A new synthesis of bicyclic *N,O*- and *N,S*-enaminals by the anionic cyclization of alk-4-ynals with amino alcohols and amino thiols*

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A reaction of alk-4-ynals with aliphatic amino alcohols or 2-aminoethanethiol in the system DMSO—KOH gives bicyclic *N,O*- and *N,S*-enaminals: 6-methylidenehexahydro-2*H*-pyrrolo[2,1-*b*][1,3]oxazines, 5-methylidenehexahydropyrrolo[2,1-*b*]oxazoles, or 5-methylidenehexahydropyrrolo[2,1-*b*]thiazoles. The reaction proceeds through the formation of equilibrium mixtures of the corresponding imines and monocyclic aminals with subsequent 5-*exo*-*dig*-cyclization catalyzed by the superbasic system DMSO—KOH.

Key words: alk-4-ynals, aminoalkanols, 2-aminoethanethiol, hexahydro-2*H*-pyrrolo[2,1-*b*]-[1,3]oxazines, hexahydropyrrolo[2,1-*b*]oxazoles, hexahydropyrrolo[2,1-*b*]thiazoles, 1,3-oxazinanes, hydroamination, anionic cyclization, dimethyl sulfoxide, potassium hydroxide.

Earlier, we have suggested[1,2] an original method for the preparation of bicyclic *N,N*-enaminals, *viz.*, 6-(arylmethylidene)octahydropyrrolo[1,2-*a*]pyrimidines and 5-(arylmethylidene)hexahydropyrrolo[1,2-*a*]imidazoles, based on the reaction of 1-(alk-1-ynyl)-1-chlorocyclopropanes with lithium derivatives of aliphatic diamines. Later, it was shown[3,4] that an anionic cyclization of alk-4-ynals with aliphatic 1,2- and 1,3-diamines in a KOH—DMSO system is more convenient and general approach to these compounds. At the same time, *N,O*- and *N,S*-analogs of these enaminals are comparatively little studied heterocyclic structures. To date, only 5-methylidenehexahydropyrrolo[2,1-*b*]oxazoles with two fused five-membered rings were obtained. They were synthesized by methods based on either the reaction of tetrahydropyrrolo[2,1-*b*]oxazol-5(6*H*)-ones with organolithium reagents[5—7] or on the reactions of aminoalkanols with diketones[8,9] or γ-oxoalkynes[9] having an activated triple bond. Compounds of this series exhibit antiinflammatory and antinociceptive activity,[10,11] whereas the presence in their structure of highly reactive 2-methylidenepyrrolidine[12] and bicyclic *N,O*-aminal[13] fragments is of considerable synthetic interest. In particular, their characteristic reactions are reduction with the simultaneous selective oxazole ring opening,[8,14] hydrolysis with the formation of cyclopentanone structures[5] or dicarbonyl compounds.[15]

At the same time, there is no data on the related 6-methylidenehexahydro-2*H*-pyrrolo[2,1-*b*][1,3]oxazines and 5-methylidenehexahydropyrrolo[2,1-*b*]thiazoles, that, apparently, results from the absence of convenient general approaches to these types of compounds. We suggested that these *N,O*- and *N,S*-enaminals, as well as 5-methylidenehexahydropyrrolo[2,1-*b*]oxazoles, can be obtained similarly to *N,N*-enaminals by the reaction of the corresponding alk-4-ynals with amino alcohols and amino thiols in the superbasic[16,17] system DMSO—KOH.

Results and Discussion

In the course of the present studies, it was found that a sequential addition of aldehydes **1a**,**b**,**d** and powdered KOH to the solutions of amino alcohols **2a—c** in DMSO (the molar ratio aldehyde : amine : KOH = 1 : 1 : 5) leads to the corresponding *N,O*-enaminals **3a—e** in 42—82% yields (Scheme 1, Table 1). The highest yields were obtained when 2,2-disubstituted aldehydes **1a**,**b** were used. The products **3a—d** with ~90% purity were isolated by the dilution of the reaction mixtures with a 10-fold amount of water with subsequent extraction of the aqueous phases with dichloromethane. The crystalline compound **3b** was additionally purified by recrystallization from hexane, while the products **3a**,**c—e**, which are dense liquids, were isolated by column chromatography on neutral Al_2O_3.

The reaction of aldehyde **1c** having no substituents at α-position to the carbonyl group did not lead to the corresponding enaminals **3** neither with 3-aminopropanol (**2a**), nor with (1-aminomethylcyclopropyl)methanol (**2c**), giving mixtures of unidentifiable compounds. It is probable that this results from the side processes involving relatively acidic hydrogen atoms in the corresponding imino alco-

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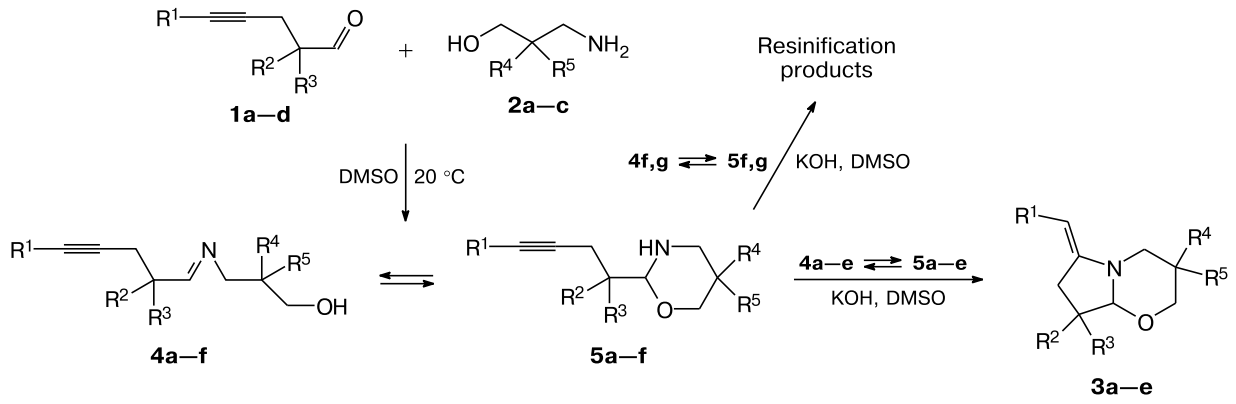
Scheme 1



Yield of compound **3**: 82% (**a**), 72% (**b**), 78% (**c**), 68% (**d**), 42% (**e**).

1: R^1 = Ph, $R^2 = R^3$ = Me (**a**)
R^1 = 2-thienyl, $R^2 = R^3$ = Me (**b**)
R^1 = Ph, $R^2 = R^3$ = H (**c**)
R^1 = 4-$F_3CC_6H_4$, $R^2 = R^3$ = H (**d**)
2: $R^4 = R^5$ = H (**a**), $R^4 = R^5$ = Me (**b**)
$R^4 + R^5 = (CH_2)_2$ (**c**)

3—5: R^1 = Ph, $R^2 = R^3$ = Me, $R^4 = R^5$ = H (**a**)
R^1 = Ph, $R^2 = R^3 = R^4 = R^5$ = Me (**b**)
R^1 = Ph, $R^2 = R^3$ = Me, $R^4 + R^5 = (CH_2)_2$ (**c**)
R^1 = 2-thienyl, $R^2 = R^3$ = Me, $R^4 = R^5$ = H (**d**)
R^1 = 4-$F_3CC_6H_4$, $R^2 = R^3 = R^4 = R^5$ = H (**e**)

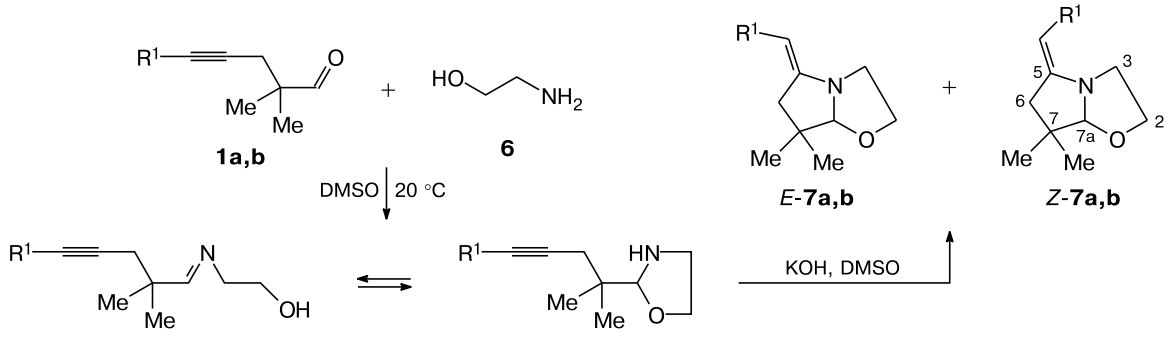
4, **5:** R^1 = Ph,
$R^2 = R^3 = R^4 = R^5$ = H (**f**)
R^1 = Ph, $R^2 = R^3$ = H,
$R^4 + R^5 = (CH_2)_2$ (**g**)

hols **4f**,**g**, which proceed significantly faster than the intramolecular hydroamination of the triple bond. However, the reaction of aldehyde **1d** bearing a 4-trifluoromethylphenyl substituent at the triple bond with 3-aminopropanol **2a** led to the product **3e** in 42% yield. In this case, it was shown that compound **3e** was formed only when an equimolar ratio of the starting reactants was used, whereas an excess of 3-aminopropanol led to the complete resinification of the reaction mixture. Apparently, this is explained by the strong polarization of the triple bond due to the –I-effect of the trifluoromethyl group, that facilitates its hydroamination and promotes the side processes of the addition of 3-aminopropoxide anion formed from the excess of 3-aminopropanol by the action of KOH in DMSO.

The structure of the amino alcohol used considerably influences the rate of this process. Thus, in the case of 3-aminopropanol **2a** and (1-aminomethylcyclopropyl)-methanol **2c**, the reaction with all the aldehydes **1** reached completion within 2 h, whereas a similar process with 3-amino-2,2-dimethylpropan-1-ol (**2b**) proceeds considerably slower and requires stirring for 24 h at room temperature to be complete. Most likely, this is due to the stronger steric influence of the dimethylmethylene fragment as compared to the methylene or cyclopropane-1,1-diyl one. Note that this reaction, like the reaction of alk-4-ynals with 1,3-diaminopropane and its derivatives studied earlier,[4] is highly stereoselective and leads to the corresponding 6-methylidenehexahydro-2*H*-pyrrolo[2,1-*b*]-[1,3]oxazines **3a—e** as the individual *E*-isomers.

Like the reaction of alk-4-ynals with 1,2-diaminoethane catalyzed by the system KOH—DMSO and described by us earlier,[4] similar reactions of aldehydes **1a**,**b** with 2-aminoethanol (**6**) proceed less stereoselectively and lead to the corresponding products **7a**,**b** as mixtures of *E*- and *Z*-isomers in the ratios 3.5 : 1 and 7.5 : 1, respectively (Scheme 2). The isomers were identified using the

Scheme 2



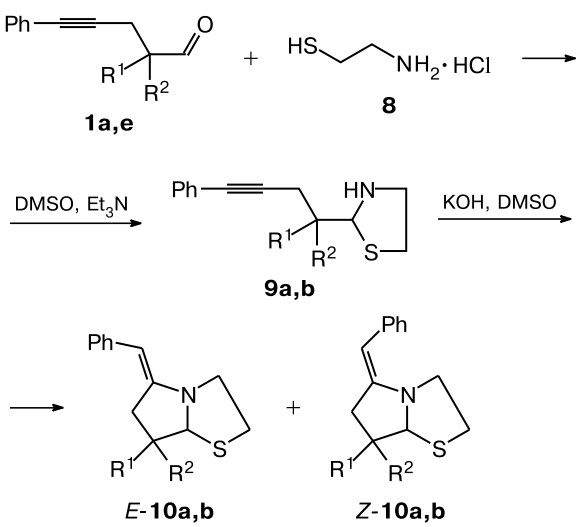
Yield of compound **7**: 75 (**a**), 64% (**b**).
1, 7: R^1 = Ph (**a**), 2-thienyl (**b**)

2D NOESY NMR spectra based on the analysis of the interactions of the protons at the double bond and the protons of the methylidene fragment at position 6. Apparently, a decrease in the stereoselectivity in the reactions of alk-4-ynals with 2-aminoethanol **6** as compared to the similar transformations involving 3-aminopropanols (**2**) results from the considerably lower steric effect of the five-membered ring formed as compared to the six-membered one.

In order to involve *N*,*S*-binucleophiles in such cyclizations, we carried out the reaction of aldehydes **1a**,**e** with 2-aminoethanethiol in DMSO with subsequent treatment of the reaction mixture with KOH. For this, we added 1 equiv. of triethylamine to the solution of the equimolar amounts of commercially available 2-aminoethanethiol hydrochloride **8** and the corresponding aldehyde **1a**,**e** in DMSO, that led to the rapid quantitative formation of the corresponding thiazolidines **9** (Scheme 3). Thus, the reaction of aldehyde **1a** with compound **8** reached completion within 30 min and after aqueous treatment of the reaction mixture, extraction with dichloromethane, washing the organic phases with water, and evaporation of the solvent, thiazolidine **9a** was isolated in 90% yield and more than 95% purity.

A subsequent addition of the excess of powdered KOH to the reaction mixtures obtained by the reaction of aldehydes **1a,e** with 2-aminoethanethiol hydrochloride **8** in the presence of triethylamine led to the previously unknown 5-benzylidenehexahydropyrrolo[2,1-*b*]thiazoles **10a**,**b** in 30—32% yields (see Scheme 3). These products, like structurally similar hexahydropyrrolo[2,1-*b*]oxazoles **7a**,**b**, were formed as mixtures of *E*- and *Z*-isomers,

Scheme 3



Yield of compound **10**: 32 (**a**), 30% (**b**).

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

however, in this case the content of *Z*-isomer was significantly lower (see Table 1), that, most likely, is explained by the larger steric effect of the thiazolidine ring as compared to the oxazolidine one.

To obtain the data on the intermediate products emerging in the course of the reactions of alk-4-ynals **1** with amino alcohols, we carried out more detailed studies of their progress in DMSO-d_6 with the monitoring the composition of the reaction mixture by ^{1}H NMR spectroscopy. The spectra recorded 10 min after mixing the solutions of the equimolar amounts of aldehyde **1a** and amino alcohols **2a** or **2b** showed the complete absence of the signals for the starting aldehyde, whereas the linear imines **4a** or **4b**, respectively, were the major products with content exceeding 90%. When these reaction mixtures were allowed to stand at room temperature, a slow formation of cyclic aminals **5a** and **5b** was observed, the content of which after 1 h was 33 and 45%, respectively, whereas after 18 h it was 54% (**4a** : **5a** = 1 : 1.2) and 86% (**4b** : **5b** = = 1 : 6) and did not change during further standing.

Similarly to the processes involving aliphatic diamines studied by us earlier,[4] the products **4** and **5** were obtained as the equilibrium mixtures, that was shown by ^{1}H NMR spectroscopy at different temperatures. Thus, heating the mixture obtained by the reaction of aldehyde **1a** with 3-aminopropanol **2a** to 50 °C led to the change of the ratio of components **4a** and **5a** from 1 : 1.2 to 1 : 0.45, which

Table 1. Reaction of alk-4-ynals **1a**—**e** with amino alcohols **2** and **6** and 2-aminoethanethiol hydrochloride **8** in DMSO in the presence of KOH[a]

Aldehyde	Amino alcohol (thiol)	*t*/h*	Product	Yield (%)
1a	**2a**	2	**3a**	82[b]
1a	**2b**	24	**3b**	72[c]
1a	**2c**	2	**3c**	78[b]
1b	**2a**	2	**3d**	68[b]
1c	**2a**	2	—[d]	—
1c	**2c**	2	—[d]	—
1d	**2a**	2	**3e**	42[b]
1a	**6**	2	**7a** (3.5 : 1)[e]	75[b]
1e	**6**	2	**7b** (7.5 : 1)[e]	64[b]
1a	**8**[f]	6	**10a** (14 : 1)[e]	32[g]
1e	**8**[f]	6	**10b** (16 : 1)[e]	30[b]

Note: *t* is the reaction time.
[a] The molar ratio alkynal : amino alcohol : KOH = 1 : 1 : 5.
[b] The yield of the product isolated by column chromatography.
[c] The yield of the product isolated by recrystallization from hexane.
[d] A complete resinification of the reaction mixture was observed.
[e] The ratio of isomers was determined using ^{1}H NMR spectra of the isolated products.
[f] An equimolar amount of triethylamine was added to the reaction mixture.
[g] The yield of the product isolated by microdistillation *in vacuo*.

returned to the initial proportion within 10 h after cooling to 23 °C. A similar experiment with a mixture of compounds **4b** and **5b** led to a reversible increase in the content of the linear product **4b** from 14% (**4b** : **5b** = 1 : 6) to 45% (**4b** : **5b** = 1 : 1.2). A comparative analysis of the spectra obtained at different temperatures allowed us to unambiguously assign the signals observed to compounds **4a**,**b** and **5a**,**b** without separation of the mixtures.

When an excess of freshly powdered KOH was added to the solution of compound **4a** in DMSO-d_6, the ^{1}H NMR spectrum of the reaction mixture recorded after 5 min showed, besides the signals for the starting compound, the presence of the signals for the products **5a** and **3a** (the ratio **4a** : **5a** : **3a** = 1 : 0.22 : 0.20). Further stirring the reaction mixture at room temperature for 30 min led to the change in the ratio of components **4a** : **5a** : **3a** to 1 : 0.45 : 0.50, with the reaction reaching completion 2 h after the beginning. Taking into account that in the absence of KOH only ~33% of imino alcohol **4a** isomerizes to oxazinane **5a** within 1 h (see above), a conclusion can be drawn that the addition of KOH slightly accelerates this reaction, with its rate and the rate of subsequent transformation of oxazinane **5a** to bicyclic enaminal **3a** being comparable.

Slightly different behavior was observed in the case of the reaction of compound **4b** with KOH in DMSO-d_6. The spectrum of the reaction mixture obtained after 10 min, besides the signals for the starting compound, also contained the signals for the products **5b** (the ratio **4b** : **5b** = 1 : 0.4) and **3b** (trace amount). Further stirring the reaction mixture at room temperature for 3 h led to the change in the ratio of components **4b** : **5b** : **3b** to 1 : 3 : 0.8, indicating significantly more rapid formation of oxazinane **5b** than its transformation to the final enaminal **3b**.

In conclusion, we accomplished a one-pot synthesis of 6-methylidenehexahydro-2*H*-pyrrolo[2,1-*b*][1,3]oxazines, 5-methylidenehexahydropyrrolo[2,1-*b*]oxazoles, and 5-methylidenehexahydropyrrolo[2,1-*b*]thiazoles by the reaction of available alk-4-ynals with amino alcohols and 2-aminoethanethiol in the presence of KOH. The reaction proceeds with the formation of three new C—heteroatom bonds. The compounds obtained seem promising for the medicinal chemistry.

Experimental

The starting compounds and the products obtained were analyzed by GC on 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. Mass spectra were obtained on a Finnigan DSQ II GLC-MS spectrometer. High resolution mass spectra were recorded on a Bruker micrOTOF II instrument with electrospray ionization (ESI). The measurements were performed on the positive ions (capillary voltage 4500 V). Masses were scanned in the range of m/z from 50 to 3000 Da, using an external or an internal calibration (Electrospray Calibrant Solution, Fluka). Solutions of compounds in acetonitrile were injected using a syringe, the flow rate 3 μL min^{-1}. Nebulizer gas was nitrogen (4 L min^{-1}), the interface temperature was 180 °C.

The starting alkynals **1a**,**b**,**e** were synthesized from the corresponding propargylic chlorides (1-chloro-3-phenylprop-2-yne, 1-chloro-3-(2-thienyl)prop-2-yne) and aldehydes (isobutyric aldehyde and cyclohexanecarbaldehyde) according to the procedures described in the work.[4] Alkynals **1c**,**d** were obtained by the cross-coupling of the corresponding iodoarenes (iodobenzene, 4-iodobenzotrifluoride) with pent-4-yne-1-ol upon treatment with a mixture of $Pd(PPh_3)_2Cl_2$—CuI in anhydrous triethylamine[18] with subsequent oxidation of forming acetylenic alcohols with pyridinium chlorochromate in dichloromethane (the overall yield on the two steps was 68% for **1c**, 75% for **1d**). The spectral data of the compounds obtained agree with those published earlier (see Ref. 19 for **1c**, Ref. 20 for **1d**).

3-Amino-2,2-dimethylpropan-1-ol (2b). Anhydrous K_2CO_3 (138 g, 1 mol) was added to a solution of ethyl cyanoacetate (28.2 g, 0.25 mol) and iodomethane (60.2 g, 0.6 mol) in anhydrous acetone (300 mL) and the mixture obtained was refluxed with stirring, monitoring the reaction progress by ^{1}H NMR spectra. After the reaction reached completion (~15—30 h), the reaction mixture was filtered, a precipitate was washed with acetone (400 mL) on the filter, the solvent was evaporated. The residue was distilled *in vacuo* to isolate a colorless liquid (23.5 g, 75%) with b.p. 80—82 °C (15 Torr), which according to the ^{1}H NMR spectra was a pure ethyl 2-cyano-2-methylpropanoate.

The product obtained was slowly added to a suspension of $LiAlH_4$ (15.2 g, 0.4 mol) in anhydrous THF (200 mL), the mixture formed was refluxed for 1 h, followed by a careful dropwise addition of water until hydrogen evolution ceased and an even white color persisted. A precipitate formed was filtered off, washed with THF (500 mL), the solvent from the organic phases was evaporated. The precipitate was additionally washed with a mixture of THF—dichloromethane (10 times), evaporating the solvent after each washing and reusing it. The residue obtained was distilled *in vacuo* to isolate a colorless compound (12.7 g, 56% calculated on the starting ethyl cyanoacetate) solidifying in the condenser (b.p. 93—95 °C (12 Torr)), which according to the NMR spectra was a pure amino alcohol **2b**. ^{1}H NMR, δ: 0.82 (s, 6 H, 2 Me); 2.63 (s, 2 H, C$\underline{H}_2$NH$_2$); 2.69 (br.s, 3 H, OH, NH$_2$); 3.41 (s, 2 H, C$\underline{H}_2$OH). ^{13}C NMR, δ: 22.2 (2 Me); 35.3 ($\underline{C}$(CH$_3$)$_2$); 51.7 (CH$_2$NH$_2$); 71.8 (CH$_2$OH).

(1-Aminomethylcyclopropyl)methanol (2c) was obtained similarly using 1,2-dibromoethane (1 equiv. with respect to ethyl cyanoacetate) instead of iodomethane. Compound **2c** was isolated by distillation *in vacuo* (b.p. 68—70 °C (1 Torr)). The yield calculated on the starting ethyl cyanoacetate was 62%. ^{1}H NMR, δ: 0.21—0.39 (m, 4 H, 2 CH$_2$, *cyclo*-C$_3$); 2.64 (s, 2 H, C$\underline{H}_2$NH$_2$); 2.71 (br.s, 3 H, OH, NH$_2$); 3.42 (s, 2 H, C$\underline{H}_2$OH). ^{13}C NMR, δ: 8.8 (2 CH$_2$, *cyclo*-C$_3$); 23.7 (C(1), *cyclo*-C$_3$); 48.5 (CH$_2$NH$_2$); 68.8 (CH$_2$OH).

Bicyclic *N*,*O*-aminals 3a—e and 9a,b (general procedure). A solution of aldehyde **1** (1 mmol) in DMSO (3 mL) was added to a solution of the corresponding amino alcohol **2** or **6** (1 mmol) in anhydrous DMSO (3 mL) with stirring. The mixture was stirred for 30 min at room temperature, followed by addition of freshly powdered KOH (280 mg, 5 mmol), the suspension obtained was stirred until the reaction reached completion (monitoring by

GLC or ^{1}H NMR spectroscopy, the reaction time is given in Table 1). Then, the reaction mixture was quenched with water (30 mL) and CH_2Cl_2 (30 mL), the organic layer was separated, the aqueous phase was extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were washed with water (4 times), dried with anhydrous K_2CO_3, the solvent was evaporated. The product was isolated from the residue by recrystallization or column chromatography (see Table 1).

(*E*)-6-Benzylidene-8,8-dimethylhexahydro-2*H*-pyrrolo[2,1-*b*][1,3]oxazine (3a) was obtained from aldehyde **1a** and 3-aminopropanol **2a** and isolated in 82% yield by chromatography on neutral Al_2O_3 (eluent hexane—diethyl ether, 10 : 1). Found (%): C, 78.72; H, 8.85; N, 5.63. $C_{16}H_{21}NO$. Calculated (%): C, 78.97; H, 8.70; N, 5.76. ^{1}H NMR, δ: 1.10 (s, 3 H, Me); 1.13 (s, 3 H, Me); 1.33 (m, 1 H, $NCH_2C\underline{H}HCH_2O$); 1.97 (m, 1 H, $NCH_2C\underline{H}HCH_2O$); 2.60 (dd, 1 H, =CC$\underline{H}$H, ^2J = 15.8 Hz, ^4J = = 1.7 Hz); 2.79 (dd, 1 H, =CC$\underline{H}$H, ^2J = 15.8 Hz, ^4J = 2.1 Hz); 3.13 (ddd, 1 H, $NC\underline{H}HCH_2CH_2O$, ^2J = 13.2 Hz, ^3J = 12.4 Hz, ^3J = 3.3 Hz); 3.68 (ddd, 1 H, $NCH_2CH_2CH\underline{H}O$, ^3J = 12.4 Hz, ^3J = 11.4 Hz, ^3J = 2.3 Hz); 3.77 (dddd, 1 H, $NC\underline{H}HCH_2CH_2O$, ^2J = 13.2 Hz, ^3J = 4.7 Hz, ^3J = 1.7 Hz, ^4J = 1.7 Hz); 4.14 (dddd, 1 H, $NCH_2CH_2CH\underline{H}O$, ^2J = 11.4 Hz, ^3J = 4.7 Hz, ^3J = 1.7 Hz, ^4J = 1.7 Hz); 4.18 (s, 1 H, NCHO); 5.81 (br.s, 1 H, PhC$\underline{H}$=); 7.01 (br.t, 1 H, Ph, J = 6.8 Hz); 7.15—7.32 (m, 4 H, Ph). ^{13}C NMR, δ: 22.0 (Me); 23.1 (C(3)); 26.7 (Me); 38.4 (C(8)); 42.9, 43.5 (C(4), C(7)); 67.3 (C(2)); 95.3, 97.5 (C(8a), Ph$\underline{C}$H=); 123.1, 126.3, 128.3 (Ph); 139.8 (C(1), Ph); 147.1 (PhCH=$\underline{C}$). MS, m/z (I_{rel} (%)): 243 $[M]^+$ (100), 242 $[M - H]^+$ (55).

(*E*)-6-Benzylidene-3,3,8,8-tetramethylhexahydro-2*H*-pyrrolo-[2,1-*b*][1,3]oxazine (3b) was obtained from aldehyde **1a** and 3-amino-2,2-dimethylpropanol **2b** and isolated in 72% yield by recrystallization from hexane. ^{1}H NMR, δ: 0.86 (s, 3 H, Me); 1.11 (s, 3 H, Me); 1.13 (s, 3 H, Me); 1.16 (s, 3 H, Me); 2.60 (dd, 1 H, =CC$\underline{H}$H, ^2J = 15.6 Hz, ^4J = 1.6 Hz); 2.81 (d, 1 H, $NC\underline{H}HCH_2CH_2O$, J = 13.0 Hz); 2.85 (dd, 1 H, =CC$\underline{H}$H, ^2J = 15.6 Hz, ^4J = 2.0 Hz); 3.39 (d, 1 H, $NCH_2CH_2CH\underline{H}O$, J = 11.1 Hz); 3.42 (dd, 1 H, $NC\underline{H}HCH_2CH_2O$, ^2J = 13.0 Hz, ^4J = 2.0 Hz); 3.66 (dd, 1 H, $NCH_2CH_2CH\underline{H}O$, ^2J = 11.1 Hz, ^4J = 2.0 Hz); 4.07 (s, 1 H, NCHO); 5.26 (br.s, 1 H, PhC$\underline{H}$=); 7.00 (br.t, 1 H, Ph, J = 6.8 Hz); 7.12—7.32 (m, 4 H, Ph). ^{13}C NMR, δ: 22.2 (Me); 23.8 (Me); 24.0 (Me); 26.4 (Me); 31.0 (C(3)); 38.5 (C(8)); 43.6 (C(7)); 54.3 (C(4)); 77.7 (C(2)); 94.4, 97.3 (C(8a), Ph$\underline{C}$H=); 122.9, 126.2, 128.3 (Ph); 140.0 (C(1), Ph); 147.4 (PhCH=$\underline{C}$). MS, m/z (I_{rel} (%)): 271 $[M^+]$ (100), 270 $[M^+ - H]$ (22). MS (ESI), found: m/z 272.2007; calculated for $C_{18}H_{25}NO$, $[M + H]^+$: m/z 272.2009.

(*E*)-6′-Benzylidene-8′,8′-dimethylhexahydrospiro[cyclopropane-1,3′-pyrrolo[2,1-*b*][1,3]oxazine] (3c) was obtained from aldehyde **1a** and [1-(aminomethyl)cyclopropyl]methanol **2c** and isolated in 72% yield by chromatography on neutral Al_2O_3 (eluent hexane—diethyl ether, 8 : 1). Found (%): C, 80.43; H, 8.49; N, 5.36. $C_{18}H_{23}NO$. Calculated (%): C, 80.26; H, 8.61; N, 5.20. ^{1}H NMR, δ: 0.25—0.50 (m, 2 H, *cyclo*-C_3); 0.60—0.89 (m, 2 H, *cyclo*-C_3); 1.83 (s, 3 H, Me); 1.25 (s, 3 H, Me); 2.68 (br.d, 1 H, =CC$\underline{H}$H, J = 15.7 Hz); 2.95 (dd, 1 H, =CC$\underline{H}$H, ^2J = 15.7 Hz, ^4J = 1.7 Hz); 3.11 (d, 1 H, $NC\underline{H}HCH_2CH_2O$, J = 13.3 Hz); 3.29 (dd, 1 H, $NCH_2CH_2CH\underline{H}O$, ^2J = 11.4 Hz, ^4J = 1.6 Hz); 3.55 (d, 1 H, $NC\underline{H}HCH_2CH_2O$, J = 13.3 Hz); 4.08 (dd, 1 H, $NCH_2CH_2CH\underline{H}O$, ^2J = 11.4 Hz, ^4J = 1.6 Hz); 4.29 (s, 1 H, NCHO); 5.33 (br.s, 1 H, PhC$\underline{H}$=); 7.07 (br.t, 1 H, Ph, J = 6.8 Hz); 7.20—7.40 (m, 4 H, Ph). ^{13}C NMR, δ: 5.1, 13.6 (C(2), C(3)); 16.7 (C(1,3′)); 22.0 (Me); 26.7 (Me); 38.3 (C(8′)); 43.5 (C(7′)); 50.5 (C(4′)); 74.4 (C(2′)); 95.3, 97.1 (C(8a′), PhC$\underline{H}$=); 122.9, 126.1, 128.1 (Ph); 139.7 (C(1), Ph); 147.5 (PhCH=$\underline{C}$). MS, m/z (I_{rel} (%)): 269 $[M]^+$ (100), 268 $[M - H]^+$ (19).

(*E*)-8,8-Dimethyl-6-(2-thienylmethylidene)hexahydro-2*H*-pyrrolo[2,1-*b*][1,3]oxazine (3d) was obtained from aldehyde **1b** and 3-aminopropanol **2a** and isolated in 68% yield by chromatography on neutral Al_2O_3 (eluent hexane—diethyl ether, 8 : 1). ^{1}H NMR, δ: 1.11 (s, 6 H, 2 Me); 1.32 (m, 1 H, $NCH_2C\underline{H}HCH_2O$); 1.97 (m, 1 H, $NCH_2C\underline{H}HCH_2O$); 2.56 (dd, 1 H, =CC$\underline{H}$H, ^2J = 16.2 Hz, ^4J = 1.7 Hz); 2.67 (dd, 1 H, =CC$\underline{H}$H, ^2J = 16.2 Hz, ^4J = 2.1 Hz); 3.11 (ddd, 1 H, $NC\underline{H}HCH_2CH_2O$, ^2J = 13.2 Hz, ^3J = 12.4 Hz, ^3J = 3.3 Hz); 3.67 (ddd, 1 H, $NCH_2CH_2CH\underline{H}O$, ^3J = 12.4 Hz, ^3J = 11.4 Hz, ^3J = 2.3 Hz); 3.69 (dddd, 1 H, $NC\underline{H}HCH_2CH_2O$, ^2J = 13.2 Hz, ^3J = 4.7 Hz, ^3J = 1.7 Hz, ^4J = 1.7 Hz); 4.11 (dddd, 1 H, $NCH_2CH_2CH\underline{H}O$, ^2J = 11.4 Hz, ^3J = 4.7 Hz, ^3J = 1.7 Hz, ^4J = 1.7 Hz); 4.18 (s, 1 H, NCHO); 5.56 (br.s, 1 H, CH=CN); 6.67 (dd, 1 H, thienyl, ^3J = 3.4 Hz, ^4J = 1.2 Hz); 6.93 (dd, 1 H, thienyl, ^3J = 5.2 Hz, ^3J = 3.4 Hz); 6.97 (dd, 1 H, thienyl, ^3J = 5.2 Hz, ^4J = 1.2 Hz). ^{13}C NMR, δ: 22.0 (Me); 23.0 (C(3)); 26.9 (Me); 38.5 (C(8)); 42.8, 43.6 (C(4), C(7)); 67.2 (C(2)); 89.6, 97.9 (C(8a), $\underline{C}$H=CN); 119.7, 120.4, 126.9 (C(1), C(4), C(5), thienyl); 143.9, 146.6 (C(2), thienyl; CH=$\underline{C}$N). MS, m/z (I_{rel} (%)): 249 $[M]^+$ (100). MS (ESI), found: m/z 250.1257, calculated for $C_{14}H_{19}NOS$, $[M + H]^+$: m/z 250.1260.

(*E*)-6-(4-Trifluoromethylbenzylidene)hexahydro-2*H*-pyrrolo [2,1-*b*][1,3]oxazine (3e) was obtained from aldehyde **1d** and 3-aminopropanol **2a** and isolated in 42% yield by chromatography on neutral Al_2O_3 (eluent hexane—diethyl ether, 10 : 1). Found (%): C, 63.85; H, 5.45; N, 5.03. $C_{15}H_{16}F_3NO$. Calculated (%): C, 63.60; H, 5.69; N, 4.94. ^{1}H NMR, δ: 1.28—1.41 (m, 1 H, $NCH_2C\underline{H}HCH_2O$); 1.81—2.24 (m, 3 H, $NCH_2C\underline{H}HCH_2O$, $=CCH_2C\underline{H}\underline{H}$); 2.68—3.10 (m, 2 H, $=CCH_2$); 3.45 (ddd, 1 H, $NC\underline{H}HCH_2CH_2O$, ^2J = 13.2 Hz, ^3J = 13.2 Hz, ^3J = 3.4 Hz); 3.75 (ddd, 1 H, $NCH_2CH_2CH\underline{H}O$, ^3J = 12.4 Hz, ^3J = 12.4 Hz, ^3J = 2.2 Hz); 3.78 (m, 1 H, $NC\underline{H}HCH_2CH_2O$); 4.07 (m, 1 H, $NCH_2CH_2CH\underline{H}O$); 4.79 (dd, 1 H, NCHO, J = 5.6 Hz, J = 2.2 Hz); 5.30 (br.s, 1 H, 4-$F_3CC_6H_4C\underline{H}$=); 7.24 (br.d, 2 H, Ph, J = 8.2 Hz); 7.46 (br.d, 2 H, Ph, J = 8.2 Hz). ^{13}C NMR, δ: 22.9 (C(3)); 28.4, 28.4 (C(7), C(8)); 42.4 (C(4)); 67.3 (C(2)); 91.3, 93.8 (C(8a), 4-$F_3CC_6H_4\underline{C}$H=); 124.0 (q, C(4), Ph, J_{CF} = 32 Hz); 125.0 (q, CF_3, J_{CF} = 270 Hz); 125.2 (q, C(3), C(5), Ph, J_{CF} = 3.7 Hz); 125.8 (C(2), C(6), Ph); 143.6 (C(1), Ph); 149.7 (4-$F_3CC_6H_4CH$=$\underline{C}$). MS, m/z (I_{rel} (%)): 283 $[M]^+$ (100), 282 $[M - H]^+$ (45).

5-Benzylidene-7,7-dimethylhexahydropyrrolo[2,1-*b*]oxazole (7a) was obtained from aldehyde **1a** and 2-aminoethanol **6** as a mixture of *E*- and *Z*-isomers (the ratio 3.5 : 1) and isolated in 75% yield by chromatography on neutral Al_2O_3 (eluent hexane—diethyl ether, 10 : 1). MS, m/z (I_{rel} (%)): 229 $[M]^+$ (100), 228 $[M - H]^+$ (18). MS (ESI), found: m/z 230.1534, calculated for $C_{15}H_{19}NO$, $[M + H]^+$: m/z 230.1539.

Isomer *E*-**7a**. ^{1}H NMR, δ: 1.18 (s, 3 H, Me); 1.19 (s, 3 H, Me); 2.70 (dd, 1 H, =CC$\underline{H}$H, ^2J = 15.6 Hz, ^4J = 2.0 Hz); 2.79 (dd, 1 H, =CC$\underline{H}$H, ^2J = 15.6 Hz, ^4J = 2.2 Hz); 3.40 (ddd, 1 H, NC$\underline{H}$H, ^2J = 10.6 Hz, ^3J = 7.7 Hz, ^3J = 6.2 Hz); 3.49 (ddd, 1 H, NC$\underline{H}$H, ^2J = 10.6 Hz, ^3J = 7.7 Hz, ^3J = 5.7 Hz); 3.82 (ddd, 1 H, OC$\underline{H}$H, ^2J = 7.7 Hz, ^3J = 7.7 Hz, ^3J = 5.7 Hz); 3.96 (ddd, 1 H, OC$\underline{H}$H, ^2J = 7.7 Hz, ^3J = 7.7 Hz, ^3J = 6.2 Hz); 4.48 (s, 1 H, NCHO); 5.68 (br.s, 1 H, PhC$\underline{H}$=); 7.10 (br.t, 1 H, Ph, J = 6.8 Hz); 7.19—7.37 (m, 4 H, Ph). ^{13}C NMR, δ: 22.1 (Me); 26.6 (Me);

39.1 (C(7)); 43.8 (C(6)); 51.3 (C(3)); 65.5 (C(2)); 102.2, 102.4 (C(7a), PhCH=); 123.9, 126.7, 128.1 (Ph); 138.6 (C(1), Ph); 152.1 (PhCH=C).

Isomer *Z*-**7a**. ^{1}H NMR, δ: 1.20 (s, 3 H, Me); 1.22 (s, 3 H, Me); 2.30 (d, 1 H, =CCHH, ^2J = 15.0 Hz); 2.70 (dd, 1 H, =CCHH, ^2J = 15.0 Hz, ^4J = 2.2 Hz); 3.11 (ddd, 1 H, NCHH, ^2J = 10.9 Hz, ^3J = 7.5 Hz, ^3J = 5.8 Hz); 3.31—3.45 (m, 1 H, NCHH); 3.73 (ddd, 1 H, OCHH, ^2J = 7.8 Hz, ^3J = 7.8 Hz, ^3J = = 5.7 Hz); 3.75—3.85 (m, 1 H, OCHH); 4.50 (s, 1 H, NCHO); 5.68 (d, 1 H, PhCH=, ^4J = 2.2 Hz); 7.20—7.55 (m, 5 H, Ph). ^{13}C NMR, δ: 22.0 (Me); 26.1 (Me); 37.9 (C(7)); 45.1 (C(6)); 52.4 (C(3)); 65.5 (C(2)); 101.8, 104.3 (C(7a), PhCH=); 124.2, 127.3, 127.8 (Ph); 137.5 (C(1), Ph); 151.2 (PhCH=C).

7,7-Dimethyl-5-(2-thienylmethylidene)hexahydropyrrolo[2,1-*b*]oxazole (7b) was obtained from aldehyde **1b** and 2-aminoethanol **6** as a mixture of *E*- and *Z*-isomers (the ratio 7.5 : 1) and isolated in 64% yield by chromatography on neutral Al_2O_3 (eluent hexane—diethyl ether, 8 : 1). Found (%): C, 66.56; H, 7.05; N, 5.84. $C_{17}H_{13}NOS$. Calculated (%): C, 66.34; H, 7.28; N, 5.95. MS, *m/z* (I_{rel} (%)): 235 $[M]^+$ (100), 234 $[M - H]^+$ (17).

Isomer *E*-**7b**. ^{1}H NMR, δ: 1.18 (s, 3 H, Me); 1.19 (s, 3 H, Me); 2.64 (br.s, 2 H, =CCH_2); 3.37—3.54 (m, 2 H, NCH_2); 3.78 (ddd, 1 H, OCHH, ^2J = 7.7 Hz, ^3J = 7.7 Hz, ^3J = 5.6 Hz); 3.92 (ddd, 1 H, OCHH, ^2J = 7.7 Hz, ^3J = 7.7 Hz, ^3J = 6.5 Hz); 4.43 (s, 1 H, NCHO); 5.88 (br.s, 1 H, CH=CN); 6.74 (dd, 1 H, thienyl, ^3J = 3.5 Hz, ^4J = 1.2 Hz); 6.96 (dd, 1 H, thienyl, ^3J = 5.1 Hz, ^3J = 3.5 Hz); 7.06 (dd, 1 H, thienyl, ^3J = 5.1 Hz, ^4J = 1.2 Hz). ^{13}C NMR, δ: 22.5 (Me); 27.4 (Me); 39.2 (C(7)); 44.0 (C(6)); 51.7 (C(3)); 65.4 (C(2)); 96.6, 103.4 (C(7a), CH=CN); 121.3, 122.2, 127.0 (C(1), C(4), C(5), thienyl); 142.7, 152.1 (C(2), thienyl and CH=CN).

Isomer *Z*-**7b**. ^{1}H NMR, δ: 1.11 (s, 3 H, Me); 1.31 (s, 3 H, Me); 2.59 (br.s, 2 H, =CCH_2); 3.23 (ddd, 1 H, NCHH, ^2J = = 10.8 Hz, ^3J = 7.0 Hz, ^3J = 5.8 Hz); 3.45—3.60 (m, 1 H, NCHH); 3.80—4.08 (m, 2 H, OCH_2); 4.47 (s, 1 H, NCHO); 5.69 (br.s, 1 H, CH=CN); 6.74 (dd, 1 H, thienyl, ^3J = 3.5 Hz, ^4J = 1.2 Hz); 6.92 (dd, 1 H, thienyl, ^3J = 5.1 Hz, ^3J = 3.5 Hz); 7.11 (dd, 1 H, thienyl, ^3J = 5.1 Hz, ^4J = 1.2 Hz). ^{13}C NMR, δ: 22.3 (Me); 28.4 (Me); 38.9 (C(7)); 45.0 (C(6)); 53.0 (C(3)); 65.4 (C(2)); 97.9, 104.6 (C(7a), CH=CN); 121.3, 122.1, 126.7 (C(1), C(4), C(5), thienyl); 140.9, 150.7 (C(2), thienyl and CH=CN).

5-Benzylidenehexahydropyrrolo[2,1-*b*]thiazoles 10a,b (general procedure). Triethylamine (100 mg, 1 mmol) was added to a solution of 2-aminoethanethiol hydrochloride **8** (115 mg, 1 mmol) and the starting aldehyde **1** (1 mmol) in anhydrous DMSO (3 mL) with stirring. The mixture was stirred for 30 min at room temperature, followed by addition of freshly powdered KOH (280 mg, 5 mmol) and the stirring was continued for 6 h until the reaction was complete (monitoring by GLC or ^{1}H NMR spectroscopy). Then, the mixture was treated with water (30 mL) and CH_2Cl_2 (30 mL), the organic layer was separated, the aqueous layer was additionally extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were washed with water (4 times), dried with anhydrous K_2CO_3, the solvent was evaporated. The target products **10a**,**b** were isolated from the residue by microdistillation *in vacuo* or column chromatography (see Table 1).

5-Benzylidene-7,7-dimethylhexahydropyrrolo[2,1-*b*]thiazole (10a) was obtained from aldehyde **1a** as a mixture of *E*- and *Z*-isomers (the ratio 14 : 1) and isolated in 32% yield by microdistillation *in vacuo* (t_{bath} = 150—160 °C (1 Torr)). Found (%): C, 73.52; H, 7.62; N, 5.87. $C_{15}H_{19}NS$. Calculated (%): C, 73.42; H, 7.80; N, 5.71. MS, *m/z* (I_{rel} (%)): 245 $[M]^+$ (100), 244 $[M - H]^+$ (25).

Isomer *E*-**10a**. ^{1}H NMR, δ: 1.25 (s, 3 H, Me); 1.32 (s, 3 H, Me); 2.62 (d, 1 H, C=CCHH, *J* = 15.7 Hz); 2.85—3.27 (m, 3 H, NHCHHCH_2S); 2.93 (dd, 1 H, C=CCHH, ^2J = 15.7 Hz, ^4J = 1.8 Hz); 4.04—4.17 (m, 1 H, $NHCH_2$CHHS); 4.68 (s, 1 H, SCHNH); 5.70 (br.s, 1 H, PhCH=); 7.03—7.35 (m, 5 H, Ph). ^{13}C NMR, δ: 25.6 (Me); 28.8 (Me); 31.7 (C(2)); 39.3 (C(7)); 43.0 (C(6)); 53.5 (C(3)); 84.4 (C(7a)); 101.3 (PhCH=); 124.2, 126.9, 128.3 (Ph); 138.7 (C(1), Ph); 149.9 (PhCH=C).

Isomer *Z*-**10a**. ^{1}H NMR, δ: 1.30 (s, 3 H, Me); 1.32 (s, 3 H, Me); 2.17 (d, 1 H, C=CCHH, *J* = 14.3 Hz); 2.73—2.84 (m, 3 H, NHCHHCH_2S); 3.12 (d, 1 H, C=CCHH, *J* = 14.3 Hz); 3.72—3.87 (m, 1 H, $NHCH_2$CHHS); 4.75 (s, 1 H, SCHNH); 5.38 (br.s, 1 H, PhCH=); 7.03—7.73 (m, 5 H, Ph).

5´-Benzylidenetetrahydro-2´*H*-spiro(cyclohexane-1,7´-pyrrolo[2,1-*b*]thiazole) (10b) was obtained from aldehyde **1e** as a mixture of *E*- and *Z*-isomers (the ratio 16 : 1) and isolated in 30% yield by chromatography on neutral Al_2O_3 (eluent hexane—dichloromethane, 5 : 1). MS, *m/z* (I_{rel} (%)): 285 $[M]^+$ (100). MS (ESI), found: *m/z* 285.1540, 286.1612, calculated for $C_{18}H_{23}NS$, $[M]^+$: *m/z* 285.1546, $[M + H]^+$: *m/z* 286.1624.

Isomer *E*-**10b**. ^{1}H NMR, δ: 1.20—1.80 (m, 10 H, 5 CH_2, *cyclo*-C_6); 2.68 (d, 1 H, C=CCHH, *J* = 16.0 Hz); 2.81 (dd, 1 H, C=CCHH, ^2J = 16.0 Hz, ^4J = 2.5 Hz); 2.80—3.23 (m, 3 H, NHCHHCH_2S); 4.02—4.14 (m, 1 H, $NHCH_2$CHHS); 4.81 (s, 1 H, SCHNH); 5.67 (br.s, 1 H, PhCH=); 7.00—7.30 (m, 5 H, Ph). ^{13}C NMR, δ: 23.0, 24.2, 26.0, 30.9, 35.8, 36.9 (C(2), C(3), C(4), C(5), C(6), C(2´)); 40.6 (C(1,7´)); 42.9 (C(6´)); 53.1 (C(3´)); 82.8 (C(7a´)); 101.1 (PhCH=); 124.0, 126.8, 128.3 (Ph); 138.7 (C(1), Ph); 149.4 (PhCH=C).

Isomer *Z*-**10b**. ^{1}H NMR, δ: 1.20—1.80 (m, 10 H, 5 CH_2, *cyclo*-C_6); 2.31 (d, 1 H, C=CCHH, *J* = 14.7 Hz); 2.74 (d, 1 H, C=CCHH, *J* = 14.7 Hz); 2.80—3.23 (m, 3 H, NHCHHCHHS); 3.69—3.80 (m, 1 H, $NHCH_2$CHHS); 4.87 (s, 1 H, SCHNH); 5.34 (br.s, 1 H, PhCH=); 7.00—7.30 (m, 5 H, Ph).

2-(2-Methyl-5-phenylpent-4-yn-2-yl)thiazolidine (9a). Triethylamine (100 mg, 1 mmol) was added to a solution of 2-aminoethanethiol hydrochloride **8** (115 mg, 1 mmol) and aldehyde **1a** (185 mg, 1 mmol) in anhydrous DMSO (3 mL) with stirring. The mixture was stirred for 30 min at room temperature and treated with water (30 mL) and CH_2Cl_2 (30 mL), the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were washed with water (4 times), dried with anhydrous K_2CO_3, the solvent was evaporated to obtain compound **9a** (220 mg, 90%) as a dense light yellow liquid. Found (%): C, 73.11; H, 7.95; N, 5.96. $C_{15}H_{19}NS$. Calculated (%): C, 73.42; H, 7.80; N, 5.71. ^{1}H NMR, δ: 1.18 (s, 3 H, Me); 1.21 (s, 3 H, Me); 1.78 (br.s, 1 H, NH); 2.50 (d, 1 H, C≡CCHH, *J* = 16.6 Hz); 2.61 (d, 1 H, C≡CCHH, *J* = 16.6 Hz); 2.67—2.82 (m, 1 H, NHCHH); 2.85—3.05 (m, 2 H, NHCHHCHHS); 3.50—3.64 (m, 1 H, SCHH); 4.63 (s, 1 H, SCHNH); 7.35—7.50 (m, 5 H, Ph). ^{13}C NMR, δ: 24.2 (Me); 24.7 (Me); 31.2 (C≡CCH_2); 35.0 (SCH_2); 37.7 (C$(CH_3)_2$); 53.0 (NCH_2); 81.2 (SCHN); 83.0, 87.5 (C≡C); 123.8 (C(1), Ph); 127.7, 128.4, 131.6 (Ph).

Reaction of aldehyde 1a with amino alcohols 2a,b in DMSO-d_6. A solution of aldehyde **1a** (47 mg, 0.25 mmol) in DMSO-d_6 (0.5 mL) was added to a solution of amino alcohol **2a** or **2b** (0.25 mmol) in anhydrous DMSO-d_6 (0.5 mL). Some (~0.4 mL) of the solution obtained was placed into an NMR tube to moni-

tor the reaction progress and the composition of the forming products by regular recording ^{1}H NMR spectra.

The solutions of compounds **4a** and **4b** in DMSO-d_6 obtained by the condensation of aldehyde **1a** with amino alcohols **2a** or **2b** for 5 min were stirred with freshly powdered KOH (70 mg, 1.25 mmol) at room temperature, monitoring the reaction progress by ^{1}H NMR spectroscopy. The ratio of the starting compounds, forming oxazinanes **5a,b** and aminals **3a,b** was determined based on the ratio of integral intensities of the imine and the aminal protons. Compounds **4a,b** and **5a,b** were characterized without isolation from the reaction mixtures.

3-(2,2-Dimethyl-5-phenylpent-4-ynylidenamino)propan-1-ol (4a). ^{1}H NMR, δ: 1.12 (s, 6 H, 2 Me); 1.64 (tt, 2 H, $NCH_2C\underline{H}_2CH_2OH$, ^3J = 6.6 Hz, ^3J = 6.6 Hz); 2.50 (s, 2 H, $C{\equiv}CCH_2$); 3.38 (td, 2 H, NCH_2, ^3J = 6.6 Hz, ^4J = 1.3 Hz); 3.41 (t, 2 H, $C\underline{H}_2OH$, J = 6.6 Hz); 3.52 (br.s, 1 H, OH); 7.29—7.40 (m, 5 H, Ph); 7.62 (t, 1 H, CH=N, J = 1.3 Hz). ^{13}C NMR, δ: 24.4 (2 Me); 29.7($C{\equiv}C\underline{C}H_2$); 33.7 ($NCH_2\underline{C}H_2CH_2O$); 39.0 ($\underline{C}(CH_3)_2$); 57.0, 58.5 ($N\underline{C}H_2C(CH_3)_2\underline{C}H_2O$); 82.2, 88.7 (C≡C); 123.2 (C(1), Ph); 128.0, 128.5, 131.2 (Ph).

2-(2-Methyl-5-phenylpent-4-yn-2-yl)-1,3-oxazinane (5a). ^{1}H NMR, δ: 0.98 (s, 6 H, 2 Me); 1.17—1.28 (m, 1 H, $NCH_2C\underline{H}HCH_2O$); 1.48—1.60 (m, 1 H, $NCH_2C\underline{H}HCH_2O$); 2.37 (s, 2 H, $C{\equiv}CCH_2$); 2.73 (ddd, 1 H, $NC\underline{H}H$, ^2J = 12.6 Hz, ^3J = 12.6 Hz, ^3J = 3.2 Hz); 2.98—3.11 (m, 1 H, $NC\underline{H}H$); 3.68 (ddd, 1 H, $OC\underline{H}H$, ^2J = 12.0 Hz, ^3J = 12.0 Hz, ^3J = 2.5 Hz); 3.84 (NCHO); 3.97—4.09 (m, 1 H, $OC\underline{H}H$); 7.30—7.42 (m, 5 H, Ph). ^{13}C NMR, δ: 22.1 (Me); 22.6 (Me); 27.0, 28.9 ($C{\equiv}C\underline{C}H_2$ and C(5), *cyclo*-C_4NO); 37.8 ($\underline{C}(CH_3)_2$); 44.2 (C(4), *cyclo*-C_4NO); 67.4 (C(6), *cyclo*-C_4NO); 82.0, 88.0 (C≡C); 93.0 (C(2), *cyclo*-C_4NO); 123.4 (C(1), Ph); 127.8, 128.5, 131.2 (Ph).

3-(2,2-Dimethyl-5-phenylpent-4-ynylidenamino)-2,2-dimethylpropan-1-ol (4b). ^{1}H NMR, δ: 0.78 (s, 6 H, 2 Me); 1.13 (s, 6 H, 2 Me); 2.53 (s, 2 H, $C{\equiv}CCH_2$); 3.16 (d, 2 H, NCH_2, J = 1.2 Hz); 3.18 (s, 2 H, $C\underline{H}_2OH$); 3.35 (br.s, 1 H, OH); 7.28—7.40 (m, 5 H, Ph); 7.56 (t, 1 H, CH=N, J = 1.2 Hz). ^{13}C NMR, δ: 22.7 (2 Me); 24.5 (2 Me); 29.8 ($C{\equiv}C\underline{C}H_2$); 36.5 ($NCH_2\underline{C}(CH_3)_2CH_2O$); 39.2 ($CH_2\underline{C}(CH_3)_2$); 68.0, 68.6 ($N\underline{C}H_2C(CH_3)_2\underline{C}H_2O$); 82.1, 88.1 (C≡C); 123.2 (C(1), Ph); 127.9, 128.5, 131.2 (Ph); 169.4 (CH=N).

5,5-Dimethyl-2-(2-methyl-5-phenylpent-4-yn-2-yl)-1,3-oxazinane (5b). ^{1}H NMR, δ: 0.65 (s, 3 H, Me); 0.99 (s, 3 H, Me); 1.02 (s, 3 H, Me); 1.03 (s, 3 H, Me); 2.41 (s, 2 H, $C{\equiv}CCH_2$); 2.52 (d, 1 H, $NC\underline{H}H$, J = 13.2 Hz); 2.62 (dd, 1 H, $NC\underline{H}H$, ^3J = 13.2 Hz, ^4J = 2.4 Hz); 3.23 (br.s, 1 H, NH); 3.27 (d, 1 H, $OC\underline{H}H$, J = 10.9 Hz); 3.52 (dd, 1 H, $OC\underline{H}H$, ^3J = 10.9 Hz, ^4J = 2.4 Hz); 3.75 (NCHO); 7.30—7.43 (m, 5 H, Ph). ^{13}C NMR, δ: 22.3 (Me); 22.5 (Me); 22.8 (Me); 23.7 (Me); 28.8 ($C{\equiv}C\underline{C}H_2$); 28.9 (C(5), *cyclo*-$C_4NO$); 37.5 ($\underline{C}(CH_3)_2$); 55.7 (C(4), *cyclo*-$C_4NO$); 77.2 (C(6), *cyclo*-$C_4NO$); 81.9, 88.6 (C≡C); 92.7 (C(2), *cyclo*-C_4NO); 123.4 (C(1), Ph); 127.8, 128.5, 131.2 (Ph).

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