Diastereoselective Addition of Radicals to Chiral 1,3-Dioxin-4-ones

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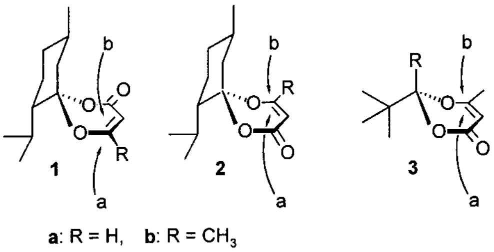
Intermolecular addition of radicals to the 1,3-dioxin-4-ones **1a,b** and **2a,b** with (–)-menthone incorporated as chiral auxiliary in 2-position were investigated. Photochemically generated radicals from 1,3-dioxolane, oxolane, and 2-propanol were added with high facial selectivity from the more exposed a-side. Intramolecular addition of 1,3-dioxolan-2-yl radicals to chiral dioxinones proceeded less efficiently and with lower selectivity also from the a-side. Nevertheless, it was possible to form the new spirocyclic compounds **22**–**27**. The 1,3-dioxin-4-ones **32a,b** possessing an unsaturated side chain were attacked by radicals at the terminal double bond. In the case of irradiation of **32b** in 1,3-dioxolane a cyclization followed the intermolecular addition of a 1,3-dioxolan-2-yl radical and the dispiro compound **36** was formed. However, the formation of dispiro compound **40** required two reaction steps starting with irradiation of **32b** and bromotrichloromethane. The achiral 1,3-dioxin-4-one **44** possessing an unsaturated side chain at C-2 was attacked by 1,3-dioxolan-2-yl radicals preferentially at C-6.

Introduction

The efficient use of 1,3-dioxin-4-ones as versatile synthons in organic synthesis has been well documented but there is still an increasing interest in mechanistic aspects because the facial selectivity in addition reactions to the C=C bond of chiral dioxinones depends on the type of reaction (Scheme 1).[1] Sato et al. reported that cuprate addition to dioxinone **1a** occurred preferentially on the face opposite the isopropyl group (b-side).[2] The same b-side preference was observed in catalytic hydrogenation of **1a**.[2] This is in accordance with results of Seebach et al. who investigated conjugate addition reactions with dialkyl cuprates and catalytic hydrogenations of chiral dioxinone **3a**.[3] Lange et al. have found that dialkyl cuprate addition to **3b** also takes place from the b-side with complete selectivity.[4] Corresponding facial selectivity of two types of dioxinones (2-*tert*-butyl- and 2-spiro-substituted) was also reported for Diels−Alder reactions with cyclopentadiene which proceed from the opposite side (a-side).[5] An attack from the a-side has also been proposed for the Diels−Alder reaction of *N*-phenylmaleimide and spirodioxinones **1** and **2** (R = alkenyl).[6] The addition of molecular fluorine to spirodioxinones is another type of ground-state reaction. The approach of fluorine proceeds with high selectivity also from the a-side.[7]

Intermolecular [2+2] photocycloadditions of alkenes to dioxinones occur preferentially from the same side as found for ground-state [4+2] cycloadditions. Demuth et al. described the a-side preference in the reaction of **1b** and **2b** for the first time.[8] Later, Sato et al. reported that **1a** and **2a** were attacked also preferentially from the a-side.[2] Lange et al. have used 2-*tert*-butyldioxinones **3**. High facial selectivity was only obtained in the photoaddition of **3b** with preferred approach from the a-side.[4] However, **3a** shows only poor facial selectivity in photoaddition with alkenes. The selectivity in intramolecular photocycloaddition of alkenes to chiral dioxinones depends on the length of the side chain.[9] In some cases addition proceeds preferentially from the b-side, which is explained by a distortion of the conformation in the triplet excited state.[10]



1 **2** **3**

a: R = H, **b**: R = CH_3

a-side attack	b-side attack
Diels-Alder reactions fluorination [2+2] cycloaddition	cuprate addition cat. hydrogenation

Scheme 1. Chiral 1,3-dioxin-4-ones

The addition of alkyl radicals to enones is an efficient route for the formation of C−C bonds.[11] However, only little work has been reported on the behaviour of dioxinones in radical reactions. This report deals with the addition of radicals to chiral 1,3-dioxin-4-ones. Since radicals should be influenced by similar stereochemical and stereoelectronic effects as nucleophiles it would be interesting to know whether alkyl radical addition takes place on the same face as preferred, for example, by cuprates (b-side). On the other hand, radical additions may be compared to

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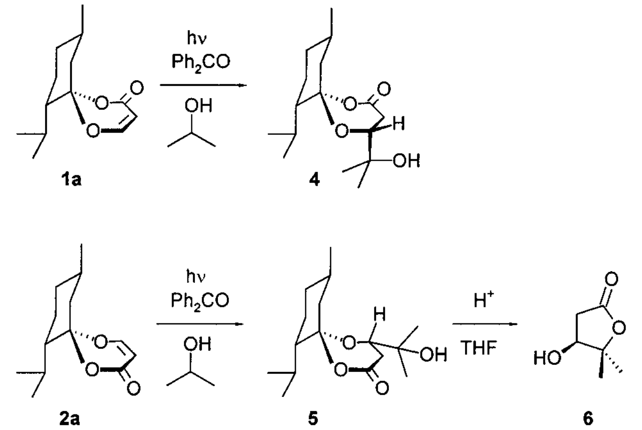
other types of reactions showing a-side preference like triplet reactions in the excited state. For example, the intramolecular photoaddition of alkenes to dioxinones are two-step reactions involving a diradical intermediate. In the first step a bond is formed at C-6.[12] If the intramolecular radical addition gives the same facial selectivity as the photocycloaddition the conformation of excited-state and ground-state spirodioxinones should be comparable.

Results and Discussion

Intermolecular Addition

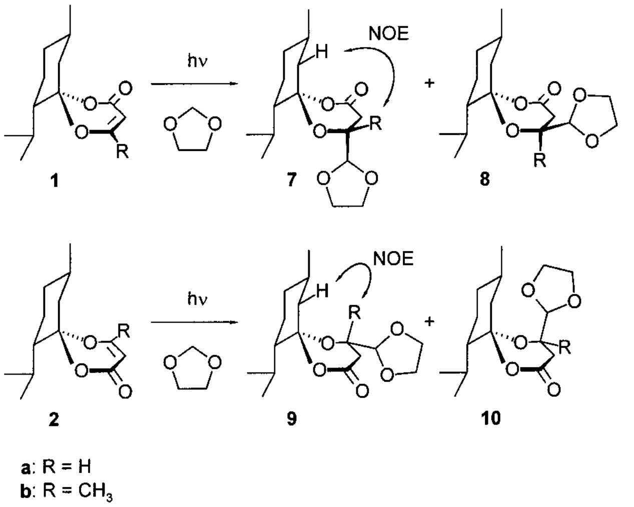
The addition reactions of photochemically generated radicals to dioxinones **1** and **2** were performed by irradiation at 350 nm.[13][14] The reaction of **1a** in 2-propanol using benzophenone as triplet sensitizer gave only one adduct **4** (28%) after chromatographic workup (Scheme 2). Sensitized irradiation of **2a** in 2-propanol gave **5** in 17% yield as a sole product. Compound **5** was converted to **6** by acid hydrolysis. The optical rotation of **6** is almost identical with the value of the known (*S*)-**6**.[15] Therefore the configuration of **5** must be the same. Accordingly the addition of the hydroxypropyl radical has taken place from the a-side. In the absence of the sensitizer no adducts were formed.



Scheme 2. Photoaddition reactions of 1,3-dioxin-4-ones

Irradiation of **1a** or **2a** in methanol was not successful. Only small amounts were converted even after ten days and we were not able to separate the complex mixture. Investigations with cyclohexane/methanol mixtures as solvents led to the formation of by-products which may result from cycloaddition reactions. There were no adducts observed when **1b** or **2b** were irradiated in 2-propanol under the same conditions as for the 6-unsubstituted 1,3-dioxin-4-ones.

The photoaddition reactions of 1,3-dioxolane were carried out without a sensitizer.[16] The product ratio was measured by ^{1}H-NMR spectroscopy from samples of the crude products. Irradiation of **1a** and **2a** in 1,3-dioxolane afforded two adducts each in a ratio of 96:4 and 90:10 (Scheme 3 and Table 1). The stereochemistry of the major adducts **7a** and **9a** were determined by NOE difference experiments (Scheme 3). Thus, both isomers resulted from the attack of a 1,3-dioxolan-2-yl radical on the a-side. Besides, an addition took place on the b-side which led to the minor adducts **8a** and **10a**. The structure of **8a** was verified by X-ray-crystallographic analysis (Figure 1).[17]



Scheme 3. Photoaddition of 1,3-dioxolane to **1** and **2**

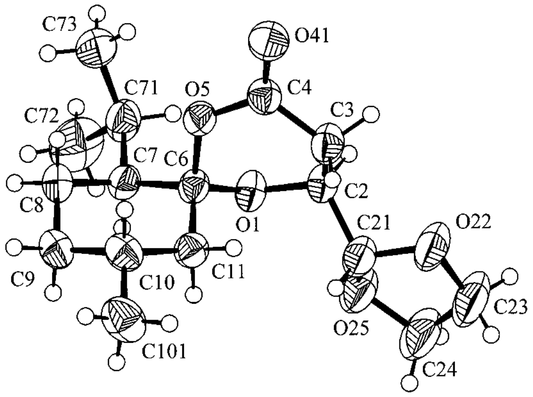


Figure 1. Crystal structure of **8a**

Table 1. Photoaddition of 1,3-dioxolan-2-yl radicals to 1,3-dioxin-4-ones

Entry	Compound	Irradiation time	Products (yield)[a]	Conversion
1	**1a**	44 h	**7a** (75%)/**8a** (3%)	100%
2	**2a**	27 h	**9a** (56%)/**10a** (6%)	83%
3	**1b**	12 d	**7b** (23%)	80%
4	**2b**	12 d	**9b** (42%)	82%

[a] Yields of isolated products.

Dioxinones **1b** and **2b** show lower reactivities in the addition to 1,3-dioxolan-2-yl radicals. Thus, irradiation must be maintained for twelve days in order to obtain the same extent of conversion as in the case of the 6-unsubstituted dioxinones. The photoaddition reaction of **1b** and 1,3-dioxolane gave only one adduct **7b** after chromatography.[18] Due to the stereochemical information obtained by a NOE experiment of **7b** the radical addition had occurred from the a-side (Scheme 3). The same a-side preference was observed

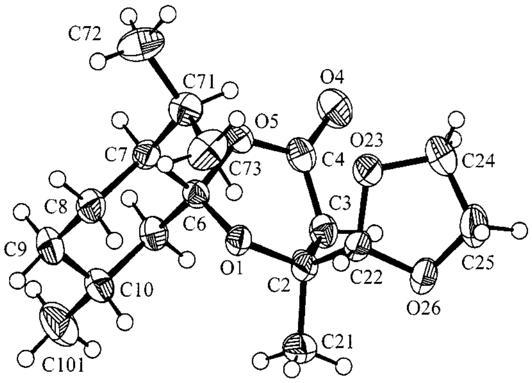


Figure 2. Crystal structure of **9b**

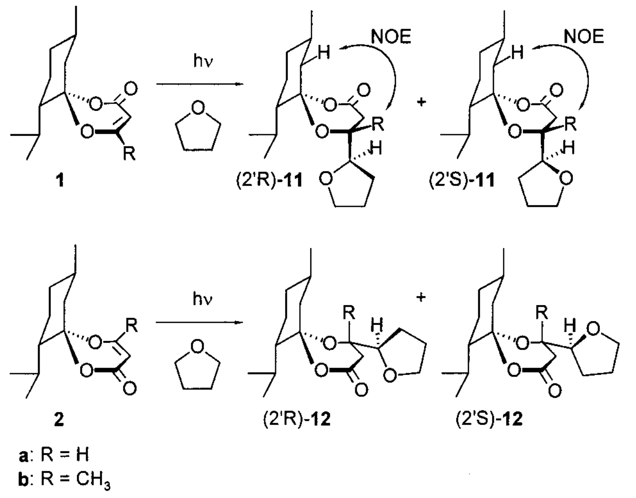
when **2b** was used. The sole adduct was **9b** of which the structure was determined by X-ray-crystallographic analysis (Figure 2).[17]

The photoaddition reaction of dioxinones and 1,3-dioxolane afforded only adducts which can be explained by the attack of a 1,3-dioxolan-2-yl radical. However, cleavage of a C−H bond at the acetal center should be preferred by the two neighbouring oxygen atoms. Surprisingly, no adduct was observed resulting from the reaction of a 1,3-dioxolan-4-yl radical and dioxinone. In order to test the possibility of a reaction at an α-ether rather than acetal center the photoaddition of THF (oxolane) was investigated.

Irradiations of dioxinones in THF were carried out under the same conditions as for the irradiations in 1,3-dioxolane.[16] Because of the lower reactivity of the 2-oxolanyl radicals irradiation of **1a** and **2a** was maintained twice as long (Table 2). In each case two adducts were formed in a ratio of 65:35 and 50:50, respectively. They were separated by HPLC and the polar product was the major isomer in case of **11a**. NOE experiments of both isomers **11** showed correlations between 11-H and the proton at the new stereogenic center in the dioxanone ring for both compounds (Scheme 4). Thus, the oxolan-2-yl radical attacked the dioxinones from the a-side. Because of the generation of an additional chiral center in the oxolanyl moiety two isomers were formed. We were not able to assign the structure of (2′*R*) and (2′*S*) isomers.

The irradiation of the dioxinones **1b** and **2b** in THF was stopped after twelve days. Two isomers were produced in a ratio of 2:1 [(2′*S*)-**11b**/(2′*R*)-**11b**] which were separated by HPLC. The separation of the isomers (2′*S*)-**12b** and (2′*R*)-**12b** failed. There is no proof of the relative configurations of isomers **11b** and **12b** but it can be assumed that the attack of the oxolan-2-yl radicals to 6-methyl-substituted dioxinones shows the same selectivity mentioned for the photoaddition reactions before. In trimethyl orthoformate the C−H bond is activated by three oxygen atoms. However, to our surprise we did not observe any product formation upon photolysis of dioxinones in the presence of this orthoester.

The groups of Seebach and Lange have correlated the stereoselectivity of conjugate addition of cuprates to 2-*tert*-butyl-1,3-dioxin-4-ones **3** with the pyramidalization of the enone moiety.[3][4] The addition occurs preferentially from the b-side, i.e. from the direction into which the centers are pyramidalized. On the other hand, Sato et al. have considered that hyperconjugation causes the facial selectivity in conjugate addition.[19] The lone-pair electrons of O-1 should interact with the antibonding orbital of the incipient bond. Since the nucleophilic attack occurs at an obtuse angle the unfavourable 1,3-diaxial interaction is small and stereoelectronic effects predominate steric demand.



Scheme 4. Photoaddition of tetrahydrofuran to **1** and **2**

Table 2. Photoaddition of oxolan-2-yl radicals to 1,3-dioxin-4-ones

Entry	Compound	Irradiation time	Products (yield)[a]	Conversion
1	**1a**	5 d	**11a** (41%/22%)	100%
2	**2a**	4 d	**12a** (22%/22%)	> 95%
3	**1b**	12 d	**11b** (6%/3%)	30%
4	**2b**	12 d	**12b** (10%)[b]	30%

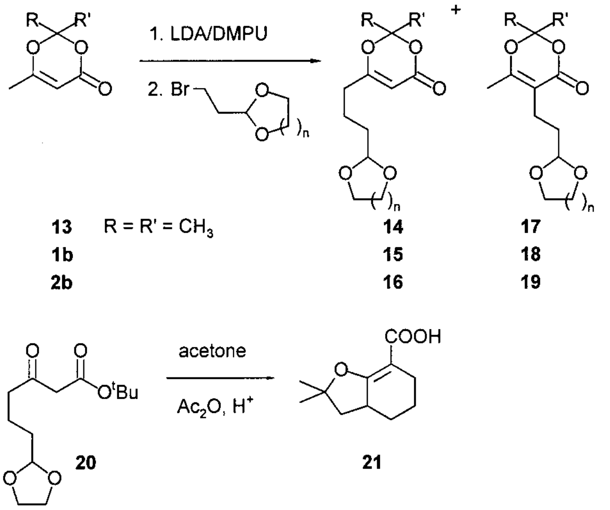
[a] Yields of isolated isomers, ratio of the products was determined by NMR to be 2:1. − [b] Isomers not separated.

In radical addition reactions a stereoelectronic effect may also compensate a steric demand and, therefore, selectivity in acyclic radical reactions where steric effects are small is often explained by electronic interactions.[20][21] A radical approaches an enone along a trajectory similar to that of a nucleophile and because of its comparable steric and stereoelectronic demand the ionic and radical addition should show the same selectivity.[22][23] Nevertheless, radicals attack dioxinones from the opposite side as shown above. Thus, the influence of hyperconjugation or non-planar enone portion is less important. Obviously, the addition occurs preferentially from the more exposed a-side of the sofa conformation as found by X-ray analyses of the dioxinones **1a**[2] and **2b**.[8] Only in the case of the addition of reactive 1,3-dioxolan-2-yl radicals to the 6-unsubstituted dioxinones **1a** and **2a** an attack from the b-side was observed as the minor pathway of the reaction. The diverse facial selectivity in the reaction of ionic nucleophiles and radicals with cyclic enones was already described by Fraser-Reid and Giese as well.[24]

Intramolecular Addition

Since so far all attempts failed to use other precursors than alcohols, acetals, and ethers in intermolecular radical addition reactions with dioxinones we were interested in radical cyclizations in order to gain more information on the behaviour of dioxinones in radical reactions. Earlier reports already showed that it is possible to form spiro systems using 1,3-dioxin-4-ones bearing an appropriate side chain at C-6.[25][26] Here a favoured process should be the well-known 5-*exo* cyclization of 5-hexenyl radicals. As a first approach we chose the 1,3-dioxolane as a unit for cyclization reactions of 1,3-dioxin-4-ones.

Two procedures to synthesize 6-substituted dioxinones are known[28], i.e. γ-alkylation of the dioxinones **1b** or **2b**[29] and treatment of appropriate *tert*-butyl β-oxo esters with ketones under acidic conditions.[30] Attempts to synthesize the achiral dioxinone **14** according to the latter method failed so far because of the lability of the dioxolane moiety under acidic conditions. Interestingly, the *tert*-butyl 6-oxo-1-cyclohexenecarboxylate was not formed as expected from the reaction of **20** in acetic acid.[31] The hexahydrobenzofuran derivative **21** was the only isolated product. Thus, the dioxinones **14−16** were prepared by γ-alkylation of the corresponding dioxinones. In all cases α-alkylated dioxinones **17−19** were also formed in smaller amounts (Scheme 5).



Scheme 5. γ-Alkylation of dioxinones

Irradiation of the achiral dioxinones **14a,b** (40 mM) and acetone as sensitizer in cyclohexane at 350 nm for 2 d gave the cyclized products **22a** and **22b** in yields of 11% and 17%, respectively. The structure of the dispiro compound **22b** was verified by X-ray-crystallographic analysis (Figure 3).[17] The intramolecular photoaddition of dioxolane to acrylate has already been reported leading to five-membered ring products in only very small amounts.[27] In some cases we observed the formation of by-products of type **23** which may result from remaining oxygen in the solution. We assume that the intermediate adduct radical is trapped by oxygen followed by hydrogen transfer. The produced hydroperoxide should be unstable under the photochemical conditions and the alcohol **23** is formed.[32] In contrast to the intermolecular reaction of 1,3-dioxolanes the cyclization reaction takes place only in the presence of a sensitizer. Unfortunately, the yields were unsatisfactory in comparison with the former reactions.

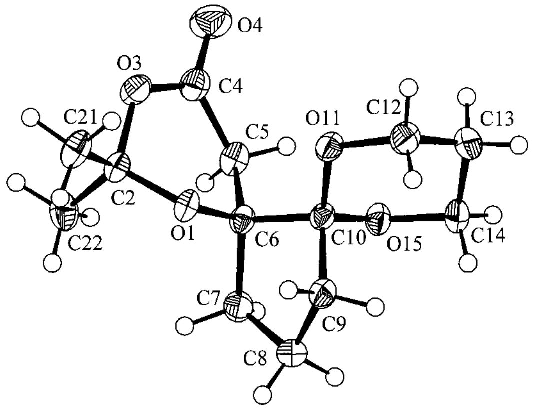


Figure 3. Crystal structure of **22b**

Irradiation of the chiral dioxinones were carried out under the same conditions as for the achiral ones. Reaction of **15** (5 mM) gave two diastereoisomers **24** and **25** after separation by HPLC in yields of 14% and 9%, respectively. The relative configuration of the major product **24** was determined by X-ray analysis of single crystals (Figure 4).[17] From these data it is obvious that the addition of the 1,3-dioxolan-2-yl radical has taken place from the a-side leading to **24**. Thus, the minor product **25** (5 mM) should be formed by an attack from the b-side. The cyclization reaction of **16** yielded two products in a ratio of 10:9 which could be separated by HPLC. Though the spectroscopic data correspond to the trispiro compounds **26** and **27**, we were not able to assign the structures to the isolated products because of the lack of certain structure determination. In summary, radicals generally attack chiral dioxinones in intermolecular addition reactions as well as in cyclization reactions preferentially from the a-side. The latter agrees with a recent investigation on cascade cyclizations of polyalkenyl-substituted chiral dioxinones by photoinduced electron transfer.[33]

In order to get further information on the relative reactivities of intra- versus intermolecular photoadditions under the conditions used in this study the dioxinone **14a** (20 mM) was irradiated for five days in 1,3-dioxolane in the presence of acetone (Scheme 8). After chromatography, **28** was isolated as the major adduct in 8% yield. There was no hints of cyclized products but the bis-1,3-dioxolanyls **29** and **30** were formed in large amounts indicating that the primary H abstraction mainly results from 1,3-dioxolane rather than **14a**. Unlike the intermolecular addition, dimerization becomes the favoured reaction because of the efficient sensitization of acetone and the low reactivity of 6-subtituted

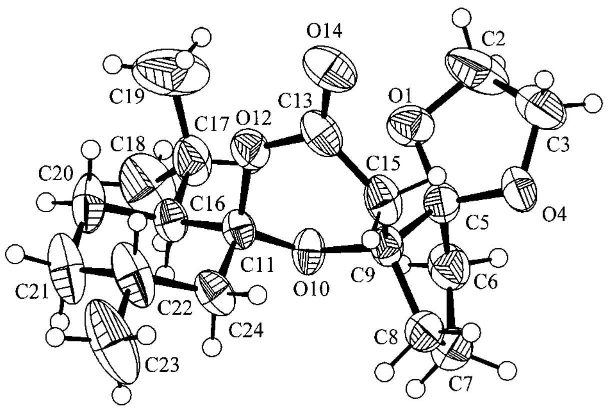
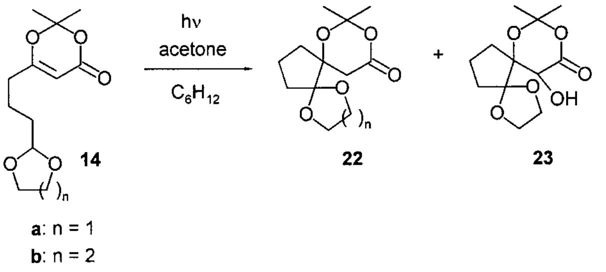
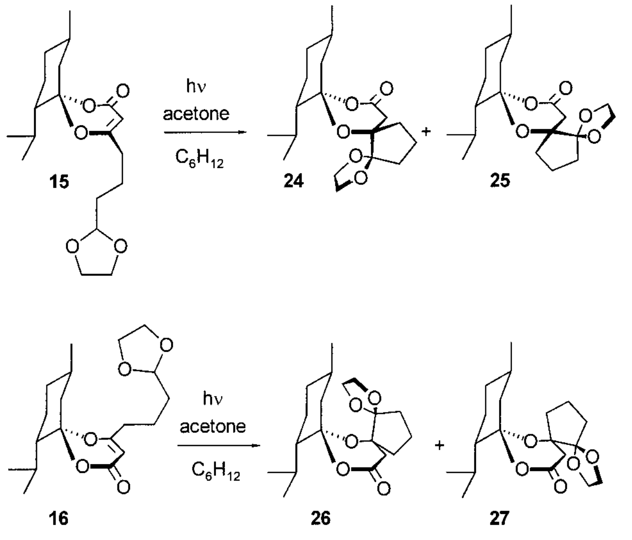


Figure 4. Crystal structure of **24**

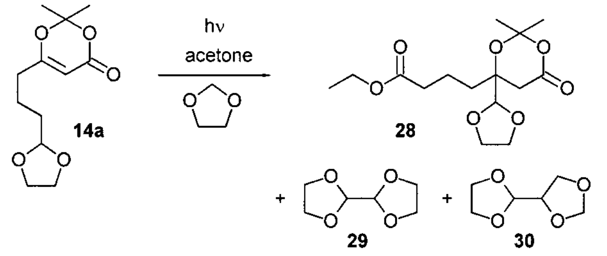
1,3-dioxin-4-ones. This latter process, i.e. the addition of 1,3-dioxolan-2-yl radicals to the C=C double bond of **14a** followed by hydrogen transfer is only observed as a side reaction. The final product **28** is probably formed by H abstraction from the internal acetal center. Alternatively, **28** could be formed by 1,6-H shift followed by ring opening of the 1,3-dioxolane and H abstraction.[34]



Scheme 6. Photocyclization of **14**



Scheme 7. Photocyclization of **15** and **16**



Scheme 8. Competition between inter- and intramolecular photoaddition

Chemoselectivity

It is known that 1,3-dioxolane adds to terminal olefins under UV irradiation in the presence of a triplet sensitizer.[34] In order to obtain information about the reactivity of dioxolanyl radicals against 1,3-dioxin-4-ones provided with a terminal olefin unit we envisaged the synthesis of compounds **32a,b**. They were prepared from the β-oxo ester **31** and (−)-menthone in acetic anhydride under acid catalysis.[30a] The yield of the dioxinones **32a,b** range from 14% to 19%. In both cases a second isomer **33a,b** was formed in smaller amounts which was separated chromatographically.

Irradiation of dioxinone **32a** (10 mM) and acetone in 1,3-dioxolane for 24 hours gave the two adducts **34** and **35** in yields of 35% and 6%, respectively. Obviously, 1,3-dioxolan-2-yl radicals preferentially attacks the terminal olefin leading to **34** rather than the double bond of the dioxinone. The by-product **35** results from the addition of 1,3-dioxolan-4-yl radicals to the terminal double bond as well. The C=C bond in the dioxinone ring cannot compete with the terminal olefin for both types of radicals.

Irradiation of the dioxinone **32b** (13 mM) and acetone in 1,3-dioxolane was carried out for 48 hours. After chromatographic workup, **36** was isolated as the main product in a yield of 14%. The structure of **36** was assigned on the basis of NMR analyses [^{1}H-^{1}H COSY, ^1J(CH) correlated, NOESY]. The NOE experiment shows a correlation between 15-H$_a$ (located at the a-side of the dioxanone) and a proton of the 1,3-dioxolan-2-ylmethyl group (Figure 5). Therefore, the methylene group C-15 and the 1,3-dioxolan-2-ylmethyl group are *cis*-fused at the new generated cyclopentane. This is in agreement with the NOE observed between the isopropyl and dioxolanylmethyl group.

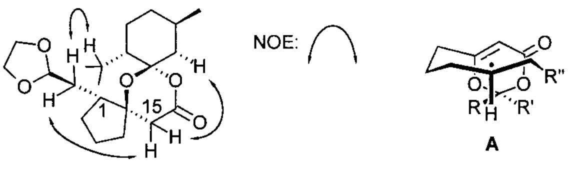


Figure 5. NOE effects of **36** and preferred formation of intermediate **A**

As found for the 6-butenyl-substituted dioxinone **32a** the dioxolanyl radicals attack the terminal olefin with high preference leading to the intermediate **A**. The following 5-*exo* cyclization under formation of **36** occurs from the a-side. Since four-membered rings are disfavoured no cyclized products were detected next to **34** and **35** in the reaction of **32a**. To explain the configuration of the newly formed cyclopentane moiety in **36** a closer look at the transition state is helpful. A pseudoequatorial position of the dioxolanylmethyl group in a chair-like transition state leads to **36** (Figure 5). Alternative transition states involving an a-side attack of the radical are unfavourable because of the steric effect of the isopropyl group.

Polyhalogenated compounds can also be added to olefins in photoreactions.[35] The addition of bromotrichloromethane to olefins by a chain reaction is achieved by bromine atom transfer. Irradiation of the dioxinone **32b** in bromotrichloromethane gave the two products **37** and **38** in a ratio of 9:1. The trichloromethyl radical reacts only with the terminal olefin. Because of the electrophilic nature of the trichloromethyl radical no addition occurs even with 6-unsubstituted dioxinones. In contrast to the reaction of **32b** in dioxolane the radical **A** is trapped by abstraction of a bromine atom indicating that cyclization is too slow to compete. Thus, under the used reaction conditions trapping of secondary radical **A** by $BrCCl_3$ is much faster than hydrogen transfer from 1,3-dioxolane. To construct spiro systems a reaction would be needed in which radical **A** leading to **32** has a longer lifetime so that cyclization becomes possible.

Dioxinone **37** can be converted to such a radical of type **A** by reduction. In a nonoptimized photoinitiated reaction of **37** and tri-*n*-butyltin hydride the reductive removal of bromine was performed and the dioxinone **39** was found as the main product beside other dehalogenated products. The only cyclized product which could be isolated after chromatographic workup was the dispirocyclic compound **40** whose structure was determined by X-ray analysis (Figure 6).[17] The configuration of **40** is in accordance with the structure of **36** showing that both cyclizations proceed preferentially from the a-side probably via chair-like transition states (Figure 5). Since an excess of tin hydride was used the cyclization reaction of **40** is followed by a reduction of the trichloromethyl to the dichloromethyl group. The formation of the dispirocyclic compound **36** starting with the alkenyl-substituted dioxinone **32b** is a one-pot reaction which is more favourable than the two-step reaction leading to **40**. From these results it can be concluded that in general, 6-haloalkyl-substituted dioxinones should be versatile precursors for spirocyclic compounds in radical cyclizations.

In the same way aryl or vinyl bromides could be used. Therefore we investigated the photoinitiated reaction of tri-*n*-butyltin hydride with achiral dioxinone **41** which was prepared from *tert*-butyl acetoacetate in two steps (Scheme 11)[30a,36] Besides the non-cyclized product **43** (6%) the indane **38** was formed in 29% yield.

The results of irradiation of the dioxinones **32a,b** in 1,3-dioxolane show that the double bond in the dioxinone ring cannot compete with that of the terminal olefin as radical trap. Radicals prefer the addition to less substituted carbon atoms in double bonds. The unfavourable effect of a substituent at C-6 also requires the ten times longer reaction times in additions of 1,3-dioxolane to dioxinones **1b** and **2b**

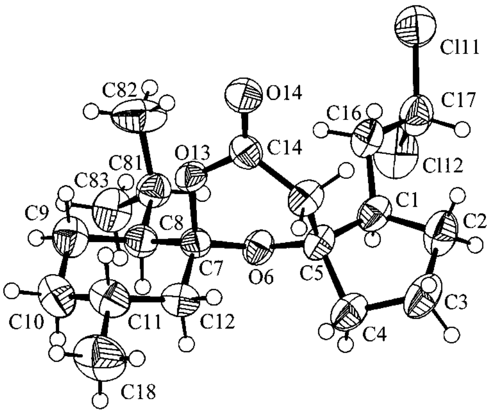
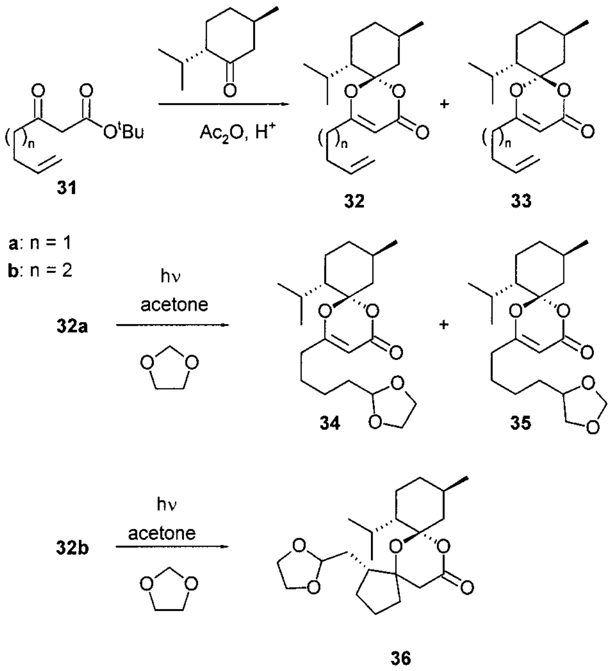
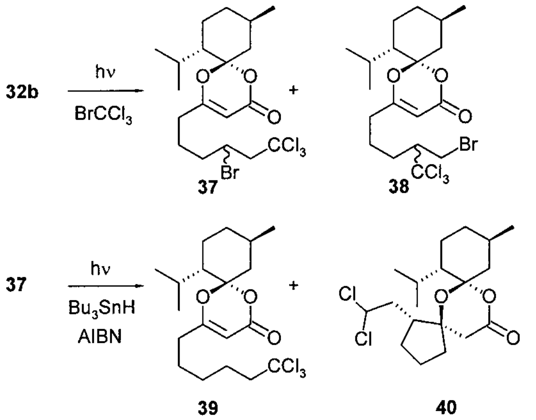


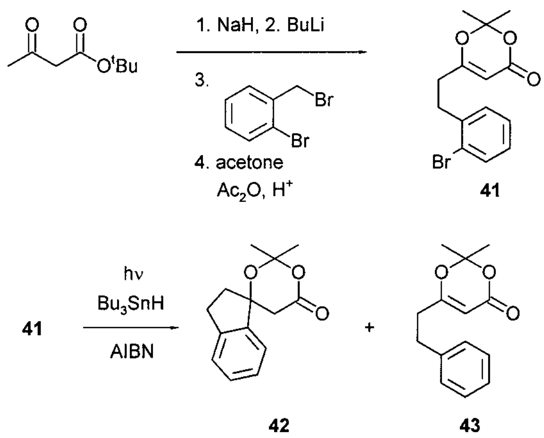
Figure 6. Crystal structure of **40**



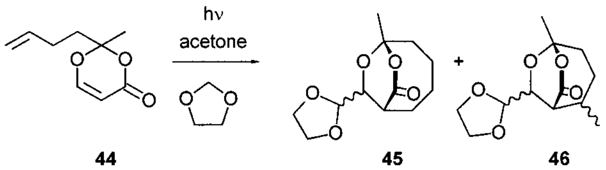
Scheme 9. Synthesis and photoaddition reactions of **32** and **33**



Scheme 10. Free-radical reaction of **32b** and **37**



Scheme 11. Synthesis and free-radical reaction of **41**



Scheme 12. Photoreaction of **44** in the presence of 1,3-dioxolane

compared to the additions to the 6-unsubstituted dioxinones **1a** and **2a**.

To establish whether 6-unsubstituted dioxinones are better radical traps for 1,3-dioxolan-2-yl radicals than terminal olefins the dioxinone **44** was prepared by refluxing 5-formyl-2,2-dimethyl-1,3-dioxane-4,6-dione in xylene.[37] Irradiation of dioxinone **44** (12 mM) and acetone in 1,3-dioxolane afforded a mixture of two products. After chromatographic workup two dioxabicyclo[3.2.2]nonanones **46** were separated in yields of 8% and 12%, respectively. Further separation gave one isomer of the dioxabicyclo[4.2.2]decanone **45** in a yield of 14%. The second isomer **45** was only enriched.

The products **45** and **46** arise from addition of the 1,3-dioxolan-2-yl radical to C-6 of 1,3-dioxin-4-one followed by a cyclization reaction via the butenyl substituent. In comparison with the reactions of **1a** and **2a** the attack of the radical should proceed with lower facial selectivity because of the conformative flexibility of **44**. Then in both intermediates the newly formed radical is trapped by the terminal olefin. If this intramolecular addition to the side chain proceeds in an 8-*endo* mode the dioxabicyclo[4.2.2]decanone **45** is formed. The alternative 7-*exo* mode cyclization leads to the dioxabicyclo[3.2.2]nonanones **46**. The 7-*exo* mode cyclization should give four possible isomers but only two were detected.

Unsubstituted dioxinones are better radical traps for nucleophiles like the dioxolanyl radical than terminal olefins reflecting the influence of the electron-withdrawing group next to the double bond in the dioxinone ring. An alkyl substituent at C-6 of the dioxinone decreases the reactivity with dioxolanyl radicals in such a way that terminal olefins become better radical traps. Thus, terminal olefins can be involved in intermolecular radical addition reactions next to a 6-substituted 1,3-dioxin-4-one.

Conclusion

We have shown that in general 1,3-dioxin-4-ones are attacked by radicals from the a-side in both inter- and intramolecular reactions. Therefore radicals behave like dienes and alkenes in Diels−Alder reactions and photochemical [2+2] cycloadditions, respectively, rather than nucleophiles in cuprate additions. The origin of this behaviour which may not be expected when considering the often observed similarities of polar and radical reactions are not yet known in detail.[11] Both Seebach's concept of pyramidalization of the enone[3][4] and Sato's hyperconjugation model[19] may not be applicable to radical reactions since diverse stereoselectivities would have been predicted. On the other hand, our free radical reactions resemble photochemical [2+2] cycloadditions via enone triplets. In both reactions open-shell-type intermediates are involved. Therefore, steric effects which were derived from X-ray analyses of **1a** and **2b** to rationalize the facial selectivity may operate as well.

Studies on the chemoselectivities of unsubstituted and 6-alkyl-substituted 1,3-dioxin-4-ones on the one side and terminal alkenes on the other side were carried out as well. In general, the highest reactivity in radical additions is observed for the unsubstituted 1,3-dioxin-4-one followed by the terminal olefin reflecting the balance of stereoelectronic effects.

Experimental Section

General Remarks: Melting points are uncorrected. − Optical rotations: Perkin−Elmer Polarimeter 241. − IR: Perkin−Elmer FTIR-Spektrometer 1600. − ^{1}H and ^{13}C NMR: Varian EM 390; Bruker AC 200 P, WM 300, AM 360 or DRX 500 with TMS as internal standard. Multipicities of ^{13}C resonances were determined by gated decoupling or by DEPT experiments. − Mass spectra: Finnigan MAT C 312 or MAT 8230, CI with isobutane. − HPLC: Kontron Pump 420 or Merck Pump L-6000, RI detector Bischoff RI 8110, column 250 × 20 mm, Merck LiChrosorb Si 60-5 or Si 60-7. − CC: Merck silica gel 60, 40−63 μm and 63−200 μm. − DC: Merck tin foil, silica gel 60 F 254 and Macherey and Nagel SIL G/UV$_{254.}$ − GC: Siemens Sichromat 3 and 1-4, Hewlett−Packard Ultra 2 (25 m, 0.2 mm) and Macherey and Nagel SE 30 (25 m, 0.2 mm). − Elemental analyses: Perkin−Elmer DIA CHN 240 and Heraeus CHN-O-Rapid. − All crystal data sets were collected with an Enraf Nonius CAD4 diffractometer. Programs used: data reduction MolEN, structure solution SHELXS-86, structure refinement SHELXL-93, graphics (with unsystematical numbering schemes) DIAMOND.

General Procedure A (Intermolecular Photoaddition): The solutions were distributed in Pyrex tubes (volume 12 mL) and deoxygenated with argon (15 min). The tubes were sealed and irradiated in a Rayonet Photochemical Reactor (model RPR-100, Southern New England) fitted with a merry-go-round apparatus and with 350-nm lamps. The reaction course was monitored by TLC (cyclohexane/ethyl acetate, 1:1). At the end of the irradiation the solvent was removed under reduced pressure and the residue was separated by HPLC (cyclohexane/ethyl acetate).

(4*R*,6*S*,7*S*,10*R*)-4-(1-Hydroxy-1-methylethyl)-7-isopropyl-10-methyl-1,5-dioxaspiro[5.5]undecan-2-one (4): A solution of 168 mg (0.75 mmol) of **1a**[38] and 20 mg (0.11 mmol) of benzophenone in 60 mL of 2-propanol was irradiated for 20 h (procedure A). The product was purified by column chromatography (diethyl ether/petroleum ether, 1:1) to yield **4** (60 mg, 28%) as an oil. − ^{1}H NMR (360 MHz, C_6D_6): δ = 0.73 (ddt, *J* = 12.2, 11.8, 3.8 Hz, 1 H), 0.80 (d, *J* = 6.6 Hz, 3 H, 10-CH_3), 0.94 (d, *J* = 7.0 Hz, 3 H, CH_3), 0.98 (s, 3 H, 1′-CH_3), 1.01 (d, *J* = 6.9 Hz, 3 H, CH_3), 1.01 (t, *J* = 12.9 Hz, 1 H, 11-H_{ax}), 1.23 (s, 3 H, 1′-CH_3), 1.28−1.80 (m, 6 H), 2.02 (ddd, *J* = 13.3, 3.3, 1.8 Hz, 1 H, 11-H_{eq}), 2.15 (dd, *J* = 16.0, 4.9 Hz, 1 H, 3-H_a), 2.40 [dsept, *J* = 7.0, 1.1 Hz, 1 H, C*H*(CH_3)$_2$], 2.51 (dd, *J* = 16.0, 8.4 Hz, 1 H, 3-H_b), 4.29 (dd, *J* = 8.4, 4.9 Hz, 1 H, 4-H). − ^{13}C NMR (90 MHz, C_6D_6): δ = 18.55 (CH_3), 22.26 (CH_3), 23.04 (CH_2, C-8), 23.61 (CH_3), 23.69 (CH_3), 24.56 [CH, *C*H(CH_3)$_2$], 28.31 (CH, C-10), 30.61 (CH_3), 34.88 (CH_2, C-9), 35.33 (CH_2, C-3), 45.17 (CH_2, C-11), 49.11 (CH, C-7), 78.82 (C, C-1′), 79.07 (CH, C-4), 110.92 (C, C-6), 176.90 (C, C-2). − MS (70 eV); *m*/*z* (%): 284 (14) [M$^+$], 269 (17), 227 (30), 199 (19), 154 (15), 139 (31), 121 (12), 113 (62), 112 (38), 97 (47), 69 (70), 55 (50), 41 (100).

(4*S*,6*R*,7*S*,10*R*)-4-(1-Hydroxy-1-methylethyl)-7-isopropyl-10-methyl-1,5-dioxaspiro[5.5]undecan-2-one (5): A solution of 95 mg (0.42 mmol) of **1b**[6] and 10 mg (0.05 mmol) of benzophenone in 30 mL of 2-propanol was irradiated for 20 h (procedure A). Purification by HPLC (ethyl acetate/cyclohexane, 1:4) yielded **5** (20 mg, 17%) as an oil. − ^{1}H NMR (300 MHz, C_6D_6): δ = 0.74 (ddt, *J* = 12.2, 12.2, 4.1 Hz, 1 H), 0.83 (d, *J* = 6.9 Hz, 3 H, CH_3), 0.92 (s, 3 H, 1′-CH_3), 0.97 (d, *J* = 6.9 Hz, 3 H, CH_3), 0.98 (d, *J* = 6.9 Hz, 3 H, CH_3), 0.98 (m, 1 H, 11-H_{ax}), 1.15 (s, 3 H, 1′-CH_3), 1.32 (ddd, J = 12.4, 4.3, 1.7 Hz, 1 H), 1.36−1.68 (m, 4 H), 1.72 (m_c, 1 H), 1.95 (ddd, *J* = 12.9, 4.3, 1.9 Hz, 1 H, 11-H_{eq}), 2.15 (dd, *J* = 16.0, 4.8 Hz, 1 H, 3-H_a), 2.34 [dsept, *J* = 6.9, 1.7 Hz, 1 H, C*H*(CH_3)$_2$], 2.54 (dd, *J* = 16.0, 8.6 Hz, 1 H, 3-H_b), 4.42 (dd, *J* = 8.6, 4.5 Hz, 1 H, 4-H). − ^{13}C NMR (75 MHz, C_6D_6): δ = 19.15 (CH_3), 22.36 (CH_3), 23.94 (CH_3 and C-8), 24.88 (CH_3), 24.95 [*C*H(CH_3)$_2$], 28.42 (C-10), 30.07 (CH_3), 34.93 (C-9), 35.50 (C-3), 45.58 (C-11), 48.54 (C-7), 78.40 (C-1′), 79.64 (C-4), 110.14 (C-6), 175.48 (C-2).

(4*S*)-4-Hydroxy-5,5-dimethyldihydrofuran-2-one (6): A solution of 168 mg (0.75 mmol) of **2a**[38] and 20 mg (0.11 mmol) of benzophenone in 60 mL of 2-propanol was irradiated for 20 h (procedure A). After removal of the solvent, the residue was treated with 2 mL of 2 M HCl in 10 mL of THF. The solution was stirred at room temperature for 4 d, and then extracted with diethyl ether. The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. Purification by distillation (Kugelrohr, 100°C bath temp./0.01 Torr) and by HPLC (ethyl acetate/cyclohexane, 7:3) yielded **6** (17 mg, 17%) as an oil: $[\alpha]^{20}_D = -11.5$ (*c* = 0.4, $CHCl_3$) {ref.[15] $[\alpha]^{20}_D = -11$ (*c* = 1.5, $CHCl_3$)}. − IR (neat): ṽ = 3417 cm^{-1} (s), 2980 (m), 2937 (m), 1760 (s, C=O), 1388 (m), 1280 (m), 1178 (m), 1126 (m), 1072 (m), 959 (m), 941 (m). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.48 (s, 3 H, 5-CH_3), 1.55 (s, 3 H, 5-CH_3), 2.55 (dd, *J* = 18.0, 3.1 Hz, 1 H, 3-H_a), 2.95 (dd, *J* = 18.0, 6.3 Hz, 1 H, 3-H_b), 3.05 (s, br., 1 H, OH), 4.21 (dd, *J* = 6.3, 3.1 Hz, 1 H, 4-H). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.06 (q, CH_3), 25.99 (q, CH_3), 38.27 (t, C-3), 73.56 (d, C-4), 88.15 (s, C-5), 175.53 (s, C-2). − MS (CI); *m*/*z* (%): 131 (100) [M$^+$ + H], 113 (16), 71 (8).

(4*RS*,6*S*,7*S*,10*R*)-4-(1,3-Dioxolan-2-yl)-7-isopropyl-10-methyl-1,5-dioxaspiro[5.5]undecan-2-one (7a and 8a): 80 mg (0.36 mmol) of **1a**[38] was dissolved in 10 mL of 1,3-dioxolane. The solution was irradiated for 44 h (procedure A). The crude mixture was separated by HPLC (cyclohexane/ethyl acetate, 3:1) to yield crystalline **8a** (3 mg, 3%) and **7a** (80 mg, 75%). − **(4*R*,6*S*,7*S*,10*R*) Isomer 7a:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.75 (d, *J* = 6.9 Hz, 3 H, CH_3), 0.80−0.93 (m, 1 H), 0.84 (d, *J* = 6.7 Hz, 3 H, CH_3), 0.86 (d, *J* = 6.7 Hz, 3 H, CH_3), 1.09 (t, *J* = 12.9 Hz, 1 H, 11-H_{ax}), 1.34−1.60 (m, 3 H), 1.61−1.78 (m, 2 H), 2.11 (ddd, *J* = 13.0, 3.6, 2.1 Hz, 1 H, 11-H_{eq}), 2.22 [dsept, *J* = 7.0, 2.2 Hz, 1 H, C*H*(CH_3)$_2$], 2.47 (dd, *J* = 17.7, 5.7 Hz, 1 H, 3-H_a), 2.56 (dd, *J* = 17.9, 9.8 Hz, 1 H, 3-H_b), 3.83−3.97 (m, 4 H, 4′-H), 4.20 (ddd, *J* = 9.5, 5.2, 3.8 Hz, 1 H, 4-H), 4.88 (d, *J* = 3.8 Hz, 1 H, 2′-H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.15 [CH_3, C(*C*H_3)$_2$], 20.66 (CH_2, C-8), 20.91 [CH_3, C(*C*H_3)$_2$], 22.45 (CH_3, 10-CH_3), 23.36 [CH, *C*H(CH_3)$_2$], 28.11 (CH, C-10), 29.02 (CH_2, C-9), 33.16 (CH_2, C-3), 43.23 (CH_2, C-11), 49.09 (CH, C-7), 64.43, 64.64 (CH_2, C-4′, C-5′), 66.59 (CH, C-4), 102.44 (CH, C-2′), 107.10 (C, C-6), 166.03 (C, C-2). − MS (70 eV); *m*/*z* (%): 299 (9) [M$^+$ + H], 298 (3) [M$^+$], 283 (2), 255 (2), 225 (8), 183 (3), 154 (10), 139 (13), 127 (64), 112 (45), 99 (21), 73 (100), 69 (29). − **(4*S*,6*S*,7*S*,10*R*) Isomer (8a, Less Polar Product):** M.p. 93°C (pentane). − IR (CH_2Cl_2): ṽ = 2930 cm^{-1} (m), 1742 (s, C=O), 1458 (w), 1372 (w), 1313 (m), 1283 (m), 1258 (m), 1196 (m), 1152 (m), 1078 (m), 1023 (m), 988 (m). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80−1.00 (m, 1 H), 0.87 (d, *J* = 7.2 Hz, 3 H, CH_3), 0.87 (d, *J* = 5.7 Hz, 3 H, CH_3), 0.94 (d, *J* = 6.9 Hz, 3 H, CH_3), 1.16−1.66 (m, 5 H), 1.67−1.93 (m, 2 H), 2.24 [dsept, *J* = 6.9, 2.0 Hz, 1 H, C*H*(CH_3)$_2$], 2.64 (dd, *J* = 16.9, 4.8 Hz, 1 H, 3-H_a), 2.72 (dd, *J* = 17.4, 9.8 Hz, 1 H, 3-H_b), 3.86−4.04 (m, 4 H, 4′-H), 4.18 (ddd, *J* = 10.0, 5.0, 3.6 Hz, 1 H, 4-H), 4.97 (d, *J* = 3.6 Hz, 1 H, 2′-H). − MS (70 eV); *m*/*z* (%): 299 (6) [M$^+$ + H], 255 (2), 225 (7) [M$^+$ − dioxolanyl], 183 (2), 154 (8) [menthone$^+$], 139 (11), 127 (66), 112 (37), 99 (21), 73 (100), 69 (30). − X-ray crystal structure analysis of **8a**: Empirical formula $C_{16}H_{26}O_5$, *M* = 298.37, 0.6 × 0.4 × 0.2 mm, *a* = 8.145(1), *b* = 9.694(1), *c* = 20.398(2) Å, *V* = 1610.6(3) Å^3, $\rho_{calcd.}$ = 1.230 g cm^{-3}, μ = 7.39 cm^{-1}, empirical absorption correction with ψ scan data (0.975 ≤ *C* ≤ 0.999), *Z* = 4, orthorhombic, space group $P2_12_12_1$ (no. 19), λ = 1.54178 Å, *T* = 293 K, ω/2θ scans, 1902 reflections collected (−*h*, +*k*, −*l*), [(sin θ)/λ] = 0.62 Å^{-1}, 1902 independent and 1812 observed reflections [$I \geq 2\,\sigma(I)$], 194 refined parameters, *R* = 0.034, wR^2 = 0.100, max. residual electron density 0.17 (−0.12) e Å^{-3}, Flack parameter 0.0(2), hydrogen atoms calculated and riding.[17]

(4*RS*,6*R*,7*S*,10*R*)-4-(1,3-Dioxolan-2-yl)-7-isopropyl-10-methyl-1,5-dioxaspiro[5.5]undecan-2-one (9a and 10a): 120 mg (0.53 mmol) of **2a**[38] was dissolved in 10 mL of 1,3-dioxolane. The solution was irradiated for 27 h (procedure A). The crude mixture was separated by HPLC (cyclohexane/ethyl acetate, 4:1) to yield recovered **2a** (20 mg) and two adducts as oils: **10a** (10 mg, 6%) and **9a** (90 mg, 56%). − **(4*S*,6*R*,7*S*,10*R*) Isomer (9a):** ^{1}H NMR (300 MHz, C_6D_6): δ = 0.62 (m_c, 1 H), 0.66 (d, *J* = 6.2 Hz, 3 H, CH_3), 0.86 (d, *J* = 6.9 Hz, 3 H, CH_3), 0.94 (d, *J* = 6.9 Hz, 3 H, CH_3), 0.98 (dd, *J* = 14.1, 12.6 Hz, 1 H, 11-H_{ax}), 1.30−1.52 (m, 5 H), 1.80 (ddd, *J* = 14.1, 2.9, 2.4 Hz, 1 H, 11-H_{eq}), 2.20 [dsept, *J* = 7.2, 1.7 Hz, 1 H, C*H*(CH_3)$_2$], 2.32 (dd, *J* = 17.6, 4.5 Hz, 1 H, 3-H_a), 2.51 (dd, *J* = 17.6, 10.5 Hz, 1 H, 3-H_b), 3.22−3.30 (m, 4 H, 4′-H), 3.74 (ddd, *J* = 10.5, 4.3, 3.3 Hz, 1 H, 4-H), 4.64 (d, *J* = 3.3 Hz, 1 H, 2′-H). − ^{13}C NMR (75 MHz, C_6D_6): δ = 19.07 [CH_3, C(*C*H_3)$_2$], 21.68 [CH_3, C(*C*H_3)$_2$], 22.73 (CH_2, C-8), 23.56 (CH_3, 10-*C*H_3), 25.53 [CH, *C*H(CH_3)$_2$], 29.33 (CH, C-10), 30.29 (CH_2, C-9), 34.36 (CH_2, C-3), 42.61 (CH_2, C-11), 50.81 (CH, C-7), 65.21, 65.43 (CH_2, C-4′,C-5′), 68.16 (CH, C-4), 103.48 (CH, C-2′), 108.71 (C, C-6), 166.25 (C, C-2). − **(4*R*,6*R*,7*S*,10*R*) Isomer (10a, Less Polar Product):** ^{1}H NMR (300 MHz, C_6D_6): δ = 0.66 (m_c, 1 H), 0.71 (d, *J* = 6.7 Hz, 3 H, CH_3), 0.89 (d, *J* = 7.0 Hz, 3 H, CH_3), 0.91 (d, *J* =

7.0 Hz, 3 H, C*H*$_3$), 1.08 (t, *J* = 12.6 Hz, 1 H, 11-H$_{ax}$), 1.25−1.52 (m, 4 H), 1.64 (m$_c$, 1 H), 1.69 (ddd, *J* = 12.4, 3.6, 1.9 Hz, 1 H, 11-H$_{eq}$), 2.22 [dsept, *J* = 6.9, 1.7 Hz, 1 H, C*H*(CH$_3$)$_2$], 2.39 (dd, *J* = 17.2, 5.5 Hz, 1 H, 3-H$_a$), 2.47 (dd, *J* = 17.2, 10.0 Hz, 1 H, 3-H$_b$), 3.14−3.30 (m, 4 H, 4′-H), 3.80 (ddd, *J* = 10.0, 5.5, 3.1 Hz, 1 H, 4-H), 4.62 (d, *J* = 3.3 Hz, 1 H, 2′-H). − ^{13}C NMR (75 MHz, C$_6$D$_6$): δ = 18.52 [CH$_3$, C(*C*H$_3$)$_2$], 21.68 [CH$_3$, C(*C*H$_3$)$_2$], 22.42 (CH$_2$, C-8), 23.64 (CH$_3$, 10-*C*H$_3$), 24.95 [CH, *C*H(CH$_3$)$_2$], 29.64 (CH, C-10 and CH$_2$, C-9), 34.15 (CH$_2$, C-3), 48.54 (CH$_2$, C-11), 51.03 (CH, C-7), 64.92, 65.22 (CH$_2$, C-4′,C-5′), 71.52 (CH, C-4), 103.74 (CH, C-2′), 108.22 (C, C-6), 165.80 (C, C-2). − MS (70 eV); *m*/*z* (%): 298 (7) [M$^+$], 283 (1), 255 (1), 225 (6), 213 (16), 154 (10), 139 (10), 127 (82), 112 (25), 99 (12), 73 (100), 69 (25).

(4*R*,6*S*,7*S*,10*R*)-4-(1,3-Dioxolan-2-yl)-7-isopropyl-4,10-dimethyl-1,5-dioxaspiro[5.5]undecan-2-one (7b): 100 mg (0.42 mmol) of **1b**[6] was dissolved in 10 mL of 1,3-dioxolane. The solution was irradiated for 12 d (procedure A). Purification by HPLC (cyclohexane/ethyl acetate, 4:1) gave recovered **1b** (20 mg) and crystalline **7b** (30 mg, 23%): M.p. 87°C. [α]$^{20}_D$ = −44.3 (*c* = 1.1, CHCl$_3$). − IR (KBr): ṽ = 2960 cm^{-1} (m), 1747 (s, C=O), 1458 (m), 1375 (m), 1319 (m), 1238 (m), 1197 (w), 1152 (m), 1112 (m), 889 (w), 570 (w). − ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 0.65 (m$_c$, 1 H), 0.70 (d, *J* = 6.4 Hz, 3 H, C*H*$_3$), 0.94 (d *J* = 7.2 Hz, 3 H, C*H*$_3$), 1.07 (t, *J* = 12.7 Hz, 1 H, 11-H$_{ax}$), 1.11 (d, *J* = 6.4 Hz, 3 H, C*H*$_3$), 1.12 (s, 3 H, 4-C*H*$_3$), 1.31 (ddd, *J* = 12.9, 3.6, 1.9 Hz, 1 H, 7-H), 1.38−1.68 (m, 4 H), 1.90 (ddd, *J* = 13.4, 3.3, 1.9 Hz, 1 H, 11-H$_{eq}$), 2.15 (d, *J* = 17.2 Hz, 1 H, 3-H$_a$), 2.61 (d, *J* = 17.2 Hz, 1 H, 3-H$_b$), 2.72 [dsept, *J* = 6.9, 1.9 Hz, 1 H, C*H*(CH$_3$)$_2$], 3.16 (ddd, *J* = 7.2, 6.9, 6.9 Hz, 1 H), 3.26 (ddd, *J* = 7.2, 6.9, 4.0 Hz, 1 H), 3.38 (ddd, *J* = 6.9, 6.4, 4.0 Hz, 1 H), 3.46 (ddd, *J* = 7.2, 6.9, 6.4 Hz, 1 H), 4.58 (s, 1 H, 2′-H). − ^{13}C NMR (75 MHz, C$_6$D$_6$): δ = 18.25 [CH$_3$, CH(*C*H$_3$)$_2$], 21.62 (CH$_2$, C-8), 22.05 [CH$_3$, CH(*C*H$_3$)$_2$], 23.84 (CH$_3$, 10-*C*H$_3$), 24.41 [CH, *C*H(CH$_3$)$_2$], 25.15 (CH$_3$, 4-*C*H$_3$), 29.70 (CH, C-10), 33.58, 34.42 (CH$_2$, C-3, C-9), 47.77 (CH$_2$, C-11), 51.44 (CH, C-7), 65.32, 65.66 (CH$_2$, C-4′, C-5′), 76.54 (C, C-4), 107.01 (C, C-6 and CH, C-2′), 166.04 (C, C-2). − MS (70 eV); *m*/*z* (%): 312 (4) [M$^+$], 297 (1), 269 (1), 256 (1), 239 (7), 155 (8), 154 (7), 141 (66), 112 (13), 73 (100), 69 (18). − C$_{17}$H$_{28}$O$_5$ (312.41): calcd. C 65.36; H 9.03; found C 64.58; H 9.30.

(4*S*,6*R*,7*S*,10*R*)-4-(1,3-Dioxolan-2-yl)-7-isopropyl-4,10-dimethyl-1,5-dioxaspiro[5.5]undecan-2-one (9b): 110 mg (0.46 mmol) of **2b**[6] was dissolved in 10 mL of 1,3-dioxolane. The solution was irradiated for 12 d (procedure A). Purification by HPLC (cyclohexane/ethyl acetate, 4:1) gave recovered **2b** (50 mg) and crystalline **9b** (60 mg, 42%): M.p. 84°C. [α]$^{20}_D$ = −16.8 (*c* = 1.0, CHCl$_3$). − IR (KBr): ṽ = 2958 cm^{-1} (m), 1744 (s, C=O), 1458 (m), 1369 (m), 1317 (m), 1109 (s), 1043 (m), 1003 (s), 811 (m), 550 (w). − ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 0.67 (m$_c$, 1 H), 0.70 (d, *J* = 6.4 Hz, 3 H, C*H*$_3$), 0.93 (d, *J* = 6.9 Hz, 3 H, C*H*$_3$), 1.01 (d, *J* = 6.9 Hz, 3 H, C*H*$_3$), 1.04 (dd, *J* = 13.4, 12.4 Hz, 1 H, 11-H$_{ax}$), 1.06 (s, 3 H, 4-C*H*$_3$), 1.26−1.37 (m, 1 H), 1.39−1.59 (m, 4 H), 1.72 (ddd, *J* = 13.4, 3.1, 1.9 Hz, 1 H, 11-H$_{eq}$), 2.10 (d, *J* = 17.4 Hz, 1 H, 3-H$_a$), 2.60 (d, *J* = 17.2 Hz, 1 H, 3-H$_b$), 2.60 [dsept, *J* = 6.9, 1.7 Hz, 1 H, C*H*(CH$_3$)$_2$], 3.15 (ddd, *J* = 6.9, 6.9, 6.7 Hz, 1 H), 3.24 (ddd, *J* = 6.9, 6.7, 4.5 Hz, 1 H), 3.37 (ddd, *J* = 6.9, 6.7, 4.1 Hz, 1 H), 3.45 (ddd, *J* = 6.9, 6.7, 6.4 Hz, 1 H), 4.54 (s, 1 H, 2′-H). − ^{13}C NMR (75 MHz, C$_6$D$_6$): δ = 19.02 [CH$_3$, CH(*C*H$_3$)$_2$], 21.72 [CH$_3$, CH(*C*H$_3$)$_2$], 22.56 (CH$_2$, C-8), 23.97 (CH$_3$, 10-*C*H$_3$), 24.68 [CH, *C*H(CH$_3$)$_2$], 24.82 (CH$_3$, 4-*C*H$_3$), 29.97 (CH, C-10), 33.54, 34.45 (CH$_2$, C-3, C-9), 46.05 (CH$_2$, C-11), 51.67 (CH, C-7), 65.32, 65.69 (CH$_2$, C-4′, C-5′), 76.78 (C, C-4), 106.84 (CH, C-2′), 107.78 (CH, C-6), 166.55 (C, C-2). − MS (70 eV); *m*/*z* (%): 312 (5) [M$^+$], 297 (1), 269 (1), 239 (6), 227 (5), 155 (8), 154 (8), 141 (84), 112 (17), 73 (100), 69 (19). − C$_{17}$H$_{28}$O$_5$ (312.41): calcd. C 65.36; H 9.03; found C 65.02; H 9.21. − X-ray crystal structure analysis of **9b**: Empirical formula C$_{17}$H$_{28}$O$_5$, *M* = 312.39, 1.0 × 0.6 × 0.5 mm, *a* = 8.997(1), *b* = 10.830(1), *c* = 17.800(2) Å, *V* = 1734.4(3) Å^3, $\rho_{calcd.}$ = 1.196 g cm^{-3}, μ = 7.07 cm^{-1}, empirical absorption correction with ψ scan data (0.947 ≤ *C* ≤ 0.999), *Z* = 4, orthorhombic, space group $P2_12_12_1$ (No. 19), λ = 1.54178 Å, *T* = 223 K, ω/2θ scans, 2037 reflections collected (+*h*, +*k*, −*l*), [(sin θ)/λ] = 0.62 Å^{-1}, 2037 independent and 1974 observed reflections [$I \geq 2\sigma(I)$], 204 refined parameters, *R* = 0.034, *wR*^{2} = 0.094, max. residual electron density 0.22 (−0.14) e Å^{-3}, Flack parameter 0.1(2), hydrogen atoms calculated and riding.[17]

(4*R*,6*S*,7*S*,10*R*,2′*RS*)-7-Isopropyl-10-methyl-4-oxolan-2′-yl-1,5-dioxaspiro[5.5]undecan-2-one (11a): 130 mg (0.58 mmol) of **1a**[38] was dissolved in 16 mL of THF. The solution was irradiated for 5 d (procedure A). Purification by HPLC (cyclohexane/ethyl acetate, 4:1) yielded the two crystalline adducts (2′*R*)-**11a** and (2′*S*)-**11a** (less polar isomer 38 mg, 22% and more polar isomer 70 mg, 41%). The isomers were separated but the stereochemistry was not assigned. − **11a (Less Polar Product):** M.p. 100°C (pentane). [α]$^{20}_D$ = +41.4 (*c* = 0.4, CHCl$_3$). − IR (neat): ṽ = 2953 cm^{-1} (s), 1747 (s, C=O), 1455 (m), 1316 (m), 1237 (m), 1154 (m), 1075 (m), 1007 (m), 972 (m). − ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 0.66 (m$_c$, 1 H), 0.74 (d, *J* = 6.4 Hz, 3 H, 10-C*H*$_3$), 0.81 (t, *J* = 12.6 Hz, 1 H, 11-H$_{ax}$), 0.90 [d, *J* = 6.9 Hz, 3 H, CH(C*H*$_3$)$_2$], 0.96 [d, *J* = 6.9 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.28 (ddd, *J* = 12.8, 3.9, 2.2 Hz, 1 H, 7-H), 1.32−1.80 (m, 8 H), 1.93 (ddd, *J* = 13.1, 3.8, 1.7 Hz, 1 H, 11-H$_{eq}$), 2.31 (dd, *J* = 17.6, 10.3 Hz, 1 H, 3-H$_a$), 2.40 [dsept, *J* = 6.9, 2.1 Hz, 1 H, C*H*(CH$_3$)$_2$], 2.42 (dd, *J* = 17.6, 4.5 Hz, 1 H, 3-H$_b$), 3.40−3.61 (m, 3 H, 2′-H, 5′-H), 3.75 (ddd, *J* = 10.1, 5.5, 4.6 Hz, 1 H, 4-H). − ^{13}C NMR (75 MHz, C$_6$D$_6$): δ = 18.31 [CH$_3$, C(*C*H$_3$)$_2$], 21.95 (CH$_2$, C-8), 22.05 [CH$_3$, C(*C*H$_3$)$_2$], 23.67 (CH$_3$, 10-*C*H$_3$), 24.81 [CH, *C*H(CH$_3$)$_2$], 25.63 (CH$_2$, C-3′), 27.55 (CH$_2$, C-2′), 29.16 (CH, C-10), 33.14, 34.42 (CH$_2$, C-3, C-9), 44.36 (CH$_2$, C-11), 50.63 (CH, C-7), 68.46 (CH$_2$, C-4′), 68.89 (CH, C-4), 80.42 (CH, C-2′), 107.07 (C, C-6), 165.74 (C, C-2). − MS (70 eV); *m*/*z* (%): 296 (5) [M$^+$], 255 (6), 211 (25), 155 (19), 154 (12), 143 (15), 139 (20), 125 (100), 112 (30), 97 (48), 83 (30), 71 (47), 69 (40). − C$_{17}$H$_{28}$O$_4$ (296.4): calcd. C 68.89; H 9.52; found C 69.14; H 9.68. − **11a (More Polar Product):** M.p. 50°C. [α]$^{20}_D$ = +27.6 (*c* = 0.6, CHCl$_3$). − IR (CH$_2$Cl$_2$): ṽ = 2954 cm^{-1} (m), 1734 (s, C=O), 1318 (w), 1237 (m), 1062 (m), 970 (w). − ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 0.64 (m$_c$, 1 H), 0.74 (d, *J* = 6.4 Hz, 3 H, 10-C*H*$_3$), 0.79 (t, *J* = 12.6 Hz, 1 H, 11-H$_{ax}$), 0.90 [d, *J* = 7.2 Hz, 3 H, CH(C*H*$_3$)$_2$], 0.96 [d, *J* = 6.9 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.25 (ddd, J = 12.9, 4.1, 2.2 Hz, 1 H, 7-H), 1.26−1.78 (m, 8 H), 1.91 (ddd, *J* = 12.9, 3.6, 1.7 Hz, 1 H, 11-H$_{eq}$), 2.13 (dd, *J* = 17.4, 4.0 Hz, 1 H, 3-H$_a$), 2.40 [dsept, *J* = 6.9, 2.2 Hz, 1 H, C*H*(CH$_3$)$_2$], 2.52 (dd, *J* = 17.4, 11.0 Hz, 1 H, 3-H$_b$), 3.46−3.56 (m, 2 H), 3.59−3.66 (m, 1 H), 3.67 (ddd, *J* = 4.0, 4.0, 11.0 Hz, 1 H, 4-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 18.16 [q, C(*C*H$_3$)$_2$], 21.77 (t, C-8), 21.93 [q, C(*C*H$_3$)$_2$], 23.49 (q, 10-*C*H$_3$), 24.58 [d, *C*H(CH$_3$)$_2$], 25.89 (t, C-3′), 27.14 (t, C-2′), 29.13 (d, C-10), 32.13, 34.26 (t, C-3, C-9), 44.38 (t, C-11), 50.22 (d, C-7), 68.90 (t, C-4′), 69.00 (d, C-4), 79.56 (d, C-2′), 108.19 (s, C-6), 167.46 (s, C-2). − MS (70 eV); *m*/*z* (%): 296 (3) [M$^+$], 225 (7), 211 (17), 155 (7), 154 (10), 143 (16), 139 (21), 125 (100), 112 (37), 97 (52), 83 (36), 71 (33), 69 (48).

(4*S*,6*R*,7*S*,10*R*,2′*RS*)-7-Isopropyl-10-methyl-4-oxolan-2′-yl-1,5-dioxaspiro[5.5]undecan-2-one (12a): 70 mg (0.31 mmol) of **2a**[38] was dissolved in 7 mL of THF. The solution was irradiated for 4 d (procedure A). Purification by HPLC (cyclohexane/ethyl acetate, 4:1) gave an oil (20 mg, 22%) and a solid (20 mg, 22%). The stereochemistry of the isomers (2′*R*)-**12a** and (2′*S*)-**12a** was not assigned.

− **12a (Less Polar Product):** − IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2966 cm^{-1} (m), 1734 (s, C=O), 1182 (m). − ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 0.64 (m$_c$, 1 H), 0.71 (d, *J* = 6.7 Hz, 3 H, 10-CH_3), 0.91 [d, *J* = 6.9 Hz, 3 H, CH(CH_3)$_2$], 0.92 [d, *J* = 6.9 Hz, 3 H, CH(CH_3)$_2$], 1.11 (t, *J* = 14.1, 12.6 Hz, 1 H, 11-H$_{ax}$), 1.28−1.55 (m, 9 H), 1.84 (ddd, *J* = 14.1, 3.3, 2.2 Hz, 1 H, 11-H$_{eq}$), 2.20 [dsept, *J* = 6.9, 1.0 Hz, 1 H, CH(CH$_3$)$_2$], 2.27 (dd, *J* = 17.6, 10.5 Hz, 1 H, 3-H$_a$), 2.42 (dd, *J* = 17.6, 4.3 Hz, 1 H, 3-H$_b$), 3.40−3.60 (m, 4 H, 4-H, 2′-H, 5′-H). − ^{13}C NMR (75 MHz, C$_6$D$_6$): δ = 19.16 [CH$_3$, C(*C*H$_3$)$_2$], 21.65 [CH$_3$, C(*C*H$_3$)$_2$], 22.86 (CH$_2$, C-8), 23.60 (CH$_3$, 10-*C*H$_3$), 25.39 [CH, *C*H(CH$_3$)$_2$], 25.66 (CH$_2$, C-3′), 27.61 (CH$_2$, C-2′), 29.50 (CH, C-10), 33.14, 34.35 (CH$_2$, C-3, C-9), 42.61 (CH$_2$, C-11), 50.79 (CH, C-7), 68.45 (CH$_2$, C-4′), 69.43 (CH, C-4), 80.45 (CH, C-2′), 108.35 (C, C-6), 166.17 (C, C-2). − MS (70 eV); *m/z* (%): 296 (4) [M$^+$], 225 (7), 211 (28), 155 (19), 154 (7) [menthone$^+$], 143 (11), 139 (11), 125 (100), 112 (22), 97 (34), 83 (20), 71 (27) [oxolanyl$^+$], 69 (22), 55 (24), 41 (56). − **12a (More Polar Product):** − IR (neat): $\tilde{\nu}$ = 2966 cm^{-1} (m), 1714 (s, C=O), 1183 (m). − ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 0.63 (m$_c$, 1 H), 0.72 (d, *J* = 6.4 Hz, 3 H, 10-CH_3), 0.91 [d, *J* = 6.9 Hz, 3 H, CH(CH_3)$_2$], 0.95 [(d, *J* = 6.9 Hz, 3 H, CH(CH_3)$_2$], 1.03 (dd, *J* = 13.8,12.6 Hz, 1 H, 11-H$_{ax}$), 1.22−1.60 (m, 9 H), 1.85 (ddd, *J* = 13.8, 2.9, 2.2 Hz, 1 H, 11-H$_{eq}$), 2.14 (dd, *J* = 17.4, 3.6 Hz, 1 H, 3-H$_a$), 2.21 [sept, *J* = 6.9 Hz, 1 H, C*H*(CH$_3$)$_2$], 2.58 (dd, *J* = 17.4, 11.0 Hz, 1 H, 3-H$_b$), 3.37−3.51 (m, 3 H, 2′-H, 5′-H), 3.62 (m$_c$, 1 H, 4-H). − ^{13}C NMR (75 MHz, C$_6$D$_6$): δ = 18.95 [CH$_3$, C(*C*H$_3$)$_2$], 21.68 [CH$_3$, C(*C*H$_3$)$_2$], 22.83 (CH$_2$, C-8), 23.54 (CH$_3$, 10-*C*H$_3$), 25.46 [CH, *C*H(CH$_3$)$_2$], 26.03 (CH$_2$, C-3′), 27.07 (CH$_2$, C-2′), 29.47 (CH, C-10), 32.40, 34.35 (CH$_2$, C-3, C-9), 42.64 (CH$_2$, C-11), 50.97 (CH, C-7), 68.56 (CH$_2$, C-4′), 69.00 (CH, C-4), 79.00 (CH, C-2′), 108.45 (C, C-6), 166.62 (C, C-2). − MS (70 eV); *m/z* (%): 296 (2) [M$^+$], 225 (5), 211 (5), 210 (7), 155 (6), 154 (15), 143 (10), 139 (27), 125 (74), 112 (44), 97 (52), 83 (49), 71 (28), 69 (58), 55 (62), 41 (100).

(4*R*,6*S*,7*S*,10*R*,2′*RS*)-7-Isopropyl-4,10-dimethyl-4-oxolan-2′-yl-1,5-dioxaspiro[5.5]undecan-2-one (11b): 70 mg (0.29 mmol) of **1b**[6] was dissolved in 7 mL of THF. The solution was irradiated for 12 d (procedure A). Purification by HPLC (cyclohexane/ethyl acetate, 3:1) gave recovered **1b** (50 mg) and two adducts (2′*R*)-**11b** and (2′*S*)-**11b** (less polar isomer 3 mg, 3% and more polar isomer 6 mg, 6%). The stereochemistry of neither isomers was assigned. − **11b (Less Polar Product):** ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 0.66 (ddt, *J* = 12.2, 12.2, 3.6 Hz, 1 H), 0.72 (d, *J* = 6.4 Hz, 3 H, 10-CH_3), 0.95 [d, *J* = 7.2 Hz, 3 H, C(CH_3)$_2$], 0.98 (s, 3 H, 4-CH_3), 1.10 [m$_c$, 1 H, therein d, *J* = 6.9 Hz, 3 H, C(CH_3)$_2$], 1.26−1.68 (m, 9 H), 1.93 (ddd, *J* = 13.4, 3.6, 1.7 Hz, 1 H, 11-H$_{eq}$), 2.22 (d, *J* = 17.2 Hz, 1 H, 3-H$_a$), 2.60 [dsept, *J* = 7.2, 1.7 Hz, 1 H, C*H*(CH$_3$)$_2$], 2.69 (d, *J* = 17.2 Hz, 1 H, 3-H$_b$), 3.45 (m$_c$, 1 H, 2′-H), 3.54−3.67 (m, 2 H, 5′-H). − **11a (More Polar Product):** ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 0.66 (ddt, *J* = 12.2, 12.2, 3.6 Hz, 1 H), 0.72 (d, *J* = 6.4 Hz, 3 H, 10-CH_3), 0.92 [d, *J* = 7.2 Hz, 3 H, C(CH_3)$_2$], 1.04 (s, 3 H, 4-CH_3), 1.05 [d, *J* = 7.9 Hz, 3 H, C(CH_3)$_2$], 1.06 (t, *J* = 12.2 Hz, 1 H, 11-H$_{ax}$), 1.29 (ddd, J = 12.9, 3.6, 1.7 Hz, 1 H), 1.37−1.74 (m, 8 H), 1.94 (ddd, *J* = 13.4, 3.6, 1.9 Hz, 1 H, 11-H$_{eq}$), 2.20 (d, *J* = 17.4 Hz, 1 H, 3-H$_a$), 2.55 [dsept, *J* = 7.2, 1.4 Hz, 1 H, C*H*(CH$_3$)$_2$], 2.78 (d, *J* = 17.4 Hz, 1 H, 3-H$_b$), 3.34 (dd, J = 8.6, 6.7 Hz, 1 H, 1′-H), 3.48 (dt, *J* = 8.1, 5.5 Hz, 1 H, 4′-H$_a$), 3.64 (dt, J = 8.1, 6.7 Hz, 1 H, 4′-H$_b$).

(4*S*,6*R*,7*S*,10*R*,2′*RS*)-7-Isopropyl-4,10-dimethyl-4-oxolan-2′-yl-1,5-dioxaspiro[5.5]undecan-2-one (12b): 75 mg (0.31 mmol) of **2b**[6] was dissolved in 16 mL of THF. The solution was irradiated for 12 d (procedure A). Purification by HPLC (cyclohexane/ethyl acetate, 3:1) gave recovered **2b** (50 mg) and a mixture of (2′*R*)-**12b** and (2′*S*)-**12b** (10 mg, 10%) as an oil. The mixture of isomers was inseparable. − **12b (Major Isomer):** ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 0.66 (m$_c$, 1 H), 0.70 (d, *J* = 6.4 Hz, 3 H, 10-CH_3), 0.89 (d, *J* = 6.7 Hz, 3 H, C(CH_3)$_2$], 0.95 [d, *J* = 7.2 Hz, 3 H, C(CH_3)$_2$], 1.05 (dd, *J* = 13.6, 12.4 Hz, 1 H, 11-H$_{ax}$), 1.06 (s, 3 H, 4-CH_3), 1.20−1.67 (m, 9 H), 1.77 (ddd, *J* = 13.6, 2.8, 2.2 Hz, 1 H, 11-H$_{eq}$), 2.15 (d, *J* = 17.6 Hz, 1 H, 3-H$_a$), 2.35 [dsept, *J* = 6.9, 1.2 Hz, 1 H, C*H*(CH$_3$)$_2$], 2.77 (d, *J* = 17.6 Hz, 1 H, 3-H$_b$), 3.38 (dd, J = 7.9, 6.9 Hz, 1 H, 2′-H), 3.43 (dt, *J* = 7.9, 5.7 Hz, 1 H, 5′-H$_a$), 3.62 (dt, J = 8.3, 6.4 Hz, 1 H, 5′-H$_b$). − **12b (Minor Isomer):** − ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 0.66 (m$_c$, 1 H), 0.72 (d, *J* = 6.7 Hz, 3 H, 10-CH_3), 0.90 (s, 3 H, 4-CH_3), 0.96 [d, *J* = 6.9 Hz, 3 H, C(CH_3)$_2$], 0.97 [d, *J* = 6.9 Hz, 3 H, C(CH_3)$_2$], 1.06 (m, 1 H, 11-H$_{ax}$), 1.20−1.68 (m, 9 H), 1.77 (ddd, *J* = 13.6, 2.8, 2.2 Hz, 1 H, 11-H$_{eq}$), 2.18 (d, *J* = 17.2 Hz, 1 H, 3-H$_a$), 2.48 [dsept, *J* = 6.9, 1.8 Hz, 1 H, C*H*(CH$_3$)$_2$], 2.66 (d, *J* = 17.2 Hz, 1 H, 3-H$_b$), 3.38−3.63 (m, 3 H, 2′-H, 5′-H).

General Procedure B (Alkylation of 1,3-Dioxin-4-ones): In a flame-dried flask, 3 mL of 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone and diisopropylamine (350 mg, 3.46 mmol) were dissolved in 20 mL of THF under argon. The solution was cooled to −78°C, *n*-butyllithium (1.9 mL, 3.0 mmol, 1.6 M in hexanes) was added. After being stirred for 20 min at this temperature, the mixture was allowed to warm to 20°C, and stirred for additional 10 min. The LDA solution was cooled to −78°C and 1,3-dioxin-4-one (2.10 mmol) in 2 mL of THF was added dropwise. After the yellow solution was stirred for 30 min, the bromide (2.1−11.0 mmol) was added, and the mixture was allowed to warm slowly to room temperature. After being stirred for 14 h, the reaction was quenched with 30 mL of a saturated ammonium chloride solution, and then extracted with diethyl ether (3 × 30 mL). The combined organic layers were washed with brine and dried (MgSO$_4$). The solvent was removed in vacuo and the resulting mixture of dioxinones was purified by column chromatography (*n*-pentane/diethyl ether).

6-[3-(1,3-Dioxolan-2-yl)propyl]-2,2-dimethyl-1,3-dioxin-4-one (14a) and 5-[2-(1,3-Dioxolan-2-yl)ethyl]-2,2,6-trimethyl-1,3-dioxin-4-one (17a): Compounds **14a** and **17a** were prepared by procedure B using 2,2,6-trimethyl-1,3-dioxin-4-one (1.73 g, 12.2 mmol) and 2-(2-bromoethyl)-1,3-dioxolane (3.64 g, 20.1 mmol). Purification by column chromotography (*n*-pentane/diethyl ether, 1:1) gave a mixture of **14a** and **17a**. This mixture was separated by HPLC (cyclohexane/ethyl acetate, 7:3) to yield **17a** (91 mg, 5%) and **14a** (436 mg, 15%). − **14a:** IR (neat): $\tilde{\nu}$ = 2951 cm^{-1} (m), 2880 (s), 1729 (s, C=O), 1633 (m), 1391 (s), 1273 (m), 1205 (m), 1140 (m), 1014 (m), 902 (w). − ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.61 (s, 6 H, 2-CH_3), 1.63 (m$_c$, 4 H), 2.21 (m, 2 H, 1′′-H), 3.75−3.95 (m, 4 H, 4′′-H), 4.80 (m$_c$, 1 H, 2′-H), 5.19 (t, *J* = 0.8 Hz, 1 H, 5-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 20.12 (t, C-2′′), 25.01 (q, 2-*C*H$_3$), 32.90, 33.36 (t, C-1′′, C-3′′), 64.93 (t, C-4′), 93.34 (d, C-5), 103.86 (d, C-2′), 106.35 (s, C-2), 161.41 (s, C-6), 171.56 (s, C-4). − MS (70 eV); *m/z* (%): 242 (1) [M$^+$], 184 (3), 183 (5), 156 (10), 99 (42), 86 (7), 73 (100), 69 (10). − **17a:** IR (neat): $\tilde{\nu}$ = 2886 cm^{-1} (m), 1716 (s, C=O), 1645 (s), 1398 (s), 1356 (m), 1270 (m), 1236 (m), 1207 (m), 1142 (m), 1031 (m), 904 (w). − ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.65 (s, 6 H, 2-CH_3), 1.83 (m, 2 H, 2′′-H), 2.00 (s, 3 H, 6-CH_3), 2.40 (m, 2 H, 1′′-H), 3.78−4.03 (m, 4 H, 4′-H), 4.87 (t, *J* = 4.7 Hz, 1 H, 2′-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 17.26 (q, 6-*C*H$_3$), 19.96 (t, C-2′′), 25.14 (q, 2-*C*H$_3$), 33.06 (t, C-1′′), 64.89 (t, C-4′), 103.97 (d, C-2′), 104.78, 104.83 (s, C-2, C-5), 161.96 (s, C-6), 163.26 (s, C-4). − MS (70 eV); *m/z* (%): 242 (5) [M$^+$], 184 (18), 167 (2), 156 (31), 141 (13), 156 (6), 111 (11), 99 (15), 97 (13), 86 (100), 73 (92).

6-[3-(1,3-Dioxan-2-yl)propyl]-2,2-dimethyl-1,3-dioxin-4-one (14b) and 5-[2-(1,3-Dioxan-2-yl)ethyl]-2,2,6-trimethyl-1,3-dioxin-4-one

(17b): Compounds **14b** and **17b** were prepared by procedure B using 2,2,6-trimethyl-1,3-dioxin-4-one (1.21 g, 8.51 mmol) and 2-(2-bromoethyl)-1,3-dioxane (1.67 g, 8.56 mmol). Purification by column chromatography (*n*-pentane/diethyl ether, 1:1) gave **17b** (68 mg, 3%) as a solid and **14b** (232 mg, 11%) as an oil. − **14b:** IR (neat): ṽ = 2960 cm^{-1} (w), 2851 (w), 1730 (s, C=O), 1633 (m), 1391 (m), 1273 (m), 1204 (m), 1146 (m), 1089 (w), 1012 (m), 901 (w). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.35 (dtt, *J* = 13.4, 2.7, 1,2 Hz, 1 H, 5′′-H_a), 1.65 (m, 4 H), 1.68 (s, 6 H, 2-CH_3), 2.11 (dtt, *J* = 13.5, 12.4, 5.0 Hz, 1 H, 5′′-H_b), 2.25 (m, 2 H, 1′-H), 3.76 (m, 2 H, 4′′-H_a), 4.10 (m, 2 H, 4′′-H_b), 4.54 (m, 1 H, 2′′-H), 5.25 (t, *J* = 0.8 Hz, 1 H, 5-H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.20 (t, C-2′), 25.07 (q, 2-CH_3), 25.81 (t, C-5′′), 33.43, 34.33 (t, C-1′, C-3′), 66.87 (t, C-4′′), 93.30 (d, C-5), 101.54 (d, C-2′′), 106.26 (s, C-2), 161.19 (s, C-6), 171.59 (s, C-4). − MS (70 eV); *m*/*z* (%): 256 (2) [M$^+$], 198 (5), 197 (6), 170 (10), 113 (29), 87 (100), 71 (18), 69 (19). − **17b:** M.p. 60−62°C. − IR (KBr): ṽ = 2948 cm^{-1} (m), 1717 (s, C=O), 1643 (m), 1408 (m), 1343 (w), 1272 (m), 1239 (m), 1206 (m), 1141 (s), 1000 (w), 894 (w). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 (dtt, *J* = 13.5, 2.6, 1.3 Hz, 1 H, 5′′-H_b), 1.65 (s, 6 H, 2-CH_3), 1.76 (m, 2 H), 1.99 (s, 3 H, 6-CH_3), 2.07 (dtt, *J* = 13.5, 12.4, 5.1 Hz, 1 H, 5′′-H_a), 2.37 (m, 2 H), 3.74 (m, 2 H, 4′′-H_a), 4.09 (m, 2 H, 4′′-H_b), 4.54 (t, *J* = 5.1 Hz, 1 H, 2′′-H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.25 (q, 6-CH_3), 19.97 (t, C-1′), 25.09 (q, 2-CH_3), 25.82 (t, C-5′′), 34.26 (C-2′), 66.67 (t, C-4′′), 101.79 (d, C-2′′), 104.75, 104.90 (s, C-5, C-2), 162.10 (s, C-6), 163.23 (s, C-4). − MS (70 eV); *m*/*z* (%): 256 (4) [M$^+$], 198 (100) [M$^+$ − acetone], 180 (10), 155 (82), 140 (31), 139 (29), 100 (85), 97 (71), 87 (95).

(6*S*,7*S*,10*R*)-4-[3-(1,3-Dioxolan-2-yl)propyl]-7-isopropyl-10-methyl-1,5-dioxaspiro[5.5]undec-3-en-2-one (15) and (6*S*,7*S*,10*R*)-3-[2-(1,3-Dioxolan-2-yl)ethyl]-7-isopropyl-4,10-dimethyl-1,5-dioxaspiro-[5.5]undec-3-en-2-one (18): Compounds **15** and **18** were prepared by procedure B using **1b**[6] (506 mg, 2.12 mmol) and 2-(2-bromoethyl)-1,3-dioxolane (955 mg, 5.28 mmol). Purification by HPLC (cyclohexane/ethyl acetate, 7:3) gave crystalline **18** (50 mg, 7%) and **15** (100 mg, 14%) as an oil. − **15:** $[\alpha]^{20}_D$ = −20.6 (*c* = 0.2, $CHCl_3$). − IR (neat): ṽ = 2954 cm^{-1} (m), 1732 (s, C=O), 1633 (m), 1456 (w), 1384 (m), 1309 (w), 1228 (m), 1142 (m), 1080 (w), 805 (w). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.8 (m_c, 1 H), 0.88 (d, *J* = 5.9 Hz, 3 H, 10-CH_3), 0.91 [d, *J* = 6.8 Hz, 3 H, $C(CH_3)_2$], 0.96 [d, *J* = 6.8 Hz, 3 H, $C(CH_3)_2$], 1.00 (dd, *J* = 13.3, 12.2 Hz, 1 H, 11-H_{ax}), 1.46−186 (m, 9 H), 2.20 [dsept, *J* = 7.0, 2.4 Hz, 1 H, $CH(CH_3)_2$], 2.27 (m, 2 H, 1′-H), 2.60 (ddd, *J* = 13.2, 5.4, 2.0 Hz, 1 H, 11-H_{eq}), 3.80−4.04 (m, 4 H, 4′′-H), 4.88 (m_c, 1 H, 2′′-H), 5.18 (s, 1 H, 3-H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.73 (q, CH_3), 20.29 (t, C-2′), 21.69 (q, CH_3), 22.58 (t, C-8), 23.32 (q, CH_3), 25.88 [d, $CH(CH_3)_2$], 28.68 (d, C-10), 33.07, 33.62 (t,C-1′,C-3′), 34.27 (t, C-9), 41.23 (t, C-11), 49.69 (d, C-7), 64.98 (t, C-4′′), 92.79 (d, C-3), 104.03 (d, C-2′′), 109.82 (s, C-6), 161.07 (s, C-4), 171.40 (s, C-2). − MS (70 eV); *m*/*z* (%): 338 (1) [M$^+$], 310 (2), 295 (2), 274 (9), 249 (3), 247 (3), 185 (47), 184 (12) [M$^+$ − menthone], 156 (34), 154 824), 139 (38), 136 (11), 112 (69), 111 (14), 99 (47), 73 (100), 69 (35). − $C_{19}H_{30}O_5$ (338.4): calcd. C 67.43; H 8.94; found C 67.54; H 8.93. − **18:** M.p. 92°C. $[\alpha]^{20}_D$ = +11.7 (*c* = 0.3, $CHCl_3$). − IR (neat): ṽ = 2954 cm^{-1} (s), 2876 (s), 1723 (s, C=O), 1644 (m), 1398 (m), 1272 (m), 1140 (m). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.85−1.14 (m, 2 H), 0.87 (d, *J* = 6.2 Hz, 3 H, 10-CH_3), 0.91 [d, *J* = 6.8 Hz, 3 H, $C(CH_3)_2$], 0.95 [d, *J* = 7.0 Hz, 3 H, $C(CH_3)_2$], 1.40−1.80 (m, 5 H), 1.81 (ddd, *J* = 8.3,4.8, 2.4 Hz, 1 H, 2′-H_a), 1.85 (ddd, *J* = 8.1, 4.7, 1.7 Hz, 1 H, 1′-H_b), 2.00 (s, 3 H, 4-CH_3), 2.24 [dsept, *J* = 2.5, 7.0 Hz, 1 H, $CH(CH_3)_2$], 2.31 (ddd, *J* = 14.1, 8.3, 6.7 Hz, 1 H, 1′-H_a), 2.46 (ddd, *J* = 14.1, 8.3, 6.3 Hz, 1 H, 1′-H_b), 2.63 (ddd, *J* = 13.3, 3.4, 2.1 Hz, 1 H, 11-H_{eq}), 3.81−4.02 (m, 4 H, 4′′-H), 4.88 (t, *J* = 4.7 Hz, 1 H, 2′′-H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.43 (q, 4-CH_3), 18.57 (q, CH_3), 19.96 (t, C-2′), 21.77 (q, CH_3), 22.14 (t, C-8), 23.33 (q, CH_3), 25.48 [d, $CH(CH_3)_2$], 28.61 (d, C-10), 33.10 (t, C-1′), 34.21 (t, C-9), 41.13 (t, C-11), 49.56 (d, C-7), 64.84 (t, C-4′′), 103.89 (s, C-3), 103.95 (d, C-2′′), 107.99 (s, C-6), 161.75 (s, C-4), 163.23 (s, C-2). − MS (70 eV); *m*/*z* (%): 338 (1) [M$^+$], 185 (16), 184 (20), 166 (3), 156 (37), 154 (3), 141 (12), 139 (9), 112 (15), 111(11), 86 (100), 73 (66), 69 (23).

(6*R*,7*S*,10*R*)-4-[3-(1,3-Dioxolan-2-yl)propyl]-7-isopropyl-10-methyl-1,5-dioxaspiro[5.5]undec-3-en-2-one (16) and (6*R*,7*S*,10*R*)-3-[2-(1,3-Dioxolan-2-yl)ethyl]-7-isopropyl-4,10-dimethyl-1,5-dioxaspiro[5.5]undec-3-en-2-one (19): Compounds **15** and **18** were prepared by procedure B using **2b**[6] (504 mg, 2.11 mmol) and 2-(2-bromoethyl)-1,3-dioxolane (2.37 g, 13.1 mmol). Purification by HPLC (cyclohexane/ethyl acetate, 7:3) gave **19** (50 mg, 7%) and **16** (90 mg, 13%). − **16:** M.p. 64°C. $[\alpha]^{20}_D$ = −2.3 (*c* = 1.0, $CHCl_3$). − IR (neat): ṽ = 2919 cm^{-1} (m), 1732 (s, C=O), 1633 (m), 1384 (m), 1281 (m), 1137 (m), 824 (m). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.87 [d, *J* = 6.9 Hz, 3 H, $C(CH_3)_2$], 0.89 (d, *J* = 6.6 Hz, 3 H, 10-CH_3), 0.95 [d, *J* = 7.0 Hz, 3 H, $C(CH_3)_2$], 1.00 (m, 1 H), 1.10 (dd, *J* = 13.7, 12.6 Hz, 1 H, 11-H_{ax}), 1.40−1.84 (m, 9 H), 2.28 (m, 2 H), 2.34 [dsept, *J* = 6.9, 1.6 Hz, 1 H, $CH(CH_3)_2$], 2.62 (ddd, *J* = 13.7, 3.6, 2.0 Hz, 1 H, 11-H_{eq}), 3.80−4.03 (m, 4 H, 4′′-H), 4.87 (m_c, 1 H, 2′′-H), 5.22 (t, *J* = 0.8 Hz, 1 H, 3-H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.26 (q, CH_3), 20.22 (t, C-2′), 21.59 (q, CH_3), 21.95 (t, C-8), 23.17 (q, CH_3), 25.12 [d, $CH(CH_3)_2$], 29.70 (d, C-10), 32.91, 33.56 (t, C-1′, C-3′), 33.96 (t, C-9), 40.59 (t, C-11), 49.36 (d, C-7), 64.96 (t, C-4′′), 93.49 (d, C-3), 103.89 (d, C-2′′), 109.46 (s, C-6), 161.61 (s, C-4), 170.81 (s, C-2). − MS (70 eV); *m*/*z* (%): 338 (5) [M$^+$], 310 (1), 295 (1), 185 (31), 184 (7), 156 (20), 154 (20), 139 (22), 136 (7), 112 (63), 111 (12), 99 (35), 73 (100), 69 (40). − **19:** $[\alpha]^{20}_D$ = −44.9 (*c* = 0.5, $CHCl_3$). − IR (neat): ṽ = 2954 cm^{-1} (s), 1723 (s, C=O), 1650 (s), 1454 (s), 1396 (s), 1310 (m), 1279 (m), 1200 (m), 1162 (m), 1092 (m), 930 (w). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85−0.96 (m, 1 H), 0.87 [d, *J* = 6.9 Hz, 3 H, $C(CH_3)_2$], 0.88 (d, *J* = 6.6 Hz, 3 H, 10-CH_3), 0.93 [d, *J* = 7.0 Hz, 3 H, $C(CH_3)_2$], 1.05 (dd, *J* = 13.6, 12.5 Hz, 1 H, 11-H_{ax}), 1.40−1.82 (m, 5 H), 1.84 (dt, *J* = 7.7, 4.7 Hz, 2 H, 2′-H), 2.00 (s, 3 H, 4-CH_3), 2.34 (dt, *J* = 14.1, 7.1 Hz, 1 H, 1′-H_a), 2.34 [dsept, *J* = 7.0, 1.5 Hz, 1 H, $CH(CH_3)_2$], 2.47 (dt, *J* = 14.2, 7.7 Hz, 1 H, 1′-H_b), 2.63 (ddd, *J* = 13.6, 3.6, 2.0 Hz, 1 H), 3.79−4.01 (m, 4 H, 4′′-H), 4.87 (t, *J* = 4.7 Hz, 1 H, 2′′-H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.35 (q, 4-CH_3), 18.26 (q, CH_3), 20.05 (t, C-2′), 21.68 (q, CH_3), 21.99 (t, C-8), 23.18 (q, CH_3), 24.14 [d, $CH(CH_3)_2$], 29.82 (d, C-10), 33.10 (t, C-1′), 34.14 (t, C-9), 40.73 (t, C-11), 49.46 (d, C-7), 64.86, 64.90 (t, C-4′′, C-5′′), 104.05 (d, C-2′′), 104.64 (s, C-3), 107.94 (s, C-6), 162.27 (s, C-4), 162.60 (s, C-2). − MS (70 eV); *m*/*z* (%): 338 (1) [M$^+$], 295 (1), 185 (17), 184 (19), 166 (3), 156 (36), 154 (4), 141 (12), 139 (10), 112 (17), 111(149, 99 (11), 97 (14), 86 (100), 73 (68), 69 (31).

General Procedure C (1,3-Dioxin-4-ones from β-Oxo Esters): Concentrated sulfuric acid (56 µL, 1.0 mmol) was added dropwise to a mixture of ketone (2.0 mmol), acetic anhydride (3.0 mmol) and β-oxo ester (1.0 mmol), and the temperature was kept below −5°C during the addition. The mixture was stirred at −5 to 0°C for 3 h and then kept at 0°C for 14 h. Under ice-cooling a cold (0°C) 10% Na_2SO_4 solution (5 mL) was added. After being stirred for 30 min at room temperature, the mixture was extracted with diethyl ether (4 × 5 mL). The combined organic layers were washed with water, dried ($MgSO_4$), and the solvent was removed in vacuo. Recrystallization or column chromatography (*n*-pentane/diethyl ether) gave the desired 1,3-dioxin-4-ones.

2,2-Dimethyl-2,3,3a,4,5,6-hexahydrobenzofuran-7-carboxylic Acid (21): Following the general procedure C, **20**[31] (500 mg, 1.94 mmol) was treated with acetone (225 mg, 3.88 mmol). Purification by column chromatography (diethyl ether/*n*-pentane, 1:9) gave **21** (84 mg, 22%) as a solid: M.p. 95°C. − IR (KBr): $\tilde{\nu}$ = 2979 cm^{-1} (w), 2940 (m), 2872 (w), 1637 (s, C=O), 1615 (sh, m), 1453 (w), 1404 (m), 1325 (m), 1224 (m), 1182 (m), 1122 (m), 1046 (m), 891 (m). − ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.17 (dddd, *J* = 13.7, 12.6, 11.1, 3.0 Hz, 1 H, 4-H$_a$), 1.39 (t, *J* = 0.5 Hz, 3 H, 2-CH_3), 1.42 (d, *J* = 0.5 Hz, 3 H, 2-CH_3), 1.45 (ddq, *J* = 13.6, 12.9, 0.7 Hz, 1 H, 3-H$_a$), 1.69 (ddddd, *J* = 13.6, 13.6, 9.4, 9.4, 3.2 Hz, 1 H, 5-H$_a$), 1.82 (dd, *J* = 13.5, 4.2 Hz, 1 H, 3-H$_b$), 1.84 (m$_c$, 1 H, 4-H$_b$), 1.95 (m$_c$, 1 H, 5-H$_b$), 2.37−2.42 (m, 2 H, 6-H), 2.59 (ddddddd, *J* = 13.0, 11.1, 4.1, 2.0, 2.0, 2.0, 2.0 Hz, 1 H, 3a-H), 13.44 (s, 1 H, OH). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 21.04 (t, C-5), 26.64 (q, 2-CH$_3$), 29.10 (t), 29.40 (d, C-3a), 29.59 (t), 30.33 (q, 2-CH$_3$), 40.93 (t, C-3), 80.91 (s, C-2), 96.19 (s, C-7), 171.68 (s, C-7a), 175.07 (c, *C*OOH). − MS (70 eV); *m*/*z* (%): 197 (5) [M$^+$ + H], 196 (29) [M$^+$], 181 (7), 178 (17), 163 (38), 150 (12), 141 (33), 135 (12), 123 (100), 95 (13), 84 (7), 79 (7). − $C_{11}H_{16}O_3$ (196.2): calcd. C 67.32; H 8.22; found C 67.27; H 8.40.

8,8-Dimethyl-1,4,7,9-tetraoxadispiro[4.0.5.3]tetradecan-10-one (22a) and 11-Hydroxy-8,8-dimethyl-1,4,7,9-tetraoxadispiro[4.0.5.3]tetradecan-10-one (23): A solution of **14a** (116 mg, 0.48 mmol) and 200 µL of acetone in 20 mL of cyclohexane was irradiated for 4 d (procedure A). Purification by HPLC (cyclohexane/ethyl acetate, 13:7) yielded **22a** (13 mg, 11%) and **23** (9 mg, 7%). − **22a:** IR (neat): $\tilde{\nu}$ = 2948 cm^{-1} (m, br.), 1748 (s, C=O), 1358 (m), 1296 (m), 1157 (m), 1032 (m), 960 (m). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.60 (q, *J* = 0.7 Hz, 3 H, 8-CH_3), 1.62 (q, *J* = 0.7 Hz, 3 H, 8-CH_3), 1.65 (m, 2 H), 1.75−2.06 (m, 4 H), 2.59 (d, *J* = 17.1 Hz, 1 H, 11-H$_a$), 2.93 (d, *J* = 17.2 Hz, 1 H, 11-H$_b$), 3.89−4.05 (m, 4 H, 2-H, 3-H). − ^{13}C NMR (50 MHz, CDCl$_3$): δ = 16.72 (t, C-13), 28.27 (q, 8-CH$_3$), 29.65 (q, 8-CH$_3$), 31.13 33.17 (t, C-12, C-14), 36.10 (t, C-11), 65.37, 65.89 (t, C-3, C-2), 82.91 (s, C-6), 105.09 (s, C-8), 116.12 (s, C-5), 168.30 (s, C-10). − MS (70 eV); *m*/*z* (%): 242 (6) [M$^+$], 184 (3), 183 (5), 167 (4), 156 (20), 140 (4), 139 (4), 113 (8), 112 (13), 99 (100), 86 (25), 69 (12). − $C_{12}H_{18}O_5$: (242.3): calcd. C 59.49; H 7.49; found C 59.47; H 7.53. − **23:** IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 3450 cm^{-1} (m, br., OH), 2944 (m), 1748 (s, C=O), 1385 (m), 1278 (m), 1109 (s), 1050 (m), 953 (w), 869 (m). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.61 (q, *J* = 0.7 Hz, 3 H, 8-CH_3), 1.64 (q, *J* = 0.7 Hz, 3 H, 8-CH_3), 1.65−2.18 (m, 6 H), 3.45 (s, 1 H, OH), 3.97−4.13 (m, 4 H, 2-H, 3-H), 4.64 (s, 1 H, 11-H). − MS (CI); *m*/*z* (%): 259 (46) [M$^+$ + H], 243 (4), 241 (5), 201 (100), 183 (31), 173 (17), 157 (8), 99 (26), 73 (2), 69 (3).

2,2-Dimethyl-1,3,8,12-tetraoxadispiro[5.0.5.3]pentadecan-4-one (22b): A solution of **14b** (98 mg, 0.38 mmol) and 100 µL of acetone in 10 mL of cyclohexane was irradiated for 2 d (procedure A). Purification by HPLC (cyclohexane/ethyl acetate, 4:1) yielded crystalline **22b** (17 mg, 17%): M.p. 112°C (pentane). − IR (KBr): $\tilde{\nu}$ = 2965 cm^{-1} (m), 2873 (m), 1743 (s, C=O), 1438 (w), 1388 (m), 1293 (m), 1227 (m), 1148 (m), 1108 (m), 1064 (m), 957 (m), 829 (m), 807 (m). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.35 (dtt, *J* = 13.3, 2.6, 1.7 Hz, 1 H, 10-H$_a$), 1.59 (q, *J* = 0.9 Hz, 3 H, 2-CH_3), 1.61 (q, *J* = 0.8 Hz, 3 H, 2-CH_3), 1.54−2.26 (m, 6 H), 2.22 (m$_c$, 1 H), 2.51 (d, *J* = 17.2 Hz, 1 H, 5-H$_A$), 3.12 (d, *J* = 17.1 Hz, 1 H, 5-H$_B$), 3.79−4.00 (m, 4 H, 9-H, 11-H). − ^{13}C NMR (50 MHz, CDCl$_3$): δ = 17.77 (t, C-14), 25.70 (2 t, C-10, C-15), 29.30 (q, 2-CH$_3$), 29.34 (q, 2-CH$_3$), 31.85 (t, C-13), 35.90 (t, C-5), 60.75, 62.05 (t, C-9, C-11), 84.19 (s, C-6), 105.22 (s, C-7), 106.25 (s, C-2), 169.06 (s, C-4). − MS (70 eV); *m*/*z* (%): 256 (69) [M$^+$], 198 (1), 181 (2), 170 (28), 154 (4), 139 (3), 113 (100), 100 (169, 85 (4). − X-ray crystal structure analysis of **22b**: Empirical formula $C_{13}H_{20}O_5$, *M* = 256.29, 0.6 × 0.5 × 0.2 mm, *a* = 7.403(1), *b* = 8.535(1), *c* = 11.186(1) Å, α = 67.27(1), β = 73.53(1), γ = 77.63(1)°, *V* = 620.75(12) Å^3, $\rho_{\text{calcd.}}$ = 1.371 g cm^{-3}, μ = 8.70 cm^{-1}, empirical absorption correction with ψ scan data (0.941 ≤ *C* ≤ 0.999), *Z* = 2, triclinic, space group *P*1bar (no. 2), λ = 1.54178 Å, *T* = 223 K, ω/2θ scans, 2740 reflections collected (−*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.62 Å^{-1}, 2534 independent and 2381 observed reflections [$I \geq 2\sigma(I)$], 166 refined parameters, *R* = 0.037, wR^2 = 0.098, max. residual electron density 0.29 (−0.23) e Å^{-3}, hydrogen atoms calculated and riding.[17]

(6*RS*,8*S*,9*S*,12*R*)-9-Isopropyl-12-methyl-1,4,7,14-tetraoxatrispiro[4.0.1.5.3.3]nonadecan-15-one (24 and 25): A solution of **15** (100 mg, 0.30 mmol) and 500 µL of acetone in 60 mL of cyclohexane was irradiated for 4 d (procedure A). Purification by HPLC (cyclohexane/ethyl acetate, 4:1) gave two crystalline products **25** (9 mg, 9%) and **24** (14 mg, 14%). − **25 (Less Polar Product):** M.p. 122°C. $[\alpha]^{20}{}_D$ = −43.3 (*c* = 0.2, CHCl$_3$). − IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2955 cm^{-1} (s), 1747 (s, C=O), 1458 (w), 1309 (m), 1253 (m), 1222 (m), 1154 (m), 1008 (m). − ^{1}H NMR (200 MHz, CDCl$_3$): δ = 0.86 [d, *J* = 7.0 Hz, 3 H, C(CH_3)$_2$], 0.87 (d, , *J* = 6.4 Hz, 3 H, 10-CH_3), 0.9 (m$_c$, 1 H), 0.92 [d, *J* = 6.7 Hz, 3 H, C(CH$_3$)$_2$], 1.26 (dd, *J* = 12.6, 13.9 Hz, 1 H, 13-H$_{ax}$), 1.32 (m, 2 H), 1.44−2.05 (m, 9 H), 2.07 (ddd, *J* = 13.9, 3.3, 1.8 Hz, 1 H, 13-H$_{eq}$), 2.29 [dsept, *J* = 7.0, 2.0 Hz, 1 H, C*H*(CH$_3$)$_2$], 2.50 (d, *J* = 16.8 Hz, 1 H, 16-H$_a$), 3.00 (d, *J* = 16.8 Hz, 1 H, 16-H$_b$), 3.92−4.09 (m, 4 H, 2-H, 3-H). − MS (70 eV); *m*/*z* (%): 338 (8) [M$^+$], 295 (3) [M$^+$ − (CH$_3$)$_2$C=CH$_2$], 253 (3), 184 (7) [M$^+$ − menthone], 167 (20), 156 (54), 139 (11), 123 (7), 112 (26), 99 (100), 86 (19), 69 (22). − HRMS: calcd. for $C_{19}H_{30}O_5$ 338.2093, found 338.2091. − **24 (More Polar Product):** M.p. 132°C; $[\alpha]^{20}{}_D$ = −5.0 (*c* = 0.4, CHCl$_3$). − IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2926 cm^{-1} (s), 1742 (s, C=O), 1458 (w), 1316 (m), 1252 (m), 1150 (m), 974 (m). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.86 [d, *J* = 6.9 Hz, 3 H, C(CH_3)$_2$], 0.88 (d, *J* = 6.4 Hz, 3 H, 12-CH_3), 0.9 (m$_c$, 1 H), 0.91 [d, *J* = 7.2 Hz, 3 H, C(CH_3)$_2$], 1.29 (dd, *J* = 13,5, 12.9 Hz, 1 H, 13-H$_{ax}$), 1.25 (m, 2 H), 1.54−2.05 (m, 9 H), 2.14 (ddd, *J* = 13.5, 3.6, 1.9 Hz, 1 H, 13-H$_{eq}$), 2.47 [dsept, *J* = 6.9, 1.9 Hz, 1 H, C*H*(CH$_3$)$_2$], 2.54 (d,, *J* = 17.4 Hz, 1 H, 16-H$_a$), 2.90 (d, *J* = 17.4 Hz, 1 H, 16-H$_b$), 3.92−4.03 (m, 4 H, 2-H, 3-H). − MS (70 eV); *m*/*z* (%): 338 (7) [M$^+$], 295 (2), 253 (2), 184 (8), 167 (18), 156 (57), 154 (14), 140 (11), 139 (28), 112 (66), 99 (100), 69 (41). − HRMS: calcd. for $C_{19}H_{30}O_5$ 338.2093, found 338.2091. − X-ray crystal structure analysis of **24**: Empirical formula $C_{19}H_{30}O_5$, *M* = 338.43, 1.2 × 1.2 × 0.3 mm, *a* = 9.833(1), *b* = 8.679(1), *c* = 10.803(1) Å, β = 95.00(1)°, *V* = 918.4(2) Å^3, $\rho_{\text{calcd.}}$ = 1.224 g cm^{-3}, μ = 7.07 cm^{-1}, empirical absorption correction with ψ scan data (0.905 ≤ *C* ≤ 0.999), *Z* = 2, monoclinic, space group $P2_1$ (no. 4), λ = 1.54178 Å, *T* = 223 K, ω/2θ scans, 2113 reflections collected (±*h*, +*k*, −*l*), [(sin θ)/λ] = 0.62 Å^{-1}, 2008 independent and 1964 observed reflections [$I \geq 2\sigma(I)$], 221 refined parameters, *R* = 0.048, wR^2 = 0.132, max. residual electron density 0.22 (−0.22) e Å^{-3}, Flack parameter −0.1(3), hydrogen atoms calculated and riding.[17]

(6*RS*,8*R*,9*S*,12*R*)-9-Isopropyl-12-methyl-1,4,7,14-tetraoxatrispiro[4.0.1.5.3.3]nonadecan-15-one (26 and 27): A solution of **16** (90 mg, 0.27 mmol) and 600 µL of acetone in 70 mL of cyclohexane was irradiated for 4 d (procedure A). Purification by HPLC (cyclohexane/ethyl acetate, 4:1) gave the less polar isomer (8 mg, 9%) as a solid, 19 mg of a not characterized oil, and the more polar isomer (9 mg, 10%) as an oil. − **Less Polar Isomer:** M.p. 66°C. $[\alpha]^{20}{}_D$ = +15.8 (*c* = 0.2, CHCl$_3$). − IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1} (s), 1751 (s, C=O), 1458 (w), 1348 (w), 1298 (m), 1214 (m), 1155 (m), 1114 (m), 981 (m). − ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.88 (d, *J* = 6.0 Hz, 3 H, 12-CH$_3$), 0.88 [d, *J* = 7.0 Hz, 3 H, C(CH_3)$_2$], 0.91 (m$_c$, 1 H), 0.92 [d, *J* = 7.0 Hz, 3 H, C(CH_3)$_2$], 1.24 (t, *J* = 12.6 Hz, 1 H, 13-

H_{ax}), 1.38 (ddd, J = 1.3, 2.4, 1.1 Hz, 1 H, 12-H), 1.43 (ddd, J = 13.1, 12.2, 3.4 Hz, 1 H), 1.56−1.77 (m, 5 H), 1.78−1.89 (m, 2 H), 1.90−1.98 (m, 2 H), 2.09 (ddd, J = 12.9, 3.4, 1.9 Hz, 1 H, 13-H_{eq}), 2.16 [dsept, J = 7.0, 1.2 Hz, 1 H, $CH(CH_3)_2$], 2.52 (d, J = 17.0 Hz, 1 H, 16-H_a), 2.94 (d, J = 17.0 Hz, 1 H, 16-H_b), 3.92−4.06 (m, 4 H, 2-H, 3-H). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.03 (t, C-18), 18.57 (q, CH_3), 21.80 (q, CH_3), 22.57 (t, C-10), 23.77 (q, 12-CH_3), 24.98 [d, $CH(CH_3)_2$], 29.77 (d, C-12), 30.77, 32.44 (t, C-17, C-19), 34.01 (t, C-11), 36.66 (t, C-16), 46.51 (t, C-13), 51.00 (d, C-9), 64.61, 66.01 (t, C-2, C-3), 83.09 (s, C-6), 109.31 (s, C-8), 116.17 (s, C-5), 169.29 (s, C-15). − MS (70 eV); *m/z* (%): 338 (10) [M^+], 295 (3) [$M^+ - (CH_3)_2C{=}CH_2$], 184 (9) [M^+ − menthone], 167 (23), 156 (37), 154 (9) [menthone$^+$], 139 (28), 125 (38), 112 (42), 111 (39), 99 (100), 83 (67), 71 (59), 69 (66). − HRMS: calcd. for $C_{19}H_{30}O_5$ 338.2093, found 338.2091. − **More Polar Isomer:** $[\alpha]^{20}_D$ = −39.6 (c = 0.3, $CHCl_3$). − IR (CH_2Cl_2): $\tilde{\nu}$ = 2954 cm^{-1} (s), 1747 (s, C=O), 1458 (w), 1311 (m), 1214 (w), 1160 (m), 1102 (w), 1050 (w), 978 (m). − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.83−0.95 (m, 2 H), 0.86 (d, J = 6.9 Hz, 6 H, CH_3), 0.9 [d, J = 7.0 Hz, 3 H, $CH(CH_3)_2$], 1.20−2.02 (m, 11 H), 2.10 (ddd, J = 13.4, 3.1, 2.0 Hz, 1 H, 13-H_{eq}), 2.20 (m_c, 1 H), 2.59 (d, J = 17.5 Hz, 1 H, 16-H_a), 2.87 (d, J = 17.5 Hz, 1 H, 16-H_b), 3.85−4.00 (m, 4 H, 2-H, 3-H). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.05 (t, C-18), 18.52 (q, CH_3), 21.74 (q, CH_3), 22.81 (t, C-10), 23.82 (q, 12-CH_3), 24.65 [d, $CH(CH_3)_2$], 30.15 (d, C-12), 31.09, 32.23 (t, C-17, C-19), 34.30 (t, C-11), 35.15 (t, C-16), 45.20 (t, C-13), 51.61 (d, C-9), 65.21, 65.85 (t, C-2, C-3), 82.37 (s, C-6), 109.33 (s, C-8), 116.18 (s, C-5), 168.79 (s, C-16). − MS (70 eV); *m/z* (%): 338 (8) [M^+], 295 (4), 253 (5), 184 (8), 167 (34), 156 (45), 139 (18), 125 (13), 123 (20), 112 (33), 111 (22), 99 (100), 85 (28), 83 (44), 71 (39), 69 (47). − HRMS: calcd. for $C_{19}H_{30}O_5$ 338.2093, found 338.2091.

Ethyl 4-[4-(1,3-Dioxolan-2-yl)-2,2-dimethyl-6-oxo-1,3-dioxan-4-yl]butyrate (28): A solution of **14a** (217 mg, 0.88 mmol) and 400 µL of acetone in 40 mL of 1,3-dioxolane was irradiated for 5 d (procedure A). The crude product was separated by HPLC (cyclohexane/ethyl acetate, 7:3). Bidioxolanyls **29** (29 mg) and **30** (16 mg) eluted first. − **28** (23 mg, 8%) was isolated as an oil. − IR (neat): $\tilde{\nu}$ = 2984 cm^{-1} (m), 2943 (m), 2892 (m), 1749 (s, C=O), 1732 (s, C=O), 1633 (w), 1387 (m), 1287 (m), 1180 (m), 1101 (m), 1946 (m), 978 (m), 814 (w). − ^1H NMR (200 MHz, $CDCl_3$): δ = 1.24 (t, J = 7.0 Hz, 3 H, CH_2CH_3), 1.59 (s, 3 H, 2′-CH_3), 1.60 (s, 3 H, 2′-CH_3), 1.61−1.82 (m, 4 H), 2.31 (m, 2 H, 2-H), 2.46 (d, J = 17.2 Hz, 1 H, 5′-H_a), 2.74 (d, J = 17.2 Hz, 1 H, 5′-H_b), 3.82−4.04 (m, 4 H, 4′′-H, 5′′-H), 4.12 (q, J = 7.0 Hz, 2 H, CH_2CH_3), 4.81 (s, 1 H, 2′′-H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.22 (q, CH_2CH_3), 18.29 (t, C-3), 28.91 (q, 2′-CH_3), 29.55 (q, 2′-CH_3), 32.25, 34.22 (t, C-2, C-4), 37.51 (t, C-5′), 60.38 (t, CH_2CH_3), 65.49, 65.87 (t, C-4′′, C-5′′), 78.53 (s, C-4′), 104.94 (s, C-2′), 105.18 (d, C-2′′), 168.16 (s, C-6′), 173.11 (s, C-1). − MS (CI); *m/z* (%): 317 (5) [M^+ + H], 299 (1) [M^+ − OH], 287 (3), 259 (12) [M^+ − acetone], 157 (34), 243 (4), 185 (9), 167 (5), 147 (100), 103 (11), 73 (31). − **[2,2′]Bi(1,3-dioxolanyl) (29):** IR (KBr): $\tilde{\nu}$ = 2895 cm^{-1} (s), 1313 (m), 1111 (s), 1033 (m), 954 (m). − ^1H NMR (90 MHz, $CDCl_3$): δ = 3.80−4.18 (m, 8 H, 4-H), 4.68 (s, 2 H, 2-H). − MS (CI); *m/z* (%): 147 (100) [M^+ + H], 75 (18), 73 (9). − **[2.4′]Bi(1,3-dioxolanyl) (30):** IR (neat): $\tilde{\nu}$ = 2889 cm^{-1} (m), 1159 (m), 1087 (s), 1035 (m), 930 (m). − ^1H NMR (90 MHz, $CDCl_3$): δ = 3.77−4.26 (m, 7 H), 4.87−5.08 (m, 3 H). − MS (CI); *m/z* (%): 147 (100) [M^+ + H].

General Procedure D (γ-Alkylation of *tert*-Butyl Acetoacetate): In a flame-dried flask, sodium hydride (880 mg, 22.0 mmol, 60% in mineral oil) was suspended in 50 mL of THF under argon and *tert*-butyl acetoacetate (3.16 g, 20.0 mmol) was added dropwise by cannula at 0°C. The mixture was stirred for 15 min at 0°C, and then *n*-butyllithium (13.1 mL, 21.0 mmol, 1.6 M in hexanes) was added over 15 min. The orange solution was stirred for additional 30 min at 0°C, and the alkyl bromide (22.0 mmol) in 5 mL of THF was added dropwise. The mixture was allowed to warm slowly to room temperature. After being stirred for 3 h at room temperature, the reaction was quenched with 100 mL of a saturated ammonium chloride solution, and the product was extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed successively with water and brine, dried ($MgSO_4$), and the solvent was removed in vacuo. Distillation gave the desired product as an oil.

***tert*-Butyl 3-Oxohept-6-enoate (31a):** Compound **31a** was prepared following the procedure D using 10 mmol of the acetoacetate and allyl bromide for alkylation. The crude product was distilled (55°C/0.01 Torr) to give **31a** (1.69 g, 85%) as an oil: − IR (neat): $\tilde{\nu}$ = 2980 cm^{-1} (m), 1743 (s, C=O), 1716 (s, C=O), 1643 (w), 1369 (m), 1320 (m), 1254 (m), 1150 (s), 916 (w). − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.47 (s, 9 H, CH_3), 2.34 (m, 2 H, 5-H), 2.64 (t, J = 7.4 Hz, 2 H, 4-H), 3.35 (s, 2 H, 2-H), 4.90 (t, J = 0.7 Hz, 2-H, enolic form), 4.99 (ddt, J = 10.1, 1.7, 1.3 Hz, 1 H, 7-H_a), 5.04 (ddt, J = 17.2, 1.7, 1.6 Hz, 1 H, 7-H_b), 5.81 (ddt, J = 17.2, 10.1, 6.5 Hz, 1 H, 6-H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.50 (t, C-5), 28.00 (q, CH_3), 41.97 (t, C-4), 50.71 (t, C-2), 81.86 [s, $C(CH_3)_3$], 90.67 (d, C-2, enolic form), 115.40 (t, C-7), 136.72 (d, C-6), 166.32 (s, C-1), 202.17 (s, C-3). − MS (CI); *m/z* (%): 199 (2) [M^+ + H], 183 (1), 143 (77), 125 (2), 101 (30), 89 (11), 87 (5), 71 (100).

(6*RS*,7*S*,10*R*)-4-But-3-enyl-7-isopropyl-10-methyl-1,5-dioxaspiro[5.5]undec-3-en-2-one (32a and 33a): Following the general procedure C, **31a** (2.96 g, 14.9 mmol) was treated with (−)-menthone (4.60 g, 29.8 mmol). The residue was purified by column chromatography. Elution with diethyl ether/*n*-pentane (3:97) gave unreacted menthone. Further elution with diethyl ether/*n*-pentane (10:90) gave a mixture of isomers which was separated by HPLC (ethyl acetate/cyclohexane, 7:93) to yield **32a** (0.56 g, 14%) as an oil and **33a** (166 mg, 4%) as a solid. − **32a (Less Polar Product):** $[\alpha]^{20}_D$ = −28.0 (c = 1.0, $CHCl_3$). − IR (neat): $\tilde{\nu}$ = 2955 cm^{-1} (m), 2923 (m), 2869 (w), 1738 (s, C=O), 1634 (m), 1383 (m), 1309 (w), 1227 (m), 1079 (w). − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.85−1.00 (m, 1 H), 0.88 (d, J = 6.1 Hz, 3 H, 10-CH_3), 0.92 [d, J = 6.8 Hz, 3 H, $C(CH_3)_2$], 0.97 [d, J = 7.0 Hz, 3 H, $C(CH_3)_2$], 1.00 (dd, J = 13.3, 12.4 Hz, 1 H, 11-H_{ax}), 1.44−1.90 (m, 5 H), 2.21 [dsept, J = 6.9, 2.4 Hz, 1 H, $CH(CH_3)_2$], 2.25−2.39 (m, 4 H, 1′-H, 2′-H), 2.60 (ddd, J = 13.3, 3.5, 2.1 Hz, 1 H, 11-H_{eq}), 5.01−5.14 (m, 2 H, 4′-H), 5.18 (s, 1 H, 3-H), 5.79 (ddt, J = 17.0, 10.2, 6.5 Hz, 1 H, 3′-H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.54 [q, $C(CH_3)_2$], 21.61 [q, $C(CH_3)_2$], 22.31 (t, C-8), 23.25 (q, 10-CH_3), 25.65 [d, $C(CH_3)_2$], 28.56 (d, C-10), 29.76 (t, C-2′), 33.04 (t, C-1′), 34.08 (t, C-9), 41.11 (t, C-11), 49.46 (d, C-7), 92.82 (d, C-3), 109.75 (s, C-6), 116.10 (t, C-4′), 135.97 (d, C-3′), 161.07 (s, C-4), 170.97 (s, C-2). − MS (70 eV); *m/z* (%): 278 (2) [M^+], 155 (10), 154 (25), 140 (5), 139 (44), 125 (22), 124 (84), 112 (100), 111 (5), 97 (18), 96 (16), 95 (16), 84 (15), 83 (21), 82 (11), 81 (10), 69 (80). − $C_{17}H_{26}O_3$ (278.4): calcd. C 73.35; H 9.41; found C 72.85; H 9.67. − **33a (More Polar Product):** M.p. 45°C. $[\alpha]^{20}_D$ = −29.1 (c = 1.0, $CHCl_3$). − IR (neat): $\tilde{\nu}$ = 2954 cm^{-1} (m), 2872 (m), 1739 (s, C=O), 1630 (m), 1449 (w), 1383 (m), 1305 (w), 1283 (m), 1219 (w), 1079 (m), 920 (m), 824 (m). − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.90−1.10 (m, 1 H), 0.88 [d, J = 6.9 Hz, 3 H, $C(CH_3)_2$], 0.89 (d, J = 6.6 Hz, 3 H, 10-CH_3), 0.95 [d, J = 7.0 Hz, 3 H, $C(CH_3)_2$], 1.10 (dd, J = 13.7, 12.5 Hz, 1 H, 11-H_{ax}), 1.40−1.84 (m, 5 H), 2.24−2.42 [m, 5 H, 1′-H, 2′-H, $CH(CH_3)_2$], 2.62 (ddd, J = 13.7, 3.7, 2.0 Hz, 1 H, 11-H_{eq}), 5.02−5.15 (m, 2 H, 4′-H), 5.21 (s, 1 H, 3-H), 5.79 (ddt, J = 17.0, 10.3, 6.0 Hz, 1 H, 3′-H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.38 [q, $C(CH_3)_2$], 21.56 [q, $C(CH_3)_2$], 22.18 (t, C-8), 23.18 (q, 10-CH_3), 25.29 [d, *C*(CH$_3$)$_2$], 29.80 (d, C-10), 29.80 (t, C-2′), 33.17 (t, C-1′), 34.05 (t, C-9), 40.74 (t, C-11), 49.55 (d, C-7), 93.67 (d, C-3), 109.60 (s, C-6), 116.17 (t, C-4′), 136.00 (d, C-3′), 161.41 (s, C-4), 170.32 (s, C-2). − MS (70 eV); *m/z* (%): 278 (3) [M$^+$], 155 (10), 154 (21), 140 (4), 139 (34), 125 (25), 124 (98), 112 (100), 111 (15), 97 (15), 96 (17), 95 (17), 84 (9), 83 (19), 82 (14), 81 (14), 69 (84). − $C_{17}H_{26}O_3$ (278.4): calcd. C 73.35; H 9.41; found C 73.11; H 9.67.

***tert*-Butyl 3-Oxooct-7-enoate (31b):** Compound **31b** was prepared following the procedure D using 20 mmol of acetoacetate and 4-bromobut-1-ene for alkylation. The crude product was distilled through a Vigreux column (77 °C/0.01 Torr) to give **31b** (2.46 g, 58%): − IR (neat): ṽ = 2978 cm^{-1} (w), 2932 (w), 1739 (s, C=O), 1715 (s, C=O), 1641 (w),1368 (m), 1319 (m), 1252 (m), 1149 (s), 914 (w). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.46 (s, 9 H, *C*H$_3$), 1.70 (quint, *J* = 7.4 Hz, 2 H, 5-H), 2.07 (m, 2 H, 6-H), 2.53 (t, *J* = 7.3 Hz, 2 H, 4-H), 3.33 (s, 2 H, 2-H), 4.89 (s, 2-H, enolic form), 4.98 (ddt, *J* = 10.0, 1.9, 1.2 Hz, 1 H, 8-H$_a$), 5.01 (ddt, *J* = 17.2, 2.1, 1.4 Hz, 1 H, 8-H$_b$), 5.76 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1 H, 7-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 22.34 (CH$_2$, C-5), 27.80 (CH$_3$, *C*H$_3$), 32.72 (CH$_2$, C-6), 41.85 (CH$_2$, C-4), 50.58 (CH$_2$, C-2), 81.68 [C, *C*(CH$_3$)$_3$], 90.41 (CH, C-2, enolic form), 115.18 (CH$_2$, C-8), 137.62 (CH, C-7), 166.30 (C, C-1), 202.90 (C, C-3). − MS (CI); *m/z* (%): 212 (13) [M$^+$], 211 (100) [M$^+$ − H], 157 (14) [M$^+$ + H − (CH$_3$)$_2$C=CH$_2$], 139 (5) [M$^+$ − OC(CH$_3$)$_3$], 113 (7).

(6*RS*,7*S*,10*R*)-7-Isopropyl-10-methyl-4-pent-4-enyl-1,5-dioxaspiro-[5.5]undec-3-en-2-one (32b and 33b): Following the general procedure C, **31b** (2.46 mg, 11.64 mmol) and (−)-menthone (3.60 g, 23.3 mmol) were allowed to react. The residue was purified by column chromatography. Elution with diethyl ether/*n*-pentane (3:97) gave unreacted menthone. Further elution with diethyl ether/*n*-pentane (10:90) gave a mixture of isomers which was separated by HPLC (ethyl acetate/cyclohexane, 7:93) to yield **32b** (0.66 g, 19%) as an oil and **33b** (0.21 g, 6%) as a solid. − **32b (Less Polar Product):** [α]$^{20}_{D}$ = −27.5 (*c* = 1.2, CHCl$_3$). − IR (neat): ṽ = 3076 cm^{-1} (w), 2954 (m), 2870 (w), 1737 (s, C=O), 1634 (m), 1456 (w), 1382 (m), 1308 (w), 1226 (m), 1070 (w), 927 (w), 805 (w). − ^{1}H NMR (200 MHz, CDCl$_3$): δ = 0.85−1.00 (m, 1 H), 0.89 (d, *J* = 6.1 Hz, 3 H, 10-C*H*$_3$), 0.92 [d, *J* = 6.7 Hz, 3 H, C(C*H*$_3$)$_2$], 0.96 [d, *J* = 7.0 Hz, 3 H, C(C*H*$_3$)$_2$], 0.99 (dd, *J* = 13.3, 12.3 Hz, 1 H, 11-H$_{ax}$), 1.45−1.87 (m, 7 H), 2.05−2.28 (m, 5 H, 1′-H, 3′-H, C*H*(CH$_3$)$_2$], 2.61 (ddd, *J* = 13.2, 3.5, 2.1 Hz, 1 H, 11-H$_{eq}$), 4.98−5.10 (m, 2 H, 5′-H), 5.17 (t, *J* = 0.8 Hz, 1 H, 3-H), 5.78 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1 H, 4′-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 18.66 [q, C(*C*H$_3$)$_2$], 21.60 [q, C(*C*H$_3$)$_2$], 22.52 (t, C-8), 23.23 (q, 10-CH$_3$), 24.98 (t, C-2′), 25.82 [d, *C*(CH$_3$)$_2$], 28.59 (d, C-10), 32.84, 33.03 (t, C-1′, C-3′), 34.17 (t, C-9), 41.15 (t, C-11), 49.62 (d, C-7), 92.64 (d, C-3), 109.69 (s, C-6), 115.64 (t, C-4′), 137.27 (d, C-3′), 160.99 (s, C-4), 171.53 (s, C-2). − MS (70 eV); *m/z* (%): 292 (2) [M$^+$], 250 (1) [M$^+$ − CH$_3$CH=CH$_2$], 155 (16), 154 (32) [menthone$^+$], 139 (56), 138 (82) [M$^+$ − menthone], 112 (100), 97 (12), 84 (30), 83 (11), 69 (63). − **33b (More Polar Product):** M.p. 53 °C. [α]$^{20}_{D}$ = −28.5 (*c* = 1.2, CHCl$_3$). − IR (neat): ṽ = 3076 cm^{-1} (w), 2955 (m), 2871 (w), 1735 (s, C=O), 1636 (m), 1456 (w), 1383 (m), 1307 (w), 1280 (m), 1217 (w), 1080 (w), 912 (w), 808 (w). − ^{1}H NMR (200 MHz, CDCl$_3$): δ = 0.85−1.10 (m, 1 H), 0.87 [d, *J* = 7.1 Hz, 3 H, C(C*H*$_3$)$_2$], 0.89 (d, *J* = 6.6 Hz, 3 H, 10-C*H*$_3$), 0.95 [d, *J* = 7.1 Hz, 3 H, C(C*H*$_3$)$_2$], 1.11 (dd, *J* = 13.7, 12.7 Hz, 1 H, 11-H$_{ax}$), 1.40−1.87 (m, 7 H), 2.02−2.31 (m, 4 H, 1′-H, 3′-H), 2.34 [dsept, *J* = 7.1, 1.7 Hz, 1 H, C*H*(CH$_3$)$_2$], 2.63 (ddd, *J* = 13.7, 3.7, 2.0 Hz, 1 H, 11-H$_{eq}$), 5.02 (ddt, *J* = 10.5, 2.0, 1.2 Hz, 1 H, 5′-H$_a$) 5.14 (m$_c$, 1 H, 5′-H$_b$), 5.21 (s, 1 H, 3-H), 5.77 (ddt, *J* = 16.9, 10.5, 6.8 Hz, 1 H, 4′-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 18.33 [q, C(*C*H$_3$)$_2$], 21.59 [q, C(*C*H$_3$)$_2$], 22.16 (t, C-8), 23.17 (q, 10-CH$_3$), 25.04 (t, C-2′), 25.28 [d, *C*(CH$_3$)$_2$], 29.79 (d, C-10), 32.82, 33.13 (t, C-1′, C-3′), 34.07 (t, C-9), 40.75 (t, C-11), 49.54 (d, C-7), 93.53 (d, C-3), 109.49 (s, C-6), 115.75 (t, C-4′), 137.24 (d, C-3′), 161.49 (s, C-4), 170.95 (s, C-2). − MS (70 eV); *m/z* (%): 292 (2) [M$^+$], 250 (1) [M$^+$ − CH$_3$CH=CH$_2$], 155 (16), 154 (31) [menthone$^+$], 139 (57), 138 (81) [M$^+$ − menthone], 112 (100), 97 (12), 95 (10), 84 (28), 83 (11), 69 (61). − $C_{18}H_{28}O_3$ (292.4): calcd. C 73.93; H 9.65; found C 73.21; H 9.75.

(6*S*,7*S*,10*R*)-4-[4-(1,3-Dioxolan-2-yl)butyl]-7-isopropyl-10-methyl-1,5-dioxaspiro[5.5]undec-3-en-2-one (34) and (6*S*,7*S*,10*R*)-4-[4-(1,3-Dioxolan-4-yl)-butyl]-7-isopropyl-10-methyl-1,5-dioxaspiro-[5.5]undec-3-en-2-one (35): A solution of **32a** (51 mg, 0.18 mmol) and 200 μL of acetone in 20 mL of 1,3-dioxolane was irradiated for 24 h (procedure A). Purification by HPLC (cyclohexane/ethyl acetate, 4:1) gave 35 (4 mg, 6%) as a solid and 34 (21 mg, 33%) as an oil. − **34 (More Polar Product):** [α]$^{20}_{D}$ = −20.0 (*c* = 0.3, CHCl$_3$). − IR (neat): ṽ = 2952 cm^{-1} (m), 2872 (m), 1732 (s, C=O), 1633 (m), 1456 (w), 1384 (m), 1309 (m), 1227 (m), 1142 (m), 1080 (m), 956 (m), 805 (m). − ^{1}H NMR (200 MHz, CDCl$_3$): δ = 0.85−0.95 (m, 1 H), 0.89 (d, *J* = 6.3 Hz, 3 H, 10-C*H*$_3$), 0.91 [d, *J* = 6.9 Hz, 3 H, C(C*H*$_3$)$_2$], 0.96 [d, *J* = 7.1 Hz, 3 H, C(C*H*$_3$)$_2$], 0.99 (dd, *J* = 12.3, 13.4 Hz, 1 H, 11-H$_{ax}$), 1.38−1.86 (m, 11 H), 2.19 [dsept, *J* = 2.0, 7.0 Hz, 1 H, C*H*(CH$_3$)$_2$], 2.22 (m, 2 H), 2.60 (ddd, *J* = 13.4, 3.4, 2.2 Hz, 1 H, 11-H$_{eq}$), 3.78−4.02 (m, 4 H, 4′′-H), 4.85 (t, *J* = 4.5 Hz, 1 H, 2′′-H), 5.16 (t, *J* = 0.7 Hz, 1 H, 3-H). − ^{13}C NMR (50 MHz, CDCl$_3$): δ = 18.70 (q, *C*H$_3$), 21.68 (q, *C*H$_3$), 22.53 (t, C-8), 23.30 (t, C-3′), 23.34 (q, *C*H$_3$), 25.74 [d, *C*H(CH$_3$)$_2$], 25.83 (t, C-2′), 28.65 (d, C-10), 33.43, 33.72 (t, C-1′, C-4′), 34.22 (t, C-9), 41.15 (t, C-11), 49.63 (d, C-7), 64.90 (t, C-4′′), 92.63 (d, C-3), 104.23 (d, C-2′′), 109.76 (s, C-6), 161.18 (s, C-4), 171.66 (s, C-2). − MS (70 eV); *m/z* (%): 352 (1) [M$^+$], 267 (1), 199 (16), 154 (17), 139 (20), 112 (73), 73 (100), 69 (37). − **35 (Less Polar Product):** M.p. 73 °C. [α]$^{20}_{D}$ = −20.0 (*c* = 0.1, CHCl$_3$). − IR (KBr): ṽ = 2931 cm^{-1} (m), 2866 (w), 1721 (s, C=O), 1636 (m), 1458 (w), 1383 (m), 1310 (w), 1227 (m), 1143 (w), 1080 (m), 928 (w). − ^{1}H NMR (200 MHz, CDCl$_3$): δ = 0.88 (d, *J* = 5.9 Hz, 3 H, 10-CH$_3$), 0.89 (m, 1 H), 0.92 [d, *J* = 6.8 Hz, 3 H, C(CH$_3$)$_2$], 0.96 [d, *J* = 7.0 Hz, 3 H, CH(CH$_3$)$_2$], 0.99 (dd, *J* = 12.6, 13.2 Hz, 1 H, 11-H$_{ax}$), 1.45−1.86 (m, 11 H), 2.20 [dsept, *J* = 2.4, 7.0 Hz, 1 H, CH(CH$_3$)$_2$], 2.24 (m, 2 H, 1′-H), 2.61 (ddd, *J* = 2.1, 3.4, 13.3 Hz, 1 H, 11 H$_{eq}$), 3.43 (dd, *J* = 9.6, 10.5 Hz, 1 H, 5′′-H), 3.92−4.03 (m, 2 H), 4.87 (s, 1 H, 2′′-H$_a$), 5.02 (s, 1 H, 2′′-H$_b$), 5.17 (s, 1 H, 3-H). − MS (CI); *m/z* (%): 353 (98) [M$^+$+H], 309 (6), 199 (79), 155 (100), 112 (8).

(1*R*,5*R*,7*S*,8*S*,11*R*)-1-(1,3-Dioxolan-2-ylmethyl)-8-isopropyl-11-methyl-6,13-dioxadispiro[4.1.5.3]pentadecan-14-one (36): A solution of **32b** (138 mg, 0.47 mmol) and 300 μL of acetone in 36 mL of 1,3-dioxolane was irradiated for 2 d (procedure A). Purification by HPLC (cyclohexane/ethyl acetate, 7:3) gave **36** (24 mg, 14%) as a solid: M.p. 80 °C. [α]$^{20}_{D}$ = +13.3 (*c* = 0.5, CHCl$_3$). − IR (KBr): ṽ = 2955 cm^{-1} (m), 1737 (s), 1457 (w), 1371 (w), 1319 (m), 1234 (m), 1152 (m), 1080 (w), 1023 (w), 957 (m). − ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.77 [d, *J* = 7.0 Hz, 3 H, C(C*H*$_3$)$_2$], 0.81 (d, *J* = 6.5 Hz, 3 H, 11-C*H*$_3$), 0.84 (m$_c$, 1 H, 10-H$_a$), 0.86 [d, *J* = 7.0 Hz, 3 H, C(C*H*$_3$)$_2$], 1.14 (dddd, *J* = 13.5, 11.1, 11.1, 7.0 Hz, 1 H, 2-H$_a$), 1.16 (dd, *J* = 13.5, 12.4 Hz, 1 H, 12-H$_{ax}$), 1.33 (ddd, *J* = 12.7, 5.1, 2.0 Hz, 1 H, 8-H), 1.39 (ddd, *J* = 13.3, 11.2, 4.4 Hz, 1 H, 1′-H$_a$), 1.49 (m$_c$, 1 H, 9-H$_a$), 1.51 (m$_c$, 1 H, 9-H$_b$), 1.52 (m$_c$, 1 H, 3-H$_a$), 1.67 (m$_c$, 1 H, 11-H), 1.70 (m$_c$, 1 H, 10-H$_b$), 1.73 (m$_c$, 1 H, 3-H$_b$), 1.75 (m$_c$, 1 H, 4-H$_a$), 1.80 (ddd, *J* = 13.2, 5.5, 2.9 Hz, 1 H, 1′-H$_b$), 1.87 (ddd, *J* = 13.0, 10.5, 9.7 Hz, 1 H, 4-H$_b$), 1.94 (dddd, *J* = 17.3, 9.5, 9.5, 3.9 Hz, 1 H, 2-H$_b$), 2.06 (ddd, *J* = 13.5, 3.6, 2.1 Hz, 1 H, 12-H$_{eq}$), 2.10 (dddd, *J* = 11.4, 11.4, 8.2, 2.8 Hz, 1 H, 1-H), 2.29 [dqq, *J* = 7.0, 7.0, 2.0 Hz, 1 H, C*H*(CH$_3$)$_2$], 2.40 (d, *J* = 17.2 Hz, 1 H, 15-H$_a$), 2.50 (d, *J* = 17.2 Hz, 1 H, 15-H$_b$), 3.77 (m$_c$, 1 H), 3.78 (m$_c$, 1 H), 3.86 (m$_c$, 1 H), 3.90 (m$_c$, 1 H), 4.84 (dd, *J* = 4.5, 5.5 Hz, 1 H, 2′-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 17.76 [q, C(*C*H$_3$)$_2$], 19.98 (t, C-3), 21.28 (t, C-9), 21.10 (q, 11-*C*H$_3$), 23.64 [q, C(*C*H$_3$)$_2$], 24.38 [d, *C*H(CH$_3$)$_2$], 26.35 (t, C-2), 29.45 (d, C-11), 33.51 (t, C-1′′), 34.13 (t, C-10), 35.05 (t, C-15), 40.23 (t, C-4), 45.32 (d, C-1), 46.96 (t, C-12), 51.05 (d, C-8), 64.58, 64.94 (t, C-4′, C-5′), 82.68 (s, C-5), 103.91 (d, C-2′), 107.88 (s, C-7), 168.09 (s, C-14). − MS (CI); *m*/*z* (%): 367 (4) [M$^+$ + H], 213 (100), 195 (8), 155 (56), 73 (64). − HRMS: calcd. for $C_{21}H_{34}O_5$ 366.2406, found 366.2405.

(6*S*,7*S*,10*R*,4′*RS*)-4-(4′-Bromo-6,6,6-trichlorohexyl)-7-isopropyl-10-methyl-1,5-dioxaspiro[5.5]undec-3-en-2-one (37) and (6*S*,7*S*,10*R*,4′*RS*)-4-(4′-Bromomethyl-5,5,5-trichloropentyl)-7-isopropyl-10-methyl-1,5-dioxaspiro[5.5]undec-3-en-2-one (38): A solution of **32b** (100 mg, 0.34 mmol) in 0.5 mL of bromotrichloromethane was irradiated for 4 h (procedure A). Separation by HPLC (cyclohexane/ethyl acetate, 93:7) gave **37** (60 mg, 36%) as an oil and a mixture of **37** and **38** (7 mg, **37**/**38** = 1:1). − **37:** ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.86−1.07 (m, 1 H), 0.89/0.88 (each d, *J* = 6.4 Hz, 3 H), 0.92 (d, *J* = 6.9 Hz, 3 H), 0.96/0.97 (each d, *J* = 6.9 Hz, 3 H), 1.01/1.02 (each t, *J* = 13.1 Hz, 1 H, 11-H$_{ax}$), 1.47−2.03 (m, 8 H), 2.06−2.39 (m, 4 H), 2.60 (m$_c$, 1 H, 11-H$_{eq}$), 3.22 (dd, *J* = 5.7, 5.7 Hz, 1 H, 5′-H$_a$), 3.49 (dd, *J* = 4.8, 15.9 Hz, 1 H, 5′-H$_b$), 4.31 (m$_c$, 1 H, 4′-H), 5.18 (s, 1 H, 3-H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 18.60 (CH$_3$), 21.63 (CH$_3$), 22.24 (CH$_2$, C-8), 23.28 (CH$_3$), 23.63 (CH$_2$, C-2), 25.77 [CH, *C*H(CH)$_3$], 28.62 (CH, C-10), 32.79 (CH$_2$, C-1′), 34.11 (CH$_2$, C-9), 38.39/38.44 (CH$_2$, C-3′), 41.20 (CH, C-11), 48.04 (CH, C-4′), 49.54 (CH, C-7), 62.67 (CH$_2$, C-5′), 93.11 (CH, C-3), 96.88 (C, C-6′), 109.92 (C, C-6), 160.77 (C, C-4), 170.49 (C, C-2). − MS (CI); *m*/*z* (%): 495 (3) [M$^+$ + H], 494 (2) [M$^+$ + H], 493 (11) [M$^+$ + H], 492 (3) [M$^+$ + H], 491 (16) [M$^+$ + H], 490 (2) [M$^+$ + H], 489 (9) [M$^+$ + H], 457 (1) [M$^+$ − Cl], 375 (1) [M$^+$ − Cl − Br], 339 (3) [M$^+$ + H − menthone], 337 (5) [M$^+$ + H − menthone], 335 (3) [M$^+$ + H − menthone], 172 (15), 155 (100) [menthone + H$^+$], 112 (6), 81 (3), 69 (4). − **38 (Mixture with 37):** − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.89 (d, *J* = 6.9 Hz, 3 H), 0.90−1.08 (m, 2 H), 0.92 (d, *J* = 6.9 Hz, 3 H), 0.97 (d, *J* = 6.9 Hz, 3 H), 1.48−2.39 (m, 12 H), 2.61 (m, 1 H), 3.60 (t, *J* = 10.3 Hz, 1 H), 3.87 (dd, *J* = 4.1, 10.3 Hz, 1 H), 4.14 (m, 1 H), 5.18 (s, 1 H).

(6*S*,7*S*,10*R*)-7-Isopropyl-10-methyl-4-(6,6,6-trichlorohexyl)-15-dioxaspiro[5.5]undec-3-en-2-one (39) and (1*R*,5*R*,7*S*,8*S*,11*R*)-1-(2,2-Dichloroethyl)-8-isopropyl-11-methyl-6,13-dioxadispiro[4.1.5.3]-pentadecan-14-one (40): A solution of **37** (41 mg, 84 μmol), (36 mg, 0.12 mmol) tributyltin hydride and AIBN (4 mg, 24 μmol) in 10 mL of benzene was irradiated for 5 d [procedure A, using a water-cooled well with a high-pressure mercury lamp (HPK 125 W, Philips) as source of light]. AIBN (2 mg, 12 μmol) was added every day. The solvent was removed in vacuo and the residue was dissolved in 10 mL of wet diethyl ether. 1,8-Diazabicyclo[5.4.0]undec-7-ene (37 mg, 0.24 mmol) was added, the mixture was treated with iodine solution (0.1 M in diethyl ether) until the iodine colour just persisted, and the suspension was filtered through a short silica cloumn (diethyl ether). Purification by HPLC (cyclohexane/ethyl acetate, 4:1) gave **39** (9 mg, 26%) as an oil, a mixture of not cyclized reduction products (11 mg) and crystalline **40** (2 mg, 6%). − **39:** $[\alpha]^{20}_{D}$ = −18.0 (*c* = 0.1, CHCl$_3$). − IR (neat): ṽ = 2955 cm^{-1} (s), 2870 (m), 1732 (s, C=O), 1633 (m), 1455 (m), 1384 (s), 1309 (m), 1227 (m), 1175 (m), 1143 (m), 1079 (m), 1002 (w), 780 (m), 695 (m). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.89 (d, *J* = 5.9 Hz, 3 H, 10-C*H*$_3$), 0.90 (m, 1 H), 0.92 [d, *J* = 6.8 Hz, 3 H, C(C*H*$_3$)$_2$], 0.92 [d, *J* = 7.0 Hz, 3 H, C(C*H*$_3$)$_2$], 1.00 (dd, *J* = 13.2, 13.2 Hz, 1 H, 11-H$_{ax}$), 1.38−1.89 (m, 11 H), 2.20 [dsept, *J* = 2.4, 6.9 Hz, 1 H, C*H*(CH$_3$)$_2$], 2.26 (m, 2 H, 1′-H), 2.61 (ddd, *J* = 2.1, 3.4, 13.3 Hz, 1 H, 11-H$_{eq}$), 2.68 (m, 2 H, 5′-H), 5.18 (s, 1 H, 3-H). − MS (CI); *m*/*z* (%): 415 (18) [M$^+$ + H], 413 (52) [M$^+$ + H], 411 (53) [M$^+$ + H], 379 (3), 377 (5), 261 (2), 259 (7), 172 (16), 155 (100), 112 (5). − **40:** M.p. 108°C. − IR (KBr): ṽ = 2959 cm^{-1} (s), 2873 (m), 1734 (s, C=O), 1457 (w), 1373 (w), 1324 (s), 1281 (w), 1237 (m), 1153 (m), 970 (m), 780 (w), 746 (m). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.88 (m$_c$, 1 H), 0.88 (d, *J* = 7.0 Hz, 3 H), 0.89 (d, *J* = 6.4 Hz, 3 H), 0.94 (d, *J* = 7.0 Hz, 3 H), 1.10−1.49 (m, 6 H), 1.52−2.17 (m, 7 H), 2.30−2.56 (m, 4 H), 2.56 (s, 2 H), 5.74 (dd, *J* = 4.4, 7.7 Hz, 1 H, 2′-H). − MS (70 eV); *m*/*z* (%): 380 (0.7) [M$^+$], 378 (3.8) [M$^+$], 376 (4.4) [M$^+$], 293 (5), 291 (3), 225 (1), 223 (1), 209 (2), 207 (12), 205 (18), 155 (44), 154 (24) [menthone$^+$], 139 (26), 137 (11), 112 (100), 97 (15), 95 (22), 69 (55). − X-ray crystal structure analysis of **40**: Empirical formula $C_{19}H_{30}O_3Cl_2$, *M* = 377.33, 0.3 × 0.2 × 0.2 mm, *a* = 11.037(5), *b* = 10.997(4), *c* = 17.043(8) Å, β = 98.53(4), *V* = 2046(2) Å^3, $\rho_{calcd.}$ = 1.225 g cm^{-3}, μ = 29.56 cm^{-1}, empirical absorption correction with ψ scan data (0.976 ≤ *C* ≤ 0.999), *Z* = 4, monoclinic, space group $P2_1$ (no. 4), λ = 1.54178 Å, *T* = 223 K, ω/2θ scans, 4621 reflections collected (+*h*, +*k*, ±*l*), [(sin θ)/λ] = 0.62 Å^{-1}, 4392 independent and 2361 observed reflections [$I \geq 2\sigma(I)$], 440 refined parameters, *R* = 0.046, wR^2 = 0.094, max. residual electron density 0.19 (−0.23) e Å^{-3}, Flack parameter −0.00(2), hydrogen atoms calculated and riding.[17]

6-[2-(Bromophenyl)ethyl]-2,2-dimethyl-1,3-dioxin-4-one (41): Following the general procedure D, 10 mmol of the acetoacetate and 2-bromobenzyl bromide were allowed to react. The crude product was distilled through a Vigreux column (145−147°C/0.02 Torr) to give *tert*-butyl 5-(2-bromophenyl)-3-oxopentanoate (0.71 g, 23%): − IR (neat): ṽ = 2978 cm^{-1} (m), 1737 (s, C=O), 1715 (s, C=O), 1643 (w), 1566 (w), 1472 (m), 1368 (m), 1321 (m), 1160 (s), 1026 (m), 752 (m). − ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.45 (s, 9 H, C*H*$_3$), 2.87 (dd, *J* = 8.7, 6.6 Hz, 1 H, 4-H$_a$), 2.88 (dd, *J* = 8.0, 6.6 Hz, 1 H, 4-H$_b$), 3.03 (dd, *J* = 8.0, 6.6 Hz, 1 H, 5-H$_a$), 3.04 (dd, *J* = 8.7, 6.6 Hz, 1 H, 5-H$_b$), 3.36 (s, 2 H, 2-H), 4.92 (s, 2-H, enolic form), 7.07 (ddd, *J* = 7.7, 6.2, 3.1 Hz, 1 H, 4′-H), 7.18−7.27 (m, 2 H, 5′-H, 6′-H), 7.52 (dd, *J* = 7.7, 1.4 Hz, 1 H, 3′-H). − ^{13}C NMR (50 MHz, CDCl$_3$): δ = 27.95 (q, *C*H$_3$), 29.99 (t, C-5), 42.62 (t, C-4), 50.67 (t, C-2), 82.05 (s, *C*(CH$_3$)$_3$), 124.26 (s, C-2′), 127.56 (d, C-3′), 128.03 (d, C-5′), 130.70 (d, C-3′), 132.85 (d, C-6′), 139.95 (s, C-1′), 166.27 (s,C-1), 201.97 (s, C-3). − MS (CI); *m*/*z* (%): no M$^+$, 313 (2) [M$^+$ − CH$_3$], 311 (6) [M$^+$ − CH$_3$], 275 (41), 273 (95), 271 (100), 255 (3), 253 (4), 235 (5), 233 (14), 229 (5), 227 (5), 193 (8), 191 (16), 157 (4), 155 (3), 117 (96), 91 (81), 75 (26). − Following the general procedure C, *tert*-butyl 5-(2-bromophenyl)-3-oxopentanoate (500 mg, 1.53 mmol) and acetone (186 mg, 3.20 mmol) were allowed to react. Recrystallization of the crude product from diethyl ether/*n*-pentane gave **41** (190 mg, 38%) as a yellow solid: M.p. 63−64°C. − IR (KBr): ṽ = 3082 cm^{-1} (w), 1724 (s, C=O), 1634 (m), 1468 (w), 1446 (w), 1387 (m), 1375 (m), 1188 (m), 1032 (m), 1006 (m), 748 (m). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.69 (s, 6 H, 2-C*H*$_3$), 2.56 (m, 2 H), 2.99 (m, 2 H), 5.26 (d, *J* = 0.7 Hz, 1 H, 5-H), 7.10 (ddd, *J* = 8.0, 6.9, 2.2 Hz, 1 H, 4′-H), 7.21 (dd, *J* = 7.7, 2.2 Hz, 1 H, 6′-H), 7.26 (ddd, *J* = 7.7, 6.8, 1.3 Hz, 1 H, 5′-H), 7.55 (dd, *J* = 7.9, 1.3 Hz, 1 H, 3′-H). − ^{13}C NMR (50 MHz, CDCl$_3$): δ = 25.04 (q, 2-*C*H$_3$), 32.40, 33.49 (t, C-1′′, C-2′′), 93.69 (d, C-5), 106.48 (s, C-2), 124.27 (s, C-2′), 127.69 (d, C-4′), 128.38 (d, C-5′), 130.28 (d, C-3′), 133.05 (d, C-6′), 138.93 (s, C-1′), 161.07 (s, C-6), 170.41 (s, C-4). − MS (CI); *m*/*z* (%): 313 (99) [M$^+$ + H], 311 (100) [M$^+$ + H], 255 (11) [M$^+$ + H − acetone], 253 (11) [M$^+$

+ H − acetone], 233 (31), 175 (28), 173 (35), 99 (13). − $C_{14}H_{15}BrO_3$ (311.2): calcd. C 54.04; H 4.86; found C 54.19; H 4.87.

Spiro Compound 42 and 2,2-Dimethyl-6-phenylethyl-1,3-dioxin-4-one (43): A solution of **41** (278 mg, 0.89 mmol), tributyltin hydride (329 mg, 1.13 mmol) and AIBN (31 mg, 0.19 mmol) in 84 mL of benzene was irradiated for 3 d [procedure A, using a water-cooled well with a high-pressure mercury lamp (HPK 125 W, Philips) as source of light]. The solution was diluted with 100 mL of wet diethyl ether and treated with iodine solution (0.1 M in ether) until the iodine colour just persisted. 1,8-Diazabicyclo[5.4.0]undec-7-ene (200 mg) was added and the mixture was filtered through a short silica column (diethyl ether). Purification by HPLC (ethyl acetate/cyclohexane, 1:4) gave **42** (60 mg, 29%) as a solid, **43** (12 mg, 6%) as an oil and recovered **41** (24 mg, 8%). − **42 (Less Polar Product):** M.p. 70°C. − IR (KBr): $\tilde{\nu}$ = 2996 cm^{-1} (w), 2930 (m), 1744 (s, C=O), 1605 (w), 1316 (m), 1293 (s), 1272 (m), 1113 (m), 948 (m), 820 (w), 761 (m). − ^1H NMR (200 MHz, $CDCl_3$): δ = 1.67 (q, *J* = 0.7 Hz, 3 H, 2-C*H*$_3$), 1.70 (q, *J* = 0.7 Hz, 3 H, 2-C*H*$_3$), 2.25 (ddd, *J* = 12.9, 7.8, 4.6 Hz, 1 H, 2′-H_a), 2.45 (ddd, *J* = 12.9, 8.3, 6.8 Hz, 1 H, 2′-H_b), 2.86 (ddd, *J* = 16.1, 7.8, 6.8 Hz, 1 H, 3′-H_a), 2.89 (s, 2 H, 5-H), 3.08 (ddd, *J* = 16.1, 8.3, 4.6 Hz, 1 H, 3′-H_b), 7.21−7.36 (m, 4 H, arom. H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.93 (q, 2-*C*H_3), 29.39 (t, C-3′), 30.11 (q, 2-*C*H_3), 39.35, 41.09 (t, C-5, C-2′), 84.33 (s, C-6), 105.96 (s, C-2), 122.91, 125.03, 127.31, 129.00 (d, 4 arom. C), 141.94 (s, C-3′a), 144.86 (s, C-7′a), 167.90 (s, C-4). − MS (70 eV); *m/z* (%): 232 (7) [M^+], 217 (4), 174 (57), 157 (30), 146 (19), 133 (17), 132 (79), 131 (25), 130 (100), 129 (91), 128 (49), 127 (20), 115 (47), 104 (33), 103 (15), 91 (6), 77 (18). − $C_{14}H_{16}O_3$ (232.3): calcd. C 72.39; H 6.94; found C 73.16; H 6.72. − **43 (More Polar Product):** IR (neat): $\tilde{\nu}$ = 2922 cm^{-1} (w), 1729 (s, C=O), 1623 (m), 1390 (m), 1272 (m), 1203 (m), 1018 (m). − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.66 (s, 6 H, 2-C*H*$_3$), 2.56 (m, 2 H), 2.42 (m, 2 H), 5.22 (t, *J* = 0.7 Hz, 1 H, 5-H), 7.17−7.33 (m, 5 H, arom. H). − MS (70 eV); *m/z* (%): 232 (2) [M^+], 174 (100) [M^+ − acetone], 156 (18), 145 (21), 128 (11), 105 (35), 104 (37), 91 (38), 77 (9), 69 (23).

2-(But-3-enyl)-2-methyl-1,3-dioxin-4-one (44): To a refluxing solution of 5-hexen-2-one (4.90 g, 49.9 mmol) in 50 mL of xylol was added hydroxymethylene Meldrum's acid[39] (1.72 g, 10.0 mmol), portionwise over 15 min. The reaction was heated under reflux for further 20 min, cooled, and the solvent was removed under reduced pressure. Purification by column chromatography (cyclohexane/ethyl acetate, 3:2) gave **44** (80 mg, 5%) as a colourless oil. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.69 (s, 3 H, 2-C*H*$_3$), 2.04 (m, 2 H), 2.20−2.30 (m, 2 H), 5.00 (ddt, *J* = 10.3, 1.2 Hz, 1 H, 4′-H_a), 5.06 (ddt, *J* = 17.2, 1.7 Hz, 1 H, 4′-H_b), 5.38 (d, *J* = 6.0 Hz, 1 H, 5-H), 5.81 (ddt, *J* = 16.9, 10.3, 6.3 Hz, 1 H, 3′-H), 7.12 (d, *J* = 5.96 Hz, 1 H, 6-H). − ^{13}C NMR (75 MHz, C_6D_6): δ = 22.27 (CH_3), 27.50 (CH_2, C-2′), 37.73 (CH_2, C-1′), 97.68 (CH, C-5), 108.03 (C, C-2), 115.17 (CH_2, C-4′), 137.26 (CH, C-3′), 157.13 (CH, C-6), 158.98 (C, C-4). − MS (CI); *m/z* (%): 169 (100) [M^+ + H], 99 (52), 71 (8).

Irradiation of 44 in 1,3-Dioxolane: A solution of **44** (24 mg, 0.14 mmol) and 100 μL of acetone in 12 mL of 1,3-dioxolane was irradiated for 20 h (procedure A). The crude mixture was separated by HPLC (cyclohexane/ethyl acetate, 7:3) to give four oils: **45** (5 mg, 14%), a complex mixture (2 mg), **46a** (3 mg, 8%), and **46b** (4 mg, 12%). − **9-(1,3-Dioxolan-2-yl)-6-methyl-7,10-dioxabicyclo[4.2.2]decan-8-one (45, Less Polar Product):** IR (neat): $\tilde{\nu}$ = 2924 cm^{-1} (m), 1754 (s, C=O), 1460 (w), 1380 (m), 1277 (m), 1234 (m), 1167 (m), 1055 (m), 971 (m). − ^1H NMR (500 MHz, $CDCl_3$): δ = 1.38 (dddd, *J* = 4.9, 10.3, 11.2, 15.2 Hz, 1 H), 1.59 (s, 3 H, 6-CH_3), 1.75−1.96 (m, 4 H), 1.92 (ddd, *J* = 1.9, 4.2, 14.5 Hz, 1 H), 1.98 (ddd, *J* = 4.0, 4.9, 14.5 Hz, 1 H), 2.18 (m, 1 H, 2-H_a), 2.91 (ddd, *J* = 2.6, 2.6, 5.2 Hz, 1 H, 1-H), 3.88 (dd, *J* = 2.4, 6.5 Hz, 1 H, 9-H), 3.87−4.07 (m, 4 H, 4′-H), 5.05 (d, *J* = 6.7 Hz, 1 H, 2′-H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.74 (t), 24.63 (t), 27.83 (t), 28.39 (q, 6-CH_3), 40.42 (d, C-1), 41.80 (t), 65.25, 65.30 (t, C-4′, C-5′), 72.79 (d, C-9), 101.65 (d, C-2′), 108.47 (s, C-6), 173.99 (s, C-8). − MS (CI); *m/z* (%): 243 (100) [M^+ + H], 225 (11), 197 (5), 73 (6). − **8-(1,3-Dioxolan-2-yl)-2,5-dimethyl-6,9-dioxabicyclo[3.2.2]nonan-7-one (46a):** IR (neat): $\tilde{\nu}$ = 2984 cm^{-1} (m), 1754 (s, C=O), 1460 (w), 1384 (m), 1297 (m), 1243 (m), 1174 (m), 1154 (m), 1060 (m), 960 (m). − ^1H NMR (500 MHz, $CDCl_3$): δ = 1.01 (d, *J* = 6.8 Hz, 3 H, 2-CH_3), 1.50 (s, 3 H, 5-CH_3), 1.58 (dddd, *J* = 6.0, 11.5, 11.5, 14.5 Hz, 1 H, 3-H_a), 1.66 (ddddd, *J* = 1.0, 3.6, 5.1, 5.1, 14.5 Hz, 1 H, 3-H_b), 1.96 (ddd,, *J* = 5.2, 11.5, 15.1 Hz, 1 H, 4-H_a), 2.01 (ddd, *J* = 3.6, 6.0, 15.1 Hz, 1 H, 4-H_b), 2.10 (dqdd, *J* = 1.4, 5.3, 6.8, 11.5 Hz, 1 H, 2-H), 2.49 (dd, *J* = 1.2, 1.3 Hz, 1 H, 1-H), 3.84−3.90 (m, 2 H, 4′-H), 3.90−4.01 (m, 2 H, 4′-H), 4.29 (d, *J* = 2.8 Hz, 1 H, 8-H), 4.88 (d, *J* = 2.8 Hz, 1 H, 2′-H). − MS (CI); *m/z* (%): 243 (100) [M^+ + H], 73 (5). − **(1*R**,2*R**,5*S**,8*S**)-8-(1,3-Dioxolan-2-yl)-2,5-dimethyl-6,9-dioxabicyclo[3.2.2]nonan-7-one (46b, More Polar Product):** IR (neat): $\tilde{\nu}$ = 2963 cm^{-1} (m), 2930 (m), 1740 (s, C=O), 1464 (w), 1288 (m), 1250 (w), 1191 (w), 1152 (m), 1060 (m), 954 (m). − ^1H NMR (500 MHz, $CDCl_3$): δ = 1.07 (d, *J* = 6.8 Hz, 3 H, 2-CH_3), 1.19 (dddd, *J* = 5.1, 11.2, 12.4, 14.6 Hz, 1 H, 3-H_a), 1.53 (s, 3 H, 5-CH_3), 1.74 (ddddd,, *J* = 0.7, 4.6, 4.9, 4.9, 14.6 Hz, 1 H, 3-H_b), 1.91 (m, 1 H, 2-H), 1.93 (ddd, *J* = 4.6, 12.4, 15.1 Hz, 1 H, 4-H_a), 2.11 (ddd, *J* = 4.6, 4.6, 15.0 Hz, 1 H, 4-H_b), 2.62 (dd, *J* = 0.9, 1.1 Hz, 1 H, 1-H), 3.83−3.91 (m, 2 H, 4′-H), 3.92−4.11 (m, 2 H, 4′-H), 4.04 (d, *J* = 3.1 Hz, 1 H, 8′-H), 4.87 (d, *J* = 3.1 Hz, 1 H, 2′-H). − MS (CI); *m/z* (%): 243 (100) [M^+ + H].

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