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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.0c01501 • Publication Date (Web): 27 Jul 2020

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Visible Light-mediated Photochemical Reactions of 2-(2'-Alkenyloxy)cycloalk-2-enones

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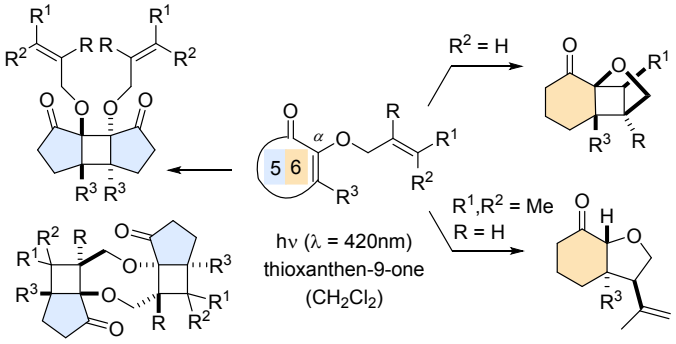
ABSTRACT



The title compounds were prepared and their reactivity was studied upon sensitized irradiation at λ = 420 nm. Thioxanthen-9-one was employed as the sensitizer at a loading of 10 mol% in small scale reactions and of 2.5 mol% on larger scale. Cyclohex-2-enones substituted by a 2'-propenyloxy, 2'-butenyloxy, 2'-pentenyloxy, or 2'-methyl-2'-propenyloxy group in 2-position gave the products of an intramolecular [2+2] photocycloadditon. The reaction proceeded with high regioselectivity (crossed product) and perfect diastereoselectivity (nine examples, 34%-99%

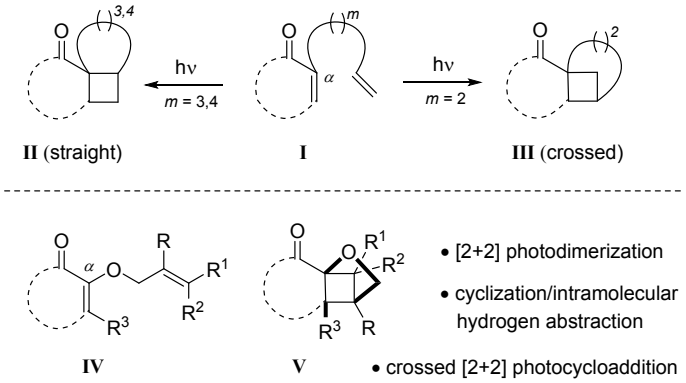
yield). If the olefin in the tether was trisubstituted (3'-methyl-2'-butenyloxy) no cycloaddition was observed. Rather, a cyclization with subsequent hydrogen abstraction occurred (three examples, 65-86% yield). The results are consistent with a reaction course via a triplet enone intermediate and the formation of a 1,4-diradical by an initial cyclization. The analogous cyclopent-2-enones were less prone to an intramolecular reaction. Instead, decomposition or intermolecular [2+2] photocycloaddition reactions prevailed. In the latter event, two main products were identified (three examples, 30-43% yield) resulting either from a head-to-head [2+2]-photodimerization or from a two-fold [2+2] photocycloaddition of the enone to the olefin. The latter reaction sequence generated pentacyclic products with a central [1,5]dioxocane ring. The structure assignment of the two product types was corroborated by single crystal X-ray analysis.

INTRODUCTION

Like most intramolecular cycloadditions, the [2+2] photocycloaddition[1] benefits from an improved regioselectivity if the two reaction partners are linked by a suitable tether. Cyclic α,β-unsaturated ketones represent the most frequently used chromophores in these reactions[2] and the preferred position for attachment of a tether is the α- or the β-position.[3] For an α-substituted enone **I** (Scheme 1) the number *m* of atoms in the tether governs the regioselectivity. A preference towards a parallel approach of the two olefins is observed if three or four atoms link the two olefinic groups (m = 3, 4) and the photocycloaddition products **II** are frequently referred to as straight products. If the tether is short (m = 2) photocycloaddition products **III** prevail in which the two olefins approach each other in a crossed fashion. The regioselectivity can be understood by the mechanistic course of the reaction[4] which involves an initial attack of the olefin on the photoexcited enone to a 1,4-diradical intermediate (vide infra). The first step of the

cycloaddition is consequently a cyclization in which the formation of five-membered rings[5] is preferred.

SCHEME 1. Regioselectivity in the Intramolecular [2+2] Photocycloaddition of α-Substituted Enones **I** and Possible Reaction Pathways of α-Allyloxy-substituted Enones **IV**



2-(2'-Alkenyloxy)cycloalk-2-enones with the general structure **IV** represent a relatively unexplored compound class in [2+2] photocycloaddition chemistry. Ikeda et al. performed experiments with three 2-allyloxycyclohex-2-enones as substrates employing a high-pressure mercury lamp as the light source and acetone as the solvent.[6] Crossed products (general structure **V**) were obtained in 53-63% yield and subsequent transformations of these products were intensively studied. We have now looked at an expanded set of substrates with two main objectives: (a) Instead of UV light it was attempted to perform the photochemical reactions with visible light. To this end, a suitable sensitizer was required which absorbs in the visible range and which does not lead to any side reactions. While visible-light mediated, sensitized reactions of styrenes and related compounds have recently received broad attention,[7] studies with cyclic enones have remained scarce.[8] (b) It was expected that other reaction pathways might be feasible depending on the structure of the chromophore and the substitution pattern of the olefin. Most

importantly, [2+2] photodimerization and hydrogen abstraction[9] were foreseen as competing reactions which would in turn lead to intriguing new structures. The results of our experimental work are summarized in this account.

RESULTS AND DISCUSSION

Figure 1 provides an overview about the compounds we employed in the present study. With regard to the olefin component, three 2'-alkenyloxy groups were employed, i.e. a 2'-propenyloxy (allyloxy) group (substrates **1**), a 2'-methyl-2'-propenyloxy (methallyloxy) group (substrates **2**), and a 3'-methyl-2'-butenyloxy (prenyloxy) group (substrates **3**). With regard to the enone component, some substituted cyclic enones (substrates **b**, **c**, **d**, **f**) were probed as starting materials apart from the unsubstituted cyclohex-2-enones (substrates **a**) and cyclopent-2-enones (substrates **e**). Cyclohex-2-enones with (*Z*)- and (*E*)-substituted 2'-alkenyloxy groups were also prepared but will be discussed in a later section.

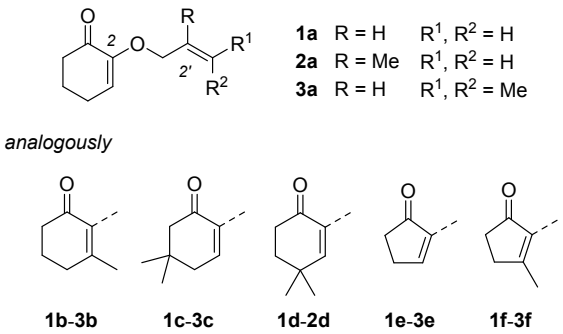


FIGURE 1. Overview about the 2-(2'-alkenyloxy)cycloalk-2-enones **1-3** employed in this study

Since the synthesis of 2-(2'-alkenyloxy)-4,4-dimethylcyclohex-2-enones was low yielding only substrates **1d** and **2d** were synthesized but not **3d**. In general, three approaches towards the [2+2] photocycloaddition precursors were taken. Starting from cyclic 1,2-diketones the alkenyloxy

group was introduced either by condensation with the respective allylic alcohol under acidic conditions (method A: TsOH in cyclohexane, reflux)[6,10] or by nucleophilic substitution of an allyl bromide via the enolate (method B: K_2CO_3 in DMF, room temperature).[11] Along these lines, 1,2-diketones **4a**, **4b**, **4e**, and **4f** (Figure 2) served as precursors for the respective 2-(2'-alkenyloxy)cycloalk-2-enones **1a-3a**, **1b-3b**, **1e-3e**, and **1f-3f**. For the synthesis of substituted cyclohexenones **1c-3c** and **1d**, **2d** epoxides **4c** and **4d** served as starting materials, which underwent nucleophilic substitution in position C2 when treated with an excess of allylic alcohol under basic conditions (method C: NaH or KOH as base).[12] As mentioned above the reaction gave low yields (6-12%) when applied to epoxide **4d** which limited the supply of starting material. Reasons for the inefficiency of the procedure were (a) difficulties in removing excess allylic alcohol and (b) formation of a side product (see the SI for further details) by dimerization of the epoxide. Since the emphasis of the study was on the [2+2] photocycloaddition chemistry alternative routes to the substituted enones were not pursued. With the exception of compounds **1a**, **2a**, and **1c**, 2-(2'-alkenyloxy)cycloalk-2-enones have not been previously employed in photochemical reactions.

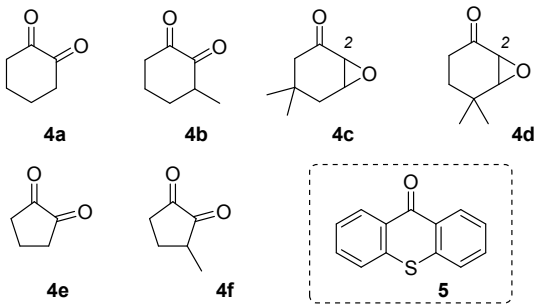
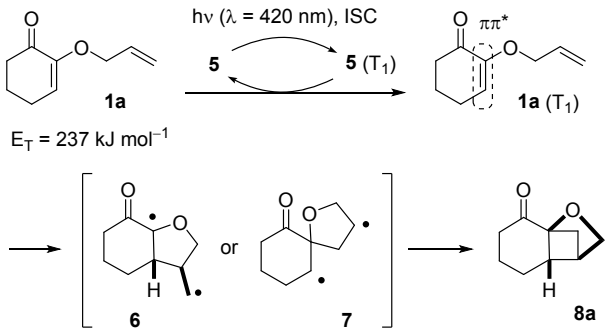


FIGURE 2. Structure of starting materials **4** for the synthesis of 2-(2'-alkenyloxy)cycloalk-2-enones and structure of thioxanthen-9-one (**5**)

Preliminary photochemical studies were performed with substrate **1a**. Its triplet energy was determined from phosphorescence experiments (77 K, CH_2Cl_2) as E_T = 235 kJ mol^{-1}. Since a wavelength of λ = 400 nm corresponds to an energy of ca. 300 kJ Es^{-1} (1 Es = 6.022 × 10^{23} photons) it seemed feasible to promote the [2+2] photocycloaddition with visible light upon judicious choice of a sensitizer. In this regard, parent thioxanthen-9-one (**5**) and its derivatives represent an excellent option and have been nicely exploited by Booker-Milburn and co-workers in [2+2] photocycloaddition reactions on large scale.[8b] In recent work on visible light-mediated reactions, we have also seen that catalyst loadings can be as low as 1 mol% for a thioxanthone sensitizer.[13] Experiments with a selection of potential sensitizers (see the SI for details) confirmed the suitability of thioxanthen-9-one (**5**) as the catalyst in the planned reaction (E_T = 268 kJ mol^{-1}).[14] Dichloromethane was established as the preferred solvent and there was no improvement in selectivity if the reaction was performed at low temperature. The reactions were run on small scale (50-200 μmol substrate, *c* = 10 mM) at a wavelength of λ = 420 nm (16 fluorescent lamps with an emission maximum at λ = 420 nm, for the emission spectrum, see the SI) and yields of product **8a** (Scheme 2) were consistently around 70% irrespective of whether 2.5, 5, or 10 mol% of **5** were used. Indeed, the low molecular weight (212 Da) of thioxanthen-9-one (**5**) made it relatively difficult to measure the exact quantity. Iridium catalysts (2.5 mol%) with a much higher molecular weight performed similar to **5** and there was a correlation between the reaction time and the triplet energy of the catalyst. Sensitizers with a triplet energy E_T > 250 kJ mol^{-1} led to a complete conversion after 2.5 hours. The reaction time increased with a decrease in triplet energy. The reaction with $Ir(ppy)_3$ (E_T = 231 kJ mol^{-1})[15] for example required five hours before no substrate was detected by TLC. The ruthenium complex $Ru(bpy)_3(PF_6)_2$ (E_T = 193 kJ mol^{-1})[16] did not promote the reaction and there was also no reaction in the absence of a sensitizer.

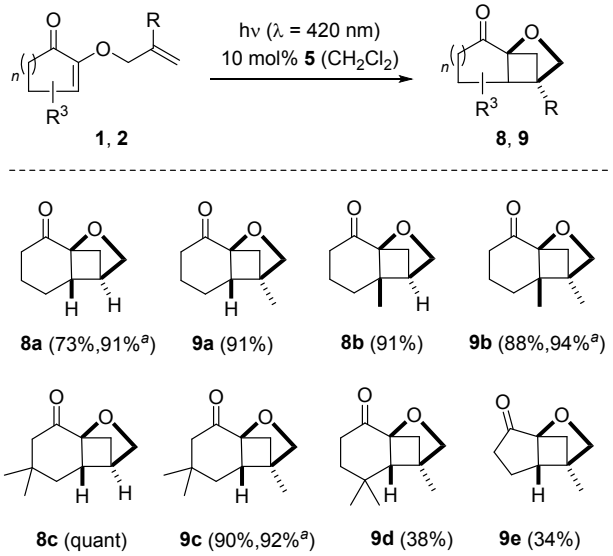
SCHEME 2. Mechanistic Proposal for the Course of the Sensitized Intermolecular [2+2] Photocycloaddition of Cyclohex-2-enone **1a**



The formation of crossed product **8a** can be easily understood by assuming an energy transfer from the triplet state T_1 of thioxanthone **5** to substrate **1a**. Intermediate **5** (T_1) is populated with high efficiency by direct excitation and rapid[17] intersystem crossing (ISC). An exothermic triplet energy transfer occurs by a spin-allowed, mutual electron-electron exchange process, often referred to as sensitization or triplet sensitization.[18] Upon energy transfer, the reactive triplet state **1a** (T_1) is generated which is ππ* in character and which is prone to undergo double bond addition.[4] Subsequently, 1,4-diradicals **6** and **7** are formed by five-membered ring closure[5] and both represent potential precursors to product **8a**. The low reduction potentials of α,β-unsaturated enones ($E_{1/2}^{red} \leq -2.0$ V)[19] render any single electron transfer (photoredox) processes not viable.

Several allyloxy- and methallyloxy-substituted cycloalk-2-enones reacted similar to substrate **1a** and the results are summarized in Scheme 3. In order to secure a reproducible reaction course, 10 mol% of the sensitizer were used for small scale reactions. Some of the reactions were also performed on larger scale (1 mmol) and at a higher concentration (c = 25 mM). In this case, only 2.5 mol% of the sensitizer were employed. Despite a longer reaction time, the chemoselectivity did not suffer and yields were as good as on small scale or even higher.

SCHEME 3. Intramolecular [2+2] Photocycloaddition of Various 2-(2'-Alkenyloxy)cycloalk-2-enones upon Irradiation with Visible Light



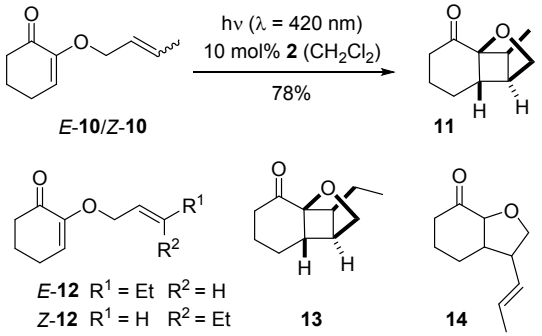
[a] Yield if the reaction was performed on 1 mmol scale.

Crossed photocycloadditon products **8a**-**8c** and **9a**-**9c** were isolated cleanly without any indication for the formation of other side products. Among the 4,4-dimethylcyclohexenones **1d** and **2d**, only the latter substrate showed a photochemical reaction. The former substrate did not react and the starting material was recovered. Since quantities were limited, the low yield of product **9d** might be associated with loss of product during chromatographic purification. Both compounds **9d** and **9e** were difficult to detect on TLC which further impaired a quantitative isolation. Cyclopentenone **1e** was converted upon sensitized irradiation (cf. Scheme 3) but no defined products could be isolated. The same observation was made when the compound was irradiated directly at λ = 350 nm (c = 10 mM, CH_2Cl_2).

The suspected intermediacy of 1,4-diradicals in the course of the [2+2] photocycloaddition implied the possibility to perform stereoconvergent reactions[20] with 1,2-disubstituted olefins in

the tether. Substrates *E*-**10**/*Z*-**10** (Scheme 4) were obtained from an *E*/*Z*-mixture (d.r. = 50/50) of crotyl alcohol (2-butenol) by condensation with 1,2-diketone **4a** (method A). Sensitized irradiation delivered photocycloaddition product **11** as a single diastereoisomer accompanied by an olefinic impurity which was removed by treatment with 3,6-bis(methoxycarbonyl)-1,2,4,5-tetrazine.[21] The yield of clean isolated product was 78% and its relative configuration was assigned based on NOESY spectra (see the SI for further details).

SCHEME 4. Stereoconvergent Formation of [2+2] Photocycloaddition Products **11** and **13**

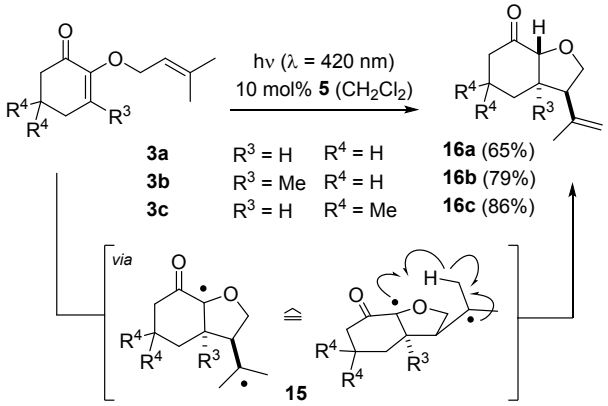


The ethyl-substituted substrates **12** were obtained in diastereomerically pure form from (*E*)- and (*Z*)-3-penten-1-ol and diketone **4a**. The compounds were individually subjected to the irradiation conditions and delivered the same product **13**. In this case, the product was not completely homogenous but was contaminated by compound **14** (yield from *E*-**12**: quant., **13**/**14** = 82/18; yield from *Z*-**12**: 90%, **13**/**14** = 83/17). By-product formation is likely to occur from the intermediate 1,4-diradical by intramolecular hydrogen abstraction (vide infra). It was possible to remove the undesired compound by oxidation and the desired product **13** was obtained in 69% yield. The outcome of the reactions suggests that 1,4-biradicals related to **6** are the major intermediates in the [2+2] photocycloaddition to products **11** and **13**. Not only do they explain the

observed stereoconvergence of the reaction but they also account for the formation of the olefinic side products.

When cyclohexenones **3a**-**3c** with a trisubstituted tethered olefin were employed as starting materials, a cyclization/reduction pathway became dominant and [2+2] photocycloaddition products were not detected. The high yields achieved for products **16a**-**16c** (Scheme 5) render some synthetic utility to this method, which represents formally a conjugate addition to the β-carbon atom of the α,β-unsaturated enone. The assignment of the relative product configuration was suggested by ^{1}H-NMR coupling constants and NOESY experiments (see the SI for detail) and the selectivity of the process is remarkable as it allows to construct three contiguous stereogenic centers with a defined configuration.

SCHEME 5. Formation of Cyclization Products **16** from 2-Dimethylallyloxy-substituted Enones **3** via 1,4-Diradicals **15**



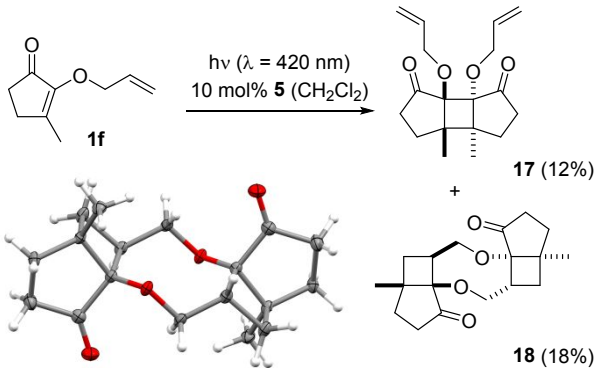
Mechanistically, the first step of the sequence occurs presumably in analogy to the C-C bond forming event previously mentioned (**1a** → **6**), i.e. the triplet of **3** undergoes intramolecular addition to the tethered olefin by a five-membered ring cyclization. However, due to steric hindrance of the substituents (R^3 and CMe_2) bond formation occurs in a *trans* fashion. In the

intermediate bicyclic 1,4-diradical **15** cyclization to a cyclobutane by C-C bond formation is not feasible but an intramolecular hydrogen abstraction[9] can readily occur that generates products **16**.

Like cyclopentenone **1e** in the [2+2] photocycloaddition study, the cyclopentenone with a prenyloxy substituent (**3e**) showed only decomposition under the conditions successfully employed for substrate **3a**. Also the cyclopentenones **1f-3f** with an additional methyl group in β-position displayed a reactivity that did not parallel the reactivity pattern of the comparable six-membered cyclic enones **1b-3b**. In this instance, however, defined products could be isolated albeit in only low to moderate yields. The preferred reaction pathway of the cyclopentenones **1f-3f** was a [2+2] photodimerization with the interesting twist that there are two double bonds available in each component. Along these lines, 2-(2'-butenyloxy)-3-methylcycloalk-2-enone (**1f**) produced a set of [2+2] photocycloaddition products from which two products **17** and **18** could be isolated (Scheme 6). Product **17** is the [2+2] photodimerization product resulting from addition of the two enone double bonds in what is commonly referred to as a *cis-anti-cis* addition.[1,2] The *cis* fusion between the five-membered rings and the four-membered ring is to be expected due to the rigidity of the skeleton while the *anti* (*trans*) configuration of the cyclopentanone rings minimizes their steric repulsion. Based on its NMR data, the second product **18** was also symmetric and – as confirmed by its crystal structure – it displays an inversion center (S_2 symmetry).[22] The crystal structure revealed that the bicyclo[3.2.0]heptane core is *cis* connected and all substituents within the cyclobutane are positioned in a *cis* fashion. The two constitutionally identical bicyclo[3.2.0]heptane fragments possess opposite absolute configuration. Given the low combined yield for compounds **17** and **18**, it is likely that other dimerization products were formed but could not be isolated in pure form. [2+2] Photodimerization in a head-to-head fashion is common for cyclopentenones[23] while the

regioselectivity of the intermolecular head-to-head double bond addition of a monosubstituted olefin to an enone has less precedence.[9d,23d,24]

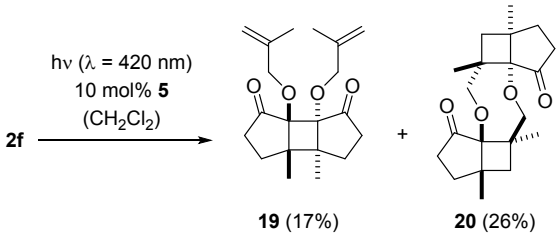
SCHEME 6. [2+2] Photodimerization of Cyclopent-2-enone **1f** and Crystal Structure[a] of Product **18**



[a] Ellipsoids in the ORTEP structure are displayed at the 50% probability level.

The overall product yield achieved in the [2+2] photodimerization of compound **2f** was slightly higher (44%) than observed for **1f**. Again two regioisomers were isolated one of which was the enone dimerization product **19** and the other the product of an enone/olefin addition. The configuration assignment for the latter product **20** was based on analogy to product **18**.

SCHEME 7. [2+2] Photodimerization of Cyclopent-2-enone **2f** to Products **19** and **20**



Remarkably, even the prenyloxy-substituted enone **3f** did not display the cyclization tendency observed with cyclohexenones **3a**-**3c**. Instead, the only product isolated from its sensitized irradiation was the head-to-head regioisomer **21** of a [2+2] photodimerization that was obtained in 34% yield. The C_2-symmetric compound displayed the same relative configuration as the previously discussed enone dimers **17** and **19** and the structure assignment could in this specific case be secured by single crystal structure analysis (Figure 3).

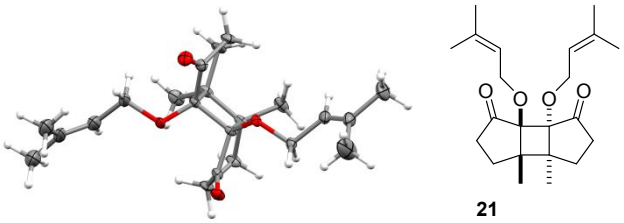


FIGURE 3. Structure of the [2+2] photodimerization product **21** (ellipsoids in the ORTEP structure are displayed at the 50% probability level) obtained by sensitized irradiation of substrate **3f** (34% yield)

The difference between the cyclopentenone and the cyclohexenone chromophore in the photochemical reactivity of their 2-(2'-alkenyloxy)-substituted derivatives is remarkable. Only in a single case (product **9e**) an intramolecular attack of the tethered olefin occurred while with all other substrates there was no indication for such an attack, not even for a cyclization to a 1,4-diradical (in analogy to the formation of intermediate **15**). The cyclization seems retarded and intermolecular [2+2] photocycloaddition reactions become competitive. The observation is important because it allows to access cyclopentenone dimers without protecting olefinic side chains.

In summary, an array of structurally diverse products has been obtained by irradiation of the title compounds in the presence of a sensitizer. The photochemical reactions of all cyclohexenone derivatives proceeded in moderate to excellent yields and with a high degree of diastereoselectivity. Intramolecular reactions were observed exclusively either as [2+2] photocycloaddition or as a cyclization/hydrogen abstraction cascade. Up to four stereogenic centers can be established in a single reaction and the products hold promise as scaffolds which enable a further functionalization at several positions. The cyclopentenone derivatives were less prone to intramolecular reactions but underwent preferentially an intermolecular reaction leading to [2+2] photodimerization products.

EXPERIMENTAL SECTION

General Methods. All air and moisture sensitive reactions were carried out in flame-dried glassware under an argon atmosphere using standard *Schlenk* techniques. For moisture sensitive reactions, tetrahydrofuran (THF), diethylether (Et_2O) and dichloromethane (CH_2Cl_2) were dried using a solvent purification system. Cyclohexane was dried over neutral aluminum oxide and stored over 4 Å molecular sieves. Dry *N,N*-dimethylformamide (DMF) was obtained in the highest available purity stored over molecular sieves and used without further purification. For photochemical reactions, dry dichloromethane was degassed by three freeze-pump-thaw cycles. Cooling baths used were ice/water (0 °C) and dry ice/ethanol (–78 °C). Technical solvents [1,2-dichloroethane (DCE), pentane (P), Et_2O, CH_2Cl_2, methanol (MeOH), ethyl acetate (EtOAc), cyclohexane] were distilled prior to use. Flash column chromatography was performed on silica 60 (230-400 mesh) and thin layer chromatography (TLC) was performed on silica coated glass plates (silica 60 F_{254}) with detection by UV-light (λ = 254 nm) and/or by staining with $KMnO_4$ solution followed by heat treatment. Infrared spectra (IR) were recorded by attenuated total

reflection (ATR) technique and are reported as wave numbers $\tilde{\nu}$ (cm^{-1}). The following abbreviations for intensities were used: vs (very strong), s (strong), m (medium), w (weak). NMR spectra were recorded at room temperature on either a 300, 400 or 500 MHz nuclear magnetic resonance spectrometer. The ^{1}H NMR spectra were referenced to the residual solvent peak of either chloroform (7.26 ppm) or C_6D_6 (7.16 ppm), and the $^{13}C\{^{1}H\}$ NMR spectra were referenced either against the central peak of $CDCl_3$ (77.16 ppm) or the residual solvent peak of C_6D_6 (128.06 ppm). ^{1}H NMR spectra were reported as follows: chemical shift in parts per million (ppm), peak shape (s - singlet, d - dublet, t - triplet, q - quartet, quint. - quintet, sept. - septet, m = multiplet), coupling constant in Hertz (Hz), and integration. Apparent multiplets which occur as a result of coupling constant equality between magnetically non-equivalent protons are marked as virtual (*virt.*). Mass spectra were measured with a mass selective quadrupole detector (EI, 70 eV). HRMS data were determined at a double-focussing magnetic sector instrument (EI, 70 eV). UV/Vis Spectra were recorded using a precision cell made of quartz with a pathway of 1 mm.

General procedure 1 (Method A): To a solution of the respective 1,2-cyclohexadione (1.0 equiv.) in dry cyclohexane (40 mL/g starting material) was added *p*-TsOH·H_2O (3.0 mol%) and the corresponding allylic alcohol (4.0 equiv.). The reaction mixture was heated at reflux in a Dean-Stark apparatus for 15 – 17 h. The solution was allowed to cool to room temperature, washed with brine (2 × 50 mL/g), dried over Na_2SO_4, and filtrated. The solvent was removed under reduced pressure and the crude product was purified using flash column chromatography (P/Et_2O).

General procedure 2 (Method B): To a solution of the respective 1,2-cyclohexadione (1.0 equiv.) in dry DMF (40 mL/g starting material) was added K_2CO_3 (1.2 equiv.) and the

respective allylbromide (1.2 equiv.). The reaction mixture was stirred at room temperature for 4.5 – 21 h. The reaction was quenched by the addition of H_2O (20 mL/g). Et_2O (40 mL/g) was added and the layers were separated. The organic layer was washed with H_2O (4 × 40 mL/g) and brine (1 × 60 mL/g), dried over Na_2SO_4, and filtrated. The solvent was removed under reduced pressure and the crude product was purified using flash column chromatography (P/Et_2O).

General procedure 3 (Method C): A round bottom flask charged with NaH (60 wt%, 1.2 equiv.) was cooled to 0 °C and the respective allylic alcohol (30 equiv.) was added dropwise. The reaction mixture was stirred for 10 min and subsequently the corresponding epoxide (1.0 equiv.) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 20 – 24 h. The mixture was diluted with Et_2O (75 mL/g) and quenched by the addition of H_2O (35 mL/g). The layers were separated and the organic layer was washed with H_2O (1 × 35 mL/g) and brine (1 × 75 mL/g), dried over Na_2SO_4, and filtrated. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (P/Et_2O).

General procedure 4 (Method B): To a solution of the respective 1,2-cyclopentadione (1.0 equiv.) in dry DMF (40 mL/g starting material) was added K_2CO_3 (1.2 equiv.) and the respective allylbromide (1.2 equiv.). The reaction mixture was stirred at room temperature for 17 – 22 h. The reaction was quenched by the addition of H_2O (20 mL/g). Et_2O (40 mL/g) was added and the layers were separated. The organic layer was washed with H_2O (4 × 40 mL/g) and brine (1 × 60 mL/g), dried over Na_2SO_4, and filtrated. The solvent was removed under reduced pressure and the crude product was purified using flash column chromatography (P/Et_2O).

2-(Allyloxy)cyclohex-2-en-1-one (1a)

According to general procedure 1, compound **1a** was synthesized starting from **4a** (1.00 g, 8.92 mmol, 1.0 equiv.), allylic alcohol (2.43 mL, 2.07 g, 35.7 mmol, 4.0 equiv.) and *p*-TsOH·H_2O (51.3 mg, 270 µmol, 3.0 mol%). Purification by flash column chromatography (SiO_2, P/Et_2O = 5/1, UV) afforded the product (667 mg, 4.38 mmol, 49%) as a colorless oil. TLC (P/Et_2O = 3/1): R_f = 0.18 [UV, $KMnO_4$]. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.97 (*virt.* quint. $^3J \cong {}^3J$ = 6.2 Hz, 2H), 2.41 (td, ^3J = 6.0, 4.7 Hz, 2H), 2.48 – 2.53 (m, 2H), 4.31 (*virt.* dt ^3J = 5.5 Hz, $^4J \cong {}^4J$ = 1.5 Hz, 2H), 5.25 (ddt, ^2J = 1.5 Hz, ^3J = 10.6 Hz, ^4J = 1.5 Hz, 1H), 5.33 (ddt, ^2J = 1.5 Hz, ^3J = 17.4 Hz, ^4J = 1.5 Hz, 1H), 5.89 (t, ^3J = 4.7 Hz, 1H), 5.98 (ddt, ^3J = 17.4, 10.6, 5.5 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 300 K): δ = 23.1 (t), 24.7 (t), 39.0 (t), 68.8 (t), 118.1 (t), 118.7 (d), 133.1 (d), 150.5 (s), 194.5 (s). UV/vis (CH_2Cl_2, *c* = 0.5 mM): λ = 259 nm (ε = 3736 cm^{-1} M^{-1}). Data of this compound were in accordance with the literature.[6b]

2-(Allyloxy)-3-methylcyclohex-2-en-1-one (1b)

According to general procedure 2, compound **1b**[12a,25] was synthesized starting from **4a** (500 mg, 3.96 mmol, 1.0 equiv.), allyl bromide (410 µL, 580 mg, 4.76 mmol, 1.2 equiv.) and K_2CO_3 (670 mg, 4.85 mmol, 1.2 equiv.). Purification by flash column chromatography (SiO_2, P/Et_2O = 9/1, UV) afforded the product (259 mg, 1.56 mmol, 39%) as a colorless oil. TLC (P/Et_2O = 3/1): R_f = 0.30 [UV, $KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 1.92 (s, 3H), 1.92 – 1.97 (m, 2H), 2.38 (t, ^3J = 6.1 Hz, 2H), 2.41 – 2.47 (m, 2H), 4.34 (*virt.* dt, ^3J = 6.0 Hz, $^2J \cong {}^4J$ = 1.4 Hz, 2H), 5.18 (*virt.* dt, ^3J = 10.3 Hz, $^2J \cong {}^4J$ = 1.4 Hz, 1H), 5.28 (*virt.* dtd, ^3J = 17.2 Hz, $^2J \cong {}^4J$ = 1.6 Hz, ^4J = 1.5 Hz, 1H), 5.99 (ddt, ^3J = 17.0, 10.3, 6.0 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 300 K): δ = 18.1 (q), 22.3 (t), 31.7 (t), 38.9 (t), 73.0 (t), 117.8 (t), 134.5 (d), 146.4 (s), 147.9 (s), 194.9 (s). IR (ATR): $\tilde{\nu}$ = 2928 (w), 1672 (vs), 1631 (m), 1431

(w), 1379 (w), 1304 (w), 1193 (s), 1153 (s), 985 (s), 926 (s). MS (EI, 70 eV): *m/z* (%) = 166 (80), 151 (100), 137 (13), 125 (17), 113 (38), 110 (93), 95 (82), 82 (78). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{10}H_{14}O_2$: 166.0982; Found: 166.0988. UV/vis (CH_2Cl_2, c = 0.5 mM): λ = 247 nm (ε = 8212 cm^{-1} M^{-1}).

2-(Allyloxy)-5,5-dimethylcyclohex-2-en-1-one (1c)

According to general procedure 3, compound **1c**[12a] was synthesized starting from epoxide **4c** (200 mg, 1.43 mmol, 1.0 equiv.), allylic alcohol (3.00 mL, 2.55 g, 43.9 mmol, 31 equiv.) and NaH (60 wt%, 72.0 mg, 1.80 mmol, 1.3 equiv.). Purification by flash column chromatography (SiO_2, P/Et_2O = 9/1 → 6/1, UV) afforded the product (115 mg, 640 µmol, 45%) as a colorless oil. TLC (P/Et_2O = 3/1): R_f = 0.31 [UV, $KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 1.06 (s, 6H), 2.31 (d, ^3J = 4.6 Hz, 2H), 2.37 (s, 2H), 4.32 (*virt.* dt, ^3J = 5.8 Hz, $^2J \cong {}^4J$ = 1.4 Hz, 2H), 5.25 (*virt.* dq, ^3J = 10.6 Hz, $^2J \cong {}^4J$ = 1.3 Hz, 1H), 5.33 (*virt.* dq, ^3J = 17.3 Hz, $^2J \cong {}^4J$ = 1.5 Hz, 1H), 5.73 (t, ^3J = 4.6 Hz, 1H), 5.98 (ddt, ^3J = 17.2, 10.8, 5.5 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 300 K): δ = 28.3 (q), 34.1 (s), 38.6 (t), 52.4 (t), 68.8 (t), 116.1 (d), 118.2 (t), 133.0 (d), 149.8 (s), 194.5 (s). IR (ATR): $\tilde{\nu}$ = 2959 (m), 1690 (vs), 1629 (m), 1467 (w), 1368 (w), 1165 (m), 999 (m). MS (EI, 70 eV): *m/z* (%) = 180 (100), 165 (10), 151 (10), 127(10), 124 (51), 109 (49), 95 (52), 83 (19). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{11}H_{16}O_2$: 180.1145; Found: 180.1145. UV/vis (CH_2Cl_2, c = 0.5 mM): λ = 261 nm (ε = 5484 cm^{-1} M^{-1}).

2-(Allyloxy)-4,4-dimethylcyclohex-2-en-1-one (1d)

KOH (85 wt%, 94.2 mg, 1.43 mmol, 1.0 equiv.) was dissolved in allylic alcohol (1.00 mL, 854 mg, 14.7 mmol, 10 equiv.). A solution of epoxide **4d** (200 mg, 1.43 mmol, 1.0 equiv.) in allylic alcohol (1.5 mL, 1.28 g, 22.1 mmol, 15 equiv.) was then added dropwise and the reaction mixture was stirred at room temperature over night. Subsequently the reaction mixture was

diluted with 15 mL Et_2O and quenched by the addition of 15 mL H_2O. The layers were separated and the aqueous layer was extracted with Et_2O (2 × 15 mL). The combined organic layers were washed with brine (1 × 50 mL), dried over Na_2SO_4, filtrated and the solvent as well as the remaining allylic alcohol were removed under reduced pressure. After purification by flash column chromatography (SiO_2, P/Et_2O = 20/1 → 6/1, UV) the product **1d** (30.5 mg, 169 µmol, 12%) was obtained as a colorless oil. TLC (P/Et_2O = 3/1): R_f = 0.28 [UV, $KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 1.18 (s, 6H), 1.82 (t, ^3J = 6.5 Hz, 2H), 2.55 (t, ^3J = 6.5 Hz, 2H), 4.27 (*virt.* dt, ^3J = 5.6 Hz, $^4J \cong {}^4J$ = 1.5 Hz, 2H), 5.24 (*virt.* dq, ^3J = 10.4 Hz, $^2J \cong {}^4J$ = 1.4 Hz, 1H), 5.32 (*virt.* dq, ^3J = 17.2 Hz, $^2J \cong {}^4J$ = 1.6 Hz, 1H), 5.59 (s, 1H), 5.97 (ddt, ^3J = 17.3, 10.8, 5.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 300 K): δ = 29.2 (q), 33.0 (s), 35.0 (t), 36.0 (t), 68.7 (t), 118.2 (t), 128.7 (d), 132.9 (d), 148.1 (s), 194.1 (s). IR (ATR): $\tilde{\nu}$ = 2958 (m), 1690 (vs), 1619 (s), 1458 (w), 1362 (m), 1261 (m), 1200 (s), 1130 (s), 1107 (s), 1014 (m), 925 (w). MS (EI, 70 eV): *m/z* (%) = 180 (24), 165 (24), 137 (4), 124 (100), 109 (23), 96 (15), 83 (11). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{11}H_{16}O_2$: 180.1145; Found: 180.1144. UV/vis (CH_2Cl_2, *c* = 0.5 mM): λ = 260 nm (ε = 7584 cm^{-1} M^{-1}).

2-(Allyloxy)cyclopent-2-en-1-one (1e)

To a solution of 1,2-cyclopentadione (**4e**) (95.0 mg, 968 µmol, 1.0 equiv.) in 5.0 mL dry cyclohexane was added *p*-TsOH·H_2O (6.10 mg, 32.1 µmol, 3.0 mol%) and allylic alcohol (210 µL, 178 mg, 3.06 mmol, 3.2 equiv.). The reaction mixture was heated at reflux using a Dean-Stark apparatus for 23 h. The solution was allowed to cool to room temperature and the solvent was removed under reduced pressure. After purification by flash column chromatography (SiO_2, P/Et_2O = 3/1, UV) the product **1e**[25] (100 mg, 720 µmol, 74%) was obtained as a colorless oil. TLC (P/Et_2O = 3/1): R_f = 0.14 [UV, $KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 2.38 –

2.48 (m, 2H), 2.52 (ddd, ^3J = 6.4, 4.2, 2.9 Hz, 2H), 4.43 (*virt.* dt, ^3J = 5.6 Hz, $^4J \cong {}^4J$ = 1.5 Hz, 2H), 5.28 (*virt.* dq, ^3J = 10.6 Hz, $^2J \cong {}^4J$ = 1.4 Hz, 1H), 5.36 (*virt.* dq, ^3J = 17.3 Hz, $^2J \cong {}^4J$ = 1.6 Hz, 1H), 5.98 (ddt, ^3J = 17.3, 10.9, 5.6 Hz, 1H), 6.39 (t, ^3J = 2.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 300 K): δ = 22.1 (t), 33.2 (t), 70.8 (t), 118.7 (t), 128.3 (d), 132.4 (d), 156.4 (s), 202.7 (s). IR (ATR): $\tilde{\nu}$ = 2925 (w), 1715 (vs), 1624 (m), 1337 (w), 1276 (w), 1119 (m), 1027 (w), 934 (w). MS (EI, 70 eV): *m/z* (%) = 138 (100), 109 (15), 95 (11), 82 (52). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_8H_{10}O_2$: 138.0675; Found: 138.0677, $[M]^+$ Calcd. for $C_7{}^{13}C_1H_{10}O_2$: 139.0709; Found: 139.0712. UV/vis (CH_2Cl_2, *c* = 0.5 mM): λ = 248 nm (ε = 5180 cm^{-1} M^{-1}).

2-(Allyloxy)-3-methylcyclopent-2-en-1-on (1f)

According to general procedure 4, compound **1f**[12a] was synthesized starting from **4f** (500 mg, 4.46 mmol, 1.0 equiv.), allyl bromide (460 µL, 650 mg, 5.35 mmol, 1.2 equiv.) and K_2CO_3 (740 mg, 5.35 mmol, 1.2 equiv.). Purification by flash column chromatography (SiO_2, P/Et_2O = 3/1, UV) afforded the product (387 mg, 2.54 mmol, 55%) as a colorless oil. TLC (P/Et_2O = 3/1): R_f = 0.24 [UV, $KMnO_4$]. ^1H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.98 (s, 3H), 2.30 – 2.39 (m, 2H), 2.43 (*virt.* dtd, ^2J = 7.1 Hz, $^3J \cong {}^3J$ = 2.5, ^3J = 1.2 Hz, 2H), 4.67 (*virt.* dt, ^3J = 5.9 Hz, $^2J \cong {}^2J$ = 1.4 Hz, 2H), 5.18 (*virt.* dq, ^3J = 10.4 Hz, $^2J \cong {}^4J$ = 1.3 Hz, 1H), 5.29 (*virt.* dq, ^3J = 17.2 Hz, $^2J \cong {}^4J$ = 1.6 Hz, 1H), 5.94 (ddt, ^3J = 17.2, 10.4, 5.8 Hz, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 300 K): δ = 15.1 (q), 27.6 (t), 33.1 (t), 70.9 (t), 117.9 (t), 134.3 (d), 151.7 (s), 155.6 (s), 203.3 (s). IR (ATR): $\tilde{\nu}$ = 2917 (w), 1699 (vs), 1643 (m), 1442 (w), 1389 (w), 1333 (m), 1204 (m), 1094 (s), 984 (m), 928 (m). MS (EI, 70 eV): *m/z* (%) = 152 (49), 137 (76), 123 (19), 112 (9), 96 (22), 84 (16), 81 (8), 69 (26), 67 (15), 55 (19), 41 (100). HRMS (EI) *m/z*: $[M]^+$ Calcd.

for $C_9H_{12}O_2$: 152.0827; Found: 152.0832. UV/vis (CH_2Cl_2, c = 0.5 mM): λ = 246 nm (ε = 10132 cm^{-1} M^{-1}).

2-[(2-Methylallyl)oxy]cyclohex-2-en-1-one (2a)

According to general procedure 1, compound **2a** was synthesized starting from **4a** (1.00 g, 8.92 mmol, 1.0 equiv.), methallylic alcohol (3.00 mL, 2.57 g, 35.7 mmol, 4.0 equiv.) and *p*-TsOH·H_2O (52.3 mg, 275 µmol, 3.0 mol%). Purification by flash column chromatography (SiO_2, P/Et_2O = 9/1 → 4/1, UV) afforded the product (682 mg, 4.10 mmol, 46%) as a colorless oil. TLC (P/Et_2O = 3/1): R_f = 0.19 [UV, $KMnO_4$]. ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ = 1.36 (*virt.* quint. $^3J \cong {}^3J$ = 6.1 Hz, 2H), 1.66 (s, 3H), 1.74 (td, ^3J = 6.0, 4.6 Hz, 2H), 2.05 – 2.21 (m, 2H), 3.90 (s, 2H), 4.86 (s, 1H), 5.11 (s, 1H), 5.30 (t, ^3J = 4.6 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 300 K): δ = 19.8 (q), 23.5 (t), 24.8 (t), 39.6 (t), 71.9 (t), 113.0 (t), 118.1 (d), 141.6 (s), 151.5 (s), 190.4 (s). UV/vis (CH_2Cl_2, c = 0.5 mM): λ = 259 (ε = 4518 cm^{-1} M^{-1}). Data of this compound were in accordance with the literature.[6b]

3-Methyl-2-[(2-methylallyl)oxy]cyclohex-2-en-1-one (2b)

According to general procedure 2, compound **2b** was synthesized starting from **4b** (500 mg, 3.96 mmol, 1.0 equiv.), methallyl bromide (480 µL, 640 mg, 4.76 mmol, 1.2 equiv.) and K_2CO_3 (0.660 mg, 4.76 mmol, 1.2 equiv.). Purification by flash column chromatography (SiO_2, P/Et_2O = 9/1, UV) afforded the product (414 mg, 2.29 mmol, 58%) as a colorless oil. TLC (P/Et_2O = 3/1): R_f = 0.29 [UV, $KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 1.82 (s, 3H), 1.90 – 1.98 (m, 5H), 2.38 (t, ^3J = 6.1 Hz, 2H), 2.44 (t, ^3J = 6.7 Hz, 2H), 4.22 (s, 2H), 4.90 (*virt.* t, $^2J \cong {}^4J$ = 2.0 Hz, 1H), 5.02 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 300 K): δ = 18.0 (q), 19.9 (q), 22.3 (t), 31.7 (t), 38.9 (t), 75.7 (t), 112.8 (t), 142.0 (s), 146.1 (s), 148.2 (s), 194.9 (s). IR

(ATR): $\tilde{\nu}$ = 2920 (w), 1673 (vs), 1632 (m), 1433 (w), 1378 (m), 1304 (m), 1193 (s), 1151 (vs), 993 (m), 895 (m). MS (EI, 70 eV): *m/z* (%) = 180 (100), 165 (37), 137 (11), 123 (21), 110 (94), 95 (74). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{11}H_{16}O_2$: 180.1145; Found: 180.1145, $[M]^+$ Calcd. for $C_{10}{}^{13}C_1H_{16}O_2$: 181.1185; Found: 181.1178. UV/vis (CH_2Cl_2, c = 0.5 mM): λ = 248 nm (ε = 7196 cm^{-1} M^{-1}).

5,5-Dimethyl-2-[(2-methylallyl)oxy]cyclohex-2-en-1-one (2c)

According to general procedure 3, compound **2c** was synthesized starting from epoxide **4c** (200 mg, 1.43 mmol, 1.0 equiv.), methallylic alcohol (2.40 mL, 2.06 g, 28.6 mmol, 20 equiv.) and NaH (60 wt%, 70.0 mg, 1.75 mmol, 1.2 equiv.). Purification by flash column chromatography (SiO_2, P/Et_2O = 9/1, UV) afforded the product (102 mg, 527 µmol, 37%) as a colorless oil. TLC (P/Et_2O = 3/1): R_f = 0.40 [UV, $KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 1.06 (s, 6H), 1.76 (s, 3H), 2.29 (d, ^3J = 4.6 Hz, 2H), 2.36 (s, 2H), 4.25 (s, 2H), 4.95 (s, 1H), 5.00 (s, 1H), 5.73 (t, ^3J = 4.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 300 K): δ = 19.4 (q), 28.3 (q), 34.2 (s), 38.5 (t), 52.4 (t), 71.6 (t), 112.9 (t), 116.3 (d), 140.5 (s), 149.9 (s), 194.3 (s). IR (ATR): $\tilde{\nu}$ = 2958 (m), 1691 (vs), 1629 (m), 1455 (w), 1368 (w), 1163 (m), 902 (w). MS (EI, 70 eV): *m/z* (%) = 194 (57), 179 (8), 151 (9), 138 (22), 127 (14), 109 (100), 95 (9), 83 (14). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{12}H_{18}O_2$: 194.1301; Found: 194.1302. UV/vis (CH_2Cl_2, c = 0.5 mM): λ = 261 nm (ε = 4374 cm^{-1} M^{-1}).

4,4-Dimethyl-2-[(2-methylallyl)oxy]cyclohex-2-en-1-one (2d)

KOH (85 wt%, 59.9 mg, 908 µmol, 1.0 equiv.) was dissolved in methallylic alcohol (1.00 mL, 851 mg, 11.8 mmol, 13 equiv.). A solution of epoxide **4d** (127 mg, 908 µmol, 1.0 equiv.) in methallylic alcohol (1.0 mL, 0.851 mg, 11.8 mmol, 13 equiv.) was then added dropwise and the

reaction mixture was stirred at room temperature over night. Subsequently the reaction mixture was diluted with 15 mL Et_2O and quenched by the addition of 15 mL H_2O. The layers were separated and the aqueous layer was extracted with Et_2O (2 × 15 mL). The combined organic layers were washed with brine (1 × 50 mL), dried over Na_2SO_4, filtrated and the solvent as well as the remaining volatiles were removed under reduced pressure. After purification by flash column chromatography (SiO_2, P/Et_2O = 6/1) the product **2d** (11.0 mg, 56.6 µmol, 6%) was obtained as a colorless oil. TLC (P/Et_2O = 3/1): R_f = 0.37 [UV, $KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 1.17 (s, 6H), 1.76 (t, ^4J = 1.2 Hz, 3H), 1.80 – 1.83 (m, 2H), 2.52 – 2.60 (m, 2H), 4.18 (s, 2H), 4.94 (*virt.* quint., $^2J \cong {}^4J$ = 1.3 Hz, 1H), 5.00 (*virt.* dq, ^2J = 2.1 Hz, $^4J \cong {}^4J$ = 1.2 Hz, 1H), 5.60 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 300 K): δ = 19.5 (q), 29.2 (q), 33.0 (s), 35.1 (t), 36.0 (t), 71.5 (t), 113.1 (t), 128.9 (d), 140.3 (s), 148.2 (s), 194.1 (s). IR (ATR): $\tilde{\nu}$ = 2958 (m), 1692 (vs), 1619 (s), 1455 (w), 1363 (m), 1201 (s), 1130 (s), 1109 (s), 1014 (m), 901 (w). MS (EI, 70 eV): *m/z* (%) = 194 (44), 179 (31), 151 (14), 138 (100), 125 (20), 109 (37), 97 (22), 83 (10). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{12}H_{18}O_2$: 194.1301; Found: 194.1301, $[M]^+$ Calcd. for $C_{11}{}^{13}C_1H_{18}O_2$: 195.1335; Found: 195.1350. UV/vis (CH_2Cl_2, c = 0.5 mM): λ = 260 nm (ε = 6300 cm^{-1} M^{-1}), 338 nm (ε = 912 cm^{-1} M^{-1}).

2-[(2-Methylallyl)oxy]cyclopent-2-en-1-one (2e)

In analogy to general procedure 4, compound **2e**[23] was synthesized starting from **4e** (100 mg, 1.02 mmol, 1.0 equiv.), methallyl bromide (150 µL, 207 mg, 1.53 mmol, 1.5 equiv.) and K_2CO_3 (211 mg, 1.53 mmol, 1.5 equiv.) in 4.0 mL dry DMF. The reaction was quenched by the addition of 5 mL H_2O and 10 mL Et_2O. The organic layer was washed with H_2O (4 × 10 mL) and brine (1 × 20 mL), dried over Na_2SO_4, filtrated and the solvent was removed under reduced pressure. Purification by flash column chromatography (SiO_2, P/Et_2O = 3/1, UV) afforded the product

(55.1 mg, 360 µmol, 35%) as a colorless oil. TLC (P/Et_2O = 1/1): R_f = 0.30 [UV, $KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 1.78 (s, 3H), 2.40 – 2.44 (m, 2H), 2.50 (dt, ^3J = 6.1, 2.8 Hz, 2H), 4.34 (s, 2H), 4.98 (s, 1H), 5.03 (s, 1H), 6.40 (t, ^3J = 2.8 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 300 K): δ = 19.4 (q), 22.1 (t), 33.2 (t), 73.8 (t), 113.7 (t), 128.5 (d, C-3), 140.0 (s), 156.5 (s), 202.6 (s). IR (ATR): $\tilde{\nu}$ = 2922 (w), 1708 (vs), 1623 (s), 1407 (w), 1336 (w), 1273 (m), 1104 (vs), 1025 (m), 902 (m), 782 (m). MS (EI, 70 eV): *m/z* (%) = 152 (100), 137 (16), 124 (10), 109 (21), 96 (90), 82 (19). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_9H_{12}O_2$: 152.0832; Found: 152.0831. UV/vis (CH_2Cl_2, *c* = 0.5 mM): λ = 248 nm (ε = 6794 cm^{-1} M^{-1}).

3-Methyl-2-[(2-methylallyl)oxy]cyclopent-2-en-1-one (2f)

According to general procedure 4, compound **2f** was synthesized starting from **4f** (500 mg, 4.46 mmol, 1.0 equiv.), methallyl bromide (550 µL, 736 mg, 5.46 mmol, 1.2 equiv.) and K_2CO_3 (740 mg, 5.35 mmol, 1.2 equiv.). Purification by flash column chromatography (SiO_2, P/Et_2O = 9/1, UV) afforded the product (621 mg, 3.74 mmol, 84%) as a colorless oil. TLC (P/Et_2O = 3/1): R_f = 0.28 [UV, $KMnO_4$]. ^{1}H NMR (300 MHz, C_6D_6, 300 K): δ = 1.57 – 1.59 (m, 3H), 1.56 – 1.67 (m, 2H), 1.64 – 1.71 (m, 3H), 1.85 – 1.90 (m, 2H), 4.79 – 4.86 (m, 2H), 4.86 (*virt.* ddq, ^2J = 2.3 Hz, ^4J = 1.6, $^4J \cong {}^4J$ = 0.8 Hz, 1H), 5.11 (*virt.* dq, ^2J = 2.3 Hz, $^4J \cong {}^4J$ = 1.1 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 300 K): δ = 14.4 (q), 19.4 (q), 26.8 (t), 33.1 (t), 73.0 (t), 112.7 (t), 142.5 (s), 151.8 (s), 152.1 (s), 201.4 (s). IR (ATR): $\tilde{\nu}$ = 2917 (w), 1700 (vs), 1646 (m), 1448 (w), 1389 (m), 1335 (m), 1204 (m), 1096 (s), 990 (m), 903 (m). MS (EI, 70 eV): *m/z* (%) = 166 (56), 151 (31), 137 (10), 110 (9), 96 (12), 84 (15), 69 (16), 55 (100), 41 (24). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{10}H_{14}O_2$: 166.0988; Found: 166.0985, $[M]^+$ Calcd. for $C_9{}^{13}C_1H_{14}O_2$: 167.1022; Found: 167.1026. UV/vis (CH_2Cl_2, *c* = 0.5 mM): λ = 248 nm (ε = 9284 cm^{-1} M^{-1}).

2-[(3-Methylbut-2-en-1-yl)oxy]cyclohex-2-en-1-one (3a)

According to general procedure 2, compound **3a** was synthesized starting from **4a** (1.00 g, 8.92 mmol, 1.0 equiv.), 3,3-dimethylallyl bromide (1.24 mL, 1.60 g, 10.7 mmol, 1.2 equiv.) and K_2CO_3 (1.48 g, 10.7 mmol, 1.2 equiv.). Purification by flash column chromatography (SiO_2, P/Et_2O = 9/1 → 4/1 → 3/1, UV) afforded the product (227 mg, 1.26 mmol, 14%) as a colorless oil. TLC (P/Et_2O = 3/1): R_f = 0.15 [UV, $KMnO_4$]. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.64 (s, 3H), 1.71 (s, 3H), 1.86 – 1.99 (m, 2H), 2.39 (td, ^3J = 6.1, 4.7 Hz, 2H), 2.47 (dd, ^3J = 7.4, 6.0 Hz, 2H), 4.23 (d, ^3J = 5.9 Hz, 2H), 5.38 (*virt.* ddq, ^3J = 8.2, 5.9 Hz, $^4J \cong {}^4J$ = 1.5 Hz, 1H), 5.85 (t, ^3J = 4.7 Hz, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 300 K): δ = 18.2 (q), 23.0 (t), 24.6 (t), 25.8 (q), 38.9 (t), 64.6 (t), 117.9 (d), 119.6 (d), 137.6 (s), 150.7 (s), 194.5 (s). IR (ATR): $\tilde{\nu}$ = 2926 (w), 1686 (vs), 1622 (m), 1444 (w), 1375 (w), 1259 (m), 1184 (s), 1148 (vs), 1003 (m), 874 (w). MS (EI, 70 eV): *m/z* (%) = 180 (27), 147 (11), 134 (8), 118 (57), 112 (100), 99 (12), 95 (7), 84 (27). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{11}H_{16}O_2$: 180.1148; Found: 180.1145, $[M]^+$ Calcd. for $C_{10}{}^{13}C_1H_{16}O_2$: 181.1185; Found: 181.1178. UV/vis (CH_2Cl_2, c = 0.5 mM): λ = 261 nm (ε = 4126 cm^{-1} M^{-1}).

3-Methyl-2-[(3-methylbut-2-en-1-yl)oxy]cyclohex-2-en-1-one (3b)

According to general procedure 2, compound **3b**[26] was synthesized starting from **4b** (500 mg, 3.96 mmol, 1.0 equiv.), 3,3-dimethylallyl bromide (550 µL, 710 mg, 4.76 mmol, 1.2 equiv.) and K_2CO_3 (0.660 mg, 4.76 mmol, 1.2 equiv.). Purification by flash column chromatography (SiO_2, P/Et_2O = 9/1 → 3/1, UV) afforded the product (197 mg, 1.01 mmol, 26%) as a colorless oil. TLC (P/Et_2O = 3/1): R_f = 0.24 [UV, $KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 1.68 (s, 3H), 1.75 (s, 3H), 1.86 – 2.03 (m, 5H), 2.38 (t, ^3J = 6.1 Hz, 2H), 2.41 – 2.45 (m, 2H), 4.32 (d, ^3J = 7.4 Hz, 2H), 5.44 (*virt.* ddq, ^3J = 7.4, 5.9 Hz, $^4J \cong {}^4J$ = 1.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (126

MHz, $CDCl_3$, 300 K): δ = 18.1 (q), 22.3 (t), 26.0 (q), 31.6 (t), 38.9 (t), 68.3 (t), 120.7 (d), 138.2 (s), 146.5 (s), 148.0 (s), 195.1 (s). IR (ATR): $\tilde{\nu}$ = 2917 (w), 1673 (vs), 1630 (m), 1433 (w), 1381 (m), 1301 (m), 1191 (s), 1148 (s), 970 (m). MS (EI, 70 eV): *m/z* (%) = 126 (100), 98 (11), 84 (23). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{12}H_{18}O_2$: 194.1300; Found: 194.1301. UV/vis (CH_2Cl_2, *c* = 0.5 mM): λ = 248 nm (ε = 6640 cm^{-1} M^{-1}).

5,5-Dimethyl-2-[(3-methylbut-2-en-1-yl)oxy]cyclohex-2-en-1-one (3c)

According to general procedure 3, compound **3c** was synthesized starting from epoxide **4c** (200 mg, 1.43 mmol, 1.0 equiv.), 3,3-dimethylallylic alcohol (4.50 mL, 3.83 g, 44.4 mmol, 31 equiv.) and NaH (60 wt%, 69.0 mg, 1.73 mmol, 1.2 equiv.). Purification by flash column chromatography (SiO_2, P/Et_2O = 9/1, P/Et_2O = 9/1 → 6/1, UV) afforded the product (45.2 mg, 217 µmol, 15%) as a colorless oil. TLC (P/Et_2O = 3/1): R_f = 0.28 [UV, $KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 1.06 (s, 6H), 1.68 (s, 3H), 1.75 (s, 3H), 2.31 (d, ^3J = 4.6 Hz, 2H), 2.36 (s, 2H), 4.28 (d, ^3J = 7.3 Hz, 2H), 5.42 (ddd, ^3J = 7.3 Hz, ^4J = 4.1, 1.5 Hz, 1H), 5.71 (t, ^3J = 4.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 300 K): δ = 18.3 (q), 25.9 (q), 28.3 (q), 34.1 (s), 38.6 (t), 52.4 (t), 64.6 (t), 115.3 (d), 119.6 (d), 137.7 (s), 150.1 (s), 194.5 (s). IR (ATR): $\tilde{\nu}$ = 2958 (m), 1691 (vs), 1627 (m), 1452 (w), 1368 (w), 1162 (s), 1108 (m), 1003 (w). MS (EI, 70 eV): *m/z* (%) = 208 (28), 175 (12), 146 (30), 140 (100), 125 (49), 112 (10), 98 (71), 84 (57). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{13}H_{20}O_2$: 208.1458; Found: 208.1445, $[M]^+$ Calcd. for $C_{12}{}^{13}C_1H_{20}O_2$: 209.1491; Found: 209.1482. UV/vis (CH_2Cl_2, *c* = 0.5 mM): λ = 263 nm (ε = 4500 cm^{-1} M^{-1}).

2-[(3-Methylbut-2-en-1-yl)oxy]cyclopent-2-en-1-one (3e)

In analogy to general procedure 4, compound **3e** was synthesized starting from **4e** (170 mg, 1.73 mmol, 1.0 equiv.), 3,3-dimethylallyl bromide (310 µL, 340 mg, 2.68 mmol, 1.5 equiv.) and K_2CO_3 (377 mg, 2.73 mmol, 1.6 equiv.) in 7.0 mL dry DMF. The reaction was quenched by the addition of 7 mL H_2O and 15 mL Et_2O. The organic layer was washed with H_2O (4 × 15 mL) and brine (1 × 30 mL), dried over Na_2SO_4, filtrated and the solvent was removed under reduced pressure. Purification by flash column chromatography (SiO_2, P/Et_2O = 3/1, UV) afforded the product (60.0 mg, 360 µmol, 21%) as a colorless solid. Mp 42 – 43 °C.TLC (P/Et_2O = 1/1): R_f = 0.35 [UV, $KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 1.70 (s, 3H), 1.76 (s, 3H), 2.41 – 2.44 (m, 2H), 2.48 – 2.60 (m, 2H), 4.40 (d, ^3J = 6.8 Hz, 2H), 5.43 (t, ^3J = 6.8 Hz, 1H), 6.36 (*virt.* q, $^3J \cong {}^4J$ = 2.5 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 300 K): δ = 18.3 (q), 22.2 (t), 25.9 (q), 33.2 (t), 66.7 (t), 119.1 (d), 127.6 (d), 138.7 (s), 156.6 (s), 202.9 (s). IR (ATR): $\tilde{\nu}$ = 2924 (w), 1715 (vs), 1623 (s), 1449 (w), 1342 (w), 1275 (w), 1110 (s), 1026 (w), 964 (w), 782 (m). MS (EI, 70 eV): *m/z* (%) = 166 (59), 148 (21), 120 (11), 110 (23), 106 (28), 99 (100). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{10}H_{14}O_2$: 166.0988; Found: 166.0983, $[M]^+$ Calcd. for $C_9{}^{13}C_1H_{14}O_2$: 167.1022; Found: 167.1021. UV/vis (CH_2Cl_2, c = 0.5 mM): λ = 250 nm (ε = 5976 cm^{-1} M^{-1}).

3-Methyl-2-[(3-methylbut-2-en-1-yl)oxy]cyclopent-2-en-1-one (3f)

According to general procedure 4, compound **3f**[26] was synthesized starting from **4f** (500 mg, 4.46 mmol, 1.0 equiv.), 3,3-dimethylallyl bromide (620 µL, 800 mg, 5.35 mmol, 1.2 equiv.) and K_2CO_3 (750 mg, 5.42 mmol, 1.2 equiv.). Purification by flash column chromatography (SiO_2, P/Et_2O = 9/1, UV) afforded the product (558 mg, 3.09 mmol, 69%) as a colorless oil. TLC (P/Et_2O = 3/1): R_f = 0.26 [UV, $KMnO_4$]. ^{1}H NMR (300 MHz, C_6D_6, 300 K): δ = 1.55 (dd, ^4J = 1.4, 0.8 Hz, 6H), 1.60 – 1.62 (m, 3H), 1.63 – 1.67 (m, 2H), 1.82 – 1.99 (m, 2H), 4.97 (*virt.*

dquint., ^3J = 7.1 Hz, $^4J \cong {}^4J$ = 0.9 Hz, 2H), 5.52 (*virt.* ddquint., ^3J = 8.4, 5.6 Hz, $^4J \cong {}^4J$ = 1.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 300 K): δ = 14.5 (q), 18.0 (q), 25.8 (q), 33.1 (t), 66.4 (t), 121.9 (d), 137.4 (s), 152.2 (s), 152.7 (s), 201.8 (s). IR (ATR): $\tilde{\nu}$ = 2915 (w), 1700 (vs), 1645 (m), 1443 (w), 1390 (m), 1338 (m), 1205 (m), 1092 (s), 969 (m), 905 (m). MS (EI, 70 eV): *m/z* (%) = 112 (90), 84 (32), 69 (100), 53 (9), 41 (74). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{11}H_{16}O_2$: 180.1145; Found: 180.1143. UV/vis (CH_2Cl_2, *c* = 0.5 mM): λ = 247 nm (ε = 9532 cm^{-1} M^{-1}).

3-Ethoxy-5,5-dimethylcyclohex-2-en-1-one

According to a modified literature procedure:[21] To a solution of dimedone (2.10 g, 15.0 mmol, 1.0 equiv.) in 46 mL dry toluene were added EtOH (3.56 mL, 2.80 g, 61.0 mmol, 4.0 equiv.) and *p*-TsOH·H_2O (139 mg, 0.73 mmol, 5.0 mol%). The reaction mixture was heated at reflux using a water separator for 90 min at which point EtOH (3.00 mL, 2.37 g, 50.3 mmol, 3.4 equiv.) was added. Subsequently, the solution was refluxed for additional 14 h. It was allowed to cool to room temperature and the solvent was removed under reduced pressure. The crude product was then filtered over a short plug of Al_2O_3 (Et_2O, UV) and the product (2.52 g, 15.0 mmol, 100%) was obtained as a pale yellow oil. TLC (P/Et_2O = 3/1): R_f = 0.17 [UV, $KMnO_4$]. ^1H NMR (300 MHz, $CDCl_3$, 300 K): δ = 1.07 (s, 6H), 1.36 (t, ^3J = 7.0 Hz, 3H), 2.21 (s, 2H), 2.27 (s, 2H), 3.90 (q, ^3J = 7.0 Hz, 2H), 5.35 (s, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 300 K): δ = 14.3 (q), 28.4 (q), 32.6 (t), 43.1 (t), 50.8 (t), 64.4 (t), 101.6 (d), 176.5 (s), 199.8 (s). Data of this compound were in accordance to the literature.[21]

5,5-Dimethylcyclohex-2-en-1-one

According to a modified literature procedure:[21] To an ice-cooled suspension of $LiAlH_4$ (138 mg, 3.63 mmol, 0.4 equiv.) in 4.0 mL dry THF a solution of **S1** (1.50 g, 8.92 mmol, 1.0 equiv.) in

7.5 mL dry THF was added dropwise. Subsequently, the reaction mixture was allowed to warm to room temperature and stirred for 3 h. The reaction mixture was then cooled to 0 °C and quenched by the addition of MeOH (approx. 10 mL) until no further gas evolution was observed. After addition of 14 mL 1 M HCl the reaction mixture was stirred for 30 min, the layers were separated and the aqueous layer was extracted with Et_2O (3 × 30 mL). The combined organic layers were washed with brine (2 × 60 mL), dried over Na_2SO_4, filtrated and the solvent was removed under reduced pressure. After purification by flash column chromatography (SiO_2, P/Et_2O = 8/1, UV) the product (663 mg, 5.34 mmol, 60%) was obtained as a colorless oil. TLC (P/Et_2O = 1/1): R_f = 0.29 [UV, $KMnO_4$]. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 1.05 (s, 6H, CH_3), 2.24 (dd, ^3J = 4.1 Hz, ^4J = 2.1 Hz, 2H, H-4), 2.27 (s, 2H, H-6), 6.02 (dt, ^3J = 10.1 Hz, ^4J = 2.1 Hz, 1H, H-2), 6.86 (dt, ^3J = 10.1, 4.1 Hz, 1H, H3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 300 K): δ = 28.5 (q), 34.0 (s), 40.0 (t), 51.9 (t), 129.1 (d), 148.5 (d), 200.1 (s). Data of this compound were in accordance to the literature.[21]

(1*SR*,6*SR*)-4,4-Dimethyl-7-oxabicyclo[4.1.0]heptan-2-one (4c)

According to a modified literature procedure:[27] To an ice-cooled solution of 5,5-dimethylcyclohex-2-en-1-one[21] (990 mg, 7.97 mmol, 1.0 equiv.) in 16 mL MeOH were dropwise added H_2O_2 (30 wt%, 3.30 mL, 1.10 g, 32.3 mmol, 4.1 equiv.) and 6M NaOH (0.64 mL, 154 mg, 3.84 mmol, 0.5 equiv.). The reaction mixture was allowed to warm to room temperature and stirred for 2 h. Subsequently, the reaction mixture was diluted with 32 mL CH_2Cl_2 and H_2O was added until proper phase separation was achieved. The aqueous layer was extracted with CH_2Cl_2 (3× 30 mL). The combined organic layers were washed with brine (2 × 80 mL), dried over Na_2SO_4, filtrated and the solvent was removed under reduced pressure. After purification by flash column chromatography (SiO_2, P/Et_2O = 2/1, $KMnO_4$) the product (901 mg, 6.43 mmol, 80%)

was obtained as a colorless oil. TLC (P/Et_2O = 2/1): R_f = 0.56 [$KMnO_4$]. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 0.92 (s, 3H), 1.06 (s, 3H), 1.74 – 1.89 (m, 2H), 2.04 (d, ^2J = 14.3 Hz, 1H), 2.66 (d, ^2J = 14.3 Hz, 1H), 3.21 (*virt.* dt ^3J = 3.8 Hz, $^3J \cong {}^3J$ = 1.0 Hz, 1H), 3.51 (dd, ^3J = 3.8, 4.7 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 300 K): δ = 28.2 (q), 31.2 (q), 37.4 (t), 37.5 (t), 48.8 (s), 54.9 (d), 57.2 (d), 207.6 (s). Data of this compound were in accordance with the literature.[27]

(1*SR*,6*SR*)-5,5-Dimethyl-7-oxabicyclo[4.1.0]heptan-2-one (4d)

According to a modified literature procedure:[27] To an ice-cooled solution of 4,4-dimethylcyclohex-2-en-1-one (2.00 g, 16.1 mmol, 1.0 equiv.) in 32 mL MeOH were dropwise added H_2O_2 (30 wt%, 8.23 mL, 80.5 mmol, 5.0 equiv.) and 6M NaOH (1.33 mL, 8.05 mmol, 0.5 equiv.). The reaction mixture was allowed to warm to room temperature and stirred for 3.5 h. Subsequently, the reaction mixture was diluted with 60 mL CH_2Cl_2 and H_2O was added until proper phase separation was achieved. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 60 mL). The combined organic layers were washed with brine (1 × 120 mL), dried over Na_2SO_4, filtrated and the solvent was removed under reduced pressure. After purification by flash column chromatography (SiO_2, P/Et_2O = 6/1, $KMnO_4$) the product (1.67 g, 11.9 mmol, 74%) was obtained as a colorless oil. TLC (P/Et_2O = 2/1): R_f = 0.68 [$KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 1.06 (s, 3H), 1.22 (s, 3H), 1.34 (dddd, ^2J = 13.7 Hz, ^3J = 7.1, 3.0 Hz, ^4J = 1.3 Hz, 1H), 1.90 (ddd, ^2J = 13.7 Hz, ^3J = 11.7, 6.4 Hz, 1H), 2.19 (ddd, ^2J = 18.9 Hz, ^3J = 11.7, 7.0 Hz, 1H), 2.40 (ddd, ^2J = 18.9 Hz, ^3J = 6.4, 3.0 Hz, 1H), 3.18 (dd, ^3J = 4.0 Hz, ^4J = 1.3 Hz, 1H), 3.23 (d, ^3J = 4.0 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 300 K): δ = 23.1 (q), 27.6 (q), 29.9 (t), 30.9 (s), 33.3 (t), 56.1 (d), 64.3 (d), 206.2 (s). Data of this compound were in accordance with the literature.[28]

General procedure 5 (Irradiation): Thioxanthone **5** (10 mol%) was dissolved in 1.0 mL dry degassed CH_2Cl_2 and transferred to a flame dried Duran phototube. The respective 2-(2'-alkenyloxy)cycloalk-2-enone (1.0 equiv.) dissolved in 1.0 mL dry degassed CH_2Cl_2 was then added and the reaction mixture was diluted with dry degassed CH_2Cl_2 until a concentration of 10 mM (relative to the substrate) was reached. The reaction mixture was irradiated at room temperature in a previously described irradiation set-up[21] (λ = 420 nm, for details about the light source, see the SI). Irradiation was continued until full conversion was reached and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (P/Et_2O).

(3*RS*,3a*SR*,7a*SR*)-Hexahydro-7*H*-3,7a-methanobenzofuran-7-one (8a)

According to general procedure 5, compound **8a** was synthesized starting from **1a** (15.6 mg, 103 µmol, 1.0 equiv.) and thioxanthone **5** (2.21 mg, 10.4 µmol, 10 mol%) over 2.5 h. Purification by flash column chromatography (SiO_2, P/Et_2O = 1/2, $KMnO_4$) afforded the product (11.2 mg, 73.6 µmol, 73%) as a colorless solid. The reaction on 1 mmol scale was performed with 152 mg **1a** (1.00 mmol, 1.0 equiv.) and 5.30 mg **5** (25.0 µmol, 2.5 mol%) in 40 mL CH_2Cl_2 (25 mM, irradiation time: 5 h). The yield was 138 mg (0.91 mmol, 91%). Mp 59 – 65 °C. TLC (P/Et_2O = 1/2): R_f = 0.11 [$KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 1.64 – 1.78 (m, 1H), 1.81 – 1.96 (m, 2H), 2.03 – 2.18 (m, 2H), 2.30 (ddd, ^3J = 11.0, 7.8, 6.4 Hz, 1H), 2.35 – 2.44 (m, 2H), 2.84 (dd, ^2J = 8.1 Hz, ^3J = 3.0 Hz, 1H), 2.88 (d, ^3J = 3.0 Hz, 1H), 3.85 (d, ^3J = 6.0 Hz, 1H), 3.94 (d, ^3J = 6.0 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 300 K): δ = 25.4 (t), 27.3 (t), 40.1 (t), 41.6 (t), 42.0 (d), 55.4 (d), 70.8 (t), 88.6 (s), 203.6 (s). Data of this compound were in accordance with the literature.[6b]

(3*RS*,3a*SR*,7a*SR*)-3a-Methylhexahydro-7*H*-3,7a-methanobenzofuran-7-one (8b)

According to general procedure 5, compound **8b** was synthesized starting from **1b** (16.8 mg, 101 µmol, 1.0 equiv.) and thioxanthone **5** (2.19 mg, 10.3 µmol, 10 mol%) over 2 h. Purification by flash column chromatography (SiO_2, P/Et_2O = 1/2, $KMnO_4$) afforded the product (15.2 mg, 91.2 µmol, 91%) as a colorless solid. Mp 38 – 47 °C. TLC (P/Et_2O = 1/2): R_f = 0.04 [$KMnO_4$]. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 0.99 (s, 3H), 1.76 (d, ^2J = 8.2 Hz), 1.84 (ddt, ^2J = 14.1 Hz, ^3J = 4.2 Hz, ^4J = 1.9 Hz, 1H), 2.00 (*virt.* qt, $^2J \cong {}^3J$ = 13.9 Hz, ^3J = 4.2 Hz, 1H), 2.08 – 2.18 (m, 1H), 2.28 (*virt.* td, $^2J \cong {}^3J$ = 14.1 Hz, ^3J = 4.3 Hz, 1H), 2.36 (ddt, ^2J = 14.5 Hz, ^3J = 4.1 Hz, ^4J = 1.9 Hz, 1H), 2.49 (td, ^2J = 14.5 Hz, ^3J = 5.8 Hz, 1H), 2.72 (d, ^3J = 3.0 Hz, 1H), 2.84 (dd, ^2J = 8.2 Hz, ^3J = 3.0 Hz, 1H), 3.86 (d, ^2J = 6.7 Hz, 1H), 3.92 (d, ^2J = 6.7 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 300 K): δ = 15.8 (q), 25.7 (t), 31.8 (t), 40.1 (t), 40.8 (t), 44.6 (d), 56.0 (s), 68.5 (t), 89.9 (s), 204.0 (s). IR (ATR): $\tilde{\nu}$ = 2925 (m), 1713 (s), 1458 (w), 1123 (w), 1043 (w), 945 (w), 862 (w). MS (EI, 70 eV): *m/z* (%) =166 (100), 163 (21), 149 (39), 123 (35), 109 (62), 95 (44), 81 (100). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{10}H_{14}O_2$: 166.0988; Found: 166.0982.

(3*RS*,3a*SR*,7a*SR*)-5,5-Dimethylhexahydro-7*H*-3,7a-methanobenzofuran-7-one (8c)

According to general procedure 5, compound **8c** was synthesized starting from **1c** (36.2 mg, 201 µmol, 1.0 equiv.) and thioxanthone **5** (4.34 mg, 20.4 µmol, 10 mol%) over 2.5 h. Purification by flash column chromatography (SiO_2, P/Et_2O = 3/1 → 1/1, $KMnO_4$) afforded the product (36.2 mg, 201 µmol, 100%) as a colorless solid. Mp 73 – 74 °C. TLC (P/Et_2O = 1/1): R_f = 0.14 [$KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 0.89 (s, 3H), 1.11 (s, 3H), 1.76 – 1.91 (m, 3H), 2.06 (dd, ^2J = 14.2 Hz, ^4J = 2.3 Hz, 1H), 2.34 – 2.45 (m, 2H), 2.81 (ddd, ^2J = 8.2 Hz,

^3J = 3.1 Hz, ^4J = 1.1 Hz, 1H), 2.84 (d, ^3J = 3.1 Hz, 1H), 3.90 (d, ^2J = 6.0 Hz, 1H), 3.97 (d, ^2J = 6.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 300 K): δ = 25.5 (q), 31.4 (q), 38.2 (t), 39.9 (s), 41.0 (t), 41.3 (d), 52.8 (d), 53.1 (t), 71.6 (t), 88.5 (s), 203.4 (s). Data of this compound were in accordance with the literature.[6b]

(3*RS*,3a*SR*,7a*SR*)-3-Methylhexahydro-7*H*-3,7a-methanobenzofuran-7-one (9a)

According to general procedure 5, compound **9a** was synthesized starting from **2a** (16.8 mg, 100 µmol, 1.0 equiv.) and thioxanthone **5** (2.24 mg, 10.6 µmol, 10 mol%) over 3 h. Purification by flash column chromatography (SiO_2, P/Et_2O = 1/2, $KMnO_4$) afforded the product (15.3 mg, 92.0 µmol, 91%) as a colorless oil. TLC (P/Et_2O = 1/2): R_f = 0.15 [$KMnO_4$]. ^1H NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 1.25 (s, 3H), 1.66 – 1.82 (m, 2H), 1.88 (*virt.* t, $^2J \cong {}^4J$ = 7.9 Hz, 1H), 1.95 – 2.04 (m, 1H), 2.14 (ddt, ^2J = 10.7 Hz, ^3J = 6.0, 2.9 Hz, 1H), 2.24 (*virt.* qd, $^3J \cong {}^3J$ = 7.7 Hz, ^4J = 3.7 Hz, 1H), 2.31 – 2.44 (m, 2H), 2.59 (d, ^2J = 7.9 Hz, 1H), 3.64 (dd, ^2J = 5.9 Hz, ^4J = 1.2 Hz, 1H), 3.74 (d, ^2J = 5.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 300 K): δ [ppm] = 12.8 (q), 23.6 (t), 27.1 (t), 40.1 (t), 45.4 (t), 49.1 (s), 57.4 (d), 75.4 (t), 87.2 (s), 204.2 (s). Data of this compound were in accordance with the literature.[6b]

(3*RS*,3a*SR*,7a*SR*)-3,3a-Dimethylhexahydro-7*H*-3,7a-methanobenzofuran-7-one (9b)

According to general procedure 5, compound **9b** was synthesized starting from **2b** (18.2 mg, 101 µmol, 1.0 equiv.) and thioxanthone **5** (2.14 mg, 10.1 µmol, 10 mol%) over 5 h. Purification by flash column chromatography (SiO_2, P/Et_2O = 1/2, $KMnO_4$) afforded the product (15.9 mg, 88.3 µmol, 88%) as a colorless solid. The reaction on 1 mmol scale was performed with 180 mg **2b** (1.00 mmol, 1.0 equiv.) and 5.40 mg **5** (25.0 µmol, 2.5 mol%) in 40 mL CH_2Cl_2 (25 mM,

irradiation time: 9 h). The yield was 169 mg (0.94 mmol, 94%). Mp 67 – 70 °C. TLC (P/Et_2O = 1/2): R_f = 0.08 [$KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 0.90 (s, 3H), 1.14 (s, 3H), 1.65 (ddt, ^2J = 13.5 Hz, ^3J = 3.9 Hz, ^4J = 1.8 Hz, 1H), 1.78 (d, ^2J = 8.2 Hz, 1H), 1.92 – 2.06 (m, 1H), 2.07 – 2.20 (m, 2H), 2.28 – 2.36 (m, 1H), 2.38 – 2.51 (m, 1H), 2.62 (d, ^2J = 8.2 Hz, 1H), 3.61 (d, ^2J = 6.5 Hz, 1H), 3.66 (dd, ^2J = 6.5 Hz, ^4J = 1.4 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 300 K): δ = 10.5 (q), 13.8 (q), 25.6 (t), 29.9 (t), 40.0 (t), 45.4 (t), 50.6 (s), 57.0 (s), 72.9 (t), 89.4 (s), 204.5 (s). IR (ATR): $\tilde{\nu}$ = 2922 (s), 1714 (vs), 1456 (w), 1385 (w), 1245 (w), 949 (w). MS (EI, 70 eV): *m/z* (%) = 180 (6), 165 (48), 135 (54), 125 (78), 110 (49), 97 (100), 83 (71). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{11}H_{16}O_2$: 180.1145; Found: 180.1145.

(3*RS*,3a*SR*,7a*SR*)-3,5,5-Trimethylhexahydro-7*H*-3,7a-methanobenzofuran-7-one (9c)

According to general procedure 5, compound **9c** was synthesized starting from **2c** (38.9 mg, 200 µmol, 1.0 equiv.) and thioxanthone **5** (4.36 mg, 20.5 µmol, 10 mol%) over 2.5 h. Purification by flash column chromatography (SiO_2, P/Et_2O = 1/1, $KMnO_4$) afforded the product (35.1 mg, 181 µmol, 90%) as a colorless solid. The reaction on 1 mmol scale was performed with 194 mg **2c** (1.00 mmol, 1.0 equiv.) and 5.30 mg **5** (25.0 µmol, 2.5 mol%) in 40 mL CH_2Cl_2 (25 mM, irradiation time: 4.5 h). The yield was 178 mg (0.92 mmol, 92%). Mp 65 – 67 °C. TLC (P/Et_2O = 1/1): R_f = 0.19 [$KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 0.90 (s, 3H), 1.12 (s, 3H), 1.23 (s, 3H), 1.68 (ddd, ^2J = 14.0 Hz, ^3J = 7.0 Hz, ^4J = 2.3 Hz, 1H), 1.75 (dd, ^2J = 14.0 Hz, ^3J = 11.1 Hz, 1H), 1.88 (*virt.* t, $^2J \cong {}^4J$ = 7.9 Hz, 1H), 2.05 (dd, ^2J = 14.2 Hz, ^4J = 2.3 Hz, 1H), 2.28 – 2.41 (m, 2H), 2.56 (dd, ^2J = 8.0 Hz, ^4J = 1.2 Hz, 1H), 3.68 (dd, ^2J = 5.9 Hz, ^4J = 1.2 Hz, 1H), 3.76 (d, ^2J = 5.9 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 300 K): δ = 12.8 (q), 25.7 (q), 31.4 (q), 36.4 (t), 39.9 (s), 44.7 (t), 48.4 (s), 53.0 (t), 54.7 (d), 76.1 (t),

87.1 (s), 204.0 (s). IR (ATR): $\tilde{\nu}$ = 2954 (m), 1714 (vs), 1468 (w), 1245 (w), 1163 (w), 1082 (w), 964 (s). MS (EI, 70 eV): *m/z* (%) = 194 (25), 179 (9), 151 (16), 124 (10), 109 (100), 95 (16), 83 (15). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{12}H_{18}O_2$: 194.1301; Found: 194.1301.

(3*RS*,3a*SR*,7a*SR*)-3,4,4-Trimethylhexahydro-7*H*-3,7a-methanobenzofuran-7-one (9d)

According to general procedure 5, compound **9d** was synthesized starting from **2d** (11.0 mg, 56.6 µmol, 1.0 equiv.) and thioxanthone **5** (1.20 mg, 5.66 µmol, 10 mol%) over 7.5 h. Purification by flash column chromatography (SiO_2, P/Et_2O = 3/1 → 1/1, $KMnO_4$) afforded the product (4.20 mg, 21.6 µmol, 38%) as a colorless oil. TLC (P/Et_2O = 1/1): R_f = 0.14 [$KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 1.17 (s, 3H), 1.32 – 1.41 (m, 6H), 1.66 – 1.75 (m, 2H), 1.88 (*virt.* t, $^2J \cong {}^4J$ = 8.4 Hz, 1H), 2.01 (d, ^4J = 8.5 Hz, 1H), 2.31 (dt, ^2J = 16.2 Hz, ^3J = 4.2 Hz, 1H), 2.50 (ddd, ^2J = 16.2 Hz, ^3J = 10.2, 7.4 Hz, 1H), 2.76 (dd, ^2J = 8.1 Hz, ^4J = 1.2 Hz, 1H), 3.61 (dd, ^2J = 5.9 Hz, ^4J = 1.2 Hz, 1H), 3.64 (d, ^2J = 5.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 300 K): δ = 13.6 (q), 24.0 (q), 32.9 (s), 33.7 (q), 37.0 (t), 41.4 (t), 45.9 (t), 49.7 (s), 65.0 (d), 76.8 (t), 86.3 (s), 205.1 (s). IR (ATR): $\tilde{\nu}$ = 2954 (m), 1719 (vs), 1458 (w), 1062 (m), 948 (w). MS (EI, 70 eV): *m/z* (%) = 194 (8), 179 (33), 164 (19), 149 (34), 138 (100), 125 (38), 109 (36), 97 (34), 81 (43). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{12}H_{18}O_2$: 194.1301; Found: 194.1298.

(3*RS*,3a*SR*,6a*SR*)-3-Methyltetrahydro-3,6a-methanocyclopenta[*b*]furan-6(2*H*)-one (9e)

According to general procedure 5, compound **9e** was synthesized starting from **2e** (30.7 mg, 202 µmol, 1.0 equiv.) and thioxanthone **5** (4.26 mg, 20.1 µmol, 10 mol%) over 19 h. Purification by flash column chromatography (SiO_2, P/Et_2O = 3/1, $KMnO_4$) afforded the product (10.4 mg, 68.3 µmol, 34%) as a colorless oil. TLC (P/Et_2O = 3/1): R_f = 0.07 [$KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 1.29 (s, 3H), 1.95 (*virt.* t, $^2J \cong {}^4J$ = 8.2 Hz, 1H), 2.02 (ddd, ^3J = 9.2, 7.7,

5.8 Hz, 2H), 2.48 (*virt.* q, $^3J \cong {}^3J$ = 8.3 Hz, 1H), 2.57 (dt, ^2J = 19.2 Hz, ^3J = 9.2 Hz, 1H), 2.62 – 2.73 (m, 2H), 4.04 (dd, ^2J = 6.2 Hz, ^4J = 1.3 Hz, 1H), 4.08 (d, ^2J = 6.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 300 K): δ = 13.8 (q), 16.9 (t), 41.3 (t), 44.2 (t), 49.0 (s), 51.3 (d), 83.1 (t), 93.0 (s), 206.3 (s). IR (ATR): $\tilde{\nu}$ = 2956 (w), 1737 (vs), 1451 (w), 1238 (w), 1038 (m), 1006 (m), 975 (s), 919 (m), 894 (m). MS (EI, 70 eV): *m/z* (%) = 151 (6), 137 (36), 123 (13), 110 (100), 96 (70), 81 (92). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_9H_{12}O_2$: 152.0832; Found: 152.0828.

(*E*/*Z*)-2-(But-2-en-1-yloxy)cyclohex-2-en-1-one (*E*-10/*Z*-10)

According to general procedure 1, compound ***E*-10/*Z*-10**[29] was synthesized starting from **4a** (1.00 g, 8.92 mmol, 1.0 equiv.), crotyl alcohol (*E*/*Z* = 1/1) (3.00 mL, 2.55 g, 35.4 mmol, 4.0 equiv.) and *p*-TsOH·H_2O (51.7 mg, 272 µmol, 3.0 mol%). Purification by flash column chromatography (SiO_2, P/Et_2O = 3/1, UV) afforded the product (510 mg, 3.07 mmol, 34%) as a colorless oil. TLC (P/Et_2O = 3/1): R_f = 0.14 [UV, $KMnO_4$]. ^1H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.72 (dd, ^3J = 6.3 Hz, ^4J = 1.1 Hz, 3H), 1.96 (*virt.* quint. $^3J \cong {}^3J$ = 6.2 Hz, 2H), 2.41 (*virt.* td, $^3J \cong {}^3J$ = 5.9 Hz, ^3J = 4.6 Hz, 2H), 2.50 (dd, ^3J = 7.4, 6.0 Hz, 2H), 4.20 (d, ^3J = 6.3 Hz, 2H), 5.62 – 5.71 (m, 1H), 5.71 – 5.83 (m, 1H), 5.88 (t, ^3J = 4.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 300 K): δ = 17.9 (q), 23.1(t), 24.7 (t), 39.0 (t), 68.6 (t), 118.1 (d), 125.9 (d), 130.9 (d), 150.6 (s), 194.5 (s). IR (ATR): $\tilde{\nu}$ = 2939 (w), 1686 (vs), 1622 (m), 1439 (w), 1365 (w), 1259 (m), 1185 (s), 1149 (vs), 1006 (m), 965 (s), 872 (w). MS (EI, 70 eV): *m/z* (%) = 166 (21), 112 (100), 95 (6), 84 (32). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{10}H_{14}O_2$: 166.0988; Found:166.0988, $[M]^+$ Calcd. for $C_9{}^{13}C_1H_{14}O_2$: 167.1022; Found: 167.1025. UV/vis (CH_2Cl_2, *c* = 0.5 mM): λ = 260 nm (ε = 4882 cm^{-1} M^{-1}).

(3*RS*,3a*SR*,7a*SR*,8*SR*)-8-Methylhexahydro-7*H*-3,7a-methanobenzofuran-7-one (11)

In analogy to general procedure 5, compound **11** was synthesized starting from *E*-**10**/*Z*-**10** (16.6 mg, 100 µmol, 1.0 equiv.) and thioxanthone **5** (2.15 mg, 10.1 µmol, 10 mol%) over 4.5 h. The solvent was removed under reduced pressure and the residue redissolved in 1.0 mL CH_2Cl_2 and dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate (5.30 mg, 26.7 µmol, 0.27 equiv.) was added.[21] The reaction mixture was stirred at room temperature for 4.5 h and the solvent was removed under reduced pressure. Purification by flash column chromatography (SiO_2, P/Et_2O = 1/2, $KMnO_4$) afforded the product (13.0 mg, 78.2 µmol, 78%) as a colorless solid. Mp 48 – 53 °C. TLC (P/Et_2O = 1/2): R_f = 0.21 [$KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 0.91 (d, ^3J = 6.4 Hz, 3H), 1.62 – 1.76 (m, 1H), 1.91 (*virt.* tdd, $^2J \cong {}^3J$ = 14.2 Hz, ^3J = 11.0 Hz, ^3J = 3.7 Hz, 1H), 2.00 – 2.07 (m, 1H), 2.11 (ddd, ^2J = 13.4 Hz, ^3J = 6.7, 3.6 Hz, 1H), 2.21 (dd, ^3J = 11.0, 6.7 Hz, 1H), 2.28 – 2.41 (m, 2H), 2.65 (d, ^3J = 2.9 Hz, 1H), 3.06 (qd, ^3J = 6.4 Hz, 2.9 Hz, 1H), 3.76 (d, ^2J = 6.5 Hz, 1H), 3.88 (d, ^2J = 6.5 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 300 K): δ = 9.7 (q), 24.4 (t), 27.1 (t), 40.1 (t), 44.4 (d), 45.0 (d), 52.7 (d), 67.5 (t), 89.1 (s), 203.8 (s). IR (ATR): $\tilde{\nu}$ = 2946 (m), 1710 (vs), 1451 (w), 1320 (w), 1094 (m), 994 (m), 930 (m), 848 (m). MS (EI, 70 eV): *m/z* (%) = 166 (20), 151 (4), 138 (5), 123 (5), 112 (100), 109 (15), 95 (11), 84 (41). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{10}H_{14}O_2$: 166.0988; Found: 166.0982.

(*E*)-2-(Pent-2-en-1-yloxy)cyclohex-2-en-1-one (*E*-12)

According to general procedure 1, compound *E*-**12** was synthesized starting from **4a** (250 mg, 2.23 mmol, 1.0 equiv.), (*E*)-pent-2-en-1-ol (0.90 mL, 770 mg, 8.92 mmol, 4.0 equiv.) and *p*-TsOH·H_2O (12.7 mg, 70.0 µmol, 3.0 mol%). Purification by flash column chromatography (SiO_2, P/Et_2O = 6/1 → 3/1, P/Et_2O = 6/1, UV) afforded the product (152 mg, 840 µmol, 38%) as a colorless oil. TLC (P/Et_2O = 3/1): R_f = 0.18 [UV, $KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 1.00 (t, ^3J = 7.5 Hz, 3H), 1.96 (dt, ^2J = 12.4 Hz, ^3J = 6.0 Hz, 2H), 2.02 – 2.13 (m,

2H), 2.41 (*virt.* td, $^3J \cong {}^3J$ = 6.0 Hz, ^3J = 4.6 Hz, 2H), 2.50 (dd, ^3J = 7.4, 6.0 Hz, 2H), 4.22 (dd, ^3J = 6.3 Hz, ^4J = 1.4 Hz, 2H), 5.64 (dtt, ^3J = 15.5, 6.3 Hz, ^4J = 1.6 Hz, 1H), 5.75 – 5.85 (m, 1H), 5.88 (t, ^3J = 4.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 300 K): δ = 13.3 (q), 23.1 (t), 24.7 (t), 25.5 (t), 39.0 (t), 68.7 (t), 118.2 (d), 123.5 (d), 137.6 (d), 150.5 (s), 194.6 (s). IR (ATR): $\tilde{\nu}$ = 2933 (w), 1686 (vs), 1623 (m), 1458 (w), 1365 (w), 1259 (m), 1185 (s), 1149 (vs), 1123 (s), 1007 (m), 967 (s), 880 (w). MS (EI, 70 eV): *m/z* (%) = 180 (11), 145 (93), 129 (11), 113 (16), 99 (100), 83 (23). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{11}H_{16}O_2$: 180.1145; Found: 180.1143. UV/vis (CH_2Cl_2, *c* = 0.5 mM): λ = 260 nm (ε = 4760 cm^{-1} M^{-1}).

(*Z*)-1-Bromopent-2-ene[30]

(*Z*)-Pent-2-en-1-ol (0.81 mL, 689 mg, 8.00 mmol, 1.0 equiv.) was dissolved in 16 mL dry Et_2O and cooled to 0 °C. PBr_3 (0.90 mL, 2.60 g, 9.60 mmol, 1.2 equiv.) was added dropwise, the reaction mixture was allowed to warm to room temperature and stirred for 4 h. The reaction was quenched by addition of 20 mL of H_2O and the layers were separated. The organic layer was washed with $NaHCO_3$ (1 × 20 mL), H_2O (1 × 20 mL) and brine (1 × 20 mL), dried over Na_2SO_4, filtrated and the solvent was removed under reduced pressure. After purification by flash column chromatography (SiO_2, P) the product (119 mg, 0.80 mmol, 10%) was obtained as a colorless oil. TLC (P): R_f = 0.67 [UV, $KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 1.03 (t, ^3J = 7.5 Hz, 3H), 2.16 (*virt.* quint.d $^3J \cong {}^3J$ = 7.5 Hz, ^4J = 1.5 Hz, 2H), 4.00 (dd, ^3J = 8.3 Hz, ^4J = 0.7 Hz, 2H), 5.60 (dt, ^3J = 10.6, 7.4 Hz, 1H), 5.70 (m, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 300 K): δ = 13.9 (q), 20.4 (t), 27.4 (t), 124.8 (d), 137.7 (d). Data of this compound were in accordance to the literature.[30]

(*Z*)-2-(Pent-2-en-1-yloxy)cyclohex-2-en-1-one (*Z*-12)

According to general procedure 2, compound *Z*-**12** was synthesized starting from **4a** (520 mg, 4.64 mmol, 1.0 equiv.), (*Z*)-1-bromopent-2-ene (830 mg, 5.57 mmol, 1.2 equiv.) and K_2CO_3 (0.770 mg, 5.57 mmol, 1.2 equiv.). Purification by flash column chromatography (SiO_2, P/Et_2O = 3/1, H/EtOAc = 24/1 → 7/3 → 0/1 UV) afforded the product (133 mg, 737 µmol, 17%) as a colorless oil. TLC (P/Et_2O = 3/1): R_f = 0.19 [UV, $KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 0.99 (t, ^3J = 7.5 Hz, 3H), 1.89 – 2.03 (m, 2H), 2.03 – 2.15 (m, 2H), 2.42 (*virt.* td, $^3J \cong {}^3J$ = 6.0 Hz, ^3J = 4.6 Hz, 2H), 2.51 (dd, ^3J = 7.5, 6.0 Hz, 2H), 4.36 (d, ^3J = 5.1 Hz, 2H), 5.43 – 5.67 (m, 2H), 5.87 (t, ^3J = 4.6 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 300 K): δ = 14.2 (q), 21.3 (t), 23.1 (t), 24.7 (t), 39.0 (t), 63.8 (t), 118.2 (d), 124.0 (d), 135.7 (d), 150.5 (s), 194.6

(s). IR (ATR): $\tilde{\nu}$ = 2933 (w), 1687 (vs), 1622 (m), 1457 (w), 1374 (w), 1259 (m), 1185 (m), 1149 (vs), 1123 (s), 1007 (m), 873 (w). MS (EI, 70 eV): *m/z* (%) = 180 (17), 145 (58), 129 (11), 113 (100), 99 (87), 84 (40). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{11}H_{16}O_2$: 180.1145; Found: 180.1145, $[M]^+$ Calcd. for $C_{10}{}^{13}C_1H_{16}O_2$: 181.1178; Found: 181.1183. UV/vis (CH_2Cl_2, c = 0.5 mM): λ = 259 nm (ε = 3754 cm^{-1} M^{-1}).

(3*RS*,3a*SR*,7a*SR*,8*SR*)-8-Ethylhexahydro-7*H*-3,7a-methanobenzofuran-7-one (13)

According to general procedure 5, compound **13** was synthesized starting from *E*-**12** (18.1 mg, 100 µmol, 1.0 equiv.) and thioxanthone **5** (2.14 mg, 10.2 µmol, 10 mol%) over 2.5 h. Purification by flash column chromatography (SiO_2, P/Et_2O = 2/1 → 1/1, $KMnO_4$) afforded a mixture of product **13** and olefinic by-product **14** (18.1 mg, 100 µmol, 100%, **13**/**14** = 82/18) as a colorless solid.

According to general procedure 5, compound **13** was synthesized starting from *Z*-**12** (18.1 mg, 100 µmol, 1.0 equiv.) and thioxanthone **5** (2.17 mg, 10.1 µmol, 10 mol%) over 2.5 h. Purification by flash column chromatography (SiO_2, P/Et_2O = 1/1, $KMnO_4$) afforded a mixture of product **13** and olefinic by-product **14** (16.3 mg, 90.4 µmol, 90%, **13**/**14** = 83/17) as a colorless solid.

The product mixture (14.2 mg, 78.8 µmol) was dissolved in 500 µL DCE and 400 µLH_2O. Subsequently $RuCl_3 \cdot xH_2O$ (1 small crystal, calc. 0.14 mg, 0.7 µmol, 3.5 mol% relative to by-product) and $NaIO_4$ (18.6 mg, 87.0 µmol, 4.3 equiv.) were added and the reaction mixture was stirred at room temperature for 20 h. The reaction was quenched by addition of 2.0 mL H_2O, diluted with 2.0 mL Et_2O and the layers were separated. The aqueous layer was extracted with Et_2O (3 × 5 mL). The combined organic layers were then washed with H_2O (1 × 10 mL) and brine (1 × 10 mL), dried over Na_2SO_4, filtrated and the solvent was removed under reduced pressure. Purification by flash column chromatography (SiO_2, P/Et_2O = 2/1, $KMnO_4$) afforded

the product (9.80 mg, 54.4 µmol, 69%) as a colorless solid. Mp 58 – 61 °C. TLC (P/Et_2O = 1/2): R_f = 0.16 [$KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 0.79 (t, ^3J = 7.5 Hz, 3H), 1.21 – 1.33 (m, 1H), 1.37 – 1.51 (m, 1H), 1.63 – 1.78 (m, 1H), 1.93 (*virt.* tdd, $^2J \cong {}^3J$ = 14.2 Hz, ^3J = 11.0 Hz, ^3J = 3.8 Hz, 1H), 1.99 – 2.09 (m, 1H), 2.09 – 2.16 (m, 1H), 2.21 (dd, ^3J = 11.0, 6.7 Hz, 1H), 2.31 – 2.43 (m, 2H), 2.71 (d, ^3J = 2.9 Hz, 1H), 2.84 (ddd, ^3J = 8.6, 6.0, 2.9 Hz, 1H), 3.75 (d, ^2J = 6.5 Hz, 1H), 3.85 (d, ^2J = 6.5 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 300 K): δ = 11.4 (q), 17.9 (t), 24.4 (t), 27.3 (t), 40.2 (t), 43.4 (d), 52.4 (d), 52.8 (d), 67.8 (t), 88.9 (s), 204.2 (s). IR (ATR): $\tilde{\nu}$ = 2956 (m), 1713 (vs), 1462 (w), 1327 (w), 1095 (m), 1013 (w), 947 (m), 851 (m). MS (EI, 70 eV): *m/z* (%) = 180 (8), 151 (6), 123 (7), 113 (100), 109 (9), 95 (12), 84 (22). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{10}H_{14}O_2$: 180.1145; Found: 180.1148.

(3*RS*,3a*RS*,7a*RS*)-3-(Prop-1-en-2-yl)hexahydrobenzofuran-7(4*H*)-one (16a)

According to general procedure 5, compound **16a** was synthesized starting from **3a** (18.4 mg, 102 µmol, 1.0 equiv.) and thioxanthone **5** (2.21 mg, 10.4 µmol, 10 mol%) over 4.5 h. Purification by flash column chromatography (SiO_2, P/Et_2O = 1/2, $KMnO_4$) afforded the product (11.9 mg, 66.0 µmol, 65%, d.r. > 95/5) as a colorless oil. TLC (P/Et_2O = 1/2): R_f = 0.05 [$KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 1.46 (*virt.* qd, $^2J \cong {}^3J$ = 12.4 Hz, ^3J = 3.8 Hz, 1H), 1.64 (*virt.* qdd, $^2J \cong {}^3J$ = 12.6 Hz, ^3J = 5.4, 3.8 Hz, 1H), 1.81 (s, 3H), 1.99 – 2.06 (m, 1H), 2.08 – 2.17 (m, 2H), 2.26 (*virt.* tdd, $^2J \cong {}^3J$ = 14.0 Hz, ^3J = 5.4 Hz, ^4J = 1.7 Hz, 1H), 2.36 (*virt.* ddt, ^2J = 14.1 Hz, ^3J = 5.1 Hz, $^3J \cong {}^4J$ = 1.8 Hz, 1H), 2.80 – 2.93 (m, 1H), 4.00 (dd, ^2J = 9.1 Hz, ^3J = 1.7 Hz, 1H), 4.10 (dd, ^2J = 9.1 Hz, ^3J = 6.3 Hz, 1H), 4.15 (dd, ^3J = 12.4 Hz, ^4J = 1.7 Hz, 1H), 4.79-4.81 (m, 1H), 5.03 (*virt.* quint., $^2J \cong {}^4J$ = 1.3 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 300 K): δ = 24.7 (q), 25.9 (t), 27.3 (t), 39.8 (t), 47.5 (d), 50.7 (d), 73.7 (t), 84.0 (d), 112.7 (t), 144.3 (s), 207.8 (s). IR (ATR): $\tilde{\nu}$ = 2929 (m), 1730 (vs), 1449 (w), 1105 (m), 1045 (m), 900 (m). MS (EI, 70 eV): *m/z*

(%) = 180 (73), 165 (8), 136 (21), 123 (17), 107 (100), 93 (46), 81 (29). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{11}H_{16}O_2$: 180.1145; Found: 180.1145, $[M]^+$ Calcd. for $C_{10}{}^{13}C_1H_{16}O_2$: 181.1178; Found: 181.1183.

(3*SR*,3a*RS*,7a*RS*)-3a-Methyl-3-(prop-1-en-2-yl)hexahydrobenzofuran-7(4*H*)-one (16b)

According to general procedure 5, compound **16b** was synthesized starting from **3b** (19.6 mg, 101 µmol, 1.0 equiv.) and thioxanthone **5** (2.16 mg, 10.2 µmol, 10 mol%) over 5 h. Purification by flash column chromatography (SiO_2, P/Et_2O = 2/1, $KMnO_4$) afforded the product (15.4 mg, 79.1 µmol, 79%, d.r. > 95/5) as a colorless solid. Mp 87 – 92 °C. TLC (P/Et_2O = 1/2): R_f = 0.08 [$KMnO_4$]. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 0.97 (s, 3H), 1.66 (*virt.* td, $^2J \cong {}^3J$ = 13.0 Hz, ^3J = 5.4 Hz, 1H), 1.73 – 1.79 (m, 1H), 1.81 (s, 3H), 1.87 – 1.98 (m, 1H), 1.98 – 2.06 (m, 1H), 2.20 – 2.34 (m, 2H), 2.52 (ddd, ^3J = 7.0, 2.1 Hz, ^4J = 0.9 Hz, 1H), 3.95 (dd, ^2J = 9.6 Hz, ^3J = 2.1 Hz, 1H), 4.19 – 4.26 (m, 2H), 4.79-4.81 (m, 1H), 5.07 (*virt.* quint., $^2J \cong {}^4J$ = 1.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 300 K): δ = 20.2 (q), 23.4 (t), 25.5 (q), 30.8 (t), 38.8 (t), 50.6 (s), 55.3 (d), 72.6 (t), 85.3 (d), 112.3 (t), 145.5 (s), 207.8 (s). IR (ATR): $\tilde{\nu}$ = 2924 (s), 1732 (vs), 1455 (w), 1377 (w), 1260 (w), 1104 (w), 1054 (m), 907 (w). MS (EI, 70 eV): *m/z* (%) = 176 (6), 149 (7), 126 (97), 111 (100), 97 (67), 93 (45). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{12}H_{18}O_2$: 194.1301; Found: 194.1299.

(3*RS*,3a*RS*,7a*RS*)-5,5-Dimethyl-3-(prop-1-en-2-yl)hexahydrobenzofuran-7(4*H*)-one (16c)

According to general procedure 5, compound **16c** was synthesized starting from **3c** (24.8 mg, 120 µmol, 1.0 equiv.) and thioxanthone **5** (2.57 mg, 12.1 µmol, 10 mol%) over 1.5 h. Purification by flash column chromatography (SiO_2, P/Et_2O = 3/1, $KMnO_4$) afforded the product (21.2 mg, 102 µmol, 86%, d.r. > 95/5) as a colorless solid. Mp 95 – 101 °C. TLC (P/Et_2O = 3/1): R_f = 0.09

[$KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 0.99 (s, 3H), 1.13 (s, 3H), 1.46 (*virt.* t, $^2J \cong {}^3J$ = 13.0 Hz, 1H), 1.70 (ddd, ^2J = 13.0 Hz, ^3J = 3.2 Hz, ^4J = 2.3 Hz, 1H), 1.81 (dd, ^4J = 1.4, 0.8 Hz, 3H), 2.06 (dd, ^2J = 13.5 Hz, ^4J = 2.3 Hz, 1H), 2.25 (ddd, ^2J = 13.5 Hz, ^4J = 1.7, 0.9 Hz), 2.36 (*virt.* tdd, $^3J \cong {}^3J$ = 12.7 Hz, ^3J = 6.8, 3.2 Hz, 1H), 2.84 (*virt.* t, $^3J \cong {}^3J$ = 6.6 Hz, 1H), 4.03 (dd, ^2J = 9.2 Hz, ^3J = 1.6 Hz, 1H), 4.10 – 4.21 (m, 2H), 4.79-4.81 (m, 1H), 5.06 (*virt.* quint., $^2J \cong {}^4J$ = 1.3 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 300 K): δ = 24.9 (q), 27.2 (q), 32.1 (q), 38.5 (s), 39.0 (t), 46.3 (d), 47.4 (d), 52.9 (t), 74.4 (t), 83.7 (d), 112.7 (t), 144.4 (s), 207.2 (s). IR (ATR): $\tilde{\nu}$ = 2957 (m), 1733 (vs), 1459 (w), 1370 (w), 1126 (w), 1060 (m), 919 (w). MS (EI, 70 eV): *m/z* (%) = 208 (100), 193 (8), 164 (28), 152 (6), 135 (44), 123 (87), 105 (26), 95 (56), 81 (10). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{13}H_{20}O_2$: 208.1458; Found: 208.1458.

(3a*SR*,3b*SR*,6a*RS*,6b*RS*)-6a,6b-Bis(allyloxy)-3a,3b-dimethyloctahydrocyclo-buta[1,2:3,4]-di[5]annulene-1,6-dione (17)

According to general procedure 5, compound **17** was synthesized starting from **1f** (61.7 mg, 405 µmol, 1.0 equiv.) and thioxanthone **5** (8.50 mg, 40.0 µmol, 10 mol%) over 14 h. Purification by flash column chromatography (SiO_2, P/Et_2O = 3/1, $KMnO_4$) afforded the product (7.10 mg, 23.3 µmol, 12%) as a colorless solid. Mp > 220 °C. TLC (P/Et_2O = 3/1): R_f = 0.47 [$KMnO_4$]. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.25 (s, 6H), 1.70 (ddd, ^2J = 14.9 Hz, ^3J = 13.1, 8.8 Hz, 2H), 2.24 – 2.41 (m, 4H), 2.54 – 2.73 (m, 2H), 4.08 (*virt.* ddt, ^2J = 12.8 Hz, ^3J = 5.4 Hz, $^4J \cong {}^4J$ = 1.5 Hz, 2H), 4.18 (*virt.* ddt, ^2J = 12.8 Hz, ^3J = 5.0 Hz, $^4J \cong {}^4J$ = 1.6 Hz, 2H), 5.07 (*virt.* dq, ^3J = 10.5 Hz, $^2J \cong {}^4J$ = 1.6 Hz, 2H), 5.18 (*virt.* dq, ^3J = 17.2 Hz, $^2J \cong {}^4J$ = 1.6 Hz, 2H), 5.71 – 5.89 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 300 K): δ = 19.1 (q), 32.7 (t), 37.2 (t), 44.2 (s), 68.4 (t), 86.1 (s), 116.1 (t), 134.8 (d), 214.2 (s). IR (ATR): $\tilde{\nu}$ = 2964 (w), 1748 (vs), 1451 (w), 1413 (w), 1186 (w), 1089 (m), 1060 (w), 988 (w), 923 (w). MS (EI, 70 eV): *m/z* (%) = 152 (66),

137 (100), 123 (31), 96 (25), 81 (19), 69 (31), 57 (34), 41 (95). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{18}H_{24}O_4$: 304.1669; Found: 304.1660.

(3a*RS*,4a*SR*,6a*SR*,9a*SR*,10a*RS*,12a*RS*)-3a,9a-Dimethyldodecahydro-1*H*,7*H*-cyclopenta[1,4]cyclobuta[1,2-*b*]cyclopenta[1,4]cyclobuta[1,2-*f*][1,5]dioxocine-1,7-dione (18)

According to general procedure 5, compound **18** was synthesized starting from **1f** (61.7 mg, 405 µmol, 1.0 equiv.) and thioxanthone **5** (8.50 mg, 40.0 µmol, 10 mol%) over 14 h. Purification by flash column chromatography (SiO_2, P/Et_2O = 3/1, $KMnO_4$) afforded the product (11.1 mg, 36.5 µmol, 18%) as a colorless solid. Mp >220 °C. TLC (P/Et_2O = 3/1): R_f = 0.30 [$KMnO_4$]. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 1.15 (s, 6H), 1.31 (dd, ^2J = 12.9 Hz, ^3J = 4.6 Hz, 2H), 1.58 – 1.70 (m, 2H), 1.72 – 1.89 (m, 4H), 2.27 – 2.47 (m, 4H), 2.67 (ddd, ^2J = 17.8 Hz, ^3J = 13.1, 8.8 Hz, 2H), 3.74 (dd, ^2J = 12.8 Hz, ^3J = 3.0 Hz, 2H), 4.46 – 4.53 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 300 K): δ = 22.7 (q), 28.9 (t), 34.0 (t), 35.8 (t), 36.0 (d), 44.5 (s), 66.8 (t), 81.3 (s), 220.2 (s). IR (ATR): $\tilde{\nu}$ = 2927 (m), 1735 (vs), 1456 (w), 1266 (w), 1114 (w), 1068 (s), 802 (w). MS (EI, 70 eV): *m/z* (%) = 304 (33), 263 (25), 248 (53), 230 (20), 208 (49), 191 (15), 175 (10), 161 (13), 152 (72), 137 (100), 113 (54), 97 (74), 84 (67), 67 (63), 55 (85), 41 (95). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{18}H_{24}O_4$: 304.1669; Found: 304.1674, $[M]^+$ Calcd. for $C_{17}{}^{13}C_1H_{24}O_4$: 305.1703; Found: 305.1723.

(3a*SR*,3b*SR*,6a*RS*,6b*RS*)-3a,3b-Dimethyl-6a,6b-bis((2-methylallyl)oxy)octahydrocyclobuta[1,2:3,4]di[5]annulene-1,6-dione (19)

According to general procedure 5, compound **19** was synthesized starting from **2f** (66.9 mg, 402 µmol, 1.0 equiv.) and thioxanthone **5** (8.50 mg, 40.0 µmol, 10 mol%) over 3 h. Purification by flash column chromatography (SiO_2, P/Et_2O = 9/1 → 3/1 → 1/1, $KMnO_4$) afforded the

product (11.3 mg, 34.0 µmol, 17%) as a colorless solid. Mp 50 – 65 °C. TLC (P/Et_2O = 3/1): R_f = 0.44 [$KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 1.26 (s, 6H), 1.66 (s, 6H), 1.69 – 1.78 (m, 2H), 2.21 – 2.42 (m, 4H), 2.63 (ddd, ^2J = 17.6 Hz, ^3J = 13.7, 9.4 Hz, 2H), 3.99 (d, ^2J = 12.7 Hz, 2H), 4.10 (d, ^2J = 12.7 Hz, 2H), 4.78 (*virt.* dt, ^4J = 3.0 Hz, $^2J \cong {}^4J$ = 1.6 Hz, 2H), 4.83 – 4.94 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 300 K): δ = 19.1 (q), 19.6 (q), 32.7 (t), 37.2 (t), 44.4 (s), 70.3 (t), 85.8 (s), 110.5 (t), 142.3 (s), 214.0 (s). IR (ATR): $\tilde{\nu}$ = 2967 (m), 1749 (vs), 1450 (w), 1186 (w), 1097 (m), 1060 (w), 897 (w). MS (EI, 70 eV): *m/z* (%) = 213 (13), 182 (25), 166 (65), 151 (44), 123 (23), 110 (41), 97 (23), 84 (46), 69 (27), 55 (100). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{20}H_{28}O_4$: 332.1982; Found: 332.1998.

(3a*RS*,4a*SR*,6a*RS*,9a*SR*,10a*RS*,12a*SR*)-3a,4a,9a,10a-Tetramethyldodecahydro-1*H*,7*H*-cyclopenta[1,4]cyclobuta[1,2-*b*]cyclopenta[1,4]cyclobuta[1,2-*f*][1,5]dioxocine-1,7-dione (20)

According to general procedure 5, compound **20** was synthesized starting from **2f** (66.9 mg, 402 µmol, 1.0 equiv.) and thioxanthone **5** (8.50 mg, 40.0 µmol, 10 mol%) over 3 h. Purification by flash column chromatography (SiO_2, P/Et_2O = 9/1 → 3/1 → 1/1, $KMnO_4$) afforded the product (17.3 mg, 52.0 µmol, 26%) as a colorless solid. Mp 25 – 30 °C. TLC (P/Et_2O = 3/1): R_f = 0.12 [$KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 0.99 (s, 6H), 1.18 (s, 6H), 1.65 (dddd, ^2J = 14.1 Hz, ^3J = 9.2, 4.0 Hz, ^4J = 0.9 Hz, 2H), 1.84 (d, ^2J = 8.3 Hz, 2H), 2.27 (dt, ^2J = 14.1 Hz, ^3J = 8.7 Hz, 2H), 2.49 – 2.68 (m, 6H), 3.95 (d, ^2J = 6.7 Hz, 2H), 4.11 (dd, ^2J = 6.7 Hz, ^4J = 1.7 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 300 K): δ = 11.6 (q), 15.0 (q), 25.0 (t), 39.6 (t), 44.7 (t), 51.1 (s), 52.2 (s), 81.0 (t), 95.4 (s), 205.5 (s). IR (ATR): $\tilde{\nu}$ = 2957 (m), 1742 (vs), 1450 (w), 1043 (w), 976 (w), 902 (w). MS (EI, 70 eV): *m/z* (%) = 151 (37), 137 (9), 123 (58), 110 (43), 95 (100), 81 (64), 67 (92), 55 (79), 41 (47). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{20}H_{28}O_4$: 332.1982; Found: 332.1983.

(3a*SR*,3b*SR*,6a*RS*,6b*RS*)-3a,3b-Dimethyl-6a,6b-bis((3-methylbut-2-en-1-yl)oxy)octa-hydrocyclobuta[1,2:3,4]di[5]annulene-1,6-dione (21)

According to general procedure 5, compound **21** was synthesized starting from **3f** (72.3 mg, 401 µmol, 1.0 equiv.) and thioxanthone **5** (8.50 mg, 40.0 µmol, 10 mol%) over 4 h. Purification by flash column chromatography (SiO_2, P/Et_2O = 9/1 → 3/1 → 1/1, $KMnO_4$) afforded the product (24.3 mg, 67.4 µmol, 34%) as a colorless solid. Mp 85 – 98 °C. TLC (P/Et_2O = 3/1): R_f = 0.44 [$KMnO_4$]. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 1.24 (s, 6H), 1.58 (s, 6H), 1.64 – 1.72 (m, 8H), 2.23 – 2.39 (m, 4H), 2.62 (ddd, ^2J = 17.6 Hz, ^3J = 13.8, 9.3 Hz, 2H), 4.05 (dd, ^2J = 11.6 Hz, ^3J = 6.9 Hz, 2H), 4.14 (dd, ^2J = 11.6 Hz, ^3J = 6.5 Hz, 2H), 5.08 – 5.26 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 300 K): δ = 18.3 (q), 19.3 (q), 25.9 (q), 32.8 (t), 37.1 (t), 44.0 (s), 64.7 (t), 86.3 (s), 121.6 (d), 135.7 (s), 214.4 (s). IR (ATR): $\tilde{\nu}$ = 2967 (m), 1748 (vs), 1448 (w), 1381 (w), 1185 (w), 1090 (m), 1060 (w), 982 (w). MS (EI, 70 eV): *m/z* (%) = 224 (13), 160 (14), 124 (11), 113 (43), 97 (21), 83 (29), 69 (100), 55 (39), 41 (64). HRMS (EI) *m/z*: $[M]^+$ Calcd. for $C_{22}H_{32}O_4$: 360.2295; Found: 360.2296.

ASSOCIATED CONTENT

^{1}H and ^{13}C{^{1}H} NMR spectra for all compounds, configuration assignment by NOESY studies, luminescence spectrum of compound **1a**, emission spectrum of the light source, UV/Vis spectra of all photochemical substrates, X-ray crystallographic data of compounds **18** and **21**. FAIR Data is available as Supporting Information for Publication and includes the primary NMR FID files for all compounds mentioned in the Experimental Section.

ACKNOWLEDGEMENT

Financial support by the European Research Council under the European Union's Horizon 2020 research and innovation programme (grant agreement No 665951 – ELICOS) is gratefully acknowledged. We thank Thomas Pickl for his help in the synthesis of starting materials and in the structure elucidation of a by-product.

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