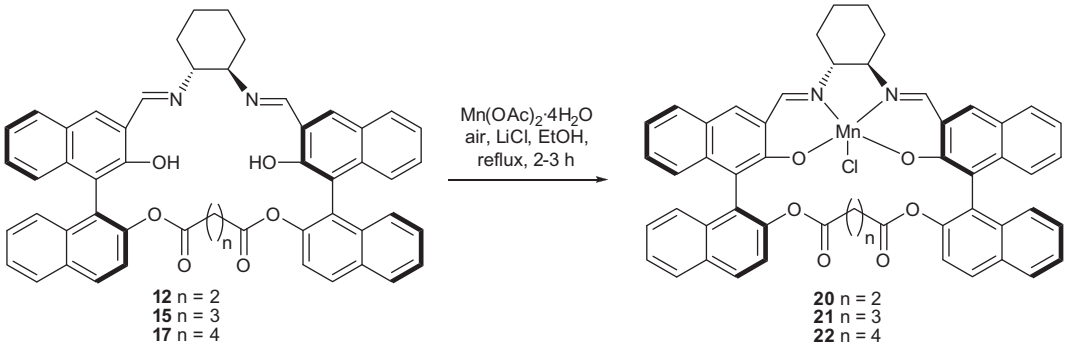


Figure 2. MALDI-TOF of spectra of compounds **12** and **17**.

2.2. Synthesis and characterization of [1+1] macrocyclic binol based MnIII(salen) complexes

Macrocyclic binol based manganese complexes were then synthesized by refluxing the corresponding macrocyclic salen ligand with $Mn(OAc)_2{\cdot}4H_2O$ in ethanol in air for 2–3 h followed by the addition of LiCl and heated for a further 1 h to afford Mn(III)(calixsalen)Cl complexes (Scheme 4). All of the metal complexes were isolated as a black or brown powder. The Mn(III)Cl complexes formed as black to brown powders and were characterized by mass spectrometry (MALDI-TOF) and IR spectroscopy. The presence of an Mn–O bond was confirmed by the absence of a γ_{OH} stretching frequency in the IR spectra. A shift in $\gamma_{C=N}$ (1620 cm^{-1}) stretching frequency in the complex compared to that of the free ligand also confirmed the metal insertion. The mass spectra of the metal complexes showed many peaks and were in contrast to the single peak observed for the free macrocyclic ligand. This was attributed to the mass fragmentations of the corresponding metal complexes and their adducts.

The manganese complexes of macrocyclic ligands **10**–**12** were also prepared by refluxing the free macrocyclic ligand with $Mn(OAc)_2{\cdot}4H_2O$ and LiCl in ethanol in the presence of air. The metal complexes synthesized were characterized by MALDI-TOF spectra.



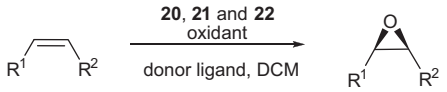
Scheme 4. Synthesis of macrocyclic [1+1] Mn(III)(binol salen)Cl complexes.

2.2.1. Asymmetric epoxidation catalyzed by chiral [1+1] macrocyclic Binol based MnIII(salen) complexes

In our initial experiments, we have carried out epoxidation reactions on 2,2-dimethylchromene using commercial bleach (4% NaOCl) and 70% *m*CPBA as terminal oxidants. An excess of NMO (5 equiv) was used in the mCPBA oxidation to prevent direct oxidation of the olefin by *m*CPBA while catalytic 4-PPNO (0.2 equiv) was used in the case of NaOCl, where it acts as a donor ligand as well as a phase-transfer reagent for the oxidation under biphasic conditions.[15] The effect of the amount of oxidant and catalyst loading on the asymmetric epoxidation of 2,2-dimethylchromene under the oxidation conditions were studied and the results are shown in Figures 3 and 4.

From the results it is evident that the optimized catalyst loading for the *m*CPBA (1.5 equiv) oxidation reaction is 2 mol %, while 4 mol % catalyst (**20**) loading is the optimized catalyst loading for the NaOCl (2 equiv) oxidation.

The optimized reaction conditions were applied for the asymmetric epoxidation of various prochiral olefins using the Mn(III)(binolsalen)Cl **20** complex as the catalyst (Scheme 5). In the catalytic process, NaOCl oxidations produced epoxides with high ee compared to *m*CPBA oxidations. The cyclic olefins produced epoxides in higher enantiomeric excess compared to acyclic olefins. The results are shown in Tables 2 and 3. Macrocyclic Mn(III)(binolsalen)Cl complexes containing succinic acid spacers were found to produce moderate catalytic activity and enantioselectivity during the asymmetric epoxidation of various unfunctionalizsed olefins. However, we thought the suitable tuning of the catalyst structure could provide a method for obtaining epoxides with high enantioselectivity. As a result, the effect of the spacer length on the enantioselective epoxidation was also studied. The optimized reaction conditions were applied for the asymmetric epoxidation of various prochiral olefins using Mn(III)(binolsalen)Cl **21** and Mn(III)(binolsalen)Cl **22** complexes as catalysts. The results are shown in Table 2. The overall catalytic activity of metal complexes containing an increased tether length was found to give higher yields and enantioselectivity. It was observed that in all the cases, the oxygen delivered from the top-face of the olefin was formed as the major enantiomer. Cyclic olefins were found to be the best substrate for the epoxidation. In the case of styrene and its derivatives, moderate enantioselectivity was observed. On the other hand, trisubstituted α-methylstyrene produced epoxides in good yield and ee. The other trisubstituted olefin, 1-phenylcyclohexene, afforded the (1*S*,2*S*)-epoxide as the major enantiomer



Scheme 5. Asymmetric epoxidation of various prochiral olefins using [1+1] binol based macrocyclic manganese complexes.

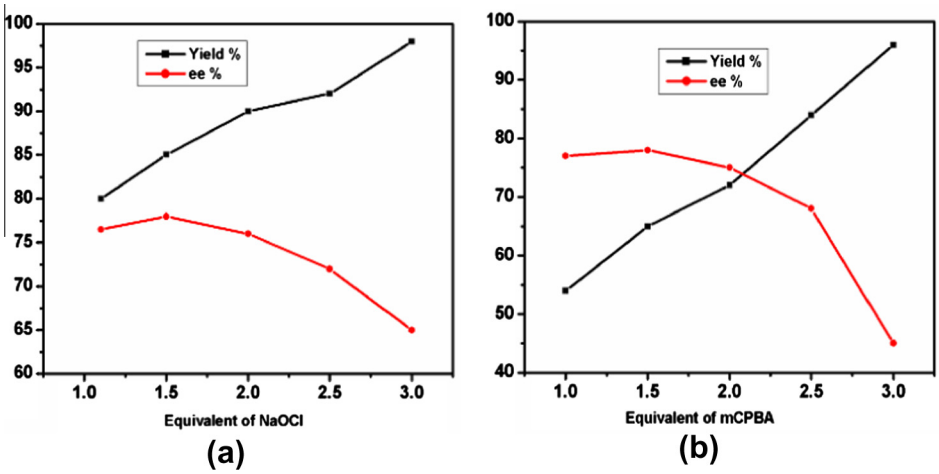


Figure 3. Effect of the amount of (a) NaOCl and (b) *m*CPBA on the enantioselective epoxidation of 2,2-dimethylchromene (4 mol % of **20** was used in both cases).

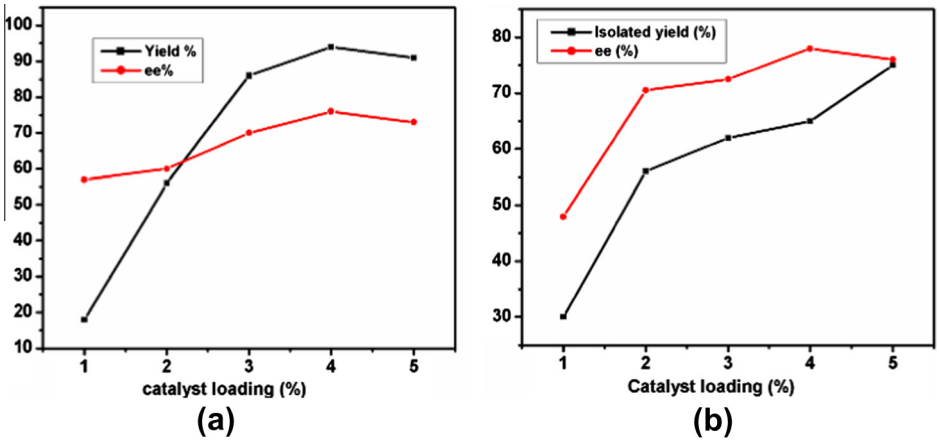
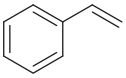
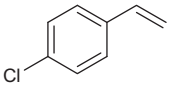
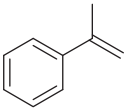
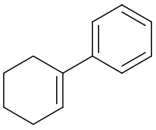
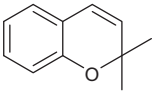
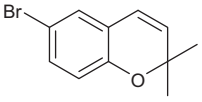
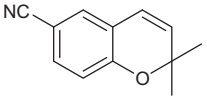


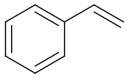
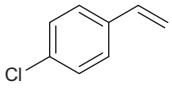
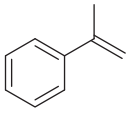
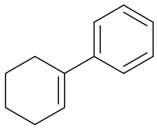
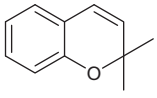
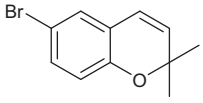
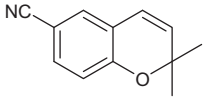
Figure 4. Effect of catalyst loading on the enantioselective epoxidation of 2,2-dimethylchromene with (a) NaOCl (2 equiv) and (b) *m*CPBA (1.5 equiv) as terminal oxidant.

Table 2
Asymmetric epoxidation of various prochiral olefins using binol based macrocyclic manganese complexes

Entry	Prochiral olefines	NaOCl 0 °C						Config.
		Yield[a] (%)			ee[b] (%)			
		20	**21**	**22**	**20**	**21**	**22**	
1		92	80	82	20	25	28	(*R*)
2		80	76	78	12	20	26	(*R*)
3		87	90	92	43	41	62	(*R*)
4		97	94	90	57	58	65	(*R*,*R*)
5		94	96	70	78	81	85	(*R*,*R*)
6		95	90	82	85	85	89	(*R*,*R*)
7		93	91	90	92	90	94	(*R*,*R*)

[a] Isolated yield.
[b] Enantiomeric excess was determined by chiral GC using a β-DEX column.

Table 3
Asymmetric epoxidation of various prochiral olefins using binol based macrocyclic manganese complexes

Entry	Prochiral olefines	mCPBA −78 °C						Config.
		Yield[a] (%)			ee[b] (%)			
		20	**21**	**22**	**20**	**21**	**22**	
1		72	70	80	25	22	30	(*R*)
2		68	67	72	22	18	25	(*R*)
3		78	72	85	47	38	60	(*R*)
4		85	80	87	61	52	63	(*R*,*R*)
5		65	70	70	78	80	84	(*R*,*R*)
6		80	68	82	84	83	87	(*R*,*R*)
7		82	73	87	87	86	92	(*R*,*R*)

[a] Isolated yield.
[b] Enantiomeric excess was determined by chiral GC using a β-DEX column.

with moderate enantiomeric excess. Irrespective of the catalyst systems, 2,2-dimethylchromene, 6-bromo-2,2-dimethylchromene, and 6-cyano-2,2-dimethylchromene afforded the (*R*,*R*)-epoxides in almost quantitative yields and with good enantiomeric excesses.

3. Conclusion

A facile method for the synthesis of [1+1] chiral macrocyclic Schiff bases is described. Chiral dialdehydes afforded [1+1] macrocycles in higher yields with chiral diamines. The catalyst structure was tuned by incorporating lengthy spacers and bulkier groups, which displayed increased catalytic activity and enantioselectivity forming epoxides in over 94% ee. Cyclic olefins were found to be better substrates than acyclic olefins with NaOCl as the oxidant of choice.

4. Experimental

4.1. General

^{1}H NMR spectra were recorded on a 400 MHz Bruker AVANCE 400 spectrometer and ^{13}C NMR spectra were recorded on a 400 MHz Bruker AVANCE 400 spectrometer, respectively, using TMS as the internal standard. IR spectra were recorded on a Perkin–Elmer FT/IR 100 spectrometer. Mass spectra were recorded on a MALDI TOF mass spectrometer. Optical rotations were measured by a Rudolph Autopol V polarimeter. All reactions were monitored by thin layer chromatography (TLC). TLC was performed on F254, 0.25 mm silica gel plates (Merck). Plates were eluted with appropriate solvent systems, and then stained with either alkali $KMnO_4$ or ceric ammonium molybdate solutions prepared in the laboratory. The developed plates were first analyzed under UV 254 nm, then stained with the appropriate reagent. Column chromatography was performed using silica gel with particle size 100–200 mesh. Enantiomeric excess values were determined by GC with a chiral β-cyclodextrin capillary column (RESTEK RT-BetaDEXse, 30 m × 0.25 mm × 0.25 μm).

4.2. General experimental procedure for synthesis of chiral binapthyl dialdehydes

At first, (*S*)-2,2′-dihydroxy-1,1′-binaphthyl-3-carbaldehyde **4** (1 mmol), diacids (0.5 mmol), and a catalytic amount of dimethylaminopyridne DMAP (0.2 mmol) were dissolved in 10 mL of dry CH_2Cl_2 and stirred for 15 min at room temperature. The solution was cooled to 0 °C and then added immediately to (1-(3-dimethylaminopropyl)-3-ethyl carbodiimide (EDCl) (1.5 mmol) under a nitrogen atmosphere. The reaction mixture was allowed to return to room temperature and stirred for 2 h. After completion of the reaction, as indicated by TLC, CH_2Cl_2 was removed under reduced pressure and the reaction mixture was diluted with EtOAc. The organic layer was washed with water dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure to give the crude compound. Purification of the crude compound by column chromatography over silica gel using 20% EtOAc in hexane as an eluent afforded pure binapthyl bis(hydroxylaldehydes) **5**–**7** as a yellow solid in 73–96% yield

4.2.1. Spectroscopic data for 5

(Yield 73%); $[\alpha]_D^{20} = -152.3$ (*c* 0.65, $CHCl_3$); IR (KBr): 795, 1117, 1142, 1253, 1290, 1440, 1505, 1632, 1652, 1752, 2859, 3029, 3190 cm^{-1}; ^{1}H NMR [400 MHz, $CDCl_3$] δ 2.04–2.40 (m, 4H), 7.29–

7.40 (m, 14H), 7.97–8.04 (m, 6H), 8.27 (s, 2H), 10.13 (s, 2H), 10.49 (s, 2H); ^{13}C NMR [400 MHz, $CDCl_3$] δ 27.9, 115.9, 121.2, 121.2, 122.3, 123.8, 124.6, 125.0, 125.2, 126.2, 126.6, 127.7, 129.1, 129.1, 129.9, 131.2, 132.5, 136.6, 137.7, 146.1, 152.8, 169.3, 196.0; ESI-MS: *m*/*z* 711 ([M+H]$^+$).

4.2.2. Spectroscopic data for 6

(Yield 97%); $[\alpha]_D^{20} = -221$ (*c* 1.4, CH_2Cl_3); IR (KBr): 754, 777, 790, 1119, 1147, 1254, 1295, 1442, 1505, 1630, 1655, 1754, 2853, 3060, 3193 cm^{-1}; ^{1}H NMR [400 MHz, $CDCl_3$] δ 0.95–0.99 (m, 2H), 1.49–1.60 (m, 4H), 7.11–7.39 (m, 14H), 7.78–7.94 (m, 6H), 8.14 (s, 2H), 10.02 (s, 2H), 10.41(s, 2H); ^{13}C NMR [400 MHz, $CDCl_3$] δ 19.2, 32.4, 116.6, 121.8, 123.1, 124.5, 125.3, 125.6, 125.8, 126.8, 127.2, 128.3, 129.7, 129.8, 131.1, 133.1, 137.2, 138.3, 146.8, 153.4, 170.5, 196.7; ESI-MS: *m*/*z* 747 ([M+Na]$^+$).

4.2.3. Spectroscopic data for 7

(Yield 95%); $[\alpha]_D^{20} = -40.1$ (*c* 0.4, $CHCl_3$); IR (KBr): 750, 773, 794, 1119, 1146, 1250, 1298, 1444, 1507, 1638, 1659, 1742, 2855, 3020, 3197 cm^{-1}; ^{1}H NMR [400 MHz, $CDCl_3$] δ 0.70–0.71 (m, 4H), 1.62–1.67 (m, 4H), 7.17–7.52 (m, 14H), 7.90–8.06 (m, 6H), 8.27 (s, 2H), 10.15 (s, 2H), 10.50 (s, 2H); ^{13}C NMR [400 MHz, $CDCl_3$] δ 25.6, 35.5, 118.9, 123.9, 124.0, 125.2, 126.6, 127.5, 127.8, 127.9, 128.9, 129.4, 130.5, 131.7, 131.8, 132.7, 134.0, 135.3, 139.4, 140.3, 149.0, 155.6, 173.1, 198.8; ESI-MS: *m*/*z* 739 ([M+H]$^+$).

4.2.4. Spectroscopic data for 8

(Yield 50%); $[\alpha]_D^{20} = -123.8$ (*c* 0.82 $CHCl_3$); IR (KBr): 756, 779, 802, 1122, 1148, 1259, 1304, 1451, 1515, 1641, 1662, 1747, 2859, 3028, 3112 cm^{-1}; ^{1}H NMR [400 MHz, $CDCl_3$] δ 1.72 (s, 3H), 7.17–7.38 (m, 7H), 7.85–7.95 (m, 3H), 8.23 (s, 1H), 10.10 (s, 1H), 10.40 (s, 1H); ^{13}C NMR [400 MHz, $CDCl_3$] δ 20.6, 116.8, 121.8, 121.9, 123.1, 124.5, 125.7, 125.7, 126.8, 127.3, 128.3, 129.6, 129.7, 130.6, 131.8, 133.2, 137.3, 138.3, 147.0, 153.4, 169.1, 196.6; ESI-MS: *m*/*z* 357 ([M+H]$^+$).

4.3. General experimental procedure for the synthesis of [*n*+*n*] macrocycles under microwave irradiation

The chiral diamine salt (1.2 equiv) and K_2CO_3 (2.4 equiv) were weighed in a boiling tube. Next, 3 mL of water was added to form a clear solution. The dialdehyde (1 equiv) was then weighed in a separate boiling tube and dissolved in 3 mL of ethanol to form a clear solution. The aldehyde solution was added in one portion to the boiling tube containing a diamine salt and potassium carbonate to form a pale yellow solution. The reverse addition however did not produce any macrocycle and resulted in polymeric materials. The yellow solution was irradiated in a domestic microwave oven for a total time period of 5 min. The immediate appearance of a yellow solid was observed and the mixture was cooled after every 1 min period of irradiation. The mixture was finally filtered, and washed with ethanol and water. Ethyl acetate was then added to the reaction mixture and the insoluble materials were filtered again. The ethyl acetate layer was dried over anhydrous Na_2SO_4 and concentrated to yield the crude product, which was purified by a short-path column chromatography over silica gel to give pure [n+n] macrocycles.

4.3.1. Spectroscopic data for 12

(Yield 97%); $[\alpha]_D^{25} = -642$ (*c* 1.0, $CHCl_3$); IR (KBr) *v* 735, 1121, 1435, 1592, 1631, 1754, 2858, 2925, 3383 cm^{-1}; ^{1}H NMR [400 MHz, $CDCl_3$] δ 1.13–1.16 (m, 2H), 1.18–1.22 (m, 4H), 1.38–1.40 (m, 2H), 1.80–1.83 (m, 4H), 3.28–3.30 (d, *J* = 9.6 Hz, 2H), 6.88–6.90 (d, *J* = 8.4 Hz, 2H), 7.13–7.33 (m, 10H), 7.37–7.41 (t, *J* = 7.6 Hz, 2H), 7.75–7.77 (d, *J* = 8.4 Hz, 2H), 7.86–7.92 (m, 6H), 8.54 (s, 2H), 12.92 (s, 2H); ^{13}C NMR [400 MHz, $CDCl_3$] δ 24.0, 32.7, 60.4, 72.7, 113.5, 114.3, 117.7, 120.6, 123.3, 123.9, 124.5, 124.7, 126.5, 127.7, 128.2, 129.0, 129.2, 129.2, 130.0, 133.5, 134.7, 135.2, 151.5, 155.4, 164.9, 171.2. MALDI-TOF-MS: *m*/*z* 788.5 ([M+H]$^+$).

4.3.2. Spectroscopic data for 13

(Yield 89%); $[\alpha]_D^{25} = -20.6$ (*c* 0.2, $CHCl_3$); IR (KBr): 732, 811, 1115, 1203, 1348, 1508, 1628, 1753, 2852, 2922, 3055 cm^{-1}; ^{1}H NMR [400 MHz, $CDCl_3$] δ 1.8–1.94 (m, 2H), 2.79–2.99 (m, 4H), 3.55 (s, 2H), 4.00 (s, 2H), 7.03–7.34 (m, 20H), 7.79–7.88 (m, 8H), 8.84 (s, 2H), 13.07 (s, 2H); ^{13}C NMR [400 MHz, $CDCl_3$] δ 23.4, 58.3, 58.5, 73.8, 113.1, 116.3, 119.3, 122.8, 123.4, 123.4, 125.3, 126.4, 127.0, 127.4, 127.5, 127.8, 128.0, 128.9, 132.2, 133.7, 134.1, 150.1, 154.1, 164. MALDI-TOF-MS: *m*/*z* 866 ([M+H]$^+$).

4.3.3. Spectroscopic data for 14

(Yield 78%); $[\alpha]_D^{25} = -312.5$ (*c* 1.0, $CHCl_3$); IR (KBr) *v* 698, 733, 890, 1115, 1204, 1345, 1443, 1631, 1751, 2859, 3058 cm^{-1}; ^{1}H NMR [400 MHz, $CDCl_3$] δ 0.69–0.76 (m, 2H), 1.00–1.40 (m, 2H), 3.45 (s, 2H), 3.54–3.61 (m, 4H), 4.24–4.27 (d, *J* = 12.2 Hz, 2H), 4.29–4.32 (d, *J* = 12.2 Hz, 2H), 6.82–7.44 (m, 22H), 7.60–7.83 (m, 8H), 8.35 (s, 2H), 12.75 (s, 2H);^{13}C NMR [400 MHz, $CDCl_3$] δ 32.9, 70.8, 71.0, 73.4, 115.2, 120.1, 121.9, 123.5, 124.9, 125.6, 126.3, 126.9, 127.5, 127.7, 127.8, 128.2, 128.3, 129.0, 129.4, 132.1, 133.6, 134.9, 137.7, 137.8, 146.9, 154.6, 167.0, 170.3. ESI-MS: *m*/*z* 947 ([M+H]$^+$).

4.3.4. Spectroscopic data for 15

(Yield 94%); $[\alpha]_D^{25} = -123.8$ (*c* 0.3, $CHCl_3$); IR (KBr) *v* 739, 1133, 1435, 1582, 1630, 1751, 2859, 2919, 3380 cm^{-1}; ^{1}H NMR [400 MHz, $CDCl_3$] δ 0.24–0.27 (m, 2H), 0.98–1.06 (m, 2H), 1.12–1.33 (m, 2H), 1.66–1.76 (m, 4H), 1.92–2.02 (m, 4H), 3.40–3.43 (dd, *J* = 4 Hz, *J* = 8 Hz, 2H), 7.08–7.10 (d, *J* = 8.4 Hz, 2H), 7.28–7.56(m, 12H), 7.88–7.90 (d, *J* = 8.4 Hz, 2H), 8.00 (s, 2H), 8.02–8.04 (d, *J* = 8.4 Hz, 2H), 8.07–8.10 (d, *J* = 8.8 Hz, 2H), 8.66 (s, 2H), 13.12 (s, 2H); ^{13}C NMR [400 MHz, $CDCl_3$] δ 18.8, 24.2, 32.8, 60.4, 73.6, 76.7, 115.2, 120.1, 121.7, 123.3, 124.8, 125.0, 125.6, 126.0, 126.7, 127.1, 128.2, 128.3, 128.6, 129.4, 132.0, 133.4, 134.3, 134.7, 146.7, 154.5, 164.9, 170.1. MALDI-TOF-MS: *m*/*z* 802 ([M+H]$^+$).

4.3.5. Spectroscopic data for 16

(Yield 91%); $[\alpha]_D^{25} = -195.3$ (*c* 0.63, $CHCl_3$); IR (KBr) *v* 692, 737, 1125, 1209, 1335, 1445, 1634, 1753, 2869, 3061 cm^{-1}; ^{1}H NMR [400 MHz, $CDCl_3$] δ 0.203–0.167 (m, 2H), 0.95–0.87 (m, 2H), 1.26–1.19 (m, 2H), 3.63–3.61 (m, 2H), 3.80–3.73 (m, 4H), 4.50–4.42 (dd, *J* = 12 Hz, *J* = 12 Hz, 4H), 7.03–7.01 (d, *J* = 8 Hz, 2H), 7.48–7.20 (m, 20H), 7.81–7.79 (d, *J* = 7.6 Hz, 2H), 7.96–7.94 (d, *J* = 8.4 Hz, 2H), 7.92 (s, 2H), 8.02–7.99 (d, *J* = 8.8 Hz, 2H), 12.94 (s, 2H), 8.54 (s, 2H); ^{13}C NMR [400 MHz, $CDCl_3$] δ 18.9, 32.1, 70.6, 73.3, 115.1, 120.0, 121.8, 123.4, 124.8, 125.6, 126.0, 126.7, 127.2, 127.6, 127.7, 128.3, 128.4, 128.8, 129.4, 132.0, 134.7, 137.7, 146.8, 154.5, 166.9, 170.25. MALDI-TOF-MS: *m*/*z* 989 ([M+H]$^+$).

4.3.6. Spectroscopic data for 17

(Yield 96%); $[\alpha]_D^{25} = -185.4$ (*c* 0.3 $CHCl_3$); IR (KBr) *v* 741, 1137, 1439, 1579, 1632, 1748, 2859, 2921, 3382 cm^{-1}; ^{1}H NMR [400 MHz, $CDCl_3$] δ −0.557 (m, 2H), −0.24 (m, 2H), 0.80–0.76 (m, 2H), 1.18–0.98 (m, 2H), 1.41–1.36 (m, 2H), 1.76–1.66 (m, 2H), 1.86–1.77 (m, 4H), 3.43–3.40 (d, *J* = 9.2 Hz, 2H), 6.93–6.91 (d, *J* = 7.6 Hz, 2H), 7.39–7.11 (m, 12H), 7.71–7.69 (d, *J* = 7.6 Hz, 2H), 7.88–7.86 (d, *J* = 7.6 Hz, 4H), 7.94–7.92 (d, *J* = 8.8 Hz, 2H), 8.53 (s, 2H), 13.03 (s, 2H); ^{13}C NMR [400 MHz, $CDCl_3$] δ 18.8, 24.2, 32.8, 60.4, 73.6, 76.7, 115.2, 120.1, 121.7, 123.3, 124.8, 125.0, 125.6, 126.0, 126.7, 127.1, 128.2, 128.3, 128.6, 129.4, 132.0, 133.4, 134.3, 134.7, 146.7, 154.5, 164.9, 170.11. MALDI-TOF-MS: *m*/*z* 816.5 ([M+H]$^+$).

4.3.7. Spectroscopic data for 18

(Yield 84%); $[\alpha]_D^{25} = -256.4$ (c 0.73, $CHCl_3$); IR (KBr): 730, 815, 1120, 1339, 1505, 1627, 1750, 2856, 2924, 3058 cm^{-1}; ^1H NMR [400 MHz, $CDCl_3$] δ −0.01 (m, 2H), −0.00 (m, 2H), 3.31–3.23 (m, 4H), 3.96–3.92 (m, 2H), 4.26 (t, J = 5.8 Hz 2H), 7.38–7.37 (d, J = 4.8 Hz, 2H), 7.47–7.39 (m, 18H), 7.55–7.53 (d, J = 8.8 Hz, 2H), 8.11–8.08 (d, J = 8 10 Hz, 4H), 8.16–8.14 (d, J = 8.8 Hz, 2H), 8.79 (s, 2H), 13.12 (s, 2H); ^{13}C NMR [400 MHz, $CDCl_3$] δ 25.2, 35.6, 59.3, 62.6, 77.3, 117.7, 122.1, 123.7, 125.8, 126.7, 127.2, 127.6, 128.0, 128.7, 129.2, 130.2, 130.3, 130.4, 130.7, 131.5, 134.0, 136.1, 137.2, 148.8, 156.3, 168.6, 172.6. ESI-MS: m/z 894 ($[M+H]^+$).

4.3.8. Spectroscopic data for 19

(Yield 89%); $[\alpha]_D^{25} = -149.8$ (c 0.1, $CHCl_3$); IR (KBr) ν 737, 1121, 1207, 1336, 1445, 1629, 1749, 2865, 3059 cm^{-1}; ^1H NMR [400 MHz, $CDCl_3$] δ −0.43–0.45 (m, 2H), −0.12 to 0.14 (m, 2H), 1.25–1.18 (m, 2H), 3.64–3.62 (m, 2H), 3.77–3.76 (m, 4H), 4.49–4.43 (dd, J = 12 Hz, J = 12 Hz, 4H), 7.19–7.18 (d, J = 5.4 Hz, 2H), 7.40–7.19 (m, 20H), 7.95–7.93 (m, 6H), 8.01–7.99 (d, J = 8.8 Hz, 2H), 8.56 (s, 2H), 12.84 (s, 2H); ^{13}C NMR [400 MHz, $CDCl_3$] δ 22.3, 32.9, 70.5, 71.8, 73.3, 115.5, 120.2, 123.5, 125.1, 125.5, 125.9, 126.6, 127.1, 127.5, 127.6, 127.6, 128.2, 128.8, 128.3, 128.3, 128.5, 129.4, 131.9, 134.0, 137.6, 146.8, 154.5, 166.3, 171.14. ESI-MS: m/z 1003 ($[M+H]^+$).

4.4. Synthesis of binol based [1+1] macrocyclic Mn(III) Cl

An ethanol solution of new ligands **12**, **15**, and **17** (1.0 mmol) was stirred with an ethanol solution of $Mn(OAc)_2{\cdot}4H_2O$ (3.0 mmol) under a nitrogen atmosphere at reflux for 6 h. The reaction mixture was cooled to room temperature. Next, lithium chloride (6.0 mmol) was added and the resulting mixture was refluxed for an additional 2 h while being exposed to air. The solvent was removed under reduced pressure and the residue was extracted with dichloromethane (3 × 10 mL). The extract was washed with water (2 × 10 mL), brine, dried over anhydrous Na_2SO_4, and then concentrated to give the crude product. The crude product was recrystallized with petroleum ether to afford the desired complexes.

4.4.1. Compound 20

Dark brown powder (73% yield). $[\alpha]_D^{25} = -43.6$ (c 0.2, $CHCl_3$); LC–MS: m/z 841.3 $[M-Cl]^+$. Anal. Calcd for $C_{52}H_{38}ClMnN_2O_6$: C, 71.19; H, 4.37; Cl, 4.04; Mn, 6.26; N, 3.19; O, 10.94. Found: C, 71.23; H, 4.40; Cl, 4.10; Mn, 6.31; N, 3.21; O, 11.01. FT-IR (KBr): 730, 1127, 1427, 1576, 1612, 1748, 2861, 2920, 3385 cm^{-1}.

4.4.2. Compound 21

Dark brown powder (80% yield). $[\alpha]_D^{25} = -123.5$ (c 0.52, $CHCl_3$); LC–MS: m/z 855.2 $[M-Cl]^+$. Anal. Calcd for $C_{53}H_{40}ClMnN_2O_6$: C, 71.42; H, 4.52; Cl, 3.98; Mn, 6.16; N, 3.14; O, 10.77. Found: C, 71.48; H, 4.58; Cl, 4.02; Mn, 6.20; N, 3.16; O, 10.81. FT-IR (KBr): 733, 1124, 1420, 1572, 1609, 1738, 2863, 2925, 3375 cm^{-1}.

4.4.3. Compound 22

Dark brown powder (86% yield). $[\alpha]_D^{25} = -19.5$ (c 0.1, $CHCl_3$); LC–MS: m/z 869.1 $[M-Cl]^+$. Anal. Calcd for $C_{54}H_{42}ClMnN_2O_6$: C, 71.64; H, 4.68; Cl, 3.92; Mn, 6.07; N, 3.09; O, 10.60. Found: C, 71.68; H, 4.71; Cl, 3.98; Mn, 6.11; N, 3.12; O, 10.65. FT-IR (KBr): 738, 1134, 1429, 1582, 1618, 1742, 2867, 2925, 3382 cm^{-1}.

4.5. General procedure for the preparation of chiral epoxides

4.5.1. Using *m*CPBA as the terminal oxidant

A solution of olefin (0.5 mmol), catalyst (0.02 mmol), and NMO·H_2O (2.5 mmol) in 5 mL of CH_2Cl_2 was cooled to the appropriate temperature. Then pre-cooled solid *m*CPBA (1.0 mmol) was added in two roughly equal portions. When the reaction was complete, NaOH (5 mL, 1.0 M) was added and the organic layer was separated. This was further washed with distilled water and the combined organic extracts were collected and dried over anhydrous Na_2SO_4. After concentration, the crude product was purified by column chromatography on silica gel.

4.5.2. Using NaOCl as the terminal oxidant

A solution of olefin (0.5 mmol), catalyst (0.02 mmol), and PPNO (0.1 mmol) in 5 mL of CH_2Cl_2 was cooled to the appropriate temperature, after which pre-cooled commercially available 4% NaOCl solution (1.0 mmol) was added dropwise to the solution in three roughly equal portions over 30 min. The resulting biphasic solution was stirred at 0 °C for 10–12 h which indicated the completion of the reaction. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 3 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated to yield the crude product, which was purified by column chromatography over silica-gel using EtOAc/hexane as eluent to yield the pure epoxide.

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11. *Crystal data for* ***8*** *(rectangular shaped crystal):* $C_{23}H_{16}O_4$, M = 536.36 monoclinic, space group P_{21}, a = 9.4831(8), b = 11.9851(12), c = 16.3703(16) Å, β = 103.336(4)°. V = 1810.4(3) Å^3, Z = 4, d_{calcd} = 1.307 mg m^{-3}, T = 293 (2) K, Enraf Nonius CAD4 diffractometer, Cu-Kα (λ = 1.5418 Å), = 0.084 mm^{-1}, collected reflections 14,120, unique 5427 (R_{int} = 0.0497), $2\lambda_{max}$ = 24.99°, Final R indices [$I > 2\sigma(I)$]: R_1 (observed) = 0.0621, wR_2 = 0.1620R (all data): R_1 = 0.0743, wR_2 = 0.1698, GOF (F_2) = 1.068. CCDC number 931673.
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