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Regio- and diastereoselectivity studies on the photocycloaddition of ketene diethyl acetal to chiral 2(5*H*)-furanones

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ABSTRACT

The photochemical [2+2] cycloaddition of 1,1-diethoxyethylene to chiral 2(5*H*)-furanones is investigated. The effect of the substituents of the lactone and the polarity of the solvents on the chemical yield, regioselectivity, and facial diastereoselectivity is evaluated. The reactions in ether proceed with excellent regioselectivity and good yields. Hydrolysis of the ketal group of the major cycloadducts afforded enantiopure cyclobutanones fused to γ-lactones.

1. Introduction

Cyclobutanone and its derivatives are useful compounds in organic synthesis.[1] In general, a four-membered cyclic ketone is synthesized either by [2+2] cycloaddition of ketenes to olefins[2] or by ring expansion of cyclopropane precursors.[3] In connection with our interest in the synthesis of cyclobutane-containing products, it was envisaged that the photochemical cycloaddition of 5-substituted 2(5*H*)-furanones to ketene ketals could be a convenient method for preparing cyclobutanones. Despite its synthetic potential, this photochemical reaction has been scarcely exploited.[4] In principle, such a process could lead to the formation of up to four products, the head-to-head (HH) and head-to-tail (HT) *anti* regioisomers[5] and the HH and HT *syn* regioisomers (Scheme 1). It has been reported that the photocycloaddition of cyclic enones to electron-rich alkenes takes place with predictable regioselectivity giving mainly HT adducts.[6] Nevertheless, slight variations of the substrate structure[7] or the reaction conditions, specially the solvent,[8] can change the regioselectivity dramatically. Controlling the regio- and stereochemical aspects of photochemical reactions has been a prime challenge to synthetic organic chemists, particularly on the preparation of highly substituted cyclobutanes with multiple stereogenic centers.[9,6d] To get a deeper insight into the factors controlling the stereochemical course of these photoadditions, we decided to study in detail the solvent and substituent effects on the regio- and diastereoselectivity of the photochemical reaction of 1,1-diethoxyethylene **2** with lactones **1a–e**. Since these chiral lactones are readily available in enantiopure form, the photoreaction should lead to the enantio-directed formation of masked cyclobutanones fused to γ-lactones.

2. Results

Lactones **1a**,[10] **1c**,[10] **1d**,[11] and **1e**[12] were synthesized following procedures described in the literature. The new furanone **1b** was easily prepared in 83% yield by the reaction of (*S*)-5-hydroxymethyl-2(5*H*)-furanone with 1-adamantanecarbonyl chloride and pyridine in CH_2Cl_2. Substrates **1a–e** and a 10-fold excess of 1,1-diethoxyethylene in acetonitrile, ether, or hexane solutions[13] were irradiated through a quartz vessel using a 125 W high-pressure mercury lamp at −20 °C. The progress of the cycloadditions was monitored by GC or ^{1}H NMR analysis and the irradiation was prolonged until complete conversion of the starting furanone. The results are listed in Table 1.

The monosubstituted lactones **1a–c**, bearing acyl groups that differ in size, were first investigated. In all the cases, a mixture of the four possible cycloadducts (**3–6**)**a–c** was formed. The chromatographic separation of the compounds was rather difficult and, in some cases, it was necessary to perform NMR analyses of samples containing minor amounts of other isomers. The *anti*/*syn* configuration of the cycloadducts was determined by the value of the coupling constant between H-4 and H-5 (∼2 Hz for the *anti* isomers **3a–c** and **5a–c** vs ∼6 Hz for the *syn* isomers **4a–c** and **6a–c**), while the connectivity was determined by HMBC experiments, wherein a correlation between the acetal carbon atom C-6 and proton H-4 is observed for the HT adducts **3a–c** and **4a–c**. Additional evidence of the regiochemical assignment was given by the ^{13}C NMR spectra, where the signal of C-5 of the HT isomers appears downfield shifted ($\delta \sim 47$ for **3a–c** and **4a–c**) compared to the HH adducts ($\delta \sim 29$ for **5a–c** and **6a–c**), according to the deshielding effect of the ketal oxygen atoms.

The photoreactions of lactones **1a–c** and olefin **2** in acetonitrile (entries 1–3) were accomplished in reasonably good yields and moderate regio- and stereoselectivity. A remarkable solvent effect was unveiled when these cycloadditions were performed in ether

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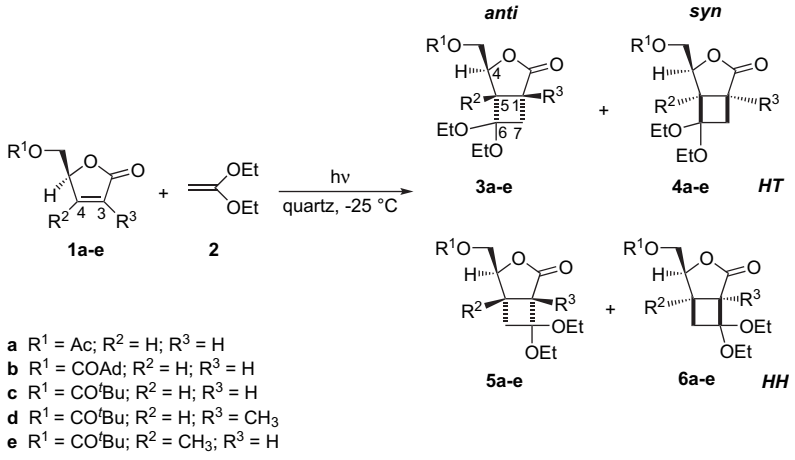


Scheme 1. Cycloadducts from the photochemical reaction of lactones **1a**–**e** with 1,1-diethoxyethylene **2**.

(entries 6–8) or hexane (entries 11–13). In these less polar solvents, the regioselectivity was notably enhanced, while the stereoselectivity decreased slightly. Because of its low solubility, the photoreaction of **1a** in hexane (entry 11) became much slower and prolonged irradiation time (11 h) was required to get a low yield of the photoadducts (37%). From these results we can conclude that the size of the acyl substituent has little influence on either the regio- or the facial selectivity of the cycloaddition. A slight increase of *anti* adducts is observed on going from the acetyl group (entries 1, 6, and 11) to the bulkier adamantyl (entries 2, 7, and 12) and pivaloyl (entries 3, 8, and 13) residues, while the regioselectivity only varies in the reactions performed in acetonitrile (entries 1–3), wherein the HT–HH ratio diminishes with increment of the substituent size.

We also examined how the introduction of a methyl group at the 3- or 4-position of the 2(5*H*)-furanone may influence the regio- and stereochemical outcome of the cycloaddition process. To that end, we performed the photochemical reaction of 1,1-diethoxyethylene with lactones **1d** (entries 4, 9, and 14) and **1e** (entries 5, 10, and 15) in acetonitrile, hexane and ether. These reactions delivered the corresponding mixtures of cycloadducts **3d**–**6d** and **3e**–**6e**.

The regio- and stereochemistry of the major adducts **3d**–**5d** were determined as indicated above, while the *anti* or *syn* relative configuration of **3e** and **4e** was inferred from the chemical shift of the angular methyl carbon on their ^{13}C NMR spectra. The 'steric compression' in the *anti* adduct **3e** is much larger, with the signal of the methyl carbon atom appearing high field shifted (δ 13.4) when compared to the *syn* adduct **4e** (δ 16.5).

As shown in Table 1, the attachment of an α-methyl group on the lactone has only a moderate influence on the regioselectivity when the reaction is performed in acetonitrile (compare entries 3 and 4), while a β-methyl group increases dramatically the proportion of the HT regioisomers (compare entries 3 and 5). Conversely, the structural modification of the substrate does not increase further the yet very high regioselectivity observed in apolar solvents (compare entries 8 and 9/10, and entries 13 and 14/15). It is also shown that the β-methyl substitution decreases the antifacial selectivity irrespective of the solvent used (entries 5, 10 and 15 vs entries 3, 8 and 13). To the contrary, α-methyl substitution increases the diastereoselectivity values (entries 4, 9 and 14 vs entries 3, 8 and 13).

The results in acetonitrile might be rationalized considering the isomeric 1,4-biradical intermediates (**I**–**IV**)**c**–**e** (Fig. 1). Substitution effects at the 2- and 3-position of cyclopentenone in its photochemical reaction with 2-methylpropene have been examined by Weedon.[15] By trapping experiments, it was found that the major 1,4-biradical intermediates were formed by bonding the less substituted end of the alkene to both the 2- and the 3-position of the enone. It was suggested that the regiochemical outcome of the reaction was determined by the extend to which isomeric 1,4-biradical intermediates partition between fragmentation to starting materials and closure to products rather than by the relative rates of formation of the biradical intermediates. Moreover, it has been

Table 1
[2+2] Photocycloaddition of 2(5*H*)-furanones **1a**–**e** to 1,1-diethoxyethylene **2**

Entry	2(5*H*)-Furanone	Solvent	*t*	Yield[a] (%)	**3**:**4**:**5**:**6**[b] (%)	HT/HH (%)	*anti*/*syn* (%)
1	**1a**	Acetonitrile	3.3 h	75	47:31:15:7	78:22	62:38
2	**1b**	Acetonitrile	1.9 h	77	50:21:22:7[c]	71:29	72:28
3	**1c**[14]	Acetonitrile	2 h	61	50:22:21:7	72:28	71:29
4	**1d**	Acetonitrile	2.3 h	87	60:20:17:3[c]	80:20	77:23
5	**1e**	Acetonitrile	35 min	85	63:31:4:2	94:6	67:33
6	**1a**	Ether	2.25 h	78	51:41:5:3	92:8	56:44
7	**1b**	Ether	2.25 h	50	52:39:6:3[c]	91:9	58:42
8	**1c**[14]	Ether	2.3 h	75	58:34:5:3	92:8	63:37
9	**1d**	Ether	2 h	64	62:31:7:–[c]	92:8	69:31
10	**1e**	Ether	1.5 h	80	51:42:4:3	93:7	55:45
11	**1a**	Hexane	11.2 h	37	48:42:6:4	90:10	54:46
12	**1b**	Hexane	1.6 h	66	57:36:4:3[c]	93:7	61:39
13	**1c**[14]	Hexane	2.5 h	72	52:39:6:3	91:9	58:42
14	**1d**	Hexane	3 h	58	50:41:9:–[c]	91:9	59:41
15	**1e**	Hexane	1.7 h	69	47:46:4:3	93:7	51:49

[a] Isolated yield of the mixture of stereoisomers after column chromatography.
[b] Isomer ratio from GC analysis of the crude reaction mixture.
[c] Isomer ratio from ^{13}C NMR analysis of the crude reaction mixture.

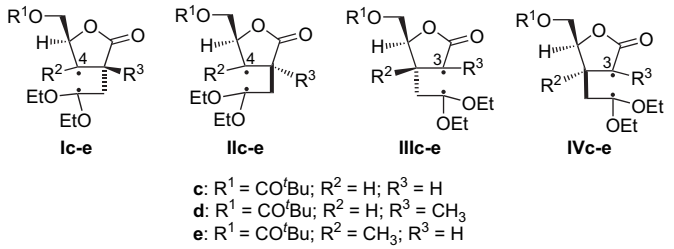
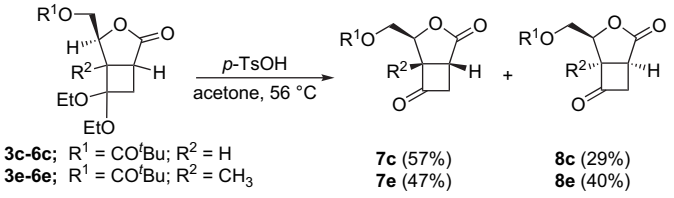


Figure 1. Isomeric 1,4-biradical intermediates (**I**–**IV**)**c**–**e**.

described that, in the biradical intermediates, radical centers at the 3-position are planar and that at the 4-position are pyramidalized.[6b]

Taking this study into account, it might be expected that a methyl substituent at the 4-position (β-position) would sterically inhibit first bond formation between its point of attachment and the less substituted end of the alkene (**IIIe** and **IVe**), but stabilize the radical center resulting from the bond formed between the less substituted end of the alkene and the α-carbon atom (**Ie** and **IIe**), which direct the product regiochemistry. Interestingly, the methyl group in biradicals **Ie** and **IIe** does not sterically inhibit closure to the cyclobutane compounds. The noteworthy diminution of the diastereoselectivity for **1e** compared to **1c** is likely due to the higher steric congestion between the methyl group, the acetalic chain and the substituent attached at the stereogenic center in the *anti* cycloadducts. The effect of a methyl group at the 3-position in the photochemical reaction is slightly different. In this case, in radicals **IIId** and **IVd**, the methyl substituent which is attached to the sp^2 hybridized radical center would interfere with cyclobutane formation giving more prominence to biradicals **Id** and **IId**, and thus showing better regioselectivity compared to lactone **1c**.

To obtain the unprotected cyclobutanones, the hydrolysis of the ketal group of photoadducts **3c**–**6c** and **3d**–**6d** was undertaken (Scheme 2). Treatment of a 58:34:5:3 mixture of **3c**–**6c** with *p*-TsOH in acetone at 56 °C afforded, after column chromatography, the enantiopure cyclobutanones **7c** and **8c** in 57 and 29% yield, respectively. Upon the foregoing conditions, a 51:42:4:3 mixture of **3e**–**6e** resulted in the formation of **7e** and **8e** in 47 and 40% yield, respectively. The isolation of the cyclobutanones derived from the minor HH adducts was not attempted in either case.



Scheme 2. Preparation of cyclobutanones.

3. Conclusions

We have studied the [2+2] photochemical reaction of chiral 5-substituted 2(5*H*)-furanones with 1,1-diethoxyethylene in acetonitrile, ether and hexane. The degree of regio- and diastereoselectivity achieved was dependent on the substituents of the lactone as well as on the polarity of the solvent. The reactions in ether proceed with excellent regioselectivity and good yields. A noticeable diminution of the regioselectivity was found when the photochemical reactions were performed in acetonitrile. The chiral 3-oxabicyclo[3.2.0]heptan-2,6-dione scaffolds reported here are valuable precursors for the elaboration of polyfunctionalized cyclobutane compounds. Active investigation in this field is being carried out in our laboratory.

4. Experimental

4.1. General

Commercially available reagents were used as-received. Solutions were concentrated using an evaporator at 15–20 Torr. Flash column chromatographies were carried out on silica gel (230–400 mesh). Melting points were determined on hot stage and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at the Servei de Ressonància Magnètica Nuclear de la Universitat Autònoma de Barcelona at 250 and 62.5 MHz or 360 and 90 MHz or 500 and 125 MHz. NMR signals were assigned with the help of DEPT, COSY, HMBC and HMQC experiments. High-resolution mass spectra (HRMS) were recorded at the Unidade de Espectrometria de Masas in the Universidade de Santiago de Compostela. Microanalyses were performed at the Servei d'Anàlisi Elemental de la Universitat Autònoma de Barcelona. Optical rotations were measured at 22±2 °C.

*4.1.1. (−)-(S)-5-Adamantanecarbonyloxymethyl-2(5H)-furanone (**1b**)*

Adamantanecarbonyl chloride (3.67 g, 17.5 mmol) was slowly added to an ice-cooled solution of (*S*)-5-hydroxymethyl-2(5*H*)-furanone (1.01 g, 8.86 mmol) and dry pyridine (1.41 mL) in dry CH_2Cl_2 (19 mL). The mixture was stirred overnight as it came to room temperature. After addition of CH_2Cl_2 (15 mL), the organic layer was successively washed with 5% HCl (3×20 mL), saturated aqueous $NaHCO_3$ (3×20 mL), and brine (2×20 mL) and dried (Na_2SO_4). Evaporation of the solvent and column chromatography of the residue (hexane–EtOAc 2:1) afforded **1b** (2.02 g, 7.31 mmol, 83% yield) as a white solid: mp 80–82 °C (white solid from EtOAc–pentane); $[\alpha]_D$ −76.2 (*c* 1.05, $CHCl_3$); IR (ATR) 2906, 2889, 2848, 1746, 1721, 1439, 1223, 1165 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.39 (dd, $J_{4,3}$=5.9 Hz, $J_{4,5}$=1.5 Hz, 1H, H-4), 6.18 (dd, $J_{3,4}$=5.6 Hz, $J_{3,5}$=1.8 Hz, 1H, H-3), 5.20 (m, 1H, H-5), 4.38 (dd, J_{gem}=12.0 Hz, $J_{6,5}$=4.4 Hz, 1H, H-6), 4.32 (dd, J_{gem}=12.0 Hz, $J_{6,5}$=3.8 Hz, 1H, H-6), 2.0–1.5 (m, 15H, Ad); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 176.8 (C=O, lactone), 172.2 (C=O, ester), 152.5 (CH, C-4), 122.8 (CH, C-3), 81.0 (CH, C-5), 61.5 (CH_2, C-6), 40.6 (C, Ad), 38.5 (Ad), 36.2 (Ad), 27.6 (Ad). Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.31; H, 7.23.

4.2. General procedure for photocycloadditions of 2(5*H*)-furanones to ketene diethyl acetal

Irradiations were performed in a small conventional photochemical reactor (two-necked vessel fitted quartz immersion type cooling jacket) using a high-pressure 125 W mercury lamp (cathodeon HPK-125), which provides maximum energy at 365 nm with substantial radiation also at 313 and 253 nm. Methanol at −15 °C was used for refrigeration of the immersion well jacket. The vessel was externally cooled at −20 °C with a dry ice-acetonitrile bath. The reaction mixture was initially degassed by passage of oxygen-free argon through the solution for 10 min and then irradiated under an atmosphere of argon. The progress of the reaction was monitored by GC or by ^{1}H or ^{13}C NMR analyses of aliquot samples.

*4.2.1. (1R,4S,5S)- and (1S,4S,5R)-4-acetyloxymethyl-6,6-diethoxy-3-oxabicyclo[3.2.0]heptan-2-one (**3a** and **4a**), and (1S,4S,5S)- and (1R,4S,5R)-4-acetyloxymethyl-7,7-diethoxy-3-oxabicyclo[3.2.0]heptan-2-one (**5a** and **6a**)*

A solution of lactone **1a** (95 mg, 0.61 mmol) and 1,1-diethoxyethylene **2** (0.82 mL, 6.10 mmol) in acetonitrile (70 mL) was irradiated for 3.3 h. The progress of the reaction was monitored by GC.

Evaporation of the solvent and column chromatography (hexane–EtOAc, 6:1) afforded a 47:31:15:7 mixture of **3a**, **4a**, **5a**, and **6a** (124 mg, 0.46 mmol, 75% yield). Repeated column chromatography (hexane–EtOAc, 6:1) provided enriched fractions of compounds **3a**–**6a**. Compound **3a**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.99 (m, 1H, H-4), 4.25 (dd, J_{gem}=12.0 Hz, $J_{8,4}$=3.2 Hz, 1H, H-8), 4.12 (dd, J_{gem}=12.0 Hz, $J_{8,4}$=4.3 Hz, 1H, H-8), 3.45–3.20 (m, 4H, H-1′), 3.01 (m, 2H, H-1, H-5), 2.60 (ddd, J_{gem}=13.3 Hz, $J_{7,1}$=9.1 Hz, $J_{7,5}$=2.7 Hz, 1H, H-7), 2.42 (dd, J_{gem}=13.3 Hz, $J_{7,1}$=3 Hz, 1H, H-7), 2.05 (s, 3H, C*H*$_3$CO), 1.20 (m, 6H, H-2′); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 178.4 (C=O, lactone), 170.3 (C=O, ester), 98.8 (C, C-6), 75.8 (CH, C-4), 65.3 (CH_2, C-8), 56.8 (CH_2, C-1′), 56.5 (CH_2, C-1′), 46.7 (CH, C-5), 36.3 (CH_2, C-6), 31.0 (CH, C-1), 20.5 (CH_3, *C*H$_3$CO), 14.9 (CH_3, C-2′), 14.8 (CH_3, C-2′). HRMS (FAB+) calcd for $[C_{13}H_{20}O_6+H]^+$): 273.1338. Found: 273.1341. Compound **4a**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.64 (m, 2H, H-4, H-8), 4.46 (dd, J_{gem}=11.3 Hz, $J_{8,4}$=1.2 Hz, 1H, H-8), 3.38 (m, 4H, H-1′), 3.16 (dd, $J_{5,1}$=8.1 Hz, $J_{5,4}$=5.7 Hz, 1H, H-5), 3.04 (ddd, $J_{1,5}$=8.1 Hz, $J_{1,7}$=7.1 Hz, $J_{1,7}$=4.3 Hz, 1H, H-1), 2.45 (m, 2H, H-7), 2.05 (s, 3H, C*H*$_3$CO), 1.19 (m, 6H, H-2′); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 178.4 (C=O, lactone), 170.7 (C=O, ester), 102.0 (C, C-6), 79.4 (CH, C-4), 64.6 (CH_2, C-8), 56.9 (CH_2, C-1′), 56.8 (CH_2, C-1′), 47.1 (CH, C-5), 35.6 (CH_2, C-7), 32.1 (CH, C-1), 20.8 (CH_3, *C*H$_3$CO), 15.0 (CH_3, C-2′), 14.8 (CH_3, C-2′). Compound **5a**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.57 (ddd, $J_{4,8}$=4.2 Hz, $J_{4,8}$=3.3 Hz, $J_{4,5}$=1.5 Hz, 1H, H-4), 4.21 (dd, J_{gem}=12.0 Hz, $J_{8,4}$=3.3 Hz, 1H, H-8), 4.08 (dd, J_{gem}=12.0 Hz, $J_{8,4}$=4.2, 1H, H-8), 3.65–3.30 (m, 5H, 4×H-1′, H-1), 2.68 (m, 1H, H-5), 2.60 (m, 1H, H-6), 2.20 (m, 1H, H-6), 2.05 (s, 3H, C*H*$_3$CO), 1.19 (m, 6H, H-2′); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 173.0 (C=O, lactone), 170.4 (C=O, ester), 99.3 (C, C-7), 82.2 (CH, C-4), 65.4 (CH_2, C-8), 57.6 (CH_2, C-1′), 57.1 (CH_2, C-1′), 50.9 (CH, C-1), 37.9 (CH_2, C-6), 29.0 (CH, C-5), 20.6 (CH_3, *C*H$_3$CO), 15.0 (CH_3, C-2′), 14.9 (CH_3, C-2′). Compound **6a**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.66 (ddd, $J_{4,8}$=6.5 Hz, $J_{4,8}$=6.5 Hz, $J_{4,5}$=5.0 Hz, 1H, H-4), 4.20 (m, 2H, H-8), 3.70–3.20 (m, 5H, 4×H-1′ and H-1), 2.95 (m, 1H, H-5), 2.30 (m, 2H, H-6), 2.05 (s, 3H, C*H*$_3$CO), 1.19 (m, 2×CH_3, H-2′); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 170.4 (2×C=O), 98.6 (C, C-7), 77.9 (CH, C-4), 57.8 (CH_2, C-1′), 57.2 (CH_2, C-1′), 51.2 (CH, C-1), 32.0 (CH_2, C-6), 28.7 (CH, C-5), 20.6 (CH_3, *C*H$_3$CO), 15.0 (CH_3, C-2′), 14.9 (CH_3, C-2′).

When the irradiation was performed through a quartz filter in ether (70 mL) for 2.25 h, from lactone **1a** (117 mg, 0.75 mmol) and **2** (1.0 mL, 7.5 mmol), after purification of the crude material by column chromatography (hexane–EtOAc, 6:1), a 51:41:5:3 mixture of **3a**–**6a** (159 mg, 0.58 mmol, 78% yield) was obtained.

When the irradiation was performed through a quartz filter in hexane (70 mL) for 11.2 h, from lactone **1a** (105 mg, 0.67 mmol) and **2** (0.9 mL, 6.7 mmol), after purification of the crude material by column chromatography (hexane–EtOAc, 6:1), provided the following fractions: (i) a 48:42:6:4 mixture of **3a**–**6a** (67 mg, 0.25 mmol, 37% yield) and (ii) unreacted lactone **1a** (20 mg, 0.13 mmol).

*4.2.2. (1R,4S,5S)- and (1S,4S,5R)-4-adamantanecarbonyloxymethyl-6,6-diethoxy-3-oxabicyclo[3.2.0]heptan-2-one (**3b** and **4b**), and (1S,4S,5S)- and (1R,4S,5R)-4-adamantanecarbonyloxymethyl-7,7-diethoxy-3-oxabicyclo[3.2.0]heptan-2-one (**5b** and **6b**)*

A solution of lactone **1b** (99 mg, 0.36 mmol) and 1,1-diethoxyethylene **2** (0.49 mL, 3.6 mmol) in acetonitrile (70 mL) was irradiated for 1.9 h. The progress of the reaction was monitored by GC. Evaporation of the solvent and column chromatography (hexane–EtOAc, 10:1) afforded a 50:22:21:7 mixture of **3b**, **4b**, **5b**, and **6b** (108 mg, 0.28 mmol, 77% yield). Repeated column chromatography (hexane–EtOAc, 10:1) provided the following fractions: (i) a mixture of **3b** and **6b** as an oil and (ii) a mixture of **4b** and **5b** as an oil. All the attempts to separate **3b** and **4b** from **6b** and **5b**, respectively, were unsuccessful and enriched fractions were analyzed. Compound **3b**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.99 (ddd, $J_{4,8}$=3.2 Hz, $J_{4,8}$=3.2 Hz, $J_{4,5}$=1.6 Hz, 1H, H-4), 4.23 (dd, J_{gem}=12.2 Hz, $J_{8,4}$=3.2 Hz, 1H, H-8), 4.09 (dd, J_{gem}=12.2 Hz, $J_{8,4}$=3.4 Hz, 1H, H-8), 3.45–3.25 (m, 4H, H-1′), 3.00 (m, 2H, H-1, H-5), 2.58 (ddd, J_{gem}=13.0 Hz, $J_{7,1}$=9.5 Hz, $J_{7,5}$=2.3 Hz, 1H, H-7), 2.42 (dd, J_{gem}=13.0 Hz, $J_{7,5}$=3.4 Hz, 1H, H-7), 2.00–1.60 (m, 15H, Ad), 1.15 (m, 6H, H-2′); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 178.7 (C=O, lactone), 177.1 (C=O, ester), 98.9 (C, C-6), 76.0 (CH, C-4), 65.1 (CH_2, C-8), 56.8 (CH_2, C-1′), 56.6 (CH_2, C-1′), 46.8 (CH, C-5), 40.8 (Ad), 38.6 (Ad), 36.5 (CH_2, C-7), 36.3 (CH_2, Ad), 31.3 (CH, C-1), 27.8 (CH, Ad), 15.0 (CH_3, C-2′), 14.9 (CH_3, C-2′). HRMS (FAB+): calcd for ($[C_{22}H_{32}O_6+H]^+$): 393.2277. Found: 393.2288. Compound **4b**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.61 (m, 2H, H-4, H-8), 4.49 (dd, J_{gem}=10.7 Hz, $J_{8,4}$=0.9 Hz, 1H, H-8), 3.40 (m, 4H, H-1′), 3.16 (dd, $J_{5,1}$=8.2 Hz, $J_{5,4}$=5.6 Hz, 1H, H-5), 3.03 (ddd, $J_{1,5}$=8.2 Hz, $J_{1,7}$=8.2 Hz, $J_{1,7}$=4.3 Hz, 1H, H-1), 2.45 (m, 2H, H-7), 2.00–1.60 (m, 15H, Ad), 1.15 (m, 6H, H-2′); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 178.5 (C=O, lactone), 177.6 (C=O, ester), 102.0 (C, C-6), 79.9 (CH, C-4), 64.4 (CH_2, C-8), 56.9 (CH_2, C-1′), 56.9 (CH_2, C-1′), 47.3 (CH, C-5), 40.7 (CH_2, Ad), 38.7 (Ad), 36.3 (Ad), 35.6 (CH_2, C-7), 32.2 (CH, C-1), 27.8 (CH, Ad), 15.1 (CH_3, C-2′), 14.9 (CH_3, C-2′). HRMS (FAB+) calcd for ($[C_{22}H_{32}O_6+H]^+$): 393.2277. Found: 393.2273. Compound **5b**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.55 (m, 1H, H-4), 4.18 (dd, J_{gem}=12.0 Hz, $J_{8,4}$=3.2 Hz, 1H, H-8), 4.04 (dd, J_{gem}=12.0 Hz, $J_{8,4}$=3.7 Hz, 1H, H-8), 3.60–3.30 (m, 5H, 4×H-1′, H-1), 2.69 (m, 1H, H-5), 2.60 (m, 1H, H-6), 2.19 (m, 1H, H-6), 2.00–1.60 (m, 15H, Ad), 1.15 (m, 2×CH_3, H-2′); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 177.1 (C=O, lactone), 173.5 (C=O, ester), 99.3 (C, C-7), 82.4 (CH, C-4), 65.1 (CH_2, C-8), 57.6 (CH_2, C-1′), 57.1 (CH_2, C-1′), 51.0 (CH, C-1), 40.6 (CH_2, Ad), 38.7 (Ad), 38.0 (CH_2, C-6), 36.4 (Ad), 28.9 (CH, C-5), 27.8 (Ad), 14.8 (CH_3, C-2′). Compound **6b**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.60 (dd, $J_{4,8}$=6.3 Hz, $J_{4,5}$=6.3 Hz, 1H, H-4), 4.10 (m, 2H, H-8), 3.50–3.20 (m, 5H, 4×H-1′, H-1), 2.95 (m, 1H, H-5), 2.25 (m, 2H, H-6), 2.00–1.60 (m, 15H, Ad), 1.15 (m, 2×CH_3, H-2′); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 173.1 (C=O, ester), 169.9 (C=O, lactone), 98.4 (C, C-7), 77.8 (CH, C-4), 62.4 (CH_2, C-8), 57.5 (CH_2, C-1′), 57.0 (CH_2, C-1′), 50.9 (CH, C-1), 40.6 (CH_2, Ad), 38.6 (Ad), 36.2 (Ad), 31.9 (CH_2, C-6), 28.6 (CH, C-5), 27.6 (CH, Ad), 13.9 (CH_3, C-2′), 11.9 (CH_3, C-2′).

When the irradiation was performed through a quartz filter in ether (70 mL) for 2.25 h, from lactone **1b** (99 mg, 0.36 mmol) and **2** (0.49 mL, 3.6 mmol), after purification of the crude material by column chromatography (hexane–EtOAc, 10:1), a 52:39:6:3 mixture of **3b**–**6b** (70 mg, 0.18 mmol, 50% yield) was obtained.

When the irradiation was performed through a quartz filter in hexane (70 mL) for 1.6 h, from lactone **1b** (109 mg, 0.39 mmol) and **2** (0.51 mL, 3.9 mmol), after purification of the crude material by column chromatography (hexane–EtOAc, 10:1), provided a 57:36:4:3 mixture of **3b**–**6b** (102 mg, 0.26 mmol, 66% yield).

*4.2.3. (1R,4S,5S)- and (1S,4S,5R)-6,6-diethoxy-3-methyl-4-pivaloyloxymethyl-3-oxabicyclo[3.2.0]heptan-2-one (**3d** and **4d**), and (1S,4S,5S)-7,7-diethoxy-3-methyl-4-pivaloyloxymethyl-3-oxabicyclo[3.2.0]heptan-2-one (**5d**)*

A solution of lactone **1d** (93 mg, 0.44 mmol) and 1,1-diethoxyethylene **2** (0.76 mL, 4.4 mmol) in acetonitrile (70 mL) was irradiated for 2.3 h. The progress of the reaction was monitored by GC. Evaporation of the solvent and column chromatography (hexane–EtOAc, 8:1) afforded a 60:20:17:3 mixture of **3d**, **4d**, **5d**, and **6d** (126 mg, 0.38 mmol, 87% yield). Repeated column chromatography (hexane–EtOAc, 10:1) provided the following fractions: (i) pure **3d** as an oil and (ii) a mixture of cycloadducts **4d** and **5d** as an oil. All the attempts to obtain any fraction that contains cycloadduct **6d** were unsuccessful. Compound **3d**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.90 (ddd, $J_{4,8}$=4.0 Hz, $J_{4,8}$=4.0 Hz, $J_{4,5}$=2.9 Hz, 1H, H-4), 4.25 (dd, J_{gem}=12.2 Hz, $J_{8,4}$=4.0 Hz, 1H, H-8), 4.05 (dd, J_{gem}=12.2 Hz, $J_{8,4}$=4.5 Hz, 1H, H-8), 3.35 (m, 4H, H-1′), 2.51 (ddd, $J_{5,7}$=2.9 Hz, $J_{5,4}$= 2.9 Hz, $J_{5,7}$=1.0 Hz, 1H, H-5), 2.49 (dd, J_{gem}=13.2 Hz, $J_{7,5}$=1.0 Hz, 1H, H-7), 2.21 (dd, J_{gem}=13.2 Hz, $J_{7,5}$=2.9 Hz, 1H, H-7), 1.45 (s, 3H, H-9),

1.19 (m, 15H, C(C*H*$_3$)$_3$, H-2′); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 180.3 (C=O, lactone), 178.1 (C=O, ester), 96.9 (C, C-6), 74.7 (CH, C-4), 65.3 (CH_2, C-8), 56.9 (CH_2, C-1′), 56.5 (CH_2, C-1′), 51.2 (CH, C-5), 43.0 (CH_2, C-7), 38.8 (C, *C*(CH$_3$)$_3$), 37.1 (C, C-1), 27.1 (CH$_3$, C(*C*H$_3$)$_3$), 20.3 (CH$_3$, C-9), 15.1 (CH$_3$, C-2′), 14.9 (CH$_3$, C-2′). HRMS (FAB+) calcd for ([($C_{17}H_{28}O_6$)+H]$^+$): 329.1964. Found: 329.1948. Compound **4d**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.60 (m, 2H, H-4, H-8), 4.47 (m, 1H, H-8), 3.70–3.25 (m, 4H, H-1′), 2.81 (ddd, $J_{5,4}$=5.7 Hz, $J_{5,7}$=1.0 Hz, $J_{5,7}$=1.0 Hz, 1H, H-5), 2.63 (dd, J_{gem}=12.9 Hz, $J_{7,5}$=1.1 Hz, 1H, H-7), 2.07 (dd, J_{gem}=12.9 Hz, $J_{7,5}$=0.9 Hz, 1H, H-7), 1.39 (s, 3H, H-9), 1.19 (m, 15H, C(C*H*$_3$)$_3$, H-2′); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 181.2 (2×C=O), 100.1 (C, C-6), 81.9 (CH, C-4), 65.2 (CH_2, C-8), 57.4 (CH_2, C-1′), 57.2 (CH_2, C-1′), 52.9 (CH, C-5), 42.8 (CH_2, C-6), 39.2 (C, C-1), 36.2 (C, *C*(CH$_3$)$_3$), 27.5 (CH$_3$, C(*C*H$_3$)$_3$), 20.5 (CH$_3$, C-9), 15.5 (CH$_3$, C-2′), 15.3 (CH$_3$, C-2′). HRMS (FAB+) calcd for ([($C_{17}H_{28}O_6$)+H]$^+$): 329.1964. Found: 329.1956. Compound **5d**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.59 (m, 1H, H-4), 4.18 (dd, J_{gem}=12.0 Hz, $J_{8,4}$=3.9 Hz, 1H, H-8), 4.02 (dd, J_{gem}=12.0 Hz, $J_{8,4}$=5.5 Hz, 1H, H-8), 3.40 (m, 4H, H-1′), 2.54 (dd, J_{gem}=12.8 Hz, $J_{6,5}$=8.8 Hz, 1H, H-6), 2.22 (m, 1H, H-5), 2.12 (dd, J_{gem}=12.8 Hz, $J_{6,5}$=4.1 Hz, 1H, H-6), 1.41 (s, 3H, H-9), 1.19 (m, 15H, C(C*H*$_3$)$_3$, H-2′).

When the irradiation was performed through a quartz filter in ether (70 mL) for 2 h, from lactone **1d** (101 mg, 0.48 mmol) and **2** (0.66 mL, 4.9 mmol), after purification of the crude material by column chromatography (hexane–EtOAc, 8:1), a 62:31:7 mixture of **3d**–**5d** (100 mg, 0.31 mmol, 64% yield) was obtained.

When the irradiation was performed through a quartz filter in hexane (70 mL) for 3 h, from lactone **1d** (118 mg, 0.56 mmol) and **2** (0.76 mL, 5.6 mmol), after purification of the crude material by column chromatography (hexane–EtOAc, 8:1), a 50:41:9 mixture of **3d**–**5d** (107 mg, 0.33 mmol, 58% yield) was obtained.

*4.2.4. (1R,4S,5S)- and (1S,4S,5R)-6,6-diethoxy-5-methyl-4-pivaloyloxymethyl-3-oxabicyclo[3.2.0]heptan-2-one (**3e** and **4e**), and (1S,4S,5S)- and (1R,4S,5R)-7,7-diethoxy-5-methyl-4-pivaloyloxymethyl-3-oxabicyclo[3.2.0]heptan-2-one (**5e** and **6e**)*

A solution of lactone **1e** (105 mg, 0.49 mmol) and 1,1-diethoxyethylene **2** (0.66 mL, 4.9 mmol) in ether (70 mL) was irradiated for 1.5 h. The progress of the reaction was monitored by GC. Evaporation of the solvent and column chromatography (hexane–EtOAc, 12:1) afforded a 51:42:4:3 mixture of **3e**, **4e**, **5e**, and **6e** (130 mg, 0.39 mmol, 80% yield). Repeated column chromatography (hexane–EtOAc, 12:1) provided enriched fractions of **3e** and **4e** which were analyzed. All attempts to obtain enriched fraction of compounds **5e** and **6e** were unsuccessful. Compound **3e**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.97 (dd, $J_{4,8}$=3.2 Hz, $J_{4,8}$=3.2 Hz, 1H, H-4), 4.38 (dd, J_{gem}=12.3 Hz, $J_{8,4}$=3.2 Hz, 1H, H-8), 4.04 (dd, J_{gem}=12.3 Hz, $J_{8,4}$=3.2 Hz, 1H, H-8), 3.20–3.55 (m, 4H, OC*H*$_2$CH$_3$), 2.49 (m, 3H, H-1, 2H-7), 1.30 (s, CH$_3$, C*H*$_3$), 1.20 (s, 9H, (C*H*$_3$)$_3$C), 1.15 (m, 6H, OCH$_2$C*H*$_3$); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 178.5 (C=O), 178.4 (C=O), 103.4 (C, C-6), 78.1 (CH, C-4), 63.5 (CH_2, C-8), 58.0 (CH_2, O*C*H$_2$CH$_3$), 57.6 (CH_2, O*C*H$_2$CH$_3$), 53.6 (C, C-5), 38.7 (C, (CH$_3$)$_3$*C*), 38.2 (CH, C-1), 34.3 (CH_2, C-7), 27.1 (CH$_3$, (*C*H$_3$)$_3$C), 14.9 (CH$_3$, 2OCH$_2$*C*H$_3$), 13.4 (*C*H$_3$). Compound **4e**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.65 (dd, J_{gem}=12.6 Hz, $J_{8,4}$=7.6 Hz, 1H, H-8), 4.47 (dd, J_{gem}=12.6 Hz, $J_{8,4}$=2.3 Hz, 1H, H-8), 4.28 (dd, $J_{4,8}$=7.6 Hz, $J_{4,8}$=2.3 Hz, 1H, H-4), 3.40 (m, 4H, OC*H*$_2$CH$_3$), 2.49 (m, 2H, H-1, H-7), 2.34 (dd, J_{gem}=12.8 Hz, $J_{7,1}$=9.8 Hz, 1H, H-7), 1.37 (s, 3H, C*H*$_3$), 1.20 (s, 9H, (C*H*$_3$)$_3$C), 1.15 (m, 6H, OCH$_2$C*H*$_3$); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 178.2 (C=O), 177.9 (C=O), 101.1 (C, C-6), 84.8 (CH, C-4), 64.1 (CH_2, C-8), 58.2 (CH_2, O*C*H$_2$CH$_3$), 57.7 (CH_2, O*C*H$_2$CH$_3$), 54.7 (C, C-5), 39.0 (CH, C-1), 38.7 (C, (CH$_3$)$_3$*C*), 33.0 (CH_2, C-7), 27.1 (CH$_3$, (*C*H$_3$)$_3$C), 14.9 (CH$_3$, 2OCH$_2$*C*H$_3$), 16.5 (*C*H$_3$).

When the irradiation was performed through a quartz filter in hexane (70 mL) for 1.7 h, from lactone **1e** (100 mg, 0.47 mmol) and **2** (0.64 mL, 4.7 mmol), after purification of the crude material by column chromatography (hexane–EtOAc, 12:1), a 47:46:4:3 mixture of **3d**, **4d**, **5d**, and **6d** (106 mg, 0.32 mmol, 69% yield) was obtained.

When the irradiation was performed through a quartz filter in acetonitrile (70 mL) for 1.5 h, from lactone **1e** (100 mg, 0.47 mmol) and **2** (0.62 mL, 4.7 mmol), after purification of the crude material by column chromatography (hexane–EtOAc, 12:1), a 63:31:4:2 mixture of **3e**, **4e**, **5e**, and **6e** (132 mg, 0.40 mmol, 85% yield) was obtained.

*4.2.5. (1R,4S,5S)-4-pivaloyloxymethyl-3-oxabicyclo[3.2.0]heptan-2,6-dione (**7c**) and (1S,4S,5R)-4-pivaloyloxymethyl-3-oxabicyclo[3.2.0]heptan-2,6-dione (**8c**)*

A (58:34:5:3) mixture of photoadducts **3c**–**6c** (111 mg, 0.35 mmol) was diluted in a solution of *p*-toluenesulfonic acid in acetone (0.01 M, 7 mL). The mixture was stirred overnight at 56 °C. Evaporation of the solvent and purification by column chromatography (from hexane–EtOAc, 4:1 to hexane–EtOAc, 3:1) afforded the *anti* HT isomer **7c** (49 mg, 0.20 mmol, 57% yield) as a white solid and the *syn* isomer **8c** (25 mg, 0.10 mmol, 29% yield) as a white solid. Compound **7c**: mp 82–83 °C (from EtOAc–hexane); $[\alpha]_D$ −193.0 (*c* 1.15, $CHCl_3$); MS (ESI+) 263 ([M+Na]$^+$, 100); IR (ATR) 2959, 1800, 1772, 1719, 1156 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.93 (ddd, $J_{4,8}$=2.9 Hz, $J_{4,8}$=2.9 Hz, $J_{4,5}$=1.5 Hz, 1H, H-4), 4.32 (dd, J_{gem}=12.2 Hz, $J_{8,4}$=2.9 Hz, 1H, H-8), 4.14 (dd, J_{gem}=12.2 Hz, $J_{8,4}$=2.9 Hz, 1H, H-8), 3.93 (dddd, $J_{5,1}$=7.4 Hz, $J_{5,7}$=3.0 Hz, $J_{5,7}$=3.0 Hz, $J_{5,4}$=1.5 Hz, 1H, H-5), 3.75 (ddd, J_{gem}=18.0 Hz, $J_{7,1}$=10.0 Hz, $J_{7,5}$=3.0 Hz, 1H, H-7), 3.49 (ddd, $J_{1,7}$=10.0 Hz, $J_{1,5}$=7.5 Hz, $J_{1,7}$=3.7 Hz, 1H, H-1), 3.35 (ddd, J_{gem}=18.0 Hz, $J_{7,1}$=3.7 Hz, $J_{7,5}$=3.0 Hz, 1H, H-7), 1.22 (s, 9H, (C*H*$_3$)$_3$C); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 202.3 (C=O, C-6), 177.5 (C=O), 176.1 (C=O, C-2), 76.1 (CH, C-4), 65.2 (CH_2, C-8), 62.5 (CH, C-5), 53.8 (CH_2, C-7), 38.7 (C, *C*(CH$_3$)$_3$), 30.7 (CH, C-1), 27.0 (CH$_3$, (*C*H$_3$)$_3$C). Anal. Calcd for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 60.00; H, 6.85. Compound **8c**: mp 115–116 °C (from EtOAc–hexane); $[\alpha]_D$ +236.0 (*c* 2.0, $CHCl_3$); IR (ATR) 2975, 2907, 2872, 1775, 1719, 1152 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.80 (ddd, $J_{4,5}$=9.0 Hz, $J_{4,8}$=5.8 Hz, $J_{4,8}$=3.5 Hz, 1H, H-4), 4.53 (dd, J_{gem}=12.6 Hz, $J_{8,4}$=3.5 Hz, 1H, H-8), 4.18 (dd, J_{gem}=12.6 Hz, $J_{8,4}$=5.8 Hz, 1H, H-8), 4.10 (m, 1H, H-5), 3.68 (ddd, J_{gem}=17.7 Hz, $J_{7,1}$=9.4 Hz, $J_{7,5}$=3.5 Hz, 1H, H-7), 3.52 (ddd, $J_{1,7}$=9.4 Hz, $J_{1,5}$=7.7 Hz, $J_{1,7}$=3.9 Hz, 1H, H-1), 3.40 (ddd, J_{gem}=17.7 Hz, $J_{7,1}$=3.9 Hz, $J_{7,5}$=3.5 Hz, 1H, H-7), 1.20 (s, 9H, (C*H*$_3$)$_3$C); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 200.6 (C=O, C-6), 177.6 (C=O), 176.0 (C=O, C-2), 76.8 (CH, C-4), 62.6 (CH_2, C-8), 61.6 (CH, C-5), 53.7 (CH_2, C-7), 38.7 (C, *C*(CH$_3$)$_3$), 30.8 (CH, C-1), 27.0 (CH$_3$, (*C*H$_3$)$_3$C). Anal. Calcd for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 59.91; H, 6.78.

*4.2.6. (1R,4S,5S)-5-methyl-4-pivaloyloxymethyl-3-oxabicyclo-[3.2.0]heptan-2,6-dione (**7e**) and (1S,4S,5R)-5-methyl-4-pivaloyloxymethyl-3-oxabicyclo[3.2.0]heptan-2,6-dione (**8e**)*

A (51:42:4:3) mixture of photoadducts **3e**–**6e** (140 mg, 0.43 mmol) was diluted in a solution of *p*-toluenesulfonic acid in acetone (0.01 M, 32 mL). The mixture was stirred overnight at 56 °C. Evaporation of the solvent and purification by column chromatography (from hexane–EtOAc, 10:1 to hexane–EtOAc, 5:1) afforded the *anti* isomer **7e** (51 mg, 0.20 mmol, 47% yield) as a white solid and the *syn* isomer **8e** (44 mg, 0.17 mmol, 40% yield) as a white solid. Compound **7e**: mp 92–93 °C (from pentane–EtOAc); $[\alpha]_D$ −148.6 (*c* 1.40, $CHCl_3$); MS (CI+/NH_3) 272 ([M+NH_4]$^+$, 100); IR (KBr) 2975, 1769, 1714, 1480, 1276, 1208 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.78 (dd, $J_{4,8}$=2.6 Hz, $J_{4,8}$=1.9 Hz, 1H, H-4), 4.41 (dd, J_{gem}=12.5 Hz, $J_{8,4}$=2.6 Hz, 1H, H-8), 4.05 (dd, J_{gem}=12.5 Hz, $J_{8,4}$=1.9 Hz, 1H, H-8), 3.80 (dd, J_{gem}=18.4 Hz, $J_{7,1}$=10.2 Hz, 1H, H-7), 3.28 (dd, J_{gem}=18.4 Hz, $J_{7,1}$=3.4 Hz, 1H, H-7), 3.10 (dd, $J_{1,7}$=10.2 Hz, $J_{1,7}$=3.4 Hz, 1H, H-1), 1.38 (s, 3H, C*H*$_3$), 1.21 (s, 9H, (C*H*$_3$)$_3$C); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 206.5 (C=O), 177.4 (C=O), 176.2 (C=O), 78.0 (CH, C-4), 68.0 (C, C-5), 62.9 (CH_2, C-8), 51.9 (CH_2, C-7), 38.7 (C,

(CH_3)$_3$*C*), 37.0 (CH, C-1), 27.1 (CH_3, (*C*H_3)$_3$C), 12.8 (*C*H_3). Anal. Calcd for $C_{13}H_{18}O_5$: C, 61.40; H, 7.14. Found: C, 61.57; H, 7.14. Compound **8e**: mp 138–140 °C (from pentane–EtOAc); $[\alpha]_D$ +202.8 (*c* 0.48, $CHCl_3$); MS (CI+/NH_3) 272 ($[M+ NH_4]^+$, 100); IR (KBr) 2975, 2940, 1770, 1715, 1479, 1358, 1150 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 4.45 (m, 2H, H-8, H-4), 4.14 (dd, J_{gem}=11.6 Hz, $J_{8,4}$=4.8 Hz, 1H, H-8), 3.67 (dd, J_{gem}=18.8 Hz, $J_{7,1}$=10.2 Hz, 1H, H-7), 3.38 (dd, J_{gem}=18.8 Hz, $J_{7,1}$=4.7 Hz, 1H, H-7), 3.16 (dd, $J_{1,7}$=10.2 Hz, $J_{1,7}$=4.7 Hz, 1H, H-1), 1.49 (s, 3H, C*H*$_3$), 1.22 (s, 9H, (C*H*$_3$)$_3$C); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 204.1 (C=O), 177.7 (C=O), 175.8 (C=O), 82.8 (CH, C-4), 68.3 (C, C-5), 62.0 (CH_2, C-8), 51.8 (CH_2, C-7), 38.8 (C, (CH_3)$_3$*C*), 37.1 (CH, C-1), 27.0 (CH_3, (*C*H_3)$_3$C), 17.2 (*C*H_3). Anal. Calcd for $C_{13}H_{18}O_5$: C, 61.40; H, 7.14. Found: C, 61.43; H, 7.15.

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References and notes

1. (a) Baktharaman, S.; Selvakumar, S.; Singh, V. K. *Org. Lett.* **2006**, *8*, 4335–4338; (b) Nemoto, H.; Fukumoto, K. *Synlett* **1997**, 863–875; (c) Bellus, D.; Ernst, B. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 797–827.
2. Snider, B. B. *Chem. Rev.* **1988**, *88*, 793–811.
3. See, for example: (a) Markham, J. P.; Staben, S. T.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 9708–9709; (b) Zhang, L.; Koreeda, M. *Org. Lett.* **2002**, *4*, 3755–3758.
4. (a) Kosugi, H.; Sekiguchi, S.; Sekita, R.; Uda, H. *Bull. Chem. Soc. Jpn.* **1976**, 520–528; (b) Tada, M.; Kokubo, T.; Sato, T. *Tetrahedron* **1972**, *28*, 2121–2125.
5. In the addition of an asymmetrical olefin to an α,β-unsaturated lactone, there are two regioisomers, the head-to-head (HH) and head-to-tail (HT) adducts, where head refers to the carbonyl end of the enone and to the more substituted end of the olefin.
6. (a) Schmidt, K.; Margaretha, P. *Arkivoc* **2008**, *viii*, 68–73; (b) Schuster, D. I.; Lem, G.; Kaprinidis, N. A. *Chem. Rev.* **1993**, *93*, 3–22; (c) Schuster, D. I. In *The Chemistry of Enones*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, NY, 1989; pp 623–756; (d) Crimmins, M. T. *Chem. Rev.* **1988**, *88*, 1453–1473; (e) Corey, E. J.; Bass, J. D.; LeMahieu, R.; Mitra, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 5570–5583.
7. (a) Suishu, T.; Shimo, T.; Somekawa, K. *Tetrahedron* **1997**, *53*, 3545–3556; (b) Lange, G. L.; Organ, M. G.; Lee, M. *Tetrahedron Lett.* **1990**, *31*, 4689–4692.
8. (a) Lange, G. L.; Decicco, C.; Lee, M. *Tetrahedron Lett.* **1987**, *28*, 2833–2836; (b) Berenjian, N.; de Mayo, P.; Sturgeon, M.-E.; Sydnes, L. K.; Weedon, A. C. *Can. J. Chem.* **1982**, *60*, 425–436.
9. (a) Hoffmann, N. *Chem. Rev.* **2008**, *108*, 1052–1103; (b) Iriondo-Alberdi, J.; Greaney, M. F. *Eur. J. Org. Chem.* **2007**, 4801–4815; (c) Margaretha, P. In *Molecular and Supramolecular Photochemistry*; Griesbeck, A. G., Mattay, J., Eds.; Marcel Dekker: New York, NY, 2005; pp 211–238; (d) Namyslo, J. C.; Kaufmann, D. E. *Chem. Rev.* **2003**, *103*, 1485–1537; (e) Lee-Ruff, E.; Mladenova, G. *Chem. Rev.* **2003**, *103*, 1449–1483; (f) Bach, T. *Synthesis* **1998**, 683–703.
10. Alibés, R.; Bourdelande, J. L.; Font, J. *Tetrahedron: Asymmetry* **1991**, *2*, 1391–1402.
11. Alibés, R.; Bourdelande, J. L.; Gregori, A.; Font, J.; Rustullet, A.; Parella, T. *J. Carbohydr. Chem.* **2003**, *22*, 501–511.
12. Alibés, R.; Bourdelande, J. L.; Font, J.; Gregori, A.; Parella, T. *Tetrahedron* **1996**, *52*, 1267–1278.
13. Initial attempts to carry out the photochemical reaction in acetone met with failure.
14. Rustullet, A.; Alibés, R.; de March, P.; Figueredo, M.; Font, J. *Org. Lett.* **2007**, *9*, 2827–2830.
15. Andrew, D.; Weedon, A. C. *J. Am. Chem. Soc.* **1995**, *117*, 5647–5663.