Cyclization of alk-4-ynals with *o*-diaminoarenes as a selective one-pot synthesis of arylmethylidene-substituted 2,3-dihydro-1*H*-pyrrolo[1,2-*a*]benzimidazoles and 7,8-dihydro-6*H*-pyrrolo[1´,2´:1,2]imidazo[4,5-*b*]pyridines*,**

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A one-pot synthesis of arylmethylidene-substituted 2,3-dihydro-1*H*-pyrrolo[1,2-*a*]-benzimidazoles based on the reaction of alk-4-ynals with 1,2-diaminobenzenes in DMSO at sequential catalysis with NH_4Br and bases was suggested. The use in these processes of KOH as a base led to the selective formation of *E*-isomers of the final products in 48—66% yields, whereas less basic K_2CO_3 gave the corresponding *Z*-isomers in 32—82% yields. Similar cyclization reactions involving 2,3-diaminopyridine gave 7,8-dihydro-6*H*-pyrrolo[1´,2´:1,2]imidazo[4,5-*b*]pyridines in up to 56% yields. The distinguishing feature of the processes under study is proceeding of their key step that is intramolecular hydroamination of the triple bond, as a 5-*exo*-*dig*-cyclization. The necessity for the application of drastic conditions required for these processes is in agreement with the results of quantum chemical calculations of PES of their most probable rate-determining step, namely, the cyclization of the corresponding benzimidazolide anions to cyclic vinyl anions.

Key words: alk-4-ynals, 1,2-diaminoarenes, 2,3-dihydro-1*H*-pyrrolo[1,2-*a*]benzimidazoles, 7,8-dihydro-6*H*-pyrrolo[1´,2´:1,2]imidazo[4,5-*b*]pyridines, hydroamination, anionic cyclization, dimethyl sulfoxide, potassium hydroxide, potassium carbonate, quantum chemical calculations.

Pyrrolobenzimidazoles play an important role in medicinal chemistry and can be regarded as privileged scaffolds in pharmaceutical studies. Investigation of their biological activity began in 1975, when these compounds were found to possess pronounced analgesic activity.[2] Later, it was shown that substituted 2,3-dihydro-1*H*-pyrrolo[1,2-*a*]-benzimidazoles can be used as inhibitors of protein-protein interaction[3] and antitumor agents.[4,5]

The common syntheses of these compounds include the rhodium-catalyzed cyclization of *N*-alkenylbenzimidazoles,[6] cyclocondensation of pyrrolidones with *o*-bromoanilines,[8] annulation of benzimidazoles through the intramolecular nucleophilic substitution,[9] and cyclopropylimine rearrangement of 2-cyclopropylbenzimidazolium salts.[10] There are also known syntheses of 2,3-dihydro-1*H*-pyrrolo[1,2-*a*]benzimidazoles based on the radical cyclization of different alkylbenzimidazoles[11] and iodocyclization of 2-alkynylbenzimidazoles.[12]

Earlier, we have suggested[13—15] an original approach to (arylmethylidene)octahydropyrrolo[1,2-*a*]pyrimidines and 5-(arylmethylidene)hexahydropyrrolo[1,2-*a*]imidazoles based on the reaction of alk-4-ynals with aliphatic diamines upon treatment with strong bases. Later, this approach was extended[16] to similar processes involving amino alcohols and amino thiols, which led to the corresponding fused oxazoles, oxazines, and thiazoles with an exocyclic double bond. Further development of these studies showed that the use of *o*-aminobenzylamine and *o*-aminobenzyl alcohol as binucleophilic reagents in the reactions with alk-4-ynals constitutes a simple, efficient, and metal-free method for the preparation of 1-arylmethylidene-1,2,3,3a-tetrahydro-5*H*-pyrrolo[1,2-*a*][3,1]benzoxazines and 1-arylmethylidene-1,2,3,3a,4,5-hexahydropyrrolo[1,2-*a*]quinazolines.[17]

Recently, we accomplished[1] a one-pot synthesis of arylmethylidene-substituted 2,3-dihydro-1*H*-pyrrolo[1,2-*a*]-benzimidazoles based on the reaction of available alk-4-ynals with 1,2-diaminobenzene, which is catalyzed sequentially by ammonium bromide and bases. By the present time, there are known only several examples of the preparation of such compounds[12] which contain an iodine

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atom, a phenyl and a phenylethynyl group as substituents in the methylidene fragment, with all of them being obtained as less sterically hindered *E*-isomers. The present work is devoted to more detailed study of the discovered[1] process for the preparation of these compounds, revealing its specific features and synthetic scope.

Results and Discussion

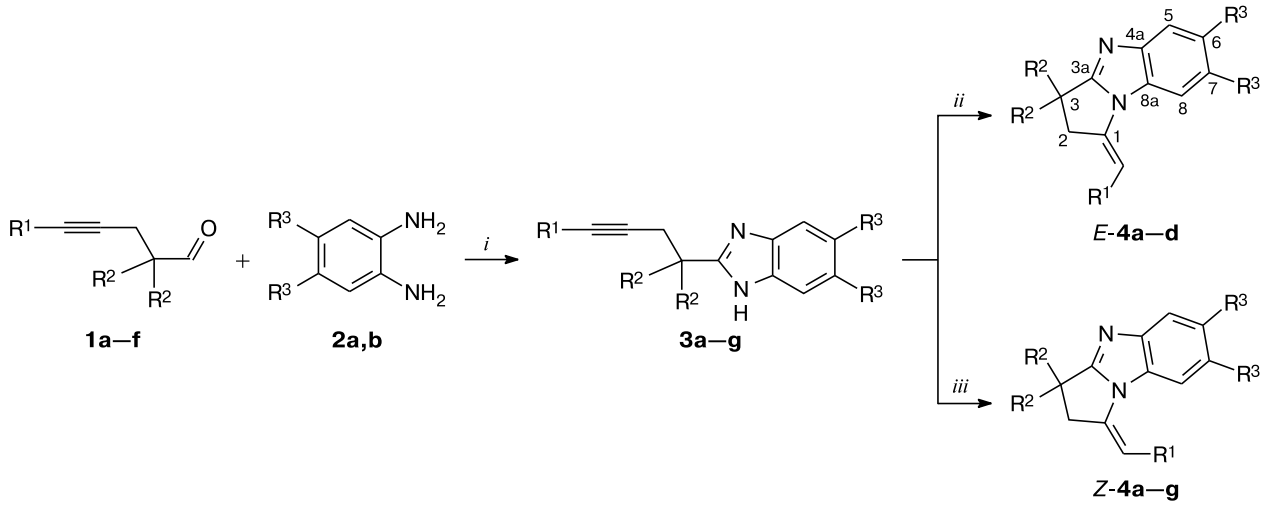
In the course of the present studies, we found that the stirring of equimolar amounts of aldehydes **1a**—**f** and *o*-diaminobenzenes **2a**,**b** in anhydrous DMSO in the presence of NH_4Br at ~20 °C led, according to the NMR spectra of the reaction mixtures, to the selective formation of the corresponding 2-alkynyl-substituted benzimidazoles **3a**—**g** (Scheme 1). Earlier,[18] a four-fold excess of NH_4Br was used in similar reactions with aromatic aldehydes, however, we showed that the process can successfully proceed with only 20 mol.% NH_4Br. In separate experiments, benzimidazoles **3a** and **3d** were isolated in the individual state in 68% and 74% yields, respectively.

It should be noted that carrying out the reaction of aldehydes **1** with aromatic diamines with contact of the reaction mixture with air is a necessary condition for benzimidazoles **3** to be formed. A control reaction of aldehyde **1a** and *o*-diaminobenzene **2a** under argon for 24 h gave, according to the NMR spectra of the reaction mixture, only 2-(1,1-dimethyl-4-phenylbut-3-yn-1-yl)-2,3-dihydro-1*H*-benzimidazole, which was an initial product of cyclocondensation of the starting compounds. Its structure was established based on characteristic signals, which are: first of all, a broad singlet at δ 5.02 corresponding to the aminal proton; a doublet with the spin-spin coupling constant J = 3.4 Hz attributed to two equivalent NH groups; as well as a multiplet for four protons of the dihydrobenzimidazole fragment in the region of δ 6.23—6.37.

The addition of a 1.5-fold molar excess of freshly powdered KOH to the solutions of benzimidazoles **3a**—**d** in DMSO with subsequent stirring of the reaction mixtures at ~20 °C for 2 h did not cause any changes in contrast to the earlier studied by us similar processes involving alkynyl-substituted 1,4-dihydro-2*H*-3,1-benzoxazines and 1,2,3,4-tetrahydroquinazolines.[17] However, raising temperature to 50 °C and prolongation the reaction to 12—48 h led to the complete transformation of compounds **3** into pyrrolobenzimidazoles **4a**—**d**, which were obtained exclusively as *E*-isomers, as was inferred from the NMR spectra of the reaction mixtures (see Scheme 1, Table 1). The latter after aqueous work-up of the reaction mixtures were isolated in 48—66% yields by recrystallization from hexane (for compounds **4a**—**c**) or by chromatography on silica gel (for compound **4d**).

Unfortunately, our attempts to involve alk-4-ynals with hydrogen atoms at α-position to the carbonyl group in

Scheme 1



Compound **1**	R^1	R^2
a	Ph	Me
b	2-thienyl	Me
c	Ph	—$(CH_2)_5$—
d	Ph	H
e	3,4-$F_2C_6H_3$	H
f	3,4-$F_2C_6H_3$	Me

2: R^3 = H (**a**), Me (**b**)

Compound **3**, **4**	R^1	R^2	R^3
a	Ph	Me	H
b	Ph	Me	Me
c	2-thienyl	Me	H
d	Ph	—$(CH_2)_5$—	H
e	Ph	H	H
f	3,4-$F_2C_6H_3$	H	H
g	3,4-$F_2C_6H_3$	Me	H

Conditions and reagents: *i.* DMSO, NH_4Br, 24 h, 20 °C; *ii.* KOH, DMSO, 50 °C; *iii.* K_2CO_3, DMSO, 90 °C.

Table 1. Reactions of alk-4-ynals **1a—f** with diamines **2a—e** in DMSO sequentially catalyzed by NH_4Br and bases[a]

Alkynal	Diamine	T_1/°C	Cyclization of intermediates **3**			Product yield (%)
			Base	τ/h	T_2/°C	
1a	**2a**	20	KOH	48	50	*E*-**4a** (56[b])
1a	**2b**	20	KOH	60	50	*E*-**4b** (66[b])
1a	**2c**	20	KOH	48	50	*E*-**4h** (62[b])
1a	**2a**	20	K_2CO_3	72	90	*Z*-**4a** (75[b])
1a	**2b**	20	K_2CO_3	48	90	*Z*-**4b** (82[b])
1a	**2c**	20	K_2CO_3	72	90	*Z*-**4h** (69[b])
1a	**2d**	20	K_2CO_3	48	90	*Z*-**4i** **:** *Z*-**4j** = = 1.1 : 1[d] (78[c])
1a	**2e**	90	K_2CO_3	24	90	*Z*-**8a** (56[b])
1b	**2a**	20	KOH	12	50	*E*-**4c** (59[b])
1b	**2a**	20	K_2CO_3	12	90	*Z*-**4c** (78[b])
1b	**2e**	90	K_2CO_3	12	90	*Z*-**8b** (51[b])
1c	**2a**	20	KOH	24	50	*E*-**4d** (48[c])
1c	**2a**	20	K_2CO_3	24	90	*Z*-**4d** (52[b])
1d	**2a**	20	KOH	24	50	—[e]
1d	**2a**	20	K_2CO_3	240	90	*Z*-**4e** (37[b])
1e	**2a**	20	K_2CO_3	24	90	*Z*-**4f** (32[b])
1f	**2a**	20	K_2CO_3	12	90	*Z*-**4g** (57[b])

[a] The molar ratio of alkynal : diamine = 1 : 1; T_1 is the temperature of the reaction carried out upon treatment with NH_4Br, T_2 is the temperature of cyclization.
[b] After recrystallization from hexane.
[c] After column chromatography.
[d] According to the ^1H NMR spectral data of isolated mixtures of products.
[e] A complete resinification of the reaction mixture was observed.

these processes were unsuccessful. Thus, the addition of KOH to a solution of benzimidazole **3e** obtained by the reaction of aldehyde **1d** with diamine **2a** led to the formation of only polymeric products. Probably, this is explained by side processes involving acidic enough hydrogen atoms in the corresponding benzimidazole **3e**, which proceed much faster than the intramolecular hydroamination of the triple bond.

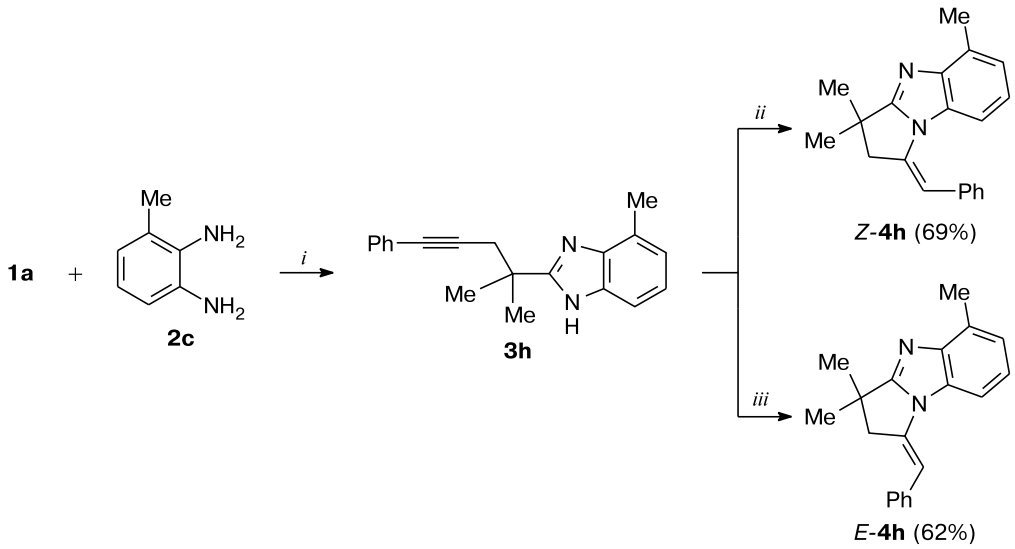
The use of less strong base (anhydrous potassium carbonate) instead of KOH with simultaneous increase in temperature to 90 °C allowed us to synthesize pyrrolobenzimidazoles **4a—g** from aldehydes **1a—f** irrespective of the presence in the latter of substituents at α-position to the carbonyl group. The yields of the final products varied within the range of 32—82% (see Table 1). Very interesting and unexpected is the fact that the use of these cyclization conditions leads to a dramatic change in the stereoselectivity of the formation of pyrrolobenzimidazoles **4**, which, in contrast to the case with KOH, are formed exclusively as more sterically hindered *Z*-isomers.

As can be seen from the given data (see Table 1), the replacement of a phenyl group with more electron-withdrawing thienyl or 3,4-difluorophenyl one considerably accelerates cyclization of benzimidazoles **3**. A similar effect is observed when two alkyl substituents are introduced at α-position of the starting aldehyde, that, most likely, is due to the increase in polarization of the triple bond and, respectively, to its ability to undergo nucleophilic addition.

The reaction of aldehyde **1a** with 1,2-diamino-3-methylbenzene (**2c**) in DMSO in the presence of NH_4Br and subsequent cyclization of obtained benzimidazole **3h** upon treatment with K_2CO_3 led to the selective formation of pyrrolobenzimidazole *Z*-**4h** in 69% yield (Scheme 2). The presence in its structure of methyl substituent at position 5, rather than at position 8, was inferred from the ^1H NMR spectrum, which exhibited a signal characteristic of the proton H(8) at δ 5.67 correlating well with similar signals in the spectra of other *Z*-isomers of pyrrolobenzimidazoles **4**. The use of KOH for cyclization of benzimidazole **3h** also led to the only product in 62% yield, which based on a combination of spectral data was characterized as the *E*-isomer of compound **4h** (see Scheme 2). Apparently, the steric and electronic influence of the methyl substituent at *ortho*-position to the five-membered ring in benzimidazole **3h** turned out to be enough for the 5-*exo*-*dig*-hydroamination proceeding exclusively with the involvement of the most remote from it nitrogen atom.

At the same time, the use of 1,2-diamino-4-methylbenzene (**2d**) in a similar reaction leads to a mixture of isomers *Z*-**4i** and *Z*-**4j** in the ratio of 1.1 : 1 in 78% total yield, which were characterized without separation. The absence of selectivity in this case indicates that the methyl

Scheme 2

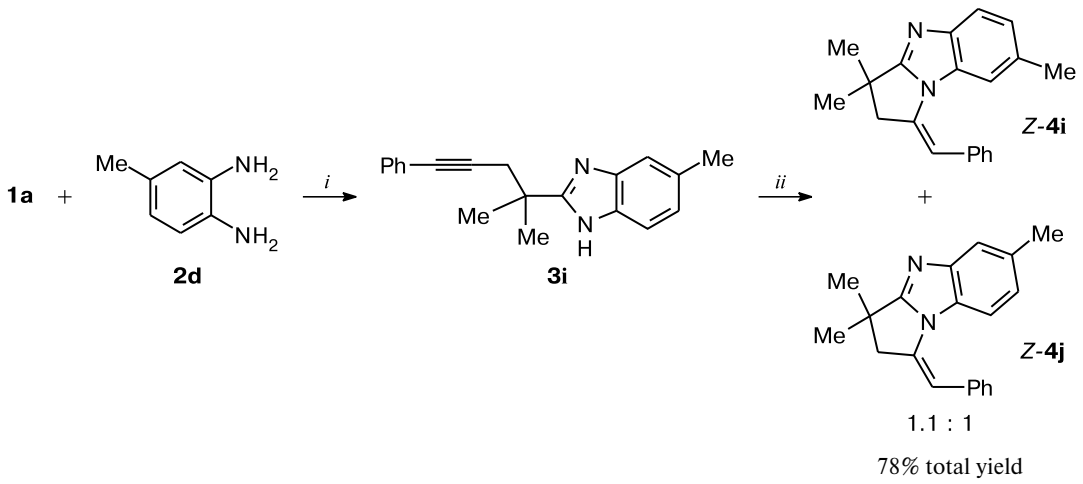


Conditions and reagents: *i.* DMSO, NH_4Br, 24 h, 20 °C; *ii.* K_2CO_3, DMSO, 90 °C; *iii.* KOH, DMSO, 50 °C.

group has little effect on the relative reactivities of nitrogen atoms in benzimidazole **3i** (Scheme 3). Compounds **4i** and **4j** were identified based on the analysis of the splitting pattern of the signal for the proton H(8). In the predominant isomer **4i**, this signal was found as a broad singlet, whereas in the minor isomer **4j** it is a doublet with the spin-spin coupling constant of 8.4 Hz due to the interaction with the neighboring proton.

The *E*- and *Z*-isomers of pyrrolobenzimidazoles **4** were identified based on the 2D proton NOESY spectra. In the case of *E*-isomers, they exhibited correlations between the signals for the methine proton at the double bond and the proton at position 8, as well as between the signals for the methylene fragment at position 2 and the signals for the *ortho*-protons of the aromatic substituent at the double bond. At the same time, the correlations between the signals for the protons of the aromatic substituent and the signal for the proton at position 8 are completely absent. Conversely, they are quite pronounced for isomers *Z*-**4**. There are also present characteristic correlations between the signals for the olefin proton and the CH_2 fragment at position 2 (Fig. 1). Apart from that, the spectra of isomers *Z*-**4** are characterized by a strong upfield shift of the signal for the proton H(8) (δ 5.3—5.9), most likely, attributed to the shielding effect of a nearby aryl substituent, whose plane is perpendicular to the plane of the pyrrolobenzimidazole core.

Scheme 3



Conditions and reagents: *i.* DMSO, NH_4Br, 24 h, 20 °C; *ii.* K_2CO_3, DMSO, 90 °C.

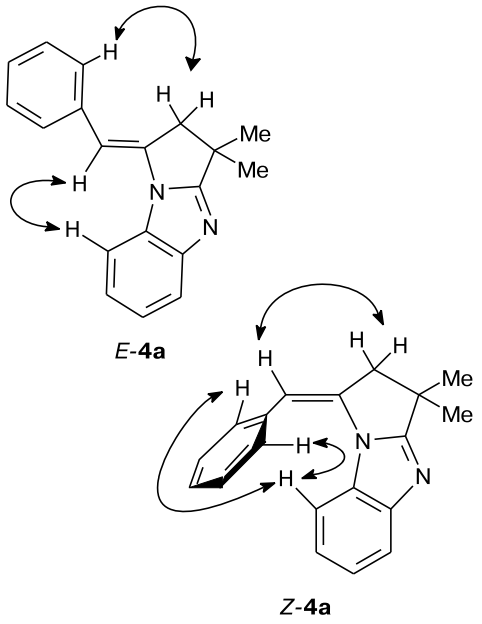


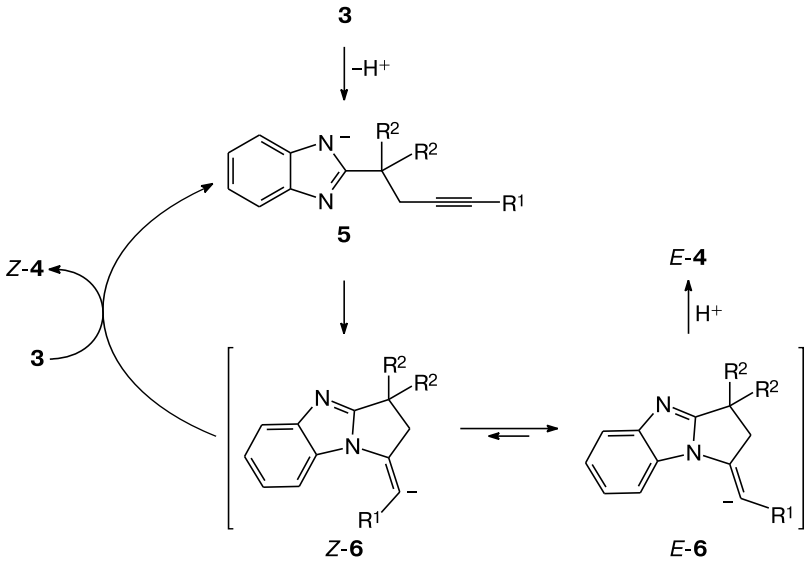
Fig. 1. Key NOE-interactions in compounds *E*-**4a** and *Z*-**4a**.

The large difference in the stereoselectivity of the formation of pyrrolobenzimidazoles **4** depending on the nature of the base used is most likely explained as follows. In the case of strongly basic KOH, the starting alkynylbenzimidazoles **3** undergo fast and complete deprotonation with the formation of the corresponding anions **5**. This fact was confirmed by characteristic upfield shifts of the signals for the aromatic protons in the spectra of solutions of compounds **3** in DMSO after addition of KOH. Then, anions **5** as a result of 5-*exo*-*dig*-cyclization are converted to vinyl anions *Z*-**6**, that agrees with the literature data on hydroamination of alkynes upon treatment with imidazoles[19] and indoles.[20] Because of the high basicity of the KOH—DMSO system, these anions live long enough to undergo isomerization to more thermodynamically stable anions *E*-**6** (according to our calculations, the energy difference is ~2.5—2.7 kcal mol^{-1}). Note that similar processes for vinyl anions obtained by the intramolecular addition of *N*-centered anions to triple bonds were described in the work.[21] In the final step, anions *E*-**6** add a proton from the reaction medium to form *E*-isomers of pyrrolobenzimidazoles **4** (Scheme 4).

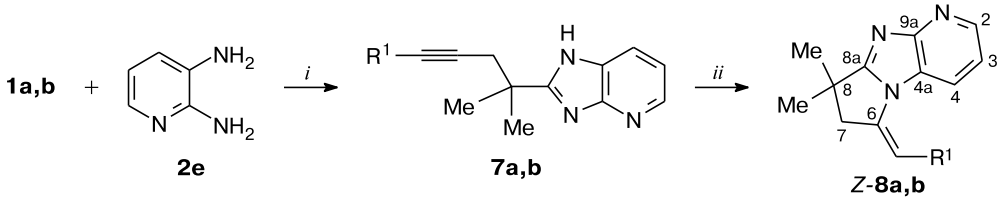
In the case of less basic K_2CO_3, the starting alkynylbenzimidazoles **3** undergo deprotonation only to a little extent. As soon as anions **5** cyclize to anions *Z*-**6**, the latter are immediately protonated upon action of the excessive starting compound **3**, regenerating anions **5**, which enter the next reaction cycle, and giving rise to *Z*-isomers of products **4** (see Scheme 4).

The present studies showed that besides *o*-diaminobenzenes **2a**—**d**, 2,3-diaminopyridine (**2e**) can be also involved in similar cyclization reactions with alk-4-ynals. In this case, the first step of the process, *i.e.*, the oxidative cyclization to the corresponding imidazopyridines **7a**,**b**, proceeds considerably slower and requires heating for 12 h at 90 °C to reach completion. The addition of a three-fold molar excess of anhydrous K_2CO_3 to the thus obtained solutions of imidazopyridines **7a**,**b** in DMSO with subsequent stirring of the reaction mixtures for 12—24 h at 90 °C led to a complete consumption of the starting compounds with the formation of arylmethylidene-substituted 7,8-dihydro-6*H*-pyrrolo[1′,2′:1,2]imidazo[4,5-*b*]pyridines *Z*-**8a**,**b**. The latter after aqueous work-up of the reaction mixture were isolated in the individual state by recrystallization from hexane in 56 and 51% yields, respectively (Scheme 5, see Table 1).

Scheme 4



Scheme 5



1, 7, 8: R^1 = Ph (**a**), 2-thienyl (**b**)

Conditions and reagents: *i.* DMSO, NH_4Br, 12 h, 90 °C; *ii.* K_2CO_3, DMSO, 90 °C.

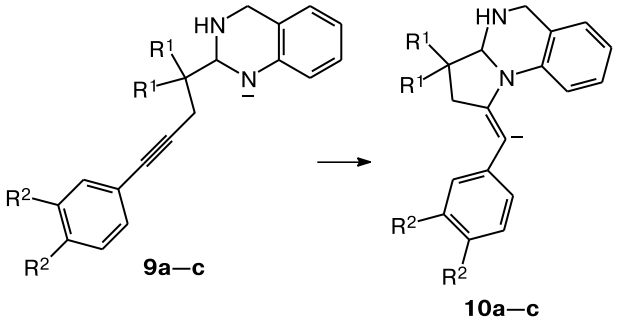
Their ^{1}H NMR spectra exhibit signals at δ 5.62—6.02 corresponding to the protons at position 4 of the tricyclic system, which are located in the same region as the signals of similar protons in pyrrolobenzimidazoles **4** (δ 5.3—5.9). This indicates that these products have the structure in which the pyridine nitrogen atom is at position remote from the arylmethylidene group. Thus, under conditions of anionic cyclization of compounds **7** the nitrogen atom of the imidazole ring which is farther from the pyridine nitrogen atom possesses considerably higher reactivity with respect to the triple bond. Note that such a regioselectivity crucially differs from the regioselectivity of similar cyclizations[22] carried out upon heating in polar solvent, which proceed exclusively as 6-*endo*-*dig*-processes with the formation of six-membered rings.

To explain the strong differences in conditions required for the intramolecular cyclization of alkynyl-substituted benzimidazoles **3** upon treatment with KOH in DMSO (12—60 h at 50 °C, see Table 1) and the earlier studied similar processes involving related 1,2,3,4-tetrahydroquinazolines (0.5—2 h at ~20 °C),[17] we carried out quantum chemical calculations of the key step of these transformations, that is, the intramolecular addition of the corresponding amide anions at the triple bond.

It is known[23] that the energy parameters of intramolecular cyclization reactions, including those involving anions obtained from the results of the B3LYP/6-31+G(d,p) calculations, are in good agreement with the experimental results. The use of similar procedure for calculations of the potential energy surface (PES) of the transformations of *N*-anions **9a—c**, formed as the intermediate products in the reaction of alk-4-ynals with *o*-aminobenzylamine,[17] to anions **10a—c** (Scheme 6, Fig. 2) showed that this process is weakly exothermic (ΔE_0 = = –(0.4—1.4) kcal mol^{-1}).

Similar method was used to calculate the PES of the cyclization of benzimidazolide anions **5a—c** to the corresponding vinyl anions *Z*-**6a—c** and *E*-**6a—c**, which most likely is a rate-determining step in the transformation of benzimidazoles **3** to pyrrolobenzimidazoles **4** (see Schemes 4 and 7, Fig. 3). The calculations showed that, in contrast to similar transformation of anions **9** to anions **10** (see Fig. 2), in this case the process is endothermic (ΔE_0 = = 12.9—18.4 kcal mol^{-1}) and has a high activation barrier. This agrees with the experimentally observed necessity for rather drastic conditions (see Table 1) for carrying out the cyclization of benzimidazoles **3** to pyrrolobenzimidazoles **4**. The formation of the latter upon heating of solutions of benzimidazoles **3** in DMSO in the presence of bases is a slow process, apparently, because of the very low equilibrium concentration of the corresponding cyclic anions **6**.

Scheme 6



9, 10: R^1 = H, R^2 = H (**a**), R^1 = Me, R^2 = H (**b**), R^1 = H, R^2 = F (**c**)

The introduction of the methyl groups at α-position of the alkynyl fragment (compound **5b**) or the fluorine atoms in benzene ring (compound **5c**) leads to some decrease in the activation energy of the direct reaction (from 25.2 to 22.6—23.3 kcal mol^{-1}) and an increase in the reverse reaction barrier (from 6.8 kcal mol^{-1} in the case of *Z*-**6a** to

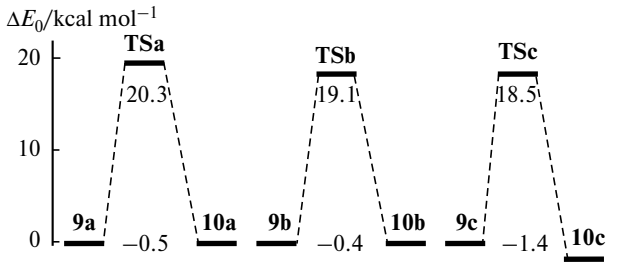
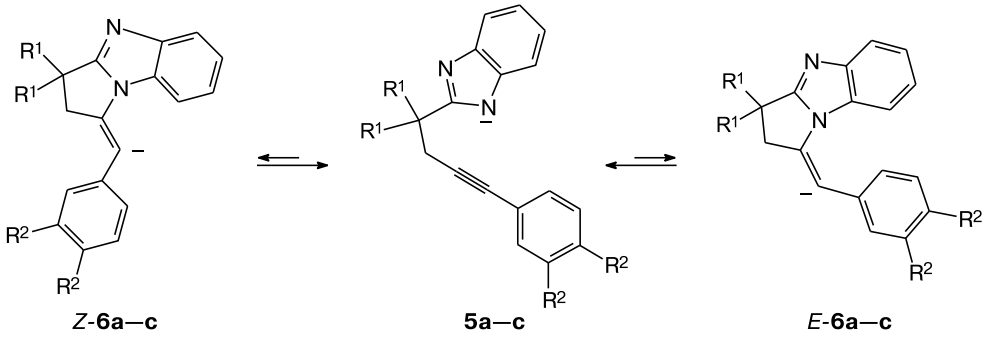


Fig. 2. Energy profile of cyclization of *N*-anions **9a—c** to anions **10a—c**.

Scheme 7



5,6: R^1 = H, R^2 = H (**a**), R^1 = Me, R^2 = H (**b**), R^1 = H, R^2 = F (**c**)

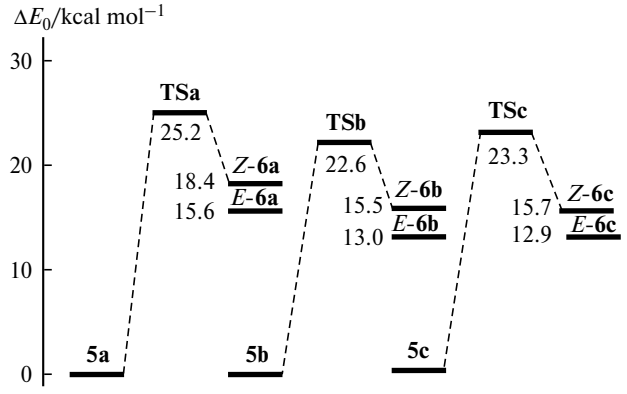


Fig. 3. Energy profile of cyclization of benzimidazolide anions **5a**—**c** to anions **6a**—**c**.

7.1—7.6 kcal mol^{-1} in cases of *Z*-**6b**,**c**, Scheme 7, see Fig. 3). These results agree with the experimentally observed dependence of the reaction time required for the complete conversion of the corresponding benzimidazoles **3** to products **4** (see Table 1).

In conclusion, we have developed a convenient one-pot synthesis of arylmethylidene-substituted 2,3-dihydro-1*H*-pyrrolo[1,2-*a*]benzimidazoles and 7,8-dihydro-6*H*-pyrrolo[1′,2′:1,2]imidazo[4,5-*b*]pyridines by the reaction of available alk-4-ynals with aromatic diamines at sequential catalysis with NH_4Br and bases. A distinguishing feature of this approach is a possibility of directing stereoselectivity of the reaction by changing the type of the base used, depending on which *Z*- or *E*-isomers of the final products can be selectively obtained. The final compounds seem promising for medicinal chemistry.

Experimental

Starting compounds and obtained products were analyzed by GC using a Hewlett-Packard 5890 Series II instrument with an HP-1 capillary column (30 m×0.153 mm) and an Hewlett-Packard 3396A automated integrator. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200p spectrometer in $CDCl_3$, using $SiMe_4$ as an internal standard. NMR monitoring of reaction progress was carried out by recording spectra of the samples of reaction mixtures.

High resolution mass spectra were recorded on a Bruker micrOTOF II instrument with electrospray ionization (ESI). The measurements were performed on positive ions (capillary voltage 4500 V). The range of scanned masses m/z from 50 to 3000 Da, external or internal calibration (Electrospray Calibrant Solution, Fluka). Compounds were syringed as solutions in acetonitrile, the flow rate was 3 μL min^{-1}. Nebulizer gas was nitrogen (4 L min^{-1}), interface temperature 180 °C.

Quantum chemical calculations of structure, vibrational frequencies, and potential energy surface (PES) were carried out by density functional theory (DFT) on the B3LYP[24,25] level in the 6-31+G (d,p) basis, using the GAUSSIAN-09, Rev/D 01 software package.[26] The character of found stationary points (the minimum or saddle point) was determined by the calculation of the eigenvalues of the energy second derivatives matrix. The belonging of a transition state (TS) to a certain transformation was controlled using results of the calculations of the internal reaction coordinate (IRC).[27] The allowance for the solvation effect of DMSO was made using the polarizable continuum model (PCM) in the self-consistent reaction field (SCRF) method.[28]

The starting alkynals **1a**—**c**,**f** were synthesized from the corresponding propargyl chlorides (1-chloro-3-phenylprop-2-yne, 1-chloro-3-(2-thienyl)prop-2-yne, 1-chloro-3-(3,4-difluorophenyl)prop-2-yne) and aldehydes (isobutyric aldehyde and cyclohexanecarbaldehyde) according to the procedures described in the work.[15] Alkynal **1d** was obtained by cross-coupling of iodobenzene with pent-4-yn-1-ol upon treatment with a mixture of $Pd(PPh_3)_2Cl_2$—CuI in anhydrous triethylamine[29] with subsequent Swern oxidation of formed 5-phenylpent-4-yn-1-ol (a total yield on two steps was 62%). The spectral data of the product agree with those published earlier.[30] Alkynal **1e** was obtained by similar cross-coupling from 4-bromo-1,2-difluorobenzene, using $Pd(PPh_3)_4$ as the catalyst, in 55% total yield on two steps.

Synthesis of 2-(alk-3-ynyl)benzimidazoles 3a,d from aldehydes 1a,c and *o*-diaminobenzene 2a (general procedure). A solution of *o*-diaminobenzene **2a** (216 mg, 2 mmol) in DMSO (3 mL) was slowly added to a solution of the corresponding aldehyde **1** (2 mmol) in DMSO (3 mL), followed by the addition of NH_4Br (39 mg, 0.4 mmol). The mixture obtained was stirred for 24 h at

~20 °C under dry air. Then, water (30 mL) and CH_2Cl_2 (50 mL) were added, the organic layer was separated. The aqueous layer was additionally extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were washed thrice with water, dried with anhydrous Na_2SO_4, the solvent was evaporated, and the residue was recrystallized from a mixture of light petroleum ether—THF to isolate products **3a**,**d**.

2-(1,1-Dimethyl-4-phenylbut-3-yn-1-yl)-1*H*-benzimidazole (3a) was obtained from aldehyde **1a** in 68% yield, m.p. 250—251 °C. ^{1}H NMR, δ: 1.55 (s, 6 H, 2 Me); 2.90 (s, 2 H, CH_2); 7.05—7.15 (m, 2 H, C(5)H, C(6)H); 7.20—7.25 (m, 5 H, Ph); 7.45—7.55 (m, 2 H, C(4)H, C(7)H); 11.90 (br.s, 1 H, NH). ^{13}C NMR, δ: 25.0 (2 CH_3); 30.9 (CH_2); 35.4 ($\underline{C}Me_2$); 81.0, 85.8 (C≡C), 113.1 (br., C(4), C(7)); 119.9 (C(5), C(6)); 121.8 (C(1), Ph), 126.2 (C(4), Ph), 126.7, 129.7 (C(2), C(3), C(5), C(6), Ph), 136.8 (br., C(3a), C(7a)); 158.8 (C(2)). MS (ESI), found: *m/z* 275.1549, calculated for $C_{19}H_{18}N_2$, $[M + H]^+$: *m/z* 275.1543.

2-[1-(3-Phenylprop-2-yn-1-yl)cyclohexyl]-1*H*-benzimidazole (3d) was obtained from aldehyde **1c** in 74% yield, m.p. 238—239 °C. ^{1}H NMR, δ: 1.23—1.96 (m, 8 H, *cyclo*-C_6); 2.52—2.67 (m, 2 H, *cyclo*-C_6); 2.86 (s, 2 H, $CH_2C{\equiv}C$); 7.14—7.25 (m, 2 H, C(5)H, C(6)H); 7.25—7.41 (m, 5 H, Ph); 7.58—7.70 (m, 2 H, C(4)H, C(7)H); 12.08 (br.s, 1 H, NH). ^{13}C NMR, δ: 22.1 (C(3), C(5), *cyclo*-C(6)); 25.0 (C(4), *cyclo*-C_6); 32.3 (C≡C$\underline{C}H_2$); 33.9 (C(2), C(6), *cyclo*-C_6); 40.7 (C(1), *cyclo*-C_6); 82.6, 86.9 (C≡C), 114.0 (br., C(4), C(7)); 120.6 (C(5), C(6)); 123.0 (C(1), Ph), 127.3 (C(4), Ph); 127.8, 130.9 (C(2), C(3), C(5), C(6), Ph); 135.9 (br., C(3a), C(7a)); 158.3 (C(2)). MS (ESI), found: *m/z* 315.1851, calculated for $C_{22}H_{22}N_2$, $[M + H]^+$: *m/z* 315.1856.

Synthesis of 1-arylmethylidene-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]-benzimidazoles (4a—j) and 6-arylmethylidene-7,8-dihydro-6*H*-pyrrolo[1´,2´:1,2]imidazo[4,5-*b*]pyridines (8a,b) (general procedure). A solution of the corresponding aromatic diamine **2** (1 mmol) in DMSO (3 mL) was added to a solution of the corresponding aldehyde **1** (1 mmol) in anhydrous DMSO (3 mL) with stirring, followed by the addition of NH_4Br (19 mg, 0.2 mmol) to the resulting mixture, which then was stirred under dry air and conditions indicated in Table 1. Then, freshly powdered KOH (84 mg, 1.5 mmol) was added (for the preparation of *E*-**4a**—**d**,**h**) or anhydrous K_2CO_3 (414 mg, 3 mmol) (for the preparation of *Z*-**4a**—**j**) and the resulting suspension was stirred under argon until reaction reached completion (^{1}H NMR monitoring, the reaction time and temperature are given in Table 1). Then, water (40 mL) and Et_2O (30 mL) were added to the reaction mixture, the organic layer was separated, whereas the aqueous phase was extracted with Et_2O (3×10 mL). The combined organic layers were washed with water thrice and dried with anhydrous K_2CO_3, the solvent was evaporated, the residue was purified by recrystallization or column chromatography to isolate a product (see Table 1).

(1*E*)-1-Benzylidene-3,3-dimethyl-2,3-dihydro-1*H*-pyrrolo-[1,2-*a*]benzimidazole (*E*-4a) was obtained from aldehyde **1a** and diamine **2a** and isolated in 56% yield by recrystallization from hexane, m.p. 135—137 °C. ^{1}H NMR, δ: 1.46 (s, 6 H, 2 Me); 3.27 (d, 2 H, CH_2, ^4J = 2.2 Hz); 6.69 (t, 1 H, PhC$\underline{H}$=, ^4J = 2.2 Hz); 7.10—7.36 (m, 7 H, Ph, C(5)H, C(6)H); 7.63—7.72 (m, 2 H, C(7)H, C(8)H). ^{13}C NMR, δ: 27.4 (2 Me), 36.4 (C(3)); 47.9 (C(2)); 108.9 (PhCH=); 111.4 (C(8)); 120.1, 122.9, 123.2 (C(5), C(6), C(7)); 126.5, 127.9, 128.7 (Ph), 129.9 (C(8a)); 135.5, 136.0 (C(1), Ph; C(1)); 149.0 (C(4a)); 167.0 (C(3a)). MS (ESI), found: *m/z* 275.1545, calculated for $C_{19}H_{18}N_2$, $[M + H]^+$: *m/z* 275.1543.

(1*Z*)-1-Benzylidene-3,3-dimethyl-2,3-dihydro-1*H*-pyrrolo-[1,2-*a*]benzimidazole (*Z*-4a) was obtained from aldehyde **1a** and diamine **2a** and isolated in 75% yield by recrystallization from hexane, m.p. 121—122 °C. ^{1}H NMR, δ: 1.57 (s, 6 H, 2 Me); 3.13 (d, 2 H, CH_2, ^4J = 1.5 Hz); 5.76 (d, 1 H, C(8)H, ^3J = 8.2 Hz); 6.18 (br.s, 1 H, PhC$\underline{H}$=); 6.77—6.89 (m, 1 H, C(7)H); 7.08—7.19 (m, 1 H, C(6)H); 7.13—7.25 (m, 2 H, Ph); 7.26—7.41 (m, 3 H, Ph); 7.67 (d, 1 H, C(5)H, ^3J = 8.1 Hz). ^{13}C NMR, δ: 26.4 (2 Me); 36.5 (C(3)); 51.6 (C(2)); 108.4 (PhCH=), 114.4 (C(8)); 119.4, 122.0, 122.5 (C(5), C(6), C(7)); 127.2, 128.2, 129.6 (Ph); 130.3 (C(8a)); 133.7, 135.9 (C(1), Ph; C(1)); 148.0 (C(4a)); 168.8 (C(3a)). MS (ESI), found: *m/z* 275.1538, calculated for $C_{19}H_{18}N_2$, $[M + H]^+$: *m/z* 275.1543.

(1*E*)-1-Benzylidene-3,3,6,7-tetramethyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]benzimidazole (*E*-4b) was obtained from aldehyde **1a** and diamine **2b** and isolated in 66% yield by recrystallization from hexane, m.p. 151—153 °C. ^{1}H NMR, δ: 1.52 (s, 6 H, 2 Me); 2.38 (s, 3 H, Me); 2.43 (s, 3 H, Me); 3.34 (d, 2 H, CH_2, ^4J = 2.2 Hz); 6.72 (t, 1 H, PhC$\underline{H}$=, ^4J = 2.2 Hz); 7.20—7.32 (m, 1 H, Ph); 7.35—7.44 (m, 4 H, Ph); 7.52 (br.s, 2 H, C(5)H, C(8)H). ^{13}C NMR, δ: 20.3 (Me); 20.5 (Me); 27.4 (2 Me), 36.3 (C(3)); 47.9 (C(2)); 108.2 (PhCH=); 111.8 (C(8)); 120.3 (C(5)); 126.3, 127.8, 128.6 (Ph); 128.4, 131.8, 131.9 (C(6), C(7), C(8a)); 135.6, 136.2 (C(1), Ph; C(1)); 147.5 (C(4a)); 166.2 (C(3a)). MS (ESI), found: *m/z* 303.1857, calculated for $C_{21}H_{22}N_2$, $[M + H]^+$: *m/z* 303.1856.

(1*Z*)-1-Benzylidene-3,3,6,7-tetramethyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]benzimidazole (*Z*-4b) was obtained from aldehyde **1a** and diamine **2b** and isolated in 82% yield by recrystallization from a mixture of hexane—THF, m.p. 157—158 °C. ^{1}H NMR, δ: 1.55 (s, 6 H, 2 Me); 1.95 (s, 3 H, Me); 2.26 (s, 3 H, Me); 3.12 (d, 2 H, CH_2, ^4J = 1.6 Hz); 5.36 (s, 1 H, C(8)H); 6.15 (br.s, 1 H, PhC$\underline{H}$=); 7.15—7.26 (m, 2 H, Ph); 7.29—7.38 (m, 3 H, Ph); 7.40 (s, 1 H, C(5)H). ^{13}C NMR, δ: 20.0 (Me); 20.1 (Me); 26.5 (2 Me); 36.4 (C(3)); 50.9 (C(2)); 107.6 (PhCH=); 115.0 (C(8)); 119.4 (C(5)); 127.0, 128.2, 129.9 (Ph); 128.7, 130.6, 131.2 (C(6), C(7), C(8a)); 134.1, 136.3 (C(1), Ph; C(1)); 146.4 (C(4a)); 168.0 (C(3a)). MS (ESI), found: *m/z* 303.1860, calculated for $C_{21}H_{22}N_2$, $[M + H]^+$: *m/z* 303.1856.

(1*E*)-3,3-Dimethyl-1-(2-thienylmethylidene)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]benzimidazole (*E*-4c) was obtained from aldehyde **1b** and diamine **1a** and isolated in 59% yield by recrystallization from hexane, m.p. 141—143 °C. ^{1}H NMR, δ: 1.47 (s, 6 H, 2 Me); 3.26 (d, 2 H, CH_2, ^4J = 2.2 Hz); 6.87 (t, 1 H, ThiC$\underline{H}$=, ^4J = 2.2 Hz); 6.94—7.01 (m, 2 H, thienyl); 7.15—7.26 (m, 3 H, thienyl, C(5)H, C(6)H); 7.58—7.70 (m, 2 H, C(7)H, C(8)H). ^{13}C NMR, δ: 27.7 (2 Me); 36.5 (C(3)); 47.9 (C(2)); 102.4 (ThiCH=); 111.4 (C(8)); 120.2, 123.0, 123.3 (C(5), C(6), C(7)); 124.4, 126.0, 129.7 (Thi); 129.7 (C(8a)); 134.1, 139.3 (C(1), Thi; C(1)); 149.0 (C(4a)); 167.3 (C(3a)). MS (ESI), found: *m/z* 281.1114, calculated for $C_{17}H_{16}N_2S$, $[M + H]^+$: *m/z* 281.1107.

(1*Z*)-3,3-Dimethyl-1-(2-thienylmethylidene)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]benzimidazole (*Z*-4c) was obtained from aldehyde **1b** and diamine **1a** and isolated in 78% yield by recrystallization from hexane, m.p. 83—85 °C. ^{1}H NMR, δ: 1.55 (s, 6 H, 2 Me); 3.11 (d, 2 H, CH_2, ^4J = 1.7 Hz); 5.91 (d, 1 H, C(8)H, ^3J = 8.1 Hz), 6.07 (br.s, 1 H, ThiC$\underline{H}$=); 6.76 (dd, 1 H, thienyl, ^3J = 3.5 Hz, ^4J = 1.2 Hz); 6.87—6.98 (m, 1 H, C(7)H); 7.00 (dd, 1 H, thienyl, ^3J = 5.2 Hz, ^3J = 3.5 Hz); 7.12—7.22 (m, 1 H, C(6)H); 7.31 (dd, 1 H, thienyl, ^3J = 5.2 Hz, ^4J = 1.2 Hz); 7.67 (d, 1 H, C(5)H, ^3J = 8.1 Hz). ^{13}C NMR, δ: 26.4 (2 Me); 36.4

(C(3)); 50.8 (C(2)); 100.3 (ThiCH=); 114.2 (C(8)); 119.4, 122.3, 122.7 (C(5), C(6), C(7)); 125.5, 127.0, 128.3 (thienyl); 130.2 (C(8a)); 135.9, 137.0 (C(1), thienyl; C(1)); 148.0 (C(4a)); 168.7 (C(3a)). MS (ESI), found: *m/z* 281.1105, calculated for $C_{17}H_{16}N_2S$, $[M + H]^+$: *m/z* 281.1107.

(1´*E*)-1´-Benzylidene-1´,2´-dihydrospiro[cyclohexane-1,3´-pyrrolo[1,2-*a*]benzimidazole] (*E*-4d) was obtained from aldehyde **1c** and diamine **2a** and isolated in 48% yield by recrystallization from hexane, m.p. 119—120 °C. ^{1}H NMR, δ: 1.40—1.83 (m, 6 H, *cyclo*-C_6); 1.85—2.16 (m, 4 H, *cyclo*-C_6); 3.38 (d, 2 H, CH_2, ^4J = 2.2 Hz); 6.78 (t, 1 H, PhC<u>H</u>=, ^4J = 2.2 Hz); 7.00—7.48 (m, 7 H, Ph, C(5´)H, C(6´)H); 7.70—7.88 (m, 2 H, C(7´)H, C(8´)H). ^{13}C NMR, δ: 22.7 (C(3), C(5), *cyclo*-C_6); 25.3 (C(4), *cyclo*-C_6); 35.8 (C(2), C(6), *cyclo*-C_6); 40.5 (C(1,3´)); 44.3 (C(2´)); 108.5 (PhCH=); 111.4 (C(8´)); 120.1, 122.8, 123.1 (C(5´), C(6´), C(7´)); 126.4, 127.8, 128.7 (Ph); 129.5 (C(8a´)); 135.8, 136.1 (C(1), Ph; C(1´)); 148.7 (C(4a´)); 166.8 (C(3a´)). MS (ESI), found: *m/z* 315,1852, calculated for $C_{22}H_{22}N_2$, $[M + H]^+$: *m/z* 315.1856.

(1´*Z*)-1´-Benzylidene-1´,2´-dihydrospiro[cyclohexane-1,3´-pyrrolo[1,2-*a*]benzimidazole] (*Z*-4d) was obtained from aldehyde **1c** and diamine **2a** and isolated in 52% yield by chromatography on SiO_2 (eluent hexane—THF, 10 : 1→5 : 1) as a dense liquid. ^{1}H NMR, δ: 1.40—1.83 (m, 6 H, *cyclo*-C_6); 1.85—2.18 (m, 4 H, *cyclo*-C_6); 3.15 (d, 2 H, CH_2, ^4J = 1.6 Hz); 5.77 (d, 1 H, C(8´)H, ^3J = 8.2 Hz); 6.16 (br.s, 1 H, PhC<u>H</u>=); 6.77—6.87 (m, 1 H, C(7´)H); 7.09—7.18 (m, 1 H, C(6´)H); 7.14—7.40 (m, 5 H, Ph); 7.71 (d, 1 H, C(5´)H, ^3J = 8.0 Hz). ^{13}C NMR, δ: 22.8 (C(3), C(5), *cyclo*-C_6); 25.4 (C(4), *cyclo*-C_6); 35.0 (C(2), C(6), *cyclo*-C_6); 40.5 (C(1,3´)); 47.4 (C(2´)); 108.1 (PhCH=); 114.3 (C(8´)); 119.3, 121.8, 122.3 (C(5´), C(6´), C(7´)); 127.0, 128.0, 129.5 (Ph), 129.9 (C(8a´)); 133.8, 135.9 (C(1), Ph; C(1´)); 147.8 (C(4a´)); 168.6 (C(3a´)). MS (ESI), found: *m/z* 315.1850, calculated for $C_{22}H_{22}N_2$, $[M + H]^+$: *m/z* 315.1856.

(1*Z*)-1-Benzylidene-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]benzimidazole (*Z*-4e) was obtained from aldehyde **1d** and diamine **2a** and isolated in 37% yield by recrystallization from hexane, m.p. 152—154 °C. ^{1}H NMR, δ: 3.12—3.23 (m, 2 H, CH_2); 3.29—3.41 (m, 2 H, CH_2); 5.75 (d, 1 H, C(8)H, ^3J = 8.1 Hz); 6.18 (br.s, 1 H, Ph C<u>H</u>=); 6.78—6.88 (m, 1 H, C(7)H); 7.09—7.19 (m, 1 H, C(6)H); 7.17—7.27 (m, 2 H, Ph); 7.26—7.39 (m, 3 H, Ph); 7.65 (d, 1 H, C(5)H, ^3J = 8.1 Hz). ^{13}C NMR, δ: 23.1 (C(3)); 34.7 (C(2)); 107.6 (PhCH=); 114.4 (C(8)); 119.2, 121.9, 122.5 (C(5), C(6), C(7)); 127.2, 128.2, 129.7 (Ph); 130.5(C(8a)); 135.0, 136.0 (C(1), Ph; C(1)); 148.4 (C(4a)); 163.0 (C(3a)). MS (ESI), found: *m/z* 247.1231, calculated for $C_{17}H_{14}N_2$, $[M + H]^+$: *m/z* 247.1230.

(1*Z*)-1-(3,4-Difluorobenzylidene)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]benzimidazole (*Z*-4f) was obtained from aldehyde **1e** and isolated in 32% yield by recrystallization from hexane, m.p. 126—128 °C. ^{1}H NMR, δ: 3.12—3.24 (m, 2 H, CH_2); 3.28—3.40 (m, 2 H, CH_2); 5.85 (d, 1 H, C(8)H, ^3J = 8.2 Hz); 6.06 (br.s, 1 H, $C_6H_3F_2C$<u>H</u>=); 6.83—7.30 (m, 5 H, C(7)H, C(6)H, $C_6H_3F_2$); 7.66 (d, 1 H, C(5)H, ^3J = 8.1 Hz). ^{13}C NMR, δ: 23.1 (C(3)); 34.9 (C(2)); 105.4 ($C_6H_3F_2$<u>C</u>H=); 113.9 (C(8)); 119.5, 122.3, 123.0 (C(5), C(6), C(7)); 117.1 (d, C(5), $C_6H_3F_2$, J_{CF} = 17.3 Hz); 118.4 (d, C(2), $C_6H_3F_2$, J_{CF} = 17.1 Hz); 126.0 (dd, C(6), $C_6H_3F_2$, J_{CF} = 5.7 Hz, J_{CF} = 3.3 Hz); 130.3 (C(8a)); 132.9 (dd, C(1), $C_6H_3F_2$, J_{CF} = 6.1 Hz, J_{CF} = 4.1 Hz); 135.9 (C(1)); 148.5 (C(4a)); 149.2 (dd, C(3), $C_6H_3F_2$, J_{CF} = 248.5 Hz, J_{CF} = 12.1 Hz); 149.8 (dd, C(4), $C_6H_3F_2$, J_{CF} = 248.8 Hz, J_{CF} = 12.1 Hz); 163.0 (C(3a)). MS (ESI), found: *m/z* 283.1042, calculated for $C_{17}H_{12}F_2N_2$, $[M + H]^+$: *m/z* 283.1041.

(1*Z*)-1-(3,4-Difluorobenzylidene)-3,3-dimethyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]benzimidazole (*Z*-4g) was obtained from aldehyde **1d** and isolated in 57% yield by recrystallization from hexane, m.p. 124—126 °C. ^{1}H NMR, δ: 1.58 (s, 6 H, 2 Me); 3.12 (d, 2 H, CH_2, ^4J = 1.5 Hz); 5.87 (d, 1 H, C(8)H, ^3J = 8.2 Hz); 6.07 (br.s, 1 H, $C_6H_3F_2C$<u>H</u>=); 6.86—6.97 (m, 1 H, C(7)H); 7.11—7.21 (m, 1 H, C(6)H); 6.83—7.12 (m, 3 H, $C_6H_3F_2$); 7.69 (d, 1 H, C(5)H, ^3J = 8.1 Hz). ^{13}C NMR, δ: 26.4 (2 Me); 36.6 (C(3)); 51.3 (C(2)); 106.3 (Ph<u>C</u>H=); 113.9 (C(8)); 119.7, 122.4, 122.9 (C(5), C(6), C(7)); 117.1 (d, C(5), $C_6H_3F_2$, J_{CF} = 17.1 Hz); 118.3 (d, C(2), $C_6H_3F_2$, J_{CF} = 17.1 Hz); 125.9 (dd, C(6), $C_6H_3F_2$, J_{CF} = 6.1 Hz, J_{CF} = 3.3 Hz); 130.1 (C(8a)); 132.8 (dd, C(1), $C_6H_3F_2$, J_{CF} = 6.1 Hz, J_{CF} = 4.1 Hz); 134.7 (C(1)); 148.0 (C(4a)); 149.3 (dd, C(3), $C_6H_3F_2$, J_{CF} = 248.5 Hz, J_{CF} = 12.1 Hz); 149.9 (dd, C(4), $C_6H_3F_2$, J_{CF} = 248.8 Hz, J_{CF} = 12.1 Hz); 168.8 (C(3a)). MS (ESI), found: *m/z* 311.1344, calculated for $C_{19}H_{16}F_2N_2$, $[M + H]^+$: *m/z* 311.1354.

(1*E*)-1-Benzylidene-3,3,5-trimethyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]benzimidazole (*E*-4h) was obtained from aldehyde **1a** and diamine **2c** and isolated in 62% yield by recrystallization from hexane, m.p. 118—120 °C. ^{1}H NMR, δ: 1.55 (s, 6 H, 2 Me); 2.72 (s, 3 H, Me); 3.39 (d, 2 H, CH_2, ^4J = 2.1 Hz); 6.78 (t, 1 H, PhC<u>H</u>=, ^4J = 2.1 Hz); 7.15 (br.d, 1 H, C(6)H, ^3J = 7.3 Hz); 7.20—7.32 (m, 2 H, C(4), Ph; C(7)H); 7.35—7.48 (m, 4 H, Ph); 7.60 (br.d, 1 H, C(8)H, ^3J = 7.7 Hz). ^{13}C NMR, δ: 17.2 (Me); 27.5 (2 Me); 36.6 (C(3)); 48.2 (C(2)); 108.6, 108.9 (C(8), Ph<u>C</u>H=); 122.7, 123.8 (C(6), C(7)); 126.4, 127.9, 128.6 (Ph), 129.4, 130.1 (C(5), C(8a)); 135.6, 136.1 (C(1), Ph; C(1)); 148.2 (C(4a)); 166.1 (C(3a)). MS (ESI), found: *m/z* 289.1698, calculated for $C_{20}H_{20}N_2$, $[M + H]^+$: *m/z* 289.1699.

(1*Z*)-1-Benzylidene-3,3,5-trimethyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]benzimidazole (*Z*-4h) was obtained from aldehyde **1a** and diamine **2c** and isolated in 69% yield by recrystallization from hexane, m.p. 129—132 °C. ^{1}H NMR, δ: 1.62 (s, 6 H, 2 Me); 2.68 (s, 3 H, Me); 3.15 (d, 2 H, CH_2, ^4J = 1.6 Hz); 5.67 (d, 1 H, C(8)H, ^3J = 8.2 Hz); 6.20 (br.s, 1 H, PhC<u>H</u>=); 6.71—6.81 (m, 1 H, C(7)H); 6.98 (d, 1 H, C(6)H, ^3J = 7.4 Hz); 7.19—7.26 (m, 2 H, Ph); 7.30—7.42 (m, 3 H, Ph). ^{13}C NMR, δ: 17.1 (Me); 26.4 (2 Me); 36.7 (C(3)); 51.5 (C(2)); 108.3 (Ph<u>C</u>H=); 112.0 (C(8)); 121.7, 123.1 (C(6), C(7)); 127.1, 128.2, 129.6 (Ph); 129.2, 130.0 (C(5), C(8a)); 133.7, 136.0 (C(1), Ph; C(1)); 147.1 (C(4a)); 168.0 (C(3a)). MS (ESI), found: *m/z* 289.1696, calculated for $C_{20}H_{20}N_2$, $[M + H]^+$: *m/z* 289.1699.

(1*Z*)-1-Benzylidene-3,3,7-trimethyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]benzimidazole (*Z*-4i) and (1*Z*)-1-benzylidene-3,3,6-trimethyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]benzimidazole (*Z*-4j) were obtained as a mixture (the ratio 1.1 : 1) from aldehyde **1a** and diamine **2c** in 78% total yield, isolated by chromatography on SiO_2 (eluent hexane—THF, 10 : 1) as a dense liquid, and characterized without separation. <u>Compound *Z*-**4i**</u>. ^{1}H NMR, δ: 1.56 (s, 6 H, 2 Me); 2.06 (s, 3 H, Me); 3.10 (br.s, 2 H, CH_2); 5.40 (br.s, 1 H, C(8)H); 6.16 (br.s, 1 H, PhC<u>H</u>=); 6.96 (d, 1 H, C(6)H, ^3J = 8.2 Hz); 7.12—7.23 (m, 2 H, Ph); 7.25—7.41 (m, 3 H, Ph); 7.53 (d, 1 H, C(5)H, ^3J = 8.2 Hz). ^{13}C NMR, δ: 21.3 (Me); 26.4 (2 Me); 36.3 (C(3)); 50.8 (C(2)); 108.0 (Ph<u>C</u>H=); 114.7 (C(8)); 118.6, 123.6 (C(5), C(6)); 127.0, 128.0, 129.8 (Ph); 128.3, 131.5 (C(7), C(8a)); 133.9, 136.1 (C(1), Ph; C(1)); 148.2 (C(4a)); 168.8 (C(3a)). <u>Compound *Z*-**4j**</u>. ^{1}H NMR, δ: 1.56 (s, 6 H, 2 Me); 2.36 (s, 3 H, Me); 3.10 (br.s, 2 H, CH_2); 5.62 (d, 1 H, C(8)H, ^3J = 8.4 Hz); 6.13 (br.s, 1 H, PhC<u>H</u>=); 6.65 (d, 1 H, C(7)H, ^3J = 8.2 Hz); 7.12—7.23 (m, 2 H, Ph); 7.25—7.41 (m, 3 H, Ph); 7.46 (br.s, 1 H, C(5)H). ^{13}C NMR, δ: 21.3 (Me); 26.3 (2 Me);

36.4 (C(3)); 51.0 (C(2)); 108.0 (PhCH=); 113.8 (C(8)); 119.2, 123.2 (C(5), C(7)); 127.1, 128.1, 129.5 (Ph); 130.3, 132.2 (C(7), C(8a)); 133.6, 135.9 (C(1), Ph; C(1)); 145.8 (C(4a)); 168.2 (C(3a)).

(8*Z*)-8-Benzylidene-6,6-dimethyl-7,8-dihydro-6*H*-pyrrolo[2´,1´:2,3]imidazo[4,5-*b*]pyridine (*Z*-8a) was obtained from aldehyde **1a** and diamine **2e** and isolated in 56% yield by recrystallization from hexane, m.p. 134—136 °C. ^{1}H NMR, δ: 1.58 (s, 6 H, 2 Me); 3.12 (d, 2 H, CH_2, ^4J = 1.7 Hz); 5.62 (dd, 1 H, C(4)H, ^3J = 8.2 Hz, ^4J = 1.6 Hz); 6.23 (br.s, 1 H, PhCH=); 6.72 (dd, 1 H, C(3)H, ^3J = 8.2 Hz, ^3J = 4.8 Hz); 7.12—7.23 (m, 2 H, Ph); 7.27—7.38 (m, 3 H, Ph); 8.32 (dd, 1 H, C(2)H, ^3J = 4.8 Hz, ^4J = 1.6 Hz). ^{13}C NMR, δ: 26.4 (2 Me); 37.2 (C(3)); 49.8 (C(7)); 109.1 (PhCH=); 117.2, 121.7 (C(3), C(4)); 123.5 (C(9a)); 127.5, 128.4, 129.6 (Ph); 134.1, 135.7 (C(1), Ph; C(8)); 144.2 (C(2)); 159.8 (C(4a)); 170.7 (C(5a)). MS (ESI), found: *m/z* 276.1506, 298.1316, 314.1054, calculated for $C_{18}H_{17}N_3$, $[M + H]^+$: *m/z* 276.1495, $[M + Na]^+$: *m/z* 298.1315, $[M + K]^+$: *m/z* 314.1054.

(8*Z*)-6,6-Dimethyl-8-(2-thienylmethylidene)-7,8-dihydro-6*H*-pyrrolo[2´,1´:2,3]imidazo[4,5-*b*]pyridine (*Z*-8b) was obtained from aldehyde **1b** and diamine **2e** and isolated in 51% yield by recrystallization from hexane, m.p. 124—126 °C. ^{1}H NMR, δ: 1.58 (s, 6 H, 2 Me); 3.13 (d, 2 H, CH_2, ^4J = 1.7 Hz); 6.02 (dd, 1 H, C(4)H, ^3J = 8.2 Hz, ^4J = 1.4 Hz); 6.13 (br.s, 1 H, ThiCH=); 6.77 (d, 1 H, thienyl, ^3J = 3.5 Hz); 6.85 (dd, 1 H, C(3)H, ^3J = 8.2 Hz, ^3J = 4.8 Hz); 7.03 (dd, 1 H, thienyl, ^3J = 5.2 Hz, ^3J = 3.5 Hz); 7.35 (d, 1 H, thienyl, ^3J = 5.2 Hz); 8.32 (dd, 1 H, C(2)H, ^3J = 4.8 Hz, ^4J = 1.4 Hz). ^{13}C NMR, δ: 26.5 (2 Me); 37.2 (C(3)); 49.7 (C(7)); 101.0 (ThiCH=); 117.6, 121.9 (C(3), C(4)); 123.7 (C(9a)); 126.1, 127.2, 128.5 (Thi); 136.7, 136.8 (C(1), Thi; C(8)); 144.3 (C(2)); 159.9 (C(4a)); 170.9 (C(5a)). MS (ESI), found: *m/z* 282.1069, 304.0881, 320.0621, calculated for $C_{16}H_{15}N_3S$, $[M + H]^+$: *m/z* 282.1059, $[M + Na]^+$: *m/z* 304.0879, $[M + K]^+$: *m/z* 320.0618.

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