Synthesis of *N*-propargylanabasine derivatives by the Mannich reaction*

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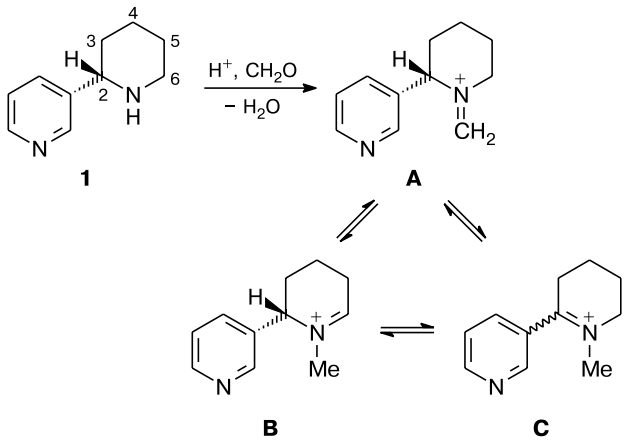
N-Propargylanabasine derivatives bearing various substituents at the carbon atom of the alkyne fragment were obtained by the reaction of anabasine hydrochloride with terminal alkynes and paraformaldehyde. The reaction proceeded with retention of the C(2) chiral center in anabasine fragment. The by-products of the reaction, including 1,3-diacetylene (the products of dimerization of alkynes) and conjugated vinylacetylenes (the rearrangement products of the Mannich adducts) were isolated and characterized.

Key words: the Mannich reaction, anabasine, alkaloids, alkynes, β-aminoalkynes.

Anabasine ((2*S*)-2-(3-pyridyl)piperidine (**1**)) is an alkaloid component of *Anabasis aphylla* L..[1] It serves as the blockator of *n*-acetylcholine receptors (*n*-AcChr) and shows neurotoxic properties toward animals and insects.[2] Anabasine salts are widely used as the insecticides,[1,3,4] as the medicines helping to give up smoking, and for the treatment of cutaneous diseases (eczema, psoriasis, *etc.*).[2,5] A quest of anabasine derivatives, combining both the useful biological activity of natural alkaloid and the minimum harmful side effects is a challenging task.[6]

To obtain the *N*-substituted anabasine derivatives, alkylation,[7—9] acylation,[9,10] and phosphorilation[4,11] reactions are used, as well as the conjugate Michael addition[12] and the Mannich reaction. The latter reaction is not well investigated. The unsuccessful attempts to involve barbituric acid derivatives[13] into it and a few examples of *N*-propargylanabasines synthesis with the use of terminal alkynes[14] have been reported. The reactions were carried out with the assistance of Ag^{I} (see Ref. 14a), Cu^{I} (see Ref. 14b,c), and Cu^{II} (see Ref. 14d) salts, the yields of the products did not exceed 32—46% (see Ref. 14c). The published data did not clarify the area of application of this reaction, particularly, the possibility to synthesize the functional derivatives of *N*-propargylanabasine. The latter can be of interest as the biologically active substances, since *N*-propargylamines are known to show the various forms of physiological activity.[15] There is no information on stereochemical structure of the products, too. The racemization of the chiral center in anabasine in the course of the reaction can not be excluded: this can result from the isomeric transformations of iminium cations **A** and **B**, the possible intermediates of the Mannich reaction,[16] through the formation of cation **C** with sp^2-hybridized C(2) atom (Scheme 1).

Scheme 1



In order to elaborate a general method for the synthesis of functional derivatives of anabasine, we for the first time undertook the systematic investigation of the synthetic and stereochemical features of condensation of anabasine (**1**) with paraformaldehyde and terminal alkynes. In contrast to the earlier published works,[14] alkaloid **1** was generated directly in the reaction media from available anabasine hydrochloride (**1**·HCl) by treatment with AcONa. Acetylene hydrocarbons **2a—d**, primary, secondary, and tertiary propargylic alcohols **3a—o** and **4a—k**, their acetates **5a—d**, containing aliphatic, alicyclic, and aromatic substituents (Scheme 2), as well as derivatives of homopropargylic alcohols **6a—c** and **7a—c** (Scheme 3) were taken as the alkyne components.

* Dedicated to Academician V. A. Tartakovsky in honor of his 75th anniversary.

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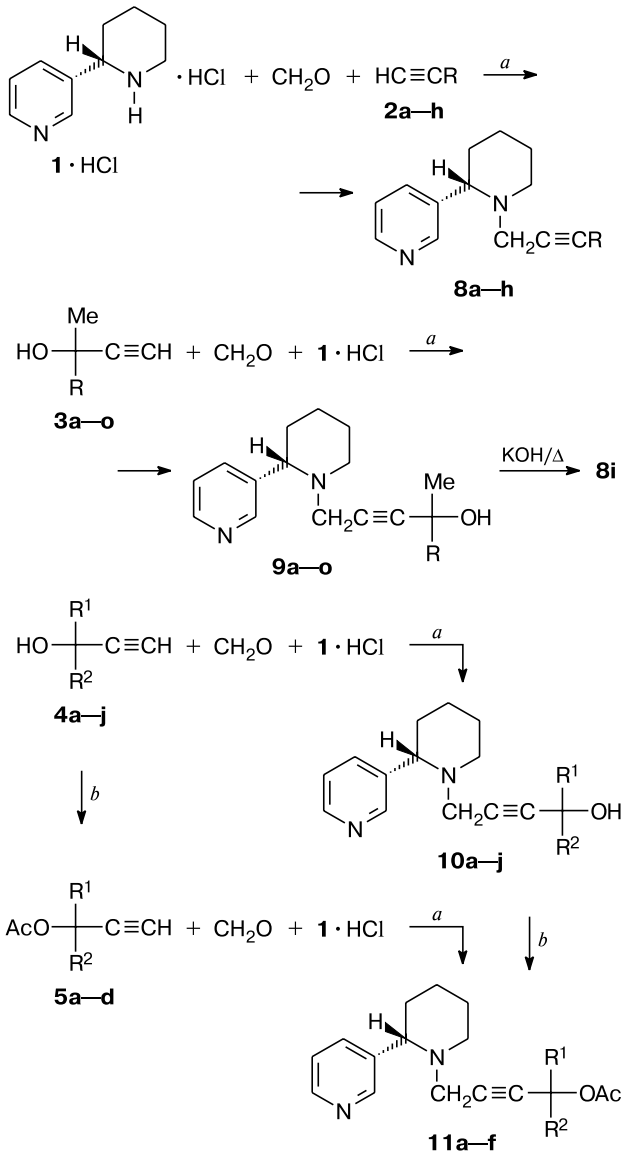
Scheme 2



a — Cu_2Cl_2—AcONa/dioxane; *b* — Ac_2O, NEt_3, DMAP/CH_2Cl_2.

2, **8**: R = Pr (**a**), Bu (**b**), $C_5H_{11}{}^n$ (**c**), $C_6H_{13}{}^n$ (**d**), $Me_2CH(CH_2)_3$— (**e**), CH_2=C(Me)— (**f**), cyclohex-1-enyl (**g**), Ph (**h**), H (**i**)

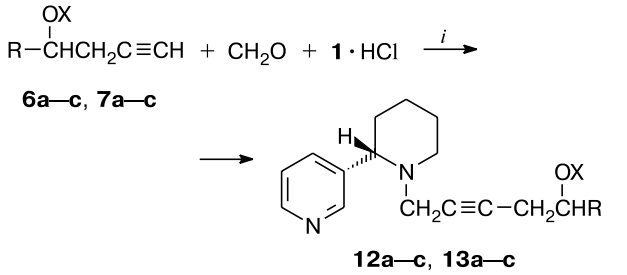
3, **9**:R = Pr (**a**), Bu (**b**), Bu^i (**c**), Bu^t (**d**), CH_2=C(Me)— (**e**), CH_2=CH$(CH_2)_2$— (**f**), Me_2C=CH$(CH_2)_2$— (**g**), $Me_2C(OMe)(CH_2)_3$— (**h**), $Me_2CH(CH_2)_3CH(Me)(CH_2)_3CH(Me)(CH_2)_3$— (**i**),

 (**j**), *cyclo*-C_3H_5 (**k**), Ph (**l**), $PhCH_2$ (**m**), $Ph(CH_2)_2$— (**n**), 4-$MeOC_6H_4(CH_2)_2$— (**o**)

4, **5**, **10**, **11**: R^1 = R^2 = H (**a**), Me (**b**), Et (**f**), Pr^i (**g**), Ph (**j**); R^1 = Me, R^2 = Et (**c**); (R^1 + R^2) = $(CH_2)_5$ (**d**), R^1 = H, R^2 = Ph (**e**); $(CH_2)_4$ (**h**), $(CH_2)_6$ (**i**)

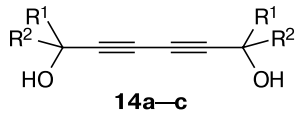
As a rule, the molar ratio anabasine : paraformaldehyde : alkyne in the reaction under study was 1 : 3 : 1.5. It was also found that an excess of alkynes **2**—**7**, which

Scheme 3

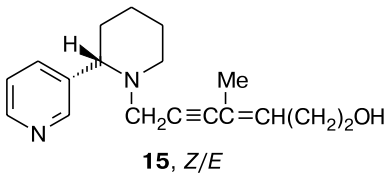


i. Cu_2Cl_2—AcONa/dioxane

6, **7**, **12**, **13**: R = H (**6**, **12**), Me (**7**, **13**); X = H (**a**), Ac (**b**), $SiMe_3$ (**c**)



R^1 = Me, R^2 = Bu^t (**a**); R^1 + R^2 = $(CH_2)_6$ (**b**); R^1 = R^2 = Ph (**c**)



under the reaction conditions undergo partial dimerization to diacetylenes **14**, promotes an increase in the yields of condensation products **8**—**13**, calculated from anabasine hydrochloride (**1** · HCl).

Copper(I) salts (Cu_2Cl_2, $Cu(OAc)_2$, and Cu_2Br_2) were used as catalysts. The type of the anion and amount of the catalyst used in the range of 0.2—1.5 equiv. turned out to have no much effect on the yields of the condensation products. However, greater excess of the catalyst increases the yield of the side products of dimerization of alkynes **14a**—**c** (Scheme 3), which makes the target compounds difficult to isolate. It is reasonable to carry out the reaction in dioxane at 60—70 °C. Addition of solvents of various polarity (benzene, DMF) does not cause an increase in the yields of condensation products. The elaborated procedure enabled us to synthesize *N*-propargylanabasine derivatives **8**—**11** of various structure in 62—85% yield. The earlier unknown compounds of terpene **9g**—**i** and norbornene **9j** series are among the synthesized products.

The selectivity of the reaction is defined by the alkyne structure. The reaction proceeds most smoothly for the derivatives of acetylene hydrocarbons **2a**—**d**. In case of propargylic alcohols **3** and **4**, the formation of hemi-acetals and aminals, the minor products of methylenation at their hydroxy group (signals in the region 4.0—4.6 ppm in the ^{1}H NMR spectra) is observed. These side processes are less pronounced in the reactions of tertiary alcohols

3e—d, **3l—o**, and **4c—l**, especially, if they contain bulky substituents R, R^1, and R^2.

The side processes also take place during the reaction of **1**·HCl with paraformaldehyde and homopropargylic alcohols **6a** and **7a** (see Scheme 3). According to the ^{1}H NMR data, the yields of condensation products **12a** and **13a** did no exceed 70% (40% isolated yield). We found that it was reasonable to use in the Mannich reaction acetylene alcohols **6a** and **7a** in form of their acetates **6b** and **7b** or trimethylsilyl ethers **6c** and **7c**. After removal of the protecting groups (trimethylsilyl group was eliminated from trimethylsilyl ethers **12c** and **13c** by treatment of the reaction mixture with aq. acid) and flash-chromatography, the corresponding condensation products **12b**,**c** and **13b**,**c** gave the individual alcohols **12a** and **13a** in 65—70% yield calculated from **1**·HCl.

The reaction of methylcyclopropylethynylcarbinol (**3k**) with anabasine is a complicated one. Along with the expected product **9k**, conjugated 1,3-enyne **15** (a mixture of *Z*,*E*-isomers, ~1 : 5) was unexpectedly obtained, formation of which results from the cyclopropylcarbinyl-homoallylic rearrangement,[17] occurring even under the mild conditions of the process.

Structures of the synthesized condensation products **8—13** and their salts were confirmed by elemental analysis data, IR, ^{1}H NMR, and mass spectra. The IR spectra of these compounds contain the absorption bands of stretching vibrations of the pyridine ring (1590, 1570 cm^{-1}) and OH group (3250—3410 cm^{-1}). The absorption bands of acetylene fragment in the region 2190—2250 cm^{-1} have low intensities.[18] The mass spectra are characterized by the presence of the molecular peak [M^+] and of the strong (40—100%) fragment ion, corresponding to the elimination of pyridine [$M^+ - C_5H_4N$]. In the ^{1}H NMR spectra of the compounds obtained, there are signals of N-CH_2 groups as AB-system in the region 2.80—3.20 ppm (J = 16.7—17.2 Hz) and of other hydrocarbon fragments of the molecules. Most of the synthesized products were converted to the corresponding hydrochlorides upon treatment with dry HCl in acetone.

The physical and chemical properties of compounds **10b—d**, obtained by us in state of noncrystallizing oils, differ from those described in the literature (in the work,[8] they are reported as crystalline substances). However, there are no NMR spectroscopy data for compounds **10b—d** in the paper,[8] whereas the synthesized by us substances are unambiguously characterized by spectroscopy methods and by chemical transformation to *N*-propargylanabasine **8i** (R = H) in the presence of a base (the retro Favorsky reaction).

The synthesized condensation products **8—13** are optically active compounds. The high negative angle of rotation values [α_D] are observed both for the free bases and for their hydrochlorides **8**·HCl—**13**·HCl and **8g**·2HCl. The samples of compound **8b**, taken from the reaction mixture in 4, 6, and 8 h after the reaction begins, have practically the same [α_D] values (230±8°), which indicates that no racemization at C(2) chiral center occurs under the reaction conditions (see Scheme 1).

Products **9a—o**, **10a**,**b**, **11a**,**b**, **12a**,**b**, and **13a**,**b**, apparently, consist of two diastereomers. However, their ^{1}H NMR spectra contain only one set of signals, excluding compounds **9d**,**m** and **11a**. In products **9d**,**m** and **11a** and their corresponding hydrochlorides, only the slight difference (Δδ 0.01—0.03) between chemical shifts of diastereotopic protons, located near the asymmetric carbon atoms is observed. According to the ^{1}H NMR data, the ratio of diastereomers is 1 : 1.

In conclusion, the condensation of anabasine hydrochloride with paraformaldehyde and terminal alkynes was systematically studied. The reaction was shown to be a convenient general method for the synthesis of chiral derivatives of *N*-propargylanabasine with various substituents at carbon atom of the alkyne fragment.

Experimental

^{1}H NMR spectra were recorded on a Bruker DRX-500 spectrometer (500.13 MHz) in DMSO-d_6 with Me_4Si as the internal standard. UV spectra were recorded on a Specord M-40 Carl Zeiss (Jena) spectrophotometer for the ethanol solutions. IR spectra were recorded on a Specord M-80 spectrophotometer, for oils as the neat samples, for solids in KBr pellets. Mass spectra were registered on a Finnigan MAT INCOS 50 instrument (EI, 70 eV) with direct inlet of the sample. Melting points were determined on the Boetius heating table and were uncorrected. The specific rotation values [α_D] (deg mL g^{-1} dm^{-1}) with chloroform solutions concentrations C/g (100 mL)$^{-1}$ were determined on a PU-7 polarimeter. Monitoring of the reaction progress was performed by TLC on Silufol (UV-254) plates in chloroform—methanol—ethyl acetate (9 : 1 : 1) with visualization in iodine vapors.

Compounds **2e**,[19a] **2f**,**d**, **3k**, **4e**, **6a**, **7a**,[19b] **3a—f**,**l**, **4f—h**,[19c] **3d—j**, **m—o**, and **4i**,**j** [19d] were synthesized according to the known procedures. Commercially available compounds **2a—d**,**h** and **4a—c** were used without additional purification. Anabasine hydrochloride (**1**·HCl), m.p. 220—222 °C, >99% purity; (S)-base, [α_D] −82.5 (*c* 0.6, EtOH).

Acetates 5a—d (general procedure). A mixture of the corresponding alcohol **4a—d** (10 mmol), dry CH_2Cl_2 (20 mL), acetic anhydride (1.2 g), triethylamine (5 mL), and 4-DMAP (20 mg) was kept for 40 h at 22—25 °C, poured into ice-cold water, and extracted with ether. The organic layer was washed with saturated solutions of $CuSO_4$, $NaHCO_3$, and NaCl, dried with $MgSO_4$. The solvents were evaporated, the residue was dissolved in *n*-hexane, filtered through Al_2O_3 (15 g), the filtrate was concentrated, and the residue was distilled *in vacuo* (2 Torr). Acetates **5a—d** were obtained, which, according to ^{1}H NMR data, were identical to the authentic samples (Aldrich), the yields were 83—90%.

Trimethylsilyl ethers 6c and 7c (general procedure). Chlorotrimethylsilane (15.0 g, 0.14 mol) was gradually added to a solution of the corresponding alcohol **6a** or **7a** (0.1 mol) and dry

pyridine (11.8 g, 0.15 mol) in dioxane (60 mL) at 0—5 °C. The mixture was stirred for 1 h at 20 °C, then was gently refluxed for 2 h; the formed pyridine hydrochloride was filtered off and washed with dioxane (30 mL). The obtained solutions of **6c** or **7c**, containing ~6% of alcohols **6a** or **7a** (GLC, Biokhrom-1, capillary column with OV-101 as stationary phase, 52 m), were used for further reactions without additional purification.

Condensation of anabasine hydrochloride (1 · HCl) with paraformaldehyde and terminal alkynes 3—7 (general procedure). Anabasine hydrochloride (**1** · HCl) (1.56 g, 7 mmol) was added in one portion to a pre-heated to ~60°C mixture of alkynes **3—7** (10—12 mmol), paraformaldehyde (0.6 g, 20 mmol), Cu_2Cl_2 (0.7 g), AcONa (1.5 g), and dioxane (40 mL). The reaction mixture was vigorously stirred for 5—8 h at 65—70 °C (TLC monitoring), concentrated on a rotary evaporator, the residue was dissolved in benzene (100 mL), filtered off the impurities, and treated with 3*N* H_2SO_4 (in case of **8a—i**, with 2 *M* HCl). The water layer, containing ammonium salts, was treated with K_2CO_3 or aq. NH_3, and extracted with benzene—ethyl acetate (2 : 1) mixture. The extract was sequentially washed with water and brine, dried with $MgSO_4$, and concentrated. The residue was dissolved in CH_2Cl_2 (1—2 mL) and chromatographed on a column (25×2.5 cm) with SiO_2 (25.0—30.0 g), eluent: NH_4OH solution (1%), and MeOH (0—10%) in CH_2Cl_2. Compounds **8a—h**, **9a—o**, **10a—d**,**i**, **11a—d** (oils) and **10h**,**j** (crystals) were thus obtained.

In case of alkynes **3d**, and **4i**,**j**, the benzene solution was concentrated and, after usual treatment, diacetylene glycols **14a—c** were obtained, which were identical to the described earlier.[20]

Anabasine derivatives hydrochlorides 8 · *n*HCl—11 · *n*HCl (*n* = 1, 2) (general procedure). A solution of HCl (10%, 0.3—0.4 mL) in dry ether was added to a solution of compounds **8—12** (40—70 mg) in acetone (0.2—0.5 mL). The formed oil was twice re-precipitated from Pr^iOH (2—6%) solution in organic solvent (acetone, ethyl acetate, or benzene), dried *in vacuo* (1 Torr) at 100—120 °C. Mono- and (or) dihydrochlorides as amorphous powders were obtained. The yields, physical and chemical properties, and elemental analysis data for compounds **8—11** and the corresponding hydrochlorides are given below.

(2*S*)-(—)-*N*-(Hex-2-yn-1-yl)-2-(3-pyridyl)piperidine (8a), light oil, the yield was 81%, $[\alpha_D]$ −243.2 (*c* 0.48). Found (%): N, 11.37. $C_{16}H_{22}N_2$. Calculated (%): N, 11.56. IR, ν/cm^{-1}: 2932, 1592, 1576, 1428, 1324, 1128, 1100, 1024, 984, 804, 716. ^{1}H NMR, δ: 0.94 (t, 3 H, Me, *J* = 6.6 Hz); 1.30—1.52 (m, 8 H, 3 CH_2 of piperidine, CH_2CH_3); 2.16 (t, 2 H, ≡CCH_2CH_2, *J* = 6.6 Hz); 2.43 (t, 1 H, NCH of piperidine, *J* = 12.0 Hz); 2.78 (d, 1 H, NCH of piperidine, *J* = 10.0 Hz); 2.84, 3.10 (both dt, 1 H, 1 H, ≡CCH_2N, *J* = 17.0 Hz, *J* = 1.8 Hz); 3.29 (dd, 1 H, NCH of piperidine, *J* = 11.3 Hz, *J* = 2.6 Hz); 7.37 (dd, 1 H, H of pyridine, *J* = 7.8 Hz, *J* = 4.8 Hz); 7.68 (br.d, 1 H, H of pyridine, *J* = 7.8 Hz); 8.44 (d, 1 H, H of pyridine, *J* = 4.8 Hz); 8.49 (br.s, 1 H, H of pyridine). MS, *m*/*z* (I_{rel} (%)): 242 [M^+] (18), 241 (12), 213 (18), 164 [$M^+ - C_5H_4N$] (100), 161 (15), 79 (14).

(2*S*)-(—)-*N*-(Hept-2-yn-1-yl)-2-(3-pyridyl)piperidine (8b), light oil, the yield was 84%, $[\alpha_D]$ −232.6 (*c* 0.36). Found (%): N, 10.64. $C_{17}H_{24}N_2$. Calculated (%): N, 10.93. IR, ν/cm^{-1}: 2928, 2856, 1588, 1576, 1428, 1324, 1126, 1100, 1022, 984, 804, 716. ^{1}H NMR, δ: 0.90 (t, 3 H, CH_3, *J* = 6.6 Hz); 1.36—1.78 (m, 10 H, 3 CH_2 of piperidine, $(CH_2)_2CH_3$); 2.20 (tt, 2 H, ≡CCH_2CH_2, *J* = 6.6 Hz, *J* = 1.8 Hz); 2.44 (dt, 1 H, NCH of piperidine, *J* = 12.0 Hz, *J* = 2.6 Hz); 2.89 (d, 1 H, NCH of piperidine, *J* = 10.4 Hz); 2.87, 3.09 (both dt, 1 H, 1 H, ≡CCH_2N, *J* = 17.1 Hz, *J* = 1.8 Hz); 3.27 (dd, 1 H, NCH of piperidine, *J* = 11.3 Hz, *J* = 2.7 Hz); 7.35 (dd, 1 H, H of pyridine, *J* = 7.8 Hz, *J* = 4.8 Hz); 7.68 (dt, 1 H, H of pyridine, *J* = 7.8 Hz, *J* = 1.6 Hz); 8.46 (dd, 1 H, H of pyridine, *J* = 4.8 Hz, *J* = 1.2 Hz); 8.47 (d, 1 H, H of pyridine, *J* = 2.2 Hz). MS, *m*/*z* (I_{rel} (%)): 256 [M^+] (18), 213 (13), 178 [$M^+ - C_5H_4N$] (100), 161 (14), 55 (16).

Hydrochloride 8b · HCl, m.p. 99—100 °C, $[\alpha_D]$ −100.1 (*c* 0.47, EtOH). Found (%): Cl, 12,68. $C_{17}H_{25}ClN_2$. Calculated (%): Cl, 12.10.

(2*S*)-(—)-*N*-(Oct-2-yn-1-yl)-2-(3-pyridyl)piperidine (8c), light oil, the yield was 80%, $[\alpha_D]$ −229.4 (*c* 0.4). Found (%): N, 10.23. $C_{18}H_{26}N_2$. Calculated (%): N, 10.36. IR, ν/cm^{-1}: 2930, 2856, 1588, 1576, 1428, 1324, 1126, 1100, 1022, 984, 804, 716. ^{1}H NMR, δ: 0.82 (t, 3 H, CH_3, *J* = 6.6 Hz); 1.25—1.80 (m, 12 H, 3 CH_2 of piperidine, $(CH_2)_3CH_3$); 2.16 (t, 2 H, ≡CCH_2CH_2, *J* = 6.6 Hz); 2.48 (t, 1 H, NCH of piperidine, *J* = 12.0 Hz); 2.84 (d, 1 H, NCH of piperidine, *J* = 10.0 Hz); 2.89, 3.10 (both d, 1 H, 1 H, ≡CCH_2N, *J* = 17.0 Hz); 3.29 (d, 1 H, NCH of piperidine, *J* = 11.0 Hz); 7.37 (dd, 1 H, H of pyridine, *J* = 7.8 Hz, *J* = 4.8 Hz); 7.68 (br.d, 1 H, H of pyridine, *J* = 7.8 Hz); 8.45 (d, 1 H, H of pyridine, *J* = 4.8 Hz); 8.47 (br.s, 1 H, H of pyridine). MS, *m*/*z* (I_{rel} (%)): 270 [M^+] (16), 213 (14), 192 [$M^+ - C_5H_4N$] (100), 161 (20), 105 (15), 79 (14), 55 (28).

A mixture of mono- and dihydrochlorides 8c · HCl and 8c · 2HCl (20—30%), m.p. 99—100 °C, $[\alpha_D]$ −96.4 (*c* 0.41, EtOH). ^{1}H NMR, δ: 0.89 (t, 3 H, CH_3, *J* = 6.7 Hz); 1.33, 1.52, 1.62, 1.82—2.03, 2.18 (all m, 4 H, 2 H, 1 H, 3 H, 2 H, 3 CH_2 of piperidine, $(CH_2)_3CH_3$); 2.29 (t, 2 H, ≡CCH_2CH_2, *J* = 6.7 Hz); 3.18 and 3.61 (t and d, 1 H each, 2 NCH of piperidine, *J* = 12.0 Hz); 3.54, 3.81 (both d, 1 H each, ≡CCH_2N, *J* = 16.0 Hz); 4.43 (d, 1 H, NCH of piperidine, *J* = 12.0 Hz); 7.82, 8.68, 8.81, 9.07 (all br.s, 1 H each, 4 H of pyridine); 12.4 (br.s, 1 H, NH).

(2*S*)-(—)-*N*-(Non-2-yn-1-yl)-2-(3-pyridyl)piperidine (8d), light oil, the yield was 79%, $[\alpha_D]$ −217.2 (*c* 0.4). Found (%): N, 9.74. $C_{19}H_{28}N_2$. Calculated (%): N, 9.85. IR, ν/cm^{-1}: 2932, 2856, 1592, 1576, 1424, 1324, 1128, 1100, 1028, 984, 804, 716. ^{1}H NMR, δ: 0.78 (t, 3 H, CH_3, *J* = 6.6 Hz); 1.28—1.81 (m, 14 H, 3 CH_2 of piperidine, $(CH_2)_4CH_3$); 2.19 (t, 2 H, ≡CCH_2CH_2, *J* = 6.6 Hz); 2.46 (t, 1 H, NCH of piperidine, *J* = 12.0 Hz); 2.86 (d, 1 H, NCH of piperidine, *J* = 10.0 Hz); 2.89, 3.09 (both d, 1 H, 1 H, ≡CCH_2N, *J* = 17.0 Hz); 3.29 (d, 1 H, NCH of piperidine, *J* = 11.0 Hz); 7.37 (dd, 1 H, H of pyridine, *J* = 7.8 Hz, *J* = 4.8 Hz); 7.68 (br.d, 1 H, H of pyridine, *J* = 7.8 Hz); 8.45 (d, 1 H, H of pyridine, *J* = 4.8 Hz); 8.47 (br.s, 1 H, H of pyridine). MS, *m*/*z* (I_{rel} (%)): 284 [M^+] (17), 213 (13), 207 (16), 206 [$M^+ - C_5H_4N$] (100), 161 (16,9), 104 (11.4), 55 (13.7).

A mixture of mono- and dihydrochlorides 8d · HCl and 8d · 2HCl (20—30%), m.p. 85—86 °C, $[\alpha_D]$ −84.2 (*c* 0.5, EtOH). ^{1}H NMR, δ: 0.88 (t, 3 H, CH_3, *J* = 6.6 Hz); 1.18—1.39, 1.49, 1.61, 1.81—1.99, 2.12 (all m, 6 H, 2 H, 1 H, 3 H, 2 H, 3 CH_2 of piperidine, $(CH_2)_4CH_3$); 2.34 (t, 2 H, ≡CCH_2CH_2, *J* = 6.6 Hz); 3.17 and 3.61 (t and d, 1 H each, 2 NCH of piperidine, *J* = 12.0 Hz); 3.55, 3.82 (both d, 1 H each, ≡CCH_2N, *J* = 16.0 Hz); 7.89, 8.72, 8.84, 9.09 (all br.s, 1 H each, 4 H of pyridine); 12.4 (br.s, 1 H, NH).

(2*S*)-(—)-(7-Methyloct-2-yn-1-yl)-2-(3-pyridyl)piperidine (8e), light oil, the yield was 76%, $[\alpha_D]$ −214.7 (*c* 0.4). Found (%): N, 9.59. $C_{19}H_{28}N_2$. Calculated (%): N, 9.85. IR, ν/cm^{-1}: 2936, 1592, 1576, 1428, 1324, 1228, 1116, 1100, 984, 896, 804, 716.

^{1}H NMR, δ: 0.88 (d, 6 H, 2 CH_3, J = 6.7 Hz); 1.30, 1.40—1.78 (both m, 3 H, 8 H, 3 CH_2 of piperidine, $(CH_2)_2CHMe_2$); 2.48 (t, 1 H, NCH of piperidine, J = 12 Hz); 2.89 (br.d, 2 H, NCH of piperidine, ≡CCHHN, J = 17.0 Hz); 3.10 (br.d, 1 H, ≡CCHHN, J = 17.0 Hz); 3.29 (dd, 1 H, NCH of piperidine, J = 11.4 Hz, J = 2.6 Hz); 7.36 (dd, 1 H, H of pyridine, J = 7.6 Hz, J = 4.6 Hz); 7.69 (br.d, 1 H, H of pyridine, J = 7.6 Hz); 8.46 (t, 2 H, 2 H of pyridine, J = 1.4 Hz). MS, m/z (I_{rel} (%)): 284 [M^+] (11), 206 [$M^+ - C_5H_4N$] (100), 161 (19), 105 (10), 55 (12).

(2*S*)-(−)-*N*-(4-Methylpent-4-en-2-yn-1-yl)-2-(3-pyridyl)piperidine (8f), fast darkening oil, the yield was 64%, [α_D] −308.6 (*c* 0.44). Found (%): N, 11.29. $C_{16}H_{20}N_2$. Calculated (%): N, 11.66. UV (EtOH), λ_{max}/nm (ε): 222 (9800). IR, ν/cm^{-1}: 2938, 1650, 1594, 1576, 1430, 1170, 1100, 1074, 968, 754, 716. ^{1}H NMR, δ: 1.32—1.78 (m, 6 H, 3 CH_2 of piperidine); 1.87 (s, 3 H, CH_3); 2.44 (td, 1 H, NCH of piperidine, J = 11.8 Hz, J = 2.4 Hz); 2.92 (br.d, 1 H, NCH of piperidine, J = 11.3 Hz); 3.02, 3.26 (both d, 1 H each, 1 H, ≡CCH_2N, J = 17.5 Hz); 3.28 (dd, 1 H, NCH of piperidine, J = 11.3 Hz, J = 2.5 Hz); 5.24 (s, 1 H, =CHH); 5.28 (t, 1 H, =CHH, J = 1.2 Hz); 7.37 (dd, 1 H, H of pyridine, J = 7.8 Hz, J = 4.7 Hz); 7.70 (br.d, 1 H, H of pyridine, J = 7.8 Hz); 8.46 (dd, 1 H, H of pyridine, J = 4.7 Hz, J = 1.5 Hz); 8.48 (d, 1 H, H of pyridine, J = 1.1 Hz). MS, m/z (I_{rel} (%)): 240 [M^+] (32), 211 (16), 162 [$M^+ - C_5H_4N$] (100).

Dihydrochloride 8f·2HCl, m.p. 115—117 °C, [α_D] −113.2 (*c* 0.43, EtOH). Found (%): Cl, 20.07. $C_{16}H_{22}Cl_2N_2$. Calculated (%): Cl, 22.63.

(2*S*)-(−)-*N*-[3-(Cyclohex-1-en-1-yl)prop-2-yn-1-yl]-2-(3-pyridyl)piperidine (8g), fast darkening oil, the yield was 63%, [α_D] −246.0 (*c* 0.42). UV (EtOH), λ_{max}/nm (ε): 228 (9600). IR, ν/cm^{-1}: 2932, 2856, 1660, 1592, 1580, 1444, 1432, 1324, 1172, 1100, 1076, 968, 756, 716. ^{1}H NMR, δ: 1.30—1.78 (m, 10 H, 3 CH_2 of piperidine, 2 CH_2 of cyclohexene); 2.06 (m, 4 H, 2 CH_2C= of cyclohexene); 2.47 (td, 1 H, NCH of piperidine, J = 11.8 Hz, J = 2.4 Hz); 2.88 (br.d, 1 H, NCH of piperidine, J = 11.2 Hz); 2.98, 3.23 (both d, 1 H, 1 H, ≡CCH_2N, J = 17.4 Hz); 3.27 (dd, 1 H, NCH of piperidine, J = 11.2 Hz, J = 2.4 Hz); 6.04 (br.s, 1 H, CH=), 7.37 (dd, 1 H, H of pyridine, J = 7.2 Hz, J = 4.8 Hz); 7.68 (d, 1 H, H of pyridine, J = 7.2 Hz); 8.49 (br.s, 2 H, 2 H of pyridine). MS, m/z (I_{rel} (%)): 280 [M^+] (41), 279 (26), 202 [$M^+ - C_5H_4N$] (100), 173 (20), 161 (78), 141 (20), 119 (43), 105 (40), 91 (57), 84 (48), 81 (42), 55 (37), 43 (80).

Dihydrochloride 8g·2HCl, m.p. 124—126 °C, [α_D] −95.8 (*c* 0.45). Found (%): Cl, 19.51. $C_{19}H_{26}Cl_2N_2$. Calculated (%): Cl, 20.07.

(2*S*)-(−)-*N*-(3-Phenylprop-2-yn-1-yl)-2-(3-pyridyl)piperidine (8h), dark oil, the yield was 67%, [α_D] −104.8 (*c* 0.5). Found (%): N, 9.82. $C_{19}H_{20}N_2$. Calculated (%): N, 10.14. IR, ν/cm^{-1}: 3032, 2932, 2228 (—C≡C—), 1600, 1592, 1576, 1492, 1428, 1324, 1112, 1100, 1028, 984, 756, 716, 692. ^{1}H NMR, δ: 1.35—1.78 (m, 6 H, 3 CH_2 of piperidine); 2.55 (dd, 1 H, NCH of piperidine, J = 11.7 Hz, J = 2.4 Hz); 3.00 (br.d, 1 H, NCH of piperidine, J = 11,2 Hz); 3.16, 3.38 (both d, 1 H each, ≡CCH_2N, J = 17.5 Hz); 3.36 (overlapped, 1 H, NCH of piperidine); 7.37 (m, 4 H, H of pyridine, 3 H of phenyl); 7.45 (m, 2 H, 2 H of phenyl); 7.75 (dd, 1 H, H of pyridine, J = 7.8 Hz, J = 1.2 Hz); 8.47 (dd, 1 H, H of pyridine, J = 4.7 Hz, J = 1.5 Hz); 8.54 (d, 1 H, H of pyridine, J = 4.7 Hz, J = 1.5 Hz). MS, m/z (I_{rel} (%)): 276 [M^+] (36), 275 (18), 198 [$M^+ - C_5H_4N$] (63), 115 (100).

A mixture of mono- and dihydrochlorides 8h·HCl and 8h·2HCl (20—30%), m.p. 131—133 °C, [α_D] −154.5 (*c* 0.45, EtOH).

(2*S*,4´*RS*)-(−)-*N*-(4-Hydroxy-4-methylhept-2-yn-1-yl)-2-(3-pyridyl)piperidine (9a), oil, the yield was 76%, [α_D] −205.2 (*c* 0.37). Found (%): N, 9.70. $C_{18}H_{26}N_2O$. Calculated (%): N, 9.78. IR, ν/cm^{-1}: 3380, 3212, 2936, 1596, 1580, 1432, 1324, 1100, 1028, 716.

Hydrochloride 9a·HCl, m.p. 108—110 °C, [α_D] −105.0 (*c* 0.44). Found (%): Cl, 11.42. $C_{18}H_{27}ClN_2O$. Calculated (%): Cl, 10.98. ^{1}H NMR, δ: 0.96 (t, 3 H, CH_3, J = 6.7 Hz); 1.19 (s, 3 H, CH_3); 1.17—2.35 (m, 5 H, 2 CH_2 of piperidine, CH of propyl); 1.92 and 2.18 (m and br.s, 3 H, 2 H, CH, CH_2 of propyl, CH_2 of piperidine); 3.19, 3.59 (td, 1 H each, 2 NCH of piperidine, J = 12.0 Hz); 3.50, 3.82 (both d, 1 H each, ≡CCH_2N, J = 17.0 Hz); 4.43 (d, 1 H, NCH of piperidine, J = 12.0 Hz); 4.9 (br.s, 2 H, NH, OH); 7.87, 8.52, 8.86, 9.01 (all s, 1 H each, 4 H of pyridine). MS, m/z (I_{rel} (%)): 286[M^+] (10), 208 [$M^+ - C_5H_4N$] (100), 161 (23), 105 (15), 78 (10), 43 (64).

(2*S*,4´*RS*)-(−)-*N*-(4-Hydroxy-4-methyloct-2-yn-1-yl)-2-(3-pyridyl)piperidine (9b), oil, the yield was 84%, [α_D] −205.3 (*c* 0.36). Found (%): N, 9.46. $C_{19}H_{28}N_2O$. Calculated (%): N, 9.71. IR, ν/cm^{-1}: 3400, 3220, 2912, 2236 (—C≡C—), 1596, 1580, 1432, 1324, 1188, 1100, 984, 808, 716. ^{1}H NMR, δ: 0.89 (t, 3 H, CH_3, J = 6.6 Hz); 1.33 (s, 3 H, CH_3); 1.31, 1.40—1.80 (two m, 3 H, 9 H, 3 CH_2 of piperidine, $(CH_2)_3CH_3$); 2.47, 2.84 (overlapped, 1 H each, 2 NCH of piperidine); 2.90, 3.11 (both d, 1 H each, ≡CCH_2N, J = 17.3 Hz); 3.34 (br.d, 1 H, NCH of piperidine, J = 11.0 Hz); 4.98 (s, 1 H, OH); 7.34 (dd, 1 H, H of pyridine, J = 7.8 Hz, J = 4.7 Hz); 7.68 (br.d, 1 H, H of pyridine, J = 7.8 Hz); 8.46 (br.d, 1 H, H of pyridine, J = 4.7 Hz); 8.50 (br.s, 1 H, H of pyridine). MS, m/z (I_{rel} (%)): 300 [M^+] (15), 222 [$M^+ - C_5H_4N$] (100), 105 (15), 55 (21), 43 (98).

(2*S*,4´*RS*)-(−)-*N*-(4-Hydroxy-4,6-dimethylhept-2-yn-1-yl)-2-(3-pyridyl)piperidine (9c), oil, the yield was 77%, [α_D] −201.6 (*c* 0.50). Found (%): N, 9.52. $C_{19}H_{28}N_2O$. Calculated (%): N, 9.71. IR, ν/cm^{-1}: 3380, 3220, 2936, 1596, 1580, 1432, 1368, 1324, 1160, 1100, 984, 924, 716. ^{1}H NMR, δ: 0.92 (t, 6 H, CH_3, J = 6.7 Hz); 1.38 (s, 3 H, CH_3); 1.30, 1.47, 1.52—1.80 (all m, 1 H, 3 H, 4 H, 3 CH_2 of piperidine, −CH_2CH); 1.83 (m, 1 H, CH_2CH); 2.49, 2.92 (overlapped, 1 H each, 2 NCH of piperidine); 2.91, 3.13 (both d, 1 H each, ≡CCH_2N, J = 17.2 Hz); 3.32 (br.d, 1 H, NCH of piperidine, J = 11.0) Hz; 4.90 (s, 1 H, OH); 7.25 (dd, 1H, H of pyridine, J = 7.8 Hz, J = 4.6 Hz); 7.69 (br.d, 1 H, H of pyridine, J = 7.8 Hz); 8.44 (br.d, 1 H, H of pyridine, J = 4.6 Hz); 8.50 (d, 1 H, H of pyridine, J = 1.7 Hz). MS, m/z (I_{rel} (%)): 300 [M^+] (15), 222 [$M^+ - C_5H_4N$] (100), 206 (23), 204 (26), 161 (42), 122 (38), 105 (28), 43 (58).

(2*S*,4´*RS*)-(−)-*N*-(4-Hydroxy-4,5,5-trimethylhex-2-yn-1-yl)-2-(3-pyridyl)piperidine (9d), oil, the yield was 80%, [α_D] −212.6 (*c* 0.41). Found (%): N, 9.20. $C_{19}H_{28}N_2O$. Calculated (%): N, 9.33. IR, ν/cm^{-1}: 3230, 2936, 1596, 1580, 1428, 1368, 1324, 1172, 1112, 916, 804, 716. ^{1}H NMR (DMSO-d_6/CCl_4, 1 : 3), δ: 1.02 (s, 9 H, Bu^t); 1.37*, 1.38* (both s, 1.5 H each, CH_3), 1.32, 1.52, 1.62—1.85 (all m, 1 H, 1 H, 4 H, 3 CH_2 of piperidine); 2.58 (t, 1 H, NCH of piperidine, J = 11.0 Hz); 2.89 (overlapped, 1 H, NCH of piperidine); 2.96, 3.11 (both d, 1 H each, ≡CCH_2N, J = 17.0 Hz); 3.16 (m,

* Signals of diastereotopic protons of two diastereomers (1 : 1).

1 H, NCH of piperidine); 4.06 (br.s, 1 H, OH); 7.25, 7.66, 8.44, 8.52 (all br.s, 1 H each, 4 H of pyridine).

Hydrochloride 9d·HCl, m.p. 101—103 °C. Found (%): Cl, 10.91. $C_{19}H_{29}ClN_2O$. Calculated (%): Cl, 10.52. ^{1}H NMR (DMSO-d_6/CCl_4, 1 : 3), δ: 1.01*, 1.03* (both s, 4.5 H each, Bu^t); 1.40*, 1.43* (both s, 1.5 H each, CH_3); 1.75, 1.98, 2.40 (all m, 1 H, 3 H, 2 H, 3 CH_2 of piperidine); 3.29 (q, 1 H, NCH of piperidine, J = 10.2 Hz); 3.51*, 3.52*, 3.79*, 3.80* (all d, 0.5 H each, ≡CCH_2N, J = 16.0 Hz); 3.59 (d, 1 H, NCH of piperidine, J = 10.2 Hz); 4.68*, 4.71* (both d, 0.5 H each, NCH of piperidine, J = 10.2 Hz); 7.85 (q, 1 H, H of pyridine, J = 6 Hz); 8.81 (br.t, 1 H, H of pyridine, J = 4.4 Hz); 9.0, 9.18 (both br.s, 1 H each, 2 H of pyridine). MS, m/z (I_{rel} (%)): 300[M^+] (19), 243 (68), 222 [$M^+ - C_5H_4N$] (100), 161 (42), 120 (19), 118 (20), 105 (21), 91 (19), 84 (24), 82 (21), 80 (24), 78 (17), 77 (18), 56 (86), 43 (98), 41 (81).

(2*S*,4′*RS*)-(−)-*N*-(4-Hydroxy-4,5-dimethylhex-5-en-2-yn-1-yl)-2-(3-pyridyl)piperidine (9e), the yield was 61%, oil, [α_D] −208.2 (*c* 0.76). Found (%): N, 9.47. $C_{18}H_{24}N_2O$. Calculated (%): N, 9.85. IR, ν/cm^{-1}: 3240, 2936, 1652, 1596, 1580, 1432, 1368, 1324, 1188, 1100, 904, 716. ^{1}H NMR, δ: 1.31, 1.41—1.78 (both m, 1 H, 5 H, CH_2 of piperidine); 1.46 (s, 3 H, CH_3); 1.81 (s, 3 H, CH_3C=); 2.46 and 2.80 (overlapped, 1 H each, CH_2N); 2.83, 3.14 (both d, 1 H each, ≡CCH_2N, J = 17.5 Hz); 3.28 (dd, 1 H, CHN, J = 11.3 Hz, J = 2.4 Hz); 4.80, 5.23, 5.41 (all s, 1 H each, =CH_2, OH); 7.35 (dd, 1 H, H of pyridine, J = 7.8 Hz, J = 4.8 Hz); 7.69 (dd, 1 H, H of pyridine, J = 7.8 Hz, J = 1.2 Hz); 8.43 (dd, 1 H, H of pyridine, J = 4.8 Hz, J = 1.5 Hz); 8.48 (d, 1 H, H of pyridine, J = 1.2 Hz). MS, m/z (I_{rel} (%)): 284 [M^+] (3.2), 206 [$M^+ - C_5H_4N$] (71), 161 (59), 119 (24), 105 (21), 92 (19), 84 (24), 77 (22), 43 (100).

(2*S*,4′*RS*)-(−)-*N*-(4-Hydroxy-4-methyloct-7-en-2-yn-1-yl)-2-(3-pyridyl)piperidine (9f), the yield was 72%, oil, [α_D] −214.1 (*c* 0.4). Found (%): N, 9.82. $C_{19}H_{26}N_2O$. Calculated (%): N, 9.78. IR, ν/cm^{-1}: 3240, 2936, 1596, 1580, 1432, 1330, 1190, 1164, 1102, 914, 804, 716. ^{1}H NMR, δ: 1.29, 1.40—1.80 (both m, 1 H, 7 H, CH_2-of piperidine, CH_2CH_2C=); 1.37 (s, 3 H, CH_3); 2.16—2.33 (m, 2 H, CH_2C=); 2.47, 2.87 (overlapped, 1 H each, ≡CH_2N); 2.90, 3.14 (both d, 1 H each, ≡CCH_2N, J = 17.0 Hz); 4.95 (dt, 1 H, CH_2=, J = 12.0 Hz, J = 1.6 Hz); 5.04 (br.d, 1 H, CH_2=, J = 17.2 Hz); 5.24 (s, 1 H, OH); 5.83 (dddd, CH=CH_2, J = 17.2 Hz, J = 12.0 Hz, J = 6.8 Hz, J = 6.6 Hz); 7.35 (dd, 1 H, H of pyridine, J = 7.8 Hz, J = 4.8 Hz); 7.69 (dd, 1 H, H of pyridine, J = 7.8 Hz, J = 1.7 Hz); 8.46 (dd, 1 H, H of pyridine, J = 4.8 Hz, J = 1.6 Hz); 8.50 (d, 1 H, H of pyridine, J = 1.7 Hz). MS, m/z (I_{rel} (%)): 298 [M^+] (4), 225 (23), 220 [$M^+ - C_5H_4N$] (100), 199 (16), 175 (22), 161 (91), 159 (22), 132 (16), 122 (38), 119 (23), 118 (23), 105 (34), 92 (28), 84 (28), 79 (20), 78 (26), 65 (17), 55 (39), 43 (85).

(2*S*,4′*RS*)-(−)-*N*-(4-Hydroxy-4,8-dimethylnon-7-en-2-yn-1-yl)-2-(3-pyridyl)piperidine (9g), the yield was 74%, oil, [α_D] −178.5 (*c* 0.62). Found (%): N, 8.40. $C_{21}H_{30}N_2O$. Calculated (%): N, 8.58. IR, ν/cm^{-1}: 3300, 2936, 2232 (—C≡C—), 1644, 1592, 1580, 1432, 1368, 1324, 1100, 984, 912, 716. ^{1}H NMR, δ: 1.28, 1.44—1.78 (both m, 1 H, 7 H, CH_2 of piperidine, CH_2CH_2CH=); 1.37 (s, 3 H, CH_3); 1.59, 1.67 (both s, 3 H each, CH_3C=); 2.16 (m, 2 H, CH_2C=); 2.48, 2.90 (overlapped, 1 H each, CH_2N); 2.92, 3.15 (both d, 1 H each, ≡CCH_2N, J = 17.2 Hz); 3.30 (overlapped, 1 H, CHN); 5.14 (s, 1 H, OH); 5.16 (t, 1 H, CH=, J = 6.6 Hz); 7.34 (dd, 1 H, H of pyridine, J = 6.2 Hz, J = 4.1 Hz); 7.68 (br.t, 1 H, H of pyridine, J = 6.2 Hz); 8.47 (dd, 1 H, H of pyridine, J = 4.1 Hz, J = 1.8 Hz); 8.50 (dd, 1 H, H of pyridine, J = 6.2 Hz, J = 2.1 Hz). MS, m/z (I_{rel} (%)): 326 [M^+] (1), 248 [$M^+ - C_5H_4N$] (19), 162 (22), 161 (59), 105 (28), 92 (22), 84 (69), 55 (57), 43 (100), 41 (99).

(2*S*,4′*RS*)-(−)-*N*-(4-Hydroxy-8-methoxy-4,8-dimethylnon-2-yn-1-yl)-2-(3-pyridyl)piperidine (9h), the yield was 67%, oil, [α_D] −186.7 (*c* 0.54). Found (%): N, 7.59. $C_{22}H_{34}N_2O_2$. Calculated (%): N, 7.81. IR, ν/cm^{-1}: 3300, 2936, 1592, 1576, 1428, 1324, 1188, 1172, 1096, 1068, 984, 716, 668. ^{1}H NMR, δ: 1.10 (s, 6 H, CH_3); 1.25—1.80 (m, 12 H, CH_2 of piperidine, $CH_2CH_2CH_2$); 1.35 (s, 3 H, CH_3); 2.48, 2.87 (overlapped, 1 H each, CH_2N); 2.90, 3.14 (both d, 1 H each, ≡CCH_2N, J = 17.2 Hz); 3.08 (s, 3 H, CH_3O); 3.32 (br.t, 1 H, CHN, J = 9.0 Hz); 5.15 (s, 1 H, OH); 7.35 (br.t, 1 H, H of pyridine, J = 6.0 Hz); 7.70 (br.t, 1 H, H of pyridine, J = 6.0 Hz); 8.46 (d, 1 H, H of pyridine, J = 2.1 Hz); 8.49, 8.53 (both s, 0.5 H each, H of pyridine). MS, m/z (I_{rel} (%)): 244 (16), 227 (23), 199 (37), 161 (36), 105 (21), 92 (20), 84 (23), 73 (100), 55 (33), 43 (78), 41 (47).

(2*S*,4′*RS*)-(−)-*N*-(4-Hydroxy-4,8,12,16-tetramethylheptadec-4-yn-1-yl)-2-(3-pyridyl)piperidine (9i), the yield was 76%, oil, [α_D] −133.4 (*c* 0.64). Found (%): N, 5.61. $C_{31}H_{52}N_2O$. Calculated (%): N, 5.98. IR, ν/cm^{-1}: 3300, 2932, 1652, 1600, 1500, 1464, 1432, 1368, 1324, 1300, 1220, 1176, 1092, 756, 716, 692. ^{1}H NMR, δ: 0.82, 0.84 (both d, 6 H each, CH_3, J = 6.6 Hz); 1.02—1.38, 1.40—1.80 (both m, 12 H, 15 H, CH_2 of piperidine, CH_2CH); 1.36 (s, 3 H, CH_3); 2.48, 2.88 (overlapped, 1 H each, CH_2N); 2.90, 3.12 (both d, 1 H each, ≡CCH_2N, J = 17.2 Hz); 3.31 (br.t, 1 H, CHN, J = 9.0 Hz); 5.0 (s, 1 H, OH); 7.32 (br.t, 1 H, H of pyridine, J = 6.0 Hz); 7.68 (br.t, 1 H, H of pyridine); 8.45 (d, 1 H, H of pyridine, J = 2.2 Hz); 8.48 (d, 1 H, H of pyridine, J = 6.0 Hz). MS, m/z (I_{rel} (%)): M^+(−), 390 [$M^+ - C_5H_4N$] (100), 243 (26), 201 (19), 175 (18), 163 (30), 161 (67), 84 (22), 57 (25), 43 (54).

(2*S*,4′*RS*)-(−)-*N*-[4-Hydroxy-4-(bicyclo[2.2.1]hept-5-en-2-yl)pent-2-yn-1-yl]-2-(3-pyridyl)piperidine (9j), the yield was 61%, oil, [α_D] −193.4 (*c* 0.35). Found (%): N, 8.09. $C_{22}H_{26}N_2O$. Calculated (%): N, 8.38. IR, ν/cm^{-1}: 3250, 2936, 2232 (—C≡C—), 1596, 1580, 1432, 1332, 1192, 1172, 1100, 1028, 984, 900, 804, 716, 700. ^{1}H NMR, δ: 1.07—1.94 (m, 13 H, CH_2 of piperidine, CH_2, CH); 1.38 (s, 3 H, CH_3); 2.76—3.03 (m, 4 H, CH_2N); 3.14 (m, 1 H, CHN); 5.12, 5.23 (both s, 1 H total, OH); 6.10, 6.22 (two m, 2 H* total, *cyclo*-CH=CH—); 7.36, 7.68, 8.47, 8.50 (all br.s, 1 H each, H of pyridine).

(2*S*,4′*RS*)-(−)-*N*-(4-Cyclopropyl-4-hydroxypent-2-yn-1-yl)-2-(3-pyridyl)piperidine (9k), the yield was 41%, oil, [α_D] −182.5 (*c* 0.7). Found (%): N, 9.74. $C_{18}H_{24}N_2O$. Calculated (%): N, 9.85. IR, ν/cm^{-1}: 3220, 2936, 1596, 1580, 1428, 1328, 1268, 1124, 1100, 1028, 984, 948, 740, 716. ^{1}H NMR, δ: 0.37, 0.51 (both m, 3 H and 1 H, CH_2 of cyclopropane), 1.05 (m, 1 H, CH of cyclopropane); 1.28, 1.36—1.84 (both m, 1 H, 5 H, CH_2 of piperidine); 1.43 (s, 3 H, CH_3); 2.46, 2.86 (overlapped, 1 H each, CH_2N); 2.92, 3.14 (both d, 1 H each, ≡CCH_2N, J = 17.6 Hz); 3.28 (t, 1 H, CHN, J = 9.0 Hz); 5.15 (s, 1 H, OH); 7.37 (dd, 1 H, H of pyridine, J = 7.9 Hz, J = 4.8 Hz); 7.71 (br.s, 1 H, H of pyridine); 8.48, 8.52 (both d, 1 H each, H of pyridine,

* Signals of diastereotopic protons of two diastereomers (1 : 1).

* Signals of *endo*/*exo*-isomers in the ratio ~4 : 5.

J = 4.8 Hz, J = 1.7 Hz). MS, m/z (I_{rel} (%)): 284 [M^+] (23), 267 (19), 224 (38), 206 [$M^+ - C_5H_4N$] (100), 161 (42), 105 (46), 91 (39), 77 (47), 65 (34), 39 (54).

(2*S*,4´*RS*)-(−)-*N*-(4-Hydroxy-4-phenylpent-2-yn-1-yl)-2-(3-pyridyl)piperidine (9l), the yield was 63%, oil, $[\alpha_D]$ −210.6 (*c* 0.33). Found (%): N, 8.49. $C_{21}H_{24}N_2O$. Calculated (%): N, 8.74. IR, ν/cm^{-1}: 3200, 2936, 1596, 1580, 1560, 1432, 1364, 1324, 1176, 1100, 1028, 788, 764, 716, 700. ^{1}H NMR, δ: 1.30, 1.51, 1.53—1.79 (all m, 1 H, 1 H, 4 H, CH_2-of piperidine); 1.66 (s, 3 H, CH_3); 2.52, 2.82 (overlapped, 1 H each, CH_2N); 2.98, 3.18 (both d, 1 H each, ≡CCH_2N, J = 17.2 Hz); 3.32 (d, 1 H, CHN, J = 12.0 Hz); 5.91 (s, 1 H, OH); 7.27 (t, 1 H, H of pyridine, J = 7.0 Hz); 7.35 (m, 3 H, H_{Ph}); 7.59 (d, 2 H, H_{Ph}, J = 7.0 Hz); 7.27 (t, 1 H, H of pyridine, J = 7.0 Hz); 7.07 (br.d, 1 H, H of pyridine, J = 7.0 Hz); 8.49 (m, 2 H, H of pyridine). MS, m/z (I_{rel} (%)): 320 [M^+] (31.3), 319 [M^+ − H] (15.3), 242 [$M^+ - C_5H_4N$] (100), 161 (30), 115 (41), 105 (33), 92 (20), 78 (18), 77 (35), 43 (63).

(2*S*,4´*RS*)-(−)-*N*-(4-Hydroxy-4-methyl-5-phenylpent-2-yn-1-yl)-2-(3-pyridyl)piperidine (9m), the yield was 59%, oil, $[\alpha_D]$ −164.2 (*c* 0.41). Found (%): N, 8.05. $C_{22}H_{26}N_2O$. Calculated (%): N, 8.38. IR, ν/cm^{-1}: 3200, 2932, 1596, 1580, 1500, 1432, 1362, 1324, 1172, 1124, 1100, 1062, 752, 716, 700. ^{1}H NMR, δ: 1.28, 1.41—1.77 (both m, 1 H, 5 H, CH_2 of piperidine); 1.60*, 1.61* (both s, 1.5 H each, CH_3); 2.01 (s, OH), 2.42, 2.79 (both t, 1 H each, CH_2N, J = 10.0 Hz); 2.90 (dd, 1 H, ≡CCH_2N, J = 17.0 Hz, J = 2.0 Hz); 3.09—3.28 (m, 4 H, CHN, ≡CCH_2N, CH_2Ar); 7.22—7.38 (m, 6 H, H pyridyl, H_{Ph}); 7.65* (br.t, 1 H, H of pyridine, J = 9.0 Hz); 8.41*, 8.48* (both s, 0.5 H each, H of pyridine); 8.47 (s, 1 H, H of pyridine). MS, m/z (I_{rel} (%)): 324 [M^+] (1), 316 (14), 298 (40), 243 (22), 225 (22), 161 (59), 155 (17), 105 (18), 92 (22), 91 (68), 84 (19), 65 (26), 43 (100).

(2*S*,4´*RS*)-(−)-*N*-(4-Hydroxy-4-methyl-6-phenylhex-2-yn-1-yl)-2-(3-pyridyl)piperidine (9n), the yield was 72%, oil, $[\alpha_D]$ −160.2 (*c* 0.67). Found (%): N, 7.99. $C_{23}H_{28}N_2O$. Calculated (%): N, 8.04. IR, ν/cm^{-1}: 3240, 2932, 1596, 1580, 1500, 1432, 1368, 1324, 1172, 1124, 1100, 1068, 1028, 984, 752, 716, 700. ^{1}H NMR, δ: 1.30, 1.46—1.77 (both m, 1 H, 5 H, CH_2 of piperidine); 1.44 (s, 3 H, CH_3); 1.85 (m, 2 H, CH_2CH_2Ph); 2.52, 2.92 (overlapped, 1 H each, CH_2N); 2.80 (m, 2 H, CH_2Ph); 2.97, 3.19 (both d, 1 H each, ≡CCH_2N, J = 17.2 Hz); 3.35 (d, 1 H, CHN, J = 12.0 Hz); 5.15 (s, 1 H, OH); 7.18 (t), 7.22 (d), 7.28 (t) (1 H, 2 H, 2 H, H_{Ph}, J = 7.0 Hz); 7.34 (dd, 1 H, H of pyridine, J = 7.6 Hz, J = 4.4 Hz); 7.68 (d, 1 H, H of pyridine, J = 4.4 Hz); 8.46, 8.54 (both br.s, 1 H each, H of pyridine). MS, m/z (I_{rel} (%)): 348 [M^+] (47), 270 [$M^+ - C_5H_4N$] (100), 161 (60), 119 (20), 105 (33), 91 (68), 77 (18), 43 (44).

(2*S*,4´*RS*)-(−)-*N*-[4-Hydroxy-4-methyl-6-(4-methoxyphenyl)hex-2-yn-1-yl]-2-(3-pyridyl)piperidine (9o), the yield was 74%, oil, $[\alpha_D]$ −159.3 (*c* 0.38). Found (%): N, 7.46. $C_{24}H_{30}N_2O_2$. Calculated (%): N, 7.40. IR, ν/cm^{-1}: 3260, 2936, 1612, 1584, 1516, 1368, 1324, 1300, 1248, 1176, 1100, 1040, 984, 820, 716. ^{1}H NMR, δ: 1.30, 1.38—1.82 (both m, 1 H, 5 H, CH_2 of piperidine); 1.35 (s, 3 H, CH_3); 1.80, 2.73 (both m, 2 H each, CH_2CH_2Ph); 2.95, 3.18 (both d, 1 H each, ≡CCH_2N, J = 17.2 Hz); 3.34 (d, 1 H, CHN, J = 12 Hz); 3.71 (s, 3 H, CH_3O); 5.12 (s, 1 H, OH); 6.72, 7.12 (both d, 2 H each, H_{Ph}, J = 7.8 Hz); 7.34 (dd, 1 H, H of pyridine, J = 7.8 Hz, J = 4.6 Hz); 7.70 (d, 1 H, H of pyridine, J = 4.6 Hz); 8.46 (d, 1 H, H of pyridine, J = 1.8 Hz); 8.53 (br.s, 1 H, H of pyridine). MS, m/z (I_{rel} (%)): 378 [M^+] (37), 360 (17), 307 (25), 300 [$M^+ - C_5H_4N$] (61), 244 (31), 243 (57), 201 (59), 187 (39), 161 (78), 121 (100), 105 (28), 84 (21), 78 (16), 77 (23), 43 (47).

(2*S*)-(−)-*N*-(4-Hydroxybut-2-yn-1-yl)-2-(3-pyridyl)piperidine (10a), oil, containing ~90% of **10a**, the yield was 63%, $[\alpha_D]$ −167.4 (*c* 0.72).

Hydrochloride 10a·HCl, m.p. 97—99 °C, $[\alpha_D]$ −94.6 (*c* 0.56). Found (%): N, 10.24; Cl, 13.52. $C_{14}H_{18}N_2O\cdot HCl$. Calculated (%): N, 10.50; Cl, 13.29. ^{1}H NMR, δ: 1.33, 1.92, 2.24 (all m, 1 H, 3 H, 2 H, CH_2 of piperidine); 3.24 (t, 1 H, CH_2N, J = 10.0 Hz); 3.58, 3.87 (both d, 1 H each, CCH_2N, J = 17 Hz); 3.62 (d, 1 H, CH_2N, J = 10.0 Hz); 4.14 (s, 2 H, CH_2O); 4.62 (d, 1 H, CHN, J = 10 Hz); 7.92, 8.84, 8.92, 9.08 (all br.s, 1 H each, H of pyridine). MS, m/z (I_{rel} (%)): 230 [M^+] (7), 161 (11), 152 [$M^+ - C_5H_4N$] (100), 105 (11), 92 (11).

(2*S*)-(−)-*N*-(4-Hydroxy-4-methylpent-2-yn-1-yl)-2-(3-pyridyl)piperidine (10b), the yield was 67%, oil (*cf.* Ref. 8: m.p. 80 °C), $[\alpha_D]$ −195.6 (*c* 0.43). Found (%): N, 10.49. $C_{16}H_{22}N_2O$. Calculated (%): N, 10.84. IR, ν/cm^{-1}: 3240, 2932, 1596, 1580, 1428, 1324, 1228, 1172, 1100, 1028, 952, 716. ^{1}H NMR, δ: 1.30, 1.44—1.77 (both m, 1 H, 5 H, CH_2 of piperidine); 1.38 (s, 6 H, CH_3); 2.44 (dt, 1 H, CH_2N, J = 11.8 Hz, J = 2.2 Hz); 2.84 (overlapped, 1 H, CH_2N); 2.87, 3.10 (both d, 1 H each, ≡CCH_2N, J = 17.1 Hz); 3.28 (dd, 1 H, CHN, J = 11.2 Hz, J = 2.4 Hz); 5.13 (s, 1 H, OH); 7.37 (dd, 1 H, H of pyridine, J = 7.8 Hz, J = 4.8 Hz); 7.72 (br.d, 1 H, H of pyridine, J = 7.8 Hz); 8.47 (dd, 1 H, H of pyridine, J = 4.8 Hz, J = 1.6 Hz); 8.51 (d, 1 H, H of pyridine, J = 1.7 Hz). MS, m/z (I_{rel} (%)): 258 [M^+] (13), 180 [$M^+ - C_5H_4N$] (81), 161 (19), 105 (20), 78 (14), 65 (16), 43 (100).

(2*S*,4´*RS*)-(−)-*N*-(4-Hydroxy-4-methylhex-2-yn-1-yl)-2-(3-pyridyl)piperidine (10c), the yield was 72%, oil (*cf.* Ref. 8: m.p. 76 °C), $[\alpha_D]$ −233.8 (*c* 0.56). Found (%): N, 10.03. $C_{17}H_{24}N_2O$. Calculated (%): N, 10.29. IR, ν/cm^{-1}: 3320, 3240, 2932, 1596, 1580, 1432, 1368, 1208, 1100, 984, 916, 768, 716. ^{1}H NMR, δ: 0.98 (t, 3 H, CH_3, J = 6.6 Hz); 1.35 (s, 3 H, CH_3); 1.32, 1.45—1.79 (both m, 1 H, 7 H, CH_2 of piperidine, CH_2CH_3); 2.49 (br.t, 1 H, CH_2N, J = 12.0 Hz); 2.80 (overlapped, 1 H, CH_2N); 2.84, 3.13 (both d, 1 H each, ≡CCH_2N, J = 17.0 Hz); 3.30 (d, 1 H, CHN, J = 11.0 Hz); 5.13 (s, 1 H, OH); 7.37 (dd, 1 H, H of pyridine, J = 7.8 Hz, J = 5.4 Hz); 7.72 (br.d, 1 H, H of pyridine, J = 7.8 Hz); 8.49, 8.51 (both s, 1 H each, H of pyridine). MS, m/z (I_{rel} (%)): 272 [M^+] (17), 194 [$M^+ - C_5H_4N$] (100), 161 (21), 105 (11), 43 (18).

(2*S*)-(−)-*N*-[3-(1-Hydroxycyclohexyl)prop-2-yn-1-yl]-2-(3-pyridyl)piperidine (10d), the yield was 86%, oil (*cf.* Ref. 8: m.p. 78 °C), $[\alpha_D]$ −187.5 (*c* 0.49). Found (%): N, 9.43. $C_{19}H_{26}N_2O$. Calculated (%): N, 9.78. IR, ν/cm^{-1}: 3320, 2936, 2216 (—C≡C—), 1592, 1580, 1428, 1324, 1112, 1100, 984, 920, 804, 736, 716. ^{1}H NMR, δ: 1.15—1.35, 1.40—1.82 (two m, 2 H, 14 H, CH_2 of piperidine, CH_2 cyclohexane); 2.54 (overlapped, 1 H, CH_2N); 2.88 (d, 1 H, CH_2N, J = 10.4 Hz); 2.95, 3.16 (both d, 1 H each, ≡CCH_2N, J = 17.2 Hz); 3.34 (br.d, 1 H, CHN, J = 10.4 Hz); 5.04 (s, 1 H, OH); 7.34 (dd, 1 H, H of pyridine, J = 7.8 Hz, J = 4.4 Hz); 7.67 (d, 1 H, H of pyridine, J = 7.8 Hz); 8.44 (d, 1 H, H of pyridine, J = 4.4 Hz); 8.48 (br.s, 1 H, H of pyridine). MS, m/z (I_{rel} (%)): 298 [M^+] (18), 221 (14), 220 [$M^+ - C_5H_4N$] (100), 161 (27), 105 (15), 78 (83), 77 (26), 51 (24), 38 (32), 36 (79).

* Signals of diastereotopic protons of two diastereomers (1 : 1).

(2*S*,4′*RS*)-(−)-*N*-(4-Hydroxy-4-phenylbut-2-yn-1-yl)-2-(3-pyridyl)piperidine (10e), the yield was 61%, oil, $[\alpha_D]$ −184.1 (*c* 0.47). Found (%): N, 8.79. $C_{20}H_{22}N_2O$. Calculated (%): N, 9.14. IR, ν/cm^{-1}: 3240, 2932, 1592, 1576, 1428, 1364, 1176, 1100, 1028, 764, 716, 700. ^{1}H NMR ($CDCl_3$), δ: 1.36, 1.58—1.78 (both m, 1 H, 5 H, CH_2 of piperidine); 2.62 and 3.02 (br.s and d, 1 H each, CH_2N, *J* = 10.0 Hz); 3.15 and 3.26 (both d, 1 H each, ≡CCH_2N, *J* = 17.0 Hz); 3.36 (br.s, 1 H, CHN); 5.52 (s, 1 H, CHO); 7.26 (overlapped, 1 H, H of pyridine); 7.35, 7.41, 7.57 (tdd, 1 H, 2 H, 2 H, H arom., *J* = 7.8 Hz); 7.73 (br.s, 1 H, H of pyridine); 8.49 (d, 1 H, H of pyridine, *J* = 4.4 Hz); 8.51, 8.56 (both d, 0.5 H each, H of pyridine, *J* = 1.8 Hz). MS, *m*/*z* (I_{rel} (%)): 306 [M^+] (16), 228 [$M^+ - C_5H_4N$] (100), 105 (11), 77 (16).

Dihydrochloride 10e·2HCl, m.p. 125—126 °C, $[\alpha_D]$ −86.5 (*c* 0.45). Found (%): Cl, 18.26. $C_{20}H_{22}N_2O \cdot 2HCl$. Calculated (%): Cl, 18.69.

(2*S*)-(−)-*N*-(4-Ethyl-4-hydroxyhex-2-yn-1-yl)-2-(3-pyridyl)piperidine (10f), the yield was 70%, oil, $[\alpha_D]$ −210.1 (*c* 0.41). Found (%): N, 9.72. $C_{18}H_{26}N_2O$. Calculated (%): N, 9.78. IR, ν/cm^{-1}: 3200—3400, 2936, 2240 (—C≡C—), 1592, 1580, 1432, 1320, 1212, 1188, 1068, 1028, 892, 844, 808, 768, 716. ^{1}H NMR, δ: 0.94, 0.96 (both t, 3 H each, CH_3, *J* = 6.6 Hz); 1.30, 1.45—1.83 (both m, 1 H, 9 H, CH_2 of piperidine, CH_2CH_3); 2.47 (overlapped, 1 H, CH_2N); 2.86 (d, 1 H, CH_2N, *J* = 12 Hz); 2.91, 3.16 (both d, 1 H each, ≡CCH_2N, *J* = 16.8 Hz); 3.32 (dd, 1 H, CHN, *J* = 12 Hz, *J* = 2.4 Hz); 4.94 (s, 1 H, OH); 7.37 (dd, 1 H, H of pyridine, *J* = 7.8 Hz, *J* = 4.6 Hz); 7.70 (d, 1 H, H of pyridine, *J* = 7.8 Hz); 8.48 (d, 1 H, H of pyridine, *J* = 4.6 Hz); 8.50 (br.s, 1 H, H of pyridine). MS, *m*/*z* (I_{rel} (%)): 286 [M^+] (8); 208 [$M^+ - C_5H_4N$] (65); 161 (26); 118 (16); 78 (20); 77 (25); 65 (33); 55 (38); 51 (34); 41 (100).

(2*S*)-(−)-*N*-(4-Hydroxy-4-isopropyl-5-methylhex-2-yn-1-yl)-2-(3-pyridyl)piperidine (10g), the yield was 60%, oil, $[\alpha_D]$ −200.4 (*c* 0.42). Found (%): N, 8.57. $C_{20}H_{30}N_2O$. Calculated (%): N, 8.91. ^{1}H NMR, δ: 0.91—1.02 (m, 12 H, CH_3); 1.28, 1.50, 1.56—1.78 (all m, 1 H, 1 H, 4 H, CH_2 of piperidine); 1.82 (m, 2 H, $CHMe_2$); 2.55 and 2.89 (br.t and d, 1 H each, CH_2N, *J* = 11.0 Hz); 2.97 and 3.19 (both d, 1 H each, ≡CCH_2N, *J* = 17.2 Hz); 3.36 (d, 1 H, CHN, *J* = 11.0 Hz); 4.50, 4.68, 4.81, 4.92 (all s, 1 H total, OH); 7.35 (dd, 1 H, H of pyridine, *J* = 7.7 Hz, *J* = 4.4 Hz); 7.69 (d, 1 H, H of pyridine, *J* = 7.7 Hz); 8.46 (d, 1 H, H of pyridine, *J* = 4.4 Hz); 8.49 (br.s, 1 H, H of pyridine).

A mixture of mono- and dihydrochlorides 10g·HCl and 10g·2 HCl (20—30%): m.p. 108—110 °C, $[\alpha_D]$ −88.6 (*c* 0.43).

(2*S*)-(−)-*N*-[3-(1-Hydroxycyclopentyl)prop-2-yn-1-yl]-2-(3-pyridyl)piperidine (10h), the yield was 72%, m.p. 110—111 °C, $[\alpha_D]$ −302.8 (*c* 1.0). Found (%): N, 9.68. $C_{18}H_{24}N_2O$. Calculated (%): N, 9.85. IR, ν/cm^{-1}: 3232, 2920, 1592, 1584, 1452, 1428, 1328, 1308, 1220, 1116, 1096, 1028, 1000, 828, 768, 720. ^{1}H NMR, δ: 1.28, 1.45—1.86 (both m, 1 H, 13 H, CH_2 of piperidine, CH_2 of cyclopentane); 2.45 (dt, 1 H, CH_2H, *J* = 11 Hz, *J* = 1.6 Hz); 2.90 (overlapped, 1 H, CH_2N); 2.93, 3.14 (both d, 1 H each, ≡CCH_2N, *J* = 17.2 Hz); 3.28 (dd, 1 H, CHN, *J* = 10.8 Hz, *J* = 1.7 Hz); 5.13 (s, 1 H, OH); 7.36 (dd, 1 H, H of pyridine, *J* = 7.8 Hz, *J* = 4.4 Hz); 7.70 (d, 1 H, H of pyridine, *J* = 7.8); 8.46 (d, 1 H, H of pyridine, *J* = 4.4 Hz); 8.50 (br.s, 1 H, H of pyridine). MS, *m*/*z* (I_{rel} (%)): 284 [M^+] (19); 206 [$M^+ - C_5H_4N$] (100); 161 (24); 105 (34); 77 (28).

(2*S*)-(−)-*N*-[3-(1-Hydroxycycloheptyl)prop-2-yn-1-yl]-2-(3-pyridyl)piperidine (10i), the yield was 64%, oil, $[\alpha_D]$ −97.4 (*c* 0.36). Found (%): N, 8.61. $C_{20}H_{28}N_2O$. Calculated (%): N, 8.97. IR, ν/cm^{-1}: 3340, 2936, 1596, 1580, 1432, 1328, 1100, 1028, 716. ^{1}H NMR, δ: 1.28, 1.42—1.84, 1.88 (all m, 1 H, 15 H, 2H, CH_2 of piperidine, CH_2 of cycloheptane); 2.52, 2.92 (overlapped, 1 H, CH_2N); 2.94, 3.14 (both m, 1 H each, ≡CCH_2N, *J* = 17.2 Hz); 3.32 (dd, 1 H, CHN, *J* = 10.8 Hz, *J* = 1.7 Hz); 5.02 (s, 1 H, OH); 7.35 (dd, 1 H, H of pyridine, *J* = 7.8 Hz, *J* = 4.4 Hz); 7.70 (d, 1 H, H of pyridine, *J* = 7.8 Hz); 8.44 (d, 1 H, H of pyridine, *J* = 4.4 Hz); 8.50 (br.s, 1 H, H of pyridine). MS, *m*/*z* (I_{rel} (%)): 312 [M^+] (16); 235 (19); 234 [$M^+ - C_5H_4N$] (100); 161 (24); 115 (38); 105 (51); 77 (51).

(2*S*)-(−)-*N*-(4-Hydroxy-4,4-diphenylbut-2-yn-1-yl)-2-(3-pyridyl)piperidine (10j), the yield was 84%, m.p. 136—137 °C, $[\alpha_D]$ −228.8 (*c* 1.0). Found (%): N, 7.34. $C_{26}H_{26}N_2O$. Calculated (%): N, 7.32. IR, ν/cm^{-1} (Nujol): 3064, 2924, 1592, 1576, 1488, 1452, 1424, 1380, 1340, 1200, 1132, 1112, 1068, 1020, 764, 744, 720, 708, 688. ^{1}H NMR, δ: 1.28, 1.45—1.86 (both m, 1 H, 5 H, CH_2 of piperidine); 2.56 (dt, 1 H, CH_2N, *J* = 11.0 Hz, *J* = 1.6 Hz); 2.90 (d, 1 H, CH_2N, *J* = 11.0 Hz); 3.10, 3.32 (both d, 1 H each, ≡CCH_2N, *J* = 17.1 Hz); 3.36 (d, 1 H, CHN, *J* = 11.0 Hz); 6.58 (s, 1 H, OH); 7.23 (t, 2 H, H arom., *J* = 7.0 Hz); 7.32 (t, 5 H, H arom., H of pyridine, *J* = 7.0 Hz); 7.55 (d, 4 H, H arom., *J* = 8.0 Hz); 7.64 (d, 1 H, H of pyridine, *J* = 7.8 Hz); 8.45 (br.s, 2 H, H of pyridine). MS, *m*/*z* (I_{rel} (%)): 382 [M^+] (26); 381 (16); 305 (22); 304 [$M^+ - C_5H_4N$] (100); 161 (31); 115 (53); 105 (58); 91 (18); 77 (52).

A mixture of mono- and dihydrochlorides 10j·HCl and 10j·2 HCl (20—30%), m.p. 136—138 °C, $[\alpha_D]$ −101.3 (*c* 0.36). ^{1}H NMR, δ: 1.52, 1.90, 2.14 (all m, 1 H, 3 H, 2 H, CH_2 of piperidine); 3.18 (t, 1 H, CH_2N, *J* = 11.0 Hz); 3.67 (overlapped, 1 H, CH_2N); 3.69, 3.97 (both d, 1 H each, ≡CCH_2N, *J* = 17.0 Hz); 4.39 (br.s, 1 H, CHN); 7.27, 7.36 (both t, 2 H, 4 H, H arom., *J* = 7.0 Hz); 7.54, 7.57 (both d, 1 H each, H arom., *J* = 8.1 Hz); 7.69 (t, 1 H, H of pyridine, *J* = 6.8 Hz); 8.44, 8.72, 8.94 (all br.s, 1 H each, H of pyridine).

(2*S*)-(−)-*N*-(4-Acetoxybut-2-yn-1-yl)-2-(3-pyridyl)piperidine (11a), the yield was 66%, oil, $[\alpha_D]$ −210.6 (*c* 0.6). Found (%): N, 10.15. $C_{16}H_{20}N_2O_2$. Calculated (%): N, 10.29. IR, ν/cm^{-1}: 2936, 1748 (OAc), 1592, 1576, 1428, 1228, 1128, 1028, 720. ^{1}H NMR, δ: 1.32, 1.41—1.76 (both m, 1 H, 5 H, of piperidine); 2.12 (s, 3 H, CH_3CO); 2.46 (t, 1 H, CH_2N, *J* = 11.8 Hz); 2.92 (d, 1 H, CH_2N, *J* = 11.0 Hz); 2.97, 3.19 (both d, 1 H each, ≡CCH_2N, *J* = 17.2 Hz); 3.26 (d, 1 H, CHN, *J* = 11.2 Hz); 4.72 (s, 2 H, CH_2O); 7.34 (dd, 1 H, H of pyridine, *J* = 7.4 Hz, *J* = 4.6 Hz); 7.68 (br.d, 1 H, H of pyridine, *J* = 7.4 Hz); 8.47 (d, 1 H, H of pyridine, *J* = 4.6 Hz); 8.50 (s, 1 H, H of pyridine). MS, *m*/*z* (I_{rel} (%)): 272 [M^+] (10); 213 (16); 194 [$M^+ - C_5H_4N$] (92); 105 (21); 92 (20); 77 (14); 51 (22); 43 (100).

Hydrochloride 11a·HCl, m.p. 179—183 °C, $[\alpha_D]$ −132.8 (*c* 0.49). Found (%): Cl, 11.72. $C_{16}H_{20}N_2O_2 \cdot HCl$. Calculated (%): Cl, 11.48.

(2*S*)-(−)-*N*-(4-Acetoxy-4-methylpent-2-yn-1-yl)-2-(3-pyridyl)piperidine (11b), the yield was 73%, oil, $[\alpha_D]$ −207.5 (*c* 0.67). Found (%): N, 9.31. $C_{18}H_{24}N_2O_2$. Calculated (%): N, 9.33. IR, ν/cm^{-1}: 2936, 1744 (OAc), 1592, 1576, 1428, 1368, 1260, 1244, 1136, 956, 716. ^{1}H NMR, δ: 1.65 (s, 6 H, CH_3); 2.49 (overlapped, 1 H, CH_2N); 2.85 (d, 1 H, CH_2N, *J* = 11.0 Hz); 2.94, 3.16 (both d, 1 H each, ≡CCH_2N, *J* = 17.1 Hz); 3.32 (d, 1 H,

CHN, J = 11.0 Hz); 7.34 (dd, 1 H, H of pyridine, J = 7.4 Hz, J = 4.6 Hz); 7.69 (d, 1 H, H of pyridine, J = 7.4 Hz); 8.46 (d, 1 H, H of pyridine, J = 4.6 Hz); 8.50 (s, 1 H, H of pyridine). MS, m/z (I_{rel} (%)): 300 [M^+] (21); 257 (23); 241 (43); 240 (62); 239 (31); 225 (40); 222 [$M^+ - C_5H_4N$] (100); 175 (18); 162 (80); 161 (70); 105 (19); 77 (23); 43 (50).

(2*S*,4´*RS*)-(−)-*N*-(4-Acetoxy-4-methylhex-2-yn-1-yl)-2-(3-pyridyl)piperidine (11c), the yield was 75%, oil, [α_D] −223.6 (*c* 0.37). Found (%): N, 9.30. $C_{19}H_{26}N_2O_2$. Calculated (%): N, 9.26. IR, ν/cm^{-1}: 2936, 2236 (—C≡C—), 1744 (OAc), 1592, 1576, 1428, 1372, 1324, 1304, 1244, 1112, 984, 940, 720. ^{1}H NMR, δ: 0.98 (t, 3 H, J = 6.6 Hz); 1.29, 1.46—1.98 (both m, 1 H, 7 H, CH_2 of piperidine, CH_2CH_3); 1.62 (s, 3 H, CH_3); 2.04 (s, 3 H, CH_3CO); 2.50 (overlapped, 1 H, CH_2N); 2.85 (d, 1 H, CH_2N, J = 11.0 Hz); 2.96, 3.15 (both d, 1 H each, ≡CCH_2N, J = 17.1 Hz); 3.33 (overlapped, 1 H, CH_2N); 7.36 (dd, 1 H, H of pyridine, J = 7.4 Hz, J = 4.6 Hz); 7.70 (d, 1 H, H of pyridine, J = 7.4 Hz); 8.42 (d, 1 H, H of pyridine, J = 4.6 Hz); 8.46 (s, 1 H, H of pyridine). MS, m/z (I_{rel} (%)): 314 [M^+] (10); 255 (15); 236 [$M^+ - C_5H_4N$] (55); 161 (52); 105 (16); 92 (20); 84 (15); 79 (16); 77 (28); 65 (18); 43 (100).

(2*S*)-(−)-*N*-[3-(1-Acetoxycyclohexyl)prop-2-yn-1-yl]-2-(3-pyridyl)piperidine (11d), the yield was 87%, oil, [α_D] −210.1 (*c* 0.55). Found (%): N, 7.98. $C_{21}H_{28}N_2O_2$. Calculated (%): N, 8.23. IR, ν/cm^{-1}: 2936, 2856, 2232 (—C≡C—), 1748 (OAc), 1592, 1560, 1444, 1428, 1368, 1328, 1300, 1264, 1236, 1180, 1100, 964, 716. ^{1}H NMR ($CDCl_3$), δ: 1.36, 1.50—1.92, 2.12 (all m, 2 H, 12 H, 2 H, CH_2 of piperidine, CH_2 of cyclohexane); 2.04 (s, 3 H, CH_3CO); 2.65 (t, 1 H, CH_2N, J = 11.2 Hz); 2.90 (d, 1 H, CH_2N, J = 11.0 Hz); 3.12 (q, 2 H, ≡CCH_2N, J = 17.0 Hz); 3.42 (d, 1 H, CHN, J = 11.0 Hz); 7.25 (overlapped, 1 H, H of pyridine); 7.70 (d, 1 H, H of pyridine, J = 7.2 Hz); 8.50, 8.60 (both br.s, 1 H each, H of pyridine). MS, m/z (I_{rel} (%)): 340 [M^+] (4.0); 280 (12); 262 [$M^+ - C_5H_4N$] (28); 161 (47); 119 (16); 105 (19); 91 (30); 84 (20); 79 (21); 77 (17); 55 (43); 44 (31); 43 (100).

(2*S*,4´*RS*)-(−)-*N*-(4-Acetoxy-4-phenylpent-2-yn-1-yl)-2-(3-pyridyl)piperidine (11e). The product was synthesized from carbinol **10e**, according to the procedure similar to that for acetates **5**. The yield was 92%, oil, [α_D] −196.4 (*c* 0.52). Found (%): N, 7.93. $C_{22}H_{24}N_2O_2$. Calculated (%): N, 8.04. IR, ν/cm^{-1}: 2936, 2268 (—C≡C—), 1740, 1228 (OAc), 1592, 1576, 1456, 1428, 1372, 1100, 1016, 956, 756, 716, 700. ^{1}H NMR, δ: 1.25, 1.42—1.78 (both m, 1 H, 5 H, CH_2 of piperidine); 2.45 (q, 1 H, CH_2N, J = 11.0 Hz); 2.87 (d, 1 H, CH_2N, J = 11.0 Hz); 3.02, 3.25 (both d, 1 H each, ≡CCH_2N, J = 17.2 Hz); 3.24 (overlapped, 1 H, CHN); 6.44 (s, 1 H, CHO); 7.35* (sextet, 1 H, H of pyridine, J = 3.9 Hz); 7.41 (d, 1H), 7.45 (t, 2 H), 7.55 (d, 2 H) (H arom., J = 8.0 Hz); 7.63*, 7.66* (both d, 0.5 H each, H of pyridine, J = 7.6 Hz); 8.38* (br.s, 0.5 H, H of pyridine), 8.46* (d, 1 H, H of pyridine, J = 4.6 Hz); 8.49* (br.s, 0.5 H, H of pyridine). MS, m/z (I_{rel} (%)): 348 [M^+] (27); 289 (29); 288 (14); 270 [$M^+ - C_5H_4N$] (100); 161 (39); 128 (53); 127 (26); 117 (22); 115 (27); 105 (26); 92 (22); 78 (13); 77 (19); 43 (60).

(2*S*)-(−)-*N*-(4-Acetoxy-4-ethylhex-2-yn-1-yl)-2-(3-pyridyl)piperidine (11f). The product was synthesized from carbinol **10f**, according to the procedure similar to that for acetates **5**. The yield was 77%, oil, [α_D] −203.6 (*c* 0.6). Found (%): N, 8.44. $C_{20}H_{28}N_2O_2$. Calculated (%): N, 8.53. IR, ν/cm^{-1}: 2976, 2936, 2240 (—C≡C—), 1744 (OAc), 1592, 1580, 1428, 1368, 1324, 1240, 1124, 1100, 1016, 960, 716. ^{1}H NMR, δ: 0.96 (t, 6 H, CH_3, J = 6.6 Hz); 1.28, 1.45—1.78 (both m, 1 H, 5 H, CH_2 of piperidine); 1.88, 1.96 (both m, 2 H each, CH_2CH_3); 2.02 (s, 3 H, CH_3CO); 2.52 (overlapped, 1 H, CH_2N); 2.86 (d, 1 H, CH_2N, J = 11.2 Hz); 2.96, 3.20 (both d, 1 H each, ≡CCH_2N, J = 17.2 Hz); 3.32 (overlapped, 1 H, CHN); 7.36 (dd, 1 H, H of pyridine, J = 7.4 Hz, J = 4.6 Hz); 7.69 (br.d, 1 H, H of pyridine, J = 7.4 Hz); 8.46 (br.s, 2 H, H of pyridine). MS, m/z (I_{rel} (%)): 328 [M^+] (14); 285 (15); 269 (24); 268 (24); 253 (11); 250 [$M^+ - C_5H_4N$] (68); 239 (24); 161 (86); 92 (24); 79 (21); 77 (22); 55 (21); 43 (100).

(2*S*)-(−)-*N*-(5-Hydroxypent-2-yn-1-yl)-2-(3-pyridyl)piperidine (12a). Method *A*. The product was obtained by the reaction of anabasine hydrochloride (**1**·HCl) (1.56 g, 7 mmol) with paraformaldehyde (0.6 g, 20 mmol) and trimethylsilyl ether **6c** (10 mmol), as described above. The yield was 71%, oil, [α_D] −179.8 (*c* 0.62). Found (%): N, 11.19. $C_{15}H_{20}N_2O$. Calculated (%): N, 11.47. ^{1}H NMR, δ: 1.30—1.78 (m, 6 H, CH_2 of piperidine); 2.34 (t, 2 H, ≡CCH_2 J = 6.8 Hz); 2.45 (dt, 1 H, CH_2N, J = 10.2 Hz, J = 1.8 Hz); 2.90 (overlapped, 1 H, CH_2N); 2.85, 3.08 (both d, 1 H each, ≡CCH_2N, J = 17.2 Hz); 3.28 (br.d, 1 H, CHN, J = 10.2 Hz); 3.52 (q, 1 H, CH_2O, J = 6.8 Hz); 4.70 (s, 1 H, OH); 7.32 (dd, 1 H, H of pyridine, J = 7.8 Hz, J = 4.7 Hz); 7.71 (d, 1 H, H of pyridine, J = 7.8 Hz); 8.44 (d, 1 H, H of pyridine, J = 4.7 Hz); 8.50 (s, 1 H, H of pyridine).

Method *B*. A mixture of acetate **12b** (0.47 g, 1.64 mmol), K_2CO_3 (0.40 g, 2.90 mmol), and MeOH (10 mL) was stirred for 4 h at 20 °C (TLC monitoring), filtered, the solvent was evaporated, and the residue was chromatographed on Al_2O_3. Compound **12a** was obtained (310 mg, 77%), which was identical with that from Method *A*.

Dihydrochloride 12a·2HCl, m.p. 144—147 °C, [α_D] −102.2 (*c* 0.47). Found (%): Cl, 22.48. $C_{15}H_{20}N_2O$·2HCl. Calculated (%): Cl, 23.03. ^{1}H NMR, δ: 1.32, 1.95, 2.09 (all m, 1 H, 3 H, 2 H, CH_2 of piperidine); 2.41 (t, 2 H, ≡CCH_2, J = 6.6 Hz); 3.11 (t, 1 H, CH_2N, J = 10.0 Hz); 3.52, 3.91 (both d, 1 H each, ≡CCH_2N, J = 16.0 Hz); 3.54 (m, 3 H, CH_2O, CH_2N); 4.51 (d, 1 H, CHN, J = 10.0 Hz); 7.84 (t, 1 H, H of pyridine, J = 5.0 Hz); 8.69, 9.08 (both br.s, 1 H each, H of pyridine); 7.82 (d, 1 H, H of pyridine, J = 5.0 Hz). MS, m/z (I_{rel} (%)): 244 [M^+] (15); 213 (15); 166 [$M^+ - C_5H_4N$] (100); 161 (16); 105 (15); 92 (14); 65 (18); 53 (26); 39 (24).

(2*S*)-(−)-*N*-(5-Acetoxypent-2-yn-1-yl)-2-(3-pyridyl)piperidine (12b). The product was obtained by the reaction of anabasine hydrochloride (**1**·HCl) (1.56 g, 7 mmol) with paraformaldehyde (0.6 g, 20 mmol) and acetate **6b** (10 mmol), as described above. The yield was 82%, oil, [α_D] −210.6 (*c* 0.6). Found (%): N, 9.63. $C_{17}H_{22}N_2O_2$. Calculated (%): N, 9.78. IR, ν/cm^{-1}: 2936, 1744 (OAc), 1592, 1580, 1428, 1380, 1324, 1240 (OAc), 1040, 984, 716. ^{1}H NMR ($CDCl_3$), δ: 1.36, 1.52—1.86 (both m, 1 H, 5 H, CH_2 of piperidine); 2.09 (s, 3 H, CH_3CO); 2.54 (m, 3 H, ≡CCH_2, CH_2N); 2.98 (overlapped, 1 H, CH_2N); 3.02, 3.15 (both d, 1 H each, ≡CCH_2N, J = 17.0 Hz); 4.18 (t, 2 H, CH_2O, J = 6.6 Hz); 7.24 (overlapped, 1 H, H of pyridine); 7.69, 8.50, 8.59 (all br.s, 1 H each, H of pyridine). MS, m/z (I_{rel} (%)): 286 [M^+] (1); 208 [$M^+ - C_5H_4N$] (32); 107 (14); 105 (14); 92 (17); 77 (12); 65 (41); 55 (18); 43 (100).

Hydrochloride 12b·HCl, m.p. 146—147 °C, [α_D] −118.5 (*c* 0.53). Found (%): Cl, 11.35. $C_{17}H_{22}N_2O_2$·HCl. Calculated (%): Cl, 10.98.

* Signals of diastereotopic protons of two diastereomers (1 : 1).

(2*S*,5´*RS*)-(−)-*N*-(5-Hydroxyhex-2-yn-1-yl)-2-(3-pyridyl)piperidine (13a). Method *A*. The product was obtained by the reaction of anabasine hydrochloride (**1**·HCl) (1.56 g, 7 mmol) with paraformaldehyde (0.6 g, 20 mmol) and trimethylsilyl ether **7c** (10 mmol), as described above. The yield was 64%, oil $[\alpha_D]$ −197.4 (*c* 0.58). Found (%): N, 10.61. $C_{16}H_{22}N_2O$. Calculated (%): N, 10.84. IR, ν/cm^{-1}: 3370, 2936, 2248 (—C≡C—), 1596, 1580, 1432, 1328, 1212, 1116, 1028, 984, 940, 732, 716. ^{1}H NMR, δ: 1.16 (d, 3 H, CH_3, *J* = 6.6 Hz); 1.28, 1.44—1.80 (both m, 1 H, 5 H, CH_2 of piperidine); 2.19 (dd, 1 H, ≡CCH_2, *J* = 6.6 Hz, *J* = 1.8 Hz); 2.31 (dd, 1 H, ≡CCH_2, *J* = 6.6 Hz, *J* = 1.2 Hz); 2.46 (t, 1 H, CH_2N, *J* = 11.0 Hz); 2.82 (overlapped, 1 H, CH_2N); 2.86, 3.08 (both d, 1 H each, ≡CCH_2N, *J* = 17.2 Hz); 3.3 (br.m, 1 H, CHN); 4.62 (s, 1 H, OH); 3.76 (m, 1 H, CHO); 7.32 (dd, 1 H, H of pyridine, *J* = 7.8, *J* = 4.7 Hz); 7.69 (d, 1 H, H of pyridine, *J* = 7.8 Hz); 8.44 (d, 1 H, H of pyridine, *J* = 4.7 Hz); 8.49 (s, 1 H, H of pyridine). MS, *m/z* (I_{rel} (%)): 258 [M^+] (23); 213 (28); 180 [$M^+ - C_5H_4N$] (100); 105 (12); 45 (35); 43 (12).

Method *B*. A mixture of acetate **13b** (0.45 g, 1.50 mmol), K_2CO_3 (0.35 g, 2.54 mmol), and MeOH (10 mL) was stirred for 4 h at 20 °C (TLC monitoring) and filtered, the solvent was evaporated, the residue was chromatographed on Al_2O_3. Compound **13a** (300 mg, 77%) was obtained, which was identical to that from Method *A*.

(2*S*,5´*RS*)-*N*-(5-Acetoxyhex-2-yn-1-yl)-2-(3-pyridyl) piperidine (13b). The product was obtained by the reaction of anabasine hydrochloride (**1**·HCl) (1.56 g, 7 mmol) with paraformaldehyde (0.6 g, 20 mmol) and acetate **7b** (10 mmol), as described above. The yield was 74%, oil, $[\alpha_D]$ −208.9 (*c* 0.5). Found (%): N, 9.13. $C_{18}H_{24}N_2O_2$. Calculated (%): N, 9.33. IR, ν/cm^{-1}: 1746, 1240 (OAc). ^{1}H NMR ($CDCl_3$), δ: 1.34* (t, 3 H, CH_3, *J* = 6.6 Hz); 1.36, 1.51—1.86 (both m, 5 H, CH_2 of piperidine); 2.07 (s, 3 H, CH_3CO); 2.46 (m, 2H, ≡CCH_2); 2.54 (t, 1 H, CH_2N, *J* = 11.0 Hz); 2.96 (br.d, 1 H, CH_2N, *J* = 11.0 Hz); 3.04, 3.14 (both d, 1 H each, ≡CCH_2N); 3.29 (d, 1 H, CHN, *J* = 11.0 Hz); 5.01 (quintet, 1 H, CHO, *J* = 6.6 Hz); 7.24 (overlapped, 1 H, H of pyridine); 7.64 (d, 1 H, H of pyridine, *J* = 7.6 Hz); 8.49 (d, 1 H, H of pyridine, *J* = 4.6 Hz); 8.57 (br.s, 1 H, H of pyridine). MS, *m/z* (I_{rel} (%)): 300 [M^+] (7); 222 [$M^+ - C_5H_4N$] (46); 161 (24); 79 (20); 77 (18); 43 (100).

(2*S*)-(−)-*N*-[7-Hydroxy-4-methylhept-4(*E*)-en-2-yn-1-yl]-2-(3-pyridyl)piperidine (15). The product was obtained by the reaction of anabasine hydrochloride (**1**·HCl) (1.56 g, 7 mmol) with paraformaldehyde (0.6 g, 20 mmol) and 3-cyclopropylbut-1-yn-3-ol (**3k**) (10 mmol), as described above. The formed mixture of compounds **9k** and **15** was separated by column chromatography on silica gel. The less polar fractions were chromatographed twice with light petroleum—CH_2Cl_2 (from 10 : 1 to 2 : 1) as the eluent. Compound **15** (0.23 g, 12%) was isolated, oil, $[\alpha_D]$ −236.0 (*c* 0.57). Found (%): N, 9.61. $C_{18}H_{24}N_2O$. Calculated (%): N, 9.85. IR, ν/cm^{-1}: 3240, 2932, 1660, 1592, 1580, 1432, 1324, 1172, 1100, 1076, 968, 756, 716. ^{1}H NMR ($CDCl_3$), δ: 1.34, 1.43—1.88 (both m, 1 H, 5 H, CH_2 of piperidine); 1.85 (s, 3 H, CH_3); 2.68 (q, 2 H, ≡CCH_2, *J* = 6.7 Hz); 2.54 (overlapped, 1 H, CH_2N); 2.92 (d, 1 H, CH_2N, *J* = 11.0 Hz); 3.16, 3.34 (both d, 1 H each, ≡CCH_2N, *J* = 16.8 Hz); 3.35 (overlapped, 1 H, CH_2N); 3.67 (t, 2 H, CH_2O, *J* = 6.7 Hz); 5.55 (t, 1 H, (*E*)-CH=, *J* = 6.7 Hz); 5.61 (t, 0.05 H, (*Z*)-CH=, *J* = 6.7 Hz); 7.34 (dd, 1 H, H of pyridine, *J* = 7.4 Hz, *J* = 4.5 Hz); 7.71, 8.47 (both d, 1 H each, H of pyridine); 8.49 (br.s, 1 H, H of pyridine).

(2*S*)-(−)-*N*-(Prop-2-yn-1-yl)-2-(3-pyridyl)piperidine (8i). A finely triturated mixture of compounds **10b**—**d** (2.0 mmol), KOH powder (0.11 g, 2.0 mmol), and diethyleneglycol (5 mL) was heated for 5—7 h at 150—170 °C (15 Torr). The cooled to 20 °C reaction mixture was diluted with ethyl acetate—benzene (1 : 1) mixture (40 mL) and extracted with 3*M* HCl (4×3 mL). The aqueous layer was treated with K_2CO_3, extracted with benzene—ethyl acetate (2 : 1) mixture. The extract was sequentially washed with water and brine, dried with $MgSO_4$, and concentrated. The residue was dissolved in CH_2Cl_2 (1—2 mL) and chromatographed on a column (25×2.5 cm) with SiO_2 (25.0—30.0 g). Compound **8i** was obtained, the yield was 62—67%, m.p. 72 °C, $[\alpha_D]$ −225.6 (*c* 0.43). Found (%): N, 13.73. $C_{13}H_{16}N_2$. Calculated (%): N, 13.99. IR, ν/cm^{-1}: 3296, 2104 (—C≡C—), 2936, 2852, 1592, 1576, 1428, 1324, 1100, 1024, 984, 756, 716. ^{1}H NMR, δ: 1.32, 1.45—1.78 (both m, 1 H, 5 H, CH_2 of piperidine); 2.46 (dt, 1 H, CH_2N, *J* = 11.0 Hz, *J* = 2.0 Hz); 2.87 (t, 1 H, ≡CH, *J* = 2.2 Hz); 2.92, 3.15 (both d, 1 H each, ≡CCH_2N, *J* = 17.2 Hz); 3.16 (br.d, 1 H, CH_2N, *J* = 10.0 Hz); 3.29 (dd, 1 H, CHN, *J* = 12.0 Hz, *J* = 1.8 Hz); 7.36 (dd, 1 H, *J* = 7.6 Hz, *J* = 4.4 Hz); 7.70 (d, 1 H, *J* = 7.6 Hz); 8.42 (d, 1 H, *J* = 4.4 Hz); 8.43 (d, 1 H, *J* = 1.6 Hz); MS, *m/z* (I_{rel} (%)): 200 [M^+] (26); 171 (11); 161 (11); 143 (15); 131 (14); 123 (26); 122 [$M^+ - C_5H_4N$] (100); 105 (46); 92 (27); 65 (35); 55 (34).

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* Signals of diastereotopic protons of two diastereomers (1 : 1).

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