Латвийский институт органического синтеза

Химия гетероциклических соединений **2015**, *51*(4), 310–319

Multicomponent reaction of 2-aminobenzimidazole, arylglyoxals, and 1,3-cyclohexanedione

Olesya N. Petrova[1], Lali L. Zamigajlo[1], Konstantin S. Ostras[1], Svetlana V. Shishkina[1], Oleg V. Shishkin[1,2], Alexander V. Borisov[3], Vladimir I. Musatov[1], Maria G. Shirobokova[1], Victoria V. Lipson[1,2,4]*

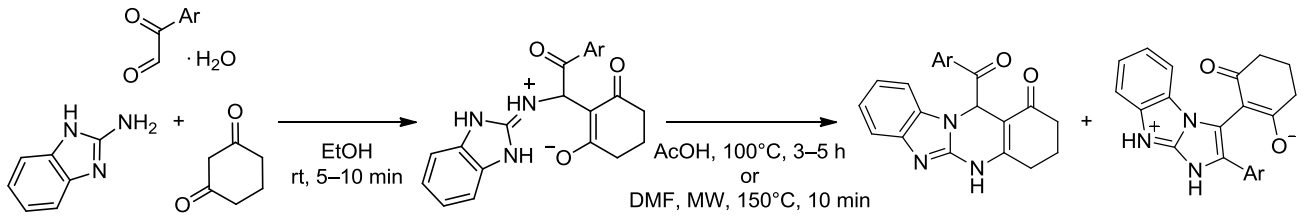
[1] *SSI "Institute for Single Crystals", 60 Lenin Ave., Kharkiv 61001, Ukraine; e-mail: info@isc.kharkov.com*

[2] *V. N. Karazin Kharkiv National University, Organic Chemistry Department, 4 Svobody Sq., Kharkiv 61077, Ukraine*

[3] *Enamine Ltd., 23 Alexandra Matrosova St., Kyiv 01103, Ukraine*

[4] *Antidiabetic Drug Laboratory, SI "V. Ya. Danilevsky Institute for Endocrine Pathology Problems", 10 Artema St., Kharkiv 61002, Ukraine; e-mail: lipson@ukr.net*

Submitted February 10, 2015
Accepted March 4, 2015

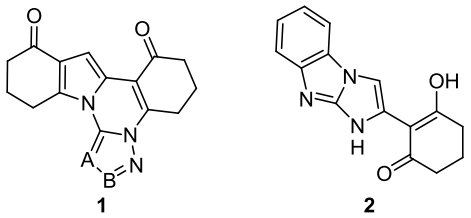


Three-component reactions of 2-aminobenzimidazole with arylglyoxals and 1,3-cyclohexanedione have been studied under conventional heating and microwave irradiation. Different product types including the Michael adduct and fused heterocyclic systems were obtained. Conditions for the selective formation of 12-aroylbenzimidazo[2,1-*b*]quinazolin-1(2*H*)-ones and 3-oxo-2-(2-aryl-1*H*-imidazo[1,2-*a*]-benzimidazol-9-ium-3-yl)cyclohex-1-enolates have been determined. The structures of all compound types were established by an X-ray diffraction study.

Keywords: 2-aminobenzimidazole, arylglyoxal, benzimidazo[2,1-*b*]quinazolinones, 1,3-cyclohexanedione, imidazo[1,2-*a*]benzimidazoliumyl-cyclohexenolates, microwave synthesis, multicomponent reaction.

Multicomponent reactions (MCRs) of amidine and guanidine binucleophiles with cyclic 1,3-diketones containing an active methylene group and carbonyl compounds in the last two decades have become a widely applicable methodology for the diversity-oriented synthesis of fused pyridine and pyrimidine systems for high-throughput screening.[1–4] Earlier the results of investigations of MCRs between different α-aminoazoles as 1,3-binucleophiles, aldehydes, and dimedone were published.[5–16] 2-Aminobenzimidazole in these reactions yielded 12-aryl-3,3-dimethyl-3,4,5,12-tetrahydrobenzimidazo[2,1-*b*]quinazolin-1(2*H*)-ones.[17] However, there are no reports concerning MCRs of this amine with arylglyoxals and cyclic 1,3-diketones in the available literature. At the same time, the presence of two carbonyl groups in the glyoxal molecule provides an additional reaction site in respect to aldehydes. In the case of oxalaldehyde, both groups participate in the cyclocondensation. We have recently published the results of our study of MCRs involving oxalaldehyde, aminoazoles, and cyclohexane-1,3-diones and leading to the formation of novel heterocyclic systems of indolo[1,2-*c*]-azolo[1,5-*a*]quinazoline-8,10-diones **1** (Fig. 1) with one aminoazole ring, one glyoxal residue, and two cyclohexenone units in their scaffolds.[18] However, in the case of 2-aminobenzimidazole, imidazo[1,2-*a*]benzimidazoles **2** with one cyclic 1,3-diketone residue in the condensed system were obtained in this reaction.

Due to the fact that the reactivity of carbonyl groups in aryglyoxals is differentiated, these compounds can act both as mono- and 1,2-bielectrophiles. In this regard, there exists an ambiguity in the orientation of their interaction in MCRs with CH acids and 1,3-binucleophilic α-aminoazoles. As a result, a problem arises in controlling the regioselectivity in these processes. In the present work, we aimed to study the three-component condensation of 2-aminobenzimidazole with 1,3-cyclohexanedione and hydrates of



1 **2**

A = CH, B = CMe, CPh, CTol, C(4-FC_6H_4);
A = N, B = CH, C(COOMe), C(CONHCH_2Ph), C(SMe), N

Figure 1. Indolo[1,2-*c*]azolo[1,5-*a*]quinazoline-8,10-diones **1** and imidazo[1,2-*a*]benzimidazoles **2**.

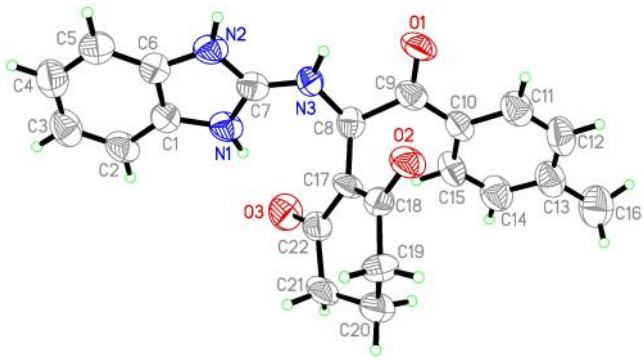


Figure 2. Molecular structure of compound **6b** with atoms represented as thermal vibration ellipsoids of 50% probability.

arylglyoxals under different reaction conditions and select the most favorable conditions for the regioselective formation of isomeric compounds. It was found that a brief stirring of equimolar amounts of 2-aminobenzimidazole (**3**), arylglyoxals **4a–c**, and 1,3-cyclohexanedione (**5**) in ethanol gives hardly soluble precipitates of compounds **6a–c** in quantitative yields (Scheme 1).

A comparison of the LC-MS spectra and analytical data of the obtained compounds **6a–c** indicated that their formation occurred from the starting reagents with elimination of one molecule of water. In ^{1}H NMR spectra of the synthesized compounds an intensive exchange of protons typical of salts is observed. These substances exist in DMSO-d_6 solutions as a mixture of two tautomers **6** and **6'** in the ratio 1:1 (Scheme 1), which was confirmed by the aromatic and aliphatic proton signals being doubled. The signal of benzimidazole NH proton was absent due to a rapid exchange with D_2O contained in the solvent. The vicinal proton signals of CH and NH^+ groups of the tautomer **6** were present in the ^{1}H NMR spectra as two doublets at 5.80–5.84 and 8.75–8.83 ppm, respectively, with coupling constants J = 4.8 and 5.2 Hz. These signals disappeared under D_2O exchange conditions. The absence of a CH group signal can be explained by the enolization of the aroyl moiety under deuterium exchange conditions. The existence of the Michael adducts **6a–c** in zwitterionic form was unequivocally established by means of a single crystal X-ray diffraction study of compound **6b** (Fig. 2).

The zwitterionic form of compound **6b** is confirmed by the analysis of geometrical parameters. Lengths of the C(18)–O(2) and C(22)–O(3) bonds (1.260(5) and 1.271(5) Å, respectively) are close to the mean value for the Csp^2–O$^-$ bond in carboxylate anion (1.254 Å).[19] The C(17) atom has sp^2 hybridization, and the C(17)–C(18) and C(17)–C(22) bonds (1.404(6) and 1.401(6) Å, respectively) are shorter than the mean value for a Csp^2–Csp^2 bond (1.455 Å) and longer than this value for a Csp^2=Csp^2 bond (1.331 Å). The length of the C(7)–N(3) bond (1.309(6) Å) is close to the mean value of a Csp^2=N bond (1.316 Å). The hydrogen atom at the N(3) atom is located from the electron density difference maps, which allows to assume the localization of the positive charge at the protonated N(3) atom. Overall, the structure of compound **6b** can be described as a superposition of two resonance structures (Fig. 3).

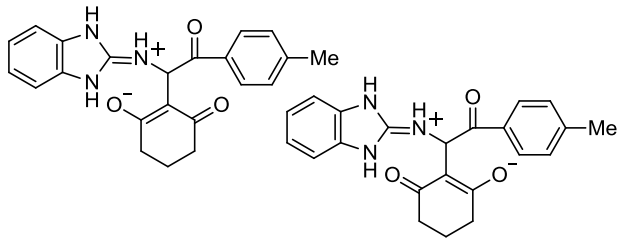
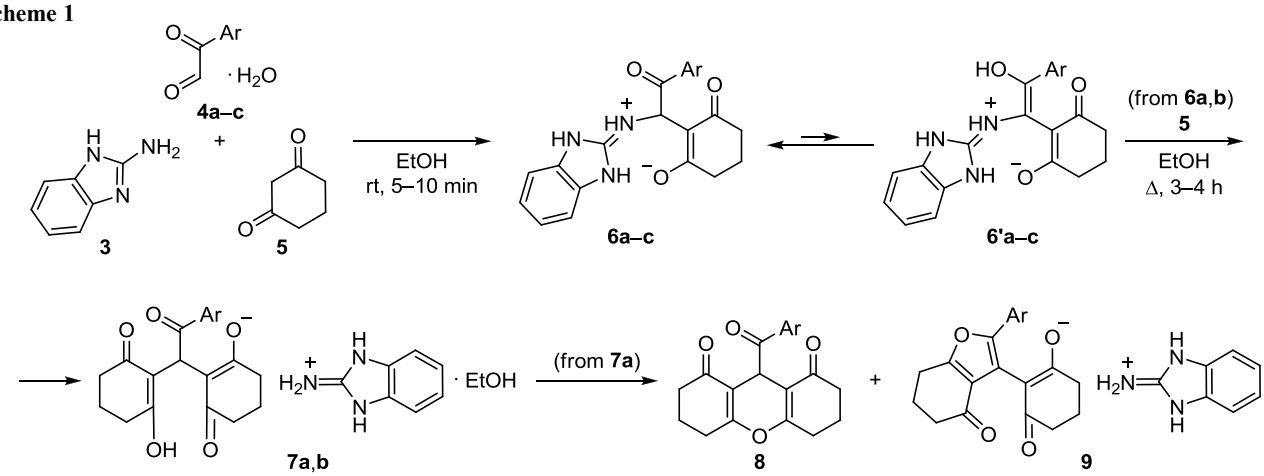


Figure 3. Resonance structures of compound **6b** according to X-ray diffraction data.

Scheme 1



6, **6'** **a** Ar = Ph, **b** Ar = 4-MeC_6H_4, **c** Ar = 4-ClC_6H_4; **7** **a** Ar = Ph, **b** Ar = 4-MeC_6H_4; **8**, **9** Ar = Ph

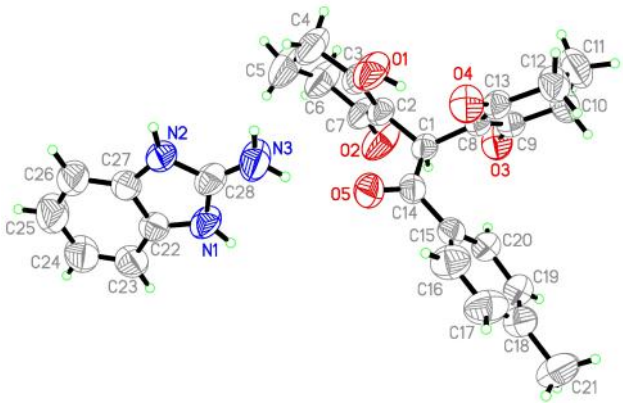


Figure 4. Molecular structure of compound **7b** with atoms represented as thermal vibration ellipsoids of 50% probability.

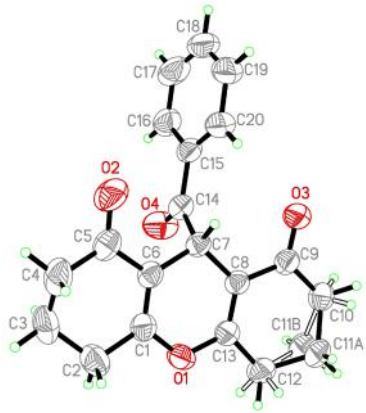


Figure 5. Molecular structure of compound **8** with atoms represented as thermal vibration ellipsoids of 50% probability.

Prolonged refluxing of adducts **6a**–**c** in alcohols did not lead to the appearance of any new compounds in the reaction mixture. However, a slow dissolution of precipitates **6a**–**c** was observed when more than 1 equiv of 1,3-diketone **5** had been added to the reaction mixture. Salts **7a**,**b** were obtained upon prolonged refluxing of such reaction mixtures (Scheme 1). It was not possible to obtain decisive information about the structure of products **7** from spectral data. Finally, their structure was determined using X-ray diffraction on a single crystal of complex salt **7b** (Fig. 4).

Compound **7b** is an organic salt which exists as a monosolvate with ethanol in the crystal phase. The solvate molecule is disordered over two positions (A and B) in the ratio 40:60. The positive charge of the organic cation is located at the protonated imino group (positions of the hydrogen atoms were determined from the electron density difference maps). The C(28)–N(3) bond length (1.311(2) Å) is close to the mean value for a Csp^2=N bond (1.316 Å) while the C(28)–N(1) and C(28)–N(2) bonds are considerably longer (1.346(2) and 1.351(2) Å, respectively). An analysis of the bond lengths in the organic anion demonstrates an elongation of the C(9)–O(3) and C(13)–O(4) bonds (1.259(2) and 1.284(2) Å, respectively) with respect to the mean length of a Csp^2–O$^-$ bond (1.254 Å). The C(8) atom has a sp^2 hybridization, and the C(8)–C(13) and C(8)–C(9) bonds are equalized (1.390(2) and 1.417(2) Å, respectively). These values considerably differ from bond lengths within the O(1)–C(3)–C(2)–C(7)–O(2) fragment where a clear location of single and double bonds is observed (O(1)–C(3) 1.336(2), C(3)–C(2) 1.366(2), C(2)–C(7) 1.433(3) Å, C(7)–O(2) 1.240(2) Å). Therefore, it can be assumed that the negative charge of the anion is located within the fragment O(3)–C(9)–C(8)–C(13)–O(4). This agrees well with the absence of a hydrogen atom at the O(3) or O(4) atoms.

Attempts to convert compounds **7a**,**b** into condensation products with 2-aminobenzimidazole (**3**) upon fusion without solvent or by refluxing in DMF or acetic acid did not lead to the desired result. In each case mixtures of xanthenedione **8** and salt **9** were obtained (Scheme 1). These compounds were separated by recrystallization from ethanol, compound **8** being the more soluble of the two. Analytical data, ^{1}H NMR spectra, and mass spectra data have confirmed that the two cyclohexenone units are connected with one arylglyoxal residue in the structure of compound **8**. Previously, a synthesis of the nearest structural analogs of compound **8** based on the reaction of arylglyoxals and dimedone has been published.[20]

^{1}H NMR spectra of compound **9** contain signals of all proton-containing groups of the partially hydrogenated benzofuran and aminobenzimidazole ring systems. As was the case with compounds **6a**–**c**, **7a**,**b**, the signal of benzimidazole NH proton was absent due to a rapid exchange with D_2O contained in the solvent (in the case of compounds **7a**,**b**, the OH signal, too, was absent). Broadening of the water signal at 3.50 ppm also was caused by an intensive proton exchange. Therefore, it is impossible to unequivocally establish whether the aminobenzimidazole fragment is covalently bound or not. A single crystal X-ray diffraction analysis of compounds **8** and **9** was used to finally corroborate the structures of the obtained products (Figs. 5 and 6).

The cyclohexenone rings of the tricyclic fragment in molecule **8** (Fig. 5) adopt slightly different conformations. The C(1)…C(6) ring adopts an asymmetric half-chair conformation. Deviations of the C(3) and C(4) atoms from the mean plane of the remaining atoms of the ring are –0.52 and 0.16 Å, respectively. The C(8)…C(13) ring is disordered over two sofa conformations (**A** and **B**) with the population ratio **A**:**B** being 84:16. The deviation of the C(11)

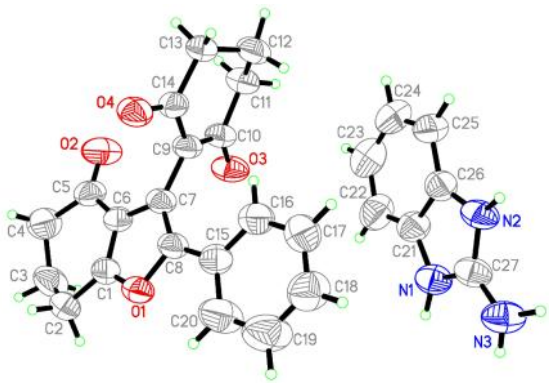


Figure 6. Molecular structure of compound **9** with atoms represented as thermal vibration ellipsoids of 50% probability.

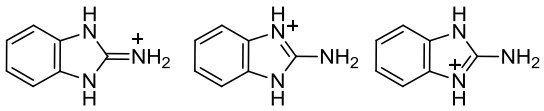


Figure 7. Resonance structures of the organic cation in compound **9** according to X-ray diffraction data.

atom from the mean plane of the remaining atoms of the ring is 0.61 Å in the conformer **A** and –0.45 Å in the conformer **B**.

Similarly to compound **7b** described above, compound **9** is an organic salt (Fig. 6). However, the location of the positive charge in compound **9** differs from that of compound **7b**, which is confirmed by the analysis of geometric parameters. The atom bonds centered at the C(27) atom are equalized (C(27)–N(1) 1.332(3), C(27)–N(2) 1.342(3), and C(27)–N(3) 1.330(3) Å) and are longer than the mean value for a Csp^2=N bond (1.316 Å), but shorter than the mean value for a Csp^2–Nsp^3 bond (1.355 Å). The N(3) atom has a slightly pyramidal configuration (the sum of valence angles centered at it is 354°). To sum up, the structure of the organic cation can be described as a superposition of three resonance structures (Fig. 7).

Such a difference in the structure of the cation between salts **7b** and **9** can be caused by the different character of the intermolecular interactions in the crystal phase. The NH groups in the crystal of compound **9** are involved in the formation of strong intermolecular hydrogen bonds (N(1)–H···O(3') (0.5–*x*, 0.5–*y*, 1–*z*), H···O 1.78 Å, N–H···O 159°; N(2)–H···O(4') (1–*x*, 1–*y*, 1–*z*) H···O 1.73 Å, N–H···O 166°; N(3)–H(3Na) ···O(4') (*x*, 1–*y*, 0.5+*z*) H···O 1.95 Å, N–H···O 170°) while only medium and weak hydrogen bonding is observed in the crystal of compound **7b** (the strongest hydrogen bond is N(3)–H(3Na)…O(3') (1+*x*, *y*, *z*) H···O 1.95 Å, N–H···O 145°).

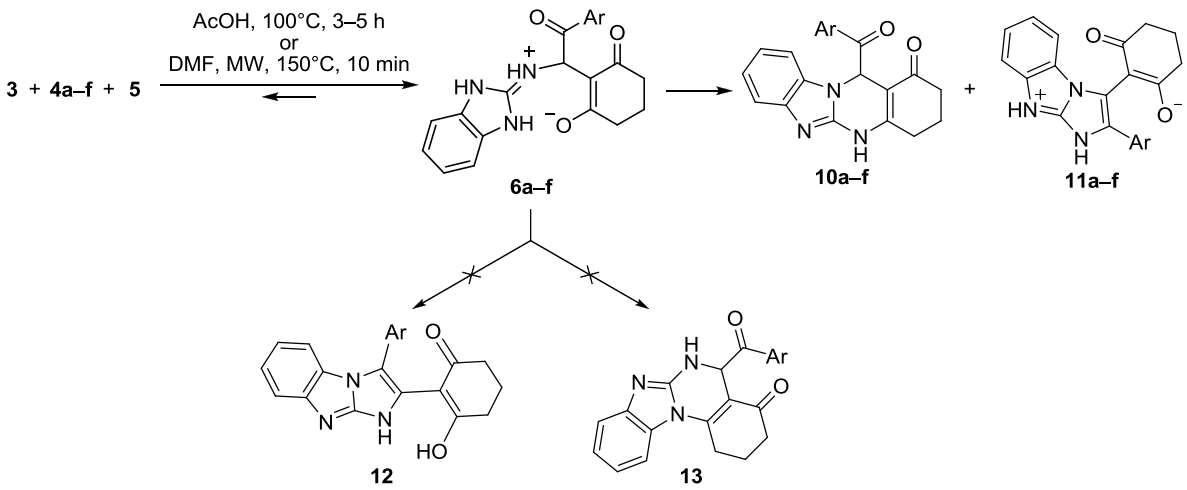
An analysis of the bond lengths in the organic anion demonstrates an unequal elongation of the C(10)–O(3) and C(14)–O(4) bonds (1.255(2) and 1.285(2) Å, respectively) with respect to the mean length of a Csp^2–O$^-$ bond (1.254 Å). The C(9) atom has sp^2 hybridization. The C(9)–C(10) and C(9)–C(14) bonds are equalized (1.411(3) and 1.402(3) Å, respectively). Therefore it can be assumed that the negative charge of the anion is located within the fragment O(3)–C(10)–C(9)–C(14)–O(4).

Table 1. Preparation of compounds **10b** and **11b** under microwave irradiation using different solvents and catalysts

Solvent	Catalyst	Reaction time	T, °C	Yield of compound, %	
				10b	**11b**
EtOH	–	10 min	150	29	67
MeCN	–	10 min	150	31	42
EtOH	HCl (15%)	10 min	150	29	49
EtOH	$Sc(OTf)_3$	10 min	150	37	46
EtOH	Et_3N	10 min	150	34	36
EtOH	$NiCl_2·6H_2O$	10 min	150	41	48
EtOH	$LiCl·H_2O$	10 min	150	34	38
DMF	–	10 min	150	19	52

Michael adducts **6a–f** initially are also formed in the three-component condensation of equimolar amounts of amine **3**, arylglyoxals **4a–f**, and diketone **5** in acetic acid at 100°C (Scheme 2). However, they turn into condensed systems under prolonged heating for 3–5 h. This reaction is selective and leads to the formation of benzimidazo[2,1-*b*]-quinazolin-1(2*H*)-ones **10a–f**. In the case of the reaction involving glyoxals **4c–e** having electron-withdrawing substituents in the *para*-position of the aryl ring, a small amount of isomeric compounds **11c–e** was obtained. In order to control the selectivity of these processes, we tried to find the optimal reaction conditions for the preferential formation of compounds **11a–f**. First we heated the reaction mixtures containing compounds **3**, **4a**,**b**, and **5** with microwaves in ethanol or acetonitrile (150°C, 10 min). Under these reaction conditions, condensed systems **10b** and **11b** were formed in amounts shown in Table 1. The use of different catalysts did not lead to the desired result either. But in the case when the reaction solution was heated with microwaves in dimethyl formamide, product **11b** was preferably formed. Under the latter reaction conditions,

Scheme 2



6,**10**,**11** **a** Ar = Ph, **b** Ar = 4-MeC_6H_4, **c** Ar = 4-ClC_6H_4, **d** Ar = 4-FC_6H_4, **e** Ar = 4-BrC_6H_4, **f** Ar = 4-MeOC_6H_4

Table 2. The reaction conditions and yields in the synthesis of compounds **10a–f** and **11a–f**

Starting compound	Reaction conditions	Yield of compound, %	
		10	**11**
4a	AcOH, 100°C, 5 h	97	–
4b	AcOH, 100°C, 3 h	64	–
4c	AcOH, 100°C, 4.5 h	55	14
4d	AcOH, 100°C, 4 h	49	5
4e	AcOH, 100°C, 5 h	46	10
4f	AcOH, 100°C, 5 h	75	–
4a	DMF, 150°C, 10 min	12	54
4b	DMF, 150°C, 10 min	19	52
4c	DMF, 150°C, 10 min	14	54
4d	DMF, 150°C, 10 min	10	65
4e	DMF, 150°C, 10 min	14	62
4f	DMF, 150°C, 10 min	18	47

compounds **11a–f** were obtained as the main products and, in all cases, compounds **11a–f** also were the first to precipitate after cooling the reaction mixture. Thus, the separation of the respective isomeric compounds was not difficult. In this way we managed to achieve a regioselectivity in the formation of isomeric products. The reaction conditions and yields of isomers **10a–f** and **11a–f** are given in Table 2.

In the three-component condensation under consideration one should not rule out the formation of isomeric products **12** and **13** simultaneously with partially hydrogenated benzimidazo[2,1-*b*]quinazolin-1(2*H*)-ones **10** and imidazo[1,2-*a*]benzimidazoles **11**. However, none of the products **12** or **13** was detected.

The identification of the structures **10** and **11** is carried out on the basis of the differences in their ^{1}H NMR spectra. In the spectra of benzimidazo[2,1-*b*]quinazolinones **10a–f**, the most characteristic are the downfield shifts of aroyl proton signals and the broad singlet of NH group at 11.19–11.34 ppm. The latter disappears in the presence of D_2O. The singlet of the 12-CH methine proton is screened by benzimidazole proton signals. In the case of compounds **11a–f**, intensive exchanges of protons are observed, and the resonance of aryl substituent protons is placed more upfield than in the spectra of compounds **10a–f**. Besides, the signals of imidazole NH groups are absent in the spectra of compounds **11a–f** due to rapid exchange with D_2O contained in the solvent. Generally, in accordance with the integral intensity of signals there is always one more proton in the aromatic region in the spectra of quinazolinones **10a–f**, compared to the spectra of the respective isomeric imidazole derivatives **11a–f**. This is due to the absence of the methine proton in the structure of compounds **11a–f**. The choice between structures **10** and **13** in favor of the former is made on the basis of the absence of magnetic interaction between CH and NH protons. A clear differentiation between structures **11** and **12** is impossible with only spectral data available. The structures of compounds **10a** and **11b** were finally confirmed by means of X-ray structural analysis (Fig. 8 and 9).

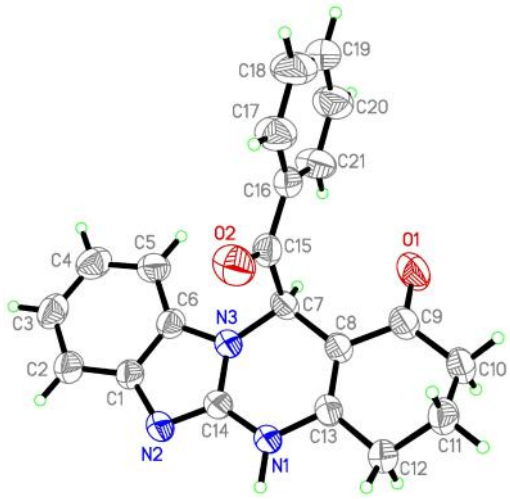


Figure 8. Molecular structure of compound **10a** with atoms represented as thermal vibration ellipsoids of 50% probability.

The cyclohexenone ring of the tetracyclic fragment in molecule **10a** (Fig. 8) adopts a sofa conformation: the deviation of the C(11) atom from the plain of the remaining atoms of the ring is –0.67 Å. The planar (within 0.02 Å) benzoyl substituent at the C(7) atom has an axial orientation and is turned with respect to the bicyclic fragment; the torsion angles C(15)–C(7)–C(8)–C(13) and C(8)–C(7)–C(15)–O(2) are 107.4(2) and –75.5(2)°, respectively.

Molecule **11b** in the crystal phase exists in the zwitterionic form (Fig. 9) similarly to compound **6b**. An analysis of the bond lengths in molecule **11b** demonstrates that the N(1)–C(9) and N(3)–C(9) bonds are equal (1.338(8) Å) and longer than the usual Csp^2=N bond (the mean value is 1.313 Å). The hydrogen atoms at the N(1) and N(3) atoms were located from the electron density difference maps. It allows to assume that the positive charge is located within the N(1)–C(9)–N(3) fragment. The C(11)–O(1) and C(15)–O(2) bond lengths (1.252(7) and 1.270(8) Å, respectively) are close to the mean value for a Csp^2–O$^-$ bond in a carboxylate anion (1.254 Å). The C(10) atom has sp^2 hybridi-

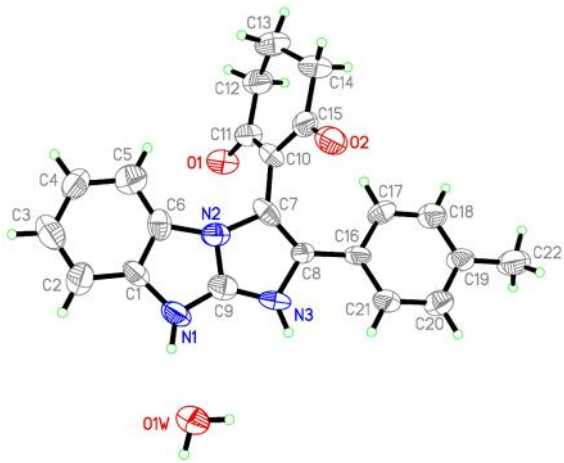
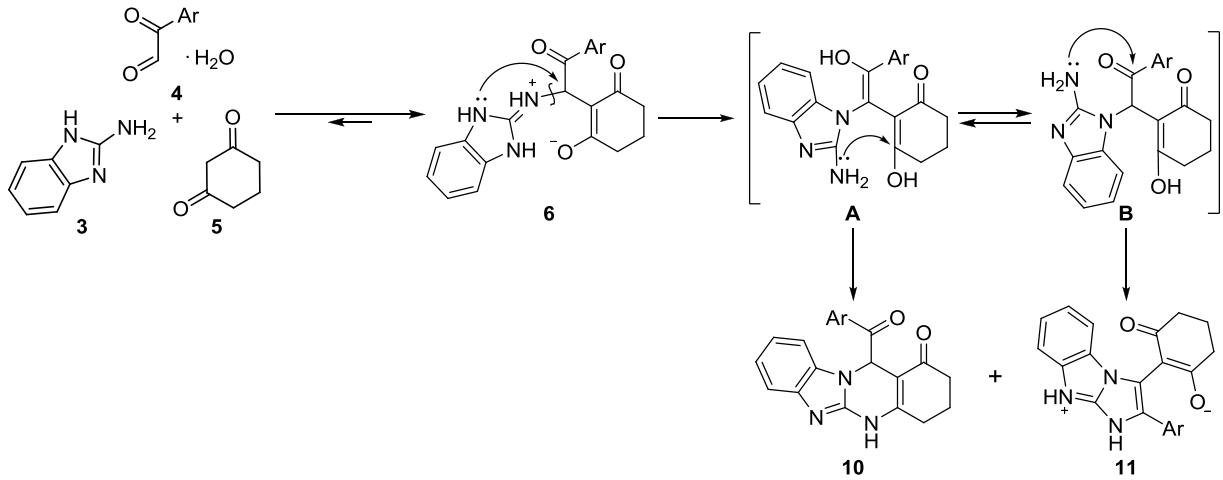


Figure 9. Molecular structure of compound **11b** with atoms represented as thermal vibration ellipsoids of 50% probability.

Scheme 3



zation, and the C(10)–C(11) and C(10)–C(15) bonds (1.408(9) and 1.407(8) Å, respectively) are shorter than the usual Csp^2–Csp^2 bond (mean value 1.455 Å) and longer than the usual Csp^2=Csp^2 bond (1.331 Å). Such delocalization of the electron density indicates that the negative charge is localized within the O(1)–C(11)–C(10)–C(15)–O(2) fragment. In a crystal, compound **11b** is observed as a monohydrate.

A possible mechanism of the one-pot reaction between α-aminoazole **3**, arylglyoxals **4**, and 1,3-diketone **5** leading to 12-aroyl-3,4,5,12-tetrahydrobenzimidazo[2,1-*b*]quinazolin-1(2*H*)-ones **10** and imidazo[1,2-*a*]benzimidazoles **11** is shown in Scheme 3. The reaction starts with the interaction of aminoazole with arylglyoxal and cyclohexanedione and gives a kinetically controlled zwitterionic compound **6**. The latter leaves the reaction sphere due to its low solubility and is not a direct synthetic precursor of benzimidazo[2,1-*b*]-quinazolinones **10** and imidazo[1,2-*a*]benzimidazoles **11**, but a prolonged heating of Michael adducts **6** in high-boiling solvents leads to the formation of a probable intermediate **A** or its tautomer **B** at the next stage of the process. In the acidic medium these intermediates convert into a mixture of compounds **10** and **11** with a predominance of the former. In contrast to this, the DMF medium provides higher yields of compounds **11**. Apparently, the enolization under acidic conditions promotes the formation of quinazolinones **10**.

Thus, in the investigated three-component condensation of 2-aminobenzimidazole with 1,3-cyclohexanedione and hydrates of arylglyoxals, kinetically controlled 2-{1-[(1,3-dihydro-2*H*-benzimidazol-2-ylidene)ammonio]-2-oxo-2-arylethyl}-3-oxocyclohex-1-en-1-olates are obtained at the first stage of the reaction, and their formation does not depend on the reaction conditions. Further transformation of these compounds in high-boiling solvents leads to their conversion into a mixture of 12-aroyl-3,4,5,12-tetrahydrobenzimidazo[2,1-*b*]quinazolin-1(2*H*)-ones and 3-oxo-2-(2-aryl-1*H*-imidazo[1,2-*a*]benzimidazol-9-ium-3-yl)cyclohex-1-enolates with a predominance of quinazolinone compounds in acidic conditions and imidazolium derivatives in DMF.

Experimental

IR spectra were recorded in KBr on a Perkin Elmer Spectrum One spectrometer. ^{1}H NMR spectra were recorded on a Varian Mercury VX-200 spectrometer (200 MHz) and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer (100 MHz) in DMSO-d_6 with TMS as internal standard. Mass spectra were recorded on a Varian 1220 L mass spectrometer with direct injection of the sample and electron ionization (EI, 70 eV). LC-MS experiments were performed on an Applied Bio-systems API 150EX LC/MS system (atmosphere pressure chemical ionization (APCI)) with Shimadzu 10-AV UV (215 and 254 nm) and ELS detectors, a Gilson-215 automatic liquid handler, a Phenomenex Luna-C18 column (5 cm × 2 mm). Elemental analysis was made on an Euro EA-3000 elemental analyzer. Melting points were determined on a Kofler apparatus and temperatures were not corrected. Reactions were monitored by a TLC (DC-Fertigfolien ALUGRAM Xtra SIL G/UV$_{254}$) in EtOAc–PhMe, 1:2, and visualized under UV light or iodine vapors. Microwave experiments were performed with a Biotage AB Emrys Creator EXP in a single-mode microwave cavity (2.45 GHz). Starting materials were purchased from commercial suppliers.

Synthesis of compounds 6a–c (General method). A mixture of 2-aminobenzimidazole (**3**) (0.27 g, 2 mmol), an arylglyoxal hydrate **4a–c** (2 mmol), and 1,3-cyclohexanedione (**5**) (0.24 g, 2 mmol) in EtOH (8–10 ml) was stirred for 5–10 min. The solid that formed was filtered, washed on the filter with EtOH, and crystallized from MeOH to give compound **6**.

2-{1-[(1,3-Dihydro-2*H*-benzimidazol-2-ylidene)ammonio]-2-oxo-2-phenylethyl}-3-oxocyclohex-1-en-1-olate (6a). Yield 0.59 g (82%), white solid, mp 218–220°C. IR spectrum, ν, cm^{-1}: ~3400 (NH), 2970–2500 (=N$^+$H, CH$_2$), 1667 (C=O), 1612 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.52 (2H, t, *J* = 6.0, CH$_2$); 1.92–2.16 (4H, m, 2CH$_2$); 5.84 (1H, d, *J* = 5.2, CH); 7.10−7.14 (2H, m, H HetAr); 7.31–7.51 (5H, m, H-3,4,5 Ph, H HetAr); 7.70 (2H, d, *J* = 7.4, H-2,6 Ph); 8.78 (1H, d, *J* = 5.2, NH). ^{1}H NMR spectrum (DMSO-d_6+ D$_2$O), δ, ppm (*J*, Hz): 1.41–1.67 (2H, m, CH$_2$); 1.83–2.22 (4H, m,

2CH_2); 7.07–7.22 (2H, m, H HetAr); 7.31–7.43 (4H, m, H-3,5 Ph, H HetAr); 7.50 (1H, t, *J* = 7.2, H-4 Ph); 7.62–7.78 (2H, m, H-2,6 Ph). ^{13}C NMR spectrum, δ, ppm: 21.0; 27.1; 33.7; 53.5; 111.2; 112.5; 119.4; 121.3; 126.1; 128.2; 132.9; 133.1; 133.8; 135.8; 137.0; 157.0; 186.9; 193.0; 196.3. Mass spectrum (EI), *m*/*z* (I_{rel}, %): 343 [M–H_2O]$^+$ (27), 286 (9), 259 (10), 258 (10), 239 (19), 238 (100), 133 (12), 105 (19), 77 (16). Found, %: C 69.88; H 5.43; N 11.49. $C_{21}H_{19}N_3O_3$. Calculated, %: C 69.79; H 5.30; N 11.63.

2-{1-[(1,3-Dihydro-2*H*-benzimidazol-2-ylidene)ammonio]-2-(4-methylphenyl)-2-oxoethyl}-3-oxocyclohex-1-enolate (6b). Yield 0.53 g (71%), white solid, mp 294–296°C. IR spectrum, ν, cm^{-1}: ~3435 (NH), 2942–2550 (=N$^+$H, CH_2), 1671 (C=O), 1618 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.49−1.66 (2H, m, CH_2); 1.96–2.15 (4H, m, 2CH_2); 2.31 (3H, s, CH_3); 5.80 (1H, d, *J* = 5.2, CH); 7.09–7.35 (6H, m, H-3,5 Ar, H HetAr); 7.61 (2H, d, *J* = 8.0, H-2,6 Ar); 8.75 (1H, d, *J* = 5.2, NH). ^{13}C NMR spectrum, δ, ppm: 21.7; 22.1; 28.2; 34.7; 53.3; 109.5; 111.1; 121.1; 122.5; 125.8; 129.1; 132.6; 133.0; 135.4; 137.4; 142.3; 156.2; 187.0; 193.1; 196.8. Mass spectrum (EI), *m*/*z* (I_{rel}, %): 357 [M–H_2O]$^+$ (8), 273 (18), 272 (13), 239 (21), 238 (100), 183 (15), 182 (25), 155 (20), 119 (46), 91 (67), 90 (19), 65 (33), 63 (22). Mass spectrum (APCI), *m*/*z*: 376 [M+H]$^+$, 374 [M–H]$^-$. Found, %: C 70.48; H 5.53; N 11.07. $C_{22}H_{21}N_3O_3$. Calculated, %: C 70.38; H 5.64; N 11.19.

2-{2-(4-Chlorophenyl)-1-[(1,3-dihydro-2*H*-benzimidazol-2-ylidene)ammonio]-2-oxoethyl}-3-oxocyclohex-1-enolate (6c). Yield 0.74 g (94%), white solid, mp 295–297°C. IR spectrum, ν, cm^{-1}: ~3400 (NH), 2970–2500 (=N$^+$H, CH_2), 1667 (C=O), 1612 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.52–1.70 (2H, m, CH_2); 1.89–2.21 (4H, m, 2CH_2); 5.82 (1H, d, *J* = 4.8, CH); 7.02–7.33 (4H, m, H HetAr); 7.47 (2H, d, *J* = 8.0, H-3,5 Ar); 7.69 (2H, d, *J* = 8.0, H-2,6 Ar); 8.83 (1H, d, *J* = 4.8, NH). ^{13}C NMR spectrum, δ, ppm: 20.9; 27.1; 34.2; 53.4; 111.3; 112.0; 121.2; 122.6; 127.4; 128.4; 129.2; 129.8; 133.8; 135.2; 138.7; 155.6; 187.8; 193.3; 196.1. Mass spectrum (EI), *m*/*z* (I_{rel}, %): 379 [M(^{37}Cl)–H_2O]$^+$ (1), 377 [M(^{35}Cl)–H_2O]$^+$ (3), 239 (15), 238 (100), 217 (14), 141 (12), 139 (35), 133 (56), 113 (5), 111 (14), 105 (10), 75 (9). Mass spectrum (APCI), *m*/*z*: 398 [M(^{37}Cl)+H]$^+$, 396 [M(^{35}Cl)+H]$^+$, 397 [M(^{37}Cl)]$^-$, 395 [M(^{35}Cl)]$^-$, 396 [M(^{37}Cl)–H]$^-$, 394 [M(^{35}Cl)–H]$^-$, 380 [M(^{37}Cl)–OH]$^+$, 378 [M(^{37}Cl)–OH]$^+$. Found, %: C 63.65; H 4.67; N 10.70. $C_{21}H_{18}ClN_3O_3$. Calculated, %: C 63.72; H 4.58; N 10.62.

Synthesis of compounds 7a,b (General method). A mixture of 2-aminobenzimidazole (**3**) (0.27 g, 2 mmol), hydrate of arylglyoxal **4a**,**b** (2 mmol), and 1,3-cyclohexanedione (**5**) (0.48 g, 4 mmol) in EtOH (20–25 ml) was refluxed for 3–4 h and the solvent evaporated *in vacuo*. The residue was crystallized from EtOAc. The precipitate was filtered and washed with EtOAc twice.

1,3-Dihydro-2*H*-benzimidazol-2-iminium 2-[1-(2-hydroxy-6-oxocyclohex-1-en-1-yl)-2-oxo-2-phenylethyl]-3-oxocyclohex-1-enolate with ethanol (1:1) (7a). Yield 0.92 g (89%), beige solid, mp 135–137°C. IR spectrum, ν, cm^{-1}: 3383–2682 (=N$^+$$H_2$, NH, CH_2, N···H, O···H), 1740 (C=O), 1683 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.14 (3H, t, *J* = 7.2, C$\underline{H}_3$$CH_2$OH); 1.50–1.68 (4H, m, 2$CH_2$); 2.01–2.21 (8H, m, 4$CH_2$); 3.94–4.05 (2H, q, *J* = 7.0, CH_3C$\underline{H}_2$OH); 6.23 (1H, s, CH); 7.05–7.15 (2H, m, H HetAr); 7.19–7.39 (5H, m, H-3,4,5 Ph, H HetAr); 7.58 (2H, d, *J* = 7.4, H-2,6 Ph); 7.93 (2H, br. s, NH_2). ^{13}C NMR spectrum, δ, ppm: 14.4; 21.0; 28.8; 32.6; 33.9; 34.9; 36.2; 38.7; 57.1; 100.1; 111.7; 113.9; 122.3; 128.9; 130.1; 131.2; 132.5; 133.5; 138.3; 152.1; 170.7; 188.2; 193.1; 196.0; 200.8. Mass spectrum (EI), *m*/*z* (I_{rel}, %): 340 [M–ABI (ABI = 2-aminobenzimidazole)]$^+$ (3), 235 (10), 218 (18), 133 [ABI]$^+$ (45), 106 (14), 105 (56), 88 (12), 77 (19), 70 (10), 61 (29), 45 (17), 43 (100). Found, %: C 66.95; H 6.30; N 7.97. $C_{29}H_{33}N_3O_6$. Calculated, %: C 67.04; H 6.40; N 8.09.

1,3-Dihydro-2*H*-benzimidazol-2-iminium 2-[1-(2-hydroxy-6-oxocyclohex-1-en-1-yl)-2-oxo-2-(4-methylphenyl)-ethyl]-3-oxocyclohex-1-enolate with ethanol (1:1) (7b). Yield 0.78 g (73%), beige solid, mp 130–133°C. IR spectrum, ν, cm^{-1}: 3371–2662 (=N$^+$$H_2$, NH, CH_2, N···H, O···H), 1742 (C=O), 1685 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.15 (3H, t, *J* = 7.2, C$\underline{H}_3$$CH_2$OH); 1.51–1.70 (4H, m, 2$CH_2$); 2.01–2.08 (8H, m, 4$CH_2$); 2.26 (3H, s, CH_3); 3.95–4.05 (2H, q, *J* = 7.2, CH_3C$\underline{H}_2$OH); 6.18 (1H, s, CH); 7.01–7.11 (4H, m, H-3,5 Ar, H HetAr); 7.21–7.28 (2H, m, H HetAr); 7.50 (2H, d, *J* = 7.8, H-2,6 Ar); 7.64 (2H, br. s, NH_2). ^{13}C NMR spectrum, δ, ppm: 14.2; 20.8; 21.1; 29.1; 31.2; 32.9; 34.6; 36.1; 38.4; 57.3; 102.1; 111.5; 113.6; 124.9; 127.7; 130.0; 130.8; 132.9; 135.2; 140.8; 152.0; 170.9; 188.0; 193.2; 195.1; 199.9. Mass spectrum (EI), *m*/*z* (I_{rel}, %): 336 [M–ABI–H_2O]$^+$ (9), 235 (35), 218 (23), 217 (8), 149 (9), 133 [ABI]$^+$ (66), 120 (9), 119 (100), 91 (40), 55 (35), 41 (45). Found, %: C 67.65; H 6.70; N 7.95. $C_{30}H_{35}N_3O_6$. Calculated, %: C 67.52; H 6.61; N 7.87.

Synthesis of compounds 8 and 9. I. Compound **7a** (0.52 g, 1 mmol) was melted on an oil bath at 135°C. The melt was dissolved in 2-PrOH to give a mixture of compounds **8** and **9**. These compounds were separated by crystallization from EtOH.

II. A solution of compound **7a** (0.52 g, 1 mmol) in DMF (10–12 ml) was refluxed for 3 h. Products **8** and **9** were precipitated by distilled H_2O (80 ml), filtered, and separated by crystallization from EtOH.

III. A solution of compound **7a** (0.52 g, 1 mmol) in acetic acid (8–10 ml) was refluxed for 3 h. Products **8** and **9** were precipitated by distilled H_2O (60 ml), filtered, and separated by crystallization from EtOH.

9-Benzoyl-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione (8). Yield 0.04 g (13%, method I), 0.05 g (15%, method II), 0.03 g (10%, method III), white solid, mp 210–212°C. IR spectrum, ν, cm^{-1}: 2953–2841 (CH_2), 1682 (C=O), 1658 (C=O), 1623 (C=C), 1176 (–O–). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.77–1.99 (4H, m, 2CH_2); 2.21–2.30 (4H, m, 2CH_2); 2.57–2.64 (4H, m, 2CH_2); 6.23 (1H, s, 9-CH); 7.44–7.63 (3H, m, H-3,4,5 Ph); 8.12 (2H, d, *J* = 7.2, H-2,6 Ph). ^{13}C NMR spectrum, δ, ppm: 20.2; 26.8; 34.1; 36.3; 113.8; 128.3; 129.3; 133.0; 137.3; 166.3; 196.8; 201.2. Mass spectrum (EI), *m*/*z* (I_{rel}, %): 322 [M]$^+$ (10), 236 (10), 235 (62), 217 (14), 175 (18), 105 (37), 86 (35), 84 (83), 77 (92), 55 (47), 51 (81), 49 (100), 47 (14). Found, %: C 74.61; H 5.71. $C_{20}H_{18}O_4$. Calculated, %: C 74.52; H 5.63.

1,3-Dihydro-2*H*-benzimidazol-2-iminium 3-oxo-2-(4-oxo-2-phenyl-4,5,6,7-tetrahydro-1-benzofuran-3-yl)cyclohex-1-enolate (9). Yield 0.35 g (78%, method I), 0.27 g (60%, method II), 0.32 g (71%, method III), yellow solid, mp 253–255°C. IR spectrum, ν, cm^{-1}: 3426 (NH), 2936–2500 (=N^+H_2, CH_2), 1682 (C=O), 1662 (C=O), 1611 (C=C), 1184 (–O–). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.88–2.12 (4H, m, $2CH_2$); 2.22–2.43 (6H, m, $3CH_2$); 2.88–2.96 (2H, m, CH_2); 6.16 (2H, br. s, NH_2); 6.80–6.86 (2H, m, H Ar); 7.03–7.10 (2H, m, H Ar); 7.23–7.38 (3H, m, H-3,4,5 Ph); 7.50 (2H, d, *J* = 7.4, H-2,6 Ph). ^{13}C NMR spectrum, δ, ppm: 20.5; 22.1; 23.1; 33.1; 35.9; 38.0; 111.5; 117.5; 119.6; 122.5; 124.5; 125.6; 127.4; 128.6; 129.3; 130.7; 141.7; 148.3; 155.0; 165.9; 186.6; 193.2; 195.4. Mass spectrum (EI), *m*/*z* (I_{rel}, %): 322 [M–ABI]$^+$ (18), 239 (17), 238 (100), 217 (10), 133 [ABI]$^+$ (30), 105 (11), 84 (18), 55 (16). Found, %: C 71.09; H 5.61; N 9.35. $C_{27}H_{25}N_3O_4$. Calculated, %: C 71.19; H 5.53; N 9.22.

Synthesis of compounds 10a–f and 11a–f (General method). I. A mixture of 2-aminobenzimidazole (**3**) (0.27 g, 2 mmol), hydrate of arylglyoxal **4a–f** (2 mmol), and 1,3-cyclohexanedione (**5**) (0.24 g, 2 mmol) in AcOH (10–12 ml) was heated at 100°C for 3–5 h. After cooling, the precipitate of compound **10a–f** was removed by filtration and washed with EtOH twice. The amorphous precipitate of compound **11a–f** that formed in the filtrate after 1–3 days was recrystallized from EtOAc.

II. A mixture of 2-aminobenzimidazole (**3**) (0.27 g, 2 mmol), hydrate of arylglyoxal **4a–f** (2 mmol), and 1,3-cyclohexanedione (**5**) (0.24 g, 2 mmol) in DMF (5 ml) was contained in a sealed microwave vial and heated in a single mode microwave reactor at 150°C for 10 min with magnetic stirring. After cooling, the precipitate of compound **11a–f** was removed by filtration and washed with EtOH twice. After 1–2 days, the precipitate of compound **10a–f** was formed in the initial filtrate. This precipitate was filtered off and recrystallized from MeOH.

12-Benzoyl-3,4,5,12-tetrahydrobenzimidazo[2,1-*b*]-quinazolin-1(2*H*)-one (10a). Beige solid, mp 288–290°C. IR spectrum, ν, cm^{-1}: 3096–2500 (NH, N···H, CH_2), 1686 (C=O), 1658 (C=O), 1637 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.79–1.96 (2H, m, CH_2); 2.23–2.38 (2H, m, CH_2); 2.62–2.67 (2H, m, CH_2); 6.91 (1H, t, *J* = 7.6, H HetAr); 7.02–7.15 (3H, m, 12-CH, H HetAr); 7.40 (1H, d, *J* = 7.8, H HetAr); 7.55 (2H, t, *J* = 7.6, H-3,5 Ph); 7.69 (1H, t, *J* = 7.2, H-4 Ph); 8.25 (2H, d, *J* = 7.8, H-2,6 Ph); 11.29 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 20.9; 27.1; 36.3; 53.5; 104.3; 109.5; 117.6; 121.1; 122.5; 129.1; 129.6; 132.6; 134.4; 135.6; 142.3; 146.3; 155.3; 193.2; 197.4. Mass spectrum (EI), *m*/*z* (I_{rel}, %): 343 [M]$^+$ (3), 239 (29), 238 (100), 237 (8), 208 (8), 105 (11), 77 (14), 51 (10). Found, %: C 73.39; H 5.07; N 12.33. $C_{21}H_{17}N_3O_2$. Calculated, %: C 73.45; H 4.99; N 12.24.

12-(4-Methylbenzoyl)-3,4,5,12-tetrahydrobenzimidazo-[2,1-*b*]quinazolin-1(2*H*)-one (10b). Beige solid, mp 296–298°C. IR spectrum, ν, cm^{-1}: 3070–2500 (NH, N···H, CH_2, CH_3), 1672 (C=O), 1657 (C=O), 1633 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.72–1.99 (2H, m, CH_2); 2.18–2.30 (2H, m, CH_2); 2.39 (3H, s, CH_3); 2.62−2.67 (2H, m, CH_2); 6.91 (1H, t, *J* = 7.2, H HetAr); 6.99–7.11 (3H, m, 12-CH, H HetAr); 7.34−7.41 (3H, m, H-3,5 Ar, H HetAr); 8.17 (2H, d, *J* = 8.0, H-2,6 Ar), 11.23 (1H, br. s, NH). ^{1}H NMR spectrum (DMSO-d_6+D_2O), δ, ppm (*J*, Hz): 1.71–2.00 (2H, m, CH_2); 2.17–2.29 (2H, m, CH_2); 2.36 (3H, s, CH_3); 2.60–2.65 (2H, m, CH_2); 6.86–7.10 (4H, m, 12-CH, H HetAr); 7.31−7.40 (3H, m, H-3,5 Ar, H HetAr); 8.10 (2H, d, *J* = 7.8, H-2,6 Ar). ^{13}C NMR spectrum, δ, ppm: 21.0; 21.7; 27.1; 36.4; 53.3; 104.4; 109.5; 117.5; 121.0; 122.5; 129.6; 129.8; 132.6; 133.0; 142.3; 145.1; 146.3; 156.2; 193.1; 196.8 (C=O). Mass spectrum (EI), *m*/*z* (I_{rel}, %): 357 [M]$^+$ (3), 238 (100), 237 (19), 119 (8), 91 (10). Found, %: C 74.02; H 5.43; N 11.83. $C_{22}H_{19}N_3O_2$. Calculated, %: C 73.93; H 5.36; N 11.76.

12-(4-Chlorobenzoyl)-3,4,5,12-tetrahydrobenzimidazo-[2,1-*b*]quinazolin-1(2*H*)-one (10c). Beige solid, mp 287–289°C. IR spectrum, ν, cm^{-1}: 3092~2500 (NH, N···H, CH_2), 1686 (C=O), 1658 (C=O), 1637 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.71–1.97 (2H, m, CH_2); 2.18–2.31 (2H, m, CH_2); 2.61–2.68 (2H, m, CH_2); 6.93 (1H, t, *J* = 7.0, H HetAr); 7.02–7.13 (3H, m, 12-CH, H HetAr); 7.41 (1H, d, *J* = 7.8, H HetAr); 7.63 (2H, d, *J* = 8.2, H-3,5 Ar); 8.28 (2H, d, *J* = 8.4, H-2,6 Ar); 11.34 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 20.9; 27.1; 36.3; 53.5; 104.1; 109.4; 117.6; 121.2; 122.6; 129.2; 131.5; 132.5; 134.2; 139.5; 142.2; 146.3; 156.5; 193.2; 196.6. Mass spectrum (EI), *m*/*z* (I_{rel}, %): 379 [M(^{37}Cl)]$^+$ (1), 377 [M(^{35}Cl)]$^+$ (3), 239 (39), 238 (100), 210 (3), 208 (9), 139 (16), 111 (12), 75 (16). Found, %: C 66.85; H 4.41; N 11.25. $C_{21}H_{16}ClN_3O_2$. Calculated, %: C 66.76; H 4.27; N 11.12.

12-(4-Fluorobenzoyl)-3,4,5,12-tetrahydrobenzimidazo-[2,1-*b*]quinazolin-1(2*H*)-one (10d). Beige solid, mp 295–297°C. IR spectrum, ν, cm^{-1}: 3072–2500 (NH, N···H, CH_2), 1683 (C=O), 1642 (C=O), 1617 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.73–1.99 (2H, m, CH_2); 2.17–2.31 (2H, m, CH_2); 2.58−2.70 (2H, m, CH_2); 6.92 (1H, t, *J* = 7.0, H HetAr); 7.01–7.14 (3H, m, 12-CH, H HetAr); 7.32−7.45 (3H, m, H-3,5 Ar, H HetAr); 8.33−8.40 (2H, dd, *J* = 8.0, *J* = 5.8, H-2,6 Ar); 11.33 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 20.8; 27.2; 36.4; 53.4; 104.0; 109.3; 115.9; 116.1; 117.5; 120.9; 122.3; 132.0; 132.5; 132.8; 142.2; 146.3; 155.4; 167.3; 192.7; 195.4. Mass spectrum (EI), *m*/*z* (I_{rel}, %): 361 [M]$^+$ (2), 239 (10), 238 (66), 88 (10), 86 (67), 84 (100), 51 (20). Found, %: C 69.69; H 4.58; N 11.55. $C_{21}H_{16}FN_3O_2$. Calculated, %: C 69.80; H 4.46; N 11.63.

12-(4-Bromobenzoyl)-3,4,5,12-tetrahydrobenzimidazo-[2,1-*b*]quinazolin-1(2*H*)-one (10e). Beige solid, mp 293–295°C. IR spectrum, ν, cm^{-1}: 3090–2500 (NH, N···H, CH_2), 1681 (C=O), 1641 (C=O), 1620 (C=C). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.74–2.01 (2H, m, CH_2); 2.18–2.31 (2H, m, CH_2); 2.60–2.67 (2H, m, CH_2); 6.94 (1H, t, *J* = 7.2, H HetAr); 7.02–7.13 (3H, m, 12-CH, H HetAr); 7.40 (1H, d, *J* = 7.6, H HetAr); 7.77 (2H, d, *J* = 8.6, H-3,5 Ar); 8.20 (2H, d, *J* = 8.6, H-2,6 Ar); 11.31 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 20.7; 26.8; 36.0; 53.2; 103.8; 109.2; 117.3; 120.9; 122.3; 128.5; 131.3; 131.9; 132.3; 134.3; 141.9; 146.0; 155.3; 193.0; 196.6. Mass spectrum (EI), *m*/*z* (I_{rel}, %): 423 [M(^{87}Br)]$^+$ (2), 421 [M(^{85}Br)]$^+$ (2),

239 (30), 238 (100), 237 (8), 185 (4), 183 (5), 157 (4), 155 (4). Found, %: C 59.82; H 3.91; N 10.05. $C_{21}H_{16}BrN_3O_2$. Calculated, %: C 59.73; H 3.82; N 9.95.

12-(4-Methoxybenzoyl)-3,4,5,12-tetrahydrobenzimidazo-[2,1-*b*]quinazolin-1(2*H*)-one (10f). Beige solid, mp 290–292°C. IR spectrum, ν, cm^{-1}: 3056–2500 (NH, N···H, CH_2), 1672 (C=O), 1652 (C=O), 1640 (C=C), 1176 (OCH_3). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.68–2.03 (2H, m, CH_2); 2.12–2.34 (2H, m, CH_2); 2.58–2.75 (2H, m, CH_2); 3.86 (3H, s, OCH_3); 6.91 (1H, t, *J* = 7.4, H HetAr); 6.98–7.15 (5H, m, 12-CH, H-3,5 Ar, H HetAr); 7.39 (1H, d, *J* = 8.0, H HetAr); 8.27 (2H, d, *J* = 8.6, H-2,6 Ar); 11.19 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 20.9; 27.1; 36.5; 53.0; 56.0; 104.5; 109.5; 114.0; 117.5; 121.0; 122.9; 128.0; 132.3; 132.6; 142.3; 146.4; 156.2; 164.3; 193.1; 195.5. Mass spectrum (EI), *m*/*z* (I_{rel}, %): 373 $[M]^+$ (6), 239 (18), 238 (100), 237 (18), 135 (4). Found, %: C 70.67; H 5.04; N 11.34. $C_{22}H_{19}N_3O_3$. Calculated, %: C 70.76; H 5.13; N 11.25.

3-Oxo-2-(2-phenyl-1*H*-imidazo[1,2-*a*]benzimidazol-9-ium-3-yl)cyclohex-1-enolate (11a). Beige solid, mp 293–295°C. IR spectrum, ν, cm^{-1}: 3053–2500 (NH, N···H, O···H, CH_2), 1667 (C=O), 1613 (C=C). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.99–2.17 (2H, m, CH_2); 2.52–2.67 (4H, m, $2CH_2$); 7.01 (1H, t, *J* = 7.4, H HetAr); 7.10−7.37 (6H, m, H-3,4,5 Ph, H HetAr), 7.66 (2H, d, *J* = 7.2, H-2,6 Ph). ^{13}C NMR spectrum, δ, ppm: 20.9; 33.7; 36.1; 106.6; 109.9; 111.2; 112.5; 119.6; 122.9; 125.8; 125.9; 126.2; 128.5; 132.0; 135.8; 137.4; 148.9; 185.1; 195.2. Mass spectrum (EI), *m*/*z* (I_{rel}, %): 343 $[M]^+$ (3), 131 (22), 130 (20), 108 (10), 77 (11), 76 (9), 40 (100). Found, %: C 73.36; H 5.06; N 12.15. $C_{21}H_{17}N_3O_2$. Calculated, %: C 73.45; H 4.99; N 12.24.

2-[2-(4-Methylphenyl)-1*H*-imidazo[1,2-*a*]benzimidazol-9-ium-3-yl]-3-oxocyclohex-1-enolate (11b). Beige solid, mp 291–293°C. IR spectrum, ν, cm^{-1}: 3034–2500 (NH, N···H, O···H, CH_2, CH_3), 1661 (C=O), 1615 (C=C). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.96–2.16 (2H, m, CH_2); 2.26 (3H, s, CH_3); 2.53–2.67 (4H, m, $2CH_2$); 7.00 (1H, t, *J* = 7.2, H HetAr); 7.06−7.24 (4H, m, H-2,6 Ar, H HetAr); 7.34 (1H, d, *J* = 7.6, H HetAr); 7.53 (2H, d, *J* = 8.2, H-2,6 Ar). ^{13}C NMR spectrum, δ, ppm: 20.8; 24.1; 33.3; 35.7; 106.5; 109.3; 112.1; 113.6; 122.76; 124.0; 125.8; 127.3; 129.1; 132.7; 135.4; 137.3; 137.7; 148.9; 185.0; 195.0. Mass spectrum (EI), *m*/*z* (I_{rel}, %): 359 (11), 358 (45), 357 $[M]^+$ (100), 356 (39), 355 (19), 301 (17), 272 (16), 271 (24), 258 (34), 118 (13), 104 (21), 90 (10), 89 (14), 82 (11), 79 (12), 77 (13), 73 (55), 56 (23), 49 (35), 44 (56). Found, %: C 74.04; H 5.26; N 11.87. $C_{22}H_{19}N_3O_2$. Calculated, %: C 73.93; H 5.36; N 11.76.

2-(2-(4-Chlorophenyl)-1*H*-imidazo[1,2-*a*]benzimidazol-9-ium-3-yl)-3-oxocyclohex-1-enolate (11c). Beige solid, mp 301–303°C. IR spectrum, ν, cm^{-1}: 3061~2500 (NH, N···H, O···H, CH_2), 1658 (C=O), 1615 (C=C). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.99–2.16 (2H, m, CH_2); 2.54–2.68 (4H, m, $2CH_2$); 7.04 (1H, t, *J* = 7.2, H HetAr); 7.12−7.26 (2H, m, H HetAr); 7.29−7.39 (3H, m, H-3,5 Ar, H HetAr); 7.67 (2H, d, *J* = 8.6, H-2,6 Ar). ^{13}C NMR spectrum, δ, ppm: 20.7; 33.4; 36.0; 106.2; 110.4; 111.3; 112.1; 119.8; 123.1; 125.5; 127.5; 128.6; 130.6; 135.2; 136.5; 137.6; 148.7; 184.8; 195.1. Mass spectrum (EI), *m*/*z* (I_{rel}, %): 378 $[M(^{37}Cl)–H]^+$ (1), 376 $[M(^{35}Cl)–H]^+$ (3), 192 (3), 190 (1), 130 (10), 95 (14), 40 (100). Found, %: C 66.87; H 4.18; N 11.04. $C_{21}H_{16}ClN_3O_2$. Calculated, %: C 66.76; H 4.27; N 11.12.

2-(2-(4-Fluorophenyl)-1*H*-imidazo[1,2-*a*]benzimidazol-9-ium-3-yl)-3-oxocyclohex-1-enolate (11d). Beige solid, mp 303–305°C. IR spectrum, ν, cm^{-1}: 3062–2500 (NH, N···H, O···H, CH_2), 1658 (C=O), 1616 (C=C). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.97–2.17 (2H, m, CH_2); 2.53–2.66 (4H, m, $2CH_2$); 6.96−7.24 (5H, m, H-3,5 Ar, H HetAr); 7.33 (1H, d, *J* = 7.4, H Ar); 7.61−7.73 (2H, dd, *J* = 8.6, *J* = 5.8, H-2,6 Ar). ^{13}C NMR spectrum, δ, ppm: 20.9; 33.7; 36.1; 106.4; 109.6; 111.1; 112.2; 115.1; 115.4; 119.7; 123.0; 125.6; 127.6; 132.6; 136.7; 137.4; 148.8; 162.7; 185.2; 195.7. Mass spectrum (EI), *m*/*z* (I_{rel}, %): 361 $[M]^+$ (8), 304 (8), 275 (12), 132 (17), 131 (10), 104 (10), 77 (10), 76 (12), 73 (22), 69 (35), 44 (100), 42 (76), 40 (13). Found, %: C 69.90; H 4.35; N 11.74. $C_{21}H_{16}FN_3O_2$. Calculated, %: C 69.80; H 4.46; N 11.63.

2-(2-(4-Bromophenyl)-1*H*-imidazo[1,2-*a*]benzimidazol-9-ium-3-yl)-3-oxocyclohex-1-enolate (11e). Beige solid, mp 293–295°C. IR spectrum, ν, cm^{-1}: 3063~2500 (NH, N···H, O···H, CH_2), 1661 (C=O), 1615 (C=C). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.99–2.16 (2H, m, CH_2); 2.53–2.67 (4H, m, $2CH_2$); 7.03 (1H, t, *J* = 7.4, H HetAr); 7.12−7.25 (2H, m, H HetAr); 7.34 (1H, d, *J* = 7.8, H HetAr); 7.46 (2H, d, *J* = 8.6, H-3,5 Ar); 7.60 (2H, d, *J* = 8.6, H-2,6 Ar). ^{13}C NMR spectrum, δ, ppm: 20.7; 33.7; 36.2; 106.4; 110.5; 111.5; 112.1; 119.1; 119.9; 123.2; 125.6; 127.9; 131.5; 135.6; 136.6; 137.5; 148.7; 185.6; 194.8. Mass spectrum (EI), *m*/*z* (I_{rel}, %): 423 $[M(^{81}Br)]^+$ (43), 421 $[M(^{79}Br)]^+$ (4), 131 (20), 127 (9), 105 (19), 103 (11), 98 (10), 79 (23), 76 (20), 72 (100), 71 (81), 69 (25), 55 (16), 44 (68), 41 (87). Found, %: C 59.65; H 3.91; N 9.84. $C_{21}H_{16}BrN_3O_2$. Calculated, %: C 59.73; H 3.82; N 9.95.

2-(2-(4-Methoxyphenyl)-1*H*-imidazo[1,2-*a*]benzimidazol-9-ium-3-yl)-3-oxocyclohex-1-enolate (11f). Beige solid, mp 287–289°C. IR spectrum, ν, cm^{-1}: 3072~2500 (NH, N···H, O···H, CH_2), 1659 (C=O), 1613 (C=C), 1179 (OCH_3). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.97–2.18 (2H, m, CH_2); 2.53–2.69 (4H, m, $2CH_2$); 3.73 (3H, s, OCH_3); 6.87 (2H, d, *J* = 8.8, H-2,6 Ar); 7.00 (1H, t, *J* = 7.4, H HetAr); 7.09−7.25 (2H, m, H HetAr); 7.34 (1H, d, *J* = 7.8, H HetAr); 7.58 (2H, d, *J* = 8.8, H-3,5 Ar). ^{13}C NMR spectrum, δ, ppm: 20.8; 33.4; 36.2; 55.4; 106.5; 108.6; 111.0; 112.7; 114.0; 119.5; 122.7; 125.9; 127.1; 127.9; 136.8; 137.8; 148.8; 158.1; 184.6; 194.9. Mass spectrum (EI), *m*/*z* (I_{rel}, %): 373 $[M]^+$ (100), 316 (30), 290 (10), 289 (52), 274 (14), 260 (11), 257 (10), 244 (15), 231 (18), 184 (23), 156 (19), 139 (11), 133 (25), 105 (13), 90 (19), 77 (21), 76 (10), 73 (54), 63 (12), 44 (93). Found, %: C 70.68; H 5.22; N 11.36. $C_{22}H_{19}N_3O_3$. Calculated, %: C 70.76; H 5.13; N 11.25.

X-Ray diffraction studies were performed on an automatic Xcalibur-3 diffractometer (graphite monochromator, Mo*K*α radiation, CCD-detector, ω-scanning). Structures were solved by direct method using the SHELXTL package.[21] Restrictions on the bond lengths in disordered fragments (Csp^3–Csp^3 1.54 Å) were applied for compound **8**.

Positions of hydrogen atoms were determined from electron density difference maps and refined by the "riding" model with $U_{iso} = nU_{eq}$ of the carrier atom (n = 1.5 for methyl groups and n = 1.2 for other hydrogen atoms). Hydrogen atoms of the protonated iminogroup in **9** and NH group in **10a** were refined in isotropic approximation. Crystallographic data and experimental parameters are listed in Table S1 (see Supplementary materials). Final atomic coordinates, geometrical parameters and crystallographic data have been deposited with the Cambridge Crystallographic Data Center (the deposit numbers are CCDC 994244 (compound **6b**), CCDC 994245 (compound **7b**), CCDC 994246 (compound **8**), CCDC 994247 (compound **9**), CCDC 994248 (compound **10a**), CCDC 994249 (compound **11b**)).

The Supplementary file containing crystallographic data, IR, ^{1}H and ^{13}C NMR, and mass spectra of synthesized compounds is available at the Journal webpage http://hgs.osi.lv.

References

1. Biggs-Houck, J. E.; Younai, A.; Shaw, J. T. *Curr. Opin. Chem. Biol.* **2010**, *14*, 371.
2. Bariwal, J. B.; Trivedi, J. C.; Van der Eycken, E. V. *Top. Heterocycl. Chem.* **2010**, *25*, 169.
3. Simon, C.; Constantieux, T.; Rodriguez, J. *Eur. J. Org. Chem.* **2004**, 4957.
4. Hügel, H. *Molecules* **2009**, *14*, 4936.
5. Quiroga, J.; Hormaza, A.; Insuasty, B.; Ortíz, A. J.; Sánchez, A.; Nogueras, M. *J. Heterocycl. Chem.* **1998**, *35*, 231.
6. Quiroga, J.; Insuasty, B.; Hormaza, A.; Saitz, C.; Jullian, C. *J. Heterocycl. Chem.* **1998**, *35*, 575.
7. Quiroga, J.; Hormaza, A.; Insuasty, B.; Saitz, C.; Jullian, C.; Cañete, A. *J. Heterocycl. Chem.* **1998**, *35*, 61.
8. Quiroga, J.; Mejía, D.; Insuasty, B.; Abonía, R.; Nogueras, M.; Sánchez, A.; Cobo, J.; Low, J. N. *Tetrahedron* **2001**, *57*, 6947.
9. Quiroga, J.; Acosta, P. A.; Cruz, S.; Abonía, R.; Insuasty, B.; Nogueras, M. *Tetrahedron Lett.* **2010**, *51*, 5443.
10. Chebanov, V. A.; Saraev, V. E.; Desenko, S. M.; Chernenko, V. N.; Shishkina, S. V.; Shishkin, O. V.; Kobzar, K. M.; Kappe, C. O. *Org. Lett*. **2007**, *9*, 1691.
11. Chebanov, V. A.; Saraev, V. E.; Desenko, S. M.; Chernenko, V. N.; Knyazeva, I. V.; Groth, U.; Glasnov, T. N.; Kappe, C. O. *J. Org. Chem*. **2008**, *73*, 5110.
12. Muravyova, E. A.; Shishkina, S. V.; Musatov, V. I.; Knyazeva I. V.; Shishkin, O. V.; Desenko, S. M.; Chebanov, V. A. *Synthesis* **2009**, 1375.
13. Lipson, V. V.; Desenko, S. M.; Borodina, V. V.; Shirobokova, M. G.; Shishkin, O. V.; Zubatyuk, R. I. *Russ. Chem. Bull., Int. Ed*. **2006**, *55*, 1224. [*Izv. Akad. Nauk, Ser. Khim.* **2006**, 1178.]
14. Lipson, V. V.; Svetlichnaya, N. V.; Shirobokova, M. G.; Musatov, V. I.; Shishkin, O. V.; Shishkina, S. V. *Russ. J. Org. Chem*. **2012**, *48*, 273. [*Zh. Org. Khim.* **2012**, *48*, 281.]
15. Petrov, A. A.; Kasatochkin, A. N.; Emelina, E. E.; Nelyubina, Yu. V.; Antipin, M. Yu. *Russ. J. Org. Chem*. **2009**, *45*, 1390. [*Zh. Org. Khim.* **2009**, *45*, 1403.]
16. Vandyshev, D.; Shikhaliev, Kh.; Potapov, A.; Krysin, M. *Chem. Heterocycl. Compd*. **2014**, *50*, 1316. [*Khim. Geterotsikl. Soedin.* **2014**, 1428.]
17. Lipson, V. V.; Desenko, S. M.; Shishkina, S. V.; Shirobokova, M. G.; Shishkin, O. V.; Orlov, V. D. *Chem. Heterocycl. Compd*. **2003**, *39*, 1041. [*Khim. Geterotsikl. Soedin.* **2003**, 1194.]
18. Petrova, O. N.; Zamigajlo, L. L.; Shishkina, S. V.; Shishkin, O. V.; Musatov, V. I.; Borisov, A. V.; Lipson, V. V. *Tetrahedron* **2013**, *69*, 11185.
19. Burgi, H.-B.; Dunitz, J. D. *Structure correlation*, Mager, T., Ed.; VCH: Weinheim, 1994, vol. 2, p. 751.
20. Bisenieks, E. A.; Makarova, N. V.; Uldrikis, Ya. R.; Dubur, G. Ya. *Chem. Heterocycl. Compd*. **1988**, *24*, 417. [*Khim. Geterotsikl. Soedin.* **1988**, 507.]
21. Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *A64*, 112.