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Synthesis of 2,3-Acetylenic Amines by Aminomethylation of Acetylenes with Geminal Diamines

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Abstract—A general and effective procedure has been developed for the synthesis of symmetrical and unsymmetrical 2,3-acetylenic amines by aminomethylation of terminal mono- and diacetylenes with geminal diamines in the presence of transition metal salts and complexes.

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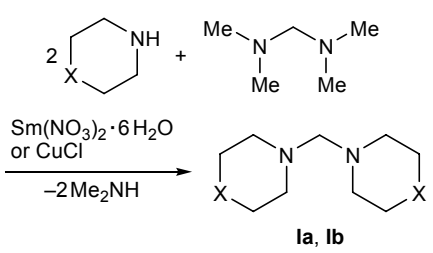
Alk-2-yn-1-amines are widely used in the synthesis of cyclic and acyclic heteroatom compounds [1–9]. A well known procedure for the synthesis of such amines is based on Mannich aminomethylation of terminal acetylenes [10] by the action of secondary amines and aldehydes or geminal diamines in the presence of copper-containing catalysts [11–17]. Dipiperidinomethane was shown to be inactive in aminomethylation of terminal acetylenes [18]. We recently found [19] that *N*,*N*,*N*′,*N*′-tetramethylmethanediamine fairly readily reacts with terminal acetylenes to give the corresponding *N*,*N*-dimethylalk-2-yn-1-amines. The proposed procedure [19] makes it possible to avoid the use of toxic solvents (dioxane, dimethylformamide, methylene chloride, acetonitrile, dimethyl sulfoxide, etc.) and ensures considerably lower consumption of the catalyst in addition to shorter reaction time.

With a view to extend the scope of aminomethylation of terminal alkynes with diamines in the presence of transition metal catalysts, as well as to develop an efficient procedure for the synthesis of various alk-2-yn-1-amines, in the present work we examined reactions of geminal diamines with terminal acetylenes and diacetylenes in the presence of catalysts which showed the highest activity in the aminomethylation of acetylenes with *N*,*N*,*N*′,*N*′-tetramethylmethanediamine [19]. We presumed that, by analogy with *N*,*N*,*N*′,*N*′-tetramethylmethanediamine [19], higher geminal diamines can also be used for aminomethylation of terminal alkynes to obtain the corresponding acetylenic amines.

Scheme 1.



Ia, **Ib**

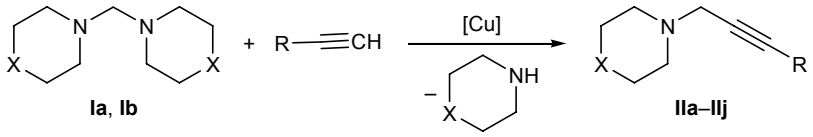
X = CH_2 (**a**), O (**b**).

First of all, we have developed a preparative procedure for the synthesis of initial geminal diamines **Ia** and **Ib** via transamination of *N*,*N*,*N*′,*N*′-tetramethylmethanediamine with piperidine and morpholine (80°C, 6 h) in the presence of 5–10 mol % of $Sm(NO_3)_2 \cdot 6H_2O$ or CuCl (Scheme 1). These catalysts ensured the best yields of the target products (Table 1). The structure of compounds **Ia** and **Ib** was confirmed by spectral methods, including ^{15}N NMR spectroscopy.

Table 1. Transamination of *N*,*N*,*N*′,*N*′-tetramethylmethanediamine with piperidine and morpholine (molar ratio diamine–amine–catalyst 1 : 2 : 0.05, 80°C, 6 h, argon)

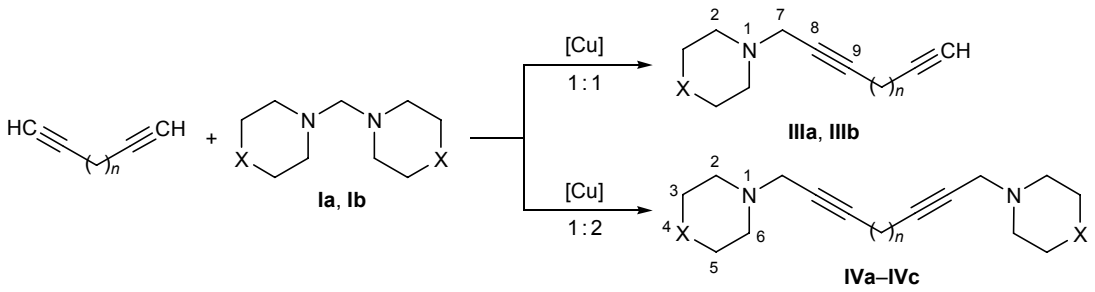
Catalyst	Initial amine	Yield of **Ia** or **Ib**, %
$Sm(NO_3)_2 \cdot 6H_2O$	Piperidine	85
CuCl	Piperidine	77
No catalyst	Piperidine	38
$Sm(NO_3)_2 \cdot 6H_2O$	Morpholine	89
CuCl	Morpholine	80
No catalyst	Morpholine	34

Scheme 2.



II, X = CH_2, R = Pr (**a**), Bu (**b**), C_5H_{11} (**c**), C_6H_{13} (**d**), Ph (**e**); X = O, R = C_6H_{13} (**f**), C_5H_{11} (**g**), Bu (**h**), Pr (**i**), Ph (**j**).

Scheme 3.



III, n = 4, X = CH_2 (**a**), O (**b**); **IV**, n = 4, X = CH_2 (**a**), O (**b**), n = 6, X = O (**c**).

Diamine **Ia** displayed in the ^{15}N NMR spectrum only one signal at δ_N 314.7 ppm due to its symmetric structure.

Symmetric diamines **Ia** and **Ib** were brought into reactions with terminal alkynes (pent-1-yne, hex-1-yne, hept-1-yne, oct-1-yne, and phenylacetylene) in the presence of CuCl or $Sm(NO_3)_2 \cdot 6H_2O$ [molar ratio **I**–alkyne–catalyst 1:1:0.05]. The reactions were carried out by heating the reactants at 80°C over a period of 6 h, and the products were the corresponding 1-[piperidino(morpholino)methyl]-2-alkyl(phenyl)acetylenes **IIa**–**IIe** whose yields ranged from 60 to 85%, depending on the initial diamine and acetylenic substrate (Scheme 2, Table 2).

Table 2. Aminomethylation of terminal alkynes with diamines **Ia** and **Ib** in the presence of CuCl (molar ratio diamine **I**–alkyne–CuCl 1:1:0.05, 80°C, 6 h)

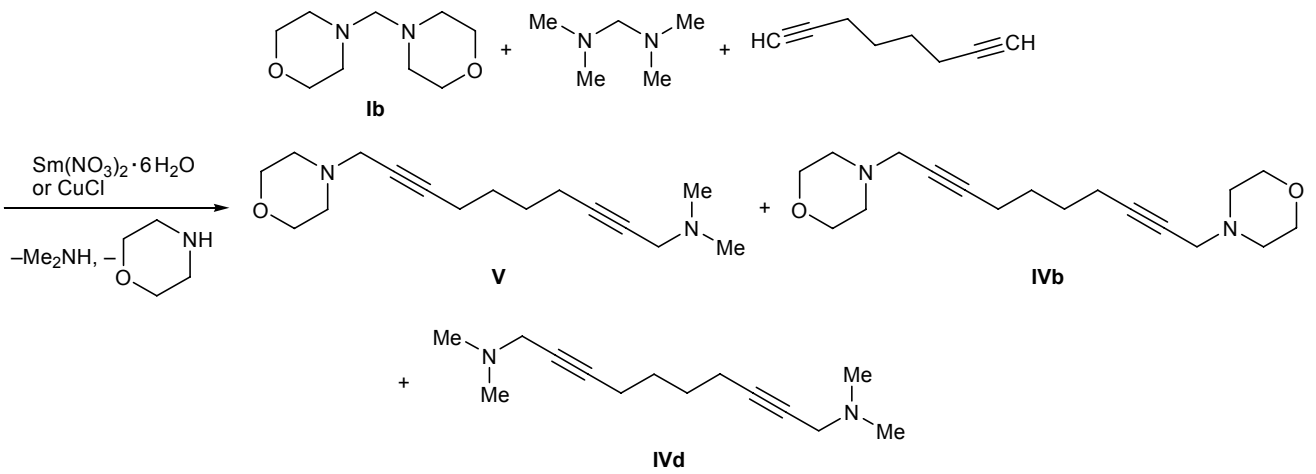
Initial diamine no.	Acetylene	Yield, %
Ia	Oct-1-yne	68
Ia	Hept-1-yne	60
Ia	Hex-1-yne	61
Ia	Pent-1-yne	64
Ib	Oct-1-yne	42
Ib	Hept-1-yne	51
Ib	Hex-1-yne	48
Ib	Pent-1-yne	73
Ia	Oct-1-yne	61[a]
Ia	Pent-1-yne	63[a]
Ia	Phenylacetylene	97
Ib	Oct-1-yne	85[a]
Ib	Hex-1-yne	64[a]
Ib	Phenylacetylene	98

[a] In the presence of $Sm(NO_3)_2 \cdot 6H_2O$ as catalyst.

We also tried to perform aminomethylation of terminal diacetylenes with diamines **Ia** and **Ib** under analogous conditions [5 mol % of $Sm(NO_3)_2 \cdot 6H_2O$ or CuCl, 80°C, 6 h]. In the reaction of octa-1,7-diyne with an equimolar amount of dipiperidinomethane (**Ia**) we obtained >90% of 1-(nona-2,7-diyn-1-yl)piperidine (**IIIa**) (Scheme 3). The downfield region of the ^{13}C NMR spectrum of **IIIa** contained four signals at δ_C 68.48, 84.55, 74.70, and 84.00 ppm, indicating the presence of four nonequivalent triple-bonded carbon atoms. The absence of a signal at δ_C 82.89 ppm (typical of methylene carbon atom in the N–CH_2–N fragment of initial diamine **Ia**), downfield shift of signals from acetylenic carbon atoms (C^8, C^9; $\Delta\delta_C$ 2.0–6.0 ppm), and the absence of a signal assignable to acetylenic proton (δ 3.13 ppm) in the ^1H NMR spectrum indicated that aminomethylation of initial octa-1,7-diyne involved only one terminal acetylenic group.

Two-dimensional heteronuclear HMBC experiments revealed couplings between 7-H (δ 3.0 ppm), on the one hand, and C^8 and C^9, on the other. In addition, the ^{13}C NMR spectrum of **IIIa** contained cross peaks between C^7 (δ_C 47.51 ppm) and C^2/C^6 in the piperidine

Scheme 4.



ring, so that compound **IIIa** was assigned the structure of monosubstituted diacetylene.

Our results allowed us to expect successful aminomethylation at both ≡CH groups in other terminal diacetylenes with geminal diamines with formation of symmetrical bis(aminomethyl) derivatives in which the acetylenic fragments are linked through polymethylene chains. As diacetylenic substrates we selected hepta-1,6-diyne, octa-1,7-diyne, and deca-1,9-diyne. By reaction of hepta-1,6-diyne with dipiperidinomethane at a ratio of 1:2 [5 mol % of CuCl or $Sm(NO_3)_2 \cdot 6H_2O$, 80°C, 6 h] we obtained 1,9-dipiperidinonona-2,7-diyne (**IVa**) in more than 70% yield. The ^{13}C NMR spectrum of **IVa** contained signals from magnetically equivalent (in pairs) carbon atoms in the acetylenic fragments at δ_C 84.42 (C^9, C^{14}) and 74.76 ppm (C^8, C^{15}). Likewise, the reactions of dimorpholinomethane with octa-1,7-diyne and deca-1,9-diyne gave 1,10-dimorpholinodeca-2,8-diyne (**IVb**) and 1,12-dimorpholinododeca-2,10-diyne (**IVc**) in 75 and 70% yield, respectively (Scheme 3).

With a view to obtain unsymmetrically substituted diamino diacetylene, octa-1,7-diyne was subjected to aminomethylation with a 1:1 mixture of *N*,*N*,*N*′,*N*′-tetramethylmethanediamine and dimorpholinomethane under the above conditions. The reaction gave a mixture of unsymmetrical 1-dimethylamino-10-morpholinodeca-2,8-diyne (**V**, yield 31%) and two symmetrically substituted products, 1,10-dimorpholinodeca-2,8-diyne (**IVb**) and 1,10-bis(dimethylamino)deca-2,8-diyne (**IVd**), at a ratio of ~1:1:1 (Scheme 4). The fraction of unsymmetrical product **V** may be increased to 60% by adding first an equimolar amount of bis(dimethylamino)methane and then (after 3 h) an equimolar amount of dimorpholinomethane.

Thus transition metal-catalyzed aminomethylation of terminal mono- and diacetylenes with geminal diamines opens a convenient and promising synthetic route to 2,3-acetylenic amines.

EXPERIMENTAL

The progress of reactions was monitored by TLC on Silufol plates using the following solvent systems: acetone–methanol (9:2 to 9:3), acetone–chloroform (9:1), and acetone–ethanol (9:1). Commercially available acetylenic substrates and solvents of chemically pure grade were used. The mass spectra were recorded on a VG-TRIO mass spectrometer. The ^1H and ^{13}C NMR spectra were measured on Jeol FX-90Q (90 and 22.5 MHz, respectively) and Bruker Avance 400 spectrometers (400.13 and 100.62 MHz, respectively) using $CDCl_3$ as solvent and tetramethylsilane as internal reference. The IR spectra were recorded in KBr on a Specord 75IR instrument. The elemental compositions were determined on a Carlo Erba 1106 analyzer. The products were analyzed by GLC on a Khrom-5 chromatograph equipped with a flame-ionization detector and a 2000×3-mm column; stationary phase SE-30; oven temperature programming from 50 to 280°C at a rate of 8 deg/min); injector temperature 300°C, detector temperature 250°C.

Geminal diamines Ia and Ib (*general procedure***).** A glass reactor equipped with a magnetic stirrer was charged under argon with 10 mmol of piperidine or morpholine, 20 mmol of *N*,*N*,*N*′,*N*′-tetramethylmethanediamine, and 0.5 mmol of CuCl or $Sm(NO_3)_2 \cdot 6H_2O$, and the mixture was stirred for 6 h at 80°C. Compounds **Ia** and **Ib** were isolated by vacuum distillation or column chromatography.

1,1′-Methylenedipiperidine (Ia). Yield 85%, bp 98–100°C (8 mm), n_D^{25} = 1.4798. IR spectrum: ν 1235 cm^{-1} (C–N–C). ^1H NMR spectrum, δ, ppm: 2.67 s (2H), 2.27 m (8H), 1.34 m (12H). ^{13}C NMR spectrum, δ_C, ppm: 24.74, 25.71, 52.74, 82.89. ^{15}N NMR spectrum: δ_N 314.7 ppm. Found, %: C 73.04; H 12.06; N 14.58. $C_{11}H_{22}N_2$. Calculated, %: C 73.08; H 12.28; N 14.64.

4,4′-Methylenedimorpoline (Ib). Yield 89%, bp 111–113°C (8 mm), n_D^{25} = 1.5314. IR spectrum, ν, cm^{-1}: 1220 (C–N–C), 1070 (C–O–C). ^1H NMR spectrum, δ, ppm: 2.79 s (2H), 2.37 m (8H), 3.57 m (8H). ^{13}C NMR spectrum, δ_C, ppm: 51.86, 66.84, 81.56. Found, %: C 55.98; H 9.64; N 14.51. $C_9H_{18}N_2O_2$. Calculated, %: C 58.06; H 9.67; N 15.07.

Aminomethylation of terminal mono- and diacetylenes (*general procedure*). A glass reactor equipped with a magnetic stirrer was charged under argon with 1–3 mmol of diamine **Ia** or **Ib**, 1 mmol of the corresponding terminal acetylene or 0.5 mmol of diacetylene, and 0.05 mmol of CuCl or $Sm(NO_3)_2 \cdot 6H_2O$, and the mixture was stirred for 6 h at 80°C. Compounds **II**–**IV** were isolated from the reaction mixture by vacuum distillation or column chromatography.

1-(Hex-2-yn-1-yl)piperidine (IIa). Yield 64%, bp 108–111°C (8 mm), n_D^{25} = 1.5293. IR spectrum, ν, cm^{-1}: 2250 (C≡C), 1240 (C–N–C). ^1H NMR spectrum, δ, ppm: 0.89 t (3H, *J* = 7 Hz), 1.21–1.54 m (4H), 2.21 t (2H), 2.39 m (4H), 2.51 m (4H), 3.19 s (2H). ^{13}C NMR spectrum, δ_C, ppm: 12.91, 18.65, 22.42, 24.42, 26.25, 27.80, 30.53, 47.20, 52.80, 75.05, 84.03. Found, %: C 78.28; H 11.61; N 7.00. $C_{11}H_{20}N$. Calculated, %: C 79.52; H 12.05; N 8.43.

1-(Hept-2-yn-1-yl)piperidine (IIb). Yield 61%, bp 125–127°C (8 mm), n_D^{25} = 1.5314. IR spectrum, ν, cm^{-1}: 2235 (C≡C), 1280 (C–N–C). ^1H NMR spectrum, δ, ppm: 0.87 t (3H, *J* = 7 Hz), 1.09–1.77 m (6H), 2.09 t (2H), 2.41 m (4H), 3.41 m (4H), 3.18 s (2H). ^{13}C NMR spectrum, δ_C, ppm: 13.27, 18.19, 21.74, 23.73, 25.52, 30.79, 47.92, 53.16, 74.75, 85.33. Found, %: C 77.20; H 11.72; N 6.92. $C_{12}H_{23}N$. Calculated, %: C 79.33; H 12.85; N 7.82.

1-(Oct-2-yn-1-yl)piperidine (IIc). Yield 60%, bp 129–131°C (8 mm), n_D^{25} = 1.5310. IR spectrum, ν, cm^{-1}: 2230 (C≡C), 1190 (C–N–C). ^1H NMR spectrum, δ, ppm: 0.87 t (3H, *J* = 7 Hz), 1.23–1.53 m (8H), 1.60 m (4H), 2.16 t (2H, *J* = 7 Hz), 2.47 m (4H). ^{13}C NMR spectrum, δ_C, ppm: 12.91, 18.65, 22.42, 24.42, 26.25, 27.80, 30.53, 47.20, 52.80, 75.05, 84.03. Found, %: C 78.28; H 11.61; N 7.00. $C_{13}H_{23}N$. Calculated, %: C 80.82; H 11.92; N 7.26.

1-(Non-2-yn-1-yl)piperidine (IId). Yield 68%, bp 148–151°C (8 mm), n_D^{25} = 1.5297. IR spectrum, ν, cm^{-1}: 2260 (C≡C), 1200 (C–N–C). ^1H NMR spectrum, δ, ppm: 0.84 t (3H, *J* = 7 Hz), 1.00–1.65 m (12H), 2.09 t (2H), 3.10 s (2H), 2.37 m (4H), 2.14 m (4H). ^{13}C NMR spectrum, δ_C, ppm: 12.91, 18.65, 22.42, 24.42, 26.25, 27.80, 30.53, 47.20, 52.80, 75.05, 84.03. Found, %: C 76.65; H 11.46; N 6.76. $C_{14}H_{25}N$. Calculated, %: C 81.16; H 12.08; N 6.76.

1-(3-Phenylprop-2-yn-1-yl)piperidine (IIe). Yield 97%, bp 124–125°C (2 mm), n_D^{25} = 1.5611. IR spectrum, ν, cm^{-1}: 2160 (C≡C), 1220 (C–N–C). ^1H NMR spectrum, δ, ppm: 2.10–2.65 m (4H), 3.29 s (2H), 3.10–3.74 m (4H), 7.04–7.34 m (5H). ^{13}C NMR spectrum, δ_C, ppm: 24.82, 25.80, 43.21, 52.80, 84.10, 84.21, 123.33, 127.92, 128.31, 131.77. Found, %: C 84.21; H 6.28; N 7.36. $C_{14}H_{17}N$. Calculated, %: C 86.60; H 6.18; N 7.22.

4-(Non-2-yn-1-yl)morpholine (IIf). Yield 85%, bp 150–153°C (8 mm), n_D^{25} = 1.5308. IR spectrum, ν, cm^{-1}: 2250 (C≡C), 1120 (C–O–C), 1040 (C–N–C). ^1H NMR spectrum, δ, ppm: 0.89 br.s (3H), 1.35 m (4H), 2.16 m (2H), 3.26 s (2H), 2.45 m (4H), 3.62 m (4H). ^{13}C NMR spectrum, δ_C, ppm: 13.24, 18.09, 21.71, 30.69, 47.47, 52.12, 66.48, 74.07, 85.82. Found, %: C 76.65; H 11.46; N 6.3. $C_{13}H_{23}NO$. Calculated, %: C 75.73; H 9.70; N 7.77.

4-(Oct-2-yn-1-yl)morpholine (IIg). Yield 51%, bp 140–143°C (8 mm), n_D^{25} = 1.5282. IR spectrum, ν, cm^{-1}: 1125 (C–O–C), 1240 (C–N–C), 2245 (C≡C). ^1H NMR spectrum, δ, ppm: 0.89 br.s (3H), 1.35 m (4H), 2.16 m (2H), 2.45 m (4H), 3.26 s (2H), 3.62 m (4H). ^{13}C NMR spectrum, δ_C, ppm: 13.24, 18.09, 21.71, 30.69, 47.47, 52.12, 66.48, 74.07, 85.82. Found, %: C 75.93; H 12.37; N 7.27. $C_{12}H_{21}NO$. Calculated, %: C 75.36; H 10.14; N 6.76.

4-(Hept-2-yn-1-yl)morpholine (IIh). Yield 64%, bp 120–123°C (8 mm), n_D^{25} = 1.5275. IR spectrum, ν, cm^{-1}: 1120 (C–O–C), 1270 (C–N–C), 2245 (C≡C). ^1H NMR spectrum, δ, ppm: 0.89 br.s (3H), 1.35 m (4H), 2.16 m (2H), 3.26 s (2H), 2.45 m (4H), 3.62 m (4H). ^{13}C NMR spectrum, δ_C, ppm: 13.24, 18.09, 21.71, 30.69, 47.47, 52.12, 66.48, 74.07, 85.82. Found, %: C 72.93; H 10.56; N 7.70. $C_{11}H_{19}NO$. Calculated, %: C 72.93; H 10.50; N 7.73.

4-(Hex-2-yn-1-yl)morpholine (IIi). Yield 73%, bp 129–130°C (8 mm), n_D^{25} = 1.4905. IR spectrum, ν, cm^{-1}: 1120 (C–O–C), 1190 (C–N–C), 2250 (C≡C).

^{1}H NMR spectrum, δ, ppm: 0.89 br.s (3H), 1.35 m (4H), 2.16 m (2H), 2.45 m (4H), 3.26 s (2H), 3.62 m (4H). ^{13}C NMR spectrum, δ_C, ppm: 13.24, 18.09, 21.71, 30.69, 47.47, 52.12, 66.48, 74.07, 85.82. Found, %: C 75.93; H 12.37; N 7.27. $C_{10}H_{17}NO$. Calculated, %: C 71.43; H 10.71; N 8.34.

4-(3-Phenylprop-2-yn-1-yl)morpholine (IIj). Yield 98%, bp 130–131°C (2 mm), n_D^{25} = 1.5657. IR spectrum, ν, cm^{-1}: 1120 (C–O–C), 1180 (C–N–C), 2265 (C≡C). ^{1}H NMR spectrum, δ, ppm: 2.10–2.65 m (4H), 3.29 s (2H), 3.10–3.74 m (4H), 7.04–7.34 m (5H). ^{13}C NMR spectrum, δ_C, ppm: 51.70, 52.38, 66.48, 81.23, 82.41, 123.23, 127.86, 128.31, 131.77. Found, %: C 78.35; H 9.12; N 8.64. $C_{13}H_{15}NO$. Calculated, %: C 77.60; H 7.45; N 6.99.

1-(Nona-2,7-diyn-1-yl)piperidine (IIIa). Yield 90%, bp 129–131°C (10 mm), n_D^{25} = 1.5294. IR spectrum, ν, cm^{-1}: 1200 (C–N–C), 1160 (C–O–C), 2260 (C≡C). ^{1}H NMR spectrum, δ, ppm: 1.81 s (1H), 2.02 br.s (4H), 1.41 m (4H), 3.01 br.s (2H) 2.30 m (4H), 1.41 m (4H), 1.22 m (2H). ^{13}C NMR spectrum, δ_C, ppm: 17.43, 17.73, 24.96, 25.8, 27.20, 27.33, 47.20, 52.70, 68.50, 74.61, 82.20, 86.00. Found, %: C 79.24; H 9.46; N 7.25. $C_{14}H_{21}N$. Calculated, %: C 82.76; H 10.34; N 6.80.

4-(Nona-2,7-diyn-1-yl)morpholine (IIIb). Yield 54%, bp 133–135°C (10 mm), n_D^{25} = 1.5287. IR spectrum, ν, cm^{-1}: 2260 (C≡C), 1040 (N–C–N). ^{1}H NMR spectrum, δ, ppm: 1.41 m (4H), 1.80 s (1H), 2.03 br.s (4H), 2.27 m (4H), 3.18 br.s (2H), 3.70 m (4H). ^{13}C NMR spectrum, δ_C, ppm: 17.34, 17.68, 27.11, 27.39, 47.90, 52.40, 66.88, 68.40, 74.70, 82.40, 85.79. Found, %: C 75.25; H 9.00; N 5.98. $C_{13}H_{17}NO$. Calculated, %: C 76.09; H 9.28; N 6.83.

1,9-Dipiperidinonona-2,7-diyne (IVa). Yield 71%, bp 196–199°C (5 mm), n_D^{25} = 1.5191. IR spectrum, ν, cm^{-1}: 2260 (C≡C), 1290 (C–N–C). ^{1}H NMR spectrum, δ, ppm: 1.37 br.m (4H), 1.80–2.20 m (4H), 2.47 m (8H), 2.93 s (4H), 6.61 m (8H). ^{13}C NMR spectrum, δ_C, ppm: 17.65, 21.90, 23.50, 25.13, 47.27, 53.62, 75.14, 83.05. Found, %: C 78.25; H 9.46; N 7.86. $C_{19}H_{30}N_2$. Calculated, %: C 79.72; H 10.48; N 9.79.

1,10-Dimorpholinodeca-2,8-diyne (IVb). Yield 75%, mp 60–61°C. IR spectrum, ν, cm^{-1}: 2260 (C≡C), 1160 (C–O–C), 1190 (C–N–C). ^{1}H NMR spectrum, δ, ppm: 1.57 m (4H), 2.18 m (4H), 2.50 m (8H), 3.19 br.s (4H), 3.70 m (8H). ^{13}C NMR spectrum, δ_C, ppm: 18.19, 27.86, 47.69, 52.41, 66.87, 74.85, 85.24. Found, %: C 68.21; H 8.88; N 8.97. $C_{18}H_{28}N_2O_2$. Calculated, %: C 71.05; H 9.22; N 9.22.

1,12-Dimorpholinododeca-2,10-diyne (IVc). Yield 70%, mp 70–72°C. IR spectrum, ν, cm^{-1}: 1120 (C–O–C), 2275 (C≡C). ^{1}H NMR spectrum, δ, ppm: 1.39 m (8H), 2.16 m (4H), 2.51 m (8H), 3.20 br.s (4H), 3.71 m (8H). ^{13}C NMR spectrum, δ_C, ppm: 18.37, 28.32, 28.64, 47.72, 52.38, 66.87, 74.59, 85.28. Found, %: C 69.98; H 9.01; N 7.47. $C_{20}H_{32}N_2O_2$. Calculated, %: C 72.20; H 9.65; N 8.42.

***N*,*N*,*N*′,*N*′-Tetramethyldeca-2,8-diyne-1,10-diamine (IVd)** [19]. Yield 20%, bp 91°C (3 mm). IR spectrum: ν 1270 cm^{-1} (C–N). ^{1}H NMR spectrum, δ, ppm: 1.47 t (4H, J = 6.87 Hz), 2.19 s (12H), 2.2–2.5 m (4H), 3.11 s (4H). ^{13}C NMR spectrum, δ_C, ppm: 18.65, 27.89, 43.80, 48.12, 75.66, 84.71. Found, %: C 75.9; H 11.30; N 11.92. $C_{14}H_{24}N_2$. Calculated, %: C 76.36; H 10.91; N 12.72.

***N*,*N*-Dimethyl-10-morpholinodeca-2,8-diyn-1-amine (V).** Yield 58%, bp 181°C (8 mm). ^{1}H NMR spectrum, δ, ppm: 1.23 m (4H), 1.41 s (4H), 2.02 m (4H), 2.19 s (6H), 2.31 br.s (4H), 3.19 s (2H), 3.21 s (2H). ^{13}C NMR spectrum, δ_C, ppm: 18.96, 26.93, 43.69, 47.60, 48.40, 52.41, 66.88, 74.70, 75.12, 84.90, 85.12. Found, %: C 73.26; H 9.93; N 10.70. $C_{16}H_{26}N_2O$. Calculated, %: C 73.28; H 9.93; N 10.69.

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