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# Synthesis of functionalized triazolo[1,5-*a*]pyrimidine derivatives

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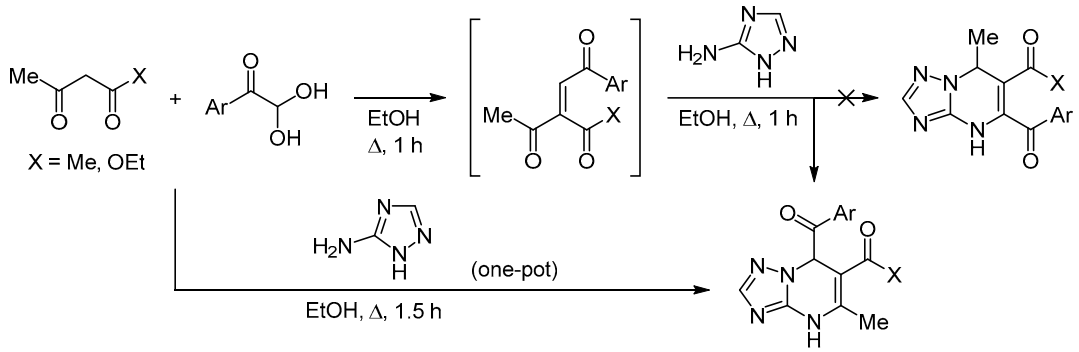


New triazolo[1,5-*a*]pyrimidines containing aroyl and acetyl or ester groups in the pyrimidine ring were synthesized in a process related to the Biginelli-like reaction, using hydrates of arylglyoxals, β-dicarbonyl compounds, and 1*H*-1,2,4-triazol-5-amine. Reaction was carried out in either sequential or one-pot procedure.

**Keywords**: acetoacetic ester, acetylacetone, arylglyoxal hydrates, 4,7-dihydro[1,2,4]triazolo[1,5-*a*]pyrimidines, 1*H*-1,2,4-triazol-5-amine, Biginelli-like reaction, three-component condensation.

One of the most innovative approaches to organic synthesis can considered multicomponent reactions that allow to significantly simplify experimental procedures, provide access to new, highly complex molecules in a single step, improve the yields of target products, that play a major role in organic and medicinal chemistry.[1–4] A classic example of multicomponent reactions employed for the preparation of dihydropyrimidine motif is the Biginelli-like reaction.[5] The formation of this heterocyclic system proceeds as a result of one-pot cyclization involving aldehydes, compounds with active methylene groups (β-dicarbonyl compounds, ketones etc.), and amidines (various derivatives of carbonic acid, as well as amino-substituted nitrogen heterocycles).[6–8] In the majority of the cases the reaction proceeds under the conditions of acidic catalysis[9-11] and could be considered to be one of the most convenient methods for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones[11] – compounds with promising physiological activity. Compounds belonging to this class have shown antihypertensive,[12] antitumor,[13] antiepileptic,[14] antioxidant,[15] anti-inflammatory,[16] as well as antibacterial activity.[17]

However, analogous condensation reactions involving arylglyoxals are practically unknown in the literature. A rare example is the work by Iranian authors[18] who describe two dihydropyrimidin-2-one derivatives that were obtained by using acetylacetone or acetoacetic ester, phenylglyoxal hydrate, and urea in the presence of Lewis acids. As later shown by the authors of another publication,[19] the studied reaction can provide either dihydropyrimidin-2-ones (**1**) or derivatives of imidazolin-2-one (**2**), depending on the electronic properties of substituent in the arylglyoxal molecule (Fig. 1). Thus, electron-donating substituents promote the formation of a six-membered ring, while five-membered ring is favored in the case of electron-withdrawing substituents. The authors also established the sequence of mechanistic steps in the studied reaction, which included the formation of a Knoevenagel condensation product with the participation of acetylacetone and arylglyoxal, the isolation of adduct formed by nucleophilic addition of urea at the activated double bond, and its further cyclization leading to compound **1** or **2**.[19]

In the current work, we studied the condensation of β-dicarbonyl compounds **3a**,**b** (acetylacetone and acetoacetic

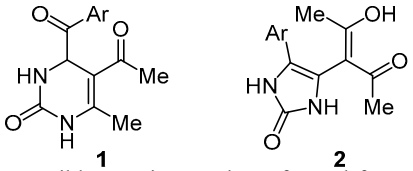

**Figure 1**. Possible reaction products formed from acetylacetone, arylglyoxal, and urea.

ester), arylglyoxals **4a**–**e**, and a typical 1,3-binucleophile, 1*H*-1,2,4-triazol-5-amine (**6**) (Scheme 1). It should be noted that the three-component condensation of aromatic aldehydes, β-dicarbonyl compounds, and aminotriazole, which led to triazolopyrimidines, has been described in the literature.[20,21] However, the replacement of aldehyde with glyoxal did not always produce the expected dihydropyrimidines,[19] providing us a reason to study the aforementioned cyclization in more detail. The reaction was performed both by sequential addition of reagents and by a one-pot procedure. In the first case, β-dicarbonyl compounds **3a**,**b** were refluxed with arylglyoxal hydrates **4a**–**c** in ethanol for 1 h, followed by treatment of the reaction mixture with aminotriazole **6**. After refluxing for an additional 1 h, the target compounds **7a**–**c**,**f**,**g** precipitated from the solution (Scheme 1, method I; Table 1).

On the other hand, the three-component condensation of compounds **3a**,**b**, arylglyoxals **4d**,**e**, and triazole **6** provided derivatives **7d**,**e**,**h** (Scheme 1, method II; Table 1).

The structures of the obtained compounds **7a**–**h** were confirmed by $^{1}$H and $^{13}$C NMR spectra, as well as by elemental analysis data. $^{1}$H NMR spectra of compounds **7a**–**e** contained singlets of methyl and acetyl group protons, a singlet of the methine proton at position 7 of the bicyclic system (6.64–6.88 ppm), singlets of the 2-CH proton in triazole ring (7.63–7.69 ppm), and the NH proton (10.76–10.92 ppm), as well as the aromatic proton multiplets. $^{1}$H NMR spectra of compounds **7f**–**h** that were synthesized by using acetoacetic ester featured a triplet and quartet of the ethoxy group protons. $^{13}$C NMR spectra contained all the carbon atom signals expected for the structures of triazolopyrimidines **7a**–**h**.

The presented experimental data theoretically were in agreement with both of the positional isomers, 7-aroyl-5-methyl- or 5-aroyl-7-methyl[1,2,4]triazolo[1,5-*a*]pyrimidines, and of the regioisomeric [1,2,4]triazolo[4,3-*a*]pyrimidines, as previously demonstrated in a review article[20] for amine **6** and arylaldehydes[21] (or cyclic ketones)[22] in a series of similar tandem reactions. It has been postulated that the formation of 5-aryl derivatives of triazolo[1,5-*a*]-pyrimidine proceeds *via* an azomethine intermediate (or *via* products of nucleophilic addition of triazole **6** at the ketone carbonyl group), while 7-aryl isomers were synthesized in the case when an enone system was formed. No other reaction products were detected by us under the experimental conditions, but the overall mechanism was supported by the experimental data.

As shown in the presented Scheme 1, the formation of products **7a**–**c**,**f**,**g** proceeded through intermediates **5a**–**c**,**f**,**g**.[19] The subsequent addition of 2-NH imino group belonging to aminotriazole **6** at the activated double bond led to the

**Scheme 1**

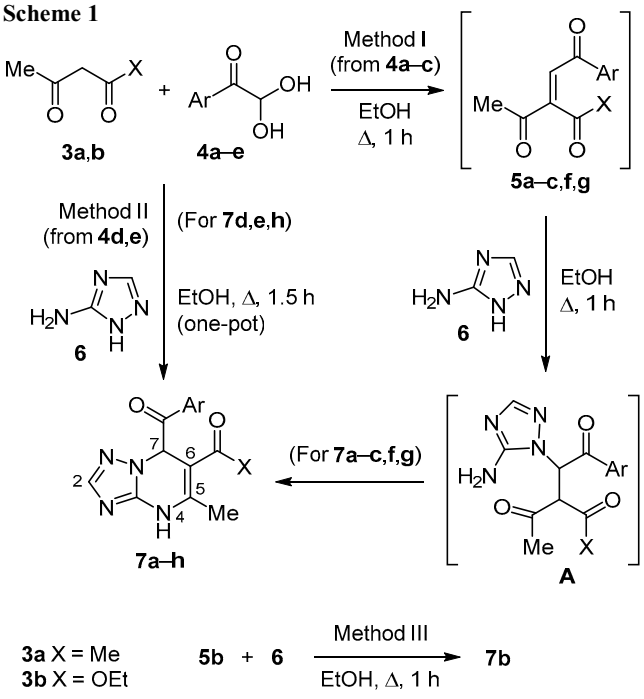


**Table 1**. Yields of triazolo[1,5-*a*]pyrimidine derivatives

| Arylglyoxal | Ar | X | Product | Yield, % |
|---|---|---|---|---|
| **4a** | 4-Et$C_6H_4$ | Me | **7a** | 71 |
| **4b** | 4-Br$C_6H_4$ | Me | **7b** | 72 (75)** |
| **4c** | 3,4-$Me_2C_6H_3$ | Me | **7c** | 83 |
| **4d** | 3,4-$Cl_2C_6H_3$ | Me | **7d*** | 83 |
| **4e** | 4-Me$C_6H_4$ | Me | **7e*** | 71 |
| **4b** | 4-Br$C_6H_4$ | OEt | **7f** | 74 |
| **4c** | 3,4-$Me_2C_6H_3$ | OEt | **7g** | 74 |
| **4d** | 3,4-$Cl_2C_6H_3$ | OEt | **7h*** | 79 |

* The compounds were obtained according to method I.
** Yield of the product according to method III.

intermediate **A**, while further cyclocondensation completed the formation of annulated pyrimidine ring. This sequence of steps was confirmed by us in the case of phenacylidene derivative **5b**, which was synthesized from acetylacetone and arylglyoxal **4b**.[19] The latter compound was used in a reaction with aminotriazole **6**, allowing to isolate dihydrotriazolopyrimidine **7b** in a high yield. This result was in a good agreement with the previously published data[23,24] regarding the interaction of enone systems with 5-aminotriazole, thus confirming the participation of the triazole ring N-2 atom in the Michael reaction.

A conclusive proof of the obtained product structures was based on X-ray structural analysis of compound **7b** (Fig. 2).

The N(1) nitrogen atom had a practically planar configuration (the sum of valence angles at the N(1) atom was equal to 358(1)°). The dihydropyrimidine ring was in a

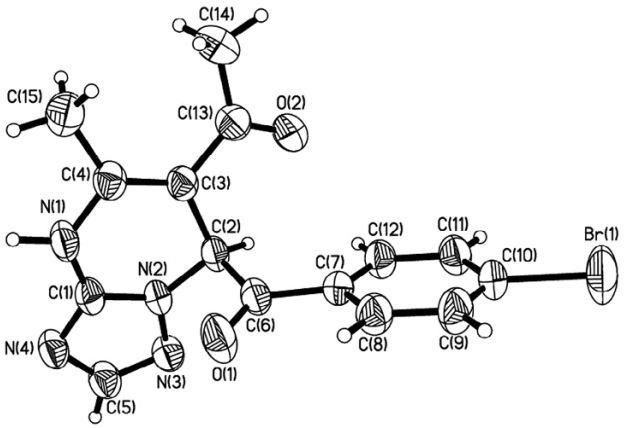


**Figure 2**. The molecular structure of compound **7b** with atoms represented by thermal vibration ellipsoids of 50% probability.

sofa conformation (the deviation of C(2) atom from the plane of other atoms was 0.347 Å, as determined with accuracy to 0.033 Å). This fact was associated with the presence of a shortened intramolecular H(1)···H(15)C contact of 2.10 Å (the sum of van der Waals radii was 2.32 Å).[25] The strong delocalization of electron density in N(2)–C(1)=N(4) fragment resulted in equalization of C(1)–N(2) and C(1)=N(4) bonds (the lengths were 1.323(1) and 1.320(1) Å, respectively), while the conjugation of this moiety with the N(1) atom was noticeably weaker (the C(1)–N(1) bond length was 1.358(1) Å).

The torsion angle C(4)–C(3)–C(13)–O(2) was equal to –170.9(1)°, facilitating the conjugation in the α,β-unsaturated C(4)=C(3)–C(13)=O(2) atom chain. As a consequence of such configuration, there were shortened intramolecular contacts H(2)···O(2) of 2.32 Å length (the average value 2.45 Å) and H(14)C···H(15)B of 2.07 Å length (the average value 2.32 Å).

The C(6)=O(1) carbonyl group at the saturated C(2) atom was practically perpendicular to the dihydropyrimidine ring plane (the torsion angle C(3)–C(2)–C(6)–O(1) was equal to 83.3(1)°), thus minimizing the intramolecular repulsion between the O(1) atom and the five-membered ring nitrogen atoms on one side and the O(2) atom on the other side. Such configuration resulted in the appearance of a shortened intramolecular contact H(2)···H(12) 2.11 Å (the average value 2.32 Å). At the same time, the C(6)=O(1) carbonyl group was practically coplanar with the benzene ring plane of the aryl substituent (torsion angle C(8)–C(7)–C(6)–O(1) equal to –14.9(1)°). The C(2)–C(6) bond with the length of 1.551(2) Å was longer than the average value (1.511 Å).[26]

The molecules formed dimers in the crystal structure, linked by paired N(1)–H(1)···N(4') hydrogen bonds (*–x*, 1 – *y*, *–z*; H···N' 1.97 Å, N–H···N' 167°).

We did not detect the formation of imidazolin-2-one derivatives analogous to compound **2** (Fig. 1) in the studied reaction, which can be explained by the higher nucleophilicity of the amino group in triazole **6** relative to urea, with the condensation accordingly proceeding at the more reactive acetyl group.

Thus, in the current work we have developed a simple and convenient method for the synthesis of functionalized 4,7-dihydro[1,2,4]triazolo[1,5-*a*]pyrimidine derivatives. The polyfunctional nature of the obtained compounds provides opportunities for their use as convenient building blocks in the synthesis of new, potentially biologically active compounds.

## Experimental

IR spectra were recorded on an Agilent Cary 630 FTIR spectrometer in KBr pellets by the diffuse reflection method. $^1$H and $^{13}$C NMR spectra were acquired on a Varian MR-400 spectrometer (400 and 100 MHz, respectively) in DMSO-$d_6$, using TMS as internal standard. Elemental analysis was performed on a EuroVector EuroEA3000 elemental analyzer. Melting points were determined on a Kofler bench. The reaction progress and purity of the obtained compounds were controlled by TLC on Silufol UV-254 plates, using 1:1 PhMe–EtOAc or 10:1 $CHCl_3$–2-PrOH mixtures as the mobile phases, with visualization in iodine vapor.

Compound **5b** was synthesized according to a procedure previously described by us.[19]

**Synthesis of compounds 7a–c,f,g** (Method I). A mixture of acetylacetone (**3a**) (0.10 ml, 1.0 mmol) or acetoacetic ester (**3b**) (0.15 ml, 1.1 mmol), arylglyoxal hydrate **4a**–**c** (1.0 mmol), and EtOH (5 ml) was refluxed for 1 h, followed by the addition of aminotriazole **6** (0.08 g, 1.0 mmol) and heating of the mixture for an additional 1 h. The reaction mixture was cooled, the precipitate was filtered off, washed with EtOH, and recrystallized from EtOH.

**Synthesis of compounds 7d,e,h** (Method II). A mixture of acetylacetone (**3a**) (0.10 ml, 1.0 mmol) or acetoacetic ester (**3b**) (0.15 ml, 1.1 mmol), arylglyoxal hydrate **4d**,**e** (1.0 mmol), aminotriazole **6** (0.08 g, 1.0 mmol), and EtOH (5 ml) was refluxed for 1.5 h. The reaction mixture was left overnight at room temperature, the precipitate that formed was filtered off, washed with EtOH, and recrystallized from EtOH.

**Synthesis of compound 7b** (Method III). A mixture of 3-acetyl-1-(4-bromophenyl)pent-2-ene-1,4-dione (**5b**) (295 mg, 1.0 mmol) and aminotriazole **6** (84 mg, 1.0 mmol) in EtOH (5 ml) was refluxed for 1 h. The reaction mixture was left overnight at room temperature, the obtained precipitate was filtered off, washed with EtOH, and recrystallized from EtOH. Yield 75%.

**1-[7-(4-Ethylbenzoyl)-5-methyl-4,7-dihydro[1,2,4]triazolo[1,5-*a*]pyrimidin-6-yl]ethanone (7a)**. Yield 0.22 g (71%), light-yellow crystals, mp 170–171°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 1.20 (3H, t, *J* = 7.6, $CH_2C\underline{H}_3$); 2.27 (3H, s, $CH_3$); 2.45 (3H, s, $CH_3$); 2.67 (2H, q, *J* = 7.6, $C\underline{H}_2CH_3$); 6.69 (1H, s, 7-CH); 7.36 (2H, d, *J* = 8.0, H Ar); 7.65 (1H, s, 2-CH); 8.04 (2H, d, *J* = 8.0, H Ar); 10.82 (1H, s, NH). $^{13}$C NMR spectrum, δ, ppm: 17.8 ($CH_3$); 22.2 ($CH_3$); 30.9 ($CH_3$); 33.3 ($CH_2$); 60.1 (C-7); 110.9 (C-6); 130.5 (2C Ar); 131.7 (2C Ar); 136.4; 149.9; 150.4; 152.4 (C-2); 152.8; 196.7 (CO); 198.6 (CO). Found, %: C 65.83; H 5.82; N 18.08. $C_{17}H_{18}N_4O_2$. Calculated, %: C 65.79; H 5.85; N 18.05.

**1-[7-(4-Bromobenzoyl)-5-methyl-4,7-dihydro[1,2,4]triazolo[1,5-*a*]pyrimidin-6-yl]ethanone (7b)**. Yield 0.26 g (72%, method I), white crystals, mp 202–204°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 2.29 (3H, s, $CH_3$); 2.46 (3H, s, $CH_3$); 6.64 (1H, s, 7-CH); 7.66 (1H, s, 2-CH); 7.75 (2H, d, *J* = 8.8, H Ar); 8.03 (2H, d, *J* = 8.4, H Ar); 10.86 (1H, s, NH). $^{13}$C NMR spectrum, δ, ppm: 22.2 ($CH_3$); 33.2 ($CH_3$); 60.2 (C-7); 111.1 (C-6); 130.0; 133.3 (2C Ar); 134.3 (2C Ar); 138.0; 149.8; 150.6 (C-2); 153.0; 196.8 (CO); 198.6 (CO). Found, %: C 49.85; H 3.66; N 15.54. $C_{15}H_{13}BrN_4O_2$. Calculated, %: C 49.88; H 3.63; N 15.51.

**1-[7-(3,4-Dimethylbenzoyl)-5-methyl-4,7-dihydro-[1,2,4]triazolo[1,5-*a*]pyrimidin-6-yl]ethanone (7c)**. Yield 0.26 g (83%), white crystals, mp 170–172°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 2.26 (3H, s, $CH_3$); 2.28 (3H, s, $CH_3$); 2.29 (3H, s, $CH_3$); 2.44 (3H, s, $CH_3$); 6.68 (1H, s, 7-CH); 7.28 (1H, d, *J* = 8.4, H Ar); 7.64 (1H, s, 2-CH); 7.82–7.86 (2H, m, H Ar); 10.78 (1H, s, NH). $^{13}$C NMR spectrum, δ, ppm: 22.0 ($CH_3$); 22.2 ($2CH_3$); 33.4 ($CH_3$); 59.9 (C-7); 110.9 (C-6); 129.3; 132.2; 132.4; 136.5; 139.1; 145.3; 149.8; 150.4 (C-2); 152.8; 196.6 (CO); 198.8 (CO). Found, %: C 65.75; H 5.81; N 18.08. $C_{17}H_{18}N_4O_2$. Calculated, %: C 65.79; H 5.85; N 18.05.

**1-[7-(3,4-Dichlorobenzoyl)-5-methyl-4,7-dihydro[1,2,4]-triazolo[1,5-*a*]pyrimidin-6-yl]ethanone (7d)**. Yield 0.29 g (83%), light-yellow crystals, mp 202–204°C. IR spectrum, ν, cm$^{-1}$: 3241, 3090, 2813, 1693, 1650, 1588, 1330, 1264, 1192, 1062, 856, 762. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 2.31 (3H, s, $CH_3$); 2.46 (3H, s, $CH_3$); 6.68 (1H, s, 7-CH); 7.69 (1H, s, 2-CH); 7.81 (1H, d, *J* = 8.0, H Ar); 8.04 (1H, d, *J* = 8.0, H Ar); 8.31 (1H, s, H Ar); 10.92 (1H, s, NH). $^{13}$C NMR spectrum, δ, ppm: 19.6 ($CH_3$); 30.6 ($CH_3$); 57.5 (C-7); 108.7 (C-6); 128.6; 130.5; 131.0; 131.7; 136.2; 136.6; 147.0; 148.3 (C-2); 150.5; 194.3 (CO); 195.2 (CO). Found, %: C 51.27; H 3.47; N 15.91. $C_{15}H_{12}Cl_2N_4O_2$. Calculated, %: C 51.30; H 3.44; N 15.95.

**1-[5-Methyl-7-(4-methylbenzoyl)-4,7-dihydro[1,2,4]-triazolo[1,5-*a*]pyrimidin-6-yl]ethanone (7e)**. Yield 0.21 g (71%), white crystals, mp 199–200°C. IR spectrum, ν, cm$^{-1}$: 3228, 3090, 2820, 1682, 1645, 1580, 1334, 1264, 1192, 968, 744. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 2.27 (3H, s, $CH_3$); 2.37 (3H, s, $CH_3$); 2.44 (3H, s, $CH_3$); 6.68 (1H, s, 7-CH); 7.33 (2H, d, *J* = 7.2, H Ar); 7.64 (1H, s, 2-CH); 8.01 (2H, d, *J* = 7.6, H Ar); 10.81 (1H, s, NH). $^{13}$C NMR spectrum, δ, ppm: 20.1 ($CH_3$); 21.7 ($CH_3$); 31.3 ($CH_3$); 57.8 (C-7); 108.8 (C-6); 129.5 (2C Ar); 129.6 (2C Ar); 134.0; 144.4; 147.7; 148.4 (C-2); 150.8; 194.6 (CO); 196.6 (CO). Found, %: C 64.87; H 5.40; N 18.96. $C_{16}H_{16}N_4O_2$. Calculated, %: C 64.85; H 5.44; N 18.91.

**Ethyl 7-(4-bromobenzoyl)-5-methyl-4,7-dihydro[1,2,4]-triazolo[1,5-*a*]pyrimidine-6-carboxylate (7f)**. Yield 0.29 g (74%), beige crystals, mp 188–190°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 0.80 (3H, t, *J* = 7.2, $OCH_2C\underline{H}_3$); 2.39 (3H, s, $CH_3$); 3.85 (2H, q, *J* = 7.2, $OC\underline{H}_2CH_3$); 6.81 (1H, s, 7-CH); 7.67 (1H, s, 2-CH); 7.78 (2H, d, *J* = 8.4, H Ar); 8.06 (2H, d, *J* = 8.8, H Ar); 10.83 (1H, s, NH). $^{13}$C NMR spectrum, δ, ppm: 16.1 ($CH_3$); 20.9 ($CH_3$); 59.3 ($CH_2$); 62.3 (C-7); 96.9 (C-6); 130.7; 133.4 (2C Ar); 134.5 (2C Ar); 137.3; 149.9; 151.5 (C-2); 153.1; 167.4; 199.4 (CO). Found, %: C 49.09; H 3.89; N 14.28. $C_{16}H_{15}BrN_4O_3$. Calculated, %: C 49.12; H 3.86; N 14.32.

**Ethyl 7-(3,4-dimethylbenzoyl)-5-methyl-4,7-dihydro-[1,2,4]triazolo[1,5-*a*]pyrimidine-6-carboxylate (7g)**. Yield 0.29 g (74%), white crystals, mp 168–170°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 0.80 (3H, t, *J* = 7.2, $OCH_2C\underline{H}_3$); 2.29 (6H, s, $2CH_3$); 2.39 (3H, s, $CH_3$); 3.84 (2H, q, *J* = 6.8, $OC\underline{H}_2CH_3$); 6.79 (1H, s, 7-CH); 7.30 (1H, d, *J* = 7.6, H Ar); 7.63 (1H, s, 2-CH); 7.83–7.89 (2H, m, H Ar); 10.76 (1H, s, NH). $^{13}$C NMR spectrum, δ, ppm: 16.1 ($CH_3$); 20.9 ($CH_3$); 21.9 ($CH_3$); 22.2 ($CH_3$); 59.4 ($CH_2$); 62.1 (C-7); 97.2 (C-6); 129.3; 132.3; 132.4; 136.1; 139.3; 145.7; 150.1 (C-2); 151.3; 152.8; 167.4; 199.2 (CO). Found, %: C 63.48; H 5.96; N 16.49. $C_{18}H_{20}N_4O_3$. Calculated, %: C 63.52; H 5.92; N 16.46.

**Ethyl 7-(3,4-dichlorobenzoyl)-5-methyl-4,7-dihydro-[1,2,4]triazolo[1,5-*a*]pyrimidine-6-carboxylate (7h)**. Yield 0.30 g (79%), white crystals, mp 184–185°C. IR spectrum, ν, cm$^{-1}$: 3385, 3132, 2960, 1701, 1682, 1581, 1556, 1364, 1254, 1209, 1114, 1028, 830, 774, 725. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 0.83 (3H, t, *J* = 6.8, $OCH_2C\underline{H}_3$); 2.39 (3H, s, $CH_3$); 3.88 (2H, q, *J* = 6.8, $OC\underline{H}_2CH_3$); 6.88 (1H, s, 7-CH); 7.68 (1H, s, 2-CH); 7.85 (1H, d, *J* = 8.4, H Ar); 8.08 (1H, d, *J* = 8.4, H Ar); 8.37 (1H, s, H Ar); 10.87 (1H, s, NH). $^{13}$C NMR spectrum, δ, ppm: 14.1 ($CH_3$); 17.8 ($CH_3$); 57.2 ($CH_2$); 60.4 (C-7); 94.7 (C-6); 129.3; 131.3; 131.8; 132.4; 136.3; 137.3; 147.8; 149.4; 151.1 (C-2); 165.3; 196.5 (CO). Found, %: C 50.45; H 3.65; N 14.72. $C_{16}H_{14}Cl_2N_4O_3$. Calculated, %: C 50.41; H 3.70; N 14.70.

**X-ray structural analysis of compound 7b** was performed on an Agilent Xcalibur-3 diffractometer at room temperature (MoKα radiation, CCD detector, graphite monochromator, ω-scanning, $2\theta_{max}$ 60°). The unit cell parameters and intensities of 8892 reflections (including 4690 independent reflections, $R_{int}$ 0.045) were determined. The crystals of compound **7b** were monoclinic, $C_{15}H_{13}BrN_4O_2$, at 22°C: *a* 8.2729(8), *b* 10.8515(9), *c* 16.9280(13) Å; β 103.166(8)°; *V* 1479.7(2) Å$^3$; *M* 361.20; *Z* 4; space group $P2_1/c$; $d_{calc}$ 1.621 g/cm$^3$; μ(MoKα) 2.791 mm$^{-1}$; *F*(000) 728. The structure was solved by a direct method. The hydrogen atom positions were determined geometrically and refined according to the "rider" model with $U_{iso}$ = 1.2$U_{eq}$ (1.5$U_{eq}$ for methyl groups), with the coordinates and isotropic temperature parameter of the hydrogen atom at N(1) atom refined independently. The structure was refined by $F^2$ using full-matrix method of least squares in anisotropic approximation for non-hydrogen atoms to $wR_2$ 0.1561 by 4690 reflections ($R_1$ 0.0636 by 2249 reflections with $F > 4\sigma(F)$, *S* 1.007). The structure was solved and refined by using the OLEX2 software suite[27] with SHELXS and SHELXL modules.[28] The crystallographic dataset, atomic coordinates, and geometric parameters of the structures were deposited at the Cambridge Crystallographic Data Center (deposit CCDC 1569908).

Supplementary information file containing $^1$H and $^{13}$C NMR spectra of compounds **7a**–**h** is available at the journal website at http://link.springer.com/journal/10593.

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