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Ring-Opening of Unsymmetrical 1,2-Dioxines Using Cobalt(II) Salen Complexes

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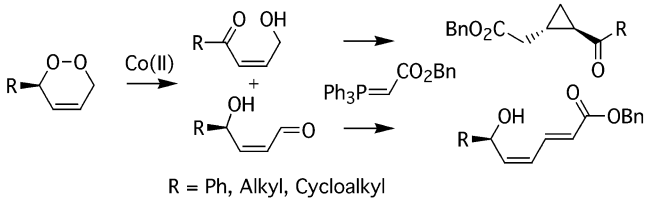


The regioselectivity of the metal-catalyzed ring opening of unsymmetrical 1,2-dioxines to *cis*-γ-hydroxyenones was investigated using two different Co(II) salen complexes. Regioselectivity was determined by direct examination of the enone ratios and by derivitization with a stabilized phosphorus ylide. The steric influence of the substituents on the 1,2-dioxine was the primary influence on regioselectivity. Temperature played little role; however, solvent and selection of Co(II) complex could be used to mildly influence the outcome of the rearrangement for selected substrates. The origins of the selectivity for the reaction are discussed.

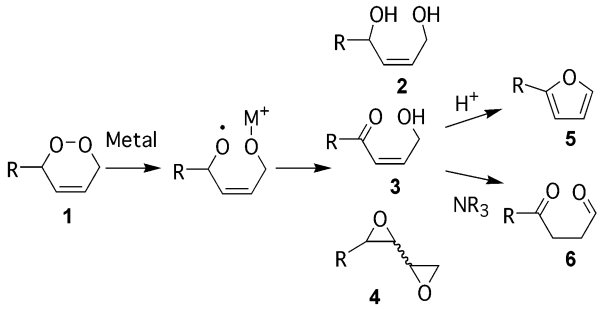
Introduction

1,2-Dioxines **1** are an important class of compounds as they are easily prepared and synthetically useful for the introduction of 1,4-oxygen functionality into organic molecules.[1−3] As a result of their weak peroxide linkage 1,2-dioxines can ring open by either homolytic or heterolytic processes to yield mixtures of 1,4-diols **2**, *cis*-γ-hydroxyenones (HEOs) **3**, and bisepoxides **4**, Scheme 1. The types of reaction products obtained are closely associated with the process by which they were generated.

Heterolytic cleavage of the peroxide bond is generally induced by removal of an α-proton by base in an E_2-like mechanism and yields exclusively HEOs, which often undergo further chemistry.[4−6]

Homolytic cleavage of the peroxide linkage may be induced by heat, light, and also transition metal catalysis and may yield mixtures of all three products (Scheme 1).[1] Transition metals react with 1,2-dioxines by a one-electron redox process whereby homolytic cleavage of the peroxide bond occurs upon addition of the metal, giving an oxygen-centered radical and a metal−oxygen bond (Scheme 1).[7] The oxy-radical can undergo disproportionation, 1,5-hydrogen abstraction, or 1,2-addition, yielding **2**, **3**, and **4**, respectively.[8]

SCHEME 1



The ring-opening reactions of 1,2-dioxines **1** with Fe(II),[9,10] Ru(II),[8] Pd(0),[11−13] and Co(II)[14−21] have been

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previously studied. In the case of bicyclic 1,2-dioxines, the reaction usually yields bisepoxides as a result of the inability of the intermediate oxy radicals to undergo 1,5-hydrogen abstraction. For monocyclic 1,2-dioxines, product ratios are closely related to the structure of the substrate and type of metal used. Ru(II) affords good yields of bisepoxides, whereas Co(II) is more selective for HEO formation.[8,14]

A complication when examining the ring opening of 1,2-dioxines derives from the instability of the products. In some strained or cyclic systems HEOs are stable; however, open chain HEOs undergo facile dehydration to furans[22−24] and rearrangement to 1,4-diketones[6,25] under mildly acidic and basic conditions, respectively (Scheme 1). The reported furan and diketone products from the transition metal ring openings of 1,2-dioxines thus imply the intermediacy of the HEO and isomeric hemiketal. An important consequence is that after dehydration to furan or rearrangement to diketone, all information on the regioselectivity of the ring opening is lost. Thus, for determination of the regioselectivity of the reaction of unsymmetrical 1,2-dioxines with transition metals it is necessary to either trap the intermediate HEO as a stable derivative or to characterize the mixtures without isolation.

The characterization of a single HEO and its *cis* and *trans* hemiketals generated from a symmetrical 1,2-dioxine using Co(II)TPP was first carried out by Foote and O'Shea using 2D ^{1}H NMR.[14] We have since reported the characterization of several HEOs generated from unsymmetrical 1,2-dioxines under basic conditions and from symmetrical 1,2-dioxines using Co(II)(salen)$_2$ catalysis.[6] Until recently, HEOs have found no synthetic utility other than in furan synthesis because of their transient nature, and consequently, the regioselectivity of the Co(II)-catalyzed ring opening for unsymmetrical 1,2-dioxines has not been investigated.

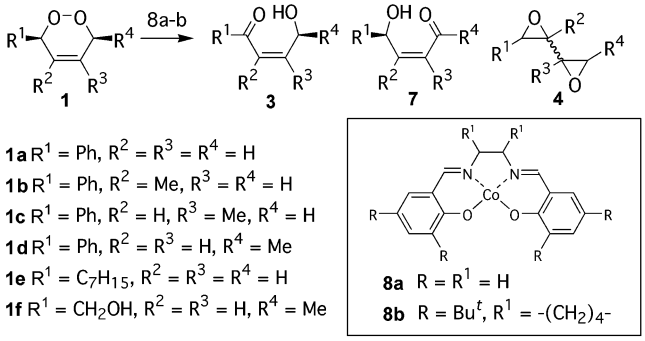
We have recently reported reactions of HEOs generating cyclopropanes,[6,26] γ-lactones,[27] and tetrahydrofurans[28] and have used Co(II) as a catalyst in these transformations. We now report on the regioselectivity of the Co(II)-catalyzed ring opening of unsymmetrical 1,2-dioxines both by direct examination of HEO ratios using NMR and by derivitization with stabilized phosphorus ylides.

TABLE 1. Product Distribution from Rearrangement of 1a−f with 8a,b

entry[a]	1,2-dioxine	catalyst	solvent	temp	ratio (**3**:**7**:**4**)[b]
1	**1a**	**8a**	$CDCl_3$	rt	24:71:5
2	**1a**	**8a**	THF	rt	21:77:2
3	**1a**	**8b**	$CDCl_3$	rt	32:64:4
4	**1a**	**8b**	CH_2Cl_2	−10	26:71:3
5	**1a**	**8b**	THF	rt	23:74:2
6	**1a**	**8b**	THF	−78	24:75:1
7[c]	**1a**	NEt_3	$CDCl_3$	rt	100:0:0
8	**1b**	**8a**	$CDCl_3$	rt	0:>95:0
9[d]	**1c**	**8a**[e]	$CDCl_3$	rt	15:63:11
10	**1c**	NEt_3	$CDCl_3$	rt	100:0:0
11	**1d**	**8a**	$CDCl_3$	rt	30:65:5
12	**1d**	**8b**	$CDCl_3$	rt	45:49:6
13	**1d**	**8b**	THF	rt	52:42:6
14[c]	**1d**	NEt_3	$CDCl_3$	rt	100:0:0
15	**1e**	**8a**	$CDCl_3$	rt	17:70:13
16	**1f**	**8a**	$CDCl_3$	rt	*f*:82[g]:tr

[a] Reactions were performed on 20 mg of 1,2-dioxine in 0.7 mL of solvent with 1.0−2.0 mol % catalyst. [b] Ratios were determined by ^{1}H NMR and represent a composite of the *cis*/*trans* hemiketal/HEO mixtures. [c] See ref 6. [d] 11% Decomposition to furan had occurred at the time of measurement. [e] **8a**·H_2O was used for the rearrangement. [f] Not detectable. [g] Absolute yield determined using phenyltrimethylsilane as internal standard.

SCHEME 2



Results and Discussion

Dioxines **1a**−**h** were chosen for this study for their ease of synthesis and because they contain combinations of groups with varying steric and electronic properties. The 1,2-dioxines were synthesized by the Rose Bengal sensitized addition of singlet oxygen to 1,3-butadienes using a previously published procedure[29,30] and are numbered so that R^1 is on the more sterically hindered side of the molecule.

The 1,2-dioxines **1a**−**f** were allowed to react with low spin square planar Co(II) salen complexes **8a,b** in $CDCl_3$, CH_2Cl_2 or THF to furnish either HEO **3** or HEO (*cis*-γ-hydroxyenal) **7** and small amounts of bisepoxides **4**, Table 1 and Scheme 2. As the product HEOs were unstable, they were characterized without isolation using COSY, ROESY, HMBC, and HMQC 2D NMR experiments. From these experiments, it was possible to assign the resonances within the ^{1}H and ^{13}C 1D spectra to either **3** or **7**.

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SCHEME 3

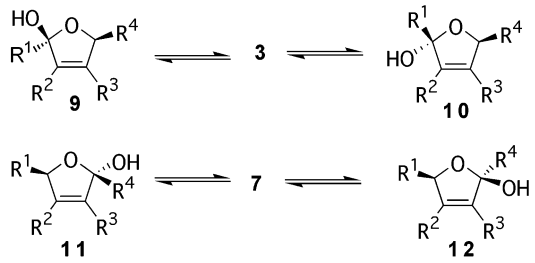

TABLE 2. Ratios of HEO/Cyclic Hemiketals Measured in $CDCl_3$ at 25 °C

dioxine	**3**:(**9**:**10**)[a]	**7**:(**11**:**12**)[a]
1a	93:7[b]	0:(49:51)
1b		0:48:52
1c	86:14[b]	0:(50:50)
1d	78:(11:11)	12:(43:45)
1e	78:22[b]	0:(50:50)
1f		12:16:72

[a] Brackets indicate that no distinction could be made between **11** and **12**. [b] Only a single hemiketal is formed upon cyclization.

Both **3** and **7** existed in equilibrium with their cyclic hemiketal (hemiacetal) anomeric mixtures **9**−**12**, and so the ratios in Table 1 represent a composite of the acyclic and cyclic isomers, Scheme 3. The relative ratios of the cyclic and acyclic isomers measured in $CDCl_3$ are given in Table 2. It was not possible to assign aryl resonances in the ^{13}C NMR of the HEO/hemiketal mixtures to specific isomers, and so aryl ^{13}C resonances were not assigned. Furthermore, only substituents attached to C2 and C5 of the cyclic hemiketals could be used to obtain diagnostic through space interactions that could be used to identify the anomer as either *cis* or *trans*. The 2D ROESY NMR of hemiketals **9**−**12** generally lacked through-space interactions between OH groups and substituents on the ring, and only **11b/12b** and **11f/12f** could be assigned as *cis* and *trans*.

In the ^1H NMR spectrum obtained from the reaction of **1a** the relative ratios of all products (**3a**, **7a**, and **4a**) could be quantified; however, it was not possible to differentiate the two cyclic hemiacetals **11a** and **12a** and so the two are quoted as a mixture. The presence of bisepoxides could be deduced from resonances in the ^1H NMR at δ 2.5−4.0 and in the ^{13}C NMR from resonances at δ 50−60 ppm. As only minor quantities of these products were seen in the reactions of **1**, their isolation and characterization was not attempted.

The reaction of **1b** was the most selective of all the 1,2-dioxines, giving solely **7b** (Table 1, entry 8). Decomposition of the ring-opened products obtained from **1c** to furan was a significant problem (entry 9). Not only was the decomposition fast, but also the decomposition of **3c** was significantly faster than that of **7c**, which may have introduced greater error in the reported ratio.

It was thought that the steric influences of the substituents on the course of the reaction could be increased if a more substituted ligand was used. Catalyst **8b** is a selective catalyst for the hydrolytic kinetic resolution of terminal epoxides and other asymmetric processes.[31,32] The reaction of **8b** with 1,2-dioxines proceeded at a rate much faster than that of **8a**. Contrary to what was expected, **8b** decreased the steric influence of substituents on the course of the reaction for **1d**, although no such effect was seen on **1a** (compare entries 1 with 3 and 11 with 12). The decreased selectivity may be due to an altered redox potential of the Co(II) center.[33,34] It should be noted that catalyst **8b** performs poorly in the desymmetrization of *meso*-1,2-dioxines.[16]

A small solvent effect was seen in the ring-opening reaction. The ring opening of **1d** was more sensitive to the steric influences of substituents in chlorinated solvents than in THF (compare entry 12 with 13), but little effect was seen in the reaction of **1a** (entries 1 and 2). Temperature had a small effect on the ratios of products obtained from the reaction. Catalyst solubility was an issue and limited the solvents that could be tested at low temperature.

When the rearrangement of **1** is catalyzed by base, the regioselectivity is governed by the acidity of the proton to be removed (entries 7, 10, and 14). The ratios in Table 2 demonstrate that when the ring opening is catalyzed by Co(II), selectivity is governed by the steric size of substituents. This means that alternate HEO isomers (either **3** or **7**) may be obtained by selecting conditions that make use of either steric or acidity differences within the 1,2-dioxine.

Reaction of Ring-Opened Products 3 and 7 with Stabilized Phosphorus Ylides. Stabilized phosphorus ylides react with HEOs to afford cyclopropanes[6] and with aldehydes to give α,β-unsaturated esters, both in near quantitative yield. Stabilized phosphorus ylides were therefore an ideal reagent to derivitize **3** and **7** so that isolable compounds could be obtained and to ensure that product assignments were accurate. When the mixtures of **3** and **7** obtained from the ring opening of **1a**,**b**,**d**−**h** were allowed to react with benzyl (triphenylphosphoranylidene)acetate, smooth transformation into either the cyclopropanes **13** and **14** or dienoate **15** was seen, Scheme 4 and Table 3. The reactions of HEOs **3a,d,e,g,h** and **7d** afforded cyclopropanes by a 1,4-addition pathway, whereas α,β-unsaturated aldehydes **7a,b,e,g,h** afforded (2*E*,4*Z*)-dienoates by a 1,2-addition pathway.

Phenyl- and methyl-substituted cyclopropanes **13a,d**[35] and **13g**[3] were spectroscopically identical with previously reported material. The remaining cyclopropanes were identified using 2D ^1H and ^{13}C NMR. The two isomers **13d** and **14** were clearly distinguishable by the presence of a methyl ketone resonance in the spectra of **14**.

All dienoates **15a,b,e,g,h** were assigned as having a 2*E*,4*Z* configuration on the basis of a 15 Hz and ≈10 Hz coupling for the two double bonds. The dienoates were typically isolated containing up to 5% of the 2*Z*,4*Z* isomer, which could be removed by recrystallization. The dienoates underwent slow polymerization at room temperature or if refrigerated over several weeks.

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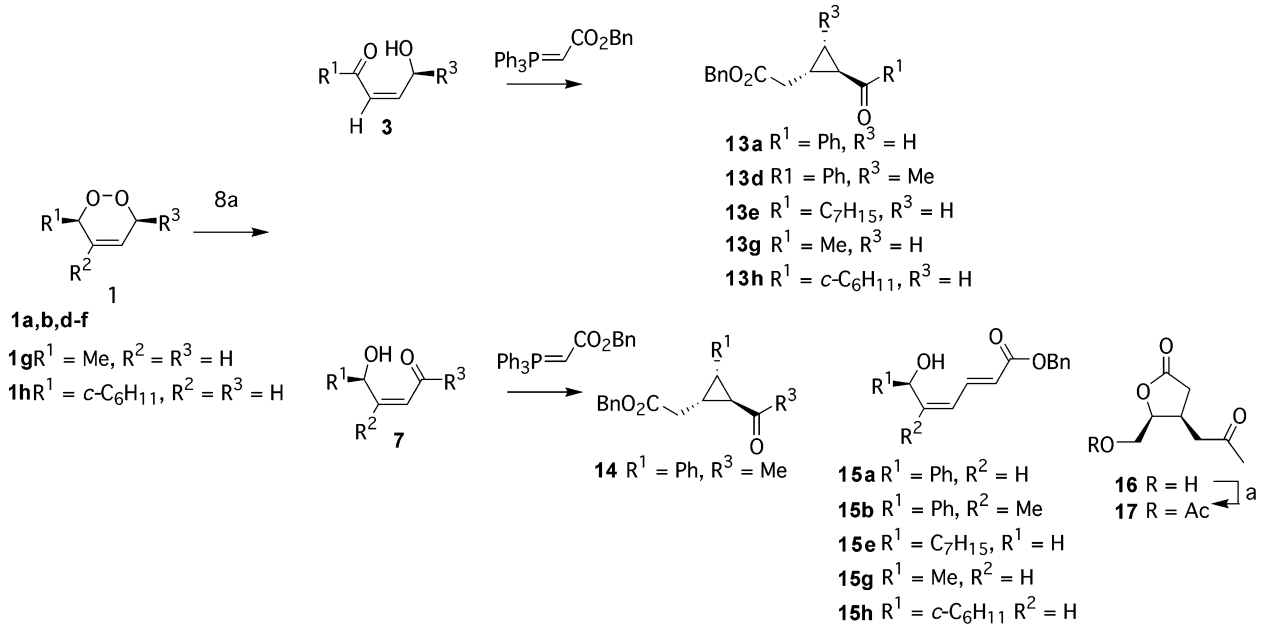
SCHEME 4[a]



[a] Reagents: (a) pyridine, Ac_2O.

TABLE 3. Reactions of 1,2-Dioxines with Benzyl (Triphenylphosphoranylidene)acetate Catalyzed by Co(II) Salen 8a

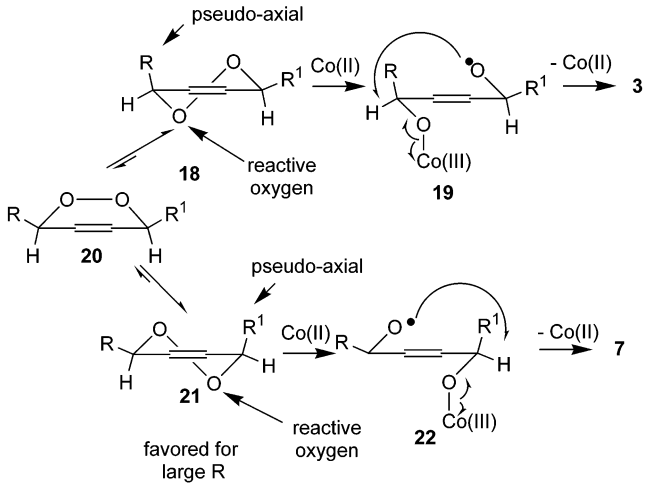
entry[a]	dioxine	derivative	yield[b]	derivative	yield[b]
1	**1a**	**13a**	18 (24)	**15a**	70 (76)
2	**1b**			**15b**	60
3	**1d**	**13d**	33 (39)	**14**	44 (61)
4[c]	**1e**	**13e**	10	**15e**	66
5[c]	**1f**			**17**	39
6	**1g**	**13g**	27[d] (37)	**15g**	58 (63)
7	**1h**	**13h**	15 (23)	**15h**	59 (77)

[a] Reactions were performed on 1.0 mmol of 1,2-dioxine with 1.0–2.0 mol % of catalyst **8a** and 1.2 mmol of benzyl triphenylphosphoranylidine acetate in CH_2Cl_2 (5 mL). [b] Yield refers to isolated yield; ratios in brackets were determined by ^{1}H NMR. [c] Ratio could not be determined accurately from the crude ^{1}H NMR. [d] Isolated as a mixture of diastereomers (*trans*:*cis* 86:14).

The reaction of hydroxymethyl-substituted 1,2-dioxine **1f** with stabilized phosphorus ylide did not give cyclopropane as expected but a hydroxymethyl *cis*-γ-lactone **16,** which was acetylated for ease of isolation. The formation of lactones from the reaction of HEOs and ylides has been previously noted and involves the hydrolysis of intermediate phosphorus-containing 1,4-addition products, in this case promoted by the γ-hydroxyl group.[28] The absolute yield of **7f** from the reaction of **1f** with **8a** was calculated from the ^{1}H NMR and found to be high (Table 1). Thus, the poor yield of **17** is attributed to the nonselective interaction of ylide and HEO.

An excellent correlation was seen between the product ratios determined by NMR experiment and by derivitization for **1a,b,d** (compare Tables 1 and 3).[36] This meant that lengthy NMR experiments with subsequent analysis was not necessary to analyze the ring opening of 3-substituted 1,2-dioxines as the ratio of cyclopropane **13** to dienoate **15** (or cyclopropane) was a good measure of the selectivity.

SCHEME 5



Mechanistic Model

Unsymmetrical 1,2-dioxines exist in two nonequivalent half-chair conformations **18** and **21** in equilibrium with a half-boat conformation **20** (Scheme 5).[37–39] These conformations may be observed using NMR when solutions of 1,2-dioxine are cooled to −100 °C.[37] In the two nonequivalent conformations **18** and **21**, one of the R-groups adopts a pseudoequatorial position and one a pseudoaxial position as a result of the *cis* nature of substitution on the 1,2-dioxine. The oxygen adjacent to

(36) Care was taken to ensure that all hydroxyenone had been consumed in the reaction as alkyl-substituted enones were slow to react by a 1,4-addition pathway.

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the pseudoequatorial position is sterically shielded by the two substituents on that face. Therefore, reactions might be expected to occur at the oxygen on the more accessible face of the 1,2-dioxine. Assuming that the relative rates of reaction of the two-half-chair conformers **18** and **21** are similar, factors that affect the relative populations of the two-half-chair conformers would be expected to influence the selectivity observed in the ring opening.

To examine the validity of this model, **1a**,**d**,**f**,**h** were examined by ^{1}H NMR at low temperature.[40] When cooled to −97 °C, slow equilibration of the two-half-chair conformers for **1a,d,h** was observed. The low-temperature ^{1}H NMR of **1a** had diagnostic peaks overlapping and so could not be used to determine the conformational preference of the molecule. 1,2-Dioxine **1h** showed a clear preference for the large cyclohexyl group to exist in a pseudoequatorial position with a 33:67 ratio of **18** and **21**.[41] This is similar to the ratio of products seen after adduction with ylide (Table 3). In the case of **1d**, a 31:69 ratio of two conformers was observed. Assignment of the two-half-chair conformers based on chemical shift[8,37,41] indicated that the methyl group in **1d** preferentially adopted a psuedoequatorial position. Thus although the conformational equilibria for **1h** could support a conformation-dependent mechanism, the conformational equilibria of **1d** does not. Thus it is unlikely that conformation is the sole determining factor for the selectivity of the reaction.

To summarize, the Co(II)-mediated ring opening of 1,2-dioxines is a process that may be used to generate HEOs regioselectively from unsymmetrical monocyclic 1,2-dioxines when there is a large steric difference in the substituents on the dioxine ring. The major HEO isomers are those with the γ-hydroxyl function on the more sterically hindered side of the 1,2-dioxine. This means that (*Z*)-4-hydroxyenals may be prepared from 3-substituted 1,2-dioxines in moderate yield. We have described the trapping of the HEOs with ylide and found that the product ratios reflect the HEO/enal ratios before trapping. We have used the process to prepare (2*E*,4*Z*)-6-hydroxy-2,4-dienoates in moderate yield. The results obtained for the reaction may help predict the ring-opening outcomes from other novel 1,2-dioxines.

Experimental Section

3-Heptyl-3,6-dihydro-1,2-dioxine, 1e. A solution of 1,3-undecadiene (930 mg, 6.1 mmol) and Rose Bengal (100 mg) in CH_2Cl_2 (100 mL) cooled to 0−5 °C was irradiated for 5 h with three 500-W tungsten lamps. The solvent was then removed in vacuo, and purification by flash chromatography afforded unreacted starting diene (317 mg, 34%) and **1e** (334 mg, 30%): R_f 0.70 (90:10 hexane/ethyl acetate); IR (neat) 3043, 2927, 1466, 1378, 1037 cm^{-1}; ^{1}H NMR (300 MHz) δ 0.86 (t, J = 6.6 Hz, 3H), 1.20−1.70 (m, 12H), 4.40−4.46 (m, 1H), 4.58−4.60 (m, 2H), 5.85−6.0 (m, 2H); ^{13}C NMR (50 MHz) δ 14.0, 22.5, 25.1, 29.0, 29.4, 31.7, 32.6, 69.7, 78.6, 123.8, 128.1; EIMS *m/z* 166 ($M^+ - H_2O$, 3), 153 (20), 97 (20), 41 (100); HRMS calcd for (M + Na^+, ESI) $C_{11}H_{20}O_2Na$ 207.1360, found 207.1358.

General Procedure for the Co(II)-Catalyzed Rearrangement of 1,2-Dioxines. To a solution of Co(II) catalyst (1−2 mg) dissolved in $CDCl_3$ (0.7 mL) was added 1,2-dioxine (20 mg). The consumption of 1,2-dioxine was monitored using ^{1}H NMR and TLC, and when complete the solution was allowed to attain ambient temperature and equilibrate for 1 h before measuring isomeric ratios. The mixtures could be stored for a short period of time (1−2 days, −15 °C) without undergoing severe decomposition. In all cases, dehydration to furan occurred after prolonged storage but could be slowed if trace acid was removed from the chloroform by passage through a short Al_2O_3 column before use.

(*Z*)-4-Hydroxy-1-phenyl-2-buten-1-one, 3a.[6] ^{1}H NMR (600 MHz) δ 3.15 (br s, 1H), 4.60 (dd, J = 5.1, 1.5 Hz, 2H), 6.63 (dt, J = 12.0, 5.1 Hz, 1H), 7.01 (dt, J = 12.0, 1.5 Hz, 1H), 7.25−7.29 (m, 3H), 7.97−8.00 (m, 2H); ^{13}C NMR (150 MHz) δ 61.1, 123.7, 128.5, 128.7, 133.2, 137.7, 147.8, 191.9.

5-Phenyl-2,5-dihydro-2-furanol, 11a/12a. Mixture of two anomers; ^{1}H NMR (600 MHz) δ 3.09−3.09 (m, D_2O exch., 1H), 3.20−3.28 (m, D_2O exch., 1H), 5.71 (br d, J = 1.2 Hz, 1H), 5.92−5.94 (m, 2H), 5.96 (ddd, J = 6.0, 2.4, 1.2 Hz, 1H), 6.17−6.21 (m, 3H), 6.30 (br s, 1H), 7.25−7.39 (m, 10H); ^{13}C NMR (150 MHz, partial) δ 86.7, 87.4, 103.2, 103.4.

(±)-(*R*,*R*)-4-Methyl-5-phenyl-2,5-dihydro-2-furanol, 11b. ^{1}H NMR (600 MHz) δ 1.61 (br s, 3H), 2.84 (br d, J = 8.4 Hz, exch. D_2O, 1H), 5.64 (m, 1H), 5.66 (m, 1H), 6.26 (dd, J = 4.2, 8.4 Hz, 1H), 7.21−7.37 (m, 5H); ^{13}C NMR (150 MHz) δ 12.0, 89.2, 103.1, 122.5, 126.7, 128.2, 129.1, 139.3, 145.1.

(±)-(*R*,*S*)-4-Methyl-5-phenyl-2,5-dihydro-2-furanol, 12b. ^{1}H NMR (600 MHz) δ 1.61 (br s, 3H), 3.03 (br d, J = 7.1 Hz, exch D_2O, 1H), 5.40 (dd, J = 1.0, 1.0 Hz, 1H), 5.60 (m, 1H), 6.12 (dq, J = 7.1, 1.2 Hz, 1H), 7.21−7.37 (m, 5H); ^{13}C NMR (150 MHz) δ 12.2, 89.9, 102.8, 122.0, 122.1, 126.9, 128.1, 139.8, 144.6. IR (neat, mixture) 3375, 2918, 1670 (weak), 1454, 1118, 1007 cm^{-1}; MS (GCQ, mixture **11b/12b**) *m/z* 175 (trace, $M^+ - H$), 158 (100, $M^+ - H_2O$).

(*Z*)-4-Hydroxy-3-methyl-1-phenyl-2-buten-1-one, 3c. ^{1}H NMR (200 MHz) δ 2.12 (d, J = 1.2 Hz, 3H), 3.60−4.40 (br s, exch. D_2O, 1H), 4.38 (br s, 2H), 6.89 (s, 1H), 7.1−7.6 (m, 3H), 7.91−7.98 (m, 2H); ^{13}C NMR (50 MHz) δ 24.2, 63.6, 122.2, 128.4, 128.5, 132.8, 138.2, 161.4, 191.9.

4-Methyl-2-phenyl-2,5-dihydro-2-furanol, 9c. ^{1}H NMR (200 MHz) δ 1.80 (d, J = 1.8 Hz, 3H), 4.59 (d, J = 13.5 Hz, 1H), 4.75 (d, J = 13.5 Hz, 1H), 5.60 (q, J = 1.2 Hz, 1H), 7.10−7.60 (m, 5H), (OH not assigned).

3-Methyl-5-phenyl-2,5-dihydro-2-furanol, 11c/12c. Major anomer: ^{1}H NMR (600 MHz) δ 1.83 (s, 3H), 3.40 (br s, exch. D_2O, 1H), 5.63 (br s, 1H), 5.73 (m, 1H), 5.91 (br s, 1H), 7.22−7.40 (m, 5H); ^{13}C NMR (150 MHz, partial) δ 11.7, 86.2, 104.6, 136.6, 141.1. Minor anomer: ^{1}H NMR (600 MHz) δ 1.83 (s, 3H), 3.39 (br s, exch. D_2O, 1H,), 5.73 (m, 1H), 5.85 (m, 1H), 6.02 (d, J = 2.6 Hz, 1H), 7.22−7.40 (m, 5H); ^{13}C NMR (150 MHz, partial) δ 11.7, 86.6, 104.9, 136.9, 140.7.

(*Z*)-4-Hydroxy-1-phenyl-2-penten-1-one, 3d. ^{1}H NMR (600 MHz) δ 1.40 (d, J = 6.6 Hz, 3H), 3.50 (br s, exch. D_2O, 1H), 4.88 (dddq, J = 6.6, 6.6, 3.6, 1.2, 1H), 6.43 (dd, J = 12.0, 6.6 Hz, 1H), 6.92 (dd, J = 12.0, 1.2 Hz, 1H), 7.20−7.45 (m, 5H); ^{13}C NMR (150 MHz) δ 22.2, 64.7, 124.5, 131.0, 137.5, 152.8, 192.4, (1 masked aromatic).

(*Z*)-5-Hydroxy-5-phenyl-3-penten-2-one, 7d. ^{1}H NMR (600 MHz) δ 2.28 (s, 3H), 3.85 (br s, exch. D_2O, 1H), 5.92 (dd, J = 6.0, 4.2 Hz, 1H), 6.24 (d, J = 12 Hz, 1H), 6.30 (dd, J = 12.0, 6.0 Hz, 1H), 7.2−7.6 (m, 5H); ^{13}C NMR (150 MHz, partial) δ 31.3, 70.1, 126.4, 133.0, 200.3.

2-Methyl-5-phenyl-2,5-dihydro-2-furanol, 11d/12d. Major anomer: ^{1}H NMR (600 MHz) δ 1.65 (s, 3H), 2.74 (br s, exch. D_2O, 1H), 5.72 (dd, J = 1.8, 1.8 Hz, 1H), 5.94 (dd, J = 6.0, 1.8 Hz, 1H), 6.08 (dd, J = 6.0, 1.8 Hz, 1H), 7.20−7.60 (m, 5H); ^{13}C NMR (150 MHz, partial) δ 26.3, 86.4, 109.9, 140.6. Minor anomer: ^{1}H NMR (600 MHz) δ 1.72 (s, 3H), 2.79 (br s, exch. D_2O, 1H), 5.87 (br s, 1H), 5.96 (dd, J = 6.0, 2.4 Hz, 1H), 6.06 (dd, J = 6.0, 1.2 Hz, 1H), 7.20−7.60 (m, 5H); ^{13}C NMR (150 MHz, partial) δ 26.8, 86.2, 109.9, 139.9.

(*Z*)-1-Hydroxy-2-undecen-4-one, 3e. ^{1}H NMR (600 MHz) δ 0.87 (t, J = 6.9 Hz, 3H), 1.24−1.53 (m, 10H), 2.51 (t, J = 7.2

(40) **1a,d,g** coalesced at −60 to −70 °C. No low-temperature coalescence was observed for **1f** down to −80 °C.

(41) The two-half-chair conformers were assigned on the basis of a downfield shift of the axial protons; see ref 37.

Hz, 2H), 3.42 (br s, exch. D_2O, 1H), 4.48 (br s, 2H), 6.26 (dt, J = 12.0, 1.8 Hz, 1H), 6.34 (dt, J = 12.0, 5.4 Hz, 1H); ^{13}C NMR (150 MHz, partial) δ 43.9, 60.8, 127.1, 202.8

2-Heptyl-2,5-dihydro-2-furanol, 9e. ^{1}H NMR (600 MHz, partial) δ 0.87 (t, J = 6.9 Hz, 3H), 1.24−1.64 (m, 12H), 4.54 (ddd, J = 14.4, 1.8, 1.8 Hz, 1H), 4.72 (ddd, J = 14.4, 2.4, 1.8 Hz, 1H), 5.80 (ddd, J = 6.0, 2.4, 1.8 Hz, 1H), 6.12 (ddd, J = 6.0, 1.8, 1.8 Hz, 1H); ^{13}C NMR (150 MHz, partial) δ 73.8, 129.9, 130.0

5-Heptyl-2,5-dihydro-2-furanol, 11e/12e. Major anomer: ^{1}H NMR (600 MHz) δ 0.87 (t, J = 6.9 Hz, 3H), 1.24−1.50 (m, 10H), 1.60 (dt, J = 7.2 Hz, 2H), 2.91 (br d, J = 6.6 Hz, exch. D_2O, 1H), 4.67 (dt, J = 4.2, 1.8 Hz, 1H), 5.83 (ddd, J = 6.0, 2.1, 1.2 Hz, 1H), 6.00 (br d, J = 6.6 Hz, 1H), 6.12−6.14 (m, 1H); ^{13}C NMR (150 MHz, partial) δ 36.9, 85.6, 102.8, 127.7, 135.2. Minor anomer: ^{1}H NMR (600 MHz) δ 0.87 (t, J = 6.9 Hz, 3H), 1.24−1.45 (m, 10H), 1.52−1.56 (m, 2H), 3.05 (br s, exch. D_2O, 1H), 4.94−4.97 (m, 1H), 5.84 (ddd, J = 6.0, 2.4, 1.2 Hz, 1H), 6.07 (br s, 1H), 6.12−6.14 (m, 1H); ^{13}C NMR (150 MHz, partial) δ 35.3, 84.9, 102.6, 127.7, 135.2.

(*Z*)-5,6-Dihydroxy-3-hexen-2-one, 7f. ^{1}H NMR (600) δ 2.27 (s, 3H), (2 masked aliphatic protons), 2.40−2.60 (br s, exch. D_2O, 2H), 4.81−4.84 (m, 1H), 6.17 (dd, J = 11.4, 6.6 Hz, 1H), 6.32 (dd, 11.4, 1.8 Hz, 1H); ^{13}C NMR (150) δ 31.2, 65.3, 68.0, 128.5, 147.1, 200.4.

(±)-(2*S*,5*S*)- 5-(Hydroxymethyl)-2-methyl-2,5-dihydro-2-furanol, 11f. ^{1}H NMR (600) δ 1.60 (s, 3H), 3.50 (br s, exch. D_2O, 1H) 3.54 (dd, J = 11.4, 5.4 Hz, 1H), 3.71 (ddd, J = 11.4, 2.4, 2.4 Hz, 1H), 4.40 (br s, exch. D_2O, 1H), 4.98−5.00 (m, 1H), 5.93 (obscured, 1H), 5.96 (dd, J = 6.0, 1.2 Hz, 1H); ^{13}C NMR (150) δ 26.9, 64.6, 85.3, 109.7, 129.6, 133.0.

(±)-(2*S*,5*R*)- 5-(Hydroxymethyl)-2-methyl-2,5-dihydro-2-furanol, 12f. ^{1}H NMR (600) δ 1.58 (s, 3H), 3.50 (br s, exch. D_2O, 1H), 3.57 (dd, J = 12.0, 2.4 1H), 3.78 (dd, 12.0, 3.0 Hz, 1H), 4.40 (br s, exch. D_2O, 1H), 4.82−4.84 (m, 1H), 5.87 (dd, J = 6.0, 1.8 Hz, 1H), 5.92 (dd, J = 6.0, 2.4 Hz, 1H); ^{13}C NMR (150) δ 25.2, 62.2, 85.0, 106.1, 128.7, 133.4.

General Procedure for the Derivitization of HEOs with Stabilized Phosphorus Ylide. To a stirred solution of Co(II) catalyst (7 mg, 0.02 mmol) in CH_2Cl_2 (5 mL) was added 1,2-dioxine (1 mmol) at ambient temperature. The red solution immediately turned a brown color, and the consumption of 1,2-dioxine was monitored using TLC. After complete rearrangement, benzyl (triphenylphosphoranylidene)acetate (492 mg, 1.2 mmol) was added, and the mixture was left to stir for 1−14 days until all intermediate HEO had been consumed (TLC, ^{1}H NMR). The solvent was then removed in vacuo, and products were purified as specified.

(±)-Benzyl 2-[(1*R*,2*S*)-2-octanoylcyclopropyl]acetate, 13e. Colorless oil purified by successive flash chromatography; R_f 0.60 (70:30 hexane/ethyl acetate); IR (neat) 2928, 2851, 1731, 1698, 1455, 1259, 1167 cm^{-1}; ^{1}H NMR (300 MHz) δ 0.80 (ddd, J = 8.1, 6.3, 4.2 Hz, 1H), 0.87 (t, J = 6.6 Hz, 3H), 1.26−1.32 (m, 10H), 1.53−1.58 (m, 1H), 1.63−1.73 (m, 1H), 1.81 (ddd, J = 8.1, 4.5, 4.2 Hz, 1H), 2.25 (dd, J = 15.9, 7.8 Hz, 1H), 2.39−2.55 (m, 3H), 5.11−5.14 (m, 2H), 7.32−7.38 (m, 5H); ^{13}C NMR (75 MHz) δ 14.0, 16.6, 20.1, 22.5, 23.8, 27.4, 29.0, 29.1, 31.6, 37.9, 43.6, 66.4, 128.1, 128.2, 128.5, 135.8, 171.6, 209.5; MS (EI) *m/z* 316 (M$^+$, 5), 232 (80), 91 (100); HRMS calcd for (M + Na$^+$, ESI) $C_{20}H_{28}O_3Na$ 339.1936, found 339.1936.

(±)-Benzyl 2-[(1*R*,2*S*)-2-cyclohexylcarbonyl)cyclopropyl]acetate, 13h. Colorless oil purified by flash chromatography; R_f 0.50 (80:20 hexane/ethyl acetate); IR (neat) 2930, 2854, 1737, 1691, 1449, 1403, 1169, 698 cm^{-1}; ^{1}H NMR (600 MHz) δ 0.78 (ddd, J = 8.4, 5.6, 4.2, 1H), 1.15−1.35 (m, 6H), 1.62−1.68 (m, 2H), 1.74−1.77 (m, 2H), 1.84−1.89 (m, 3H), 2.24 (dd, J = 15.6 8.4, 1H), 2.42 (dddd, J = 10.8, 10.8, 3.6, 3.6 Hz, 1H), 2.50 (dd, J = 15.6, 6.0 Hz, 1H); 5.10−5.14 (m, 2H), 7.31−7.37 (m, 5H); ^{13}C NMR (50 MHz) δ 16.6, 20.1, 25.5, 25.6, 25.8, 25.9, 28.2, 28.2, 37.9, 51.3, 66.3, 128.1, 128.2, 128.5, 135.7, 171.5, 211.9; EIMS *m/z* 300 (M$^+$, 20), 259 (15), 91 (100); HRMS calcd for (M + Na$^+$, ESI) $C_{19}H_{24}O_3Na$ 323.1623, found 323.1619.

(±)-Benzyl 2-[(1*S*,2*R*,3*R*)-2-acetyl-3-phenylcyclopropyl]-acetate, 14. Colorless oil; R_f 0.25 (CH_2Cl_2); IR (neat) 3031, 1737, 1698, 603, 1498, 1421, 1356, 1164, 699 cm^{-1}; ^{1}H NMR (300 MHz) δ 2.03−2.14 (m, 2H), 2.26−2.36 (m, 2H), 2.28 (s, 3H), 2.91 (dd, J = 8.1 Hz, 1H), 5.06 (d, J = 12.4 Hz, 1H), 5.08 (d, J = 12.4 Hz, 1H), 7.13−7.38 (m, 10H); ^{13}C NMR (75 MHz) δ 26.4, 30.6, 32.5, 32.8, 33.1, 66.3, 126.9, 128.2, 128.2, 128.3, 128.5, 128.7, 135.4, 135.7, 171.7, 206.3; EIMS *m/z* 308 (M$^+$, 5), 290 (10), 217 (10), 91 (100). Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 77.97; H, 6.64.

Benzyl (2*E*,4*Z*)-6-Hydroxy-6-phenyl-2,4-hexadienoate, 15a. Colorless oil purified by successive flash chromatography; R_f 0.26 (70:30 hexane/ethyl acetate); IR (neat) 3418, 3031, 1713, 1638, 1269, 1168, 1026 cm^{-1}; ^{1}H NMR (200 MHz) δ 2.33 (br d, J = 3.0 Hz, 1H), 5.19 (s, 2H), 5.75 (br dd, J = 9.0, 3.0 Hz, 1H), 5.91−6.03 (m, 2H), 6.25 (dd, J = 10.8, 11.6 Hz, 1H), 7.33−7.44 (m, 10H), 7.87 (ddd, J = 15.4, 11.6, 1.0 Hz, 1H); ^{13}C NMR (150 MHz) δ 66.3, 69.8, 123.2, 125.6, 125.9, 126.6, 126.6, 127.7, 128.1, 128.1, 128.5, 128.6, 135.8, 139.0, 140.9, 142.2, 166.6; MS (EI) *m/z* 294 (10), 278 (50), 263 (30), 105 (30), 91 (100); HRMS calcd for $C_{19}H_{18}O_3$ 294.1255, found 294.1247.

Benzyl (2*E*,4*Z*)-6-Hydroxy-5-methyl-6-phenyl-2,4-hexadienoate, 15b. Colorless solid purified by chromatography then recrystallization (CH_2Cl_2/hexane); mp 110 °C (softens at 92 °C); R_f 0.22 (70:30 hexane/ethyl acetate); IR (Nujol) 3414, 1678, 1626, 1603, 1292, 1157, 1044 cm^{-1}; ^{1}H NMR (300 MHz) δ 1.76 (s, 3H), 2.10 (br d, J = 3.0 Hz, 1H), 5.17−5.23 (m, 2H), 5.95 (d, J = 15.0 Hz, 1H), 5.99 (d, J = 3.0 Hz, 1H), 6.14 (dpent, J = 11.7, 0.6 Hz, 1H), 7.27−7.40 (m, 10H), 7.91 (dd, J = 15.0, 11.7 Hz, 1H); ^{13}C NMR (75 MHz) δ 18.5, 66.2, 71.1, 121.1, 125.5, 125.6, 127.4, 128.1, 128.2, 128.4, 128.5, 136.1, 139.4, 141.2, 149.0, 167.0; EIMS *m/z* 308 (M$^+$, 4), 291 (10), 201 (20), 91 (100). Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 77.71; H, 6.38.

Benzyl (2*E*,4*Z*)-6-Hydroxy-2,4-tridecadienoate, 15e. Colorless oil purified by successive flash chromatography; R_f 0.30 (70:30 hexane/ethyl acetate); IR (neat) 3412, 2928, 1711, 1640, 1607, 1455, 1269, 1168, 910, 732 cm^{-1}; ^{1}H NMR (300 MHz) δ 0.87 (t, J = 6.6 Hz, 3H), 1.23−1.70 (m, 12H), 1.73 (br s, 1H), 4.63−4.71 (m, 1H), 5.16−5.24 (m, 2H), 5.78 (ddd, J = 11.7, 9.6, 1.2 Hz, 1H), 5.96 (d, J = 15.3 Hz, 1H), 6.15 (ddd, J = 11.7, 11.7, 1.2 Hz, 1H), 7.29−7.39 (m, 5H), 7.63 (ddd, J = 15.3, 11.7, 1.2 Hz, 1H); ^{13}C NMR (75 MHz) δ 14.0, 25.1, 25.5, 29.1, 29.4, 31.7, 37.3, 66.2, 67.9, 122.7, 127.0, 128.1, 128.2, 128.5, 135.9, 139.2, 142.3, 166.6; EIMS *m/z* 316 (M$^+$, 5), 225 (30), 91 (100); HRMS calcd for $C_{20}H_{28}O_3$ 316.2038, found 316.2027.

Benzyl (2*E*,4*Z*)-6-Hydroxy-2,4-heptadienoate, 15g. Colorless oil purified by flash chromatography; R_f 0.29 (70:30 hexane/ethyl acetate); IR (neat) 3413, 2972, 1713, 1638, 1608, 1455, 1377, 1269, 1135, 1104 cm^{-1}; ^{1}H NMR (300 MHz) δ 1.30 (d, J = 6.3 Hz, 3H); 1.73 (br s, 1H), 4.84−4.93 (m, 1H), 4.93−5.19 (m, 2H), 5.82 (dddd, J = 10.8, 9.9, 0.9, 0.9 Hz, 1H), 5.96 (ddd, J = 15.0, 0.9, 0.9 Hz, 1H), 6.09 (dddd, J = 11.7, 10.8, 0.9, 0.9 Hz, 1H), 7.28−7.39 (m, 5H), 7.63 (ddd, J = 15.0, 11.7, 0.9, 1H); ^{13}C NMR (50 MHz) δ 23.4, 64.0, 66.2, 122.7, 126.1, 128.2, 128.5, 135.9, 139.0, 143.2, 166.6, (1 masked aromatic); EIMS *m/z* 232 (M$^+$, 5), 214 (20), 201 (40), 91 (100); HRMS calcd for (MH$^+$) $C_{14}H_{17}O_3$ 233.1177, found 233.1182.

Benzyl (2*E*,4*Z*)-6-Cyclohexyl-6-hydroxy-2,4-hexadienoate, 15h. Colorless solid purified by chromatography then recrystallization; mp 54−56 °C (CH_2Cl_2/hexane); R_f 0.31 (80:20 hexane/ethyl acetate); IR (Nujol) 3509, 1692, 1633, 1607, 1307, 1275, 733 cm^{-1}; ^{1}H NMR (300 MHz) δ 0.85−1.26 (m, 5H), 1.38−1.48 (m, 1H), 1.57−1.69 (m, 5H), 1.93 (d, J = 12.6 Hz, 1H), 4.40 (dd, J = 9.0, 7.2 Hz, 1H), 5.16−5.25 (m, 2H), 5.80 (dd, J = 10.2, 10.2 Hz, 1H), 5.97 (d, 15.0 Hz, 1H), 6.22 (dd, J = 11.4, 11.4 Hz, 1H), 7.32−7.39 (m, 5H), 7.62 (ddd, J = 15.0, 11.4, 0.6 Hz, 1H); ^{13}C NMR (50 MHz) δ 25.9, 26.0, 26.3, 28.5, 28.5, 43.9, 66.2, 72.1, 122.7, 127.8, 128.1, 128.5, 136.0, 139.4, 141.2, 166.6 (1 masked aromatic); EIMS *m/z* 300 (M$^+$, 10), 283 (40), 91 (100). Anal. Calcd for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05. Found: C, 75.83; H, 8.11.

(±)-[(2*R*,3*S*)-5-Oxo-3-(2-oxopropyl)tetrahydro-2-furanyl]-methyl Acetate, 17. To a stirred solution of *N,N*′-bis-(salicylidene)ethylenediaminocobalt(II) (12 mg, 0.037 mmol) in CH_2Cl_2 (10 mL) was added 1,2-dioxine **1f** (500 mg, 3.84 mmol). After 30 min benzyl (triphenylphosphoranylidene)-acetate (1.95 g, 4.7 mmol) was added, and the reaction mixture was allowed to stir for 14 days. The mixture was then evaporated, and acetic anhydride (2 mL) and pyridine (2 mL) were added. The reaction mixture was stirred for another 16 h and then concentrated in vacuo (0.01 mmHg). From the complex mixture of compounds was isolated, by flash chromatography, the major component as a colorless oil (321 mg, 39%): R_f 0.60 (ethyl acetate); IR (neat) 2960, 1782, 1744, 1714, 1422, 1366, 1237, 1168, 1049, 735 cm^{-1}; ^1H NMR (600 MHz) δ 2.09 (s, 3H), 2.19 (s, 3H), 2.30 (dd, J = 17.4, 9.6 Hz, 1H), 2.68 (dd, J = 17.4, 8.4 Hz, 1H), 2.68−2.77 (m, 2H), 3.15 (m, 1H), 4.06 (dd, J = 12.6, 4.2 Hz, 1H), 4.32 (dd, 12.6, 3.6 Hz, 1H), 4.87 (ddd, J = 7.2, 4.2, 3.6 Hz, 1H); ^{13}C NMR (150 MHz) δ 20.7, 29.8, 32.6, 33.9, 42.8, 62.9, 78.3, 170.0, 175.3, 205.7; EIMS *m/z* 215 (MH^+, 10), 154 (50), 43 (100); HRMS calcd for (MH^+) $C_{10}H_{15}O_5$ 215.0919, found 215.0919.

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Supporting Information Available: General experimental methods; VT NMR of **1a**, **1d**, and **1h**; and ^1H or ^{13}C NMR of **1e**, **13e,h**, **15a,e,g**, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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