

SYNTHESIS OF SUBSTITUTED 6-(1H-1,2,3-TRIAZOL-1-YL)-4,7-DIHYDRO-1,3,5-DIOXAZEPINE

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A convenient method was developed for the synthesis of 6-(1H-1,2,3-triazol-1-yl)-4,7-dihydro-1,3,5-dioxazepines, using deoxygenation of 1-(5-nitro-1,3-dioxan-5-yl)-1H-1,2,3-triazoles with triethyl phosphite.

Keywords: 1,3,5-dioxazepines, geminal nitroazides, 5-nitro-1,3-dioxanes, 1,2,3-triazoles, triethyl phosphite, deoxygenation, 1,3-dipolar cycloaddition, oxidative azidation.

Deoxygenation of nitroaromatic compounds in the presence of organic trivalent phosphorus derivatives led to the formation of a wide range of nitrogen-containing heterocycles [1-4]. This stepwise reaction involved the formation of nitrene [5-8] and, in the cases when a nucleophilic center was present at the *ortho* position, led to the formation of condensed heterocyclic system. Both five-membered and six-membered nitrogen-containing heterocyclic systems have been constructed by such approach [9-11]. The lack of a required reactive group at the *ortho* position might result in benzene ring expansion *via* enclosure at C–C bond yielding 3*H*-azepines [12, 13].

Nature of both nitroalkane and reducing agent affects course and scope of the reaction. Several methods are currently known for deoxygenation of primary and secondary nitroalkanes with trivalent phosphorus compounds, leading to the formation of nitriles [14-17], amines [18], and derivatives of oximes [15, 19-21].

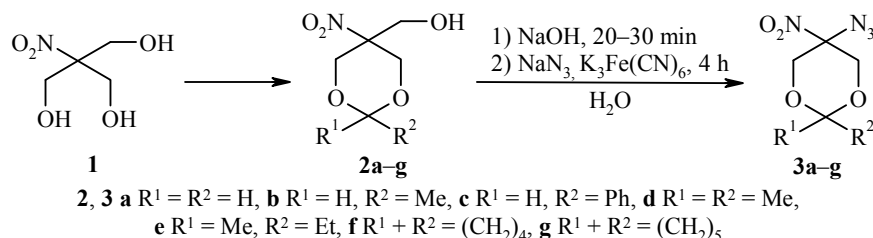
There is insufficient information available about the reactivity of tertiary nitro compounds under analogous conditions. Although it is known that the reaction of 2-halo-2-nitropropanes with triethyl phosphite results in phosphate esters of oximes [20], and α -chloronitrocycloalkanes react with triphenylphosphine, giving ring expansion products [22], the deoxygenation of geminal nitro nitroso compounds with triethyl phosphite, on the other hand, occurs at the nitroso group regardless of the substrate structure. This reaction is accompanied by nitrogen atom insertion at the C–N bond with the formation of nitrimines [23].

In this work, for a series of 1-(5-nitro-1,3-dioxan-5-yl)-1H-1,2,3-triazole derivatives, we studied the possibility of nitro group transformation by the action of triethyl phosphite. The starting compounds were synthesized in three steps from 2-hydroxymethyl-2-nitropropane-1,3-diol (**1**). In the first step, the nitro alcohol **1** was condensed with dimethoxymethane [24], aldehydes, or ketones [25] in the presence of acidic catalysts,

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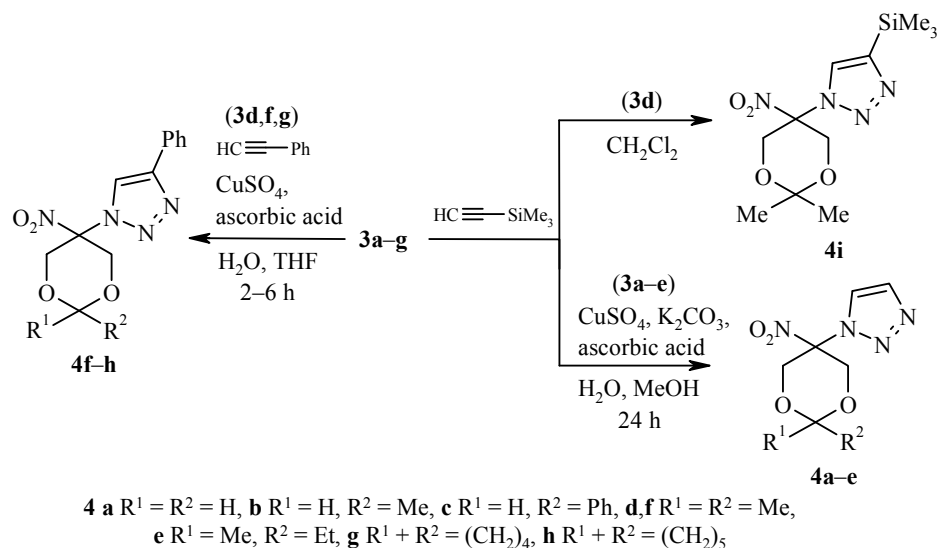
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giving compounds **2a,b,c** or **2d-g**, respectively. The hydroxymethyl derivatives **2a-g** were further subjected to oxidative azidation in the presence of $K_3[Fe(CN)_6]$ under basic conditions, yielding 5-azido-5-nitro-1,3-dioxanes **3a-g** [26].



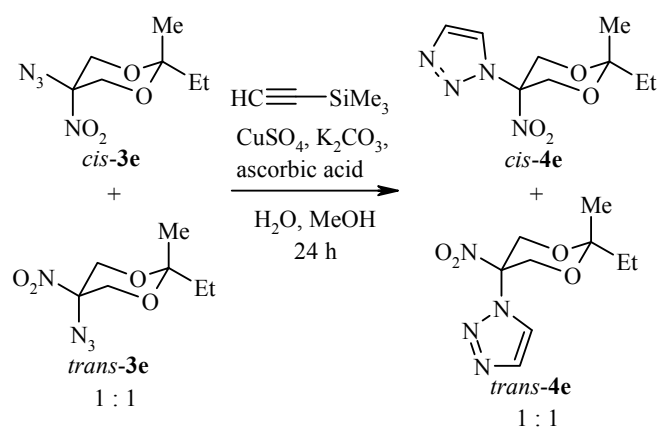
As shown previously [27], heterocyclic α -nitroazides are highly reactive in 1,3-dipolar cycloaddition to terminal acetylenes under thermal cyclization conditions, giving a mixture of 1,4- and 1,5-triazoles, regardless of the structure of aliphatic heterocycle. Performing the cyclization in the presence of copper(I) salts resulted in selective formation of 1,4-substituted triazoles.

In the current work, we used both 1-substituted and 1,4-disubstituted 1,2,3-triazoles. The mono-substituted triazoles **4a-e** were synthesized from the corresponding nitroazides **3a-e** and trimethylsilyl acetylene (TMSA). The reaction was performed at room temperature in aqueous methanolic medium in the presence of copper sulfate, ascorbic acid, and potassium carbonate [28]. The process was found to be selective, without the formation of trimethylsilyl-substituted triazoles (according to NMR spectroscopy, LC/MS), irrespective of the structure of 5-azido-5-nitro-1,3-dioxane. The yield of target products practically was not affected by order of the reactant addition, while reaction rate was mostly determined by the solubility of the reactants.



Using the example of equimolar (1:1) mixture of *cis*-**3e** and *trans*-**3e** stereoisomers [26], it was shown that the cycloaddition reaction occurred with equal success for both compounds. The ratio of *cis*-1-(2-ethyl-2-methyl-5-nitro-1,3-dioxan-5-yl)-1*H*-1,2,3-triazole (*cis*-**4e**) and *trans*-1-(2-ethyl-2-methyl-5-nitro-1,3-dioxan-5-yl)-1*H*-1,2,3-triazole (*trans*-**4e**) remained unchanged at 1:1, as determined from NMR spectra, including a NOESY 2D NMR experiment.

The 1,4-disubstituted triazoles **4f-h** were obtained by addition of azides **3d,f,g** to phenylacetylene in the presence of ascorbic acid and copper(II) sulfate, while 1-(2,2-dimethyl-5-nitro-1,3-dioxan-5-yl)-4-trimethylsilyl-1*H*-1,2,3-triazole (**4i**) was synthesized from azide **3d** and TMSA without a catalyst [27].



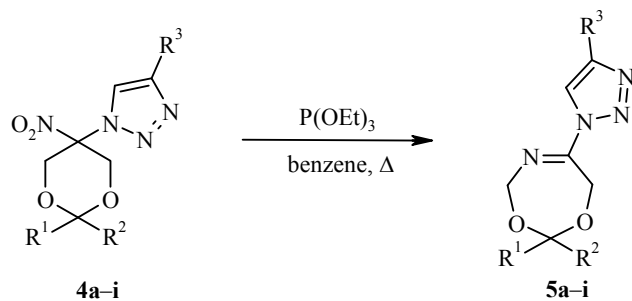
All triazoles **4a-i** were colorless crystalline compounds, which infrared spectra contained bands of asymmetric ($1563\text{-}1585\text{ cm}^{-1}$) and symmetric ($1332\text{-}1380\text{ cm}^{-1}$) vibrations of nitro group. The intensity of these bands depended on the molecular structure. In comparison, spirodioxanes **4g,h** had significantly more intense asymmetric vibration bands and weaker bands of symmetric vibrations.

The character of ^1H NMR signals of dioxane ring methylene protons (positions 4 and 6) was defined by the presence of methine proton at position 2 of the ring. The spectra of compounds **4a,d-i** contained resonance signals due to non-equivalent axial and equatorial protons as two doublets with geminal spin-spin coupling constants of $12.2\text{-}13.2\text{ Hz}$, which is characteristic of substituted 1,3-dioxanes [29]. Each of doublets was transformed into a double triplet in the spectra of compounds **4b,c** ($^2J = 12.2\text{ Hz}$, $^4J = 1.6\text{ Hz}$). The assignment of ^{13}C NMR signals was based on HSQC and HMBC 2D NMR spectra (Table 1). The HMBC spectrum of spirodioxane **4g** showed that the 1,4- CH_2 and 2,3- CH_2 methylene protons of the cyclopentane ring ($1.58\text{-}1.66\text{ ppm}$ and $1.87\text{-}1.94\text{ ppm}$, respectively), as well as equatorial (4.85 ppm) and axial (5.11 ppm) methylene protons of dioxane ring correlated with the C-5 carbon atom (111.2 ppm). On the other hand, the axial protons of dioxane (5.11 ppm) formed cross peaks with both quaternary carbon atoms C-5 and C-8 (111.2 and 91.2 ppm , respectively). Thus, we conclude that the carbon atom at the dioxane ring position 5 gave a relatively upfield signal ($90.4\text{-}91.7\text{ ppm}$) compared to the carbon atom at position 2 of the studied compounds ($92.9\text{-}111.2\text{ ppm}$). All the obtained compounds were clearly detected as positive molecular ions $[\text{M}+\text{H}]^+$ under APCI (100%).

Deoxygenation reaction of 1-(5-nitro-1,3-dioxan-5-yl)-1H-1,2,3-triazoles **4a-i** was studied in benzene with excess of triethyl phosphite (5-10 equiv.). The reaction progress was controlled by TLC and LC/MS. The target products were isolated by column chromatography after the removal of solvent and unreacted triethyl phosphite.

TABLE 1. The Detected $^1\text{H}\text{-}^{13}\text{C}$ Correlations in the HSQC and HMBC Spectra of Compound **4g**

^1H , δ , ppm	^{13}C , δ , ppm	
	HSQC	HMBC
1.58-1.66	22.5; 22.9	22.5; 22.9; 32.8; 35.2; 111.2
1.87-1.94	32.8; 35.2	22.5; 22.9; 32.8; 35.2; 111.2
4.85	63.4	63.4; 111.2
5.11	63.4	63.4; 91.2; 111.2
7.38	128.4	125.3
7.48	128.8	125.3; 128.8
7.89	125.3	125.3; 128.4; 146.9
9.19	120.9	146.9

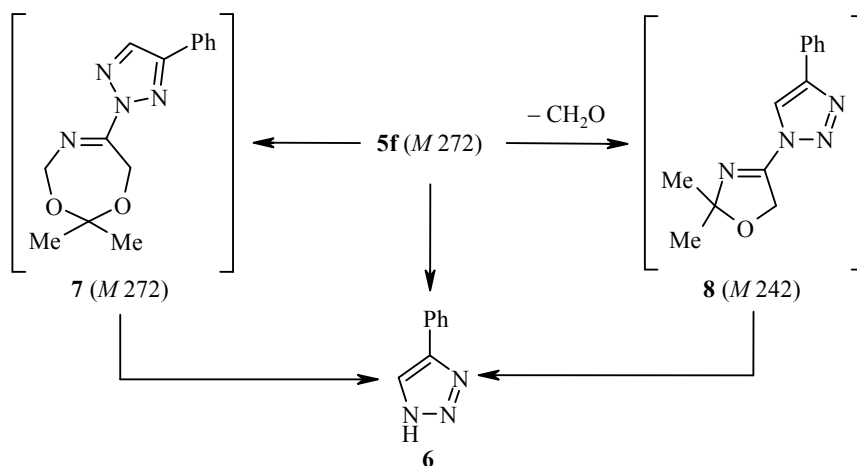


- 4, 5 a** $R^1 = R^2 = R^3 = H$, **b** $R^1 = R^3 = H, R^2 = Me$, **c** $R^1 = R^3 = H, R^2 = Ph$, **d** $R^1 = R^2 = Me, R^3 = H$,
e $R^1 = Me, R^2 = Et, R^3 = H$, **f** $R^1 = R^2 = Me, R^3 = Ph$, **g** $R^1 = R^2 = (CH_2)_4, R^3 = Ph$,
h $R^1 = R^2 = (CH_2)_5, R^3 = Ph$, **i** $R^1 = R^2 = Me, R^3 = SiMe_3$

We found that the reaction started at room temperature and was accompanied by selective formation of 4,7-dihydro-1,3,5-dioxazepines **5a-i**. The reaction rate was not sensitive to the structure of nitro compounds and was mostly determined by the excess of triethyl phosphite. Increasing the temperature allowed us to shorten reaction time from 35-40 h to 5-15 h, while resulted in substantially lower yields of some target compounds. It was shown by LC/MS in the case of nitrodioxane **4f** that deoxygenation at 80-110°C temperature was accompanied by partial degradation, forming 4-phenyl-1,2,3-triazole (**6**).

The analysis of LC/MS results showed that three compounds were formed during the degradation. Besides the target product **5f** (retention time 2.68 min, m/z 273 $[M+H]^+$ (100), 255 $[M+H-N_2]^+$ (20)) and 4-phenyl-1,2,3-triazole (**6**) (retention time 1.82 min, m/z 146 $[M+H]^+$ (100)), we also observed chromatographic peaks due to compounds with retention times 2.57 min (compound **7**, m/z 273 $[M+H]^+$ (100)) and 2.62 min (compound **8**, m/z 243 (41), 215 (25), 146 (100)). Presence of molecular ion m/z 273 and the lack of nitrogen elimination during ionization and the increased polarity of the compound, as well, suggested the possible formation of 2-substituted 1,2,3-triazole **7** due to migration of dioxazepine substituent at the triazole ring position 2. Similar thermal rearrangements were described in the literature for several 1-alkyl-substituted 1,2,3-triazoles [30-32], while in our hands, thermolysis of nitrodioxane **4f** did not result in the formation of 2-substituted 1,2,3-triazole even at 110°C.

The peak with m/z 243 may belong to protonated ion of oxazoline **8**, formed by recyclization of dioxazepine ring. Thus, the mechanism leading to 4-phenyl-1,2,3-triazole (**6**) is not quite obvious. This compound may be formed either directly from dioxazepine **5f** or from the products of its transformation.

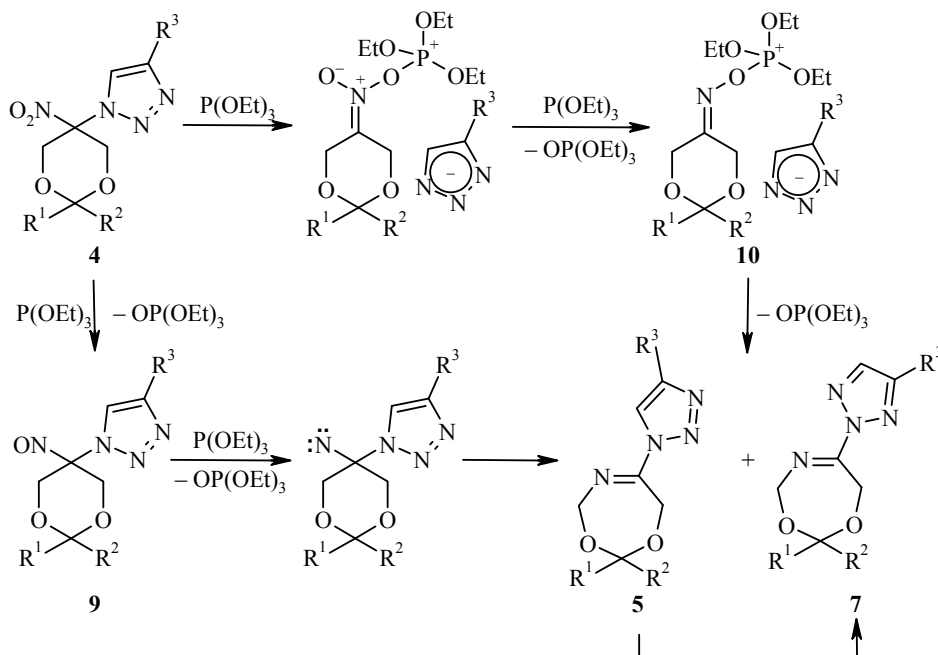


Thermolysis of dioxazepine **5f** showed that 4-phenyl-1,2,3-triazole (**6**) was formed upon heating in toluene (110°C) even in the absence of phosphorus compounds. The reaction proceeded slowly, with 2-substituted 1,2,3-triazole **7** as the sole by-product.

Deoxygenation reactions in the studied series of compounds were apparently stepwise and occurred analogously to deoxygenation of geminal chloronitrocycloalkanes with triphenylphosphine [22]. The performed study showed that reaction of 1-(5-nitro-1,3-dioxan-5-yl)-1*H*-1,2,3-triazoles **4a-i** with triethyl phosphite occurred without noticeable heat effect or changes in the color of solution, which was not characteristic to deoxygenation of nitroso compounds [23]. The attempts to detect intermediate 1-(5-nitroso-1,3-dioxan-5-yl)-1*H*-1,2,3-triazoles **9** by chromatographic methods (LC/MS and TLC) also was not successful. Even with insufficient amount and gradual addition of triethyl phosphite, the target 4,7-dihydro-1,3,5-dioxazepine **5** was detected immediately.

Thus, the most probable mechanism of dioxane ring expansion was through the stage of ion pair **10**, while the formation of 2-substituted 1,2,3-triazole **7** could occur either directly from ion pair **10** or by rearrangement of the target product **5**.

The 4,7-dihydro-1,3,5-dioxazepines **5a-i** were colorless, crystalline solids. The infrared spectra of these compounds lacked vibrational bands of nitro group, while a strong band appeared in the region of C=N bond vibration (1691-1700 cm⁻¹). The downfield region of ¹³C NMR spectrum contained resonance signals due to vicinal triazole carbon atoms and another signal at 152-153 ppm. The ¹H-¹³C HMBC spectrum of



spirodioxazepine **5g** allowed to establish that the C-9 carbon signal with chemical shift of 152.1 ppm correlated with the signals of 7-CH₂ and 10-CH₂ methylene protons of 4,7-dihydro-1,3,5-dioxazepine ring (5.40 and 5.19 ppm, respectively). The ¹H-¹⁵N HMBC spectrum of compound **5g** showed correlation of triazole ring proton (9.00 ppm) with all three nitrogen atoms of triazole (264, 353 and 359 ppm), as well as correlation of 4,7-dihydro-1,3,5-dioxazepine ring methylene protons with the nitrogen atom at 288 ppm (Table 2). The obtained results indicate different hybridization of carbon atom adjacent to methylene groups (CH₂O) and the presence of iminium fragment C=N in the structure.

All 4,7-dihydro-1,3,5-dioxazepines **5a-i** gave clear mass spectral signals of positively charged ions [M+H]⁺ (100%) under the conditions of chemical ionization. The presence of phenyl substituent in the triazole ring led to partial extrusion of nitrogen and the appearance of a weak signal (*I*_{rel} 16-20%) in the mass spectra of products **5f-h**, corresponding to the ion [M+H-N₂]⁺.

TABLE 2. The Observed Correlations in HSQC and HMBC Spectra of Compound **5g**

^1H , δ , ppm	^{13}C , δ , ppm		^{15}N , δ , ppm
	HSQC	^1H - ^{13}C HMBC	^1H - ^{15}N HMBC
1.66	23.3	23.3; 34.8; 114.7	–
1.89	34.8	23.3; 34.8; 114.7	–
5.19	62.2	62.2; 114.7; 152.1	288
5.40	75.2	75.2; 114.7; 152.1	288
7.36	128.5	125.6	–
7.44	128.9	125.6; 128.9; 129.6; 146.8	–
7.95	125.6	125.6; 128.5; 146.8;	–
9.00	118.1	118.1; 146.8	264; 353; 359

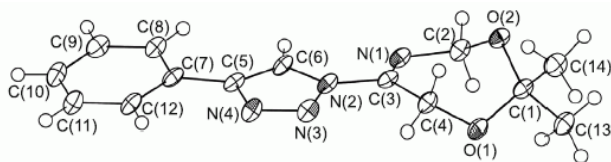


Fig. 1. Molecular structure of compound **5f** with atoms represented by thermal vibration ellipsoids of 50% probability.

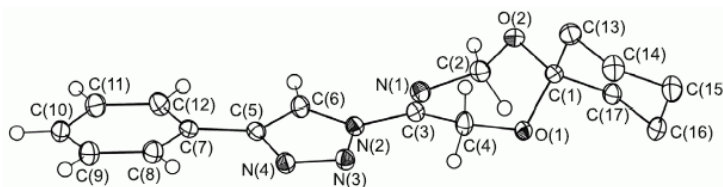


Fig. 2. Molecular structure of compound **5h** with atoms represented by thermal vibration ellipsoids of 50% probability. The methylene hydrogen atoms at C(13)–C(17) are omitted for clarity.

The structure of these new heterocyclic compounds was finally confirmed by X-ray structural analysis. For compounds **5f,h**, the 4,7-dihydro-1,3,5-dioxazepine ring was determined to be in "twist-chair" conformation (Fig. 1, 2), the torsion angle C(2)–N(1)–C(3)–C(4) in both structures was close to 0° ($-2.6(5)^\circ$ in the molecule **5f** and $-5.87(17)^\circ$ in the molecule **5h**). The C=N bond was practically coplanar to the phenyltriazole fragment: the dihedral angle between triazole ring plane and the plane defined by atoms N(1)–C(3)–N(2) was $5.38(18)^\circ$ in the molecule **5f** and $16.45(10)^\circ$ in the molecule **5h**. At the same time, there was no conjugation between C(3)=N(1) bond and the phenyltriazole ring, because in both cases the C(3)–N(2) bond was ordinary (its length was $1.432(4)$ Å in the molecule **5f** and $1.4333(13)$ Å in the molecule **5h**), while C(3)=N(1) was a double bond (its length was $1.265(4)$ Å in the molecule **5f** and $1.2597(14)$ Å in the molecule **5h**). Analogous situation was observed in the *N*-imidoylbenzotriazole series [33, 34]. The intermolecular interactions of both compounds in crystalline state were presented by CH \cdots O and CH \cdots N contacts.

A few described in the literature 4,7-dihydro-1,3,5-dioxazepines were obtained by thermolysis and photolysis from 1-azirine cycloadducts with diphenyl ketene in 1:2 ratio [35].

Thus, we have demonstrated for the first time the possibility of nitro group deoxygenation in 1-(5-nitro-1,3-dioxan-5-yl)-1*H*-1,2,3-triazole derivatives, leading to a series of 6-(1*H*-1,2,3-triazol-1-yl)-4,7-dihydro-1,3,5-dioxazepine derivatives. The developed method can be used for the preparation of previously unavailable 4,7-dihydro-1,3,5-dioxazepines, enabling characterization of the properties and reactivity of 1,3,5-dioxazepine rings containing a triazole substituent at position 6.

EXPERIMENTAL

IR spectra were recorded on a Thermo Nicolet 360 FTIR instrument in KBr pellets. ^1H and ^{13}C NMR spectra were acquired on a Varian Mercury Plus instrument (400 and 100 MHz, respectively) in DMSO-d_6 , with TMS as internal standard. The HSQC, ^1H - ^{13}C HMBC, and ^1H - ^{15}N HMBC correlation spectra of compounds **4g** and **5g** were acquired on a Bruker Avance II spectrometer (300 MHz for ^1H nuclei, 76 MHz for ^{13}C nuclei, and 30 MHz for ^{15}N nuclei) in DMSO-d_6 at 21°C . The ^{15}N NMR chemical shift values were determined with accuracy to 1 ppm relative to NH_3 as external standard. The LC/MS analysis was performed on a Thermo Finnigan Surveyor MSQ with gradient elution and chemical ionization at atmospheric pressure with simultaneous recording of positive and negative ions. Elemental analysis was performed on a Perkin Elmer 2400 Series II CHN-analyzer. Melting points were determined on a Boetius hot stage. Durasil H silica gel (40-63 μm) was used for purification of the obtained compounds by column chromatography.

Compounds **1** [36], **2a** [24], **2b** [37], **3a-f** [26], and **4f,i** [27] were synthesized according to published procedures. Phenylacetylene, trimethylsilylacetylene, and triethyl phosphite used in this work were purchased from Sigma-Aldrich.

(5-Nitro-1,3-dioxan-5-yl)methanol (2a) [24]. Yield 63%. Mp $47\text{--}48^\circ\text{C}$ (EtOH). IR spectrum, ν , cm^{-1} : 1057 (C–O); 1350, 1544 (NO_2); 2782, 2879, 2946, 3007 (C–H), 3451 (O–H). ^1H NMR spectrum, δ , ppm (J , Hz): 3.67 (2H, d, $^3J = 5.6$, CH_2OH); 3.97 (2He, d, $^2J = 12.0$) and 4.50 (2Ha, d, $^2J = 12.0$, $2\text{OCH}_2\text{C}$); 4.70 (1He, d, $^2J = 5.8$) and 4.85 (1Ha, d, $^2J = 5.8$, OCH_2O); 5.44 (1H, t, $^3J = 5.6$, CH_2OH).

(2-Methyl-5-nitro-1,3-dioxan-5-yl)methanol (2b) [37]. Yield 56%. Mp $67\text{--}68^\circ\text{C}$ (EtOH). IR spectrum, ν , cm^{-1} : 1066 (C–O); 1354, 1550 (NO_2); 2804, 2901, 2944, 2995 (C–H), 3485 (O–H). ^1H NMR spectrum, δ , ppm (J , Hz): 1.15 (3H, d, $^3J = 5.0$, CH_3CH); 3.60 (2H, d, $^3J = 5.6$, CH_2OH); 3.93 (2He, d, $^2J = 12.8$) and 4.58 (2Ha, d, $^2J = 12.8$, 2OCH_2); 4.74 (1H, q, $^3J = 5.0$, CH_3CH); 5.37 (1H, t, $^3J = 5.6$, CH_2OH).

Preparation of Substituted (5-Nitro-1,3-dioxan-5-yl)methanols 2c-g (General Method). Ketone or aldehyde (1.3 mmol) was added to a solution of 2-hydroxymethyl-2-nitropropane-1,3-diol (**1**) (1.2 mmol) in anhydrous THF (5 ml). The obtained mixture was stirred at room temperature and treated by gradual addition of $\text{BF}_3\cdot\text{Et}_2\text{O}$ (1.2 mmol). The solution was maintained for 1-3 h at room temperature (control by TLC). After the reaction was complete, the mixture was quenched with saturated aqueous NaHCO_3 (10 ml) and extracted with ethyl acetate (2×10 ml). The organic layer was dried over Na_2SO_4 and evaporated at reduced pressure. The residue was purified by silica gel column chromatography (1:3 EtOAc-*n*-hexane). The yields of 5-nitro-1,3-dioxanes **2c,d** [38] were 86 and 73%, respectively.

(2-Ethyl-2-methyl-5-nitro-1,3-dioxan-5-yl)methanol (2e) – mixture of stereoisomers (~1:1, according to ^1H NMR data). Yield 78%. Mp $50\text{--}62^\circ\text{C}$. IR spectrum, ν , cm^{-1} : 1047, 1098 (C–O); 1351, 1547, 1561 (NO_2); 2893, 2933, 2950, 2988 (C–H); 3384, 3420 (O–H). **cis-Isomer (cis-2e)**. ^1H NMR spectrum, δ , ppm (J , Hz): 0.77 (3H, t, $^3J = 7.5$, CH_3CH_2); 1.36 (3H, s, CH_3); 1.52 (2H, q, $^3J = 7.5$, CH_3CH_2); 3.70 (2H, d, $^3J = 5.7$, CH_2OH); 4.07 (2He, d, $^2J = 13.2$) and 4.37 (2Ha, d, $^2J = 13.2$, 2OCH_2); 5.46 (1H, t, $^3J = 5.7$, CH_2OH). ^{13}C NMR spectrum, δ , ppm: 7.2 (CH_3CH_2); 17.5 (CH_3C); 32.9 (CH_3CH_2); 61.3 (C-4,6); 62.5 (CH_2OH); 87.9 (C-5); 99.8 (C-2). **trans-Isomer (trans-2e)**. ^1H NMR spectrum, δ , ppm (J , Hz): 0.82 (3H, t, $^3J = 7.5$, CH_3CH_2); 1.20 (3H, s, CH_3); 1.77 (2H, q, $^3J = 7.5$, CH_3CH_2); 3.75 (2H, d, $^3J = 5.7$, CH_2OH); 4.02 (2He, d, $^2J = 13.2$) and 4.31 (2Ha, d, $^2J = 13.2$, 2OCH_2); 5.48 (1H, t, $^3J = 5.7$, CH_2OH). ^{13}C NMR spectrum, δ , ppm: 8.2 (CH_3CH_2); 22.8 (CH_3C); 25.7 (CH_3CH_2); 60.7 (C-4,6); 62.6 (CH_2OH); 87.1 (C-5); 100.4 (C-2). Mass spectrum, m/z (I_{rel} , %): 206 $[\text{M}+\text{H}]^+$ (100) (for both isomers).

(8-Nitro-6,10-dioxaspiro[4.5]dec-8-yl)methanol (2f). Yield 80%. Mp $101\text{--}103^\circ\text{C}$ (CHCl_3). IR spectrum, ν , cm^{-1} : 1065, 1107 (C–O); 1339, 1546 (NO_2); 2874, 2961 (C–H); 3404, 3345 (O–H). ^1H NMR spectrum, δ , ppm (J , Hz): 1.50-1.63 (4H, m, 2CH_2); 1.70 (2H, t, $^3J = 7.2$, CH_2); 1.87 (2H, t, $^3J = 7.2$, CH_2); 3.70 (2H, d, $^3J = 5.6$, CH_2OH); 4.00 (2He, d, $^2J = 13.2$) and 4.38 (2Ha, d, $^2J = 13.2$, 2OCH_2); 5.38 (1H, t, $^3J = 5.6$, CH_2OH). ^{13}C NMR spectrum, δ , ppm: 20.9 (C-2,3); 29.3 and 34.4 (C-1,4); 60.6 (C-7,9); 62.3 (CH_2OH); 87.5 (C-8); 96.9 (C-5). Mass spectrum, m/z (I_{rel} , %): 218 $[\text{M}+\text{H}]^+$ (100).

(3-Nitro-1,5-dioxaspiro[5.5]undec-3-yl)methanol (2g). Yield 88%. Mp 95-96°C (EtOH) (mp 96-97°C (decomp.) (MeOH-H₂O) [39]). IR spectrum, ν , cm⁻¹: 1056, 1106 (C-O); 1352, 1554 (NO₂); 2856, 2934 (C-H); 3403 (O-H). ¹H NMR spectrum, δ , ppm (*J*, Hz): 1.30-1.53 (8H, m, 4CH₂); 1.76-1.82 (2H, m, CH₂); 3.71 (2H, d, ³*J* = 5.4, CH₂OH); 4.04 (2He, d, ²*J* = 13.2) and 4.33 (2Ha, d, ²*J* = 13.2, 2OCH₂); 5.36 (1H, t, ³*J* = 5.4, CH₂OH). ¹³C NMR spectrum, δ , ppm: 21.9 and 22.0 (C-8,10); 24.8 (C-9); 28.6 and 34.8 (C-7,11); 60.3 (C-2,4); 62.4 (CH₂OH); 87.6 (C-3); 98.2 (C-6). Mass spectrum, *m/z* (*I*_{rel}, %): 232 [M+H]⁺ (100).

Preparation of Geminal Azidonitro-1,3-dioxanes 3a-g (General Method). 5-Hydroxymethyl-5-nitro-1,3-dioxane **2a-g** (10 mmol) was added to a solution of NaOH (2.00 g, 50 mmol) in water (10 ml). The mixture was stirred at room temperature for 20-30 min; then treated with a solution of NaN₃ (3.25 g, 50 mmol) in water (10 ml) and poured into a vigorously stirred solution of K₃Fe(CN)₆ (16.46 g, 50 mmol) in water (70 ml). The reaction mixture was stirred for 4 h at room temperature and extracted with EtOAc (3×20 ml). The combined extract was washed with water and dried over Na₂SO₄. The solvent was removed at reduced pressure, the residue was purified by silica gel column chromatography (CH₂Cl₂). The yields of azidonitrodioxanes **3a-f** were 64, 66, 81, 71, 70, and 60%, respectively. The properties of compounds **3a-f** matched those reported previously [26].

3-Azido-3-nitro-1,5-dioxaspiro[5.5]undecane (3g). Yield 75%. Colorless oil. IR spectrum, ν , cm⁻¹: 1111 (C-O), 1335, 1557 (NO₂), 2124 (N₃), 2861, 2939 (C-H). ¹H NMR spectrum, δ , ppm (*J*, Hz): 1.34-1.47 (6H, m, 3CH₂); 1.66-1.78 (4H, m, 2CH₂); 4.16 (2He, d, ²*J* = 12.8) and 4.46 (2Ha, d, ²*J* = 12.8, 2OCH₂). ¹³C NMR spectrum, δ , ppm: 21.9 (C-8,10); 24.6 (C-9); 31.5 and 31.9 (C-7,11); 61.4 (C-2,4); 94.2 (C-3); 99.1 (C-6). Found, %: C 44.65; H 5.81; N 22.87. C₉H₁₄N₄O₄. Calculated, %: C 44.63; H 5.83; N 23.13.

Preparation of 1-(5-Nitro-1,3-dioxan-5-yl)-1H-1,2,3-triazoles 4a-i (General Method). A. A solution of K₂CO₃ (6.25 mmol) and ascorbic acid (1 mmol) in water (10 ml) was stirred at room temperature and treated by adding a solution of trimethylsilylacetylene (6 mmol) in MeOH (20 ml), followed by solution of CuSO₄·5H₂O (0.5 mmol) in water (10 ml) and then solution of 5-azido-5-nitro-1,3-dioxane **3a-e** in MeOH (20 ml). The reaction mixture was stirred for 24 h at room temperature and extracted with CH₂Cl₂ (3×10 ml). The combined extract was washed with water (20 ml) and dried over Na₂SO₄. The solvent was removed at reduced pressure, and the residue was purified by silica gel column chromatography, using a 1:1 mixture of EtOAc-*n*-hexane as mobile phase.

B. A solution of 5-azido-5-nitro-1,3-dioxane **3d,f,g** (0.1 mol) and phenylacetylene (0.12 mol) in THF (20 ml) was treated at room temperature by adding a solution of ascorbic acid (0.05 mol) in water (10 ml), followed by solution of CuSO₄·5H₂O (0.015 mol) in water (5 ml). The reaction mixture was stirred for 2-6 h at room temperature. After the reaction was complete according to TLC, the mixture was diluted with water (20 ml) and extracted with CH₂Cl₂ (4×20 ml). The organic layer was dried over Na₂SO₄, the solvent was removed at reduced pressure, and the residue was purified by silica gel column chromatography, using 1:1 mixture of EtOAc-*n*-hexane as mobile phase.

The yield and properties of triazole **4i** matched those reported in the literature [27].

1-(5-Nitro-1,3-dioxan-5-yl)-1H-1,2,3-triazole (4a). Yield 65% (method A). Mp 93-95°C (EtOH). IR spectrum, ν , cm⁻¹: 1154 (C-O); 1332, 1569 (NO₂); 2855, 2869, 2933, 2983 (C-H); 3117, 3151 (=C-H). ¹H NMR spectrum, δ , ppm (*J*, Hz): 4.85 (2He, d, ²*J* = 12.4, 2OCH₂C); 4.92 (1He, d, ²*J* = 6.0) and 5.02 (1Ha, d, ²*J* = 6.0, OCH₂O); 5.15 (2Ha, d, ²*J* = 12.4, 2OCH₂C); 7.97 (1H, d, ³*J* = 1.2, H-4 triazole); 8.73 (1H, d, ³*J* = 1.2, H-5 triazole). ¹³C NMR spectrum, δ , ppm: 67.7 (C-4,6); 90.7 (C-5); 92.9 (C-2); 124.7 (C-5 triazole); 134.1 (C-4 triazole). Mass spectrum, *m/z* (*I*_{rel}, %): 201 [M+H]⁺ (100). Found, %: C 36.02; H 4.01; N 27.96. C₆H₈N₄O₄. Calculated, %: C 36.00; H 4.03; N 27.99.

1-(2-Methyl-5-nitro-1,3-dioxan-5-yl)-1H-1,2,3-triazole (4b). Yield 41% (method A). Mp 116-119°C (EtOH). IR spectrum, ν , cm⁻¹: 1113 (C-O); 1337, 1572 (NO₂); 2855, 2897, 2928, 2950 (C-H); 3143, 3168 (=C-H). ¹H NMR spectrum, δ , ppm (*J*, Hz): 1.14 (3H, d, ³*J* = 5.2, CH₃CH); 4.78 (2He, dt, ²*J* = 12.2, ⁴*J* = 1.6, 2CH₂); 5.07 (1H, q, ³*J* = 5.2, CH₃CH); 5.23 (2Ha, dt, ²*J* = 12.2, ⁴*J* = 1.6, 2CH₂); 7.97 (1H, d, ³*J* = 1.2, H-4 triazole); 8.79 (1H, d, ³*J* = 1.2, H-5 triazole). ¹³C NMR spectrum, δ , ppm: 19.5 (CH₃); 66.1 (C-4,6); 90.4 (C-5); 99.2

(C-2); 126.0 (C-5 triazole); 134.6 (C-4 triazole). Mass spectrum, m/z (I_{rel} , %): 215 $[M+H]^+$ (100). Found, %: C 39.44; H 4.67; N 26.23. $C_7H_{10}N_4O_4$. Calculated, %: C 39.25; H 4.71; N 26.16.

1-(5-Nitro-2-phenyl-1,3-dioxan-5-yl)-1H-1,2,3-triazole (4c). Yield 60% (method A). Mp 150-151°C (EtOH). IR spectrum, ν , cm^{-1} : 1116 (C–O); 1340, 1585 (NO_2); 2855, 2887, 2923, 2958 (C–H); 3113, 3151 (=C–H). ^1H NMR spectrum, δ , ppm (J , Hz): 5.04 (2He, dt, $^2J = 12.2$, $^4J = 1.6$) and 5.42 (2Ha, dt, $^2J = 12.2$, $^4J = 1.6$, 2CH₂); 5.97 (1H, s, CH); 7.22-7.25 (2H, m, H Ph); 7.30-7.34 (3H, m, H Ph); 8.00 (1H, d, $^3J = 1.2$, H-4 triazole); 8.87 (1H, d, $^3J = 1.2$, H-5 triazole). ^{13}C NMR spectrum, δ , ppm: 68.5 (C-4,6); 90.6 (C-5); 100.7 (C-2); 125.8 (C-2,6 Ph); 126.0 (C-3,5 Ph); 126.1 (C-5 triazole); 129.1 (C-4 Ph); 134.0 (C-4 triazole); 136.0 (C-1 Ph). Mass spectrum, m/z (I_{rel} , %): 277 $[M+H]^+$ (100). Found, %: C 52.04; H 4.51; N 20.17. $C_{12}H_{12}N_4O_4$. Calculated, %: C 52.17; H 4.38; N 20.28.

1-(2,2-Dimethyl-5-nitro-1,3-dioxan-5-yl)-1H-1,2,3-triazole (4d). Yield 73% (method A). Mp 104-105°C (EtOH). IR spectrum, ν , cm^{-1} : 1103 (C–O); 1375, 1570 (NO_2); 2852, 2922, 2998 (C–H); 3149, 3164 (=C–H). ^1H NMR spectrum, δ , ppm (J , Hz): 1.39 (3H, s, CH₃); 1.42 (3H, s, CH₃); 4.80 (2He, d, $^2J = 13.2$) and 5.06 (2Ha, d, $^2J = 13.2$, 2CH₂); 7.95 (1H, d, $^3J = 1.2$, H-4 triazole); 8.71 (1H, d, $^3J = 1.2$, H-5 triazole). ^{13}C NMR spectrum, δ , ppm: 21.6 (CH₃); 24.9 (CH₃); 61.9 (C-4,6); 91.3 (C-5); 99.6 (C-2); 124.9 (C-5 triazole); 134.1 (C-4 triazole). Mass spectrum, m/z (I_{rel} , %): 229 $[M+H]^+$ (100). Found, %: C 42.15; H 5.21; N 24.49. $C_8H_{12}N_4O_4$. Calculated, %: C 42.10; H 5.30; N 24.55.

1-(2-Ethyl-2-methyl-5-nitro-1,3-dioxan-5-yl)-1H-1,2,3-triazole (4e) was obtained as 1:1 mixture of stereoisomers, according to ^1H NMR spectral data. Yield 52% (method A). Mp 50-54°C. IR spectrum, ν , cm^{-1} : 1107 (C–O); 1337, 1564 (NO_2); 2887, 2936, 2950, 2985 (C–H); 3119 (=C–H). **trans-Isomer (trans-4e)**. ^1H NMR spectrum, δ , ppm (J , Hz): 0.69 (3H, t, $^3J = 7.6$, CH_3CH_2); 1.40 (3H, s, CH₃); 1.67 (2H, q, $^3J = 7.6$, CH_3CH_2); 4.85 (2He, d, $^2J = 12.8$) and 5.00 (2Ha, d, $^2J = 12.8$, 2OCH₂); 7.95 (1H, d, $^3J = 1.6$, H-4 triazole); 8.73 (1H, d, $^3J = 1.6$, H-5 triazole). ^{13}C NMR spectrum, δ , ppm: 7.1 (CH_3CH_2); 20.3 (CH_3C); 30.9 (CH_3CH_2); 61.7 (C-4,6); 91.2 (C-5); 101.0 (C-2); 125.1 (C-5 triazole); 133.9 (C-4 triazole). **cis-Isomer (cis-4e)**. ^1H NMR spectrum, δ , ppm (J , Hz): 0.83 (3H, t, $^3J = 7.4$, CH_3CH_2); 1.39 (3H, s, CH₃); 1.70 (2H, q, $^3J = 7.4$, CH_3CH_2); 4.76 (2He, d, $^2J = 12.8$) and 5.10 (2Ha, d, $^2J = 12.8$, 2OCH₂); 7.94 (1H, d, $^3J = 1.6$, H-4 triazole); 8.69 (1H, d, $^3J = 1.6$, H-5 triazole). ^{13}C NMR spectrum, δ , ppm: 7.0 (CH_3CH_2); 18.2 (CH_3C); 28.1 (CH_3CH_2); 61.6 (C-4,6); 91.2 (C-5); 100.8 (C-2); 124.4 (C-5 triazole); 133.8 (C-4 triazole). Mass spectrum, m/z (I_{rel} , %): 243 $[M+H]^+$ (100) (for both isomers). Found, %: C 44.25; H 5.76; N 23.31. $C_9H_{14}N_4O_4$. Calculated, %: C 44.63; H 5.83; N 23.13.

1-(2,2-Dimethyl-5-nitro-1,3-dioxan-5-yl)-4-phenyl-1H-1,2,3-triazole (4f). Yield 87% (method B). Mp 161-163°C (EtOH) (mp 53-56°C [27] reported for crude product). ^1H NMR spectrum, δ , ppm (J , Hz): 1.43 (3H, s, CH₃); 1.44 (3H, s, CH₃); 4.86 (2He, d, $^2J = 12.8$) and 5.10 (2Ha, d, $^2J = 12.8$, 2CH₂); 7.38 (1H, t, $^3J = 7.2$, H-4 Ph); 7.48 (2H, t, $^3J = 7.6$, H-3,5 Ph); 7.90 (2H, d, $^3J = 7.2$, H-2,6 Ph); 9.18 (1H, s, H-5 triazole). ^{13}C NMR spectrum, δ , ppm: 21.4 (CH₃); 24.7 (CH₃); 61.8 (C-4,6); 91.6 (C-5); 99.6 (C-2); 120.9 (C-5 triazole); 125.3 (C-2,6 Ph); 128.4 (C-4 Ph); 128.8 (C-3,5 Ph); 129.4 (C-1 Ph); 146.9 (C-4 triazole). Mass spectrum, m/z (I_{rel} , %): 305 $[M+H]^+$ (100). 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-(8-Nitro-6,10-dioxaspiro[4.5]dec-8-yl)-4-phenyl-1H-1,2,3-triazole (4g). Yield 82% (method B). Mp 187-189°C (EtOH). IR spectrum, ν , cm^{-1} : 1143 (C–O); 1339, 1564 (NO_2); 2855, 2881, 2929, 2968 (C–H); 3106, 3136 (=C–H). ^1H NMR spectrum, δ , ppm (J , Hz): 1.58-1.66 (4H, m, 2CH₂); 1.87-1.94 (4H, m, 2CH₂); 4.85 (2He, d, $^2J = 12.8$) and 5.11 (2Ha, d, $^2J = 12.8$, 2OCH₂); 7.38 (1H, t, $^3J = 7.2$, H-4 Ph); 7.48 (2H, t, $^3J = 7.6$, H-3,5 Ph); 7.89 (2H, d, $^3J = 7.2$, H-2,6 Ph); 9.19 (1H, s, H-5 triazole). ^{13}C NMR spectrum, δ , ppm: 22.5 and 22.9 (C-2,3); 32.8 and 35.2 (C-1,4); 63.4 (C-7,9); 91.2 (C-8); 111.2 (C-5); 120.9 (C-5 triazole); 125.3 (C-2,6 Ph); 128.4 (C-4 Ph); 128.8 (C-3,5 Ph); 129.3 (C-1 Ph); 146.9 (C-4 triazole). Mass spectrum, m/z (I_{rel} , %): 331 $[M+H]^+$ (100). Found, %: C 58.41; H 5.57; N 16.84. $C_{16}H_{18}N_4O_4$. Calculated, %: C 58.17; H 5.49; N 16.96.

1-(3-Nitro-1,5-dioxaspiro[5.5]undec-3-yl)-4-phenyl-1H-1,2,3-triazole (4h). Yield 76% (method B). Mp 167-169°C (EtOH). IR spectrum, ν , cm^{-1} : 1142 (C–O); 1338, 1564 (NO_2); 2854, 2885, 2926, 2968 (C–H);

3136 (=C–H). ¹H NMR spectrum, δ, ppm (*J*, Hz): 1.37-1.50 (6H, m, 3CH₂); 1.72-1.78 (4H, m, 2CH₂); 4.86 (2He, d, ²*J* = 12.8) and 5.09 (2Ha, d, ²*J* = 12.8, 2OCH₂); 7.39 (1H, t, ³*J* = 7.2, H-4 Ph); 7.48 (2H, t, ³*J* = 7.6, H-3,5 Ph); 7.89 (2H, d, ³*J* = 7.2, H-2,6 Ph); 9.17 (1H, s, H-5 triazole). ¹³C NMR spectrum, δ, ppm: 21.9 (C-8,10); 24.6 (C-9); 29.8 and 33.0 (C-7,11); 61.2 (C-2,4); 91.7 (C-3); 99.5 (C-6); 120.9 (C-5 triazole); 125.3 (C-2,6 Ph); 128.4 (C-4 Ph); 128.8 (C-3,5 Ph); 129.4 (C-1 Ph); 146.9 (C-4 triazole). Mass spectrum, *m/z* (*I*_{rel.}, %): 345 [M+H]⁺ (100). Found, %: C 59.32; H 5.94; N 16.14. C₁₇H₂₀N₄O₄. Calculated, %: C 59.29; H 5.85; N 16.27.

Preparation of 6-(1*H*-1,2,3-Triazol-1-yl)-4,7-dihydro-1,3,5-dioxazepines 5a-i (General Method). A mixture of 1-(5-nitro-1,3-dioxan-5-yl)-1*H*-1,2,3-triazole **4a-i** (0.5 mmol) and triethyl phosphite (3 mmol) in benzene (10 ml) was stirred at reflux. After the completion of reaction (5-15 h, TLC), the solvent was removed by distillation at reduced pressure. The residue was purified by silica gel column chromatography, using 1:5 mixture of EtOAc–*n*-hexane as mobile phase. The product could be purified as needed by crystallization from ethyl alcohol.

6-(1*H*-1,2,3-Triazol-1-yl)-4,7-dihydro-1,3,5-dioxazepine (5a). Yield 41%. Mp 102-105°C (EtOH). IR spectrum, *v*, cm⁻¹: 1009, 1097 (C–O); 1694 (C=N); 2906, 2954, 2991 (C–H); 3127, 3164 (=C–H). ¹H NMR spectrum, δ, ppm (*J*, Hz): 4.99 (2H, s, OCH₂O); 5.25 (2H, t, ⁵*J* = 1.6, CCH₂O); 5.41 (2H, t, ⁵*J* = 1.6, NCH₂O); 7.88 (1H, d, ³*J* = 1.2, H-4 triazole); 8.53 (1H, d, ³*J* = 1.2, H-5 triazole). ¹³C NMR spectrum, δ, ppm: 65.2 (C-7); 77.9 (C-4); 95.0 (C-2); 121.9 (C-5 triazole); 133.9 (C-4 triazole); 152.1 (C-6). Mass spectrum, *m/z* (*I*_{rel.}, %): 169 [M+H]⁺ (100). Found, %: C 42.95; H 4.91; N 33.12. C₆H₈N₄O₂. Calculated, %: C 42.86; H 4.80; N 33.32.

2-Methyl-6-(1*H*-1,2,3-triazol-1-yl)-4,7-dihydro-1,3,5-dioxazepine (5b). Yield 72%. Mp 67-70°C (EtOH). IR spectrum, *v*, cm⁻¹: 1004, 1119 (C–O); 1699 (C=N); 2915, 2988 (C–H); 3135, 3160 (=C–H). ¹H NMR spectrum, δ, ppm (*J*, Hz): 1.34 (3H, d, ³*J* = 5.2, CHCH₃); 5.11 (1H, dt, ²*J* = 16.8, ⁵*J* = 1.6, CCH₂O); 5.24-5.29 (2H, m, CCH₂O, CHCH₃); 5.33 (1H, dt, ²*J* = 16.8, ⁵*J* = 1.4) and 5.51 (1H, dt, ²*J* = 14.8, ⁵*J* = 1.6, NCH₂O); 7.88 (1H, d, ³*J* = 1.2, H-4 triazole); 8.53 (1H, d, ³*J* = 1.2, H-5 triazole). ¹³C NMR spectrum, δ, ppm: 18.6 (CH₃); 62.8 (C-7); 75.3 (C-4); 99.9 (C-2); 121.9 (C-5 triazole); 133.9 (C-4 triazole); 152.1 (C-6). Mass spectrum, *m/z* (*I*_{rel.}, %): 183 [M+H]⁺ (100). Found, %: C 46.35; H 5.62; N 30.41. C₇H₁₀N₄O₂. Calculated, %: C 46.15; H 5.53; N 30.75.

6-(1*H*-1,2,3-Triazol-1-yl)-2-phenyl-4,7-dihydro-1,3,5-dioxazepine (5c). Yield 89%. Mp 97-100°C (EtOH). IR spectrum, *v*, cm⁻¹: 1012, 1088 (C–O); 1695 (C=N); 2875, 2902, 2925, 2974 (C–H); 3131, 3148 (=C–H). ¹H NMR spectrum, δ, ppm (*J*, Hz): 5.29 (2H, br. s, CCH₂O); 5.44 (1H, dt, ²*J* = 14.8, ⁵*J* = 1.6) and 5.49 (1H, dt, ²*J* = 14.8, ⁵*J* = 1.6, NCH₂O); 6.14 (1H, s, CHPh); 7.35-7.52 (5H, m, H Ph); 7.91 (1H, d, ³*J* = 1.2, H-4 triazole); 8.57 (1H, d, ³*J* = 1.2, H-5 triazole). ¹³C NMR spectrum, δ, ppm: 63.2 (C-7); 75.8 (C-4); 100.9 (C-2); 121.9 (C-5 triazole); 126.0 (C-2,6 Ph); 128.2 (C-3,5 Ph); 128.7 (C-4 Ph); 133.9 (C-4 triazole); 137.0 (C-1 Ph); 152.0 (C-6). Mass spectrum, *m/z* (*I*_{rel.}, %): 245 [M+H]⁺ (100). Found, %: C 58.94; H 4.88; N 23.05. C₁₂H₁₂N₄O₂. Calculated, %: C 59.01; H 4.95; N 22.94.

2,2-Dimethyl-6-(1*H*-1,2,3-triazol-1-yl)-4,7-dihydro-1,3,5-dioxazepine (5d). Yield 61%. Mp 86-87°C (EtOH). IR spectrum, *v*, cm⁻¹: 1009, 1086 (C–O); 1698 (C=N); 2878, 2926, 2944, 2993 (C–H); 3134, 3159 (=C–H). ¹H NMR spectrum, δ, ppm (*J*, Hz): 1.44 (6H, s, 2CH₃); 5.20 (2H, t, ⁵*J* = 1.8, CCH₂O); 5.37 (2H, t, ⁵*J* = 1.8, NCH₂O); 7.87 (1H, br. s, H-4 triazole); 8.52 (1H, br. s, H-5 triazole). ¹³C NMR spectrum, δ, ppm: 23.3 (2CH₃); 60.5 (C-7); 73.1 (C-4); 102.4 (C-2); 121.8 (C-5 triazole); 133.8 (C-4 triazole); 151.7 (C-6). Mass spectrum, *m/z* (*I*_{rel.}, %): 197 [M+H]⁺ (100). Found, %: C 48.95; H 6.20; N 28.50. C₈H₁₂N₄O₂. Calculated, %: C 48.97; H 6.16; N 28.56.

2-Ethyl-2-methyl-6-(1*H*-1,2,3-triazol-1-yl)-4,7-dihydro-1,3,5-dioxazepine (5e). Yield 81%. Mp 65-68°C (EtOH). IR spectrum, *v*, cm⁻¹: 1003, 1087 (C–O); 1700 (C=N); 2856, 2883, 2942, 2974 (C–H); 3134, 3164 (=C–H). ¹H NMR spectrum, δ, ppm (*J*, Hz): 0.88 (3H, t, ³*J* = 7.6, CH₂CH₃); 1.36 (3H, s, CH₃); 1.77 (2H, q, ³*J* = 7.6, CH₂CH₃); 5.16 (1H, dt, ²*J* = 17.2, ⁵*J* = 1.6) and 5.21 (1H, dt, ²*J* = 17.2, ⁵*J* = 1.6, CCH₂O); 5.34 (1H, dt, ²*J* = 15.2, ⁵*J* = 1.6) and 5.39 (1H, dt, ²*J* = 15.2, ⁵*J* = 1.6, NCH₂O); 7.86 (1H, d, ³*J* = 1.2, H-4 triazole); 8.51 (1H, d, ³*J* = 1.2, H-5 triazole). ¹³C NMR spectrum, δ, ppm: 8.1 (CH₂CH₃); 19.9 (CH₃); 28.1 (CH₂CH₃); 60.4 (C-7);

73.0 (C-4); 104.5 (C-2); 121.8 (C-5 triazole); 133.8 (C-4 triazole); 151.8 (C-6). Mass spectrum, m/z (I_{rel} , %): 211 $[M+H]^+$ (100). Found, %: C 51.35; H 6.75; N 26.61. $C_9H_{14}N_4O_2$. Calculated, %: C 51.42; H 6.71; N 26.65.

2,2-Dimethyl-6-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-4,7-dihydro-1,3,5-dioxazepine (5f). Yield 37% (63% at reaction temperature of 50°C). Mp 103-105°C (EtOH). IR spectrum, ν , cm^{-1} : 1017, 1084 (C–O); 1701 (C=N); 2888, 2928, 2972, 2988 (C–H); 3164 (=C–H). 1H NMR spectrum, δ , ppm (J , Hz): 1.46 (6H, s, 2CH₃); 5.23 (2H, t, $^5J = 1.6$, CCH₂O); 5.42 (2H, t, $^5J = 1.6$, NCH₂O); 7.36 (1H, t, $^3J = 7.4$, H-4 Ph); 7.45 (2H, t, $^3J = 7.6$, H-3,5 Ph); 7.96 (2H, d, $^3J = 7.2$, H-2,6 Ph); 9.00 (1H, s, H-5 triazole). ^{13}C NMR spectrum, δ , ppm: 23.3 (2CH₃); 60.5 (C-7); 73.3 (C-4); 102.5 (C-2); 117.8 (C-5 triazole); 125.5 (C-2,6 Ph); 128.3 (C-4 Ph); 128.9 (C-3,5 Ph); 129.5 (C-1 Ph); 146.6 (C-4 triazole); 151.7 (C-6). Mass spectrum, m/z (I_{rel} , %): 273 $[M+H]^+$ (100), 245 $[M+H-N_2]^+$ (18). Found, %: C 61.52; H 5.94; N 20.32. $C_{14}H_{16}N_4O_2$. Calculated, %: C 61.75; H 5.92; N 20.58.

9-(4-Phenyl-1*H*-1,2,3-triazol-1-yl)-6,11-dioxo-8-azaspiro[4.6]undec-8-ene (5g). Yield 52% (67% at reaction temperature of 50°C). Mp 135-137°C (EtOH). IR spectrum, ν , cm^{-1} : 1008 (C–O); 1691 (C=N); 2851, 2875, 2928, 2957 (C–H); 3142 (=C–H). 1H NMR spectrum, δ , ppm (J , Hz): 1.64-1.68 (4H, m, 2CH₂); 1.89 (4H, t, $^3J = 7.0$, 2CH₂); 5.19 (2H, t, $^5J = 1.6$, CCH₂O); 5.40 (2H, t, $^5J = 1.6$, NCH₂O); 7.36 (1H, t, $^3J = 7.4$, H-4 Ph); 7.44 (2H, t, $^3J = 7.6$, H-3,5 Ph); 7.95 (2H, d, $^3J = 7.2$, H-2,6 Ph); 9.00 (1H, s, H-5 triazole). ^{13}C NMR spectrum, δ , ppm: 23.3 (C-2,3); 34.8 (C-1,4); 62.2 (C-10); 75.2 (C-7); 114.7 (C-5); 118.1 (C-5 triazole); 125.6 (C-2,6 Ph); 128.5 (C-4 Ph); 128.9 (C-3,5 Ph); 129.6 (C-1 Ph); 146.8 (C-4 triazole); 152.1 (C-9). ^{15}N NMR spectrum, δ , ppm: 264 (N-1' triazole); 288 (N-8); 353 (N-3' triazole); 359 (N-2' triazole). Mass spectrum, m/z (I_{rel} , %): 299 $[M+H]^+$ (100), 271 $[M+H-N_2]^+$ (16). Found, %: C 64.39; H 6.21; N 18.64. $C_{16}H_{18}N_4O_2$. Calculated, %: C 64.41; H 6.08; N 18.78.

10-(4-Phenyl-1*H*-1,2,3-triazol-1-yl)-7,12-dioxo-9-azaspiro[5.6]dodec-9-ene (5h). Yield 65%. Mp 148-151°C (EtOH). IR spectrum, ν , cm^{-1} : 1015 (C–O); 1697 (C=N); 2850, 2947 (C–H); 3146 (=C–H). 1H NMR spectrum, δ , ppm (J , Hz): 1.38-1.53 (6H, m, 3CH₂); 1.77 (4H, t, $^3J = 5.8$, 2CH₂); 5.23 (2H, br. s, CCH₂O); 5.42 (2H, br. s, NCH₂O); 7.36 (1H, t, $^3J = 7.4$, H-4 Ph); 7.45 (2H, t, $^3J = 7.6$, H-3,5 Ph); 7.95 (2H, d, $^3J = 7.2$, H-2,6 Ph); 8.98 (1H, s, H-5 triazole). ^{13}C NMR spectrum, δ , ppm: 22.4 (C-2,4); 24.6 (C-3); 31.7 (C-1,5); 59.8 (C-11); 72.6 (C-8); 102.4 (C-6); 117.8 (C-5 triazole); 125.5 (C-2,6 Ph); 128.3 (C-4 Ph); 128.7 (C-3,5 Ph); 129.5 (C-1 Ph); 146.6 (C-4 triazole); 151.9 (C-10). Mass spectrum, m/z (I_{rel} , %): 313 $[M+H]^+$ (100), 285 $[M+H-N_2]^+$ (20). Found, %: C 65.51; H 6.32; N 17.87. $C_{17}H_{20}N_4O_2$. Calculated, %: C 65.37; H 6.45; N 17.94.

2,2-Dimethyl-6-[4-(trimethylsilyl)-1*H*-1,2,3-triazol-1-yl]-4,7-dihydro-1,3,5-dioxazepine (5i). Yield 72%. Mp 91-94°C (EtOH). IR spectrum, ν , cm^{-1} : 846 (Si–C); 1022, 1094 (C–O); 1699 (C=N); 2900, 2927, 2960, 2993 (C–H); 3153 (=C–H). 1H NMR spectrum, δ , ppm (J , Hz): 0.27 (9H, s, 3CH₃Si); 1.43 (6H, s, 2CH₃); 5.18 (2H, br. s, CCH₂O); 5.37 (2H, br. s, NCH₂O); 8.52 (1H, s, H-5 triazole). ^{13}C NMR spectrum, δ , ppm: -1.48 (Si(CH₃)₃); 23.3 (2CH₃); 60.9 (C-7); 73.2 (C-4); 102.4 (C-2); 127.2 (C-5 triazole); 145.7 (C-4 triazole); 151.7 (C-6). Mass spectrum, m/z (I_{rel} , %): 269 $[M+H]^+$ (100). Found, %: C 49.34; H 7.70; N 20.46. $C_{11}H_{20}N_4O_2Si$. Calculated, %: C 49.23; H 7.51; N 20.88.

Thermolysis of 2,2-Dimethyl-6-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-4,7-dihydro-1,3,5-dioxazepine (5f). A solution of dioxazepine **5f** (272 mg, 1.00 mmol) in toluene (10 ml) was refluxed for 15 h. The solvent was removed at reduced pressure, the residue was separated by silica gel column chromatography, giving 103 mg (71%) of 4-phenyl-1,2,3-triazole (**6**) as colorless crystals with mp 144-146°C (EtOH) (mp 147-148°C (MeOH–H₂O) [40]). IR spectrum, ν , cm^{-1} : 516, 696, 767, 841, 877, 916, 973, 1004, 1084, 1132, 1202, 1230, 1307, 1375, 1454, 1468, 2862, 2963, 3117, 3160. 1H NMR spectrum, δ , ppm (J , Hz): 7.33 (1H, t, $^3J = 7.4$, H-4 Ph); 7.44 (2H, t, $^3J = 7.6$, H-3,5 Ph); 7.84 (2H, d, $^3J = 7.6$, H-2,6 Ph); 8.26 (1H, s, H-5); 14.98 (1H, br. s, NH). ^{13}C NMR spectrum, δ , ppm: 125.4 (C-2,6 Ph); 127.9 (C-4 Ph); 128.7 (C-3,5Ph, C-5); 130.4 (C-1 Ph); 146.7 (C-4). Mass spectrum, m/z (I_{rel} , %): 146 $[M+H]^+$ (100).

X-Ray Structural Analysis of Compounds 5f,h. Crystals of compound **5f** were obtained by slow evaporation of MeOH solution at room temperature and ambient pressure. The crystals were rhombic, space group *Pbca*; a 9.132(3), b 14.614(5), c 20.428(7) Å; V 2726.0(16) Å³; Z 8 (Z' 1); d_{calc} 1.327 g·cm⁻³; $F(000) = 1152$.

The intensities of 14276 reflections were determined at 100 K temperature on a Bruker APEX II DUO diffractometer (MoK α , λ 0.71073 Å, ω -scanning, $2\theta < 53^\circ$) and 2780 independent reflections (R_{int} 0.0839) were used in the further refinement.

Crystals of compound **5h** were obtained by crystallization from 1:1 mixture of MeOH–2-PrOH. The crystals were monoclinic, $P2_1/n$ space group; a 5.6366(3), b 14.4327(8), c 18.6719(10) Å; β 91.778(1) $^\circ$; V 1518.25(14) Å 3 ; Z 4 (Z' 1); d_{calc} 1.367 g·cm $^{-3}$; $F(000)$ 664. The intensities of 19506 reflections were determined at 120 K temperature on a Bruker APEX II diffractometer (MoK α , λ 0.71073 Å, ω -scanning, $2\theta < 61^\circ$) and 4614 independent reflections (R_{int} 0.0326) were used in the further refinement.

The structures were solved by direct method and sequential synthesis of electron density. Hydrogen atom positions were determined from differential Fourier syntheses. Refinement was performed by F^2_{hkl} in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were refined in isotropic approximation according to the "rider" model. Calculations were performed with the SHELXTL 5.10 software suite [41]. The X-ray absorption by the crystal was accounted for by using the SADABS-2008/1 program [42].

The final value of unreliability factors for crystals of compound **5f**: R_1 0.0784 (calculated by F_{hkl} for 2081 reflections with $I > 2\sigma(I)$), wR_2 0.2144 (calculated by F^2_{hkl} for all 2780 reflections), the number of refinement parameters 182, $GOOF$ 1.103.

The final value of unreliability factors for crystals of compound **5h**: R_1 0.0458 (calculated by F_{hkl} for 3875 reflections with $I > 2\sigma(I)$), wR_2 0.1160 (calculated by F^2_{hkl} for all 4614 reflections), the number of refinement parameters 208, $GOOF$ 1.064.

The complete crystallographic data sets for compounds **5f,h** were deposited at the Cambridge Crystallographic Data Center (deposits CCDC 999308 and CCDC 999309, respectively).

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