Turkish Journal of Chemistry
http://journals.tubitak.gov.tr/chem/
Research Article

Turk J Chem
(2015) 39: 824 – 834

doi:10.3906/kim-1411-68

# Conversion of racemic allylic hydroperoxides into corresponding chiral 1/2,3-triols by using catalytic $OsO_4$ and chiral cinchona ligands in the absence of co-oxidant

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**Received:** 26.11.2014 • **Accepted/Published Online:** 13.05.2015 • **Printed:** 28.08.2015

**Abstract:** For the first time, removal of oxygen atoms from allylic hydroperoxide functionality and reintroduction to the double bond was achieved using catalytic $OsO_4$ and chiral cinchona alkaloid derivatives in an acetone–water mixture to give corresponding chiral 1/2,3-triol with an enantioselectivity up to 99% ee. The hydroperoxide group was used as both a co-oxidant and a source of hydroxyl groups. This protocol is thought to have potential to provide opportunities for chiral synthesis of 1/2,3-triols from corresponding allylic hydroperoxides in the absence of co-oxidant in one stage for the first time in the literature.

**Key words:** Chiral 1/2,3-triols, chiral cinchona alkaloids derivatives, allylic hydroperoxide, intramolecular atom transfer.

## 1. Introduction

Polyhydroxylated organic compounds including inositols, quercitols, conduritols, glucose, glycerol, ethylene glycol, and cyclic triols are an important class of compounds found in plants and they are often used in the production of industrial materials.[1,2] Additionally, most cyclitols possess a wide range of important biological activities such as glycosidase inhibitory effect and antibiotic effect.[3–6] Recently, the enantioselective synthesis of polyhydroxylated organic compounds has received considerable attention due to their useful biological activity and synthetic utility.[7,8] Consistently increasing demand for the production of enantiomerically pure compounds has led to the development of different strategies for the synthesis of chiral compounds. Among the employed strategies, asymmetric synthesis has an important place, as it represents an efficient access to the required enantiomer.[9]

Asymmetric synthesis of biologically active cyclitols and derivatives plays an important role in synthetic organic chemistry.[10–17] In particular, asymmetric construction of 1,2,3-triols is a key transformation in the synthesis of polyhydroxyl groups.[18]

Sharpless was the first to develop an asymmetric syn dihydroxylation reaction of olefins using a catalytic amount of $OsO_4$ and cinchona alkaloid as a chiral ligand in the presence of co-oxidants such as hydrogen peroxide, N-methylmorpholine oxide N-oxide (NMO), $NaIO_4$, or molecular oxygen.[18–21]

Recently we reported osmium-catalyzed racemic synthesis of 1/2,3-triols from corresponding allylic hydroperoxides, without the need for co-oxidant, in an acetone–water mixture (9:1) (Scheme 1, method A).[22] Ad-

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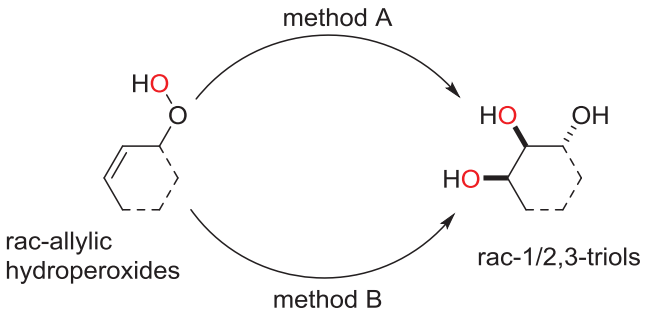
On the occasion of his retirement, we dedicate this paper to our supervisor Prof Dr Metin BALCI

ditionally, analogous reactions of intramolecular oxygen atom transfer were achieved by zeolite-confined osmium (0) nanoclusters as the result of the synthesis of racemic 1/2,3-triols from corresponding allylic hyroperoxides in the absence of co-oxidant (Scheme 1, method B).[23]




Reaction conditions, method A: cat.$OsO_4$, acetone-water (9:1), rt, 30-94% in 7 examples, 22-65 h.
Method B: 0.01 mmol% zeolite-Os (0), acetone: water (4:1), rt, 58-93% in 10 examples, 36-60 h.

**Scheme 1.** One-pot synthesis of racemic 1/2,3-triols from racemic allylic hydroperoxides.[22,23]

In Scheme 1, oxidation reactions were evolved to effectuate the synthesis of various racemic 1/2,3-triols via intramolecular oxygen atom transfer from racemic allylic hydroperoxides in the absence of co-oxidant. On the other hand, these two methods were also the pioneering examples for the synthesis of 1/2,3-triols from allylic hydroperoxides via intramolecular oxygen atom transfer.

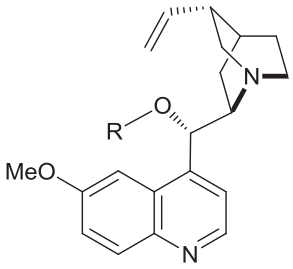
With this background, the objective of the present study was to develop an asymmetric version of this catalytic reaction. For this purpose, chiral cinchona alkaloid derivatives were used as chiral ligands with a catalytic amount of $OsO_4$ in an acetone–water mixture at room temperature. As expected, intramolecular oxygen atom transfer from the allylic hydroperoxide group to the double bond of the same molecule was achieved under mild conditions. In this protocol, an easy, facile, and applicable method was employed for the synthesis of chiral 1/2,3-triols. An effective method for the one-pot synthesis of 1/2,3-triols involves chiral cinchona alkaloids and the hydroperoxide group serving as both the co-oxidant and substrate. The use of cinchona alkaloids provides chirality, oxygen atom on the hydroperoxide group, and cat. $OsO_4$ oxides to the double bond on allylic hydroperoxide containing racemic olefins in acetone/water media.

## 2. Results and discussion

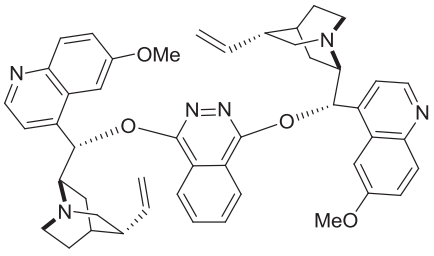
Some chiral cinchona alkaloids, **1b**, **1c**, **1d**, and **1e**, were prepared according to the literature procedures,[14–17] and other chiral cinchona ligands, **1a**, **1f**, and **1g**, were obtained from chemical suppliers (Figure).

As reported in the literature, when an amount of catalytic $OsO_4$ was used with chiral cinchona alkaloids in the dihydroxylation reaction of olefins, enantiomeric excess was quite high.[20] According to information based on the literature, the chiral ligands **1a**–**g** were treated with an equivalent amount of osmium tetraoxide, used as catalyst, in the synthesis of asymmetric triols in this study.

The cyclic or linear allylic hydroperoxides **2a**–**g** were prepared by the photooxygenation of corresponding alkenes.[17,24–32] For each of the allylic hydroperoxides, enantioselectivity and catalytic activity of the composed reaction solution were examined. Hence, the reaction temperature and the amount of chiral ligand were measured, while some findings about molecular structure were obtained for the developed asymmetric reaction.

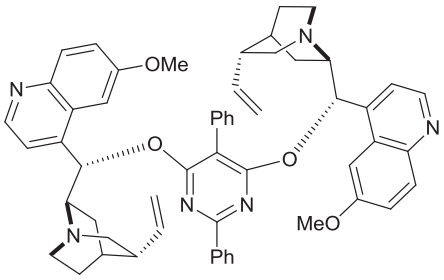



R=H (Quinidine), **1a,** (1*S*)-(6-methoxyquinolin-4-yl)(5-vinylquinuclidin-2-yl)methanol
R=Ac, **1b,** (1S)-(6-methoxyquinolin-4-yl)(5-vinylquinuclidin-2-yl)methyl acetate
R=$SiMe_3$, **1c,** 2-((*S*)-(6-methoxyquinolin-4-yl)((trimethylsilyl)oxy)methyl)-5-vinylquinuclidine
R=Bz, **1d,** (1*S*)-(6-methoxyquinolin-4-yl)(5-vinylquinuclidin-2-yl)methyl benzoate
R=Ts, **1e,** (1*S*)-(6-methoxyquinolin-4-yl)(5-vinylquinuclidin-2-yl)methyl 4-methylbenzenesulfonate




$(QD)_2$PHAL, **1f**

1-((*S*)-(6-methoxyquinolin-4-yl)((1*R*,2*S*,4*R*,5*S*)-5-vinylquinuclidin-2-yl)methoxy)-4-((1*S*)-(6-methoxyquinolin-4-yl)((2*S*)-5-vinylquinuclidin-2-yl)methoxy)phthalazine




$(QD)_2$PYR, **1g**

(1*R*,2*S*,4*R*,5*S*)-2-((1*S*)-(6-methoxyquinolin-4-yl)((6-((1*S*)-(6-methoxyquinolin-4-yl)((2*S*)-5-vinylquinuclidin-2-yl)methoxy)-2,5-diphenylpyrimidin-4-yl)oxy)methyl)-5-vinylquinuclidine

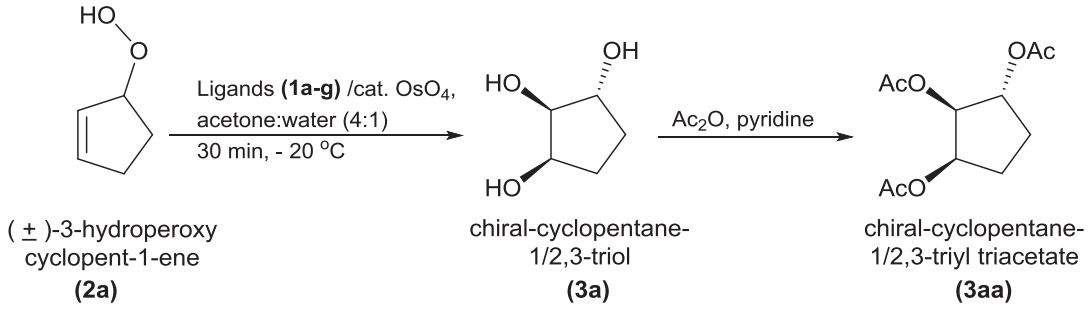
**Figure.** Chiral cinchona ligands used in this work.

In initial experiments in the present study, as a selected sample molecule 3-hydroperoxycyclopent-1-ene (**2a**) was reacted with ligand **1a**–**g** in the presence of cat. $OsO_4$ at a constant temperature and time (at –20 °C, in 30 min) in a solvent mixture such as acetone/water (4/1) (Table 1). To investigate the synthesis of racemic triols, the chiral ligand QD **1a** and cat. $OsO_4$ were primarily chosen and then other chiral ligands were tested in the presence of cat. $OsO_4$, including QDAc **1b**, $QDSiMe_3$ **1c**, QDBz **1d**, QDTs **1e**, $(QD)_2$PHAL **1f**, and $(QD)_2$PYR **1g** to optimize the reaction conditions. Among the chiral ligands, $QDSiMe_3$ **1c** was the most effective in the synthesis of chiral-cyclopentane-1/2,3-triol (**3a**) with a yield of 45%. The chiral triol **3a** was converted into corresponding chiral 1/2,3-triacetate **3aa** derivative $[\alpha]_D^{25} = -47$ (c 0.5, MeOH, 32% ee) for structural characterization and HPLC analysis (Table 1, entry 3; see supporting information, on the journal's website).

Results in assays performed with different amounts of $QDSiMe_3$ **1c** and cat. $OsO_4$ show that 2.6 mmol of hydroperoxides using as starting material with 0.4 mol % of $QDSiMe_3$ **1c** and cat. $OsO_4$ would be a more suitable system in enantioselectivity and synthesis of corresponding asymmetric 1/2,3-triol **3a**. The chiral triol **3a** was converted into corresponding **3aa** (Table 1, entry 9) and the conversion yield of **3a** was also quite high under these reaction conditions (conv. 92%). Although there were 1/2,3-triol molecules in higher conversion yields in Table 1, the high enantioselectivity reactions were taken into account. The reaction had to be interrupted at an appropriate time in order to capture high enantioselectivity; otherwise, a considerable increase would be seen in the racemic triols rate in the result of the reaction.

After determining the ligand type and ligand/$OsO_4$ rate, the effects of different parameters such as

**Table 1.** Effects of chiral ligands (1a–g) and cat. $OsO_4$ in the synthesis of chiral cyclopentane-1/2,3-triol **3a**[a] and its conversion into chiral chiral cyclopentane-1/2,3-triyl triacetate **3aa**.[d]




| Entry | $OsO_4$ (mol %) | Ligand (**1a**–**g**) (mol %) | Conversion (%)[b] | Yield (%)[c] | ee (%)[d] |
|---|---|---|---|---|---|
| 1 | 0.1 | 1a (0.1) | 88 | 78 | 6 |
| 2 | 0.1 | 1b (0.1) | 85 | 75 | 12 |
| **3** | **0.1** | **1c (0.1)** | **88** | **45** | **32** |
| 4 | 0.1 | 1d (0.1) | 85 | 55 | 28 |
| 5 | 0.1 | 1e (0.1) | 86 | 82 | 5 |
| 6 | 0.1 | 1f (0.1) | 88 | 67 | 10 |
| 7 | 0.1 | 1g (0.1) | 86 | 68 | 20 |
| 7 | 1.0 | 1c (1.0) | 98 | 85 | 15 |
| 8 | 0.2 | 1c (0.2) | 90 | 65 | 22 |
| **9** | **0.4** | **1c (0.4)** | **92** | **58** | **36** |
| 10 | 0.6 | 1c (0.6) | 93 | 68 | 19 |

[a] The reaction was carried out with **2a** (2.6 mmol) in acetone/water (v/v = 4/1) in 30 min at –20 °C in the presence of $OsO_4$ and chiral ligand.

[b] For **3a**, determined by $^1$H NMR,

[c] Total isolated yields of enantiomers from **2a** to **3aa**,

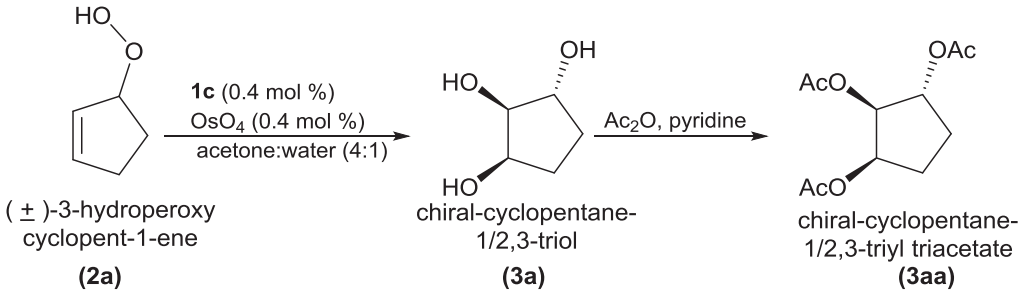
[d] For **3aa**, determined by HPLC with a Chiralcel AS column.

reaction time and temperature on the reactivity and enantioselectivity were investigated (Table 2). At the end of the trial studies, the reaction conditions giving the highest conversion and enantioselectivity were determined. It was found that temperature and reaction time play a crucial role in the synthesis of asymmetric 1/2,3-triols (Table 2, entries 1–11).

When the reaction was carried out with increasing time (30, 45, and 60 min) at the same temperature (such as –20 °C), for cyclopentane-1/2,3-triol (**3a**) conversion increased from 88% to 92%, yield from 45% to 58%, and ee from 32% to 36% (Table 2, entries 1–3). The chiral triacetate **3aa** was prepared from chiral triol **3a** with acetic anhydrate in pyridine. Optical rotatory of the chiral triacetate **3aa** was identified (Table 3, entries 1–3). The same conditions were applied to 3-hydroperoxycyclopent-1-ene (**2a**) at –40 °C for synthesis of chiral triols **3a** and in the result of the reaction synthesized chiral triol **3a** was convert to **3aa** in $Ac_2O$/pyridine solvent mixture; differences were observed in ee values of cyclopentane-1/2,3-triacetate (**3aa**): 16% ee in 30 min, 18% ee in 45 min, and 7% ee in 60 min (Table 2, entries 4–6).

When the reaction was carried out with increasing time as in entries 1–3 and at –70 °C, ee values of cyclopentane-1/2,3-triacetate (**3aa**) increased, although some differences were observed in conversions and yields

**Table 2.** Effects of temperature and time in the synthesis of chiral cyclopentane-1/2,3-triol **3a**[a] and its conversion into chiral chiral cyclopentane-1/2,3-triyl triacetate **3aa**.[e]




| Entry | Temperature (°C)[b] | Time (min) | Conversion (%)[c] | Yield (%)[d] | ee (%)[e] |
|---|---|---|---|---|---|
| **1** | **–20** | **30** | **88** | **45** | **32** |
| 2 | –20 | 45 | 90 | 46 | 33 |
| 3 | –20 | 60 | 92 | 58 | 36 |
| 4 | –40 | 30 | 68 | 35 | 16 |
| 5 | –40 | 45 | 73 | 40 | 18 |
| 6 | –40 | 60 | 78 | 45 | 7 |
| 7 | –70 | 30 | 50 | 20 | 4 |
| 8 | –70 | 45 | 48 | 25 | 9 |
| 9 | –70 | 60 | 60 | 41 | 20 |
| 10 | 0 | 30 | 92 | 35 | 15 |
| **11** | **0** | **60** | **99** | **52** | **46** |

[a] The reaction was carried out with **2a** (2.6 mmol) in acetone/water (v/v = 4/1) at the corresponding temperatures and in times in the presence of $OsO_4$ (0.4 mol %) and **1c** (0.4 mol %).

[b] Adjusted by Cryostat.

[c] For **3a**, determined by $^1$H NMR,

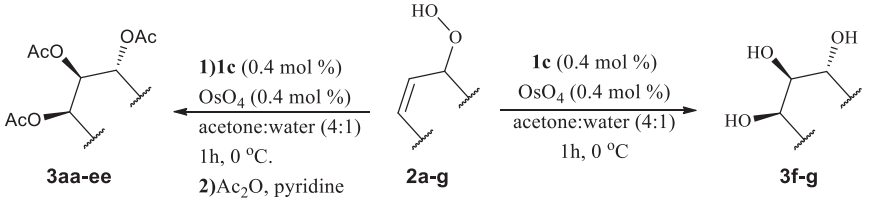
[d] Total isolated yields of enantiomers from **2a** to **3aa**,

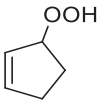
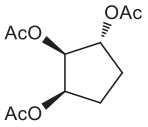
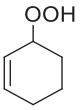
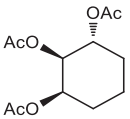
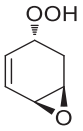
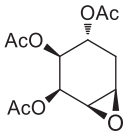
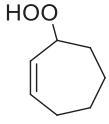
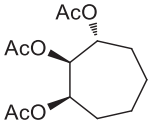
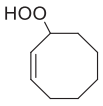
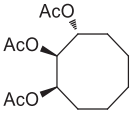
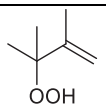
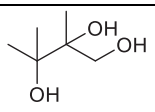
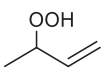
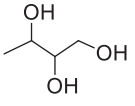
[e] For **3aa**, determined by HPLC with a Chiralcel AS column.

(Table 2, entries 7–9). However, ee values of cyclopentane-1/2,3-triacetate (**3aa**) at –40 °C and –70g° C were lower than those at –20 °C. It should be noted that the ee values of cyclopentane-1/2,3-triacetate (**3aa**) seem to be reduced as the temperature decreases. When the reaction temperature increased to 0 °C, cyclopentane-1/2,3-triol (**3a**) was obtained with a yield of 35% in 30 min and 52% in 60 min (Table 2, entries 10 and 11). It was determined that the reaction conditions such as 0 °C and 1 h were the most effective in the synthesis of cyclopentane-1/2,3-triol (**3a**) and the product was obtained in 99% conversion of cyclopentane-1/2,3-triol (**3a**) with 46% ee of cyclopentane-1/2,3-triacetate (**3aa**) (Table 2, entry 11).

Corresponding asymmetric 1/2,3-triols were synthesized from racemic allylic hydroperoxides using the optimized conditions as a result of experiments. The results of the reaction of $QDSiMe_3$ **1c**/cat. $OsO_4$ with various allylic hydroperoxides and the acetate derivatives of some asymmetric 1/2,3-triols are summarized in Table 3. For the characterization and HPLC analyses of some chiral triols, **3a**, **3b**, **3c**, **3d**, and **3e**, these triols were converted into the corresponding triacetates **3aa**, **3bb**, **3cc**, **3dd**, and **3ee** as reported in the literature. However, some triols such as **3h** and **3g** were not converted into corresponding acetates, because the triols **3g**

**Table 3.** Synthesis of chiral 1/2,3-triols from racemic allylic hydroperoxides[a] and its conversion into chiral 1/2,3-triacatate.




| Entry | Substrate | Product | Conversion (%)[b] | Yields (%)[c] | ee (%)[d] | $[\alpha]_D^{25e}$ |
|---|---|---|---|---|---|---|
| 1 |  2a |  3aa | 99 | 52 | 46 | -47.0 |
| 2 |  2b |  3bb | 99 | 44 | 25 | +10.0 |
| 3 |  2c |  3cc | 98 | 58 | 41 | -2.0 |
| 4 |  2d |  3dd | 92 | 60 | 35 | +5.0 |
| 5 |  2e |  3ee | 98 | 55 | 90 | -7.0 |
| 6 |  2f |  3f | 99 | 48 | 99 | +28.0 |
| 7 |  2g |  3g | 99 | 54 | 89 | +25.0 |

[a] The reaction was carried out with **2a**–**g** (2.6 mmol) in acetone/water (v/v = 4/1) at 0 °C and in 1 h in the presence of $OsO_4$ (0.4 mol %) and **1c** (0.4 mol %).

[b] For the triols (**3a**, **f** , **g**), determined by $^1$H NMR.

[c] Total isolated yields of enantiomers from **2a**–**e** to **3aa**–**ee** and total isolated yields of enantiomers from **2f**, **g** to **3f**, **g**.

[d] For **3aa**–**3ee,** determined by HPLC with a Chiralcel AS column.

[e] Determined by ADP 220 Bs polarimeter.

and **3h** were decomposed into reaction media. NMR spectroscopic data of the triacetates were completely in agreement with those given in the literature.[22]

The results show that the structures of allylic hydroperoxides had a considerable influence on the enantioselectivity. The use of chiral cinchona alkaloids as chiral catalysts for the trihydroxylation of allylic hydroperoxides offers an attractive means of accomplishing this reaction. It can be summarized that the allylic hydroperoxides that have five, six, and seven carbon membered rings led to lower enantioselectivities (Table 3, entries 1–4), whereas straight carbon chain and wide ringed allylic hydroperoxides were more selective (Table 3, entries 5–8).

As the result of this asymmetric reaction, *rac*-3-hydroperoxycyclopent-1-ene (**2a**) was converted into chiral cyclopentane-1/2,3-triol (**3a**) with the yield of 52% and for **3aa** 46% ee (Table 3, entry 1). *rac*-3-Hydroperoxycyclohex-1-ene (**2b**) was oxidized to chiral cyclohexane-1/2,3-triol (**3b**) with the yield of 44% and for **3bb** 25% ee (Table 3, entry 2). The reaction of *rac*-3-hydroperoxy-7-oxabicyclo [4.1.0] hept-4-ene (**2c**) with **1c**/$OsO_4$ gave chiral 7-oxabicyclo [4.1.0] heptane-2/3,4-triol (**3c**) in the yield of only 58% and for **3cc** 41% ee (Table 3, entry 3). *rac*-3-Hydroperoxycycloheptene-1-ene (**2d**) was converted into chiral cycloheptane-1/2,3-triol (**3d**) in the yield of 60% and for **3dd** 35% ee (Table 3, entry 4). *rac*-3-Hydroperoxycyclooct-1-ene (**2e**), *rac*-3-hydroperoxy-2,3-dimethylbut-1-ene (**2f**), and *rac*-3-hydroperoxybut-1-ene (**2g**) gave the products chiral cyclooctane-1/2,3-triol (**3e**), chiral 2,3-dimethylbutane-1/2,3-triol (**3f**), and chiral butane-1/2,3-triol (**3g**) with ee values (for cyclohexane 1/2,3-triacetate (**3ee**) 90% ee, for **3f** 99% ee, and for **3g** 89% ee, respectively) higher than **3aa**–**dd** (Table 3, entries 5–7). All racemic 1/2,3-triols and 1/2,3-triacetates were identified by $^1$H and $^{13}$C NMR spectroscopy in comparison with literature data.[22,23] The ratios of enantiomers for chiral 1/2,3-triols and chiral 1/2,3-triacetates were measured by HPLC spectroscopy using chiral Daicel HPLC Column OD-H, but absolute configurations were not determined.

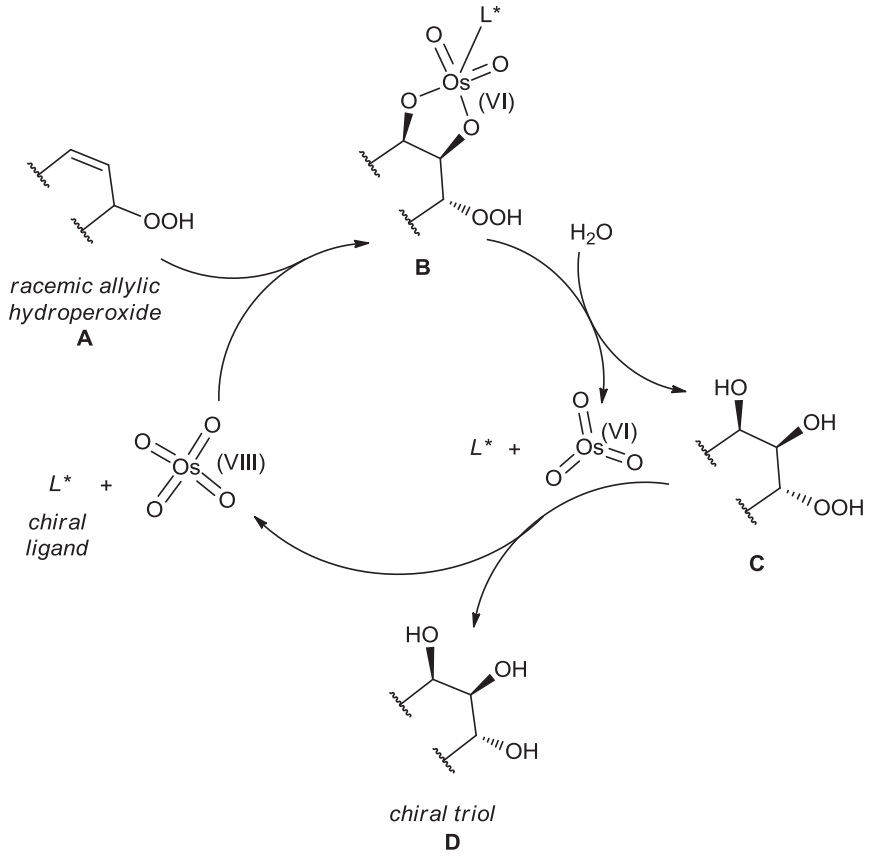
The proposed mechanism for the one-pot synthesis of chiral 1/2,3-triols from racemic allylic hydroperoxides in the presence of cat. $OsO_4$ and chiral ligands is summarized in Scheme 2.

According to the mechanism, chiral complex was obtained with the chiral ligand and osmium tetraoxide ($OsO_4$) in the reaction media. The chiral osmate ester **B** was also obtained by dihydroxylation reaction of allylic hydoperoxide **A** and the chiral ligand. Then the oxidized intermediate **C** and L*.$OsO_3$ were formed by the hydrolysis of chiral osmate ester **B**. By transferring one oxygen atom from hydroperoxide in **C** structure to $OsO_3$, chiral 1/2,3-triol **D** was obtained with an applicable enantioselectivity rate, and then osmium tetroxide, which is recreated to sustain the next catalytic cycle, was used and applied as a practically and efficiently reagent.

## 3. Experimental

### 3.1. General procedure-I for the synthesis of the allylic hydroperoxides[22–32]

First 10 mmol of olefin and TPP (5–10 mg) was dissolved in $CH_2Cl_2$. The solution was placed in a jacketed glass balloon and irradiated using a tungsten lamp (500 W) with air bubbling (oxygen gas) at room temperature. The photooxygenation reaction was monitored by TLC. Most of the reactions were completed over the time period of 8–24 h. The solvent ($CH_2Cl_2$) was evaporated at 20 °C and 20 mmHg at the end of the reaction. The residue was separated by (silica gel) thin layered chromatography (TLC) with hexane:methylene chloride.




**Scheme 2.** The suggested mechanism for the synthesis of asymmetric 1/2,3-triols from the racemic allylic hydroperoxides.

### 3.2. General procedure-II for the synthesis of the chiral 1/2,3-triols

In a typical synthesis of the 1/2,3- triols, $OsO_4$ (1.7 mg in 1 mL of acetone, 2.65 mg, 0.4 mol %) and chiral ligand (0.4 mol %) were reacted at 0 °C and stirred for 10 min. In another container, 2.6 mmol of allylic hydroperoxide was dissolved in the acetone/$H_2O$ (v/v: 4/1) mixture at 0 °C. After that, the allylic hydroperoxide solution was added slowly to the chiral ligand/$OsO_4$ mixture solution at 0 °C. The reaction continued under vigorous stirring at 0 °C for 60 min. The progress of the catalytic reaction was monitored by TLC. Then the solvent was removed by using a rotary evaporator. Finally, the crude residue was directly purified by column chromatography on silica gel using EtOAc-hexane as the eluent to separate the synthesized asymmetric 1/2,3-triols. The 1/2,3-triols were determined by $^1$H NMR and $^{13}$C NMR spectra taken in $D_2O$ or $CDCl_3$. For further characterization, the triols **3a**, **3b**, **3c**, **3d**, and **3e** were converted into the corresponding chiral triacetates **3aa**, **3bb**, **3cc**, **3dd**, and **3ee**, respectively, and the triacetates were prepared as in the literature.[22] The chiral triols **3f** and **3g** and chiral acetate derivatives **3aa**, **3bb**, **3cc**, **3dd**, and **3ee** were also determined by HPLC with a Chiralcel AS column (see supporting materials). Both the NMR and IR spectra of racemic molecules (see supporting materials) were exactly the same in the literature.[22,23] The chiral 1/2,3-triols and chiral 1/2,3-triacetates were identified by HPLC spectroscopy (chiral Daicel HPLC Column OD-H).

***Racem-allylic hydroperoxide molecules:***

*rac*-3-hydroperoxycyclopent-1-ene (**2a**), *rac*-3-hydroperoxycyclohex-1-ene (**2b**), *rac*-3-hydroperoxy-7-oxabicyclo[4.1.0]hept-4-ene (**2c**), *rac*-3-hydroperoxy- cyclohept-1-ene (**2d**), *rac*-3-hydroperoxycyclooct-1-ene (**2e**), *rac*-3-hydroperoxy-2,3-dimethylbut-1-ene (**2f**), *rac*-3-hydroperoxybut-1-ene (**2g**).

***Chiral triacetates molecules:***

***Cyclopentane-1/2,3-triacetate (3aa).*** It was prepared according to general procedure II. The ee was determined to be 46% using HPLC analysis on a Chiralcel AS column (hexane/2-propanol 90:10, 0.6 mL/min, $\lambda$ = 227 nm). Retention times were 18.2 (minor) and 20.5 (major). $[\alpha]_D^{25}$ = –47 (c 0.5, MeOH).

***Cyclohexane-1/2,3- triacetate (3bb).*** It was prepared according to general procedure II. The ee was determined to be 25% using HPLC analysis on a Chiralcel AS column (hexane/2-propanol 90:10, 0.6 mL/min, $\lambda$ = 227 nm). Retention times were 12.6 (major) and 15.1 (minor). $[\alpha]_D^{25}$ = +10 (c 0.5, MeOH).

***7-Oxabicyclo[4.1.0]heptane-2/3,4- triacetate (3cc).*** It was prepared according to general procedure II. The ee was determined to be 41% using HPLC analysis on a Chiralcel AS column (hexane/2-propanol 90:10, 0.6 mL/min, $\lambda$ = 227 nm). Retention times were 15.9 (minor) and 17.5 (major). $[\alpha]_D^{25}$ = –2 (c 0.5, MeOH).

***Cycloheptane-1/2,3-t triacetate (3dd).*** It was prepared according to general procedure II. The ee was determined to be 35% using HPLC analysis on a Chiralcel AS column (hexane/2-propanol 90:10, 0.6 mL/min, $\lambda$ = 227 nm). Retention times were 17.9 (major) and 20.1 (minor). $[\alpha]_D^{25}$ = +5 (c 0.5, MeOH).

***Cyclooctane-1/2,3- triacetate (3ee).*** It was prepared according to general procedure II. The ee was determined to be 99% using HPLC analysis on a Chiralcel AS column (hexane/2-propanol 90:10, 0.6 mL/min, $\lambda$ = 227 nm). Retention times were 13.7 (minor) and 15.3 (major). $[\alpha]_D^{25}$ = –7 (c 0.5, MeOH).

***Chiral triols molecules:***

***2,3-Dimethylbutane-1,2,3-triol (3f).*** It was prepared according to general procedure II. The ee was determined to be 99% using HPLC analysis on a Chiralcel AS column (hexane/2-propanol 90:10, 0.6 mL/min, $\lambda$ = 227 nm). Retention times were 10.5 (major) and 12.8 (minor). $[\alpha]_D^{25}$ = +28 (c 0.5, MeOH).

***Butane-1,2,3-triol (3g).*** It was prepared according to general procedure II. The ee was determined to be 99% using HPLC analysis on a Chiralcel AS column (hexane/2-propanol 90:10, 0.6 mL/min, $\lambda$ = 227 nm). Retention times were 13.5 (major) and 14.8 (minor). $[\alpha]_D^{25}$ = +25 (c 0.5, MeOH).

## 4. Conclusion

The present study reports a new method for the synthesis of asymmetric triols from racemic allylic hydroperoxides in the absence of a co-oxidant and in the presence of chiral ligand and cat. $OsO_4$. We assumed that the chiral ligand and cat. $OsO_4$ were created as the chiral complex in reaction media and so this formation can be likened to chiral ligand/cat. $OsO_4$ in a Sharpless asymmetric dihydroxylation reaction. The synthesis of asymmetric 1/2,3-triols was carried out by the catalytic cycle of chiral ligand and cat. $OsO_4$. Later, the reaction process continues similarly to the dihydroxilation reaction formed by the cat. $OsO_4$/NMO system. This method provides many advantages such as one-pot synthesis, absence of a co-oxidant, catalytic oxidation, and being practical and economic; moreover it ensures the high yielded synthesis of asymmetric triols with considerable enantioselectivity under very mild conditions. Synthesized triols using the new method can be employed as starting materials for the synthesis of most natural products. The new catalytic chiral system for

the synthesis of chiral 1/2,3-triols is thought to be a good candidate to be used in synthetic organic chemistry owing to its chirality, effectiveness, and simplicity. Further applications of this method for the synthesis of asymmetric triols are in progress and the improvements will be reported.

**Acknowledgment**

This study was supported partially by the Scientific and Technological Research Council of Turkey (TÜBİTAK) (Project No: 109T815).

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