Synthesis of 1,2,3-triazoles from heterocyclic α-nitro azides

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Noncatalytic and Cu(I)-catalyzed dipolar cycloadditions of heterocyclic α-nitro azides to substituted alkynes were studied. Catalytic cyclization gave 1,4-disubstituted triazoles only. The effect of the substituents in alkynes and that of the nature of the starting heterocycles on the isomer ratio of triazoles were examined. New representatives of 1,2,3-triazoles were obtained; their physicochemical properties were studied. A comparative analysis of the spectral characteristics of the resulting regioisomeric triazole derivatives was performed.

Key words: geminal nitro azides, 1,3-dipolar cycloaddition, 1,2,3-triazoles.

Having unique properties, 1,2,3-triazole derivatives occupy an important place in organic chemistry. They find applications as intermediates in organic synthesis, exhibit a wide spectrum of biological activity,[1—4] and can be used as optical bleaching agents[5] and components of chemiluminescent formulations.[6]

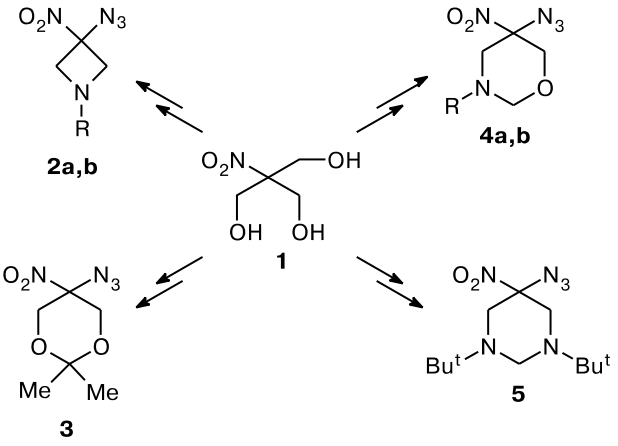
The 1,2,3-triazole ring contributes 168 kJ mol^{-1} to the enthalpy of formation of the compound;[7] along with high chemical and thermal stability, this makes the compounds of this class attractive as components of high-energy formulations.[8—11]

Substituted 1,2,3-triazoles are most commonly obtained by 1,3-dipolar cycloaddition of azides to alkynes. Elevated temperature is usually required for the reaction to occur. Nonsymmetric alkynes yield mixtures of 1,4- and 1,5-disubstituted isomers. The reaction is regiospecific when silyl-substituted alkynes,[12] ynamines,[13] and Grignard reagents[14,15] are used as dipolarophiles. In the last few years, selective synthesis of 1,4-disubstituted 1,2,3-triazoles has been implemented most often by means of catalysis with Cu^{I} ions,[16] while 1,5-disubstituted derivatives have been selectively obtained in the presence of ruthenium complex salts.[17]

Despite much research dealing with the mechanism of [3+2] cycloaddition, it still remains not fully understood how the reaction pathway depends on the structure of the starting azides. Very scarce and contradictory data on the reactivity of geminal nitro azides[18—20] preclude any predictions of the effect of the α-nitro group on the 1,3-dipolar addition to alkynes.

To find out how the structure of a nitroheterocycle influences the cycloaddition regioselectivity, here we employed heterocyclic α-nitro azides **2**—**5** prepared from easily accessible 2-(hydroxymethyl)-2-nitropropane-1,3-diol (**1**) by oxidative azidation of sodium salts of secondary nitroalkanes[21] (Scheme 1).

Scheme 1



R = NO_2 (**a**), Bu^t (**b**)

We studied both thermal and Cu^{I}-catalyzed cycloadditions of heterocyclic α-nitro azides to but-2-yne-1,4-diol (**6**), phenylacetylene (**7**), propargyl alcohol (**8**), and trimethylsilylacetylene (**9**), which are most commonly used for this purpose.

Thermal cyclization of 3-azido-1,3-dinitroazetidine (**2a**) and 5-azido-2,2-dimethyl-5-nitro-1,3-dioxane (**3**) with internal alkyne **6** gave 1,4,5-trisubstituted triazoles **10** and **11** (Scheme 2, Table 1). The reactions were carried out in boiling solvents (toluene, benzene) and melted but-2-yne-1,4-diol. When the temperature of the cyclization of azide **2a** with alkyne **6** was lowered from 110 to 80 °C

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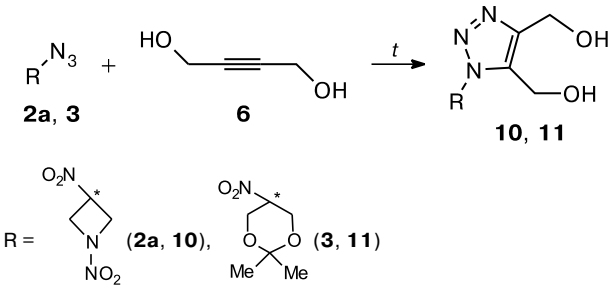
Table 1. Outcomes of the cyclization reactions of nitro azides **2a** and **3** with but-2-yne-1,4-diol (**6**)

Compound	*T*/°C	*t*/h	Yields (%) of triazoles **10** and **11**	M.p./°C
2a	110	5	62	185—190
	80	24	85	
3	80	48	35	135—137
	70*	24	52	

* In the presence of excess alkynediol **6**.

(replacement of toluene by benzene), the yield of 4,5-bis-(hydroxymethyl)-1,2,3-triazole (**10**) was increased to 85%, though the reaction time was extended as well.

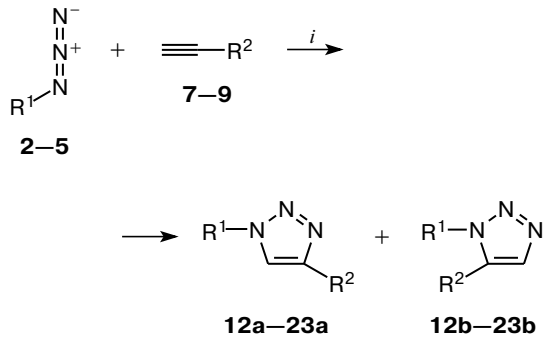
Scheme 2



Nitro azide **3** is less reactive toward but-2-yne-1,4-diol (**6**). In benzene (80 °C), the slow formation of triazole **11** is accompanied by decomposition of the starting azide **3**. A solvent-free reaction in the presence of excess alkynediol **6** allows higher yields of the target product in a shorter cyclization time.

As expected, thermal cyclization of α-nitro azides with terminal alkynes **7** and **8** proceeds slowly to give mixtures of regioisomers **a** (1,4-disubstituted) and **b** (1,5-disubstituted) (Scheme 3, Table 2). The reactions were carried out in toluene or with no solvent added, in an excess of the substituted alkyne. Since nitro azides containing electron-donating (*tert*-butyl) substituents are less stable,[21] the cyclizations of nitro azides **2b**, **4b**, and **5** were studied at room temperature.

Scheme 3



The ratio of the reaction products was determined by analyzing the chemical shifts of the ^{1}H NMR signals for the proton of the triazole ring. The proton in position 5 of the triazole ring of 1,4-disubstituted isomers is less shielded (and, accordingly, is always manifested as a lower-field signal in the ^{1}H NMR spectrum) than the proton in position 4 of 1,5-disubstituted isomers.[22,23]

We found that the nature of the terminal acetylene is decisive for the cyclization reaction. With trimethylsilylacetylene (**9**), the cyclizations selectively give 1,4-disubstituted triazoles, regardless of the structure of heterocyclic α-nitro azide.

Cycloaddition of phenylacetylene (**7**) is usually not regiospecific, yielding 1,4- and 1,5-isomers in equal amounts.[19] With sterically hindered azides, 4-phenyltriazole is a predominant cycloadduct,[24] with few exceptions of a predominant 1,5-isomer.[25] Apparently, the exceptions include α-nitro azides as well. Cyclization reactions of azides **2a**, **3**, and **4a** with phenylacetylene produce 1,5-disubstituted isomer (**b**) as a major product. This is confirmed by the literature data[19] on the preferential formation of 5-phenyltriazole (73%) from 1-azido-1-nitroethane (α-nitro azide) and phenylacetylene and on the formation of a mixture of isomers from 1-azido-2-nitroethane and phenylacetylene, the 1,4-disubstituted isomer being predominant.

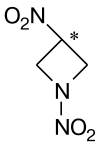
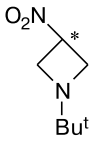
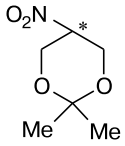
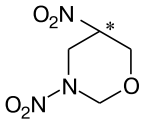
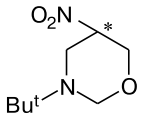
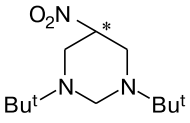
Except for azide **2a**, the reactions with propargyl alcohol (**8**) mainly give the 1,4-isomer (**a**). Cycloadditions of nitro azides **2a,b**, **3**, **4b**, and **5** in excess propargyl alcohol as well as cycloadditions at elevated temperatures are all nonselective (see Table 2). The ratio of regioisomeric cycloadducts is virtually independent of the reaction conditions. Little changes were noticed only for compounds **2a** and **3**. A decrease in the temperature augments the fraction of the 1,4-disubstituted isomer.

5-Azido-3-*tert*-butyl-5-nitrotetrahydro-1,3-oxazine (**4b**) and 5-azido-1,3-di-*tert*-butyl-5-nitrohexahydropyrimidine (**5**) decompose under the reaction conditions in 10 h.

The substituent in position 1 of the azetidine ring also has some influence on the outcome of the reaction. Cycloaddition of nitro azide **2a** containing the *N*-nitro group to propargyl alcohol mainly yields the 1,5-disubstituted isomer. In contrast, the 1,4-disubstituted isomer is slightly dominant in the products obtained from *N*-*tert*-butyl-substituted nitro azide **2b**.

Cyclizations of α-nitro azides with alkyne **9** proceed slowly, and a tenfold excess of the alkyne is required. With a lower ratio of the reactants, the reaction does not reach completion even upon prolonged heating. The synthesis at elevated temperatures allows substantial reduction in the reaction time. As expected, the 1,4-disubstituted isomer is the only product in all cases.

Table 2. Outcomes of the thermal cyclizations of azides **2a,b**, **3**, **4a,b**, and **5**

Starting compounds and substituents				*T*/°C	*t*/h	Yields (%) of the products (%)	Ratio of the isomers (1,4 : 1,5)
R^1N_3	R^1	$HC{\equiv}CR^2$	R^2				
2a		**7**	Ph	110	15	65	19 : 81 (**12a** : **12b**)
		8	CH_2OH	110	11	85	28 : 72 (**13a** : **13b**)
				18[a]	110	90	36 : 64 (**13a** : **13b**)
		9	Me_3Si	55	7	78	100 (**14a**)
2b		**8**	CH_2OH	18[a]	240	78	53 : 47 (**15a** : **15b**)
				60[a]	7	91	54 : 46 (**15a** : **15b**)
		9	Me_3Si	18[a]	360	62	100 (**16a**)
3		**7**	Ph	110	11	74	37 : 63 (**17a** : **17b**)
		8	CH_2OH	110	13	72	64 : 36 (**18a** : **18b**)
				20[a]	160	76	74 : 26 (**18a** : **18b**)
		9	Me_3Si	55	13	76	100 (**19a**)
4a		**7**	Ph	110	12	48	34 : 66 (**20a** : **20b**)
		8	CH_2OH	110	10	47	64 : 36 (**21a** : **21b**)
4b		**9**	Me_3Si	18[a]	840	58	100 (**22a**)
5		**9**	Me_3Si	18[a]	960	70	100 (**23a**)

[a] In the presence of excess alkyne.

Because the reactions of nitro azides with terminal alkynes (except for alkyne **9**) give both isomers, selective methods of 1,3-dipolar cycloaddition are wanted.

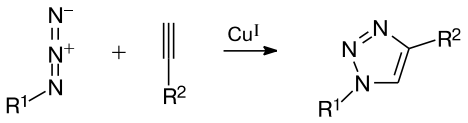
Selective synthesis of 1,4-disubstituted triazoles was implemented by Cu^I-catalyzed cycloaddition of a nitro azide to a terminal alkyne in the system ascorbic acid—cupric sulfate.[26] In all the reactions studied, the yields were increased to 70—96%, the 1,4-disubstituted isomer being the only reaction product (Scheme 4, Table 3). Another benefit is a much higher rate of the reaction completed within 3 h against 10—15 h for thermal cyclization.

Table 3. Outcomes of the copper(I)-catalyzed cyclizations of azides **2a,b**, **3**, **4a,b**, and **5**

Starting compounds and substituents		*t*/h	Yields (%) of the products (%)	M.p./°C
R^1N_3	$HC{\equiv}CR^2$			
2a	**7**	2	71 (**12a**)	163—168
	8	2	96 (**13a**)	115—117
2b	**7**	2	66 (**24**)	131—133
	8	2	62 (**15a**)	115—117
	9	72	20 (**16a**)	88—86
3	**7**	1.5	86 (**17a**)	53—56
		4	44 (**17a**)[a]	
	8	2	86 (**18a**)	165—167
4a	**7**	1	89 (**20a**)	154—156
		3.5	54 (**20a**)[a]	
	8	3	83 (**21a**)	—
4b	**7**	0.5	60 (**25**)	150—153
5	**8**	0.5	84 (**26**)	150—152

[a] In the presence of Cu_2Cl_2 (0.3 equiv.).

Scheme 4



2—5 **7—9** **12a**, **13a**, **15a—18a**, **20a**, **21a**, **24—26**

We found that the use of trimethylsilylacetylene in catalytic cycloaddition results in appreciably lower yields and longer reaction times.

When the "Sharpless catalyst" was replaced by cuprous chloride, the same products were obtained in lower yields, although the amount of cuprous chloride used was twice as high as that of the copper component of the Sharpless catalyst (see Table 3).

1,5-Disubstituted azetidinyltriazoles **12b** and **13b** differ substantially in physicochemical properties from their 1,4-regioisomers **12a** and **13a** and can easily be isolated in the individual state simply by recrystallization.

Structures **12b** and **13b** were examined by ^1H, ^{13}C, and $\{^1H—^{15}N\}$HMBC NMR spectroscopy (Table 4, Figs 1 and 2).

The signals for the carbon atoms in 1,5-disubstituted triazoles (**b**) are more closely located than the signals for the same atoms in 1,4-disubstituted triazoles. The signals for the C(4) and C(5) atoms in 1,4-disubstituted triazoles are shifted downfield and upfield, respectively. A similar spectral pattern has been observed for 1-ethyl-4(5)-nitro-1,2,3-triazoles.[27]

The $\{^1H—^{15}N\}$HMBC NMR spectra of triazoles **b** reveal couplings of the proton of the triazole ring with all three N atoms of the triazole ring (in 1,4-disubstituted triazoles, the ring proton couples only with the N(1) and N(3) atoms). Also, the CH_2 protons of the hydroxymethyl group couple with the N(1) atom and weakly couple with the N(3) atom. The absence of the coupling with the N(1) atom in 1,4-disubstituted triazoles provides evidence for the correct location of the hydroxymethyl group in position 4 of the triazole ring. In phenyltriazoles, no couplings were revealed between the N atoms and the phenyl protons in both regioisomers. These compounds can be distinguished only by the couplings between the N atoms and the proton of the triazole ring,

Table 4. Comparative table of the ^1H, ^{13}C, and ^{15}N NMR signals for triazoles **12a**,**b** and **13a**,**b**

Atom	δ			
	12a	**12b**	**13a**	**13b**
$\underline{N}—NO_2$	−224	−222	−223	−223
$N—\underline{N}O_2$	−19	−20	−20	−19
$C—\underline{N}O_2$	−2	1	−1	1
$C—C\underline{H}_2—N—NO_2$	5.50 (s, 4 H)	5.15 (d, 2 H, *J* = 11.2 Hz); 5.21 (d, 2 H, *J* = 11.2 Hz)	5.43 (s, 4 H)	5.40 (d, 2 H, *J* = 11.8 Hz); 5.59 (d, 2 H, *J* = 11.8 Hz)
Atoms of the triazole fragment				
N(1)	−138	−142	−140	−142
N(2)	—	−16	—	−15
N(3)	−28	−21	−22	−23
C(4)	147.09	133.61	149.15	132.30
C(5)	128.66	139.19	124.08	138.79
$C(4)—\underline{H}$	—	8.11	—	7.80
$C(5)—\underline{H}$	9.02	—	8.53	—

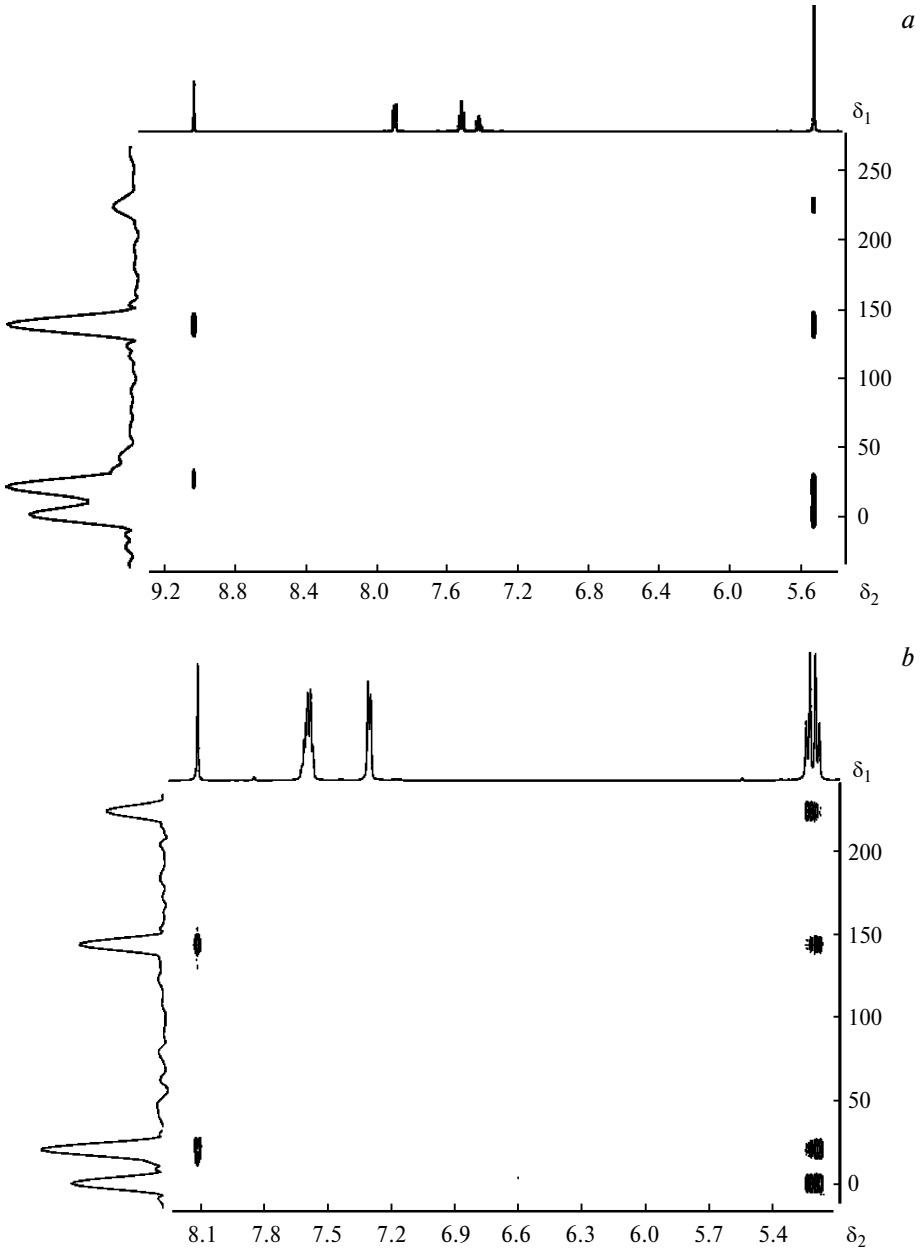


Fig. 1. {^{1}H—^{15}N}HMBC NMR spectra of compounds **12a** (*a*) and **12b** (*b*).

which are similar with those in hydroxymethyl analogs (see Figs 1 and 2).

It should be noted that the protons of the *N*-nitroazetidine ring are manifested as different signals (a singlet for 1,4-disubstituted triazoles and two doublets for 1,5-disubstituted triazoles, see Table 4), which can be due to the different rates of the conformational changes of the azetidine ring (in 1,5-disubstituted triazoles, the rate is lower).

To sum up, we were the first to study 1,3-dipolar cycloaddition of heterocyclic α-nitro azides to substituted alkynes, both with and without copper(I) salts as catalysts. We examined the properties of new 1,2,3-triazole derivatives, which are of interest as intermediates in the synthesis of various classes of chemical (specifically, high-energy) compounds.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC200 (200 MHz), Bruker AM300 (300 MHz), and Bruker AMX 400 instruments (400 MHz) in $CDCl_3$ and DMSO-d_6. {^{1}H—^{15}N}-HMBC NMR spectra were recorded on a Bruker AV600 instrument (600 MHz) in DMSO-d_6 with nitromethane as a standard. IR spectra were recorded on a Thermo Nicolet 360 FTIR

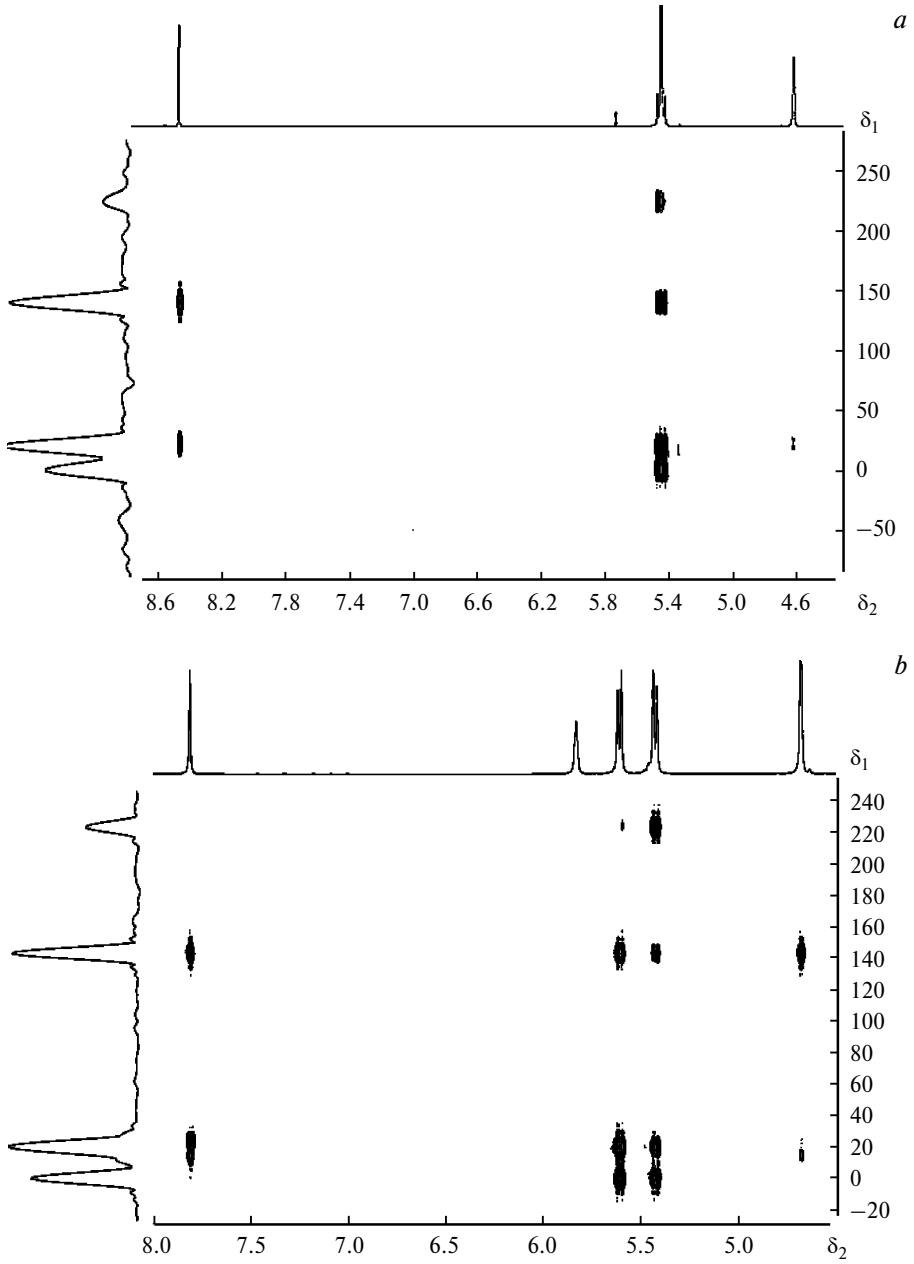


Fig. 2. {^{1}H—^{15}N}HMBC NMR spectra of compounds **13a** (*a*) and **13b** (*b*).

spectrometer (KBr pellets, 7 mm in diameter). Melting points were determined on a Boetius hot stage (heating rate 2 deg · min^{-1}). The course of the reactions was monitored by TLC on Sorbfil plates.

The starting nitro azides were prepared as described earlier.[21] But-2-yne-1,4-diol (**6**), phenylacetylene (**7**), propargyl alcohol (**8**) were purchased from Aldrich. Trimethylsilylacetylene (**9**) was synthesized as described earlier.[28]

Cycloaddition of α-nitro azides to substituted alkynes

Cycloaddition of α-nitro azides to internal alkyne 6 (but-2-yne-1,4-diol). 1-(1,3-Dinitroazetidin-3-yl)-4,5-bis(hydroxymethyl)-1*H*-1,2,3-triazole (10). A mixture of 3-azido-1,3-dinitroazetidine (**2a**) (2.42 g, 12.9 mmol) and but-2-yne-1,4-diol (**6**) (1.11 g, 12.9 mmol) in benzene (50 mL) was heated to boiling with vigorous stirring and left for 24 h. On cooling, the precipitate that formed was filtered off and washed with benzene. Yield 3 g (85%), m.p. 185—190 °C (decomp.). IR, ν/cm^{-1}: 3498, 3280 (OH); 3052, 3037, 2987, 2929 (CH), 1579, 1538, 1341, 1272 (NO_2). ^{1}H NMR (200 MHz, DMSO-d_6), δ: 4.55 (s, 2 H, C(4)—C$\underline{H}_2$—OH); 4.71 (s, 2 H, C(5)—C$\underline{H}_2$—OH); 5.37 (d, 3 H, N—CH_2—O, OH, J = 11.8 Hz); 5.59 (d, 2 H, N—CH_2—C, J = 11.8 Hz); 5.81 (s, 1 H, OH). ^{13}C NMR (50 MHz, DMSO-d_6), δ: 52.33 (C(5)—$\underline{C}H_2$—OH); 54.02 (C(4)—$\underline{C}H_2$—OH); 64.72 (N—$\underline{C}H_2$—C); 87.70 (C—NO_2); 135.71 (N—$\underline{C}$(5)(CH_2)=C); 144.65 (C=$\underline{C}$(4)(CH_2)—N). Found (%): C, 30.60; H, 3.61;

N, 30.75. $C_7H_{10}N_6O_6$. Calculated (%): C, 30.66; H, 3.68; N, 30.65.

1-(2,2-Dimethyl-5-nitro-1,3-dioxan-5-yl)-4,5-bis(hydroxymethyl)-1*H*-1,2,3-triazole (11). A mixture of 5-azido-2,2-dimethyl-5-nitro-1,3-dioxane (**3**) (10 g, 49.5 mmol) and but-2-yne-1,4-diol (**6**) (12 g, 140 mmol) was heated to 70 °C. The resulting melt was stirred for 24 h, cooled, and washed with 15% NaCl (50 mL). The precipitate that formed was filtered off, washed with ice water, and dried in air. Yield 7.5 g (52%), m.p. 135—137 °C. IR, ν/cm^{-1}: 3345 (OH); 3000, 2960, 2892 (CH), 1568, 1343 (NO_2). ^{1}H NMR (300 MHz, DMSO-d_6), δ: 1.40 (s, 6 H, Me); 4.53 (d, 2 H, C$\underline{H}_2$OH, J = 5.4 Hz); 4.64 (d, 2 H, C$\underline{H}_2$OH, J = 4.8 Hz); 4.88 (d, 2 H, O—CH_2—C, J = 12.9 Hz); 4.97 (d, 2 H, O—CH_2—C, J = 12.9 Hz); 5.27 (t, 1 H, OH, J = 5.1 Hz); 5.70 (t, 1 H, OH, J = 4.3 Hz). ^{13}C NMR (75 MHz, DMSO-d_6), δ: 21.41 (Me); 24.92 (Me); 51.00 (C(5)—$\underline{C}H_2$—OH); 53.84 (C(4)—$\underline{C}H_2$—OH); 62.65 (O—$\underline{C}H_2$—C); 95.11 (C—NO_2); 100.07 (O—$\underline{C}$(Me)$_2$—O); 135.26 (N—$\underline{C}$(CH_2)=C(CH_2)); 146.08 (C(CH_2)=$\underline{C}$(CH_2)—N). Found (%): C, 41.73; H, 5.65; N, 19.34. $C_{10}H_{16}N_4O_6$. Calculated (%): C, 41.67; H, 5.59; N, 19.44.

Cyclization of α-nitro azides with terminal alkynes. Method *A*. A mixture of a nitro azide and propargyl alcohol in a molar ratio of 1 : 15 was kept at room temperature for 7—10 days until the starting azide was consumed completely (monitoring by TLC). The excess propargyl alcohol was removed *in vacuo* and the residue was examined by ^{1}H NMR spectroscopy.

Method *B*. A terminal alkyne (1.2 mol) was added to a mixture of the starting azide (1 mol) and toluene. The reaction mixture was refluxed until the starting azide was consumed completely (monitoring by TLC). The solvent and the excess alkyne were removed *in vacuo*. The residue was examined by ^{1}H NMR spectroscopy.

1-(1,3-Dinitroazetidin-3-yl)-4-phenyl-1*H*-1,2,3-triazole (12a) and 1-(1,3-dinitroazetidin-3-yl)-5-phenyl-1*H*-1,2,3-triazole (12b). A reaction of 3-azido-1,3-dinitroazetidine with phenylacetylene was carried out according to method ***B***. Yield 65% (a mixture of regioisomers, **12a** : **12b** = 19 : 81). 1,4-Isomer. ^{1}H NMR (300 MHz, DMSO-d_6), δ: 5.50 (s, N—CH_2—C); 7.29—7.58 (m, Ph); 9.0 (s, CH). 1,5-Isomer. ^{1}H NMR (300 MHz, DMSO-d_6), δ: 5.15 (d, N—CH_2—C, J = 10.3 Hz); 5.21 (d, N—CH_2—C, J = 10.3 Hz); 7.29—7.58 (m, Ph); 7.88 (d, Ph, J = 8.1 Hz); 8.11 (s, CH).

[1-(1,3-Dinitroazetidin-3-yl)-1*H*-1,2,3-triazol-4-yl]methanol (13a) and [1-(1,3-dinitroazetidin-3-yl)-1*H*-1,2,3-triazol-5-yl]methanol (13b). A reaction of 3-azido-1,3-dinitroazetidine with propargyl alcohol was carried out according to methods ***A*** and ***B***. **Method *A*.** Yield 90% (a mixture of regioisomers, **13a** : **13b** = = 36 : 64). 1,4-Isomer. ^{1}H NMR (400 MHz, DMSO-d_6), δ: 4.61 (s, CH_2); 5.39—5.47 (m, N—CH_2—C); 8.45 (s, CH). 1,5-Isomer. ^{1}H NMR (400 MHz, DMSO-d_6), δ: 4.65 (s, CH_2); 5.39—5.47 (m, N—CH_2—C); 5.59 (d, N—CH_2—C, J = 11.2 Hz); 5.77 (s, OH); 7.78 (s, CH). **Method *B*.** Yield 85% (a mixture of regioisomers, **13a** : **13b** = 28 : 72). 1,4-Isomer. ^{1}H NMR (200 MHz, DMSO-d_6), δ: 4.62—4.67 (m, C$\underline{H}_2$—OH); 5.37—5.62 (m, N—CH_2—C, OH); 8.45 (s, CH). 1,5-Isomer. ^{1}H NMR (200 MHz, DMSO-d_6), δ: 4.62—4.67 (m, C$\underline{H}_2$—OH); 5.37—5.62 (m, N—CH_2—C); 5.85 (s, OH); 7.80 (s, CH).

[1-(1-*tert*-Butyl-3-nitroazetidin-3-yl)-1*H*-1,2,3-triazol-4-yl]methanol (15a) and [1-(1-*tert*-butyl-3-nitroazetidin-3-yl)-1*H*-1,2,3-triazol-5-yl]methanol (15b). A reaction of 3-azido-1-*tert*-butyl-3-nitroazetidine (**2b**) with propargyl alcohol was carried out according to methods ***A*** and ***B***. **Method *A*.** Yield 78% (a mixture of regioisomers, **15a** : **15b** = 53 : 47). 1,4-Isomer. ^{1}H NMR (300 MHz, DMSO-d_6), δ: 4.09 (d, N—CH_2—C, J = 10.3 Hz); 4.23—4.33 (m, N—CH_2—C); 4.60 (s, C$\underline{H}_2$—OH); 8.52 (s, CH). 1,5-Isomer. ^{1}H NMR (300 MHz, DMSO-d_6), δ: 4.23—4.33 (m, N—CH_2—C); 4.62 (s, C$\underline{H}_2$—OH); 7.78 (s, CH). **Method *B*.** Yield 91% (a mixture of regioisomers, **15a** : **15b** = = 54 : 46). 1,4-Isomer. ^{1}H NMR (300 MHz, DMSO-d_6), δ: 4.09 (d, N—CH_2—C, J = 10.0 Hz); 4.24—4.32 (m, N—CH_2—C); 4.60—4.62 (m, C$\underline{H}_2$—OH); 5.27 (t, OH, J = 5.1 Hz); 8.51 (s, CH). 1,5-Isomer. ^{1}H NMR (300 MHz, DMSO-d_6), δ: 4.24—4.32 (m, N—CH_2—C); 4.60—4.62 (m, C$\underline{H}_2$—OH); 5.55 (t, OH, J = 5.1 Hz); 7.77 (s, CH).

1-(2,2-Dimethyl-5-nitro-1,3-dioxan-5-yl)-4-phenyl-1*H*-1,2,3-triazole (17a) and 1-(2,2-dimethyl-5-nitro-1,3-dioxan-5-yl)-5-phenyl-1*H*-1,2,3-triazole (17b). A reaction of 5-azido-2,2-dimethyl-5-nitro-1,3-dioxane with phenylacetylene was carried out according to method ***B***. Yield 74% (a mixture of regioisomers, **17a** : **17b** = 37 : 63). 1,4-Isomer. ^{1}H NMR (300 MHz, DMSO-d_6), δ: 1.34 (s, Me); 4.86 (d, O—CH_2—C, J = 12.8 Hz); 5.12 (d, O—CH_2—C, J = 12.5 Hz); 7.37—7.61 (m, Ph); 7.90 (d, Ph, J = 7.3 Hz); 9.25 (s, CH). 1,5-Isomer. ^{1}H NMR (300 MHz, DMSO-d_6), δ: 1.34 (s, Me); 4.54 (d, O—CH_2—C, J = 12.5 Hz); 4.65 (d, O—CH_2—C, J = 13.2 Hz); 7.33 (d, Ph, J = 6.6 Hz); 7.37—7.61 (m, Ph); 7.95 (s, CH).

[1-(2,2-Dimethyl-5-nitro-1,3-dioxan-5-yl)-1*H*-1,2,3-triazol-4-yl]methanol (18a) and [1-(2,2-dimethyl-5-nitro-1,3-dioxan-5-yl)-1*H*-1,2,3-triazol-5-yl]methanol (18b). A reaction of 5-azido-2,2-dimethyl-5-nitro-1,3-dioxane with propargyl alcohol was carried out according to methods ***A*** and ***B***. **Method *A*.** Yield 76% (a mixture of regioisomers, **18a** : **18b** = 74 : 26). 1,4-Isomer. ^{1}H NMR (300 MHz, DMSO-d_6), δ: 1.41 (s, Me); 4.58 (s, C$\underline{H}_2$—OH); 4.79 (d, O—CH_2—C, J = 13.2 Hz); 5.07 (d, O—CH_2—C, J = 13.2 Hz); 8.59 (s, CH). 1,5-Isomer. ^{1}H NMR (300 MHz, DMSO-d_6), δ: 1.41 (s, Me); 4.63 (s, C$\underline{H}_2$—OH); 4.86 (d, O—CH_2—C, J = 13.2 Hz); 4.98 (d, O—CH_2—C, J = 13.2 Hz); 7.80 (s, CH). **Method *B*.** Yield 72% (a mixture of regioisomers, **18a** : **18b** = 64 : 36). 1,4-Isomer. ^{1}H NMR (300 MHz, DMSO-d_6), δ: 1.41 (s, Me); 4.58 (s, C$\underline{H}_2$—OH); 4.79 (d, O—CH_2—C, J = 12.5 Hz); 5.07 (d, O—CH_2—C, J = 13.2 Hz); 8.59 (s, CH). 1,5-Isomer. ^{1}H NMR (300 MHz, DMSO-d_6), δ: 1.41 (s, Me); 4.64 (s, C$\underline{H}_2$—OH); 4.86 (d, O—CH_2—C, J = 12.5 Hz); 4.98 (d, O—CH_2—C, J = 13.2 Hz); 7.80 (s, CH).

3,5-Dinitro-5-(4-phenyl-1*H*-1,2,3-triazol-1-yl)tetrahydro-1,3-oxazine (20a) and 3,5-dinitro-5-(5-phenyl-1*H*-1,2,3-triazol-1-yl)tetrahydro-1,3-oxazine (20b). A reaction of 5-azido-3,5-dinitrotetrahydro-1,3-oxazine (**4a**) with phenylacetylene was carried out according to method ***B***. Yield 48% (a mixture of regioisomers, **20a** : **20b** = 34 : 66). 1,4-Isomer. ^{1}H NMR (400 MHz, DMSO-d_6), δ: 9.27 (s, CH). 1,5-Isomer. ^{1}H NMR (400 MHz, DMSO-d_6), δ: 7.96 (s, CH).

[1-(3,5-Dinitrotetrahydro-1,3-oxazin-5-yl)-1*H*-1,2,3-triazol-4-yl]methanol (21a) and [1-(3,5-dinitrotetrahydro-1,3-oxazin-5-yl)-1*H*-1,2,3-triazol-5-yl]methanol (21b). A reaction of 5-azido-3,5-dinitrotetrahydro-1,3-oxazine with propargyl alcohol was carried out according to method ***B***. Yield 47% (a mixture of regioisomers, **21a** : **21b** = 64 : 36). 1,4-Isomer. ^{1}H NMR (400 MHz, DMSO-d_6), δ: 8.66 (s, CH). 1,5-Isomer. ^{1}H NMR (400 MHz, DMSO-d_6), δ: 8.32 (s, CH).

1-(1,3-Dinitroazetidin-3-yl)-5-phenyl-1*H*-1,2,3-triazole (12b). Phenylacetylene (**7**) (0.14 g, 1.35 mmol) was added to 3-azido-

1,3-dinitroazetidine (**2a**) (0.20 g, 1.06 mmol) in toluene (30 mL). The reaction mixture was refluxed for 6 h. On cooling, the precipitate that formed was filtered off and washed with toluene. Yield 0.13 g (41%), light cream-colored crystals, m.p. 193.5—195 °C. IR, ν/cm^{-1}: 3151 (CH_{tr}), 3065, 3028 (CH_{Ph}), 2968 (CH), 1591, 1553, 1353, 1299 (NO_2). ^{1}H NMR (300 MHz, DMSO-d_6), δ: 5.15 (d, 2 H, CH_2, J = 11.2 Hz); 5.21 (d, 2 H, CH_2, J = = 11.2 Hz); 7.29 (d, 2 H, Ph, J = 6.4 Hz); 7.59 (m, 3 H, Ph); 8.11 (s, 1 H, CH). ^{13}C NMR (50 MHz, DMSO-d_6), δ: 64.50 (CH_2); 87.20 (C—NO_2); 124.59 (p-C_{Ph}); 128.46 (o-C_{Ph}); 129.50 (m-C_{Ph}); 130.64 (*ipso*-C_{Ph}); 133.61 (C=<u>C</u>H—N); 139.19 (N—<u>C</u>(Ph)=CH). Found (%): C, 45.47; H, 3.36; N, 28.99. $C_{11}H_{10}N_6O_4$. Calculated (%): C, 45.52; H, 3.47; N, 28.96.

[1-(1,3-Dinitroazetidin-3-yl)-1*H*-1,2,3-triazol-5-yl]methanol (13b). A solution of 3-azido-1,3-dinitroazetidine (**2a**) (0.65 g, 3.46 mmol) and propargyl alcohol (0.30 g, 5.36 mmol) in toluene (30 mL) was refluxed for 11 h. On cooling, the precipitate that formed was filtered off. The crude product was purified by preparative TLC followed by recrystallization from ethyl acetate. Yield 0.40 g (47%), m.p. 188—190 °C. IR, ν/cm^{-1}: 3250 (OH), 3163 (CH_{tr}), 3052, 2994 (CH), 1579, 1532, 1340 (NO_2). ^{1}H NMR (200 MHz, DMSO-d_6), δ: 4.66 (d, 2 H, C<u>H</u>$_2$—OH, J = 3.8 Hz); 5.40 (d, 2 H, N—CH_2—C, J = 11.8 Hz); 5.59 (d, 2 H, N—CH_2—C, J = 11.8 Hz); 5.84 (s, 1 H, OH); 7.80 (s, 1 H, CH). ^{13}C NMR (50 MHz, DMSO-d_6), δ: 52.46 (CH_2—OH); 64.46 (N—<u>C</u>H$_2$—C); 87.24 (C—NO_2); 132.30 (C=<u>C</u>H—N); 138.79 (N—<u>C</u>(CH$_2$)=CH). Found (%): C, 29.45; H, 3.38; N, 34.50. $C_6H_8N_6O_5$. Calculated (%): C, 29.51; H, 3.30; N, 34.42.

Synthesis of 1,2,3-triazoles

Synthesis of trimethylsilyl-1,2,3-triazoles. Method *A*. A mixture of a nitro azide and trimethylsilylacetylene (**9**) in a molar ratio of 1 : 10 was kept at room temperature for 20—30 days until the starting azide was consumed completely (monitoring by TLC). The excess trimethylsilylacetylene (**9**) was removed. When needed, the product was recrystallized from chloroform—hexane.

Method *B*. A mixture of a nitro azide and trimethylsilylacetylene (**9**) in a molar ratio of 1 : 10 was kept in CH_2Cl_2 at 55 °C for 7—13 h. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. When needed, the product was purified by preparative TLC.

1-(1,3-Dinitroazetidin-3-yl)-4-trimethylsilyl-1*H*-1,2,3-triazole (14a) was obtained according to method ***B***. Yield 78%, m.p. 132—135 °C. IR, ν/cm^{-1}: 3123 (CH_{tr}), 3037, 2967 (CH), 1588, 1538, 1343, 1288 (NO_2), 1247, 843 (TMS). ^{1}H NMR (200 MHz, DMSO-d_6), δ: 0.3 (s, 9 H, Si—Me); 5.4 (s, 4 H, CH_2); 8.6 (s, 1 H, CH). ^{13}C NMR (50 MHz, DMSO-d_6), δ: −1.17 (Si—Me); 65.16 (CH_2); 86.46 (C—NO_2); 132.01 (N—<u>C</u>H=C); 146.15 (CH=<u>C</u>(TMS)—N). Found (%): C, 33.60; H, 4.82; N, 29.48. $C_8H_{14}N_6O_4Si$. Calculated (%): C, 33.56; H, 4.93; N, 29.35.

1-(1-*tert*-Butyl-3-nitroazetidin-3-yl)-4-trimethylsilyl-1*H*-1,2,3-triazole (16a) was obtained according to method ***A***. Yield 62%, m.p. 86—88 °C. IR, ν/cm^{-1}: 3113 (CH_{tr}), 2967 (CH), 1560, 1365, 1352 (NO_2), 1249, 854, 840 (TMS). ^{1}H NMR (300 MHz, DMSO-d_6), δ: 0.31 (s, 9 H, Si—Me); 0.97 (s, 9 H, C—Me); 4.10 (d, 2 H, CH_2, J = 9.1 Hz); 4.33 (d, 2 H, CH_2, J = 9.1 Hz); 8.72 (s, 1 H, CH). ^{13}C NMR (50 MHz, DMSO-d_6), δ: −1.23 (Si—Me); 23.64 (C—<u>Me</u>); 52.05 (<u>C</u>—Me); 55.84 (CH_2); 89.46 (C—NO_2); 131.75 (N—<u>C</u>H=C); 146.02 (CH=<u>C</u>(TMS)—N). Found (%): C, 48.47; H, 7.81; N, 23.49. $C_{12}H_{23}N_5O_2Si$. Calculated (%): C, 48.46; H, 7.79; N, 23.55.

1-(2,2-Dimethyl-5-nitro-1,3-dioxan-5-yl)-4-trimethylsilyl-1*H*-1,2,3-triazole (19a) was obtained according to method ***B***. Yield 76%, m.p. 126—127 °C. IR, ν/cm^{-1}: 3094, 2999, 2959, 2900 (CH), 1563, 1377 (NO_2), 1254, 840 (TMS). ^{1}H NMR (300 MHz, DMSO-d_6), δ: 0.28 (s, 9 H, Si—Me); 1.39 (s, 3 H, Me); 1.44 (s, 3 H, Me); 4.77 (d, 2 H, CH_2, J = 12.8 Hz); 5.11 (d, 2 H, CH_2, J = 12.8 Hz); 8.76 (s, 1 H, CH). ^{13}C NMR (75 MHz, DMSO-d_6), δ: −1.27 (Si—Me); 20.79 (Me); 25.58 (Me); 61.94 (CH_2); 91.29 (C—NO_2); 99.54 (O—<u>C</u>(Me)$_2$—O); 129.85 (N—<u>C</u>H=C); 145.98 (CH=<u>C</u>(TMS)—N). Found (%): C, 44.00; H, 6.79; N, 18.52. $C_{11}H_{20}N_4O_4Si$. Calculated (%): C, 43.98; H, 6.71; N, 18.65.

3-*tert*-Butyl-5-nitro-5-(4-trimethylsilyl-1*H*-1,2,3-triazol-1-yl)tetrahydro-1,3-oxazine (22a) was obtained according to method ***A***. Yield 58%, m.p. 121—124.5 °C. IR, ν/cm^{-1}: 3141 (CH_{tr}), 2973 (CH), 1565, 1345 (NO_2), 1251, 846 (TMS). ^{1}H NMR (300 MHz, DMSO-d_6), δ: 0.30 (s, 9 H, Si—Me); 1.08 (s, 9 H, C—Me); 3.51 (d, 1 H N—CH_2—C, J = 12.5 Hz); 4.13 (d, 1 H, N—CH_2—O, J = 8.1 Hz); 4.31 (d, 1 H, O—CH_2—C, J = 12.5 Hz); 4.46 (d, 1 H, N—CH_2—C, J = 12.5 Hz); 4.61 (d, 1 H, N—CH_2—O, J = 8.1 Hz); 5.15 (d, 1 H, O—CH_2—C, J = 12.5 Hz); 8.79 (s, 1 H, CH). ^{13}C NMR (75 MHz, DMSO-d_6), δ: −1.24 (Si—Me); 26.37 (C—<u>Me</u>); 50.40 (N—<u>C</u>H$_2$—C); 52.96 (<u>C</u>—Me); 67.97 (C—<u>C</u>H$_2$—O); 80.21 (N—CH_2—O); 93.19 (C—NO_2); 129.65 (N—<u>C</u>H=C); 145.81 (CH=<u>C</u>(TMS)—N). Found (%): C, 47.66 H, 7.59; N, 21.42 $C_{13}H_{25}N_5O_3Si$. Calculated (%): C, 47.68; H, 7.70; N, 21.39.

1,3-Di-*tert*-butyl-5-nitro-5-(4-trimethylsilyl-1*H*-1,2,3-triazol-1-yl)hexahydropyrimidine (23a) was obtained according to method ***A***. Yield 70%, m.p. 138—141.5 °C. IR, ν/cm^{-1}: 3122 (CH_{tr}), 2983, 2966 (CH), 1566, 1555, 1363 (NO_2), 1252, 845, 832 (TMS). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.31 (s, 9 H, Si—Me); 1.12 (s, 18 H, C—Me); 3.21 (d, 1 H, N—CH—N, J = 8.8 Hz); 3.28 (d, 2 H, N—CH_2—C, J = 12.1 Hz); 3.83 (d, 1 H, N—CH—N, J = 8.8 Hz); 4.18 (d, 2 H, N—CH_2—C, J = 12.1 Hz); 7.79 (s, 1 H, CH). ^{13}C NMR (75 MHz, DMSO-d_6), δ: −1.24 (Si—Me); 26.05 (C—<u>Me</u>); 50.96 (N—<u>C</u>H$_2$—C); 53.40 (<u>C</u>—Me); 63.01 (N—CH_2N); 95.20 (C—NO_2); 129.35 (N—<u>C</u>H=C); 145.51 (CH=<u>C</u>(TMS)—N). Found (%): C, 53.42; H, 9.03; N, 21.87. $C_{17}H_{34}N_6O_2Si$. Calculated (%): C, 53.37; H, 8.96; N, 21.97.

Copper(I)-catalyzed synthesis of 1,2,3-triazoles

Freshly prepared aqueous solutions of ascorbic acid and $CuSO_4 \cdot 5H_2O$ were added to a solution of an azide and an alkyne in THF; the molar ratio of azide : alkyne : ascorbic acid : $CuSO_4$ was 1 : 1.2 : 0.5 : 0.15. The reaction mixture was stirred at room temperature for 1—3 h and diluted with water. The product was extracted with ethyl acetate. The extract was dried with Na_2SO_4 and concentrated *in vacuo*. When needed, the product was purified by preparative TLC with ethyl acetate—hexane as an eluent (see Table 3).

1-(1,3-Dinitroazetidin-3-yl)-4-phenyl-1*H*-1,2,3-triazole (12a). IR, ν/cm^{-1}: 3130 (CH_{tr}), 3104 (CH_{Ph}), 3032, 2979 (CH), 1558, 1343, 1289 (NO_2). ^{1}H NMR (300 MHz, DMSO-d_6), δ: 5.50 (s, 4 H, CH_2); 7.40 (m, 1 H, Ph); 7.51 (t, 2 H, Ph, J = 7.6 Hz); 7.88 (d, 2 H, Ph, J = 8.1 Hz); 9.02 (s, 1 H, CH). ^{13}C NMR (75 MHz, DMSO-d_6), δ: 64.96 (CH_2); 86.81 (C—NO_2); 122.69 (p-C_{Ph});

125.44 (*o*-C_{Ph}); 128.66 (N—C̲H=C); 129.16 (*m*-C_{Ph}); 129.48 (*ipso*-C_{Ph}); 147.09 (CH=C̲(Ph)—N). Found (%): C, 45.56; H, 3.39; N, 29.05. $C_{11}H_{10}N_6O_4$. Calculated (%): C, 45.52; H, 3.47; N, 28.96.

[1-(1,3-Dinitroazetidin-3-yl)-1*H*-1,2,3-triazol-4-yl]methanol (13a). IR, ν/cm^{-1}: 3341 (OH), 3154 (CH_{tr}), 2970 (CH), 1584, 1559, 1355, 1338, 1281 (NO_2). ^{1}H NMR (300 MHz, DMSO-d_6), δ: 4.61 (s, 2 H, CH_2—OH); 5.39 (s, 1 H, OH); 5.43 (s, 4 H, N—CH_2—C); 8.44 (s, 1 H, CH). ^{13}C NMR (75 MHz, DMSO-d_6), δ: 54.82 (CH_2—OH); 65.04 (N—C̲H_2—C); 86.75 (C—NO_2); 124.08 (N—C̲H=C); 149.15 (CH=C̲(CH_2)—N). Found (%): C, 29.54; H, 3.25; N, 34.49. $C_6H_8N_6O_5$. Calculated (%): C, 29.51; H, 3.30; N, 34.42.

[1-(1-*tert*-Butyl-3-nitroazetidin-3-yl)-1*H*-1,2,3-triazol-4-yl]methanol (15a). IR, ν/cm^{-1}: 3199 (OH), 3143 (CH_{tr}), 2978 (CH), 1566, 1370, 1353 (NO_2). ^{1}H NMR (300 MHz, DMSO-d_6), δ: 0.96 (s, 9 H, Me); 4.09 (d, 2 H, N—CH_2—C, *J* = 9.5 Hz); 4.31 (d, 2 H, N—CH_2—C, *J* = 9.5 Hz); 4.60 (d, 2 H, CH_2—OH, *J* = 5.1 Hz); 5.34 (t, 1 H, OH, *J* = 5.1 Hz); 8.53 (s, 1 H, CH). ^{13}C NMR (75 MHz, DMSO-d_6), δ: 23.63 (Me); 52.06 (C̲—Me); 54.88 (C̲H_2—OH); 55.81 (N—C̲H_2—C); 89.75 (C—NO_2); 123.98 (N—C̲H=C); 149.03 (CH=C̲(CH_2)—N). Found (%): C, 47.12; H, 6.68; N, 27.36. $C_{10}H_{17}N_5O_3$. Calculated (%): C, 47.05; H, 6.71; N, 27.43.

1-(2,2-Dimethyl-5-nitro-1,3-dioxan-5-yl)-4-phenyl-1*H*-1,2,3-triazole (17a). IR, ν/cm^{-1}: 3128 (CH_{tr}), 3103 (CH_{Ph}), 3092, 2999 (CH), 1572, 1380 (NO_2). ^{1}H NMR (300 MHz, DMSO-d_6), δ: 1.43 (s, 3 H, Me); 1.44 (s, 3 H, Me); 4.85 (d, 2 H, CH_2, *J* = 13.2 Hz); 5.11 (d, 2 H, CH_2, *J* = 12.5 Hz); 7.39 (t, 1 H, Ph, *J* = 7.3 Hz); 7.50 (t, 2 H, Ph, *J* = 7.3 Hz); 7.89 (d, 2 H, Ph, *J* = 8.1 Hz), 9.25 (s, 1 H, CH). ^{13}C NMR (75 MHz, DMSO-d_6), δ: 21.38 (Me); 24.95 (Me); 61.89 (CH_2); 91.51 (C—NO_2); 99.69 (O—C̲(Me)$_2$—O); 121.08 (*p*-C_{Ph}); 125.40 (*o*-C_{Ph}); 128.63 (N—C̲H=C); 129.06 (*m*-C_{Ph}); 129.44 (*ipso*-C_{Ph}); 147.07 (CH=C̲(Ph)—N). Found (%): C, 55.30; H, 5.27; N, 18.47. $C_{14}H_{16}N_4O_4$. Calculated (%): C, 55.26; H, 5.30; N, 18.41.

[1-(2,2-Dimethyl-5-nitro-1,3-dioxan-5-yl)-1*H*-1,2,3-triazol-4-yl]methanol (18a). IR, ν/cm^{-1}: 3298 (OH), 3145 (CH_{tr}), 3009, 2935 (CH), 1575, 1360 (NO_2). ^{1}H NMR (300 MHz, DMSO-d_6), δ: 1.41 (s, 6 H, Me); 4.58 (d, 2 H, CH_2—OH, *J* = 4.4 Hz); 4.79 (d, 2 H, O—CH_2—C, *J* = 12.5 Hz); 5.07 (d, 2 H, O—CH_2—C, *J* = 12.5 Hz); 5.38 (t, 1 H, OH, *J* = 5.1 Hz); 8.60 (s, 1 H, CH). ^{13}C NMR (75 MHz, DMSO-d_6), δ: 21.58 (Me); 24.78 (Me); 54.82 (CH_2—OH); 61.93 (O—C̲H_2—C); 91.52 (C—NO_2); 99.64 (O—C̲(Me)$_2$—O); 122.50 (N—C̲H=C); 148.94 (CH=C̲(CH_2)—N). Found (%): C, 41.90; H, 5.38; N, 21.64. $C_9H_{14}N_4O_5$. Calculated (%): C, 41.86; H, 5.46; N, 21.70.

3,5-Dinitro-5-(4-phenyl-1*H*-1,2,3-triazol-1-yl)tetrahydro-1,3-oxazine (20a). IR, ν/cm^{-1}: 3140 (CH_{tr}), 3109 (CH_{Ph}), 3046, 3030 (CH), 1579—1570, 1293 (NO_2), 1011 (COC). ^{1}H NMR (300 MHz, DMSO-d_6), δ: 4.97 (d, 1 H, O—CH_2—C, *J* = 12.4 Hz); 5.17 (d, 1 H, O—CH_2—C, *J* = 12.4 Hz); 5.30 (m, 2 H, O—CH_2—C, N—CH_2—C); 5.92 (m, 2 H, O—CH_2—C, N—CH_2—C); 7.41 (m, 1 H, Ph); 7.52 (t, 2 H, Ph, *J* = 8.0 Hz); 7.90 (d, 2 H, Ph, *J* = 7.1 Hz); 9.30 (s, 1 H, CH). ^{13}C NMR (75 MHz, DMSO-d_6), δ: 49.43 (N—C̲H_2—C); 68.86 (C—C̲H_2—O); 76.51 (N—CH_2—O); 90.73 (C—NO_2); 121.59 (*p*-C_{Ph}); 125.37 (*o*-C_{Ph}); 128.71 (N—C̲H=C); 129.06 (*m*-C_{Ph}); 129.22 (*ipso*-C_{Ph}); 147.18 (CH=C̲(Ph)—N). Found (%): C, 45.04; H, 3.80; N, 26.23. $C_{12}H_{12}N_6O_5$. Calculated (%): C, 45.00; H, 3.78; N, 26.24.

[1-(3,5-Dinitrotetrahydro-1,3-oxazin-5-yl)-1*H*-1,2,3-triazol-4-yl]methanol (21a). IR, ν/cm^{-1}: 3386 (OH), 3155 (CH_{tr}), 3039, 2941, 2887 (CH), 1576, 1339, 1290 (NO_2), 1083, 1022 (C—O). ^{1}H NMR (300 MHz, DMSO-d_6), δ: 4.60 (d, 2 H, CH_2—OH, *J* = 5.1 Hz); 4.89 (d, 1 H, O—CH_2—C, *J* = 12.5 Hz); 5.10 (d, 1 H, O—CH_2—C, *J* = 12.5 Hz); 5.19 (d, 1 H, N—CH_2—C, *J* = 15.4 Hz); 5.28 (d, 1 H, O—CH_2—N, *J* = 11.7 Hz); 5.43 (m, 1 H, OH); 5.86 (m, 2 H, O—CH_2—C, N—CH_2—C); 8.67 (s, 1 H, CH). ^{13}C NMR (50 MHz, DMSO-d_6), δ: 49.57 (N—C̲H_2—C); 54.82 (CH_2—OH); 68.99 (C—C̲H_2—O); 76.64 (N—CH_2—O); 90.84 (C—NO_2); 123.11 (N—C̲H=C); 149.23 (CH=C̲(CH_2)—N). Found (%): C, 30.68; H, 3.77; N, 30.69. $C_7H_{10}N_6O_6$. Calculated (%): C, 30.66; H, 3.68; N, 30.65.

1-(1-*tert*-Butyl-3-nitroazetidin-3-yl)-4-phenyl-1*H*-1,2,3-triazole (24). IR, ν/cm^{-1}: 3128 (CH_{tr}), 3085, 3066 (CH_{Ph}), 3034, 2969 (CH), 1565, 1353 (NO_2). ^{1}H NMR (300 MHz, DMSO-d_6), δ: 0.99 (s, 9 H, Me); 4.17 (d, 2 H, CH_2, *J* = 8.8 Hz); 4.37 (d, 2 H, CH_2, *J* = 9.5 Hz); 7.40 (m, 1 H, Ph); 7.50 (t, 2 H, Ph, *J* = 7.0 Hz); 7.91 (d, 2 H, Ph, *J* = 7.3 Hz); 9.14 (s, 1 H, CH). ^{13}C NMR (75 MHz, DMSO-d_6), δ: 23.63 (Me); 52.08 (C̲—Me); 55.66 (CH_2); 89.91 (C—NO_2); 122.57 (*p*-C_{Ph}); 125.44 (*o*-C_{Ph}); 128.53 (N—C̲H=C); 129.03 (*m*-C_{Ph}); 129.65 (*ipso*-C_{Ph}); 147.12 (CH=C̲(Ph)—N). Found (%): C, 59.75; H, 6.40; N, 23.21. $C_{15}H_{19}N_5O_2$. Calculated (%): C, 59.79; H, 6.36; N, 23.24.

3-*tert*-Butyl-5-nitro-5-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-tetrahydro-1,3-oxazine (25). IR, ν/cm^{-1}: 3122 (CH_{tr}), 3092 (CH_{Ph}), 3027, 3006, 2970 (CH), 1563, 1367 (NO_2). ^{1}H NMR (300 MHz, DMSO-d_6), δ: 1.09 (s, 9 H, Me); 3.64 (d, 1 H, N—CH_2—C, *J* = 11.7 Hz); 4.18 (d, 1 H, N—CH_2—O, *J* = 7.3 Hz); 4.43 (d, 2 H, N—CH_2—C, O—CH_2—C, *J* = 11.0 Hz); 4.60 (d, 1 H, N—CH_2—O, *J* = 7.3 Hz); 5.12 (d, 1 H, O—CH_2—C, *J* = 11.7 Hz); 7.44 (m, 3 H, Ph); 7.90 (d, 2 H, Ph, *J* = 7.3 Hz); 9.28 (s, 1 H, CH). ^{13}C NMR (75 MHz, DMSO-d_6), δ: 26.41 (Me); 50.34 (N—C̲H_2—C); 53.05 (C̲—Me); 67.87 (C—C̲H_2—O); 80.33 (N—CH_2—O); 93.47 (C—NO_2); 120.84 (*p*-C_{Ph}); 125.39 (*o*-C_{Ph}); 128.62 (N—C̲H=C); 129.05 (*m*-C_{Ph}); 129.54 (*ipso*-C_{Ph}); 146.94 (CH=C̲(Ph)—N). Found (%): C, 58.08; H, 6.44; N, 21.08. $C_{16}H_{21}N_5O_3$. Calculated (%): C, 57.99; H, 6.39; N, 21.13.

[1-(1,3-Di-*tert*-butyl-5-nitrohexahydropyrimidin-5-yl)-1*H*-1,2,3-triazol-4-yl]methanol (26). IR, ν/cm^{-1}: 3278 (OH), 3176 (CH_{tr}), 2974 (CH), 1559, 1367, 1346 (NO_2). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.12 (s, 18 H, Me); 3.46 (m, 3 H, N—CH—N, N—CH_2—C); 3.62 (d, 1 H, N—CH—N, *J* = 8.8 Hz); 3.93 (d, 2 H, N—CH_2—C, *J* = 11.7 Hz); 4.80 (s, 2 H, CH_2—OH); 7.89 (s, 1 H, CH). ^{13}C NMR (75 MHz, DMSO-d_6), δ: 26.07 (Me); 50.93 (N—C̲H_2—C); 53.51(C̲—Me); 54.82 (CH_2—OH); 63.13 (N—CH_2—N); 95.48 (C—NO_2); 122.12 (N—C̲H=C); 148.46 (CH=C̲(CH_2)—N). Found (%): C, 52.82; H, 8.36; N, 24.68. $C_{15}H_{28}N_6O_3$. Calculated (%): C, 52.92; H, 8.29; N, 24.69.

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