The photomediated reaction of alkynes with cycloalkanes†

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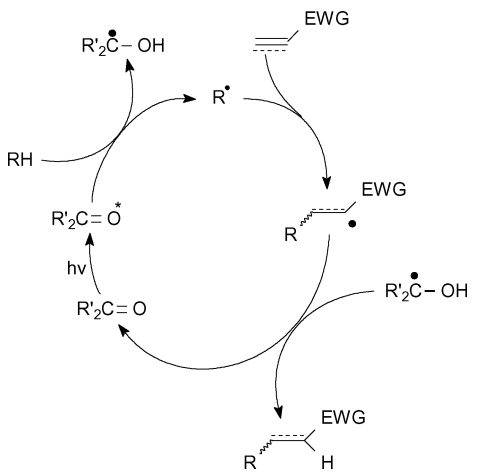
In the presence of a photomediator such as benzophenone, alkynes with electron-withdrawing groups react with cycloalkanes to give vinyl cycloalkanes. The reaction involves the regiospecific addition of a photochemically generated cycloalkyl radical to the β-carbon of the alkyne. The stereochemical outcome of the reaction depends on the nature of the photomediator and alkyne used.

Introduction

The introduction of a functional group at an unactivated carbon atom, such as those of an alkane or an ether, or the involvement of such an atom in carbon–carbon bond formation, are synthetic problems of obvious importance and considerable difficulty.[1] These problems have been addressed in a variety of ways, many of which involve the generation of an alkyl radical from an appropriate precursor and its subsequent reaction with the precursor of the group that is to be introduced. This indirect generation of the alkyl radical can be achieved in a wide variety of ways, including the reaction of alkyl halides with tributyltin hydride[2] or tris(trimethyl)silane,[3] the photolysis of nitrites[4] or alkylcobalt compounds,[5] the thermal decomposition of thiohydroxamic esters,[6] metal catalysis,[7] *etc.* Most of these methods are however limited by the fact that they involve toxic reagents or require the synthesis of the appropriate radical precursor. The direct generation of alkyl radicals by the homolytic cleavage of a C–H bond has been used less frequently and generally involves peroxides or photomediation.[8] Once generated, these radicals can participate in carbon–carbon bond forming reactions, producing a variety of functionalised systems. Vinyl and allyl groups can, for example, be introduced in this way by an addition–elimination sequence involving the radical and the appropriate stannane,[9,10] sulfide or related derivatives.[11,12] A chain transfer reaction involving triflones[13] has been used to carry out the alkenylation, alknylation and allylation of alkane- and ether-derived radicals. The reaction of these and related radicals with 2-chloroethylsulfonyl oxime ethers[14] results in the introduction of an oxime ether group, hydrolysis of which gives acylated derivatives. Once again, an evaluation of a particular process has to include a consideration of the nature of the reagents required, the by-products produced – for example, the use of triflones[13] and chloroethylsulfonyl oxime ethers[14] results in the formation of SO_2 – and the problems associated with the synthesis of any reactant.

Although often beset with problems of control and efficiency, the potential of photochemically initiated processes for the production of radicals is well established. In terms of unactivated systems, cyclopentane for example has been functionalised using a variety of photochemical methods,[15] all of which involve the generation of a cyclopentyl radical by homolysis of a C–H bond. Indeed, in the context of the discussion above, it was found that the reactions of triflones[13] and 2-chloroethylsulfonyl oxime ethers[14] were amenable to photoinitiation as well as initiation using an AIBN-related compound. In experimental terms the photoinduced hydrogen abstraction reactions of ketones are particularly attractive as a method of producing alkyl radicals, the process relying on the alkoxy radical character of carbonyl groups in the (n → π*) triplet state.[16] Thus, following absorption of a photon and intersystem crossing, ketones such as benzophenone are able to abstract a hydrogen atom from a substrate containing an appropriate C–H bond. The resulting alkyl radicals can react in a variety of ways including recombination, disproportionation and further hydrogen abstraction. Most usefully and because of their nucleophilic properties,[17] they would be expected to react with molecules containing electron deficient carbon–carbon multiple bonds (Scheme 1). This approach has been used in the reaction of enones with 1,3-dioxolanes,[18] the reaction of enals with dioxolanes and alcohols,[19] and the functionalisation of cycloalkanes with alkenyl nitriles[20] and ketene dithioacetal *S*,*S*-dioxides.[21] The mechanistic framework for the process suggests that the use of "catalytic" quantities of the carbonyl compound functioning as the photomediator should be sufficient. However, in practice there are many ways in which this molecule can be diverted from performing the required role and so larger amounts are in general required.



Scheme 1

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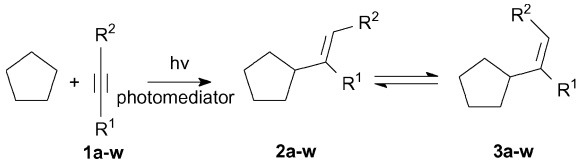
† Photomediated functionalisation and carbon–carbon bond formation in unactivated molecules. Part 1.

This paper describes the photochemical reaction of alkynes with cycloalkanes such as cyclopentane (Scheme 2). Reactions of this type were first reported in 1969 by Buchi, and independently by Grovenstein, who noted that the irradiation of a cyclohexane solution of ethyl propiolate[22] or dimethyl acetylenedicarboxylate[23] gave very small amounts of products resulting from alkyne insertion into a C–H bond of the cycloalkane. In view of the reaction times and yields involved – 24 h and 5%, and 14 days and 10%, respectively – it is not surprising that the system has not been revisited for over 30 years. The analogous reaction of saturated ethers with DMAD has also been noted,[24,25] with yields of up to 80% being reported for THF. Although the acetone initiation of the addition of DMAD to cyclic ethers was reported,[24] all of the other reactions of ethers and cycloalkanes involved direct irradiation. The possible involvement of an anion–cation radical pair as an intermediate in the reactions[25] of ethers under such conditions was also considered, but a radical chain mechanism initiated by unidentified agents was in general the preferred mechanistic framework.



a R^1 = H; R^2 = CO_2Me
b R^1 = H; R^2 = CO_2Et
c R^1 = H; R^2 = CO_2Pr
d R^1 = H; R^2 = CO_2Bu^i
e R^1 = H; R^2 = $CO_2CH_2CH(Me)Et$
f R^1 = H; R^2 = CO_2CH_2Ph
g R^1 = H; R^2 = $CO_2(CH_2)_2OMe$
h R^1 = H; R^2 = CO_2CH_2c-pentyl
i R^1 = H; R^2 = $CO_2CH_2CH{=}CH_2$
j R^1 = H; R^2 = $CO_2CH_2CH{=}CMe_2$
k R^1 = H; R^2 = $CO_2(CH_2)_2Cl$
l R^1 = H; R^2 = $CO_2(CH_2)_2Br$
m R^1 = H; R^2 = CO_2SiMe_3
n R^1 = H; R^2 = CN
o R^1 = H; R^2 = CO_2H
p R^1 = H; R^2 = SO_2Tol
q R^1 = H; R^2 = COMe
r R^1 = H; R^2 = Ph
s R^1 = H; R^2 = OCH_2CH_3
t R^1 = H; R^2 = $pNO_2C_6H_4$
u R^1 = CH_3; R^2 = $(CH_2)_2CH_3$
v R^1 = Ph; R^2 = Ph
w R^1 = c-pentylCH_2; R^2 = CO_2Me
x R^1 = c-hexyl$(CH_2)_2$; R^2 = CO_2Me
y R^1 = R^2 = CO_2Me
z R^1 = R^2 = CO_2Et
aa R^1 = R^2 = CO_2Bu^i
bb R^1 = R^2 = CO_2Bu^t

Scheme 2

We have found that the use of a photomediator such as benzophenone has a significant impact on the reaction of alkynes with cycloalkanes in terms of yield and reaction time, and here we report results relating to cycloalkanes of various sizes and to alkynes carrying a wide variety of functional groups. The results are important in that they relate to functionalisation and carbon–carbon bond formation in an unactivated system, and also because they suggest that photoinduced hydrogen abstraction in certain circumstances may be a synthetically useful method of generating radicals.[20,21]

Results and discussion

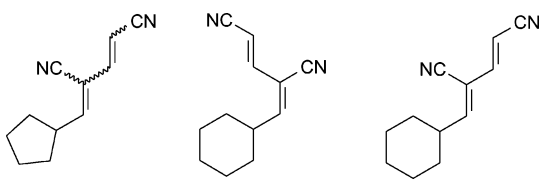
Initial experiments were carried out with cyclopentane and involved irradiating a solution of the alkyne **1** (0.15 M) and photomediator (1 equiv.) in the cycloalkanes, through Pyrex glass and using 350 nm lamps, until no alkyne remained (GC) (Scheme 2). Evaporation of the cyclopentane and removal of the photomediator by chromatography gave a substituted alkene as a mixture of *E* and *Z* isomers (Table 1). The reaction of methyl propiolate **1a** in the presence of benzophenone is typical of those involving monosubstituted alkynes. This gave a 1.6 : 1 (GC) mixture of methyl (*E*)- and (*Z*)-3-cyclopentyl-2-propenoate, **2a** and **3a**, which following chromatography were obtained in isolated yields of 32 and 36%, respectively (Table 1). The reaction is regiospecific, with the structures of the products being consistent with the concept that the reaction involves the conjugate addition of a nucleophilic cycloalkyl radical to the electron-deficient alkyne.

Table 1 The benzophenone-mediated reaction of alkynes with cyclopentane

Alkyne **1**	Time[a]/h	Products (yield, %)		*E*/*Z*[b]
1a	2.75	**2a** (37)	**3a** (22)	1.5 : 1
1b	2.5	**2b** (40)	**3b** (30)	1.5 : 1
1d	3.2	**2d** (42)	**3d** (27)	1.5 : 1
1f	3.3	**2f** (30)[c]	**3f** (20)	1.5 : 1[d]
1g	4.5	**2g** (34)[c]	**3g** (15)	1.6 : 1
1h	6.5	**2h** (40)	**3h** (25)	1.4 : 1
1i	4.5	**2i** (35)	**3i** (17)	1.5 : 1
1j	7.5	**2j** (34)	**3j** (29)	1.4 : 1
1k	2.0	**2k**[e]	**3k** (27)	1.7 : 1
1l	4.5	**2l** (25)	**3l** (22)	1.8 : 1
1m	3.0	Mixture of **2m**, **3m**, **2o** and **3o** (46 : 35 : 17 : 1)[e]		
1n	1.3	**2n**[e]	**3n** (16)	1 : 1.5
1o	1.5	**2o** (24)	**3o**[e]	1.8 : 1
1p	3.0	Mixture of **2p** and **3p** (56%)[e]		6.4 : 1
1q	11.5	**2q** (18)	**3q**[e]	3.9 : 1
1r–x	No reaction			
1y	2.5	**2y** (50)	**3y**[e]	1 : 45
1z	3.0	**2z** (43)	**3z**[e]	1 : 42
1aa	1.5	**2aa** (46)	**3aa** (3)	1 : 30
1bb	3.15 (22[f])	**2bb** (21[f])	**3bb** (7[f])	1 : 12 (1 : 4[f])

[a] Complete reaction of alkyne (GC). [b] GC. [c] Product contains some benzophenone. [d] ^{1}H NMR. [e] Product could not be satisfactorily isolated. [f] Results obtained using acetophenone as photomediator. Products co-eluted from SiO_2 with benzophenone.

The effectiveness of a range of potential photomediators in promoting the reaction was investigated and it was found that the reaction time and yield, and the product composition, were relatively insensitive to the structure of the photomediator used (Table 2). Exceptions to this pattern were 2-acetylnaphthalene, the lowest triplet state of which is of the π,π* type, and 4-methoxyacetophenone, the behaviour of which can again be explained on the basis that most molecules on excitation end up in the π,π* state.



A series of experiments involving benzophenone showed that the photomediator concentration could be reduced by a factor of six without affecting the reaction time or the yield (Table 3). At lower concentrations the time taken to complete the reaction increased dramatically. The only other low MW products formed in these reactions were cyclopentenone and cyclopentanol (GC–MS), the result of reaction between the cyclopentyl radicals and O_2 that had survived the degassing which preceded irradiation. There is a strong correlation between reaction time and the

Table 2 A comparison of the reaction of methyl propiolate **1a** with cyclopentane using different photomediators[a]

Photomediator	Time[b]/h	Yield[c] (%)	*Z*/*E*	ROH/R_2C=O[d] (%)
Ph_2CO	2.75	86	1 : 1.46	1.5/1
PhCOMe	5.00	86	1 : 1.26	0.7/1
(2-Naphthyl)COMe	No reaction			
4-$MeOC_6H_4COMe$	106 (86[e])	70	1 : 1.44	5/4
4-$F_3CC_6H_4COMe$	1.75	97	1 : 1.30	1.3/0.6
PhCHO	1.25	84	1 : 1.32	0.4/0.2
4-$MeOC_6H_4COPh$	3.50	92	1 : 1.33	4/2
$(3\text{-}F_3CC_6H_4)_2CO$	2.00	96	1 : 1.34	2/1
$(4\text{-}MeOC_6H_4)_2CO$	5.00	88	1 : 1.27	3/1

[a] Cyclopentane solution of the alkyne (0.15 M) containing photomediator (1 equiv.), 350 nm. [b] Complete consumption (GC) of alkyne. [c] GC, decane as IS. [d] ROH: cyclopentanol, R_2C=O: cyclopentanone. [e] Duplicate experiment: 79% of the alkyne had reacted after 86 h.

Table 3 The effect of benzophenone concentration on the reaction of methyl propiolate **1** with cyclopentane[a]

[Benzophenone]/M	Time/h[b]	Yield (%)[c]	*Z*/*E*	ROH/R_2C=O[d] (%)
0.15	2.75	86	1 : 1.46	1.5/1
0.10	3.00	93	1 : 1.30	2/1
0.05	3.00	92	1 : 1.33	3/1
0.022	3.00	95	1 : 1.32	3/2
0.014	102[e]	91	1 : 1.27	5/4

[a] Cyclopentane solution of the alkyne (0.15 M) and photomediator, 350 nm. [b] Complete consumption (GC) of alkyne. [c] GC, decane as IS. [d] ROH: cyclopentanol, R_2C=O: cyclopentanone. [e] 95% conversion of the alkyne had occurred after 5 h.

amount of these materials present in the product mixture (Tables 2 and 3). Interestingly, the normally efficient photoreduction of benzophenone forming benzpinacol is not competitive with the alkyne/cycloalkane reaction and the diol is formed in only very small quantities, if at all. The stereochemistry of the products was assigned on the basis of the ^{1}H NMR coupling constants, 15.6 and 11.5 Hz, displayed by the α-H in **2a** and **3a**, respectively. In common with all the reactions involving monosubstituted alkynes, the secondary *cis–trans* photoisomerisation that is a feature of the reactions of acetylenedicarboxylates (see below) does not occur here. In this context it is worth noting that the rate of inversion of vinyl radicals is much faster than the final hydrogen abstraction step,[26] and so the geometry of the product is not determined by the stereochemistry of the addition of the cycloalkyl radical to the alkyne (Scheme 1).

A GC analysis of the crude product indicated that the alkenes **2** and **3** were the only alkyne-derived low molecular weight products formed in the reaction. It is assumed that the mass balance for the reaction in terms of the alkyne is completed by the formation of polyacetylene oligomers which are not detected by GC and which are lost during chromatography. Compounds of this type have been identified among the products formed in reactions of propiolonitrile **1n** and cycloalkanes that involved higher concentrations of the alkyne and longer reaction times than normal. Thus the dimeric species **4** was identified as a minor product from the reaction of cyclopentane with **1n** using GC–MS on the basis of its molecular ion and fragmentation pattern. The compounds **5** and **6** were isolated from the corresponding reaction of cyclohexane with **1n** and characterised spectroscopically.

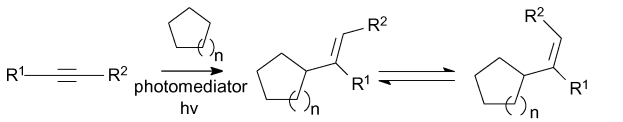
The cyclopentyl radicals display chemoselectively to the extent that they react exclusively with the alkyne in propiolate esters containing benzyl (**1f**), ether (**1g**), alkenyl (**1i** and **1j**), haloalkyl (**1k** and **1l**) and trimethylsilyl (**1m**) groups (Table 1). The same selectivity is displayed by alkynes containing other electron-withdrawing groups such as a nitrile (**1n**), an acid (**1o**), or a sulfone (**1p**). However, the crude product obtained from the reaction of cyclopentane with 3-butyn-2-one **1q** is more complex (GC) and the one product successfully isolated, the *E* isomer **2q**, was obtained in only 18% yield. The failure of **1r** and **1s** to react underlines the fact an electron-withdrawing group (EWG) on the alkyne is an essential pre-requisite for reaction with cycloalkyl radicals. In the same way, the failure of **1t** to react presumably reflects the fact that the influence of the nitro group is excessively attenuated by the linking aromatic ring. The result helps to identify the level of elecron-withdrawal that is required for these alkyne–cycloalkyl radical reactions. Although the lack of an EWG may obviously be responsible for the inertness of **1u** and **1v**, steric factors may also play a role in these reactions, as the disubstituted alkynes **1w** and **1x** also fail to react despite the presence in both of an EWG.

Cyclopentane reacts with acetylenedicarboxylates **1y–bb** (Scheme 2) (Table 1) in a parallel but somewhat less efficient manner, forming dialkyl 2-cyclopentyl-2-butenedioates. The stereochemistry of the adducts was assigned on the basis that the olefinic and cycloalkyl methine hydrogens of the *E* isomers **3y–bb**, which are *cis* to ester groups, appear at lower field in the ^{1}H NMR spectrum relative to those of the *Z* isomers **2y–bb**. The reactions of acetylenedicarboxylates with cycloalkanes are highly stereoselective, with the *Z* isomers predominating as a result of a secondary photosensitised isomerisation of the initially formed alkenes. As would be expected, the product ratio in this case is photomediator dependent. Thus, whereas the benzophenone-promoted reaction of DMAD **1y** with cyclohexane gave a *Z*/*E* ratio of 19 : 1 for **7y/8y**, the use of acetophenone, which has a higher triplet energy, resulted in a 4 : 1 mixture of **7y** and **8y**, as in this case both isomers are photoactive in terms of the photosensitised isomerisation process; a 2.5 : 1 ratio was obtained

Table 4 The photomediated reaction of alkynes with cyclohexane, cycloheptane and cyclooctane[a]

Cycloalkane	Alkyne	Time[b]/h	Products (isolated yield, %)		E/Z[c]
Cyclohexane	**1a**	4.5	**7a** (19)	**8a** (15)	1.5 : 1
Cyclohexane	**1b**	4.5	**7b** (26)	**8b** (17)	1.5 : 1
Cyclohexane	**1c**	8.5	**7c/8c** (27)[d]		1.4 : 1
Cyclohexane	**1e**	5.5	**7e/8e** (37)[d]		1.5 : 1
Cyclohexane	**1k**	2.0	**7k** (26)[e]	**8k** (14)	1.5 : 1
Cyclohexane	**1l**	4.0	**7l** (18)	**8l** (15)	1.5 : 1
Cyclohexane	**1n**	2.0	**7n** (11)[f]	**8n** (15)[f]	1 : 1.5
Cyclohexane	**1o**	2.5	**7o/8o** (28)[d]		2.5 : 1
Cyclohexane	**1p**	5.5	**7p/8p** (30)[d]		6.8 : 1
Cyclohexane	**1y**	13.5	**7y** (31)		1 : 19[g]
Cyclohexane[h]	**1y**	20.0	**7y** (12)	**8y** (3)	1 : 4[i]
Cyclohexane[j]	**1y**	6.5	**7y** (17)[c]	**8y** (7)[c]	1 : 2.5[g]
Cycloheptane	**1a**	2.5	**9a** (21)	**10a** (17)	1.3 : 1
Cycloheptane	**1b**	2.6	**9b** (20)	**10b** (20)	1.3 : 1
Cycloheptane	**1d**	2.7	**9d** (20)	**10d** (16)	1.4 : 1
Cycloheptane	**1n**	1.5	**9n** (26)[e]	**10n** (37)[e]	1 : 2
Cycloheptane	**1p**	3.0	**9p/10p** (17)[d,k]		5.4 : 1
Cycloheptane	**1y**	No reaction			
Cyclooctane	**1a**	3.0	**11a** (18)	**12a** (24)	1.4 : 1
Cyclooctane	**1b**	3.5	**11b** (24)	**12b** (22)	1.3 : 1
Cyclooctane	**1n**	1.0	**11n** (9)	**12n** (23)[l]	1 : 2.4
Cyclooctane	**1p**	1.5	**9p/10p** (47)[d]		4.6 : 1
Cyclooctane	**1y**	No reaction			

[a] Photomediator: benzophenone. [b] Complete reaction of alkyne (GC). [c] GC. [d] Chromatography gave a mixture of stereoisomers. [e] Contains a trace of benzophenone. [f] Separated on $AgNO_3/SiO_2$. [g] Small amounts of cyclohexanol and cyclohexanone were also formed. [h] Photomediator: acetophenone. [i] Isolated product. [j] Photomediator: benzaldehyde. [k] Traces of benzpinacol were also formed. [l] Contains a trace of **11n**.



1a-c, 1e, 1k
1l, 1n-p, 1y

7a n = 2, R^1 = H, R^2 = CO_2Me **8a**
7b n = 2, R^1 = H, R^2 = CO_2Et **8b**
7c n = 2, R^1 = H, R^2 = CO_2Pr **8c**
7e n = 2, R^1 = H, R^2 = $CO_2CH_2CH(Me)Et$ **8e**
7k n = 2, R^1 = H, R^2 = $CO_2(CH_2)_2Cl$ **8k**
7l n = 2, R^1 = H, R^2 = $CO_2(CH_2)_2Br$ **8l**
7n n = 2, R^1 = H, R^2 = CN **8n**
7o n = 2, R^1 = H, R^2 = CO_2H **8o**
7p n = 2, R^1 = H, R^2 = SO_2Tol **8p**
7y n = 2, R^1 = R^2 = CO_2Me **8y**
9a n = 3, R^1 = H, R^2 = CO_2Me **10a**
9b n = 3, R^1 = H, R^2 = CO_2Et **10b**
9d n = 3, R^1 = H, R^2 = CO_2Bu^i **10d**
9n n = 3, R^1 = H, R^2 = CN **10n**
9p n = 3, R^1 = H, R^2 = SO_2Tol **10p**
11a n = 4, R^1 = H, R^2 = CO_2Me **12a**
11b n = 4, R^1 = H, R^2 = CO_2Et **12b**
11n n = 4, R^1 = H, R^2 = CN **12n**
11p n = 4, R^1 = H, R^2 = SO_2Tol **12p**

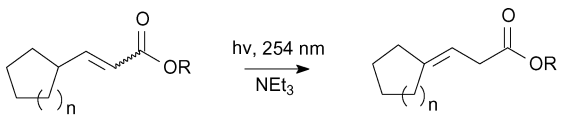
Scheme 3

with benzaldehyde (Scheme 3, Table 4). The significantly reduced stereoselectivity observed with di-*t*-butyl acetylenedicarboxylate **1bb** in the presence of benzophenone (Table 1) presumably reflects a steric preference for the *E* isomer. The use of acetophenone in this case again results in a further reduction of stereoselectivity.

The effect of cycloalkane ring size on the outcome of the reaction was considered in a series of experiments involving C_5–C_8 cycloalkanes. Reaction occurred in all cases with monosubstituted alkynes. Cyclopentane, giving overall isolated yields of up to 70% (Scheme 2, Table 1), was significantly more reactive than the C_6–C_8 cycloalkanes, which gave yields varying in a non-systematic way between 17 and 47% (Scheme 3, Table 4). The pattern of reactivity observed for the reaction of the cycloalkanes with DMAD **1y** was somewhat different, for although cyclopentane again gave significantly higher yields than cyclohexane, the larger ring systems did not react at all (Table 4). The observation that cyclopentane is more reactive than cyclohexane in reactions involving their respective radicals has also been made in relation to the bromination of these systems, where the former reacts 7–8 times faster.[27] The difference in reactivity in this case was attributed to the larger amount of eclipsing strain relief that occurs when a cyclopentyl radical is formed, essentially an I-strain[28] effect. Although this would account for the relative reactivity of cyclohexane and cyclopentane, it does not provide a basis for understanding the behaviour of the other cycloalkanes. A rationale based on the steric accessibility of the hydrogen atoms in the cycloalkanes has some merit. It is reasonable to suggest that the hydrogen atoms in cyclopentane are less sterically hindered because of its smaller bond angle. The larger bond angles in the other cycloalkanes would lead to any particular hydrogen in these systems being subject to greater steric hindrance by the hydrogens on adjacent carbons. This would result in reduced reactivity for C_6–C_8 with the propiolates, and a complete lack of reactivity for C_7 and C_8 when DMAD with its greater steric demand is involved.

Such an analysis would suggest that cyclobutane should be even more reactive than cyclopentane. Although no information relating to the reaction of of cyclobutane with alkynes is currently available, a study[25] of the reaction of cyclic ethers with alkynes has shown that four- and five-membered cyclic ethers add to DMAD under direct radiation, whereas six- and seven-membered systems are unreactive. A different effect may however be involved here, as it has been suggested[29] that there is a correlation between reactivity and the torsion angle defined by the α-hydrogens and the p-type non-bonded orbital on oxygen.

A useful extension of this photochemical functionalisation of cycloalkanes lies in the fact that the vinylcycloalkanes which are the primary photoproducts at >300 nm undergo a photochemical double bond migration at 254 nm. It has already been shown[30] that ethyl β-cyclopentyl- and β-cyclohexylpropenoates react to give β,γ-unsaturated esters. In view of the ready availability of the appropriate propenoates from the cycloalkane–alkyne reactions discussed above we have been able to show that the reaction can be extended to other propenoates including β-cycloheptyl and β-cyclooctyl systems (Scheme 4).



2d *E*, n = 1, R = Bu^i — **13** n = 1, R = Bu^i
3e *Z*, n = 2, R = $CH_2CH(Me)Et$ — **14** n = 2, R = $CH_2CH(Me)Et$
3f *Z*, n = 1, R = Bn — **15** n = 2, R = Bn
10a *Z*, n = 3, R = Me — **16** n = 3, R = Me
12a *Z*, n = 4, R = Me — **17** n = 4, R = Me

Scheme 4

Of particular interest in this regard is the observation that the double bond in dimethyl (*Z*)-2-cyclopentyl-2-butendioate **2y** undergoes a double migration, *via* the corresponding *E* isomer **3y**, forming initially the cyclopentylidene derivative **18** and ultimately the cyclopentene **19** (Scheme 5, Fig. 1).

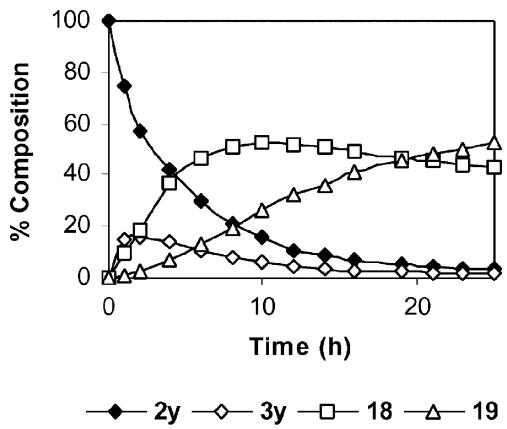
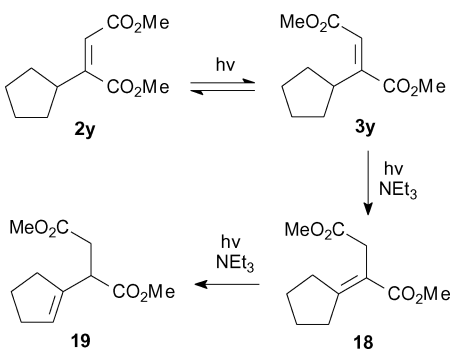


Fig. 1 The photodeconjugation reaction of dimethyl (*Z*)-cyclopentyl-2-butenedioate **2y** in the presence of triethylamine.



Scheme 5

The results reported here demonstrate that the photomediated reaction of electron-deficient alkynes with cycloalkanes, particularly cyclopentane, is a genuine alternative to the other available methods for carbon–carbon bond formation with, or functionalisation of, such unactivated systems. The fact that the reactions can be carried out[31] using sunlight as a source of UV radiation, and with supported photomediators, further enhances the approach from the clean/green chemistry perspective.

Experimental

All starting materials were distilled before use. The alkynes used, with the exception of those whose preparation is described below, were commercially available or were prepared by literature methods. The photochemical reactions between the cycloalkanes and the alkynes were carried out in cylindrical Pyrex tubes using a Rayonet Photochemical Reactor, RPR-100, equipped with sixteen 350 nm mercury lamps. IR spectra were measured on a Perkin–Elmer Spectrum 1 FT-IR. ^{1}H NMR and ^{13}C NMR were measured on a Jeol JNM-LA400 spectrometer at probe temperatures using $CDCl_3$ as solvent and TMS as internal standard. GC analyses were carried out on an RTX-5 (Restek) column. GC–MS analyses were carried out on a Micromass GCT spectrometer coupled to an Agilent 6890 capillary gas chromatograph equipped with an HP5 column.

2-Methoxyethyl propiolate 1g

1g was prepared using a Mitsonobu reaction.[32] A solution of 2-methoxyethanol (1.62 g, 21.4 mmol) and triphenylphosphine (5.05 g, 19.2 mmol) in dry ether (25 ml) was added to a solution of propynoic acid (1.50 g, 21.4 mmol) and diethyl azodicarboxylate (3.50 g, 20 mmol), also in dry ether (15 ml). During the addition there was a slight temperature rise followed by the precipitation of a white solid. The mixture was stirred for 24 h at rt after which the solid was removed by filtration and the solvent by evaporation. The resulting pale yellow liquid was distilled and chromatographed on SiO_2 (ether–petroleum ether) to give **1g** as a colourless liquid (1.20 g, 42%): ν_{max}(film)/cm^{-1} 3258, 2118, 1717; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.97 (1H, s, C≡CH), 3.40 (3H, s, OMe), 3.64 (2H, t, J = 6.0 Hz, CH_2OMe), 4.28 (2H, t, J = 6.0 Hz, C(O)OCH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 75.6, 74.6, 70.0, 65.3, 59.2. $C_6H_{12}O_3$ requires: C, 56.24; H, 6.29%; found: C, 56.59; H, 6.47%.

Cyclopentylmethyl propiolate 1h

1h was prepared as described above for **1g** in 55% yield: ν_{max}(film)/cm^{-1} 3262, 2119, 1714, 1230; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.61 (2H, m), 1.47–1.60 (4H, m), 1.67–1.72 (2H, m), 2.18 (1H, m, OCH_2CH), 2.82 (1H, s, C≡CH), 4.02 (2H, d, J = 7.0 Hz, OCH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 75.4, 74.4, 70.2, 38.2, 29.2, 25.1. $C_9H_{12}O_2$ requires: C, 71.03; H, 7.95%; found: C, 70.69; H, 7.58%.

Methyl 4-cyclopentyl-2-butynoate 1w

A solution of *n*-BuLi (2.5 M in hexanes, 9.0 ml, 2.5 mmol) was added, under N_2, to a cold (−20 °C) stirred solution of diisopropylamine (0.10 g, 1.0 mmol) and propynoic acid (0.70 g,

10.0 mmol) in dry THF. After 10 min HMPA (15 ml) was added slowly and the solution was stirred for 15 min at −20 °C and at −10 °C for a further 1.5 h. Cyclopentymethyl bromide[33] (1.71 g, 10.5 mmol) was then added and the mixture was stirred at room temperature for 24 h. After this period methyl iodide (5.7 g, 40 mmol) was added and stirring was continued at room temperature for a further 24 h. The mixture was then poured into ice-cold water, ether was added and the aqueous layer extracted with further ether. The combined organic extracts were washed with water and brine, and after drying ($MgSO_4$) and filtering the solvent was evaporated to give a brown oil (0.9 g). Chromatography on silica (4% ether in petroleum ether) gave **1w** (0.36 g, 21%) as a clear oil: ν_{max}(film)/cm^{-1} 2236, 1716, 1255; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20–1.30 (2H, m), 1.50–1.68 (4H, m), 1.80 (2H, m), 2.08 (1H, m, CH), 2.31 (2H, d, J = 6.8 Hz, C≡CCH_2), 3.73 (3H, s, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 89.4, 72.8, 52.5, 38.0, 32.0, 25.0, 24.3. $C_{10}H_{14}O_2$ requires: C, 72.26; H, 8.49%; found: C, 72.38; H, 8.15%.

Methyl 5-cyclohexyl-2-pentynoate 1x

1x was prepared as described above for **1w** in 39% yield: ν_{max}(film)/cm^{-1} 2237, 1716, 1252; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89–0.90 (2H, m), 1.10–1.30 (2H, m), 1.35 (1H, m, CH), 1.47 (2H, q, J = 7.3 Hz, C≡CCH_2CH_2), 1.63–1.71 (6H, m), 2.34 (2H, t, J = 7.3 Hz, C≡CCH_2), 3.76 (3H, s, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 90.1, 72.6, 52.5, 36.6, 34.8, 32.6, 26.4, 26.0, 16.0. $C_{12}H_{18}O_2$ requires: C, 74.19; H, 9.34%; found: C, 74.07; H, 9.34%.

General procedure for photochemical reactions using benzophenone as photomediator

A solution of benzophenone (0.08 g, 0.43 mmol), and when required dodecane (0.37 g, 2 mmol), in cycloalkane (40 ml) was degassed with N_2 for 20 min. The alkyne (3 mmol) was added and the stirred solution was irradiated until all the alkyne had been consumed (GC). The crude product mixture contained the *cis* and *trans* alkene products, and also trace amounts of the cycloalkanol and cycloalkanone (GC–MS) corresponding to the cycloalkane used. Subsequent to the removal of excess solvent the products (Tables 1 and 4) were isolated by chromatography on silica (50 g) using 5% ether–petroleum ether as eluant. All products were obtained as clear sweet-smelling oils and were characterised in the ususal way on the basis of IR and analytical data (Table 5), and ^{1}H and ^{13}C NMR spectroscopy (Tables 6 and 7).

Isolation of (2*E*,4*E*)-4-(cyclohexylmethylene)-2-pentenedinitrile 5 and (2*E*,4*Z*)-4-(cyclohexylmethylene)-2-pentenedinitrile 6. A solution of benzophenone (0.08 g, 0.43 mmol) in cyclohexane (20 ml) was degassed with N_2 for 20 min. Propionitrile (0.43 g, 8.4 mmol) was added and the solution was irradiated for 31 h, at which point product formation had ceased (GC). The crude product contained the expected alkenes **7n** and **8n** (GC, 1 : 1.4) and a small amount of benzpinacol (^{1}H NMR). Chromatography on silica (40 g, 0–20% ether in petroleum ether) initially gave fractions containing mixtures of **7n**, **8n** and benzophenone. Further elution gave **5** (0.01 g) and **6** (0.02 g). **5**: ν_{max}(film)/cm^{-1} 2222, 1622, 965; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88–1.36 (5H, m), 1.58–1.78 (5H, m), 2.56 (1H, m, C*H*CH=C), 5.84 (1H, d, J_{trans} = 16.1 Hz, NCC*H*=CH), 6.57(1H, d, J_{vic} = 10.7 Hz, CHC*H*=C), 7.22 (1H, d, J_{trans} = 16.1 Hz, NCCH=C*H*), 3.76 (3H, s, OCH_3); *m*/*z* (EI) 186 (M$^+$, 7%), 185(5), 105(25), 103(9), 82(48), 67(100). HRMS (EI): calcd. for $C_{12}H_{14}N_2$ 186.1157, found: 186.1155. **6**: ν_{max}(film)/cm^{-1} 2222, 1622, 965; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88–1.38 (5H, m), 1.58–1.77 (5H, m), 2.65 (1H, m, C*H*CH=C), 5.72 (1H, d, J_{trans} = 16.1 Hz, NCC*H*=CH), 6.53(1H, d, J_{vic} = 10.2 Hz, CHC*H*=C), 6.89 (1H, d, J_{trans} = 16.1 Hz, NCCH=C*H*); *m*/*z* (EI) 186 (M$^+$, 8%), 185(1), 105(27), 103(11), 82(50), 67(100). HRMS (EI): calcd. for $C_{12}H_{14}N_2$ 186.1157, found: 186.1173.

The reaction of propionitrile with cyclopentane under these conditions resulted in the formation of two major products, **2n** and **3n**, and traces of a third, GCMS analysis of which suggested it was a 4-(cyclopentylmethylene)-2-pentenedinitrile **4**: *m*/*z* (EI) 172 (M$^+$, 12%), 171(19), 144(10), 130(9), 105(78), 103(30), 68(100), 67(14). HRMS (EI): calcd. for $C_{11}H_{12}N_2$ 172.1000, found: 172.0986.

Photodeconjugation reactions

Irradiation of isobutyl (*E*)-3-cyclopentyl-2-propenoate 2d. Et_3N (1 drop) was added to a degassed solution of **2d** (0.16 g, 0.08 mmol) in cyclopentane in a quartz tube and this was then irradiated in a Rayonet reactor using 254 nm lamps. The reaction was monitored by GC, which indicated the formation of two products. One of these, which was identified (GC) as isobutyl (*Z*)-3-cyclopentyl-2-propenoate **3d**, disappeared as the reaction proceeded. Irradiation was discontinued after 10 h when all of the **2d** had reacted. Elution of the crude product from silica (20 g) with ether–petroleum ether gave isobutyl 3-cyclopentylidenepropanoate **13** (0.1 g, 59%) as a colourless liquid: ν_{max}(film)/cm^{-1} 1735; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (6H, d, J = 6.6 Hz, *Me*$_2$CH), 1.60–1.75 (4H, m), 1.93 (1H, m, Me$_2$C*H*), 2.20 (2H, t, J = 7.0 Hz, CH$_2$C*H*$_2$C=), 2.25 (2H, t, J = 7.0 Hz, CH$_2$C*H*$_2$C=), 3.00 (2H, d, J = 7.1 Hz, CH_2CO), 3.80 (2H, d, J = 6.6 Hz, OCH_2), 5.40 (1H, t, J = 7.1 Hz, C*H*=C); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 142.6, 106.6, 65.9, 30.5, 28.7, 24.1, 23.0, 21.5, 14.3. $C_{12}H_{20}O_2$ requires: C, 73.43; H, 10.27%; found: C, 73.20; H, 9.96%.

Irradiation of 2-methylbutyl (*Z*)-3-cyclohexyl-2-propenoate 3e. Irradiation of **3e** as indicated above for 18.5 h resulted in the formation of 2-methylbutyl 3-cyclohexylidenepropanoate **14** (53%), which was obtained as a colourless liquid: ν_{max}(film)/cm^{-1} 1738; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (3H, t, J = 7.6 Hz, *Me*CH$_2$), 0.85 (3H, d, J = 7.3 Hz, *Me*CH), 1.07–2.04 (13H, m), 2.98 (2H, d, J = 7.3 Hz, CH_2CO), 3.79 and 3.88 (2H, dds, J_{vic} = 6.5, J_{gem} = 10.6 Hz, OCH_2), 5.18 (1H, t, J = 7.3 Hz, CH=C); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 142.9, 112.4, 69.1, 36.8, 34.0, 32.9, 28.8, 28.3, 27.4, 26.6, 25.9, 16.2, 11.1. $C_{14}H_{24}O_2$ requires: C, 75.00; H, 10.71%; found: C, 74.73; H, 10.49%.

Irradiation of benzyl (*Z*)-3-cyclopentyl-2-propenoate 3f. In the same way the irradiation of **3f** for 5.5 h resulted in the formation of benzyl 3-cyclopentylidenepropanoate **15** (70%), which was obtained as a colourless liquid: ν_{max}(film)/cm^{-1} 1734, 736, 696; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45–1.80 (4H, m), 2.20 (2H, t, J = 7.0 Hz, CH$_2$C*H*$_2$C=), 2.25 (2H, t, J = 7.0 Hz, CH$_2$C*H*$_2$C=), 3.00 (2H, d, J = 7.1 Hz, CH_2CO), 5.04 (2H, s, OCH_2), 5.36 (1H,

Table 5 IR and analytical data

Alkenoate	ν_{max}/cm^{-1}			Analytical data		
	CO	C=C	Other bands	C (Found (%) [Requires (%)])	H (Found (%) [Requires (%)])	HRMS CI, $M^+ + H$: Found (Calculated)
2a ($C_9H_{14}O_2$)[34]	1724	1658	983	—	—	—
3a ($C_9H_{14}O_2$)	1721	1642	816	69.82 [70.10]	8.85 [9.15]	—
2b ($C_{10}H_{16}O_2$)[35]	1724	1656	—	—	—	—
3b ($C_{10}H_{16}O_2$)	1720	1643	816	71.21 [71.39]	9.36 [9.59]	—
2d ($C_{12}H_{20}O_2$)	1720	1652	—	73.06 [73.43]	10.17 [10.27]	—
3d ($C_{12}H_{20}O_2$)	1720	1642	820	73.20 [73.43]	9.96 [10.27]	
3f ($C_{15}H_{18}O_2$)	1718	1639	818, 736, 696	78.54 [78.23]	8.20 [7.88]	—
2g ($C_{11}H_{18}O_3$)	1717	1651	—	66.65 [66.64]	8.73 [9.15]	—
3g ($C_{11}H_{18}O_3$)	1720	1642	820	66.65 [66.64]	8.50 [9.15]	—
2h ($C_{14}H_{22}O_2$)	1720	1652	—	75.42 [75.63]	9.75 [9.97]	—
3h ($C_{14}H_{22}O_2$)	1720	1641	820	75.35 [75.63]	9.64 [9.97]	—
2i ($C_{11}H_{16}O_2$)	1718	1650	984, 929	—	—	—
3i ($C_{11}H_{16}O_2$)[a]	1719	1641	986, 929	—	—	—
2j ($C_{13}H_{20}O_2$)	1716	1653	—	74.85 [74.96]	9.75 [9.68]	—
3j ($C_{13}H_{20}O_2$)	1721	1642	—	74.65 [74.96]	9.65 [9.68]	
3k ($C_{10}H_{15}ClO_2$)	1720	1640	818	—	—	202.0752[b] (202.0761)
2l ($C_{10}H_{15}BrO_2$)	1719	1649	982-	48.89 [48.58]	6.08 [6.07]	—
3l ($C_{10}H_{15}BrO_2$)	1721	1640	819	48.75 [48.58]	6.19 [6.07]	—
2m ($C_{11}H_{20}O_2Si$)[c]	—	—	—	—	—	212.1222[b] (212.1233)
3m ($C_{11}H_{20}O_2Si$)[c]	—	—	—	—	—	212.1243[b] (212.1233)
2n ($C_8H_{11}N$)[a]	—	1631	2222, 971	—	—	121.0888[b] (121.0891)
3n ($C_8H_{11}N$)	—	1621	2218	—	—	121.0898[b] (121.0891)
2o ($C_8H_{12}O_2$)[36]	1687	1644	3100, 986	—	—	140.0836[b] (140.0837)
3o ($C_8H_{12}O_2$)[36]	1693	1634	3100, 826	—	—	140.0838[b] (140.0837)
2p ($C_{14}H_{18}O_2S$)[a]	—	1624[d]	1597, 1315, 1140, 976, 815[d]	—	—	250.1031[b] (250.1028)
3p ($C_{14}H_{18}O_2S$)[a]	—			—	—	250.1021[b] (250.1028)
2q ($C_9H_{14}O$)[35]	1673	1623	—	—	—	—
2y ($C_{11}H_{16}O_4$)	1722	1642	—	62.44 [62.25]	7.29 [7.60]	—
2z ($C_{13}H_{20}O_4$)	1728	1646	—	64.78 [64.98]	8.51 [8.39]	—
2aa ($C_{17}H_{28}O_4$)	1727	1642	—	69.24 [68.89]	9.35 [9.52]	—
3aa ($C_{17}H_{28}O_4$)	1721	1638	—	68.54 [68.89]	9.38 [9.52]	—
2bb ($C_{17}H_{28}O_4$)	1721	1643	838	68.82 [68.89]	9.41 [9.52]	—
3bb ($C_{17}H_{28}O_4$)	1718	1630	842	68.89 [68.89]	9.28 [9.52]	—
7a ($C_{10}H_{16}O_2$)[38]	1724	1651	983	—	—	—
8a ($C_{10}H_{16}O_2$)[39]	1724	1644	820	—	—	—
7b ($C_{11}H_{18}O_2$)[22]	1724	1652	983	—	—	—
8b ($C_{11}H_{18}O_2$)[22]	1724	1644	820	—	—	—
7c ($C_{12}H_{20}O_2$)[a,34]	1719	1650	—	—	—	—
8e ($C_{14}H_{24}O_2$)	1722	1638	816	74.84 [75.01]	10.39 [10.70]	—
7k ($C_{11}H_{17}ClO_2$)[a]	1721	1650	892	—	—	—
8k ($C_{11}H_{17}ClO_2$)	1720	1637	818	—	—	217.0995[e] (217.0995)
7l ($C_{11}H_{17}BrO_2$)	1720	1650	982	—	—	260.0414[b] (260.0412)
8l ($C_{11}H_{17}BrO_2$)	1720	1638	818	—	—	—
7n ($C_9H_{13}N$)[40]	—	1629	967, 2222	—	—	135.1049[b] (135.1048)
8n ($C_9H_{13}N$)[41]	—	1624	2219	—	—	135.1047[b] (135.1048)
7o ($C_9H_{14}O_2$)[a,38]	1689[d]	1639[d]	3100, 984, 827[d]	—	—	—
8o ($C_9H_{14}O_2$)[a]				—	—	—
7p ($C_{15}H_{20}O_2S$)[a]	—	1624[d]	1597, 1316, 1142, 972, 811[d]	—	—	—
8p ($C_{15}H_{20}O_2S$)[a]				—	—	264.1178[b](264.1184)
7y ($C_{12}H_{18}O_4$)[37]	1723	1644	—	—	—	—
8y ($C_{12}H_{18}O_4$)[37]	1723	1635	—	—	—	—
9a ($C_{11}H_{18}O_2$)	1725	1652	—	72.25 [72.49]	9.80 [9.95]	—
10a ($C_{11}H_{18}O_2$)	1724	1642	816	72.11 [72.49]	9.73 [9.95]	—
9b ($C_{12}H_{20}O_2$)[42]	1719	1648	—	—	—	—
10b ($C_{12}H_{20}O_2$)	1720	1641	818	73.48 [73.43]	10.06 [10.27]	—
9d ($C_{14}H_{24}O_2$)	1720	1650	—	74.95 [74.95]	10.43 [10.78]	—
10d ($C_{14}H_{24}O_2$)	1721	1641	816	74.72 [74.95]	10.61 [10.78]	—
9n ($C_{10}H_{15}N$)[a]	—	1627[d]	2221[d]	—	—	150.1281[e] (150.1283)
10n ($C_{10}H_{15}N$)[a]				—	—	150.1277[e] (150.1283)
9p ($C_{16}H_{22}O_2S$)[a]	—	1620[d]	1595, 1313, 1140, 970, 809[d]	—	—	278.1344[b] (278.1341)
10p ($C_{16}H_{22}O_2S$)[a]					—	278.1341[b] (278.1341)
11a ($C_{12}H_{20}O_2$)	1725	1653	—	73.38 [73.43]	10.13 [10.27]	—
12a ($C_{12}H_{20}O_2$)	1724	1642	829	73.21 [73.43]	10.15 [10.27]	—
11b ($C_{13}H_{22}O_2$)	1721	1651	—	74.33 [74.24]	10.18 [10.54]	—
12b ($C_{13}H_{22}O_2$)	1720	1640	830	74.26 [74.24]	10.23 [10.54]	—
11n ($C_{11}H_{17}N$)[a]	—	1627	2221, 970,	—	—	163.1277[b] (163.1283)
12n ($C_{11}H_{17}N$)	—	1618	2219	—	—	163.1278[b] (163.1283)
11p ($C_{17}H_{24}O_2S$)[a]	—	1620[d]	1597, 1315, 1142, 975, 811[d]	—	—	292.1497[b] (292.1497)
12p ($C_{16}H_{22}O_2S$)[a]	—			—	—	292.1490[b] (292.1497)

[a] Obtained as a mixture with its stereoisomer. [b] EI. [c] Obtained as a mixture with its stereoisomer and the corresponding acids. [d] For mixtutre of stereoisomers. [e] CI, $M^+ + H$.

Table 6 NMR data for photoproducts obtained from cyclopentane

Alkene	δ_H/ppm	δ_C/ppm
2a[34]	1.38–1.50 (m, 2H), 1.58–1.78 (m, 4H), 1.80–1.90 (m, 2H), 2.59 (m, 1H, H_4), 3.72 (s, 3H, OCH_3), 5.80 (d, 1H, H_2, *J* 15.6), 6.95 (dd, 1H, H_3, *J* 15.6, *J* 8.0).	167.2, 153.6, 118.7, 51.1, 42.6, 32.2, 25.0
3a	0.82–0.90 (m, 2H), 1.20–1.38 (m, 2H), 1.58–1.78 (m, 2H), 1.87–1.96 (m, 2H), 3.65 (m, 1H, H_4), 3.70 (s, 3H, OCH_3), 5.68 (d, 1H, H_2, *J* 11.5), 6.12 (dd, 1H, H_3, *J* 11.5, *J* 10.0).	166.9,155.6, 117.4, 50.8, 39.0, 33.3, 25.5
2b[35]	1.30 (t, 3H, CH_3CH_2, *J* 7.0Hz), 1.36–1.41 (m, 2H), 1.59–1.80 (m, 4H), 1.81–1.88 (m, 2H), 2.60 (m, 1H, H_4), 4.18 (q, 2H, OCH_2, *J* 7.0), 5.80 (dd, 1H, H_2, *J* 15.6, *J* 1.0), 6.95 (dd, 1H, H_3, *J* 15.6, *J* 8.0).	—
3b	1.28 (t, 3H, CH_3CH_2, *J* 7.0 Hz), 1.59–1.70 (m, 6H), 1.91–1.99 (m, 2H), 3.69 (m, 1H, H_4), 4.16 (q, 2H, OCH_2, *J* 7.0), 5.67 (dd, 1H, H_2, *J* 11.3, *J* 1.1), 6.10 (dd, 1H, H_3, *J* 11.3, *J* 9.8).	167.0, 155.3, 117.9, 59.7, 39.1, 33.3, 26.0, 14.2
2d	0.90 (d, 6H, $(CH_3)_2CH$, *J* 6.7), 1.33–1.38 (m, 2H), 1.57–1.78 (m, 4H), 1.88–1.95 (m, 2H), 1.92 (m, 1H, $(CH_3)_2CH$), 2.54 (m, 1H, H_4), 3.86 (d, 2H, OCH_2, *J* 6.7), 5.76 (d, 1H, H_2, *J* 15.4), 6.90 (dd, 1H, H_3, *J* 15.4, *J* 7.6).	167.1, 153.2, 118.9, 70.2, 42.8, 32.1, 27.7, 25.1, 19.2.
3d	0.95 (d, 6H, $(CH_3)_2CH$, *J* 6.7), 1.23–1.28 (m, 2H), 1.59–1.71 (m, 4H), 1.93–1.98 (m, 3H), 3.68 (m, 1H, H_4), 3.89 (d, 2H, OCH_2, *J* 6.7), 5.68 (d, 1H, H_2, *J* 11.5), 6.11 (dd, 1H, H_3, *J* 11.5, *J* 10.0)	166.7, 155.1, 118.0, 70.0, 39.2, 33.4, 27.7, 25.5, 19.2.
2f[a]	5.86 (dd, 1H, H_2, *J* 15.6, *J* 0.98), 6.14 (dd, 1H, H_3, *J* 15.6, *J* 8.0).	—
3f	1.20–1.35 (m, 2H), 1.58–1.80 (m, 4H), 1.87–1.99 (m, 2H), 3.72 (m, 1H, H_4), 5.15 (s, 2H, Ph–CH_2), 5.73 (dd, 1H, H_2, *J* 11.5, *J* 0.98), 6.14 (dd, 1H, H_3, *J* 11.5, *J* 10.0), 7.10–7.40 (m, 5H, Ph).	166.2, 155.9, 136.0, 128.5, 128.3, 128.1, 117.6, 65.6, 39.2, 33.6, 25.5.
2g	1.36–1.43 (m, 2H), 1.58–1.73 (m, 4H), 1.81–1.84 (m, 2H), 3.40 (s, 3H, OCH_3), 3.63 (t, 2H, CH_2OCH_3, *J* 6.0), 4.28 (t, 2H, $COOCH_2$, *J* 6.0), 5.84 (d, 1H, H_2, *J* 15.6), 6.98 (dd, 1H, H_3, *J* 15.6, *J* 7.8).	166.9, 154.2, 118.9, 70.5, 63.2, 58.9, 42.7, 32.2, 25.1.
3g	0.85 (m, 1H), 1.16–1.25 (m, 2H), 1.61–1.69 (m, 4H), 1.92 (m, 1H), 3.38 (s, 3H, OCH_3), 3.62 (t, 2H, CH_2OCH_3, *J* 6.0), 4.26 (t, 2H, $COOCH_2$, *J* 6.0), 5.73 (d, 1H, H_2, *J* 11.7), 6.14 (dd, 1H, H_3, *J* 11.7, *J* 10.2).	167.1, 156.0, 118.3, 71.2, 63.5, 59.6, 39.9, 34.0, 26.2.
2h	1.26–1.36 (m, 2H), 1.37–1.46 (m, 2H), 1.50–1.82 (m, 12H), 2.22 (m, 1H, OCH_2CH), 2.58 (m,1H, H_4), 4.00 (d, 2H, OCH_2, *J* 6.8), 5.80 (d, 1H, H_2, *J* 15.6), 6.94 (dd, 1H, H_3, *J* 15.6, *J* 7.8).	167.5, 153.7, 119.6, 68.5, 43.1, 38.8, 38.7, 29.7, 25.5.
3h	1.20–1.32 (m, 2H), 1.55–1.90 (m, 12H), 2.22 (m, 1H, OCH_2CH), 3.69 (m,1H, H_4), 3.99 (d, 2H, OCH_2, *J* 6.8), 5.67 (d, 1H, H_2, *J* 11.7), 6.10 (dd, 1H, H_3, *J* 11.7, *J* 9.75).	167.1, 155.4, 118.4, 68.2, 39.5, 38.8, 33.7, 29.7, 25.8, 25.6.
2i	1.37 (m, 2H), 1.59–1.69 (m, 4H), 1.83 (m, 2H), 2.58 (m, 1H, H_4), 4.63 (d, 2H, OCH_2, *J* 5.8), 5.23 and 5.31 (ds, 2H, CH=CH_2, *J* 10.2, *J* 15.6), 5.80 (d, 1H, H_2, *J* 15.6), 5.96 (m, 1H, CH=CH_2), 6.00 (dd, 1H, CHC*H*=CH, *J* 8.3, *J* 15.6).	166.5, 154.0, 132.3, 118.9, 118.0, 64.8, 42.8, 32.2, 25.1.
3i[a]	1.18 (m, 2H), 1.57–1.62 (m, 4H), 1.83 (m, 2H), 3.62 (m, 1H, H_4), 4.53 (d, 2H, OCH_2, *J* 5.8), 5.15 and 5.23 (ds, 2H, CH=CH_2, *J* 10.2, *J* 17.0), 5.63 (d, 1H, H_2, *J* 11.7), 5.85 (m, 1H, CH=CH_2), 6.07 (t, 1H, H_3, *J* 11.7)	166.1, 155.9, 132.6, 117.9, 117.5, 64.5, 39.1, 33.3, 25.5.
2j	1.34–1.39 (m, 2H), 1.51–1.57 (m, 4H), 1.65–1.80 (m, 2H), 1.68 (s, 3H, CH_3C), 1.72 (s, 3H, CH_3C), 2.54 (m, 1H, H_4), 4.58 (d, 2H, OCH_2, *J* 7.3), 5.32 (t, 1H, (C=C*H*CH_2, *J* 7.3), 5.75 (d, 1H, H_2, *J* 15.7), 6.92 (dd, 1H, H_3, *J* 15.7, *J* 7.7).	167.0, 153.6, 138.0, 119.2, 118.7, 61.0, 42.8, 32.3, 25.7, 25.2, 18.0.
3j	1.14–1.20 (m, 2H), 1.47–1.61 (m, 4H), 1.65 (s, 3H, CH_3C), 1.70 (s, 3H, CH_3C), 1.83–1.87 (m, 2H), 3.60 (m, 1H, H_4), 4.53 (d, 2H, OCH_2, *J* 7.3), 5.30 (t, 1H, (C=C*H*CH_2, *J* 7.3), 5.62 (dd, 1H, H_2, *J* 11.3, *J* 1.01), 6.04 (dd, 1H, H_3, *J* 11.3, *J* 9.9).	166.5, 155.5, 137.8, 118.9, 117.9, 60.7, 39.1, 33.4, 25.7, 25.5, 18.02.
3k	1.25 (m, 2H), 1.60–1.72 (m, 4H), 1.91 (m, 2H), 3.67 (m, 1H, H_4), 3.71 (t, 2H, CH_2Cl, *J* 5.8), 4.36 (t, 2H, OCH_2, *J* 5.8), 5.73 (d, 1H, H_2, *J* 11.7), 6.18 (t, 1H, H_3, *J* 11.7).	166.0, 156.6, 117.0, 63.3, 41.5, 39.1, 33.2, 25.4.
2l	1.37 (m, 2H), 1.52–1.70 (m, 4H), 1.83 (m, 2H), 2.59 (m, 1H, H_4), 3.54 (t, 2H, CH_2Br, *J* 6.3),4.43 (t, 2H, OCH_2, *J* 6.3), 5.80 (d, 1H, H_2, *J* 15.6), 7.01 (dd, 1H, H_3, *J* 8.3, *J* 15.6).	167.0, 155.0, 118.5, 63.6, 42.9, 32.3, 28.9, 25.3.
3l	1.22 (m, 2H), 1.62–1.72 (m, 4H), 1.91 (m, 2H), 3.54 (t, 2H, CH_2Br, *J* 6.3), 3.68 (m, 1H, H_4), 4.42 (t, 2H, OCH_2, *J* 6.3), 5.70 (d, 1H, H_2, *J* 11.7), 6.19 (t, 1H, H_3, *J* 11.7).	165.9, 156.8, 117.2, 63.3, 39.4, 33.4, 28.9, 25.6.
2m[b]	0.28 (s, 9H, CH_3), 1.19–1.82 (m, 8H), 2.52 (m, 1H, H_4), 5.67 (d, 1H, H_2, *J* 15.6), 6.83 (dd, 1H, H_3, *J* 7.8, *J* 15.6).	—
3m[b]	0.28 (s, 9H, CH_3), 1.19–1.82 (m, 8H), 3.59 (m, 1H, H_4), 5.57 (d, 1H, H_2, *J* 11.2), 6.04 (t, 1H, H_3, *J* 11.2).	—
2n[a]	1.30 (m, 2H), 1.55–1.77 (m, 4H), 1.88 (m, 2H), 2.51 (m, 1H, H_4), 5.20 (d, 1H, H_2, *J* 15.6), 6.63 (dd, 1H, H_3, *J* 8.3, *J* 15.6).	160.0, 117.6, 97.6, 43.8, 32.0, 25.0.
3n	1.35 (m, 2H), 1.63–1.74 (m, 4H), 1.94 (m, 2H), 3.00 (m, 1H, H_4), 5.19 (d, 1H, H_2, *J* 10.7), 6.38 (t, 1H, H_3, *J* 10.7).	159.7, 116.2, 97.3, 42.5, 32.8, 25.4.
2o[36]	1.38 (m, 2H), 1.43–1.70 (m, 4H), 1.86 (m, 2H), 2.56 (m, 1H, H_4), 5.78 (d, 1H, H_2, *J* 15.1), 7.03 (t, 1H, H_3, *J* 8.3, *J* 15.1), 10.32 (br s, 1H, OH)	172.4, 156.5, 118.6, 42.9, 32.2, 25.2.
3o[36]	1.26 (m, 2H), 1.51–1.70 (m, 4H), 1.88 (m, 2H), 3.66 (m, 1H, H_4), 5.68 (d, 1H, H_2, *J* 11.2), 6.21 (t, 1H, H_3, *J* 11.2), 10.31 (br s, 1H, OH)	172.3, 158.0, 117.1, 39.1, 33.2, 25.4.
2p[a]	1.35 (m, 2H), 1.59–1.67 (m, 4H), 1.84 (m, 2H), 2.42 (s, 3H, CH_3), 2.61 (m, 1H, H_3), 6.29 (d, 1H, H_1, *J* 15.1), 6.93 (dd, 1H, H_2, *J* 7.8, *J* 15.1), 7.31 and 7.74 (d, 2H, *J* 8.3).	151.3, 151.0, 143.8, 139.1, 137.5, 129.6, 128.6, 128.5, 127.4, 127.2, 41.7, 37.6, 33.0, 31.7, 25.2, 24.8, 21.2[c].
3p[a]	1.35 (m, 2H), 1.59–1.67 (4H, m), 1.84 (2H, m,), 2.42 (s, 3H, CH_3), 3.71 (m, 1H, H_3), 6.11 (t, 1H, H_2, *J* 10.7), 6.19 (d, 1H, H_1, *J* 10.7), 7.31 and 7.77 (d, 2H, *J* 8.3).	
2q[35]	1.40 (m, 2H), 1.64–1.78 (m, 4H), 1.86 (m 2H), 2.42 (s, 3H, $COCH_3$), 2.60 (1H, H_4), 6.05 (d, 1H, H_2, $J_{t,ans}$ = 14.9), 6.77 (dd, 1H, H_3, *J* 10.2, *J* 14.9).	—
2y	1.52–1.58 (m, 8H), 2.68 (m, 1H, HCC=C), 3.65 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 5.74 (d, 1H, C=CH, *J* 1.46).	169.3, 165.4, 155.0, 117.0, 52.0, 51.6, 44.3, 30.0, 24.6.
2z	1.27 (t, 3H, CH_3CH_2, *J* 7.1), 1.33 (t, 3H, CH_3CH_2, *J* 7.1), 1.52–1.58 (m, 8H), 2.75 (m, 1H, HCC=C), 4.10 (q, 2H, CH_3CH_2, *J* 7.1), 4.30 (q, 2H, CH_3CH_2, *J* 7.1), 5.77 (d, 1H, C=CH, *J* 1.47).	168.9, 165.0, 155.0, 117.0, 61.1, 60.5, 44.3, 30.7, 24.7, 14.0.
2aa	0.85 (d, 6H, Me, *J* 6.3), 0.87 (d, 6H, Me, *J* 6.3), 1.53–1.91 (m, 8H, CH_2), 1.93 (m, 2H, C*H*Me), 2.67 (m, 1H, HCC=C), 3.80 and 3.92 (ds, 4H, OCH_2, *J* 6.8), 5.71 (s, 1H, C=CH).	168.9, 164.9, 154.5, 116.9, 71.3, 70.6, 44.3, 30.8, 27.5, 24.6, 19.1, 19.0.
3aa	0.96 (d, 6H, Me, *J* 6.3), 0.97 (d, 6H, Me, *J* 6.3), 1.58–1.95 (m, 8H, CH_2), 1.98(m, 2H, C*H*Me), 2.79 (m, 1H, CHC=C), 3.94 and 4.00 (ds, 4H, OCH_2, *J* 6.8), 6.49 (s, 1H, C=CH).	168.9, 164.9, 154.5, 125.2, 71.2, 70.7, 38.7, 31.5, 27.6, 26.4, 19.1, 18.8.
2bb	1.34–1.80 (m, 8H), 1.38 (s, 9H, $C(CH_3)_3$), 1.52 (s, 9H, $C(CH_3)_3$), 2.66 (m, 1H, HCC=C), 5.59 (s, 1H, C=CH).	168.2, 164.5, 153.3, 118.2, 82.0, 80.5, 44.3, 30.5, 28.0, 27.9, 24.7.
3bb	1.45 (s, 9H, $C(CH_3)_3$), 1.46 (s, 9H, $C(CH_3)_3$), 1.40–1.80 (m, 8H), 3.70 (m, 1H, HCC=C), 6.25 (s, 1H, C=CH).	167.0, 164.9, 152.0, 125.9, 81.7, 81.0, 38.8, 31.4, 28.0, 27.8, 26.4.

[a] Obtained as a mixture with its stereoisomer. [b] Obtained as a mixture with its stereoisomer and the corresponding acids. [c] For mixture of stereoisomers.

Table 7 NMR data for photoproducts obtained from cyclohexane, cycloheptane and cyclooctane

	δ_H/ppm	δ_C/ppm
7a[38]	1.12–1.34 (m, 5H), 1.65–1.77 (m, 5H), 2.13 (m, 1H, H_4), 3.72 (s, 3H, OMe), 5.78 (d, 1H, H_2, *J* 15.7), 6.91 (dd, 1H, H_3, *J* 6.9, *J* 15.7).	167.4, 154.4, 118.3, 51.2, 40.3, 32.2, 25.7, 25.5.
8a[39]	0.99–1.30 (m, 5H), 1.54–1.72 (m, 5H), 3.24 (m, 1H, H_4), 3.63 (s, 3H, OMe), 5.58 (d, 1H, H_2, *J* 11.3), 5.96 (t, 1H, H_3, *J* 11.3).	166.7, 155.9, 117.1, 50.9, 37.3, 32.2, 25.8, 25.4.
7b[22]	1.12–1.30 (m, 4H), 1.28 (t, 3H, Me, *J* 6.9), 1.65–1.83 (m, 6H), 2.13 (m, 1H, H_4), 4.17 (q, 2H, CH_2O, *J* 6.9), 5.74 (d, 1H, H_2, *J* 15.7), 6.90 (dd, 1H, H_3, *J* 6.9, *J* 15.7)	167.0, 154.1, 118.7, 60.0, 40.3, 31.6, 25.8 25.6, 14.1
8b[22]	1.12–1.39 (m, 4H), 1.33 (t, 3H, Me, *J* 6.9), 1.65–1.73 (m, 6H), 3.27 (m, 1H, H_4), 4.15 (q, 2H, CH_2O, *J* 6.9), 5.66 (d, 1H, H_2, *J* 11.7), 6.02 (dd, 1H, H_3, *J* 9.8, *J* 11.7)	166.4, 155.5, 117.6, 59.7, 37.3, 32.3, 25.8, 25.4, 14.2.
7c[a,34]	0.86–1.28 (m, 5H), 0.88 (t, 3H, Me, *J* 7.3), 1.57–1.69 (m, 5H), 1.58 (m, 3H, MeCH_2), 2.04 (m, 1H, H_4), 3.99 (t, 2H, CH_2O, *J* 6.9), 5.71 (d, 1H, H_2, *J* 15.7), 6.82 (dd, 1H, H_3, *J* 6.5, *J* 15.7).	167.1, 154.1, 118.7, 65.3, 40.2, 32.2, 25.6, 25.4, 22.0, 10.3.
8c	0.87–1.29 (m, 5H), 0.89 (t, 3H, Me, *J* 7.3), 1.56–1.69 (m, 5H), 1.58 (m, 3H, MeCH_2), 3.22 (m, 1H, H_4), 3.99 (t, 2H, CH_2O, *J* 6.9), 5.57 (d, 1H, H_2, *J* 11.7), 5.95 (t, 1H, H_3, *J* 11.7).	166.8, 155.4, 117.6, 65.8, 37.3, 31.5, 25.8, 25.3, 21.9, 10.4.
7e[a]	0.80 (d, 3H, *Me*CH, *J* 6.5), 0.86 (t, 3H, *Me*CH_2, *J* 6.5), 0.99–1.66 (m, 13H), 2.07 (m, 1H, H_4), 3.86 and 3.96 (dd, 1H, CH_2O, *J* 6.5, *J* 10.9), 5.70 (d, 1H, H_2, *J* 15.7), 6.87 (dd, 1H, H_3, *J* 6.5, *J* 15.7).	167.1, 154.1, 118.7, 68.7, 40.3, 32.2, 30.5, 26.2, 25.8, 25.6, 16.3, 11.1.
8e	0.80 (d, 3H, *Me*CH, *J* 6.5), 0.86 (t, 3H, *Me*CH_2, *J* 6.5), 0.99–1.66 (m, 13H), 3.21 (m, 1H, H_4), 3.84 and 3.94 (dd, 1H, CH_2O, *J* 6.5, *J* 10.9), 5.60 (d, 1H, H_2, *J* 11.7), 5.94 (t, 1H, H_3, *J* 11.7).	166.7, 155.2, 117.6, 68.5, 37.3, 30.6, 30.0, 26.0, 25.8, 25.4, 16.4, 11.1.
7k[a]	1.03–1.48 (m, 5H), 1.54–1.71 (m, 5H), 2.03 (m, 1H, H_4), 3.63 (t, 2H, CH_2Cl, *J* 5.8), 4.30 (t, 2H, OCH_2, *J* 5.8), 5.70 (d, 1H, H_2, *J* 15.6), 6.91 (dd, 1H, H_3, *J* 6.3, *J* 15.6).	166.5, 155.6, 118.0, 63.8, 41.6, 40.4, 31.5, 25.7, 25.6.
8k	0.85–1.37 (m, 5H), 1.59–1.66 (m, 5H), 3.19 (m, 1H, H_4), 3.63 (t, 2H, CH_2Cl, *J* 5.8), 4.27 (t, 2H, OCH_2, *J* 5.8), 5.60 (d, 1H, H_2, *J* 11.2), 6.02 (t, 1H, H_3, *J* 11.2).	165.7, 156.8, 116.7, 63.4, 41.5, 37.4, 32.2, 25.7, 25.3.
7l	0.84–1.34 (m, 5H), 1.66–1.78 (m, 5H), 2.15 (m, 1H, H_4), 3.54 (t, 2H, CH_2Br, *J* 6.3), 4.43 (t, 2H, OCH_2, *J* 6.3), 5.81 (dd, 1H, H_2, J_{LR} 0.9, *J* 15.6), 6.99 (dd, 1H, H_3, *J* 6.3, *J* 15.6).	166.3, 155.5, 117.9, 63.4, 40.3, 31.4, 28.7, 25.7, 25.5.
8l	0.83–1.41 (m, 5H), 1.64–1.73 (m, 5H), 3.27 (m, 1H, H_4), 3.54 (t, 2H, CH_2Br, *J* 6.3), 4.42 (t, 2H, OCH_2, *J* 6.3), 5.70 (dd, 1H, H_2, J_{LR} 0.9, *J* 11.7), 6.10 (t, 1H, H_3, *J* 11.7).	165.0, 156.9, 116.7, 63.2, 37.4, 32.2, 28.8, 25.8, 25.4.
7n[40]	0.88–1.39 (m, 5H), 1.62–1.77 (m, 5H), 2.13 (m, 1H, H_4), 5.24 (d, 1H, H_2, *J* 16.6), 6.66 (dd, 1H, H_3, *J* 6.8, *J* 16.6).	—
8n[41]	0.88–1.39 (m, 5H), 1.62–1.76 (m, 5H), 2.60 (m, 1H, H_4), 5.22 (d, 1H, H_2, *J* 10.7), 6.29 (t, 1H, H_3, *J* 10.7).	—
7o[a,38]	0.88–1.38 (m, 5H), 1.66–1.78 (m, 5H), 2.18 (m, 1H, H_4), 5.76 (d, 1H, H_2, *J* 15.6), 7.02 (dd, 1H, H_3, *J* 6.8, *J* 15.6), 10.83 (br s, OH).	172.6, 172.1, 158.1, 157.1, 118.2, 117.0, 40.3, 37.3, 32.0, 31.3, 25.7, 25.5, 25.2[b].
8o[a]	0.88–1.38 (m, 5H), 1.66–1.78 (m, 5H), 3.28 (m, 1H, H_4), 5.66 (dd, 1H, H_2, *J* 11.2), 6.15 (t, 1H, H_3, *J* 11.2), 10.83 (br s, OH).	
7p[a]	1.10–1.28 (m, 5H), 1.64–1.73 (m, 5H), 2.15 (m, 1H, H_3), 6.25 (d, 1H, H_1, *J* 15.1), 2.42 (s, 3H, Me), 6.90 (dd, 1H, H_2, *J* 6.3, *J* 15.1), 7.31 and 7.73 (d, 2H, *J* 8.3).	151.3, 151.0, 144.0, 137.6, 129.7, 128.5, 127.2, 126.8, 39.7, 36.3, 31.8, 31.1, 25.6, 25.4, 25.0, 21.5[b].
8p[a]	1.10–1.28 (m, 5H), 1.64–1.73 (m, 5H), 2.42 (s, 3H, Me), 3.31 (m, 1H, H_3), 6.00 (t, 1H, H_2, *J* 10.7), 6.19 (d, 1H, H_1, *J* 10.7), 7.31 and 7.78 (d, 2H, *J* 8.3).	
7y[37]	1.10–1.40 (m, 5H), 1.70–1.90 (m, 5H), 2.30 (m, 1H, HCC=C), 3.71 (s, 3H, OMe), 3.84 (s, 3H, OMe), 5.76 (d, 1H, C=CH, J_{LR} 1.2)	169.3, 165.6, 156.2, 116.8, 52.0, 51.6, 42.2, 31.0, 26.0, 25.7.
8y[37]	1.10–1.40 (m, 5H), 1.70–1.90 (m, 5H), 3.30 (m, 1H, HCC=C), 3.68 (s, 3H, OMe), 3.70 (s, 3H, OMe), 6.31 (s, 1H, C=CH)	—
9a	1.38–1.82 (m, 12H), 2.30 (m, 1H, H_4), 3.72 (s, 3H, OMe), 5.74 (dd, 1H, H_2, J_{LR} 1.46, *J* 15.6), 6.97 (dd, 1H, H_3, *J* 7.6, *J* 15.6,).	168.0, 155.0, 118.0, 51.3, 42.3, 33.4, 28.3, 26.0.
10a	1.25–1.80 (m, 12H), 3.40 (m, 1H, H_4), 3.72 (s, 3H, OMe), 5.61 (d, 1H, H_2, *J* 11.5), 6.12 (dd, 1H, H_3, *J* 10.5, *J* 11.5).	166.7, 156.6, 116.0, 51.0, 38.5, 34.1, 28.3, 26.4.
9b[42]	1.33 (t, 3H, $MeCH_2$, *J* 7.1), 1.60–1.80 (m, 12H), 2.30 (m, 1H, H_4), 4.15 (q, 2H, OCH_2, *J* 7.1), 5.74 (dd, 1H, H_2, J_{LR} 1.2, *J* 15.8), 6.95 (dd, 1H, H_3, *J* 7.6, *J* 15.8)	167.2, 154.1, 117.9, 60.1, 42.3, 33.3, 28.3, 26.0, 14.3.
10b	1.28 (t, 3H, $MeCH_2$, *J* 7.1), 1.60–1.80 (m, 12H), 3.46 (m, 1H, H_4), 4.15 (q, 2H, OCH_2, *J* 7.1), 5.60 (dd, 1H, H_2, J_{LR} 1.0, *J* 11.5), 6.10 (dd, 1H, H_3, *J* 10.0, *J* 11.5).	166.0, 156.6, 116.0, 59.7, 38.5, 34.2, 28.4, 26.4, 14.3.
9d	0.95 (d, 6H, Me_2CH, *J* 6.6), 1.38–1.80 (m, 12H), 1.95 (m, 1H, Me_2CH), 2.34 (m, 1H, H_4), 3.90 (d, 2H, OCH_2, *J* 6.6), 5.75 (dd, 1H, H_2, J_{LR} 1.2, *J* 15.6,), 6.95 (dd, 1H, H_3, *J* 7.6, *J* 15.6).	167.2, 155.2, 118.1, 70.2, 42.2, 33.3, 28.2, 27.7, 26.0, 19.0.
10d	0.95 (d, 6H, Me_2CH, *J* 6.6), 1.25–1.31 (m, 2H), 1.34–1.76 (m, 10H), 1.95 (m, 1H, Me_2CH), 3.45 (m, 1H, H_4), 3.89 (d, 2H, OCH_2, *J* 6.6), 5.62 (d, 1H, H_2, *J* 11.5), 6.10 (dd, 1H, H_3, *J* 10.0, *J* 11.5).	166.1, 156.0, 116.2, 70.0, 38.6, 34.3, 28.3, 27.7, 23.6, 19.2.
9n[c]	1.34–1.76 (m, 12H), 2.32 (m, 1H, H_4), 5.23 (d, 1H, H_2, *J* 16.6), 6.69 (dd, 1H, H_3, *J* 7.8, *J* 16.6).	161.5, 117.9, 96.9, 43.4, 32.9, 28.0, 26.1.
10n[c]	1.37–1.75 (m, 12H), 2.75 (m, 1H, H_4), 5.17 (d, 1H, H_2, *J* 10.7), 6.38 (t, 1H, H_3, *J* 10.7).	160.6, 116.2, 95.9, 42.5, 33.6, 28.2, 26.2.
9p[a]	1.22–1.72 (m, 12H), 2.29 (m, 1H, H_3), 2.35 (s, 3H, Me), 6.12 (d, 1H, H_1, *J* 15.1), 6.88 (dd, 1H, H_2, *J* 7.3, *J* 15.1), 7.23 and 7.66 (d, 2H, *J* 8.3).	151.8, 145.1, 137.8, 129.7, 127.9, 127.4, 41.6, 32.9, 28.0, 26.0, 21.5.
10p[d]	1.22–1.72 (m, 12H), 2.35 (s, 3H, Me), 3.37 (m, 1H, H_3), 6.00 (t, 1H, H_2, *J* 10.7), 6.04 (d, 1H, H_1, *J* 10.7), 7.23 and 7.72 (d, 2H, *J* 8.3).	151.9, 145.1, 137.8, 129.7, 127.9, 127.4, 37.2, 33.4, 28.0, 25.9, 21.5.
11a	1.40–1.80 (m, 14H), 2.20 (m, 1H, H_4), 3.72 (s, 3H, OMe), 5.75 (dd, 1H, H_2, J_{LR} 1.46, *J* 15.5), 6.95 (dd, 1H, H_3, *J* 7.6, *J* 15.5).	168.1, 156.0, 118.0, 51.0, 40.6, 30.4, 27.2, 24.8, 26.3.
12a	1.30–1.80 (m, 14H), 3.60 (m, 1H, H_4), 3.70 (s, 3H, OMe), 5.62 (dd, 1H, H_2, J_{LR} 1.2, *J* 11.5), 6.13 (dd, 1H, H_3, *J* 10.0, *J* 11.5,).	165.1, 157.2, 115.6, 51.0, 36.2, 32.0, 26.9, 25.1, 26.3.
11b	1.26 (t, 3H, $MeCH_2$, *J* 7.0), 1.49–1.66 (m, 10H), 1.69–1.72 (m, 4H), 2.35 (m, 1H, H_4), 4.15 (q, 2H, OCH_2, *J* 7.0), 5.72 (dd, 1H, H_2, J_{LR} 1.0, *J* 15.7), 6.92 (dd, 1H, H_3, *J* 7.3, *J* 15.7)	167.2, 155.3, 118.5, 60.1, 40.6, 30.5, 27.2, 25.9, 24.8, 14.3.
12b	1.22 (t, 3H, $MeCH_2$, *J* 7.3), 1.30–1.35 (m, 2H), 1.45–1.60 (m, 12H), 3.49 (m, 1H, H_4), 4.10 (q, 2H, OCH_2, *J* 7.3), 5.52 (dd, 1H, H_2, J_{LR} 1.0, *J* 11.4), 6.03 (dd, 1H, H_3, *J* 10.3, *J* 11.4).	166.5, 156.6, 116.0, 59.7, 36.3, 32.1, 26.9, 26.4, 25.1, 14.3.
11n[a]	1.45–1.70 (m, 14H), 2.38 (m, 1H, H_4), 5.23 (d, 1H, H_2, *J* 16.6), 6.68 (dd, 1H, H_3, *J* 7.3, *J* 16.6).	161.8, 117.8, 97.0, 41.6, 31.9, 26.9, 25.8, 24.6.
12n	1.49–1.75 (m, 12H), 2.82 (m, 1H, H_4), 5.15 (d, 1H, H_2, *J* 10.7), 6.40 (t, 1H, H_3, *J* 10.7).	160.9, 116.1, 96.0, 40.7, 31.2, 26.8, 25.9, 24.8.
11p[a]	1.27–1.74 (m, 14H), 2.43 (s, 3H, Me), 2.45 (m, 1H, H_3), 6.20 (d, 1H, H_1, *J* 15.1), 6.93 (dd, 1H, H_2, *J* 7.3, *J* 15.1). 7.23 and 7.65 (d, 2H, *J* 8.3).	152.3, 152.1, 144.0, 138.0, 129.8, 128.0, 127.4, 127.1, 39.8, 36.1, 31.3, 30.2, 26.9, 26.6, 26.1, 25.6, 24.6, 21.5[b].
12p[a]	1.27–1.74 (m, 14H), 2.43 (s, 3H, Me), 3.54 (m, 1H, H_3), 6.05 (t, 1H, H_2, *J* 10.7), 6.13 (d, 1H, H_1, *J* 10.7), 7.23 and 7.72 (d, *J* 8.3).	

[a] Obtained as a mixture with its stereoisomer. [b] For mixture of stereoisomers. [c] Obtained as a mixture with benzophenone. [d] Obtained as a mixture with benzopinacol.

t, J = 7.1 Hz, C*H*=C), 7.20–7.40 (5H; m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 147.5, 136.0, 128.5, 128.3, 128.1, 111.1, 66.2, 35.0, 33.6, 36.3. $C_{15}H_{18}O_2$ requires: C, 78.23; H, 7.88%; found: C, 78.32; H, 8.05%.

Irradiation of methyl (*Z*)-3-cycloheptyl-2-propenoate 10a. Irradiation of **10a** in the standard way for 5 h resulted in the formation of methyl 3-cycloheptylidenepropanoate **16** (70%), which was obtained as a colourless liquid: ν_{max}(film)/cm^{-1} 1741; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.49–1.57 (8H, m), 2.21–2.36 (4H, m, (H_2C)C=CH)), 3.03 (2H, d, J = 6.8 Hz, CH_2CO), 3.60 (3H, s, OCH_3), 5.33 (1H, t, J = 6.8 Hz, CH=C); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 145.0, 116.0, 52.2, 37.6, 33.2, 30.2, 29.0, 26.0. $C_{11}H_{18}O_2$ requires: C, 72.49; H, 9.95%; found: C, 72.22; H, 10.27%.

Irradiation of methyl (*Z*)-3-cyclooctyl-2-propenoate 12a. Irradiation of **12a** as described above for 6.5 h resulted in the formation of methyl 3-cyclooctylidenepropanoate **17** (67%), which was obtained as a colourless liquid: ν_{max}(film)/cm^{-1} 1742; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43–1.54 (6H, m), 1.56–1.68 (6H, m), 2.14–2.23 (4H, m, (H_2C)C=CH), 3.07 (2H, d, J = 7.0 Hz, CH_2CO), 3.68 (3H, s, OCH_3), 5.36 (1H, t, J = 7.0 Hz, CH=C); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 145.1, 116.0, 51.6, 37.5, 33.4, 29.0, 27.2, 26.9, 26.1, 25.9, 25.8. $C_{11}H_{18}O_2$ requires: C, 73.43; H, 10.27%; found: C, 73.34; H, 10.19%.

Irradiation of dimethyl (*Z*)-2-cyclopentyl-2-butendioate 2y. A solution of **2y** (0.22 g, 1.00 mmol) in cyclopentane (20 ml) containing 3 drops of NEt_3 was irradiated in a quartz tubes using 254 nm lamps for 25 h. At this point no **2y** remained and two products had formed in a 1 : 1 ratio. The crude product was chromatographed on silica gel (ether–petroleum ether, 0–20%), the first product eluting being dimethyl 2-cyclopent-1-en-1-ylsuccinate **19** (0.07 g, 30%): ν_{max}(film)/cm^{-1} 1738; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 (2H, m), 2.26–2.34 (4H, m), 2.55 (1H, dd, J_{gem} = 16.5, J_{vic} = 5.5 Hz, *H*CHCO), 2.94 (1H, dd, J_{gem} = 16.5, J_{vic} = 9.8 Hz, HC*H*CO), 3.65 (1H, m, CHCO), 3.68 (3H, s, OCH_3), 3.71 (3H, s, OCH_3), 5.55 (1H, broad s, CH=C); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 172.3, 139.6, 127.8, 52.7, 51.2, 43.2, 35.0, 33.3, 32.4, 22.9. $C_{11}H_{16}O_4$ requires: C, 62.25; H, 7.60%; found: C, 62.36; H, 7.81%. Further elution gave dimethyl 2-cyclopentylidenesuccinate **18** (0,06 g, 26%): ν_{max}(film)/cm^{-1} 1740, 1719; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67–1.76 (4H, m), 2.40 (2H, t, J = 7.0 Hz, CH_2C=C), 2.82 (2H, t, J = 7.0 Hz, CH_2C=C), 3.35 (2H, s, CH_2CO), 3.68 (3H, s, OCH_3), 3.72 (3H, s, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 167.5, 165.3, 116.6, 51.8, 51.4, 35.8, 34.5, 34.1, 26.9, 25.5. $C_{11}H_{16}O_4$ requires: C, 62.25; H, 7.60%; found: C, 62.23; H, 7.74%.

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