Reactions of tetrahydropyrido[4,5-*d*][1,2,4]triazolo[1,5-*a*]-pyrimidin-4-ones with activated alkynes. Synthesis of [1,2,4]triazolo[1´,5´:1,2]pyrimido[4,5-*d*]azocines

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Triazolo[1´,5´:1,2]pyrimido[4,5-*d*]azocines were synthesized by the tandem expansion of the tetrahydropyridine ring in tetrahydropyridotriazolopyrimidines by the action of activated alkynes. Under these conditions, triazolopyridopyrimidines benzylated at the nitrogen atom of the pyrimidine moiety undergo the Hofmann cleavage of the tetrahydropyridine ring to form 5-vinyltriazolo[1,5-*a*]pyrimidines.

Key words: tandem ring expansion, tandem cleavage, [1,2,4]triazolo[1´,5´:1,2]pyrimido-[4,5d]azocines, 5-vinyltriazolo[1,5-*a*]pyrimidines.

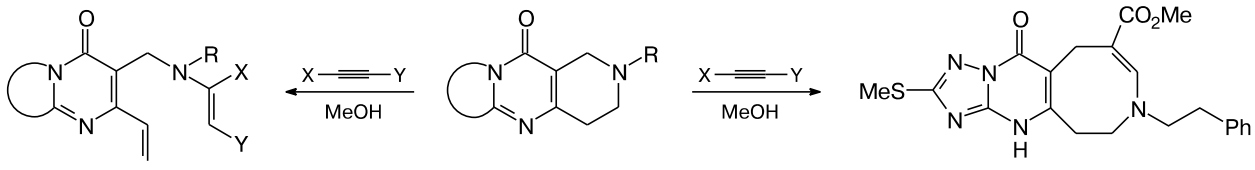
Tandem transformations of fused tetrahydropyridines by the action of alkynes containing electron-withdrawing substituents is a fairly efficient method for the synthesis of tetrahydroazocines fused to the pyrrole,[1] thiophene,[2] indole,[3] benzene,[4] and pyrimidine[5] heterocycles. Recently, we have shown[6] that the annulation of the isoxazole, thiazole, or thiadiazole rings to the pyrimidine ring of tetrahydropyrido[4,3-*d*]pyrimidines results in the change in the pathway of the transformation of their tetrahydropyridine moiety by the action of activated alkynes. Instead of the expansion of the tetrahydropyridine moiety to form the azocine moiety, the former undergoes the Hofmann cleavage to give 5- or 7-vinyl-substituted azolopyrimidines **1** (Scheme 1).[6]

Only the reaction of *N*-phenylethyl-substituted tetrahydropyrido(methylthio)triazolopyrimidine with methyl propiolate resulted in the tetrahydropyridine ring expansion to give triazolopyrimidoazocine **2** (see Scheme 1).[6] It was of interest to find the factors responsible for this pathway of transformations of triazole-fused pyridopyrimidines.

Pyridotriazolopyrimidines **3** and **4** were synthesized by the condensation of 1-benzyl- and 1-methyl-3-methoxycarbonylpiperidin-4-ones, respectively, with 3-amino-5-methylthio[1,2,4]triazole in polyphosphoric acid (PPA) according to a procedure described previously.[7] Compound **5** was prepared according to a procedure described in our earlier publication[5] (Scheme 2).

The reactions of compounds **3**—**5** with methyl propiolate and acetylacetylene were performed in refluxing methanol. As in the case of *N*-phenylethyl-substituted triazolopyridopyrimidine **5**, the main direction of the reaction involved the tetrahydropyridine ring expansion. After 0.5—24 h, triazolopyrimidoazocines **6**—**9** were obtained in 52—85% yields (Scheme 3).

Scheme 1



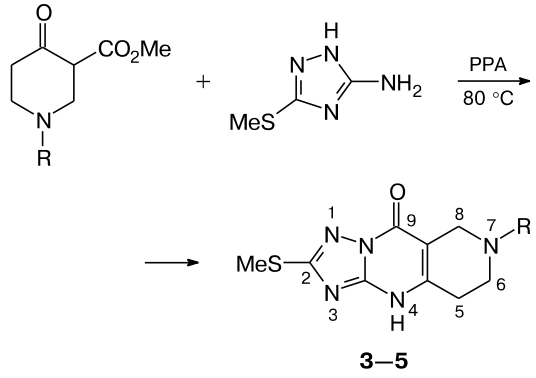
1 **2**

R = Me, Pr^i, Br, CH_2CH_2Ph; X = H, CO_2Me; Y = CO_2Me, COMe

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1587—1591, August, 2012.

1066-5285/12/6108-1603

Scheme 2



R = Me (**3**), Bn (**4**), CH_2CH_2Ph (**5**)

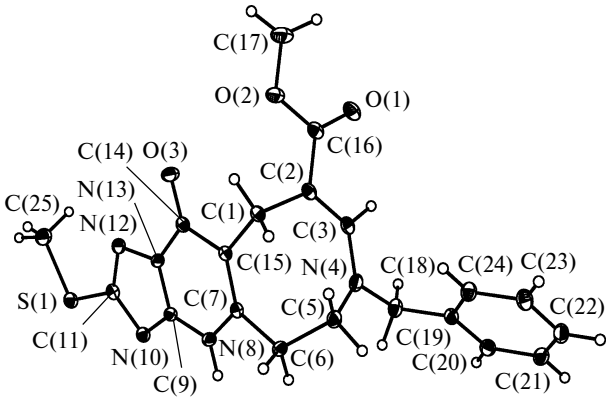


Fig. 1. Molecular structure of compound **7** with displacement ellipsoids drawn at the 50% probability level.

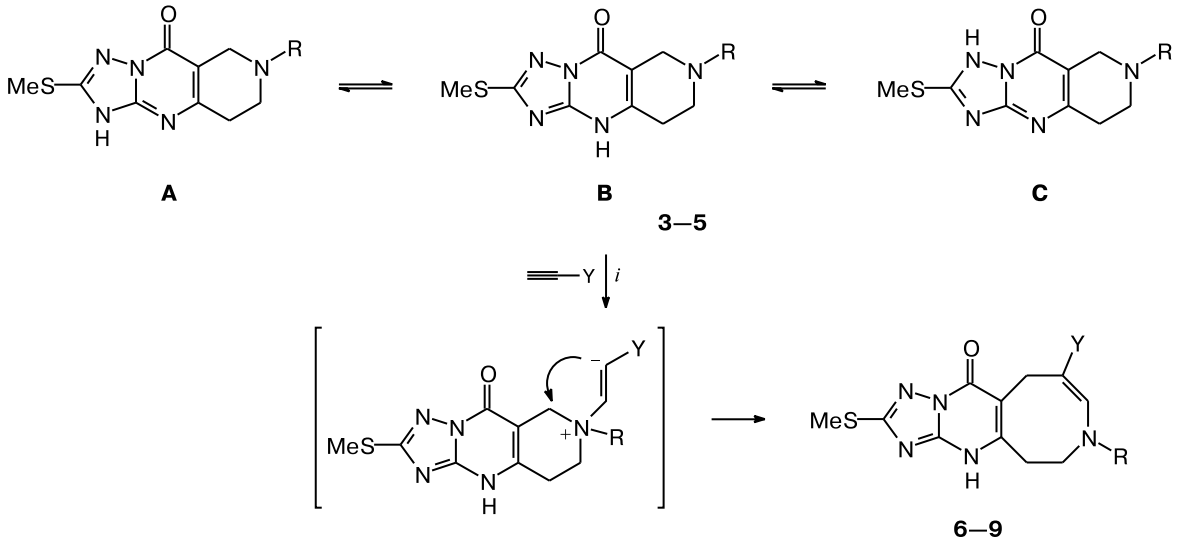
Since pyridotriazolopyrimidines **3**—**5** can exist in solution as mixtures of tautomers **A**, **B**, and **C** (see Refs 8 and 9), the resulting azocines **6**—**9** can adopt three tautomeric forms of the triazolopyrimidine moiety. A single crystal of triazolopyrimidoazocine **7** was obtained by the crystallization from DMSO, and the three-dimensional structure of **7** was established by X-ray diffraction (Fig. 1).

The triazolopyrimidine moiety is almost planar and exists in the tautomeric form **B**, which is unambiguously evidenced by the C(9)—N(10) (1.319(2) Å) and C(11)—N(12) (1.327(2) Å) bond lengths in the triazole ring. The tetrahydroazocine moiety adopts a distorted boat conformation. These results suggest that the tetrahydropyridine ring expansion occurs in the tautomeric form **B**.

To confirm this suggestion, we performed the benzylation of pyridotriazolopyrimidine **4** with benzyl chloride in DMF in the presence of sodium hydride (Scheme 4).

According to the X-ray diffraction data (Fig. 2), the benzylation occurs at the pyrimidine nitrogen atom, and the tautomeric form **B** in compound **10** is fixed, which is unambiguously evidenced by the N(1)—C(2) (1.323(2) Å) and N(3)—C(3A) (1.320(2) Å) bond lengths. The tetrahydropyridine moiety in compound **10** adopts an unsymmetrical chair conformation (the carbon atom C(6) and the nitrogen atom N(7) deviate from the mean plane passing through the other atoms of the ring by 0.339(4) and –0.426(3) Å, respectively). The triazolopyrimidine moiety is nearly planar. The phenyl rings are almost perpen-

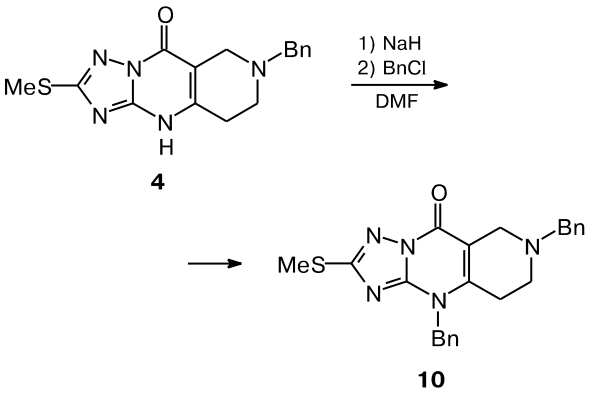
Scheme 3



i. MeOH, refluxing.

Compound	**6**	**7**	**8**	**9**
R	Me	Bn	Bn	CH_2CH_2Ph
Y	CO_2Me	CO_2Me	COMe	COMe

Scheme 4



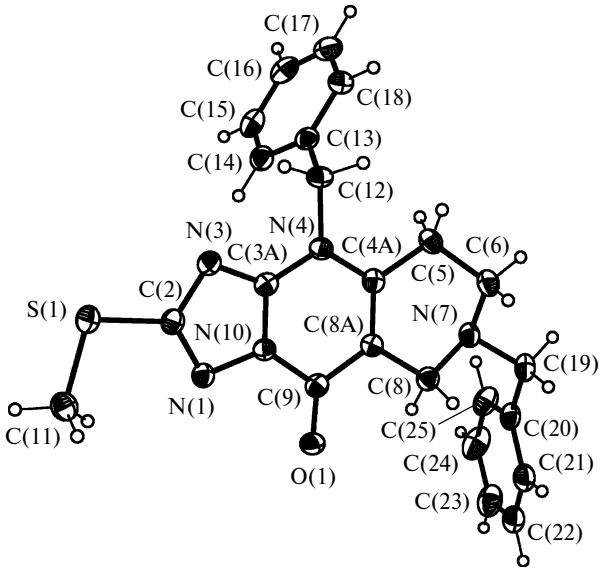


Fig. 2. Molecular structure of compound **9** with displacement ellipsoids drawn at the 50% probability level.

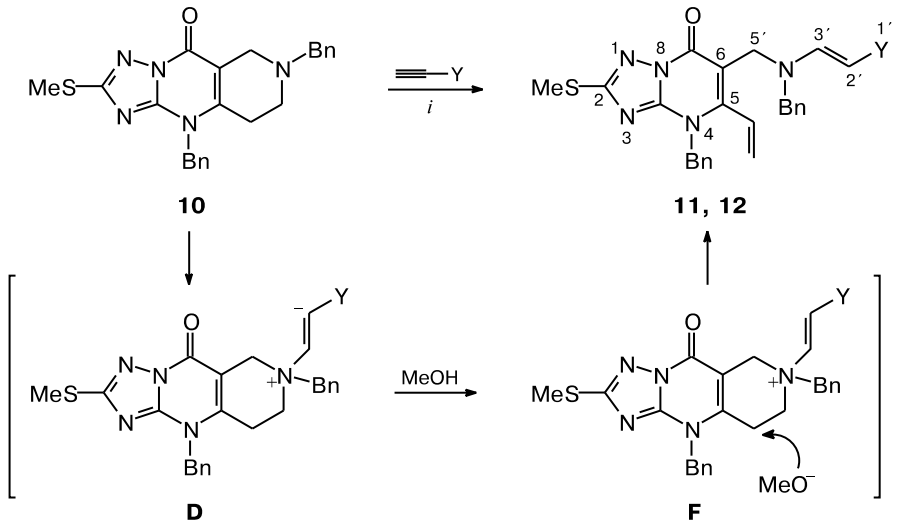
dicular to the plane of the triazolopyrimidine moiety (the angles between the corresponding planes are 80.89(5) and 87.06(5)°).

We expected that the tandem reactions of triazolopyridopyrimidine **10** with acetylacetylene and methyl propiolate in methanol would give triazolopyrimidoazocines. However, we obtained not the expected tetrahydrotriazolopyrimidoazocines but products of the Hofmann cleavage of the tetrahydropyridine ring, *viz.*, 5-vinyl[1,2,4]triazolo[1,5-*a*]pyrimidines **11** and **12** in 85 and 89% yields, respectively (Scheme 5).

Apparently, due to the electron-donating effect of the enamine group fixed by the benzyl radical in the zwitterion **D**, the electron deficiency on the methylidene group in position 7 decreases so that the nucleophilic attack on this group is hardly possible. The anionic center of the zwitterion **D** deprotonates methanol, and the ammonium ion **F** undergoes the Hofmann cleavage by the action of resulting methoxide anion.

These results suggest that the tetrahydropyridine ring expansion of tetrahydrotriazolopyridopyrimidines **3**—**5** to form the azocine moiety, as compared with their analogs, tetrahydropyridopyrimidines, fused to the isoxazole, thiazole, and thiadiazole rings, takes place due to the electron-withdrawing effect of triazole, which leads to an increase in the electron deficiency on the methylidene group in position 7. The expansion of the tetrahydropyridine ring occurs apparently in the tautomeric

Scheme 5



Y = CO_2Me (**11**), COMe (**12**)

form **A**, which is transformed into the more stable form **B** in azocine.

Therefore, we performed for the first time the efficient synthesis of tetrahydrotriazolopyrimido[4,5-*d*]azocines representing a new heterocyclic system.

Experimental

The IR spectra were recorded on an Infralyum FT–801 Fourier-transform infrared spectrometer as KBr pellets. The LCMS spectra were obtained using a system composed of an Agilent 1100 liquid chromatograph, an Agilent Technologies LC/MSD VL mass spectrometer (electrospray mode, atmospheric-pressure chemical ionization), and an ELSD Sedex 75 detector. High-resolution mass spectra were measured on a JEOL JMS-T100LP-DART 100 instrument (DART ionization). The ^{1}H NMR spectra were recorded on Bruker-400 and JEOL JNM-ECA600* instruments (for ^{1}H, operating at 400 and 600 MHz, respectively) in $CDCl_3$ or DMSO-d_6 using residual signals of the solvents or $SiMe_4$ as the internal standard. The elemental analysis was performed on a Carlo Erba 1106 instrument. The melting points were measured in open capillaries on a SMP10 instrument. The course of the reactions was monitored by TLC using Silufol UV-254 and Sorbfile plates (visualization was performed in an UV chamber rated at 254 nm, with iodine vapor or a $KMnO_4$ solution, 3 g L^{-1}). All solvents used in the work were purified by distillation and dried. Methyl propiolate, acetylacetylene, and dimethyl acetylenedicarboxylate were purchased from Acros Organics and Merck and were used without additional purification.

X-ray diffraction study of compounds 7 and 9. The unit cell parameters and intensities of reflections were measured on Bruker SMART APEX II CCD (compound **7**) and Bruker SMART 1K CCD (compound **9**) automated three-circle diffractometers (λMo-Kα radiation, graphite monochromator, φ- and ω-scanning technique). Absorption corrections were applied using the SADABS program (version 2.03[10] for **7** and version 2.01[11] for **9**). Principal crystallographic data are given in Table 1. The structures of compounds **7** and **9** were solved by direct methods and refined by the full-matrix least-squares method using F^2 with anisotropic displacement parameters for nonhydrogen atoms. In the crystal structure of compound **7**, there is one dimethyl sulfoxide molecule of solvation per asymmetric unit. In both structures, the hydrogen atoms were positioned geometrically and refined isotropically with fixed positional (a riding model) and thermal (U_{iso}(H) = 1.5U_{eq}(C) for CH_3 groups and U_{iso}(H) = = 1.2U_{eq}(C) for all other groups) parameters. All calculations were carried out with the use of the SHELXTL program package.[12] Tables of atomic coordinates, bond lengths, bond angles, torsion angles, and anisotropic displacement parameters for compounds **7**·$(CH_3)_2SO$ and **9** were deposited with the Cambridge Crystallographic Data Centre.

Table 1. Principal crystallographic characteristics and the structure refinement statistics for compounds **7**·$(CH_3)_2SO$ and **9**

Compound	**7**·$(CH_3)_2SO$	**9**
Molecular formula	$C_{22}H_{27}N_5O_4S_2$	$C_{23}H_{23}N_5OS$
Crystal dimensions/mm^3	0.22×0.26×0.30	0.02×0.21×0.24
Molecular weight	489.61	417.52
T/K	100	120
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	22.5841(8)	11.4893(7)
b/Å	11.2441(4)	13.3297(9)
c/Å	9.0681(3)	13.3537(9)
β/deg	96.1750(10)	93.5780(10)
V/Å^3	2289.37(14)	2041.1(2)
Z	4	
d_{calc}/g cm^{-3}	1.420	1.359
F(000)	1032	880
μ/mm^{-1}	0.273	0.184
$2\theta_{max}$/deg	61.6	60.0
Number of reflections	30106	23628
measured unique	7122	5942
with $I > 2\sigma(I)$	5713	3845
Number of parameters refinement	302	272
R_1 ($I > 2\sigma(I)$)	0.0388	0.0544
wR_2 (based on all data)	0.0958	0.1389
GOOF	1.002	1.008
T_{min}/T_{max}	0.923/0.942	0.957/0.996
(ρ_{max}/ρ_{min})/eÅ^{-3}	0.450/–0.299	0.375/–0.336

Synthesis of 7-*R*-2-methylthio-5,6,7,8-tetrahydropyrido-[4,3-*d*][1,2,4]triazolo[1,5-*a*]pyrimidin-9(4*H*)-ones 3—5 (general procedure). A solution of 1-alkyl-3-carbomethoxypiperidin-4-one hydrochloride (20 mmol) and 3-amino-5-methylthio[1,2,4]-triazole (2.35 g, 20 mmol) in polyphosphoric acid (20 mL) was heated at 80 °C for 8—20 h (the course of the reaction was monitored by TLC, chloroform—methanol, 9 : 1, as the eluent). The reaction mixture was cooled, water (50 mL) was added, and the mixture was neutralized with a 15% NaOH solution. The crystals that formed were filtered off, washed with water and ethanol, and recrystallized from DMF.

7-Methyl-2-methylthio-5,6,7,8-tetrahydropyrido[4,3-*d*]-[1,2,4]triazolo[1,5-*a*]pyrimidin-9(4*H*)-one (3). Yield 30%, colorless crystals, m.p. 198—200 °C. Found (%): C, 47.60; H, 5.01; N, 27.76. $C_{10}H_{13}N_5OS$. Calculated (%): C, 47.79; H, 5.21; N, 27.87. IR, ν/cm^{-1}: 1695 (C=O). ^{1}H NMR (400 MHz, DMSO-d_6), δ: 2.50 (s, 3 H, NCH_3); 2.51—2.54 (m, 2 H, C(6)H_2); 2.55—2.61 (m, 2 H, C(5)H_2); 2.56 (s, 3 H, SCH_3); 3.45 (s, 2 H, C(8)H_2). MS (ESI+), *m/z*: 282 $[M + H]^+$.

7-Benzyl-2-methylthio-5,6,7,8-tetrahydropyrido[4,3-*d*]-[1,2,4]triazolo[1,5-*a*]pyrimidin-9(4*H*)-one (4). Yield 75%, colorless crystals, m.p. 250—252 °C (with decomposition). Found (%): C, 58.55; H, 5.34; N, 21.47. $C_{16}H_{17}N_5OS$. Calculated (%): C, 58.70; H, 5.23; N, 21.39. IR, ν/cm^{-1}: 1639 (C=O). ^{1}H NMR (400 MHz, DMSO-d_6), δ: 2.56 (s, 3 H, SCH_3); 2.73 (m, 2 H, C(6)H_2); 2.77 (m, 2 H, C(5)H_2); 3.30 (s, 2 H, $\underline{CH_2}$Ph); 3.74 (s, 2 H, C(8)H_2); 7.28—7.38 (m, 5 H, Ph). MS (ESI+), *m/z*: 328 $[M + H]^+$.

2-Methylthio-7-(ethyl-2-phenyl)-5,6,7,8-tetrahydropyrido-[4,3-*d*][1,2,4]triazolo[1,5-*a*]pyrimidin-9(4*H*)-one (5). Yield 47%, colorless crystals, m.p. 254—256 °C (with decomposition). Found (%): C, 59.63; H, 5.30; N, 20.44. $C_{17}H_{19}N_5OS$. Calculat-

* We thank the staff of the Shared Research and Education Center of Peoples´ Friendship University of Russia for recording the NMR spectra.

ed (%): C, 59.80; H, 5.61; N, 20.51. IR, ν/cm^{-1}: 1698 (C=O). ^{1}H NMR (400 MHz, DMSO-d$_6$), δ: 2.47 (t, 2 H, C(6)H$_2$, *J* = 7.0 Hz); 2.56 (s, 3 H, SCH$_3$); 2.75 (t, 2 H, C(5)H$_2$, *J* = 7.0 Hz); 3.26 (m, 2 H, CH$_2$CH$_2$Ph); 3.77 (s, 2 H, C(8)H$_2$); 3.85 (m, 2 H, CH$_2$CH$_2$Ph); 7.08—7.20 (m, 5 H, Ph). MS (ESI+), *m/z*: 342 [M + H]$^+$.

Synthesis of triazolo[1′,5′:1,2]pyrimido[4,5-*d*]azocines 6—9 (general procedure). Methyl propiolate or acetylacetylene (0.74 mmol) was added to a solution of the corresponding pyridotriazolopyrimidine (**3**, **4**, or **5**) (0.20 g, 0.61 mmol) in methanol (20 mL). The reaction mixture was refluxed for 30—60 min (the course of the reaction was monitored by TLC, ethyl acetate as the eluent). The precipitate that formed was filtered off, washed with methanol, and dried.

Methyl 7-methyl-2-methylthio-11-oxo-4,5,6,7,10,11-hexahydro[1,2,4]triazolo[1′,5′:1,2]pyrimido[4,5-*d*]azocine-9-carboxylate (6). Yield 55%, colorless crystals, m.p. 172—174 °C. Found (%): C, 50.19; H, 5.03; N, 20.92. $C_{14}H_{17}N_5O_3S$. Calculated (%): C, 50.14; H, 5.11; N, 20.88. IR, ν/cm^{-1}: 1682 (C=O), 1650 (C=O). ^{1}H NMR (400 MHz, DMSO-d$_6$), δ: 2.56 (s, 3 H, SCH$_3$); 2.89 (s, 3 H, NCH$_3$); 3.20 (t, 2 H, C(5)H$_2$, *J* = 6.5 Hz); 3.53 (s, 3 H, OCH$_3$); 3.69 (t, 2 H, C(6)H$_2$, *J* = 6.5 Hz); 3.79 (s, 2 H, CH$_2$(10)); 7.25 (s, 1 H, C(8)H). MS (ESI+), *m/z*: 336 [M + H]$^+$.

Methyl 7-benzyl-2-methylthio-11-oxo-4,5,6,7,10,11-hexahydro[1,2,4]triazolo[1′,5′:1,2]pyrimido[4,5-*d*]azocine-9-carboxylate (7). Yield 88%, colorless crystals m.p. 274—276 °C. Found (%): C, 58.43; H, 5.23; N, 16.96. $C_{20}H_{21}N_5O_3S$. Calculated (%): C, 58.38; H, 5.14; N, 17.02. IR, ν/cm^{-1}: 1685 (C=O), 1646 (C=O). ^{1}H NMR (600 MHz, DMSO-d$_6$), δ: 2.59 (s, 3 H, SCH$_3$); 3.05 (t, 2 H, C(5)H$_2$, *J* = 5.8 Hz); 3.58 (s, 3 H, OCH$_3$); 3.85 (m, 2 H, C(6)H$_2$); 3.85 (s, 2 H, C(10)H$_2$); 4.41 (s, 2 H, CH$_2$Ph); 7.08—7.11 (m, 2 H, Ph); 7.20—7.23 (m, 3 H, Ph); 7.55 (s, 1 H, C(8)H). MS (ESI+), *m/z*: 412 [M + H]$^+$.

9-Acetyl-7-benzyl-2-methylthio-5,6,7,10-tetrahydro[1,2,4]triazolo[1′,5′:1,2]pyrimido[4,5-*d*]azocin-11(4*H*)-one (8). Yield 78%, colorless crystals m.p. 265—268 °C. Found (%): C, 60.71; H, 5.29; N, 17.83. $C_{20}H_{21}N_5O_2S$. Calculated (%): C, 60.74; H, 5.35; N, 17.71. IR, ν/cm^{-1}: 1679 (C=O). ^{1}H NMR (600 MHz, DMSO-d$_6$), δ: 2.15 (s, 3 H, COCH$_3$); 2.58 (s, 3 H, SCH$_3$); 3.03 (m, 2 H, C(5)H$_2$); 3.83 (m, 2 H, C(6)H$_2$); 3.83 (m, 2 H, C(10)H$_2$); 4.46 (s, 2 H, CH$_2$Ph); 7.11—7.22 (m, 5 H, Ph); 7.62 (s, 1 H, C(8)H); 12.39 (s, 1 H, NH). MS (ESI+), *m/z*: 396 [M + H]$^+$.

9-Acetyl-2-methylthio-7-(2-phenylethyl)-5,6,7,10-tetrahydro[1,2,4]triazolo[1′,5′:1,2]pyrimido[4,5-*d*]azocin-11(4*H*)-one (9). Yield 77%, colorless crystals m.p. 246—249 °C. Found (%): C, 61.67; H, 5.75; N, 17.19. $C_{21}H_{23}N_5O_2S$. Calculated (%): C, 61.59; H, 5.66; N, 17.10. IR, ν/cm^{-1}: 1675 (C=O). ^{1}H NMR (400 MHz, DMSO-d$_6$), δ: 1.94 (s, 3 H, COCH$_3$); 2.56 (s, 3 H, SCH$_3$); 2.75 (t, 2 H, CH$_2$CH$_2$Ph, *J* = 7.4 Hz); 3.26 (m, 2 H, C(5)H$_2$); 3.47 (t, 2 H, CH$_2$CH$_2$Ph, *J* = 7.4 Hz); 3.76 (m, 2 H, C(6)H$_2$); 3.86 (m, 2 H, C(10)H$_2$); 7.09—7.15 (m, 5 H, Ph); 7.19 (s, 1 H, C(8)H). MS (ESI+), *m/z*: 410 [M + H]$^+$.

4,7-Dibenzyl-2-methylthio-5,6,7,8-tetrahydro-[4,3-*d*]-[1,2,4]triazolo[1,5-*a*]pyrimidin-9(4*H*)-one (10). To a solution of compound **4** (1.10 g, 3.38 mmol) in anhydrous DMF (3.0 mL), NaH (0.16 g, 4.06 mmol; 60% in Vaseline oil) was added. The reaction mixture was heated at 60 °C for 2 h, benzyl chloride (4.06 mmol) was added, and the mixture was stirred at 80 °C for 20 h (TLC monitoring, Sorbfile, chloroform—methanol, 19 : 1, as the eluent). Then the mixture was cooled, and water (40 mL) was added dropwise. The precipitate of triazolopyridopyrimidine **10** that formed was filtered off and recrystallized from acetonitrile. Compound **10** was obtained in a yield of 0.85 g (60%), yellow crystals, m.p. 220—222 °C. Found (%): C, 66.03; H, 5.62; N, 16.85. $C_{23}H_{23}N_5OS$. Calculated (%): C, 66.16; H, 5.55; N, 16.77. IR, ν/cm^{-1}: 1676 (C=O). ^{1}H NMR (600 MHz, CDCl$_3$), δ: 2.66—2.63 (m, 2 H, C(5)H$_2$); 2.68 (s, 3 H, SCH$_3$); 2.67—2.74 (m, 2 H, C(6)H$_2$); 3.58 (s, 2 H, N(7)CH$_2$Ph); 3.68 (s, 2 H, C(8)H$_2$); 5.41 (s, 2 H, N(4)CH$_2$Ph); 7.15—7.13 (m, 2 H, N(7)CH$_2$Ph); 7.27—7.33 (m, 3 H, N(7)CH$_2$Ph); 7.20—7.40 (m, 5 H, N(4)CH$_2$Ph). MS (ESI+), *m/z*: 418 [M + H]$^+$.

Methyl (2*E*)-3-{benzyl[(4-benzyl-5-vinyl-2-methylthio-7-oxo-4,7-dihydro[1,2,4]triazolo[1,5-*a*]pyrimidin-6-yl)methyl]-amino}acrylate (11). A solution of triazolopyridopyrimidine **10** (0.20 g, 0.48 mmol) and methyl propiolate (0.048 g, 0.55 mmol) in a mixture of toluene (10 mL) and methanol (5 mL) was refluxed for 2 h (TLC monitoring, Silufol, chloroform—methanol, 9 : 1, as the eluent). The solvent was evaporated *in vacuo*, and the residue was recrystallized from an ethyl acetate—hexane mixture. Compound **11** was obtained in a yield of 0.21 g (89%), yellow crystals, m.p. 140—145 °C. Found (%): C, 64.50; H, 5.49; N, 14.03. $C_{27}H_{27}N_5O_3S$. Calculated (%): C, 64.65; H, 5.43; N, 13.96. IR, ν/cm^{-1}: 1697 (C=O), 1671 (C=O). ^{1}H NMR (600 MHz, CDCl$_3$), δ: 2.68 (s, 3 H, SCH$_3$); 3.61 (s, 3 H, OMe); 4.33 (s, 2 H, NCH$_2$Ph); 4.43 (s, 2 H, C(5′)H$_2$); 4.55 (d, 1 H, C(2′)H, *J* = 13.1 Hz); 5.34 (s, 2 H, N(4)CH$_2$Ph); 5.47 (d, 1 H, CH$_2$=, *J* = 17.9 Hz); 5.86 (d, 1 H, CH$_2$=, *J* = 11.7 Hz); 6.31 (dd, 1 H, CH=CH$_2$, *J* = 11.7 Hz, *J* = 17.9 Hz); 7.08—7.05 (m, 2 H, Ph); 7.14—7.11 (m, 2 H, Ph); 7.22—7.16 (m, 3 H, Ph); 7.35—7.28 (m, 3 H, Ph); 7.60 (d, 1 H, C(3′)H, *J* = 13.1). MS HRMS (DART+), Found: *m/z* 502.1873 [M + H]$^+$. $C_{27}H_{28}N_5O_3S$. Calculated: [M + H] = 502.1867.

4-Benzyl-6-({benzyl[(1*E*)-3-oxobut-1-en-1-yl]amino}methyl)-5-vinyl-2-methylthio[1,2,4]triazolo[1,5-*a*]pyrimidin-7(4*H*)-one (12). Compound **12** was synthesized according to the above-described procedure from compound **10** (0.20 g, 0.48 mmol) and acetylacetylene (0.045 mL, 0.55 mmol) in a yield of 0.21 g (85%), yellow crystals, m.p. 170—172 °C. Found (%): C, 66.85; H, 5.52; N, 14.48. $C_{27}H_{27}N_5O_2S$. Calculated (%): C, 66.78; H, 5.60; N, 14.42. IR, ν/cm^{-1}: 1692 (C=O), 1600 (C=O). ^{1}H NMR (600 MHz, CDCl$_3$), δ: 2.04 (s, 3 H, CH$_3$C=O); 2.68 (s, 3 H, SCH$_3$); 4.36 (s, 2 H, =CHNCH$_2$Ph); 4.45 (s, 2 H, C(5′)H$_2$); 5.11 (br.s, 1 H, =CHCOCH$_3$); 5.34 (s, 2 H, N(4)CH$_2$Ph); 5.47 (d, 1 H, CH$_2$=CH, *J* = 17.9 Hz); 5.88 (d, 1 H, CH$_2$=CH, *J* = 11.7 Hz); 6.29 (dd, 1 H, CH$_2$=CH, *J* = 11.7 Hz, *J* = 17.9 Hz); 7.02—7.35 (m, 10 H, Ph); 7.60 (br.s, 1 H, CH=CH). MS (ESI+), *m/z*: 486 [M + H]$^+$.

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Received July 1, 2011;
in revised form February 8, 2012