Dipolar Cycloaddition Reactions with Heterocyclic Bicyclo[2.2.0]hexenes. – A Contribution to the *syn – anti* Selectivity of *cis*-3,4-Disubstituted Cyclobutenes[1)]

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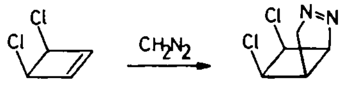
In order to examine the possible preference for *anti* or *syn* attack in bicyclic cyclobutenes, a series of heterocyclic bicyclo[2.2.0]hexenes, **3** – **8**, has been subjected to the reaction towards 1,3-dipoles, particularly diazoalkanes. All dipolar cycloadditions exclusively lead to *anti*-configurated tricyclic products with varying regiochemistry in the cases of **4** – **8**. Similarly, the Pd-catalyzed methylene transfer reactions only yield *anti* products. These results are in remarkable contrast to the known cycloaddition of, e.g., dichlorocyclobutene (**1**) or the carbonate **24**.

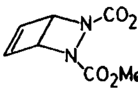
Dipolare Cycloadditionen mit heterocyclischen Bicyclo[2.2.0]hexenen. – Ein Beitrag zur ***syn/anti*-Selektivität *cis*-3,4-disubstituierter Cyclobutene**[1)]

Um die Tendenz zum bevorzugten *anti*- oder *syn*-Angriff in bicyclischen Cyclobutenen zu untersuchen, wurde eine Reihe heterocyclischer Bicyclo[2.2.0]hexene, **3** – **8**, mit 1,3-Dipolen, insbesondere Diazoalkanen, umgesetzt. Alle dipolaren Cycloadditionen führen ausschließlich zu *anti*-konfigurierten Produkten mit unterschiedlicher Regiochemie in den Fällen **4** – **8**. Ebenso werden bei Pd-katalysierten Methylentransfer-Reaktionen nur *anti*-Produkte erhalten. Diese Ergebnisse stehen in bemerkenswertem Gegensatz zu den bekannten Cycloadditionen von beispielsweise Dichlorcyclobuten (**1**) oder dem Carbonat **24**.

The *syn* addition of 1,3-dipoles to *cis*-3,4-disubstituted cyclobutenes (e.g. **1** to **2**) represents a remarkable phenomenon because of the contra-sterical effects coming into force in this reaction[2)].



1 **2**



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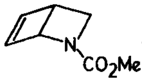

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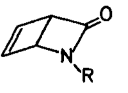
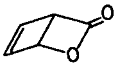


5, R = i-C_3H_7
6, R = CH_3
7, R = H



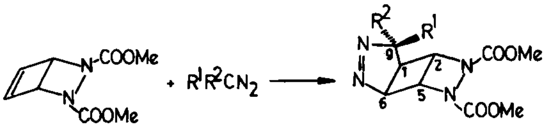
8

As possible explanations for that effect intramolecular interactions in the cyclobutene, pyramidalization at the olefinic C atoms and intermolecular LUMO(dipole)-n(cyclobutene) interactions have been postulated. In order to investigate the influence of hetero substituents in 3,4-position in a clearly defined sterical arrangement the reactivity of the bicycles **3** – **8**[3)] with diazoalkanes **9a** – **e** has been studied.

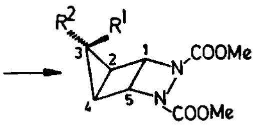
In addition to that the bridging of the substituents in 3,4-position facilitates structural assignments to the tricyclic adducts, since in these adducts the central four-membered ring should be nearly planar. Thus, it should be possible to differentiate *syn* and *anti* adducts with the help of the dependence of the vicinal coupling on dihedral angles. Extraordinarily large *trans* couplings, as can be observed in bicyclic adducts of 3,4-dichloro- or 3,4-dibromocyclobutenes, are therefore not to be expected. Part of the work (regarding compound **3**) has been published in preliminary form[4)].

The reaction of diazomethane with **3** yields 50% of the tricyclic pyrazoline **10a**.

Apart from 55% of a photoproduct, on which we will report separately, photolysis of the pyrazoline **10a** yields 45% of the housane **11a**. Both, NMR spectroscopical data of **10a** and **11a**, prove the *anti* structure and therefore the *anti* cycloaddition.



3 **9** **10a – e**



11a – e

a, $R^1 = R^2 = H$
b, $R^1 = R^2 = CH_3$
c, $R^1 = C_6H_5$ $R^2 = CH_3$
d, $R^1 = R^2 = C_6H_5$
e, R^1R^2C = Fluorenylidene

In the ^1H-NMR spectrum of **10a** a doublet ($^3J_{2\text{-H}/5\text{-H}}$ = 4 Hz) appears at δ = 4.30. Since in a *syn* structure each proton of the four-membered ring should show two large *cis* couplings (dihedral angle ca. 0°) the single doublet split proves the *anti* structure. This doublet can be assigned to 2-H by means of ^{13}C-NMR spectroscopy. Thus, in the ^1H-coupled ^{13}C-NMR spectrum the C-2 signal shows a more complex fine structure than that of C-5 and can be correlated with the doublet proton resonance at δ = 4.30 by means of selective ^1H decoupling. The proton 5-H, vicinal to the azo group, absorbs at lower field (δ = 4.75).

In the case of the housane **11a** the *anti* geometry can be proved by the missing W coupling. The signal of the *exo* proton 3-H_x (R^2 = H) appears as a distinct quartet caused

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by similar coupling of ^2J = 6 Hz with 3-H_n (R^1 = H), and ^3J = 6 Hz with 2-H/4-H. The ^4J-coupling with 1-H/5-H (typical of housanes with W-H,H structural element[5]), is not present in **11a**.

Diazopropane **9b** adds faster than diazomethane **9a**, which indicates that the reaction is HOMO-(dipole-)controlled. The ^{1}H-NMR spectrum of the adduct **10b** reflects the *anti* structure in the shape of four partly broadened doublets: each cyclobutane proton shows merely one larger coupling.

In the ^{1}H-coupled ^{13}C-NMR spectrum of the pyrazoline **10b** it is remarkable that the methyl carbon signal at higher field (δ = 20.6) shows only quartet fine structure (^3J = 4.5 Hz) whereas that at δ = 26.6 appears as a quintet (^3J = 4.5 Hz). Thus, the latter can be assigned to the *exo* methyl group R^2 = CH_3, since only that group has 1-H as a favourable ^3J coupling partner apart from the *endo* methyl neighbouring group. Furthermore, it is interesting that C-6 shows a ^3J diagonal coupling constant of 5 Hz with 2-H; ^3J(C-2/6-H) and ^3J(C-5/1-H) are traceable as well.

Photolysis of **10b** yields 42% of the tricyclic housane **11b** and, analogous to **10a**, another photoproduct on which we will report separately. Simulation experiments of the AA'XX' spectrum of the cyclobutane protons of the symmetrical housane **11b** indicate the existence of a negative diagonal coupling ($^4J < 0$ Hz) which leads to the pseudo doublets observed for 1-H/5-H and 2-H/4-H, respectively. The negative sign of the diagonal coupling, which obviously is particularly large for such housanes (compare the following asymmetric housanes) supports the assumed *anti* structure[6].

The methyl C-atoms of **11b** can clearly be differentiated in the ^{13}C-NMR spectrum (δ = 14.6 and 23.6). The *endo* methyl C-atom (R^1 = CH_3), which is exposed to the γ-effect of the CH groups in the positions 1 and 5, absorbs at higher field. Furthermore, the *exo* methyl C-atom (R^2 = CH_3) shows sextet fine structure because of its *cis* coupling with 2-H/4-H and also with the *endo* methyl group. On the other hand, the *endo* methyl group displays a pure quartet fine structure.

Methylphenyldiazomethane **9c** adds considerably slower than **9a** or **9b** and leads to two stereoisomeric pyrazolines **10c** (7%) and **10c'** (1%). Due to the small amount of **10c'** that side-product has only been characterized ^{1}H-NMR spectroscopically. The doublet ^{1}H-resonances show that both isomers have *anti* configuration. The main product **10c** bears the phenyl group in *endo* position (R^1 = C_6H_5). That should be due to kinetic reasons: during the approach of the linear dipole the transition state with the flat phenyl group in *endo* position possesses lower repulsion.

The proof for the *exo* position of the methyl group again results from the ^{13}C-NMR spectrum. The methyl C-atom shows a doublet fine structure which is caused by the vicinal coupling with 1-H in *cis* position.

Photolysis of **10c** yields the tricyclic housane **11c** in a highly stereoselective way. The *endo* arrangement of the phenyl group clearly follows from the triplet fine structure (^3J = 3 Hz) of the methyl C-atom at δ = 25.2 caused by the two vicinal *cis* protons 2-H/4-H.

Diphenyldiazomethane **9d** and diazofluorene **9e** add within some days and yield 53 and 49% of the two pyrazolines **10d** and **10e**, respectively. The diagonal coupling ^3J (C-2/6-H) of 10 Hz for **10d** can be proved in the following way. Decoupling of 2-H (δ = 4.07) only leaves a reduced ^3J coupling constant, $^3J_{red}$ (C-2/6-H) = 2.2 Hz for C-2 (Fig. 1). The result for C-6 is ^1J: $^1J_{red}$ = 162:37 = 4.4. Consequently, the original diagonal coupling amounts to ^3J(C-2/6-H) = 2.2 × 4.4 Hz = 9.7 Hz (measured: 10 Hz). The relatively large value of the ^3J(C-2/6-H) coupling can probably be explained by the double coupling pathway.

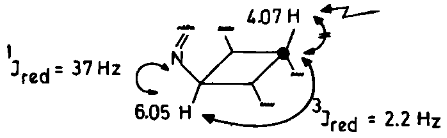
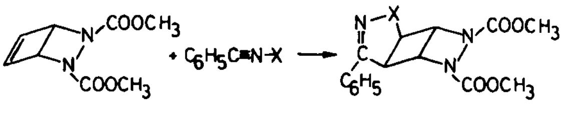


Figure 1. Proof of the diagonal coupling ^3J(C-2/6-H) = 10 Hz in **10d** by decoupling the proton 2-H (δ = 4.07) and observation of the reduced coupling constant $^3J_{red}$ = $^3J(^1J_{red}/^1J)$

Both by thermolysis (80 − 110°C in toluene) and by photolysis, the housanes **11d** and **11e** can be obtained, which, corresponding to the housanes **11a − c** cause pseudo doublets in the ^{1}H-NMR spectra.

In order to check whether the observed *anti* selectivity is only restricted to cycloadditions of diazoalkanes or whether it is generally valid, **3** was treated with benzonitrile oxide **12f** and diphenylnitrile imine **12g**. In both cases again only the *anti* tricycles **13f** and **13g** could be isolated.



3

12f, X = O

12g, X = N-C_6H_5

13f, X = O

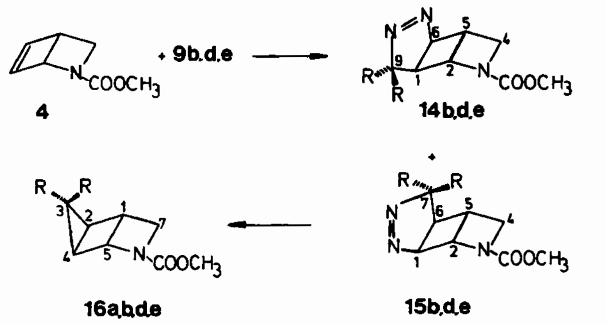
13g, X = N-C_6H_5

The urethane **4** adds to diazopropane (**9b**), diphenyldiazomethane (**9d**), and diazofluorene (**9e**) to yield regioisomeric *anti* cycloadducts **14** and **15**.

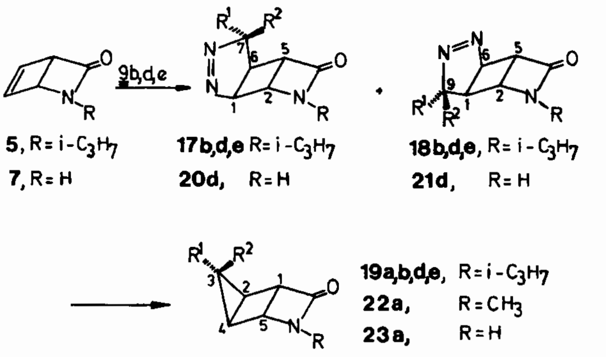
The isomers are formed in similar proportions with slight preference of **15**. Separation of the isomers is accomplished by fractional crystallization or HPLC. At ambient temperature the ^{1}H- and ^{13}C-NMR spectra of **14** and **15** show exchange broadening due to restricted N − C rotation of the carbamate group. Since besides the resonances of C-1, C-2, C-4, 2-H, and OCH_3 that of 1-H is affected in all compounds, the chemical shift of this broadened resonance provides a simple means to distinguish between the isomers. The analysis of the splitting patterns of the ^{1}H resonances assisted by decoupling experiments confirms the structural assignments. Thus, a relatively large *trans* coupling $^3J_{5,6}$ = 2.1 − 2.4 Hz is observed for the compounds **15**. The corresponding coupling on the other side of the ring $^3J_{1,2}$ is too small to be detected. In the isomers **14** the *trans* coupling

$^3J_{5,6}$ and the cross-ring coupling $^4J_{2,6}$ are of similar magnitude (1–2 Hz).

Both regioisomers are photolyzed or thermolyzed to yield the same *anti* housane **16**. Exchange broadening of the resonance of 4-H together with decoupling experiments demonstrate the presence of large cross-ring couplings: $^4J_{1,4}$ = 2.5–3 Hz, $^4J_{2,5}$ = 3.5 Hz.

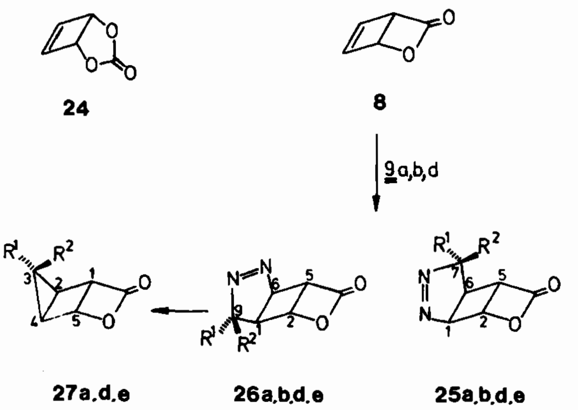


Among the lactams **5** has been treated with the diazoalkanes **9b**, **9d**, and **9e** (**9a** turned out to be insufficiently reactive hitherto). **7** reacted with **9a** and **9d**, however, **20a** could not be obtained in pure state so far.



Again, only *anti* addition is observed. Compared with the urethane **4** the lactams **5** and **7** give rise to higher regioselectivity in the formation of the two possible *anti* cycloadducts **17**, **18**, **20**, and **21**. Thus, in the reactions of **5** with **9b** and **9d** only the pyrazolines **17b** and **17d**, respectively, have been isolated in high yield. Both isomers **17e** and **18e** are formed in the reaction of diazofluorene (**9e**) with **5** in a ratio of 3:1 as determined by ^{13}C NMR of the crude product. In contrast to the lactam **5** the cycloaddition of the parent lactam **7** with diphenyldiazomethane (**9d**) proceeds less regioselectively yielding a 2:1 mixture of **20d** and **21d**. Assignment of the regioisomers has been achieved by the use of the one-sided *trans* coupling $^3J_{5,6}$ as described above for the isomeric urethanes **14** and **15**. Photolysis or thermolysis of the pyrazolines **17**, **18**, **20**, and **21** afford the housanes **19**, **22**, and **23**. The ^{1}H-NMR spectra, recorded at 60 or 80 MHz in $CDCl_3$ as solvent, are not amenable to a first-order analysis since the proton resonances of 2-H and 4-H are not resolved.

Particularly instructive results were expected from the bicyclic lactone **8**. The structure of **8** is extraordinarily similar to that of the carbonate **24**. The fundamental differences between **8** and **24** should lie in the electronic structures of the carbonate or lactone skeleton, respectively. The carbonate **24** adds to diazomethane and other dipoles both in *anti* and in *syn* geometry with a small preference for the *anti* attack (2:1)[2b].



Diazomethane adds to **8** to give two products in a ratio of 3:1, which, however, do not prove to be *syn/anti* isomers but instead are the regioisomers **25a** and **26a**, respectively. Analogous behaviour is observed for the diazoalkanes **9b** and **9d**.

The structural assignment of the isomers is based on the ^{1}H-chemical shifts and coupling constants. Use of the anisotropy of N=N, established above for **10a**, allows to distinguish between the regioisomers via the chemical shifts of the protons 2-H and 5-H.

The compounds **25** and **26** have the smallest vicinal coupling $^3J_{2,5}$ (ca. 2 Hz) of all pyrazolines described in this work. This reduced *cis* coupling is explained easily by the high electronegativity of the oxygen in position 3. As a result, the *cis* coupling now has the same magnitude as the *trans* coupling $^3J_{5,6}$ and the cross-ring coupling $^4J_{2,6}$ in **25** and **26**, respectively, leading to triplet patterns in both isomers.

Photolysis or thermolysis of isomer mixtures **25**/**26** afford only one housane in each case. The ^{1}H-NMR spectra of the housanes **27** show similar patterns for the resonances of 1-H and 5-H. In the case of **27e** the largest separation of the resonances of 2-H and 4-H is obtained which can further be enlarged by use of C_6D_6 as a solvent. Thus, first-order analysis reveals as large cross-ring couplings ($^4J_{2,5}$ = 3.7 Hz and $^4J_{1,4}$ = 2.7 Hz) as have been verified for housanes **16**. Interestingly, the *cis* coupling $^3J_{1,5}$ has a value of only 1 Hz in this compound. The housanes which can be derived from diazomethane but which cannot be prepared by dipolar cycloadditions with diazomethane, because of its too low or complex reactivity, are accessible by other methods. When treating the bicyclic cyclobutenes **3**, **4**, **5**, **6**, **7**, and **8** with an etheric solution of diazomethane in the presence of Pd(II) acetate, the tricycles **11a**, **16a**, **19a**, **22a**, **23a**, and **27a** can be isolated in good yields. Thus, these methylene additions also take a strictly *anti*-selective course.

Conclusions

All dipolar cycloadditions carried out with the bicyclic cyclobutenes **3**–**8** exclusively lead to *anti*-configurated tricyclic pyrazolines with varying regiochemistry in the cases of **4**–**8**. Similarly, the Pd-catalyzed methylene transfer reactions only yield *anti* products. In connection with the photoelectron spectra of these compounds we will report on the causes for this *anti* preference, which can be attributed both to destabilizing influences of the hetero atoms and to certain pyramidalizations of the olefinic C-atoms.

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Experimental

Melting points: Büchi SMP-20 (uncorrected). – IR: Infrared Spectrophotometer 297, Perkin Elmer. Ratio Recording Infrared Spectrophotometer 1420, Perkin Elmer. – UV: Spectrometer M 4 QIII, Carl Zeiss. – ^{1}H NMR: WP 80, Bruker. EM 360-A Varian. – ^{13}C NMR: XL 100, Varian. – MS: Varian-MAT CH 5. – Photolyses were carried out with a 150-W high-pressure mercury lamp (TQ 150, Hanau), Duran filter.

Dimethyl (1α,2β,5β,6α)-3,4,7,8-Tetrazatricyclo[4.3.0.0^{2,5}]non-7-ene-3,4-dicarboxylate (**10a**): A solution of diazomethane (ca. 33 mmol) in ether is added slowly to a cooled solution of **3** (2.30 g, 11.6 mmol) in 20 ml of ether. After 12 h at 0°C the solvent is evaporated to 10 ml, and the solution is stored at –20°C for 24 h The crystals are filtered to the exclusion of air and give analytically pure material; yield 1.39 g (50%), m.p. 120°C. – IR (KBr): 1690–1760 cm^{-1} (C=O), 1530 (N=N). – UV (Ethanol): λ_{max} (lg ε) = 240 (2.98), 325 nm (2.50). – ^{1}H NMR (80 MHz, CDCl$_3$): δ = 3.0–3.25 (m; 1H, 1-H), 3.80 (s; 3H, OCH$_3$), 3.85 (s; 3H, OCH$_3$), 4.30 (d, *J* = 4 Hz; 1H, 2-H), 4.75 (mc; 3H, 5-H, CH$_2$), 5.8 (m; 1H, 6-H). – ^{13}C NMR (CDCl$_3$): δ = 36.4 (d; C-1), 53.6, 53.7 (s; OCH$_3$), 66.2 (d; C-5), 68.1 (d; C-2), 81.8 (t; C-9), 92.3 (d; C-6), 159.1 (s; CO). – MS (70 eV): *m/z* (%) = 240 (10, M$^+$), 212 (2, M – N$_2$), 167 (8, M – NCO$_2$CH$_3$).

$C_9H_{12}N_4O_4$ (240.2) Calcd. C 45.00 H 5.03 N 23.32
Found C 45.10 H 5.04 N 23.53

Dimethyl (1α,2β,5β,6α)-9,9-Dimethyl-3,4,7,8-tetrazatricyclo[4.3.0.0^{2,5}]non-7-ene-3,4-dicarboxylate (**10b**): 2-Diazopropane is prepared from acetone hydrazone (3.00 g, 41.6 mmol), red mercury oxide (12 g), ether (20 ml), and potassium hydroxide in ethanol (3 M) according to the literature procedure[7]; it is collected with ether in a cold trap (–78°C). This red solution is added dropwise at 0°C to **3** (2.00 g, 10.1 mmol) in 10 ml ether. After 2 h the red solution is pipetted from the precipitate, evaporated to ca. 4 ml and kept at –10°C for 24 h. The formed precipitate is filtered, combined with the first precipitate and washed with ether/pentane; yield 1.64 g (61%), m.p. 135°C. – IR (KBr): 1740, 1720 cm^{-1} (C=O), 1540 (N=N). – UV (CHCl$_3$): λ_{max} (lg ε) = 328 nm (2.41). – ^{1}H NMR (80 MHz, CDCl$_3$): δ = 1.25 (s; 3H, *exo*-CH$_3$), 1.62 (s; 3H, *endo*-CH$_3$), 2.85 (d, *J* = 5 Hz; 1H, 1-H), 3.88 (s; 3H, OCH$_3$), 3.92 (s; 3H, OCH$_3$), 4.60 (d, *J* = 4 Hz; 1H, 2-H), 4.82 (d, *J* = 4 Hz; 1H, 5-H), 5.87 (d, *J* = 5 Hz; 1H, 6-H). – ^{13}C NMR (CDCl$_3$): δ = 20.7 (q; *endo*-CH$_3$), 26.7 (q; *exo*-CH$_3$), 47.0 (d; C-1), 53.55, 53.59 (q; OCH$_3$), 64.0 (d; C-2), 64.4 (d; C-5), 92.7 (d; C-6), 91.6 (s; C-9), 158.9 (s; CO). – MS (70 eV): *m/z* (%) = 268 (2, M$^+$), 240 (2, M – N$_2$).

$C_{11}H_{16}N_4O_4$ (268.2) Calcd. C 49.25 H 6.01 N 20.89
Found C 49.02 H 6.03 N 20.77

Dimethyl (1α,2β,5β,6α,9β)-9-Methyl-9-phenyl-3,4,7,8-tetrazatricyclo[4.3.0.0^{2,5}]non-7-ene-3,4-dicarboxylate (**10c**): 1-Phenyldiazoethane is prepared from acetophenone hydrazone (4.50 g, 33.0 mmol), yellow mercury oxide (14.8 g), sodium sulfate (4 g), and potassium hydroxide in ethanol (1 ml, 1 M). A solution of 1-phenyldiazoethane in ether (50 ml) is added dropwise to **3** (4.00 g, 20.2 mmol) in 10 ml of ether. After 24 h at 0°C three quarters of the solvent are removed in vacuo. After 4 d the precipitate is filtered and washed with ether/pentane: 350 mg **10c**. Further 100 mg of **10c** are isolated from the filtrate by chromatography using neutral alumina (250 g, ethyl acetate/chloroform = 1:9). After that a very little amount of **10c′** is eluted as colorless oil; yield 450 mg (7%) of **10c** and 50 mg (1%) of **10c′**; m.p. (**10c**) 150°C.

10c: IR (KBr): 1750 cm^{-1}, 1725 (C=O), 1540 (N=N). – UV (CHCl$_3$): λ_{max} (lg ε) = 320 nm (2.21). – ^{1}H NMR (80 MHz, CDCl$_3$): δ = 1.48 (s; CH$_3$), 3.22 (d, *J* = 5 Hz; 1H, 1-H), 3.87–3.90 (s superimposed on d; 1H, 2-H), 3.87 (s; 3H, OCH$_3$), 3.94 (s; 3H, OCH$_3$), 4.68 (d, *J* = 4 Hz; 1H, 5-H), 5.92 (d, *J* = 5 Hz; 1H, 6-H), 7.2–7.6 (m; 5H, aromatic H). – ^{13}C NMR (CDCl$_3$): δ = 29.2 (q; CH$_3$), 47.2 (d; C-1), 53.6 (q; OCH$_3$), 53.7 (q; OCH$_3$), 64.0 (d; C-5), 64.8 (d; C-2), 92.4 (d; C-6), 98.4 (s; C-9), 125.9, 127.5, 128.7, 139.7 (aromatic C), 159.0, 159.2 (s; CO). – MS (70 eV): *m/z* (%) = 330 (1, M$^+$), 302 (2, M – N$_2$).

$C_{16}H_{18}N_4O_4$ (330.3) Calcd. C 58.17 H 5.49 N 16.96
Found C 58.23 H 5.72 N 16.81

10c′: ^{1}H NMR (60 MHz, CDCl$_3$): δ = 1.90 (s; 3H, CH$_3$), 3.20 (d, *J* = 5 Hz; 1H, 1-H), 3.84 (s; 3H, OCH$_3$), 3.90 (s; 3H, OCH$_3$), 4.65 (d, *J* = 4 Hz; 1H, 2-H), 4.84 (d, *J* = 4 Hz; 1H, 5-H), 5.80 (d, *J* = 5 Hz; 1H, 6-H), 6.90–7.50 (m; 5H, aromatic H).

Dimethyl (1α,2β,5β,6α)-9,9-Diphenyl-3,4,7,8-tetrazatricyclo[4.3.0.0^{2,5}]non-7-ene-3,4-dicarboxylate (**10d**): Diphenyldiazomethane (1.95 g, 10.1 mmol) in 10 ml of ether is added to **3** (2.00 g, 10.1 mmol) in 10 ml of ether. After 3 d at ambient temperature the precipitate is filtered and washed with little ether/pentane. After evaporating the filtrate to a smaller volume further pyrazoline precipitates at –20°C; yield 2.10 g (53%), m.p. 152°C. – IR (KBr): 1740 cm^{-1}, 1710 (C=O), 1540 (N=N). – UV (Methanol): λ_{max} (lg ε) = 335 nm (2.32), 240 (2.97). – ^{1}H NMR (80 MHz, CDCl$_3$): δ = 3.80 (d; 1H, 1-H), 3.85 (s; 3H, OCH$_3$), 3.90 (s; 3H, OCH$_3$), 4.07 (d, *J* = 4 Hz; 1H, 2-H), 4.80 (d, *J* = 4 Hz; 1H, 5-H), 6.05 (d, *J* = 4.5 Hz; 1H, 6-H), 7.00–7.75 (m; aromatic H). – ^{13}C NMR (CDCl$_3$): δ = 47.5 (d; C-1), 53.6 (q; OCH$_3$), 53.7 (q; OCH$_3$), 63.7 (d; C-5), 65.3 (d; C-2), 94.4 (d; C-6), 104.4 (s; C-9), 125.8, 127.5, 127.7, 127.9, 128.6, 128.7, 138.6, 141.1 (aromatic C), 158.9, 159.1 (s; CO). – MS (70 eV): *m/z* (%) = 364 (30, M – N$_2$), 305 [100, M – (N$_2$ + CO$_2$CH$_3$)].

$C_{21}H_{20}N_4O_4$ (392.4) Calcd. C 64.28 H 5.14 N 14.28
Found C 64.29 H 5.20 N 14.01

Dimethyl (1α,2β,5β,6α)-9-Fluorenylidene-3,4,7,8-tetrazatricyclo[4.3.0.0^{2,5}]non-7-ene-3,4-dicarboxylate (**10e**): Diazofluorene (1.94 g, 10.1 mmol) in 10 ml of ether is added to **3** (2.00 g, 10.1 mmol) in 10 ml of ether. After 1 week at 0°C the precipitate is filtered. The filtrate is evaporated to half the volume. After adding 2 ml of pentane at 0°C further product precipitates. Owing to the thermolability of the product all operations have to be carried out below ambient temperature; yield 1.93 g (49%), m.p. 139°C. – IR (KBr): 1765 cm^{-1}, 1730 (C=O), 1535 (N=N). – UV (Methanol): λ_{max} (lg ε) = 330 nm (2.53), 268 (4.08). – ^{1}H NMR (80 MHz, [D$_6$]acetone): δ = 3.37 (d, *J* = 5 Hz; 1H, 1-H), 3.63 (s; 3H, OCH$_3$), 3.92 (s; 3H, OCH$_3$), 5.05 (d, *J* = 4.5 Hz; 1H, 2-H), 5.22 (d, *J* =

4.5 Hz; 1 H, 5-H), 6.54 (d, J = 5 Hz; 1 H, 6-H), 7.10–8.20 (m; 8 H, aromatic H). – MS (70 eV): m/z (%) = 362 (30%, M – N_2).

$C_{21}H_{18}N_4O_4$ (390.4) Calcd. C 64.61 H 4.65 N 14.35
Found C 64.50 H 4.68 N 14.24

Dimethyl (1α,2β,4β,5α)-6,7-Diazatricyclo[3.2.0.0^{2,4}]heptane-6,7-dicarboxylate (**11a**). – a) A solution of diazomethane (from 21.4 g Diazald) in 180 ml of ether is added dropwise within 3 h to **3** (3.00 g, 15.1 mmol) and palladium(II) acetate (43 mg) in 80 ml of ether at –10°C. After 24 h at ambient temperature the solution is filtered and the solvent is removed in vacuo. The oily residue is diluted with 2 ml of ether. Within hours most of the product crystallizes. Another crop of crystals can be obtained from the filtrate by chromatography using deactivated alumina (5% H_2O; ethyl acetate/chloroform = 1:19); yield 1.60 g (50%), m.p. 111–113°C (from ether).

b) 900 mg (3.75 mmol) of **10a** is irradiated in 190 ml of acetonitrile for 17 h at ambient temperature (photoreactor of Gräntzel, Karlsruhe, $\lambda \approx$ 320 nm). After evaporating the solvent in vacuo the remaining yellow oil is subjected to column chromatography using neutral alumina (70 g, ethyl acetate/chloroform = 1:19); yield 290 mg (45%), m.p. 112–113°C. – IR (KBr): 1740 cm^{-1}, 1710 (C=O). – ^1H NMR (80 MHz, $CDCl_3$): δ = 0.50 (dt, J_{gem} = 6 Hz; J_{vic} = 1 Hz; 1 H, 3-*endo*-H), 1.02 (q, J_{gem} = J_{vic} = 6 Hz; 1 H, 3-*exo*-H), 2.37 (m; 2 H, 2-H, 4-H), 3.90 (s; 6 H, OCH_3), 4.48 („d"; 2 H, 1-H, 5-H). – ^{13}C NMR ($CDCl_3$): δ = 8.2 („dd", AB*X*; C-3), 20.2 (dm; C-2, C-4), 53.3 (q; OCH_3), 66.6 (dm; C-1, C-5), 159.9 (s; CO). – MS (70 eV): m/z (%) = 212 (8, M$^+$), 153 (14, M – CO_2CH_3),

$C_9H_{12}N_2O_4$ (212.2) Calcd. C 50.94 H 5.70 N 13.20
Found C 50.89 H 5.77 N 13.16

Dimethyl (1α,2β,4β,5α)-3,3-Dimethyl-6,7-diazatricyclo[3.2.0.0^{2,4}]-heptane-6,7-dicarboxylate (**11b**): **10b** (1.70 g, 6.34 mmol) is irradiated in 190 ml of acetonitrile for 18 h at ambient temperature as described for **11a**. After evaporating the solvent in vacuo the remaining oil is subjected to column chromatography on neutral alumina (ethyl acetate/chloroform = 1:19). **11b** is obtained as a colorless oil; yield 530 mg (42%). – IR (film): 1760 cm^{-1}, 1715 (C=O). – ^1H NMR (60 MHz, $CDCl_3$): δ = 1.08 (s; 6 H, *exo*- and *endo*-CH_3), 2.14 (XX'; 2 H, 2-H, 4-H), 3.80 (s; 6 H, OCH_3), 4.46 (AA'; 2 H, 1-H, 5-H). – ^{13}C NMR ($CDCl_3$): δ = 14.6 (q; *endo*-CH_3), 21.4 (b.s; C-3), 23.6 (qsext; *exo*-CH_3), 32.1 (dm; C-2, C-4), 53.21 (q; OCH_3), 64.7 (dq; C-1, C-5), 160.1 (s; C=O). – MS (70 eV): m/z (%) = 240 (8, M$^+$), 181 (70, M – CO_2CH_3).

$C_{11}H_{16}N_2O_4$ (240.3) Calcd. C 54.99 H 6.71 N 11.66
Found C 54.00 H 6.71 N 11.28

Dimethyl (1α,2β,3α,4β,5α)-3-Methyl-3-phenyl-6,7-diazatricyclo-[3.2.0.0^{2,4}]heptane-6,7-dicarboxylate (**11c**): **10c** (410 mg, 1.24 mmol) is irradiated in 190 ml of acetonitrile for 9.5 h at ambient temperature as described for **11a**. After evaporating the solvent in vacuo the residue is subjected to chromatography on neutral alumina (40 g, ethyl acetate/chloroform = 1:19); yield 130 mg (35%), m.p. 138°C. – IR (KBr): 1730 cm^{-1}, 1700 (C=O). – ^1H NMR (60 MHz, $CDCl_3$): δ = 1.35 (s; 3 H, *exo*-CH_3), 2.64 (XX'; 2 H, 2-H, 4-H), 3.82 (s; 3 H, OCH_3), 4.20 (AA'; 2 H, 1-H, 5-H), 7.35 (b.s.; 5 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 25.2 (qt; *exo*-CH_3), 32.2 (s; C-3), 33.1 (dm; C-2, C-4), 53.3 (q; OCH_3), 65.3 (ddt; C-1, C-5), 127.0, 128.6, 128.8, 138.3 (aromatic C), 160.1 (s; C=O). – MS (70 eV): m/z (%) = 302 (23, M$^+$), 243 (15, M – CO_2CH_3).

$C_{16}H_{18}N_2O_4$ (302.3) Calcd. C 63.57 H 6.00 N 9.26
Found C 63.37 H 6.11 N 8.99

Dimethyl (1α,2β,4β,5α)-3,3-Diphenyl-6,7-diazatricyclo[3.2.0.0^{2,4}]-heptane-6,7-dicarboxylate (**11d**): **10d** (1.00 g, 2.50 mmol) is refluxed for 2 h in 20 ml of dry toluene. After removing the solvent in vacuo the remaining oil is dissolved in a few ml of ether. After some hours **11d** crystallizes; yield 864 mg (95%), m.p. 203°C. – IR (KBr): 1700–1760 cm^{-1} (C=O). – ^1H NMR (60 MHz, $CDCl_3$): δ = 3.05 (XX'; 2 H, 2-H, 4-H), 3.80 (s; 3 H, OCH_3), 4.30 (AA'; 2 H, 1-H, 5-H), 6.90–7.50 (m; 10 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 35.1 (dm; C-2, C-4), 39.6 (s; C-3), 57.4 (q; OCH_3), 65.3 (dm; C-1, C-5), 126.5, 127.5, 128.3, 128.7, 130.2, 135.7, 141.8 (aromatic H), 159.9 (s; CO). – MS (70 eV): m/z (%) = 364 (20, M$^+$), 305 (100, M – CO_2CH_3).

$C_{21}H_{20}N_2O_4$ (364.4) Calcd. C 69.22 H 5.53 N 7.69
Found C 68.90 H 5.56 N 7.46

Dimethyl (1α,2β,4β,5α)-3-Fluorenylidene-6,7-diazatricyclo-[3.2.0.0^{2,4}]heptane-6,7-dicarboxylate (**11e**): **10e** (600 mg, 1.54 mmol) in 50 ml of dry toluene is heated to 80°C for 2 h. After evaporation of the solvent the remaining yellow oil is dissolved in dry ether (1 ml). **11e** crystallizes after a while; yield 530 mg (95%), m.p. 196°C. – IR (KBr): 1750 cm^{-1}, 1715 (C=O). – ^1H NMR (100 MHz, $CDCl_3$): δ = 3.25 (XX'; 2 H, 2-H, 4-H), 3.90 (s; 6 H, OCH_3), 5.28 (AA'; 2 H, 1-H, 5-H), 6.85–7.95 (m; 8 H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 37.0 (dm; C-2, C-4), 37.3 (s; C-3), 53.6 (q; OCH_3), 66.0 (dm; C-1, C-5), 118.8, 119.7, 120.5, 123.8, 126.7, 127.0, 127.1, 127.2, 138.7, 142.1, 142.5, 143.9 (aromatic C), 159.9 (s; C=O). – MS (70 eV): m/z (%) = 362 (12, M$^+$), 303 (100, M – CO_2CH_3).

$C_{21}H_{18}N_2O_4$ (362.4) Calcd. C 69.60 H 5.00 N 7.73
Found C 69.44 H 4.99 N 7.71

Dimethyl (1α,2β,5β,6α)-9-Phenyl-7-oxa-3,4,8-triazatricyclo-[4.3.0.0^{2,5}]non-8-ene-3,4-dicarboxylate (**13f**): **3** (400 mg, 2.02 mmol) and dry triethylamine (224 mg, 2.22 mmol) are dissolved in 5 ml of ether. The mixture is stirred at 0°C and benzohydroximoyl chloride (313 mg, 2.02 mmol) in 10 ml of ether is added dropwise. A crystalline precipitate forms immediately. The solid is filtered, washed with a little water, and dried. The product is recrystallized from ethanol; yield 390 mg (61%), m.p. 179°C. – IR (KBr): 1750 cm^{-1}, 1720 (CO), 1600, 1550, 1490 (C=C). – ^1H NMR (100 MHz, $CDCl_3$): δ = 3.88 (s; 3 H, OCH_3), 3.95 (s; 3 H, OCH_3), 4.80–4.96 (m; 3 H, 1-H, 2-H, 5-H), 5.48 (d; 1 H, 6-H), 7.40–7.70 (m; 5 H, aromatic H). – MS (70 eV): m/z (%) = 317 (8, M$^+$), 145 (21, M – $C_6H_8N_2O_4$).

$C_{17}H_{15}N_3O_5$ (317.3) Calcd. C 56.78 H 4.76 N 13.24
Found C 56.90 H 4.85 N 12.95

Dimethyl (1α,2β,5β,6α)-7,9-Diphenyl-3,4,7,8-tetrazatricyclo-[4.3.0.0^{2,5}]non-8-ene-3,4-dicarboxylate (**13g**): To a solution of **3** (400 mg, 2.02 mmol) and *N*-phenylbenzohydrazonoyl chloride (464 mg, 2.02 mmol) in 10 ml of dry benzene, triethylamine (222 mg, 2.20 mmol) in 5 ml of benzene is added. After some minutes the solution becomes turbid. The mixture is kept at ambient temperature for 24 h and the solid is filtered. The filtrate is evaporated and the residue dissolved in 1 ml of ethanol. At 0°C greenish yellow crystals appear which display a green fluorescence in solution; yield 520 mg (66%), m.p. 168°C. – IR (KBr): 1750 cm^{-1}, 1710 (CO). – UV ($CHCl_3$): λ_{max} (lg ε) = 420 nm (3.57). – ^1H NMR (60 MHz, $CDCl_3$): δ = 3.90 (s; 6 H, OCH_3), 4.70–4.90 (m; 3 H, 1-H, 2-H, 5-H), 5.30 (d; 1 H, 6-H), 6.80–7.80 (m; 10 H, aromatic H). – MS (70 eV): m/z (%) = 392 (3, M$^+$), 299 (15), 220 (100, M – $C_6H_8N_2O_4$).

$C_{21}H_{20}N_4O_4$ (392.4) Calcd. C 64.28 H 5.14 N 14.28
Found C 64.29 H 5.21 N 14.01

Methyl (1α,2β,5β,6α)-9,9-Dimethyl-3,7,8-triazatricyclo[4.3.0.0^{2,5}]non-7-ene-3-carboxylate (**14b**) *and Methyl (1α,2β,5β,6α)-7,7-Dimethyl-3,8,9-triazatricyclo[4.3.0.0^{2,5}]non-8-ene-3-carboxylate* (**15b**): A solution of 2-diazopropane in ether (from 2.5 g of acetone hydrazone) is distilled into a cooled receiver (−78°C) containing **4** (800 mg, 5.80 mmol). The mixture is stirred and the temperature raised to 20°C. The solid is filtered and washed with a little ether. The colourless crystals of **15b** have m.p. 132−133°C. The filtrate is concentrated and the remaining oil is distilled in a kugelrohr apparatus (90−100°C/0.02 Torr). **14b** is obtained as a colourless oil; ratio **14b**/**15b** ≈ 1:1; yield 700 mg (56%).

15b: IR (KBr): 1535 cm^{-1} (N=N), 1700 (C=O). − UV (CH_3CN): λ_{max} (lg ε) = 329 nm (2.4). − ^{1}H NMR (80 MHz, $CDCl_3$, 60°C): δ = 1.18 (s; 3H, *endo*-CH_3), 1.56 (s; 3H, *exo*-CH_3), 2.49 (dd, *J* = 4.8 Hz, *J* = 2.3 Hz; 1H, 6-H), 2.67 (ddt, *J* = 6.8 Hz, *J* = 4.3 Hz, *J* = 2.3 Hz, *J* = 2.3 Hz; 1H, 5-H), 3.76 (s; 3H, OCH_3), 3.93 (ddd, *J* = 9.0 Hz, *J* = 2.3 Hz, *J* = 1.2 Hz; 1H, 4-*endo*-H), 4.31 (dd, *J* = 9.0 Hz, *J* = 6.8 Hz; 1H, 4-*exo*-H), 4.56 (b.d, *J* = 4.3 Hz; 1H, 2-H), 5.63 (d, *J* = 4.8 Hz; 1H, 1-H). − ^{13}C NMR ($CDCl_3$, 60°C): δ = 20.7 (q; *endo*-CH_3), 26.7 (q; *exo*-CH_3), 31.9 (d; C-5), 47.0 (d; C-6), 52.1 (q; OCH_3), 55.8 (t; C-4), 63.5 (d; C-2), 90.8 (s; C-7), 94.8 (d; C-1), 155.8 (s; CO_2CH_3). − MS (70 eV): *m/z* (%) = 181 (7, M − N_2), 180 (43, M − N_2 − H).

14b: IR (KBr): 1540 cm^{-1} (N=N), 1700 (C=O). − UV (CH_3CN): λ_{max} (lg ε) = 331 nm (2.46). − ^{1}H NMR ($CDCl_3$): δ = 1.20 (s; 3H, *endo*-CH_3), 1.59 (s; 3H, *exo*-CH_3), 2.57 (b.d, *J* = 5.0 Hz; 1H, 1-H), 2.9 (m; 1H, 5-H), 3.70 (s; 3H, OCH_3), 4.05−4.45 (m; 3H, CH_2, 2-H), 5.50 (dt, *J* = 5.0 Hz, *J* = 1.3 Hz; 1H, 6-H). − ^{13}C NMR ($CDCl_3$, 60°C): δ = 20.9 (q; *endo*-CH_3), 27.1 (q; *exo*-CH_3), 35.2 (d; C-5), 48.6 (d; C-1), 52.1 (q; OCH_3), 53.8 (t; C-4), 63.1 (d; C-2), 90.8 (s; C-9), 92.9 (d; C-6), 155.6 (s; CO_2CH_3). − MS (70 eV): *m/z* (%) = 181 (36, M − N_2), 180 (80, M − N_2 − H).

$C_{10}H_{15}N_3O_2$ (209.3) Calcd. C 57.40 H 7.23 N 20.08
Found C 57.24 H 7.18 N 19.74

Methyl (1α,2β,5β,6α)-9,9-Diphenyl-3,7,8-triazatricyclo[4.3.0.0^{2,5}]non-7-ene-3-carboxylate (**14d**) *and Methyl (1α,2β,5β,6α)-7,7-Diphenyl-3,8,9-triazatricyclo[4.3.0.0^{2,5}]non-8-ene-3-carboxylate* (**15d**): **4** (0.8 g, 5.8 mmol) and diphenyldiazomethane (**9d**) (1.1 g, 5.8 mmol) are heated in 10 ml of toluene to 80°C for 11 h. After cooling the precipitate is filtered and washed with a little ether. The solid consists of **14d** and **15d**, ratio 2:3; yield 1.5 g (79%). − Separation of the isomers is accomplished by HPLC (RP 8, methanol/water, 7.5:2.5).

15d: m.p. 135°C. − IR (KBr): 1535 cm^{-1} (N=N), 1700 (C=O), 1595 (C=C). − UV (acetonitrile): λ_{max} (lg ε) = 335 nm (2.39). − ^{1}H NMR ($CDCl_3$): δ = 2.15 (m; 1H, 5-H), 3.52 (dd, *J* = 4.3 Hz, *J* = 2.4 Hz; 1H, 6-H), 3.76 (s; 3H, OCH_3), 3.99 (ddd, *J* = 8.8 Hz, *J* = 2.2 Hz, *J* = 1.0 Hz; 1H, 4-*endo*-H), 4.20 (dd, *J* = 8.8 Hz, *J* = 6.6 Hz; 1H, 4-*exo*-H), 4.64 (b.d, *J* = 4.2 Hz; 1H, 2-H), 5.89 (b.d, *J* = 4.3 Hz; 1H, 1-H), 7.0−7.5 (m; 10H, aromatic H). − ^{13}C NMR ($CDCl_3$, 60°C, mixture of **14d** and **15d**): δ = 33.7 (d; C-5), 47.2 (d; C-6), 52.2 (q; CO_2CH_3), 55.9 (t; CH_2), 63.2 (d; C-2), 96.7 (d; C-1), 104.2 (s; C-7), 126.0, 126.2, 127.3, 127.5, 127.6, 127.9, 128.5 (d; phenyl, *o*-, *m*-, *p*-C), 140.3, 141.7 (s; phenyl, *ipso*-C), 155.7 (s; C=O). − MS (20 eV): *m/z* (%) = 305 (21, M − N_2), 304 (79, M − N_2 − H), 290 (33, M − N_2 − CH_3), 180 (100), 138 (35).

14d: m.p. 149−152°C (dec.). − IR (KBr): 1540 cm^{-1} (N=N), 1688 (C=O), 1595 (C=C). − UV ($CHCl_3$): λ_{max} (lg ε) = 333 nm (2.49). − ^{1}H NMR ($CDCl_3$, 60°C): δ = 2.96 („b.q.“, *J* = 4.6 Hz; 1H, 5-H), 3.54 (d, *J* = 4.6 Hz; 1H, 1-H), 3.69 (s; 3H, OCH_3), 3.88 (b.d, *J* = 4.6 Hz; 1H, 2-H), 4.30 („d“, *J* = 5.3 Hz; 2H, CH_2), 5.68 (dt, *J* = 4.6 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz; 1H, 6-H), 7.0−7.8 (m; 10H, aromatic H). − ^{13}C NMR ($CDCl_3$, 60°C, mixture of **14d** and **15d**): δ = 34.2 (d; C-5), 48.8 (d; C-1), 52.0 (q; CO_2CH_3), 53.6 (t; CH_2), 64.6 (d; C-2), 94.2 (d; C-6), 103.9 (s; C-9), 126.0, 126.2, 127.2, 127.5, 127.6, 127.9, 128.5 (d; phenyl, *o*-, *m*-, *p*-C), 139.6, 142.3 (s; phenyl, *ipso*-C), 155.5 (s; C=O). − MS (20 eV): *m/z* (%) = 305 (27, M − N_2), 304 (85, M − N_2 − H), 290 (44, M − N_2 − CH_3), 180 (100), 138 (40).

$C_{20}H_{19}N_3O_2$ (333.4) Calcd. C 72.05 H 5.74 N 12.60
Found C 72.68 H 5.80 N 12.70

Methyl (1α,2β,5β,6α)-9-Fluorenylidene-3,7,8-triazatricyclo[4.3.0.0^{2,5}]non-7-ene-3-carboxylate (**14e**) *and Methyl (1α,2β,5β,6α)-7-Fluorenylidene-3,8,9-triazatricyclo[4.3.0.0^{2,5}]non-8-ene-3-carboxylate* (**15e**): **4** (800 mg, 5.8 mmol) and diazofluorene (**9e**) (1.1 g, 5.8 mmol) are refluxed in 7 ml of ether for 24 h. After cooling the precipitate is filtered and washed with a little ether. The solid contains the isomers in the ratio **15e**/**14e** = 2:1; yield 1.3 g (72%). Separation can be achieved by means of HPLC (RP 8, eluent methanol/water, 8:2).

15e: m.p. 131−132°C. − IR (KBr): 1530 cm^{-1} (N=N), 1687 (C=O). − UV ($CHCl_3$): λ_{max} (lg ε) = 346 nm (2.01) sh, 330 (2.34) sh. − ^{1}H NMR ($CDCl_3$, 60°C): δ = 2.99 (dd, *J* = 4.9 Hz, *J* = 2.1 Hz; 1H, 6-H), 3.14 (ddd, *J* = 7.1 Hz, *J* = 4.2 Hz, *J* = 2.4 Hz, *J* = 2.0 Hz; 1H, 5-H), 3.79 (s; 3H, OCH_3), 3.88 (ddd, *J* = 9.0 Hz, *J* = 2.4 Hz, *J* = 1.1 Hz; 1H, 4-*endo*-H), 4.26 (dd, *J* = 9.0 Hz, *J* = 7.1 Hz, 1H, 4-*exo*-H), 4.89 (b.d, *J* = 4.2 Hz; 1H, 2-H), 6.09 (d, *J* = 4.9 Hz; 1H, 1-H), 6.8−7.9 (m; 8H, aromatic H). − ^{13}C NMR ($CDCl_3$, 65°C, mixture of **14e** and **15e**): δ = 33.8 (d; C-5), 45.8 (d; C-6), 52.3 (q; OCH_3), 55.8 (t; C-4), 63.7 (d; C-2), 97.3 (d; C-1), 104.2 (s; C-7), 120.0, 120.6, 122.8, 126.1, 127.2, 128.1, 129.2 (d; phenyl, *o*-, *m*-, *p*-C), 139.5, 140.9, 142.5, 144.9 (s; phenyl, *ipso*-C), 155.6 (s; C=O). − MS (70 eV): *m/z* (%) = 303 (22, M^+ − N_2).

14e: m.p. 96−97°C. − IR (KBr): 1530 cm^{-1} (N=N), 1690 (C=O). − UV ($CHCl_3$): λ_{max} (lg ε) = 326 nm (2.20) sh. − ^{1}H NMR ($CDCl_3$): δ = 3.10 (d, *J* = 5.1 Hz; 1H, 1-H), 3.26 (dddd, *J* = 6.7 Hz, *J* = 4.1 Hz, *J* = 2.5 Hz, *J* = 1.4 Hz; 1H, 5-H), 3.75 (s; 3H, OCH_3), 4.25 (dd, *J* = 9.2 Hz, *J* = 2.5 Hz; 1H, 4-*endo*-H), 4.39 (dd, *J* = 9.2 Hz, *J* = 6.7 Hz; 1H, 4-*exo*-H), 4.71 (b.d, *J* = 4.1 Hz; 1H, 2-H), 6.00 (dt, *J* = 5.1 Hz, *J* = 1.4 Hz, *J* = 1.4 Hz; 1H, 6-H), 6.8−7.9 (m; 8H, aromatic H). − ^{13}C NMR ($CDCl_3$, 65°C, mixture of **14e** and **15e**): δ = 36.3 (d; C-5), 44.6 (d; C-1), 52.0 (q; OCH_3), 53.8 (t; C-4), 65.1 (d; C-2), 95.6 (d; C-6), 104.1 (s; C-9), 123.0, 125.8 (d; phenyl, *o*-, *m*-, *p*-C), 139.9, 140.4 (s; phenyl, *ipso*-C), 155.2 (s; C=O). − MS (70 eV): *m/z* (%) = 303 (65, M − N_2).

$C_{20}H_{17}N_3O_2$ (331.4) Calcd. C 72.49 H 5.17 N 12.68
Found C 72.38 H 5.34 N 12.68

Methyl (1α,2β,4β,5α)-6-Azatricyclo[3.2.0.0^{2,4}]heptane-6-carboxylate (**16a**)[8]: The procedure is the same as described for **11a**, section a); from 1.40 g (10.0 mmol) of **4**, purification by kugelrohr distillation (50°C/0.04 Torr), colourless liquid, m.p. approx. −20°C; yield 1.3 g (85%). − IR (film): 1705 cm^{-1} (C=O). − ^{1}H NMR ($CDCl_3$): δ = 0.45 (dt, *J* = 5.4 Hz, *J* = 1.5 Hz, *J* = 1.5 Hz; 1H, 3-*endo*-H), 0.87 (q, *J* = 5.4 Hz; 1H, 3-*exo*-H), 1.88 (m; 1H, 2-H), 2.15 (b.s; 1H, 4-H), 2.58 (dq, *J* = 6.1 Hz, *J* = 3.0 Hz; 1H, 1-H), 3.72 (s; 3H, OCH_3), 3.94 (ddd, *J* = 8.8 Hz, *J* = 2.8 Hz, *J* = 1.2 Hz; 1H, 7-*endo*-H), 4.20 (dd, *J* = 8.8 Hz, *J* = 6.1 Hz; 1H, 7-*exo*-H), 4.3 (5-H, superimposed by 7-H). − ^{13}C NMR ($CDCl_3$, 60°C): δ = 20.6 (d, C-4), 10.0 („dd“, AB*X*; C-3), 18.6 (d; C-2), 35.8 (d; C-1), 51.8 (q; OCH_3), 52.9 (t; CH_2), 65.2 (d; C-5), 156.7 (s; C=O). − MS (70 eV): *m/z* (%) = 153 (25, M^+), 138 (67, M − CH_3), 94 (98, M − CO_2CH_3).

$C_8H_{11}NO_2$ (153.2) Calcd. C 62.73 H 7.24 N 9.14
Found C 62.21 H 7.66 N 9.10

Methyl (1α,2β,4β,5α)-3,3-Dimethyl-6-azatricyclo$[3.2.0.0^{2,4}]$*heptane-6-carboxylate* (**16b**): **14b** or **15b** (600 mg, 2.90 mmol) and benzophenone (60 mg) are dissolved in 500 ml of dry acetone and irradiated for 3 h at 0°C. The solvent is removed, and the remaining oil is subjected to column chromatography using silica gel and chloroform. **16b** is eluted as a colourless oil which is purified by kugelrohr distillation (65°C/0.01 Torr); yield 395 mg (76%). – IR (film): 1710 cm^{-1} (C=O). – ^1H NMR ($CDCl_3$): δ = 0.98 (s; 3H, *endo*-CH_3), 1.04 (s, 3H, *exo*-CH_3), 1.61 (t, *J* = 3.7 Hz; 1H, 2-H), 1.93 (b.s; 1H, 4-H), 2.50 (dq, *J* = 6.5 Hz, *J* = 2.5 Hz; 1H, 1-H), 3.70 (s; 3H, OCH_3), 3.91 (ddd, *J* = 8.7 Hz, *J* = 2.5 Hz, *J* = 1.0 Hz; 1H, 7-*endo*-H), 4.14 (dd, *J* = 8.7 Hz, *J* = 6.5 Hz; 1H, 7-*exo*-H), 4.2 (mc; 1H, 5-H). – ^{13}C NMR ($CDCl_3$, 55°C): δ = 14.5 (q; CH_3), 20.8 (s; C-3), 23.7 (q; CH_3), 31.6 (d; C-2), 32.3 (d; C-1), 32.9 (d; C-4), 51.8 (q; OCH_3), 52.4 (t; C-7), 62.9 (d; C-5), 156.8 (s; C=O). – MS (70 eV): *m/z* (%) = 181 (68, M^+), 180 (99, M – H), 166 (100, M – CH_3).

Methyl (1α,2β,4β,5α)-3,3-Diphenyl-6-azatricyclo$[3.2.0.0^{2,4}]$*heptane-6-carboxylate* (**16d**): a) **14d** or **15d** (400 mg, 1.20 mmol) is heated to 120°C in 10 ml of xylene for 2 h. After removing the solvent in vacuo the remaining oil crystallizes on addition of ether; yield 297 mg (81%).

b) **14d** or **15d** (400 mg, 1.20 mmol) and benzophenone (40 mg) are irradiated in dry acetone (400 ml) for 4 h. The solvent is evaporated, and the oily residue is filtered through silica gel (chloroform/ethyl acetate, 19:1); yield 321 mg (88%), m.p. 102–103°C (from toluene). – IR (KBr): 1700 cm^{-1} (C=O), 1599 (C=C). – ^1H NMR ($CDCl_3$, 60°C): δ = 2.40 (dq, *J* = 5.8 Hz, *J* = 2.9 Hz; 1H, 1-H), 2.57 (t, *J* = 3.6 Hz; 1H, 2-H), 2.86 (b.t, *J* = 3.6 Hz; 1H, 4-H), 3.71 (s; 3H, OCH_3), 4.05 (m; 3H, 5-H, CH_2), 6.9–7.5 (m; 10H, aromatic H). – ^{13}C NMR ($CDCl_3$, 60°C): δ = 34.0 (d; C-2), 35.1 (d; C-1), 36.6 (d; C-4), 39.6 (s; C-3), 52.0 (t; C-7), 52.0 (q, OCH_3), 63.6 (d; C-5), 125.9, 126.4, 126.9, 128.1, 128.2, 128.4, 130.7 (d; phenyl, *o*-, *m*-, *p*-C), 137.0, 143.3 (s; phenyl, *ipso*-C), 156.6 (s; C=O). – MS (70 eV): *m/z* (%) = 305 (48, M^+), 304 (85, M – H), 290 (48, M – CH_3).

$C_{20}H_{19}NO_2$ (305.4) Calcd. C 78.66 H 6.27 N 4.59
Found C 78.64 H 6.26 N 4.49

Methyl (1α,2β,4β,5α)-3-Fluorenylidene-6-azatricyclo$[3.2.0.0^{2,4}]$*heptane-6-carboxylate* (**16e**): **4** (800 mg, 5.8 mmol) and 9-diazofluorene (1.1 g, 5.8 mmol) are heated to 80°C in 5 ml of dry toluene. After cooling the precipitate is filtered and washed with a little ether; yield 0.9 g (45%), m.p. 173–174°C (from toluene). – IR (KBr): 1710 cm^{-1} (C=O). – ^1H NMR ($CDCl_3$, 50°C): δ = 2.72 (t, *J* = 3.5 Hz; 1H, 2-H), 3.08 (b.t, *J* = 2.5 Hz; 1H, 4-H), 3.34 (dq, *J* = 6.7 Hz, *J* = 2.5 Hz; 1H, 1-H), 3.74 (s; 3H, OCH_3), 4.11 (ddd, *J* = 8.5 Hz, *J* = 2.3 Hz, *J* = 1.2 Hz; 1H, 7-*endo*-H), 4.26 (dd, *J* = 8.5 Hz, *J* = 6.7 Hz; 1H, 7-*exo*-H), 5.00 (b.s; 1H, 5-H), 6.8–7.9 (m; 8H, aromatic H). – MS (70 eV): *m/z* (%) = 303 (94, M^+), 288 (38, M – CH_3), 244 (56, M – CO_2CH_3).

$C_{20}H_{17}NO_2$ (303.4) Calcd. C 79.19 H 5.57 N 4.62
Found C 79.41 H 5.75 N 4.60

(1α,2β,5β,6α)-3-Isopropyl-7,7-dimethyl-3,8,9-triazatricyclo$[4.3.0.0^{2,5}]$*non-8-en-4-one* (**17b**): A solution of dimethyldiazomethane in ether (from 5.0 g of acetone hydrazone) is distilled into a cooled receiver (–78°C) containing **5** (1.22 g, 8.90 mmol). The mixture is stirred and the temperature raised to 20°C. The solution is evaporated to ca. 15 ml, and 15 ml of *n*-hexane is added. **17b** is obtained as colourless crystals; yield 1.3 g (70%), m.p. 117–118°C. – IR (KBr): 1530 cm^{-1} (N=N), 1720 (C=O). – UV (EtOH): λ_{max} (lg ε) = 328 nm (2.36). – ^1H NMR ($CDCl_3$): δ = 1.19 (s; 3H, *endo*-CH_3), 1.58 (s; 3H, *exo*-CH_3), 1.35 [d, *J* = 6.8 Hz; 3H, $CH(CH_3)_2$], 1.38 [d, *J* = 6.8 Hz; 3H, $CH(CH_3)_2$], 2.59 (dd, *J* = 4.6 Hz, *J* = 2.0 Hz; 1H, 6-H), 3.27 (dd, *J* = 2.8 Hz, *J* = 2.0 Hz; 1H, 5-H), 3.97 [sept, *J* = 6.8 Hz; 1H, $CH(CH_3)_2$], 3.99 (d, *J* = 2.8 Hz; 1H, 2-H), 5.51 (d, *J* = 4.6 Hz; 1H, 1-H). – ^{13}C NMR ($CDCl_3$): δ = 20.6 [q; $CH(CH_3)_2$], 20.7 [q; $CH(CH_3)_2$], 20.8 (q; *endo*-CH_3), 26.7 (q; *exo*-CH_3), 41.8 (d; C-6), 44.8 [d; $CH(CH_3)_2$], 50.0 (d; C-5), 51.6 (d; C-2), 88.9 (s; C-7), 94.3 (d; C-1), 168.0 (s; C-4). – MS (70 eV): *m/z* (%) = 179 (2, M^+ – N_2), 164 (3, M – N_2 – CH_3).

$C_{11}H_{17}N_3O$ (207.3) Calcd. C 63.74 H 8.27 N 20.27
Found C 64.06 H 8.43 N 20.34

(1α,2β,5β,6α)-3-Isopropyl-7,7-diphenyl-3,8,9-triazatricyclo$[4.3.0.0^{2,5}]$*non-8-en-4-one* (**17d**): The preparation of **17d** is carried out analogous to the synthesis of **14d** and **15d** from **9d** (1.0 g, 7.3 mmol) and **5** (1.4 g, 7.3 mmol); yield 2.2 g (89%), m.p. 165–167°C (dec.). – IR (KBr): 1535 cm^{-1} (N=N), 1730 (C=O). – UV (EtOH): λ_{max} (lg ε) = 336 nm (2.47). – ^1H NMR ($CDCl_3$): δ = 1.38 (d, *J* = 6.8 Hz; 3H, *endo*-CH_3), 1.43 (d, *J* = 6.8 Hz; 3H, *exo*-CH_3), 2.83 (dd, *J* = 3.0 Hz, *J* = 2.5 Hz; 1H, 5-H), 3.59 (dd, *J* = 4.3 Hz, *J* = 2.5 Hz; 1H, 6-H), 4.00 (d, *J* = 3.0 Hz; 1H, 2-H), 4.02 [sept, *J* = 6.8 Hz; 1H, $CH(CH_3)_2$], 5.70 (d, *J* = 4.3 Hz; 1H, 1-H), 7.0–7.5 (m; 10H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 20.6 [q; $CH(CH_3)_2$], 20.7 [q; $CH(CH_3)_2$], 42.0 (d; C-6), 44.6 [d; $CH(CH_3)_2$], 50.9 (d; C-2), 51.6 (d; C-5), 96.1 (d; C-1), 101.9 (s; C-7), 126.2 (d; *o*-C), 127.4 (d; *p*-C), 127.6 (d; *o*-C), 127.7 (d; *p*-C), 128.5 (d; *m*-C), 128.6 (d; *m*-C), 139.6 (s; *ipso*-C), 141.3 (s; *ipso*-C), 167.5 (s; C-4). – MS (70 eV): *m/z* (%) = 303 (15, M – N_2).

$C_{21}H_{21}N_3O$ (331.4) Calcd. C 76.11 H 6.39 N 12.68
Found C 76.13 H 6.43 N 12.65

(1α,2β,5β,6α)-7-Fluorenylidene-3-isopropyl-3,8,9-triazatricyclo$[4.3.0.0^{2,5}]$*non-8-en-4-one* (**17e**) *and (1α,2β,5β,6α)-9-Fluorenylidene-3-isopropyl-3,7,8-triazatricyclo*$[4.3.0.0^{2,5}]$*non-7-en-4-one* (**18e**): **5** (1.4 g, 10.0 mmol) and 9-diazofluorene (**9e**) (1.9 g, 10.0 mmol) are refluxed in 15 ml of dry ether for 18 h. After cooling the colourless crystals are filtered (**18e**), yield 0.9 g (28%), m.p. 103–105°C (dec.). The filtrate is evaporated and the residue dissolved in 7 ml of ether/*n*-hexane (2:1). At –25°C colourless crystals precipitate (**17e**); yield 1.7 g (51%), m.p. 128°C (dec.).

17e: IR (KBr): 1540 cm^{-1} (N=N), 1740 (C=O), 1600, 1540 (C=C). – UV ($CHCl_3$): λ_{max} (lg ε) = 346 nm (1.78) sh, 330 (2.22) sh. – ^1H NMR ($CDCl_3$): δ = 1.38 [d, *J* = 6.8 Hz; 3H, $CH(CH_3)_2$], 1.42 [d, *J* = 6.8 Hz; 3H, $CH(CH_3)_2$], 3.07 (dd, *J* = 4.8 Hz, *J* = 2.1 Hz; 1H, 6-H), 3.77 (dd, *J* = 2.9 Hz, *J* = 2.1 Hz; 1H, 5-H), 4.02 [sept, *J* = 6.8 Hz; 1H, $CH(CH_3)_2$], 4.35 (d, *J* = 2.9 Hz; 1H, 2-H), 5.95 (d, *J* = 4.8 Hz; 1H, 1-H), 6.7–8.1 (m; 8H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 20.5 [q; $CH(CH_3)_2$], 20.7 [q; $CH(CH_3)_2$], 40.4 (d; C-6), 44.9 [d; $CH(CH_3)_2$], 51.9 (d; C-2, C-5), 96.5 (d; C-1), 101.7 (s; C-7), 120.0, 120.5, 122.5, 125.9, 127.2, 127.9, 129.2, 129.3 (d; phenyl, *o*-, *m*-, *p*-C), 139.6, 140.2, 142.3, 144.2 (s; phenyl, *ipso*-C), 167.3 (s; C=O).

18e: IR (KBr): 1540 cm^{-1} (N=N), 1735 (C=O), 1610, 1540 (C=C). – UV ($CHCl_3$): λ_{max} (lg ε) = 326 nm (2.28) sh. – ^1H NMR ($CDCl_3$): δ = 0.99 [d, *J* = 6.5 Hz; 3H, $CH(CH_3)_2$], 1.15 [d, *J* = 6.5 Hz; 3H, $CH(CH_3)_2$], 2.85 (dd, *J* = 5.0 Hz, *J* = 1.0 Hz; 1H, 1-H), 3.65 [sept, *J* = 6.5 Hz; 1H, $CH(CH_3)_2$], 3.91 (dd, *J* = 2.9 Hz, *J* = 1.0 Hz; 1H, 5-H), 4.04 (b.d, *J* = 2.9 Hz; 1H, 2-H), 6.00 (b.d, *J* = 5.0 Hz; 1H, 6-H), 6.7–7.9 (m; 8H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 20.4 [q; $CH(CH_3)_2$], 20.6 [q; $CH(CH_3)_2$], 45.2 [d; $CH(CH_3)_2$], 46.3 (d; C-1), 52.2 (d; C-2), 53.4 (d; C-5), 91.2 (d; C-6), 101.8 (s; C-9), 122.8, 126.1, 128.2 (d; phenyl, *o*-, *m*-, *p*-C), 139.8, 144.4 (s; phenyl, *ipso*-C), 164.9 (s; C-4).

$C_{21}H_{19}N_3O$ (329.4) Calcd. C 76.57 H 5.81 N 12.76
Found C 76.93 H 5.85 N 12.15

(1α,2β,5β,6α)-7,7-Diphenyl-3,8,9-triazatricyclo[4.3.0.0^{2,5}]non-8-en-4-one (**20d**) *and (1α,2β,5β,6α)-9,9-Diphenyl-3,7,8-triazatricyclo[4.3.0.0^{2,5}]non-7-en-4-one* (**21d**): **7** (476 mg, 5.00 mmol) and diphenyldiazomethane (**9d**) (1.1 g, 5.7 mmol) are heated to 80°C in 4 ml of dry toluene for 80°C. After cooling the precipitate is filtered and washed with ether. The resulting mixture of **20d** and **21d** (2:1) could not be separated; yield 1.3 g (90%), m.p. 157°C (dec.). – IR (KBr): 1545 cm^{-1} (N=N), 1735 (C=O). – UV (Ethanol): λ_{max} (lg ε) = 333 nm (2.48).

20d: ^{1}H NMR (CDCl$_3$): δ = 2.93 ("bq", *J* = 2.5 Hz; 5-H), 3.63 (dd, *J* = 4.2 Hz, *J* = 2.0 Hz; 6-H), 4.01 (d, *J* = 3.0 Hz; 1H, 2-H), 5.70 (d, *J* = 4.2 Hz; 1H, 1-H), 6.55 (b.s; 1H, NH), 7.0–7.6 (m; 10H, aromatic H). – ^{13}C NMR (CDCl$_3$): δ = 41.2 (d; C-6), 49.5 (d; C-2), 54.7 (d; C-5), 97.0 (d; C-1), 101.9 (s; C-7), 126.2, 126.3, 127.3, 127.6, 127.9, 128.6, 128.7 (d; phenyl, *o*-, *m*-, *p*-C), 139.6, 141.1 (s; phenyl, *ipso*-C), 169.6 (s; C=O). Signals of aromatic C are superimposed by those of the other isomer.

21d: ^{1}H NMR (CDCl$_3$): δ = 3.20 (b.d, *J* = 3.0 Hz; 1H, 2-H), 3.39 (d, *J* = 4.3 Hz; 1H, 1-H), 3.75 (b.t, *J* = 2.5 Hz; 1H, 5-H), 5.80 (dt, *J* = 4.3 Hz, *J* = 1.2 Hz; 1H, 6-H), 6.55 (b.s; 1H, NH), 7.0–7.6 (m; 10H, aromatic H). – ^{13}C NMR (CDCl$_3$): δ = 49.7 (d; C-1), 50.6 (d; C-2), 55.8 (d; C-5), 89.1 (d; C-6), 126.2, 126.3, 127.3, 127.6, 127.9, 128.6, 128.7 (d; phenyl, *o*-, *m*-, *p*-C), 139.6, 141.0 (s; phenyl, *ipso*-C), 167.5 (s; C=O). Signals of aromatic C are superimposed by those of the other isomer.

$C_{18}H_{15}N_3O$ (289.3) Calcd. C 74.72 H 5.23 N 14.52
Found C 74.70 H 5.13 N 14.24

(1α,2β,4β,5α)-6-Isopropyl-6-azatricyclo[3.2.0.0^{2,4}]heptan-7-one (**19a**): From **5** (1.4 g, 10.0 mmol) as described for **11a**, section a). Purification by kugelrohr distillation (70°C/0.1 Torr), colourless liquid; yield 1.3 g (84%). – IR (film): 1730 cm^{-1} (C=O). – ^{1}H NMR (CDCl$_3$): δ = 0.81 (dt, *J* = 5.6 Hz, *J* = 1.4 Hz; 1H, 3-*endo*-H), 1.18 (q, *J* = 5.6 Hz; 1H, 3-*exo*-H), 1.26 [d, *J* = 6.6 Hz; 3H, CH(C*H*$_3$)$_2$], 1.29 [d, *J* = 6.6 Hz; 3H, CH(C*H*$_3$)$_2$], 2.17 (m; 2H, 4-H, 2-H), 3.15 (dd, *J* = 2.5 Hz, *J* = 1.8 Hz; 1H, 1-H), 3.66 (dd, *J* = 3.0 Hz, *J* = 1.8 Hz; 1H, 5-H), 3.91 [sept, *J* = 6.6 Hz; 1H, C*H*(CH$_3$)$_2$]. – ^{13}C NMR (CDCl$_3$): δ = 16.4 („dd", AB*X*; C-3), 18.3 (d; C-2), 21.1 [q; CH(*C*H$_3$)$_2$], 24.4 (d; C-4), 44.4 [d; *C*H(CH$_3$)$_2$], 53.2 (d; C-5), 54.5 (d, C-1), 169.1 (s; C=O). – MS (70 eV): *m/z* (%) = 151 (16, M$^+$), 66 (100, M – iPr – NCO).

$C_9H_{13}NO$ (151.2) Calcd. C 71.49 H 8.67 N 9.26
Found C 70.94 H 8.68 N 9.14

(1α,2β,4β,5α)-6-Isopropyl-3,3-dimethyl-6-azatricyclo[3.2.0.0^{2,4}]heptan-7-one (**19b**): **17b** (500 mg, 2.4 mmol) and benzophenone (60 mg) are irradiated in 500 ml of dry acetone at 0°C for 5 h. After evaporation of the solvent the residue is filtered through silica gel using chloroform. Purification by kugelrohr distillation yields **19b**, 365 mg (84%). – IR (film): 1740 cm^{-1} (C=O). – ^{1}H NMR (CDCl$_3$): δ = 1.01 (s; 3H, CH$_3$), 1.15 (s; 3H, CH$_3$), 1.26 [d, *J* = 6.8 Hz; 6H, CH(C*H*$_3$)$_2$], 1.93 (m; 2H, 2-H, 4-H), 3.16 (m; 1H, 1-H), 3.66 (m; 1H, 5-H), 3.95 [sept, *J* = 6.8 Hz; 1H, C*H*(CH$_3$)$_2$]. – ^{13}C NMR (CDCl$_3$): δ = 14.6 (q; *endo*-CH$_3$), 20.8 [q; CH(*C*H$_3$)$_2$], 21.1 [q; CH(*C*H$_3$)$_2$], 24.1 (q; *exo*-CH$_3$), 28.4 (s; C-3), 30.6 (d; C-2), 36.5 (d; C-4), 44.3 [d; *C*H(CH$_3$)$_2$], 51.3 (d; C-5), 51.7 (d; C-1), 169.0 (s; C=O). – MS (70 eV): *m/z* (%) = 179 (2, M$^+$), 164 (7, M – CH$_3$), 122 (32), 94 (81, M – iPr – NCO).

(1α,2β,4β,5α)-6-Isopropyl-3,3-diphenyl-6-azatricyclo[3.2.0.0^{2,4}]heptan-7-one (**19d**). – a) *Thermolysis of* **17d**: **17d** (500 mg, 1.50 mmol) is thermolyzed at 130°C in 10 ml of xylene for 2 h. After evaporation of the solvent the remaining oil is dissolved in a little ether. The precipitate is filtered and recrystallized from ether/ethanol (2:1); yield 362 mg (79%), m.p. 115–117°C.

b) *Photolysis of* **17d**: **17d** (500 mg, 1.50 mmol) is photolyzed as described for **16d**; yield 340 mg (74%). – IR (KBr): 1715 cm^{-1} (C=O). – ^{1}H NMR (CDCl$_3$): δ = 1.25 [d, *J* = 6.6 Hz; 3H, CH(C*H*$_3$)$_2$], 1.34 [d, *J* = 6.6 Hz; 3H, CH(C*H*$_3$)$_2$], 2.86 (m; 2H, 4-H, 2-H), 3.05 (m; 1H, 1-H), 3.46 (m; 1H, 5-H), 3.97 [sept, *J* = 6.6 Hz; 1H, C*H*(CH$_3$)$_2$], 6.8–7.6 (m; 10H, aromatic H). – ^{13}C NMR (CDCl$_3$): δ = 20.9 [q; CH(*C*H$_3$)$_2$], 21.2 [q; CH(*C*H$_3$)$_2$], 34.2 (d; C-4), 40.1 (d; C-2), 44.4 [d; *C*H(CH$_3$)$_2$], 46.4 (s; C-3), 51.8 (d; C-5), 53.1 (d; C-1), 126.1, 126.2, 127.1, 128.2, 128.6, 130.4 (d; phenyl, *o*-, *m*-, *p*-C), 136.7, 142.8 (s; phenyl, *ipso*-C), 167.9 (s; C=O). – MS (70 eV): *m/z* (%) = 303 (9, M$^+$), 260 (10, M – C$_3$H$_7$), 219 (100), 77 (15, C$_6$H$_5$).

$C_{21}H_{21}NO$ (303.4) Calcd. C 83.13 H 6.98 N 4.62
Found C 83.02 H 6.86 N 4.84

(1α,2β,4β,5α)-3-Fluorenylidene-6-isopropyl-6-azatricyclo[3.2.0.0^{2,4}]heptan-7-one (**19e**): **5** (500 mg, 3.60 mmol) and 9-diazofluorene (**9e**) (730 mg, 3.80 mmol) are heated to 80°C in 8 ml of toluene for 11 h. After cooling the precipitate is filtered and washed with a little ether; yield 660 mg (60%), m.p. 153–154°C (from toluene). – IR (KBr): 1730 cm^{-1} (C=O). – ^{1}H NMR (CDCl$_3$): δ = 1.35 [d, *J* = 6.6 Hz; 6H, CH(C*H*$_3$)$_2$], 3.04 (m; 2H, 4-H, 2-H), 3.95 (m; 1H, 1-H), 4.03 [sept, *J* = 6.6 Hz; 1H, C*H*(CH$_3$)$_2$], 4.42 (m; 1H, 5-H), 6.7–7.9 (m; 8H, aromatic H). – ^{13}C NMR (CDCl$_3$): δ = 20.9 [q; CH(*C*H$_3$)$_2$], 21.1 [q; CH(*C*H$_3$)$_2$], 36.3 (d; C-2), 41.4 (d; C-4), 43.8 (s; C-3), 44.7 [d; *C*H(CH$_3$)$_2$], 52.4 (d; C-5), 53.6 (d; C-1), 118.7, 119.5, 120.3, 124.4, 126.4, 126.7, 126.8, 127.1 (d; aromatic C), 138.1, 142.0, 143.6, 144.2 (s; aromatic C), 167.7 (s; C=O). – MS (70 eV): *m/z* (%) = 301 (6, M$^+$), 216 (100, M – iPr – NCO).

$C_{21}H_{19}NO$ (301.4) Calcd. C 83.69 H 6.36 N 4.65
Found C 83.42 H 6.45 N 4.89

(1α,2β,4β,5α)-6-Methyl-6-azatricyclo[3.2.0.0^{2,4}]heptan-7-one (**22a**): From **6** (1.1 g, 10.0 mmol) as described for **11a**, section a). Purification by kugelrohr distillation (40°C/0.02 Torr), colourless liquid; yield 1.0 g (81%). – IR (film): 1730 cm^{-1} (C=O). – ^{1}H NMR (CDCl$_3$): δ = 0.86 (dt, *J* = 5.5 Hz, *J* = 1.4 Hz; 1H, 3-*endo*-H), 1.24 (q; *J* = 5.5 Hz; 1H, 3-*exo*-H), 2.07 (dtd, *J* = 5.5 Hz, *J* = 3.5 Hz, *J* = 3.5 Hz, *J* = 1.4 Hz; 1H, 2-H), 2.22 (dddd, *J* = 5.5 Hz, *J* = 3.5 Hz, *J* = 2.8 Hz, *J* = 1.4 Hz; 1H, 4-H), 2.91 (s; 3H, CH$_3$), 3.29 (dd, *J* = 2.8 Hz, *J* = 1.9 Hz; 1H, 1-H), 3.67 (dd, *J* = 3.5 Hz, *J* = 1.9 Hz; 1H, 5-H). – ^{13}C NMR (CDCl$_3$): δ = 16.3 ("dd", AB*X*; C-3), 18.5 (d; C-2), 22.3 (d; C-4), 27.6 (q; NCH$_3$), 56.4 (d; C-5, C-1), 170.9 (s; C=O). – MS (70 eV): *m/z* (%) = 123 (27, M$^+$), 94 (76, M – CHO), 66 (100, M – CH$_3$NCO).

C_7H_9NO (123.2) Calcd. C 68.27 H 7.37 N 11.37
Found C 68.32 H 7.65 N 11.40

(1α,2β,4β,5α)-6-Azatricyclo[3.2.0.0^{2,4}]heptan-7-one (**23a**): From **7** (1.0 g, 10.0 mmol) as described for **11a**, section a). Purification by sublimation (70°C/0.02 Torr); yield 0.6 g (51%), m.p. 66°C. – IR (KBr): 1740 cm^{-1} (C=O). – ^{1}H NMR (CDCl$_3$): δ = 0.85 (dt, *J* = 5.5 Hz, *J* = 1.3 Hz; 1H, 3-*endo*-H), 1.23 (q, *J* = 5.5 Hz; 1H, 3-*exo*-H), 2.11 (m; 2H, 4-H, 2-H), 3.35 (dd, *J* = 3.3 Hz, *J* = 1.8 Hz; 1H, 1-H), 3.69 (dd, *J* = 4.5 Hz, *J* = 1.8 Hz; 1H, 5-H), 7.05 (b.s; 1H, NH). – ^{13}C NMR (CDCl$_3$): δ = 17.2 (dd; C-3), 17.9 (d; C-2), 25.0 (d; C-4), 51.7 (d; C-5), 57.5 (d; C-1), 172.0 (s; C=O). – MS (70 eV): *m/z* (%) = 109 (23, M$^+$), 80 (81, M$^+$ – CHO), 66 (100, M – HNCO), 53 (67, HNCO).

C_6H_7NO (109.1) Calcd. C 66.04 H 6.47 N 12.83
Found C 66.16 H 6.44 N 12.76

(1α,2β,5β,6α)-3-Oxa-8,9-diazatricyclo[4.3.0.0^{2,5}]non-8-en-4-one (**25a**) *and (1α,2β,5β,6α)-3-Oxa-7,8-diazatricyclo[4.3.0.0^{2,5}]non-7-*

en-4-one (**26a**): A solution of diazomethane (ca. 47 mmol) in 100 ml of ether, dried over KOH, is added dropwise to an ice-cooled solution of **8** (550 mg, 7.13 mmol) in 50 ml of ether to the exclusion of air and light. After 2 d at 0°C the solvent is evaporated at 0°C in vacuo. The solid is washed with a little ether; yield 450 mg (50%), m.p. 77°C (mixture of 75% **25a** and 25% **26a**). – IR (KBr): 1800–1850 cm^{-1} (C=O), 1540 (N=N). – UV ($CHCl_3$): λ_{max} (lg ε) = 322 nm (2.41). – ^1H NMR (60 MHz, $CDCl_3$, mixture of **25a** and **26a**), **25a**: δ = 3.02 (m; 1H, 6-H), 3.52 (m; 1H, 5-H), 4.65 (m; 2H, 7-H), 4.83 (d, *J* = 2 Hz; 1H, 2-H), 5.62 (m; 1H, 1-H). – **26a**: δ = 4.02 (b.d, *J* = 2 Hz; 1H, 5-H), 4.51 (t, *J* = 2 Hz; 1H, 2-H), further resonances superimposed by **25a**. – ^{13}C NMR ($CDCl_3$, mixture of **25a** and **26a**), **25a**: δ = 30.7 (d; C-6), 58.7 (d; C-5), 72.0 (d; C-2), 81.9 (t; C-7), 94.5 (d; C-1), 167.8 (s; C-4). – **26a**: δ = 38.9 (d; C-1), 59.1 (d; C-5), 74.9 (d; C-2), 79.2 (t; C-9), 86.3 (d; C-6), 166.8 (s; C-4). – MS (70 eV): *m/z* (%) = 138 (2, M^+), 110 (2, M – N_2, CO), 81 (16, M – N_2 – COH), 66 (56, M – N_2 – CO_2).

(1α,2β,5β,6α)-7,7-Dimethyl-3-oxa-8,9-diazatricyclo[4.3.0.0^{2,5}]non-8-en-4-one (**25b**) *and (1α,2β,5β,6α)-9,9-Dimethyl-3-oxa-7,8-diazatricyclo[4.3.0.0^{2,5}]non-7-en-4-one* (**26b**): A solution of 2-diazopropane (ca. 30 mmol) in ether is added dropwise at 0°C to a solution of **8** (620 mg, 8.10 mmol) in 50 ml of ether. The mixture is kept at –10°C for about 12 h and then stirred at 20°C for 2 d. After evaporation of the solvent at 0°C the remaining solid is washed with ether; yield 550 mg (41%), m.p. 83°C (mixture of 85% **25b** and 15% **26b**). – IR (KBr): 1790–1860 cm^{-1} (C=O), 1520 (N=N). – UV ($CHCl_3$): λ_{max} (lg ε) = 325 nm (2.42). – ^1H NMR (60 MHz, $CDCl_3$, mixture of **25b** and **26b**), **25b**: δ = 1.25 (s; 3H, *exo*-CH_3), 1.60 (s; 3H, *endo*-CH_3), 2.80 (dd, *J* = 5 Hz, *J* = 2 Hz; 1H, 6-H), 3.78 (t, *J* = 2 Hz; 1H, 5-H), 4.93 (d, *J* = 2 Hz; 1H, 2-H), 5.67 (d, *J* = 5 Hz; 1H, 1-H). – **26b**: δ = 1.25 (s; 3H, *exo*-CH_3), 1.60 (s; 3H, *endo*-CH_3), 2.70 (d, *J* = 5 Hz; 1H, 1-H), 4.08 (b.d, *J* = 2 Hz; 1H, 5-H), 4.77 (t, *J* = 2 Hz; 1H, 2-H), 5.6 (superimposed by 1-H signal of **25b**). – ^{13}C NMR ($CDCl_3$, mixture of **25b** and **26b**), **25b**: δ = 20.8 (q; *endo*-CH_3), 26.4 (q; *exo*-CH_3), 41.3 (d; C-6), 54.0 (d; C-5), 70.5 (d; C-2), 90.0 (s; C-7), 94.9 (d; C-1), 168.5 (s; C-4). – **26b**: δ = 20.8 (q; *endo*-CH_3), 27.0 (q; *exo*-CH_3), 49.1 (d; C-1), 57.2 (d; C-5), 72.0 (d; C-2), 86.8 (d; C-6), 90.3 (s; C-9), 166.7 (s; C-4). – MS (70 eV): *m/z* (%) = 166 (2, M^+), 138 (6, M – N_2, CO), 110 (30, M – N_2 – CO).

$C_8H_{10}N_2O_2$ (166.2) Calcd. C 57.82 H 6.07 N 16.86
Found C 57.80 H 6.01 N 16.88

(1α,2β,5β,6α)-7,7-Diphenyl-3-oxa-8,9-diazatricyclo[4.3.0.0^{2,5}]non-8-en-4-one (**25d**) *and (1α,2β,5β,6α)-9,9-Diphenyl-3-oxa-7,8-diazatricyclo[4.3.0.0^{2,5}]non-7-en-4-one* (**26d**): Diphenyldiazomethane (1.37 g; 7.70 mmol) is added at 0°C to a solution of **8** (590 mg, 7.70 mmol) in 100 ml of ether. The mixture is stirred at room temperature for 12 h. The white solid is filtered; yield 610 mg (30%), m.p. 151°C (mixture of 85% **25d** and 15% **26d**). – IR (KBr): 1800–1850 cm^{-1} (C=O), 1540 (N=N). – UV ($CHCl_3$): λ_{max} (lg ε) = 332 nm (2.41). – ^1H NMR (60 MHz, $CDCl_3$, mixture of **25d** and **26d**), **25d**: δ = 3.25 (t, *J* = 2 Hz; 1H, 5-H), 3.82 (dd, *J* = 4 Hz, *J* = 2 Hz; 1H, 6-H), 4.94 (d, *J* = 2 Hz; 1H, 2-H), 5.95 (d, *J* = 4 Hz; 1H, 1-H), 6.90–7.50 (m; 10H, aromatic H). – **26d**: δ = 3.71 (d, *J* = 4 Hz; 1H, 1-H), 4.15 (m; 2H, 2-H, 5-H), 5.9 (6-H, superimposed by 1-H signal of **25d**), aromatic H superimposed by **25d**. – ^{13}C NMR ($CDCl_3$, mixture of **25d** and **26d**), **25d**: δ = 41.9 (d; C-6), 55.6 (d; C-5), 69.8 (d; C-2), 96.6 (d; C-1), 103.0 (s; C-7), 126.2, 127.4, (d; phenyl, *o*-C), 127.9, 128.2 (d; phenyl, *p*-C), 128.7, 128.9 (d; phenyl, *m*-C), 139.0, 140.0 (s; phenyl, *ipso*-C), 168.0 (s; C-4). – **26d**: δ = 49.1 (d; C-1), 56.8 (d; C-5), 73.1 (d; C-2), 88.2 (d; C-6), 103.9 (s; C-9), 168.0 (s; C-4), aromatic C superimposed by signals of **25d**. – MS (70 eV): *m/z* (%) = 290 (1, M^+), 262 (4, M – N_2, CO), 234 (20, M – N_2–CO).

$C_{18}H_{14}N_2O_2$ (290.3) Calcd. C 74.47 H 4.86 N 9.65
Found C 74.45 H 4.85 N 9.73

(1α,2β,5β,6α)-7-Fluorenylidene-3-oxa-8,9-diazatricyclo[4.3.0.0^{2,5}]non-8-en-4-one (**25e**) *and (1α,2β,5β,6α)-9-Fluorenylidene-3-oxa-7,8-diazatricyclo[4.3.0.0^{2,5}]non-7-en-4-one* (**26e**): Diazofluorene (1.24 g, 6.46 mmol) in 10 ml of dry ether is added dropwise at 0°C to a solution of **8** (620 mg, 6.46 mmol) in 50 ml of ether. The mixture is kept at 0°C for 2 weeks. The solid is filtered; yield 930 mg (50%), m.p. 128°C (mixture of 70% **25e** and 30% **26e**). – IR (KBr): 1800–1850 cm^{-1} (C=O), 1520 (N=N). – UV ($CHCl_3$): λ_{max} (lg ε) = 328 nm (2.31) sh, 268 (4.21). – ^1H NMR (60 MHz, mixture of **25e** and **26e**, $CDCl_3$), **25e**: δ = 3.27 (d, *J* = 5 Hz; 1H, 6-H), 4.23 (t, *J* = 2 Hz; 1H, 5-H), 5.17 (d, *J* = 2 Hz; 1H, 2-H), 6.08 (d, *J* = 5 Hz; 1H, 1-H), 6.50–7.80 (m; 8H, aromatic H). – **26e**: δ = 3.15 (d, *J* = 3 Hz; 1H, 1-H), 4.42 (d, *J* = 2 Hz; 1H, 5-H), 5.03 (t, *J* = 2 Hz; 1H, 2-H), 6.00 (d, *J* = 3 Hz; 1H, 6-H), 6.50–7.80 (m; 8H, aromatic H). – ^{13}C NMR ($CDCl_3$, mixture of **25e** and **26e**), **25e**: δ = 39.8 (dt; C-6), 56.1 (ddd; C-5), 70.6 (dddd; C-2), 91.1 (ddd; C-1), 102.3 (s; C-7), 120.2, 120.9, 122.6, 125.6, 127.5, 128.3, 129.6, 129.7 (d; aromatic C), 139.3, 139.6, 142.4, 143.5 (s; aromatic C), 167.7 (s; C-4). – **26e**: δ = 39.8 (d; C-1), 56.1 (ddd; C-5), 73.3 (dddd; C-2), 89.4 (dt; C-6), 102.6 (s; C-9), 166.1 (s; C-4), aromatic C superimposed by signals of **25e**. – MS (70 eV): *m/z* (%) = 288 (1, M^+), 260 (25, M – N_2, CO), 232 (42, M – N_2 – CO), 231 (100, M – N_2 – COH), 216 (92, M – N_2 – CO_2).

$C_{18}H_{12}N_2O_2$ (288.3) Calcd. C 74.99 H 4.20 N 9.72
Found C 74.59 H 4.20 N 9.78

(1α,2β,4β,5α)-6-Oxatricyclo[3.2.0.0^{2,4}]heptan-7-one (**27a**): a) From **8** (500 mg, 6.48 mmol) in 50 ml ether as described for **11a**, section a). After evaporation of the solvent the oily residue is distilled; yield 190 mg (30%), b.p. 36°C/0.01 Torr.

b) From a mixture of **25a** und **26a** (100 mg, 0.72 mmol) as described for **11a**, section b). After evaporation of the solvent a colourless oil is obtained; yield 70 mg (88%). – IR (film): 1800–1845 cm^{-1} (C=O). – ^1H NMR (60 MHz, $CDCl_3$): δ = 0.97 (td, *J* = 1 Hz, *J* = 5 Hz; 1H, 3-*endo*-H), 1.35 (q, *J* = 5 Hz; 1H, 3-*exo*-H), 2.38 (m; 2H, 2-H, 4-H), 3.67 (b.p. *J* = 4 Hz; 1H, 1-H), 4.17 (dd, *J* = 4 Hz, *J* = 1 Hz; 1H, 5-H). – ^{13}C NMR ($CDCl_3$): δ = 16.3 (dd; C-3), 18.1 (d; C-2), 23.4 (d; C-4), 57.9 (d; C-1), 73.6 (d; C-5), 169.6 (s; C-7). – MS (70 eV): *m/z* (%) = 66 (100, N – CO_2).

(1α,2β,4β,5α)-3,3-Diphenyl-6-oxatricyclo[3.2.0.0^{2,4}]heptan-7-one (**27d**): a) The mixture of **25d** and **26d** (500 mg, 1.80 mmol) is dissolved in 20 ml of dry toluene and refluxed under nitrogen for 12 h. After evaporation of the solvent 1 ml of ether is added and the oily residue crystallizes; yield 310 mg (69%), m.p. 122°C.

b) The mixture of **25d** and **26d** (100 mg, 0.34 mmol) is irradiated as described for **11a**, section b). After evaporation of the solvent the oily residue crystallizes on addition of 1 ml of ether; yield 80 mg (90%), m.p. 122°C. – IR (KBr): 1780–1840 cm^{-1} (C=O). – ^1H NMR (60 MHz, $CDCl_3$): δ = 3.00 (m; 2H, 2-H, 4-H), 3.45 (m; 1H, 1-H), 4.40 (b.d, *J* = 3.5 Hz; 1H, 5-H), 6.83–7.42 (m; 10H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 33.0 (d; C-2), 38.5 (d; C-4), 47.0 (s; C-3), 56.6 (d; C-1), 72.1 (d; C-5), 126.7, 127.6 (d; phenyl, *p*-C), 128.4, 128.9 (d; phenyl, *m*-C), 126.2, 130.1 (d; phenyl, *o*-C), 135.8, 141.4 (s; phenyl, *ipso*-C), 168.9 (s; C-7). – MS (70 eV): *m/z* (%) = 262 (5, M^+), 234 (16, M – CO).

$C_{18}H_{14}O_2$ (262.3) Calcd. C 82.42 H 5.38
Found C 82.42 H 5.43

(1α,2β,4β,5α)-3-Fluorenylidene-6-oxatricyclo[3.2.0.0^{2,4}*]heptan-7-one* (**27e**): The mixture of **25e** and **26e** (400 mg, 1.38 mmol) is heated in 50 ml of dry toluene under nitrogen to 80°C for 3 h. After removal of the solvent in vacuo a red oil is obtained which crystallizes on addition of 1 ml of ether; yield 240 mg (66%), m.p. 225°C (dec.). – IR (KBr): 1790–1860 cm^{-1} (C=O). – ^{1}H NMR (60 MHz, C_6H_6): δ = 2.37 (dd, J = 3.5 Hz, J = 3.5 Hz; 1H, 2-H), 2.53 (dd, J = 2.5 Hz, J = 1 Hz; 1H, 4-H), 3.42 (dd; J = 2.5 Hz, J = 1 Hz; 1H, 1-H), 4.43 (dd, J = 3.5 Hz, J = 1 Hz; 1H, 5-H), 6.00–7.63 (m; 8H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 34.8 (d"dt"; C-2), 39.5 (dd"t"; C-4), 44.1 (s; C-3), 57.1 (ddd; C-1), 72.6 (db.d; C-5), 118.7, 119.6, 120.5, 123.6, 126.7, 127.3 (d; aromatic C), 138.3, 142.0, 142.3, 142.9 (s; aromatic C), 168.4 (s; C-7). – MS (70 eV): m/z (%) = 260 (100, M$^+$), 232 (35, M – CO), 231 (90, M – COH).

$C_{18}H_{12}O_2$ (260.3) Calcd. C 83.06 H 4.65
Found C 82.94 H 4.61

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3: 19839-41-9 / **4**: 33707-39-0 / **5**: 37657-09-3 / **6**: 31638-95-6 / **7**: 4432-69-3 / **8**: 22980-23-0 / **9a**: 334-88-3 / **9b**: 2684-60-8 / **9c**: 22293-10-3 / **9d**: 883-40-9 / **9e**: 832-80-4 / **10a**: 105367-52-0 / **10b**: 105367-55-3 / **10c**: 105252-63-9 / **10c'**: 105367-56-4 / **10d**: 105367-57-5 / **10e**: 105367-58-6: **11a**: 105367-53-1 / **11b**: 105367-59-7 / **11c**: 105252-64-0 / **11d**: 105367-60-0 / **11e**: 105367-61-1 / **13f**: 105252-50-4 / **13g**: 105280-87-3 / **14b**: 105252-51-5 / **14d**: 105252-65-1 / **14e**: 105252-67-3 / **15b**: 105252-52-6 / **15d**: 105252-66-2 / **15e**: 105252-68-4 / **16a**: 105367-54-2 / **16b**: 105252-69-5 / **16d**: 105252-70-8 / **16e**: 105252-71-9 / **17b**: 105252-53-7 / **17d**: 105252-72-0 / **17e**: 105252-73-1 / **18e**: 105252-54-8 / **19a**: 105252-55-9 / **19b**: 105252-74-2 / **19d**: 105252-75-3 / **19e**: 105280-88-4 / **20d**: 105252-56-0 / **21d**: 105252-57-1 / **22a**: 105252-58-2 / **23a**: 105252-59-3 / **25a**: 105252-60-6 / **25b**: 105252-76-4 / **25d**: 105252-78-6 / **25e**: 105252-80-0 / **26a**: 105252-61-7 / **26b**: 105252-77-5 / **26d**: 105252-79-7 / **26e**: 105252-81-1 / **27a**: 105252-62-8 / **27d**: 105280-89-5 / **27e**: 105252-82-2 / benzohydroximoyl chloride: 698-16-8 / benzohydrazonoyl chloride: 15424-14-3

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