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Geminally Activated Nitroethenes in Reactions with Sodium Azide. Synthesis of Functionalized 1,2,3-Triazoles

V. M. Berestovitskaya[a], R. I. Baichurin[a], N. I. Aboskalova[a], L. V. Baichurina[b], E. V. Trukhin[a], A. V. Fel'gendler[b], and M. A. Gensirovskaya[a]

[a] *Herzen State Pedagogical University of Russia, nab. reki Moiki 48, St. Petersburg, 191186 Russia*
e-mail: kohrgpu@yandex.ru

[b] *Kirov Military Medical Academy, St. Petersburg, Russia*

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Abstract—Reactions of geminally activated alkoxycarbonyl(acetyl, benzoyl, cyano)nitroethenes with sodium azide provided a series of functionally substituted 1,2,3-triazoles. Their structure was characterized by IR, ^{1}H, and ^{13}C–{^{1}H} NMR spectroscopy.

Keywords: geminally activated nitroalkenes, 2-nitroacrylates, *gem*-acylnitroethenes, 2-nitroacrylonitriles, sodium azide, 1,2,3-triazoles

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Conjugated nitroethenes are highly reactive compounds and convenient synthons for different classes of organic substances [1]. The introduction of ester, nitrile or acyl groups into the *gem*-position to the nitro function broadens significantly the range of synthetic possibilities of these unsaturated nitro compounds as a result of increasing electrophilicity of the double bond and the possibility of participation of substituents in additional transformations [2].

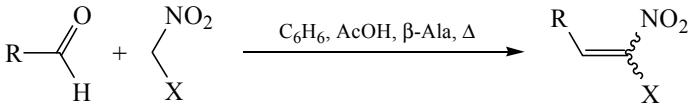
Reactions of [4π + 2π] cycloaddition are of particular interest where the geminally activated nitroethenes serve as dieno- or dipolarophiles and which may result in functionalized carbocyclic and heterocyclic structures. It is known that electron deficient nitroethenes like *gem*-bromonitrostyrenes [3, 4] and *gem*-dinitrostyrenes [5] react readily with inorganic 1,3-dipole sodium azide. The originally formed 1,2,3-triazolines underwent aromatization by dehydrobromination or denitration to form nitro-containing 1,2,3-triazoles. Similar reactions of *gem*-acylnitroethenes of furan, thiophene and indole series, as well as two spicemens of *gem*-acetylnitrostyrenes afforded 4-acyl-1,2,3-triazoles [6–10]. Some alkoxycarbonyl-substituted 1,2,3-triazoles were obtained reacting α-nitrocinnamic esters as well as their indole and furan analogs with sodium azide [10–12]. It should be noted that no information exists on the preparation of cyano-containing 1,2,3-triazoles by the reaction of *gem*-cyanonitroethenes with sodium azide; some of them could be synthesized only by using sodium trimethylsilyl azide instead of sodium azide [13, 14]. This reagent has been also successfully applied to the synthesis of 4-alkoxycarbonyl-5-aryl-1,2,3-triazoles [13, 15].

Increased interest in the 1,2,3-triazoles is due to a wide range of their practically useful properties. Many of them show antifungal, antimicrobial, and antiviral activity [3, 16–21]. For example, 5-(4-bromophenyl)-4-nitro-1,2,3-triazole and its *p*-nitrophenyl analog exhibit tuberculostatic and antifungal activity [3]. Structures of Tazobactam and Cefatrizine antibiotics contain a triazole ring [17]. 1,2,3-Triazole derivatives are used as herbicides, light stabilizers and optical brighteners. Therefore, the search for a simple and convenient preparative method of the synthesis of substituted 1,2,3-triazoles containing ester, nitrile, or acyl groups is very important.

Here we report on the synthesis of functionally substituted 1,2,3-triazoles by reacting *gem*-activated nitroethenes **1**–**14** containing ethoxycarbonyl, acetyl, benzoyl, or nitrile function with sodium azide.

Starting β-aryl-α-nitroacrylates **1**, **2** [22], **4** [23], *gem*-acetylnitrostyrenes **5** [24], **6**, **7** [25, 26], *gem*-

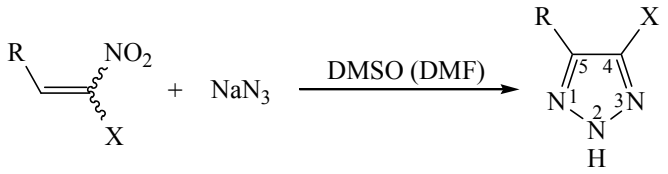
Scheme 1.



3, **11**, **12**

X = COOEt, R = 4-BrC_6H_4 (**3**); X = C(O)Ph, R = 4-ClC_6H_4 (**11**), 4-BrC_6H_4 (**12**).

Scheme 2.



1–**14** **15**–**28**

X = COOEt, R = 4-$Me_2NC_6H_4$ (**1**, **15**), 4-ClC_6H_4 (**2**, **16**), 4-BrC_6H_4 (**3**, **17**), 4-$O_2NC_6H_4$ (**4**, **18**); X = C(O)Me, R = 4-$Me_2NC_6H_4$ (**5**, **19**), 4-ClC_6H_4 (**6**, **20**), 4-$O_2NC_6H_4$ (**7**, **21**); X = C(O)Ph, R = Ph (**8**, **22**), 4-$MeOC_6H_4$ (**9**, **23**), 4-$Me_2NC_6H_4$ (**10**, **24**), 4-ClC_6H_4 (**11**, **25**), 4-BrC_6H_4 (**12**, **26**); X = CN, R = 4-$MeOC_6H_4$ (**13**, **27**), 1-Me-3-indolyl (**14**, **28**).

benzoylnitrostyrenes **10**, **8** [24, 27], and *gem*-cyanonitroethenes **13** [28], **14** [29] were prepared by the known procedures.

Substituted *gem*-nitroethenes **3**, **11**, **12** were synthesized by boiling mixtures of the corresponding aldehydes and nitro-containing CH acids (ethyl nitroacetate or nitroacetophenone) in benzene in the presence of acetic acid and β-alanine similar to the procedures reported in [22, 27, 30]. 1-Benzoyl-2-(4-bromophenyl)-1-nitroethene **12** was obtained for the first time (Scheme 1).

Compound **3** was synthesized previously from an appropriate aldehyde and ethyl nitroacetate in the presence of $TiCl_4$ (Δ, 48 h) [12] or from a Schiff base and nitroacetic acid [31], but the specific method of its preparation and the melting point were absent. According to Ciller et al. [32], nitroethene **11** was obtained from α-nitroacetophenone and a Schiff base by the method [33], but its melting point and spectral characteristics also were not given.

Previously, the structure of compounds **1**, **2**, **4**, **5**, **8**–**10**, **13** has been studied [6, 22, 34, 35]. Analysis of the structure of geminally substituted nitroethenes **3**, **6**, **7**, **11**, **12** and **14** by means of ^1H, ^{13}C–{^1H} NMR, UV, and IR spectroscopy showed that compounds **3**, **6** and **7** are possessed the *Z*-configuration, and compounds **11**, **12**, **14** had the *E*-configuration.

α-Nitroacrylates **1**–**4**, *gem*-acetyl(benzoyl)nitrostyrenes **5**–**12**, and α-nitroacrylonitriles **13**, **14** were brought into the reaction of 1,3-dipolar cycloaddition with sodium azide (2–4 mol) in DMSO or DMF; yields of the desired 1,2,3-triazoles **15**–**28** reached 86%. In most cases (with the initial nitroalkenes **2**–**4**, **6**–**9**, **11**–**14**), the reaction proceeded at room temperature. α-Nitroacrylate **1** and *gem*-acylnitroethenes **5**, **10** bearing *para*-dimethylamino-substituted benzene ring reacted at heating (Scheme 2).

Melting points of 1,2,3-triazoles **16**, **18**, **22**, **23**, **27** corresponded to those for samples obtained by the other methods [13, 16, 36–38]. Compounds **15**, **19**–**21**, **24**–**26**, **28** were synthesized for the first time.

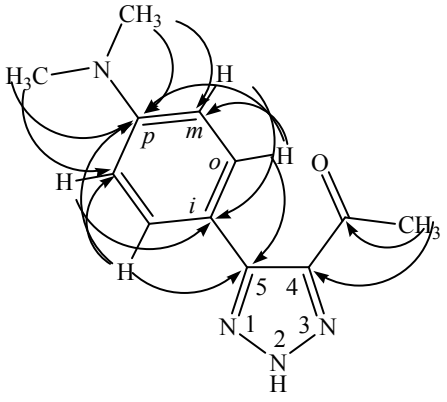
Triazoles **16** and **17** containing an ethoxycarbonyl group were obtained recently [12] from the corresponding α-nitrocinnamic ester and sodium azide in DMSO at heating (50°C) for 1.5 hours, but with somewhat lower yields (e. g., the yield of **17** equaled 62% [12] instead of 86%).

The structure of 1,2,3-triazoles **15**–**28** was confirmed by spectroscopy methods. For example, in the IR spectra there were absorption bands of stretching vibrations of NH (3152–3443 cm^{-1}) and carbonyl groups (1655–1728 cm^{-1}). In addition, the spectra of compounds **27** and **28** contained absorption due to the stretching vibrations of the nitrile function (2237–2238 cm^{-1}).

In the ^1H and ^{13}C–{^1H} NMR spectra of derivatives **15**–**28** there were the signals of all the structural fragments of the molecules. In particular, the ^1H NMR

spectra of alkoxycarbonyl-containing 1,2,3-triazoles **15**–**18** contained a quartet and a triplet signals of $COOCH_2CH_3$ fragment at 4.25–4.33 and 1.21–1.28 ppm, respectively. In the ^1H NMR spectra of acetyl-containing 1,2,3-triazoles **19**, **20**, and **21** the singlet signals of acetyl groups appeared at 2.59, 2.72, and 2.74 ppm, respectively. The signals in the region 14.25–14.46, 61.37–61.67, and 160.92–161.63 ppm in the $^{13}C–\{^1H\}$ NMR spectra of 1,2,3-triazoles **15**, **17**, and **18** corresponded to ethoxy groups.

The signals of acetyl group in the spectrum of compound **19** appeared at 29.03 and 193.10 ppm, whereas the nitrile group in compounds **27** and **28** resonated at 114.29 and 114.38 ppm, respectively. The validity of the signals assignement in the NMR spectra of 1,2,3-triazoles **15**–**28** was confirmed by two-dimensional $^1H–^{13}C$ HMQC and $^1H–^{13}C$ HMBC spectroscopy. For example, in compounds **19**, the signal in the weaker field (142.14 ppm) was unambiguously assigned to the carbon atom C^5 of the triazole ring owing to the presence of cross peaks with *ortho*-protons (7.73 ppm) of aromatic substituent in the $^1H–^{13}C$ HMBC spectrum. The signal of acetyl group at 2.59 ppm correlated with the signal of the carbon atom of C^4 of the triazole ring (140.83 ppm). Moreover, it should be noted that for all compounds **15**–**28** obtained the signal of the carbon atom C^5 of triazole ring appeared in a weaker field than that of the C^4 atom. Moreover, in most cases, the signals of the carbon atoms C^4 and C^5 of the triazole ring and the *ipso*-carbon atom of the aromatic substituent are broadened, indicating a possible prototropic transformations caused by NH- proton migration.



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In summary, a simple method for the synthesis of functionalized 1,2,3-triazoles by reacting geminally activated nitroalkenes with sodium azide was developed. The obtained alkoxycarbonyl, acetyl, benzoyl, and cyano functionalized triazoles are of interest as potential biologically active substances.

EXPERIMENTAL

Physicochemical studies were carried out using the equipment of the Center for Collective Use of the faculty of chemistry of the Herzen State Pedagogical University of Russia.

^1H, $^{13}C–\{^1H\}$, $^1H–^{13}C$ HMQC, and $^1H–^{13}C$ HMBC NMR spectra were recorded on a Jeol JNM-ECX400A spectrometer operating at 399.78 (^1H) and 100.53 MHz (^{13}C) and using chloroform-*d* or DMSO-d_6 as the solvent and internal standart. IR spectra were registered on a Shimadzu IR-Prestige-21 Fourier spectrometer from chloroform solutions (40 mg mL^{-1}) or KBr pellets. Electron absorption spectra of ethanol or acetonitrile solutions were recorded on a Shimadzu UV 2401PC spectrometer using quartz cells (l = 1.01 mm). Elemental analysis was performed on a EuroVector EA 3000 analyzer (CHN Dual).

gem-Activated nitroalkenes **1**, **2**, **4**–**10**, **13**, **14** were prepared according to the known methods [22–29].

***Z*-Ethyl 3-(4-bromophenyl)-2-nitropropenoate (3).** A mixture of 3.3 g (25 mmol) of ethyl nitroacetate, 5.55 g (30 mmol) of *p*-bromobenzaldehyde, a catalytic amount (0.19 g) of β-alanine, and 4 mL of glacial acetic acid in 40 mL of anhydrous benzene was refluxed for 5 h in a flask equipped with a Dean–Stark trap. After cooling, the reaction mixture was washed with brine and dried with calcined $MgSO_4$. Benzene was evaporated on a rotary evaporator, and the residue was placed into the refrigerator. After treatment with ethanol the resulting crystalline solid was filtered off and dried. Yield 2.92 g (39%), colorless crystals, mp 69–71°C (ethanol). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1730 (C=O), 1646 (C=C), 1540, 1370 (NO_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm (J, Hz): 1.34 t (3H, CH_3, ^3J = 7.2), 4.35 q (2H, OCH_2, ^3J = 7.2), 7.25 d and 7.53 d (4H, $H^{o,m}$, BrC_6H_4, ^3J = 8.5), 7.45 (1H, =CH). $^{13}C–\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 14.11 (CH_3), 63.35 (OCH_2), 127.08 (C^{ipso}, BrC_6H_4), 127.88 (C^p, BrC_6H_4), 131.08 (C^o, BrC_6H_4), 132.82 (C^m, BrC_6H_4), 131.67 (=CH), 140.60 (=CNO_2), 159.06 (C=O). UV spectrum (ethanol), λ_{max}, nm (ε, mol L^{-1} cm^{-1}): 292 (19550).[1] Found, %: C 44.32, 44.18; H 3.45, 3.33;

[1] The UV spectra of nitroethenes of **3**, **6**, **7**, **11**, **12, 14** contain absorption bands in a longwave region above 270 nm.

N 4.75, 4.73. $C_{11}H_{10}BrNO_4$. Calculated, %: C 44.02; H 3.36; N 4.67.

***Z*-4-(4-Chlorophenyl)-3-nitro-3-buten-2-one (6).** IR spectrum ($CHCl_3$), ν, cm^{-1}: 1695 (C=O), 1634 (C=C), 1540, 1364 (NO_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.45 s (3H, CH_3), 7.35 d and 7.40 d (4H, ClC_6H_4, ^3J = 8.9), 7.34 s (1H, =CH). $^{13}C–\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 25.30 (CH_3), 127.34 (C^{ipso}, ClC_6H_4), 129.98, 131.19 ($C^{o,m}$, ClC_6H_4), 138.92 (C^p, ClC_6H_4), 130.92 (=CH), 148.10 (=CNO_2), 187.72 (C=O). UV spectrum (CH_3CN), λ_{max}, nm (ε, mol L^{-1} cm^{-1}): 294 (19100).

***Z*-3-Nitro-4-(4-nitrophenyl)-3-butene-2-one (7).** IR spectrum ($CHCl_3$), ν, cm^{-1}: 1701 (C=O), 1630 (C=C), 1544, 1530, 1349 (NO_2, Ar-NO_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.49 s (3H, CH_3), 7.59 d and 8.28 d ($H^{o,m}$, 4H, $O_2NC_6H_4$, ^3J = 8.9), 7.47 s (1H, =CH). $^{13}C–\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 25.44 (CH_3), 124.58 (C^m, $O_2NC_6H_4$), 130.45 (C^o, $O_2NC_6H_4$), 135.06 (C^{ipso}, $O_2NC_6H_4$), 149.40 (C^p, $O_2NC_6H_4$), 129.28 (=CH), 149.67 (=CNO_2), 187.24 (C=O). UV spectrum (CH_3CN), λ_{max}, nm (ε, mol L^{-1} cm^{-1}): 291 (19000).

***E*-3-(4-chlorophenyl)-2-nitro-1-phenylpropene-1-one (11)** was prepared analogously to compound **5** from nitroacetophenone and *p*-chlorobenzaldehyde; reaction time 6 h (after benzene was removed the residue was treated with methanol). Yield 39%, pale yellow crystals, mp 58–60°C (petroleum ether). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1679 (C=O), 1641 (C=C), 1532, 1326 (NO_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.29 d and 7.34 d ($H^{m,o}$, 4H, ClC_6H_4, ^3J = 8.7), 7.48 t [2H, H^m, $C(O)C_6H_5$, *J* = 7.6], 7.64 t [1H, H^p, $C(O)C_6H_5$, *J* = 7.5], 7.93 d [2H, H^o, $C(O)C_6H_5$, *J* = 8.4], 8.27 s (1H, =CH). $^{13}C–\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 127.49 (C^{ipso}, ClC_6H_4), 129.83 (C^m, ClC_6H_4), 132.26 (C^o, ClC_6H_4), 138.77 (C^p, ClC_6H_4), 129.31 (C^o, COC_6H_5), 129.48 (C^m, COC_6H_5), 134.92 (C^{ipso}, COC_6H_5), 135.29 (C^p, COC_6H_5), 136.00 (=CH), 145.19 (=CNO_2), 188.10 (C=O). UV spectrum (ethanol), λ_{max}, nm (ε, mol L^{-1} cm^{-1}): 322 (20000). Found, %: C 62.78, 62.73; H 3.54, 3.61; N 5.03, 4.99. $C_{15}H_{10}ClNO_3$. Calculated, %: C 62.62; H 3.50; N 4.87.

***E*-3-(4-Bromophenyl)-2-nitro-1-phenylpropene-1-one (12)** was prepared analogously to compound **5** from nitroacetophenone and *p*-bromobenzaldehyde. Yield 53%, pale yellow crystals, mp 90–92°C (ethanol). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1678 (C=O), 1641 (C=C), 1529, 1325 (NO_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.26 d and 7.46 d (4H, $H^{o,m}$, BrC_6H_4, ^3J = 8.6), 7.49 t [2H, H^m, $C(O)C_6H_5$, *J* = 7.6], 7.64 t [1H, H^p, $C(O)C_6H_5$, *J* = 7.5], 7.93 d [2H, H^o, $C(O)C_6H_5$, *J* = 8.3], 8.25 s (1H, =CH). $^{13}C–\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 127.23 (C^{ipso}, BrC_6H_4), 127.78 (C^p, BrC_6H_4), 132.23 (C^o, BrC_6H_4), 132.68 (C^m, BrC_6H_4), 129.17 (C^o, COC_6H_5), 129.37 (C^m, COC_6H_5), 134.76 (C^{ipso}, COC_6H_5), 135.20 (C^p, COC_6H_5), 136.00 (=CH), 145.12 (=CNO_2), 187.96 (C=O). UV spectrum (ethanol), λ_{max}, nm (ε, mol L^{-1} cm^{-1}): 323 (30000). Found, %: C 54.38, 54.41; H 3.10, 3.14; N 4.28, 4.34. $C_{15}H_{10}BrNO_3$. Calculated, %: C 54.24; H 3.03; N 4.22.

***E*-3-(1-Methyl-3-indolyl)-2-nitropropenenitrile (14).** IR spectrum ($CHCl_3$), ν, cm^{-1}: 2225 (C≡N), 1580, 1590 (C=C, C=N^+), 1285, 1300 (NOO^-). ^1H NMR spectrum [$(CD_3)_2SO$], δ, ppm (*J*, Hz): 3.98 s (3H, NCH_3), 7.32–7.44 m (2H, $H^{5,6}$), 7.64 d (1H, H^7, $^3J_{7,6}$ = 8.9), 8.08 d (1H, H^4, $^3J_{4,5}$ 7.2), 8.59 s (1H, H^2), 8.99 s (1H, =CH). $^{13}C–\{^1H\}$ NMR spectrum [$(CD_3)_2SO$], δ_C, ppm: 34.90 (NCH_3), 114.43 (CN), 107.15 (C^3), 112.59 (C^7), 120.25 (C^4), 124.29 (C^5), 125.23 (C^6), 127.97 (C^{3a}), 138.62 (C^{7a}), 140.66 (C^2), 115.26 (=CNO_2), 141.59 (=CH). UV spectrum (ethanol), λ_{max}, nm (ε, mol L^{-1} cm^{-1}): 445 (46000).

Ethyl 5-(4-*N*,*N*-dimethylaminophenyl)-1,2,3-triazole-4-carboxylate (15). A mixture of 0.422 g (1.6 mmol) of ethyl 3-(4-*N*,*N*-dimethylaminophenyl)-2-nitropropenoate **1** and 0.416 g (6.4 mmol) of sodium azide in 7 mL of DMSO was stirred at 60°C for 3 h. The reaction mixture was poured into finely crushed ice. The separated oily product was extracted with diethyl ether. The extract was dried with calcinated magnesium sulfate, and then the solvent was evaporated. After treatment of the residue with ethanol the precipitate was filtered off and dried. Yield 0.205 g (49%), beige crystals, mp 109–110°C (petroleum ether : benzene = 1 : 1). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1722 (C=O), 3175 br, 3421 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.28 t (3H, CH_3, ^3J = 7.2), 2.97 s [6H, $N(CH_3)_2$], 4.33 q (2H, OCH_2, ^3J = 7.2), 6.68 d and 7.72 d (4H, $H^{m,o}$, NC_6H_4, ^3J = 9.0), 12.24 br.s (NH). $^{13}C–\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 14.25 (CH_3), 40.27 (NCH_3), 61.37 (OCH_2), 111.69 (C^m, NC_6H_4), 113.77 (C^{ipso}, NC_6H_4), 130.22 (C^o, NC_6H_4), 151.37 (C^p, NC_6H_4), 132.88 (C^4), 144.86 br (C^5), 161.63 (C=O). Found, %: C 60.12, 60.15; H 6.39, 6.27; N 21.73, 21.75. $C_{13}H_{16}N_4O_2$. Calculated, %: C 59.99; H 6.20; N 21.52.

Ethyl 5-(4-chlorophenyl)-1,2,3-triazole-4-carboxylate (16). A mixture of 0.256 g (1 mmol) of ethyl

3-(4-chlorophenyl)-2-nitropropenoate **2** and 0.130 g (2 mmol) of sodium azide in 7 mL of DMSO was stirred at room temperature for 3 h, then poured into finely crushed ice. The precipitate was filtered off, washed with distilled water, and dried. Yield 0.181 g (72%), colorless crystals, mp 171–172°C (ethanol) {mp 172–172.5°C (water) [36]. IR spectrum (KBr), ν, cm^{-1}: 1709 (C=O), 3219 br (NH). ^1H NMR spectrum [$(CD_3)_2SO$], δ, ppm (*J*, Hz): 1.22 t (3H, CH_3, ^3J = 7.1), 4.25 q (2H, OCH_2, ^3J = 7.1), 7.52 d and 7.78 d (4H, ClC_6H_4, ^3J = 9.0). Found, %: C 52.37, 52.43; H 4.11, 4.14; N 16.61, 16.56. $C_{11}H_{10}ClN_3O_2$. Calculated, %: C 52.50; H 4.01; N 16.70.

Ethyl 5-(4-bromophenyl)-1,2,3-triazole-4-carboxylate (17) was prepared analogously to compound **16** from ethyl 3-(4-bromophenyl)-2-nitropropenoate **3** and sodium azide. Yield 86%, colorless crystals, mp 173–175°C (ethanol : water = 2 : 1) (mp 173–174°C [12]). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1728 (C=O), 3200 br, 3418 (NH). ^1H NMR spectrum [$(CD_3)_2SO$], δ, ppm (*J*, Hz): 1.21 t (3H, CH_3, ^3J = 7.1), 4.25 q (2H, OCH_2, ^3J = 7.1), 7.65 d and 7.70 br. d (4H, BrC_6H_4, ^3J = 8.4 Hz), 15.86 br.s (NH). $^{13}C–\{^1H\}$ NMR spectrum [$(CD_3)_2SO$], δ_C, ppm: 14.46 (CH_3), 61.40 (OCH_2), 123.29, 128.32 br, 131.62, 131.71 (BrC_6H_4), 135.03 br (C^4), 145.75 br (C^5), 161.29 (C=O).

Ethyl 5-(4-nitrophenyl)-1,2,3-triazole-4-carboxylate (18) was prepared analogously to compound **16** from ethyl 2-nitro-3-(4-nitrophenyl)propenoate **4** and sodium azide in DMF; reaction time 2 h. Yield 69%, pale yellow crystals, mp 169–170°C (ethanol) {mp 170–171°C (water) [36, 37]}. IR spectrum (KBr), ν, cm^{-1}: 1718 (C=O), 1523, 1347 (NO_2), 3219 br (NH). ^1H NMR spectrum [$(CD_3)_2SO$], δ, ppm (*J*, Hz): 1.23 t (3H, CH_3, ^3J = 7.1), 4.27 q (2H, OCH_2, ^3J = 7.1), 8.05 d and 8.28 d (4H, $H^{o,m}$, $O_2NC_6H_4$, ^3J = 8.7), 15.96 br.s (NH). $^{13}C–\{^1H\}$ NMR spectrum [$(CD_3)_2SO$], δ_C, ppm: 14.41 (CH_3), 61.67 (OCH_2), 123.82 (C^m, $O_2NC_6H_4$), 136.04 (C^{ipso}, $O_2NC_6H_4$), 130.80 (C^o, $O_2NC_6H_4$), 148.10 (C^p, $O_2NC_6H_4$), 134.34 (C^4), 144.93 br (C^5), 160.92 (C=O). Found, %: C 50.46, 50.42; H 3.76, 3.69; N 21.26, 21.32. $C_{11}H_{10}N_4O_4$. Calculated, %: C 50.38; H 3.84; N 21.37.

4-Acetyl-5-(4-*N*,*N*-dimethylaminophenyl)-1,2,3-triazole (19) was prepared analogously to compound **15** from 4-(4-*N*,*N*-dimethylaminophenyl)-3-nitro-3-buten-2-one **5** and sodium azide in DMF. Yield 42%, beige crystals, mp 176–178°C (ethanol : water = 2 : 1). IR spectrum (KBr), ν, cm^{-1}: 1657 (C=O), 3152 br (NH). ^1H NMR spectrum [$(CD_3)_2SO$], δ, ppm (*J*, Hz): 2.59 s [3H, $C(O)CH_3$], 2.94 s [6H, $N(CH_3)_2$], 6.74 d and 7.73 d (4H, $H^{m,o}$, $NC_6\underline{H}_4$, ^3J = 8.5), 15.56 br.s (NH). $^{13}C–\{^1H\}$ NMR spectrum [$(CD_3)_2SO$], δ_C, ppm: 29.03 (CH_3), 40.27 (NCH_3), 111.81 (C^m, NC_6H_4), 114.12 br (C^{ipso}, NC_6H_4), 130.35 (C^o, NC_6H_4), 151.57 (C^p, NC_6H_4), 140.83 (C^4), 142.14 br (C^5), 193.10 (C=O). Found, %: C 62.73, 62.78; H 6.22, 6.29; N 24.50, 24.45. $C_{12}H_{14}N_4O$. Calculated, %: C 62.59; H 6.13; N 24.33.

4-Acetyl-5-(4-chlorophenyl)-1,2,3-triazole (20) was prepared analogously to compounds **16** from 4-(4-chlorophenyl)-3-nitro-3-buten-2-one **6** and sodium azide in DMF; reaction time 2.5 h. Yield 73%, pale yellow crystals, mp 154–156°C (CCl_4). IR spectrum (KBr), ν, cm^{-1}: 1696 (C=O), 3436 br (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.72 s (3H, CH_3), 7.42 d and 7.84 br. d (4H, ClC_6H_4, ^3J = 8.5), 12.22 br.s (NH). Found N, %: 18.88, 18.90. $C_{10}H_8ClN_3O$. Calculated N, %: 18.96.

4-Acetyl-5-(4-nitrophenyl)-1,2,3-triazole (21) was prepared analogously to compounds **16** from 3-nitro-4-(4-nitrophenyl)-3-buten-2-one **7** and sodium azide in DMF; reaction time 2.5 h. Yield 38%, pale yellow crystals, mp 146–148°C (benzene). IR spectrum (KBr), ν, cm^{-1}: 1685 (C=O), 1521, 1345 (NO_2), 3236 br (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.74 s (3H, CH_3), 8.15 d and 8.29 d (4H, OC_6H_4, ^3J = 8.9), 12.48 br.s (NH). Found N, %: 24.04, 24.25. $C_{10}H_8N_4O_3$. Calculated N, %: 24.14.

4-Benzoyl-5-phenyl-1,2,3-triazole (22) was prepared analogously to compounds **16** from 1,3-diphenyl-2-nitropropen-1-one **8** and sodium azide in DMF; reaction time 4 h. Yield 75%, colorless crystals, mp 121–122°C (benzene) (mp 120.5–122°C [16]). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1662 (C=O), 3198 br, 3421 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.34–7.44 m (3H, $H^{m,p}$), 7.60–7.70 m (2H, H^o), 7.39 t [2H, H^m, $C(O)C_6H_5$, *J* = 7.5], 7.53 t [1H, H^p, $C(O)C_6H_5$, *J* = 7.3], 8.01 d [2H, H^o, $C(O)C_6H_5$, *J* = 7.5], 13.53 br.s (NH). $^{13}C–\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 127.52 (C^{ipso}, C_6H_5), 128.68 (C^m, C_6H_5), 128.90 (C^o, C_6H_5), 129.83 (C^p, C_6H_5), 128.47 (C^m, COC_6H_5), 130.61 (C^o, COC_6H_5), 133.66 (C^p, COC_6H_5), 137.02 (C^{ipso}, COC_6H_5), 140.97 (C^4), 145.84 br (C^5), 188.44 (C=O). Found N, %: 16.80, 16.81. $C_{15}H_{11}N_3O$. Calculated N, %: 16.87.

4-Benzoyl-5-(4-methoxyphenyl)-1,2,3-triazole (23) was prepared analogously to compound **16** from 3-(4-

methoxyphenyl)-2-nitro-1-phenylpropen-1-one **9** and sodium azide in DMF; reaction time 2.5 h. Yield 58%, colorless crystals, mp 119–120°C (benzene) (mp 126–128°C [38]). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1658 (C=O), 3158 br, 3421 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.77 s (3H, OCH_3), 6.84 d and 7.65 d (4H, $H^{m,o}$, OC_6H_4, ^3J = 8.2), 7.41 t [2H, H^m, $C(O)C_6H_5$, *J* = 7.3], 7.54 t [1H, H^p, $C(O)C_6H_5$, *J* = 7.0], 8.05 d [2H, H^o, $C(O)C_6H_5$, *J* = 7.0], 13.75 br.s (NH). $^{13}C–\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 55.41 (OCH_3), 114.14 (C^m, OC_6H_4), 119.60 br (C^{ipso}, OC_6H_4), 130.38 (C^o, OC_6H_4), 160.86 (C^p, OC_6H_4), 128.42 (C^m, COC_6H_5), 130.61 (C^o, COC_6H_5), 133.47 (C^p, COC_6H_5), 137.27 (C^{ipso}, COC_6H_5), 140.71 br (C^4), 145.35 br (C^5), 188.31 (C=O). Found N, %: 14.98, 15.00. $C_{16}H_{13}N_3O_2$. Calculated N, %: 15.05.

4-Benzoyl-5-(4-*N*,*N*-dimethylaminophenyl)-1,2,3-triazole (24) was prepared analogously to compound **15** from 3-(4-*N*,*N*-dimethylaminophenyl)-2-nitro-1-phenylpropen-1-one **10** and sodium azide. Yield 60%, beige crystals, mp 126–127°C (ethanol). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1655 (C=O), 3174 br, 3423 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.92 s [6H, $N(CH_3)_2$], 6.60 d and 7.65 d (4H, $H^{m,o}$, NC_6H_4, ^3J = 8.8), 7.41 t [2H, H^m, $C(O)C_6H_5$, *J* = 7.6], 7.52 t [1H, H^p, $C(O)C_6H_5$, *J* = 7.4], 8.09 d [2H, H^o, $C(O)C_6H_5$, *J* = 7.4], 13.94 br.s (NH). $^{13}C–\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 40.28 (NCH_3), 111.91 (C^m, NC_6H_4), 113.75 br (C^{ipso}, NC_6H_4), 129.95 (C^o, NC_6H_4), 151.37 (C^p, NC_6H_4), 128.30 (C^m, COC_6H_5), 130.68 (C^o, COC_6H_5), 133.06 (C^p, COC_6H_5), 137.83 (C^{ipso}, COC_6H_5), 140.20 (C^4), 144.71 br (C^5), 188.43 (C=O). Found N, %: 19.29, 19.34. $C_{17}H_{16}N_4O$. Calculated N, %: 19.17.

4-Benzoyl-5-(4-chlorophenyl)-1,2,3-triazole (25) was prepared analogously to compound **16** from 3-(4-chlorophenyl)-2-nitro-1-phenylpropen-1-one **11** and sodium azide. Yield 46%, colorless crystals, mp 154–156°C (ethanol : water = 2 : 1). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1662 (C=O), 3207 br, 3420 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.34 d and 7.70 d (4H, $H^{m,o}$, ClC_6H_4, ^3J = 8.5), 7.46 t [2H, H^m, $C(O)C_6H_5$, *J* = 7.7], 7.59 t [1H, H^p, $C(O)C_6H_5$, *J* = 7.4], 8.04 d [2H, H^o, $C(O)C_6H_5$, *J* = 8.2], 9.03 br.s (NH). $^{13}C–\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 126.90 (C^{ipso}, ClC_6H_4), 128.90 (C^m, ClC_6H_4), 130.24 (C^o, ClC_6H_4), 135.83 (C^p, ClC_6H_4), 128.55 (C^m, COC_6H_5), 130.56 (C^o, COC_6H_5), 133.82 (C^p, COC_6H_5), 136.92 (C^{ipso}, COC_6H_5), 141.36 (C^4), 146.51 (C^5), 188.01 (C=O). Found, %: C 63.68, 63.73; H 3.71, 3.68; N 14.95, 15.02. $C_{15}H_{10}ClN_3O$. Calculated, %: C 63.50; H 3.55; N 14.81.

4-Benzoyl-5-(4-bromophenyl)-1,2,3-triazole (26) was prepared analogously to compound **16** from 3-(4-bromophenyl)-2-nitro-1-phenylpropene-1-one **12** and sodium azide. Yield 41%, colorless crystals, mp 164–166°C (ethanol : water = 2 : 1). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1663 (C=O), 3200 br, 3420 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.51 d and 7.65 d (4H, $H^{m,o}$, BrC_6H_4, ^3J = 8.4), 7.47 t [2H, H^m, $C(O)C_6H_5$, *J* = 7.7], 7.60 t [1H, H^p, $C(O)C_6H_5$, *J* = 7.4], 8.05 d [2H, H^o, $C(O)C_6H_5$, *J* = 7.6], 12.31 br.s (NH). $^{13}C–\{^1H\}$ NMR spectrum ($CDCl_3$), δ_C, ppm: 124.08 (C^{ipso}, BrC_6H_4), 127.26 (C^p, BrC_6H_4), 130.36 (C^o, BrC_6H_4), 131.77 (C^m, BrC_6H_4), 128.47 (C^m, COC_6H_5), 130.46 (C^o, COC_6H_5), 133.76 (C^p, COC_6H_5), 136.78 (C^{ipso}, COC_6H_5), 141.29 br (C^4), 146.58 br (C^5), 187.91 (C=O). Found N, %: 12.86, 12.93. $C_{15}H_{10}BrN_3O$. Calculated N, %: 12.80.

5-(4-Methoxyphenyl)-1,2,3-triazole-4-carbonitrile (27) was prepared analogously to compound **16** from 2-nitro-3-phenylpropenenitrile **13** and sodium azide in DMF. Yield 31%, colorless crystals, mp 198–200°C {mp 197–198°C (ethyl acetate) [13]}. IR spectrum (KBr), ν, cm^{-1}: 2238 (C≡N), 3187 (NH). ^1H NMR spectrum [$(CD_3)_2SO$], δ, ppm (*J*, Hz): 3.79 s (3H, OCH_3), 7.11 d and 7.77 d (4H, $H^{m,o}$, OC_6H_4, ^3J = 8.5), 9.05 br.s (NH). $^{13}C–\{^1H\}$ NMR spectrum [$(CD_3)_2SO$], δ_C, ppm: 55.94 (OCH_3), 114.29 (CN), 115.44 (C^m, OC_6H_4), 118.26 (C^{ipso}, OC_6H_4), 128.75 (C^o, OC_6H_4), 161.43 (C^p, OC_6H_4), 115.64 (C^4), 146.14 (C^5). Found, %: C 59.88, 60.13; H 4.15, 4.09; N 27.86, 27.83. $C_{10}H_8N_4O$. Calculated, %: C 59.99; H 4.03; N 27.99.

5-(1-Methyl-3-indolyl)-1,2,3-triazole-4-carbonitrile (28) was prepared analogously to compound **16** from 3-(1-methyl-3-indolyl)-2-nitro-propenenitrile **14** and sodium azide; reaction time 1 day. Yield 30%, beige crystals, mp 138–140°C. IR spectrum (KBr), ν, cm^{-1}: 2237 (C≡N), 3192, 3443 (NH). ^1H NMR spectrum [$(CD_3)_2SO$], δ, ppm (*J*, Hz): 3.87 s (3H, NCH_3), 7.20 m (1H, 3-indolyl), 7.28 m (1H, 3-indolyl), 7.53 d (1H, 3-indolyl, *J* = 8.0), 7.95 s (1H, H^2, 3-indolyl), 7.99 d (1H, 3-indolyl, *J* = 7.9), 16.12 br.s (NH). $^{13}C–\{^1H\}$ NMR spectrum [$(CD_3)_2SO$], δ_C, ppm: 33.49 (NCH_3), 114.38 (CN), 100.51, 111.17, 120.62, 121.35, 123.22, 125.10, 130.34, 137.34 (3-indolyl), 115.41 (C^4), 143.37 br (C^5). Found, %: C 64.75, 64.79; H 4.15, 4.19; N 31.55, 31.58. $C_{12}H_9N_5$. Calculated, %: C 64.56; H 4.06; N 31.37.

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