Pergamon

Tetrahedron 56 (2000) 417–424

TETRAHEDRON

Asymmetric Epoxidation of Unfunctionalized Alkenes with Ammonium and Phosphonium Monopersulfates Catalyzed by Chiral Mn(III)–Salen Complexes

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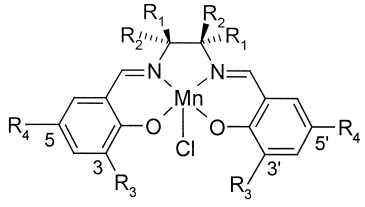
Received 16 June 1999; revised 20 October 1999; accepted 11 November 1999

Abstract—Simple *cis*-disubstituted and trisubstituted alkenes were enantioselectively epoxidized in mild conditions using various Mn(III)–salen complexes as catalysts and quaternary ammonium and phosphonium monopersulfates (Bu_4NHSO_5, Ph_4PHSO_5) as oxidants together with amine *N*-oxides as additives. The effect of the catalyst structure on the stereochemical outcome of the epoxidation reactions was studied. Generally, the 1,2-diphenylethylenediamine-derived complexes were found to give higher asymmetric induction compared to their 1,2-diaminocyclohexane-derived counterparts. Particularly high yields of epoxides (up to 98%) and good enantiomeric excesses (ee up to 93%) were obtained in the epoxidation of 2,2-dialkylchromenes and trisubstituted alkenes.

Optically active epoxides are valuable intermediates in organic chemistry because they can undergo stereospecific ring-opening reactions giving rise to a wide variety of biologically and pharmaceutically important compounds. During the last decade, chiral (salen)Mn(III) complexes have emerged as efficient and practical catalysts for the asymmetric epoxidation of various unfunctionalized *cis*-disubstituted, tri- and tetra-substituted alkenes.[1–3] Several different stoichiometric oxidants have been discovered to be effective oxygen atom donors in these reactions, most of the epoxidations being conducted using iodosylbenzene[2] or NaOCl[3]. Other common oxidants that have been explored with (salen)Mn(III) complexes such as **1**–**8** (Scheme 1) include MCPBA,[4] molecular oxygen,[5] dimethyldioxirane,[6] H_2O_2,[7] periodates,[8] and recently also potassium monopersulfate (Oxone®, $2KHSO_5–KHSO_4–K_2SO_4$).[4,9]

Oxone is a strong, cheap and versatile oxidising agent that has previously been studied in metalloporphyrin-catalyzed oxidations.[10] It is an efficient single oxygen atom donor since it contains a non-symmetrical O–O bond which is heterolytically cleaved during the oxidation cycle catalyzed by transition metal complexes (porphyrins, salen compounds). It has some disadvantages: it is insoluble in organic solvents, buffering is needed due to its acidity, and it sometimes bleaches the metal catalysts and donor ligands during oxidation reactions. On the other hand, it has recently been successfully applied to the asymmetric epoxidation of *trans*-alkenes using chiral ketones as catalysts.[11] Tetrabutylammonium monopersulfate (Bu_4NHSO_5) is a solid easily prepared from Oxone.[12,13] Unlike Oxone, it is readily soluble in various organic solvents and usually used in CH_2Cl_2 for the mild oxidation of sensitive compounds.[12,14] It has also been used in oxidations catalyzed by transition metal complexes with varying results.[15]

Very recently, simple alkenes were epoxidized in this laboratory with Bu_4NHSO_5 catalyzed by Mn(III)–salen complexes **1** and **5** together with *N*-methylmorpholine *N*-oxide acting as proximal ligand.[16] Generally, the results were good, with electron-rich alkenes the yields and ee's of the corresponding epoxides exceeded 90%. Surprisingly, asymmetric epoxidations conducted using commercially available "Jacobsen's" catalyst **5**, in many cases the catalyst of choice, gave considerably lower yields and ee's



Scheme 1. (*S*,*S*)-**1**: R_1=Ph, R_2=H, R_3=*t*-Bu, R_4=Me. (*R*,*R*)-**1**: R_1=H, R_2=Ph, R_3=*t*-Bu, R_4=Me. (*S*,*S*)-**2**: R_1=Ph, R_2=H, R_3=*t*-Bu, R_4=*t*-Bu. (*S*,*S*)-**3**: R_1=Ph, R_2=H, R_3=*t*-Bu, R_4=OSi(*i*-Pr)$_3$. (*S*,*S*)-**4**: R_1=Ph, R_2=H, R_3=C(Me)$_2$Ph, R_4=Me. (*S*,*S*)-**5**: R_1,R_1=–(CH$_2$)$_4$–, R_2=H, R_3=*t*-Bu, R_4=*t*-Bu.(*R*,*R*)-**6**: R_1=H, R_2,R_2=–(CH$_2$)$_4$–, R_3=*t*-Bu, R_4=Me. (*R*,*R*)-**7**: R_1=H, R_2,R_2=–(CH$_2$)$_4$–, R_3=*t*-Bu, R_4=C(Ph)$_3$. (*R*,*R*)-**8**: R_1=H, R_2,R_2=–(CH$_2$)$_4$–, R_3=C(Me)$_2$Ph, R_4=*t*-Bu.

Keywords: asymmetric reactions; epoxidations; catalysts.

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0040–4020/00/$ - see front matter
PII: S0040-4020(99)01008-X

compared with the values obtained using catalyst **1**. These results prompted the further study of the Bu_4NHSO_5/NMO oxidation system. Here we report the results of the asymmetric epoxidation of simple alkenes using structurally varied catalysts **1**–**8** together with Bu_4NHSO_5 and amine *N*-oxides. Also a quaternary phosphonium monopersulfate, Ph_4PHSO_5, which has earlier been used as a mild oxidant in kinetic and mechanistic studies concerning certain Mn(III)-porphyrins,[17] was studied as a potential oxidant in asymmetric salen-catalyzed epoxidations.

Results and Discussion

Asymmetric epoxidation of 6,7-dihydro-5*H*-benzocycloheptene with monopersulfates under different reaction conditions

Tetrabutylammonium monopersulfate is easily prepared by two similar methods from Oxone and Bu_4NHSO_4.[12,15a] The original procedure by Trost et al. gave a product with Bu_4NHSO_5 content of 37% (the rest consisting of Bu_4NHSO_4 and $[Bu_4N]_2SO_4$) and the modification of Campestrini et al. afforded Bu_4NHSO_5 with a purity of 88%. Here, the epoxidations were performed using the purer oxidant, which produced the epoxides with somewhat higher asymmetric induction.[16] Tetraphenylphosphonium monopersulfate was obtained using a similar procedure from Oxone and Ph_4PCl with a purity of 89%.[17a] The epoxidations were conducted in CH_3CN containing the substrate, oxidant, nitrogen heterocycle additive, and salen catalyst **1**–**8** in a molar ratio of 0.40:0.56–0.65:0.10–0.40:0.0012–0.0028. The results are summarized in Tables 1 and 2.

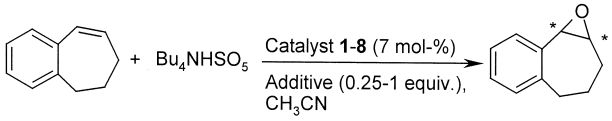
First, the epoxidation of a simple model substrate, 6,7-dihydro-5*H*-benzocycloheptene, was studied under different reaction conditions using the catalyst **1** (results in Table 1) together with Bu_4NHSO_5. The reaction proceeded smoothly at 2°C giving the epoxide of 89% ee in 59% yield (entry 1). Lowering the temperature from 2 to −18°C increased the yield to 72% but had practically no effect on the ee of the epoxide (entry 2). Further lowering of the temperature resulted in retardation of the reaction rate (entry 3) and a slight increase in ee. After 5 h reaction time at −46°C the ^1H NMR analysis of the reaction mixture showed the presence of the epoxide and alkene in a ratio of 85:15, the isolated yield of the epoxide being 57% (at −74°C the epoxide/olefin ratio was only 34:66 after 5 h). Epoxidations were also conducted in CH_2Cl_2, which resulted in longer reaction times (e.g. at −18°C reaction time extended from 1.5 to 2.5 h, entry 2), but the yield and ee of the epoxide were practically identical in both solvents.

Using an aromatic amine *N*-oxide, picoline *N*-oxide, as an additive in the place of NMO gave equally good yields and ee's (entry 5). On the other hand, imidazole was not an effective donor ligand. The rate of the epoxidation reaction was similar to that using the amine *N*-oxides but the yield of the epoxide and enantioselectivity were lower (entry 6). The reason may be the tendency of imidazole to degrade in the presence of many oxidants, e.g. $KHSO_5$,[10] although in some cases it has been used successfully in asymmetric epoxidations of chromene derivatives.[9] Also, when the epoxidation was performed using substoichiometric amount of the *N*-oxide additives the ee of the epoxide was slightly reduced (entry 4).

Electronic and steric effects in asymmetric epoxidations with monopersulfates

It was earlier reported, that when the epoxidation of

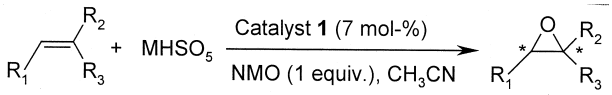
Table 1. Asymmetric epoxidation of 6,7-dihydro-5*H*-benzocycloheptene with Bu_4NHSO_5 and catalysts **1**–**8** (reactions were performed in CH_3CN (2.2 ml). Molar ratio of alkene:oxidant:additive:catalyst=0.40:0.65:0.10–0.40:0.012–0.028)

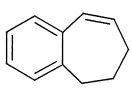
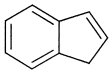
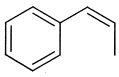
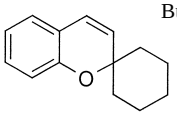


Entry	Catalyst	Additive (equiv.)[a]	Temperature (°C)	Time (h)	Yield[b] (%)	ee[c] (%)	Epoxide configuration[d]
1	(*S*,*S*)-**1**	NMO (1.0)	2	1	59	89	5*S*,6*R*-(+)
2	(*S*,*S*)-**1**	NMO (1.0)	−18	1.5 (2.5)[e]	72	90	5*S*,6*R*-(+)
3	(*S*,*S*)-**1**	NMO (1.0)	−46	5	57 (80)[f]	92	5*S*,6*R*-(+)
4	(*S*,*S*)-**1**	NMO (0.25)	−18	1.75	74	84	5*S*,6*R*-(+)
5	(*R*,*R*)-**1**	PicNO (1.0)	2	1	72	89	5*R*,6*S*-(−)
6	(*R*,*R*)-**1**	Imid. (1.0)	2	1	67	80	5*R*,6*S*-(−)
7	(*S*,*S*)-**2**	NMO (1.0)	−18	1.25	78	88	5*S*,6*R*-(+)
8	(*S*,*S*)-**3**	NMO (1.0)	2	3.5	62	80	5*S*,6*R*-(+)
9	(*S*,*S*)-**4**	NMO (1.0)	2	3	70	80	5*S*,6*R*-(+)
10	(*S*,*S*)-**5**	NMO (1.0)	2	2.5	52	72	5*S*,6*R*-(+)
11	(*R*,*R*)-**6**	NMO (1.0)	2	3.5	60	74	5*R*,6*S*-(−)
12	(*R*,*R*)-**7**	NMO (1.0)	2	3	49	60	5*R*,6*S*-(−)
13	(*R*,*R*)-**8**	NMO (1.0)	2	1.5	66	83	5*R*,6*S*-(−)

[a] Relative to olefin. NMO=*N*-methylmorpholine *N*-oxide, PicNO=picoline *N*-oxide, Imid.=imidazole.
[b] Yield of the isolated epoxide.
[c] Determined by ^1H NMR analysis in the presence of $Eu(hfc)_3$.
[d] Determined by comparison of the sign of $[\alpha]_D$ to the literature values.
[e] Reaction was conducted in CH_2Cl_2.
[f] Yield in parentheses is calculated from the reacted olefin.

Table 2. Asymmetric epoxidation of various alkenes with monopersulfates using catalyst **1** (for general conditions see Table 1. Reactions with Ph_4PHSO_5 were performed in 3.2 ml of CH_3CN)



Entry	Alkene	Oxidant ($MHSO_5$)	Temperature (°C)	Time (h)	Yield (%)	ee (%)
1		Bu_4NHSO_5	−18	1.5	72	90
2	〃	Ph_4PHSO_5	−18	1.25	78	91
3		Bu_4NHSO_5	−18	1	75	72
4	〃	Ph_4PHSO_5	2	1	79	71
5	〃	Ph_4PHSO_5	−18	1	78	75
6		Bu_4NHSO_5	−18	1	72[a]	87[b]
7	〃	Ph_4PHSO_5	2	1	64[c]	88[b]
8	〃	Ph_4PHSO_5	−18	1.25	66[d]	89[b]
9		Bu_4NHSO_5	−18	1.25	86	91
10	〃	Ph_4PHSO_5	−18	1.5	86	89
11		Bu_4NHSO_5	−18	1	97	93
12[e]	〃	Bu_4NHSO_5	−18	2.5	86	85
13	〃	Ph_4PHSO_5	−18	1	98	91

[a] A mixture of *cis*- and *trans*-epoxides (8.3:1).
[b] ee of the *cis*-epoxide.
[c] A mixture of *cis*- and *trans*-epoxides (7.8:1).
[d] A mixture of *cis*- and *trans*-epoxides (9.4:1).
[e] Reaction was performed using complex **5** (7 mol%) as the catalyst.

benzocycloheptene with Bu_4NHSO_5 was catalyzed by commercially available "Jacobsen's" catalyst **5** the reaction proceeded more slowly and the ee of the epoxide dropped considerably (from 90 to ca. 70%) compared to the reaction catalyzed by **1**.[16] The reason for this difference is not clear, probably the catalyst **5** is partially deactivated during the catalytic cycle by some unknown mechanism (see Ref. 15 for similar comments). In fact, when the epoxidation was conducted in a two-phase system using aqueous Oxone as the oxidant, catalyst **5** was completely bleached during the reaction (as indicated by TLC and disappearance of the color of the catalyst). With some other oxidants (e.g. H_2O_2) both of these catalysts **1** and **5** give comparable yields and ee's in epoxidations of various simple alkenes.[7b] Therefore, the electronic and steric effects of substituents on the different 1,2-diphenylethylenediamine- and 1,2-diaminocyclohexane-derived catalysts were studied (Table 1, entries 6–13). In almost all cases the 1,2-diphenylethylenediamine-derived catalysts gave better ee's than the corresponding 1,2-diaminocyclohexane-derived complexes.

Altering the electronic and steric environment around the metal center of the salen catalyst strongly affects the stereochemical outcome of the epoxidations. Jacobsen et al. have reported that Mn(III)–salen complexes bearing electron-donating groups exhibited higher asymmetric induction than those bearing electron-withdrawing groups.[18] Here, introduction of electron-donating groups [e.g. $OSi(i\text{-}Pr)_3$ in catalyst **3**] at the 5 and 5′ positions of the salicylide ligand (see Scheme 1 for the numbering in salen complexes) attenuated the reactivity of the catalyst as expected, but at the same time both the enantioselectivity and yield of the epoxide were lowered considerably compared to reactions catalyzed by, e.g. **1** (entry 2 vs. 8). This somewhat differs from the results obtained using H_2O_2 as the oxidant in the asymmetric epoxidation of benzocycloheptene, where the

difference in selectivity between catalysts **1** and **3** was not so pronounced.[7b]

Increasing the steric bulk of the substituents on the *para* (5,5′) positions of the 1,2-diaminocyclohexane-derived catalysts from methyl (**6**) and *tert*-butyl (**5**) to triphenylmethyl (**7**) resulted in considerably decreased enantioselectivity (entries 10–12). Presumably the large triphenylmethyl group blocks all sides of the catalyst making the side-on approach of the olefin more difficult.[1a] Increasing the size of the substituents at the *ortho* (3,3′) positions had variable effects. Introduction of bulky $C(Me)_2Ph$ groups on the *ortho* positions of 1,2-diphenylethylenediamine-derived salen ligand (catalyst **4**) resulted in decreased asymmetric induction compared to catalyst **1** as expected on the basis of earlier studies.[19] On the other hand, 1,2-diaminocyclohexane-derived catalyst **8** bearing $C(Me)_2Ph$ groups on the *ortho* positions was found to be more reactive and selective (difference in ee 11%) than catalyst **5** bearing *t*-Bu substituents (entry 10 vs. 13). Our earlier observations show that *both* 1,2-diphenylethylenediamine- (**4**) *and* 1,2-diaminocyclohexane-derived catalysts (**8**) bearing $C(Me)_2Ph$ groups at the *ortho* positions show decreased asymmetric induction during the asymmetric epoxidation of simple alkenes with oxidants like NaOCl and H_2O_2 compared to catalysts **1** and **5** having *t*-Bu groups in *ortho* positions (difference in ee ca. 10%).[19] The reason for this reversed difference in reactivity and enantioselectivity between catalyst **5** and **8** is not fully clear. X-ray crystal structure analysis of **8**[20] gives no straight answer, since the analysis shows that the salen ligand adopts the near planar conformation typical for most Mn(III)–salen complexes.[21] In fact, the structure of the complex **8** closely resembles the known X-ray structures of the catalysts **5**[21a] and **6**.[21b] One possible explanation is that complex **5** is less stable than the more hindered catalyst **8** towards the oxidative degradation induced by the monopersulfate oxidant during the catalytic cycle.

One problem in comparing the selectivities of different types of salen complexes is that the structures of the actual active catalysts [Mn(V)–oxo complexes] are not fully known and may differ from the Mn(III) complexes.[1c] In fact, some research groups have proposed a bent or twisted structure[22] for the active catalyst while others hold to the planar model.[21b] Also, it is not fully clear which is the actual direction of the alkene approach to the metal center in Mn-oxo complex. Here again, different kinds of approaches have been proposed at various times by several research groups.[1,22c,23] For example, Jacobsen et al. have proposed alternative approach models for 1,2-diaminocyclohexane-derived and 1,2-diphenylethylene-derived catalysts.[2a,3a] The common feature in these models is that they all can reasonably well explain the stereochemical outcome in the asymmetric epoxidation.[1c] While the exact mechanism of the asymmetric Mn–salen catalyzed epoxidation reactions remains to be elucidated, it is apparent from the results shown here that the reaction conditions play a fundamental role.[24]

Asymmetric epoxidation of various alkenes with monopersulfates

Bu_4NHSO_5 has previously been reported to cause catalyst deactivation when used with metalloporphyrins.[15a,b] It was assumed that Bu_4NHSO_4 present as an impurity inhibits epoxidation of olefins by Bu_4NHSO_5.[17a] The mechanism of this action is not known yet. Ph_4PHSO_5 was then presumed to react more selectively with metalloporphyrins than Bu_4NHSO_5. Therefore, the epoxidation of various di- and tri-substituted aromatic alkenes was performed using both monopersulfates as oxidants together with NMO and catalyst (*S*,*S*)-**1** (Table 2).

All the reactions proceeded smoothly with high yields and enantioselectivity. Also both of the oxidants gave almost identical yields and ee's with most of the substrates. Only the epoxidation of indene gave a some what moderate ee (entries 3–5). Here, the possibility for partial epoxide ring opening with subsequent kinetic resolution cannot be ruled out. With this alkene Ph_4PHSO_5 produced slightly better results compared to Bu_4NHSO_5. The epoxidation of (*Z*)-1-phenyl-1-propene produced the corresponding epoxide with a stereoselectivity (*cis*/*trans*=7–9, entries 6–8) comparable with the results obtained earlier with the MCPBA/NMO-system.[4] Here, the use of Ph_4PHSO_5 resulted in slightly lower yield but higher stereoselectivity than Bu_4NHSO_5. Particularly useful values (yield, ee) were obtained for electron-rich substrates spiro[chromen-2,1′-cyclohexane] (entries 9 and 10) and 1,1-diphenyl-1-propene (entries 11–13). We also saw the difference in reactivity between 1,2-diphenylethylenediamine- and 1,2-diaminocyclohexane-derived catalysts (catalyst **1** vs. **5**), the first-mentioned giving again both higher yields and ee's. For example, the epoxidation of 1,1-diphenyl-1-propene with Bu_4NHSO_5 proceeded with ee's of 93 and 84% using catalysts **1** and **5**, respectively.

In conclusion, ammonium and phosphonium monopersulfates were found to be useful oxidants in Mn(III)–salen catalyzed asymmetric epoxidations. These readily synthesized oxidants might find more general use since they are readily soluble in various organic solvents unlike, e.g. Oxone and PhIO. The reaction system presented here offers mild reaction conditions, as illustrated by comparing the Mn(III)–salen catalyzed oxidation of alkenes by Bu_4NHSO_5/NMO with that of Oxone (see also Ref. 9). A number of salen complexes were synthesized and evaluated in the epoxidation with monopersulfates including two new catalysts **4** and **8**. The 1,2-diphenylethylenediamine-derived complex **1** was found to be the catalyst of choice.

Experimental

General

NMR spectra were recorded at 200 MHz on a Varian Gemini 2000 spectrometer in $CDCl_3$ with Me_4Si as internal standard. IR spectra were acquired by use of a Nicolet Protege 460 FTIR spectrometer. Optical rotation was measured with a Jasco DIP-1000 polarimeter at ambient temperature. EI-MS was acquired by use of a JEOL JMS-SX102 mass spectrometer. FAB-MS was recorded on a Finnigan Mat 8200 BE instrument by bombardment of the samples (in 3-nitrobenzyl alcohol matrix) with Xe. Elemental analyses were performed by the Analytische

Laboratorien Prof. Dr. Malissa und G. Reuter GmbH in Lindlar, Germany. TLC was conducted on Merck aluminum plates coated with silica gel 60 F_{254}. TLC plates were visualized with UV and molybdatophosphoric acid–$Ce(SO_4)_2$–H_2SO_4 with subsequent heating at 120°C. Flash chromatography and dry column flash chromatography[25] were performed using Merck silica gel 60 (230–400 mesh ASTM). (*Z*)-Phenyl-1-propene was obtained from Tokyo Chemical Industry Co. 6,7-Dihydro-5*H*-benzocycloheptene, spiro-[chromen-2,1′-cyclohexane], and 1,1-diphenyl-1-propene were prepared as indicated in the literature.[7b] Oxone was purchased from Sigma–Aldrich Chemie. Bu_4NHSO_4 and Ph_4PCl were obtained from Fluka Chemie. Synthesis of the catalysts **1** and **3** is described in a previous paper.[7b] Catalyst **5** was from Fluka Chemie.

2-Hydroxy-5-methyl-3-(1-methyl-1-phenylethyl)benzaldehyde (salicylaldehyde precursor of 4). Prepared from 4-methyl-2-(1-methyl-1-phenylethyl)phenol[26] using the procedure of Deng and Jacobsen.[27] Yellowish crystals (from ethanol at −18°C), yield 68%, mp 70–71°C. IR (KBr): 3085, 3052, 3023, 2968, 2938, 2847, 1644, 1599, 1492, 1443, 1324, 1264, 1218, 973, 863, 764, 749, 695 cm^{-1}. ^1H NMR: δ 1.73 (6H, s, CMe_2), 2.40 (3H, s, Ar–CH_3), 7.12–7.26 (6H, m, Ph+Ar–H), 7.53 (1H, d, J=2.1 Hz, Ar–H), 9.79 (1H, s, CHO), 11.17 (1H, s, OH). ^{13}C NMR: δ 20.7, 29.3, 41.8, 120.5, 125.4, 125.5, 127.9, 128.1, 131.8, 135.5, 137.4, 149.8, 158.3, 196.7. HRMS (EI) *m*/*z*: calcd for $C_{17}H_{18}O_2$ 254.1307, found 254.1299.

3-*tert*-Butyl-2-hydroxy-5-triphenylmethylbenzaldehyde (salicylaldehyde precursor of 7). 2-*tert*-Butyl-4-triphenylmethylphenol[28] (6.58 g, 16.8 mmol) was suspended in dry benzene (10 ml) under Ar atmosphere together with 2,6-lutidine (0.8 ml, 6.87 mmol). $SnCl_4$ (0.22 ml, 1.88 mmol) was added dropwise and the yellowish mixture was stirred under Ar for 80 min. Solid paraformaldehyde (1.7 g, 56.6 mmol) was then added and the mixture refluxed for 3 h. The mixture was cooled and stirring was continued while water (30 ml) and ethyl acetate (30 ml) were added. The mixture was transferred to a separating funnel, and the reaction flask was rinsed with additional water (30 ml) and ethyl acetate (30 ml). The mixture was acidified with 2 M HCl. The resulting emulsion was filtered through a short pad of Celite to facilitate phase separation, and the Celite was washed several times with ethyl acetate. The aqueous layer was extracted with more ethyl acetate (2×25 ml) and the combined organic extracts were washed with 2 M HCl (25 ml), water (40 ml) and saturated NaCl solution (40 ml). Drying with anhydrous Na_2SO_4, and subsequent evaporation in vacuo yielded a yellowish solid, 6.72 g (95%), mp 190–193°C (lit.[21b] mp 189–190°C). Recrystallization from chloroform–methanol afforded a white solid, mp 203°C. IR (KBr): 3086, 3059, 3031, 2991, 2957, 2950, 2909, 2866, 1646, 1615, 1492, 1442, 1415, 1330, 1277, 1202, 1161, 1031, 873, 776, 763, 751, 703, 647, 634 cm^{-1}. ^1H NMR: δ 1.26 (9H, s, *t*-Bu), 7.16–7.32 (16H, m, Ph+Ar–H), 7.35 (^1H, d, J=2.3 Hz, Ar-H), 9.69 (1H, s, CHO), 11.81 (1H, s, OH). ^{13}C NMR: δ 29.2, 34.9, 64.3, 119.4, 126.1, 127.5, 130.9, 132.9, 136.9, 137.5, 138.2, 146.3, 159.5, 197.2. HRMS (EI) *m*/*z:* calcd for $C_{30}H_{28}O_2$ 420.2089, found 420.2090.

5-*tert*-Butyl-2-hydroxy-3-(1-methyl-1-phenylethyl)benzaldehyde (salicylaldehyde precursor of 8). Prepared as above from 4-*tert*-butyl-2-(1-methyl-1-phenylethyl)phenol.[26] The oily product was purified by dry column flash chromatography (eluent hexane–THF) to afford a pale solid, yield 68%, mp 76–77.5°C. IR (KBr): 3082, 3060, 3027, 2966, 2872, 2835, 1641, 1603, 1460, 1440, 1332, 1267, 1212, 1156, 882, 758, 695 cm^{-1}. ^1H NMR: δ 1.38 (9H, s, *t*-Bu), 1.75 (6H, s, CMe_2), 7.12–7.32 (5H, m, Ph), 7.41 (1H, d, J=2.4 Hz, Ar–H), 7.76 (1H, d, J=2.4 Hz, Ar–H), 9.83 (1H, s, CHO), 11.22 (1H, s, OH). ^{13}C NMR: δ 29.3, 31.4, 34.3, 42.1, 120.1, 125.4, 125.6, 127.9, 128.2, 132.1, 137.1, 141.6, 149.8, 158.3, 197.1. HRMS (EI) *m*/*z*: calcd for $C_{20}H_{24}O_2$ 296.1777, found 296.1782.

(*S*,*S*)-*N*,*N*′-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-diphenylethylenediamine (ligand of catalyst 2). (*S*,*S*)-1,2-Diphenylethylenediamine (0.25 g, 1.18 mmol) and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde[27] (0.55 g, 2.35 mmol) were refluxed in absolute ethanol (10 ml) for 3 h. A small amount of water was added to the reaction mixture, then it was allowed cool to 2°C and kept at that temperature for 2 h. The product was collected by suction filtration to afford a yellow powder, yield 0.53 g (70%), mp 197–198°C (lit.[29] mp 199–200°C). IR (KBr): 3087, 3062, 3030, 2958, 2909, 2869, 1626, 1598, 1469, 1454, 1442, 1362, 1250, 1174, 876, 776, 700 cm^{-1}. ^1H NMR: δ 1.22 (18H, s, *t*-Bu), 1.42 (18H, s, *t*-Bu), 4.72 (2H, s, CH–N), 6.98 (2H, d, J=2.4 Hz, Ar–H), 7.18 (10H, s, Ph), 7.31 (2H, d, J=2.4 Hz, Ar–H), 8.40 (2H, s, CH=N), 13.59 (2H, s, OH). ^{13}C NMR: δ 29.4, 31.4, 34.0, 34.9, 80.0, 117.7, 126.2, 127.0, 127.3, 127.9, 128.1, 136.2, 139.7, 139.9, 157.8, 167.1. HRMS (EI) *m*/*z*: calcd for $C_{44}H_{56}N_2O_2$ 644.4342, found 644.4329.

(*S*,*S*)-*N*,*N*′-Bis[5-methyl-3-(1-methyl-1-phenylethyl)salicylidene]-1,2-diphenylethylenediamine (ligand of catalyst 4). Prepared as above from (*S*,*S*)-1,2-diphenylethylenediamine (220 mg, 1.04 mmol) and 2-hydroxy-5-methyl-3-(1-methyl-1-phenylethyl)benzaldehyde (528 mg, 2.08 mmol). Yellow powder, yield 635 mg (91%), mp 103–105°C. IR (KBr): 3082, 3056, 3028, 2964, 2915, 2869, 1627, 1599, 1492, 1453, 1442, 1264, 1029, 860, 776, 764, 697 cm^{-1}. ^1H NMR: δ 1.69 (6H, s, CH_3), 1.72 (6H, s, CH_3), 2.29 (6H, s, Ar-CH_3), 4.47 (2H, s, CH–N), 6.76 (2H, d, J=1.9 Hz, Ar–H), 7.0–7.25 (22H, m, Ph+Ar–H), 8.11 (2H, s, CH=N), 12.88 (2H, s, OH). ^{13}C NMR: δ 20.7, 29.3, 30.0, 42.0, 80.3, 118.4, 124.9, 125.6, 126.3, 127.3, 127.8, 128.0, 128.1, 130.5, 131.2, 135.9, 139.2, 150.6, 157.3, 166.5. HRMS (EI) *m*/*z*: calcd for $C_{48}H_{48}N_2O_2$ 684.3716, found 684.3713.

(*R*,*R*)-*N*,*N*′-Bis(3-*tert*-butyl-5-methylsalicylidene)-1,2-cyclohexanediamine (ligand of catalyst 6). (*R*,*R*)-1,2-Cyclohexanediamine (1.22 g, 10.7 mmol) and 3-*tert*-butyl-2-hydroxy-5-methylbenzaldehyde (4.12 g, 21.4 mmol) were refluxed in absolute ethanol (50 ml) for 1 h and stirred overnight at 70°C. Water was added and the mixture was cooled at 2°C for 2 h to give yellow powder, yield 3.35 g (68%), mp 134–135°C (lit.[21b] mp 134–135°C). IR (KBr): 2992, 2956, 2942, 2860, 1628, 1595, 1466, 1441, 1357, 1317, 1265, 1233, 1211, 1165, 866, 772 cm^{-1}. ^1H NMR: δ 1.40 (18H, s, *t*-Bu), 1.4–2.0 (8H, m, CH_2), 2.20 (6H, s, CH_3), 3.30 (2H, m, CH–N), 6.78 (2H, d, J=1.8 Hz, Ar–H), 7.04 (2H, d,

J=1.8 Hz, Ar–H), 8.23 (2H, s, CH=N), 13.6 (2H, brs, OH). ^{13}C NMR: δ 20.5, 24.3, 29.3, 33.0, 34.6, 72.0, 118.2, 126.3, 129.6, 130.1, 136.6, 157.9, 165.4. HRMS (EI) *m*/*z*: calcd for $C_{30}H_{42}N_2O_2$ 462.3246, found 462.3242.

(*R*,*R*)-*N*,*N*′-Bis(3-*tert*-butyl-5-triphenylmethylsalicylidene)-1,2-cyclohexanediamine (ligand of catalyst 7).[21b] (*R*,*R*)-1,2-Cyclohexanediamine (0.141 g, 1.24 mmol), 3-*tert*-butyl-2-hydroxy-5-triphenylmethylbenzaldehyde (1.04 g, 2.47 mmol), and anhydrous Na_2SO_4 (1.5 g) were refluxed gently in chloroform (10 ml) for 22 h. The cooled reaction mixture was filtered and the filtrate evaporated. The crude product was purified by flash chromatography (eluent *n*-hexane–THF) to afford yellow foam, yield 1.01 g (89%). IR (KBr): 3085, 3056, 3029, 2999, 2956-2934, 2861, 1628, 1595, 1492, 1467, 1442, 1279, 1203, 1185, 1160, 1038, 873, 749, 703, 648, 635 cm^{-1}. ^{1}H NMR: δ 1.23 (18H, s, *t*-Bu), 1.4–1.8 (8H, m, CH_2), 3.29 (2H, m, CH–N), 6.90 (2H, d, J=2.4 Hz, Ar–H), 7.13 (2H, d, J=2.4 Hz, Ar-H), 7.15–7.26 (30H, m, Ph), 8.17 (2H, s, CH=N), 13.91 (2H, s, OH). ^{13}C NMR: δ 24.2, 29.3, 33.3, 34.8, 64.4, 72.2, 117.4, 125.8, 127.5, 131.1, 131.3, 133.5, 135.7, 135.9, 146.9, 158.6, 165.6. MS (EI) *m*/*z* 918 $(M)^+$. Anal. Calcd for $C_{66}H_{66}N_2O_2$: C, 86.24; H, 7.24; N, 3.05. Found: C, 85.71; H, 7.32; N, 2.88.

(*R*,*R*)-*N*,*N*′-Bis[5-*tert*-butyl-3-(1-methyl-1-phenylethyl)-salicylidene]-1,2-cyclohexanediamine (ligand of catalyst 8). (*R*,*R*)-1,2-Cyclohexanediamine (72 mg, 0.631 mmol) and 5-*tert*-butyl-2-hydroxy-3-(1-methyl-1-phenylethyl)-benzaldehyde (374 mg, 1.262 mmol) were refluxed in absolute ethanol (6 ml) for 3 h. Water was added to the reaction mixture and it was cooled to 2°C and kept at that temperature for 2 h. The product was collected by suction filtration to afford a yellow powder, yield 379 mg (90%), mp 97–99°C. IR (KBr): 3083, 3057, 3022, 2963, 2933, 2862, 1628, 1598, 1465, 1442, 1361, 1272, 1161, 771, 762, 698 cm^{-1}. ^{1}H NMR: δ 1.28 (18H, s, *t*-Bu), 1.54 (4H, m, CH_2), 1.65–1.80 (4H, m, CH_2), 1.69 (6H, s, CH_3), 1.73 (6H, s, CH_3), 3.12 (2H, m, CH–N), 6.96 (2H, d, J=2.4 Hz, Ar–H), 7.10–7.30 (10H, m, Ph), 7.42 (2H, d, J=2.4 Hz, Ar–H), 8.09 (2H, s, CH=N), 13.19 (2H, s, OH). ^{13}C NMR: δ 24.3, 28.9, 30.2, 31.5, 33.1, 34.1, 42.3, 72.3, 117.9, 125.0, 125.6, 126.3, 127.3, 127.9, 135.6, 139.7, 150.7, 157.4, 165.4. HRMS (EI) *m*/*z*: calcd for $C_{46}H_{58}N_2O_2$ 670.4498, found 670.4495.

[(*S*,*S*)-*N*,*N*′-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-diphenylethylenediamine]chloromanganese(III) (catalyst 2). Solid $Mn(OAc)_2\cdot 4H_2O$ (0.40 g, 1.63 mmol) was added to a solution of (*S*,*S*)-*N*,*N*′-bis(3,5-di-*tert*-butyl-salicylidene)-1,2-diphenylethylenediamine (0.51 g, 0.79 mmol) in absolute ethanol (10 ml), and the dark brown mixture was refluxed for 2 h under air. Solid LiCl (0.11 g, 2.60 mmol) was then added and the mixture was refluxed for an additional 2 h and then stirred at 70°C overnight. The reaction mixture was cooled, and then water was added resulting in the precipitation of a brown powder which was collected by suction filtration. The powder was redissolved in CH_2Cl_2 and extracted with water and brine. The organic phase was dried over anhydrous Na_2SO_4, and solvent evaporated to afford a brown powder, yield 0.54 g (93%), mp >300°C. IR (KBr): 3063, 3027, 2956, 2904, 2867, 1610, 1534, 1455, 1429, 1317, 1252, 1174, 857, 700, 579 cm^{-1}. MS (FAB) *m*/*z* 697.6 $(M-Cl)^+$. Anal. Calcd for $C_{44}H_{54}ClMnN_2O_2\cdot 1/2H_2O$: C, 71.19; H, 7.47; N, 3.77. Found: C, 71.36; H, 7.47; N, 3.66.

[(*S*,*S*)-*N*,*N*′-Bis[5-methyl-3-(1-methyl-1-phenylethyl)-salicylidene]-1,2-diphenylethylenediamine]chloromanganese(III) (catalyst 4). Prepared as catalyst **2** from (*S*,*S*)-*N*,*N*′-bis[5-methyl-3-(1-methyl-1-phenylethyl)-salicylidene]-1,2-diphenylethylenediamine (602 mg, 0.88 mmol), total reaction time 4 h. Brown powder, yield 650 mg (96%), mp 244°C. IR (KBr): 3085, 3055, 3028, 2963, 2920, 2869, 1611, 1539, 1494, 1429, 1342, 1299, 1223, 819, 774, 699, 554 cm^{-1}. MS (EI) *m*/*z* 772 $(M)^+$, 737 $(M-Cl)^+$. Anal. Calcd for $C_{48}H_{46}ClMnN_2O_2\cdot H_2O$: C, 72.86; H, 6.18; N, 3.54. Found: C, 73.03; H, 6.18; N, 3.36.

[(*R*,*R*)-*N*,*N*′-Bis(3-*tert*-butyl-5-methylsalicylidene)-1,2-cyclohexanediamine]chloromanganese(III) (catalyst 6). Prepared as catalyst **2** from (*R*,*R*)-*N*,*N*′-bis(3-*tert*-butyl-5-methylsalicylidene)-1,2-cyclohexanediamine (406 mg, 0.88 mmol), total reaction time 16 h. Brown powder, yield 468 mg (97%), mp >300°C (lit.[21b] mp 311–312°C). IR (KBr): 3032, 3006, 2940, 2910, 2865, 1616, 1543, 1431, 1387, 1338, 1305, 1238, 1208, 1172, 825, 781, 570 cm^{-1}. MS (EI) *m*/*z* 550 $(M)^+$, 515 $(M-Cl)^+$. Anal. Calcd for $C_{30}H_{40}ClMnN_2O_2\cdot H_2O$: C, 63.32; H, 7.44; N, 4.92. Found: C, 63.72; H, 7.85; N, 4.55.

[(*R*,*R*)-*N*,*N*′-Bis(3-*tert*-butyl-5-triphenylmethylsalicylidene)-1,2-cyclohexanediamine]chloromanganese(III) (catalyst 7). $Mn(OAc)_2\cdot 4H_2O$ (0.53 g, 2.16 mmol) dissolved in absolute ethanol (5 ml) was added to a suspension of (*R*,*R*)-*N*,*N*′-bis(3-*tert*-butyl-5-triphenylmethylsalicylidene)-1,2-cyclohexanediamine (0.80 g, 0.87 mmol) in absolute ethanol (10 ml), and the brown mixture was refluxed for 2 h under air. Solid LiCl (0.12 g, 2.83 mmol) was then added and the mixture was further refluxed for 1 h. The reaction mixture was treated as above to afford a brown powder, yield 0.79 g (90%), mp >300°C (lit.[21b] mp 325–326°C). IR (KBr): 3083, 3056, 3028, 2999, 2938, 2864, 1621, 1607, 1534, 1491, 1433, 1341, 1308, 1184, 1036, 872, 712, 703, 651, 575 cm^{-1}. MS (FAB) *m*/*z* 971.4 $(M-Cl)^+$. Anal. Calcd for $C_{66}H_{64}ClMnN_2O_2\cdot H_2O$: C, 77.29; H, 6.49; N, 2.73. Found: C, 77.34; H, 6.48; N, 2.55.

[(*R*,*R*)-*N*,*N*′-Bis[5-*tert*-butyl-3-(1-methyl-1-phenylethyl)-salicylidene]-1,2-cyclohexanediamine]chloromanganese-(III) (catalyst 8). Prepared as catalyst **2** from (*R*,*R*)-*N*,*N*′-bis[5-*tert*-butyl-3-(1-methyl-1-phenylethyl)salicylidene]-1,2-cyclohexanediamine (359 mg, 0.535 mmol), total reaction time 4 h. Brown powder, yield 394 mg (97%), mp 263–265°C. IR (KBr): 3087, 3054, 3021, 2960, 2865, 1613, 1538, 1434, 1339, 1311, 1264, 1249, 836, 700, 554 cm^{-1}. MS (FAB) *m*/*z* 723.6 $(M-Cl)^+$. Anal. Calcd for $C_{46}H_{56}ClMnN_2O_2$: C, 72.76; H, 7.43; N, 3.69. Found: C, 72.84; H, 7.55; N, 3.31.

Preparation of the oxidants

Bu_4NHSO_5.[12] To a solution of Oxone (3.4 g, 11.2 mmol of $KHSO_5$) in distilled water (35 ml) was added Bu_4NHSO_4 (3.4 g, 10 mmol). The solution was stirred for 20 min and

then extracted with CH_2Cl_2 (70 ml). The organic phase was dried over $MgSO_4$, filtered, and evaporated. The crude product was washed with *n*-hexane (20 ml) and dried in vacuo to produce Bu_4NHSO_5 as a white powder (2.5–2.6 g, 70–73%). The purity was determined iodometrically to be 88%.

Ph_4PHSO_5.[17a] To a solution of Oxone (6.0 g, 19.7 mmol of $KHSO_5$) in distilled water (60 ml) was added a solution of Ph_4PCl (3.0 g, 8.0 mmol) in CH_2Cl_2 (60 ml). The mixture was stirred vigorously for 10 min after which the layers were separated. The organic phase was dried over $MgSO_4$, filtered, and evaporated. The crude product was washed with cold water (20 ml), dried in vacuo and crystallized once from CH_2Cl_2–*n*-hexane to produce Ph_4PHSO_5 as a white powder (2.5 g, 69%). The purity was determined iodometrically to be 89%.

General procedure for the asymmetric epoxidation of unfunctionalized alkenes with monopersulfates catalyzed by 1–8. To a cooled solution of the alkene (0.4 mmol), additive (0.1–0.4 mmol), and catalyst (0.0012–0.0028 mmol) in acetonitrile (2.2–3.2 ml) was added the monopersulfate oxidant (0.56–0.65 mmol) in two portions during 20–30 min. The mixture was stirred at the indicated temperature. After all the olefin had reacted (monitored by TLC) the reaction was quenched by adding Me_2S (ca. 1.0 mmol). Excess solid K_2CO_3 was added, the mixture was allowed to reach room temperature and then filtered. The filtrate was concentrated and the residue was purified by flash chromatography (eluent *n*-hexane–ethyl acetate). The ee of the epoxide was determined by ^1H NMR analysis in the presence of the chiral shift reagent tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium, Eu(hfc)$_3$. ^1H NMR and chiroptical data of the obtained epoxides are presented in a previous paper.[7b]

Typical asymmetric epoxidation of (*Z*)-1-phenyl-1-propene with monopersulfates catalyzed by 1 (Table 2, entry 8). To a cooled (−18°C) solution of (*Z*)-1-phenyl-1-propene (48 mg, 0.406 mmol), NMO (48 mg, 0.41 mmol), and catalyst **1** (18.5 mg, 0.00285 mmol) in acetonitrile (3.2 ml) was added Ph_4PHSO_5 (89%, 300 mg, 0.59 mmol) in two portions during 30 min. After 75 min the reaction was quenched by adding Me_2S (80 μl, 1.1 mmol). Excess solid K_2CO_3 was added, the mixture was allowed to reach room temperature and then filtered through a short pad of Florisil and the filtrate concentrated. ^1H NMR analysis of the residue indicated the presence of *cis* and *trans* epoxides in a 9.4:1 ratio. The residue was purified by flash chromatography (eluent *n*-hexane–ethyl acetate) to afford the *cis* epoxide in a 66% yield (containing a trace of the *trans* isomer). The ee of the *cis* epoxide was determined to be 89% by ^1H NMR analysis in the presence of Eu(hfc)$_3$. The absolute configuration was determined to be (1*R*,2*S*) by measuring the optical rotation: $[\alpha]_D^{20}$ −36.4 (*c* 0.5, $CHCl_3$, 89% ee) [lit.:[30] $[\alpha]_D^{20}$ +47.5 (*c* 1.17, $CHCl_3$) for (1*S*,2*R*)-isomer]. ^1H NMR: δ 1.08 (3H, d, *J*=5.5 Hz), 3.34 (1H, dq, *J*=4.3 and 5.5 Hz), 4.06 (1H, *J*=4.3 Hz), 7.2–7.4 (5H, m).

Acknowledgements

This work was partially supported by the Technology Development Centre of Finland (TEKES). I thank Mr Jorma Matikainen (PhD) for running the mass spectra.

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