



Lead(IV) acetate mediated cleavage of β -hydroxy ethers: enantioselective synthesis of α -acetoxy carbonyl compounds

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ABSTRACT

α -Acetoxy aldehydes or α -acetoxy ketones can be efficiently synthesized by treating 2,3-epoxy primary alcohols with lead tetraacetate. The reaction, which proceeds with complete regio- and stereoselectivity facilitates the enantioselective synthesis of α -acetoxy carbonyl compounds from allyl alcohols, via Sharpless epoxidation. Cyclic β -hydroxy ethers, with an oxygenated five-, six- or seven-membered ring, are transformed into α -acetoxy ethers.

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1. Introduction

The α -hydroxy carbonyl group occupies an important place in organic chemistry, being found in a wide variety of biologically active natural products.^{1a–e} Chiral α -hydroxy ketones (acyloins) are also versatile synthetic intermediates in asymmetric synthesis. Reduction of the acyloin carbonyl group affords either the *threo* or the *erythro* 1,2-diols, which are very useful building blocks.² Wittig olefination allows the synthesis of chiral allylic alcohols, which have been utilized in the synthesis of pheromones.³ Chiral acyloins have been used for synthesizing *syn* or *anti* aldols with high diastereoselectivity utilizing boron-mediated aldol condensation⁴ or titanium enolates.⁵ Other examples of the synthetic scope of chiral α -hydroxy ketones are the synthesis of chiral β -lactams⁶ and γ -butyrolactones.⁷

Numerous methods for introducing a hydroxyl group into the α -position to a carbonyl moiety have been reported. These include the direct oxidation of ketone/enol with transition metal salts,⁸ hypervalent iodine reagents⁹ or molecular oxygen,¹⁰ or the most widely used procedure, involving enolates. Among these, the use of molybdenum peroxy complexes¹¹ or of 2-sulfonyloxaziridines, perhaps the most widely employed enolate hydroxylation agent,¹²

should be emphasized. Most of the above cited methods are restricted to ketones. The corresponding α -hydroxylation of aldehydes is often complicated by undesired self-condensation of the enolates and the instability of the hydroxylated products.^{11c} Frequently, α -hydroxy carbonyl compounds are made using multistep transformations; these routes include nucleophilic acylation with masked acyl anions¹³ or the monooxidation of *vic*-diols,¹⁴ among others.

Several chemical methods for the preparation of chiral α -hydroxy carbonyl compounds have been described in the literature.¹⁵ Stereoselective versions of some of the above methods have also been reported;¹⁶ they include the enantioselective oxidation of chiral enolates,¹⁷ the oxidation of non-chiral enolates with chiral oxidants¹⁸ or the use of DITOX, a chiral dithiane oxide.¹⁹ More recently, the desymmetrization of *meso*-diols through acylation and oxidation,²⁰ the asymmetric reductive coupling of alkynes and aldehydes,²¹ the asymmetric dihydroxylation of substituted allenes,²² or the asymmetric rearrangement of α,α -disubstituted α -amino aldehydes²³ and α -siloxy aldehydes²⁴ have been utilized for synthesizing chiral α -hydroxy ketones. An alternative procedure to obtain enantiomerically pure acyloins involves the chemoenzymatic dynamic kinetic resolution (DKR) of these²⁵ or of the precursor allylic alcohols.²⁶

Lead(IV) acetate (LTA, lead tetraacetate) has long been considered one of the most useful reagents in organic chemistry because of its ability to bring about various reactions under mild conditions

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and its low cost.²⁷ LTA is commonly used for oxidative cleavage (C–C bond cleavage),²⁸ decarboxylations,²⁹ acetoxylation,³⁰ and formation of cyclic ethers (C–O bond formation).³¹ It is less often used for C–C bond formation,³² and C–N bond formation.³³ More recently, some new applications have been reported, such as the preparation of aryl lead triacetate, utilized in the direct arylation of nucleophiles,³⁴ and a very interesting multistage hetero-domino transformation;³⁵ both examples allow the construction of unique carbon substitution patterns. Very recently an interesting LTA mediated oxidative fragmentation of homoallylic alcohols³⁶ and an oxidative cleavage of allyl alcohols induced by the O₃/LTA system³⁷ have been reported.

Brockson et al. trying to synthesize the corresponding epoxy tetrahydrofuran from 8,9-epoxy-*p*-menthan-10-ol (**1d**) found that the treatment of this epoxy alcohol with LTA led to the α -acetoxy ketone **2d** instead of the desired furan; in a similar way, epoxy alcohols **1b** and **1c** were converted into the corresponding α -acetoxy carbonyl compounds **2b** and **2c**.³⁸ These authors indicate that the reaction was efficient in the case of linear α,β -epoxy alcohols but did not proceed well in the case of cyclic substrates³⁹ and could be utilized as a degradative procedure for the structural determination of α,β -unsaturated ketones or alcohols.

In order to explore the scope and limitations of this reaction and establish its synthetical potential, the behavior against LTA of a series of 2,3-epoxy alcohols, including chiral substrates, was studied in our laboratory. The results of this investigation, which highlight the regio- and stereoselectivity of the process and its application to the synthesis of optically active α -hydroxy carbonyl compounds, starting from epoxy alcohols prepared utilizing the asymmetric Sharpless epoxidation, have been recently communicated.⁴⁰

In this paper we report an expanded study on this subject, including other examples of 2,3-epoxy alcohols and the behavior of cyclic β -hydroxy ethers, with an oxygenated five-, six- or seven-membered ring, against this reagent.

2. Results and discussion

When 2,3-epoxyhexanol (**1a**) was treated with LTA in benzene at 50 °C for 20 min 2-acetoxypentanal (**2a**) was obtained in 73% yield (Table 1). In a similar way, Brockson et al. had transformed the epoxy alcohol **1b** into the α -acetoxy aldehyde **2b**.³⁸ 2,3-Epoxy alcohols bearing an alkyl group on the C-2 (compounds **1c–i**) led to the corresponding α -acetoxy ketones **2c–i**; cyclic epoxides of this type (compounds **1h–i**) gave cyclohexanone derivatives (ketones **2h–i**). 3,3-Dialkyl-2,3-epoxyalcohols (**1j–k**) showed a different behavior to that of the above mentioned epoxy alcohols, affording a mixture of products. Acyclic compounds, such as alcohol **1j**, always produced a complex mixture, whereas the more rigid cyclic epoxy alcohols, such as the bicyclic alcohol **1k**, led to a mixture of compounds including the α -acetoxy ketone **2k** as a minor constituent.

The results obtained when chiral epoxy alcohols (entries 8 and 9) were utilized as the substrate reaction deserve special mention. The enantiopure compound **1i** was transformed into the α -acetoxy ketone **2i** as the only isomer. Epoxy alcohol **1h**, a 6:1 mixture of diastereoisomers, gave a mixture of diastereomeric acetoxy ketones **2h** in identical proportion. However, the 3,3-dialkyl-2,3-epoxyalcohol **1k** afforded the minor α -acetoxy ketone **2k** with retention of the configuration on the α -carbon.

The regio- and stereoselectivities observed in the course of the above transformations lead us to propose the mechanism shown in Scheme 1.⁴¹ The complete stereoselectivity exhibited by chiral epoxides, such as compounds **1h–i**, can be explained by the nucleophilic attack of acetate anion in the intermediate oxonium **I**. The unsatisfactory results provided by the 3,3-dialkyl-2,3-epoxy alcohols, such as compounds **1j–k**, can be attributed to the formation of

Table 1

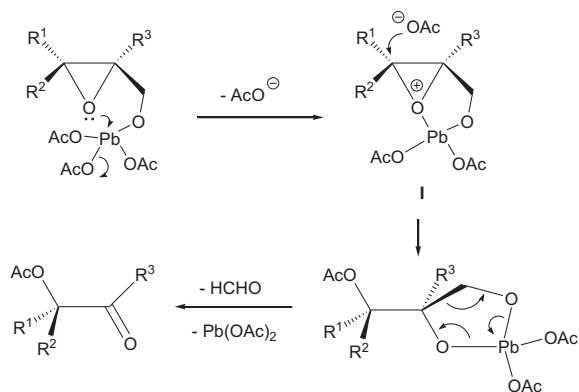
Reaction of 2,3-epoxy alcohols with LTA. Synthesis of α -acetoxy aldehydes and α -acetoxy ketones

Entry	Epoxy alcohol	Time	Product	%	
1	1a ⁴³	20 min	2a	73	
2	1b	2 h	2b	87 ³⁸	
3	1c	2 h	2c	91 ³⁸	
4	1d	2 h	2d	87 ³⁸	
5	1e ⁴⁴	20 min	2e	77	
6	1f ⁴⁵	1 h	2f	96	
7	1g	1 h	2g	82	
8	1h ^{a46}	1.5 h	2h ^a	94	
9	1i	2 h	2i	97	
10	1j ⁴⁷	2 h	Complex mixture		
11	1k ⁴⁸	2 h	2k ⁴⁹ + Complex mixture	26	

^aDiastereomeric ratio: 6:1.

a tertiary carbenium ion resulting from the oxonium ring opening, which undergoes different side reactions. The observed retention in the α carbon configuration for compound **2k**, which results after the attack of an acetate anion on the carbenium ion by the less hindered α side, seems to corroborate this assumption (entry 8).⁴²

In view of the complete stereoselectivity observed for chiral compounds **1h–i**, the enantioselective synthesis of α -acetoxy carbonyl compounds from allyl alcohols, via Sharpless epoxidation, was investigated. Epoxy alcohols **3a–f** were prepared, with >95% enantiomer excess, with the Sharpless L-(+)-DET reagent (Table 2). Treatment of these compounds with LTA in benzene under heating afforded in high yield the corresponding α -acetoxy carbonyl derivatives **4a–f**. Compounds **4a–e** were obtained with >95%



R¹ or R²: H; R³: Alkyl or H

Scheme 1. Mechanism of the reaction of 2,3-epoxy alcohols with LTA.

Table 2
Enantioselective synthesis of α -acetoxy aldehydes and α -acetoxy ketones

Entry	Epoxy alcohol	Time	Product	%
1		20 min		93
2		1 h		87
3		1 h		83
4		1 h		95
5		1 h		59
6		4 h		81
7		45 min		92

^a70% ee.

^bDiastereomeric ratio: 6:1.

Table 3
Reaction of some β -hydroxy ethers with LTA

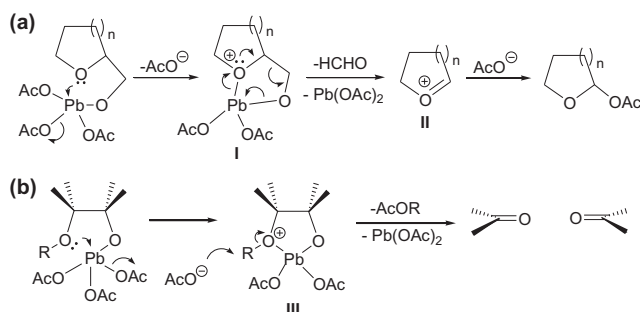
Entry	Epoxy alcohol	Time	Product	% ^a
1		12 h		48
2		12 h		75
3		12 h		78
4		12 h		66
5		8 h		63
6		30 min		55
7		4 h		83

^a Run under reflux.

enantiomer excess, as it could be expected. The acetoxy cyclohexanone derivative **4f** resulted in only 70% enantiomer excess; the lower enantioselectivity observed in this case can be attributed to the 3,3-dialkyl substitution pattern of epoxy alcohol **3f**, which can react via carbocationic intermediate. Epoxy alcohol **3g**, a 6:1 mixture of diastereomers obtained after the Sharpless epoxidation of the corresponding enantiopure allyl alcohol, led to a mixture of α -acetoxy ketones **4g** in the approximate 6:1 ratio. The absolute configuration of compounds **2e–h** and **4a–g** was proposed on the basis of the reaction mechanism; compounds **2h** and **4e** showed similar $[\alpha]_D$ values to those reported in the literature.^{49,54}

In order to explore the scope and limitation of this reaction the behavior of other type of β -hydroxy ethers was investigated (Table 3). When compounds **5a–e** with an oxygenated five-, six- or seven-membered ring, were treated with LTA under the above mentioned conditions α -acetoxy ethers **6a–d** were obtained. The unsaturated hydroxy ether **5f** gave a mixture of the corresponding unsaturated α -acetoxy ether **6e** and of the hydroxy aldehyde **6f**, resulting from the hemiketal ring opening. A mechanism, which can explain the formation of hemiketal acetates **6a–e** is depicted in Scheme 2(a). The cleavage of intermediate oxonium **I** leads to the more stable ion **II**, which is then attacked by the acetate anion. On the other hand, compound **5g**, with an acyclic ether moiety, was transformed into

the ketoaldehyde **6g** under the same conditions. The nucleophilic attack of acetate anion on the alkyl group of intermediate **III** causes the carbon–oxygen bond rupture and the subsequent usual carbon–carbon bond rupture (Scheme 2(b)).



Scheme 2. Mechanism of the reaction of acyclic and cyclic β -hydroxy ethers with LTA.

Finally, it should be mentioned that the use of the hypervalent iodine (III) reagent (diacetoxyiodo)benzene (DIB), instead of LTA, has also been investigated. 2,3-Epoxy alcohols remained unaltered and the other β -hydroxy ethers were also transformed into α -acetoxy ethers after prolonged reaction times (from 1 to 4 days) in benzene under reflux.

3. Conclusion

The treatment of β -hydroxy ethers with LTA causes a carbon–carbon cleavage, which proves to be a useful synthetic tool. α -Acetoxy aldehydes or α -acetoxy ketones can be efficiently synthesized by treating 2,3-epoxy primary alcohols with lead tetraacetate in benzene under heating. The reaction, which proceeds with complete regio- and stereoselectivity facilitates the enantioselective synthesis of α -acetoxy carbonyl compounds from allyl alcohols, via Sharpless epoxidation. Under these reaction conditions, cyclic β -hydroxy ethers, with an oxygenated five-, six- or seven-membered ring, are transformed into α -acetoxy ethers, whereas acyclic β -hydroxy ethers lead to carbonyl compounds: ketones or aldehydes.

4. Experimental

4.1. General

All reactions were carried out under argon atmosphere. Dichloromethane (DCM) was dried over calcium hydride and benzene over sodium-benzophenone. Chromatography separations were carried out by flash column on silica gel 60 (230–400 mesh) using hexanes–Et₂O (H–E) mixtures.

Instrumentation: Infrared (IR) spectra were obtained using Perkin–Elmer Spectrum Models 782 and 983G spectrophotometers, with samples between sodium chloride plates. Data are presented as the frequency of absorption (cm^{−1}). Only selected absorbancies ($\nu_{\max}$) are reported. Proton and Carbon-13 nuclear magnetic resonance (¹H NMR or ¹³C NMR) spectra were recorded on a Varian 400 or 500 spectrometer. Chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane. Data are presented as follows: chemical shift, multiplicity (s=singlet, br s=broad singlet, d=double, t=triplet, m=multiplet), coupling constant (*J*) in hertz (Hz). The signals of the ¹³C NMR were assigned utilizing DEPT experiments and on the basis of heteronuclear correlations.

4.2. General procedure for the cleavage of β -hydroxy ethers

To a solution of β -hydroxy ether (1 mmol) in dry benzene (10 mL) was added lead (IV) acetate (1.3 mmol) and the reaction mixture was heated at 50 °C (when aldehydes are obtained) or at reflux (when ketones or acetoxy ethers are formed) for the specified time (monitored by TLC). Then, the reaction was quenched with 5% Na₂SO₃, extracted with Et₂O, washed with water, brine, dried (Na₂SO₄), and concentrated. The residue was chromatographed on silica gel (hexanes/ether) to give the corresponding α -acetoxy carbonyl or α -acetoxy ether compound.

4.3. General procedure for Sharpless epoxidation

To a mixture of activated 4 Å molecular sieves (0.3 g) in dry CH₂Cl₂ (10 mL) were added successively at −25 °C (+)-diethyl *l*-tartarate (0.22 mL, 1.3 mmol) and Ti(O^{*i*}-Pr)₄ (0.42 mL, 1.4 mmol) under argon atmosphere. After stirring for 10 min *tert*-butyl hydroperoxide (TBHP) 5.0–6.0 M solution in decane (0.5 mL, 2.6 mmol) was added dropwise and the resulting mixture was stirred at −25 °C for 45 min. Then a solution of allyl alcohol (1 mmol) in dry CH₂Cl₂ (5 mL) was added and the resulting mixture was stirred for 12–15 h Et₂O (20 mL) was then added at −25 °C and a 30% aqueous solution of NaOH (0.5 mL) and brine (0.5 mL) were added. The resulting mixture was warmed up to room temperature, Na₂SO₄ and Celite were added. The mixture was filtered in vacuum and extracted with ether, the combined organic phases were dried (Na₂SO₄) and the solvent was removed. The resulting crude product was purified by flash column chromatography (hexanes–ether mixtures) as eluent to afford the corresponding 2,3-epoxy alcohol.

The enantiomeric excesses were determined by ¹H NMR, utilizing europium (III) tris [3-(heptafluoropropylhydroxymethylene)-*d*-camphorate] [Eu(hfc)₃] as chiral shift reagent.

Typical experimental procedure: 10 mg of Europium(III) tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorate] (Eu(hfc)₃) was added to a solution of benzoates obtained from alcohols **3a–f** (15 mg) in CDCl₃ (0.5 mL) containing 1% of TMS, and the resulting yellow solution was allowed to stand for 15 min. Then, the solution was added to an NMR tube and the ¹H NMR spectrum recorded. The relative intensities (peak heights or peak areas) of the resonance signal of oxygenated methylene protons were measured and the percentage of each enantiomer in the sample calculated.

4.4. Experimental data

Compounds **1g**, **1i**, **3b**, **3g**, **5b–f** are intermediates of our synthetic research and are a part of unpublished results.

4.4.1. 6-Acetoxy-2,3-epoxy-2,6-dimethyloct-7-en-1-ol (1f). Colorless oil (35% ether/hexanes). ¹H NMR (CDCl₃, 500 MHz) δ : 1.25 (s, 6H), 1.52 (s, 3H), 1.55 (s, 3H), 1.62 (m, 2H), 1.85 (m, 2H), 1.99 (s, 6H), 1.90–2.10 (m, 4H), 3.02 (t, *J*=6.4 Hz, 2H), 3.54 (d, *J*=12.2 Hz, 2H), 3.64 (d, *J*=12.2 Hz, 2H), 5.12 (d, *J*=11.0 Hz, 2H), 5.14 (dd, *J*=17.5, 3.9 Hz, 2H), 5.97 (dd, *J*=17.5, 11.0 Hz, 1H), 5.99 (dd, *J*=17.5, 11.0 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ : 14.06 (CH₃), 14.07 (CH₃), 22.08 (CH₃), 22.09 (CH₃), 22.8 (2 CH₂), 23.6 (CH₃), 23.7 (CH₃), 36.23 (CH₂), 36.25 (CH₂), 59.7 (2 CH), 61.0 (2C), 65.3 (2 CH₂), 82.3 (C), 82.4 (C), 113.5 (CH₂), 113.6 (CH₂), 141.2 (CH), 141.4 (CH), 140.9 (C), 169.9 (2C); IR (film): 3430, 1645, 1240, 1149, 1030, 930, 875 cm^{−1}. HRMS (EI) *M*⁺ *m/z*: calcd for C₁₂H₂₀O₄ 228,1362, found: 228,1378.

4.4.2. 2,3-Epoxy-2-propylheptan-1-ol (1g). Colorless oil (25% ether/hexanes). ¹H NMR (CDCl₃, 500 MHz) δ : 0.82–1.02 (m, 6H), 1.19–1.78 (m, 10H), 3.02 (dd, *J*=66.7, 5.4 Hz, 1H), 3.59 (d, *J*=12.1 Hz, 1H), 3.74 (d, *J*=12.2 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ : 14.0 (CH₃), 14.5 (CH₃), 18.5 (CH₂), 22.6 (CH₂), 27.7 (CH₂), 28.9 (CH₂), 31.0 (CH₂), 60.5

(CH), 63.3 (C), 63.4 (CH₂). HRMS (EI) M^+ m/z : calcd for C₁₀H₂₀O₂ 172,1463, found: 172,1449.

4.4.3. Methyl (3R)-5-((1'S,2'R,4'aS,5'S,6'S,8'aR)-5',6'-epoxy-5'-(hydroxymethyl)-1',2',4'-trimethyldecahydronaphthalen-1'-yl)-3-methylpentanoate (1i). Colorless oil (30% ether/hexanes), $[\alpha]_D^{25} +4.8$ (c 0.5, CHCl₃). ¹H NMR (CDCl₃, 500 MHz) δ : 0.76 (d, $J=6.6$ Hz, 3H), 0.79 (s, 3H), 0.92 (d, $J=6.6$ Hz, 3H), 1.24 (dd, $J=3.9$, 3.9 Hz, 1H), 1.08 (s, 3H), 1.12 (m, 1H), 1.17 (s, 3H), 1.13 (m, 1H), 1.22–1.34 (m, 3H), 1.34–1.42 (m, 2H), 1.46–1.60 (m, 2H), 1.80–1.89 (m, 3H), 1.97 (m, 1H), 2.04 (m, 1H), 2.13 (dd, $J=14.8$, 8.1 Hz, 1H), 2.31 (dd, $J=14.8$, 6.0 Hz, 1H), 3.29 (d, $J=3.2$ Hz, 1H), 3.63 (dd, $J=12.3$, 8.7 Hz, 1H), 3.64 (s, 3H), 3.99 (dd, $J=12.3$, 2.2 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ : 15.7 (CH₃), 16.7 (CH₂), 19.6 (CH₃), 19.9 (CH₃), 22.7 (CH₃), 29.08 (CH₂), 29.14 (CH₂), 29.26 (CH₃), 31.1 (CH), 34.5 (CH₂), 34.6 (C), 35.6 (CH₂), 37.5 (CH), 39.0 (C), 41.6 (CH₂), 44.3 (CH), 51.4 (CH₃), 57.5 (CH), 61.2 (CH₂), 63.9 (C), 173.6 (C); IR (film): 3450, 1739, 1716, 1699, 1684, 1558, 1507, 1457, 1306, 1233, 1038, 897, 788, 747 cm⁻¹. HRMS (EI) M^+ m/z : calcd for C₂₁H₃₆O₄ 352.2614, found: 352.2608.

4.4.4. (1R,2R,4aS,8aS)-1,2-Epoxy-1-(hydroxymethyl)-2,5,5,8a-tetramethyldecahydronaphthalene (1k). Colorless syrup (25% ether/hexanes). ¹H NMR (CDCl₃, 500 MHz) δ : 0.80 (s, 3H), 0.84 (s, 3H), 0.96 (s, 3H), 1.29 (s, 3H), 3.49 (ddd, $J=13.1$, 13.1, 4.6 Hz, 1H), 1.21–1.45 (m, 4H), 1.47–1.62 (m, 2H), 1.75–1.87 (m, 2H), 1.90–2.00 (m, 2H), 3.55 (d, $J=10.9$ Hz, 1H), 3.87 (dd, $J=10.9$, 4.5 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ : 16.2 (CH₃), 17.2 (CH₂), 18.4 (CH₂), 21.4 (CH₃), 21.6 (CH₃), 29.4 (CH₂), 33.0 (C), 33.5 (CH₃), 34.0 (CH₂), 37.2 (C), 41.4 (CH₂), 43.2 (CH), 57.0 (CH₂), 64.5 (C), 71.3 (C). HRMS (EI) M^+ m/z : calcd for C₁₅H₂₆O₂ 238,1933, found: 238,1941.

4.4.5. 2-Acetoxy-2-pentanol (2a). Colorless oil (10% ether/hexanes), $[\alpha]_D^{25} -7.2$ (c 1.2, CHCl₃). ¹H NMR (CDCl₃, 500 MHz) δ : 0.93 (t, $J=7.3$ Hz, 3H), 1.34–1.52 (m, 2H), 1.61–1.86 (m, 2H), 2.15 (s, 3H), 4.98 (dd, $J=8.4$, 4.6 Hz, 1H), 9.50 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ : 13.8 (CH₃), 18.3 (CH₂), 20.6 (CH₃), 30.7 (CH₂), 78.2 (CH), 170.7 (C), 198.3 (C); IR (film): 1737, 1729, 1468, 1372, 1247, 1105, 1017, 799, 750 cm⁻¹.

4.4.6. 3-Acetoxy-2-pentanone (2e). Colorless oil (15% ether/hexanes). ¹H NMR (CDCl₃, 500 MHz) δ : 0.97 (t, $J=7.4$ Hz, 3H), 1.75 (m, 1H), 1.84 (m, 1H), 2.14 (s, 3H), 2.15 (s, 3H), 4.94 (dd, $J=7.9$, 4.5 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ : 9.4 (CH₃), 20.5 (CH₃), 23.8 (CH₂), 26.2 (CH₂), 79.6 (CH), 170.7 (C), 205.3 (C); IR (film): 1775, 1724, 1549, 1378, 1235, 1181, 1111, 1061 cm⁻¹.

4.4.7. 3,6-Diacetoxy-6-methyloct-7-en-2-one (2f). Colorless oil (20% ether/hexanes). ¹H NMR (CDCl₃, 500 MHz) δ : 1.46 (s, 3H), 1.60–1.95 (m, 4H), 1.93 (s, 3H), 2.07 (s, 6H), 4.96 (m, 1H), 4.83 (m, 1H), 5.13 (d, $J=11.0$ Hz, 1H), 5.14 (br d, $J=17.5$ Hz, 1H), 5.90 (dd, $J=17.5$, 11.0 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ : 20.6 (CH₃), 22.1 (CH₃), 23.6 (CH₃), 24.5 (CH₂), 26.1 (CH₃), 35.0 (CH₂), 78.3 (CH), 82.1 (C), 113.8 (CH₂), 140.9 (CH), 169.8 (C), 170.5 (C), 205.0 (C). HRMS (EI) M^+ m/z : calcd for C₁₃H₂₀O₅ 256,1311, found: 256,1302.

4.4.8. 5-Acetoxy-4-one (2g). Colorless oil (15% ether/hexanes). ¹H NMR (CDCl₃, 500 MHz) δ : 0.90 (t, $J=6.9$ Hz, 3H), 0.92 (t, $J=7.4$ Hz, 3H), 1.49–1.15 (m, 4H), 1.95–1.51 (m, 4H), 2.13 (s, 3H), 2.36 (dt, $J=17.4$, 7.3 Hz, 1H), 2.47 (dt, $J=17.4$, 7.2 Hz, 1H), 4.98 (dd, $J=8.5$, 4.2 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ : 13.7 (CH₃), 13.9 (CH₃), 16.7 (CH₂), 20.7 (CH₃), 22.4 (CH₂), 27.4 (CH₂), 30.1 (CH₂), 40.5 (CH₂), 78.5 (CH), 170.7 (C), 207.5 (C); IR (film): 1746, 1730, 1462, 1370, 1230 cm⁻¹.

4.4.9. (2S,4S)-2-Acetoxy-4-(1-propen-2-yl)-cyclohexanone (2h). Colorless oil (15% ether/hexanes), $[\alpha]_D^{25} -14.7$ (c 0.6, CHCl₃). ¹H NMR (CDCl₃, 500 MHz) signals assignable to the major isomer δ : 1.62 (m, 1H), 1.76 (m, 1H), 1.80 (m, 1H), 2.11 (m, 1H), 2.15 (s, 3H), 2.31

(m, 1H), 2.64–2.40 (m, 3H), 4.78 (br s, 1H), 4.80 (t, $J=1.4$ Hz, 1H), 5.26 (ddd, $J=12.9$, 6.3, 0.8 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ : 20.7 (CH₃), 31.8 (CH₂), 37.4 (CH₂), 39.5 (CH₂), 42.7 (CH), 75.6 (CH), 110.4 (CH₂), 146.4 (C), 169.9 (C), 204.1 (C); IR (film): 1751, 1731, 1441, 1375, 1231, 1149, 1073, 979, 894, 772 cm⁻¹. HRMS (EI) M^+ m/z : calcd for C₁₁H₁₆O₃ 196,1099, found: 196,1102.

4.4.10. Methyl (3R)-5-((1'S,2'R,4'aS,6'R,8'aR)-6'-acetoxy-1',2',4'-trimethyl-5'-oxo-decahydronaphthalen-1'-yl)-3-methylpentanoate (2i). Colorless oil (30% ether/hexanes), $[\alpha]_D^{25} +16.4$ (c 0.5, CHCl₃). ¹H NMR (CDCl₃, 500 MHz) δ : 0.66 (s, 3H), 0.73 (d, $J=6.7$ Hz, 3H), 0.97 (d, $J=6.7$ Hz, 3H), 1.33 (s, 3H), 1.42 (ddd, $J=13.3$, 13.3, 3.5 Hz, 1H), 1.45 (ddd, $J=13.2$, 13.3, 3.6 Hz, 1H), 1.80 (m, 1H), 1.85 (m, 1H), 1.95 (m, 1H), 2.13 (s, 3H), 2.29 (dt, $J=13.4$, 3.5 Hz, 1H), 2.31 (dd, $J=14.9$, 6.1 Hz, 1H), 3.66 (s, 3H), 5.65 (dd, $J=11.3$, 8.6 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ : 15.6 (CH₃), 18.9 (CH₂), 19.1 (CH₃), 19.8 (CH₃), 20.7 (CH₃), 27.3 (CH₂), 28.9 (CH₂), 30.1 (CH₃), 30.9 (CH), 30.95 (CH₂), 35.05 (CH₂), 35.12 (CH₂), 37.2 (CH), 40.1 (C), 41.4 (CH₂), 48.2 (C), 49.8 (CH), 51.4 (CH₃), 72.4 (CH), 170.2 (C), 173.5 (C), 209.6 (C); IR (film): 1746, 1722, 1462, 1437, 1373, 1238, 1173, 1089, 1013, 984, 789, 753 cm⁻¹. HRMS (EI) M^+ m/z : calcd for C₂₂H₃₆O₅ 380.2563, found: 380.2572.

4.4.11. (2R,4aS,8aS)-2-Acetoxy-2,5,5,8a-tetramethyl-(2H)-octahydronaphthalen-1-one (2k). Colorless syrup (10% ether/hexanes). ¹H NMR (CDCl₃, 500 MHz) δ : 0.87 (s, 3H), 0.93 (s, 3H), 1.12 (s, 3H), 1.44 (s, 3H), 1.14–1.67 (m, 7H), 3.49 (br d, $J=12.3$ Hz, 1H), 1.84 (m, 1H), 1.96 (dt, $J=12.8$, 3.2 Hz, 1H), 2.02 (s, 3H), 2.31 (ddd, $J=13.2$, 13.2, 5.0 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ : 18.2 (CH₂), 19.3 (CH₂), 19.7 (CH₃), 21.5 (CH₃), 22.1 (CH₃), 26.7 (CH₂), 33.0 (CH₃), 33.9 (C), 34.2 (CH₂), 37.2 (CH₂), 41.1 (CH₂), 49.5 (CH), 81.6 (C), 170.0 (C), 214.3 (C). HRMS (EI) M^+ m/z : calcd for C₁₆H₂₆O₃ 266.1882, found: 266.1894.

4.4.12. (2S,3S)-2,3-Epoxy-1-decanol (3a). Colorless oil (20% ether/hexanes), $[\alpha]_D^{25} -29.3$ (c 1.2, CHCl₃). ¹H NMR (CDCl₃, 500 MHz) δ : 0.76 (t, $J=7.2$ Hz, 3H), 1.10–1.26 (m, 8H), 1.26–1.39 (m, 2H), 1.40–1.49 (m, 2H), 2.65 (br s, 1H), 2.78–2.86 (m, 2H), 3.49 (dd, $J=12.7$, 4.5 Hz, 1H), 3.78 (dd, $J=12.7$, 2.4 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ : 14.0 (CH₃), 22.6 (CH₂), 25.9 (CH₂), 29.2 (CH₂), 31.6 (CH₂), 31.7 (CH₂), 56.1 (CH), 58.7 (CH), 61.8 (CH₂). HRMS (EI) M^+ m/z : calcd for C₁₀H₂₀O₂ 172,1463, found: 172,1452.

4.4.13. (2S,3S)-2,3-Epoxy-5,9-dimethyldec-8-en-1-ol (3b). Colorless oil (20% ether/hexanes). ¹H NMR (CDCl₃, 500 MHz) δ : 0.96 (d, $J=6.9$ Hz, 3H), 0.98 (d, $J=6.9$ Hz, 3H), 1.56 (s, 6H), 1.68 (s, 6H), 1.16–1.82 (m, 10H), 1.90–2.07 (m, 4H), 2.85 (m, 2H), 2.95–3.01 (m, 2H), 3.58–3.70 (m, 2H), 3.87–3.45 (m, 2H), 5.05–5.12 (m, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ : 17.7 (2 CH₃), 19.6 (CH₃), 20.0 (CH₃), 25.5 (CH₂), 25.5 (CH₂), 25.8 (2 CH₃), 30.6 (CH), 31.1 (CH), 36.9 (CH₂), 37.4 (CH₂), 38.9 (2 CH₂), 54.8 (CH), 54.9 (CH), 58.4 (CH), 58.9 (CH), 61.71 (CH₂), 61.73 (CH₂), 124.5 (2 CH), 131.5 (2C). HRMS (EI) M^+ m/z : calcd for C₁₂H₂₂O₂ 198,1620, found: 198,1611.

4.4.14. (E)-5-(2S,3S)-8-Acetoxy-2,3-epoxy-2,6-dimethyloct-6-en-1-ol (3d). Colorless oil (30% ether/hexanes), $[\alpha]_D^{25} -5.5$ (c 1.4, CHCl₃). ¹H NMR (CDCl₃, 500 MHz) δ : 1.21 (s, 3H), 1.59–1.75 (m, 2H), 1.66 (s, 3H), 1.99 (s, 3H), 1.99–2.23 (m, 2H), 2.95 (t, $J=6.3$ Hz, 1H), 3.50 (dd, $J=12.1$, 7.2 Hz, 1H), 3.60 (br d, $J=12.1$ Hz, 1H), 4.53 (d, $J=7.0$ Hz, 2H), 5.32 (t, $J=7.0$ Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ : 14.2 (CH₃), 16.4 (CH₃), 21.0 (CH₃), 26.3 (CH₂), 36.1 (CH₂), 59.7 (CH), 61.2 (CH₂), 65.4 (CH₂), 72.1 (C), 119.0 (CH), 140.9 (C), 171.1 (C); IR (film): 3320, 1738, 1450, 1383, 1028, 953 cm⁻¹. HRMS (EI) M^+ m/z : calcd for C₁₂H₂₀O₄ 228,1362, found: 228,1373.

4.4.15. Methyl (1S,4aR,5S)-1,4a-dimethyl-6-methylene-5-((2S,3S)-2',3'-epoxy-4'-hydroxy-3'-methylbutyl)-decahydronaphthalene-1-

carboxylate (**3g**). Colorless syrup (20% ether/hexanes). ^1H NMR (CDCl_3 , 500 MHz) δ : 0.54 (s, 3H), 0.93–1.04 (m, 2H), 1.11 (s, 3H), 1.22 (s, 3H), 1.44 (m, 1H), 1.55–1.96 (m, 9H), 2.10 (br d, $J=13.5$ Hz, 1H), 2.35 (m, 1H), 2.94 (dd, $J=6.8$, 4.1 Hz, 1H), 3.44 (d, $J=12.1$ Hz, 1H), 3.54 (s, 3H), 3.60 (d, $J=12.1$ Hz, 1H), 4.67 (s, 1H), 4.86 (s, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ : 12.4 (CH_3), 14.4 (CH_3), 20.0 (CH_2), 23.3 (CH_2), 26.1 (CH_2), 28.8 (CH_3), 38.2 (CH_3), 38.6 (CH_2), 39.4 (CH_2), 40.2 (C), 44.3 (C), 51.2 (CH_3), 54.3 (CH), 56.2 (CH), 62.2 (CH), 59.9 (C), 60.1 (CH), 65.6 (CH_2), 107.5 (CH_2), 180.9 (C); IR (film): 3446, 1724, 1645, 1449, 1384, 1154, 1033, 891 cm^{-1} . HRMS (EI) M^+ m/z : calcd for $\text{C}_{20}\text{H}_{32}\text{O}_4$ 336.2301, found: 336.2308.

4.4.16. (*R*)-2-Acetoxy-nonanal (**4a**). Colorless oil (10% ether/hexanes), $[\alpha]_D^{25} +15.2$ (c 1.2, CHCl_3). ^1H NMR (CDCl_3 , 500 MHz) δ : 0.87 (t, $J=7.2$ Hz, 3H), 1.22–1.35 (m, 8H), 1.36–1.45 (m, 2H), 1.67–1.76 (m, 1H), 1.77–1.86 (m, 1H), 2.17 (s, 3H), 4.98 (dd, $J=8.4$, 4.8 Hz, 1H), 9.51 (s, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ : 14.1 (CH_3), 20.6 (CH_2), 22.6 (CH_2), 25.0 (CH_2), 28.7 (CH_2), 29.0 (CH_2), 29.2 (CH_2), 31.7 (CH_2), 78.4 (CH), 170.3 (C), 198.4 (C); IR (film): 1742, 1371, 1233, 1045 cm^{-1} . HRMS (EI) M^+ m/z : calcd for $\text{C}_{11}\text{H}_{20}\text{O}_3$ 200.1412, found: 200.1406.

4.4.17. (*R*)-2-Acetoxy-4,8-dimethylnon-7-enal (**4b**). Colorless oil (10% ether/hexanes). ^1H NMR (CDCl_3 , 500 MHz) δ : 0.93 (d, $J=6.6$ Hz, 3H), 0.95 (d, $J=6.6$ Hz, 3H), 1.59 (s, 6H), 1.67 (s, 6H), 2.16 (s, 6H), 1.10–2.12 (m, 14H), 5.12–5.01 (m, 2H), 9.50 (d, $J=0.8$ Hz, 2H); ^{13}C NMR (CDCl_3 , 125 MHz) δ : 17.7 (CH_3), 18.9 (CH_3), 20.1 (CH_3), 20.7 (CH_3), 25.2 (CH_2), 25.4 (CH_2), 25.8 (CH_3), 27.05 (CH_3), 28.8 (CH), 29.0 (CH), 35.3 (CH_2), 35.5 (CH_2), 36.2 (CH_2), 37.3 (CH_2), 76.9 (2C), 124.3 (CH), 124.5 (CH), 131.67 (C), 131.74 (C), 170.6 (C), 170.7 (C), 198.3 (CH), 198.4 (CH); IR (film): 1742, 1454, 1230 cm^{-1} . HRMS (EI) M^+ m/z : calcd for $\text{C}_{13}\text{H}_{22}\text{O}_3$ 226.1569, found: 226.1580.

4.4.18. (*R,Z*)-2-Acetoxyoct-5-enal (**4c**). Colorless oil (10% ether/hexanes), $[\alpha]_D^{25} +13.4$ (c 1.3, CHCl_3). ^1H NMR (CDCl_3 , 500 MHz) δ : 0.95 (t, $J=7.5$ Hz, 3H), 1.79 (m, 1H), 1.88 (m, 1H), 1.96–2.01 (m, 3H), 2.18 (m, 1H), 2.18 (s, 3H), 4.98 (dd, $J=8.6$, 4.6 Hz, 1H), 45.28 (m, 1H), 5.44 (m, 1H), 9.51 (s, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ : 14.0 (CH_3), 20.56 (CH_2), 20.64 (CH_3), 22.4 (CH_2), 28.4 (CH_2), 77.8 (CH), 126.5 (CH), 134.0 (CH), 170.6 (C), 198.3 (C); IR (film): 1744, 1720, 1462, 1453, 1370, 1302, 1227, 1135, 1089, 1032, 971 cm^{-1} . HRMS (EI) M^+ m/z : calcd for $\text{C}_{10}\text{H}_{16}\text{O}_3$ 184.1099, found: 184.1105.

4.4.19. (*R,E*)-3-Acetoxy-6-methyloct-6-en-2-one (**4d**). Colorless oil (15% ether/hexanes), $[\alpha]_D^{25} +1.1$ (c 0.9, CHCl_3). ^1H NMR (CDCl_3 , 500 MHz) δ : 1.62 (s, 3H), 1.69–1.87 (m, 2H), 1.95 (s, 3H), 1.98–2.08 (m, 2H), 2.06 (s, 3H), 2.07 (s, 3H), 4.44 (d, $J=6.6$ Hz, 2H), 4.83 (m, 1H), 5.26 (t, $J=6.6$ Hz, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ : 16.3 (CH_3), 20.6 (CH_3), 20.9 (CH_3), 26.0 (CH_3), 28.1 (CH_2), 61.0 (CH_2), 78.0 (C), 119.6 (CH), 140.2 (C), 170.4 (C), 171.0 (C), 205.2 (C); IR (film): 1739, 1729, 1711, 1583, 1449, 1369, 1235, 1025, 955, 790 cm^{-1} . HRMS (EI) M^+ m/z : calcd for $\text{C}_{13}\text{H}_{20}\text{O}_5$ 256.1311, found: 256.1302.

4.4.20. (*R*)-2-Acetoxy-cyclohexanone (**4e**). Colorless oil, $[\alpha]_D^{25} +76$ (c 1.2, CHCl_3). ^1H NMR (CDCl_3 , 500 MHz) δ : 1.57 (ddd, 13.3, 13.3, 4.1 Hz, 1H), 1.64–1.76 (m, 2H), 1.91 (m, 1H), 2.02 (m, 1H), 2.09 (s, 3H), 2.23 (m, 1H), 2.39 (ddt, $J=13.7$, 6.1, 1.0 Hz, 1H), 2.51 (m, 1H), 5.10 (m, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ : 20.7 (CH_3), 23.8 (CH_2), 27.1 (CH_2), 33.1 (CH_2), 40.7 (CH_2), 76.5 (CH), 170.0 (C), 204.5 (C). HRMS (EI) M^+ m/z : calcd for $\text{C}_8\text{H}_{12}\text{O}_3$ 156.0786, found: 156.0795.

4.4.21. (*R*)-2-Acetoxy-2,6,6-trimethylcyclohexanone (**4f**). Colorless oil, $[\alpha]_D^{25} +14.5$ (c 0.9, CHCl_3); ^1H NMR (CDCl_3 , 500 MHz) δ : 1.12 (s, 3H), 1.21 (s, 3H), 1.43 (s, 3H), 1.50–2.0 (m, 5H), 2.03 (s, 3H), 2.35 (m, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ : 19.0 (CH_3), 21.4 (CH_3), 25.3 (CH_3), 26.3 (CH_3), 27.2 (CH_3), 37.6 (CH_2), 39.0 (CH_2), 45.0 (C), 81.5 (C), 170.2

(C), 212.7 (C). HRMS (EI) M^+ m/z : calcd for $\text{C}_{11}\text{H}_{18}\text{O}_3$ 198.1256, found: 198.1268.

4.4.22. Methyl (1*S*,4*aR*,5*S*)-5'-((*R*)-2'-acetoxy-3'-oxobutyl)-1,4*a*-dimethyl-6-methylenedecahydronaphthalene-1-carboxylate (**4g**). Colorless syrup (20% ether/hexanes), $[\alpha]_D^{25} +14.1$ (c 1.6, CHCl_3). ^1H NMR (CDCl_3 , 500 MHz) δ : 0.50 (s, 3H), 1.06 (ddd, $J=13.3$, 13.3, 4.0 Hz, 1H), 1.07 (ddd, $J=13.8$, 13.8, 3.0 Hz, 1H), 1.18 (s, 3H), 1.33 (dd, $J=12.5$, 3.1 Hz, 1H), 1.53 (m, 1H), 1.70–1.94 (m, 8H), 2.00 (m, 1H), 2.13 (s, 3H), 2.17 (s, 3H), 2.42 (dt, $J=11.7$, 3.1 Hz, 1H), 3.61 (s, 3H), 4.59 (s, 1H), 4.94 (s, 1H), 4.97 (d, 10.0 Hz, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ : 12.7 (CH_3), 19.9 (CH_2), 20.8 (CH_3), 25.2 (CH_3), 26.17 (CH_3), 26.20 (CH_2), 28.8 (CH_3), 38.2 (CH_2), 38.6 (CH_2), 39.1 (CH_2), 40.1 (C), 44.4 (C), 51.3 (CH_3), 51.6 (CH), 56.3 (CH), 77.8 (CH), 107.0 (CH_2), 147.3 (C), 170.8 (C), 177.6 (C), 205.9 (C); IR (film): 1750, 1725, 1644, 1445, 1374, 1248, 1227, 1155, 1046, 983, 893, 756 cm^{-1} . HRMS (EI) M^+ m/z : calcd for $\text{C}_{21}\text{H}_{32}\text{O}_5$ 364.2250, found: 364.2242.

4.4.23. 1-((2*S*,3*aR*,5*aS*,9*aS*,9*bR*)-3*a*,6,6,9*a*-Tetramethyldodecahydronaphtho[2,1-*b*]furan-2-yl)ethanol (**5b**). Colorless syrup (15% ether/hexanes). ^1H NMR (CDCl_3 , 500 MHz) δ : 0.76 (s, 3H), 0.77 (s, 3H), 0.80 (s, 3H), 0.90 (dd, $J=12.5$, 8.2 Hz, 1H), 0.97 (ddd, $J=12.3$, 12.3, 3.5 Hz, 1H), 1.03 (d, $J=6.2$ Hz, 3H), 1.13 (s, 3H), 1.12 (ddd, $J=14.2$, 4.9 Hz, 1H), 1.16–1.43 (m, 5H), 1.50 (dd, $J=13.5$, 5.4 Hz, 1H), 1.60 (m, 1H), 1.66–1.73 (m, 2H), 1.93 (dt, $J=11.7$, 3.2 Hz, 1H), 2.65 (br s, 1H), 3.59 (m, 1H), 3.66 (ddd, $J=8.7$, 8.7, 6.5 Hz, 1H); IR (film): 3457, 1445, 1379, 1274, 1120, 1060, 948 cm^{-1} . HRMS (EI) M^+ m/z : calcd for $\text{C}_{18}\text{H}_{32}\text{O}_2$ 280.2402, found: 280.2417.

4.4.24. 2-((2*S*,3*aR*,5*aS*,9*aS*,9*bR*)-3*a*,6,6,9*a*-Tetramethyldodecahydronaphtho[2,1-*b*]furan-2-yl)propan-2-ol (**5c**). Colorless syrup (15% ether/hexanes), $[\alpha]_D^{25} -24.3$ (c 0.9, CHCl_3). ^1H NMR (CDCl_3 , 400 MHz) δ : 0.81 (s, 3H), 0.83 (s, 3H), 0.85 (s, 3H), 0.90–1.08 (m, 2H), 1.11 (s, 3H), 1.16 (s, 3H), 1.22 (s, 3H), 1.09–1.81 (m, 10H), 1.85–1.97 (m, 2H), 3.71 (dd, $J=9.8$, 5.2 Hz, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ : 15.9 (CH_2), 18.4 (CH_2), 20.9 (CH_3), 21.3 (CH_2), 24.1 (CH_2), 24.4 (CH_3), 25.4 (CH_3), 28.8 (CH_3), 33.3 (C), 33.4 (CH_3), 35.3 (C), 40.1 (CH_2), 40.8 (CH_2), 42.4 (CH_2), 57.0 (CH), 60.0 (CH), 70.6 (C), 80.9 (C), 86.2 (CH); IR (film): 3449, 1646, 1461, 1378, 1124, 1010 cm^{-1} . HRMS (EI) M^+ m/z : calcd for $\text{C}_{19}\text{H}_{34}\text{O}_2$ 294.2559, found: 294.2548.

4.4.25. 1-((2*R*,3*aR*,5*S*,5*aS*,9*aR*,9*bR*)-5-Acetoxy-2-3*a*,6,6,9*a*-tetramethyldodecahydronaphtho[2,1-*b*]furan-2-yl) ethanol (**5d**). Colorless syrup (20% ether/hexanes). ^1H NMR (CDCl_3 , 500 MHz) δ : 0.81 (s, 3H), 0.82 (s, 3H), 0.85 (s, 3H), 0.87 (s, 3H), 0.92 (s, 3H), 0.925 (s, 3H), 0.99 (s, 6H), 1.02 (d, $J=6.4$ Hz, 3H), 1.09 (d, $J=6.5$ Hz, 3H), 1.15 (s, 3H), 1.17 (s, 3H), 1.05–1.80 (m, 10H), 1.97 (s, 6H), 2.09–2.16 (m, 2H), 2.59 (br s, 2H), 3.52 (m, 1H), 3.67 (ddd, $J=8.7$, 8.7, 6.5 Hz, 1H), 3.74 (m, 1H), 3.79 (m, 1H), 3.86 (dd, $J=11.3$, 6.0 Hz, 1H), 5.05–5.14 (m, 2H); IR (film): 3447, 1737, 1460, 1377, 1241, 1030 cm^{-1} . HRMS (EI) M^+ m/z : calcd for $\text{C}_{20}\text{H}_{34}\text{O}_4$ 338.2457, found: 338.2466.

4.4.26. ((5*aR*,7*aS*,11*aS*,11*bR*)-5*a*,8,8,11*a*-Tetramethyltetradecahydronaphtho[2,1-*b*]oxepin-4-yl)methanol (**5e**). Colorless syrup (15% ether/hexanes), $[\alpha]_D^{25} +5.47$ (c 0.7, CHCl_3). ^1H NMR (CDCl_3 , 500 MHz) δ : 0.72 (s, 3H), 0.73 (s, 3H), 0.79 (s, 3H), 0.76–0.88 (m, 2H), 1.07 (ddd, 13.4, 13.4, 4.2 Hz, 1H), 1.12 (s, 3H), 1.12–1.80 (m), 2.02 (br s, 1H), 3.21 (dd, $J=10.7$, 9.0 Hz, 1H), 3.33 (dd, $J=10.7$, 3.6 Hz, 1H), 3.79 (m, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ : 16.1 (CH_2), 18.5 (CH_2), 20.8 (CH_2), 21.1 (CH_3), 22.4 (CH_2), 24.5 (CH_3), 27.9 (CH_2), 32.3 (CH_2), 33.3 (CH_3), 33.3 (C), 39.0 (C), 39.4 (CH_2), 39.5 (CH_2), 42.1 (CH_2), 56.4 (CH), 58.3 (CH), 66.3 (CH_2), 70.3 (CH), 78.5 (C); IR (film): 3438, 1453, 1382, 1092, 1040 cm^{-1} . HRMS (EI) M^+ m/z : calcd for $\text{C}_{19}\text{H}_{34}\text{O}_2$ 294.2559, found: 294.2570.

4.4.27. ((5*aR*,7*aS*,11*aS*,11*bR*)-5*a*,8,8,11*a*-Tetramethyl-3-methylenetetradecahydronaphtho[2,1-*b*]oxepin-4-yl)methanol (**5f**). Colorless

syrup (15% ether/hexanes), $[\alpha]_D^{25} +70.9$ (c 0.6, CHCl₃). ¹H NMR (CDCl₃, 500 MHz) δ : 0.71 (s, 3H), 0.76 (s, 3H), 0.78 (s, 3H), 1.06 (ddd, $J=13.4$, 13.4, 4.1 Hz, 1H), 1.15 (s, 3H), 1.16–1.65 (m, 14H), 1.95 (ddd, $J=10.7$, 8.3, 1.5 Hz, 1H), 2.04 (br s, 1H), 2.49 (m, 1H), 3.33 (dd, $J=10.9$, 9.0 Hz, 1H), 3.43 (dd, $J=11.0$, 4.0 Hz, 1H), 4.24 (m, 1H), 4.74 (s, 1H), 4.58 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ : 16.1 (CH₂), 18.8 (CH₂), 20.4 (CH₂), 21.5 (CH₃), 22.7 (CH₂), 23.8 (CH₃), 30.6 (CH₂), 33.4 (C), 33.5 (CH₃), 38.3 (C), 39.0 (CH₂), 40.4 (CH₂), 42.0 (CH₂), 53.4 (CH), 56.3 (CH), 66.2 (CH₂), 72.8 (CH), 106.9 (CH₂), 150.9 (C); IR (film): 3461, 1643, 1454, 1412, 1095, 1041, 888, 756 cm⁻¹. HRMS (EI) M^+ m/z : calcd for C₂₀H₃₄O₂ 306,2559, found: 306,2559.

4.4.28. 2-Acetoxytetrahydro-2H-pyran (6a). Colorless oil. ¹H NMR (CDCl₃, 500 MHz) δ : 1.52 (m, 1H), 1.61–1.67 (m, 1H), 1.76 (dt, $J=9.7$, 3.1 Hz, 1H), 1.80 (dd, $J=9$, 2 Hz, 1H), 1.84 (t, $J=5.0$ Hz, 1H), 2.08 (d, $J=2.0$ Hz, 1H), 0.86 (s, 3H), 0.86 (s, 3H), 0.89–2.07 (m, 24H), 1.12 (dd, $J=11.5$, 4.9 Hz, 1H), 5.93 (t, $J=3$ Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ : 18.7 (CH₂), 21.2 (CH₃), 24.9 (CH₂), 29.2 (CH₂), 63.4 (CH₂), 92.7 (CH), 169.8 (C).

4.4.29. (3aR,5aS,9aS,9bR)-2-Acetoxy-3a,6,6,9a-Tetramethyldodecahydronaphtho[2,1-b]furan (6b). Colorless syrup (5% ether/hexanes). ¹H NMR (CDCl₃, 500 MHz) δ : 0.81 (s, 3H), 0.81 (s, 3H), 0.82 (s, 3H), 0.85 (s, 3H), 0.86 (s, 3H), 0.89–2.07 (m, 24H), 1.12 (s, 3H), 1.24 (s, 3H), 2.02 (s, 3H), 2.03 (s, 3H), 2.09–2.20 (m, 2H), 6.19 (dd, $J=11.7$, 5.8 Hz, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ : 15.1 (CH₃), 15.3 (CH₃), 18.2 (CH₂), 18.3 (CH₂), 20.4 (CH₂), 20.9 (CH₂), 21.0 (CH₃), 21.4 (CH₃), 22.8 (CH₃), 23.0 (CH₃), 30.0 (CH₂), 30.3 (CH₂), 33.0 (C), 33.1 (C), 33.4 (CH₃), 33.5 (CH₃), 36.0 (C), 36.1 (C), 39.5 (CH₂), 39.6 (CH₂), 39.9 (CH₂), 40.0 (CH₂), 42.3 (CH₂), 42.4 (CH₂), 56.6 (CH), 56.97 (CH), 57.0 (CH), 60.0 (CH), 82.9 (C), 84.3 (C), 97.4 (CH), 98.6 (CH), 170.4 (C), 170.7 (C); IR (film): 1743, 1588, 1461, 1380, 1238, 1219, 1121, 1082, 1042, 969 cm⁻¹. HRMS (EI) M^+ m/z : calcd for C₁₈H₃₀O₃ 294,2195, found: 294,2204.

4.4.30. (3aR,5S,5aS,9aS,9bR)-2,5-Diacetoxy-3a,6,6,9a-tetramethyldodecahydronaphtho[2,1-b]furan (6c). Major isomer: colorless syrup (15% ether/hexanes), $[\alpha]_D^{25} +16.6$ (c 0.8, CHCl₃). ¹H NMR (CDCl₃, 500 MHz) δ : 0.88 (s, 3H), 0.92 (s, 3H), 0.99 (s, 3H), 1.23 (s, 3H), 1.10–1.90 (m, 11H), 2.03 (s, 3H), 2.04 (s, 3H), 2.18 (ddd, $J=11.1$, 11.1, 4.1 Hz, 1H), 2.20 (dd, $J=11.0$, 4.0 Hz, 1H), 5.17 (ddd, $J=11.1$, 11.1, 4.1 Hz, 1H), 6.23 (d, $J=5.5$ Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ : 16.6 (CH₃), 18.1 (CH₂), 21.5 (CH₃), 21.8 (CH₃), 22.0 (CH₃), 24.1 (CH₃), 30.3 (CH₂), 33.4 (C), 35.4 (C), 35.8 (CH₃), 39.9 (CH₂), 43.7 (CH₂), 47.1 (CH₂), 56.6 (CH), 59.4 (CH), 71.5 (CH), 82.4 (C), 97.5 (CH), 170.1 (C), 170.4 (C); IR (film): 1737, 1459, 1377, 1240, 1033, 974 cm⁻¹.

Minor isomer: colorless syrup (10% ether/hexanes), $[\alpha]_D^{25} +51.7$ (c 0.9, CHCl₃). ¹H NMR (CDCl₃, 500 MHz) δ : 0.88 (s, 3H), 0.97 (s, 3H), 0.99 (s, 3H), 1.07 (ddd, $J=12.8$, 12.8, 4.0 Hz, 1H), 1.26 (m, 1H), 1.35 (s, 3H), 1.32–1.50 (m, 4H), 1.50–1.75 (m, 4H), 1.82 (ddd, $J=13.8$, 12.6, 5.0 Hz, 1H), 2.04 (s, 3H), 2.05 (s, 3H), 2.14–2.23 (m, 2H), 5.15 (ddd, $J=11.0$, 11.0, 4.0 Hz, 1H), 6.22 (dd, $J=6.2$, 5.1 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ : 16.4 (CH₃), 18.1 (CH₂), 21.4 (CH₃), 21.8 (CH₃), 22.0 (CH₃), 24.3 (CH₃), 30.0 (CH₂), 33.4 (C), 35.6 (C), 35.8 (CH₃), 39.7 (CH₂), 43.7 (CH₂), 46.7 (CH₂), 59.5 (CH), 59.8 (CH), 71.2 (CH), 81.2 (C), 98.6 (CH), 170.1 (C), 170.7 (C); IR (film): 1746, 1457, 1365, 1240, 1030, 965 cm⁻¹. HRMS (EI) M^+ m/z : calcd for C₂₀H₃₂O₅ 352,225, found: 352,231.

4.4.31. (5aR,7aS,11aS,11bR)-4-Acetoxy-5a,8,8,11a-tetramethyltetradecahydronaphtho[2,1-b]oxepine (6d). Colorless syrup (3% ether/hexanes). ¹H NMR (CDCl₃, 500 MHz) signals assignable to the major isomer δ : 0.71 (s, 6H), 0.79 (s, 3H), 1.07 (ddd, $J=13.4$, 13.4, 4.0 Hz, 1H), 1.16 (s, 3H), 1.98 (s, 3H), 1.21–1.81 (m, 14H), 6.03 (dd, $J=9.6$, 2.0 Hz, 1H, 2H), ¹³C NMR (CDCl₃, 125 MHz) signals assignable to the major isomer δ : 16.2 (CH₃), 18.66 (CH₂), 20.97 (CH₂), 21.3 (CH₃), 21.6 (CH₃), 22.2 (CH₂), 24.1 (CH₃), 26.6 (CH₂), 33.4 (CH₃), 35.5 (CH₂), 39.17

(CH₂), 39.5 (CH₂), 42.1 (CH₂), 56.19 (CH), 60.3 (CH), 79.5 (C), 91.6 (CH), 169.7 (C); IR (film) 1744, 1456, 1384, 1260, 1018, 800 cm⁻¹. HRMS (EI) M^+ m/z : calcd for C₂₀H₃₄O₃ 322,2508, found: 322,2514.

4.4.32. (5aR,7aS,11aS,11bR)-4-Acetoxy-5a,8,8,11a-tetramethyl-3-methylenetetradecahydronaphtho[2,1-b]oxepine (6e) and 4-((1R,2R,5aR,8aS)-2-hydroxy-2,5,5,8a-tetramethyldecahydronaphthalen-1-yl)-2-methylenebutanal (6f). Compounds **6e** and **6f** were obtained as a mixture in a 1:1 ratio.

Compound **6e**. Colorless syrup (5% ether/hexanes). ¹H NMR (CDCl₃, 500 MHz) signals assignable to the major isomer δ : 0.71 (s, 6H), 0.79 (s, 3H), 0.75–0.90 (m, 2H), 1.15–1.37 (m, 4H), 1.25 (s, 3H), 1.54–1.66 (m, 13H), 2.05 (s, 3H), 2.47 (ddd, $J=13.0$, 6.6, 3.7 Hz, 1H), 4.89 (s, 1H), 4.90 (s, 1H), 6.35 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz) signals assignable to the major isomer δ : 15.6 (CH₃), 18.7 (CH₂), 19.9 (CH₂), 21.4 (CH₃), 21.5 (CH₃), 22.2 (CH₃), 33.2 (CH₂), 33.3 (CH₃), 33.4 (C), 38.3 (C), 40.0 (CH₂), 41.7 (CH₂), 42.3 (CH₂), 55.9 (CH), 59.1 (CH), 81.9 (C), 92.7 (CH), 110.8 (CH₂), 148.2 (C), 169.6 (C); IR (film): 2936, 1733, 1650, 1452, 1386, 1242, 1132, 994, 934, 756 cm⁻¹. HRMS (EI) M^+ m/z : calcd for C₂₁H₃₄O₃ 334,2508, found: 334,2519.

Compound **6f**. Colorless syrup (20% ether/hexanes), $[\alpha]_D^{25} +20.4$ (c 1.0, CHCl₃). ¹H NMR (CDCl₃, 500 MHz) δ : 0.75 (s, 3H), 0.76 (s, 3H), 0.85 (s, 3H), 0.90 (dd, $J=12.2$, 2.2 Hz, 1H), 0.94 (dd, $J=12.8$, 12.8, 3.6 Hz, 1H), 1.09 (t, $J=3.9$ Hz, 1H), 1.12 (s, 3H), 1.22 (ddd, $J=13.4$, 13.4, 3.2 Hz, 1H), 1.25 (ddd, $J=13.4$, 13.4, 3.1 Hz, 1H), 1.30–1.8 (m, 9H), 1.84 (dt, $J=12.3$, 3.3 Hz, 1H), 2.2–2.40 (m, 2H), 5.95 (s, 1H), 6.30 (s, 1H), 9.50 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ : 15.4 (CH₂), 18.4 (CH₂), 20.4 (CH₂), 21.4 (CH₃), 23.9 (CH₂), 24.0 (CH₃), 26.9 (CH₃), 31.5 (CH₂), 33.2 (C), 33.3 (CH₃), 38.9 (C), 39.6 (CH₂), 41.9 (CH₂), 44.2 (CH₂), 56.1 (CH), 61.6 (CH), 74.0 (C), 134.0 (CH₂), 150.9 (C), 195.0 (CH). IR (film): 3457, 1687, 1650, 1461, 1387, 1124, 939, 756 cm⁻¹. HRMS (EI) M^+ m/z : calcd for C₁₉H₃₂O₂ 292,2402, found: 292,2395.

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