Intramolecular [4+2] Cycloaddition of Furfurylsubstituted Homoallylamines to Allylhalides, Acryloyl chloride and Maleic anhydride

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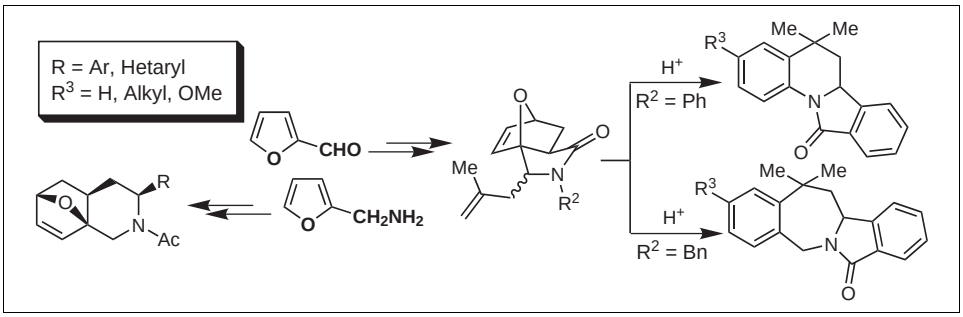

Acylation of 4-(furyl-2)-4-*R*-aminobut-1-enes and 4-*R*-4-furfurylaminobut-1-enes with maleic anhydride, acryloyl chloride or allylhalides provided 3-aza-10-oxatricyclo[5.2.1.0^{1,5}]decenes. The tricycles are formed *via* an initial amide formation followed by a stereoselective *exo*-IMDAF (Intramolecular Diels-Alder of Furan). In case of competing cycloaddition (for compounds possessing two furan or two dienophilic moieties) the most substituted fivemembered cycle is preferably annulated. Refluxing of 4-*R*-4-furfurylaminobut-1-enes in acetic anhydride led to *exo*-3-aza-11-oxatricyclo[6.2.1.0^{1,6}]undecenes with the pseudoequatorial substituent *R*-4. Treatment of 3-aza-10-oxatricyclo[5.2.1.0^{1,5}]decenes with PPA at 90–110 °C promoted cyclic ether opening, aromatization and intramolecular cyclization reactions sequence to give the corresponding tetracyclic compounds – tetrahydroisoindolo[2,1-*a*]quinolines and tetrahydroisoindolo[2,1-*b*][2]benzazepines in good yields. Unusual products of *ipso*-substitution in aromatic ring were obtained on cyclization of *N*-*p*-*R*-substituted 2-allyl-4-oxo-3-aza-10-oxatricyclo[5.2.1.0^{1,5}]dec-8-enes.

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Introduction.

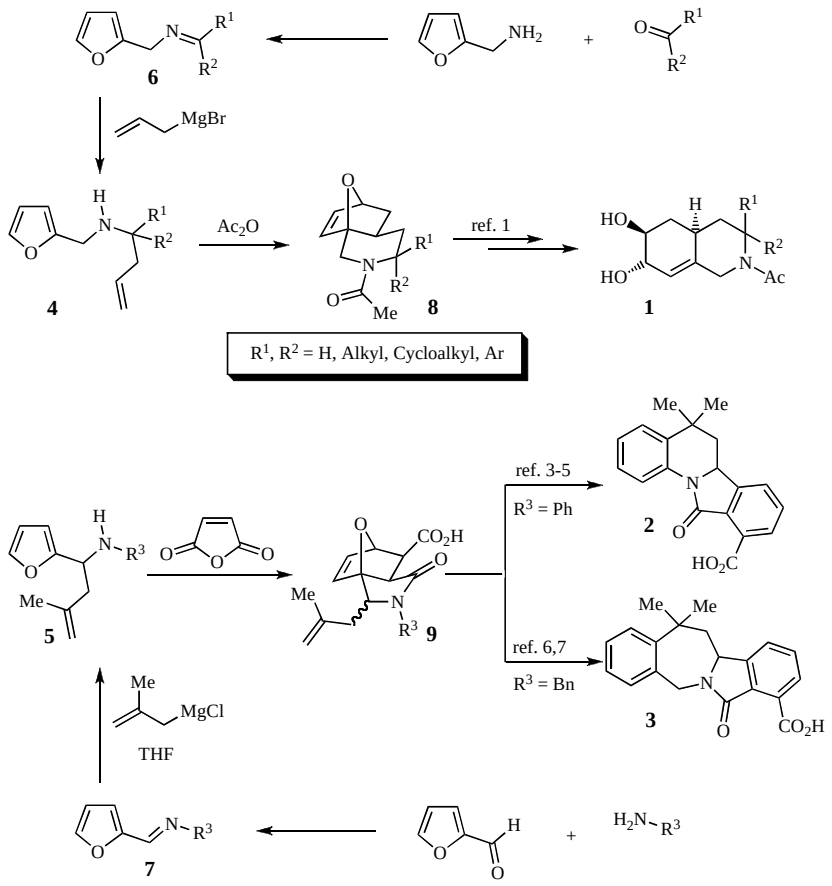
Recently we have proposed several effective synthetic approaches to the potential biologically active compounds such as hydrogenated hydroxyisoquinolines **1** [1,2], isoindolo[2,1-*a*]quinoline- **2** [3-5] and isoindolo[2,1-*b*]benzazepinecarboxylic acids **3** [6,7] (Scheme 1) using furylsubstituted homoallylamines **4**, **5** as starting materials. Amines **4** and **5** were obtained from easily available imines **6** and **7** correspondingly. The intramolecular furan Diels–Alder reaction (IMDAF) [8] between the alkenyl fragment and the furan core in the amines **4** or **5** was the key step of the transformations mentioned above.

The present study had two major aims. First it was interesting to investigate the competing intramolecular cycloaddition processes in the case of amines **4** and **5** possessing several potential diene and/or dienophilic centers. The second aim was to synthesize a series of carboxyl non substituted isoindolo[2,1-*a*]quinolines **2** (-benzazepines **3**) as their further functionalization could allow us to find some perspective ways for the construction of the patented pharmacophores analogues [9-14].

Results and Discussion.

We have chosen the reaction sequence shown in Scheme 1 to solve these problems basing on the array of butenylamines **10a–f**, **11a–c**, and **12a–c** as starting materials. It is worth noting that the homoallylamines **10a,f** [2], **11a–c** [3], and **12a–c** [6,7] were obtained and characterized by our group earlier, and the aryl- **10b**, hetaryl substituted amines **10c–e** were first synthesized. Amines **10–12** (Fig. 1) were obtained in 71–86% yield except the pyridylsubstituted compound **10e** moderate yield of which could be explained by the low solubility of

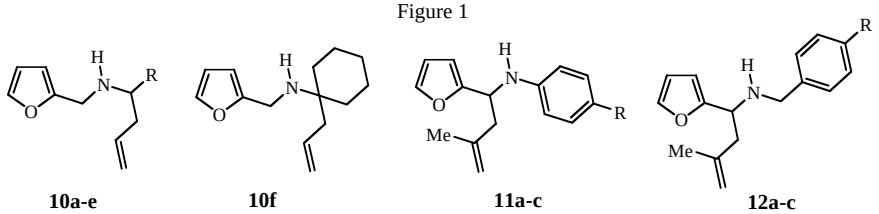
Scheme 1



the intermediate imine-allylmagnesium bromide complex both in ether and THF.

As we have shown earlier [3], cycloaddition of maleic anhydride to 4-furyl-4-aminobutenes **5** was preceded by the preliminary *N*-acylation leading to in the analogous manner through the formation of the intermediate *N*-acryloyl derivative **13a** (R=H). Since the intermediates **13** possessed two dienophilic fragments (allyl and *N*-acryloyl) in their molecules two competing ways of the [4+2] intra-

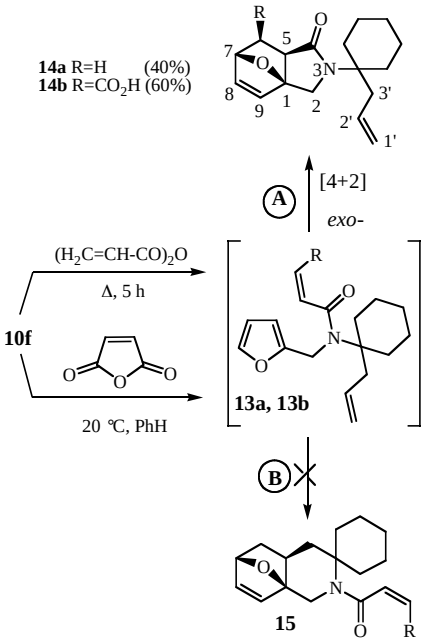
Figure 1



Compound	**10a**	**10b**	**10c**	**10d**	**10e**	**10f**	**11a**	**11b**	**11c**	**12a**	**12b**	**12c**
R	Ph	C_6H_4OMe-p	Thienyl-2	Furyl-2	Py-3		H	Me	OMe	H	Me	OMe
Yield, %	72	78	82	78	50	84	76	75	86	83	83	71

the formation of the intermediate maleinamide **13b** (R=CO_2H, Scheme 2). Obviously the interaction between acrylic anhydride and amine **10f** proceeded molecular cycloaddition were theoretically possible: **A** (isoindole formation) and **B** (formation of isoquinolines).

Scheme 2

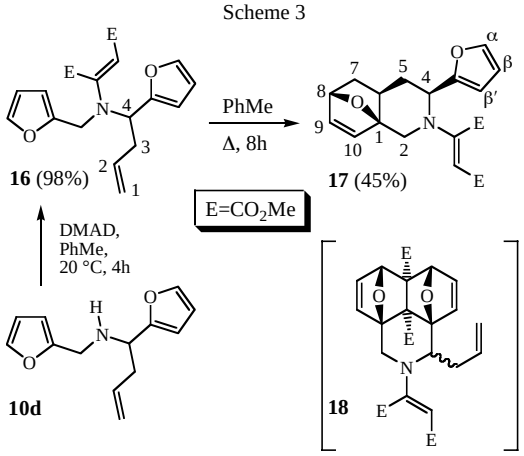


Actually the way **A** resulting in the formation of *N*-cyclohexyl substituted *exo*-oxoepoxyisoindolones **14** realized that was established experimentally. Reaction proceeded regio- and stereospecifically giving corresponding *exo*-oxoepoxyisoindolone **14a** and *exo*-isoindolonecarboxylic acid **14b** in satisfactory yields. It's worth noting that six-membered cycle annulation (products of type **15** formation) is commonly preferable compared to the five-membered cycle formation (products of type **14** formation). We explain our experimental data in terms of higher reactivity of the electron deficient olefin fragment (*viz* R-CH=CH→CO) in IMDAF reactions compared to the electron rich allylic one.

The structure of compounds **14a,b** was established relying on the ^{1}H NMR spectroscopic data (see the Experimental section). In particular, the H atoms of the olefin fragment CH_2=CH- in these compounds gave the signals at δ 5.02–5.04 (H-1′) and 5.81 (H-2′) ppm. The *exo*-configuration of the Diels-Alder adducts **14** was confirmed by comparing the values of spin-spin coupling constants of oxabicyclo[2.2.1]heptene moiety H-atoms with the literature data [15-17]. Thus $J_{7,6endo}$ value in **14b** was close to zero which fact confirmed the *exo*-orientation of CO_2H-group and 5-amide substituent. In case of *exo*-orientation 6-H atom would give a signal with $J_{6exo,7}$ greater than 3 Hz (usually 4.0–4.5 Hz) [15]. The spatial structure of the adduct **14a** was established in the same manner.

Interaction between difuryl derivative **10d** and dimethyl acetylenedicarboxylate (DMAD) in mild reaction conditions proceeded as Michael addition of secondary amine to a triple bond (Scheme 3) resulting in the formation of *cis-N*-dimethoxycarbonylvinylsubstituted homoallylamine **16** in a quantitative yield. *Cis*-orientation of the methoxycarbonyl fragments (E) was established by comparing with the literature data [18,19].

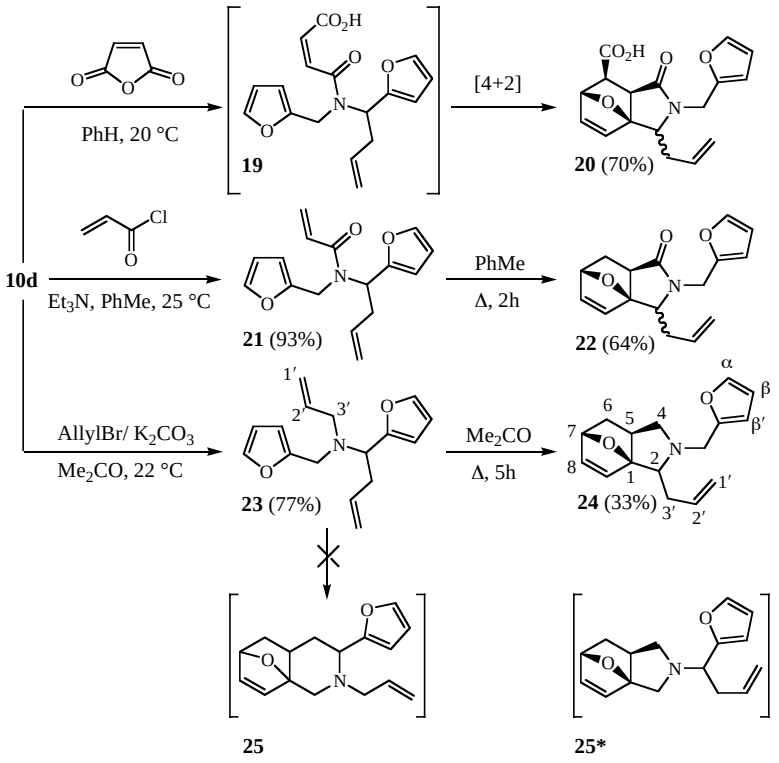
Scheme 3



While the thermal cyclization of homoallylamine **10d** was not observed even after prolonged boiling in xylene, the intramolecular Diels-Alder reaction of its *N*-vinyl-substituted analogue **16** proceeded smoothly in boiling toluene giving *exo*-4-furylsubstituted isoquinoline **17**. Its stereochemistry was established based on the ^{1}H NMR data. Thus the *exo*-orientation of C_5–C_6 bond in the oxabicyclo[2.2.1]heptene fragment was determined similarly to the compounds **8** [2], and the pseudooequatorial position of the 4-furyl substituent (*cis-* in relation to the *oxa*-bridge) was confirmed by considering $J_{4,5ax}$=11.0 and $J_{4,5eqv}$=7.0 Hz values. According to these values as well as by analogy with the 4-thienyl-substituted tricycle **26c** (as indicated below, Fig. 2) the piperidine moiety in the molecule of **17** has the "slightly twisted tub" conformation. Obviously the easiness of thermal [4+2] cycloaddition in case of alkene **16** was determined by the flattening of the amide fragment owing to the conjugation of the unshared electron pair of the nitrogen atom with the multiple bond, and as a consequence the approach of the furan and allylic substituents in the IMDAF intermediate.

It should be emphasized that the reaction of amine **10d** with double molar excess of DMAD as well as boiling of enamine **16** with the equimolar amount of DMAD in toluene did not lead to the formation of the prospective pincer-addition product **18** [20-22] (Scheme 3). In each case a mixture of DMAD addition products to both furan rings in bisfuran **16** was isolated from a multicomponent reaction mixture in a low combined yield along with a small amount of isoquinoline **17**. Their spatial structure was not studied in detail.

Scheme 4



The interaction between homoallylamine **10d** and maleic anhydride proceeded smoothly as a regio- and stereospecific process (Scheme 4). Initially formed maleinamide **19** (was not isolated) cyclized instantly to *exo*-adduct **20**. The latter was isolated as a mixture of two geometrical isomers based on the orientation of the allyl group in relation to the 1,7-oxabridge. The ratio of isomers was ~1:6 according to the ^{1}H NMR spectroscopic data (Scheme 4).

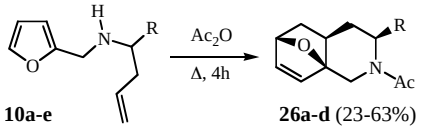
Interaction between acryloyl chloride and amine **10d** in the presence of NEt_3 brought to the formation of *N*-acryloylamide **21** in almost a quantitative yield. The intramolecular cyclization of diene **21** into the epoxyisoindolone **22** began as early as at 25–30 °C that brought to the contamination of obtained amide **21** with about 7% of adduct **22** according to the ^{1}H NMR data. Heating of acryloylamide **21** in toluene led to the rapid formation of *exo*-adduct **22**. *Exo*-epoxyisoindolone **22** was isolated as a mixture of two diastereoisomers in a ratio of ~1:2 (similarly to the isomers **20**).

Geometrical isomers of the isoindolones **20** and **22** were not separated. Compound **20** was isolated as white powder almost insoluble in chloroform and acetone. In the case of 3-aza-10-oxabicyclo[5.2.1.0^{1,5}]-decene **22** isolated from the reaction mixture as a light-yellow oil, separation of the geometrical isomers appeared to be impossible owing to the equal retention factor of these isomers.

Alkylation of amine **10d** with allylbromide in the presence of potash proceeded smoothly giving diallylderivative **23** in good yield (Scheme 4). Heating of furfurylamine **23** in acetone was accompanied by considerable resinification of the reaction mixture (we suppose it took place owing to the side intermolecular [4+2] cycloaddition reactions). According to the ^{1}H NMR spectrum of the reaction mixture product **24** was also formed as a mixture of geometrical isomers but only one of them was isolated as an individual substance after the column chromatography in 33% yield. It was not possible to establish the orientation of allyl radical in relation to the oxabridge. It is interesting to note that in the latter case we observed no traces of the prospective alternative IMDAF products such as the isomeric epoxyisoindole **25*** and isoquinoline **25** in the reaction mixture. This fact means that when the competing intramolecular [4+2] cycloaddition is possible the fivemembered rings **24** would preferably be formed compared to the sixmembered ones **25** (the entropic factor). The absence of the isomer **25*** among the IMDAF products is the example of a well known *qem*-dialkyl effect (angle compression Thorpe-Ingold effect) or of the "reactive rotamer effect" proposed by E. Jung, both phenomena being principally the same [23-25].

Unsymmetrically substituted butenylamines **10a–d** cyclized in boiling acetic anhydride giving *exo*-adducts **26a–d** in satisfactory yields (Scheme 5). The only

Scheme 5



10a-e **26a-d** (23-63%)

a R=Ph; **b** R=C_6H_4OMe-*p*; **c** R=Thienyl-2; **d** R=Furyl-2; **e** R=Py-3

exception was the impossibility to produce 4-(3-pyridyl)-substituted tricycle **26e** (condensed derivative of anabasine, R=Py-3) because of the resinification of starting amine **10e** in the reaction conditions. The ^{1}H NMR spectra of the obtained *exo*-3-aza-11-oxatricyclo-[6.2.1.0^{1,6}]undec-9-enes **26** contained characteristic signals of the three spin-linked bicyclic H-atoms: H-10 (d, δ 5.99–6.36 ppm), H-9 (dd, 6.26–6.42 ppm), and H-8 (dd, 4.85–4.94 ppm) with $J_{8,9}$=0.9–1.8 and $J_{9,10}$=5.8–6.0 Hz.

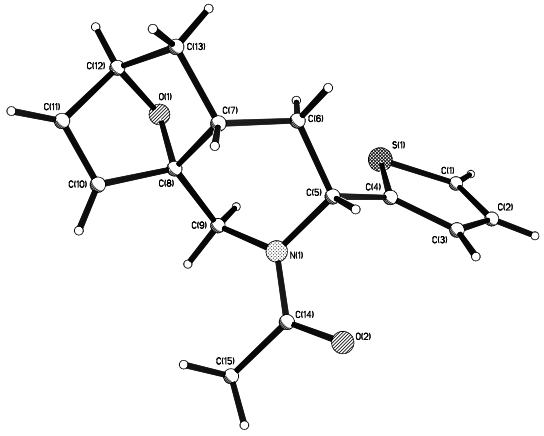


Figure 2. The X-ray crystal structures of isoquinoline **26c**

But the widening of H-2 and H-4 signals (because of the slow rotation of the acetyl fragment around the amide bond) did not allow to determine the orientation of the C-4 substituent using the NMR spectral data. To solve this problem we generated a monocrystal of the tricycle **26c** and its molecular structure was unambiguously elucidated by X-ray data (Fig. 2).

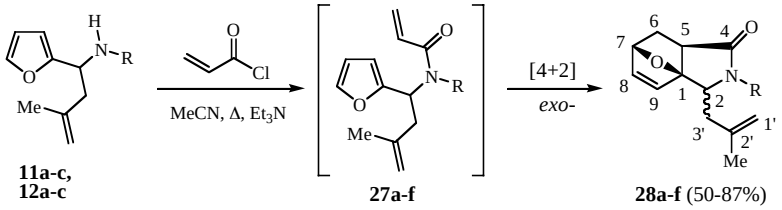
The X-ray analysis [26] of 3-acetyl-4-(2-thienyl)-3-aza-11-oxatricyclo[6.2.1.0^{1,6}]undec-9-ene **26c** showed that compound $C_{15}H_{17}NO_2S$ crystallized in monoclinic lattice, the space group $P2_1/n$. Oxabicyclo[2.2.1]heptene moiety of the **26c** molecule was *exo*-annulated at C(7)-C(8) bond with piperidine one (Fig. 2, crystallographic numeration used). Piperidine cycle had "twist-boat" conformation proved by the values of torsion angles between the planes N(1)C(5)C(6)C(7), C(5)C(6)C(7)C(8), C(6)C(7)C(8)C(9), C(7)C(8)C(9)N(1), C(8)C(9)N(1)C(5), and C(9)N(1)C(5)C(6) equal to 32.1, –63.8, 32.7, 25.9, –62.3, and 31.8° correspondingly. *N*(1)-Acetyl substituent in the piperidine ring occupied the "pseudoaxial" position, and C(5)-thienyl one – "pseudoequatorial". H-Atom at C(7) was "pseudoaxial" oriented in piperidine cycle (*trans*- according to thienyl cycle), and it was *endo*-oriented in oxabicyclo[2.2.1]heptene fragment.

Compounds **26a,b,d** were proposed to have the same conformation of the piperidine fragment with "pseudoequatorial" orientation of *R*-substituent at C-4 on the basis of the data mentioned above above (these products have almost identical ^{1}H NMR data).

Noncarboxyl substituted isoindolo[2,1-*a*]quinolines **2** and isoindolo[2,1-*b*][2]benzazepines **3** were synthesized basing on the same starting material – furylsubstituted homoallylamines **5** (Scheme 1). Acylation of homoallylamines **11a–c** and **12a–c** with acryloyl chloride was carried out in boiling acetonitrile in the presence of excess triethylamine (Scheme 6). Resulting *N*-phenyl(benzyl)-3-aza-4-oxo-10-oxatricyclo [5.2.1.0^{1,5}]dec-8-enes **28a–f** were isolated in satisfactory to high yields. The use of toluene as the reaction medium in case of **11c** results in lowering tricyclic product **28c** yield: 48% compared to 66% in acetonitrile.

Initial acylation of furfurylamines **11**, **12** with acryloyl chloride led to the intermediate amides **27a–f**, which underwent further [4+2] cycloaddition to give cycloadducts **28**. That was confirmed using amine **11a** as a model compound. In this case two individual products **27a** and **28a** were isolated by column chromatography of the reaction mixture in the ratio of 2:1 in 75% overall yield. Their structure was confirmed based on the array of spectroscopic data. Heating of acryloylamide **27a** at 100 °C led to the tricyclic product **28a** formation.

Scheme 6



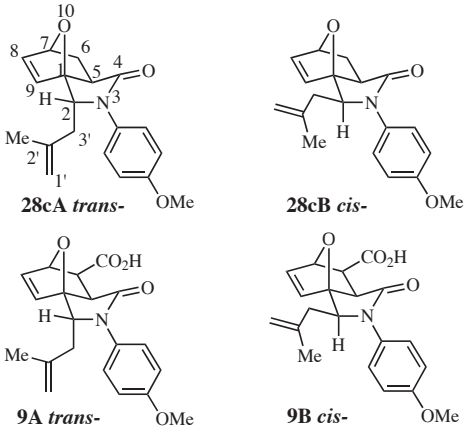
11a-c, 12a-c **27a-f** **28a-f** (50-87%)

Compound	**28a**	**28b**	**28c**	**28d**	**28e**	**28f**
R	Ph	C_6H_4Me-*p*	C_6H_4OMe-*p*	Bn	$CH_2C_6H_4Me$-*p*	$CH_2C_6H_4OMe$-*p*
Yield, %	50	64	66	86	68	87

The cycloaddition reaction proceeded stereospecifically and only the *exo*-adducts **28** were formed according to the ^{1}H NMR spectra of crude reaction mixtures. The structure of adducts **28** was established based on H-5, H-6 and H-7 oxabicycloheptene protons *J* values compared to the literature data [15,27-31] as well as by analogy with compounds **14a**, **20**, **22**.

Exo-3-aza-10-oxatricyclo[5.2.1.0^{1,5}]decenes **28** were isolated as the mixtures of geometric isomers **A** and **B** (Figure 3). The **A**/**B** isomeric ratio varied from 10/1 to 2/1 depending on the *N*-substituent nature. The isomers of compounds **28a–e** were separated by column chromatography that allowed to thoroughly analyse their steric structure.

The orientation of the methallyl fragment at C-2 in the isomeric pairs **28A**/**28B** was established basing on ^{1}H NMR NOE values and by comparison of δ_H and δ_C values in these pairs. It was interesting to compare the data received for the **28A**/**28B** isomeric pairs with those for the pairs of their carboxylic analogues **9** synthesized earlier [3] (Scheme 1). The measurements were obtained for all the isomers **28A**/**28B**, and the data described below are given only for the methoxyphenyl substituted pairs of compounds **28cA**/**28cB** and **9A**/**9B** (Figure 3).



NOE, %	Isomer				Interatomic dist. (calc.), d (Å)	
	9A (*trans*)	**9B** (*cis*)	**28cA** (*trans*)	**28cB*** (*cis*)	(*trans*)	(*cis*)
$\eta_{H-2,H-5}$	<1	2.5	<1	3.1	2.92	2.21
$\eta_{H-2,H-9}$	<1	4.5	<1	3.3	2.70	2.07
$\eta_{H-5,H-9}$	2.2	2.5	2.7	2.6	2.21	2.24

* As the signals of 2H-3' and H-6B protons in **28cB** isomer are appreciably overlapped in $CDCl_3$ the NOE and exact *J* measurements were carried out in C_6D_6 solutions.

Figure 3. ^{1}H NMR NOE values ($\eta H_i,H_j$) and interatomic distances (d) in the isomeric pairs **28cA**/**28cB** and **9A**/**9B** (400 MHz, $CDCl_3$).

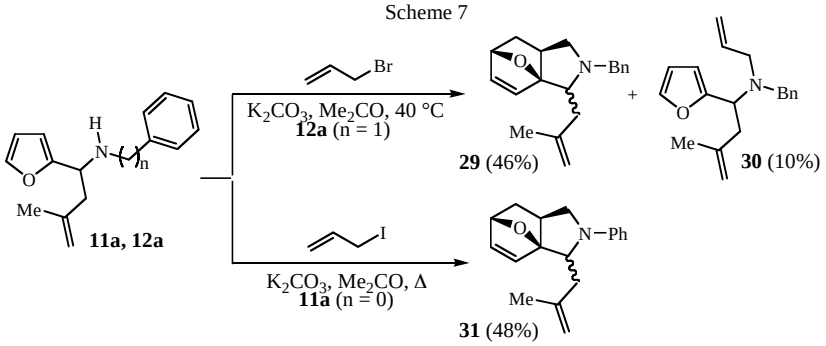
^{1}H NMR NOE values indicating the increase of H_i intensity when H_j signal was saturated ($\eta_{Hi}\{H_j\}$, %) are represented in table of Figure 3 for H-2, H-5 and H-9 protons of **28cA**/**28cB** and **9A**/**9B** isomeric pairs in the averaged mode: $\eta_{Hi,Hj}=[\eta_{Hi}\{H_j\}+\eta_{Hj}\{H_i\}]/2$ (%), where H_i, H_j: H-2, H-5, H-9; $H_i \neq H_j$.

Interatomic distances d (Å) between the specified hydrogen atoms in the isomers with *cis*- and *trans*-orientation of the 2-alkenyl fragment in relation to the 1,7-oxabridge obtained by the molecular modeling are represented in Figure 3. The analysis of the data summarised in the table of Figure 3 shows that $\eta_{H-2,H-5}$ and $\eta_{H-2,H-9}$ values could be compared with $\eta_{H-5,H-9}$ values only in the case of the isomers with *cis*-orientation of H-2 and H-5 protons in which molecules $d_{H-2,H-5} \approx d_{H-2,H-9} \approx d_{H-5,H-9}$, whereas in the isomers with *trans*-orientation of this protons $d_{H-2,H-5}$ and $d_{H-2,H-9}$ appreciably exceed $d_{H-5,H-9}$.

It is possible to note certain correlation between δ_H and δ_C values in **28cA**/**28cB** and **9A**/**9B** isomeric pairs based on their configuration established, that could be used as the criteria for determining configuration of the analogous compounds. Thus, the following correlations can be used for the NMR spectra of the $CDCl_3$ solutions: $\delta_{H-3'}$ (*trans*) > $\delta_{H-3'}$ (*cis*) ($\Delta\delta$~0.2); δ_{C-9} (*cis*) > δ_{C-9} (*trans*) ($\Delta\delta$~2). For example, application of these correlations to the data obtained for the **28aA**/**28aB** isomeric pair in which: $\delta_{H-3'}$ (**28aA**)=2.40 and 2.54 > $\delta_{H-3'}$ (**28aB**)=2.28 ppm; δ_{C-9} (**28aB**)=134.0 > δ_{C-9} (**28aA**)=132.0 ppm ($\Delta\delta$=2), allows to assert that compounds **28aA** and **28aB** are the isomers with the *trans*- and *cis*-orientation of H-2 and H-5 protons in relation to the 1,7-oxabridge accordingly [31].

Interaction between aminobutenes **11a**, **12a** and allylhalides resulted in the formation of *exo*-3-aza-10-oxatricyclo[5.2.1.0^{1,5}]dec-8-enes **29**, **31** (Scheme 7). *N*-Benzylsubstituted amine **12a** easily underwent alkylation with allylbromide at 40 °C to form the allyl derivative **30**. Cycloaddition started on boiling the reaction mixture in acetone (established by TLC). A mixture of allyl

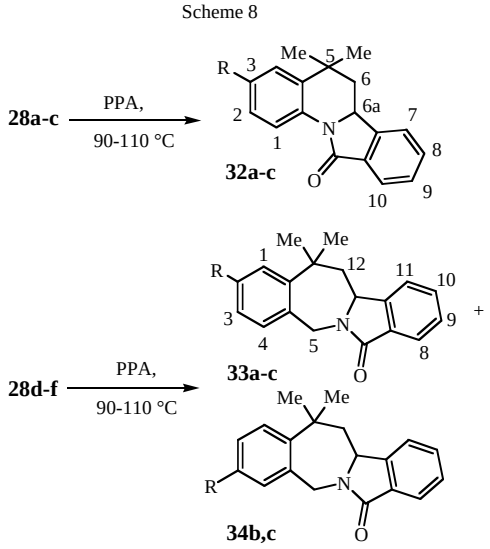
Scheme 7



derivative **30**/adduct **29** was formed in the ratio of 1/2.6 according to the ^{1}C NMR data. Heating of the obtained mixture at 100 °C in toluene led to the formation of **30**/**29**=1/5 mixture. *N*-Phenylsubstituted aminobutene **11a** underwent alkylation only after preliminary substitution of bromine atom in allylbromide for iodine. The intermediate allyl derivative instantly underwent [4+2] cycloaddition in boiling acetone to form the desired tricycle **31**. Obviously it can be explained by the fact that nitrogen atom in the intermediate *N*-benzyl-*N*-allylderivative **30** is pyramidal (sp^3), whereas in the intermediate *N*-phenyl-*N*-allyl derivative nitrogen atom is flat (sp^2) due to the conjugation with the aromatic ring and therefore leads to the formation of the ordered six-membered transition state that favors [4+2] cycloaddition process.

Intramolecular cyclization of the methallyl fragment in tricycles **28a–f** was carried out in PPA at 90–110 °C (Scheme 8). *N*-Phenylsubstituted adducts **28a–c** and *N*-benzylsubstituted adduct **28d** easily underwent intramolecular electrophilic substitution in this reaction conditions to give desired isoindolo[2,1-*a*]quinolines **32a–c** and isoindolo[2,1-*b*][2]benzazepine **33a** in good yields. Products **32a–c** and **33a** existed as single conformers with the pseudo-axial H-6*a* (11*b*) according to the ^{1}H NMR data.

Scheme 8

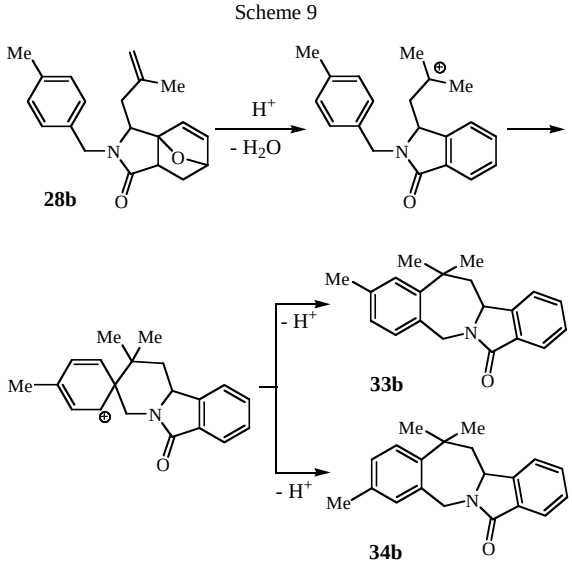


Compound	**32a**	**32b**	**32c**	**33a**	**33b**	**34b**	**33c**	**34c**
R	H	Me	OMe	H	Me	Me	OMe	OMe
Yield, %	61	70	64	61	6	20	15	15

In the case of *N*-*p*-methyl- and *N*-*p*-methoxy-benzyl-substituted adducts **28e**,**f** the cyclization brought to the formation of the mixtures containing two products possessing benzazepine fragment in their molecules according to the ^{1}H NMR data. These products had almost identical retention factor and equal molecular mass that made their chromatographic separation impossible. In the case of methyl substituted product **33b** the isomers formed were separated by multiple fractional crystallization. It should be notified that the yield of a **33b+34b** mixture isolated after the first recrystallization was around 65 %. The low yield of products **33c+34c** (30 %) was due to the considerable resinification of the reaction mixture in the reaction conditions.

The NOE experiment showed that compounds **33b** and **34b** were the isomers according to the position of the methyl group in the aromatic ring. Thus the ^{1}H NMR spectrum of **33b** contained the signals analogous to those in the ^{1}H NMR spectrum of **34b**. The greatest difference in the chemical shifts of equal multiples was observed for the methyl-substituted benzene ring and equal to 0.05 ppm. It gave us grounds to suggest the products **33b** and **34b** to be the regioisomers judging by the arrangement of the methyl-substituted benzene ring relative to the remaining part of the molecule. This suggestion was confirmed by measuring the NOE values indicating the increase of H_i intensity when H_j signal was saturated ($\eta_{Hi}\{H_j\}$, %). On saturation of the high field signal of the Me-13 group at δ 1.50 ppm in the case of **34b** or at δ 1.52 ppm in the case of **33b** the intensity increase of the doublet signals at δ 7.25 ppm with ^3J=8.0 Hz (η=21%) or at δ 7.17 ppm with ^4J=1.5 Hz (η=23%) was observed correspondingly. Since only H-1 situated alongside one of the Me-13 groups can show the intensity increase in the present experiment, the data obtained have given the evidence of the fact that the methyl substituent in the benzene ring was attached to C-2 in case of **33b**, and to C-3 in case of **34b**. The analogous process occurred in the case of **28f**, but unfortunately we did not manage to isolate the products formed (**33c**, **34c**) in pure form.

Scheme 9



Formation of the unusual regioisomer **34b** (**34c**) could be explained in terms of *ipso*-substitution in the aromatic ring. Thus, the tertiary carbo-cation formed upon protonation of the methallyl fragment attacked the quaternary carbon atom attached to the aminomethene group [32-34] and subsequent 1,2-shift resulted in the formation of the regioisomers **33b** and **34b** (Scheme 9).

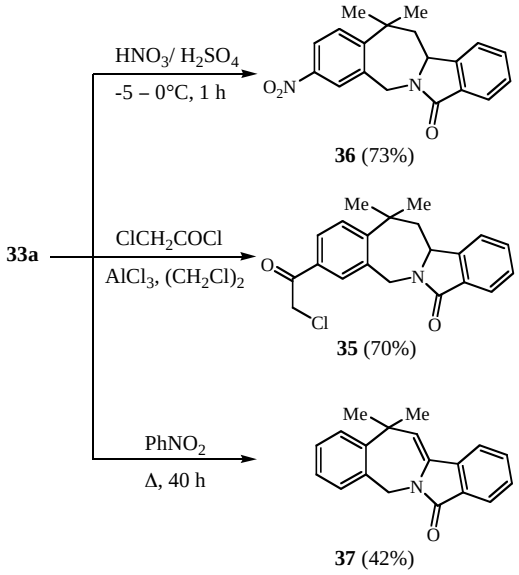
It is significant that we have not observed similar *ipso*-substitution in the synthesis of [2]benzazepines earlier [6,7,35,36].

Unfortunately we did not succeed in carrying out the desired cyclization of adducts **29**, **31** into tetracyclic non-oxygenated amines similar to **2**, **3** (**32–34**). Products formed from **29** or **31** in acidic conditions turned out to be very unstable.

Isoindolo[2,1-*b*][2]benzazepines **33** underwent regio-selective electrophilic substitution in the benzazepine unit. Thus, heating of **33a** with chloroacetylchloride in dichloroethane in the presence of $AlCl_3$ brought to the formation of the acylation product **35** (Scheme 10). Nitration of the compound **33a** with the nitration mixture at –5–0°C proceeded with high-regioselectivity giving 3-nitrosubstituted product **36**. At room temperatures (~25°C) the selectivity of the process failed and a mixture of mono- and dinitrosubstituted products was formed.

The position of the substituents in the aromatic ring in the molecules of **35**, **36** was established by comparison of their NMR data with those of 3-nitro-8-carboxyisoindolo-[2,1-*b*][2]benzazepine obtained earlier [6,37].

Scheme 10



The long-term reflux of tetrahydroisoindolobenzazepine **33a** in nitrobenzene lead to the oxidation of the tetrahydrobenzazepine fragment to form dihydroiso-indolo[2,1-*b*][2]benzazepine **37**.

The data obtained showed that isoindolo[2,1-*b*][2]-benzazepine system underwent electrophilic substitution at milder conditions and contained a less mobile H-11*b* proton compared to 8-carboxysubstituted analogues **3** [6].

In conclusion, we have shown that, starting from 2-furfural and 2-furfurylamine, complex ring systems: isoindolo[2,1-*a*]quinolines, isoindolo[2,1-*b*][2]benzazepines and 3-aza-11-oxatricyclo[6.2.1.0^{1,6}]undecenes, could be obtained in a few steps. The IMDAF reaction of furfurylsubstituted homoallylamines with allylhalides, acryloyl chloride and maleic anhydride occurred with high stereoselectivity when competitive ways were possible. *Exo*-products were exclusively formed; the positional relationship of the oxygen bridge and the allylic function in the diastereoisomers formed was established. In the process of isoindolobenzazepine synthesis the unusual *ipso*-substitution was discovered.

EXPERIMENTAL

All reagents were purchased from Acros Chemical Co. All solvents were used without further purification. Melting points were determined using a Fisher–Johns melting point apparatus and are uncorrected. IR spectra were obtained in KBr pellets for solids or in thin film for oils (Fourier-transform infrared spectrometer "Infralum FT-801"). NMR spectra ^{1}H (400 MHz) and ^{13}C (100.6 MHz) were recorded for solutions (2–5%) in deuteriochloroform or DMSO-d_6 at 30°C and traces of chloroform (^{1}H NMR δ 7.24, ^{13}C NMR 77.00 ppm) or DMSO-d_5H (^{1}H NMR δ 2.49, ^{13}C NMR 39.43 ppm) were used as the internal standard. Mass spectra were obtained by electron ionization at 70 eV on a HP MS 5988 mass spectrometer or a Finnegan MAT95XL chromatomass spectrometer. The purity of the obtained substances and the composition of the reaction mixtures were controlled by TLC Sorbfil UV_{254} plates. The separation of the final products was carried out by column chromatography on Al_2O_3 (activated, neutral, 50–200 mm) or by fractional crystallization.

X-Ray data of compound **26c** were collected on an "Inraf-Nonius Cad-4" 3-circle diffractometer at 293 K using graphite monochromated Mo Kα radiation (λ=0.71073 Å, ω-scanning, 2=2θ=60°) [38]. The structures were solved by direct methods using the SHELXS97 [39] program and refined by least-squares method in an anisotropic approximation using the SHELXL97 package [40]. The H-atoms were located geometrical and refined in arid approximation.

Crystal data for **26c** [26]: crystal dimensions: 0.47 × 0.34 × 0.22 mm, colorless prisms, $C_{15}H_{17}NO_2S$, M 275.36, space group $P2_1/n$, monoclinic, a=6.422(5), b=7.546(7), c=28.130(9) Å, β=90.77(3)°, V=1363.1 (17) Å^3, $d_{(calcd.)}$=1.342 g × cm^{-3} and Z=4, μ=0.235 cm^{-1}, F(000)=584. Intensities of 4096 reflections with I≥0.5σI (3933 are independent of symmetry) were measured. The final R_1 value are 0.0592 ($wR_2(F^2)$=0.2010) for 3933 with I ≥ 2σI (R_{int}=0.0176) reflections, GOOF=1.000.

4-*R*-4-*N*-Furfurylamino-1-butenes (**10b–e**).

Typical Procedure.

The freshly obtained [37,41] aldimine (0.30 mol) was slowly added drop-wise to a stirred solution of allylmagnesium bromide

prepared from allyl bromide (39 mL, 0.45 mol) and magnesium turnings (22.0 g, 0.90 mol) in ether (300 mL) or THF (300 mL) for **10e** at reflux. After the addition of the Schiff base, the reaction mixture was stirred for 1 h at room temperature. The cooled reaction mixture was poured into saturated aqueous NH_4Cl solution (300 mL) under ice cooling and extracted with ether (3 × 100 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was distilled in *vacuo* to give products **10b–e** as colourless oils.

4-*N*-Furfurylamino-4-(4-methoxyphenyl)butene-1 (**10b**).

Yield 60.1 g (78%); bp 167–169 °C/4 mmHg; ir: 3320 (NH), and 1612 (C=C) cm^{-1}; ^1H nmr ($CDCl_3$, 400 MHz) δ 1.93 (brs, 1H, NH), 2.38–2.42 (m, 2H, H-3), 3.51 (d, 1H, *J*=14.6 Hz, NCH_2-A), 3.62 (t, 1H, *J*=6.9 Hz, H-4), 3.67 (d, 1H, *J*=14.6 Hz, NCH_2-B), 3.80 (s, 3H, OMe), 5.05 (brdd, 1H, *J*=1.1, 10.2 Hz, H-1*cis*), 5.09 (dd, 1H, *J*=1.1, 16.9 Hz, H-1*trans*), 5.68 (m, 1H, *J*=6.6, 7.6, 10.2, 16.9 Hz, H-2), 6.08 (dd, 1H, *J*=3.2, 0.8 Hz, H-β′), 6.29 (dd, 1H, *J*=3.2, 1.8 Hz, H-β), 6.90 (AA′, 2H, *J*~8.7 Hz, H-Ph), 7.27 (BB′, 2H, *J*~8.7 Hz, H-Ph), 7.36 (dd, 1H, *J*=1.8, 0.8 Hz, H-α).

Anal. Calcd. for $C_{16}H_{19}NO_2$: C, 74.70; H, 7.39; N, 5.44. Found: C, 74.74; H, 7.42; N, 5.39.

4-*N*-Furfurylamino-4-(2-thienyl)butene-1 (**10c**).

Yield 57.3 g (82%); bp 130–131 °C/1 mmHg; ir: 3320 (NH), and 1630 (C=C) cm^{-1}; ^1H nmr ($CDCl_3$, 400 MHz) δ 1.91 (brs, 1H, NH), 2.47 (brt, 2H, *J*=6.7 Hz, H-3), 3.60 (d, 1H, *J*=14.7 Hz, NCH_2-A), 3.77 (d, 1H, *J*=14.7 Hz, NCH_2-B), 3.97 (t, 1H, *J*=6.7 Hz, H-4), 5.05 (m, 1H, *J*=9.5 Hz, H-1*cis*), 5.08 (m, 1H, *J*=17.1 Hz, H-1*trans*), 5.69 (m, 1H, *J*=6.7, 9.5, 17.1 Hz, H-2), 6.09 (dd, 1H, *J*=3.4, 0.9 Hz, H-β′), 6.27 (dd, 1H, *J*=3.4, 1.8 Hz, H-β), 6.90–6.95 (m, 2H, *J*=2.1, 3.4, 4.3 Hz, H-β and H-β′ (thienyl)), 7.19 (dd, 1H, *J*=2.1, 3.4 Hz, H-α (thienyl)), 7.32 (dd, 1H, *J*=1.8, 0.9 Hz, H-α).

Anal. Calcd. for $C_{13}H_{15}NOS$: C, 66.95; H, 6.43; N, 6.00. Found: C, 66.96; H, 6.46; N, 6.08.

4-*N*-Furfurylamino-4-(2-furyl)butene-1 (**10d**).

Yield 50.8 g (78%); bp 133–134 °C/3 mmHg; ir: 3325 (NH), and 1641 (C=C) cm^{-1}; ^1H nmr ($CDCl_3$, 400 MHz) δ 1.87 (brs, 1H, NH), 2.51 (brt, 2H, *J*=6.7 Hz, H-3), 3.60 (d, 1H, *J*=14.7 Hz, NCH_2-A), 3.75 (d, 1H, *J*=14.7 Hz, NCH_2-B), 3.77 (t, 1H, *J*=6.7 Hz, H-4), 5.07 (m, 1H, *J*=1.2, 17.1 Hz, H-1*trans*), 5.11 (m, 1H, *J*=1.2, 10.1 Hz, H-1*cis*), 5.70 (ddt, 1H, *J*=6.7, 10.1, 17.1 Hz, H-2), 6.11 (dd, 1H, *J*=3.1, 0.6 Hz, H-β′), 6.18 (dd, 1H, *J*=3.4, 0.6 Hz, H-β′*), 6.27 (dd, 1H, *J*=3.4, 1.8 Hz, H-β*), 6.31 (dd, 1H, *J*=3.1, 1.8 Hz, H-β), 7.32 (dd, 1H, *J*=1.8, 0.6 Hz, H-α*), 7.36 (dd, 1H, *J*=1.8, 0.6 Hz, H-α).

Anal. Calcd. for $C_{13}H_{15}NO_2$: C, 71.88; H, 6.91; N, 6.45. Found: C, 71.98; H, 6.90; N, 6.44.

4-*N*-Furfurylamino-4-(3-pyridyl)butene-1 (**10e**).

Yield 34.2 g (50%); bp 139–141 °C/2 mmHg; ir: 3300 (NH), and 1647 (C=C) cm^{-1}; ^1H nmr ($CDCl_3$, 400 MHz) δ 1.99 (brs, 1H, NH), 2.39 (dd, 2H, *J*=6.8, 7.0 Hz, H-3), 3.50 (d, 1H, *J*=14.7 Hz, NCH_2-A), 3.67 (d, 1H, *J*=14.7 Hz, NCH_2-B), 3.70 (t, 1H, *J*=6.8 Hz, H-4), 5.02 (m, 1H, *J*=1.3, 9.5 Hz, H-1*cis*), 5.09 (dd, 1H, *J*=1.3, 17.4 Hz, H-1*trans*), 5.66 (m, 1H, *J*=6.7, 9.5, 17.4 Hz, H-2), 6.06 (dd, 1H, *J*=3.2, 0.8 Hz, H-β′), 7.25 (brdd, 1H, *J*=4.8, 7.9 Hz, H-5*), 6.27 (dd, 1H, *J*=3.2, 1.9 Hz, H-β), 7.33 (dd, 1H, *J*=1.9, 0.8 Hz, H-α), 7.70 (dt, 1H, *J*=1.8, 7.9 Hz, H-4*), 8.50 (d, 1H, *J*=4.8 Hz, H-6*), 8.54 (d, 1H, *J*=1.8 Hz, H-2*).

Anal. Calcd. for $C_{14}H_{16}N_2O$: C, 73.68; H, 7.01; N, 12.28. Found: C, 73.65; H, 7.14; N, 12.39.

3-(1-Allylcyclohexyl)-10-oxa-3-azatricyclo[5.2.1.$0^{1,5}$]dec-8-en-4-on (**14a**).

Acrylic anhydride 6.60 mL (57.0 mmol) was added to a solution of 2.50 g (11.4 mmol) of allylamine **10f** in *o*-xylene (15 mL). The mixture was refluxed for 5 h (TLC monitoring). Then the reaction mass was poured into H_2O (150 mL) and concentrated Na_2CO_3 solution was added until pH 10–11. The solution was extracted with Et_2O (3 × 70 mL), combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by column chromatography on Al_2O_3 (25 × 2 cm, using hexane/ethyl acetate, 30:1 as eluent). Compound **14a**: white acicular crystals; yield 1.20 g (4.40 mmol, 40%); mp 95 °C (hexane–ethyl acetate); R_f 0.25 (hexane–ethyl acetate, 1:1); ir: 1667 (N–C=O), and 1627 (C=C) cm^{-1}; ms: m/z M^+ 273 (2), 261 (3), 232 (17), 220 (3), 204 (2), 178 (3), 161 (2), 140 (3), 121 (4), 107 (2), 91 (2), 82 (8), 81 (100), 67 (5), 55 (10), 53 (9), 41 (11); ^1H nmr ($CDCl_3$, 400 MHz) δ 1.31–1.61 (m, 8H, $(CH_2)_4$), 1.51 (dd, ^3J=8.7, ^2J=11.8 Hz, H-6*endo*), 2.14 (m, 1H, H-*o*-cyclohexyl), 2.16 (ddd, 1H, ^3J=3.3, 4.5, ^2J=11.8 Hz, H-6*exo*), 2.35 (brd, 1H, H-*o*-cyclohexyl), 2.42 (dd, 1H, ^3J=3.3, 8.7 Hz, H-5*endo*), 2.49 (dd, 1H, ^3J=8.1, ^2J=13.9 Hz, H-3′B), 2.54 (dd, 1H, ^3J=7.2, ^2J=13.9 Hz, H-3′A), 3.87 (d, 1H, ^2J=11.7 Hz, H-2B), 3.96 (d, 1H, ^2J=11.7 Hz, H-2A), 5.03 (d, 1H, ^3J=4.5 Hz, H-7), 5.02–5.08 (m, 2H, H-1′), 5.81 (dddd, 1H, ^3J=7.2, 8.1, 9.4, 17.3 Hz, H-2′), 6.36 (m, 2H, H-8 and H-9).

Anal. Calcd. for $C_{17}H_{23}NO_2$: C, 74.72; H, 8.42; N, 5.12. Found: C, 74.75; H, 8.37; N, 5.14.

3-(1-Allylcyclohexyl)-10-oxa-3-azatricyclo[5.2.1.$0^{1,5}$]dec-8-en-4-on-6-carboxylic acid (**14b**).

Amine **10f** 2.10 g (9.58 mmol) was dissolved in 15 mL of benzene. Then an equimolar amount of maleic anhydride 0.94 g (9.58 mmol) was added in one portion to the obtained solution. The reaction mixture was stirred for 2 d at room temperature. Then the crystalline product was collected by filtration, washed with benzene (2 × 10 mL), ether (2 × 10 mL) and dried at 100 °C to give desired product **14b** as white powder. Yield 1.82 g (5.75 mmol, 60%); mp 87–110 °C with decomposition; ir: 1667 (C=O), 2980 (OH), and 1627 (C=C) cm^{-1}; ms: m/z $[M-41]^+$ 273 (1), 261 (3), 232 (3), 204 (3), 178 (2), 176 (2), 140 (6), 121 (7), 98 (4), 94 (3), 91 (3), 82 (6), 81 (100), 79 (7), 77 (5), 67 (5), 55 (10), 53 (12), 43 (14), 41 (13); ^1H nmr ($CDCl_3$, 400 MHz) δ 1.30–1.85 (m, 8H, $(CH_2)_4$), 2.10–2.30 (m, 2H), 2.53 (d, 2H, ^3J=7.6 Hz, H-3′), 2.83 (d, 1H, ^3J=9.2 Hz, H-6), 2.88 (d, 1H, ^3J=9.2 Hz, H-5), 3.92 (d, 1H, ^2J=12.2 Hz, H-2B), 4.00 (d, 1H, ^2J=12.2 Hz, H-2A), 5.07 (brd, 1H, ^3J=16.2 Hz, H-1′trans), 5.09 (brd, 1H, ^3J=10.7 Hz, H-1′cis), 5.42 (brs, 1H, ^3J=1.5 Hz, H-7), 5.81 (m, 1H, ^3J=7.6, 10.7, 16.2 Hz, H-2′), 6.41 (d, 1H, ^3J=5.8 Hz, H-9), 6.52 (dd, 1H, ^3J=1.5, 5.8 Hz, H-8).

Anal. Calcd. for $C_{18}H_{23}NO_4$: C, 68.13; H, 7.25; N, 4.41. Found: C, 68.30; H, 7.18; N, 4.45.

Dimethyl (*E*)-2-[(1-(2-furyl)-3-butenyl)furfurylamino]-2-butenedioate (**16**).

DMAD 1.13 mL (9.21 mmol) was added to a solution of 2.0 g (9.21 mmol) of allylamine **10d** in toluene (10 mL). The mass was

feebly getting warm and dark. The reaction mixture was stirred for 4 h at room temperature (TLC monitoring). Then toluene was stripped in vacuo. Compound **16**: brown oil, yield 3.25 g (9.05 mmol, 98%); R_f 0.31 (hexane–ethyl acetate, 3 : 1); ir: 1733 (O–C=O), and 1680 (C=C) cm^{-1}; ms: m/z M^+ 359 (9), 318 (5), 286 (5), 238 (17), 208 (4), 179 (6), 178 (11), 146 (5), 121 (26), 103 (17), 93 (11), 91 (15), 82 (6), 81 (100), 77 (14), 53 (15); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 2.71 (m, 2H, 2H-3), 3.62 (s, 3H, CO_2Me), 3.94 (s, 3H, CO_2Me), 4.13 (d, 1H, ^2J=16.9 Hz, NCH_2-A), 4.20 (d, 1H, ^2J=16.9 Hz, NCH_2-B), 4.56 (t, 1H, ^3J=7.5 Hz, H-4), 4.89 (s, 1H, E–C*H*=C), 5.06 (m, 1H, ^3J=10.3, ^2J=1.5 Hz, H-1*cis*), 5.09 (m, 1H, ^3J=17.1, ^2J=1.5 Hz, H-1*trans*), 5.71 (ddt, 1H, ^3J=10.3, 17.1, 7.0 Hz, H-2), 6.03 (dd, 1H, ^3J=3.2, ^4J=0.8 Hz, H-β′*), 6.24 (dd, 1H, ^3J=3.2, ^4J=1.8 Hz, H-β*), 6.31 (dt, 1H, ^3J=3.2, 0.8 Hz, H-β′), 6.33 (dd, 1H, ^3J=3.2, 1.8 Hz, H-β), 7.28 (dd, 1H, ^3J=1.7, ^4J=0.8 Hz, H-α*), 7.38 (dd, 1H, ^3J=1.7, ^4J=0.8 Hz, H-α).

Anal. Calcd. for $C_{19}H_{21}NO_6$: C, 63.50; H, 5.84; N, 3.89. Found: C, 63.65; H, 5.70; N, 3.80.

Dimethyl (*E*)-2-[4-(2-furyl)-11-oxa-3-azatricyclo[6.2.1.0^{1,6}]-undec-9-en-3-yl]-2-butenedioate (**17**).

Procedure A. DMAD 1.1 mL (9.20 mmol) was added to a solution of 2.0 g (9.20 mmol) allylamine **10d** in toluene (10 mL). The resulting mixture was refluxed for 15 h (TLC monitoring). After removal of toluene, the crude product was purified by column chromatography on Al_2O_3 (4 × 17 cm, using hexane/ethyl acetate, 10:1 as eluent). Yield (**17**) 0.6 g (2.20 mmol, 24%).

Procedure B. The solution of 2.20 g (6.13 mmol) compound **16** in toluene (15 mL) was refluxed for 8 h. After removal of toluene, the crude product was purified by column chromatography on Al_2O_3 (3 × 15 cm, eluent hexane/ethyl acetate, 10:1). Yield (**17**) 0.99 g (2.75 mmol, 45%).

Compound **17**: white needles, mp 117–118.5 °C (ethyl acetate–hexane); R_f 0.24 (ethyl acetate–hexane, 1 : 1); ir: 1726 (O–C=O), and 1680 (C=C) cm^{-1}; ms: m/z M^+ 359 (29), 328 (9), 300 (26), 286 (32), 282 (8), 268 (11), 178 (13), 121 (8), 103 (10), 94 (45), 91 (23), 82 (7), 81 (100), 77 (21), 65 (9), 53 (22); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.42–1.66 (m, 3H, H-6 and H-7), 1.86 (dt, 1H, ^2J=13.6, ^3J=11.0 Hz, H-5*ax*), 2.34 (ddd, 1H, ^2J=13.6, ^3J=7.0, 3.0 Hz, H-5*eqv*), 3.61 (s, 3H, CO_2Me), 3.71 (d, 1H, ^2J=15.1 Hz, H-2B), 3.83 (d, 1H, ^2J=15.1 Hz, H-2A), 3.96 (s, 3H, CO_2Me), 4.57 (d, 1H, ^3J=7.0, 11.0 Hz, H-4*ax*), 4.85 (s, 1H, E–C*H*=CE), 4.91 (dd, 1H, ^3J=4.4, 1.7 Hz, H-8), 6.23 (dd, 1H, ^3J=3.2, ^4J=0.8 Hz, H-β′), 6.32 (dd, 1H, ^3J=3.2, 1.8 Hz, H-β), 6.30 (dd, 1H, ^3J=5.8, 1.4 Hz, H-9), 6.50 (d, 1H, ^3J=5.8 Hz, H-10), 7.36 (dd, 1H, ^3J=1.8, ^4J=0.8 Hz, H-α).

Anal. Calcd. for $C_{19}H_{21}NO_6$: C, 63.50; H, 5.84; N, 3.89. Found: C, 63.68; H, 6.03; N, 3.94.

2-Allyl-3-(2-furylmethyl)-4-oxo-10-oxa-3-azatricyclo[5.2.1.0^{1,5}]-dec-8-ene-6-carboxylic acid (**20**).

Amine **10d** 3.0 g (13.8 mmol) was added to a solution of 1.36 g (13.8 mmol) of maleic anhydride in benzene (25 mL). The reaction mixture was stirred at 0–5 °C for 2 h. Then the crystalline product was collected by filtration, washed with benzene (2 × 30 mL), ether (30 mL) and dried in air to give desired product **20**. Compound **20**: 3.01 g (9.66 mmol, 70%) white powder, mixture of isomers in the ~1:6 ratio; mp 132–133.5 °C; ir: 3360 (OH), 1708 (N–C=O), and 1684 (C=C) cm^{-1}; ms: m/z M^+ 315 (5), 274 (5), 234 (4), 194 (53), 176 (15), 121 (9), 98 (17), 96 (62), 91 (12), 81 (100), 78 (21), 77 (17), 65 (13), 53 (42), 41 (14), 39 (25); **20** (maj): ^{1}H nmr (DMSO, 400 MHz) δ 2.47 (d, 1H, ^3J=9.3 Hz, H-5), 2.52–2.62 (m, 2H, 2H-3′), 2.79 (d, 1H, ^3J=9.3 Hz, H-6), 3.79 (dd, 1H, ^3J=6.4, 3.8 Hz, H-2), 4.29 (d, 1H, ^2J=16.1 Hz, NCH_2-B), 4.58 (d, 1H, ^2J=16.1 Hz, NCH_2-A), 4.95 (d, 1H, ^3J=1.7 Hz, H-7), 5.11 (dd, 1H, ^3J=10.2, ^2J=1.8 Hz, H-1′*cis*), 5.18 (dd, 1H, ^3J=17.2, ^2J=1.8 Hz, H-1′*trans*), 5.75 (m, 1H, ^3J=17.2, 10.2, 7.0 Hz, H-2′), 6.31 (brdd, 1H, ^3J=3.2, ^4J=0.8 Hz, H-β′), 6.38 (dd, 1H, ^3J=3.2, 1.8 Hz, H-β), 6.44 (dd, 1H, ^3J=5.8, 1.7 Hz, H-8), 6.65 (d, 1H, ^3J=5.8 Hz, H-9), 7.57 (dd, 1H, ^3J=1.8, ^4J=0.8 Hz, H-α), 12.15 (brs, 1H, CO_2H); **20** (min): δ 2.48 (d, 1H, ^3J=9.3 Hz, H-5), 2.52–2.62 (m, 2H, 2H-3′), 2.77 (d, 1H, ^3J=9.3 Hz, H-6), 3.97 (dd, 1H, ^3J=10.5, 4.5 Hz, H-2), 4.12 (d, 1H, ^2J=16.1 Hz, NCH_2-B), 4.72 (d, 1H, ^2J=16.1 Hz, NCH_2-A), 5.01 (d, 1H, ^3J=1.8 Hz, H-7), 5.02 (brd, 1H, ^3J~10.0 Hz, H-1′*cis*), 5.11 (brd, 1H, ^3J~17.0 Hz, H-1′*trans*), 5.75 (m, 1H, H-2′), 6.31 (brdd, 1H, ^3J=3.2, ^4J=0.8 Hz, H-β′), 6.34 (brdd, 1H, ^3J=5.7, 1.8 Hz, H-8), 6.41 (dd, 1H, ^3J=3.2, 1.9 Hz, H-β), 6.47 (dd, 1H, ^3J=5.7 Hz, H-9), 7.59 (m, 1H, ^3J=1.9, 0.8 Hz, H-α), 12.15 (brs, 1H, CO_2H).

Anal. Calcd. for $C_{17}H_{17}NO_5$: C, 64.76; H, 5.39; N, 4.40. Found: C, 64.80; H, 5.42; N, 4.37.

4-*N*-Furfurylamino-*N*-acryloyl-4-(2-furyl)butene-1 (**21**).

Triethylamine 4.09 mL (29.30 mmol) and acryloyl chloride 1.99 mL (24.40 mmol) were added to a solution of allylamine **10d** (2.12 g, 9.76 mmol) in 20 mL of toluene. The reaction mass was feebly getting warm and white triethylamine hydrochloride precipitated. The mixture was stirred for 5 h at room temperature (TLC monitoring), diluted with H_2O (100 mL) and a solution of Na_2CO_3 was added until pH 9–10. The organic products were extracted with $CHCl_3$ (4 × 50 mL), combined organic layers were washed with saturated Na_2CO_3 solution (2 × 50 mL), dried over $MgSO_4$ and concentrated. The column chromatography on Al_2O_3 (15 × 1.5 cm, using ethyl acetate/hexane, 1:5 as eluent) gave compound **21** 2.50 g (9.00 mmol) contaminated with about 5–7 percent of tricycle **22** (according to NMR). Mobile yellow oil, yield 93%; R_f 0.71 (ethyl acetate–hexane, 1:1); ir: 1665 (C=O, and C=C) cm^{-1}; ^{1}H nmr (DMSO, 400 MHz) δ 2.60 (m, 2H, ^3J=6.7, 7.6, 8.6 Hz, H-3); 3.35 (d, 1H, ^2J=14.7 Hz, NCH_2-B), 3.80 (d, 1H, ^2J=14.7 Hz, NCH_2-A), 5.12 (m, 1H, ^3J=10.1, ^2J=1.8 Hz, H-1*cis*), 5.20 (m, 1H, ^3J=17.1, ^2J=1.8 Hz, H-1*trans*), 5.48 (dd, 1H, ^3J=10.3, ^2J=2.0 Hz, H-1′*cis*), 5.78 (m, 1H, ^3J=10.1, 17.1, 7.6 Hz, H-2), 5.81 (dd, 1H, ^3J=10.3, 16.8 Hz, H-2′), 6.14 (brd, 1H, ^3J=3.2 Hz, H-β′*), 6.19 (brd, 1H, ^3J=3.2 Hz, H-β′), 6.31 (dd, 1H, ^3J=3.2, ^4J=1.8 Hz, H-β*), 6.33 (dd, 1H, ^3J=3.2, 1.8 Hz, H-β), 6.39 (dd, 1H, ^3J=16.8, ^2J=2.1 Hz, H-1′*trans*), 6.43 (dd, 1H, ^3J=8.6, 6.7 Hz, H-4), 7.37 (dd, 1H, ^3J=1.8, ^4J=0.8 Hz, H-α*), 7.39 (dd, 1H, ^3J=1.8, ^4J=0.8 Hz, H-α).

Anal. Calcd. for $C_{16}H_{17}NO_3$: C, 68.32; H, 6.04; N, 4.98. Found: C, 68.20; H, 6.09; N, 5.02.

3-(2-Furylmethyl)-2-allyl-10-oxa-3-azatricyclo[5.2.1.0^{1,5}]dec-8-en-4-one (**22**).

Triethylamine (4.1 mL, 29.30 mmol) and acryloyl chloride (2.0 mL, 24.40 mmol) were added to a solution of allylamine **10d** 2.12 g (9.76 mmol) in toluene (20 mL). The reaction mass was feebly getting warm and white triethylamine hydrochloride precipitates. The mixture was refluxed for 3 h (TLC monitoring), then diluted with H_2O (100 mL) and a solution of Na_2CO_3 was added until pH 9–10. The organic

products were extracted with $CHCl_3$ (4 × 50 mL). The combined organic layers were washed with saturated Na_2CO_3 solution (2 × 50 mL), dried over $MgSO_4$ and concentrated. The column chromatography on Al_2O_3 (22 × 2 cm, using ethyl acetate/hexane, 1:5 as eluent) gave tricycle **22** 1.75 g (6.24 mmol). Viscous pale yellow oil, yield 64%; mixture of diastereoisomers in the ~1:2 ratio; R_f 0.32 (ethyl acetate–hexane, 1:1); ir: 1686 (C=O and C=C) cm^{-1}; ms: m/z M^+ 281 (4), 240 (8), 216 (59), 160 (18), 121 (9), 98 (17), 96 (15), 81 (100), 77 (9), 53 (21), 41 (14); ^1H nmr (DMSO, 400 MHz) **22** (maj): δ 1.43 (m, 1H, H-6), 1.84 (m, 1H, H-6), 2.40 (m, 1H, H-5), 2.60 (m, 2H, ^3J=3.9, 6.5, 7.6 Hz, H-3′), 3.73 (d, 1H, ^3J=6.5, 3.9 Hz, H-2), 4.27 (d, 1H, ^2J=15.8 Hz, NCH_2-B), 4.63 (d, 1H, ^2J=15.8 Hz, NCH_2-A), 4.95 (dd, 1H, ^3J=4.4, 1.7 Hz, H-7), 5.11 (m, 1H, ^3J=10.7, ^2J=1.6 Hz, H-1′*cis*), 5.19 (dd, 1H, ^3J=17.1, ^2J=1.6 Hz, H-1′*trans*), 6.19 (brd, 1H, ^3J=3.2 Hz, H-β′), 5.70–5.83 (m, 1H, H-2′), 6.33 (dd, 1H, ^3J=3.2, 1.8 Hz, H-β), 6.39 (dd, 1H, ^3J=5.9, 1.7 Hz, H-8), 6.47 (dd, 1H, ^3J=5.9 Hz, H-9), 7.58 (dd, 1H, ^3J=1.8, ^4J=0.8 Hz, H-α); **22** (min): 1.43 (m, 1H, H-6A), 1.84 (m, 1H, H-6B), 2.40 (m, 1H, H-5), 2.60 (m, 2H, H-3′), 4.03 (d, 1H, ^3J=10.4, 4.4 Hz, H-2), 4.11 (d, 1H, ^2J=16.2 Hz, NCH_2-B), 4.75 (d, 1H, ^2J=16.2 Hz, NCH_2-A), 4.99 (dd, 1H, ^3J=4.3, 1.7 Hz, H-7), 5.12 (m, 1H, ^3J=10.1, ^2J=1.8 Hz, H-1′*cis*), 5.20 (m, 1H, ^3J=17.1, ^2J=1.8 Hz, H-1′*trans*), 5.56–5.66 (m, 1H, H-2′), 6.19 (brd, 1H, ^3J=3.2 Hz, H-β′), 6.33 (dd, 1H, ^3J=3.2, 1.8 Hz, H-β), 6.39 (dd, 1H, ^3J=5.9, 1.7 Hz, H-8), 6.47 (dd, 1H, ^3J=5.9 Hz, H-9), 7.62 (dd, 1H, ^3J=1.8, ^4J=0.8 Hz, H-α).

Anal. Calcd. for $C_{16}H_{17}NO_3$: C, 68.32; H, 6.04; N, 4.98. Found: C, 68.27; H, 6.09; N, 5.00.

4-*N*-Furfurylamino-*N*-allyl-4-(2-furyl)butene-1 (**23**).

A solution of allylbromide (4.0 mL, 46.0 mmol) in 10 mL of acetone was added dropwise to a stirred solution of homoallylamine **10d** (5.0 g, 23.0 mmol), 8.50 g (46.0 mmol) of dry NaI and 9.5 g (69.0 mmol) of K_2CO_3 in 20 mL of acetone. The reaction mixture was stirred for 4 h at room temperature (TLC monitoring), taken up into H_2O (100 mL) and extracted with ether (3 × 70 mL). Combined organic layers were washed with saturated Na_2CO_3 solution (2 × 50 mL), dried over $MgSO_4$ and evaporated *in vacuo*. The residue (dark-red oil) was purified by column chromatography on Al_2O_3 (4 × 1.5 cm, using hexane as eluent). Compound **23**: pale yellow oil 4.55 g (17.70 mmol), yield 77%; R_f 0.58 (ethyl acetate–hexane, 1:2); ir: 1640 (C=C) cm^{-1}; ms: m/z M^+ 257 (4), 217 (10), 216 (59), 136 (18), 121 (4), 108 (6), 94 (5), 81 (100), 77 (5), 53 (8), 41 (6); ^1H nmr ($CDCl_3$, 400 MHz) δ 2.60 (m, 2H, ^3J=5.0, 7.6 Hz, H-3), 2.85 (dd, 1H, ^2J=14.1, ^3J=6.9 Hz, H-3′B), 3.32 (ddt, 1H, ^2J=14.1, ^3J=6.9, 1.6 Hz, H-3′A), 3.35 (d, 1H, ^2J=14.7 Hz, NCH_2-A), 3.80 (d, 1H, ^2J=14.7 Hz, NCH_2-B), 3.87 (t, 1H, ^3J=7.6 Hz, H-4), 4.96 (m, 1H, ^3J=10.1, ^2J=1.5 Hz, H-1′*cis*), 5.02 (m, 1H, ^3J=17.1, ^2J=1.5 Hz, H-1′*trans*), 5.12 (m, 1H, ^3J=10.1, ^2J=1.8 Hz, H-1*cis*), 5.20 (m, 1H, ^3J=17.1, ^2J=1.8 Hz, H-1*trans*), 5.73 (ddt, 1H, ^3J=10.1, 17.1, 6.9 Hz, H-2′), 5.78 (m, 1H, ^3J=10.1, 17.1, 7.6, 5.0 Hz, H-2), 6.14 (brd, 1H, ^3J=3.2 Hz, H-β′*), 6.19 (brd, 1H, ^3J=3.2 Hz, H-β′), 6.31 (dd, 1H, ^3J=3.2, ^4J=1.8 Hz, H-β*), 6.33 (dd, 1H, ^3J=3.2, 1.8 Hz, H-β), 7.37 (dd, 1H, ^3J=1.8, ^4J=0.8 Hz, H-α*), 7.39 (dd, 1H, ^3J=1.8, ^4J=0.8 Hz, H-α).

Anal. Calcd. for $C_{16}H_{19}NO_2$: C, 74.70; H, 7.39; N, 5.44. Found: C, 74.76; H, 7.42; N, 5.46.

3-(2-Furylmethyl)-2-allyl-10-oxa-3-azatricyclo[5.2.1.$0^{1,5}$]dec-8-en (**24**).

Procedure A. A solution of amine **10d** (3.0 g, 13.80 mmol) in 15 mL of acetone was added dropwise to a stirred mixture of K_2CO_3 (7.6 g, 55.20 mmol) and allylbromide (2.4 mL, 27.60 mmol) in 25 mL of acetone. After the complete amine addition the reaction mixture was refluxed for 1 h and poured into 100 mL of water. The organic products were extracted with ether (3 × 50 mL), combined organic layers were dried over $MgSO_4$ and evaporated to give dark-brown residue. Its further column chromatography on Al_2O_3 (4 × 5 cm, using hexane/ethyl acetate, 10:1 as eluent) gave pure **24**: 1.17 g (4.60 mmol), yield 33 %.

Procedure B. A solution of diallylderivative **23** 2.0 g (7.78 mmol) in 10 mL of benzene was refluxed for 30 min (TLC monitoring). Benzene was removed under reduced pressure, the residual brown oil was purified by column chromatography on Al_2O_3 (4 × 5 cm, using hexane/ethyl acetate, 10:1 as eluent) to give **24**: 0.59 g (2.33 mmol), yield 30 %.

Compound **24**: pale yellow oil; R_f 0.47 (ethyl acetate–hexane, 1:1); ir: 1640 (C=C) cm^{-1}; ms: m/z M^+ 257 (5), 217 (8), 216 (63), 136 (16), 121 (4), 108 (5), 94 (7), 81 (100), 77 (6), 53 (11), 41 (6); ^1H nmr ($CDCl_3$, 400 MHz) δ 1.28 (dd, 1H, ^2J=11.3, ^3J=7.3 Hz, H-6*endo*), 1.66 (ddd, 1H, ^2J=11.3, ^3J=4.3, 2.8 Hz, H-6*exo*), 1.98 (dddd, 1H, J=2.8, 7.3, 6.7, 10.4 Hz, H-5), 2.24 (dd, 1H, ^2J=8.2, ^3J=10.4 Hz, H-4B), 2.30–2.45 (m, 2H, H-3′), 2.93 (dd, 1H, ^3J=5.5, 7.3 Hz, H-4′), 3.23 (dd, 1H, ^2J=8.2, ^3J=6.7 Hz, H-4A), 3.68 (d, 1H, ^2J=14.3 Hz, H-2B), 3.88 (d, 1H, ^2J=14.3 Hz, H-2A), 4.94 (dd, 1H, ^3J=4.3, 1.5 Hz, H-7), 5.12 (m, 1H, ^3J=17.0, ^2J=1.5 Hz, H-1′*trans*), 5.14 (m, 1H, ^3J=10.1, ^2J=1.5 Hz, H-1′*cis*), 5.93 (ddt, 1H, ^3J=17.0, 10.1, 6.4 Hz, H-2′), 6.18 (dd, 1H, ^3J=3.1, ^4J=0.8 Hz, H-β′), 6.24 (dd, 1H, ^3J=5.8, 1.5 Hz, H-8), 6.29 (dd, 1H, ^3J=3.1, 1.8 Hz, H-β), 6.43 (d, 1H, ^3J=5.8 Hz, H-9), 7.35 (dd, 1H, ^3J=1.8, ^4J=0.8 Hz, H-α).

Anal. Calcd. for $C_{16}H_{19}NO_2$: C, 74.70; H, 7.39; N, 5.44. Found: C, 74.64; H, 7.43; N, 5.57.

3-Acetyl-3-aza-11-oxatricyclo[6.2.1.$0^{1,6}$]undec-9-enes (**26a–d**).

Typical Procedure.

Homoallylamine **10a–e** (0.1 mol) was refluxed in a 20-fold molar excess of acetic anhydride for 3–6 h (TLC control). Excess anhydride was distilled off under reduced pressure, the residue was diluted with water (200 mL), basified with $NaHCO_3$ to pH 9–10, extracted with ethyl acetate (3 × 70 mL), dried over $MgSO_4$ and evaporated. The residue was recrystallized from hexane–ethyl acetate or purified by chromatography on Al_2O_3 (using hexane as eluent). Tricyclic compounds **26a–d** were isolated as colorless crystals.

3-Acetyl-3-aza-4-phenyl-11-oxatricyclo[6.2.1.$0^{1,6}$]undec-9-ene (**26a**).

Yield 9.14 g (34%); mp 117–118 °C; ir: 1639 (C=C, and N–C=O) cm^{-1}; ms: m/z M^+ 269 (16), 228 (8), 227 (26), 210 (12), 208 (15), 188 (9), 186 (8), 146 (7), 138 (33), 104 (13), 96 (46), 91 (19), 81 (100), 53 (12), 43 (21); ^1H nmr ($CDCl_3$, 400 MHz) δ 1.35–1.80 and 2.20–2.40 (m, 6H, H-4, 2H-5, H-6, 2H-7), 2.04 (s, 3H, Ac), 3.35 (brd, 1H, J=14.3 Hz, H-2A), 4.87 (dd, 1H, J=1.8, 4.3 Hz, H-8), 5.01 (brd, 1H, J=14.3 Hz, H-2B), 6.28 (brdd, 1H, J=1.8, 5.8 Hz, H-9), 6.41 (d, 1H, J=5.8 Hz, H-10), 7.15–7.35 (m, 5H, H-Ph).

Anal. Calcd. for $C_{17}H_{19}NO_2$: C, 75.84; H, 7.06; N, 5.20. Found: C, 75.58; H, 7.20; N, 5.25.

3-Acetyl-3-aza-4-(4-methoxyphenyl)-11-oxatricyclo[6.2.1.0^{1,6}]-undec-9-ene (**26b**).

Yield 18.84 g (63%); mp 100–102 °C; ir: 1640 (C=C, and N–C=O) cm^{-1}; ms: m/z M$^+$ 299 (100), 257 (20), 240 (24), 238 (27), 218 (15), 195 (8), 161 (12), 134 (18), 121 (7), 81 (23), 43 (7); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.35–1.95 (m, 5H, 2H-5, H-6, 2H-7), 2.31 (brs, 3H, Ac), 3.13 (brd, 1H, *J*=15.0 Hz, H-2A), 3.77 (s, 3H, OMe), 4.75 (m, 1H, H-4), 4.88 (m, 1H, H-8), 5.45 (brd, 1H, *J*=15.0 Hz, H-2B), 6.28 (m, 1H, H-9), 6.39 (m, 1H, H-10), 6.85 (AA′, 2H, H-Ph), 7.20 (BB′, 2H, H-Ph).

Anal. Calcd. for $C_{18}H_{21}NO_3$: C, 72.24; H, 7.02; N, 4.68. Found: C, 72.30; H, 6.80; N, 4.82.

3-Acetyl-3-aza-4-(2-thienyl)-11-oxatricyclo[6.2.1.0^{1,6}]undec-9-ene (**26c**).

Yield 7.70 g (28%); mp 108–108.5 °C; ir: 1636 (C=C, and N–C=O) cm^{-1}; ms: m/z M$^+$ 275 (30), 233 (34), 216 (22), 214 (22), 194 (16), 152 (18), 138 (22), 110 (18), 97 (17), 96 (32), 91 (7), 81 (100), 53 (14), 43 (30); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.35–1.65, 1.70–1.95 and 2.30–2.50 (m, 5H, 2H-5, H-6, 2H-7), 2.16 (brs, 3H, Ac), 3.37 (m, 1H, H-4), 4.73 (brd, 1H, *J*=15.6 Hz, H-2A), 4.89 (dd, 1H, *J*=1.2, 3.7 Hz, H-8), 5.41 (brd, 1H, *J*=15.6 Hz, H-2B), 6.30 (brdd, 1H, *J*=1.2, 5.8 Hz, H-9), 6.38 (d, 1H, *J*=5.8 Hz, H-10), 6.90–7.00 (m, 2H, H-β and H-β′), 7.18 (dd, 1H, *J*=1.2, 4.6 Hz, H-α).

Anal. Calcd. for $C_{15}H_{17}NO_2S$: C, 65.45; H, 6.18; N, 5.09. Found: C, 65.73; H, 6.03; N, 5.16.

3-Acetyl-3-aza-4-(2-furyl)-11-oxatricyclo[6.2.1.0^{1,6}]undec-9-ene (**26d**).

Yield 5.96 g (23%); mp 114–116 °C; ir: 1667 (C=C, and N–C=O) cm^{-1}; ms: m/z M$^+$ 259 (5), 218 (6), 179 (6), 178 (54), 138 (28), 136 (31), 96 (32), 91 (8), 81 (100), 77 (6), 53 (14), 43 (18); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.35–1.60, 1.70–1.95 and 2.20–2.50 (m, 5H, 2H-5, H-6, 2H-7), 2.18 (brs, 3H, Ac), 3.32 (brd, 1H, *J*=15.3 Hz, H-2A), 4.77 (m, 1H, H-4), 4.89 (dd, 1H, *J*=1.5, 4.0 Hz, H-8), 5.14 (brd, 1H, *J*=15.3 Hz, H-2B), 6.28 (brdd, 1H, *J*=1.5, 5.8 Hz, H-9), 6.37 (d, 1H, *J*=5.8 Hz, H-10), 6.20 (dd, 1H, *J*=0.9, 3.4 Hz, H-β′), 6.27 (dd, 1H, *J*=1.8, 3.4 Hz, H-β), 7.33 (dd, 1H, *J*=0.9, 1.8 Hz, H-α).

Anal. Calcd. for $C_{15}H_{17}NO_3$: C, 69.49; H, 6.56; N, 5.40. Found: C, 69.65; H, 6.56; N, 5.46.

2-Methallyl-3-aza-4-oxo-10-oxatricyclo[5.2.1.0^{1,5}]dec-8-enes (**28a–f**). Typical Procedure.

Acryloyl chloride (9.0 mL, 0.11 mol) was added dropwise to a stirred solution of corresponding amine **11a–c** or **12a–c** (0.05 mol) and triethylamine (20.8 mL, 0.15 mol) in acetonitrile (100 mL). After the complete addition of acryloyl chloride the reaction mixture was refluxed for 6–8 h (TLC monitoring). The reaction mixture was cooled, poured into water (300 mL), basified with 25 % aqueous ammonia to pH ~10–11, extracted with chloroform (6×80 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Resulting residue was purified by column chromatography on Al_2O_3 (3.5 × 30 cm, using hexane/ethyl acetate, 10:1 as eluent) to give a mixture of isomers. Final separation of the isomers **28aA** and **28aB**, **28bA** and **28bB**, **28cA** and **28cB**, **28dA** was carried out by column chromatography of isomeric mixture (0.5 g) on Al_2O_3 (1.5 × 20 cm, using hexane/ethyl acetate, from 50:1 to 10:1 as eluent).

2-Methallyl-3-aza-4-oxo-3-phenyl-10-oxatricyclo[5.2.1.0^{1,5}]dec-8-ene (**28a**).

Yield 7.03 g (50%); ratio of isomers **A**/**B** = 6/1; ir: 1640 (C=C), and 1690 (N–C=O) cm^{-1}; ms: m/z M$^+$ 281 (10), 226 (42), 172 (100), 135 (11), 117 (7), 91 (6), 77 (12), 55 (22).

Anal. Calcd. for $C_{18}H_{19}NO_2$: C, 76.87; H, 6.76; N, 4.98. Found: C, 76.89; H, 6.74; N, 5.16.

Compound **28aA**.

Colourless oil, R_f 0.44 (ethyl acetate–hexane, 1:1); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.60 (dd, 1H, *J*=8.8, 11.8 Hz, H-6*endo*), 1.69 (s, 3H, Me-2′), 2.20 (ddd, 1H, *J*=3.4, 4.6, 11.8 Hz, H-6*exo*), 2.40 (dd, 1H, *J*=10.1, 16.1 Hz, H-3′B), 2.54 (dd, 1H, *J*=3.9, 16.1 Hz, H-3′A), 2.66 (dd, 1H, *J*=3.4, 8.8 Hz, H-5), 4.64 (dd, 1H, *J*=3.9, 10.1 Hz, H-2), 4.81 (brs, 1H, H-1′A), 4.86 (brs, 1H, H-1′B), 4.99 (dd, 1H, *J*=1.7, 4.6 Hz, H-7), 6.33 (dd, 1H, *J*=1.7, 5.9 Hz, H-8), 6.47 (d, 1H, *J*=5.9 Hz, H-9), 7.14 (d, 2H, *J*=7.8 Hz, H-Ph), 7.32 (brt, 1H, *J*=7.8 Hz, H-Ph), 7.43 (t, 2H, *J*=7.8 Hz, H-Ph). ^{13}C nmr ($CDCl_3$, 100.6 MHz) δ 173.1 (s, C-4), 140.4 (s, C-2′), 137.5 (s, C-1″), 136.4 (d, C-8, *J*=175.6 Hz), 132.0 (d, C-9, *J*=177.8 Hz), 128.7 (d, 2C, C-3″, 5″, *J*=162.5 Hz), 125.4 (d, C-4″, *J*=163.5 Hz), 123.1 (d, 2C, C-2″, 6″, *J*=161.8 Hz), 113.2 (t, C-1′, *J*=155.7 Hz), 91.3 (s, C-1), 78.2 (d, C-7, *J*=164.8 Hz), 59.4 (d, C-2, *J*=145.0 Hz), 46.6 (d, C-5, *J*=138.0 Hz), 37.7 (t, C-3′, *J*=127.0 Hz), 28.6 (t, C-6, *J*=138.0 Hz), 22.6 (q, Me-2′, *J*=126.3 Hz).

Compound **28aB**.

White crystals, mp 112–114 °C (ethyl acetate–hexane); R_f 0.34 (ethyl acetate–hexane, 1 : 1); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.61 (dd, 1H, *J*=8.8, 11.8 Hz, H-6*endo*), 1.71 (s, 3H, Me-2′), 2.27 (ddd, 1H, *J*=3.5, 4.5, 11.8 Hz, H-6*exo*), 2.28 (m, 2H, H-3′), 2.53 (dd, 1H, *J*=3.5, 8.8 Hz, H-5), 4.76 (dd, 1H, *J*=6.4, 8.2 Hz, H-2), 4.75 (brs, 1H, H-1′B), 4.80 (brs, 1H, H-1′A), 5.08 (dd, 1H, *J*=1.7, 4.5 Hz, H-7), 6.27 (dd, 1H, *J*=1.7, 5.8 Hz, H-8), 6.36 (d, 1H, *J*=5.8 Hz, H-9), 7.20 (t, 1H, *J*=7.8 Hz, H-Ph), 7.27 (d, 2H, *J*=7.8 Hz, H-Ph), 7.37 (t, 2H, *J*=7.8 Hz, H-Ph). ^{13}C nmr ($CDCl_3$, 100.6 MHz) δ 173.4 (s, C-4), 140.3 (s, C-2′), 136.7 (s, C-1″), 135.0 (d, C-8, *J*=175.5 Hz), 134.0 (d, C-9, *J*=177.0 Hz), 128.7 (d, 2C, C-3″, 5″, *J*=162.0 Hz), 126.1 (d, C-4″, *J*=162.7 Hz), 125.3 (d, 2C, C-2″, 6″, *J*=161.5 Hz), 113.6 (t, C-1′, *J*=155.8 Hz), 90.3 (s, C-1), 78.2 (d, C-7, *J*=165.0 Hz), 58.8 (d, C-2, *J*=140.5 Hz), 47.7 (d, C-5, *J*=136.8 Hz), 34.8 (t, C-3′, *J*=130.0 Hz), 28.6 (t, C-6, *J*=137.8 Hz), 23.0 (q, Me-2′, *J*=126.0 Hz).

2-Methallyl-3-aza-4-oxo-3-(4-methylphenyl)-10-oxatricyclo-[5.2.1.0^{1,5}]dec-8-ene (**28b**).

Yield 9.44 g (64%); ratio of isomers **A**/**B** = 2.7/1; ir: 1640 (C=C), and 1685 (N–C=O) cm^{-1}; ms: m/z M$^+$ 295 (34), 240 (38), 186 (100), 118 (6), 91 (16), 77 (4), 65 (8), 55 (22), 39 (7).

Anal. Calcd. for $C_{19}H_{21}NO_2$: C, 77.29; H, 7.12; N, 4.75. Found: C, 77.17; H, 7.15; N, 4.66.

Compound **28bA**.

White crystals, mp 106.5–108.5 °C (ethyl acetate–hexane); R_f 0.20 (ethyl acetate–hexane, 1:1); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.64 (dd, 1H, *J*=8.9, 11.8 Hz, H-6*endo*), 1.73 (s, 3H, Me-2′), 2.26 (ddd, 1H, *J*=3.3, 4.5, 11.8 Hz, H-6*exo*), 2.35 (s, 3H, Me-

4″), 2.42 (dd, 1H, *J*=10.3, 16.0 Hz, H-3′B), 2.58 (dd, 1H, *J*=3.8, 16.0 Hz, H-3′A), 2.57 (dd, 1H, *J*=3.3, 8.9 Hz, H-5), 4.62 (dd, 1H, *J*=3.8, 10.3 Hz, H-2), 4.84 (brs, 1H, H-1′A), 4.90 (m, 1H, H-1′B), 5.05 (dd, 1H, *J*=1.7, 4.5 Hz, H-7), 6.38 (dd, 1H, *J*=1.7, 5.9 Hz, H-8), 6.52 (d, 1H, *J*=5.9 Hz, H-9), 7.18 (BB′, 2H, *J*~8.2 Hz, H-Ph), 7.33 (AA′, 2H, *J*~8.2 Hz, H-Ph).

Compound **28bB**.

White crystals, mp 96–97.5 °C (ethyl acetate–hexane); R_f 0.14 (ethyl acetate–hexane, 1:1); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.65 (dd, 1H, *J*=8.8, 11.8 Hz, H-6*endo*), 1.74 (s, 3H, Me-2′), 2.30 (ddd, 1H, *J*=3.5, 4.5, 11.8 Hz, H-6*exo*), 2.35 (s, 3H, Me-4″), 2.30 (d, 2H, *J*=7.4 Hz, H-3′), 2.68 (dd, 1H, *J*=3.5, 8.8 Hz, H-5), 4.75 (t, 1H, *J*=7.4 Hz, H-2), 4.77 (dd, 1H, *J*=0.8, 1.4 Hz, H-1′B), 4.83 (t, 1H, *J*=0.8 Hz, H-1′A), 5.12 (dd, 1H, *J*=1.7, 4.5 Hz, H-7), 6.30 (dd, 1H, *J*=1.7, 5.8 Hz, H-8), 6.39 (d, 1H, *J*=5.8 Hz, H-9), 7.15–7.22 (AA′BB′, 4H, H-Ph).

2-Methallyl-3-aza-4-oxo-3-(4-methoxyphenyl)-10-oxatricyclo-[5.2.1.0^{1,5}]dec-8-ene (**28c**).

Yield 10.26 g (66%); ratio of isomers **A**/**B** = 2/1; ir: 1640 (C=C), and 1685 (N–C=O) cm^{-1}; ms: m/z M$^+$ 311 (48), 256 (28), 202 (100), 186 (9), 117 (8), 77 (10), 65 (4), 55 (29), 39 (7).

Anal. Calcd. for $C_{19}H_{21}NO_3$: C, 73.31; H, 6.75; N, 4.50. Found: C, 73.15; H, 6.83; N, 4.47.

Compound **28cA**.

White crystals, mp 91.5–92 °C (ethyl acetate–hexane); R_f 0.47 (ethyl acetate–hexane, 1:1); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.60 (dd, 1H, *J*=8.9, 11.8 Hz, H-6*endo*), 1.68 (s, 3H, Me-2′), 2.21 (ddd, 1H, *J*=3.4, 4.5, 11.8 Hz, H-6*exo*), 2.39 (dd, 1H, *J*=4.1, 15.9 Hz, H-3′A), 2.54 (dd, 1H, *J*=10.0, 15.9 Hz, H-3′B), 2.64 (dd, 1H, *J*=3.4, 8.9 Hz, H-5), 3.75 (s, 3H, OMe-4″), 4.54 (dd, 1H, *J*=4.1, 10.0 Hz, H-2), 4.80 (brd, 1H, *J*=0.8 Hz, H-1′A), 4.85 (brd, 1H, *J*=0.8 Hz, H-1′B), 5.01 (dd, 1H, *J*=1.7, 4.5 Hz, H-7), 6.34 (dd, 1H, *J*=1.7, 6.0 Hz, H-8), 6.47 (d, 1H, *J*=6.0 Hz, H-9), 6.86 (BB′, 2H, *J*~8.9 Hz, H-Ph), 7.29 (AA′, 2H, *J*~8.9 Hz, H-Ph); ^{13}C nmr ($CDCl_3$, 100.6 MHz) δ 173.2 (s, C-4), 157.4 (s, C-4″), 140.6 (s, C-2′), 136.4 (d, C-8, *J*=175.5 Hz), 132.2 (d, C-9, *J*=177.5 Hz), 130.4 (s, C-1″), 125.6 (d, 2C, C-2″ and 6″, *J*=160.5 Hz), 114.1 (d, 2C, C-3″ and 5″, *J*=160.5 Hz), 113.2 (t, C-1′, *J*=155.5 Hz), 91.6 (s, C-1), 78.3 (d, C-7, *J*=164.5 Hz), 60.2 (d, C-2, *J*=144.8 Hz), 55.2 (q, OMe-4″, *J*=144.0 Hz), 46.3 (d, C-5, *J*=137.7 Hz), 38.0 (t, C-3′, *J*=127.5 Hz), 28.6 (t, C-6, *J*=138.0 Hz), 22.6 (q, Me-2′, *J*=126.2 Hz).

Compound **28cB**.

Pale yellow oil, R_f 0.36 (ethyl acetate–hexane, 1:1); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.60 (dd, 1H, *J*=8.8, 11.8 Hz, H-6*endo*), 1.69 (s, 3H, Me-2′), 2.22 (dd, 1H, *J*=10.2, 13.8 Hz, H-3′B), 2.25 (ddd, 1H, *J*=3.5, 4.5, 11.8 Hz, H-6*exo*), 2.27 (dd, 1H, *J*=4.5, 13.8 Hz, H-3′A), 2.52 (dd, 1H, *J*=3.5, 8.8 Hz, H-5), 3.76 (s, 3H, OMe-4″), 4.67 (dd, 1H, *J*=4.5, 10.2 Hz, H-2), 4.72 (brs, 1H, H-1′B), 4.78 (m, 1H, H-1′A), 5.07 (dd, 1H, *J*=1.7, 4.5 Hz, H-7), 6.26 (dd, 1H, *J*=1.7, 5.8 Hz, H-8), 6.35 (d, 1H, *J*=5.8 Hz, H-9), 6.89 (BB′, 2H, *J*~8.9 Hz, H-Ph), 7.15 (AA′, 2H, *J*~8.9 Hz, H-Ph); ^{1}H nmr (C_6D_6, 400 MHz) δ 1.35 (dd, 1H, $J_{6endo,6exo}$=11.7, $J_{5,6endo}$=8.7 Hz, H-6*endo*), 1.71 (s, 3H, Me-2′), 2.31 (dd, 1H, $J_{5,6endo}$=8.7, $J_{5,6exo}$=3.5 Hz, H-5), 2.42 (ddd, 1H, $J_{6endo,6exo}$=11.8, $J_{7,6exo}$=4.5, $J_{5,6exo}$=3.5 Hz, H-6*exo*), 2.49 (dd, 1H, $J_{2,3'A}$=3.6, $J_{3'A,3'B}$=13.7 Hz, H-3′A), 2.62 (dd, 1H, $J_{2,3'B}$=10.9, $J_{3'A,3'B}$=13.7 Hz, H-3′B), 3.40 (s, 3H, OMe-4″), 4.45 (dd, 1H, $J_{2,3'B}$=10.9, $J_{2,3'A}$=3.6 Hz, H-2), 4.73 (dd, 1H, $J_{7,8}$=1.7, $J_{7,6exo}$=4.5 Hz, H-7), 4.94 (brs, 1H, H-1′), 4.95 (brs, 1H, H-1′), 5.82 (dd, 1H, $J_{8,9}$=5.8, $J_{7,8}$=1.7 Hz, H-8), 6.05 (d, 1H, ^3J=5.8 Hz, H-9), 6.89 (BB′, 2H, H-3″ and H-5″), 7.39 (AA′, 2H, H-2″ and H-6″); ^{13}C nmr ($CDCl_3$, 100.6 MHz) δ 173.7 (s, C-4), 157.9 (s, C-4″), 140.3 (s, C-2′), 135.0 (d, C-8, *J*=175.0 Hz), 134.0 (d, C-9, *J*=176.5 Hz), 129.4 (s, C-1″), 127.1 (d, 2C, C-2″ and 6″, *J*=160.3 Hz), 114.1 (d, 2C, C-3″ and 5″, *J*=160.0 Hz), 113.6 (t, C-1′, *J*=155.8 Hz), 90.5 (s, C-1), 78.3 (d, C-7, *J*=164.5 Hz), 59.2 (d, C-2, *J*=140.0 Hz), 55.2 (q, OMe-4″, *J*=144.2 Hz), 47.6 (d, C-5, *J*=137.0 Hz), 35.0 (t, C-3′, *J*=128.5 Hz), 28.5 (t, C-6, *J*=137.5 Hz), 23.0 (q, Me-2′, *J*=126.3 Hz).

2-Methallyl-3-aza-4-oxo-3-benzyl-10-oxatricyclo[5.2.1.0^{1,5}]dec-8-ene (**28d**).

Colourless oil, yield 12.68 g (86%); ratio of isomers **A**/**B** = 10/1; ir: 1640 (C=C), and 1685 (N–C=O) cm^{-1}; R_f 0.17 (ethyl acetate–hexane, 1:5); ms: m/z M$^+$ 295 (9), 240 (53), 186 (100), 160 (4), 134 (2), 106 (8), 91 (84), 65 (8), 55 (24), 27 (4); ^{1}H nmr ($CDCl_3$, 400 MHz, isomer **A**) δ 1.60 (dd, 1H, *J*=8.8, 11.6 Hz, H-6*endo*), 1.70 (s, 3H, Me-2′), 2.24 (ddd, 1H, *J*=2.9, 4.5, 11.6 Hz, H-6*exo*), 2.37 (dd, 1H, *J*=8.1, 15.3 Hz, H-3′B), 2.51 (dd, 1H, *J*=5.7, 15.3 Hz, H-3′A), 2.56 (dd, 1H, *J*=2.9, 8.8 Hz, H-5), 3.89 (dd, 1H, *J*=5.7, 8.1 Hz, H-2), 4.05 (d, 1H, *J*=15.3 Hz, NCH_2-B), 4.82 (brs, 1H, H-1′A), 4.90 (brs, 1H, H-1′B), 5.03 (dd, 1H, *J*=1.6, 4.5 Hz, H-7), 5.10 (d, 1H, *J*=15.3 Hz, NCH_2-A), 6.33 (dd, 1H, *J*=1.6, 5.9 Hz, H-8), 6.43 (d, 1H, *J*=5.9 Hz, H-9), 7.19–7.33 (m, 5H, H-Ph). *Anal*. Calcd. for $C_{19}H_{21}NO_2$: C, 77.29; H, 7.12; N, 4.75. Found: C, 77.41; H, 7.18; N, 4.76.

2-Methallyl-3-aza-4-oxo-3-(4-methylbenzyl)-10-oxatricyclo-[5.2.1.0^{1,5}]dec-8-ene (**28e**).

Yield 10.51 g (68%); ratio of isomers **A**/**B** = 8.4/1; ir: 1645 (C=C), and 1680 (N–C=O) cm^{-1}; ms: m/z M$^+$ 309 (12), 254 (16), 200 (20), 174 (7), 120 (27), 105 (100), 90 (4), 64 (4), 54 (12), 38 (5).

Anal. Calcd. for $C_{20}H_{23}NO_2$: C, 77.67; H, 7.44; N, 4.53. Found: C, 77.61; H, 7.40; N, 4.34.

Compound **28eA**.

White crystals, mp 101.5–103 °C (ethyl acetate–hexane); R_f 0.35 (ethyl acetate–hexane, 1:1); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.60 (dd, 1H, *J*=8.8, 11.7 Hz, H-6*endo*), 1.72 (s, 3H, Me-2′), 2.24 (ddd, 1H, *J*=3.3, 4.4, 11.7 Hz, H-6*exo*), 2.30 (s, 3H, Me-4″), 2.37 (dd, 1H, *J*=8.3, 15.1 Hz, H-3′B), 2.52 (dd, 1H, *J*=5.7, 15.1 Hz, H-3′A), 2.57 (dd, 1H, *J*=3.3, 8.8 Hz, H-5), 3.87 (dd, 1H, *J*=5.7, 8.3 Hz, H-2), 4.00 (d, 1H, *J*=15.4 Hz, NCH_2-B), 4.83 (s, 1H, H-1′A), 4.91 (brs, 1H, H-1′B), 5.03 (dd, 1H, *J*=1.3, 4.4 Hz, H-7), 5.07 (d, 1H, *J*=15.4 Hz, NCH_2-A), 6.34 (dd, 1H, *J*=1.3, 5.9 Hz, H-8), 6.44 (d, 1H, *J*=5.9 Hz, H-9), 7.10 (s, 4H, H-Ph).

Compound **28eB**.

Pale yellow oil, R_f 0.44 (ethyl acetate–hexane, 1:1); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.59 (dd, 1H, *J*=8.8, 11.8 Hz, H-6*endo*), 1.59 (s, 3H, Me-2′), 2.21 (ddd, 1H, *J*=3.5, 4.6, 11.8 Hz, H-6*exo*), 2.32 (s, 3H, Me-4″), 2.37 (dd, 1H, *J*=10.2, 13.6 Hz, H-3′B), 2.40 (dd, 1H, *J*=3.5, 8.8 Hz, H-5), 2.47 (dd, 1H, *J*=4.6, 13.6 Hz, H-3′A), 4.03 (d, 1H, *J*=15.2 Hz, NCH_2-B), 4.07 (dd, 1H, *J*=4.6, 10.2 Hz, H-2), 4.69 (brs, 1H, H-1′B), 4.78 (brs, 1H, H-1′A), 4.89 (d, 1H, *J*=15.2 Hz, NCH_2-A), 5.03 (dd, 1H, *J*=0.9, 4.6 Hz, H-7), 6.24 (m, 2H, H-8 and H-9), 7.12 (s, 4H, H-Ph).

2-Methallyl-3-aza-4-oxo-3-(4-methoxybenzyl)-10-oxatricyclo-[5.2.1.0^{1,5}]dec-8-ene (**28f**).

White crystals, yield 14.14 g (87%); ratio of isomers **A**/**B** = 4.5/1 (inseparable mixture of isomers); mp 57.5–64 °C (ethyl acetate–hexane); R_f 0.25 (ethyl acetate–hexane, 1:3); ir: 1640 (C=C), and 1675 (N–C=O) cm^{-1}; ms: m/z M$^+$ 325 (24), 270 (6), 217 (6), 136 (21), 121 (100), 91 (4), 77 (7), 55 (18), 39 (4); ^{1}H nmr ($CDCl_3$, 400 MHz, isomer **A**) δ 1.60 (dd, 1H, J=8.9, 11.7 Hz, H-6*endo*), 1.71 (s, 3H, Me-2′), 2.23 (ddd, 1H, J=3.5, 4.5, 11.7 Hz, H-6*exo*), 2.36 (dd, 1H, J=8.3, 15.2 Hz, H-3′B), 2.51 (dd, 1H, J=5.7, 15.2 Hz, H-3′A), 2.56 (brdd, 1H, J=3.5, 8.9 Hz, H-5), 3.76 (s, 3H, OMe-4′′), 3.87 (dd, 1H, J=5.7, 8.3 Hz, H-2), 3.98 (d, 1H, J=15.4 Hz, NCH_2-B), 4.82 (brs, 1H, H-1′A), 4.90 (brs, 1H, H-1′B), 5.02 (dd, 1H, J=1.7, 4.5 Hz, H-7), 5.04 (d, 1H, J=15.4 Hz, NCH_2-A), 6.33 (dd, 1H, J=1.7, 5.9 Hz, H-8), 6.43 (d, 1H, J=5.9 Hz, H-9), 6.83 (BB′, 2H, H-Ph), 7.12 (AA′, 2H, H-Ph).

Anal. Calcd. for $C_{20}H_{23}NO_3$: C, 73.85; H, 7.08; N, 4.31. Found: C, 73.75; H, 7.12; N, 4.30.

4-*N*-Phenylamino-*N*-acryloyl-4-(2-furyl)butene-1 (**27a**).

Was isolated along with **28a** (see Scheme 6). White crystals, yield 3.51 g (25%); mp 65.5–66.5 °C (ethyl acetate–hexane); R_f 0.68 (ethyl acetate–hexane, 1 : 3); ir: 1645 (N–C=O and C=C) cm^{-1}; ms: m/z M$^+$ 281 (13), 238 (3), 226 (44), 172 (100), 161 (2), 148 (3), 135 (18), 117 (10), 107 (3), 91 (8), 77 (13), 65 (2), 55 (23), 39 (3), 27 (4); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.79 (s, 3H, Me-2), 2.43 (dd, 1H, $J_{3A,3B}$=14.7, $J_{3B,4}$=8.6 Hz, H-3B), 2.54 (dd, 1H, $J_{3A,3B}$=14.7, $J_{3A,4}$=6.7 Hz, H-3A), 4.80 (brs, 2H, H-1B), 4.85 (brs, 2H, H-1A), 5.48 (dd, 1H, $J_{2',1'cis}$=10.3, $J_{1'cis,1'trans}$=2.0 Hz, H-1′*cis*), 5.81 (dd, 1H, $J_{2',1'cis}$=10.3, $J_{2',1'trans}$=16.8 Hz, H-2′), 6.08 (brd, 1H, $J_{\beta,\beta'}$=3.2 Hz, H-β′), 6.25 (dd, 1H, $J_{\beta,\beta'}$=3.2, $J_{\alpha,\beta}$=1.7 Hz, H-β), 6.39 (dd, 1H, $J_{1'cis,1'trans}$=2.0, $J_{1'trans,2'}$=16.8 Hz, H-1′*trans*), 6.43 (dd, 1H, $J_{4,3A}$=6.7, $J_{4,3B}$=8.6 Hz, H-4), 7.20–7.32 (m, 5H, H-Ph), 7.37 (dd, 1H, $J_{\alpha,\beta}$=1.7, $J_{\alpha,\beta'}$=0.7 Hz, H-α).

Anal. Calcd. for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.79; H, 6.75; N, 4.90.

Compounds **9A** and **9B** were synthesized earlier [3].

2-Methallyl-3-aza-3-benzyl-10-oxatricyclo[5.2.1.0^{1,5}]dec-8-en (**29**) and *N*-Allyl-2-methyl-4-*N*-benzylamino-4-(2′-furyl)but-1-en (**30**).

Potash (7.38 g, 0.054 mol) and allylbromide (3.72 mL, 0.043 mol) were added to a solution of amine **12a** (8.59 g, 0.036 mol) in 80 mL of acetone. The reaction mixture was refluxed for 3 h (TLC monitoring). Inorganic precipitate was filtered off and washed with acetone (2 × 60 mL). The residue obtained after acetone evaporation was refluxed in toluene (50 mL) for 4 h (TLC monitoring). Toluene was removed *in vacuo*, products **29**, **30** were separated by column chromatography on Al_2O_3 (2.5 × 25 cm, using hexane as eluent). In case of *N*-allylderivative **30** the eluent was removed under reduced pressure at room temperature.

Compound **29**.

Colourless viscous oil; yield 46% (4.65 g); R_f 0.37 (ethyl acetate–hexane, 1:100); ir: 1640 (C=C) cm^{-1}; ms: m/z [M–55]$^+$ 226 (93), 131 (3), 117 (2), 91 (100), 81 (3), 65 (6), 41 (9), 28 (4); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.28 (dd, 1H, $J_{6exo,6endo}$=11.4, $J_{6endo,5}$=7.5 Hz, H-6*endo*), 1.67 (ddd, 1H, $J_{6exo,6endo}$=11.4, $J_{6exo,7}$=4.4, $J_{6exo,5}$=3.0 Hz, H-6*exo*), 1.83 (s, 3H, Me-2′), 1.97 (dddd, 1H, $J_{4ax,5}$=10.5, $J_{4eqv,5}$=6.6, $J_{6endo,5}$=7.5, $J_{6exo,5}$=3.0 Hz, H-5*endo*), 2.09 (dd, 1H, $J_{4eqv,4ax}$=8.5, $J_{4ax,5}$=10.5 Hz, H-4*ax*), 2.43 (dd, 1H, $J_{A,B}$=15.3, $J_{2,3'A}$=5.8 Hz, H-3′A), 2.48 (dd, 1H, $J_{A,B}$=15.3, $J_{2,3'B}$=8.1 Hz, H-3′B), 3.11 (dd, 1H, $J_{4eqv,4ax}$=8.5, $J_{4eqv,5}$=6.6 Hz, H-4*eqv*), 3.11 (dd, 1H, $J_{2,3'B}$=8.1, $J_{2,3'A}$=5.8 Hz, H-2), 3.47 (d, 1H, $J_{A,B}$=12.8 Hz, NCH_2-B), 4.05 (d, 1H, $J_{A,B}$=12.8 Hz, NCH_2-A), 4.88 (s, 1H, H-1′A), 4.91 (s, 1H, H-1′B), 4.98 (dd, 1H, $J_{7,6exo}$=4.4, $J_{8,7}$=1.7 Hz, H-7), 6.23 (dd, 1H, $J_{8,9}$=5.9, $J_{8,7}$=1.7 Hz, H-8), 6.43 (d, 1H, $J_{8,9}$=5.9 Hz, H-9), 7.24–7.33 (m, 5H, H-Ph).

Anal. Calcd. for $C_{19}H_{23}NO$: C, 81.10; H, 8.24; N, 4.98. Found: C, 81.23; H, 8.39; N, 5.11.

Compound **30**.

Colourless oil, yield 10% (1.01 g); R_f 0.78 (ethyl acetate–hexane, 1:100); ir: 1645 (C=C) cm^{-1}; ms: m/z [M–55]$^+$ 226 (100), 131 (3), 91 (64), 68 (3), 41 (4); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.64 (brs, 3H, Me-2), 2.55 (dd, 1H, $J_{A,B}$=14.1, $J_{3B,4}$=7.7 Hz, H-3B), 2.67 (ddd, 1H, $J_{A,B}$=14.1, $J_{3A,4}$=7.7, $J_{3A,1}$=0.7 Hz, H-3A), 2.80 (dd, 1H, $J_{3'A,3'B}$=14.2, $J_{3'B,2'}$=8.0 Hz, H-3′B), 3.19 (d, 1H, $J_{A,B}$=13.9 Hz, NCH_2Ph-B), 3.29 (ddt, 1H, $J_{3'A,3'B}$=14.2, $J_{3'A,2'}$=4.7, $J_{3'A,1'}$=1.6 Hz, H-3′A), 4.05 (t, 1H, $J_{4,3}$=7.7 Hz, H-4), 3.92 (d, 1H, $J_{A,B}$=13.9 Hz, NCH_2Ph-A), 4.69 (dq, 1H, $J_{1,1}$=1.0, $J_{1trans,Me}$=2.0 Hz, H-1*trans*), 4.76 (brs, 1H, $J_{1,1}$=1.0 Hz, H-1*cis*), 5.12 (ddd, 1H, $J_{2',1'cis}$=10.2, $J_{1'cis,3'A}$=1.6, $J_{1',1'}$=0.9 Hz, H-1′*cis*), 5.12 (ddd, 1H, $J_{2',1'trans}$=17.3, $J_{1'trans,3'A}$=1.6, $J_{1',1}$=0.9 Hz, H-1′*trans*), 5.81 (dddd, 1H, $J_{2',1'trans}$=17.3, $J_{2',1'cis}$=10.2, $J_{2',3'B}$=8.0, $J_{2',3'A}$=4.7 Hz, H-2′), 6.15 (dd, 1H, $J_{\beta,\beta'}$=3.1, $J_{\alpha,\beta'}$=0.9 Hz, H-β′), 6.36 (dd, 1H, $J_{\beta,\beta'}$=3.1, $J_{\alpha,\beta}$=1.8 Hz, H-β), 7.22–7.39 (m, 5H, H-Ph), 7.42 (dd, 1H, $J_{\alpha,\beta}$=1.8, $J_{\alpha,\beta'}$=0.9 Hz, H-α).

Anal. Calcd. for $C_{19}H_{23}NO$: C, 81.10; H, 8.24; N, 4.98. Found: C, 81.20; H, 8.21; N, 4.99.

2-Methallyl-3-aza-3-phenyl-10-oxatricyclo[5.2.1.0^{1,5}]dec-8-en (**31**).

Sodium iodide dihydrate (7.66 g, 0.041 mol) was added to a solution of allylbromide (3.5 mL, 0.04 mol) in 60 mL of acetone and the reaction mixture was stirred for 1 h at 22 °C. Then potash (7.33 g, 0.053 mol) and amine **11a** (3.0 g, 0.013 mol) were added and the reaction mass was refluxed for 18 h until the disappearance of the starting material spot (TLC control). The inorganic precipitate was filtered off and washed with acetone (2 × 50 mL). The residue obtained after acetone evaporation was purified by column chromatography on Al_2O_3 (4.5 × 30 cm, using hexane as eluent).

Compound **31**.

Viscous yellow oil; yield 48% (1.67 g); ratio of isomers 10/1; R_f 0.41 (ethyl acetate–hexane, 1:50); ir: 1640 (C=C) cm^{-1}; ms: m/z M$^+$ 267 (18), 212 (100), 171 (16), 144 (10), 115 (7), 104 (34), 91 (11), 77 (49), 65 (9), 51 (20), 39 (29); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.55 (dd, 1H, $J_{6exo,6endo}$=11.5, $J_{6endo,5}$=7.5 Hz, H-6*endo*), 1.90 (ddd, 1H, $J_{6exo,6endo}$=11.5, $J_{6exo,7}$=4.5, $J_{6exo,5}$=2.5 Hz, H-6*exo*), 1.90 (s, 3H, Me-2′), 2.25 (dd, 1H, $J_{A',B'}$=17.3, $J_{2,3'B}$=10.8 Hz, H-3′B), 2.34 (ddt, 1H, $J_{4ax,5}$=$J_{4eqv,5}$=8.7, $J_{6endo,5}$=7.5, $J_{6exo,5}$=2.5 Hz, H-5*endo*), 2.69 (brdd, 1H, $J_{A',B'}$=17.3, $J_{2,3'A}$=1.8 Hz, H-3′A), 2.92 (t, 1H, $J_{4eqv,4ax}$=$J_{4ax,5}$=8.7 Hz, H-4*ax*), 3.87 (t, 1H, $J_{4eqv,4ax}$=$J_{4eqv,5}$=8.7 Hz, H-4*eqv*), 4.24 (dd, 1H, $J_{2,3'B}$=10.8, $J_{2,3'A}$=1.8 Hz, H-2), 4.94 (brs, 1H, H-1′A), 5.00 (brs, 1H, H-1′B), 5.03 (dd, 1H, $J_{7,6exo}$=4.5, $J_{8,7}$=1.7 Hz, H-7), 6.38 (dd, 1H, $J_{8,9}$=5.9, $J_{8,7}$=1.7 Hz, H-8), 6.50 (d, 1H, $J_{8,9}$=5.9 Hz, H-9),

6.59 (d, 2H, $J_{m,o}$=7.8 Hz, H-Ph*ortho*), 6.70 (t, 1H, $J_{m,p}$=7.3 Hz, H-Ph*para*), 7.25 (dd, 2H, $J_{m,o}$=7.8, $J_{m,p}$=7.3 Hz, H-Ph*metha*).

Anal. Calcd. for $C_{18}H_{21}NO$: C, 81.86; H, 7.92; N, 5.24. Found: C, 81.81; H, 7.94; N, 5.33.

Isoindolo[2,1-*a*]quinolines **32a–c** and Isoindolo[2,1-*b*][2]benzazepines **33a–c**, **34b,c**.

Typical Procedure.

A mixture of corresponding adduct **28** (0.01 mol) and 30 mL of PPA was stirred for 1–2 h (TLC monitoring) at 90–110 °C (TLC monitoring). At the end of the reaction, the mixture was cooled and diluted with water (100 mL). After that four 60-mL extractions with chloroform were performed. The organic layers were combined, dried ($MgSO_4$) and concentrated. The resulting residue was purified by chromatography on Al_2O_3 (2.5 × 20 cm, using hexane/ethyl acetate, 5:1 as eluent) to obtain the products **32a–c**, **33a** as white crystals. In case of adduct **28e** cyclization the obtained isomeric mixture (**33b**/**34b** = 1/3) was three times recrystallized (hexane–ethyl acetate) to isolate the desired product **34b**. The mother solution contained the isomeric mixture **33b**/**34b** in ratio 1/3.5.

5,5-Dimethyl-5,6,6a,11-tetrahydro-11-oxoisoindolo[2,1-*a*]quinoline (**32a**).

White crystals, yield 1.60 g (61%); mp 118–119 °C (hexane–ethyl acetate); R_f 0.66 (ethyl acetate–hexane, 2:1); ir: 1675 (N–C=O) cm^{-1}; ms: m/z M^+ 263 (47), 248 (100), 232 (13), 222 (5), 204 (7), 115 (11), 91 (7), 77 (8), 39 (3); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.41 (s, 3H, Me-5), 1.49 (s, 3H, Me-5), 1.63 (dd, 1H, *J*=12.9, 13.1 Hz, H-6*ax*), 2.29 (dd, 1H, *J*=2.7, 13.1 Hz, H-6*eq*), 4.81 (dd, 1H, *J*=2.7, 12.9 Hz, H-6a), 7.14 (dt, 1H, *J*=1.3, 7.5 Hz, H-3), 7.29 (dt, 1H, *J*=1.5, 7.5 Hz, H-2), 7.41 (dd, 1H, *J*=1.5, 7.6 Hz, H-4), 7.48–7.52 (m, 2H, H-7 and H-9), 7.60 (dt, 1H, *J*=1.2, 7.4 Hz, H-8), 7.94 (dd, 1H, *J*=1.2, 8.3 Hz, H-10), 8.50 (dt, 1H, *J*=1.3, 7.5 Hz, H-1); ^{13}C nmr ($CDCl_3$, 100.6 MHz) δ 165.6 (C=O), 144.4 (s), 134.9 (s), 134.5 (s), 132.5 (s), 131.8 (d), 128.2 (d), 126.6 (d), 126.5 (d), 124.0 (d), 123.9 (d), 121.6 (d), 120.3 (d), 55.4 (d, C-6a), 43.4 (t, C-6), 33.4 (s, C-5), 32.1 (q, Me-5), 30.8 (q, Me-5).

Anal. Calcd. for $C_{18}H_{17}NO$: C, 82.13; H, 6.46; N, 5.32. Found: C, 82.20; H, 6.48; N, 5.39.

3,5,5-Trimethyl-5,6,6a,11-tetrahydro-11-oxoisoindolo[2,1-*a*]-quinoline (**32b**).

White crystals, yield 1.94 g (70%); mp 187.5–189 °C (hexane–ethyl acetate); R_f 0.58 (ethyl acetate–hexane, 3:1); ir: 1685 (N–C=O) cm^{-1}; ms: m/z M^+ 277 (54), 262 (100), 247 (21), 232 (16), 218 (5), 124 (5), 108 (6), 102 (4), 77 (6), 51 (2); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.40 (s, 3H, Me-5), 1.48 (s, 3H, Me-5), 1.61 (dd, 1H, *J*=12.6, 13.2 Hz, H-6*ax*), 2.28 (dd, 1H, *J*=1.6, 13.2 Hz, H-6*eq*), 2.35 (s, 3H, Me-3), 4.79 (dd, 1H, *J*=1.6, 12.6 Hz, H-6a), 7.10 (dd, 1H, *J*=1.5, 8.3 Hz, H-2), 7.20 (d, 1H, *J*=1.5 Hz, H-4), 7.48–7.52 (m, 2H, H-7 and H-9), 7.58 (dt, 1H, *J*=1.2, 7.9 Hz, H-8), 7.93 (dd, 1H, *J*=1.2, 7.9 Hz, H-10), 8.38 (d, 1H, *J*=8.3 Hz, H-1).

Anal. Calcd. for $C_{19}H_{19}NO$: C, 82.31; H, 6.86; N, 5.05. Found: C, 82.29; H, 6.82; N, 5.10.

5,5-Dimethyl-5,6,6a,11-tetrahydro-3-methoxy-11-oxoisoindolo-[2,1-*a*]quinoline (**32c**).

White crystals, yield 1.87 g (64%); mp 146.5–148 °C (hexane–ethyl acetate); R_f 0.67 (ethyl acetate–hexane, 1:1); ir: 1680 (N–C=O) cm^{-1}; ms: m/z M^+ 293 (72), 278 (100), 263 (20), 248 (6), 235 (10), 220 (5), 207 (8), 191 (4), 146 (3), 131 (3), 115 (3), 103 (5), 89 (4), 77 (8), 63 (3), 51 (2); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.40 (s, 3H, Me-5), 1.48 (s, 3H, Me-5), 1.62 (dd, 1H, *J*=12.9, 13.3 Hz, H-6*ax*), 2.28 (dd, 1H, *J*=2.6, 13.3 Hz, H-6*eq*), 3.83 (s, 3H, OMe-3), 4.79 (dd, 1H, *J*=2.6, 12.9 Hz, H-6a), 6.86 (dd, 1H, *J*=2.9, 9.0 Hz, H-2), 6.94 (d, 1H, *J*=2.9 Hz, H-4), 7.48–7.51 (m, 2H, H-7 and H-9), 7.59 (dt, 1H, *J*=1.2, 7.9 Hz, H-8), 7.92 (dd, 1H, *J*=1.2, 7.9 Hz, H-10), 8.43 (d, 1H, *J*=9.0 Hz, H-1).

Anal. Calcd. for $C_{19}H_{19}NO_2$: C, 77.82; H, 6.48; N, 4.78. Found: C, 77.78; H, 6.45; N, 4.79.

13,13-Dimethyl-7-oxo-5,11b,12,13-tetrahydro-7*H*-isoindolo-[2,1-*b*][2]benzazepine (**33a**).

White crystals, yield 1.69 g (61%); mp 106.5–108.5 °C (hexane–ethyl acetate); R_f 0.46 (ethyl acetate–hexane, 1:1); ir: 1680 (N–C=O) cm^{-1}; ms: m/z M^+ 277 (100), 262 (22), 234 (23), 221 (11), 193 (6), 145 (17), 132 (24), 129 (15), 115 (10), 103 (5), 91 (18), 77 (5); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.54 (s, 3H, Me-13), 1.61 (s, 3H, Me-13), 1.59 (dd, 1H, $J_{12ax,12eqv}$=14.1, $J_{11b,12ax}$=12.0 Hz, H-12*ax*), 2.27 (dd, 1H, $J_{12ax,12eqv}$=14.1, $J_{11b,12eqv}$=3.2 Hz, H-12*eqv*), 4.70 (d, 1H, $J_{A,B}$=15.5 Hz, H-5B), 4.91 (dd, 1H, $J_{11b,12ax}$=12.0, $J_{11b,12eqv}$=3.2 Hz, H-11b), 5.32 (d, 1H, $J_{A,B}$=15.5 Hz, H-5A), 7.19 (dt, 1H, $J_{9,10}$=$J_{8,9}$=7.7, $J_{9,11}$=1.0 Hz, H-9), 7.24 (dd, 1H, $J_{10,11}$=7.7, $J_{9,11}$=1.5 Hz, H-11), 7.37–7.43 (m, 4H), 7.51 (dt, 1H, $J_{9,10}$=$J_{10,11}$=7.7, $J_{8,10}$=1.0 Hz, H-10), 7.82 (d, 1H, $J_{8,9}$=8.1 Hz, H-8).

Anal. Calcd. for $C_{19}H_{19}NO$: C, 82.31; H, 6.86; N, 5.05. Found: C, 82.27; H, 6.81; N, 5.15.

2,13,13-Trimethyl-7-oxo-5,11b,12,13-tetrahydro-7*H*-isoindolo-[2,1-*b*][2]benzazepine (**33b**) and 3,13,13-Trimethyl-7-oxo-5,11b,12,13-tetrahydro-7*H*-isoindolo[2,1-*b*][2]benzazepine (**34b**). Total yield of the isomers mixture 0.76 g (26%). Ratio of isomers **33b**/**34b** = 1/3.

Compound **33b**.

Was isolated along with **34b**. ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.52 (s, 3H, Me-13), 1.56 (dd, 1H, $J_{12ax,12eqv}$=14.1, $J_{11b,12ax}$=12.0 Hz, H-12*ax*), 1.58 (s, 3H, Me-13), 2.24 (dd, 1H, $J_{12ax,12eqv}$=14.1, $J_{11b,12eqv}$=3.2 Hz, H-12*eqv*), 2.30 (s, 3H, Me-2), 4.62 (d, 1H, $J_{A,B}$=15.5 Hz, H-5B), 4.87 (dd, 1H, $J_{11b,12ax}$=12.0, $J_{11b,12eqv}$=3.2 Hz, H-11b), 5.27 (d, 1H, $J_{A,B}$=15.5 Hz, H-5A), 6.98 (dd, 1H, $J_{3,4}$=7.6, $J_{1,3}$=1.5 Hz, H-3), 7.17 (d, 1H, $J_{1,3}$=1.5 Hz, H-1), 7.28 (d, 1H, $J_{4,3}$=7.6 Hz, H-4), 7.39 (d, 1H, $J_{10,11}$=7.5 Hz, H-11), 7.39 (t, 1H, $J_{8,9}$=$J_{10,9}$=7.5 Hz, H-9), 7.49 (dt, 1H, $J_{10,9}$=$J_{10,11}$=7.5, $J_{8,10}$=1.5 Hz, H-10), 7.78 (dd, 1H, $J_{8,9}$=7.5, $J_{8,10}$=1.5 Hz, H-8); ^{13}C nmr ($CDCl_3$, 100.6 MHz) δ 166.4 (s, N-C=O), 146.4 (s), 145.7 (s), 137.2 (s), 133.0 (s), 131.8 (s), 131.1 (d), 131.0 (d), 127.9 (d), 127.1 (d), 127.0 (d), 123.6 (d), 121.4 (d), 59.3 (d, C-11b), 47.1 (t, C-12), 46.1 (t, C-5), 37.5 (s, C-13), 32.6 (q, Me-13), 25.7 (q, Me-13), 21.2 (q, Me-2).

Compound **34b**.

White crystals, yield 0.38 g (13%); mp 150.5–152 °C (hexane–ethyl acetate); R_f 0.57 (ethyl acetate–hexane, 1:1); ir: 1675 (N–C=O) cm^{-1}; ms: m/z M^+ 291 (100), 276 (31), 248 (55), 235 (13), 220 (10), 207 (8), 186 (14), 159 (26), 146 (33), 129 (30), 115 (22),

105 (29), 91 (14), 77 (19), 63 (5), 51 (5), 41 (4); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.50 (s, 3H, Me-13), 1.57 (s, 3H, Me-13), 1.54 (dd, 1H, $J_{12ax,12eqv}$=14.1, $J_{11b,12ax}$=12.0 Hz, H-12*ax*), 2.24 (dd, 1H, $J_{12ax,12eqv}$=14.1, $J_{11b,12eqv}$=3.2 Hz, H-12*eqv*), 2.29 (s, 3H, Me-3), 4.64 (d, 1H, $J_{A,B}$=15.5 Hz, H-5B), 4.88 (dd, 1H, $J_{11b,12ax}$=12.0, $J_{11b,12eqv}$=3.2 Hz, H-11b), 5.25 (d, 1H, $J_{A,B}$=15.5 Hz, H-5A), 7.03 (dd, 1H, $J_{1,2}$=8.0, $J_{2,4}$=2.0 Hz, H-2), 7.22 (d, 1H, $J_{2,4}$=2.0 Hz, H-4), 7.25 (d, 1H, $J_{1,2}$=8.0 Hz, H-1), 7.39 (d, 1H, $J_{10,11}$=7.5 Hz, H-11), 7.39 (t, 1H, $J_{8,9}$=$J_{10,9}$=7.5 Hz, H-9), 7.49 (dt, 1H, $J_{10,9}$=$J_{10,11}$=7.5, $J_{8,10}$=1.5 Hz, H-10), 7.78 (dd, 1H, $J_{8,9}$=7.5, $J_{8,10}$=1.5 Hz, H-8); ^{13}C nmr ($CDCl_3$, 100.6 MHz) δ 166.4 (s, NCO), 145.7 (s), 143.6 (s), 136.0 (s), 135.8 (s), 131.7 (s), 131.7 (d, C-4, *J*=155.5 Hz), 131.0 (d, C-10, *J*=161.0 Hz), 128.1 (d, C-2, *J*=155.5 Hz), 127.8 (d, C-9, *J*=161.5 Hz), 126.1 (d, C-1, *J*=155.0 Hz), 123.5 (d, C-8, *J*=164.0 Hz), 121.4 (d, C-7, *J*=161.0 Hz), 59.3 (d, C-11b, *J*=141.0 Hz), 47.1 (t, C-12, *J*=128.5 Hz), 46.3 (t, C-5, *J*=137.0 Hz), 37.2 (s, C-13), 32.6 (q, Me-13, *J*=127.0 Hz), 25.6 (q, Me-13, *J*=126.0 Hz), 20.3 (q, Me-3, *J*=126.5 Hz).

Anal. Calcd. for $C_{20}H_{21}NO$: C, 82.47; H, 7.22; N, 4.81. Found: C, 82.40; H, 6.99; N, 4.89.

13,13-Dimethyl-7-oxo-5,11b,12,13-tetrahydro-2-methoxy-7*H*-isoindolo[2,1-*b*][2]benzazepine (**33c**) and 13,13-Dimethyl-7-oxo-5,11b,12,13-tetrahydro-3-methoxy-7*H*-isoindolo[2,1-*b*][2]-benzazepine (**34c**).

Slow-moving colorless oil, total yield of isomeric mixture 0.92 g (30%). Ratio of isomers **33c/34c** = 1/1; R_f 0.60 (ethyl acetate–hexane, 1:1); ir: 1680 (N–C=O) cm^{-1}; ms: m/z M$^+$ 307 (100), 292 (20), 264 (57), 251 (15), 236 (5), 220 (4), 204 (4), 186 (32), 175 (27), 161 (30), 145 (20), 131 (20), 121 (35), 115 (20), 103 (22), 91 (24), 77 (26), 63 (7), 51 (7); ^{1}H nmr isomer mixture spectrum ($CDCl_3$, 400 MHz) δ 1.52 (s, 6H, Me-13), 1.56 (dd, 2H, *J*=14.1, 12.1 Hz, H-12*ax*), 1.58 (s, 3H, Me-13), 1.60 (s, 3H, Me-13), 2.25 (dd, 2H, *J*=14.1, 3.3 Hz, H-12*eqv*), 3.79 (s, 3H, OMe), 3.80 (s, 3H, OMe), 4.62 (d, 1H, *J*=15.5 Hz, H-5), 4.67 (d, 1H, *J*=15.5 Hz, H-5), 4.88 (dd, 1H, *J*=12.1, 3.3 Hz, H-11b), 4.90 (dd, 1H, *J*=12.1, 3.3 Hz, H-11b), 5.26 (d, 1H, *J*=15.5 Hz, H-5), 5.28 (d, 1H, *J*=15.5 Hz, H-5), 6.69 (dd, 1H, *J*=8.7, 2.9 Hz), 6.75 (dd, 1H, *J*=8.2, 2.5 Hz), 6.96 (d, 1H, *J*=2.5 Hz), 6.98 (d, 1H, *J*=2.9 Hz), 7.29 (d, 1H, *J*=8.7 Hz), 7.34 (d, 1H, *J*=8.2 Hz), 7.40–7.44 (m, 2H), 7.49–7.54 (m, 2H), 7.81 (dd, 2H, *J*=7.5, 1.7 Hz).

Anal. Calcd. for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56. Found: C, 78.25; H, 6.93; N, 4.63.

3-Chloroacetyl-13,13-dimethyl-7-oxo-5,11b,12,13-tetrahydro-7*H*-isoindolo[2,1-*b*][2]benzazepine (**35**).

Chloroacetyl chloride (1.73 mL, 0.022 mol) was added to a stirred suspension of $AlCl_3$ (4.81 g, 0.036 mol) in dry dichloroethane (60 mL). After 0.5 h stirring at room temperature isoindolobenzazepine **33a** 2.0 g (7.2 mmol) was added and resulting mass was stirred for 20 h at 24 °C. Then the reaction mixture was poured into 100 mL of ice water and basified with 25% aqueous ammonia solution to pH ~ 8–9. Obtained precipitate was filtered off and washed with chloroform (3 × 50 mL). The water phase was extracted with $CHCl_3$ (3 × 30 mL). Organic phases were collected, washed with water (1 × 40 mL), dried over $MgSO_4$ and concentrated. The crude product was recrystallized from hexane–ethyl acetate mixture to give desired chloroacetylderivative **35** as colorless crystals. Yield 1.78 g (70%); mp 141.5–143.5 °C with decomposition; R_f 0.13 (ethyl acetate–hexane, 1 : 2); ir: 1675 (N–C=O), and 1700 (C=O) cm^{-1}; ms: m/z M$^+$ 353 (^{35}Cl, 100), 338 (18), 304 (21), 289 (4), 276 (8), 220 (4), 185 (6), 171 (16), 159 (11), 132 (25), 129 (9), 115 (7), 77 (5); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.57 (s, 3H, Me-13), 1.63 (s, 3H, Me-13), 1.58 (dd, 1H, $J_{12ax,12eqv}$=14.2, $J_{11b,12ax}$=12.1 Hz, H-12*ax*), 2.30 (dd, 1H, $J_{12ax,12eqv}$=14.2, $J_{11b,12eqv}$=3.1 Hz, H-12*eqv*), 4.62 (d, 1H, $J_{A,B}$=14.7 Hz, ClC*H*$_A$H$_B$), 4.72 (d, 1H, $J_{A,B}$=15.7 Hz, H-5B), 4.73 (d, 1H, $J_{A,B}$=14.7 Hz, ClCH$_A$*H*$_B$), 4.94 (dd, 1H, $J_{11b,12ax}$=12.1, $J_{11b,12eqv}$=3.1 Hz, H-11b), 5.40 (d, 1H, $J_{A,B}$=15.7 Hz, H-5A), 7.42 (dd, 1H, $J_{10,11}$=7.5, $J_{9,11}$=1.1 Hz, H-11), 7.43 (dt, 1H, $J_{9,11}$=1.1, $J_{9,10}$=$J_{8,9}$=7.5 Hz, H-9), 7.51 (dd, 1H, $J_{8,10}$=1.1, $J_{8,9}$=7.5 Hz, H-8), 7.53 (dt, 1H, $J_{8,10}$=1.1, $J_{9,10}$=$J_{10,11}$=7.5 Hz, H-10), 7.80 (d, 1H, $J_{1,2}$=8.3 Hz, H-1), 7.83 (dd, 1H, $J_{1,2}$=8.3, $J_{2,4}$=2.0 Hz, H-2), 7.97 (d, 1H, $J_{2,4}$=2.0 Hz, H-4).

Anal. Calcd. for $C_{21}H_{20}NO_2Cl$: C, 71.28; H, 5.70; N, 3.96; Cl, 10.02. Found: C, 71.17; H, 5.68; N, 4.03; Hal, 9.83.

3-Nitro-13,13-dimethyl-7-oxo-5,11b,12,13-tetrahydro-7*H*-isoindolo[2,1-*b*][2]benzazepine (**36**).

Potassium nitrate 0.37 g (3.63 mmol) was added portion wise to a stirred solution of **33a** 1.00 g (3.60 mmol) in 15 mL of conc. sulfuric acid at –10 °C. Then the reaction mixture was stirred at –5–0 °C for 1 h and poured into 50 mL of ice water. The obtained precipitate was collected by filtration, washed with water to pH~7 and dried in air. Then the crude product was purified by recrystallization (*i*-PrOH–DMF) to give the desired nitroderivative **36** as white crystals. Yield 0.85 g (73%); mp 191.5–192 °C; R_f 0.71 (ethyl acetate–chloroform, 1:1); ir: 1693 (N–C=O), 1344 (as.-NO_2), and 1512 (s.-NO_2) cm^{-1}; ms: m/z M$^+$ 322 (100), 305 (88), 293 (13), 275 (51), 263 (23), 233 (17), 217 (17), 204 (7), 191 (13), 158 (20), 146 (46), 115 (82), 89 (48), 77 (66), 51 (28), 39 (35); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.59 (s, 3H, Me-13), 1.64 (s, 3H, Me-13), 1.60 (dd, 1H, $J_{12ax,12eqv}$=14.3, $J_{11b,12ax}$=12.0 Hz, H-12*ax*), 2.33 (dd, 1H, $J_{12ax,12eqv}$=14.3, $J_{11b,12eqv}$=3.0 Hz, H-12*eqv*), 4.74 (d, 1H, $J_{A,B}$=15.8 Hz, H-5A), 4.96 (dd, 1H, $J_{11b,12ax}$=12.0, $J_{11b,12eqv}$=3.0 Hz, H-11b), 5.44 (d, 1H, $J_{A,B}$=15.8 Hz, H-5B), 7.43 (d, 1H, $J_{10,11}$=7.3 Hz, H-11), 7.44 (t, 1H, $J_{9,10}$=$J_{8,9}$=7.3 Hz, H-9), 7.55 (d, 1H, $J_{8,9}$=7.3 Hz, H-8), 7.54 (t, 1H, $J_{9,10}$=$J_{10,11}$=7.3 Hz, H-10), 7.82 (d, 1H, $J_{1,2}$=8.3 Hz, H-1), 8.07 (dd, 1H, $J_{1,2}$=8.3, $J_{2,4}$=2.4 Hz, H-2), 8.28 (d, 1H, $J_{2,4}$=2.0 Hz, H-4).

Anal. Calcd. for $C_{19}H_{18}N_2O_3$: C, 70.79; H, 5.63; N, 8.69. Found: C, 70.72; H, 5.67; N, 8.72.

13,13-Dimethyl-7-oxo-5,13-dihydro-7*H*-isoindolo[2,1-*b*][2]-benzazepine (**37**).

A mixture of amide **33a** 0.5 g (1.81 mmol) and nitrobenzene (30 mL) was refluxed for 40 h (TLC monitoring). After that the reaction mixture was concentrated *in vacuo* and the crude product was purified by column chromatography on Al_2O_3 (1.5 × 18 cm, using hexane/ethyl acetate, 10:1 as eluent). The obtained yellow oil crystallizes to give the product **37**. Beige crystals, yield 0.21 g (42%); mp 122–124 °C (ethyl acetate–hexane); R_f 0.69 (ethyl acetate–hexane, 1:1); ir: 1680 (N–C=O) cm^{-1}; ms: m/z M$^+$ 275 (18), 260 (100), 245 (11), 232 (26), 202 (4), 130 (17), 102 (11), 77 (4), 39 (4); ^{1}H nmr ($CDCl_3$, 400 MHz) δ 1.74 (s, 6H, Me-13), 5.24 (brs, 2H, H-5), 5.82 (s, 1H, H-12), 7.24 (dt, 1H, *J*=1.4, 7.4 Hz, H-2), 7.31 (dt, 1H, *J*=1.4, 7.4 Hz, H-3), 7.39 (dd, 1H, *J*=1.4, 7.4 Hz, H-1), 7.41 (dt, 1H, *J*=1.4, 7.5 Hz, H-9), 7.43 (dd, 1H, *J*=1.4, 7.4 Hz, H-4), 7.51 (dt, 1H, *J*=1.4, 7.5 Hz, H-10), 7.60 (dd, 1H, *J*=1.4, 7.5 Hz, H-11), 7.81 (dd, 1H, *J*=1.4, 7.5 Hz, H-11).

Anal. Calcd. for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09. Found: C, 82.90; H, 6.14; N, 5.11.

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REFERENCES AND NOTES

[1] F. I. Zubkov, E. V. Nikitina, K. F. Turchin, G. G. Aleksandrov, A. A. Safronova, R. S. Borisov, A. V. Varlamov, *J. Org. Chem.*, **69**, 432 (2004).

[2] F. I. Zubkov, E. V. Nikitina, K. F. Turchin, A. A. Safronova, R. S. Borisov, A. V. Varlamov, *Russ. Chem. Bull.* (Engl. transl.), **53**, 860 (2004).

[3] F. I. Zubkov, E. V. Boltukhina, K. F. Turchin, R. S. Borisov, A. V. Varlamov, *Tetrahedron*, **61**, 4099 (2005).

[4] E. V. Boltukhina, F. I. Zubkov, E. V. Nikitina, A. V. Varlamov, *Synthesis*, 1859 (2005).

[5] F. I. Zubkov, E. V. Boltukhina, E. V. Nikitina, A. V. Varlamov, *Russ. Chem. Bull.* (Engl. transl.), **53**, 2816 (2004).

[6] F. I. Zubkov, E. V. Boltukhina, K. F. Turchin, A. V. Varlamov, *Tetrahedron*, **60**, 8455 (2004).

[7] F. I. Zubkov, E. V. Boltukhina, A. P. Krapivko, A. V. Varlamov, *Chem. Heterocycl. Compd.* (Engl. transl.), **39**, 1534 (2003).

[8] Last IMDAF review: F. I. Zubkov, E. V. Nikitina, A. V. Varlamov, *Russ. Chem. Rev.* (Engl. transl.), **74**, 639 (2005).

[9] Y. Ishihara, Y. Kiyota, G. Goto, *Chem. Pharm. Bull.,* **38**, 3024 (1990).

[10] Y. Ishihara, T. Doi, H. Nagabukuro, Y. Ishichi, WO Patent 00/18391.

[11] Y. Ishihara, Y. Fujisawa, N. Furuyama, WO Patent 9846590 [*Chem. Abstr.*, **129**, 330744a (1998)].

[12] G. Goto, Y. Ishihara, M. Miyamoto, EP Patent 655451 [*Chem. Abstr.*, **123**, 198832x (1995)].

[13] G. Goto, Y. Ishihara, JP Patent 02042078 [*Chem. Abstr.*, **113**, 40431z (1990)].

[14] Z. Sui, J. Altom, V. N. Nguyen, J. Fernandez, J. I. Bernstein, J. J. Hiliard, J. F. Barrett, B. L. Podlogar, K. A. Ohemeng, *Bioorg. Med. Chem.*, **6**, 735 (1998).

[15] D. Bilović, *Croat. Chem. Acta*, **40** (1), 15 (1968) [*Chem. Abstr.*, **69**, 486751 (1968)].

[16] D. Bilović, *Croat. Chem. Acta*, **38**, 293 (1966) [*Chem. Abstr.*, **66**, 55416 (1967)].

[17] D. Prajapati, D. R. Borthakur, J. S. Sandhu, *J. Chem. Soc., Perkin Trans. 1*, 1197 (1993).

[18] T. N. Borisova, L. G. Voskressensky, T. A. Soklakova, L. N. Kulikova, A. V. Varlamov, *Mol. Diversity*, **6**, 207 (2003).

[19] A. V. Varlamov, T. N. Borisova, L. G. Voskressensky, T. A. Soklakova, L. N. Kulikova, A. I. Chernyshev, G. G. Alexandrov, *Tetrahedron Lett.,* **43**, 6767 (2002).

[20] C. Marchionni, P. Vogel, P. Roversi, *Tetrahedron Lett.*, **37**, 4149 (1996).

[21] M. Lautens, E. Fillion, *J. Org. Chem.,* **61**, 7994 (1996).

[22] M. Lautens, E. Fillion, *J. Org. Chem.,* **62**, 4418 (1997).

[23] M. E. Jung, *Synlett*, 186 (1990).

[24] M. E. Jung, J. Gervay, *J. Am. Chem. Soc.*, **113**, 224 (1991).

[25] M. E. Jung, M. Kiankarimi, *J. Org. Chem.*, **63**, 2968 (1998).

[26] Full crystallographic data (atomic coordinates, bond lengths, bond angles and thermal parameters) for structure **26c** have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication numbers CCDC 281912. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[27] K. Paulvannan, *Tetrahedron Lett.,* **40**, 1851 (1999).

[28] F. Kienzle, *Helv. Chim. Acta,* **58**, 123 (1975).

[29] C. Rogers, B. A. Keay, *Can. J. Chem.*, **70**, 2929 (1992).

[30] W. L. Nelson, D. R. Allen, *J. Heterocycl. Chem.*, **9**, 561 (1972).

[31] our stereochemical results compare favorably to those reported in the recent article: I. N. N. Namboothiri, M. Ganesh, S. M. Mobin, M. Cojocaru, *J. Org. Chem.*, **70**, 2235 (2005).

[32] O. G. Ausheva, V. A. Glushkov, S. N. Shurov, Yu. V. Shklyaev, *Russ. Chem. Bull., Int. Ed.,* **50**, 1648 (2001).

[33] V. A. Glushkov, O. G. Ausheva, Yu. V. Shklyaev, *Russ. Chem. Bull., Int. Ed.*, **51**, 709 (2002).

[34] V. A. Glushkov, O. G. Ausheva, Shurov, S. N.; Shklyaev, Yu. V. *Russ. Chem. Bull., Int. Ed.*, **51**, 894 (2002).

[35] C. O. Puentes, V. V. Kouznetsov, *J. Heterocycl. Chem.*, **39**, 595 (2002).

[36] V. V. Kouznetsov, S. V. Lantsetov, A. E. Aliev, A. V. Varlamov, N. S. Prostakov, *Zh. Org. Khim.*, **28**, 74 (1992) [*Russ. J. Org. Chem.* (Engl. Transl.), **28**, 61 (1992)].

[37] A. V. Varlamov, V. V. Kouznetsov, F. I. Zubkov, A. I. Chernyshev, G. G. Alexandrov, A. R. Palma, L. Vargas, S. Salas, *Synthesis,* 849 (2001).

[38] SMART (control) and SAINT (integration) software, version 5.0 Bruker AXS Inc., Madison, WI, 1997.

[39] G. M. Sheldrick, SHELXS-97 – Program for the solution of crystal structures. University of Göttingen, Germany, 1997.

[40] G. M. Sheldrick, SHELXL-97 – Program for the refinement of crystal structures. University of Göttingen, Germany, 1997.

[41] A. V. Varlamov, V. V. Kouznetsov, F. I. Zubkov, A. I. Chernyshev, O. V. Shurupova, L. M. Vargas, A. R. Palma, J. R. Castro, A. J. Rosas-Romero, *Synthesis*, 771 (2002).