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Epoxidation of 4-Alkylidenecyclopentenones: A Route to the 1-Oxaspiro[2.4]hept-6-en-5-one Framework

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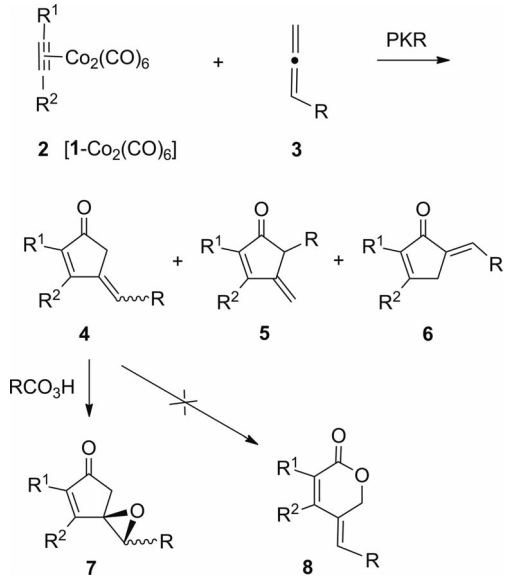
Thanks to their lack of polarity, the exocyclic double bonds of 4-alkylidenecyclopentenones **4** are selectively epoxidized by MCPBA to give spiroepoxycyclopentenones **7**, which feature the nonclassical 1-oxaspiro[2.4]hept-6-en-5-one framework. Under acidic conditions, compounds **7** undergo ring-opening to afford 4-hydroxy-4-(1-hydroxyalkyl)cyclopentenones **10**.

Introduction

4-Alkylidenecyclopentenones are rare unsaturated cyclic enones, the chemistry of which has been only little studied, unquestionably because of their very small number of synthesis procedures.[1] We recently developed a straightforward route to these cyclopentenones **4** (Scheme 1), as well as the cyclopentenone minor products **5** and **6**, through cobalt-mediated intermolecular Pauson–Khand reactions (PKRs) between alkynes **1** and allenes **3**.[2,3] Consequently, studies on their chemical reactivities and potential utility became possible.[4,5]

In another context, the 1-oxaspiro[2.4]hept-6-en-5-one (spiroepoxycyclopentenone) framework forms the structural core of several natural products such as streptazone A[6] and guaianolides related to cyclotagitinin C[7] or arborescin,[8] and also of an antitumor agent.[9] Spiroepoxycyclopentenones are also useful intermediates for the synthesis of plant-derived leads for drug discovery.[10] Consequently, we focused our attention on the epoxidation of the doubly unsaturated systems of 4-alkylidenecyclopentenones **4**. Basic epoxidation conditions (H_2O_2 + NaOH), as classically used for enones,[11] were inappropriate for these cyclopentenones **4**, which turned out to be very sensitive to basic media because of their very easy enolisation.[4] Epoxidation of α,β-enones with peroxy acids is often difficult because competitive Baeyer–Villiger oxidation leads mostly to enol esters and acyloxyoxiranes.[12] However, the exocyclic double bonds in 4-alkylidenecyclopentenones **4** did not appear to be polarized, with poor conjugation with the α,β-double bonds. Indeed, analysis of the ^{13}C NMR spectra of these compounds showed the chemical shifts of the carbon atoms of these exocyclic double bonds to be very close together.[2c,5] Consequently, because of the differences in polarity between the two double bond types, the selective epoxidation of the exocyclic double bonds in cyclopentenones **4** by use of peroxy acids seemed possible. We had already disclosed in a preliminary note that treatment of 4-alkylidenecyclopentenones **4** with a peracid does lead to spiroepoxycyclopentenones **7** (Scheme 1),[5] and not to enol lactones **8** as previously published.[13] These methodologies (PKRs of allenes, selective epoxidation) might represent valuable synthetic transformations for the preparation of cyclopentanoid natural products,[6–10,14] or for the synthesis of functionalized butenolide-type steroidal systems, which are of great medicinal therapeutic potential.[15] We therefore report here a full account of the selective epoxidation of the



Scheme 1. Pauson–Khand reactions of allenic compounds.

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exocyclic double bonds in cyclopentenones **4** and the acid-catalyzed ring-opening of the obtained spiro compounds **7**, which leads to dihydroxylated cyclopentenones **10** (Table 3).

Results and Discussion

Synthesis of 4-Alkylidenecyclopentenones

We have already described most of the starting 4-alkylidenecyclopentenones **4** (and **5**) used in this study.[2c] Some new ones were prepared by the same Pauson–Khand methodology. In particular, the functionalized 4-alkylidenecyclopentenones **4j**–**m** (shown in Table 2, below) were obtained as (*E* + *Z*) mixtures through PKRs between acetylene and the α-allenic alcohol **3d** (further acetylation of cyclopentenone **4i** gave **4j**) or the silylated allenes **3c**, **3e** and **3f**.

Previously, the *E* or *Z* configurations of the alkyl-substituted 4-alkylidenecyclopentenones **4** had been easily assigned by comparison of the ^{13}C NMR spectra of the two isomers, with both their C-3 and their C-5 carbon nuclei depending on the configurations of the exocyclic double bonds.[2c] Thus, for the new cyclopentenone **4k** (Figure 1), the C-5 carbon of isomer (*E*)-**4k** resonates at high field (δ = 37.6 ppm) relative to the analogous C signal of isomer (*Z*)-**4k** (δ = 40.5 ppm) because of the shielding due to a positive *cis* γ-effect from the allylic carbon atom (C-4)=C–**C**H$_2$.[2c,16] A similar shielding effect is observed for the C-3 (δ = 154.9 ppm) of the isomer (*Z*)-**4k**, whereas for isomer (*E*)-**4k** this C-3 signal is shifted downfield (δ = 160.9 ppm) .

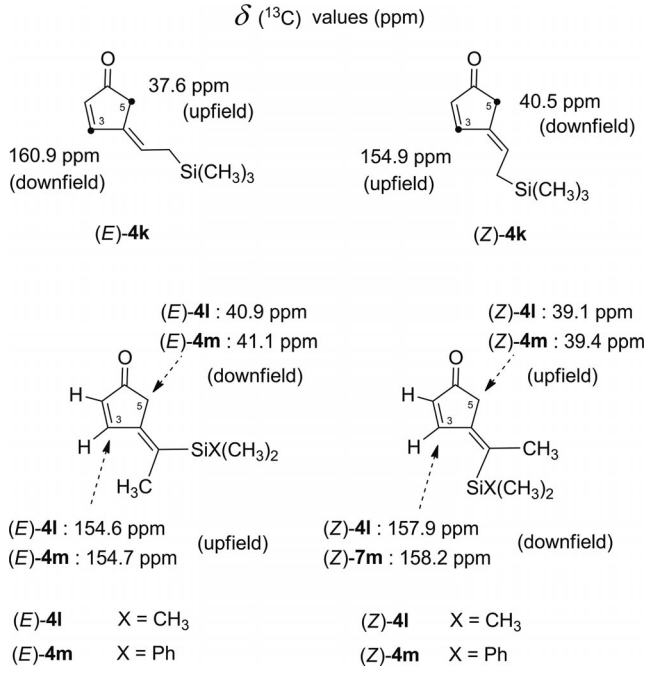


Figure 1. ^{13}C NMR data for cyclopentenones (*E*)- and (*Z*)-**4k**–**m**.

A reverse situation is observed with the silylated cyclopentenones (*E*)- and (*Z*)-**4l** and (*E*)- and (*Z*)-**4m**, because the silicon atom has been demonstrated to induce a negative γ-effect.[17] The shielding positive *cis* γ-effect of the allylic methyl group (C-4)=C(*CH$_3$*)SiX(CH$_3$)$_2$ is now more influential for the chemical shifts of both C-3 and C-5, so signal of C-5 of cyclopentenones (*E*)-**4l** and (*E*)-**4m** (δ = 40.9 and 41.1 ppm, respectively) is observed downfield, whereas for isomers (*Z*)-**4l** and (*Z*)-**4m** it is found upfield (δ = 39.1 and 39.4 ppm). Similarly, the C-3 carbon atoms are shielded in cyclopentenones (*E*)-**4l** and (*E*)-**4m**, because of the positive γ-effect of the allylic methyl group, and deshielded in isomers (*Z*)-**4l** and (*Z*)-**4m** (Figure 1).

Epoxidation of 4-Alkylidenecyclopentenones 4

The 4-alkylidenecyclopentenones **4** (and **5**) were each treated with two equivalents of *meta*-chloroperbenzoic acid (MCPBA) under classical conditions in toluene at 0–20 °C. They all gave **7** or **9** (Table 1) with unoptimized 50–86% yields. As would be expected, the (*E*)-4-alkylidenecyclopentenones (*E*)-**4c**–**h** gave *trans*-**7c**–**h** (Entries 3–8) whereas the cyclopentenone (*Z*)-**4h** afforded *cis*-**7h** (Entry 9). The 5-alkyl-substituted cyclopentenone **5h** furnished a 90:10 mixture of the two isomers *trans*-**9i** and *cis*-**9i** (Entry 10). As anticipated, the epoxidation mainly occurred on the less hindered side of the exocyclic double bond, *anti* to the hexyl group at C-5.

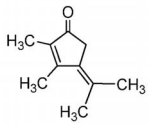
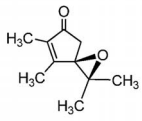
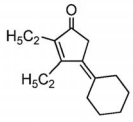
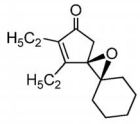
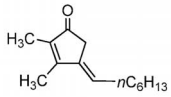
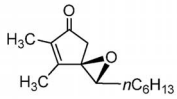
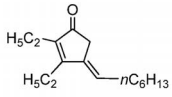
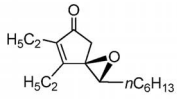
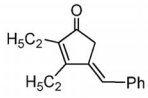
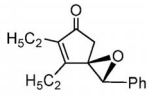
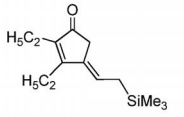
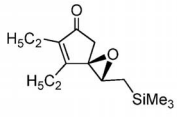
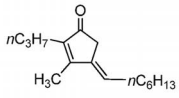
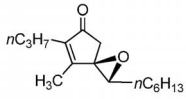
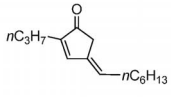
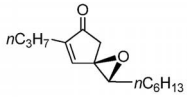
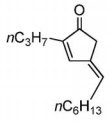
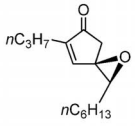
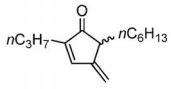
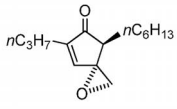
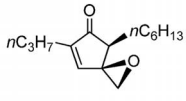
We next looked at the epoxidation of functionalized 4-alkylidenecyclopentenones **4j**–**m** (Table 2). They gave the corresponding spiroepoxycyclopentenones **7j**–**m** as *trans* + *cis* mixtures of isomers with *trans*/*cis* ratios similar to the *E*/*Z* ratios of the starting cyclopentenones (Entries 1–4).

Structures and Stereochemical Assignments of Spiroepoxycyclopentenones 7

The chemical structures of compounds **7** had to be elucidated. The literature had provided one example of a reaction between a peracid and an 4-alkylidenecyclopentenone: cyclopentenone **4j** (Scheme 2) was reported to afford the enol lactone **8j** resulting from a Baeyer–Villiger reaction.[13]

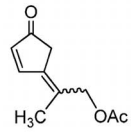
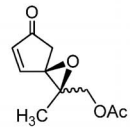
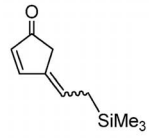
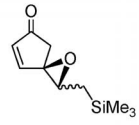
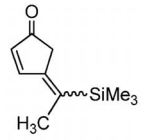
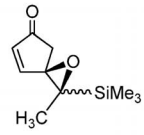
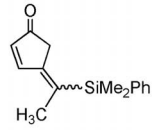
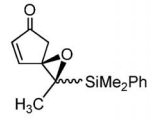
The published IR and ^1H NMR spectroscopic data for this compound **8j** do not, however, fit an enol lactone structure such as the model lactone **8n** (Figure 2), also found in the literature.[18] Compounds **7j** and **8j** displayed similar IR absorptions [**7j**: 1718 (C=O acetate) and 1685 cm^{-1} (C=O ketone); **8j**: 1722 cm^{-1}], whereas the enol lactone **8n** showed an absorption at 1755 cm^{-1}. A comparison of the ^1H NMR spectroscopic data for **7j** and for the enol lactones **8j** (supposed) and **8n** is provided in Figure 2. There is a significant discrepancy between the NMR spectroscopic data published for compound **8j** and those for the model enol lactone **8n**. In particular, the chemical shifts corresponding to the vinylic protons of compound **8j**, at δ = 6.43 and 7.34 ppm, are inconsistent with an enol ester function, and the triplet (δ = 2.69 ppm) and quartet (δ = 4.24 ppm) corresponding to the C*H$_2$* groups are unrealistic. In contrast, these data [chemical shifts and coupling constants (*J*)], ex-

Table 1. Epoxidation of 4-alkylidenecyclopentenones **4**–**5**.

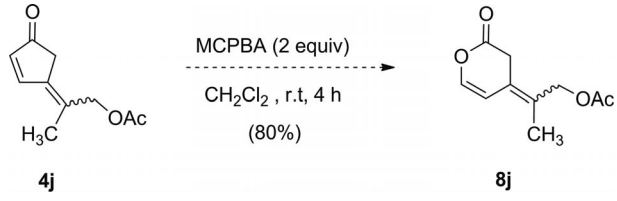
Entry	4-Alkylidene-cyclopentenones **4**		Epoxide **7** (**9**)[a]		Yield[b]
1	**4a**		**7a**		76
2	**4b**		**7b**		57
3	**4c**		**7c**		81
4	**4d**		**7d**		69
5	**4e**		**7e**		70
6	**4f**		**7f**		84
7	**4g**		**7g**		86
8	(*E*)-**4h**		*trans*-**7h**		50
9	(*Z*)-**4h**		*cis*-**7h**		72
10	**5h**		*trans*-**9h**		47
			trans/*cis* 90:10[c]		
			cis-**9h**		

[a] Epoxidation reactions were carried out with MCPBA (2 equiv.) in toluene at 0–20 °C on 1–5 mmol scales. [b] Yields of isolated product(s) after flash chromatography. [c] Ratio of isomers was obtained by ^{1}H NMR spectroscopy.

Table 2. Epoxidation of functionalized 4-alkylidenecyclopentenones **4**.

Entry	4-Alkylidene-cyclopentenones **4** (*E*/*Z*)		Epoxide **7**[a] (*trans*/*cis*)		Yield[c]
1	**4j**		**7j**		67
	(53:46)		(53:46)[b]		
2	**4k**		**7k**		66
	(80:20)		(80:20)[b]		
3	**4l**		**7l**		82
	(64:36)		(64:36)[b]		
4	**4m**		**7m**		87
	(60:40)		(60:40)		

[a] Epoxidations were carried out with MCPBA (2 equiv.) in toluene at 0–20 °C on 1–5 mmol scales. [b] *trans*/*cis* ratios were determined from ^{1}H NMR spectra. [c] Yields of isolated epoxides (mixtures of *trans* + *cis* stereoisomers) after flash chromatography, except for **7m**, for which the *cis* and *trans* stereoisomers were separated.



Scheme 2. Reported reaction between MCPBA and 4-alkylidenecyclopentenone **4j**.

cept for the given multiplicities, match those for our compound **7j**. We thus concluded that the structure of an enol lactone had been given erroneously to compound **8j** and that it should in fact be considered identical with **7j**.

With regard to the ^{13}C NMR spectra of compounds **7a**–**m**, the chemical shifts of the five carbon atoms (C-*n*) of the cyclopentenone rings and the carbon atoms of the epoxy functions are consistent for the proposed spiro structures **7**. Treatment of 4-alkylidenecyclopentenones **4** with MCPBA

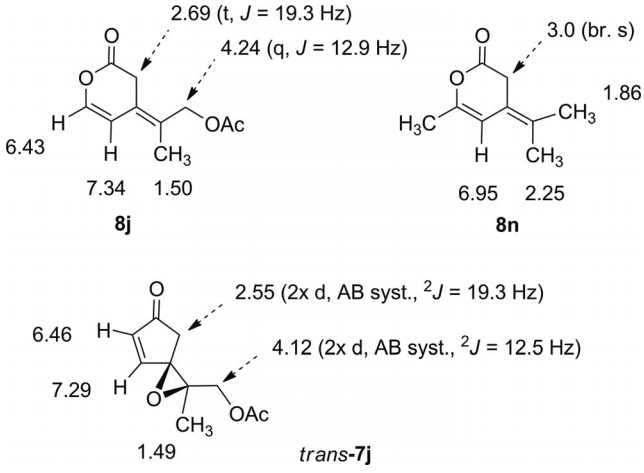


Figure 2. Comparison of the ^{1}H NMR spectra for structures **7j**, **8j** and **8n**.

does therefore indeed result in the selective epoxidation of their exocyclic double bonds.

The *trans* or *cis* configuration of the epoxide function of **7** is the result of the *E* or *Z* configuration in the original 4-alkylidenecyclopentenone **4**. As in the parent cyclopentenones (*E*)- and (*Z*)-**4**, however, the two isomers *trans*- and *cis*-**7** can easily be recognized thanks to their different ^{13}C NMR spectra. In particular, the C-5 signals of *trans*-**7h** and *trans*-**7k** are shifted upfield (δ = 37.9 and 37.5 ppm, respectively, Figure 3) because of the positive *cis* γ-effects of the first methylene groups of the R substituents, whereas for isomers *cis*-**7h** and *cis*-**7k** they are shifted downfield (δ = 39.8 and 40.9 ppm, respectively, Δ = 2–3 ppm). Alternatively, the C-3 signals are shifted downfield for *trans*-**7h** and *trans*-**7k** and upfield for isomers *cis*-**7h** and *cis*-**7k**.

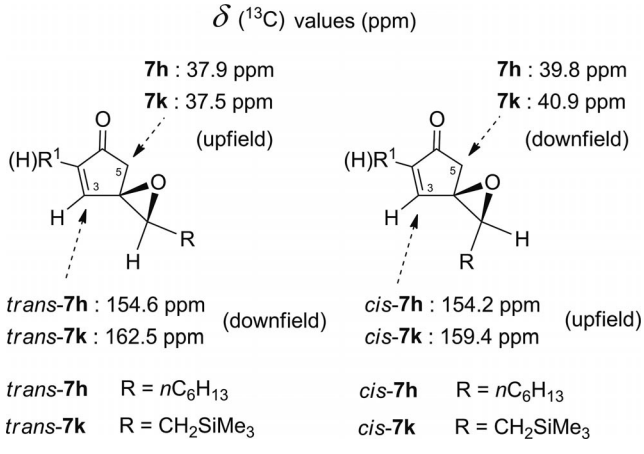


Figure 3. ^{13}C NMR data for spiroepoxycyclopentenones *trans* and *cis*-**7h** and *trans* and *cis*-**7k**.

The cases of the silylated compounds *trans*- and *cis*-**7l** and *trans*- and *cis*-**7m** (Figure 4) are also worth some comment. As in the cases of the parent silylated cyclopentenones (*E*)- and (*Z*)-**4l** and (*E*)- and (*Z*)-**4m**, opposite chemical shifts are observed for C-3 and C-5, because of the above-mentioned negative γ-effect of silicon and the dominating positive *cis* γ-effect of the C(CH_3)SiX(CH_3)$_2$ methyl groups. The C-5 carbon atoms of *trans*-**7l** and *trans*-**7m** are deshielded, whereas those of stereoisomers *cis*-**7l** and *cis*-**7m** are shifted upfield. Similarly, the C-3 carbon atoms are deshielded for *cis*-**7l** and *cis*-**7m** but shifted upfield for *trans*-**7l** and *trans*-**7m** (Figure 4).

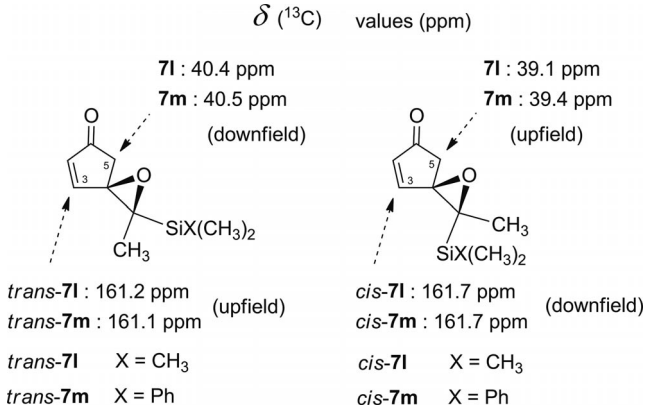


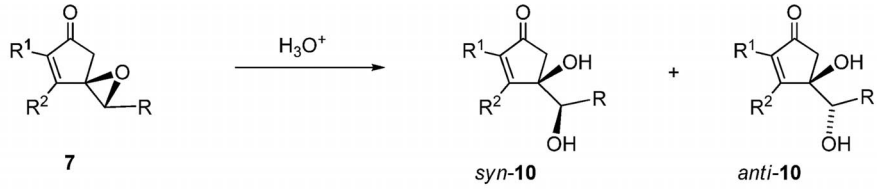
Figure 4. ^{13}C NMR data for *trans*- and *cis*-**7l** and *trans*- and *cis*-**7m**.

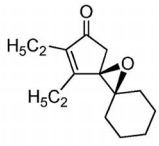
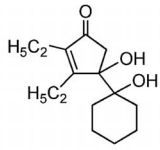
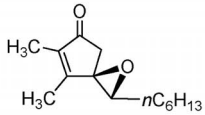
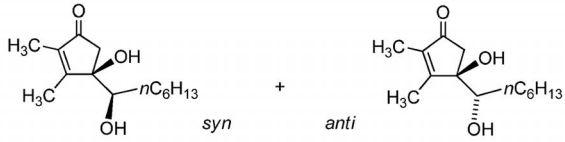
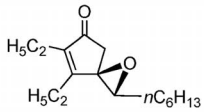
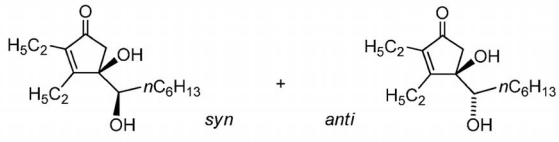
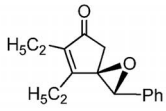
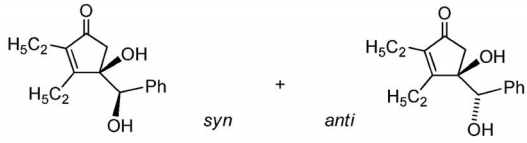
Acid-Catalyzed Ring-Opening of Spiroepoxycyclopentenones 7

Epoxides are valuable synthetic intermediates, due to their reactivity with numerous reagents to give addition products.[19] Ring-opening of **7** was thus expected to give interesting dihydroxylated cyclopentenones **10** (Table 3), the structures of which are related to several natural products such as pentenocine B, an interleukine inhibitor.[20] We therefore examined the ring-opening of **7** under acidic conditions as reported in Table 3. Compounds **7** reacted with sulfuric acid (0.75 M) to give the 4-hydroxy-4-(1-hydroxyalkyl)cyclopentenones **10**. Spiroepoxycyclopentenone **7b** gave the dihydroxylated cyclopentenone **10b** (Table 3, Entry 1). The cyclopentenones (*E*)-**7c** and (*E*)-**7d** both afforded mixtures of the two *syn* and *anti* diastereomers of dihydroxylated cyclopentenones **10c** and **10d**, respectively. The diastereomers *anti*-**10c** and *anti*-**10d** were the major ones in both cases (Entries 2 and 3). The phenyl-substituted compound **7e** did not react under the above conditions, undoubtedly because of its low solubility. However, addition of a solvent such as *t*BuOH or THF allowed the ring-opening of the epoxide bridge to occur (Entries 4 and 5). The diastereoselectivity was then dependent on the nature of this solvent. The diastereomer *anti*-**10e** was still the major diastereomer produced when the reaction was carried out with added *t*BuOH, but an equal mixture of *syn*- and *anti*-**10e** diastereomers was obtained when THF was added.

In order to determine the configurations of the major diastereomers **10c**–**e**, these diastereomers were transformed into the cyclic acetals **11c**–**e** (Scheme 3), with which several NOE 1D NMR experiments were carried out. With acetal **11c**, irradiation of the diastereomeric proton H_a of the methylene (C-5)H_2 group at δ = 2.94 ppm (d, part A of an

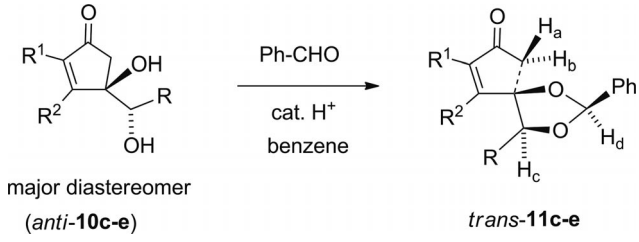
Table 3. Acid-catalyzed ring-opening of spiroepoxycyclopentenones **7**.



Entry	7	Epoxy-cyclopentenone	10	Dihydroxy-cyclopentenones	Yield [%][a] *syn*-**10** + *anti*-**10**	Ratio[d] *syn*/*anti*
1	**7b**		**10b**		64	–
2	**7c**		**10c**		67	12:88
3	**7d**		**10d**		48	25:75
4	**7e**		**10e**		46[b]	43:57
5	**7e**		**10e**		56[c]	50:50

[a] Yields of isolated products after flash chromatography. [b] Reaction carried out with added *t*BuOH. [c] The reaction was carried out with added THF. [d] *syn*/*anti* ratios were obtained from isolated pure diastereomers *syn*- and *anti*-**10c**–**e**.

AB system, ^2J = 18.3 Hz) resulted in the enhancement (21%) of proton H_b (δ = 2.53 ppm, part B of an AB system, ^2J = 18.3 Hz) together with a small increase (0.5%) for the acetal proton H_d at δ = 6.00 ppm (Figure 5). This irradiation had no effect on the dioxolane proton H_c, which is too far away. On the other hand, irradiation of the diastereomeric proton H_b (δ = 2.53 ppm) resulted in the enhancement (21%) of proton H_a (δ = 2.94 ppm) and of the dioxolane proton H_c (6.3%) at δ = 4.14 ppm (dd, ^3J = 3.4 Hz and ^3J = 9.0 Hz). From these two NMR experiments we can infer that the methylene (C-5)H_2 group and the H_c proton of acetal **11c** are *cis*, so that the (C-5)H_2/*n*C_6H_{13} relationship for this acetal **11c** is *trans* (*trans*-**11c**). Had such a NOE experiment been performed with the other diastereomer of acetal **11c** (*cis*-**11c**), the signal of proton H_c would not have been increased. Consequently, the relative stereochemistry of the two hydroxy groups of the major diastereomer **10c** is *anti*.



Scheme 3. Synthesis of acetals **11c**–**e** from the major diastereomers of dihydroxylated cyclopentenones **10c**–**e**.

For acetals **11d** and **11e**, irradiation of proton H_c (at δ = 4.15 and 5.40 ppm, respectively) resulted in the enhancement of both protons H_b and H_d (Figure 6), which also confirms the *anti* relationships of the two OH groups of the major dihydroxylated cyclopentenone products *anti*-**10c** and *anti*-**10d**.

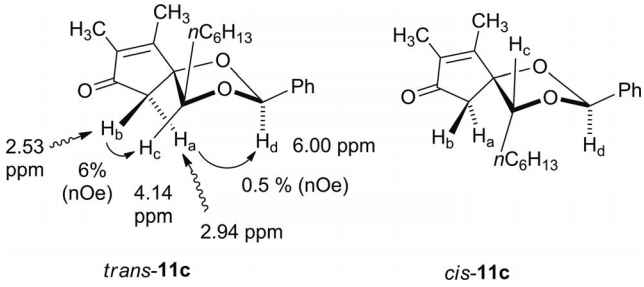


Figure 5. NOE 1D experiments (500 MHz) with acetal *trans*-**11c**.

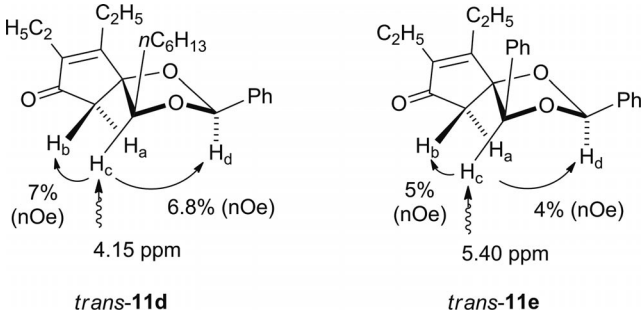
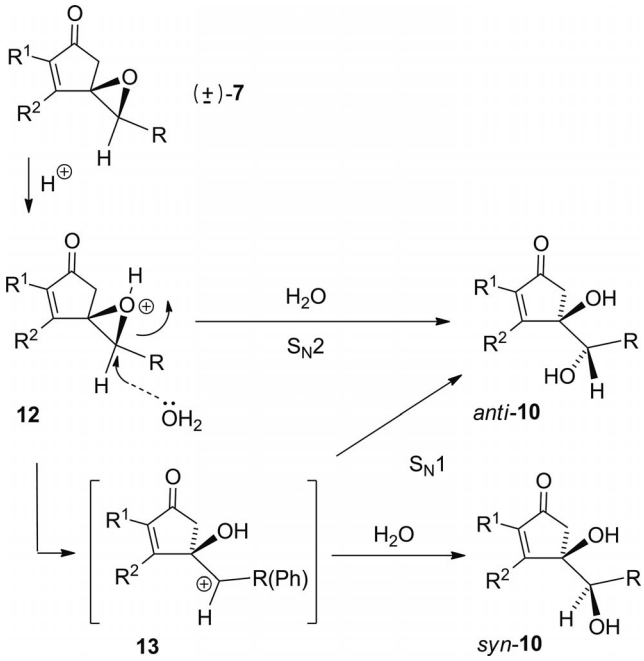


Figure 6. NOE 1D experiments (500 MHz) with acetals *trans*-**11d** and *trans*-**11e**.

From a mechanistic point of view, the major diastereomers *anti*-**10c** and *anti*-**10d** should mainly be the results of favoured S_N2 ring-opening of the protonated epoxide bridges of cations **12** (Scheme 4), whereas *syn*-**10c** and *syn*-**10d** should be produced from carbocations **13** through S_N1 substitution reactions. This last substitution route should be more significant when the R group is a phenyl group, which should stabilize the carbocation **13**, which would explain why **7e** (R = Ph) gave an about equal mixture of *syn*- and *anti*-dihydroxylated cyclopentenones **10e**.



Scheme 4. Ring-opening mechanism for spiroepoxycyclopentenones.

Conclusions

In summary, this study demonstrates that epoxidation of 4-alkylidenecyclopentenones **4** occurs regioselectively on their exocyclic double bonds to afford spiroepoxycyclopentenones **7**. The acidic ring-opening of these epoxides diastereoselectively gives dihydroxylated cyclopentenones **10**, which might be interesting dihydroxylated synthons for the synthesis of cyclopentanoid targets.[14]

Experimental Section

General: All reactions were carried out under nitrogen in oven-dried glassware with use of standard syringe, cannula and septa techniques. Tetrahydrofuran was distilled from deep-purple sodium-benzophenone dianion and stored under nitrogen. Dichloromethane was distilled from calcium hydride and stored under nitrogen. Thin-layer chromatography (TLC) was performed with precoated Kieselgel 60 F_{254} plates (Merck). Detection was achieved by UV (254 nm) followed by charring with *p*-anisaldehyde (4%), acetic acid (5%) and sulfuric acid (5%) in ethanol (86%). Flash chromatography was performed on silica gel 60 (40–63 μm, Merck) by Still's procedure.[21] IR spectra were recorded with a Perkin–Elmer 298 spectrophotometer or a Perkin–Elmer Spectrum One FT-IR instrument; they were recorded from thin films on NaCl plates for oils or from KBr discs for solids. ^1H and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz, respectively, with Bruker DRX 300 or ALS 300 instruments. NOE 1D experiments were recorded at 500 MHz with a Bruker DRX 500 instrument. ^1H NMR chemical shifts were measured in $CDCl_3$ and are reported in ppm relative to the solvent shift of residual chloroform at δ = 7.26 ppm. Multiplicities are described as s (singlet), d (doublet), dd, ddd, etc. (doublet of doublets, doublet of doublets of doublets, etc.), t (triplet), q (quartet), m (multiplet), and further qualified as br (broad), app (apparent); coupling constants (^nJ) are reported in Hz. ^{13}C NMR chemical shifts were obtained in $CDCl_3$ and are reported in ppm relative to $CHCl_3$ at δ = 77.16 ppm. All the carbons were assigned with the aid of Dept 135 experiments. Low- and high-resolution mass spectra were obtained with a ThermoFinnigan MAT 95 XL spectrometer in the Electron Impact (EI, ionization potential of 70 eV) mode or Chemical Ionisation (CI, isobutane as the reagent gas) modes. Low-resolution mass spectra were also obtained with the ElectroSpray Ionisation (ESI) mode and a ThermoFinnigan LCQ Advantage spectrometer. GC–MS were obtained with a Focus DSQ ThermoElectron spectrometer. Microanalyses were carried out by the "Service Central d'analyse du CNRS", Solaize, France. Melting points (m.p.s) were not corrected. PE refers to petroleum ether with a boiling range of 40–60 °C.

Starting Materials: Octacarbonyldicobalt was purchased from Strem Chemicals, Inc. as a solid stabilized with hexane (1–5%). It was used as received and stored under nitrogen at 0 °C. Acetylene (**1a**, dissolved) was purchased from Air Liquide. But-2-yne (**1b**), hex-3-yne (**1c**) and 3-(trimethylsilyl)buta-1,2-diene (**3e**) were commercially available from Aldrich. 3-Methylbuta-1,2-diene (**3a**),[22] phenylallene (**3b**),[23] 4-(trimethylsilyl)buta-1,2-diene (**3c**)[24] and 2-methylbuta-2,3-dien-1-ol (**3d**)[25] were prepared as reported in the literature.

3-[Dimethyl(phenyl)silyl]buta-1,2-diene (3f): A solution of 1-(tosyloxy)but-2-yne (11 g, 49 mmol) in THF (20 mL) was added dropwise under nitrogen at –30 °C to a solution of dimethyl(phenyl)silyl cuprate, previously prepared at –10 °C from a THF solution of dimethyl(phenyl)silyllithium (1.1 M, 150 mL) and a suspension of copper cyanide (6.6 g, 73 mmol) in THF (50 mL).[26] After having been stirred at –30 °C for 1 h, the mixture was allowed to warm to room temperature. The reaction mixture was quenched with a saturated ammonium chloride solution (70 mL), and extracted with diethyl ether (3× 60 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated under reduced pressure. Purification by distillation gave allene **3f** (4.1 g, 31%) containing disilane $Me_2PhSi–SiPhMe_2$ (about 5 mol-%), which can be recognized by its ^1H and ^{13}C NMR spectra and GC–MS analysis.[27]

Compound 3f: Colourless liquid, b.p. 65 °C (14 Torr). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.54 (m, 2 H, H_{ar}), 7.3 (m, 3 H, H_{ar}), 4.34 (q, ^5J = 3.2 Hz, 2 H, H_2C=C=C), 1.67 (t, ^5J = 3.2 Hz, 3 H, CH_3), 0.38 (s, 6 H, 2× SiCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 210.0 (C=*C*=C), 137.9 [C_q, *C*(Ph)$_i$], 133.9 [2× *C*H(Ph)$_o$], 129.4 [*C*H(Ph)$_p$], 127.9 [2× *C*H(Ph)$_m$], 88.2 [C=C=*C*(Si)], 68.0 (H_2C=C=C), 15.7 [C=C=C(Si)*C*H$_3$], –3.3 [2× Si*C*H$_3$] ppm. IR (thin film): $\tilde{\nu}$ = 1960 (allene), 1225(SiMe), 1105(SiPh) cm^{-1}. GC–MS (EI): *m*/*z* (%) = 188 (12) $[M]^+$, 173 (7) $[M – CH_3]^+$, 135 (100) $[SiPh(CH_3)_2]^+$, 105 (11). HRMS (EI): calcd. for $C_{12}H_{16}Si$ $[M]^+$ 188.1021; found 188.1030.

1,2-Dimethyl-1,2-diphenyldisilane:[25] ^1H NMR (300 MHz, $CDCl_3$): δ = 7.53–7.56 (m, 4 H, H_{ar}), 7.38 (m, 6 H, H_{ar}), 0.34 (s, 12 H, 4× SiCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.9 [2× *C*(Ph)$_i$], 133.1 [4× *C*H(Ph)$_o$], 129.4 [2× *C*H(Ph)$_p$], 129.3 [4× *C*H(Ph)$_m$], 1.0 [4× Si*C*H$_3$] ppm. GC–MS (EI): *m*/*z* (%) = 270 (9) $[M]^+$, 255 (2) $[M – CH_3]^+$, 197 (14), 135 (100) $[SiPh(CH_3)_2]^+$, 105 (6).

Synthesis of 4-Alkylidenecyclopentenones 4 and 5: Cyclopentenones **4b**–**d**, **4g**, **4h** and **5h**, prepared by our PKR methodology, are already described.[2c] New cyclopentenones **4a**, **4e**, **4f** and **4i**–**m** were similarly synthesized as follows.

Synthesis of 4-Alkylidenecyclopentenones 4

General Procedure for the Preparation of (Alkyne)hexacarbonyldicobalt Complexes 2a–c:[2c] An alkyne **1** (1.2 mmol) was added at 0 °C to a stirred solution of $Co_2(CO)_8$ (1 mmol) in CH_2Cl_2 [2.5 mL per mmol of $Co_2(CO)_8$], and the mixture was stirred at this temperature for 30 min. The reaction was complete when the emission of carbon monoxide stopped. In the case of complex **2a**, acetylene gas (after condensation of acetone through a cooled trap) was bubbled through the solution of $Co_2(CO)_8$ for 1 h. The mixture was allowed to warm to room temperature and stirred until all $Co_2(CO)_8$ was consumed (ca. 2–3 h). The mixture was then filtered through a short plug of Celite®. Washing with dichloromethane and evaporation of solvent under vacuum with a rotary evaporator (without heating) gave the crude dicobalt complex **2** as a purple viscous precipitate; yields ranged from 95 to 100%.

General Procedure for the Synthesis of 4-Alkylidenecyclopent-2-enones 4:[2c] A solution of an allene **3** (1.5 mmol) in CH_2Cl_2 (1 mL) was added at –78 °C (or –40 °C) to a stirred solution of an (alkyne)-hexacarbonyldicobalt complex **2** (1 mmol) in a CH_2Cl_2/THF mixture (1:1, 10 mL). Solid NMO (6 mmol) was then added over 5 min. After 15 min at this temperature, the mixture was allowed to warm to room temperature by removal of the cold bath (1 h) and stirred until the starting complex had disappeared (1 to 3 h). The solution was filtered through a small plug of silica gel (washing of the precipitate with ether) and concentrated under vacuum. This operation was repeated several times if necessary, to eliminate most of the cobalt clusters. The crude product was purified by flash chromatography (PE/Et_2O mixtures as eluents) to afford the corresponding 4-alkylidenecyclopentenone **4**.

4-Isopropylidene-2,3-dimethylcyclopent-2-enone (4a): The cycloaddition between (but-2-yne)dicobalthexacarbonyl complex (**2b**, 605 mg, 1.78 mmol) and 3-methylbuta-1,2-diene (**3a**, 332 mg, 2.67 mmol) by the General Procedure, promoted by NMO (1.251 g, 10.68 mmol) in CH_2Cl_2/THF (1:1, 10 mL), gave the cyclopentenone **4a** (283 mg, 77%) after flash chromatography (PE/Et_2O 90:10). Yellow oil; R_f = 0.33 (PE/Et_2O 50:50). ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.90 (s, 2 H, 5-H), 2.27 [s, 3 H, (C-3)CH_3], 2.06 [s, 3 H, (C-4)=CC$H_{3\text{-}trans}$], 1.83 [s, 3 H, (C-4)=CC$H_{3\text{-}cis}$], 1.77 [s, 3 H, (C-2)-CH_3] ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 204.6 (C-1, *C*=O), 163.7 [C-3, *C*=C(C=O)], 139.7 [C-2, C=*C*(C=O)], 130.8 and 130.5 [2× C_q, C-4 and (C-4)=C_q], 40.7 [C-5, (C=O)*C*H$_2$], 24.9 [(C-4)=C(*C*H$_{3\text{-}cis}$)], 21.3 [(C-4)=C(*C*H$_{3\text{-}trans}$)], 17.2 [(C-3)*C*H$_3$], 8.2 [(C-2)*C*H$_3$] ppm. IR (thin film): $\tilde{\nu}$ = 2970, 2910, 2850, 1685 (C=O), 1640, 1390, 1340, 1280, 1200, 945, 770, 670 cm^{-1}. MS (EI): *m*/*z* (%) = 150 (71) $[M]^+$, 135 (11) $[M – CH_3]^+$, 122 (29), 107 (65), 91 (20), 79 (26), 77 (19), 65 (17), 53 (43), 51 (32), 41 (67), 39 (100), 28 (58), 27 (50). $C_{10}H_{14}O$ (150.22): calcd. C 79.96, H 9.39; found C 79.99, H 9.23.

(*E*)-4-Benzylidene-2,3-diethylcyclopent-2-enone (4e): The cycloaddition between (hex-3-yne)hexacarbonyldicobalt complex (**2c**, 13.1 g, 35.6 mmol) and phenylallene (**3b**, 4.96 g, 42.7 mmol) by the General Procedure, promoted by NMO (13.1 g, 35.61 mmol) in CH_2Cl_2/THF (1:1), gave the cyclopentenone (*E*)-**4e** (3.4 g, 35%) after flash chromatography (PE/Et_2O 85:15). Yellow solid; m.p. 95 °C; R_f = 0.33 (PE/Et_2O 80:20). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.43 (m, 5 H, H_{ar}), 6.67 [s, 1 H, (C-4)=C*H*], 3.26 (s, 2 H, 5-H), 2.68 [q, ^3J = 7.5 Hz, 2 H, (C-3)CH_2], 2.36 [q, ^3J = 7.5 Hz, 2 H, (C-2)CH_2], 1.25 (t, ^3J = 7.5 Hz, 3 H, CH_3), 1.10 (t, ^3J = 7.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 Mz, $CDCl_3$): δ = 205.4 (C-1, *C*=O), 169.5 (C-3), 136.9 (C-2), 136.2 [2× C_q, C-4 and C(Ph)$_i$], 129.0 and 128.8 [2× *C*H(Ph)$_o$ and 2× *C*H(Ph)$_m$], 127.7 [*C*H(Ph)$_p$], 123.3 [(C-4)=*C*H(Ph)], 40.0 (C-5), 19.8 [(C-3)*C*H$_2$], 17.4 [(C-2)*C*H$_2$], 14.5 (*C*H$_3$), 13.9 (*C*H$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3060, 2960, 2930, 2870, 1680, 1600, 1450, 755, 690 cm^{-1}. MS (EI): *m*/*z* (%) = 226 (100) $[M]^+$, 211 (55) $[M – CH_3]^+$, 197 (27), 169 (27), 141 (17), 115 (16), 91 (11).

(*E*)-2,3-Diethyl-4-[2-(trimethylsilyl)ethylidene]cyclopent-2-enone (4f): The cycloaddition between (hex-3-yne)hexacarbonyldicobalt complex (**2c**, 1.53 g, 4 mmol) and 4-(trimethylsilyl)buta-1,2-diene (**3c**, 0.66 g, 4 mmol) by the General Procedure, promoted by NMO (2.8 g, 24 mmol) in CH_2Cl_2/THF (1:1, 30 mL), gave the cyclopentenone (*E*)-**4f** (527 mg, 56%) after flash chromatography (PE/Et_2O 80:20). Yellow oil; R_f = 0.33 (PE/Et_2O 80:20). ^1H NMR (300 MHz, $CDCl_3$): δ = 5.83 [t, ^3J = 8.9 Hz, 1 H, (C-4)=C*H*CH_2SiMe$_3$], 2.82 (s, 2 H, 5-H), 2.51 [q, ^3J = 7.7 Hz, 2 H, (C-3)CH_2], 2.26 [q, ^3J = 7.5 Hz, 2 H, (C-2)CH_2], 1.62 [d, ^3J = 8.9 Hz, 2 H, (C-4)=CHCH_2SiMe$_3$], 1.14 (t, ^3J = 7.7 Hz, 3 H, CH_3), 1.03 (t, ^3J = 7.5 Hz, 3 H, CH_3), 0.04 [s, 9 H, 3× SiCH_3] ppm. ^{13}C NMR (75 Mz, $CDCl_3$): δ = 205.4 (C-1, *C*=O), 168.9 (C-3), 142.3 (C-4), 133.6 (C-2), 122.3 [(C-4)=*C*HCH$_2$SiMe$_3$], 37.7 (C-5), 22.1 (*C*H$_2$SiMe$_3$), 19.3 [(C-3)*C*H$_2$], 16.7 [(C-2)*C*H$_2$], 14.1 (*C*H$_3$), 13.5 (*C*H$_3$), –1.5 (3× Si*C*H$_3$) ppm. IR (thin film): $\tilde{\nu}$ = 2968, 2878, 1693 (C=O), 1247 (C=C), 1247 and 838 (Si–Me) cm^{-1}. MS (EI): *m*/*z* (%) = 236 (29) $[M]^+$, 221 (34) $[M – CH_3]^+$, 207 (10) $[M – C_2H_5]^+$, 91 (6), 75 (13), 73 (100) $[SiMe_3]^+$. HRMS (EI): calcd. for $C_{14}H_{24}OSi$ $[M]^+$ 236.1596; found 236.1605.

4-[2-Hydroxy-1-(methyl)ethylidene]cyclopent-2-enone (4i): Gaseous acetylene (**1a**) was bubbled for 1.5 h through a solution of octacar-

bonylcobalt complex $Co_2(CO)_8$ (13 mmol, 1.1 equiv.) in CH_2Cl_2 (16 mL per g of complex) at room temperature in order to obtain a solution of (acetylene)hexacarbonylcobalt complex (**2a**). 2-Methylbuta-2,3-dien-1-ol (**3d**, 1 g, 11.9 mmol) was then added together with anhydrous THF (35 mL). The mixture was cooled down to –40 °C, *N*-methylmorpholine oxide (1 equiv.) was added, and the mixture was allowed to warm to –30 °C. Then the mixture was cooled down to –40 °C again, and the remaining 5 equiv. of *N*-methylmorpholine oxide were added portionwise. The reaction mixture was stirred at room temperature for 18 h and was then filtered through a silica gel plug with washing with diethyl ether. The filtrate was concentrated under vacuum and the crude product was purified by flash chromatography (gradient from PE/Et_2O 10:90 to pure Et_2O as the eluent) to afford cyclopentenone (*E* + *Z*)-**4i** (632 mg, 38%, *E*/*Z* 53:47). R_f = 0.18 (Et_2O). ^{1}H NMR (300 MHz $CDCl_3$): (*E*)-**4i**: δ = 8.04 (d, ^3J = 5.8 Hz, 1 H, 3-H, *H*C=CHCO), 6.24 (d, ^3J = 5.8 Hz, 1 H, 2-H, HC=C*H*CO), 4.21 (s, 2 H, CH_2OH), 2.94 (s, 2 H, 5-H), 2.45 (s, 1 H, O*H*), 2.00 (s, 3 H, CH_3) ppm. (*Z*)-**4i**: δ = 8.13 (d, ^3J = 5.7 Hz, 1 H, *H*C=CHCO), 6.19 (d, ^3J = 5.7 Hz, 1 H, HC=C*H*CO), 4.35 (s, 2 H, CH_2OH), 2.89 (s, 2 H, 5-H), 2.45 (br. s, 1 H, O*H*), 1.90 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): (*E*)-**4i**: δ = 207.0 (*C*=O), 156.7 (C-3), 135.8 (C-2), 134.2 (C_q), 133.5 (C_q), 64.7 (*C*H_2OH), 38.2 [C-5, (C=O)*C*H_2], 15.6 (*C*H_3) ppm. (*Z*)-**4i**: δ = 206.7 (*C*=O), 155.4 (C-3), 136.0 (C-2), 133.9 (C_q), 132.8 (C_q), 62.7 (*C*H_2OH), 38.9 (C-5), 18.4 (*C*H_3) ppm. IR (thin film): $\tilde{\nu}$ = 3400, 2970, 2920, 2860, 2240, 1700, 1670, 1530, 1440, 1385 cm^{-1}. MS (CI): *m*/*z* (%) = 139 [M + H]$^+$.

4-[2-Acetoxy-1-(methyl)ethylidene]cyclopent-2-enone (4j): Triethylamine (0.1 mL, 1.24 mmol) and 4-(dimethylamino)pyridine (13.7 mg, 10 mol-%) were added under nitrogen to a solution of cyclopentenone (*E* + *Z*)-**4i** (155 mg, 1.13 mmol) in CH_2Cl_2 (5 mL). The mixture was cooled to 5 °C, and acetic anhydride (0.2 mL, 2 mmol) was added. The reaction mixture was stirred at room temperature for 1 h and was then quenched with water (5 mL) with a few drops of a saturated solution of $NaHCO_3$ and extracted with CH_2Cl_2 (3× 5 mL). The organic layers were collected, washed with water (5 mL), dried with Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by flash chromatography (PE/Et_2O 2:3, then 1:3) to afford acetate (*E* + *Z*)-**4j** (167 mg, 83%, *E*/*Z* 53:47). R_f = 0.20 (PE/Et_2O 40:60). ^{1}H NMR (300 MHz, $CDCl_3$): (*E*)-**4j**: δ = 8.02 (d, ^3J = 5.8 Hz, 1 H, *H*C=CHCO), 6.30 (d, ^3J = 5.8 Hz, 1 H, HC=C*H*CO), 4.63 (s, 2 H, CH_2–OAc), 3.01 [s, 2 H, (C=O)CH_2], 2.08 [s, 3 H, O(C=O)CH_3], 1.96 (s, 3 H, CH_3) ppm. (*Z*)-**4j**: δ = 8.10 (d, ^3J = 5.7 Hz, 1 H, *H*C=CHCO), 6.27 (d, ^3J = 5.7 Hz, 1 H, HC=C*H*CO), 4.78 (s, 2 H, CH_2–OAc), 2.93 [s, 2 H, (C=O)CH_2], 2.08 [s, 3 H, O(C=O)CH_3], 1.89 (s, 3 H, CH_3) ppm. IR (thin film): $\tilde{\nu}$ = 2975, 2920, 2860, 2240, 1730, 1700, 1670, 1530, 1440, 1385 cm^{-1}.

4-[2-(Trimethylsilyl)ethylidene]cyclopent-2-enone (4k): As described in the General Procedure NMO (13.1 g, 35.61 mmol) was added portionwise at –40 °C over 30 min to a solution of 4-(trimethylsilyl)buta-1,2-diene (**3c**, 4 g, 31.8 mmol) and (acetylene)hexacarbonyldicobalt complex (**2a**, 6.6 g, 21.2 mmol), prepared as for **4i** from $Co_2(CO)_8$ (8.06 g, 23.6 mmol) and acetylene, in CH_2Cl_2/THF (1:1, 100 mL) stirred at –40 °C. After warming up, dilution with ethyl ether, stirring at room temperature for 18 h and workup, purification by flash chromatography (PE/Et_2O 80:20) gave the cyclopentenone (*E* + *Z*)-**4k** (2.36 g, 62%, *E*/*Z* 80:20). R_f = 0.32 (PE/Et_2O 75:25). ^{1}H NMR (300 MHz, $CDCl_3$): (*E*)-**4k**: δ = 7.70 (d, ^3J = 5.1 Hz, 1 H, 3-H, C*H*=CCO), 6.12 (d, ^3J = 5.1 Hz, 1 H, 2-H, C=C*H*CO), 5.90 [t, ^3J = 8.9 Hz, 1 H, (C-4)=C*H*CH$_2$], 2.84 [s, 2 H, 5-H, (C=O)CH_2], 1.66 (d, ^3J = 8.9 Hz, 2 H, SiCH_2), 0.05 (s, 9 H, 3× SiCH_3) ppm. (*Z*)-**4k**: δ = 7.98 (d, ^3J = 5.3 Hz, 1 H, 3-H), 6.21 (d, ^3J = 5.3 Hz, 1 H, 2-H), 5.75 [t, ^3J = 9.2 Hz, 1 H, (C-4)=C*H*CH$_2$], 2.96 (s, 2 H, 5-H), 1.79 (d, ^3J = 9.2 Hz, 2 H, CH_2Si), 0.05 (s, 9 H, 3× SiCH_3) ppm. ^{13}C NMR (75 Mz, $CDCl_3$): (*E*)-**4k**: δ = 206.7 (C-1, *C*=O), 160.9 (C-3), 135.8 (C_q, C-4), 131.3 (C-2), 129.7 [(C-4)=*C*H], 37.6 (C-5), 22.9 (Si*C*H$_2$), –1.5 (3× Si*C*H$_3$) ppm. (*Z*)-**4k**: δ = 207.5 (C-1), 154.9 (C-3), 133.6 (C_q, C-4), 132.9 (C-2), 127.8 [(C-4)=*C*H], 40.5 (C-5), 20.9 (Si*C*H$_2$), –1.7 (3× Si*C*H$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 2955, 2886, 1699 (C=O), 1645, 1537, 1247 and 834 (SiCH$_3$) cm^{-1}. MS (EI): *m*/*z* (%) = 180 (34) [M]$^+$, 165 (8) [M – CH$_3$]$^+$, 91 (15) [M – H – SiMe$_3$]$^+$, 73 (100) [SiMe$_3$]$^+$. HRMS (EI): calcd. for $C_{10}H_{16}OSi$ [M]$^+$ 180.0970; found 180.0974.

4-[1-(Trimethylsilyl)ethylidene]cyclopent-2-enone (4l): Treatment of 3-(trimethylsilyl)buta-1,2-diene (**3e**, 1 g, 7.9 mmol), (acetylene)-hexacarbonyldicobalt complex (**2a**, 2.97 g, 9.5 mmol) and NMO (6.7 g, 57 mmol) by the General Procedure at –40 °C gave the cyclopentenone **4l** as a mixture of *E* and *Z* stereoisomers (570 mg, 40%, *E*/*Z* 64:36) after purification by flash chromatography (PE/Et_2O 75:25). R_f = 0.21 (PE/Et_2O 75:25). ^{1}H NMR (300 MHz, $CDCl_3$): (***E***)-**4l**: δ = 8.14 [d, ^3J = 5.6 Hz, 1 H, *H*C=CH(C=O)], 6.25 [d, 1 H, ^3J = 5.6 Hz, HC=C*H*(C=O)], 2.96 [s, 2 H, (C=O)CH_2], 1.99 [s, 3 H, (C-4)=CCH_3], 0.17 (s, 9 H, 3× SiCH_3) ppm. (*Z*)-**4l**: δ = 7.96 [d, ^3J = 5.6 Hz, 1 H, *H*C=CH(C=O)], 6.24 [d, ^3J = 5.6 Hz, 1 H, HC=C*H*(C=O)], 2.92 [s, 2 H, (C=O)CH_2], 1.88 [s, 3 H, (C-4)=CCH_3], 0.23 (s, 9 H, 3× SiCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): (***E***)-**4l**: δ = 207.5 (*C*=O), 154.6 (C-3), 143.7 (C-2), 139.1 (C-4, C_q=CSiMe$_3$), 132.9 [(C-4)=C_qSiMe$_3$], 40.9 [(C=O)*C*H$_2$], 17.7 [(C-4)=C*C*H$_3$], –0.8 (3× Si*C*H$_3$) ppm. **(*Z*)-4l**: δ = 205.7 (*C*=O), 157.9 (C-3), 146.1 (C-2), 141.3 (C-4), 133.6 [(C-4)=C_qSi], 39.1 [(C=O)*C*H$_2$], 20.4 [C-(4)=C*C*H$_3$], 0.12 (3× Si*C*H$_3$) ppm. GC–MS (EI): *m*/*z* (%) = 180 (32) [M]$^+$, 165 (37) [M – CH$_3$]$^+$, 135 (6), 109 (7), 106 (11), 97 (17), 91 (83), 73 (100) [SiMe$_3$]$^+$, 75 (27). HRMS (EI): calcd. for $C_{10}H_{16}OSi$ [M]$^+$ 180.0970; found 180.0971.

4-[1-(Dimethylphenylsilyl)ethylidene]cyclopent-2-enone (4m): Treatment of 3-(dimethylphenylsilyl)buta-1,2-diene (**3f**, 1.5 g, 8 mmol), (acetylene)dicobalt complex **2a** (3 g, 9.6 mmol) and NMO (6.75 g, 58 mmol) by the General Procedure at –40 °C gave the cyclopentenone **4m** as a mixture of *E* and *Z* isomers (602 mg, 31%, *E*/*Z* 60:40) after purification by flash chromatography (PE/Et_2O 75:25). R_f = 0.32 (PE/Et_2O 70:30). ^{1}H NMR (300 MHz, $CDCl_3$): (*E*)-**4m**: δ = 8.18 (d, ^3J = 5.6 Hz, 1 H, 3-H), 7.62 (br. s, 1 H, H$_{ar}$), 7.52–7.39 (br. s, 4 H, H$_{ar}$), 6.28 (d, ^3J = 5.6 Hz, 1 H, 2-H), 2.79 [s, 2 H, (C=O)CH_2], 2.08 [s, 3 H, (C-4)=CCH_3], 0.48 (s, 6 H, 2× SiCH_3) ppm. (*Z*)-**4m**: δ = 7.72 (d, ^3J = 5.5 Hz, 1 H, 3-H), 7.62 (br. s, 1 H, H$_{ar}$), 7.52–7.39 (m, 4 H, H$_{ar}$), 6.17 (d, ^3J = 5.5 Hz, 1 H, 2-H), 2.99 [s, 2 H, (C=O)CH_2], 1.96 [s, 3 H, (C-4)=CCH_3], 0.43 (s, 6 H, 2× SiCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): (*E*)-**4m**: δ = 207.7 (C-1, *C*=O), 154.7 (C-3), 145.3 (C_q, C-4), 139.4 [(C-4)=*C*(SiPhMe$_2$)], 137.6 [*C*(Ph)$_i$], 133.8 [2× *C*H(Ph)$_o$], 129.5 (C-2), 128.2 [*C*(Ph)$_p$], 127.9 [2× *C*H(Ph)$_{met}$], 41.1 [(C=O)*C*H$_2$], 18.5 [(C-4)=C*C*H$_3$], –1.9 (2× Si*C*H$_3$) ppm. (*Z*)-**4m**: δ = 206.2 (*C*=O), 158.2 (C-3), 147.5 (C-4), 139.2 [(C-4)=*C*(SiPhMe$_2$)], 137.3 [*C*(Ph)$_i$], 133.8 [2× *C*H(Ph)$_o$], 129.6 (C-2), 128.2 [*C*(Ph)$_p$], 127.9 [2× *C*H(Ph)$_{met}$], 39.4 [(C=O)*C*H$_2$], 20.9 [(C-4)=C*C*H$_3$], 0.1 (2× Si*C*H$_3$) ppm. GC–MS (EI): *m*/*z* (%) = 242 (73) [M]$^+$, 227 (26) [M – CH$_3$]$^+$, 168 (27), 135 (100) [SiPhMe$_2$]$^+$, 105 (36), 75 (42). HRMS (EI): calcd. for $C_{15}H_{18}OSi$ [M]$^+$ 242.1127; found 242.1131.

General Procedure for Epoxidation of 4-Alkylidenecyclopentenones 4 (or 5): *m*-Chloroperbenzoic acid (4 mmol) was added at 0 °C to a solution of a cyclopentenone **4** (or **5**, 2 mmol) in toluene (10 mL). The reaction mixture was stirred until completion (2–18 h) and then concentrated in vacuo. Filtration on silica gel with petroleum ether/ether 95:5 as eluent, followed by purification by flash

chromatography, gave **7** (or **9**). If *m*-chlorobenzoic acid remained, the epoxide **7** (or **9**) was dissolved in CH_2Cl_2, which was washed with water to which few drops of a saturated $NaHCO_3$ solution had been added. The organic layer was washed again with water, dried with Na_2SO_4, filtered and concentrated in vacuo.

Spiroepoxycyclopentenone 7a: Epoxidation of cyclopentenone **4a** (300 mg, 2 mmol) by the General Procedure (Table 1, Entry 1) gave the spiroepoxycyclopentenone **7a** (253 mg, 76%) after flash chromatography (PE/Et_2O 70:30). Yellow oil; R_f = 0.18 (PE/Et_2O 70:30). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.66 [d, ^2J = 18.8 Hz, 1 H, (C=O)CH_aH$_b$], 2.43 [d, ^2J = 18.8 Hz, 1 H, (C=O)CH$_a$$H_b$], 1.96 [s, 3 H, (C-3)C$H_3$], 1.78 [s, 3 H, (C-2)C$H_3$], 1.54 [s, 3 H, (C-4)-O-CCH_3CH$_3$], 1.40 [s, 3 H, (C-4)-O-CH$_3$CH_3] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.0 (C-1, *C*=O), 165.2 (C-3), 143.3 (C-2), 70.1 (C-4, C_q–O), 64.2 [(C-4)-O-*C*(CH$_3$)$_2$], 40.6 (C-5), 25.5 [(C-4)-O-C*C*H$_3$], 20.7 [(C-4)-O-C*C*H$_3$], 14.6 [(C-3)*C*H$_3$], 8.8 [(C-2)-*C*H$_3$] ppm. IR (thin film): $\tilde{\nu}$ = 3332, 2986, 2907, 1669, 1589, 1392, 1368, 1200, 1076, 915, 891 cm^{-1}. MS (EI): *m*/*z* (%) = 166 (6) [M]$^+$, 124 (40) [M – C(CH$_3$)$_2$]$^+$, 80 (100), 77 (20), 43 (36). HRMS (EI): calcd. for $C_{10}H_{14}O_2$ [M]$^+$ 166.0994; found 166.0992.

Spiroepoxycyclopentenone 7b: Epoxidation of cyclopentenone **4b** (130 mg, 0.6 mmol) by the General Procedure (Table 1, Entry 2) gave **7b** (80 mg, 57%) after flash chromatography (PE/Et_2O 80:20). Yellowish oil; R_f = 0.22 (PE/Et_2O 80:20). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.65 [d, ^2J = 18.5 Hz, 1 H, (C=O)CH_aH$_b$], 2.43 [d, ^2J = 18.5 Hz, 1 H, (C=O)CH$_a$$H_b$], 2.48–2.33 [m, 2 H, (C-3)CH_2], 2.28 [qd, ^3J = 7.5, ^5J = 2.3 Hz, 2 H, (C-2)CH_2], 1.90–1.45 (m, 10 H, 5× CH_2), 1.11 (t, ^3J = 7.5 Hz, 3 H, CH_3), 1.06 (t, ^3J = 7.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.2 (C-1, *C*=O), 169.7 (C-3), 148.6 (C-2), 70.3 (C-4, *C*–O), 68.9 [(C-4)-O-C_q], 40.9 [(C=O)*C*H$_2$], 35.2, 30.5, 25.5, 25.4 and 24.9 (5× *C*H$_2$), 20.7 and 17.1 (2× *C*H$_2$CH$_3$), 13.0 and 12.9 (2× *C*H$_3$) ppm. IR (thin film): $\tilde{\nu}$ = 2960, 2920, 2850, 1705, 1620, 1450, 1380, 1240, 960, 835 cm^{-1}. MS (EI): *m*/*z* (%) = 234 (7) [M]$^+$, 152 (100), 136 (13), 108 (33), 93 (20), 67 (24). HRMS (EI): calcd. for $C_{15}H_{22}O_2$ [M]$^+$ 234.1620; found 234.1621.

Spiroepoxycyclopentenone *trans*-7c: Epoxidation of cyclopentenone (*E*)-**4c** (207 mg, 1 mmol) by the General Procedure (Table 1, Entry 3) gave *trans*-**7c** (203 mg, 81%) after flash chromatography (PE/Et_2O 80:20). Yellow oil; R_f = 0.33 (PE/Et_2O 70:30). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.26 [t, ^3J = 5.6 Hz, 1 H, (C-4)-O-C*H*], 2.56 [d, ^2J = 19.0 Hz, 1 H, (C=O)CH_aH$_b$], 2.41 [d, ^2J = 19.0 Hz, 1 H, (C=O)CH$_a$$H_b$], 1.80 (s, 3 H, C$H_3$), 1.78 (s, 3 H, C$H_3$), 1.60–1.20 (m, 10 H, 5× CH_2), 0.88 (t, ^3J = 6.6 Hz, 3 H, CH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.5 (*C*=O), 165.4 (C-3), 141.8 (C-2), 66.0 (C-4, C_q-O-CH), 60.5 [(C-4)-O-*C*H], 37.6 [(C=O)*C*H$_2$], 32.1, 31.1, 29.5, 26.6 and 22.9 (5× *C*H$_2$), 14.4 (CH$_2$*C*H$_3$), 10.7 [(C-3)*C*H$_3$], 8.83 [(C-2)*C*H$_3$] ppm. IR (thin film): $\tilde{\nu}$ = 2936, 1685, 1670, 1376, 1220, 1163, 1040, 965, 848, 813 cm^{-1}. MS (ESI): *m*/*z* (%) = 223 (100) [M + H]$^+$, 254.9 (22) [M + H + CH$_3$OH]$^+$, 277.2 (51) [M + Na + CH$_3$OH]$^+$, 445.1 (49) [2 M + H]$^+$.

Spiroepoxycyclopentenone *trans*-7d: Epoxidation of cyclopentenone (*E*)-**4d** (234 mg, 1 mmol) (Table 1, Entry 4) by the General Procedure gave *trans*-**7d** (173 mg, 69%) after flash chromatography (PE/Et_2O 90:10). Yellow oil; R_f = 0.28 (PE/Et_2O 80:20). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.26 (t, ^3J = 5.5 Hz, 1 H, C_q-O-C*H*), 2.55 [d, ^2J = 19.2 Hz, 1 H, (C=O)CH_aH$_b$], 2.41 [d, ^2J = 19.2 Hz, 1 H, (C=O)CH$_a$$H_b$], 2.27 [q, ^3J = 7.5 Hz, 2 H, (C-3)CH_2], 2.14 [qd, ^3J = 7.5, ^5J = 2.5 Hz, 2 H, (C-2)CH_2], 1.43 (m, 10 H, 5× CH_2), 1.08 (t, ^3J = 7.5 Hz, 3 H, CH_3), 1.05 (t, ^3J = 7.5 Hz, 3 H, CH_3), 0.88 (t, ^3J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.5 (*C*=O), 169.5 (C-3), 146.9 (C-2), 65.2 (C-4, C_q-O-CH), 60.6 [(C-4)-O-*C*H], 37.8 [(C=O)*C*H$_2$], 31.8, 30.9, 29.3, 26.4 and 22.7 (5× *C*H$_2$), 17.9 (*C*H$_2$CH$_3$), 17.0 (*C*H$_2$CH$_3$), 14.2, 14.0 and 13.2 (3× *C*H$_3$) ppm. IR (thin film): $\tilde{\nu}$ = 2860, 2820, 1660, 1650, 1400, 1375, 1250, 1165, 915, 790 cm^{-1}. MS (EI): *m*/*z* (%) = 250 (6) [M]$^+$, 221 (8), 179 (12), 152 (100), 137 (13), 108 (31), 57 (25). HRMS (CI): calcd. for $C_{16}H_{26}O_2$ [M + H]$^+$ 251.1933; found 251.1931.

Spiroepoxycyclopentenone *trans*-7e: Epoxidation of cyclopentenone (*E*)-**4e** (226 mg, 1 mmol) by the General Procedure (Table 1, Entry 5) gave *trans*-**7e** (169 mg, 70%) after flash chromatography (PE/Et_2O 80:20). Yellow solid; m.p = 60–61 °C; R_f = 0.22 (PE/Et_2O 80:20). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31 (m, 5 H, 5× CH_{ar}), 4.34 (s, 1 H, O–C*H*Ph), 2.45 [d, ^2J = 19.0 Hz, 1 H, (C=O)CH_aH$_b$], 2.29 [m, 4 H, (C-3)CH_2 and (C-2)CH_2], 2.15 [d, ^2J = 19.0 Hz, 1 H, (C=O)CH$_a$$H_b$], 1.21 (t, ^3J = 7.7 Hz, 3 H, CH_3), 1.07 (t, ^3J = 7.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 209.9 (*C*=O), 168.0 (C-3), 147.6 (C-2), 135.5 ($C_{q\text{-}ar}$), 128.6 (2× *C*H$_{ar}$), 128.4 (*C*H$_{ar}$), 126.2 (2× *C*H$_{ar}$), 68.5 (C-4, C_q-O-CH), 61.5 [(C-4)-O-*C*H], 37.9 [(C=O)-*C*H$_2$], 18.0 [(C-3)*C*H$_2$], 17.0 [(C-2)*C*H$_2$], 14.0 (*C*H$_3$), 13.1 (*C*H$_3$) ppm. IR (thin film): $\tilde{\nu}$ = 3060, 3040, 2960, 2930, 2870, 1700, 1630, 1495, 1460, 1450, 1380, 1240, 905, 810, 760 cm^{-1}. MS (EI): *m*/*z* (%) = 242 (45) [M]$^+$, 215 (37), 185 (18), 136 (24), 108 (100), 91 (52), 77 (32), 43 (60).

Spiroepoxycyclopentenone *trans*-7f: Epoxidation of cyclopentenone **4f** (237 mg, 1 mmol) by the General Procedure (Table 1, Entry 6) gave *trans*-**7f** (212 mg, 84%) after flash chromatography (PE/Et_2O 80:20). R_f = 0.30 (PE/Et_2O 80:20). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.36 (dd, ^3J = 7.7, ^3J = 7.5 Hz, 1 H, O–C*H*CH$_2$Si), 2.53 [d, ^2J = 18.8 Hz, 1 H, (C=O)CH_aH$_b$], 2.44 [d, ^2J = 18.8 Hz, 1 H, (C=O)-CH$_a$$H_b$], 2.27 [q, ^3J = 7.5 Hz, 2 H, (C-3)CH_2], 2.15 [q, ^3J = 7.7 Hz, 2 H, (C-2)CH_2], 1.18–1.07 (m, 1 H, CH_aH$_b$Si), 1.09 (t, ^3J = 7.7 Hz, 3 H, CH_3), 1.05 (t, ^3J = 7.5 Hz, 3 H, CH_3), 0.80 (dd, ^2J = 14.3, ^3J = 7.7 Hz, 1 H, CH$_a$$H_b$Si), 0.08 (s, 9 H, 3× SiCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.3 (*C*=O), 169.6 (C-3), 146.8 (C-2), 65.8 (C-4, C_q–O), 58.8 (O–*C*H), 38.0 [(C=O)*C*H$_2$], 18.9 (*C*H$_2$SiMe$_3$), 17.8 and 17.3 (2× *C*H$_2$CH$_3$), 13.9 and 13.2 (2× CH$_2$*C*H$_3$), –1.1 (3× Si*C*H$_3$) ppm. IR (thin film): $\tilde{\nu}$ = 2969, 2878, 1705, 1663, 1464, 1381, 1249, 1186, 1059, 963, 846 cm^{-1}. MS (EI): *m*/*z* (%) = 252 (1) [M]$^+$, 251 (2), 237 (6) [M – CH$_3$]$^+$, 225 (6), 223 (5) [M – C$_2$H$_5$]$^+$, 209 (2), 195 (2). 73, (100) [Si(CH$_3$)$_3$]$^+$. HRMS (ESI): calcd. for $C_{14}H_{24}O_2SiNa$ [M + Na]$^+$ 275.1441; found 275.1443.

Spiroepoxycyclopentenone *trans*-7g: Epoxidation of cyclopentenone (*E*)-**4g** (600 mg, 2.5 mmol) by the General Procedure (Table 1, Entry 7) gave *trans*-**7g** (535 mg, 86%) after flash chromatography (PE/Et_2O 80:20). Yellow oil; R_f = 0.55 (PE/Et_2O 50:50). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.25 (t, ^3J = 5.6 Hz, 1 H, O–C*H*), 2.55 [d, ^2J = 19.2 Hz, 1 H, (C=O)CH_aH$_b$], 2.35 [d, ^2J = 19.2 Hz, 1 H, (C=O)CH$_a$$H_b$], 2.22 [t, ^3J = 7.5 Hz, 2 H, (C-2)CH_2], 1.8 [s, 3 H, (C-3)CH_3], 1.58 (m, 2 H, CH_2), 1.45 [quint, ^3J = 7.5 Hz, 2 H, (C-2)CH$_2$CH_2CH$_3$], 1.38 (m, 8 H, 4× CH_2), 1.05 (t, ^3J = 6.8 Hz, 3 H, CH_3), 0.9 (t, ^3J = 7.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.0 (*C*=O), 165.2 (C-3), 145.6 (C-2), 65.7 (C-4), 60.3 (O–*C*H), 37.5 [(C=O)*C*H$_2$], 31.8 [(C-3)*C*H$_3$], 30.8 [(C-2)*C*H$_3$], 29.2 (O–CH*C*H$_2$), 26.4, 25.5, 22.6 and 21.5 (4× *C*H$_2$), 14.2 [(C-2)-CH$_2$*C*H$_2$], 14.0 and 13.2 (2× *C*H$_3$) ppm. IR (thin film): $\tilde{\nu}$ = 2958, 2928, 2858, 1707 (C=O), 1457, 1387, 1267, 1228, 1082, 960, 812 cm^{-1}. MS (CI): *m*/*z* (%) = 251 (100) [M + H]$^+$, 235 (19), 154 (19), 93 (15), 81 (21), 69 (35). HRMS (CI): calcd. for $C_{16}H_{27}O_2$ [M + H]$^+$ 251.2011; found 251.2007.

Spiroepoxycyclopentenone *trans*-7h: Epoxidation of cyclopentenone (*E*)-**4h** (300 mg, 1 mmol) by the General Procedure (Table 1, Entry 8) gave *trans*-**7h** (162 mg, 50%) after flash chromatography (PE/Et_2O 80:20). Yellow oil; R_f = 0.44 (PE/Et_2O 70:30). ^{1}H NMR

(300 MHz, $CDCl_3$): δ = 6.73 [s, 1 H, C*H*=C(C=O)], 3.21 [dd (t_{app}), ^2J = 6.0, ^2J = 5.8 Hz, 1 H, (C-4)-O-C*H*], 2.63 [d, ^2J = 19.2 Hz, 1 H, (C=O)CH_aH_b], 2.46 [d, ^2J = 19.2 Hz, 1 H, (C=O)CH_aH_b], 2.21 [t, ^3J = 7.5 Hz, 2 H, (C-2)CH_2], 1.60–1.45 (m, 2 H, O–CHCH_2), 1.52 [quint, ^3J = 7.5 Hz, 2 H, (C-2)CH_2CH_2], 1.45–1.15 (m, 10 H, 4× CH_2), 0.94 (t, ^3J = 7.3 Hz, 3 H, CH_3), 0.89 (t, ^3J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.0 (*C*=O), 154.7 (C-3), 151.0 (C-2), 64.6 (C-4, C_q-O-CH), 63.1 [(C-4)-O-*C*H], 38.0 [(C=O)*C*H_2], 31.8, 30.9, 29.2, 26.9, 26.2, 22.6 and 20.8 (7× *C*H_2), 14.2 and 14.0 (2× *C*H_3) ppm. IR (thin film): $\tilde{\nu}$ = 2958, 2927, 2858, 1714 (CO), 1458, 1379, 1254, 1045, 968 cm^{-1}. HRMS (CI): calcd. for $C_{15}H_{25}O_2$: $[M + H]^+$ 237.1855; found 237.1853.

Spiroepoxycyclopentenone *cis*-7h: Epoxidation of cyclopentenone (*Z*)-**4h** (230 mg, 1.05 mmol) by the General Procedure (Table 1, Entry 9) gave *cis*-**7h** (177.4 mg, 72%) after flash chromatography (PE/Et_2O 80:20). Yellow oil; R_f = 0.36 (PE/Et_2O 70:30). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.85 [d, ^4J = 1.2 Hz, 1 H, C*H*=C(C=O)], 3.36 [dd (t_{app}), ^2J = 6.2, ^2J = 6.0 Hz, 1 H, O–C*H*], 2.69 [d, ^2J = 19.2 Hz, 1 H, (C=O)CH_aH_b], 2.58 [d, ^2J = 19.2 Hz, 1 H, (C=O)-CH_aH_b], 2.24 [td, ^3J = 7.5, ^4J = 1.2 Hz, 2 H, (C-2)CH_2], 1.80–1.60 (m, 2 H, O–CHCH_2), 1.53 [quint, ^3J = 7.5 Hz, 2 H, (C-2)CH_2CH_2], 1.60–1.20 (m, 8 H, 4× CH_2), 0.94 (t, ^3J = 7.5 Hz, 3 H, CH_3), 0.89 (t, ^3J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.5 (*C*=O), 154.2 (C-3), 150.8 (C-2), 64.4 (C-4, C_q-O-CH), 65.3 [(C-4)-O-*C*H], 39.8 [(C=O)*C*H_2], 32.2, 30.9, 29.1, 26.3, 25.2, 22.6 and 20.8 (7× *C*H_2), 14.1 and 13.9 (2× *C*H_3) ppm. IR (thin film): $\tilde{\nu}$ = 2958, 2928, 2858, 1707 (C=O), 1457, 1387, 1267, 1228, 1082, 960, 812 cm^{-1}. MS (CI): *m*/*z* (%) = 237 (100) $[M + H]^+$, 222 (11), 208 (41), 190 (47).

Spiroepoxycyclopentenone 9h: Epoxidation of cyclopentenone **5h** (221 mg, 0.93 mmol) by the General Procedure (Table 1, Entry 10) gave a mixture of *trans*-**9h** and *cis*-**9h** (112 mg, 47%, *trans*-**9h**/*cis*-**9h** 90:10) after flash chromatography (PE/Et_2O 95:5).

Isomers (*trans* + *cis*)-9h: Yellow oil; R_f = 0.34 (PE/Et_2O 90:10). IR (thin film): $\tilde{\nu}$ = 2960, 2930, 2860, 1700 (C=O), 1460, 1386, 1270, 1229, 1082, 960, 812 cm^{-1}.

Isomer *trans*-9h: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.70 [s, 1 H, C*H*=C(C=O)], 3.29 [d, ^2J = 4.3 Hz, 1 H, (C-4)-O-CH_aH_b], 3.09 [d, ^2J = 4.3 Hz, 1 H, (C-4)-O-CH_aH_b], 2.53 [t, ^3J = 5.3 Hz, 1 H, (C=O)-C*H*], 2.23 [t, ^3J = 6.8 Hz, 2 H, (C-2)CH_2], 1.51 [m, 2 H, (C-2)-CH_2CH_2], 1.2–1.4 (m, 10 H, 5× CH_2), 0.96 (t, ^3J = 7.3 Hz, CH_3), 0.84 (t, ^3J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 207.3 (*C*=O), 153.1 (C-3), 151.6 (C-2), 64.8 (C-4, C_q–O), 51.8 [(C-4)-O-*C*H_2], 48.4 [(C=O)*C*H], 31.7 [(C-2)*C*H_2], 31.7, 29.7, 27.1, 26.0, 22.8 and 20.9 (6× *C*H_2), 14.2 and 14.0 (2× *C*H_3) ppm.

Isomer *cis*-9h: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.92 (s, 1 H, C*H*=CCO), 3.29 [d, ^2J = 4.3 Hz, 1 H, (C-4)-O-CH_aH_b], 3.08 [d, ^2J = 4.3 Hz, 1 H, (C-4)-O-CH_aH_b], 2.44 [t, ^3J = 5.3 Hz, 1 H, (C=O)-C*H*], 2.22 [t, ^3J = 6.8 Hz, 2 H, (C-2)CH_2], 1.50 [m, 2 H, (C-2)-CH_2CH_2], 1.2–1.4 (m, 10 H, 5× CH_2), 1.25 (t, ^3J = 7.3 Hz, CH_3), 0.85 (t, ^3J = 6.8 Hz, CH_3) ppm.

Spiroepoxycyclopentenone 7j: Epoxidation of cyclopentenone (*E* + *Z*)-**4j** (160 mg, 0.89 mmol) by the General Procedure (Table 2, Entry 1) gave (*trans* + *cis*)-**7j** (117 mg, 67%, *trans*/*cis* 53:46) after flash chromatography (PE/Et_2O 80:20).

Isomers (*trans* + *cis*)-7j: Yellow oil; R_f = 0.24 (PE/Et_2O 70:30).

Isomer (major) *trans*-7j: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34 [d, ^3J = 6.0 Hz, 1 H, *H*C=CH(C=O)], 6.43 [d, ^3J = 6.0 Hz, 1 H, HC=C*H*(C=O)], 4.27 (d, ^2J = 12.0 Hz, 1 H, H_aH_bC–OAc), 4.20 (d, ^2J = 12.0 Hz, 1 H, H_aH_bC–OAc), 2.67 [d, ^2J = 19.2 Hz,1 H, (C=O)-H_aH_b], 2.44 [d, ^2J = 19.2 Hz, 1 H, (C=O)H_aH_b], 2.09 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.1 (*C*=O), 170.5 (*C*=O), 158.3 (C-3), 139.4 (C-2), 69.7 (C_q–O), 65.8 (C_q–O), 63.7 (*C*H_2–OAc), 38.6 [(C=O)*C*H_2], 20.8 (*C*H_3), 18.5 (*C*H_3) ppm.

Isomer (minor) *cis*-7j: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 [d, ^3J = 5.8 Hz, 1 H, *H*C=CH(C=O)], 6.46 [d, ^3J = 5.8 Hz, 1 H, HC=C*H*(C=O)], 4.14 (d, ^2J = 12.5 Hz, 1 H, H_aH_bC–OAc), 4.09 (d, ^2J = 12.5 Hz, 1 H, H_aH_bC–OAc), 2.71 [d, ^2J = 19.2 Hz, 1 H, (C=O)-H_aH_b], 2.47 [d, ^2J = 19.2 Hz, 1 H, (C=O)H_aH_b], 2.09 (s, 3 H, CH_3), 1.49 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.1 (*C*=O), 170.6 (*C*=O), 158.4 (C-3), 139.5 (C-2), 69.4 (*C*q–O), 67.3 (*C*q–O), 63.9 (*C*H_2–OAc), 38.1 [(C=O)*C*H_2], 20.8 (*C*H_3), 16.2 (*C*H_3) ppm.

Spiroepoxycyclopentenone (7k): Epoxidation of cyclopentenone (*E* + *Z*)-**4k** (220 mg, 1.22 mmol) by the General Procedure (Table 2, Entry 2) gave (*trans* + *cis*)-**7k** (157 mg, 66%, *trans*/*cis* = 80:20) after flash chromatography (PE/Et_2O 80:20.

Isomers (*trans* + *cis*)-7k: R_f = 0.21 (PE/Et_2O 80:20). IR (thin film): $\tilde{\nu}$ = 2955, 2884, 1719 (C=O), 1350, 1248, 1118, 1165, 969, 840 cm^{-1}.

Isomer (major) *trans*-7k: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.13 [d, ^3J = 5.7 Hz, 1 H, C*H*=CH(C=O)], 6.31 [d, ^3J = 5.7 Hz, 1 H, CH=C*H*(C=O)], 3.31 (t_{app}, $^3J_{app}$ = 6.8 Hz, 1 H, O-C*H*-CH_aH_bSi), 2.53 [d, ^2J = 19.2 Hz, 1 H, (C=O)CH_aH_b], 2.37 [d, ^2J = 19.2 Hz, 1 H, (C=O)CH_aH_b], 0.97 (dd, ^2J = 14.5, ^3J = 6.6 Hz, 1 H, CH_aH_bSi), 0.83 (dd, ^2J = 14.5, ^3J = 6.8 Hz, 1 H, CH_aH_bSi), 0.06 (s, 9 H, 3× SiCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.1 (*C*=O), 162.5 (C-3), 137.7 (C-2), 66.6 (C-4, C_q-O-CH), 61.5 (O-*C*H-CH_2Si), 37.5 [(C=O)*C*H_2], 18.9 [*C*H_2Si(CH_3)$_3$], –1.1 (3× Si*C*H_3) ppm.

Isomer (minor) *cis*-7k: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26 [d, ^3J = 5.8 Hz, 1 H, C*H*=CH(CO)], 6.43 [d, ^3J = 5.8 Hz, 1 H, CH=C*H*(C=O)], 3.46 (m, 1 H, O-C*H*-CH_2Si), 2.62 [d, ^2J = 19.2 Hz, 1 H, (C=O)CH_aH_b], 2.51 [d, ^2J = 19.2 Hz, 1 H, (C=O)-CH_aH_b], 1.10–1.25 (m, 2 H, CH_2Si), 0.06 (s, 9 H, 3× SiCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.9 (*C*=O), 159.4 (C-3), 139.2 (C-2), 65.9 (C-4, C_q-O-CH), 62.6 (O-*C*H-CH_2Si), 40.9 [(C=O)-*C*H_2], 17.5 [*C*H_2Si(CH_3)$_3$], –1.1 (3× Si*C*H_3) ppm. MS (CI): *m*/*z* (%) = 197 (100) $[M + H]^+$, 154 (9), 125 (7), 107 (18), 81 (25), 69 (36). HRMS (CI): calcd. for $C_{10}H_{17}O_2Si$: $[M + H]^+$ 197.0998; found 197.1009.

Spiroepoxycyclopentenone 7l: Epoxidation of cyclopentenone (*E* + *Z*)-**4l** (180.4 mg, 1 mmol) by the General Procedure (Table 2, Entry 3) gave (*trans* + *cis*)-**7l** (162 mg, 82%, *trans*/*cis* = 64:36) after flash chromatography (PE/Et_2O 80:20).

Isomers (*trans* + *cis*)-7l: R_f = 0.46 (PE/Et_2O 80:20).

Isomer (major) *trans*-7l: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43 [d, ^3J = 5.9 Hz, 1 H, *H*C=CH(C=O)], 6.63 [d, ^3J = 5.9 Hz, 1 H, CH=C*H*(C=O)], 2.63 [d, ^2J = 19.0 Hz, 1 H, (C=O)CH_aH_b], 2.45 [d, ^2J = 19.0 Hz, 1 H, (C=O)CH_aH_b], 1.40 (s, 3 H, O–CCH_3), 0.14 (s, 9 H, 3× SiCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.3 (*C*=O), 161.2 (C-3), 138.0 (C-2), 68.3 (C-4, C_q–O), 62.0 (O-*C*-Si), 40.4 [(C=O)*C*H_2], 17.1 (O-C*C*H_3), –2.6 (3× Si*C*H_3) ppm.

Isomer (minor) *cis*-7l: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30 [d, ^3J = 5.9 Hz, 1 H, *H*C=CH(C=O)], 6.34 [d, ^3J = 5.9 Hz, 1 H, C=C*H*(C=O)], 2.68 [d, ^2J = 19.0 Hz, 1 H, (C=O)CH_aH_b], 2.46 [d, ^2J = 19.0 Hz, 1 H, (C=O)CH_aH_b], 1.33 (s, 3 H, OCCH_3), 0.18 (s, 9 H, 3× SiCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.13 (*C*=O), 161.7 (C-3), 137.4 (C-2), 66.6 (C-4), 61.6 (O-*C*-Si), 38.8 [(C=O)*C*H_2], 20.3 (O–C*C*H_3), –1.9 (3× Si*C*H_3) ppm. GC–MS (EI): *m*/*z* (%) = 196 (6) $[M]^+$, 181 (5), 154 (4), 153 (11), 116 (4), 101 (4),

85 (13)75 (20), 73 (100). HRMS (EI): calcd. for $C_{10}H_{16}O_2Si$: $[M]^+$ 196.0919; found 196.0920.

Spiroepoxycyclopentenone 7m: Epoxidation of cyclopentenone (*E* + *Z*)-**4m** (300 mg, 1.23 mmol) by the General Procedure (Table 2, Entry 4) gave *trans*-**7m** (168 mg, 53%) and its isomer *cis*-**7m** (108 mg, 34%) after flash chromatography (PE/Et_2O 80:20).

Isomer (major) *trans*-7m: R_f = 0.33 (PE/Et_2O 60:40). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.01 [d, ^3J = 5.9 Hz, 1 H, *H*C=C(C=O)], 7.60–7.50 (m, 2 H, H_{ar}), 7.41–7.36 (m, 3 H_{ar}), 6.41 [d, ^3J = 5.9 Hz, 1 H, CH=C*H*(C=O)], 2.53 [d, ^2J = 19.0 Hz, 1 H, (C=O)CH_aH$_b$], 2.24 [d, ^2J = 19.0 Hz, 1 H, (C=O)CH$_a$*H*$_b$], 1.43 (s, 3 H, CH_3), 0.43 and 0.40 (2× CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.6 (*C*=O), 161.1 (C-3), 138.4 (C-2), 135.5 [C(Ph)$_i$], 134.1 [2× *C*H-(Ph)$_o$], 129.9 [*C*H(Ph)$_p$], 128.3 [2× *C*H(Ph)$_m$], 68.6 (C-4, C_q–O), 61.9 (O-*C*-Si), 40.5 [(C=O)*C*H$_2$], 17.9 (*C*H$_3$), –3.6 and –3.9 (2× Si*C*H$_3$) ppm. GC–MS (EI): *m*/*z* (%) = 258 (4) $[M]^+$, 243 (5), 162 (11), 136 (13), 135 (100), 105 (12). HRMS (EI): calcd. for $C_{15}H_{18}O_2Si$: $[M]^+$ 258.1076; found 258.1066.

Isomer (minor) *cis*-7m: R_f = 0.40 (PE /Et_2O 60:40). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.50 (m, 2 H, H_{ortho}), 7.41–7.36 (m, 3 H, H_{meta} + H_{para}), 6.94 [d, ^3J = 5.9 Hz, 1 H, *H*C=C(C=O)], 6.20 [d, ^3J = 5.9 Hz, 1 H, CH=C*H*(C=O)], 2.68 [d, ^2J = 19.2 Hz, 1 H, (C=O)CH_aH$_b$], 2.45 [d, ^2J = 19.2 Hz, 1 H, (C=O)CH$_a$*H*$_b$], 1.25 (s, 3 H, CH_3), 0.48 and 0.46 (2× CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.4 (*C*=O), 161.7 (C-3), 137.4 (C-2), 135.8 [C(Ph)$_i$], 134.1 [2× *C*H(Ph)$_o$], 129.8 [*C*H(Ph)$_p$], 128.3 [2× *C*H(Ph)$_m$], 69.9 (C-4, C_q–O), 61.5 (O-C_q-Si), 39.0 [(C=O)*C*H$_2$], 20.9 (*C*H$_3$), –3.2 and –3.4 (2× Si*C*H$_3$) ppm.

General Procedure for the Acidic Ring-Opening of Spiroepoxycyclopentenones 7: A spiroepoxycyclopentenone **7** (1 mmol) was mixed with H_2SO_4 (0.75 M, 7.2 mL, 5.5 mmol, 11 equiv.). The mixture was stirred at room temperature overnight (15 h). A solution of $NaHCO_3$ (1 M, 11 mL, 11 mmol) was added, and the mixture was extracted with CH_2Cl_2 (2× 10 mL) and ether (10 mL). The organic layers were collected, dried with Na_2SO_4, and then concentrated in vacuo. Flash chromatography on silica gel yielded a dihydroxylated cyclopentenone **10**.

2,3-Diethyl-4-hydroxy-4-(1-hydroxycyclohexyl)cyclopentenone (10b): Ring-opening of epoxide **7b** (80 mg, 0.34 mmol) by the General Procedure (Table 3, Entry 1) gave **10b** (55 mg, 64%) after flash chromatography. Yellow oil; R_f = 0.24 (PE/Et_2O 75:25). ^1H NMR (300 MHz, $CDCl_3$): δ = 3.20–2.60 (br. s, 2 H, 2× O*H*), 2.67 [dq, ^2J = 13.3, ^3J = 7.6 Hz, 1 H, (C-3)CH_aH$_b$CH$_3$], 2.64 [d, ^2J = 18.2 Hz, 1 H, (C=O)CH_aH$_b$], 2.50 [dq, ^2J = 13.3, ^3J = 7.6 Hz, 1 H, (C-3)CH$_a$*H*$_b$CH$_3$], 2.35 [d, ^2J = 18.2 Hz, 1 H, (C=O)CH$_a$*H*$_b$], 2.22 [dq, ^2J = 13.6, ^3J = 7.6 Hz, 1 H, (C-2)CH_aH$_b$CH$_3$], 2.16 [dq, ^2J = 13.6, ^3J = 7.5 Hz, 1 H, (C-2)CH$_a$*H*$_b$CH$_3$], 1.70–1.00 (m, 10 H, 5× CH_2), 1.19 (t, ^3J = 7.6 Hz, 3 H, CH_3), 1.01 (t, ^3J = 7.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.7 (C-1, *C*=O), 175.0 (C-3, *C*=C-CO), 144.6 (C-2, C=*C*-CO), 84.2 (C-4, C_q–O), 76.5 (C_q–O), 47.5 [C-5, (C=O)*C*H$_2$], 32.4 [(C-3)*C*H$_2$], 31.5 [(C-2)-*C*H$_2$], 25.6, 21.6, 21.5, 21.4 and 16.7 (5× *C*H$_2$), 14.1 (*C*H$_3$), 13.1 (*C*H$_3$) ppm. IR (thin film): $\tilde{\nu}$ = 3520, 3340, 2920, 2870, 1685, 1630, 1450, 1380, 1160 cm^{-1}. MS (CI): *m*/*z* (%) = 253 $[M + H]^+$.

4-Hydroxy-4-(1-hydroxyheptyl)-2,3-dimethylcyclopent-2-enone (10c): Ring-opening of **7c** (90 mg, 0.40 mmol) by the General Procedure (Table 3, Entry 2) gave *anti*-**10c** (58 mg, 59%) and its diastereomer *syn*-**10c** (8 mg, 8%) after flash chromatography.

Isomer *anti*-10c: Colourless oil; R_f = 0.43 (Et_2O). ^1H NMR (300 MHz, $CDCl_3$): δ = 3.79 [br. d, ^3J = 9.4 Hz, 1 H, C*H*(OH)], 3.30–2.80 (m, 2 H, 2× O*H*), 2.49 [d, ^2J = 18.1 Hz, 1 H, (C=O)-CH_aH$_b$], 2.37 [d, ^2J = 18.1 Hz, 1 H, (C=O)CH$_a$*H*$_b$], 2.05 (s, 3 H, CH_3), 1.70 (s, 3 H, CH_3), 1.20–1.40 (m, 10 H, 5× CH_2), 0.87 (t, ^3J = 6.8 Hz, 3 H, CH$_2$CH_3) ppm.

Isomer *syn*-10c: Colourless oil; R_f = 0.22 (Et_2O). ^1H NMR (300 MHz, $CDCl_3$): δ = 3.84 [br. d, ^3J = 10.2 Hz, 1 H, C*H*(OH)], 3.20–2.60 (m, 2 H, 2× O*H*), 2.79 [d, ^2J = 18.8 Hz, 1 H, (C=O)-CH_aH$_b$], 2.20 [d, ^2J = 18.8 Hz, 2 H, (C=O)CH$_a$*H*$_b$], 1.98 (s, 3 H, CH_3), 1.72 (s, 3 H, CH_3), 1.30–1.05 (m, 10 H, 5× CH_2), 0.87 (t, ^3J = 6.8 Hz, 3 H, CH$_2$CH_3) ppm.

2,3-Diethyl-4-hydroxy-4-(1-hydroxyheptyl)cyclopent-2-enone (10d): Ring-opening of epoxide **7d** (72 mg, 0.29 mmol) by the General Procedure (Table 3, Entry 3) gave *anti*-**10d** (30.5 mg, 36%) and its diastereomer *syn*-**10d** (10 mg, 12%) after flash chromatography.

Isomer *anti*-10d: White solid; R_f = 0.39 (PE/Et_2O 20:80). ^1H NMR (300 MHz, $CDCl_3$): δ = 3.79 [br. d, ^3J = 9.4 Hz, 1 H, C*H*(OH)], 3.10–2.70 (br. s, 2 H, 2× O*H*), 2.50 [m, 2 H, (C-3)CH_2], 2.49 [d, ^2J = 18.1 Hz, 1 H, (C=O)CH_aH$_b$], 2.35 [d, ^2J = 18.1 Hz, 1 H, (C=O)CH$_a$*H*$_b$], 2.20 [q, ^3J = 7.7 Hz, 2 H, (C-2)CH_2], 1.42–1.10 (m, 10 H, 5× CH_2), 1.21 (t, ^3J = 7.6 Hz, 3 H, CH_3), 1.02 (t, ^3J = 7.7 Hz, 3 H, CH_3), 0.86 (t, ^3J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.5 (*C*=O), 173.3 (C-3), 144.7 (C-2), 81.4 (C-4, C_q–O), 75.9 [*C*H(OH)], 46.7 [(C=O)*C*H$_2$], 31.9 [(C-3)*C*H$_2$], 31.7 [(C-2)*C*H$_2$], 29.3, 26.7, 22.7, 20.5 and 16.6 (5× *C*H$_2$), 14.2, 14.0 and 13.2 (3× *C*H$_3$) ppm. IR (thin film): $\tilde{\nu}$ = 3360, 2960, 2920, 2870, 2855, 1680, 1640, 1460, 1375, 1195, 1150, 1130 cm^{-1}. MS (CI): *m*/*z* (%) = 269 $[M + H]^+$. HRMS (EI): calcd. for $C_{16}H_{28}O_3$ $[M]^+$ 268.2039; found 268.2115.

Isomer *syn*-10d: White solid; m.p 76–77 °C; R_f = 0.14 (PE/Et_2O 20:80). ^1H NMR (300 MHz, $CDCl_3$): δ = 3.84 [dd, ^3J = 7.9, ^3J = 3.4 Hz, 1 H, C*H*(OH)], 3.20–2.50 (br. s, 2 H, 2× O*H*), 2.78 [d, ^2J = 18.1 Hz, 1 H, (C=O)CH_aH$_b$], 2.21 [d, ^2J = 18.1 Hz, 1 H, (C=O)-CH$_a$*H*$_b$], 2.55–2.20 [m, 2 H, (C-3)CH_2], 2.22 [q, ^3J = 7.6 Hz, 2 H, (C-2)CH_2], 1.45–1.10 (m, 10 H, 5× CH_2), 1.19 (t, ^3J = 7.5 Hz, 3 H, CH_3), 1.03 (t, ^3J = 7.6 Hz, 3 H, CH_3), 0.86 (t, ^3J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.4 (*C*=O), 172.6 (C-3), 144.5 (C-2), 82.6 (C-4, C_q–O), 75.3 [*C*H(OH)], 45.1 [(C=O)*C*H$_2$], 31.8 [(C-3)*C*H$_2$], 31.3 [(C-2)*C*H$_2$], 29.2, 26.3, 22.6, 19.9 and 16.6 (5× *C*H$_2$), 14.1, 13.7 and 12.9 (3× *C*H$_3$) ppm. IR (thin film): $\tilde{\nu}$ = 3420, 2920, 2850, 1685, 1640, 1455, 1380 cm^{-1}. MS (CI): *m*/*z* (%) = 269 $[M + H]^+$.

2,3-Diethyl-4-hydroxy-4-(1-hydroxy-1-phenylmethyl)cyclopent-2-enone (10e): Ring-opening of epoxide **7e** (43 mg, 0.18 mmol) by the General Procedure (Table 3, Entry 4) but with addition of *t*BuOH as solvent (2 mL) gave *anti*-**10e** (12 mg, 26%) and its diastereomer *syn*-**10e** (9 mg, 20%) after flash chromatography. In a second experiment (Table 3, Entry 5), by the General Procedure but with addition of THF as solvent (5 mL), ring-opening of epoxide **7e** (120 mg, 0.5 mmol) gave cyclopentenone *anti*-**10e** (36 mg, 28%) and its diastereomer *syn*-**10e** (36 mg, 28%) after flash chromatography.

Isomer *anti*-10e: Yellow oil; R_f = 0.20 (PE/Et_2O 80:20). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.34 (m, 5 H, H_{ar}), 4.87 [s, 1 H, C*H*(OH)], 2.84 [d, ^2J = 17.7 Hz, 1 H, (C=O)CH_aH$_b$], 2.50 [dq, ^2J = 14.0, ^3J = 7.5 Hz, 1 H, (C-3)CH_aH$_b$], 2.44 [dq, ^2J = 14.0, ^3J = 7.5 Hz, 1 H, (C-3)CH$_a$*H*$_b$], 2.90–2.20 (br. s, 2 H, 2× O*H*), 2.25–2.05 [m, 2 H, (C-2)CH_2], 2.13 [d, ^2J = 17.7 Hz, 1 H, (C=O)CH$_a$*H*$_b$], 1.22 (t, ^3J = 7.5 Hz, 3 H, CH_3), 0.95 (t, ^3J = 7.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.0 (*C*=O), 172.4 (C-3), 145.0 (C-2), 139.2 [*C*(Ph)$_i$], 128.7 [*C*H(Ph)$_p$], 128.5 [2× *C*H(Ph)$_m$], 127.4 [2× *C*H-(Ph)$_o$], 81.8 [C-4, C_q(OH)], 77.4 [*C*H(OH)], 46.3 [(C=O)*C*H$_2$], 20.2 [(C-3)*C*H$_2$], 16.7 [(C-2)*C*H$_2$], 14.1 (*C*H$_3$), 12.9 (*C*H$_3$) ppm. IR (thin

film): $\tilde{\nu}$ = 3400, 3050, 2970, 2935, 2885, 1695, 1640, 1450, 1380, 735, 705 cm^{-1}. HRMS (EI): calcd. for $C_{16}H_{20}O_3$ $[M]^+$ 260.1413; found 260.1424.

Isomer *syn*-10e: Yellow oil; R_f = 0.16 (PE/Et_2O 80:20). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.21 (m, 5 H, H_{ar}), 4.99 [s, 1 H, C*H*(OH)], 3.90–2.40 (br. s, 2 H, 2× O*H*), 2.85 [d, ^2J = 18.1 Hz, 1 H, (C=O)-CH_aH$_b$], 2.57 [q, ^3J = 7.5 Hz, 2 H, (C-3)CH_2], 2.20 [d, ^2J = 18.1 Hz, 1 H, (C=O)CH$_a$$H_b$], 2.06 [dq, ^2J = 13.4, ^3J = 7.5 Hz, 1 H, (C-2)-CH_aH$_b$], 1.96 [dq, ^2J = 13.4, ^3J = 7.5 Hz, 1 H, (C-2)CH$_a$$H_b$], 1.28 (t, ^2J = 7.5 Hz, 3 H, CH_3), 0.75 (t, ^3J = 7.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.8 (*C*=O), 171.6 (C-3), 144.9 (C-2), 138.5 [*C*(Ph)$_i$], 128.3 [*C*(Ph)$_p$], 128.1 [2× *C*(Ph)$_m$], 126.8 [2× *C*(Ph)$_o$], 82.9 [C-4, C_q(OH)], 77.4 [*C*H(OH)], 45.0 [C-5, (C=O)-*C*H$_2$], 20.9 [(C-3)*C*H$_2$], 16.4 [(C-2)*C*H$_2$], 14.3 (*C*H$_3$), 12.3 (*C*H$_3$) ppm. IR (thin film): $\tilde{\nu}$ = 3400, 3060, 3030, 2965, 2935, 2875, 1690, 1635, 1490, 1460, 1450, 1375, 1195, 735, 700 cm^{-1}. HRMS (CI): calcd. for $C_{16}H_{21}O_3$ $[M + H]^+$ 261.1491; found 261.1488.

General Procedure for Acetalization of Dihydroxylated Cyclopentenones 10: A crystal of *para*-toluenesulfonic acid was added to a solution of a dihydroxylated cyclopentenone **10** (0.15 mmol) and distilled benzaldehyde (15.5 mg, 0.15 mmol) in benzene (2.5 mL) under a Dean–Stark apparatus. The mixture was heated at reflux for 1–2 h. After cooling, the mixture was filtered over neutral alumina (grade III), which was further eluted with ether. Evaporation of the solvents followed by flash chromatography gave the acetal **11**. In order to prevent the hydrolysis of the acetal **11** on the silica gel column, the column was prepared with a 1% triethylamine PE/Et_2O mixture of solvents and then eluted with this solvent mixture.

Acetal *trans*-11c: Acetalization of the major isomer of dihydroxylated cyclopentenone *anti*-**10c** (35 mg, 0.15 mmol) by the General Procedure gave *trans*-**11c** (10 mg, 21%) after flash chromatography (PE/Et_2O gradient 95:5 to 40:60). Yellow oil; R_f = 0.33 (PE/Et_2O 80:20). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.54 (m, 2 H, H_{ar}), 7.40 (m, 3 H, H_{ar}), 5.98 [s, 1 H, O-C*H*(Ph)-O], 4.14 (dd, ^3J = 9.1, ^3J = 3.4 Hz, 1 H, C*H*–O), 2.92 [d, ^2J = 18.5 Hz, 1 H, (C=O)CH_aH$_b$], 2.51 [d, ^2J = 18.5 Hz, 1 H, (C=O)CH$_a$$H_b$], 1.99 [s, 3 H, (C-3)C$H_3$], 1.72 [s, 3 H, (C-2)C$H_3$], 1.56 [m, 2 H, CH(OH)C$H_2$], 1.10–1.40 (m, 8 H, 4× CH_2), 0.88 (t, ^3J = 6.8 Hz, 3 H, CH_3) ppm. At 500 MHz (Bruker DRX 500 instrument), irradiation of proton H_a of the (C=O)CH_aH$_b$ group at δ = 2.94 ppm resulted in the enhancement of proton $\mathbf{H}_b$ [(C=O)CH$_a$$H_b$] at δ = 2.53 ppm (21% nOe) and of the acetal proton O-C***H***(Ph)-O at δ = 6.00 ppm (0.5% nOe). Irradiation of proton $\mathbf{H}_b$ [(C=O)CH$_a$$H_b$] at δ = 2.53 ppm resulted in the enhancement of $\mathbf{H}_a$ (21% nOe) and of the dioxolane proton C***H***(nC$_6$H$_{13}$)-O at δ = 4.14 ppm (6% nOe).

Acetal *trans*-11d: Acetalization of the major isomer of dihydroxylated cyclopentenone *anti*-**10d** (27 mg, 0.1 mmol) by the General Procedure gave *trans*-**11d** (13 mg, 36%) after flash chromatography (PE/Et_2O gradient 90:10 to 70:30). Yellow oil; R_f = 0.44 (PE/Et_2O 90:10). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.55 (m, 2 H, H_{ar}), 7.40 (m, 3 H, H_{ar}), 5.94 [s, 1 H, O-C*H*(Ph)-O], 4.12 [dd, ^3J = 8.7, ^3J = 3.4 Hz, 1 H, C*H*(nC$_6$H$_{13}$)-O], 2.94 [d, ^2J = 18.5 Hz, 1 H, (C=O)-CH_aH$_b$], 2.48 [d, ^2J = 18.5 Hz, 1 H, (C=O)CH$_a$$H_b$], 2.44 [q, ^3J = 7.5 Hz, 2 H, (C-3)CH_2], 2.13–132 [m, 2 H, (C-2)CH_2], 1.20–1.70 (m, 8 H, 4× CH_2), 1.04 (t, ^3J = 7.5 Hz, 3 H, CH$_2$CH_3), 1.00 (t, ^3J = 7.1 Hz, 3 H, CH$_2$CH_3), 0.86 (t, ^3J = 6.8 Hz, 3 H, CH$_2$CH_3) ppm. At 500 MHz, irradiation of proton C*H*(nC$_6$H$_{13}$)-O at δ = 4.15 ppm resulted in the enhancement of proton (C=O)CH$_a$$\mathbf{H}_b$ at δ = 2.51 ppm (7% nOe) and of the acetal proton O-C***H***(Ph)-O at δ = 5.97 ppm (6.8% nOe).

Acetal *trans*-11e: Acetalization of the major isomer of dihydroxylated cyclopentenone *anti*-**10e** (40 mg, 0.15 mmol) by the General Procedure gave *trans*-**11e** (25 mg, 47%) after flash chromatography (PE/Et_2O 75:25). Yellow oil; R_f = 0.16 (PE/Et_2O 75:25). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.65–7.75 (m, 2 H, H_{ar}), 7.40–7.50 (m, 3 H, H_{ar}), 7.20–7.35 (m, 5 H, H_{ar}), 6.20 [s, 1 H, O-C*H*(Ph)-O], 5.39 [s, 1 H, O-C_q-C*H*(Ph)-O], 3.10 [d, ^2J = 18.0 Hz, 1 H, (C=O)-CH_aH$_b$], 2.95 [d, ^2J = 18.0 Hz, 1 H, (C=O)CH$_a$$H_b$], 1.73–2.33 (m, 4 H, 2× CH_2CH$_3$), 0.84 (t, ^3J = 7.5 Hz, 3 H, CH$_2$CH_3), 0.75 (t, ^3J = 7.5 Hz, 3 H, CH$_2$CH_3) ppm. At 500 MHz, irradiation of proton C*H*(Ph)–O at δ = 5.40 ppm resulted in the enhancement of proton (C=O)CH$_a$$\mathbf{H}_b$ at δ = 2.97 ppm (5% nOe), of the acetal proton O-C***H***(Ph)-O at δ = 6.20 ppm (4% nOe) and of the *ortho*-protons of the phenyl group CH$_c$(***Ph***)–O at δ = 7.27 ppm (3.6% nOe).

Supporting Information (see footnote on the first page of this article): The ^1H and ^{13}C NMR spectra of cyclopentenones **10** and acetals **11** are provided.

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[1] a) G.-J. Martin, C. Rabiller, G. Mabon, *Tetrahedron Lett.* **1970**, *11*, 3131–3132; b) G.-J. Martin, C. Rabiller, G. Mabon, *Tetrahedron* **1972**, *28*, 4027–4037.
[2] a) M. Ahmar, F. Antras, B. Cazes, *Tetrahedron Lett.* **1995**, *36*, 4417–4420; b) F. Antras, M. Ahmar, B. Cazes, *Tetrahedron Lett.* **2001**, *42*, 8153–8156; c) F. Antras, S. Laurent, M. Ahmar, H. Chermette, B. Cazes, *Eur. J. Org. Chem.* **2010**, 3312–3336.
[3] For other non-general syntheses of 4-alkylidenecyclopentenones **4**, see: a) D. J. Pasto, S.-H. Yang, J. A. Muellerleile, *J. Org. Chem.* **1992**, *57*, 2976–2978; b) A. S. K. Hashmi, J. W. Bats, J.-H. Choi, L. Schwarz, *Tetrahedron Lett.* **1998**, *39*, 7491–7494; c) W. Huang, T. T. Tidwell, *Synthesis* **2000**, 457–470; d) R. Ballini, G. Bosica, D. Fiorini, M. V. Gil, M. Petrini, *Org. Lett.* **2001**, *3*, 1265–1267; e) P. Cao, X.-S. Sun, B.-H. Zhu, Q. Shen, Z. Xie, Y. Tang, *Org. Lett.* **2009**, *11*, 3048–3051.
[4] a) F. Antras, M. Ahmar, B. Cazes, *Tetrahedron Lett.* **2002**, *43*, 5029–5031; b) S. Laurent, N. Chorfa, M. Ahmar, B. Cazes, *Synlett* **2006**, 681–684.
[5] M. Ahmar, S. Thomé, B. Cazes, *Synlett* **2006**, 279–282.
[6] C. Puder, P. Krastel, A. Zeeck, *J. Nat. Prod.* **2000**, *63*, 1258–1260.
[7] P. K. Chowdhury, N. C. Barua, R. P. Sharma, J. N. Barua, W. Herz, K. Watanabe, J. F. Blount, *J. Org. Chem.* **1983**, *48*, 732–738.
[8] a) F. Bohlmann, L. Hartono, J. Jakupovic, S. Huneck, *Phytochemistry* **1985**, *24*, 1003–1007; b) R. Ortet, S. Prado, E. Mouray, O. P. Thomas, *Phytochemistry* **2008**, *69*, 2961–2965.
[9] K. Sakai, M. Yamashita, K. Yamada, N. Toida, *Jpn. Kokai Tokkyo Koho* **1987**; *Chem. Abstr.* **1987**, *107*, 154158.
[10] E. F. Makkiyi, R. F. M. Frade, T. Lebl, E. G. Jaffray, S. E. Cobb, A. L. Harvey, A. M. Z. Slawin, R. T. Hay, N. J. Westwood, *Eur. J. Org. Chem.* **2009**, 5711–5715.
[11] T. Bauer, in: *Houben–Weyl, Methoden der organischen Chemie*, E21e, Georg Thieme Verlag, Stuttgart, Germany, **1995**, p. 4649.
[12] a) H. M. Walton, *J. Org. Chem.* **1957**, *22*, 1161–1165; b) G. R. Krow, *Org. React.* **1993**, *43*, 251–798.
[13] A. G. Schultz, L. O. Lockwood Jr, *J. Org. Chem.* **2000**, *65*, 6354–6361.
[14] B. Heasley, *Eur. J. Org. Chem.* **2009**, 1477–1489.
[15] a) A. Guzman, J. M. Muchowski, A. M. Strosberg, J. M. Sims, *Can. J. Chem.* **1981**, *59*, 3241–3247; b) C. P. Melero, M. Medarde, A. San Feliciano, *Molecules* **2000**, *5*, 51–81; c) B. Heasley, *Chem. Eur. J.* **2012**, *18*, 3092–3120.
[16] a) J. W. De Haan, L. J. M. Van de Ven, *Org. Magn. Reson.* **1973**, *5*, 147–153; b) M. Ahmar, J.-J. Barieux, B. Cazes, J. Gore,

Tetrahedron **1987**, *43*, 513–526; c) E. Kleinpeter, P. R. Seidl, *J. Phys. Org. Chem.* **2004**, *17*, 680–685.
[17] a) W. Kitching, M. Marriott, W. Adcock, D. Doddrell, *J. Org. Chem.* **1976**, *41*, 1671–1673; b) J. Schraml, V. Chvalovsky, M. Mägi, E. Lippmaa, *Collect. Czech. Chem. Commun.* **1979**, *44*, 854–865.
[18] D. A. Otieno, G. Pattenden, C. R. Popplestone, *J. Chem. Soc. Perkin Trans. 1* **1977**, 196–201.
[19] a) R. J. Gritter, in: *The Chemistry of Ether Linkage* (Ed.: S. Patai), Interscience Publishers, London, **1967**, p. 373; b) M. Bartok, K. L. Lang, in: *The chemistry of ethers, crown-ethers, hydroxyl groups and their sulfur analogues* (Ed.: S. Patai), Wiley, Chichester, UK, **1980**, p. 609; c) Y. Sawaki, in: *The chemistry of hydroxyl, ether and peroxide groups*, Supplement E2 (Ed.: S. Patai), Wiley, Chichester, UK, **1993**, p. 587; d) J. Gorzynski Smith, *Synthesis* **1984**, 629–656; e) B. Rickborn, in: *Comprehensive Organic Synthesis* (Eds.: B. M. Trost, I. Fleming, G. Pattenden), Pergamon Press, New York, **1991**, vol. 3, chapter 3.3, p. 733–775.
[20] T. Sugahara, H. Fukuda, Y. Iwabuchi, *J. Org. Chem.* **2004**, *69*, 1744–1747.
[21] W. C. Still, M. Khan, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923–2925.
[22] a) Y. J. Ginzburg, *J. Gen. Chem. (USSR)* **1940**, *10*, 513–516; *Chem. Abstr.* **1940**, *34*, 7843; b) G. F. Hennion, J. A. Sheeman, *J. Am. Chem. Soc.* **1949**, *71*, 1964; c) J. Chengebroyen, M. Linke, M. Robitzer, C. Sirlin, M. Pfeffer, *J. Organomet. Chem.* **2003**, *687*, 313–321.
[23] J.-L. Moreau, M. Gaudemar, *J. Organomet. Chem.* **1976**, *108*, 159–164.
[24] M. Montury, B. Psaume, J. Gore, *Synth. Commun.* **1982**, *12*, 402–407.
[25] D. Djahanbini, B. Cazes, J. Gore, *Tetrahedron* **1987**, *43*, 3441–3452.
[26] I. Fleming, F. Roessler, *J. Chem. Soc., Chem. Commun.* **1980**, 276–277.
[27] a) K. A. Trankler, J. Y. Corey, N. P. Rath, *J. Organomet. Chem.* **2003**, *86*, 66–74; b) Z. Li, K. Iida, Y. Tomisaka, A. Yoshimura, T. Hirao, A. Nomoto, A. Ogawa, *Organometallics* **2007**, *26*, 1212–1226.

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