

# Lead(IV) acetate mediated cleavage of $\beta$ -hydroxy ethers: enantioselective synthesis of $\alpha$ -acetoxy carbonyl compounds

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## ABSTRACT

$\alpha$ -Acetoxy aldehydes or  $\alpha$ -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  $\alpha$ -acetoxy carbonyl compounds from allyl alcohols, *via* Sharpless epoxidation. Cyclic  $\beta$ -hydroxy ethers, with an oxygenated five-, six- or seven-membered ring, are transformed into  $\alpha$ -acetoxy ethers.

## 1. Introduction

The  $\alpha$ -hydroxy carbonyl group occupies an important place in organic chemistry, being found in a wide variety of biologically active natural products.<sup>1a-e</sup> Chiral  $\alpha$ -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.<sup>2</sup> Wittig olefination allows the synthesis of chiral allylic alcohols, which have been utilized in the synthesis of pheromones.<sup>3</sup> Chiral acyloins have been used for synthesizing *syn* or *anti* aldols with high diastereoselectivity utilizing boron-mediated aldol condensation<sup>4</sup> or titanium enolates.<sup>5</sup> Other examples of the synthetic scope of chiral  $\alpha$ -hydroxy ketones are the synthesis of chiral  $\beta$ -lactams<sup>6</sup> and  $\gamma$ -butyrolactones.<sup>7</sup>

Numerous methods for introducing a hydroxyl group into the  $\alpha$ -position to a carbonyl moiety have been reported. These include the direct oxidation of ketone/enol with transition metal salts,<sup>8</sup> hypervalent iodine reagents<sup>9</sup> or molecular oxygen,<sup>10</sup> or the most widely used procedure, involving enolates. Among these, the use of molybdenum peroxy complexes<sup>11</sup> or of 2-sulfonyloxaziridines, perhaps the most widely employed enolate hydroxylation agent,<sup>12</sup> should be emphasized. Most of the above cited methods are restricted to ketones. The corresponding  $\alpha$ -hydroxylation of aldehydes is often complicated by undesired self-condensation of the enolates and the instability of the hydroxylated products.<sup>11c</sup> Frequently,  $\alpha$ -hydroxycarbonyl compounds are made using multistep transformations; these routes include nucleophilic acylation with masked acyl anions<sup>13</sup> or the monooxidation of vic-diols,<sup>14</sup> among others.

Several chemical methods for the preparation of chiral  $\alpha$ -hydroxy carbonyl compounds have been described in the literature.<sup>15</sup> Stereoselective versions of some of the above

methods have also been reported;<sup>16</sup> they include the enantioselective oxidation of chiral enolates,<sup>17</sup> the oxidation of non-chiral enolates with chiral oxidants<sup>18</sup> or the use of DITOX, a chiral dithiane oxide.<sup>19</sup> More recently, the desymmetrization of *meso*-diols through acylation and oxidation,<sup>20</sup> the asymmetric reductive coupling of alkynes and aldehydes,<sup>21</sup> the asymmetric dihydroxylation of substituted allenes,<sup>22</sup> or the asymmetric rearrangement of  $\alpha,\alpha$ -disubstituted  $\alpha$ -amino aldehydes<sup>23</sup> and  $\alpha$ -siloxy aldehydes<sup>24</sup> have been utilized for synthesizing chiral  $\alpha$ -hydroxy ketones. An alternative procedure to obtain enantiomerically pure acyloins involves the chemoenzymatic dynamic kinetic resolution (DKR) of these<sup>25</sup> or of the precursor allylic alcohols.<sup>26</sup>

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 and its low cost.<sup>27</sup> LTA is commonly used for oxidative cleavage (C–C bond cleavage),<sup>28</sup> decarboxylations,<sup>29</sup> acetoxylation,<sup>30</sup> and formation of cyclic ethers (C–O bond formation).<sup>31</sup> It is less often used for C–C bond formation,<sup>32</sup> and C–N bond formation.<sup>33</sup> More recently, some new applications have been reported, such as the preparation of aryl lead triacetate, utilized in the direct arylation of nucleophiles,<sup>34</sup> and a very interesting multistage hetero-domino transformation;<sup>35</sup> both examples allow the construction of unique carbon substitution patterns. Very recently an interesting LTA mediated oxidative fragmentation of homoallylic alcohols<sup>36</sup> and an oxidative cleavage of allyl alcohols induced by the O<sub>3</sub>/LTA system<sup>37</sup> have been reported.

Brocksom et al trying to synthesize the corresponding epoxy tetrahydrofuran from 8,9-epoxy-*p*-menthan-10-ol (**1d**) found that

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the treatment of this epoxy alcohol with LTA led to the  $\alpha$ -acetoxy ketone **2d** instead of the desired furan; in a similar way, epoxy alcohols **1b** and **1c** were converted into the corresponding  $\alpha$ -acetoxy carbonyl compounds **2b** and **2c**.<sup>38</sup> These authors indicate that the reaction was efficient in the case of linear  $\alpha,\beta$ -epoxy alcohols but did not proceed well in the case of cyclic substrates<sup>39</sup> and could be utilized as a degradative procedure for the structural determination of  $\alpha,\beta$ -unsaturated ketones or alcohols.

In order to explore the scope and limitations of this reaction and establish its synthetical potential, the behavior 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  $\alpha$ -hydroxy carbonyl compounds, starting from epoxy alcohols prepared utilizing the asymmetric Sharpless epoxidation, have been recently communicated.<sup>40</sup>

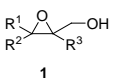
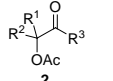
In this paper we report an expanded study on this subject, including other cyclic examples of 2,3-epoxy alcohols and the behaviour of cyclic  $\beta$ -hydroxy ethers, with an oxygenated five-, six- or seven-membered ring, against this reagent.

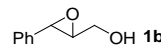
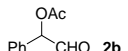


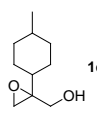
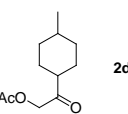
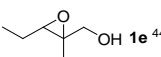

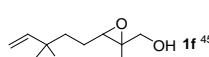
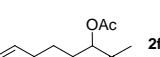
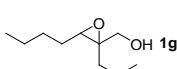
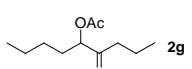
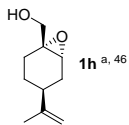
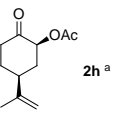
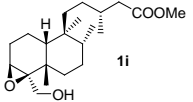
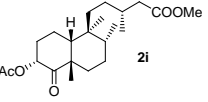
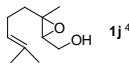
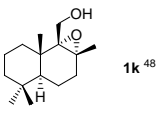
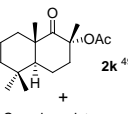
## 2. Results and discussion

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  $\alpha$ -acetoxy aldehyde **2b**.<sup>38</sup> 2,3-Epoxyalcohols bearing an alkyl group on the C-2 (compounds **1c-i**) led to the corresponding  $\alpha$ -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 behaviour 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  $\alpha$ -acetoxy ketone **2k** as a minor constituent.

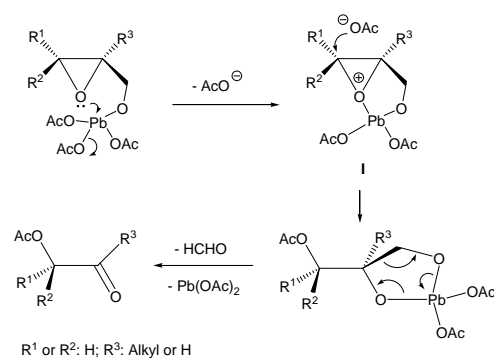
The results obtained when chiral epoxy alcohols (entries 8 and 9) were utilized as the substrate reaction deserve special mention. The enantiopure compound **1i** was transformed into the  $\alpha$ -acetoxy ketone **2i** as the only isomer. Epoxy alcohol **1h**, a 6:1 mixture of diastereoisomers, gave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

**Table 1.** Reaction of 2,3-epoxy alcohols with LTA. Synthesis of  $\alpha$ -acetoxy aldehydes and  $\alpha$ -acetoxy ketones.

Entry	Epoxy alcohol	Time	Product	%
1		LTA benzene, $\Delta$ 20 min		73

2		2 h		87 <sup>38</sup>
3		2 h		91 <sup>38</sup>
4		2 h		87 <sup>38</sup>
5		20 min		77
6		1 h		96
7		1 h		82
8		1.5 h		94
9		2 h		97
10		2 h	Complex mixture	
11		2 h	 Complex mixture	26

<sup>a</sup> Diastereomeric ratio: 6:1.

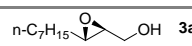
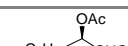
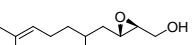
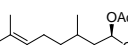
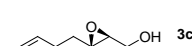

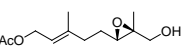
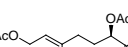




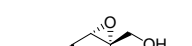
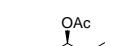


**Scheme 1.** Mechanism of the reaction of 2,3-epoxy alcohols with LTA.

The regio- and stereoselectivities observed in the course of the above transformations lead us to propose the mechanism shown in Scheme 1.<sup>41</sup> 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-epoxyalcohols, such as compounds **1j-k**, can be attributed to the formation of a tertiary carbenium ion resulting from the oxonium ring opening, which undergoes different side reactions. The observed retention in the  $\alpha$  carbon configuration for compound **2k**, which results after the attack of an acetate

anion on the carbenium ion by the less hindered  $\alpha$  side, seems to corroborate this assumption (entry 8).<sup>42</sup>

**Table 2.** Enantioselective synthesis of  $\alpha$ -acetoxy aldehydes and  $\alpha$ -acetoxy ketones.

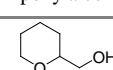
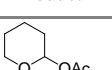
Entry	Epoxy alcohol	Time	Product	%
1	 <b>3a</b> <sup>50</sup>	20 min	 <b>4a</b>	93
2	 <b>3b</b>	1 h	 <b>4b</b>	87
3	 <b>3c</b> <sup>51</sup>	1 h	 <b>4c</b>	83
4	 <b>3d</b> <sup>52</sup>	1 h	 <b>4d</b>	95
5	 <b>3e</b> <sup>47</sup>	1 h	 <b>4e</b> <sup>54</sup>	59
6	 <b>3f</b> <sup>53</sup>	4 h	 <b>4f</b> <sup>a</sup>	81
7	 <b>3g</b> <sup>b</sup>	45 min	 <b>4g</b> <sup>b</sup>	92

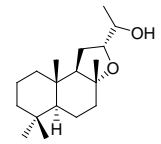
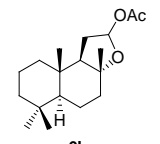
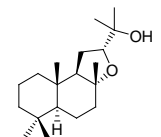
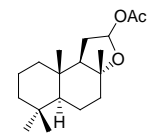
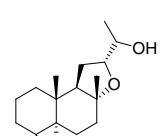
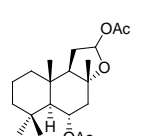
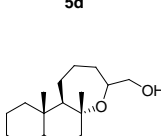
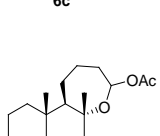
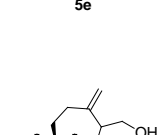
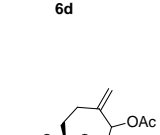
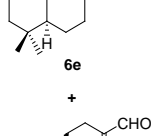
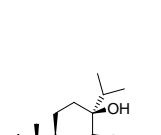
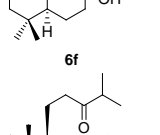
<sup>a</sup> 70% ee.

<sup>b</sup> Diastereomeric ratio: 6:1.

In view of the complete stereoselectivity observed for chiral compounds **1h-i**, the enantioselective synthesis of  $\alpha$ -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  $\alpha$ -acetoxy carbonyl derivatives **4a-f**. Compounds **4a-e** were obtained with >95% 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

**Table 3.** Reaction of some  $\beta$ -hydroxy ethers with LTA.

Entry	Epoxy alcohol	Time	Product	% <sup>a</sup>
1	 <b>5a</b>	12 h	 <b>6a</b>	48

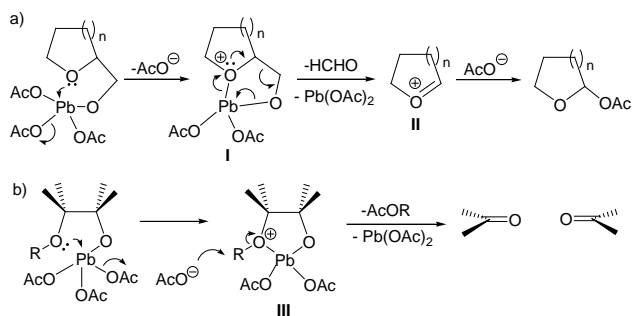
2	 <b>5b</b>	12 h	 <b>6b</b>	75
3	 <b>5c</b>	12 h	 <b>6b</b>	78
4	 <b>5d</b>	12 h	 <b>6c</b>	66
5	 <b>5e</b>	8 h	 <b>6d</b>	63
6	 <b>5f</b>	30 min	 <b>6e</b> +  <b>6f</b>	55
7	 <b>5g</b> <sup>55</sup>	4 h	 <b>6g</b> <sup>55</sup>	83

<sup>a</sup> Run under reflux.

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  $\alpha$ -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.<sup>49,54</sup>

In order to explore the scope and limitation of this reaction the behaviour of other type of  $\beta$ -hydroxy ethers was investigated. When compounds **5a-e** with an oxygenated five-, six- or seven-membered ring, were treated with LTA under the above mentioned conditions  $\alpha$ -acetoxy ethers **6a-d** were obtained. The unsaturated hydroxy ether **5f** gave a mixture of the corresponding unsaturated  $\alpha$ -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  $\beta$ -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  $\beta$ -hydroxy ethers were also transformed into  $\alpha$ -acetoxy ethers after prolonged reaction times (from 1 to 4 days) in benzene under reflux.

### 3. Conclusion

The treatment of  $\beta$ -hydroxy ethers with LTA causes a carbon-carbon cleavage which proves to be a useful synthetic tool.  $\alpha$ -Acetoxy aldehydes or  $\alpha$ -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  $\alpha$ -acetoxy carbonyl compounds from allyl alcohols, *via* Sharpless epoxidation. Under these reaction conditions, cyclic  $\beta$ -hydroxy ethers, with an oxygenated five-, six- or seven-membered ring, are transformed into  $\alpha$ -acetoxy ethers, whereas acyclic  $\beta$ -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-Et<sub>2</sub>O (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<sup>-1</sup>). Only selected absorbancies ( $\nu_{\max}$ ) are reported. Proton and Carbon-13 nuclear magnetic resonance (<sup>1</sup>H NMR or <sup>13</sup>C NMR) spectra were recorded on a Varian 400 or 500 spectrometer. Chemical shifts are expressed in

parts per million ( $\delta$  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 <sup>13</sup>C NMR were assigned utilizing DEPT experiments and on the basis of heteronuclear correlations.

### 4.2 General procedure for the cleavage of $\beta$ -hydroxy ethers

To a solution of  $\beta$ -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% Na<sub>2</sub>SO<sub>3</sub>, extracted with Et<sub>2</sub>O, washed with water, brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated. The residue was chromatographed on silica gel (Hexanes/Ether) to give the corresponding  $\alpha$ -acetoxy carbonyl or  $\alpha$ -acetoxy ether compound.

### 4.3 General procedure for Sharpless epoxidation

To a mixture of activated 4 Å molecular sieves (0.3 g) in dry CH<sub>2</sub>Cl<sub>2</sub> (10 mL) were added successively at -25°C (+)-diethyl L-tartrate (0.22 mL, 1.3 mmol) and Ti(O-<sup>*i*</sup>Pr)<sub>4</sub> (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 CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added and the resulting mixture was stirred for 12 - 15 h. Et<sub>2</sub>O (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, Na<sub>2</sub>SO<sub>4</sub> and celite were added. The mixture was filtered in vacuum and extracted with ether, the combined organic phases were dried (Na<sub>2</sub>SO<sub>4</sub>) 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 <sup>1</sup>H-NMR, utilizing europium (III) tris [3-(heptafluoropropylhydroxymethylene)-*d*-camphorate] [Eu(hfc)<sub>3</sub>] as chiral shift reagent.

Typical experimental procedure: 10 mg of Europium(III) tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorate] (Eu(hfc)<sub>3</sub>) was added to a solution of benzoates obtained from alcohols **3a-f** (15 mg) in CDCl<sub>3</sub> (0.5 mL) containing 1% of TMS, and the resulting yellow solution was stand for 15 min. Then, the solution was added to an NMR tube and the <sup>1</sup>H-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**, **5c**, **5d**, **5e** and **5f** 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). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$ : 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 14.06 ( $\text{CH}_3$ ), 14.07 ( $\text{CH}_3$ ), 22.08 ( $\text{CH}_3$ ), 22.09 ( $\text{CH}_3$ ), 22.8 (2  $\text{CH}_2$ ), 23.6 ( $\text{CH}_3$ ), 23.7 ( $\text{CH}_3$ ), 36.23 ( $\text{CH}_2$ ), 36.25 ( $\text{CH}_2$ ), 59.7 (2 CH), 61.0 (2 C), 65.3 (2  $\text{CH}_2$ ), 82.3 (C), 82.4 (C), 113.5 ( $\text{CH}_2$ ), 113.6 ( $\text{CH}_2$ ), 141.2 (CH), 141.4 (CH), 140.9 (C), 169.9 (2 C); IR (film): 3430, 1645, 1240, 1149, 1030, 930, 875  $\text{cm}^{-1}$ . HRMS (EI)  $\text{M}^+$   $m/z$ : calcd for  $\text{C}_{12}\text{H}_{20}\text{O}_4$  228,1362, found: 228,1378.

#### 4.4.2. 2,3-Epoxy-2-propylheptan-1-ol (**1g**)

Colorless oil (25% ether/hexanes).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 14.0 ( $\text{CH}_3$ ), 14.5 ( $\text{CH}_3$ ), 18.5 ( $\text{CH}_2$ ), 22.6 ( $\text{CH}_2$ ), 27.7 ( $\text{CH}_2$ ), 28.9 ( $\text{CH}_2$ ), 31.0 ( $\text{CH}_2$ ), 60.5 (CH), 63.3 (C), 63.4 ( $\text{CH}_2$ ). HRMS (EI)  $\text{M}^+$   $m/z$ : calcd for  $\text{C}_{10}\text{H}_{20}\text{O}_2$  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'a-trimethyldecahydronaphthalen-1'-yl)-3-methylpentanoate (**1i**)

Colorless oil (30% ether/hexanes),  $[\alpha]_{\text{D}}^{25} = +4.8$  (c 0.5,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 15.7 ( $\text{CH}_3$ ), 16.7 ( $\text{CH}_2$ ), 19.6 ( $\text{CH}_3$ ), 19.9 ( $\text{CH}_3$ ), 22.7 ( $\text{CH}_3$ ), 29.08 ( $\text{CH}_2$ ), 29.14 ( $\text{CH}_2$ ), 29.26 ( $\text{CH}_3$ ), 31.1 (CH), 34.5 ( $\text{CH}_2$ ), 34.6 (C), 35.6 ( $\text{CH}_2$ ), 37.5 (CH), 39.0 (C), 41.6 ( $\text{CH}_2$ ), 44.3 (CH), 51.4 ( $\text{CH}_3$ ), 57.5 (CH), 61.2 ( $\text{CH}_2$ ), 63.9 (C), 173.6 (C); IR (film): 3450, 1739, 1716, 1699, 1684, 1558, 1507, 1457, 1306, 1233, 1038, 897, 788, 747  $\text{cm}^{-1}$ . HRMS (EI)  $\text{M}^+$   $m/z$ : calcd for  $\text{C}_{21}\text{H}_{36}\text{O}_4$  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).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 16.2 ( $\text{CH}_3$ ), 17.2 ( $\text{CH}_2$ ), 18.4 ( $\text{CH}_2$ ), 21.4 ( $\text{CH}_3$ ), 21.6 ( $\text{CH}_3$ ), 29.4 ( $\text{CH}_2$ ), 33.0 (C), 33.5 ( $\text{CH}_3$ ), 34.0 ( $\text{CH}_2$ ), 37.2 (C), 41.4 ( $\text{CH}_2$ ), 43.2 (CH), 57.0 ( $\text{CH}_2$ ), 64.5 (C), 71.3 (C). HRMS (EI)  $\text{M}^+$   $m/z$ : calcd for  $\text{C}_{15}\text{H}_{26}\text{O}_2$  238,1933, found: 238,1941.

#### 4.4.5. 2-Acetoxypentanal (**2a**)

Colorless oil (10% ether/hexanes),  $[\alpha]_{\text{D}}^{25} = -7.2$  (c 1.2,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 13.8 ( $\text{CH}_3$ ), 18.3 ( $\text{CH}_2$ ), 20.6 ( $\text{CH}_3$ ), 30.7 ( $\text{CH}_2$ ), 78.2 (CH), 170.7

(C), 198.3 (C); IR (film): 1737, 1729, 1468, 1372, 1247, 1105, 1017, 799, 750  $\text{cm}^{-1}$ .

#### 4.4.6. 3-Acetoxy-2-pentanone (**2e**)

Colorless oil (15% ether/hexanes).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 9.4 ( $\text{CH}_3$ ), 20.5 ( $\text{CH}_3$ ), 23.8 ( $\text{CH}_2$ ), 26.2 ( $\text{CH}_2$ ), 79.6 (CH), 170.7 (C), 205.3 (C); IR (film): 1775, 1724, 1549, 1378, 1235, 1181, 1111, 1061  $\text{cm}^{-1}$ .

#### 4.4.7. 3,6-Diacetoxy-6-methyloct-7-en-2-one (**2f**)

Colorless oil (20% ether/hexanes).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 20.6 ( $\text{CH}_3$ ), 22.1 ( $\text{CH}_3$ ), 23.6 ( $\text{CH}_3$ ), 24.5 ( $\text{CH}_2$ ), 26.1 ( $\text{CH}_3$ ), 35.0 ( $\text{CH}_2$ ), 78.3 (CH), 82.1 (C), 113.8 ( $\text{CH}_2$ ), 140.9 (CH), 169.8 (C), 170.5 (C), 205.0 (C). HRMS (EI)  $\text{M}^+$   $m/z$ : calcd for  $\text{C}_{13}\text{H}_{20}\text{O}_5$  256,1311, found: 256,1302.

#### 4.4.8. 5-Acetoxy-nonan-4-one (**2g**)

Colorless oil (15% ether/hexanes).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 13.7 ( $\text{CH}_3$ ), 13.9 ( $\text{CH}_3$ ), 16.7 ( $\text{CH}_2$ ), 20.7 ( $\text{CH}_3$ ), 22.4 ( $\text{CH}_2$ ), 27.4 ( $\text{CH}_2$ ), 30.1 ( $\text{CH}_2$ ), 40.5 ( $\text{CH}_2$ ), 78.5 (CH), 170.7 (C), 207.5 (C); IR (film): 1746, 1730, 1462, 1370, 1230  $\text{cm}^{-1}$ .

#### 4.4.9. (2S,4S)-2-Acetoxy-4-(1-propen-2-yl)-cyclohexanone (**2h**)

Colorless oil (15% ether/hexanes),  $[\alpha]_{\text{D}}^{25} = -14.7$  (c 0.6,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) signals assignable to the major isomer  $\delta$ : 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 20.7 ( $\text{CH}_3$ ), 31.8 ( $\text{CH}_2$ ), 37.4 ( $\text{CH}_2$ ), 39.5 ( $\text{CH}_2$ ), 42.7 (CH), 75.6 (CH), 110.4 ( $\text{CH}_2$ ), 146.4 (C), 169.9 (C), 204.1 (C); IR (film): 1751, 1731, 1441, 1375, 1231, 1149, 1073, 979, 894, 772  $\text{cm}^{-1}$ . HRMS (EI)  $\text{M}^+$   $m/z$ : calcd for  $\text{C}_{11}\text{H}_{16}\text{O}_3$  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'a-trimethyl-5'-oxo-decahydronaphthalen-1'-yl)-3-methylpentanoate (**2i**)

Colorless oil (30% ether/hexanes),  $[\alpha]_{\text{D}}^{25} = +16.4$  (c 0.5,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 15.6 ( $\text{CH}_3$ ), 18.9 ( $\text{CH}_2$ ), 19.1 ( $\text{CH}_3$ ), 19.8 ( $\text{CH}_3$ ), 20.7 ( $\text{CH}_3$ ), 27.3 ( $\text{CH}_2$ ), 28.9 ( $\text{CH}_2$ ), 30.1 ( $\text{CH}_3$ ), 30.9 (CH), 30.95 ( $\text{CH}_2$ ), 35.05 ( $\text{CH}_2$ ), 35.12 ( $\text{CH}_2$ ), 37.2 (CH), 40.1 (C), 41.4 ( $\text{CH}_2$ ), 48.2 (C), 49.8 (CH), 51.4 ( $\text{CH}_3$ ), 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  $\text{cm}^{-1}$ . HRMS (EI)  $M^+$   $m/z$ : calcd for  $\text{C}_{22}\text{H}_{36}\text{O}_5$  380.2563, found: 380.2572.

4.4.11. (2*R*,4*aS*,8*aS*)-2-Acetoxy-2,5,5,8*a*-tetramethyl-(2*H*)-octahydronaphthalen-1-one (**2k**)

Colorless syrup (10% ether/hexanes).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 18.2 ( $\text{CH}_2$ ), 19.3 ( $\text{CH}_2$ ), 19.7 ( $\text{CH}_3$ ), 21.5 ( $\text{CH}_3$ ), 22.1 ( $\text{CH}_3$ ), 26.7 ( $\text{CH}_2$ ), 33.0 ( $\text{CH}_3$ ), 33.9 (C), 34.2 ( $\text{CH}_2$ ), 37.2 ( $\text{CH}_2$ ), 41.1 ( $\text{CH}_2$ ), 49.5 (CH), 81.6 (C), 170.0 (C), 214.3 (C). HRMS (EI)  $M^+$   $m/z$ : calcd for  $\text{C}_{16}\text{H}_{26}\text{O}_3$  266.1882, found: 266.1894.

4.4.12. (2*S*,3*S*)-2,3-Epoxy-1-decanol (**3a**)

Colorless oil (20% ether/hexanes),  $[\alpha]_{\text{D}}^{25} = -29.3$  (c 1.2,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 14.0 ( $\text{CH}_3$ ), 22.6 ( $\text{CH}_2$ ), 25.9 ( $\text{CH}_2$ ), 29.2 ( $\text{CH}_2$ ), 29.3 ( $\text{CH}_2$ ), 31.6 ( $\text{CH}_2$ ), 31.7 ( $\text{CH}_2$ ), 56.1 (CH), 58.7 (CH), 61.8 ( $\text{CH}_2$ ). HRMS (EI)  $M^+$   $m/z$ : calcd for  $\text{C}_{10}\text{H}_{20}\text{O}_2$  172,1463, found: 172,1452.

4.4.13. (2*S*,3*S*)-2,3-Epoxy-5,9-dimethyldec-8-en-1-ol (**3b**)

Colorless oil (20% ether/hexanes).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 17.7 (2  $\text{CH}_3$ ), 19.6 ( $\text{CH}_3$ ), 20.0 ( $\text{CH}_3$ ), 25.5 ( $\text{CH}_2$ ), 25.5 ( $\text{CH}_2$ ), 25.8 (2  $\text{CH}_3$ ), 30.6 (CH), 31.1 (CH), 36.9 ( $\text{CH}_2$ ), 37.4 ( $\text{CH}_2$ ), 38.9 (2  $\text{CH}_2$ ), 54.8 (CH), 54.9 (CH), 58.4 (CH), 58.9 (CH), 61.71 ( $\text{CH}_2$ ), 61.73 ( $\text{CH}_2$ ), 124.5 (2 CH), 131.5 (2 C). HRMS (EI)  $M^+$   $m/z$ : calcd for  $\text{C}_{12}\text{H}_{22}\text{O}_2$  198,1620, found: 198,1611.

4.4.14. (*E*)-5-((2*S*,3*S*)-8-Acetoxy-2,3-epoxy-2,6-dimethyloct-6-en-1-ol (**3d**)

Colorless oil (30% ether/hexanes),  $[\alpha]_{\text{D}}^{25} = -5.5$  (c 1.4,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 14.2 ( $\text{CH}_3$ ), 16.4 ( $\text{CH}_3$ ), 21.0 ( $\text{CH}_3$ ), 26.3 ( $\text{CH}_2$ ), 36.1 ( $\text{CH}_2$ ), 59.7 (CH), 61.2 ( $\text{CH}_2$ ), 65.4 ( $\text{CH}_2$ ), 72.1 (C), 119.0 (CH), 140.9 (C), 171.1 (C); IR (film): 3320, 1738, 1450, 1383, 1028, 953  $\text{cm}^{-1}$ . HRMS (EI)  $M^+$   $m/z$ : calcd for  $\text{C}_{12}\text{H}_{20}\text{O}_4$  228,1362, found: 228,1373.

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

Colorless syrup (20% ether/hexanes).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 12.4 ( $\text{CH}_3$ ), 14.4 ( $\text{CH}_3$ ), 20.0 ( $\text{CH}_2$ ), 23.3 ( $\text{CH}_2$ ), 26.1 ( $\text{CH}_2$ ), 28.8 ( $\text{CH}_3$ ), 38.2 ( $\text{CH}_3$ ), 38.6 ( $\text{CH}_2$ ), 39.4 ( $\text{CH}_2$ ), 40.2 (C), 44.3 (C), 51.2 ( $\text{CH}_3$ ), 54.3 (CH), 56.2 (CH), 62.2 (CH), 59.9 (C), 60.1 (CH), 65.6 ( $\text{CH}_2$ ), 107.5 ( $\text{CH}_2$ ), 180.9 (C); IR (film): 3446, 1724, 1645, 1449, 1384, 1154, 1033, 891  $\text{cm}^{-1}$ . 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-Acetoxyonanal (**4a**)

Colorless oil (10% ether/hexanes),  $[\alpha]_{\text{D}}^{25} = +15.2$  (c 1.2,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 14.1 ( $\text{CH}_3$ ), 20.6 ( $\text{CH}_2$ ), 22.6 ( $\text{CH}_2$ ), 25.0 ( $\text{CH}_2$ ), 28.7 ( $\text{CH}_2$ ), 29.0 ( $\text{CH}_2$ ), 29.2 ( $\text{CH}_2$ ), 31.7 ( $\text{CH}_2$ ), 78.4 (CH), 170.3 (C), 198.4 (C); IR (film): 1742, 1371, 1233, 1045  $\text{cm}^{-1}$ . 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).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 17.7 ( $\text{CH}_3$ ), 18.9 ( $\text{CH}_3$ ), 20.1 ( $\text{CH}_3$ ), 20.7 ( $\text{CH}_3$ ), 25.2 ( $\text{CH}_2$ ), 25.4 ( $\text{CH}_2$ ), 25.8 ( $\text{CH}_3$ ), 27.05 ( $\text{CH}_3$ ), 28.8 (CH), 29.0 (CH), 35.3 ( $\text{CH}_2$ ), 35.5 ( $\text{CH}_2$ ), 36.2 ( $\text{CH}_2$ ), 37.3 ( $\text{CH}_2$ ), 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  $\text{cm}^{-1}$ . 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),  $[\alpha]_{\text{D}}^{25} = +13.4$  (c 1.3,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 14.0 ( $\text{CH}_3$ ), 20.56 ( $\text{CH}_2$ ), 20.64 ( $\text{CH}_3$ ), 22.4 ( $\text{CH}_2$ ), 28.4 ( $\text{CH}_2$ ), 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  $\text{cm}^{-1}$ . 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),  $[\alpha]_{\text{D}}^{25} = +1.1$  (c 0.9,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 16.3 ( $\text{CH}_3$ ), 20.6 ( $\text{CH}_3$ ), 20.9 ( $\text{CH}_3$ ), 26.0 ( $\text{CH}_3$ ), 28.1 ( $\text{CH}_2$ ), 61.0 ( $\text{CH}_2$ ), 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  $\text{cm}^{-1}$ .

HRMS (EI)  $M^+$   $m/z$ : calcd for  $C_{13}H_{20}O_5$  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)  $\delta$ : 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)  $\delta$ : 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  $C_8H_{12}O_3$  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)  $\delta$ : 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)  $\delta$ : 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  $C_{11}H_{18}O_3$  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)  $\delta$ : 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)  $\delta$ : 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  $C_{21}H_{32}O_5$  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)  $\delta$ : 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  $C_{18}H_{32}O_2$  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),  $[\alpha]_D = -24.3$  (c = 0.9,  $CHCl_3$ ).  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$ : 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)  $\delta$ : 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  $C_{19}H_{34}O_2$  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)  $\delta$ : 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  $C_{20}H_{34}O_4$  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),  $[\alpha]_D = +5.47$  (c = 0.7,  $CHCl_3$ ).  $^1H$  NMR ( $CDCl_3$ , 500 MHz)  $\delta$ : 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)  $\delta$ : 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  $C_{19}H_{34}O_2$  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),  $[\alpha]_D = +70.9$  (c = 0.6,  $CHCl_3$ ).  $^1H$  NMR ( $CDCl_3$ , 500 MHz)  $\delta$ : 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);  $^{13}C$  NMR ( $CDCl_3$ , 125 MHz)  $\delta$ : 16.1 ( $CH_2$ ), 18.8 ( $CH_2$ ), 20.4 ( $CH_2$ ), 21.5 ( $CH_3$ ), 22.7 ( $CH_2$ ), 23.8 ( $CH_3$ ), 30.6 ( $CH_2$ ), 33.4 (C), 33.5 ( $CH_3$ ), 38.3 (C), 39.0 ( $CH_2$ ), 40.4 ( $CH_2$ ), 42.0 ( $CH_2$ ), 53.4 (CH), 56.3 (CH), 66.2 ( $CH_2$ ), 72.8 (CH), 106.9 ( $CH_2$ ), 150.9 (C); IR (film): 3461, 1643, 1454, 1412, 1095, 1041, 888, 756  $cm^{-1}$ . HRMS (EI)  $M^+$   $m/z$ : calcd for  $C_{20}H_{34}O_2$  306,2559, found: 306,2559.

#### 4.4.28. 2-Acetoxytetrahydro-2*H*-pyran (**6a**)

Colorless oil.  $^1H$  NMR ( $CDCl_3$ , 500 MHz)  $\delta$ : 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), 2.09

(s, 3H), 3.89 (ddd,  $J = 11.3, 9, 3.1$  Hz, 1H), 3.60 (dd,  $J = 11.5, 4.9$  Hz, 1H), 5.93 (t,  $J = 3$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 18.7 ( $\text{CH}_2$ ), 21.2 ( $\text{CH}_3$ ), 24.9 ( $\text{CH}_2$ ), 29.2 ( $\text{CH}_2$ ), 63.4 ( $\text{CH}_2$ ), 92.7 (CH), 169.8 (C).

4.4.29. (3*aR*,5*aS*,9*aS*,9*bR*)-2-Acetoxy-3*a*,6,6,9*a*-Tetramethyldodecahydronaphtho[2,1-*b*]furan (**6b**)

Colorless syrup (5% ether/hexanes).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 0.81 (s, 3H), 0.81 (s, 3H), 0.82 (s, 3H), 0.85 (s, 3H), 0.86 (s, 3H), 0.86 (s, 3H), 0.89 – 2.07 (m, 24H), 1.12 (s, 3H), 1.24 (s, 3H), 2.02 (s, 3 H), 2.03 (s, 3 H), 2.09 – 2.20 (m, 2H), 6.19 (dd,  $J = 11.7, 5.8$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 15.1 ( $\text{CH}_3$ ), 15.3 ( $\text{CH}_3$ ), 18.2 ( $\text{CH}_2$ ), 18.3 ( $\text{CH}_2$ ), 20.4 ( $\text{CH}_2$ ), 20.9 ( $\text{CH}_2$ ), 21.0 ( $\text{CH}_3$ ), 21.4 ( $\text{CH}_3$ ), 22.8 ( $\text{CH}_3$ ), 23.0 ( $\text{CH}_3$ ), 30.0 ( $\text{CH}_2$ ), 30.3 ( $\text{CH}_2$ ), 33.0 (C), 33.1 (C), 33.4 ( $\text{CH}_3$ ), 33.5 ( $\text{CH}_3$ ), 36.0 (C), 36.1 (C), 39.5 ( $\text{CH}_2$ ), 39.6 ( $\text{CH}_2$ ), 39.9 ( $\text{CH}_2$ ), 40.0 ( $\text{CH}_2$ ), 42.3 ( $\text{CH}_2$ ), 42.4 ( $\text{CH}_2$ ), 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  $\text{cm}^{-1}$ . HRMS (EI)  $\text{M}^+$   $m/z$ : calcd for  $\text{C}_{18}\text{H}_{30}\text{O}_3$  294,2195, found: 294,2204.

4.4.30. (3*aR*,5*S*,5*aS*,9*aS*,9*bR*)-2,5-Diacetoxy-3*a*,6,6,9*a*-tetramethyldodecahydronaphtho[2,1-*b*]furan (**6c**)

Major isomer: Colorless syrup (15% ether/hexanes),  $[\alpha]_{\text{D}} = +16.6$  ( $c = 0.8$ ,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 16.6 ( $\text{CH}_3$ ), 18.1 ( $\text{CH}_2$ ), 21.5 ( $\text{CH}_3$ ), 21.8 ( $\text{CH}_3$ ), 22.0 ( $\text{CH}_3$ ), 24.1 ( $\text{CH}_3$ ), 30.3 ( $\text{CH}_2$ ), 33.4 (C), 35.4 (C), 35.8 ( $\text{CH}_3$ ), 39.9 ( $\text{CH}_2$ ), 43.7 ( $\text{CH}_2$ ), 47.1 ( $\text{CH}_2$ ), 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  $\text{cm}^{-1}$ .

Minor isomer: Colorless syrup (10% ether/hexanes),  $[\alpha]_{\text{D}} = +51.7$  ( $c = 0.9$ ,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 16.4 ( $\text{CH}_3$ ), 18.1 ( $\text{CH}_2$ ), 21.4 ( $\text{CH}_3$ ), 21.8 ( $\text{CH}_3$ ), 22.0 ( $\text{CH}_3$ ), 24.3 ( $\text{CH}_3$ ), 30.0 ( $\text{CH}_2$ ), 33.4 (C), 35.6 (C), 35.8 ( $\text{CH}_3$ ), 39.7 ( $\text{CH}_2$ ), 43.7 ( $\text{CH}_2$ ), 46.7 ( $\text{CH}_2$ ), 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  $\text{cm}^{-1}$ . HRMS (EI)  $\text{M}^+$   $m/z$ : calcd for  $\text{C}_{20}\text{H}_{32}\text{O}_5$  352,225, found: 352,231.

4.4.31. (5*aR*,7*aS*,11*aS*,11*bR*)-4-Acetoxy-5*a*,8,8,11*a*-tetramethyltetradecahydronaphtho[2,1-*b*]oxepine (**6d**)

Colorless syrup (3% ether/hexanes).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) signals assignable to the major isomer  $\delta$ : 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),  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz) signals assignable to the major isomer  $\delta$ : 16.2 ( $\text{CH}_3$ ), 18.66 ( $\text{CH}_2$ ), 20.97 ( $\text{CH}_2$ ), 21.3 ( $\text{CH}_3$ ), 21.6 ( $\text{CH}_3$ ), 22.2 ( $\text{CH}_2$ ) 24.1 ( $\text{CH}_3$ ), 26.6 ( $\text{CH}_2$ ), 33.4 ( $\text{CH}_3$ ), 35.5 ( $\text{CH}_2$ ), 39.17 ( $\text{CH}_2$ ), 39.5 ( $\text{CH}_2$ ), 42.1 ( $\text{CH}_2$ ), 56.19 (CH), 60.3 (CH), 79.5 (C), 91.6 (CH), 169.7 (C); IR (film) 1744, 1456, 1384,

1260, 1018, 800  $\text{cm}^{-1}$ . HRMS (EI)  $\text{M}^+$   $m/z$ : calcd for  $\text{C}_{20}\text{H}_{34}\text{O}_3$  322,2508, found: 322,2514.

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

Compounds **6e** and **6f** were obtained as a mixture in a 1:1 ratio.

**6e**. Colorless syrup (5% ether/hexanes).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) signals assignable to the major isomer  $\delta$ : 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz) signals assignable to the major isomer  $\delta$ : 15.6 ( $\text{CH}_3$ ), 18.7 ( $\text{CH}_2$ ), 19.9 ( $\text{CH}_2$ ), 21.4 ( $\text{CH}_3$ ), 21.5 ( $\text{CH}_3$ ), 22.2 ( $\text{CH}_3$ ), 33.2 ( $\text{CH}_2$ ), 33.3 ( $\text{CH}_3$ ), 33.4 (C), 38.3 (C), 40.0 ( $\text{CH}_2$ ), 41.7 ( $\text{CH}_2$ ), 42.3 ( $\text{CH}_2$ ), 55.9 (CH), 59.1 (CH), 81.9 (C), 92.7 (CH), 110.8 ( $\text{CH}_2$ ), 148.2 (C), 169.6 (C); IR (film): 2936, 1733, 1650, 1452, 1386, 1242, 1132, 994, 934, 756  $\text{cm}^{-1}$ . HRMS (EI)  $\text{M}^+$   $m/z$ : calcd for  $\text{C}_{21}\text{H}_{34}\text{O}_3$  334,2508, found: 334,2519.

**6f**. Colorless syrup (20% ether/hexanes),  $[\alpha]_{\text{D}} = +20.4$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 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);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 15.4 ( $\text{CH}_2$ ), 18.4 ( $\text{CH}_2$ ), 20.4 ( $\text{CH}_2$ ), 21.4 ( $\text{CH}_3$ ), 23.9 ( $\text{CH}_2$ ), 24.0 ( $\text{CH}_3$ ), 26.9 ( $\text{CH}_3$ ), 31.5 ( $\text{CH}_2$ ), 33.2 (C), 33.3 ( $\text{CH}_3$ ), 38.9 (C), 39.6 ( $\text{CH}_2$ ), 41.9 ( $\text{CH}_2$ ), 44.2 ( $\text{CH}_2$ ), 56.1 (CH), 61.6 (CH), 74.0 (C), 134.0 ( $\text{CH}_2$ ), 150.9 (C), 195.0 (CH); IR (film): 3457, 1687, 1650, 1461, 1387, 1124, 939, 756  $\text{cm}^{-1}$ . HRMS (EI)  $\text{M}^+$   $m/z$ : calcd for  $\text{C}_{19}\text{H}_{32}\text{O}_2$  292,2402, found: 292,2395.

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