Synthesis of bicyclic *N,N*-enaminals by cyclization of alk-4-ynals with aliphatic diamines in DMSO upon treatment with KOH*

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A cyclization of alk-4-ynals with aliphatic diamines in DMSO upon treatment with KOH was found to lead to bicyclic *N,N*-enaminals. The studies of this reaction showed that 1,3-diaminopropane and *N*-methyl-1,3-diaminopropane gave (*E*)-6-(arylmethylidene)octahydropyrrolo[1,2-*a*]pyrimidines in 45—78% yields, whereas 1,2-diaminoethane gave 5-(arylmethylidene)hexahydropyrrolo[1,2-*a*]imidazoles as mixtures of *E*- and *Z*-isomers in up to 75% total yield. The mechanism of these new cascade cyclization reactions includes formation of the equilibrium mixtures of imines and cyclic aminals with subsequent intramolecular hydroamination of the triple bond having considerable ionic character.

Key words: alk-4-ynals, 1,2-diaminoethane, 1,3-diaminopropanes, hexahydropyrrolo[1,2-*a*]-imidazoles, octahydropyrrolo[1,2-*a*]pyrimidines, hexahydropyrimidines, imidazolidines, hydroamination, cascade cyclization, dimethyl sulfoxide.

In the last years, researchers pay serious attention to cyclization of available alk-4-ynals, alk-5-ynals, as well as corresponding ketones, upon their reaction with amines as a versatile approach to the synthesis of various nitrogen-containing heterocyclic compounds. Thus, recently there was described a new strategy for the synthesis of annulated isoquinolines based on the reaction of *o*-alkynylbenzaldehydes with aromatic amines bearing an additional nucleophilic center either in the presence of Au^I (see Refs 2 and 3), Ag^I (see Ref. 4), and Cu^I salts (see Ref. 5) or in the absence of metal-containing catalysts.[6] A number of works in the last years were devoted to the new approach to the synthesis of 1,2-dihydroisoquinolines based on the reaction of *o*-alkynylbenzaldehydes with amines and various nucleophiles in the absence of catalysts[7] or in the presence of carbophilic Lewis acids such as AgOTf,[8,9] $Au(PPh_3)Cl/AgNTf_2$,[10] $In(OTf)_3$,[10,11] Cu^I or Pd^{II} salts (see Refs 12—14), $CuSO_4/C_{12}H_{25}SO_3Na$,[15] and $Mg(ClO_4)_2/Cu(OTf)_2$[16]. A multi-component reaction of 2-alkynylbenzaldehyde with 1,2-diaminobenzene and iodine in the presence of CuI opens a pathway to the synthesis of iodoisoquinolines annulated with benzimidazole.[17] A reaction of substituted alk-4-ynones with amines catalyzed by AgOTf or a mixture of AuCl, AgOTf, and Ph_3P gave pyrroles.[18] A condensation of chiral amines with ω-oxoalkynoates in the presence of alcohols effected a diastereoselective synthesis of chiral 2-alkoxy-5-methoxycarbonylmethylidenepyrrolidines and the corresponding piperidines.[19] Recently, a CuCl-catalyzed four-component reaction between 2-ethynylbenzaldehyde, secondary amine, formaldehyde, and diaminoalkane resulted in the synthesis of 3-aminomethyl-substituted annulated isoquinoline structures.[20]

A distinguishing feature of the most reactions mentioned above is obtaining of nitrogen-containing heterocycles with the endocyclic double bond. Formation of products with the exocyclic double bond in the reaction of amines with alk-4-ynals and alk-5-ynals was observed only in the case when a triple bond activated by an ester group was present in the alkynals.[19] Also note that before our studies, no information was available on the carrying out these cyclization reactions in the presence of strong bases.

We discovered a one-pot method for the synthesis of bicyclic *N,N*-enaminals — 6-(arylmethylidene)octahydropyrrolo[1,2-*a*]pyrimidines and 5-(arylmethylidene)hexahydropyrrolo[1,2-*a*]imidazoles, based on the cyclization of available alk-4-ynals with aliphatic diamines in DMSO upon treatment with KOH.[1] Compounds of these series exhibit a wide range of biological activity,[21,22] while the presence in their structure of highly active enamine and aminal fragments with the shared nitrogen atom makes it possible to involve them in the selective reduction and dehydration reactions, proceeding with both retention and transformation of the starting bicyclic system.[23] The present work is devoted to the in-depth study of the discovered process[1] leading to these compounds, its mechanism, and the scope of its synthetic application.

* Dedicated to Academician of the Russian Academy of Sciences M. P. Egorov on the occasion of his 60th birthday.
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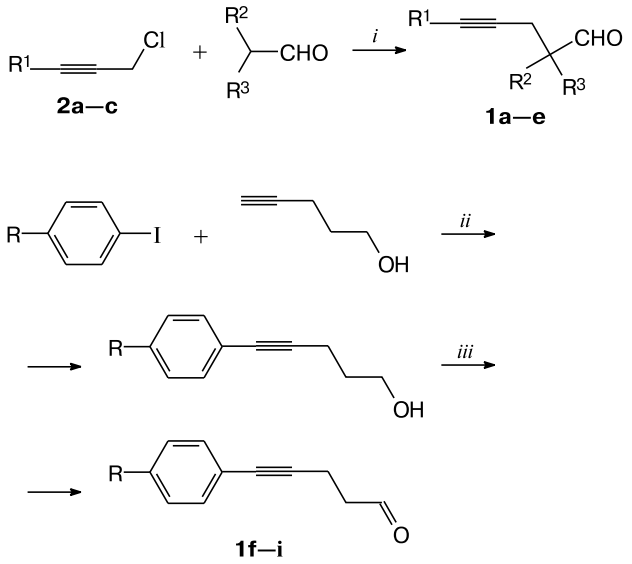
Results and Discussion

The starting alkynals **1a—e** were obtained in 56—70% yields by the reaction of 3-substituted propargyl chlorides **2a—c** with isobutyraldehyde, cyclohexanecarbaldehyde, and tetrahydropyran-4-carbaldehyde in a 30% aqueous NaOH—toluene two-phase system in the presence of a mixture of catalytic amounts of NaI and tetrabutylammonium iodide according to the procedure[24] suggested for the preparation of aldehyde **1a** (Scheme 1).

Scheme 1



Compound **1**	R^1	R^2	R^3	Yield (%)
a	Ph	Me	Me	70
b	4-FC_6H_4	Me	Me	58
c	2-thienyl	Me	Me	65
d	Ph	—$(CH_2)_5$—		62
e	Ph	—$(CH_2)_2O(CH_2)_2$—		56

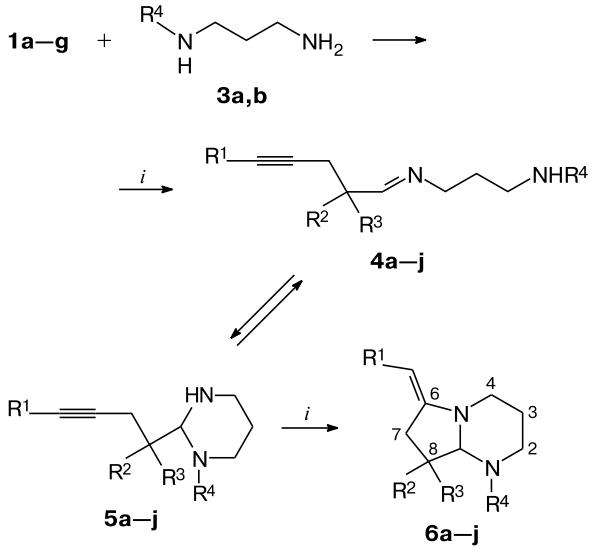
1: R = H (**f**), F_3C (**g**), Me (**h**), OMe (**i**)
2: R^1 = Ph (**a**), 4-FC_6H_4 (**b**), 2-thienyl (**c**)

Reagents and conditions: *i.* 30% aqueous NaOH, toluene, NaI, Bu_4NI, 50 °C; *ii.* $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, 20 °C; *iii.* Py·CrO_3·HCl, CH_2Cl_2, 20 °C.

Alkynals **1f—i** unsubstituted at α-position were obtained by a cross-coupling of the corresponding iodoarenes (iodobenzene, 4-iodobenzotrifluoride, 4-iodotoluene, and 4-iodoanisole) with pent-4-yn-1-ol upon treatment with a mixture of $Pd(PPh_3)_2Cl_2$ and CuI in anhydrous triethylamine[25] with subsequent oxidation of the alcohols obtained with pyridinium chlorochromate in dichloromethane (see Scheme 1).

A sequential addition of aldehydes **1a—g** and powdered KOH to solutions of 1,3-diaminopropanes **3a**,**b** in DMSO (the molar ratio amine : aldehyde : KOH = 5 : 1 : 5) led to the formation of the corresponding (*E*)-6-(arylmethylidene)octahydropyrrolo[1,2-*a*]pyrimidines **6a—j** in 42—78% yields (Scheme 2, Table 1). The best yields were observed in the case of 2,2-disubstituted aldehydes **1a—e**, apparently, because of the exception of the side processes proceeding due to the presence of acidic hydrogen atoms at α-position to the carbonyl group. Products **6a**,**b** having ~90% purity were isolated by simple dilution of the reaction mixture with a 10-fold amount of water with subsequent separation of the crystalline precipitate by filtration and its washing with water. Additional purification of products **6a**,**b**, as well as isolation of compounds **6c—j**, was performed by recrystallization from hexane.

Scheme 2



Compound **4, 5, 6**	R^1	R^2	R^3	R^4
a	Ph	Me	Me	H
b	Ph	Me	Me	Me
c	4-FC_6H_4	Me	Me	Me
d	2-thienyl	Me	Me	Me
e	Ph	—$(CH_2)_5$—		H
f	Ph	—$(CH_2)_5$—		Me
g	Ph	—$(CH_2)_2O(CH_2)_2$—		Me
h	Ph	H	H	H
i	Ph	H	H	Me
j	4-$F_3CC_6H_4$	H	H	Me

3: R^4 = H (**a**), Me (**b**)

Reagents and conditions: *i.* DMSO, KOH, 20 °C.

It should be noted that this reaction proceeds with high stereoselectivity: in all the cases compounds **6** were exclusively formed as *E*-isomers. The isomers were identified using their NOESY-2D proton spectra based on the analysis of the interaction of protons at the double bond and the protons of the methylidene fragment at position 7. As it is seen from the data obtained (see Table 1), the

Table 1. The products of the reaction of alk-4-ynals **1a—i** with diaminoalkanes **3a,b** and **7** in DMSO in the presence of KOH (the molar ratio alkynal : diaminoalkane : KOH = 1 : 5 : 5)

Aldehyde	Diamino-alkane	τ/h	Product	Yield (%)
1a	**3a**	2	**6a**	77[b]
1a	**3b**	10	**6b**	78[b]
1b	**3b**	15	**6c**	60[b]
1c	**3b**	10	**6d**	58[b]
1d	**3a**	2	**6e**	52[b]
1d	**3b**	10	**6f**	65[b]
1e	**3b**	10	**6g**	72[b]
1f	**3a**	2	**6h**	42[b]
1f	**3b**	15	**6i**	51[b]
1g	**3b**	10	**6j**	45[b]
1h	**3a**	10	—[a]	—
1i	**3b**	10	—[a]	—
1a	**7**	2	**10a**[c]	75[d]
1d	**7**	2	**10b**[c]	63[d]

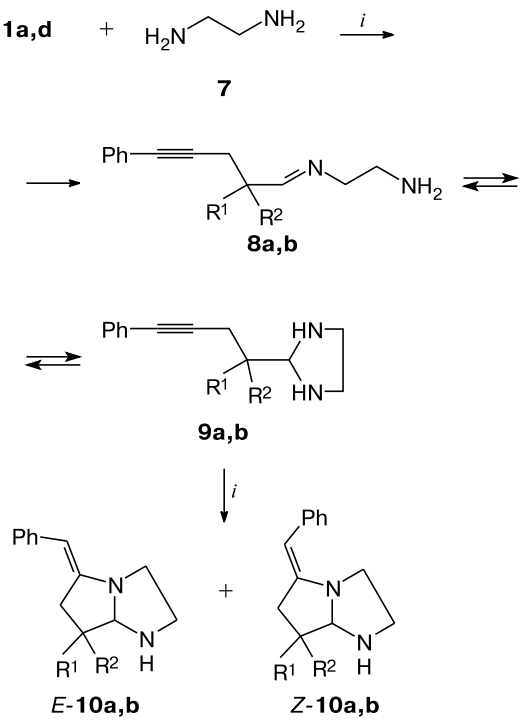
[a] No product was formed, a complete resinification of the reaction mixture was observed.
[b] The yield of the product isolated by crystallization from hexane is given.
[c] The ratio of isomers was determined from the NMR spectra of isolated products: for compound **10a** $E/Z = 5 : 1$, for compound **10b** $E/Z = 4.5 : 1$.
[d] The yield of the product isolated by column chromatography is given.

structure of the diamine used considerably influences the rate of the process. Thus, the reaction of 1,3-diaminopropane (**3a**) with all the aldehydes **1** under study reached completion within two hours, whereas similar processes with *N*-methyl-1,3-diaminopropane (**3b**) proceeded slower and required stirring for 10—15 h to be completed.

No formation of the corresponding enaminals **6** was observed when aldehydes **1h** and **1i** with *p*-tolyl and *p*-methoxyphenyl substituents at the triple bond were used as the starting compounds. It is possible that this results from the low polarization of the triple bond in the initial adducts of these aldehydes with diamines because of more donor character of the aryl substituents used, that interferes with the intramolecular hydroamination and directs the process along the side channels.

Unlike reactions with diaminopropanes **3a**,**b**, similar processes with 1,2-diaminoethane (**7**) proceed less selectively. Thus, the reaction of aldehydes **1a**,**d** with a fivefold molar excess of 1,2-diaminoethane (**7**) and powdered KOH in anhydrous DMSO leads to the corresponding hexahydropyrrolo[1,2-*a*]imidazoles **10a**,**b** as mixtures of *E*- and *Z*-isomers in 75 and 63% yields, respectively (Scheme 3, see Table 1). Most likely, such a difference can be explained by a significantly smaller steric effect of the five-membered ring formed in the course of this process as compared to the six-membered one. Unlike products **6**, both compounds **10a** and **10b** were obtained as dense liquids, which were isolated by column chromatography on neutral Al_2O_3.

Scheme 3



8, 9, 10: R^1, R^2 = Me (**a**), $R^1 + R^2 = -(CH_2)_5-$ (**b**)

Reagents and conditions: *i*. DMSO, KOH, 20 °C.

In order to gather data on the intermediate products emerging in the course of these reactions, a more detailed study of their proceeding in DMSO-d_6 with the periodical checking of the reaction mixture by NMR spectroscopy was performed. Thus, it was shown that the addition of aldehyde **1a** to 1,3-diaminopropane (**3a**) or 1,2-diaminoethane (**7**) over a short period of time (10—20 min) led to the equilibrium mixtures of the corresponding linear imines **4a** and **8a** and cyclic aminals **5a** and **9a** in quantitative yields (Table 2). The ratio of components in the mixtures obtained did not virtually depend on the excess of the diamine used (in the range from 1 : 1 to 1 : 10), and no formation of noticeable amounts of adducts at both amino groups even at the equimolar ratio of reagents was observed at all.

The presence of the equilibrium between compounds **8a** and **9a**, as well as between **4a** and **5a,** was confirmed by NMR spectroscopy at different temperatures. Thus, upon heating the reaction mixture obtained by the reaction of aldehyde **1a** with 1,2-diaminoethane to 50 °C, the ratio of components **8a** and **9a** changed from 1 : 5.5 to 1 : 2.3 and was completely restored to the initial value upon subse-

Table 2. The reaction of aldehydes **1a** and **1f** with diamines **3a**,**b** and **7** in DMSO-d_6 and the subsequent reactions of the products **4a**,**b**, **5a**,**i**, **8a**, **9a** with KOH

Starting aldehyde	Diamine	Molar ratio aldehyde : diamine	Condensation products	Reaction time with KOH[b]/h	Product (yield)[c]
1a	**3a**	1 : 1	**4a**, **5a** (1 : 50)[a]	2	**6a** (96%)
		1 : 3	**4a**, **5a** (1 : 45)[a]	2	**6a** (98%)
1a	**7**	1 : 1	**8a**, **9a** (1 : 5.7)[a]	2	**10a** (95%)
		1 : 3	**8a**, **9a** (1 : 5.6)[a]	2	**10a** (94%)
		1 : 10	**8a**, **9a** (1 : 5.5)[a]	2	**10a** (90%)
1a	**3b**	1 : 1.5	**4b**	15	**6b** (56%)
		1 : 3		15	**6b** (84%)
		1 : 10		15	**6b** (90%)
1f	**3b**	1 : 1	**5i**	15	**6i** (62%)
		1 : 3		15	**6i** (64%)

[a] The ratio was determined at 23 °C.
[b] The molar ratio alkynal : KOH = 1 : 5.
[c] Determined based on the comparison of integral intensities of the signals in the ^{1}H NMR spectrum of the products and dioxane (δ 3.56) taken as an internal standard.

quent cooling to 23 °C. In similar experiment with a mixture of compounds **4a** and **5a**, heating to 50 °C led to a reversible increase in the content of linear product **4a** from ~2% (**4a** : **5a** = 1 : 50) to 25% (**4a** : **5a** = 1 : 3).

The reaction of aldehyde **1a** with *N*-methyl-1,3-diaminopropane (**3b**) in DMSO-d_6 exclusively led to linear product **4b** in quantitative yield, whereas a similar reaction with aldehyde **1f** unsubstituted at α-position gave only cyclic aminal **5i**. Most likely, such a difference is explained by the steric influence of two methyl groups, hindering cyclization of imine **4b** to the corresponding aminal **5b** and significantly shifting the equilibrium to the side of the former.

Compounds **4a**,**b**, **5a**,**i**, **8a**, and **9a** in the reaction mixtures were identified by a comparison of the NMR spectra of these mixtures with the spectra of the corresponding products obtained by the condensation of aldehydes **1a**,**f** with excess of diamines **2a**—**c** in CH_2Cl_2 in the presence of anhydrous Na_2SO_4. In all the cases, the overall yield of the condensation products determined based on the correlation of the integral intensities of their signals and the signal of dioxane taken as an internal standard has proved to be quantitative.

Stirring the solutions of the reaction products, obtained from aldehydes **1a**,**f** and diamines **3a**,**b** and **7**, in DMSO-d_6 with freshly powdered KOH led to the disappearance of the signals for these compounds in the NMR spectra and the appearance of the signals for the corresponding aminals **6a**,**b**,**i** and **10a**, whose yields after the reaction reached completion were determined from the correlation of the integral intensities of the signal for the aminal proton (δ 2.7—4.05) and that of dioxane (δ 3.56) used as an internal standard. The results obtained are given in Table 2.

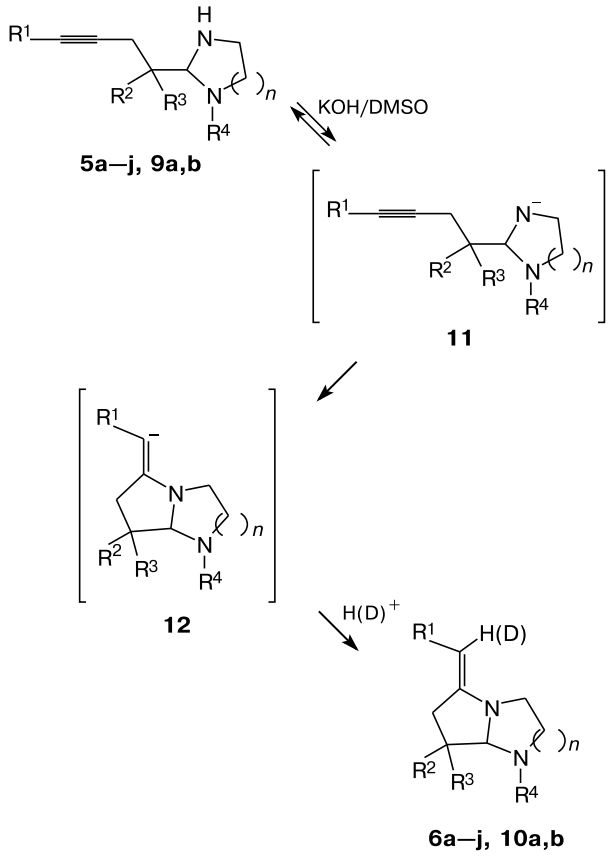
In the case of cyclization of imine **4b**, the NMR spectra of the reaction mixture showed no appearance of the corresponding cyclic product **5b** in the course of the reaction at various conversions of the starting compound, that, most likely, indicates that the process of its formation is significantly slower than subsequent addition at the C≡C bond, thus being a limiting step of the whole process.

As it is seen from the data given in Table 2, excess of diamine, excluding the case of the reaction of aldehyde **1a** with *N*-methyl-1,3-diaminopropane (**3b**), virtually does not affect the yields of the final products **6** and **10**, which in the case of 2,2-disubstituted aldehydes are almost quantitative even at the equimolar ratio aldehyde : diamine. This fact can be useful if this reaction is carried out with expensive or hardly separable diaminoalkanes.

It should be noted that in all the reactions of alkynals **1** with diamines in DMSO-d_6 in the presence of KOH, the observed integral intensity of the signal for the proton at the double bond (δ 5.1—5.3) in the NMR spectra of products **6** and **10** was much lower than the calculated intensity, that indicates a considerable extent of the deuteroexchange in the course of the process under study. Taking into account the data of a separate experiment, which showed that stirring compound **6b** under the same conditions (KOH in DMSO-d_6 at ~20 °C) did not lead to the deuteroexchange, a conclusion can be drawn that the intramolecular addition of the amino group at the triple bond in aminals **5** and **9** bears considerable ionic character and proceeds with involvement of the corresponding amide anions **11**, transforming to vinyl anions **12**, which then add a proton (or a deuterium cation) from the reaction medium (Scheme 4).

In conclusion, we suggested a simple method for the preparation of various 6-(arylmethylidene)octahydropyrrolo[1,2-*a*]pyrimidines and 5-(arylmethylidene)hexahydropyrrolo[1,2-*a*]imidazoles based on the reaction of available alk-4-ynals with aliphatic diaminoalkanes in the

Scheme 4



n = 1, 2

presence of KOH in DMSO, which gives an opportunity to further study these polyfunctional and highly reactive substrates. The intermediates emerging in the course of these multi-step processes were established. This approach has the advantage over methods described earlier[26] of using available starting compounds, as well as of a possibility to obtain a wider scope of bicyclic *N,N*-enaminals, including those containing no substituents at α-position to the carbon atom of the NCHN fragment.

Experimental

GLC analysis of starting compound and products obtained was carried out on a Hewlett-Packard 5890 Series II instrument with an HP-1 capillary column (30 m × 0.153 mm) and a Hewlett-Packard 3396A automatic integrator. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200p spectrometer for solutions in $CDCl_3$, using Me_4Si as an internal standard. Mass spectra were recorded on a Finningan DSQ II GLC-MS spectrometer.

1-Chloro-3-phenylprop-2-yne (**2a**) was obtained by chlorination of 3-phenylprop-2-yn-1-ol upon treatment with $SOCl_2$ in CCl_4 in the presence of an equimolar amount of triethylamine according to the procedure[27] in 87% yield. 1-Chloro-3-(4-fluorophenyl)prop-2-yne (**2b**) was obtained similarly from 3-(4-fluorophenyl)prop-2-yn-1-ol in 82% yield, 1-chloro-3-(2-thienyl)prop-2-yne (**2c**) was synthesized by the reaction of 3-(2-thienyl)prop-2-yn-1-ol with $SOCl_2$ in diethyl ether under conditions described in the work[28] (77% yield).

2,2-Dimethyl-5-phenylpent-4-ynal (1a) was synthesized from chloride **2a** and freshly distilled isobutyraldehyde according to the procedure described in the work.[24] Similar procedure was used to obtain 5-(4-fluorophenyl)-2,2-dimethylpent-4-ynal (**1b**), 2,2-dimethyl-5-(2-thienyl)pent-4-ynal (**1c**), 1-(3-phenylprop-2-ynyl)cyclohexanecarbaldehyde (**1d**), and 4-(3-phenylprop-2-ynyl)tetrahydropyran-4-carbaldehyde (**1e**).

5-(4-Fluorophenyl)-2,2-dimethylpent-4-ynal (1b) was obtained from chloride **2b** and isobutyraldehyde in 58% yield and isolated by microdistillation *in vacuo* (bath temperature 110—120 °C, 1 Torr). ^{1}H NMR, δ: 1.23 (s, 6 H, 2 Me); 2.61 (s, 2 H, C≡CCH_2); 6.92—7.05 (m, 2 H, Ph); 7.35—7.45 (m, 2 H, Ph); 9.60 (s, 1 H, CHO). ^{13}C NMR, δ: 21.3 (2 Me); 27.5 (C≡C$\underline{C}H_2$); 45.8 ($\underline{C}Me_2$); 82.27, 85.3 (C≡C); 115.5 (d, C(3), C(5), Ph, J = 22.1 Hz); 119.5 (d, C(1), Ph, J = 3.7 Hz); 133.4 (d, C(2), C(6), Ph, J = 8.4 Hz); 162.2 (d, C(4), Ph, J = 248 Hz); 204.6 (CHO).

2,2-Dimethyl-5-(2-thienyl)pent-4-ynal (1c) was obtained from chloride **2c** and isobutyraldehyde in 65% yield and isolated by microdistillation *in vacuo* (bath temperature 120—130 °C, 1 Torr). ^{1}H NMR, δ: 1.22 (s, 6 H, 2 Me); 2.59 (s, 2 H, C≡CCH_2); 6.95 (dd, 1 H, C(4)H, J = 5.2 Hz, J = 3.6 Hz); 7.14 (dd, 1 H, C(3)H, J = 3.6 Hz, J = 1.2 Hz); 7.19 (dd, 1 H, C(5)H, J = 5.2 Hz, J = 1.2 Hz); 9.59 (s, 1 H, CHO). ^{13}C NMR, δ: 21.4 (2 Me); 27.8 (C≡C$\underline{C}H_2$); 45.9 ($\underline{C}Me_2$); 78.3, 89.7 (C≡C); 123.4 (C(2), thienyl); 126.4, 126.9, 131.5 (thienyl); 204.6 (CHO).

1-(3-Phenylprop-2-ynyl)cyclohexanecarbaldehyde (1d) was obtained from chloride **2a** and cyclohexanecarbaldehyde in 62% yield and isolated by microdistillation *in vacuo* (bath temperature 160—170 °C, 1 Torr). ^{1}H NMR, δ: 1.20—1.71 (m, 8 H, *cyclo*-C_6); 1.95—2.10 (m, 2 H, *cyclo*-C_6); 2.56 (s, 2 H, C≡CCH_2); 7.25—7.45 (m, 5 H, Ph); 9.64 (s, 1 H, CHO). ^{13}C NMR, δ: 22.3, 25.5, 28.7, 30.5 (5 CH_2, *cyclo*-C_6, C≡C$\underline{C}H_2$); 49.1 (C_{quat}); 83.5, 85.1 (C≡C); 123.4 (C(1), Ph); 127.1, 128.2, 131.6 (Ph); 206.0 (CHO).

4-(3-Phenylprop-2-ynyl)tetrahydropyran-4-carbaldehyde (1e) was obtained from chloride **2a** and tetrahydropyran-4-carbaldehyde in 62% yield and isolated by microdistillation *in vacuo* (bath temperature 160—170 °C, 1 Torr). ^{1}H NMR, δ: 1.75 (ddd, 2 H, C$\underline{H}$HC(CHO)C$\underline{H}$H, J = 13.9 Hz, J = 10.5 Hz, J = 4.3 Hz); 2.05 (ddd, 2 H, C$\underline{H}$HC(CHO)C$\underline{H}$H, J = 13.9 Hz, J = 4.3 Hz, J = 2.8 Hz); 2.58 (s, 2 H, C≡CCH_2); 3.49 (ddd, 2 H, C$\underline{H}$HOC$\underline{H}$H, J = 12.0 Hz, J = 10.5 Hz, J = 2.8 Hz); 3.82 (ddd, 2 H, C$\underline{H}$HOC$\underline{H}$H, J = 12.0 Hz, J = 4.3 Hz, J = 4.3 Hz); 7.25—7.45 (m, 5 H, Ph); 9.63 (s, 1 H, CHO). ^{13}C NMR, δ: 26.9 (C≡C$\underline{C}H_2$); 30.3 (C(3), C(5), *cyclo*-C_5O); 46.9 (C(4), *cyclo*-C_5O); 64.3 (C(2), C(6), *cyclo*-C_5O); 83.8, 84.0 (C≡C); 122.8 (C(1), Ph); 128.0, 128.2, 131.5 (Ph); 204.3 (CHO).

Alkynals **1f—i** were obtained by the cross-coupling of the corresponding iodoarenes (iodobenzene, 4-iodobenzotrifluoride, 4-iodotoluene, and 4-iodoanisole) with pent-4-yn-1-ol upon treatment with a mixture of $Pd(PPh_3)_2Cl_2$ and CuI in anhydrous triethylamine[25] with subsequent oxidation of the acetylenic alcohol formed with pyridinium chlorochromate in dichloromethane (the yield for the two steps was 68% for **1f**, 75% for **1g**, 77% for **1h**, and 65% for **1i**). Spectral characteristics of the compounds obtained agreed with the published data (see Ref. 29 for **1f**, as well as Ref. 30 for **1g—i**).

Synthesis of bicyclic aminals 6a—j and 10a,b from acetylenic aldehydes 1a—g and diamines 3a,b and 7 (general procedure). A solution of aldehyde **1** (1 mmol in DMSO (3 mL) was added slowly to a solution of the corresponding diamine (5 mmol) in anhydrous DMSO (3 mL) with stirring. The mixture obtained was stirred for 30 min at ~20 °C, followed by addition of freshly powdered KOH (280 mg, 5 mmol) and stirring a suspension for 2—10 h until reaction reached completion (GLC or NMR monitoring). Then, water (30 mL) and CH_2Cl_2 (30 mL) were added to the reaction mixture, the organic layer was separated, the aqueous layer was additional extracted with dichloromethane (3×10 mL). The combined organic layers were washed with water 4 times, dried with anhydrous K_2CO_3, the solvent was evaporated, whereas the residue was subjected to recrystallization or column chromatography to isolate the target product, which according to the NMR and elemental analysis data was one of the corresponding aminals **6** or **10** with more than 95% purity (see Table 1).

5-Benzylidene-7,7-dimethylhexahydro-1*H*-pyrrolo[1,2-*a*]-imidazole (10a) was obtained from aldehyde **1a** and 1,2-diaminoethane **7** as a mixture of *E*- and *Z*-isomers (the ratio of 5 : 1) and isolated in 75% yield by chromatography on neutral Al_2O_3 (eluent hexane—diethyl ether, 10 : 1).

5´-Benzylidenehexahydrospiro[cyclohexane-1,7´-pyrrolo-[1,2-*a*]imidazole] (10b) was obtained from aldehyde **1d** and 1,2-diaminoethane (**7**) in 63% yield as a mixture of *E*- and *Z*-isomers (the ratio of 4 : 1) and isolated by chromatography on neutral Al_2O_3 (eluent hexane—diethyl ether, 5 : 1).

(*E*)-6-Benzylidene-8,8-dimethyloctahydropyrrolo[1,2-*a*]pyrimidine (6a) was obtained from aldehyde **1a** and 1,3-diaminopropane (**3a**) and isolated in 77% yield by recrystallization from hexane.

(*E*)-6-Benzylidene-1,8,8-trimethyloctahydropyrrolo[1,2-*a*]-pyrimidine (6b) was obtained from aldehyde **1a** and *N*-methyl-1,3-diaminopropane (**3b**) and isolated in yield 78% by recrystallization from hexane.

Spectral characteristics of compounds **6a**,**b** and **10a**,**b** correspond to those described earlier.[26]

(*E*)-6-(4-Fluorobenzylidene)-1,8,8-trimethyloctahydropyrrolo[1,2-*a*]pyrimidine (6c) was obtained from aldehyde **1b** and *N*-methyl-1,3-diaminopropane (**3b**) and isolated in 60% yield by recrystallization from hexane. Found (%): C, 74.71; H, 8.21 N, 9.98. $C_{17}H_{23}FN_2$. Calculated (%): C, 74.42; H, 8.45; N, 10.21. ^{1}H NMR, δ: 1.12 (s, 3 H, Me); 1.27 (s, 3 H, Me); 1.60—1.74 (m, 1 H, $NCH_2C\underline{H}HCH_2N$); 1.78—2.00 (m, 1 H, $NCH_2C\underline{H}HCH_2N$); 2.04—2.21 (m, 1 H, $MeNC\underline{H}HCH_2CH_2N$); 2.32 (s, 3 H, NCH_3); 2.46 (br.d, 1 H, $=CC\underline{H}H$, J = 15.6 Hz); 2.51 (ddd, 1 H, $MeNC\underline{H}HCH_2CH_2N$, ^2J = 12.0 Hz, ^3J = 12.0 Hz, ^3J = 4.0 Hz); 2.66 (br.d, 1 H, $=CC\underline{H}H$, J = 15.6 Hz); 2.73 (s, 1 H, NCHN); 2.94 (ddd, 1 H, $MeNCH_2CH_2C\underline{H}HN$, ^2J = 10.9 Hz, ^3J = 3.4 Hz, ^3J = 3.4 Hz); 3.50—3.62 (m, 1 H, $MeNCH_2CH_2C\underline{H}HN$); 5.15 (br.s, 1 H, 4-$FC_6H_4C\underline{H}$=); 6.85—7.15 (m, 4 H, Ph). ^{13}C NMR, δ: 22.5 (Me); 24.1 (C(3); 28.1 (Me); 38.3 (C(8); 42.3 (NMe); 43.0, 45.8 (C(4), C(7)); 56.3 (C(2)); 90.1, 92.0 (N$\underline{C}$HN, 4-$FC_6H_4\underline{C}$H=); 115.0 (d, C(3), C(5), Ph, J = 21 Hz); 127.4 (d, C(2), C(6), Ph, J = 7.2 Hz); 136.0 (d, C(1), Ph, J = 2.7 Hz); 148.6 (4-FC_6H_4CH=$\underline{C}$); 162.0 (d, C(4), Ph, J = 242 Hz). MS, m/z: 274 [M^+], 273 [M — H]$^+$.

(*E*)-1,8,8-Trimethyl-6-(2-thienylmethylidene)octahydropyrrolo[1,2-*a*]pyrimidine (6d) was obtained from aldehyde **1c** and *N*-methyl-1,3-diaminopropane (**3b**) and isolated in 58% yield by recrystallization from hexane. Found (%): C, 96.32; H, 8.69; N, 10.97. $C_{15}H_{22}N_2S$. Calculated (%): C, 68.65; H, 8.45; N, 10.68. ^{1}H NMR, δ: 1.13 (s, 3 H, Me); 1.30 (s, 3 H, Me); 1.60—1.74 (m, 1 H, $NCH_2C\underline{H}HCH_2N$); 1.76—2.00 (m, 1 H, $NCH_2C\underline{H}HCH_2N$); 2.00—2.15 (m, 1 H, $MeNC\underline{H}HCH_2CH_2N$); 2.29 (s, 3 H, NMe); 2.44 (br.d, 1 H, $=CC\underline{H}H$, J = 16.5 Hz); 2.50 (ddd, 1 H, $MeNC\underline{H}HCH_2CH_2N$, ^2J = 12.0 Hz, ^3J = 12.0 Hz, ^3J = 3.9 Hz); 2.69 (br.d, 1 H, $=CC\underline{H}H$, J = 16.5 Hz); 2.75 (s, 1 H, NCHN); 2.93 (ddd, 1 H, $MeNCH_2CH_2C\underline{H}HN$, ^2J = 10.9 Hz, ^3J = 3.4 Hz, ^3J = 3.4 Hz); 3.50—3.62 (m, 1 H, $MeNCH_2CH_2C\underline{H}HN$); 5.48 (br.s, 1 H, ThiC$\underline{H}$=); 6.65 (dd, 1 H, thienyl, J = 3.4 Hz, J = 1.4 Hz); 6.88—6.98 (m, 2 H, thienyl). ^{13}C NMR, δ: 22.6 (Me); 24.0 (C(3)); 28.1 (Me); 38.5 (C(8)); 42.3 (NMe); 42.9, 45.9 (C(4), C(7)); 56.2 (C(2)); 87.4, 90.3 (N$\underline{C}$HN, Thi$\underline{C}$H=), 119.4, 120.2, 127.0 (thienyl); 144.1 (C(1), thienyl); 146.2 (ThiCH=$\underline{C}$). MS, m/z: 262 [M^+], 261 [M — H]$^+$.

(*E*)-6´-Benzylidenehexahydro-1´*H*-spiro[cyclohexane-1,8´-pyrrolo[1,2-*a*]pyrimidine] (6e) was obtained from aldehyde **1d** and 1,3-diaminopropane (**3a**) and isolated in 52% yield by recrystallization from hexane. Spectral characteristics of this compound correspond to those described earlier.[26]

(*E*)-6´-Benzylidene-1´-methylhexahydro-1´*H*-spiro[cyclohexane-1,8´-pyrrolo[1,2-*a*]pyrimidine] (6f) was obtained from aldehyde **1d** and *N*-methyl-1,3-diaminopropane (**3b**) and isolated in 52% yield by recrystallization from hexane. Found (%): C, 80.67; H, 9.69; N, 9.21. $C_{20}H_{28}N_2$. Calculated (%): C, 81.03; H, 9.52; N, 9.45. ^{1}H NMR, δ: 1.10—2.00 (m, 12 H, *cyclo*-C_6H_{10}, $NCH_2C\underline{H}_2CH_2N$); 2.03—2.18 (m, 1 H, $MeNC\underline{H}HCH_2CH_2N$); 2.33 (br.d, 1 H, $=CC\underline{H}H$, J = 16.4 Hz); 2.36 (s, 3 H, NMe); 2.50 (ddd, 1 H, $MeNC\underline{H}HCH_2CH_2N$, ^2J = 11.8 Hz, ^3J = 11.8 Hz, ^3J = 4.0 Hz); 2.71 (s, 1 H, NCHN); 2.88—3.00 (m, 1 H, $MeNCH_2CH_2C\underline{H}HN$); 3.12 (br.d, 1 H, $=CC\underline{H}H$, J = 16.4 Hz); 3.52—3.64 (m, 1 H, $MeNCH_2CH_2C\underline{H}HN$); 5.18 (br.s, 1 H, PhC$\underline{H}$=); 6.98 (br.t, 1 H, Ph, J = 6.8 Hz); 7.15—7.30 (m, 4 H, Ph). ^{13}C NMR, δ: 22.3, 23.8, 23.9, 26.4, 28.7, 37.6, 39.8 (5 CH, *cyclo*-C_6; C(3´), C(7´)); 42.4 (C(1,8´)), 43.0 (C(4´)); 43.2 (NMe); 56.8 (C(2´)); 90.3 (N$\underline{C}$HN); 93.0 (Ph$\underline{C}$H=C); 122.8, 126.3, 128.3 (Ph); 140.1 (C(1), Ph); 147.1 (PhCH=$\underline{C}$). MS, m/z: 296 [M^+], 295 [M — H]$^+$.

(*E*)-6´-Benzylidene-1´-methyldecahydro-1´*H*-spiro[pyran-4,8´-pyrrolo[1,2-*a*]pyrimidine] (6g) was obtained from aldehyde **1e** and *N*-methyl-1,3-diaminopropane (**3b**) and isolated in 72% yield by recrystallization from hexane. Found (%): C, 76.17; H, 8.56; N, 9.23. $C_{19}H_{26}N_2O$. Calculated (%): C, 76.47; H, 8.78; N, 9.39. ^{1}H NMR, δ: 1.39 (br.dd, 2 H, $C\underline{H}_2CH_2OCH_2CH_2$, J = 15 Hz, J = 15 Hz), 1.61—1.75 (m, 1 H, $NCH_2C\underline{H}HCH_2N$); 1.77—2.25 (m, 3 H, $NCH_2C\underline{H}HCH_2N$, $C\underline{H}HCH_2OCH_2C\underline{H}H$); 2.13—2.32 (m, 1 H, $MeNC\underline{H}HCH_2CH_2N$); 2.40 (s, 3 H, NMe); 2.43 (d, 1 H, $=CC\underline{H}H$, J = 16.3 Hz); 2.53 (ddd, 1 H, $MeNC\underline{H}HCH_2CH_2N$, ^2J = 12.0 Hz, ^3J = 12.0 Hz, ^3J = 4.0 Hz); 2.77 (s, 1 H, NCHN); 2.96 (ddd, 1 H, $MeNCH_2CH_2C\underline{H}HN$, ^2J = 11.5 Hz, ^3J = 3.2 Hz, ^3J = 3.2 Hz); 3.24 (br.d, 1 H, $=CC\underline{H}H$, J = 16.3 Hz); 3.52 (ddd, 1 H, $CH_2OCH\underline{H}$, ^2J = 12.0 Hz, ^3J = 12.0 Hz, ^3J = 2.0 Hz); 3.53—3.63 (m, 1 H, $MeNCH_2CH_2C\underline{H}HN$); 3.64 (ddd, 1 H, $CH_2OCH\underline{H}$, ^2J = 12.4 Hz, ^3J = 12.4 Hz, ^3J = 2.3 Hz); 3.85—4.02 (m, 2 H, CH_2OCH_2); 5.22 (br.s, 1 H, PhC$\underline{H}$=); 7.02 (br.t, 1 H, Ph, J = 6.8 Hz); 7.15—7.35 (m, 4 H, Ph). ^{13}C NMR, δ: 23.6 (C(3´)); 29.3, 37.3 (C(4), C(5), *cyclo*-C_5O); 39.3 (C(7´)); 40.2 (C(4, 8´)); 42.9 (C(4´)); 43.0 (NMe); 56.7 (C(2´)); 64.2, 66.6 (C(2), C(6), *cyclo*-C_5O), 89.5 (N$\underline{C}$HN); 93.6 (Ph$\underline{C}$H=C); 123.1, 126.4, 128.4 (Ph); 139.7 (C(1), Ph); 145.9 (PhCH=$\underline{C}$).

(*E*)-6-Benzylideneoctahydropyrrolo[1,2-*a*]pyrimidine (6h) was obtained from aldehyde **1f** and 1,3-diaminopropane (**3a**) and isolated in 42% yield by recrystallization from hexane. Found (%): C, 78.65; H, 8.23; N, 13.36. $C_{14}H_{18}N_2$. Calculated (%): C, 78.46; H, 8.47; N, 13.07. ^{1}H NMR, δ: 1.48—1.78 (m, 3 H, $NCH_2C\underline{H}_2CH_2N$, $=CCH_2C\underline{H}H$); 2.03 (br.s, 1 H, NH); 2.22 (dddd, 1 H, $=CCH_2C\underline{H}H$, ^2J = 11.6 Hz, ^3J = 8.7 Hz, ^3J = 5.8 Hz, ^3J = 2.9 Hz); 2.55—3.03 (m, 4 H, $=CCH_2$, $NC\underline{H}HCH_2C\underline{H}HNH$); 3.21 (br.d, 1 H, $NCH_2CH_2C\underline{H}HNH$, J = 13.5 Hz); 3.70 (br.d, 1 H, $NC\underline{H}HCH_2CH_2NH$, J = 12.2 Hz); 3.87 (dd, 1 H, $NC\underline{H}N$, J = 8.1 Hz, J = 5.8 Hz); 5.21 (br.s, 1 H, $PhC\underline{H}$=); 6.99 (br.t, 1 H, Ph, J = 6.8 Hz); 7.15—7.30 (m, 4 H, Ph). ^{13}C NMR, δ: 24.8, 27.2, 28.6 (C(3), C(7), C(8)); 43.3, 44.8 (C(2), C(4)); 75.3 (NCHN); 93.3 (Ph$\underline{C}$H=); 122.7, 126.0, 128.1 (Ph); 139.6 (C(1), Ph); 147.5 (PhCH=$\underline{C}$). MS, m/z: 214 [M^+], 213 [M — H]$^+$.

(*E*)-6-Benzylidene-1-methyloctahydropyrrolo[1,2-*a*]pyrimidine (6i) was obtained from aldehyde **1f** and *N*-methyl-1,3-diaminopropane (**3b**) and isolated in 51% yield by recrystallization from hexane. Found (%): C, 78.56; H, 9.03; N, 12.01. $C_{15}H_{20}N_2$. Calculated (%): C, 78.90; H, 8.83; N, 12.27. ^{1}H NMR, δ: 1.60—1.74 (m, 1 H, $NCH_2C\underline{H}HCH_2N$); 1.76—2.23 (m, 4 H, $NCH_2C\underline{H}HCH_2N$, $=CCH_2C\underline{H}_2$, $MeNC\underline{H}HCH_2CH_2N$); 2.29 (s, 3 H, NMe); 2.57—2.81 (m, 2 H, $=CC\underline{H}H$, $MeNC\underline{H}HCH_2CH_2N$); 2.91—3.07 (m, 2 H, $=CC\underline{H}H$, $MeNCH_2CH_2C\underline{H}HN$); 3.08 (dd, 1 H, $NC\underline{H}N$, J = 7.5 Hz, J = 5.9 Hz); 3.60—3.72 (m, 1 H, $MeNCH_2CH_2C\underline{H}HN$); 5.25 (br.s, 1 H, $PhC\underline{H}$=); 7.00 (br.t, 1 H, Ph, J = 6.8 Hz); 7.15—7.30 (m, 4 H, Ph). ^{13}C NMR, δ: 23.8, 27.5, 27.7 (C(3), C(7), C(8)); 41.5 (NMe); 42.7 (C(4)); 55.2 (C(2)); 82.5 (N$\underline{C}$HN); 93.8 (Ph$\underline{C}$H=); 122.9, 126.2, 128.2 (Ph); 139.8 (C(1), Ph); 148.2 (PhCH=$\underline{C}$). MS, m/z: 228 [M^+], 227 [M — H]$^+$.

(*E*)-1-Methyl-6-(4-trifluoromethylbenzylidene)octahydropyrrolo[1,2-*a*]pyrimidine (6j) was obtained from aldehyde **1g** and *N*-methyl-1,3-diaminopropane (**3b**) and isolated in 45% yield by recrystallization from hexane. Found (%): C, 65.21; H, 6.21; N, 9.69. $C_{16}H_{19}F_3N_2$. Calculated (%): C, 64.85; H, 6.46; N, 9.45. ^{1}H NMR, δ: 1.60—1.74 (m, 1 H, $NCH_2C\underline{H}HCH_2N$); 1.76—2.23 (m, 4 H, $NCH_2C\underline{H}HCH_2N$, $=CCH_2C\underline{H}_2$, $MeNC\underline{H}HCH_2CH_2N$); 2.26 (s, 3 H, NMe); 2.57—2.80 (m, 2 H, $=CC\underline{H}H$, $MeNC\underline{H}HCH_2CH_2N$); 2.88—3.08 (m, 2 H, $=CC\underline{H}H$, $MeNCH_2CH_2C\underline{H}HN$); 3.16 (dd, 1 H, $NC\underline{H}N$, J = 7.2 Hz, J = 5.7 Hz); 3.60—3.73 (m, 1 H, $MeNCH_2CH_2C\underline{H}HN$); 5.20 (br.s, 1 H, $PhC\underline{H}$=); 7.21 (br.d, 2 H, Ph, J = 8.3 Hz); 7.43 (br.d, 2 H, Ph, J = 8.3 Hz). ^{13}C NMR, δ: 23.7, 27.4, 28.3 (C(3), C(7), C(8)); 41.4 (NMe); 42.5 (C(4)); 55.2 (C(2)); 82.5 (N$\underline{C}$HN); 93.8 (4-$F_3CC_6H_4\underline{C}$H=); 123.9 (q, C(4), Ph, J = 32 Hz); 124.8 (q, CF_3, J = 270 Hz); 125.0 (q, C(3), C(5), Ph, J = 3.7 Hz); 125.6 (C(2), C(6), Ph); 143.8 (C(1), Ph); 150.5 (4-$F_3CC_6H_4$-CH=$\underline{C}$). MS, m/z: 296 [M^+], 295 [M — H]$^+$.

Reaction of aldehydes 1a and 1f with diamines in DMSO-d_6. A solution of aldehyde **1a** or **1f** (0.1 mmol) was added to a solution of diamine **3a**, **3b**, or **7** (amounts are given in Table 2) and dioxane (~10 mg) (used as an internal standard) in anhydrous DMSO-d_6 (0.3 mL), followed by a short-time heating to ~50 °C. The NMR spectra recorded after cooling the tubes to ~20 °C showed the absence of the signal for the aldehyde proton in all the cases. The composition of the mixture formed was determined by a comparison of its spectrum with the spectra of products obtained by an alternative method by the reaction of aldehydes **1a**,**f** with the corresponding diamines in CH_2Cl_2 in the presence of Na_2SO_4 (see below). Results are given in Table 2.

Solutions of the products of condensation of aldehydes **1a** or **1f** with diamines **3a**, **3b**, or **7** (see Table 2) were stirred with freshly powdered KOH (28 mg, 0.5 mmol) at ~20 °C, monitoring the reaction progress with ^{1}H NMR spectra. In the case of mixtures of products **8a** and **9a**, as well as **4a** and **5a**, the spectra recorded after 2 h showed their complete conversion to aminals **10a** and **6a**, respectively. In the case of using compounds **4b** and **5i**, the conversion after 2 h was 65 and 73%, respectively, the reaction reached completion within 15 h. The yields of aminals **6** and **10** calculated based on the comparison of integral intensities of the signal for the proton of the NCHN fragment and the signal for dioxane are given in Table 2.

Condensation of aldehydes 1a,f with diaminoalkanes 3a,b and 7. Independent synthesis of compounds 4a,b, 5a,i, 8a, 9a. Anhydrous Na_2SO_4 (5 g) was added to a solution of one of diaminoalkanes **3a**,**b** or **7** (20 mmol) in CH_2Cl_2 (20 mL), then, a solution of the corresponding aldehyde **1** (5 mmol) in CH_2Cl_2 (5 mL) was added over 5 min. The mixture obtained was allowed to stand at ~20 °C for 24 h, then, thrice washed with water, and dried with anhydrous Na_2SO_4. The solvent was evaporated *in vacuo* to yield dense oily compounds, which are (NMR data) either mixtures of the corresponding adducts **8a** and **9a** or **4a** and **5a** (characterized without separation), or derivatives **4b** or **5i** with the purity exceeding 90%.

***N*^{1}-(2,2-Dimethyl-5-phenylpent-4-ynylidene)ethane-1,2-diamine (8a).** ^{1}H NMR, δ: 1.15 (s, 6 H, 2 Me); 1.80 (br.s, 2 H, NH_2); 2.45 (s, 2 H, $C{\equiv}CCH_2$); 2.88 (t, 2 H, $C\underline{H}_2NH_2$, J = 5.8 Hz); 3.43 (br.t, 2 H, $=NCH_2$, J = 5.8 Hz); 7.17—7.43 (m, 5 H, Ph); 7.59 (br.s, 1 H, CH=N). ^{13}C NMR, δ: 24.6 (2 Me); 30.5 ($C{\equiv}C\underline{C}H_2$); 39.2 ($\underline{C}(Me)_2$); 42.2 ($CH_2NH_2$); 61.1 ($=NCH_2$); 82.6, 87.2 (C≡C); 123.7 (C(1), Ph); 127.6, 128.1, 131.5 (Ph); 171.4 (CH=N).

2-(2-Methyl-5-phenylpent-4-yn-2-yl)imidazolidine (9a). ^{1}H NMR, δ: 1.04 (s, 6 H, 2 Me); 1.80 (br.s, 2 H, 2 NH); 2.41 (s, 2 H, $C{\equiv}CCH_2$); 2.84—2.92 (m, 4 H, NCH_2CH_2N); 3.62 (s, 1 H, NCHN); 7.17—7.43 (m, 5 H, Ph). ^{13}C NMR, δ: 23.0 (2 Me); 29.7 ($C{\equiv}C\underline{C}H_2$); 37.3 ($\underline{C}(Me)_2$); 46.8 ($N\underline{C}H_2\underline{C}H_2N$); 81.7 (NCHN); 82.5, 88.0 (C≡C); 123.8 (C(1), Ph); 127.5, 128.1, 131.4 (Ph).

***N*^{1}-(2,2-Dimethyl-5-phenylpent-4-ynylidene)propane-1,3-diamine (4a).** ^{1}H NMR, δ: 1.14 (s, 6 H, 2 Me); 1.43—1.57 (m, 2 H, $NCH_2C\underline{H}_2CH_2N$; 1.55 (br.s, 2 H, NH_2); 2.51 (s, 2 H, $C{\equiv}CCH_2$); 2.57 (t, 2 H, $C\underline{H}_2NH_2$, J = 6.7 Hz); 3.38 (br.t, 2 H, $=NCH_2$, J = 6.8 Hz); 7.20—7.45 (m, 5 H, Ph); 7.64 (br.s, 1 H, CH=N).

2-(2-Methyl-5-phenylpent-4-yn-2-yl)hexahydropyrimidine (5a). ^{1}H NMR, δ: 1.12 (s, 6 H, 2 Me); 1.44 (br.s, 2 H, 2 NH); 1.43—1.57 (m, 2 H, $NCH_2C\underline{H}_2CH_2N$); 2.50 (s, 2 H, $C{\equiv}CCH_2$); 2.76—2.94 (m, 2 H, $NC\underline{H}HCH_2C\underline{H}HN$); 3.19—3.32 (m, 2 H, $NC\underline{H}HCH_2C\underline{H}HN$); 3.41 (s, 1 H, NCHN); 7.27—7.51 (m, 5 H, Ph). ^{13}C NMR, δ: 22.8 (2 Me); 27.6, 29.6 ($C{\equiv}C\underline{C}H_2$; C(5), *cyclo*-$C_4N_2$); 37.4 ($\underline{C}(Me)_2$); 46.2 (C(4), C(6), *cyclo*-C_4N_2); 77.9 (C(2), *cyclo*-C_4N_2); 82.3, 87.7 (C≡C); 123.7 (C(1), Ph); 127.2, 127.9, 131.2 (Ph).

***N*^{1}-(2,2-Dimethyl-5-phenylpent-4-ynylidene)-*N*^{3}-methylpropane-1,3-diamine (4b).** ^{1}H NMR, δ: 1.19 (s, 6 H, 2 Me); 1.50 (br.s, 1 H, NH); 1.75 (tt, 2 H, $NCH_2C\underline{H}_2CH_2N$, J = 6.8 Hz, J = 6.8 Hz); 2.35 (s, 3 H, NMe); 2.49 (s, 2 H, $C{\equiv}CCH_2$); 2.57 (t, 2 H, $C\underline{H}_2NHCH_3$, J = 6.8 Hz); 3.43 (br.t., 2 H, $=NCH_2$, J = 6.8 Hz); 7.20—7.45 (m, 5 H, Ph); 7.61 (br.s, 1 H, CH=N).

^{13}C NMR, δ: 24.6 (2 Me); 30.5, 30.8 (C≡C<u>C</u>H$_2$, NCH$_2$<u>C</u>H$_2$-CH$_2$N); 36.4 (NMe); 39.2 (<u>C</u>(Me)$_2$); 49.9 (MeN<u>C</u>H$_2$); 59.3 (=NCH$_2$); 82.5, 87.2 (C≡C); 123.8 (C(1), Ph); 127.5, 128.1, 131.4 (Ph); 169.9 (CH=N).

1-Methyl-2-(4-phenylbut-3-ynyl)hexahydropyrimidine (5i). ^{1}H NMR, δ: 1.35—1.50 (m, 1 H, NCH$_2$C<u>H</u>HCH$_2$N); 1.55—1.76 (m, 3 H, C≡CCH$_2$C<u>H</u>$_2$, NH); 1.89—2.11 (m, 1 H, NCH$_2$C<u>H</u>H-CH$_2$N); 2.18 (s, 3 H, NMe); 2.27 (ddd, 1 H, NC<u>H</u>HCH$_2$-CH$_2$NMe, ^2J = 12 Hz, ^3J = 3.2 Hz, ^3J = 3.2 Hz); 2.36—2.67 (m, 3 H, C≡CCH$_2$, NC<u>H</u>HCH$_2$CH$_2$NMe); 2.83—2.96 (m, 1 H, NCH$_2$CH$_2$C<u>H</u>HNMe); 2.93 (dd, 1 H, NCHN, J = 8.3 Hz, J = 3.2 Hz); 2.96—3.08 (m, 1 H, NCH$_2$CH$_2$C<u>H</u>HNMe); 7.15—7.40 (m, 5 H, Ph). ^{13}C NMR, δ: 15.1 (C≡C<u>C</u>H$_2$); 26.8 (C(5), *cyclo*-C$_4$N$_2$); 32.4 (C≡CCH$_2$<u>C</u>H$_2$); 40.1 (NMe); 45.0 (C(4), *cyclo*-C$_4$N$_2$); 55.6 (C(6), *cyclo*-C$_4$N$_2$); 77.3 (C(2), *cyclo*-C$_4$N$_2$); 80.5, 90.0 (C≡C); 123.8 (C(1), Ph); 127.4, 128.0, 131.4 (Ph).

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