96. New Polycyclic Compounds from Photochemical Rearrangements of Some Substituted 2-Azatricyclo[5.2.2.$0^{1,5}$]undeca-4,8,10-trien-3-ones

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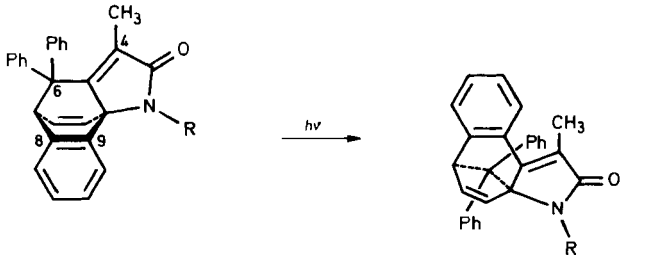
(5.III.91)

The products formed on UV irradiation of several tricyclic compounds (*i.e.* **3**, **6**, **8**, **15**, and **17**, *Schemes 2–4*) were studied in detail. A marked dependence of the reaction course on the type and site of substitution was found. Among the several light-induced transformations, a novel rearrangement, *i.e.* **11** to **9** (*Scheme 3*) was identified. The formation of the polycyclic compound **13** on irradiation of **8a** (*Scheme 3*) resulted from an unexpected skeletal rearrangement with dearomatization of one benzene ring. The structures of compounds **10**, **11**, and **13** were established by X-ray crystallography (*Figs. 1–3*). An attempt was made to give a general mechanistic picture of all observed photochemical results (*Schemes 4–6*).

1. Introduction. – Recently, we described a new photochemical rearrangement of 2-azabenzotricyclo[5.2.2.$0^{1,5}$]undecatrien-3-ones to 2-azabenzotricyclo[6.2.1.$0^{1,5}$]undecatrien-3-ones (**1a,b** → **2a,b**, *Scheme 1*), proceeding in a regiospecific way [1]. It was demonstrated that the course of the photochemical reaction of the starting tricyclic compounds is strongly dependent on the substituents at C(6) and also at C(8)–C(9). The

Scheme 1



1a R = H
b R = COCHPh$_2$

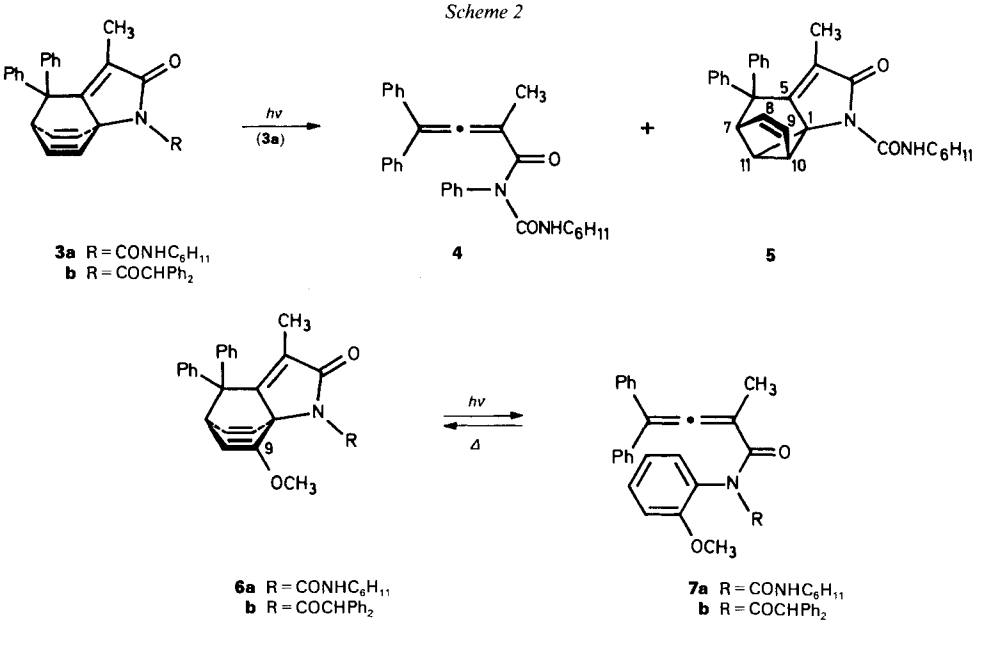
2a R = H
b R = COCHPh$_2$

observed skeletal rearrangement was previously known as a thermal reaction, which is only possible for compounds having an electron-withdrawing group at C(4) [2]. We now report on the photochemical behaviour of some new 2-azatricyclo[5.2.2.$0^{1,5}$]undeca-4,8,10-trien-3-ones possessing diverse substituents at C(8)–C(9) as well as at the N-atom.

2. Results and Discussion. – The starting compounds were obtained as described in [1] and [3] from 2-methyl-4,4-diphenylbuta-2,3-dienoic acid and the corresponding substituted carbodiimide or ketenimine (see *Exper. Part*).

Urea **3b** with an unsubstituted C(8)=C(9) bond was previously shown to give a complex reaction mixture on irradiation [1]. Carboxamide **3a**, however, gave a photolysate[1]) containing the *retro-Diels-Alder* allene **4** and the di-π-methane product **5** (*Scheme 2*). The structure of **4** was mainly evidenced by the Me signal at characteristically low field (1.97 ppm) in the ^{1}H-NMR spectrum and by the signal of C(3) in the ^{13}C-NMR spectrum (207.5 ppm), while the structure of **5** was based on the replacement of one of the double bonds at C(8) and C(10) by a cyclopropane ring adjacent to the remaining double bond, as evidenced by the coupling constants (*vide infra* and *Exper. Part*). On irradiation under the same conditions, the 9-methoxy derivatives **6a, b** gave the allenic carboxamides **7a, b** as the sole photoproducts (*Scheme 2*). The latter recyclized in the dark and at room temperature back to **6a, b**. The structure of **7a, b** was based on the very close similarity of their ^{1}H- and ^{13}C-NMR spectra to those of known allenic carboxamides [3].

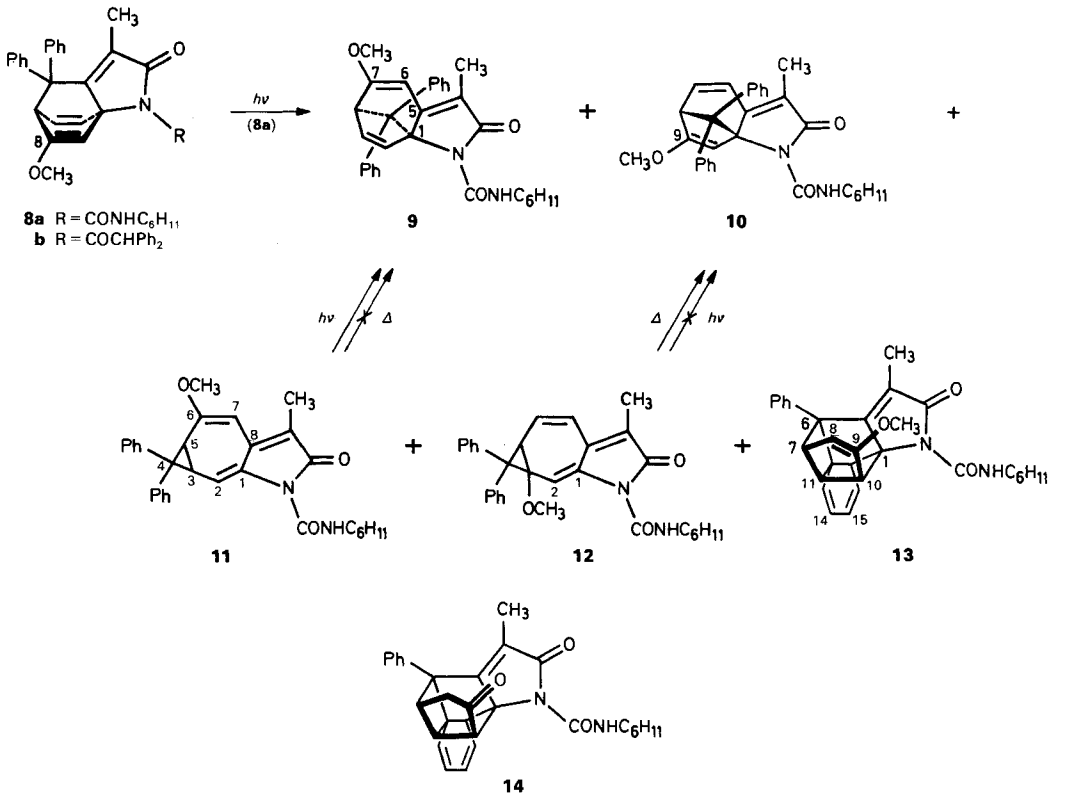
Scheme 2



The 8-methoxy derivative **8a**, however, unlike **6a, b**, afforded a complex photolysate, which was chromatographically separated to give three colourless (**9**, **10**, and **13**) and two yellow products (**11** and **12**) in low yields (*Scheme 3*). The positional isomers **9** and **10** were distinguished on the basis of the ^{1}H-NMR analysis. The vicinal coupling constants ^3J(H–C(9), H–C(10)) = 5.7 Hz for **9** and ^3J(H–C(6), H–C(7)) = 9.1 Hz for **10** compare

[1]) The ^{1}H-NMR spectrum of the fresh photolysate had to be measured at –10° to detect the thermally unstable photoproducts **4** and **5**.

Scheme 3



well with those of the parent compounds [1] [4]. On the other hand, the longest wavelength absorption of **9** is at 327 nm, while **10** absorbs at 291 nm. The structure of **10** was established by X-ray crystallography (see *Chapt. 4*). The yellow products **11** and **12** were obtained as a chromatographically unresolvable mixture, which afforded pure **11** on recrystallization from benzene. The NMR data of **12** were obtained after subtraction of the signals of **11** from those of the mixture. The structures of **11** and **12** were easily deduced from the NMR data and confirmed for the former by X-ray crystallography (see *Chapt. 4*)

Compound **12** shows ^{1}H-NMR signals for 3 olefinic protons (8.22 (*s*, H–C(2)), 6.12 (*d*, H–C(7)), and 6.50 ppm (*dd*, H–C(6))), while in the spectrum of **11**, only 2 olefinic protons appear (8.08 (*d*, H–C(2)) and 5.24 ppm (*s*, H–C(7))). Only **11** has the enol-ether fragment CH_3O–C=CH (^{1}H-NMR: 5.24 ppm (*s*, H–C(7)); ^{13}C-NMR: 93.1 ppm (C(7))). The presence of a cyclopropane ring in the structure of both **11** and **12** was evidenced by the large ^1J(C,H) constants (**11**: 160.7 (H–C(3)) and 162.3 Hz (H–C(5)); **12**: 157.3 Hz (H–C(5))) [5] [6]. The assignments for the ^{1}H- and ^{13}C-NMR signals of **11** were supported by the HETCOR spectrum for the ^{1}H,^{13}C-connectivities (see *Exper. Part*).

In separate experiments, compound **11** was shown to be photochemically unstable, affording **9** on direct irradiation; in contrast, **12** was stable under the same conditions, but was converted to **10** in benzene solution at room temperature in the dark. It should be

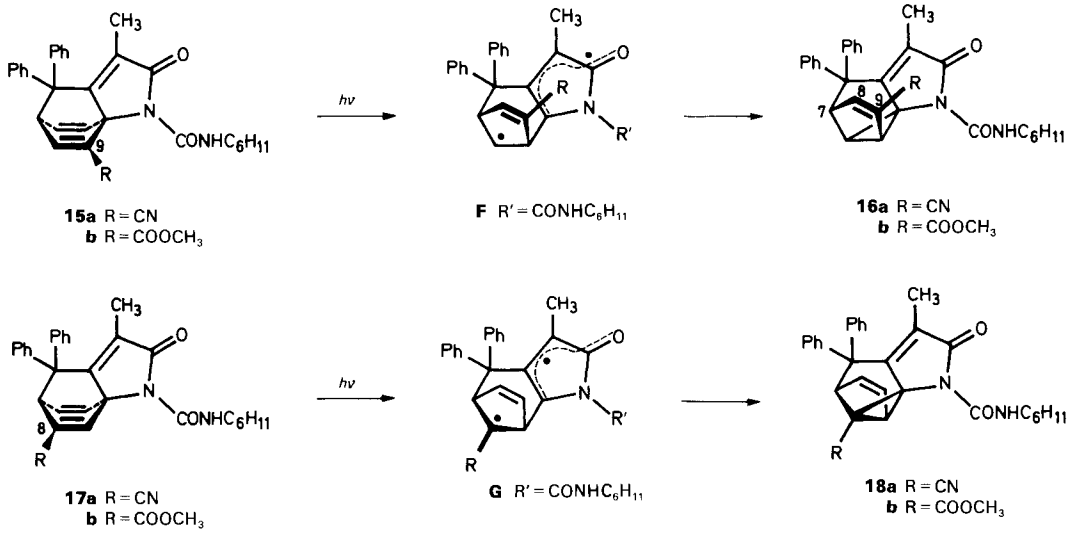
pointed out that **10** was detected in trace amounts in the fresh photolysate, *i.e.* a direct photochemical path to **10** cannot be excluded.

The spectral data of the colourless photoproduct **13** revealed the presence of an enol-ether fragment, together with only one Ph substituent and also four methine protons. On mild acid-catalysed hydrolysis, the enol-ether function was converted into a $COCH_2$ fragment, one of the protons of which showed a large coupling constant ($^3J(H,H) = 6.0$ Hz) indicating the presence of the fragment $COCH_2CH$. The latter could be only interpreted as evidence for a 'deep-seated' skeletal rearrangement of **8a** leading to **13**. The structure of **13** was established again by a single-crystal X-ray analysis (see *Chapt. 4*) and the ketone derived from **13** by acid-catalysed hydrolysis, therefore, has structure **14** (*Scheme 3*).

The 8-methoxy derivative **8b** gave, on irradiation, a rather complex mixture; no pure compound could be isolated from this by means of TLC.

The tricyclic compounds **15a, b** and **17a, b** bearing electron-withdrawing substituents at C(9) and at C(8), respectively, gave, on direct irradiation, the corresponding tetracyclo-[5.3.1.$0^{1,5}$.$0^{10,11}$] derivatives **16a, b** and **18a, b** (*Scheme 4*).

Scheme 4

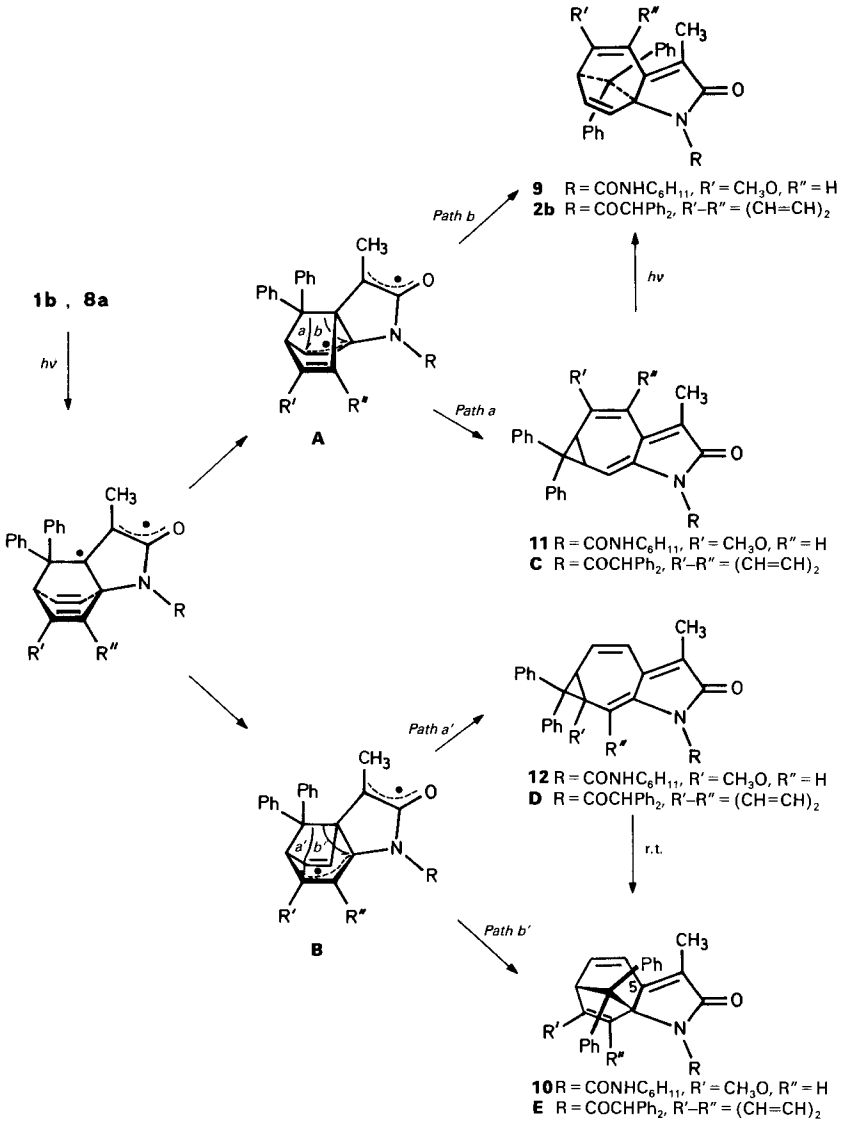


The elucidation of the structures of these di-π-methane rearrangement products was based on the NMR data.

As can be seen from the coupling constants and from decoupling experiments in the ^{1}H-NMR spectra (see *Exper. Part*), only 1 olefinic proton (H–C(8)) in **16** is adjacent to a methine proton (H–C(7)), which, in turn, is coupled with one of the 2 cyclopropane protons. In **18**, however, 2 olefinic protons show vicinal coupling with 2 methine protons in the fragment CH–CH=CH–CH. The assumption that 2 H (for **16**) or 1 H (for **18**) are part of a cyclopropane ring was supported by the characteristically large values of the $^1J(C,H)$ constants (**16b**: 185.5 and *ca.* 178 Hz; **18a**: 176.3 Hz) [5] [6]. The full assignment of the ^{1}H- and ^{13}C-NMR signals of **18** was achieved on the basis of the HETCOR spectra (see *Exper. Part*).

3. Mechanistic Considerations. – In addition to the regiospecificity, the rearrangement **1b** → **2b** [1] (*Scheme 1*) was found to be independent of wavelength and solvent changes and could neither be sensitized nor quenched. It can formally be considered to proceed *via* 1,2-bond shifts, which can be expected to be affected significantly by substituents. Surprisingly, the unsubstituted **3a** rearranged to the *retro-Diels-Alder* product **4** and the di-π-methane product **5** (*Scheme 2*), but not to the expected unsubstituted tricyclo[6.2.1.$0^{1,5}$]undecatrienone of type **2**. The formation of **4** and **5** was not influenced by O_2.

Scheme 5

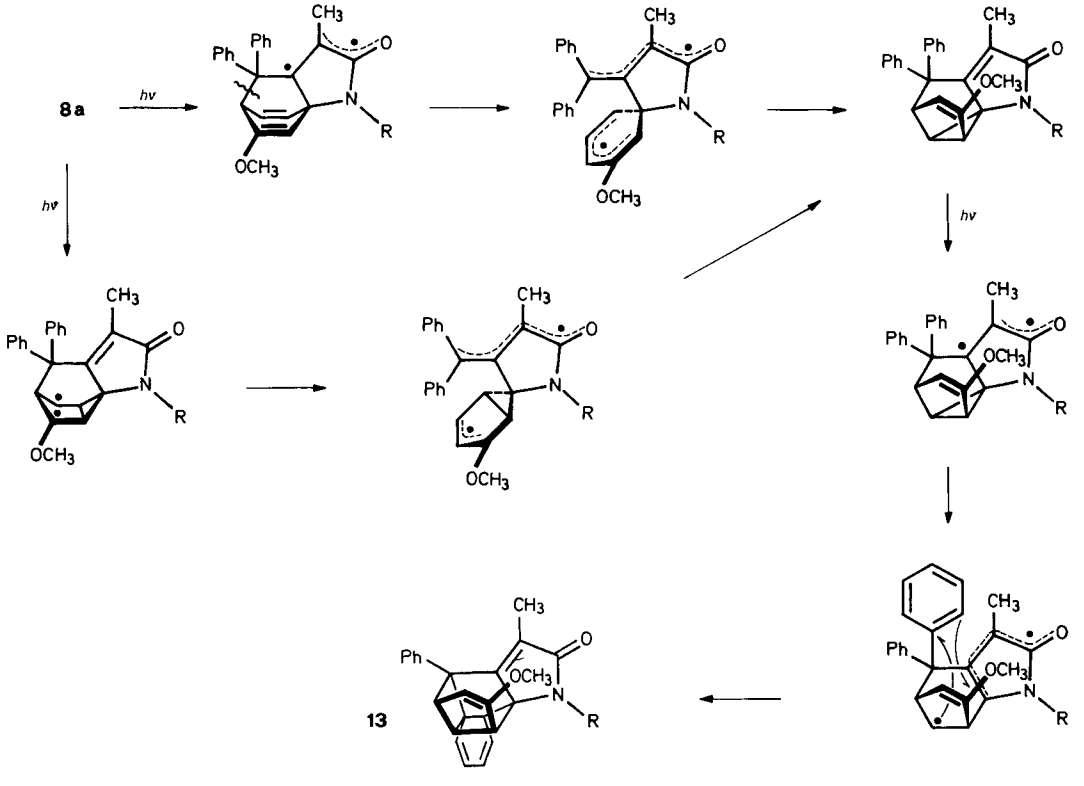


Considerably more informative was the direct irradiation of 8-methoxy-substituted **8a** yielding **9**–**13** (*Scheme 3*). The thermal instability of **12** deserves a special note, since on standing at room temperature it gave **10** as a sole product. An interesting difference in photochemical behaviour between products **11** and **12** was observed. On direct irradiation, **11** gave **9**, the photochemically allowed product according to orbital-symmetry considerations, whereas **12** was inert. Isomer **11** also afforded **9** on sensitization with 2-acetylnaphthalene (E_T = 59 kcal/mol [7]); this conversion was O_2- and solvent-independent.

The formation of compounds **9**–**12** from **8a**, as well as of **2b** from **1b**, can be envisaged to pass through the two biradicals **A** and **B** (*Scheme 5*). We consider the *Paths a* and *a'* leading to **11** and **12** particularly informative for explaining the regiospecificity of the rearrangement in the case of the benzo derivative **1b** (see *Scheme 1*). Indeed, a product **E** most likely would require intermediate **D** as a precursor; but the formation of **D** should be unfavourable on steric and energetic grounds, thus explaining the surprising regiospecificity depicted in *Scheme 1*.

Tentative reaction sequences for the formation of photoproduct **13**, which is obviously the result of a profound rearrangement, are given in *Scheme 6*. In this connection, two features deserve special mentioning, the participation of the Ph substituent in a

Scheme 6



cyclisation reaction and the shift of the MeO-bearing double bond. The formation of **13** proceeds *via* an intermediate since it was found to be sensitized by benzene and affected by a change in solvent. Its formation is wavelength-independent. It can, therefore, be concluded that the formation of **13** proceeds along a different path than that of **11** and **12**, the latter remaining unaffected by a change in solvent or quenching (O_2 included). Compounds **11** and **12** were also obtained through benzene sensitization – an indication that their formation probably occurs *via* a singlet reaction.

The formation of the *retro-Diels-Alder* product **7** from **6** (*Scheme 2*) was unaffected by the presence of O_2 and solvent changes, could not be sensitized by 2-acetylnaphthalene, but was sensitized by benzene. A particularly interesting case illustrating the effect of substitution on regioselectivity arises with compounds **15a**, **b** and **17a**, **b** which bear electron-withdrawing groups instead of the MeO groups in **6** and **8**, respectively. The reaction course is completely different and leads to the di-π-methane products **16** and **18** (*Scheme 4*). The results allow us to postulate that in the case of C(9) substitution, the stabilisation of the incipient double bond appears to govern the formation of **16** (*via* **F**), while in the case of C(8) substitution, the stabilisation of the radical is decisive (→ **G** →**18**) [8]. The absence of di-π-methane products arising as artifacts from C(8)–C(11) bond formation points to the preferential position of the radical at C(1). The formation of **16** and **18** was wavelength, solvent, O_2, and piperilene independent, but could be sensitized by benzene. On sensitization with 2-acetylnaphthalene, only the formation of **18a** was observed.

4. Crystal Structure Determination of 10, 11, and 13. – Crystals of **10**, **11**, and **13** obtained from benzene/hexane (**10**, **11**) or Et_2O (**13**) were used for X-ray structure determination[2]).

The intensities were collected at 297 K on a *Nicolet-R3* diffractometer in the *Wyckoff* ω-scan mode using graphite-monochromated MoK_α radiation ($\lambda = 0.71069$ Å). The intensities were corrected for *Lorentz* and polarisation effects and, for **11** for decay, since the standard intensities decreased linearly by 9% during the data collection. No corrections were applied for absorption. The structures were solvent by direct methods (SHELXS-86 [9]), which in each case yielded the positions of all non-H-atoms, and refined on *F* by full-matrix least-squares procedures using the program SHELX-76 [19].

In **10**, there is disorder within the cyclohexyl ring. This was successfully resolved by refining two conformations of the ring with 50% site-occupation factors. The positions of the disordered atoms were refined with isotropic temperature factors, while all other non-H-atoms were refined with anisotropic thermal parameters. The H-atom attached to the amide N-atom was located in a difference *Fourier* map, and its position and temperature factor were allowed to refine with a N–H bond-length constraint of 1.02 Å. All other H-atoms were placed in geometrically calculated positions with a C–H bond length of 1.08 Å. During refinement, their positions were constrained to ride on the C-atom to which they were bonded, and a common overall isotropic temperature factor was refined. No attempt was made to determine the absolute configuration.

The asymmetric unit of **11** contains two independent molecules **11A** and **11B** and one highly disordered benzene solvent molecule. The cyclohexane ring in one of the molecules is possibly disordered, but a disordered model for this could not be successfully refined. Consequently, the ordered model contains some atoms with large thermal vibration ellipsoids. Two sets of six C-atoms with 50% site occupation factors were refined for the benzene molecule, but the solvent appears to occupy many orientations within its cavity. All non-H-atoms were refined with anisotropic thermal parameters, except those of the solvent molecule which were refined with isotropic temperature factors only. The H-atom attached to the amide N-atom was located in a difference *Fourier* map, and its position was allowed to refine. All other H-atoms were placed in geometrically calculated positions with a C–H bond length

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[2]) Atomic coordinates, bond lengths, and angles have been deposited with the *Cambridge Crystallographic Data Centre*, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

of 1.08 Å, and during refinement their positions were constrained to ride on the C-atom to which they were bonded. Individual isotropic temperature factors were refined for all H-atoms. H-atoms were not included for the highly disordered solvent molecule.

For **13**, there was no disorder evident in the structure. All non-H-atoms were refined with anisotropic thermal parameters. All H-atoms were located in a difference *Fourier* map, and their positions were allowed to refine together with individual isotropic temperature factors. A light bond-length constraint of 1.02 Å was applied to the N–H bond.

Crystallographic data are given in *Table 1*, and views of the molecules are shown in *Figs. 1–3* (50% probability ellipsoids for anisotropically refined atoms, arbitrary spheres for the remaining atoms).

The crystal structures of **10**, **11**, and **13** show each one intramolecular H-bond between NH(2) and the O-atom at the dihydropyrrole ring (O(1)), thereby forming a distorted 6-membered ring (*Table 2*). This H-bonded 6-membered ring is part of a

Table 1. *Crystallographic Data for Compounds* **10**, **11**, *and* **13**

	10	**11**	**13**
Crystallised from	benzene/hexane	benzene/hexane	Et_2O
Colour	colourless	pale yellow	colourless
Space group	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$
Atoms in the asymmetric unit	$C_{31}H_{32}N_2O_3$	$2(C_{31}H_{32}N_2O_3)\cdot C_6H_6$	$C_{31}H_{32}N_2O_3$
Cell parameters[a])			
a [Å]	10.833(2)	12.715(2)	11.363(5)
b [Å]	13.229(2)	24.669(4)	11.505(4)
c [Å]	18.195(3)	9.077(2)	12.120(5)
α [°]	90	95.65(1)	111.04(3)
β [°]	90	98.84(1)	98.31(3)
γ [°]	90	84.32(1)	114.76(3)
V [Å^3]	2607.4(8)	2789.6(8)	1258.9(9)
D_x [g cm^{-3}]	1.224	1.237	1.268
Linear absorption coeff. [cm^{-1}]	0.734	0.735	0.761
2θ (max)	46°	50°	50°
Total reflections measured	2745	10318	5256
Symmetry-independent reflections	2540	9775	4407
Reflections used in refinement ($I > 2\sigma(I)$)	1392	5187	3248
Variables	331	779	453
Final R	0.0638	0.0709	0.0503
wR	0.0596	0.0719	0.0513
Goodness of fit s	1.225	1.548	1.544
Weighting factor g ($w = [\sigma^2(F) + gF^2]^{-1}$)	0.0010	0.00084	0.00066
$\sigma(d_{(c-c)})$ [Å]	0.01–0.05	0.005–0.01	0.003–0.006

[a]) The cell dimensions were obtained from 25 accurately centered reflections with $20° < 2\theta < 28°$, $28° < 2\theta < 30°$, and $28° < 2\theta < 32°$, respectively.

Table 2. *Hydrogen-Bonding Distances* [Å] *and Angles* [°] *in* **10**, **11**, *and* **13**

	10	**11A**	**11B**	**13**
H(2)–O(1)	1.81(4)	1.95(4)	1.84(4)	1.88(3)
N(2)–O(1)	2.69(1)	2.668(5)	2.672(5)	2.710(3)
N(2)–H(2)–O(1)	142(14)	140(3)	140(3)	138(2)
C(1)–O(1)–H(2)	92(5)	96(1)	98(1)	98.0(8)

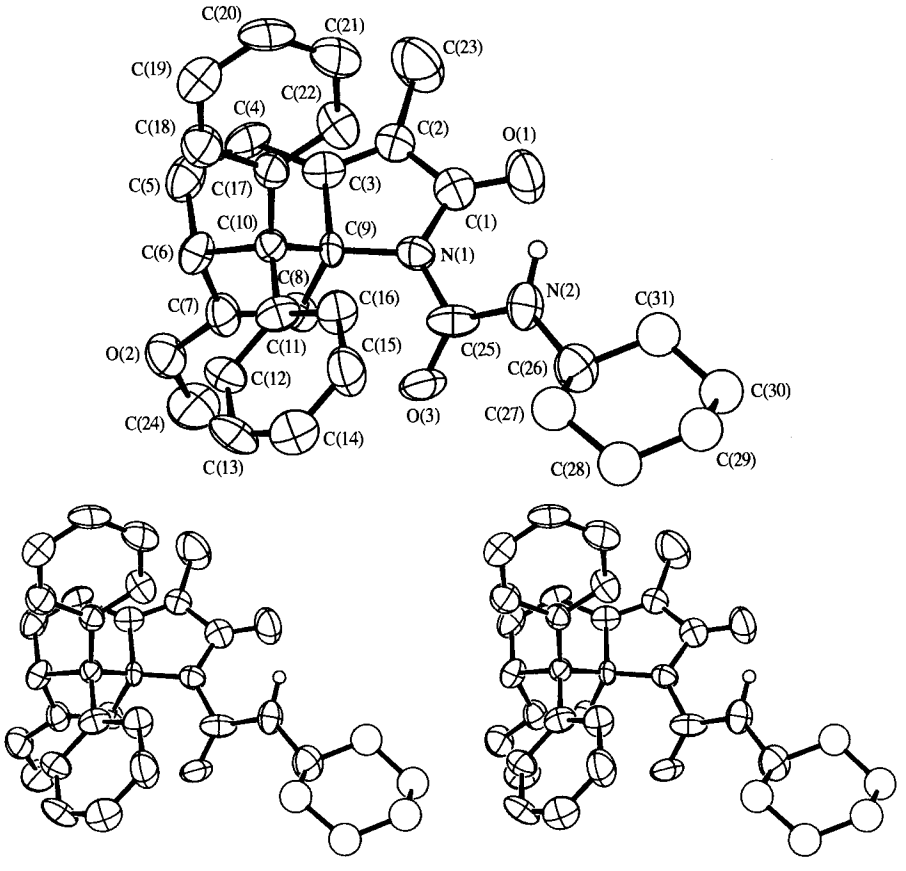

Fig. 1. *Molecular structure of* **10** *showing the atom-numbering scheme and stereoview of the crystal structure*

relatively planar system which includes the amide group and the attached 5-membered lactam ring. The maximum deviations from planarity are 0.46 Å in **10** (O(3)), 0.19 and 0.12 Å for C(26) in **11A** and **11B**, respectively, and 0.07 Å in **13** (C(3)). In **11A** and **11B**, the fused 5- and 7-membered rings are also planar with a maximum deviation from the plane of 0.09 and 0.10 Å, respectively. The cyclopropane ring of **11A** and **11B** forms an angle with the plane of the 7-membered ring of 114.0 and 116.4°, respectively.

Except for the Ph groups, the C–C bond lengths in each of the three structures are characteristic of isolated single and double bonds [11]. Even where the possibility exists for conjugation, as, *e.g.*, in the O(1)=C(1)–C(2)=C(3)–C(4)=C(5) moiety of **10**, the bond lengths are indicative of formally alternating single and double bonds. Bond lengths within the amide groups also show no unusual trends.

The two symmetry-independent molecules of **11** exhibit no significant differences, with most bond lengths differing by less than 0.02 Å, which is within the 3σ limits of the standard deviations of these parameters. The maximum bond-length difference is 0.06 Å within one of the Ph rings. Similary, the maximum bond-angle difference between the independent molecules is 4.1° with most differences being less than 2.3°.

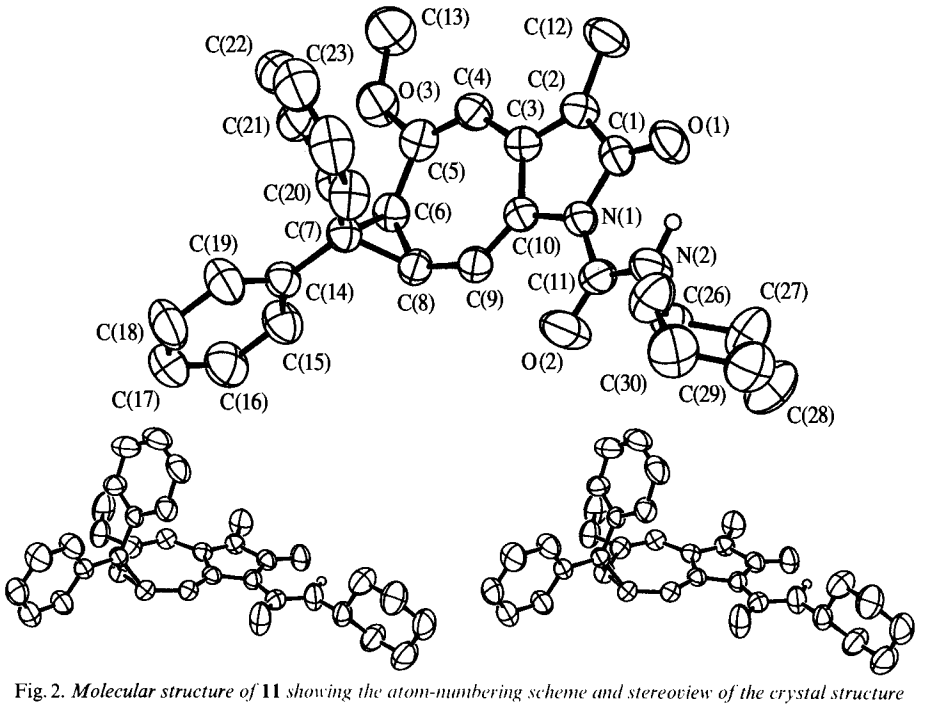

Fig. 2. *Molecular structure of* **11** *showing the atom-numbering scheme and stereoview of the crystal structure*

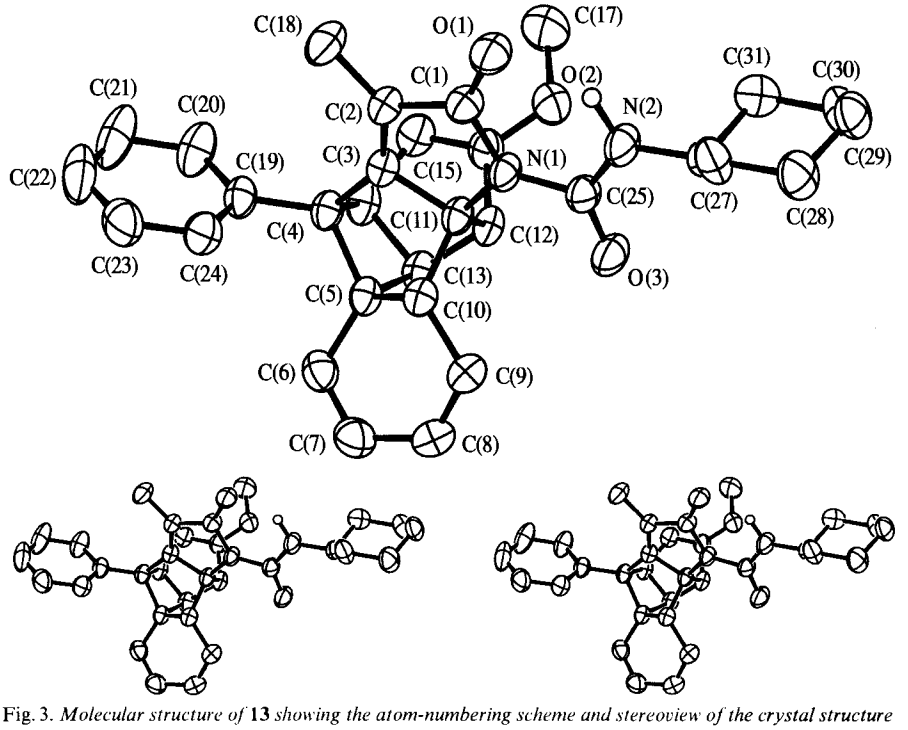

Fig. 3. *Molecular structure of* **13** *showing the atom-numbering scheme and stereoview of the crystal structure*

The bond lengths within the cyclopropane ring of **11** are of interest. In **11**, the so-called 'vicinal' C–C bonds of the cyclopropane ring starting at the Ph-substituted C-atom (C(6)–C(7) 1.537(5) and 1.540(5) Å and C(7)–C(8) 1.527(6) and 1.529(6) Å for **11A** and **11B**, resp.) are significantly longer than the distal C(6)–C(8) bond (1.496(6) and 1.485(6) Å, resp.). It has been shown [12–15] that substituents on cyclopropane rings which have π orbitals available for interaction with the π orbitals of the cyclopropane ring cause lengthening of the 'vicinal' C–C bonds and shortening of the distal C–C bond of the cyclopropane ring. The bond-length trends in **11** are entirely consistent with this observation and indicate that the π-eletron systems of the Ph groups are interacting with the π orbitals of the cyclopropane ring. The angles between the normals of the planes of the Ph substituents and the distal C(6)–C(8) vector are, for molecules **11A** and **11B**, 0.8 and 8.6°, respectively, for the Ph defined by C(14) to C(19) and 88.4 and 83.8°, respectively, for the Ph defined by C(20) to C(25). Angles of 0° represent the bisecting position, while those of 90° represent the parallel position, as described previously [12] [13] [15]. The bisecting position is required if the substituent is a π-electron acceptor, but if the substituent acts as a π-electron donor to the cyclopropane ring, either the bisecting or perpendicular orientation is allowed, depending on the orbitals involved [12] [13] [15–17].

It has been noted previously [13] that some cyclopropanes with more than one Ph group at the same cyclopropane C-atom exhibit an arrangement where one of the Ph groups adopts the perpendicular position, while the other does not adopt a specific orientation and lies somewhere between the two ideal positions. It was concluded from those observations that distortion of the cyclopropane C–C bond lengths could be explained in therms of π-electron donation from the Ph group to the cyclopropane ring, at least for the group that was in the perpendicular position, although it was uncertain how the skew Ph group might be interacting. The orientation of the Ph groups in **11** is consistent with the earlier results. While it is not possible for both Ph groups of **11** to adopt the bisecting position because of steric hindrance, one Ph group lies very close to the perpendicular position, while the other is almost in the bisecting position. This conformation strongly suggests that the Ph groups of **11** are interacting with the cyclopropane ring by π-electron donation from the Ph groups to the cyclopropane ring.

We thank the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for financial support.

Experimental Part

General. See [3]. The wavelength dependence of reactivity was measured on an *Applied Photophysics Monochromator* 900 W apparatus.

1. Starting Materials. – The tricyclic compounds under investigation were prepared starting from 2-methyl-4,4-diphenylbuta-2,3-dienoic acid [18] and the corresponding carbodiimide or ketenimine [1] [3]. The latter compounds were prepared from the corresponding ureas or amides using the $Ph_3P/CCl_4/Et_3N$ dehydration system [19]. They were characterized by the IR spectra (two strong bands in the region 2150–2105 cm^{-1} for the carbodiimides and one strong band at *ca.* 2000 cm^{-1} for the ketenimines) and used as crude products.

N-Cyclohexyl-4-methyl-3-oxo-6,6-diphenyl-2-azatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-2-carboxamide (**3a**). Yield 76%. Colourless crystals (Et_2O/hexane). M.p. 163.0–164.0°. UV (MeCN): 260 (sh, 2450). IR ($CHCl_3$): 3310*m*, 3000*m*, 2940*s*, 2855*m*, 1710*s*, 1665*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.55 (*d*, J = 7.7, NH); 7.4–7.1 (*m*, 10 arom. H); 6.46 (*dd*, J = 7.0, 1.5, H–C(9), H–C(10)); 6.25 (*t*, J = 7.0, H–C(8), H–C(11)); 4.52 (*tt*, J = 7.0, 1.5, H–C(7)); 4.0–3.8 (*m*, CHN); 2.1–1.1 (*m*, 10 H, C_6H_{11}); 1.62 (*s*, Me). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 174.2 (*s*, C(3));

160.2 (*s*, C(5)); 151.0 (*s*, NCON); 143.6 (*s*, arom. C); 133.6, 132.6 (2*d*, C(8) to C(11)); 128.7, 128.0, 126.7 (3*d*, arom. CH); 126.1 (*s*, C(4)); 72.7 (*s*, C(1)); 58.8 (*s*, C(6)); 52.4 (*d*, C(7)); 48.4 (*d*, CHN); 33.1, 25.6, 24.6 (3*t*, CH_2); 11.5 (*q*, Me). CI-MS: 326 (100, $[M + 1 - C_6H_{11}NCO]^+$).

(1RS,7SR)-N-Cyclohexyl-9-methoxy-4-methyl-3-oxo-6,6-diphenyl-2-azatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-2-carboxamide (**6a**). Yield 51%. Colourless crystals (Et_2O). M.p. 170.0–172.0°. UV (MeCN): 260 (2500). IR (KBr): 3315*m*, 2940*m*, 2865*m*, 1718*s*, 1685*m*, 1660*m*, 1605*w*. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.53 (*d*, *J* = 8.0, NH); 7.3–7.0 (*m*, 10 arom. H); 6.42 (*d*, *J* = 6.0, H–C(10)); 6.35 (*t*, *J* = 6.5, H–C(11)); 4.79 (*d*, *J* = 6.8, H–C(8)); 4.28 (br. *t*, *J* = 6.0, H–C(7)); 4.45–4.25 (*m*, CHN); 3.49 (*s*, MeO); 2.0–1.2 (*m*, 10 H, C_6H_{11}); 1.64 (*s*, Me). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 174.5 (*s*, C(3)); 159.6, 158.6 (2*s*, C(5), C(9)); 151.0 (*s*, NCON); 144.0, 143.6 (2*s*, arom. C); 135.9, 129.5 (2*d*, C(10), C(11)); 128.6, 128.3, 128.2, 127.7 (4*d*, arom. CH); 126.7, 126.6 (2*d*, 1*s*, arom. CH, C(4)); 96.5 (*d*, C(8)); 72.3 (*s*, C(1)); 59.6 (*s*, C(6)); 56.7 (*q*, MeO); 50.1 (*d*, C(7)); 48.3 (*d*, CHN); 33.0, 25.6, 24.6 (3*t*, CH_2); 11.8 (*q*, Me). MS (70 eV): 481 (13), 480 (46, M^+), 356 (25), 355 (100, $[M - C_6H_{11}NCO]^+$), 354 (42), 340 (33), 205 (54), 203 (25), 202 (21), 191 (33), 165 (21), 149 (13), 128 (13), 97 (17).

(1RS,7SR)-2-(Diphenylacetyl)-9-methoxy-4-methyl-6,6-diphenyl-2-azatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one (**6b**). Yield 55%. Colourless crystals (Et_2O/hexane). M.p. 154.0–158.0°. IR ($CHCl_3$): 3075*w*, 3050*m*, 3025*m*, 2955*m*, 1710*s*, 1695*s*, 1665*m*, 1635*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.55–7.15 (*m*, 20 arom. H); 6.72 (*s*, CHCO); 6.35–6.25 (*m*, H–C(10), H–C(11)); 4.77 (*d*, *J* = 6.7, H–C(8)); 4.27 (br. *t*, *J* = 6.7, H–C(7)); 3.42 (*s*, MeO); 1.61 (*s*, Me). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 172.0 (*s*, C(3)); 170.9 (*s*, NCOCH); 159.9, 158.5 (2*s*, C(5), C(9)); 144.0, 143.6 (2*s*, arom. *C*–C(6)); 139.3, 139.1 (2*s*, arom. *C*–CH); 135.9 (*s*, C(10) or C(11)); 129.8, 129.6, 129.4, 129.2, 128.6, 128.4, 128.2, 127.8, 127.0, 126.8, 126.7, 126.6 (12*d*, C(11) or C(10), arom. CH); 96.6 (*d*, C(8)); 72.1 (*s*, C(1)); 59.9 (*s*, C(6)); 56.2 (*q*, MeO); 55.8 (*d*, *C*HCO); 12.0 (*q*, Me). MS (70 eV): 549 (29, M^+), 355 (17, $[M - Ph_2C{=}C{=}O]^+$), 317 (17), 299 (12), 205 (21), 167 (100), 165 (54).

(1RS,7SR)-N-Cyclohexyl-8-methoxy-4-methyl-3-oxo-6,6-diphenyl-2-azatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-2-carboxamide (**8a**). Yield 70%. Colourless crystals (hexane). M.p. 162.0–165.0°. UV (MeCN): 260 (4000). IR ($CHCl_3$): 3280*m*, 2945*m*, 2920*m*, 2845*m*, 1710*s*, 1670*m*, 1645*m*, 1600*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.58 (*d*, *J* = 8.1, NH); 7.3–7.2 (*m*, 10 arom. H); 6.51 (*dd*, *J* = 7.3, 1.3, H–C(10)); 6.25 (*t*, *J* = 7.3, H–C(11)); 5.17 (*d*, *J* = 2.5, H–C(9)); 4.2–4.1 (*m*, H–C(7)); 3.95–3.8 (*m*, CHN); 3.28 (*s*, MeO); 2.05–1.2 (*m*, 10 H, C_6H_{11}); 1.60 (*s*, Me). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 174.4 (*s*, C(3)); 163.2, 162.4 (2*s*, C(5), C(8)); 151.1 (*s*, NCON); 142.9, 141.8 (2*s*, arom. C); 134.8, 132.6 (2*d*, C(10), C(11)); 128.8, 128.6, 128.2, 127.8, 126.8 (5*d*, arom. CH); 124.8 (*s*, C(4)); 97.6 (*d*, C(9)); 71.1 (*s*, C(1)); 58.3 (*s*, C(6)); 55.8 (*q*, MeO); 48.5 (*d*, CHN); 33.2, 25.6, 24.6 (3*t*, CH_2); 11.2 (*q*, Me). MS (70 eV): 480 (4, M^+), 356 (25), 355 (100, $[M - C_6H_{11}NCO]^+$), 340 (50), 205 (42), 191 (25), 165 (21), 77 (20).

(1RS,7SR)-2-(Diphenylacetyl)-8-methoxy-4-methyl-6,6-diphenyl-2-azatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one (**8b**). Yield 41%. Colourless crystals (THF). M.p. 181.0–186.0°. IR ($CHCl_3$): 3100–2950*m*, 1710*s*, 1680*s*, 1630*s*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.55–7.1 (*m*, 20 arom. H); 6.78 (*s*, CHCO); 6.35 (*d*, *J* = 7.0, H–C(10)); 6.24 (*t*, *J* = 7.0, H–C(11)); 5.01 (*d*, *J* = 2.3, H–C(9)); 4.14 (br. *d*, *J* = 7.0, H–C(7)); 3.25 (*s*, MeO); 1.58 (*s*, Me). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 171.9 (*s*, C(3)); 171.1 (*s*, NCON); 163.1, 162.6 (2*s*, C(5), C(8)); 142.8, 141.8 (2*s*, arom. *C*–C(6)); 139.1, 139.0 (2*s*, arom. *C*–CH); 134.8, 132.7 (2*d*, C(10), C(11)); 129.4, 129.2, 128.7, 128.5, 128.4, 128.2, 127.8, 127.1, 126.9 (9*d*, arom. CH); 125.3 (*s*, C(4)); 97.7 (*d*, C(9)); 70.8 (*s*; C(1)); 58.5 (*s*, C(6)); 55.7 (*q*, MeO); 55.6, 55.5 (2*d*, C(7), *C*HCO); 11.4 (*q*, Me). MS (70 eV): 549 (4, M^+), 355 (100, $[M - Ph_2C{=}C{=}O]^+$), 340 (54), 205 (29), 194 (33), 165 (83).

(1RS,7SR)-9-Cyano-N-cyclohexyl-4-methyl-3-oxo-6,6-diphenyl-2-azatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-2-carboxamide (**15a**). Yield 30%. Colourless crystals (THF/hexane). M.p. 150.0–153.0°. UV (MeCN): 260 (8500). IR ($CHCl_3$): 3320*m*, 3000*m*, 2930*s*, 2855*m*, 2220*m*, 1715*s*, 1675*m*, 1620*w*. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.38 (*d*, *J* = 8.0, NH); 7.3–7.1 (*m*, 10 arom. H); 6.97 (*d*, *J* = 6.5, H–C(8)); 6.59 (*dd*, *J* = 7.0, 1.5, H–C(10)); 6.27 (*t*, *J* = 7.0, H–C(11)); 4.69 (*td*, *J* = 6.5, 1.5, H–C(7)); 4.0–3.85 (*m*, CHN); 2.1–1.2 (*m*, 10 H, C_6H_{11}); 1.64 (*s*, Me). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 173.1 (*s*, C(3)); 156.8 (*s*, C(5)); 150.4 (*s*, NCON); 149.1 (*d*, C(8)); 142.0 (*s*, arom. C); 132.2, 131.9 (2*d*, C(10), C(11)); 128.7, 128.5, 128.4, 128.1, 127.5, 127.3 (6*d*, arom. CH); 118.9 (*s*, C≡N); 113.6 (*s*, C(9)); 72.0 (*s*, C(1)); 58.8 (*s*, C(6)); 53.1 (*d*, C(7)); 48.8 (*d*, CHN); 32.9, 25.6, 24.6, 24.5 (4*t*, CH_2); 11.4 (*q*, Me). MS (70 eV): 475 (83, M^+), 393 (8), 350 (100, $[M - C_6H_{11}NCO]^+$), 335 (29), 250 (8), 205 (67).

Methyl (1RS,7SR)-2-(N-Cyclohexylcarbamoyl)-4-methyl-3-oxo-6,6-diphenyl-2-azatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carboxylate (**15b**). Yield 30%. Colourless crystals (Et_2O/hexane). M.p. 140.0–146.0°. UV (MeCN): 262 (7800). IR ($CHCl_3$): 3310*m*, 2930*s*, 2855*m*, 1700*s*, 1665*m*, 1625*w*. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.53 (*d*, *J* = 8.0, NH); 7.4–7.1 (*m*, 10 arom. H); 6.91 (*d*, *J* = 6.5, H–C(8)); 6.54 (*dd*, *J* = 6.5, 1.5, H–C(10)); 6.30 (*t*, *J* = 6.5, H–C(11)); 4.58 (*td*, *J* = 6.5, 1.5, H–C(7)); 4.45–4.25 (*m*, CHN); 3.65 (*s*, COOMe); 2.1–1.1 (*m*, 10 H, C_6H_{11}); 1.62 (*s*, Me). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 173.4 (*s*, C(3)); 163.8 (*s*, *C*OOMe); 157.8 (*s*, C(5)); 151.3 (*s*, NCON); 143.0 (*d*, C(8)); 142.8 (*s*, arom. C); 134.9 (*s*, C(9)); 133.2, 132.3 (2*d*, C(10), C(11)); 128.7, 182.3, 128.2,

128.1, 127.0 (5*d*, arom. CH); 127.4 (*s*, C(4)); 72.1 (*s*, C(1)); 58.5 (*s*, C(6)); 52.3 (*d*, C(7)); 51.7 (*q*, COO*Me*); 48.3 (*d*, CHN); 33.0, 32.9, 25.6, 24.6, 24.4 (5*t*, CH_2); 11.3 (*q*, Me). MS (70 eV): 383 (100, $[M - C_6H_{11}NCO]^+$), 368 (20), 351 (20), 205 (71), 146 (56).

(1RS,7SR)-8-Cyano-N-cyclohexyl-4-methyl-3-oxo-6,6-diphenyl-2-azatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-2-carboxamide (**17a**). Yield 37%. Colourless crystals ((i-Pr)$_2$O/hexane). M.p. 164.0–170.0°. UV (MeCN): 260 (7000). IR ($CHCl_3$): 3310*m*, 2990*m*, 2925*s*, 2850*m*, 1705*s*, 1670*s*. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.40 (*d*, *J* = 8.0, NH); 7.4–7.1 (*m*, 10 arom. H, H–C(9)); 6.51 (*dd*, *J* = 7.2, 1.7, H–C(10)); 6.42 (*dd*, *J* = 7.2, 6.0, H–C(11)); 4.67 (*dt*, *J* = 6.0, 1.7, H–C(7)); 3.9–3.7 (*m*, CHN); 2.1–1.2 (*m*, 10 H, C_6H_{11}); 1.63 (*s*, Me). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 173.1 (*s*, C(3)); 156.8 (*s*, C(5)); 150.6 (*s*, NCON); 147.3 (*d*, C(9)); 141.7, 141.0 (2*s*, arom. C); 132.8, 132.5 (2*d*, C(10), C(11)); 128.8, 128.7, 128.3, 127.8, 127.4 (5*d*, arom. CH); 118.8 (*s*, C≡N); 115.7 (*s*, C(8)); 72.6 (*s*, C(1)); 58.4 (*s*, C(6)); 55.0 (*d*, C(7)); 48.7 (*d*, CHN); 33.0, 25.5, 24.6 (3*t*, CH_2); 11.6 (*q*, Me). MS (70 eV): 350 (75, $[M - C_6H_{11}NCO]^+$), 335 (29), 205 (100).

Methyl (1RS,7SR)-2-(N-Cyclohexylcarbamoyl)-4-methyl-3-oxo-6,6-diphenyl-2-azatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-8-carboxylate (**17b**). Yield 24%. Colourless crystals (Et_2O/hexane). M.p. 148.0–151.0°. UV (MeCN): 262 (7750). IR ($CHCl_3$): 3305*m*, 3000*m*, 2930*s*, 2850*m*, 1705*s*, 1660*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.48 (*d*, *J* = 8.0, NH); 7.35 (*d*, *J* = 2.0, H–C(9)); 7.3–7.1 (*m*, 10 arom. H); 6.45 (*dd*, *J* = 7.1, 2.0, H–C(10)); 6.41 (*dd*, *J* = 7.1, 5.8, H–C(11)); 5.04 (*dt*, *J* = 5.8, 2.0, H–C(7)); 4.0–3.8 (*m*, CHN); 3.49 (*s*, COOMe); 2.1–1.1 (*m*, C_6H_{11}); 1.65 (*s*, Me). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 173.6 (*s*, C(3)); 163.7 (*s*, *C*OOMe); 158.7 (*s*, C(5)); 150.8 (*s*, NCON); 142.6 (*s*, arom. C); 142.1 (*d*, C(9)); 137.7 (*s*, C(8)); 134.0, 131.8 (2*d*, C(10), C(11)); 128.8, 128.4, 128,1, 128.0, 127.0 (5*d*, arom. CH); 73.1 (*s*, C(1)); 58.5 (*s*, C(6)); 52.0 (*d*, C(7)); 51.5 (*q*, COO*Me*); 48.6 (*d*, CHN); 33.1, 25.6, 24.6 (3*t*, CH_2); 11.8 (*q*, Me). MS (70 eV): 383 (70, $[M - C_6H_{11}NCO]^+$), 328 (46), 207 (100), 191 (46).

2. Irradiation. – A soln. of the tricyclic compound (0.5 mmol) in 250 ml of Et_2O[3]) (**8a**, **15b**) or in a mixture of Et_2O/THF 5:1 (250 ml; for the remaining compounds) was irradiated with a 15-W *Hanau* low-pressure Hg lamp under Ar for 30 min (**6a**, **17a**), for 40 min (**3a**, **8b**, **15a**), for 1 h (**15b**), or for 2 h (**6b**, **8a**, **17b**). The solvent was evaporated and the residue analysed by NMR at −10° in the case of **3a**, **6a**, and **6b** or subjected to prep. TLC separation with petroleum ether/AcOEt/acetone 10:1:1 (**15a**) or 15:1:1 (in the remaining cases). The crude products were analysed by NMR at −10° (**15a**, **15b**, **17a**, and **17b**) or recrystallized to afford pure products **9** and **13**. The yellow zone obtained in the case of **8a** afforded, after elution with $CHCl_3$ and removal of the solvent, a mixture of **11** and **12** in a ratio of *ca.* 1:1 (20%). This mixture was dissolved in dry benzene and kept at r.t. in the dark for 14 days and then subjected to prep. TLC separation with petroleum ether/AcOEt/acetone 15:1:1 to give a yellow (R_f 0.65) and a colourless, but UV (254 nm)-active, zone (R_f 0.45). Both zones were eluted with $CHCl_3$, the solvent was removed, and the residue was recrystallized to give yellow **11** and colourless **10**, respectively.

N-*Cyclohexyl*-N′-*(2-methyl-4,4-diphenylbuta-2,3-dienoyl)*-N′-*phenylurea* (**4**). **3a**/**4**/**5** 5:3:1. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.96 (*d*, *J* = 7.4, NH); 7.5–6.9 (*m*, 15 arom. H); 3.7–3.6 (*m*, CHN); 2.0–1.0 (*m*, 10 H, C_6H_{11}); 1.97 (*s*, Me). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 207.5 (*s*, C(3)); 170.6 (*s*, C(1)); 153.6 (*s*, NCON); 137.6 (*s*, arom. C–N); 134.5 (*s*, arom. C); 112.3 (*s*, C(4)); 100.9 (*s*, C(2)); 49.5 (*d*, CHN); 32.7, 23.8 (2*t*, CH_2); 17.8 (*q*, Me).

(1RS,7RS,10SR,11RS)-N-Cyclohexyl-4-methyl-3-oxo-6,6-diphenyl-2-azatetracyclo[5.3.1.0^{1,5}.0^{10,11}]undeca-4,8-diene-2-carboxamide (**5**). ^{1}H-NMR (250 MHz, $CDCl_3$): 8.96 (*d*, *J* = 7.5, NH); 7.5–7.0 (*m*, 10 arom. H); 5.68 (*dd*, *J* = 5.5, 2.5, H–C(8)); 4.86 (*dd*, *J* = 5.5, 2.5, H–C(9)); 4.17 (*dd*, *J* = 6.7, 5.5, H–C(11)); 3.8–3.7 (*m*, CHN); 3.66 (*dd*, *J* = 6.7, 2.5, H–C(10)); 2.0–1.0 (*m*, 13 H, Me, C_6H_{11}).

N-*Cyclohexyl*-N′-*(2-methoxyphenyl)*-N′-*(2-methyl-4,4-diphenylbuta-2,3-dienoyl)urea* (**7a**). **6a**/**7a** 1:1. ^{1}H-NMR (250 MHz, $CDCl_3$): 9.00 (*d*, *J* = 7.2, NH); 7.4–7.05 (*m*, 10 arom. H); 6.99 (*dd*, *J* = 7.8, 1.5, 1 arom. H); 6.79 (*td*, *J* = 7.8, 1.8, 1 arom. H); 6.5–6.4 (*m*, 2 arom. H); 3.7–3.6 (*m*, CHN); 3.56 (*s*, MeO); 2.01 (*s*, Me); 2.05–1.1 (*m*, 10 H, C_6H_{11}). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 206.9 (*s*, C(3)); 170.9 (*s*, C(1)); 154.2, 153.2 (2*s*, arom. C–O, NCON); 134.6 (*s*, arom. C); 120.0, 110.8 (2*d*, arom. CH); 111.9 (*s*, C(4)); 100.3 (*s*, C(2)); 54.9 (*q*, MeO); 49.3 (*d*, CHN); 32.6 (*t*, CH_2); 17.6 (*q*, Me).

N-*(2-Methoxyphenyl)*-N-*(2-methyl-4,4-diphenylbuta-2,3-dienoyl)-2,2-diphenylacetamide* (**7b**). **6b**/**7b** 1:1. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.5–6.5 (*m*, 24 arom. H); 5.98 (*s*, CHCO); 3.36 (*s*, MeO); 2.06 (*s*, Me). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 210.3 (*s*, C(3)); 176.1 (*s*, COCH); 172.0 (*s*, C(1)); 153.1 (*s*, arom. C); 134.1 (*s*, arom. C); 130.0–126.0 (arom. CH); 120.3, 110.9 (2*s*, arom. C); 113.2 (*s*, C(4)); 57.3 (*q*, MeO); 54.7 (*d*, CHCO); 16.3 (*q*, Me).

(1RS,8SR)-N-Cyclohexyl-7-methoxy-4-methyl-3-oxo-11,11-diphenyl-2-azatricyclo[6.2.1.0^{1,5}]undeca-4,6,9-triene-2-carboxamide (**9**). Yield 5%. Colourless crystals (benzene/hexane). M.p. 199.0–203.0°. UV (MeCN): 327 (12200). IR (KBr): 3419*w*, 3305*m*, 2927*m*, 2852*m*, 1720*s*, 1674*m*, 1639*m*, 1595*m*. ^{1}H-NMR (250 MHz,

[3]) The Et_2O and THF solvents were deaerated prior to use and passed over neutral Al_2O_3 to eliminate peroxides.

$CDCl_3$): 8.25 (*d*, *J* = 7.0, NH); 7.2–7.0 (*m*, 10 arom. H); 6.43 (*dd*, *J* = 5.7, 3.5, H–C(9)); 5.99 (*d*, *J* = 5.7, H–C(10)); 4.96 (*d*, *J* = 2.0, H–C(6)); 4.12 (br. *t*, *J* ≈ 2.5, H–C(8)); 3.55 (*s*, MeO); 3.5–3.3 (*m*, CHN); 1.78 (*s*, Me); 1.95–1.1 (*m*, 10 H, C_6H_{11}); irrad. at 3.35 (*m*, CHN)→8.25 (*s*, NH); irrad. at 4.12 (br. *t*, H–C(8))→6.43 (*d*, *J* = 5.7, H–C(9)); 4.96 (*s*, H–C(6)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 174.4 (*s*, C(3)); 170.5 (*s*, C(5)); 153.4 (*s*, C(7)); 151.0 (*s*, NCON); 144.6, 141.4 (2*s*, arom. C); 137.0, 129.4, 128.4, 127.5, 127.4, 126.1, 126.0 (7*d*, C(9), C(10), arom. CH); 118.7 (*s*, C(4)); 88.1 (*d*, C(6)); 79.6 (*s*, C(1)); 74.1 (*s*, C(11)); 55.8 (*q*, MeO); 55.0 (*d*, C(8)); 48.4 (*d*, CHN); 32.9, 32.6, 25.8, 24.5, 24.4 (5*t*, CH_2); 7.9 (*q*, Me). MS (70 eV): 481 (8), 480 (25, $M^{+\cdot}$), 356 (29), 355 (100, $[M - C_6H_{11}NCO]^+$), 165 (21).

*(1*RS,*8*RS*)*-N-*Cyclohexyl-9-methoxy-4-methyl-3-oxo-11,11-diphenyl-2-azatricyclo[6.2.1.0^{1,5}]undeca-4,6,9-triene-2-carboxamide* (**10**). Yield 8%. Colourless crystals (benzene/hexane). M.p. 215.0–223.0°. UV (MeCN): 291 (12400). IR (KBr): 3300*w*, 2929*s*, 2852*m*, 1718*s*, 1676*m*, 1655*s*. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.22 (*d*, *J* = 7.0, NH); 7.3–7.0 (*m*, 10 arom. H); 6.70 (*dd*, *J* = 9.1, 5.5, H–C(7)); 6.18 (*d*, *J* = 9.1, H–C(6)); 4.58 (*s*, H–C(10)); 4.03 (*d*, *J* = 5.5, H–C(8)); 3.68 (*s*, MeO); 3.5–3.3 (*m*, CHN); 1.84 (*s*, Me); 1.8–1.1 (*m*, 10 H, C_6H_{11}); irrad. at 3.4 (*m*, CHN)→8.22 (*s*, NH). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 174.1 (*s*, C(3)); 162.4 (*s*, C(5)); 152.3, 150.7 (2*s*, C(9), NCON); 144.7, 143.9 (2*s*, arom. C); 140.4 (*d*, C(7)); 128.9, 127.4, 126.1, 125.9 (4*d*, arom. CH); 123.3 (*s*, C(4)); 120.2 (*d*, C(6)); 96.4 (*d*, C(10)); 78.1 (*s*, C(1)); 72.9 (*s*, C(11)); 57.4 (*q*, MeO); 51.8 (*d*, C(8)); 48.4 (*d*, CHN); 32.9, 32.6, 25.7, 24.6, 24.4 (5*t*, CH_2); 8.0 (*q*, Me). MS (70 eV): 481 (16), 480 (25, $M^{+\cdot}$), 356 (33), 355 (100, $[M - C_6H_{11}NCO]^+$), 165 (21).

*(3*RS,*5*SR*)*-N-*Cyclohexyl-6-methoxy-9-methyl-10-oxo-4,4-diphenyl-11-azatricyclo[6.3.0.0^{3,5}]undeca-1,6,8-triene-11-carboxamide* (**11**). Yield 9%. Yellow prisms (benzene/hexane). M.p. 169.0–171.0°. UV (MeCN): 322 (14600). IR ($CHCl_3$): 3275*m*, 2990*w*, 2930*m*, 2850*m*, 1690*s*, 1660*s*, 1620*s*. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.95 (*d*, *J* = 7.7, NH); 8.08 (*d*, *J* = 6.8, H–C(2)); 7.4–7.0 (*m*, 10 arom. H); 5.24 (*s*, H–C(7)); 3.9–3.7 (*m*, CHN); 3.80 (*s*, MeO); 2.72 (*d*, *J* = 9.3, H–C(5)); 2.60 (*dd*, *J* = 9.3, 6.8, H–C(3)); 2.05–1.2 (*m*, 10 H, C_6H_{11}); 1.67 (*s*, Me); irrad. at 8.08 (*d*, *J* = 6.8, H–C(2))→2.60 (*d*, *J* = 9.3, H–C(3)); irrad. at 2.72 (*d*, *J* = 9.3, H–C(5))→2.60 (*d*, *J* = 6.8, H–C(3)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 171.1 (*s*, C(10)); 160.3 (*s*, C(8)); 152.3 (*s*, NCON); 145.7, 138.6, 136.6, 135.2 (4*s*, C(1), C(6), arom. C); 121.5 (*s*, C(9)); 119.5 (*d*, C(2)); 93.1 (*d*, C(7)); 55.7 (*q*, MeO); 48.3 (*d*, CHN); 40.9 (*s*, C(4)); 36.4 (*d*, C(5)); 32. 8 (*t*, CH_2); 30.5 (*d*, C(3)); 25.4, 24.6 (2*t*, CH_2); 7.9 (*q*, Me). MS (70 eV): 481 (4), 480 (17, $M^{+\cdot}$), 256 (29), 255 (100, $[M - C_6H_{11}NCO]^+$), 165 (25).

*(3*RS,*5*SR*)*-N-*Cyclohexyl-3-methoxy-9-methyl-10-oxo-4,4-diphenyl-4-azatricyclo[6.3.0.0^{3,5}]undeca-1,6,8-triene-11-carboxamide* (**12**). Yield 11%. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.86 (*d*, *J* = 8.0, NH); 8.22 (*s*, H–C(2)); 7.5–7.0 (*m*, 10 arom. H); 6.50 (*dd*, *J* = 12.5, 6.7, H–C(6)); 6.12 (*d*, *J* = 12.5, H–C(7)); 3.9–3.7 (*m*, CHN); 3.30 (*s*, MeO); 2.79 (*d*, *J* = 6.7, H–C(5)); 2.05–1.2 (*m*, 10 H, C_6H_{11}); 1.69 (*s*, Me). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 170.8 (*s*, C(10)); 152.0 (*s*, NCON); 141.2, 139.5, 137.0, 135.6 (4*s*, C(1), C(8), arom. C); 129.0, 128.3, 128.1, 127.6, 126.9, 126.5, 126.3, 125.9, 123.7 (9*d*, arom. CH); 120.3 (*d*, C(2)); 71.6 (*s*, C(3)); 56.6 (*q*, MeO); 51.7 (*s*, C(4)); 48.3 (*d*, CHN); 39.5 (*d*, C(5)); 32.8, 25.4, 24.6 (3*t*, CH_2); 7.9 (*q*, Me).

*(1*RS,*6*SR,*7*RS,*10*RS,*11*SR,*12*RS,*17*RS*)*-N-*Cyclohexyl-9-methoxy-4-methyl-3-oxo-6-phenyl-2-azahexacyclo[8.7.0.0^{1,5}.0^{6,12}.0^{7,11}.0^{12,17}]heptadeca-4,8,13,15-tetraene-2-carboxamide* (**13**). Yield 5%. Colourless crystals (Et_2O). M.p. 183.0–186.0°. IR (KBr): 3450*m*, 3302*m*, 2931*m*, 2856*m*, 1711*s*, 1697*s*, 1677*s*, 1612*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.43 (*d*, *J* = 7.7, NH); 7.4–7.2 (*m*, 5 arom. H); 6.56 (br. *d*, *J* = 8.8, H–C(16)); 6.05–5.85 (*m*, H–C(13), H–C(14), H–C(15)); 4.47 (*d*, *J* = 3.1, H–C(8)); 3.95 (*d*, *J* = 8.0, H–C(10)); 3.9–3.7 (*m*, CHN); 3.65 (*dd*, *J* = 6.7, 3.1, H–C(7)); 3.48 (*s*, MeO); 3.11 (br. *s*, H–C(17)); 3.04 (*t*, *J* = 7.5, H–C(11)); 2.05–1.95 (*m*, 2 H, C_6H_{11}); 1.8–1.2 (*m*, 8 H, C_6H_{11}); 1.10 (*s*, Me); irrad. at 6.56 (H–C(16))→6.05–5.85 (H–C(13) to H–C(15)) changed and 3.11 (*d*, *J* ≈ 2.0, H–C(17)); irrad. at 4.47 (H–C(8))→3.65 (*d*, *J* = 6.7, H–C(7)); irrad. at 3.95 (H–C(10))→3.04 (*d*, *J* = 6.7, H–C(11)); irrad. at 3.65 (H–C(7))→4.47 (*s*, H–C(8)) and 3.04 (*d*, *J* = 8.0, H–C(11)); irrad. at 3.04 (H–C(11))→3.95 (*s*, H–C(10)) and 3.65 (*d*, *J* = 3.1, H–C(7)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 175.4 (*s*, C(3)); 170.3, 167.9 (2*s*, C(5), C(9)); 151.8 (*s*, NCON); 138.4 (*s*, arom. C); 128.5, 127.2, 127.1, 126.6, 126.2, 124.7 (6*d*, arom. CH, C(13), C(14), C(15), C(16)); 121.5 (*s*, C(4)); 93.3 (*d*, C(8)); 74.0 (*s*, C(1)); 57.5, 54.6, 52.3, 47.5 (4*d*, C(7), C(10), C(11), C(17)); 56.0 (*q*, MeO); 56.0, 55.2 (2*s*, C(6), C(12)); 48.2 (*d*, CHN); 33.0, 25.4, 24.7 (3*t*, CH_2); 7.2 (*q*, Me). MS (70 eV): 480 (17, $M^{+\cdot}$), 355 (50, $[M - C_6H_{11}NCO]^+$), 340 (13), 260 (40), 259 (100).

*(1*RS,*6*SR,*7*RS,*10*RS,*11*SR,*12*RS,*17*RS*)*-N-*Cyclohexyl-4-methyl-3,9-dioxo-6-phenyl-2-azahexacyclo-[8.7.0.0^{1,5}.0^{6,12}.0^{7,11}.0^{12,17}]heptadeca-4,13,15-triene-2-carboxamide* (**14**). A soln. of **13** (9.0 mg) in undried $CHCl_3$ was kept at r.t. in the dark for 1 month. The solvent was removed and the residue recrystallized from hexane/Et_2O: pure **14** (6.0 mg, 67%). Colourless crystals. M.p. 175.0–177.0° (dec.). IR (KBr): 3444*w*, 3315*m*, 2930*m*, 2854*m*, 1734*s*, 1711*s*, 1530*s*. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.37 (*d*, *J* = 7.3, NH); 7.45–7.1 (*m*, 5 arom. H); 6.52 (*dd*, *J* = 8.8, 1.0, H–C(13) or H–C(16)); 6.1–5.9 (*m*, 3 olef. H); 3.9–3.7 (*m*, CHN); 3.84 (*d*, *J* = 7.0, H–C(14)); 3.73 (br. *t*, *J* = 6.3, H–C(7)); 3.11 (*t*, *J* = 6.5, H–C(11)); 3.04 (br. *s*, H–C(17)); 2.39 (*dd*, *J* = 18.5, 6.0, 1 H–C(8)); 2.18 (*d*,

J = 18.5, 1 H–C(8)); 2.1–1.1 (*m*, 10 H, C_6H_{11}); 1.17 (*s*, Me). MS (70 eV): 466 (21, M^{+}), 341 (20), 322 (12), 197 (100), 117 (32).

*(1*RS,7SR,*10*SR,*11*SR*)-9-Cyano-*N*-cyclohexyl-4-methyl-3-oxo-6,6-diphenyl-2-azatetracyclo[5.3.1.0^{1,5}.0^{10,11}]-undeca-4,8-diene-2-carboxamide* (**16a**). Yield 26%. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.43 (*d*, J = 7.8, NH); 7.45–7.05 (*m*, 10 arom. H); 5.67 (*d*, J = 2.9, H–C(8)); 4.38 (*dd*, J = 5.6, 2.9, H–C(7)); 4.24 (*dd*, J = 7.0, 5.6, H–C(11)); 3.91 (*d*, J = 7.0, H–C(10)); 3.75–3.65 (*m*, CHN); 2.0–1.1 (*m*, 10 H, C_6H_{11}); 1.63 (*s* Me); irrad. at 3.91 (*d*, J = 7.0, H–C(10))→4.24 (*d*, J = 5.6, H–C(11)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 173.9 (*s*, C(3)); 165.1 (*s*, C(5)); 154.0 (*d*, C(8)); 150.7 (*s*, NCON); 145.2, 138.1 (2*s*, arom. C); 129.2, 128.9, 128.4, 127.7, 127.4 (5*d*, arom. CH); 114.9, 112.7 (2*s*, C(9), C≡N); 66.3, 64.2 (2*s*, C(1), C(6)); 65.2 (*d*, C(7)); 48.4 (*d*, CHN); 43.8, 37.8 (2*d*, C(10), C(11)); 32.9, 32.8, 25.5, 24.5 (4*t*, CH_2); 10.1 (*q*, Me).

*Methyl (1*RS,7SR,*10*SR,*11*SR*)-2-(*N*-Cyclohexylcarbamoyl)-4-methyl-3-oxo-6,6-diphenyl-2-azatetracyclo-[5.3.1.0^{1,5}.0^{10,11}]undeca-4,8-diene-9-carboxylate* (**16b**). Yield 34%. IR ($CHCl_3$): 3300*m*, 2990*w*, 2930*s*, 2850*m*, 1720*s*, 1705*s*, 1670*m*, 1540*s*. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.45 (*d*, J = 7.5, NH); 7.45–7.0 (*m*, 10 arom. H); 5.75 (*d*, J = 2.4, H–C(8)); 4.35–4.30 (*m*, H–C(7)); 4.23 (*dd*, J = 6.5, 5.4, H–C(11)); 3.93 (*d*, J = 6.5, H–C(10)); 3.75–3.65 (*m*, CHN); 3.66 (*s*, COOMe); 2.0–1.1 (*m*, 10 H, C_6H_{11}); 1.61 (*s*, Me). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 174.3 (*s*, C(3)); 166.5, 163.8 (2*s*, C(5), *C*OOMe); 150.6 (*s*, NCON); 148.7 (*d*, C(8)); 145.2, 138.5 (2*s*, arom. C); 134.2 (*s*, C(9)); 129.0, 128.5, 128.2, 127.8, 127.5, 127.2, 126.9 (7*d*, arom. CH); 66.0, 64.0 (2*s*, C(1), C(6)); 64.3 (*d*, ^1J(C,H) = 146.8, C(7)); 51.8 (*q*, COO*Me*); 48.2 (*d*, CHN); 44.3 (*d*, ^1J(C,H) = 185.5, C(10) or C(11)); 36.0 (*d*, ^1J(C,H) = *ca.* 178, C(11) or C(10)); 32.8, 25.2, 24.5 (3*t*, CH_2); 10.1 (*q*, Me). MS (70 eV): 383 (5, [M – $C_6H_{11}NCO$]$^{+}$), 322(5), 224(4), 205(5), 202(4), 165(9).

*(1*RS,7RS,*10*RS,*11*RS*)-11-Cyano-*N*-cyclohexyl-4-methyl-3-oxo-6,6-diphenyl-2-azatetracyclo[5.3.1.0^{1,5}.0^{10,11}]undeca-4,8-diene-2-carboxamide* (**18a**). Yield 12%. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.36 (*d*, J = 7.7, NH); 7.4–7.2 (*m*, 8 arom. H); 6.99 (*m*, 2 arom. H); 5.60 (*dd*, J = 5.5, 2.4, H–C(8)); 4.94 (*dd*, J = 5.5, 2.5, H–C(9)); 4.50 (*d*, J = 2.5, H–C(10)); 4.45 (*d*, J = 2.4, H–C(7)); 3.8–3.6 (*m*, CHN); 2.0–1.2 (*m*, 10 H, C_6H_{11}); 1.60 (*s*, Me). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 173.4 (*s*, C(3)); 163.8 (*s*, C(5)); 150.1 (*s*, NCON); 144.7, 138.4 (2*s*, arom. C); 138.8 (*d*, C(8) or C(9)); 129.9, 129.4, 128.6, 127.8, 127.4, 125.9, (6*d*, C(9) or C(8), arom. CH); 117.6 (*s*, C≡N); 68.9, 65.9, 38.8 (3*s*, C(1), C(6), C(11)); 67.1 (*d*, C(7)); 48.4 (*d*, CHN); 41.5 (*d*, ^1J(C,H) = 176.3, C(10)); 33.1, 32.6, 25.3, 24.6 (4*t*, CH_2); 10.4 (*q*, Me).

*Methyl (1*RS,7RS,*10*RS,*11*RS*)-2-(*N*-Cyclohexylcarbamoyl)-4-methyl-3-oxo-6,6-diphenyl-2-azatetracyclo-[5.3.1.0^{1,5}.0^{10,11}]undeca-4,8-diene-11-carboxylate* (**18b**). Yield 10%. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.59 (br. *s*, NH); 7.5–7.2 (*m*, 8 arom. H); 7.06 (*d*, J = 7.7, 2 arom. H); 5.64 (*dd*, J = 5.3, 2.4, H–C(8)); 5.05 (*dd*, J = 5.3, 2.1, H–C(9)); 4.90 (*d*, J = 2.1, H–C(10)); 4.66 (*d*, J = 2.4, H–C(7)); 3.90 (*s*, COOMe); 3.8–3.6 (*m*, CHN); 2.0–1.0 (*m*, 10 H, C_6H_{11}); 1.54 (*s*, Me). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 174.5 (*s*, C(3)); 169.3 (*s*, *C*OOMe); 165.6 (*s*, C(5)); 151.2 (*s*, NCON); 145.6, 139.1 (2*s*, arom. C); 139.2, 129.6, 128.3, 128.0, 127.9, 127.0, 126.8, 126.4 (8*d*, C(8), C(9), arom. CH); 126.6 (*s*, C(4)); 68.8, 64.1, 54.8 (3*s*, C(1), C(6), C(11)); 66.5 (*d*, C(7)); 52.8 (*q*, COO*Me*); 48.5 (*d*, CHN); 43.2 (*d*, C(10)); 32.8, 25.4, 24.6 (3*t*, CH_2); 10.2 (*q*, Me).

3. Irradiation of 11. – A soln. of **11** (4.0 mg) in dry Et_2O (30 ml) was irradiated under the same conditions as above for 25 min. The solvent was evaporated and the residue shown to consist mainly of **9** (TLC, ^{1}H-NMR).

4. Sensitization Experiments. – *Sensitization of* **11** *with 2-Acetylnaphthalene*. A soln. of 2 mg **11** and 14 mg of the sensitizer in 4 ml of deaerated Et_2O/THF 1:1 was irradiated at 282 nm: the sensitizer absorbs more than 97% of the light. The sole presence of **9** as a photoproduct was detected.

Sensitization of **17a** *with 2-Acetylnaphthalene*. A soln. of 2 mg **17a** and 7 mg of the sensitizer in 4 ml of deaerated Et_2O/THF 1:1 was irradiated at 350 nm: the sensitizer absorbs more than 99% of the light. The sole presence of **18a** as a photoproduct was detected. Under the same conditions, **17b** failed to undergo a reaction.

Sensitizations with Benzene. Irradiation of O_2-free benzene solns. of **8a** at 254 nm (more than 99% of the light is absorbed by the solvent) led to the formation of **11**, **12**, and **13**. Compound **13** was not observed in the photolysate when the irradiation was conducted in the presence of O_2. Compounds **6**, **15**, and **17** were irradiated under the same conditions: **6** afforded **7**, **15** gave **16**, and **17** gave **18**; in all three cases the reaction course was unaffected by O_2. Irradiation of **12** yielded **10**.

Attempts to effect sensitization with acetophenone, benzophenone, and xanthone were unseccessful.

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