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Formation of Bicyclic Pyrroles and Furans Through an Enone Allene Photocycloaddition and Fragmentation Sequence

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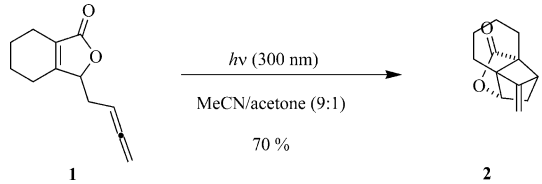
The [2+2] photocycloaddition of allenes **15**–**18**, **23** and **26** was studied. Irradiation of a solution of these substrates in acetonitrile at 300 nm resulted in the clean conversion of the starting materials into a mixture of photoproducts. The major product in all cases was a bicyclic pyrrole or furan fused to an eight membered ring (43–70 % yield). The formation of these products is thought to be a result of a heteroatom-induced fragmentation of the straight adduct (**7**). This is supported by irradiation of the carbon analogue **32** which allowed the isolation of straight adduct **45** after catalytic hydrogenation in 27 %. The minor crossed photoproducts were isolated in 10–20 % yield. The observed major/minor ratio of 4:1 was not affected by the variation of substituents on the cyclohexene ring. Introduction of a substituent on the allene had a more significant effect on the ratio which changed to 2:1.

Introduction

The construction of fused polycyclic structures is one of the major challenges in the realm of natural products synthesis.[1] Among the established methods available to the synthetic organic chemist, the intramolecular enone-olefin [2+2] photocycloaddition has proven to be a powerful methodology for the construction of cyclobutane-containing ring systems in a single operation.[2]

In connection with our study towards the total synthesis of solanoeclepin A, the use of allenes as olefinic partners in the intramolecular enone olefin [2+2] photocycloaddition is of special interest to us.[3] For the construction of the tricyclic core of the natural product we designed a strategy relying on an intramolecular butenolide allene [2+2] photocycloaddition. This strategy was first tested using model substrate **1** in which the allene and the butenolide double bond are connected by a two-atom tether. It appeared that this mode of [2+2] photocycloaddition of an allene with an α,β-unsaturated carbonyl compound was unknown in the literature when we began our studies about five years ago.[4] We were therefore pleased to find that exposure of a solution of photo substrate **1** to UV light (300 nm) resulted in the smooth formation of the desired crossed cycloadduct **2** in 70 % yield (Scheme 1). Thus, only the internal allene double bond reacted and did so solely in a crossed fashion. The success of this reaction stimulated us to further study this type of intramolecular [2+2] photocycloaddition of allenes.



Scheme 1.

In contrast to enone allenes like **1** simple enone olefins with a two-atom tether have been the subject of numerous photochemical studies.[2] Among these, substrates such like **3** (X = NR or O) were shown to be easily accessible from the condensation of a cyclic 1,3-diketone with allylamine or allyl alcohol.[5] This ease of preparation attracted our attention.[6] We envisaged that similar condensation with propargyl alcohol[7a] or propargylamine[7b] would result in the formation of acetylenic substrates, suitable for Crabbé homologation to the corresponding allenes **4** (Scheme 2).[8] Enone allenes of type **4** are the subject of this article.

$X = CH_2$, NR, O

Scheme 2.

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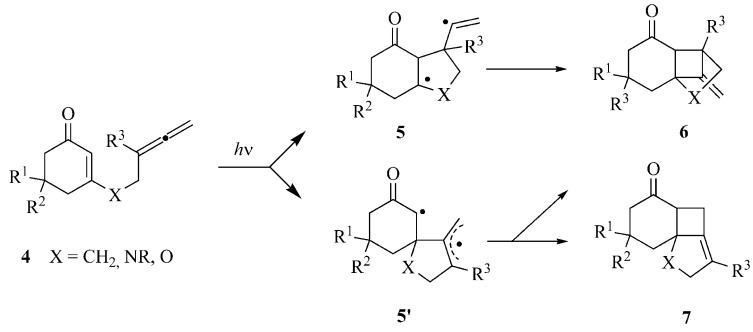
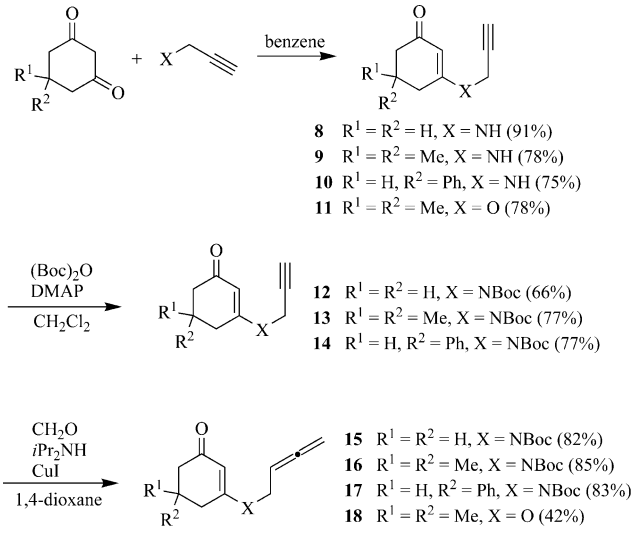


Scheme 3. Proposed mechanism for the formation of the straight and crossed adduct.

Mechanistically, substrates like **1** and **4** are highly interesting because they can provide several products, depending on which double bond of the allene will react and in what fashion, crossed or straight. For alkenes it is rather predictable which regioisomer is formed from the [2+2] photocycloaddition. This regioselectivity is dictated by the length of the tether, generally giving the crossed adduct with a two-atom tether and the straight adduct with a three-atom tether through initial five-membered ring formation. When this initial five-membered ring formation (the so-called Rule of Five) is applied to substrate **4**, two 1,4-biradical intermediates (**5** and **5′**) can be considered (Scheme 3)[9] of which allylic intermediate **5′** is most likely being generated.[10] This intermediate can give ring-closure at either the internal position giving crossed product **6** or at the primary position giving straight product **7**. The alternative five-membered ring formation would lead to the less stable diradical **5** which then should also close to the crossed product **6**. In other words, ring closure on the internal alkene of the allene is expected to lead to crossed product **6** and on the terminal alkene to the straight product **7**. In the case of **1** only the crossed product was observed (Scheme 1), but the geometry of **4** is different from **1**. Such considerations stimulated us to investigate the photochemistry of compounds **4** and the results are detailed herein.

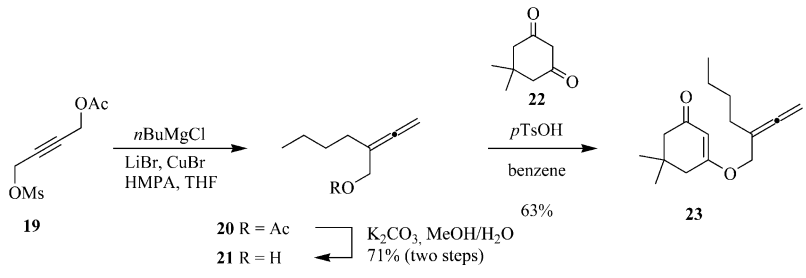
Results and Discussion

The syntheses of the photo substrates **15**–**18** are outlined in Scheme 4. Condensation of the cyclohexane-1,3-diones with propargylamine and propargyl alcohol provided acetylenes **8**–**11** in good yield. Subsequent Boc-protection of amines **12**–**14** and homologation of the acetylenes to the corresponding allenes using the method of Crabbé resulted in the formation of the desired photo substrates **15**–**18** (Scheme 4).



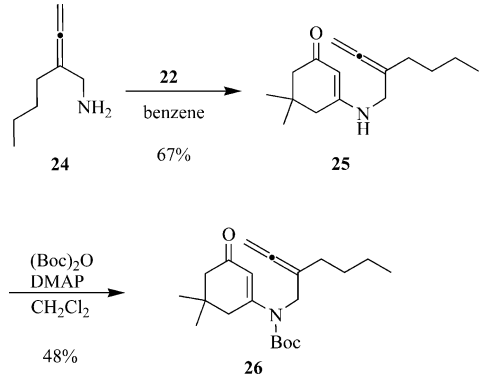
Scheme 4.

The butyl-substituted allenic alcohol **21** was prepared as follows (Scheme 5). Treatment of mesylate **19**[11] with the in situ formed *n*-butylcopper intermediate [from *n*-butylmagnesium chloride, copper(I) bromide and lithium bromide] in the presence of HMPA led to the formation of the corresponding *n*-butyl-substituted allene **20** which,[12] after saponification of the acetate using K_2CO_3 in aqueous methanol, resulted in the formation of the allene **21** in 71% over two steps. On condensation of **21** with dimedone (**22**) the desired photo substrate **23** was obtained in 63% yield (Scheme 5).



Scheme 5.

α-Allenic amine **24** was prepared via a literature procedure[13] and used in the coupling with **22** resulting in the formation of enamine **25** in 67%. After subsequent Boc-protection photo substrate **26** was obtained in 48% yield (Scheme 6).

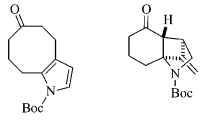
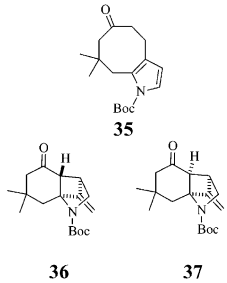
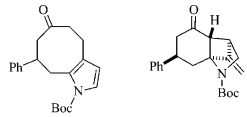
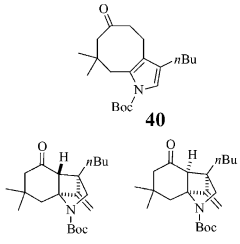
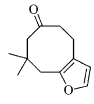
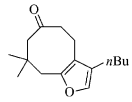


Scheme 6.

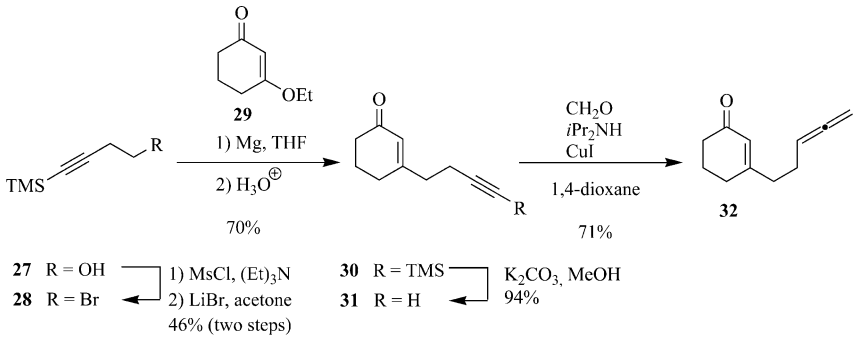
In order to compare the results of the heteroatom tethered enone allenes with the all-carbon analogue we also synthesized compound **32**. To this end commercially available alcohol **27** was converted into its mesylate and then exposed to LiBr in acetone to afford bromine **28** in a modest yield over two steps. Treatment of **28** with magnesium (in refluxing THF!) resulted in the formation of the Grignard reagent which was then cooled to 0 °C and added to **29**.[14] Acidic workup provided enone **30** which on desilylation using K_2CO_3 in methanol led to acetylene **31**. Conversion to the desired allene **32** by using the Crabbé procedure (Scheme 7) proceeded in 71% yield.[15]

With the photo substrates in hand the stage was set to investigate the [2+2] photocycloadditions. Gratifyingly, irradiation of a solution of **16** in acetonitrile at 300 nm resulted in complete consumption of the starting material and clean formation of two new products according to TLC after 10 min. The ^{1}H NMR spectrum of the crude reaction mixture, however, showed the formation of three products in a ratio of 74:18:8 (Table 1, entry 2). The ^{1}H NMR spectrum of the major compound showed two doublets at δ = 7.13 and 5.98 ppm with a coupling constant of 3.4 Hz. Such a pattern fits with the 2,3-*ortho* coupling of a pyrrole system.[16] The two minor photoproducts showed no pyrrole

Table 1. Result of the irradiation experiments.

Entry	Starting material	Product(s)	Ratio[a]	% Yield[b]
1	**15**	 **33** **34**	80:20	**(33)** 61 **(34)** 10
2	**16**	 **35** **36** **37**	74:18:8	**(35)** 70 **(36)** 15
3	**17**	 **38** **39**	83:17	**(38)** 68 **(39)** 10
4	**26**	 **40** **41** **42**	66:34	**(40)** 43 **(41)** 20
5	**18**	 **43**		40
6	**23**	 **44**		42

[a] Determined with ^{1}H NMR spectroscopy. [b] Isolated yields.



Scheme 7.

signals but two singlets at δ = 4.69 and 4.67 ppm and at δ = 4.45 and 4.55 ppm, suggesting the presence of exocyclic methylene protons and therefore the formation of two different crossed cycloadducts. Attempted separation of the mixture resulted in two chromatographic fractions. The first fraction proved to be an inseparable mixture of the major and a minor photoproduct. The second fraction provided a crystalline compound (m.p. 103–104 °C) of which the structure was elucidated by single-crystal X-ray analysis, confirming the formation of a crossed adduct. Furthermore, the X-ray structure revealed a *cis* ring fusion of the six- and the four-membered ring (Figure 1). In analogy to the work of Tamura et al. it was expected that the second minor photoproduct was **37** which is the thermodynamically less stable epimer of **36**.[5] Chemical evidence was obtained by treatment of the crude reaction mixture with a catalytic amount of DBU in CH_2Cl_2. This resulted in the clean conversion of **37** into **36** according to ^{1}H NMR spectroscopy. At this stage the mixture could be fully separated and from the major compound crystals could be obtained (m.p. 119–121 °C). Single-crystal X-ray crystallography confirmed the presence of a pyrrole fused with an eight-membered ring (Figure 1).

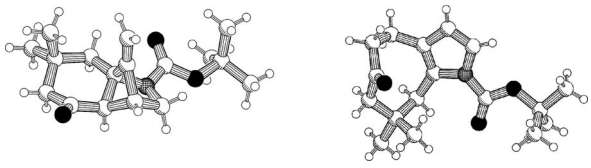
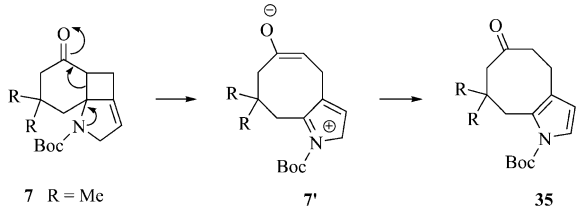


Figure 1. X-ray structures of ketone **36** and pyrrole **35**.

The formation of such a bicyclic system can be rationalized by a retro-Mannich type fragmentation of the straight adduct from reaction of the terminal double bond of the allene.[17] The highly strained nature of **7** probably triggers the fragmentation generating zwitterionic intermediate **7′**. Protonation and deprotonation then lead to bicyclic product **35** (Scheme 8).



Scheme 8. Proposed fragmentation pathway leading to bicyclic pyrrole **35**.

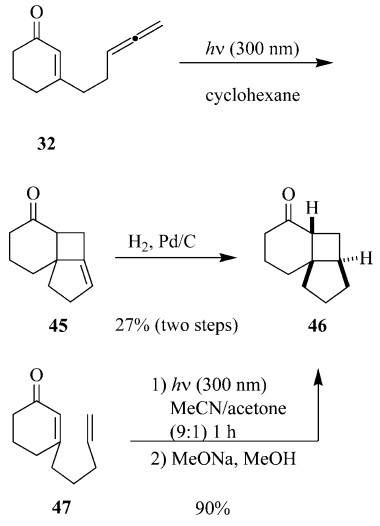
Irradiating a solution of **15** under the same conditions resulted in the clean conversion of the starting material and formation of two new products according to TLC after 10 min. Surprisingly, only two products could be detected by ^{1}H NMR in a ratio of 80:20 (Table 1, entry 1). The major product was pyrrole **33** showing two doublets at δ = 7.13 and 6.01 ppm and the minor crossed adduct **34** which showed two singlets at δ = 4.67 and 4.56 ppm. The mixture proved to be stable against base and no epimerization could be detected. Therefore, by analogy to **36** it was concluded that **34** is the crossed adduct having its 4.6 rings *cis*-fused. Purification of the mixture resulted in the isolation of pyrrole **33** and tricyclic ketone **34** in 61% and 10% yield, respectively.

Irradiation of a solution of **17** for 10 min caused complete conversion of the starting material and formation of two new products according to TLC. Examination of the crude reaction mixture with ^{1}H NMR showed the formation of pyrrole **38** and tricyclic ketone **39** in a ratio of 83:17, along with some unidentified photoproducts (Table 1, entry 3). Purification provided two chromatographic fractions. The first fraction was an inseparable mixture from which pyrrole **38** could be crystallized in 68% yield. The second fraction provided tricyclic ketone **39** which was stable against base. The relative stereochemistry at the benzylic position could not be readily determined from the ^{1}H NMR spectrum because **39** does not adopt a regular chair conformation. However, the preference of substituents on the cyclohexane ring to occupy an equatorial position in the reaction led us to assign the presented relative stereochemistry.[18]

Irradiation of **26** for 15 min resulted in the complete conversion of the starting material into two products. Examination of the crude reaction mixture with ^{1}H NMR showed the formation of pyrrole **40** along with crossed adduct **41** and a trace of the thermodynamically less stable *trans* isomer **42** (Table 1, entry 4). Surprisingly, the ratio between the pyrrole and the crossed adduct dropped to 66:34 relative to 74:26 for substrate **16**. Purification of the mixture provided pyrrole **40** and tricyclic ketone **41** in 43% and 20% yield, respectively.

We then directed our attention to the oxygen analogs which, in analogy, could lead to the formation of bicyclic furans. The irradiation of a solution of **18** for 35 min resulted in the complete consumption of the starting material. Examination of the crude reaction mixture indeed revealed the formation of the expected furan by its two doublets at δ = 7.24 and 6.23 ppm with a coupling constant of 1.8 Hz, along with some unidentified photoproducts. Purification of the mixture provided 40% of bicyclic furan **43**. The *n*-butyl-substituted analog **23**, gave the expected furan **44** after 1.5 h of irradiation in 42% isolated yield (Table 1, entry 6).

The outcome of the irradiation of substrate **32** is now very interesting because this substrate has a carbon at the β-position. A fragmentation pathway of straight cycloadduct **45** is not likely to occur and therefore we hoped to isolate this compound, thereby obtaining evidence for the intermediacy of **7** in the formation of the bicyclic heterocycles. Irradiation of a solution of **32** in cyclohexane with 300 nm UV light for 1 h resulted in the complete consumption of the starting material according to TLC (Scheme 9). The main photoproduct was most probably tricyclic unsaturated ketone **45** (^{13}C signals at δ = 146.7 ppm for a quaternary carbon and 118.4 for a tertiary carbon), but this compound could not be obtained pure, because it was not fully stable (Scheme 9).



Scheme 9.

It was therefore decided to reduce the double bond by catalytic hydrogenation. This resulted in the isolation of the saturated product **46** as a sole isomer in 27% over two steps from **32**. The synthesis of this tricyclic ketone from enone alkene **47** has been reported before by Maradyn and Weedon[19] and by Becker et al.[20] However, no explicit spectroscopic data were given for **46**.[21] We therefore prepared **47** by addition of the Grignard reagent from 5-bromo-1-pentene to 3-ethyoxycyclohex-2-enone followed by aqueous acidic workup.[22] Irradiation of **47** for 1 h resulted in the complete consumption of the starting material. ^{1}H NMR showed the formation of two products in a ratio of 91:9. Treatment of the mixture with catalytic NaOMe in methanol at room temp. resulted in a clean conversion of the minor to the major product according to ^{1}H NMR spectroscopy. This product appeared identical to **46** obtained in two steps from **32** by comparison of ^{1}H and ^{13}C NMR spectra.

Conclusions

In conclusion, irradiation of enone allenes of type **4** leads preferably to straight cycloaddition of the terminal double bond of the allene, independent of the tether type (N, O or C). The products are not stable in the case of a heteroatom in the tether and fragment to a pyrrole or furan ring. In this manner unique bicyclic pyrroles and furans are obtained in very few steps from readily available starting materials. Some of these products were earlier published by Winkler and Ragains,[4] but we have here presented a more comprehensive study with details on byproducts, including X-ray structures of both bicyclic pyrrole **35** and crossed adduct **36**. Variation of the substituents on the cyclohexenone ring of the photo substrates had only a minor effect on the straight/crossed ratio of the [2+2] photocycloaddition. The introduction of an *n*-butyl substituent on the allene changed the ratio in favor of the crossed adduct. Furthermore, we have reported the synthesis of enone allene **32**. Irradiation of this substrate led to the straight adduct, providing evidence for the proposed fragmentation pathway leading to the formation of the bicyclic heterocycles. That the mode of cycloaddition of **4** is fully different from that of **1** (crossed on the internal alkene) must be ascribed to stereoelectronic factors.

Experimental Section

General Remarks: All reactions involving oxygen- or moisture-sensitive compounds were carried out under a dry nitrogen atmosphere. THF was distilled from sodium/benzophenone and CH_2Cl_2 and acetonitrile were distilled from CaH_2. The acetone used for the irradiation experiments was of spectrophotometric grade. All commercially available chemicals were used as received. NMR spectra were recorded on a Bruker ARX 400 operating at 400 and 100 MHz for ^{1}H and ^{13}C. Unless otherwise stated, $CDCl_3$ was used as solvent. Chemical shifts are given in ppm (δ) and were referred to internal solvent signals. IR spectra were measured using a Bruker IFS 28 FT-spectrometer and wavelengths (ν) are reported in cm^{-1}. Mass spectra and accurate mass determinations were performed on a JEOL JMX SX/SX102A, coupled to a JEOL MS-MP7000 data system. The photoreaction was carried out in a quarts reaction vessel with a Rayonet RPR 300 nm. Elemental analyses were preformed by Dornis & Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

General Procedure for the Formation of the Vinylogous Amides and Ethers: To a suspension of the appropriate 1,3-diketone was added propargylamine (1 equiv.) in benzene (0.5 M). The resulting mixture was warmed to reflux and stirred overnight. The reaction mixture was concentrated in vacuo and the solid residue was recrystallized from a mixture of PE/EtOAc.

3-(Prop-2-ynylamino)cyclohex-2-enone (8): Prepared according to the general procedure from 1,3-cyclohexanedione (3.7 g, 33.3 mmol). Recrystallization afforded **8** as yellow crystals (4.5 g, 91%). All spectroscopic data were in agreement with the literature.[23] **5,5-Dimethyl-3-(prop-2-ynylamino)cyclohex-2-enone (9):** Prepared according to the general procedure from 5,5-dimethyl-1,3-cyclohexanedione (5.1 g, 36.3 mmol). Recrystallization afforded **9** as yellow crystals (5.0 g, 78%); m.p. 148–149 °C. ^{1}H NMR: δ = 5.45 (br. s, 1 H), 5.14 (s, 1 H), 3.86 (m, 2 H), 2.28 (t, J = 2.4 Hz, 1 H), 2.22 (s, 1 H), 2.18 (s, 1 H), 1.06 (s, 6 H) ppm. ^{13}C NMR: δ = 197.5, 163.8, 95.9, 78.8, 72.6, 50.5, 42.9, 33.1, 32.6, 28.5 ppm. IR: $\tilde{\nu}$ = 3441, 3307, 1591 cm^{-1}.

5-Phenyl-3-(prop-2-ynylamino)cyclohex-2-enone (10): Prepared according to the general procedure from 5-phenyl-1,3-cyclohexanedione (1.0 g, 5.3 mmol). Recrystallization afforded **10** as yellow crystals (0.9 g, 75%); m.p. 162–163 °C. ^{1}H NMR: δ = 7.34 (t, J = 7.5 Hz, 2 H), 7.27–7.23 (m 3 H), 5.25 (s, 1 H), 5.10 (br. s, 1 H), 3.89 (d, J = 2.7 Hz, 2 H), 3.38–3.34 (m 1 H), 2.73–2.45 (m, 4 H), 2.32 (s, 1 H) ppm. ^{13}C NMR: δ = 196.9, 162.5, 143.2, 129.0, 127.3, 126.9, 98.1, 78.4, 73.3, 43.8, 40.2, 37.1, 33.0 ppm. IR: $\tilde{\nu}$ = 3441, 3307, 1590 cm^{-1}.

3-(Prop-2-ynyloxy)cyclohex-2-enone (11): A mixture of 5,5-dimethyl-1,3-cyclohexanedione (1 g, 7.1 mmol), propargyl alcohol (1.3 mL, 21.4 mmol) and *p*TsOH (1.6 g, 9.3 mmol) in benzene (50 mL) was refluxed for 1.5 h under Dean–Stark conditions. The reaction was cooled to room temp. and washed with saturated $NaHCO_3$. The organic layer was dried with $MgSO_4$ and concentrated in vacuo to give an oil which crystallized on standing. Recrystallization from PE/EtOAc afforded **11** as colorless crystals

(0.98 g, 78%); m.p. 50–52 °C. ^{1}H NMR: δ = 5.45 (s, 1 H), 4.66 (d, J = 2.4 Hz, 2 H), 2.57 (t, J = 2.4 Hz, 1 H), 2.30 (s, 2 H), 2.22 (s, 2 H), 1.07 (s, 6 H) ppm. ^{13}C NMR: δ = 199.1, 174.3, 102.2, 76.3, 55.8, 50.4, 42.3, 32.4, 28.0 ppm. IR: $\tilde{\nu}$ = 3243, 2960, 1655, 1011 cm^{-1}.

5,5-Dimethyl-3-(2-vinylidenehexylamino)cyclohex-2-enone (25): To a suspension of 5,5-dimethyl-1,3-cyclohexanedione (56 mg, 0.4 mmol) in 5 mL of benzene was added crude allene **24**[13] (50 mg, 0.4 mmol). The resulting mixture was heated to reflux and stirred for 1 h. The solvent was removed and the residue was purified by chromatography (PE/EtOAc, 1:1 + 10% Et_3N) to afford **25** as a yellow oil (66 mg, 67%), R_f = 0.27. ^{1}H NMR: δ = 5.08 (s, 1 H), 4.99 (br. s, 1 H), 4.88–4.85 (m. 2 H), 3.56 (d, J = 4.2 Hz, 2 H), 2.18 (s, 2 H), 2.15 (s, 2 H), 1.96–1.92 (m, 2 H), 1.42–1.36 (m, 2 H), 1.34–1.28 (m, 2 H), 1.04 (s, 6 H), 0.89 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR: δ = 204.2, 196.7, 162.3, 100.6, 96.1, 79.3, 60.3, 50.3, 43.7, 32.7, 29.4, 29.4, 28.2, 22.2, 13.8 ppm. IR: $\tilde{\nu}$ = 3407, 1959, 1584, 1518 cm^{-1}.

General Procedure for the Preparation of Vinylogous Carbamates: To a suspension of vinylogous amide was added Boc_2O (2 equiv.) and DMAP (10 mol-%) in CH_2Cl_2 (0.4 M). The resulting mixture was stirred at room temperature until complete conversion was observed with TLC. Then imidazole was added (1 equiv.) and the mixture was stirred for 1 h.[24] The mixture was washed with 1 N HCl (2 × 25 mL), saturated $NaHCO_3$ (2 × 25 mL), dried with $MgSO_4$ and concentrated in vacuo.

***tert*-Butyl *N*-(3-Oxocyclohex-1-enyl)-*N*-(prop-2-ynyl)carbamate (12):** Prepared according to the general procedure from **8** (1.0 g, 6.7 mmol) and isolated as a light brown oil, which crystallized on standing. Recrystallization from *n*-hexane afforded **12** as colorless crystals (1.1 g, 66%); m.p. 71–72 °C. ^{1}H NMR: δ = 5.94 (s, 1 H), 4.30 (d, J = 2.4 Hz, 2 H), 2.74 (t, J = 5.9 Hz, 2 H), 2.39 (t, J = 6.3 Hz, 2 H), 2.26 (t, J = 2.4 Hz, 1 H), 2.00 (m, 2 H), 1.52 (s, 9 H) ppm. ^{13}C NMR: δ = 198.9, 162.0, 151.5, 115.2, 82.8, 78.2, 72.4, 38.6, 36.6, 29.9, 27.8, 22.8 ppm. IR: $\tilde{\nu}$ = 3307, 1715, 1650 cm^{-1}.

***tert*-Butyl *N*-(5,5-Dimethyl-3-oxocyclohex-1-enyl)-*N*-(prop-2-ynyl)carbamate (13):** Prepared according to the general procedure from **9** (1.0 g, 5.6 mmol) and isolated as a light brown oil, which crystallized on standing. Recrystallization from *n*-hexane afforded **13** as colorless crystals (1.2 g, 77%); m.p. 106–107 °C. ^{1}H NMR: δ = 5.95 (s, 1 H), 4.31 (d, J = 2.4 Hz, 2 H), 2.62 (s, 2 H), 2.27 (t, J = 2.4 Hz, 1 H), 2.24 (s, 2 H), 1.52 (s, 9 H), 1.07 (s, 6 H) ppm. ^{13}C NMR: δ = 199.2, 159.9, 151.7, 114.9, 82.9, 78.2, 77.2, 72.4, 50.3, 43.8, 38.7, 33.8, 27.9 ppm. IR: $\tilde{\nu}$ = 3307, 1716, 1650 cm^{-1}.

***tert*-Butyl *N*-(3-Oxo-5-phenylcyclohex-1-enyl)-*N*-(prop-2-ynyl)carbamate (14):** Prepared according to the general procedure from **10** (0.5 g, 2.2 mmol) and purified by chromatography (PE/EtOAc, 1:2) to afford **14** as a colorless oil, which crystallized on standing (1.2 g, 77%); R_f = 0.50; m.p. 62–63 °C. ^{1}H NMR: δ = 7.35 (t, J = 7.4 Hz, 2 H), 7.28–7.24 (m, 3 H), 6.03 (s, 1 H), 4.47 (dd, J = 17.9, 2.4 Hz, 1 H), 4.18 (dd, J = 17.9, 2.4 Hz, 1 H), 3.35–3.29 (m, 1 H), 3.07–2.95 (m, 2 H), 2.70–2.58 (m, 2 H), 2.29 (t, J = 2.4 Hz, 1 H), 1.50 (s, 9 H) ppm. ^{13}C NMR: δ = 198.9, 161.5, 152.0, 143.2, 129.1, 127.3, 127.0, 115.4, 83.7, 78.6, 73.0, 44.2, 41.7, 39.3, 38.3, 28.3 ppm. IR: $\tilde{\nu}$ = 3307, 1717, 1651 cm^{-1}.

***tert*-Butyl *N*-(5,5-Dimethyl-3-oxocyclohex-1-enyl)-*N*-(2-vinylidenehexyl)carbamate (26):** Prepared according to the general procedure from **25** (60 mg, 0.24 mmol). Purification of the crude product by chromatography (PE/EtOAc, 4:1) gave **26** as a colorless oil (30 mg, 48%); R_f = 0.30. ^{1}H NMR: δ = 5.71 (s, 1 H), 4.79–4.76 (m, 2 H), 4.06 (t, J = 3.7 Hz, 2 H), 2.62 (s, 2 H), 2.22 (s, 2 H), 1.93–1.88 (m, 2 H), 1.49 (s, 9 H), 1.46–1.40 (m, 2 H), 1.37–1.32 (m, 2 H), 1.06 (s, 6 H), 0.90 (t, J = 7.3 Hz, 3 H) ^{13}C NMR ppm. δ = 204.4, 199.6, 161.0, 152.4, 114.2, 100.9, 82.0, 78.9, 50.7, 50.4, 43.9, 33.9, 29.3, 29.0, 27.9, 22.2, 13.7. IR: $\tilde{\nu}$ = 1961, 1711, 1640, 1593 cm^{-1}.

General Procedure for the Formation of Allenes: To a solution of the acetylene in 1,4-dioxane (0.05 M) was added paraformaldehyde (2.5 equiv.), copper iodide (0.5 equiv.) and diisopropylamine (2 equiv.). The resulting mixture was heated to reflux and stirred overnight. Then the reaction mixture was cooled to room temperature and quenched with saturated $NaHSO_4$ (30 mL). The reaction mixture was diluted with water (30 mL) and extracted with CH_2Cl_2 (4 × 25 mL). The combined organic layers were washed with brine (2 × 25 mL), dried with $MgSO_4$ and concentrated in vacuo.

***tert*-Butyl *N*-(Buta-2,3-dienyl)-*N*-(3-oxocyclohex-1-enyl)carbamate (15):** Prepared according to the general procedure from **12** (0.5 g, 2.0 mmol). The residue was purified by chromatography (PE/EtOAc, 1:2) to give **15** as a colorless oil (0.44 g, 82%); R_f = 0.41. ^{1}H NMR: δ = 5.76 (s, 1 H), 5.19–5.13 (m, 1 H), 4.84–4.80 (m, 2 H), 4.16–4.13 (m, 2 H), 2.73 (t, J = 5.9 Hz, 2 H), 2.36 (t, J = 6.9 Hz, 2 H), 2.01–1.94 (m, 2 H), 1.49 (s, 9 H) ppm. ^{13}C NMR: δ = 208, 198.5, 162.5, 151.7, 114.7, 86.7, 81.7, 77.2, 47.1, 36.4, 29.9, 27.6, 22.8 ppm. IR: $\tilde{\nu}$ = 1958, 1714, 1647 cm^{-1}.

***tert*-Butyl *N*-(Buta-2,3-dienyl)-*N*-(5,5-dimethyl-3-oxocyclohex-1-enyl)carbamate (16):** Prepared according to the general procedure from of **13** (0.5 g, 1.8 mmol). The residue was purified by chromatography (PE/EtOAc, 1:1) to afford **16** as a colorless oil (0.45 g, 85%); R_f = 0.47. ^{1}H NMR: δ = 5.77 (s, 1 H), 4.82–5.19 (m, 1 H) 4.82–4.79 (m, 2 H), 4.16–4.13 (m, 2 H), 2.59 (s, 2 H), 2.21 (s, 2 H), 1.48 (s, 9 H), 1.04 (s, 6 H) ppm. ^{13}C NMR: δ = 208.1, 199.0, 160.5, 152.0, 114.3, 86.8, 82.1, 77.4, 50.2, 47.5, 43.8, 33.7, 27.8 ppm. IR: $\tilde{\nu}$ = 1957, 1723, 1652 cm^{-1}.

***tert*-Butyl *N*-(Buta-2,3-dienyl)-*N*-(3-oxo-5-phenylcyclohex-1-enyl)-carbamate (17):** Was prepared according to the general procedure from **14** (0.5 g, 1.5 mmol). The residue was purified by chromatography (PE/EtOAc, 2:1) to give a colorless oil, which crystallized on standing. Recrystallization from *n*-hexane afforded **17** as colorless crystals (0.43 g, 83%); R_f = 0.43; m.p. 68–69 °C. ^{1}H NMR: δ = 7.34 (t, J = 6.1 Hz, 2 H), 7.32–7.24 (m, 3 H), 5.86 (s, 1 H), 5.22–5.16 (m, 1 H), 4.87–4.83 (m, 2 H), 4.38–432 (m, 1 H), 4.09–4.03 (m, 1 H), 3.33–3.25 (m, 1 H), 3.07–2.91 (m, 2 H), 2.69–2.56 (m, 2 H), 1.47 (s, 9 H) ppm. ^{13}C NMR: δ = 208.0, 198.3, 161.8, 151.9, 142.9, 128.5, 126.8, 126.5, 114.4, 86.9, 82.3, 77.7, 47.3, 43.7, 41.3, 37.9, 27.8 ppm. IR: $\tilde{\nu}$ = 3007, 1957, 1715, 1647, 1592 cm^{-1}.

3-(Buta-2,3-dienyloxy)-5,5-dimethylcyclohex-2-enone (18): Prepared according to the general procedure from **11** (2.4 g, 15.8 mmol). The residue was purified by chromatography (PE/EtOAc, 2:1) to afford **18** as a yellow oil (1.26 g, 42%); R_f = 0.28. ^{1}H NMR: δ = 5.32 (s, 1 H), 5.27 (m, 1 H), 4.88 (dt, J = 6.8, 2.4 Hz, 2 H), 4.40 (dt, J = 6.8, 2.4 Hz, 2 H), 2.27 (s, 2 H), 2.20 (s, 2 H), 1.06 (s, 6 H), ^{13}C NMR ppm. δ = 209.4, 199.2, 175.3, 101.9, 85.5, 76.9, 65.9, 60.1, 50.5, 42.6, 32.2. IR: $\tilde{\nu}$ = 2975, 1957, 1703, 1680, 1650, 1591 cm^{-1}.

2-Vinylidenehexan-1-ol (21): LiBr (5.63 g, 64.8 mmol) and CuBr (9.3 g, 64.8 mmol) were dried under vacuum (2 Torr) at 150 °C for 2 h. THF (130 mL) was added and the mixture was stirred for 15 min and then allowed to cool to –78 °C. To this mixture was added *n*-butylmagnesium chloride (2 M *solution* in THF, 35 mL). After being stirred for 15 min HMPA (32 mL) was added followed by a solution of **19**[11] (12.2 g, 59 mmol) in THF (10 mL). The resulting mixture was slowly warmed up to room temperature for 20 min and stirred for an additional 30 min. Saturated NH_4Cl (100 mL) was added and the mixture was filtered through celite.

The filtrate was extracted with *n*-pentane (3 × 100 mL). The combined organic layers were washed with water (200 mL) and brine (200 mL), dried with $MgSO_4$ and concentrated in vacuo. The residue was dissolved in methanol (100 mL) and added to a solution of K_2CO_3 (12.2 g, 88.5 mmol) in methanol (100 mL). The resulting mixture was stirred at room temp. for two days and part of the solvent was then distilled off. To the resulting suspension was added brine (100 mL) and the aqueous phase was extracted with *n*-pentane (3 × 100 mL). The combined organic layers were washed with water (200 mL) and brine (200 mL), dried with $MgSO_4$ and concentrated via distillation (25 °C, 100 Torr). The remainder was purified by column chromatography to afford **21** as a yellow oil (5.3 g, 71%). ^{1}H NMR: δ = 4.78 (m, 2 H), 4.05 (t, J = 3 Hz, 2 H), 2.01 (m, 2 H), 1.50–1.25 (m, 4 H), 0.91 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR: δ = 204.8, 104.6, 77.9, 63.1, 29.8, 28.6, 22.6, 14.1 ppm. IR: $\tilde{\nu}$ = 3319, 2927, 1957 cm^{-1}.

5,5-Dimethyl-3-(2-vinylidenepentyloxy)cyclohex-2-enone (23): To a solution of **21** (1.0 g, 7.9 mmol) in 50 mL of benzene was added **22** (2.2 g, 15.6 mmol) and *p*TsOH (150 mg, 0.79 mmol). The resulting mixture was stirred at reflux under Dean–Stark conditions for 3 h. The mixture was cooled to room temp. and washed with saturated $NaHCO_3$. The organic layer was dried en concentrated in vacuo. The residue was purified (PE/EtOAc, 7:3) to afford **23** as a yellow oil (1.2 g, 63%); R_f = 0.25. ^{1}H NMR: δ = 5.37 (s, 1 H), 4.84 (q, J = 2.4 Hz, 2 H), 4.38 (t, J = 2.2 Hz, 2 H), 2.30 (s, 2 H), 2.22 (s, 2 H), 2.05–1.99 (m, 2 H), 1.44–1.32 (m, 4 H), 1.08 (s, 6 H), 0.92 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR: δ = 206.5, 199.3, 175.6, 101.9, 98.7, 76.9, 69.2, 50.5, 42.6, 32.3, 29.3, 28.4, 28.1, 22.1, 13.7 ppm. IR: $\tilde{\nu}$ = 2957, 1960, 1659, 1608 cm^{-1}.

General Procedure for the Irradiation Experiments: A solution of the photo substrate was degassed by bubbling argon though for 30 min and the solution was kept under argon during the irradiation. When complete conversion was observed according to TLC the solvent was removed and the residue was purified using standard flash column chromatography.

Irradiation of Photo Substrate 16: After irradiating a solution of **16** (100 mg, 0.34 mmol) in 30 mL of MeCN for 15 min the solvent was removed and the residue was dissolved in 5 mL of CH_2Cl_2 to which a catalytic amount of DBU was added. The resulting mixture was stirred overnight. Then the reaction mixture was washed with saturated aqueous NH_4Cl (2 × 5 mL), dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by chromatography (PE/Et_2O, 1:1.5) to give two chromatographic fractions. The first fraction provided **35** as a white solid (70 mg, 70%). Recrystallization from *n*-hexane afforded crystals suitable for X-ray analysis; R_f = 0.68; m.p. 119–121 °C. ^{1}H NMR: δ = 7.12 (d, J = 3.4 Hz, 1 H), 5.98 (d, J = 3.4 Hz, 1 H), 3.07 (s, 2 H), 2.76 (t, J = 6.1 Hz, 2 H), 2.55 (t, J = 6.1 Hz, 2 H), 2.23 (s, 2 H), 1.57 (s, 9 H), 1.01 (s, 6 H) ppm. ^{13}C NMR: δ = 212.1, 149.4, 129.4, 120.8, 110.7, 83.1, 52.8, 52.8, 48.4, 36.3, 35.9, 57.8, 21.8 ppm. IR: $\tilde{\nu}$ = 1736, 1694 cm^{-1}. HR-MS: *m*/*z* calcd. for: $C_{17}H_{26}O_3N$ 292.1913; found 292.1912 [M + H]$^+$. $C_{17}H_{25}NO_3$ (291.39): C 70.07, H 8.65, N 4.81; found C 70.05, H 8.72, N 4.78. The second fraction provided tricyclic ketone **36** as a white solid (15 mg, 15%). Recrystallisation from *n*-pentane gave crystals suitable for X-ray analysis; R_f = 0.30; m.p. 103–104 °C. ^{1}H NMR (C_6D_6): δ = 4.69 (s, 1 H), 4.67 (s, 1 H), 3.44 (d, J = 8.3 Hz, 1 H), 3.39 (d, J = 8.3 Hz, 1 H), 3.36 (s, 1 H), 2.61 (s, 1 H), 2.43 (d, J = 15.3 Hz, 1 H), 2.63 (d, J = 15.3 Hz, 1 H), 2.23 (d, J = 13.9 Hz, 1 H), 2.11 (d, J = 13.9 Hz, 1 H), 1.46 (s, 9 H), 1.11 (s, 3 H), 1.04 (s, 3 H) ppm. ^{13}C NMR: δ = 208.2, 156.6, 151.7, 96.8, 80.2, 76.5, 57.8, 53.4, 52.7, 44.9, 36.9, 36.5, 32.8, 29.6, 28.6 ppm. IR: $\tilde{\nu}$ = 1713, 1685, 897 cm^{-1}. HR-MS: *m*/*z* calcd. for $C_{17}H_{26}O_3N$: 292.1913; found 292.1902 [M + H]$^+$.

X-ray Crystal Structure Analysis of 35: $C_{17}H_{25}NO_3$, M = 291.39; T = 293 K, λ = 0.71073 Å; orthorhombic, $P2_12_12_1$; a = 9.9164(4) Å, b = 11.1617(3) Å, c = 14.8053(7) Å; V = 1638.77(11) Å^3, Z = 4, D_c = 1.181 g cm^{-3}; 2405 observed unique reflections; R_1 = 0.0519, wR_2 = 0.0803 [$I > 2\sigma(I)$].

X-ray Crystal Structure Analysis of 36: $C_{17}H_{25}NO_3$, M = 291.38; T = 208 K, λ = 0.71073 Å; triclinic, P-1; a = 6.7979(6) Å, b = 11.2185(7) Å, c = 11.6611(7) Å, α = 78.521(4)°, β = 79.840(6)°, γ = 75.451(5)°; V = 836.04(10) Å^3, Z = 2, D_c = 1.157 g cm^{-3}; 2619 observed unique reflections; R_1 = 0.0734, wR_2 = 0.1796 [$I > 2\sigma(I)$].

Irradiation of Photo Substrate 15: After irradiating a solution of **15** (100 mg, 0.38 mmol) in 30 mL of MeCN for 10 min the solvent was removed and the residue was purified by chromatography (PE/Et_2O, 2:1) to give two chromatographic fractions. The first fraction provided **33** as a white solid (61 mg, 61%); R_f = 0.40, m.p. 52–53 °C. ^{1}H NMR: δ = 7.13 (d, J = 3.2 Hz, 1 H), 6.01 (d, J = 3.2 Hz, 1 H), 2.99 (t, J = 5.6 Hz, 2 H), 2.67 (t, J = 5.9 Hz, 2 H), 2.59 (t, J = 5.6 Hz, 2 H), 2.32 (t, J = 6.3 Hz, 2 H), 1.83–1.78 (m, 2 H), 1.59 (s, 9 H) ppm. ^{13}C NMR: δ = 215.2, 149.7, 129.9, 124.7, 120.3, 111.2, 83.5, 48.8, 40.2, 28.1, 24.7, 24.3, 22.3 ppm. IR: $\tilde{\nu}$ = 1734, 1698 cm^{-1}. HR-MS: *m*/*z* calcd. for $C_{15}H_{22}O_3N$: 264.1599; found 264.1599 [M + H]$^+$. The second fraction provided tricyclic ketone **34** as a white solid (10 mg, 10%); R_f = 0.25; m.p. 129–130 °C. ^{1}H NMR: δ = 4.67 (s, 1 H), 4.56 (s, 1 H), 3.45–3.41 (m, 3 H), 2.65 (d, J = 15.4 Hz, 1 H), 2.55 (s, 1 H), 2.40–2.32 (m, 2 H), 2.25–2.19 (dt, J = 13.7, 5.6 Hz, 1 H), 2.11–2.05 (m, 1 H), 1.87–1.76 (tq, J = 13.4, 3.9 Hz, 1 H), 1.48 (s, 9 H) ppm. ^{13}C NMR (C_6D_6): δ = 205.5, 155.9, 149.8, 94.9, 79.5, 77.5, 58.7, 52.0, 45.9, 40.6, 28.9, 24.9, 22.9 ppm. IR: $\tilde{\nu}$ = 1770, 1726 cm^{-1}. HR-MS: *m*/*z* calcd. for $C_{15}H_{22}O_3N$: 264.1599; found 264.1597 [M + H]$^+$.

Irradiation of Photo Substrate 17: After irradiating a solution of **17** (100 mg, 0.34 mmol) in 30 mL of MeCN for 10 min the solvent was removed and the residue was purified by chromatography (PE/Et_2O, 1:1) to give a solid. Recrystallization from *n*-hexane afforded **38** as colorless crystals (68 mg, 68%); R_f = 0.47; m.p. 156–157 °C. ^{1}H NMR: δ = 7.36–7.31 (m, 4 H), 7.23 (t, J = 6.8 Hz, 1 H), 7.15 (d, J = 3.2 Hz, 1 H), 6.01 (d, J = 3.2 Hz, 1 H), 3.68 (d, J = 14.2 Hz, 1 H), 3.25–3.18 (m. 2 H), 3.16–3.03 (m, 2 H), 2.85 (td, J = 12.4, 4.6 Hz, 1 H), 2.75 (td, J = 14.2, 4.6 Hz, 1 H), 2.53 (dt, J = 12.6, 5.1 Hz, 1 H), 2.41 (d, J = 12.2 Hz, 1 H), 1.48 (s, 9 H) ppm. ^{13}C NMR: δ = 212.5, 149.3, 145.8, 129.4, 128.8, 127.1, 126.7, 125.3, 121.3, 110.8, 83.6, 49.0, 48.2, 43.2, 32.9, 28.2, 21.4 ppm. IR: $\tilde{\nu}$ = 1742, 1702 cm^{-1}. HR-MS: *m*/*z* calcd. for $C_{21}H_{26}O_3N$: 340.1913; found 340.1903 [M + H]$^+$. Anal. calcd. for $C_{21}H_{25}NO_3$ (339.43): C 74.31, H 7.42, N 4.13; found C 74.28, H 7.53, N 4.06. The second chromatographic fraction provided tricyclic ketone **39** as a colorless oil (10 mg, 10%). ^{1}H NMR: δ = 7.36–7.31 (m, 2 H), 7.27–7.24 (m, 3 H), 4.76 (s, 1 H), 4.69 (s, 1 H), 3.53–3.47 (0, 3 H), 3.24–3.16 (m, 1 H), 2.93 (dd, J = 15.0, 4.2 Hz, 1 H), 2.71–2.52 (m, 4 H), 1.46 (s, 9 H) ppm. ^{13}C NMR: δ = 206.4, 155.7, 148.9, 143.2, 128.7, 127.2, 127.1, 95.7, 80.2, 76.9, 58.4, 51.9, 48.3, 45.2, 40.8, 32.5, 28.7 ppm. IR: $\tilde{\nu}$ = 2947, 1699 cm^{-1}. HR-MS: *m*/*z* calcd. for $C_{21}H_{26}O_3N$: 340.1913; found 340.1918 [M + H]$^+$.

Irradiation of Photo Substrate 26: After irradiating a solution of **26** (40 mg, 0.12 mmol) in 30 mL of MeCN for 15 min the solvent was removed and the residue was purified by chromatography (n-pentane/Et_2O, 6:1) to give two chromatographic fractions. The first fraction provided **40** as a colorless oil (17 mg, 43%); R_f = 0.26. ^{1}H NMR: δ = 6.91 (s, 1 H), 3.07 (br. s, 2 H), 2.74 (t, J = 6.1 Hz, 2 H), 2.54 (t, J = 6.1 Hz, 2 H), 2.34 (t, J = 8.1 Hz, 2 H), 2.25 (s, 2 H), 1.61–1.51 (m, 2 H), 1.57 (s, 9 H), 1.47–1.41 (m, 2 H), 1.03 (s, 6 H), 0.95 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR: δ = 212.2, 149.5, 129.5,

124.5, 124.3, 117.5, 82.7, 52.9, 47.9, 36.3, 36.1, 31.8, 27.9, 24.6, 22.5, 19.4, 13.8 ppm. IR: $\tilde{\nu}$ = 1738, 1700 cm^{-1}. HR-MS: *m/z* calcd. for $C_{21}H_{34}O_3N$: 348.2539; found 348.2506 $[M + H]^+$. The second fraction provided tricyclic ketone **41** as colorless oil (8 mg, 20%); R_f = 0.14. ^1H NMR: δ = 5.32 (s, 1 H), 5.09 (s, 1 H), 3.98–3.92 (m, 2 H), 3.67 (s, 0.5 H), 3.59 (s, 0.5 H), 2.40–1.96 (m, 4 H), 1.67–1.51 (m, 3 H), 1.46 (s, 9 H), 1.43–1.27 (m, 3 H), 1.09 (s, 3 H), 0.945–0.91 (m, 6 H) ppm. ^{13}C NMR (C_6D_6): δ = 206.7, 156.2, 151.3, 108.7, 79.9, 58.3, 57.5, 55.8, 53.7, 40.3, 39.7, 32.1, 31.5, 28.9, 27.4, 23.9, 15.9, 14.4 ppm. IR: $\tilde{\nu}$ = 1707 cm^{-1}. HR-MS: *m/z* calcd. for $C_{21}H_{33}O_3N$: 347.2460; found 347.2441 $[M + H]^+$.

Irradiation of Photo Substrate 18: After irradiating a solution of **18** (58 mg, 0.3 mmol) in 30 mL of MeCN for 35 min and the solvent was removed and the residue was purified by chromatography (PE/EtOAc, 4:1) to afford **43** as colorless oil (23 mg, 40%); R_f = 0.23. ^1H NMR: δ = 7.24 (d, J = 1.8 Hz, 1 H), 6.23 (d, J = 1.8 Hz, 1 H), 2.78 (t, J = 2.5 Hz, 2 H), 2.64–2.61 (m, 4 H), 2.31 (s, 3 H), 1.03 (s, 6 H) ppm. ^{13}C NMR: δ = 212.5, 150.2, 140.4, 118.7, 111.9, 52.4, 46.43, 36.3, 28.8, 21.56 ppm. IR: $\tilde{\nu}$ = 2958, 1697 cm^{-1}. HR-MS: *m/z* calcd. for $C_{12}H_{17}O_2$: 193.1229; found 193.1230 $[M + H]^+$.

Irradiation of Photo Substrate 23: After irradiating a solution of **23** (75 mg, 0.3 mmol) in 30 mL of MeCN for 1.5 h and the solvent was removed and the residue was purified by chromatography (PE with 5% EtOAc) to afford of **44** as a colorless oil (32 mg, 42%); R_f = 0.31. ^1H NMR: δ = 7.03 (s, 1 H), 2–72–2.69 (m, 2 H), 2.62–2.59 (m, 2 H), 2.57 (s, 2 H), 2.34–2.29 (m, 4 H), 1.53 (q, J = 8.3 Hz, 2 H), 1.43–1.34 (m, 2 H), 1.02 (s, 6 H), 0.94 (t, J = 7.3 Hz, 3 H) ppm. ^{13}C NMR: δ = 209.8, 150.5, 136.9, 125.3, 118.9, 52.1, 46.0, 39.5, 35.7, 31.8, 28.8, 23.5, 22.6, 19.3, 13.9 ppm. IR: $\tilde{\nu}$ = 2958, 2932, 2871, 1703 cm^{-1}. HR-MS: *m/z* calcd. for $C_{16}H_{25}O_2$: 248.1776; found 248.1789 $[M + H]^+$.

4-Bromo-but-1-ynyl-trimethylsilane (28): To a solution of methanesulfonyl chloride (8.2 mL, 104 mmol) in CH_2Cl_2 (30 mL) was added a mixture of alcohol **27** (10.0 g, 70 mmol) and triethylamine (14.4 mL, 104 mmol). The resulting mixture was stirred for 20 h at room temp. The mixture was diluted with CH_2Cl_2 and washed with water and brine, dried with $MgSO_4$ and the solvent removed to give the mesylate as a red liquid. This crude mesylate was dissolved in acetone (120 mL) and added to a mixture of LiBr (23.28 g, 268 mmol) in acetone (70 mL) at 0 °C and the mixture was stirred at room temp. for 19 h. After the addition of water the mixture was extracted with CH_2Cl_2 (3 × 50 mL) and the combined organic phases were washed with water and brine and dried using $MgSO_4$. The solvent was removed under reduced pressure and the residue was distilled (44 °C, 2 mbar) to afford **28** as a colorless liquid (6.4 g, 46%). ^1H NMR: δ = 3.42 (t, J = 7.5 Hz, 2 H), 2.77 (t, J = 7.5 Hz, 2 H), 0.15 (s, 9 H) ppm. ^{13}C NMR: δ = 103.0, 86.8, 29.0, 24.1 ppm. IR: $\tilde{\nu}$ = 3008, 2960, 2171, 1663 cm^{-1}.

3-(4-Trimethylsilane-but-3-ynyl)-cyclohex-2-enone (30): To a suspension of Mg turnings (0.61 g, 25 mmol) in THF (3 mL) was added 1,2-dibromoethane (8 μL). The mixture was heated to reflux and a solution of 1,2-dibromoethane and bromide **28** in THF (6 mL) was added dropwise. The mixture was refluxed for 2 h and then cooled to 0 °C. To this mixture was added dropwise a solution of 3-ethoxy-2-cylohexene-1-one (**29**) (2.96 mL, 20.5 mmol) in THF (4 mL). The mixture was stirred at 0 °C for 20 min, then allowed to warm to room temp. and stirred overnight. Then an aqueous solution of HCl (2 M) was added in small portions until all Mg was dissolved. The mixture was stirred for an additional hour and then extracted with diethyl ether (3 × 20 mL). The combined organic phases were washed with water and brine and dried with $MgSO_4$. The solvent was removed and the residue purified by chromatography (PE/EtOAc, 2:1) to give **30** as a yellow oil (3.2 g, 70%); R_f = 0.3. ^1H NMR: δ = 5.87 (s, 1 H), 2.41 (s, 4 H), 2.36–2.29 (m, 4 H), 2.01–1.95 (m, 4 H), 0.13 (s, 9 H) ppm. ^{13}C NMR: δ = 199.4, 163.5, 126.2, 104.9, 85.9, 37.1, 36.4, 29.3, 22.4, 17.8 ppm. IR: $\tilde{\nu}$ = 3008, 2961, 2174, 1663 cm^{-1}.

3-But-3-ynyl-cyclohex-2-enone (31): To a solution of **30** (3.15 g, 14.4 mmol) in MeOH (50 mL) was added K_2CO_3 (1.98 g, 14.4 mmol) and the mixture was stirred for 4 h. After the mixture was concentrated in vacuo water was added (20 mL). The aqueous layer was extracted with diethyl ether (3 × 20 mL) and the combined organic phases were washed with water, brine and dried using $MgSO_4$. The solvent was removed and the residue was purified by column chromatography to give **31** as a yellow oil (1.99 g, 94%). ^1H NMR: δ = 5.92 (s, 1 H), 2.44–2.30 (m, 8 H), 2.04–1.98 (m, 3 H) ppm. ^{13}C NMR: δ = 199.4, 163.2, 126.1, 82.3, 69.4, 37.1, 36.2, 29.3, 22.4, 16.2 ppm. IR: $\tilde{\nu}$ = 36.72, 3308, 3012, 2928, 1663 cm^{-1}.

3-Penta-3,4-dienyl-cyclohex-2-enone (32): According to the general procedure for the formation of allenes from acetylenes, starting from **31** (0.2 g, 1.3 mmol) allene **321** (0.19 g, 71%) was obtained as a yellow oil after column chromatography (PE/EtOAc, 5:4); R_f = 0.32. ^1H NMR: δ = 5.86 (s, 1 H), 5.12–5.05 (m, 1 H), 4.69–4.66 (m, 2 H), 2.35–2.26 (m, 6 H), 2.22–2.17 (m, 2 H), 2.00–1.95 (m, 2 H) ppm. ^{13}C NMR: δ = 208.3, 199.6, 165.1, 125.8, 88.5, 75.5, 36.8, 29.5, 25.2, 22.5 ppm. IR: $\tilde{\nu}$ = 3011, 2954, 2927, 1955, 1 661 cm^{-1}.

Irradiation of Photo Substrate 32: After irradiating a solution of **32** (100 mg, 0.62 mmol) in 20 mL of cyclohexane for 1 h the solvent was removed and the residue was dissolved in THF (2 mL) and Pd/C was added (2 mol-%) and stirred under hydrogen atmosphere for 3 h at room temp. The reaction mixture was filtered through celite and reduced in vacuo. The residue was purified (PE/EtOAc, 9:1) to give **46** as a colorless oil (28 mg, 28%); R_f = 0.21. ^1H NMR: δ = 2.58 (dt, J = 17.8, 3.6 Hz, 1 H), 2.48 (dd, J = 11.3, 7.0 Hz, 1 H), 2.43–2.24 (m, 1 H), 2.19–1.98 (m, 4 H), 1.97–1.80 (m, 3 H), 1.64–1.54 (m, 5 H), 1.35–1.33 (m, 1 H) ppm. ^{13}C NMR: δ = 215.4, 49.8, 47.1, 40.2, 39.4, 39.3, 32.8, 32.7, 26.7, 24.8, 21.0 ppm. IR: $\tilde{\nu}$ = 2928, 2850, 1697 cm^{-1}. HR-MS: *m/z* calcd. for $C_{11}H_{16}O_2$: 164.1201; found 164.1197.

Irradiation of Photo Substrate 47: After irradiating a solution of **47** (120 mg, 0.73 mmol) in 30 mL of MeCN/acetone (9:1) for 1 h the solvent was removed. The residue was dissolved in 1 mL of MeOH and a catalytic amount of NaOMe (30% in MeOH) was added and the mixture was stirred overnight. The reaction was quenched by addition of 10% $KHSO_4$ and the mixture was extracted with EtOAc (2 × 5 mL). The combined organic phases were dried using $MgSO_4$ and the solvent removed. The residue was purified (PE/EtOAc, 9:1) to give a colorless oil (109 mg, 90%). All spectroscopic data were consistent with those obtained after irradiation and hydrogenation of **32**.

CCDC-663375 (for **35**) and -663374 (for **36**) contain supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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