Pergamon

Tetrahedron 54 (1998) 4873–4888

TETRAHEDRON

Photochemical [2+2] Cycloaddition of Cyclic Enones to (5R)-5-Menthyloxy-2[5H]-furanone

Samuel Bertrand, Norbert Hoffmann* and Jean-Pierre Pete

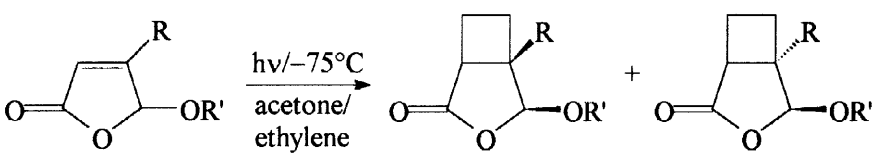
Unité Mixte de Recherche, n° 6519, CNRS,
Université de Reims Champagne-Ardenne, UFR Sciences, B.P. 1039
F-51687 REIMS Cedex 2, France.

Received 10 November 1997; accepted 17 February 1998

Abstract: The [2+2] Photocycloaddition of different cyclic enones to (5R)-5-menthyloxy-2[5H]-furanone is investigated. The diastereoselectivity relative to the chiral acetal centre and the regio and the exo/endo ratios of the products have been determined. By variation of the structure of cyclic enones, the diastereoselectivity could be optimised to 9/1. The results lead to the conclusion that the photochemically excited cyclopentenone transfer its energy to the (5R)-5-menthyloxy-2[5H]-furanone. The subsequent reaction of the excited furanone with cyclopentenone in its ground state is less stereoselective, as already observed. However, cyclic enones which furnish mixed adducts with (5R)-5-menthyloxy-2[5H]-furanone with high facial diastereoselectivity, react in their T_1 state.

Introduction

The [2+2] photocycloaddition has been frequently applied to organic synthesis[1]. Particular attention has been paid to its application in asymmetric synthesis.[2,3] Therefore, a lot of work has been done to investigate the mechanism as well as the regio, exo/endo and diastereoselectivity of this reaction.[4,5] Most frequently, the reaction was carried out with cyclic enones. In this context, the triplet sensitised [2+2] photocycloaddition of ethylene to (5R)-5-menthyloxy-2[5H]-furanone **1** and other 5-alkyloxy-2[5H]-furanones (Scheme 1) has been studied.[6,7] A remarkable influence of the achiral substituent R at β position on the diastereoselectivity, has been observed.



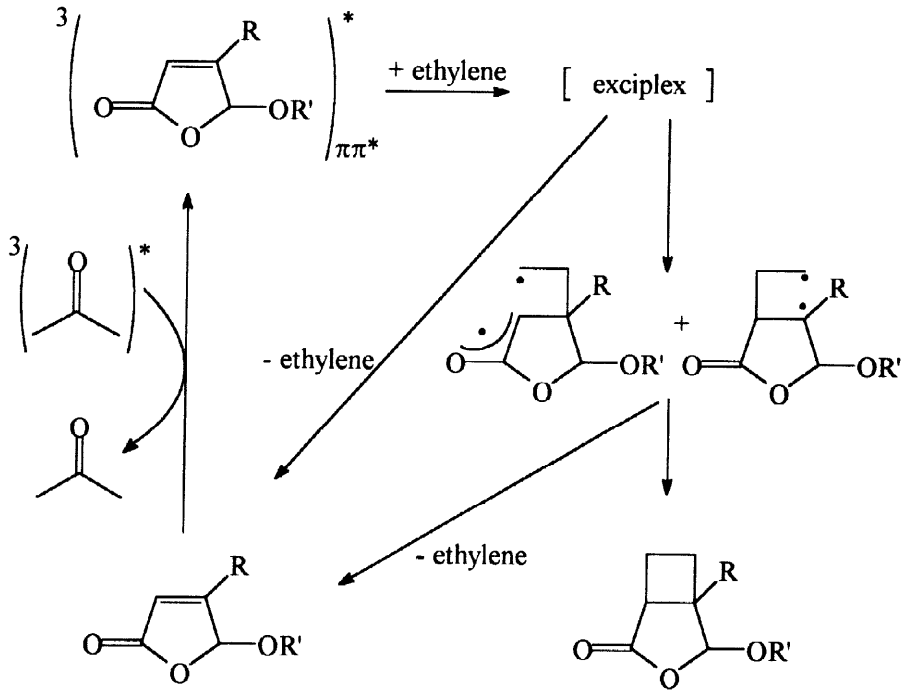
R' = Me, Et, *i*-Pr				
	R = H	4	:	1
	R = *i*-Pr	1	:	3.6
	R = Ph	2.6	:	1

Scheme 1: Diastereoselectivity of the photochemical [2+2] cycloaddition of ethylene to different 5-alkyloxy-2[5H]-furanones.

5-Alkoxy-2[5H]-furanones can be electronically excited by absorption of photons or most commonly by sensitisation (Scheme 2). The photochemical reaction proceeds from the $^3\pi\pi^*$ state. A triplet exciplex generated,[4f] in the first step with the alkene, reacts towards more stable 1,4 biradicals or returns to the substrates in their ground state. The biradical intermediates have also two possibilities to react. Either they form the final products (cyclobutanes) or dissociate to furnish the starting compounds in the ground state.

E-mail: norbert.hoffmann@univ-reims.fr - Fax: intern. + 33 3 26 05 31 66

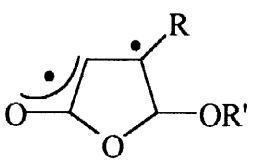
0040-4020/98/$19.00
PII: S0040-4020(98)00171-9



Scheme 2: Mechanism of the photosensitized [2+2] cycloaddition of ethylene to 5-alkoxy-2[5H]furanones.

In the case of simple cyclic enones (eg. cyclopentenone, cyclohexenone) reacting with substituted alkenes, competition between these two processes was reported to explain the observed regioselectivity. The interpretation was essentially justified by trapping of different 1,4 biradical intermediates by H_2Se.[5] A different regioselectivity was observed for the cycloadducts and the trapping products.

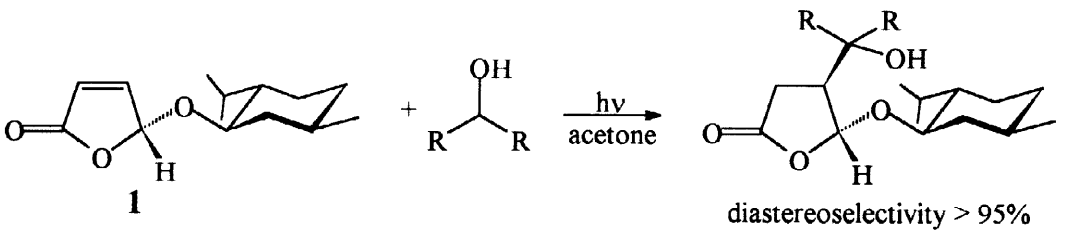
In order to get information on the diastereoselection of the photocycloaddition of ethylene and 5-alkoxy-2[5H]-furanones, a temperature effect on the ratio of diastereoisomers was determined.[7] The diastereoisomeric ratio was also found to be influenced significantly by substituents at the β position (Scheme 1). It has been concluded that the diastereoselectivity is predominantly generated during the formation of 1,4 diradicals. Therefore, the diastereoselection is governed by the structure of the vibrationally relaxed $^3\pi\pi^*$ excited sate of furanones. The structure of the $^3\pi\pi^*$ sate is different from the structure in the ground state, since the electrons of the π bond between the α and the β carbon are partially deconjugated with formation of an oxoallyl radical and an alkyl radical moiety (Scheme 3). The influence of the acetal centre is diminished, while the achiral substituent R gains influence.[7]



Scheme 3: $^3\pi\pi^*$ excited and vibrationally relaxed furanones have diradical structure.

In contrast to addition reactions of **1** in the ground state which are known to proceed diastereospecifically with respect to the chiral acetal centre, products of the photochemical [2+2] cycloaddition were obtained with moderate or low diastereoselectivity.

For example, the addition of photochemically generated symmetric ketyl radicals to **1** is completely diastereoselective (Scheme 4).[8] The same diastereoselectivity was observed for other ground state reactions of **1**.[9]



Scheme 4: Photochemical induced radical addition of alcohols to (5R)-5-menthyloxy-2[5H]-furanone **1**.

The observation that cycloaddition reactions of 5-alkyloxy-2[5H]-furanones from its $^3\pi\pi^*$ excited state are less diastereoselective while the addition of radical species to these furanones in its ground state are diastereospecific led us to the hypothesis that cycloaddition of photochemical excited cycloenones to (5R)-5-menthyloxy-2[5H]-furanone **1** might be diastereospecific with respect to the acetal centre of the furanone, since photochemically excited and vibrationally relaxed cyclenones have essentially free radical properties.

In agreement with this idea, several examples are known, where the [2+2] photocycloaddition of $^3\pi\pi^*$ excited enones to alkenes are highly diastereoselective with respect to a chiral centre adjacent to the olefinic bond.[10]

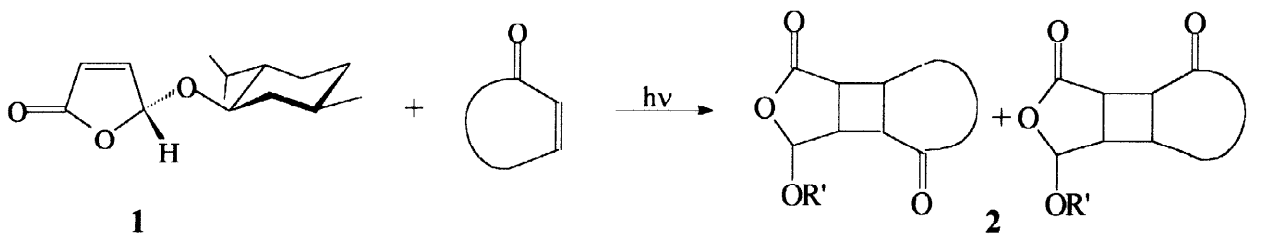
Cycloenones like cyclopentenone having their lowest absorption bands at lower energies than alkyloxyfuranones, can be excited selectively in the presence of furanones. For the same reason, the triplet energies of cyclic enones were expected to range below the corresponding energies of alkoxyfuranones. Therefore, sensitisation of the furanones by the cyclic enones should not be an important process.

Results and Discussion

We started our investigation with the irradiation of cyclopentenone at λ = 366 nm, in acetonitrile, in the presence of (5R)-5-menthyloxy-2[5H]-furanone **1** (Scheme 5, Table: run 1). Irradiation at this wavelength provided the best results. The isolated products were formed under kinetic control (irreversible reaction). Four stereoisomers of mixed adducts of **1** and cyclopentenone were formed in equal quantity. Contrary to our initial estimation, no facial stereoselectivity ((**2a** + **2b**) : (**2c** + **2d**) = 1 : 1) was obtained. Interestingly, an important regioselectivity ((**2a** + **2c**) : (**2b** + **2d**) = 8 : 1) was observed, when the reaction was carried out in *n*-hexane as solvent (run 2). The formation of the less polar regioisomers **2a** and **2c** is favoured by the low polarity of this

solvent. No endo-cycloadducts could be detected in the reaction mixture and small amounts of cyclopentenone dimers (5 %) were also isolated.

The absence of facial selectivity in the approach of cyclopentenone to the chiral furanone might indicate that an energy transfer between the $^3\pi\pi^*$ excited state of cyclopentenone to the chiral furanone **1** was involved as indicated in Scheme 6. The cycloaddition process would implicate the triplet excited state of **1** and cyclopentenone in its ground state to generate the 1,4 diradical intermediates. In the T_1 state of **1** the (C-C)-π bond has been cleaved to generate a diradical species (Scheme 3). The considerable modification of the structure has direct implications on the steric side differentiation caused by the 5-alkoxy substituent in the neighbourhood of the reaction centre (for details see ref.[7]). Even a two step or multi step selection process, as it has been discussed in the literature for this kind of reactions,[5,11] cannot improve the stereoselectivity significantly. The product ratios of the regio isomers and the exo/endo isomers are also in accordance with reactions from $^3\pi\pi^*$ excited furanones.



1 **2**

different stereoisomers

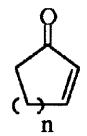
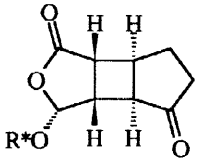
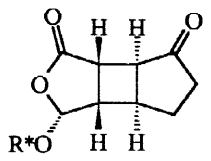
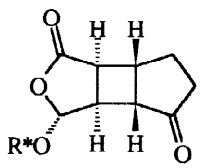
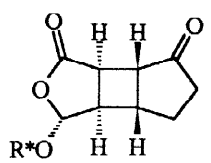
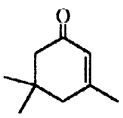
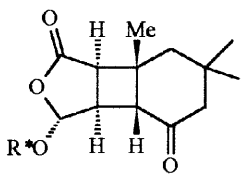
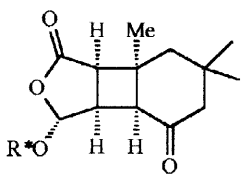
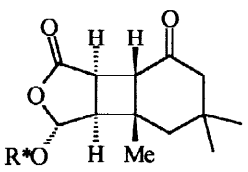
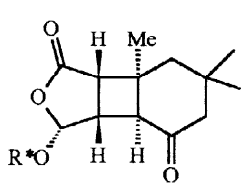
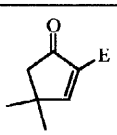
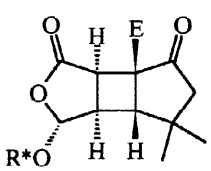
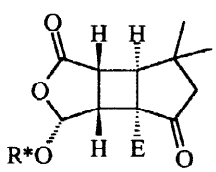
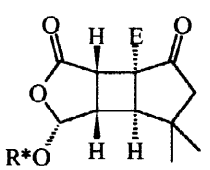
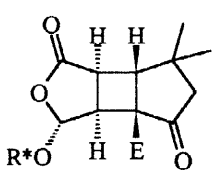
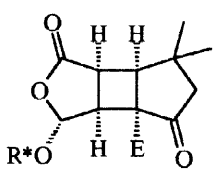
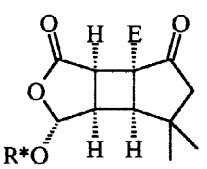
Scheme 5: Photochemical [2+2] cycloaddtition of cyclic enones to **1** providing different stereoisomers of cyclobutanes **2**.

Based on the fact that furanones (α,β-unsaturated lactones) have higher singlet excitation energies, it has been assumed previously that the corresponding triplet energies should also be higher than those of the enones. However, recent theoretic treatments of the problem leads to the conclusion that the triplet energy of the furanone and the cyclic enones are rather comparable.[12] Further on, it has been shown that energy transfer from the photochemical excited enone to an alkyne is also possible.[13]

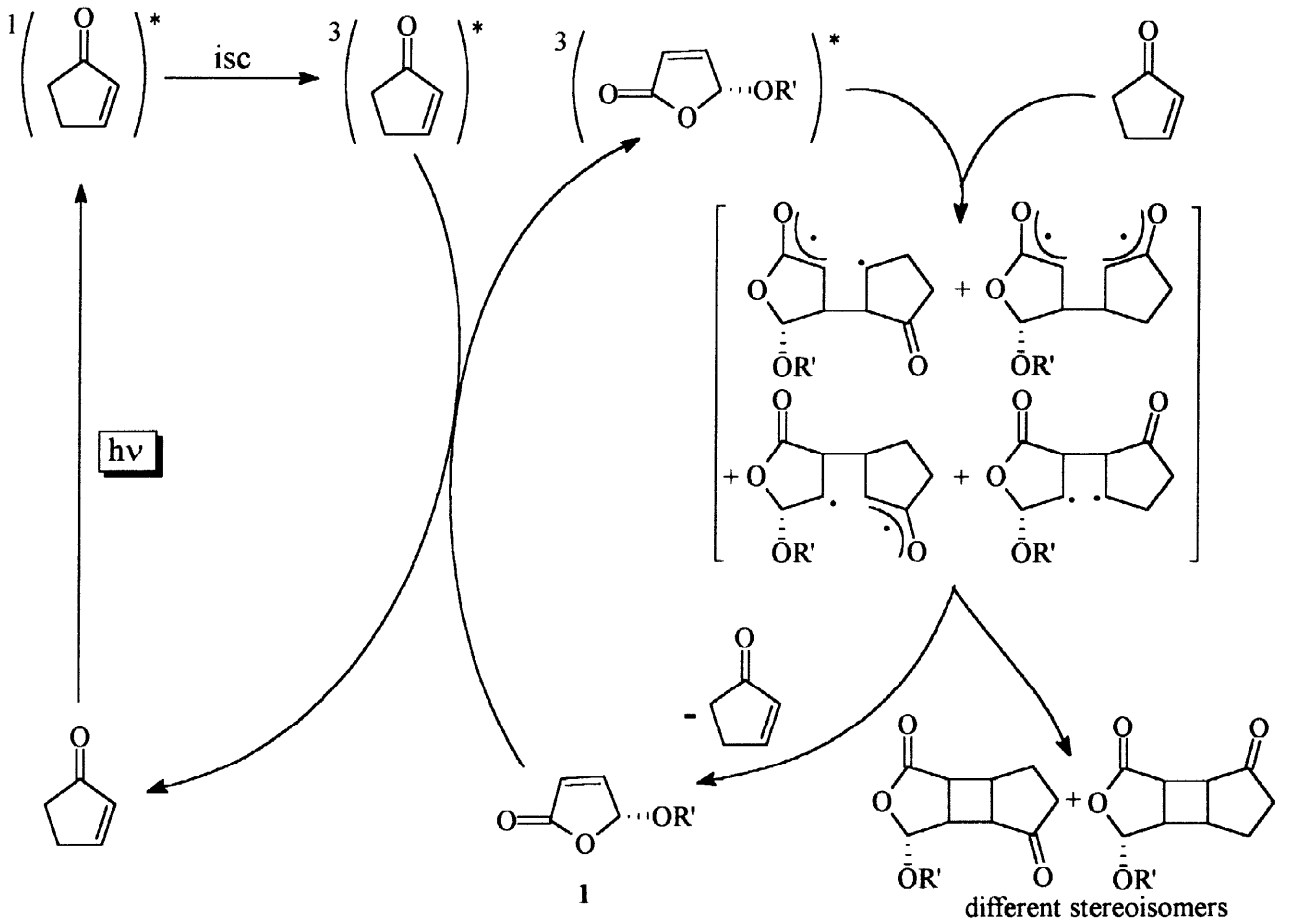
In order to avoid such an energy transfer from the excited enone, we anticipated that an easier deformation of the excited enone or an increase of the electrophilic character of the enone should decrease the energy level of the corresponding $^3\pi\pi^*$ excited state and the energy transfer would become unfavourable.

Irradiation in the same conditions at λ = 366 nm, in acetonitrile and in the presence of **1**, cyclohexenone, cycloheptenone and cyclooctenone gave no mixed cycloadducts (Table, runs 3 - 5). Cyclodimers of the cycloenone, which were efficiently formed, were the only new isolable products from the reaction. The high yields of cyclodimers indicates that the triplet excited state of these enones has been produced. Other more efficient deactivation pathways than the energy transfer have to be considered too (e.g. via the ground state of the trans configuration of cyclooctenone, which is known to react with cis cyclooctenone).

Table: Results of the [2+2] photocycloaddition in acetonitrile of cyclic enones to (5R)-5-menthyloxy-2[5H]-furanone **1**.

Run	Enone	Conv (%)	Yield (%)[a]	Structure (relative quantity)	Other products (yield)
1	 n=1	90	47	 **2a** 1)  **2b** (1)  **2c** (1)  **2d** (1)	cyclodimers (5%)
2[b]	n=1	100	50	**2a** (8), **2b** (1), **2c** (8), **2d** (1).	cyclod. (6%)
3	n=2	40	80	-	cyclod.
4	n=3	100	90	-	cyclod.
5	n=4	100	80	-	cyclod.
6		45	80	 **2e** (1)  **2f** (2)  **2g** (1.5)  **2h** (1)	-
7	 E = CO_2Me **3**	100[c]	53	 **2i** (0.7)  **2j** (0.1)  **2k** (0.1)  **2l** (0.7)  **2m** (0.2)  **2n** (0.2)	-

R*OH = (-)-menthol. [a] Based on the conversion. [b] This reaction was carried out in *n*-hexane as solvent. [c]The reaction was also carried out at $\lambda = 350$ nm. The results are comparable.

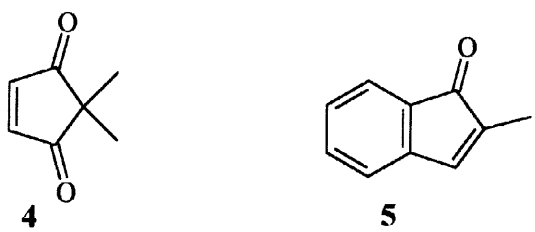


Scheme 6: Proposed mechanism for the [2+2] photocycloaddition of cyclopentenone to (5R)-5-menthyloxy-2[5H]-furanone **1** which includes an energy transfer from the excited enone to **1**.

Of particular interest was the absence of mixed cycloadducts from **1** and cyclohexenone. When this enone was replaced by the more hindered isophorone in the reaction mixture, there was a dramatic change: cyclodimers of isophorone could not be detected; mixed cycloadducts with **1** are formed with high facial selectivity ((**2e** + **2f** + **2g**) : **2h** = 82 : 18), favouring an approach of the enone anti to the menthyloxy group of the furanone; an endo product **2f** was also isolated (run 6). This facial selectivity can hardly be attributed to a cycloaddition of the excited furanone **1*** to isophorone. In this case it would be difficult to explain why **1*** is adding to isophorone and not on the corresponding and less hindered cyclohexenone or to the furanone **1** in its ground state. The formation of furanone dimers had been observed as a side reaction in the photosensitized cycloaddition of ethylene.[14] The high facial selectivity is also similar to the previous results reported for the reaction of chiral cyclopentenes with excited enones. Finally, formation of a mixture of exo and endo cycloadducts probably reflects the increased steric hindrance in the β position of the excited isophorone as compared with non substituted enones.[15]

Similarly, excited **3** was expected to have a lower triplet energy than cyclopentenone (Table, run 7). In agreement with this expectation, when **3** was irradiated in the presence of **1**, a mixture of six mixed cycloadducts could be isolated (run 7). As for isophorone, the facial selectivity favouring an anti approach relatively to the menthyloxy group of the chiral furanone, was high ((**2i** + **2l** + **2m** + **2n**) : (**2j** + **2k**) = 9:1). Here again, the appearance of significant amounts of endo cycloadducts **2m**, **2n** can be attributed to the steric hindrance of the large carboxymethyl group on **3***. No adducts similar to **2k** and **2n** could be observed in the reaction of **1** with isophorone. Their formation might be prevented by the steric effect of the methyl group in the β position.

Finally, 5,5-dimethylcyclopent-2-ene-1,4-dione **4** and 2-methylindenone **5** (Scheme 7) did not furnish mixed cycloadducts when irradiated in the same conditions and only degradation of these products could be detected, although **4** and **5** should have lower triplet energies than **1** due to the substitution with electronically active groups.[16]



4 **5**

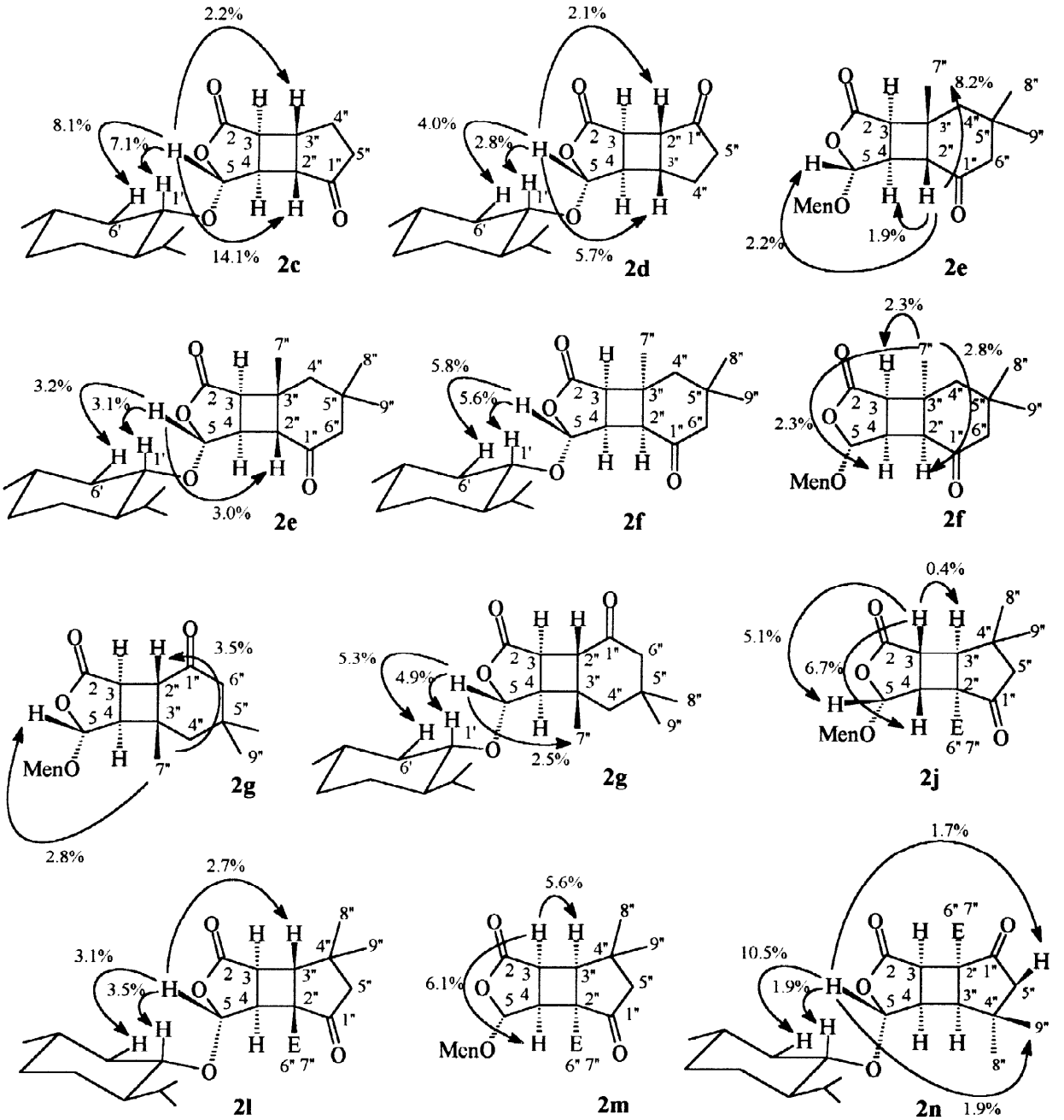
Scheme 7

Determination of the structures

The assignment of the syn/anti isomers with respect to the menthyloxy substituent was essentially based on the coupling constant of the acetalic centre with the proton in position 4. In the case of the anti isomers **2c**, **2d**, **2e**, **2f**, **2g**, **2i**, **2l**, **2m** and **2n**, small or no coupling is observed while important coupling constants are measured for the same protons of the syn isomers **2a**, **2b**, **2h**, **2j** and **2k**.[7,14] The assignment of the regio and the exo/endo isomers was based on nOe measurements (Scheme 8).

Conclusion

[2+2] Photocycloadditon of (5R)-5-menthyloxy-2[5H]-furanone **1** can be carried out with a number of cyclic enones. The diastereoselectivity observed in these reactions indicates an energy transfer from the triplet excited cyclopentenone to the furanone **1**. The $^3\pi\pi^*$ excited **1** reacts with ground state cyclopentenone to yield cyclobutanes without facial diastereoselectivity. The best values for facial selectivity (1/8 and1/9) are obtained when **1** was irradiated with isophorone and the enone ester **3**. In these cases energy transfer from the $^3\pi\pi^*$ excited enone to **1** becomes unefficient. High facial diastereoselectivity in the [2+2] photocycloaddition of cyclic enones to (5R)-5-menthyloxy-2[5H]-furanone **1** is obtained only if **1** reacts from its ground state, while low diastereoselectivity is observed when **1** reacts at its T_1 state via sensitisation.



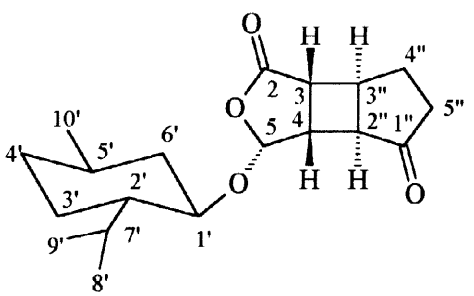
Scheme 8: Nuclear Overhouser effects detected in the mixed [2+2] cycloadducts **2**.

Experimental Section

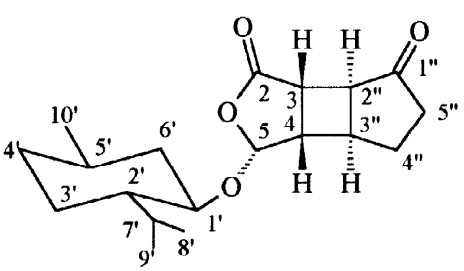
General Remarks: Melting points have been determined with a Büchi apparatus. IR spectra were recorded as KBr pellet or as film on a Spectrafile IR^{TM} Plus MIDAC. Mass spectra were recorded on a JEOL D-300 spectrometer. Microanalyses were performed by the analytical department of the UFR Sciences of the Université de Reims. NMR data were recorded at 250 MHz for ^{1}H and at 62 MHz for ^{13}C on a Bruker spectrometer. $CDCl_3$ was used as solvent. Chemical shifts are reported in ppm relative to TMS. Coupling

constants are denoted in Hz. Optical rotation values were obtained from a Pelkin-Elmer 241 spectrometer using a sodium lamp at 589 nm and a mercury lamp at 578, 546, 436 and 365 nm in dichloromethane as solvent. The (5R)-5-menthyloxy-2[5H]-furanone **1** was synthesized according to the procedure previously described.[17] 2-Carboxymethyl-4,4-dimethylcyclopent-2-en-1-one **3** has been prepared from dimedone.[18] Acetonitrile was distilled on calcium hydride and *n*-hexane was distilled.

Irradiation of **1**: A solution of 12 - 15 mmol of (5R)-5-menthyloxy-2[5H]-furanone (4.10^{-2} mol/L) and the 3 - 4 mmol of cyclic enone (10^{-2} mol/L) was irradiated at 350 nm (Rayonet, 30°C) or at 366 nm (Philips HPW 125W lamp, 20°C) during 60 - 150 h. The solution was then evaporated and the resulting crude oil was purified by flash chromatography (silca gel, ethylacetate / petroleum ether 1:5).

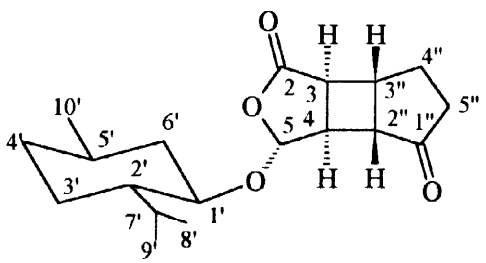


Cyclobutane **2a**: Yield: 103 mg.
$C_{19}H_{28}O_4$; M = 320.43; F = 87°C. IR: ν = 2945, 2925, 2870, 2805, 1775, 1740, 1360, 1165, 1155, 1040, 955, 910 cm^{-1}. MS (70 eV): *m/z* (%) = 320 (2.5, M^+), 276 (0.3), 264 (0.3), 248 (1), 238 (1.8), 183 (7), 165 (100), 139 (62), 95(41). Anal.: found: C 70.98, H 8.59; calculated C 71.22, H 8.81. ^1H NMR ($CDCl_3$): δ = 0.84 (d, J = 6.7 Hz, 3H, H8'-H9'), 0.91 (d, J = 6.7 Hz, 3H, H8'-H9'), 0.94 (d, J = 7.6 Hz, 3H, H10'), 0.81-1.10 (m, 3H, H3'ax-H4'ax-H6'ax), 1.15-1.47 (m, 2H, H2'-H5'), 1.58-1.73 (m, 2H, H3'eq-H4'eq), 2.03-2.20 (m, 3H, H6'eq-H7'-H4''), 2.22-2.36 (m, 1H, H4''), 2.44 (ddd, J = 19.4/8.7/3.8 Hz, 1H, H5''), 2.65 (ddd, J = 19.4/8.7/3.8 Hz, 1H, H5''), 2.89 (td, J = 6.5/2.7 Hz, 1H, H4), 2.98 (dd, J = 6.5/3.6Hz, 1H, H2''), 3.11 (m, 1H, H3''), 3.23 (m, 1H, H3), 3.64 (td, J = 10.7/4.2 Hz, 1H, H1'), 5.87(d, J = 6.5 Hz, 1H, H5) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.8 (C8'-C9'), 20.9 (C8'-C9'), 22.2 (C10'), 23.2 (C3'), 25.8 (C7'), 27.3 (C4''), 31.4 (C5'), 34.2 (C4'), 36.4 (C5''), 39.1 (C3''), 39.2 (C4), 39.6 (C6'), 41.9 (C3), 43.2 (C2''), 47.7 (C2'), 78.3 (C1'), 100.0 (C5), 176.6 (C2), 219.2 (C1'') ppm.
$[\alpha_D]^{21}$ = -74.0, $[\alpha_{578}]^{21}$ = -78.0, $[\alpha_{546}]^{21}$ = -85.0, $[\alpha_{436}]^{21}$ = -109.0, $[\alpha_{365}]^{21}$ = -20.0; (c = 0.98).

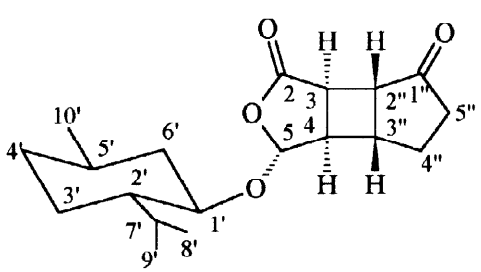


Cyclobutane **2b**: Yield: 99 mg.
$C_{19}H_{28}O_4$; M = 320.43; F = 135°C. IR: ν = 2955, 2925, 2870, 2805, 1780, 1740, 1360, 1165, 1155, 1100, 940, 920 cm^{-1}. MS (70 eV): *m/z* (%) = 320 (4.5, M^+), 276 (0.7), 261 (1.0), 249 (1.3), 235 (3.2), 206 (4), 183 (7), 165 (100), 138 (62), 83 (52). Anal.: found: C 70.96, H 8.90; calculated: C 71.22, H 8.81. ^1H NMR ($CDCl_3$): δ = 0.85 (d, J = 6.7 Hz, 3H, H8'-H9'), 0.93 (d, J = 7.2 Hz, 3H, H10'), 0.94 (d, J = 6.7 Hz, 3H, H8'-H9'), 0.83-1.10 (m, 3H, H3'ax-H4'ax-H6'ax), 1.19-1.47 (m, 2H, H2'-H5'), 1.62-1.75 (m, 2H, H3'eq-H4'eq), 1.88-2.09 (m, 3H, H6'eq-H4''), 2.19 (dsept, J = 6.7/2.3 Hz, 1H, H7'), 2.34-2.71 (m, 2H, H5''), 2.75 (d, J = 6.1 Hz, 1H, H2''), 2.88 (td, J = 6.5/5.3 Hz, 1H, H4), 2.94 (dd, J = 6.5/2.3 Hz, 1H, H3), 3.54 (m, 1H, H3''), 3.64 (td, J = 10.7/4.2 Hz, 1H, H1'), 5.80 (d, J = 5.3 Hz, 1H, H5)

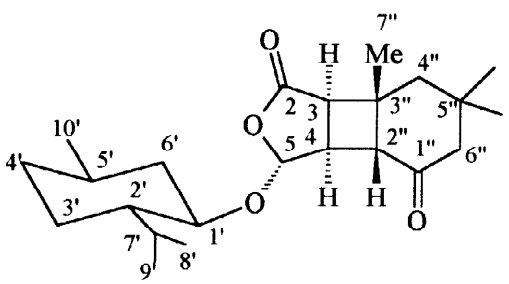
ppm. ^{13}C NMR ($CDCl_3$): δ = 15.9 (C8'-C9'), 20.9 (C8'-C9'), 22.2 (C10'), 23.2 (C3'), 25.7 (C7'), 26.8 (C4''), 31.4 (C5'), 33.7 (C3''), 34.3 (C4'), 35.6 (C5''), 40.0 (C6'), 40.5 (C4), 42.6 (C3), 45.7 (C2''), 47.8 (C2'), 78.7 (C1'), 101.0 (C5), 174.9 (C2), 217.4 (C1'') ppm.
$[\alpha_D]^{21}$ = -254.0, $[\alpha_{578}]^{21}$ = -270.1, $[\alpha_{546}]^{21}$ = -315.3, $[\alpha_{436}]^{21}$ = -625.1, $[\alpha_{365}]^{21}$ = -1270.1, (c=1.01).



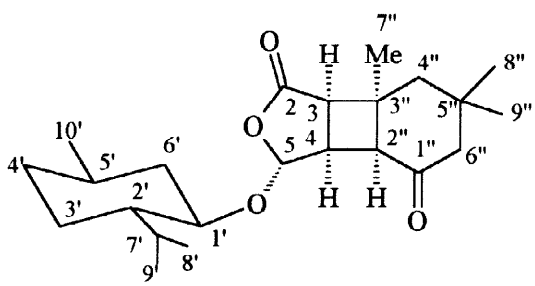
Cyclobutane **2c**: Yield: 105 mg.
$C_{19}H_{28}O_4$; M = 320.43; F = 159°C. IR: ν = 3000, 2960, 2930, 2875, 1780, 1740, 1360, 1170, 1145, 1100, 925, 910 cm^{-1}. MS (70 eV): *m/z* (%) = 320 (0.2, M^+), 261 (0.1), 248 (0.3), 238 (0.7), 206 (2.1), 165 (41), 138 (47), 83 (100). Anal.: found: C 70.97, H 8.95; calculated: C 71.22, H 8.81. ^1H NMR ($CDCl_3$): δ = 0.76 (d, J = 7.2 Hz, 3H, H10'), 0.83 (d, J = 6.9 Hz, 3H, H8'-H9'), 0.92 (d, J = 6.9 Hz, 3H, H8'-H9'), 0.83-1.16 (m, 3H, H3'ax-H4'ax-H6'ax), 1.22-1.73 (m, 4H, H2'-H3'eq-H4'eq-H5'), 1.99 (dsept, J = 6.9/2.3 Hz, 1H, H7'), 2.22-2.30 (m, 2H, H6'eq-H4''), 2.33 (d, J = 14.9/6.2 Hz, 1H, H4''), 2.45 (dd, J = 9.0/6.3 Hz, 1H, H5''), 2.65 (dd, J = 9.0/6.3 Hz, 1H, H5''), 2.78 (m, 2H, H3-H2''), 3.04 (m, 2H, H4-H3''), 3.58 (td, J = 10.7/4.2, 1H, H1'), 5.67(s, 1H, H5) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.6 (C8'-C9'), 20.7 (C8'-C9'), 22.2 (C10'), 23.1 (C3'), 25.4 (C7'), 26.6 (C4''), 31.5 (C5'), 34.2 (C4'), 35.7 (C5''), 37.7 (C3''), 38.2 (C4), 39.8 (C6'), 44.7 (C3), 46.4 (C2''), 47.7 (C2'), 76.3 (C1'), 102.9 (C5), 176.5 (C2), 216.6 (C1'') ppm.



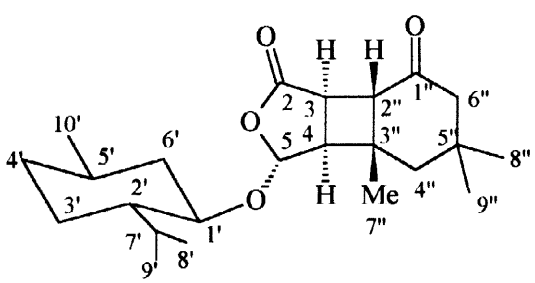
Cyclobutane **2d**: Yield: 98 mg.
$C_{19}H_{28}O_4$; M = 320.43; F = 112°C. IR: ν = 2960, 2920, 2870, 1770, 1720, 1455, 1390, 1355, 1130, 930 cm^{-1}. MS (70 eV): *m/z* (%) = 320 (0.9, M^+), 261 (2.1), 238 (3.7), 220 (4), 206 (2.1), 183 (11), 165 (100), 138 (47), 81 (45). Anal.: found: C 70.93, H 8.64; calculated: C 71.22, H 8.81. ^1H NMR ($CDCl_3$): δ = 0.76 (d, J = 6.9 Hz, 3H, H8'-H9'), 0.85 (d, J = 6.9 Hz, 3H, H8'-H9'), 0.93 (d, J = 7.6Hz, 3H, H10'), 0.81-1.17 (m, 3H, H3'ax-H4'ax-H6'ax), 1.22-1.47 (m, 2H, H2'-H5'), 1.68-1.73 (m, 2H, H3'eq-H4'eq), 1.97 (dsept, J = 6.9/2.3 Hz, 1H, H7'), 2.06-2.09 (m, 1H, H6'eq), 2.22-2.34 (m, 2H, H4''), 2.44 (ddd, J = 19.7/7.6/3.4 Hz, 1H, H5''), 2.63 (ddd, J = 19.7/11.8/9.5 Hz, 1H, H5''), 2.79 (m, 2H, H3-H2''), 3.04 (m, 2H, H4-H3''), 3.58 (td, J = 10.7/4.2 Hz, 1H, H1') 5.63 (s, 1H; H5) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.8 (C8'-C9'), 20.7 (C8'-C9'), 22.1 (C10'), 23.2 (C3'), 25.5 (C7'), 26.9 (C4''), 31.7 (C5'), 34.0 (C4'), 35.6 (C5''), 37.9 (C3''), 38.1 (C4), 39.9 (C6'), 44.1 (C3), 46.1 (C2''), 47.6 (C2'), 77.2 (C1'), 101.6 (C5), 177.5 (C2), 216.9 (C1'') ppm.
$[\alpha_D]^{21}$ = -220.0, $[\alpha_{578}]^{21}$ = -231.1, $[\alpha_{546}]^{21}$ = -286.3, $[\alpha_{436}]^{21}$ = -321.1, $[\alpha_{365}]^{21}$ = -362.1, (c=1.02).



Cyclobutane **2e**: Yield: 82 mg.
$C_{23}H_{36}O_4$; M = 376.59; F = 128°C. IR: ν = 2960, 2920, 2870, 1770, 1720, 1455, 1390, 1355, 1130, 900 cm^{-1}. MS (70 eV): *m/z* (%) = 377 (0.3, M^+), 318 (0.3), 277 (19), 221 (36), 191 (42), 139 (100), 109 (55), 81 (85). Anal. found: C 73.08, H 9.67; calculated: C 73.35, H 9.66. ^{1}H NMR ($CDCl_3$): δ = 0.83 (d, J = 6.9 Hz, 3H, H8'-H9'), 0.88 (d, J = 6.9 Hz, 3H, H8'-H9'), 0.92 (d, J = 7.6 Hz, 3H, H10'), 0.81-1.22 (m, 3H, H3'ax-H4'ax-H6'ax), 1.12 (s, 3H, H8''-H9''), 1.20 (s, 3H, H7''), 1.21 (s, 3H, H8''-H9''), 1.20-1.45 (m, 2H, H2'-H5'), 1.58 (d, J = 13.4 Hz, 1H, H4''), 1.59-1.69 (m, 2H, H3'eq-H4'eq), 2.02 (d, J = 13.4 Hz, 1H; H4''), 2.04-2.15 (m, 2H, H6'eq-H7'), 2.33 (m, 2H, H6''), 2.90 (dd, J = 3.4/1.7 Hz, 1H, H2''), 3.43-3.50 (m, 2H, H4-H3), 3.59(td, J = 10.7/4.2 Hz, 1H, H1'), 5.74 (dd, J = 3.0/1.7 Hz, 1H, H5) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.3 (C8'-C9'), 20.7 (C8'-C9'), 22.2 (C10'), 23.5 (C3'), 24.8 (C7''), 26.1 (C7'), 31.4 (C5'), 33.3 (C5''), 34.2 (C4'), 35.0 (C8''-C9''), 35.7 (C8''-C9''), 39.5 (C6'), 41.3 (C4), 42.6 (C3''), 45.3 (C4''), 47.6 (C2'), 49.0 (C3), 51.8 (C2''), 52.5 (C6''), 78.3 (C1'), 99.8 (C5), 173.0 (C2), 204.2 (C1'') ppm.
$[\alpha_D]^{21}$ = -166.6, $[\alpha_{578}]^{21}$ = -173.3, $[\alpha_{546}]^{21}$ = -196.6, $[\alpha_{436}]^{21}$ = -304.9, $[\alpha_{365}]^{21}$ = -354.9, (c=0.96).



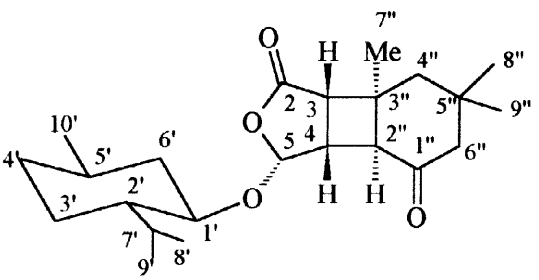
Cyclobutane **2f**: Yield: 158 mg.
$C_{23}H_{36}O_4$; M = 376.59; F = 109°C. IR: ν = 2920, 2860, 1780, 1695, 1465, 1340, 1090, 930 cm^{-1}. MS (70 eV): *m/z* (%) = 377 (4, M^+), 362 (1), 332 (3), 279 (4), 221 (60), 140 (55), 139 (63), 83 (41), 69 (69), 55 (100). Anal.: found: C 73.04, H 9.78; calculated: C 73.35, H 9.66. ^{1}H NMR ($CDCl_3$): δ = 0.75 (d, J = 6.9 Hz, 3H, H8'-H9'), 0.85 (d, J = 6.9 Hz, 3H, H8'-H9'), 0.89 (s, 3H, H8''-H9''), 0.92 (d, J = 7.6 Hz, 3H, H10'), 1.00 (s, 3H, H8''-H9''), 0.74-1.07 (m, 3H, H3'ax-H4'ax-H6'ax), 1.27-1.47 (m, 4H, H2'-H5'-H4''), 1.52 (s, 3H, H7''), 1.57-1.69 (m, 2H, H3'eq-H4'eq), 1.89-2.01 (m, 2H, H6'eq-H7'), 2.07 (d, J = 18.0 Hz, 1H, H6''), 2.22 (d, J = 18.0 Hz, 1H, H6''), 2.72 (dd, J = 11.1/1.5 Hz, 1H, H4), 2.93 (dd, J = 6.9/2.5 Hz, 1H, H2''), 3.23 (dd, J = 11.1/1.5 Hz, 1H, H3), 3.46 (td, J = 10.7/4.2 Hz, 1H, H1'), 5.50 (s, 1H, H5) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.5 (C8'-C9'), 20.8 (C8'-C9'), 22.1 (C10'), 23.1 (C3'), 25.3 (C7'), 27.4 (C8''-C9''), 31.1 (C8''-C9''), 31.4 (C5'), 32.2 (C5''), 32.9 (C7''), 34.2 (C4'), 39.3 (C3''), 39.5 (C4), 39.9 (C6'), 42.9 (C4''), 47.7 (C2'), 48.8 (C3), 49.4 (C2''), 53.5 (C6''), 76.9 (C1'), 100.4 (C5), 176.4 (C2), 212.4 (C1'') ppm.
$[\alpha_D]^{21}$ = +50.0, $[\alpha_{578}]^{21}$ = +52.2, $[\alpha_{546}]^{21}$ = +64.4, $[\alpha_{436}]^{21}$ = +162.2, $[\alpha_{365}]^{21}$ = +471.8, (c=1.01).



Cyclobutane **2g**: Yield: 119 mg.
$C_{23}H_{36}O_4$; M = 376.59; F = 114°C. IR: ν = 2960, 2920, 2870, 1780, 1705, 1455, 1340, 1290, 1155, 1090, 1040, 930 cm^{-1}. MS (70 eV): *m/z* (%) = 377 (4, M^+), 358 (1.5), 330 (1.2), 251 (1.5), 239 (9), 221 (92), 194 (72), 139 (67), 83 (100). Anal.: found: C 73.16, H 9.57; calculated: C 73.35, H 9.66. ^{1}H NMR

($CDCl_3$): δ = 0.76 (d, J = 6.9 Hz, 3H, H8'-H9'), 0.85 (d, J = 6.9 Hz, 3H, H8'-H9'), 0.94 (d, J = 7.6 Hz, 3H, H10'), 0.74-1.02 (m, 3H, H3'ax-H4'ax-H6'ax), 1.07 (s, 3H, H8''-H9''), 1.08 (s, 3H, H8''-H9''), 1.38 (s, 3H, H7''), 1.29-1.49 (m, 2H, H2'-H5'), 1.55 (d, J = 14.5 Hz, 1H, H4''), 1.53-1.70 (m, 2H, H3'eq-H4'eq), 1.75 (d, J = 14.5 Hz, 1H, H4''), 1.90-2.17 (m, 2H, H6'eq-H7'), 2.23 (m, 2H, H6''), 2.57 (dd, J = 3.6/1.3 Hz, 1H, H2''), 2.78 (dd, J = 7.8/1.3 Hz, 1H, H3), 3.31 (dd, J = 7.8/3.6 Hz, 1H, H4), 3.54 (td, J = 10.7/4.2 Hz, 1H, H1'), 5.62 (s, 1H, H5) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.6 (C8'-C9'), 20.7 (C8'-C9'), 22.2 (C10'), 23.1 (C3'), 25.3 (C7'), 26.2 (C7''), 28.7 (C8''-C9''), 31.3 (C5'), 31.6 (C8''-C9''), 34.2 (C4'), 35.3 (C5''), 37.6 (C4), 39.7 (C6'), 40.6 (C3''), 47.7 (C2'), 49.1 (C3), 49.8 (C4''), 51.9 (C2''), 52.5 (C6''), 76.3 (C1'), 100.0 (C5), 177.7 (C2), 209.9 (C1'') ppm.

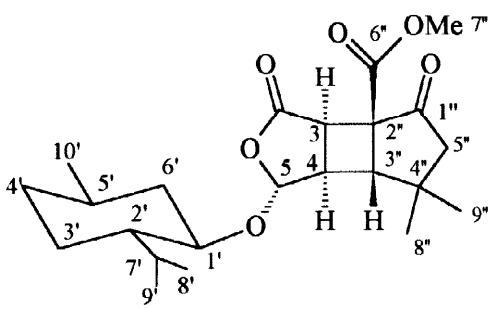
$[\alpha_D]^{21}$ = -67.7, $[\alpha_{578}]^{21}$ = -69.2, $[\alpha_{546}]^{21}$ = -77.7, $[\alpha_{436}]^{21}$ = -114.1, $[\alpha_{365}]^{21}$ = -110.5, (c=0.99).



Cyclobutane **2h**: Yield: 80 mg.

$C_{23}H_{36}O_4$; M = 376.59; F = 121°C. IR: ν = 2960, 2915, 2875, 1780, 1710, 1455, 1335, 1290, 1160, 1100, 1045, 925 cm^{-1}. MS (70 eV): ***m/z*** (%) = 377 (0.9, M^+), 358 (2), 332 (2), 251 (1.5), 239 (13), 221 (78), 194 (62), 139 (100). Anal.: found: C 73.19, H 9.61; calculated: C 73.35, H 9.66. ^1H NMR ($CDCl_3$): δ = 0.83 (d, J = 6.9 Hz, 3H, H8'-H9'), 0.87 (d, J = 6.9 Hz, 3H; H8'-H9'), 0.88 (s, 3H, H8''-H9''), 0.89 (d, J = 7.2 Hz, 3H, H10'), 0.78-1.09 (m, 3H, H3'ax-H4'ax-H6'ax), 1.04 (s, 3H, H8''-H9''), 1.18-1.44 (m, 2H, H2'-H5'), 1.46 (s, 3H, H7''), 1.52-1.72 (m, 3H, H3'eq-H4'eq-H4''), 1.83-1.95 (m, 1H, H6'eq), 1.96 (d, J = 14.1 Hz, 1H, H4''), 2.07-2.22 (m, 1H, H7'), 2.09 (d, J = 16.8 Hz, 1H, H6''), 2.67 (d, J = 16.8 Hz, 1H, H6''), 2.80 (d, J = 3.1 Hz, 1H, H2''), 2.93 (d, J = 8.7 Hz, 1H, H3), 3.41-3.69 (m, 2H, H1'-H4), 5.73 (d, J = 7.2 Hz, 1H, H5) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.3 (C8'-C9'), 21.0 (C8'-C9'), 22.0 (C10'), 22.5 (C3'), 25.3 (C7'), 27.7 (C7''), 30.6 (C8''-C9''), 31.4 (C5''), 31.9 (C8''-C9''), 32.9 (C5'), 33.4 (C4), 33.8 (C4'), 37.0 (C3''), 40.3 (C6'), 43.0 (C4''), 46.7 (C3), 48.0 (C2'), 50.8 (C6''), 53.3 (C2''), 81.8 (C1'), 104.0 (C5), 175.1 (C2), 211.1 (C1'') ppm.

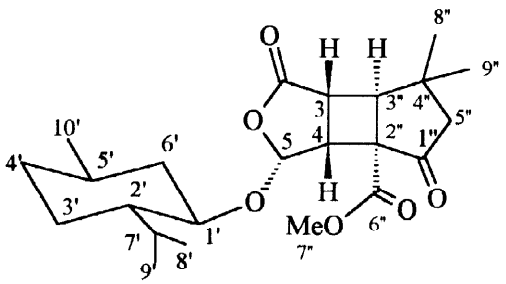
$[\alpha_D]^{21}$ = -76.7, $[\alpha_{578}]^{21}$ = -89.2, $[\alpha_{546}]^{21}$ = -107.3, $[\alpha_{436}]^{21}$ = -129.3, $[\alpha_{365}]^{21}$ = -141.5, (c=0.99).



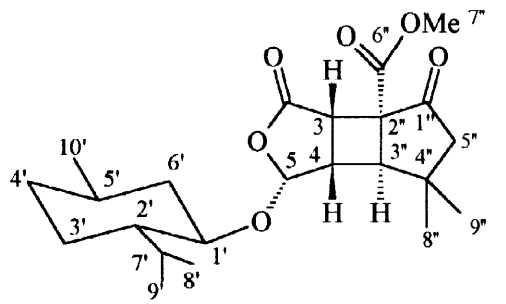
Cyclobutane **2i**: Yield: 275 mg.

$C_{23}H_{34}O_6$; M = 406.23. IR: ν = 2945, 2870, 1710, 1630, 1320, 1240, 1110, 1030, 935 cm^{-1}. MS (70 eV): ***m/z*** (%) = 406 (7, M^+), 323 (35), 269 (31), 251 (100), 224 (51), 192 (72), 139 (97). Anal.: found: C 67.71, H 8.56; calculated: C 67.94, H 8.43. ^1H NMR ($CDCl_3$): δ = 0.73 (d, J = 6.9 Hz, 3H, H8'-H9'), 0.84 (d, J = 6.9 Hz, 3H, H8'-H9'), 0.93 (d, J = 7.6 Hz, 3H, H10'), 0.69-1.01 (m, 3H, H3'ax-H4'ax-H6'ax), 1.05-1.45 (m, 2H, H2'-H5'), 1.16 (s, 3H, H8''-H9''), 1.25 (s, 3H, H8''-H9''), 1.58-1.72 (m, 2H, H3'eq-H4'eq), 1.88-2.09 (m, 2H, H6'eq-H7'), 2.28 (d, J = 16.9 Hz, 1H, H5''), 2.58 (d, J = 16.9 Hz, 1H, H5''), 2.80 (dd, J = 6.7/4.3 Hz, 1H, H4), 2.92 (d, J = 6.7 Hz, 1H, H3), 3.57 (td, J = 10.2/4.6 Hz,

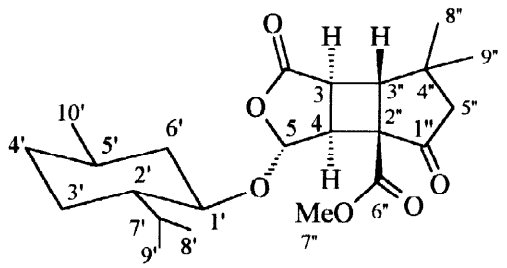
1H, H1'), 3.72 (m, 1H, H3''), 3.73 (s, 3H, H7''), 5.55 (s, 1H, H5) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.5 (C8'-C9'), 20.7 (C8'-C9'), 22.2 (C10'), 22.8 (C8''-C9''), 23.1 (C3'), 25.4 (C7'), 27.5 (C8''-C9''), 31.3 (C5'), 34.2 (C4'), 36.2 (C4''), 38.6 (C4), 39.7 (C6'), 41.1 (C3), 47.6 (C2'), 52.4 (C5''), 52.7 (C3''), 57.7 (C7''), 58.7 (C2''), 76.7 (C1'), 102.7 (C5), 166.6 (C6''), 173.0 (C2), 203.7 (C1'') ppm.
$[\alpha_D]^{21}$ = -18.1, $[\alpha_{578}]^{21}$ = -17.6, $[\alpha_{546}]^{21}$ = -17.6, $[\alpha_{436}]^{21}$ = -1.7, $[\alpha_{365}]^{21}$ = +93.2, (c=0.98).



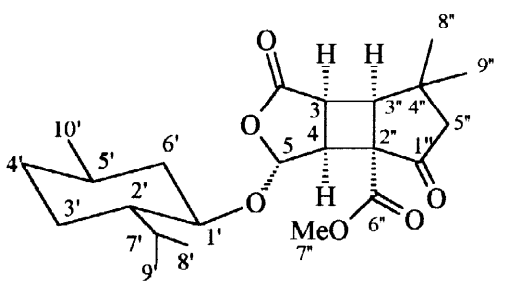
Cyclobutane **2j**: Yield: 43 mg.
$C_{23}H_{34}O_6$; M = 406.23. IR: ν = 2945, 2870, 1750, 1710, 1450, 1340, 1215, 1025, 950 cm^{-1}. MS (70 eV): *m/z* (%) = 406 (1.5, M^+), 357 (3), 269 (43), 251 (94), 237 (51), 138 (100). Anal.: found: C 67.81, H 8.30; calculated: C 67.94, H 8.43. ^{1}H NMR ($CDCl_3$): δ = 0.76 (d, J = 6.9 Hz, 3H, H8'-H9'), 0.81 (d, J = 6.9 Hz, 3H, H8'-H9'), 0.85 (d, J = 7.6 Hz, 3H, H10'), 0.72-1.02 (m, 3H, H3'ax-H4'ax-H6'ax), 1.07-1.48 (m, 2H, H2'-H5'), 1.18 (s, 3H, H8''-H9''), 1.23 (s, 3H, H8''-H9''), 1.60-1.75 (m, 2H, H3'eq-H4'eq), 2.02-2.15 (m, 2H, H6'eq-H7'), 2.23 (d, J = 18.7 Hz, 1H, H5''), 2.55 (d, J = 18.7 Hz, 1H, H5''), 2.92 (dd, J = 7.6/6.1 Hz, 1H, H3), 3.12 (dd, J = 7.6/6.9 Hz, 1H, H4), 3.23 (d, J = 6.1 Hz, 1H, H3''), 3.57 (td, J = 10.2/4.6 Hz, 1H, H1'), 3.71 (s, 3H, H7''), 5.93 (d, J = 6.9 Hz, 1H, H5) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.7 (C8'-C9'), 20.7 (C8'-C9'), 22.1 (C10'), 22.5 (C8''-C9''), 23.0 (C3'), 25.3 (C7'), 29.5 (C8''-C9''), 31.3 (C5'), 34.1 (C4'), 38.5 (C4''), 39.6 (C6'), 40.2 (C4), 41.2 (C3), 47.5 (C2'), 58.6 (C5''), 60.2 (C7''), 76.6 (C1'), 78.9 (C3''), 90.3 (C2"), 102.6 (C5), 150.8 (C6''), 173.0 (C2), 203.7 (C1'') ppm.
$[\alpha_D]^{21}$ = -126.5, $[\alpha_{578}]^{21}$ = -133.3, $[\alpha_{546}]^{21}$ = -146.2, $[\alpha_{436}]^{21}$ = -208.3, $[\alpha_{365}]^{21}$ = -184.0, (c=1.02).



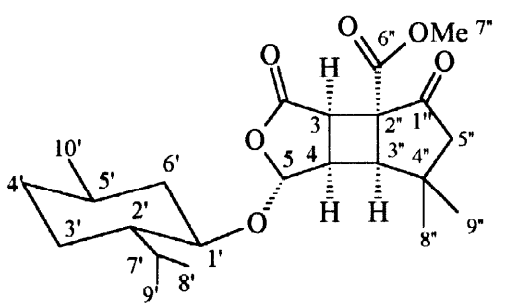
Cyclobutane **2k**: Yield: 41 mg.
$C_{23}H_{34}O_6$; M = 406.23. IR: ν = 2945, 2870, 1750, 1720, 1450, 1290, 1215, 1025, 925 cm^{-1}. MS (70 eV): *m/z* (%) = 406 (2.7, M^+), 321 (2.7), 251 (79), 234 (39), 192 (100), 136 (48). Anal.: found: C 67.62, H 8.15; calculated: C 67.94, H 8.43. ^{1}H NMR ($CDCl_3$): δ = 0.86 (d, J = 6.9 Hz, 3H, H8'-H9'), 0.93 (d, J = 6.9 Hz, 3H, H8'-H9'), 0.94 (d, J = 7.6 Hz, 3H, H10'), 0.72-0.99 (m, 3H, H3'ax-H4'ax-H6'ax), 1.04-1.47 (m, 2H, H2'-H5'), 1.05 (s, 3H, H8''-H9''), 1.09 (s, 3H, H8''-H9''), 1.60-1.74 (m, 2H, H3'eq-H4'eq), 2.02-2.28 (m, 2H, H6'eq-H7'), 2.28 (d, J = 18.3 Hz, 1H, H5''), 2.53 (d, J = 18.3 Hz, 1H, H5''), 2.95 (ddd, J = 7.3/5.7/5.3 Hz, 1H, H4), 3.21 (d, J = 7.3 Hz, 1H, H3), 3.49 (d, J = 6.1 Hz, 1H, H3''), 3.63 (td, J = 10.2/4.6 Hz, 1H, H1'), 3.77 (s, 3H, H7''), 5.80 (d, J = 5.7 Hz, 1H, H5) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.0 (C8'-C9'), 20.8 (C8'-C9'), 22.1 (C10'), 23.0 (C8''-C9''), 23.3 (C3'), 25.8 (C7'), 27.7 (C8''-C9''), 31.3 (C5'), 34.2 (C4'), 38.9 (C4''), 40.6 (C6'), 42.9 (C4), 47.8 (C2'), 48.9 (C3), 50.3 (C5''), 51.7 (C7''), 52.7 (C3''), 57.7 (C2"), 79.0 (C1'), 100.3 (C5), 166.5 (C6''), 171.2 (C2), 202.3 (C1'') ppm.
$[\alpha_D]^{21}$ = -285.5, $[\alpha_{578}]^{21}$ = -297.8, $[\alpha_{546}]^{21}$ = -342.9, $[\alpha_{436}]^{21}$ = -639.1, $[\alpha_{365}]^{21}$ = -1237.8 (c=1.00).



Cyclobutane **2l**: Yield: 283 mg.
$C_{23}H_{34}O_6$; M = 406.23. IR: ν = 2945, 2870, 2250, 1750, 1715, 1605, 1455, 1300, 1225, 1165, 1115, 935 cm^{-1}. MS (70 eV): *m/z* (%) = 406 (12, M^+), 336 (10), 267 (19), 218 (42), 192 (93), 135 (95), 121 (100). Anal.: found: C 67.73, H 8.27; calculated: C 67.94, H 8.43. ^1H NMR ($CDCl_3$): δ = 0.80 (d, J = 6.9 Hz, 3H, H8'-H9'), 0.91 (d, J = 7.6 Hz, 3H, H10'), 0.95 (s, 3H, H8''-H9''), 0.96 (d, J = 6.9 Hz, 3H, H8'-H9'), 0.74-1.04 (m, 3H, H3'ax-H4'ax-H6'ax), 1.21-1.47 (m, 2H, H2'-H5'), 1.27 (s, 3H, H8''-H9''), 1.51-1.73 (m, 2H, H3'eq-H4'eq), 1.92-2.18 (m, 2H, H6'eq-H7'), 2.14 (d, J = 16.4 Hz, 1H, H5''), 2.33 (d, J = 16.4 Hz, 1H, H5''), 2.93 (d, J = 3.4 Hz, 1H, H4), 3.02 (dd, J = 5.0/3.4 Hz, 1H, H3), 3.57 (td, J = 10.2/4.6 Hz, 1H; H1'), 3.98 (s, 3H, H7''), 4.26 (d, J = 5.0 Hz, 1H, H3''), 5.71 (s, 1H, H5) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.5 (C8'-C9'), 20.7 (C8'-C9'), 22.2 (C10'), 22.8 (C8''-C9''), 23.1 (C3'), 25.4 (C7'), 27.5 (C8''-C9''), 31.3 (C5'), 34.2 (C4'), 36.2 (C4''), 38.6 (C4), 39.7 (C6'), 41.1 (C3), 47.6 (C2'), 52.4 (C5''), 52.7 (C3''), 57.7 (C7''), 58.7 (C2''), 76.7 (C1'), 102.7 (C5), 166.6 (C6''), 173.0 (C2), 203.7 (C1'') ppm.
$[\alpha_D]^{21}$ = -134.8, $[\alpha_{578}]^{21}$ = -140.0, $[\alpha_{546}]^{21}$ = -159.9, $[\alpha_{436}]^{21}$ = -275.3, $[\alpha_{365}]^{21}$ = -275.6, (c=1.01).



Cyclobutane **2m**: Yield: 82 mg.
$C_{23}H_{34}O_6$; M = 406.23. IR: ν = 3405, 2940, 2870, 1750, 1720, 1600, 1455, 1370, 1220, 1130, 925 cm^{-1}. MS (70 eV): *m/z* (%) = 406 (7, M^+), 269 (12), 251 (69), 211 (44), 192 (66), 169 (97), 137 (100). Anal.: found: C 67.74, H 8.33; calculated: C 67.94, H 8.43. ^1H NMR ($CDCl_3$): δ = 0.77 (d, J = 6.9 Hz, 3H, H8'-H9'), 0.89 (d, J = 7.6 Hz, 3H, H10'), 0.96 (d, J = 6.9 Hz, 3H, H8'-H9'), 0.98 (s, 3H, H8''-H9''), 0.82-1.05 (m, 3H, H3'ax-H4'ax-H6'ax), 1.20-1.48 (m, 2H, H2'-H5'), 1.30 (s, 3H, H8''-H9''), 1.62-1.75 (m, 2H, H3'eq-H4'eq), 1.90-2.10 (m, 2H, H6'eq-H7'), 2.04 (d, J = 16.8 Hz, 1H, H5''), 2.28 (d, J = 16.8 Hz, 1H, H5''), 2.49 (d, J = 9.9 Hz, 1H, H3), 2.57 (dd, J = 9.9/6.9 Hz, 1H, H4), 3.54 (td, J = 10.2/4.6 Hz, 1H, H1'), 3.98 (s, 3H, H7''), 5.28 (d, J = 6.9 Hz, 1H, H3''), 5.62(s, 1H, H5) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.4 (C8'-C9'), 20.8 (C8'-C9'), 22.1 (C10'), 22.7 (C8''-C9''), 22.9 (C3'), 25.7 (C7'), 28.5 (C8''-C9''), 31.3 (C5'), 34.1 (C4'), 38.0 (C4''), 38.2 (C4), 39.4 (C6'), 42.8 (C3), 47.5 (C2'), 54.7 (C5''), 55.6 (C7''), 73.7 (C3''), 77.6 (C1'), 87.2 (C2''), 109.5 (C5), 158.5 (C6''), 171.0 (C2), 198.8 (C1'') ppm.
$[\alpha_D]^{21}$ = -118.3, $[\alpha_{578}]^{21}$ = -122.6, $[\alpha_{546}]^{21}$ = -140.6, $[\alpha_{436}]^{21}$ = -241.7, $[\alpha_{365}]^{21}$ = -242.2, (c=0.99).



Cyclobutane **2n**: Yield: 84 mg.
$C_{23}H_{34}O_6$; M = 406.23. IR: ν = 3405, 2945, 2855, 1750, 1715, 1430, 1370, 1220, 1110, 935 cm^{-1}. MS (70 eV): *m/z* (%) = 406 (1, M^+), 338 (3.7), 287 (23), 209 (34), 192 (61), 169 (88), 137 (100). Anal.: found: C 67.64, H 8.21; calculated: C 67.94, H 8.43. ^1H NMR ($CDCl_3$): δ = 0.79 (d, J = 6.9 Hz, 3H, H8'-H9'), 0.82 (d, J = 7.6 Hz, 3H, H10'), 0.92 (s, 3H, H8''-

H9''), 0.95 (d, J = 6.9 Hz, 3H, H8'-H9'), 0.74-1.04 (m, 3H, H3'ax-H4'ax-H6'ax), 1.17-1.47 (m, 2H, H2'-H5'), 1.23 (s, 3H, H8''-H9''), 1.53-1.76 (m, 2H, H3'eq-H4'eq), 2.02-2.18 (m, 2H, H6'eq-H7'), 2.08 (d, J = 16.8 Hz, 1H; H5''), 2.29 (d, J = 16.8 Hz, 1H, H5''), 2.75 (ddd, J = 6.5/6.1/4.2 Hz, 1H, H4), 2.83 (d, J = 6.1 Hz, 1H, H3), 3.59 (td, J = 10.2/4.6 Hz, 1H, H1'), 3.96 (s, 3H, H7''), 4.60 (d, J = 6.5 Hz, 1H, H3''), 5.62 (d, J = 4.2 Hz, 1H, H5) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.5 (C8'-C9'), 20.9 (C8'-C9'), 22.2 (C10'), 22.4 (C8''-C9''), 23.0 (C3'), 25.2 (C7'), 29.7 (C8''-C9''), 31.4 (C5'), 34.2 (C4'), 38.5 (C4''), 39.4 (C6'), 39.9 (C4), 41.0 (C3), 47.5 (C2'), 55.2 (C5''), 56.6 (C7''), 74.5 (C3''), 78.9 (C1'), 90.1 (C2''), 100.6 (C5), 158.9 (C6''), 169.4 (C2), 199.9 (C1'') ppm.
$[\alpha_D]^{21}$ = -12.8, $[\alpha_{578}]^{21}$ = -11.4, $[\alpha_{546}]^{21}$ = -10.0, $[\alpha_{436}]^{21}$ = -2.8, $[\alpha_{365}]^{21}$ = +42.8, (c=1.00).

Acknowledgements

We are grateful to *Prof. Dr. Dr. h.c. H.-D. Scharf* (RWTH Aachen, Germany) for the donation of chemicals. S. B. thanks the *Région Champagne-Ardenne* for a fellowship.

References and Notes

1. a) Dilling, W.L. *Chem. Rev.* **1966**, *66*, 373 - 393; b) Crimmins, M.T. *Chem. Rev.* **1988**, *88*, 1453 - 1473; c) Crimmins, M.T.; Reinhold, T.L. *Organic Reactions* **1993**, *44*, 297 - 588; d) Winkler, J.D.; Bowen, C.M.; Liotta, F. *Chem. Rev.* **1995**, *95*, 2003 - 2020; e) Crimmins, M.T. *Comprehensive Organic Synthesis*, Vol. 5 (Trost, B.M.; Fleming, I.; Paquette, L.A.; ed.), Pergamon Press, Oxford, **1991**, p. 123 - 150.
2. a) Rau, H. *Chem Rev.* **1983**, *83*, 535 - 547; b) Demuth, M.; Mikhail, G. *Synthesis* **1989**, 145 - 162; c) Jarosz, S. *Wiadomosci Chemiczne* **1983**, *37*, 167 - 192; d) Inoue, Y. *Chem Rev.* **1992**, *92*, 741 - 770; e) Pete, J.-P. *Advances in Photochemistry*, Vol. 21, (Neckers, D.C.; Volman, D.H.; von Bünau, G.; eds.) Wiley, **1996**, pp 135 - 216; f) Demuth, M.; Palomer, A.; Sluma, H.D.; Dey, A.K.; Krüger, C.; Tay, Y.H. *Angew. Chem.* **1986**, *98*, 1093 - 1095; *Angew. Chem., Int. Ed. Eng.* **1986**, 25, 1117 - 1119; g) Lange, G.L.; Decicco, C.; Lee, M. *Tetrahedron Lett.* **1987**, *28*, 2833 - 2836; h) Lange, G.L.; Decico, C. *Tetrahedron Lett.* **1988**, *29*, 2613 - 2614; i) Organ, M.G.; Froese, R.D.J.; Goddard, J.D.; Taylor, N.J.; Lange, G.L. *J. Am. Chem. Soc.* **1994**, *116*, 3312 - 3323; j) Bruneel, K.; De Keukeleire, D.; Vandewalle, M. *J. Chem. Soc. Perkin Trans. I* **1984**, 1697 - 1700; k) Bonvalet, C.; Bouquant, J.; Feigenbaum, A.; Pete, J.-P.; Scholler, D. *Bull. Soc. Chim. Fr.* **1994**, *131*, 687 - 692; l) Tanaka, M.; Tomioka, K.; Koga, K. *Tetrahedron* **1994**, *50*, 12829 - 12842; m) Meyers, A.I.; Fleming, S.A. *J. Am. Chem. Soc.* **1986**, *108*, 306 - 307; n) Faure, S.; Piva-Le Blanc, S.; Piva, O.; Pete, J.-P. *Tetrahedron Lett.* **1997**, *38*, 1045 - 1048; o) Matsui, T.; Morooka, T.; Nakayama, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 417 - 419; p) Sato, M.; Abe, Y.; Takayama, K.; Sekiguchi, K.; Kaneko, C.; Inoue (née Suzaki), N.; Furuya, T.; Inukai, N. *J. Heterocyclic Chem.* **1991**, *28*, 241 - 252; q) Iwaoka, T.; Murohashi, T.; Katagiri, N.; Sato, M.; Kaneko, C. *J. Chem. Soc. Perkin Trans. I* **1992**, 1393-1397; r) Alibés, R.; Bourdelande, J.L.; Font, J.; Gregori, A.; Parella, T. *Tetrahedron* **1996**, *52*, 1267 - 1278; s) Alibés, R.; Bourdelande, J.L.; Font, J.; Parella, T. *Tetrahedron* **1996**, *52*, 1279 - 1292; t) Baldwin, S.W.; Mazzuckelli, T.J. *Tetrahedron Lett.* **1986**, *27*, 5975 - 5978; u) Tolbert, L.M.; Ali, M.B. *J. Am. Chem. Soc.* **1982**, *104*, 1742 - 1744; v) Herzog, H.; Koch, H.; Scharf, H.-D.; Runsink, J. *Chem. Ber.* **1987**, *120*, 1737 - 1740; w) Herzog, H.; Koch, H.; Scharf, H.-D.; Runsink, J. *Tetrahedron* **1986**, *42*, 3547 - 3558.

3. For derivatives of cinnamic acid see for example: a) Vaida, M.; Addadi, L.; Leiserowitz, L.; Lahav, M. *J. Am. Chem. Soc.* **1989**, *111*, 1029 - 1034; b) Chung, C.-M.; Kunita, A.; Hayashi, K.; Nakamura, F.; Saigo, K.; Hasegawa, M. *J. Am. Chem. Soc.* **1991**, *113*, 7316 - 7322; c) Green, B.S.; Hagler, A.T.; Rabinsohn, Y.; Rejtö, M. *Israel J. Chem.* **1976/77**, *15*, 124 - 130; d) Ito, Y.; Borecka, B.; Trotter, J.; Scheffer, J.R. *Tetrahedron Lett.* **1995**, *36*, 6083 - 6086; e) Meyer, U.; Lahrahar, N.; Marsau, P.; Hopf, H.; Greiving, H.; Desvergne, J.-P.; Bouas-Laurent, H.; *Liebigs Ann. Chem.* **1997**, 381 - 384; f) Haag, D.; Scharf, H.-D. *J. Org. Chem.* **1996**, *61*, 6127 - 6135; g) Braussaud, N.; Hoffmann, N.; Scharf, H.-D. *Tetrahedron* **1997**, *53*, 14701 - 14712.
4. a) Schuster, D.I. *The Chemistry of the Enones* (Patai, S.; Rappoport, Z.; eds.), Wiley, New York, **1989**, p 623 - 756; b) Schuster, D.I.; Lem, G.; Kaprinidis, N.A. *Chem. Rev.* **1993**, *93*, 3 - 22; c) Becker, D.; Haddad, N, *Organic Photochemistry*, Vol. 10 (Padwa, S.; ed.), Marcel Dekker, New York, **1989**, p 1 - 162; d) Margaretha, P. *Chimia* **1975**, *29*, 203 - 209; e) Corey, E.J.; Bass, J.D.; LeMahieu, R.; Mitra, R.B. *J. Am. Chem. Soc.* **1964**, *86*, 5570 - 5583; f) Loutfy, R.O. de Mayo, P. *J. Am. Chem. Soc.* **1977**, *99*, 3559 - 3565; g) Robson, R.; Grubb, P.W.; Barltrop, J.A. *J. Chem. Soc.* **1964**, 2153 - 2164; h) Scharf, H.-D. *Tetrahedron Lett.* **1967**, 4231 - 4236; i) Gleiter, R.; Fischer, E. *Chem. Ber.* **1992**, *125*, 1899 - 1911.
5. Andrew, D.; Hastings, D.J.; Weedon, A.C. *J. Am. Chem. Soc.* **1994**, *116*, 10870 - 10871.
6. a) Scharf, H.-D.; Janus, J.; Müller, E. *Tetrahedron*, **1979**, *35*, 25 - 29; b) Hoffmann, N.; Scharf, H.-D.; Runsink, J. *Tetrahedron Lett.* **1989**, *30*, 2637 - 2638; c) Hoffmann, N.; Scharf, H.-D. *Liebigs Ann. Chem.* **1991**, 1273 - 1277; d) Curtius, F.W.; Scharf, H.-D. *Tetrahedron Asymm.* **1996**, *7*, 2957 - 2961; e) Hoffmann, N.; Scharf, H.-D. *Photochemical Key Steps in Organic Chemistry* (Mattay, J.; Griesbeck, A.; ed.), VCH, Weinheim, **1994**, p. 97 - 104.
7. Hoffmann, N.; Buschmann, H.; Raabe, G.; Scharf, H.-D. *Tetrahedron* **1994**, *50*, 11167 - 11186.
8. a) Hoffmann, N. *Tetrahedron Asymm.* **1994**, *5*, 879 - 886; b) Hoffmann, N. *Photochemical Key Steps in Organic Chemistry* (Mattay, J.; Griesbeck, A.; ed.), VCH, Weinheim, **1994**, p. 81 - 85.
9. See for example: a) Feringa, B.L.; de Lange. B.; Jansen, J.F.G.A.; de Jong, J.C.; Lubben, J.C.; Faber, W.; Schudde, E.P. *Pure Appl. Chem.* **1992**, *64*, 1865 - 1871; b) Feringa, B.L.; de Jong, J.C. *Bull. Soc. Chim. Belge* **1992**, *101*, 627 - 640; c) Krief, A.; Lecomte, Ph.; Demoute, J.P.; Dumont, W. *Synthesis* **1990**, 275 - 278; d) Pelter, A.; Ward, R.S.; Qianrong, L.; Pis, J. *Tetrahedron Asymm.* **1994**, *5*, 909 - 920.
10. a) White, J.D.; Gupta, D.N. *J. Am. Chem. Soc.* **1968**, *90*, 6171 - 6177; b) Baldwin, S.W.; Crimmins, M.T. *J. Am. Chem. Soc.* **1980**, *102*, 1198 - 1200; c) Sato, M.; Takayama, K.; Abe, Y.; Furuya, T.; Inukai, N.; Kaneko, C. *Chem. Pharm. Bull.* **1990**, *38*, 336 - 339.
11. a) Buschmann, H.; Scharf, H.-D.; Hoffmann, N.; Esser, P. *Angew. Chem., Int. Ed. Eng.* **1991**, *30*, 477 - 515; *Angew. Chem.* **1991**, *103*, 480 - 518; b) Buschmann, H.; Scharf, H.-D.; Hoffmann, N.; Plath, M.W.; Runsink, J. *J. Am. Chem. Soc.* **1989**, *111*, 5367 - 5373.
12. Froese, R.D.J.; Lange, G.L. (University of Guelph) personal communication.
13. Froese, R.D.J.; Lange, G.L.; Goddard, J.D. *J. Org. Chem.* **1996**, *61*, 952 - 961.
14. Hoffmann, N. *Dissertation, RWTH Aachen* **1992**.
15. Lange, G.L.; Decicco, C.; Tan, S.L.; Chamberlain, G. *Tetrahedron Lett.* **1985**, *26*, 4707 - 4710.
16. a) Schuster, D.I.; Dunn, D.A.; Heibel, G.E.; Brown, P.B.; Rao, J.M.; Woning, J. Bonneau, R. *J. Am. Chem. Soc.* **1991**, *113*, 6245 - 6255; b) Kelly, J.M.; Mc Murry, T.B.M.; Work, D.N. *J. Chem. Soc. Perkin Trans. 2* **1990**, 981 -983.
17. a) Martel, J.; Tessier, J.; Demoute, J.P. *Eur; Pat. Appl.* 23454 (Roussel Uclaf) (**1980**); b) Feringa, B.L.; de Jong, J.C. *J. Org. Chem.* **1988**, *53*, 1125 - 1127; c) Esser, P. *Dissertation, RWTH Aachen* **1994**.
18. a) Froborg, J.; Magnusson, G. *J. Am. Chem. Soc.* **1978**, *100*, 6728 - 6733; b) Liu, H.J.; Ulibarri, G.; Brown, E. *Can. J. Chem.* **1992**, *70*, 1545 - 1554.