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Regio- and Stereoselective Addition of HO/OOH to Allylic Alcohols

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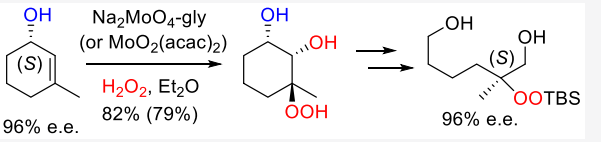
ABSTRACT: A range of allylic alcohols are shown to readily react with ethereal H_2O_2 in the presence of catalytic amounts of Na_2MoO_4-gly or $MoO_2(acac)_2$, affording the C=C trans hydroxylation−hydroperoxylation products in good yields with high regio- and stereoselectivity. Use of enantiomers of cyclic substrates resulted in corresponding enantiopure diol-*tert*-hydroperoxides. The possibility of further conversion of the diol-*tert*-hydroperoxides into triols or linear building blocks with an isolated *tert*-peroxy group containing a quaternary center is also exemplified.



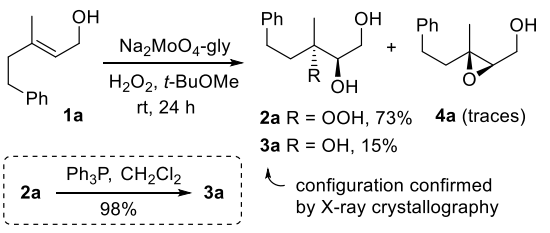
INTRODUCTION

Perhydrolysis of epoxides is one of the reactions that allow for facile incorporation of peroxy bonds into carbon frameworks under mild conditions in synthetically useful yields, representing a rather useful synthetic tool in peroxide chemistry.[1] For this reason, installation of epoxy functionality sometimes also becomes an indispensable part of the whole synthetic plan and thus holds, though in an inexplicit way, a special place in the synthesis of organic peroxides. During the course of studies on perhydrolysis of epoxides, we became aware of those protocols of, e.g., Scettri ($Ti(OiPr)_4$),[2] Yamamoto ($VO(OiPr)_3$, $WO_2(acac)_2$),[3] and Yamazaki (MTO, methyltrioxorhenium),[4] where allylic or homoallylic alcohols reacted smoothly with H_2O_2 in the presence of a proper transition metal catalyst to furnish corresponding epoxides. These findings prompted us to consider whether molybdenum species could also promote epoxidation of alkenes in ethereal H_2O_2—should it be possible to form epoxides under the perhydrolysis conditions, the epoxidation and the perhydrolysis might occur in one flask and thus tremendously simplify the overall synthesis.

RESULTS AND DISCUSSION

One of our initial experiments is shown in Scheme 1, with **1a** as the substrate and Na_2MoO_4-gly[5] as the catalyst. The expected epoxide (**4a**) indeed was detectable on TLC (also verified spectroscopically after chromatographic separation) after 1 h of reaction. With the progress of the reaction, another two products (**2a** and **3a**) formed gradually. Further extension of the reaction to 24 h led to complete disappearance of starting **1a** and the intermediate **4a**, leaving only **2a** and **3a** as the major species in the reaction mixture. The structures of **2a** and **3a** were fully secured by ^1H and ^{13}C NMR, IR, and MS. Treatment of **2a** with Ph_3P gave **3a**, confirming the presence of the peroxy bond. Later, the relative configuration of (racemic) **3a** was established by X-ray diffraction.[6]

Scheme 1. Hydroxyhydroperoxylation of 1a



Several other linear allylic alcohols of different alkene geometry and/or different substitution patterns also reacted smoothly under the same conditions,[7] affording the expected products (entries 2−8, Table 1). In the case of **1g** and **1h**, partial relative configuration of the products was assigned by the NOE's observed with the acetonides (Figure 1, **3g′** and **3h′**, respectively) of **3g** and **3h**, respectively.

With the feasibility of the highly anticipated tandem epoxidation−perhydrolysis achieved, we next turned our attention to cyclic substrates, because in such conformation restrained cases, the stereoselectivity might be even better, and determination of relative configuration would be much easier. More importantly, it would be more likely to acquire otherwise not-so-easily attainable enantiopure *tert*-hydroperoxides (vide infra).[8]

Allylic alcohols **1i−m** (Figure 2) were first examined. The substituent at the C=C appeared to have critical influence on the reaction. Conjugation of the double bond with a phenyl ring (**1i**) or a vinyl group (**1j**) apparently complicated the reaction (leading to complex mixtures), while an electron-withdrawing ester group (**1k**) turned off the reaction completely; no products

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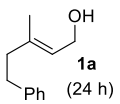
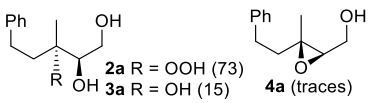
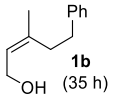
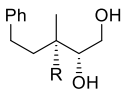
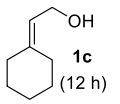
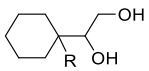
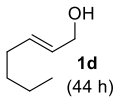
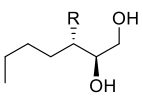
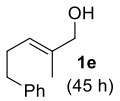
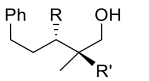
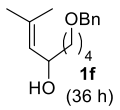
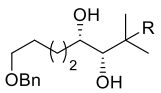
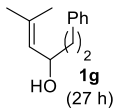
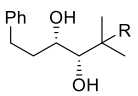
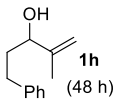
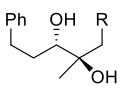
Table 1. Outline of the results with 1a−h[a]

entry	substrate (time)	products[b] (isolated yield%)
1[c]	 **1a** (24 h)	 **2a** R = OOH (73) **3a** R = OH (15) **4a** (traces)
2	 **1b** (35 h)	 **2b** R = OOH (77) **3b** R = OH (14)
3	 **1c** (12 h)	 **2c** R = OOH (82) **3c** R = OH (11)
4	 **1d** (44 h)	 **2d** R = OOH (60) **3d** R = OH (20)
5	 **1e** (45 h)	 **2e** R = OOH, R' = OH (38) **2e'** R = OH, R' = OOH (18) **3e** R, R' = OH (30)
6	 **1f** (36 h)	 **2f** R = OOH (72) **3f** R = OH (11)
7[d]	 **1g** (27 h)	 **2g** R = OOH (74) **3g** R = OH (24)
8[d]	 **1h** (48 h)	 **2h** R = OOH (25) **3e** R = OH (30)

[a]Performed at rt in H_2O_2-saturated *t*-BuOMe with Na_2MoO_4-gly as the catalyst. [b]Relative configuration deduced with reference to that of **3a**, **3g**, and **3h**. [c]Relative configuration determined by X-ray diffraction. [d]Relative configuration determined by NOE (cf. Figure 1).

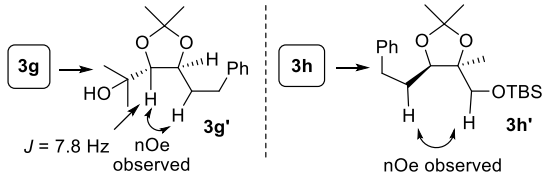


Figure 1. NOE's observed with acetonides **3g′** and **3h′**.

were detected under the same conditions over 16 h of reaction. However, both **1l** and **1m** reacted (separately) with H_2O_2 smoothly, affording the expected products in high yields with high stereoselectivity. In the case of **1m**, the hydroperoxy product (racemic **2m**) was a solid; its configuration was verified by single crystal X-ray crystallographic analysis.[6]

The above results showed that the configurations of the two newly installed stereogenic centers were controlled by the OH at the allylic position. In other words, use of a single enantiomer of a cyclic substrate should result in the corresponding optically active tertiary hydroperoxide. Subsequent efforts were thus made using optically active cyclic alcohols (obtained through enzymatic resolution of the racemates, with tabular summary of the resolution results shown in the Supporting Information).

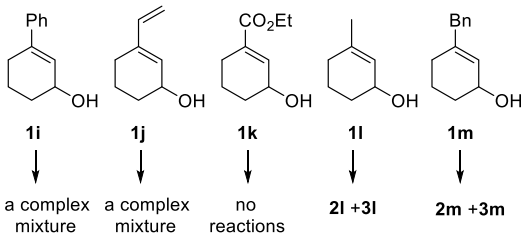


Figure 2. Some cyclic substrates initially tested (cf. the text).

With the optically active allylic alcohols as substrates, we proceeded to examine their hydroxyhydroperoxylation under the aforementioned conditions. Thus, (*S*)-**1l** furnished **2l** in 82% yield (Table 2, entry 1). The H-2/H-3 coupling constant of **2l** was found to be 3.1 Hz (equatorial/axial coupling),[9] revealing a *cis* relationship between the OH at C-2 and C-3 (cf. structure **A** or **B**, Scheme 2). This is also fully consistent with the X-ray analysis[6] of racemic **2m**. Selective protection of the OOH with TBSCl followed by oxidative cleavage of the vicinal diol and $NaBH_4$ reduction of the dialdehyde afforded **5** (without any loss of enantiopurity all the way from **2l**). Conversion of **5** into the known[10] triol **6** finally verified the absolute configuration at the C-1 of **2l**.

By then, we had noticed that $MoO_2(acac)_2$ was particularly potent in perhydrolysis of epoxides (compared with ketones and ketals),[11] and subsequent examination of $MoO_2(acac)_2$ showed that the products were the same.[12] Although the yields were slightly lower, this disadvantage was compensated by the greatly accelerated reaction rate as exemplified in entry 1 (Table 2). Therefore, most other substrates were thus tested using $MoO_2(acac)_2$ as the catalyst.[13]

We also examined **1y** and **1z** (Scheme 3), which gave a known expoxide or triol and thus provided further evidence for the stereochemical course of the formal hydroxyhydroperoxylation reaction. These two substrates reacted substantially slower than those simple ones listed in Table 2. Thus, after stirring at ambient temperature for 12 h, the reaction mixture of **1y** still contained substantial amounts of unreacted/intermediate epoxide **4y**[14a] (isolated in 18% yield) in addition to the expected product **2y** and the known[14b] **3y**. A similar phenomenon was also observed with **1z**. In this case, the reaction was further extended to 42 h to allow for full consumption of **1z** to be converted into **2z** and the known[14b] **3z**.

It should be noted that although in some cases **3** is not listed in Table 2 (entries 6−8 and 12, simply because of isolation/characterization difficulty), formation of diol-hydroperoxide **2** was always accompanied by formation of triol **3**. In an effort to clarify the origin of **3**, the isolated diol-hydroperoxide **2** was re-exposed to the same ethereal $H_2O_2/MoO_2(acac)_2$ conditions again for 12 h, and no **3** could be detected in the reaction mixture. On the other hand, addition of activated powdered 4 Å molecular sieves to the reaction system raised the ratio of **2**/**3** from 7:1 to 11:1.[15] On the basis of these observations, it was concluded that triol **3** must be generated via hydrolysis of the intermediate epoxide **4** rather than deterioration of diol-hydroperoxide **2**.

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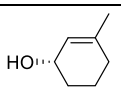
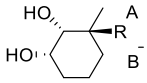
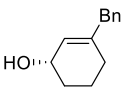
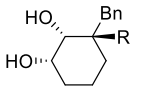
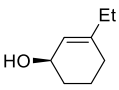
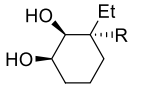
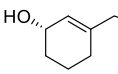
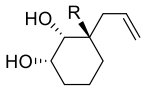
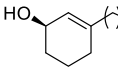
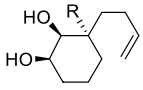
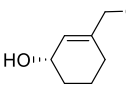
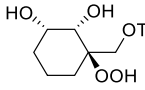
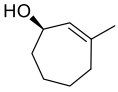
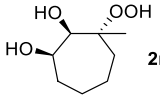
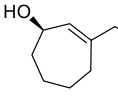
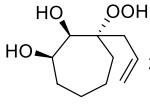
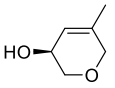
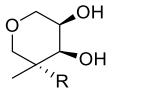
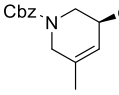
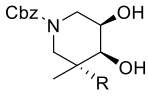
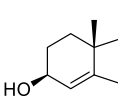
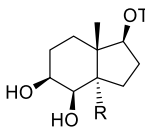
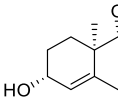
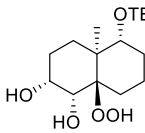
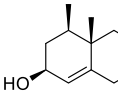
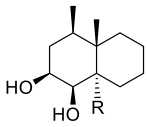
J. Org. Chem. XXXX, XXX, XXX−XXX

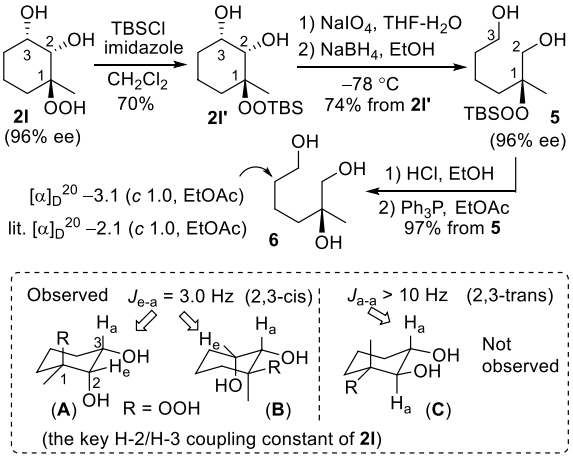
Table 2. Outline of the Results with 1l–u[a]

entry	substrate (catalyst/time)	products (isolated yield%)
1	 (*S*)-**1l** (A/12 h) (B/4 h)	 A **2l** R = OOH (82) **3l** R = OH (13) B **2l** R = OOH (79) **3l** R = OH (9)
2	 (*S*)-**1m** (B/15 h)	 **2m** R = OOH (80) **3m** R = OH (7)
3	 (*R*)-**1n** (B/4 h)	 **2n** R = OOH (78) **3n** R = OH (11)
4	 (*S*)-**1o** (B/10 h)	 **2o** R = OOH (78) **3o** R = OH (10)
5	 (*R*)-**1p** (B/12 h)	 **2p** R = OOH (69) **3p** R = OH (10)
6	 (*S*)-**1q** (B/12 h)	 **2q** (45)
7	 (*R*)-**1r** (B/6 h)	 **2r** (79)
8	 (*R*)-**1s** (B/12 h)	 **2s** (62)
9	 (*S*)-**1t** (B/12 h)	 **2t** R = OOH (84) **3t** R = OH (12)
10	 (*S*)-**1u** (B/13 h)	 **2u** R = OOH (79) **3u** R = OH (12)
11	 **1v** (A/6 h)	 **2v** R = OOH (87) **3v** R = OH (7)
12	 **1w** (B/17 h)	 **2w** (42)
13	 **1x** (B/27 h)	 **2x** R = OOH (53) **3x** R = OH (20)

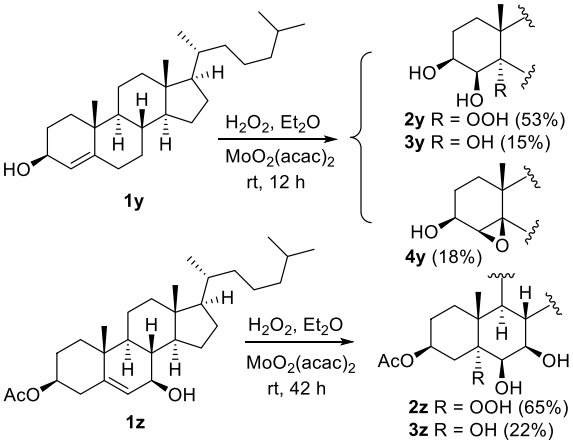
[a]Performed at rt in ethereal H_2O_2 in the presence of the indicated catalyst (A = Na_2MoO_4-gly, B = $MoO_2(acac)_2$).

Isolation and full characterization of the diol-hydroperoxides also made it possible to establish the stereochemical course of

Scheme 2. Elaboration of 2l into 5



Scheme 3. Hydroxyhydroperoxylation of 1y–z



the overall transformation: As illustrated in Scheme 4 with conversion of **1l** to **2l** and **3l** (part (A), the upper left scheme), in the cyclic substrate cases the epoxidation occurred with a clear-cut cis facial selectivity (cis to the allylic OH), strongly suggesting that the reaction was mediated by a cyclic transition state (which excluded epoxidation on the other face of the C=C) with both the allylic OH and the H_2O_2 (which eventually oxidized the C=C to give an epoxy ring) bound to the Mo catalyst. The subsequent perhydrolysis also showed distinct regio- as well as stereoselectivity; the attack by the OOH exclusively occurred at the quaternary epoxy carbon center with full configuration inversion, substantially better than the ca. 85% inversion observed in the perhydrolysis[16] of oxetanes. The observation that no reaction (via path c) occurred at the other epoxy carbon center (which was less substituted and thus would be more suitable for S_N2 substitution) suggested that the inversion at the quaternary center was more likely to be achieved via an S_N1 ion pair mechanism (with one side of the planar carbocation blocked by the counterion/leaving group) as reasoned for the perhydrolysis of oxetanes in our previous[16] work.

The knowledge from the cyclic substrates, together with the structures as well as the configurations of the products from the noncyclic substrates, also allowed us to get a stereochemical overview (Scheme 4, exemplified with **1g**, **1e**, and **1h**) of the reaction for the open-chain cases. Thus, at the first step of transformation (epoxidation) the open-chain substrates **1g**, **1e**,

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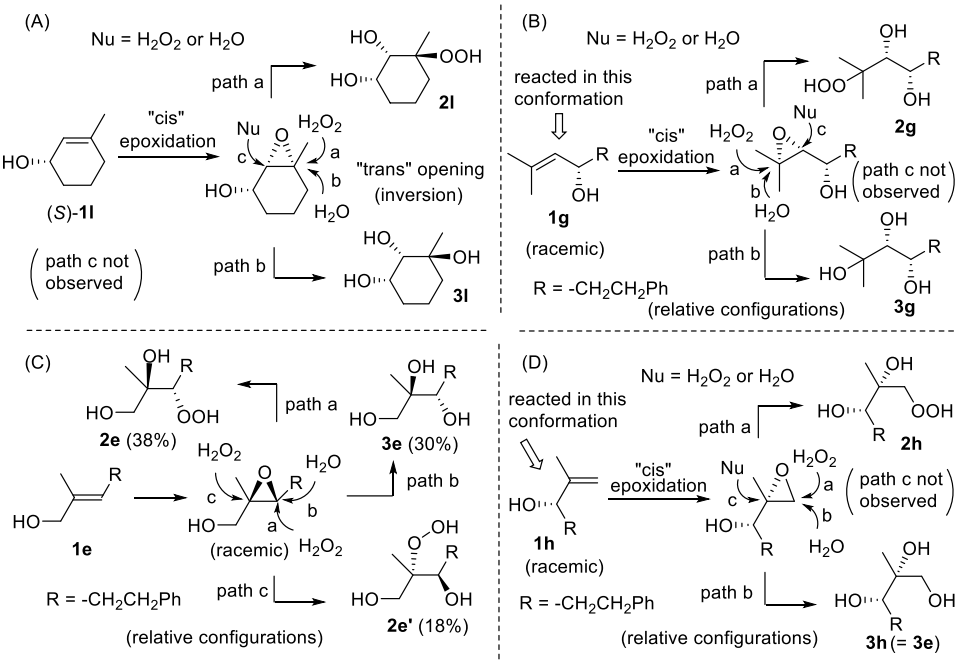
J. Org. Chem. XXXX, XXX, XXX–XXX

Scheme 4. Stereochemical Overview of the Addition of OH/OOH to Allylic Alcohols



and **1h** must react in those conformations as depicted in Scheme 4 (parts (B), (C), and (D), respectively), and the regio- and stereoselectivity in the subsequent perhydrolysis in each selected case must be as depicted in the corresponding subschemes.

With the aid of the schematic summaries in Scheme 4, it becomes much easier to identify the evidence for the dominating perhydrolysis mechanism: In the case of **1g**, the OOH attack exclusively occurred at the more crowded quaternary epoxy carbon center (with full configuration inversion) rather than the less crowded tertiary epoxy carbon center. Therefore, the S_N2 mechanism could be excluded, leaving the S_N1 ion pair as the only possible alternative. This conclusion is the same as what is reached above for the cyclic substrates. However, it must be noted that such preference for a S_N1 ion pair perhydrolysis mechanism at the quaternary epoxy carbon center holds only when the quaternary center is not adjacent to the allylic center. If the positions of the two epoxy carbon centers are "switched" as in **1e** (part (C), Scheme 4), the steric crowding around the tertiary center becomes smaller (compared with that in **1g**, because the liner $-CH_2CH_2Ph$ is smaller in size than the branched $-CH(OH)CH_2CH_2Ph$); the S_N2 substitution at the tertiary epoxy carbon center not only is in operation, but also has gained the upper hand in competition with the S_N1 ion pair mechanism at the quaternary center, providing **2e** as the major product (38%). Further reduction of the steric crowding around the tertiary epoxy carbon center in **1e** into a nonsubstituted CH_2 (as the terminal epoxy center in **1h**) leads to tremendous facilitation of the S_N2 substitution at this site; the perhydrolysis exclusively occurred at the terminal center via the S_N2 mechanism, giving **2h** as the only product (part (C), Scheme 4).[17]

In the case of **1d** (Table 1), a disubstituted alkene, neither of the two epoxy carbon centers of the intermediate epoxide are quaternary. This made the S_N1 ion pair mechanism strongly disfavored. Therefore, the perhydrolysis/hydrolysis of the epoxide derived from **1d** most likely occurred through an S_N2 mechanism, with full configuration inversion. What deserves mentioning here is that although both epoxy carbon centers in this case are disubstituted, the nucleophilic attacks took place preferentially at the carbon center beta to the allylic OH, confirming that the epoxy carbon center beta to allylic OH is more susceptible to perhydrolysis. Besides, the slower reaction/longer reaction time observed with **1d** (compared with, e.g., **1a**) also indicated that the mechanism of the perhydrolysis of the intermediate epoxide in this case must be different from that with the substrates with a quaternary epoxy carbon center (such as the intermediate epoxide derived from **1a**).

It is perhaps noteworthy that the combination of $MoO_2(acac)_2$ and H_2O_2 has been used by Su and Wang in a recently[18] reported protocol for the synthesis of triols from alkenes, where the main reactions were completed in a (35% aqueous H_2O_2−MeCN) biphasic system in the presence of an additional (synthetic) ligand. Judging from the reaction conditions, their crude product mixtures very likely contained some hydroperoxides in addition to the triols directly formed from the competing hydrolysis (which is expected to be much more severe than observed in this work). However, because the hydroperoxides were neither isolated nor characterized, but directly reduced with Ph_2S, it is not possible to assess the value of that protocol in synthesis of hydroperoxides in comparison with the present work.

CONCLUSIONS

A molybdenum mediated method for hydroxylation−hydroperoxylation of the C=C in allylic alcohols has been developed. With Na_2MoO_4-gly or $MoO_2(acac)_2$ as the catalyst, an array of allylic alcohols were converted into the corresponding diol-hydroperoxides in good yields. The reaction occurred in a highly stereoselective manner, with the product configuration fully controlled by the allylic OH of the substrates. As a consequence of using ethereal H_2O_2 (instead of the previously[18] aqueous H_2O_2), the whole transformation did not require any additional ligand. Competing hydrolysis at the perhydrolysis step was also effectively suppressed. A range of diol-*tert*-hydroperoxides thus become readily accessible. Isolation of the hydroperoxides also

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J. Org. Chem. XXXX, XXX, XXX−XXX

made it possible to look into the stereochemical course of the tandem epoxidation−perhydrolysis reaction. As diol-hydroperoxides could be readily reduced to corresponding alcohols in high yields, the present protocol also provides a stereocontrolled approach to the corresponding triols with a newly installed trans diol subunit, which are not accessible through, e.g., conventional OsO_4 cis[19] dihydroxylation. Finally, as illustrated through conversion of **2l** into **5** (a flexible optically active chiral *tert*-peroxy building block), this new access to **2** also opens up an entry to the otherwise not-so-easily attainable enantiopure peroxy group-containing isolated quaternary stereogenic centers.[20]

EXPERIMENTAL SECTION

General Considerations. Although no explosions were experienced in this work, generally speaking, organic peroxides are potentially hazardous compounds and must be handled with great care: Avoid direct exposure to strong heat or light, mechanical shock, oxidizable organic materials, or transition metal ions. A safety shield should be used for all reactions involving H_2O_2. All solvents and reagents were used as received from commercial sources. Novozyme 435[21] and Lipase AK were purchased from Strem and Sigma, respectively. H_2O_2-saturated Et_2O (ethereal hydrogen peroxide) was prepared using a literature procedure[22] with a slight modification: Et_2O (60 mL) was placed in a separatory funnel and "washed" with three portions (20 mL each) of NaCl-saturated H_2O_2 (prepared by stirring the commercially available 30% aqueous hydrogen peroxide (60 mL) with an excess of powdered NaCl (ca. 30 g) at ambient temperature until the initially cloudy liquid phase became a clear solution; the supernatant was used; performed behind a safety shield!). The ethereal layer was then dried over anhydrous $MgSO_4$ (ca. 2 g). The supernatant (ca. 1 M in H_2O_2 as titrated with 0.1 M $KMnO_4$) was used directly in the $MoO_2(acac)_2$ catalyzed hydroxylation−hydroperoxylation. H_2O_2-saturated *t*-BuOMe was prepared similarly, except with *t*-BuOMe to replace Et_2O. Column chromatography was performed on silica gel (300−400 mesh) under slightly positive pressure. PE stands for petroleum ether (chromatography solvent, bp 60−90 °C).

Melting points were uncorrected (measured on a hot-stage melting point apparatus equipped with a microscope). Optical rotations were measured on an Anton Paar MCP5500 polarimeter. IR spectra were measured with a Nicolet 380 infrared spectrophotometer. NMR spectra were recorded with a Bruker Avance III 400 NMR spectrometer (operating at 400 MHz for ^1H) or a Bruker Avance III HD 500 NMR (operating at 500 MHz for ^1H) or a Bruker Avance III HD 600 NMR (operating at 600 MHz for ^1H) instrument as stated below. ESI-MS data were acquired with a Shimadzu LCMS-2010 eV mass spectrometer or an Agilent Technologies 6120 Quadrupole LC/MS. ESI-HRMS data were obtained with a Bruker Maxis 4 G TOF MS spectrometer or a Thermo Scientific Q Exactive HF Orbitrap-FT MS.

Synthesis of Substrates 1a−h. Substrates **1a−c**, **1e**, and **1h** are known compounds and were prepared according to the literature.[23] Substrate **1d** is commercially available and was used as received.

*8-(Benzyloxy)-2-methyloct-2-en-4-ol (**1f**).* A commercially available solution of 2-methylprop-1-enyl magnesium bromide (0.5 M, in THF, 2.4 mL, 1.2 mmol) was added to a solution of 5-benzyloxypentanal (198 mg, 1.03 mmol) in dry THF (4 mL) stirred in an ice−water bath under N_2 (balloon). After completion of the addition, stirring was continued while the bath was allowed to warm to ambient temperature naturally. When TLC showed completion of the reaction (ca. 5 h), aq. sat. NH_4Cl (5 mL) was added. The mixture was extracted with Et_2O (10 mL × 3). The combined organic layers were washed with brine (10 mL) and dried over anhydrous Na_2SO_4. Removal of the drying agent by filtration and the solvent by rotary evaporation gave an oily residue, which was purified by column chromatography (5:1 PE/EtOAc) on silica gel to afford **1f** as a colorless oil (220 mg, 0.89 mmol, 87%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−7.24 (m, 5H), 5.15 (dd, J = 8.8, 1.3 Hz, 1H), 4.49 (s, 2H), 4.32 (dt, J = 8.5, 6.3 Hz, 1H), 3.46 (t, J = 6.6 Hz, 2H), 1.72 (s, 3H), 1.67 (s, 3H), 1.64−1.56 (m, 3H), 1.47−1.34 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 138.5, 134.9, 128.3, 128.1, 127.6, 127.4, 72.8, 70.2, 68.5, 37.4, 29.6, 25.7, 22.0, 18.1; FT-IR (film) 3418, 3087, 3063, 3030, 2933, 2859, 2792, 2729, 1675, 1604, 1496, 1453, 1375, 1363, 1204, 1101, 1028, 908, 735, 697 cm^{-1}. ESI-MS m/z 271.3 ($[M + Na]^+$); ESI-HRMS calcd. for $C_{16}H_{24}O_2Na$ ($[M + Na]^+$) 271.1669, found 271.1663.

*5-Methyl-1-phenylhex-4-en-3-ol (**1g**).* A commercially available solution of 2-methylprop-1-enyl magnesium bromide (0.5 M, in THF, 14.4 mL, 7.2 mmol) was added to a solution of 3-phenylpropanal (0.8 mL, 6.0 mmol) in dry THF (24 mL) stirred in an ice−water bath under N_2 (balloon). After completion of the addition, stirring was continued while the bath was allowed to warm to ambient temperature naturally. When TLC showed completion of the reaction (ca. 3 h), aq. sat. NH_4Cl (10 mL) was added. The mixture was extracted with Et_2O (30 mL × 3). The combined organic layers were washed with brine (10 mL) and dried over anhydrous Na_2SO_4. Removal of the drying agent by filtration and the solvent by rotary evaporation gave an oily residue, which was purified by column chromatography (15:1 PE/EtOAc) on silica gel to afford **1g** as a colorless oil (967 mg, 5.1 mmol, 85%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.34−7.19 (m, 5H), 5.27−5.23 (m, 1H), 4.39 (dt, J = 8.8 Hz, 6.5 Hz, 1H), 2.76−2.63 (m, 2H), 2.00−1.90 (m, 1H), 1.83−1.79 (m, 1H), 1.77 (s, 3H), 1.69 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.0, 135.4, 128.33, 128.26, 127.9, 125.7, 68.1, 39.1, 31.7, 25.7, 18.2; FT-IR (film) 3362, 3062, 3026, 2969, 2928, 2859, 1675, 1603, 1496, 1453, 1376, 1043, 1030, 1005, 914, 844, 747, 699 cm^{-1}; EI-MS m/z (%) 85 (100), 91 (37), 175 (36), 190 (M^+, 33); EI-HRMS calcd. for $C_{13}H_{18}O$ (M^+) 190.1358, found 190.1356.

General Procedure for Na_2MoO_4-gly Mediated Conversion of 1a−h into 2a−h. These experiments were mostly performed in H_2O_2-saturated *t*-BuOMe using the general procedure shown below just to illustrate that in case the more conventional H_2O_2-saturated Et_2O cannot be employed for safety reason, the reaction still can be carried out to acquire the expected products.

The allyl alcohol **1** (0.3 mmol) was dissolved in freshly prepared[16] H_2O_2-saturated *t*-BuOMe (3.0 mL). Na_2MoO_4-gly[5] (11 mg, 0.03 mmol) was added. The mixture was stirred at ambient temperature until TLC showed consumption of the starting **1**. The mixture was diluted with Et_2O and washed with H_2O. Phases were separated. The aq. layer was back extracted with EtOAc (10 mL × 3). The combined organic layers were washed in turn with H_2O (5 mL) and brine (5 mL) and dried over anhydrous Na_2SO_4. The drying agent was removed by filtration. The filtrate was concentrated on a rotary evaporator. The residue was purified by column chromatography on silica gel to give the product **2** and **3**.

Data for (2R,3S*)-3-Hydroperoxy-3-methyl-5-phenylpentane-1,2-diol (**2a**).* **2a** was obtained as a colorless oil, 33 mg, 73% from **1a**, along with 14% of recovered **1a**, chromatography using 1:1 to 1:2 PE/EtOAc; ^1H NMR (400 MHz, $CDCl_3$) δ 7.26−7.11 (m, 5H), 4.34 (br s, 1H), 3.90 (d, J = 5.5 Hz, 1H), 3.74 (d, J = 10.6 Hz, 1H), 3.64 (dd, J = 11.3 Hz, 7.5 Hz, 1H), 2.71 (td, J = 13.0, 4.5 Hz, 1H), 2.59 (td, J = 12.5, 5.0 Hz, 1H), 2.04 (td, J = 13.0, 4.3 Hz, 1H), 1.63 (td, J = 13.8, 5.2 Hz, 1H), 1.23 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.1, 128.4, 128.3, 125.9, 85.0, 75.8, 62.7, 35.2, 29.2, 18.5; FT-IR (film) 3365, 3089, 3062, 3028, 2979, 2939, 2864, 1602, 1496, 1454, 1367, 1205, 1151, 1090, 1028, 740, 699 cm^{-1}. ESI-MS m/z 249.2 ($[M + Na]^+$); ESI-HRMS calcd. for $C_{12}H_{18}O_4Na$ ($[M + Na]^+$) 249.1097, found 249.1102.

Data for (2R,3S*)-3-Methyl-5-phenylpentane-1,2,3-triol (**3a**).* **3a** was obtained as a white solid, 7 mg, 15% from **1a**, chromatography using 1:1 to 1:2 PE/EtOAc; mp 108−109 °C. ^1H NMR (500 MHz, CD_3OD) δ 7.26−7.11 (m, 5H), 3.82 (dd, J = 10.5 Hz, 2.7 Hz, 1H), 3.59−3.51 (m, 2H), 2.75 (td, J = 12.7, 4.9 Hz, 1H), 2.67 (td, J = 13.2, 4.9 Hz, 1H), 1.86 (td, J = 13.2, 4.9 Hz, 1H), 1.72 (td, J = 12.8, 5.0 Hz, 1H), 1.19 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3OD) δ 144.3, 129.35, 129.32, 126.6, 78.2, 74.7, 64.0, 42.5, 30.5, 22.2; FT-IR (film) 3197, 3024, 2999, 2941, 2961, 2887, 2863, 1605, 1494, 1453, 1368, 1314, 1196, 1087, 1063, 1029, 992, 949, 885, 789, 742, 721, 699 cm^{-1}; ESI-MS m/z 233.1 ($[M + Na]^+$); ESI-HRMS calcd. for $C_{12}H_{18}O_3Na$ ($[M + Na]^+$) 233.1148, found 233.1154.

Data for (2S,3S*)-3-Hydroperoxy-3-methyl-5-phenylpentane-1,2-diol (**2b**).* **2b** was obtained as a white solid, 48 mg, 77% from **1b**,

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J. Org. Chem. XXXX, XXX, XXX−XXX

along with 7.5% of recovered **1b**, chromatography using 1:1 to 1:2 PE/EtOAc; mp 105−106 °C. ^{1}H NMR (400 MHz, CD_3OD) δ 7.35−7.10 (m, 5H), 3.86 (dd, J = 8.0, 2.9 Hz, 1H), 3.74 (dd, J = 11.5, 2.6 Hz, 1H), 3.53 (dd, J = 12.5 Hz, 5.0 Hz, 1H), 2.78−2.62 (m, 2H), 1.93−1.76 (m, 2H), 1.21 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3OD) δ 144.1, 129.3, 126.7, 85.7, 76.4, 63.8, 37.2, 30.5, 18.0; FT-IR (film of a concd. solution in CH_2Cl_2) 3366, 3060, 3026, 2941, 1603, 1496, 1454, 1377, 1188, 1090, 1062, 1030, 903, 747, 699, 668 cm^{-1}; ESI-MS m/z 249.2 ([M + Na]$^+$); ESI-HRMS calcd. for $C_{12}H_{18}O_4Na$ ([M + Na]$^+$) 249.1097, found 249.1101.

Data for (2S,3S*)-3-Methyl-5-phenylpentane-1,2,3-triol (**3b**).* **3b** was obtaind as a white solid, 9 mg, 14% from **1b**, chromatography using 1:1 to 1:2 PE/EtOAc; mp 105−106 °C. ^{1}H NMR (500 MHz, CD_3OD) δ 7.26−7.11 (m, 5H), 3.77 (dd, J = 10.5 Hz, 2.7 Hz, 1H), 3.59−3.51 (m, 2H), 2.69 (t, J = 8.8 Hz, 2H), 1.89−1.81 (m, 1H), 1.76−1.68 (m, 1H), 1.22 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD) δ 144.2, 129.3, 126.6, 78.6, 74.8, 63.9, 41.7, 30.9, 23.0; FT-IR (film of a concd. solution in CH_2Cl_2) 3391, 3025, 2927, 1602, 1496, 1454, 1375, 1061, 1029, 747, 699 cm^{-1}; ESI-MS m/z 233.1 ([M + Na]$^+$); ESI-HRMS calcd. for $C_{12}H_{18}O_3Na$ ([M + Na]$^+$) 233.1148, found 233.1152.

*Data for 1-(1-Hydroperoxycyclohexyl)ethane-1,2-diol (**2c**).* **2c** was obtained as a colorless oil, 49 mg, 82% from **1c**, chromatography using 1:1 to 1:2 and finally 1:3 PE/EtOAc; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 4.22 (s, 2H), 3.82−3.68 (m, 3H), 1.94 (d, J = 13.8 Hz, 1H), 1.87 (d, J = 13.9 Hz, 1H), 1.69−1.44 (m, 5H), 1.38−1.14 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 83.8, 75.8, 62.5, 29.6, 28.7, 25.6, 21.1, 21.0; FT-IR (film) 3373, 2936, 2862, 1448, 1154, 1076, 1018, 929, 878, 819, 739 cm^{-1}; ESI-MS m/z 221.1 ([M + COOH]$^-$); ESI-HRMS calcd. for $C_8H_{16}O_4Cl$ ([M + Cl]$^-$) 211.0743, found 211.0744.

*Data for 1-(1-Hydroxycyclohexyl)ethane-1,2-diol (**3c**).* **3c** was obtained as a white solid, 6 mg, 11% from **1c**, chromatography using 1:1 to 1:2 and finally 1:3 PE/EtOAc; mp 111−112 °C. ^{1}H NMR (400 MHz, CD_3OD) δ 3.78 (dd, J = 11.3, 3.3 Hz, 1H), 3.55 (dd, J = 11.1, 7.8 Hz, 1H), 3.36 (dd, J = 8.0, 3.2 Hz, 1H), 1.71−1.43 (m, 9H), 1.29−1.18 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3OD) δ 79.0, 74.0, 63.6, 34.6, 33.5, 27.0, 22.52, 22.48; FT-IR (film of a concd. solution in CH_2Cl_2) 3307, 2930, 2856, 1446, 1400, 1337, 1263, 1090, 1063, 1023, 971, 908, 879 cm^{-1}; ESI-MS m/z 183.1 ([M + Na]$^+$); ESI-HRMS calcd. for $C_8H_{16}O_3Na$ ([M + Na]$^+$) 183.0992, found 183.0998.

Data for (2R,3S*)-3-Hydroperoxyheptane-1,2-diol (**2d**).* **2d** was obtained as a colorless oil, 28 mg, 60% from **1d**, chromatography using 1:1 to 1:2, then 1:3 PE/EtOAc, and finally MeOH; ^{1}H NMR (500 MHz, CD_3OD) δ 3.86 (q, J = 5.4 Hz, 1H), 3.77 (q, J = 5.1 Hz, 1H), 3.66 (dd, J = 11.3, 4.3 Hz, 1H), 3.58 (dd, J = 11.3, 6.8 Hz, 1H), 1.66−1.48 (m, 3H), 1.44−1.31 (m, 3H), 0.93 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3OD) δ 86.9, 73.3, 64.6, 29.2, 28.6, 23.8, 14.4; FT-IR (film) 3348, 2957, 2933, 2873, 1466, 1380, 1215, 1066, 988, 881 cm^{-1}; ESI-MS m/z 209.1 ([M + COOH]$^-$); ESI-HRMS calcd. for $C_7H_{16}O_4Na$ ([M + Na]$^+$) 187.0941, found 187.0932.

Data for (2R,3S*)-Heptane-1,2,3-triol (**3d**).* **3d** was obtained as a a white solid, 9 mg, 20% from **1d**, chromatography using first 1:1, then 1:2, and finally 1:3 PE/EtOAc and finally MeOH; mp 76−78 °C. ^{1}H NMR (400 MHz, CD_3OD) δ 3.72 (dd, J = 11.2, 3.6 Hz, 1H), 3.56 (dd, J = 11.2, 6.6 Hz, 1H), 3.52−3.41 (m, 2H), 1.72−1.64 (m, 1H), 1.58−1.48 (m, 1H), 1.44−1.29 (m, 4H), 0.94 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3OD) δ 76.3, 73.6, 64.7, 33.8, 29.1, 23.9, 14.5; FT-IR (film of a concd. solution in CH_2Cl_2) 3260, 2953, 2938, 2914, 2872, 2856, 1487, 1458, 1439, 1315, 1083, 1042, 1005, 962, 888, 875, 730 cm^{-1}; EI-MS m/z (%) 69 (100), 87 (62), 44 (33), 117 ([M − CH_2OH]$^+$, 13), 147 ([M − H]$^+$, 0.97); ESI-HRMS calcd. for $C_6H_{13}O_2$ ([M − CH_2OH]$^+$) 117.0916, found 117.0919.

Data for (2R,3S*)-3-Hydroperoxy-2-methyl-5-phenylpentane-1,2-diol (**2e**).* **2e** was obtained as a colorless oil, 20 mg, 38% from **1e**, chromatography using first 2:3, then 1:1 PE/EtOAc, and finally EtOAc; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (br s, 1H), 7.30−7.15 (m, 5H), 3.90 (dd, J = 10.8, 2.3 Hz, 1H), 3.78 (d, J = 11.8 Hz, 1H), 3.66 (br s, 1H), 3.41 (d, J = 11.8 Hz, 1H), 2.97 (ddd, J = 13.6, 9.6, 4.8 Hz, 1H), 2.71 (dt, J = 13.6, 8.1 Hz, 1H), 1.94−1.74 (m, 2H), 1.06 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 141.6 (quat), 128.49 (CH), 128.44 (CH), 126.0 (CH), 89.3 (CH), 75.0 (quat), 66.3 (CH_2), 32.6 (CH_2), 29.4 (CH_2), 21.1 (CH_3) (assigned with the aid of DEPT 135); FT-IR (film) 3348, 3085, 3062, 3026, 2935, 2864, 1603, 1496, 1454, 1382, 1244, 1115, 1041, 918, 752, 700 cm^{-1}; ESI-MS m/z 249.2 ([M + Na]$^+$); ESI-HRMS calcd. for $C_{12}H_{18}O_4Na$ ([M + Na]$^+$) 249.1097, found 249.1096.

Data for (2R,3S*)-2-Hydroperoxy-2-methyl-5-phenylpentane-1,3-diol (**2e′**).* **2e** was obtained as a colorless oil, 14 mg, 18% from **1e**, chromatography using first 2:3, then 1:1 PE/EtOAc, and finally EtOAc; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.34 (s, 1H), 7.30−7.17 (m, 5H), 3.91−3.84 (m, 2H), 3.78 (d, J = 12.7 Hz, 1H), 3.46 (br s, 2H), 2.97 (ddd, J = 13.7, 9.8 Hz, 4.9 Hz, 1H), 2.66 (ddd, J = 13.9, 9.3, 7.3 Hz, 1H), 1.90−1.74 (m, 2H), 1.07 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 141.7 (quat), 128.53 (CH), 128.47 (CH), 126.0 (CH), 85.8 (quat), 74.0 (CH), 64.7 (CH_2), 33.5 (CH_2), 32.7 (CH_2), 16.4 (CH_3) (assigned with the aid of DEPT 135); FT-IR (film) 3365, 3086, 3062, 3026, 2929, 2860, 1603, 1496, 1454, 1376, 1257, 1223, 1044, 933, 751, 700 cm^{-1}; ESI-MS m/z 249.1 ([M + Na]$^+$); ESI-HRMS calcd. for $C_{12}H_{18}O_4Na$ ([M + Na]$^+$) 249.1097, found 249.1094.

Data for (2R,3S*)-2-Methyl-5-phenylpentane-1,2,3-triol (**3e**).* **3e** was obtained as a colorless oil, 19 mg, 30% from **1e**, chromatography using first 2:3, then 1:1 PE/EtOAc, and finally EtOAc; ^{1}H NMR (400 MHz, CD_3OD) δ 7.26−7.11 (m, 5H), 3.56 (d, J = 11.0 Hz, 1H), 3.51 (dd, J = 10.6, 1.3 Hz, 1H), 3.44 (d, J = 11.1 Hz, 1H), 2.91 (ddd, J = 13.4, 10.5, 4.6 Hz, 1H), 2.61 (ddd, J = 13.5, 10.0, 7.0 Hz, 1H), 2.02−1.93 (m, 1H), 1.69−1.59 (m, 1H), 1.08 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3OD) δ 143.8, 129.5, 129.3, 126.7, 75.6, 75.3, 68.8, 34.01, 34.00, 19.0; FT-IR (film) 3406, 3085, 3062, 3026, 2927, 1603, 1496, 1454, 1381, 1257, 1044, 941, 833, 750, 700 cm^{-1}; ESI-MS m/z 233.2 ([M + Na]$^+$); ESI-HRMS calcd. for $C_{12}H_{18}O_3Na$ ([M + Na]$^+$) 233.1148, found 233.1150. (note that **3e** = **3h**.)

Data for (3R,4S*)-8-(Benzyloxy)-2-hydroperoxy-2-methyloctane-3,4-diol (**2f**).* **2f** was obtained as a colorless oil, 49 mg, 72% from **1f**, chromatography using 1:1 PE/EtOAc; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.36−7.25 (m, 5H), 4.49 (s, 2H), 3.82 (dd, J = 7.5, 4.2 Hz, 1H), 3.49 (t, J = 6.3 Hz, 2H), 3.42−3.28 (m, 2H), 2.62 (br s, 1H), 1.74−1.59 (m, 3H), 1.57−1.38 (m, 3H), 1.29 (s, 3H), 1.23 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 138.1, 128.3, 127.7, 127.6, 84.8, 76.7, 72.9, 70.1, 69.4, 34.9, 29.3, 22.5, 20.9; FT-IR (film) 3388, 3092, 3059, 3030, 2980, 2939, 2863, 2798, 1603, 1496, 1454, 1365, 1206, 1151, 1100, 1074, 1028, 911, 737, 698 cm^{-1}; ESI-MS m/z 321.2 ([M + Na]$^+$); ESI-HRMS calcd. for $C_{16}H_{26}O_5Na$ ([M + Na]$^+$) 321.1673, found 321.1672.

Data for (3R,4S*)-8-(Benzyloxy)-2-methyloctane-2,3,4-triol (**3f**).* **3f** was obtained as a colorless oil, 7 mg, 11% from **1f**, chromatography using 1:1 PE/EtOAc; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.27 (m, 5H), 4.50 (s, 2H), 3.98−3.92 (m, 1H), 3.49 (t, J = 6.4 Hz, 2H), 3.13−3.08 (m, 1H), 3.01−2.72 (m, 3H), 1.73−1.61 (m, 3H), 1.59−1.40 (m, 3H), 1.28 (s, 3H), 1.27 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 138.4, 128.4, 127.7, 127.6, 76.4, 74.1, 72.9, 71.2, 70.2, 34.1, 29.5, 27.3, 26.2, 22.4; FT-IR (film) 3417, 3087, 3064, 3030, 2930, 2857, 2794, 1603, 1496, 1454, 1365, 1307, 1162, 1101, 1028, 949, 804, 736, 698 cm^{-1}; ESI-MS m/z 305.2 ([M + Na]$^+$); ESI-HRMS calcd. for $C_{16}H_{26}O_4Na$ ([M + Na]$^+$) 305.1723, found 305.1725.

Data for (3S,4R*)-5-Hydroperoxy-5-methyl-1-phenylhexane-3,4-diol (**2g**).* **2g** was obtained as a colorless oil, 53 mg, 74% from **1g**, chromatography using 2:1 to 3:2 PE/EtOAc; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.29−7.14 (m, 5H), 3.86 (dd, J = 8.0, 5.3 Hz, 1H), 3.44 (s, 1H), 3.35 (s, 1H), 3.22 (s, 1H), 2.81−2.64 (m, 2H), 2.07−1.97 (m, 1H), 1.88−1.78 (m, 1H), 1.30 (s, 3H), 1.21 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.5, 128.39, 128.34, 125.9, 85.0, 76.7, 69.1, 36.8, 32.0, 22.4, 20.8; FT-IR (film) 3420, 3086, 3063, 3026, 2981, 2939, 2861, 1603, 1496, 1454, 1383, 1234, 1145, 1099, 1045, 997, 775, 748, 700 cm^{-1}; ESI-MS m/z 263.2 ([M + Na]$^+$); ESI-HRMS calcd. for $C_{13}H_{20}O_4Na$ ([M + Na]$^+$) 263.1254, found 263.1256.

Data for (3R,4S*)-2-Methyl-6-phenylhexane-2,3,4-triol (**3g**).* **3g** was obtained as a colorless oil, 16 mg, 24% from **1g**, chromatography using 2:1 to 3:2 PE/EtOAc; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.19 (m, 5H), 4.01 (dd, J = 8.0, 5.2 Hz, 1H), 3.37−3.04 (m, 4H), 2.83−2.67 (m, 2H), 2.07−1.97 (m, 1H), 1.91−1.81 (m, 1H), 1.31 (s, 3H), 1.27 (s,

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J. Org. Chem. XXXX, XXX, XXX−XXX

3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.6, 128.42, 128.38, 125.9, 76.6, 74.3, 70.6, 36.0, 31.9, 27.3, 26.1; FT-IR (film) 3398, 3084, 3062, 3026, 2974, 2927, 2859, 1603, 1496, 1454, 1386, 1158, 1096, 1044, 990, 949, 805, 749, 700 cm^{-1}; ESI-MS m/z 247.1 ($[M + Na]^+$); ESI-HRMS calcd. for $C_{13}H_{20}O_3Na$ ($[M + Na]^+$) 247.1305, found 247.1308.

Data for (2R,3S*)-1-Hydroperoxy-2-methyl-5-phenylpentane-2,3-diol (**2h**).* **2h** was obtained as a white solid, 17 mg, 25% from **1h**, along with 18 mg (33%) of unreacted **1h**, chromatography using 1:1 to 1:2 PE/EtOAc; mp 62−63 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 10.30 (s, 1H), 7.31−7.18 (m, 5H), 4.24 (d, J = 13.3 Hz, 1H), 3.91 (d, J = 13.3 Hz, 1H), 3.57 (t, J = 6.3 Hz, 1H), 3.06 (br s, 2H), 2.94 (dt, J = 13.5, 7.4 Hz, 1H), 2.68 (dt, J = 13.8, 8.1 Hz, 1H), 1.88−1.78 (m, 2H), 1.10 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.5, 128.52, 128.46, 126.1, 80.8, 76.7, 74.8, 32.87, 32.84, 21.3; FT-IR (film of a concd. solution in CH_2Cl_2) 3398, 3085, 3061, 3026, 2927, 1603, 1496, 1454, 1381, 1257, 1043, 940, 749, 700 cm^{-1}; ESI-MS m/z 249.2 ($[M + Na]^+$; ESI-HRMS calcd. for $C_{12}H_{18}O_4Na$ ($[M + Na]^+$) 249.1097, found 249.1093.

Data for (2R,3S*)-2-Methyl-5-phenylpentane-1,2,3-triol (**3h** = **3e**).* **3h** = **3e** was obtained as a colorless oil, 19 mg, 30% from **1h**, chromatography using 1:1 to 1:2 PE/EtOAc; cf. the data for **3e** given above immediately below the data for **2e′**.

Conversion of Hydroperoxide 2a into Triol 3a. Ph_3P (31 mg, 0.118 mmol) was added to a solution of **2a** (23 mg, 0.102 mmol) in CH_2Cl_2 (2 mL) stirred at ambient temperature. After completion of the addition, stirring was continued at the same temperature until TLC showed completion of the reaction (ca. 1 h). The mixture was concentrated on a rotary evaporator. The residue was purified by column chromatography (first 2:1, then 1:1 PE/EtOAc) on silica gel to give **3a** as a white solid (21 mg, 0.999 mmol, 98%). Data for **3a**: cf. those given above under "Data for **3a**".

2-((4R,5S*)-2,2-Dimethyl-5-phenethyl-1,3-dioxolan-4-yl)-propan-2-ol (**3g′**).* A small drop of concd. H_2SO_4 (ca. 10 mg) was added to a mixture of **3g** (59 mg, 0.26 mmol) in acetone (3 mL) stirred at ambient temperature. Stirring was then continued for 12 h (when TLC showed full consumption of the starting **3g**). The reaction mixture was poured into aq. sat. $NaHCO_3$ (5 mL) and then extracted with Et_2O (10 mL × 3). The combined organic layers were washed with water (3 mL) and brine (3 mL) and dried over anhydrous Na_2SO_4. Removal of the drying agent by filtration and the solvent by rotary evaporation gave a residue, which was purified by column chromatography (6:1 PE/EtOAc) on silica gel to afford **3g′** as a colorless oil (61 mg, 0.23 mmol, 88%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.30−7.15 (m, 5H), 3.98 (td, J = 8.6, 3.0 Hz, 1H), 3.55(d, J = 7.8 Hz, 1H), 2.91 (ddd, J = 13.8, 10.3, 5.3 Hz, 1H), 2.70 (ddd, J = 13.8, 10.3, 6.6 Hz, 1H), 2.14 (s, 1H), 1.96−1.81 (m, 2H), 1.43 (s, 6H), 1.23 (s, 3H), 1.13 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 141.8, 128.36, 128.34, 125.9, 108.4, 86.8, 76.3, 69.7, 37.3, 32.6, 27.6, 27.5, 27.1, 24.6; FT-IR (film) 3481, 3087, 3063, 3027, 2984, 2932, 2858, 1604, 1496, 1455, 1379, 1370, 1250, 1216, 1170, 1061, 929, 874, 749, 700, 668 cm^{-1}; ESI-MS m/z 287.1 ($[M + Na]^+$); ESI-HRMS calcd. for $C_{16}H_{24}O_3Na$ ($[M + Na]^+$) 287.1618, found 287.1619.

tert-Butyldimethyl(((4R,5S*)-2,2,4-trimethyl-5-phenethyl-1,3-dioxolan-4-yl)methoxy)silane (**3h′**).* A solution of triol **3h** (21 mg, 0.1 mmol), TBSCl (18 mg, 0.12 mmol), imidazole (9 mg, 0.13 mmol) in dry DMF (1 mL) was stirred in an ice−water bath for 20 min (TLC showed completion of the reaction). Water (5 mL) was added to quench the reaction. The mixture was extracted with Et_2O (10 mL × 3). The combined organic layers were washed with water (5 mL) and brine (5 mL) before being dried over anhydrous Na_2SO_4. Filtration and rotary evaporation left an oily residue, which was purified by column chromatography (5:1 PE/EtOAc) on silica gel to furnish **3h**-TBS (= **3e**-TBS; (2*R**,3*S**)-1-((*tert*-butyldimethylsilyl)oxy)-2- methyl-5-phenylpentane-2,3-diol) as a colorless oil (28 mg, 0.86 mmol, 86%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.31−7.16 (m, 5H), 3.75 (d, J = 9.9 Hz, 1H), 3.53−3.47 (m, 1H), 3.47 (d, J = 9.8 Hz, 1H), 3.10 (s, 1H), 2.98 (ddd, J = 13.6, 10.3, 4.9 Hz, 1H), 2.81 (d, J = 6.7 Hz, 1H), 2.67 (ddd, J = 13.6, 9.7, 7.0 Hz, 1H), 1.91−1.83 (m, 1H), 1.69−1.59 (m, 1H), 1.06 (s, 3H), 0.90 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.1, 128.5, 128.4, 125.8, 76.9, 73.3, 68.4, 33.8, 33.0, 25.8, 20.7, 18.1, −5.6, −5.7; FT-IR (film) 3465, 3085, 3063, 3027, 2954, 2929, 2857, 1604, 1496, 1471, 1463, 1389, 1362, 1329, 1256, 1087, 1006, 974, 938, 838, 778, 749 cm^{-1}; ESI-MS m/z 347.3 ($[M + Na]^+$); ESI-HRMS calcd. for $C_{18}H_{32}O_3Na$ ($[M + Na]^+$) 347.2013, found 347.2004.

The **3h**-TBS (22 mg, 0.068 mmol) obtained above was dissolved in acetone (2 mL). To this solution was added *p*-TsOH·H_2O (1 mg, 0.006 mmol). The solution was stirred at ambient temperature for 3 h, when TLC showed completion of the reaction. Aq. sat. $NaHCO_3$ (2 mL) was added. The mixture was extracted with Et_2O (10 mL × 2). The combined organic layers were washed with water (3 mL) and brine (3 mL) before being dried over anhydrous Na_2SO_4. Filtration and rotary evaporation left an oily residue, which was purified by column chromatography (5:1 PE/EtOAc) on silica gel to give acetonide **3h′** as a colorless oil (25 mg, 0.068 mmol, 86%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.34−7.20 (m, 5H), 3.80 (t, J = 6.5 Hz, 1H), 3.69 (d, J = 9.8 Hz, 1H), 3.30 (d, J = 9.7 Hz, 1H), 2.93 (dt, J = 14.4, 7.3 Hz, 1H), 2.71 (dt, J = 14.3, 8.3 Hz, 1H), 2.01−1.93 (m, 2H), 1.46 (s, 3H), 1.39 (s, 3H), 1.28 (s, 3H), 0.89 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.9, 128.4, 128.3, 125.8, 106.7, 82.4, 81.6, 65.4, 33.2, 30.2, 28.6, 26.5, 25.8, 21.5, 18.1, −5.6, −5.7; FT-IR (film) 3086, 3064, 3028, 2984, 2956, 2931, 2858, 1604, 1497, 1471, 1455, 1377, 1369, 1296, 1252, 1216, 1194, 1095, 1045, 1002, 938, 837, 815, 776, 749 cm^{-1}; ESI-MS m/z 387.4 ($[M + Na]^+$); ESI-HRMS calcd. for $C_{21}H_{36}O_3SiNa$ ($[M + Na]^+$) 387.2326, found 387.2335.

Synthesis of Cyclic Substrates 1l−u. Cyclic (racemic) substrates **1l**, **1m**, **1n**, **1o**, **1p**, **1q**, **1r**, and **1u** are known compounds and were prepared according to the literature procedures.[24]

*Data for (±)-3-Ethylcyclohex-2-en-1-ol (**1n**).* **1n** was obtained as a colorless oil, chromatography using 4:1 PE/EtOAc): ^1H NMR (500 MHz, $CDCl_3$) δ 5.48 (br s, 1H), 4.20 (br s, 1H), 2.03−1.85 (m, 4H), 1.84−1.68 (m, 2H), 1.62−1.50 (m, 3H), 1.00 (t, J = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 144.1, 122.3, 65.9, 32.0, 30.2, 28.5, 19.1, 12.0. FT-IR (film) 3389, 2962, 2928, 2855, 1668, 1456, 1066 cm^{-1}; EI-MS m/z (%) 126 (M^+, 2), 108 (4), 97 (100), 91 (6), 79 (24), 67 (13), 55 (22), 41 (20), 39 (13); EI-HRMS calcd. for $C_8H_{14}O$ (M^+) 126.1039, found 126.1041.

*Data for (±)-3-Methylcyclohept-2-en-1-ol (**1r**, No Data Available in the Literature).* **1r** was obtained as a colorless oil, 603 mg, 4.8 mmol, 96% by $NaBH_4/CeCl_3$/MeOH reduction from the corresponding ketone, chromatography using 3:1 PE/EtOAc): ^1H NMR (500 MHz, $CDCl_3$) δ 5.48−5.45 (m, 1H), 4.35 (br s, 1H), 2.13−1.97 (m, 2H), 1.93−1.85 (m, 1H), 1.84−1.77 (m, 1H), 1.72 (s, 3H), 1.68 (br s, 1H), 1.66−1.56 (m, 3H), 1.39−1.30 (m, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 138.7, 131.6, 71.4, 36.6, 34.0, 27.1, 26.3, 25.7. EI-MS m/z (%) 126 (M+, 40), 111 (84), 97 (100), 83 (64), 69 (55), 55 (78), 43 (55), 41 (83); EI-HRMS calcd. for $C_8H_{14}O$ (M^+) 126.1039, found 126.1035.

*(±)-3-Allylcyclohept-2-en-1-ol (**1s**).* $CeCl_3·7H_2O$ (857 mg, 2.3 mmol) was added to a solution of the known[25] ketone (320 mg, 2.1 mmol) in MeOH (5 mL). The mixture was stirred at ambient temperature until a homogeneous solution was obtained. Stirring was then continued in an ice−water bath, while $NaBH_4$ (87 mg, 2.3 mmol) was introduced. After completion of the addition, the mixture was stirred at the same temperature for another 10 min (TLC showed completion of the reaction). Water (5 mL) was then added to quench the reaction. The mixture was extracted with EtOAc (20 mL × 3). The combined organic layers were washed with brine (10 mL) and dried over anhydrous Na_2SO_4. Removal of the drying agent by filtration and the solvent by rotary evaporation gave **1s** as a colorless oil (310 mg, 2.0 mmol, 95%). ^1H NMR (500 MHz, $CDCl_3$) δ 5.75 (ddt, J = 17.0, 10.1, 6.8 Hz, 1H), 5.50−5.47 (m, 1H), 5.05−4.99 (m, 2H), 4.37 (d, J = 7.7 Hz, 1H), 2.71 (d, J = 6.8 Hz, 2H), 2.10−1.99 (m, 2H), 1.94−1.85 (m, 1H), 1.84−1.74 (m, 2H), 1.67−1.53 (m, 3H), 1.34−1.21 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 140.4, 136.3, 132.7, 116.2, 71.6, 44.4, 36.6, 32.4, 27.4, 26.0. FT-IR (film) 3349, 2924, 2853, 1445, 1260, 1030, 911, 801 cm^{-1}; EI-MS m/z (%) 152 (M^+, 4), 134 (5), 111 (100), 93 (40), 79 (20), 67 (35), 55 (56), 43 (20), 41 (37); EI-HRMS calcd. for $C_{10}H_{16}O$ (M^+) 152.1196, found 152.1193.

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J. Org. Chem. XXXX, XXX, XXX−XXX

*(±)-5-Methyl-3,6-dihydro-2H-pyran-3-ol (**1t**).* Alcohol **1t** was obtained using the same procedure above for "Synthesis of (racemic) **1s**", except the starting 7-membered cyclic ketone was replace with the known[26] 5-methyl-2*H*-pyran-3(6*H*) -one. Data for **1t** (a colorless oil, 180 mg, 1.6 mmol, 72%; chromatography using 1:1 PE/EtOAc): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.70 (br s, 1H), 4.02−3.90 (m, 3H), 3.83 (br d, J = 11.7 Hz, 1H), 3.64 (dd, J = 11.7, 2.6 Hz, 1H), 1.65 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 137.8, 121.3, 70.6, 68.7, 63.0, 18.6; FT-IR (film) 3359, 2920, 2849, 1659, 1646, 1632, 1470, 668 cm^{-1}; ESI-MS m/z 137.05 ([M + Na]$^+$); ESI-HRMS calcd. for $C_6H_{10}O_2Na$ ([M + Na]$^+$) 137.0573, found 137.0575.

*Novozyme 435 Resolution of (±)-3-(3-Butenyl)-cyclohex-2-en-1-ol (**1p**, Typical Procedure[24a]).* Novezyme 435 (7.0 mg, ca. 2.2% of the substrate weight) was added to a 1 M solution of racemic **1p** (304 mg, 2.0 mmol) in *n*-hexane (2 mL) and vinyl butanoate (228 mg, 2 mol equiv with respect to **1p**). The mixture was stirred at ambient temperature (ca. 24 °C) for about 5 h. The solid enzyme was filtered off through Celite with suction. The filtrate was concentrated on a rotary evaporator. The residue was subjected to column chromatography on silica gel (10:1 to 4:1 PE/EtOAc) to give in turn the butanoate of (*R*)-**1p′** (along with some unreacted vinyl butanoate) and pure (*S*)-**1p** as a colorless oil (147 mg, 0.96 mmol, 48% yield from racemic **1p** 96% ee). The ester (*R*)-**1p′** (along with small amounts of **1p**) was dissolved in MeOH (2 mL), to which aq. NaOH (4 M, 0.5 mL, 2 mmol) was added. The solution was stirred at ambient temperature until TLC showed completion of the hydrolysis (the reaction mixture might turn yellowish due to self-condensation of the acetaldehyde generated from the hydrolysis of the unreacted vinyl butanoate). The mixture was extracted with EtOAc (10 mL × 2). The combined organic layers were washed with brine (10 mL) and dried over anhydrous Na_2SO_4. Removal of the drying agent by filtration and the solvent by rotary evaporation gave an oily residue, which was purified by column chromatography (4:1 PE/EtOAc) on silica to give (*R*)-**1p** as a yellowish oil (135 mg, 0.88 mmol, 44%, 97% ee).

Substrates **1l**, **1n**, **1o**, **1q**, **1r**, **1s**, and **1t** were all resolved using the above procedure. Substrate **1m** was resolved using the same procedure, but with 2:1 *n*-hexane/EtOAc to replace *n*-hexane as the solvent. Compound **1u** was resolved using lipase AK according to the literature.[24f]

*Data for (R)-3-Methylcyclohex-2-en-1-ol ((R)-**1l**).* (*R*)-**1l** was obtained as a yellowish oil; 20.8 g, 185 mmol, 43%; chromatography using 4:1 PE/EtOAc; $[\alpha]_D^{25}$ +88.5 (*c* 1.0 $CHCl_3$) (lit.[24a] $[\alpha]_D^{22}$ +96.0 (*c* 0.423, $CHCl_3$). 94% ee as determined by HPLC on a CHIRALPAK AD-H column (ϕ 0.46 × 25 cm, particle size = 5 μm) eluting with 98:2 of *n*-hexane/*i*-PrOH at a flow rate of 0.7 mL/min with UV detector set to 214 nm. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.48 (m, 1H), 4.16 (m, 1H), 1.83−1.96 (m, 2H), 1.70−1.81 (m, 2H), 1.67 (s, 3H), 1.52−1.61 (m, 2H).

*Data for (S)-3-Methylcyclohex-2-en-1-ol ((S)-**1l**).* (*S*)-**1l** was obtained as a colorless oil, 22.9 g, 204 mmol, 48%; chromatography using 4:1 PE/EtOAc; $[\alpha]_D^{25}$ −92.6 (*c* 1.0 $CHCl_3$) (lit.[24a] $[\alpha]_D^{24}$ −96.3 (*c* 0.458, $CHCl_3$)), 97% ee as determined by HPLC on a CHIRALPAK AD-H column (ϕ 0.46 × 25 cm, particle size = 5 μm) eluting with 98:2 of *n*-hexane/*i*-PrOH at a flow rate of 0.7 mL/min with UV detector set to 214 nm. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.48 (m, 1H), 4.16 (m, 1H), 1.83−1.96 (m, 2H), 1.70−1.81 (m, 2H), 1.67 (s, 3H), and 1.52−1.61 (m, 2H).

*Data for (R)-3-Benzylcyclohex-2-en-1-ol ((R)-**1m**).* (*R*)-**1m** was obtained as a colorless oil, 162 mg, 0.86 mmol, 45%; chromatography using 4:1 PE/EtOAc; $[\alpha]_D^{25}$ +30.8(*c* 1.0 $CHCl_3$), 92% ee as determined by HPLC on a CHIRALPAK IB column (ϕ 0.46 × 25 cm, particle size = 5 μm) eluting with 98:2 of *n*-hexane/*i*-PrOH at a flow rate of 0.7 mL/min with UV detector set to 214 nm. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31−7.26 (m, 2H), 7.23−7.15 (m, 3H), 5.55 (br s, 1H), 4.22 (br s, 1H), 3.31 (d, J = 15.9 Hz, 1H), 3.28 (d, J = 16.6 Hz, 1H), 1.96−1.67 (m, 4H), 1.64 (br s, 1H), 1.61−1.50 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 141.6, 139.4, 128.9, 128.3, 126.1, 125.7, 66.0, 44.2, 31.8, 28.2, 19.1.

*Data for (S)-3-Benzylcyclohex-2-en-1-ol ((S)-**1m**).* (*S*)-**1m** was obtained as a colorless oil, 145 mg, 0.77 mmol, 40%; chromatography using 4:1 PE/EtOAc; $[\alpha]_D^{25}$ −50.8 (*c* 1.0 $CHCl_3$), 98% ee as determined by HPLC on a CHIRALPAK IB column (ϕ 0.46 × 25 cm, particle size = 5 μm) eluting with 98:2 of *n*-hexane/*i*-PrOH at a flow rate of 0.7 mL/min with UV detector set to 214 nm. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31−7.26 (m, 2H), 7.23−7.15 (m, 3H), 5.55 (br s, 1H), 4.22 (br s, 1H), 3.31 (d, J = 16.7 Hz, 1H), 3.28 (d, J = 15.7 Hz, 1H), 1.96−1.67 (m, 4H), 1.61−1.50 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 141.6, 139.3, 128.9, 128.3, 126.1, 125.7, 66.0, 44.2, 31.8, 28.2, 19.1.

*Data for (R)-3-Ethylcyclohex-2-en-1-ol ((R)-**1n**).* (*R*)-**1n** was obtained as a yellowish oil, 49 mg, 0.39 mmol, 39%; chromatography using 4:1 PE/EtOAc; $[\alpha]_D^{25}$ +73.4 (*c* 1.0 $CHCl_3$), 96% ee as determined by HPLC on a CHIRALPAK IG column (ϕ 0.46 × 25 cm, particle size = 5 μm) eluting with 95:5 of *n*-hexane/*i*-PrOH at a flow rate of 0.7 mL/min with UV detector set to 214 nm. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.48 (br s, 1H), 4.20 (br s, 1H), 2.04−1.54 (m, 9H), 1.00 (t, J = 7.5 Hz, 3H).

*Data for (S)-3-Ethylcyclohex-2-en-1-ol ((S)-**1n**).* (*S*)-**1n** was obtained as a yellowish oil, 57 mg, 0.45 mmol, 45%; chromatography using 4:1 PE/EtOAc; $[\alpha]_D^{25}$ −62.2 (*c* 1.0 $CHCl_3$) (lit.[27] $[\alpha]_D$ −27.9 (*c* 0.4, $CHCl_3$); (lit.[24b] $[\alpha]_D^{20}$ −61 (*c* unknown, $CHCl_3$), 77% ee)), 87% ee as determined by HPLC on a CHIRALPAK IG column (ϕ 0.46 × 25 cm, particle size = 5 μm) eluting with 95:5 of *n*-hexane/*i*-PrOH at a flow rate of 0.7 mL/min with UV detector set to 214 nm. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.48 (br s, 1H), 4.20 (br s, 1H), 2.02−1.56 (m, 9H), 1.00 (t, J = 7.5 Hz, 3H).

*Data for (R)-3-Allylcyclohex-2-en-1-ol ((R)-**1o**).* (*R*)-**1o** was obtained as a colorless oil, 190 mg, 1.37 mmol, 46%; chromatography using 4:1 PE/EtOAc; $[\alpha]_D^{20}$ +65.4 (*c* 1.0 $CHCl_3$), 99% ee as determined by GC on a DB-WAX quartz capillary column (ϕ 0.25 mm × 30 m, df (dimension of film) = 0.25 μm) with the injector temperature set to 250 °C, the column temperature changed from 50 to 250 °C at a rate of 10 °C/min, N_2 as carrier gas (at a flow rate of 2 mL/min), and the effluents detected using a H_2 flame ionization detector. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.80 (ddt, J = 16.8, 10.3, 6.9 Hz, 1H), 5.56−5.53 (m, 1H), 5.08−5.05 (m, 1H), 5.04−5.03 (m, 1H), 4.21 (br s, 1H), 2.72 (d, J = 6.7 Hz, 1H), 2.01−1.86 (m, 2H), 1.85−1.70 (m, 2H), 1.63−1.55 (m, 2H), 1.49 (br s, 1H, −OH).

*Data for (S)-3-Allylcyclohex-2-en-1-ol ((S)-**1o**).* (*S*)-**1o** was obtained as a colorless oil, 201 mg, 1.45 mmol, 48%; chromatography using 4:1 PE/EtOAc; $[\alpha]_D^{20}$ −54.9 (*c* 1.0 $CHCl_3$), 91% ee as determined by GC on a DB-WAX quartz capillary column (ϕ 0.25 mm × 30 m, df (dimension of film) = 0.25 μm) with the injector temperature set to 250 °C, the column temperature changed from 50 to 250 °C at a rate of 10 °C/min, N_2 as carrier gas (at a flow rate of 2 mL/min), and the effluents detected using a H_2 flame ionization detector. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83−5.73 (m, 1H), 5.53 (br s, 1H), 5.05 (br d, J = 7.8 Hz, 1H), 5.02 (br s, 1H), 4.20 (br s, 1H), 2.71 (d, J = 6.7 Hz, 2H), 2.01−1.85 (m, 2H), 1.83−1.69 (m, 2H), 1.63−1.53 (m, 2H).

*Data for (R)-3-(3-Butenyl)-cyclohex-2-en-1-ol ((R)-**1p**).* (*R*)-**1p** was obtained as a yellowish oil, 135 mg, 0.88 mmol, 44%; chromatography using 10:1 PE/EtOAc for the corresponding butanoate and 4:1 PE/EtOAc for the alcohol; $[\alpha]_D^{25}$ +64.6 (*c* 1.0, $CHCl_3$), 97% ee as determined by HPLC on a CHIRALPAK IF3 column (ϕ 0.46 × 25 cm, particle size = 3 μm) eluting with 98:2 of *n*-hexane/*i*-PrOH at a flow rate of 0.7 mL/min with UV detector set to 214 nm. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.80 (ddt, J = 17.0, 10.1, 6.5 Hz, 1H), 5.51 (br s, 1H), 5.01 (br d, J = 17.1 Hz, 1H), 4.95 (br d, J = 10.1 Hz, 1H), 4.19 (br s, 1H), 2.21−2.14 (m, 2H), 2.08−2.03 (m, 2H), 2.00−1.85 (m, 2H), 1.83−1.69 (m, 2H), 1.62−1.53 (m, 2H), 1.46 (br s, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 141.7, 138.3, 124.0, 114.6, 65.9, 36.8, 31.9, 31.7, 28.5, 19.0.

*Data for (S)-3-(3-Butenyl)-cyclohex-2-en-1-ol ((S)-**1p**).* (*S*)-**1p** was obtained as a yellowish oil, 147 mg, 0.96 mmol, 48%; chromatography using 4:1 PE/EtOAc; $[\alpha]_D^{25}$ −66.5 (*c* 1.0, $CHCl_3$), 96% ee as determined by HPLC on a CHIRALPAK IF3 column (ϕ 0.46 × 25 cm, particle size = 3 μm e) eluting with 98:2 of *n*-hexane/*i*-PrOH at a flow rate of 0.7 mL/min with UV detector set to 214 nm. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.80 (ddt, J = 17.1, 10.2, 6.5 Hz, 1H), 5.51 (br s, 1H),

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J. Org. Chem. XXXX, XXX, XXX−XXX

5.01 (br d, J = 17.1 Hz, 1H), 4.95 (br d, J = 10.1 Hz, 1H), 4.19 (br s, 1H), 2.21−2.14 (m, 2H), 2.08−2.03 (m, 2H), 2.00−1.85 (m, 2H), 1.83−1.69 (m, 2H), 1.62−1.53 (m, 2H), 1.46 (br s, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 141.7, 138.3, 124.0, 114.6, 65.9, 36.8, 31.9, 31.7, 28.5, 19.0.

*Data for (R)-3-(((tert-Butyldimethylsilyl)oxy)methyl)-cyclohex-2-en-1-ol ((R)-**1q**).* (*R*)-**1q** was obtained as a yellowish oil, 140 mg, 0.58 mmol, 29%; chromatography using 5:1 PE/EtOAc; $[\alpha]_D^{25}$ +34.4 (*c* 1.0, $CHCl_3$), 97% ee as determined by HPLC on a CHIRALPAK OD-H column (ϕ 0.46 × 25 cm, particle size = 5 μm) eluting with 98:2 of *n*-hexane/*i*-PrOH at a flow rate of 0.7 mL/min with UV detector set to 214 nm. ^1H NMR (500 MHz, $CDCl_3$) δ 5.77−5.74 (m, 1H), 4.23 (br s, 1H), 4.02 (s, 2H), 1.99−1.71 (m, 4H), 1.63−1.57 (m, 2H), 0.91 (s, 9H), 0.07 (s, 6H).

*Data for (S)-3-(((tert-Butyldimethylsilyl)oxy)methyl)-cyclohex-2-en-1-ol ((S)-**1q**).* (*S*)-**1q** was obtained as a yellowish oil, 241 mg, 0.99 mmol, 50%; chromatography using 5:1 PE/EtOAc; $[\alpha]_D^{25}$ −28.5 (*c* 1.0, $CHCl_3$), 92% ee as determined by HPLC on a CHIRALPAK OD-H column (ϕ 0.46 × 25 cm, particle size = 5 μm) eluting with 98:2 of *n*-hexane/*i*-PrOH at a flow rate of 0.7 mL/min with UV detector set to 214 nm. ^1H NMR (500 MHz, $CDCl_3$) δ 5.77−5.74 (m, 1H), 4.23 (br s, 1H), 4.02 (s, 2H), 1.95−1.81 (m, 3H), 1.78−1.70 (m, 1H), 1.65−1.57 (m, 2H), 0.91 (s, 9H), 0.07 (s, 6H).

*Data for (R)-3-Methylcyclohept-2-en-1-ol ((R)-**1r**).* (*R*)-**1r** was obtained as a yellowish oil, 120 mg, 0.95 mmol, 33%; chromatography using 5:1 PE/EtOAc; $[\alpha]_D^{25}$ +18.0 (*c* 1.0, $CHCl_3$), 98% ee as determined by HPLC on a CHIRALPAK IG column (ϕ 0.46 × 25 cm, particle size = 5 μm) eluting with 95:5 of *n*-hexane/*i*-PrOH at a flow rate of 0.7 mL/min with UV detector set to 214 nm. ^1H NMR (500 MHz, $CDCl_3$) δ 5.46 (br s, 1H), 4.35 (br s, 1H), 2.13−2.06 (m, 1H), 2.00 (dd, J = 14.9, 7.1 Hz, 1H), 1.93−1.86 (m, 1H), 1.84−1.78 (m, 1H), 1.72 (s, 3H), 1.67−1.51 (m, 4H), 1.40−1.29 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 138.7, 131.5, 71.4, 36.6, 34.0, 27.0, 26.3, 25.7.

*Data for (S)-3-Methylcyclohept-2-en-1-ol ((S)-**1r**).* (*S*)-**1r** was obtained as a yellowish oil, 186 mg, 1.47 mmol, 52%; chromatography using 5:1 PE/EtOAc; $[\alpha]_D^{25}$ −5.7 (*c* 1.0, $CHCl_3$), 72% ee as determined by HPLC on a CHIRALPAK IG column (ϕ 0.46 × 25 cm, particle size = 5 μm) eluting with 95:5 of *n*-hexane/*i*-PrOH at a flow rate of 0.7 mL/min with UV detector set to 214 nm. ^1H NMR (500 MHz, $CDCl_3$) δ 5.47−5.44 (m, 1H), 4.34 (d, J = 7.1 Hz, 1H), 2.12−2.05 (m, 1H), 2.03−1.96 (m, 1H), 1.92−1.85 (m, 1H), 1.8−1.75 (m, 1H), 1.71 (s, 3H), 1.69 (s, 1H), 1.64−1.55 (m, 3H), 1.39−1.29 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 138.7, 131.6, 71.4, 36.6, 33.9, 27.1, 26.3, 25.7.

*Data for (R)-3-Allylcyclohept-2-en-1-ol ((R)-**1s**).* (*R*)-**1s** was obtained as a colorless oil, 80 mg, 0.53 mmol, 28%; chromatography using 4:1 PE/EtOAc): $[\alpha]_D^{25}$ +19.0 (*c* 1.0, $CHCl_3$), 98% ee as determined by HPLC on a CHIRALPAK AD-H column (ϕ 0.46 × 25 cm, particle size = 5 μm) eluting with 98:2 of *n*-hexane/*i*-PrOH at a flow rate of 0.7 mL/min with UV detector set to 214 nm. ^1H NMR (500 MHz, $CDCl_3$) δ 5.76 (ddt, J = 16.9, 10.1, 6.8 Hz, 1H), 5.49 (br s, 1H), 5.07−5.00 (m, 2H), 4.39 (d, J = 6.9 Hz, 1H), 2.72 (d, J = 6.7 Hz, 2H), 2.12−1.99 (m, 2H), 1.96−1.87 (m, 1H), 1.86−1.76 (m, 1H), 1.72−1.51 (m, 4H), 1.36−1.21 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 140.5, 136.3, 132.6, 116.2, 71.7, 44.4, 36.6, 32.4, 27.3, 26.0.

*Data for (S)-3-Allylcyclohept-2-en-1-ol ((S)-**1s**).* (*S*)-**1s** was obtained as a colorless oil, 186 mg, 1.47 mmol, 52%; chromatography using 4:1 PE/EtOAc; $[\alpha]_D^{25}$ −8.9 (*c* 1.0, $CHCl_3$), 42% ee as determined by HPLC on a CHIRALPAK AD-H column (ϕ 0.46 × 25 cm, particle size = 5 μm) eluting with 98:2 of *n*-hexane/*i*-PrOH at a flow rate of 0.7 mL/min with UV detector set to 214 nm. ^1H NMR (500 MHz, $CDCl_3$) δ 5.75 (ddt, J = 16.9, 10.1, 6.8 Hz, 1H), 5.48 (br s, 1H), 5.07−4.98 (m, 2H), 4.37 (d, J = 6.8 Hz, 1H), 2.70 (d, J = 6.7 Hz, 2H), 2.13−1.98 (m, 2H), 1.95−1.86 (m, 1H), 1.85−1.74 (m, 2H), 1.66−1.53 (m, 3H), 1.34−1.20 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 140.4, 136.3, 132.7, 116.2, 71.6, 44.4, 36.6, 32.4, 27.4, 26.0.

*Data for (S)-5-Methyl-3,6-dihydro-2H-pyran-3-ol ((S)-**1t**).* (*S*)-**1t** was the enantiomer obtained after hydrolysis of the ester, a colorless oil, 151 mg, 1.32 mmol, 35%; chromatography using 1:1 PE/EtOAc; $[\alpha]_D^{25}$ +206.1 (*c* 1.0, $CHCl_3$), 94% ee as determined by HPLC on a CHIRALPAK IE3 column (ϕ 0.46 × 25 cm, particle size = 3 μm) eluting with 80:20 of *n*-hexane/*i*-PrOH at a flow rate of 0.7 mL/min with UV detector set to 214 nm. ^1H NMR (500 MHz, $CDCl_3$) δ 5.69 (s, 1H), 4.02−3.89 (m, 3H), 3.82 (d, J = 11.6 Hz, 1H), 3.63 (d, J = 11.6 Hz, 1H), 2.00 (d, J = 4.8 Hz, 1H), 1.64 (s, 3H).

*Data for (R)-5-Methyl-3,6-dihydro-2H-pyran-3-ol ((R)-**1t**).* (*R*)-**1t** was the enantiomer isolated directly from the enzyme resolution mixture, a colorless oil, 187 mg, 1.64 mmol, 43%; chromatography using 1:1 PE/EtOAc; $[\alpha]_D^{25}$ −183.3 (*c* 0.5, $CHCl_3$), 84% ee as determined by HPLC on a CHIRALPAK IE3 column (ϕ 0.46 × 25 cm, particle size = 3 μm) eluting with 80:20 of *n*-hexane/*i*-PrOH at a flow rate of 0.7 mL/min with UV detector set to 214 nm. ^1H NMR (500 MHz, $CDCl_3$) δ 5.69 (br s, 1H), 3.99−3.87 (m, 3H), 3.80 (dd, J = 11.8, 1.3 Hz, 1H), 3.62 (dd, J = 11.7, 2.6 Hz, 1H), 2.25 (br s, 1H), 1.63 (s, 3H). The absolute configuration of (*R*)-**1t** was also confirmed by CBS reduction of the corresponding ketone (using (*R*)- CBS-methyl-oxazaborolidne/BH_3), which according to the empirical rule, should give (*R*)-**1t**, and the product showed a negative optical rotation $[\alpha]_D^{25}$ −117.4 (*c* 0.8, $CHCl_3$).

*Data for (S)-1-(Benzyloxycarbonyl)-3-hydroxy-5-methyl-1,2,3,6-tetrahydro- pyridine ((S)-**1u**).* (*S*)-**1u** was the enantiomer obtained after hydrolysis of the ester, a colorless oil, 90 mg, 0.36 mmol, 36%; chromatography using 2:1 PE/EtOAc; $[\alpha]_D^{25}$ −81.3 (*c* 1.0, $CHCl_3$), $[\alpha]_D^{25}$ −43.4 (*c* 1.3, EtOH), 99% ee as determined by HPLC on a CHIRALPAK AD-H column (ϕ 0.46 × 25 cm, particle size = 5 μm) eluting with 95:5 of *n*-hexane/*i*-PrOH at a flow rate of 0.7 mL/min with UV detector set to 220 nm. ^1H NMR (500 MHz, $CDCl_3$) δ 7.39−7.28 (m, 5H), 5.64 (br s, 1H), 5.21−5.11 (m, 2H), 4.24−4.09 (m, 1H), 4.06−3.88 (m, 1H), 3.74−3.61 (m, 2H), 3.53−3.43 (m, 1H), 1.72 (s, 3H).

*Data for (R)-1-(Benzyloxycarbonyl)-3-hydroxy-5-methyl-1,2,3,6-tetrahydro- pyridine ((R)-**1u**).* (*R*)-**1u** was the enantiomer isolated directly from the enzyme resolution mixture, a colorless oil, 130 mg, 0.53 mmol, 53%; chromatography using 2:1 PE/EtOAc; $[\alpha]_D^{25}$ +60.1 (*c* 1.0, $CHCl_3$), $[\alpha]_D^{25}$ +38.3 (*c* 1.3, EtOH) (lit.[24f] $[\alpha]_D$ +44 (*c* 1.3, EtOH)), 79% ee as determined by HPLC on a CHIRALPAK AD-H column (ϕ 0.46 × 25 cm, particle size = 5 μm) eluting with 95:5 of *n*-hexane/*i*-PrOH at a flow rate of 0.7 mL/min with UV detector set to 220 nm. ^1H NMR (500 MHz, $CDCl_3$) δ 7.42−7.27 (m, 5H), 5.64 (br s, 1H), 5.20−5.11 (m, 2H), 4.16 (d, J = 28.1 Hz, 1H), 4.06−3.87 (m, 1H), 3.70 (d, J = 17.8 Hz, 2H), 3.55−3.42 (m, 1H), 1.72 (s, 3H).

Synthesis of Substrates 1v−z. These compounds were all synthesized according to the literature.[28]

*Data for (2R,4aR,5R)-5-((tert-butyldimethylsilyl)oxy)-4a-methyl-2,3,4,4a,5,6,7,8-octahydronaphthalen-2-ol (**1w**).* **1w** was obtained as a colorless oil, 340 mg, 1.15 mmol, chromatography using 4:1 PE/EtOAc; $[\alpha]_D^{25}$ −53.5 (*c* 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 5.37 (br s, 1H), 4.16 (br s, 1H), 3.20 (dd, J = 10.8, 5.0 Hz, 1H), 2.17−2.07 (m, 1H), 1.98−1.87 (m, 2H), 1.82−1.68 (m, 2H), 1.65−1.53 (m, 2H), 1.49−1.38 (m, 2H), 1.34−1.15 (m, 2H), 1.03 (s, 3H), 0.88 (s, 9H), 0.02 (s, 3H), 0.02 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 145.4, 125.5, 79.4, 67.8, 41.2, 34.1, 31.4, 31.3, 29.1, 25.8, 24.4, 18.1, 17.1, −3.9, −4.9.

*Data for (2S,4R,4aS,6R)-4,4a-dimethyl-6-(prop-1-en-2-yl)-2,3,4,4a,5,6,7,8-octahydronaphthalen-2-ol (**1x**).* **1x** was obtained as a colorless oil, 918 mg, 4.17 mmol, 91% yield from corresponding ketone, chromatography using 5:1 PE/EtOAc; $[\alpha]_D^{25}$ +105.1 (*c* 1.0, $CHCl_3$) (lit.[29] $[\alpha]_D$ +208 (*c* 1.1, $CHCl_3$)). ^1H NMR (500 MHz, $CDCl_3$) δ 5.32 (br d, J = 1.6 Hz, 1H), 4.70−4.66 (m, 2H), 4.28−4.21 (m, 1H), 2.37−2.21 (m, 2H), 2.11 (ddd, J = 14.1, 4.1, 2.6 Hz, 1H), 1.89−1.75 (m, 3H), 1.70 (s, 3H), 1.63 (s, 1H), 1.55−1.47 (m, 1H), 1.42−1.32 (m, 2H), 1.25−1.16 (m, 1H), 0.99 (s, 3H), 0.95 (t, J = 12.7 Hz, 1H), 0.89 (d, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 150.2, 146.0, 124.2, 108.5, 68.0, 44.6, 40.8, 39.3, 38.2, 37.2, 32.9, 32.3, 20.8, 18.2, 15.4.

*Data for Cholest-4-en-3β-ol (**1y**).* **1y** was obtained as a white solid, 189 mg, 0.48 mmol, chromatography using 6:1 PE/EtOAc; mp 133−135 °C (lit.[28e] 135−136 °C). $[\alpha]_D^{25}$ +56.1 (*c* 0.1, $CHCl_3$) (lit.[30] $[\alpha]_D$ +47.5 (*c* 1.0, $CHCl_3$)). ^1H NMR (500 MHz, $CDCl_3$) δ 5.27 (br d, J =

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J. Org. Chem. XXXX, XXX, XXX−XXX

1.5 Hz, 1H), 4.18−4.11 (m, 1H), 2.25−2.14 (m, 1H), 2.04−1.91 (m, 3H), 1.86−1.66 (m, 3H), 1.55−1.19 (m, 13H), 1.04 (s, 3H), 1.17−0.92 (m, 8H), 0.90 (d, J = 6.5 Hz, 3H), 0.86 (d, J = 6.6 Hz, 3H), 0.86 (d, J = 6.6 Hz, 3H), 0.76−0.70 (m, 1H), 0.67 (s, 3H).

*Data for 7β-Hydroxycholest-5-en-3β-yl acetate (**1z**).* **1z** was obtained as a white solid, 724 mg, 1.63 mmol, chromatography using 4:1 PE/EtOAc; mp 111−112 C (lit.[28e] 110−111 °C). $[\alpha]_D^{25}$ −12.4 (c 0.1, $CHCl_3$) (lit.[30] $[\alpha]_D$ −132.6 (c 0.1, $CHCl_3$), lit.[31] $[\alpha]_D^{23}$ −9 (c 0.1, $CHCl_3$)). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.30 (br s, 1H), 4.66−4.55 (m, 1H), 3.89−3.82 (m, 1H), 2.38−2.28 (m, 2H), 2.02 (s, 3H), 1.93−1.75 (m, 4H), 1.64−1.24 (m, 12H), 1.21−0.95 (m, 9H), 1.05 (s, 3H), 0.91 (d, J = 6.5 Hz, 3H), 0.86 (d, J = 6.6 Hz, 3H), 0.85 (d, J = 6.6 Hz, 3H), 0.68 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 170.5, 142.3, 126.3, 73.4, 73.2, 55.9, 55.4, 48.1, 42.9, 40.7, 39.5, 37.6, 36.6, 36.5, 36.2, 35.7, 28.5, 28.0, 27.7, 26.3, 23.8, 22.8, 22.5, 21.4, 21.0, 19.1, 18.7, 11.8.

$MoO_2(acac)_2$ Mediated Formal Hydroxylation−Hydroperoxylation of 1l (Typical Procedure). To a solution of (*S*)-**1l** (449 mg, 4.0 mml) in freshly prepared H_2O_2-saturated Et_2O (20 mL) was added $MoO_2(acac)_2$ (65 mg, 0.2 mmol). The pale yellow−greenish transparent solution was stirred at ambient temperature for 4 h (TLC showed completion of the reaction). Aq. sat. NaCl (4 mL) was added to quench the reaction. Phases were separated. The aq. layer was extracted with EtOAc (20 mL × 5). The combined organic layers were dried over anhydrous Na_2SO_4. Removal of the drying agent by filtration and the solvent by rotary evaporation left an oily residue, which was purified by column chromatography (1:1 PE/EtOAc) on silica gel to give diol-hydroperoxide **2l** (colorless sticky oil, 512 mg, 3.16 mmol, 79% from **1l**) and triol **3l** (52 mg, 0.36 mmol, 9% from **1l**).

*Data for (1S,2S,3S)-3-Hydroperoxy-3-methylcyclohexane-1,2-diol (**2l**).* **2l** was obtained as a colorless sticky oil, 512 mg, 3.16 mmol, 79%; less polar than **3l**, chromatography using 1:1 PE/EtOAc; $[\alpha]_D^{25}$ +18.9 (c 1.0, MeOH). ^{1}H NMR (500 MHz, CD_3OD) δ 3.85 (dt, J = 2.9, 7.6 Hz, 1H), 3.75 (d, J = 3.1 Hz, 1H), 1.59−1.42 (m, 6H), 1.28 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, CD_3OD) δ 84.2, 72.0, 68.5, 29.1, 27.1, 20.7, 18.6; FT-IR (film) 3386, 2941, 1370, 1061 cm^{-1}; ESI-MS m/z 185.10 ([M + Na]$^+$); ESI-HRMS calcd. for $C_7H_{14}O_4Na$ ([M + Na]$^+$) 185.0784, found 185.0779.

*Data for (1S,2S,3S)-1-methylcyclohexane-1,2,3-triol (**3l**).* **3l** was obtained as a colorless sticky oil, 52 mg, 0.36 mmol, 9%; more polar than **2l**, chromatography using 1:1 PE/EtOAc; $[\alpha]_D^{25}$ +9.2 (c 1.0, MeOH). ^{1}H NMR (500 MHz, CD_3OD) δ 3.94−3.89 (m, 1H), 3.43 (d, J = 2.7 Hz, 1H), 1.62−1.45 (m, 5H), 1.35−1.27 (m, 2H), 1.22 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, CD_3OD) δ 75.8, 72.6, 68.5, 32.2, 27.2, 26.3, 18.8; FT-IR (film) 3387, 2937, 1059, 1032 cm^{-1}; ESI-MS m/z 169.00 ([M + Na]$^+$); ESI-HRMS calcd. for $C_7H_{14}O_3Na$ ([M + Na]$^+$) 169.0835, found 169.0834.

*Data for (1S,2S,3R)-3-Benzyl-3-hydroperoxycyclohexane-1,2-diol (**2m**).* **2m** was obtained as a white solid, 96 mg, 0.40 mmol, 80%; less polar than **3m**, chromatography using 2:1 PE/EtOAc; mp 84−86 °C. $[\alpha]_D^{25}$ +29.2 (c 1.0, MeOH). ^{1}H NMR (500 MHz, CD_3OD) δ 7.37−7.33 (m, 2H), 7.24−7.12 (m, 3H), 3.80 (ddd, J = 10.9, 5.2, 2.9 Hz, 1H), 3.64 (d, J = 2.6 Hz, 1H), 3.03 (d, J = 13.9 Hz, 1H), 2.98 (d, J = 13.9 Hz, 1H), 1.64−1.53 (m, 2H), 1.51−1.38 (m, 4H), 1.29 (br s, 1H); ^{13}C{^{1}H} NMR (125 MHz, CD_3OD) δ 137.4, 130.7, 127.1, 125.4, 85.8, 70.3, 68.6, 38.1, 27.1, 26.9, 18.5; FT-IR (KBr) 3347, 2925, 1455, 1031, 997, 730, 696, 660 cm^{-1}; ESI-MS m/z 261.00 ([M + Na]$^+$); ESI-HRMS calcd. for $C_{13}H_{18}O_4Na$ ([M + Na]$^+$) 261.1097, found 261.1098.

*Data for (1R,2S,3S)-1-benzylcyclohexane-1,2,3-triol (**3m**).* **3m** was obtained as a colorless sticky oil, 8 mg, 0.036 mmol, 7%; more polar than **2m**, chromatography using 1:1 PE/EtOAc; $[\alpha]_D^{25}$ +14.6 (c 0.5, MeOH). ^{1}H NMR (500 MHz, CD_3OD) δ 7.28−7.22 (m, 4H), 7.19−7.15 (m, 1H), 3.89−3.84 (m, 1H), 3.40 (d, J = 2.5 Hz, 1H), 2.88 (d, J = 13.5 Hz, 1H), 2.77 (d, J = 13.5 Hz, 1H), 1.65−1.44 (m, 5H), 1.33−1.24 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, CD_3OD) δ 137.2, 130.7, 127.3, 125.6, 74.5, 73.5, 68.6, 45.1, 30.4, 27.2, 18.7; FT-IR (film) 3420, 2936, 2862, 1452, 997, 703 cm^{-1}; ESI-MS m/z 244.95 ([M + Na]$^+$); ESI-HRMS calcd. for $C_{13}H_{18}O_3Na$ ([M + Na]$^+$) 245.1148, found 245.1148.

*Data for (1R,2R,3R)-3-ethyl-3-hydroperoxycyclohexane-1,2-diol (**2n**).* **2n** was obtained as a white solid, 4.45 g, 25.3 mmol, 78%; less polar than **3n**, chromatography using 1:1 PE/EtOAc; mp 69−70 °C. $[\alpha]_D^{25}$ −13.3 (c 1.0, MeOH). ^{1}H NMR (500 MHz, CD_3OD) δ 3.81−3.76 (m, 1H), 3.73 (d, J = 2.7 Hz, 1H), 1.70 (q, J = 7.5 Hz, 2H), 1.64 (br d, J = 13.8 Hz, 1H), 1.60−1.41 (m, 4H), 1.40−1.30 (m, 1H), 0.90 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, CD_3OD) δ 85.8, 70.1, 68.6, 27.3, 26.6, 25.5, 18.6, 5.4. FT-IR (film in $CHCl_3$) 3374, 2940, 2880, 1459, 1382, 1069, 1042, 996, 829 cm^{-1}; ESI-MS m/z 198.95 ([M + Na]$^+$); ESI-HRMS calcd. for $C_8H_{16}O_4Na$ ([M + Na]$^+$) 199.0941, found 199.0941.

*Data for (1R,2R,3R)-1-Ethylcyclohexane-1,2,3-triol (**3n**).* **3n** was obtained as a colorless oil, 560 mg, 3.5 mmol, 11%; more polar than **2n**, chromatography using 1:3 PE/EtOAc; $[\alpha]_D^{25}$ −10.7 (c 1.0, MeOH). ^{1}H NMR (500 MHz, CD_3OD) δ 3.89 (ddd, J = 10.0, 5.5, 2.9 Hz, 1H), 3.51 (d, J = 2.7 Hz, 1H), 1.65−1.54 (m, 4H), 1.54−1.41 (m, 3H), 1.39−1.33 (m, 1H), 0.91 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, CD_3OD) δ 74.4, 73.2, 68.6, 31.5, 30.4, 27.5, 18.8, 5.4. FT-IR (film) 3396, 2940, 2880, 1459, 1395, 1151, 1069, 1041, 996, 962, 874, 834 cm^{-1}; ESI-MS m/z 182.90 ([M + Na]$^+$); ESI-HRMS calcd. for $C_8H_{16}O_3Na$ ([M + Na]$^+$) 183.0992, found 183.0994.

*Data for (1S,2S,3R)-3-Allyl-3-hydroperoxycyclohexane-1,2-diol (**2o**).* **2o** was obtained as a colorless sticky oil, 74 mg, 0.39 mmol, 78%; less polar than **3o**, chromatography using 2:1 PE/EtOAc; $[\alpha]_D^{25}$ +9.4 (c 1.0, MeOH). ^{1}H NMR (500 MHz, CD_3OD) δ 6.00−5.90 (m, 1H), 5.10−5.02 (m, 2H), 3.84−3.77 (m, 2H), 2.51 (dd, J = 14.4, 6.8 Hz, 1H), 2.42 (dd, J = 14.4, 7.7 Hz, 1H), 1.62−1.35 (m, 6H); ^{13}C{^{1}H} NMR (125 Hz, CD_3OD) δ 133.8, 116.2, 85.4, 70.6, 68.5, 37.8, 27.2, 26.9, 18.5; FT-IR (film) 3348, 2943, 1051, 999, 668 cm^{-1}; ESI-MS m/z 211.00 ([M + Na]$^+$); ESI-HRMS calcd. for $C_9H_{16}O_4Na$ ([M + Na]$^+$) 211.0941, found 211.0940.

*Data for (1R,2S,3S)-1-Allylcyclohexane-1,2,3-triol (**3o**).* **3o** was obtained as a colorless sticky oil, 10 mg, 0.058 mmol, 11%; more polar than **2o**, chromatography using 1:1 PE/EtOAc; $[\alpha]_D^{25}$ +3.5 (c 0.5, MeOH). ^{1}H NMR (500 MHz, CD_3OD) δ 5.96−5.89 (m, 1H), 5.10−5.04 (m, 2H), 3.82−3.87 (m, 1H), 3.49 (d, J = 2.5 Hz, 1H), 2.35 (dd, J = 14.0, 7.0 Hz, 1H), 2.26 (dd, J = 14.0, 7.8 Hz, 1H), 1.63−1.27 (m, 7H); ^{13}C{^{1}H} NMR (125 Hz, CD_3OD) δ 133.5, 116.8, 74.2, 73.9, 68.5, 43.8, 30.4, 27.4, 18.7; FT-IR (film) 3393, 2939, 1049, 999, 669 cm^{-1}; ESI-MS m/z 194.95 ([M + Na]$^+$); ESI-HRMS calcd. for $C_9H_{16}O_3Na$ ([M + Na]$^+$) 195.0992, found 195.0991.

*Data for (1R,2R,3S)-3-(But-3-en-1-yl)-3-hydroperoxycyclohexane-1,2-diol (**2p**).* **2p** was obtained as a colorless sticky oil, 70 mg, 0.34 mmol, 69%; less polar than **3p**, chromatography using 2:1 PE/EtOAc; $[\alpha]_D^{25}$ −14.3 (c 1.0, MeOH). ^{1}H NMR (500 MHz, CD_3OD) δ 5.87 (ddt, J = 17.0, 10.3, 6.6 Hz, 1H), 5.03 (ddt, J = 17.1, 1.9, 1.6 Hz, 1H), 4.91 (ddt, J = 10.2, 2.0, 1.0 Hz, 1H), 3.82−3.77 (m, 1H), 3.75 (d, J = 2.5 Hz, 1H), 2.24−2.09 (m, 2H), 1.81−1.72 (m, 2H), 1.69−1.63 (m, 1H), 1.62−1.49 (m, 4H), 1.48−1.36 (m, 2H); ^{13}C{^{1}H} NMR (125 Hz, CD_3OD) δ 139.3, 112.8, 85.5, 70.4, 68.6, 32.6, 27.3, 27.0, 26.2, 18.6; FT-IR (film) 3403, 2938, 1709, 1448, 1054, 997 cm^{-1}; ESI-MS m/z 225.05 ([M + Na]$^+$); ESI-HRMS calcd. for $C_{10}H_{18}O_4Na$ ([M + Na]$^+$) 225.1097, found 225.1092.

*Data for (1S,2R,3R)-1-(But-3-en-1-yl)-cyclohexane-1,2,3-triol (**3p**).* **3p** was obtained as a colorless sticky oil, 10 mg, 0.054 mmol, 10%; more polar than **2p**, chromatography using 1:1 PE/EtOAc; $[\alpha]_D^{25}$ −31.7 (c 0.1, MeOH). ^{1}H NMR (500 MHz, CD_3OD) δ 5.86 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.02 (ddt, J = 17.1, 2.0, 1.6 Hz, 1H), 4.91 (ddt, J = 10.2, 2.1, 1.2 Hz, 1H), 3.90 (ddd, J = 9.7, 5.5, 2.9 Hz, 1H), 3.52 (d, J = 2.5 Hz, 1H), 2.24−2.09 (m, 2H), 1.71−1.45 (m, 6H), 1.41−1.27 (m, 2H); ^{13}C{^{1}H} NMR (125 Hz, CD_3OD) δ 139.2, 112.9, 74.1, 73.6, 68.6, 38.7, 30.7, 27.4, 26.3, 18.7; FT-IR (film) 3393, 2937, 1709, 1447, 1053, 998 cm^{-1}; ESI-MS m/z 208.95 ([M + Na]$^+$); ESI-HRMS calcd. for $C_{10}H_{18}O_3Na$ ([M + Na]$^+$) 209.1148, found 209.1147.

*Data for (1S,2S,3R)-3-(((tert-Butyldimethylsilyl)oxy)methyl)-3-hydro- peroxycyclohexane-1,2-diol (**2q**).* **2q** was obtained as a colorless sticky oil, 33 mg, 0.11 mmol, 45%; chromatography using 1:1 PE/EtOAc; $[\alpha]_D^{25}$ +5.0 (c 1.0, MeOH). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (s, 1H), 4.10 (br s, 1H), 4.01 (d, J = 10.7 Hz, 1H), 4.01−3.96 (m, 1H), 3.87 (d, J = 10.6 Hz, 1H), 2.88 (br s, 1H), 2.03 (br s, 1H), 1.72−1.51 (m, 7H), 0.92 (s, 9H), 0.12 (s, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 85.0, 70.4, 69.1, 67.2, 28.2, 25.8, 25.4, 18.1, −5.6; ^{13}C{^{1}H} NMR (125 MHz, CD_3OD) δ 85.9, 69.0, 68.5, 63.4, 27.5, 25.1,

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J. Org. Chem. XXXX, XXX, XXX−XXX

23.8, 18.2, 17.9, −6.7; FT-IR (film) 3411, 2926, 2855, 1717, 1457, 1056, 1022 cm^{-1}; ESI-MS m/z 315.10 ($[M + Na]^+$); ESI-HRMS calcd. for $C_{13}H_{28}O_5SiNa$ ($[M + Na]^+$) 315.1598, found 315.1600.

*Data for (1R,2R,3R)-3-Hydroperoxy-3-methylcycloheptane-1,2-diol (**2r**).* **2r** was obtained as a colorless sticky oil, 18 mg, 0.10 mmol, 68%; chromatography using 1:1 PE/EtOAc; $[\alpha]_D^{25}$ −5.8 (c 0.5, MeOH). ^1H NMR (500 MHz, CD_3OD) δ 4.02 (br d, J = 9.8 Hz, 1H), 3.92 (br s, 1H), 1.98−1.88 (m, 1H), 1.77−1.70 (m, 1H), 1.67−1.42 (m, 6H), 1.31 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD) δ 84.7, 77.7, 70.7, 34.3, 29.7, 23.6, 22.5, 20.9; FT-IR (film) 3340, 2931, 2868, 1456, 1101, 1034, 1009 cm^{-1}; ESI-MS m/z 198.95 ($[M + Na]^+$); ESI-HRMS calcd. for $C_8H_{16}O_4Na$ ($[M + Na]^+$) 199.0941, found 199.0932.

*Data for (1R,2R,3S)-3-Allyl-3-hydroperoxycycloheptane-1,2-diol (**2s**).* **2s** was obtained as a colorless sticky oil, 50 mg, 0.25 mmol, 62%; chromatography using 1:1 PE/EtOAc; $[\alpha]_D^{25}$ −29.2 (c 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 9.02 (s, 1H), 6.00−5.91 (m, 1H), 5.19−5.09 (m, 2H), 4.15−4.07 (m, 2H), 3.43 (br s, 2H), 2.67 (dd, J = 14.8, 6.5 Hz, 1H), 2.48 (dd, J = 14.8, 7.7 Hz, 1H), 1.97−1.88 (m, 1H), 1.83−1.76 (m, 1H), 1.74−1.62 (m, 2H), 1.61−1.45 (m,4H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 134.3, 118.0, 86.7, 77.4, 71.5, 39.0, 31.7, 29.8, 23.2, 20.9; FT-IR (film) 3371, 2933, 2866, 1457, 1093, 1003, 915 cm^{-1}; ESI-MS m/z 225.05 ($[M + Na]^+$); ESI-HRMS calcd. for $C_{10}H_{18}O_4Na$ ($[M + Na]^+$) 225.1097, found 225.1103.

*Data for (3R,4R,5R)-5-Hydroperoxy-5-methyltetrahydro-2H-pyran-3,4-diol (**2t**).* **2t** was obtained as a colorless oil, 78 mg, 0.47 mmol, 84%; less polar than **3t**, chromatography using 1:3 PE/EtOAc; $[\alpha]_D^{25}$ −31.9 (c 1.0, MeOH). ^1H NMR (500 MHz, CD_3OD) δ 3.91 (ddd, J = 9.5, 4.8, 3.3 Hz, 1H), 3.83 (d, J = 3.2 Hz, 1H), 3.59 (d, J = 12.1 Hz, 1H), 3.55 (dd, J = 10.7, 4.8 Hz, 1H), 3.46 (dd, J = 9.8, 9.8 Hz, 1H), 3.44 (d, J = 12.1 Hz, 1H), 1.21 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD) δ 82.6, 69.3, 67.3, 65.8, 65.3, 16.0; FT-IR (film) 3374, 2923, 1098, 1061 cm^{-1}; ESI-MS m/z 186.95 ($[M + Na]^+$); ESI-HRMS calcd. for $C_6H_{12}O_5Na$ ($[M + Na]^+$) 187.0577, found 187.0579.

*Data for (3R,4R,5R)-3-Methyltetrahydro-2H-pyran-3,4,5-triol (**3t**).* **3t** was obtained as a colorless oil, 10 mg, 0.067 mmol, 12%; more polar than **2t**, chromatography using 15:1 CH_2Cl_2/MeOH; $[\alpha]_D^{25}$ −18.8 (c 1.0, MeOH). ^1H NMR (500 MHz, CD_3OD) δ 4.00 (ddd, J = 9.9, 4.9, 3.3 Hz, 1H), 3.58−3.54 (m, 2H), 3.48 (d, J = 11.7 Hz, 1H), 3.41 (dd, J = 10.3, 10.3 Hz, 1H), 3.27 (d, J = 11.6 Hz, 1H), 1.28 (br s, 2H), 1.14 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD) δ 73.3, 71.0, 70.8, 65.7, 65.0, 20.8; FT-IR (film) 3386, 2924, 1095, 1058 cm^{-1}; ESI-MS m/z 170.95 ($[M + Na]^+$); ESI-HRMS calcd. for $C_6H_{12}O_4Na$ ($[M + Na]^+$) 171.0628, found 171.0623.

*Data for (3R,4R,5R)-1-(Benzyloxycarbonyl)-3-hydroperoxy-4,5-dihydroxy-3-methylpiperidine (**2u**).* **2u** was obtained as a colorless oil, 54 mg, 0.18 mmol, 79%; chromatography using 1:1 PE/EtOAc; $[\alpha]_D^{25}$ −0.52 (c 1.0, MeOH), $[\alpha]_D^{25}$ +0.43 (c 1.0, MeOH) (another measurement at c 1.0 in MeOH), $[\alpha]_D^{25}$ +1.1 (c 0.5 MeOH), $[\alpha]_D^{25}$ +1.7 (c 0.25 MeOH), 92% pure as determined by HPLC analysis on a CHIRALPAK IC column (ϕ 0.46 × 25 cm, particle size = 5 μm) eluting with 50:50 of n-hexane/i-PrOH at a flow rate of 0.7 mL/min with the UV detector set to 214 nm. This compound in solution exists as a nearly 1:1 mixture of two conformers (cf. also the NMR at different temperatures, Figure S5 in the Supporting Information) as shown by ^1H and ^{13}C NMR. ^1H NMR (500 MHz, CD_3OD) δ 7.39−7.25 (m, 5H), 5.18−5.05 (m, 2H), 3.98−3.70 (m, 4H), 3.12−2.95 (m, 2H), 1.30 and 1.28 (two singlets, 3H altogether); $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD) δ 158.1 and 157.6, 138.1 and 137.9, 129.5 and 129.4, 129.1 and 128.9, 128.8 and 128.6, 84.4 and 83.9, 71.7 and 71.5, 68.5 and 68.4, 66.6 and 66.3, 46.7 and 46.6, 45.1 and 44.5, 18.8. FT-IR (film) 3401, 2939, 1678, 1437, 1221, 1096, 978, 698 cm^{-1}; ESI-MS m/z 320.25 ($[M + Na]^+$); ESI-HRMS calcd. for $C_{14}H_{19}O_6NNa$ ($[M + Na]^+$) 320.1105, found 320.1106. Reduction of this sample using Ph_3P in CH_2Cl_2 gave the corresponding triol in 100% yield, with ^1H NMR in full consistence with that for **3u** below and an optical rotation of $[\alpha]_D^{25}$ +7.6 (c 0.5, MeOH), confirming that the optical rotation of **2u** is indeed very small in magnitude.

*Data for (3R,4R,5R)-1-(Benzyloxycarbonyl)-3,4,5-trihydroxy- 3-methylpiperidine (**3u**).* **3u** was obtained as a colorless oil, 8 mg, 0.028 mmol, 12%; chromatography using 1:3 PE/EtOAc; $[\alpha]_D^{25}$ +8.1 (c 0.5, MeOH). ^1H NMR (600 MHz, MeOD) δ 7.39−7.26 (m, 5H), 5.19−5.02 (m, 2H), 3.99−3.87 (m, 2H), 3.66 (d, J = 13.6 Hz, 1H), 3.50 (s, 1H), 3.10−2.90 (m, 2H), 1.23 and 1.21 (two singlets, 3H altogether). $^{13}C\{^1H\}$ NMR (150 MHz, CD_3OD) δ 158.0 and 157.7, 138.2, 129.5, 129.0 and 129.0, 128.8, 75.4 and 75.3, 72.6 and 72.5, 68.3, 66.5 and 66.2, 50.2 and 50.2, 44.8 and 44.6, 24.0, and 23.9. FT-IR (film) 3399, 2930, 1681, 1434, 1094, 1056, 978, 697 cm^{-1}; ESI-MS m/z 304.25 ($[M + Na]^+$); ESI-HRMS calcd. for $C_{14}H_{19}O_5NNa$ ($[M + Na]^+$) 304.1155, found 304.1151.

*Data for (1S,3aS,4S,5S,7aR)-1-((tert-butyldimethylsilyl)oxy)-3a-hydroperoxy-7a-methyloctahydro-1H-indene-4,5-diol (**2v**).* **2v** was obtained as a white solid, 145 mg, 0.44 mmol, 87%; less polar than **3v**, chromatography using 1:1 PE/EtOAc; mp 148−150 °C. $[\alpha]_D^{25}$ +25.6 (c 1.0, MeOH). ^1H NMR (500 MHz, CD_3OD) δ 4.24 (d, J = 3.9 Hz, 1H), 4.15 (dd, J = 8.6, 6.4 Hz, 1H), 4.08 (ddd, J = 11.7, 5.3, 4.2 Hz, 1H), 2.17−2.08 (m, 1H), 2.06−1.93 (m, 2H), 1.79−1.68 (m, 1H), 1.66−1.51 (m, 3H), 1.27−1.21 (m, 1H), 1.12 (s, 3H), 0.88 (s, 9H), 0.00 (d, J = 8.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD) δ 94.7, 77.9, 69.2, 68.3, 46.8, 30.2, 27.7, 25.4, 24.9, 23.4, 17.5, 15.4, −5.7, −6.0. FT-IR (KBr) 3463, 3250, 2955, 1467, 1391, 1250, 1126, 1094, 1030, 895, 832, 780 cm^{-1}; ESI-MS m/z 355.15 ($[M + Na]^+$); ESI-HRMS calcd. for $C_{16}H_{32}O_5SiNa$ ($[M + Na]^+$) 355.1911, found 355.1911.

*Data for (1S,3aS,4S,5S,7aR)-1-((tert-Butyldimethylsilyl)oxy)-7a-methyloctahydro-3aH-indene-3a,4,5-triol (**3v**).* **3v** was obtained as a white solid, 12 mg, 0.038 mmol, 7%; more polar than **2v**, chromatography using 1:2 PE/EtOAc; mp 178−181 °C. $[\alpha]_D^{25}$ +37.6 (c 0.33, MeOH). ^1H NMR (500 MHz, CD_3OD) δ 4.23 (dd, J = 8.6, 6.5 Hz, 1H), 4.12−4.07 (m, 1H), 3.69 (d, J = 3.8 Hz, 1H), 2.30−2.22 (m, 1H), 2.18−2.08 (m, 1H), 1.77−1.65 (m, 2H), 1.64−1.48 (m, 2H), 1.30−1.22 (m, 2H), 1.05 (s, 3H), 0.89 (s, 9H), 0.02 (d, J = 3.9 Hz, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD) δ 83.2, 78.2, 74.4, 68.6, 45.5, 30.0, 30.0, 28.0, 25.5, 25.0, 17.5, 14.5, −5.7, −6.0. FT-IR (KBr) 3427, 2954, 2857, 1472, 1250, 1088, 1061, 1027, 940, 903, 836, 776 cm^{-1}; ESI-MS m/z 339.20 ($[M + Na]^+$); ESI-HRMS calcd. for $C_{16}H_{32}O_4SiNa$ ($[M + Na]^+$) 339.1962, found 339.1964.

*Data for (1R,2R,4aS,5R,8aR)-5-((tert-Butyldimethylsilyl)oxy)-8a-hydroperoxy-4a-methyldecahydronaphthalene-1,2-diol (**2w**).* **2w** was obtained as a white solid, 59 mg, 0.17 mmol, 42%; less polar than **3w**, chromatography using 1:1 PE/EtOAc; mp 190−192 °C. $[\alpha]_D^{25}$ −47.6 (c 0.25, MeOH). ^1H NMR (500 MHz, CD_3OD) δ 4.08−4.00 (m, 2H), 3.79 (dd, J = 9.6, 6.1 Hz, 1H), 1.93−1.69 (m, 4H), 1.64−1.41 (m, 6H), 1.36−1.26 (m, 2H), 1.14 (s, 3H), 0.87 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD) δ 87.3, 73.3, 71.3, 67.9, 42.0, 30.3, 30.1, 25.0, 25.0, 24.3, 18.0, 17.5, 13.7, −5.3, −6.0; FT-IR (KBr) 3536, 3437, 3129, 2936, 1458, 1251, 1092, 1053, 834, 773 cm^{-1}; ESI-MS m/z 369.10 ($[M + Na]^+$); ESI-HRMS calcd. for $C_{17}H_{34}O_5SiNa$ ($[M + Na]^+$) 369.2068, found 369.2065.

*Data for (1S,2S,4R,4aS,6R,8aS)-8a-Hydroperoxy-4,4a-dimethyl-6-(prop-1-en-2-yl)decahydronaphthalene-1,2-diol (**2x**).* **2x** was obtained as a white solid, 72 mg, 0.27 mmol, 53% from **1x**; less polar than **3x**, chromatography using 1:1 PE/EtOAc; mp 119−121 °C. $[\alpha]_D^{25}$ +58.7 (c 1.0, EtOAc). ^1H NMR (500 MHz, CD_3OD) δ 4.70 (br s, 1H), 4.65 (br s, 1H), 4.12−4.04 (m, 2H), 2.27 (tt, J = 12.7, 4.0 Hz, 1H), 2.06−1.88 (m, 2H), 1.88−1.79 (m, 1H), 1.76 (dd, J = 13.0, 4.6 Hz, 1H), 1.71 (s, 3H), 1.59 (q, J = 12.5 Hz, 1H), 1.54−1.44 (m, 3H), 1.24 (dd, J = 12.4, 2.9 Hz, 1H), 1.09 (s, 3H), 0.75 (d, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD) δ 150.6, 107.5, 85.3, 71.7, 67.5, 39.7, 39.5, 38.1, 34.1, 33.8, 25.4, 25.3, 19.5, 16.1, 13.9. FT-IR (KBr) 3527, 3200, 2949, 2611, 2379, 1453, 1133, 1038, 890 cm^{-1}; ESI-MS m/z 293.25 ($[M + Na]^+$); ESI-HRMS calcd. for $C_{15}H_{30}O_4N$ ($[M + NH_4]^+$) 288.2169, found 288.2170.

*Data for (1S,2S,4R,4aS,6R,8aS)-4,4a-Dimethyl-6-(prop-1-en-2-yl)octahydronaphthalene-1,2,8a(1H)-triol (**3x**).* **3x** was obtained as a white solid, 26 mg, 0.10 mmol, 20% from **1x**; more polar than **2x**, chromatography using 1:2 PE/EtOAc; mp 138−140 °C. $[\alpha]_D^{25}$ +31.4 (c 1.0 EtOAc). ^1H NMR (500 MHz, CD_3OD) δ 4.69 (br s, 1H), 4.65 (br s, 1H), 4.15−4.09 (m, 1H), 3.44 (d, J = 3.6 Hz, 1H), 2.32−2.21 (m, 2H), 1.95−1.85 (m, 1H), 1.80−1.70 (m, 1H), 1.71 (s, 3H), 1.62−1.43 (m, 4H), 1.32−1.24 (m, 2H), 1.04 (s, 3H), 0.77 (d, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD) δ 150.6, 107.4, 77.4, 74.8, 67.7,

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J. Org. Chem. XXXX, XXX, XXX−XXX

39.7, 38.4, 38.2, 34.3, 33.6, 31.5, 25.3, 19.5, 14.9, 13.9. FT-IR (KBr) 3342, 2945, 2480, 1641, 1458, 1376, 1145, 1039, 997, 951, 889 cm^{-1}; ESI-MS m/z 277.25 ($[M + Na]^+$); ESI-HRMS calcd. for $C_{15}H_{30}O_3N$ ($[M + NH_4]^+$) 272.2220, found 272.2221.

Data for Cholestane-5α-hydroperoxy-3β,4β-diol ***2y*****).** **2y** was obtained as a white solid, 58 mg, 0.13 mmol, 53% from **1y**; less polar than **3y**, chromatography using 2:1 PE/EtOAc; Mp 164−166 °C. $[\alpha]_D^{25}$ +45.7 (c 1.0 THF). ^1H NMR (500 MHz, d_6-DMSO) δ 10.40 (s, 1H), 4.35 (d, J = 4.4 Hz, 1H), 3.95 (d, J = 7.3 Hz, 1H), 3.87−3.76 (m, 2H), 1.88 (d, J = 12.3 Hz, 1H), 1.75 (br s, 2H), 1.67−0.91 (m, 30H), 0.85 (d, J = 6.3 Hz, 3H), 0.82 (d, J = 6.4 Hz, 6H), 0.59 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, d_6-DMSO) δ 85.2, 71.8, 67.0, 56.5, 56.2, 46.1, 42.8, 40.2, 39.4, 39.3, 36.1, 35.7, 34.9, 31.4, 28.3, 27.9, 26.2, 25.8, 25.6, 24.2, 23.8, 23.1, 22.8, 20.6, 18.9, 16.9, 12.4. FT-IR (KBr) 3349, 2941, 2867, 1468, 1379, 1333, 1110, 1050, 1014, 951, 921, 831, 796 cm^{-1}; ESI-MS m/z 459.55 ($[M + Na]^+$); ESI-HRMS calcd. for $C_{27}H_{48}O_4Na$ ($[M + Na]^+$) 459.3445, found 459.3448.

Data for Cholestane-3β,4β,5α-triol ***(3y)*****.** **3y** was obtained as a white solid, 16 mg, 0.038 mmol, 15% from **1y**; more polar than **2y**, chromatography using 1:1 PE/EtOAc; mp 207−209 °C (lit.[28b] 211−212 °C (EtOH)). $[\alpha]_D^{25}$ +24.3 (c 0.5, MeOH), $[\alpha]_D^{25}$ +40.8 (c 0.5, pyridine) (lit.[32] $[\alpha]_D^{25}$ +43 (c unknown, pyridine)). ^1H NMR (500 MHz, CD_3OD) δ 4.05 (ddd, J = 12.1, 5.0, 4.1 Hz, 1H), 3.43 (d, J = 3.5 Hz, 1H), 2.19−2.11 (m, 1H), 2.00 (dt, J = 12.3, 3.1 Hz, 1H), 1.90−1.79 (m, 1H), 1.72 (dq, J = 3.8, 12.6 Hz, 1H), 1.64−0.98 (m, 27H), 1.15 (s, 3H), 0.92 (d, J = 6.5 Hz, 3H), 0.88 (d, J = 6.6 Hz, 3H), 0.88 (d, J = 6.6 Hz, 3H), 0.68 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD) δ 79.2, 76.7, 69.3, 57.7, 57.7, 47.6, 43.9, 41.5, 40.7, 39.4, 37.4, 37.2, 36.1, 32.4, 32.1, 29.4, 29.2, 26.8, 26.8, 25.2, 25.0, 23.2, 23.0, 21.7, 19.2, 16.2, 12.6. ESI-MS m/z 443.60 ($[M + Na]^+$).

Data for 4β,5β-Epoxycholestan-3β-ol ***(4y)*****.** **4y** was obtained as a white solid, 18 mg, 0.045 mmol, 18% from **1y**): Mp 47−50 °C (lit.[28e] mp 96−97 °C (EtOH)), $[\alpha]_D^{25}$ −2.4 (c 1.0, $CHCl_3$), $[\alpha]_D^{25}$ −4.0 (c 0.7, $CHCl_3$), $[\alpha]_D^{25}$ −4.6 (c 0.5, $CHCl_3$), (lit.[33] $[\alpha]_D^{21}$ +4 (c 1.4, $CHCl_3$), $[\alpha]_D^{20}$ +5.4 (c 1.0, $CHCl_3$), $[\alpha]_D^{21}$ +4.3 (c 0.8, $CHCl_3$)). ^1H NMR (500 MHz, $CDCl_3$) δ 4.05 (br s, 1H), 3.13 (d, J = 4.4 Hz, 1H), 2.29 (br s, 1H), 2.10 (dt, J = 4.4, 13.6 Hz, 1H), 1.98 (dt, J = 12.7, 3.3 Hz, 1H), 1.88−1.72 (m, 2H), 1.62−1.48 (m, 3H), 1.45−1.21 (m, 11H), 1.18−0.92 (m, 14H), 0.90 (d, J = 6.5 Hz, 3H), 0.86 (d, J = 6.6 Hz, 3H), 0.86 (d, J = 6.6 Hz, 3H), 0.67 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 68.9, 64.2, 63.7, 56.2, 56.1, 47.0, 42.5, 39.7, 39.5, 36.1, 36.1, 35.7, 35.0, 31.1, 30.3, 28.2, 28.0, 26.1, 25.9, 24.3, 23.8, 22.8, 22.5, 21.3, 19.1, 18.6, 11.9.[34]

Data for 5α-Hydroperoxy-6β,7β-dihydroxycholestan-3β-yl Acetate ***(2z)*****.** **2z** was obtained as a white solid, 80 mg, 0.16 mmol, 65% from **1z**; mp 195−197 °C. $[\alpha]_D^{25}$ +25.7 (c 0.5, EtOAc). ^1H NMR (500 MHz, d_6-DMSO) δ 10.82 (s, 1H), 5.04−4.96 (m, 1H), 4.69 (d, J = 5.0 Hz, 1H), 3.79 (br s, 1H), 3.51 (br s, 2H), 2.13−2.04 (m, 1H), 1.97 (s, 3H), 1.93−1.70 (m, 5H), 1.55−0.93 (m, 22H), 1.11 (s, 3H), 0.88 (d, J = 6.4 Hz, 3H), 0.84 (d, J = 6.6 Hz, 3H), 0.84 (d, J = 6.6 Hz, 3H), 0.62 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, d_6-DMSO) δ 170.2, 86.1, 72.1, 71.5, 70.7, 55.9, 55.4, 44.3, 43.5, 39.4, 38.6, 38.2, 36.2, 35.8, 32.1, 31.5, 30.0, 28.8, 27.9, 27.3, 27.0, 23.8, 23.1, 22.9, 21.6, 21.2, 19.1, 18.2, 12.5; FT-IR (KBr) 3409, 3184, 2944, 1719, 1469, 1366, 1261, 1131, 1086, 1031, 689 cm^{-1}; ESI-MS m/z 517.65 ($[M + Na]^+$); ESI-HRMS calcd. for $C_{29}H_{54}O_6N$ ($[M + NH_4]^+$) 512.3946, found 512.3946.

Data for 5α,6β,7β-Trihydroxycholestan-3β-yl Acetate ***(3z)*****.** **3z** was obtained as a white solid, 26 mg, 0.054 mmol, 22% from **1z**; mp 180−182 °C (lit.[14b] 178−179 °C). $[\alpha]_D^{25}$ +24.9 (c 1.0, EtOAc) (lit. $[\alpha]_D$ data not available). ^1H NMR (500 MHz, CD_3OD) δ 5.20−5.12 (m, 1H), 3.69 (dd, J = 10.1, 3.8 Hz, 1H), 3.38 (d, J = 3.6 Hz, 1H), 2.18 (t, J = 12.2 Hz, 1H), 2.00 (s, 3H), 1.94−1.79 (m, 3H), 1.70−0.99 (m, 23H), 1.15 (s, 3H), 0.94 (d, J = 6.2 Hz, 3H), 0.88 (d, J = 6.6 Hz, 6H), 0.71 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD) δ 171.3, 77.8, 76.0, 72.3, 71.3, 55.6, 55.5, 43.9, 43.3, 40.1, 39.3, 38.1, 37.4, 36.8, 36.0, 35.8, 31.9, 28.4, 27.8, 26.7, 26.5, 23.6, 21.8, 21.6, 21.0, 19.9, 18.0, 16.2, 11.3; $^{13}C\{^1H\}$ NMR (125 MHz, d_6-DMSO) δ 169.8, 77.1, 75.1, 71.3, 70.7, 55.4, 55.0, 43.3, 43.0, 38.9, 37.9, 37.2, 37.0, 35.7, 35.3, 31.7, 28.4, 27.4, 26.8, 26.6, 23.3, 22.7, 22.4, 21.1, 20.8, 18.7, 16.6, 12.0; FT-IR (KBr) 3443, 2951, 1737, 1467, 1383, 1240, 1132, 1078, 1029, 895, 709 cm^{-1}; ESI-MS m/z 501.65 ($[M + Na]^+$); ESI-HRMS calcd. for $C_{29}H_{54}O_5N$ ($[M + NH_4]^+$) 496.3997, found 496.3997.

(*S*)-2-((*tert*-Butyldimethylsilyl)peroxy)-2-methylhexane-1,6-diol (5). Elaboration of 2l into 6 via 5. Imidazole (4.5 g, 66 mmol) was added to a solution of **2l** (7.2 g, 44.3 mmol) in CH_2Cl_2 (180 mL) and acetone (60 mL) stirred in an ice−water bath. The mixture was stirred at the same temperature for 10 min. A solution of TBSCl (7.4 g, 48.8 mmol) in CH_2Cl_2 (30 mL) was introduced slowly over 30 min. After completion of the addition, stirring was continued in the cooling bath for another 4 h. Water (50 mL) was added to quench the reaction. The mixture was extracted with CH_2Cl_2 (50 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4. Removal of the drying agent by filtration and the solvent by rotary evaporation left an oily residue, which was purified by column chromatography (4:1 PE/EtOAc) on silica gel to afford **2l′** as a colorless oil (8.6 g, 31.1 mmol, 70% from **2l**) along with unreacted starting **2l** (700 mg, 4.4 mmol, 10%). Data for **2l′**: $[\alpha]_D^{25}$ +5.8 (c 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 4.01 (ddd, J = 6.9, 3.5, 3.4 Hz, 1H), 3.88 (d, J = 3.3 Hz, 1H), 3.05 (br s, 1H), 2.27 (br s, 1H), 1.75−1.66 (m, 1H), 1.63−1.41 (m, 5H), 1.36 (s, 3H), 0.93 (s, 9H), 0.14 (s, 3H), 0.13 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 84.9, 74.9, 69.3, 31.7, 28.7, 26.2, 19.8, 18.2, 18.2, −5.7; FT-IR (film) 3422, 2933, 1250, 1061, 834, 784 cm^{-1}; ESI-MS m/z 299.10 ($[M + Na]^+$); ESI-HRMS calcd. for $C_{13}H_{28}O_4SiNa$ ($[M + Na]^+$) 299.1649, found 299.1650.

The **2l′** (6.7 g, 24.2 mmol) obtained above was dissolved in a mixture of THF (90 mL) and H_2O (30 mL). The mixture was stirred at ambient temperature, while powdered $NaIO_4$ (10.3 g, 48.4 mmol) was added in three portions (the clear solution became turbid with the addition). After completion of the addition, the mixture was stirred at ambient temperature for 1.5 h (TLC showed completion of the reaction). Solids were filtered off through Celite (with suction). The filter cake was washed with Et_2O (30 mL). The combined filtrate and washing were partially concentrated on a rotary evaporator to remove most of the volatiles. The concentrated mixture was extracted with Et_2O (30 mL × 2). The combined organic layers were washed with brine (30 mL) and dried over anhydrous Na_2SO_4. Removal of the drying agent by filtration and the solvent by rotary evaporation gave the intermediate dialdehyde as a colorless oil (6.5 g), which was immediately dissolved in EtOH (120 mL). To this solution (stirred in an EtOH−dry ice bath, ca. −70 °C, to avoid side reactions) was added $NaBH_4$ (1.83 g, 48.4 mmol). The mixture was then stirred at the same temperature for another 30 min. Water (30 mL) was added. The mixture was concentrated on a rotary evaporator to remove most of the EtOH. The residue was extracted with EtOAc (50 mL × 2). The combined organic layers were washed with brine (30 mL) and dried over anhydrous Na_2SO_4. Removal of the drying agent by filtration and the solvent by rotary evaporation left an oily residue, which was purified by column chromatography (2:1 PE/EtOAc) on silica gel to afford diol **5** as a colorless oil (5.0 g, 18.0 mmol, 74% from **2l′**). Data for **5**: $[\alpha]_D^{25}$ −20.4 (c 1.0, $CHCl_3$), 96% ee as determined by HPLC on a CHIRALPAK AD-H column (ϕ 0.46 cm × 25 cm, particle size 5 μm) eluting with 95:5 of n-hexane/i-PrOH at a flow rate of 0.7 mL/min with UV detector set to 214 nm. ^1H NMR (500 MHz, $CDCl_3$) δ 3.65−3.59 (m, 3H), 3.56 (dd, J = 11.7, 6.9 Hz, 1H), 2.44 (t, J = 6.4 Hz, 1H), 1.84 (br s, 1H), 1.61−1.48 (m, 4H), 1.43−1.33 (m, 2H), 1.11 (s, 3H), 0.91 (s, 9H), 0.14 (s, 3H), 0.14 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, cdcl$_3$) δ 84.9, 67.5, 62.5, 33.6, 33.1, 26.1, 19.6, 18.5, 18.2, −5.7; FT-IR (film) 3365, 2931, 2859, 1250, 1054, 837, 784 cm^{-1}; ESI-MS m/z 301.20 ($[M + Na]^+$); ESI-HRMS calcd. for $C_{13}H_{30}O_4SiNa$ ($[M + Na]^+$) 301.1806, found 301.1803.

Part of **5** (25 mg, 0.09 mmol) obtaineda above was dissolved EtOH (1 mL). Aq. HCl (2 N, 90 μL) was added. The mixture was stirred at ambient temperature for 30 min (TLC showed completion of the reaction). Anhydrous Na_2SO_4 was added (to remove the traces of water in the mixture). The mixture was filtered and concentrated on a rotary evaporator. The residue was dissolved in EtOAc (1 mL). Ph_3P (31.5 mg, 0.12 mmol) was added. The mixture was then stirred at ambient temperature for ca. 10 min (TLC showed completion of the reaction), concentrated on a rotary evaporator, and purified by column chromatography (1:15 MeOH/CH_2Cl_2) on silica gel to give the known ((*S*)-2-methylhexane-1,2,6-triol (**6**) as a colorless oil (13 mg,

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J. Org. Chem. XXXX, XXX, XXX−XXX

0.088 mmol, 97% from **5**). Data for **6**: $[\alpha]_D^{25}$ −3.1 (*c* 1.0, EtOAc) (lit.[35] $[\alpha]_D^{20}$ −2.1 (*c* 1.0, EtOAc)). ^{1}H NMR (500 MHz, CD_3OD) δ 3.56 (t, *J* = 6.5 Hz, 2H), 3.35 (s, 2H), 1.57−1.37 (m, 6H), 1.12 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3OD) δ 72.2, 68.9, 61.5, 37.8, 32.9, 22.3, 19.5; ^{1}H NMR (500 MHz, d_6-DMSO) δ 4.46 (t, *J* = 5.7 Hz, 1H), 4.35 (t, *J* = 5.2 Hz, 1H), 3.96 (s, 1H), 3.18−3.09 (m, 2H), 1.41−1.21 (m, 7H), 0.97 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, d_6-DMSO) δ 71.5, 69.0, 60.9, 38.4, 33.5, 24.1, 19.7.

Conversion of (*S*)-1l into 3l (without Separation of the Hydroperoxide 2l). To a solution of (*S*)-**1l** (224 mg, 2.0 mml) in freshly prepared H_2O_2−saturated Et_2O (10 mL) was added $MoO_2(acac)_2$ (32.6 mg, 0.1 mmol). The pale yellow−greenish transparent solution was stirred at ambient temperature for ca. 5 h (TLC showed completion of the reaction). The flask was placed in an ice−water bath. Me_2S (0.73 mL, 10 mmol) was added slowly (the yellow color of the reaction mixture gradually faded). The mixture was then stirred at ambient temperature overnight.

The solvent was removed by rotary evaporation. The oily residue was purified by column chromatography (initially 1:1, then 1:3 PE/EtOAc) on silica gel to give triol **3l** (colorless sticky oil, 265 mg, 1.81 mmol, 91% from **1l**). Data for **3l**: cf. those given above.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c01280.

^{1}H and $^{13}C\{^1H\}$ NMR, IR spectra for all new compounds, and tabular summary for enzymatic resolution of **1l**−**1u** (PDF)

X-ray crystallographic data for compounds **3a**, **2v**, **2m**, and **2x** (CIF)

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Notes

The authors declare no competing financial interest.

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(7) In these experiments *t*-BuOMe was used to replace Et_2O just to show its experimental feasibility. In many cases we examined, H_2O_2-*t*-BuOMe and H_2O_2-Et_2O are interchangeable.

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