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Photorearrangement of N-Alkanoyl β-Enaminones. Application to the Synthesis of α-Amino-β,γ-Unsaturated Acid Derivatives[1]

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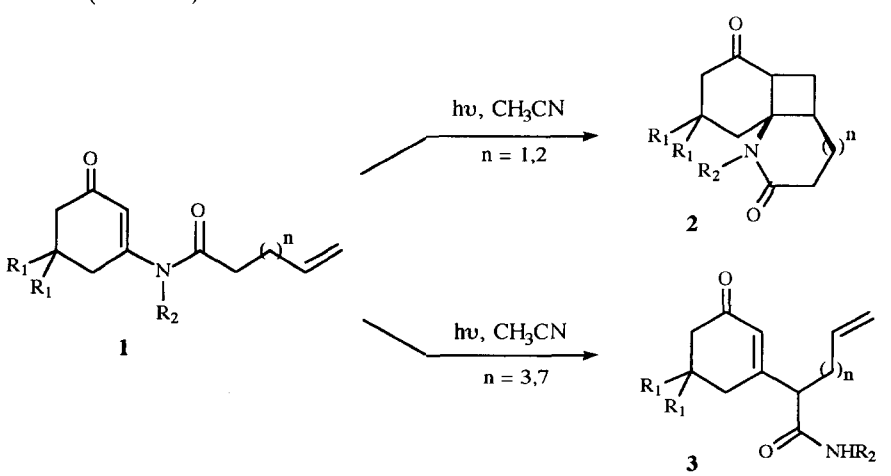
(Dedicated to Professor H-D. Scharf on the occasion of his 65th birthday)

Abstract: *The irradiation of N-alkanoyll-β-enaminones lead to the formation of spiranic β-lactams which undergo C-N bond cleavage during chromatography on alumina giving cycloalkenones functionalized at position 3. This new rearrangement has been applied to the synthesis of α-amino-β,γ-unsaturated amides in one step and gives convenient yields.*

β-Enaminones are very attractive molecules readily available from the corresponding β-diketones. Their photoreactivity has been extensively studied and numerous synthetic applications have been recognized.[2] Interestingly, small modifications of the nitrogen substituents have been shown to induce very different photoprocesses. Depending on the substitution, photo-Fries rearrangements or electrocyclizations have been described. For example, N-aryl β-enaminones were reported to undergo photocyclization to give the indole skeleton[3], while N-acryloyl cyclic β-enaminones rearranged into isoquinoline derivatives.[4]

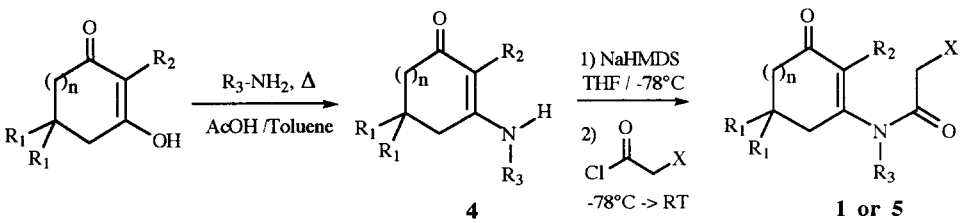
In the presence of alkenes, [2+2] photocycloadditions analogous to the De Mayo reaction of β-diketones can also be observed.[5] Owing to the great potential of cyclobutane adducts as precursors of various polycyclic structures[6] we have recently explored the synthetic interest of intramolecular [2+2] photocycloadditions of N-alkenoyl β-enaminones.[7] The reaction was shown to be efficient and to occur regio- and stereoselectively with enones **1** having a pentenoyl or hexenoyl chain (n=1,2), thus leading to the expected cyclobutane derivatives **2**. Surprisingly, compounds **1** possessing longer alkenoyl chains (n=3,7) prefer to rearrange to 3-C-alkylated cyclohexenones **3**. (Scheme 1).



Scheme 1

The good overall yields for this photochemical rearrangement led us to explore its scope, limits and mechanism.[8] We wish to report here the results of our investigation and to present applications for the synthesis of highly functionalized molecules such as unusual α-alkoxy or α-amino acid derivatives.

The starting materials were synthesized in a few steps according to scheme 2. Condensation of a primary amine with 1,3-diones[9] affords quantitatively β-enaminones **4**. After deprotonation with NaHMDS[10] and treatment with the appropriate acid chloride, the requisite N-alkanoyl enaminones **1** or **5** were isolated in good yields. Results are collected in Table 1.



Scheme 2

Table 1. Preparation of N-alkanoyl β-enaminones **1** and **5**:

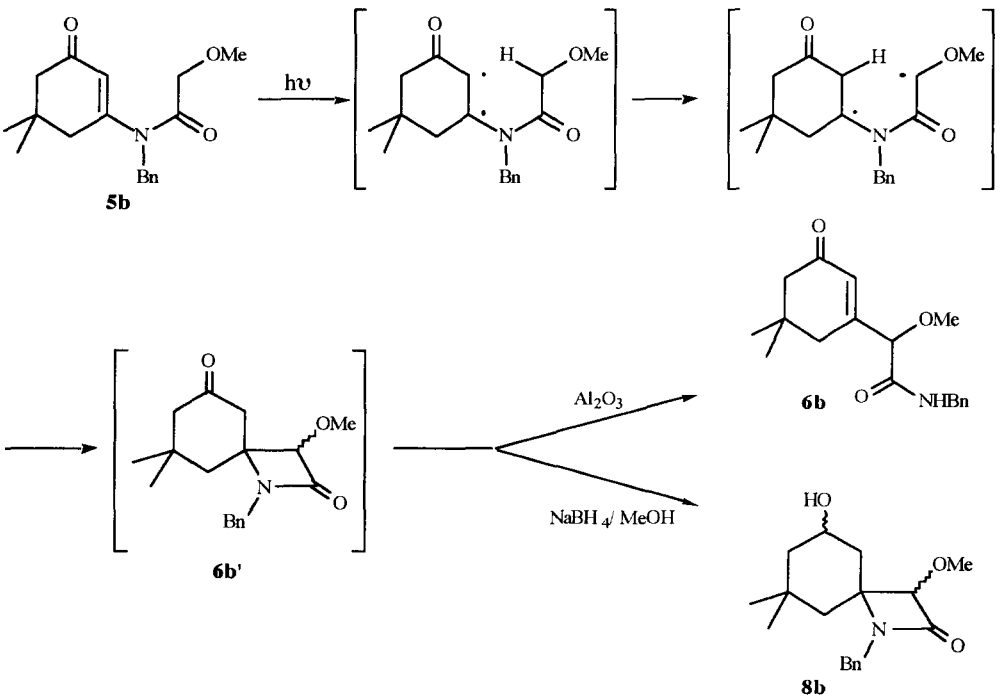
n	R_1	R_2	**4**	R_3	Product	X	Yield (%)
1	Me	H	**4a**	$PhCH_2$	**1a**	$(CH_2)_3CH=CH_2$	76
1	Me	H	**4a**	$PhCH_2$	**1b**	$(CH_2)_7CH=CH_2$	76
1	Me	H	**4a**	$PhCH_2$	**5a**	Me	75
1	Me	H	**4a**	$PhCH_2$	**5b**	OMe	73
1	Me	H	**4a**	$PhCH_2$	**5c**	O-Allyl	50
1	Me	H	**4b**	n-Hexyl	**5d**	O-Allyl	50
1	H	H	**4c**	$PhCH_2$	**5e**	OMe	58
0	H	Me	**4d**	$PhCH_2$	**5f**	OMe	55
1	H	H	**4e***	H	**5g**	OMe	41
1	Me	H	**4a**	$PhCH_2$	**5h**	H	77

* Commercial

According to the structure of the product **3**, the presence of a double bond in the side-chain seems not to be essential for the efficiency of the photorearrangement. In order to verify this hypothesis, β-enaminones **5a** (X=Me) and **5b** (X=OMe) have been submitted to irradiation under the same conditions as above. As expected, the rearranged products **6a** and **6b** were isolated respectively in 58% and 73% yield, confirming thus the possibility to apply this reaction to substrates other than N-alkenoyl β-enaminones **1**.

Mechanistically, we have supposed that a hydrogen atom abstraction occurs, leading from compound **5b**, for example, initially to a spiranic keto β-lactam **6b'** according to scheme 3. Due to its amidoketone structure and to the strain of the four-membered ring, this spiranic β-lactam is highly sensitive to base and could undergo β-elimination during chromatography on alumina. Furthermore, according to this hypothesis, convenient substitution of the lateral chain by an electron rich substituent (X=OMe) could stabilize the 1,4-biradical intermediate formed after initial hydrogen abstraction, through the captodative effect.[11]

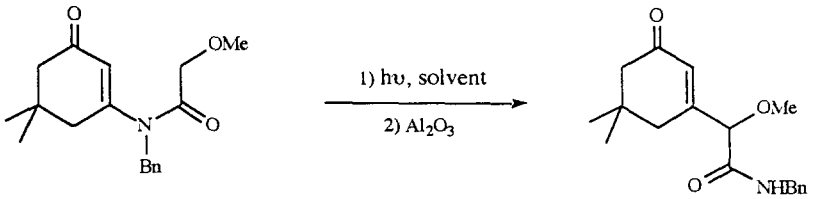
Spectroscopic data collected on the crude product obtained after photolysis of **5b** support the formation of a β-lactam intermediate **6b'**. In the IR spectrum, the intense signal at 1740 cm^{-1} is characteristic of the β-lactam function. The ^{13}C-NMR spectrum shows two quaternary centers at 207 and 166 ppm which can be attributed to the unconjugated ketone and to the β-lactam carbons respectively. A third quaternary center at 65 ppm corresponds to the spiranic carbon. It is worth noting that the proton spectrum (in $CDCl_3$) of the aforementioned structure **6b'** evolves slowly to the rearranged compound **6b**. Such intramolecular γ-hydrogen abstractions by excited enones have already been observed[12,13] and spiranic derivatives of high synthetic value can be thus synthesized.[14-16]



Scheme 3

In order to confirm the formation of the spiranic keto β-lactam entity, the crude product obtained after concentration of the solvent used for the irradiation, was submitted to the action of $NaBH_4$. Selective reduction of the keto function occurred giving a complex mixture of hydroxy β-lactams **8b**. The presence of the β-lactam function was fully confirmed by IR.

From a practical point of view, various conditions of irradiation (nature of the solvent and the wavelength value) have been tested on substrate **5b** (Scheme 4) and the results are summarized in Table 2. In all cases, the rearranged compound **6b** was obtained as the major product but better yields were observed when the irradiation was carried out in acetonitrile at 366 nm.



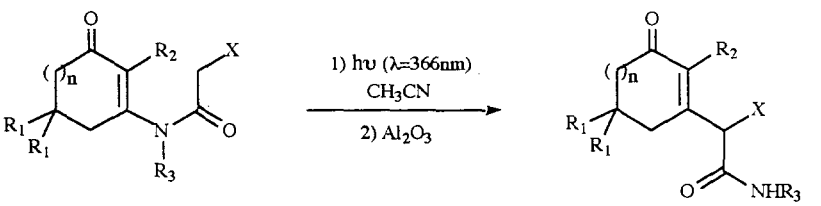
5a **6a**

Scheme 4

Table 2: Optimization of irradiation conditions for **5a**:

Solvent	CH_3CN	CH_3CN	MeOH	CH_2Cl_2	Ph-H
Wavelength	313nm	366nm	366nm	366nm	366nm
Chemical Yields	51%	68%	65%	55%	47%

The above conditions have been used for the irradiation of the other substrates **5c-h** (Scheme 5) and all the results are given in Table 3.



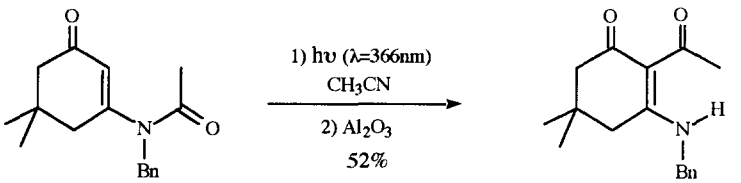
1/5 **3/6**

Scheme 5

Table 3: Irradiation of enaminones **1** and **5**.

1/5	n	R_1	R_2	R_3	X	**3/6**	Yield (%)
1a	1	Me	H	$PhCH_2$	$(CH_2)_3CH=CH_2$	**3a**	55
1b	1	Me	H	$PhCH_2$	$(CH_2)_7CH=CH_2$	**3b**	72
5a	1	Me	H	$PhCH_2$	Me	**6a**	58
5b	1	Me	H	$PhCH_2$	OMe	**6b**	73
5c	1	Me	H	$PhCH_2$	OAllyl	**6c**	50
5d	1	Me	H	n-Hexyl	OAllyl	**6d**	40
5e	1	H	H	$PhCH_2$	OMe	**6e**	51
5f	0	H	Me	$PhCH_2$	OMe	**6f**	38
5g	1	H	H	H	OMe	**6g**	0
5h	1	Me	H	$PhCH_2$	H	**6h**	0

The rearrangement appears to be a general process and gives the expected 3-functionalized cycloalkenones **6**. It is interesting to note that substrates bearing an allyloxy chain undergo only H-abstraction, and not [2+2] photocycloaddition. This phenomenon could be due either to the stabilization of the 1,4-biradical formed, or to an unfavourable conformation for the cycloaddition. Furthermore, the reaction seems to be dependent on the nature of the substituent attached on the nitrogen atom : when R_3=H, the starting material is recovered unchanged. As already noted for similar reactions, this lack of reactivity could be due to an unfavourable conformation of the substrate[17] which prevents hydrogen abstraction. The degree of substitution of the side chain is also of importance : enaminone **5h** (X=H) shows low photochemical reactivity and after lengthy irradiation, compound **7h** was the sole product isolated besides the starting material (Scheme 6). Its formation results from a photo-Fries reaction.[18] This particular reactivity of **5h** might be due to some difficulty to produce a primary radical by hydrogen abstraction.

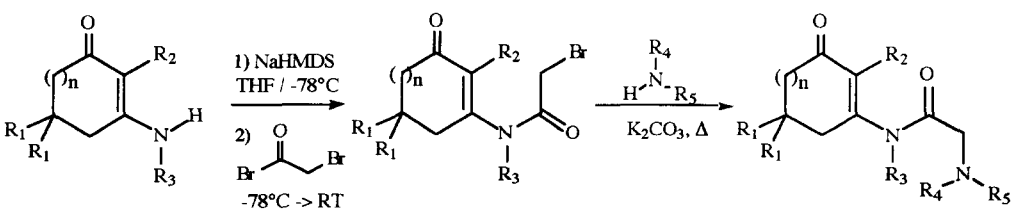


5h **7h**

Scheme 6

Due to the importance of α-amino, β,γ-unsaturated acids and their derivatives, in particular as enzyme inhibitors[19], we have investigated the possibility of gaining an access to this type of compound by the photorearrangement of β-enaminones **10**, which bear an amino group on the side chain (X=NR_2). We have considered more particularly substrates which possess the bis(allyl)amino group. This well-known protective group of the amino function[20] can be easily cleaved under different conditions such as palladium catalysis[21], oxidative conditions[22] or isomerization with rhodium catalysts.[23]

The starting materials **10 - 11** were synthesized in moderate to good yields, according to a process relatively similar to that of β-enaminones **5**.(Table 4 and scheme 7).



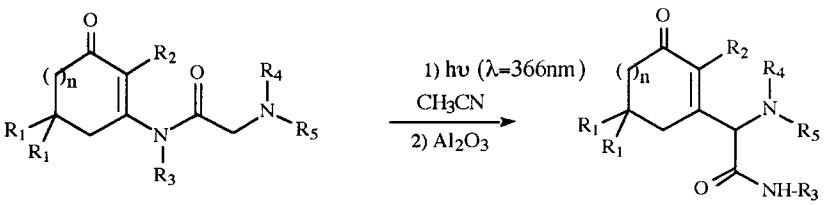
4 **9** **10 / 11**

Scheme 7

Table 4 : Preparation of enaminones **10** and **11**.

4	n	R_1	R_2	R_3	R_4	R_5	**10 /11**	C.y. (%)
a	1	Me	H	$PhCH_2$	Ethyl	Ethyl	**10a**	95
a	1	Me	H	$PhCH_2$	Allyl	Allyl	**10b**	76
a	1	Me	H	$PhCH_2$	Me	$PhCH_2$	**10c**	83
b	1	Me	H	n-Hexyl	Allyl	Allyl	**10d**	63
c	1	H	H	H	Allyl	Allyl	**10e**	47
d	0	H	Me	$PhCH_2$	Allyl	Allyl	**10f**	67
f	1	Me	H	CH_2CO_2Me	Allyl	Allyl	**10g**	50
a	1	Me	H	$PhCH_2$	H	(S)-Phenylethyl	**11a**	57
a	1	Me	H	$PhCH_2$	Allyl	(S)-Phenylethyl	**11b**	58

Irradiation of compounds **10** and **11**was conducted at 366 nm in acetonitrile solutions and the results are collected in Table 5. Except for **10e** (where R_3=H), and whatever the size or the nature of the substituents of the starting materials, the photorearrangement occurs and leads to cycloalkenones **12**, which possess the expected α-amino β,γ-unsaturated amide functionality. Moreover, access to certain unnatural dipeptides is possible as shown with **10g** which leads to **12g** in relatively good yields.



10 **12**

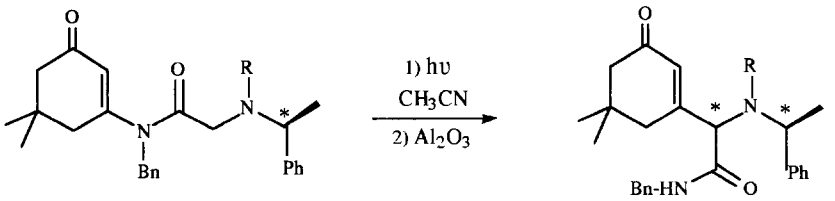
Scheme 8

Table 5 : Photochemical preparation of α-amino β,γ-unsaturated amides **12** .

10	n	R_1	R_2	R_3	R_4	R_5	**12**	Yield (%)
a	1	Me	H	$PhCH_2$	Ethyl	Ethyl	**a**	74
b	1	Me	H	$PhCH_2$	Allyl	Allyl	**b**	73
c	1	Me	H	$PhCH_2$	Me	$PhCH_2$	**c**	75
d	1	Me	H	n-Hexyl	Allyl	Allyl	**d**	77
e	1	H	H	H	Allyl	Allyl	**e**	0
f	0	H	Me	$PhCH_2$	Allyl	Allyl	**f**	54
g	1	Me	H	CH_2CO_2Me	Allyl	Allyl	**g**	45

Finally, we have also examined the possibility of achieving asymmetric induction by using enaminones which bear a chiral group on the nitrogen. The cheap and commercially available α-methylbenzylamine was chosen for

this purpose and two enaminones **11a** and **11b** were synthesized and submitted to irradiation. In the case of **11a** (R_4=H), no reaction occurs and this lack of reactivity has to be compared with previous results observed with unsubstituted enaminone **5g**. However, compound **11b** leads to the rearranged compound **13b** in good yield but with low diastereoselectivity.



11a (R = H) **13a** 0%

11b (R = Allyl) **13b** 55% (d.e. <20%)

Scheme 9

In conclusion, we have described a new rearrangement of β-enaminones which can furnish in one step highly functionalized 3-substituted cycloalkenones. This reaction has been applied with success to the synthesis of α-amino β,γ-unsaturated amides or dipeptides.

EXPERIMENTAL SECTION:

General: The NMR spectra were recorded in $CDCl_3$ using a Brü ker AC 250 instrument. FT-IR spectra were carried out in $CHCl_3$ on a IR MIDAC spectrometer. Mass spectra were obtained on a D-300 JEOL apparatus at the UFR Pharmacy of the University of Reims. Elemental analyses were determined on a CHN 2400 Perkin Elmer apparatus. Chromatography was performed on Merck aluminium oxide (70-230 mesh).

Preparation of enaminones **4**:

To a solution of the 1,3-dione (10 mmol.) in toluene (100ml) is added the primary amine (10 mmol.) and p-toluenesulfonic acid or propionic acid,in catalytic amounts. The mixture is heated at reflux for 10 hours. The solvent is removed by distillation and the crude product is purified by recrystallization in hexane or chromatographied on alumina (eluent: AcOEt / hexanes: 40 / 60).

3-Benzylamino-5,5-dimethylcyclohex-2-enone: **4a**

87%. F=123°C. ^{13}C-NMR: 28.0; 32.5; 42.9; 46.6; 50.0; 95.1; 127.1; 127.3; 128.5; 136.8; 163.8; 196.6. ^{1}H-NMR: 1.22 (s, 6H); 2.00 (s, 2H); 2.23 (s, 2H); 4.15 (d, 2H, J = 5.5 Hz); 5.00 (s, 1H); 6.50 (m, 1H); 7.18-7.31 (m, 5H). IR: 3440; 2980; 1590; 1515; 1470; 1260. MS: 230 ($M^{+\cdot}$+1, 3); 229 ($M^{+\cdot}$, 12); 144 (57); 91 (100). Anal. Calcd. for $C_{15}H_{19}NO$: C: 78.56, H: 8.35, N: 6.10. Found: C: 78.78, H: 8.12, N: 6.16.

3-Hexylamino-5,5-dimethylcyclohex-2-enone: **4b**

85%. F=113°C. ^{13}C-NMR: 13.8; 22.3; 26.5; 28.1; 28.2; 31.2; 32.6; 42.8; 43.2; 50.2; 94.6; 463.45; 196.3. ^{1}H-NMR: 0.90 (t, 3H, J = 6.8 Hz); 1.05 (s, 6H); 1.25-1.35 (m, 6H); 1.60 (tt, 2H, J= 6.75 and 6.75 Hz); 2.15 (s, 2H); 3.10 (dt, 2H, J = 6.75 and 6.75 Hz); 5.10 (s, 1H); 5.65-5.75 (ma, 1H). IR: 3420; 3250; 2950; 2850; 1580-1500; 1460; 1360; 1240; 1140; 900. MS: 224 ($M^{+\cdot}$+1, <5); 223 ($M^{+\cdot}$,<5); 181 (100); 180 (57); 57 (47). Anal. Calcd. for $C_{14}H_{25}NO$: C: 75.28, H: 11.23, N: 6.27. Found: C: 75.48, H: 11.67, N: 6.11.

3-Benzylamino-cyclohex-2-enone: **4c**

62%. ^{13}C-NMR: 22.0; 29.6; 36.4; 47.1; 97.4; 127.6; 127.8; 128.8; 136.7; 164.4; 197.4. ^{1}H-NMR: 1.95 (m, 2H); 2.25 (t, 2H, J = 6.3 Hz); 2.40 (t, 2H, J = 6.3 Hz); 4.20 (d, 2H, J = 5.25 Hz); 5.15 (s, 1H); 5.50 (sl, 1H); 7.20-7.40 (m, 5H). IR: 3430; 3000; 1585; 1470; 1360; 1260; 1190; 1140; 800; 720. MS: 201 ($M^{+}\cdot$, 4); 173 (38); 145 (22); 144 (68); 91 (100). Anal. Calcd. for $C_{13}H_{15}NO$: C: 77.58, H: 7.51, N: 6.96. Found: C: 77.50, H: 7.66, N: 7.01.

3-Benzylamino-2-methylcyclopent-2-enone: **4d**

92%. F=135°C. ^{13}C-NMR: 6.2; 24.6; 32.8; 47.3; 100.1; 126.8; 127.5; 128.7; 138.1; 173.2; 202.4. ^{1}H-NMR: 1.62 (s, 3H); 2.25-2.35 (m, 2H); 2.50-2.65 (m, 2H); 4.50 (d, 2H, J = 6.25 Hz); 5.90-6.00 (m, 1H); 7.25-7.40 (m, 5H). IR: 1590; 1410; 1340; 1200; 1130; 1070; 1040. MS: 202 ($M^{+}\cdot$+1, 10); 201 ($M^{+}\cdot$, 40); 91 (100). Anal. Calcd. for $C_{13}H_{15}NO$: C: 77.58, H: 7.51, N: 6.96. Found: C: 77.46, H: 7.54, N: 6.86.

3-*N*-Carbomethoxymethylamino-5,5-dimethylcyclohexen-2-enone: **4f**

73%. ^{13}C-NMR: 28.1; 32.7; 42.9; 43.9; 50.2; 52.4; 96.5; 161.7; 169.6; 197.0. ^{1}H-NMR: 1.02 (s, 6H); 2.10 (s, 2H); 2.19 (s, 2H); 3.72 (s, 3H); 3.79 (d, 2H); 4.91 (s, 1H); 5.36 (N-H). IR: 3240; 1751; 1590; 1450; 1425; 1365; 1205; 1165; 990. MS: 212 ($M^{+}\cdot$+1, 10); 211 ($M^{+}\cdot$, 8); 155 (67); 152 (36); 123 (61); 96 (95); 95 (98); 67 (53). Anal. Calcd. for $C_{11}H_{17}NO_3$: C: 62.54, H: 8.11, N: 6.63. Found: C: 62.88, H: 7.91, N: 6.53.

Preparation of β-enaminones **1a,b** and **5a-h**

To a solution of enaminone **4** (10 mmol.) in anhydrous THF, is added at -78°C, NaHMDS (11mmol.). The mixture is stirred for 4 hours at this temperature. The acid chloride (12 mmol.) in THF (3ml) is then added dropwise. The reaction mixture is stirred overnight at RT. After hydrolysis with brine (50ml) and extraction with ether (3 x 50ml), the organic layers are dried over $MgSO_4$. After concentration, the crude product is chromatographied on alumina (eluent: AcOEt / hexanes: 20 / 80). All compounds are isolated as syrups.

N-Benzyl, *N*-(5,5-dimethyl-3-oxo-cyclohex-1-enyl) hept-6-enamide: **1a**

76%. ^{13}C-NMR: 24.7; 27.8; 28.2; 34.4; 34.6; 43.5; 50.0; 50.6; 114.6; 123.0; 127.2; 127.5; 128.62; 136.5; 138.1; 159.8; 172.5; 199.0. ^{1}H-NMR: 1.00 (s, 6H); 1.40 (quint, 2H, J=7.6 Hz); 1.70 (quint, 2H, J=7.6 Hz); 2.05 (q, 2H, J=7.6 Hz); 2.20 (s, 2H); 2.40 (s, 2H); 2.41 (t, 2H, J=7.6 Hz); 4.80 (s, 2H); 4.90-5.05 (m, 2H); 5.72 (s, 1H); 5.75 (ddt, 1H, J=10, 18 and 7.6 Hz); 7.20-7.30 (m, 5H). IR: 3080; 3020; 2960, 2920; 2880; 1660; 1620; 1450; 1380; 1370. MS: 340 ($M^{+}\cdot$+1, <5); 339 ($M^{+}\cdot$,<5); 311 (40); 214 (22); 201 (20); 91 (100); 77 (5); 54 (40). UV (CH_3CN) ε_{278}= 6600; ε_{216}= 5900. Anal. Calcd. for: $C_{22}H_{29}NO_2$: C: 77.84, H: 8.61, N: 4.13. Found : C: 77.95, H: 9.01, N: 3.89.

N-Benzyl, *N*-(5,5-dimethyl-3-oxo-cyclohex-1-enyl)-undec-10-enamide: **1b**

76% ^{13}C-NMR: 25.3; 27.8; 28.7; 28.9; 29.1; 33.3; 33.5; 34.7; 43.5; 50.4; 50.6; 114.0; 122.9; 127.1; 127.6; 128.6; 136.5; 138.9; 159.8; 172.6; 198.9. ^{1}H-NMR : 1.00 (s, 6H); 1.20-1.40 (m, 10H); 1.60 (quint, 2H, J=6.9 Hz); 2.05 (s, 2H); 2.25 (quint, 2H, J=7.6 Hz); 2.38 (t, 2H, J=7.6 Hz); 2.41 (s, 2H); 4.80 (s, 2H); 4.90-5.00 (m, 2H); 5.70 (s, 1H); 5.80 (ddt, 1H, J=17, 11.5 and 6.9 Hz); 7.15-7.35 (m, 5H). IR : 3000; 2920; 1650; 1620; 1500; 1390; 1370; 1230-1200; 1050; 920. MS : 396 ($M^{+}\cdot$+1, <5); 395 ($M^{+}\cdot$, <5); 372 (60); 243 (45); 91 (100); 77 (5). UV (CH_3CN) ε_{280}= 7800; ε_{208}= 5900. Anal. Calcd. for: $C_{26}H_{37}NO_2$: C: 78.94, H: 9.43, N: 3.54. Found: C: 78.73, H: 9.69, N: 3.51.

N-Benzyl, *N*-(5,5-dimethyl-3-oxo-cyclohex-1-enyl)-propionamide: **5a**

75%. ^{13}C-NMR: 9.6; 27.9; 28.2; 33.5; 43.6; 50.6; 50.7; 122.9; 127.2; 127.6; 128.7; 136.60, 160.0; 173.4; 199.1. ^{1}H-NMR: 1.00 (s, 6H); 1.16 (t, 3H, J=7.2 Hz); 2.22 (s, 2H); 2.45 (s, 2H); 2.43 (q, 2H, J= 7.2 Hz); 4.81 (s, 2H); 5.72 (s, 1H); 7.15-7.35 (m, 5H). IR: 2960; 1640; 1620; 1450; 1385; 1370; 1185. MS: 286 ($M^{+\cdot}$+1, 100); 285 ($M^{+\cdot}$, <5); 257 (75); 201 (40); 91 (45); 57 (42). UV (CH_3CN) ε_{278}= 8700; ε_{220}= 4900. Anal. Calcd. for: $C_{18}H_{23}NO_2$: C: 75.76, H: 8.12, N: 4.91. Found: C: 75.42, H: 8.29, N: 5.36

N-Benzyl, *N*-(5,5-dimethyl-3-oxo-cyclohex-1-enyl)-2-methoxy-acetamide: **5b**

73%. ^{13}C-NMR: 27.9; 33.2; 42.9; 49.95; 50.7 59.4; 71.7; 122.7; 127.4; 127.7; 128.7; 136.0; 158.8; 169.0; 198.9. ^{1}H-NMR: 0.93 (s, 6H); 2.15 (s, 2H); 2.36 (s, 2H); 3.34 (s, 3H); 4.06 (s, 2H); 4.75 (s, 2H); 5.70 (sl, 1H); 7.10-7.30 (m, 5H). IR: 3000, 2950, 2920, 1660, 1620, 1450, 1370, 1230-1190, 920. MS: 302 ($M^{+\cdot}$, <5), 301 ($M^{+\cdot}$, <5), 273 (20), 91 (100), 83 (30), 65 (15). Anal. Calcd. for: $C_{18}H_{23}NO_3$: C : 71,73, H : 7.69, N : 4.65. Found: C : 71.71, H : 7.80, N : 4.48.

2-Allyloxy, *N*-benzyl, *N*-(5,5-dimethyl-3-oxo-cyclohex-1-enyl)-acetamide: **5c**

50%. ^{13}C-NMR: 27.9; 33.2; 42.8; 50.1; 50.7; 69.3; 72.9; 118.1; 122.8; 127.5; 127.8; 128.8; 133.5; 136.1; 158.9; 169.2; 199.0. ^{1}H-NMR: 0.95 (s, 6H); 2.18 (s, 2H); 2.42 (s, 2H); 4.02 (dt, 2H, J=6-1 Hz); 4.17 (s, 2H); 4.80 (s, 2H); 5.15-5.30 (m, 2H); 5.70 (sl, 1H); 5.85 (ddt, 1H, J=17, 11 and 6 Hz), 7.15-7.35 (m 5H). IR: 3000, 2940, 1650, 1400-1390, 1220-1200, 1190. MS : 328 ($M^{+\cdot}$+1, 100), 327 ($M^{+\cdot}$, <5), 299 (50), 228 (60), 91 (99), 65 (60). Anal. Calcd. for : $C_{20}H_{25}NO_3$: C : 73.37, H : 7.70, N : 4.28. Found: C : 73.26, H : 7.86, N : 4.12.

2-Allyloxy, *N*-(5,5-dimethyl-3-oxo-cyclohex-1-enyl), *N*-hexyl-acetamide: **5d**

50%. ^{13}C-NMR: 13.9; 22.4; 26.3; 28.0; 28.2; 31.3; 33.3; 42.7; 46.1; 50.8; 69.2; 72.2; 118.1; 122.9; 133.6; 158.7; 168.9; 199.1. ^{1}H-NMR: 0.87 (t, 3H, J=6.3 Hz); 1.10 (s ,6H); 1.20-1.30 (m, 6H); 1.50 (m, 2H); 2.25 (s, 2H); 2.43 (s, 2H); 3.52 (t, 2H, J=7.8 Hz); 4.01 (dt, 2H, J= 5.9 and 1.2 Hz); 4.12 (s, 2H); 5.10-5.30 (m, 2H); 5.82 (s, 1H); 5.87 (ddt,1H, J=16, 10 and 5.9 Hz). IR : 3040, 3010, 2940, 1650, 1400, 1220-1190. MS: 322 ($M^{+\cdot}$+1, <5), 321 ($M^{+\cdot}$, <5), 293 (12), 250 (20), 222 (50), 167 (40), 166 (100), 83 (55), 55 (50). Anal. Calcd. For: $C_{19}H_{31}NO_3$: C : 70.99, H : 9.72, N : 4.36. For: C : 70.91, H : 9.95, N : 4.37.

N-Benzyl, *N*-(3-oxo-cyclohex-1-enyl)-2-methoxyacetamide: **5e**

58%. ^{13}C-NMR: 21.9; 29.2; 36.8; 50.1; 59.0; 71.7; 123.4; 127.3; 127.6; 128.6; 136.1; 161.2; 168.9; 198.8. ^{1}H-NMR: 1.90 (quint, 2H, J=6.1 Hz); 2.35 (t, 2H, J=6.1 Hz); 2.50 (t, 2H, J=6.1 Hz); 3.35 (s, 3H); 4.10 (s, 2H); 4.80 (s, 2H); 5.70 (s, 1H); 7.10-7.40 (m, 5H). IR : 2980, 2920, 1640, 1600, 1390, 1340, 1220-1200, 1175, 1120. MS : 274 ($M^{+\cdot}$+1, <5), 273 ($M^{+\cdot}$, <5), 245 (100), 91 (99), 65 (55). Anal. Calcd. For: $C_{16}H_{19}NO_3$: C : 70.31, H : 7.01, N : 5.12. Found: C : 70.37, H : 7.23, N : 5.01.

N-Benzyl, *N*-(2-methyl-3-oxo-cyclopent-1-enyl)-2-methoxyacetamide: **5f**

55 %. ^{13}C-NMR: 8.5; 28.1; 34.2; 49.3; 59.3; 71.6; 126.70, 127.9; 128.2; 128.6; 136.1; 165.7; 167.7; 207.3. ^{1}H-NMR: 1.45 (s, 3H); 2.40-2.49 (m, 2H); 2.52-2.60 (m, 2H); 3.35 (s, 3H); 3.95 (s, 2H); 4.80 (s, 2H); 7.20-7.30 (m, 5H). IR: 3000, 1670, 1635, 1400, 1220, 1190, 1120. MS: 274 ($M^{+\cdot}$+1, <5), 273 ($M^{+\cdot}$, 5), 245 (18), 91 (100), 65 (17). Anal. Calcd. For: $C_{16}H_{19}NO_3$: C : 70.31, H : 7.01, N : 5.12. Found: C: 70.06, H : 7.28. N : 5.09.

2-Methoxy, *N*-(3-oxo-cyclohex-1-enyl)-acetamide: **5g**

41%. ^{13}C-NMR: 21.3; 28.3; 36.5; 59.1; 71.8; 112.4; 153.9; 168.1; 199.5. ^{1}H-NMR: 2.05 (quint, 2H, J=6 Hz); 2.37 (t, 2H, J= 6 Hz); 2.57 (t, 2H, J=6 Hz); 3.47 (s, 3H); 3.95 (s, 2H); 6.66 (s, 1H); 8.00 (ma, 1H). IR : 3350, 2980, 1640, 1600, 1485, 1170, 1105. MS : 184 (M^{+}·+1, 18), 183 (M^{+}·, 35), 155 (25), 127 (60), 95 (100). Anal. Calcd. For: $C_9H_{13}NO_3$: C : 59.00, H : 7.15, N : 7.65. Found: C : 58.92, H : 7.25, N : 7.60.

N-Benzyl, *N*-(5,5-dimethyl-3-oxo-cyclohex-1-enyl)-acetamide: **5h**

77%. ^{13}C-NMR: 22.8; 27.7; 33.2; 43.1; 50.3; 50.4; 122.9; 127.1; 127.4; 128.5; 136.2; 159.5; 169.5; 198.8. ^{1}H-NMR: 1.00 (s, 6H); 2.15 (s, 3H); 2.20 (s, 2H); 2.42 (s, 2H); 4.80 (s, 2H); 5.75 (s, 1H); 7.15-7,35 (m, 5H). IR : 3000, 2940, 1615, 1420, 1380, 1370. MS : 272 (M^{+}·+1, 1), 271 (M^{+}·, 1), 243 (25), 228 (8), 91 (100). HRMS Calcd. For: $C_{17}H_{21}NO_2$: 271.358. Found: 271.1537.

Irradiation of substrates **1** and **5** :

A solution of the starting material **1** or **5** in acetonitrile (c = 10^{-2} M) is degassed under argon and submittted to irradiation at 366 nm(HPW 125 W Philips) at room temperature. After concentration under reduced pressure the product is purified on alumina. All compounds are isolated as syrups.

2-(5,5-Dimethyl-3-oxo-cyclohex-1-enyl)-hept-6-enoic acid benzylamide: **3a**

65%. ^{13}C-NMR : 26.7; 27.6; 28.3; 28.9; 33.4; 34.6; 40.6; 43.8; 51.1; 53.3; 115.1; 126.5; 127.6; 127.8; 128.5; 137.9; 160.7; 170.3; 199.8. ^{1}H-NMR : 0,90 (s, 3H); 0.95 (s, 3H); 1.25-2.50 (m, 10H); 2.95 (t, 1H, J = 7.5 Hz); 4.40 (d, 2H, J= 6 Hz); 4.90-5.10 (m, 2H); 5.75 (ddt, 1H, J = 16.9, 10.2 and 6.7 Hz); 5.90 (s, 1H); 6.00 (t, 1H, J = 6 Hz); 7.15-7.40 (m, 5H). IR: 3390, 3010, 2935, 1705, 1665, 1605, 1505, 1430, 1230, 1180, 1115. MS : 340 (M^{+}·+1, 10), 338 (M^{+}·, 20), 220 (20), 106 (60), 91 (99), 83 (100).

2-(5,5-Dimethyl-3-oxo-cyclohex-1-enyl)-dodec-11-enoic acid benzylamide: **3b**

72%. ^{13}C-NMR : 27.7; 28.8; 27.4; 29.0; 29.2; 29.3; 29.5; 33.4; 33.7; 36.7; 40.6; 43.8; 51.0; 55.5; 114.2; 126.4; 127.5; 127.7; 128.8; 138.0; 139.0; 161.0; 170.50; 199.9. ^{1}H-NMR : 0.95 (s,3H); 1.00 (s, 3H); 1.15-1.40 (m, 10 H); 1.60 (m, 2H); 2.00 (quint, 2H, J= 7.4 Hz); 2.17 (s, 2H); 2.20 (s, 2H); 3.00 (t, 1H, J= 7.4 Hz); 4,40 (d, 2H, J= 5,6 Hz); 4,90-5,05 (m, 2H); 5,80 (ddt, 1H, J= 17, 10 and 6 Hz); 5,95 (s, 1H); 6,25 (t, 1H, J= 5,6 Hz); 7,20-7,35 (m, 5H). IR: 3000, 2920, 1660, 1620, 1230-1200.MS: 396 (M^{+}·+1, <5), 395 (M^{+}·,<5), 270 (20), 149 (70), 106 (60), 91 (100).

N-Benzyl-2-(5,5-dimethyl-3-oxo-cyclohex-1-enyl)-propionamide: **6a**:

58%. ^{13}C-NMR : 15.0; 27.6; 28.3; 33.4; 40.8; 43.8; 49.0; 51.1; 125.8; 127.7; 127.9; 128.7; 138.0; 161.7; 171.0; 199.9. ^{1}H-NMR: 0.90 (s, 3H); 0.95 (s, 3H); 1.35 (d, 3H, J= 7 Hz); 2.15 (s, 2H); 2.10 (d, 1H, J_{AB}= 18 Hz); 2.25 (d, 1H, J_{AB}= 18 Hz); 3.18 (q, 1H, J = 7 Hz); 4.40 (d, 2H, J= 5.7 Hz); 5.82 (s, 1H); 6.08 (ma, 1H); 7.20-7.40 (m, 5H). IR: 3420, 2950, 1650, 1495, 1370, 1220-1200. MS : 286 (M^{+}·+1, 15), 285 (M^{+}·, 55), 152 (100), 105 (65), 91 (99).

N-Benzyl-2-(5,5-dimethyl-3-oxo-cyclohex-1-enyl)-2-methoxy-acetamide: **6b**

73%. ^{13}C-NMR : 27.4; 28.3; 33.5; 39.3; 43.0; 51.3; 57.4; 84.3; 126.7; 127.7; 127.8; 128.8; 137.7; 156.0; 167.9; 199.4. ^{1}H-NMR : 0.95 (s, 3H); 1.00 (s, 3H); 2.25 (d, 2H, J=2.6 Hz); 2.20 (d, 1H, J_{AB}=18 Hz); 2.30 (d, 1H, J_{AB}= 18 Hz); 3.35 (s, 3H); 4.20 (s, 1H); 4.45 (d, 2H, J=6 Hz); 6.15 (s, 1H); 7.05 (ma, 1H); 7.20-7.40 (m, 5H). IR : 3390, 3000, 1650, 1500, 1410, 1205. MS: 302 (M^{+}·+1, <5), 301 (M^{+}, <5), 270 (4), 168 (100), 91 (70). Anal Calcd for $C_{18}H_{23}NO_3$: C : 71.73, H : 7.69, N : 4.65. Found : C : 71.55, H : 7.84, N : 4.49.

2-Allyloxy-*N*-benzyl-2-(5,5-dimethyl-3-oxo-cyclohex-1-enyl)-acetamide: **6c**:

50%. ^{13}C-NMR : 27.5; 28.6; 33.6; 39.4; 43.1; 51.4; 70.7; 81.6; 118.7; 126.7; 127.7; 127.5; 128.7; 132.9; 156.6; 168.2; 199.5. ^{1}H-NMR : 1.00 (s, 3H); 1.05 (s, 3H); 2.30 (d, 2H, J= 2 Hz); 2.20 (dd, 1H, J_{AB}= 18Hz and J=2 Hz); 2.40 (dd, 1H, J_{AB}= 18Hz and J=2Hz); 3.95 (ddt, 1H, J = 12, 6 and 1Hz); 4.00 (dd, 1H, J_{AB}= 18 Hz and J=2 Hz); 4.35 (sl, 1H); 4.45 (d, 2H, J= 6 Hz); 5.15-5.25 (m, 2H); 5.30 (s, 1H); 5.85 (ddt, 1H, J=16, 11 and 6 Hz); 6.15 (sl, 1H); 7.00 (sl, 1H); 7.20-7.40 (m, 5H). IR: 3350, 2950, 2875, 1715, 1665, 1530, 1455, 1365, 1255, 1125, 1075, 1025. MS : 328 (M^{+}·+1, <5), 327 (M^{+}·, <5), 270 (<5), 153 (60), 91 (100).

2-Allyloxy-*N*-hexyl-2-(5,5-dimethyl-3-oxo-cyclohex-1-enyl)-acetamide: **6d**:

40%. ^{13}C-NMR : 13.9; 22.4; 26.4; 27.5; 28.6; 29.4; 31.3; 33.6; 39.0; 39.5; 51.4; 70.6; 81.6; 118.4; 126.4; 133.0; 156.8; 168.0; 199.5. ^{1}H-NMR: 0.89 (t, 3H, J=6.7 Hz); 1.00 (s, 3H); 1.10 (s, 3H); 1.20-1.40 (m, 6H); 1.50 (quint, 2H J= 6.3 Hz); 2.15 (d, 1H, J_{AB}= 18 Hz); 2.27 (d, 2H, J=2.4Hz); 2.41 (d, 1H, J_{AB} = 18 Hz), 4.00 (ddt, 1H, J = 13, 6 and 1.2Hz); 4.10 (ddt, 1H, J = 13, 6 and 1.2 Hz); 5.20-5.40 (m, 2H); 5.88 (ddt, 1H, J = 16, 13 and 6 Hz); 6.20 (sl, 1H); 6.70 (ma, 1H). IR: 3400, 2920, 1650, 1500, 1440, 1360, 1230-1200, 1115, 1070. MS: 322 (M^{+}·+1, 10), 321 (M^{+}·, <5), 264 (9), 153 (100).

N-Benzyl-2-methoxy-2-(3-oxo-cyclohex-1-enyl)-acetamide: **6e**:

51%. ^{13}C-NMR : 29.3; 25.4; 37.6; 42.9; 57.5; 84.2; 126.5; 127.5; 128.6; 158.6; 168.0; 199.2. ^{1}H-NMR: 2.1-2.6 (m, 6H); 3.30 (s, 3H); 4.20 (s, 1H); 4.45 (d, 2H, J=5.5Hz), 6.10 (s, 1H); 7.10 (ma, 1H); 7.20-7.40 (m, 5H). IR: 3400, 2980, 2910, 1650, 1510, 1490, 1080, 1020, 990.MS: 274 (M^{+}·+1, <5), 273 (M^{+}·, <5), 242 (5), 140 (100), 125 (20). Anal. Calcd. for $C_{15}H_{19}NO_3$: C : 70.31, H : 7.01, N : 5.12. Found: C: 69.91, H : 7.08, N : 4.92.

N-Benzyl-2-methoxy-2-(2-methyl-3-oxo-cyclopent-1-enyl)-acetamide: **6f**:

38%. ^{13}C-NMR : 8.4; 25.3; 29.6; 39.7; 43.0; 79.2; 127.6; 128.7; 137.6; 141.1; 164.4; 168.2; 209.3. ^{1}H-NMR: 1.75 (s, 3H); 2.20-2.50 (m, 4H); 3.20 (s, 3H); 4.40 (d, 2H, J=5.5 Hz); 4.70 (s, 1H); 7.00 (ma, 1H); 7.10-7.40 (m, 5H). IR: 3480, 2920, 1660, 1490, 1220-1190. MS: 274 (M^{+}·+1,<5), 273 (M^{+}·, <5), 140 (99), 139 (40), 91 (100), 85 (40), 83 (65).

spiranic β-lactam **6b'**:

^{13}C-NMR: 25.1; 31.6; 32.6; 41.7; 43.6; 44.7; 53.2; 58.6; 64.9; 89.0; 127.6; 128.5; 136.0; 166.7; 207.5. IR: 3000, 2940, 2920, 1740, 1700, 1220-1200. MS: 302 (M^{+}·+1,<5), 301 (M^{+}·, <5), 168 (100), 91 (70).

1-Benzyl-8-hydroxy-3-methoxy-6,6-dimethyl-1-azaspiro[3,5]nonan-2-one **8b**:

After concentration, the crude product obtained from the irradiation of **5b** was dissolved in methanol and sodium tetrahydroboride was added portionwise at 0°C. The mixture was stirred 3 hours then carefully hydrolyzed with water. The salts were filtered and the solution concentrated under reduced pressure. Compound **8b** was isolated by chromatography on silica gel (Eluent AcOEt / hexanes : 80 /20).

^{13}C-NMR: 27.0; 31.3; 34.2; 35.6; 41.4; 43.4; 45.7; 58.8; 64.0; 66.6; 88.3; 127.6; 127.8; 128.6; 136.7; 166.7.

^{1}H-NMR: 0.90 (s, 3H); 1.10 (s, 3H); 1.40-1.70 (m, 5H); 2.00-2.10 (m, 1H); 3.60 (m, 1H); 3.70 (s, 3H); 4.00 (m, 1H); 4.20 (s, 1H); 4.35 (d, J_{AB}= 13.7 Hz, 1H); 4.20 (s, 1H); 4.35 (d, J_{AB}= 13.7 Hz, 1H); 7.20-7.41 (m, 5H). IR : 3450, 2900, 1720, 1445, 1400, 1340, 1240-1200, 1100, 1040. MS : 304 (M^{+}·+1, <5), 303 (M^{+}·, <5), 170 (100), 152 (95), 91 (75), 85 (70).

Preparation of β-enaminones **10** and **12**:

NaHMDS (12mmol) is added to a solution of enaminone **4** (10 mmol.) in THF (100ml) at -78°C. After 5 hours, bromoacetylbromide is carrefully added to the reaction mixture which is further stirred overnight at room temperature under argon. After hydrolysis with brine and extraction with ether, the organic layer is dried over $MgSO_4$. After hydrolysis, the resulting N-(cycloalkenyl) bromoacetamides **9** were rapidily filtered over a short column of alumina and used therefore without further purification.The crude product is added to a suspension of potassium carbonate (12 mmol.) in acetonitrile (120ml).Then, the amine $R_4(R_5)NH$ is added and the reaction mixture is heated overnight. After filtration and concentration, the product is purified by chromatography on alumina. All compounds are isolated as syrups.

N-Benzyl, N-(5,5-dimethyl-3-oxo-cyclohex-1-enyl)-2-diethylaminoacetamide: **10a**

95%. ^{13}C-NMR: 11.4; 27.9; 33.3; 42.9; 47.1; 50.3; 50.7; 57.4; 121.6; 127.1; 127.5; 128.6; 136.6; 160.4; 171.5; 199.2. ^{1}H-NMR: 0.95 (t, 6H, J = 6 Hz); 0.96 (s, 6H); 2.16 (s, 2H); 2.47 (s, 2H); 2.55 (q, 4H, J= 6 Hz); 3.30 (s, 2H); 4.90 (s, 2H); 5.70 (s, 1H); 7.10-7.30 (m, 5H). IR : 2960, 1640, 1380, 1360, 1300, 1190, 1150. MS : 343 (M^{+}·+1, <5), 342 (M^{+}·, <5), 91 (100), 86 (99), 58 (40). UV (CH_3CN) ε 276= 9700; ε 222= 5500. Anal. Calcd. for: $C_{21}H_{30}N_2O_2$: C : 73.63, H : 8.83, N : 8.18. Found: C : 73.25, H : 9.09, N : 7.95.

N-Benzyl, N-(5,5-dimethyl-3-oxo-cyclohex-1-enyl)-2-(diallylamino)acetamide: **10b**

76%. ^{13}C-NMR: 27.9; 33.3; 43.0; 50.2; 50.6; 56.0; 57.0; 118.3; 122.2; 127.2; 127.5; 128.6; 134.7; 136.5; 159.7; 170.7; 199.0. ^{1}H-NMR: 0.97 (s, 6H); 2.20 (s, 2H); 5.10-5.20 (m, 4H); 5.70 (t, 1H, J = 1.1 Hz); 5.80 (ddt, 2H, J = 16.8, 13.0, 6.5 Hz); 7.15-7.30 (m, 5H). IR : 3000, 1640, 1620, 1420, 1210, 930. MS : 367 (M+.+1,<5); 366 (M+.,<5); 325 (19); 110 (99); 91 (100). UV: (CH_3CN) ε 278= 8100; ε 220= 6400.Anal. Calcd. for: $C_{23}H_{30}N_2O_2$: C : 75.36, H : 8.25, N : 7.64. Found: C : 75.21, H : 8.41, N : 7.41.

N-Benzyl, *N*-(5,5-dimethyl-3-oxo-cyclohex-1-enyl)-2-[benzyl,methylamino]acetamide: **10c**

83%. ^{13}C-NMR: 27.8; 33.3; 42.6; 43.07; 50.5; 60.6; 59.7; 61.5; 121.7; 127.0; 127.2; 127.5; 128.2; 128.6; 129.0; 136.4; 137.6; 159.9; 170.5; 199.0. ^{1}H-NMR: 0.90 (s, 6H); 2.13 (s, 2H); 2.32 (s, 2H); 2.35 (s, 3H); 3.20 (s, 2H); 3.58 (s, 2H); 4.85 (s, 2H); 5.70 (s, 1H); 7.10-7.45 (m, 10H). IR : 3010; 2950; 1655; 1620; 1440; 1390; 1350. MS : 390 (M^{+}·+1, <5); 389 (M^{+}·,<5); 134 (95); 105 (100); 91 (99); 83 (95); 77 (85). UV (CH_3CN) ε 281= 8200; ε 207= 24200. Anal. Calcd. For: $C_{21}H_{30}N_2O_2$: C : 73.63, H : 8.83, N : 8.18. Found: C : 73.25, H : 9.09, N : 7.95.

N-(5,5-Dimethyl-3-oxo-cyclohex-1-enyl) *N*-hexyl 2-diallylaminoacetamide: **10d**

63%. ^{13}C-NMR: 13.8; 22.4; 26.4; 28.1; 28.4; 31.3; 33.3; 42.9; 46.35; 50.8; 55.8; 57.0; 118.3; 122.8; 134.9; 159.6; 170.2; 199.2. ^{1}H-NMR: 0.88 (t, 3H, J = 6.5 Hz); 1.10 (s, 6H); 1.20-1.40 (m, 6H); 1.45-1.60 (m, 2H); 2.28 (s, 2H); 2.42 (s, 2H); 3.15 (d, 4H, J = 6.5 Hz); 3.32 (s, 2H); 3.52 (t, 2H, J = 7.6 Hz); 5.10-5.30 (m, 4H); 5.79 (ddt, 2H, J = 17.0, 10.0 and 7.0 Hz); 5.80 (s, 1H). IR : 3000; 1640; 1610; 1500; 1410; 1200; 1100. MS : 361 (M^{+}·+1,<5); 360 (M+.,<5); 319 (50); 111 (100); 110 (99); 68 (85). UV (CH_3CN) ε 281= 7300; ε 214= 7300. Anal. Calcd. for: $C_{22}H_{36}N_2O_2$: C : 73.29, H : 10.06, N : 7.77. Found: C : 73.08, H : 10.18, N : 7.83.

N-(5,5-dimethyl-3-oxo-cyclohex-1-enyl)-2-diallylaminoacetamide: **10e**

47%. ^{13}C-NMR: 21.3; 28.1; 36.5; 57.3; 57.6; 11.8; 119.0; 133.6; 154.1; 170.1; 199.4. ^{1}H-NMR: 2.05 (quint., 2H, J = 6.5 Hz); 2.37 (t, 2H, J = 6.5 Hz); 2.58 (t, 2H, J = 6.5 Hz); 3.10 (s, 2H); 3.60 (d, 4H, J = 6.5 Hz); 5.15-5.30 (m, 4H); 5.80 (ddt, 2H, J = 15, 10 and 6.5 Hz); 6.55 (sl, 1H); 8.90 (sl, 1H). IR : 3220; 3000; 1630; 1590; 1430; 1410;

1210. MS : 249 ($M^{+\cdot}$+1,<5); 248 ($M^{+\cdot}$,<5); 207 (95); 111 (98); 110 (99); 96 (56); 81 (61); 68 (100). UV (CH_3CN) ε 271= 9700. Anal. Calcd. for: $C_{14}H_{20}N_2O_2$: C : 67.72, H : 8.12, N : 11.28. Found: C : 67.72, H : 8.19, N : 11.16.

N-Benzyl, *N*-(3-oxo-cyclopent-1-enyl)-2-diallylaminoacetamide: **10f**

67%. ^{13}C-NMR: 8.6; 28.0; 34.04; 49.1; 55.8; 57.0; 118.3; 127.7; 128.0; 128.4; 134.6; 135.4; 136.5; 166.8; 169.4; 207.5. ^{1}H-NMR: 1.40 (s, 3H); 2.40-2.50 (m, 2H); 2.55-2.70 (m, 2H); 3.10 (d, 4H, J = 6.5 Hz); 3.15 (s, 2H); 4.80 (s, 2H); 5.10-5.20 (m, 4H); 5.60-5.80 (m, 2H); 7.10-7.35 (m, 5H). IR : 2960; 2920; 2800; 1640; 1430; 1400; 1315; 1230-1200; 1100; 1080; 1000. MS : 339 ($M^{+\cdot}$+1, <5); 338 ($M^{+\cdot}$,<5); 297 (40); 111 (42); 110 (95); 91 (100).

N-Carbomethoxymethyl, *N*-(5,5-dimethyl-3-oxo-cyclohex-1-enyl)-2-diallylaminoacetamide: **10g**

50%. ^{13}C-NMR: 27.8; 33.1; 42.6; 48.5; 50.6; 55.0; 55.9; 56.6; 118.4; 134.2; 159.6; 168.7; 170.5; 198.7. ^{1}H-NMR: 1.04 (s, 6H); 2.19 (s, 2H); 2.43 (s, 2H); 3.09 (d, 2H, J = 6.7 Hz); 3.30 (s, 2H); 3.68 (s, 3H); 4.26 (s, 2H); 5.11 (m, 4H); 5.72 (m, 2H); 5.75 (s, 1H). IR : 1750; 1665; 1625; 1385; 1365; 1205; 995. MS : 348 ($M^{+\cdot}$, 29); 307 (31); 110 (100); 68 (35).

N-Benzyl, *N*-(5,5-dimethyl-3-oxo-cyclohex-1-enyl)-2-[(1S)-1-(phenyl)ethyl]aminoacetamide: **11a**

57%. ^{13}C-NMR: 17.5; 28.2; 28.5; 32.9; 40.9; 43.4; 49.0; 49.4; 56.2; 99.9; 126.7; 127.4; 127.7; 127.9; 128.6; 128.9; 137.7; 139.8; 163.4; 167.9; 197.0. ^{1}H-NMR: 0.90 (s, 6H); 1.51 (d, 3H, J = 7 Hz); 2.05 (s, 2H); 2.28 (s, 2H); 3.63 (d, 1H, J_{AB} = 17.5Hz); 3.75 (d, 1H, J_{AB} = 17.5Hz); 4.22 (d, 2H, J = 5.7 Hz); 5.1 (q, 1H, J = 7 Hz); 5.2 (s, 1H); 6.58 (ma, 1H); 7.00-7.30 (m, 10H). IR : 3430; 3010; 2950; 1685; 1575. MS : 391 ($M^{+\cdot}$+1,<5); 390 ($M^{+\cdot}$,<5); 243 (10); 105 (100); 91 (70); 83 (60). UV (CH_3CN) ε 291= 2500, ε 211= 1400.
$[\alpha]_D$ = -1,14 (c = 0,07, $CHCl_3$).

N-Benzyl *N*-(5,5-dimethyl-3-oxo-cyclohex-1-enyl)-2-[allyl,1-(phenyl)ethyl]aminoacetamide: **11b**

58%. ^{13}C-NMR: 18.5; 27.8; 28.0; 33.4; 43.1; 50.4; 50.7; 52.7; 53.9; 59.8; 117.6; 121.9; 127.1; 127.5; 128.5; 128.6; 136.0; 136.5; 143.6; 159.8; 171.4; 199.0. ^{1}H-NMR: 0.92 (s, 3H); 0.95 (s, 3H); 1.35 (d, 3H, J = 6.5 Hz); 2.15 (s, 2H); 2.25 (d, 1H, J_{AB} = 17.5 Hz); 2.38 (d, 1H, J_{AB} = 17.5 Hz); 3.28 (d, 2H, J = 6.5 Hz); 3.39 (d, 1H, J_{AB} = 16 Hz); 3.45 (d, 1H, J_{AB} = 16 Hz); 4.14 (q, 1H, J = 6.5 Hz); 4.78 (s, 2H); 5.05-5.25 (m, 2H); 5.62 (s, 1H); 5.82 (ddt, 1H, J = 16.4, 9.9 and 6.5 Hz); 7.10-7.30 (m, 10H). IR : 3000; 1500; 1460; 1200. UV (CH_3CN) ε 281= 8200, ε 207= 24000. $[\alpha]_D$ = -12 (c = 0,39, $CHCl_3$).

Irradiation of compounds **10** and **11** was carried out as described for **1** and **5**.

N-Benzyl-2-diethylamino-2-(5,5-dimethyl-3-oxo-cyclohex-1-enyl)-acetamide: **12a**

74%. ^{13}C-NMR: 11.5; 27.4; 28.45; 33.6; 41.4; 43.2; 43.6; 51.2; 127.4; 127.7; 128.6; 129.1; 137.9; 157.2; 169.7; 199.4. ^{1}H-NMR: 0.95 (t, 6H, J = 7 Hz); 1.00 (s, 3H); 1.05 (s, 3H); 2.20 (s, 2H); 2.25 (s, 2H); 2.47 (dq, 2H, J = 14 and 7 Hz); 2.67 (dq, 2H, J = 14 and 7 Hz); 3.80 (s,1H); 4.40 (d, 1H, J_{AB} = 5.7 Hz); 4.45 (d, 1H, J_{AB} = 5.7 Hz); 6.10 (s, 1H); 7.20-7.40 (m, 6H). IR : 3600; 3200; 300; 1650; 1500; 1420; 1210; 920. MS : 343 ($M^{+\cdot}$+1,<5); 342 ($M^{+\cdot}$, <5); 91 (52); 86 (100); 58 (58).

N-Benzyl-2-diallylamino-2-(5,5-dimethyl-3-oxo-cyclohex-1-enyl)-acetamide: **12b**

73%. ^{13}C-NMR: 27.9; 28.0; 33.7; 41.6; 43.2; 51.2; 53.2; 70.9; 118.5; 127.5; 127.7; 128.6; 129.2; 134.0; 137.8; 156.8; 169.1; 199.3. ^{1}H-NMR: 1.00 (s, 3H); 1.05 (s, 3H); 2.22 (s, 2H); 2.25 (dd, 1H, J_{AB} = 17.9 Hz and J = 1.1 Hz); 2.35 (dd, 1H, J_{AB} = 17.9 Hz and J = 1.1 Hz); 3.08 (dd, 2H, J_{AB} = 14.5 Hz and J = 7 Hz); 3.30 (dd, 2H, J_{AB} = 14.5 Hz and J = 7 Hz); 3.95 (s, 1H); 4.38 (dd, 1H, J_{AB} = 14.5 Hz and J = 6 Hz); 4.50 (dd, 1H, J_{AB} = 14.5 Hz and J = 6 Hz); 5.10-5.20 (m, 4H); 5.75 (ddt, 2H, J = 16, 9 and 6 Hz); 6.06 (s, 1H); 7.15 (t, 1H, J = 5.8 Hz); 7.20-7.50 (m, 5H). IR : 360; 2960; 1660; 1500; 1460; 1365; 1230-1200; 995. MS : 367 (M+.+1,<5); 366 (M+.,<5); 232 (99); 110 (65); 91 (99); 57 (100). Anal. Calcd. for: $C_{23}H_{30}N_2O_2$: C : 74.54, H : 8.53, N : 7.90. Found: C : 74.44, H : 8.49, N : 8.13.

N-Benzyl-2-(benzyl,methylamino)-2-(5,5-dimethyl-3-oxo-cyclohex-1-enyl)-acetamide: **12c**

75%. ^{13}C-NMR: 27.3; 28.7; 33.6; 39.7; 41.2; 43.3; 51.2; 59.7; 75.9; 127.4; 127.5; 127.8; 128.4; 128.6; 128.9; 137.4; 137.8; 157.0; 168.9; 199.3. ^{1}H-NMR: 1.00 (s, 3H); 1.10 (s, 3H); 2.20 (s, 3H); 2.25 (s, 2H); 2.35 (s, 2H); 3.50 (d, 1H, J_{AB} = 13.0 Hz); 3.60 (d, 1H, J_{AB} = 13 Hz); 3.65 (s, 1H); 4.45 (d, 2H, J = 6 Hz); 6.20 (s, 1H); 7.10-7.35 (m, 10H + NH). IR : 3390; 3010; 2970; 1655; 1505; 1440; 1365; 1240; 1215. MS : 391 ($M^{+\cdot}$+1,<5); 390 ($M^{+\cdot}$,<5); 256 (80); 91 (99); 57 (100).

2-Diallylamino-2-(5,5-dimethyl-3-oxo-cyclohex-1-enyl)-*N*-hexyl-acetamide: **12d**

77%. ^{13}C-NMR: 13.9; 22.5; 26.6; 28.0; 28.2; 29.5; 31.4; 33.9; 39.2; 41.9; 51.5; 53.3; 71.0; 118.5; 129.4; 134.2; 156.9; 169.2; 199.5. ^{1}H-NMR: 0.85 (t, 3H, J = 6.5 Hz); 1.05 (s, 3H); 1.10 (s, 3H); 1.20-1.40 (m, 6H); 1.50 (quint., 2H, J = 6.5 Hz); 2.20 (d, 1H, J_{AB} = 16.8 Hz); 2.20 (s, 2H); 2.35 (d, 1H, J_{AB} = 16.8 Hz); 3.00-3.15 (m, 2H); 3.20-3.35 (m, 4H); 3.90 (s, 1H); 5.10-5.25 (m, 4H); 5.70-5.90 (m, 2H); 6.10 (s, 1H); 6.75 (ma, 1H). IR : 3400; 3010; 2960; 1655; 1530; 1440; 1365; 1230. MS : 362 ($M^{+\cdot}$+1,<5); 361 ($M^{+\cdot}$,<5); 232 (99); 110 (95); 96 (100).

N-Benzyl-2-diallylamino-2-(2-methyl-3-oxo-cyclopent-1-enyl)-acetamide: **12f**

54%. ^{13}C-NMR: 9.1; 28.1; 33.9; 43.4; 53.8; 65.6; 118.6; 127.6; 127.8; 128.8; 133.9; 137.9; 141.9; 165.0; 169.4; 209.2. ^{1}H-NMR: 1.75 (t, 3H, J = 2 Hz); 2.37 (t, 2H, J = 5.0 Hz); 2.40-2.70 (m, 2H); 3.05 (dd, 1H, J_{AB} = 15 Hz and J = 6.0 Hz); 3.25 (dd, 1H, J_{AB} = 15 Hz and J = 6.0 Hz); 4.42 (s, 1H); 4.45 (d, 2H, J = 7.0 Hz); 5.05-5.20 (m, 4H); 5.75 (ddt, 2H, J = 17, 10 and 7.0 Hz); 7.15-7.40 (m, 5H + 1NH). IR : 3360; 2990; 2910; 1660; 1500; 1430; 1160. MS : 338 ($M^{+\cdot}$+1,<5); 337 ($M^{+\cdot}$,<5); 204 (100); 91 (30); 83 (30).

N-Carbomethoxymethyl-2-(diallylamino)-2-(5,5-dimethyl-3-oxo-cyclohex-1-enyl)-acetamide: **12g**

45%. ^{13}C-NMR: 27.9; 33.9; 40.7; 51.3; 52.2; 53.2; 56.9; 70.3; 118.5; 129.5; 134.2; 156.5; 168.7; 168.8; 199.3. ^{1}H-NMR: 1.05 (s, 3H); 1.06 (s, 3H); 2.24 (dd, 1H, J_{AB} = 18 Hz, J = 1.4 Hz); 2.29 (s, 2H); 2.38 (dd, 1H, J_{AB} = 18 Hz, J = 1.4 Hz); 3.14 (dd, 1H, J_{AB} = 14.6 Hz, J = 6.7 Hz); 3.32 (dd, 1H, J_{AB} = 14.6 Hz, J = 5.8 Hz); 3.78 (s, 3H); 4.00 (s, 1H); 4.06 (dd, 1H, J_{AB} = 18.2 Hz, J = 5.4 Hz); 4.11 (dd, 1H, J_{AB} = 18.2 Hz, J = 5.8 Hz); 5.15-5.30 (m, 4H); 5.81 (ddt, 2H, J = 16.1, 9.7 and 5.9 Hz); 6.05 (s, 1H); 7.23 (m, 1H). IR : 3335; 1755; 1670; 1520; 1445; 1370; 1210; 995; 910. MS : 320 ($M^{+\cdot}$, 3); 293 (26); 204 (100); 136 (24); 107 (31); 96 (92); 81 (61); 69 (73); 55 (52).

2-[Allyl-(1-phenylethyl)-amino]-*N*-benzyl-2-(5,5-dimethyl-3-oxo-cyclohex-1-enyl)-acetamide: **13b**

58%. ^{13}C-NMR: Major diastereoisomer: 16.7; 27.9; 28. 4; 43.2;43.4; 51.3; 51.6; 58.1; 69.05; 117.06; 127.5; 127.6; 127.9; 128.6; 137.1; 142.1; 159.3; 169.7; 199.6. Minor diastereoisomer: 18.4; 27.6; 28.6; 33.8; 43.2; 43.4; 51.3; 51.6; 58.6; 68.7; 116.7; 127.5; 127.6; 127.9; 128.6; 137.6; 142.1; 158.1; 170.2; 199.6. ^{1}H-NMR: 0.90 (s, 6H); 1.00 (s, 6H); 1.35 (d, 6H, J = 6 Hz); 2.20 (s, 4H); 2.10 (s, 4H); 3.40 (d, 4H, J = 6 Hz); 3.90 (s, 2H); 4.10 (q, 1H, J = 6Hz); 4.20 (dd, 2H, J_{AB} = 18 Hz and J = 6Hz); 4.30 (dd, 2H, J_{AB} = 18 Hz and J = 6Hz); 4.40 (q, 1H, J = 6.0 Hz); 5.00-5.15 (m, 4H); 5.70-5.80 (m, 2H); 5.90 (s, 1H); 6.10 (s, 1H); 6.45 (ma, 1 NH); 7.10-7.40 (m, 10H). IR : 3400; 3000; 1650; 1500; 1460; 1200. MS : 431 ($M^{+\cdot}$+1,<5); 430 ($M^{+\cdot}$,<5); 298 (5); 192 (80); 105 (99); 91 (100).

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