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Efficient photochemical synthesis of 2-vinylcyclopropanecarbaldehydes, precursors of cyclopropane components present in pyrethroids, by using the oxa-di-π-methane rearrangement

Diego Armesto *, Maria J. Ortiz *, Antonia R. Agarrabeitia, Noureddin El-Boulifi

Departamento de Química Orgánica I, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain

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ABSTRACT

A comparative study on the triplet photoreactivity of a series of β,γ,δ,ε-unsaturated aldehydes **14a**–**f** and **15**, using 3-methoxyacetophenone and 4-phenylbenzophenone as sensitizers, has been carried out. When 3-methoxyacetophenone is used as the triplet sensitizer, the aldehydes undergo oxa-di-π-methane rearrangement (ODPM) to afford the corresponding cyclopropanecarbaldehydes **16a**–**f** and **17** in yields ranging from 14% to 62% in addition in most cases to products resulting from decarbonylation. However, when 4-phenylbenzophenone is used as the photosensitizer ODPM products are obtained exclusively in almost quantitative yield. These are additional examples of the recently described, unexpected influence of the nature of the triplet sensitizer on the photoreactivity of organic compounds.

1. Introduction

Pyrethrins are natural insecticides produced by the flowers of *Chrysanthemum cinerafolis* and *Chrysanthemum coccineum*.[1] The major components of these insecticides are esters of chrysanthemic acid **1** and pyrethric acid **2** with substituted optically active cyclopentenolones **3a**–**c** (Fig. 1). The pyrethroids, compounds structurally related to the natural pyrethrins, are usually more active than the natural products, and have higher thermal and photochemical stabilities. Pyrethrins and pyrethroids are lipophilic insecticides that act on the nervous system of insects with high efficiency, but they have low toxicity to mammals in general, and humans in particular, and they are biodegradable.[1,2] These properties make these substances an important family of ecological insecticides, which is the reason that they are widely used for domestic applications.

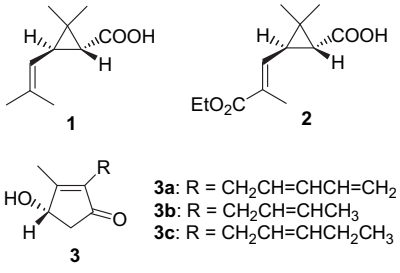

Fig. 1. Components of natural pyrethrins.

The key step in the synthetic routes to pyrethrins and pyrethroids is the construction of the substituted cyclopropanecarboxylic acid moiety that is then esterified with the appropriate alcohol. Many methods exist for the preparation of these acids, most of which are patented.[1] However, none of these synthetic approaches can be considered to be general. Among them, the addition of ethyl diazoacetate to differently substituted 1,3-butadienes and the addition of sulfur or phosphorus ylides to methyl penta-2,4-dienoates[3] have been widely used to obtain most of the common vinylcyclopropanecarboxylic acids, but all of these procedures have limitations and can be used for the synthesis of only a few pyrethroids.

In the early 90s, our group investigated a novel and potentially general methodology for the preparation of cyclopropanecarboxylic acids present in pyrethrins and pyrethroids. The key step in this synthetic approach is the 1-aza-di-π-methane (1-ADPM) rearrangement of β,γ-unsaturated oxime acetates.[4] For example, aldehydes **4**, previously considered to be unreactive in the oxa-di-π-methane (ODPM) rearrangement, were transformed into the

* Corresponding authors. Tel.: +34 913 944 316; fax: +34 913 944 103; e-mail addresses: darmesto@quim.ucm.es (D. Armesto), mjortiz@quim.ucm.es (M.J. Ortiz).

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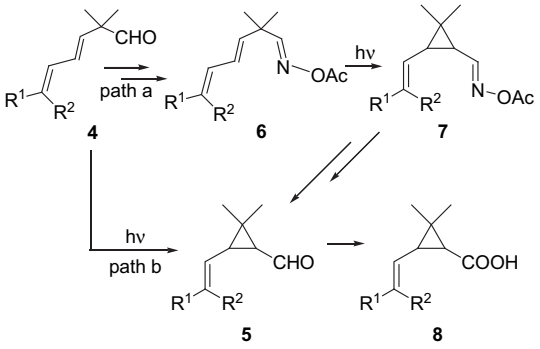
corresponding cyclopropanecarbaldehydes **5** by a route involving their conversion to oxime acetates **6**, followed by acetophenone triplet sensitized irradiation that yields the corresponding cyclopropane oxime acetates **7**, as shown in Scheme 1 (path a). Thermal elimination of acetic acid in **7** affords the corresponding nitriles, which are reduced to form aldehydes **5**. Finally, oxidation of **5** by conventional methods gives the cyclopropanecarboxylic acids **8** (Scheme 1, path a). This method proved to have general applicability and was patented.[5]



Scheme 1. Synthesis of cyclopropanecarboxilic acids via 1-ADPM and ODPM rearrangements.

Some years later, studies carried out in our laboratory demonstrated that, contrary to the common belief, suitable substituted β,γ-unsaturated aldehydes do undergo ODPM rearrangement, with high chemical efficiencies and in some cases high degrees of diastereoselectivity (Scheme 1, path b).[6] These results open a new and easier route to compounds **8**. The results of recent investigations in our group demonstrate that the nature of the sensitizer plays an important role on the photochemical reactivity of β,γ-unsaturated ketones. Thus, β,γ-unsaturated acyclic ketones **9**, previously described as being unreactive in the ODPM mode, afford the corresponding cyclopropyl ketones **10** in high yields when they are irradiated using sensitizers with triplet energies that are slightly higher than those of the β,γ-alkene moiety. In some cases, rearranged enones **11**, resulting from photoinduced 1,3-acyl migration in **9**, were also obtained depending on the sensitizer used to promote the reaction (Fig. 2).[7]

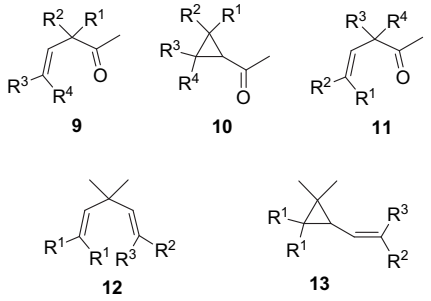


Fig. 2. Triplet photoreactivity of β,γ-unsaturated acyclic ketones and 1,4-dienes.

This surprising influence of the nature of the sensitizer on the triplet reactivity of organic compounds was further demonstrated in a recent study of the di-π-methane rearrangement (DPM) of a series of acyclic 1,4-dienes **12**. Some compounds in the series probed were previously reported to undergo the DPM rearrangement only very inefficiently when common triplet sensitizers, such as acetophenone or benzophenone, were used. Based on these earlier findings, it was concluded that most acyclic 1,4-dienes do not undergo the DPM reaction in the triplet excited state, as has been stated in books and monographs on this topic. However, our recent observations show that 1,4-dienes **12** do rearrange to the corresponding vinylcyclopropanes **13** in high yield when suitable triplet sensitizers are used (Fig. 2).[8]

Based on the observations described above, we have carried out a study on the comparative photoreactivity of a series of β,γ,δ,ε-unsaturated aldehydes **14a**–**f** and **15** using 3-methoxyacetophenone and 4-phenylbenzophenone as triplet sensitizers. The effort was aimed at determining if the corresponding ODPM products **16** and **17**, structurally related to cyclopropane components present in pyrethrins and pyrethroids, could be obtained in high yields and if alternative reaction modes, previously unreported for these compounds, could be observed (Fig. 3).

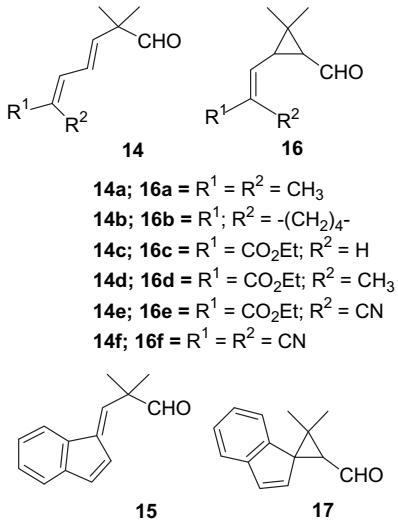
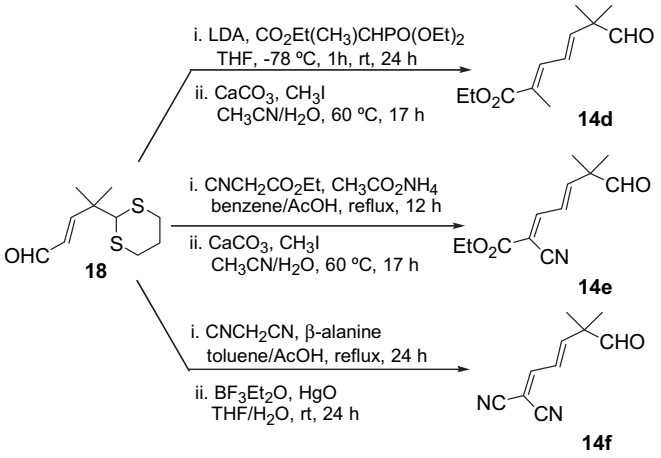


Fig. 3. Starting aldehydes (**14** and **15**) and ODPM photoproducts (**16** and **17**).

The sensitizers used in the study were selected based on the following considerations. 3-Methoxyacetophenone has been used as triplet sensitizer previously to study the photoreactivity of compounds **14a** and **14b**, This selection was based on the fact that the triplet energy (E_T=71.0 kcal mol^{-1})[9] of this sensitizer is approximately 11–13 kcal mol^{-1} higher than those of the diene moieties present in **14a**,**b**. This energy difference ensures that efficient energy transfer would take between the triplet excited state of the sensitizer and the diene. In addition, the absorption spectrum of 3-methoxyacetophenone does not overlap to a large extend with those of aldehydes **14** and **15**. 4-Phenylbenzophenone was selected as sensitizer used in this effort since excellent yields of products were obtained using this sensitizer in our previous studies on the photoreactivity of β,γ-unsaturated ketones and acyclic 1,4-dienes.[7,8] However, it should be noted that the triplet energy (E_T=61.0 kcal mol^{-1})[9] of this sensitizer is slightly higher than those of the diene moieties present in **14** and **15**. Again, the absorption spectrum of phenylbenzophenone overlaps only minimally with those **14** and **15**.

2. Results and discussion

The synthesis of **14a**,**b**,[4] **14c**,[5] and **15**[4] has been reported previously. Aldehydes **14d**–**f**, described here for the first time, were prepared from aldehyde **18**[4] by using conventional methods (Scheme 2). Compounds **14** and **15** were obtained with the stereochemistry shown in Scheme 2 in ca. 50% isolated yields.



Scheme 2. Synthetic route for aldehydes (**14d**–**f**).

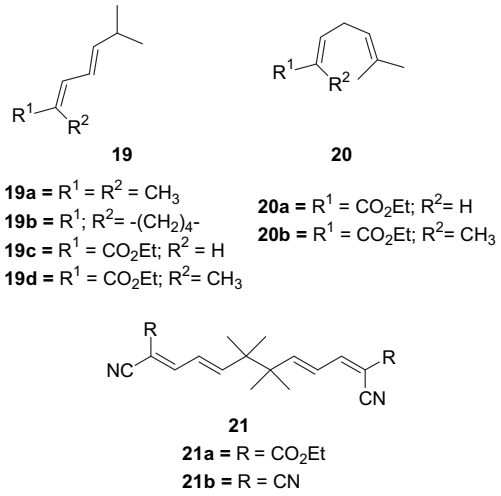


Fig. 4. Decarbonylation products (**19**–**21**).

Irradiation of **14a**,**b** in the presence of 3-methoxyacetophenone has been described previously by us. Under these conditions, aldehydes **14a**,**b** afford the corresponding ODPM products **16a**,**b** in moderate yields (52% and 47%, respectively).[6]

3-Methoxyacetophenone-sensitized irradiation of aldehydes **14c**–**f** and **15** affords the corresponding cyclopropanes **16c**–**f** and **17**, resulting from ODPM rearrangements, in isolated yields ranging from 14% to 65% (Fig. 3 and Table 1). In addition to the ODPM process, another reaction mode is followed under these conditions. Thus, photosensitized reaction of **14c** also gives an inseparable mixture of dienes **19c** and **20a**, resulting from decarbonylation, in 4% overall yield (Fig. 4). This reaction mode was also observed to take place in the reaction **14d** that yields **19d** and **20b**, in 18% overall yield (Fig. 4). However, for unknown reasons, the photoinduced decarbonylation of **14e** and **14f** affords the respective tetraenes **21a** and **21b**, resulting from dimerization of the radicals formed by decarbonylation (Fig. 4 and Table 1). Finally, aldehyde **15** does not undergo competitive decarbonylation and, as a result, it reacts to produce the ODPM product **17** (65%) exclusively. In each case, increasing the irradiation time brings about complete consumption of the starting material without improving the yield of ODPM product.

Table 1
Reaction conditions and yields of products in the irradiation of β,γ,δ,ε-unsaturated aldehydes **14** and **15**

Compd	Sens.[a]	Irrad. time (min)	ODPM (yield, %)	Dienes (yield, %)	S.M. (yield, %)
14a	3-MAP	15	**16a** (52)	**19a** (6)	**14a** (30)
14a	4-PBP	15	**16a** (94)		
14b	3-MAP	20	**16b** (47)	**19b** (6)	**14b** (30)
14b	4-PBP	20	**16b** (94)		
14c	3-MAP	45	**16c** (22)	**19c**, **20a** (4)	**14c** (52)
14c	4-PBP	45	**16c** (96)		
14d	3-MAP	60	**16d** (14)	**19d**, **20b** (18)	**14d** (55)
14d	4-PBP	60	**16d** (92)		
14e	3-MAP	45	**16e** (47)	**21a** (4)	**14e** (39)
14e	4-PBP	45	**16e** (95)		
14f	3-MAP	60	**16f** (34)	**21b** (4)	**14f**(34)
14f	4-PBP	60	**16f** (93)		
15	3-MAP	180	**17** (65)		**15** (19)
15	4-PBP	180	**17** (95)		

[a] 3-MAP=3-methoxyacetophenone; 4-PBP=4-phenylbenzophenone.

In our previous study, the decarbonylation process was not observed to participate in photoreactions of **14a** and **14b**. Therefore, the photochemical behavior of these two aldehydes was reinvestigated. A careful analysis of the photoreaction mixture showed that compounds **19a** (6%) and **19b** (6%), formed by respective decarbonylation of **14a** and **14b**, are present (Fig. 4 and Table 1). The fact that these alkenes were not detected in the earlier effort was probably a consequence of their low boiling points that led to their evaporation during conventional workup procedures. It is worth noting at this point that the decarbonylation process observed for compounds **14** is formally a Norrish type I reaction, which is commonly observed in the direct irradiation promoted reactions of carbonyl compounds. However, in the cases described above, the processes are not taking place by direct irradiation of the carbonyl group but rather by triplet sensitization of the diene unit. This is a situation that has been seldom observed.[7,10]

When aldehydes **14a**–**f** and **15** are irradiated for the same time periods using 4-phenybenzophenone as the sensitizer, the decarbonylation pathway is suppressed and the corresponding ODPM products **16** and **17** are obtained in almost quantitative isolated yields (Fig. 3 and Table 1). The results confirm that the nature of the triplet sensitizer has an important influence on the outcome of these photochemical reactions.

The results described above demonstrate that by using a sensitizer with a triplet energy that is close to the acceptor diene the yield of the rearrangement products increase and those of the decarbonylation products decrease. It can be argued that the lower yield observed in the photoreactions promoted by using 3-methoxyacetophenone as sensitizer are a result of the fact that the alkenes formed by decarbonylation can act as quenchers of the sensitizer, which leads to diminished efficiencies of the reaction. However, an increased yield of product is also observed in the reactions of **15**, substances that do not decarbonylate when 3-methoxyacetophenone is used as sensitizer. Another factor to take into account is that the triplet energy of 4-phenybenzophenone (E_T=61.0 kcal mol^{-1})[9] is lower than that of the alkene unit present in cyclopropanes **16** and **17**. This factor prevents intermolecular energy transfer and, therefore, destruction of the photoproducts. The possibility that the decarbonylation products observed in the photoreactions sensitized by 3-methoxyacetophenone could arise by direct absorption of light was also considered, but this option was discarded based on the fact that the concentrations used in these processes insures that more than 99% of the light is being absorbed by the sensitizer. Furthermore, aldehydes **15** do not undergo decarbonylation under the same irradiation conditions that are used for **14**, even though decarbonylation is the only reaction observed upon direct irradiation of **15**.

3. Conclusions

For many years a general consensus has been that the main requirement in photochemical reactions promoted by triplet sensitization is that efficient energy transfer from the triplet sensitizer to the acceptor molecule be insured. It was generally believed that once this energetic requirement is achieved the triplet excited substrate would follow a particular reaction pathway, independent of the nature of the sensitizer used. However, recent studies carried out by us show that organic molecules can react by different triplet pathways depending on the nature of the triplet sensitizer used.[7,8] The photoreactivity described above for compounds **14** and **15** is yet another example of this interesting behavior. Specifically, irradiation of aldehydes **14** and **15** using 4-phenybenzophenone as sensitizer, which has a triplet energy that is slightly above the acceptor alkene, affords the corresponding cyclopropanes **16** and **17** in almost quantitative yields without competition from decarbonylation processes. In contrast, decarbonylation becomes a highly competitive reaction pathway in reactions of these substances when sensitized by 3-methoxyacetophenone, with an energy approximately 11–13 kcal mol^{-1} higher than the triplet energy of the acceptor moieties present in **14** and **15**. The high yields of products obtained in all reactions studied suggest that the ODPM rearrangement of β,γ,δ,ε-unsaturated aldehydes using 4-phenybenzophenone as triplet sensitizer is a general, highly efficient synthetic route for the preparation of cyclopropanecarboxylic acids present in pyrethrins and pyrethroids.

4. Experimental section

4.1. General

Starting materials and reagents are commercially available unless synthesis is described. The solvents were dried and distilled, before use. Spectral data of the known compounds were in accordance with the literature data. Flash chromatography was performed using silica gel 60 (40–63 mm). ^1H and ^{13}C NMR spectra were measured on a BRUKER AC-200 spectrometer at 200 and 50 MHz, respectively, in $CDCl_3$ solution. Chemical shifts (δ) were expressed in parts per million (ppm) relative to tetramethylsilane (TMS), and coupling constants J were given in hertz (Hz). Infrared spectra were recorded as a thin film using NaCl plate on a PERKIN–ELMER 781 spectrophotometer. UV/visible spectra were measured on PERKIN–ELMER LAMBDA 3B in CH_2Cl_2 solution. Mass spectra were registered by electron impact at 70 eV in a VGI2-250 spectrometer. High resolution mass spectra were determined by electro spray ionization in the positive mode (ESI^+) in a Accurate-Mass Q-TOF LC/MS 6520 (Agilent Technologies). Combustion analyses (C, H, N) were obtained on a LECO CHNS-932 apparatus at the Universidad Complutense de Madrid analysis services and were within 0.4% of the theoretical values.

Aldehydes **14a**,**b**[4] and **15**[4] were synthesized by the methods previously described. Aldehyde **14c** was synthesized by a modification of the procedure previously described.[5]

4.2. (3*E*,5*E*)-6-Ethoxycarbonyl-2,2-dimethylhexa-3,5-dienal (14c)

This compound was synthesized in two steps from (*E*)-4-(1,3-dithian-2-yl)-4-methylpent-2-enal (**18**).[4] To a solution of lithium diisopropylamide (9.2 mmol) in dry THF (30 mL), prepared from diisopropylamine (1.3 mL, 9.2 mmol) and BuLi (5.7 mL, 9.2 mmol of 1.6 M solution in hexane), at −78 °C under an atmosphere of argon, was added slowly dropwise ethyl 2-(diethoxyphosphoryl)acetate (2.05 g, 9.2 mmol). The mixture was stirred for 45 min and then a solution of **18** (1.8 g, 8.3 mmol) in dry THF (50 mL) was added dropwise. The reaction mixture was kept at −78 °C for 2 h, allowed to warm at room temperature, and stirred for 24 h before being quenched with saturated NH_4Cl solution and extracted with Et_2O. The combined organic phases were dried, filtered, and concentrated to dryness. Flash chromatography (hexane/Et_2O 97:3) afforded ethyl (2*E*,4*E*)-6-(1,3-dithian-2-yl)-6-methylhepta-2,4-dienoate[5] (1.94 g, 81%) as a yellow solid. Mp 96–98 °C (hexane). Found: C, 58.8; H, 7.7; S, 22.4. $C_{14}H_{22}O_2S_2$ requires C, 58.70; H, 7.74; S, 22.39%. IR (KBr): 1730, 1650, 1630 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ=1.20 (s, 6H, $2CH_3$), 1.21 (t, J=7.1 Hz, 3H, CH_3), 1.66–1.84 (m, 1H, $1/2CH_2$), 1.96–2.06 (m, 1H, $1/2CH_2$), 2.78–2.83 (m, 4H, $2CH_2S$), 3.99 (s, 1H, CH), 4.12 (q, J=7.1 Hz, 2H, CH_2O), 5.78 (d, J=15.4 Hz, 1H, CH=C*H*CO_2Et), 6.03–6.20 (m, 2H, CH=CH), 7.17–7.29 (m, 1H, C*H*=$CHCO_2$Et); ^{13}C NMR (50 MHz, $CDCl_3$): δ=14.3, 25.1, 25.9, 31.3, 41.7, 60.1, 60.2, 120.7, 126.2, 144.7, 149.8, 167.0; MS: m/z (%)=119 (M^+−167, 100). HRMS-ESI^+: found 287.1137. $C_{14}H_{22}O_2S_2+H^+$ requires 287.1140.

The removal of the thioacetal group was carried out by the method of Procter and co-workers.[11] A solution of the protected aldehyde (1.93 g, 6.75 mmol), $CaCO_3$ (2.02 g, 20.2 mmol), CH_3I (4.2 mL, 67.5 mmol) in a 4:1 mixture of CH_3CN/H_2O (40 mL) was stirred at 60 °C for 17 h. The solution was filtered on silica gel, washed with Et_2O, and evaporated to dryness. Flash chromatography (hexane/Et_2O 95:5) afforded (3*E*,5*E*)-**14c**[5] (1.22 g, 86%) as a colorless oil. Found: C, 67.4; H, 8.1. $C_{11}H_{16}O_3$ requires C, 67.32; H, 8.22%. IR (neat): 2840, 2730, 1740, 1710 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ=1.18 (s, 6H, $2CH_3$), 1.22 (t, J=7.1 Hz, 3H, CH_3), 4.13 (q, J=7.1 Hz, 2H, CH_2O), 5.82 (d, J=15.4 Hz, 1H, CH=C*H*CO_2Et), 5.99 (d, J=15.6, 1H, CH=CH), 6.17 (dd, J=15.6, 10.3 Hz, 1H, CH=CH), 7.19 (dd, J=15.4, 10.3 Hz, 1H, C*H*=$CHCO_2$Et), 9.34 (s, 1H, CHO); ^{13}C NMR (50 MHz, $CDCl_3$): δ=14.2, 21.3, 49.2, 60.3, 121.9, 128.7, 143.3, 143.6, 166.7, 201.1; MS: m/z (%)=43 (15), 79 (32), 93 (100), 167 (M^+−29, 91); HRMS-ESI^+: found 197.1175. $C_{11}H_{16}O_3+H^+$ requires 197.1178; UV (CH_2Cl_2): λ_{max} (ε)=255 nm (39,127), 313 nm (1765).

4.3. (3*E*,5*E*)-6-Ethoxycarbonyl-2,2-dimethylhepta-3,5-dienal (14d)

This compound was synthesized following the same procedure as in **14c**, from diisopropylamine (0.9 mL, 6.2 mmol), BuLi (3.9 mL, 6.3 mmol of 1.6 M solution in hexane), ethyl 2-(diethoxyphosphoryl) propanoate (1.4 g, 6.2 mmol), and **18** (1.22 g, 5.7 mmol) in dry THF (50 mL). Flash chromatography (hexane/Et_2O 97:3) afforded ethyl (2*E*,4*E*)-6-(1,3-dithian-2-yl)-2,6-dimethylhepta-2,4-dienoate (1.5 g, 87%) as a yellow oil. Found: C, 60.0; H, 8.0; S, 21.3. $C_{15}H_{24}O_2S_2$ requires C, 59.96; H, 8.05; S, 21.34%. IR (neat): 1697, 1635 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ=1.21 (s, 6H, $2CH_3$), 1.22 (t, J=7.1 Hz, 3H, CH_3), 1.63–1.82 (m, 1H, $1/2CH_2$), 1.87 (d, J=1.3 Hz, 3H, CH_3C=C), 1.93–2.09 (m, 1H, $1/2CH_2$), 2.77–2.83 (m, 4H, $2CH_2S$), 4.00 (s, 1H, CH), 4.11 (q, J=7.1 Hz, 2H, CH_2O), 6.09 (d, J=15.3 Hz, 1H, CH=CH), 6.28 (dd, J=15.3, 10.7 Hz, 1H, CH=CH), 7.13 (dd, J=10.7, 1.3 Hz, 1H, CH=C); ^{13}C NMR (50 MHz, $CDCl_3$): δ=12.8, 14.4, 25.3, 26.0, 31.3, 41.8, 60.3, 60.5, 123.7, 126.5, 138.3, 148.4, 168.4; MS: m/z (%)=43 (11), 91 (7), 119 (100), 194 (M^+−106, 9). HRMS-ESI^+: found 301.1296. $C_{15}H_{24}O_2S_2+H^+$ requires 301.1297.

The removal of the thioacetal group was carried out by the method of Procter and co-workers.[11] A solution of the protected aldehyde (1.5 g, 5 mmol), $CaCO_3$ (1.5 g, 15 mmol), CH_3I (3.1 mL, 50 mmol) in a 4:1 mixture of CH_3CN/H_2O (40 mL) was stirred at 60 °C for 17 h. The solution was filtered on silica gel, washed with Et_2O, and evaporated to dryness. Flash chromatography (hexane/Et_2O 95:5) afforded (3*E*,5*E*)-**14d** (1.22 g, 67%) as a colorless oil. Found: C, 68.5; H, 8.6. $C_{12}H_{18}O_3$ requires C, 68.54; H, 8.63%. IR (neat): 2810, 2707, 1705, 1637 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ=1.19 (s, 6H, $2CH_3$), 1.23 (t, J=7.1 Hz, 3H, CH_3), 1.88 (d, J=1.3 Hz, 3H, CH_3C=C), 4.13 (q, J=7.1 Hz, 2H, CH_2O), 5.95 (d, J=15.5 Hz, 1H, CH=CH), 6.32 (dd, J=15.5, 11.7 Hz, 1H, CH=CH), 7.10 (dd, J=11.7, 0.6 Hz,

1H, CH=C), 9.35 (s, 1H, CHO); ^{13}C NMR (50 MHz, $CDCl_3$): δ=13.1, 14.7, 21.8, 49.8, 60.9, 126.7, 128.3, 137.7, 142.3, 168.7, 201.9; MS: *m*/*z* (%)=43 (100), 71 (30), 113 (15), 141 (M^+−69, 14); HRMS-ESI$^+$: found 211.1333. $C_{12}H_{18}O_3$+H^+ requires 211.1335; UV (CH_2Cl_2): λ_{max} (ε)= 261 nm (6989), 313 nm (1).

4.4. (3*E*,5*E*)-6-Cyano-6-ethoxycarbonyl-2,2-dimethylhexa-3,5-dienal (14e)

A solution of **18** (2 g, 9.3 mmol), ethyl cyanoacetate (4.7 g, 41.6 mmol), acetic acid (2.4 mL), and ammonium acetate (855 mg, 11.1 mmol) in benzene (40 mL) was refluxed for 12 h. The water generated during the condensation was azeotropically removed by using a Dean−Stark trap. The mixture was then cooled, diluted with Et_2O, and washed with water. The organic layers were dried ($MgSO_4$), filtered, and concentrated to dryness. Flash chromatography (hexane/Et_2O 95:5) afforded ethyl (2*E*,4*E*)-2-cyano-6-(1,3-dithian-2-yl)-6-methylhepta-2,4-dienoate (2,7 g, 94%) as a yellow oil. Found: C, 57.8; H, 6.8; N, 4.5; S, 20.6. $C_{15}H_{21}NO_2S_2$ requires C, 57.84; H, 6.80; N, 4.50; S, 20.59%. IR (neat): 2227, 1724, 1624 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ=1.27 (s, 6H, $2CH_3$), 1.29 (t, *J*=7.1 Hz, 3H, CH_3), 1.66−1.85 (m, 1H, 1/$2CH_2$), 1.98−2.11 (m, 1H, 1/$2CH_2$), 2.80−2.86 (m, 4H, $2CH_2S$), 4.04 (s, 1H, CH), 4.25 (q, *J*=7.1 Hz, 2H, CH_2O), 6.48−6.71 (m, 2H, CH=CH), 7.81 (d, *J*=10.2 Hz, 1H, CH=C); ^{13}C NMR (50 MHz, $CDCl_3$): δ=14.1, 24.8, 25.6, 31.1, 42.6, 59.4, 62.2, 104.7, 114.2, 123.9, 155.7, 159.8, 162.0; MS: *m*/*z* (%)=45 (15), 106 (7), 119 (M^+−192, 100); HRMS-ESI$^+$: found 312.1090. $C_{15}H_{21}NO_2S_2$+H^+ requires 321.1093.

The removal of the thioacetal group was carried out by the method of Vedejs and Fuchs.[12] To a stirred suspension of red mercuric oxide (2.8 g, 13 mmol) in THF (100 mL of 15% aqueous) under an argon atmosphere, $BF_3{\cdot}Et_2O$ (1.7 mL, 13 mmol) was added. Then, a solution of the protected aldehyde (2.7 g, 8.7 mmol) in THF (20 mL) was added through a dropping funnel. The stirred mixture was maintained at room temperature for 20 min and then gently refluxed for 2 h to complete the reaction. The mixture was allowed to cool to room temperature and the mercuric salts were precipitated by addition of 30 mL of Et_2O and then filtered. The filtrate was washed with saturated $NaHCO_3$ solution, then with brine and finally dried. The organic extracts were filtered and concentrated to dryness. Flash chromatography (hexane/EtAcO 95:5) afforded the aldehyde (3*E*,5*E*)-**14e** (1.1 g, 54%) as a yellow oil. Found: C, 65.1; H, 6.8; N, 6.3. $C_{12}H_{15}NO_3$ requires C, 65.14; H, 6.83; N, 6.33%. IR (neat): 2814, 2754, 2230, 1728, 1626, 1589 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ=1.13 (s, 6H, $2CH_3$), 1.15 (t, *J*=7.1 Hz, 3H, CH_3), 4.12 (q, *J*=7.1 Hz, 2H, CH_2O), 6.37−6.55 (m, 2H, CH=CH), 7.64 (dd, *J*=8.9, 1.7 Hz, 1H, CH=C), 9.35 (s, 1H, CHO); ^{13}C NMR (50 MHz, $CDCl_3$): δ=14.2, 21.4, 50.3, 62.2, 106.2, 114.0, 125.9, 153.2, 154.7, 161.9, 200.3; MS: *m*/*z* (%)=77 (66), 91 (67), 147 (100), 192 (71), 221 (M^+, 2); HRMS-ESI$^+$: found 222.1130. $C_{12}H_{15}NO_3$+H^+ requires 222.1131; UV (CH_2Cl_2): λ_{max} (ε)=276 nm (29,355), 313 nm (8889).

4.5. (*E*)-6,6-Dicyano-2,2-dimethylhexa-3,5-dienal (14f)

A solution of **18** (1.5 g, 13.2 mmol), malononitrile (2 g, 9.3 mmol), β-alanine (280 mg, 3.1 mmol), and acetic acid (4 mL) in toluene (40 mL) was refluxed for 24 h. The water generated during the condensation was azeotropically removed by using a Dean−Stark trap. The mixture was then cooled, diluted with Et_2O, and washed with water. The organic layers were dried ($MgSO_4$), filtered, and concentrated to dryness. Flash chromatography (hexane/EtAcO 8:2) afforded [(2*E*)-4-(1,3-dithian-2-yl)-4-methylpent-2-enylidene]malononitrile (2,25 g, 92%) as a yellow oil. Found: C, 59.0; H, 6.1; N, 10.6; S, 24.2. $C_{13}H_{16}N_2S_2$ requires C, 59.05; H, 6.10; N, 10.59; S, 24.25%. IR (neat): 2255, 2231, 1620 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ=1.26 (s, 6H, $2CH_3$), 1.66−1.85 (m, 1H, 1/$2CH_2$), 1.98−2.08 (m, 1H, 1/$2CH_2$), 2.80−2.85 (m, 4H, $2CH_2O$), 4.03 (s, 1H, CH), 6.53 (dd, *J*=15.3, 10.7 Hz, 1H, CH=CH), 6.71 (d, *J*=15.3 Hz, 1H, CH=CH), 7.42 (d, *J*=10.7 Hz, 1H, CH=C); ^{13}C NMR (50 MHz, $CDCl_3$): δ=24.9, 25.7, 31.3, 43.1, 59.2, 85.3, 111.1, 112.9, 123.6, 160.7, 162.1; MS: *m*/*z* (%)=75 (6), 106 (9), 119 (100), 264 (M^+, 1); HRMS-ESI$^+$: found 265.0832. $C_{13}H_{16}N_2S_2$+H^+ requires 265.0834.

The removal of the thioacetal group was brought about following the same procedure as in **14e** using red mercuric oxide (671 mg, 3.1 mmol) in THF (100 mL of 15% aqueous), $BF_3{\cdot}Et_2O$ (440 mg 3.1 mmol), and the protected aldehyde (500 mg, 2.06 mmol) in THF (20 mL). Flash chromatography (hexane/EtAcO 8:2) afforded the aldehyde (*E*)-**14f** (207 mg, 58%) as a yellow oil. Found: C, 68.9; H, 5.8; N, 16.1. $C_{10}H_{10}N_2O$ requires C, 68.95; H, 5.79; N, 16.08%. IR (neat): 2870, 2740, 2100, 1700, 1630 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ=1.28 (s, 6H, $2CH_3$), 6.51−6.69 (m, 2H, CH=CH), 7.42 (dd, *J*=8.3, 2.2 Hz, 1H, CH=C), 9.24 (s, 1H, CHO); ^{13}C NMR (50 MHz, $CDCl_3$): δ=21.4, 50.4, 85.3, 111.0, 112.9, 125.2, 155.5, 159.8, 199.9; MS: *m*/*z* (%)=39 (48), 43 (28), 79 (41), 104 (37), 118 (77), 131 (41), 145 (100), 174 (M^+, 2); HRMS-ESI$^+$: found 175.0871. $C_{10}H_{10}N_2O$+H^+ requires 175.0872; UV (CH_2Cl_2): λ_{max} (ε)=283 nm (23,663), 313 nm (7285).

4.6. Preparative photolyses; general procedure

The photolyses were carried out in a quartz immersion well apparatus with a Pyrex filter and a 400 W medium pressure Hg arc lamp. Solutions of the compounds and the sensitizer (3-methoxyacetophenone or 4-phenylbenzophenone) in dry CH_2Cl_2 were purged for 1 h with argon and irradiated under a positive pressure of argon. After completion of the irradiation, the solvent was evaporated under reduced pressure, and the sensitizers and the products were separated by flash chromatography on silica gel.

*4.6.1. 3-Methoxyacetophenone-sensitized irradiation of **14a**.* Compound (*E*)-**14a** (200 mg, 1.34 mmol) and 3-methoxyacetophenone (890 mg, 5.9 mmol) in CH_2Cl_2 (160 mL) was irradiated for 15 min. Chromatography (hexane/Et_2O 8:2) gave alkene (*E*)-**19a** (10 mg, 6%) as a colorless oil, starting aldehyde **14a** (60 mg, 30%) as a 4:1 mixture of *E*/*Z* isomers and cyclopropylaldehyde (*E*)-**16a**[4] (104 mg, 52%). Further elution with Et_2O afforded 5 mg of highly polar material.

Compound (*E*)-**14a** (200 mg, 1.34 mmol) and 3-methoxyacetophenone (890 mg, 5.9 mmol) in CH_2Cl_2 (160 mL) was irradiated for 45 min. Chromatography (hexane/Et_2O 98:2) gave alkene (*E*)-**19a** (12 mg, 7%), starting aldehyde (*E*)-**14a** (2 mg, 1%), and cyclopropylaldehyde **16a**[4] (74 mg, 37%) as a 5:1 mixture of *E*/*Z* isomers. Further elution with Et_2O afforded 65 mg of highly polar material.

*4.6.1.1. Compound (E)-**19a**.* Found: C, 87.0; H, 13.0. C_9H_{14} requires C, 87.02; H, 12.98%. IR (neat): 1630 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.94 (d, *J*=6.7 Hz, 6H, $CH(CH_3)_2$), 1.68 (br s, 6H, $2CH_3C$=C), 2.18−2.35 (m, 1H, $CH(CH_3)_2$), 5.46 (dd, *J*=15.1, 6.9 Hz, 1H, CH=CH), 5.71 (d, *J*=10.7 Hz, 1H, CH=C), 6.15 (ddd, *J*=15.1, 10.7, 1.1 Hz, 1H, CH=CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ=18.0, 22.5, 25.5, 27.0, 31.2, 123.5, 125.0, 132.7, 139.0; HRMS-ESI$^+$: found 125.1329. C_9H_{16}+H^+ requires 125.1331.

*4.6.2. 4-Phenylbenzophenone-sensitized irradiation of **14a**.* Compound (*E*)-**14a** (160 mg, 1.05 mmol) and 4-phenylbenzophenone (880 mg, 3.4 mmol) in CH_2Cl_2 (160 mL) was irradiated for 15 min. Chromatography (hexane/Et_2O 98:2) gave cyclopropylaldehyde **16a**[4] (150 mg, 94%) as a 6:1 mixture of *E*/*Z* isomers. Further elution with Et_2O afforded 5 mg of highly polar material.

*4.6.3. 3-Methoxyacetophenone-sensitized irradiation of **14b**.* Compound (*E*)-**14b** (200 mg, 1.13 mmol) and 3-methoxyacetophenone (800 mg,

5.3 mmol) in CH_2Cl_2 (160 mL) was irradiated for 20 min. Chromatography (hexane/Et_2O 95:5) gave alkene (*E*)-**19b** (10 mg, 6%) as a colorless oil, starting aldehyde **14b** (60 mg, 30%) as a 3:2 mixture of *E*/*Z* isomers, and cyclopropylaldehyde **16b**[4] (94 mg, 47%) as a 8:1 mixture of *E*/*Z* isomers. Further elution with Et_2O afforded 7 mg of highly polar material.

Compound (*E*)-**14b** (200 mg, 1.13 mmol) and 3-methoxyacetophenone (800 mg, 5.3 mmol) in CH_2Cl_2 (160 mL) was irradiated for 45 min. Chromatography (hexane/Et_2O 95:5) gave alkene (*E*)-**19b** (10 mg, 6%), starting aldehyde (*E*)-**14b** (8 mg, 4%), and cyclopropylaldehyde **16b**[4] (72 mg, 36%) as a 6:1 mixture of *E*/*Z* isomers. Further elution with Et_2O afforded 37 mg of highly polar material.

*4.6.3.1. Compound (E)-**19b**.* Found: C, 87.7; H, 12.3. $C_{11}H_{18}$ requires C, 87.92; H, 12.08%. IR (neat): 1630 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ=1.02 (d, *J*=6.6, 6H, $CH(CH_3)_2$), 1.62–1.73 (m, 4H, $2CH_2$), 2.27–2.36 (m, 5H, $CH(CH_3)_2$ and $2CH_2$), 5.50 (dd, *J*=14.9, 7.1 Hz, 1H, CH=CH), 5.91 (dt, *J*=10.7, 2.2 Hz, 1H, CH=C), 6.08 (ddd, *J*=14.9, 10.7, 1.0 Hz, 1H, CH=CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ=22.4, 26.1, 26.2, 29.0, 30.1, 33.7, 120.2, 124.9, 125.3, 138.3; HRMS-ESI$^+$: found 151.1485. $C_{11}H_{18}+H^+$ requires 151.1488.

*4.6.4. 4-Phenylbenzophenone-sensitized irradiation of **14b**.* Compound (*E*)-**14b** (170 mg, 0.95 mmol) and 4-phenylbenzophenone (255 mg, 0.98 mmol) in CH_2Cl_2 (160 mL) was irradiated for 20 min. Chromatography (hexane/Et_2O 98:2) gave cyclopropylaldehyde (*E*)-**16b**[4] (160 mg, 94%). Further elution with Et_2O afforded 5 mg of highly polar material.

*4.6.5. 3-Methoxyacetophenone-sensitized irradiation of **14c**.* Compound (3*E*,5*E*)-**14c** (200 mg, 1.02 mmol) and 3-methoxyacetophenone (1.6 g, 10.6 mmol) in CH_2Cl_2 (160 mL) was irradiated for 45 min. Chromatography (hexane/Et_2O 97:3) gave a 9:1 mixture of alkenes (2*E*,4*E*)-**19c** and (*E*)-**20a** (7 mg, 4%) as a colorless oil, aldehyde (3*Z*,5*E*)-**14c** (21 mg, 10%) as a yellow oil, aldehyde (3*E*,5*E*)-**14c** (84 mg, 42%), and cyclopropylaldehyde **16c** (44 mg, 22%) as a yellow oil and as a 1:2 mixture of (Z_{cyclo},E_{C-C}/E_{cyclo},E_{C-C}) isomers. Further elution with Et_2O afforded 10 mg of highly polar material.

Compound (3*E*,5*E*)-**14c** (200 mg, 1.02 mmol) and 3-methoxyacetophenone (1.6 g, 10.6 mmol) in CH_2Cl_2 (160 mL) was irradiated for 120 min. Chromatography (hexane/Et_2O 97:3) gave a 6:1 mixture of alkenes (2*E*,4*E*)-**19c** and (*E*)-**20a** (21 mg, 12%), aldehyde (3*Z*,5*E*)-**14c** (4 mg, 2%), aldehyde (3*E*,5*E*)-**14c** (8 mg, 4%), and cyclopropylaldehyde **16c** (68 mg, 34%) as a 1:5 mixture of (Z_{cyclo},E_{C-C}/E_{cyclo},E_{C-C}) isomers. Further elution with Et_2O afforded 50 mg of highly polar material.

*4.6.5.1. Compound (3Z,5E)-**14c**.* Found: C, 67.3; H, 8.2. $C_{11}H_{16}O_3$ requires C, 67.32; H, 8.22%. IR (neat): 2840, 2730, 1740, 1720 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ=1.20 (s, 6H, $2CH_3$), 1.24 (t, *J*=7.2 Hz, 3H, CH_3), 4.13 (q, *J*=7.2 Hz, 2H, CH_2O), 5.62 (d, *J*=11.1 Hz, 1H, CH=CH), 5.93 (d, *J*=15.7 Hz, 1H, CH=C*H*CO_2Et), 6.50 (t_{exp}, *J*=11.1 Hz, 1H, CH=CH), 7.51–7.37 (ddd, *J*=15.7, 11.1, 1.0 Hz, 1H, C*H*=$CHCO_2Et$), 9.35 (s, 1H, CHO); ^{13}C NMR (50 MHz, $CDCl_3$): δ=14.3, 21.4, 49.4, 60.1, 118.2, 127.3, 143.9, 144.2, 166.3, 201.5; MS: *m*/*z* (%)=43 (21), 79 (40), 93 (100), 167 (M^+–29, 93); HRMS-ESI$^+$: found 197.1176. $C_{11}H_{16}O_3+H^+$ requires 197.1178.

*4.6.5.2. Compound (Z_{cyclo},E_{C-C}/E_{cyclo},E_{C-C})-**16c**.* ^1H NMR (200 MHz, $CDCl_3$): δ=1.21 (s, 1H, CH_3, Z_{cyclo},E_{C-C}), 1.22 (t, *J*=7.1 Hz, 3H, CH_3, Z_{cyclo},E_{C-C} and E_{cyclo},E_{C-C}), 1.22 (s, 2H, CH_3, E_{cyclo},E_{C-C}), 1.25 (s, 1H, CH_3, Z_{cyclo},E_{C-C}), 1.36 (s, 2H, CH_3, E_{cyclo},E_{C-C}), 1.95–2.15 (m, 1.33H, CH, Z_{cyclo},E_{C-C} and E_{cyclo},E_{C-C}), 2.36 (dd, *J*=9.9, 5.0 Hz, 0.66H, CH, E_{cyclo},E_{C-C}), 4.11 (q, *J*=7.1 Hz, 0.66H, CH_2O, Z_{cyclo},E_{C-C}), 4.12 (q, *J*=7.1 Hz, 1.33H, CH_2O, E_{cyclo},E_{C-C}), 5.91 (d, *J*=15.4 Hz, 0.33H, CH=C*H*CO_2Et, Z_{cyclo},E_{C-C}), 5.94 (d, *J*=15.4 Hz, 0.66H, CH=C*H*CO_2Et, E_{cyclo},E_{C-C}), 6.59 (dd, *J*=15.4, 9.9 Hz, 0.33H, C*H*=$CHCO_2Et$, Z_{cyclo},E_{C-C}), 7.14 (dd, *J*=15.4, 10.2 Hz, 0.66H, C*H*=$CHCO_2Et$, E_{cyclo},E_{C-C}), 9.45 (d, *J*=4.4 Hz, 0.33H, CHO, Z_{cyclo},E_{C-C}), 9.57 (d, *J*=5.0 Hz, 0.66H, CHO, E_{cyclo},E_{C-C}); ^{13}C NMR (50 MHz, $CDCl_3$): δ=14.2 (E_{cyclo},E_{C-C}), 15.2 (Z_{cyclo},E_{C-C}), 15.6 (Z_{cyclo},E_{C-C}), 21.1 (E_{cyclo},E_{C-C}), 22.2 (E_{cyclo},E_{C-C}), 28.5 (Z_{cyclo},E_{C-C}), 29.7 (Z_{cyclo},E_{C-C}), 33.1 (E_{cyclo},E_{C-C}), 36.7 (E_{cyclo},E_{C-C}), 38.5 (Z_{cyclo},E_{C-C}), 43.0 (Z_{cyclo},E_{C-C}), 44.6 (E_{cyclo},E_{C-C}), 60.3 (E_{cyclo},E_{C-C}), 65.8 (Z_{cyclo},E_{C-C}), 122.9 (E_{cyclo},E_{C-C}), 123.7 (Z_{cyclo},E_{C-C}), 142.7 (Z_{cyclo},E_{C-C}), 145.0 (E_{cyclo},E_{C-C}), 166.2 (Z_{cyclo},E_{C-C} and E_{cyclo},E_{C-C}), 198.7 (E_{cyclo},E_{C-C}), 199.2 (Z_{cyclo},E_{C-C}).

*4.6.5.3. Compounds (2E,4E)-**19c** and (E)-**20a**.* ^1H NMR (200 MHz, $CDCl_3$): δ=0.97 (d, *J*=6.7 Hz, 5.4H, $CH(CH_3)_2$, **19c**), 1.21 (t, *J*=7.1 Hz, 3H, CH_3), 1.54 (s, 0.3H, CH_3C=C, **20a**), 1.66 (s, 0.3H, CH_3C=C, **20a**), 2.26–2.43 (m, 0.9H, $CH(CH_3)_2$, **19c**), 2.80 (t_{exp}, *J*=6.4 Hz, 0.2H, CH_2, **20a**), 4.10 (q, *J*=7.1 Hz, 0.2H, CH_2O, **20a**), 4.12 (q, *J*=7.1 Hz, 1.8H, CH_2O, **19c**), 5.07 (t, *J*=6.4 Hz, 0.1H, C*H*=$C(CH_3)_2$, **20a**), 5.72 (d, *J*=15.3 Hz, 0.9H, CH=C*H*CO_2Et, **19c**), 5.74 (d, *J*=15.6 Hz, 0.1H, CH=C*H*CO_2Et, **20a**), 5.95–6.14 (m, 1.8H, CH=CH, **19c**), 6.86 (dt, *J*=15.6, 6.2 Hz, 0.1H, C*H*=$CHCO_2Et$, **20a**), 7.12–7.25 (m, 0.9H, C*H*=$CHCO_2Et$, **19c**); ^{13}C NMR (50 MHz, $CDCl_3$): δ=14.2 (**19c** and **20a**), 17.5 (**20a**), 21.7 (**19c**), 25.5 (**20a**), 30.7 (**20a**), 31.4 (**19c**), 60.0 (**19c** and **20a**), 119.0 (**20a**), 119.3 (**19c**), 121.0 (**20a**), 125.4 (**19c**), 145.1 (**19c**), 147.6 (**20a**), 151.0 (**19c** and **20a**), 167.1 (**19c** and **20a**).

*4.6.6. 4-Phenylbenzophenone-sensitized irradiation of **14c**.* Compound (3*E*,5*E*)-**14c** (200 mg, 1.02 mmol) and 4-phenylbenzophenone (1.1 g, 4.25 mmol) in CH_2Cl_2 (160 mL) was irradiated for 45 min. Chromatography (hexane/Et_2O 97:3) gave cyclopropylaldehyde (E_{cyclo},Z_{C-C})-**16c** (6 mg, 3%) as a yellow oil and cyclopropylaldehyde **16c** (186 mg, 93%) as a 1:4 mixture of (Z_{cyclo},E_{C-C}/E_{cyclo},E_{C-C}) isomers. Further elution with Et_2O afforded 4 mg of highly polar material.

*4.6.6.1. Compound (E_{cyclo},Z_{C-C})-**16c**.* Found: C, 67.3; H, 8.2. $C_{11}H_{16}O_3$ requires C, 67.32; H, 8.22%. IR (neat): 2840, 2730, 1740, 1720 cm^{-1}; IR ($CHCl_3$): 2860, 2740, 1710, 1630 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ=1.18 (s, 3H, CH_3), 1.24 (t, *J*=7.1 Hz, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.76 (t_{exp}, *J*=5.4 Hz, 1H, CH), 3.57–3.64 (m, 1H, CH), 4.12 (q, *J*=7.1 Hz, 2H, CH_2O), 5.71–5.85 (m, 2H, CH=CH), 9.28 (d, *J*=5.8 Hz, 1H, CHO); ^{13}C NMR (50 MHz, $CDCl_3$): δ=14.4, 21.9, 22.2, 31.0, 34.1, 46.3, 60.2, 121.5, 145.6, 166.0, 199.5; MS: *m*/*z* (%)=71 (43), 93 (60), 125 (19), 149 (100), 167 (M^+–29, 71); HRMS-ESI$^+$: found 197.1175. $C_{11}H_{16}O_3+H^+$ requires 197.1178.

*4.6.7. 3-Methoxyacetophenone-sensitized irradiation of **14d**.* Compound (3*E*,5*E*)-**14d** (250 mg, 1.19 mmol) and 3-methoxyacetophenone (2 g, 13.3 mmol) in CH_2Cl_2 (160 mL) was irradiated for 60 min. Chromatography (hexane/Et_2O 97:3) gave a 6:1 mixture of alkenes (2*E*,4*E*)-**19d** and (*E*)-**20b** (21 mg, 10%) as a colorless oil, alkene (2*Z*,4*E*)-**19d** (18 mg, 8%) as a colorless oil, aldehyde (3*E*,5*E*)-**14d** (92 mg, 37%), aldehyde (3*E*,5*Z*)-**14d** (46 mg, 28%) as a yellow oil, and cyclopropylaldehyde **16d** (35 mg, 14%) as a yellow oil and as a 1:5 mixture of (Z_{cyclo},E_{C-C}/E_{cyclo},E_{C-C}) isomers. Further elution with Et_2O afforded 2 mg of highly polar material.

Compound (3*E*,5*E*)-**14d** (250 mg, 1.19 mmol) and 3-methoxyacetophenone (2 g, 13.3 mmol) in CH_2Cl_2 (160 mL) was irradiated for 120 min. Chromatography (hexane/Et_2O 97:3) gave a 5:1 mixture of alkenes (2*E*,4*E*)-**19d** and (*E*)-**20b** (18 mg, 8%), alkene (2*Z*,4*E*)-**19d** (9 mg, 4%), aldehyde (3*E*,5*E*)-**14d** (25 mg, 10%), aldehyde (3*E*,5*Z*)-**14d** (12 mg, 5%), and cyclopropylaldehyde **16d** (12 mg, 5%) as a 1:2 mixture of (Z_{cyclo},E_{C-C}/E_{cyclo},E_{C-C}) isomers. Further elution with Et_2O afforded 95 mg of highly polar material.

*4.6.7.1. Compound (3E,5Z)-**14d**.* Found: C, 68.5; H, 8.6. $C_{12}H_{18}O_3$ requires C, 68.54; H, 8.63%. IR (neat): 2810, 2707, 1705, 1637 cm^{-1};

^{1}H NMR (200 MHz, $CDCl_3$): δ=1.17 (s, 6H, 2 CH_3), 1.26 (t, J=7.1 Hz, 3H, CH_3), 1.90 (br s, 3H, CH_3C=C), 4.16 (q, J=7.1 Hz, 2H, CH_2O), 5.74 (d, J=15.6 Hz, 1H, CH=CH), 6.35 (d, J=11.0 Hz, 1H, CH=C), 7.17 (dd, J=15.6, 11.0 Hz, 1H, CH=CH), 9.32 (s, 1H, CHO); ^{13}C NMR (50 MHz, $CDCl_3$): δ=14.7, 21.1, 21.8, 37.0, 60.8, 126.7, 128.7, 139.6, 140.9, 154.0, 202.1; MS: m/z (%)=43 (100), 71 (30), 113 (15), 141 (M^+−69, 14); HRMS-ESI$^+$: found 211.1333. $C_{12}H_{18}O_3$+H^+ requires 211.1335.

*4.6.7.2. Compound (Z_{cyclo},E_{C-C}/E_{cyclo},E_{C-C})-**16d**.* ^{1}H NMR (200 MHz, $CDCl_3$): δ=1.21 (s, 0.5H, CH_3, Z_{cyclo},E_{C-C}), 1.22 (t, J=7.1 Hz, 2.5H, CH_3, E_{cyclo},E_{C-C}), 1.22 (s, 2.5H, CH_3, E_{cyclo},E_{C-C}), 1.23 (t, J=7.1 Hz, 0.5H, CH_3, Z_{cyclo},E_{C-C}), 1.28 (s, 2.5H, CH_3, E_{cyclo},E_{C-C}), 1.37 (s, 0.5H, CH_3, Z_{cyclo},E_{C-C}), 1.86 (d, J=1.4 Hz, 2.5H, CH_3C=C, E_{cyclo},E_{C-C}), 1.85−2.00 (m, 1.5H, CH and CH_3C=C, E_{cyclo},E_{C-C} and Z_{cyclo},E_{C-C}), 2.10 (t_{exp}, J=5.1 Hz, 0.166H, CH, Z_{cyclo},E_{C-C}), 2.38 (dd, J=9.6, 5.0 Hz, 0.834H, CH, E_{cyclo},E_{C-C}), 4.12 (q, J=7.1 Hz, 1.66H, CH_2O, E_{cyclo},E_{C-C}), 4.13 (q, J=7.1 Hz, 0.33H, CH_2O, Z_{cyclo},E_{C-C}), 6.39 (dd, J=9.6, 1.4 Hz, 0.83H, CH=C, E_{cyclo},E_{C-C}), 6.93 (dd, J=9.4, 1.5 Hz, 0.166H, CH=C, Z_{cyclo},E_{C-C}), 9.43 (d, J=5.8 Hz, 0.166H, CHO, Z_{cyclo},E_{C-C}), 9.47 (d, J=4.5 Hz, 0.83H, CHO, E_{cyclo},E_{C-C}); ^{13}C NMR (50 MHz, $CDCl_3$): δ=13.2 (Z_{cyclo},E_{C-C}), 13.3 (E_{cyclo},E_{C-C}), 14.5 (Z_{cyclo},E_{C-C}), 14.7 (E_{cyclo},E_{C-C}), 21.7 (E_{cyclo},E_{C-C}), 22.8 (E_{cyclo},E_{C-C}), 23.1 (Z_{cyclo},E_{C-C}), 32.3 (Z_{cyclo},E_{C-C}), 33.3 (E_{cyclo},E_{C-C}), 34.6 (E_{cyclo},E_{C-C}), 35.6 (Z_{cyclo},E_{C-C}), 42.9 (Z_{cyclo},E_{C-C}), 45.6 (E_{cyclo},E_{C-C}), 61.0 (Z_{cyclo},E_{C-C} and E_{cyclo},E_{C-C}), 130.5 (E_{cyclo},E_{C-C}), 131.4 (Z_{cyclo},E_{C-C}), 135.3 (Z_{cyclo},E_{C-C}), 144.2 (E_{cyclo},E_{C-C}), 167.9 (Z_{cyclo},E_{C-C}), 168.0 (E_{cyclo},E_{C-C}), 199.7 (E_{cyclo},E_{C-C}), 200.4 (Z_{cyclo},E_{C-C}).

*4.6.7.3. Compound (2Z,4E)-**19d**.* Found: C, 72.5; H, 9.9. $C_{11}H_{18}O_2$ requires C, 72.49; H, 9.95%. IR (neat): 1708, 1635 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.97 (d, J=6.7 Hz, 6H, $CH(CH_3)_2$), 1.25 (t, J=7.1 Hz, 3H, CH_3), 1.87 (br s, 3H, CH_3C=C), 2.30−2.43 (m, 1H, $CH(CH_3)_2$), 4.15 (q, J=7.1 Hz, 2H, CH_2O), 5.80 (dd, J=15.3, 6.7 Hz, 1H, CH=CH), 6.33 (d, J=11.2 Hz, 1H, CH=C), 7.01 (dd, J=15.3, 11.8 Hz, 1H, CH=CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ=14.4, 20.7, 22.1, 31.5, 60.2, 124.8, 141.0, 142.0, 148.7, 189.2; MS: m/z(%)=43 (100), 57 (20), 71 (27), 140 (2), 154 (1), 181 (M^+−7), 182 (M^+, 2); HRMS-ESI$^+$: found 183.1384. $C_{11}H_{18}O_2$+H^+ requires 183.1386.

*4.6.7.4. Compounds (2E,4E)-**19d** and (E)-**20b**.* ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.98 (d, J=6.7 Hz, 5H, $(CH_3)_2CH$, **19d**), 1.21 (t, J=6.9 Hz, 0.5H, CH_3, **20b**), 1.22 (t, J=7.1 Hz, 2.5H, CH_3, **19d**), 1.57 (br s, 0.5H, CH_3C=C, **20b**), 1.63 (br s, 0.5H, CH_3C=C, **20b**), 1.78 (br s, 0.5H, CH_3C=C, **20b**), 1.86 (d, J=1.0 Hz, 2.5H, CH_3C=C, **19d**), 2.28−2.45 (m, 0.83H, $CH(CH_3)_2$, **19d**), 2.78 (t_{exp}, J=7.3 Hz, 0.33H, CH_2, **20b**), 4.10 (q, J=6.9 Hz, 0.33H, CH_2O, **20b**), 4.12 (q, J=7.1 Hz, 1.66H, CH_2O, **19d**), 5.05 (t, J=7.3 Hz, 0.166H, CH=C $(CH_3)_2$, **20b**), 5.97 (dd, J=15.1, 6.8 Hz, 0.83H, CH=CHCH$(CH_3)_2$, **19d**), 6.23 (ddd, J=15.1, 11.0, 0.9 Hz, 0.83H, CH=CHCH$(CH_3)_2$, **19d**), 6.63 (td, J=7.5, 1.4 Hz, 0.166H, CH=CCO_2Et, **20b**), 7.09 (d, J=11.0 Hz, 0.83H, CH=C, **19d**); ^{13}C NMR (50 MHz, $CDCl_3$): δ=12.4 (**20b**), 12.6 (**19d**), 14.4 (**19d** and **20b**), 17.9 (**20b**), 22.1 (**19d**), 25.7 (**20b**), 27.9 (**20b**), 31.9 (**19d**), 60.5 (**19d**), 64.2 (**20b**), 120.4 (**19d** and **20b**), 123.1, 125.4, 138.8, 140.6, 140.8, 149.8, 168.7 (**19d** and **20b**).

*4.6.8. 4-Phenylbenzophenone-sensitized irradiation of **14d**.* Compound (3*E*,5*E*)-**14d** (83 mg, 1.02 mmol) and 4-phenylbenzophenone (80 mg, 0.31 mmol) in CH_2Cl_2 (160 mL) was irradiated for 60 min. Chromatography (hexane/Et_2O 97:3) gave cyclopropylaldehyde **16d** (76 mg, 92%) as a 1:5 mixture of (Z_{cyclo},E_{C-C}/E_{cyclo},E_{C-C}) isomers. Further elution with Et_2O afforded 5 mg of highly polar material.

*4.6.9. 3-Methoxyacetophenone-sensitized irradiation of **14e**.* Compound (3*E*,5*E*)-**14e** (200 mg, 0.9 mmol) and 3-methoxyacetophenone (7.1 g, 47.3 mmol) in CH_2Cl_2 (280 mL) was irradiated for 45 min. Chromatography (hexane/EtAcO 98:2) gave aldehyde (3*E*,5*Z*)-**14e** (78 mg, 39%) as a yellow oil, cyclopropylaldehyde (E_{cyclo},Z_{C-C})-**16e** (94 mg, 47%) as a yellow oil, and tetraene **21a** (14 mg, 4%) as a yellow oil. Further elution with Et_2O afforded 4 mg of highly polar material.

Compound (3*E*,5*E*)-**14e** (200 mg, 0.9 mmol) and 3-methoxyacetophenone (7.1 g, 47.3 mmol) in CH_2Cl_2 (280 mL) was irradiated for 90 min. Chromatography (hexane/EtAcO 98:2) gave aldehyde (3*E*,5*E*)-**14e** (16 mg, 8%), cyclopropylaldehyde (E_{cyclo}, Z_{C-C})-**16e** (64 mg, 32%), and tetraene **21a** (21 mg, 6%). Further elution with Et_2O afforded 75 mg of highly polar material.

*4.6.9.1. Compound (3E,5Z)-**14e**.* Found: C, 65.1; H, 6.8; N, 6.3. $C_{12}H_{15}NO_3$ requires C, 65.14; H, 6.83; N, 6.33%. IR (neat): 2814, 2754, 2230, 1728, 1626, 1589 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ=1.26 (s, 6H, $2CH_3$), 1.29 (t, J=7.1 Hz, 3H, CH_3), 4.26 (q, J=7.1 Hz, 2H, CH_2O), 6.40 (d, J=15.6 Hz, 1H, CH=CH), 7.20 (d, J=11.3 Hz, 1H, CH=C), 7.54 (dd, J=15.6, 11.3 Hz, 1H, CH=CH), 9.38 (s, 1H, CHO); ^{13}C NMR (50 MHz, $CDCl_3$): δ=14.2, 21.4, 50.3, 62.3, 104.5, 116.8, 126.0, 153.4, 156.2, 161.5, 200.5; MS: m/z (%)=77 (65), 91 (63), 147 (100), 192 (68), 221 (M^+, 2); HRMS-ESI$^+$: found 222.1130. $C_{12}H_{15}NO_3$+H^+ requires 222.1131.

*4.6.9.2. Compound (E_{cyclo},Z_{C-C})-**16e**.* Found: C, 65.1; H, 6.8; N, 6.3. $C_{12}H_{15}NO_3$ requires C, 65.14; H, 6.83; N, 6.33%. IR (neat): 2820, 2750, 2230, 1728, 1625 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ=1.28 (t, J=7.1 Hz, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 2.21 (t_{exp}, J=4.6 Hz, 1H, CH), 2.78 (dd, J=11.2, 4.7 Hz, 1H, CH), 4.25 (q, J=7.1 Hz, 2H, CH_2O), 7.22 (d, J=11.2 Hz, 1H, CH=C), 9.45 (d, J=4.5 Hz, 1H, CHO); ^{13}C NMR (50 MHz, $CDCl_3$): δ=14.1, 21.2, 22.7, 34.9, 36.0, 46.6, 62.6, 109.4, 113.6, 159.9, 160.9, 196.7; MS: m/z (%)=41 (100), 39 (98), 53 (40), 77 (76), 148 (15), 192 (57), 193 (22); HRMS-ESI$^+$: found 222.1129. $C_{12}H_{15}NO_3$+H^+ requires 222.1131.

*4.6.9.3. Compound **21a**.* Found: C, 68.7; H, 7.4; N, 7.1. $C_{22}H_{28}N_2O_4$ requires C, 68.73; H, 7.34; N, 7.29%. IR (neat): 2235, 1625, 1589 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ=1.26 (s, 12H, $4CH_3$), 1.29 (t, J=7.1 Hz, 6H, $2CH_3$), 4.26 (q, J=7.1 Hz, 4H, $2CH_2O$), 6.48−6.73 (m, 4H, CH=CH), 7.81 (d, J=10.2 Hz, 2H, CH=C); ^{13}C NMR (50 MHz, $CDCl_3$): δ=14.2, 20.6, 50.3, 62.2, 106.2, 114.0, 125.9, 153.2, 154.7, 161.9; HRMS-ESI$^+$: found 385.2125. $C_{22}H_{28}N_2O_4$+H^+ requires 385.2049.

*4.6.10. 4-Phenylbenzophenone-sensitized irradiation of **14e**.* Compound (3*E*,5*E*)-**14e** (200 mg, 0.9 mmol) and 4-phenylbenzophenone (4.9 g, 18.9 mmol) in CH_2Cl_2 (160 mL) was irradiated for 45 min. Chromatography (hexane/EtAcO 98:2) gave cyclopropylaldehyde (E_{cyclo},E_{C-C})-**16e** (174 mg, 87%) and cyclopropylaldehyde (Z_{cyclo},E_{C-C})-**16e** (16 mg, 8%). Further elution with EtAcO afforded 5 mg of highly polar material.

*4.6.11. 3-Methoxyacetophenone-sensitized irradiation of **14f**.* Compound (*E*)-**14f** (200 mg, 1.15 mmol) and 3-methoxyacetophenone (7.4 g, 49.3 mmol) in CH_2Cl_2 (160 mL) was irradiated for 60 min. Chromatography (hexane/Et_2O 8:2) gave aldehyde (*E*)-**14f** (68 mg, 34%), cyclopropylaldehyde (*Z*)-**16f** (26 mg, 13%) as a yellow oil, cyclopropylaldehyde (*E*)-**16f** (42 mg, 21%) as a yellow oil, and tetraene (4*E*,8*E*)-**21b** (15 mg, 4%) as a yellow oil. Further elution with Et_2O afforded 21 mg of highly polar material.

Compound (*E*)-**14f** (200 mg, 1.15 mmol) and 3-methoxyacetophenone (7.4 g, 49.3 mmol) in CH_2Cl_2 (160 mL) was irradiated for 120 min. Chromatography (hexane/Et_2O 8:2) gave aldehyde (*E*)-**14f** (18 mg, 9%), cyclopropylaldehyde (*Z*)-**16f** (20 mg, 10%), cyclopropylaldehyde (*E*)-**16f** (40 mg, 20%), and tetraene (4*E*,8*E*)-**21b** (26 mg, 7%). Further elution with Et_2O afforded 60 mg of highly polar material.

*4.6.11.1. Compound (Z)-**16f**.* Found: C, 68.9; H, 5.8; N, 16.1. $C_{10}H_{10}N_2O$ requires C, 68.95; H, 5.79; N, 16.08%. IR (neat): 2854, 2744,

2235, 1709, 1595 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ=1.27 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 2.47 (dd, J=11.0, 7.8 Hz, 1H, CH), 2.71 (dd, J=7.8, 1.8 Hz, 1H, CH), 7.77 (d, J=11.0 Hz, 1H, CH=C), 9.82 (d, J=1.8 Hz, 1H, CHO); ^{13}C NMR (50 MHz, $CDCl_3$): δ=14.9, 28.3, 36.8, 38.4, 45.9, 87.9, 111.2, 112.3, 165.0, 197.3; MS: m/z (%)=39 (100), 43 (40), 77 (48), 119 (72), 145 (33), 146 (14), 156 (11), 173 (M^+−1, 3); HRMS-ESI$^+$: found 175.0870. $C_{10}H_{10}N_2O+H^+$ requires 175.0872.

*4.6.11.2. Compound (E)-**16f**.* Found: C, 68.9; H, 5.8; N, 16.1. $C_{10}H_{10}N_2O$ requires C, 68.95; H, 5.79; N, 16.08%. IR (neat): 2854, 2744, 2235, 1709, 1595 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ=1.32 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 2.33 (dd, J=4.8, 3.7 Hz, 1H, CH), 2.97 (dd, J=11.2, 4.8 Hz, 1H, CH), 6.86 (d, J=11.2 Hz, 1H, CH=C), 9.52 (d, J=3.7 Hz, 1H, CHO); ^{13}C NMR (50 MHz, $CDCl_3$): δ=20.7, 22.6, 35.9, 38.4, 46.9, 88.6, 111.2, 112.5, 165.6, 195.6; MS: m/z (%)=39 (100), 43 (36), 77 (40), 119 (76), 145 (35), 173 (M^+−1, 5).

*4.6.11.3. Compound **21b**.* Found: C, 74.4; H, 6.4; N, 19.2. $C_{18}H_{18}N_4$ requires C, 74.46; H, 6.25; N, 19.29%. IR (neat): 2110, 1630 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ=1.34 (s, 12H, $4CH_3$), 6.61 (d, J=15.0 Hz, 2H, 2CH=CH), 6.76 (dd, J=15.0, 11.1 Hz, 2H, 2CH=CH), 7.42 (d, J=11.1 Hz, 2H, 2CH=C); ^{13}C NMR (50 MHz, $CDCl_3$): δ=29.4, 42.9, 84.9, 111.2, 113.5, 122.2, 160.8, 161.8; HRMS-ESI$^+$: found 291.1607. $C_{18}H_{18}N_4+H^+$ requires 291.1610.

*4.6.12. 4-Phenylbenzophenone-sensitized irradiation of **14f**.* Compound (*E*)-**14f** (200 mg, 1.15 mmol) and 4-phenylbenzophenone (5.2 g, 20.1 mmol) in CH_2Cl_2 (160 mL) was irradiated for 60 min. Chromatography (hexane/Et_2O 8:2) gave cyclopropylaldehyde (*Z*)-**16f** (49 mg, 27%) and cyclopropylaldehyde (*E*)-**16f** (112 mg, 66%). Further elution with Et_2O afforded 5 mg of highly polar material.

*4.6.13. 3-Methoxyacetophenone-sensitized irradiation of **15**.* Compound (*E*)-**15** (200 mg, 1.1 mmol) and 3-methoxyacetophenone (4.8 g, 32.0 mmol) in CH_2Cl_2 (270 mL) was irradiated for 180 min. Chromatography (hexane/Et_2O 97:3) gave aldehyde **15** (38 mg, 19%) as a 1:1 mixture of *E*/*Z* isomers and cyclopropylaldehyde **17**[4] (124 mg, 62%) as a 6:1 mixture of *E*/*Z* isomers. Further elution with Et_2O afforded 30 mg of highly polar material.

Compound (*E*)-**15** (220 mg, 1.1 mmol) and 3-methoxyacetophenone (4,8 g, 32.0 mmol) in CH_2Cl_2 (270 mL) was irradiated for 300 min. Chromatography (hexane/Et_2O 97:3) gave aldehyde (*E*)-**15** (7 mg, 3%) and cyclopropylaldehyde **17** (84 mg, 40%) as a 9:1 mixture of *E*/*Z* isomers. Further elution with Et_2O afforded 67 mg of highly polar material.

*4.6.14. 4-Phenylbenzophenone-sensitized irradiation of **15**.* Compound (*E*)-**15** (200 mg, 1.0 mmol) and 4-phenylbenzophenone (2.9 g, 11.2 mmol) in CH_2Cl_2 (160 mL) was irradiated for 180 min. Chromatography (hexane/Et_2O 97:3) gave cyclopropylaldehyde **17** (190 mg, 95%) as a 6:1 mixture of *E*/*Z* isomers. Further elution with Et_2O afforded 5 mg of highly polar material.

*4.6.15. Direct irradiation of **15**.* Compound (*E*)-**15** (200 mg, 1.0 mmol) in CH_2Cl_2 (160 mL) was irradiated for 180 min. Chromatography (hexane/Et_2O 97:3) gave (*E*)-1-(2-methylpropylidene)-1*H*-indene (105 mg, 62%) as a colorless oil. Further elution with Et_2O afforded 15 mg of highly polar material. Found: C, 91.7; H, 8.3. $C_{13}H_{14}$ requires C, 91.71; H, 8.29%. IR (neat): 1640, 1610 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ=0.94 (d, J=6.8 Hz, 6H, CH(CH_3)$_2$), 2.18–2.35 (m, 1H, C*H*(CH_3)$_2$), 6.44 (d, J=5.7 Hz, 1H, indene), 6.57 (d, J=10.7 Hz, CH=C), 6.80 (m, 1H, indene), 7.06–7.21 (m, 3H, indene), 7.43–7.49 (m, 1H, indene); ^{13}C NMR (50 MHz, $CDCl_3$): δ=22.5, 31.2, 119.1, 121.1, 125.0, 125.6, 128.0, 132.1, 135.2, 137.0, 141.7, 142.0; HRMS-ESI$^+$: found 171.1083. $C_{13}H_{14}+H^+$ requires 171.1085.

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Supplementary data

These data include copies of ^1H NMR spectra for all new compounds. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.09.012. These data include MOL files and InChIKeys of the most important compounds described in this article.

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