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Convenient Asymmetric (Salen)Mn(III)-catalyzed Epoxidation of Unfunctionalized Alkenes with Hydrogen Peroxide Using Carboxylate Salt Cocatalysts

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Abstract: Asymmetric epoxidation of unfunctionalized alkenes is reported using chiral (salen)Mn(III) complexes **1-5** together with a carboxylate salt cocatalyst in the presence of either aqueous H_2O_2 or anhydrous urea-H_2O_2 adduct as oxidant. Several simple soluble salts (acetates, formates, benzoates) were studied all giving good yields of epoxides with moderate to excellent enantioselectivity. For example, 1,1-diphenyl-1-propene was converted into the corresponding epoxide of 96 % ee in 84 % yield. Generally, this epoxidation method gave better results than a previously described system using nitrogen heterocycles as cocatalysts.

Chiral (salen)Mn(III) complexes have emerged as the most efficient and practical catalysts for the asymmetric epoxidation of unfunctionalized olefins.[1] High yields of epoxides and moderate to excellent enantiomeric excesses (ee) have been reported for reactions of a variety of disubstituted *cis*-alkenes with oxidants such as iodosylarenes (mainly PhIO),[2] sodium hypochlorite,[3] peracids,[4] O_2/aldehyde,[5] and dimethyldioxirane.[6] Also H_2O_2[7,8] and periodates[9] were recently applied as feasible terminal oxidants. This salen-based epoxidation methodology has recently been expanded to include the enantioselective synthesis of certain mono-, tri- and tetrasubstituted epoxides.[4a,10]

Hydrogen peroxide is particularly attractive oxidant as it is cheap, reasonably stable, readily available, and gives only water as a by-product. The problems in transition metal complex-catalyzed (porphyrins[11] and salen-based catalysts) epoxidations with hydrogen peroxide are the homolytic cleavage of its weak O-O bond (formation of radicals), its relative ease of dismutation, and the oxidative destruction of catalysts by H_2O_2. The heterolytic bond cleavage producing the reactive metal-oxo species [e.g. (salen)Mn(V)=O] can be favoured by using nitrogen heterocycle cocatalysts acting as bases or as axial ligands on the transition metal catalyst.[12] Typical nitrogenous bases used are imidazoles, pyridines, and tertiary amine *N*-oxides. In the case of metalloporphyrin-catalyzed epoxidations these axial ligands have been used alone or together with other additives like carboxylic acids,[12b-c] and soluble bases.[12d] Recently, Katsuki et al. used a complex system containing a salen catalyst with four stereogenic centers together with two cocatalysts, *N*-methylimidazole and an ammonium salt (NH_4ClO_4, NH_4PF_6), for the epoxidation of chromene derivatives.[8b] All these systems suffer from the same disadvantages, namely from the oxidative destruction of the heterocyclic cocatalyst and from their relative complexity. On the other hand, Mansuy et al. discovered recently that a simple ammonium

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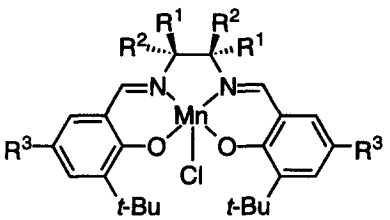
salt, like ammonium acetate, *alone* can act as a very efficient cocatalyst for the metalloporphyrin-catalyzed epoxidation of simple alkenes by H_2O_2.[13] Also, other bases like sodium carbonate have been shown to promote the porphyrin-catalyzed epoxidation without requiring any other additive.[12d] (Salen)Mn(III) complexes have been used as catalysts together with H_2O_2, without the presence of additives, in the asymmetric oxidation of sulfides to sulfoxides.[14]

Here is reported that simple soluble carboxylate salts are efficient cocatalysts in asymmetric epoxidations catalyzed by chiral (salen)Mn(III) complexes (**1-5**) giving comparable or better results (yield, ee) than typical nitrogen heterocycles under identical conditions.



(*S,S*)-**1**: R^1= Ph, R^2= H, R^3= Me
(*S,S*)-**2**: R^1= Ph, R^2= H, R^3= OSi(*i*-Pr)$_3$
(*R,R*)-**3**: R^1= H, R^2= Ph, R^3= Br
(*S,S*)-**4**: R^1,R^1= -$(CH_2)_4$-, R^2= H, R^3= *t*-Bu
(*R,R*)-**5**: R^1= H, R^2,R^2= -$(CH_2)_4$-, R^3= OSi(*i*-Pr)$_3$

RESULTS AND DISCUSSION

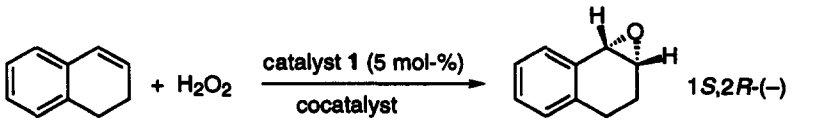
Cocatalyst effect in the asymmetric epoxidation of 1,2-dihydronaphthalene

The effect of the carboxylate salts studied (NH_4OAc, NH_4O_2CH, NaOAc, and $PhCO_2Na$) were compared with typical nitrogenous ligands used in transition metal complex-catalyzed epoxidations. 1,2-Dihydronaphthalene was epoxidized using 30 % aqueous hydrogen peroxide and 5 mol-% of the catalyst (*S,S*)-**1** together with 40-60 mol-% of the cocatalyst in CH_2Cl_2-CH_3OH (1:1) at 2 °C. The results are summarized in Table 1.

When 1,2-dihydronaphthalene was oxidized with H_2O_2 catalyzed by (*S,S*)-**1** in the presence of nitrogenous bases *N*-methylimidazole, and 4-*tert*-butylpyridine moderate yields of the epoxide were obtained with enantioselectivities ranging from 59 % to 64 % (entries 1-2). Similar results were observed in previous study using imidazoles or pyridines as ligand together with catalysts (*S,S*)-**1** and (*R,R*)-**4**.[7] Also, previously was found that pyridine *N*-oxide is not a suitable ligand for epoxidations with H_2O_2 and catalyst (*S,S*)-**1**.[7] Here, on the other hand, *N*-oxides (*N*-methylmorpholine *N*-oxide, 4-phenylpyridine *N*-oxide) gave significantly higher ee's than the amines mentioned above (entries 3-4).

When carboxylate salts were used as cocatalysts both the yields and ee's were higher than with nitrogenous bases (entries 5-11). NH_4OAc gave somewhat better yields than the other salts under most conditions (entries 5, 6, and 8). The amount of the salt (NH_4OAc) could be reduced from 40 mol-% to 20 mol-% without any significant effect on the yield and ee of the epoxide (entry 6). Also the simple inorganic base $NaHCO_3$ was able to promote the epoxidation (entry 12). Lowering the reaction temperature from 2 °C to -18 °C had only a marginal effect on the ee of the product (entry 6 *vs* 8, see also Table 2). As expected, reaction at room temperature gave lower enantioselectivity (difference in ee 4-6 %, entries 1 and 5). Finally, the epoxidation was performed using anhydrous urea-hydrogen peroxide adduct[8a] as the oxidant together with ammonium acetate. The yield and selectivity were quite similar with those obtained using 30 % aq. H_2O_2 (entry 6 *vs* 7).

Table 1. Asymmetric Epoxidation of 1,2-Dihydronaphthalene Catalyzed by (*S,S*)-**1**[a]



entry	cocatalyst[b] (mol. equiv.)	temp. (°C)	time (h)	yield (%)[c]	ee (%)[d]
1	*N*-MeIm (0.6)	2	1.25	51	64 (60)[e]
2	*t*-BuPy (0.6)	2	1.5	60	59
3	NMO (0.4)	2	2	74	69
4	PPNO (0.4)	2	1.5	61	69
5	NH_4OAc (0.4)	RT	1.25	73	61
6	"	2	1.25	73 (70)[f]	67 (66)[f]
7[g]	"	2	1	68	67
8	"	-18	4	73	68
9	NH_4O_2CH (0.4)	2	1.25	65	68
10	NaOAc (0.4)	2	1	68	69
11	NaO_2CPh (0.4)	2	1.25	69	67
12	$NaHCO_3$ (0.2)	2	1	62	66

a) Reactions were performed in 0.5 mmol scale of the alkene in CH_2Cl_2-CH_3OH (1:1, 1.5 ml) with molar ratio of alkene: H_2O_2: cocatalyst: salen= 1: 2.5-3: 0.4-0.6: 0.05. b) *N*-MeIm= *N*-methylimidazole, *t*-BuPy= 4-*tert*-butylpyridine, NMO= *N*-methylmorpholine *N*-oxide, PPNO= 4-phenylpyridine *N*-oxide. c) Yield of the isolated epoxide. d) Determined by ^1H NMR in the presence of $Eu(hfc)_3$. e) Value in parenthesis is for the reaction performed at RT (from ref. 7). f) Value in parenthesis is for the reaction using 0.2 mol. equiv. of NH_4OAc. g) Reaction was performed using urea-H_2O_2 (3 mol. equiv.) as the oxidant.

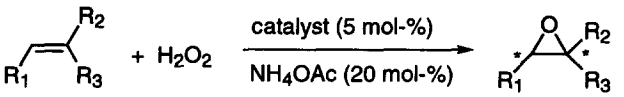
Asymmetric epoxidation of various olefins with H_2O_2 and NH_4OAc

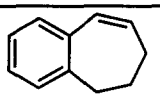
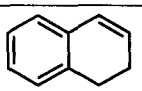
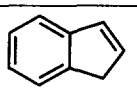
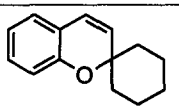
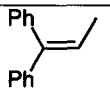
Results of asymmetric epoxidation of other unfunctionalized alkenes using ammonium acetate as the cocatalyst are summarized in Table 2. First, both the steric and electronic effects of substituents on the different 1,2-diphenylethanediamine- and 1,2-diaminocyclohexane-derived catalysts were studied using 6,7-dihydro-5*H*-benzocycloheptene as the olefinic substrate (entries 1-4, 7). In all cases the selectivity obtained was reasonably high 1,2-diaminocyclohexane-derived catalysts (*S,S*)-**4** and (*R,R*)-**5** giving slightly better ee's than the other catalysts. Jacobsen et al. has reported that (salen)Mn(III) catalysts bearing electron-donating groups exhibited higher asymmetric induction than those bearing electron-withdrawing groups.[15] Electron-donating substituents at the 5 and 5' positions of the salicylide ligand in catalysts (*S,S*)-**2** and (*R,R*)-**5** attenuated the reactivity of the catalyst as shown by longer reaction times (entries 2 and 7). This trend was also observed with other substrates, e.g. with 1,2-dihydronaphthalene (entry 8). On the other hand, introduction of an electron-withdrawing Br-substituent in the salicylide ligand [catalyst (*R,R*)-**3**] accelerated the epoxidation reaction, but at the same time enantioselectivity was considerably lowered (entry 3).

Other disubstituted alkenes studied showed highest yields and selectivities when epoxidized using either catalysts (*S,S*)-**1** or (*S,S*)-**2** (entries 9-11). Particularly promising results were obtained with spiro[chromen-2,1'-cyclohexane], a member of a synthetically important class of olefins.[16] The chromene oxide was

produced in useful yield and showed ee-values exceeding 90 %. This epoxidation methodology was also applied to the epoxidation of a trisubstituted alkene, 1,1-diphenyl-1-propene. Here, both the yield and the ee of the corresponding epoxide reached excellent values (entries 12-13).

Table 2. Asymmetric Epoxidation of Various Olefins with H_2O_2 and NH_4OAc[a]



entry	alkene	catalyst	temp (°C)	time (h)	yield (%)[b]	ee (%)[c]	epoxide config[d]
1		(*S,S*)-**1**	2	1.25	70	85	5*S*,6*R*-(+)
2[e]	"	(*S,S*)-**2**	2	5	78	83	5*S*,6*R*-(+)
3	"	(*R,R*)-**3**	2	1	71	67	5*R*,6*S*-(-)
4	"	(*S,S*)-**4**	2	1.5	71	87	5*S*,6*R*-(+)
5	"	(*S,S*)-**4**	-18	2	71	87	5*S*,6*R*-(+)
6[f]	"	(*S,S*)-**4**	2	1	73	84	5*S*,6*R*-(+)
7[e]	"	(*R,R*)-**5**	2	6	54 (75)[g]	89	5*R*,6*S*-(-)
8[h]		(*S,S*)-**2**	2	5	54 (63)[g]	64	1*S*,2*R*-(-)
9		(*S,S*)-**1**	2	2	63	75	1*S*,2*R*-(+)
10		(*S,S*)-**4**	2	1.25	90	91	(+)[i]
11[h]	"	(*S,S*)-**4**	-18	2.75	87	90	(+)[i]
12		(*S,S*)-**4**	2	1	86	92	*R*-(+)
13[h]	"	(*S,S*)-**4**	-18	4	84	96	*R*-(+)

a) Reactions (2 °C) were performed in CH_2Cl_2-CH_3OH (1:1,1.5 ml) with molar ratio of alkene: H_2O_2: NH_4OAc: salen= 1: 3: 0.2: 0.05. b) Yield of the isolated epoxide. c) Determined by ^1H NMR in the presence of $Eu(hfc)_3$. d) Determined by comparison of the sign of $[\alpha]_D$ to the literature values. e) 5 mol. equiv. of H_2O_2 was used in 2 ml of CH_2Cl_2-CH_3OH (3:5). f) NaOAc was used as the cocatalyst. g) Yield in parenthesis is calculated from the reacted olefin. h) 4 mol. equiv. of H_2O_2 was used in 2 ml of CH_2Cl_2-CH_3OH (3:5). i) Absolute configuration not determined.

Possible roles of the cocatalyst in the asymmetric epoxidation

The exact role of the carboxylate additives during the catalytic cycle is not clear. Nitrogen heterocycles are believed to act as ligands to the salen metal catalyst and as bases.[1,11-12] Another possible mode of action is to assist dissociation of unreactive μ-oxo dimers to reactive monomeric oxo complexes.[17] Nitrogenous bases may also improve the epoxide yield by lowering the Lewis acidity of Mn(III) complexes.[18,19]

In the case of carboxylate additives two different roles are possible. First, the carboxylates can act as bases promoting the formation of HO_2^- from H_2O_2 which facilitates the formation of the hydroperoxy complex (salen)Mn(III)-O-OH from (salen)Mn(III).[12d] In fact, the apparent pH of 30 % H_2O_2 (8.9 M) was raised from pH 2.6 to ca. pH 6 when the carboxylates were dissolved in H_2O_2 in the same proportions as used in the epoxidation reactions.[12c] Moreover, the use of a carboxylic acid in the place of the corresponding acid salt resulted in a dramatic retardation of the reaction rate. For example, epoxidation of 1,2-dihydronaphthalene in the presence of benzoic acid (20 mol-%) only produced a 19:81 mixture of the epoxide and alkene (determined by ^1H NMR) after 2.5 h reaction time. Also, practically no reaction was oserved in the absence of additives. The importance of the basicity of the cocatalyst was further pointed by the fact that also $NaHCO_3$ as an additive gave satisfactory results (Table 1, entry 12).

Another possibility is that the reaction sequence from (salen)Mn(III) to (salen)Mn(V)=O proceeds *via* a peroxyacylmanganese species, (salen)Mn(III)-O-OCOR, as proposed by Montanari et al. for the manganese-porphyrin-catalyzed epoxidation of alkenes with H_2O_2 in the presence of a lipophilic nitrogen heterocycle ligand and a carboxylic acid cocatalyst.[12b-c] Also, the reaction with molecular oxygen with (salen)Mn(III) in the presence of an aldehyde has been proposed to provide peroxyacylmanganese species.[5b] It was suggested that this active species, in the absence of a donor ligand, would directly epoxidize olefins, but the same reaction in the presence of the ligand (e.g. *N*-alkylimidazole) would proceed by way of oxo species. This was supported by the fact that the sense of enantioface selection observed in the absence of the donor ligand is opposite to that observed in the presence of the axial ligand. In our epoxidation experiments the same enantioface selection without any inversions was observed with all the additives (see Table 1). The possibility of carboxylates acting as axial ligands on the salen complexes cannot be ruled out. On the other hand, results obtained in the presence of $NaHCO_3$, presumably not capable of functioning as a ligand to the salen metal, indicate that basicity is a *sufficient* property of the additives in salen-catalyzed epoxidations.

While the exact mechanism of the action of the carboxylate salts during the asymmetric epoxidation reaction remains to be elucidated, their practical significance is obvious. It was shown that carboxylate salts together with chiral salen complexes and hydrogen peroxide are able to promote the asymmetric epoxidation of di- and trisubstituted alkenes in a straighforward manner with high yields and enantioselectivity. The aforementioned good properties of hydrogen peroxide together with the high stability[13] of the carboxylate salts under the reaction conditions make this at the moment one of the most convenient methods for the enantioselective transition metal complex-catalyzed epoxidation of unfunctionalized olefins.

EXPERIMENTAL

General. ^1H NMR spectra were recorded at 200 MHz on a Varian Gemini 200 spectrometer using $CDCl_3$ as solvent and with tetramethylsilane as internal standard. Optical rotation was measured with a JASCO DIP-1000 digital polarimeter at ambient temperature. EI-MS were aquired by use of a JEOL JMS-SX102 mass spectrometer. FAB-MS were recorded on a Finnigan Mat 8200 BE mass spectrometer by bombardment of the samples (in 3-nitrobenzyl alcohol matrix) with Xe. Elemental analyses were performed by the Analytische Laboratorien Prof. Dr. H. Malissa und G. Reuter GmbH in Lindlar Germany. Thin layer chromatography (TLC) was conducted on Merck aluminum plates coated with 0.25 mm of 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 was performed using Merck silica gel 60 (230-400 mesh ASTM). 1,2-Dihydronaphthalene and 6,7-dihydro-5*H*-benzocycloheptene were prepared by reduction with $NaBH_4$ and subsequent dehydration from α-tetralone and 1-benzosuberone, respectively.[20] Spiro[chromen-2,1'-cyclohexane][21] and 1,1-diphenyl-1-propene[22] were prepared as indicated in the literature. 30 % aq. H_2O_2 (PERDROGEN®) was purchased from Riedel-de Haen. Urea-hydrogen peroxide adduct (UHP) was prepared as indicated in the literature, and dried under high vacuum before use.[23] The hydrogen peroxide content of aq. H_2O_2 and UHP was determined by iodometric titration.

The catalysts. Catalyst **4** was purchased from Fluka Chemie. Catalysts **1-3**, and **5** were prepared by literature methods from the corresponding salicylaldehyde and optically active commercial diamine.[3a,24] The free ligands were analyzed with ^1H NMR, ^{13}C NMR, and MS(EI). Analyses of the Mn(III) complexes:
(*S,S*)-**1**.[3a] MS(EI) *m/z* 648 $(M)^+$, 613 $(M\text{-}Cl)^+$. Anal. Calcd. for $C_{38}H_{42}ClMnN_2O_2$: C, 70.31; H, 6.52; N, 4.32. Found: C, 69.80; H, 6.75; N, 4.18.
(*S,S*)-**2.** MS(FAB) *m/z* 929 $(M\text{-}Cl)^+$. Anal. Calcd. for $C_{54}H_{78}ClMnN_2O_4Si_2$: C, 67.16; H, 8.14; N, 2.90. Found: C, 66.47; H, 8.44; N, 2.90.
(*R,R*)-**3.** MS(EI) *m/z* 776 $(M)^+$, 778 $(M+2)^+$, 780 $(M+4)^+$. Anal. Calcd. for $C_{36}H_{36}Br_2ClMnN_2O_2$: C, 55.51; H, 4.66; N, 3.60. Found: C, 55.31; H, 4.69; N, 3.61.
(*R,R*)-**5.**[24d] MS(FAB) *m/z* 831 $(M\text{-}Cl)^+$. Anal. Calcd. for $C_{46}H_{76}ClMnN_2O_4Si_2$: C, 63.68; H, 8.83; N, 3.23. Found: C, 63.63; H, 9.07; N, 3.19.

General procedure for the asymmetric epoxidation of 1,2-dihydronaphthalene with aq. hydrogen peroxide catalyzed by (*S,S*)-1 (Table 1). To a cooled (2 °C) solution of 1,2-dihydronaphthalene (65 mg, 0.5 mmol), donor ligand (0.2 mmol), and catalyst (*S,S*)-**1** (16.5 mg, 0.025 mmol) in CH_2Cl_2-CH_3OH (1:1, 1.6 ml) was added precooled 30 % aqueous H_2O_2 (8.9 M, 0.16 ml, 1.42 mmol) in four portions during 40 minutes. The mixture was stirred at 2 °C and the reaction was monitored by TLC. After the reaction had reached completion, the mixture was diluted with CH_2Cl_2 and transferred into a separatory funnel containing water. The organic layer was separated, dried over Na_2SO_4, and concentrated. The residue was analyzed by ^1H NMR and the epoxide was isolated by flash chromatography on silica gel (hexane/EtOAc, gradient elution). The ee of the epoxide was determined by ^1H NMR in the presence of the chiral shift reagent tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III), $Eu(hfc)_3$.

Asymmetric epoxidation with urea-hydrogen peroxide adduct (Table 1, entry 7). The reaction was carried out as above except that urea-hydrogen peroxide adduct (UHP, 1.5 mmol as H_2O_2) was added as a solid in two roughly equal portions in 30 minutes.

Asymmetric epoxidation using $NaHCO_3$ as the cocatalyst (Table 1, entry 12). The reaction was carried out as above except that the hydrogen peroxide solution (8.9 M, 0.17 ml, 1.51 mmol) contained $NaHCO_3$ (8.8 mg, 0.105 mmol).

General procedure for the asymmetric epoxidation of various alkenes with aq. hydrogen peroxide and NH_4OAc (Table 2). The reactions were performed as above in general procedure for Table 1 using 0.47 mmol of the alkene, 0.10 mmol of NH_4OAc, 0.024 mmol of the catalyst **1-5**, and 1.33-1.38 mmol of aqueous H_2O_2 in CH_2Cl_2-CH_3OH (1:1, 1.5 ml).

Asymmetric epoxidation of 6,7-dihydro-5*H*-benzocycloheptene catalyzed by (*S,S*)-2 and (*R,R*)-5 (Table 2, entries 2 and 7). To a cooled (2 °C) solution of 6,7-dihydro-5*H*-benzocycloheptene (68 mg, 0.47 mmol), NH_4OAc (8 mg, 0.10 mmol), and catalyst (*S,S*)-**2** or (*R,R*)-**5** (0.024 mmol) in CH_2Cl_2-CH_3OH (3:5, 2 ml) was added precooled aq. H_2O_2 (0.15 ml, 1.33 mmol) in four portions during 40 minutes. The mixture was stirred at 2 °C and after 1.5 h more H_2O_2 (4 x 30 ml, 1.07 mmol) was added in 30 min intervals. The reaction catalyzed by (*S,S*)-**2** reached completion after 5 hours, and the reaction catalyzed by (*R,R*)-**5** was stopped after 6 hours (^{1}H NMR showed the presence of the olefin and the epoxide in a ratio of 28:72).

Asymmetric epoxidation of 1,2-dihydronaphthalene catalyzed by (*R,R*)-3 (Table 2, entry 8). The reaction was performed as above using 64 mg of 1,2-dihydronaphthalene (0.49 mmol), NH_4OAc (8 mg, 0.10 mmol), catalyst (*R,R*)-**3** (24 mg, 0.025 mmol), and 1.33 mmol of H_2O_2 in CH_2Cl_2-CH_3OH (3:5, 2 ml). After 1.5 h more H_2O_2 (2 x 30 ml, 0.53 mmol) was added in 30 min intervals. After 5 h the reaction mixture was worked-up and analyzed as above.

Asymmetric epoxidation of spiro[chromen-2,1'-cyclohexane] and 1,1-diphenyl-1-propene catalyzed by (*S,S*)-2 at -18 °C (Table 2, entries 11 and 13). The reactions were performed as above using 0.46 mmol of the alkene, 0.10 mmol of NH_4OAc, 0.024 mmol of (*S,S*)-**2**, and 1.33 mmol of H_2O_2 in CH_2Cl_2-CH_3OH (3:5, 2 ml). After 1.5 h more H_2O_2 (2 x 30 ml, 0.53 mmol) was added in 30 min intervals.

Asymmetric epoxidation of 6,7-dihydro-5*H*-benzocycloheptene catalyzed by (*S,S*)-4 and NaOAc (Table 2, entry 6). The reaction was performed as in general procedure for Table 2 using 0.46 mmol of the alkene, 0.10 mmol of NaOAc, 0.023 mmol of (*S,S*)-**4**, and 1.25 mmol of aq. H_2O_2 in CH_2Cl_2-MeOH (1:1, 1.5 ml).

^{1}H NMR and chiroptical data of the obtained epoxides

(1*S*,2*R*)-1,2-Epoxy-1,2,3,4-tetrahydronaphthalene; [25] ^{1}H NMR: δ 1.76 (1H, ddd, *J*= 5.6, 13.8 and 13.8 Hz), 2.35-2.59 (2H, m), 2.78 (1H, ddd, *J*= 6.4, 13.4 and 15.0 Hz), 3.74 (1H, m), 3.85 (1H, d, *J*= 4.2 Hz), 7.05-7.45 (4H, m). $[\alpha]^{23}_D$ - 90.8 (*c* 0.94, $CHCl_3$, 69 % ee).

(5*S*,6*R*)-5,6-Epoxy-6,7,8,9-tetrahydro-5*H*-benzocycloheptene;[26] ^{1}H NMR: δ 1.50-1.95 (3H, m), 2.15 (1H, m), 2.68-2.98 (2H, m), 3.41 (1H, m), 4.03 (1H, d, *J*= 4.4 Hz), 7.08 (1H, m), 7.25 (2H, m), 7.50 (1H, m). $[\alpha]^{23}_D$ +21.7 (*c* 0.98, $CHCl_3$, 85 % ee).

(1*S*,2*R*)-1,2-Epoxyindan;[27] ^{1}H NMR: δ 2.99 (1H, dd, *J*= 2.9 and 18.0 Hz), 3.24 (1H, d, *J*= 18.4 Hz), 4.15 (1H, dd, *J*= 2.8 and 2.9 Hz), 4.28 (1H, dd, *J*= 1.1 and 2.6 Hz), 7.20-7.35 (3H, m), 7.52 (1H, d, *J*= 6.8 Hz). $[\alpha]^{24}_D$ +15.7 (*c* 0.94, $CHCl_3$, 75 % ee).

3,4-Epoxyspiro[chroman-2,1'-cyclohexane]; ^{1}H NMR: δ 1.26-2.14 (10H, m), 3.49 (1H, d, *J*= 4.4 Hz), 3.87 (1H, d, *J*= 4.4 Hz), 6.83-6.96 (2H, m), 7.20-7.35 (2H, m). HRMS(EI) *m/z*: calcd. for $C_{14}H_{16}O_2$ 216.1150, found 216.1159. $[\alpha]^{24}_D$ +11.2 (*c* 1.03, $CHCl_3$, 90 % ee).

(*R*)-1,1-Diphenyl-1-propeneoxide; [28] ^{1}H NMR: δ 1.18 (3H, d, *J*= 5.4 Hz), 3.49 (1H, q, *J*= 5.4 Hz), 7.28-7.43 (10H, m). $[\alpha]^{24}_D$ + 20.2 (*c* 1.02, $CHCl_3$, 92 % ee).

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