DOI 10.1007/s10593-019-02525-2

*Chemistry of Heterocyclic Compounds* **2019**, *55*(8), 704–715

# Synthesis of β-azolyl- and β-azolylcarbonylenamines and their reactions with aromatic azides

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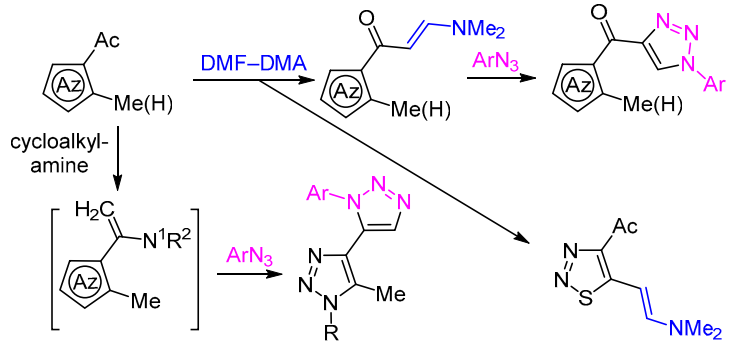
Translated from Khimiya Geterotsiklicheskikh Soedinenii, 2019, *55*(8), 704–715

Submitted March 13, 2019
Accepted April 16, 2019




Synthesis of 4-acetyl-substituted azoles (1,2,3-triazole, 1,2,3-thiadiazole, and 1,2-oxazole) is reported. Organocatalytic reactions of 4-acetyl-1,2,3-triazoles with aryl azides were used to obtain bis-1,2,3-triazoles containing directly linked ring systems. The reactions of 4-acetylazoles with DMF–DMA led to the formation of enamines. It was found that the acetyl and methyl groups in 4-acetyl-5-methyl-1,2,3-thiadiazole competed for the role of reactive site. The obtained enamines reacted with aryl azides, forming bisheterocycles that were linked by a carbonyl group. The structures of the synthesized compounds were proved by NMR spectroscopy, mass spectrometry, and X-ray structural analysis.

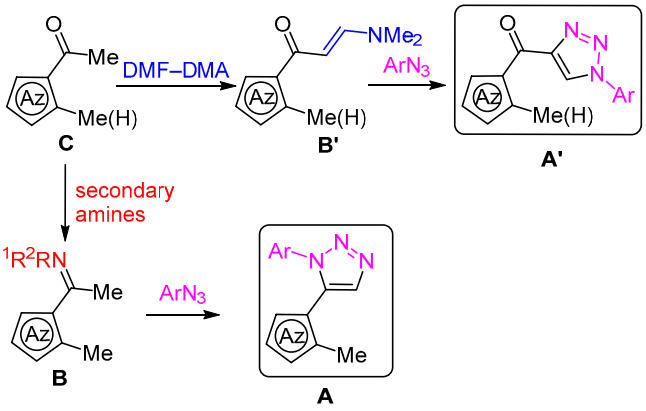
**Keywords**: bistriazoles, enamines, enaminones, 1,2-oxazoles, 1,2,3-thiadiazoles, 1,2,3-triazoles.

Molecules containing chains of azole rings and other heterocycles (known as stick-like molecules) are attractive objects of study in medicinal chemistry,[1] organic synthesis,[2] materials chemistry,[3] and organic electronics.[4] For these reasons, it is important to continue research in the synthesis of bisazoles on the basis of 1,2,3-triazole, 1,2,3-thiadiazole, and 1,2-oxazole, either directly bonded or linked by a carbonyl group. The most common method for obtaining 1,2,3-triazoles *via* the reactions of acetylenes with azides[5] has limited applicability to the synthesis of azolyltriazoles due to the limited availability of azolylacetylenes. On the other hand, a more promising route to these compounds relies on the reactions of azides with the significantly more available enamines.[6] In addition, compounds containing an azolyl enamine moiety are of interest to medicinal chemists as potential lead compounds for the discovery of new biologically active compounds.[7] Taking into account all of this, our research was aimed at developing a convenient method for the preparation of 3-azolyl enamines, and their reactions with aromatic azides were studied.

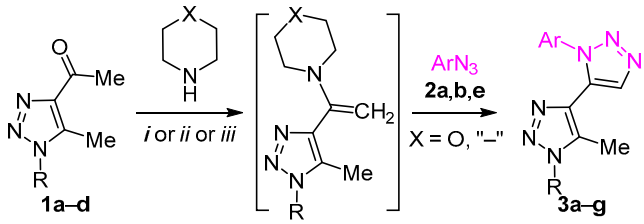
We have previously shown that the reactions of β-azolyl enamines with aromatic and aliphatic azides provide an effective method for the synthesis of (1,2,3-triazolyl-4-yl)-5-azoles (4–5-bonding).[8] Thus, we planned to prepare bisazoles where position 4 of azole and position 5 of 1,2,3-triazole were linked either by a single bond (structure **A**, Scheme 1) or through a carbonyl group (structure **A'**), using the reactions of aromatic and aliphatic azides with α-azolyl enamines (structure **B**) and 3-azolyl enaminones (structure **B'**). It should be noted that the synthesis of α-azolyl enamines **B** and their reactions with azides have not been described in the literature prior to the current study, while bicyclic ensembles **A** that were synthesized by another method (from 1,2,3-triazolylacetylenes) have been represented by only a few examples.[9] The synthesis of enamines **B** was proposed starting from secondary amines, using reactions with the acetylazoles **C**.

The starting materials **C** selected from 1,2,3-triazole series were 1-substituted 4-acetyl-5-methyl-1,2,3-triazoles **1a–n** and 4-acetyl-1,2,3-triazoles **1o–r**, as well as 1,2,3-thiadiazole **1s** and 4-acetyl-1,2-oxazole **1t** (Fig. 1).

**Scheme 1**. The planned routes of synthesis for bisazoles **A** and **A'**




**Scheme 2**. Synthesis of bistriazoles **3a–g** (structures **A**)




*i*: $TiCl_4$, 95–105°C, 7–36 h; *ii*: CaO, 120°C, 72 h
*iii*: no additives, 95–120°C,12–48 h

**3 a** R = Ar = Ph (48%); **b** R = Ph, Ar = 4-$O_2NC_6H_4$ (49%); **c** R = Me, Ar = Ph (40%); **d** R = Me, Ar = 4-$O_2NC_6H_4$ (50%); **e** R = Me, Ar = 4-$ClC_6H_4$ (41%); **f** R = 4-$BrC_6H_4CH_2$ (70%), Ar = 4-$O_2NC_6H_4$ (70%); **g** R = *n*-Bu, Ar = 4-$O_2NC_6H_4$ (61%)

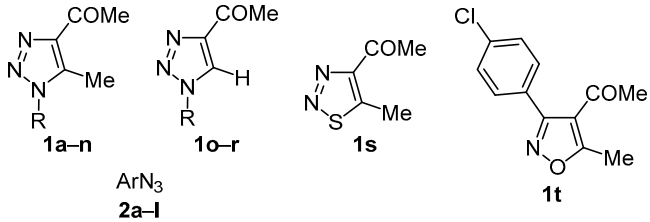
For the purpose of obtaining enamines **B**, we treated 4-acetyl-1,2,3-triazoles **1a**,**b** with boiling morpholine and pyrrolidine under various conditions (in the presence of CaO or *p*-TsOH, without solvent or in PhMe solution while removing the solvent by distillation) over several hours. In none of these experiments, the starting ketones **1a**,**b** participated in the reaction. Nevertheless, we added aryl azides **2** to the studied reaction mixtures with the expectation that even minimal amounts of enamines **B**, which would be in equilibrium with the starting ketones **C**, would participate in the reaction, forming bistriazoles **A**. Indeed, refluxing ketones **1a–d** for many hours with a large excess of aryl azides **2a**,**b**,**e** under various combinations of reaction conditions (in morpholine or pyrrolidine, without additives, or in the presence of CaO or $TiCl_4$) led to the formation of the target compounds **3a–g** in 40–70% yields (Scheme 2).

The structure of compounds **3a–g** as bicyclic ensembles was established by NMR experiments as well as by monocrystal X-ray structural analysis of compound **3d** (Fig. 2).

It should be noted that we could not obtain the analogous triazoles from ketones of 1,2,3-thiadiazole (compound **1s**) and isoxazole (compound **1t**) series. Thus, as a result of generating the previously unknown 1-(1,2,3-triazol-4-yl) enamines **B** followed by their reactions with aromatic azides **2a**,**b**,**e**, a new method has been developed for obtaining bicyclic 1,2,3-triazoles that are not accessible by other methods.

In order to synthesize alternative bisheterocyclic structures **A'** containing an azole moiety and triazole ring linked by a carbonyl group, we performed studies aimed at advancing the methodology for the preparation of enaminones **B'** and studied their interaction with azides. We have previously synthesized enamines of 1,2,3-triazole series by reactions of 5-methyl-1,2,3-triazoles with the Bredereck's reagent (1-*tert*-butoxy-*N*,*N*,*N*',*N*'-tetramethylmethanediamine) in high boiling point solvents.[8b] The attempts to obtain the respective enaminones from 5-methyl-1,2,3-triazoles by using the considerably less costly dimethylformamide dimethylacetal (DMF–DMA) were unsuccessful.[8]

Taking into account the high cost of the Bredereck's reagent, we repeated the attempts to synthesize enaminones by reactions of 5-methyl-1,2,3-triazoles with DMF–DMA in various solvents with the addition of Lewis acids or various bases, including *N*-methylimidazole,[8c] as well as under solvent-free conditions. Acceptable yields of enaminones **4a–r** were achieved only after prolonged heating of ketones **1b–i**,**k–t** at 80–110°C in DMF–DMA solution without additives (Scheme 3). The optimal procedure included the removal of unreacted DMF–DMA by distillation, with an option for reuse of the recovered reagent. Depending on the solubility of the obtained




**1 a** R = Me, **b** R = Ph, **c** R = 4-$O_2NC_6H_4$, **d** R = 2-$O_2NC_6H_4$, **e** R = 4-$MeC_6H_4$,**f** R = 4-*i*-$PrC_6H_4$, **g** R = 3-$FC_6H_4$, **h** R = 2-Cl-4-$MeC_6H_3$, **i** R = 2-$O_2N$-5-$ClC_6H_3$, **j** R = $C_6F_5$, **k** R = 4-$BrC_6H_4CH_2$, **l** R = 3-$ClC_6H_4$, **m** R = *n*-Bu, **n** R = allyl, **o** R = Ph, **p** R = 4-$MeC_6H_4$, **q** R = 2-$O_2NC_6H_4$,**r** R = 4-$O_2NC_6H_4$

**2 a** Ar = Ph, **b** Ar = 4-$O_2NC_6H_4$, **c** Ar = 2-$O_2NC_6H_4$, **d** Ar = 4-*i*-$PrC_6H_4$, **e** Ar = 4-$ClC_6H_4$, **f** Ar = 3-$FC_6H_4$, **g** Ar = $C_6F_5$, **h** Ar = 2-Cl-4-$MeC_6H_3$, **i** Ar = 2-F-4-$O_2NC_6H_3$, **j** Ar = 4-$BrC_6H_4CH_2$, **k** Ar = 2-$O_2N$-5-$ClC_6H_3$, **l** Ar = 4-$MeC_6H_4$

**Figure 1**. Structures of the starting acetylazoles **1a–t** and azides **2a–l**.

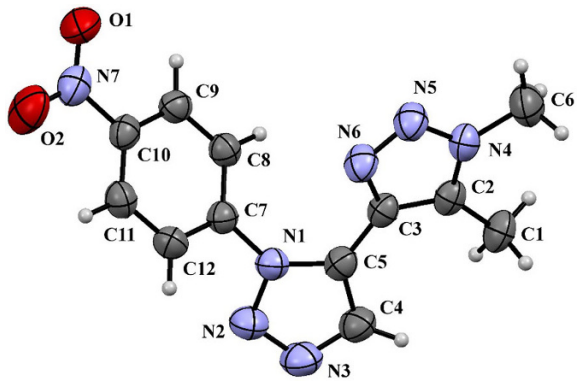


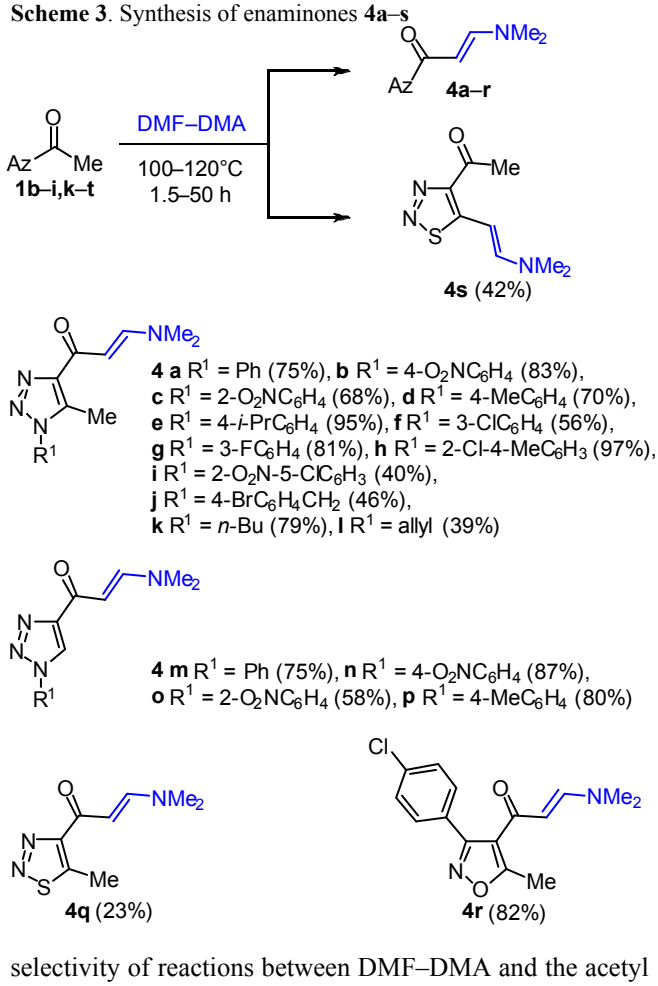

**Figure 2**. The molecular structure of bistriazole **3d** with atoms represented by thermal vibration ellipsoids of 50% probability.

products in organic solvents, purification was performed either by column chromatography or recrystallization from organic solvents. The obtained azolyl enaminones **4a**–**r** were crystalline compounds with high melting points. The employed method provided access to a wide range of enamines containing various azole rings in their structure. Taking into account the value of 1,2,3-triazolyl enaminones as unique building blocks for organic synthesis, as well as their potential as lead structures for drug discovery research, we put particular emphasis on the preparation of 1-aryl-1,2,3-triazolyl enaminones **4b**–**j**,**n**–**p** with a wide variety of substituents in the phenyl ring, as well as the 1-*n*-butyl- and 1-allyltriazoles **4k**,**l**. At the same time, the reactions of pentafluoro derivative **1j** with DMF–DMA gave an intractable product mixture that could not be separated preparatively into individual compounds. According to HPLC–HRMS analysis, its major components were products arising from the substitution of one or two fluorine atoms in the initially formed 1-(5-methyl-1-(perfluorophenyl)-1*H*-1,2,3-triazol-4-yl-l)prop-2-en-1-one with methoxy groups by the action of MeOH, which was liberated from DMF–DMA reagent during the synthesis. Apparently, the general method for the preparation of enaminones was unsuitable in the case of ketone containing a pentafluorophenyl group, due to the reactivity of fluorine atoms of the polyfluorinated phenyl ring in the basic medium containing DMF–DMA.

It should be noted that the reactions of 4-acetyl-1,2,3-triazoles **1o**–**r** lacking substituents at position 5, as well as 4-acetyl-5-methylazoles **1b**–**n** and 1,2-oxazole **1t** containing a 4-acetyl group along with 5-methyl group produced individual compounds **4a**–**p**,**r** with the participation of acetyl group only. An alternative transformation with the participation of 5-methyl group was observed only in the reaction of 1,2,3-thiadiazole **1s** with DMF–DMA, forming not only enaminone **4q**, but also a product with enamine moiety at position 5 – compound **4s**. The location of the enamine moiety in the molecules of compounds **4q**,**s** was determined on the basis of two-dimensional $^{1}$H–$^{13}$C HMBC and $^{1}$H–$^{13}$C HSQC experiments. Besides that, monocrystal X-ray structural analysis was performed for enaminone **4q**, allowing to conclusively prove the structures of both isomers (Fig. 3). It should be noted that, according to the results of X-ray structural analysis, enaminone **4q** existed in the form of *E*-isomer. This was in agreement with the high spin-spin coupling constant ($J$ = 12.6 Hz) between the alkene group protons in its $^{1}$H NMR spectrum. This constant for enaminones **4q**,**r** belonging to 1,2,3-triazole and isoxazole series was equally large (12.3–12.6 Hz), providing strong evidence that these compounds are also in the *E*-form.

It should be noted that the proton signals of 5-methyl and 4-acetyl groups in $^{1}$H NMR spectrum of the starting 1,2,3-thiadiazole **1s** were practically equivalent and therefore could not be assigned. At the same time, the chemical shifts of protons in the respective methyl groups in the series of 1,2,3-triazoles **1b**–**r** differed by only 0.10 to 0.25 ppm, while for isoxazole **1t** this difference reached 0.57 ppm. This observation was in agreement with the

**Scheme 3**. Synthesis of enaminones **4a**–**s**




selectivity of reactions between DMF–DMA and the acetyl group in triazoles **1b**–**r** and isoxazole **1t** and the ambivalence of acetyl and methyl groups in 1,2,3-thiadiazole **1s**. By comparing the chemical shifts of methyl and acetyl group protons in the starting ketones **1b**–**t** with the chemical shifts of methyl group protons in enaminones **4a**–**r**, it was possible to define a rule, according to which the electrophilic DMF–DMA reagent reacted exclusively with the methyl group giving a more downfield proton NMR signal.

Thus, we have achieved a substantial progress in developing a general and effective method for the synthesis of azolyl enaminones in good yields, using the reactions of 5-acetyl-substituted 1,2,3-triazoles containing various aryl substituents at position 1, as well as other azoles with DMF–DMA.

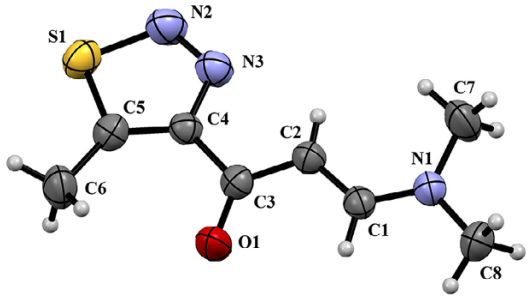
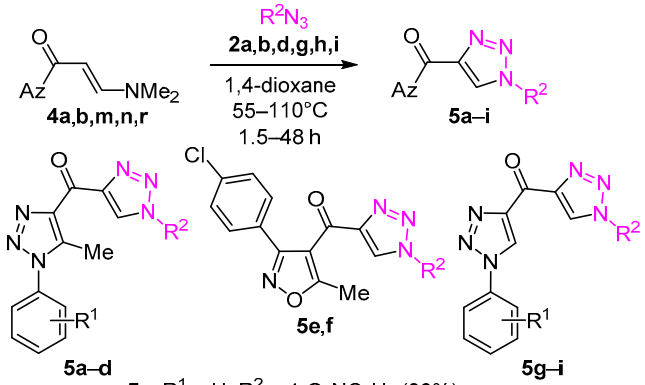



**Figure 3**. The molecular structure of enaminone **4q** with atoms represented by thermal vibration ellipsoids of 50% probability.

The possibility of using the obtained enaminones **4** for the synthesis of bisheterocyclic systems in which the azole moiety and the 1,2,3-triazole ring are linked *via* a carbonyl group was demonstrated using the reactions of enaminones **4a**,**b**,**n**,**m**,**r**, with aryl azides **2a**,**b**,**d**,**g**,**h**,**i**. As a result, 4-(1,2,3-triazole-4-carbonyl)azoles **5a–i** were obtained in good yields (Scheme 4). The structures of compounds **5a–i** were proved on the basis of $^{1}$H and $^{13}$C NMR spectra. The characteristic $^{1}$H NMR signals were those of the newly formed 1,2,3-triazole ring protons at 8.52–9.96 ppm, while $^{13}$C NMR spectra contained the characteristic C=O group signals at 175.3–180.4 ppm.

**Scheme 4**. Synthesis of triazolylcarbonylazoles **5a–i**




**5** **a** $R^1$ = H, $R^2$ = 4-$O_2NC_6H_4$ (86%)
**b** $R^1$ = 4-$NO_2$, $R^2$ = 4-$O_2NC_6H_4$ (65%)
**c** $R^1$ = H, $R^2$ = $C_6F_5$ (60%)
**d** $R^1$ = H, $R^2$ = 2-F-4-$O_2NC_6H_3$ (42%)
**e** $R^2$ = Ph (63%); **f** $R^2$ = 4-$O_2NC_6H_4$ (39%)
**g** $R^1$ = H, $R^2$ = 2-Cl-4-$MeC_6H_3$ (79%)
**h** $R^1$ = H, $R^2$ = 2-F-4-$O_2NC_6H_3$ (41%)
**i** $R^1$ = 4-$NO_2$, $R^2$ = 4-*i*-$PrC_6H_4$ (18%)

Thus, as a result of this study, a new aproach was developed for the synthesis of previously difficult to obtain bis-1,2,3-triazole system containing two rings with direct bonding between the carbon atoms at positions 4 and 5, as well as bisheterocyclic structures where the 1,2,3-triazole ring and a second azole ring are linked *via* a carbonyl group. The synthesis of the first type of bisheterocycles apparently involved a new type of enamines – α-(1,2,3-triazol-4-yl) enamines. In addition, a dual reactivity of 4-acetyl-5-methyl-1,2,3-thiadiazole in reactions with DMF–DMA was identified. The second 1,2,3-triazole ring in the bisheterocyclic structures of both types was assembled mostly by using the same aryl azides as in the synthesis of the starting acetylazoles. For this reason, the developed approach was highly productive even with a limited range of available reactants.

## Experimental

$^{1}$H, $^{13}$C, and $^{19}$F NMR spectra were acquired on a Bruker Avance II 400 spectrometer (400, 100, and 376 MHz, respectively) in DMSO-$d_6$, $CDCl_3$, or DMF-$d_7$ solutions. The residual signals of DMSO, $CHCl_3$, and DMF were used as internal standards for $^{1}$H and $^{13}$C NMR spectra. The chemical shifts of $^{19}$F NMR signals were measured relative to the $CFCl_3$ signal. Mass spectra with EI ionization were recorded on a GCMS-QP 2010 Ultra mass spectrometer (70 eV). Elemental analysis (C, H, and N) was performed on a PerkinElmer 2400 II automatic analyzer. HPLC-MS analysis of the compounds with electrospray ionization was performed using an Agilent 6540 UHD Accurate-Mass Q-TOF LC/MS tandem quadrupole time-of-flight exact mass-selective detector. Analytical chromatographic separations were performed using an Agilent 1290 Infinity UPLC instrument equipped with a Zorbax Extend-$C_{18}$ RRHT, 2.1 × 50 mm column, the particle size of stationary phase was 1.8 μm (Agilent 727700-902) at thermostat temperature of 50°C. The reaction progress and purity of the obtained compounds were controlled by TLC method on Sorbfil UV-254 plates, using visualization under UV light. KSKG silica gel with 40–100 μm particle size was used for the column chromatography. The volatile components were evaporated, and solutions were concentrated at reduced pressure. The solid and liquid phases were separated by centrifugation at 3000 rpm. Melting points were determined on a Stuart SMP10 melting point apparatus.

All solvents were prepared according to the standard procedures. The petroleum ether fraction with 70–100°C bp was used.

Methyltriazolyl ketones **1a**,[10a] **1b**,**c**,**e**,**m**,[10b] **1d**,[10c] **1l**,[10d] **1o**,[10e] **1r**,[10f] **1s**,[10g,h] **1t**[10i], azides **2a–h**,**j–l**[11], and enaminones **4a**,**b**[10a] were synthesized according to literature procedures. Azide **2i** was obtained from a commercial source.

**Synthesis of methyl triazolyl ketones 1f**,**h**,**i** (General method). A solution of the appropriate azide **2d**,**h**,**k** (10.0 mmol) and acetylacetone (2.0 g, 20.0 mmol) in DMF (20 ml) was treated by adding $Et_3N$ (2.02 g, 20.0 mmol) and DBU (0.76 g, 5.00 mmol), while for the synthesis of compound **1h** only $Et_3N$ (20.0 mmol) was used as base. The reaction mixture was stirred at room temperature for 12 h. The solution was then diluted with $H_2O$ (20 ml), the precipitate that formed was filtered off after 10 min, washed with $H_2O$ (10 ml), and dried in a vacuum desiccator over $P_4O_{10}$.

**1-{5-Methyl-1-[4-(propan-2-yl)phenyl]-1*H*-1,2,3-triazol-4-yl}ethanone (1f)** was obtained from azide **2d**. Yield 2.262 g (93%), light-beige powder, mp 81–83°C. $^{1}$H NMR spectrum (DMSO-$d_6$), δ, ppm (*J*, Hz): 1.27 (6H, d, *J* = 6.9, $CH(C\underline{H}_3)_2$); 2.51 (3H, s, 5-$CH_3$); 2.64 (3H, s, $CH_3CO$); 2.94–3.13 (1H, m, $C\underline{H}(CH_3)_2$); 7.33–7.68 (4H, m, H Ar). $^{13}$C NMR spectrum (DMSO-$d_6$), δ, ppm: 9.7; 23.6; 27.5; 33.2; 125.3; 127.5; 132.8; 137.6; 142.7; 150.5; 193.3. Mass spectrum, *m*/*z* ($I_{rel}$, %): 243 $[M]^+$ (30), 200 (40), 158 (100). Found, %: C 69.01; H 6.65; N 17.13. $C_{14}H_{17}N_3O$. Calculated, %: C 69.11; H 7.04; N 17.27.

**1-[1-(3-Fluorophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]-ethanone (1g)**. A solution of azide **2f** (1.371 g, 10 mmol) and acetylacetone (1.201 g, 12.00 mmol) in $CHCl_3$ (6 ml) was treated with $Et_3N$ (1.011 g, 10.00 mmol) and DBU (0.166 g, 1.10 mmol). The solution was maintained in a sealed vessel for 2 h at 60°C. The volatile components were removed by evaporation to dryness, the oily residue was extracted with boiling petroleum ether. Yield 1.58 g

(72%), light-beige powder, mp 89–91°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.52–2.64 (3H, m, 5-$CH_3$); 2.66–2.78 (3H, m, $CH_3CO$); 7.25 (3H, d, *J* = 7.6, H-4,5,6 Ar); 7.48–7.61 (1H, m, H-2 Ar). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 10.0; 27.7; 113.0 (d, *J* = 24.8); 117.1 (d, *J* = 20.9); 120.9 (d, *J* = 3.5); 131.1 (d, *J* = 8.9); 135.7–138.1 (m); 143.6; 162.7 (d, *J* = 250.0); 194.1. $^{19}$F NMR spectrum ($CDCl_3$), δ, ppm: –109.54. Mass spectrum, *m*/*z* ($I_{rel}$, %): 219 $[M]^+$ (14), 191 $[M–N_2]^+$ (4), 176 (18), 148 (81), 43 (100). Found, %: C 59.96; H 4.55; N 19.08. $C_{11}H_{10}FN_3O$. Calculated, %: C 60.27; H 4.60; N 19.17.

**1-[1-(2-Chloro-4-methylphenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]ethanone (1h)** was obtained from azide **2h**. Yield 2.01 g (80%), colorless powder, mp 114–115°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm (*J*, Hz): 2.34 (3H, s, 4-$CH_3$ Ar); 2.44 (3H, s, 5-$CH_3$); 2.65 (3H, s, $CH_3CO$); 7.38–7.49 (1H, m, H-5 Ar); 7.58 (1H, d, *J* = 8.0, H-6 Ar); 7.66 (1H, d, *J* = 1.0, H-3 Ar). $^{13}$C NMR spectrum (DMSO-$d_6$), δ, ppm: 9.0; 20.6; 27.5; 129.1; 129.2; 129.6; 129.9; 130.6; 139.0; 142.3; 143.3; 193.2. Mass spectrum, *m*/*z* ($I_{rel}$, %): 251 $[M]^+$ (4), 250 $[M]^+$ (2), 249 $[M]^+$ (12), 221 $[M–N_2]^+$ (4), 206 (23), 178 (50), 43 (100). Found, %: C 57.36; H 4.80; N 16.75. $C_{12}H_{12}ClN_3O$. Calculated, %: C 57.72; H 4.84; N 16.83.

**1-[1-(5-Chloro-2-nitrophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]ethanone (1i)** was obtained from azide **2k**. Yield 2.47 g (88%), light-yellow powder, mp 141–142°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm (*J*, Hz): 2.49 (3H, s, 5-$CH_3$); 2.66 (3H, s, $CH_3CO$); 8.01–8.12 (1H, m, H-6 Ar); 8.19–8.28 (1H, m, H-3 Ar); 8.39 (1H, dd, *J* = 8.8, *J* = 1.5, H-4 Ar). $^{13}$C NMR spectrum (DMSO-$d_6$), δ, ppm: 9.1; 27.6; 127.8; 128.5; 129.6; 132.5; 139.2; 139.7; 142.4; 193.1. Mass spectrum, *m*/*z* ($I_{rel}$, %): 282 $[M]^+$ (8), 281 $[M]^+$ (4), 280 $[M]^+$ (26), 252 $[M–N_2]^+$ (9), 43 (100). Found, %: C 47.12; H 3.53; N 20.06. $C_{11}H_9ClN_4O_3$. Calculated, %: C 47.07; H 3.23; N 19.96.

**1-[5-Methyl-1-(pentafluorophenyl)-1*H*-1,2,3-triazol-4-yl]ethanone (1j)**. A mixture of azide **2g** (525 mg, 2.50 mmol) and acetylacetone (250 mg, 2.50 mmol) in $CHCl_3$ (3 ml) was treated by adding $Et_3N$ (252 mg, 2.49 mmol) and DBU (103 mg, 0.68 mmol). The reaction mixture was maintained at room temperature for 1.5 h, followed by evaporation of the volatile components to dryness. The product was extracted from the precipitate with boiling petroleum ether, the extract was concentrated to a minimum volume, and the residue was crystallized from petroleum ether. The precipitate was separated and dried. The yield of the crude product was 415 mg (57%), colorless crystalline powder, suitable for using in the subsequent synthetic steps. Analytically pure product was obtained by column chromatography (eluent PhH), mp 82–83°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.52 (3H, s, $CH_3CO$); 2.76 (3H, s, $CH_3$). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.9; 27.6; 136.5–137.2 (m); 139.4 (ddd, *J* = 13.9, *J* = 8.9, *J* = 4.0); 140.0; 141.5–142.2 (m); 144.5 (dt, *J* = 13.4, *J* = 7.2); 143.1; 193.5. $^{19}$F NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): –143.56÷–144.13 (2F, m), –147.42 (1F, t, *J* = 21.5), –158.31÷–159.08 (2F, m). Mass spectrum, *m*/*z* ($I_{rel}$, %): 291 $[M]^+$ (5), 263 $[M–N_2]^+$ (2), 221 (45), 208 (10), 194 (10), 43 (100). Found, %: C 45.02; H 2.05; N 14.71. $C_{11}H_6F_5N_3O$. Calculated, %: C 45.37; H 2.08; N 14.43.

**1-[1-(4-Bromobenzyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]ethanone (1k)**. A solution of azide **2j** (2.364 g, 10.00 mmol) and acetylacetone (1.202 g, 12.00 mmol) in anhydrous 1,4-dioxane (4 ml) was treated by adding $Et_3N$ (1.215 g, 12.00 mmol) and DBU (0.154 g, 1.01 mmol). The solution was heated for 23 h at 95°C, and the volatile components were removed by evaporation. The residue was triturated with cold $H_2O$. The obtained oil was dried to remove residual $H_2O$ and EtOH. The crude product was isolated by fractional crystallization from petroleum ether. Yield 0.539 g (18%), light-brown amorphous material, mp 86–87°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.45 (3H, s, $CH_3CO$); 2.67 (3H, s, 5-$CH_3$); 5.45 (2H, s, $CH_2$); 7.05 (2H, d, *J* = 8.4, H Ar); 7.47 (2H, d, *J* = 8.4, H Ar). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 9.1; 27.7; 51.0; 122.8; 128.9; 132.3; 133.0; 136.7; 144.1; 194.2. Mass spectrum, *m*/*z* ($I_{rel}$, %): 296 $[M]^+$ (2), 295 $[M]^+$ (14), 294 $[M]^+$ (3), 293 $[M]^+$ (14), 266 (25), 265 $[M–N_2]^+$ (4), 264 (25), 252 (19), 250 (21), 224 (8), 222 (7), 54 (100). Found, %: C 49.12; H 4.08; N 14.35. $C_{12}H_{12}BrN_3O$. Calculated, %: C 49.00; H 4.11; N 14.29.

**1-[(5-Methyl-1-prop-2-en-1-yl)-1*H*-1,2,3-triazol-4-yl]ethanone (1n)**. A solution of diazoacetylacetone (1.261 g, 10.00 mmol) and allylamine (1.427 mg, 25.00 mmol) in $CHCl_3$ (6 ml) was maintained at room temperature for 24 h. The volatile components were evaporated to dryness. The obtained oily residue was treated with $H_2O$ (8 ml) and concentrated HCl (0.8 ml). The product was extracted with $Et_2O$, and the extract was evaporated to dryness. Yield 1.082 g (66%), colorless oil that was suitable for subsequent syntheses without additional purification. An analytically pure sample was obtained by converting ketone **1n** into the corresponding semicarbazone **1n'**, followed by its decomposition to ketone **1n** in acidic medium (see the Supplementary information file). $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.53 (3H, d, *J* = 0.8, $CH_3$); 2.67 (3H, d, *J* = 1.4, $CH_3$); 4.93 (1H, d, *J* = 5.4, $C\underline{H}_2CH=CH_2$); 5.01–5.12 (1H, m, $C\underline{H}_2CH=CH_2$); 5.30 (2H, dd, *J* = 10.3, *J* = 0.6, $CH_2CH=C\underline{H}_2$); 5.87–5.95 (1H, m, $CH_2C\underline{H}=CH_2$). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 8.9; 27.6; 50.1; 119.1; 130.5; 136.9; 143.8; 194.3. Mass spectrum, *m*/*z* ($I_{rel}$, %): 165 $[M]^+$ (43), 136 (30), 122 (21), 54 (100). Found, %: C 58.19; H 6.58; N 25.52. $C_8H_{11}N_3O$. Calculated, %: C 58.17; H 6.71; N 25.44.

**Synthesis of methyl triazolyl ketones 1p,q** (General method). A solution of (3*E*)-4-(dimethylamino)but-3-en-2-one (1.131 g, 10.00 mmol) and the appropriate azide **2c**,**l** (10.00 mmol) in PhMe (4 ml) was heated at 50–105°C for 6–23 h. After cooling, the volatile components were evaporated to dryness and the residue was separated on a chromatography column (eluent PhH (for compound **1p**) or $CHCl_3$ (for compound **1q**)). The fractions containing the product were combined, evaporated to dryness, and the residue was crystallized from petroleum ether.

**1-[1-(4-Methylphenyl)-1*H*-1,2,3-triazol-4-yl]ethanone (1p)** was obtained from azide **2l**, the reaction was

performed at 105°C for 23 h. Yield 965 mg (48%), colorless crystals, mp 115–116°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.42 (3H, s, $CH_3$); 2.73 (3H, s, $CH_3$); 7.33 (2H, d, *J* = 8.1, H Ar); 7.61 (2H, d, *J* = 8.4, H Ar); 8.44 (1H, s, H triazole). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 21.1; 27.2; 120.7; 123.3; 130.4; 134.1; 139.8; 148.4; 192.8. Mass spectrum, *m*/*z* ($I_{rel}$, %): 201 $[M]^+$ (13), 173 $[M–N_2]^+$ (3), 158 (83), 144 (7), 130 (100). Found, %: C 65.66; H 5.56; N 21.00. $C_{11}H_{11}N_3O$. Calculated, %: C 65.66; H 5.51; N 20.88.

**1-[1-(2-Nitrophenyl)-1*H*-1,2,3-triazol-4-yl]ethanone (1q)** was obtained from azide **2c**, the reaction was performed at 55°C for 6 h. Yield 1.3 g (56%), colorless crystals, mp 133–134°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.75 (3H, s, $CH_3$); 7.61 (1H, dd, *J* = 7.8, *J* = 1.3, H Ar); 7.80 (2H, t, *J* = 8.0, H Ar); 7.84 (1H, t, *J* = 8.0, H Ar); 8.15 (1H, dd, *J* = 8.1, *J* = 1.4, H Ar); 8.38 (1H, s, H triazole). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 27.4; 125.9; 127.2; 128.0; 129.6; 131.6; 134.2; 144.3; 148.2; 192.3. Mass spectrum, *m*/*z* ($I_{rel}$, %): 232 $[M]^+$ (1), 204 $[M–N_2]^+$ (2), 145 (3), 43 (100). Found, %: C 51.88; H 3.78; N 24.31. $C_{10}H_8N_4O_3$. Calculated, %: C 51.73; H 3.47; N 24.13.

**Synthesis of bistriazoles 3a**,**b**,**f** (General method). A suspension of $TiCl_4$ (1.32 g, 7.00 mmol) in anhydrous 1,4-dioxane (6 ml) was cooled to –7÷–10°C and treated by the addition of anhydrous morpholine (5.94 ml, 68.90 mmol). The reaction mixture was stirred for 5 min at room temperature, then the appropriate ketone **1a**,**b**,**k** (2.00 mmol) and azide **2a**,**b** (5.00 mmol) were added. The reaction mixture was stirred for 7–36 h at 95–105°C. The solids were separated, washed with hot 1,4-dioxane (2×7 ml) and $CHCl_3$. The liquid phases were combined and evaporated to dryness. The residue was treated with 1 N HCl, then with $H_2O$. The crude product was purified by column chromatography (eluent $CHCl_3$ – petroleum ether, 1:1 (for compound **3a**); petroleum ether, $CHCl_3$ – petroleum ether, gradient from 1:1 to 2:1 (for compound **3b**); petroleum ether, $CHCl_3$ – petroleum ether, 1:1, $CHCl_3$, then $CHCl_3$–EtOAc, 1:1 (for compound **3f**)).

**5-Methyl-1,3'-diphenyl-1*H*,3'*H*-4,4'-bis-1,2,3-triazole (3a)**. The reaction was performed at 95°C for 36 h. Yield 290 mg (48%), colorless oil. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.07 (3H, s, $CH_3$); 7.40–7.45 (2H, m, H Ar); 7.45–7.51 (3H, m, H Ar); 7.50–7.60 (5H, m, H Ar); 8.03 (1H, s, H triazole). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 9.3; 124.9; 125.0; 128.7; 129.4; 129.5; 129.7; 129.9; 133.0; 133.2; 134.7; 135.7; 136.6. Mass spectrum, *m*/*z* ($I_{rel}$, %): 302 $[M]^+$ (4), 274 $[M–N_2]^+$ (14), 245 (32), 204 (15), 143 (73), 77 (100). Found, %: C 67.79; H 4.29; N 27.94. $C_{17}H_{14}N_6$. Calculated, %: C 67.54; H 4.67; N 27.80.

**5-Methyl-3'-(4-nitrophenyl)-1-phenyl-1*H*,3'*H*-4,4'-bis-1,2,3-triazole (3b)**. The reaction was performed at 105°C for 7 h. Yield 340 mg (49%), light-pink powder, mp 211–213°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm (*J*, Hz): 2.33 (3H, s, $CH_3$); 7.62–7.65 (5H, m, H Ph); 7.87 (2H, d, *J* = 9.0, H Ar); 8.33 (1H, s, H triazole); 8.40 (2H, d, *J* = 9.1, H Ar). $^{13}$C NMR spectrum (DMSO-$d_6$), δ, ppm: 9.6; 125.3; 125.6; 126.7; 129.4; 130.2; 130.4; 132.3; 134.7; 134.8; 135.9; 141.7; 148.0. Mass spectrum, *m*/*z* ($I_{rel}$, %): 347 $[M]^+$ (4), 319 $[M–N_2]^+$ (13), 290 (10), 274 (10), 244 (24), 77 (100). Found, %: C 58.54; H 3.75; N 28.54. $C_{17}H_{13}N_7O_2$. Calculated, %: C 58.79; H 3.77; N 28.23.

**1-(4-Bromobenzyl)-5-methyl-3'-(4-nitrophenyl)-1*H*,3'*H*-4,4'-bis-1,2,3-triazole (3f)**. The reaction was performed for 33 h at 95°C. Yield 616 mg (70%), colorless powder, mp 191–195°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm (*J*, Hz): 2.19 (3H, s, $CH_3$); 5.63 (2H, s, $CH_2$); 7.16 (2H, d, *J* = 8.4, H Ar); 7.58 (2H, d, *J* = 8.4, H Ar); 7.76 (2H, d, *J* = 9.0, H Ar); 8.26 (1H, s, H triazole); 8.36 (2H, d, *J* = 9.0, H Ar). $^{13}$C NMR spectrum (DMSO-$d_6$), δ, ppm: 8.0; 50.3; 121.3; 124.7; 126.2; 129.1; 131.7; 131.8; 133.9; 134.2; 134.6; 141.2; 147.4. Mass spectrum, *m*/*z* ($I_{rel}$, %): 442 $[M]^+$ (2), 441 $[M]^+$ (5), 440 $[M]^+$ (2), 439 $[M]^+$ (5), 414 $[M–N_2]^+$ (10), 413 $[M–N_2]^+$ (48), 412 $[M–N_2]^+$ (22), 411 $[M–N_2]^+$ (48), 382 (11), 338 (21), 90 (100). Found, %: C 49.16; H 2.97; N 22.35. $C_{18}H_{14}BrN_7O_2$. Calculated, %: C 49.11; H 3.21; N 22.27.

**1,5-Dimethyl-3'-phenyl-1*H*,3'*H*-4,4'-bis-1,2,3-triazole (3c)**. Method I. A mixture of ketone **1a** (278 mg, 2.00 mmol), azide **2a** (1.073 g, 9.00 mmol), and CaO (221 mg, 3.94 mmol) in anhydrous morpholine (2 ml) was stirred at 120°C for 72 h. The volatile components were evaporated to dryness, the residue was separated on a chromatography column (using a sequence of eluents: $CHCl_3$–EtOAc, 2:1; $CHCl_3$–EtOAc, 1:1; $CHCl_3$–EtOAc, 1:2). The last portions of eluate containing the product were combined and evaporated to dryness. The oily residue was treated with petroleum ether and left overnight at cold temperature.

Method II. A solution of ketone **1a** (278 mg, 2.00 mmol) and azide **2a** (550 mg, 4.61 mmol) in anhydrous pyrrolidine (2 ml) was stirred at 70–80°C for 8 h. The volatile components were evaporated to dryness. The crude product was purified in the way described in method I. Yield 71 mg (15%, method I), 192 mg (40%, method II), light-yellow powder, mp 86–91°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.02 (3H, s, $CH_3$); 3.95 (3H, s, $NCH_3$); 7.40–7.43 (5H, m, H Ph); 7.91 (1H, s, H triazole). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 8.0; 34.7; 124.8; 128.9; 129.2; 132.4; 132.8; 134.4; 136.6. Mass spectrum, *m*/*z* ($I_{rel}$, %): 240 $[M]^+$ (11), 212 $[M–N_2]^+$ (23), 183 (56), 169 (14), 56 (100). Found, %: C 59.62; H 4.75; N 34.87. $C_{12}H_{12}N_6$. Calculated, %: C 59.99; H 5.03; N 34.98.

**Synthesis of bistriazoles 3d**,**e**,**g** (General method). A solution of the appropriate ketone **1a**,**g** (2.00 mmol) and azide **2b**,**e** (5.00 mmol) in anhydrous morpholine (2 ml) was stirred at 95–120°C for 12–48 h. The volatile components were evaporated to dryness, the residue was purified by column chromatography (eluent $CHCl_3$, followed by $CHCl_3$–EtOAc, 1:1 (for compound **3d**); $CHCl_3$, followed by $CHCl_3$–EtOAc, 1:3 (for compound **3e**); petroleum ether, petroleum ether – $Et_3N$, 93:1; petroleum ether – $Et_3N$ – EtOAc, 93:1:186 (for compound **3g**)).

**1,5-Dimethyl-3'-(4-nitrophenyl)-1*H*,3'*H*-4,4'-bis-1,2,3-triazole (3d)**. The reaction was performed for 48 h at 110°C. The product was isolated by column chromatography and then additionally purified by crystallization from EtOH. Yield 285 mg (50%), colorless powder, mp 160–165°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm (*J*, Hz): 2.32 (3H,

s, $CH_3$); 4.00 (3H, s, $NCH_3$); 7.78 (2H, d, $J$ = 9.1, H Ar); 8.07 (1H, s, H triazole); 8.36 (2H, d, $J$ = 9.1, H Ar). $^{13}$C NMR spectrum (DMSO-$d_6$), δ, ppm: 7.9; 34.5; 124.4; 125.8; 129.1; 133.6; 133.7; 140.0; 141.3; 147.2. Mass spectrum, *m*/*z* ($I_{rel}$, %): 285 $[M]^+$ (9), 257 $[M–N_2]^+$ (42), 228 (10), 214 (7), 201 (9), 182 (20), 56 (100). Found, %: C 50.91; H 3.89; N 34.18. $C_{12}H_{11}N_7O_2$. Calculated, %: C 50.53; H 3.89; N 34.37.

**3'-(4-Chlorophenyl)-1,5-dimethyl-1*H*,3'*H*-4,4'-bis-1,2,3-triazole (3e)**. The reaction was performed for 26 h at 120°C. The product obtained after column chromatography was crystallized from heptane. Yield 203 mg (41%), light-brown powder, mp 120–123°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.17 (3H, s, $CH_3$); 4.00 (3H, s, $NCH_3$); 7.43–7.47 (4H, m, $J$ = 8.9, H Ar); 7.90 (1H, s, H triazole). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 8.2; 34.9; 126.3; 128.8; 129.4; 132.2; 134.3; 135.1; 135.3. Mass spectrum, *m*/*z* ($I_{rel}$, %): 276 $[M+2]^+$ (6), 275 $[M+1]^+$ (3), 274 $[M]^+$ (17), 246 $[M–N_2]^+$ (5), 217 (20), 183 (23), 56 (100). Found, %: C 52.11; H 3.97; N 30.39. $C_{12}H_{11}ClN_6$. Calculated, %: C 52.47; H 4.04; N 30.59.

**1-Butyl-5-methyl-3'-(4-nitrophenyl)-1*H*,3'*H*-4,4'-bis-1,2,3-triazole (3g)**. The reaction was performed at 95°C over 12 h. The product isolated by column chromatography was crystallized from PhH – petroleum ether mixture. Yield 400 mg (61%), light-yellow amorphous material, mp 91–93°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.95 (3H, t, $J$ = 7.4, $N(CH_2)_3C\underline{H}_3$); 1.28–1.46 (2H, m, $N(CH_2)_2C\underline{H}_2CH_3$); 1.80–1.95 (2H, m, $NCH_2C\underline{H}_2CH_2CH_3$); 2.25 (3H, s, $CH_3$); 4.27 (2H, t, $J$ = 7.3, $NC\underline{H}_2(CH_2)_2CH_3$); 7.74 (2H, d, $J$ = 9.0, H Ar); 7.90 (1H, s, H triazole); 8.29 (2H, d, $J$ = 8.9, H Ar). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 8.3; 13.4; 19.7; 31.6; 48.2; 124.5; 125.7; 129.0; 131.9; 132.4; 134.4; 141.5; 147.8. Mass spectrum, *m*/*z* ($I_{rel}$, %): 327 $[M]^+$ (7), 299 $[M–N_2]^+$ (25), 298 (100). Found, %: C 55.03; H 5.45; N 29.87. $C_{15}H_{17}N_7O_2$. Calculated, %: C 55.04; H 5.23; N 29.95.

**Synthesis of enaminones 4c–s** (General method). A mixture of the appropriate ketone **1** (3.00 mmol) and DMF–DMA (4.3 g, 4.8 ml, 36.00 mmol) was heated at 100–120°C (the temperature of the oil bath) for 1.5–50 h. The excess of DMF–DMA was evaporated, the crude enaminone was purified by crystallization from EtOH, PhH, or petroleum ether, or by column chromatography (eluent EtOAc, a mixture of EtOAc – petroleum ether, $CHCl_3$–EtOAc, or $CHCl_3$–EtOH).

**3-(Dimethylamino)-1-[5-methyl-1-(2-nitrophenyl)-1*H*-1,2,3-triazol-4-yl]prop-2-en-1-one (4c)**. The reaction was performed over 22 h at 110°C. The crude product was treated by petroleum ether, $H_2O$, then crystallized from EtOH. Yield 615 mg (68%), light-yellow powder, mp 228–229°C (decomp.). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm (*J*, Hz): 2.48 (3H, d, $J$ = 6.6, $CH_3$); 2.91 (3H, s, $NCH_3$); 3.17 (3H, s, $NCH_3$); 6.07 (1H, d, $J$ = 12.6, $C\underline{H}$=CHN$(CH_3)_2$); 7.78 (1H, d, $J$ = 12.6, CH=C$\underline{H}$N$(CH_3)_2$); 7.91–7.94 (2H, m, H Ar); 7.98–8.08 (1H, m, H Ar); 8.31 (1H, dd, $J$ = 8.4, $J$ = 1.3, H Ar). $^{13}$C NMR spectrum (DMSO-$d_6$), δ, ppm: 9.0; 92.9; 99.5; 125.6; 128.0; 129.6; 132.1; 134.6; 137.5; 143.8; 145.5; 153.3; 180.6. Mass spectrum, *m*/*z* ($I_{rel}$, %): 301 $[M]^+$ (16), 229 (22), 98 (100). Found, %: C 55.91; H 5.21; N 23.47. $C_{14}H_{15}N_5O_3$. Calculated, %: C 55.81; H 5.02; N 23.24.

**3-(Dimethylamino)-1-[5-methyl-1-(methylphenyl)-1*H*-1,2,3-triazol-4-yl]prop-2-en-1-one (4d)**. The reaction was performed at 110°C over 22 h. The product was purified by column chromatography (eluent EtOAc), then crystallized from *i*-PrOH. Yield 568 mg (70%), light-yellow needles, mp 190–193°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm (*J*, Hz): 2.41 (3H, s, $CH_3$); 2.51 (3H, s, $CH_3$); 2.90 (3H, br. s, $NCH_3$); 3.15 (3H, br. s, $NCH_3$); 6.08 (1H, d, $J$ = 12.6, $C\underline{H}$=CHN$(CH_3)_2$); 7.42 (2H, d, $J$ = 8.2, H Ar); 7.45–7.50 (2H, m, H Ar); 7.75 (1H, d, $J$ = 12.6, CH=C$\underline{H}$N$(CH_3)_2$). $^{13}$C NMR spectrum (DMSO-$d_6$), δ, ppm: 9.6; 20.6; 92.7; 125.1; 130.0; 133.1; 135.7; 139.4; 143.9; 153.0; 180.9. Mass spectrum, *m*/*z* ($I_{rel}$, %): 270 $[M]^+$ (36), 242 $[M–N_2]^+$ (2), 227 (5), 198 (37), 132 (100). Found, %: C 66.52; H 6.74; N 20.57. $C_{15}H_{18}N_4O$. Calculated, %: C 66.64; H 6.71; N 20.73.

**3-(Dimethylamino)-1-{5-methyl-1-[4-(propan-2-yl)-phenyl]-1*H*-1,2,3-triazol-4-yl}prop-2-en-1-one (4e)**. The reaction was performed at 110°C for 20 h. The crude product was purified by crystallization from PhH. Yield 850 mg (95%), light-yellow powder, mp 190–192°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.28 (6H, d, $J$ = 6.9, $CH(C\underline{H}_3)_2$); 2.61 (3H, s, 5-$CH_3$); 2.96–2.99 (4H, m, $NCH_3$, $C\underline{H}(CH_3)_2$); 3.14 (3H, s, $NCH_3$); 6.27 (1H, d, $J$ = 12.6, $C\underline{H}$=CHN$(CH_3)_2$); 7.34 (2H, d, $J$ = 8.7, H Ar); 7.38 (2H, d, $J$ = 8.6, H Ar); 7.85 (1H, d, $J$ = 12.6, CH=C$\underline{H}$N$(CH_3)_2$). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 10.2; 23.8; 33.9; 37.4; 45.0; 125.2; 127.5; 144.4; 150.6; 153.3; 182.7. Mass spectrum, *m*/*z* ($I_{rel}$, %): 298 $[M]^+$ (49), 270 $[M–N_2]^+$ (3), 226 (62), 184 (19), 160 (81), 98 (100). Found, %: C 68.53; H 7.31; N 19.07. $C_{17}H_{22}N_4O$. Calculated, %: C 68.43; H 7.43; N 18.78.

**1-[1-(3-Chlorophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]-3-(dimethylamino)-prop-2-en-1-one (4f)**. The reaction was performed at 100°C for 24 h. The product was purified by column chromatography (eluent EtOAc), then crystallized from a PhH – petroleum ether mixture. Yield 488 mg (56%), light-yellow powder, mp 128–129°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.63 (3H, s, $CH_3$); 2.95 (3H, s, $NCH_3$); 3.14 (3H, s, $NCH_3$); 6.24 (1H, d, $J$ = 12.6, $C\underline{H}$=CHN$(CH_3)_2$); 7.30–7.40 (1H, m, H Ar); 7.44–7.56 (3H, m, H Ar); 7.83 (1H, d, $J$ = 12.6, CH=C$\underline{H}$N$(CH_3)_2$). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 10.3; 37.4; 45.1; 93.6; 123.4; 125.6; 129.8; 130.5; 135.3; 136.3; 136.9; 144.7; 153.5; 182.4. Mass spectrum, *m*/*z* ($I_{rel}$, %): 292 $[M]^+$ (14), 291 $[M]^+$ (8), 290 $[M]^+$ (43), 273 (10), 218 (46), 152 (66), 98 (100). Found, %: C 57.92; H 4.99; N 19.62. $C_{14}H_{15}ClN_4O$. Calculated, %: C 57.83; H 5.20; N 19.27.

**3-(Dimethylamino)-1-[1-(3-fluorophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]prop-2-en-1-one (4g)**. The reaction was performed at 100°C for 7.5 h. The crude product was washed with petroleum ether and crystallized from PhH – petroleum ether mixture. Yield 667 mg (81%), light-brown powder, mp 157–158°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.67 (3H, s, $CH_3$); 2.98 (3H, s, $NCH_3$); 3.17 (3H, s, $NCH_3$); 6.27 (1H, d, $J$ = 12.4, $C\underline{H}$=CHN$(CH_3)_2$); 7.26 (3H,

s, H Ar); 7.44–7.62 (1H, m, H Ar); 7.85 (1H, d, *J* = 12.4, CH=CHN(CH$_3$)$_2$). $^{13}$C NMR spectrum (CDCl$_3$), δ, ppm (*J*, Hz): 10.2; 37.4; 44.8, 93.3, 112.9 (d, *J* = 25.0); 116.5 (d, *J* = 21.0); 120.9 (d, *J* = 3.0); 130.9 (d, *J* = 9.0); 136.2; 137.1 (d, *J* = 10.0); 144.6; 153.4; 162.7 (d, *J* = 258.0); 182.3. $^{19}$F NMR spectrum (CDCl$_3$), δ, ppm: –110.0. Mass spectrum, *m*/*z* (*I*$_{rel}$, %): 275 [M+1]$^+$ (7), 274 [M]$^+$ (36), 257 (8), 202 (41), 176 (12), 162 (14), 136 (100). Found, %: C 61.38; H 5.72; N 20.65. $C_{14}H_{15}FN_4O$. Calculated, %: C 61.30; H 5.51; N 20.43.

**1-[1-(2-Chloro-4-methylphenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]-3-(dimethylamino)prop-2-en-1-one (4h)**. The reaction was performed at 120°C for 24 h. The crude product was treated with petroleum ether and crystallized from PhH – petroleum ether mixture. Yield 886 mg (97%), light-yellow powder, mp 160–162°C. $^1$H NMR spectrum (CDCl$_3$), δ, ppm (*J*, Hz): 2.43 (3H, s, CH$_3$); 2.46 (3H, s, CH$_3$); 2.96 (3H, s, NCH$_3$); 3.15 (3H, s, NCH$_3$) 6.28 (1H, d, *J* = 12.6, CH=CHN(CH$_3$)$_2$); 7.22–7.28 (2H, m, H Ar); 7.40 (1H, d, *J* = 0.4, H Ar); 7.85 (1H, d, *J* = 12.6, CH=CHN(CH$_3$)$_2$). $^{13}$C NMR spectrum (CDCl$_3$), δ, ppm: 9.5; 21.1; 37.3; 44.9; 93.8; 128.5; 128.8; 130.9; 131.0; 131.4; 138.0; 142.5; 143.9; 153.4; 182.6. Mass spectrum, *m*/*z* (*I*$_{rel}$, %): 306 [M+2]$^+$ (22), 305 [M+1]$^+$ (13), 304 [M]$^+$ (66), 287 (9), 241 (15), 234 (25), 232 (71), 166 (100). Found, %: C 58.93; H 5.25; N 18.66. $C_{15}H_{17}ClN_4O$. Calculated, %: C 59.11; H 5.62; N 18.38.

**1-[1-(5-Chloro-2-nitrophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]-3-(dimethylamino)prop-2-en-1-one (4i)**. The reaction was performed at 150°C for 12 h. The crude product was purified by column chromatography (eluent CHCl$_3$–EtOAc, 1:1, then EtOAc), followed by crystallization from PhH – petroleum ether mixture. Yield 403 mg (40%), light-yellow crystals, mp 192–194°C (decomp.). $^1$H NMR spectrum (CDCl$_3$), δ, ppm (*J*, Hz): 2.54 (3H, s, CH$_3$); 2.96 (3H, s, NCH$_3$); 3.16 (3H, s, NCH$_3$); 6.23 (1H, d, *J* = 12.5, CH=CHN(CH$_3$)$_2$); 7.50 (1H, d, *J* = 2.0, H Ar); 7.72 (1H, dd, *J* = 8.8, *J* = 1.9, H Ar); 7.85 (1H, d, *J* = 12.5, CH=CHN(CH$_3$)$_2$); 8.16 (1H, d, *J* = 8.8, H Ar). $^{13}$C NMR spectrum (CDCl$_3$), δ, ppm: 9.6; 37.4; 45.1; 93.5; 127.1; 129.9; 130.3; 131.6; 138.1; 140.4; 143.8; 144.3; 153.7; 181.9. Mass spectrum, *m*/*z* (*I*$_{rel}$, %): 337 [M]$^+$ (5), 336 [M]$^+$ (3), 335 [M]$^+$ (15), 265 (7), 263 (22), 98 (100). Found, %: C 50.05; H 4.11; N 20.59. $C_{14}H_{14}ClN_5O_3$. Calculated, %: C 50.08; H 4.20; N 20.86.

**1-(1-[4-Bromobenzyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]-3-(dimethylamino)prop-2-en-1-one (4j)**. The reaction was performed at 105°C for 3.5 h. The crude product was purified by column chromatography (eluent CHCl$_3$, then CHCl$_3$–EtOAc, 1:1, then EtOAc). The fractions containing the product were evaporated to dryness, the residue was crystallized from PhH – petroleum ether mixture. Yield 482 mg (46%), light-yellow powder, mp 158–160°C. $^1$H NMR spectrum (CDCl$_3$), δ, ppm (*J*, Hz): 2.49 (3H, s, CH$_3$); 2.94 (3H, br. s, NCH$_3$); 3.13 (3H, br. s, NCH$_3$); 5.44 (2H, s, CH$_2$); 6.21 (1H, d, *J* = 12.6, CH=CHN(CH$_3$)$_2$); 7.02 (2H, d, *J* = 8.4, H Ar); 7.44 (2H, d, *J* = 8.4, H Ar); 7.80 (1H, d, *J* = 12.6, CH=CHN(CH$_3$)$_2$). $^{13}$C NMR spectrum (CDCl$_3$), δ, ppm: 9.1; 50.8; 93.7; 122.4; 128.8; 132.2; 133.6; 135.6; 145.0; 153.4; 182.6. Mass spectrum, *m*/*z* (*I*$_{rel}$, %): 351 [M]$^+$ (4), 350 [M]$^+$ (20), 349 [M]$^+$ (4), 348 [M]$^+$ (22), 333 (13), 331 (14), 276 (6), 98 (100). Found, %: C 51.38; H 4.84; N 16.09. $C_{15}H_{17}BrN_4O$. Calculated, %: C 51.59; H 4.91; N 16.04.

**1-(1-Butyl-5-methyl-1*H*-1,2,3-triazol-4-yl)-3-(dimethylamino)prop-2-en-1-one (4k)**. The reaction was performed at 110°C for 50 h. The crude product was crystallized from petroleum ether. Yield 562 mg (79%), light-yellow powder, mp 93–95°C. $^1$H NMR spectrum (CDCl$_3$), δ, ppm (*J*, Hz): 0.90 (3H, t, *J* = 7.4, (CH$_2$)$_3$CH$_3$); 1.25–1.33 (2H, m, (CH$_2$)$_2$CH$_2$CH$_3$); 1.77–1.85 (2H, m, CH$_2$CH$_2$CH$_2$CH$_3$); 2.56 (3H, s, CH$_3$); 2.90 (3H, d, *J* = 2.2, NCH$_3$); 3.09 (3H, br. s, NCH$_3$); 4.21 (2H, t, *J* = 7.3, CH$_2$(CH$_2$)$_2$CH$_3$); 6.16 (1H, d, *J* = 12.7, CH=CHN(CH$_3$)$_2$); 7.76 (1H, d, *J* = 12.7, CH=CHN(CH$_3$)$_2$). $^{13}$C NMR spectrum (CDCl$_3$), δ, ppm: 9.1; 13.4; 19.6; 31.7; 37.3; 44.9; 47.2; 93.5; 135.2; 144.3; 153.1; 182.8. Mass spectrum, *m*/*z* (*I*$_{rel}$, %): 236 [M]$^+$ (44), 219 (26), 193 (6), 164 (20), 151 (16), 42 (100). Found, %: C 61.20; H 8.28; N 23.51. $C_{12}H_{20}N_4O$. Calculated, %: C 60.99; H 8.53; N 23.71.

**3-(Dimethylamino)-1-[5-methyl-1-(prop-2-en-1-yl)-1*H*-1,2,3-triazol-4-yl]prop-2-en-1-one (4l)**. The reaction was performed at 100°C for 5 h. The crude product was purified by column chromatography (eluted with the sequence of CHCl$_3$, 1:1 CHCl$_3$–EtOAc mixture, and EtOH). The ethanol eluate contained the product and was evaporated to dryness. The residue was purified by chromatography using a second column (eluent PhH–Et$_3$N, 93:1, then CHCl$_3$–Et$_3$N, 93:1), followed by crystallization from petroleum ether. Yield 258 mg (39%), light-yellow powder, mp 75–77°C. $^1$H NMR spectrum (CDCl$_3$), δ, ppm (*J*, Hz): 2.55 (3H, s, CH$_3$); 2.91 (3H, s, NCH$_3$); 3.10 (3H, s, NCH$_3$); 4.89 (2H, d, *J* = 5.3, CH$_2$CH=CH$_2$); 5.02 (1H, d, *J* = 17.1, CH$_2$CH=CH$_2$); 5.24 (1H, d, *J* = 10.4, CH$_2$CH=CH$_2$); 5.87–5.95 (1H, m, CH$_2$CH=CH$_2$); 6.18 (1H, d, *J* = 12.6, CH=CHN(CH$_3$)$_2$); 7.78 (1H, d, *J* = 12.6, CH=CHN(CH$_3$)$_2$). $^{13}$C NMR spectrum (CDCl$_3$), δ, ppm: 8.9; 37.2; 44.9; 49.8; 93.3; 118.3; 131.0; 135.6; 144.4; 153.1; 182.4. Mass spectrum, *m*/*z* (*I*$_{rel}$, %): 220 [M]$^+$ (74), 203 (46), 177 (7), 148 (30), 98 (100). Found, %: C 59.86; H 6.97; N 25.28. $C_{11}H_{16}N_4O$. Calculated, %: C 59.98; H 7.32; N 25.44.

**3-(Dimethylamino)-1-(1-phenyl-*1H*-1,2,3-triazol-4-yl)prop-2-en-1-one (4m)**. The reaction was performed at 120°C for 6 h. The crude product was purified by column chromatography (eluted with the sequence of CHCl$_3$, EtOAc, and EtOH). Yield 545 mg (75%), light-yellow needles, mp 188–189°C. $^1$H NMR spectrum (DMSO-*d*$_6$), δ, ppm (*J*, Hz): 2.93 (3H, s, NCH$_3$); 3.17 (3H, s, NCH$_3$); 6.01 (1H, d, *J* = 12.5, CH=CHN(CH$_3$)$_2$); 7.50 (1H, t, *J* = 7.4, H Ar); 7.60 (2H, t, *J* = 7.8, H Ar); 7.84 (1H, d, *J* = 12.5, CH=CHN(CH$_3$)$_2$); 7.97 (2H, d, *J* = 7.9, H Ar); 9.20 (1H, s, H triazole). $^{13}$C NMR spectrum (DMSO-*d*$_6$), δ, ppm: 37.1; 44.5; 91.8; 120.2; 123.8; 128.8; 129.8; 136.4; 149.8; 153.7; 178.5. Mass spectrum, *m*/*z* (*I*$_{rel}$, %): 242 [M]$^+$ (71), 225 (8), 185 (7), 173 (21), 171 (27), 98 (100). Found, %: C 64.68; H 5.99; N 22.78. $C_{13}H_{14}N_4O$. Calculated, %: C 64.45; H 5.82; N 23.13.

**3-(Dimethylamino)-1-[1-(4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl]prop-2-en-1-one (4n)**. The reaction was performed at 120°C for 18 h. The crude product was washed with $Et_2O$, then with petroleum ether, and dried. Yield 750 mg (87%), light-yellow crystals, mp 281–284°C (decomp.). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm (*J*, Hz): 2.95 (3H, s, $NCH_3$); 3.19 (3H, s, $NCH_3$); 5.99 (1H, d, *J* = 12.5, C<u>H</u>=CHN$(CH_3)_2$); 7.86 (1H, d, *J* = 12.5, CH=C<u>H</u>N$(CH_3)_2$); 8.22–8.37 (2H, m, H Ar); 8.39–8.52 (2H, m, H Ar); 9.36 (1H, s, H triazole). $^{13}$C NMR spectrum (DMSO-$d_6$), δ, ppm: 31.1; 92.5; 121.5; 124.8; 125.9; 141.3; 147.5; 150.7; 154.4; 178.7. Mass spectrum, *m*/*z* ($I_{rel}$, %): 287 $[M]^+$ (64), 242 (10), 216 (21), 215 (57), 98 (100). Found, %: C 54.31; H 4.92; N 24.44. $C_{13}H_{13}N_5O_3$. Calculated, %: C 54.35; H 4.56; N 24.38.

**3-(Dimethylamino)-1-[1-(2-nitrophenyl)-1*H*-1,2,3-triazol-4-yl]prop-2-en-1-one (4o)**. The reaction was performed at 120°C for 2.5 h. The crude product was purified by column chromatography (eluent EtOAc, then EtOAc–EtOH, 10:1), then crystallized from PhH – EtOAc – petroleum ether mixture. Yield 500 mg (58%), light-yellow powder, mp 156–157°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.98 (3H, s, $NCH_3$); 3.19 (3H, s, $NCH_3$); 6.18 (1H, d, *J* = 10.8, C<u>H</u>=CHN$(CH_3)_2$); 7.59 (1H, dd, *J* = 7.8, *J* = 1.1, H Ar); 7.70 (1H, td, *J* = 7.9, *J* = 1.3, H Ar); 7.78 (1H, td, *J* = 7.7, *J* = 1.3, H Ar); 7.99 (1H, br. s, CH=C<u>H</u>N$(CH_3)_2$); 8.08 (1H, dd, *J* = 8.1, *J* = 1.3, H Ar); 8.36 (1H, s, H triazole). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 37.4; 45.1; 93.0; 125.7; 126.4; 127.7; 130.0; 131.0; 133.9; 144.5; 150.3; 154.4; 179.9. Mass spectrum, *m*/*z* ($I_{rel}$, %): 287 $[M]^+$ (27), 215 (36), 98 (100). Found, %: C 54.06; H 4.76; N 24.68. $C_{13}H_{13}N_5O_3$. Calculated, %: C 54.35; H 4.56; N 24.38.

**3-(Dimethylamino)-1-[1-(4-methylphenyl)-1*H*-1,2,3-triazol-4-yl]prop-2-en-1-one (4p)**. The reaction was performed at 120°C for 22 h. The crude product was treated with $Et_2O$, the solids were separated and crystallized from PhH – petroleum ether mixture. Yield 615 mg (80%), light-yellow powder, mp 213–215°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.40 (3H, s, $CH_3$); 2.97 (3H, s, $NCH_3$); 3.16 (3H, s, $NCH_3$); 6.19 (1H, d, *J* = 9.6, C<u>H</u>=CHN$(CH_3)_2$); 7.30 (2H, d, *J* = 8.2, H Ar); 7.57–7.74 (2H, m, H Ar); 7.94 (1H, br. s, CH=C<u>H</u>N$(CH_3)_2$); 8.43 (1H, s, H triazole). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 21.1; 37.4; 45.1; 92.9; 120.4; 122.9; 130.3; 134.5; 139.1; 150.2; 154.1; 180.5. Mass spectrum, *m*/*z* ($I_{rel}$, %): 256 $[M]^+$ (86), 228 $[M–N_2]^+$ (4), 187 (24), 185 (35), 98 (100). Found, %: C 65.40; H 6.50; N 21.75. $C_{14}H_{16}N_4O$. Calculated, %: C 65.61; H 6.29; N 21.86.

**1-[3-(4-Chlorophenyl)-5-methyl-1,2-oxazol-4-yl]-3-(dimethylamino)prop-2-en-1-one (4r)**. The reaction was performed at 100°C for 1.5 h. The volatile components were removed by evaporation to dryness. The crude product was purified by column chromatography (eluent – $CHCl_3$ followed by $CHCl_3$–EtOAc, gradient from 12.5:1 to 4:1), then crystallized from MeOH. Yield 715 mg (82%), light-yellow powder, mp 88–89°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.63 (6H, s, N$(CH_3)_2$); 3.06 (3H, s, $CH_3$); 4.95 (1H, d, *J* = 12.3, C<u>H</u>=CHN$(CH_3)_2$); 7.40 (2H, d, *J* = 8.5, H Ar); 7.54 (1H, br. s, CH=C<u>H</u>N$(CH_3)_2$); 7.61 (2H, d, *J* = 8.6, H Ar). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 12.7; 37.0; 45.0; 76.8; 77.1; 77.4; 127.9; 128.6; 130.3; 135.7; 160.2. Mass spectrum, *m*/*z* ($I_{rel}$, %): 292 $[M]^+$ (8), 291 $[M]^+$ (5), 290 $[M]^+$ (24), 273 (12), 246 (11), 98 (100). Found, %: C 61.98; H 5.55; N 9.97. $C_{15}H_{15}ClN_2O_2$. Calculated, %: C 61.97; H 5.20; N 9.64.

**Synthesis of 3-(dimethylamino)-1-(5-methyl-1,2,3-thiadiazol-4-yl)prop-2-en-1-one (4q) and 1-{5-[2-(dimethylamino)ethenyl]-1,2,3-thiadiazol-4-yl}ethanone (4s)**. A solution of ketone **1s** (213 mg, 1.50 mmol) in DMF–DMA (1.06 ml, 23.0 mmol) was heated in a sealed vessel at 80°C for 1 h. The volatile components were removed by evaporation to dryness, the residue was separated by column chromatography (eluting first with $CHCl_3$, then with $CHCl_3$–EtOAc, gradient from 4:1 to 1:10). Enamine **4s** ($R_f$ 0.68, EtOAc) was isolated from the first fractions, yield 125 mg (42%), yellow-green needles, mp 120–122°C (decomp.), while the last fractions gave enaminone **4q** ($R_f$ 0.34, EtOAc), yield 68 mg (23%), light-yellow needles, mp 131–132°C.

**Compound 4q**. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.93 (6H, d, *J* = 16.5, N$(CH_3)_2$); 3.16 (3H, s, $CH_3$); 6.37 (1H, d, *J* = 12.6, C<u>H</u>=CHN$(CH_3)_2$); 7.84 (1H, d, *J* = 12.6, CH=C<u>H</u>N$(CH_3)_2$). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 11.0 ($NCH_3$); 37.5 ($NCH_3$); 45.2 ($CH_3$); 95.2 (C-β); 154.4 (C-4); 156.5 (C-5); 157.8 (C-α); 181.7 (C=O). Mass spectrum, *m*/*z* ($I_{rel}$, %): 197 $[M]^+$ (11), 154 (19), 98 (100). Found, %: C 48.66; H 5.31; N 21.32. $C_8H_{11}N_3OS$. Calculated, %: C 48.71; H 5.62; N 21.30.

**Compound 4s**. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.74 (3H, s, $CH_3$); 2.97 (6H, s, N$(CH_3)_2$); 6.46 (1H, d, *J* = 13.3, C<u>H</u>=CHN$(CH_3)_2$); 7.06 (1H, d, *J* = 13.3, CH=C<u>H</u>N$(CH_3)_2$). $^{13}$C NMR spectrum (DMSO-$d_6$), δ, ppm: 29.1 ($CH_3$); 40.9 (N$(CH_3)_2$); 85.1 (C-β); 149.3 (C-4); 154.6 (C-5); 162.4 (C-α); 191.4 (C=O). Mass spectrum, *m*/*z* ($I_{rel}$, %): 197 $[M]^+$ (38), 169 $[M–N_2]^+$ (18), 127 (91), 42 (100). Found, *m*/*z*: 220.0514 $[M+Na]^+$. $C_8H_{11}N_3NaOS$. Calculated, *m*/*z*: 220.0515. Found, %: C 49.04; H 5.71; N 21.64. $C_8H_{11}N_3OS$. Calculated, %: C 48.71; H 5.62; N 21.30.

**Synthesis of 4-triazolylcarbonyl-1,2,3-triazoles 5a–i** (General method). A solution of enaminone **4a**,**b**,**m**,**n**,**r** (1.0 mmol) and the appropriate azide **2a**,**b**,**d**,**g**,**h**,**i** (1.5–7.0 mmol) in 1,4-dioxane (5–10 ml) was heated at 55–110°C for 1.5–48 h. The solvent was removed by evaporation, the crude product was purified by column chromatography or by recrystallization.

**(5-Methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)[1-(4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl]methanone (5a)** was obtained from enaminone **4a** (256 mg, 1.0 mmol) and azide **2b** (328 mg, 2.0 mmol). The reaction was performed at 110°C for 16 h. After cooling the reaction mixture, the solids were separated, refluxed in EtOH (6 ml) for 10 min, the precipitate was separated and then washed with a small amount of EtOH. Yield 323 mg (86%), light-brown powder, mp 235–238°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm (*J*, Hz): 2.65 (3H, s, $CH_3$); 7.58–7.77 (5H, m, H Ph); 8.39 (2H, d, *J* = 9.1, H Ar); 8.47 (2H, d, *J* = 9.1, H Ar); 9.94 (1H, s, H triazole). $^{13}$C NMR spectrum

(DMSO-$d_6$), δ, ppm: 9.9; 121.8; 125.3; 125.4; 128.7; 129.7; 130.2; 135.0; 140.1; 140.5; 142.2; 145.6; 147.4; 177.0. Mass spectrum, *m*/*z* ($I_{rel}$, %): 347 $[M–N_2]^+$ (11), 319 $[M–N_2]^+$ (2), 290 (7), 244 (8), 77 (100). Found, %: C 57.55; H 3.63; N 26.10. $C_{18}H_{13}N_7O_3$. Calculated, %: C 57.60; H 3.49; N 26.12.

**[5-Methyl-1-(4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl]-[1-(4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl]methanone (5b)** was obtained from enaminone **4b** (301 mg, 1.0 mmol) and azide **2b** (492 mg, 3.0 mmol). The reaction was performed at 100°C for 16.5 h. The crude product was purified by column chromatography (eluent PhH, PhH–HOAc, 55:1, then $CHCl_3$–EtOAc, 1:1), then crystallized from 1,4-dioxane–*i*-PrOH mixture. Yield 273 mg (65%), light-beige powder, mp 226–229°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm (*J*, Hz): 2.72 (3H, s, $CH_3$); 8.04 (2H, d, *J* = 8.9, H Ar); 8.40 (2H, d, *J* = 9.2, H Ar); 8.48 (2H, d, *J* = 9.1, H Ar); 8.52 (2H, d, *J* = 9.0, H Ar); 9.96 (1H, s, H triazole). $^{13}$C NMR spectrum (DMSO-$d_6$), δ, ppm: 10.1; 121.7; 125.1; 125.4; 126.7; 128.9; 139.7; 140.4; 140.7; 145.4; 142.3; 147.3; 148.2; 176.7. Mass spectrum, *m*/*z* ($I_{rel}$, %): 392 $[M–N_2]^+$ (37), 318 (11), 290 (15), 244 (35), 117 (100). Found, %: C 51.53; H 2.99; N 26.90. $C_{18}H_{12}N_8O_5$. Calculated, %: C 51.43; H 2.88; N 26.66.

**(5-Methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)[1-(pentafluorophenyl)-1*H*-1,2,3-triazol-4-yl]methanone (5c)** was obtained from enaminone **4a** (256 mg, 1.0 mmol) and azide **2g** (418 mg, 2.0 mmol). The reaction was performed at 60°C for 1.5 h. The crude product was purified by column chromatography (eluent $CHCl_3$), then crystallized from heptane. Yield 252 mg (60%), colorless crystals, mp 147–149°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.73 (3H, s, $CH_3$); 7.48 (2H, dd, *J* = 7.4, *J* = 2.0, H Ar); 7.54–7.69 (3H, m, H Ar); 9.42 (1H, s, H triazole). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 10.4; 125.3; 129.8; 130.4; 132.5; 135.1; 136.8; 139.4; 140.2; 141.4; 142.5; 144.0; 145.0; 176.2. $^{19}$F NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): –144.69÷–145.25 (2F, m); –148.89 (1F, t, *J* = 21.4); –158.82÷–159.32 (2F, m). Mass spectrum, *m*/*z* ($I_{rel}$, %): 392 $[M–N_2]^+$ (9), 335 (8), 317 (6), 234 (7), 77 (100). Found, %: C 51.55; H 2.48; N 19.72. $C_{18}H_9F_5N_6O$. Calculated, %: C 51.44; H 2.16; N 20.00.

**[1-(2-Fluoro-4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl]-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)methanone (5d)** was obtained from enaminone **4a** (256 mg, 1.0 mmol) and azide **2i** (273 mg, 1.5 mmol). The reaction was performed at 104°C for 1.5 h. The crude product was purified by column chromatography (eluent PhH–HOAc, 53:1, then PhH–EtOAc–HOAc, 53:53:1), followed by refluxing of the product in EtOH for 5 min and separation of the solids. Yield 163 mg (42%), light-yellow powder, mp 215–217°C (decomp.). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm (*J*, Hz): 2.65 (3H, s, $CH_3$); 7.69 (5H, s, H Ph); 8.34–8.37 (2H, m, H Ar); 8.57 (1H, d, *J* = 10.8, H Ar); 9.79 (1H, d, *J* = 1.7, H triazole). $^{13}$C NMR spectrum (DMSO-$d_6$), δ, ppm (*J*, Hz): 10.0; 113.4 (d, *J* = 13.5); 120.7 (d, *J* = 2.0); 125.5; 126.2; 129.3 (d, *J* = 9.0); 129.8; 130.3; 131.7 (d, *J* = 4.0); 134.9; 140.3; 143.1 (d, *J* = 283.0); 148.2 (d, *J* = 9.0); 152.0; 154.5; 176.5. $^{19}$F NMR spectrum (DMSO-$d_6$), δ, ppm: –118.20. Mass spectrum, *m*/*z* ($I_{rel}$, %): 365 $[M–N_2]^+$ (9), 308 (5), 291 (4), 262 (7), 77 (100). Found, %: C 55.16; H 3.16; N 25.14. $C_{18}H_{12}FN_7O_3$. Calculated, %: C 54.96; H 3.08; N 24.93.

**[3-(4-Chlorophenyl)-5-methyl-1,2-oxazol-4-yl](1-phenyl-1*H*-1,2,3-triazol-4-yl)methanone (5e)** was obtained from enaminone **4r** (291 mg, 1.0 mmol) and azide **2a** (833 mg, 7.0 mmol). The reaction was performed at 90°C for 20 h. The crude product was purified by column chromatography (eluent $CHCl_3$, then $CHCl_3$–EtOAc, 4:1), followed by crystallization from PhH – petroleum ether mixture. Yield 231 mg (63%), colorless crystals, mp 97–99°C. $^1$H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.66 (3H, s, $CH_3$); 7.33 (2H, d, *J* = 8.6, H Ar); 7.45–7.62 (5H, m, H Ph); 7.65–7.77 (2H, m, H Ar); 8.52 (1H, s, H triazole). $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 13.5; 115.7; 120.7; 125.1; 127.9; 128.9; 129.7; 130.1; 135.9; 136.2; 147.9; 161.3; 173.8; 181.1. Mass spectrum, *m*/*z* ($I_{rel}$, %): 366 $[M]^+$ (3), 365 $[M]^+$ (2), 364 $[M]^+$ (9), 336 $[M–N_2]^+$ (6), 335 (13), 265 (6), 43 (100). Found, %: C 62.94; H 3.34; N 15.04. $C_{19}H_{13}ClN_4O_2$. Calculated, %: C 62.56; H 3.59; N 15.36.

**[3-(4-Chlorophenyl)-5-methyl-1,2-oxazol-4-yl][1-(4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl]methanone (5f)** was obtained from enaminone **4r** (291 mg, 1.0 mmol) and azide **2b** (492 mg, 3.0 mmol). The reaction was performed at 55°C for 4 h. The crude product was purified by column chromatography (eluent $CHCl_3$–EtOAc, 1:1), then crystallized twice from a mixture of DMF–$H_2O$ and EtOH. Yield 160 mg (39%), colorless crystals, mp 152–154°C. $^1$H NMR spectrum (DMF-$d_7$), δ, ppm (*J*, Hz): 2.69 (3H, s, $CH_3$); 7.46–7.60 (2H, m, H Ar); 7.61–7.75 (2H, m, H Ar); 8.40 (2H, d, *J* = 9.1, H Ar); 8.57 (2H, d, *J* = 9.1, H Ar); 9.81 (1H, s, H triazole). $^{13}$C NMR spectrum (DMF-$d_7$), δ, ppm: 12.6; 115.8; 121.6; 125.6; 127.7; 128.0; 128.9; 130.4; 135.3; 140.8; 147.9; 148.0; 161.2; 174.1; 180.4. Mass spectrum, *m*/*z* ($I_{rel}$, %): 411 $[M]^+$ (2), 410 $[M]^+$ (1), 409 $[M]^+$ (5), 381 $[M–N_2]^+$ (6), 380 (7), 43 (100). Found, %: C 56.04; H 3.20; N 16.92. $C_{19}H_{12}ClN_5O_4$. Calculated, %: C 55.69; H 2.95; N 17.09.

**[1-(2-Chloro-4-methylphenyl)-1*H*-1,2,3-triazol-4-yl]-(1-phenyl-1*H*-1,2,3-triazol-4-yl)methanone (5g)** was obtained from enaminone **4m** (242 mg, 1.0 mmol) and azide **2h** (336 mg, 2.0 mmol). The reaction was performed at 100°C for 16 h. The crude product was purified by column chromatography (eluting with a sequence of PhH, $CHCl_3$, and 1:1 mixture of $CHCl_3$–$Me_2CO$), then crystallized from PhH – petroleum ether mixture. Yield 287 mg (79%), light-yellow powder, mp 202–203°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm (*J*, Hz): 2.44 (3H, s, $CH_3$); 7.44 (1H, d, *J* = 8.0, H Ar); 7.56 (1H, t, *J* = 7.4, H Ar); 7.61–7.73 (4H, m, H Ar); 8.05 (2H, d, *J* = 7.6, H Ar); 9.57 (1H, s, H triazole); 9.75 (1H, s, H triazole). $^{13}$C NMR spectrum (DMSO-$d_6$), δ, ppm: 20.5; 66.4; 120.9; 127.8; 128.0; 128.2; 128.3; 128.9; 129.4; 129.9; 130.7; 131.4; 132.1; 136.1; 142.6; 144.8; 146.0; 175.3. Mass spectrum, *m*/*z* ($I_{rel}$, %): 338 $[M–N_2]^+$ (3), 337 $[M–N_2]^+$ (2), 336 $[M–N_2]^+$ (9), 308 (16), 273 (27), 245 (16), 205 (8), 77 (100). Found, %: C 59.08; H 3.76; N 23.03. $C_{18}H_{13}ClN_6O$. Calculated, %: C 59.27; H 3.59; N 23.04.

**[1-(2-Fluoro-4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl]-(1-phenyl-1*H*-1,2,3-triazol-4-yl)methanone (5h)** was obtained from enaminone **4m** (242 mg, 1.0 mmol) and azide **2i** (273 mg, 1.5 mmol). The reaction was performed at 100°C for 2.5 h. The crude product was purified by column chromatography (eluting with the sequence of PhH, $CHCl_3$, and 1:1 $CHCl_3$–EtOH mixture). The solids were then briefly treated with boiling EtOH, filtered off, and dried. Yield 155 mg (41%), light-yellow powder, mp 247–248°C (decomp.). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm (*J*, Hz): 7.57 (1H, t, *J* = 7.3, H Ar); 7.65 (2H, t, *J* = 7.7, H Ar); 8.04 (2H, d, *J* = 7.7, H Ar); 8.26–8.42 (2H, m, H Ar); 8.57 (1H, d, *J* = 10.9, H Ar); 9.75 (2H, s, H triazole). $^{13}$C NMR spectrum (DMSO-$d_6$), δ, ppm (*J*, Hz): 113.4 (d, *J* = 25.0): 120.8; 126.8; 127.9; 129.2 (d, *J* = 11.0); 129.5; 129.9; 131.5 (d, *J* = 6.0); 136.1; 145.2; 146.1; 148.4 (d, *J* = 8.3); 152.1; 154.6; 175.1. $^{19}$F NMR spectrum (DMSO-$d_6$), δ, ppm: –118.05. Mass spectrum, *m*/*z* ($I_{rel}$, %): 379 $[M]^+$ (1), 351 $[M–N_2]^+$ (8), 323 (18), 282 (6), 277 (8), 77 (100). Found, %: C 53.79; H 2.43; N 25.90. $C_{17}H_{10}FN_7O_3$. Calculated, %: C 53.83; H 2.66; N 25.85.

**[1-(4-Isopropylphenyl)-1*H*-1,2,3-triazol-4-yl][1-(4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl]methanone (5i)** was obtained from enaminone **4n** (287 mg, 1.0 mmol) and azide **2d** (515 mg, 3.2 mmol). The reaction was performed at 90–100°C for 48 h. The crude product was purified by column chromatography (eluent PhH, then PhH–$Me_2CO$–HOAc, 121:53:1). The first fractions of the eluate contained unreacted azide (360 mg). The fractions of eluate that contained the product were combined and evaporated to dryness. The residue was treated with boiling EtOH for 5 min, and the solids were separated. Yield 72 mg (18%), light-yellow powder, mp 246–250°C (decomp.). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm (*J*, Hz): 1.26 (6H, d, *J* = 6.9, $CH(C\underline{H}_3)_2$); 2.98–3.06 (1H, m, $C\underline{H}(CH_3)_2$); 7.52 (2H, d, *J* = 8.4, H Ar); 7.95 (2H, d, *J* = 8.4, H Ar); 8.39 (2H, d, *J* = 9.0, H Ar); 8.50 (2H, d, *J* = 9.0, H Ar); 9.71 (1H, s, H triazole); 9.96 (1H, s, H triazole). $^{13}$C NMR spectrum (DMSO-$d_6$), δ, ppm: 23.6; 33.1; 120.9; 121.7; 125.5; 127.7; 128.0; 128.7; 134.0; 140.4; 145.7; 145.9; 147.4; 150.1; 175.31. Mass spectrum, *m*/*z* ($I_{rel}$, %): 403 $[M]^+$ (10), 375 $[M–N_2]^+$ (11), 347 (19), 332 (26), 304 (40), 287 (10), 130 (100). Found, *m*/*z*: 404.1471 $[M+H]^+$. $C_{20}H_{18}N_7O_3$. Calculated, *m*/*z*: 404.1466. Found, %: C 59.62; H 4.36; N 24.42. $C_{20}H_{17}N_7O_3$. Calculated, %: C 59.55; H 4.25; N 24.31.

**X-ray structural analysis of compounds 3d and 4q** was performed on an Xcalibur 3 single crystal diffractometer according to the standard method (MoKα radiation, graphite monochromator, 295(2) K, ω-scanning with a step of 1°). The structures were solved and refined using the SHELXTL software suite.[12] The structures were solved by direct method with ShelXS program, the structures were refined with ShelXL program using a full-matrix method of least squares by $F^2$ in anisotropic approximation for non-hydrogen atoms. The hydrogen atoms were placed in the calculated positions and included in the refinement according to the riding model. The complete X-ray structural datasets for compounds **3d** and **4q** were deposited at the Cambridge Crystallographic Data Center (deposits CCDC 1901947 and CCDC 1901951, respectively).

Supplementary information file containing descriptions of the procedures used for the preparation and purification of compounds **1b**,**c**,**d**,**m**,**n**,**o**,**s**,**t**, as well as $^1$H–$^{13}$C HMBC and $^1$H–$^{13}$C HSQC spectra of compound **4s** is available from the journal website at http://link.springer.com/journal/10593.

*This work received financial support from the Russian Foundation for Basic Research (grant 18-03-00715) and by the directive No. 211 of the Government of the Russian Federation (contract No. 02.A03.21.0006).*

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