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[2+2] Photocycloadditions and Photorearrangements of 2-Alkenylcarboxamido-2-cycloalken-1-ones

Catherine Meyer, Olivier Piva,*,† and Jean-Pierre Pete*

Laboratoire des Réactions Sélectives et Applications Associé au CNRS, UMR 6519, Université de Reims, Champagne-Ardenne, BP 1039, 51687 Reims cedex 2, France

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Abstract—While intermolecular photocycloaddition of alkenes with 2-carboxamidocyclo-2-pent-1-enones was not an efficient process, photolysis of 2-alkenylcarboxamido-2-cycloalken-1-ones led regio- and stereospecifically to a faster [2+2] intramolecular reaction and therefore to the corresponding cyclobutanes. However, photorearrangements involving three different intramolecular H-abstraction processes, compete with the observed cycloaddition. To explain the results, we propose that different deactivation pathways are available to the excited state, depending on the conformers present in the starting material.

During recent years, [2+2] photocycloadditions have been widely used for the synthesis of polycyclic molecules and applied to natural product synthesis.[1] The mechanism of the reaction of cyclic enones with alkenes involves addition of the excited enone triplet to ground-state alkene via 1,4-biradicals. These intermediates can either close to the corresponding cyclobutanes or revert to the starting materials.[2] With disymmetric alkenes, complex mixtures of regio- and stereoisomers may result, while control of the regioselectivity could be expected for intramolecular photocycloadditions.[3]

Recently, we reported intramolecular photocycloadditions of unsaturated esters of 3-carboxy-2-cyclohexen-1-ones with high regio and *syn*/*anti* stereocontrol.[4] Facial selectivity was finally achieved when a removable chiral tether group was placed between the enone and the alkenyl moiety.[5] In continuation in our interest for the study of stereoselective [2+2] photocycloadditions, introduction of functional groups at C-2 appears highly attractive. While 2-alkenyl-,[6] 2-alkenyloxy-[7] and 2-[*N*-acyl-*N*-(2-propenyl)-amino]cyclohex-2-enones[8] have been already considered, little attention has been paid to the photoreactivity of *N*-alkyl-*N*-alkenylamido-2-cycloalken-1-ones. We, therefore, carried out a study on conjugated cycloalkenones bearing a carbamido group (general structures **2** and **7**) at C-2 in order to determine the factors affecting selectivity and competition between photocycloaddition and intramolecular H-abstraction (Fig. 1).[9,10]

β-Ketoamides **2** were prepared by dehydrogenation of *N*,*N*-dialkyl-2-oxo-cycloalkanecarboxamides **1** using a mixture of cupric acetate and lead tetraacetate[11] (Scheme 1, Table 1).

This procedure was not successful for the synthesis of β-ketoamides **7**, which possess an unsaturated nitrogen substituent. The reaction sequence starting from β-ketoester **3**[12,13] is presented in Scheme 2. The unsaturated ketoacid **6** served as common intermediate, while the alkenylamino group was introduced in the final reaction step. Ketoamides **7** were obtained in satisfactory yields (Table 2). It should be noted that compounds, differently substituted at nitrogen, exist as rotameric mixtures around the amide bond.

We examined first the photocycloaddition of **2a** with cyclopentene (70 equiv.) at 366 nm in acetonitrile. After 96 h, photocycloadduct **8a** (14%) and the rearranged compound **9a** (20%) were isolated and identified (74% conversion of **2a**). Compound **8a** was characterized by a molecular ion at *m*/*z*=249 in the mass spectrum, as well as by the disappearance of the sp^2-C-atoms and the appearance of tertiary carbons at 40.0, 44.6 and 45.2 ppm, and a quaternary carbon at 59.0 ppm (cyclobutane) in the ^{13}C NMR spectrum. The

2 (R_1, R_2 = Alkyl) **7**

Fig. 1.

Keywords: photocycloaddition; amides; cyclopentenones; cyclohexenones; lactams.

* Corresponding authors. Fax: +33-4-72-44-81-36;
e-mail: piva@copssg.univ-lyon1.fr
† Present address: Laboratoire de Chimie Organique, Photochimie et Synthèse, UMR CNRS 5622, Université Claude Bernard-Lyon I, 43, Bd du 11 novembre 1918, 69622, Villeurbanne cedex, France.

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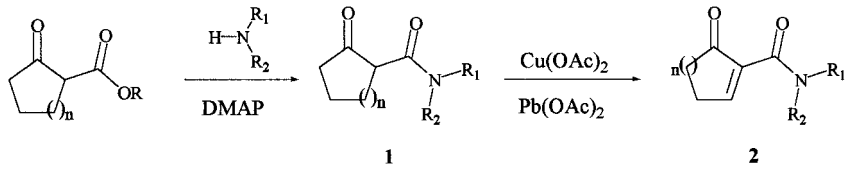


Scheme 1.

Table 1. Preparation of unsaturated amides **2**

1	*N*	R_1	R_2	Yield (%)	**2**	Yield (%)
a	1	Et	Et	65	**a**	74
b	1	$-(CH_2)_5-$		66	**b**	43
c	1	*i*-Pr	*i*-Pr	29	**c**	38
d	2	*i*-Pr	*i*-Pr	22	**d**	34
e	2	$-(CH_2)_5-$		94	**e**	30
f	2	$-(CH_2)_2-O-(CH_2)_2-$		94	**f**	24

absence of a ketone group in **9a** and ^{13}C NMR signals of two sp^2-C-atoms and a signal at 86.5 ppm, attributed to a tertiary carbon vicinal to a nitrogen and an oxygen atom, are indicative of an oxazinone structure.

The photoreactivity of **2b**–**2e** was then examined in the presence of cyclopentene and the results are summarised in Scheme 3 and Table 3.

In all enones, cycloaddition was inefficient and very long irradiation times, independent of the nature of the solvent were required. Rearranged compounds **9** and **10** were usually the major photoreaction products albeit in low yields. Polar material was not characterised.

Table 2. Preparation of unsaturated ketoamides **7**

7	*m*	R	Yield[a] (%)
a	1	Allyl	61
b	1	Me	44
c	1	*tert*-Bu	70
d	2	Me	64
e	3	Me	51
f	4	Me	92

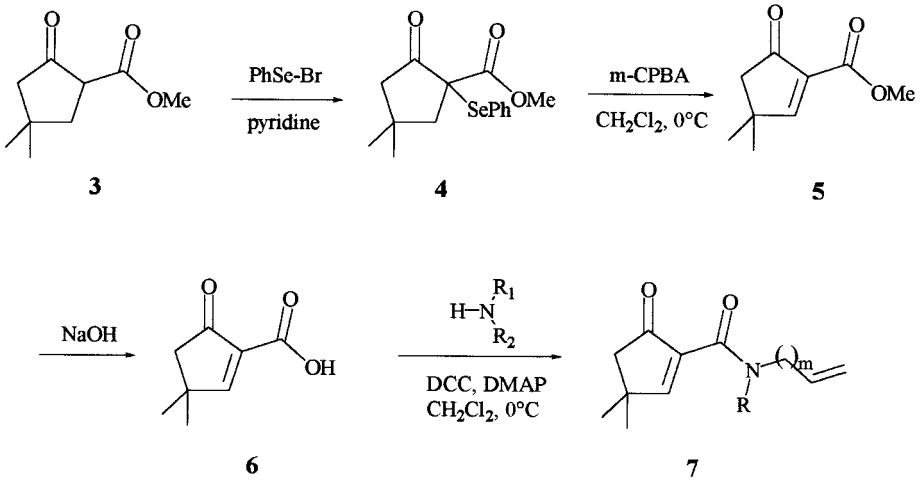
[a] Yield based on consumption of **4**.

Cyclohexenones **2d**–**2f** did not give rise to photocycloadducts and only very small amounts of rearranged compounds **9d**, **10e**, and **9f** were detected.

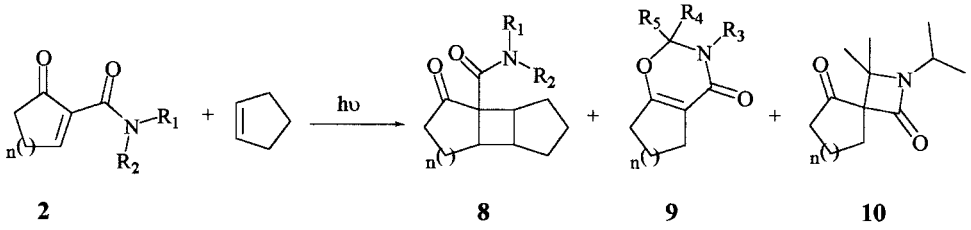
Next, the photoreactivity of *N*-alkenyl 2-carboxamido-2-cyclopenten-1-ones **7** was examined. Irradiation of **7a** at 366 nm in acetonitrile gave formation of **11a** (41%) and **12a** (14%). The structure of **11a** was derived from disappearance of one allyl group and of the conjugated double bond, as well as from the presence of a quaternary carbon at 61 ppm and two tertiary carbons at 31.4 and 50.9 ppm (cyclobutane). Analogous photocycloadducts arose from irradiation of **7b**–**7d** (Scheme 4, Table 4).

The stereochemistry of compound **11a** was determined by nOe experiments as indicated in Scheme 4. The relative stereochemistry thus established was accepted for **11b**–**11d** based on comparable NMR data. Dioxenones **12a** and **12b** (minor reaction products) resulted from rearrangements as described for **2**. Structures **9** and **12** were established from relevant NMR spectra (Table 5).

The reaction appeared more efficient in toluene. Cycloadduct **11a** was isolated in 71% yield while the use of acetonitrile delivered the same compound in lower yield. Interestingly, β-lactam **13c** rather than **12c** was isolated from irradiation of **7c** (R=*tert*-Bu). Finally, the efficiency of the process was really affected by the length of the chain; **14f** was the sole product isolated from the irradiation of **7f** (*n*=4). A similar adduct **17**



Scheme 2.



Scheme 3.

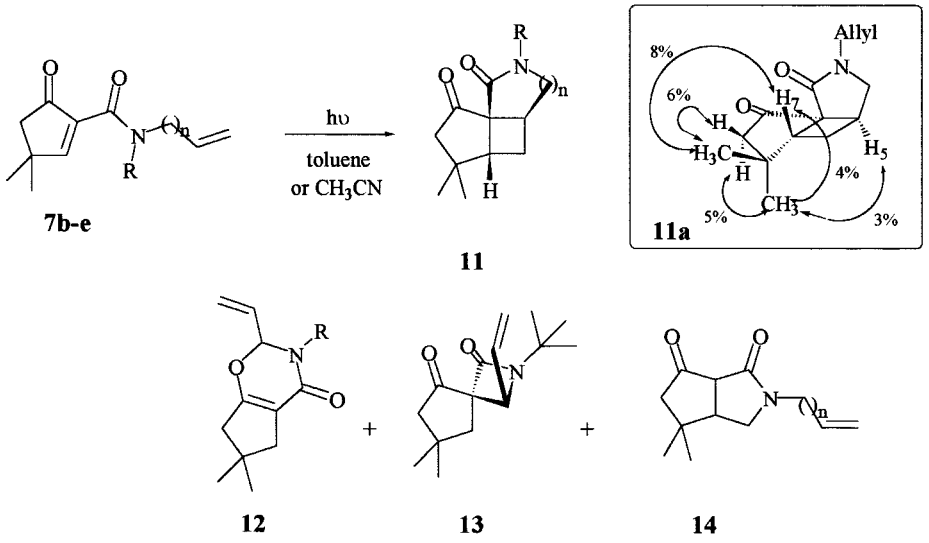
Table 3. Irradiation of amides **2** with cyclopentene

Starting material	R_1	R_2	R_3	R_4	R_5	Irradiation time (h)	Conv. (%)	**8**[a] (%)	**9** (%)	**10** (%)
2a	Et	Et	Et	Me	H	96	74	14	20	
2b	*i*-Pr	*i*-Pr	*i*-Pr	Me	Me	40	100	(a)	–	2
2c	$-(CH_2)_5-$		$-(CH_2)_4-$		H	122	100	31	15	
2d	Et	Et	Et	Me	H	240	100	–	26	–
2e	*i*-Pr	*i*-Pr	–	–	–	104	100	–	–	12
2f	$-(CH_2)_5-$		$-(CH_2)_4-$		H	220	100	–	8	–

[a] **8b** (20%), which could be detected in the reaction mixture from the ^{1}H NMR spectra, could not be isolated in a pure form.

and compound **16** were obtained from oxoamide **15** for which no unsaturated chain were fixed on the nitrogen atom (Scheme 5).

It appears that intramolecular hydrogen abstraction followed by cyclisation of the corresponding biradical intermediates give rise to formation of **14**, **16** and **17**. Abstractions of a δ-hydrogen by the excited carbonyl group is expected to lead to a biradical intermediate such as **Bir1**. Cyclization of the methylene radical site will occur either on the ketyl site to give **16** or at C-3 of the starting cyclopentenone to produce **17** under its enolized form. The high yield of the bicyclic alcohol **16** is in agreement with previous reports on δ-H abstraction processes, especially



Scheme 4.

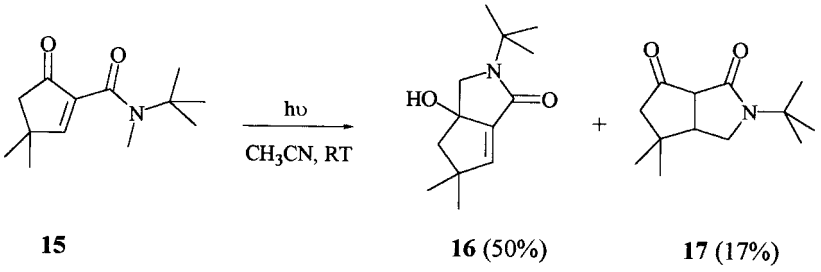
Table 4. Irradiation of amides **7**

Starting compound	N	R	Conversion (%)	**11** (%)[a]	**12** (%)[a]	**13** (%)[a]	**14** (%)[a]
7a	1	Allyl	100 85[b]	71 41[b]	9 14[b]	–	–
7b	1	Me	100	36	4	–	30
7c	1	*tert*-Bu	100	50	–	12	–
7d	2	Me	100	28	–	–	58
7e	3	Me	100	39	[c]	–	26
7f	4	Me	100	[c]		–	46

[a] Yields of isolated compounds.
[b] Reaction in acetonitrile.
[c] Not detected.

Table 5. NMR data of compounds **9** and **12**

Product	H_2 (ppm)	C_2 ppm)	C_4 (ppm)	C_5 (ppm)	C_6 (ppm)
9a	5.39, q, *J*=6.0 Hz	86.5	167.4	109.2	162.6
9b	–	95.0	164.6	108.5	162.8
9c	5.08, dd, *J*=9.5, 4.2 Hz	88.1	168.6	108.7	165.4
9d	5.26, q, *J*=6.0 Hz	83.8	163.8	107.1	160.8
12a	5.58, d, *J*=6.1 Hz	88.9	165.3	108.4	153.2
12b	5.52, d, *J*=6.5 Hz	91.1	165.1	108.3	158.4



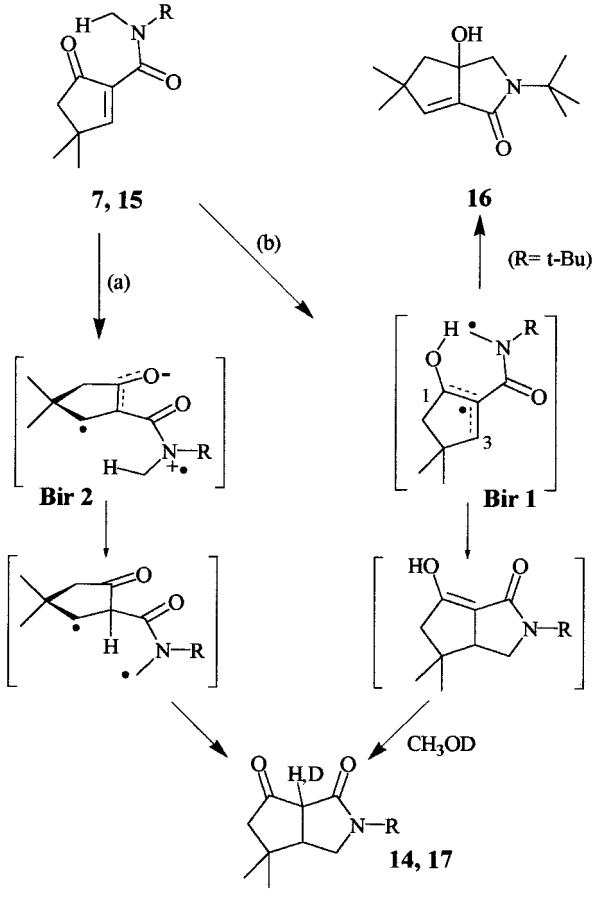
Scheme 5.

important for ortho alkoxy acetophenones,[14] β-alkoxy-[15] and β-alkylamino-ketones.[16] However, another pathway has to be considered to explain the formation of **14** and the surprising hydrogen abstraction from the *N*-methyl group even in the presence of *N*-allyl substituents as in **7b**, **7d**. A direct β-H abstraction from the methyl group by C-2 of the excited enone and cyclization of **Bir2** might also produce **14**. In order to test which of (a) or (b) pathway was really followed by the excited enone in the formation of **14**, we carried out the reaction in CH_3OD (Scheme 6). If an enol intermediate was involved as in path (b), incorporation of a deuterium atom would be expected. When **7b** was irradiated in CH_3OD, until complete disappearance of the starting material, the crude reaction mixture was next examined in ^{13}C NMR, without any purification. No incorporation of deuterium could be detected in **14**. Although the hydrogen atom situated between the keto- and amido-groups is expected to be very acidic, no exchange of this proton of **15** could be detected, in the conditions used for the NMR analysis.

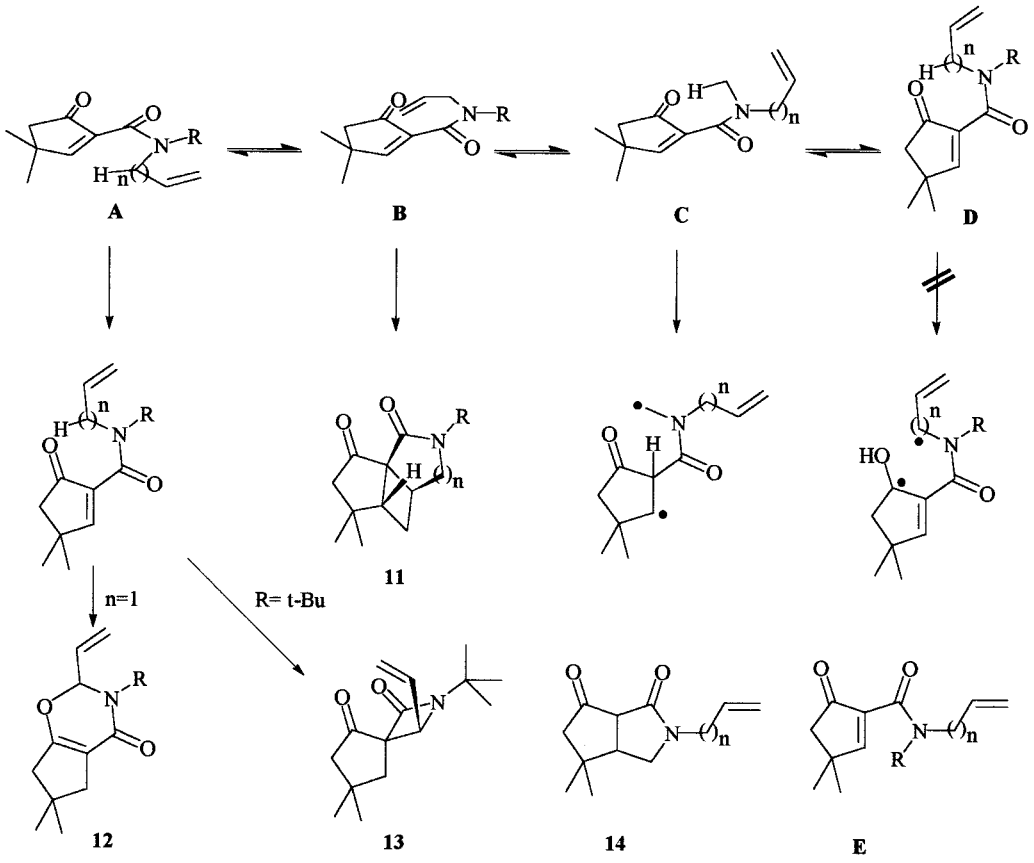
These results seem to exclude an enolic intermediate in the process. The preference for an hydrogen abstraction from the *N*-methyl rather than from the *N*-allyl group was unexpected but might indicate that an electron transfer precedes hydrogen migration, with formation of a radical cation as intermediate. An important increase of acidity is expected for the C–H bonds close to nitrogen radical cations, and migration of the less hindered methyl hydrogen atom would be prefered.[17]

Depending on the nature of the substituents present on the nitrogen atom, several rearranged products involving various intramolecular hydrogen abstraction processes were observed. The competition between δ-H abstraction by the excited carbonyl, γ-H abstraction by the β-carbon and β-H abstraction by the α-carbon of the excited enone, is possible if various conformers of the starting enone are simultaneously present in the excited state. The population of conformers depends on the relative size and the nature of the substituents on the nitrogen and the competition between addition and rearrangement processes might be steered by the conformational equilibrium. Cycloadduct **11** and rearranged products **12**–**14** are expected to result from conformers **A**–**C** respectively, as indicated in Scheme 7.

In order to know if the product distribution during the irradiation of **7b** was determined by the relative stability of the



Scheme 6.



Scheme 7.

products, the relative energy of **11b**, **12b** and **14b** was computed.[18] The intramolecular [2+2] photocycloadduct **11b** was found to be more stable than **12b** and **14b**. PM3 calculations were also performed to verify if the conformers **A**–**E** were available from **7b**. They indicate that conformation **E**, having the two carbonyl groups in a coplanar and head-to-head arrangement, is highly energetic and avoided. All possible conformers appeared to be non planar and very low energy differences were calculated for conformers **A**–**C**. The great proximity between the *N*-methyl hydrogens and C-2 in conformer **C** (2.5 Å) favours a β-H abstraction by the α-carbon of the excited enone. The distance (2.9 Å) of allylic hydrogens and C-3 in conformer **A** makes possible a γ-H abstraction by C-3.[19] Cyclization of the delocalized biradical can produce either the dioxenones or the β-lactam compound.

In conclusion, we have reported that irradiation of unsaturated oxoamides afforded the expected [2+2] photoadducts but also the formation of isomers which resulted from competitive H-abstraction leading to spiranic β-lactams, oxazinones and/or azadiquinane derivatives.

Experimental

General

Solvents were distilled according to standard procedures before use under an argon atmosphere: THF, toluene and diethylether over sodium/benzophenone, methylene chloride over calcium hydride. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 250 spectrometer in chloroform, using tetramethylsilane as internal standard. Chemical shifts are expressed in ppm. IR spectra were recorded on a IR Mirdac spectrometer. Elemental analyses were performed on a CHN 2400 Perkin–Elmer apparatus. Mass spectra were recorded at the Faculty of Pharmacy, University of Reims on a JEOL D300 spectrometer at 70 eV.

Preparation of amides 1

General procedure: To a solution of methyl 2-oxocyclopentane carboxylate (2.00 g, 14.1 mmol) or ethyl 2-oxocyclohexane carboxylate (2.40 g, 14.1 mmol) in toluene (30 ml) were added DMAP (0.516 mg, 4.2 mmol) and the amine (28.2 mmol). The mixture was heated to reflux for 50–84 h. After removal of toluene by distillation under atmospheric pressure, oxoamides **1** were purified by flash-chromatography on silica (EtOAc/Petroleum ether: 40/60).

***N*,*N*-Diethyl-2-oxocyclopentanecarboxamide**: **1a**[20] 65%. ^{1}H NMR: 1.08 (3H, t, *J*=7.2 Hz), 1.15 (3H, t, *J*=7.2 Hz), 1.72–1.89 (1H, m), 2.07–2.35 (4H, m), 2.38–2.50 (1H, m), 3.17–3.64 (5H, m). ^{13}C NMR: 12.9 (CH_3), 14.4 (CH_3), 21.0 (CH_2), 27.6 (CH_2), 38.4 (CH_2), 40.4 (CH_2), 42.1 (CH_2), 51.5 (CH), 168.1 (C=O), 214.6 (C=O). MS: 184 ($M^{+\cdot}$+1, 14), 183 ($M^{+\cdot}$, 26), 128 (56), 72 (85), 58 (100). IR: 2970, 1745, 1635, 1450, 1100 cm^{-1}.

Piperidyl-2-oxocyclopentanecarboxamide: **1b**[21] 66%. ^{1}H NMR: 1.43–1.59 (6H, m), 1.74–1.85 (1H, m), 2.01–2.02 (4H, m), 2.31–2.46 (1H, m), 3.30–3.61 (5H, m). ^{13}C NMR: 20.7 (CH_2), 24.3 (CH_2), 25.3 (CH_2), 26.3 (CH_2), 27.2 (CH_2), 38.2 (CH_2), 42.9 (CH_2), 47.0 (CH_2), 51.3 (CH), 166.5 (C=O), 214.1 (C=O). MS: 196 ($M^{+\cdot}$+1, 48), 195 ($M^{+\cdot}$, 20), 140 (38), 84 (100). IR: 2950, 2860, 1745, 1630, 1440, 1255, 1130, 1015 cm^{-1}. Elemental analysis: Calcd for $C_{11}H_{17}NO_2$: C 67.66, H 8.78, N 7.17. Found: C 67.37, H 9.11, N 6.98.

***N*,*N*-Diisopropyl-2-oxocyclopentanecarboxamide**: **1c** 29%. ^{1}H NMR: 1.15 (3H, t, *J*=6.7 Hz), 1.26 (3H, d, *J*=6.7 Hz), 1.32 (6H, d, *J*=6.7 Hz), 1.73–2.28 (5H, m), 2.35–2.50 (1H, m), 3.35 (1H, t, *J*=8.4 Hz), 3.49 (1H, hept, *J*=6.7 Hz), 4.10 (1H, hept, *J*=6.7 Hz). ^{13}C NMR: 14.0 (CH_3), 20.3 (CH_3), 21.0 ($2CH_3$), 21.1 (CH_2), 27.6 (CH_2), 38.5 (CH_2), 45.9 (CH), 48.8 (CH), 53.0 (CH), 167.5 (C=O), 214.6 (C=O). MS: 212 ($M^{+\cdot}$+1, 48), 211 ($M^{+\cdot}$, 4), 100 (26), 86 (100). IR: 2970, 1745, 1630, 1440, 1340, 1210, 1140, 1040 cm^{-1}. Elemental analysis: Calcd for $C_{12}H_{21}NO_2$: C 68.21, H 10.02, N 6.63. Found: C 68.45, H 10.42, N 6.83.

***N*,*N*-Diisopropyl-2-oxocyclohexanecarboxamide**: **1d** 22%. ^{1}H NMR (d^6-DMSO): 1.12 (3H, d, *J*=6.7 Hz), 1.13 (3H, d, *J*=6.7 Hz), 1.34 (3H, d, *J*=6.7 Hz), 1.39 (3H, d, *J*=6.7 Hz), 1.50–2.37 (7H, m), 2.46–2.50 (1H, m), 3.34–3.44 (2H, m), 3.72 (1H, hept, *J*=6.7 Hz). ^{13}C NMR: 20.4 (CH_3), 20.6 (CH_3), 20.7 (CH_3), 21.0 (CH_3), 23.5 (CH_2), 27.2 (CH_2), 30.6 (CH_2), 41.9 (CH_2), 45.9 (CH), 48.7 (CH), 55.7 (CH), 168.1 (C=O), 207.9 (C=O). MS: 226 ($M^{+\cdot}$+1, 4), 225 ($M^{+\cdot}$, 31), 182 (67), 100 (100), 86 (100), 58 (90). IR: 2960, 2875, 1705, 1630, 1450, 1350, 1320, 1210, 1050 cm^{-1}. Elemental analysis: Calcd for $C_{13}H_{23}NO_2$: C 69.30, H 10.29, N 6.22. Found: C 69.25, H 10.55, N 6.10.

Piperidyl-2-oxocyclohexanecarboxamide: **1e**[22] 94%. ^{1}H-NMR: 1.34–2.32 (13H, m), 2.40–2.59 (1H, m), 3.15–3.19 (2H, m), 3.41–3.57 (3H, m). ^{13}C NMR: 23.3 (CH_2), 24.2 (CH_2), 25.3 (CH_2), 26.0 (CH_2), 26.9 (CH_2), 30.2 (CH_2), 41.6 (CH_2), 42.6 (CH_2), 46.6 (CH_2), 53.9 (CH), 167.5 (C=O), 207.3 (C=O). MS: 210 ($M^{+\cdot}$+1, 8), 209 ($M^{+\cdot}$, 5), 140 (22), 84 (100). IR: 3390, 2945, 2860, 1705, 1640, 1445, 1345, 1190 cm^{-1}. Elemental analysis: Calcd for $C_{12}H_{19}NO_2$: C 68.87, H 9.15, N 6.69. Found: C 69.08, H 9.35, N 6.74.

Morpholyl-2-oxocyclohexanecarboxamide: **1f**[23] 94%. ^{1}H NMR: 1.64–1.87 (2H, m), 1.95–2.39 (5H, m), 2.48–2.58 (1H, m), 3.29–3.33 (2H, m), 3.43–3.69 (6H, m), 3.77–3.85 (1H, m). ^{13}C NMR: 23.5 (CH_2), 26.9 (CH_2), 25.3 (CH_2), 30.0 (CH_2), 41.8 (CH_2), 42.1 (CH_2), 46.1 (CH_2), 53.1 (CH), 66.4 (CH_2), 167.9 (C=O), 207.1 (C=O). MS: 212 ($M^{+\cdot}$+1, 10), 211 ($M^{+\cdot}$, 5), 86 (100). IR: 3390, 2970, 2940, 1705, 1630, 1450, 1430, 1110 cm^{-1}. Elemental analysis: Calcd for $C_{11}H_{17}NO_3$: C 62.54, H 8.11, N 6.63. Found: C 62.39, H 8.33, N 6.59.

Preparation of unsaturated amides 2

General procedure: To a solution of amide **1** (2 mmol) in benzene (23 ml) was added cupric acetate (0.182 g, 1 mmol). After 30 min at rt, lead tetraacetate (0.886 g, 2 mmol) was added. The reaction mixture was stirred overnight at rt. After filtration on florisil and concentration under vacuo, the unsaturated amides **2** were purified by flash-chromatography on silica (EtOAc/petroleum ether: 80/20).

***N*,*N*-Diethyl-2-oxocyclopent-2-enecarboxamide**: **2a** 74%. ^{1}H NMR: 1.02 (3H, t, *J*=7.2 Hz), 1.08 (3H, t, *J*=7.2 Hz), 2.36–2.40 (2H, m), 2.61–2.66 (2H, m), 3.08 (2H, q, *J*=7.2 Hz), 3.36 (2H, q, *J*=7.2 Hz), 7.66 (1H, t, *J*=2.8 Hz). ^{13}C NMR: 12.6 (CH_3), 14.0 (CH_3), 27.0 (CH_2), 34.2 (CH_2), 38.7 (CH_2), 42.6 (CH_2), 143.6 (C^{IV}), 161.9 (CH), 164.1 (C=O), 204.6 (C=O). MS: 182 ($M^{+\cdot}$+1, 17), 181 ($M^{+\cdot}$, 12), 109 (44), 72 (100). IR: 3485, 2975, 1620, 1440, 1285, 1035 cm^{-1}.

Piperidyl-2-oxocyclopent-2-enecarboxamide: **2b** 43%. ^{1}H NMR: 1.46–1.55 (6H, m), 2.38–2.42 (2H, m), 2.63–2.68 (2H, m), 3.14 (2H, t, *J*=5.2 Hz), 3.54 (2H, t, *J*=5.2 Hz), 7.74 (1H, t, *J*=2.7 Hz). ^{13}C NMR: 24.1 (CH_2), 25.2 (CH_2), 26.2 (CH_2), 27.1 (CH_2), 34.3 (CH_2), 42.4 (CH_2), 47.9 (CH_2), 143.3 (C^{IV}), 160.7 (CH), 163.3 (C=O), 204.5 (C=O). MS: 194 ($M^{+\cdot}$+1, 3), 193 ($M^{+\cdot}$, 12), 84 (100). IR: 2945, 1710, 1630, 1445, 1235, 1210, 1030 cm^{-1}.

***N*,*N*-Diisopropyl-2-oxocyclopent-2-enecarboxamide**: **2c** 38%. ^{1}H NMR: 1.10 (6H, d, *J*=6.8 Hz), 1.41 (6H, d, *J*=6.8 Hz), 2.41 (2H, m), 2.66 (2H, m), 3.40 (1H, hept, *J*=6.8 Hz), 3.57 (1H, hept, *J*=6.8 Hz), 7.63 (1H, t, *J*=2.7 Hz). ^{13}C NMR: 20.2 (CH_3), 20.2 (CH_3), 20.6 (CH_3), 20.6 (CH_3), 27.0 (CH_2), 34.2 (CH_2), 45.7 (CH), 51.0 (CH), 145.1 (C^{IV}), 160.8 (CH), 164.1 (C=O), 204.9(C=O). MS: 210 ($M^{+\cdot}$+1, 9), 209 ($M^{+\cdot}$, 10), 166 (62), 109 (100), 100 (89), 86 (100). IR: 1710, 1620, 1450, 1050 cm^{-1}.

***N*,*N*-Diisopropyl-2-oxocyclohex-2-enecarboxamide**: **2d** 34%. ^{1}H NMR: 1.13 (6H, d, *J*=6.8 Hz), 1.45 (6H, d, *J*=6.8 Hz), 2.00–2.10 (2H, m), 2.39–2.50 (4H, m), 3.42 (1H, hept, *J*=6.8 Hz), 3.62 (1H, hept, *J*=6.8 Hz), 6.93 (1H, t, *J*=4.2 Hz). ^{13}C NMR: 20.4 (CH_3), 20.5 (CH_3), 22.4 (CH_2), 25.4 (CH_2), 38.0 (CH_2), 45.6 (CH), 51.0 (CH), 140.5 (C^{IV}), 146.2 (CH), 166.7 (C=O), 195.7 (C=O). MS: 224 ($M^{+\cdot}$+1, 4), 223 ($M^{+\cdot}$, 6), 123 (100), 100 (58). HMRS: Calcd for $C_{13}H_{21}NO_2$: 223.1567. Found: 223.1572. IR: 3690, 3610, 2975, 1670, 1445, 1370, 1215, 1020 cm^{-1}. UV(CH_2Cl_2) ε_{227}=5000, ε_{252}=2300, ε_{366}=27. Elemental analysis: Calcd for $C_{13}H_{21}NO_2$: C 69.92, H 9.48, N 6.27. Found: C 69.19, H 8.10, N 5.81.

Piperidyl-2-oxocyclohex-2-enecarboxamide: **2e** 30%. ^{1}H NMR: 1.46–1.60 (6H, m), 1.89–2.05 (2H, m), 2.36–2.46 (4H, m), 3.52–3.57 (2H, m), 7.00 (1H, t, *J*=4.0 Hz). ^{13}C NMR: 22.2 (CH_2), 24.2 (CH_2), 25.2 (CH_2), 25.4 (CH_2), 26.0 (CH_2), 37.8 (CH_2), 42.3 (CH_2), 48.0 (CH_2), 138.6 (C^{IV}), 148.5 (CH), 165.6 (C=O), 195.3 (C=O). MS: 208 ($M^{+\cdot}$+1, 32), 207 ($M^{+\cdot}$, 28), 179 (16), 84 (100). HMRS: Calcd for $C_{12}H_{17}NO_2$: 207.1255. Found: 207.1259. IR: 3690, 3020, 2945, 1680, 1470, 1445, 1210 cm^{-1}. UV(CH_2Cl_2) ε_{228}=5100, ε_{305}=2500, ε_{366}=27.

Morpholyl-2-oxocyclohex-2-enecarboxamide: **2f** 24%. ^{1}H NMR: 2.01–2.09 (4H, m), 2.44–2.50 (4H, m), 3.21 (2H, t, *J*=4.8 Hz), 3.61 (2H, t, *J*=4.8 Hz), 3.65–3.69 (2H, m), 7.12 (1H, t, *J*=4.0 Hz). ^{13}C NMR: 22.2 (CH_2), 25.6 (CH_2), 37.8 (CH_2), 42.0 (CH_2), 47.3 (CH_2), 66.6 ($2CH_2$), 138.0 (C^{IV}),

150.2 (CH), 165.8 (C═O), 195.3 (C═O). MS: 210 ($M^{+\cdot}$+1, 37), 209 ($M^{+\cdot}$, 84), 181 (49), 123 (100). HMRS: Calcd for $C_{11}H_{15}NO_3$: 209.1048. Found: 209.1052.

Preparation of amides 7

4,4-Dimethyl-2-methoxycarbonyl-2-phenylselanylcyclopentan-1-one: **4** To a solution of 4,4-dimethyl-2-methoxycarbonyl-cyclopentan-1-one **3**[24] (4.05 g, 23.8 mmol) in methylene chloride (15 ml) was added at 0°C, pyridine (2.3 ml, 28.6 mmol). After 5 min, a solution of phenylselenyl bromide (6.74 g, 28.6 mmol) in methylene chloride (5 ml) was added dropwise. After complete transformation (TLC), the reaction mixture was quenched with a saturated aqueous solution of ammonium chloride (10 ml) and extracted twice with ethyl acetate (20 ml). The organic layer was washed with water and dried over $MgSO_4$. After concentration, the product was purified by flash-chromatography on silica (EtOAc/hexane: 10/90) giving **4** as an oil (5.54 g). 72%. ^{1}H NMR: 1.00 (3H, s); 1.12 (3H, s); 2.03 ($1H_{AB}$, J_{AB}=14.5 Hz); 2.20 (2H, s); 3.68 (3H, s); 2.61 ($1H_{AB}$, J=14.5 Hz); 7.30–7.47 (3H, m); 7.60–7.68 (2H, m). ^{13}C NMR: 28.6 (CH_3); 29.2 (CH_3); 33.9 (C); 47.6 (CH_2); 52.1 (CH_2); 52.8 (OCH_3); 56.8 (C); 127.0 (C); 128.7 (CH); 129.5 (CH); 137.4 (C); 170.0 (CO_2); 208.8 (C═O). MS: 326 (M^++1, 100); 211(47); 183 (62); 157 (100); 137 (43); 83 (72), 77 (90). IR: 2955; 1720; 1440; 1250 cm^{-1}.

3,3-Dimethyl-5-oxo-1-cyclopentene-1-carboxylic acid methyl ester: **5** To a solution of **4** (5.54 g, 17.0 mmol) in methylene chloride (10 ml) was added (by small amounts) at 0°C, m-CPBA (6.76 g, 3.2 mmol). After 3 h, water (4 ml) was added and the mixture was extracted with methylene chloride. The organic layers were washed with brine and dried over $MgSO_4$. Removal of the solvent gave **5**, which was used without purification. ^{1}H NMR: 1.28 (6H, s); 2.43 (2H, s); 3.83 (3H, s); 8.14 (1H, s). ^{13}C NMR: 27.4 ($2CH_3$); 39.0 (C); 51.2 (CH_2); 52.0 (OCH_3); 162.4 (C^{IV}); 170.4 (CO_2); 180.3 (CH); 202.6 (C═O).

3,3-Dimethyl-5-oxo-1-cyclopentene carboxylic acid: **6** Methyl ester **5** (3.06 g, 17 mmol) was added to an aqueous 0.5 M NaOH solution (110 ml) and the mixture was stirred overnight at rt. After extraction with methylene chloride and acidification to pH 2, the acid was extracted with methylene chloride. The organic layers were dried over $MgSO_4$, filtered and concentrated under vacuo. Acid **6** (2.01 g) was used without further purification. ^{1}H NMR: 1.34 (6H, s); 2.57 (2H, s); 8.41 (1H, s). ^{13}C NMR: 27.0 ($2CH_3$); 40.0 (C); 50.3 (CH_2); 161.9(C^{IV}); 170.0 (CO_2H); 183.5 (CH); 208.5 (C═O).

Synthesis of *N*-alkenyl-*N*-alkyl-oxocarboxamides 7

General procedure: To a solution of **6** (2.75 g, 17.8 mmol) in methylene chloride (13 ml) were added DMAP (0.110 g, 0.9 mmol) and the amine (19.6 mmol). After cooling to 0°C, dicyclohexylcarbodiimide (3.86 g, 18.7 mmol) dissolved in the same solvent was added dropwise. After 10 min, the cooling bath was removed, the solution was allowed to warm up to rt and was stirred overnight. After filtration and washing of the urea with DCM, the solution was concentrated. Amides **7** were purified by flash chromatography on silica. (EtOAc/hexane: 50/50).

***N*,*N*-Bisallyl-(3,3-dimethyl-5-oxo-1-cyclopentene)-carboxamide**: **7a** Obtained as an oil in 61%. ^{1}H NMR: 1.20 (6H, s), 2.31 (2H, s), 3.77 (2H, d, J=5.6 Hz), 4.06 (2H, d, J=5.6 Hz), 5.09–5.26 (4H, m), 5.66 (2H, m), 7.50 (1H, s). ^{13}C NMR: 27.5 ($2CH_3$), 39.8 (C), 46.6 (CH_2), 50.0 (CH_2), 50.2 (CH_2), 117.4 (CH_2), 117.5 (CH_2), 132.2 (CH), 133.2 (CH), 139.8 (C^{IV}), 164.5 (OCN), 170.8 (CH), 203.9 (C═O). IR: 2960, 1715, 1645, 1625, 1415, 1305 cm^{-1}. MS *m/z*: 234 (70, $M^{+\cdot}$+1), 233 ($M^{+\cdot}$, 85), 192 (82), 137 (87), 96 (83), 69 (100). HRMS: Calcd for $C_{14}H_{19}NO_2$: 233.1411. Found: 233.1416. UV (CH_2Cl_2): ε_{229}=5800, ε_{366}=10.

***N*-Allyl-*N*-methyl-(3,3-dimethyl-5-oxo-cyclopentene)-carboxamide**: **7b** Obtained as an oil in 44% (2 rotamers) 50/50 at RT. ^{1}H NMR: Rotamer 1: 1.27 (6H, s), 2.38 (2H, s), 2.85 (3H, s), 3.77 (2H, dt, J=5.7, 1.5 Hz), 5.13–5.32 (2H, m), 5.68–5.88 (1H, m), 7.50 (1H, s). Rotamer 2: 1.30 (6H, s), 2.39 (2H, s), 2.98 (3H, s), 4.08 (2H, dt, J=6.1, 1.5 Hz), 5.13–5.32 (2H, m), 5.68–5.88 (1H, m), 7.58 (1H, s). ^{13}C NMR: Rotamer 1: 27.3 ($2CH_3$), 32.1 (CH_3), 39.6 (C), 49.1 (CH_2), 49.9 (CH_2), 117.2 (CH_2), 131.8 (CH), 139.4 (C), 164.0 (NCO), 170.7 (CH), 203.6 (C═O). Rotamer 2: 27.3 ($2CH_3$), 35.3 (CH_3), 39.6 (C), 49.8 (CH_2), 52.9 (CH_2), 117.4 (CH_2), 132.7 (CH), 139.9 (C), 164.4 (NCO), 171.6 (CH), 203.9 (C═O). IR: 2960, 2930, 1710, 1625, 1485, 1465, 1400, 1305 cm^{-1}. MS *m/z*: 208 (100, $M^{+\cdot}$+1), 207 ($M^{+\cdot}$, 45), 192 (7), 137 (23), 110 (15), 70 (100). HRMS: Calcd for $C_{12}H_{19}NO_2$: 207.1255. Found: 207.1259. UV (CH_2Cl_2): ε_{230}=6300, ε_{327}=300, ε_{366}=80.

***N*-Allyl-*N*-*t*-butyl-(3,3-dimethyl-5-oxo-cyclopentene)-carboxamide**: **7c** Obtained in 70% from **6** as a mixture of 2 rotamers (4/96). ^{1}H NMR: Rotamer 1: 1.22 (6H, s), 1.49 (9H, s), 2.32 (2H, s), 3.84–3.87 (2H, m), 5.09–5.17 (2H, m), 5.76 (1H, ddt, J=16.8, 10.7, 4.9 Hz), 7.33 (1H, s). Rotamer 2: 1.22 (6H, s), 1.49 (9H, s), 2.32 (2H, s), 3.84–3.87 (2H, m), 5.09–5.17 (2H, m), 5.76 (1H, ddt, J=16.8–10.7–4.9 Hz), 7.47 (1H, s). ^{13}C NMR: 27.6 ($2CH_3$), 28.5 (CH_3), 39.6 (C), 48.5 (CH_2), 50.0 (CH_2), 57.7 (C), 115.9 (CH_2), 136.5 (CH), 142.0 (C), 165.9 (NCO), 168.2 (CH), 204.5 (C═O). IR: 2965, 2930, 1870, 1720, 1640, 1610, 1450, 1395, 1375, 1365, 1295, 1225, 1200, 925 cm^{-1}. MS *m/z*: 250 (4, $M^{+\cdot}$+1), 249 (17, $M^{+\cdot}$), 234 (11), 192 (42), 137 (100), 69 (79). HRMS: Calcd for $C_{15}H_{23}NO_2$: 249.1723. Found: 249.1729. Elemental analysis: Calcd for $C_{15}H_{23}NO_2$: C, 72.25, H, 9.30, N, 5.62. Found: C, 71.71, H, 9.40, N, 5.76. UV (CH_2Cl_2): ε_{270}=370, ε_{366}=9.

***N*-But-3-enyl-*N*-methyl-(3,3-dimethyl-5-oxo-cyclopentene)-carboxamide**: **7d** Obtained in 64% as an oil (mixture of 2 rotamers). ^{1}H NMR: Rotamer 1: 1.27 (6H, s), 2.23–2.39 (2H, s), 2.36 (2H, s), 2.87 (3H, s), 3.22 (2H, t, J=7.2 Hz), 5.01–5.04 (2H, m), 5.64 (1H, ddt, J=17.2, 10.3 and 6.9 Hz), 7.48 (1H, s). Rotamer 2: 1.27 (6H, s), 2.23–2.39 (2H, m), 2.36 (2H, s), 2.99 (3H, s), 3.51 (2H, t, J=7.2 Hz), 5.01–5.14 (2H, m), 5.82 (1H, ddt, J=17.0, 10.1 and 6.9 Hz), 7.51 (1H, s). ^{13}C NMR: Rotamer 1: 27.1 ($2CH_3$), 30.9 (CH_2), 31.9 (CH_3), 39.3 (C^{IV}), 46.0 (CH_2), 49.5 (CH_2), 116.1 (CH_2), 133.6 (CH), 139.5 (C^{IV}), 163.5 (C═O), 170.5 (CH), 203.2 (C═O). Rotamer 2: 27.1 ($2CH_3$), 32.1 (CH_2), 35.7 (CH_3),

39.3 (C^{IV}), 46.0 (CH_2), 49.5 (CH_2), 116.8 (CH_2), 134.5 (CH), 139.8 (C^{IV}), 164.0 (C=O), 170.8 (CH), 203.5 (C=O). IR: 2960, 2930, 1710, 1625, 1485, 1435, 1405, 1305 cm^{-1}. MS *m/z*: 222 ($M^{+\cdot}$+1, 24), 221($M^{+\cdot}$, 23), 180 (15), 137 (33), 83 (100), 69 (38). HRMS: Calcd for $C_{13}H_{19}NO_2$: 221.1411. Found: 221.1416. UV (CH_2Cl_2): ε_{229}=5700, ε_{366}=7.

***N*-Methyl-*N*-pent-4-enyl-(3,3-dimethyl-5-oxo-cyclopentene)-carboxamide**: **7e** Obtained in 51% as an oil (mixture of 2 rotamers). ^{1}H NMR: Rotamer 1: 1.28 (6H, s), 1.58–1.75 (2H, m), 1.94–2.02 (2H, m), 2.37 (2H, s), 2.88 (3H, s), 3.15 (2H, t, *J*=7.6 Hz), 4.96–5.08 (2H, m), 5.72 (1H, ddt, *J*=16.8, 10.3, 6.9 Hz), 7.47 (1H, s). Rotamer 2: 1.28 (6H, s), 1.58–1.75 (2H, m), 2.07–2.15 (2H, m), 2.37 (2H, s), 2.99 (3H, s), 3.45 (2H, t, *J*=7.4 Hz), 4.96–5.08 (2H, m), 5.84 (1H, ddt, *J*=16.8, 10.3, 6.5 Hz), 7.54 (1H, s). ^{13}C NMR: Rotamer 1: 26.1 (CH_2), 27.7 ($2CH_3$), 30.5 (CH_2), 32.4 (CH_3), 39.9 (C), 46.7 (CH_2), 50.1 (CH_2), 114.9 (CH_2), 137.1 (CH), 140.2 (C^{IV}), 164.5 (C=O), 170.9 (CH), 204.0 (C=O). Rotamer 2: 27.3 (CH_2), 27.7 ($2CH_3$), 30.7 (CH_2), 36.1 (CH_3), 39.9 (C), 50.1 (CH_2), 50.2 (CH_2), 115.6 (CH_2), 137.8 (CH), 140.3 (C^{IV}), 164.5 (C=O), 171.7 (CH), 204.2 (C=O). IR: 2960, 2920, 2860, 1720, 1645, 1455, 1405, 1395, 1305 cm^{-1}. MS *m/z*: 236 (7, $M^{+\cdot}$+1), 235(10, $M^{+\cdot}$), 220 (14, $M^{+\cdot}$–CH_3), 166 (16), 151 (15), 137 (100), 98 (74), 69 (94). HRMS: Calcd for $C_{14}H_{21}NO_2$: 235.1567. Found: 235.1572. UV (CH_2Cl_2): ε_{270}=150, ε_{366}=12.

***N*-Hex-5-enyl-*N*-methyl-(3,3-dimethyl-5-oxo-cyclopentene)-carboxamide**: **7f** Obtained as an oil in 92%. ^{1}H NMR: Rotamer 1: 1.28 (6H, s), 1.42–1.62 (4H, m), 2.37 (2H, s), 2.86 (3H, s), 3.14 (2H, t, *J*=7.4 Hz), 4.95–5.06 (2H, m), 5.67–5.89 (1H, m), 7.48 (1H, s). Rotamer 2: 1.28 (6H, s), 1.42–1.62 (4H, m), 2.38 (2H, s), 2.99 (3H, s), 3.45 (2H, t, *J*=7.2 Hz), 4.95–5.06 (2H, m), 5.67–5.89 (1H, m), 7.54 (1H, s). ^{13}C NMR: Rotamer 1: 25.6 (CH_2), 27.6 ($2CH_3$), 32.3 (CH_3), 33.0 (CH_2), 39.7 (C), 46.8 (CH_2), 50.0 (CH_2), 50.4 (CH_2), 114.5 (CH_2), 137.7 (CH), 140.2 (C), 164.3 (NCO), 170.8 (CH), 203.8 (C=O). Rotamer 2: 26.1 (CH_2), 27.6 ($2CH_3$), 33.2 (CH_2), 35.9 (CH_3), 39.7 (C), 46.8 (CH_2), 50.1 (CH_2), 50.4 (CH_2), 114.9 (CH_2), 138.3 (CH), 140.5 (C), 164.3 (NCO), 171.4 (CH), 204.0 (C=O). IR: 2935, 1720, 1645, 1455, 1405, 1305 cm^{-1} MS *m/z*: 250 (13, $M^{+\cdot}$+1), 249(18, $M^{+\cdot}$), 234 (20), 166 (20), 137 (100), 112 (63), 69 (79). HRMS: Calcd for $C_{15}H_{23}NO_2$: 249.1723. Found: 249.1729. UV (CH_2Cl_2): ε_{270}=180, ε_{366}=5.

***N*-*t*-Butyl-*N*-methyl,-(3,3-dimethyl-5-oxo-cyclopentene)-carboxamide**: **15** Obtained in 76% (one rotamer). ^{1}H NMR: 1.27 (9H, s), 1.47 (6H, s), 2.36 (3H, s), 7.52 (1H, s). ^{13}C NMR: 27.7 ($2CH_3$), 27.9 ($3CH_3$), 33.8 (CH_3), 39.5 (C), 49.1 (CH_2), 57.0 (C), 142.7 (C), 165.2 (NCO), 171.2 (CH), 203.9 (CO). IR: 2960, 1705, 1625, 1385 cm^{-1}. MS *m/z*: 224 (5, $M^{+\cdot}$+1), 223 (19, $M^{+\cdot}$), 208 (51), 168 (13), 137 (100), 110 (10), 69 (88). HRMS: Calcd for $C_{15}H_{23}NO_2$: 249.1723. Found: 249.1729. Elemental analysis: Calcd for $C_{13}H_{21}NO_2$: C 69.92, H 9.48, N 6.27. Found: C 69.56, H 9.65, N 6.31. UV (CH_2Cl_2): ε_{269}=430, ε_{366}=6.

Intermolecular photocycloadditions

General procedure: A solution of amides **2** (0.25 mmol) and cyclopentene (1.5 ml, 16 mmol) in acetonitrile (15 ml) was deoxygenated under argon during 15 min and irradiated at 366 nm until consumption of the starting material. After concentration, the crude mixture was purified by preparative TLC (EtOAc/hexane: 80/20).

1-(*N*,*N*-Diethyl)-10-oxotricyclo[5.3.0.0^{2,6}]decanecarboxamide: **8a** Viscous oil, 14%. ^{1}H NMR: 1.15 (3H, t, *J*=6.8 Hz), 1.26 (3H, t, *J*=6.8 Hz), 1.38–1.87 (6H, m), 1.90–1.96 (1H, m), 2.10–2.26 (1H, m), 2.46–2.58 (1H, m), 2.52 and 2.85 (AB, J_{AB}=6.5 Hz, 2H), 2.75–2.91 (1H, m), 3.11 (1H, t, *J*=6.1 Hz), 3.33 and 3.66 (AB, J_{AB}=11.2 Hz, 1H, q, *J*=6.8 Hz and 1H, q, *J*=6.8 Hz), 3.34 and 3.67 (AB, J_{AB}=15.4 Hz, 1H, q, *J*=6.8 Hz and 1H, q, *J*=6.8 Hz). ^{13}C NMR: 12.5 (CH_3), 13.9 (CH_3), 24.9 (CH_2), 25.7 (CH_2), 29.3 (CH_2), 32.6 (CH_2), 37.8 (CH_2), 38.8 (CH_2), 40.0 (CH), 42.2 (CH_2), 44.6 (CH), 45.2 (CH), 59.0 (C), 166.9 (C), 217.2 (C). MS *m/z*: 250 (9, $M^{+\cdot}$+1), 249(4, $M^{+\cdot}$), 182 (100), 149 (18), 108 (32), 72 (93). HRMS: Calcd for $C_{15}H_{23}NO_2$: 249.1723. Found: 249.1729.

1-Piperidinyl-10-oxotricyclo[5.3.0.0^{2,6}]decanecarboxamide: **8c** 31%. ^{13}C NMR: 24.4 (CH_2), 25.0 (CH_2), 25.6 (CH_2), 25.7 (CH_2), 26.2 (CH_2), 29.4 (CH_2), 32.4 (CH_2), 37.6 (CH_2), 39.9 (CH), 43.2 (CH_2), 44.7 (CH), 45.1 (CH), 47.5 (CH_2), 59.0 (C), 166.1 (NCO), 217.2 (C=O). MS *m/z*: 262 ($M^{+\cdot}$+1, 3), 261 ($M^{+\cdot}$, 11), 194 (100), 149 (13), 109 (28).

3-Ethyl-4-methyl-2-oxo-5-oxa-3-azabicyclo[3.4]non-1-ene: **9a** 20%. ^{1}H NMR: 1.14 (3H, t, *J*=7.1 Hz), 1.58 (3H, d, *J*=5.8 Hz), 1.89–2.03 (2H, m), 2.43–2.59 (4H, m), 3.19 and 3.68 (AB, J_{AB}=13.9 Hz, 1H, q, *J*=7.1 Hz and 1H, q, *J*=7.1 Hz), 5.39 (1H, q, *J*=2.8 Hz). ^{13}C NMR: 14.2 (CH_3), 18.2 (CH_3), 19.8 (CH_2), 25.9 (CH_2), 31.1 (CH_2), 36.7 (CH_2), 86.5 (CH), 109.2 (C^{IV}), 162.6 (C–O), 167.4 (NC=O). IR: 1660, 1630, 1430 cm^{-1}. MS *m/z*: 182 (12, $M^{+\cdot}$+1), 181(18, $M^{+\cdot}$), 110 (50), 56 (100). HRMS: Calc for $C_{10}H_{15}NO_2$: 181.1099. Found: 181.1103.

2-Oxo-9-oxa-3-azatricyclo[8.3.0.0.^{3,8}]tridec-1-ene: **9c** 15%. ^{1}H NMR: 1.10–2.20 (8H, m), 2.40–2.70 (5H, m), 4.20–4.30 (1H, m), 5.08 (1H, dd, *J*=9.5 and 4.2 Hz). ^{13}C NMR: 19.8 (CH_2), 21.3 (CH_2), 23.5 (CH_2), 26.0 (CH_2), 30.8 (CH_2), 31.2 (CH_2), 88.1 (CH), 108.7 (C^{IV}), 165.4 (C–O), 168.6 (C=O). IR: 2930, 1660, 1635, 1440, 1430, 1210 cm^{-1}.

3-Ethyl-4-methyl-2-oxo-5-oxa-3-azabicyclo[4.4]dec-1-ene: **9d** Oil, 26%. ^{1}H NMR: 1.15 (3H, t, *J*=7.1 Hz), 1.55 (3H, d, *J*=6.0 Hz), 1.61–1.70 (4H, m), 2.11–2.15 (2H, m), 2.26–2.29 (2H, m), 3.19 (1H, d, J_{AB}=14.1 Hz), 3.68 (1H, d, J_{AB}=14.1 Hz), 5.26 (1H, q, *J*=6.0 Hz). ^{13}C NMR: 14.0 (CH_3), 18.1 (CH_3), 21.4 (CH_2), 22.0 (CH_2), 22.1 (CH_2), 27.2 (CH_2), 36.9 (CH_2), 83.8 (CH), 107.1 (C^{IV}), 160.8 (C–O), 163.7 (NC=O). IR: 3000, 2935, 1665, 1630, 1480, 1430, 1210 cm^{-1}. MS *m/z*: 196 ($M^{+\cdot}$+1, 23), 195 ($M^{+\cdot}$, 41), 180 (37), 125 (40), 56 (100).

3,3-Dimethyl-2-isopropyl-1,5-dioxo-2-azaspiro[3.4]octane: **10b** Oil, 2%. ^{1}H NMR: 1.24–1.46 (12H, m); 1.50–2.45 (6H, m); 3.49–3.68 (1H, m). ^{13}C NMR: 19.8 (CH_2), 21.8 ($2CH_3$); 21.9 (CH_3); 25.1 (CH_3); 27.8 (CH_2); 38.9 (CH_2); 44.3 (CH);61.8 (C^{IV}); 71.3 (C^{IV}); 165.8 (C=O); 213.4 (C=O). IR: 1745, 1720, 1215 cm^{-1}.

3,3-Dimethyl-2-isopropyl-1,5-dioxo-2-azaspiro[3.5]nonane: **10e** 12%. ^{1}H NMR: 1.32 (3H, d, J=6.9 Hz); 1.34 (3H, d, J=6.9 Hz); 1.37 (3H, s); 1.45 (3H, s); 1.47–2.24 (7H, m); 2.60–2.70 (1H, m); 3.50 (1H, hept, J=6.9 Hz). ^{13}C NMR: 21.9 ($2CH_3$); 22.3 (CH_2); 22.4 (CH_3); 23.5 (CH_3); 26.5 (CH_2); 29.8 (CH_2); 42.4 (CH_2); 43.8 (CH); 62.6 (C); 71.9 (C); 166.0 (C=O); 207.4 (C=O). IR: 3020, 1745, 1700, 1335, 1220 cm^{-1}. MS *m/z*: 224 ($M^{+\cdot}$+1, 7), 208 (17), 138 (100), 123 (61), 110 (49), 95 (59), 67 (64).

Intramolecular [2+2] photocycloaddition

A solution of ketoamides **7** (0.84 mmol) in toluene (24 ml) previously deoxygenated under argon was irradiated at 366 nm until complete consumption of starting material (16–18 h). The solvent was removed by concentration and the crude mixture was purified by preparative TLC (EtOAc/hexane: 60/40).

3-Allyl-8.8-dimethyl-2.10-dioxo-3-azatricyclo[5.3.0.0$^{1.5}$] decane: **11a** Solid, 71%. ^{1}H NMR: 1.07 (3H, s), 1.12 (3H, s), 2.04 (1H, ddd, J_{AB}=13.2 Hz, J=4.0 Hz and 9.2 Hz), 2.18 (1H, dd, J_{AB}=17.0 Hz, J=1.0 Hz), 2.49 (1H, ddd, J_{AB}= 13.2 Hz, J=6.2 Hz and 8.4 Hz), 2.64 (1H, dd, J_{AB}= 17.0 Hz, J=1.0 Hz), 2.69–2.80 (2H, m), 3.32 (1H, dd, J_{AB}=10.0 Hz, J=3.8 Hz) 3.65 (1H, dd, J_{AB}=10.0 Hz, J=9.8 Hz), 3.84 (1H, ddt, J_{AB}=15.2 Hz, J=6.2 Hz and 1.3 Hz), 4.02 (1H, ddt, J_{AB}=15.2 Hz, J=6.0 Hz and 1.3 Hz), 5.18–5.26 (2H, m), 5.76 (1H, ddt, J=17.4 Hz, 9.8 Hz and 6.1 Hz). ^{13}C NMR: 22.4 (CH_3), 26.6 (CH_2), 28.1 (CH_3), 31.4 (CH), 36.9 (C^{IV}), 45.4 (CH_2), 50.9 (CH), 51.1 (CH_2), 53.2 (CH_2), 61.0 (C^{IV}), 171.0 (C=O), 212.8 (C=O). IR: 2960, 1745, 1680, 1445 cm^{-1}. MS *m/z*: 234 ($M^{+\cdot}$+1, 12), 233 ($M^{+\cdot}$, 60), 164 (100), 137 (20), 69 (73). Elemental analysis calcd for $C_{14}H_{19}NO_2$: C 72.07, H 8.21, N 6.00. Found: C 72.26, H 8.22, N 6.06.

3,8,8-Trimethyl-2.10-dioxo-3-azatricyclo[5.3.0.0$^{1.5}$] decane: **11b** Oil, 36%. ^{1}H NMR: 1.05 (3H, s), 1.11 (3H, s), 2.04 and 2.48 (AB, J_{AB}=13.2 Hz, 1H, dd, J=9.2, 4.0 Hz and 1H, dd, J=8.4, 6.3 Hz), 2.16 and 2.64 (AB, J_{AB}=17.2 Hz, 2H), 2.68–2.83 (2H, m), 2.88 (3H, s), 3.34 and 3.69 (AB, J_{AB}=9.9 Hz, 1H, J=4.0 Hz and 1H, d, J=9.7 Hz). ^{13}C NMR: 22.4 (CH_3), 26.6 (CH_2), 28.1 (CH_3), 29.8 (CH_3), 31.4 (CH), 36.9 (C), 50.7 (CH), 51.0 (CH_2), 55.9 (CH_2), 60.7 (C), 171.2 (C), 213.1 (C). IR: 2945, 1740, 1680, 1505, 1405, 1330, 1265, 1155. MS *m/z*: 208 (30, $M^{+\cdot}$+1), 207 (100, $M^{+\cdot}$), 192 (57), 178 (19), 164 (52), 139 (50), 124 (69), 70 (100). HRMS: Calcd for $C_{12}H_{17}NO_2$: 207.1255. Found: 207.1259.

3-*t*-Butyl-8.8-dimethyl-2.10-dioxo-3-azatricyclo[5.3.0.0$^{1.5}$] decane: **11c** Solid, 50%. ^{1}H NMR: 1.05 (3H, s), 1.10 (3H, s), 1.43 (9H, s), 2.00 and 2.44 (AB, J_{AB}=13.2 Hz, 1H, dd, J=8.9–3.8 Hz and 1H, dd, J=8.2–6.3 Hz), 2.14 and 2.61 (AB, J_{AB}=17.2 Hz, 1H, d, J=1.1 Hz and 1H), 3.9 Hz and 1H, d, J=9.7 Hz). ^{13}C NMR: 22.3 (CH_3), 26.5 (CH_2), 27.4 ($3CH_3$), 27.9 (CH_3), 30.4 (CH), 36.6 (C), 50.7 (CH), 51.0 (CH_2), 52.2 (CH_2), 54.3 (C), 62.1 (C), 171.6 (C), 214.0 (C). IR: 2960, 1745, 1665, 1465, 1405, 1290, 1230 cm^{-1}. MS *m/z*: 250 (7, $M^{+\cdot}$+1), 249 (35, $M^{+\cdot}$), 234 (100), 206 (55), 137 (16). HRMS: Calcd for $C_{15}H_{23}NO_2$: 249.1723. Found: 249.1729.

3,10,10-Trimethyl-2.12-dioxo-3-azatricyclo[7.3.0.0$^{1.5}$] dodecane: **11e** 39%. ^{1}H NMR: 1.07 (3H, s), 1.08 (3H, s), 1.26–1.41 (1H, m), 1.54–1.91 (4H, m), 2.08–2.26 (2H, m), 2.09 (1H, dd, J_{AB}=16.9 Hz, J=1.2 Hz),), 2.76 (1H, dd, J_{AB}=16.9 Hz, J=1.2 Hz), 2.91–3.03 (2H, m), 2.99 (3H, s), 3.81–3.94 (1H, m). ^{13}C NMR: 22.1 (CH_3), 22.7 (CH_2), 24.2 (CH_3), 27.6 (CH_2), 29.2 (CH_3), 34.6 (CH_2), 36.4 (C^{IV}), 36.6 (CH_2), 46.5 (CH), 48.1 (CH_2), 50.6 (CH), 63.9 (C^{IV}), 169.0 (C=O), 214.0 (C=O). IR: 2935, 1730, 1630, 1455, 1265, 1140 cm^{-1}. MS *m/z*: 236 ($M^{+\cdot}$+1, 6), 235 ($M^{+\cdot}$, 27), 220 (32), 207 (31), 192 (30), 152 (100). Elemental analysis calcd for $C_{14}H_{21}NO_2$: C 71.46, H 9.00, N 5.95. Found: C 71.46, H 9.30, N 6.08.

3-Allyl-8,8-dimethyl-2-oxo-4-vinyl-5-oxa-3-azabicyclo[3,4]-non-1-ene: **12a** Oil, 9%. ^{1}H NMR: 1.14 (3H, s), 1.15 (3H, s), 2.10–2.45 (4H, m), 3.52 (1H, ddt, J_{AB}=16.0 Hz, J=6.6 and 1.2 Hz), 4.51–4.52 (1H, ddt, J_{AB}=16.0 Hz, J=4.7 and 1.7 Hz), 5.14–5.25 (2H, m), 5.31–5.44 (2H, m), 5.58 (1H, d, J=6.1 Hz), 6.04 (1H, ddd, J=17.5, 9.9 and 6.1 Hz). ^{13}C NMR: 29.9 (CH_3), 30.1 (CH_3), 36.6 (C^{IV}), 41.1 (CH_2), 44.6 (CH_2), 46.2 (CH_2), 88.9 (C^{IV}), 108.4 (C^{IV}), 117.3 (CH_2), 120.5 (CH_2), 131.5 (CH), 133.4 (CH), 153.2 (C-O), 165.3 (C=O). IR: 2955, 2930, 2870, 1670, 1455, 1415 cm^{-1}. UV (CH_2Cl_2): ε_{229}=5500, ε_{263}=2700, ε_{366}=8. MS *m/z*: 234 ($M^{+\cdot}$+1, 5), 233 ($M^{+\cdot}$, 28), 218 (9), 205 (13), 192 (10), 149 (100), 138 (37), 123 (34). HRMS: Calcd for $C_{14}H_{19}NO_2$: 233.1411. Found: 233.1416.

3,10,10-Trimethyl-2-oxo-4-vinyl-5-oxa-3-azabicyclo[3,4]-non-1-ene: **12b** Oil, 4%. ^{1}H NMR: 1.14 (3H, s), 1.15 (3H, s), 2.29–2.37 (4H, m), 2.90 (3H, s), 5.38–5.45 (2H, m), 5.52 (1H, d, J=6.4 Hz), 6.04 (1H, ddd, J=16.8, 10.5 and 6.4 Hz). ^{13}C NMR: 29.7 (CH_3), 29.9 (CH_3), 30.0 (CH_3), 36.3 (C^{IV}), 41.1 (CH_2), 46.2 (CH_2), 91.1 (CH), 108.3 (C^{IV}), 120.7 (CH_2), 131.4 (CH), 158.4 (C–O), 165.1 (C^{IV}). IR: 2955, 2935, 1740, 1670, 1470, 1445, 1410 cm^{-1}. MS *m/z*: 208 ($M^{+\cdot}$+1, 24), 207 ($M^{+\cdot}$, 17), 156 (29), 138 (64), 123 (95), 95 (60), 83 (57). HRMS: Calcd for $C_{12}H_{17}NO_2$: 207.1255. Found: 207.1259.

2-*t*-Butyl-7,7-dimethyl-1,5-dioxo-3-vinyl-2-azaspiro[3.4]-octane: **13c** Oil, 11%. ^{1}H NMR: 1.00 (3H, s), 1.18 (3H, s), 1.33 (9H, s), 1.99–2.20 (2H, m), 2.03 (1H, d, J_{AB}=13.5 Hz), 2.36 (1H, d, J_{AB}=13.5 Hz), 3.92 (1H, d, J=9.9 Hz), 5.22 (1H, dd, J=9.9 and 1.3 Hz), 5.30 (1H, dd, J=17.2 and 1.3 Hz), 6.18 (1H, ddd, J=17.2, 9.9 and 9.9 Hz). ^{13}C NMR: 28.2 (CH_3), 28.3 ($2CH_3$), 28.5 (CH_3), 28.6 (CH_3), 34.5 (C^{IV}), 44.5 (CH_2), 54.4 (CH_2), 55.0 (C^{IV}), 65.5 (CH), 69.6 (C^{IV}), 119.8 (CH_2), 136.0 (CH), 165.9 (C=O), 212.2 (C=O). IR: 2960, 1725, 1680, 1465, 1390, 1370, 1270, 1255, 1145 cm^{-1}.

3-Allyl-6,6-dimethyl-2,8-dioxo-3-azabicyclo[3.3.0] octane: **14b** Oil. Yield 30%. ^{1}H NMR: 1.08 (3H, s), 1.10 (3H, s), 2.18 (1H, d, J_{AB}=17.7 Hz), 2.21 (1H, d, J_{AB}=17.7 Hz), 2.77 (1H, ddd, J=8.9, 8.9 and 5.8 Hz), 3.28 (1H, d, J=8.9 Hz), 3.26–3.48 (2H, m), 3.78–3.94 (2H, m), 5.14–5.21 (2H, m), 5.68 (1H, ddt, J=16.6, 10.5 and 6.3 Hz). ^{13}C NMR: 232.9 (CH_3), 29.4 (CH_3), 36.8 (C^{IV}), 44.4 (CH), 45.5 (CH_2), 46.5 (CH_2), 51.4 (CH_2), 56.6 (CH), 118.6 (CH_2), 131.8 (CH), 167.1 (C=O), 208.6 (C=O). IR: 2960, 1755, 1680, 1645, 1465, 1440, 1415, 1270 cm^{-1}. MS *m/z*: 208 ($M^{+\cdot}$+1, 47),

207 ($M^{+\cdot}$, 50), 123 (84), 85 (100). HRMS: Calcd for $C_{12}H_{17}NO_2$: 207.1255. Found: 207.1259.

3-(4-Butenyl)-6,6-dimethyl-2,8-dioxo-3-azabicyclo[3.3.0] octane: **14c** Oil. Yield 58%. ^{1}H NMR: 1.12 (3H, s), 1.11 (3H, s), 2.10–2.41 (4H, m), 2.80 (1H, ddd, J=8.9, 8.9 and 5.8 Hz), 3.26 (1H, d, J=8.9 Hz), 3.32 (2H, t, J=6.5 Hz), 3.38–3.53 (2H, m), 5.01–5.11 (2H, m), 5.75 (1H, ddt, J=17.2, 10.3 and 6.8 Hz). ^{13}C NMR: 23.0 (CH_3), 29.4 (CH_3), 31.6 (CH_2), 36.7 (C^{IV}), 41.8 (CH_2), 44.5 (CH), 47.1 (CH_2), 51.2 (CH_2), 56.7 (CH), 117.0 (CH_2), 139.4 (CH), 167.4 (C·O), 208.6 (C·O). IR: 2955, 2930, 1755, 1685, 1640, 1435, 1275 cm^{-1}. MS *m/z*: 222 ($M^{+\cdot}$+1, 7), 221 ($M^{+\cdot}$, 20), 180 (84), 85 (100). HRMS: Calcd for $C_{13}H_{19}NO_2$: 221.1411. Found: 221.1416.

6,6-Dimethyl-2,8-dioxo-3-(4-pentenyl)-3-azabicyclo[3.3.0] octane: **14e** Oil. Yield 26%. ^{1}H NMR: 1.09 (6H, s), 1.58 (2H, quint, J=7.5 Hz), 2.00 (2H, dd, J=14.1 and 6.9 Hz), 2.14 (1H, d, J_{AB}=17.5 Hz), 2.22 (1H, d, J_{AB}=17.5 Hz), 2.78 (1H, ddd, J=9.1, 9.1 and 5.6 Hz), 3.22–3.29 (3H, m), 3.32 (1H, dd, J_{AB}=10.4 Hz and J=5.6 Hz), 3.46 (1H, dd, J_{AB}= 10.4 Hz and J=9.1 Hz), 4.92–5.02 (2H, m), 5.75 (1H, ddt, J=17.2, 10.3 and 6.5 Hz). ^{13}C NMR: 22.8 (CH_3), 26.1 (CH_2), 29.2 (CH_3), 30.7 (CH_2), 36.6 (C^{IV}), 42.2 (CH_2), 44.3 (CH), 46.8 (CH_2), 51.3 (CH_2), 56.5 (CH), 115.0 (CH_2), 137.1 (CH), 167.2 (C═O), 208.6 (C═O). IR: 2960, 2920, 1755, 1680, 1440, 1275 cm^{-1}. MS *m/z*: 236 ($M^{+\cdot}$+1, 22), 235 ($M^{+\cdot}$, 29), 180 (86), 124 (28), 97 (64), 83 (66). HRMS: Calcd for $C_{14}H_{21}NO_2$: 235.1567. Found: 235.1572.

6,6-Dimethyl-2,8-dioxo3-(5-hexenyl)-3-azabicyclo[3.3.0] octane: **14f** Oil. Yield 46%. ^{1}H NMR: 1.13 (6H, s), 1.30–1.59 (4H, m), 2.07 (2H, dd, J=14.0 and 7.3 Hz), 2.19 (1H, d, J_{AB}=17.4 Hz), 2.23 (1H, d, J_{AB}=17.4 Hz), 2.79 (1H, ddd, J=9.1, 9.1 and 5.6 Hz), 3.23–3.30 (2H, m), 3.28 (1H, d, J=9.1 Hz), 3.34 (1H, dd, J_{AB}=10.4 Hz and J=5.6 Hz), 3.48 (1H, dd, J_{AB}=10.4 Hz and J=9.1 Hz), 4.94–5.05 (2H, m), 5.77 (1H, ddt, J=17.1, 10.4 and 6.7 Hz). ^{13}C NMR: 22.7 (CH_3), 25.7 (CH_2), 26.1 (CH_2), 29.2 (CH_3), 32.8 (CH_2), 36.5 (C^{IV}), 42.4 (CH_2), 44.2 (CH), 46.7 (CH_2), 51.2 (CH_2), 56.4 (CH), 114.5 (CH_2), 137.9 (CH), 167.0 (C═O), 208.5 (C═O). IR: 2930, 1755, 1685, 1640, 1435, 1370, 1270 cm^{-1}. MS *m/z*: 250 ($M^{+\cdot}$+1, 18), 249 ($M^{+\cdot}$, 45), 234 (15), 208 (100), 180 (92), 168 (67), 124 (38), 111 (30), 96 (70). HRMS: Calcd for $C_{15}H_{23}NO_2$: 249.1723. Found: 249.1729.

3-*t*-Butyl-7,7-dimethyl-2-oxo-3-azabicyclo[3.3]oct-1-en-5-ol: **16** Oil, 50%. ^{1}H NMR: 1.09 (3H, s), 1.15 (3H, s), 1.33 (3H, s), 1.39 (3H, s), 1.80 (1H, d, J_{AB}=13.3 Hz), 2.04 (1H, 1H, J_{AB}=13.3 Hz), 3.15 (1H, s), 3.32 (1H, dd, J=10.2 and 0.5 Hz), 3.58 (1H, dd, J=10.2 and 0.5 Hz), 6.18 (1H, s). ^{13}C NMR: 27.2 (CH_3), 27.3 ($2CH_3$), 28.1 (CH_3), 28.6 (CH_3), 36.6 (C^{IV}), 50.3 (C^{IV}), 52.1 (CH_2), 58.8 (CH_2), 81.1 (C^{IV}), 142.5 (CH), 142.8 (CH), 164.7 (C═O). IR: 3270, 2955, 2935, 1745, 1675, 1645, 1465, 1455, 1360. UV (CH_2Cl_2) ε_{270}=490. MS *m/z*: 224 ($M^{+\cdot}$+1, 7), 223 ($M^{+\cdot}$, 33), 208 (100), 180 (17), 168 (19), 137 (26). HRMS: Calcd for $C_{13}H_{21}NO_2$: 223.1567. Found: 223.1572.

3-*t*-Butyl-7,7-dimethyl-2-oxo-3-azabicyclo[3.3]oct-1-en-5-ol: **17** Oil, 17%. ^{1}H NMR: 1.11 (6H, s), 1.39 (9H, s), 2.17 (1H, d, J_{AB}=17.4 Hz), 2.22 (1H, d, J_{AB}=17.4 Hz), 2.66 (1H, ddd, J=8.9, 8.9 and 5.3 Hz), 3.21 (1H, d, J=9.0 Hz), 3.40 (1H, dd, J_{AB}=10.6 Hz and J=5.3 Hz), 3.58 (1H, dd, J_{AB}=10.6 Hz and J=8.8 Hz). ^{13}C NMR: 22.7 (CH_3), 27.2 ($2CH_3$), 29.0 (CH_3), 36.7 (C^{IV}), 43.2 (CH), 45.2 (CH_2), 51.4 (CH_2), 54.2 (C^{IV}), 57.7 (CH), 167.2 (C═O), 208.9 (C═O). IR: 2960, 1745, 1665, 1405, 1290, 1130. MS *m/z*: 224 ($M^{+\cdot}$+1, 7), 223 ($M^{+\cdot}$, 42), 208 (100), 180 (28), 168 (42), 151 (9). HRMS: Calcd for $C_{13}H_{21}NO_2$: 223.1567. Found: 223.1572.

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