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Synthesis of *N*-substituted tetrapropargylamines by catalytic aminomethylation of α,ω-diacetylenes

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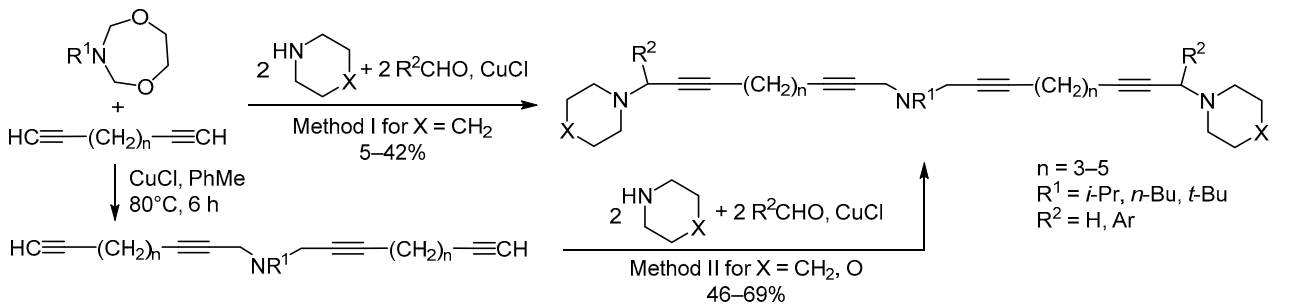

A catalytic method was developed for the synthesis of *N*-substituted tetrapropargylamines by reactions of α,ω-diacetylenes with 1,5,3-dioxazepanes, aldehydes (benzaldehydes, formaldehyde), and cyclic secondary amines.

Keywords: copper(I) chloride, α,ω-diacetylenes, 1,5,3-dioxazepanes, tetrapropargylamines, aminomethylation.

Multicomponent reactions represent a very common methodology for organic synthesis.[1] According to literature data,[2] three-component condensation of amines, aldehydes, and acetylenes (A^3-coupling) provides an effective approach for the synthesis of propargylamines. A modification of this reaction is the double aminomethylation of terminal acetylenes, which leads to dipropargylamines and includes several variants: a) a reaction of 1,7-octadiyne with aromatic aldehydes and cyclic secondary amines with the formation of dipropargylamines,[3] b) a reaction of terephthalaldehyde with phenylacetylene and piperidine or morpholine,[4] c) a reaction of secondary diamines with benzaldehyde and phenylacetylene.[5] Double aminomethylation can be also performed by using a primary amine[6] or *N*-methylformamide.[7] Di- and tetrapropargylamines were obtained by heterocyclization of piperazine, formaldehyde, and α,ω-dipropargylic alcohols.[8] Multicomponent reactions of α,ω-diacetylenes with secondary amines and terephthalaldehyde or reactions of α,ω-diacetylenes with primary amines and aldehydes (polycoupling) led to the formation of polymeric products.[9]

Quite limited data are available on methods used for the synthesis of azatetraynes belonging to propargylamine series.[8,10] We recently proposed a procedure for the preparation of cyclic and acyclic azatetraynes by reactions of *N*-substituted bis(ethoxymethyl)amines[11] or 1,5,3-dioxazepanes[12] with α,ω-diacetylenic hydrocarbons in the presence of copper salts as catalysts. Our interest toward propargylamines was motivated by their applications in the role of biologically active compounds[13] and building blocks for organic synthesis.[10e,14]

In a continuation of our research aimed at the synthesis of azatetraynes,[11,12] as well as in order to develop an effective method for the preparation of triazatetraynes belonging to the propargylamine series, we studied the reaction of *N*-substituted 1,5,3-dioxazepanes with α,ω-diacetylenes, aldehydes (halogenated benzaldehydes, formaldehyde), and cyclic secondary amines in the presence of CuCl as catalyst that has shown high activity in aminomethylation reactions of terminal acetylenes.[15]

In the case of reaction between *N*-(*n*-butyl)-1,5,3-dioxazepane, 1,7-octadiyne, piperidine (**2a**) as secondary amine, and *p*-bromobenzaldehyde (**3c**), it was established that this synthesis can be performed by a one-pot four-component condensation of the starting reagents (Scheme 1, method I) with the formation of the target compound –

Scheme 1

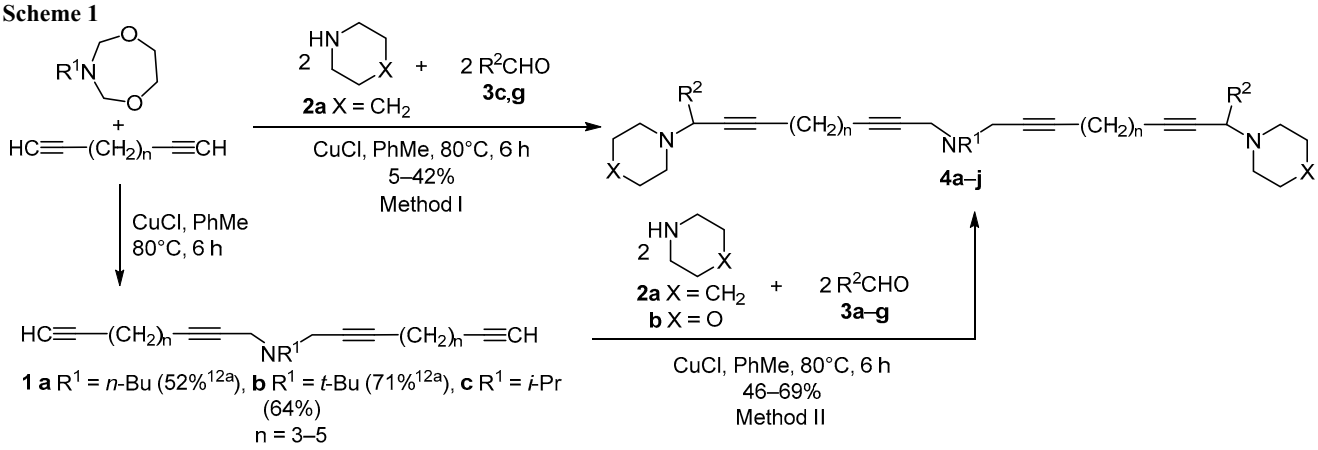

Table 1. Yields of compounds **4a**–**j**

Azatetrayne	R^1	Amine	X	Aldehyde	R^2	Product	n	Yield,%	
								Method I*	Method II**
1a	*n*-Bu	**2a**	CH_2	**3a**	*m*-FC_6H_4	**4a**	4	7	34 (65)
1a	*n*-Bu	**2a**	CH_2	**3b**	*m*-ClC_6H_4	**4b**	4	5	29 (56)
1a	*n*-Bu	**2a**	CH_2	**3c**	*p*-BrC_6H_4	**4c**	4	9	27 (51)
1a	*n*-Bu	**2a**	CH_2	**3d**	*m*-$CF_3C_6H_4$	**4d**	4	–	31 (59)
1b	*t*-Bu	**2a**	CH_2	**3e**	*p*-FC_6H_4	**4e**	4	–	36 (53)
1b	*t*-Bu	**2a**	CH_2	**3f**	*p*-ClC_6H_4	**4f**	3	–	34 (48)
1b	*t*-Bu	**2b**	O	**3c**	*p*-BrC_6H_4	**4g**	4	–	33 (46)
1a	*n*-Bu	**2a**	CH_2	**3g**	H	**4h**	4	39	34 (65)
1a	*n*-Bu	**2a**	CH_2	**3g**	H	**4i**	5	42	36 (69)
1c	*i*-Pr	**2a**	CH_2	**3g**	H	**4j**	3	25	37 (58)

* Yield calculated relative to 1,5,3-dioxazepane.
** Overall yield. Yield relative to azatetrayne **1** is indicated in parentheses.

10-(4-bromophenyl)-*N*-[10-(4-bromophenyl)-10-(piperidin-1-yl)deca-2,8-diyn-1-yl]-*N*-butyl-10-(piperidin-1-yl)deca-2,8-diyne-1-amine (**4c**). Compound **4c** can be also obtained by a two-step procedure (method II) involving isolation of azatetrayne intermediate **1**,[12a] which subsequently reacted with piperidine (**2a**) and *p*-bromobenzaldehyde (**3c**).

The one-pot procedure (method I) was performed by first mixing *n*-butyl-1,5,3-dioxazepane with 1,7-octadiyne for 6 h under argon atmosphere at 80°C in PhMe medium in the presence of CuCl catalyst (5 mol %), followed by the addition of piperidine (**2a**), *p*-bromobenzaldehyde (**3c**), CuCl (5 mol %), and continuing the stirring for 6 h at 80°C. Triazatetraacetylene **4c** was formed under these conditions in approximately 9% yield (Table 1).

A two-step procedure (method II) involved the initial isolation of azatetrayne **1a**, and in this case the yield of triazatetrayne **4c** reached 51% when calculated from azatetrayne **1a**. The reaction was performed in PhMe medium under argon atmosphere in the presence of CuCl (5 mol %) at 80°C over the course of 6 h. Under these conditions, the aminomethylation of azatetraynes **1a**–**c** was performed with benzaldehydes **3a**–**g** (*m*-, *p*-fluorobenzaldehyde, *m*-, *p*-chlorobenzaldehyde, *p*-bromobenzaldehyde, *m*-(trifluoromethyl)benzaldehyde), 1,6-hexadiyne, and morpholine (**2b**). As a result, method II was used to obtain triazatetraynes **4a**–**g** in 46–65% yields (27–37% overall yield calculated from azatetrayne **1**). This reaction was not successful with *o*-fluorobenzaldehyde (the starting azatetrayne **1a** did not participate in the reaction), which could be probably explained by steric effects. The reaction with formaldehyde proceeded with the formation of target products **4h**–**j** in 25–42% yields according to method I and in 58–69% yields according to method II (34–37% overall yields). It should be noted that the four-component reactions (method I) along with products **4a**–**c**,**h**–**j** also gave the corresponding azatetraynes **1a**,**c**. The reaction did not occur in the absence of catalyst.

The structures of compounds **4a**–**j** were determined by using ^1H and ^{13}C NMR spectroscopy and mass spectrometry. ^1H and ^{13}C NMR spectra of compounds **4a**–**j** lacked signals that would be characteristic for terminal triple bond atoms in azatetraynes **1**. The signals of magnetically nonequivalent *sp*-hybridized carbon atoms were assigned on the basis of ^1H–^{13}C HMBC experiment. The formation of compounds **4a**–**g** was deduced from the presence of tertiary carbon atom signal in ^{13}C NMR spectrum in the range of 61.2–61.5 ppm (multiplicity determined using a DEPT-135 experiment) and ^1H NMR singlet in the range of 4.50–4.54 ppm. The formed asymmetric center affected the NMR parameters of the adjacent aromatic substituent, for example, the chemical shifts of *ortho*-protons in the *p*-fluoro-substituted phenyl ring in compound **4e** were observed as separate doublets. However, in the case of *p*-bromo-substituted analog

(compound **4c**), all four protons of the substituted aromatic ring were observed as a narrow singlet at 7.45 ppm, apparently due to overlapping signals of magnetically non-equivalent protons. In the case of compound **4e**, $^{1}H–^{15}N$ HMBC experiment allowed to determine the chemical shifts of two nitrogen atoms, one of which belonged to piperidine ring (303.6 ppm) and the other was part of the *N*-*tert*-butyl substituent (307.8 ppm).

Mass spectra (atmospheric pressure chemical ionization) of compounds **4a**–**i** featured peaks of $[M+H]^+$ ions corresponding to the molecular mass values of these compounds, which served as additional confirmation of their structures. The strongest peak in MALDI–TOF mass spectrum of compound **4g** was that of protonated molecular ion $[M+H]^+$ with *m*/*z* 818.2719, containing two atoms of ^{81}Br isotope, while the strongest mass spectral peak for compound **4c** was that of an ion with *m*/*z* 836.1969.

Thus, we have described a CuCl-catalyzed method for the synthesis of new *N*-substituted tetrapropargylamines by a four-component reaction of α,ω-diacetylenes with *N*-substituted 1,5,3-dioxazepanes, formaldehyde, and piperidine, as well as aminomethylation reaction of dipropargylamines with aldehydes and cyclic secondary amines.

Experimental

IR spectra were recorded on a Bruker VERTEX 70v spectrometer for samples prepared as thin films. One-dimensional (^{1}H and ^{13}C) and two-dimensional homonuclear (COSY, NOESY) and heteronuclear ($^{1}H–^{13}C$ HSQC, $^{1}H–^{13}C$ HMBC) NMR spectra were acquired on Bruker Avance 400 (400 and 101 MHz) and Bruker Ascend 500 (500 and 126 MHz) spectrometers for samples in $CDCl_3$ solutions. Residual signals of $CDCl_3$ solvent were used as internal standards (7.28 ppm for ^{1}H nuclei and 77.10 ppm for ^{13}C nuclei). ^{19}F NMR spectra were acquired on a Bruker Avance 400 spectrometer (376 MHz), using $CFCl_3$ as internal standard (0.0 ppm). Heteronuclear two-dimensional $^{1}H–^{15}N$ HMBC spectra were acquired on a Bruker Ascend 500 spectrometer at 51 MHz resonance frequency for ^{15}N nuclei, using $MeNO_2$ as standard (380 ppm, chemical shift values recalculated relative to $MeNO_2$). GC-MS analysis (EI ionization at 70 eV for compound **1c**) was performed using a Shimadzu GC 2010 gas chromatograph with GCMS-QP2010 Ultra mass selective detector. High-resolution mass spectra (MALDI–TOF) of compounds **1c**, **4a**–**j** were recorded on a Bruker Autoflex III spectrometer using sinapic acid matrix, samples were prepared by the dried-droplet method from chloroform solutions (1:10). Mass spectra (APCI) of compounds **4a**–**i** were recorded on a Shimadzu LCMS-2010 EV instrument using atmospheric pressure chemical ionization (sample injection by syringe, 0.1 ml/min, eluent MeCN–H_2O, 95:5) in positive ion mode at 4.5 kV capillary voltages; interface temperature 250°C, heater temperature 200°C, evaporator temperature 230°C; the nebulizer gas (nitrogen) flow rate was 2.5 l/min. Individual compounds were purified by column chromatography on KSK silica gel (50–160 μm). TLC analysis was performed on Sorbfil PTSKh-AF-A plates, visualization in iodine vapor.

The starting materials (amines, α,ω-diacetylenes, aldehydes) with ≥98% assay were commercially available and used without additional purification. *N*-Alkyl-1,5,3-dioxazepanes and azatetraynes **1a–c** were obtained according to a literature procedure.[12a]

***N*-(Octa-2,7-diyn-1-yl)-*N*-(propan-2-yl)octa-2,7-diyn-1-amine (1c)**. A Schlenk vessel was placed over a magnetic stirrer, flushed with argon stream, and charged with 1,5,3-dioxazepane (1 mmol), α,ω-diacetylene (2 mmol), CuCl (0.05 mmol, 5 mg), and PhMe (5 ml). The mixture was stirred at 80°C for 6 h. The reaction mixture was filtered through a layer of silica gel, the solvent was evaporated at reduced pressure on a rotary evaporator. The product was isolated by silica gel column chromatography. Yield 171 mg (64%), yellow oil, R_f 0.63 (Me_2CO–PhH, 2:1). IR spectrum, ν, cm^{-1}: 669, 755, 1118, 1216, 1326, 1385, 1432, 2118, 2957. ^{1}H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 1.12 (6H, d, ^{3}J = 6.5, $CH(C\underline{H}_3)_2$); 1.73 (4H, pent, ^{3}J = 7.0, $2CH_2C\underline{H}_2CH_2$); 1.97 (2H, t, *J* = 2.5, $2C{\equiv}C\underline{H}$); 2.32–2.34 (8H, m, $2C\underline{H}_2CH_2C\underline{H}_2$); 2.92 (1H, pent, ^{3}J = 6.5, $C\underline{H}(CH_3)_2$); 3.50 (4H, s, $2NC\underline{H}_2C{\equiv}C$). ^{13}C NMR spectrum (100 MHz), δ, ppm: 17.6 and 17.9 ($\underline{C}H_2CH_2\underline{C}H_2$); 20.2 ($CH_3$); 27.7 ($CH_2\underline{C}H_2CH_2$); 39.5 ($N\underline{C}H_2C{\equiv}C$); 51.1 ($\underline{C}H(CH_3)_2$); 68.8 ($C{\equiv}C$); 76.5 ($C{\equiv}C$); 83.6 ($\underline{C}{\equiv}\underline{C}$). Mass spectrum, *m*/*z* (I_{rel}, %): 267 $[M]^+$ (6), 252 $[M–CH_3]^+$ (100), 224 $[M–CH(CH_3)_2]^+$ (63), 158 $[HN(CH_2C{\equiv}C)CH_2C{\equiv}C(CH_2)_3C{\equiv}CH]^+$ (17), 91 $[C{\equiv}C(CH_2)_3C{\equiv}CH]^+$ (42), 77 $[N(CHC)CH_2C{\equiv}C]^+$ (63). Found, *m*/*z*: 266.3389 $[M–H]^+$. $C_{19}H_{24}N$. Calculated, *m*/*z*: 266.1909.

Synthesis of triazatetraacetylenes 4a–j. Method I. A two-necked flask was placed on a magnetic stirrer and charged under argon flow with 3-alkyl-1,5,3-dioxazepane (1 mmol), 1,7-octadiyne (2 mmol), CuCl (5 mg, 0.05 mmol), and PhMe (3 ml). The mixture was stirred at 80°C for 6 h, then treated by adding piperidine (2 mmol), aldehyde **3a**–**c**,**g** (2 mmol), CuCl (5 mg, 0.05 mmol), and PhMe (3 ml). Stirring was continued under argon atmosphere at 80°C for 6 h. The reaction mixture was filtered through a thin silica gel layer, the solvent was removed by evaporation at reduced pressure on a rotary evaporator. The product was isolated by column chromatography.

Method II. A two-neck flask was flushed with argon and charged with azatetraacetylene **1a–c** (1 mmol),[12a] piperidine (**2a**) or morpholine (**2b**) (2 mmol), aldehyde **3a**–**g** (2 mmol), CuCl (5 mg, 0.05 mmol), and PhMe (3 ml). The mixture was stirred under argon atmosphere at 80°C for 6 h. The product was isolated according to method I.

***N*-Butyl-10-(3-fluorophenyl)-*N*-[10-(3-fluorophenyl)-10-(piperidin-1-yl)-deca-2,8-diyn-1-yl]-10-(piperidin-1-yl)-deca-2,8-diyn-1-amine (4a)**. Yield 225 mg (65%), brown oil, R_f 0.65 (hexane–EtOAc, 1:2). IR spectrum, ν, cm^{-1}: 764, 1089, 1111, 1155, 1283, 1466, 1590, 1614, 2933. ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 0.91–0.93 (3H, m, CH_3); 1.32–1.38 (2H, m, $C\underline{H}_2CH_3$); 1.40–1.48 (6H, m, $CH_3CH_2C\underline{H}_2$, $2N(CH_2CH_2)_2C\underline{H}_2$); 1.53–1.63 (8H, m, $2N(CH_2C\underline{H}_2)_2CH_2$); 1.67–1.74 (8H, m, $2C{\equiv}CCH_2(C\underline{H}_2)_2CH_2C{\equiv}C$); 2.27 (4H, s, $2NCH_2C{\equiv}CC\underline{H}_2(CH_2)_3C{\equiv}C$); 2.34–2.39 (4H, m, $2NCH_2C{\equiv}C(CH_2)_3C\underline{H}_2C{\equiv}C$); 2.42–2.47 (8H, m, $2N(C\underline{H}_2CH_2)_2CH_2$); 2.47–2.52 (2H, m, $NC\underline{H}_2(CH_2)_2CH_3$);

3.39 (4H, s, 2NC$\underline{H}_2$C≡C); 4.54 (2H, s, 2C≡CC$\underline{H}$Ar); 6.94–6.97 (2H, m, H Ar); 7.31–7.33 (6H, m, H Ar). ^{13}C NMR spectrum (125 MHz), δ, ppm (*J*, Hz): 14.0 (CH_3); 18.3 ($\underline{C}H_2$C≡CCHAr, NCH$_2$C≡C$\underline{C}H_2$); 20.6 ($CH_3\underline{C}H_2$); 24.4 (N(CH_2CH_2)$_2\underline{C}H_2$); 26.2 (N($CH_2\underline{C}H_2$)$_2CH_2$); 28.0 and 28.1 (C≡C–CH_2($\underline{C}H_2$)$_2CH_2$C≡C); 29.6 ($CH_3CH_2\underline{C}H_2$); 42.6 (N$\underline{C}H_2$C≡C); 50.5 (N($\underline{C}H_2CH_2$)$_2CH_2$); 52.6 (CH_3(CH_2)$_2\underline{C}H_2$N); 61.5 (C≡C$\underline{C}$H(Ar)N); 75.4 (NCH$_2\underline{C}$≡C); 75.9 (C≡$\underline{C}$CHAr); 84.4 (NCH$_2$C≡$\underline{C}$); 87.8 ($\underline{C}$≡CCHAr); 114.1 (d, J_{CF} = 21.1, C Ar); 115.3 (d, J_{CF} = 22.0, C Ar); 123.9 (C Ar); 129.2 (d, *J* = 8.0, C Ar); 142.2 (C Ar); 162.8 (d, J_{CF} = 243.4, CF Ar). ^{19}F NMR spectrum (376 MHz, $CDCl_3$), δ, ppm: –17.96 (FC_6H_4). Mass spectrum (APCI), *m*/*z* (I_{rel}, %): 692 $[M+H]^+$ (100). Found, *m*/*z*: 692.3790 $[M+H]^+$. $C_{46}H_{60}F_2N_3$. Calculated, *m*/*z*: 692.4755. Found, *m*/*z*: 714.3651 $[M+Na]^+$. $C_{46}H_{59}F_2N_3Na$. Calculated, *m*/*z*: 714.4775. Found, *m*/*z*: 730.3234 $[M+K]^+$. $C_{46}H_{59}F_2N_3K$. Calculated, *m*/*z*: 730.4314.

***N*-Butyl-10-(3-chlorophenyl)-*N*-[10-(3-chlorophenyl)-10-(piperidin-1-yl)deca-2,8-diyn-1-yl]-10-(piperidin-1-yl)-deca-2,8-diyn-1-amine (4b)**. Yield 202 mg (56%), brown oil, R_f 0.87 (hexane–EtOAc, 1:2). IR spectrum, ν, cm^{-1}: 685, 762, 992, 1038, 1113, 1324, 1383, 1468, 1595, 1642, 2235, 2933. ^{1}H NMR spectrum (400 MHz), δ, ppm (*J*, Hz): 0.91–0.93 (3H, m, CH_3); 1.31–1.38 (2H, m, C$\underline{H}_2CH_3$); 1.40–1.49 (6H, m, $CH_3CH_2C\underline{H}_2$, 2N(CH_2CH_2)$_2C\underline{H}_2$); 1.53–1.62 (8H, m, 2N($CH_2C\underline{H}_2$)$_2CH_2$); 1.66–1.74 (8H, m, 2C≡CCH$_2$(C$\underline{H}_2$)$_2CH_2$C≡C); 2.24–2.29 (4H, m, 2NCH$_2$C≡CC$\underline{H}_2$(CH_2)$_3$C≡C); 2.33–2.38 (4H, m, 2NCH$_2$C≡C(CH_2)$_3C\underline{H}_2$C≡C); 2.43–2.47 (8H, m, 2N(C$\underline{H}_2CH_2$)$_2CH_2$); 2.50 (2H, t, ^3J = 7.5, NC$\underline{H}_2$(CH_2)$_2CH_3$); 3.39 (4H, s, 2NC$\underline{H}_2$C≡C); 4.52 (2H, s, 2C≡CC$\underline{H}$Ar); 7.24–7.27 (4H, m, H Ar); 7.46 (2H, d, *J* = 7.5, H Ar); 7.58 (2H, s, H Ar). ^{13}C NMR spectrum (100 MHz), δ, ppm: 14.0 (CH_3); 18.3 ($\underline{C}H_2$C≡CCHAr, NCH$_2$C≡C$\underline{C}H_2$); 20.6 ($CH_3\underline{C}H_2$); 24.4 (N(CH_2CH_2)$_2\underline{C}H_2$); 26.1 (N($CH_2\underline{C}H_2$)$_2CH_2$); 28.0 and 28.1 (C≡C–CH_2($\underline{C}H_2$)$_2CH_2$C≡C); 29.6 ($CH_3CH_2\underline{C}H_2$); 42.6 (N$\underline{C}H_2$C≡C); 50.5 (N($\underline{C}H_2CH_2$)$_2CH_2$); 52.6 (CH_3(CH_2)$_2\underline{C}H_2$N); 61.5 (C≡C$\underline{C}$H(Ar)N); 75.3 (NCH$_2\underline{C}$≡C); 75.7 (C≡$\underline{C}$CHAr); 84.4 (NCH$_2$C≡$\underline{C}$); 88.0 ($\underline{C}$≡CCHAr); 126.6 (C Ar); 127.4 (C Ar); 128.5 (C Ar); 129.2 (C Ar); 129.2 (C Ar); 133.9 (C Ar); 141.5 (C Ar). Mass spectrum (APCI), *m*/*z* (I_{rel}, %): 724 $[M+H]^+$ (100). Found, *m*/*z*: 667.4379 $[M–Bu+H]^+$. $C_{42}H_{51}Cl_2N_3$. Calculated, *m*/*z*: 667.3460.

10-(4-Bromophenyl)-*N*-[10-(4-bromophenyl)-10-(piperidin-1-yl)deca-2,8-diyn-1-yl]-*N*-butyl-10-(piperidin-1-yl)-deca-2,8-diyn-1-amine (4c). Yield 207 mg (51%), brown oil, R_f 0.68 (hexane–EtOAc, 1:2). IR spectrum, ν, cm^{-1}: 503, 767, 832, 869, 1011, 1088, 1382, 1441, 1452, 2233, 2931. ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 0.91–0.93 (3H, m, CH_3); 1.29–1.37 (2H, m, C$\underline{H}_2CH_3$); 1.38–1.49 (6H, m, 2N(CH_2CH_2)$_2C\underline{H}_2$, C$\underline{H}_2CH_2CH_3$); 1.63–1.72 (8H, m, 2C≡CCH$_2$(C$\underline{H}_2$)$_2CH_2$C≡C); 2.20–2.29 (4H, m, 2NCH$_2$C≡CC$\underline{H}_2$(CH_2)$_3$C≡C); 2.30–2.37 (4H, m, 2C$\underline{H}_2$C≡CCHAr); 2.40–2.52 (8H, m, 2N(C$\underline{H}_2CH_2$)$_2CH_2$); 2.48–2.52 (2H, t, ^3J = 9.2, NC$\underline{H}_2$(CH_2)$_2CH_3$); 3.39 (4H, s, 2NC$\underline{H}_2$C≡C); 4.54 (2H, s, C≡CC$\underline{H}$Ar); 7.45 (8H, s, H Ar). ^{13}C NMR spectrum (125 MHz), δ, ppm: 14.0 (CH_3); 18.3 ($\underline{C}H_2$C≡CCHAr, NCH$_2$C≡C$\underline{C}H_2$); 20.7 ($CH_3\underline{C}H_2$); 24.4 (N(CH_2CH_2)$_2\underline{C}H_2$); 26.2 (N($CH_2\underline{C}H_2$)$_2CH_2$); 28.0 and 28.1 (C≡C–CH_2($\underline{C}H_2$)$_2CH_2$C≡CH); 29.7 ($CH_3CH_2\underline{C}H_2$); 42.6 (N$\underline{C}H_2$C≡C); 50.5 (N($\underline{C}H_2CH_2$)$_2CH_2$); 52.7 (CH_3(CH_2)$_2\underline{C}H_2$N); 61.4 (C≡C$\underline{C}$H(Ar)N); 75.4 (NCH$_2\underline{C}$≡C); 75.9 (C≡$\underline{C}$CHCAr); 84.4 (NCH$_2$C≡$\underline{C}$); 87.8 ($\underline{C}$≡CHAr); 121.1 (C Ar); 130.2 (C Ar); 131.0 (C Ar); 138.4 (C Ar). Mass spectrum (APCI), *m*/*z* (I_{rel}, %): 812 $[M+H]^+$ (100). Found, *m*/*z*: 834.1924/836.1969/838.1973 (35/100/58) $[M+Na]^+$. $C_{46}H_{59}Br_2N_3Na$. Calculated, *m*/*z*: 834.2973/836.2953/838.2933. Found, *m*/*z*: 850.1737/852.1741/854.1514 (5/12/5) $[M+K]^+$. $C_{46}H_{59}Br_2KN_3$. Calculated, *m*/*z*: 850.2713/852.2692/854.2672.

***N*-Butyl-(10-piperidin-1-yl)-*N*-{10-(piperidin-1-yl)-10-[3-(trifluoromethyl)phenyl]deca-2,8-diyn-1-yl}-10-[3-(trifluoromethyl)phenyl]deca-2,8-diyn-1-amine (4d)**. Yield 233 mg (59%), brown oil, R_f 0.6 (hexane–EtOAc, 1:2). IR spectrum, ν, cm^{-1}: 702, 769, 1073, 1163, 1269, 1330, 1444, 1616, 2250, 2858, 2931. ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 0.90–0.94 (3H, m, CH_3); 1.30–1.36 (2H, m, C$\underline{H}_2CH_3$); 1.40–1.48 (6H, m, C$\underline{H}_2CH_2CH_3$, N(CH_2CH_2)$_4C\underline{H}_2$); 1.52–1.61 (8H, m, N($CH_2C\underline{H}_2$)$_2CH_2$); 1.68–1.74 (8H, m, C≡CCH$_2$(C$\underline{H}_2$)$_2CH_2$C≡C); 2.27 (4H, br. s, NCH$_2$C≡CC$\underline{H}_2$); 2.36–2.41 (4H, m, NCH$_2$C≡C(CH_2)$_3C\underline{H}_2$); 2.42–2.51 (10H, m, 2N(C$\underline{H}_2CH_2$)$_2CH_2$, NC$\underline{H}_2$(CH_2)$_2CH_3$); 3.37 (4H, s, NC$\underline{H}_2$C≡C); 4.50 (2H, s, C≡CC$\underline{H}$(Ar)N); 7.46 (2H, t, *J* = 7.5, CH(Ar)); 7.53 (2H, d, *J* =7.5, CH(Ar)); 7.78 (2H, d, *J* = 7.5, CH(Ar)); 7.86 (2H, s, CH(Ar)). ^{13}C NMR spectrum (125 MHz), δ, ppm: 14.0 (CH_3); 18.2 ($\underline{C}H_2$C≡CCH(Ar)N); 18.3 (NCH$_2$C≡C$\underline{C}H_2$); 20.6 ($CH_3\underline{C}H_2$); 24.4 (N(CH_2CH_2)$_2\underline{C}H_2$); 26.1 (N($CH_2\underline{C}H_2$)$_2CH_2$); 28.0 and 28.1 (C≡CCH_2($\underline{C}H_2$)$_2CH_2$C≡C); 29.6 (NCH$_2\underline{C}H_2CH_2CH_3$); 42.6 (N$\underline{C}H_2$C≡C); 50.5 (N($\underline{C}H_2CH_2$)$_2CH_2$); 52.6 ($CH_2CH_2\underline{C}H_2$N); 61.5 ($CH_2$C≡C$\underline{C}$H(Ar)N); 75.4 (NCH$_2\underline{C}$≡C); 75.6 (C≡$\underline{C}$CHCAr); 84.4 (NCH$_2$C≡$\underline{C}$); 88.3 ($\underline{C}$≡CCHAr); 124.1 (CH Ar); 125.2 (CH Ar); 125.4 (CF_3); 128.4 (CH Ar); 130.4 ($\underline{C}CF_3$ Ar); 131.8 (CH(Ar)); 140.5 (C Ar). Mass spectrum (APCI), *m*/*z* (I_{rel}, %): 792 $[M+H]^+$ (100). Found, *m*/*z*: 792.5355 $[M+H]^+$. $C_{48}H_{60}F_6N_3$. Calculated, *m*/*z*: 792.4691.

***N*-(*tert*-Butyl)-10-(4-fluorophenyl)-*N*-[10-(4-fluorophenyl)-10-(piperidin-1-yl)deca-2,8-diyn-1-yl]-10-(piperidin-1-yl)deca-2,8-diyn-1-amine (4e)**. Yield 183 mg (53%), brown oil, R_f 0.65 (hexane–EtOAc, 1:2). IR spectrum, ν, cm^{-1}: 773, 856, 1024, 1037, 1143, 1267, 1390, 1601, 2257, 2856, 2934. ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 1.19 (9H, s, C(CH_3)$_3$); 1.40–1.46 (4H, m, 2N(CH_2CH_2)$_2C\underline{H}_2$); 1.51–1.63 (8H, m, 2N($CH_2C\underline{H}_2$)$_2CH_2$); 1.67–1.72 (8H, m, 2C≡CCH$_2$(C$\underline{H}_2$)$_2CH_2$C≡C); 2.22–2.27 (4H, m, 2NCH$_2$C≡CC$\underline{H}_2$); 2.34–2.37 (4H, m, 2C$\underline{H}_2$C≡CCHAr); 2.42–2.46 (8H, m, 2N(C$\underline{H}_2CH_2$)$_2CH_2$); 3.60 (4H, s, 2NC$\underline{H}_2$C≡C); 4.52 (2H, s, 2C≡C–CHAr); 7.32–7.33 (4H, dd, *J* = 8.5, H Ar); 7.53–7.55 (4H, t, *J* = 8.5, H Ar). ^{13}C NMR spectrum (125 MHz), δ, ppm (*J*, Hz): 18.4 ($\underline{C}H_2$C≡CCHAr); 18.5 (NCH$_2$C≡C$\underline{C}H_2$); 24.5 (N(CH_2CH_2)$_2\underline{C}H_2$); 26.1 (N($CH_2\underline{C}H_2$)$_2CH_2$); 27.5 (CH_3); 27.9 and 28.2 (C≡CCH_2($\underline{C}H_2$)$_2CH_2$C≡CH); 36.7 (N$\underline{C}H_2$C≡C); 50.4 (N($\underline{C}H_2CH_2$)$_2CH_2$); 54.9 (CH_3)$_3\underline{C}$N); 61.2 (–CH_2C≡C$\underline{C}$H); 76.3 (NCH$_2\underline{C}$≡C); 77.9 (C≡$\underline{C}$CHAr); 83.6 ($\underline{C}$≡CCHAr); 87.6 (NCH$_2$C≡$\underline{C}$); 114.6 (d, *J* = 21.3, CH Ar); 130.0 (d, *J* = 7.9, CH Ar); 134.9 (C Ar); 162.1 (d, *J* = 243.8, CF Ar).

^{15}N NMR (51 MHz), δ, ppm: 303.6 ($N(CH_2CH_2)_2CH_2$); 307.8 ($NCH_2C{\equiv}C$). Mass spectrum (APCI), *m/z* (I_{rel}, %): 692 $[M+H]^+$ (100). Found, *m/z*: 692.2827 $[M+H]^+$. $C_{46}H_{60}F_2N_3$. Calculated, *m/z*: 692.4755. Found, *m/z*: 714.2365 $[M+Na]^+$. $C_{46}H_{59}NaF_2N_3$. Calculated, *m/z*: 714.4575. Found, *m/z*: 730.2128 $[M+K]^+$. $C_{46}H_{59}KF_2N_3$. Calculated, *m/z*: 730.4314.

***N*-(*tert*-Butyl)-9-(4-chlorophenyl)-*N*-[9-(4-chlorophenyl)-9-(piperidin-1-yl)nona-2,7-diyn-1-yl]-9-(piperidin-1-yl)nona-2,7-diyn-1-amine (4f)**. Yield 167 mg (48%), brown oil, R_f 0.87 (Me_2CO–PhH, 1:1). IR spectrum, ν, cm^{-1}: 598, 770, 1017, 1089, 1201, 1265, 1390, 1430, 1453, 1608, 2254, 2868, 2933. ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 1.21 (9H, m, $C(CH_3)_3$); 1.42–1.50 (4H, m, $2N(CH_2CH_2)_2C\underline{H}_2$); 1.55–1.80 (8H, m, $2C{\equiv}CCH_2C\underline{H}_2CH_2C{\equiv}C$, $N(CH_2C\underline{H}_2)_2CH_2$); 2.30–2.52 (16H, m, $2C{\equiv}CC\underline{H}_2CH_2C\underline{H}_2C{\equiv}C$, $2N(C\underline{H}_2CH_2)_2CH_2$); 3.72 (4H, s, $2NC\underline{H}_2C{\equiv}C$); 4.61 (2H, s, $C{\equiv}CC\underline{H}Ar$); 7.32 (4H, d, ^3J = 8.0, H Ar); 7.56 (4H, br. s, H Ar). ^{13}C NMR spectrum (125 MHz), δ, ppm: 18.2; 18.4; 24.1; 25.7; 27.5; 28.0; 37.2; 50.5; 55.3; 61.3; 77.2; 77.3 (overlapping with $CDCl_3$ signals); 83.2; 83.5; 128.2 (C Ar); 130.1; 130.8; 133.0. Mass spectrum (APCI), *m/z* (I_{rel}, %): 696 $[M+H]^+$ (100). Found, *m/z*: 694.4112 $[M–H]^+$. $C_{44}H_{54}Cl_2N_3$. Calculated 694.3695.

10-(4-Bromophenyl)-*N*-[10-(4-bromophenyl)-10-(morpholin-4-yl)deca-2,8-diyn-1-yl]-*N*-(*tert*-butyl)-10-(morpholin-4-yl)deca-2,8-diyn-1-amine (4g). Yield 188 mg (46%), brown oil, R_f 0.75 (PhH–$CHCl_3$–hexane–Et_2O, 1:1:1:2). IR spectrum, ν, cm^{-1}: 731, 817, 854, 1167, 1364, 1453, 1589, 2259, 2825, 2857, 2942. ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 1.20 (9H, s, $C(CH_3)_3$); 1.63–1.71 (8H, m, $2C{\equiv}CCH_2(C\underline{H}_2)_2CH_2C{\equiv}C$); 2.20–2.35 (8H, m, $2C{\equiv}CC\underline{H}_2(CH_2)_2C\underline{H}_2C{\equiv}C$); 2.51 (8H, s, $2N(C\underline{H}_2CH_2)_2O$); 3.64 (4H, s, $2NC\underline{H}_2C{\equiv}C$); 3.69–3.72 (8H, m, $2N(C\underline{H}_2CH_2)_2O$); 4.49 (2H, s, $2C{\equiv}CC\underline{H}Ar$); 7.45 (8H, dd, ^3J = 8.8, H Ar). ^{13}C NMR spectrum (125 MHz), δ, ppm: 18.3 ($\underline{C}H_2C{\equiv}CCH$–Ar); 18.5 ($NCH_2C{\equiv}C\underline{C}H_2$); 27.4 ($CH_3$); 27.9 and 28.1 ($C{\equiv}CCH_2(\underline{C}H_2)_2CH_2C{\equiv}C$); 36.9 ($N\underline{C}H_2C{\equiv}C$); 49.7 (CHAr); 55.3 ($\underline{C}(CH_3)_3$); 61.0 ($N(\underline{C}H_2CH_2)_2O$); 67.1 ($N(CH_2\underline{C}H_2)_2O$); 75.2 ($NCH_2\underline{C}{\equiv}C$); 76.8 ($C{\equiv}\underline{C}CHC$–Ar); 84.2 ($NCH_2C{\equiv}\underline{C}$); 88.7 ($\underline{C}{\equiv}CHAr$); 121.5 (C Ar); 130.2 (CH Ar); 131.0 (CH Ar); 137.5 (C Ar). Mass spectrum (APCI), *m/z* (I_{rel}, %): 816 $[M+H]^+$(100). Found, *m/z*: 816.4077/818.4026/820.4202 (16/43/16) $[M+H]^+$. $C_{44}H_{56}Br_2N_3O_2$. Calculated, *m/z*: 816.2739/818.2719/820.2698.

***N*-Butyl-10-(piperidin-1-yl)-*N*-[10-(piperidin-1-yl)deca-2,8-diyn-1-yl]deca-2,8-diyn-1-amine (4h)**. Yield 163 mg (65%), brown oil, R_f 0.4 (Et_2O–$CHCl_3$–Me_2CO, 1:1:1). IR spectrum, ν, cm^{-1}: 1115, 1203, 1324, 1443, 1454, 2234, 2858, 2932. ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 0.83 (3H, t, ^3J = 7.2, CH_3); 1.25 (2H, q, ^3J = 7.2, $C\underline{H}_2CH_3$); 1.30–1.36 (6H, m, $2N(CH_2CH_2)_2C\underline{H}_2$, $C\underline{H}_2CH_2CH_3$); 1.52 (16H, br. s, $2N(CH_2C\underline{H}_2)_2CH_2$, $2C{\equiv}CCH_2(C\underline{H}_2)_2CH_2C{\equiv}C$); 2.13 (8H, s, $2NCH_2C{\equiv}CC\underline{H}_2(CH_2)_2C\underline{H}_2C{\equiv}C$); 2.38 (10H, br. s, $NC\underline{H}_2(CH_2)_2CH_3$, $N(C\underline{H}_2CH_2)_2CH_2$); 3.12 (4H, s, $2NC\underline{H}_2C{\equiv}C$); 3.26 (4H, s, $N(C\underline{H}_2C{\equiv}C)_2$). ^{13}C NMR spectrum (125 MHz), δ, ppm: 13.9 (CH_3); 18.2 ($\underline{C}H_2C{\equiv}CCH$–Ar, $NCH_2C{\equiv}C\underline{C}H_2$); 20.5 ($CH_3\underline{C}H_2$); 24.9 ($N(CH_2CH_2)_2\underline{C}H_2$); 25.8 ($N(CH_2\underline{C}H_2)_2CH_2$); 27.8 and 27.9 ($C{\equiv}C$–$CH_2(\underline{C}H_2)_2CH_2C{\equiv}CH$); 29.5 ($CH_3CH_2\underline{C}H_2$); 42.4 ($N(\underline{C}H_2C{\equiv}C)_2$); 47.9 ($NC\underline{H}_2C{\equiv}C$); 52.5 ($CH_3(CH_2)_2\underline{C}H_2N$); 53.2 ($N(\underline{C}H_2CH_2)_2CH_2$); 75.2 (C≡C); 75.4 (C≡C); 84.4 (C≡C); 87.6 (C≡C). Mass spectrum (APCI), *m/z* (I_{rel}, %): 504 $[M+H]^+$ (100). Found, *m/z*: 504.3535 $[M+H]^+$. $C_{34}H_{54}N_3$. Calculated, *m/z*: 504.4318.

***N*-Butyl-11-(piperidin-1-yl)-*N*-[11-(piperidin-1-yl)undeca-2,9-diyn-1-yl]undeca-2,9-diyn-1-amine (4i)**. Yield 183 mg (69%), brown oil, R_f 0.68 (PhH–Me_2CO–*i*-PrOH, 2:1:0.5). IR spectrum, ν, cm^{-1}: 993, 1104, 1116, 1179, 1325, 1340, 1366, 1453, 2257, 2857, 2932. ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 0.88–0.91 (3H, m, CH_3); 1.28–1.37 (2H, m, $C\underline{H}_2CH_3$); 1.38–1.55 (18H, m, $2N(CH_2C\underline{H}_2)_2CH_2$, $2N(CH_2CH_2)_2C\underline{H}_2$, $C\underline{H}_2CH_2CH_3$, $2C{\equiv}C(CH_2)_2C\underline{H}_2(CH_2)_2C{\equiv}C$); 1.56–1.65 (8H, m, $2C{\equiv}CCH_2C\underline{H}_2CH_2C\underline{H}_2CH_2C{\equiv}C$); 2.15–2.20 (8H, br. s, $2C{\equiv}CC\underline{H}_2(CH_2)_3C\underline{H}_2C{\equiv}C$); 2.20–2.25 (2H, m, $NC\underline{H}_2(CH_2)_2CH_3$); 2.40–2.50 (8H, m, $2N(C\underline{H}_2CH_2)_2CH_2$); 3.17–3.20 (4H, m, $2NC\underline{H}_2C{\equiv}C$); 3.34 (4H, s, $2NC\underline{H}_2C{\equiv}C$). ^{13}C NMR spectrum (125 MHz), δ, ppm: 14.0 (CH_3); 18.6 and 19.1 ($C{\equiv}C\underline{C}H_2(CH_2)_3\underline{C}H_2C{\equiv}C$); 20.6 ($CH_3\underline{C}H_2$); 24.0 ($N(CH_2CH_2)_2\underline{C}H_2$); 25.8 ($N(CH_2\underline{C}H_2)_2CH_2$); 27.8, 28.0, and 28.4 ($C{\equiv}C$–$CH_2(\underline{C}H_2)_3CH_2C{\equiv}CH$); 29.6 ($CH_3CH_2\underline{C}H_2$); 42.5 ($N(\underline{C}H_2C{\equiv}C)_2$); 48.0 ($2N\underline{C}H_2C{\equiv}C$); 52.6 ($CH_3(CH_2)_2\underline{C}H_2N$); 53.3 ($N(\underline{C}H_2CH_2)_2CH_2$); 75.1 ($NCH_2\underline{C}{\equiv}C$), 75.3 ($C{\equiv}\underline{C}CH_2$); 84.7 ($NCH_2C{\equiv}\underline{C}$); 84.9 ($\underline{C}{\equiv}CH_2$). Mass spectrum (APCI), *m/z* (I_{rel}, %): 532 $[M+H]^+$ (100). Found, *m/z*: 554.4797 $[M+Na]^+$. $C_{36}H_{57}N_3Na$. Calculated, *m/z*: 554.4450. Found, *m/z*: 570.4558 $[M+K]^+$. $C_{36}H_{57}N_3K$. Calculated, *m/z*: 570.4190.

***N*-Isopropyl-(9-piperidin-1-yl)-*N*-[9-(piperidin-1-yl)nona-2,7-diyn-1-yl]nona-2,7-diyn-1-amine (4j)**. Yield 134 mg (58%), yellow oil, R_f 0.35 (Et_2O–Me_2CO–$CHCl_3$, 1:1:1). IR spectrum, ν, cm^{-1}: 993, 1038, 1104, 1068, 1104, 1168, 1251, 1310, 1325, 1365, 1439, 1451, 1466, 2257, 2854, 2931. ^{1}H NMR spectrum (500 MHz), δ, ppm (*J*, Hz): 1.11 (6H, d, ^3J = 6.5, $CH(C\underline{H}_3)_2$); 1.44 (4H, br. s, $2N(CH_2CH_2)_2C\underline{H}_2$); 1.64 (8H, t, ^3J = 5.8, $2N(CH_2C\underline{H}_2)_2CH_2$); 1.69–1.73 (4H, m, $2C{\equiv}CCH_2C\underline{H}_2CH_2C{\equiv}C$); 2.30–2.34 (8H, m, $2C{\equiv}CC\underline{H}_2CH_2C\underline{H}_2C{\equiv}C$); 2.50 (8H, br. s, $2N(C\underline{H}_2CH_2)_2CH_2$); 2.89 (1H, pent, ^3J = 6.5, $C\underline{H}(CH_3)_2$); 3.24 (4H, s, $2NC\underline{H}_2C{\equiv}C$), 3.47 (4H, s, $N(C\underline{H}_2C{\equiv}C)_2$). ^{13}C NMR spectrum (125 MHz), δ, ppm: 18.0, 18.1 ($\underline{C}H_2CH_2\underline{C}H_2$); 20.3 ($CH_3$); 23.9 ($N(CH_2CH_2)_2\underline{C}H_2$); 25.8 ($N(CH_2\underline{C}H_2)_2CH_2$); 28.1 ($CH_2\underline{C}H_2CH_2$); 39.5 ($N(\underline{C}H_2C{\equiv}C)_2$); 48.0 ($2N\underline{C}H_2C{\equiv}C$); 50.9 (CHN); 53.3 ($N(\underline{C}H_2CH_2)_2CH_2$); 75.6 ($C{\equiv}\underline{C}CH_2N(CH_2CH_2)_2CH_2$); 76.5 ($NCH_2\underline{C}{\equiv}C$); 83.6 ($NCH_2C{\equiv}\underline{C}$); 84.3 ($\underline{C}{\equiv}CCH_2N(CH_2CH_2)_2CH_2$). Found, *m/z*: 460.4028 $[M–H]^+$. $C_{31}H_{46}N_3$. Calculated, *m/z*: 460.3692.

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