Asymmetric Intramolecular [2 + 2] Photocycloadditions: α- and *β*-Hydroxy Acids as Chiral Tether Groups

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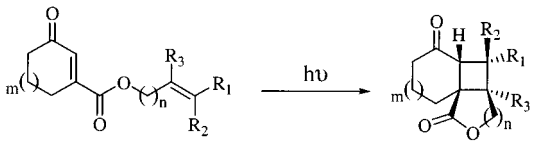
Chiral α- and *β*-hydroxy acids such as (*S*)-lactic acid, (*S*)-phenyllactic acid, (*S*)-mandelic acid, or (3*R*)-3-hydroxybutyric acid have been used as tether groups for intramolecular and diastereoselective [2 + 2] photocycloaddition of 3-oxocyclohexene carboxylic acid derivatives. Total regiocontrol toward the straight adduct and high diastereoselectivities (up to 94%) were observed in the case of butenyl lactate **11**. After separation of the two diastereoisomers, cleavage of the chiral tether under basic conditions afforded cyclobutane lactones in good yield and enantiomeric pure form. An X-ray structure has been recorded that confirmed the relative and absolute configuration of the three contiguous stereogenic centers assigned according to CD spectra.

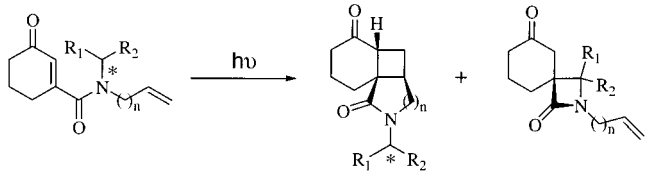
[2 + 2] photocycloaddition is one of the major photochemical reactions applied to total synthesis.[1,2] While the intermolecular processes suffer generally of a lack of regio- and/or syn/anti stereocontrol, the intramolecular reactions seem far more interesting.[3] In this context, we previously investigated intramolecular photocycloadditions starting from cycloalkenone carboxylate derivatives. This chromophoric system has been widely used for intermolecular reactions and applied to the synthesis of natural products.[4,5] Interestingly, the ester group compared to the acetal moiety has been considered as a poor linking unit[6] before our own successful investigations.[7]

Irradiation of enone derivatives connected to the alkenyl chain by a carboxylic "connector" was extremely efficient. To our delight, only one regio- and stereoisomer of the expected cyclobutane derivatives was usually detected (Scheme 1). However, some dimeric side products[7] could be observed during irradiation mainly at low temperature or under high concentration conditions.

Scheme 1



Scheme 2



With the aim to develop an asymmetric version of this process, oxoesters were first replaced by oxoamides bearing at least one chiral group on the nitrogen atom. Unfortunately, a competitive hydrogen abstraction took place leading to spiranic *β*-lactam derivatives (Scheme 2).[8] Related spiranic structures were recently reported to exhibit important biological properties such as cholesterol absorption inhibition.[9]

To avoid these hydrogen abstraction processes, we decided to turn back to oxoesters and to introduce a chiral tether group connected both to the unsaturated oxoester chromophore and to the alkenyl chain. While chiral centers present on the alkenyl side-chain have been already reported to direct efficiently diastereoselective intramolecular [2 + 2] photocycloadditions, the use of chiral removable tether groups could represent an im-

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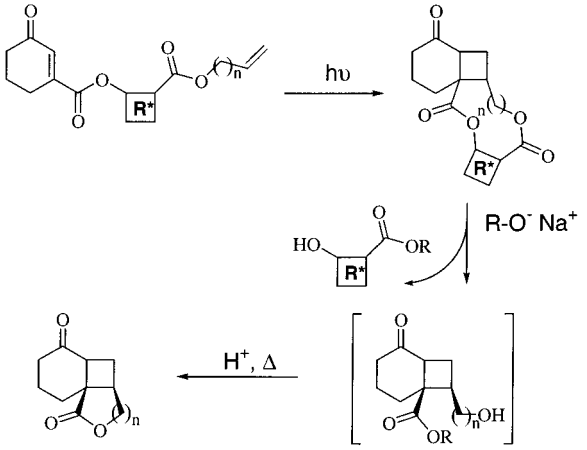
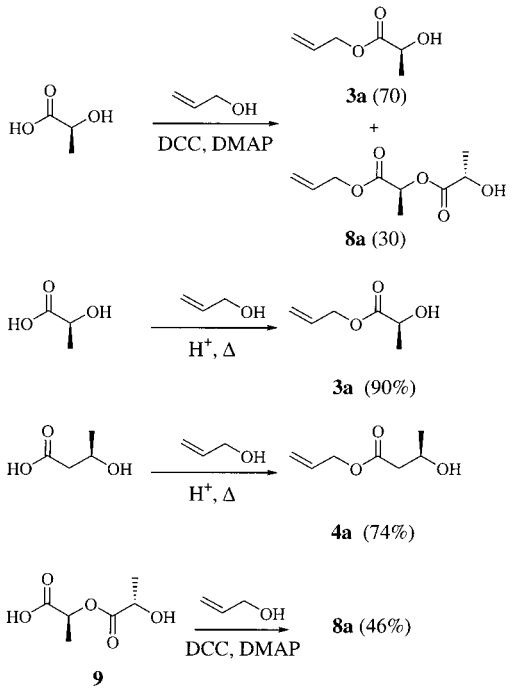
Scheme 3



provement for further applications to the synthesis of natural products.[10] For our purposes, chiral α- and *β*-hydroxy acids that are easily prepared or commercially available[11] might be interesting chiral linkers. Therefore, we first tested the use of (*S*)-lactic acid, (*S*)-phenyllactic acid, (*S*)-mandelic acid, and (3*R*)-hydroxybutyric acid as cheap reagents.[12] Due to a high conformational mobility, the intramolecular photocycloaddition of oxoesters having a long and unsubstituted alkenyl chain (Scheme 1, $n > 3$) appeared to be inefficient or without regiocontrol. The introduction of a chiral tether linked by esters groups was expected to rigidify the system[13] and to allow a conformation favorable to the overlap of the orbitals of the biradical intermediate[14] with the *π*-system of the isolated double bond. Furthermore, a chiral auxiliary bounded by two ester functionalities could not only direct a diastereoselective approach of the unsaturated chain toward the enone moiety but also be easily removed in one single step (Scheme 3).

The starting materials **10**−**19** were prepared from 3-oxocyclohexene and 3-oxocyclopentene carboxylic acids **1** and **2**[15] and unsaturated hydroxyesters **3a**−**f**, allyl (3*R*)-3-hydroxybutyrate **4a**, or allylbislactate **8a**, respectively. Allyl lactate **3a** was conveniently obtained by heating (*S*)-lactic acid **1** in pure allyl alcohol in the presence of a trace of acid.[16] Similarly, (3*R*)-allyl hydroxybutyrate **4a** was obtained directly from the biopolymer of 3-hydroxybutyric acid (PHB), in the presence of diluted sulfuric acid and allyl alcohol[17] (Scheme 4).

Scheme 4



The high cost of other unsaturated alcohols excluded their use as the solvent for the preparation of **3b**−**f**, and a more suitable and general synthetic approach was designed for these compounds (Scheme 5). Protection of methyl lactate as a silyl ether was accomplished using standard procedures.[18] Saponification of **5** by LiOH[19] produced the acid **6** esterified with 3-buten-1-ol to give **7b**, using a DCC activation.[20] The final deprotection to **3b** was carried out in the presence of *n*-Bu_4NF.[21] Finally, this procedure was extended to the preparation of compounds **3c**−**d**. Butenyl derivatives **3e** and **3f** were directly prepared from (*S*)-phenyllactic acid and (*S*)-mandelic acid by heating with 3-buten-1-ol in acetonitrile and in the presence of catalytic amount of tetracyanoethylene (TCNE) according to a procedure first described by Masaki et al.[22]

The dimeric structure **8a** was prepared as pure material from bislactic acid **9** isolated as a byproduct during distillation of polymeric lactic acid. The moderate yield for **8a** could be explained by the formation of a side product resulting from the condensation of the acid **9** and DCC as already observed with other α-hydroxy acids.[23]

Condensation of the unsaturated hydroxy esters **3a**−**f**, **8a**, and **4a** with carboxylic acid **1** and **2**, in the presence of DCC and DMAP,[20] afforded the expected substrates **10**−**19** in good yields (Scheme 6, Table 1).

When the allyl monolactate **10** was irradiated in dichloromethane, no intramolecular cycloaddition could be detected, and the head-to-tail photodimer **20** of the cyclohexenone moiety could be isolated with quite low yields (20−30%). In contrast, when the allyl bislactate **12** was irradiated under the same conditions, only two

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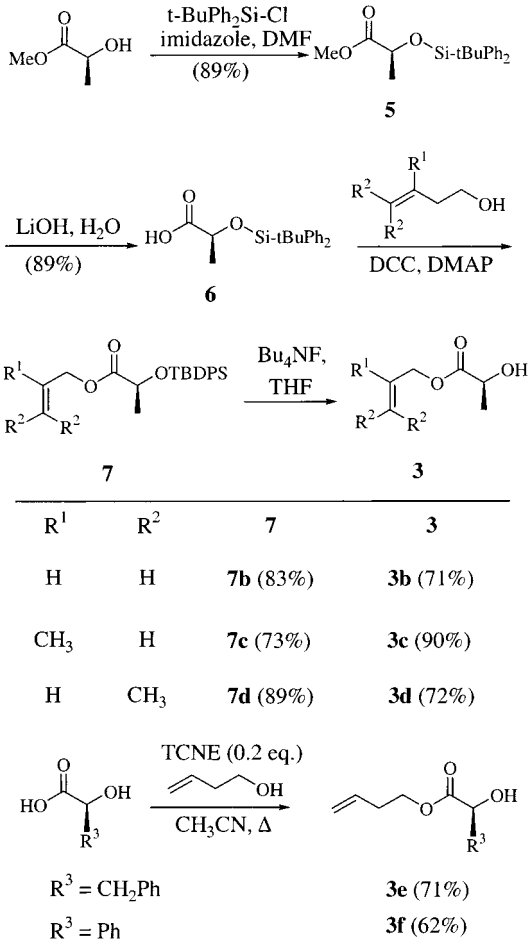
Scheme 5



R^1	R^2	7	3
H	H	**7b** (83%)	**3b** (71%)
CH_3	H	**7c** (73%)	**3c** (90%)
H	CH_3	**7d** (89%)	**3d** (72%)
$R^3 = CH_2Ph$			**3e** (71%)
$R^3 = Ph$			**3f** (62%)

cycloadducts **21** (41%) and **22** (24%) were obtained (Scheme 7).

The structures of these cycloadducts were determined thanks to their spectroscopic data. According to the mass spectrum, they both presented a parent peak at m/z = 324 indicating a $C_{16}H_{20}O_7$ molecular formula when their respective ^{1}H NMR and ^{13}C NMR spectra showed unambiguously that they are regioisomers.

For **21**, the proton that appeared at 4.45 ppm as a doublet of doublet (J = 11.2, 5.5 Hz) was identified as H_a characteristic of a straight arrangement in this kind of adducts.[7] The relative configuration on the cyclobutane ring was deduced from the lactone **23** obtained by methanolysis of **21** (Scheme 8). NOE experiments indicated a correlation between H_a and one H_d, and no relationship between H_a and H_c. Moreover, due to the high strain of the molecule, the polycyclic structures could only possess a cis/syn/cis relative arrangement around the four-membered ring.[24] For **22**, the ^{1}H NMR presents a doublet at 3.15 ppm (J = 8.7 Hz) attributed to H_a, indicating the presence of only one vicinal proton having the trans relative configuration.

To determine the absolute configuration of the three new contiguous stereogenic centers in **21**, CD spectra recorded for this compound and lactone **23** present a negative Cotton effect.[25] This negative value of the dichroic band and the application of the octant's rule indicate a (1*R*,5*R*,7*R*) configuration for **23** and determines without ambiguity the configuration of the asymmetric centers created in **21** during the cycloaddition step (Scheme 9).

This attribution is in agreement with those already described from CD spectra of cyclobutane derivatives.[26]

Scheme 6

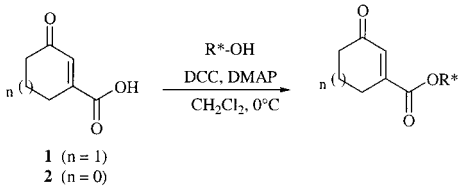
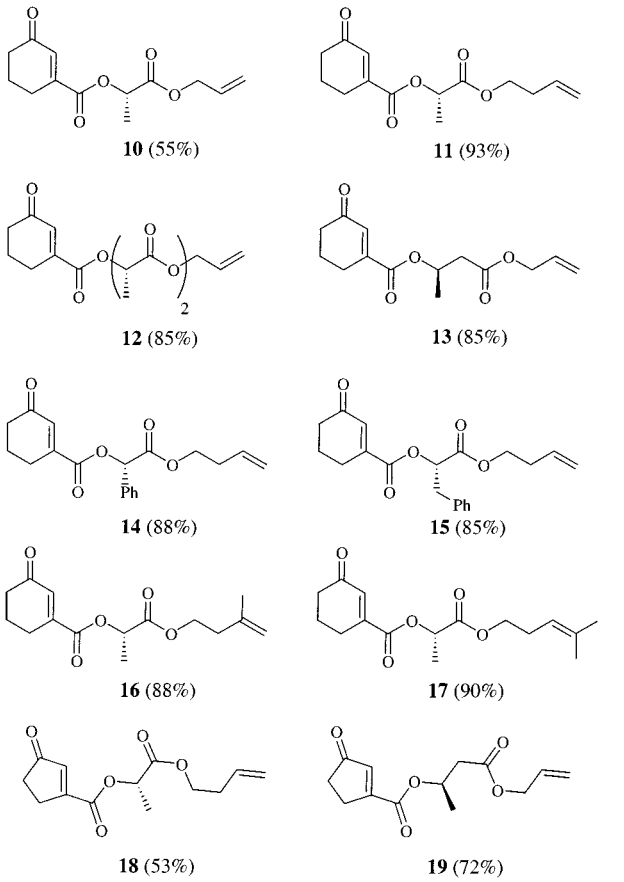
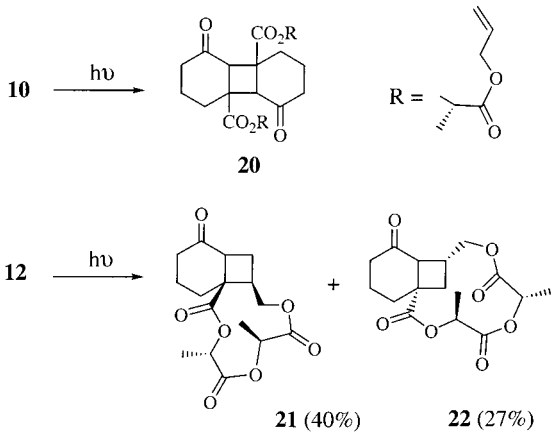


Table 1. Synthesis of Substrates 10−19



Scheme 7



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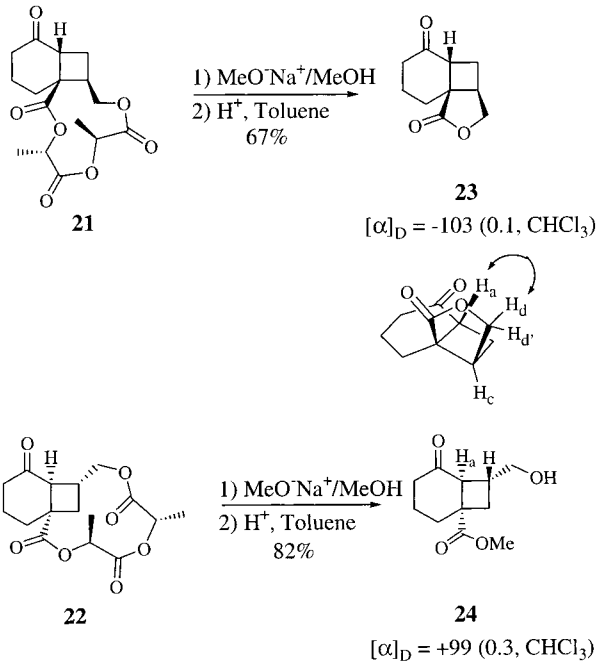
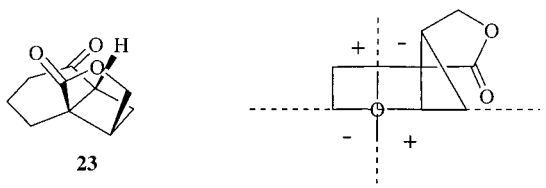
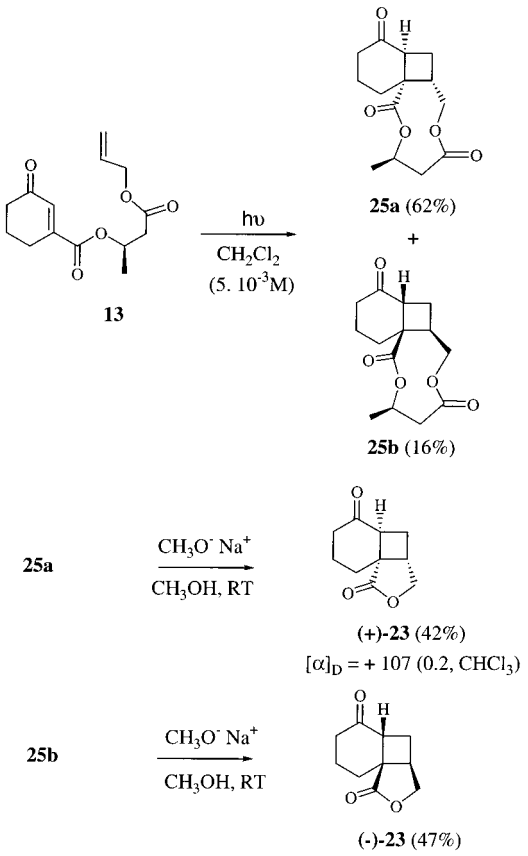
Scheme 8



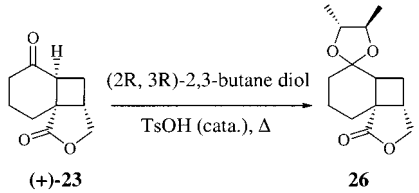
Scheme 9



Scheme 10



Scheme 11



Furthermore, we were delighted to obtain crystals of **21** for which an X-ray structure was recorded. The ORTEP representation (see the Supporting Information) shows unambiguously the relative configuration of the three stereogenic centers created after irradiation. Knowing the absolute configuration of the stereogenic centers of the tether groups, we were able to confirm the configuration determined from the CD spectra.

The absolute configuration of the adduct **21** appears to be (1*R*,4*S*,7*S*,11*R*,13*R*) and, therefore, (1*R*,5*R*,7*R*) for **23**. Similarly, the configuration of the new asymmetric centers of **22** could be elucidated using CD spectra of **22** and **24**.

Irradiation of allyl 3-hydroxybutyrate derivative **13** was next performed under similar conditions (Scheme 10). Only two cycloadducts could be isolated and identified, by NMR spectroscopy, as head-to-head regioisomers: **25a** (62%), **25b** (16%). While the regiocontrol appeared to be total, the stereochemical control was moderate (de = 64%).

Nevertheless, the two adducts **25a** and **25b**, conveniently separated, underwent methanolysis under basic conditions and led, respectively, to the two enantiomers of butyrolactone **23**. According to the study of allylbislactate adduct **14** described above, we were able to assign the configuration of the asymmetric centers and the structures for the two major isomers **25a** and **25b**. Furthermore, derivatization[27] of the keto group by a commercially available chiral 1,2-diol-like (2*R*,3*R*)-2,3-butanediol allows the determination of the enantiomeric purity of the cycloadduct (Scheme 11).

These results indicate that formation of a nine-membered ring macrolide from **13** was much more favorable than eight-membered ring derivatives from **10**. The absence of intramolecular photocycloaddition from **10** might result from conformational restrictions and a short linking unit between the cyclohexenone and ethylenic groups. Then, we turned back to the monolactate **11** bearing a butenyl chain that should deliver under irradiation macrolactone **27**, which should possess a nine-membered ring like **25**.

As expected, irradiation of ester **11** produced, in a very clean reaction and in high yield, only two stereoisomers **27a** and **27b** identified as before using ^{1}H NMR spectroscopy. The diastereoselectivity, measured by the same method on the crude mixture of the irradiation carried out in CH_2Cl_2 and at 20 °C, reached 86% for 92% chemical yield (Scheme 12). The cleavage of the tether group of the unseparable adducts **27**, in situ followed by lactonization, gave the tricyclic valerolactones **28a** and **28b**.

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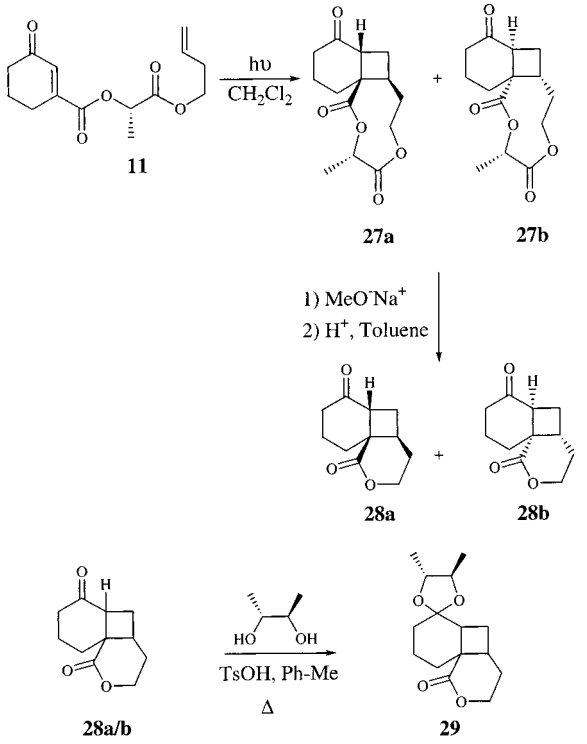
Scheme 12



Scheme 13

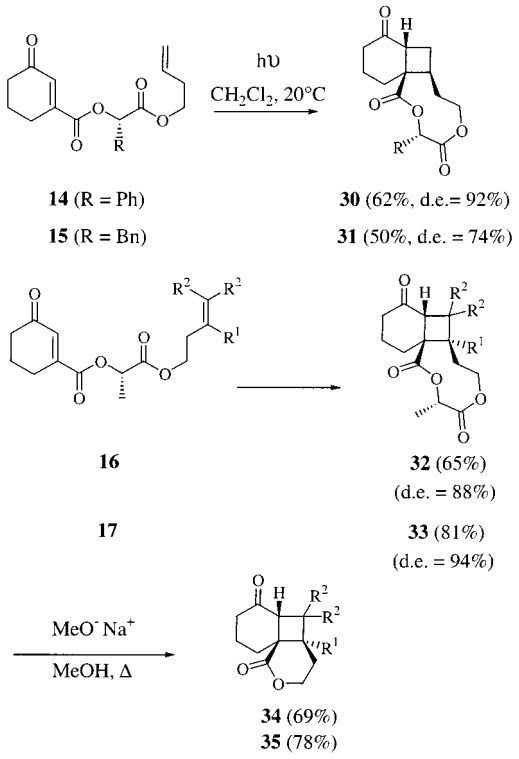


Table 2. Influence of the Temperature of Irradiation on the Diastereoselectivity for 11

T (°C)	time (h)	yield (%)	**27a**/**27b**	de[a] (%)	oligomers
20	12	92	93:7	86	−
−20	40	78	96:4	92	+
−40	50	42	97:3	94	++

[a] de determined by ^{1}H NMR (500 MHz).

The ee (88%) determined after derivatization of lactones **28** with (2*R*,3*R*)-2,3-butanediol to ketals **29a** and **29b** confirmed again that no dramatic decrease of the selectivity occurred during the removal of the chiral entity. While the relative configuration on **28** has been already assigned thanks to previous studies,[7a] the determination of the absolute configuration of the major diastereoisomer **27a** was next achieved using the same method as for bislactate adduct **21**. The sign of the Cotton effect was also negative. By using, octants' rule, the (1*R*,6*S*,8*R*) configuration was assigned to the major diastereoisomer (−)-**27a**.

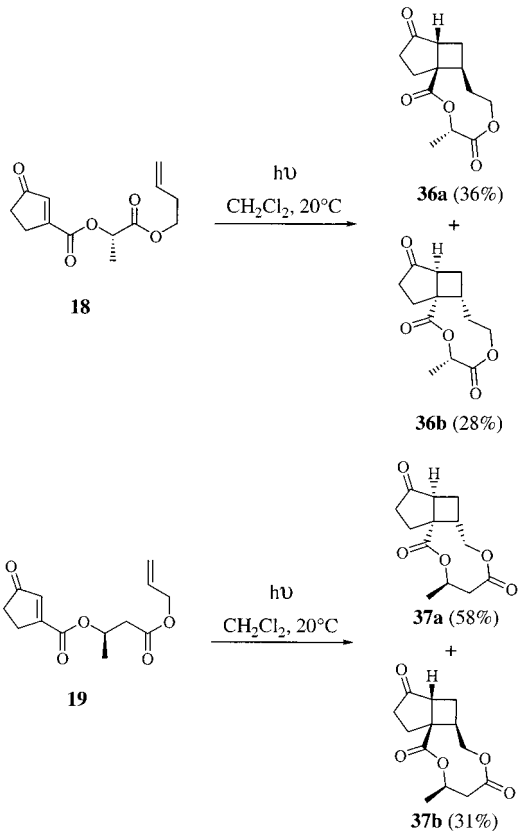
To improve the diastereoselectivity of the process, irradiations of **11** were performed at various temperatures (Table 2). We observed that a decrease of the temperature was accompanied by an increase of the selectivities. Unfortunately, the rate of the cycloaddition dramatically slowed and the diminution of the yield observed at −40 °C can be explained by the formation of some oligomer species.[7b] The range of temperature 0−20 °C appeared as a good range for obtaining **27a** with de higher than 90% together with convenient yields.

The reaction was next generalized to other substrates **14**−**19**. Changing the nature of the tether group from (*S*)-lactic acid to more bulky compounds such as (*S*)-mandelic acid or (*S*)-phenyllactic acid has no influence on the regioselectivity of the process; Irradiation of **14** and **15** at rt in methylene chloride led to the straight adducts **30** and **31** with, respectively, 92% and 74% de (Scheme 13). Therefore, an increase of the diastereoselectivity can be achieved by simply switching a methyl group with a phenyl ring on the tether moiety. Lactic derivatives **16** and **17** substituted on the alkenyl chain by alkyl groups were also irradiated and delivered cycloadducts **32** and **33** in good yields and high selectivities (88 and 94%). The tether group was conveniently removed by methanolysis to furnish new tricyclic valerolactones **34** and **35** without loss of optical purity. Finally, esters **18** and **19**, which possess a cyclopentane core, were transformed into macrocyclic lactones with still high regioselectivities but less important diastereoselectivities, 12 and 30%, respectively (Scheme 14). The exact reason for this difference between esters prepared from **1** or **2** is still unclear.

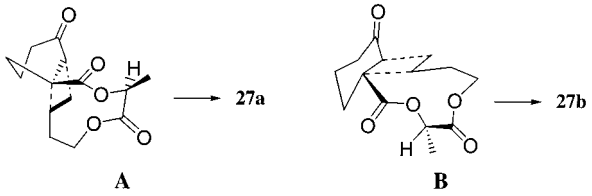
While the determination of the relative and absolute configuration of the asymmetric centers has been achieved, and in order to generalize this approach, we examined models that might explain the selective approach of the alkene moiety toward the enone part.

The tricyclic skeleton of the cycloadducts introduces steric restrictions, and the configurations of the three asymmetric centers present around the cyclobutane ring are not independent. Furthermore, we have to consider that the asymmetric induction is obtained during the first step of the photocycloaddition process. Despite the multistep nature of the cycloaddition process and the nonplanar structure of the triplet excited state of the cyclohexenone chromophore, we anticipated that the observed asymmetric induction was the result of conformational restrictions in the transition step, imposed by the carboxyl group and the methyl group on the chiral auxiliary. We present a rationale for these results, with a chiral induction obtained during an 9-*exo*-*trig* addition of the distorted cyclohexenone triplet onto the terminal alkene. In the case of the lactate tether derivative **11**, we have represented in Scheme 15 two possible diastereomeric transition states **A** and **B** for the first step of a cycloaddition process involving the formation of a nine-

Scheme 14



Scheme 15



membered ring lactone, which could lead to the major and the minor adducts, respectively. We assume that in both transition states the methyl group of the linker has to adopt a pseudoequatorial position. Then, the stereochemistry of the two major isomers might be the result of a competition between s-syn or s-trans conformations of the carboxylic connector. An s-syn conformation of the double bond of the conjugated ester and a syn conformation of the carboxylic group and the hydrogen atom fixed on the stereogenic center of the linker[28] induce the favorable transition state **A** and formation of **27a**. In contrast, formation of **27b** would require transition state **B**, having an s-trans conformation of the α,*β*-unsaturated carboxylic moiety (Scheme 15). Such an explanation is supported by previous observations from Lange's and Scharf's groups to connect the diastereoselectivities observed for intermolecular processes with the conformation of related oxoesters.[15b,29] However, it has also been pointed out that the structure of the cycloadducts can be determined by the relative rates of cyclization and fragmentation of the biradical intermediates.[14] Then, further studies would be needed to give a better understanding of the stereochemical control of such an intramolecular process.[30]

In conclusion, this study has shown the advantages of the use of α- and *β*-hydroxy acids as chiral tethers for highly diastereoselective intramolecular photocycloadditions. It should be pointed out that after our preliminary communication[12] diastereoselctive intramolecular cycloadditions directed by chiral linkers derived from amino acids appeared in the literature.[31,32] However, even if the diastereoselectivities are of the same order, these chiral moieties seem difficult to remove. In our case, enantiomerically pure tricyclic lactones could be prepared after the cleavage in one single step of the chiral auxiliary. Work is now in progress to synthesize and test other chiral hydroxy acids as tether groups, to improve the selectivities, to generalize the process to other substrates, and to apply this method to the synthesis of natural products.[33]

Experimental Section

General Methods. All manipulations with air-sensitive reagents were carried out under a dry argon atmosphere using standard Schlenk techniques. Solvents were purified according to standard procedures: THF and ether on sodium/benzophenone, methylene chloride on CaH_2. Reagents were purchased from Aldrich Chemical Co. or Acros Organics. Analytical TLC was performed using Merck SI F 254 plates. Column flash chromatography was performed by using Kieselgel 60 (230−400 mesh). The ^{1}H NMR and ^{13}C NMR spectra were recorded at 250 and 62.5 MHz, respectively, in $CDCl_3$; chemical shifts (*δ*) are given in ppm and referred to tetramethylsilane. FTIR spectra were measured with KBr plates on a spectrafile IR PLUS MIDAC.

Direct Esterification of (*S*)-Lactic Acid and (3*R*)-3-Hydroxybutyric Acid. In a 50 mL flask equipped with a cooler were placed (*S*)-lactic acid (10 g, 0.11 mol), benzene (6 mL), and 12 N sulfuric acid (0.1 mL). The mixture was heated to reflux with removal of water (Dean Stark system). Unsaturated alcohol (0.44 mol, 4 equiv) was rapidly added, and reflux was maintained for 4 h. After neutralization with sodium acetate, the ester formed was purified by distillation under reduced pressure.

Allyl lactate[34] **(3a):** liquid, 90%; ^{1}H NMR (250 MHz, $CDCl_3$) *δ* 1.40 (d, 3H, J = 6.9 Hz), 2.58 (m, 1H, OH), 4.28 (q, 1H, q, J = 6.9 Hz), 4.66 (ddd, 2H, J = 5.7, 2.6, 1.1 Hz), 5.25 (ddt, 1H, J = 10.3, 2.6, 1.1 Hz), 5.32 (ddt, 1H, J = 17.1, 3, 1.5 Hz), 5.90 (ddt, 1H, J = 17.1, 10.3, 5.7 Hz); $[\alpha]^{21}_D$ = −10 (1.38, $CHCl_3$).

(*R*)-Allyl 3-hydroxybutyrate[35] **(4a):** liquid, 74%; ^{1}H NMR (250 MHz, $CDCl_3$) *δ* 1.23 (d, 3H, J = 6.4 Hz), 2.46 (dd, 1H, J_{AB} = 16.4 Hz, J = 8.0 Hz), 2.51 (dd, 1H, J_{AB} = 16.4 Hz, J = 4.2 Hz), 2.91 (1H, sl, OH), 4.21 (ddq, 1H, J = 8.0, 4.2, 6.4 Hz), 4.61 (ddd, 2H, J = 5.7, 1.5, 1.1 Hz), 5.25 (ddt, 1H, J = 10.3, 1.5, 1.1 Hz), 5.32 (dq, 1H, J = 17.7, 1.5 Hz), 5.92 (ddt, 1H, J = 17.7, 10.3, 5.7 Hz); ^{13}C NMR (62 MHz, $CDCl_3$) *δ* 22.4, 42.7, 64.2, 65.2, 118.4, 131.8, 172.3; IR (neat) *ν* 3576, 2936, 1730, 1315, 1178 cm^{-1}; MS (EI, 70 eV) *m*/*z* 145 ($M^{\bullet+}$ + 1, 15), 129; $[\alpha]^{21}_D$ = −36 (1.08, $CHCl_3$).

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Access to lactates 3b−d. Methyl 2-[(1,1-Dimethylethyl)diphenylsilyl]oxypropanoate[36] (5). To a solution of (*S*)-methyl lactate (2.00 g, 19.2 mmol) in DMF (70 mL) were successively added *tert*-butyldiphenylsilyl chloride (28.8 mmol) and imidazole (67.2 mmol). After being stirred overnight, the mixture was diluted with brine (100 mL) and extracted with ether (5 × 50 mL). The organic layer was washed successively with a cooled aqueous 5% HCl solution and brine and dried over $MgSO_4$. After concentration under vacuum, the residue was purified by flash chromatography (hexanes/AcOEt = 97:3) to afford **5** (89%) as a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.11 (s, 9H), 1.39 (d, 3H, J = 6.8 Hz), 3.58 (s, 3H), 4.30 (q, 1H, J = 6.8 Hz), 7.30−7.50 (m, 6H), 7.60−7.75 (m, 4H); ^{13}C NMR (62 MHz, $CDCl_3$) δ 19.2, 21.2, 26.8, 51.5, 68.9, 127.5, 127.6, 129.7, 132.3, 132.9, 135.7, 135.8, 177.6; IR (neat) ν 2936, 2860, 1755, 1429, 1114 cm^{-1}; MS (EI, 70 eV) *m*/*z* 342 (M^+), 285, 213, 183, 153, 105.

2-[(1,1-Dimethylethyl)diphenylsilyl]oxypropanoic Acid[37] (6). To a solution of ester **5** (2 g, 5.8 mmol) in THF (90 mL) at 0 °C was dropwise added an ice-cooled 0.2 M solution of LiOH (11.8 mmol) in water in 20 mn. After being stirred overnight, the mixture was concentrated by half and extracted with ether (2 × 20 mL). The organic layer was washed with an aqueous saturated solution of sodium hydrogenocarbonate (20 mL). The aqueous layers were combined, carefully acidified to pH 4 with a 1 N solution of potassium hydrogenosulfate, and extracted with ether (4 × 50 mL). The ethereal phase was dried over Na_2SO_4, and the solvent was removed by concentration: solid, 89%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.15 (s, 9H), 1.39 (d, 3H, J = 6.7 Hz), 4.36 (q, 1H, J = 6.7 Hz), 7.37−7.53 (m, 6H), 7.68−7.74 (m, 4H); ^{13}C NMR (62 MHz, $CDCl_3$) δ 19.1, 21.0, 26.8, 68.9, 127.7, 127.8, 130.1, 132.3, 132.9, 135.6, 135.7, 177.6; IR (neat) ν 3072, 1730, 1429, 1240, 1103 cm^{-1}; MS (EI, 70 eV) *m*/*z* 271 (31), 200 (20), 199 (100), 139 (38); HMRS calcd. for $C_{19}H_{25}O_3Si$ ($M^{\bullet+}$ + 1) 329.15729, found 329.15725.

3-Butenyl 2-[(1,1-Dimethylethyl)diphenylsilyl]oxypropanoate (7b). In a two-necked flask, acid **6** (1.64 g, 5 mmol) and DMAP (0.610 g, 5 mmol) were added to a solution of 3-butenol (0.360 g, 5 mmol) in dichloromethane (5 mL). The mixture was flushed with argon, and after cooling with an external ice−water bath, a solution of DCC (1.03 g, 5 mmol) in the same solvent (2 mL) was dropwise added. The external bath was removed and the solution stirred overnight at rt. After filtration and wash of the urea with dichloromethane, the resulting solution was concentrated and purified by flash hromatography on silica (hexanes/AcOEt 10/90) giving **7b** (1.591 g, 4.1 mmol) as an oil: 83%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.13 (s, 9H), 1.39 (d, 3H, J = 6.9 Hz), 2.30 (dq, 2H, J = 6.87, 1.3 Hz), 4.05 (dt, 2H, J = 6.9, 3.9 Hz), 4.32 (q, 1H, J = 6.9 Hz), 5.03−5.12 (m, 2H), 5.73 (ddt, 1H, J = 17.1, 10.3, 6.9 Hz), 7.35−7.50 (m, 6H); 7.68−7.76 (m, 4H); ^{13}C NMR (62 MHz, $CDCl_3$) δ 19.2, 21.3, 26.8, 32.9, 63.5, 68.9, 117.1, 127.5, 127.6, 129.7, 133.2, 133.5, 133.8, 135.7, 135.8, 173.6; IR (neat) ν 2922, 2860, 1755, 1429, 1114 cm^{-1}; MS (EI, 70 eV) *m*/*z* 382 ($M^{\bullet+}$), 325, 297, 271, 253, 199, 181, 139, 123, 105; $[\alpha]^{21}_D$ = −47.6 (1.1, CH_2Cl_2).

(3-Methyl)-3-butenyl 2-[(1,1-Dimethylethyl)diphenylsilyl]oxypropanoate (7c). Same procedure as for **7b** using 3-methyl-3-butenol instead of 3-butenol: 73%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.10 (s, 9H), 1.36 (d, 3H, J = 6.9 Hz), 1.71 (s, 3H), 2.23 (t, 2H, J = 6.9 Hz), 4.04 (dt, 1H, J_{AB} = 10.7 Hz, J = 6.9 Hz), 4.14 (dt, 1H, J_{AB} = 10.7 Hz, J = 6.9 Hz), 4.27 (q, 1H, J = 6.9 Hz), 4.66 (sl, 1H), 4.76 (sl, 1H), 7.33−7.50 (m, 6H), 7.65−7.72 (m, 4H); ^{13}C NMR (62 MHz, $CDCl_3$) δ 19.2, 21.2, 22.3, 26.8, 36.4, 62.6, 68.9, 112.2, 127.5, 127.6, 129.7, 133.2, 133.5, 135.7, 135.8, 141.3, 173.6; IR (neat) ν 2922, 2860, 1755, 1140, 1105 cm^{-1}; MS (EI, 70 eV) *m*/*z* 397 ($M^{\bullet+}$ + 1, 4), 271, 199, 181, 139; $[\alpha]^{21}_D$ = −42 (0.4, $CHCl_3$). Anal. Calcd for $C_{24}H_{32}O_3Si$: C, 72.68; H, 8.13. Found: C, 72.59; H, 8.45.

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(4-Methyl)-3-pentenyl 2-[(1,1-Dimethylethyl)diphenylsilyl]oxypropanoate (7d). Same procedure as for **7b** using 4-methyl-3-pentenol[35] instead of 3-butenol: 89%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.11 (s, 9H), 1.38 (d, 3H, J = 6.9 Hz), 1.60 (s, 3H), 1.69 (d, 3H, J = 1.1 Hz), 2.23 (q, 2H, J = 7.2 Hz), 3.91 (dt, 1H, J = 10.7, 7.2 Hz), 4.00 (dt, 1H, J = 10.3, 7.2 Hz), 4.29 (q, 1H, J = 6.9 Hz), 5.04 (t, 1H, J = 7.2 Hz), 7.30−7.50 (m, 6H), 7.60−7.75 (m, 4H); ^{13}C NMR (62 MHz, $CDCl_3$) δ 17.7, 19.2, 21.3, 25.7, 26.8, 27.4, 64.2, 68.9, 119.1, 127.5, 127.6, 129.7, 129.9, 133.2, 135.7, 135.9, 173.7; IR (neat) ν 2922, 2850, 1755, 1430, 1140 cm^{-1}; $[\alpha]^{21}_D$ = −37 (1.1, $CHCl_3$). Anal. Calcd for $C_{25}H_{34}O_3Si$: C, 73.12; H, 8.34. Found: C, 73.24; H, 8.54.

(*S*)-3-Butenyl Lactate (3b). Tetrabutylammonium fluoride (2.09 g, 8 mmol) was added at once and at 0 °C to a solution of ester **7b** (1.54 g, 4 mmol) dissolved in THF (50 mL). After 1.5 h stirring at rt, the mixture was diluted with brine (25 mL) and extracted with ether. The organic layer was washed with a 5% HCl aqueous solution and then dried over $MgSO_4$. After removal of the solvents, the crude product was purified by flash chromatography on silica (hexanes/AcOEt 70/30) giving **3b** (0.822 g, 5.7 mmol) as a liquid: 71%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.41 (d, 3H, J = 6.9 Hz), 2.30−2.50 (m, 2H), 3.61 (m, OH), 4.15−4.40 (m, 3H), 5.00−5.20 (m, 2H), 5.77 (ddt, 1H, J = 17.1, 10.3, 6.9 Hz); ^{13}C NMR (62 MHz, $CDCl_3$) δ 20.2, 32.9, 64.4, 66.7, 117.5, 133.3, 177.9; IR (neat) ν 3460, 2978, 1738, 1269, 1211, 1126 cm^{-1}; $[\alpha]^{21}_D$ = −11.7 (0.65, $CHCl_3$).

(*S*)-(3-Methyl)-3-butenyl Lactate (3c). Same procedure as above starting from **7c**: 90%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.38 (d, 3H, J = 6.9 Hz), 1.74 (s, 3H), 2.35 (t, 2H, J = 6.8 Hz), 2.80 (s, 1H), 4.23 (dt, 1H, J_{AB} = 11.1 Hz, J = 6.8 Hz), 4.24 (d, 1H, J = 6.9 Hz), 4.33 (dt, 1H, J_{AB} = 11.1 Hz, J = 6.8 Hz), 4.72 (s, 1H), 4.80 (s, 1H); ^{13}C NMR (62 MHz, $CDCl_3$) δ 20.3, 22.2, 36.5, 63.4, 66.6, 112.5, 141.0, 175.6; IR (neat) ν 3440, 2990, 2935, 1745, 1455, 1265, 1215, 1130, 1055, 890 cm^{-1}.

(*S*)-(4-Methyl)-3-pentenyl Lactate (3d). Same procedure as above starting from **7d**: 72%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.40 (d, 3H, J = 6.9 Hz), 1.63 (s, 3H), 1.71 (d, 3H, J = 1.1 Hz), 2.35 (q, 2H, J = 7.25 Hz), 2.73 (s, 1H), 4.10 (dt, 1H, J_{AB} = 10.7 Hz, J = 6.9 Hz), 4.19 (dt, 1H, J_{AB} = 10.7 Hz, J = 6.9 Hz), 4.26 (q, 1H, J = 6.9 Hz), 5.08 (t, 1H, J = 7.2 Hz); ^{13}C NMR (62 MHz, $CDCl_3$) δ 17.7, 20.3, 25.6, 27.4, 65.1, 66.6, 118.6, 134.9, 175.7; IR (neat) ν 3450, 2985, 2920, 1730, 1455, 1380, 1265, 1215, 1130 cm^{-1}; MS (EI, 70 eV) *m*/*z* 173 ($M^{\bullet+}$ + 1, 8), 129, 119, 116. Anal. Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.36. Found: C, 63.07; H, 9.84.

Esterification Initiated with Tetracyanoethylene (TCNE). (*S*)-3-Butenyl Phenyllactate (3e). A solution of phenyllactic acid (1.01 g, 6.6 mmol) and 3-butenol (0.61 g, 8.5 mmol) dissolved in methylene chloride (10 mL) was heated at 50 °C in the presence of TCNE (0.169 g, 1.3 mmol). After 3 days, the solvent was removed under reduced pressure and the mixture purified by flash chromatography (AcOEt/hexanes 20/80) to give **3e** as an oil (0.976 g, 4.4 mmol): oil, 67%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.39 (dt, 2H, J = 6.8, 6.6 Hz), 2.71 (d, 1H, J = 6.1 Hz), 2.95 (dd, 1H, J_{AB} = 14.1 Hz, J = 6.8 Hz), 3.11 (dd, 1H, J_{AB} = 14.4 Hz, J = 4.6 Hz), 4.21 (t, 2H, J = 6.8 Hz), 4.43 (ddd, 1H, J = 6.8, 6.1, 4.6 Hz), 5.12 (m, 2H), 5.75 (ddt, 1H, J = 17.1, 10.3, 6.6 Hz), 7.18−7.38−7 (m, 5H); ^{13}C NMR (62 MHz, $CDCl_3$) δ 32.8, 40.5, 64.5, 71.1, 117.5, 126.8, 128.3, 129.4, 133.4, 136.3, 174.0; IR (neat) ν 3455, 2945, 1735, 1454, 1271, 1095 cm^{-1}; MS (EI, 70 eV) *m*/*z* 220 ($M^{\bullet+}$, 31), 202, 148, 131, 121, 103; $[\alpha]^{21}_D$ = −15 (0.9, $CHCl_3$). Anal. Calcd for $C_9H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 70.85; H, 6.97.

(*S*)-3-Butenyl Mandelate (3f). Same procedure as above using mandelic acid (1.0 g, 6.6 mmol): oil, 62%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.33 (tdd, 2H, J = 6.9, 6.5, 1.4 Hz), 3.52 (s, 1H), 4.21 (t, 2H, J = 6.9 Hz), 4.98 (d, 1H, J = 17 Hz), 4.99 (d, 1H, J = 10.7 Hz), 5.17 (s, 1H), 5.64 (ddt, 1H, J = 17.0, 10.7, 6.9 Hz), 7.25−7.55 (m, 5H); ^{13}C NMR (62 MHz, $CDCl_3$) δ 32.8, 64.9, 72.8, 117.5, 126.4, 128.3, 128.4, 133.1, 138.3, 173.5; IR (neat) ν 3425, 2985, 1750, 1720, 1625, 1375, 1255, 1215, 1160, 1080 cm^{-1}; MS (EI, 70 eV) *m*/*z* 206 ($M^{\bullet+}$, 8), 131, 105. $[\alpha]^{21}_D$ = +176 (0.4, $CHCl_3$). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.74; H, 7.28.

Allyl Bislactate (8a). Prepared from bis lactic acid and allyl alcohol using the DCC activation as described above for **7b**: liquid, 46%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.48 (d, 3H, J = 6.9 Hz), 1.54 (d, 3H, J = 7.1 Hz), 2.79 (sl, 1H, OH), 4.35 (dq, 1H, J = 6.9, 5.9 Hz), 4.64 (dt, 2H, J = 5.7, 1.5 Hz), 5.21 (q, 1H, J = 7.1 Hz), 5.26 (ddt, 1H, J = 10.3, 1.4, 1.3 Hz), 5.33 (ddt, 1H, J = 17.1, 1.4, 1.5 Hz), 5.98 (ddt, 1H, J = 17.1, 10.3, 5.7 Hz); ^{13}C NMR (62 MHz, $CDCl_3$) δ 16.8, 20.4, 65.9, 66.7, 69.3, 118.8, 131.3, 169.8, 175.0; IR (neat) ν 3487, 1742, 1655, 1454, 1203, 1128, 1089, 978 cm^{-1}; MS (EI, 70 eV) m/z 204 (M^+), 145, 131, 114; $[\alpha]^{25}_D$ = −38 (1.04, $CHCl_3$). Anal. Calcd for $C_9H_{14}O_5$: C, 53.50; H, 7.00. Found: C, 53.10; H, 7.30.

(1*S*)-1-(1-Allyloxycarbonyl)ethyl 3-Oxocyclohex-1-enecarboxylate (10). Prepared by condensation of 3-oxocyclohex-1-enecarboxylic acid with **3a** according to a protocol similar to that for the formation of **7b**: oil, 55%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.57 (d, 3H, J = 6.9 Hz), 2.07 (q, 2H, J = 6.1 Hz), 2.46 (t, 2H, J = 6.1 Hz), 2.61 (td, 2H, J = 6.1, 1.9 Hz), 4.65 (dt, 2H, J = 5.7, 1.1 Hz), 5.22 (q, 1H, J = 6.9 Hz); 5.31 (2H, m); 5.90 (1H, ddt, J = 17.1, 10.3, 5.7 Hz); 6.82 (1H, t, J = 1.9 Hz); ^{13}C NMR (62 MHz, $CDCl_3$) δ 16.7, 21.9, 24.6, 37.5, 65.8, 69.4, 118.6, 131.3, 133.5, 147.9, 165.7, 169.7, 199.6; IR (neat) ν 2957, 2853, 1720, 1684, 1456, 1375, 1251, 1223, 1186, 1097, 1047, 966, 922, 731 cm^{-1}; MS (EI, 70 eV) m/z 253 (M^+ + 1), 167, 123; UV (CH_2Cl_2) λ_{max} (ϵ) 238 (12340), 355 (30); $[\alpha]^{25}_D$ = +11.3 (c 1.18, $CHCl_3$). Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.89; H, 6.39. Found: C, 61.71; H, 6.53.

(1*S*)-1-(1-But-3-enyloxycarbonyl)ethyl 3-Oxocyclohex-1-enecarboxylate (11). Prepared by condensation of 3-oxocyclohex-1-enecarboxylic acid with **3b** according to a protocol similar to that for the formation of **7b**: oil, 93%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.55 (d, 3H, J = 7.0 Hz), 2.08 (tt, 2H, J = 6.5, 6.0 Hz), 2.41 (qt, 2H, J = 6.6, 1.2 Hz), 2.47 (t, 2H, J = 6.5 Hz), 2.61 (td, 2H, J = 6.0, 1.8 Hz), 4.14−4.30 (m, 2H), 5.05−5.16 (m, 2H), 5.19 (q, 1H, J = 7.0 Hz), 5.76 (ddt, 1H, J = 17.1, 10.3, 6.7 Hz), 6.82 (t, 1H, J = 1.8 Hz); ^{13}C NMR (62 MHz, $CDCl_3$) δ 16.9, 22.1, 24.7, 32.9, 64.4, 69.6, 117.5, 133.5, 133.6, 148.0, 165.8, 170.1, 199.8; IR (neat) ν 2947, 1755, 1730, 1693, 1454, 1253, 1228, 1203, 1103, 914, 738 cm^{-1}; MS (EI, 70 eV) m/z 267 ($M^{\bullet+}$ + 1), 212, 195, 167, 148, 123, 112; $[\alpha]^{25}_D$ = +6 (c 0.99, $CHCl_3$). Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.14; H, 6.81. Found: C, 63.21; H, 6.91.

(1*S*)-[1-(1-Allyloxycarbonyl)-1-(1*S*)-ethyloxycarbonyl]-ethyl 3-Oxocyclohex-1-enecarboxylate (12). Prepared by condensation of 3-oxocyclohex-1-enecarboxylic acid with **8a** according to a protocol similar to that for the formation of **7b**: oil, 85%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.55 (d, 3H, J = 7.2 Hz), 1.64 (d, 3H, J = 6.8 Hz), 2.07 (tt, 2H, J = 7.2, 6.1 Hz), 2.47 (t, 2H, J = 7.2 Hz), 2.61 (dt, 2H, J = 6.1, 1.9 Hz), 4.64 (dt, 2H, J = 5.7, 1.5 Hz), 5.20 (q, 1H, J = 7.2 Hz), 5.24 (1H, q, J = 6.8 Hz), 5.27 (1H, dt, 1H, J = 10.3, 1.1 Hz), 5.33 (ddt, 1H, J = 17.1, 1.5, 1.1 Hz), 5.90 (ddt, 1H, J = 17.1, 10.3, 5.7 Hz), 6.83 (t, 1H, J = 1.9 Hz); ^{13}C NMR (62 MHz, $CDCl_3$) δ 16.7, 16.8, 22.1, 24.7, 37.6, 65.9, 69.3, 69.4, 118.9, 131.3, 133.7 147.9, 165.9, 169.6, 169.7, 199.7; IR (neat) ν 2997, 1755, 1680, 1454, 1379, 1190, 1103, 964 cm^{-1}; MS (EI, 70 eV) m/z 325 ($M^{\bullet+}$ + 1), 268, 195, 178, 167, 123; $[\alpha]^{25}_D$ = −11.5 (c 0.12, $CHCl_3$). Anal. Calcd for $C_{16}H_{20}O_7$: C, 59.25; H, 6.21. Found: C, 59.46; H, 6.41.

(1*R*)-1-(2-Allyloxycarbonyl-1-methyl)ethyl 3-Oxocyclohex-1-enecarboxylate (13). Prepared by condensation of 3-oxocyclohex-1-enecarboxylic acid with **4a** according to a protocol similar that for to the formation of **7b**: oil, 85%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.37 (d, 3H, J = 6.5 Hz), 2.04 (tt, 2H, J = 6.5, 6.1 Hz), 2.43 (2H, t, J = 6.1 Hz), 2.55 (dt, 2H, J = 6.5, 1.9 Hz), 2.60 (dd, 1H, J = 15.6, 5.3 Hz), 2.72 (dd, 1H, J = 15.6, 7.6 Hz), 4.57 (dt, 2H, J = 5.7, 1.5 Hz), 5.22 (ddt, 1H, J = 10.3, 1.5, 1.1 Hz), 5.30 (ddt, 1H, J = 17.1, 1.5, 1.4 Hz), 5.40 (ddq, 1H, J = 7.6, 6.5, 5.3 Hz), 5.88 (ddt, 1H, J = 17.1, 10.3, 6.1 Hz), 6.69 (t, 1H, J = 1.9 Hz); ^{13}C NMR (62 MHz, $CDCl_3$) δ 19.6, 21.9, 24.6, 37.5, 40.4, 65.3, 68.6, 118.5, 131.7, 132.9, 148.8, 165.9, 169.4, 199.9; IR (neat) ν 2941, 1735, 1724, 1685, 1246, 1070, 995 cm^{-1}; MS (EI, 70 eV) m/z 267 (M^+ + 1), 178, 124, 123, 112; UV (CH_2Cl_2) λ_{max} (ϵ) 239 (14 100), 358 (30); $[\alpha]^{21}_D$ = −31 (c 1.1, $CHCl_3$). Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.14; H, 6.81. Found: C, 62.91; H, 7.10.

1-(1*S*)-(1-Butenyloxycarbonyl-1-phenyl)methyl 3-Oxocyclohex-1-enecarboxylate (14). Prepared by condensation of 3-oxocyclohex-1-enecarboxylic acid with **3f** according to a protocol similar that for to the formation of **7b**: oil, 88%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.09 (tt, 2 H, J = 6.9, 6.1 Hz), 2.54 (q, 2 H, J = 6.5 Hz), 2.49 (t, 2 H, J = 6.9 Hz), 2.66 (td, 2 H, J = 6.1, 1.5 Hz), 4.20 (t, 2 H, J = 6.7 Hz), 4.92−5.05 (m, 3 H), 5.66 (ddt, 1 H, J = 16.8, 10, 6.9 Hz), 6.89 (t, 1 H, J = 1.5 Hz), 7.35−7.53 (m, 5 H); ^{13}C NMR (62 MHz, $CDCl_3$) δ 22.0, 24.6, 32.7, 37.6, 64.7, 75.2, 117.4, 127.4, 128.7, 129.3, 133.1, 133.2, 133.8, 147.8, 165.7, 168.1, 199.7; IR (neat) ν 3071, 2954, 1752, 1726, 1686, 1497, 1455, 1224, 1180, 1078, 1046, 965, 916, 740, 697 cm^{-1}; MS (70 eV) m/z 328 ($M^{\bullet+}$, 12), 316, 256, 124, 123, 105; $[\alpha]^{21}_D$ = +82 (c = 1.10, $CHCl_3$). Anal. Calcd for $C_{19}H_{20}O_5$: C, 69.49; H, 6.13. Found: C, 69.38; H, 6.42.

1-(1*S*)-(1-But-3-enyloxycarbonyl-1-phenyl)ethyl 3-Oxocyclohex-1-enecarboxylate (15). Prepared by condensation of 3-oxocyclohex-1-enecarboxylic acid with **3e** according to a protocol similar to that for the formation of **7b**: oil, 85%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.04 (quint, 2 H, J = 6.1 Hz), 2.36 (dq, 2 H, J = 1.1, 6.7 Hz), 2.44 (t, 2 H, J = 6.1 Hz), 2.53 (t, 2 H, J = 6.1 Hz), 3.13 (dd, 1 H, J_{AB} = 14.3 Hz, J = 8.6 Hz), 3.26 (dd, 1 H, J_{AB} = 14.3 Hz, J = 4.4 Hz), 4.19 (t, 2 H, J = 6.7 Hz), 5.08 (m, 2 H), 5.29 (dd, 1 H, J = 8.6, 4.4 Hz), 5.71 (ddt, 1 H, J = 17.1, 10.3, 6.7 Hz), 6.74 (s, 1 H), 7.15−7.35 (m, 5 H); ^{13}C NMR (62 MHz, $CDCl_3$) δ 21.9, 24.6, 32.7, 37.3, 37.5, 64.7, 73.9, 117.4, 127.1, 128.5, 129.2, 133.4, 133.5, 135.5, 147.7, 165.5, 168.9, 199.6; IR (neat) ν 3070, 3030, 2951, 1753, 1726, 1686, 1454, 1247, 1218, 1186, 1083, 964, 916, 740, 701 cm^{-1}; MS (70 eV) m/z 343 ($M^{\bullet+}$ + 1, 22), 202 (54), 148 (100), 131 (91), 123 (73), 103 (46); $[\alpha]^{21}_D$ = −46.6 (c = 0.96, $CHCl_3$). Anal. Calcd for $C_{20}H_{22}O_5$: C, 70.15; H, 6.48. Found: C, 70.40; H, 6.97.

1-(1*S*)-[1-(3-Methyl)but-3-enyloxycarbonyl]ethyl 3-oxocyclohex-1-enecarboxylate (16). Prepared by condensation of 3-oxocyclohex-1-enecarboxylic acid with **3c** according to a protocol similar to that for the formation of **7b**: oil, 88%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.54 (d, 3H, J = 7.2 Hz), 1.74 (s, 3H), 2.07 (tt, 2H, J = 6.9, 6.1 Hz), 2.35 (dd, 2H, J = 6.9, 6.7 Hz), 2.46 (t, 2H, J = 6.9 Hz), 2.60 (td, 2H, J = 6.1, 1.9 Hz), 4.22 (dt, 1H, J_{AB} = 11.1 Hz, J = 6.7 Hz), 4.33 (dt, 1H, J_{AB} = 11.1 Hz, J = 6.9 Hz), 4.72 (s, 1H), 4.80 (s, 1H), 5.17 (q, 1H, J = 7.2 Hz), 6.81 (t, 1H, J = 1.9 Hz); ^{13}C NMR (62 MHz, $CDCl_3$) δ 16.8, 22.0, 22.2, 24.7, 36.5, 37.6, 63.4, 69.6, 112.5, 133.6, 141.1, 148.0, 165.8, 170.1, 199.9; IR (neat) ν 2960, 1730, 1695, 1455, 1315, 1555, 1205, 1100, 965, 900 cm^{-1}; MS (70 eV) m/z 280 ($M^{\bullet+}$, 14), 213, 123; $[\alpha]^{21}_D$ = +1.1 (c = 0.5, $CHCl_3$); HMRS calcd for $C_{15}H_{20}O_2$ 280.13107, found 280.13130.

1-(1*S*)-[1-(4-Methyl)pent-3-enyloxycarbonyl]ethyl 3-Oxocyclohex-1-enecarboxylate (17). Prepared by condensation of 3-oxocyclohex-1-enecarboxylic acid with **3d** according to a protocol similar to that for the formation of **7b**: oil, 90%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.54 (d, 3H, J = 7.0 Hz), 1.62 (s, 3H), 1.69 (d, 3H, J = 0.8 Hz), 2.07 (m, 2H), 2.33 (td, 2H, J = 6.9, 7.2 Hz), 2.46 (t, 2H, J = 6.9 Hz), 2.61 (td, 2H, J = 6.1, 1.9 Hz), 4.08 (dt, 1H, J_{AB} = 10.7 Hz, J = 6.9 Hz), 4.17 (dt, 1H, J_{AB} = 10.7 Hz, J = 7.2 Hz), 5.06 (tt, 1H, J = 7.5, 1.5 Hz), 5.18 (q, 1H, J = 7.0 Hz), 6.81 (t, 1H, J = 1.9 Hz); ^{13}C NMR (62 MHz, $CDCl_3$) δ 16.8, 17.7, 22.0, 24.6, 25.6, 27.4, 37.6, 65.0, 69.5, 118.7, 133.5, 134.8, 148.0, 165.7, 170.0, 199.8; IR (neat) ν 2960, 2885, 1730, 1680, 1455, 1215, 1090, 965, 740 cm^{-1}; MS (70 eV) m/z 294 ($M^{\bullet+}$, 28), 260, 213, 143, 123, 112; $[\alpha]^{21}_D$ = +9 (c = 1.3, $CHCl_3$). Anal. Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53. Found: C, 64.89; H, 7.68.

1-(1*S*)-(1-But-3-enyloxycarbonyl-1-phenyl)ethyl 3-Oxocyclopent-1-enecarboxylate (18). Prepared by condensation of 3-oxocyclopent-1-enecarboxylic acid with **3b** according to a protocol similar to that for the formation of **7b**: oil, 53%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.58 (d, 3H, J = 6.8 Hz), 2.41 (dddt, 2H, J = 6.7, 1.5, 1.1, 6.5 Hz), 2.54 (m, 2H), 2.88 (dt, 2H, J = 2.3, 4.6 Hz), 5.05−5.16 (m, 2H), 5.23 (q, 1H, J = 6.8 Hz), 5.76 (ddt, 1H, J = 17.1, 10.3, 6.7 Hz), 6.83 (t, 1H, J = 2 Hz); ^{13}C NMR (62 MHz, $CDCl_3$) δ 16.7, 27.2, 32.8, 35.4, 60.1, 64.3, 69.5, 117.4, 133.3, 138.7, 162.8, 163.5, 208.5; IR (neat) ν 2950, 1730,

1275, 1205, 1130 cm^{-1}; MS (70 eV) *m/z* 252 ($M^{\bullet+}$, 11), 224, 199, 153, 109; UV (CH_2Cl_2) λ_{max} (ϵ) 235 (13 700), 339 (30); $[\alpha]^{21}_D$ = +2.4 (*c* = 1.0, $CHCl_3$).

1-(1*R*)-(2-Allyloxycarbonyl-1-methyl)ethyl 3-Oxocyclopent-1-enecarboxylate (19). Prepared by condensation of 3-oxocyclopent-1-enecarboxylic acid with **4a** according to a protocol similar to that for the formation of **7b**: oil, 72%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.40 (d, 3 H, *J* = 6.5 Hz), 2.52 (m, 2 H), 2.64 (dd, 1 H, *J* = 15.6, 5.7 Hz), 2.75 (dd, 1 H, *J* = 15.6, 7.2 Hz), 2.83 (dt, 2 H, *J* = 2.3, 4.6 Hz), 4.59 (dt, 2 H, *J* = 5.7, 1.1 Hz), 5.20−5.36 (m, 2 H), 5.45 (ddq, 1 H, *J* = 6.5, 5.7, 7.2 Hz), 5.89 (ddt, 1 H, *J* = 17.1, 10.3, 5.7 Hz), 6.72 (t, 1 H, *J* = 2 Hz); ^{13}C NMR (62 MHz, $CDCl_3$) δ 19.7, 27.3, 35.4, 40.5, 65.3, 68.7, 118.5, 131.7, 138.1, 163.4, 164.0, 169.4, 208.8; IR (neat) ν 2985, 2936, 1727, 1612, 1439, 1280, 1250, 1219, 1185, 1060, 990, 741 cm^{-1}; MS (70 eV) *m/z* 252 ($M^{\bullet+}$, 2), 195, 127, 126, 109; $[\alpha]^{21}_D$ = −31.3 (*c* = 0.3, $CHCl_3$). Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.89; H, 6.39. Found: C, 61.68; H, 6.57.

Irradiation of Oxoesters. Typical Procedure. Ester **12** (0.324 g, 1 mmol) dissolved in methylene chloride (200 mL) was poured into Pyrex tubes that were deoxygenated with an argon stream, fitted with septa, and placed around a HPW 125 Philips lamp. The solution was irradiated at rt until complete disappearance of the starting material. The solvent was removed by concentration and the crude product purified by flash chromatography (AcOEt/hexanes 30/70).

(1*R*,4*S*,7*S*,11*R*,13*R*)-4,7-Dimethyl-3,6,9-trioxatricyclo[11.4.0^{1,13}.0^{1,11}]heptadeca-2,5,8,14-tetraone (21): solid, 40%; mp = 151 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.53 (d, 3H, *J* = 7.2 Hz), 1.58 (d, 3H, *J* = 6.8 Hz), 1.65−2.20 (m, 4H), 2.25−2.50 (m, 3H), 2.55−2.70 (m, 2H), 3.66 (t, 1H, *J* = 10 Hz), 3.96 (dd, 1H, J_{AB} = 11.2 Hz, *J* = 12.4 Hz), 4.45 (dd, 1H, J_{AB} = 11.2 Hz, *J* = 5.5 Hz), 5.12 (q, 1H, *J* = 6.8 Hz), 5.40 (q, 1H, *J* = 7.2 Hz); ^{13}C NMR (62 MHz, $CDCl_3$) δ 15.4, 16.1, 20.8, 23.1, 29.3, 37.8, 41.3, 42.5, 49.1, 63.7, 69.8, 71.3, 168.9, 172.6, 210.7; IR (neat) ν 2961, 2885, 1743, 1705, 1454, 1265, 1078 cm^{-1}; MS (EI, 70 eV) *m/z* 324 ($M^{\bullet+}$), 181, 135, 123; UV (CH_2Cl_2) λ_{max} (ϵ) 240 (100), 297 (25); $[\alpha]^{21}_D$ = −146 (*c* 0.36, $CHCl_3$). Anal. Calcd for $C_{16}H_{20}O_7$: C, 59.25; H, 6.21. Found: C, 59.20; H, 6.34.

(1*S*,4*S*,7*S*,11*S*,12*S*)-4,7-Dimethyl-3,6,9-trioxatricyclo[9.5.1.0^{1,12}]heptadeca-2,5,8,13-tetraone (22): solid, 27%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.53 (d, 3H, *J* = 7.2 Hz), 1.54 (d, 3H, *J* = 6.8 Hz), 1.70−2.25 (m, 4H), 2.26−2.65 (m, 3H), 3.42 (d, 1H, *J* = 2.7 Hz), 4.06 (d, 1H, J_{AB} = 11.1 Hz), 4.30 (dd, 1H, J_{AB} = 11.1 Hz, *J* = 2.3 Hz), 4.96 (q, 1H, *J* = 7.2 Hz), 5.27 (q, 1H, *J* = 6.8 Hz); ^{13}C NMR (62 MHz, $CDCl_3$) δ 15.9, 16.8, 20.0, 30.8, 31.3, 34.1, 40.0, 45.6, 48.0, 66.8, 69.8, 71.8, 169.2, 169.9, 176.5, 212.4; IR (neat) ν 2947, 2872, 1755, 1705, 1454, 1265, 1190, 1078 cm^{-1}; MS (EI, 70 eV) *m/z* 324 ($M^{\bullet+}$), 181, 135, 123; HMRS calcd for $C_{16}H_{21}O_7$ ($M^{\bullet+}$ + 1) 325.12872, found 325.12883; $[\alpha]^{21}_D$ = +33 (*c* 0.36, $CHCl_3$).

Procedures for the Cleavage of the Tether Group. Procedure A. Cycloadduct **21** (0.100 g, 0.31 mmol) was dissolved in methanol (3 mL) in a 5 mL flask. Sodium methylate (0.054 g, 1 mmol) was introduced at once, and the resulting mixture was stirred for 4 h. The solvent was next removed by concentration, and the crude product was dissolved in methylene chloride and acidified with an aqueous 1 N HCl solution. The aqueous solution was extracted with dichloromethane, and the combined organic layers were dried over $MgSO_4$ and concentrated. The crude mixture was purified by flash chromatography on silica (AcOEt/hexanes 30/70).

Procedure B. Adduct **22** (0.081 g, 0.25 mmol) was first cleaved following procedure A. The crude mixture obtained after extraction was dissolved in toluene and heated under reflux in the presence of a catalytic amount of (−)-camphorsulfonic acid and by using a Dean−Stark apparatus. After the mixture was heated for 4 h, toluene was distilled and the crude material purified by flash chromatography on silica (AcOEt/hexanes 30/70).

10-Oxatricyclo[6.3.0^{1,6}.0^{1,8}]undeca-5,11-dione (23). Cleavage of **21** according to procedure A: solid, 67%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.60−2.10 (m, 3H), 2.10−2.60 (m, 5H), 2.83 (dd, 1H, *J* = 4.0, 10.0 Hz), 2.94 (tq, 1H, *J* = 1.1, 7.0 Hz), 4.14 (dd, 1H, *J* = 1.1, 9.5 Hz), 4.30 (dd, 1H, *J* = 6.0, 9.5 Hz); ^{13}C NMR (62 MHz, $CDCl_3$) δ 22.2, 27.1, 27.4, 36.9, 40.4, 44.9, 51.1, 71.8, 180.6, 210.7; IR (neat) ν 3022, 1768, 1705, 1228, 1153 cm^{-1}; MS (EI, 70 eV) *m/z* 180 ($M^{\bullet+}$), 152, 136, 121, 118, 107; HMRS calcd for $C_{10}H_{12}O_3$ ($M^{\bullet+}$) 180.07864, found 180.07862; $[\alpha]^{21}_D$ = −103 (*c* 0.16, $CHCl_3$).

Methyl 7-Hydroxymethyl-5-oxabicyclo[4.2.0^{1,6}]octanecarboxylate (24). Cleavage of **22** according to procedure B: liquid, 82%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.60−1.80 (OH, m), 1.75−2.15 (m, 4H), 2.15−2.30 (m, 2H), 2.35−2.50 (m, 2H), 2.56 (ddt, 1H, *J* = 8.7, 6.1, 2.6 Hz), 3.15 (d, 1H, *J* = 8.7 Hz), 3.67 (d, 2H, *J* = 6.1 Hz); ^{13}C NMR (62 MHz, $CDCl_3$) δ 20.5, 30.8, 31.7, 36.7, 38.4, 44.4, 49.4, 52.2, 65.5, 175.9, 211.7; IR (neat) ν 3474, 3022, 2947, 1730, 1693, 1454, 1228 cm^{-1}; MS (EI, 70 eV) *m/z* 212 ($M^{\bullet+}$), 182, 164, 155, 135, 123, 95, 79; HMRS calcd for $C_{11}H_{16}O_4$ ($M^{\bullet+}$) 212.10486, found 212.10485; $[\alpha]^{21}_D$ = +99 (*c* 0.31, $CHCl_3$).

(1*S*,4*R*,9*S*,11*S*)-4-Methyl-3,7-dioxatricyclo[9.4.0^{1,11}.0^{1,9}]pentadeca-2,6,12-trione (25a): solid, 62%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.38 (d, 3H, *J* = 6.5 Hz), 1.85−2.48 (m, 9H), 2.63−2.75 (m, 1H), 2.78 (dd, 1H, J_{AB} = 11.4 Hz, *J* = 6.1 Hz), 3.47 (dd, 1H, *J* = 6.1, 9.9 Hz), 4.06 (dd, 1H, J_{AB} = 12.2 Hz, *J* = 6.9 Hz), 4.33 (dd, 1H, J_{AB} = 12.2 Hz, *J* = 4.6 Hz), 5.36 (tq, 1H, *J* = 6.5, 6.1 Hz); ^{13}C NMR (62 MHz, $CDCl_3$) δ 19.8, 21.1, 23.7, 28.7, 39.1, 42.0, 43.2, 52.6, 65.6, 67.4, 171.1, 173.9, 211.9; IR (neat) ν 2986, 2936, 2860, 1730, 1693, 1454, 1354, 1253, 1190, 1064 cm^{-1}; MS (EI, 70 eV) *m/z* 266 ($M^{\bullet+}$), 198, 180, 162, 152, 135, 124, 112, 107; $[\alpha]^{21}_D$ = +130 (*c* 0.21, $CHCl_3$). Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.14; H, 6.81. Found: C, 63.04; H, 6.93.

(1*R*,4*R*,9*R*,11*R*)-4-Methyl-3,7-dioxatricyclo[9.4.0^{1,11}.0^{1,9}]pentadeca-2,6,12-trione (25b): solid, 16%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.43 (d, 3H, *J* = 6.5 Hz), 1.80−2.20 (m, 4H), 2.25−2.70 (m, 7H), 3.65 (dd, 1H, *J* = 11.4, 7.2 Hz), 3.88 (dd, 1H, J_{AB} = 11.8 Hz, *J* = 1.5 Hz), 4.56 (dd, 1H, J_{AB} = 11.8 Hz, *J* = 3.0 Hz), 5.48 (ddq, 1H, *J* = 6.5, 6.1, 2.7 Hz); ^{13}C NMR (62 MHz, $CDCl_3$) δ 20.2, 20.3, 24.4, 31.0, 38.7, 40.8, 42.9, 43.7, 51.3, 65.9, 68.4, 170.8, 174.8, 212.4; IR (neat) ν 2936, 2885, 1743, 1705, 1454, 1253, 1178, 989 cm^{-1}; MS (EI, 70 eV) *m/z* 266 ($M^{\bullet+}$), 180, 140, 135, 124, 107; $[\alpha]^{21}_D$ = −150 (*c* 0.20, $CHCl_3$).

Ketal 26. A solution of lactone **23** (0.114 g, 0.63 mmol) and (2*R*,3*R*)-2,3-butane diol in toluene (5 mL) was heated in the presence of a catalytic amount of *p*-toluenesulfonic acid under reflux for 4 h using a Dean−Stark apparatus. The solvent was removed by concentration under vacuo. The crude product was purified by flash chromatography on silica (AcOEt/hexanes 20/80) (0.148 g, 0.59 mmol): 92%; ^{1}H NMR (500 MHz, $CDCl_3$) (major diastereoisomer) δ 1.21 (d, 3H, *J* = 6.0 Hz), 1.27 (d, 3H, *J* = 6.0 Hz), 1.50−1.60 (m, 2H), 1.60−1.87 (m, 4H), 1.94 (ddd, 1H, *J* = 12.2, 8.2, 6.8 Hz), 2.37 (ddd, 1H, *J* = 11.8, 8.2, 3.4 Hz), 2.47 (dd, 1H, *J* = 8.2, 3.4 Hz), 2.98 (dt, 1H, *J* = 13.6, 6.8 Hz), 3.56 (dq, 1H, *J* = 8.5, 6.0 Hz), 3.69 (dq, 1H, *J* = 8.5, 6.0 Hz), 4.14 (dd, 1H, J_{AB} = 9.5 Hz, *J* = 1.0 Hz), 4.24 (dd, 1H, J_{AB} = 9.5 Hz, *J* = 5.7 Hz); ^{1}H NMR (500 MHz, $CDCl_3$) (minor diastereoisomer) δ (characteristic signal) 3.06 (dt, 1H, *J* = 13.6, 6.8 Hz); ^{13}C NMR (62 MHz, $CDCl_3$) δ = 16.3, 17.2, 19.5, 25.1, 33.0, 37.9, 42.9, 49.0, 71.6, 78.4, 78.7, 107.4, 182.5; IR (neat) ν 2972, 2936, 1768, 1379, 1165, 1090 cm^{-1}; MS (EI, 70 eV) *m/z* 252 ($M^{\bullet+}$, 33), 224 (29), 127 (100).

(1*R*,4*S*,9*S*,11*R*)-4-Methyl-3,6-dioxatricyclo[9.4.0^{1,11}.0^{1,9}]pentadeca-2,5,12-trione (27a): ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.51 (d, 3H, *J* = 6.9 Hz), 1.70−2.50 (m, 10H), 2.50−2.67 (m, 1H), 3.55 (dd, 1H, *J* = 11.0, 7.2 Hz), 3.79 (ddd, 1H, J_{AB} = 11.0, *J* = 12.2, 3.4 Hz), 4.77 (ddd, 1H, J_{AB} = 11.0 Hz, *J* = 5.0, 1.5 Hz), 5.21 (q, 1H, *J* = 6.8 Hz); ^{13}C NMR (62 MHz, $CDCl_3$) δ = 15.3, 21.1, 28.0, 28.8, 31.4, 38.3, 42.1, 42.9, 52.8, 64.9, 74.5, 171.5, 176.1, 211.6; IR (neat) ν 2947, 1755, 1718, 1466, 1253, 1053 cm^{-1}; MS (EI, 70 eV) *m/z* 266 ($M^{\bullet+}$, 18), 238 (21), 148 (55), 110 (24); $[\alpha]^{21}_D$ = −232 (0.41, $CHCl_3$).

(1*S*,4*S*,9*R*,11*S*)-4-Methyl-3,6-dioxatricyclo[9.4.0^{1,11}.0^{1,9}]pentadeca-2,5,12-trione (27b): ^{1}H NMR (250 MHz, $CDCl_3$) (characteristic signal) δ 4.58 (ddd, 1H, J_{AB} = 11.0 Hz, *J* = 5.0, 1.5 Hz).

(1*R*,6*S*,8*R*)-3-Oxatricyclo[6.4.0^{1,6}.0^{1,8}]-2,9-dodecadione (28): 88%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.73−1.87 (m, 2H),

1.93−2.25 (m, 3H), 3.13 (dd, 1H, J = 11.0, 6.6 Hz), 4.29 (ddd, 1H, J_{AB} = 11.4 Hz, J = 8.8, 2.9 Hz), 4.48 (ddd, 1H, J_{AB} = 11.4 Hz, J = 6.1, 3.4 Hz); ^{13}C NMR (62 MHz, $CDCl_3$) δ 20.1, 27.6, 28.9, 31.4, 35.3, 38.8, 45.0, 46.6, 67.3, 175.3, 211.1; IR (neat) ν 2936, 2872, 1718, 1265, 1293, 1153, 1064 cm^{-1}. Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.03; H, 7.27. Found: C, 68.11; H, 7.58.

Ketal (29). Prepared using the same protocol than **26**, from (2*R*,3*R*)-2,3-butanediol and **28a**/**28b**: ^{1}H NMR (250 MHz, $CDCl_3$) major adduct: δ 1.20 (d, 3H, J = 5.6 Hz), 1.21 (d, 3H, J = 5.4 Hz), 1.52 (ddd, 1H, J_{AB} = 14.2 Hz, J = 11.4, 4.2 Hz), 1.70−1.90 (m, 5H), 1.95 (m, 1H), 2.03 (m, 1H), 2.16 (d, 1H, J_{AB} = 14.2 Hz), 2.30−2.40 (m, 2H), 2.64 (dd, 1H, J = 9.2, 8.6 Hz), 3.53 (dq, 1H, J = 8.2, 6.0 Hz), 3.61 (dq, 1H, J = 8.2, 6.0 Hz), 4.29 (ddd, 1H, J_{AB} = 11.0 Hz, J = 7.1, 3.4 Hz), 4.54 (ddd, 1H, J_{AB} = 11.0 Hz, J = 7.9, 2.9 Hz); ^{1}H NMR (250 MHz, $CDCl_3$) minor adduct (characteristic signal): δ 2.57 (dd, 1H, J = 9.2, 8.6 Hz); ^{13}C NMR (62 MHz, $CDCl_3$) major adduct: δ 16.8, 16.9, 19.8, 25.2, 28.3, 30.8, 32.7, 36.0, 42.0, 43.7, 67.3, 78.0, 78.1, 107.3, 174.9; IR (neat) ν 2922, 2860, 1718, 1454, 1265, 1178, 1089 cm^{-1}; MS (EI, 70 eV) m/z 266 ($M^{\bullet+}$, 14), 149 (16), 141 (25), 127 (100).

(1*R*,4*S*,9*S*,11*R*)-4-Phenyl-3,6-dioxatricyclo[9.4.0^{1,11}.0^{1,9}]-pentadecane-2,5,12-trione (30): solid, 62%; ^{1}H NMR ($CDCl_3$) δ 1.49 (d, 1 H, J = 15.2 Hz), 1.80−2.20 (m, 4 H), 2.20−2.65 (m, 5 H), 2.67−2.80 (m, 1 H), 3.60 (dd, 1 H, J = 11.2, 8.2 Hz), 3.74 (ddd, 1 H, J_{AB} = 11.2 Hz, J = 12.2, 3.2 Hz), 4.89 (dd, 1 H, J_{AB} = 11.2 Hz, J = 5.0 Hz), 6.07 (s, 1 H), 7.39−7.41 (m, 3 H,), 7.50−7.55 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.0, 28.2, 29.9, 31.6, 38.2, 42.0, 43.0, 52.9, 65.4, 79.9, 126.9, 128.8, 129.4, 132.1, 169.3, 175.7, 211.4; IR (neat) ν 2947, 2860, 1743, 1705, 1454, 1228, 1103, 1028, 702 cm^{-1}; MS (70 eV) m/z 328 ($M^{+\bullet}$, 17), 222, 195, 178, 150, 123, 118, 105; $[\alpha]^{21}_D$ = −141 (c = 0.97, $CHCl_3$). Anal. Calcd for $C_{19}H_{20}O_5$: C, 69.49; H, 6.13. Found: C, 69.70; H, 6.07.

(1*R*,4*S*,9*S*,11*R*)-4-Benzyl-3,6-dioxatricyclo[9.4.0^{1,11}.0^{1,9}]-pentadecane-2,5,12-trione (31): solid, 50%; ^{1}H NMR ($CDCl_3$) δ 1.50−2.55 (m, 11 H), 3.05 (d, 2 H, J = 6.7 Hz), 3.41 (dd, 1 H, J = 11.2, 7.8 Hz), 3.64 (td, 1 H, J_{AB} = 11.4 Hz, J = 11.4, 3.0 Hz), 4.72 (dd, 1 H, J_{AB} = 11.4 Hz, J = 4.0 Hz), 5.22 (t, 1 H, J = 6.7 Hz), 7.10−7.30 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 20.8, 28.0, 28.8, 31.5, 36.2, 38.2, 42.1, 42.7, 52.8, 65.3, 78.9, 127.1, 128.5, 129.2, 135.5, 170.5, 176.1, 211.9; MS (70 eV) m/z 342 ($M^{\bullet+}$, 14), 148, 131. Anal. Calcd for $C_{20}H_{22}O_5$: C, 70.15; H, 6.48. Found: C, 69.88; H, 6.82.

(1*R*,4*S*,9*S*,11*R*)-4,9-Dimethyl-3,6-dioxatricyclo-[9.4.0.^{1,11}.0^{1,9}]tetradecane-2,5,12-trione (32): solid, 65%; ^{1}H NMR ($CDCl_3$) δ 1.29 (s, 3H), 1.51 (s, 3H), 1.60−1.80 (m, 1H), 1.96 (td, 1H, J = 13.0, 3.3 Hz), 1.98 (t, 2H, J = 10.8 Hz), 2.05−2.15 (m, 1H), 2.10 (t, 1H, J = 11.0 Hz), 2.30−2.42 (m, 2H), 2.50−2.60 (m, 2H), 3.57 (t, 1H, J = 10.4 Hz), 3.93 (ddd, 1H, J_{AB} = 12.0 Hz, J = 12.2, 3.9 Hz), 4.74 (dd, 1H, J_{AB} = 12.0 Hz, J = 6.0 Hz), 5.14 (q, 1H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 15.3, 19.7, 21.4, 24.4, 36.6, 37.3, 38.2, 69.6, 112.5, 133.6, 141.1, 148.0, 165.8, 170.1, 199.9; IR (neat) ν 2980, 2870, 1755, 1720, 1465, 1380, 1240, 1140, 1105, 1065 cm^{-1}; MS (70 eV) m/z 280 ($M^{\bullet+}$, 17), 213, 209, 163, 135, 123, 107; $[\alpha]^{21}_D$ = −156 (c 0.9, $CHCl_3$). Anal. Calcd for $C_{15}H_{20}O_5$: C, 69.27; H, 7.19. Found: C, 64.26; H, 7.31.

(1*R*,4*S*,9*R*,11*R*)-4,10,10-Trimethyl-3,6-dioxatricyclo-[9.4.0^{1,9}.0^{1,11}]pentadecane-2.5 12-trione (33): oil, 81%; ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 3H), 1.15 (s, 3H), 1.38 (dd, 1H, J = 15.4, 1.2 Hz), 1.51 (d, 3H, J = 7.0 Hz), 1.71 (m, 1H), 1.80−2.20 (m, 3H), 2.25−2.40 (m, 3H), 2.72 (ddd, 1H, J = 14.2, 7.4, 2.8 Hz), 3.16 (s, 1H), 3.69 (ddd, 1H, J_{AB} = 11.0 Hz, J = 13.0, 2.5 Hz), 4.89 (ddd, 1H, J_{AB} = 11.0 Hz, J = 4.6, 1.0 Hz), 5.17 (q, 1H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 15.6, 20.3, 25.6, 26.7, 27.3, 30.2, 38.6, 40.1, 49.3, 53.1, 53.3, 65.7, 74.7, 172.0, 177.5, 210.7; IR (neat) ν 2960, 2895, 1755, 1695, 1455, 1240, 1055 cm^{-1}; MS (70 eV) m/z 294 ($M^{\bullet+}$, 28), 222, 213, 176, 149, 135, 123, 111, 107; $[\alpha]^{21}_D$ = −232 (c 0.9, $CHCl_3$). Anal. Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53. Found: C, 65.53; H, 7.81.

(1*R*,6*S*,8*R*)-6-Methyl-3-oxatricyclo[6.4.0^{1,6}.0^{1,8}]dodecane-2,9-dione (34): solid, 69%; ^{1}H NMR ($CDCl_3$) δ 1.13 (s, 3H), 1.74 (ddd, 1H, J = 14.5, 6.8, 3.1 Hz), 1.80−2.40 (m, 7H), 2.07 (dd, 1H, J = 12.5, 8.1 Hz), 2.17 (dd, 1H, J = 12.5, 10.5 Hz), 3.07 (dd, 1H, J = 10.5, 8.1 Hz), 4.26 (ddd, 1H, J_{AB} = 11.6 Hz, J = 8.1, 3.1 Hz), 4.42 (ddd, 1H, J_{AB} = 11.6 Hz, J = 6.8, 3.2 Hz); ^{13}C NMR ($CDCl_3$) δ 21.0, 23.1, 25.7, 35.3, 37.4, 38.3, 38.6, 42.8, 49.2, 66.2, 175.4, 211.5; IR (neat) ν 2935, 2875, 1730, 1695, 1455, 1405, 1265, 1190, 1065 cm^{-1}; MS (70 eV) m/z 208 ($M^{\bullet+}$, 14), 190, 149, 139, 135, 126, 123, 109; $[\alpha]^{21}_D$ = −89 (c 0.9, $CHCl_3$). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.19; H, 7.75. Found: C, 69.03; H, 7.91.

(1*R*,6*S*,8*R*)-7,7-Dimethyl-3-oxatricyclo[6.4.0^{1,6}.0^{1,8}]dodecane-2,9-dione (35): solid, 78%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.05 (s, 3H), 1.14 (s, 3H), 1.86−2.06 (m, 5H), 2.13 (m, 1H), 2.29 (ddd, 1H, J_{AB} = 18.0 Hz, J = 9.5, 5.3 Hz), 2.41 (ddd, 1H, J_{AB} = 18.0 Hz, J = 5.6, 5.1 Hz), 2.53 (t, 1H, J = 9.5 Hz), 2.88 (s, 1H), 4.19 (ddd, 1H, J_{AB} = 11.0 Hz, J = 2.0, 12.1 Hz), 4.46 (ddd, 1H, J_{AB} = 11.0 Hz, J = 3.9, 2.6 Hz); ^{13}C NMR ($CDCl_3$) δ 18.9, 23.8, 26.7, 32.1, 38.2, 40.0, 41.0, 45.3, 55.9, 67.5, 176.9, 209.4; IR (neat) ν 2960, 2895, 1730, 1680, 1480, 1390, 1205, 1055, 980 cm^{-1}; MS (70 eV) m/z 222 ($M^{\bullet+}$, 25), 194, 179, 167, 149, 137, 124, 118, 111, 107; $[\alpha]^{21}_D$ = −63 (c 0.9, $CHCl_3$). Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.36; H, 8.21.

(1*S*,4*S*,9*S*,11*R*)-4-Methyl-3,6-dioxatricyclo[9.3.0^{1,11}.0^{1,9}]-tetradecane-2,5,12-trione (36a): solid, 36%; ^{1}H NMR ($CDCl_3$) δ 1.67 (d, 3H, J = 6.9 Hz), 1.70−1.90 (m, 1H), 1.90−2.55 (m, 6H), 2.65−2.90 (m, 2H), 3.14 (dd, 1H, J = 11.2, 4.4 Hz), 4.19 (ddd, 1H, J_{AB} = 11.4 Hz, J = 7.2, 4.2 Hz), 4.53 (ddd, 1H, J_{AB} = 11.4 Hz, J = 6.5, 4.6 Hz), 5.00 (q, 1H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 16.1, 25.8, 29.9, 33.1, 37.3, 42.9, 44.1, 55.1, 63.8, 74.9, 171.1, 176.5, 218.6; IR (neat) ν = 2922, 2850, 1743, 1440, 1280, 1165, 1055 cm^{-1}; MS (70 eV) m/z 252 ($M^{\bullet+}$, 22), 224, 109; $[\alpha]^{21}_D$ = +197 (c = 0.3, $CHCl_3$).

(1*R*,4*S*,9*R*,11*S*)-4-Methyl-3,6-dioxatricyclo[9.3.0^{1,11}.0^{1,9}]-tetradecane-2,5,12-trione (36b): solid, 28%; ^{1}H NMR ($CDCl_3$) δ 1.67 (d, 3H, J = 6.9 Hz), 1.70−1.90 (m, 1H), 1.90−2.55 (m, 6H), 2.65−2.90 (m, 2H), 3.14 (dd, 1H, J = 12.2, 4.4 Hz), 4.19 (ddd, 1H, J_{AB} = 11.4 Hz, J = 7.2, 4.2 Hz), 4.53 (ddd, 1H, J_{AB} = 11.4 Hz, J = 6.5, 4.6 Hz), 5.00 (q, 1H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$): δ 15.5, 27.3, 29.1, 32.4, 37.2, 43.5, 54.9, 65.1, 74.6, 171.8, 175.7, 218.1.

(1*S*,4*R*,9*S*,11*S*)-4-Methyl-3,7-dioxatricyclo[9.4. 0^{1,11}.0^{1,9}]-tetradecane-2,6,12-trione (37a): solid, 58%; ^{1}H NMR ($CDCl_3$) δ 1.39 (d, 3 H, J = 6.1 Hz), 1.90−2.50 (m, 5 H), 2.51 (ddd, 1 H, J = 9, 3, 1.9 Hz), 3.65−2.83 (m, 3 H), 3.07 (dd, 1 H, J = 9.3, 5 Hz), 3.87 (d, 1 H, J_{AB} = 12.2 Hz), 4.61 (dd, 1 H, J_{AB} = 12.2 Hz, J = 2 Hz), 5.50 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.1, 23.1, 30.2, 36.7, 40.7, 42.9, 44.1, 52.7, 64.9, 67.4, 170.6, 173.9, 218.6; IR (neat) ν = 2961, 2922, 1743, 1454, 1304, 1190, 1039 cm^{-1}; MS (70 eV) m/z 252 ($M^{\bullet+}$, 27), 166, 148, 138, 127, 120, 109.

(1*R*,4*R*,9*R*,11*R*)-4-Methyl-3,7-dioxatricyclo[9.4 0^{1,11}.0^{1,9}]-tetradecane-2,6,12-trione (37b): solid, 31%; ^{1}H NMR ($CDCl_3$) δ 1.40 (d, 3 H, J = 6.5 Hz), 2.05 (ddd, 1 H, J = 12.6, 8.5, 4.6 Hz), 2.15−2.44 (m, 4 H), 2.51 (ddd, 1 H, J = 9.1, 4.6, 1.9 Hz), 2.60−2.80 (m, 2 H), 2.94 (m, 1 H), 3.14 (dd, 1 H, J = 11, 4.6 Hz), 4.26 (dd, 1 H, J_{AB} = 11.8 Hz, J = 8.8 Hz), 4.31 (dd, 1 H, J_{AB} = 11.8 Hz, J = 6.8 Hz), 5.42 (ddq, 1 H, J = 8.0, 4.6, 6.5 Hz); ^{13}C NMR ($CDCl_3$) δ 19.9, 23.4, 29.0, 37.5, 39.9, 42.9, 43.1, 52.8, 67.1, 67.5, 171.2, 173.2, 217.9; $[\alpha]^{21}_D$ −224 (c = 0.6, $CHCl_3$).

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Supporting Information Available: ORTEP structure and tables of X-ray crystallography data of compound **21**. ^{1}H and ^{13}C spectra of **3b**,**c**, **7b**, **16**, **18**, **22**−**24**, **27**, **36**, and **37**. This material is available free of charge via the Internet at htpp://pubs.acs.org.

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