Synthesis of 6-hydrazino-3,4-dimethyl-1*H*-pyrazolo[3,4-*d*]pyrimidine and its application for the construction of a pyrazolo[4,3-*e*][1,2,4]triazolo[4,3-*a*]pyrimidine system

A. V. Komkov, A. S. Shashkov, S. V. Baranin, and V. A. Dorokhov*†

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (499) 135 5328. E-mail: svbar@ioc.ac.ru

A new representative of heterocyclic hydrazines, *viz.*, 6-hydrazino-3,4-dimethyl-1*H*-pyrazolo[3,4-*d*]pyrimidine (**3**) was synthesized from diacetyl ketene *N*,*S*-acetal. A condensation of hydrazine **3** with amide acetals or aldehydes and subsequent cyclization furnished pyrazolo[4,3-*e*][1,2,4]triazolo[4,3-*a*]pyrimidines, whose structure was confirmed by ^{1}H, ^{13}C, and $^{1}H/^{15}N$ HMBC NMR spectroscopy. Reactions of hydrazine **3** with acetylacetone, ethyl acetoacetate, diethyl malonate, and acetic anhydride were studied.

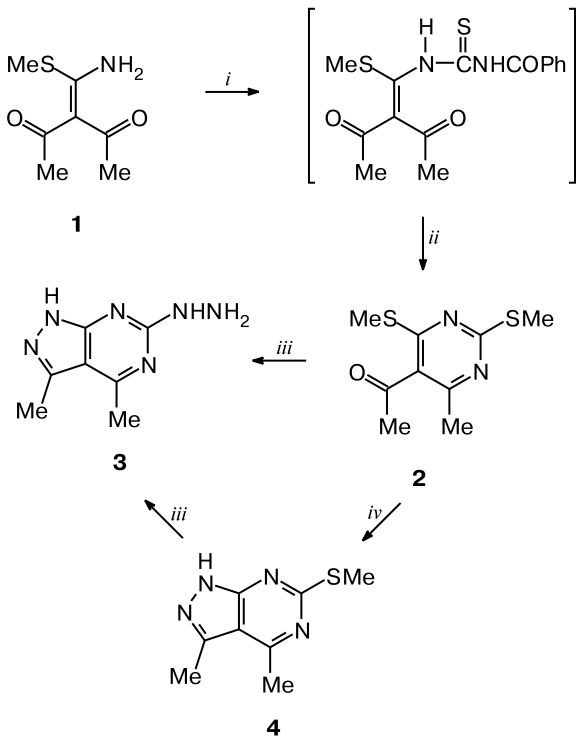
Key words: diacetyl ketene *N*,*S*-acetal, 5-acetyl-6-methyl-2,4-di(methylsulfanyl)pyrimidine, hydrazine, 6-hydrazino-1*H*-pyrazolo[3,4-*d*]pyrimidine, amide acetals, aldehydes, condensation, oxidative cyclization, pyrazolo[4,3-*e*][1,2,4]triazolo[4,3-*a*]pyrimidines, 6-(1*H*-pyrazol-1-yl)-1*H*-pyrazolo[3,4-*d*]pyrimidines.

The present work is a continuation of our studies on the application of diacetyl ketene *N*,*S*-acetal[1] obtained by us in heterocyclic synthesis. Earlier this reagent was used in the preparation of functionally substituted 2-pyrimidinones,[2] 2-pyrimidinethiones,[3] 4-pyrimidinethiones,[4,5] 4-methylsulfanyl- and 4-methylsulfonylpyrimidines,[5] 4-pyridinones,[6] pyrazoles,[7] pyridino[2,3-*d*]pyrimidines,[3,4] pyrimido[4,5-*d*]pyrimidines,[2,3] and pyrazolo[3,4-*d*]pyrimidines.[5,7]

Recently,[3] the reaction of diacetyl ketene *N*,*S*-acetal **1** and benzoylisothiocyanate with subsequent cyclization was used to synthesize 5-acetyl-6-methyl-2,4-di(methylsulfanyl)pyrimidine (**2**) (Scheme 1). In order to prepare new functionalized pyrazolo[3,4-*d*]pyrimidines, we studied reactions of pyrimidine **2** with hydrazine hydrate. It was found that reflux of compound **2** in hydrazine hydrate led to the formation of 6-hydrazino-3,4-dimethyl-1*H*-pyrazolo[3,4-*d*]pyrimidine (**3**) in high yield, *i.e.*, the pyrazole ring closure was accompanied by the substitution for the MeS group with the hydrazine one. It should be noted that the use of milder conditions for this reaction (reflux of the same mixture of reagents in butanol) gave 6-methylsulfanylpyrazolopyrimidine **4**, which upon reflux in hydrazine hydrate was also converted to hydrazine **3**.

Compound **3** is a white crystalline compound poorly soluble in organic solvents. Its structure was confirmed by mass spectrum and ^{1}H and ^{13}C NMR spectra.

Scheme 1



Reagents and conditions: *i.* PhCONCS, C_6H_6, 20 °C; *ii.* 1) MeONa, MeOH, Δ, 2) MeI, 20 °C; *iii.* $NH_2NH_2 \cdot H_2O$, Δ; *iv.* $NH_2NH_2 \cdot H_2O$, BuOH, Δ.

† Deceased.

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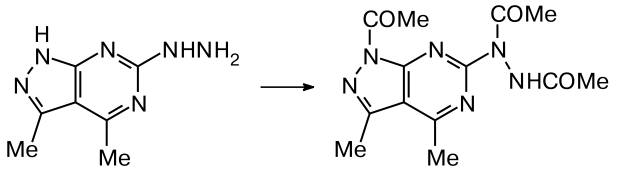
The reactivity of hydrazine **3** with respect to acetic anhydride and β-dicarbonyl compounds was studied. It was found that a prolonged reflux of hydrazine **3** with a large excess of Ac_2O in benzene resulted in the formation of a white crystalline triacetyl-substituted derivative **5** (Scheme 2), whose structure was confirmed by mass spectrum, ^1H and ^{13}C NMR spectra, and 2D $^1H/^{15}N$ HMBC NMR spectrum (see Experimental).

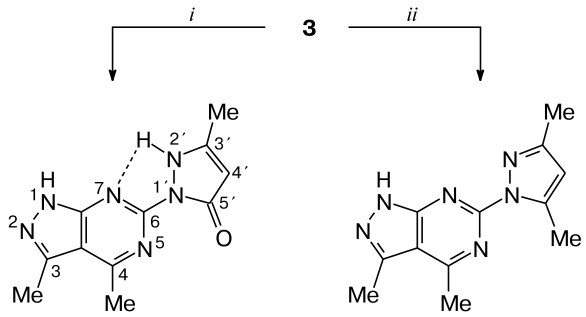
Scheme 2



Reagents and conditions: Ac_2O, C_6H_6, Δ.

The reaction of hydrazine **3** with ethyl acetoacetate or acetylacetone upon reflux in acetic acid smoothly gave, respectively, pyrazolo[3,4-*d*]pyrimidinyl-substituted pyrazolone **6** or pyrazole **7** in high yields (Scheme 3).

Scheme 3

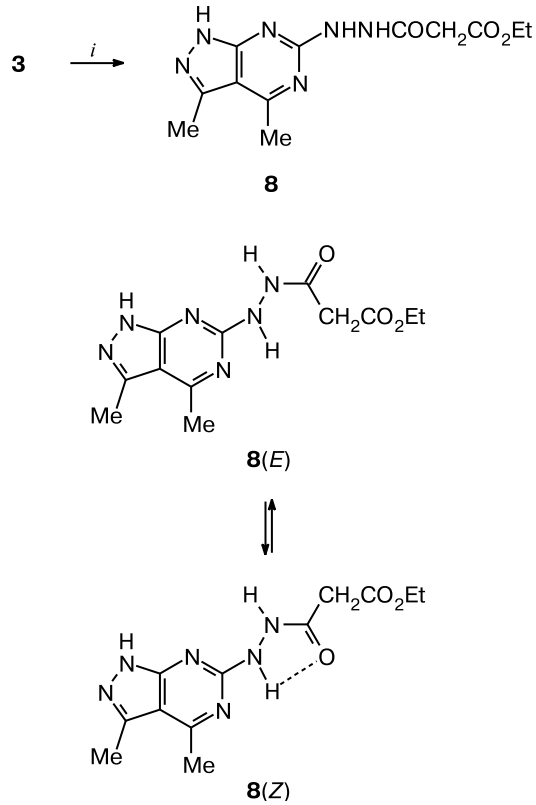


Reagents and conditions: *i*. $MeCOCH_2COOEt$, AcOH, Δ; *ii*. $MeCOCH_2COMe$, AcOH, Δ.

The structure of colorless compounds **6** and **7** was confirmed by mass spectra, ^1H and ^{13}C NMR spectra, and 2D $^1H—^{15}N$ HMBC NMR spectra. It should be noted that pyrazolone **6** exclusively exists in the enamine form, which was indicated by the ^1H NMR spectra in DMSO-d_6 and $CDCl_3$. This is probably due to the presence in molecule **6** of a strong intramolecular hydrogen bond stabilizing the enamine form. The oxy form of the pyrazole ring in compound **6** is excluded based on the 2D $^1H/^{15}N$ HMBC NMR spectrum, in which a characteristic upfield chemical shift for atom N(2′) is observed (δ −164, the correlation peak with the protons of the 3′-Me group; *cf.* with δ −78 for atom N(2′) in pyrazole **7**).

A solvent-free heating of hydrazine **3** with diethyl malonate led to the formation of hydrazide **8**, which failed to be cyclized neither by reflux in acetic acid nor by treatment with MeONa in MeOH (Scheme 4).

Scheme 4



Reagents and conditions: *i*. $EtO_2CCH_2CO_2Et$, 160—170 °C.

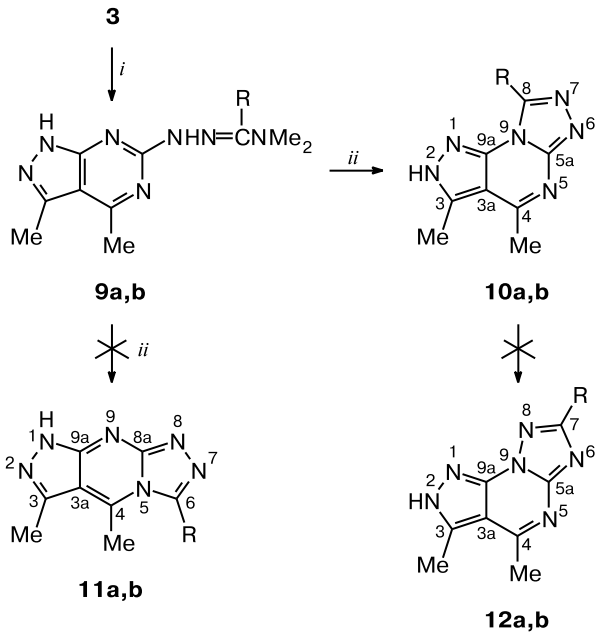
The structure of a colorless compound **8** was confirmed by physicochemical methods. It should be noted that in the ^1H and ^{13}C NMR spectra and 2D $^1H—^{15}N$ HMBC NMR spectrum, a double set of signals for the hydrazide fragment is observed, indicating the presence of *E*- and *Z*-isomers in molecule **8**. This fact, apparently, is explained by the slow rotation around the N—CO bond in the hydrazide fragment.

Further studies of the reactivity of hydrazine **3** showed that it can be used for the construction of pyrazolo[4,3-*e*]-[1,2,4]triazolo[4,3-*a*]pyrimidines. The molecules with the pyrazolotriazolopyrimidine structure contain two fragments isomeric to purines: the pyrazolopyrimidine and the triazolopyrimidine ones. Compounds having such fragment are of interest because of their biological properties. Thus, for example, some of similar compounds are known to be selective human A_3 adenosine receptor antagonists,[8,9]

exhibit antiinflammatory activity,[10–12] or belong to the class of strong xantineoxidase inhibitors.[13]

We found that reflux of hydrazine **3** with an excess of dimethylformamide or dimethylacetamide dimethylacetal in benzene led to the formation of amidrazones **9a**,**b**, which in refluxing *o*-xylene were converted to pyrazolo[4,3-*e*]-[1,2,4]triazolo[4,3-*a*]pyrimidines **10a**,**b**, *i.e.*, the cyclization took place at atom N(7) of the pyrimidine ring of amiderazines **9**, rather than at atom N(5), which would result in the formation of the alternative structure **11a**,**b** (Scheme 5).

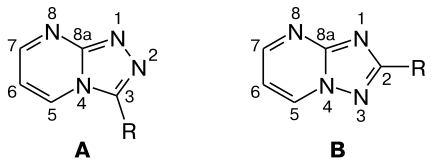
Scheme 5



R = H (**a**), Me (**b**)

Reagents and conditions: *i.* $(MeO)_2C(R)NMe_2$, C_6H_6, Δ; *ii. o*-xylene, Δ.

Besides, a possibility of the formation of other alternative structures (**12a**,**b**), *i.e.*, the Dimroth rearrangement products, was excluded based on the spectroscopic data. Thus, it is known[14] that the 1,2,4-triazolo[4,3-*a*]pyrimidine system (**A**), being a fragment of heterocycles **10a**,**b**, can undergo isomerization to the thermodynamically more stable [1,5-*a*] system (**B**) either thermally, or under acidic or basic conditions.



Amidrazones **9a**,**b** are well soluble in chloroform, whereas pyrazolotriazolopyrimidines **10a**,**b** are poorly soluble in organic solvents, including DMSO. The structure of compounds **9a**,**b** and **10a**,**b** was confirmed by spectroscopic methods. Their mass spectra (EI) are characterized by strong peaks of molecular ions (the tricycles **10a**,**b** virtually give no fragmentation). The ^{1}H NMR spectrum of amidrazone **9a** ($CDCl_3$) exhibits a singlet for the proton CH= at δ 7.65, whereas for pyrazolotriazolopyrimidine **10a** (DMSO-d_6) the singlet for proton H(8) is found at δ 9.26. The 2D ^{1}H—^{15}N HMBC NMR spectrum of compound **10b** is shown in Fig. 1.

The presence of the upfield signal for atom N(9) at δ −208 and the downfield signal for atom N(7) in the region δ −102 (the correlation peaks of the protons of 8-Me group, respectively, with atoms N(9) and N(7)) confirmed the structure of compound **10b** and excluded the formation of tricycle **12b**, in which chemical shifts for both N atoms should be found in the low field region (the correlation peaks of the protons of 7-Me group with atoms N(6) and N(8)). Besides, in the spectrum of the alternative structure **11b** chemical shift for atom N(5) in both correlation peaks with the 4-Me and 6-Me protons should be identical and found in the high field. The actual chemical shift for atom N(5) is observed at δ −140 (the correlation peak only with the protons of the 4-Me group; *cf.* also with δ −136 for atom N(5) in amidrazone **9b**), that confirms the structure **10b**. The high-field chemical shift for atom N(2) at δ −159 (the correlation peak with the protons of the 3-Me group) in compound **10b** indicates the position of the proton at atom N(2) in the pyrazole ring (*cf.* with δ −85 for atom N(2) in amidrazone **9b**, which has a proton at atom N(1)). Chemical shifts for proton H(8) in the ^{1}H NMR spectrum (δ 9.26) and atom C(8) in the ^{13}C NMR spectrum (δ 132.44) in compound **10a** also confirm its structure and exclude the formation of compound **12a** (*cf.*[14] with δ 9.25 for H(3) and δ 135.8 for C(3) in compound **A**, δ 8.26 for H(2) and δ 156.3 for C(2) in compound **B** in the ^{1}H and ^{13}C NMR spectra recorded in DMSO-d_6 for R = H).

To sum up, the data of the 2D ^{1}H—^{15}N HMBC NMR spectra unambiguously confirm the structure **10a**,**b** and exclude the structures **11a**,**b** and **12a**,**b**.

Continuing with the studies of the reactivity of hydrazine **3**, we found that it reacted with aromatic aldehydes, resulting in obtaining of white crystalline hydrazones **13a**,**b**. When this reaction was run in refluxing acetic acid in the presence of sulfuric acid, the aldehydes also underwent condensation at the methyl group of the pyrimidine ring, which led to the formation of compounds **14a**,**b** as yellow crystals (Scheme 6). Hydrazones **13a**,**b** were converted to pyrazolotriazolopyrimidines **15a**,**b**, similar in structure to compounds **10a**,**b**, by the oxidative cyclization using $CuCl_2$ according to the method suggested in the work.[15]

The structure of pyrazolotriazolopyrimidines **15a**,**b** was established by spectroscopic methods.

Unlike for tricycles **10a**,**b**, the molecular ion peak in the mass spectrum (EI) of compound **15b** appeared to be

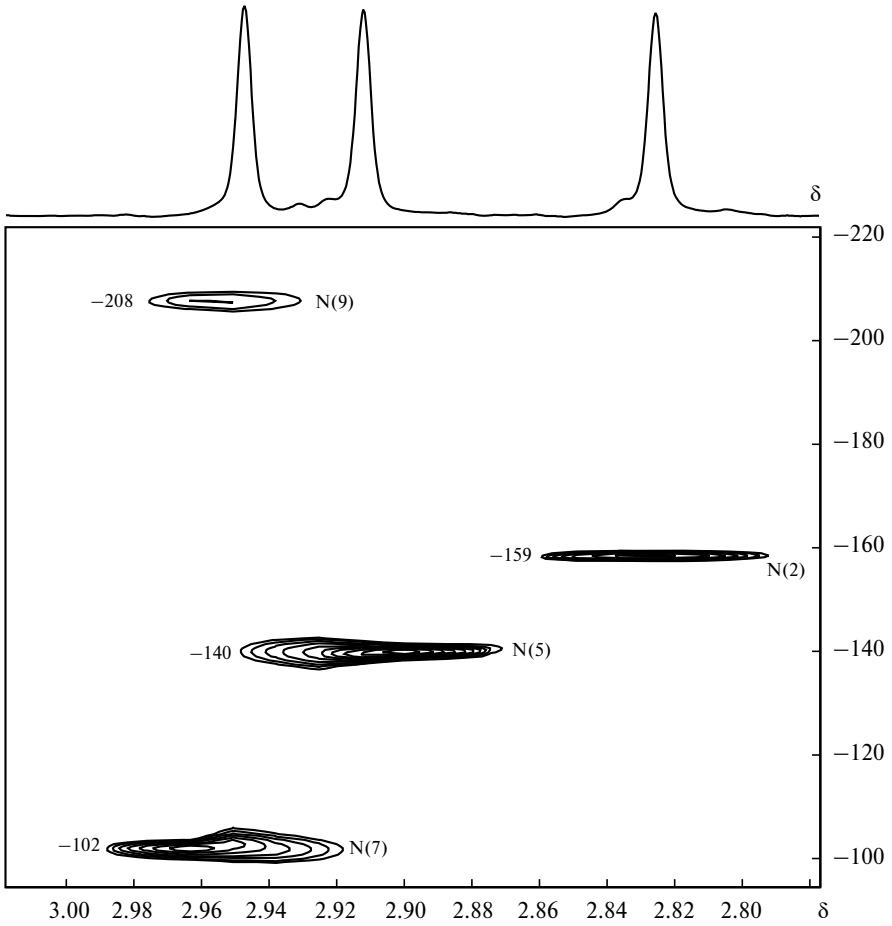
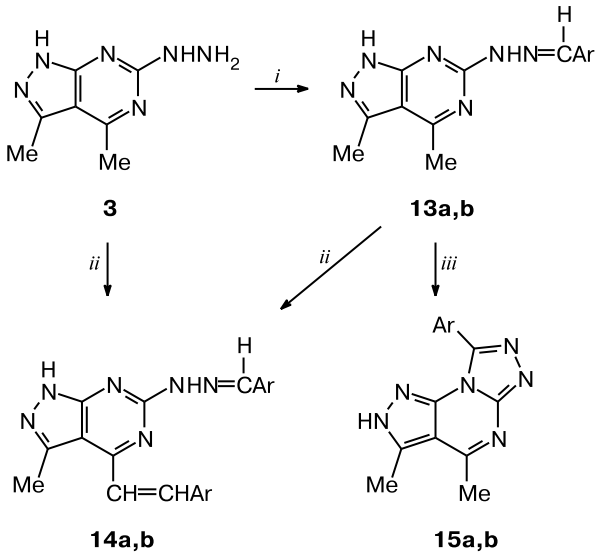


Fig. 1. 2D $^{1}H—^{15}N$ HMBC NMR spectrum of compound **10b**.

Scheme 6



Ar = 4-$EtOC_6H_4$ (**a**), 4-BrC_6H_4 (**b**)

Reagents and conditions: *i*. ArCHO, EtOH, Δ; *ii*. ArCHO, AcOH, H_2SO_4, Δ; *iii*. $CuCl_2$, DMF, 110 °C.

weak, and was absent in the spectrum of heterocycle **15a**. However, in the high resolution mass spectra obtained by electrospray ionization (ESI), the peaks of the ions $[M + H]^+$ were observed for compounds **15a,b**, that confirmed the formation of suggested pyrazolotriazolopyrimidines. The 2D $^{1}H—^{15}N$ HMBC NMR spectrum of compound **15b** exhibited a downfield signal for N(5) at δ −127 (the correlation peak of the 4-Me protons with atom N(5)) and an upfield signal N(2) in the region δ −171 (the correlation peak of the 3-Me protons with atom N(2)). The ^{13}C NMR spectra exhibit the signal for atom C(8) at δ 145.80 in compound **15a** and δ 145.04 in heterocycle **15b** (*cf.* the data in Ref. 14: the chemical shifts δ 144.8 for C(3) and δ 165.6 for C(2), respectively, in compounds **A** and **B** for R = Ar). The spectral data given unambiguously confirm the structure of compounds **15a**,**b**.

It should be noted that earlier,[16,17] it was reported that only 4-imino-1,5-diphenylpyrazolo[4,3-*e*][1,2,4]triazolo[4,3-*a*]pyrimidines were synthesized from 5-amino-1-phenyl-1*H*-pyrazolo-4-carboxylic acid amide

In conclusion, we suggested an approach to the construction of the little studied pyrazolo[4,3-*e*][1,2,4]-

triazolo[4,3-*a*]pyrimidine system based on diacetyl ketene *N*,*S*-acetal.

Experimental

^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer (300 MHz), ^{13}C NMR spectra and 2D ^{1}H—^{13}C and ^{1}H—^{15}N HMBC NMR spectra were recorded on a Bruker Avance 600 spectrometer (600, 150, and 60.8 MHz for ^{1}H, ^{13}C, and ^{15}N, respectively). Residual signals of the deuterated solvents (7.27 for $CDCl_3$ and 2.50 for DMSO-d_6) were used as references in the ^{1}H NMR spectra, whereas in the ^{13}C NMR spectra as those were used the multiplet signals of the deuterated solvents (39.50 for DMSO-d_6 and 77.00 for $CDCl_3$). The signals in the ^{1}H and ^{13}C NMR spectra of NMR spectra were assigned based on the 2D ^{1}H—^{13}C HMBC NMR spectra. Chemical shifts for ^{15}N were measured relative to the external standard $MeNO_2$ (the upfield chemical shifts are given as negative values) based on the analysis of the 2D ^{1}H—^{15}N HMBC NMR spectra. IR spectra were recorded on a Specord-M 82 spectrometer, mass spectra were measured on a Kratos MS-30 instrument (EI, 70 eV, temperature of the ionizing chamber 250 °C, direct injection of compounds). High resolution mass spectra were recorded on a Bruker micrOTOF II instrument using electrospray ionization (ESI). The measurements were performed on the positive ions (capillary voltage 4500 V). The masses range scanning (*m*/*z* 50—3000 Da), external and internal calibration (Electrospray Calibrant Solution, Fluka). Solutions of samples in methanol were injected with a syringe, the flow rate 3 μL min^{-1}. Sprayer gas nitrogen (4 L min^{-1}), interface temperature 180 °C. Amide acetals purchased from Lancaster and aldehydes from Acros were used in the syntheses. 5-Acetyl-6-methyl-2,4-di(methylsulfanyl)pyrimidine (**2**) was synthesized according to the procedure p ublished earlier.[3]

6-Hydrazino-3,4-dimethyl-1*H*-pyrazolo[3,4-*d*]pyrimidine (3). A mixture of pyrimidine **2** (0.456 g, 2 mmol) and hydrazine hydrate (6 mL, 123 mmol) was refluxed for 4 h and cooled to 20 °C. A precipitate was filtered off and washed with ethanol (6 mL) to obtain a white hydrazine **3** (0.306 g, 86%), m.p. >360 °C. Found (%): C, 47.22; H, 5.68; N, 47.25. $C_7H_{10}N_6$. Calculated (%): C, 47.18; H, 5.66; N, 47.16. MS, *m*/*z* (I_{rel} (%)): 178 $[M]^+$ (100), 149 $[M - NNH]^+$ (28), 148 $[M - NNH_2]^+$ (12), 133 $[M - NNH - NH_2]^+$ (11). ^{1}H NMR (DMSO-d_6), δ: 2.46 (s, 3 H, 3-Me); 2.56 (s, 3 H, 4-Me); 4.15 (br.s, 2 H, NH_2); 7.92 (br.s, 1 H, NH); 12.30 (br.s, 1 H, $NH_{pyrazole}$). ^{13}C NMR (DMSO-d_6 + + CF_3COOH), δ: 14.49 (3-Me); 21.96 (4-Me); 108.40 (C(3a)); 143.06 (C(3)); 155.92, 159.31 (C(6), C(7a)); 165.06 (C(4)).

3,4-Dimethyl-6-methylsulfanyl-1*H*-pyrazolo[3,4-*d*]pyrimidine (4). A mixture of pyrimidine **2** (0.16 g, 0.7 mmol) and hydrazine hydrate (0.85 mL, 17.5 mmol) in BuOH (5 mL) was refluxed for 3 h and cooled to 20 °C. A precipitate was filtered off and washed with BuOH (5 mL) and light petroleum to obtain a white compound **4** (0.09 g, 65%), m.p. 237—240 °C (subl.). Found (%): C, 49.63; H, 5.21; N, 28.72; S, 16.22. $C_8H_{10}N_4S$. Calculated (%): C, 49.46; H, 5.19; N, 28.84; S, 16.51. MS, *m*/*z* (I_{rel} (%)): 194 $[M]^+$ (100), 193 $[M - H]^+$ (44), 163 $[M - H - 2\,Me]^+$ (15), 148 $[M - SCH_2]^+$ (34), 133 $[M - SCH_2 - Me]^+$ (19), 121 $[M - MeSCN]^+$ (30). ^{1}H NMR ($CDCl_3$), δ: 2.68 (s, 6 H, 2 Me); 2.79 (s, 3 H, Me); 10.75 (br.s, 1 H, NH).

1-Acetyl-6-(1,2-diacetyl)hydrazino-3,4-dimethyl-1*H*-pyrazolo[3,4-*d*]pyrimidine (5). A mixture of hydrazine **3** (0.072 g, 0.4 mmol) and acetic anhydride (0.30 mL, 3.2 mmol) in benzene (5 mL) was refluxed for 8 h until complete dissolution, cooled to 20 °C, and diluted with light petroleum (12 mL). A precipitate formed was filtered off and washed with light petroleum to obtain a white compound **5** (0.071 g, 58%), m.p. 192—193 °C. Found (%): C, 51.48; H, 5.35; N, 27.36. $C_{13}H_{16}N_6O_3$. Calculated (%): C, 51.30; H, 5.30; N, 27.62. MS, *m*/*z* (I_{rel} (%)): 304 $[M]^+$ (1), 262 $[M - COCH_2]^+$ (55), 220 $[M - 2\,COCH_2]^+$ (55), 178 $[M - 3\,COCH_2]^+$ (100), 149 $[M - 3\,COCH_2 - N_2 - H]^+$ (40). ^{1}H NMR ($CDCl_3$), δ: 2.17 (s, 3 H, MeCONH); 2.63 (s, 3 H, MeCON); 2.65 (s, 3 H, 3-Me); 2.77 (s, 3 H, MeCON); 2.78 (s, 3 H, 4-Me); 8.46 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 15.13 (3-Me); 20.79, 22.50, 24.17, 25.39 (3 MeCON, 4-Me); 112.64 (C(3a)); 146.78 (C(3)); 156.37, 158.17 (C(6), C(7a)); 164.84 (C(4)); 167.94 (NCO); 169.41 (NHCO); 170.73 (NCO). ^{15}N NMR ($CDCl_3$), δ: −240 (NH) (correlation with proton NH); −213 (NH—NCOMe) (correlation with proton NH); −115 (N(5)) (correlation with protons 4-Me); −70 (N(2)) (correlation with protons 3-Me).

3,4-Dimethyl-6-(3-methyl-5-oxo-1*H*,2*H*-pyrazol-1-yl)-1*H*-pyrazolo[3,4-*d*]pyrimidine (6). A mixture of (0.142 g, 0.8 mmol) hydrazine **3** and ethyl acetoacetate (0.40 mL, 3.2 mmol) in AcOH (4 mL) was refluxed for 7 h. The reaction mixture was allowed to stand at 20 °C for 12 h. A precipitate was filtered off, washed with chloroform (2 mL) to obtain colorless compound **6** (0.137 g, 70%), m.p. 354—356 °C (decomp.). Found (%): C, 54.21; H, 4.83; N, 34.48. $C_{11}H_{12}N_6O$. Calculated (%): C, 54.09; H, 4.95; N, 34.41. MS, *m*/*z* (I_{rel} (%)): 244 $[M]^+$ (100), 216 $[M - CO]^+$ (8), 203 $[M - MeCN]^+$ (11), 148 (19), 147 (11), 133 (12). IR (KBr), ν/cm^{-1}: 3250—2750 (NH, CH); 1636 (CO); 1595, 1512, 1484, 1444. ^{1}H NMR (DMSO-d_6), δ: 2.15 (s, 3 H, 3′-Me); 2.62 (s, 3 H, 3-Me); 2.81 (s, 3 H, 4-Me); 5.44 (s, 1 H, H(4′)); 12.51 (br.s, 1 H, N(2′)H); 13.43 (br.s, 1 H, N(1)H). ^{1}H NMR ($CDCl_3$), δ: 2.43 (s, 3 H, 3′-Me); 2.72 (s, 3 H, 3-Me); 2.91 (s, 3 H, 4-Me); 5.52 (s, 1 H, H(4′)); 12.50 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d_6 + CF_3COOH), δ:12.97, 14.16 (3-Me, 3′-Me); 21.56 (4-Me); 90.30 (C(4′)); 110.46 (C(3a)); 143.86 (C(3)); 151.37 (C(3′)); 151.49, 155.07 (C(6), C(7a)); 158.63 (C(5′)); 164.52 (C(4)). ^{15}N NMR (DMSO-d_6 + CF_3COOH), δ: −164 (N(2′)) (correlation with protons 3′-Me); −150 (N(5)) (correlation with protons 4-Me); −76 (N(2)) (correlation with protons 3-Me).

3,4-Dimethyl-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-1*H*-pyrazolo[3,4-*d*]pyrimidine (7). A mixture of hydrazine **3** (0.125 g, 0.7 mmol) and acetylacetone (0.29 mL, 2.8 mmol) in AcOH (4 mL) was refluxed for 4 h. The reaction mixture was allowed to stand at 20 °C for 12 h. A precipitate was filtered off and washed with light petroleum (10 mL) to obtain colorless compound **7** (0.122 g, 72%), m.p. 310—312 °C. Found (%): C, 59.32; H, 5.85; N, 34.70. $C_{12}H_{14}N_6$. Calculated (%): C, 59.49; H, 5.82; N, 34.69. MS, *m*/*z* (I_{rel} (%)): 242 $[M]^+$ (100), 227 $[M - Me]^+$ (26), 201 $[M - MeCN]^+$ (12), 163 (15), 148 (12), 102 (35). ^{1}H NMR (DMSO-d_6), δ: 2.21 (s, 3 H, 3′-Me); 2.60 (s, 3 H, 5′-Me); 2.64 (s, 3 H, 3-Me); 2.82 (s, 3 H, 4-Me); 6.11 (s, 1 H, H(4′)); 13.37 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 13.02 (3′-Me); 13.93 (5′-Me); 14.10 (3-Me); 21.84 (4-Me); 108.81 (C(4′)); 109.80 (C(3a)); 141.55 (C(5′)); 142.20 (C(3)); 148.79 (C(3′)); 153.86, 155.48 (C(6), C(7a)); 163.87 (C(4)). ^{15}N NMR (DMSO-d_6), δ: −164 (N(1′)) (correlation with protons 5′-Me and proton H(4′)); −125 (N(5)) (correlation with protons 4-Me); −78 (N(2′)) (correlation with protons 3′-Me); −74 (N(2)) (correlation with protons 3-Me).

3,4-Dimethyl-6-[2-(ethoxycarbonyl)acetyl]hydrazino-1*H*-pyrazolo[3,4-*d*]pyrimidine (8). A mixture of hydrazine **3** (0.064 g, 0.36 mmol) and ethyl malonate (2.0 mL, 13.2 mmol) was heated

in an oil bath at 160—170 °C for 5 h and cooled to 20 °C. A precipitate was filtered off and washed with light petroleum (10 mL) to obtain colorless compound **8** (0.074 g, 70%), m.p. 266—268 °C. Found (%): C, 49.28; H, 5.55; N, 28.71. $C_{12}H_{16}N_6O_3$. Calculated (%): C, 49.31; H, 5.52; N, 28.75. MS, *m/z* (I_{rel} (%)): 292 $[M]^+$ (55), 247 $[M - C_2H_5O]^+$ (15), 220 $[M - C_2H_4 - CO_2]^+$ (10), 205 $[M - CH_2CO_2Et]^+$ (26), 178 $[M - C_2H_4 - CO_2 - CH_2CO]$ (100), 149 (87). IR (KBr), ν/cm^{-1}: 3282, 3213, 3144, 3014, 1746 (CO_2Et); 1671 (CON); 1619, 1596, 1554, 1517. ^{1}H NMR (DMSO-d_6), δ (for major/minor isomer, the ratio 3.5 : 1): 1.28/1.12 (t, 3 H, MeCH$_2$, *J* = 7.2 Hz); 2.50/2.50 (s, 3 H, 3-Me); 2.61/2.61 (s, 3H , 4-Me); 3.30/3.22 (s, 2 H, CH_2); 4.10/4.00 (q, 2 H, CH_2O, *J* = 7.2 Hz); 8.97/9.20 (br.s, 1 H, NH); 10.0/9.35 (br.s, 1 H, NHCO); 12.72/12.91 (br.s, 1 H, N(1)H). ^{13}C NMR (DMSO-d_6), δ (for major/minor isomer): 13.98/13.85 (MeCH$_2$); 14.49/14.49 (3-Me); 21.91/21.91 (4-Me); 40.68/39.46 (CH_2); 60.50/60.25 (CH_2O); 106.96/106.96 (C(3a)); 142.03/142.03 (C(3)); 156.73/156.73 (C(7a)); 161.15/161.15 (C(6)); 163.53/163.53 (C(4)); 164.70/170.65 (NCO); 167.21/167.00 (COO). ^{15}N NMR (DMSO-d_6), δ (for major/minor isomer): −278/−274 (NH_{pyrim}) (correlation with proton NHCO in major isomer and NH_{pyrim} in minor isomer); −249/−248 (NHCO) (correlation with protons NHCO and CH_2 in both isomers); −203/−201 (N(1)) (correlation with proton N(1)H); −138/−138 (N(5)) (correlation with protons 4-Me); −85/−85 (N(2)) (correlation with protons 3-Me and N(1)H).

3,4-Dimethyl-6-(dimethylaminomethylidene)hydrazino-1*H*-pyrazolo[3,4-*d*]pyrimidine (9a). A mixture of hydrazine **3** (0.089 g, 0.5 mmol) and DMF dimethyl acetal (0.13 mL, 1.0 mmol) in benzene (4 mL) was refluxed for 4 h and cooled to 20 °C. A precipitate was filtered off, then chloroform (5 mL) was added to this precipitate, the undissolved residue of the unreacted hydrazine **3** was filtered off, chloroform was evaporated *in vacuo*, the residue was washed with light petroleum to obtain amidrazone **9a** (0.085 g, 73%), m.p. >360 °C. Found (%): C, 51.22; H, 6.36; N, 41.82. $C_{10}H_{15}N_7$. Calculated (%): C, 51.49; H, 6.48; N, 42.03. MS, *m/z* (I_{rel} (%)): 233 $[M]^+$ (100), 189 $[M - Me_2N]^+$ (52), 178 $[M - MeNCN]^+$ (45), 163$[M - Me_2NCN]^+$ (94). ^{1}H NMR ($CDCl_3$), δ: 2.52 (s, 3 H, 3-Me); 2.61 (s, 3 H, 4-Me); 2.93 (s, 6 H, NMe_2);7.65 (s, 1 H, CH=); 8.02 (br.s, 1 H, NH); 12.05 (br.s, 1 H, $NH_{pyrazole}$). ^{13}C NMR ($CDCl_3$), δ: 14.96 (3-Me); 22.25 (4-Me); 38.07 (NMe_2); 106.96 (C(3a)); 142.99 (C(3)); 154.45 (CH=); 157.48, 160.29 (C(6), C(7a)); 163.85 (C(4)). ^{15}N NMR ($CDCl_3$), δ: −310 and −240 (NMe_2 and NH) (correlation with proton CH=); −136 (N(5)) (correlation with protons 4-Me); −85 (N(2)) (correlation with protons 3-Me).

3,4-Dimethyl-6-[1-(dimethylamino)ethylidene]hydrazino-1*H*-pyrazolo[3,4-*d*]pyrimidine (9b). A mixture of hydrazine **3** (0.10 g, 0.56 mmol) and dimethylacetamide dimethyl acetal (0.33 mL, 2.24 mmol) in benzene (4 mL) was refluxed for 8 h. Then, the reaction mixture was treated similarly as described for amidrazone **9a** to obtain amidrazone **9b** (0.072 g, 52%), m.p. > 360 °C. Found (%): C, 53.18; H, 6.78; N, 39.36. $C_{11}H_{17}N_7$. Calculated (%): C, 53.42; H, 6.93; N, 39.65. MS, *m/z* (I_{rel} (%)): 247 $[M]^+$ (12), 163 (6), 101 (100). ^{1}H NMR ($CDCl_3$), δ: 2.11 (s, 3 H, Me); 2.53 (s, 3 H, 3-Me); 2.62 (s, 3 H, 4-Me); 2.99(s, 6 H, NMe_2); 7.59 (br.s, 1 H, NH); 12.08 (br.s, 1 H, $NH_{pyrazole}$). ^{13}C NMR ($CDCl_3$), δ: 12.95 (Me); 14.93 (3-Me); 22.19 (4-Me); 38.63 (NMe_2); 106.90 (C(3a)); 142.80 (C(3)); 157.47, 160.30 (C(6), C(7a)); 161.24 (C—NMe_2); 163.62 (C(4)). ^{15}N NMR ($CDCl_3$), δ: −136 (N(5)) (correlation with protons 4-Me); −85 (N(2)) (correlation with protons 3-Me).

3,4-Dimethyl-2*H*-pyrazolo[4,3-*e*][1,2,4]triazolo[4,3-*a*]-pyrimidine (10a). Amidrazone **9a** (0.065 g, 0.28 mmol) was refluxed in *o*-xylene (5 mL) for 8 h and cooled to 20 °C. A precipitate was filtered off and washed with chloroform (5 mL) to obtain compound **10a** (0.042 g, 80%), m.p. > 360 °C. Found (%): C, 50.82; H, 4.48; N, 44.44. $C_8H_8N_6$. Calculated (%): C, 51.06; H, 4.28; N, 44.66. MS, *m/z* (I_{rel} (%)): 188 $[M]^+$ (100), 101 (38), 83 (33). ^{1}H NMR (DMSO-d_6), δ: 2.72 (s, 3 H, 3-Me); 2.76 (s, 3 H, 4-Me); 9.26 (s, 1 H, H(8)); 13.60 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 11.33 (3-Me); 22.90 (4-Me); 103.80 (C(3a)); 132.44 (C(8)); 139.66 (C(3)); 153.70 (C(5a)); 161.15 (C(4)) (chemical shifts for C(3a) and C(5a) were obtained from the 2D ^{1}H/^{13}C HMBC NMR spectrum, whereas that of C(9a) was not found because of the low solubility of compound **10a** in DMSO-d_6). ^{13}C NMR (DMSO-d_6 + CF_3COOH), δ: 12.06 (3-Me); 23.92 (4-Me); 107.62 (C(3a)); 134.53 (C(8)); 143.00, 149.35 (C(5a), C(9a)); 143.29 (C(3)); 171.80 (C(4)). ^{15}N NMR (DMSO-d_6 + + CF_3COOH), δ: −214 (N(9)) (correlation with proton H(8)); −163 (N(2)) (correlation with protons 3-Me); −148 (N(5)) (correlation with protons 4-Me).

3,4,8-Trimethyl-2*H*-pyrazolo[4,3-*e*][1,2,4]triazolo[4,3-*a*]-pyrimidine (10b) was synthesized similarly to compound **10a** by reflux of amidrazone **9b** in *o*-xylene. The yield was 79%, m.p. > 360 °C. Found (%): C, 53.38; H, 4.90; N, 41.28. $C_9H_{10}N_6$. Calculated (%): C, 53.45; H, 4.99; N, 41.56. MS, *m/z* (I_{rel} (%)): 202 $[M]^+$ (100), 132 (4), 101 (13). ^{1}H NMR (DMSO-d_6 + + CF_3COOH), δ: 2.83 (s, 3 H, 3-Me); 2.91 (s, 3 H, 4-Me); 2.95 (s, 3 H, 8-Me); 14.70 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d_6 + + CF_3COOH), δ: 11.70 (3-Me); 12.34 (8-Me); 23.67 (4-Me); 107.00 (C(3a)); 142.15 (C(3)); 143.47 (C(8)); 144.39, 149.37 (C(5a), C(9a)); 170.59 (C(4)). ^{15}N NMR (DMSO-d_6 + CF_3COOH), δ: −208 (N(9)) (correlation with protons 8-Me); −159 (N(2)) (correlation with protons 3-Me); −140 (N(5)) (correlation with protons 4-Me); −102 (N(7)) (correlation with protons 8-Me).

3,4-Dimethyl-6-(4-ethoxybenzylidene)hydrazino-1*H*-pyrazolo[3,4-*d*]pyrimidine (13a). A mixture of hydrazine **3** (0.078 g, 0.44 mmol) and 4-ethoxybenzaldehyde (0.12 mL, 0.88 mmol) in EtOH (5 mL) was refluxed for 4 h and cooled to 20 °C. A precipitate was filtered off and washed with light petroleum to obtain a white compound **13a** (0.125 g, 92%), m.p. 274—275 °C. Found (%): C, 61.79; H, 6.05; N, 27.10. $C_{16}H_{18}N_6O$. Calculated (%): C, 61.92; H, 5.85; N, 27.08. ^{1}H NMR (DMSO-d_6), δ: 1.31 (t, 3 H, MeCH$_2$, *J* = 7.0 Hz); 2.50 (s, 3 H, 3-Me); 2.62 (s, 3 H, 4-Me); 4.05 (q, 2 H, CH_2, *J* = 7.0 Hz); 6.95 (d, 2 H, C_6H_4, *J* = 7.8 Hz); 7.58 (d, 2 H, C_6H_4, *J* = 7.8 Hz); 8.08 (br.s, 1 H, CH=); 11.12 (br.s, 1 H, NH); 12.81 (br.s, 1 H, $NH_{pyrazole}$).

6-(4-Bromobenzylidene)hydrazino-3,4-dimethyl-1*H*-pyrazolo[3,4-*d*]pyrimidine (13b) was synthesized similarly to compound **13a** from hydrazine **3** and 4-bromobenzaldehyde. The yield was 85%, m.p. 345—347 °C. Found (%): C, 48.53; H, 4.00; N, 24.69. $C_{14}H_{13}BrN_6$. Calculated (%): C, 48.71; H, 3.79; N, 24.35. ^{1}H NMR (DMSO-d_6), δ: 2.50 (s, 3 H, 3-Me); 2.62 (s, 3 H, 4-Me); 7.60 (s, 4 H, C_6H_4); 8.11 (s, 1 H, CH=); 11.38 (br.s, 1 H, NH); 12.88 (br.s, 1 H, $NH_{pyrazole}$).

6-(4-Ethoxybenzylidene)hydrazino-4-[2-(4-ethoxyphenyl)-vinyl]-3-methyl-1*H*-pyrazolo[3,4-*d*]pyrimidine (14a). Acetic acid (5 mL) and concentrated H_2SO_4 (3 drops) were added to a mixture of hydrazine **3** (0.089 g, 0.50 mmol) and 4-ethoxybenzaldehyde (0.28 mL, 2.0 mmol), and the mixture was refluxed for 3 h and cooled to 20 °C. A precipitate was filtered off, treated with aqueous NH_3, washed with water, and dried to obtain a yellow compound **14a** (0.203 g, 92%), m.p. 288—289 °C. Found (%):

C, 67.67; H, 5.98; N, 18.68. $C_{25}H_{26}N_6O_2$. Calculated (%): C, 67.85; H, 5.92; N, 18.99. MS, *m/z* (I_{rel} (%)): 442 $[M]^+$ (10), 295 $[M - EtOC_6H_4CN]^+$ (66), 163 $[EtOC_6H_4CHNNH_2]^+$ (100), 121 $[EtOC_6H_4]^+$ (70). ^{1}H NMR (DMSO-d_6), δ: 1.34 (t, 3 H, MeCH$_2$, *J* = 7.2 Hz); 1.35 (t, 3 H, MeCH$_2$, *J* = 7.2 Hz); 2.64 (s, 3 H, 3-Me); 4.06 (q, 2 H, CH_2O, *J* = 7.2 Hz); 4.08 (q, 2 H, CH_2O, *J* = 7.2 Hz); 6.98 (d, 2 H, *m*-$H_{C_6H_4C=N}$, *J* = 8.4 Hz); 7.01 (d, 2 H, *m*-$H_{C_6H_4C=C}$, *J* = 8.4 Hz); 7.43 (d, 1 H, Pyrim-CH=, *J* = 15.6 Hz); 7.61 (d, 2 H, *o*-$H_{C_6H_4C=N}$, *J* = 8.4 Hz); 7.70 (d, 2 H, *o*-$H_{C_6H_4C=C}$, *J* = 8.4 Hz); 8.00 (d, 1 H, C_6H_4CH=, *J* = 15.6 Hz); 8.13 (s, 1 H, CH=N); 11.04 (br.s, 1 H, NH); 12.90 (br.s, 1 H, $NH_{pyrazole}$). ^{13}C NMR (DMSO-d_6), δ: 14.54 (Me—CH_2); 14.60 (Me—CH_2); 15.14 (3-Me); 63.16 (CH_2); 63.29 (CH_2); 105.74 (C(3a)); 114.68 (*m*-$C_{C_6H_4C=N}$); 114.96 (*m*-$C_{C_6H_4C=C}$); 119.88 (Pyrim-CH=); 127.78 (*o*-$C_{C_6H_4C=N}$); 127.82 (*ipso*-$C_{C_6H_4C=N}$, *ipso*-$C_{C_6H_4C=C}$); 129.60 (*o*-$C_{C_6H_4C=C}$); 137.27 (C_6H_4CH=); 141.38 (CH=N); 141.75 (C(3)); 157.88 (C(4)); 158.23 (C(6)); 158.32 (C(7a)); 159.22 (*p*-$C_{C_6H_4C=N}$); 159.90 (*p*-$C_{C_6H_4C=C}$).

6-(4-Bromobenzylidene)hydrazino-4-[2-(4-bromophenyl)-vinyl]-3-methyl-1*H*-pyrazolo[3,4-*d*]pyrimidine (14b). Acetic acid (5 mL) and conc. H_2SO_4 (3 drops) were added to a mixture of hydrazone **13b** (0.060 g, 0.17 mmol) and 4-bromobenzaldehyde (0.064 g, 0.35 mmol), and the mixture was refluxed for 4 h and cooled to 20 °C. A precipitate was filtered off, treated with aqueous NH_3, washed with water, and dried to obtain a yellow compound **14b** (0.086 g, 97%), m.p. 303—305 °C. Found (%): C, 48.92; H, 3.44; N, 16.12. $C_{21}H_{16}Br_2N_6$. Calculated (%): C, 49.24; H, 3.15; N, 16.41. ^{1}H NMR (DMSO-d_6), δ: 2.65 (s, 3 H, 3-Me); 7.61 (d, 1 H, Pyrim-CH=, *J* = 15.6 Hz); 7.63 (s, 4 H, C_6H_4C=N); 7.65 (d, 2 H, *m*-$H_{C_6H_4C=C}$, *J* = 7.8 Hz); 7.73 (d, 2 H, *o*-$H_{C_6H_4C=C}$, *J* = 7.8 Hz); 7.99 (d, 1 H, C_6H_4CH=, *J* = 15.6 Hz); 8.16 (s, 1 H, CH=N); 11.34 (br.s, 1 H, NH); 13.00 (br.s, 1 H, $NH_{pyrazole}$). ^{13}C NMR (DMSO-d_6), δ: 15.08 (3-Me); 106.29 (C(3a)); 121.83 (*p*-$C_{C_6H_4C=N}$); 122.89 (*p*-$C_{C_6H_4C=C}$); 123.42 (Pyrim-CH=); 128.14 (*o*-$C_{C_6H_4C=N}$); 129.90 (*o*-$C_{C_6H_4C=C}$); 131.71 (*m*-$C_{C_6H_4C=N}$); 131.98 (*m*-$C_{C_6H_4C=C}$); 134.57 (*ipso*-$C_{C_6H_4C=C}$); 134.60 (*ipso*-$C_{C_6H_4C=N}$); 136.29 (C_6H_4CH=); 140.13 (CH=N); 141.85 (C(3)); 157.37 (C(4)); 158.02 (C(6)); 158.26 (C(7a)).

8-(4-Ethoxyphenyl)-3,4-dimethyl-2*H*-pyrazolo[4,3-*e*][1,2,4]-triazolo[4,3-*a*]pyrimidine (15a). Dimethylformamide (4 mL) was added to hydrazone **13a** (0.10 g, 0.32 mmol) and heated until complete dissolution, then $CuCl_2$ (0.086 g, 0.64 mmol) was added, and the reaction mixture was heated in an oil bath for 2.5 h. DMF was evaporated *in vacuo*. Aqueous ammonia (5 mL) was added to the residue, a precipitate was filtered off and washed with water until the washings ceased to be colored in violet. A black precipitate obtained was extracted with refluxing methanol (3×50 mL) to yield the reaction product **15a**. Methanol was evaporated *in vacuo*, the residue was washed with chloroform (5 mL) to obtain a yellowish compound **15a** (0.028 g, 28%), m.p. 265—268 °C. HRMS (MCBP) (ESI): found: *m/z* 309.1449 $[M + H]^+$. $C_{16}H_{16}N_6O$. Calculated: $[M + H]^+$ = 309.1458. MS (EI), *m/z* (I_{rel} (%)): 216 (9), 184 (33), 182 (49), 148 (25), 138 (39), 121 (30), 91 (100), 57 (80). ^{1}H NMR (DMSO-d_6), δ: 1.36 (t, 3 H, MeCH$_2$, *J* = 6.0 Hz); 2.71 (s, 3 H, 3-Me); 2.73 (s, 3 H, 4-Me); 4.11 (q, 2 H, CH_2, *J* = 6.0 Hz); 7.07 (d, 2 H, $H_{C_6H_4}$, *J* = 7.2 Hz); 8.06 (d, 2 H, $H_{C_6H_4}$, *J* = 7.2 Hz); 14.10 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 11.30 (3-Me); 14.46 (MeCH$_2$); 23.00 (4-Me); 63.17 (CH_2); 104.62 (C(3a)); 113.91 (*m*-$C_{C_6H_4}$); 119.35 (*ipso*-$C_{C_6H_4}$); 130.47 (*o*-$C_{C_6H_4}$); 138.74 (C(3)); 144.30 (C(9a)); 145.80 (C(8)); 154.70 (C(5a)); 159.63 (*p*-$C_{C_6H_4}$); 160.85 (C(4)).

8-(4-Bromophenyl)-3,4-dimethyl-2*H*-pyrazolo[4,3-*e*][1,2,4]-triazolo[4,3-*a*]pyrimidine (15b) was synthesized similarly to compound **15a** from hydrazone **13b**. The yield was 31%, m.p. >360 °C. HRMS (MCBP) (ESI): found: *m/z* 343.0299 (for isotope ^{79}Br) $[M + H]^+$, 345.0286 (for isotope ^{81}Br) $[M + H]^+$. $C_{14}H_{11}BrN_6$. Calculated: $[M + H]^+$ = 343.0301 (for isotope ^{79}Br) and 345.0281 (for isotope ^{81}Br). MS (EI), *m/z* (I_{rel} (%)): 342 $[M]^+$(12) for isotope ^{79}Br, 344 $[M]^+$ (10) for isotope ^{81}Br, 184 (70), 183 (49), 182 (55), 163 (28),148 (54), 147 (47), 91 (100). ^{1}H NMR (DMSO-d_6), δ: 2.71 (s, 3 H, 3-Me); 2.76 (s, 3 H, 4-Me); 7.76 (d, 2 H, C_6H_4, *J* = 7.2 Hz); 8.11 (d, 2 H, C_6H_4, *J* = 7.2 Hz); 13.50 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 11.34 (3-Me); 23.05 (4-Me); 104.78 (C(3a)); 123.32, 126.46 (*p*-$C_{C_6H_4}$, *ipso*-$C_{C_6H_4}$); 130.94, 131.30 (*o*-$C_{C_6H_4}$, *m*-$C_{C_6H_4}$); 139.02 (C(3)); 144.28 (C(9a)); 145.04 (C(8)); 155.03 (C(5a)); 161.46 (C(4)). ^{15}N NMR (DMSO-d_6, δ: −171 (N(2)) (correlation with protons 3-Me); −127 (N(5)) (correlation with protons 4-Me).

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