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# Asymmetric Mn(III)-salen catalyzed epoxidation of unfunctionalized alkenes with in situ generated peroxycarboxylic acids

Pekka Pietikäinen*

*Department of Chemistry, Laboratory of Organic Chemistry, University of Helsinki, BOX 55, FIN-00014, Helsinki, Finland*

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## Abstract

Unfunctionalized aromatic alkenes were enantioselectively epoxidized with peroxycarboxylic acids prepared in situ from urea-$H_2O_2$ (and other anhydrous adducts of $H_2O_2$) and carboxylic acid anhydrides (maleic, phthalic, and acetic anhydride) using chiral Mn(III)-salen complexes as catalysts and *N*-methylmorpholine *N*-oxide (NMO) as an additive. Experimental results were compared with those reported earlier that employed aqueous hydrogen peroxide as the primary oxidant and the method presented here was found to offer both higher enantioselectivities and shorter reaction times. This novel epoxidation system was also compared with the Jacobsen's MCPBA/NMO system, and some differences in reactivity and selectivity were observed. These differences could possibly be explained assuming the presence of alternative mechanistic pathways during the catalytic cycle of the asymmetric epoxidation. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Asymmetric reactions; Epoxidations; Catalysts; Peroxyacids; Hydrogen peroxide

## 1. Introduction

The enantioselective epoxidation of alkenes is an important reaction in organic synthesis because the resulting epoxide can be stereospecifically opened by nucleophiles to produce various optically active 1,2-difunctional compounds. One of the most challenging aims has been the achievement of high enantioselectivity in the epoxidation of unfunctionalized alkenes. Presently, chiral Mn(III)-salen complexes (e.g. catalysts **1–4** in Scheme 1) are the most efficient and practical catalysts for the asymmetric epoxidation of various *cis*-disubstituted, tri- and tetra-substituted alkenes [1,2]. Many stoichiometric oxidants are able to donate the oxygen atom in transition metal catalyzed epoxidations the most frequently utilized being iodosylarenes [3–5], NaOCl [1,6,7], molecular oxygen [8], and $H_2O_2$ [9–12].

Recently, *m*-chloroperoxybenzoic acid (MCPBA) was used in Mn(III)-salen catalyzed low temperature epoxidation of various alkenes [13,14]. High yields of epoxides and enantiomeric excesses (ee) were reported particularly when the reactions were conducted at −74°C using excess of *N*-methylmorpholine *N*-oxide (NMO) as an additive. On the other hand, MCPBA is both shock sensitive and potentially explosive, and the commercial oxidant is usually contaminated with substantial amounts of *m*-chlorobenzoic acid and water [15,16]. Therefore, search for safe alternatives

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* Present address: Orion Corporation Fermion, Box 28, FIN-02101 Espoo, Finland. Tel.: +358-9-4294528; fax: +358-9-4294597.
*E-mail address:* pekka.pietikainen@orion.fi (P. Pietikäinen).

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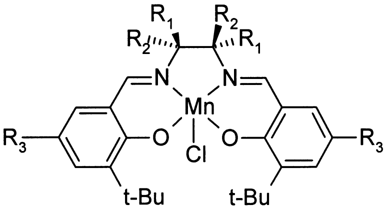


Scheme 1. (*S*,*S*)-**1**: $R_1$,$R_1$ = –$(CH_2)_4$–, $R_2$ = H, $R_3$ = *t*-Bu. (*R*,*R*)-**2**: $R_1$ = H, $R_2$,$R_2$ = –$(CH_2)_4$–, $R_3$ = OSi(*i*-Pr)$_3$. (*S*,*S*)-**3**: $R_1$ = Ph, $R_2$ = H, $R_3$ = Me. (*S*,*S*)-**4**: $R_1$ = Ph, $R_2$ = H, $R_3$ = OSi(*i*-Pr)$_3$.

for MCPBA is sensible especially if large-scale syntheses are desired. Magnesium monoperoxyphthalate (MMPP) is presently the most widely used substitute for MCPBA but it suffers from low solubility [15–17]. MMPP has previously been used as an oxidant in epoxidations catalyzed by metalloporphyrins under phase-transfer conditions [18]. In addition, Jacobsen et al. reported that asymmetric salen catalyzed epoxidations with MMPP proceeded well in the presence of an aqueous phase, whereas reactions under anhydrous conditions at low temperatures resulted in very low reactivity [13,14]. Unfunctionalized alkenes have also been epoxidized using 40% peracetic acid together with Mn-salen complexes in one instance however, only moderate enantioselectivity was observed [8].

It is also possible to epoxidize alkenes with peroxycarboxylic acids generated in situ from carboxylic acid anhydrides and either aqueous $H_2O_2$ or more preferably anhydrous urea-$H_2O_2$ (UHP) [15–25]. Most commonly used anhydrides include acetic anhydride and trifluoroacetic anhydride [15,16,19,20], phthalic anhydride [21,22], and particularly maleic anhydride [22–25]. For example, peroxyacetic acid generated from excess acetic anhydride and 30% $H_2O_2$ has been used in the Mn-porphyrin catalyzed epoxidation of non-functionalized alkenes [26]. The present paper shows — as a part of the search for mild asymmetric epoxidation methods [9,12,27,28] — the possibility of using in situ generated peroxyacids as terminal oxidants in the asymmetric epoxidation of simple aromatic alkenes catalyzed with chiral Mn(III)-salen complexes. UHP itself is a easy-to-handle solid source of anhydrous $H_2O_2$ alternative to concentrated hydrogen peroxide for use in various oxidation reactions including Mn(III)-salen catalyzed epoxidations [9,12,15,16,19]. UHP is easily prepared by crystallizing urea from aqueous $H_2O_2$ [29], and it is also commercially available. In addition to UHP, other anhydrous adducts of hydrogen peroxide, triphenylphosphine oxide-$H_2O_2$ ($Ph_3PO{\cdot}0.5H_2O_2$, POHP) [30] and sodium percarbonate ($Na_2CO_3{\cdot}1.5H_2O_2$, SPC) [31] were tested as $H_2O_2$ donors [20]. For comparison, peroxylauric acid was also tested as possible alternative for MCPBA [32].

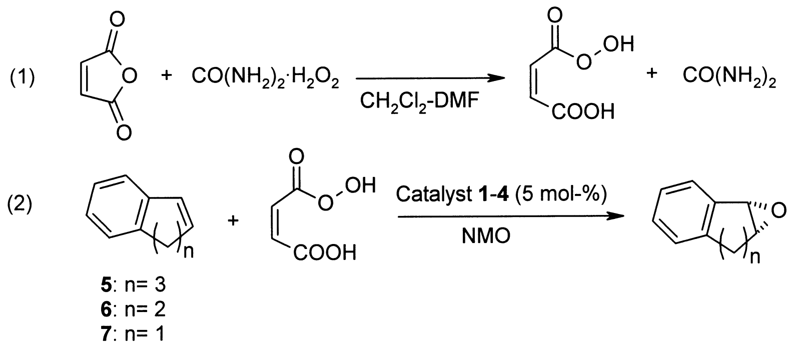
## 2. Results and discussion

### 2.1. Asymmetric epoxidation with in situ generated peroxyacids under different conditions

Unfunctionalized aromatic alkenes, 6,7-dihydro-5H-benzocycloheptene (**5**), 1,2-dihydronaphthalene (**6**), and indene (**7**), were enantioselectively epoxidized with peroxycarboxylic acids formed in situ from anhydrous adducts of $H_2O_2$ and carboxylic acid anhydrides (maleic, phthalic, and acetic anhydride) using chiral Mn(III)-salen complexes **1–4** (5–7 mol%) as catalysts and *N*-methylmorpholine *N*-oxide (NMO) as an additive. Typical epoxidation procedure showing maleic anhydride and UHP is outlined in Scheme 2. The results are summarized in Tables 1 and 2.

The peroxyacids were prepared using slight excess of the anhydride over $H_2O_2$ at room temperature for 0.5–1 h in order to obtain peroxyacids essentially free from $H_2O_2$ [24,26,33]. This was further favored by using $CH_2Cl_2$-DMF mixture as the reaction medium. For example, reaction of maleic anhydride with concentrated $H_2O_2$ in solvents with low dielectric constant (e.g. $CH_2Cl_2$) has been reported to be slow and incomplete even at reflux temperatures, but in the presence of small amounts of water-miscible solvents of high dielectric constant (e.g. DMF) rapid conversion to peroxymaleic acid takes place [24].

The epoxidation reactions (Eq. (2) in Scheme 2) were very facile and proceeded generally within 1 h upon addition of the alkene, catalyst and NMO to a suspension of the peroxyacid in $CH_2Cl_2$-DMF (4:1) at 2 or $-18^\circ$C (reaction medium was buffered in the case of peroxyacetic acid). The rate of the epoxidation was strongly dependent on the presence of NMO. While the reaction could be conducted even with substoichiometric amounts of the additive (0.2 mol% was enough to induce complete reaction) its absence



Scheme 2. Typical epoxidation procedure utilizing in situ generated peroxymaleic acid.

resulted in significant retardation of the epoxidation (incomplete reaction after 24 h). Also, epoxidations in the absence of Mn-salen complexes were negligible under the usual reaction conditions.

Benzocycloheptene (**5**) was initially used as the model olefin to test the efficiency of different carboxylic anhydrides and $H_2O_2$ adducts with catalysts **1** and **2** (Table 1, entries 1–7). The enantioselectivity obtained with catalyst **2** was slightly higher, while at the same time the yield of the corresponding epoxide was lower compared with reactions conducted using catalyst **1**. Particular attention was paid to maleic

Table 2
Asymmetric Mn(III)-salen (**3**) catalyzed epoxidation of 1,2-dihydronaphthalene (**6**) with different oxidants at 2°C[a]

| Entry | Oxidant | Time (h) | Isolated yield (%) | ee (%)[b] |
|---|---|---|---|---|
| 1 | 30% $H_2O_2$ | 2 | 74 | 69 |
| 2 | urea·$H_2O_2$ | 2 | 72 | 69 |
| 3 | $Ph_3PO{\cdot}0.5H_2O_2$ | 3 | 70 | 65 |
| 4 | $Na_2CO_3{\cdot}1.5H_2O_2$ | 6 | traces | – |
| 5 | urea·$H_2O_2$/maleic anhydride | 0.75 | 70 | 73 |

[a] See experimental section for reaction conditions.
[b] Determined by $^1H$ NMR in the presence of $Eu(hfc)_3$.

Table 1
Asymmetric Mn(III)-salen catalyzed epoxidation with in situ generated peroxyacids[a]

| Entry | Alkene | Catalyst | Oxidant[b] | Temp (°C) | Time (h) | Yield[c] (%) | ee[d] (%) | Epoxide configuration[e] |
|---|---|---|---|---|---|---|---|---|
| 1 | 5 | 1 | UHP/MA | 2 | 1.5 | 71 | 87 | 5*S*,6*R*−(+) |
| 2 | 5 | 1 | POHP/MA | 2 | 0.5 | 81 | 88 | 5*S*,6*R*−(+) |
| 3 | 5 | 1 | POHP/MA | −18 | 0.75 | 81 | 90 | 5*S*,6*R*−(+) |
| 4 | 5 | 2 | POHP/MA | −18 | 1.5 | 73 | 92 | 5*R*,6*S*−(−) |
| 5 | 5 | 1 | UHP/PA[f] | 2 | 4 | 54 | 87 | 5*S*,6*R*−(+) |
| 6 | 5 | 1 | UHP/$Ac_2O$ | −18 | 0.5 | 80 | 89 | 5*S*,6*R*−(+) |
| 7 | 5 | 1 | Peroxylauric acid | −18 | 2.75 | 66 | 91 | 5*S*,6*R*−(+) |
| 8 | 6 | 3 | UHP/MA | −18 | 1 | 70 | 73 | 1*S*,2*R*−(−) |
| 9 | 6 | 3 | POHP/MA | −70 | 1 | 69 | 66 | 1*S*,2*R*−(−) |
| 10 | 7 | 1 | UHP/MA | 2 | 0.5 | 41 | 73 | 1*S*,2*R*−(+) |
| 11 | 7 | 3 | UHP/MA | −18 | 0.5 | 50 | 80 | 1*S*,2*R*−(+) |
| 12 | 7 | 4 | UHP/MA | −18 | 1.25 | 40 | 81 | 1*S*,2*R*−(+) |

[a] See experimental section for reaction conditions.
[b] MA = maleic anhydride, PA = phthalic anhydride.
[c] Isolated yield.
[d] Determined by $^1H$ NMR in the presence of $Eu(hfc)_3$.
[e] Determined by comparison of the sign of $[a]_D$ to the literature values ([12]).
[f] Reaction was performed in MeOH-$CH_2Cl_2$ (1:1).

anhydride since it may be used in non-buffered systems unlike acetic and trifluoroacetic anhydrides [22–25]. Also, peroxymaleic acid has in some cases been observed to be more reactive than most peroxyacids with the exception of trifluoroperoxyacetic acid [23]. Here, highest chemical yields were obtained by using maleic or acetic anhydrides. Reactions performed with UHP/phthalic anhydride or peroxylauric acid afforded lower yields however, comparable ee-values were obtained in all cases. Enantioselectivity in oxidations with peroxymaleic acid was independent of the $H_2O_2$ adduct used (entries 1–2). On the other hand, reactions performed using POHP were faster and produced higher chemical yields compared to epoxidations induced by UHP. The slight difference in reactivity can be attributed to the higher solubility of POHP in organic solvents [30].

Dihydronaphthalene (**6**) and indene (**7**) were epoxidized with equal efficiency using both POHP and UHP as the source of $H_2O_2$ (Table 1, entries 8–12). With these alkenes highest selectivities were obtained using the 1,2-diphenylethylenediamine derived complexes **3** and **4** as catalysts. Epoxidation of indene was very facile but at the same time the chemical yield was only moderate compared to earlier reaction systems [12,28]. It is possible that the highly sensitive indene epoxide reacts with maleic acid resulting in epoxide ring opening products as similar behavior of other sensitive epoxides has been reported earlier [23,25].

Generally, lowering the reaction temperature from 2 to $-18^\circ$C had marginal positive effect on the yield and ee of the epoxides however, reaction temperatures below $-18^\circ$C were not beneficial for the reaction (entry 2 versus 3). For example, epoxidation of alkene **6** with POHP/MA and catalyst **3** at $-70^\circ$C produced the corresponding epoxide of 66% ee in 69% yield compared with 73% ee and 70% yield at $-18^\circ$C (entry 8 versus 9). In the case of the less soluble UHP/MA-system the reactions were impractically slow at $-70^\circ$C. Likewise reactions conducted using phthalic anhydride started to slacken when the temperature was decreased below $0^\circ$C.

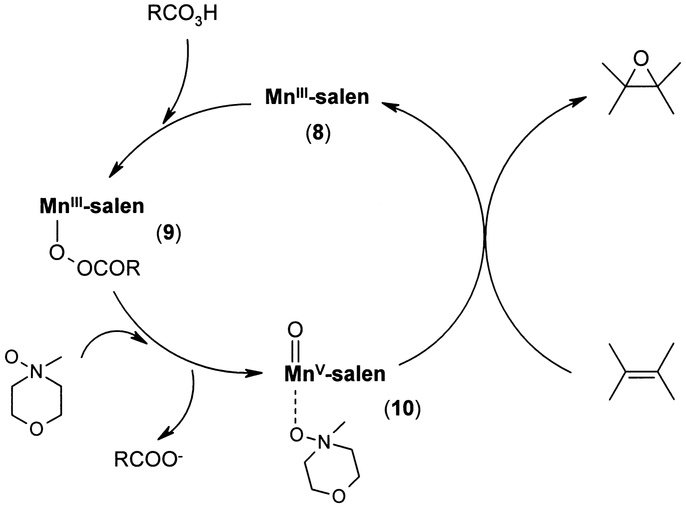
### 2.2. *Comparison of the peroxyacid epoxidation with other oxidation systems utilizing $H_2O_2$*

Experimental results obtained here were compared with those reported earlier employing aqueous $H_2O_2$ and UHP as oxidants [12]. In general, 3–5% higher enantioselectivities were obtained using in situ generated peroxyacids compared to hydrogen peroxide. Also epoxidations proceeded considerably faster: with peroxyacids reaction times were usually within 1 h, while reactions conducted using $H_2O_2$ took 2–4 h to reach completion [12]. These differences in enantioselectivity and reactivity are illustrated in Mn(III)-salen (**3**) catalyzed epoxidation of 1,2-dihydronaphthalene (**6**) with aqueous $H_2O_2$, anhydrous $H_2O_2$ adducts, and peroxymaleic acid (Table 2 for results). The results show that all the oxidants with the exception of $Na_2CO_3{\cdot}1.5H_2O_2$ (SPC) give similar epoxide yields, but in situ generated peroxymaleic acid affords up to 8% higher enantioselectivity. The very low reactivity of SPC is presumably due to its low solubility to the solvent system. Similar differences in reactivity between UHP and SPC have been reported before [9].

In addition to the carboxylic anhydrides, other derivatives capable of generating activated oxidants in situ with $H_2O_2$ were tested. All the systems studied, namely benzoyl imidazole [20,34], ethyl chloroformate and cyanoformate [35,36], nitriles (benzonitrile, trichloroacetonitrile) [20], and formamide [37] generally produced unsatisfactory results. The only exception was trichloroacetonitrile that in some cases gave similar results compared with the system presented here. For example, epoxidation of 1,2-dihydronaphthalene (**6**) with trichloroacetonitrile/UHP [20] in the presence of NMO and catalyst **3** produced the corresponding epoxide with 72% ee in 70% yield (for comparison, see Table 2, entry 5).

### 2.3. *Possible catalytic routes for the asymmetric epoxidation with peroxyacids*

While the enantiomeric excesses obtained here are reasonably high they sometimes fall short of the selectivities obtained with the MCPBA/NMO system introduced by Jacobsen et al. [13,14]. Also, the temperature dependence is somewhat different. Here, decreasing the reaction temperature considerably below $-18^\circ$C did not improve the ee's in contrast to the case of MCPBA where lowering the temperature to $-74^\circ$C is highly favorable to the attainment of high enantioselectivities [13,14]. In some cases inferior enantioselectivity has been obtained with the MCPBA/NMO system when the epoxidation has



Scheme 3. Possible catalytic route for the asymmetric epoxidation with peroxyacids.

been conducted at 0°C instead of −74°C [13,38]. In addition, the NMO additive has divergent functions in these reaction systems. Generally, NMO and other nitrogen heterocycles are considered to act as axial ligands to the salen metal catalysts (e.g. Scheme 3) and as bases, and they are also believed to prevent the formation of unreactive μ-oxo dimers [1,2,12]. In the case of Jacobsen's epoxidation system NMO has some additional roles. Jacobsen et al. observed that NMO and MCPBA generate a 1:1 salt which is unreactive towards alkenes but oxidizes the (salen)Mn(III) catalyst [13]. Also, excess NMO was critical in preventing the uncatalyzed epoxidation pathways that take place in the absence of the additive [13,14].

Based on these differences in reactivity and selectivity, it is reasonable to assume that the oxidation method introduced here might operate with different mechanistic pathway than the Jacobsen's system. In Scheme 3 is presented one possible catalytic route for the asymmetric epoxidation with peroxyacids. In the case of in situ generated peroxyacids, the reaction sequence from (salen)Mn(III) (**8**) to (salen)Mn(V)=O (**10**), which is the actual active oxidant, most likely proceeds via a peroxyacylmanganese species **9** [(salen)Mn(III)-O-OCOR] [12,39,40]. Similar pathway has been proposed by Montanari et al. for the Mn-porphyrin catalyzed epoxidation of alkenes with $H_2O_2$ in the presence of nitrogen heterocycle ligands and carboxylic acid cocatalysts [39,40]. In an alternative sequence peroxyacyl intermediate **9** is assumed as the active species without the presence of the oxo compound **10** [2]. The Mn-salen catalyzed epoxidation with molecular oxygen/pivalaldehyde (or peroxyacetic acid) has been proposed to provide, in certain conditions, [(salen)Mn(III)-O-OCOR] as the active oxidant which epoxidized alkenes directly [2,8]. Likewise, acylperoxoiron(III) porphyrin species from Fe(III)-porphyrins and MCPBA have been suggested by Morishima et al. as potent oxidants for olefin epoxidations especially at low temperatures [41]. Therefore, the presence of **9** as active species in Mn-salen catalyzed epoxidation with MCPBA/NMO seems reasonable [2], although the exact mechanistic role of NMO in this reaction system is not clear [14].

Finally, the involvement of other reactive species during the catalytic cycle cannot be ruled out. In fact, Groves and Stern have reported the existence of two different oxidative species in the Mn-porphyrin catalyzed epoxidation with MCPBA in the presence of tetramethylammonium hydroxide [42]. The other oxidant prevailing at low temperatures (−78°C) was the (porphyrin)Mn(V)=O, while the other, favored above 0°C, was suggested to be a Mn(IV)=O species. This species also performed alkene epoxidation but with less diastereoselectivity: significant amounts of *trans*-epoxide were formed from *cis*-alkene.

In conclusion, in situ generated peroxyacids were shown to be effective oxidants in the asymmetric epoxidation of unfunctionalized alkenes catalyzed by Mn(III)-salen complexes. Especially, the combination of maleic anhydride with the commercially available UHP and NMO makes up a feasible reaction system. When compared with the analogous epoxidations using $H_2O_2$ [12], addition of carboxylic anhydrides resulted in pronounced increase in reactivity and enantioselectivity. Finally, differences in selectivity and reactivity between the reaction system presented here and the Jacobsen's MCPBA/NMO-system could be reasonably explained assuming that different mechanistic pathways were operating during the catalytic cycles.

## 3. Experimental

### 3.1. General

$^1$H NMR spectra were recorded in $CDCl_3$ at 200 MHz on a Varian Gemini 2000 spectrometer. Optical rotation was measured with a JASCO DIP-1000 digital polarimeter at ambient temperature. TLC was conducted on Merck silica gel 60 $F_{254}$ plates. Flash chromatography was performed using Merck silica gel 60 (230–400 mesh ASTM). 6,7-Dihydro-5H-benzocycloheptene (**5**), 1,2-dihydronaphthalene (**6**), and Mn-salen catalysts **2–4** were prepared as previously described [12]. Indene (**7**) was from Merck and was freshly distilled before use. Catalyst **1** was purchased from Fluka Chemie. Anhydrous adducts of $H_2O_2$ (UHP [29], POHP [30], and SPC [31]) and peroxylauric acid [32] were prepared as indicated in the literature. The $H_2O_2$ content was determined by iodometric titration.

### 3.2. Typical asymmetric epoxidation with in situ prepared peroxymaleic acid

POHP or UHP (0.75 mmol as $H_2O_2$) was added to a solution of maleic anhydride (100 mg, 1.0 mmol) in $CH_2Cl_2$-DMF (4:1, 1.0 ml) and the resulting suspension was stirred at room temperature for 30 min and then cooled to 2 to −18°C. Then a pre-cooled solution of the alkene **5–7** (0.49 mmol), NMO (130 mg, 1.11 mmol), and Mn-salen catalyst **1–4** (0.024–0.032 mmol) in $CH_2Cl_2$ (1.5 ml) was added and the reaction mixture was stirred at 2 to −18°C. After completion of the reaction (monitored by TLC), excess of dimethylsulfide (ca. 2.0 mmol) was added and the mixture was stirred for 15 min at room temperature. Then $CH_2Cl_2$ (7 ml) and saturated $NaHCO_3$ solution (3 ml) were added and the phases separated. The organic phase was washed with water, dried over anhydrous $Na_2SO_4$, and concentrated. The residue was purified by flash chromatography (the silica gel was buffered with $Et_3N$) eluting with hexane-ethyl acetate. The ee of the epoxide was determined by $^1$H NMR in the presence of the chiral shift reagent tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III), Eu(hfc)$_3$. $^1$H NMR and typical chiroptical data of the obtained epoxides are presented in a previous paper [12].

### 3.3. Asymmetric epoxidation with peroxyphthalic acid

UHP (0.75 mmol as $H_2O_2$) was added to a solution of phthalic anhydride (150 mg, 1.01 mmol) in MeOH (1.5 ml) and the resulting suspension was stirred at room temperature for 30 min and then cooled to 2°C. Then a pre-cooled solution of the alkene **5** (68 mg, 0.47 mmol), NMO (130 mg, 1.11 mmol), and catalyst **1** (15.3 mg, 0.024 mmol) in $CH_2Cl_2$ (1.5 ml) was added and the reaction mixture was stirred at 2°C. After completion of the reaction the mixture was treated as above.

### 3.4. Asymmetric epoxidation with peroxyacetic acid

UHP (1.06 mmol as $H_2O_2$) was suspended in $CH_2Cl_2$-DMF (4:1, 1.0 ml), acetic anhydride (160 μl, 1.69 mmol) was added, and the resulting suspension was stirred at room temperature for 1 h. $Na_2HPO_4$ (0.3 g, 2.0 mmol) was added and the mixture was cooled to −18°C. A pre-cooled solution of the alkene **5** (68.5 mg, 0.475 mmol), NMO (230 mg, 1.96 mmol), and catalyst **1** (19 mg, 0.030 mmol) in $CH_2Cl_2$ (2.5 ml) was added and the reaction mixture was stirred at −18°C. After completion of the reaction the mixture was treated as above.

### *3.5. Asymmetric epoxidation with peroxylauric acid*

A pre-cooled solution of peroxylauric acid (165 mg, 0.76 mmol) in $CH_2Cl_2$ (2.5 ml) was added to a cooled (−18°C) solution of the alkene **5** (67 mg, 0.465 mmol), NMO (150 mg, 1.28 mmol), and catalyst **1** (15.5 mg, 0.024 mmol) in $CH_2Cl_2$ (2 ml). The mixture was stirred, and after completion of the reaction, treated with excess of $Me_2S$. The mixture was filtered through a small plug of Florisil and the filtrate concentrated in vacuo. The residue was treated as above.

### *3.6. Asymmetric epoxidations with anhydrous $H_2O_2$ adducts [12]*

Solid anhydrous $H_2O_2$ adduct (UHP, POHP or SPC, 1.4 mmol as $H_2O_2$) was added in two roughly equal portions in 20 min to a cooled solution of the alkene **6** (65 mg, 0.5 mmol), NMO (70 mg, 0.52 mmol), and catalyst **3** (16 mg, 0.025 mmol) in MeOH-$CH_2Cl_2$ (1:1, 2 ml). The mixture was stirred at 2°C, and after completion of the reaction, treated as above.

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